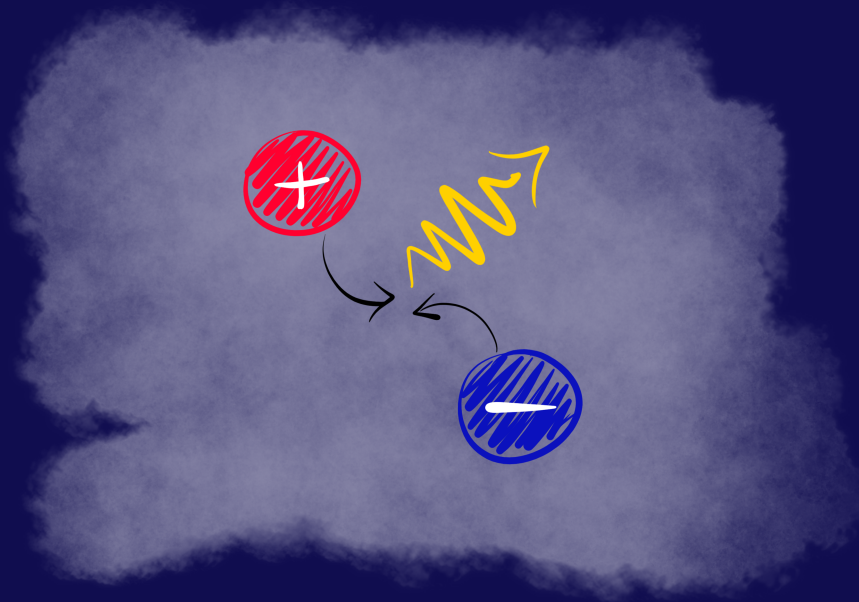


Simulating the dynamics of charges and excitons in organic light emitting diode structures and blends

Giacomo Cotelli



Dissertation
der Universität Bayreuth
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Dovie'andi se tovyu sagain.

– Matrim Cauthon (*The Eye of the World*, Robert Jordan)

English abstract

Organic light-emitting diodes (OLEDs) represent the most commercially successful example of organic optoelectronic devices to date. The use of organic materials enables the production of thin, flexible, and high-contrast devices that are nowadays widespread across high-end displays, from smartphones to TV screens. Nonetheless, both device efficiency and operational lifetime remain active targets of ongoing research and development.

The four publications collected in this thesis investigate the physical processes that govern OLED efficiency or, in other words, how the dynamics of charge carriers and excitons determine device performance. The tool chosen for this task is the simulation of full OLED stacks and of organic thin films with a kinetic Monte Carlo (kMC) approach. By explicitly modelling the dynamics of individual charges and excitons in the material, kMC naturally bridges molecular-scale material properties and macroscopic device observables, providing a powerful framework for the rational analysis and design of OLED devices.

In the first and second publication, simulation of whole OLED stacks are carried out to study how morphological and energetic factors play out in determining the internal quantum efficiency of devices.

The first publication, *“Simulation of charge and exciton dynamics across nanostructured rough interfaces in organic light emitting devices”*, investigates how roughness at organic-organic interfaces affects the efficiency of OLED devices. Intermixing or corrugation between organic layers may result from device fabrication and has been indicated as a potential cause for reduced device efficiency and stability. Simulations reveal that interfacial roughness leads to a spatial redistribution of carriers and excitons, but does not affect the overall efficiency of OLED devices. In contrast, controlled interfacial morphology may offer a handle for boosting the injection of charges across energy barriers in the device, or tuning the position of the recombination zone in OLEDs.

The second publication, *“Sweet spot of energy-level alignment in hyperfluorescent organic light-emitting diodes”*, addresses the issue of efficiency in hyperfluorescent (HF) OLEDs. HF-OLEDs combine a thermally activated delayed fluorescence (TADF) sensitizer and a fluorescent terminal emitter (TE) to achieve narrowband emission with in principle high internal quantum efficiency. However, HF-OLEDs are often outperformed by devices containing the sensitizer alone, a sign that the addition of a terminal emitter introduces new loss mechanisms as well. The simulation of accurate “digital twins” of real OLED devices led to identify the generation of non-emissive intermolecular (charge-transfer) excited states as one such new loss mechanism. This channel can be deactivated if the energy of the intermolecular state lies at least 150 meV above the singlet energy level of the terminal emitter, providing a clear design rule for efficient HF-OLEDs.

In the third and fourth publications, the focus shifts on the simulation of the photophysics of small-molecule organic semiconductors. Spectroscopic characterisation of organic thin films is a widely used preliminary step in OLED research, serving both to assess the suitability of candidate materials for device applications and to study efficiency loss mechanisms in a simpler setting than a full device stack.

The third publication, *“Spectral diffusion due to charge carrier relaxation of intermolecular charge-transfer states in donor:acceptor blends of disordered organic semiconductors”*, examines the dynamic processes which govern luminescence from intermolecular charge transfer (CT) states in blends of small-molecule organic materials. This study relates the spectral diffusion of the CT state emission spectrum to the relaxation dynamics of charge carriers in an energetically disordered medium, in a comprehensive framework able to unify multiple experimental observations.

Finally, the fourth publication, *“The rates are not what they seem: understanding the time dependence of exciton-exciton annihilation ‘constants’ in a TADF system”*, focuses on the issues associated with the evaluation of annihilation dynamics from photoluminescence measurements. Through kMC simulations, the kinetic coefficients of spin-dependent annihilation processes can be precisely quantified, revealing that under pulsed

excitation these coefficients exhibit a time-dependence governed by the exciton diffusivity. Because this time-dependence is usually unknown or neglected in standard analyses, this study urges caution when interpreting experimental data – particularly when the extracted annihilation coefficients are subsequently used as input parameters in device-scale OLED simulations.

In conclusion, this thesis provides both mechanistic insights and practical design guidelines for developing more efficient and stable OLED devices, using kinetic Monte Carlo simulations to bridge molecular-scale processes and device-level performance.

Deutsche Zusammenfassung

Organische Leuchtdioden (*Organic Light-Emitting Diodes*, OLEDs) stellen das bislang kommerziell erfolgreichste Beispiel für organische optoelektronische Bauelemente dar. Der Einsatz organischer Materialien ermöglicht die Herstellung dünner, flexibler und kontrastreicher Bauelemente, die heute in hochwertigen Displays, von Smartphones bis hin zu Fernsehbildschirmen, weit verbreitet sind. Dennoch bleiben sowohl die Effizienz als auch die Betriebsdauer der Bauelemente Gegenstand aktueller Forschung und Entwicklung.

Die vier in dieser Arbeit zusammengefassten Publikationen untersuchen die physikalischen Prozesse, welche die OLED-Effizienz bestimmen, oder anders ausgedrückt, wie die Dynamik von Ladungsträgern und Exzitonen die Leistungsfähigkeit des Bauelements beeinflusst. Als Methode wurde hierfür die Simulation vollständiger OLED-Schichtstapel sowie organischer Dünnschichten mithilfe von kinetischen Monte-Carlo-Methode (kMC) gewählt. Durch die explizite Modellierung der Dynamik einzelner Ladungen und Exzitonen im Material schlägt kMC dabei eine natürliche Brücke zwischen Materialeigenschaften auf molekularer Ebene und makroskopischen Kenngrößen des Bauelements; dies bietet einen leistungsfähigen Rahmen für die gezielte Analyse und das Design von OLEDs.

In der ersten und zweiten Publikation werden Simulationen vollständiger OLED-Schichtstapel durchgeführt, um zu untersuchen, wie sich morphologische und energetische Faktoren auf die interne Quanteneffizienz der Bauelemente auswirken.

Die erste Publikation, *„Simulation of charge and exciton dynamics across nanostructured rough interfaces in organic light emitting devices“* untersucht, wie sich die Rauheit an organisch-organischen Grenzflächen auf die Effizienz von OLEDs auswirkt. Durch den Herstellungsprozess können Vermischungen oder Korrugation an den Grenzflächen organischer Schichten entstehen, welche bereits als mögliche Ursache für eine verringerte Effizienz und Stabilität der Bauelemente identifiziert wurden. Die Simulationen zeigen, dass Grenzflächenrauheit zwar zu einer räumlichen Umverteilung von Ladungsträgern und Exzitonen führt, die Gesamteffizienz der OLEDs jedoch nicht beeinträchtigt. Im Gegensatz dazu könnte eine gezielte Steuerung der Grenzflächenmorphologie bieten, die Ladungsinjektion über Energiebarrieren im Bauelement zu verbessern oder die Position der Rekombinationszone in der OLED zu optimieren.

Die zweite Publikation, *„Sweet spot of energy-level alignment in hyperfluorescent organic light-emitting diodes“*, befasst sich mit der Effizienz von hyperfluoreszierenden (HF) OLEDs. HF-OLEDs kombinieren einen Sensibilisator auf Basis thermisch aktivierter verzögerter Fluoreszenz (*Thermally Activated Delayed Fluorescence*, TADF) mit einem fluoreszierenden Endemitter (*Terminal Emitter*, TE), um eine schmalbandige Emission bei prinzipiell hoher interner Quanteneffizienz zu erzielen. Allerdings bleiben HF-OLEDs hinter Bauelementen zurück, die lediglich den Sensibilisator enthalten; dies deutet darauf hin, dass die Zugabe eines Endemitters auch neue Verlustmechanismen einführt. Die Simulation „digitaler Zwillinge“ realer OLEDs identifizierte die Bildung nichtemittierender, zwischenmolekularer angeregter Zustände als einen solchen neuen Verlustmechanismus. Dieser Kanal kann deaktiviert werden, wenn die Energie des intermolekularen Zustands mindestens 150 meV über dem Singulett-Energieniveau des Endemitters liegt. Dies liefert eine klare Designregel für effiziente HF-OLEDs.

In der dritten und vierten Publikation verlagert sich der Schwerpunkt auf die Simulation der Photophysik niedermolekularer organischer Halbleiter. Die spektroskopische Charakterisierung organischer Dünnschichten ist ein weit verbreiteter erster Schritt in der OLED-Forschung. Sie dient sowohl der Beurteilung der Eignung von Kandidatenmaterialien für Bauelementanwendungen als auch der Untersuchung von Effizienzverlustmechanismen in einem einfacheren Modell als einem kompletten Bauelement.

Die dritte Publikation, *„Spectral diffusion due to charge carrier relaxation of intermolecular charge-transfer states in donor:acceptor blends of disordered organic semiconductors“*, untersucht die dynamischen Prozesse, die

die Lumineszenz von intermolekularen CT-Zuständen in Mischungen niedermolekularer organischer Halbleiter bestimmen. Diese Studie verknüpft die spektrale Diffusion des CT-Emissionsspektrums mit der Relaxationsdynamik von Ladungsträgern in einem energetisch ungeordneten Medium in einem umfassenden Rahmen, der mehrere experimentelle Beobachtungen vereinheitlichen kann.

Die vierte Publikation, *„The rates are not what they seem: understanding the time dependence of exciton-exciton annihilation ‘constants’ in a TADF system“*, befasst sich mit den Problemen der Auswertung der Annihilationsdynamik anhand von Photolumineszenzmessungen. Mithilfe von kMC-Simulationen lassen sich die kinetischen Koeffizienten spinabhängiger Annihilationsprozesse präzise quantifizieren. Dabei zeigt sich, dass diese Koeffizienten unter gepulster Anregung eine Zeitabhängigkeit aufweisen, die von der Exziton-diffusivität bestimmt wird. Da diese Zeitabhängigkeit in Standardanalysen üblicherweise unbekannt ist oder vernachlässigt wird, mahnt diese Studie zur Vorsicht bei der Interpretation experimenteller Daten – insbesondere, wenn die ermittelten Annihilationskoeffizienten anschließend als Eingangsparameter in OLED-Simulationen auf Bauelementebene verwendet werden.

Zusammenfassend liefert diese Arbeit sowohl mechanistische Einblicke als auch praktische Designrichtlinien für die Entwicklung effizienterer und stabilerer OLED-Bauelemente. Dies gelingt durch kinetische Monte-Carlo-Simulationen, die als Brücke zwischen molekularen Prozessen und der Leistungsfähigkeit von Bauelementen dient.

Riassunto in italiano

I diodi organici a emissione di luce (*organic light-emitting diodes*, OLEDs) sono ad oggi il più chiaro esempio di successo commerciale di dispositivi optoelettronici a base organica. L'uso di materiali organici permette di produrre dispositivi sottili, flessibili e ad alto contrasto, ad oggi ampiamente diffusi negli schermi di dispositivi elettronici di alta gamma, dagli smartphone ai televisori. Ciononostante, l'efficienza energetica e il tempo di vita dei dispositivi rimangono a tutt'oggi un obiettivo di ricerca e sviluppo.

Le quattro pubblicazioni raccolte in questa tesi indagano i processi fisici che governano l'efficienza degli OLED o, detto altrimenti, come i processi dinamici che coinvolgono portatori di carica ed eccitoni determinano l'efficienza dei dispositivi. Lo strumento principe selezionato a questo scopo è la simulazione a livello di intero *stack* OLED o di film sottile, seguendo un approccio Monte Carlo cinetico (*kinetic Monte Carlo*, kMC). Trattando i processi dinamici al livello del singolo portatore di carica o eccitone nel materiale, l'approccio kMC è in grado di rapportare in modo naturale le proprietà su scala molecolare con gli osservabili macroscopici a livello di dispositivo. Ciò offre un potente strumento per l'analisi e la progettazione razionale di dispositivi OLED.

Nella prima e seconda pubblicazione sono stati simulati interi *stack* OLED per studiare come fattori morfologici ed energetici influiscono sull'efficienza interna (*internal quantum efficiency*) dei dispositivi.

La prima pubblicazione, "*Simulation of charge and exciton dynamics across nanostructured rough interfaces in organic light emitting devices*" ("*Simulazione delle dinamiche di cariche ed eccitoni attraverso interfacce nanostrutturate in diodi organici a emissione di luce*"), studia come la rugosità superficiale all'interfaccia fra due *layer* organici influenza l'efficienza di un dispositivo OLED. Il processo di fabbricazione del dispositivo può comportare la presenza di parziale mescolamento o rugosità fra *layer* organici, fattori identificati come possibili cause di ridotta efficienza e stabilità. Le simulazioni rivelano che la rugosità interfacciale comporta la redistribuzione spaziale di portatori di carica ed eccitoni, ma non influenza l'efficienza complessiva del dispositivo OLED. Viceversa, la progettazione controllata di una morfologia interfacciale può favorire l'iniezione di carica attraverso una barriera energetica nel dispositivo o permettere il controllo della posizione della zona di ricombinazione fra portatori di carica all'interno dell'OLED.

La seconda pubblicazione, "*Sweet spot of energy-level alignment in hyperfluorescent organic light-emitting diodes*" ("*Allineamento ottimale dei livelli energetici in OLED iperfluorescenti*") considera il problema dell'efficienza in OLED iperfluorescenti (*hyperfluorescent OLED*, HF-OLED). Gli HF-OLED combinano un materiale sensibilizzante che sfrutta la fluorescenza ritardata attivata termicamente (*thermally activated delayed fluorescence*, TADF) per riciclare eccitoni in stato di tripletto e trasferirli verso un emettitore finale (*terminal emitter*) fluorescente, in modo da ottenere al contempo uno spettro d'emissione con ridotta ampiezza spettrale e un'elevata efficienza interna. Tuttavia, gli HF-OLED vengono spesso superati in termini d'efficienza da dispositivi che contengono il solo sensibilizzante – un'indicazione del fatto che l'aggiunta dell'emettitore finale comporta l'introduzione di nuovi meccanismi di perdita d'efficienza. La simulazione di "gemelli digitali" di dispositivi OLED reali ha permesso di identificare quale uno di questi nuovi meccanismi la generazione di stati eccitati intermolecolari non emissivi (con carattere di trasferimento di carica). Questo canale di perdita d'efficienza può essere disattivato se l'energia dello stato eccitato intermolecolare è almeno 150 meV maggiore rispetto all'energia dello stato di singoletto dell'emettitore finale. Ciò fornisce una chiara linea guida per la progettazione di HF-OLED ad alta efficienza.

Nella terza e quarta pubblicazione, l'attenzione si sposta verso la simulazione di processi fotofisici in semiconduttori basati su piccole molecole organiche. La caratterizzazione spettroscopica di film sottili a base organica è un passaggio preliminare molto diffuso nella ricerca sugli OLED. Questa caratterizzazione è utile a studiare l'idoneità di un materiale per l'uso in un dispositivo e per studiare meccanismi di perdita d'efficienza in un contesto meno complesso rispetto ad un intero *stack* OLED.

La terza pubblicazione, *“Spectral diffusion due to charge carrier relaxation of intermolecular charge-transfer states in donor:acceptor blends of disordered organic semiconductors”* (*“Diffusione spettrale di stati intermolecolari a trasferimento di carica dovuta al rilassamento dei portatori di carica in miscele donatore:accettore di semiconduttori organici disordinati”*), esamina i processi dinamici che governano la luminescenza di stati eccitati intermolecolari a trasferimento di carica (*charge transfer*, CT) in miscele di semiconduttori organici. Lo studio mette in relazione la diffusione spettrale dello spettro d’emissione da stati CT con le dinamiche di rilassamento dei portatori di carica in un materiale caratterizzato da disordine energetico. Ciò fornisce un quadro di riferimento che unifica e giustifica numerose osservazioni sperimentali.

Infine, la quarta pubblicazione, *“Understanding the time dependence of exciton-exciton annihilation ‘constants’ in a TADF system”* (*“Capire la dipendenza temporale delle ‘costanti’ di annichilazione eccitone-eccitone in un sistema TADF”*), si concentra sulle problematiche relative alla valutazione delle dinamiche di annichilazione fra eccitoni tramite misure di fotoluminescenza. Le simulazioni kMC permettono di quantificare accuratamente i coefficienti cinetici dei vari processi d’annichilazione (dipendenti dallo spin degli stati eccitonici coinvolti). L’analisi rivela che, durante misure in stato transiente, questi coefficienti mostrano una dipendenza dal tempo governata dalla diffusività degli eccitoni. Poiché, nei comuni metodi d’analisi, questa dipendenza dal tempo è tipicamente ignota o trascurata, questo studio raccomanda cautela nell’interpretazione dei dati sperimentali – in particolar modo quando i coefficienti di annichilazione così estratti servono a parametrizzare successive simulazioni a livello di dispositivo.

In conclusione, questa tesi fornisce sia una comprensione dei meccanismi microscopici, sia linee guida per la progettazione di dispositivi OLED più efficienti e più stabili, usando un approccio Monte Carlo cinetico per connettere i processi su scala molecolare e le prestazioni dei dispositivi OLED.

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Since the digital revolution of the late 20th century, electronic displays have become a signature of modern times: in the last couple decades, display technology has witnessed a fast, steady development, acquiring an increasing market relevance within which liquid-crystal displays (LCDs) have had a for a long time a dominant share. In recent years, however, the LCD primate has been rapidly eroded by the innovative OLED technology, standing for *organic light emitting diodes* [1, 2]. Compared to LCDs, OLEDs offer a wider colour gamut, increased contrast, lower response times, and reduced energy consumption. In addition, due to the flexibility of organics, OLED devices can be made extremely thin, lightweight and flexible: foldable phones have already hit the market and prototypes for rollable displays have been presented [3, 4]. Nevertheless, low light generation efficiencies, reduced long-term reliability and higher production costs remain some of the main detracting features of the OLED technology. In common fluorescent devices, only 5% of injected electrons at best are converted to usable light. Efficiencies can be increased to 20-30% by using organometallic phosphors or fully organic *thermally activated delayed fluorescence* (TADF) dyes. However, phosphors suffer from long response times and TADF dyes provide an insufficient colour purity. Furthermore, fluorescent and TADF OLEDs suffer from rapid material degradation, and the lifetimes of blue emitters often do not exceed a few hundred hours. The research work presented in this thesis aims at clarifying some factors which affect OLED efficiency, aiding in the search for design principles for efficient and long-lasting OLED devices.

OLED research gathers the joint effort of multiple disciplines: the search for new materials propels organic design and synthesis, while device-level research seeks optimal designs to make the emitters truly shine. Empirical experimentation, however, is often inherently bound to a trial-and-error methodology, whereas a general, deeper understanding of the workings and limitations of OLEDs is imperative to overcome the current challenges. Computational simulation of organic thin films and OLEDs provides then a powerful complementary route. Simulations can be seen as “idealized experiments with an adjustable degree of complexity” [5]. Furthermore, simulations are able to resolve charge and exciton dynamics at the microscopic scale, allowing to look “under the hood” into the processes that collectively determine macroscopic device observables. Because simulation offers a means to examine these processes directly, simulations are complementary to experimental characterisation and enable a deep mechanistic understanding of material and device physics.

The work presented in this thesis focuses on kinetic Monte Carlo simulations at the device scale, aiming at a better understanding of the factors that govern efficiency in OLED devices. The thesis is structured as follows. Part I includes an introduction to the physics of small-molecule organic materials as are usually employed in OLEDs (Chapter 2), to the OLED

technology (Chapter 3), and to relevant modelling techniques (Chapter 4). Part II gives an overview of the contents of this thesis, including a short summary of the constituting publications (Chapter 5) and the author contributions to each of them (Chapter 6). The publications are reproduced in their original form in Part III. Chapter 7 investigates how inhomogeneity at organic-organic interfaces affects the electrooptical behaviour of OLEDs. Chapter 8 reports a joint empirical and simulation study on selected hyperfluorescent devices to clarify the origin of their unexpectedly low efficiency. Chapter 9 the photophysical properties of charge-transfer states in donor:acceptor blends and how they relate to the charge transport dynamics. Finally, Chapter 10 critically considers common approaches to quantifying and modelling efficiency losses by exciton-exciton annihilation, with the aim to improve our mechanistic understanding of the phenomenon. Overall conclusions are drawn in Chapter 11.

PART I
INTRODUCTION

Introduction to the physics of organic semiconductors

2

This chapter describes the properties of organic semiconductor materials starting from the molecular basis, detailed in Section 2.1. To understand the physics of OLEDs, we need to understand the mechanisms involved in the transport of charge carriers, the generation of excitons and the resulting photophysical phenomena. The formalism employed to describe charge transport is presented in Section 2.2, while injection and extraction processes at the electrodes are introduced in Section 2.3. Finally, an overview of relevant photophysical processes is presented in Section 2.4, and a brief description of intermolecular excited states is given in Section 2.5.

2.1 Energy structure of an organic semiconductor

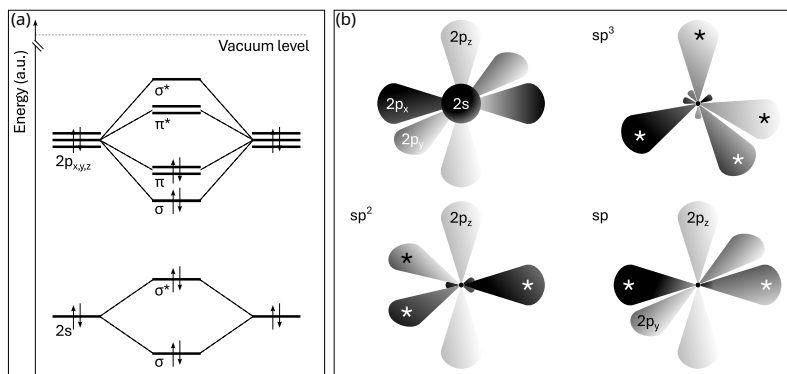
Organic molecules are composed of carbon, hydrogen, and heteroatoms such as nitrogen, oxygen or phosphorus. Atoms are linked by covalent (polar) bonds and chemical and electronic properties of organic materials can be well described by the *linear combination of atomic orbitals* (LCAO) model, according to which atomic orbitals combine into *molecular orbitals* (MO) by constructive or destructive interference of their wavefunctions [6]. Molecular orbitals are characterised by their symmetry: in σ bonds, the electron density is localised along the axis connecting the two atoms, while in π bonds the density is symmetrically localised above and below the axis. Non-bonding orbitals n – not involved in chemical bonding – may also appear when heteroatoms with lone electron pairs are present. An example MO diagram is presented in Figure 2.1. The *molecular ground state* is obtained by filling MOs with electrons to obtain the lowest-energy configuration. Then, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) can be identified.

π -type MOs are responsible for many of the properties that make organic materials suitable for optoelectronic applications: the small splitting between different π -type orbitals (as compared to σ orbitals) produces electronic transitions in the visible range (for light emission) and allows to easily ionise the molecules by adding or removing an electron (for charge transport). Furthermore, adjacent π orbitals may form a *conjugated system*, whereby the superposition of multiple π MOs allows charges to delocalise over large portions of the molecular scaffold, increasing their mobility and further reducing the energy differences between π orbitals.

The vibrations of the molecular scaffold – i.e., the oscillation of atomic nuclei around their equilibrium geometry – generally happen on much longer timescales than electron motion and can be considered separately (*Born-Oppenheimer approximation*). In addition to *electronic* energy levels, we can then define *vibrational (sub)levels* of the molecular scaffold. The

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Figure 2.1: (a) Orbital diagram for two atoms of carbon whose frontier orbitals $2s$ and $2p_{x,y,z}$ combine to generate bonding (σ , π) and antibonding (σ^* , π^*) orbitals. Upward and downward pointing arrows indicate electrons with opposite spin. The core orbital $1s$ is omitted. (b) Representation of the frontier orbitals in an isolated carbon atom (top left) and after sp^3 , sp^2 or sp hybridisation. Hybridised orbitals are marked with a star symbol.



molecular ground state thus corresponds to the lowest vibrational energy level in the lowest electronic energy level. Whereas the energy difference between electronic energy levels is often of the order of 1 eV, the splitting between adjacent vibrational energy levels is much smaller – of the order of 0.1 eV. Thermal energy is too small to promote electronic transitions (differently from inorganic semiconductors) but may suffice to populate higher vibrational states.

2.1.1 Intermolecular interactions in the solid state

The shape and occupation of the MOs determine the electron density surrounding a molecule: electronegative atoms such as oxygen and nitrogen are surrounded by a higher electron density, at the expenses of less electronegative elements such as carbon and hydrogen. The presence of electron-rich and electron-poor regions (also depending on molecular symmetry) results in a *permanent molecular dipole*. Additionally, the molecular electron density may be affected by the presence of external electric dipoles or charges, resulting in an *induced dipole*, while fast fluctuations in the electron density create *instantaneous dipoles*. Solid-state organic semiconductors are characterised by weak intermolecular interactions between such permanent, induced and instantaneous dipole moments.

Crystalline materials display high structural regularity and both short- and long-range order, while *amorphous* organic materials are morphologically disordered. Because of their ordering, crystalline materials may display different properties depending on the crystallographic axis they are probed from. In contrast, amorphous materials are *isotropic*, i.e., their properties do not depend on the probing direction. Additionally, in a crystalline semiconductor MOs may strongly overlap, so that additional charges or excitations may *delocalise* over multiple molecular units. Vice versa, in an amorphous semiconductor charges and excitations are *localised* on individual molecules due to the weak intermolecular interactions and the structural disorder. This thesis focuses on the study of *amorphous organic semiconductors* (AOS).

2.1.2 Charged molecules in the solid state

By electrochemical means, an electron may be added to or removed from a molecule, obtaining an anion or a cation respectively (Figure 2.2a). For

convenience, the *extraction* of an *electron* is rather referred as the *injection* of a *hole*, as the leftover electron gap can be modelled as an analogous quasiparticle with positive charge. Electrons are generally extracted from the HOMO and injected to the LUMO. For an isolated molecule in the gas phase, the energy required to add or remove an electron from a molecule then corresponds to its HOMO or LUMO energy (*Koopman's theorem*). In contrast, in the solid state, a charged molecule polarises its environment and produces small morphological rearrangements of the surrounding molecules, as schematised in Figure 2.2b. The environmental response in turn affects the energy of the charged molecule. Hence, when a charge carrier moves through the material, a “wave” of polarisation and geometrical distortion follows in its wake, which can be interpreted as a quasiparticle called *polaron*.

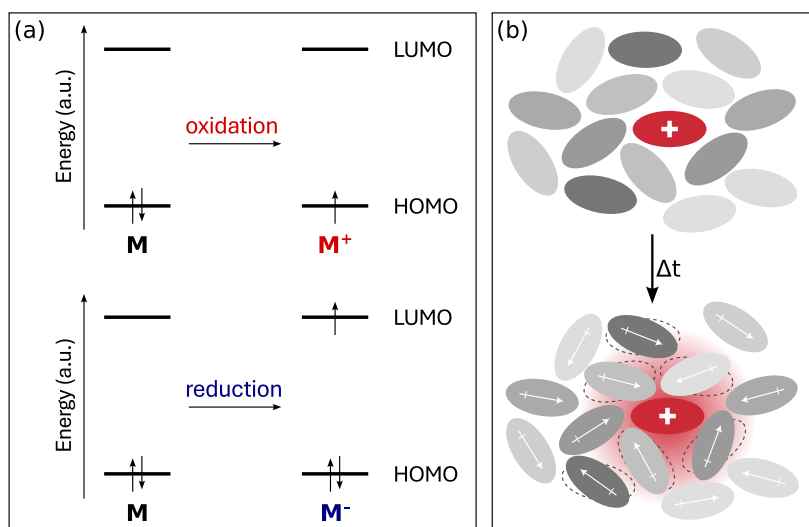


Figure 2.2: (a) Electronic energy level diagram indicating the occupation of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for a neutral molecule M and the corresponding cation M⁺ (top) and anion M⁻ (bottom). (b) Schematic representation of the electrical polarisation and geometrical distortion of the environment surrounding a charged molecule in the solid state.

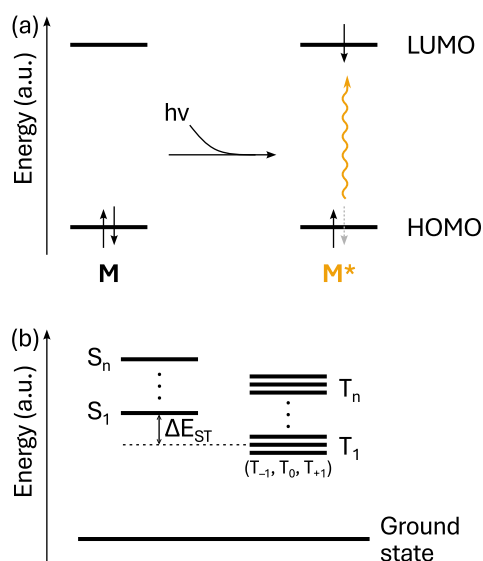
In the solid state, then, we define – rather than a HOMO (LUMO) energy – an *ionisation energy* IE (*electron affinity* EA) corresponding to the energy required to remove an electron from the material (gained by adding an electron to the material) with respect to the *vacuum level*, defined as the energy of a stationary electron a few nanometres from the material surface [7]. The IE can be obtained by measuring the kinetic energy of electrons emitted from the material under ultraviolet excitation (*ultra-violet photoelectron spectroscopy*, UPS). The EA may be measured as the energy of photons emitted under electron irradiation (*inverse photoelectron spectroscopy*, IPES or its low-energy version LEIPS). However, the measurement of EA with these techniques is associated with large uncertainties, so that the value is rather obtained indirectly from the IP and the optical gap (see next section). In addition, electrochemical methods are also available, such as *cyclic voltammetry* (CV). Such measurements are often carried out in solution and do not yield reliable values to evaluate film properties. Finally, first-principles calculations of IE and EA require a refined approach to introduce solid-state effects, the discussion of which is beside the point of this chapter.

2.1.3 Excited states, excitons, optical and electrical gap

In their ground state, organic molecules usually possess an even number of electrons with paired spins, so that the molecular ground state is

normally a *singlet* state with total spin quantum number $S_{GS} = 0$. Energy can be supplied to the molecule to reach an *excited state*. In a first approximation, the lowest-lying excited states correspond to a promotion of one electron from HOMO to LUMO and can be interpreted as a bound electron-hole pair sitting on the same (overall neutral) molecule, as shown in the schematic in Figure 2.3a. The spins of the electrons and the hole may combine to define a *singlet excited state* (S_1) with $S_S = 0$, or three *triplet excited states* (T_1^-, T_1^0, T_1^+) with $S_T = 1$ and $m_s = -1, 0, 1$ respectively, where m_s is the magnetic quantum number, i.e., the projection of the total spin along a chosen axis. The three triplet states are degenerate, unless specific perturbations (e.g. an external magnetic field) are applied. A generic excited state structure is shown in Figure 2.3b.

Figure 2.3: (a) Electronic energy level diagram indicating the occupation of the HOMO and LUMO for a molecule in the ground state (M) and excited state (M^*) in an intuitive approximated picture. (b) Energy level diagram depicting the ground state, the singlet and triplet excited manifolds, and the singlet-triplet energy gap ΔE_{ST} .



The gap between the HOMO and LUMO energy levels (more precisely, the difference between IE and EA) is identified as the *electrical gap*. Due to electron-hole interactions, however, the *optical gap* (i.e. the energy of the excited state proper) is lower. We can write:

$$E_S = E_{EA} - E_{IE} - E_B \quad (2.1)$$

where E_B identifies the *exciton binding energy*, which may range in value from 0.2 eV to over 1 eV [8]. Contributions to the binding energy include a Coulombic term and an exchange term. The Coulombic term is comparable, regardless of the excited state spin, whereas the exchange term is larger for triplet states. As a consequence, triplet states have a larger binding energy than singlet states, resulting in a generally positive *singlet-triplet energy gap* $\Delta E_{ST} = E_{S1} - E_{T1} \geq 0$.

2.1.4 Energetic disorder

While the properties of an AOS are macroscopically isotropic, at the microscopic level each individual molecule experiences a slightly different environment due to the morphological disorder. Furthermore, molecules in the solid state may be physically constrained in different geometries. These individual differences affect the electronic and excitonic energy levels of each molecule, globally resulting in the energetic disorder of

the material. The distribution of molecular energies can be described as a *density of states* (DOS), shown in Figure 2.4. In AOSs, the DOS often shows a Gaussian profile (*Gaussian disorder model*, [9, 10]) centred on the average IE, EA, S_1 or T_1 energy, and with a characteristic width in the range of $\sigma = 0 - 200\text{meV}$ [11, 12]. Charge carriers are more susceptible to polarisation changes in their environment than neutral excitons, thus IE and EA typically show a larger disorder than singlet and triplet exciton energies. Depending on the strength of the intermolecular interactions – particularly in the presence of strong permanent dipole moments – short-range spatial correlations between the energy of neighbouring sites may appear. The resulting disordered energetic panorama has then a globally Gaussian DOS, but is characterised by reduced energy differences between neighbouring sites (*correlated Gaussian disorder model* [13]).

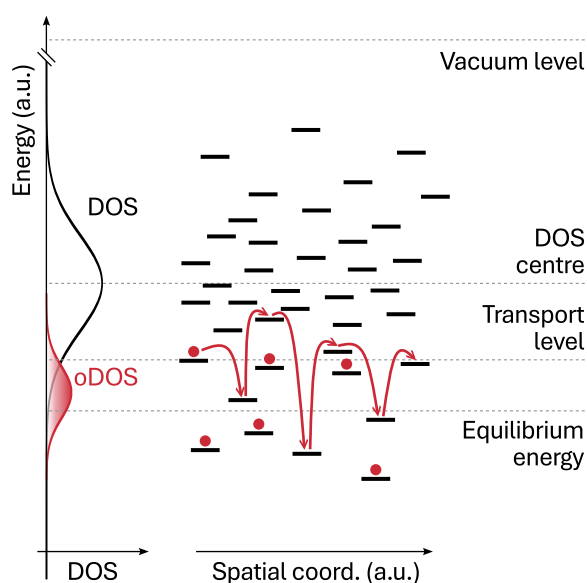


Figure 2.4: Schematic representation of a Gaussian density of states (DOS) and the corresponding occupied density of states (oDOS, enlarged for visibility) as a function of carrier energy. An example trajectory for a charge carrier within the oDOS is indicated: charge transport happens via subsequent hopping between molecular sites with different energies, following a trapping/thermally activated de-trapping mechanism.

When excitons or charge carriers are introduced in a material, their distribution in the DOS defines an *occupied density of states* (oDOS, enlarged for visibility in Figure 2.4). The oDOS is typically centred at a lower energy than the DOS maximum and may have a different width than the DOS. In a system with Gaussian disorder with variance of σ^2 which has reached thermal equilibrium, the oDOS itself can be well described as a Gaussian distribution with equal variance σ^2 , centred at $\Delta E = -\frac{\sigma^2}{k_B T}$ below the DOS centre (where $k_B T$ is the thermal energy) [9]. However, optoelectronic devices often operate under nonequilibrium conditions [14, 15], in which case the oDOS may be centred at higher energies and exhibit a narrower linewidth, as charge carriers or excitons closer to the DOS centre relax faster than those already in the low-energy tail. The oDOS may furthermore evolve in time, for example if charge carriers and excitons relax by diffusing through the material [16, 17]. Stankevych *et al.* [12] have recently shown that, under nonequilibrium conditions, the electronic oDOS width is around 2/3 of the full DOS width for many common organic materials. Melianas *et al.* [18] reported consistent conclusions on the nonequilibrium behaviour of charge transport in interfacial solar cells simulated under reverse bias (conceptually identical to an OLED device).

The relaxation of charge carriers and excitons within the DOS is affected by the diffusion kinetics and may be “frustrated” at low temperatures [14, 19–22], if endothermic hops – occasionally needed to surpass an obstacle in an energetically disordered landscape – are prevented. Frustrated relaxation produces an increase in the average carrier and exciton energy at low temperatures which contrasts with the expected thermal population. This effect is particularly relevant for species with a short-range type diffusion such as charge carriers and triplet excitons, as shown by Athanasopoulos *et al.* [14].

2.2 Charge transport processes

In AOSs, the structural disorder prevents large coupling between energy levels on different molecules, and the small dielectric screening (relative dielectric constant $\epsilon_r \approx 3$) further hinders charge delocalisation. Consequently, charge carriers are generally *localised* on single molecules. Charge transfer then happens by a “hopping mechanism” involving a series of non-coherent, thermally activated charge carrier hops between individual molecules. In particular, Baranovskii *et al.* [23] have demonstrated that hopping charge transport commonly follows a “multiple trapping” mechanism, whereby charge carriers in the low-energy tail of the DOS may reach – through a thermally activated hop – a so-called *transport energy* level closer to the centre of the DOS. Carriers are thereby more mobile due to the larger number of available sites with similar energy and may proceed throughout the material. Eventually, carriers relax back to a low-energy site and repeat the process, as shown in Figure 2.4. Previous modelling efforts [24–27] furthermore revealed that charge transport through a disordered energy landscape is filamentary, as charge carriers do not explore the whole volume of the semiconductor: rather, they seek paths of least resistance formed by the random disposition of low-energy sites.

Charge transport can be more complex in an optoelectronic device, where host:guest blends are common. Emissive guests often act as charge carrier traps, in which case charge transport is trap-limited up to a threshold guest concentration, past which percolative, trap-mediated transport is observed instead [28].

The rate of charge transfer is controlled by (i) the *coupling* between molecular sites, (ii) the *static disorder* due to different molecular energies, geometries and orientations, and (iii) the *dynamic disorder* introduced by the coupling of electronic states with inter- and intramolecular vibrations. Two common expressions for hopping rates are those derived by Miller and Abrahams [29] and by Marcus [30]. When static disorder prevails, hopping rates can be calculated according to the Miller-Abrahams theory, usually in the approximated form derived by Fishchuk *et al.* [31] for $|\Delta E_{ij}| \gg k_B T$, which reads:

$$k_{ij}^{\text{MA}}(r_{ij}) = v_0 \exp(-2\alpha r_{ij}) \exp\left(-\frac{|\Delta E_{ij}| + \Delta E_{ij}}{2k_B T}\right) \quad (2.2)$$

where v_0 is the intrinsic hopping attempt rate¹, α is the inverse wavefunction decay length, r_{ij} is the intersite distance, ΔE_{ij} is the energy difference

1: In some cases, for computational convenience, the *attempt rate at nearest-neighbour distance* v_1 is used instead, and the distance-dependent term reads $\exp[-2\alpha(r_{ij} - a)]$, where a is the nearest-neighbour distance. Hence the prefactors are $v_1 = v_0 \exp(-2\alpha a)$.

between sites and $k_B T$ is the thermal energy. The first exponential expresses the inter-site coupling and the second exponential introduces a parametric dependence on temperature, under the assumption that the transfer for $\Delta E \neq 0$ eV is activated by the absorption or emission of a single phonon (vibrational quantum). The approximated formula can be effectively applied when $\sigma \gg k_B T$ and $\sigma > eaF$, where e is the unit charge, a is the unit-length hop in the direction of the applied electric field and F is the field intensity [32]. Outside the region of validity, the full expression should be used [31, 32].

When dynamic disorder (i.e., environment reorganisation after a hop) prevails, the Marcus theory offers a better description of the hopping rates. The initial and final state are described as a pair of displaced harmonic oscillators characterised by a *reorganisation energy* λ , as shown in Figure 2.5a. The transfer rate reads:

$$k_{ij}^{\text{Ma}} = \frac{|J_{ij}|^2}{\hbar} \sqrt{\frac{\pi}{\lambda k_B T}} \cdot \exp \left[-\frac{(\Delta E_{ij} + \lambda)^2}{4\lambda k_B T} \right] \quad (2.3)$$

where J_{ij} is a coupling term, $k_B T$ is the thermal energy, $\hbar$ is Planck's constant, and ΔE_{ij} is the energy difference between the initial and final site energies. The semiclassical treatment in Equation 2.3 strictly holds when thermal energy is much higher than the vibrational energy of the molecules and $\lambda \gg J$, otherwise a quantum-mechanical treatment of vibrations (Marcus-Levich-Jortner rate) is needed [6].

Figure 2.5b briefly compares the energy difference dependence of Equation 2.2 and Equation 2.3.

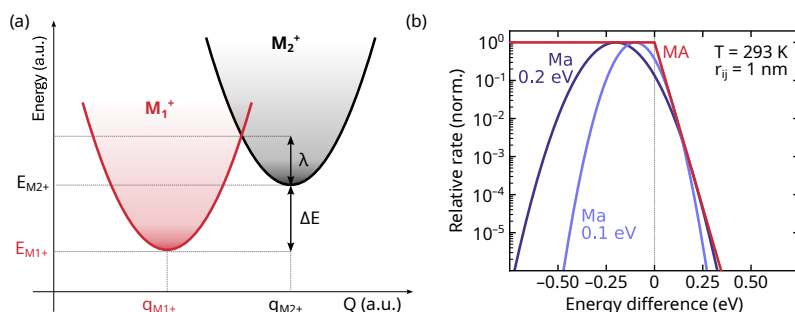


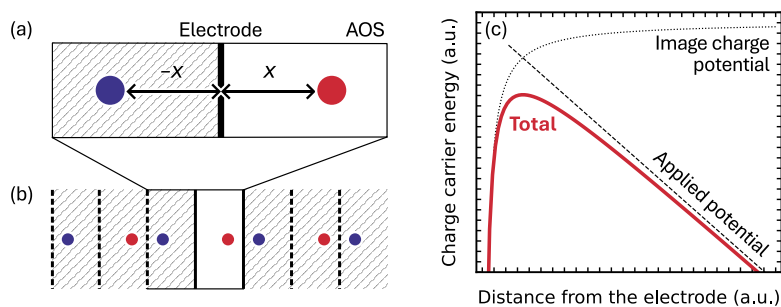
Figure 2.5: (a) Schematic representation of the cationic states of molecules M_1 and M_2 as parabolic energy surfaces shifted along a coordinate Q and energetically offset by a value ΔE . The reorganisation energy λ , according to the Marcus theory, is also indicated. (b) Comparison of charge transfer rates as a function of the energy offset between sites, according to the approximated Miller-Abrahams (MA, red) or Marcus (Ma, light and dark blue) expressions. Marcus rates are calculated for $\lambda = 0.1$ eV (light blue) or 0.2 eV (dark blue).

2.3 Charge injection and extraction at the electrodes

The electrochemical doping of electrons and holes in an organic amorphous semiconductor requires a charge transfer between a (metal) electrode and the organic material. Good injection requires proper alignment between the electrode workfunction and IP or EA of the organic semiconductors, to minimise injection energy barriers. Additionally, the electrostatic interaction between a metal surface and a charge carrier inside an organic material can be modelled as the interaction between the “real” charge carrier and an “image charge” with opposite sign², placed at an equal distance from the metal-organic interface in the opposite

2: Differences in the relative permittivity ϵ_r between adjacent organic layers can also lead to the formation of image charges at organic-organic interfaces, but the effect is generally negligible as most materials have similar ϵ_r in the range of 3-4.

Figure 2.6: (a) Schematic of the spatial relationship between a “real” charge carrier (red, e.g. hole) and an image charge with opposite sign at a metal-organic interface. (b) Schematic of the infinite series of image charges generated by a point charge placed between two facing metal electrodes. (c) Charge carrier energy as a function of the distance from a metal surface, alongside with its components.



direction (Figure 2.6a). This interaction is always attractive and represents the major driving force for charge injection inside organics. The energy required to inject a charge carrier into an organic material is [33]:

$$E = \int_{-\infty}^x \frac{q^2}{4\pi\epsilon_0\epsilon_r} \cdot \frac{1}{(2x')^2} dx' = -\frac{1}{16\pi\epsilon_0\epsilon_r \cdot x} \quad (2.4)$$

The image charge of each charge carrier furthermore interacts with all other charge carriers in the system, most importantly affecting the Coulombic potential close to the electrodes. OLED devices and solar cells possess two facing electrodes, hence each “real” charge interacts with two “first order” image charges. Each image charge in turn acquires an image charge at the opposite electrode, thus generating an infinite, periodic series of image charges (Figure 2.6c). Given that the usual size of devices is in the tens of nanometres, however, the effect from “second-order” image charges and further iterations is negligible.

If an external bias is applied to the organic semiconductor, the potential landscape close to the electrode – including contributions from the applied field and the electrode-charge interactions – shows a maximum, as displayed in Figure 2.6c. Thermionic injection can then be evaluated with the Schottky model [34, 35].

The electric behaviour of a device depends on the efficiency of charge injection into the organic semiconductor: if the electrodes provide an insufficient supply of charge carriers, the electric current transiting through the device is *injection limited*. Vice versa, if the electrodes supply enough charge carriers, the current density in the device will be eventually limited by its own space charge, which shields the applied electric field (*space-charge limited current*). In the latter case, electrodes are called *ohmic*, although misleadingly they do not obey Ohm’s law – rather, the current density J scales with voltage V and device thickness d as $J \propto \frac{V^2}{d^3}$ (Mott-Gurney equation).

2.4 Photophysical processes

The Jablonski diagram in Figure 2.7a presents an overview on intramolecular photophysical processes. Subsection 2.4.1 details radiative photophysical processes, while Subsection 2.4.2 discusses internal conversion and spin-flip processes. Finally, Subsection 2.4.4 describes bimolecular energy transfer processes.

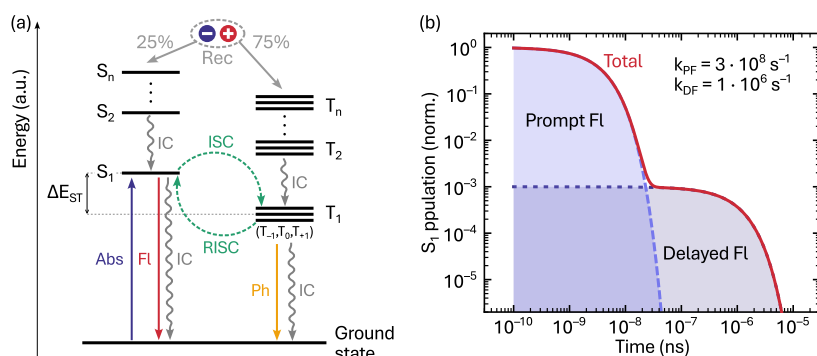


Figure 2.7: (a) Jablonski diagram indicating the relevant monomolecular photophysical processes: absorption (Abs), fluorescent emission (Fl), phosphorescent emission (Ph), internal conversion (IC), intersystem crossing (ISC) and reverse intersystem crossing (RISC). (b) Time-resolved decay of the S_1 population of a TADF emitter (red continuous line), exhibiting the characteristic double-decay, divided in a *prompt* (dashed line) and a *delayed* (dotted line) component.

2.4.1 Radiative processes: absorption and emission

A molecule in the ground state may reach an excited state due to the *absorption* of a photon (*photoexcitation*), or by the injection of an electron and a hole (*electrical excitation*). Depending on the excitation method, the radiative decay from the excited state (via the emission of a photon) is identified as *photoluminescence* (PL) or *electroluminescence* (EL).

The intensity of an electronic transition from state $|i\rangle$ to state $|f\rangle$ can be calculated from Fermi's golden rule as:

$$k_{i \rightarrow f} = \frac{2\pi}{\hbar} \cdot |\langle f | \mathbf{H} | i \rangle|^2 \cdot \rho(E_f) \quad (2.5)$$

where $\hbar$ is the reduced Planck constant and $\mathbf{H}$ is the Hamiltonian operator, of which we consider the off-diagonal element $\langle f | \mathbf{H} | i \rangle$, and $\rho(E_f)$ is the density of states $|f\rangle$ at energy E_f .

Under the Born-Oppenheimer approximation, we decouple electronic motion from molecular vibrations, as the former happen on a much faster timescale, and solve the *electronic* and the *nuclear problem* independently. We then decompose Equation 2.5 in terms of electronic, vibronic and spin contributions:

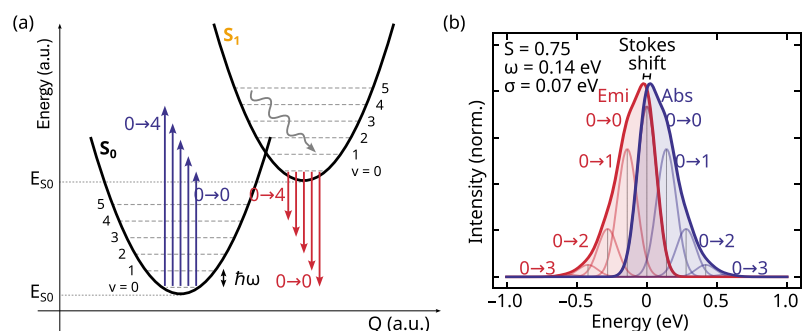
$$k_{i \rightarrow f} = \frac{2\pi}{\hbar} \cdot |\langle \psi_f | e \mathbf{r} | \psi_i \rangle|^2 \cdot |\langle s_f | s_i \rangle|^2 \cdot \quad (2.6)$$

$$\sum_{v,v'} |\langle \chi_{v',f} | \mathbf{H} | \chi_{v,i} \rangle|^2 \cdot \rho(E_f) \quad (2.7)$$

where $|\psi_i\rangle$, $|s_i\rangle$, and $|\chi_{v,i}\rangle$ are the electronic, spin, and vibrational wavefunctions of the initial state i (including the vibrational quantum number v), and likewise for the final state f (with vibrational quantum number v'), e is the elementary charge and $\mathbf{r}$ is the position operator. Due to the electronic overlap term $\langle \psi_f | e \mathbf{r} | \psi_i \rangle$, transitions between orbitals centred on the same molecular fragment (e.g. $\pi \rightarrow \pi^*$ transitions) are more likely than transitions between orbitals farther apart (e.g. charge-transfer transitions).

The spin term $\langle s_f | s_i \rangle$ imposes total spin conservation, allowing only transitions within the same manifold (singlets to singlets, triplets to triplets). In organic semiconductors, only singlet excited states are thus spectroscopically accessible from the singlet ground state. Likewise, the radiative decay is only allowed from a singlet excited state (*fluorescence*), whereas triplets are normally dark. The spin-forbidden radiative decay from triplet states (*phosphorescence*) may be observed in the presence

Figure 2.8: (a) Schematic representation of the first two singlet states (ground state S_0 and first excited state S_1) as parabolic potential energy surfaces offset along an arbitrary coordinate Q . Dashed lines indicate vibronic states with given quantum numbers. Upwards (downwards) pointing straight arrows indicate subsets of the possible vibronically-coupled absorption (emission) processes, the grey wavy arrow indicates fast internal conversion between vibronic states of S_1 . (b) Emission (red) and absorption (blue) spectra resolved in terms of individual vibronic transitions.



of sizable *spin-orbit coupling* (SOC), a relativistic interaction between the magnetic dipole of an electron and its orbital motion inside the electrostatic potential of the nuclei. As the intensity of SOC scales with the fourth power of the atomic number, heavy nuclei are generally required to observe phosphorescence. Careful molecular design allows to obtain sizable SOC also in fully organic molecules, e.g. if the lowest excited states have an intermolecular charge-transfer character.

Finally, the *Franck-Condon factors* $\langle \chi_{v',f} | \mathbf{H} | \chi_{v,i} \rangle$ express how electronic transitions couple with the vibrational motion of the nuclei. The relative intensities of the vibrationally-coupled electronic transitions determine a *vibronic* structure of the emission and absorption spectra, which appear in Figure 2.8a as a set of vertical arrows from and towards different vibronic levels v, v' . Emission only takes place from the lowest vibrational level of the lowest excited state ($S_1, v' = 0$), as *internal conversion* from higher states is a fast process (*Kasha's rule*). We can describe an emission spectrum as the sum of individual electronic-vibronic coupled transitions, as shown in Figure 2.8b. Each transition produces a (Gaussian) peak with a characteristic width σ , offset by one vibrational quantum $\hbar\omega$ from the next peak (assuming ground state and excited state are a pair of displaced, coupled harmonic oscillators with equal vibrational quantum $\hbar\omega$). The different equilibrium geometry between the ground and excited state determines an offset between the 0-0 peak positions in absorption and emission (*Stokes shift*).

2.4.2 Nonradiative processes: internal conversion and spin flip

Decay from an excited state may also happen without the emission of a photon by *internal conversion*. The *energy gap law* relates the internal conversion rate to the energy gap ΔE between the initial and final state:

$$k_{IC} \propto \exp \left(-\gamma \cdot \frac{\Delta E}{\hbar\omega} \right) \quad (2.8)$$

where γ is a constant and $\hbar\omega$ is the vibrational quantum.

As indicated in Figure 2.7a, nonradiative transitions between excited states are also possible, particularly between the lowest singlet and triplet excited states. *Intersystem crossing* (ISC) identifies the conversion of singlet excitons to triplet excitons, whereas the opposite process is called *reverse intersystem crossing* (RISC) converts triplets to singlets. Both processes

are spin-forbidden and commonly mediated by SOC. Being opposite processes, their rates are linked by a Boltzmann factor:

$$\frac{k_{RISC}}{k_{ISC}} = \exp\left(-\frac{\Delta E_{ST}}{k_B T}\right) \quad (2.9)$$

where ΔE_{ST} is the singlet-triplet gap and $k_B T$ is the thermal energy at temperature T . In organic semiconductors, $\Delta E_{ST} > 0$ so that ISC is always favoured over RISC. For RISC to be efficient, a small ΔE_{ST} at most of the order of room-temperature thermal energy (25 meV) is required.

In the presence of a sizable RISC rate, *thermally activated delayed fluorescence* (TADF) may be observed. If a fraction of singlet excitons converted to triplets via ISC reverts to the singlet state via RISC, the transient singlet population shows a characteristic double decay (Figure 2.7b), where the *prompt fluorescence* arises from direct decay from the singlet excited state and the *delayed fluorescence* results from one or more ISC-RISC cycles.

2.4.3 Photoluminescence quantum yield

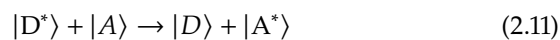
The *photoluminescence quantum yield* (PLQY, η) of an organic emitter is calculated as the ratio between its radiative recombination rate k_r and the sum of all possible decay processes:

$$\eta = \frac{k_r}{\sum k_i} \quad (2.10)$$

The PLQY is normally discussed in a low-excitation regime, when the only channel for nonradiative decay is the intramolecular internal conversion. PLQY can be further reduced in the presence of loss processes due to energy transfer, as described in the next section.

2.4.4 Energy transfer processes

An excited-state molecule (donor, D^*) may transfer its excitation energy to another molecule (acceptor, A) in a process:

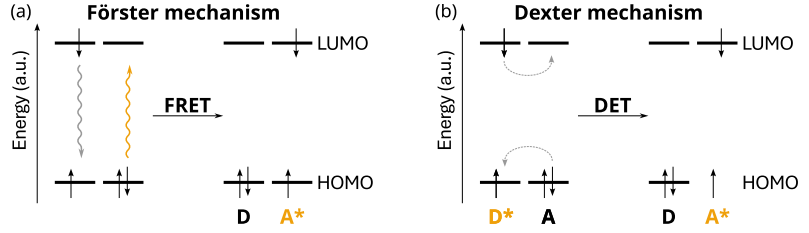


Energy transfer processes are schematised in Figure 2.9a,b.

Energy transfer rates can be calculated via Fermi's golden rule: under different regimes, the *Förster mechanism* (or *Förster resonance energy transfer*, FRET) and the *Dexter mechanism* are obtained. In the Förster mechanism (Figure 2.9a), energy transfer happens via the interaction of molecular transition dipole moments, as if exchanging a “virtual” photon: the donor and acceptor molecules can be interpreted as classical antennae exchanging a signal. Although no real photon is emitted, the donor molecule is required to have a sizable emission in the spectral region where the acceptor absorbs. In the long-field limit, molecules can be treated as point dipoles and the Förster rate reads:

$$k_{D \rightarrow A}^F(r_{DA}) = \frac{1}{\tau_D} \left(\frac{R_0}{r_{DA}} \right)^6 \quad (2.12)$$

Figure 2.9: Schematics for the (a) Förster resonance energy transfer and (b) Dexter energy transfer. (c,d) Schematics for (c) exciton-exciton annihilation or (d) exciton polaron quenching.



where τ_D is the donor excited state lifetime, r_{DA} is the donor-acceptor intermolecular distance, and R_0 is the Förster radius³:

$$R_0^6 \propto \eta_D \cdot n^{-4} \cdot J \cdot \kappa^2 \quad (2.13)$$

where η_D is the PLQY of the donor, n is the refractive index of the medium, J is the spectral overlap between donor absorption and acceptor emission and κ^2 is the orientational factor. The spectral overlap is calculated as:

$$J = \int f_D(\lambda) \cdot \varepsilon_A(\lambda) \cdot \lambda^4 d\lambda \quad (2.14)$$

where f_D is the donor emission spectrum, ε_A is the absorption emission spectrum and λ is the wavelength.

The orientation factor is calculated as:

$$\kappa = \hat{\mu}_D \cdot \hat{\mu}_A - 3(\hat{\mu}_D \cdot \hat{r}_{DA})(\hat{\mu}_A \cdot \hat{r}_{DA}) \quad (2.15)$$

where $\hat{\mu}_i$ indicates the normalised transition dipole moment of the respective fluorophore and $\hat{r}_{DA}$ is the unit vector corresponding to the intermolecular distance. The Förster transfer rate depends in fact on the alignment of the transition dipoles of the donor and acceptor. In most cases, an isotopically averaged value $\kappa^2 = 2/3$ is employed, although it strictly holds only in solution, whereas in the solid state orientations are fixed.

In the *Dexter mechanism*, energy transfer happens via an electron exchange, as depicted in Figure 2.9b. Sizable orbital overlap (hence close contact) is required and the energy transfer rate reads:

$$k_{D \rightarrow A}^D(r_{DA}) = \nu_0 \exp(-2\alpha r_{DA}) \quad (2.16)$$

where ν_0 is the attempt frequency, r_{DA} is again the donor-acceptor distance, and α is the inverse wavefunction decay length.

The steep exponential dependence on intermolecular distance and the usual $(1/\alpha) < 1$ nm makes Dexter transfer a short-range process. Conversely, common Förster radii fall in the 1-5 nm range, hence Förster transfer may be long-range. The Förster mechanism is of particular relevance for energy transfer processes originating from singlet states, which have a short radiative lifetime, while Dexter transfer is relevant for dark, long-lived triplet excitons.

When dealing with energetically disordered systems, the energy transfer parameters (R_0 , ν_0 ...) are usually taken as constants and an exponential (approximated Miller-Abrahams, Equation 2.2) or Gaussian (Marcus-type, Equation 2.3) energy-dependent term is often attached to Equation 2.13 and Equation 2.16.

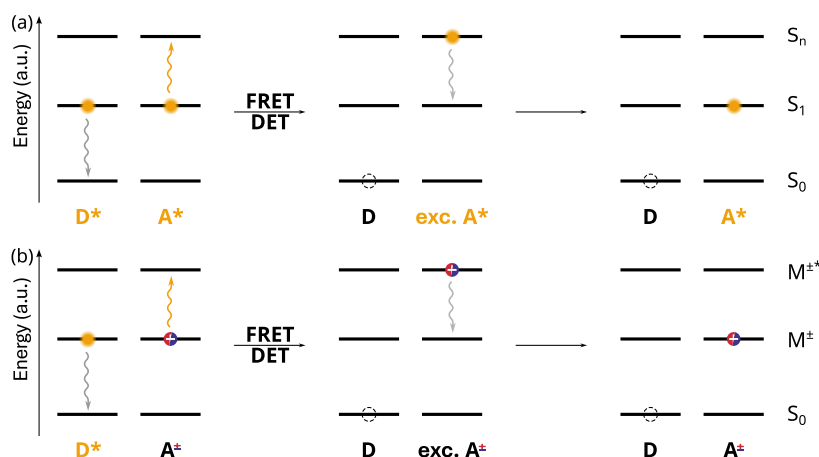


Figure 2.10: Schematics for the (a) exciton-exciton annihilation and (b) exciton polaron quenching processes.

If the acceptor is in the ground state, energy transfer results in the *diffusion* of excitons throughout the material. If the acceptor is a charged or excited molecule, an *exciton-polaron quenching* (EPQ) or *exciton-exciton annihilation* (EEA) event takes place, respectively. A schematic view of these processes is given in Figure 2.10. EPQ (EEA) raises the acceptor to an excited polaronic state (higher excited state), whose extra energy is quickly dispersed to yield back the original state of the acceptor.

Spin conservation imposes that singlet-singlet annihilation results in a singlet state and singlet-triplet annihilation in a triplet state. Triplet-triplet annihilation (TTA) may yield a singlet, triplet or quintet excited state with a 1:3:5 probability ratio, although quintet states may usually be neglected as energetically inaccessible.

EEA can be observed under continuous-wave photoexcitation as a non-linear dependence of the intensity of emitted light on the intensity of the excitation radiation. Likewise, the decay of the transient exciton population after an excitation pulse deviates from a (double) exponential. Kinetic annihilation rates are often extracted by fitting experimental transient photoluminescence profiles to a rate equation model (see Chapter 4) including quadratic annihilation terms [36]. The limitations of this technique are addressed in Section 4.2 and Chapter 10.

Modelling studies have shown that EEA (particularly TTA) is influenced by exciton diffusion [37–40] thus, in a host-guest system, is affected by the energy level alignment [41] and guest concentration [42]. In fact, comparison between kMC simulation and experiment [36, 43] further led to identify two extreme regimes for TTA, i.e. a long-range, Förster-mediated, single-step mechanism versus a short-range, Dexter-mediated, multiple-steps mechanism. Saxena *et al.* [44] have simulated TTA in simple polymer morphologies and in the presence of quenching impurities, highlighting the relevance of filamentary transport also for exciton transport. Similar results have been obtained for TPQ [45, 46].

Although TTA offers a (lossy) pathway to convert dark triplet excitons to emissive singlet excitons in OLEDs, both EPQ and EEA are generally regarded as efficiency loss processes, as the excitation energy of the donor is effectively lost. Due to the large amount of free polarons in an OLED under operation, EPQ is particularly detrimental [45–49]. The reduction of OLED efficiency (“roll-off”) at increasing luminance is instead attributed to EEA due to the larger exciton density [50–54]. For both EPQ and EEA,

the large energy density present on the acceptor before thermalisation often facilitates chemical damage to the material.

2.5 Intermolecular excited states

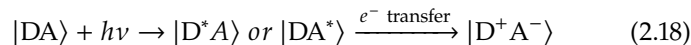
Sufficient interaction between a donor (D) and an acceptor (A) molecule may result in the formation of delocalised *intermolecular excited states*, which can be described as the quantum-mechanical admixture of the local excited states and intermolecular charge-transfer (CT) states:

$$|DA\rangle^* = c_D \cdot |D^*A\rangle + c_A \cdot |DA^*\rangle + c_{CT} \cdot |D^+A^-\rangle \quad (2.17)$$

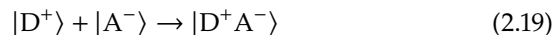
where $|D^*A\rangle$ ($|DA^*\rangle$) is the local donor (acceptor) excited state, $|D^+A^-\rangle$ is a charge-transfer state (neglecting the unlikely $|D^-A^+\rangle$ state), and the coefficients are normalised so that $c_D^2 + c_A^2 + c_{CT}^2 = 1$.

Emission from D:A blends with large IE or EA offset is often observed [55–61]: the intermolecular excited state has then prevalent CT character ($|DA\rangle^* \cong |D^+A^-\rangle$) and can be effectively understood as an emissive electron-hole pair. In recent literature, the names “CT state” and “exciplex” are used interchangeably to identify such intermolecular excited states, although the latter term was historically reserved for those with some covalent character.

In a D:A system, it is possible to reach a CT states by photoexcitation of either component, followed by electron transfer:



or by electrical generation of anions (A^-) and cations (D^+):



As the molecules involved only interact in the excited state, no new absorption features appear. Vice versa, emission from CT states appears as a broad, featureless peak due to an intrinsically large linewidth. The vibronic structure has seldom been analysed and results appear to be widely dependent on the chosen system [62]. The lifetime of CT states is characteristically longer than that of local excited states due to the scarce overlap between the electron and hole wavefunction. The same scarce overlap often grants intermolecular excited states a reduced ΔE_{ST} [58, 63, 64], hence high RISC rates [58–61, 64–66].

Introduction to OLEDs

This chapter gives an introduction to organic light emitting diodes (OLED)s. Section 3.1 provides a brief history of OLEDs, while Section 3.2 describes the structure and working principles of these devices. Section 3.3 discusses the factors determining OLED efficiency, while Section 3.4 addresses the issue of the lifetime. Finally, Section 3.5 gives an overview on the OLED fabrication techniques.

3.1 A brief history of OLEDs

Organic light emitting diodes (OLEDs) exploit the *electroluminescence* effect, that is the emission of visible light due to the application of an external voltage. While the effect has been known for over a century in inorganic materials [67] and over seventy years in organics [68], in both cases applications have taken several decades to come into being [69].

Electroluminescence from organic materials was first observed in the early 1950s at the Nancy-Université (Nancy, France) by André Bernanose and coworkers [68], who worked on thin layers of acridine and carbazole deposited on cellulose films. The work of Pope [70], Helfrich and Schneider [71, 72], and others [73–75], expanded the portfolio of electroluminescent materials to organic crystals, particularly anthracene. These first experiments were far from viable devices: due to the large crystal thickness and the poor quality of electrical contacts, observing light emission required the application of humongous voltages of hundreds to thousands of volts at kilohertz frequencies. In 1975, Roger Partridge patented a polymer-based device [76] whose structure was remarkably close to modern-day designs. Partridge correctly identified the need for an amorphous film and proper energy level alignment between the electrodes and the emissive medium as requirements for viable OLEDs. By the time his results became publicly available in 1983 [77–80], electroluminescence under low applied voltages had been achieved by Vincett and Roberts [81, 82] in thin films of amorphous anthracene sandwiched between an aluminium cathode and a gold anode, as is still commonly done to this day. Further advancements were made by Tang and VanSlyke employing vacuum-deposited organic thin films [83] and by Burroughes *et al.* with spin-coated polymers [84]. In the following years, the interest for the new technology was sparked and multilayer structures (commonly produced by vacuum evaporation) increased in complexity [85], while the library of available organic compounds progressively grew. Electroluminescence from intermolecular excited states was also reported both at an interface [55] and in a blend [86].

With the first commercial applications dating as far as the late 1990s [87, 88], OLED usage in electronic appliances has seen a steady increase during the first decades of the XXI century, representing nowadays a good share of the display market. Red, green and blue OLEDs can be

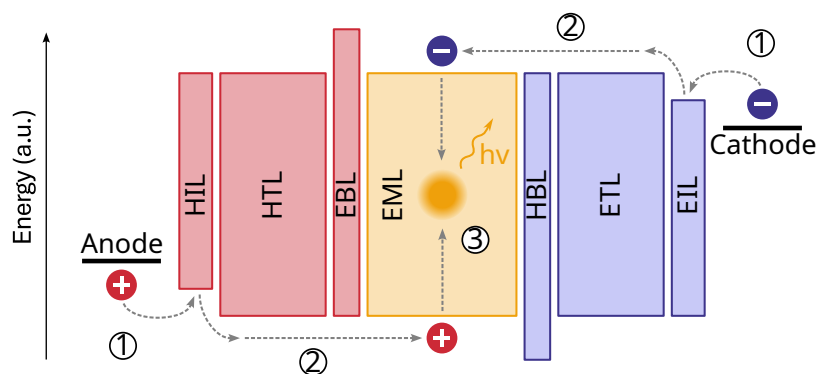
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used in three-colour pixels, while “white” OLEDs with a broad emission spectrum have been developed for general illumination. Intense research and investments are funnelled every year into this promising technology, whose full potential has not yet been achieved. For example, blue OLEDs are to this day inferior in terms of both efficiency and operative lifetime, compared to red and green devices, and the development of efficient and stable blue organic fluorophores is an open challenge.

3.2 Structure of an OLED

An OLED is composed of a thin film of amorphous organic semiconductor sandwiched between two electrodes. Figure 3.1 gives an overview on the physical processes involved in OLED operation, namely charge injection, charge transport and recombination. Due to the applied electric field, holes are injected at the anode and electrons at the cathode. Under the effect of the applied voltage, the charge carriers migrate through the device toward the opposite electrode. When an electron and a hole meet, their radiative recombination results in the emission of light.

Figure 3.1: Schematic representation of an OLED stack displaying the layer sequence with their abbreviations and the physical processes leading to light emission. From left to right: anode, hole injection layer (HIL), hole transport layers (HTL), electron blocking layer (EBL), emissive layer (EML), hole blocking layer (HBL), electron transport layers (ETL), electron injection layer (EIL), and cathode. Dashed grey arrows indicate the ideal path charge carriers take upon (1) injection at the electrodes, (2) charge transport and (3) recombination and light emission.



Modern OLEDs are multilayer structures, where each layer is composed of a neat, doped or blended organic material optimised for a specific function. Figure 3.1 shows, from left to right, the anode, a *hole injection layer* (HIL) to favour the doping of the material from the electrode, a *hole transport layer* (HTL), and an *electron blocking layer* (EBL) to confine electrons within the next *emissive layer* (EML). In the EML charge carriers are expected to encounter and recombine to form excitons, which will decay by emitting light. Symmetrically follow a number of layers optimised for electron injection and transport and the cathode. While injection and transport layers are often neat films, in the EML the emitter material is commonly doped in a charge-transporting host to avoid concentration quenching. Not all device structures may include all layers, and one layer may serve multiple functions. In fact, a champion single-layer, blue OLED device with over 27% EQE (see Section 3.3) has been recently achieved [89] by careful material and layer design.

3.3 Efficiency of OLED devices

The efficiency of OLED devices is quantified via two figures of merit [90], namely the *internal quantum efficiency* (η_{IQE}) – that is the fraction of

charge carriers that are converted into photons inside the device – and the *external quantum efficiency* (η_{EQE}) – that is, the fraction of charge carriers which result into photons *that escape the device* and can be perceived by a detector or an eye. Whereas η_{EQE} can be experimentally measured, η_{IQE} is not directly accessible. On the contrary, device modelling allows to obtain both η_{IQE} and η_{out} , as described in Chapter 4.

The η_{IQE} can be separated into a number of contributions, representing the ideal steps that convert injected charge carriers into photons:

- ▶ the *exciton generation probability* (η_{gen}), is the chance that two injected opposite-sign carriers and generate an exciton,
- ▶ the *singlet-to-triplet ratio* (η_{ST}) relates to the probability that a generated exciton is emissive,
- ▶ the *emission efficiency* (η_r) is the probability that the exciton decays radiatively by emitting a photon.

Overall, we can write:

$$\eta_{IQE} = \eta_{gen} \cdot \eta_{ST} \cdot \eta_r \quad (3.1)$$

Finally, the *outcoupling efficiency* (η_{out}) is the probability that a photon escapes the device (normally $\leq 30\%$, see Subsection 3.3.4) and thus connect η_{IQE} and η_{EQE} as:

$$\eta_{EQE} = \eta_{IQE} \cdot \eta_{out} \quad (3.2)$$

Each term of Equation 3.1 and Equation 3.2 shall be analysed separately in the following.

3.3.1 Generation efficiency and charge balance

To achieve a high generation efficiency (η_{gen}), charge carriers with opposite sign must be able to meet, which can be best achieved if a roughly equal number of electrons and holes are injected into the EML and meet towards the centre of the layer, rather than at the edges [91–93]. Charge balance inside the EML is a crucial prerequisite for efficient OLED operation, albeit a nontrivial one to achieve in practice: many organic materials are in fact good hole conductors but do not conduct well electrons [94, 95], leading to unbalanced charge transport.

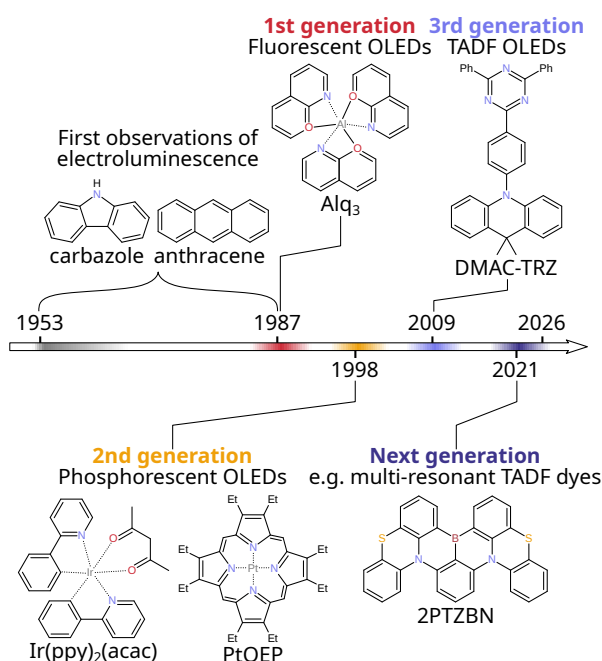
Unbalanced charge transport favours the accumulation of charge carriers at the sides of the EML, enhancing losses by exciton-polaron quenching [96]. Charge imbalance also shifts the *recombination zone* towards the sides of the device, which can alter the outcoupling efficiency (η_{out}) [97–99] or result in interfacial emission [96], a parasitic process which “pollutes” the colour point of the device by adding an undesired and often uncontrolled source of emission.

Various strategies can be implemented in order to achieve balanced charge transport: for example, the transport materials can be engineered via chemical modifications [100], additional layers may be introduced to favour injection of the minority carrier [101], or a cohost blend may be used to separate efficient electron and hole transport on different materials [102]. Research on this topic is ongoing.

3.3.2 Excited state spins and the OLED generations

Electrons and holes are injected into a semiconductor with a random spin up or spin down and may then recombine into a singlet or a triplet excited state with a 1:3 ratio [6], according to spin statistics. Specific systems with singlet yields in excess of 25% have been occasionally reported [103], but are not commonly used. The 25% probability to generate an emissive singlet state posed a hard limit on the efficiency of purely fluorescent “first generation” OLEDs, developed in the late 1980s [83]. OLED research has since progressed via several “generations” to optimise η_{ST} through emitter design, as schematically shown in Figure 3.2.

Figure 3.2: Timeline of the OLED generations and representative emitters.



To overcome the 25% barrier, Baldo *et al.* introduced the concept of “triplet gathering” [104], triggering the “second generation” of OLED devices based on phosphorescent emitters. Phosphors manage $\eta_{ST} = 100\%$ as a result of fast intersystem crossing [105, 106], converting all singlet excitons to emissive triplets. Phosphorescence is however a spin-forbidden process: efficient phosphors must incorporate heavy atoms such as platinum and iridium. This requirement increases material cost and draws upon a finite, non-sustainable resource. Additionally, low triplet emission rates translate to long lifetimes, which increase response times and favour energy transfer processes, leading to efficiency losses and material degradation. Nevertheless, blue phosphorescent OLEDs outperform fluorescent devices and represent the industrial standard to this day.

Triplet-triplet annihilation (TTA) and thermally activated delayed fluorescence (TADF) were later identified as candidate solutions to convert non-emissive triplet excitons into emissive singlets. “Sacrificing” a triplet state via TTA gains a 25% chance of converting the surviving triplet to a singlet exciton, yielding a maximum $\eta_{ST} = 62.5\%$ [107–112]. Conversely, TADF exploits thermally activated *reverse intersystem crossing* (RISC, see Subsection 2.4.2) to convert triplet states into emissive singlets, leading to a potential $\eta_{ST} = 100\%$. First observed in 1929 by Frances Perrin [113] and later in 1961 by Parker and Hatchard on eosin solutions [114], TADF

was brought to prominence in the OLED field in the late 2000s, thanks to the pioneering work of the Adachi group [115]. TADF underlies the “third generation” of OLED devices: red, blue and green devices with $\eta_{\text{EQE}} > 20\%$ have been obtained [116–126]. Although RISC involves a spin-forbidden transition, careful emitter design lifts the requirement for heavy atoms: the spatial separation of the electron and hole wavefunctions on distinct portions of the molecular scaffold minimises the singlet-triplet energy gap [127–129], granting a sizable RISC rate (see Equation 2.9). In such donor-acceptor type emitters, the charge-transfer character of excited states leads however to undesirably broad emission spectra [130]. More recently, *multiresonant* TADF (MR-TADF) materials [131] have been developed: through a short-range separation between the electron and hole wavefunctions, localised on alternated atoms of a bidimensional conjugated system, MR-TADF dyes pair RISC capabilities with very narrow emission spectra. On the downside, the enforced planarity of MR-TADF systems encourages aggregation and lowers the threshold for concentration quenching [132]. In terms of raw triplet recycling capabilities, MR-TADF dyes are furthermore still inferior to donor-acceptor TADF dyes [131–136]. Donor:acceptor blends have also demonstrated promising RISC capabilities [58, 61, 65, 66] from intermolecular excited states with charge-transfer character (Section 2.5). Because of the large separation between the electron and hole wavefunctions, such blends often surpass regular TADF dyes in terms of raw triplet recycling capabilities [58, 60, 61, 65] although, for the same reason, emission rates (hence PLQY) are low and their emission spectra rather broad. Champion devices still top $\eta_{\text{EQE}} > 20\%$ [66].

The most recent “generation 3.5” is based on the “hyperfluorescence” (HF) approach [137, 138], which relies on the synergistic combination of the triplet gathering capabilities of a TADF *sensitiser* and the fast, narrowband emission of a fluorescent *terminal emitter*. Singlet excitons are generated on the sensitiser and transferred towards the terminal emitter via the Förster mechanism; Dexter-mediated triplet transfer is detrimental [39, 139]. While HF devices may achieve $\eta_{\text{EQE}} > 20\%$ [138, 140, 141], they seldom outshine corresponding devices containing the sensitiser alone [142, 143], an issue which is approached in Chapter 8. The analogous “hyperphosphorescent” [144] approach, where the sensitiser is a phosphor, suffers from similar drawbacks as phosphorescent devices. Conversely, efficient blue, green [102, 145, 146] and white [147–149] OLEDs have been fabricated by substituting the host and sensitiser with a bipolar cohost capable of RISC, in which the terminal emitter is doped. Electron and hole transport can be then separately fine-tuned on the cohost components, overcoming the need for a single host with good transport properties for both carriers.

3.3.3 Recombination efficiency and excitonic losses

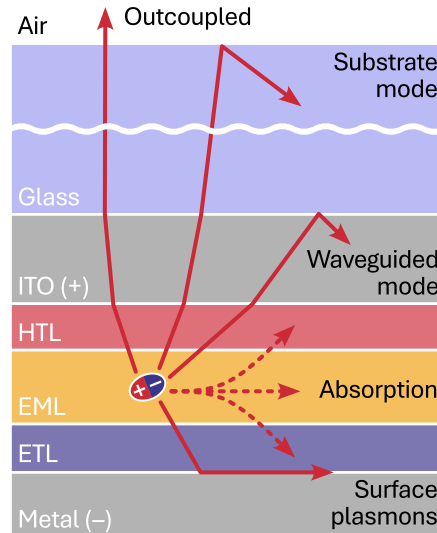
The PLQY (see Subsection 2.4.3) is commonly employed to estimate η_r , as the same factors which limit photoluminescence efficiency will also be present under electrical excitation, including losses via internal conversion to the ground state and singlet exciton conversion to dark triplet states. Detrimental intermolecular processes also include losses via *exciton-exciton annihilation* (EEA) and *exciton-polaron quenching* (EPQ),

described in Subsection 2.4.4. EPQ (EEA) is favoured in the presence of a high charge carrier (exciton) density, as the average distance between the involved species decreases. In a scenario with strong charge imbalance, device efficiency will then be undermined not only by a reduced η_{gen} , but also by enhanced EPQ leading to decreased η_r . For example, triplet-polaron quenching (TPQ) has been often identified as the main loss mechanism in phosphorescent OLEDs [47, 150, 151]. At the same time, EEA represents the primary cause for the OLED efficiency roll-off at high luminance, when the exciton density leads on average to sufficiently short exciton-exciton distances [47, 50–54, 150–152]. Such losses can however be reduced by effective triplet confinement via energy level engineering [41]. Interestingly, a simulation study by van Eersel *et al.* [153] identified a “compensation mechanism” between losses by EPQ and EEA: reducing EPQ yields a higher exciton density which in turn favours EEA losses, thus decreasing the η_r gain.

3.3.4 Outcoupling efficiency

The outcoupling efficiency η_{out} refers to the probability that a photon generated inside the OLED stack escapes the device, usually from a transparent indium-tin oxide (ITO) anode capped in glass. The $\sim 10^2$ nm of organic material and the few micrometres of inorganics on top constitute an optical microcavity [154, 155]: the outcoupling efficiency η_{out} is reduced by several optical loss processes (indicated in Figure 3.3) such as internal reflection at the glass-air interface (*substrate mode*) and at the ITO-glass interface (*waveguided mode*), light *absorption* from the layers, and coupling to the metal electrodes (*plasmon mode*).

Figure 3.3: Example OLED stack and relevant optical processes inside the microcavity.



The refraction index of the organic layers ($n = 1.5 - 1.6$) allows to estimate a maximum $\eta_{\text{out}} \approx \frac{1}{(2n^2)} \approx 20\%$ [156, 157], thus representing a “soft cap” for OLED efficiency, assuming unitary IQE. More precisely, η_{out} depends on the wavelength of the emitted photons (dependent on the emitter), as well as the position within the device where the photon is emitted (related to the layer thickness and charge transport efficiency), the emission angle (related to the molecular orientation of the emitter), plus the refraction index and absorption coefficients of all layers. For

example, η_{out} can be raised by enforcing a favourable orientation of the emitter at the molecular scale [158]. Optical modelling tools may also be used to optimise device structures as shown in Refs. [155, 159]. Additional outcoupling structures can be placed either inside the device stack (e.g. scattering layers, corrugated diffraction layers) or outside it (e.g. arrays of microlenses, Bragg mirrors).

3.3.5 Efficiency roll-off

The efficiency of an OLED device decreases at increasing luminance (intensity of light output), a phenomenon identified as *efficiency roll-off*. Higher luminance is obtained by increasing the applied voltage, resulting in a higher current density, thus higher charge carrier and exciton densities within the device. Higher charge and exciton densities however favour losses by EPQ and EEA. Particularly, singlet-singlet annihilation and singlet-triplet annihilation have been identified as the main causes of the roll-off in fluorescent devices, including both “first generation” fluorescent devices and TADF devices [50–54]. In the presence of charge imbalance, *singlet-polaron quenching* (SPQ) may also contribute to the roll-off to a large extent [49], while in phosphorescent devices *triplet-polaron quenching* (TPQ) is the prevalent loss mechanism [45–47, 151].

3.4 Lifetime and degradation

Under constant current, the luminance of an OLED device decreases in time, while the bias required to drive the device increases [160–162]. The luminance drop has been shown to primarily arise from a reduction in the exciton generation efficiency (η_{gen}), rather than the recombination efficiency (η_{r}), a picture consistent with the progressive creation of deep, dark carrier traps [161, 163, 164] as a result of irreversible (electro)chemical and morphological damage to the organic materials. Material degradation is often associated with the transient highly-excited species generated by EPQ and EEA processes [48, 49, 165], particularly TPQ [48, 150]: the large energy density present on the acceptor before thermalisation may exceed bond dissociation energies and prompt electro- or photochemical damage to the material, leaving non-emissive, trapping sites inside the material thus reducing the device lifetime [108, 166–170]. Modelling efforts have furthermore shown that charge transport in OLED device is not homogeneous: due to energetic disorder (see Subsection 2.1.4), current through the device is characteristically filamentary as charge carriers follow percolation paths formed by the random distribution of low-energy sites [24, 26, 27]. Shen and Giebink have associated such locally increased charge (hence exciton) density with localised, inhomogeneous device degradation [25].

In terms of stability, OLEDs are to this day far inferior to LCD screens: lifetimes for red, green and blue OLED are limited to few hundreds or thousands of hours at most [168], particularly for blue-emitting devices [91, 130, 171] because of the high photon energies involved. Lifetime enhancement of OLED devices is still a widely open topic for research.

Optimising stacks to run on lower driving currents implicitly reduces the risk of material degradation and the overall power consumption.

3.5 Fabrication of OLED devices

The fabrication of OLED stacks requires the sequential deposition of the active layers. A common technique is *physical vacuum deposition* (PVD), involving the controlled heating of a material source under ultra-high vacuum. For materials which cannot be directly deposited, chemical precursors may be evaporated instead and made to react *in situ* (*chemical vapour deposition*). Material purity and quality of the vacuum are paramount to ensure functionality and reproducibility of devices. Pixels are defined by the application of photolithographed shadow-masks, which obstruct the path between the material source and the substrate.

PVD and CVD have serious drawbacks: by design, large amounts of precious organics end up on the mask and are wasted at each run. Furthermore, for devices which require a whole panel apiece (e.g., large television screens), one defect may lead to discard the whole panel, raising consumer prices to cover for losses. The expensive vacuum machinery involved in the process inherently restricts the maximum size of devices that can be fabricated.

To address these fabrication challenges, focus has recently shifted towards processing from solution [172, 173]. Chemical design enables to engineer the solubility of organic materials, allowing direct deposition on the substrate via printing and coating techniques such as inkjet printing or roll-to-roll, master-blade and spin coating. In inkjet printing, tiny drops of material are deposited on a moving substrate, which can be performed on an industrial scale [174–176]. In spin-coating the precursor solution is dropped on a rotating substrate to accelerate drying and favour the formation of a homogeneous film. Solution-processing only requires an inert atmosphere, rather than high vacuum conditions, and is inherently more efficient than PVD in terms of material and energy consumption, since the material is only coated where needed. Solution processing also opens the way to new classes of materials whose molecular weight is too large for PVD, e.g. emissive polymers and dendrimers. Restrictions on maximum substrate size are also partly lifted. However, several new variables enter the game, such as material solubility and solvent viscosity, evaporation rate and wetting ability, plus drying and annealing conditions to ensure solvents are removed. Such requirements add a further layer of complexity in the choice of material and solvent combinations.

To this day, the performances of solution-processed OLEDs are yet inferior to those of analogue devices produced by PVD [172, 177, 178] and furthermore show reduced stability and lifetime [179]. Several potential issues have been pointed out: solvent-solute interaction may impact morphological aspects, e.g. favouring the formation of aggregates [180–182] or leading to roughness or intermixing at the organic-organic interfaces by partial redissolution of the underlying material upon deposition of the next layer [183–186]. Vice versa, vacuum deposition yields flat and homogeneous interfaces between organic layers [187–189], save for spontaneous organisation of a layer due to interactions with the substrate

[190–192]. Additional substances such as solvents and impurities may impact on charge transport.

Although simulation studies have approached the issue of the decreased performances in solution-processed OLEDs compared to vacuum-evaporated devices, precise agreement with experiment has not been yet reached. For example, Sanderson *et al.* [193] obtained realistic film morphologies from molecular dynamics simulations of material deposition and performed kinetic Monte Carlo simulations informed by first-principle calculations. However, no significant differences were observed between devices with morphologies obtained by (simulated) vacuum-deposition or (simulated) solution-processing. This indicates that both deeper empirical characterisation and further refinements of the simulation techniques methodologies are required.

Modelling techniques

Over the last decades, numerous models have been developed to study the charge transport and photophysical properties of organic semiconductors. Figure 4.1 schematically compares some common approaches. Basic physics can be reproduced by representing the organic semiconductor as a continuum, neglecting the disordered and discrete nature of the material, such as in the drift-diffusion approach for charge transport (Section 4.1) and in the rate equation description of photophysics (Section 4.2). A drift-diffusion simulation typically relies on a monodimensional description of the device, represented as a stack of homogeneous layers in which material properties and charge carrier or exciton density vary continuously, as schematised in Figure 4.1a. These models exploit a small number of effective parameters such as charge mobility, diffusion coefficients, and photophysical coefficients, which conceptually emerge from a spatial averaging of material properties. Models are usually parametrised on a case-by-case basis by comparison with experiment, thus lack predictive power. The calculation is however extremely lightweight, and equations can be conveniently extended to include additional processes such as charge trapping and heat or ion transport.

However, for a more accurate description of organic materials, modelling must explicitly include the effects of spatial inhomogeneities, energetic disorder, and bimolecular loss processes. Mesoscale simulation techniques, introduced in Section 4.3 enable to connect “microscopic” material properties – such as the frontier orbital energy levels of materials – with macroscopic observables – for example, the current density through a device. Techniques such as Master Equation (Subsection 4.3.1) and kinetic Monte Carlo (Subsection 4.3.2) enable a full three-dimensional description of the material as a collection of molecular sites. While much more computationally demanding, these techniques offer superior precision and flexibility in exchange. The next development of modelling approaches is expected improve on the accuracy of the description by lifting the “molecular site” approximation and explicitly considering size and orientation of molecular components.

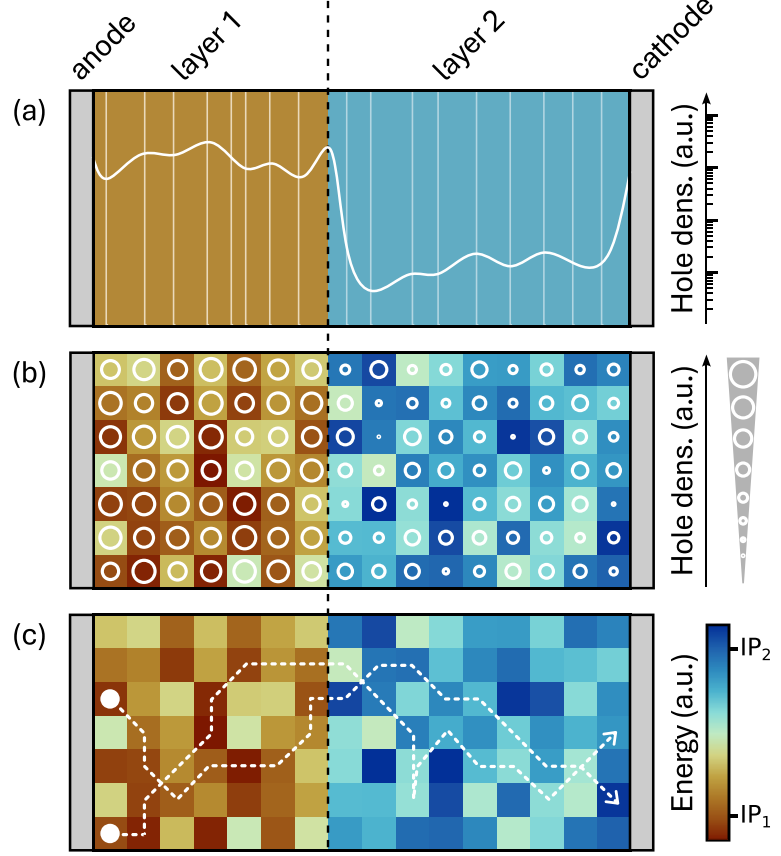
Finally, optical models – not treated in this chapter as they are not relevant to the present thesis – allow to calculate the light outcoupling efficiency due to microcavity effects and can be coupled as a final step after the simulation of electronic and excitonic behaviour of the device.

4.1 Drift-diffusion (DD)

Macroscopically, charge transport can be considered the result of the combined motion of directed charge transfer under the effect of an applied field (*carrier drift*) and of Brownian-type *diffusion*, isotropic in

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Figure 4.1: Schematic representation of the description of charge transport in a bi-layer, according to (a) 1D drift-diffusion, (b) master equation and (c) kinetic Monte Carlo techniques. In a 1D drift-diffusion model (a), charge density is described as a continuum distribution (white line). The solved master equation (b) instead returns an occupation probability for each site, indicated by white circles of different sizes and dependent on the site energy (heatmap). Kinetic Monte Carlo (c) returns real-time occupation of charge carriers on the lattice, which can then be averaged to obtain the spatially resolved charge density. Figure freely adapted from Ref. [194].



principle. The *drift current* and the *diffusion current* can be calculated as:

$$\mathbf{J}_{\text{drift}} = q(n\mu_n - p\mu_p)\nabla V \quad \mathbf{J}_{\text{diffusion}} = q \cdot (D_n\nabla n + D_p\nabla p) \quad (4.1)$$

where q is the unit charge, n (p) is the electron (hole) number density with gradient ∇n (∇p), while μ_n (μ_p) is the electron (hole) mobility, D_p (D_n) is the electron (hole) diffusion coefficient, and ∇V is the applied field. Diffusion coefficients and mobilities are connected by Einstein's law as:

$$D_{n,p} = \mu_{n,p} \frac{k_B T}{q} \quad (4.2)$$

where additionally $k_B T$ is the thermal energy.

Further, the Poisson equation relates the electrical potential to the number densities of electrons (n) and holes (p) as:

$$\nabla^2 V = \frac{q}{\epsilon_0 \epsilon_r} (n - p) \quad (4.3)$$

where ϵ_0 is the dielectric permittivity of the vacuum and ϵ_r the relative permittivity of the medium, which is $\epsilon_r \approx 3 - 4$ for most organic semiconductors.

Modelling involves the self-consistent (numerical) solution of the Poisson equation and a set of differential equation which describe the evolution of charge density as a function of time and position within the device:

$$\frac{\partial i}{\partial t} = \nabla \cdot \mathbf{J}_{\text{total},i} + G(i) - R(n, p) \quad (4.4)$$

where i may be n (electrons) or p (holes), $G(i)$ is a generation term, e.g. representing charge injection at the electrodes, and $R(n, p)$ is a recombination term. Depending on the properties of the material, a Langevin [195] or Shockley-Read-Hall [196] rate expression for recombination may be used, otherwise the rate may be left as a fitting parameter.

The main advantage of drift-diffusion models lies in their computational lightweight and the fact that computational effort does not scale with system size or carrier density, differently from mesoscale approaches, hence DD models are particularly attractive for large-scale or high carrier density cases.

DD models are able to reproduce the basic physics of organic semiconductors, e.g. differentiating between injection limited and space-charge limited current behaviour [197]. Simulations of simple OLED devices have also been carried out using the DD approach [198]. However, due to the simplified approach to charge transport, DD modelling faces the challenge of accurately describing the complex dependencies of charge mobility and other parameters on field, temperature, charge density, etc. [24]. Reliance on effective parameters derived from fitting empirical data reduces the predictive power of the DD approach: for example, a parametrisation obtained under steady-state conditions does not allow to describe non-equilibrium, time-dependent processes such as charge carrier relaxation, and vice versa. Furthermore, as DD models are usually one-dimensional, energetic disorder can only be accounted for as an effective change in mobility and the inherent spatial inhomogeneity of charge transport is not represented at all.

For the same reason, DD models struggle to include non-local processes such as exciton diffusion, exciton-exciton annihilation and exciton-polaron quenching: these processes can only be treated as efficient “loss rates” fitted to empirical data. Lacking a direct dependence on material energy levels, energy barriers between layers are also not easily included, although an improved DD method has been proposed by Cottaar *et al.* [199]. Zeder *et al.* [200] introduced a hybrid methodology in which a 1D-DD for the calculation of carrier densities is coupled to a Master Equation model for a more physically sound treatment of exciton diffusion and losses.

4.2 Rate equation (RE)

Similarly to the DD approach to charge transport, it is possible to describe the photophysics of a system via a number of coupled differential equations. Commonly used formulas are given in Equation 4.5 and Equation 4.6:

$$\begin{cases} \frac{\partial S}{\partial t} = G_S - (k_{r,S} + k_{IC,S}) \cdot S - k_{ISC} \cdot S + k_{RISC} \cdot T + \\ \quad - k_{SSA} \cdot S^2 - k_{STA} \cdot S \cdot T + \frac{1}{4} k_{TTA} \cdot T^2 - k_{SPQ} \cdot S \cdot (n + p) \quad (4.5) \\ \frac{\partial T}{\partial t} = G_T - (k_{r,T} + k_{IC,T}) \cdot T + k_{ISC} \cdot S - k_{RISC} \cdot T + \\ \quad - \frac{5}{4} k_{TTA} \cdot T^2 - k_{TPQ} \cdot T \cdot (n + p) \quad (4.6) \end{cases}$$

where S , T , n and p indicate the number density for singlets, triplets, electrons and holes, $G_{S(T)}$ is a singlet (triplet) generation term, $k_{r,S(T)}$ and $k_{IC,S(T)}$ are the photophysical coefficients for radiative recombination and internal conversion of singlets (triplets), and $k_{(R)ISC}$ is the coefficient for (reverse) intersystem crossing. A distribution of photophysical coefficients may sometimes be needed, e.g. due to conformational disorder [201–203]. Quadratic terms in Equation 4.5 and Equation 4.6 describe bimolecular processes such as singlet- or triplet-polaron quenching (SPQ, TPQ), singlet-singlet, singlet-triplet and triplet-triplet annihilation (SSA, STA, TTA) with prefactors reflecting spin statistics. The equations can be extended to multiple components (e.g. host and guest) and relevant energy transfer mechanisms.

Fitting such equations to experimental data allows in principle the extraction of effective kinetic coefficients for relevant photophysical processes [203–205]. The resulting values are usually case-dependent and cannot be generalised. Commonly, annihilation coefficients are taken as time-independent constants. In a minority of cases, a time-dependence is effectively treated using equations inspired to Smoluchowski's formula for particle aggregation in solution [206, 207]. Such equations generally take a form:

$$k \propto a + \frac{b}{\sqrt{\pi Dt}} \quad (4.7)$$

where k is the annihilation coefficient, D is an effective diffusion rate, t is time and a and b are arbitrary constants. This expression qualitatively matches the result obtained by Förster for an ensemble of nondiffusive donor and acceptors [208].

Recently, more refined rate equation models have been developed to improve the physical significance and numerical stability of extracted parameters. Bazrafshan *et al.* [40] introduced an effective treatment of exciton relaxation via the concept of the *transport energy level* derived from charge transport studies. Similarly, the approach proposed by Niyonkuru *et al.* [209] consider the inhomogeneity in the distribution of guest sites in a host, resulting in a distribution of annihilation coefficients. Both models show improved agreement with experiment and kMC simulations, compared to the regular rate equation approaches described above.

4.3 Mesoscale models

Mesoscale simulation techniques such as Master Equation (ME) and kinetic Monte Carlo (kMC) represent the organic material as a collection of molecular sites in real space, each site ideally corresponding to an individual molecule or monomer unit. Molecular sites are commonly arranged on a grid for computational convenience [9, 35, 210], but *off-lattice* simulation tools have also been developed [211] with similar results. The three-dimensional description naturally includes the effects of local inhomogeneities and of distance-dependent processes, granting a higher precision and flexibility compared to drift-diffusion models. Mesoscale techniques disregard the atomistic detail of the sites, rather focusing on the effective coupling between them: due to this coarse-graining approach, ME and kMC simulations connect molecular-scale calculations

(e.g. density functional theory, DFT) to device-level properties, hence the “mesoscale” name.

Mesoscale techniques adopt a stochastic approach, describing the time evolution of a system as a *Markov chain* of events in which the probability of each event taking place only depends on the current state of the system. This approach allows to describe physical systems which are in principle deterministic but are too complex to allow for analytical treatment: time-dependent properties are then directly accessible, while steady-state properties are obtained as time-averages. “Macroscopic” transition probabilities between states can be computed from the “microscopic” rates of the physical processes involved. For example, given two states ξ and ξ' corresponding to different configurations of charge carriers on a number of molecular sites, the transition rate $w_{\xi \rightarrow \xi'}$ relates to the carrier hop rates required to reach the configuration in state ξ' from the one in state ξ .

Given all transition rates, it is in principle possible to calculate a (time-dependent) probability P_ξ to find the system in state ξ , with energy E_ξ . Microscopic reversibility and the principle of *detailed balance* impose that, at thermodynamic equilibrium, for each forward transition $\xi \rightarrow \xi'$ with rate $w_{\xi \rightarrow \xi'}$, a backward transition $\xi' \rightarrow \xi$ with rate $w_{\xi' \rightarrow \xi}$ is defined such that:

$$\frac{w_{\xi' \rightarrow \xi}}{w_{\xi \rightarrow \xi'}} = \exp\left(-\frac{E_{\xi'} - E_\xi}{k_B T}\right) \quad (4.8)$$

where $k_B T$ is the thermal energy.

Parametrisation options for mesoscale techniques are depicted in Figure 4.2. In general, transition rates may be derived from experiment, from first-principles methods, or calculated according to formulas derived from quantum-mechanics. Differently from continuum models, mesoscale techniques do not employ effective parameters such as charge mobility or diffusion coefficients: rather, more fundamental properties such as material energy levels or photophysical rates are employed, hence the higher flexibility and true predictive power, at the cost of a largely increased computational cost.

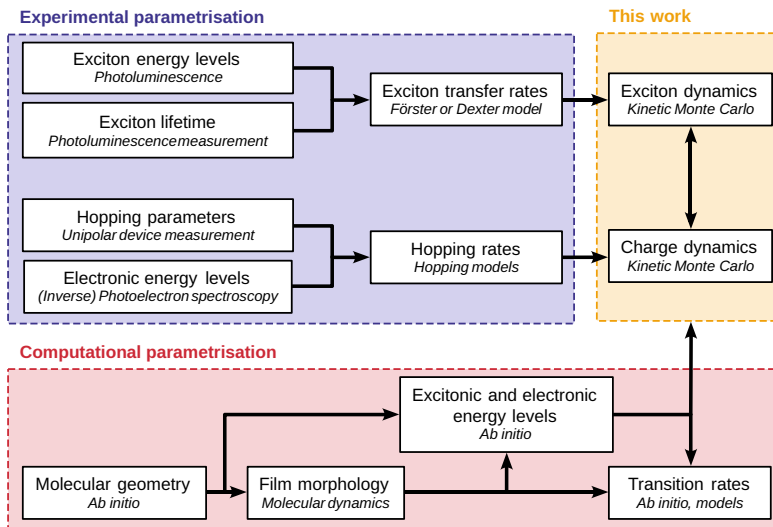


Figure 4.2: Device simulation workflow via kinetic Monte Carlo (yellow square): the necessary parameters can be obtained either from experiment, or from a fully computational path. The output of the kMC simulation can then be piped into an optical modelling software.

The combination of molecular dynamics simulations and first-principle methods may be employed to calculate individual inter-site hopping rates [193, 212–214]: this (computationally demanding) approach points towards a fully virtual workflow connecting molecular design to device properties.

4.3.1 Master equation (ME)

The Master Equation (ME) approach revolves around the solution of the eponymous equation:

$$\frac{dP_{\xi}(t)}{dt} = \sum_{\xi' \neq \xi} [-w_{\xi \rightarrow \xi'} P_{\xi}(t) + w_{\xi' \rightarrow \xi} P_{\xi'}(t)] \quad (4.9)$$

where P_{ξ} is the probability of finding the system in state ξ at time t , and $w_{\xi \rightarrow \xi'}$ expresses the transition rate towards another state ξ' . At the steady state, the ME is solved by imposing that the left-hand term is zero, i.e. that the *probability flux* between states is null. The ME is solved on a grid of molecular sites with a local occupation probability (white circles in Figure 4.1). Solutions to the ME are in the form of time- and space-dependent probability distributions for particles such as charge carriers and excitons, or events such as radiative recombination or exciton losses. The knowledge of the P_i terms and of the properties of the corresponding states then allows to calculate system observables.

The main difficulty with solving the ME is the large number of states potentially involved: n charge carriers may distribute on N molecular sites to generate $n!/(n! \cdot N!)$ states. Even for small systems, calculation of an exact solution becomes rapidly unfeasible and approximate methods are required [215]. Furthermore, the treatment of on-site charge density as a continuous occupation probability, rather than a direct representation of point charges, complicates the accurate treatment of Coulomb interactions [216].

Nevertheless, approximated ME approaches have been successfully applied to both reproduce and predict the behaviour of OLED devices [217–219]. The 3D-ME approach proposed by Taherpour *et al.* [220], based on the solution of a hierarchical chain of equations, furthermore highlights the development of spatial correlations between the positions of charges and excitons in OLED devices under operation, respectively because of Coulomb repulsion and exciton-exciton annihilation events.

4.3.2 Kinetic Monte Carlo (kMC)

Kinetic Monte Carlo (kMC) methods offer an alternative approach to the solution of the Markov chain. In fact, most states of the system have a vanishing probability (P_{ξ}), meaning that only a very limited subset is dominant. Rather than searching for a solution to the master equation, then, kMC methods sample the probability distribution searching for these dominant states, one configuration at a time, using random numbers. The advantage over a ME approach lies in the smaller number of transitions to consider, as only the subset of states accessible from the current state of the system – according to a selected set of rules –

is accounted for. Examples of such “rules” include restricting charge hopping within a certain maximum distance from the starting site, past which hopping rates are assumed to be negligible. Only elementary transitions are considered, e.g. a single carrier hop, a single exciton decay, etc.

While the implementation details may vary, the basic kMC algorithm requires to create a list of possible events given the state of the system, calculate their rates, randomly select an event, change the system accordingly and update the simulation time. In the *Bortz-Kalos-Lebowitz* (BKL) rejection-free algorithm [221], which is the basis for the simulation codes employed in this work (Part 6), the e -th event is selected if the following condition is met:

$$\sum_{i=1}^{e-1} k_i < \left(r \cdot \sum_{i=1}^N k_i \right) \leq \sum_{i=1}^e k_i \quad (4.10)$$

where $r \in [0, 1)$ is a random number drawn from a uniform distribution and N is the total number of possible events.

While in the ME approach time is a continuous variable, in kMC models time is divided into a sequence of discrete “Monte Carlo steps”. Particularly, in *variable timestep* kMC algorithms such as the BKL algorithm, the simulation clock is advanced according to the system *waiting time*. The waiting time for each event is calculated as the inverse of the corresponding rate, and it can be demonstrated [222, 223] that waiting times follow an exponential distribution, therefore the global clock at each timestep should be advanced by:

$$\Delta t = \frac{1}{\sum_i k_i} \log r' \quad (4.11)$$

where k_i is the rates for the i -th event and $r' \in [0, 1)$ is a second random number, again drawn from a uniform distribution (note that $\langle \log r' \rangle = -1$). Ref. [224] contains a derivation of Equation 4.11.

kMC models allow to simulate both steady-state and time-dependent properties. For steady state simulations, the system is equilibrated until observables do not change anymore in time, from which point the desired properties is obtained as a time-average. For time-dependent simulations, measurement is performed throughout the simulation after setting up the system in a state to which it cannot revert. Simulations are typically performed in multiple replicates to grant higher numerical stability and independence on the starting configuration. As more statistics is gathered, kMC results converge to a hypothetical exact solution of the ME.

Raw data generated by kMC simulations usually include particle or event counts and their distribution in space and/or time. The emission energy statistics may be converted to an emission spectrum by extracting the frequency histogram of emission energies, the time-averaged occupation of each site is directly related to the charge or exciton density [194].

Just as in the ME approach, the fully three-dimensional treatment offered by kMC modelling allows an accurate and fully predictive modelling of organic amorphous materials, including factors such as energetic disorder and spatially inhomogeneous charge and exciton density. Early achievements included the successful prediction of the current-voltage and emission profile in a white OLED device [225]. Similar models

have been applied to a wide array of devices, including phosphorescent, fluorescent, TADF and hyper-fluorescent devices [150, 226] with excellent experimental agreement. Greater accuracy comes however at a higher computational cost compared to DD modelling and, while the algorithm outline is simple, producing an efficient code requires significant effort. Furthermore, as kMC relies on the collection of statistics, it is rather sensitive to statistical noise, limiting its applicability in cases with signal-to-noise ratio, e.g. in low-current regimes where the diffusive behaviour of charges prevails. Taherpour *et al.* have recently proposed a *multiverse* kMC approach [227] in which the collection of statistics is improved by making use of the rates for unselected events, in addition to the execution of the selected event: such an approach is most effective in the presence of many events with comparable rates (e.g. charge transport in a low-disorder system), while it yields comparable statistics to regular kMC if few high rates dominate (e.g. charge transport in a system with sizable disorder).

kMC is nowadays a mature and established technique, which has demonstrated to reliably model transport and interaction properties of both charge carriers and excitons in many cases. It is now possible to employ it alongside experiment to further the field of organic optoelectronics – as done in this thesis – both in terms of specific device optimisation (Chapter 8) and with the broader aim of in-depth mechanistic description of less-investigated systems, such as inhomogeneous interfaces (Chapter 7) and donor:acceptor blends (Chapter 9), or to clarify the precise kinetics of loss processes (Chapter 10).

PART II

OVERVIEW

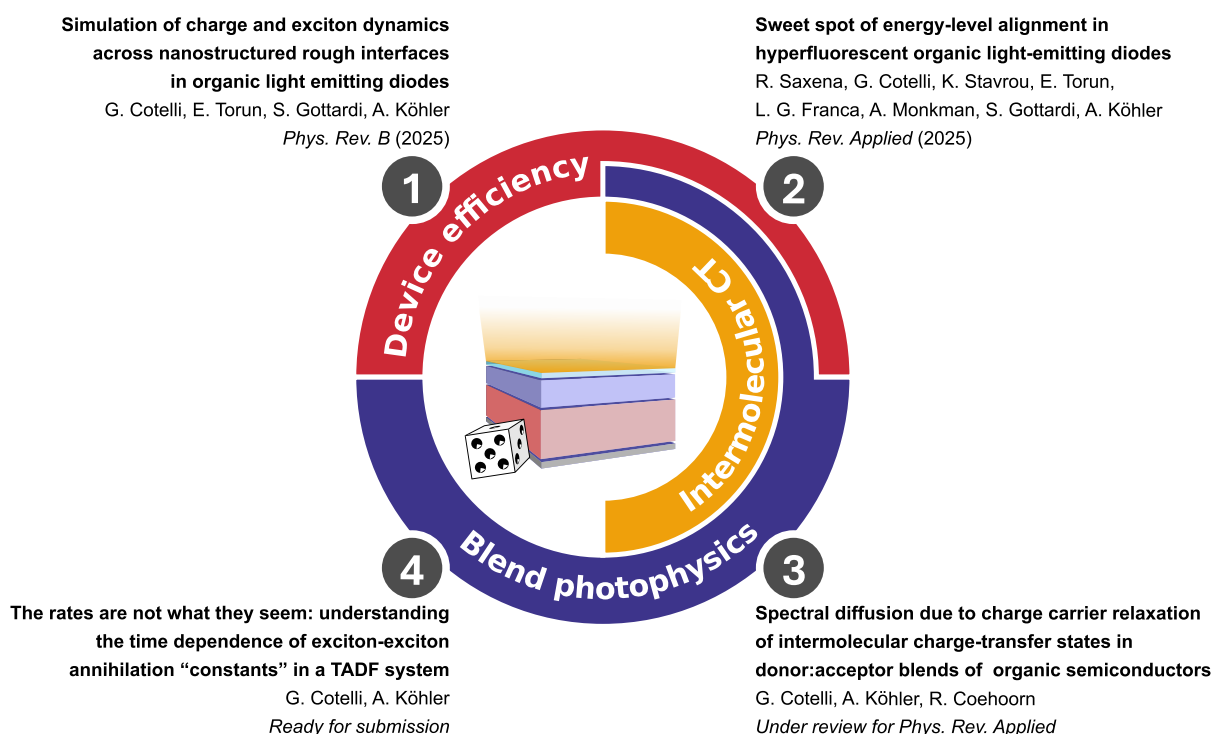
Overview of the contents of the publications

5

This thesis addresses the electronic and photophysical processes governing the efficiency of organic light-emitting diodes (OLEDs). As a display and lighting technology, OLEDs enable the fabrication of thin, flexible, high-contrast panels that have become increasingly prevalent in consumer and industrial applications. Despite their commercial success, improving device efficiency and operational stability remains an active area of research: high efficiency directly reduces energy consumption, whilst long operational lifetime is critical for commercial viability and for minimising electronic waste.

Advancing device performance requires a deep and reliable understanding of the underlying physics of OLEDs at the microscopic level. The primary methodological tool employed in this work is kinetic Monte Carlo (kMC) simulation of OLED device operation. kMC explicitly models individual charge and exciton hopping events between molecular sites by applying rates derived from quantum chemistry. This approach naturally bridges molecular-scale material properties and macroscopic device observables, providing a fully predictive tool with a mechanistic insight that continuum or mean-field methods cannot capture. Thus, kMC is a powerful framework for the rational analysis and design of OLED devices.

The results of this work have appeared in four publications, which are outlined in the following figure.



Publications 1 and 2 (Chapter 7 and Chapter 8) investigate how structural and energetic factors influence carrier and exciton distributions within the OLED device stack, and how these in turn determine the *internal quantum efficiency* (IQE) of devices.

Achieving high efficiency and long operational lifetime in OLEDs requires precise control over the spatial distribution of charges and excitons within the device stack, which in turn depends not only on the electronic properties of the constituent materials but also on the morphology of the interfaces between them. The sequential deposition of organic layers may yield interfaces with some degree of roughness or intermixing. Such morphological irregularities are known to influence local electric fields and charge accumulation, yet their quantitative impact on carrier and exciton dynamics at the device level has never been systematically addressed. Understanding how morphological irregularities influence carrier and exciton dynamics at the device level is therefore important for interpreting device behaviour and for identifying structural factors that may contribute to efficiency losses or accelerated degradation. While an experimental characterisation is impractical, kMC simulation permits a precise control of the simulation conditions, enabling a systematic study of the effects of nanoscale roughness on device performances. In the **first publication**, I investigated how the shape and amplitude of periodically corrugated organic-organic interfaces affect charge transport and recombination in unipolar and bipolar devices. A key finding is that, whereas interfacial roughness can strongly redistribute carriers and excitons spatially, it does not affect the overall internal quantum efficiency of bipolar devices. This observation hints at the fact that interfacial inhomogeneity may not be the root cause of the inferior performances of solution-processed OLEDs (which are expected to present significant interfacial inhomogeneities), as compared to vacuum-evaporated analogues. In contrast, this work demonstrates that controlled interfacial morphology may offer a handle for tuning charge injection and the localisation of the recombination zone in OLEDs by purely morphological means.

The **second publication** addresses a different class of efficiency losses, related to the energy level alignment of the emissive layer components in *hyperfluorescent* (HF) OLEDs. HF devices pair a sensitiser, capable of harvesting triplet excitons through thermally activated delayed fluorescence (TADF), with a terminal emitter that provides fast, spectrally pure emission. In principle, this synergistic combination grants an IQE approaching 100% while retaining the colour purity demanded by modern display applications. In practice, however, HF devices frequently show a lower IQE than devices containing the TADF sensitiser alone, suggesting that the introduction of the terminal emitter opens additional loss channels. kMC simulations informed by thoroughly characterised real devices (fabricated by my colleague Rishabh Saxena) are ideal tools for the detailed study of exciton losses. We identified as one such loss channels the population of a dark intermolecular excited state formed between the sensitiser and terminal emitter, at the expenses of emissive singlet excitons on the terminal emitter. Naturally, this intermolecular state can only be populated if energetically accessible, and its energy depends on the energetic alignment of the frontier orbitals of the sensitiser and terminal emitter. By comparing real HF devices and their “digital

twins” in simulation, we identified two design principles for HF devices: (i) to prevent the population of the intermolecular excited state, its energy should be at least 150 meV above the lowest singlet energy level (typically on the terminal emitter); (ii) device IQE can be further increased by using a terminal emitter with TADF capabilities, to avoid the accumulation of triplet excitons.

Publications 3 and 4 (Chapter 9 and Chapter 10) investigate the dynamics of excited states in organic semiconductors, with a focus on processes that are experimentally observable but difficult to interpret without microscopic insight.

Donor:acceptor blends have emerged as promising emitters and triplet sensitiser for OLEDs due to the formation of emissive intermolecular charge-transfer (CT) states. Due to the large spatial separation of the electron and hole wavefunctions, such states display a minimal singlet-triplet energy gap, hence appealing triplet gathering capabilities. A well-known but poorly understood feature of CT state emission is that its spectrum is not static. Rather, it redshifts in time and varies with other factors such as blend composition and excitation conditions. Whereas experimental studies have documented these spectral shifts and identified qualitative trends, a comprehensive mechanistic rationalisation is still missing. The **third publication** fills this knowledge gap by presenting a unified framework to understand numerous experimental observations in terms of spectral diffusion due to the relaxation of charge carriers in an energetically disordered panorama. By extending a KMC framework to treat CT states as photophysically active species, I simulated their emission under both optical and electrical excitation to disentangle contributions from the energetic disorder, the blend composition, and the excitation pathway. This study demonstrates the direct link between the dynamics of charge carriers and the CT state emission properties, and provides the basis for an informed selection of materials for future OLED applications.

Besides the inherent emitter efficiency, the IQE of OLED devices is reduced by energy transfer events between the charged and neutral excited states generated in the active layers. As the current through the device increases, the growing exciton density in the emissive layer raises the probability of bimolecular excitonic losses via exciton-exciton annihilation and exciton-polaron quenching, reducing the fraction of excitons that decay radiatively and thus limiting the achievable brightness at acceptable efficiency. Additionally, material degradation is directly linked to the short-lived but highly energetic intermediate states reached during these processes. A quantitative understanding of excitonic loss processes at the molecular level is therefore a prerequisite for identifying which channels dominate under realistic operating conditions, and for designing emitter systems and device architectures that mitigate them effectively. The **fourth publication** focuses on exciton-exciton annihilation, a bimolecular loss process directly responsible for the efficiency roll-off observed in OLEDs at high luminance, hence one of the key remaining obstacles to deploying OLEDs in high-brightness applications. In this study, I exploited the molecular-level detail of kMC simulations to observe the kinetics of exciton-exciton annihilation in a host:guest blend after an excitation pulse. Such an approach is experimentally used to

quantify annihilation processes in the form of kinetic coefficients to be incorporated into predictive device models. Achieving an accurate estimate is therefore of considerable practical importance, yet the standard spectroscopic approaches used to characterise it rest on simplifying assumptions whose validity is not always guaranteed. This work provides a more robust physical picture of exciton-exciton annihilation in host:guest systems, providing a more reliable basis for predictive simulations of the OLED efficiency and roll-off behaviour.

In conclusion, this doctoral thesis advances the organic electronics field by elucidating four aspects of exciton and charge dynamics relevant to OLED efficiency and lifetime. The work includes the impact of device morphology on carrier and exciton distributions, the identification and quantification of intrinsic loss mechanisms in state-of-the-art emitter systems, and the development of a more reliable physical framework for characterising exciton dynamics in organic semiconductors. Together, the studies aim to bridge the gap between molecular-scale material properties and macroscopic device observables, providing both mechanistic insight and practically applicable design rules for the design of more efficient and stable OLED devices.

This chapter collects the statements of the author contributions to each publication. For published works, statements are included in the published text and are here reproduced. For submitted works, author contributions have been approved in writing by all authors.

Publication 1 Simulation of charge and exciton dynamics across nanostructured rough interfaces in organic light emitting devices

Published 29th July 2025 in
Physical Review B **112**, 035307,
DOI: 10.1103/36kq-7pvt

Giacomo Cotelli, Engin Torun, Stefano Gottardi, Anna Köhler

G.C., A.K., and S.G. conceived the project. G.C. performed kMC simulations under the supervision of S.G., E.T., and A.K. G.C. and A.K. wrote the paper with input from all authors.

Publication 2 Sweet spot of energy-level alignment in hyper-fluorescent organic light-emitting diodes

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Rishabh Saxena*, Giacomo Cotelli*, Kleitos Stavrou, Engin Torun, Larissa G. Franca, Andrew P. Monkman, Stefano Gottardi, Anna Köhler. (*These authors contributed equally.)

R.S. conceived the project. R.S. and K.S. conducted device fabrication and characterization. R.S. and L.G.F. carried out photophysical measurements. G.C. performed the KMC simulations with inputs from R.S. and E.T. A.P.M., S.G., and A.K. supervised group members involved in the project. R.S., G.C. and A.K. wrote the manuscript with inputs from all the authors.

Publication 3 Spectral diffusion due to charge carrier relaxation of intermolecular charge-transfer states in donor:acceptor blends of disordered organic semiconductors

Under review for *Physical Review Applied*
(code NQ10575)

Giacomo Cotelli, Anna Köhler, Reinder Coehoorn

G.C. and R.C. conceived the project. G.C. implemented the CT state model and performed kMC simulations under the supervision of R.C. and A.K. G.C., A.K. and R.C. wrote the paper.

Publication 4 The rates are not what they seem: understanding the time dependence of exciton-exciton annihilation “constants” in a TADF system

Ready for submission

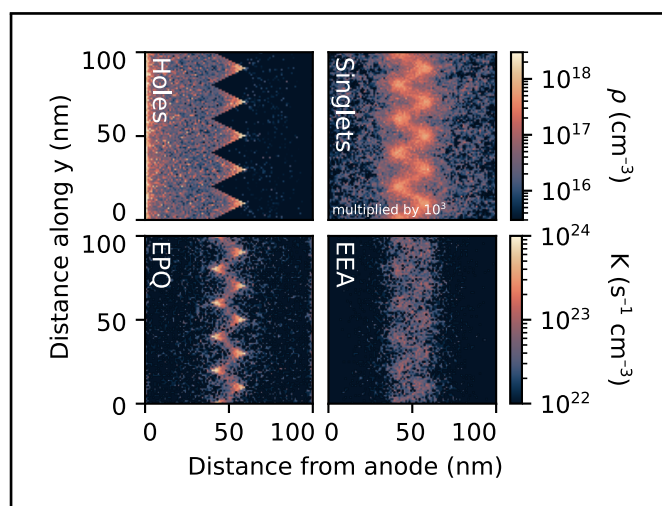
Giacomo Cotelli and Anna Köhler

G.C. conceived the project, implemented the kMC algorithm and performed the simulations under the supervision of A.K. G.C. and A.K. wrote the paper.

PART III
PUBLICATIONS

Simulation of charge and exciton dynamics across nanostructured rough interfaces in organic light emitting devices

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Simulation of charge and exciton dynamics across nanostructured rough interfaces in organic light emitting devices

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In organic semiconductor devices, the deposition of organic layers may result in intermixed regions or rough interfaces between layers. To examine how roughness at organic-organic interfaces influences device performance, we conducted mesoscopic device simulations using a three-dimensional kinetic Monte Carlo algorithm. We simulated devices containing interfaces with periodic corrugation of either triangular or rectangular cross section. Our results show how the shape and size of interfacial roughness impacts on both charge and exciton dynamics of unipolar and bipolar devices. We first analyzed bilayer devices where the two layers are energetically offset. We find interfaces with triangular cross section display strong carrier funneling to the tips. This funneling translates to pronounced inhomogeneity in the spatial distribution of charge carriers, excitons, and excitonic losses. The tips act as injection hot spots, increasing the current density by up to two orders of magnitude, depending on the energy offset, compared to a flat-interface device. In contrast, the internal quantum efficiency of bipolar devices is surprisingly unaffected by interfacial morphology. In bipolar three-layer devices, we used this enhancement in current density to improve charge injection toward the central emissive layer. The recombination zone within the emissive layer can also be tuned through the configuration and size of the morphology.

DOI: [10.1103/36kq-7pvt](https://doi.org/10.1103/36kq-7pvt)

I. INTRODUCTION

During recent decades, organic light emitting diodes (OLEDs) have attracted increasing attention as innovative light sources for the display and lighting industry: high contrast, low energy consumption, and the possibility to fabricate transparent and flexible devices are among the strong points in favor of conventional LEDs. The manufacture of OLEDs from solution, as an alternative to the well-established vacuum-evaporation techniques, has recently seen intense development, owing to the possibility to exploit well-established industrial-scale printing technologies [1–6] on a virtually unlimited substrate size and with a promisingly low waste fraction, leading altogether to lower fabrication costs.

Nevertheless, in terms of performances, solution-processed OLEDs still lag behind their vacuum-evaporated counterparts [5–9] and the causes behind this are yet to be fully clarified. Morphological effects have been suggested to be at play: the higher performances of vacuum-deposited films have been associated with their better film quality, e.g., in terms of reduced component segregation or aggregation [10–12]. Films

produced by vacuum evaporation are usually more homogeneously flat and more densely packed than the corresponding solution-processed films, producing sharp, flat interfaces between adjacent layers [13–15], although curiously, in rare occurrences, the opposite case of solution processing yielding better results than evaporation has also been reported [16,17]. A crucial aspect of OLED fabrication involves the deposition of subsequent layers: the complex, multilayered structures which represent the state of the art for vacuum-deposited devices prove yet a tough challenge for solution processing, as the coating of an upper layer may lead to the partial dissolution or swelling of the layer below, thereby creating an intermixed or corrugated interface [18–21].

The effect of such inhomogeneous interfaces has been rarely studied: several works have addressed, by indirect spectroscopic means, the diffusion of small molecules in a host (e.g., C₆₀ in a polymer matrix, [22,23]) or the intermixing between adjacent layers under heating [24], reporting that layer interpenetration may proceed in both cases to a surprisingly large extent. Similarly, it is also well known that severe roughness may be present at the interface between electrodes and injection layers, especially when indium-tin oxide is used as the cathode [25,26]. Such inhomogeneity and the subsequent creation of pinholes has been suggested to reduce the lifetime of devices by locally shorting the circuit [25,27]. On the other hand, engineered interfaces have been suggested as means by which to improve light outcoupling [28], but they are often flattened out with a suitable interlayer before the active layers.

In terms of simulation studies, the topic of inhomogeneous interfaces between layers has been occasionally approached in the field of organic photovoltaics: for example, Buxton and

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Clarke [29] addressed the effects of a periodic, sinusoidal roughness at the interface between two materials via a 2D drift-diffusion model, while Watkins *et al.* [30] ran three-dimensional kinetic Monte Carlo simulations on bicomponent blends with varying degrees of intermixing. Such theoretical studies helped elucidate the working principles of a good bulk heterojunction, observing how phase separation influences the generation and diffusion of charge carriers in photovoltaic devices, therefore affecting device efficiency.

To this day, however, the field of organic light emitting devices (OLEDs) has not benefited from similar studies: in this work, we aim to address this issue with an analysis of the effects of interfacial inhomogeneity between adjacent layers via kinetic Monte Carlo simulations of ideal OLED devices of increasing complexity.

In Sec. II, an overview on the simulation methodology is provided, along with relevant parameters. In Sec. III A, we analyze the impact of inhomogeneous interfaces on charge transport in hole-only bilayer devices, while the corresponding bipolar devices are presented in Sec. III B to observe the effect of interfacial morphology on exciton dynamics and losses. These observations are translated in Sec. III C to three-layer devices containing two interfaces. Finally, in Sec. IV we present a unified picture on the effects of interfacial roughness on charge transport, discuss by extrapolation how morphological features on a larger length scale may impact the device behavior, and speculate on the possible role of roughness in aggravating device degradation under some conditions.

II. METHODS

Three-dimensional kinetic Monte Carlo (3D kMC) simulations were performed using the commercial software BUMBLEBEE [31], which in earlier studies showed good agreement with experiment for a wide array of devices, including phosphorescent, fluorescent, thermally activated delayed fluorescent (TADF), and hyperfluorescent devices [32–39].

Devices are modeled as a collection of molecular sites arranged on a simple cubic grid, with periodic boundary conditions along the directions parallel to the electrodes. Each molecular site can host an electron, a hole, a singlet exciton, or a triplet exciton. Intermolecular charge transport in the hopping regime is described using a Miller-Abrahams-type rate [40]. Energetic disorder is described according to the Gaussian disorder model [41], assuming a spatially uncorrelated Gaussian density of states (DOS) centered on the material-specific ionization energy (IP) or electronic affinity (EA) value. Correlated disorder produces qualitatively similar results, favoring a more homogeneous charge distribution, similar to the effect of a smaller degree of uncorrelated disorder (see Fig. S4 in the Supplemental Material [42]). Injection layers are not explicitly modeled: instead, an energy barrier is placed at each injecting electrode. Coulomb interactions are explicitly calculated within a 10 nm cutoff radius from each charge carrier, while a layer average is employed for carriers outside the cutoff radius [43].

A hole and an electron sitting on the same molecular site generate an exciton, the spin of which is randomly determined with a singlet (S) to triplet (T) relative probability of 1:3, as prescribed by spin statistics. On-site exciton energies are

TABLE I. Simulation parameters employed in this study.

Parameter	Value
Lattice step	1 nm
Device area	$100 \times 100 \text{ nm}^2$
Temperature	293 K
Injection energy barrier	0.2 eV
Explicit Coulomb calculation cutoff distance ^a	10 nm
Charge hopping cutoff distance	Two neighbors
Excitonic neighbor cutoff distance	Four neighbors
Electronic disorder (IP/EA)	0.10 eV [46]
Excitonic disorder (S_1/T_1)	0.05 eV [37]
Singlet exciton binding energy	1.00 eV [47]
Triplet exciton binding energy	1.25 eV ^b
Förster radius (exciton transfer, $\Delta E < 0.5 \text{ eV}$)	1.5 nm [36]
Förster radius (exciton transfer, $\Delta E \geq 0.5 \text{ eV}$)	3.5 nm [36]
Förster radius (EPQ, EPA)	3.5 nm [36]
Miller-Abrahams or Dexter prefactor (nearest neighbor attempt rate)	$3.33 \times 10^{10} \text{ s}^{-1}$ [46]
Miller-Abrahams or Dexter wave function decay length	0.3 nm [46]

^aChosen for performance as in Refs. [40,43].

^bChosen as 0.25 eV higher than the singlet binding energy.

again extracted from a spatially uncorrelated Gaussian DOS. Exciton dissociation is naturally included as a result of either charge carrier leaving the exciton site, incurring a supplementary energy cost equal to the exciton binding energy. Exciton diffusion and loss processes are explicitly modeled: diffusion results from an exciton transfer to a free site, while transfer to a site already occupied by a polaron or a second exciton, respectively, results in exciton-polaron quenching (EPQ) or exciton-exciton annihilation (EEA). Upon EPQ, the exciton is lost and only the polaron is left; upon EEA, the diffusing exciton is lost, while the remaining exciton may change its spin state in accordance with spin conservation: singlet-singlet annihilation (SSA) results in a singlet, triplet-singlet (TSA) and singlet-triplet annihilation (STA) result in a triplet, and triplet-triplet annihilation (TTA) results in a singlet (25%) or triplet (75%) exciton (high-energy quintet states are neglected). Exciton diffusion, quenching, and annihilation phenomena are introduced via both the Dexter and Förster mechanisms, respectively, with a dependency $k_D \propto e^{-r}$ and $k_F \propto r^{-6}$ on the distance r between the origin and destination site; only excitons with a nonzero radiative rate may be transferred via the Förster mechanism. A Miller-Abrahams-type factor accounts for the exciton energy difference between the origin and destination site.

General simulation parameters are indicated in Table I: this set of values, determined in previous studies, has proven to realistically describe charge transport and excitonic phenomena both in phosphorescent [32,34–36] and (hyper)fluorescent [37,39] devices. In the spirit of simulating ideal symmetric devices as described below, we assume equal mobility parameters for holes and electrons, differently from previous works

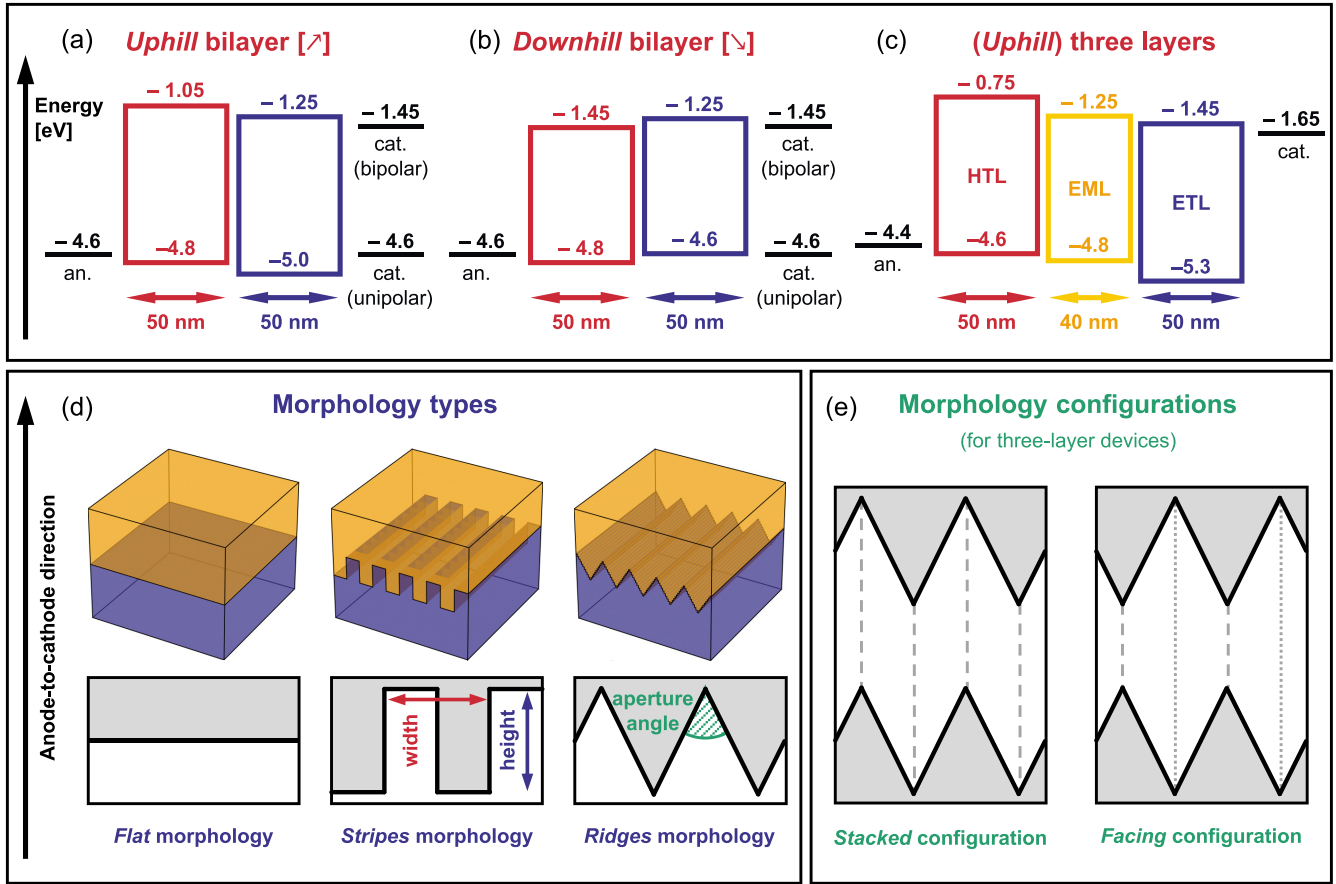


FIG. 1. Device schematics and morphology information. (a–c) Energy diagrams for the energetically and structurally symmetric devices simulated in this study: in the uphill bilayer structure (a), a $+0.2$ eV energy barrier is present across the interface in the direction of the applied field, representing an energy barrier for both types of charge carriers; in the downhill bilayer structure (b), the offset across the interface is -0.2 eV. Electrons are only present in bipolar devices, while unipolar devices are hole only. In the three-layer structure (c), a $+0.2$ eV energy barrier is present for either carrier type between its respective transport layer and the emissive layer (EML), and a $+0.5$ eV barrier between the EML and the opposite transport layer (double serving as a blocking layer). (d) Depictions of the interfacial morphologies studied in this work and (e) their possible configurations within three-layer devices.

[37]. Each simulation is run in five independent replicates corresponding to different disorder configurations.

Schematics for the bilayer and three-layer devices studied in this work are presented in Figs. 1(a)–1(c): to limit the complexity and the number of parameters to consider, the stacks are chosen as geometrically and energetically symmetric. We indicate as *uphill* (respectively, *downhill*) those devices in which charge carriers encounter a positive (respectively, negative) energy offset between adjacent layers in the direction of carrier drift. Material parameters, detailed in Table II, are comparable with common (fluorescent) transport materials. In bilayer devices, due to the symmetric choice of hole and electron energy levels, the two materials have the same exciton energy, so that no energy barrier for exciton diffusion is present across the interface.

Our devices are composed of two or three neat layers stacked between flat electrodes. To introduce roughness at the organic-organic interfaces, we attribute each site to a “material” according to the desired interface shape. The material determines the on-site electronic parameters (IP, EA) and on-site excitonic parameters (singlet or triplet energy, Förster or

Dexter transfer rates). The “resolution” of the morphology is determined by the lattice step (1 nm).

To capture the basic physics of the system, we introduced periodic interfacial roughness with simple geometric features: namely, we report results for a reference *flat* morphology and two rough interfaces with periodic corrugation and either triangular (*ridges*) or rectangular (*stripes*) cross section, displayed in Fig. 1(d). Specifically, the ridges and stripes morphology corrugate along one axis parallel to the electrodes and have constant cross section along the other: we indicate as *width* the corrugation period (along a direction parallel to the electrodes) and as *height* the amplitude of the oscillation (along the anode-to-cathode direction). For the ridges morphology, we furthermore define an *aperture angle* $\alpha = 2 \times \arctan[\text{width}/(2 \times \text{height})]$.

Details on the calculation of current density, internal quantum efficiency, charge or exciton density [44], and event rates are given in Sec. S4 of the Supplemental Material [42]. Density maps displayed in the following sections were generated using the LIPARI color map from Ref. [45] as supplied in the CMCRAMERI module for PYTHON3.

TABLE II. Material parameters employed in this study.

	IP (eV)	EA (eV)	S_1 (eV) ^a	T_1 (eV) ^a	$k_{S,rad}, k_{T,IC}$ (s ⁻¹) ^b
<i>Uphill bilayers</i>					
Hole transport layer	-4.80	-1.05	2.75	2.50	$10^8, 10^4$
Electron transport layer	-5.00 ^c	-1.25	2.75	2.50	$10^8, 10^4$
<i>Downhill bilayers</i>					
Hole transport layer ^d	-4.80	-1.45	2.35	2.10	$10^8, 10^4$
Electron transport layer ^d	-4.60 ^e	-1.25	2.35	2.10	$10^8, 10^4$
<i>Uphill three layers</i>					
Hole transport	-4.60	-0.75	2.85	2.60	0, 0
Electron transport	-5.30	-1.45	2.85	2.60	0, 0
Emissive layer	-4.80	-1.25	2.55	2.30	$10^8, 10^4$

^a $S_1=EA-IP$ -(binding energy).^bRate for the radiative decay from the singlet state and internal conversion from the triplet state; rates for (reverse) intersystem crossing, internal conversion from the singlet state, and radiative decay from the triplet state are zero.^cLowered to -5.10, -5.20, -5.30 eV to test performances at increasing energy barrier in Fig. 4.^dDefined so as to obtain the same built-in voltage for uphill and downhill bipolar devices.^eRaised to -4.50, -4.40, -4.30 eV to test performances at increasing energy offset in Fig. 4.

III. RESULTS

A. Unipolar bilayers

We analyzed the effect of interfacial morphology on charge transport in unipolar (hole-only) bilayer devices [Fig. 1(a)]. In Fig. 2, we consider how differently shaped interfaces affect the spatial distribution of charges. Figure 3 reports the current voltage curve for representative devices. The impact of the energetic offset across the interface is addressed in Fig. 4.

Figure 2(a) presents the hole distribution at a modeled 6.0 V applied bias in uphill devices containing interfaces with various morphologies: a flat interface, three ridges interfaces with varying feature size, and a stripes interface. In all cases,

holes injected from the anode [left electrode in Fig. 2(a)] trivially accumulate at the interface due to the IP difference between layers. The hole distribution at the interface is influenced by the morphology: in devices which contain a ridges morphology, charge carriers are funneled toward the convex tips of the interface, leading to an enhanced charge carrier density there, as compared to a stripes morphology [Fig. 2(b)]. As a result of this funneling, the tips act as injection points toward the adjacent layer, determining within it a spatially inhomogeneous hole distribution characterized by “plumes” of injected carriers. The areas between the tips are instead depleted from charges. This charge carrier funneling translates to an inhomogeneous, quasifilamentary current flow. The

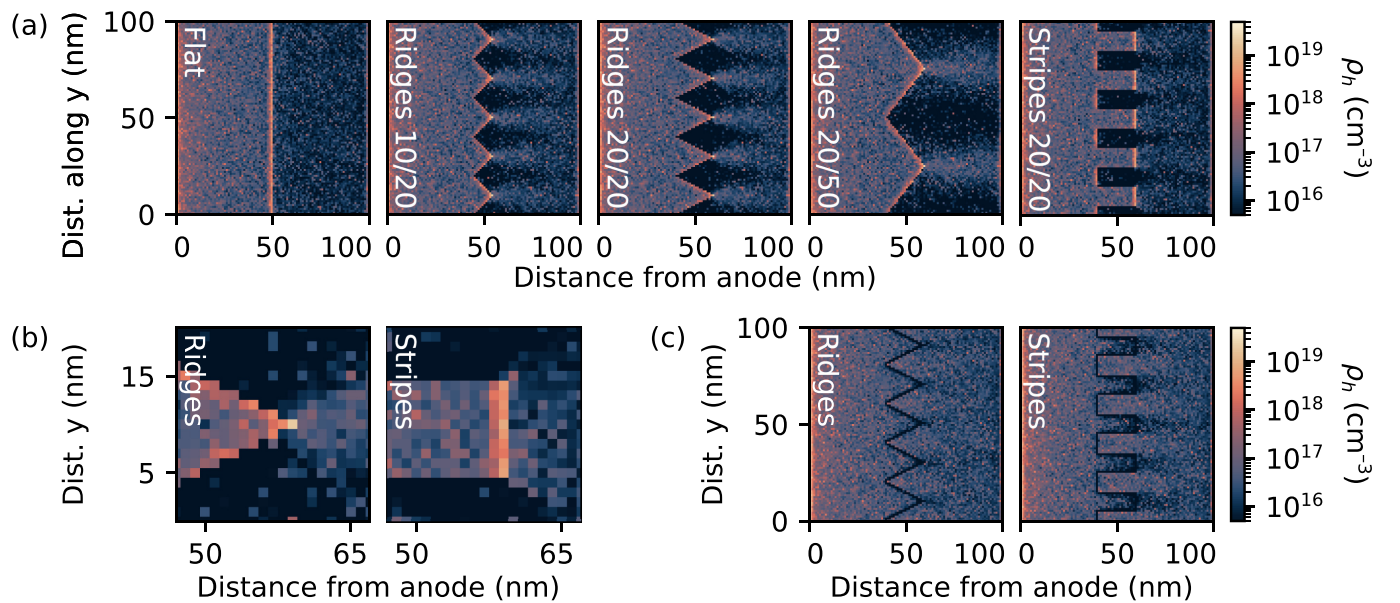


FIG. 2. Unipolar bilayers, heat maps. Charge-density maps at 6.0 V applied bias in (a) hole-only uphill bilayers with (left to right) a flat morphology, three ridges morphologies, and a stripes morphology. Feature size is indicated as height/width in nanometers. (b) Zoom-in on the tips of a ridges device and a stripes device at equal feature size (20 nm high, 20 nm wide). (c) Charge-density maps at 6.0 V applied bias in hole-only downhill bilayers with stripes or ridges morphology. In all figure parts, holes move from the left to the right.

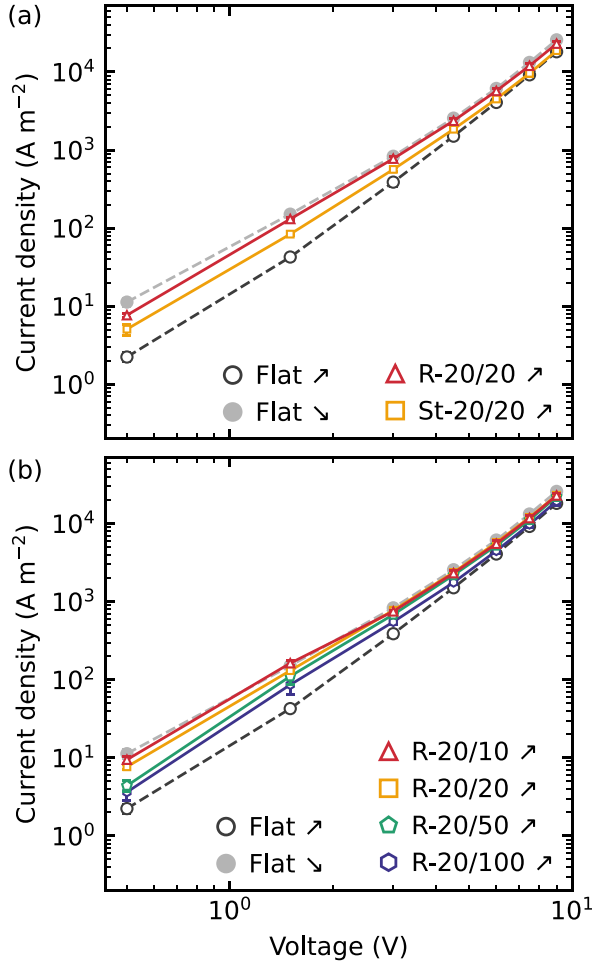


FIG. 3. Unipolar bilayers, current density. Current density vs voltage (JV) curves of devices containing (a) a ridges (Δ) or stripes ($\square$) interface 20 nm wide, 20 nm high or (b) ridges interfaces with 20 nm high and increasing width (10 nm Δ , 20 nm $\square$, 50 nm $\diamond$, 100 nm $\circ$). Curves for flat uphill ($\circ$) or downhill ($\bullet$) devices are reported for reference. Uncertainty on the current density is smaller than the symbol size; lines are provided as a guide to the eye.

effect is significantly softened with a stripes morphology. The area between the stripes fingers is still depleted of charge density, but the injection occurs over the whole interfacial line in the direction of the electric field, as shown in the video in the Supplemental Material [42]. Correspondingly, there are no noticeable size effects (see Supplemental Material [42], Fig. S3). Finally, Fig. 2(c) compares the distribution of holes in downhill devices containing a ridges or stripes interface under a modeled 6.0 V applied bias. Both devices exhibit a charge-density gradient from anode to cathode and a carrier-depleted region at the interface, as charge carriers cannot hop back to the left-side layer. Aside from that, the interfacial morphology shows little effect on device properties (also see Fig. S3 in the Supplemental Material [42]).

Considering the JV curves of uphill devices at varying interfacial morphology for equal feature size [Fig. 3(a)], we observe a higher current density at any given voltage in the order ridges > stripes > flat. This effect is particularly strong at low voltages and for small aperture angles (Fig. 3(b) and

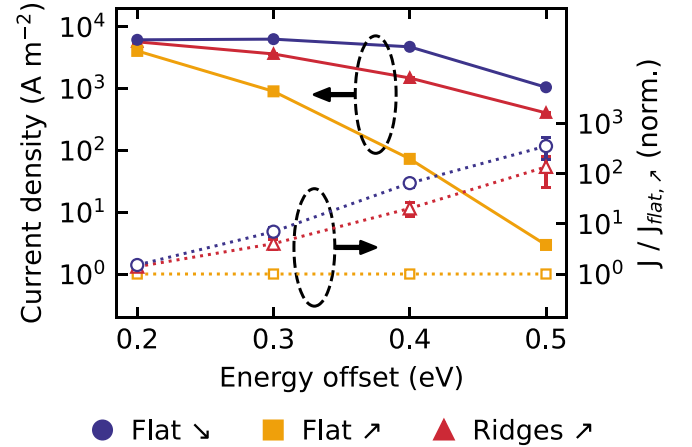


FIG. 4. Unipolar bilayers, effect of the energy offset. Current density at 6.0 V (filled markers) and relative current density compared to the uphill flat-interface device ($J_i/J_{\text{flat,uphill}}$, empty markers) vs the energy offset across the interface for hole-only downhill ($\circ$) and uphill ($\square$) flat-interface bilayer devices, and for an uphill bilayer with a 20 nm high, 20 nm wide ridges interface (Δ). Uncertainty on the absolute current density is smaller than the symbol size; lines are provided as a guide to the eye.

Supplemental Material [42], Fig. S7(c)). In fact, it can render the current in the devices with a ridges interface close to that of a flat downhill device, implying that the energetic barrier becomes irrelevant, thus effectively improving charge injection through the interface. Such injection boost becomes even more relevant when a higher barrier is present at the interface. In Fig. 4 we compare the current density at 6.0 V for an uphill ridges device (20 nm high, 20 nm wide, red triangles) and a flat device (uphill and downhill) as a function of the energy offset across the interface. In the flat downhill device, the increasing energy offset produces an increasing extraction barrier at the cathode. Remarkably, the current density in the ridges devices is significantly higher (up to a factor of 100 for a 0.5 eV offset) compared to the flat uphill device. In fact, it becomes strikingly close to the current density of the barrierless flat downhill device. Hence, it is possible to use a ridges morphology to significantly boost charge injection across interfaces featuring a large energy barrier. This will be explored further for the case of a three-layer device in Sec. III C. Vice versa, consistently with previous observations on charge distribution, downhill devices show no influence of morphology on current density (see Fig. S7(b) in the Supplemental Material [42]).

B. Bipolar bilayers

In Fig. 5–7, we analyze the behavior of uphill bilayer devices containing ridges interfaces, and in which both electrons and holes are injected. We report the spatial distribution of holes, singlet excitons, and losses due to exciton-polaron quenching (EPQ) and exciton-exciton annihilation (EEA) (Fig. 5). We analyze which loss processes reduce the internal electroluminescence quantum efficiency (IQE) (Fig. 6), then compare devices with different ridges width (corrugation period) in terms of current density [Fig. 7(a)] and IQE [Fig. 7(b)]. We refer to the Supplemental Material [42]

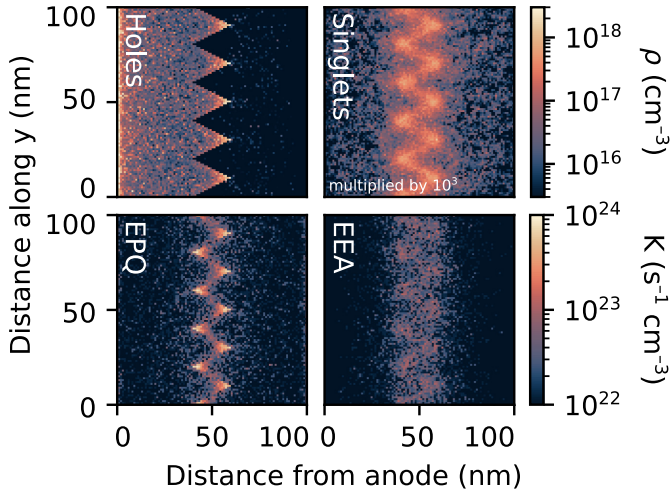


FIG. 5. Bipolar bilayers, density maps. Density maps for holes, singlets, exciton-polaron quenching (EPQ), and exciton-exciton annihilation (EEA) events in a bipolar bilayer device containing a ridges morphology 20 nm high, 20 nm wide, under 4.0 V applied bias. Holes move from left to right; electrons move from right to left. The energy barrier across the interface is +0.2 eV for both types of carriers; no barrier is present for excitons.

(Fig. S12) for a brief treatment of downhill devices which, as in unipolar devices, show little influence of the morphology on device behavior.

Figure 5 illustrates the distribution of holes, singlet excitons, and losses via EPQ or EEA in a device containing a 20 nm high, 20 nm wide ridges interface at 6.0 V. The hole distribution shows that, analogous to unipolar devices, carriers are funneled toward the tips of the interface (see Supplemental Material, Figs. S9–S11 [42] for electron distribution). Comparing the absolute values of hole density at the tips in the bipolar device ($2 \times 10^{18} \text{ cm}^{-3}$, i.e., 2×10^{-3} charges per site) and the analogous unipolar device ($2 \times 10^{19} \text{ cm}^{-3}$, i.e.,

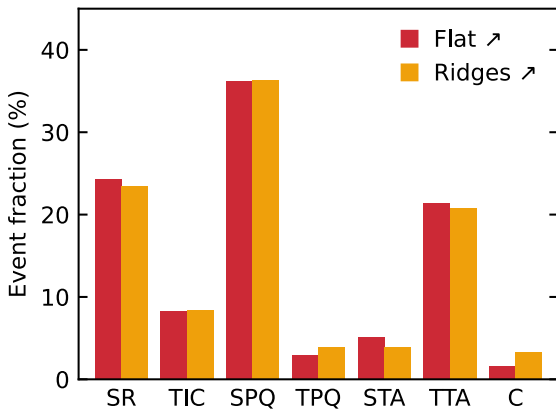


FIG. 6. Bipolar bilayers, loss processes. Comparison of excitonic events in uphill bipolar bilayers with either a flat or ridges (20 nm high, 20 nm wide) interface, under 4.0 V applied bias. Abbreviations: SR, singlet radiative decay; TIC, triplet internal conversion; SPQ (TPQ), singlet (triplet) polaron quenching; STA (TTA), singlet (triplet) triplet annihilation; C, collection of carriers at the opposite electrode.

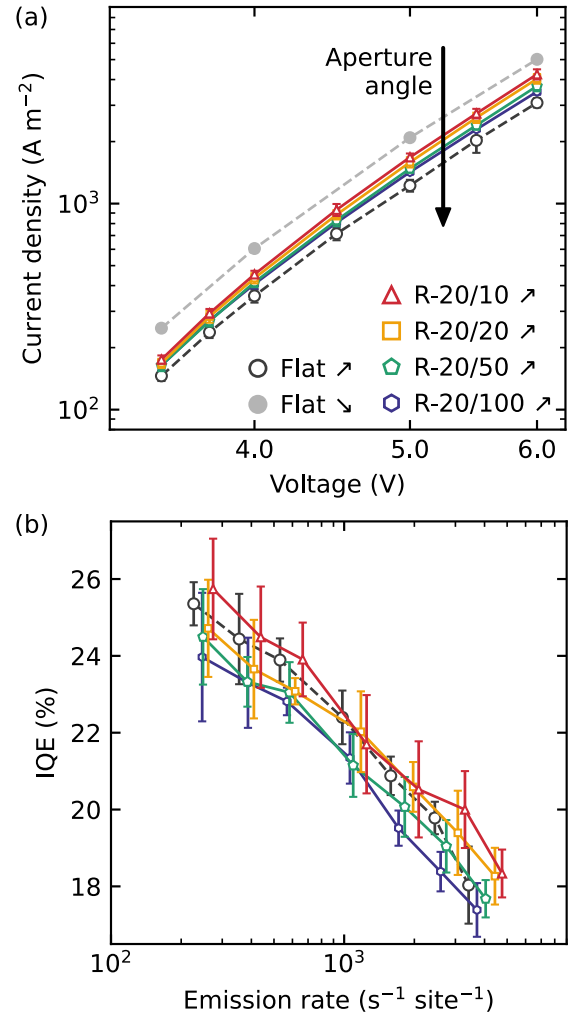


FIG. 7. Bipolar bilayers, current density, and efficiency. Comparison of (a) current density vs voltage and (b) IQE vs emission rate ($\propto$ luminance) between devices containing ridges interfaces 20 nm high with increasing width (10 nm $\triangle$, 20 nm $\square$, 50 nm $\diamond$, 100 nm $\circ$). Curves for flat uphill ($\circ$) or downhill ($\bullet$) devices are reported for reference. Uncertainty on the absolute current density is smaller than the symbol size; lines are provided as a guide to the eye.

2×10^{-2} charges per site) shows that charge accumulation seems to be hindered by recombination at the interface. Notably, holes (Fig. 5, top left) and electrons (see Supplemental Material [42], Fig. S9) accumulate separately on alternate tips. The singlet density (Fig. 5, top right) is highest around the tips of the morphology. The inner volume of each tip becomes a hot spot for EPQ losses (Fig. 5, bottom left) due to the high local charge density there. In contrast, EEA events (Fig. 5, bottom right) are more spread out, likely due to exciton diffusion.

Analyzing in more detail reveals that the EPQ losses result mainly from singlet-polaron quenching (SPQ), whereas the EEA losses arise predominantly from triplet-triplet annihilation (TTA), as displayed in Fig. 6. In particular, Fig. 6 compares the fractions of radiative decay and nonradiative losses at 6.0 V for the ridges and flat devices. Despite the inhomogeneous spatial distribution of loss events in the ridges

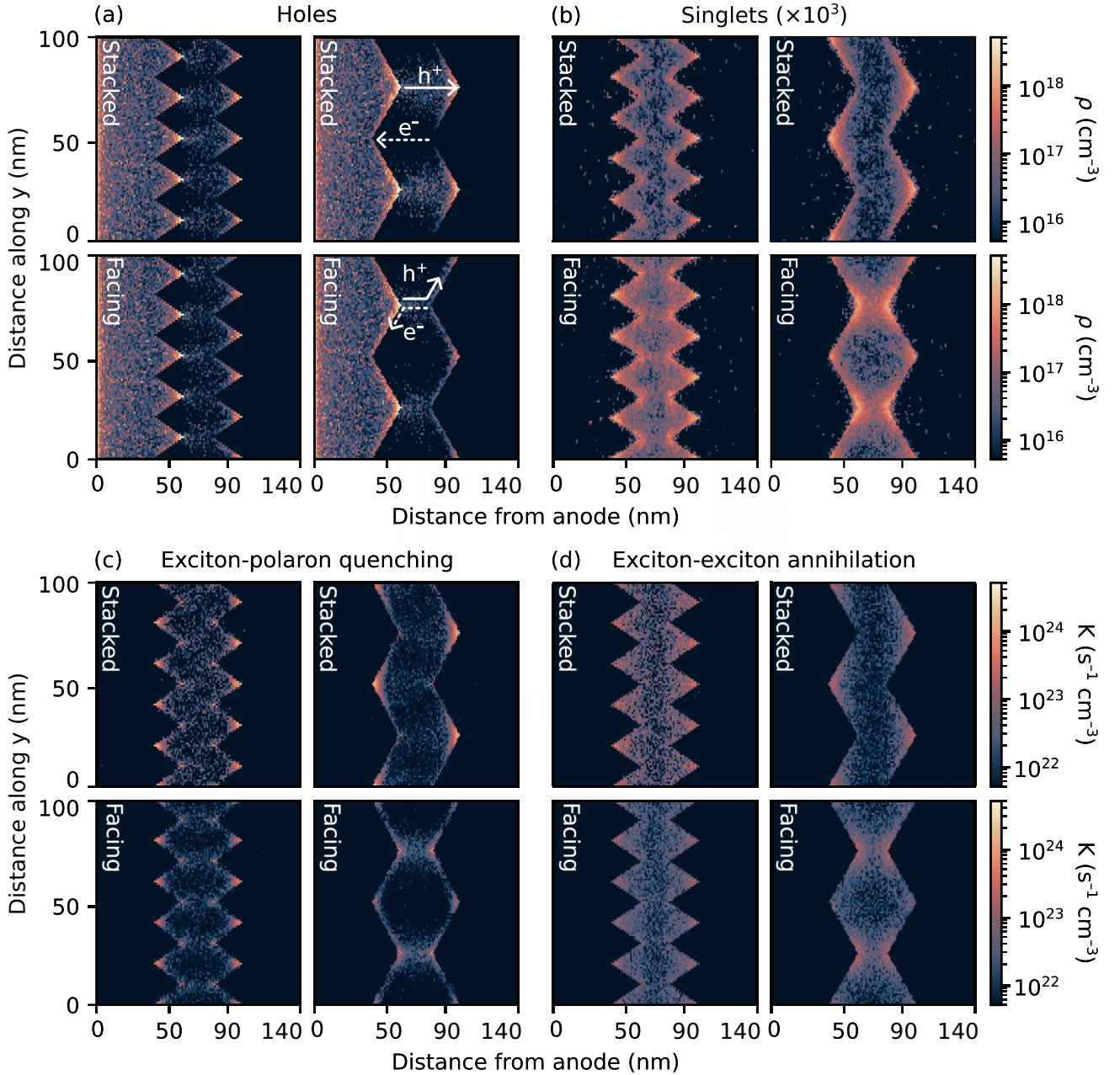


FIG. 8. Bipolar three layers, density maps. Density maps for (a) holes, (b) singlets, and (c) EPQ and (d) EEA events at 5.0 V for bipolar three-layer devices with ridges morphologies at varying size (in each panel, left: 20 nm high, 20 nm wide; right: 20 nm high, 50 nm wide) and offset (in each panel, top: stacked offset; bottom: facing offset).

device, its internal quantum efficiency (IQE) is strikingly close to that of the flat device (23%).

Figure 7(a) shows that, as in unipolar bilayers, bipolar ridges bilayers exhibit an increased current density compared to the flat uphill device; the current density also increases for narrower aperture angles, though the effect is weaker than for the unipolar bilayers. In fact, unlike in unipolar devices, bipolar ridges devices always show a lower current density compared to the flat downhill device. IQE [Fig. 7(b)] and IQE roll-off with luminance are not significantly affected by the interface shape or feature size, except for a minor drop in IQE at increasing width (see Supplemental Material [42], Sec. S6.3).

C. Bipolar three layers

In simulating three-layer devices, we have a double aim: firstly, to explore to which extent interfacial roughness may impact realistic devices and, secondly, to check whether a nanostructured interfacial morphology may be exploited to improve charge injection across an energy barrier, as suggested by the data of the unipolar bilayers.

We designed a simple three-layer structure [Fig. 1(c)] in which a pair of flat or ridges interfaces is placed between each transport layer (HTL and ETL) and the central emissive layer (EML). The EML material presents a 0.2 eV energy barrier for hole and electron injection from the corresponding

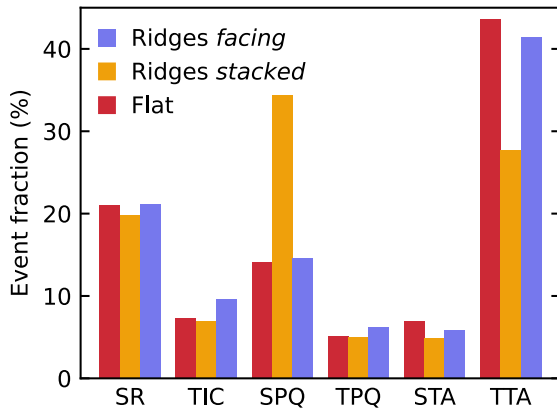


FIG. 9. Bipolar three layers, loss processes. Comparison of excitonic events in three-layer devices containing a flat interface or a ridges interface (20 nm high, 50 nm wide) either with stacked or facing offset, under 5.0 V applied bias. Abbreviations: SR, singlet radiative decay; TIC, triplet internal conversion; SPQ (TPQ), singlet (triplet) polaron quenching; STA (TTA), singlet (triplet) triplet annihilation. Blocking layers prevent carrier collection at the opposite electrode.

transport layers, which also serve as blocking layers for the opposite charge carriers by means of a 0.5 eV energy barrier. The blocking function of HTL and ETL is crucial to grant carrier confinement within the EML: we find exciton generation within the transport layers to prevail otherwise (see Supplemental Material [42], Figs. S17 and S18). With two ridges interfaces, multiple configurations are possible, depending on the lateral offset: as we employ periodic morphologies, we

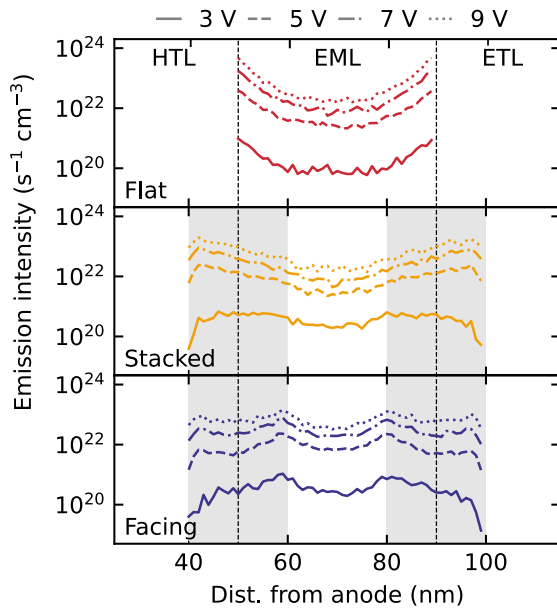


FIG. 10. Bipolar three layers, emission profiles. Emission profile in the anode-to-cathode direction for bipolar three layers containing a flat interface or a ridges interface 20 nm high, 50 nm wide either with stacked or facing offset. The dashed black lines indicate the position of the interfaces in the flat device. In the ridges devices, shadowed areas indicate regions where roughness implies EML- or transport-layer material may be present.

consider the extremes of in-phase (*stacked*) and out-of-phase (*facing*) offset [Fig. 1(e)].

In Fig. 8, we consider how the width and offset of ridges morphologies affect the distribution of holes [Fig. 8(a)], singlet excitons [Fig. 8(b)], and the resulting exciton-polaron quenching [Fig. 8(c)] and exciton-exciton annihilation [Fig. 8(d)] events. The different loss processes (Fig. 9) and the emission profiles (Fig. 10) in a pair of ridges devices with different offset are finally compared against a flat device.

Figure 8(a) displays the hole distribution at a 5.0 V applied bias in ridges devices for two different aperture angles and for a stacked versus facing offset. As before, holes are funneled to the tips of the HTL-EML interface from where they are injected. This leads to inhomogeneous, quasifilamentary current flow with a charge shadowing effect in the areas between the tips. In both stacked and facing devices, holes accumulate inside the tips (i.e., in the concavities) of the EML-ETL interface as well. Similarly, by symmetry, electrons accumulate at the tips of the EML-ETL interface and in the valleys between the tips of the HTL-EML interface (see Supplemental Material [42], Fig. S15(a)). As a result, the electron and hole currents (indicated as white arrows in [Fig. 8(a)]) are spatially separated in the stacked offset, while there is some overlap (in the neck between the tips) for a facing offset. The degree of overlap between the electron and hole current also depends on the feature size: it is larger for a 50 nm wide ridges morphology [bottom right of Fig. 8(a)] than for a 20 nm wide morphology [bottom left of Fig. 8(a)].

These filamentary currents determine the resulting singlet exciton distribution [Fig. 8(b)]. For the stacked offset, the scarce overlap between the hole and electron currents inside the EML results in exciton generation mainly in the concavities of the tips on either side of the EML, where electrons or holes accumulate. In contrast, for the facing offset, exciton generation is also strong in the crossover region of electron and hole current, i.e., at the narrow “necks” of the EML. The distribution for triplet excitons is similar, yet the excitons are more spread out due to the longer lifetime of the triplets, which allows for diffusion (see Supplemental Material [42], Fig. S15(b)). These sites of high charge and exciton density act as a hot spot for EPQ and EEA losses [respectively, Figs. 8(c) and 8(d)]. A detailed analysis in Fig. 9 shows that SPQ is the predominant loss mechanism for the ridges device with stacked offset, while TTA dominates in the flat device and in the ridges device with facing offset, in line with the observed distribution of charge and exciton density.

Consistent with the results for the bipolar bilayers, we find only minor differences in the IQE between the flat and ridges device. In fact, the devices with the facing offset and the flat devices give identical IQEs, and only those with the stacked offset are about 2% lower (see Supplemental Material [42], Fig. S19).

Even though the overall IQE hardly varies, we find that the presence of nanostructured interfaces between the transport and emissive layers leads to a conspicuous change in the emission profile along the anode-to-cathode axis. Figure 10 compares the emission profiles for the flat device and two ridges devices (20 nm high, 50 nm wide) with either stacked or facing offset. As the intensity is plotted against distance from

the anode, at some distance the charge transport layer extends into the EML and vice versa. In the flat device, the majority of radiative decay events happens within 7 nm from the HTL-ETL or ETL-EML interface. In the presence of two ridges interfaces, however, the emission profile is instead flattened out. The facing ridges devices presented in the bottom panel of Fig. 10 exhibit an almost flat emission profile scarcely affected by voltage. Further examples are given in Fig. S21 [42].

IV. DISCUSSION

To clarify the influence of rough interfaces within OLEDs, we have performed 3D-kinetic Monte Carlo simulations of ideal, symmetric bilayer and three-layer devices, both unipolar and bipolar, revealing that the microscopic behavior of a device can be significantly influenced by purely geometrical modifications of the interface morphology, namely, the introduction of rough features between adjacent layers. The presence of roughness considerably affects both charge and exciton dynamics in a shape- and size-dependent fashion. We shall first focus on the injection properties resulting from morphological variation.

In the presence of an energy barrier for charge transfer between layers, ridges morphologies (with triangular cross section) induce charge accumulation at the tips. The tips then act as injection points, determining the onset of quasifilamentary currents and leading to a strongly inhomogeneous distribution of charge carriers and excitons at the interface and in the adjacent layer. Ridges devices characteristically show enhanced charge injection across the energy barrier, yielding a significant rise in the current-voltage curve, compared to a flat-interface device. Conversely, devices containing a stripes morphology (with rectangular cross section) display negligible enhancement except at low voltage.

We attribute the increased current density through ridges devices to an enhanced carrier mobility at the tips, resulting from the locally larger charge density: higher occupation translates to a higher Fermi level, as visible from the occupied density of states (oDOS) at the tips in Fig. 11. We argue that the key difference between ridges and stripes devices is that, in ridges devices, the sloping interface allows charge carriers to “slide” alongside the interface: thus, both carrier drift and diffusion enable charge funneling toward a favorable injection point (i.e., the tip). Vice versa, in stripes devices, charge carriers meet a wall and need to diffuse in a direction parallel to its surface, in order to find a good spot to progress over the energy barrier or funnel forward into the stripes. This results in a weaker carrier funneling (further discussion is provided in the Supplemental Material [42], Sec. S5.2). The difference in carrier motion is clearly visible in the video provided as Supplemental Material [42]. The fact that downhill devices exhibit virtually no influence of the morphology on device behavior agrees well with this reasoning.

Consistently with the reasoning, equivalent morphologies in bipolar bilayer devices produce a smaller increase in current density [see Fig. 7(a)] compared to the flat device. The reason is that the recombination of charge carriers at the interfaces reduces the occupation at the tips [see Fig. 11(b)], thus producing a lower Fermi level. In contrast, in a three-layer structure, carrier recombination occurs in the central layer,

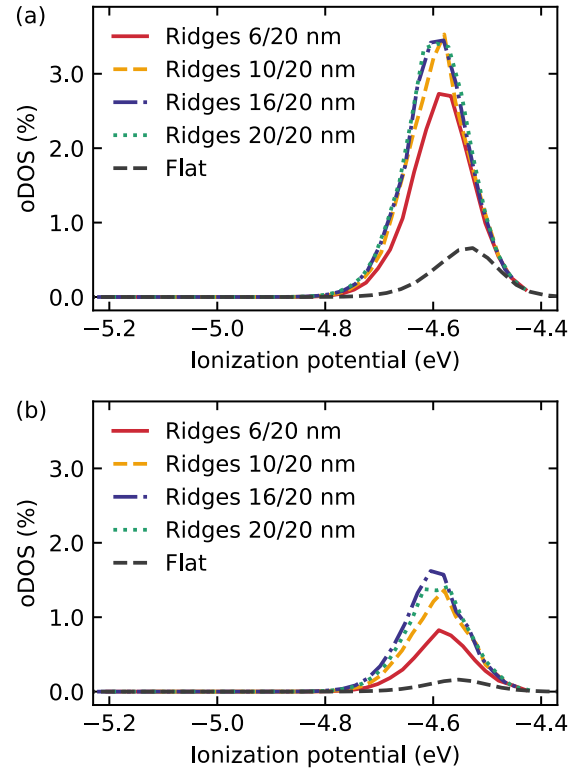


FIG. 11. oDOS. Occupied density of states at the tips of ridges interfaces in (a) unipolar or (b) bipolar uphill bilayer devices under 6.0 V bias. Devices contain a ridges interface 20 nm wide with varying height, as indicated. A flat device is reported for comparison.

and not at the tips of the charge injection layers [compare Fig. 5 versus Fig. 8(b)]. The charge carrier occupation at the tips remains high, thus preserving the injection boost that we reported for unipolar devices.

It is worth briefly mentioning that, in ridges devices, the Fermi level at the tips (E_F) strongly depends on the size of the ridges features, but such dependence cannot be tracked back to a universal trend with aperture angle α . Figure 11 reports the oDOS at the tips of ridges interfaces with varying sizes, in unipolar and bipolar devices. When the height is varied at constant width, DOS occupation increases, as charge funneling is more efficient. The dependence of tip occupation on aperture angle is detailed further in the Supplemental Material [42], Sec. S8 (including Refs. [48,49]).

We now consider the impact of interfacial morphology on emission. In bipolar devices with two and with three layers, we have observed a surprisingly minor impact of roughness on internal quantum efficiency (IQE) and IQE roll-off owing to a trade-off between loss mechanisms [Fig. 7(b)]. For the bilayer ridges devices, charge accumulation at the tip sites surprisingly does not increase exciton-polaron quenching (EPQ). We attribute this to the fact that a nominally flat interface and one with ridges resemble each other insofar, that for both interfaces, sites of high carrier density are also sites with a high probability for exciton formation, and hence for EPQ. Whether these sites are tail states in the DOS or geometric traps such as tips does not seem to matter much.

This is different for three-layer devices. The most noticeable difference is that, in three-layer devices, even for flat

interfaces the fraction of exciton-exciton annihilation events—more precisely, triplet-triplet annihilation (TTA)—increases drastically. In bilayer devices, TTA happens half as often as singlet-polaron quenching (SPQ), while in three-layer devices, TTA happens more than twice as often as SPQ (Figs. 6 and 9). The reason is that the sites of charge accumulation and exciton formation are separated in three-layer devices. High carrier densities only prevail in the charge transport layers. Once carriers enter the central emissive layer, they recombine to form excitons and are hence no longer present as charges. This is the case for the flat device and the ridges device with facing offset: sites of high carrier density are at the tips of the charge injection layer, while sites of high exciton density are at the same tips, yet inside the emissive layer, thus precluding strong SPQ. We recall the carrier pathways indicated by white arrows in Fig. 8(a) that result in efficient exciton formation at the necks, while charge accumulation, e.g., of holes, inside the EML only occurs comparatively weakly at the concave side of the tips, e.g., adjacent to the electron transport layer (ETL). For the stacked offset, however, this is different. Charges, e.g., holes, injected into the EML accumulate strongly at the concave tips to the next layer, e.g., the ETL [Fig. 8(a)]. These regions of charge accumulation are also the sites where excitons form [Fig. 8(b)], hence leading to a dominance of SPQ. The surprising feature is that this interplay between SPQ and TTA losses does not affect the overall emission efficiency, consistent with studies on simulated phosphorescent devices by van Eersel *et al.* [35].

Nevertheless, the three-layer structure can be used to fine tune the overlap between the hole and electron currents and thus to modulate the recombination zone inside the EML. As shown in Fig. 10, this can be used to achieve a surprisingly homogeneous, voltage-independent emission profile across the emissive layer. The disadvantage of such an approach is that increased carrier concentrations at tips can possibly enhance local degradation. Shen and Giebink [50] have associated filamentary charge transport with lifetime reduction in flat-interface simulated OLEDs similar to our model systems. Further simulations are, however, needed to verify whether the locally enhanced charge density and concentration of EPQ events in our model systems lead to a shorter device lifetime, compared to a flat-interface scenario where filamentary charge transport is rather caused by energetic disorder [51–53].

As a final note, our simulations could only explore morphologies up to a width scale of tens of nanometers, which is the upper threshold for state of the art kMC. Surface atomic force microscopy performed on as-deposited films [14,15,54–58] shows variations in film thickness usually of the order of 10 nm, but generally on a width scale of micrometers along the directions parallel to the electrodes. Such analysis may, however, reflect roughness arising from the substrate, reducing the effective thickness variations of internal layers. Nevertheless, we extrapolate from our simulations that, in the presence of corrugation on a large width scale, charge carrier funneling would be rather ineffective. Macroscopic effects such as the *JV* enhancement already vanish for a 20 nm high, 100 nm wide ridges morphology [Figs. 3(b) and 7(a)]. We emphasize that this 100 nm wide morphology still affects the microscopic behavior of the device by producing a

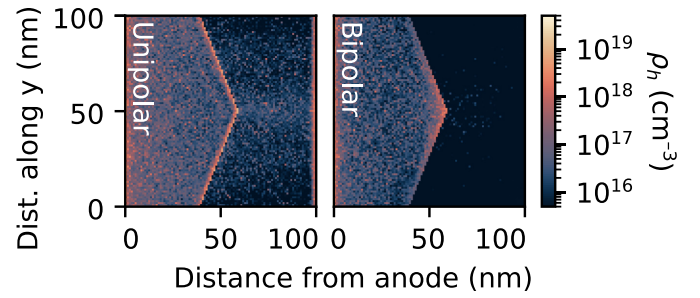


FIG. 12. Wide morphologies. Hole density maps at 6.0 V in a unipolar (left) or bipolar (right) uphill bilayer with a 20 nm high, 100 nm wide ridges morphology. Holes move from left to right.

visible inhomogeneity in charge distribution both in unipolar and bipolar uphill bilayers, displayed in Fig. 12.

V. CONCLUSIONS

We have employed three-dimensional kinetic Monte Carlo simulations of bi- and three-layer devices to elucidate the charge and exciton dynamics across rough organic-organic interfaces. We compared two interfacial morphologies with periodic corrugation and either rectangular (stripes) or triangular (ridges) cross section against a reference flat interface.

We detect significant impact of the interfacial morphology only when associated with an energy barrier for charge transport, in which case funneling of charge carriers to the tips of the interface creates an inhomogeneous distribution of charge density. Such funneling is favored in the presence of a ridges interface (particularly for smaller aperture angles). Significant inhomogeneities in charge and exciton density are present even for corrugations over a 100 nm width scale.

As the tips of the injection layer act as hot spots for charge injection, the current density of a ridges-interface device can be significantly enhanced compared to the reference flat-interface device, thus lowering the device operating voltage. Interfacial roughness does not affect the overall internal quantum efficiency of bi- and three-layer devices, although it favors exciton-polaron quenching losses over exciton-exciton annihilation processes. The interfacial morphology furthermore influences the recombination profile inside the emissive layer, yielding a flatter and less voltage-dependent profile compared to a flat-interface device.

On the downside, we draw attention to the possible role of roughness in aggravating device degradation due to the focusing of charge transport and losses in the tip volume, even when macroscopic properties such as the *JV* of the pristine device appear unaffected.

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G.C., A.K., and S.G. conceived the project. G.C. performed kMC simulations under the supervision of S.G., E.T., and A.K. G.C., and A.K. wrote the paper with input from all authors.

The authors declare no competing interests.

DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

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Simulation of charge and exciton dynamics across nanostructured rough interfaces in organic light emitting devices

Supplementary Material

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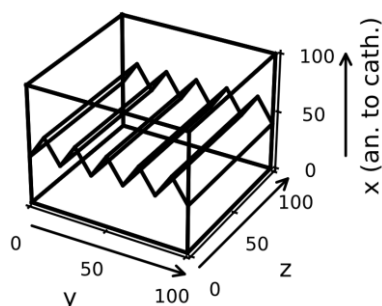
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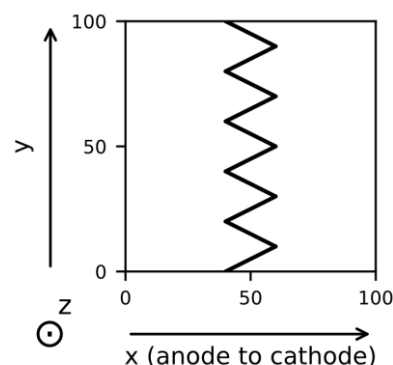
Section S1. List of abbreviations

EEA	Exciton-exciton annihilation (singlet or triplet with singlet or triplet)
EPQ	Exciton-polaron quenching (singlet or triplet with electron or hole)
SPQ	Singlet-polaron quenching (with electron or hole)
SSA	Singlet-singlet annihilation
STA	Singlet-triplet annihilation
TPQ	Triplet-polaron quenching (with electron or hole)
TSA	Triplet-singlet annihilation
TTA	Triplet-triplet annihilation

Section S2. Axes conventions



(a) Axes conventions, 3D

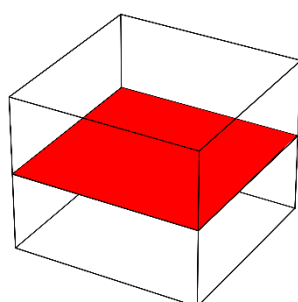


(b) Axes conventions, density maps

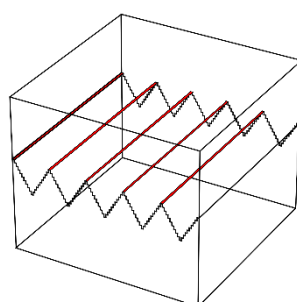
Figure S1: Axes conventions.

Section S3. Tip sites

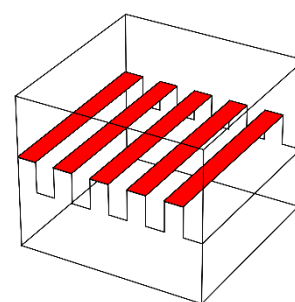
We identify as *tip sites* the interface sites located farther from the injecting electrode for each charge carrier, e.g. the highlighted sites in the following figure (assuming injection from the bottom electrode resulting in a current along +x).



(a) Flat



(b) Ridges



(c) Stripes

Figure S2: Tip/edge sites.

Section S4. Formulas

4.1. Current density and IQE

Under steady-state conditions, the current density in each replicate simulation is calculated as:

$$J_i = \frac{e}{l_y \cdot l_z} \cdot [\text{dfh}(t_{\max}) - \text{dfh}(t_{\max}/2)]$$

where l_y, l_z are the device sizes along the y and z axis (voltage is applied along the x axis), e is the unit charge and $\text{dfh}(i)$ indicates the cumulative count of downfield hops at timestep i ($t_{\max}$ is the last timestep).

Similarly, internal quantum efficiency in each replicate simulation is calculated as:

$$IQE_i = \frac{R(t) - R(t/2)}{\text{dfh}(n) - \text{dfh}(n/2)}$$

where, in addition, $R(i)$ indicates the cumulative count of recombination events at timestep i .

After N replicates have been simulated, the average current density and IQE are obtained as the average value of the individual replicates:

$$\bar{X} = \frac{1}{N} \cdot \sum_{i=1}^N X_i$$

where X is IQE or J .

Uncertainties on the average values are calculated as:

$$\delta_X = \chi \cdot \frac{1}{(N-1)^{1/2}} \cdot \left[\frac{1}{N} \sum_{i=1}^N (X_i^2) - \bar{X}^2 \right]^{1/2}$$

where χ expresses the width of the 95% confidence interval.

4.2. Charge/exciton density and loss rates

Density maps presented in the main text and in the following document display the distribution of the local density of charges and excitons, and of the local rates for excitonic loss processes. In accordance with Ref. [1], the charge/exciton density per site $\rho_{i,s}$ is calculated as:

$$\rho_{(x,y,z),s} = \frac{\Delta t_{(x,y,z),s}}{\Delta t_{\text{tot}}} \cdot \frac{1}{V}$$

where $\Delta t_{i,s}$ is overall time interval during which site (x, y, z) hosts a particle of type s (hole, electron, singlet, triplet), Δt_{tot} is the global simulation time and V is the site volume (here 1 nm^3).

Rates for EPQ and EEA losses are obtained as:

$$K_{(x,y,z),e} = \frac{n_{(x,y,z),e}}{\Delta t_{tot}} \cdot \frac{1}{V}$$

where $n_{(x,y,z),e}$ is the number of events of kind e taking place on site (x, y, z) , divided by time and volume unit.

The results displayed in the colourmaps are obtained by averaging $\rho_{(x,y,z),s}$ or $K_{(x,y,z),e}$ along the z axis (Figure S1, here $N_z = 100$ sites) and over the simulation replicates (here $R = 5$), e.g.:

$$\bar{X}_{(x,y,z),s} = \frac{1}{R} \frac{1}{N_z} \sum_{r=1}^R \sum_{z=1}^{N_z} \rho_{(x,y,z),s}(r)$$

Section S5. Unipolar bilayers

5.1. Colourmaps

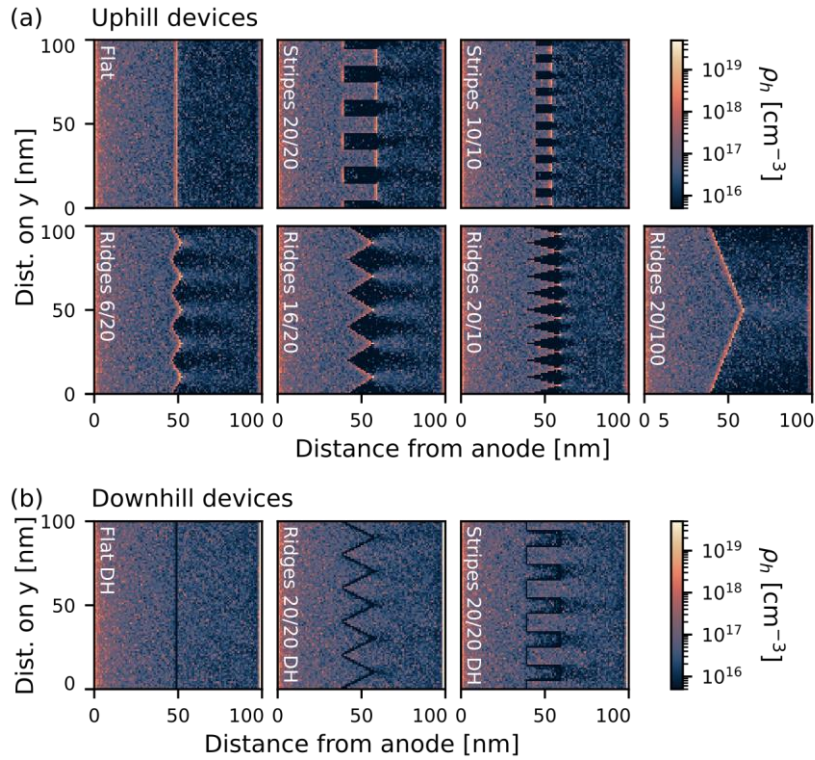


Figure S3: Charge density in unipolar *uphill* and *downhill* devices. Averaged hole density at 6 V applied bias in hole-only (a) *uphill* and (b) *downhill* bilayer devices containing various interfacial morphologies.

(a) *Top row: uphill bilayers with a flat, 20 nm high / 20 nm wide stripes, 10 nm high / 10 nm wide stripes interface. Bottom row: uphill bilayers with a 6 nm high / 20 nm wide ridges, 16 nm high / 20 nm wide ridges, 20 nm high / 10 nm wide ridges, 20 nm high / 100 nm wide ridges interface.*

(b) *Downhill bilayers with a flat, 20 nm high / 20 nm wide ridges, 20 nm high / 20 nm wide stripes interface.*

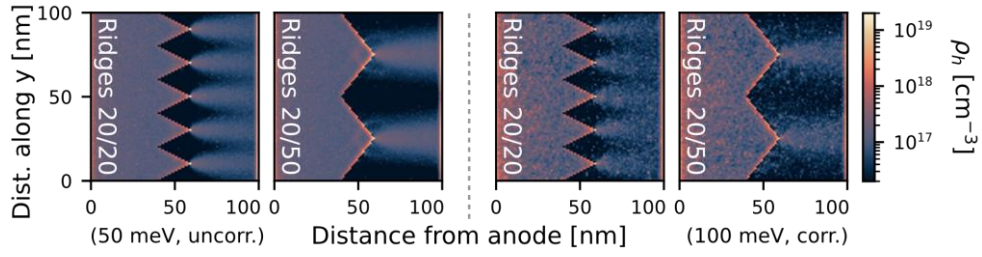


Figure S4: Charge density in unipolar *uphill* devices at varying disorder. Averaged hole density at 6 V applied bias in hole-only *uphill* bilayer devices containing 20 nm high / 20 nm wide or 20 nm high / 50 nm wide *ridges* interfaces. *Left panel:* uncorrelated disorder with $\sigma_{IP} = 50$ meV (the rest of this work employs $\sigma_{IP} = 100$ meV). *Right panel:* correlated disorder with $\sigma_{IP} = 100$ meV (the rest of this work employs uncorrelated disorder). Reducing σ_{IP} does not qualitatively alter the hole distribution although, for the 20 nm high / 50 nm wide *ridges* morphology, artifacts due to the Coulomb cutoff radius appear as a halo around the tips. Correlated disorder produces effects analogous to an uncorrelated disorder with smaller σ_{IP} .

5.2. Stripes vs. ridges: mechanism and profiles

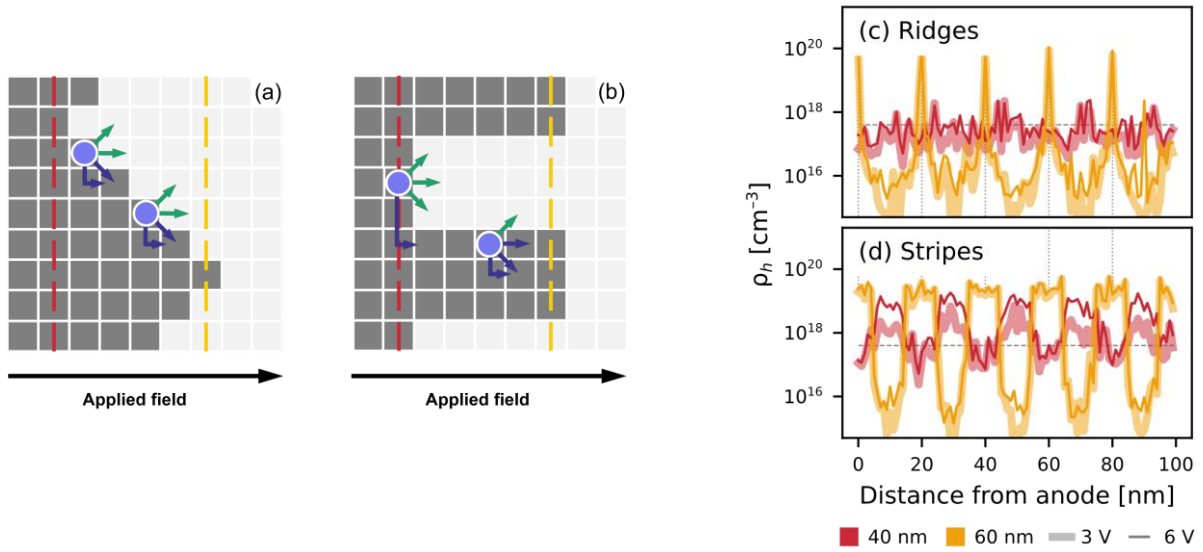


Figure S5: Different behaviour of charge carriers at a *stripes* vs *ridges* interface. (a,b) Schematic of sample charge carriers at the interface of a (a) *ridges* or (b) *stripes* morphology, with indication of possible hopping options (hopping against the applied field is neglected). Long arrows indicate paths that take more than one nearest-neighbour hopping step, diagonal arrows indicate non-nearest-neighbour hopping with one component parallel and one perpendicular to the applied field direction; green arrows indicate hops that lead to crossing the interface, dark blue arrows hops that do not. The red and yellow dashed lines indicate the positions along the morphology where the profiles in (c,d) have been extracted.

(c,d) Hole density profile at the concave and convex edge (40 nm and 60 nm from the anode respectively) in a hole-only bilayer with a (c) *ridges* or (d) *stripes* morphology (20 nm high / 20 nm wide in both cases) under 3 V and 6 V applied bias. The grey dashed line corresponds to the baseline of the bulk, reported for reference. For the *ridges* morphology, the hole distribution profile shows little change at varying voltage, with significant accumulation only at the convex tip of each ridge. Conversely, for a *stripes* morphology, the accumulation at the concave edge (red lines) significantly deviates from the bulk baseline in a voltage-dependent fashion, i.e. increases at decreasing applied voltage, consistently with a picture of hindered diffusion at increasing applied bias.

5.3. Inhomogeneity in charge distribution

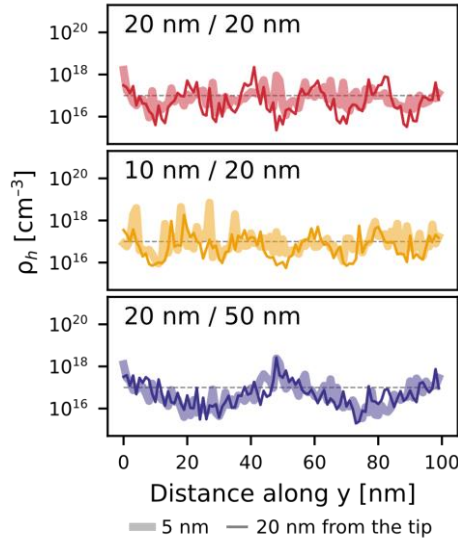


Figure S6: Charge distribution profile along the y axis, at 5 nm and 20 nm distance from the tip of three *ridges* interface with different feature size. Note how, for the 20 nm wide *ridges*, the inhomogeneous charge distribution generated by the tips of the morphology is clearly visible at 5 nm from the tips, and fades to random noise at 20 nm from the tips. Vice versa, for a 50 nm wide *ridges* morphology the profiles at 5 and 20 nm from the tips are precisely superimposable, showing an inhomogeneous charge density even at large distances from the interface.

5.4. JV curves

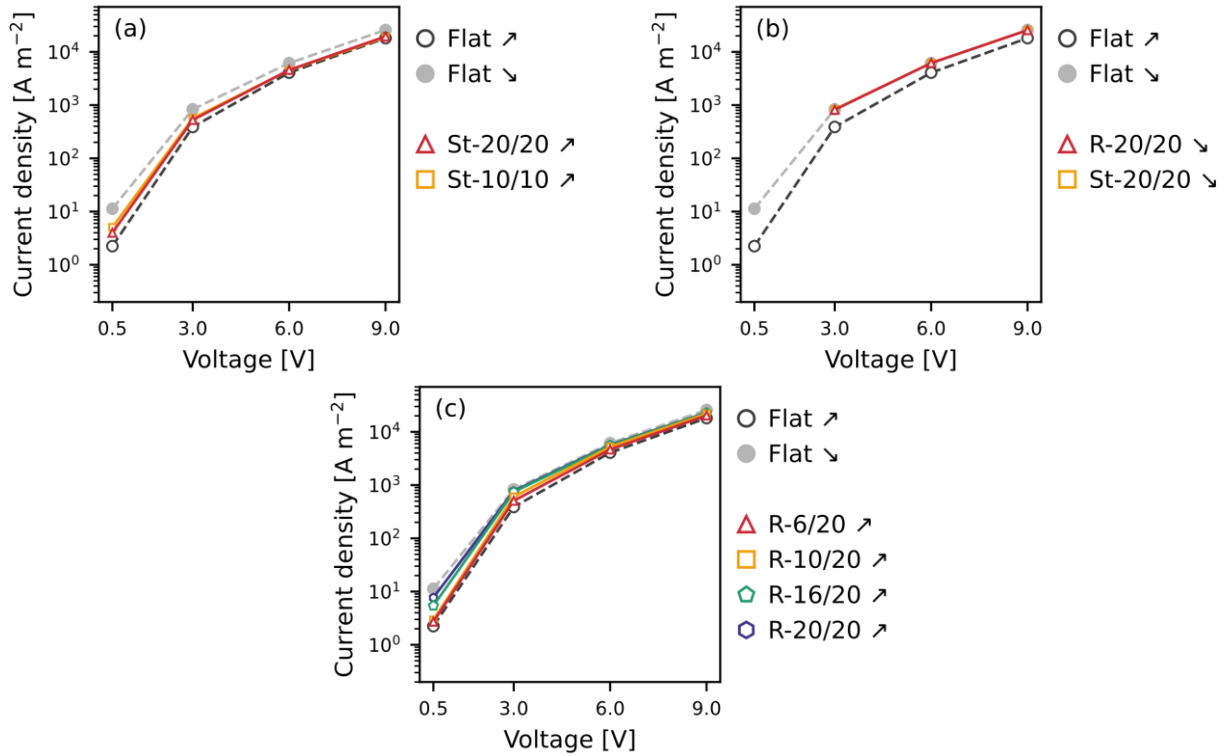


Figure S7: Unipolar bilayers, JV curve comparisons. Current density/voltage curves for several unipolar *uphill* bilayer devices containing different morphologies. Legend: R = *ridges*, St = *Stripes*, ↗ = *uphill* (positive energy gap, i.e. energy barrier), ↘ = *downhill* (negative energy gap). (a) *stripes uphill* bilayers 10 nm high / 10 nm wide vs 20 nm high / 20 nm wide (no difference observed); (b) *downhill* devices at varying morphology shape (no difference observed); (c) *ridges uphill* devices at 20 nm width and varying height (current density increases with increasing height, i.e. decreasing aperture angle).

5.5. Device schematics for unipolar bilayers with varying energy gap across the interface

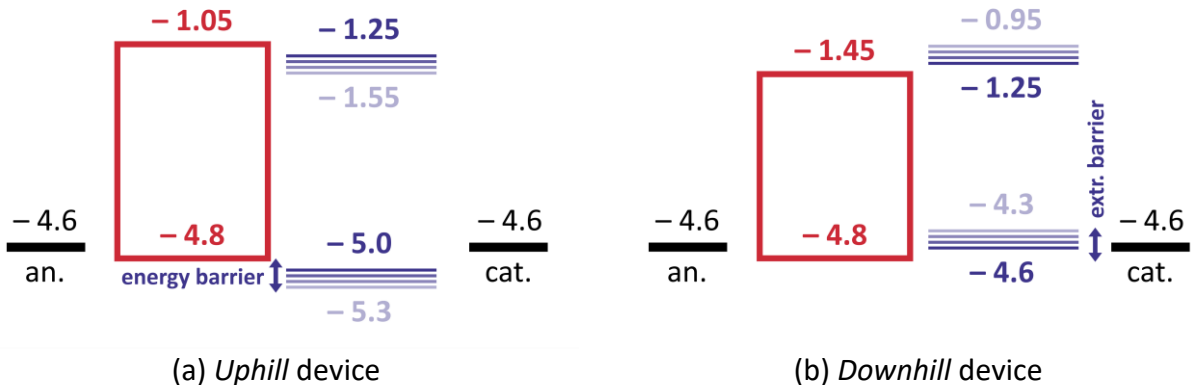


Figure S8: Schematics. Bilayer devices with varying energy barrier across the interface.

Section S6. Bipolar bilayers

6.1. Colourmaps

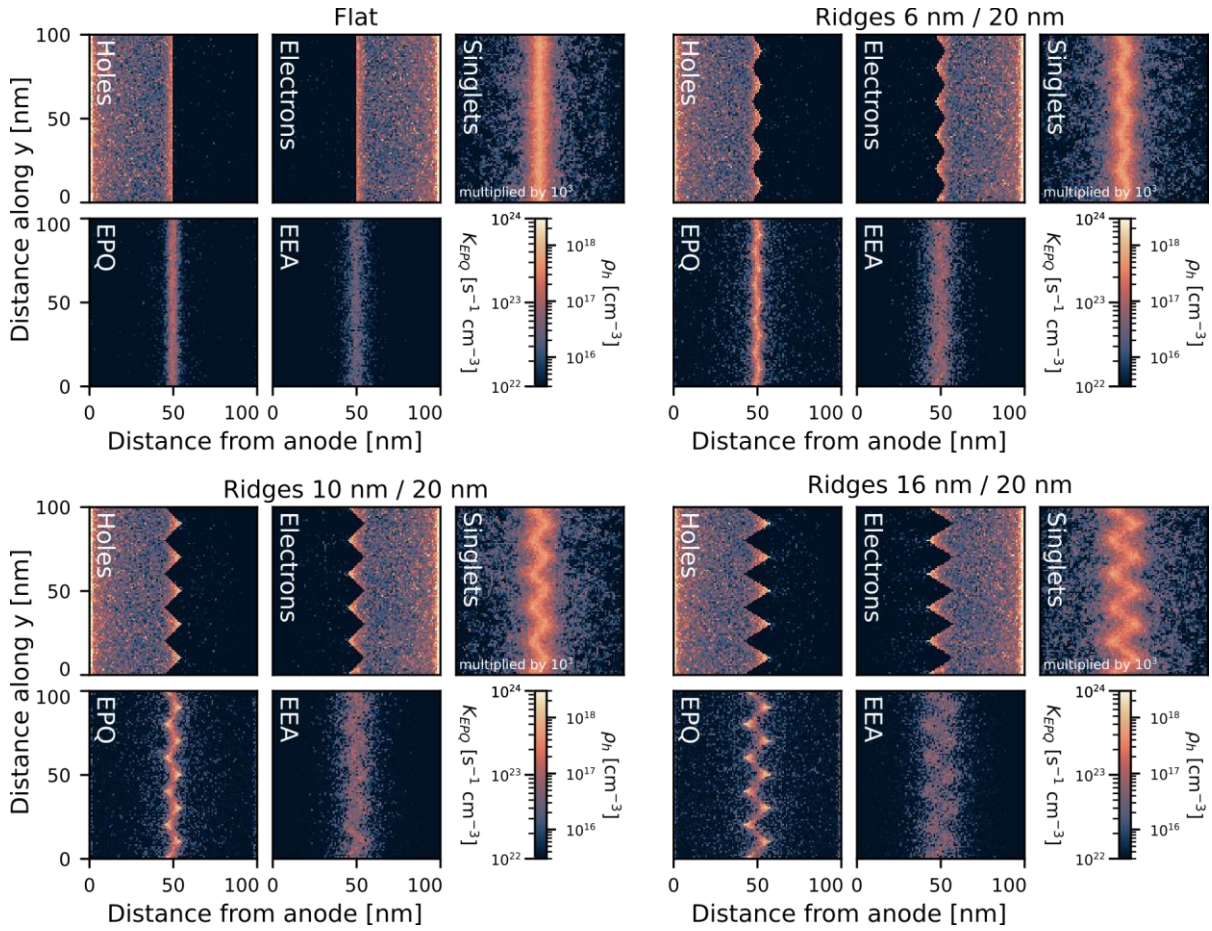


Figure S9: Bipolar *flat uphill* devices. Density maps showing the spatial distribution of the (*top row*) hole, electron and singlet density and (*bottom row*) the EPQ and EEA rates at 4 V applied bias in bipolar *uphill* bilayers with the indicated morphologies.

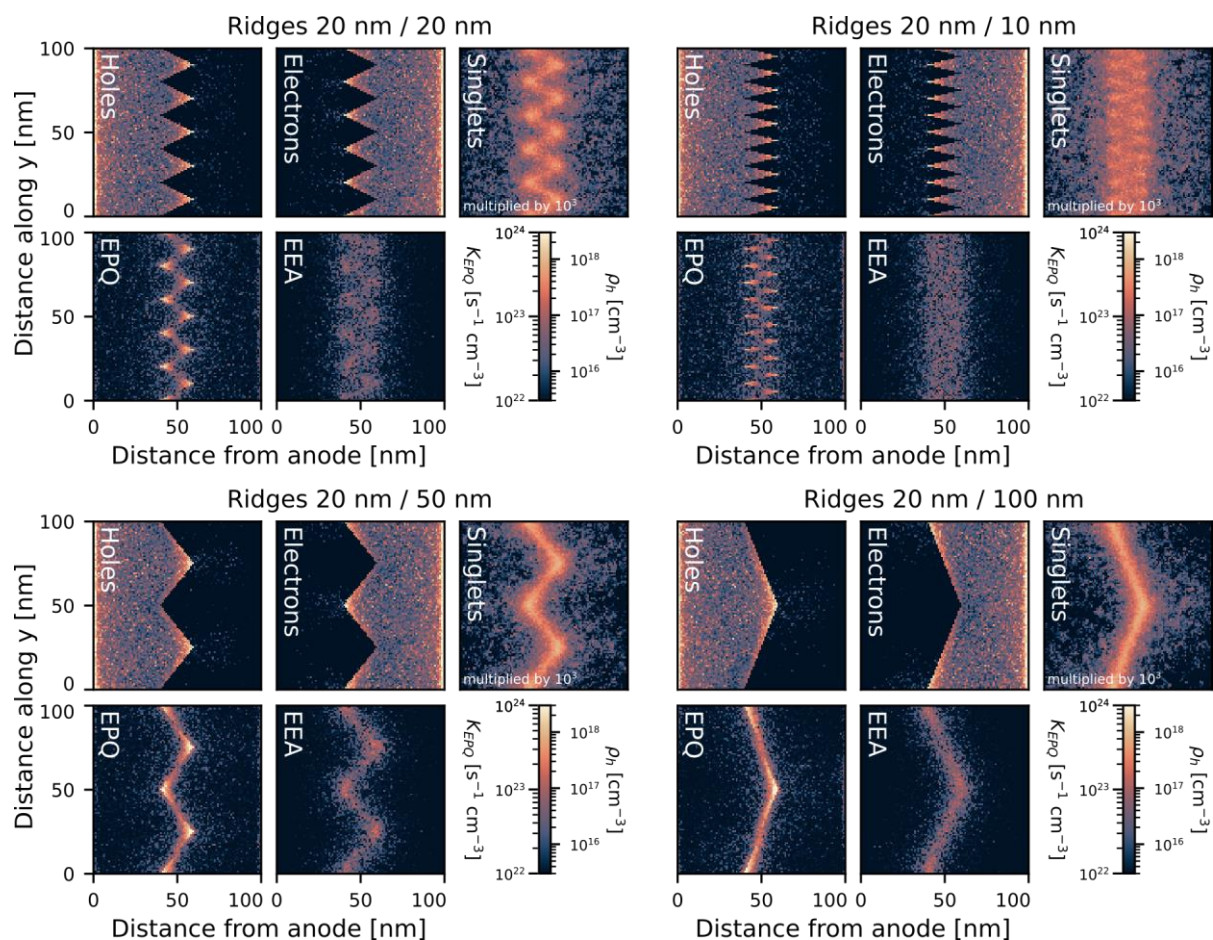


Figure S10: Bipolar *ridges uphill* devices. Density maps showing the spatial distribution of the (*top row*) hole, electron and singlet density and (*bottom row*) the EPQ and EEA rates at 4 V applied bias in bipolar *uphill* bilayers with the indicated morphologies.

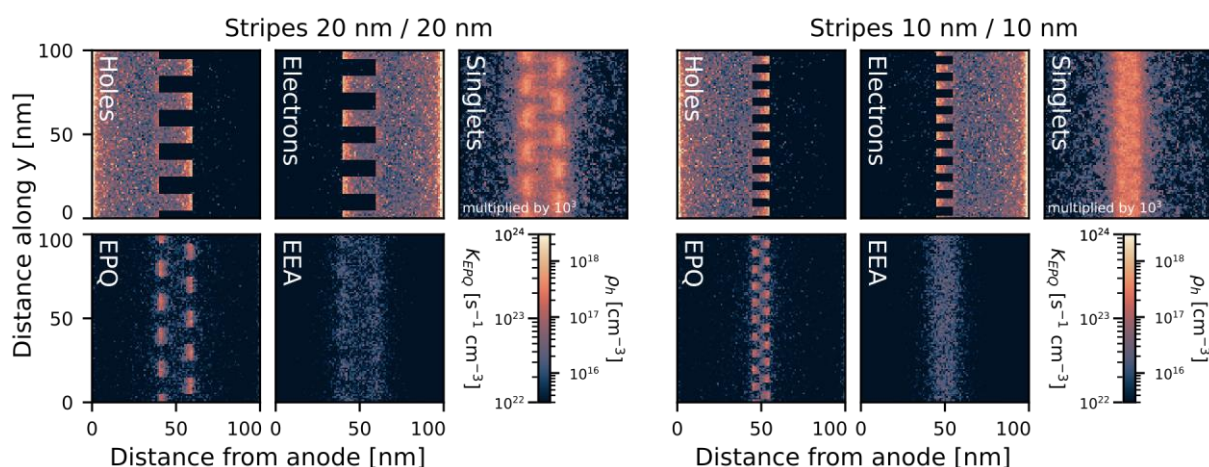


Figure S11: Bipolar *stripes uphill* devices. Colourmaps showing the spatial distribution of the (*top row*) hole, electron and singlet density and (*bottom row*) the EPQ and EEA rates at 4 V applied bias in bipolar *uphill* bilayers with the indicated morphologies.

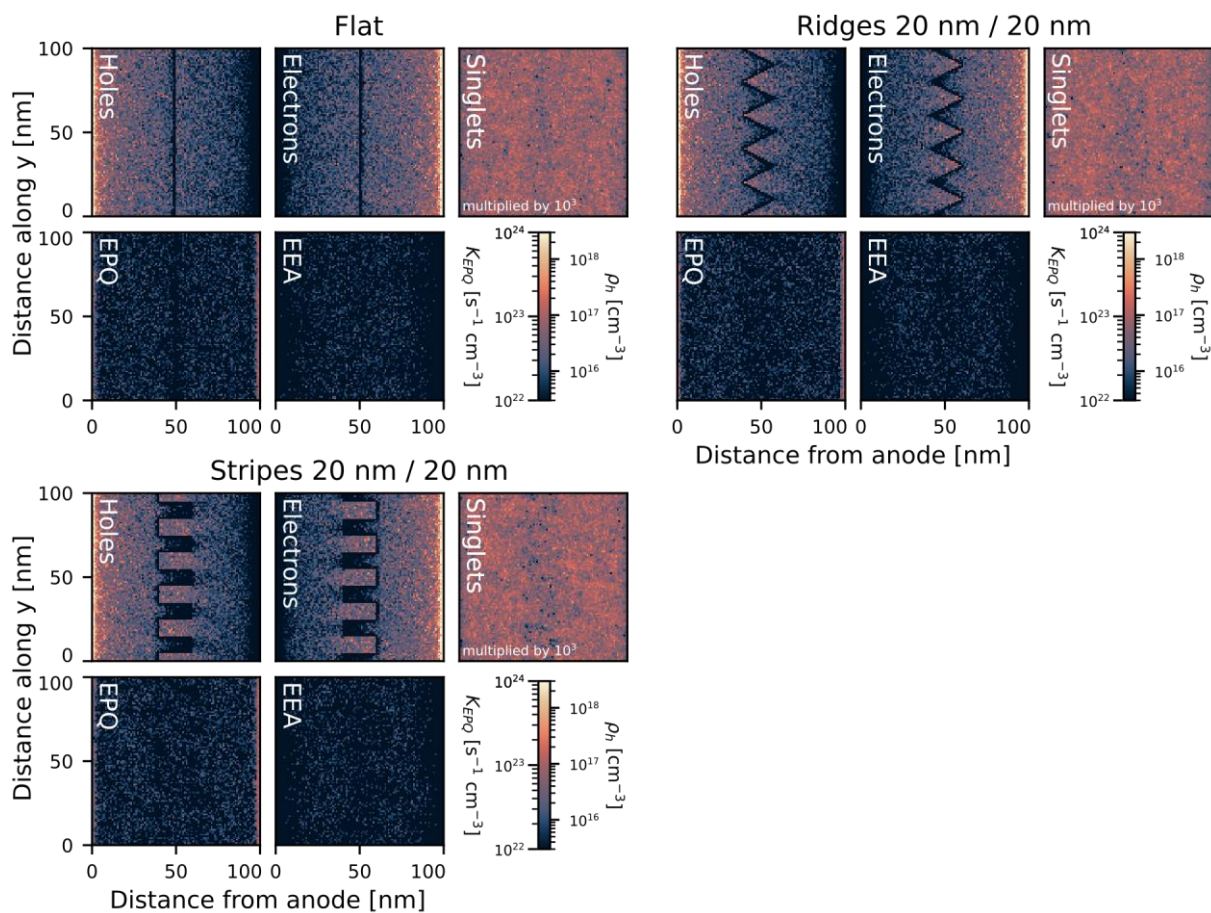


Figure S12: Bipolar *flat*, *ridges* and *stripes downhill* devices. Colourmaps showing the spatial distribution of the (*top row*) hole, electron and singlet density and (*bottom row*) the EPQ and EEA rates at 4 V applied bias in bipolar *downhill* bilayers with the indicated morphologies.

6.2. JV and IQE/L curves

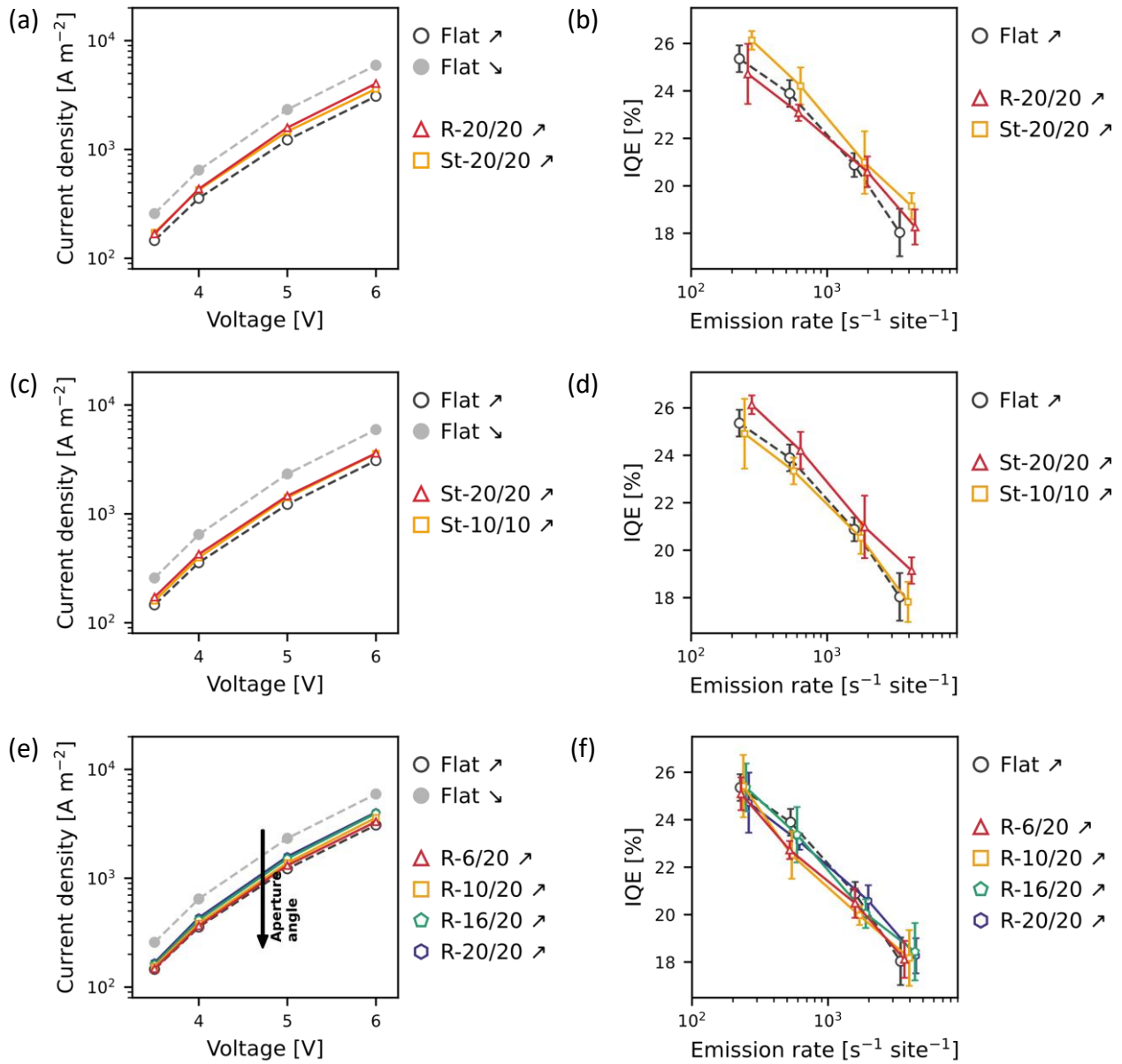


Figure S13: Bipolar bilayers (JV and IQE/L curve comparisons). Legend: R = *ridges*, St = *Stripes*, ↗ = *uphill* (positive energy gap, i.e. energy barrier), ↘ = *downhill* (negative energy gap). Current density/voltage curves (left column) and internal quantum efficiency (IQE) vs total emission rate (right column) for devices containing: (a,b) 20 nm high / 20 nm wide *ridges* or *stripes* interfaces; (c,d) *stripes* interfaces 20 nm high / 20 nm wide or 10 nm high / 10 nm wide; (e,f) *ridges* interfaces 20 nm wide with varying height.

6.3. Losses in bipolar bilayers

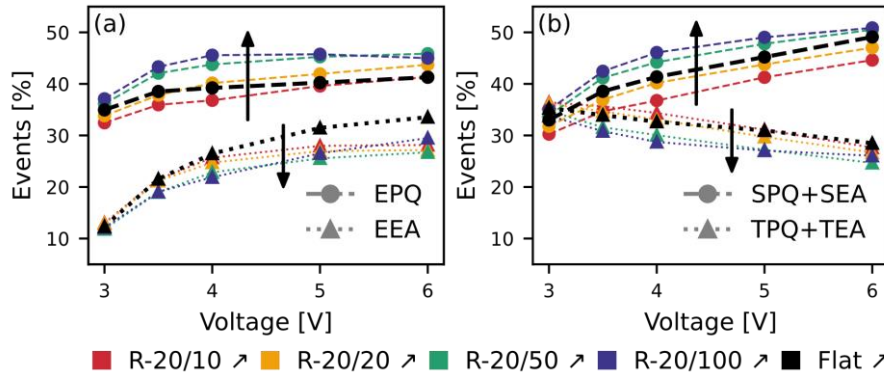


Figure S14: Bipolar *ridges* bilayers (JV and IQE/L curve comparisons). Legend: R = *ridges*, ↗ = *uphill* (positive energy gap, i.e. energy barrier), feature size is indicated as *height/width* in nm. Arrows indicate the direction of increasing aperture angle. Comparison of the losses (a) by process (i.e. EPQ vs. EEA) and (b) by spin of the lost excitons.

We observe a trend of slightly decreasing IQE at increasing morphology width, reported in Figure 3d of the main text. From Figure S17, we can attribute this reduced IQE to an increase in EPQ (particularly SPQ) losses, at quasi-constant EPA contribution. We explain this increase in EPQ as the result of an increasing charge imbalance at the interface, due to the large spatial separation between the accumulation points electrons and holes. Excitons are likely generated inside the tips by direct extraction of a carrier from the layer beside the interface: charge imbalance disfavours the process, leaving many free carriers inside each tip. The high carrier concentration in turn favours EPQ, thus increasing losses.

Section S7. Bipolar three-layers

7.1. Colourmaps

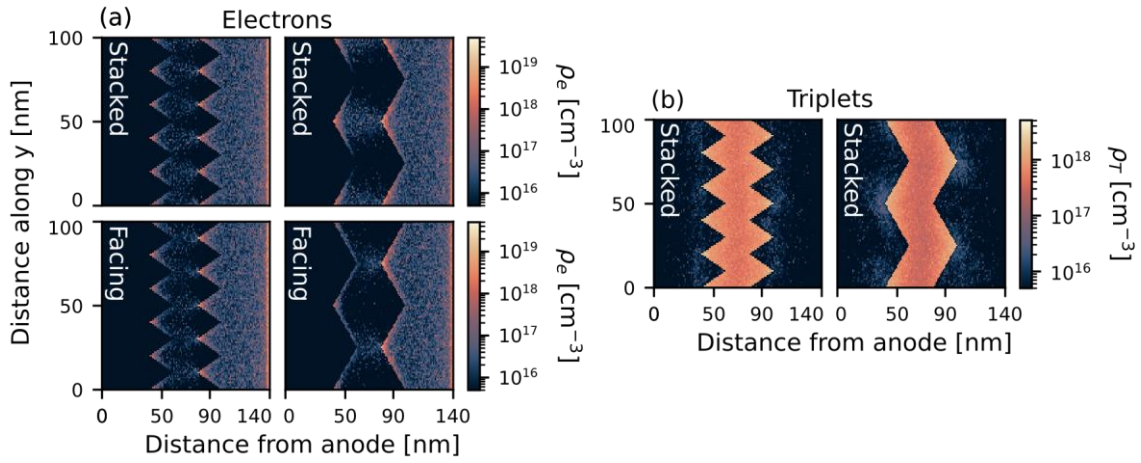


Figure S15: Electron and triplet density in *ridges* three-layers. (a) Electron density maps at 5 V applied bias in bipolar *uphill* three-layers with *ridges* morphology with varying size and offset. *Left column*: 20 nm high / 20 nm wide, *right column*: 20 nm high / 50 nm wide. (b) Triplet density in the same *uphill* three-layers with *ridges* morphology, with varying size and *stacked* offset.

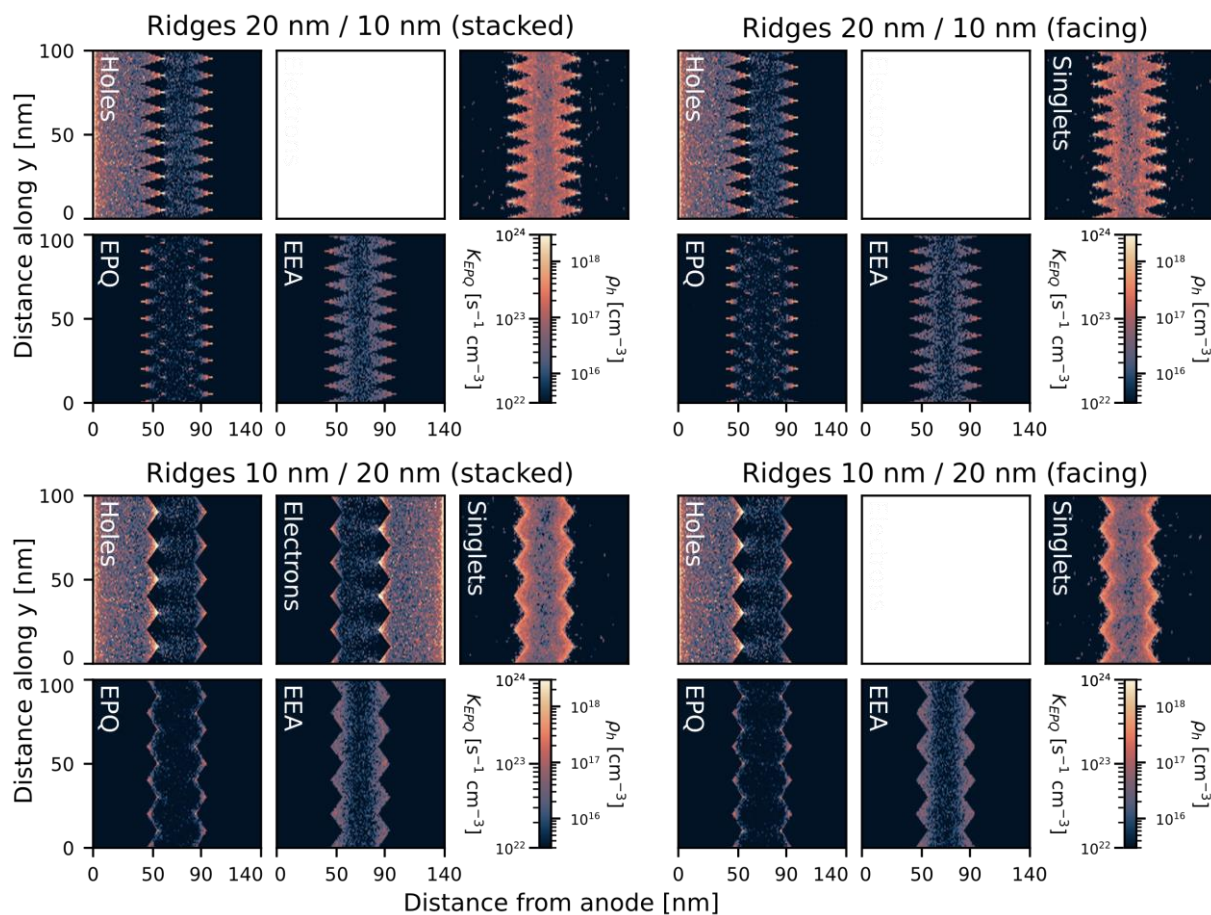


Figure S16: More ridges three-layers. Colourmaps showing the spatial distribution of (*top row*) hole, electron and singlet density and (*bottom row*) EPQ and EEA rates at 5 V applied bias in bipolar three-layers with the indicated morphologies.

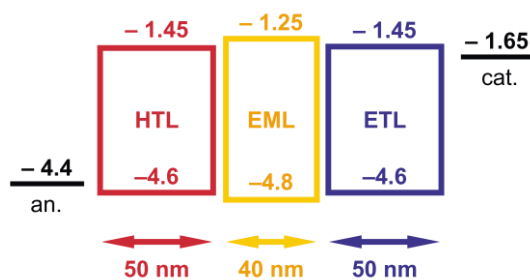


Figure S17: Schematic for a three-layer device with no charge confinement. In the device displayed, a 0.2 eV energy barrier is present for holes at the HTL-EML interface and for electrons at the EML-ETL interface. Conversely, a -0.2 eV gap (i.e. no barrier) is present for holes at the EML-ETL interface and for electrons at the HTL-EML interface. As a result, carriers encounter an injection barrier for entering the EML, but no barrier for extraction, and can easily escape under the applied voltage.

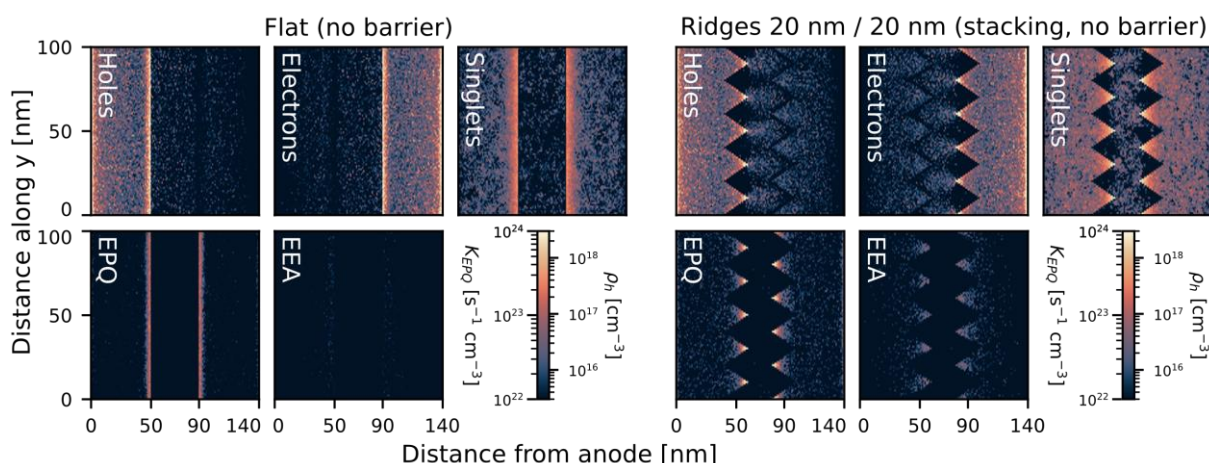


Figure S18: Three-layer devices with no charge confinement. Density maps showing the spatial distribution of (*top row*) hole, electron and singlet density and (*bottom row*) EPQ and EEA rates at 5 V applied bias in bipolar bilayers with no charge confinement within the EML, containing the indicated morphologies. As a result of the scarce carrier confinement in the EML, excitons are rather generated mostly in the transport layers.

7.2. JV and IQE/L curves

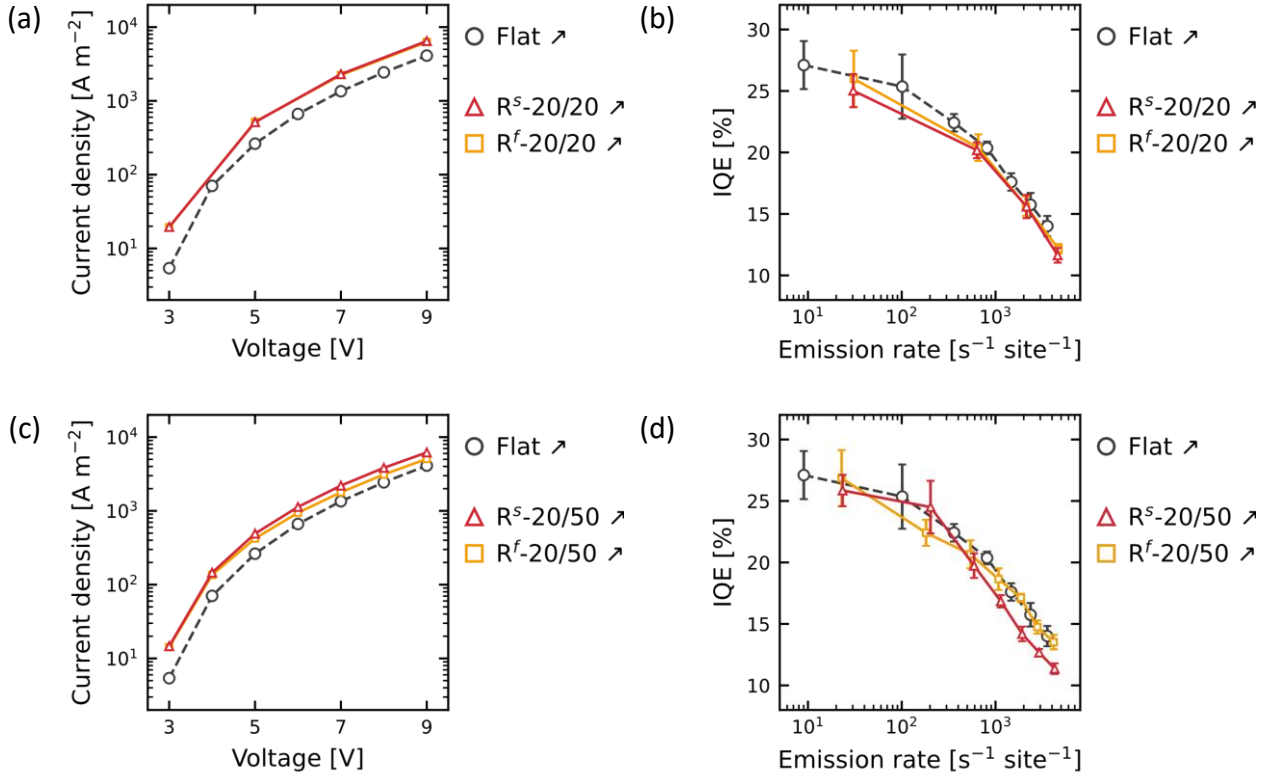


Figure S19: Three-layer devices (JV and IQE/L curve comparisons). Legend: R = *ridges*, St = *Stripes*, $\nearrow$ = *uphill* (positive energy gap, i.e. energy barrier), $\searrow$ = *downhill* (negative energy gap), superscript s = *stacking* offset (in-phase), superscript f = *facing* offset (out-of-phase). Current density/voltage curves (*left column*) and internal quantum efficiency (IQE) vs total emission rate (*right column*) for devices containing: (a,b) *ridges* interfaces 20 nm high / 20 nm wide with *stacked* or *facing* offset; (c,d) *ridges* interfaces 20 nm high / 50 nm wide with *stacked* or *facing* offset.

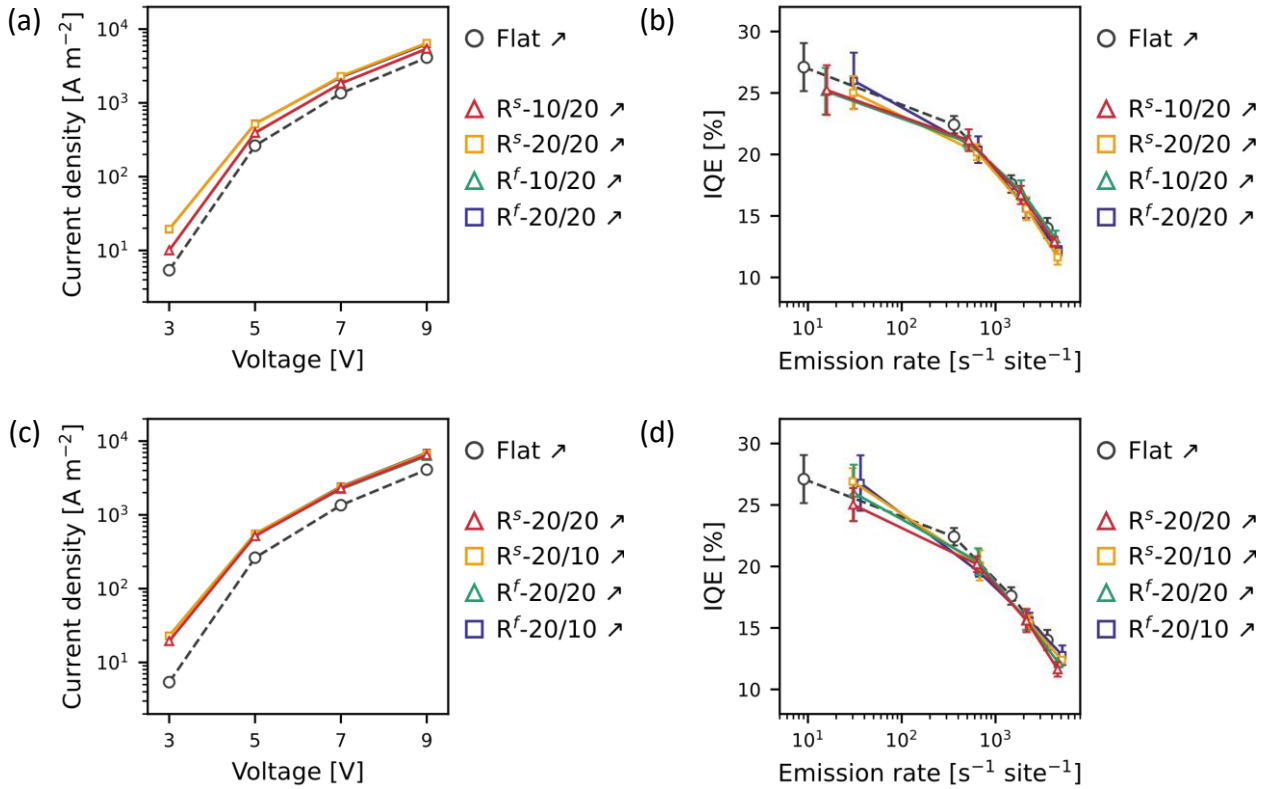


Figure S20: More three-layer devices (JV and IQE/L curve comparisons). Legend: R = *ridges*, St = *Stripes*, $\nearrow$ = *uphill* (positive energy gap, i.e. energy barrier), $\searrow$ = *downhill* (negative energy gap), superscript *s* = *stacking* offset (in-phase), superscript *f* = *facing* offset (out-of-phase). Current density/voltage curves (*left column*) and internal quantum efficiency (IQE) vs total emission rate (*right column*) for devices containing: (a,b) *ridges* interfaces 20 nm wide, 20 nm or 10 nm high, with *stacked* or *facing* offset; (c,d) *ridges* interfaces 20 nm wide, 20 nm or 10 nm high, with *stacked* or *facing* offset.

7.3. Emission profiles

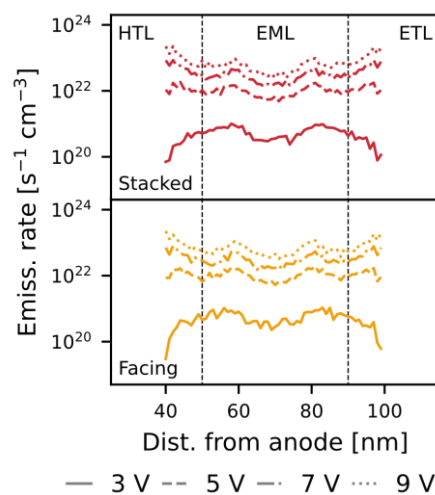


Figure S21: Emission profile. Emission profile along the anode-to-cathode axis for a three-layers device containing a pair of 20 nm high / 20 nm wide *ridges* interfaces, either with a *stacked* (top) or *facing* (bottom) offset.

Section S8. Effects of morphology size

8.1. Carrier density and occupied density of states at the tips vs morphology size

In *uphill ridges* bilayer devices, the charge density at the tips – and in turn the filling of the occupied density of states (oDOS), thus the local Fermi level (E_F) – strongly depends on the size of the *ridges* features, but such dependence cannot be tracked back to a universal trend with aperture angle α . Figure S22a reports the oDOS at the tips of *ridges* interfaces with varying height at constant width, in which case DOS occupation increases with height, as charge funnelling is understandably more “efficient”.

However, at constant height and increasing width (Figure S22b) we note an unexpected behaviour, in that the DOS occupation shows an initial increase with increasing width, peaking for a width around 50 nm. In fact, while each tip is less “efficient” in funnelling carriers at increasing width, the smaller number of tips in the device means that more charge carriers are available for each tip.

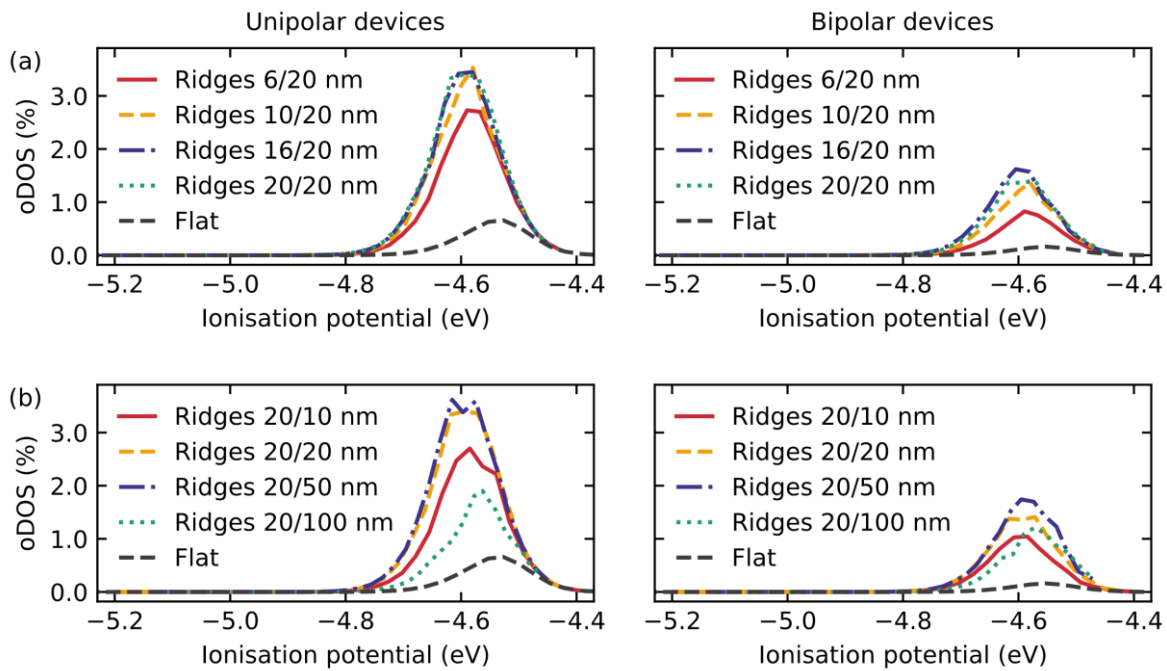


Figure S22: oDOS at varying morphology size. Occupied density of states at the tips of *ridges* interfaces in (top row) unipolar or (bottom row) bipolar *uphill* bilayer devices under 6.0 V bias. Devices contain (a) a *ridges* interface 20 nm wide with varying height or (b) a *ridges* interface 20 nm high with varying width, as indicated. A *flat* device is reported for comparison.

The trend of oDOS occupation with morphology width, although counterintuitive, can be reproduced with a simple model according to the given reasoning. We define (in arbitrary length units u):

- L , the device size, in the $[1, +\infty)$ u range.
- w , the width of the *ridge*, in the $[1, L]$ u range. For a macroscopic device, normally $L \gg w$ where the limit for $w \rightarrow L$ corresponds to a flat interface, for large L .
- h , the height of the *ridge* (a constant),
- $\alpha = 2 \cdot \arctan[w/(2 \cdot h)]$, the aperture angle.

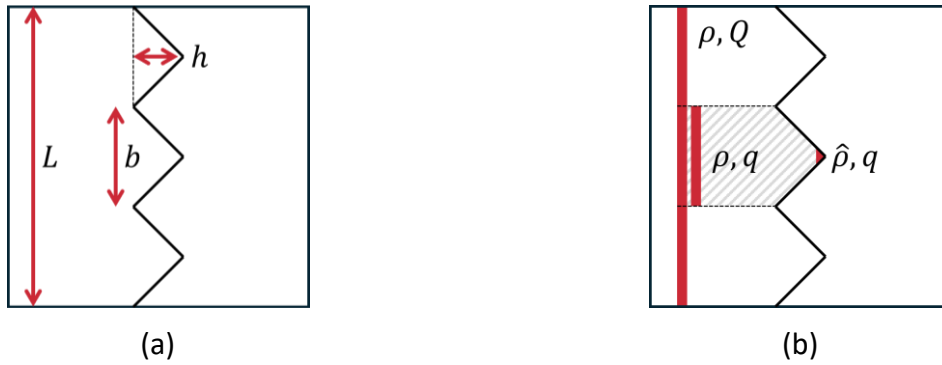


Figure S23: Model parameters. Schematics indicating (a) device length, morphology width and height (cf. Figure S1b) and (b) charge density (ρ , $\hat{\rho}$) and number of charges (Q , q) in different regions of the device.

Considering slices of unit thickness parallel to the electrodes (the argument holds even though charge density is not constant along the anode-cathode axis), we calculate:

- the charge density ρ in a slice of unit thickness far from the interface $\rho = Q/(L^2 \cdot u)$, where Q is the number of injected charge carriers,
- the number q of charge carriers which (on average) reach each tip: in a section of device limited by the tip (hashed area in Figure S23), $\rho = q/(L \cdot w \cdot u)$, hence $q = \rho \cdot (L \cdot w \cdot u)$.

Assuming the tip has unit volume, the charge density at the tip $\hat{\rho}$ is:

$$\hat{\rho} = \frac{q}{L \cdot u^2} \cdot \phi(w, h) = \rho \cdot w \cdot \phi(w, h)$$

where $\phi(w, h)$ is a function describing the “funnelling efficiency”, i.e. the likelihood of a charge carrier in the section of device limited by the tip to be funnelled to the very tip.

The function $\phi(w, h)$ is unknown but we argue that:

- ϕ should decrease monotonically with increasing α , converging to *flat* behaviour,
- for very small w , all carriers are funnelled: $\lim_{w \rightarrow u} \hat{\rho} = q/L = \rho \cdot w$, hence $\lim_{w \rightarrow 1} \phi = 1$,
- for very large w , the aperture angle tends to a straight angle and no carrier is funnelled: $\lim_{w \rightarrow L} \hat{\rho} = \rho \cdot w \cdot \phi(w, h) = \rho$, hence $\lim_{w \rightarrow L} \phi = 1/w = 1/L$.

Note that:

- for $\phi(w) = w^{-\alpha}$, then $\hat{\rho} = \rho \cdot w^{1-\alpha}$ which decreases monotonically for any $\alpha > 1$,
- for functions with a steeper decrease than power laws, $\hat{\rho}(w)$ may have a maximum. For example, for $\phi(w) = \exp(-\alpha w)$, $\hat{\rho}(w)$ reaches a maximum for $w = \alpha^{-1}$.

Figure S23 reports $\hat{\rho}(w)$ in *unipolar uphill ridges* devices, showing a maximum $w = 50$ nm. A normalisation $\hat{\rho}/n_t$ (where $n_t = L/w$ is the number of tips in the device) yields a curve which is proportional to $\phi(w)$, which can be fit with a stretched exponential. Consistently with our reasoning, then, $\phi(w)$ displays a faster decay than power law, which produces a maximum in $\hat{\rho}(w)$.

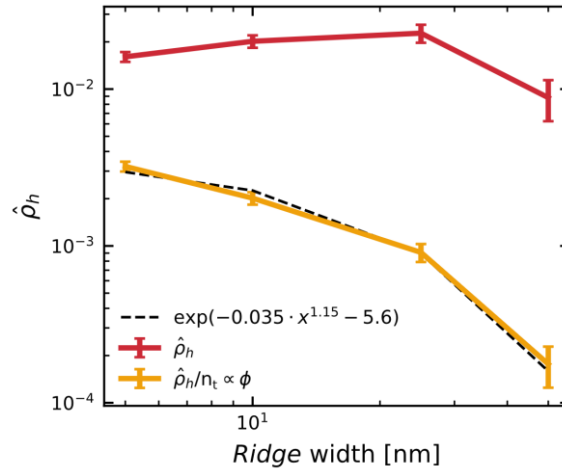


Figure S24: Charge density at the tips in unipolar *uphill ridges* devices. Absolute charge density, and charge density normalised by number of tips n_t , at the tips of *ridges* morphology with varying width in unipolar *uphill* devices.

8.2. Current density vs morphology size

A higher occupation at the tips translates to a higher local Fermi level (E_F) there. Carrier mobility is thus locally enhanced, yielding a higher current through the tip. When *ridges* height is varied at

constant width, carrier density and E_F at the tips increase monotonically with decreasing opening angle, and so does the overall device current density.

However, devices with constant *ridges* height and varying width show again an unexpected behaviour, in that the charge density at the tips shows a maximum for a width of 50 nm, but current density decreases monotonically with increasing width as the higher carrier mobility contrasts with the smaller number of injecting sites. Again, it is possible to obtain a consistent model.

We can calculate the Fermi level by rearranging eq. 6.6 in Ref. [2]:

$$E_F = E_0 + \sigma \cdot \sqrt{2} \operatorname{erf}^{-1}(2\hat{\rho} - 1)$$

where the last term expresses the degree of DOS filling and $\hat{\rho}$ is the average charge density at the tips from kMC calculations. Expectedly, a peak at $w = 50$ nm is observed.

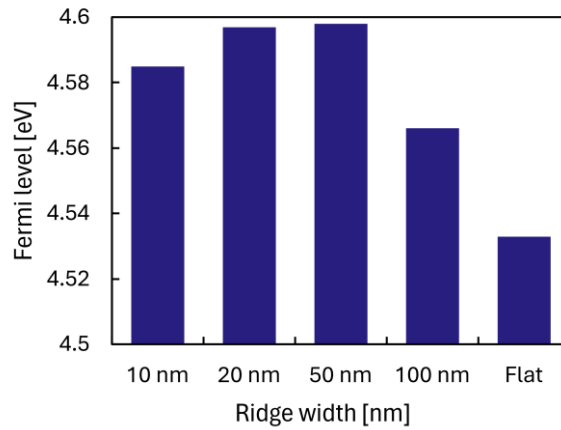


Figure S25: Fermi level. Fermi level at the tips of *ridges* morphology with varying width in unipolar *uphill* devices. A *flat* device is presented for reference.

We calculate the mobility for a carrier at a tip of the interface by rearranging eq. 5 from Ref. [3]:

$$\begin{aligned} \mu &\propto \exp\left(-\frac{\Delta E}{k_B T}\right) = \exp\left(-\frac{E_t - E_F}{k_B T}\right) \\ &\propto \exp\left(\frac{E_F}{k_B T}\right) \end{aligned}$$

where $\Delta E = E_t - E_F$ is the energy barrier between the Fermi level E_F and the transport level E_t .

We compare the *relative* mobility $\bar{\mu} = \mu/\mu_{\text{Flat}}$ to easily get rid of all multiplicative constants:

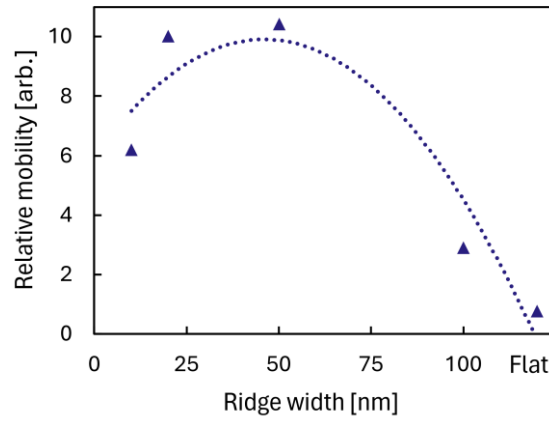


Figure S26: Relative mobility. Relative hole mobility at the tips of *ridges* morphology with varying width in unipolar *uphill* devices. A *flat* device is presented for reference. The dashed line is a guide to the eye.

The resulting current density J is directly proportional to the mobility and the number of injecting tips ($n_t = L/w$):

$$J \propto \bar{\mu} n_t$$

This qualitatively leads to the trend of monotonically decreasing current density with increasing width we observed in kMC simulations:

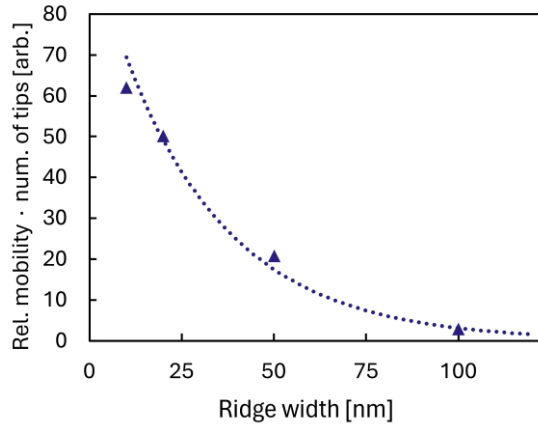


Figure S27: Current density. Trend of current density with *ridges* width in unipolar *uphill* devices. The dashed line is a guide to the eye.

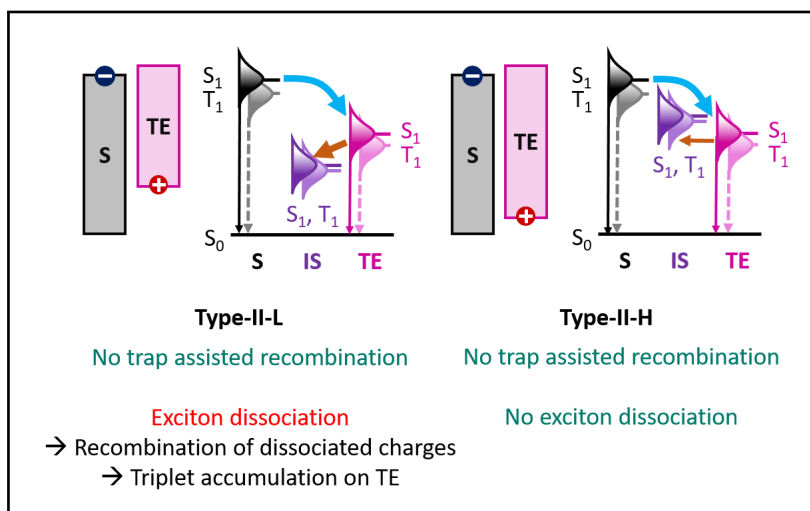
Note that this simple model only considers the current which is flowing through the tips. As the opening angle increases, however, charge funnelling is less efficient, and more charge carriers cross the interface far from the tip. Indeed, kMC shows a less sharp dependence of current density on *ridges* width than what this model would predict.

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Sweet spot of energy-level alignment in hyperfluorescent organic light-emitting diodes

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Sweet spot of energy-level alignment in hyperfluorescent organic light-emitting diodes

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We investigate loss mechanisms in hyperfluorescent organic light-emitting diodes (HF-OLEDs) with the emissive layer consisting of a host, a thermally activated delayed fluorescence (TADF) sensitizer, and a terminal emitter. We focus on understanding how the relative energy levels between the TADF sensitizer and terminal emitter impact device efficiency and roll-off through the formation and subsequent dissociation of an intermolecular state. Using a combined experimental and kinetic Monte Carlo (KMC) simulation-based approach, we analyzed HF-OLEDs incorporating either multiresonant (MR) or fluorescent (non-MR) terminal emitters. We find that selecting terminal emitters with ionization potential and electron affinity values that position the intermolecular state at least 150 meV above the singlet energy of the terminal emitter effectively suppresses the losses due to exciton dissociation. Furthermore, we show that using the MR emitter, which exhibits reverse intersystem crossing (RISC), significantly reduces residual triplet-related losses compared with the non-MR emitter. This further mitigates exciton dissociation losses, thereby improving the external quantum efficiency (EQE). These findings provide clear guidelines for selecting terminal emitters and optimizing energy level alignment to address intermolecular state-related loss pathways in HF-OLEDs.

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I. INTRODUCTION

Organic light-emitting diodes (OLEDs) have played a crucial role in transforming the display technology owing to their remarkable attributes such as high efficiency, flexibility, and potential for cost-effective manufacturing. Achieving high efficiency in OLEDs requires utilizing both singlet and triplet excitons. One approach involves using phosphorescent emitters, which incorporate heavy metals [1]. However, a heavy metal-free alternative is the use of thermally activated delayed fluorescence (TADF) emitters. This approach, pioneered by Adachi and coworkers, enables the efficient conversion of triplet excitons to

singlet states through thermal activation, resulting in subsequent emission [2]. Although the first TADF emitters were organometallic complexes [3,4], subsequent developments have focused on purely organic TADF emitters. Despite their promising features, TADF emitters still face some challenges. They produce broad emission spectra, which compromise the color purity of OLEDs. For efficient TADF, the emitter must have a small energy gap between the lowest singlet and triplet states. This small gap can be achieved by reducing the overlap of electron and hole wave functions, which results in a charge-transfer (CT) character of the lowest energy singlet and triplet excited states. Unfortunately, the CT nature inherently implies broader emission spectra [5,6].

Initially investigated in standalone TADF OLED configurations, these emitters have now found novel applications in hyperfluorescent OLEDs (HF-OLEDs) [7]. In HF-OLEDs, the emissive layer (EML) typically consists of a host matrix, a TADF sensitizer, and a fluorescent terminal emitter. This composition facilitates efficient energy transfer of excitons generated on the TADF sensitizer to the fluorescent emitters [7,8]. The synergistic combination of TADF and fluorescence mechanisms takes advantage

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of the high triplet harvesting efficiency characteristic of the TADF sensitizer materials, coupled with the narrower emission spectra and enhanced operational lifetime provided by fluorescent emitters [7,9]. However, it has been noted that HF-OLEDs utilizing fluorescent terminal emitters often exhibit lower external quantum efficiency (EQE) compared with identical OLEDs without the terminal emitters [10,11]. This raises the question of what causes these efficiency losses and how to engineer the energy levels of the terminal emitter to prevent them.

There have been suggestions that loss processes associated with triplet states on the terminal emitter may contribute to the poor performance of some HF-OLEDs [5,12,13]. To address this, it was proposed to replace the commonly used fluorescent terminal emitter with an emitter that converts triplets to singlets via a TADF mechanism, while maintaining a narrow emission spectrum. This can be achieved using multiresonant (MR) emitters, which have a narrow emission spectrum due to their rigidity and a CT character resulting from a very short-range translation of the electron and hole wave functions [6]. Although this approach has produced some highly efficient OLEDs [14–16], there are instances where the use of MR emitters did not improve device efficiency and roll-off [13,16,17]. Stavrou *et al.* have also shown that the precise photophysical parameters, such as radiative lifetimes and intersystem crossing rate, of the TADF sensitizer play a critical role in the achievable EQE increase and its resistance to roll-off in MR-TADF-based hyperfluorescent OLEDs [16]. In our work, we perform a combined experimental and modeling study to understand how MR emitters might further improve device performance and, in particular, what energy level requirements are necessary for this improvement. We found that two conditions must be met. First, the ionization potential (IP) and electron affinity (EA) of the TADF sensitizer and the terminal emitter need to be designed such that any possible intermolecular state, such as an intermolecular charge-transfer state or an exciplex, between the TADF sensitizer and the terminal emitter would be higher in energy than the lowest energy singlet excited state of the terminal emitter. Second, the terminal emitter must have efficient reverse intersystem crossing (RISC) to eliminate any remaining triplets from the device.

There are two limiting cases when two chromophores are so close that their electronic systems interact. When the two chromophores have very distinct electron affinities, so that a full charge transfer takes place, the wave function of the resulting state will have significant ionic contributions and the state is referred to as a charge-transfer (CT) state. Conversely, for chromophores with similar electron affinities, only partial charge transfer may occur and, thus, covalent contributions from resonance interaction dominate. The species is called an exciplex [18], though this

terminology is not always strictly adhered to, given the continuous transition between the two limits. Here, we are not concerned with the nature of any intermolecular state but with its energy and, henceforth, refer to it simply as the intermolecular state (IS). Thus, a central element in our study is designing the relative alignment of the energy levels of the TADF sensitizer and the terminal emitter. In principle, the IP and EA of the TADF sensitizer and terminal emitter may be nested, similar to energy level alignment prevailing in a type-I heterojunction architecture that promotes Förster-type resonance energy transfer (FRET). They can also be offset from each other, resembling the alignment known from a type-II heterojunction architecture that is conducive to the formation of an intermolecular state (Fig. 1).

To motivate our choice of materials, we briefly recall the advantages and disadvantages of each sensitizer-terminal emitter alignment. With a type-I-like alignment, the terminal emitter serves as a trap for both holes and electrons so that trap-assisted recombination of charges results in (nonemissive) triplet generation on the terminal emitter. This constitutes a significant efficiency loss process in type-I architecture-based HF-OLEDs [5,19], unless MR emitters are used as terminal emitters and employed at very low concentrations [20]. Furthermore, it allows for FRET, yet precludes significant charge-transfer interaction (Fig. 1). In contrast, a type-II-like alignment allows for charge-transfer interactions with the formation of an intermolecular state. Since the terminal emitter acts as a trap for either holes or electrons, but not both, direct recombination and, hence, exciton generation on the terminal emitter can be avoided, though at the expense of creating a charge recombination site. Hence, one solution is to use a type-II-like alignment but to aim for a minimal population of the intermolecular state formed between the TADF sensitizer and terminal emitter. For this, it is important to consider the energy of the intermolecular state. It was already recognized in the late 90s that the energy of an intermolecular state between two molecules may—in theory—be lower or higher than the singlet state energies of either molecule, yet a higher energy intermolecular state would not be stable, if it forms at all [21]. When the intermolecular state energy is lower than the singlet energy of the terminal emitter (“type-II-L” in Fig. 1), it will become populated instead of the terminal emitter’s singlet state and may subsequently dissociate [22]. This is a well-recognized issue, exploited in the working principle of organic solar cells [18,21]. While the dissociation of excited states is, in principle, a known efficiency loss mechanism for OLEDs [22–25], its impact on the efficiency of hyperfluorescent OLEDs is not yet fully understood nor appreciated [21–25]. Moreover, the subsequent recombination of dissociated charges can increase triplet accumulation on the terminal emitter, further reducing OLED efficiency and worsening roll-off.

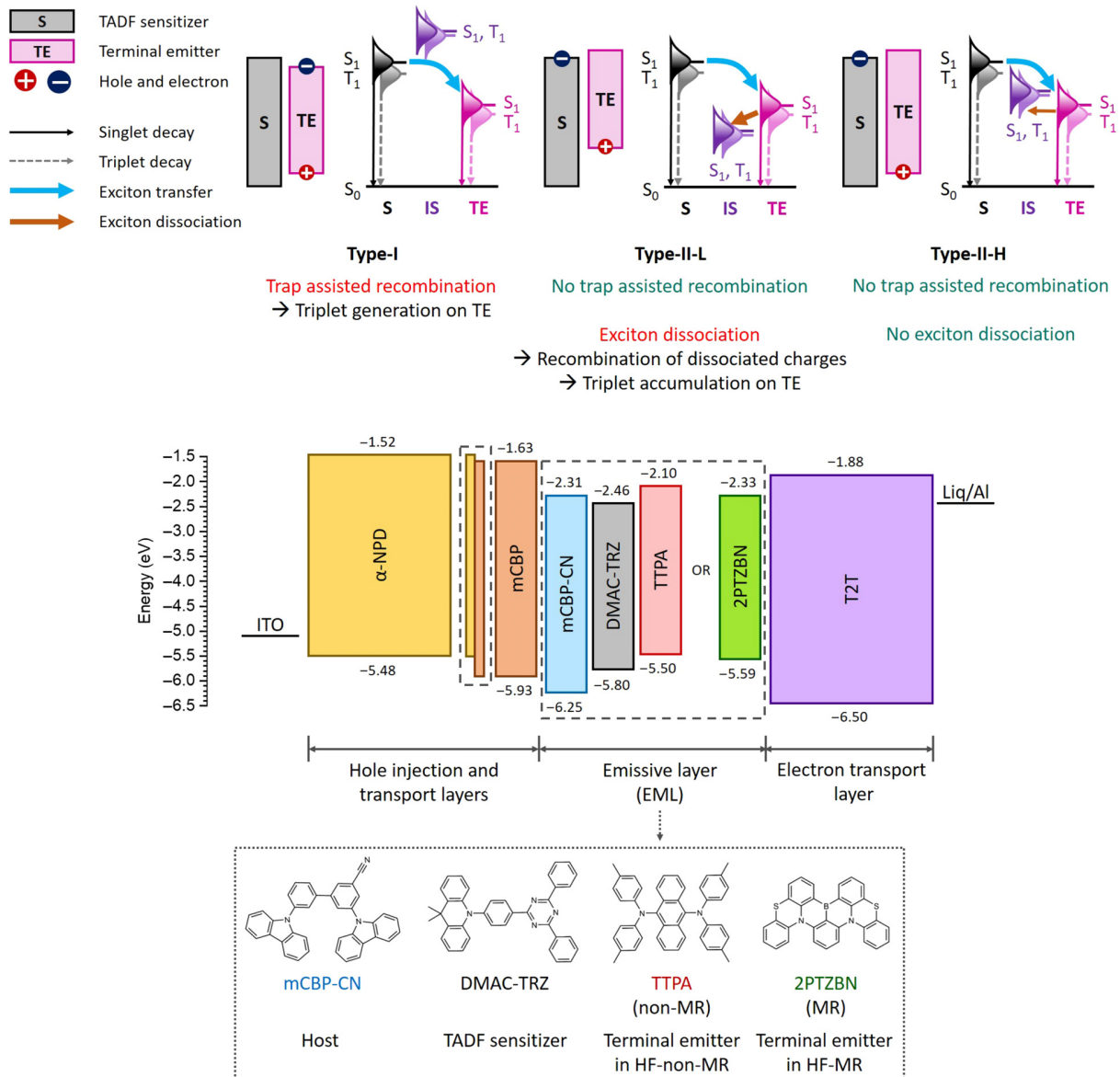


FIG. 1. OLED architecture and materials. (top) Energy level diagrams and Jablonski diagrams for type-I, II-L, and II-H heterojunction-like alignments between the TADF sensitizer and terminal emitter. (middle) Layer structure of the OLEDs studied in this work. Within the emissive layer, mCBP-CN is used as the host matrix and DMAC-TRZ is either used as an emitter (in ref-TADF OLEDs) or as a sensitizer (in HF-OLEDs). In HF-non-MR OLEDs, the non-MR fluorescent emitter TTPA acts as the terminal emitter whereas, in HF-MR OLEDs, the MR emitter 2PTZBN acts as the terminal emitter. Refer to Table II for more details on the device nomenclature and emissive layer composition. (bottom) Chemical structures of mCBP-CN, DMAC-TRZ, TTPA, and 2PTZBN are shown.

One promising approach to address this issue lies in fine tuning the energy of the intermolecular state by chemical design (i.e., modifying the IP and EA values of the molecules) such that an intermolecular state would be higher than the singlet energy of the terminal emitter (“type-II-H” in Fig. 1). This adjustment can effectively prevent (or minimize) exciton dissociation by transforming the occupation of the intermolecular state into a thermally

activated process. This aspect has not yet been systematically studied in HF-OLEDs. Therefore, the key question in our study is whether such HF-OLEDs can be engineered by modifying the IP and EA values suitably. If so, what specific requirements regarding energy level alignment and terminal emitter properties need to be considered when designing such OLEDs to effectively suppress exciton dissociation?

II. METHODS

A. Experimental procedures

The materials used are as follows: N,N-bis(naphthalene-1-yl)-N,N-bis(phenyl)benzidine (α -NPD), 3,3'-Di(9H-carbazol-9-yl)-1,1'-biphenyl (mCBP), 3,3'-di(carbazol-9-yl)-5-cyano-1,1'-biphenyl (mCBP-CN), 10-(4-(4,6-Diphenyl-1,3,5-triazin-2-yl)phenyl)-9,9-dimethyl-9,10-dihydroacridine (DMAC-TRZ), 9,10 Bis[N,N-di-(p-tolyl)-amino]anthracene (TPPA), [1,4] benzothiazino[4'',3'',2'':1',8'] [1,4]benzazaborino[4',3',2':4,5] [1,4] benza-zaborino [3,2,1 kl] phenothiazine (2PTZBN), 2,4,6-tris(biphenyl-3-yl)-1,3,5-triazine (T2T), 8 hydroxyquinolino-lato-lithium (Liq), dipyrzino[2,3-f:2',3'-h] quinoxaline-2,3,6,7,10,11 hexacarbonitrile (HAT-CN) and aluminum (Al). α -NPD, mCBP, and T2T were purchased from Sigma-Aldrich, while mCBP-CN was purchased from Ossila and sublimed before use. Sublimed DMAC-TRZ, TPPA, and 2PTZBN were purchased from Lumtec and were used as received.

The devices were fabricated on patterned indium tin oxide (ITO) coated glass substrates ($2.5 \times 2.5 \times 0.1$ cm) with a sheet resistance of $15 \Omega/\text{sq}$ (VisionTek Systems). The substrates were cleaned by sonication in acetone and isopropanol, followed by oxygen plasma treatment. Subsequently, the cleaned substrates were placed in a deposition chamber (Kurt J. Lesker Super Spectros), where both the small molecule and cathode layers were thermally evaporated under vacuum pressures lower than 10^{-7} mbar. The device areas were either 4 or 8 mm².

The OLEDs were fabricated with the following configuration: ITO/ α -NPD (35 nm)/mCBP: α -NPD (1:1, 5 nm)/mCBP (10 nm)/EML (25 nm)/T2T (40 nm)/Liq (3 nm)/Al (100 nm). For the symmetric electron-only device, the emissive layer is sandwiched between the well-known electron transport material T2T, with the device configuration: ITO/Liq (3 nm)/T2T (40 nm)/EML (25 nm)/T2T (40 nm)/Liq (3 nm)/Al (100 nm). Symmetric hole-only devices were fabricated with the configuration: ITO/ α -NPD (35 nm)/mCBP: α -NPD (1:1, 5 nm)/mCBP (10 nm)/EML (25 nm)/mCBP (10 nm)/mCBP: α -NPD (1:1, 5 nm)/ α -NPD (35 nm)/HAT-CN (10 nm)/Al (100 nm). HAT-CN was introduced in hole-only devices to block the injection of electrons from the cathode into the EML.

The devices were transferred into a calibrated 6-inch integrating sphere (Labsphere) within the glovebox. Electrical properties were assessed using a Keithley 2400 source meter. For the OLEDs, the emission spectra were recorded simultaneously using a calibrated fiber-coupled spectrometer (Ocean Optics USB4000) and a photodiode for low luminance measurements. All the evaluations were conducted at room temperature under a nitrogen atmosphere.

The thin film samples were kept in a continuous flow He-cryostat with a temperature controller. The samples

were excited at 355 nm by a Q-switched laser from QS laser (MPL15100-DP). Emission from the samples was directed onto a spectrograph (Oriel MS257) and detected using a gated iCCD camera (iStar A-DH334T-18F-03). The measurements were conducted under vacuum (10^{-5} mbar) or in a He-filled atmosphere. Fluorescence and phosphorescence spectra were recorded at low temperatures (either 5 K or 77 K). The time-resolved PL measurements of the thin films were performed with exponentially increasing delay and gating times, with the gating time set to be 10 times lower compared with the delay time. The photoluminescence quantum yield of the thin film samples was measured in a N₂-filled integrating sphere fitted with a JASCO FP-8600 spectrofluorometer.

B. Kinetic Monte Carlo simulations

For a comprehensive understanding of the efficiency loss processes, we performed three-dimensional kinetic Monte Carlo (KMC) simulations by using the algorithm implemented in the commercial software BUMBLEBEE [22, 26–33]. In this approach, the device is modeled as a collection of molecular sites arranged on a simple cubic grid with a lattice spacing of 1 nm. Each site may host an electron, a hole, a singlet exciton, or a triplet exciton and is, therefore, assigned an energy level for the ionization potential, electron affinity, singlet, and triplet energies. Injection layers are not explicitly modeled but a 0.2 eV energy barrier is positioned at both injecting electrodes. The charge transport is described as a hopping process using a Miller-Abrahams-type (MA) rate [31], with a wave function decay length for hopping of 0.3 nm and a nearest neighbor attempt-to-hop frequency of $3.33 \times 10^{10} \text{ s}^{-1}$ for both holes and electrons. A temperature of 293 K is assumed. Unlike previous studies [22,34], we found that a reduced electron mobility prefactor to model electron trapping in an effective way was unnecessary. Hence, we assumed equal hole and electron mobility parameters in all the materials. The decision to use the MA formalism is further supported by recent theoretical and KMC reports demonstrating that the Miller-Abrahams formalism is more appropriate for describing charge transport in amorphous organic semiconductor films than the Marcus formalism [35–37].

The software defines an exciton when a hole and an electron occupy the same molecular site. Its spin is determined probabilistically according to spin statistics, favoring a relative singlet-to-triplet probability of 1:3. Exciton formation is associated with an additional energy stabilization equal to the exciton binding energy. This is also taken into account as a further energy penalty when the hole or electron leaves the exciton site, thus causing the dissociation of the exciton. The energy levels considered in the KMC model are illustrated in Fig. 1. We do not explicitly consider the electronic character of each state (i.e., whether

it is of an intramolecular charge-transfer or a localized nature, or of an intermolecular CT or exciplex-like nature), yet we consider the spin. Excitonic processes are explicitly modeled, including the radiative and nonradiative decay of the singlet and triplet states, intersystem crossing (ISC), RISC, exciton diffusion, and losses resulting from interactions with polarons (exciton-polaron quenching) or other excitons (exciton-exciton annihilation). In exciton-exciton annihilation, the spin of the surviving exciton may or may not change, adhering to the spin conservation principle: singlet-singlet annihilation (SSA) results in a singlet, singlet-triplet annihilation (STA) results in a triplet, and triplet-triplet annihilation (TTA) results in either a singlet or triplet with a relative probability of 1:3. Exciton-polaron quenching and exciton-exciton annihilation processes are treated as on-site processes. Exciton diffusion, quenching, and annihilation phenomena are introduced via both the Dexter and Förster mechanisms, as discussed in Sec. S1 of the Supplemental Material [32] (including Refs. [22,26–30,32,34,38,39]).

The KMC simulations help to identify the processes occurring within the device [22,26,28,29,40]. However, this necessitates precise knowledge of the energy levels of the materials, or more specifically, their relative energy offsets and energetic disorder. The IP and EA values depicted in Fig. 1 were determined through a methodology involving the fabrication and characterization of unipolar hole-only and electron-only devices, in conjunction with the KMC simulations (for details regarding parameter refinement, see Sec. S1 of the Supplemental Material) [32]. In brief, we based the initial IP values for all the materials, except 2PTZBN, on literature values derived from photoelectron spectroscopy data. For 2PTZBN, we used cyclic voltammetry values as initial estimates due to the absence of photoelectron spectroscopy data [41]. We then estimated the EA values by adding the optical gap plus the singlet exciton binding energy to the IP values. We used a singlet exciton binding energy of 1.0 eV for all the materials, except for mCBP-CN, DMAC-TRZ, and 2PTZBN, where we used a value of 0.7 eV due to the intramolecular charge-transfer character of their lowest singlet states [42,43]. These binding energy values are consistent with an inverse photoemission spectroscopy study by Yoshida *et al.* [44], and similar values have also been used in other related studies [22,34,45]. To adjust for the impact of the local environment, we refined these starting values for the IP and EA values of each material by running the KMC simulations for hole-only and electron-only devices with these IP and EA values. The current density-voltage curves obtained from the KMC were compared with those obtained experimentally (Figs. S1–S8 in the Supplemental Material [32]), and the IP and EA values were adjusted until good agreement was obtained. This procedure is further detailed in the Secs. S1.1 and S1.2 in the Supplemental Material [32] (including Refs. [22,32,34,41–48]).

TABLE I. Material-specific parameters used for the KMC simulations. When two values are indicated for the same material, the literature value (left-hand side) is compared with the refined value (right-hand side).

	α -NPD	mCBP	mCBP-CN	DMAC-TRZ	TPA	2PTZBN	T2T
E_{IP} [eV]	–5.40 [7]	–5.475 ^a	–6.00 [34]	–5.925 ^a	–5.80 [50]	–5.19 [41]	–6.50 [34]
E_{EA} [eV]	–1.52 ^b	–1.63 ^b	–2.24 ^b	–2.305 ^a	–2.40 ^b	–2.73 [41]	–1.94 ^b
E_S [eV]	3.12 [51]	3.37 [34]	3.31 ^d	2.71 ^d	2.46 ^d	2.50 ^d	3.56 [52]
E_T [eV]	2.38 [51]	2.90 [34]	2.78 ^d	2.63 ^d	1.60 [53]	2.37 ^d	2.80 [52]
$k_{R,S}, k_{NR,S}$ [s ^{–1}]	10 ⁸ , 10 ⁸ ^c	10 ⁸ , 10 ⁸ ^c	2.1 × 10 ⁷ ^d , 0 ^e	2.2 × 10 ⁷ ^d , 0 ^e	3.9 × 10 ⁷ ^d , 0 ^e	3.4 × 10 ⁷ ^d , 0 ^e	10 ⁸ , 10 ⁸ ^c
k_{ISC} [s ^{–1}]	0 ^c	0 ^c	10 ⁸ ^c	4.0 × 10 ⁷ ^d	6.6 × 10 ⁷ ^d	1.9 × 10 ⁷ ^d	0 ^c
k_{RISC} [s ^{–1}]	0 ^c	0 ^c	0 ^c	1.5 × 10 ⁶ ^d	0 ^c	2.9 × 10 ⁵ ^d	0 ^c
$k_{R,T}, k_{NR,T}$ [s ^{–1}]	0, 10 ⁴ ^c	0, 10 ⁴ ^c	0, 10 ⁴ ^c	0 ^e , 7.3 × 10 ⁴ ^d	0, 10 ⁴ ^c	0 ^e , 4.6 × 10 ⁴ ^d	0, 10 ⁴ ^c

^aRefined value, see Sec. III B in the main text and Sec. S1 in the Supplemental Material [32] for details.

^bEstimated from the IP value, singlet energy (E_S), and assumed singlet exciton binding energy, see Sec. III B in the main text and Sec. S1 in the Supplemental Material [32] for more details.

^cBUMBLEBEE default (assumed) value.

^dMeasured or derived value, see Sec. S2 in the Supplemental Material [32] for more details.

^eAssumed in the fitting of experimental data, see Sec. S2 in the Supplemental Material [32].

Table I summarizes both the initial and final obtained values for IP and EA of this procedure. Note that this method is not guaranteed to produce the most correct absolute IP and EA values, yet we expect it to yield very reliable values relative to each other for the set of materials investigated.

Furthermore, we required excitonic parameters, including singlet and triplet energies, as well as photophysical rate constants such as radiative and nonradiative decay rates of singlet and triplet states, ISC rate, and RISC rate. We obtained these parameters through time-resolved spectroscopy on films (refer to Sec. S2 and Figs. S12–S14 in the Supplemental Material) [32] (including Refs. [54,55]). The spectroscopic data are also summarized in Table I and essentially match the literature values [41,43,49,56,57].

III. RESULTS AND DISCUSSION

A. Electrical and optical characterization

We first aim to investigate the impact of the RISC in the terminal emitter on efficiency loss processes in the OLEDs with a type-II-like energy level alignment between sensitizer and terminal emitter. For this, we fabricated OLEDs with the emissive layer sandwiched between hole injection/transport layers and an electron transport layer. Figure 1 shows the schematic layer structure of the OLED stack under investigation (refer to Sec. II A for the fabrication details and chemical names). For the emissive layer, we chose mCBP-CN as the host matrix. The host matrix is doped with DMAC-TRZ, serving as the TADF sensitizer, which enables percolative hole and electron transport, provided it is added at 10% or more [58]. The combination of mCBP-CN with DMAC-TRZ is a well-studied workhorse; it is known that no intermolecular state forms between them [16,56,58]. The chemical structures of EML materials are shown in Fig. 1.

We tested two different terminal emitters for HF-OLEDs based on a type-II-H-like level alignment. The first is a common fluorescent emitter, i.e., TTPA, henceforth referred to as the non-MR emitter [7,57,59]. Since triplet generation on the terminal emitter plays a crucial role in governing the efficiency loss processes in OLEDs, we also tested a second terminal emitter, 2PTZBN, which is itself a TADF emitter and has a narrow emission spectrum due to its MR character. We refer to it as the MR emitter. Both TTPA and 2PTZBN have similar ionization potentials ($E_{IP,TTPA} = -5.50$ eV and $E_{IP,2PTZBN} = -5.59$ eV) and a similar optical gap ($S_{1,TTPA} = 2.46$ eV and $S_{1,2PTZBN} = 2.50$ eV); the key difference is that the non-MR emitter TTPA does not exhibit RISC, while the MR emitter 2PTZBN does, with a rate of $k_{RISC} = 2.9 \times 10^5$ s⁻¹, as determined from the transient PL measurements (Supplemental Material [32], Sec. S2). TTPA is used as the terminal emitter in HF-non-MR OLEDs, while 2PTZBN is used as the terminal emitter in HF-MR OLEDs.

TABLE II. Device nomenclature and emissive layer composition. Device names and the respective concentration of mCBP-CN, DMAC-TRZ, TTPA, and 2PTZBN in the emissive layer of these devices.

Device name	mCBP-CN (host)	DMAC-TRZ (sensitizer)	TTPA (non-MR)	2PTZBN (MR)
host-only	100%	—	—	—
ref-TADF	90%	10%	—	—
ref-non-MR	99%	—	1%	—
HF-non-MR	89%	10%	1%	—
ref-MR	99%	—	—	1%
HF-MR	89%	10%	—	1%

We also considered the following reference OLEDs to assess the influence of the respective omitted components: (i) a reference TADF OLED, comprising a mCBP-CN matrix with TADF emitter DMAC-TRZ (10 wt %) and no terminal emitter, (ii) a reference non-MR OLED, comprising an mCBP-CN matrix without TADF sensitizer but with the non-MR emitter (1 wt %), and (iii) a reference MR OLED, comprising an mCBP-CN matrix without TADF sensitizer but with the MR emitter (1 wt %). The combinations and concentrations of host, sensitizer, and terminal emitter studied as EMLs in this study, along with the corresponding device nomenclature, are summarized in Table II.

Before considering the OLEDs, some aspects of the hole- and electron-only devices merit closer examination and discussion. Figure 2 shows the current density-voltage (J - V) characteristics of the hole- and electron-only devices for various emissive layer compositions including host-only, ref-TADF, HF-non-MR, and HF-MR configurations (see Table II for host, sensitizer, and terminal emitter combinations and concentrations in the EML). Upon doping with 10 wt % DMAC-TRZ, both the hole and electron currents in ref-TADF devices decrease compared with the host-only devices. This aligns with recent findings on varied DMAC-TRZ:mCBP-CN concentration ratios in the emissive layer [58]. It implies that at a concentration of 10 wt % DMAC-TRZ or higher, transport primarily occurs via the DMAC-TRZ sites. Consequently, the host material's contribution to charge transport is minimal. Hence, importantly, the critical factors influencing charge dynamics within the emissive layer of HF-OLEDs are the IP and EA offsets between the TADF sensitizer and the terminal emitter.

Moreover, doping with either terminal emitter results in decreased electron and hole currents (Fig. 2). Specifically, the reduction in hole current is more pronounced with 1 wt % TTPA (HF-non-MR device) compared with 1 wt % 2PTZBN (HF-MR device), implying lower (less negative) ionization potentials for both TTPA and 2PTZBN relative to DMAC-TRZ, with TTPA acting as a deeper hole

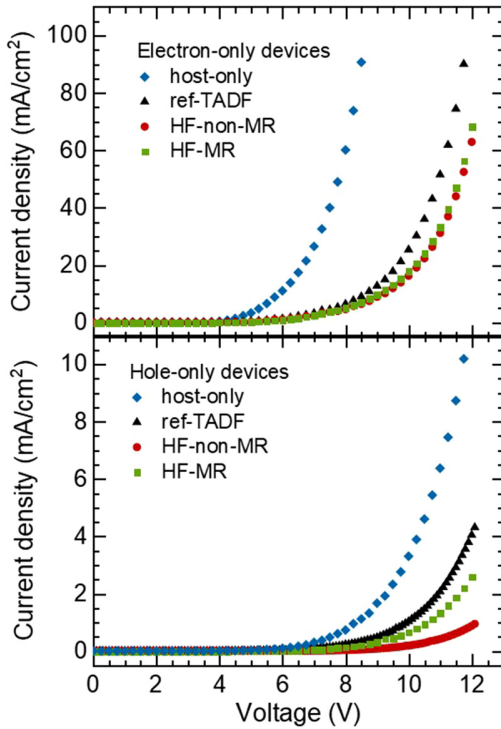


FIG. 2. Unipolar device characteristics. J - V characteristics of (top) the electron-only devices and (bottom) the hole-only devices for host-only, ref-TADF, HF-non-MR, and HF-MR devices. Refer to Table II for details on device nomenclature and emissive layer composition.

trap. Conversely, the electron current decreases similarly for both terminal emitters, which we attribute to dilution effects caused by a dopant with a lower (less negative) electron affinity than DMAC-TRZ [60]. We ruled out the possibility that the terminal emitters act as electron traps (see Figs. S20 and S21 in the Supplemental Material [32]). For this, the terminal emitter would need to have more negative electron affinities than the DMAC-TRZ. However, considering the ionization potentials and optical gaps detailed in Table I, such low electron affinities would imply unrealistically low exciton binding energies for a luminescent compound. Hence, the electron affinity of DMAC-TRZ sets a lower bound. Note that the charges are primarily transported by the DMAC-TRZ sites, which are 10 wt % of the total sites. A terminal emitter concentration of 0.5–5 wt %, hence, implies a relative trap and barrier concentration of 5–50%. Therefore, from our analysis of single carrier devices, we conclude that, indeed, both terminal emitters form type-II heterojunctions with the sensitizer DMAC-TRZ.

With this information, we can now consider the HF-OLEDs. Figure 3(a) presents the EQE-current density (EQE- J) curves for the ref-TADF OLED, ref-non-MR fluorescent OLED, and HF-non-MR OLED. Comparing

OLEDs with and without the non-MR terminal emitter, i.e., the ref-TADF (10 wt % DMAC-TRZ and mCBP-CN) and HF-non-MR (1 wt % TTPA, 10 wt % DMAC-TRZ, and mCBP-CN) OLEDs, it is evident that adding the non-MR emitter TTPA introduces additional loss channels. Omitting the TADF sensitizer to create the ref-non-MR (1 wt % TTPA and mCBP-CN) fluorescent OLED results in an even worse performance. Figure 3(b) depicts the electroluminescence (EL) spectra of the ref-TADF and HF-non-MR OLEDs. The EL of the HF-non-MR OLED exhibits some contribution from the TADF sensitizer DMAC-TRZ, consistent with a Förster radius for the energy transfer from DMAC-TRZ to TTPA of 2.1 nm (Fig. S15 in the Supplemental Material [32]). Increasing the concentration of TTPA from 0.5 to 1 to 2 to 5 wt %, decreases the contribution of DMAC-TRZ emission in the EL spectra (Fig. S16 in the Supplemental Material [32]). However, the EQE also decreases due to a significant build-up of triplet population on the non-MR fluorescent emitter TTPA with its increased concentration (Fig. S16 in the Supplemental Material [32]). In the ref-non-MR OLED, an additional emission peak centered around 450 nm is observed, which is absent in the ref-TADF and HF-non-MR OLEDs. This peak likely originates from recombination at the interface with the hole transport layer, as it does not correspond to emission from either the host or the non-MR emitter (see Fig. S12 in the Supplemental Material [32]), and the devices are electron-dominated. This additional peak is suppressed when the TADF sensitizer is added, as charge transport then occurs primarily via percolation on the sensitizer itself.

Figure 3(c) presents the EQE-current density (EQE- J) curves for the ref-TADF (10 wt % DMAC-TRZ and mCBP-CN) OLED, ref-MR (1 wt % 2PTZBN and mCBP-CN) OLED, and HF-MR (1 wt % 2PTZBN, 10 wt % DMAC-TRZ, and mCBP-CN) OLED. Considering the two reference OLEDs, ref-TADF OLED exhibits higher EQE and lower roll-off in comparison with ref-MR OLED, attributed to a lower RISC rate in 2PTZBN compared with DMAC-TRZ ($2.9 \times 10^5 \text{ s}^{-1}$ vs $1.5 \times 10^6 \text{ s}^{-1}$). On the other hand, comparing OLEDs with and without the MR terminal emitter, i.e., ref-TADF and HF-MR OLEDs, suggests that adding the MR terminal emitter maintains peak EQE. This is in contrast to the case of HF-non-MR OLEDs, emphasizing the advantageous effect of utilizing a terminal emitter that also demonstrates RISC, effectively mitigating loss processes associated with triplets. The benefits of triplet harvesting on 2PTZBN become more apparent when considering that, unlike HF-non-MR OLEDs, the EQE of HF-MR OLEDs remains similar as the 2PTZBN concentration increases from 0.5 to 1 to 2 wt %, dropping significantly only when the concentration is further increased to 5 wt % (Fig. S17 in the Supplemental Material [32]). Nevertheless, the HF-MR OLEDs still exhibit slightly increased roll-off compared with the ref-TADF OLEDs

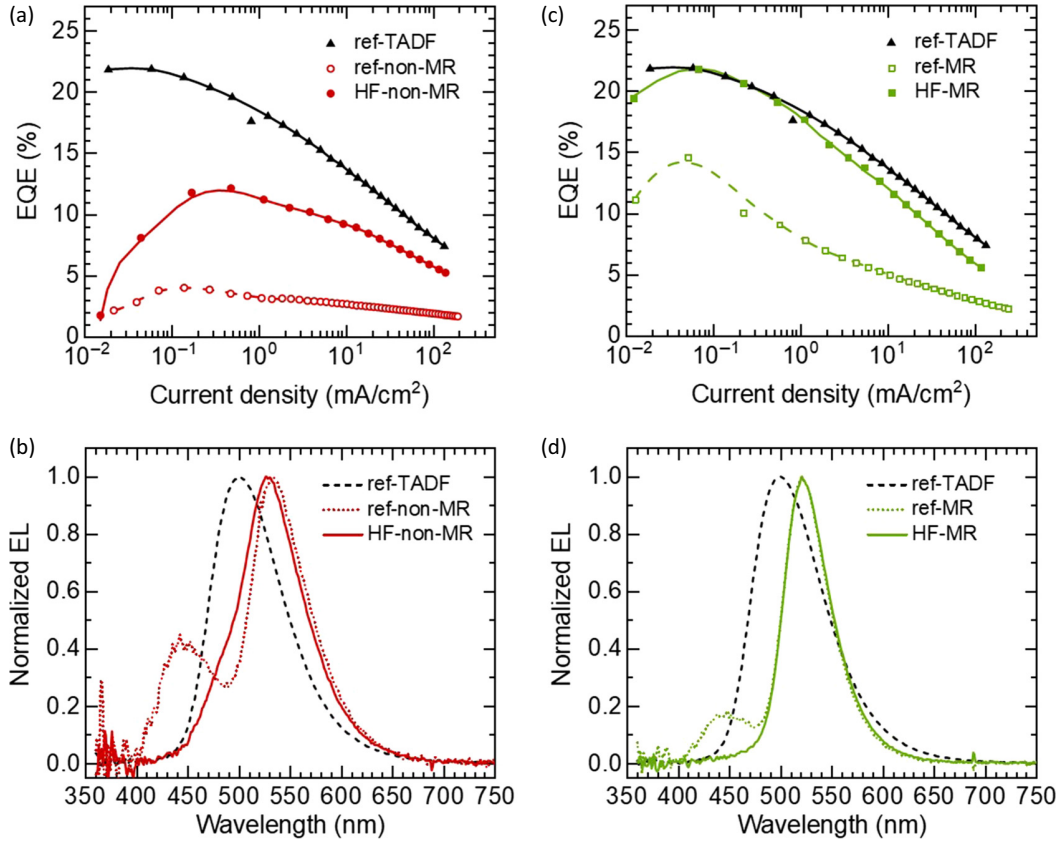


FIG. 3. OLED characteristics. (a) EQE as a function of current density (EQE- J curves) and (b) electroluminescence spectra for the ref-TADF, ref-non-MR, and HF-non-MR OLEDs. (c) EQE- J curves and (d) electroluminescence spectra for the ref-TADF, ref-MR, and HF-MR OLEDs.

at higher current densities, which is further examined in Sec. IV B. Moreover, the narrow EL spectrum of HF-MR OLED, corresponding to the 2PTZBN emission spectrum (Figs. S15 and S25 in the Supplemental Material [32]), contrasts with the broader emission spectra of the ref-TADF OLED [Fig. 3(d)]. Analogous to the case of the HF-non-MR OLED, omitting the sensitizer in the ref-HF-MR OLED results in the appearance of an additional peak around 450 nm, which is presumably due to recombination at the interface with the hole transport layer.

B. Efficiency loss processes

To identify what is causing the losses, we combined the electronic parameters optimized via KMC with the excitonic parameters determined through spectroscopy to simulate the bipolar devices. Figure 4 shows a comparison between the experimentally measured and simulated J - V characteristics and EQE- J curves for the ref-TADF (10 wt % DMAC-TRZ and mCBP-CN), HF-non-MR (1 wt % TTPA, 10 wt % DMAC-TRZ, and mCBP-CN), and HF-MR (1 wt % 2PTZBN, 10 wt % DMAC-TRZ, and mCBP-CN) OLEDs, demonstrating a satisfactory agreement in

all cases. Limitations in KMC statistics at low current density prevented us from running simulations at current densities below 0.2–0.3 mA cm⁻². We calculated the external quantum efficiency (EQE) as the product of the internal quantum efficiency and a constant 33% light out-coupling efficiency. This choice is based on the previously reported emitter orientation factor for DMAC-TRZ doped in mCBP-CN [46,61]. Minor discrepancies between the experimentally measured and simulated EQE data may, therefore, result from differences in outcoupling efficiency across devices. Additionally, changes in the emission profile within the EML as a function of current density, an effect not accounted for in our modeling, could further contribute to these differences.

In both HF systems, electron-hole recombination primarily occurs on the TADF sensitizer DMAC-TRZ sites, followed by energy transfer to terminal emitter sites. Consistent with our observations on the energy level alignment of materials in Sec. IV A, significant hole density is present on both DMAC-TRZ and terminal emitter sites, while electrons predominantly accumulate on DMAC-TRZ sites (see Figs. S20 and S21 in the Supplemental Material [32]), thus determining exciton generation.

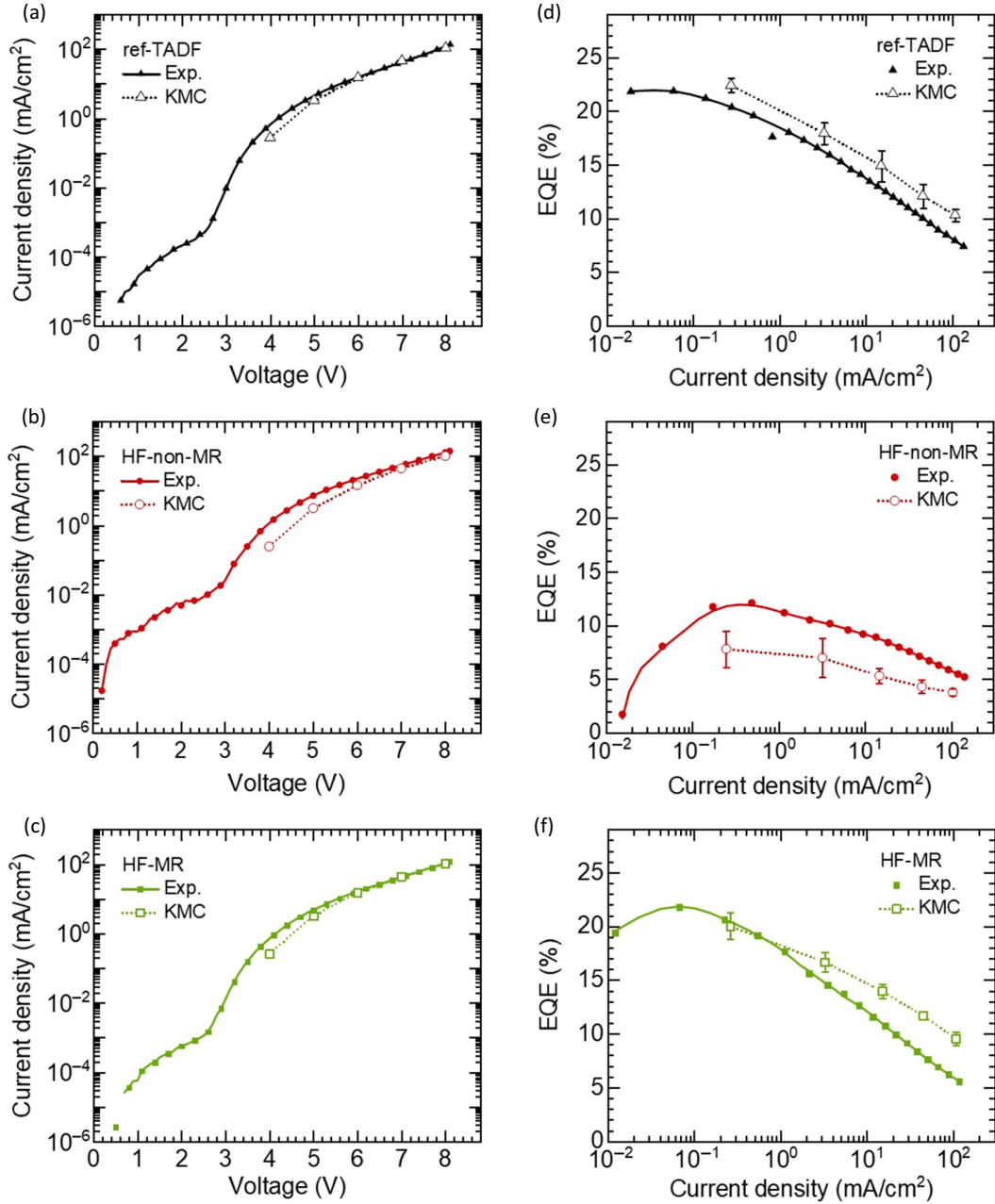


FIG. 4. Comparison of experimental and simulation data. J - V characteristics of the (a) ref-TADF, (b) HF-non-MR, and (c) HF-MR OLEDs. EQE- J curves of the (d) ref-TADF, (e) HF-non-MR, and (f) HF-MR OLEDs. Experimental data (solid symbol and solid line) and the data obtained from the KMC simulations (open symbols) are shown. Dotted lines serve as a guide to the eye for the simulation data. The error bars are calculated as the standard deviation of the current density or EQE over the simulation replicates. In (a)–(c), the error bars for the simulated current density are smaller than the symbol size.

With KMC results at hand, we can analyze the impact of each kind of loss process in the three devices. Figures 5(a)–5(c) present simulation results depicting the relative contributions of various excitonic processes to the efficiency roll-off observed in ref-TADF, HF-non-MR, and HF-MR OLEDs. At low current densities (e.g., 3 mA/cm²), we observe merely triplet nonradiative decay (gray) and

exciton-polaron quenching (shades of blue) across all the devices, while exciton-exciton annihilation (yellow and orange) starts contributing significantly at higher current densities (e.g., 45 mA/cm²).

We attribute the significant exciton-polaron quenching in all the devices to charge imbalance within the EML, which arises due to a difference of 0.45 eV in the ionization

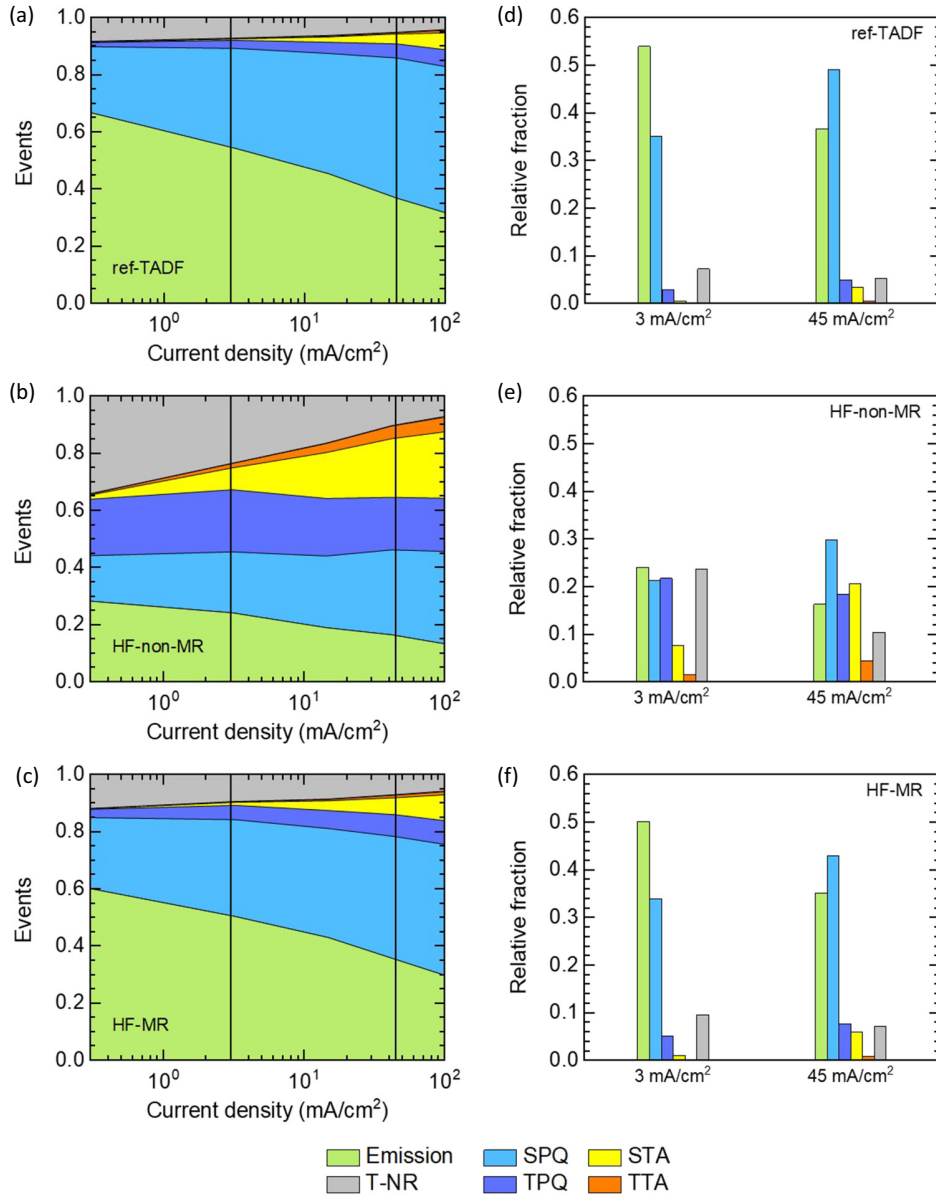


FIG. 5. Efficiency loss processes. The relative contributions of the different excitonic processes that occur are shown as a function of current density for the (a) ref-TADF, (b) HF-non-MR, and (c) HF-MR OLEDs. The different excitonic processes include singlet emission, singlet-polaron quenching, singlet-triplet annihilation, triplet nonradiative decay, triplet-polaron quenching, and triplet-triplet annihilation. The reference lines at 3 mA/cm² and 45 mA/cm² in (a)–(c) indicate the current densities at which the contributions of different excitonic processes to the overall efficiency loss are compared in the (d) ref-TADF, (e) HF-non-MR, and (f) HF-MR OLEDs.

potential between α -NPD and mCBP (Fig. 1 and Table I). At the interface between the α -NPD:mCBP mixed layer and the pure mCBP layer, the higher ionization potential of mCBP produces an energy barrier that hinders hole transport. This hindrance leads to an unbalanced charge distribution in the EML, reducing recombination efficiency and leaving an excess of free electrons, which can effectively quench excitons on both the sensitizer and terminal

emitters (see Sec. S3 in the Supplemental Material for a further discussion [32]).

Let us briefly discuss the nature of the annihilation processes. From the simulated singlet and triplet exciton profiles [panels (c) and (d) in Figs. S18, S20, and S21 in the Supplemental Material [32]], we observe that the triplet density is one to two orders of magnitude higher than the singlet density in all the devices. Therefore, we argue

that, in all three devices, the most relevant annihilation process for singlet excitons is Förster-mediated singlet-triplet annihilation (STA), as the singlet density is too low to yield a significant amount of singlet-singlet annihilation (SSA). Similarly, triplet excitons are more likely to undergo Dexter-mediated triplet-triplet annihilation (TTA) than triplet-singlet annihilation. The relatively high fraction of STA (compared with TTA) can be explained by the long-range nature of Förster interactions, which favor the STA loss pathway despite the low singlet density. In contrast, TTA is hindered by the short-range nature of Dexter interactions, despite the higher triplet density. We recall that, in our devices, triplets predominantly localize on the terminal emitters (see Figs. S20 and S21 in the Supplemental Material [32]) at a concentration of only 1%.

When comparing the efficiency loss processes between the ref-TADF OLED [Fig. 5(a)] and HF-non-MR OLED [Fig. 5(b)], the HF-non-MR OLED shows higher contributions from triplet-related loss processes, such as triplet-polaron quenching (TPQ), STA, and TTA [as quantified in Fig. S22 in the Supplemental Material [32], Figs. 5(d) and 5(e)]. We attribute this increase to the increased triplet accumulation on the non-MR fluorescent emitter TTPA (Fig. S20 in the Supplemental Material [32]), which does not exhibit RISC and, thus, has a long triplet lifetime.

When comparing the efficiency loss processes in the ref-TADF OLED [Fig. 5(a)] and the HF-MR OLED [Fig. 5(c)], we observe similarities and differences. Both OLEDs show strikingly similar profiles where singlet-polaron quenching is the dominant loss process, with increased contributions from TPQ and STA at higher current densities. At 45 mA/cm², the HF-MR OLED exhibits slightly higher contributions from TPQ and STA compared with the ref-TADF OLED [as quantified in Fig. S22 in the Supplemental Material [32], Figs. 5(d) and 5(f)]. We attribute this to a slower RISC rate on the MR emitter 2PTZBN compared with the TADF sensitizer DMAC-TRZ. This slower RISC rate likely causes the higher roll-off of the HF-MR OLED compared with the ref-TADF OLED, as shown in Fig. 2(c). This finding may also explain the higher efficiency roll-off observed in MR-emitter-based HF-OLEDs compared with ref-TADF OLEDs in other related studies [13,16,17].

C. Role of intermolecular states

We now address the formation and role of intermolecular states in type-II architecture-based HF-OLEDs. In a type-II-like alignment between the TADF sensitizer and terminal emitter, the energy level alignment allows excitons to dissociate into geminate pairs on neighboring sites, leading to the creation of an intermolecular CT or exciplex state through the loss of an exciton. To better understand this further loss mechanism, we examine the energetics

involved. We define the “IS-S₁ offset” as the energy difference between the sensitizer-terminal emitter intermolecular state and the lowest singlet state, which in a HF-OLED is the terminal emitter singlet state. The formation and population of the IS is favorable if the IS-S₁ offset is negative (type-II-L) and unfavorable if the IS-S₁ offset is positive (type-II-H), as displayed in Fig. 1. For our molecules, the IS forms with a hole residing on a terminal emitter site and an electron residing on a nearby TADF sensitizer site. As outlined previously [22,62], we estimate the IS energy (E_{IS}) according to

$$E_{IS} = E_{EA, \text{sensitizer}} - E_{IP, TE} - E_b, \quad (1)$$

i.e., based on the electron affinity of the sensitizer ($E_{EA, \text{sensitizer}}$) and the ionization potential ($E_{IP, TE}$) of each terminal emitter (detailed in Table S2 in the Supplemental Material [32]), plus a Coulomb interaction term acting as the intermolecular state binding energy (E_b). In our KMC model, we use an intersite distance of 1 nm and a dielectric constant of 3, which results in a binding energy of 0.48 eV for the intermolecular state. The resulting IS energies are then 2.56 eV and 2.65 eV for the HF-non-MR and HF-MR OLEDs, respectively (see Table S2 in the Supplemental Material [32]). Comparing these values with the experimentally determined singlet energies of the non-MR terminal emitter TTPA (2.46 eV) and the MR terminal emitter 2PTZBN (2.50 eV), we find that the IS-S₁ offset in HF-non-MR and HF-MR OLEDs is approximately 100 and 150 meV, respectively. A summary of these energy levels is presented in Figs. 6(a) and 7(a) for HF-non-MR and HF-MR OLEDs, respectively.

Of course, the statistical variation in the intermolecular distances and orientations implies a Gaussian distribution of these energies rather than sharp values. Moreover, there are also intermolecular states from nonnearest-neighbor sites, as well as intermolecular states formed between any combination of the host, TADF sensitizer, and terminal emitter (see Table S2 in the Supplemental Material [32] for relevant intermolecular state energies). These effects are explicitly considered in the KMC simulations and, hence, in the results presented in Figs. 4–7. The values quoted in our discussion pertain to the mean value of the distribution from nearest-neighbor sensitizer-terminal emitter intermolecular states, which is sufficient to grasp the essential physics of the system and to explain the observed behavior of the OLEDs.

To investigate the impact of the intermolecular state formation on efficiency loss in hyperfluorescent OLEDs, we conducted KMC simulations of hypothetical “model” HF-OLEDs. The configuration of these model devices was kept identical to that of “pristine” HF-OLEDs (Fig. 1). However, in these model devices, we disfavored intermolecular state formation by having the highest possible IS-S₁ offset, which can be obtained when the IP

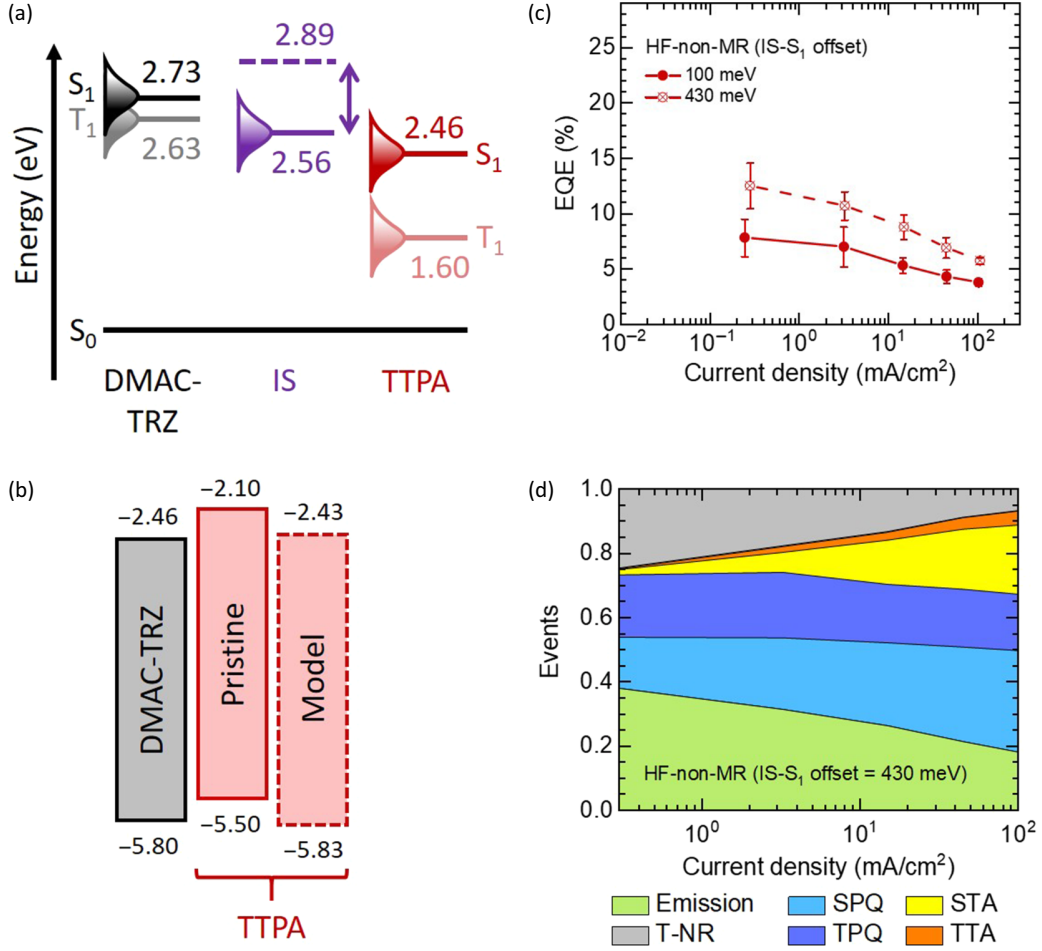


FIG. 6. Impact of the intermolecular state formation on efficiency loss in the HF-non-MR OLEDs. (a) Singlet and triplet energies for DMAC-TRZ (black) and TTPA (red). The TTPA (hole) and DMAC-TRZ (electron) intermolecular state energy is shown in purple for the pristine (solid line) and the model (dashed line) HF-non-MR OLEDs. The IS- S_1 offset, defined as the energy difference between the intermolecular state and TTPA singlet energy, is 100 meV for the pristine and 430 meV for the model HF-non-MR OLEDs. (b) A schematic illustration of the ionization potential and electron affinity of TTPA in the pristine and model HF-non-MR OLEDs. (c) Simulated EQE- J curves for the pristine (IS- S_1 offset = 100 meV) and the model (IS- S_1 offset = 430 meV) HF-non-MR OLEDs. (d) Relative contribution of various excitonic processes to the overall efficiency loss in the model HF-non-MR OLED.

and EA values of the terminal emitter and sensitizer are equal. To achieve this, we shifted both the IP and EA of the terminal emitter to lower energies, such that $E_{IP,TE}^{model} = E_{IP,TE}^{pristine} + \Delta_{TE}$ and likewise for EA. The shift was $\Delta_{TTPA} = -0.33$ eV for TTPA [Fig. 6(b)] and $\Delta_{2PTZBN} = -0.18$ eV for 2PTZBN [Fig. 7(b)]. Although the IP and EA values of the sensitizer and terminal emitter are not exactly equal after the shift, the IP and EA offsets between the sensitizer and terminal emitter are less than ± 30 meV [see Figs. 6(b) and 7(b)], which is comparable to the room temperature thermal energy. To maintain consistency in the electronic parameters between the pristine and model devices, while still ensuring a high IS- S_1 offset to suppress IS formation, it was not considered essential to exactly match the IP and EA values of the sensitizer and

terminal emitter. Doing so would have required independently adjusting the IP and EA of the terminal emitters, which would in turn alter their IP-EA gap. Moreover, we emphasize that lowering the energy levels further would result in the formation of the reverse intermolecular states (type II-L), with holes on the sensitizer and electrons on the terminal emitter. A comparison of the energy levels in pristine and model devices is displayed in Figs. 6(b) and 7(b) for HF-non-MR and HF-MR OLEDs, respectively. All the other simulation parameters, as per the simulation results shown in Figs. 4 and 5, remain unchanged. We note that the simulations implicitly take into account that, for this energy level arrangement, the formation of an intermolecular state between the sensitizer and the terminal emitter is less likely than the occurrence of energy transfer.

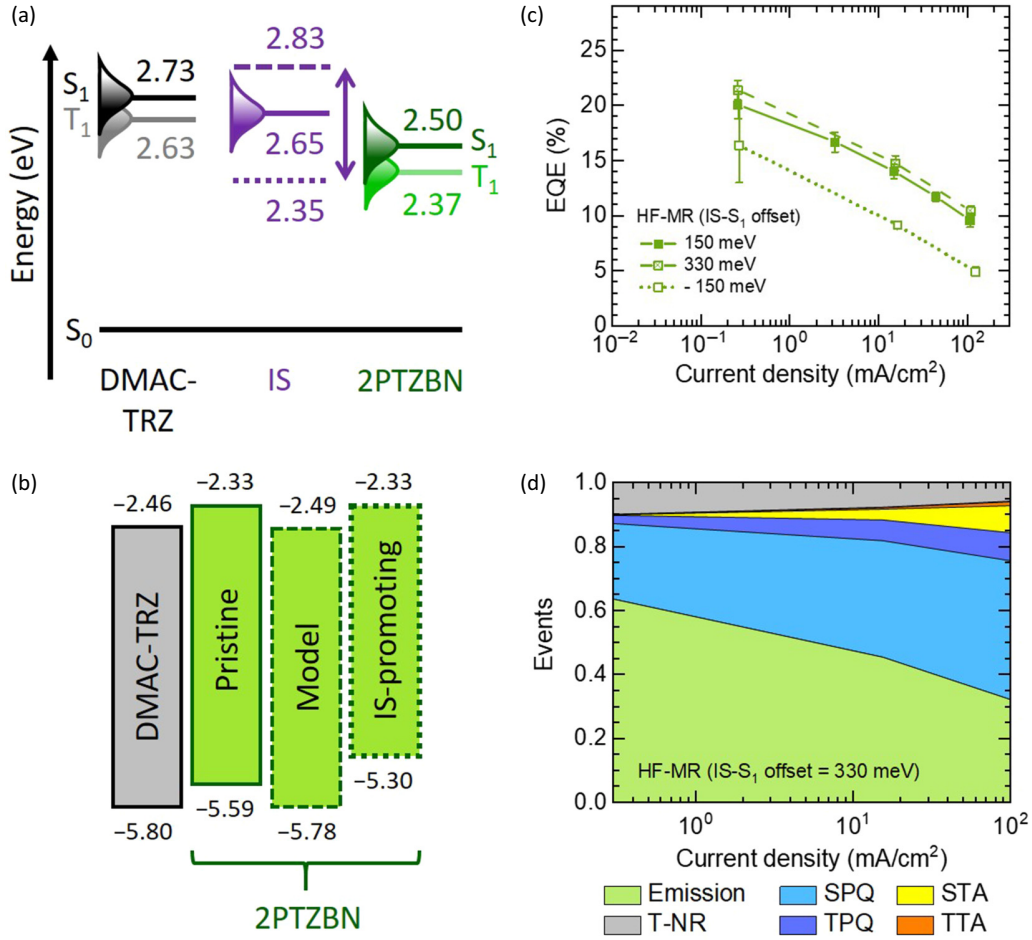


FIG. 7. Impact of the intermolecular state formation on efficiency loss in the HF-MR OLEDs. (a) Singlet and triplet energies for DMAC-TRZ (black) and 2PTZBN (green). The 2PTZBN (hole) and DMAC-TRZ (electron) intermolecular state energy is shown in purple for the pristine (solid line), model (dashed line), and IS-promoting (dotted line) HF-MR OLEDs. The IS- S_1 offset, defined as the energy difference between the intermolecular state and 2PTZBN singlet energy, is 150 meV for the pristine, 330 meV for the model, and -150 meV for the IS-promoting HF-MR OLEDs. (b) A schematic illustration of the ionization potential and electron affinity of 2PTZBN in the pristine, model, and IS-promoting HF-MR OLEDs. (c) Simulated EQE- J curves for the pristine (IS- S_1 offset = 150 meV), model (IS- S_1 offset = 330 meV), and IS-promoting (IS- S_1 offset = -150 meV) HF-MR OLEDs. (d) Relative contribution of various excitonic processes to the overall efficiency loss in the model HF-MR OLED.

In Figs. 6 and 7, we compare the simulated EQE- J curve and the efficiency roll-off between the model devices and their pristine counterparts. Let us first analyze the HF-non-MR OLEDs. As shown in Fig. 6(a), the IS- S_1 offset in pristine and model HF-non-MR OLED is approximately 100 and 430 meV, respectively, with the latter being the purposefully designed maximum IS- S_1 offset. We expect that model devices will not exhibit any efficiency loss due to intermolecular state formation and dissociation. Therefore, it provides a benchmark to test whether the pristine HF-non-MR OLED with an IS- S_1 offset of 100 meV is effective in preventing losses arising from intermolecular state formation and dissociation. As illustrated in Fig. 6(c), the peak EQE of the model and the pristine OLEDs are

about 12% and 8%, respectively, reducing to 6% and 4% at $100 \text{ mA}/\text{cm}^2$ due to roll-off. This implies that the pristine, i.e., the real OLED, obtains only about two-thirds of the maximum possible efficiency, suggesting that significant losses may occur due to exciton dissociation into an intermolecular state, followed by either its separation into free charges or its nonradiative decay [63]. This strong effect may be surprising, yet it is worth recalling that one needs to consider not only the formation and thermal population of the intermolecular state 100 meV above the terminal emitter singlet state, but also the fact that the density of state (DOS) of the intermolecular state is disorder-broadened into a Gaussian shape with a standard deviation of about 50–100 meV. Hence, in particular, the tail states of the

DOS of the intermolecular state can be populated easily and, thus, act as particularly active dissociation sites (type II-H in Fig. 1).

The relative contributions of various excitonic processes to the efficiency roll-off observed in the model HF-non-MR OLED, as depicted in Fig. 6(d), mirror those of the pristine HF-non-MR OLED in Fig. 5(b). However, model OLEDs exhibit a reduction in triplet-related quenching processes, such as TPQ, STA, TTA, and nonradiative triplet decay, as quantified in Fig. S23 in the Supplemental Material [32], and thus emission is more likely. We consider that, in the pristine OLED, charges resulting from exciton dissociation may recombine again and, as a result, increase the triplet concentration.

We next consider the impact of the IS-S₁ offset in pristine and model HF-MR OLEDs. The maximum offset that can be obtained for our system by minimizing the IP difference and EA difference is 330 meV [Figs. 7(a) and 7(b)]. This compares against the IS-S₁ offset of 150 meV in the pristine system. As illustrated in Fig. 7(c), the model HF-MR OLED shows only a 1–2% enhancement in peak EQE compared with the pristine HF-MR OLED, i.e., they are equivalent within the device performance error, implying that intermolecular state dissociation does not play a role in the HF-MR OLED with an IS-S₁ offset of 150 meV. This is further confirmed by the negligible difference in the relative contributions of various excitonic processes to the efficiency roll-off observed in the pristine and model HF-MR OLEDs [c.f., Figs. 5(c) versus 7(d), further quantified in Fig. S23 in the Supplemental Material [32]].

To summarize, if we compare the HF-non-MR OLED and the HF-MR OLED, we find that in the HF-non-MR OLED, there is an IS-S₁ offset of 100 meV that is insufficient to suppress intermolecular state formation and population, subsequent dissociation, and recombination to the triplet state. In contrast, in the HF-MR OLED with an IS-S₁ offset of 150 meV, intermolecular state formation and population, dissociation, and increased triplet formation are not an issue. The difference between the two systems is the IS-S₁ offset of 100 meV against 150 meV, and the non-MR versus the MR nature of the terminal emitter. We would expect a slightly larger IS-S₁ offset in the HF-MR OLED to perhaps reduce any intermolecular state-related effects, yet not to eliminate them entirely. We, therefore, attribute the disappearance of the intermolecular state-related losses to the important role played by RISC in the MR emitter. This reasoning is further supported by the negligible change in the EQE-*J* curve when the IS-S₁ offset in the HF-MR OLED is reduced from 150 to 100 meV (Fig. S24 in the Supplemental Material [32]). We argue as follows. The intermolecular state-related losses in the HF-non-MR OLED ultimately stem from increased triplet accumulation on TTPA. Due to the absence of RISC, it acts as a triplet trap. In the HF-MR OLED with the MR terminal emitter, even if there is an increased (transient)

formation of triplet states from intermolecular state formation, dissociation, and recombination, such triplets are converted back into singlets due to their sufficient RISC rate.

Naturally, the question arises: Is RISC all we need? To check this, we simulated an IS-promoting device where, as illustrated in Fig. 7(b), by keeping the electron affinity of 2PTZBN unaltered while shifting the ionization potential such that $E_{\text{IP,TE}}^{\text{IS-promoting}} = E_{\text{IP,TE}}^{\text{pristine}} + 0.30$ eV, a negative IS-S₁ offset of –150 meV results. As shown in Fig. 7(c), the IS-promoting HF-MR OLED is only about 70% efficient compared with the pristine HF-MR OLED. Evidently, if the additional amount of triplet state created through the intermolecular state formation and dissociation becomes too large, the RISC rate no longer suffices to remove them. It then becomes an issue of the relative rates of additional triplet formation versus conversion into singlets. Thus, we can conclude that RISC alone is not sufficient to eliminate the losses associated with intermolecular state formation and dissociation: a positive IS-S₁ offset is required first of all. Having RISC on the terminal emitter, however, mitigates the losses further.

IV. CONCLUSIONS

In summary, our experiments show that the HF-non-MR OLED with the non-MR fluorescent terminal emitter shows lower EQE compared with the reference TADF OLED. In contrast, the HF-MR OLED employing the MR terminal emitter achieves comparable peak EQE to the reference TADF OLED. However, it exhibits slightly higher roll-off, attributed to slower RISC in the MR emitter relative to the TADF sensitizer. The KMC simulations identify triplet-polaron quenching and singlet-triplet annihilation as primary contributors to this roll-off difference.

Our study of intermolecular state formation and dissociation in HF-OLEDs with type-II heterojunction-like alignment between the TADF sensitizer and terminal emitter highlights strategies for minimizing losses. We find that intermolecular state formation results in efficiency loss. We attribute this loss to the intermolecular state dissociation, followed by recombination in a statistical singlet-triplet ratio, ultimately leading to an increased triplet population on the terminal emitter. This loss channel can be significantly suppressed if the intermolecular state energy is at least 150 meV above the singlet energy of the terminal emitter. This requires a suitable choice of the relative ionization potential and electron affinity levels of the terminal emitter and TADF sensitizer. When the intermolecular state energy falls below this threshold, partial suppression persists but it is limited by the disorder-broadened DOS in the amorphous films. Residual triplet-related losses, including triplet-polaron quenching, singlet-triplet annihilation, and triplet nonradiative decay, can be further mitigated by using terminal emitters with

RISC, such as MR emitters. Ultimately, it is essential that the RISC rate of the terminal emitter is higher than the rate of additional triplet state population resulting from the formation of any intermolecular state.

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R.S. conceived the project. R.S. and K.S. conducted device fabrication and characterization. R.S. and L.G.F. carried out photophysical measurements. G.C. performed the KMC simulations with inputs from R.S. and E.T. A.P.M., S.G., and A.K. supervised group members involved in the project. R.S., G.C. and A.K. wrote the manuscript with inputs from all the authors.

DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

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The Sweet Spot of Energy Level Alignment in Hyperfluorescent OLEDs

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Section S1: Parameter optimization

Material parameters detailed in Table 1 of the main text were first obtained from literature and tested against experimental J-V curves of unipolar electron- and hole- only devices (EOD, HOD), yielding significant deviations. To rectify this divergence, we undertook a refinement process by systematically adjusting the simulation parameters to match the J-V curves of devices with increasing complexity. Upon refinement, we found that the IP values for all materials demonstrated variations of up to 75 meV, except for 2PTZBN, which required a considerable adjustment of 400 meV to match the experimental J-V characteristics of the corresponding hole-only device (Figure S4). The initial literature values for the IP of all materials, except 2PTZBN, were derived from photoelectron spectroscopy data. For 2PTZBN, we used cyclic voltammetry values as initial estimates due to the absence of photoelectron spectroscopy data,[1] and it is well known that the values in amorphous films can substantially differ from those obtained from cyclic voltammetry measurements performed in solutions, justifying our 400 meV correction. We also refined the energy disorder for DMAC-TRZ to 140 meV, as only with this change could we reproduce the experimental data (Figure S3). Such a value is reasonable for a donor-acceptor type material with a permanent dipole moment, such as DMAC-TRZ.

For all materials except 2PTZBN, we initially estimated the EA by adding the optical gap and singlet exciton binding energy to the IP. We assumed a singlet exciton binding energy of 1.0 eV for all materials except mCBP-CN and DMAC-TRZ, where we applied a value of 0.7 eV due to the intramolecular charge transfer character of their lowest singlet state.[2,3] These values were chosen based on an inverse photoemission spectroscopy study by Yoshida *et al.* [4] and similar values have also been applied in other related studies.[5-7] The EA of 2PTZBN was obtained by shifting the EA measured via cyclic voltammetry by 400 meV, for consistency with the IP refinement.[1] Subsequently, we further refined the EAs for all materials as described below.

The detailed parameter refinement procedure is given in the following. We emphasize that the optimised values for the IP and EA energy levels may not reflect perfect, absolute values for any given material. Indeed, simulations are sensitive to offsets between IP or EA energy levels rather than the absolute values themselves. We therefore obtained a good estimate for the IP offsets between α -NPD:mCBP, mCBP:mCBP-CN, DMAC-TRZ:TTPA, and DMAC-

TRZ:2PTZBN. Similarly, we have a good estimate for the EA offsets between T2T:mCBP-CN and mCBP-CN:DMAC-TRZ. Conversely, the system is not strongly sensitive to the IP offset between mCBP-CN:T2T and EA offsets between DMAC-TRZ:TTPA, DMAC-TRZ:2PTZBN, and mCBP-CN:mCBP. For these offsets, we cannot get an estimate with the present devices; however, they are not crucial for our study. This set of parameters satisfactorily reproduces the electronic behaviour of the unipolar hole-only and electron-only devices (Figure S6 and S8) as well as bipolar OLEDs (Figure 4 of the main text). Furthermore, it allows us to discuss with reasonable accuracy the CT states in which the electron is localised on DMAC-TRZ and the hole on TTPA or 2PTZBN, since we know the relevant IP and EA values reasonably well from optimisation.

Section S1.1: Hole-only devices (HODs)

Literature parameters yielded extremely low current density values for all HODs (Figure S1), with a particularly low value obtained for the HF-MR HOD.

In the host-only HOD, we detected intense hole accumulation at the α -NPD:mCBP interface, understandable in terms of the 600 meV energy difference between the IP of the two materials. Agreement with experimental data was greatly improved (Figure S2) by reducing the IP offset to 450 meV by symmetrically raising (lowering) the IP of α -NPD (mCBP) by 75 meV, which falls well within the usual 100 meV error bar for photoelectron spectroscopy measurements. No further optimisation of mCBP-CN parameters was necessary.

Applying these corrected parameters to the reference TADF HOD yielded an overestimated current density, compared to experiment. Relevant DMAC-TRZ parameters were tested to observe what may improve the agreement: ionization potential (from -5.92 eV to -5.68 eV), doping percentage (from 8 mol% to 12 mol%) and the nearest-neighbour hop attempt rate for holes (from $3.33 \times 10^8 \text{ s}^{-1}$ to $3.33 \times 10^{10} \text{ s}^{-1}$) did not affect the result significantly. The experimental J-V curve could only be reproduced by assuming a $\sigma_{\text{IP}} = 140$ meV for DMAC-TRZ (Figure S3). The value is slightly higher than commonly expected for organic semiconducting materials, but it may be understandable for a material with a permanent dipole moment such as DMAC-TRZ.[8-10] For the sake of consistency, in the following, $\sigma_{\text{EA}} = 140$ meV is also assumed for DMAC-TRZ.

Finally, material parameters for the two terminal emitters (TTPA and 2PTZBN) were tested. Introducing the previous corrections, the HF-non-MR HOD was nicely reproduced without need of further optimisations. Conversely, the HF-MR HOD showed current density values lower by several orders of magnitude than the experimentally measured values. This discrepancy was fixed by raising the IP of 2PTZBN by 400 meV (Figure S4). This large variation cannot be justified in terms of experimental error; however, we underline that the only available measurement of the IP of 2PTZBN is performed by cyclic voltammetry in solution,[1] and as such cannot be fully trusted to accurately represent the properties of the material as a thin film dopant. Our adjustment is therefore not inconsistent with measurement. For the sake of consistency, the EA of 2PTZBN is also raised by 400 meV compared to the literature value.

Figure S5 displays a comparison between experimental data and simulation results according to the best fit obtained.

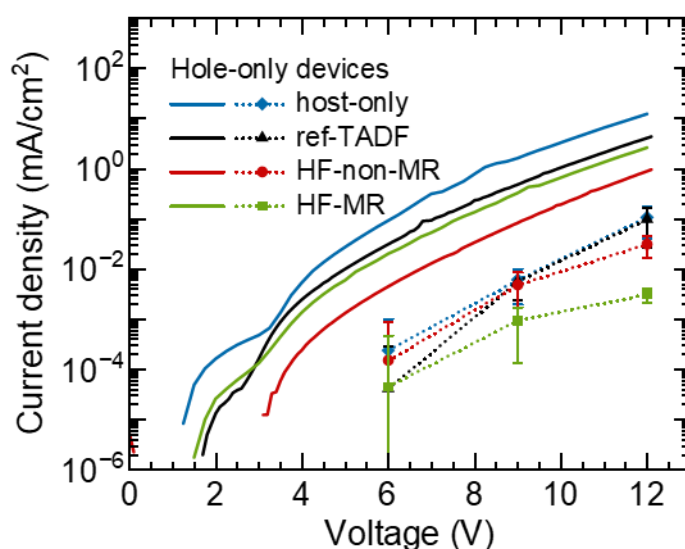


Figure S1: Comparison between experimental data and simulation results for all HODs, employing the default set of Bumblebee parameters plus material data from literature as-obtained. A large underestimate of the simulated current density is observed for all HODs, and a specifically high discrepancy is obtained for the HF-MR HOD.

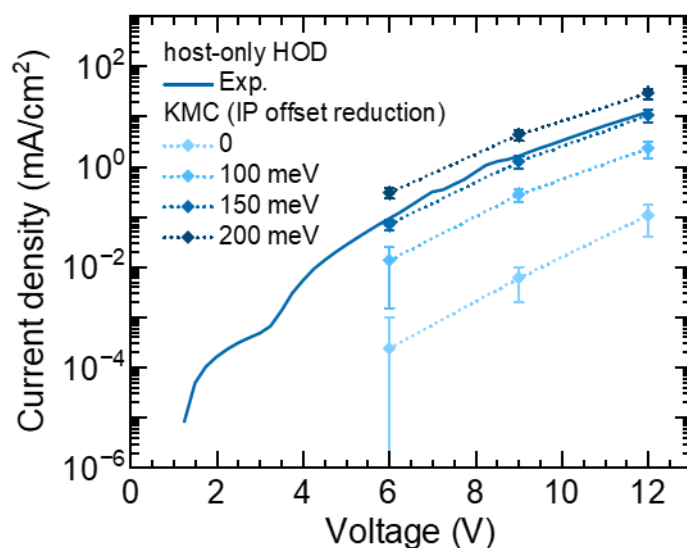


Figure S2: Comparison between experimental data and simulation results for the host-only HOD at varying IP offset between α -NPD and mCBP. The offset reduction is obtained by a symmetrical raise of the α -NPD and lowering of the mCBP ionization potentials. A reduction of the gap by 150 meV (± 75 meV on α -NPD and mCBP, respectively) offers the best fit.

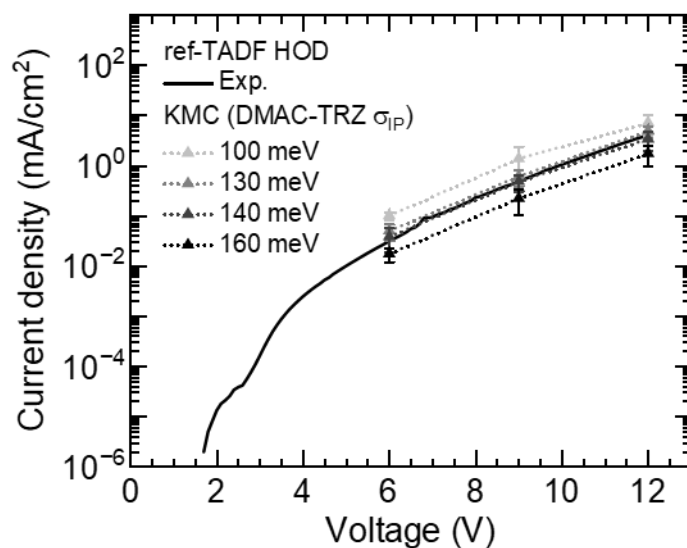


Figure S3: Comparison between experimental data and simulation results for the reference TADF HOD at varying σ_{IP} of DMAC-TRZ, with 140 meV offering the best fit.

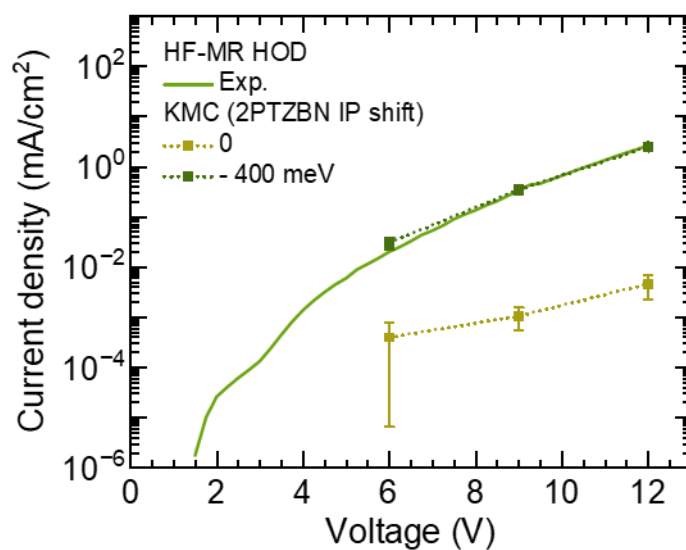


Figure S4: Comparison between experimental data and simulation results for the HF-MR HOD using the literature value for the ionization potential of 2PTZBN, and with a 400 meV decrease offering the best fit.

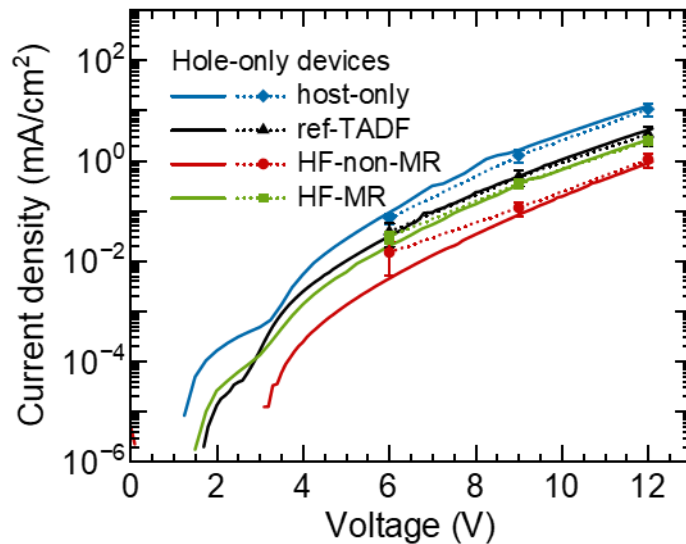


Figure S5: Comparison between experimental data and simulation results according to the best fit, for all HODs reported in this study.

Section S1.2: Electron-only devices (EODs)

Electron affinities were calculated as IP + optical gap + singlet stabilisation energy (1 eV for all materials except mCBP-CN and DMAC-TRZ, 0.7 eV for the latter due to the intramolecular charge transfer character of their lowest singlet state). The procedure detailed in the previous section was applied on EODs. Figure S6 shows the results for the host-only EOD simulated with literature parameters: the largely overestimated J-V curve could be improved by increasing the EA offset between mCBP-CN and T2T by 130 meV. This was obtained again by symmetrically raising (lowering) the EA of mCBP-CN (T2T) by 65 meV.

With these parameters, the J-V curve for the reference TADF EOD (with $\sigma_{\text{EA}} = \sigma_{\text{IP}} = 140$ meV) was underestimated. To improve agreement, the EA of DMAC-TRZ was lowered by 60 meV (Figure S7).

With these optimised parameters, the HF-non-MR and HF-MR EODs are naturally reproduced with no further optimisation required. Figure S8 displays a comparison between experimental data and simulation results according to the best fit.

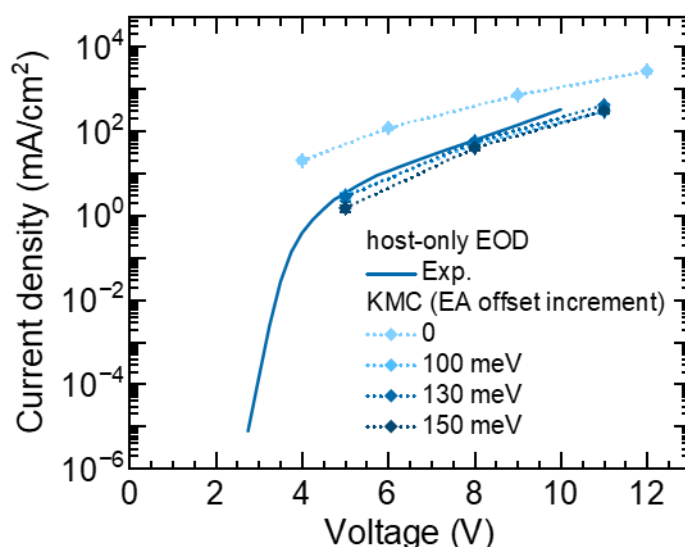


Figure S6: Comparison between experimental data and simulation results for the host-only EOD, at varying EA offset between mCBP-CN and T2T. The offset increase is obtained by a symmetrical raise of the T2T and lowering of the mCBP-CN electron affinities. An increase of the gap by 130 meV (± 65 meV on mCBP-CN and T2T, respectively) offers the best fit.

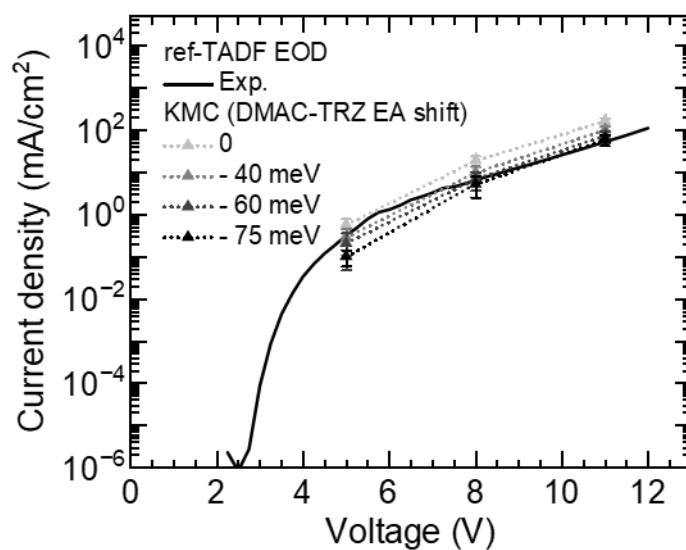


Figure S7: Comparison between experimental data and simulation results for the reference TADF EOD, at varying electron affinities for DMAC-TRZ. Reducing the electron affinity of DMAC-TRZ by 60 meV offers the best fit.

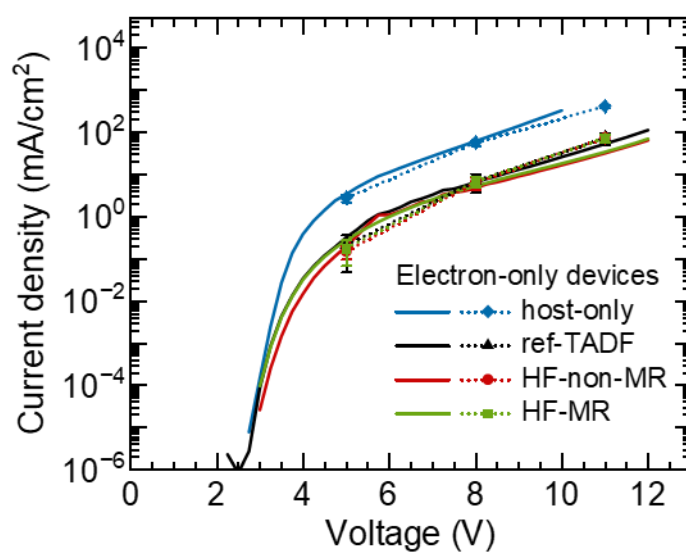


Figure S8: Comparison between experimental data and simulation results according to the best fit, for all EODs reported in this study.

Section S1.3: Förster and Dexter interaction parameters

We describe the diffusion of singlets as a Dexter-type process plus a Förster-type process, while the diffusion of non-emissive triplets only has a Dexter-type contribution. Similarly, exciton-exciton annihilation (EEA) and exciton-polaron quenching (EPQ) – which are introduced as diffusion processes to a site occupied resp. by a polaron or a second exciton – are described as a Dexter-type processes plus, only in the case of singlets, a Förster type process. All rates include a Miller-Abrahams-type term to treat the exciton energy difference between the origin and destination site.[11]

Dexter rates are calculated as:

$$k_{da}^D = \nu_{1\text{nm}}^D \exp\left(-2 \cdot \frac{r_{da}}{\lambda}\right) \cdot \varphi_{MA}(\Delta E_{da})$$

where $\nu_{1\text{nm}}^D$ is the nearest-neighbour attempt frequency, r_{da} is the distance between individual donor-acceptor sites, λ the wavefunction decay length and φ_{MA} is an energy-dependent Miller-Abrahams term (see below). The $\nu_{1\text{nm}}^D$ and λ parameters are not process-specific, i.e. equal for all Dexter-mediated processes.

Förster rates are calculated as:

$$k_{da}^F = (k_{r,d} + k_{nr,d}) \cdot \left(\frac{R_0}{r_{da}}\right)^6 \cdot \varphi_{MA}(\Delta E_{da})$$

where $k_{(n)r,d}$ is the (non-)radiative decay rate for the donor species and R_0 is a process-specific Förster radius.

The energy-dependent Miller-Abrahams term φ_{MA} is:

$$\varphi_{MA}(\Delta E_{da}) = \exp\left(-\frac{|\Delta E_{da}| + \Delta E_{da}}{2k_B T}\right)$$

where ΔE_{da} is exciton energy difference between the donor and acceptor sites, k_B is the Boltzmann constant and T is temperature.

Normally, in hyperfluorescent devices, the Förster rates for singlet interactions are much higher than the Dexter rates: Förster-mediated SPQ and STA are then the prevalent loss mechanism for singlet excitons, while non-emissive triplets are only lost through Dexter-mediated TPQ and TTA.

Experimental determination of Förster and Dexter parameters for EPQ and EEA is non-trivial. The Bumblebee default parameter set (Table S1) has shown good agreement with experimental data in previous studies. [5,7,12-17] Since this parameter set favours Förster-type interactions, it will be referred to as the “mainly Förster” parameter set. To check the validity of this parameter set, we compared it with an opposite limiting picture, dominated by Dexter interactions: in the “mainly Dexter” parameter set (Table S1), the Förster radius for SPQ is arbitrarily lowered to 1.5 nm and the Dexter prefactor is adjusted to $166.5 \cdot 10^{10} \text{ s}^{-1}$ to match the experimental roll-off of our devices. Since the simulation software does not allow to set process-specific Dexter prefactors, this change will affect all Dexter-mediated excitonic events (diffusion, quenching, annihilation). However, triplet annihilation losses are minor in all three devices, so we may assume that the change will almost exclusively work in favour of TPQ.

Figure S9 shows external quantum efficiency vs. current density (EQE-J) curves calculated for the reference TADF, HF-non-MR and HF-MR devices studied in this work with the two parameter sets; the current density is naturally unaffected by EPQ/EEA parameters. EQE is calculated as the product between the simulated internal quantum efficiency (IQE) and an assumed outcoupling efficiency of 33%. The “mainly Förster” and “mainly Dexter” sets produce a similar roll-off in the reference TADF and HF-MR devices, and in both cases the “mainly Dexter” set yields a higher EQE; conversely, in the HF-non-MR device, the “mainly Dexter” parameter set produces a visible decrease in EQE compared to the “mainly Förster” set, with reduced roll-off. A comparison of the fraction of losses per process is presented in Figure S10: by design, the “mainly Dexter” parameter set favours triplet losses. In the TADF and HF-MR devices, triplets mostly reside on sites with triplet recycling capabilities, so that triplet lifetime is short and TPQ mostly takes the share of losses which, using the “mainly Förster” set, were due to SPQ; vice versa, In the HF-non-MR device, long-living triplets accumulate on the non-MR terminal emitter, determining a large share of TPQ already with the “mainly Förster” set: the “mainly Dexter” set further exacerbates these losses, causing a major EQE drop compared to the “mainly Förster” set.

The two parameter sets were also tested by comparing EQE-J curves for the two HF devices at varying terminal emitter concentration (Figure S11). While the quantitative match is less than impressive in all cases and for both parameter sets, it is still possible to verify that the “mainly Dexter” set produces a slight EQE overestimate for the HF-MR device and an increasing

underestimate for the HF-non-MR device, which make it a less suitable choice compared to the “mainly Förster set”.

In conclusion, we can infer that various sets of Förster and Dexter EPQ parameters, despite representing significantly different microscopic scenarios, can lead to comparable and satisfactory macroscopic outcomes. If we assess the EQE-J curves illustrated in Figure S9 individually, we may demonstrate reasonable alignment with experimental data, although adjustments to the unknown outcoupling efficiency may be necessary. However, it is only after a comprehensive examination encompassing all three OLEDs (ref-TADF, HF-non-MR, and HF-MR) along with HF-non-MR and HF-MR OLEDs with varying concentrations of terminal emitters from 0.5 - 5 wt% (Figures S9, S10 and S11) that we can draw a reasonable conclusion: the chosen “mainly Förster” parameter set enables the closest replication of experimental results within reasonable limits. This, in turn, allows for the accurate interpretation of the device behaviour discussed in this study.

Table S1: Comparison between the two set of parameters employed in the present section. The parameters changed to obtain the mainly Dexter parameter set are indicated in bold in the last column.

		Mainly Förster	Mainly Dexter
Dexter	Prefactor, all processes [s^{-1}]	3.33×10^{10}	166.5×10^{10} (50 times higher)
	Decay length, all processes [nm]	0.3	0.3
Förster	Diffusion radius [nm]	if $\Delta E \leq 0.5$ eV	1.5
		if $\Delta E > 0.5$ eV	3.5
	Exciton-exciton annihilation radius [nm]	3.5	3.5
	Exciton-polaron quenching radius [nm]	3.5	1.5

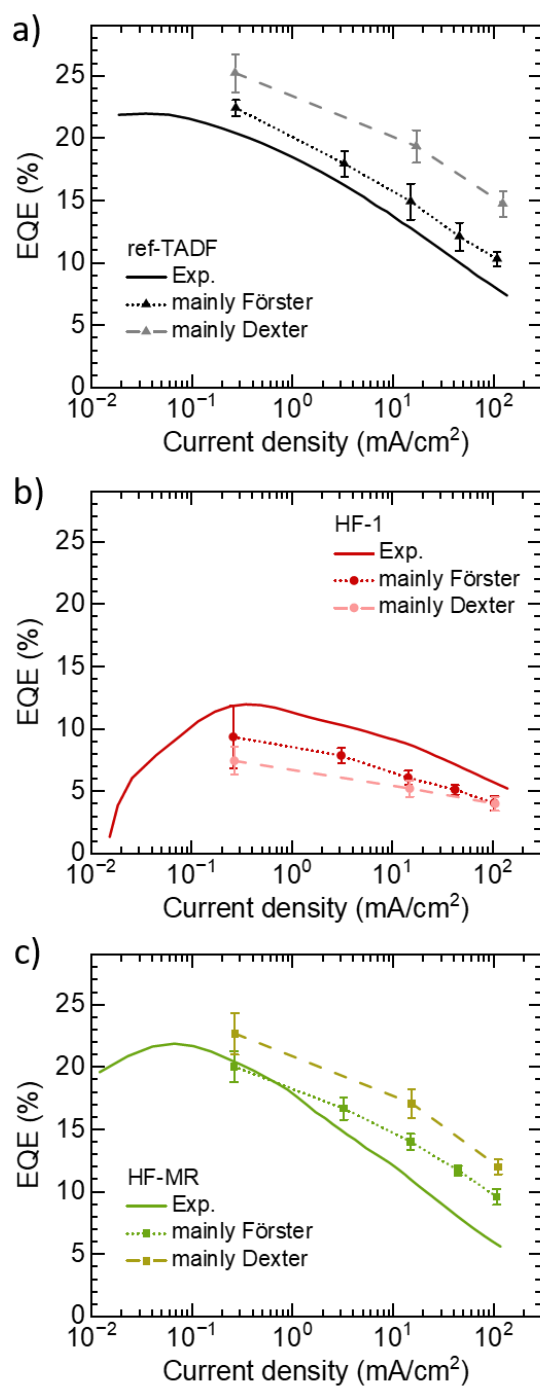


Figure S9: Comparison between experimental (full lines) and simulated (dots) EQE-J curves for the three bipolar devices considered in this study: (left) reference TADF, (center) HF-non-MR and (right) HF-MR and for the two parameter sets indicated in Table S1.

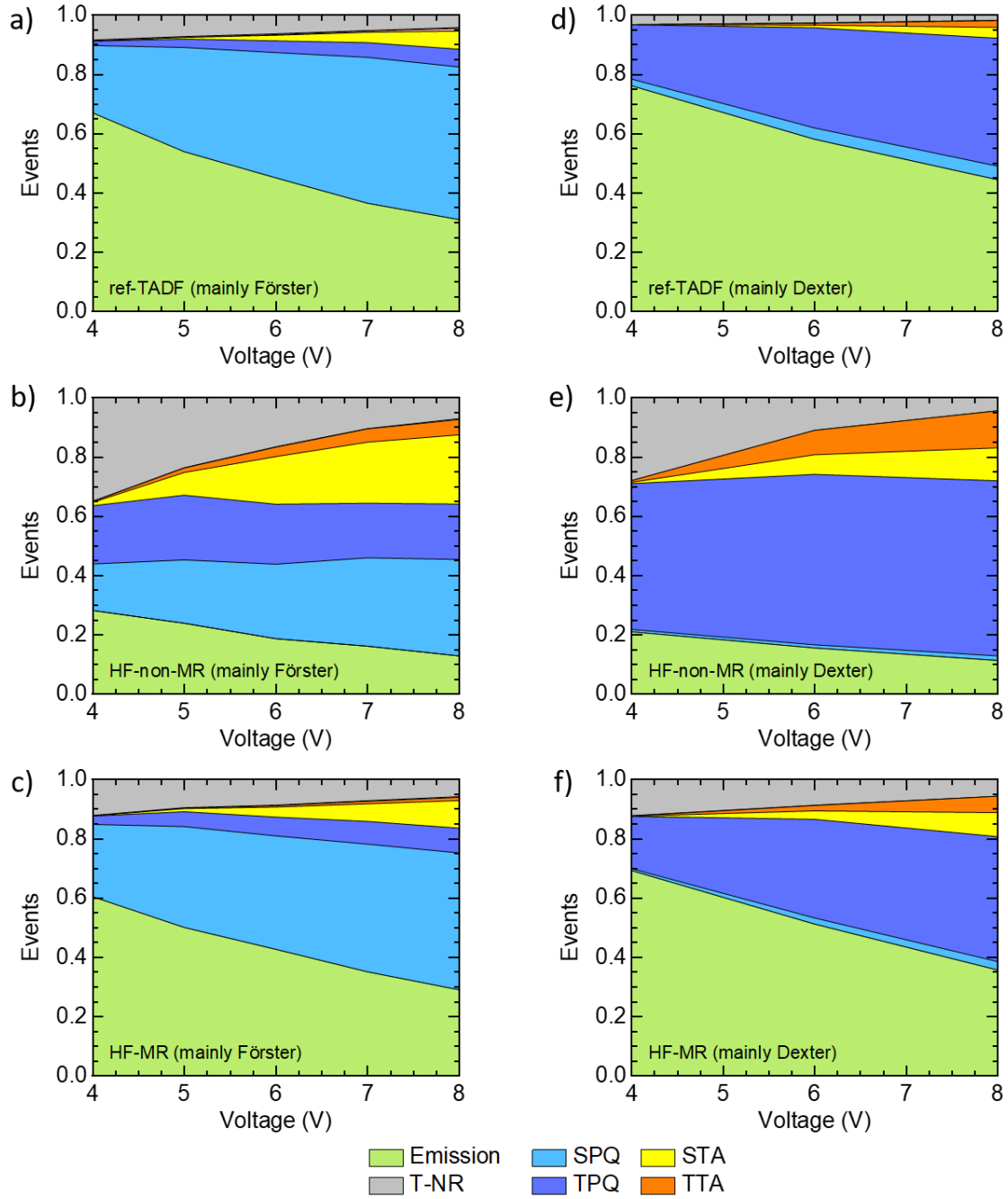


Figure S10: Event plot comparison between the three devices studied in this work: (a) and (d) reference TADF, (b) and (e) HF-non-MR, (c) and (f) HF-MR) and with the two parameter sets (mainly Förster, mainly Dexter). The predominance of (Förster-mediated) SPQ in the mainly Förster case and of (Dexter-mediated) TPQ in the mainly Dexter case can be observed.

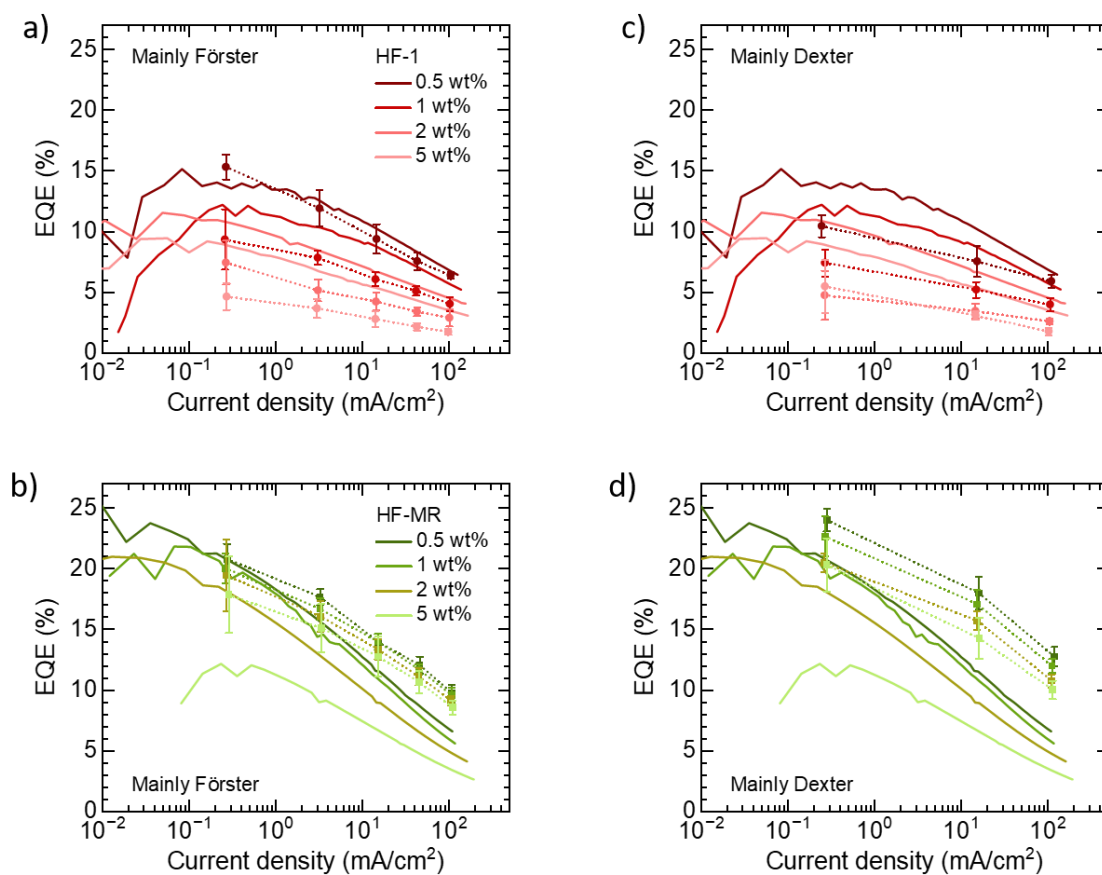


Figure S11: Comparison between experimental (full lines) and simulated (dots) EQE vs. J curves for the (top) HF-non-MR and (bottom) HF-MR devices at varying terminal emitter concentration (TADF sensitizer concentration: 10%). Simulations are performed using either the (left) mainly Förster or (right) mainly Dexter parameter set.

Section S2: Photophysical data

Determination of photophysical rate constants:

- Prompt fluorescence lifetime (τ_{PF}) and delayed fluorescence lifetime (τ_{DF}) were determined from the monoexponential fits of the prompt and delayed components of the photoluminescence (PL) decay at room temperature (shown in Figure S13 and S25).
- Photoluminescence quantum efficiency (ϕ_{PL}) was determined under N₂ atmosphere. ϕ_{PL} for host-only, reference TADF, reference non-MR, and reference MR films were determined as 11%, 92%, 37% and 57% respectively.
- ϕ_{DF}/ϕ_{PF} was determined from the ratio of the integrated DF and PF in the PL decay curves.
- Since, $\phi_{PL} = \phi_{PF} + \phi_{DF} \Rightarrow \phi_{PF} = \frac{\phi_{PL}}{1 + \phi_{DF}/\phi_{PF}}$ and $\phi_{DF} = \phi_{PL} - \phi_{PF}$.
- Assuming negligible nonradiative singlet decay rate, ISC quantum efficiency, $\phi_{ISC} = 1 - \phi_{PF}$.
- RISC quantum efficiency is then determined as: $\phi_{rISC} = \frac{\phi_{DF}}{\phi_{ISC} \phi_{PL}}$
- Radiative singlet decay rate, $k_S = \frac{\phi_{PF}}{\tau_{PF}}$.
- Intersystem crossing rate, $k_{ISC} = \frac{\phi_{ISC}}{\tau_{PF}}$.
- Reverse intersystem crossing rate, $k_{RISC} = \frac{1}{\phi_{ISC} \tau_{DF}} \left(\frac{\phi_{DF}}{\phi_{PF}} \right)$.
- Nonradiative triplet decay rate, $k_{NR}^T = \frac{k_{rISC}}{\phi_{rISC}} - k_{RISC}$

Photophysical rates thus obtained are summarized in Table 1 of the main text. These rates were then used in KMC simulations, obtaining a straightforward match with the experimental photoluminescence decay curves without further optimisation, as shown in Figure S14.

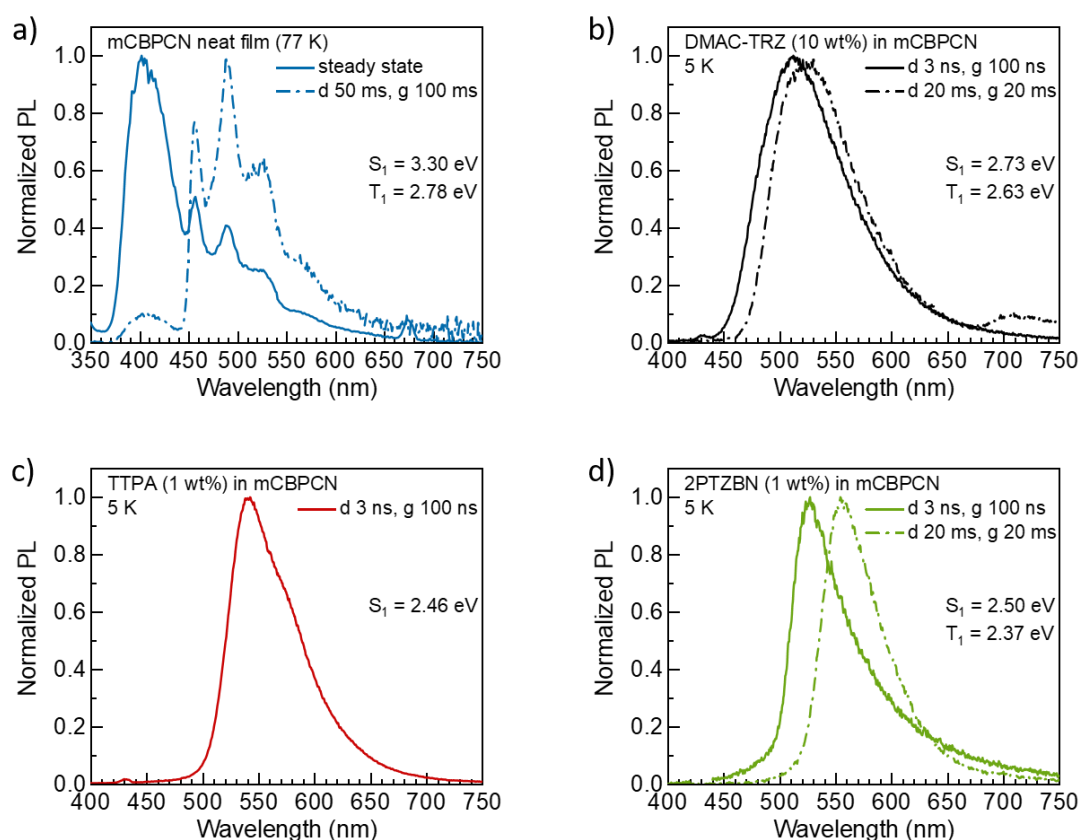


Figure S12: (a) 77 K steady state and phosphorescence (delay time = 50 ms, gating time = 100 ms) spectra obtained for host-only (neat mCBP-CN) film, (b) 5 K prompt fluorescence (delay time = 3 ns, gating time = 100 ns) and phosphorescence (delay time = 20 ms, gating time = 20 ms) spectra obtained for ref-TADF (10 wt% DMAC-TRZ in mCBP-CN) film, (c) 5 K prompt fluorescence (delay time = 3 ns, gating time = 100 ns) spectrum obtained for ref-non-MR (1 wt% TTPA in mCBP-CN) film. Phosphorescence spectrum could not be obtained for ref-non-MR film. (d) 5 K prompt fluorescence (delay time = 3 ns, gating time = 100 ns) and phosphorescence (delay time = 20 ms, gating time = 20 ms) spectra obtained for ref-MR (1 wt% 2PTZBN in mCBP-CN) film. Singlet and triplet energies obtained from the onset of prompt fluorescence and phosphorescence spectra are also mentioned.

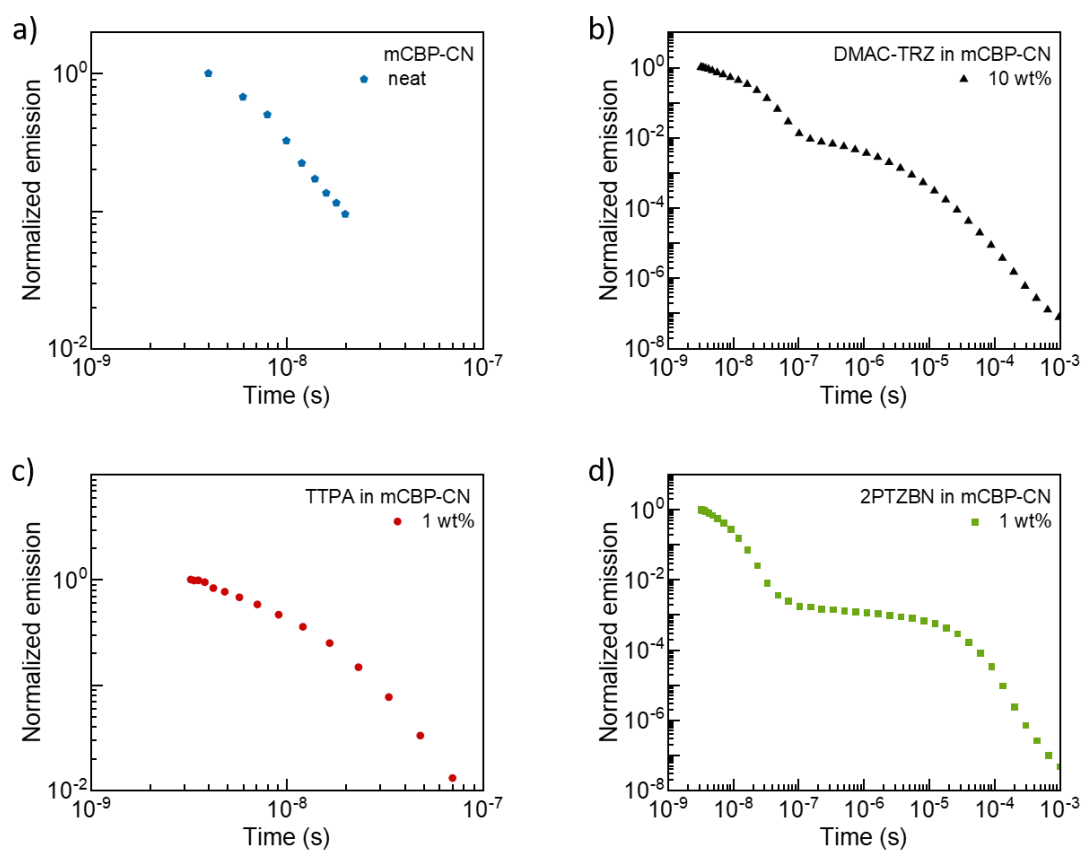


Figure S13: Photoluminescence decay curves obtained at room temperature for (a) host-only (neat mCBP-CN), (b) ref-TADF (10 wt% DMAC-TRZ in mCBP-CN), (c) ref-non-MR (1 wt% TTPA in mCBP-CN) and (d) ref-MR (1 wt% 2PTZBN in mCBP-CN) films.

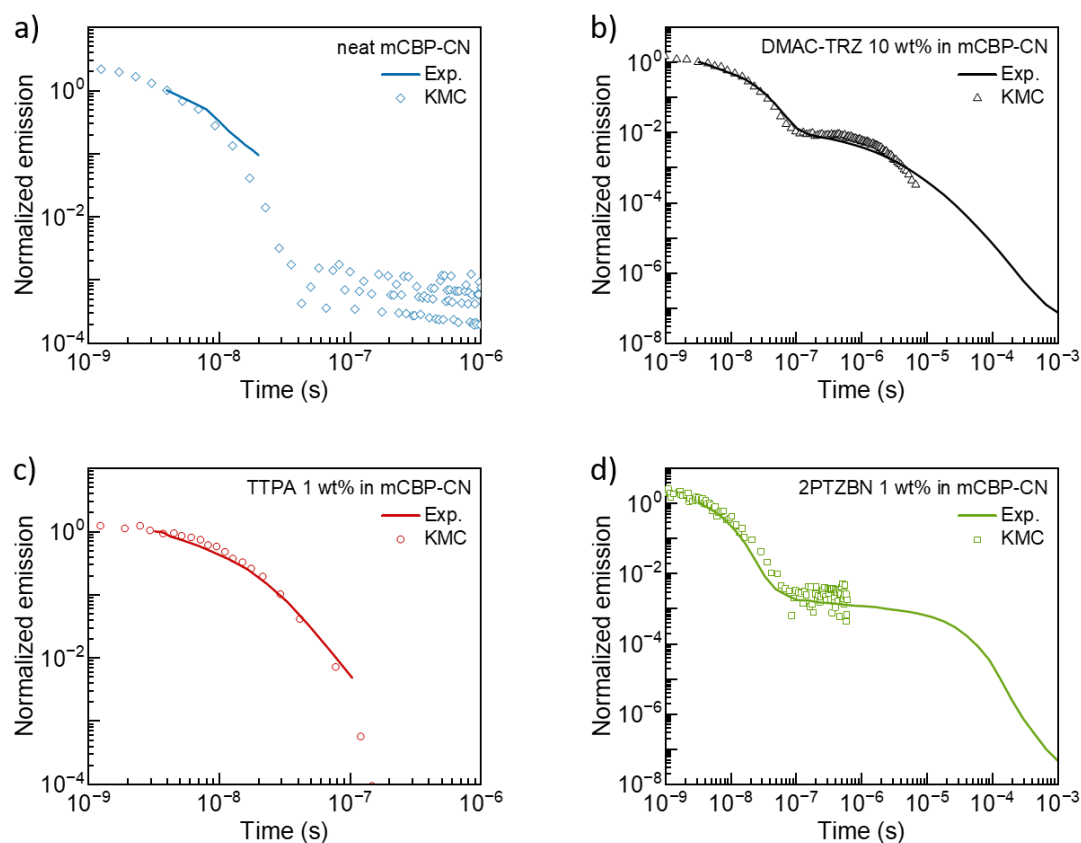


Figure S14: Comparison between experimental (solid lines) and simulated (open circles) photoluminescence decay curves for (a) host-only (neat mCBP-CN), (b) ref-TADF (10 wt% DMAC-TRZ in mCBP-CN), (c) ref-non-MR (1 wt% TTPA in mCBP-CN) and (d) ref-MR (1 wt% 2PTZBN in mCBP-CN) films.

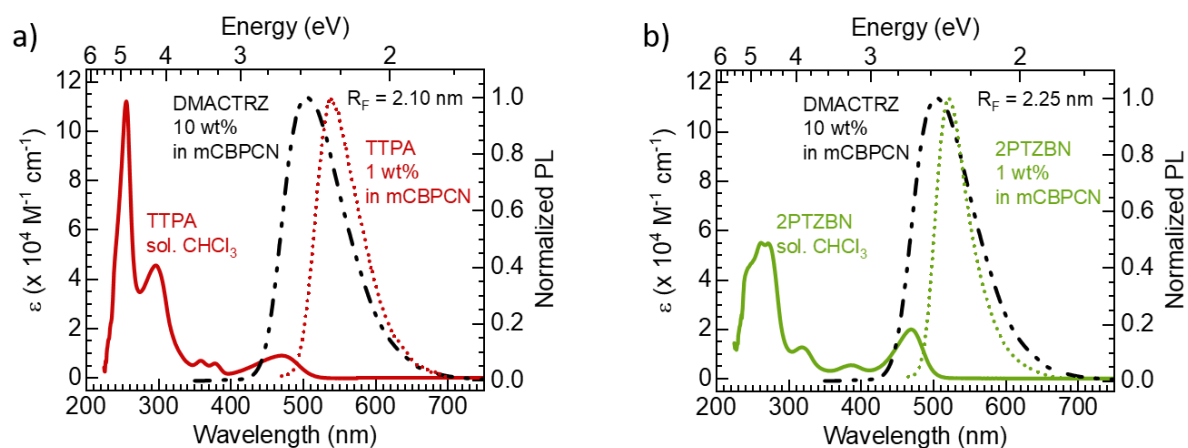


Figure S15: Molar extinction coefficient of (a) TTPA and (b) 2PTZBN in chloroform solution (solid line) and normalized steady state photoluminescence spectrum for thin film of 10 wt% DMAC-TRZ in mCBP-CN (dash-dot line), which were used for calculating the Förster radius between DMAC-TRZ and TTPA (2.1 nm) and 2PTZBN (2.25 nm). Also shown is the steady state photoluminescence spectrum for thin film of (a) 1 wt% TTPA and (b) 1 wt% 2PTZBN in mCBP-CN (dotted line).

Section S3: Effect of the co-evaporated α -NPD:mCBP (1:1) layer

In the simulated TADF and HF devices, the co-evaporated α -NPD:mCBP (1:1) layer (5 nm) between the neat α -NPD and neat mCBP hole transport layers does not significantly influence charge transport. Figures S18, 20 and 21 show that hole occupation on mCBP sites in the co-evaporated layer is negligible, while charge transport exclusively happens through α -NPD sites. This is consistent with the 0.45 eV difference between the ionisation potentials (IPs) of α -NPD and mCBP, where α -NPD has a lower (less negative) IP. Consequently, high-energy mCBP sites in the co-evaporated layer remain largely unoccupied, while the substantial density of α -NPD sites (50%) ensures effective charge transport.

Section S4: Further OLED results

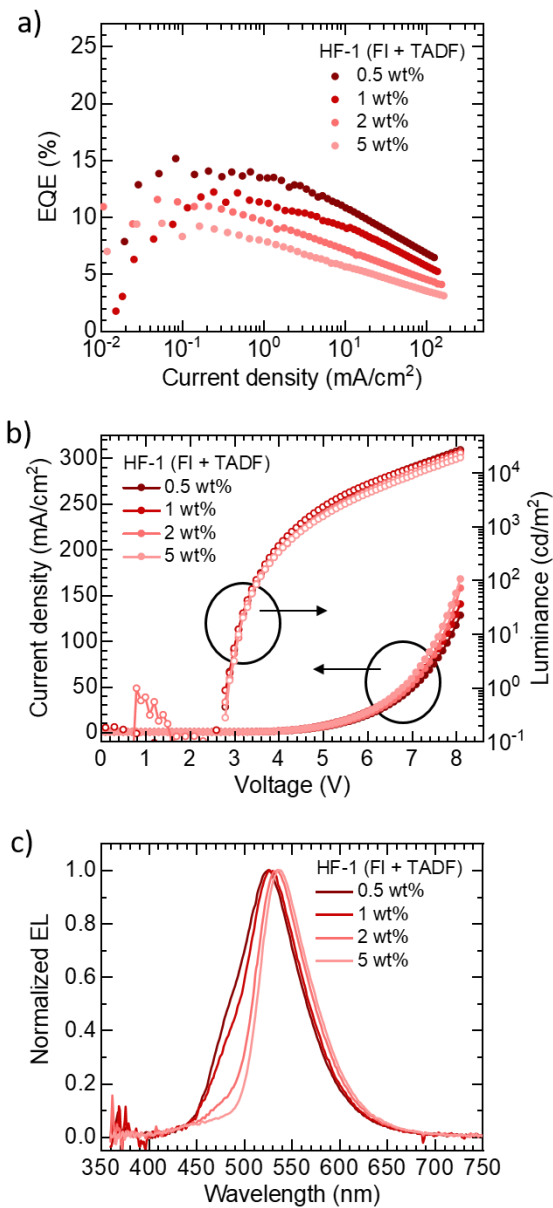


Figure S16: (a) EQE as a function of current density (b) current density-voltage-luminance characteristics and (c) electroluminescence spectra of the HF-non-MR OLEDs with varied concentration of TTPA in the emissive layer (DMAC-TRZ concentration: 10 wt%).

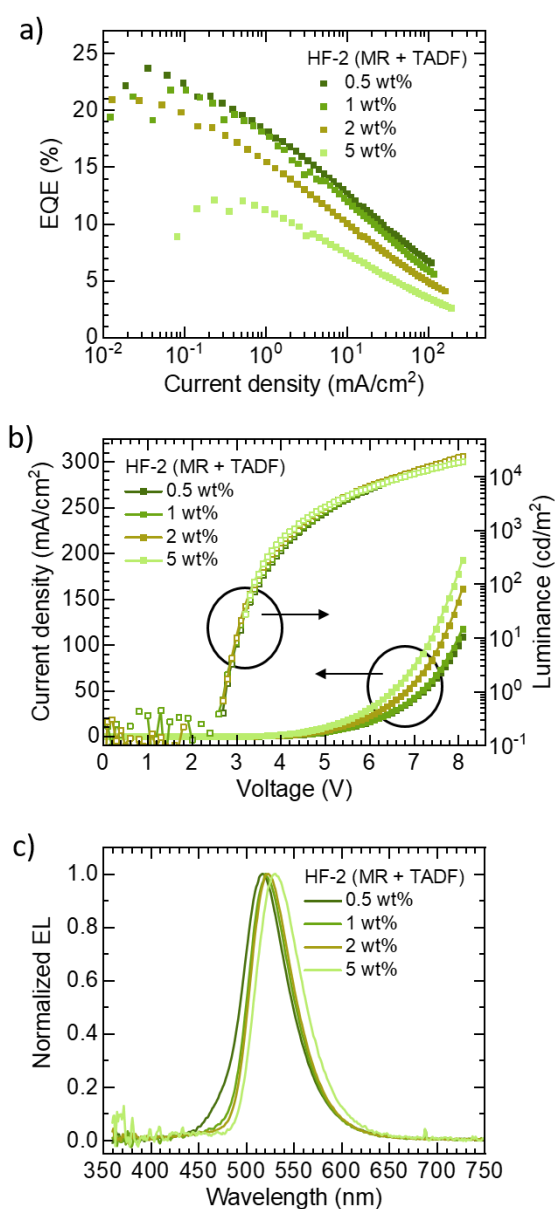


Figure S17: (a) EQE as a function of current density (b) current density-voltage-luminance characteristics and (c) electroluminescence spectra of the HF-MR OLEDs with varied concentration of 2PTZBN in the emissive layer (DMAC-TRZ concentration: 10 wt%).

Section S5: Further simulation results

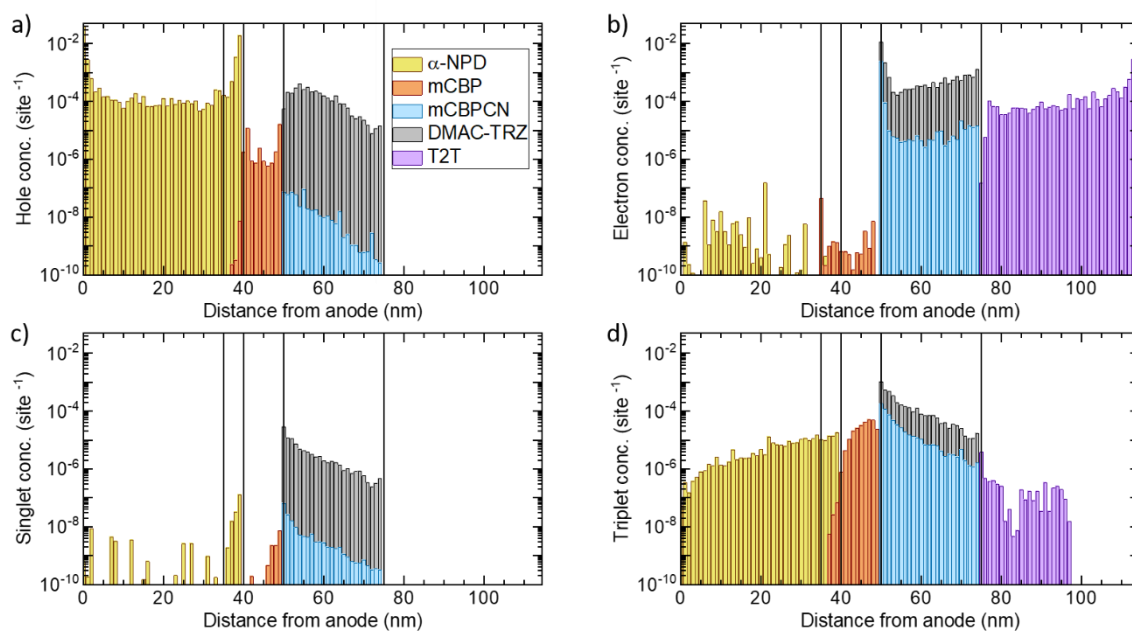


Figure S18: Material resolved profiles for (a) hole concentration, (b) electron concentration, (c) singlet concentration and (d) triplet concentration obtained from KMC simulations for reference TADF device.

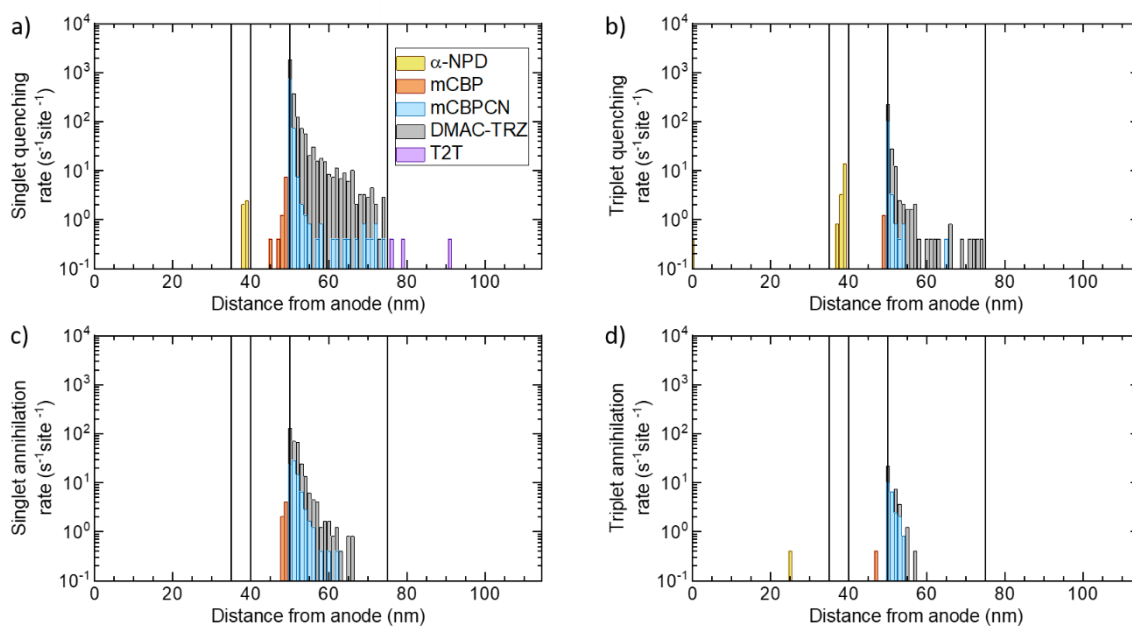


Figure S19: Material resolved profiles for (a) singlet quenching rate, (b) triplet quenching rate, (c) singlet annihilation rate and, (d) triplet annihilation rate obtained from KMC simulations for reference TADF device.

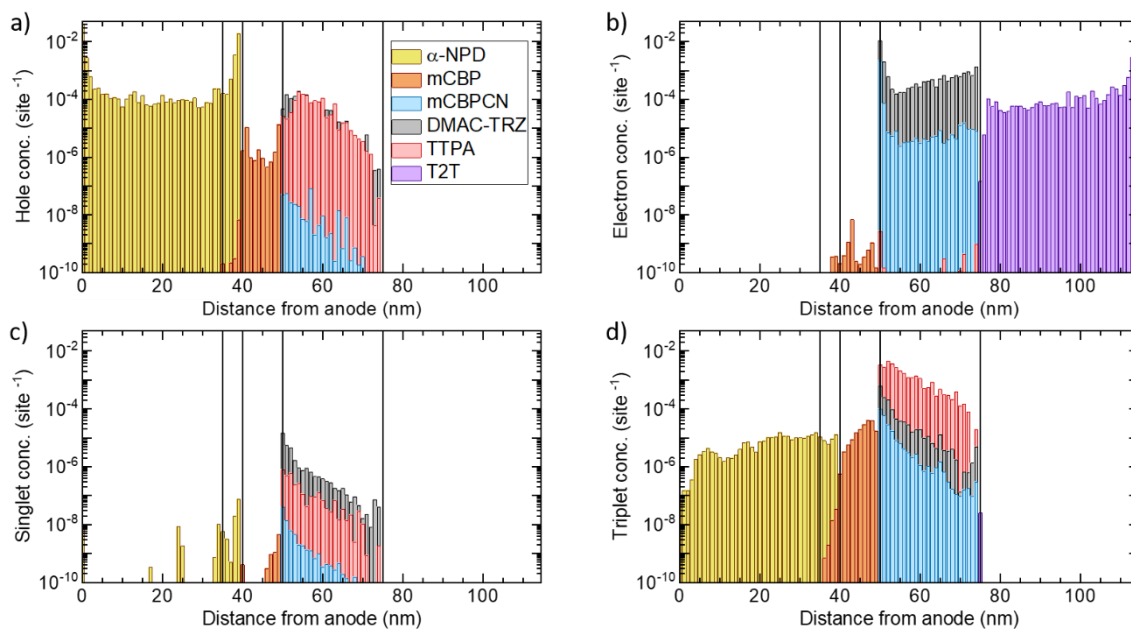


Figure S20: Material resolved profiles for (a) hole concentration, (b) electron concentration, (c) singlet concentration and (d) triplet concentration obtained from KMC simulations for HF-non-MR device.

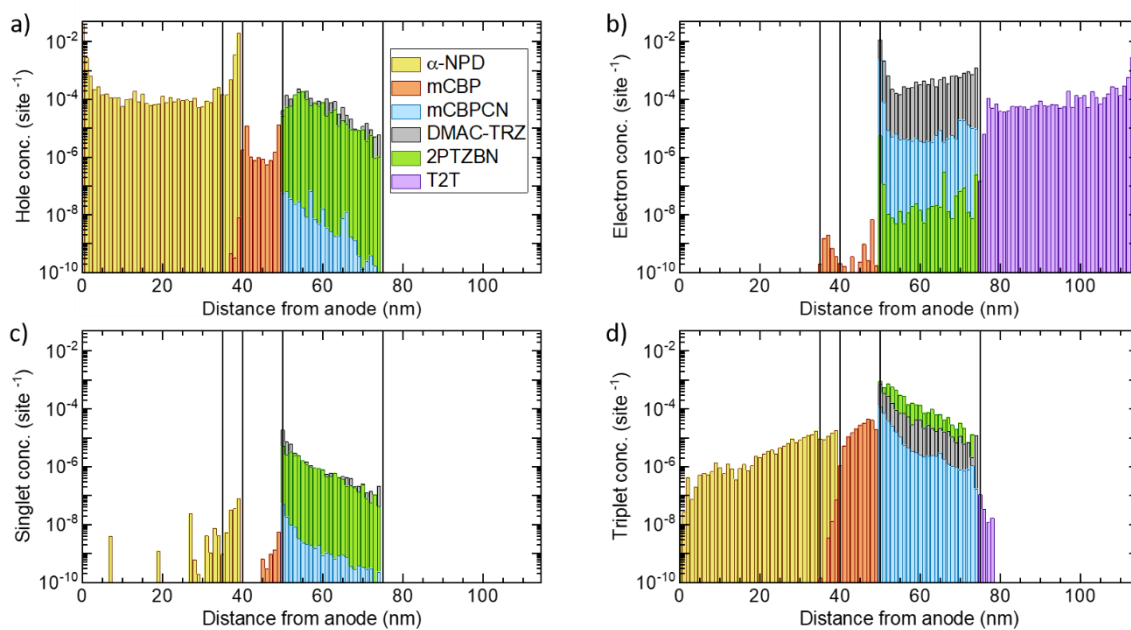


Figure S21: Material resolved profiles for (a) hole concentration, (b) electron concentration, (c) singlet concentration and (d) triplet concentration obtained from KMC simulations for HF-MR device.

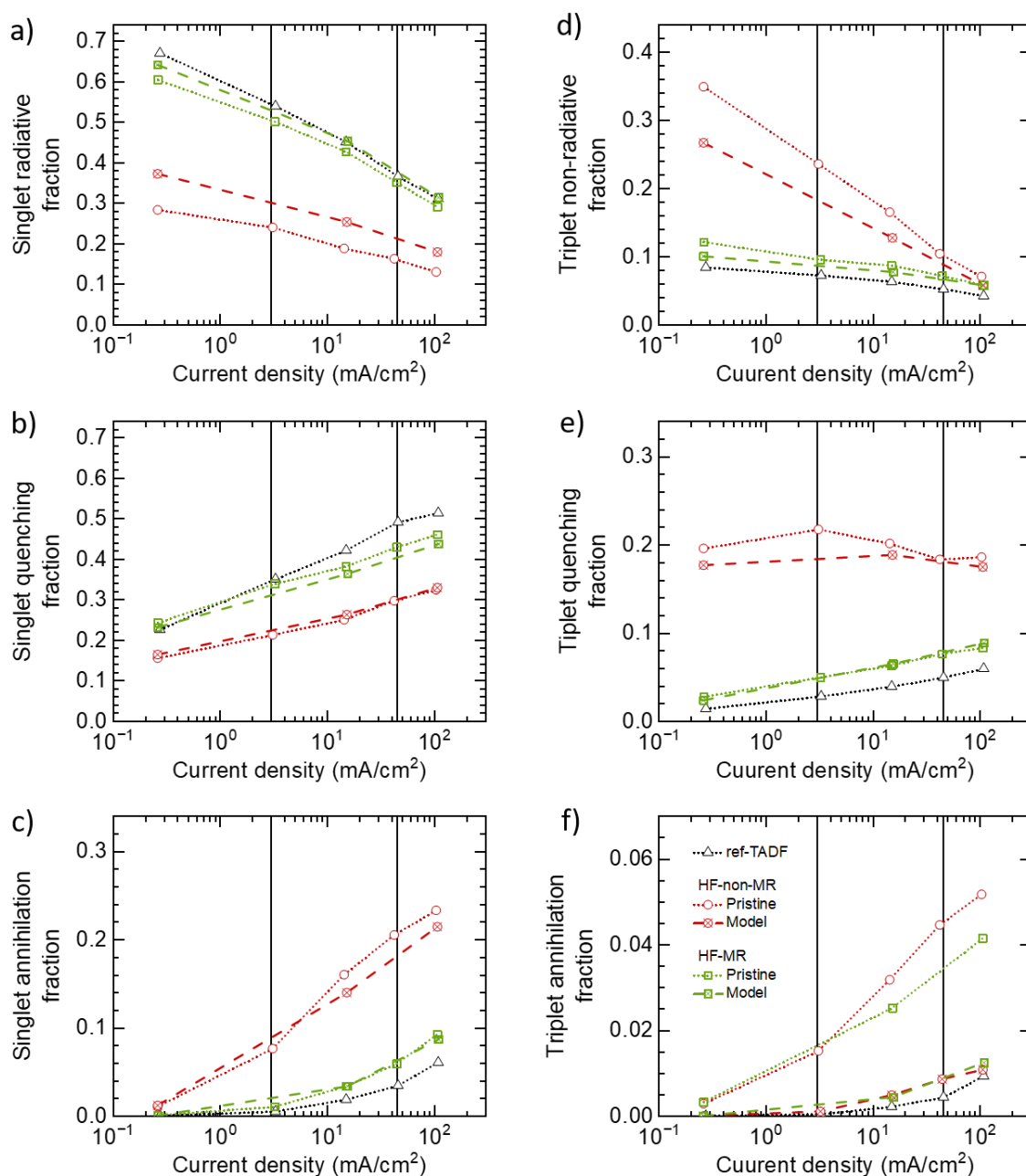


Figure S22: Comparison of (a) singlet radiative fraction, (b) singlet quenching fraction, (c) singlet annihilation fraction, (d) triplet non-radiative fraction, (e) triplet quenching fraction and, (f) triplet annihilation fraction between ref-TADF (black triangles), pristine HF-non-MR (open red circles), pristine HF-MR (open green squares), model HF-non-MR (crossed red circles) and model HF-MR (crossed green squares) devices. Different fractions represent the contribution of respective excitonic processes to the overall efficiency loss. Lines serve as a guide to the eye.

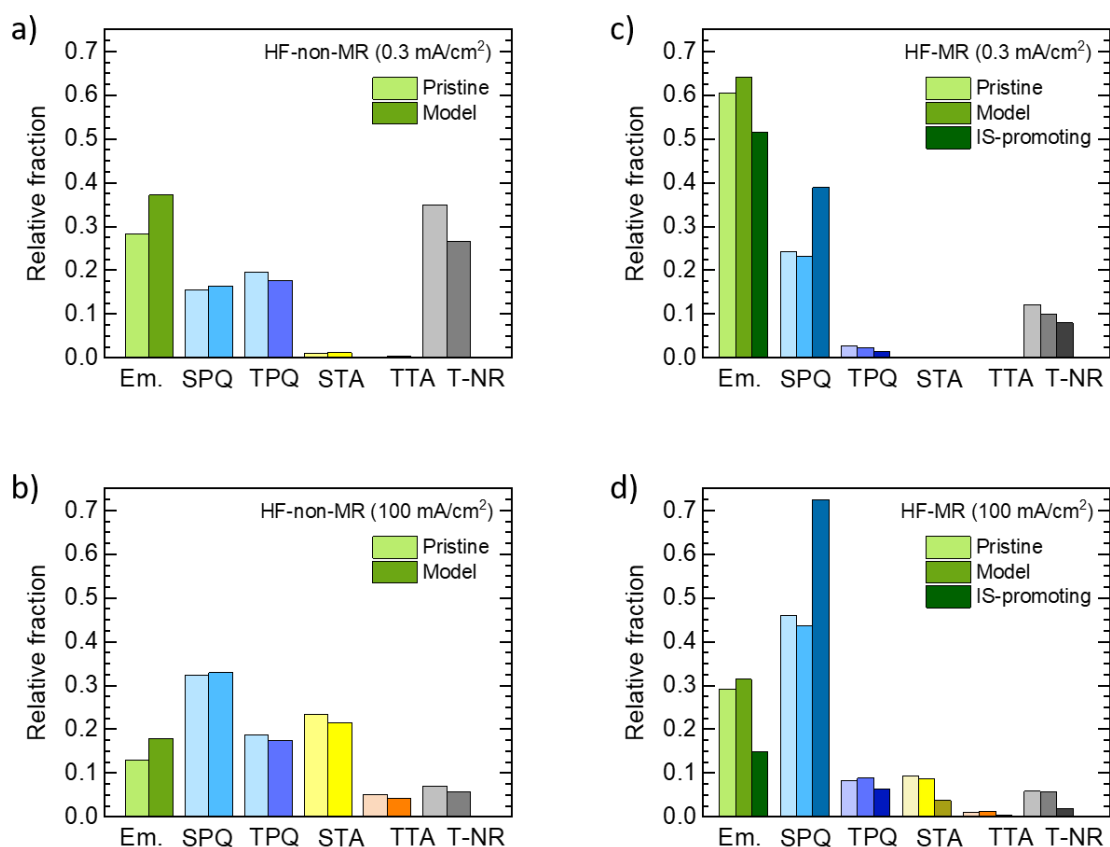


Figure S23: (a) and (b) compare the excitonic process contributions between pristine and model HF-non-MR OLEDs at current densities of 0.3 mA/cm² and 100 mA/cm², respectively. (c) and (d) compare the excitonic process contributions between pristine, model and IS-promoting (dark shade) HF-MR OLEDs at current densities of 0.3 mA/cm² and 100 mA/cm², respectively.

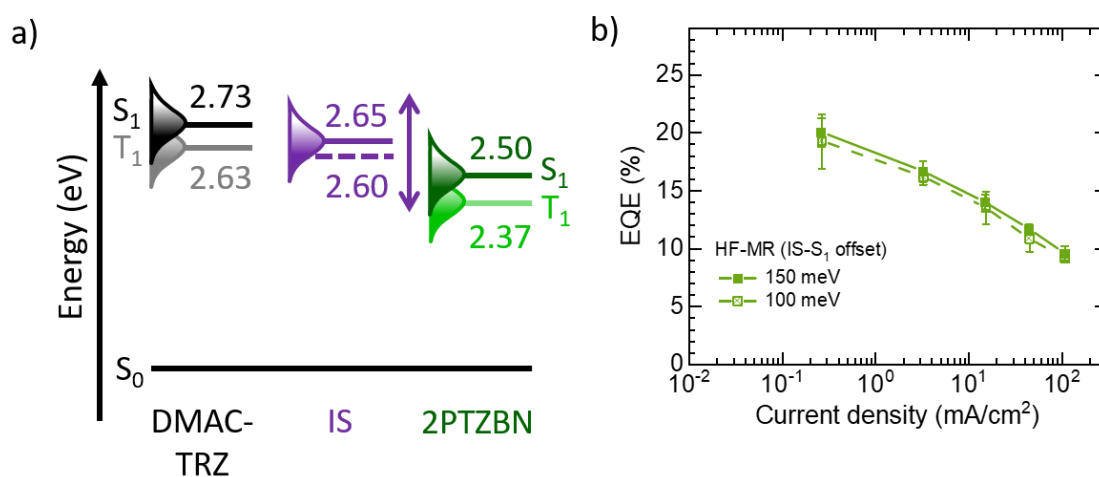


Figure S24: (a) Singlet and triplet energy for DMAC-TRZ (black) and 2PTZBN (green) are shown. The 2PTZBN (hole):DMAC-TRZ (electron) intermolecular state energy is shown in purple, for both the pristine HF-MR OLEDs with a 150 meV IS- S_1 offset (solid line) and the HF-MR OLED with a reduced 100 meV IS- S_1 offset (dashed line). (b) Simulated EQE-J curves for the HF-MR OLEDs with IS- S_1 offsets of 150 meV (pristine) and 100 meV.

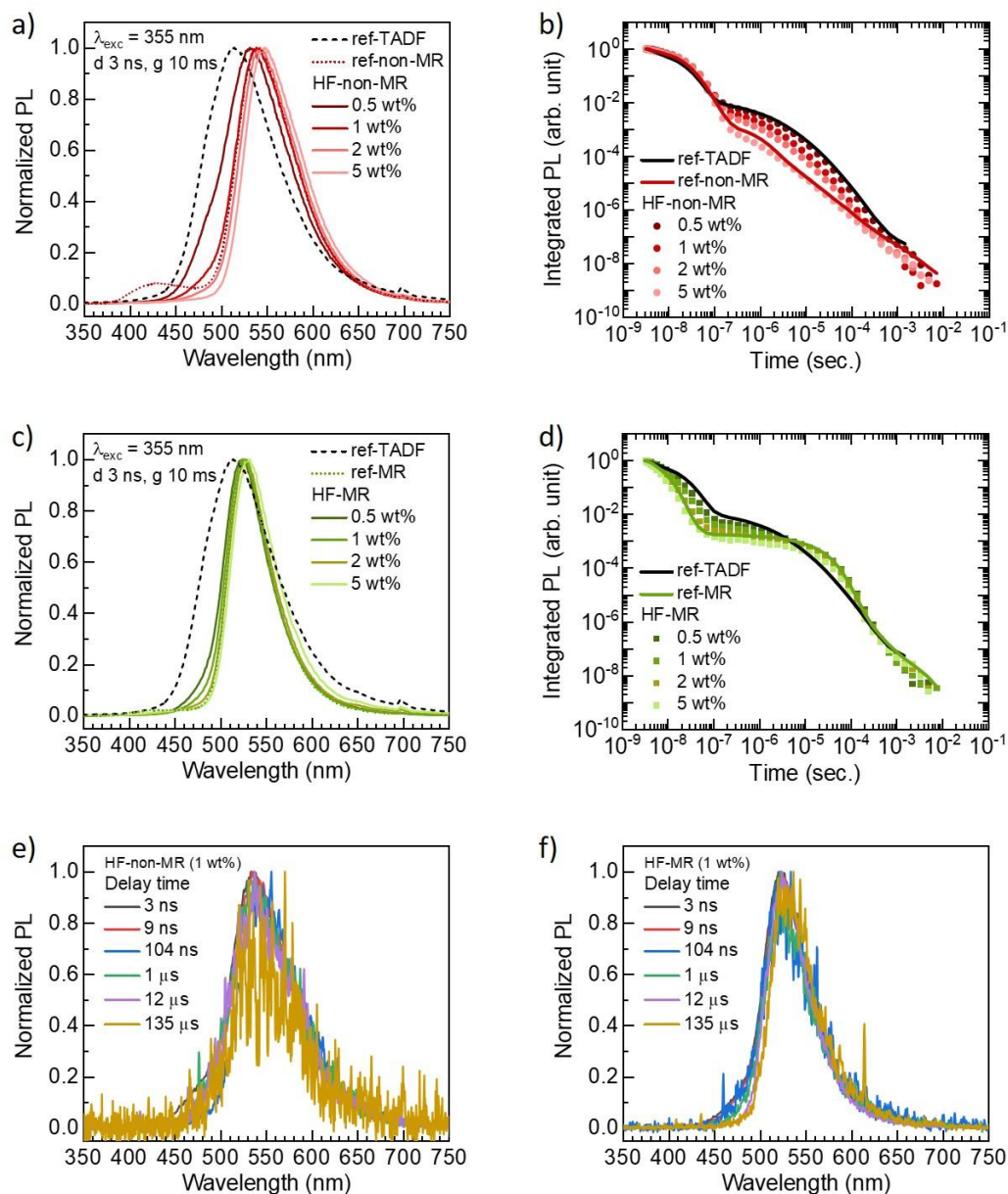
Section S6: Further photophysical data

Figure S25: (a) quasi-steady state spectra (delay time: 3 ns, integration time: 10 ms) and (b) room temperature photoluminescence decay curves for ref-TADF film, ref-non-MR film and HF-non-MR films with varied concentrations of terminal emitter. (c) quasi-steady state spectra (delay time: 3 ns, integration time: 10 ms) and (d) room temperature photoluminescence decay curves for ref-TADF film, ref-MR film and HF-MR films with varied concentrations of terminal emitter (excitation wavelength: 355 nm). Also shown are the normalized PL spectra at different delay times (with integration times about 10 times shorter) for (e) HF-non-MR (TTPA concentration = 1 wt%) and (f) HF-MR (2PTZBN concentration = 1 wt%) films.

Section S7: Energies of intermolecular states between different materials

Table S2: Intermolecular (IS) state energies, where electrons and holes reside on different materials within the emissive layer.

Electron		Hole		$E_{IS}^{[b]}$ (eV)
Material	Electron affinity (eV) ^[a]	Material	Ionization potential (eV) ^[a]	
mCBP-CN	-2.305	DMAC-TRZ	-5.8	3.02
DMAC-TRZ	-2.46	mCBP-CN	-6.25	3.31
mCBP-CN	-2.305	TTPA	-5.5	2.72
TTPA	-2.1	mCBP-CN	-6.25	3.67
DMAC-TRZ	-2.46	TTPA	-5.5	2.56
TTPA	-2.1	DMAC-TRZ	-5.8	3.22
mCBP-CN	-2.305	2PTZBN	-5.59	2.81
2PTZBN	-2.33	mCBP-CN	-6.25	3.44
DMAC-TRZ	-2.46	2PTZBN	-5.59	2.65
2PTZBN	-2.33	DMAC-TRZ	-5.8	2.99

^[a] Optimized electron affinity (E_{EA}) and ionization potential (E_{IP}) values. See section S1 for more details. ^[b] $E_{IS} = E_{EA} - E_{IP} - E_b$, where $E_b = 0.48$ eV is the Coulomb energy between an electron-hole pair separated by 1 nm in a medium with a dielectric constant of 3.

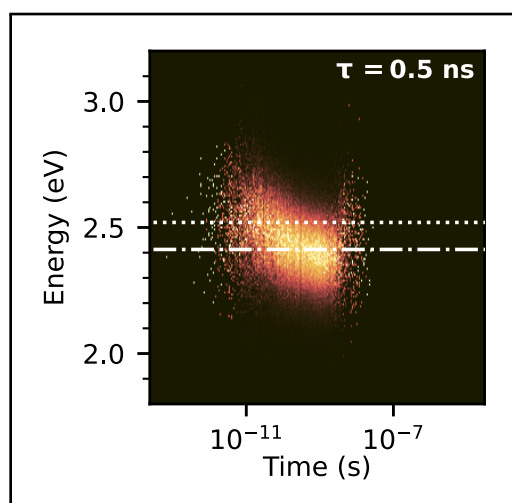
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Spectral diffusion due to charge carrier relaxation of intermolecular charge-transfer states in donor:acceptor blends of disordered organic semiconductors

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Spectral diffusion due to charge carrier relaxation of intermolecular charge-transfer states in donor:acceptor blends of disordered organic semiconductors

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Intermolecular charge-transfer (CT) states, often called “exciplexes”, exhibit promising triplet-recycling capabilities which enable small-molecule organic semiconductor materials in blends to act as emitters in organic light-emitting diodes (OLEDs). Alternatively, in OLEDs, an exciplex-forming blend of a donor- and an acceptor-type material can act as a sensitizer for fluorescent or phosphorescent emitter molecules. While OLEDs based on exciplex-forming blends are increasingly common, the dynamic processes that determine the time-resolved and time-integrated exciplex emission spectrum after optical and electrical excitation have not yet been studied in detail. We present a comprehensive study of these dynamic processes for two- and three-component blends, using three-dimensional kinetic Monte Carlo simulations that include radiative decay from CT states. Under both, photoexcitation and electrical excitation, CT state emission exhibits a time-dependent spectral diffusion, resulting from relaxation of the charge carrier pairs within the exciplex density of states (DOS). We disentangle the effects of the CT state lifetime, the frontier orbital energetic disorder of the components and the blend composition ratio on the emission spectrum. Furthermore, we highlight similarities and differences between the photoluminescent and electroluminescent emission of CT states. Our work shows that studying the emission of binary and ternary blends of donor and acceptor materials proves a valuable tool to understand the charge dynamics within such systems and may eventually provide an effective method to probe properties such as the material-specific energetic disorder and the occupation of the DOS spectroscopically.

Keywords: Monte Carlo methods, Carrier generation & recombination, Excitons, Organic LEDs

I. INTRODUCTION

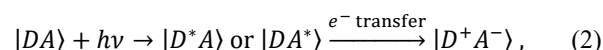
Organic semiconductor blends containing an electron-rich donor (D) and an electron-poor acceptor (A) material often show a characteristically broad emission, redshifted with respect to that of either component, due to the formation of intermolecular excited states [1]–[7]. Formally, such states can be described by a quantum-mechanical mixing of the local excited states and a charge-transfer (CT) state:

$$|DA\rangle^* = c_D \cdot |D^*A\rangle + c_A \cdot |DA^*\rangle + c_{CT} \cdot |D^+A^-\rangle, \quad (1)$$

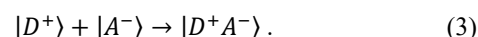
where $|D^*A\rangle$ ($|DA^*\rangle$) indicates the local donor (acceptor) excited state and $|D^+A^-\rangle$ is the CT state (neglecting the unlikely $|D^-A^+\rangle$ state), and where, due to normalization of these component states, the three coefficients satisfy the expression $c_D^2 + c_A^2 + c_{CT}^2 = 1$ [8]. For strong donor-acceptor pairs, i.e., pairs with a strongly reduced energy of the CT state as compared to the lowest-energy localized states on the donor and acceptor, charge-transfer character dominates and $c_D, c_A \ll c_{CT}$, so that $|DA\rangle^* \cong |D^+A^-\rangle$. Such a situation occurs in the case of a sufficiently strong offset of the semiconducting gaps of the two materials. Effectively, the

intermolecular excited state can be then understood as an emissive electron-hole (geminate) pair. In addition to the broad, featureless, redshifted emission spectrum, CT states also show absorption from the ground state [9]. This absorption is however very weak, as is expected from the long radiative decay time via the Strickler-Berg relation [10].

CT states may be generated by *photoexcitation* of either component, creating a local excited state (exciton) which evolves to an intermolecular CT state via electron transfer:



Alternatively, CT states may also form via *electrical excitation*, i.e., via the interaction between an anion (A^-) and a cation (D^+) created by injection of charge carriers from the electrodes:



In the field of organic photovoltaics (OPV), photogenerated intermolecular CT states are well-known precursors to charge separation. Their properties determine the efficiency of solar cells and, over the last decades, much work on this subject has been carried out (e.g. [11]–[16]). More recently, observations of efficient singlet exciton harvesting from intermolecular CT states [4]–[7],[17]–[19]

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SPECTRAL DIFFUSION DUE TO CHARGE CARRIER...

has sparked the interest of the OLED community as well. The localisation of the hole and electron on distinct molecules creates a spatial separation between the hole and electron wavefunction. This separation results in a very small energy gap between the singlet and triplet CT states, granting these systems efficient reverse inter-system crossing (rISC) capabilities. While the broad emission spectra of donor:acceptor (D:A) blends is less than ideal to produce OLED devices with good colour purity, such blends have found application in white OLEDs [20]–[22]. Efficient blue and green OLEDs have also been produced by combining a bipolar cohost and an emissive dopant [23]–[27], similar to the working principle of hyperfluorescent devices. These devices require that the emission of the cohost matches the absorption of the terminal emitter: predicting valid cohost-dopant combinations in turn requires a fundamental understanding of the emission properties of D:A blends. Research on intermolecular CT state emission for OLED applications has revealed some general trends which transcend the exact choice of materials. For example, the emission of CT states characteristically redshifts over time [4],[5],[28]. Conversely, it can be blueshifted by adding an excess of the donor or acceptor material [29] or an inert spacer [30],[31]. Other properties of the CT state emission, such as its effective radiative lifetime and width, have received less attention, despite being crucial to achieve efficient OLED devices.

To further improve the efficiency of light-emitting devices through better material choices, a comprehensive understanding of the photoluminescent (PL) and electroluminescent (EL) properties of D:A blends should be developed. This work aims at presenting a unified explanation of experimental observations within a single framework, providing the basis for an informed selection of materials. Three-dimensional kinetic Monte Carlo (3D-kMC) simulations of two- and three-component blends with a systematic variation of parameters such as energetic disorder, CT state lifetime and composition are used to disentangle the effect of each parameter. We focus on a study of the effect of CT state relaxation on the PL and EL peak energy and width. Modelling EL from CT states has not been demonstrated before in devices, where, in regions with a high electron and hole density, a certain ambiguity could exist concerning the pairing of electrons and holes leading to a photophysically active species. We show how it is possible to deal with this ambiguity in a practical manner. The relaxation process is described as the result of electron and hole hopping to (on average) lower-energy sites, in the presence of the other charge carrier, as in the work of Deotare *et al.* [28]. We find that most observations on the PL and EL emission of D:A blends can be understood from such a process. As schematised in Figure 1, the electron and hole DOS generate a joint “CT state DOS”, centred at

$$E_{CT} = E_{IE,D} - E_{EA,A} - E_B, \quad (4)$$

where $E_{IE,D}$ ($E_{EA,A}$) is the average ionisation energy of the donor (electron affinity of the acceptor) and E_B is the CT state

binding energy. The estimated width (standard deviation) of the CT state DOS is

$$\sigma_{CT} = (\sigma_{IE,D}^2 + \sigma_{EA,A}^2)^{1/2}, \quad (5)$$

where $\sigma_{IE,D}$ ($\sigma_{EA,A}$) is the width of the ionisation energy (electron affinity) distribution of the donor (acceptor) material, assuming Gaussian disorder [32]. In Equation 5, a possible distribution of CT state binding energies is neglected.

Charge carrier relaxation is known to result in the formation of an *occupied* density of states (oDOS) that is shifted towards lower energies and with a reduced width [32],[33]. In fact, kMC modelling [28] and magnetic field-dependent measurements [28],[34] support the picture of CT state diffusion via the alternate hopping of the electron and the hole, a so-called “inchworm” motion [28]. This way, CT states may explore their surroundings in search of low-energy sites. A schematic representation of the relaxation process is given in Figure 2. As a result of energetic disorder, such

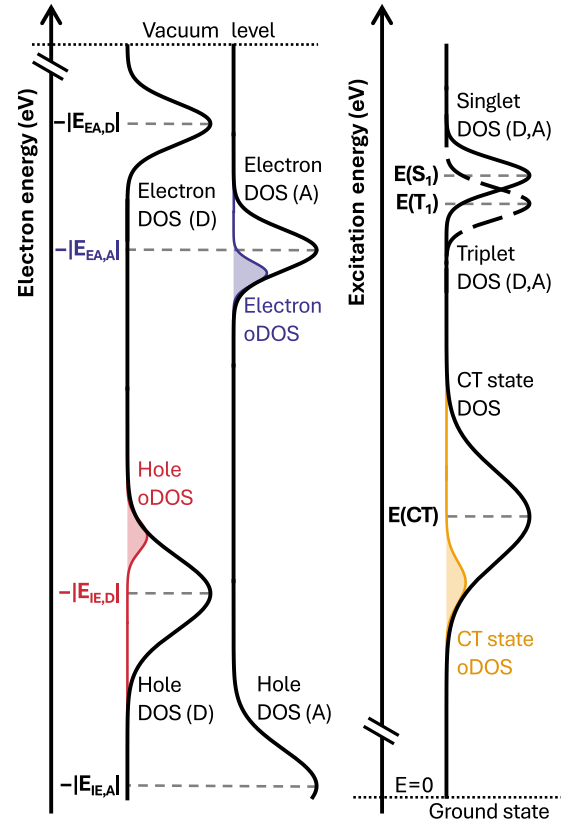


FIG. 1. Electronic and excitonic (occupied) density of states. (Left) Energy level scheme illustrating the relationship between the density of states (DOS) and the occupied density of states (oDOS) for holes on the donor molecules (D^+) and electrons on the acceptor molecules (A^-). (Right) DOS for the intermolecular charge transfer state D^+A^- . Also indicated is the DOS for the intramolecular S_1 and T_1 states of the donor and the acceptor: since their optical gaps are chosen to be identical, the energies $E(S_1)$ and $E(T_1)$ of the D and A molecules are equal.

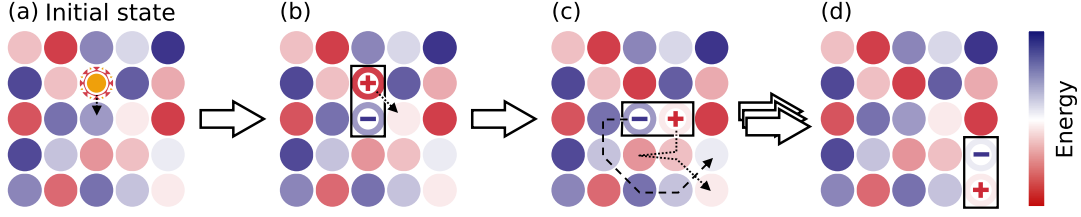


FIG. 2. Relaxation mechanism. Schematic of the proposed relaxation mechanism of CT state diffusion via charge carrier hopping. (a) A singlet exciton S (orange-coloured starred symbol) on a donor site generates a CT state (indicated by a rectangular box) via electron transfer to an adjacent acceptor molecule, then (b) within one hop the hole relaxes to a lower energy site. In time, (c) the electron-hole pair relaxes via a sequence of hops to (d) a lower-energy position. Saturated deep blue and deep red colours indicate high-energy electron and hole states, respectively, as indicated by the bar scale at the right-hand-side of the figure.

relaxation takes place in a nonequilibrium regime and is limited by the intrinsic CT state lifetime, resulting in a time-dependent spectral diffusion of the CT state emission. A key result of this work is that the relaxation process is in general only partial. Full relaxation would lead to a redshift over an energy $\sigma_{CT}^2/k_B T$, i.e., the thermal equilibrium energy, with k_B the Boltzmann constant and T the temperature, as has been observed for excitons [35]. For CT states with $\sigma_{CT} \approx 0.15$ eV, the expected redshift would then be about 0.9 eV at room temperature. However, we explain why in actual systems the redshift is only about 0.2 eV.

Studying the sensitivity of the spectral diffusion to the blend composition and the properties of the constituent materials is key to successful application of D:A blends, e.g. to predict suitable combinations of D:A cohosts and dopants for efficient energy transfer in hyperfluorescent OLEDs. As has been shown recently, CT state emission studies of large sets of D:A materials may also be employed to deduce the values of E_{IE} and E_{EA} of the constituent materials [36]. The effective average exciplex binding energy that follows from such studies is affected by the effect of spectral diffusion due to exciplex relaxation. Our work quantifies that effect.

In Sec. II, we present the simulation methodology and relevant parameters. The simulation results are described in Section 3. In Sec. III A, we study the CT state photoluminescence of equimolar blends and discuss its dependence on the energetic disorder and the CT state lifetime. In Sec. III B, we discuss the sensitivity of the PL spectra of binary blends to the D:A ratio. In Sec. III C, the PL emission from ternary D:A:spacer blends is studied. We also show how the findings can be extended to electroluminescent devices, focusing in Sec. III D on the sensitivity to the CT state lifetime and in Sec. III E on the sensitivity to an applied electric field. A summary and outlook are given in Sec. IV.

II. METHODS

This work extends the Kinetic Monte Carlo algorithm developed by Mesta et al. [37] and van Eersel et al. [38], as reviewed recently in Ref. [39], by including CT state

photophysics. We first give an overview on the general model (Sec. II A) and then discuss the choice of the values of the model parameters that are used in this work (Sec. II B).

A. Model for charge transport and CT state photophysics

The organic film is described as a collection of molecular sites on a simple cubic lattice, with donor, acceptor and (in some simulations) high-energy gap spacer molecules at random positions. The photoluminescence (PL) simulations are carried out for large cubic simulation boxes with fully periodic boundary conditions. The electroluminescence (EL) simulations are carried out for devices in which the simulation box is bounded by the electrodes along one axis and with periodic boundary conditions in the directions perpendicular to that axis. Each site is assigned an ionisation energy E_{IE} , electron affinity E_{EA} , singlet (S_1) energy E_S , and triplet (T_1) energy E_T , extracted from spatially uncorrelated Gaussian distributions [32] that are centred on material-specific E_{IE} , E_{EA} , E_S and E_T values, respectively, and with a width representing the energetic disorder. Positional disorder is not included in the model, as energetic disorder has been found to generally dominate [40]. Each site can host up to one electron and one hole. An electron and a hole sitting on the same site define an exciton, which dissociates when either charge carrier leaves the exciton site. Carrier hopping from site i to site j is described using a variable-range hopping rate with a Miller-Abrahams-type energy dependence [41],[42]:

$$k_{ij}^{\text{hop}} = \nu_1 \cdot \exp\left(-2 \cdot \frac{r_{ij}-a}{\alpha}\right) \cdot \exp\left(-\frac{|\Delta E_{ij}| + \Delta E_{ij}}{2k_B T}\right), \quad (6)$$

where ν_1 is the nearest-neighbour hopping attempt rate, α is the wavefunction decay length, a is the lattice spacing, and r_{ij} and ΔE_{ij} are the distance and energetic difference between sites i and j , respectively. ΔE_{ij} includes Coulomb interactions with all charges in the system, and the exciton or CT state binding energy. In the EL case, the injection or extraction barrier, image charges from the electrodes, and the applied field are also included in ΔE_{ij} . Coulomb interactions are

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included explicitly with all charges within a cutoff radius of 10 nm, as in Refs. [37],[38], while the contributions due to more remote charges are included by solving a one-dimensional Poisson equation.

An electron-hole pair is treated as a CT state when: (a) the hole sits on a donor-material site, (b) the electron sits on an acceptor-material site and (c) the electron-hole separation distance r_{eh} is smaller than a dissociation distance R_d . The selected value of R_d and the sensitivity of the simulation results to this parameter are discussed briefly in Sec. II B and more in detail in Section S1 of the Supplemental Material [43]. The simulations can be used to study CT state relaxation under PL conditions with a finite fluence, or under EL conditions with a finite current density. In such cases, there are generally multiple electrons and holes in the simulated system. This situation is treated as follows. Each carrier can only take part in one CT state. When multiple “CT state candidates” which fit the criteria (discussed above) are present, the CT state that is lowest in energy forms. While this rule implies a bias towards low-energy CT states, in this study we generally operate at such low concentration conditions that, realistically, each electron will have at most one hole in its vicinity and vice versa. The energy of the CT state that is formed by an electron-hole pair is given by

$$E_{CT,eh} = E_{IE,h} - E_{EA,e} - E_C(r_{eh}) - e(\mathbf{F} \cdot \mathbf{r}_{eh}), \quad (7)$$

where $E_{IE,h}$ ($E_{EA,e}$) is the ionisation energy (electron affinity) on the site where the hole (electron) resides, $E_C(r_{eh})$ is the Coulomb interaction energy at an electron-hole distance r_{eh} , and the last term represents the interaction energy between the dipole moment of the CT state and the local electrostatic field $\mathbf{F}$ [44]. We take $E_C(r_{eh}) = e^2/(4\pi\epsilon_0\epsilon_r r_{eh})$, with ϵ_0 the vacuum dielectric permittivity and ϵ_r the relative permittivity. We neglect non-Coulombic contributions to the binding energy, in agreement with experimental literature suggesting that exchange energy contributions are at least one order of magnitude smaller than the Coulombic term [6],[18],[45].

In the most general form of the model, CT states possess a spin, and are labelled as a singlet or triplet. When the dissociation of an exciton results in a CT state, the spin of the CT state is taken equal to that of the exciton. When two free charge carriers generate a CT state, its spin is randomly extracted favouring a chosen singlet:triplet ratio. We assume that the spin of a CT state does not change if one of the charge carriers hops to another site that is still within a distance R_d from the other charge. If, due to a hop of one of the charges, r_{eh} exceeds R_d , then the CT state is treated as “dissociated” and all information on the mutual spin of the two charge carriers is lost.

CT states are treated as photophysically active species, and are therefore assigned rates for radiative decay, non-radiative decay, intersystem crossing (ISC) and reverse intersystem crossing (rISC). The radiative decay rate, $k_{rad,CT}$, is expected to decrease with increasing electron-hole separation distance, due to the reduced overlap of the electron and hole wavefunctions. However, we find that the results of

photoluminescence simulations are almost insensitive to such an effect, as is briefly discussed in Sec. II B.

The present model does not include vibrational contributions to the emission spectra. While this additional source of broadening has proven crucial to reproduce experimental emission spectra [16],[46], we are interested here in studying the effects of the disorder and the composition on the occupation of the DOS and the emission spectrum.

B. Modelling restrictions and parameter values

To limit the parameter space, we restrict in this work the applications of the model as follows:

- (a) The donor and acceptor materials are taken to have equal charge transport gaps and optical gaps (5 eV and 4 eV, respectively), offset by an energy of $\Delta = 2$ eV. This offset provides a large driving force for exciton dissociation. In fact, an offset of $\Delta = 1$ eV would already be sufficient to achieve >99% exciton dissociation (see Section S2 of the Supplemental Material [43], in agreement with measurements [3],[18],[47],[48]). However, taking $\Delta = 2$ eV ensures that the emission from local excitons (at ~4 eV) and CT states (below 3 eV) is well separated.
- (b) We neglect diffusion of the local excitons, as the lifetime of excitons in the donor:acceptor blend is effectively shortened to a few picoseconds due to the dissociation processes that leads to intermolecular CT state formation (see Figure S8 of the Supplemental Material [43]).
- (c) The weak ground-state absorption of CT states is assumed to prevent Förster-type diffusion. Short-range diffusion, for which experimental evidence is available [49], is treated as a result of (repeated) hopping of a single electron or hole in the presence of the oppositely charged carrier. Transfer of the entire pair, to another donor *and* another acceptor, is neglected.
- (d) We work at a very low exciton and charge carrier density ($\sim 10^{-3}$ site $^{-1}$) and can therefore ignore interaction processes between excited species (exciton-exciton annihilation) or with free polarons (exciton-polaron quenching).
- (e) We assume that within the PL and EL simulations only singlet excitons and CT states are generated. We note that introducing triplet excitations would only result in an increased *effective* lifetime of the corresponding singlet excitation. Thus, we also neglect ISC and rISC.
- (f) The non-radiative decay rate of the excitons and CT states, which only reduces the emission intensity by a certain factor, is taken to be zero for all species.

When simulating a PL experiment, the dissociation distance R_d , which represents the maximum distance at which information on the mutual spin of carriers is maintained, should be taken relatively large. Otherwise, the dissociation and subsequent reassociation of CT states at the boundaries of the electron-hole distance range with a width R_d may result in spin flips that violate the principle of detailed balance. We

find that, under realistic PL conditions, the electron-hole distance of optically generated pairs is seldom larger than the second-nearest-neighbour distance (1.41 nm). Taking $R_d > 3$ nm is therefore found to suffice to prevent such artifacts in transient PL simulations (see Figure S2 of the Supplemental Material [43]). In the PL simulations, we use $R_d = 10$ nm. As the maximum electron-hole separation distance r_{eh} is very small, it makes little difference to PL studies whether the CT state radiative decay rate $k_{rad,CT}$ depends on r_{eh} or is a constant, as shown in Figure S4 of the Supplemental Material [43].

In contrast, under electrical excitation, oppositely charged carriers are injected from the opposite sides of the device. As a result, the distribution of electron-hole pair distances in the device is at any time very wide. When $k_{rad,CT}$ would be taken constant (distance independent), emission from CT states with a very large r_{eh} would dominate the emission profile (Figure S5 and S6 of the Supplemental Material [43]). When using a more physically realistic approach in which $k_{rad,CT}$ decreases following a steep exponential function with increasing r_{eh} , the simulation results qualitatively match experimental observations more closely, as shown in Sec. III D. We find that these results are virtually identical to results of EL simulations with $R_d = 1.5$ nm and with a distance-independent radiative decay rate (see Figure S7 of the Supplemental Material [43]). The EL simulations are therefore carried out using this small value of R_d .

An overview of the default simulation parameters is given in Table I. We will study the sensitivity of the simulation results to some of these parameters. For the lattice spacing $a = 1$ nm and the relative permittivity $\epsilon_r = 3$ assumed in this study, the Coulombic CT state binding energy is $E_B = 0.48$ eV for a nearest-neighbour electron-hole pair.

III. RESULTS AND DISCUSSION

A. PL emission spectrum of equimolar D:A blends

We first study the CT state emission spectrum of an equimolar donor:acceptor (D:A) blend under photoexcitation, leading to an exciton on a donor site. Figure 3 shows the dependence of these spectra for various values of the radiative lifetime of the CT states, using otherwise the set of default parameters that is given in Table I. The radiative decay rate that corresponds to the shortest lifetime that has been considered ($\tau_{rad,CT} = 0.03$ ns, Figure 3b) is equal to the rate ν_1 of each of the charge transfer processes that leads to exciton dissociation. Photogenerated singlet excitons on donor sites dissociate within a few picoseconds by electron transfer to a nearby acceptor site (Figure S8 of the Supplemental Material [43]). The resulting CT states are found to be mostly first nearest-neighbour (1NN, 80-90%) or second-nearest neighbour (2NN, 5-15%) electron-hole pairs (see Figure S10 and S11 of the Supplemental Material [43]). When only transfer to 1NN sites is considered, the initial average CT state energy is $E_{CT} = 2.52$ eV (from Equation 4, with

TABLE I: Simulation parameters.

Parameter	Value
Lattice parameter, a	1 nm
Size of the simulated system (PL)	$150 \times 150 \times 150 \text{ nm}^3$
Size of the simulated system (EL)	$90 \times 50 \times 50 \text{ nm}^3$
Temperature, T	293 K
Relative permittivity, ϵ_r	3
Coulomb cutoff radius, R_c	10 nm ^(a)
Nearest-neighbour hopping attempt rate, ν_1	$3.33 \cdot 10^{10} \text{ s}^{-1}$ ^(b)
Wavefunction decay length, α	0.1 nm
$ E_{EA,D} - E_{IE,D} $ and $ E_{EA,A} - E_{IE,A} $	5.0 eV
Offset energy $\Delta = E_{IE,A} - E_{IE,D} $	2.0 eV
$ E_{IE,D} - E_{IE,S} $ and $ E_{EA,A} - E_{EA,S} $	0.2 eV ^(c)
Singlet energy for D and A, $E_{S,(D,A)}$	4.0 eV ^(d)
Singlet energy for the spacer, $E_{S,S}$	5.6 eV ^(d)
Electronic disorder (all materials), $\sigma_{IE,EA}$	0.10 eV ^(e)
Excitonic disorder (all materials), σ_S	0.05 eV
Singlet exciton decay rate (all materials), $k_{rad,CT}$	$2.0 \cdot 10^9 \text{ s}^{-1}$
CT state dissociation distance (PL), $R_{d,PL}$	10 nm
CT state dissociation distance (EL), $R_{d,EL}$	1.5 nm

The material properties refer to the donor (D), acceptor (A), and spacer (S) materials. Under default conditions, the optically and electrically generated CT states are singlets, and ISC and rISC are neglected. For EL simulations, the barrier for charge injection from the electrodes is 0.2 eV. The decay rate $k_{rad,CT}$ is equal to $2.0 \cdot 10^8 \text{ s}^{-1}$ except in Sec. II, where it is systematically varied from $3.33 \cdot 10^{10} \text{ s}^{-1}$ ($k_{rad,CT} = \nu_1$) to $2.0 \cdot 10^6 \text{ s}^{-1}$ ($k_{rad,CT} = 6.0 \cdot 10^{-5} \cdot \nu_1$). $k_{rad,CT}$ is constant for electron-hole distances $r_{eh} < R_d$, see Section S1 of the Supplemental Material [43].

^(a) Chosen for performance as in Ref. [50],[51].

^(b) Typical value, see Ref. [52].

^(c) The charge transport gap of the spacer is thus 6.6 eV.

^(d) The singlet exciton binding energy for the donor, acceptor and spacer is thus 1.0 eV [53].

^(e) Systematically varied for the donor and acceptor material in Sec. III B from 0 eV to 0.15 eV.

$E_B = 0.48$ eV) and the initial distribution width is $\sigma_{CT} = 0.141$ eV (from Equation 5), as shown in Figure 3a. The DOS of holes on D sites and electrons on A sites is then uniformly populated. As shown in Figure 3b-d, which display

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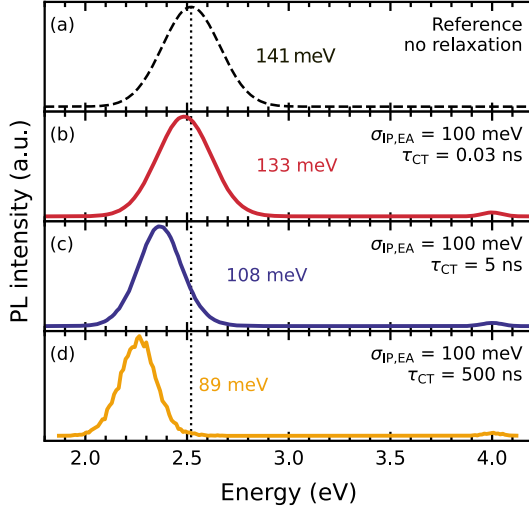


FIG. 3. Photoluminescence spectra. Calculated PL spectra of an equimolar D:A blend with electronic disorder energies of 0.10 eV. (a) Initial distribution of CT state energies that is expected from Equations 4 and 5, which assume dissociation to a 1NN CT state. The average energy is 2.52 eV (vertical dotted line). (b-d) Simulated steady-state PL spectra for a CT state lifetime of 0.03 ns, 5 ns and 500 ns, respectively. The standard deviation of the resulting emission profiles is indicated next to the curve. The figures also show the weak residual exciton emission around 4.0 eV (<1% of the total intensity).

actual simulation results, CT state relaxation leads not only to a redshift but also to a narrowing of the distribution. The relaxation of about 0.1 – 0.2 eV that is expected for $\tau_{\text{rad,CT}} = 5 - 500$ ns, which is a typical range for CT state lifetimes [2]–[5],[28], is similar to values that have been reported in the literature from time-resolved PL experiments [4],[5],[28].

The sensitivity of the CT state emission to the energetic disorder of the donor ionisation energy (IE) and the acceptor electron affinity (EA) is shown in Figure 4. Particularly, Figure 4a shows the effect of varying $\sigma = \sigma_{\text{IE,D}} = \sigma_{\text{EA,A}}$ and Figure 4b shows the effect of varying only $\sigma_{\text{EA,A}}$, with $\sigma_{\text{IE,D}} = 0.10$ eV. In general, an increase of the energetic disorder leads to a broader and more redshifted emission spectrum. As in the systems shown in Figure 3, the spectra are primarily determined by electron-hole pairs at a 1NN distance, whereas pairs further apart contribute only weakly to the high-energy tail (see Section S4 of the Supplemental Material [43]). In Figures 4c,d, the peak redshift and emission width are given as a function of the total disorder $\sigma_{\text{CT}} = (\sigma_{\text{IE,D}}^2 + \sigma_{\text{EA,A}}^2)^{1/2}$. Interestingly, data for varying $\sigma_{\text{IE,D}} = \sigma_{\text{EA,A}}$ and for varying $\sigma_{\text{EA,A}}$ at a fixed value of $\sigma_{\text{IE,D}}$ fall neatly on the same line, indicating that the redshift and width of the CT state emission only depend on the total disorder, rather than the individual energetic disorder of donor or acceptor. Specifically, the width of the CT state emission

is directly proportional to the total disorder:

$$\sigma_{\text{CT,sim}} = c \cdot (\sigma_{\text{IE,D}}^2 + \sigma_{\text{EA,A}}^2)^{1/2} \quad (8)$$

where, for a CT state lifetime of 5 ns, $c = 0.75$. We may argue that the parameter c is not only (by definition) equal to the ratio $\sigma_{\text{CT,sim}}/\sigma_{\text{CT}}$, but that it also represents the relative widths of the oDOS for electrons and holes in the respective DOS:

$$c \equiv \frac{\sigma_{\text{CT,sim}}}{\sigma_{\text{CT}}} = \frac{\sigma_{\text{IE,oDOS}}}{\sigma_{\text{IE,D}}} = \frac{\sigma_{\text{EA,oDOS}}}{\sigma_{\text{EA,A}}} \quad (9)$$

In fact, if $\sigma_{\text{IE,oDOS}}/\sigma_{\text{IE,D}} \neq \sigma_{\text{EA,oDOS}}/\sigma_{\text{EA,A}}$, varying $\sigma_{\text{EA,A}}$ at a fixed $\sigma_{\text{IE,D}}$ or jointly varying $\sigma_{\text{EA,A}} = \sigma_{\text{IE,D}}$ would not be equivalent. Simulations would then show a dependence of the emission width on $\sigma_{\text{EA,A}}$ and $\sigma_{\text{IE,D}}$ individually and not, as we observe, on total disorder alone.

It is well known that relaxation in a Gaussian DOS under equilibrium conditions leads to an oDOS with a width that is equal to the DOS width [54]. In such a case, one would expect a redshift to the thermal equilibrium energy, i.e., by $\sigma_{\text{CT}}^2/(k_{\text{B}}T) \approx 0.8$ eV for $\sigma_{\text{CT}} = 0.141$ eV, and with $c = 1$. The much smaller redshift (~ 0.2 eV) that is obtained from the simulations proves that equilibrium conditions are not reached. In such a case, the relatively fast relaxation of higher-energy charges, as compared to the relatively slow relaxation of charges that have already been partially relaxed, leads to a narrowing of the oDOS. This is analogous to the situation in

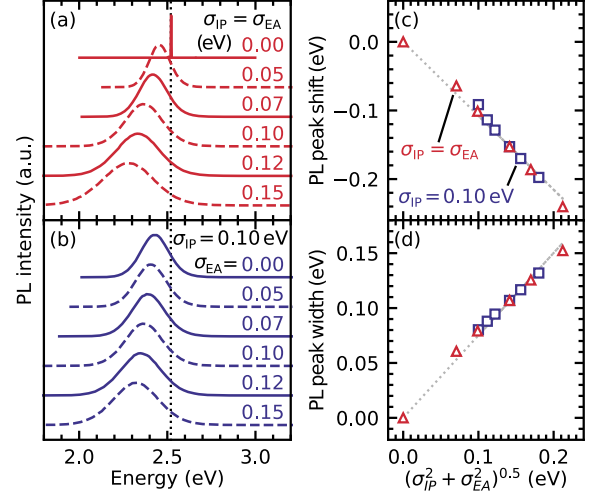


FIG. 4. Effect of energetic disorder on the time-integrated PL emission. (a,b) Simulated steady-state photoluminescence spectra for equimolar D:A blends with a lifetime $\tau_{\text{rad,CT}} = 5$ ns and varying disorder. Spectral relaxation for systems with (a) equal disorder for IE and EA and (b) varying EA disorder at a constant IE disorder of 0.10 eV. The vertical dotted line indicates the emission peak position in the absence of relaxation. Panels (c) and (d) show the peak shift and the emission width as a function of the total disorder energy $(\sigma_{\text{IE,D}}^2 + \sigma_{\text{EA,A}}^2)^{1/2}$, respectively for the cases shown in panel (a) (red triangles) and (b) (blue squares).

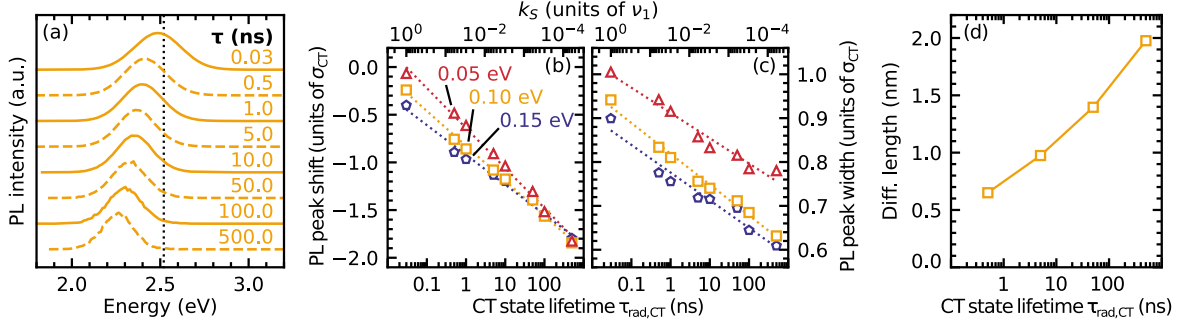


FIG. 5. Effect of the CT state lifetime on the time-integrated PL emission. (a) Simulated steady-state photoluminescence spectra for equimolar D:A blends with 0.10 eV disorder for each IE and EA, and varying lifetime τ . The vertical dotted line indicates the emission peak position in the absence of relaxation. (b) Steady state peak shift and (c) width of the emission spectra, parametric against CT state lifetime, for a disorder of (Δ) 0.05 eV, ($\square$) 0.10 eV and ($\diamond$) 0.15 eV for each IE and EA. The width is given in units of σ_{CT} and thus corresponds to the parameter c in Equation 9. The top horizontal axis reports the CT radiative decay rate relative to the charge hopping attempt frequency. The linear dotted lines are guides to the eye. (d) Average CT state diffusion length as a function of $\tau_{rad,CT}$.

infrared-cleansed thermally stimulated luminescence (TSL) experiments at low temperatures, that can provide the width of the DOS of neat films and the oDOS of charges after photoexcitation, and which has shown c values around 0.66 for a large set of neat films of disordered organic semiconductor materials [33]. The c value is expected to depend on the detailed conditions that determine the degree to which the system is out-of-equilibrium, such as the temperature, the radiative lifetime and (in the case of CT states in D:A blends) the constraints due to the Coulomb interaction and the positional disorder due to the randomly dispersed donor and acceptor molecules. In Ref. [33], spatially correlated energetic disorder was also found to play a role. For the systems studied, the parameter c is expected to decrease with increasing CT lifetime, as long as the system is out of equilibrium. Such a decrease is indeed found, as will be shown in Figure 5c.

Figure 5 shows the sensitivity of the time-integrated PL spectra to a variation of the CT state lifetime from 0.03 ns to 500 ns. Emission spectra for $\sigma_{IE,D} = \sigma_{EA,A} = 0.10$ eV are displayed in Figure 5a. Similar observations hold for 0.05 eV and 0.15 eV disorder, presented in Figure S12 of the Supplemental Material [43]. Figure 5b and c show that, in the range of CT state lifetimes under study, the PL emission spectrum is increasingly redshifted and narrower with increasing lifetime. The peak redshift and emission width vary approximately linearly with $\log_{10}(\tau_{rad,CT})$.

Interestingly, the data sets for different energetic disorders do not fall on the same line: the peak position redshifts more slowly for larger disorders (see Figure 5b). This is likely due to the increasing depth of tail states with increasing disorder, which reduces the charge carrier mobility. On the other hand, the dynamics of the emission width (normalised to the total disorder, Figure 5c) is almost independent of the energetic disorder, i.e., shows a similar slope when displayed as a function of $\log_{10}(\tau_{rad,CT})$. We remark that, even for a 0.03 ns

lifetime (i.e., for $k_{rad,CT} = \nu_1$) the emission profiles do *not* correspond to the relaxation-free curve predicted by Equation 4 and 5. That may be understood as a result of the availability of multiple initial carrier relaxation pathways in a three-dimensional blend, so that the average time at which the first relaxation process occurs is smaller than ν_1^{-1} . Figure 5d shows that the average diffusion length of the CT state, when taking $\sigma_{IE,D} = \sigma_{EA,A} = 0.10$ eV, also varies in an approximately linear fashion with $\log_{10}(\tau_{rad,CT})$. For CT state lifetimes below 1 μ s, and for the simulation parameters that have been assumed, the average diffusion length is smaller than 2 nm. We note that Ref. [28] finds much larger diffusion distances of 5-10 nm in two-dimensional kMC simulations of CT state diffusion at a planar interface between pure m-MTDATA and pure 3TPYMB. The discrepancy with our findings can be understood from (i) the absence of the spatial randomness of the donor and acceptor molecules in a 2D interfacial system, (ii) the use of a relatively small disorder energy ($\sigma_{IE,D} = \sigma_{EA,A} = 0.06$ eV in Ref. [28] vs 0.10 eV in this study), (iii) the use of a much larger lattice parameter ($a = 2.5$ nm in Ref. [28] vs 1.0 nm), and (iv) the use of a relatively large CT state lifetime (3.3 μ s in Ref. [28]).

Figure 6 complements these views on the relaxation process by showing the simulated energy- and time-resolved emission for D:A blends with $\tau_{rad,CT} = 0.5$ ns (Figure 6a) and 500 ns (Figure 6b), and for $\sigma_{IE,D} = \sigma_{EA,A} = 0.10$ eV. These figures ease comparisons with previous experimental studies on the time dependence of CT state emission [4],[5],[28]. The simulations yield an almost linear dependence of the emission redshift (Figure 6c) and width (Figure 6d) on $\log_{10}(\text{time})$, followed over five orders of magnitude. This behaviour is in agreement with the simulations of short-range exciton diffusion by Hoffmann *et al.* [35]. The slopes of the peak redshift and the relative emission peak width in Figures 6c and 6d are similar to the results for $\sigma_{IE,D} = \sigma_{EA,A} = 0.10$ eV in Figure 5, although

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slightly larger. The difference may be understood by considering that the TRPL experiments probe the peak position and width after a certain delay time t_{delay} , whereas time-integrated experiments for a radiative decay time $\tau_{\text{rad,CT}} = t_{\text{delay}}$ approximately probe the average peak positions and width until $t = t_{\text{delay}}$. These averages will also decrease with increasing t_{delay} , but with a reduced slope when plotted on a logarithmic timescale.

B. Effect of the composition of binary D:A blends on the PL emission

Empirically, the CT state emission is known to shift to shorter wavelengths when using a non-equimolar blend [29] – which will be studied in this section – or when diluting the donor and acceptor materials with an inert, high energy gap “spacer” [30],[31] – which will be studied in Sec. III C.

Figure 7 shows simulation results for blends with a range of D:A ratios, obtained for $\sigma_{\text{IE,D}} = \sigma_{\text{EA,A}} = 0.10$ eV, and $\tau_{\text{rad,CT}} = 5$ ns. The simulated emission profiles are shown in Figure 7a. Figures 7b,c show the dependence of the emission redshift and width on the blend composition. The simulations show a blueshift (with respect to the equimolar peak energy) of up to about +0.06 eV when varying the concentration towards the limit of strong dilution. Figure S14 of the Supplemental Material [43] shows that the extent of this blueshift is in good agreement with Ref. [29]. The spectra show a broadening of up to about +0.014 eV (i.e. $\sim 10\%$ of the CT state DOS width of an equimolar blend before relaxation). Consistent with the symmetry of the simulated D:A system,

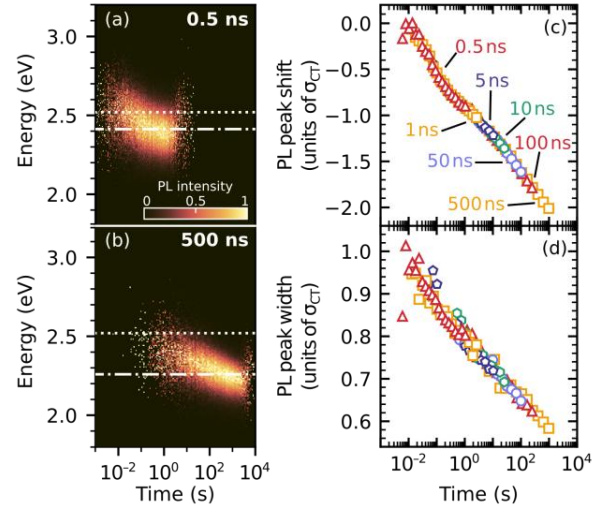


FIG. 6. Transient PL emission spectra. (a,b) Simulated time-resolved CT state emission, normalised in intensity to the peak maximum for each slice, for an equimolar D:A blend with a CT state lifetime of (a) 0.5 ns and (b) 500 ns, and a disorder of 0.10 eV for each IE and EA. The white dotted line indicates the emission peak position in the absence of relaxation, the dash-dotted line indicates the steady-state emission peak position for the given lifetime. (c) Time-dependent peak shift and (d) width of the simulated transient photoluminescence emission peak for CT states with different radiative lifetime $\tau_{\text{rad,CT}}$, plotted against time.

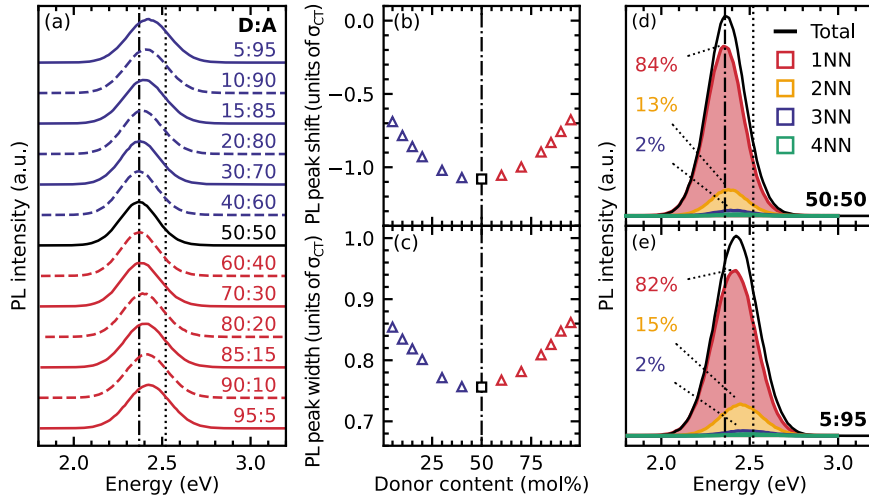


FIG. 7. Effect of blend composition (D:A ratio) on PL emission. (a) Simulated steady-state photoluminescence spectra for blends with varying D:A composition for a disorder of 0.10 eV for each IE and EA, and a CT state lifetime of 5 ns. (b) Position and (c) width of the emission peak as a function of blend composition. The dash-dotted line indicates the 50:50 composition. (d,e) Decomposition of the emission spectra in terms of electron-hole distance (nearest- to fourth-nearest neighbour) for a (d) 50:50 and (e) 5:95 blend. In panels (a,c,d), the vertical dotted line indicates the emission peak position in the absence of relaxation, the dash-dotted line indicates the steady-state peak position for a 50:50 D:A blend.

the effect is symmetric with respect to the equimolar composition.

The observed blueshift may be understood from Figures 7d,e, which show the emission profile for a 50:50 or 5:95 blend, resolved in terms of electron-hole distance. Recent literature [30],[31],[55] attributes the blueshift to an increased electron-hole distance, and hence a lower Coulombic binding energy, due to the lower content of D or A in non-equimolar blends. In our simulations, that would translate to an increased fraction of emission from second- or even third-nearest neighbour (2NN, 3NN) electron-hole pairs. However, the emission from 2NN pairs increases only from 13% for a 50:50 D:A blend (Figure 7d) to about 15% for a 5:95 D:A blend (Figure 7e). This small change is not sufficient to produce the observed blueshift. Rather, in the 5:95 case the emission from 1NN pairs (red-shaded curves in Figure 7d,e) is itself broader and less redshifted than in the 50:50 case, explaining the differences in the overall profile. We attribute this lack of redshift to frustrated carrier relaxation [56]: a low donor (acceptor) content reduces both the number of low-energy hole (electron) sites and the percolation pathways to reach them.

Interestingly, simulations show sizable charge carrier relaxation even for systems in which the donor or acceptor concentrations are very small. That may be understood as the result of relaxation due to electron transfer in the vicinity of a hole that stays on the same donor (in the small donor concentration limit), or an analogous hole relaxation process (in the small acceptor concentration limit).

C. PL emission from ternary D:A:spacer blends

Simulation results for diluted donor:acceptor blends, obtained by introducing a spacer material, are shown in Figure 8. As shown in the energy diagram in Figure 8a, the spacer material has a high energy gap, so that D:A CT states are well-confined, and so that the spacer does not form CT states with either D or A. The IE (EA) of the spacer is offset by 0.2 eV with respect to the IE (EA) of the donor (acceptor) to enable charge transport through the spacer without generating carrier traps. The energetic disorder is $\sigma_{IE,S} = \sigma_{EA,S} = 0.10$ eV. The energy levels that are shown in the figure are consistent with the energy level differences that are given in Table I.

Figure 8b shows simulated emission profiles for D:A:S blends with equal D:A ratio and 0 mol% (50:50:0) to 90 mol% (5:5:90) spacer content. The figure shows that the emission spectrum blueshifts and broadens with increasing spacer content. The blueshift is +0.16 eV for a 5:5:90 blend, compared to a 50:50:0 composition, and the corresponding increase in peak width is +0.04 eV. The blueshift and broadening follow a surprisingly linear trend with the fraction of spacer (see Figure S13 of the Supplemental Material [43]). These results are in fair agreement with measurements in Ref. [30] (see Figure S15 of the Supplemental Material [43]).

Figures 8c and 8d show the emission profile for a 50:50:0 or 5:5:90 D:A:S composition, resolved in terms of the electron-hole distance. In a 5:5:90 blend (Figures 8d), the

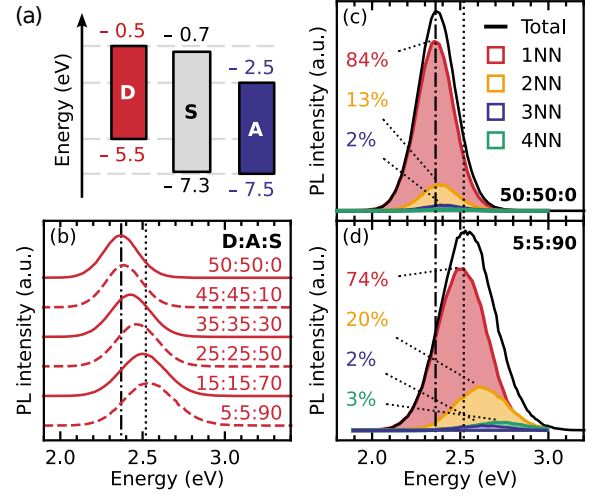


FIG. 8. Effect of blend composition (inert spacer) on PL emission. (a) Energy levels of the donor, acceptor and inert spacer materials. (b) Simulated steady-state photoluminescence spectra for blends with equimolar D:A ratio and a varying fraction (0 to 90 mol%) of inert spacer. (c,d) Decomposition of the emission spectra in terms of electron-hole distance (nearest- to fourth-nearest neighbour) for blends with (c) no spacer and (d) 90 mol% spacer. In panels (b-d), the dotted line indicates the emission peak position in the absence of relaxation, the dash-dotted line indicates the steady-state peak position of a 50:50 D:A blend without spacer.

1NN emission spectrum is largely blueshifted (+0.14 eV) and broadened (+40%) as compared to a 50:50:0 blend (Figure 8c), so that its peak energy (2.54 eV) and width (0.15 eV) are almost equal to the values calculated with Equations 4 and 5 in the absence of relaxation. We argue that, like in non-equimolar D:A blends, a reduced donor or acceptor content hinders carrier relaxation, as the system contains less low-energy sites to relax to. Differently from our observations on non-equimolar D:A blends, however, emission from 2NN pairs increases at increasing spacer content: the 2NN contribution almost doubles from 13% in a 50:50:0 blend to 20% in a 5:5:90 blend. Increased 2NN contributions produce a major broadening of the peak and further blueshift. As a result, the overall 5:5:90 emission peak reaches a width of 0.15 eV, slightly wider than the value of 0.141 eV predicted by Equation 5, which only considers 1NN pairs. We note that the peak shift and broadening are found to be almost independent of the specific distance dependence of $k_{rad,CT}$ that has been assumed in the simulations. The simulations in Figure 8 have been carried out assuming an exponential dependence $k_{rad,CT}(r_{eh}) = k_{rad,CT}(a) \cdot \exp[-(r_{eh} - a)/\lambda]$, with $a = 1$ nm the lattice constant and a decay length $\lambda = 3$ nm. The simulated spectra overlap perfectly with simulation results for $\lambda = 0.5$ nm or 1 nm, shown in Figure S13 of the Supplemental Material [43].

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D. EL emission – effect of the CT state lifetime

After having discussed the PL emission from intermolecular CT states in thin films, we move to EL emission from such states in devices. The device structure is:

$$\text{anode} | \text{D (30 nm)} | \text{D:A blend (50:50, 30 nm)} | \text{A (30 nm)} | \text{cathode},$$

as displayed in Figure 9a. Near-Ohmic injection from the electrodes, which are not explicitly modelled, is introduced by taking a 0.2 eV injection barrier [57]. Figure 9b shows the simulated emission spectra for devices with CT state lifetimes from 0.5 to 500 ns and $\sigma_{\text{IE,D}} = \sigma_{\text{EA,A}} = 0.10$ eV, for an applied voltage of a 7.5 V, corresponding to a device-averaged field $F = 8.3 \times 10^7 \text{ V m}^{-1}$. For a binary blend-based device, the effect of the applied field on the CT state emission spectrum is negligible, as we will show in Sec. III E. No excitons are formed, so that no emission is recorded for energies above approximately 2.7 eV.

As in the PL case, the EL emission redshifts and narrows for longer CT state lifetimes. Figure 9c shows that the EL peak position redshifts linearly in $\log_{10}(\text{time})$, with a slightly smaller slope than in the PL case. As compared to the PL case, the EL emission is redshifted by around 0.08 eV. Such a difference, which has often been reported in the literature [6],[54]–[56], may be understood as the result of charge carrier relaxation during charge transport, which in EL devices may proceed to a larger extent than in a photoexcited thin film due to longer carrier lifetimes (i.e., the time to reach the emissive layer plus the CT state lifetime). Furthermore, Figure 9d shows that the emission profile is consistently narrower for PL than for EL. We suggest that this difference reflects that under electrical excitation CT states are generated via a different process than under photoexcitation, viz. a Shockley-Read-Hall-like recombination mechanism within which, before recombination, one carrier resides on an energetically deep site in the tail of the DOS, which acts as a trap site. The potential well of this “cold” carrier constitutes a trap for a “hot” carrier. The “cold” carrier cannot easily escape from its deep site, so that further relaxation due to the hopping of the captured “hot” carrier is limited.

E. EL emission – effect of the applied external field

Figure 10 presents the simulated EL emission as a function of the applied external field. The simulations were carried out for the blend device shown in Figure 9a and for a bilayer device with a structure

$$\text{anode} | \text{D (45 nm)} | \text{A (45 nm)} | \text{cathode},$$

shown in Figure S16a of the Supplemental Material [43]. The simulations for a bilayer device have been added with the purpose to study in more detail the effect of the electric field on the CT state energy. According to Equation 7, the electric field F in the device at the position of the CT state due to the externally applied voltage should modulate the CT state energy by a quantity $|e(\mathbf{F} \cdot \mathbf{r}_{eh})|$, where $\mathbf{r}_{eh}$ is the electron-

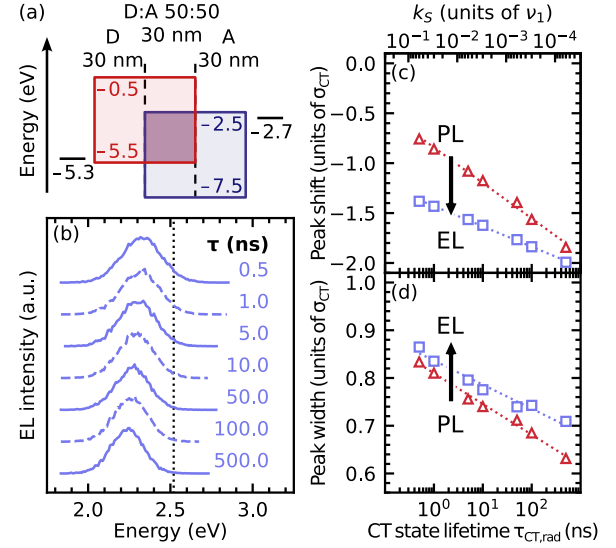


FIG. 9. Effect of the CT state lifetime on EL emission. (a) Energy diagram for an OLED device with structure “anode | donor (30 nm) | D:A blend (50:50, 30 nm) | acceptor (30 nm) | cathode”. The IE and EA of the donor and acceptor have 0.10 eV disorder each. (b) Simulated steady-state electro-luminescence spectra, parametric in the CT state lifetime $\tau_{\text{rad,CT}}$, under 7.5 V applied bias ($5.6 \times 10^7 \text{ V m}^{-1}$). The dotted line indicates the emission peak position in the absence of relaxation, as derived from the PL. (c) Peak shift and (d) width of (□) steady-state electroluminescence and (Δ) steady-state photoluminescence emission for identical blends. The top horizontal axis reports the CT radiative decay rate relative to the charge hopping attempt frequency. The linear dotted lines are guides to the eye.

hole distance vector. When applying a voltage $V = 10 \text{ V}$ across a 100 nm device, and when taking $r_{eh} \approx 1 \text{ nm}$ in the direction parallel to the applied field, the corresponding shift is expected to be of the order of $\pm 0.1 \text{ eV}$, depending on the relative alignment of the field with respect to the static dipole moment of the CT state. In Figure 10, this field effect is displayed by showing CT state peak energies and widths that have been obtained using the full expression for the CT state energy (Equation 7) or by omitting the field-term from the calculation of the state energy. We note that omitting the field term already in the simulations, when calculating the dynamics of CT states, is found to lead to the same peak energies and distributions as omitting the field term only in the post-processing of the data. That shows that the dynamics of the CT-state formation and relaxation processes is, for the devices and conditions studied, not influenced by the field.

We first focus on the bilayer device (Figure 10a,c,d). In this device, the static dipole moments of the CT states that are formed at the internal interface have all an antiparallel alignment with the field, thus increasing the CT state energy.

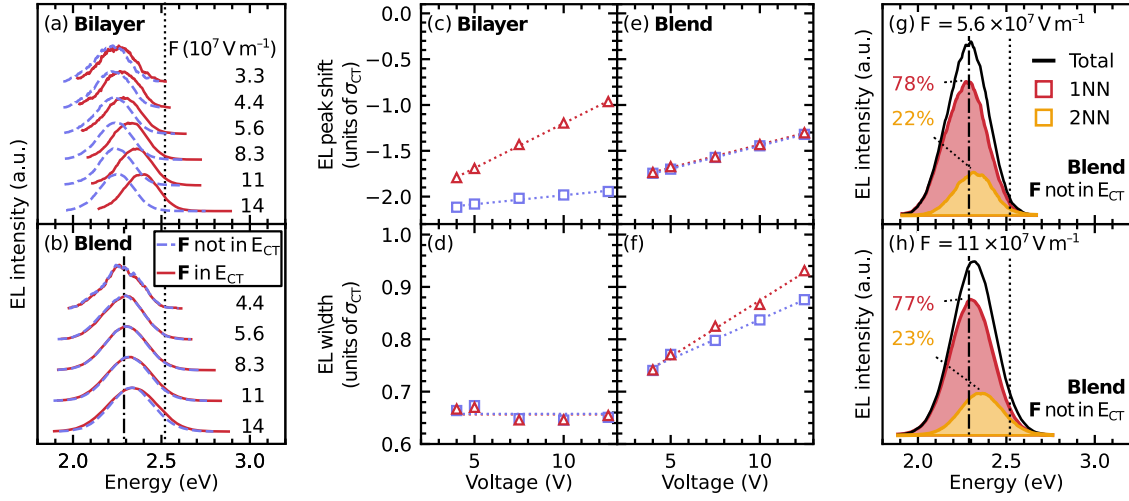


FIG. 10. Effect of the applied electric field on EL emission. (a,b) Simulated steady-state electroluminescence spectra (smoothed data), parametric in the externally applied field F , either by including (red, full curves) or omitting (blue, dashed curves) the field-dependent term in Equation 7 for (a) an interfacial device with the structure “anode | D (45 nm) | A (45 nm) | cathode” and for (b) the blend device in Figure 9a. For the sake of simplicity, the value of F that is displayed is equal to V/L (with V the applied voltage and L the thickness of the semiconducting layer). This neglects the built-in voltage. (c,e) Peak shift and (d,f) width of the steady-state electroluminescence emission for the bilayer (c,d) and blend (e,f) devices; the dotted lines are guides to the eye. (g,h) Decomposition of two emission spectra from panel (b) in terms of the electron-hole distance for the blend device under an applied field of (g) $5.6 \times 10^7 \text{ V m}^{-1}$ (5 V) or (h) $11 \times 10^7 \text{ V m}^{-1}$ (10 V). In both cases we neglect the field-dependence of the CT state energies. In panels (a,b,g,h), the vertical dotted lines indicate the emission peak position in the absence of relaxation, while the vertical dash-dotted lines indicate the steady-state peak position under an applied field of $5.6 \times 10^7 \text{ V m}^{-1}$ (5 V).

That effect is indeed seen from Figures 10a,c (red triangles and full curves). This large blueshift is consistent with experimental results in Refs. [44],[55]. If the field contribution is not included in the CT state energy (blue squares and dashed line in Figure 10a,c), we only observe a minor reduction of the EL peak redshift at high fields. Figure 10d shows that the width of the EL spectra is essentially independent of the voltage and of the method used (including or ignoring the effect of the field on the CT state). This further confirms that the degree of charge carrier relaxation is unaffected by the electric field contribution to the CT state energy.

The situation is different for the blend device (Figure 10b,e,f). The emission profile in this device is quite homogeneous throughout the central emissive layer (EML), as shown in Figure S5c of the Supplemental Material [43]. Emission at the edges of the EML, where it is more likely that CT states align with the field due to geometrical constraints, represent only a small contribution to the overall spectrum. Figure 10e shows that the peak position shifts slightly to the blue with increasing voltage. The relaxation of the charge carriers within the DOS is thus slightly reduced, in line with the interpretation of Ref. [16]. The figure also shows that this increase is independent on whether the field contribution is considered for calculating the CT state energy, indicating that the dipole moment vectors of the CT states are randomly

oriented and do not align with the electric field before recombination. The modulations of the CT state energy by the electric field then averages out to zero. That is consistent with experimental data [16],[55] and with the simulations in Ref. [16]. Figure 10f shows that the peak width increases with increasing voltage, even when the field contribution is not included in the calculation of the CT state energies (blue squares). That is consistent with the finding that the degree of relaxation decreases with increasing voltage, so that less peak narrowing is expected. When including the field contribution (red triangles), the randomness of the static dipole moments of the CT states is expected to give rise to an increase of the peak width when the field-induced contribution is of the same order of magnitude or larger than the zero-field width. The figure shows that such a situation occurs when V is larger than approximately 6 V.

We can summarize the findings from this study of the sensitivity of the spectrum to the layer structure and the applied field as follows. In the bilayer device, the CT states are at all fields strongly relaxed and their dipole moments are at all fields antiparallel with respect to the applied field. In contrast, in the blend device the distribution of dipole orientations does not show a preference with respect to the applied field, and the degree of relaxation of the CT states is, at all voltages that have been considered, less than in the bilayer device and decreases further with increasing voltage.

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Contrary to our interpretation, it has been suggested [55] that the slight blueshift observed in bilayer and blend devices may reflect an increased mean electron-hole distance. We can confidently rule this out. In our simulations of the bilayer device, CT states are only allowed to form at the interface ($R_d = 1$ nm), so the electron-hole distance is fixed. Hence it cannot be the cause for the blueshift. For the blend device, Figures 10g and h display the emission spectra for two different electric fields, resolved in terms of the electron-hole distance, and show that the distribution of electron-hole distances of the emitting species does not change with field.

IV. SUMMARY AND CONCLUSIONS

We have extended three-dimensional kinetic Monte Carlo (kMC) simulations that describe the photophysics of disordered organic semiconductor materials and the functioning of OLEDs by including the photophysics of intermolecular charge transfer (CT) states. In the model, CT states are treated as photophysically active species that can decay radiatively. Simulations have been used to analyse the effects of energetic relaxation processes on the emission from CT states that are optically or electrically generated. From experimental studies, it is known that the emission from such states redshifts over time [4],[5],[28]. Such observations have been proposed to arise from a varying (time-dependent) degree of charge transfer [7], a varying electron-hole distance [55], a varying medium polarizability [6], or as a consequence of conformational disorder producing correlated distributions of CT state energies and emission rates [57]. In principle, also relaxation in the CT state density of states due to long-range Förster type processes could contribute. Deotare *et al.* [28] interpreted the time-dependent redshift as a result of charge carrier relaxation within the electron and hole densities of states. The model postulates an asynchronous, alternate (“inchworm”) diffusion of the carrier pair, caused by short-range hops of the charge carriers. A comparison between measurements and a two-dimensional kinetic Monte Carlo (kMC) model of a linear interface showed a good quantitative agreement. This picture was also supported by magnetic field-dependent measurements [28],[34]. Our simulations show that such a process can also be applied on three-dimensional blends of donor and acceptor materials, providing a realistic explanation of observed redshifts of the emission spectra, and that energetic relaxation also leads to spectral narrowing. These effects have been shown to depend sensitively on the blend composition. Our simulation results are also consistent

with the experimental finding that the emission energy of electrically generated CT states is slightly redshifted compared to that of optically generated CT states. The simulations have shown that, for the systems studied, CT state emission is predominantly due to electrons and holes on nearest-neighbour sites and that, for the representative set of simulation parameters that has been assumed, the CT state diffusion length varies linearly with $\log_{10}(\tau_{\text{rad,CT}})$. Even when $\tau_{\text{rad,CT}}$ is as large as ~ 1 μs , the simulated diffusion length is only ~ 2 nm. CT state diffusion is limited by the energetic disorder of the frontier orbitals, the spatial disorder of the donor and acceptor molecules in the 1:1 blend, and the small value of ϵ_r (taken equal to 3) that makes the formation of more extended CT states less likely. The finding of much larger diffusion lengths from optical and magnetic field studies in Ref. [28], of 5-10 nm for the specific system of m-MTDATA:3TPyMB, suggests that it will be of interest to study the material-specificity of the various simulation parameters and/or the dependence on the deposition conditions.

In future extensions of this work, additional photophysical properties of CT states should be included, such as non-radiative decay, bimolecular energy loss process (quenching by polarons or annihilation by excitons or another CT state) and spin-related processes such as ISC, rISC and (non)radiative decay from triplet states. It would also be of interest to study the sensitivity of the simulation results to material-specific refinements, such as a sensitivity of the frontier orbital energy to the dielectric environment in the blend system and the effect of distributions of donor-acceptor distances and of the corresponding transfer integrals for charge transport.

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G.C. and R.C. conceived the project. G.C. implemented the CT state model and performed kMC simulations under the supervision of R.C. and A.K. G.C., A.K. and R.C. wrote the paper. The authors declare no competing interests.

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Spectral diffusion due to charge carrier relaxation of intermolecular charge-transfer states in donor:acceptor blends of disordered organic semiconductors

Supplemental Material

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S1 Dependence of the steady-state EL and PL emission on the dissociation distance (R_d) and the distance-dependence of rates (λ)

The dissociation distance R_d indicates the maximum distance at which an electron-hole pair may be identified as a CT state, rather than as a pair of free carriers. A CT state has a finite radiative lifetime and an energy calculated as per Equation 7 of the main text.

The parameter λ quantifies the decrease of the CT state radiative decay rate $k_{\text{rad,CT}}$ with increasing electron-hole separation distance r_{eh} . As the overlap between the electron and hole wavefunction decreases with increasing separation distance, the radiative decay rate is expected to decrease quite steeply. We assume an exponential decay:

$$k_{\text{rad,CT}}(r_{\text{eh}}) = k_{\text{rad,CT}}(a) \cdot \exp\left(\frac{r_{\text{eh}} - a}{\lambda}\right) \quad (1)$$

where $k_{\text{rad,CT}}(r_{\text{eh}})$ is the CT state recombination rate as a function of the electron-hole separation distance r_{eh} , $k_{\text{rad,CT}}(a)$ is the recombination rate for nearest-neighbour CT states at a distance a (here $a = 1$ nm) and λ is a parameter which regulates the decay. The parameter λ relates to the electron and hole wavefunction overlap. Its calculation is beside the point of the present work, and it is therefore left as a free parameter.

Section S1.1 analyses the photoluminescence (PL) case, in which the choice of R_d or λ is mostly inconsequential. Section 1.2 analyses the electroluminescence (EL) case, where more caution must be exercised when choosing the parameter values.

S1.1 Photoluminescence

Figure S1 compares the transient PL decay curves (Figure S1a) and the steady-state PL emission spectra (Figure S1b) for a 50:50 donor:acceptor (D:A) blend with a CT state lifetime of 5 ns, parametric against the dissociation distance R_d . For simplicity, the system only contains singlet excitons and CT states. Emission rates are independent on the electron-hole separation distance: this represents an unphysical, worst-case scenario.

Both transient PL profiles and steady-state spectra are virtually unaffected by the choice of R_d , as long as it is larger than nearest-neighbour distance (1 nm). In fact, under PL conditions, photogenerated CT states form as nearest (1NN) or second-nearest (2NN) neighbour and seldom dissociate further (see also Section S4). $R_d = 1$ nm (1NN distance) neglects 2NN CT states, as is visible by the reduced CT state content in Figure S1a. In Figure S1b, a minor broadening of the steady-state spectra at increasing R_d is the result of minor emission from longer-range CT states.

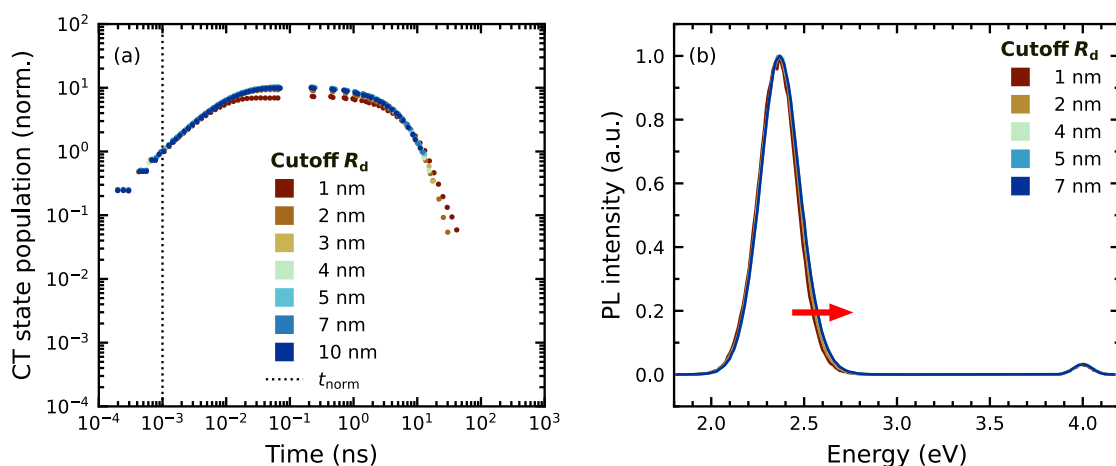


Figure S1. Sensitivity to R_d (PL). Simulated (a) transient PL curves and (b) steady-state PL emission for a 50:50 D:A blend with a CT state lifetime of 5 ns, for various values of the dissociation distance R_d . In Figure S1a, the initial singlet exciton population is 10^{-3} site $^{-1}$ and the CT state population is normalised at $t = 0.001$ ns. The dissociation kinetics does not depend on R_d , so that the CT state population is supposed to be equal in all simulation at early times.

When triplet CT states are allowed in the system, a bit more care must be taken with R_d . From the algorithm point of view, R_d marks the transition between a CT state (with spin) and a free charge carrier pair (with no spin). In other words, when carriers hop at a distance larger than R_d , the information on mutual spin orientation is lost: if they hop back to form a CT state, its state will be randomly extracted favouring the selected singlet:triplet ratio. This caveat does not apply to our main results, where we have considered singlet-only systems for simplicity. Figure S2 shows transient PL profiles for a 50:50 D:A blend with a 5 ns lifetime, parametric against R_d . The photophysical rates for singlet CT state decay, ISC and rISC are $1.72 \cdot 10^6$ s $^{-1}$, $1.79 \cdot 10^7$ s $^{-1}$ and $4.92 \cdot 10^6$ s $^{-1}$ respectively. The singlet:triplet ratio for CT state generation is 1:3. Convergence is observed for $R_d > 3$ nm.

Mechanisms which may lead to artificial spin-flip are depicted in Figure S3. We suggest that the best approach is to consider a large R_d value, so as to avoid these kinds of artifacts, and prevent unphysical long-range emission by using a small λ value.

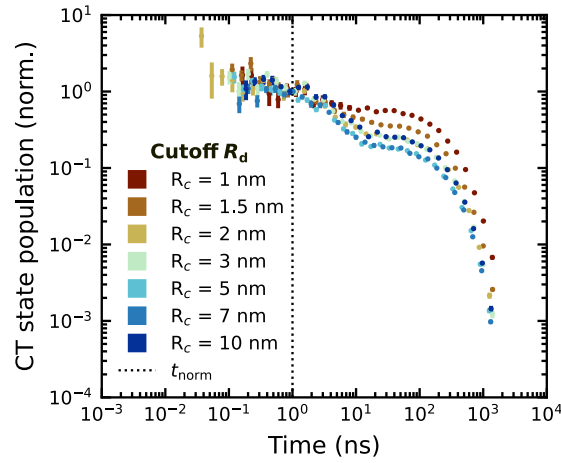


Figure S2: Sensitivity to R_d (transient PL). Simulated transient PL curves for a 50:50 D:A blend with $k_{\text{rad,CT}} = 1.72 \cdot 10^6 \text{ s}^{-1}$, $k_{\text{ISC}} = 1.79 \cdot 10^7 \text{ s}^{-1}$ and $k_{\text{RISC}} = 4.92 \cdot 10^6 \text{ s}^{-1}$, for various values of the dissociation distance R_d . The initial singlet exciton population is $10^{-3} \text{ site}^{-1}$, the CT state population is normalised at $t = 1 \text{ ns}$. The dissociation kinetics do not depend on R_d for $R_d > 3 \text{ nm}$.

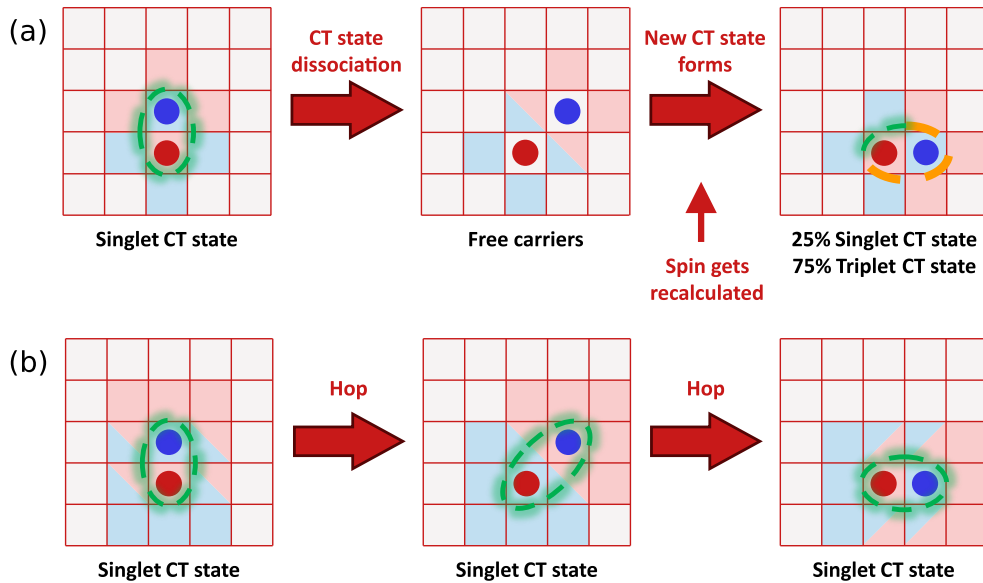


Figure S3: Artificial spin-flip mechanism (transient PL). Schematic view of charge carrier hopping (a) leading to artificial spin-flip for $R_d = 1 \text{ nm}$, vs (b) proper accounting of the CT state spin for $R_d = 1.5 \text{ nm}$. The red (blue) shadowed areas indicate the sites to which the hole (electron) may hop without dissociation of the CT state.

As CT states are generated as short-range geminate pairs, the exact choice of λ is also not so influential, as in most cases $r_{\text{eh}} \leq 2$ nm. Figure S4 compares the transient PL decay curves (Figure S4a) and the steady-state PL emission spectra (Figure S4b) for a 50:50 (D:A) blend with a CT state lifetime of 5 ns, parametric against the parameter λ . $R_d = 10$ nm and only singlet CT states are considered. In all cases, the influence of λ is small, and it reflects the physical effect of decreased rates leading to increased lifetimes.

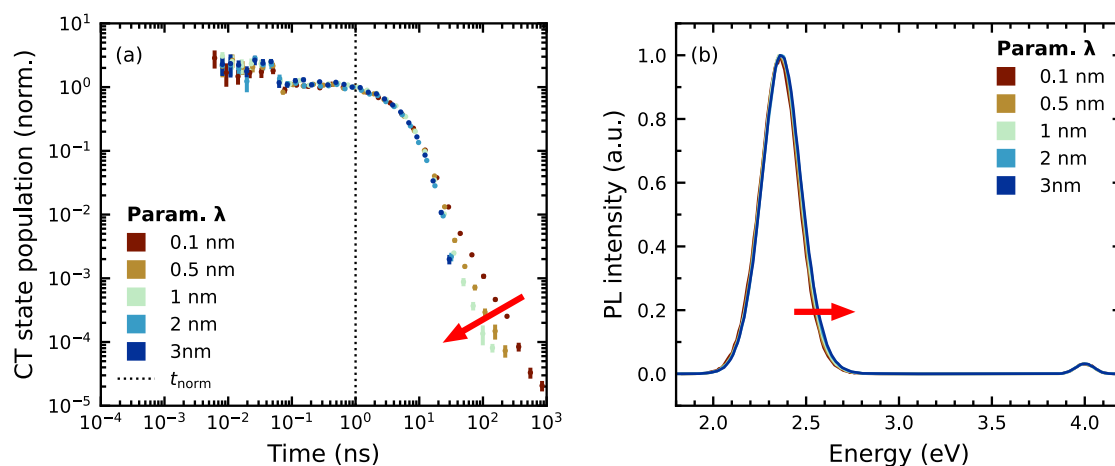


Figure S4. Sensitivity to λ (PL). Simulated (a) transient PL curves and (b) steady-state PL emission for a 50:50 D:A blend with a CT state lifetime of 5 ns, for various values of the parameter λ at a fixed $R_d = 10$ nm. In Figure S4a, initial singlet exciton population is 10^{-3} site $^{-1}$. The CT state population is normalised at $t = 1$ ns.

S1.2 Electroluminescence

We have simulated a three-layer device with the structure:

anode | D (30 nm) | D:A blend (50:50, 30 nm) | A (30 nm) | cathode,

displayed in Figure 9a of the main text. The electrodes are not explicitly modelled. Instead, a 0.2 eV injection barrier is included. The CT state lifetime is 5 ns. Under electrical excitation, charge carriers with opposite sign are injected from opposite sides of the device. Our observations on the reduced separation distance of photogenerated CT states do not apply anymore.

In Figure S5 we study the dependence of steady-state EL emission on the dissociation distance. Figure S5a compares the steady-state EL emission spectra, parametric against R_d . Again, emission rates are independent on the electron-hole separation distance to observe the worst-case scenario. A major blueshift of the emission peak from ~ 2.3 eV to over 2.6 eV is observed at increasing R_d . Figure S5b displays the total emission intensity as a function of electron-hole distance: the large emission blueshift at increasing R_d can be understood as the result of increasing contribution of long-range CT states, whose Coulombic stabilisation energy approaches zero (thus the emission energy approaches the nominal $E_{EA,A} - E_{IE,D} = 3$ eV value). Particularly, we highlight the minimum in emission intensity around $r_{eh} = 1.4 - 2$ nm for all curves. We argue that up to $r_{eh} = 2$ nm electron-hole pairs indeed form geminate pairs which may be identified as CT states; for larger r_{eh} values, the increase in emission intensity reflects the possibility for free carriers in the transport layers to recombine with carriers within the emissive layers (roughly, the chance of finding an opposite charge carrier at distance r goes with r^2).

In fact, Figure S5c and d display distribution profiles along the anode-to-cathode axis for the total electron and hole density and for the density of electron and holes involved in CT state emission (analogous to an exciton emission profile). A comparison of the emission profiles for $R_d = 1.5$ nm (Figure S5c) and 10 nm (Figure S5d) shows that, for larger R_d values, charge carriers outside the central emissive layers are involved in CT state emission.

In other words, we argue that the major emission blueshift with increasing R_d is to be regarded as an artifact arising from an improper parameter choice, i.e., *at most* electron-hole pairs with $r_{eh} \leq 2$ nm should be identified as CT states.

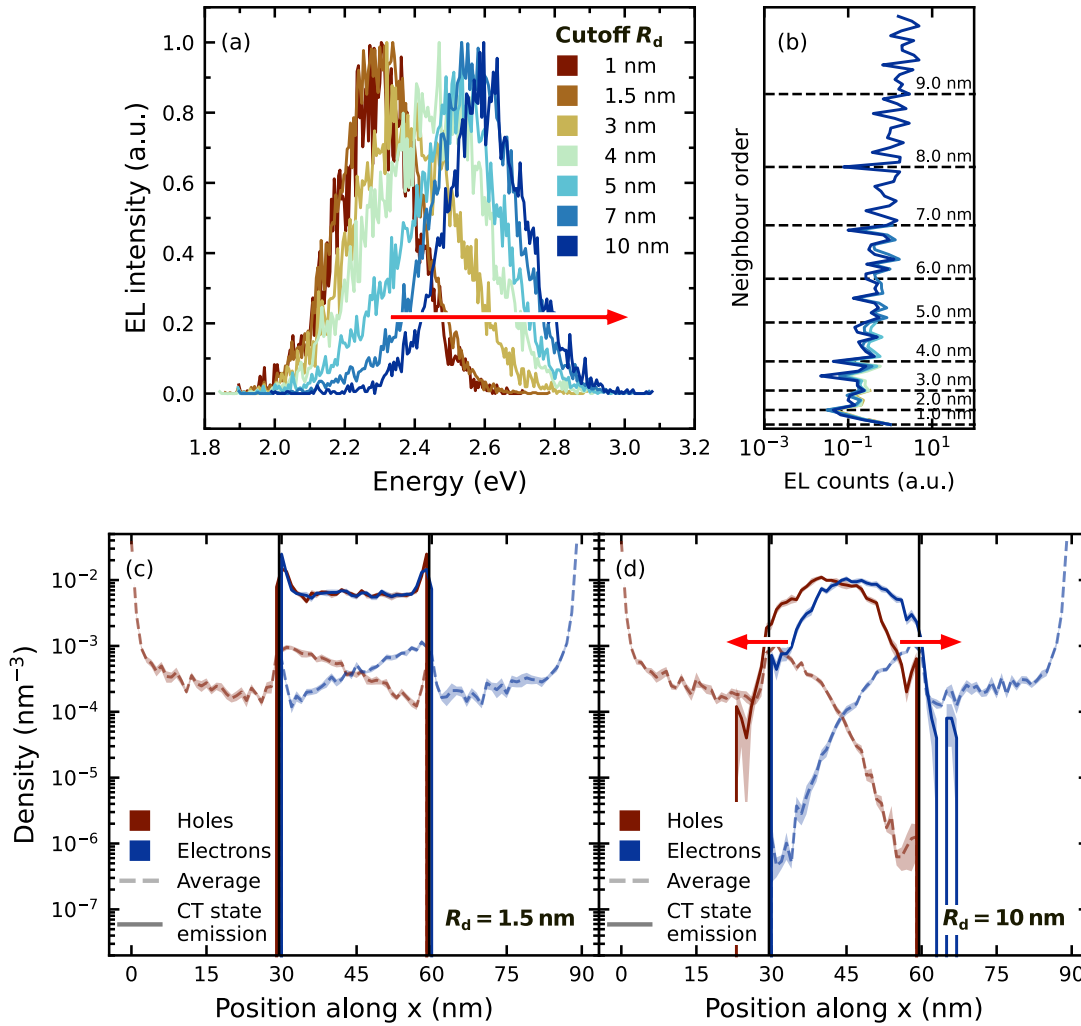


Figure S5: Sensitivity to R_d (EL). (a) Simulated steady-state EL emission for a three-layer device indicated in Figure 9a of the main text, with a CT state lifetime of 5 ns, for various values of the dissociation distance R_d , and (b) electron-hole distance-resolved total emission intensity. (c,d) Distribution profiles for the total carrier density (dashed lines) and the density of carriers involved in CT state emission (full lines) are shown for a dissociation distance of (c) 1.5 nm and (d) 10 nm. In panels c and d, the shadowed areas indicate the uncertainty.

In Figure S6 we study the dependence of steady-state EL emission on the parameter λ . Figure S6a compares the steady-state EL emission spectra, parametric against λ . Similarly to the behaviour with increasing R_d , a major blueshift of the emission peak from ~ 2.3 eV to over 2.6 eV is observed at increasing λ . Note however how the sensitivity is scarce up to $\lambda = 1$ nm.

Figure S6b displays the total emission intensity as a function of λ and Figure S6c and d show distribution profiles along the anode-to-cathode axis for the total electron and hole density and for the density of electron and holes involved in CT state emission, for $\lambda = 0.5$ nm (Figure S6c) and 3 nm (Figure S6d). As before: for larger λ values, charge carriers outside the central emissive layers are involved in CT state emission, producing the observed blueshift.

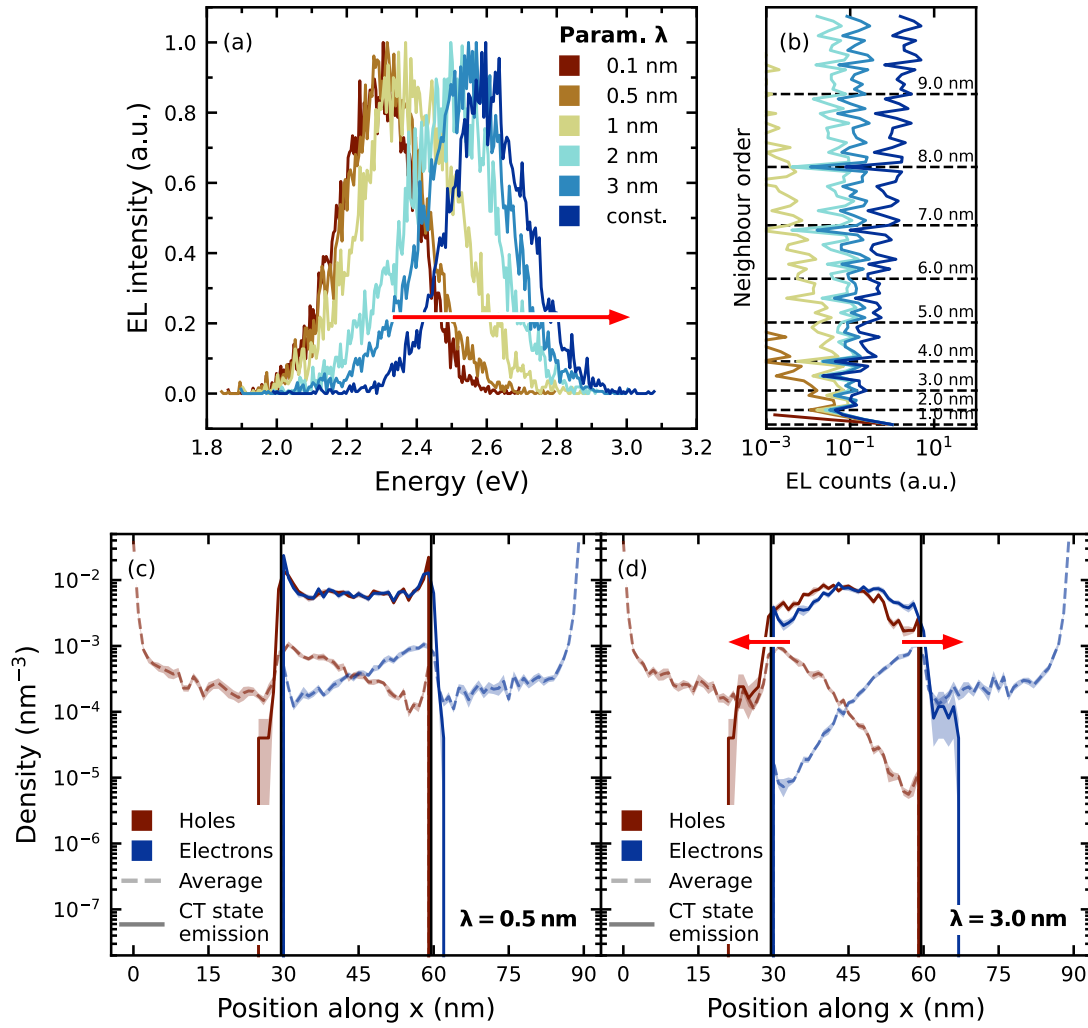


Figure S6: Sensitivity to λ (EL). (a) Simulated steady-state EL emission for a three-layer device indicated in Figure 9a of the main text, with a CT state lifetime of 5 ns, for various values of the parameter λ , and (b) electron-hole distance-resolved total emission intensity. (c,d) Distribution profiles for the total carrier density (dashed lines) and the density of carriers involved in CT state emission (full lines) are shown for a λ value of (c) 0.5 nm and (d) 3 nm. In panels c and d, the shadowed areas indicate the uncertainty.

Figure S7 shows that reducing R_d with constant $k_{\text{rad,CT}}$ rates is virtually equal to using a large R_d with a smaller λ value. For our study, we chose $R_d = 1.5$ nm, corresponding to $\lambda = 0.1 - 0.5$ nm.

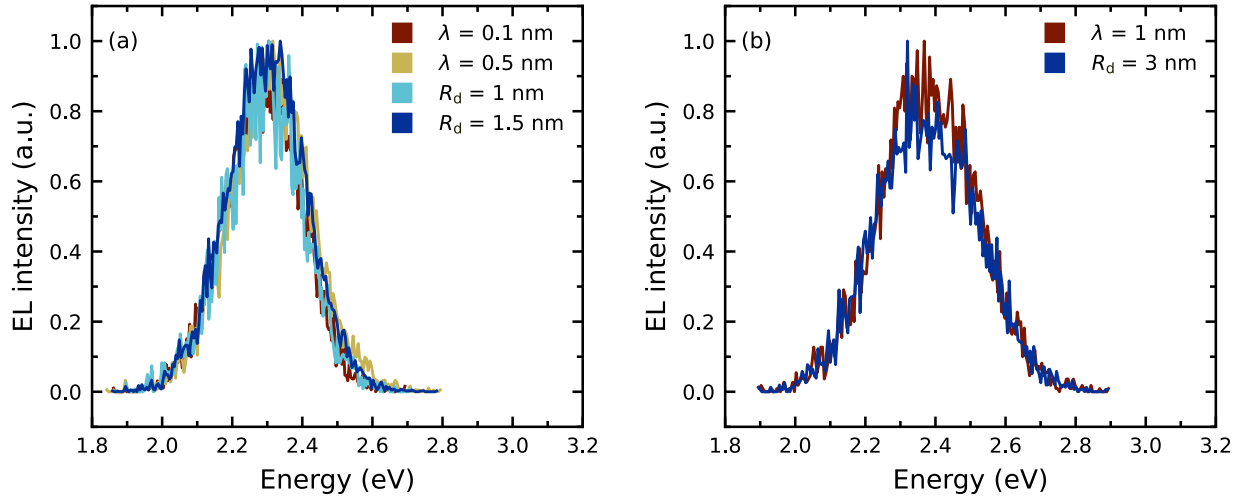


Figure S7: Sensitivity against λ (EL). Simulated steady-state EL emission for a three-layer device indicated in Figure 9a of the main text, with a CT state lifetime of 5 ns, for various combinations of R_d and λ . Where R_d is indicated, rates are distance-independent ($\lambda \rightarrow +\infty$); where λ is indicated, $R_d = 10$ nm.

S2 Dependence on the ionisation energy or electron affinity gap

We consider a donor (D) and an acceptor (A) material with equal energy gap. The energy offset is symmetric: $|E_{\text{IE,D}} - E_{\text{IE,A}}| = |E_{\text{EA,D}} - E_{\text{EA,A}}| = \Delta$, where $E_{\text{IE},i}$ ($E_{\text{EA},i}$) is the ionisation energy (electron affinity) of species i . Simulations for an equimolar D:A blend have been performed for different values of Δ : Figure S8 shows that, for $\Delta > 1$ eV, CT state formation is almost quantitative. The decay of the exciton population is then dominated by dissociation rather than recombination.

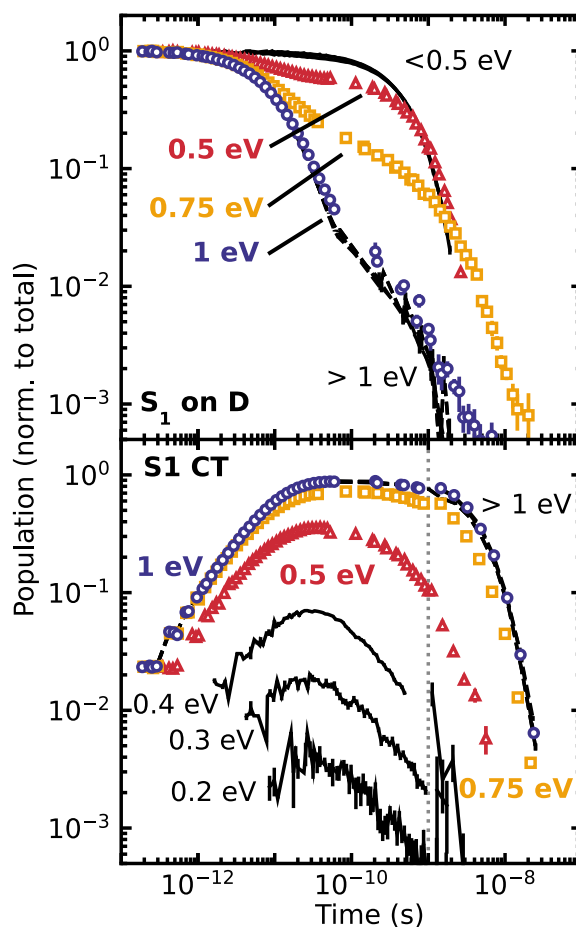


Figure S8: Transient photoluminescence kinetics vs. energy offset. Transient population of (top) singlet excitons on donor sites and (bottom) singlet CT states in an equimolar D:A blend. The lifetime of singlet excitons (CT states) is 0.5 ns (5 ns), initial exciton population is 10^{-3} site $^{-1}$. Black lines indicate the curves for $\Delta < 0.5$ eV (negligible CT state formation) and $\Delta > 1$ eV (almost quantitative CTs state formation). Lines for $\Delta = 0.5$ eV, 0.75 eV and 1 eV are highlighted in red triangles, yellow squares and blue circles respectively.

S3 Dependence on the inverse wavefunction decay length α

In the Miller-Abrahams formalism for carrier hopping (Equation 6 of the main text), the wavefunction decay length α is left as a free parameter. In our study we have employed $\alpha = 10 \text{ nm}^{-1}$ in all cases. For the lattice spacing $a = 1 \text{ nm}$ that is used, the hopping process is then almost nearest-neighbour type. Figure S9 shows the peak redshift and width for the steady-state emission of an equimolar D:A blend with $\sigma_{\text{IE,D}} = \sigma_{\text{EA,A}} = 0.10 \text{ eV}$. Relaxation dynamics appear to be linear in $\log(\text{time})$, with comparable slopes for all cases, but to proceed to a higher extent (even for shorter times) for smaller α values (i.e. increased carrier delocalisation). This behaviour is understandable as a result of increased accessibility of neighbouring sites with smaller α values, favouring carrier relaxation, in agreement with the results of Athanasopoulos *et al.* [1].

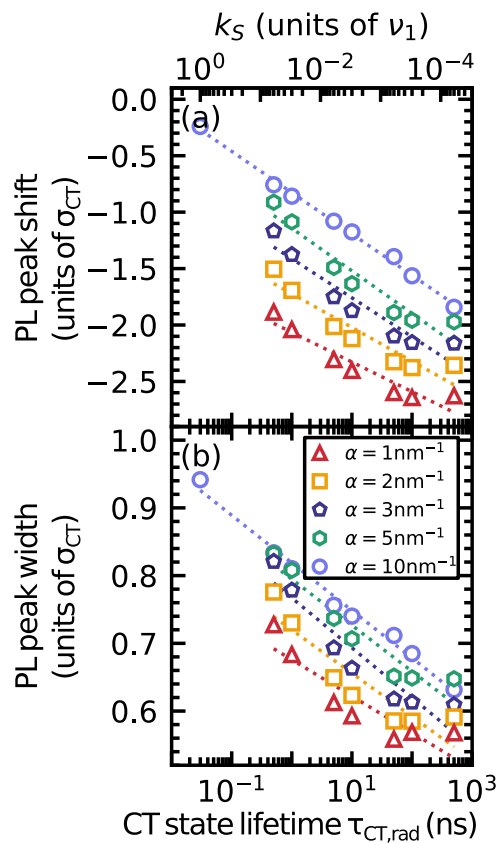


Figure S9: Effect of the inverse wavefunction decay length α on steady state PL. (a) Peak shift and (b) width of the simulated steady-state photoluminescence emission spectra, parametric against CT state lifetime, for several values of the inverse wavefunction decay length α . The top horizontal axis reports the CT radiative decay rate relative to the charge hopping attempt frequency. The linear dotted lines are guides to the eye.

S4 Decomposing SSPL spectra in terms of neighbour contributions

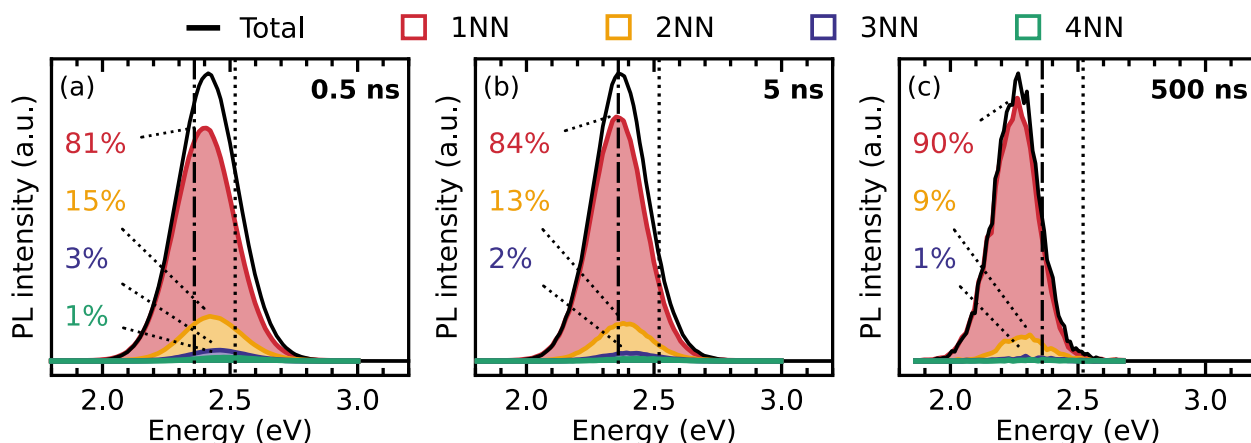


Figure S10: Distance-resolved emission spectra (lifetime). Decomposition of the steady-state PL spectra in terms the electron-hole distance (nearest- to fourth-nearest neighbour) for a 50:50 D:A blend with (a) 0.5 ns, (b) 5 ns, and (c) 500 ns lifetime. The disorder energy of the donor IE and the acceptor EA is 0.10 eV. The dotted lines indicate the emission peak position in the absence of relaxation, and the dash-dotted lines indicate the steady-state peak position for a 50:50 D:A blend with 5 ns lifetime.

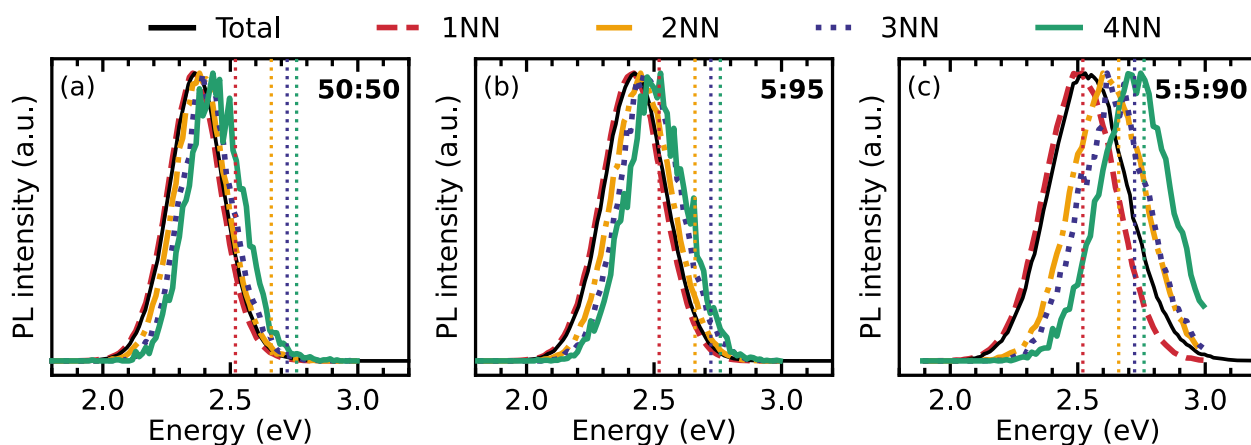


Figure S11: Distance-resolved emission spectra (composition). Decomposition of the steady-state PL spectra in terms the electron-hole distance (nearest- to fourth-nearest neighbour) for a D:A(:S) blend with composition: (a) 50:50, (b) 5:95, and (c) 5:5:90. CT state lifetime is 5 ns and disorder is 0.10 eV on donor IE and acceptor EA. The spectra are normalised to the peak intensity to better visualise the blueshift. Thin dotted lines indicate the corresponding peak position in the absence of diffusion.

S5 Further simulation results

S5.1 Effect of the CT state lifetime in a D:A blend (PL)

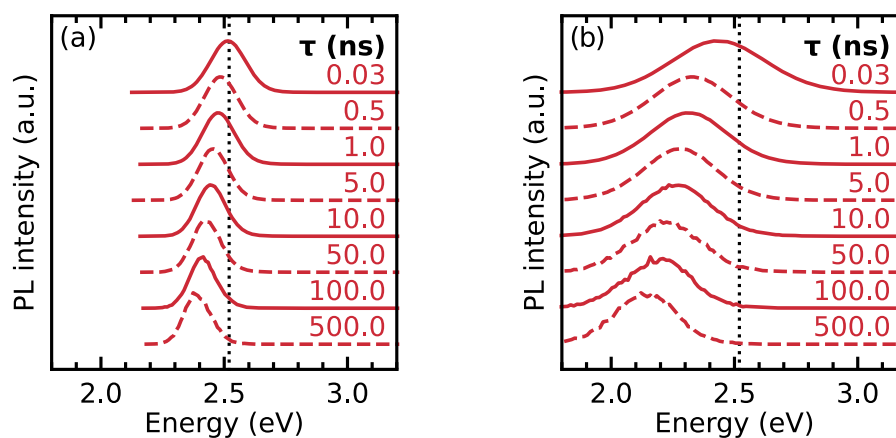


Figure S12: Effect of the CT state lifetime (PL). Simulated steady-state photoluminescence spectra for equimolar D:A blends with (a) 0.05 eV or (b) 0.15 eV disorder energy for each IE and EA, and varying lifetime $\tau_{\text{rad,CT}}$. The dotted line indicates the emission peak position in the absence of relaxation.

S5.2 Effect of the spacer concentration in a D:A:S blend (PL)

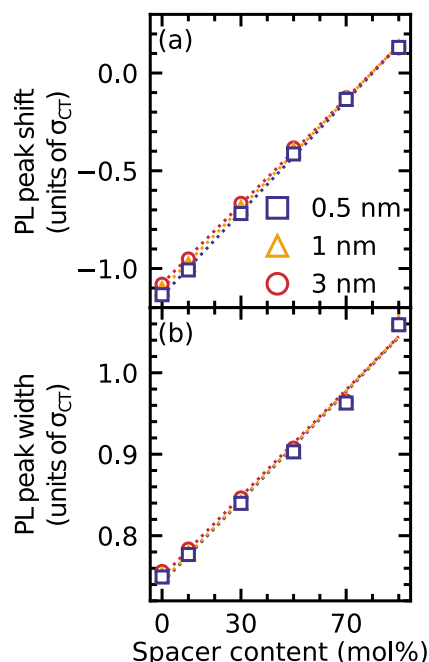


Figure S13: Effect of an inert spacer (PL). Extracted (a) peak redshift and (b) width of the steady-state PL emission for D:A:S blend with equimolar D:A ratio and varying spacer content. Simulations have been performed for $\lambda = 0.5$ nm, 1 nm, or 3 nm (see Section S1 for more details on the parameter λ) with virtually identical results. The linear dotted lines are guides to the eye.

S5.3 Comparison against experimental emission spectra for D:A and D:A:S blends (PL)

In the following Figures S14 and S15, we compare our simulation results to experimental studies in Ref. [2],[3]. Ref. [2] reports the emission spectra of blends of BCFN (donor) and TPCz (acceptor) with varying donor:acceptor ratio. Ref. [3] reports the emission spectra of blends of TSBPA (donor) and PO-T2T (acceptor) in a 50:50 ratio (presumably by weight), diluted in a variable amount of UGH-3 (spacer). Experimental weight ratios have been converted to molar ratios and compared against our closest simulations. The simulation results have been shifted along the energy axis to match the peak position of the leftmost (low-energy) spectrum. The disorder energy is 0.10 eV for each IE and EA, CT state lifetime is 5 ns: although these parameters are not precisely known for the experimental systems, a good agreement in the redshift is obtained. Experimental peak width is affected by vibrational broadening, thus understandably broader than in simulation. Experimental peak width is affected by vibrational broadening, thus understandably broader than in simulation.

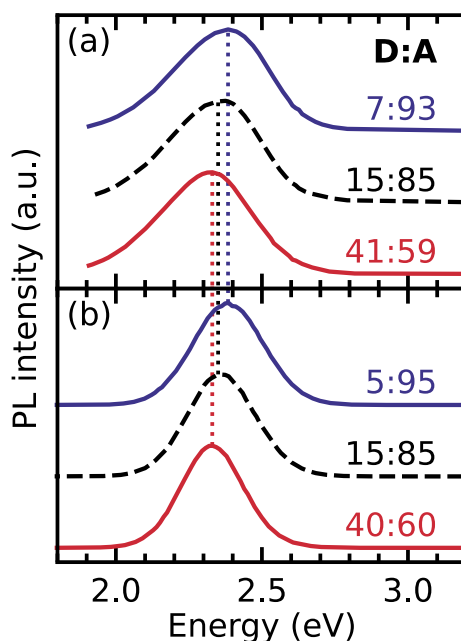


Figure S14: Effect of the blend composition, experimental comparison. Comparison between (a) measurements from Ref. [2] and (b) simulation results for blends with varying D:A ratio. Thin dotted lines indicate the peak position of the experimental spectrum.

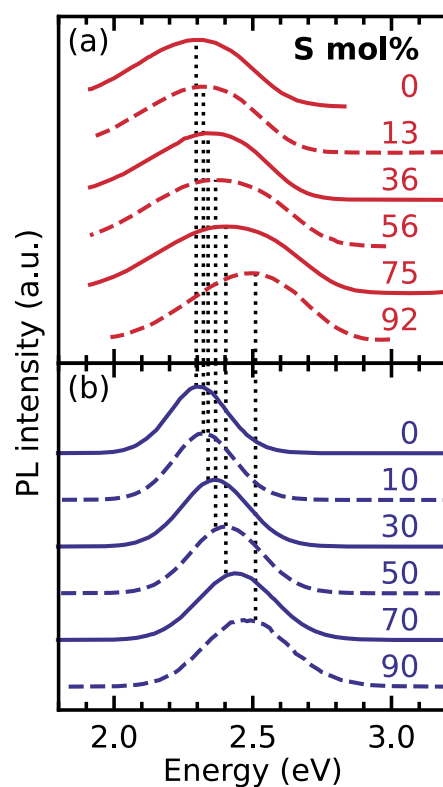


Figure S15: Effect of the blend composition, experimental comparison. Comparison between (a) measurements from Ref. [3] and (b) simulation results for D:A:S blends with an equimolar D:A ratio and varying spacer content. Thin dotted lines indicate the peak position of the experimental spectrum.

S5.4 Effect of the applied voltage, unsmoothed data (EL)

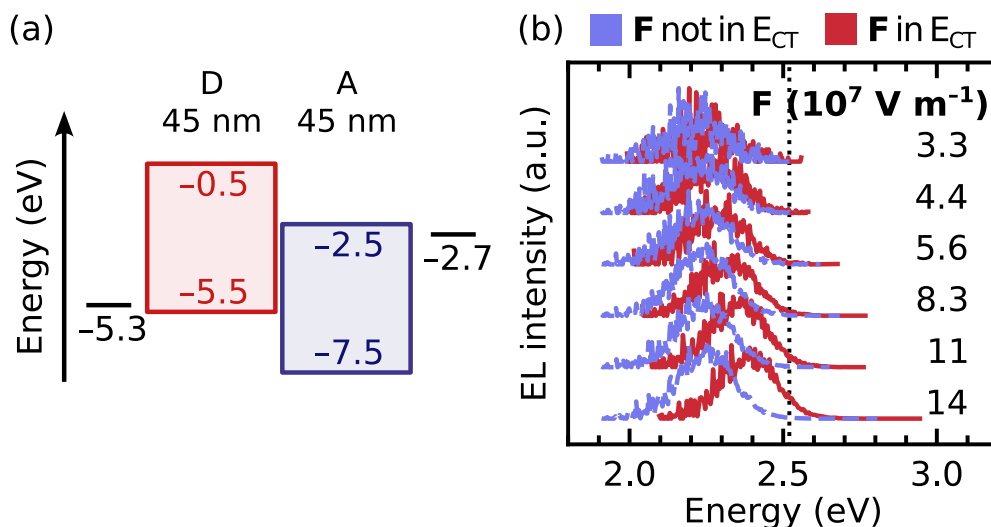


Figure S16: Effect of voltage (EL, interfacial device). (a) Energy diagram for an OLED device with layer structure “anode | donor (45 nm) | acceptor (45 nm) | cathode”. The IE of the donor and the EA of the acceptor have 0.10 eV disorder each. The CT state dissociation distance is $R_d = 1$ nm (i.e., CT states can only form within 1 nm of the interface). (b) Simulated steady-state electroluminescence spectra (non-smoothed data), parametric in the applied bias, either by including or ignoring the contribution of the applied field to the CT state energy (Equation 7 of the main text). The dotted line indicates the emission peak position in the absence of relaxation.

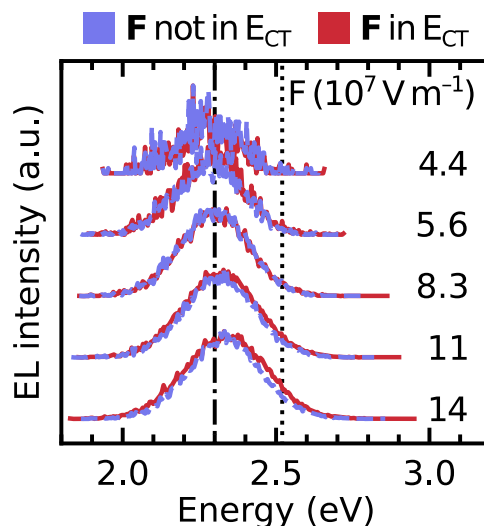


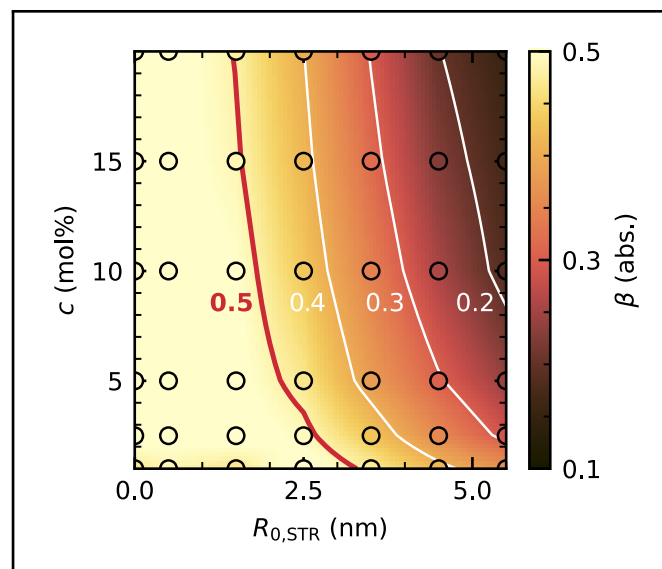
Figure S17: Effect of voltage (EL, blend device). Simulated steady-state EL spectra (non-smoothed data) for the blend device show in Figure 9a of the main text, parametric in the applied bias, either by including or ignoring the contribution of the applied field to the CT state energy (Equation 7 of the main text). The dotted line indicates the emission peak position in the absence of relaxation while the dash-dotted line indicates the steady-state peak position under a $5.6 \times 10^7 \text{ V m}^{-1}$ (5 V) field.

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**The rates are not what they seem:
understanding the time dependence of
exciton-exciton annihilation “constants”
in a TADF system**

Ready for submission



The rates are not what they seem: understanding the time dependence of exciton-exciton annihilation “constants” in a TADF system

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Exciton-exciton annihilation is a key non-radiative loss mechanism in organic optoelectronic devices, responsible for example for the efficiency roll-off observed in organic light-emitting diodes (OLEDs) at high luminance and implicated in the photochemical degradation of active layer materials. Accurate quantification of exciton-exciton annihilation is therefore essential both for the characterisation of organic semiconductors and for the parametrisation of device-level models. Using three-dimensional kinetic Monte Carlo simulations, we investigate the kinetics of exciton-exciton annihilation in systems comprising a thermally activated delayed fluorescence (TADF) emitter dispersed in an inert host. TADF materials sustain a coexisting singlet and triplet exciton population via reverse intersystem crossing (RISC), resulting in different competing spin-dependent annihilation processes. We show that the annihilation coefficients are in general time-dependent, scaling as $t^{-0.5}$ for realistic material parameters. This dependence originates from the spatially inhomogeneous depletion of the exciton population, which gives rise to a progressively correlated exciton distribution. A larger exciton diffusivity reduces the exponent of the time dependence $t^{-\beta}$, but a truly time-independent regime requires exceptional energy transfer parameters unlikely to be encountered in practice. These findings challenge the common practice of fitting transient PL data with time-independent rate constants. We further demonstrate that fit quality is an unreliable indicator of the accuracy of the extracted parameters, cautioning against the use of this method without appropriate scrutiny.

Keywords: Monte Carlo methods, Excitons, Organic LEDs — *email: anna.koehler@uni-bayreuth.de

I. INTRODUCTION

The internal quantum efficiency of optoelectronic devices, including organic light-emitting diodes (OLEDs) and organic photovoltaic (OPV) devices, is governed by excited-state dynamics within their organic active layers, which typically consist of small-molecule or polymeric amorphous materials. Given the weakly interacting nature of such materials, neutral and charged molecular excitations are strongly localised on individual molecules or short polymer segments. The photoluminescence (PL) quantum yield is consequently determined by a complex interplay of processes, including exciton generation and dissociation, exciton diffusion, and both radiative and non-radiative decay pathways. Among these, exciton-exciton annihilation (EEA) is a non-radiative decay mechanism in which the interaction between two excited-state molecules causes one (the donor) to relax to the ground state, while the other (the acceptor) is promoted to a higher-lying excited state. The excess energy of the acceptor is subsequently dissipated through rapid thermalisation back to the lowest excited state. When excitons of differing spin undergo EEA, the annihilation products must comply with total spin conservation. Singlet-singlet annihilation yields a singlet exciton, singlet-triplet annihilation produces a triplet exciton, and triplet-triplet annihilation can land in a singlet, triplet, or quintet state in a 1:3:5 statistical ratio, although

quintet states may generally be neglected as energetically inaccessible.

Because each annihilation event effectively results in the loss of an exciton, EEA can reduce the internal quantum efficiency of OLEDs. At low luminance (i.e., low exciton density), losses are generally dominated by exciton-polaron quenching (energy transfer from an excited species towards a charged one). At increasing luminance, the higher exciton densities favour exciton-exciton interactions [1]–[10], so that EEA increasingly contributes to the decrease in OLED efficiency (“roll-off”). Furthermore, the large excitation energy deposited on the highly excited acceptor prior to thermalisation may exceed bond dissociation energies and result in the photochemical degradation of the active materials, hence reducing the operational lifetime of devices [11]–[16]. By contrast, in the case of triplet fusion, TTA is employed to convert two triplet excitons into a singlet exciton with a 25% probability, providing a pathway for triplet harvesting [11],[17]–[21] and photon up-conversion [22]. Besides, EEA is also widely exploited to probe exciton diffusion in organic semiconductors and extract exciton diffusion lengths [23]–[26].

A solid understanding of EEA kinetics is a prerequisite for a reliable modelling of optoelectronic devices, in order to define rational design principles. For example, the extraction of precise exciton diffusion length is critical for optimising the blend morphology and estimating the charge generation

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efficiency in OPVs. An accurate quantification of excitonic losses is equally essential to design mitigation strategies in OLEDs, or vice versa to engineer efficient photon up-conversion and triplet harvesting systems. For these reasons, the quantification and modelling of EEA is still a matter of interest [8],[26]–[32].

Mechanistic studies are most commonly conducted using three-dimensional kinetic Monte Carlo (kMC) simulations [6],[7],[26],[33]–[36], whereas experiments rely on fluence-dependent PL measurements. Transient PL curves are usually fit to a phenomenological kinetic rate equation to extract kinetic rate “constants” – better termed *coefficients* – for the relevant annihilation processes [37],[38]. As a simplifying approximation, these coefficients are often treated as time independent constants [26],[31],[32],[37],[38], although in principle time-dependent coefficients may be expected from a transient PL measurement.

Since annihilation parameters extracted from these fits feed directly into drift-diffusion and other device-level models (e.g. Refs. [9],[10],[38]), any shortcomings in the description of the underlying photophysics will cause systematic errors at the characterisation stage to propagate into predictions of device behaviour. In this study, we leverage the microscopic insight offered by three-dimensional kMC simulations to quantify the time dependence of exciton-exciton annihilation coefficients for a host:guest system under transient PL conditions. Previous literature has argued that the annihilation coefficients may be the time-dependent [30],[39]–[41] following Förster’s argument for energy transfer [39]. Here, we address the origin and nature of the time-dependence in the annihilation coefficients. Specifically, we consider a system comprising a thermally activated delayed fluorescence (TADF) emitter dispersed in an inert host. Unlike purely fluorescent or phosphorescent emitters, whose photophysics is dominated by singlet or triplet excitons respectively, TADF dyes sustain coexisting populations of singlet and triplet excitons for an extended period following the initial excitation pulse. This markedly complex photophysics means that a quantitative description of EEA in TADF systems requires careful consideration of the interplay between competing spin-dependent annihilation processes.

In short, we find that the kinetic coefficients for exciton-exciton annihilation are in general time-dependent and scale as $t^{-0.5}$ for realistic systems. The exponent can be smaller in the presence of substantial exciton diffusion, but a truly time-independent regime requires exceptional energy transfer parameters.

The paper is structured as follows: the simulation methodology is outlined in Sec. II, whereas the results are presented in Sec. III and compared against the existing literature in Sec. IV, allowing us to draw our conclusions in Sec. V.

II. METHODS

The organic material is represented as a fully periodic $100 \times 100 \times 100 \text{ nm}^3$ cubic lattice of molecular sites with lattice

constant $a = 1 \text{ nm}$. A fraction c of sites are randomly assigned as guest molecules, dispersed in an energetically inaccessible host that acts as an inert spacer. Each site may host at most one exciton, either singlet or triplet. As a representative system, we consider the TADF emitter DMAC-TRZ, with the photophysical rates measured in mCBP-CN in Ref. [42] and listed in Table I along with the other simulation parameters. The singlet and triplet energy levels of each guest site are drawn independently from a spatially uncorrelated Gaussian density of states [43], centred on the nominal singlet or triplet energy of the material and with variance σ^2 .

TABLE I: Simulation parameters.

<i>Parameter</i>	<i>Value</i>
Lattice parameter (a)	1 nm
Size of the simulated system	$100 \times 100 \times 100 \text{ nm}^3$
Temperature (T)	293 K
Guest fraction (c)	10 mol% ^(a)
Initial exciton density [$S(0)$, TRPL]	10^{19} cm^{-3} ^(b)
Singlet energy (guest)	2.73 eV [42]
Triplet energy (guest)	2.63 eV [42]
Singlet and triplet energy disorder (σ , guest)	0.05 eV [48]
Singlet radiative decay rate ($k_{S,r}$)	$2.2 \cdot 10^7 \text{ s}^{-1}$ [42]
Singlet internal conversion rate ($k_{S,ic}$)	0 s^{-1} [42]
Triplet radiative decay rate ($k_{T,r}$)	0 s^{-1} [42]
Triplet internal conversion rate ($k_{T,ic}$)	$7.3 \cdot 10^4 \text{ s}^{-1}$ [42]
Intersystem crossing rate (k_{ISC})	$4.0 \cdot 10^7 \text{ s}^{-1}$ [42]
Reverse intersystem crossing rate (k_{RISC})	$1.5 \cdot 10^6 \text{ s}^{-1}$ [42]
Förster radius for singlet energy transfer ($R_{0,STR}$)	1.5 nm [7] ^(c)
Förster radius for singlet-singlet annihilation ($R_{0,SSA}$)	3.5 nm [7]
Förster radius for singlet-triplet annihilation ($R_{0,STA}$)	3.5 nm [7]
Dexter hopping attempt rate (ν_0)	$3.3 \cdot 10^{10} \text{ s}^{-1}$ [7],[49] ^(d)
Dexter inverse wavefunction decay length (α)	3.3 nm^{-1} [7],[49] ^(d)
Maximum distance for excitonic processes	5 neighbours per side ^(e)

^(a) Changed in Figure 6 between 1 mol% and 20 mol%.

^(b) Corresponding to 10% of guest sites in a 10 mol% blend, changed in Figure 7 from 10^{18} to $2 \cdot 10^{19} \text{ cm}^{-3}$. We will show that transient PL results are not sensitive to this value.

^(c) Changed in Figure 4, 5, and 6 between 0 nm and 5.5 nm.

^(d) Chosen equal for triplet diffusion, triplet-triplet annihilation and triplet-singlet annihilation.

^(e) The cutoff was increased to 7 neighbours per side when Förster radii in excess 3.5 nm were used, but results were found not to differ compared to a 5-neighbour cutoff.

In transient PL simulations, singlet excitons are initially generated on a fraction ϕ of guest sites, proportional to the fluence of the excitation pulse, giving an initial singlet exciton density $S(0) = \phi c a^{-3}$. The system is then allowed to evolve in time and time-dependent observables can be directly obtained. In steady-state PL simulations, singlet excitons are generated continuously on empty guest sites at a constant rate G , assuming a uniform absorption profile throughout the sample, consistently with the three-dimensional periodicity of the lattice. Observables are computed as time averages once the system has reached a stationary state.

We only consider energy transfer events between guest sites. Energy transfer from an excited-state donor to a ground-state (excited-state) acceptor results in exciton transfer (EEA). Higher excited states are not explicitly modelled; instead, instantaneous thermalisation is assumed to follow each EEA event. The relevant energy transfer parameters are listed in Table I. Note that energy transfer parameters are specific to the states involved in the interaction and differ, in principle, for each combination of donor and acceptor spin state – the latter being either the ground state or an excited state of a given spin.

In our simulations, we distinguish four spin-specific EEA channels: singlet-singlet (SSA), singlet-triplet (STA), triplet-singlet (TSA), and triplet-triplet (TTA) annihilation, where the first (second) label denotes the spin state of the donor (acceptor). Although STA and TSA involve the same species to yield the same product (a triplet by total spin conservation), they differ in the spin state of the donor: in STA (TSA), a singlet (triplet) is transferred, so the process is generally mediated by a Förster (Dexter) interaction. For this reason, in a fluorescent system, STA rates are usually much larger than TSA rates.

For simplicity, we assume that energy transfer from singlet (triplet) states only takes place via the Förster (Dexter) mechanism. Furthermore, we take equal Förster radii for SSA and STA and equal Dexter attempt rates for TSA and TTA. The general case is discussed in Sec. S6 of the Supporting Information and does not qualitatively differ.

The Förster rate reads:

$$\xi_{i \rightarrow j}^F = \frac{1}{\tau_D} \left(\frac{R_0}{r_{ij}} \right)^6 \cdot \Phi(\Delta E_{ij}) \quad (1)$$

where τ_D is the excited state lifetime of the donor, r_{ij} is the donor-acceptor distance, and the Förster radius R_0 summarises the spectral overlap between the emission of the donor and the absorption of the acceptor, the donor PL quantum yield, and the relative orientation of the donor and acceptor transition dipoles [44]. For simplicity and consistency with previous studies, we consider an isotropic R_0 , even though molecular orientations are fixed in the solid state. The factor $\Phi(\Delta E_{ij})$ is discussed below.

The Dexter rate reads:

$$\xi_{i \rightarrow j}^D = \nu_0 \exp(-2\alpha r_{ij}) \cdot \Phi(\Delta E_{ij}) \quad (2)$$

where ν_0 is the hopping attempt frequency and α is the inverse wavefunction decay length.

Because we use material-averaged energy transfer parameters (namely the Förster radius R_0 and the attempt frequency ν_0) in place of site-specific spectral or orbital overlaps, we introduce the energy-dependent factor $\Phi(\Delta E_{ij})$ to include the effect of energetic disorder. The factor depends solely on the energy difference between the states involved in the transition at the donor and acceptor sites and takes the form of an approximated Miller-Abrahams-type dependence [45],[46]:

$$\Phi_{\text{aMA}}(\Delta E_{ij}) = \exp\left(-\frac{|\Delta E_{ij}| + \Delta E_{ij}}{2k_B T}\right) \quad (3)$$

with $k_B T$ the thermal energy at temperature T . Alternatively, in Sec. S3 of the Supporting Information we also use a Marcus-type energy dependence [47]:

$$\Phi_{\text{Ma}}(\Delta E_{ij}) = \sqrt{\frac{1}{4\pi\lambda k_B T}} \exp\left[-\frac{(\Delta E_{ij} + \lambda)^2}{4\lambda k_B T}\right] \quad (4)$$

where the relaxation energy λ expresses the energy dissipated to reach the equilibrium geometry in the excited state and typically lies in the 0-0.2 eV range. Sec. S3 shows that an approximate Miller-Abrahams-type dependence and Marcus-type dependence yield the same qualitative results, consistently with the conclusion of Saxena *et al.* [33].

Simulations are performed using an in-house implementation of the Bortz-Kalos-Lebowitz (BKL) algorithm, with each simulation repeated across multiple independent replicates to accumulate statistics over approximately 10^6 individual excitons. In the following figures, error bars are displayed when appropriate and are generally smaller than symbol size. Where lines are used instead of markers, shaded areas equivalently indicate the statistical error margin. Some areas (indicated in the captions) are not shown in plots due to large statistical noise, generally because of the very low exciton population.

III. RESULTS AND DISCUSSION

Figure 1a shows the simulated time evolution of the singlet and triplet exciton densities for the parameter set indicated in Table I under pulsed excitation (markers). The populations of singlets and triplets can also be derived by solving the general rate equations:

$$\begin{cases} \frac{dS(t)}{dt} = -(k_{S,r} + k_{S,ic} + k_{ISC}) S(t) + k_{rISC} T(t) \\ \quad - k_{SSA} [S(t)]^2 - (k_{STA} + k_{TSA}) S(t) T(t) \\ \quad + \frac{1}{4} k_{TTA} [T(t)]^2 \\ \frac{dT(t)}{dt} = -(k_{T,r} + k_{T,ic} + k_{rISC}) T(t) + k_{ISC} S(t) \\ \quad - \frac{5}{4} k_{TTA} [T(t)]^2 \end{cases} \quad (5)$$

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where $S(t)$ [$T(t)$] is the time-dependent singlet (triplet) number density, $k_{i,r}$ ($k_{i,ic}$) is the radiative decay (internal conversion) rate of species i , $k_{(r)ISC}$ is the (reverse) intersystem crossing rate, and k_{XYA} is the annihilation coefficient between excitons with spin X and Y .

The solid lines in Figure 1 show the populations calculated using Equation 5 in the annihilation-free case (i.e. all $k_{XYA} = 0 \text{ cm}^3 \text{ s}^{-1}$), to serve as reference. The prompt and delayed fluorescence contributions are clearly distinguishable in the singlet decay curve. Both simulated populations, however, deviate markedly from the annihilation-free case. Analysis of the simulation statistics reveals that a substantial fraction of singlet excitons is lost to singlet-singlet annihilation (SSA, 17% of total exciton decays) and singlet-triplet annihilation (STA, 36%). Conversely, triplet-singlet (TSA) and triplet-triplet (TTA) annihilation amount to less than 1% of total decays, as reverse intersystem crossing (RISC) effectively outcompetes both processes. The deviation of the simulated singlet population curve from the annihilation-free case indicates the role of annihilation as an effective additional channel for non-radiative decay, whereas for the triplet population it only reflects the reduced availability of singlet excitons for intersystem crossing (ISC).

From the transient number densities of excitons and annihilation events we can calculate the annihilation coefficients as the number density of annihilation events per unit time normalised to the number density of the involved exciton species [50]:

$$k_{XYA}(t) = \frac{1}{X(t) \cdot Y(t)} \cdot \frac{dN_{XYA}(t)}{dt} \quad (6)$$

where $X(t)$ and $Y(t)$ are the transient populations of excitons with given spin and $N_{XYA}(t)$ is the number density of the corresponding annihilation events as a function of time. The resulting transient annihilation coefficients for SSA and STA are shown in Figure 1b. Calculation is not possible for TTA and TSA, due to the extremely low statistics.

From Figure 1b, we can immediately observe that the SSA and STA coefficients are time-dependent and that, between 10^{-11} s and $2 \cdot 10^{-8} \text{ s}$, they follow the same functional dependence on time, differing only by a small scale factor. We can split their time evolution in three regimes. In regime (i), up to a delay time of 10^{-11} s , the SSA coefficient is constant in time. In regime (ii), between 10^{-11} s and $2 \cdot 10^{-8} \text{ s}$, the SSA and STA coefficients exhibit a $t^{-0.5}$ dependence. In regime (iii), beyond $2 \cdot 10^{-8} \text{ s}$, the STA coefficient shows a broad “bump” peaking around $3 \cdot 10^{-7} \text{ s}$ before decreasing.

We interpret these results as follows. The scale factor between the SSA and STA coefficients originates from the energy-dependent correction term (Equation 3 and 4): singlet states are typically close in energy, so SSA may involve a small activation barrier. By contrast, triplet states lie on average 100 meV below singlets, so STA is generally downhill in energy, therefore marginally faster. Regarding the time dependence, the constant SSA coefficient in regime (i) results from the annihilation of nearest-neighbour exciton

pairs. We attribute the subsequent decrease in regime (ii) to the spatially inhomogeneous depletion of the exciton population [30],[40],[41]: because the energy transfer rates decay steeply with distance ($\propto r^{-6}$ for Förster-mediated SSA and STA), closely spaced exciton pairs annihilate preferentially over more distant ones. Hence, the immediate vicinity of each surviving exciton is rapidly depleted, increasing the distance to the nearest surviving exciton. In other words, the positions of the surviving excitons develop a degree of spatial correlation over time, as will be discussed in detail below. Finally, in regime (iii), the exciton population is dominated by triplets, hence the occurrence of SSA and STA is no longer governed by energy transfer kinetics but rather by the availability of singlet excitons regenerated via RISC.

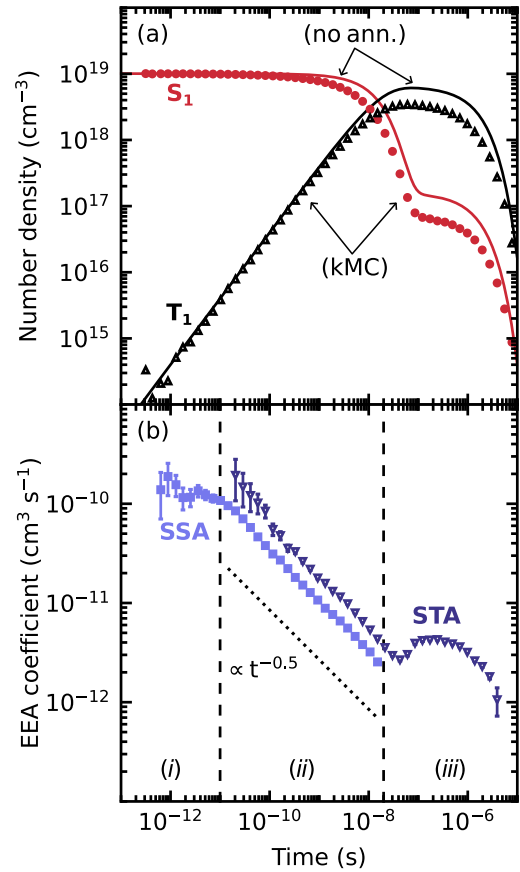


FIG. 1. Transient population for singlet (red) and triplet (black) excitons, calculated either from kMC simulations using the parameters in Table I (markers) or by solving the general rate equation (Equation 5) for the annihilation-free case (lines). (b) Annihilation coefficients for singlet-singlet annihilation (SSA, light blue squares) and singlet-triplet annihilation (STA, dark blue triangles) as a function of time. SSA (STA) rates are not shown for $t \geq 2 \cdot 10^{-8} \text{ s}$ ($t \leq 10^{-11} \text{ s}$) due to large statistical noise. The vertical dashed lines separate the three regimes (numbered in italic at the bottom of the panel), whereas the oblique dotted line indicates a $t^{-0.5}$ time dependence.

We then attribute the broad “bump” in the STA coefficient to the regeneration via RISC of singlet excitons in random clusters of triplets too far apart to give rise to TTA. In fact, the time at which this feature peaks changes depending on the RISC rate, as shown in Figure S8b.

This interpretation is corroborated by the time evolution of the mean donor-acceptor distance for SSA and STA, shown in Figure 2. The same three regimes can be identified: a constant regime (i), a time-dependent regime (ii), and a final regime featuring a broad bump (iii). Additionally, while statistical noise in the exciton populations (denominators of Equation 6) prevents a reliable estimate of the SSA coefficient for $t \geq 2 \cdot 10^{-8}$ s, the mean donor-acceptor distance can be evaluated throughout the entire simulation. The perfect overlap in Figure 2 of the curves for SSA and STA for $t \geq 10^{-11}$ s suggests that – were more statistics available – the coefficients displayed in Figure 1 would also follow an identical time evolution across the whole simulation interval.

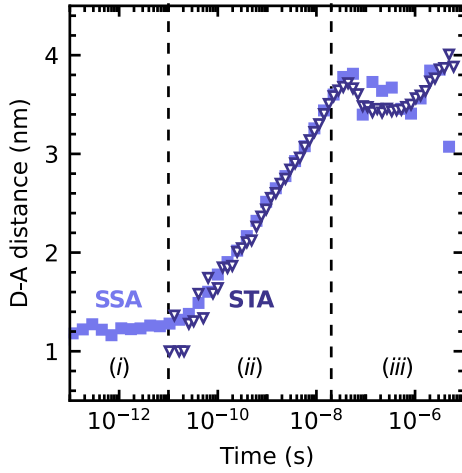


FIG. 2. Mean donor-acceptor distance for SSA (filled squares) and STA (empty triangles) as a function of time, for the system of Figure 1. The vertical dashed lines separate the three regimes identified in Figure 1 (numbered in italic at the bottom).

We have anticipated that the spatially inhomogeneous depletion of the exciton population leads to the development of a spatial correlation between the positions of surviving excitons over time. This correlation can be quantified through the radial distribution function (RDF, Equation S1 of the Supporting Information), which expresses the probability to find two excitons at a distance r and at a time t after the irradiation pulse. Rather than resolving the RDF by spin species, here we consider the cumulative (spin-independent) RDF, which is sufficient to discuss the relevant physics without loss of generality. A more detailed analysis is provided in Sec. S1 of the Supporting Information. Figure 3 shows the cumulative RDF against the exciton-exciton distance, parametric in time, for the system of Figure 1.

At short range, the RDF decays rapidly in time: SSA eliminates virtually all nearest-neighbour exciton pairs within

10^{-11} s of the excitation pulse, after which the depletion region progressively extends to distances of up to 5 nm from each surviving exciton, in good agreement with the results of Taherpour *et al.* for phosphorescent systems [30].

We can then explain the identical time dependence of the SSA and STA coefficients in Figure 1b as follows. At early times, the exciton population consists entirely of singlets, and SSA between neighbouring excitons proceeds rapidly relative to ISC. Consequently, the spatially inhomogeneous depletion of the exciton population has already proceeded to some extent by the time a significant triplet population is generated by ISC. Thus, the average donor-acceptor distance for SSA and STA events (Figure S2) follows the same time evolution, as both processes sample the same underlying spatial distribution and depend on the same Förster radius $R_{0,SSA} = R_{0,STA}$. (The general case for $R_{0,SSA} \neq R_{0,STA}$ is discussed in Sec. S6 of the Supporting Information.) Since triplet diffusion is too slow to replenish the locally depleted regions on the timescale of SSA and STA, the evolution of the RDF in time is ultimately dictated by SSA alone. As a consequence, TTA is further suppressed: by the time a substantial triplet population has developed, SSA has already depleted virtually all closely spaced exciton pairs, preventing efficient TTA.

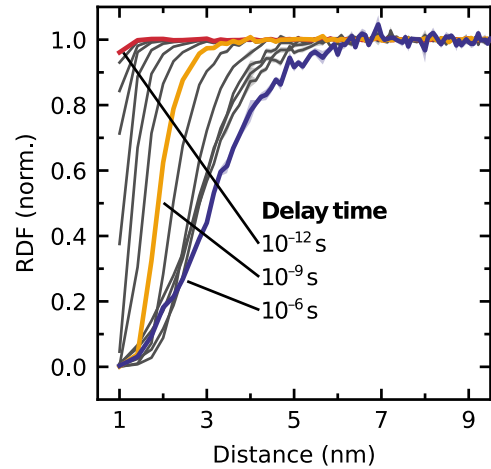


FIG. 3. Exciton radial distribution function (spin-independent) against the exciton-exciton distance for the system of Figure 1, parametric against time.

From the fast decrease of the RDF in time, it is also clear that singlet exciton diffusion (enabled with a Förster radius $R_{0,STR} = 1.5$ nm) cannot compensate for the spatially inhomogeneous depletion of excitons due to EEA. We have therefore repeated the simulations for different values of the Förster radius $R_{0,STR}$ ranging from 0 nm (no diffusion) to 5.5 nm. For comparison, Förster radii usually fall in the 1-2 nm range due to poor self-spectral overlap [7],[24],[26],[51].

The resulting annihilation coefficients are reported in Figure 4 for SSA (Figure 4a) and STA (Figure 4b) as a function of time, parametric against $R_{0,STR}$. As before, the time dependence of the SSA and STA coefficients is fully

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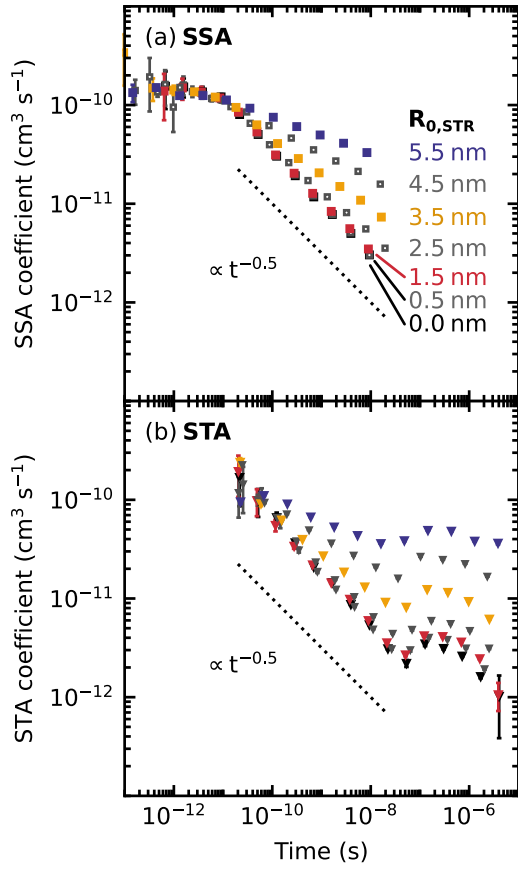


FIG. 4. Annihilation coefficients for (a) singlet-singlet annihilation and (b) singlet-triplet annihilation as a function of time, parametric against the Förster radius for singlet exciton transfer $R_{0,STR}$. SSA (STA) rates are not shown for $t \geq 2 \cdot 10^{-8}$ s ($t \leq 10^{-11}$ s) due to large statistical noise. The black dashed line indicates a $\propto t^{-0.5}$ dependence against time.

comparable across values of $R_{0,STR}$, up to a small scale factor. The same three regimes identified in Figure 1 are again present. In regime (ii), in particular, the coefficients exhibit a general $t^{-\beta}$ dependence, where the exponent β decreases monotonically with increasing exciton diffusivity. For $R_{0,STR} \lesssim 1.5$ nm, the exponent is $\beta = 0.5$, while it decreases to $\beta = 0.18$ for $R_{0,STR} = 5.5$ nm.

We understand the variations in the exponent β as the result of the competition between two opposing effects, namely the inhomogeneous depletion of the exciton population driven by EEA, and the homogenising effect of exciton diffusion. Hence, $\beta = 0.5$ describes a “slow diffusion” limit where EEA outcompetes exciton diffusion, whereas a hypothetical “fast diffusion” limit (not reached within our parameter set) would display $\beta = 0$, i.e., time-independent coefficients. Intermediate regimes show a continuous variation of β .

It is noteworthy that, even in a system with $R_{0,STR}$ as large as 5.5 nm, the exciton density is far from spatially

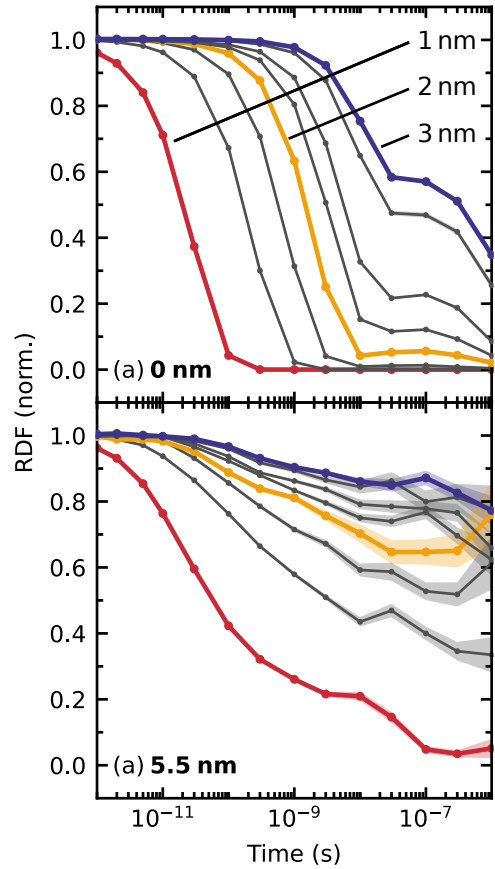


FIG. 5. Exciton radial distribution function (spin-independent) against time, parametric against the exciton-exciton distance, for systems with a Förster radius for singlet exciton transfer ($R_{0,STR}$) of (a) 0 nm, that is in the absence of singlet exciton diffusion, and (b) 5.5 nm. On a cubic lattice, inter-site distances take discrete rather than continuous values; the distances shown correspond to the first eight neighbour shells, with integer-valued separations highlighted in red (1 nm), yellow (2 nm) and blue (3 nm).

homogeneous. Figure 5 shows the cumulative RDF against time for exciton-exciton distances up to 3 nm, for the extreme cases of no diffusion (implemented as $R_{0,STR} = 0$ nm, Figure 5a) and $R_{0,STR} = 5.5$ nm (Figure 5b). In the absence of diffusion, the decay of the RDF at short distances is very rapid, exhausting the nearest-neighbour exciton population by 10^{-10} s. Even for $R_{0,STR} = 5.5$ nm, the RDF at any distance decreases monotonically, albeit much more slowly (Figure 5b). We conclude that a spatially homogeneous exciton distribution is not a prerequisite for EEA to proceed at a nearly constant rate: the occasional occurrence of a closely spaced exciton pair is sufficient. Indeed, whereas the *average* exciton-exciton distance (as inferred from the RDF) decreases in time, the mean donor-acceptor distance at which annihilation events occur remains approximately constant for $R_{0,STR} > 4.5$ nm (Figure S11c of the Supporting Information).

As a side note, the effect of triplet diffusion is visible as a “bump” in the RDF at long delay times ($> 10^{-7}$ s). Because Dexter-mediated TTA is active at much shorter distances than SSA and STA, triplet excitons can reside in closer proximity without undergoing annihilation. The same effect is visible in Figure 3 ($R_{0,STR} = 1.5$ nm) as a crossover of the curves for delay times between 10^{-9} s and 10^{-6} s, for exciton-exciton distances below 3 nm.

To further characterise the effect of exciton diffusion on the annihilation coefficients, we performed additional simulations in which the guest fraction c was varied from 1 to 20 mol%, and for a neat guest film (100 mol%). The guest content governs the availability of exciton percolation pathways and can therefore substantially influence exciton diffusion. For each value of c , simulations were run across multiple values of the Förster radius for singlet energy transfer $R_{0,STR}$, dependent on the self-spectral overlap of the guest emitter. For each simulation we extracted the exponent of the SSA time dependence $t^{-\beta}$. We remind that $\beta = 0.5$ indicates that exciton diffusion does not compensate significantly for the spatially inhomogeneous depletion of the exciton population, whereas $\beta < 0.5$ indicates partial replenishment of the depleted regions due to singlet diffusion.

The results are summarised in the heat map in Figure 6, which shows β as a function of c and $R_{0,STR}$. The red contour marks the boundary at $\beta = 0.5$, corresponding to the slow-diffusion limit. A true fast-diffusion limit, characterised by time-independent coefficients, is not reached for any of the simulated systems. Rather, for $R_{0,STR} \leq 1.5$ nm, the value of the exponent seems to converge to $\beta = 0.5$ regardless of the guest concentration. In fact, even for a neat guest system, β is

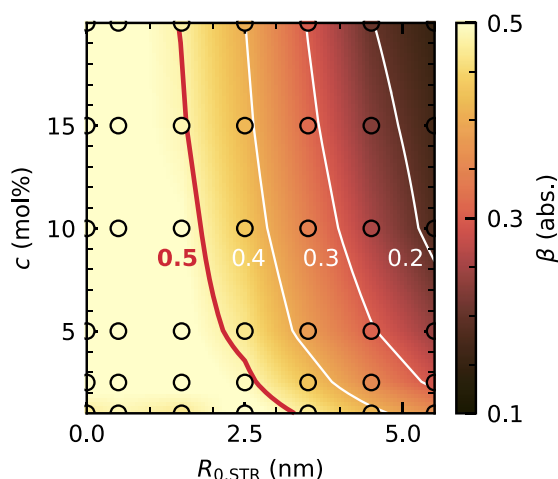


FIG. 6. Heat map showing the exponent of the time dependence $t^{-\beta}$ of the singlet-singlet annihilation coefficient, for different values of the guest fraction (c) and of the Förster radius for singlet exciton transfer ($R_{0,STR}$). The heatmap is interpolated on a 100×100 grid from the data points indicated as circle markers. The red line indicates an approximate boundary for the slow-diffusion regime, where $\beta \approx 0.5$ (light yellow region on the bottom left corner).

larger than 0.4 for all $R_{0,STR} \leq 1.5$ nm (Figure S14 of the Supporting Information). We conclude that most realistic systems fall into the slow-diffusion regime, where annihilation coefficients scale with time as $t^{-0.5}$.

Finally, we consider the effect of the excitation density on the annihilation kinetics, comparing the photophysics under pulsed and continuous illumination. Pulsed-excitation simulations were performed with an initial exciton density ϕ ranging from 10^{18} to $2 \cdot 10^{19}$ cm^{-3} (corresponding to a fraction of initially excited guest sites ranging from 1% to 20% in a 10 mol% blend). Expectedly, the fraction of excitons lost to EEA increases with increasing excitation density.

Counterintuitively, however, the SSA and STA coefficients shown in Figure 7a are entirely independent of the excitation power. We rationalise this as follows: after the excitation pulse, the time evolution of the annihilation coefficients is governed by the annihilation dynamics within randomly distributed clusters of excited guest molecules. A higher excitation power increases the number of such clusters, hence of the overall EEA losses, but does not alter the dynamics inside the clusters themselves, which are rather determined by the microscopic photophysical and energy transfer rates. This interpretation is supported by the cumulative RDFs calculated for the highest and lowest excitation powers tested (Figure 7b). The two curves overlap for all delay times and distances, confirming that the systems are microscopically identical despite their different total exciton densities. To verify that this independence on excitation density is not an artefact of the slow-diffusion regime, we repeated the simulations with a larger exciton transfer radius ($R_{0,STR} = 3.5$ nm), placing the system outside the slow-diffusion regime. The same conclusions were reached (Figure S15 of the Supporting Information).

Let us now consider the same host:guest system under continuous irradiation, modelled as a constant rate G for the generation of singlet excitons on empty sites (assuming a homogeneous emission profile). G is varied from $3 \cdot 10^{-18}$ to 10^{-12} $\text{cm}^{-3} \text{s}^{-1}$, corresponding to steady-state singlet exciton densities from $1.5 \cdot 10^{15}$ to $7.5 \cdot 10^{17}$ cm^{-3} . In all cases, the triplet exciton density exceeds the singlet density by about one order of magnitude, reflecting the long triplet lifetime in TADF emitters. Figure 8a shows the SSA, STA, and TTA coefficients as a function of G . Although the number of STA events exceeds that of SSA events by at least one order of magnitude, the corresponding kinetic coefficients are comparable. This can again be understood by recognising that the annihilation coefficients reflect the microscopic kinetics within clusters of photogenerated excitons, rather than the macroscopic number of events. The reduced singlet density suppresses the frequency of SSA events but does not alter the rate at which annihilation proceeds when two singlet excitons encounter one another.

Continuous irradiation also afforded sufficient statistics to reliably extract the coefficients for triplet-triplet annihilation. TTA accounts for at most 0.3% of total exciton decays even at the highest triplet densities reached in these simulations ($7.4 \cdot 10^{18}$ cm^{-3}), which are far higher than those recorded at

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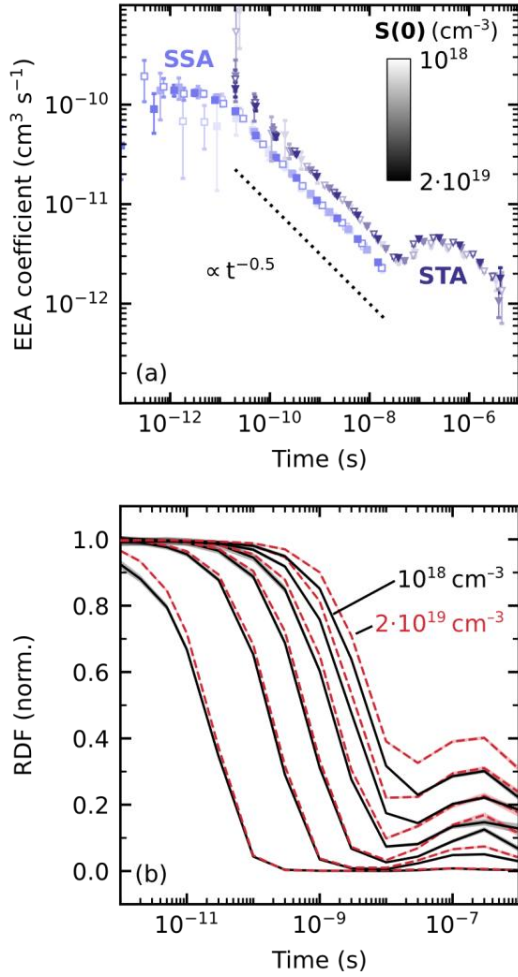


FIG. 7. (a) Annihilation coefficients for singlet-singlet (SSA, light blue) and singlet-triplet (STA, dark blue) annihilation as a function of time, parametric against the initial exciton density (from 10^{17} to $2 \cdot 10^{19} \text{ cm}^{-3}$, light to dark colour gradient). SSA (STA) rates are not shown for $t \geq 2 \cdot 10^{-8} \text{ s}$ ($t \leq 10^{-11} \text{ s}$) due to large statistical noise. The black dashed line indicates a $t^{-0.5}$ dependence against time. (b) Exciton radial distribution function (spin-independent) against time, for the highest and lowest initial exciton density, 10^{18} cm^{-3} (solid black lines) and $2 \cdot 10^{19} \text{ cm}^{-3}$ (red dashed lines).

any time under pulsed excitation. TTA coefficients exhibit the same functional dependence on exciton density as the SSA and STA coefficients, but are three orders of magnitude smaller, consistently with the considerably weaker Dexter parameters governing TTA.

To understand why the annihilation coefficients are dependent on the excitation power under continuous illumination but not under pulsed excitation, we examine the time-averaged, cumulative RDF under continuous illumination, shown in Figure 8b as a function of the exciton-exciton distance and parametric against the singlet generation rate. Under continuous illumination, the RDF depends on the excitation power: as the exciton generation rate increases, the

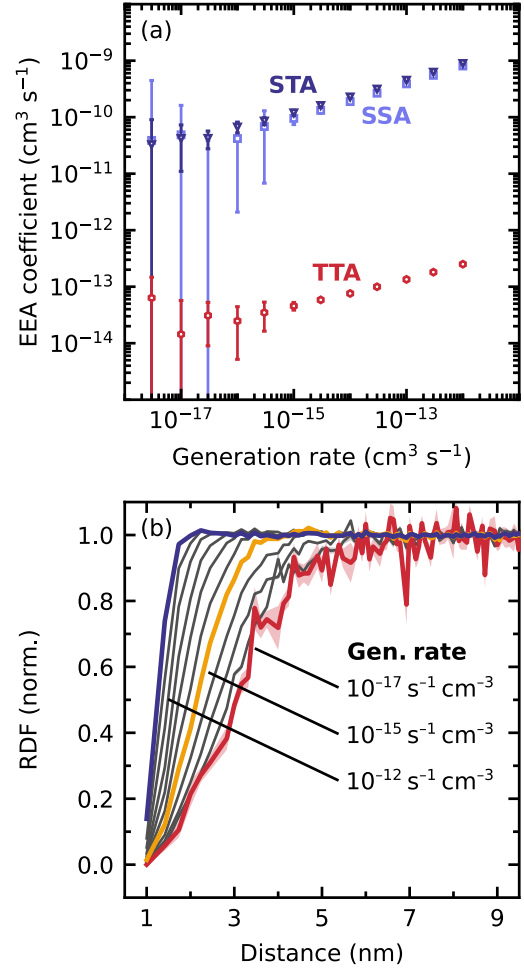


FIG. 8. (a) Annihilation coefficients for singlet-singlet (SSA), singlet-triplet (STA) and triplet-triplet (TTA) annihilation in a 10 mol% host:guest system under continuous irradiation, reported against the singlet generation rate. For generation rates below $10^{-16} \text{ cm}^{-3} \text{ s}^{-1}$ (equivalently, singlet densities below 10^{17} cm^{-3}) the large uncertainties on the exciton density and the small extent of annihilation translate to large uncertainties on the annihilation coefficients. (b) Excitonic radial distribution function (spin-independent) reported against the exciton-exciton distance, parametric against the singlet generation rate.

inflection point of the RDF shifts at shorter distances and the slope of the line increases. By contrast, we have observed in Figure 7b that the RDF under pulsed excitation is fully comparable at all times for all initial exciton densities, i.e., is independent on the excitation power.

We can then conclude that the increase of the annihilation coefficients with increasing excitation power under continuous illumination is not a consequence of the higher exciton density. Rather, it follows from the power-dependency of the RDF. The continuous generation of new excitons on random sites across the material disrupts the spatial correlation between surviving excitons promoted by

EEA, and maintains a more spatially uniform exciton distribution, thereby increasing the probability of short-range encounters. Differently, under pulsed excitation the microscopic dynamics are not affected by the macroscopic exciton density, hence the annihilation coefficients are independent on the excitation power, as discussed just above.

IV. DISCUSSION

This study addresses the kinetics of EEA in a host:TADF guest system through the analysis of kinetic annihilation coefficients, defined as the number density of annihilation events per unit time normalised to the number density of the involved exciton species (Equation 6). The time evolution of the annihilation coefficients reflects the microscopic annihilation kinetics independently of the total number of annihilation events. In general, we find that these coefficients are not constant but scale with time according to a power-law dependence $t^{-\beta}$, where the exponent β is determined by the exciton diffusivity. Power-law dependences of this form have been experimentally observed for both small-molecule and polymeric organic semiconductors [29],[40],[25].

For static or weakly diffusive systems, we find $\beta = 0.5$, consistent with the result derived by Förster [39] for the energy transfer between randomly dispersed, immobile excited-state donors and fluorescence quenchers (acceptors). The time dependency is then a consequence of the spatially inhomogeneous distribution of donor-acceptor pairs. Yokota and Tanimoto [52] extended Förster's framework to account for the diffusion of excited molecules in solution under continuous irradiation, but did not derive an expression for the time dependence of the energy transfer coefficients in the transient PL regime. In this study, we have carried out simulations over a wide range of guest concentrations and Förster radii for singlet exciton transfer, showing that increasing exciton diffusivity systematically reduces the exponent β while preserving the $t^{-\beta}$ functional form. We can in fact generalise our results by reporting the value of β versus the exciton diffusion coefficient on the master plot in Figure 9. We can identify a threshold value for the singlet diffusion coefficient ($D_{\text{limit}} = 2 \cdot 10^{-7} \text{ cm}^2 \text{ s}^{-1}$) below which singlet diffusion is “slow” compared to exciton annihilation ($\beta = 0.5$), and above which one enters a transition regime where β progressively decreases. One expects that sufficiently fast diffusion would ultimately yield time-independent coefficients ($\beta \rightarrow 0$). However, this limit is not reached within our parameter range. In fact, despite the scarce literature on singlet diffusion in small-molecule host:guest systems, there are indications [53] that diffusion coefficients for real systems fall around or below D_{limit} . Exciton diffusivity in neat systems can be much higher, up to $D \sim 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ [54],[55], placing such systems in the transition regime.

A functionally similar time dependence has occasionally been introduced in the literature [25],[27],[56]–[59] through expressions inspired by Smoluchowski's theory of diffusion-

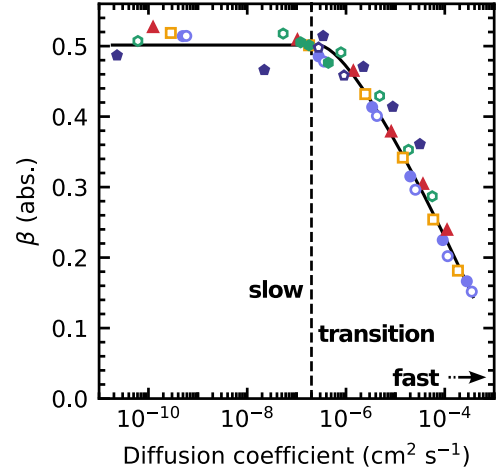


FIG. 9. Master plot showing the exponent of the time dependence $t^{-\beta}$ of the singlet-singlet annihilation coefficient against the singlet exciton diffusion coefficient for all simulated data sets, indicated by different marker styles. The solid black line is a guide to the eye, while the dashed vertical line indicates an ideal limit for the slow-diffusion regime for a diffusion coefficient $D_{\text{limit}} = 2 \cdot 10^{-7} \text{ cm}^2 \text{ s}^{-1}$.

limited particle aggregation [60],[61] which takes the general form

$$k(t) = 4\pi\gamma D + \frac{4\pi\gamma^2 D}{\sqrt{\pi Dt}} \quad (7)$$

where k is the annihilation coefficient, γ is an effective capture radius, and D is the diffusion coefficient. The first and second term of the sum represent the fast- and slow-diffusion regimes, respectively. Our results recover both limiting cases of Equation 7: $k \propto t^{-0.5}$ for $D \rightarrow 0$ and $k = \text{const.}$ for $D \rightarrow +\infty$. Discrepancies arise, however, for intermediate values of D . Within the Smoluchowski framework, the exponent of the time dependence is constant at -0.5 , with the diffusion coefficient controlling only the relative weight of the time-dependent term. In contrast, our results are best described (in the intermediate regime between 10^{-11} s and $2 \cdot 10^{-8} \text{ s}$) by a variable exponent $0 < \beta \leq 0.5$ that depends effectively on the exciton diffusivity.

To understand the discrepancy, we revisit the assumptions underlying the Smoluchowski formalism. The derivation assumes (i) a diffusion-limited reaction, in which local depletion at early times is subsequently replenished by particle diffusion, and (ii) a completely absorbing boundary condition, i.e., a reaction that happens with unity probability below a characteristic separation γ , and with zero probability beyond it (a correction to this assumption, introducing a reaction probability at the boundary, has been proposed by Ansari-Rad in Ref. [8]). While we find that EEA is indeed diffusion-limited, we argue that a “hard” boundary does not adequately describe Förster-mediated singlet annihilation. Rather, the power-law decay of Förster rates with distance gives rise to a “soft” absorbing boundary, where annihilation may happen across a range of distances with varying

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probability. It is therefore reasonable that our results differ from the Smoluchowski framework in the intermediate regime. Conversely, Smoluchowski-like models may remain appropriate to describe triplet-triplet annihilation, when the fast exponential decay of Dexter TTA rates with distance may be reasonably approximated as a hard boundary.

It is worth highlighting a further distinction between systems dominated by singlet and triplet excitons. Previous studies have shown that triplet diffusion coefficients [8],[50],[56],[62] are time-dependent, indicating a non-equilibrium transport regime due to energetic relaxation. By contrast, in our simulations, singlet exciton diffusion is always Brownian (Figure S12 of the Supporting Information) even in the presence of substantial exciton relaxation (Figure S2). We attribute this difference to two concurring factors: firstly, the singlet exciton dynamics involve considerably shorter timescales (nanosecond) compared to triplet excitons (milliseconds). Secondly, because singlet energy transfer involves a long-range Förster process, it is less affected by kinetic frustration effects, as compared to Dexter-mediated triplet diffusion [63],[64].

We have attributed the time dependence of annihilation coefficients to the fast depletion of the exciton density in the immediate vicinity of each surviving exciton. This depletion produces a progressive spatial correlation between the positions of the surviving excitons, which we have quantified through the excitonic radial distribution function. Our results are in excellent agreement with the Master Equation results of Taherpour *et al.* [30], who derived analytical expressions for the RDF of both immobile and diffusive triplet excitons in the absence of disorder. The close relationship between the RDF and the annihilation coefficients is further validated by the fact that the annihilation coefficients can be calculated as the RDF-weighted, spatially averaged Förster transfer rate, as demonstrated for both pulsed and continuous irradiation in Sec. S4 of the Supporting Information.

In contrast, Cook *et al.* noticed that a spectral redshift of the singlet emission accompanied a decrease in the annihilation coefficients and concluded that trapping of the singlets in low-energy sites in the polymer causes the annihilation to slow down [25]. Our results are at variance with this interpretation. While both the average exciton energy and the annihilation coefficients decrease similarly in time (compare Figure S2 and S6 of the Supporting Information), they are not correlated. In fact, the annihilation rates remain fully comparable when changing the disorder parameter σ between 0 meV and 150 meV (Figure S6), despite a time-dependent redshift of up to 120 meV, depending on σ (Figure S2). In general, SSA and STA rates are rather insensitive to both the energetic disorder and the exact functional formula of the energy dependence (compare Figure S2 and S3 of the Supporting Information). This behaviour is obviously dissimilar from the case of triplet-dominated systems, and we attribute the difference to the long-range character of Förster-mediated processes, as previously discussed for the exciton diffusion coefficients.

Additionally, our simulations show that – while the annihilation of high-energy excitons proceeds with

marginally higher rates due to the energy factor $\Phi(\Delta E) = 1$ for $\Delta E \leq 0$ (Equation 3) – the depletion of the high-energy tail of the singlet energy distribution is only slightly accelerated by EEA, as compared to the energy relaxation driven by exciton diffusion (Figure S2).

In conclusion, we consider the implications of our results for the quantification of exciton-exciton annihilation from PL measurements. A widely used approach in the field consists of fitting power-dependent transient PL profiles to a kinetic rate equation to extract the annihilation coefficients. In these fits, the annihilation coefficients are often assumed to be time-independent constants (e.g. in Ref. [31],[32],[37],[38]), at variance with the time-dependence established in this work. Nevertheless, the fits are often in fair agreement with experimental data (e.g. in Ref. [32]), which prompts the question of whether the quality of the fit is a reliable indicator of the accuracy of the extracted coefficients and of the validity of the underlying physical model. Figure 10 shows that our simulated data can in fact be fitted to the rate equation in Equation 5 under the assumption of time-independent coefficients, yielding ostensibly reasonable values for the SSA and STA coefficients and a good fit (thick red line). However, an equally good fit is obtained when STA is entirely neglected and the SSA coefficient is the sole fit parameter – that is, when a physically incorrect model is assumed (thin blue line). This naive example illustrates a fundamental limitation of the fitting approach: the quality of the fit is little sensitive to the chosen physical model. In turn, the results of the fit may depend heavily on the assumptions built into it. This leads us to question the physical significance of annihilation coefficients obtained in this way, and by

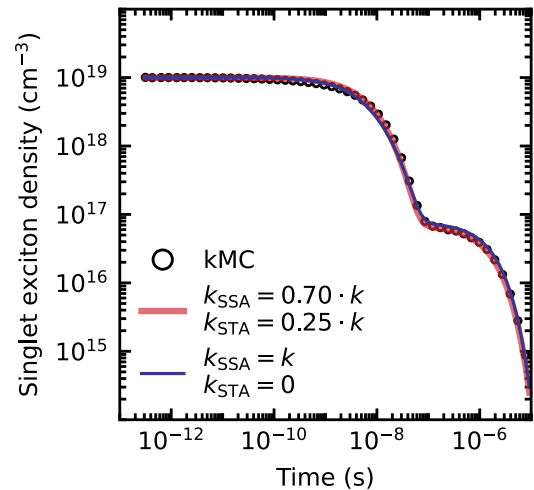


FIG. 10. (Markers) Transient singlet exciton population simulated using the parameters in Table I. (Lines) Fit to the rate equation in Equation 5, either leaving both the SSA and STA coefficients as fit parameters (thick red line) or the sole SSA coefficient (i.e., assuming that the STA coefficient is null, thin blue line). The fitted coefficient is $k = 1.5 \cdot 10^{-11} \text{ cm}^{-3} \text{ s}^{-1}$. The coefficients for TSA and TTA are assumed null in all cases.

extension urge caution when using them to parametrise device-level simulations or extract exciton diffusion lengths.

V. SUMMARY AND CONCLUSIONS

Using kinetic Monte Carlo simulations, we have investigated exciton-exciton annihilation under both transient and steady-state conditions in a host:guest system with a TADF emitter as the guest. We have demonstrated that the annihilation coefficients are in general time-dependent, scaling as $t^{-0.5}$ for realistic material parameters. Stronger exciton diffusion can reduce this exponent while maintaining the functional formula $t^{-\beta}$, at variance with the widely used Smoluchowski equation, which we argue is ill-suited to describe the photophysics of singlet-dominated systems due to its underlying assumption of a hard interaction boundary. Besides, we have shown that reaching a truly time-independent regime requires exceptional energy transfer parameters unlikely to be encountered in practice.

The time dependence of annihilation coefficients originates from the spatially inhomogeneous depletion of the exciton population through annihilation events, which gives rise to a spatially correlated exciton distribution. Contributions from the energetic relaxation are conversely negligible. We emphasise that these conclusions are not specific to the particular system under study: since singlet diffusion, SSA, and STA are all Förster-mediated processes whose rates scale identically with the material photophysical parameters, results for other systems are expected to differ quantitatively but not qualitatively from the general trends outlined in this work.

Ultimately, our results directly challenge the common practice of fitting transient PL curves with time-independent “rate constants”. We have shown that, while a reasonable fit can generally be obtained, the quality of the fit is an unreliable estimator of the accuracy of the extracted parameters, whose values can vary substantially depending on the assumptions of the fitting model. Additionally, such time-independent coefficients are sometimes treated as fluence-dependent quantities. Our results provide no support for this practice: the coefficients solely reflect the microscopic dynamics within randomly distributed exciton clusters, which are independent of the global exciton density. Differently, under continuous illumination the steady replenishment of excitons at random positions does render the coefficients fluence-dependent. We therefore urge caution when interpreting experimental transient PL data, particularly when the extracted parameters are intended to inform steady-state device simulations.

VI. ACKNOWLEDGEMENTS

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**The rates are not what they seem:
understanding the time dependence of exciton-exciton
annihilation “constants” in a TADF system**

Supplemental Material

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S1. Abbreviations

EEA	exciton-exciton annihilation (generic term for annihilation processes)
MSD	mean squared displacement
(o)DOS	(occupied) density of states
RDF	radial distribution function
σ_g	guest energetic disorder parameter (excitonic DOS width)
SSA	singlet-singlet annihilation
STA	singlet-triplet annihilation
TSA	triplet-singlet annihilation
TTA	triplet-triplet annihilation

S2. Radial distribution function

The radial distribution function (RDF) $g(r, t)$ is calculated as the frequency histogram of the exciton-exciton distances r at a given delay time t after the excitation pulse. The histogram is normalised by the number $n(r)$ of lattice sites at distance r and the material-averaged exciton density ρ , so that $\lim_{r \rightarrow +\infty} g(r, t) \rightarrow 1$.

$$g_{XY}(r, t) = \frac{N(r_{XY} = r)(t)}{\rho(t) \cdot n(r)} \quad (\text{S1})$$

Spin-specific RDFs (g_{SS} , g_{ST} and g_{TT}) are obtained by considering only the distances between excitons with given spins. These RDFs are however extremely noisy when the exciton population is scarce so, in the main article text, we show rather the “cumulative” RDF calculated from the distances between all excitons, regardless of spin. Because we work in the special case where SSA and STA have the same Förster transfer parameters ($R_{0,SSA} = R_{0,STA}$), and because triplet diffusion is negligible on the timescales of SSA and STA, then the RDFs $g_{SS}(r, t) \approx g_{ST}(r, t) \approx g(r, t)$, as shown in Figure S1. The general case ($R_{0,SSA} \neq R_{0,STA}$) is discussed in Section S6.

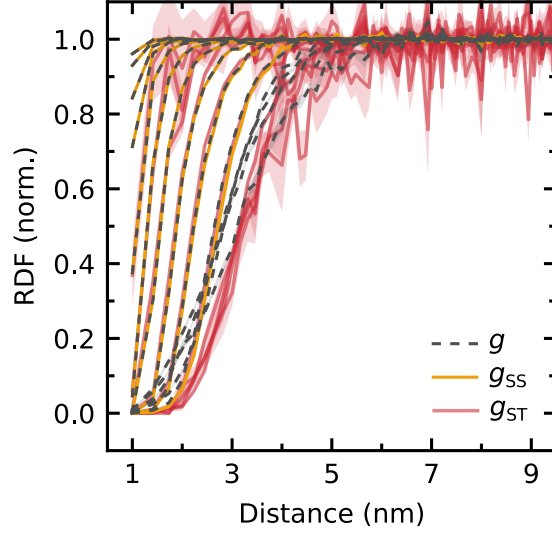


Figure S1. Comparison between the cumulative radial distribution function g and the spin-specific correlation functions g_{SS} and g_{ST} against the exciton-exciton distance, parametric against time (from 10^{-12} s to 10^{-6} s) for the system with parameters listed in Table I of the main text. The three RDFs overlap well until $\sim 10^{-7}$ s, then triplet diffusion increases the RDF value at short-range (g_{TT} is not shown).

S3. Effect of the energetic disorder

We have carried out simulations for host:guest systems with a varying energetic disorder σ_g ranging from 0 to 0.2 eV, equal for the singlet and triplet energy levels. Singlet and triplet energies are uncorrelated both spatially and on the same site. The energy dependence of the energy transfer rates may take an approximate Miller-Abrahams form or a Marcus form, respectively in Equation 3 and 4 of the main text.

Let us consider the usual system with parameters listed in Table I of the main text. First, we analyse the role of exciton diffusion and EEA in determining the average singlet energy. Figure S2 shows the average energy (peak position, panels a,c,e,g) and width (standard deviation, panels b,d,f,h) of the oDOS as a function of time, parametric against the disorder strength σ . The mean energy (width) of the singlet oDOS is calculated as the average emission energy (width) of the transient emission spectrum, which samples the singlet oDOS homogeneously at any given time. The redshift and narrowing of the oDOS are a combination of two factors: (i) the relaxation of excitons within the oDOS, mediated by exciton diffusion, and (ii) the depletion of the high-energy part of the DOS via EEA, since energy transfer happens preferentially downwards in energy, hence surviving excitons have on average lower energy. The different contributions can be appreciated by comparing a system with (i) energetic relaxation due to exciton diffusion in the absence of EEA (Figure S2a,b), (ii) EEA in the absence of exciton diffusion (Figure S2c,d), and (iii) EEA and exciton diffusion (Figure S2e,f).

Additionally, Figure S2g,h shows a system with EEA and exciton diffusion, where the on-site singlet and triplet energies are correlated. The on-site energy levels $\varepsilon_{S(T),i}$ are then obtained as:

$$\varepsilon_{S(T),i} = E_{S(T)} + \sigma_g \sqrt{-2 \cdot \log(1 - \zeta) \cdot \cos(2\pi\zeta)} \quad (\text{S2})$$

where $E_{(S),T}$ is the average singlet (triplet) energy for the material, σ is the disorder parameter and ζ is a random value in the $[0,1)$ interval.

In the presence of exciton diffusion, a large redshift is observed in time (Figure S2a). The small narrowing of the oDOS (Figure S2b) indicates that exciton transport happens in the nonequilibrium regime. Additionally, past the ~ 300 ns mark, the average singlet energy may increase because of triplets undergoing rISC on sites with randomly high singlet energies. Even in the absence of diffusion, EEA alone yields a sizable oDOS redshift (Figure S2c) but causes no oDOS narrowing (Figure S2d). When both processes are enabled, we attribute the dynamics of the oDOS primarily to exciton relaxation. Note both the mean energy and width of the oDOS show a “rebound” after the onset of RISC, due to the regeneration of singlet excitons. The “rebound” is smaller but still present if the on-site singlet and triplet energies are correlated (Figure S2g,h).

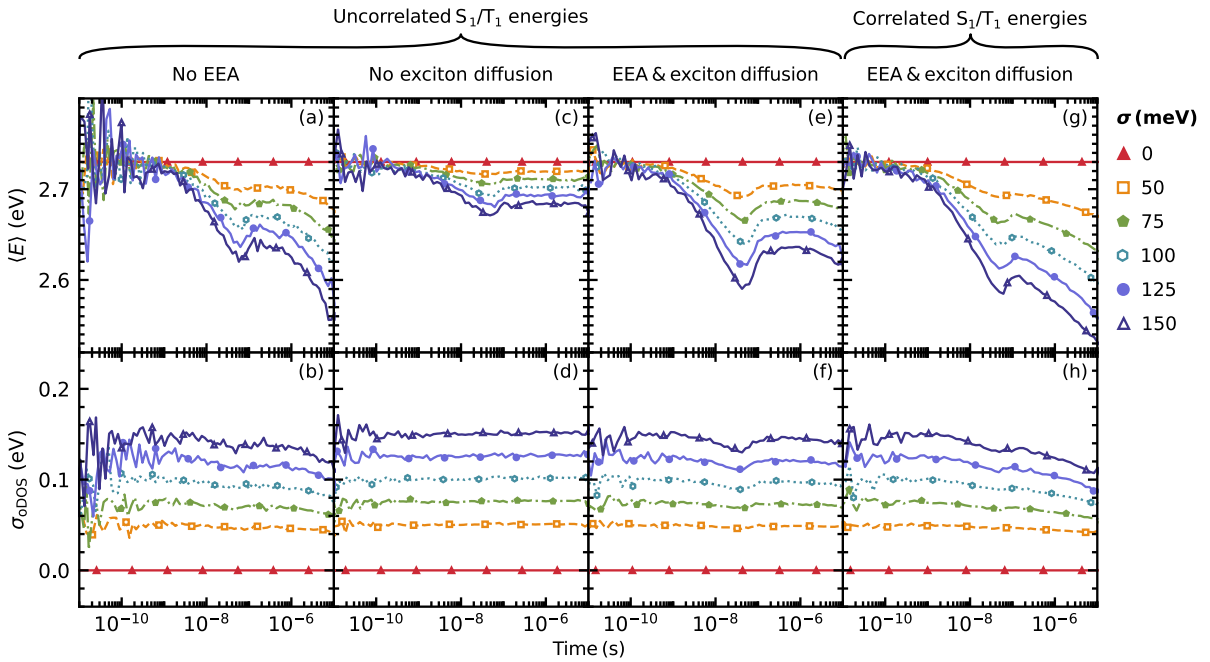


Figure S2. Effect of the energetic disorder (singlet oDOS).

(a,c,e,g) Mean value $\langle E \rangle$ and (b,d,f,h) standard deviation σ_{oDOS} of the occupied density of states for singlet excitons as a function of time, parametric against the energetic disorder parameter σ . We compare systems (a,b) with exciton diffusion ($R_{0,\text{diff}} = 1.5$ nm), without exciton-exciton annihilation, (c,d) with EEA, but without exciton diffusion, (e,f) with exciton diffusion and EEA, (e,f) with exciton diffusion and EEA, additionally with correlated on-site energy levels.

Figure S3 shows that results are not qualitatively different if a Marcus energy dependence (Equation 4 of the main text) is used.

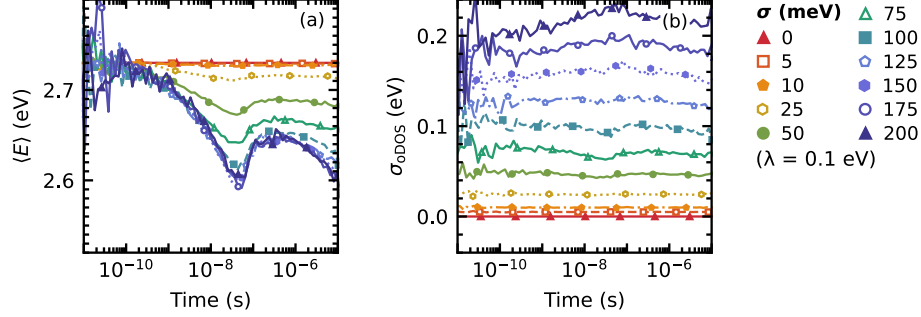


Figure S3. Effect of the energetic disorder (singlet oDOS, Marcus dependence).

(a) Mean value $\langle E \rangle$ and (b) standard deviation σ_{oDOS} of the occupied density of states for singlet excitons as a function of time, parametric against the energetic disorder parameter σ .

Regardless of the exact functional form of $\Phi(\Delta E)$, exciton losses by both SSA and STA increase at decreasing disorder (Figure S4), which we attribute to a higher exciton mobility. However, the diffusion coefficient in the absence of disorder is only 2-3 times higher than for the largest disorder tested, $\sigma_g = 0.20$ eV (Figure S5) and is not seemingly sufficient to alter the slow diffusion regime.

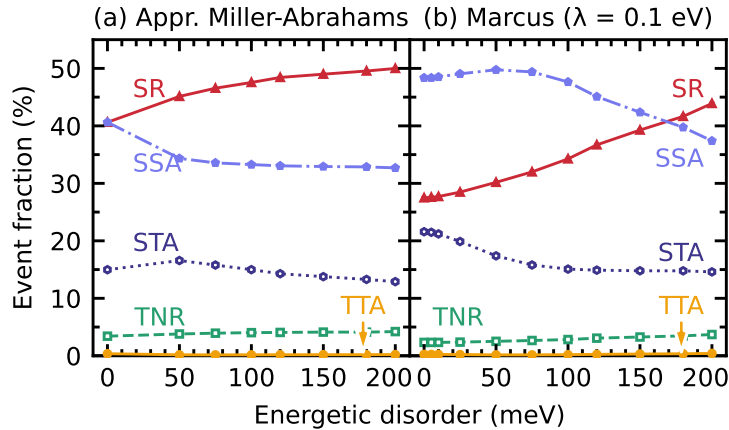


Figure S4. Fraction of excitons that decay by singlet recombination (SR), triplet internal conversion (TIC), singlet-singlet annihilation (SSA), singlet-triplet annihilation (STA), and triplet-triplet annihilation (TTA) as a function of disorder, either using (a) a Miller-Abrahams or (b) a Marcus energy dependence with a relaxation energy $\lambda = 0.1$ eV. Note that, for $\sigma_g = 0$ eV, results for the two rates differ as $\Phi_{\text{MA}}(0 \text{ eV}) = 1$ while $\Phi_{\text{Ma}}(0 \text{ eV}) = \exp(\lambda/4\pi k_B T) \cdot (4\pi\lambda k_B T)^{-0.5}$, which exceeds 1 for $\lambda \lesssim 0.35$ eV, that is for most reasonable values.

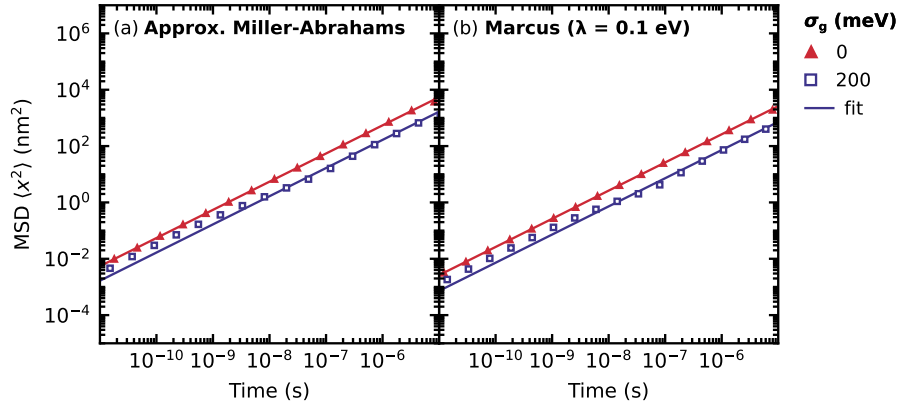


Figure S5. Mean squared displacement (MSD, $\langle x^2 \rangle$) as a function of time, parametric against the disorder parameter σ_g , using (a) a Miller-Abrahams energy dependence or a (b) Marcus energy dependence with a relaxation energy $\lambda = 0.1$ eV. Continuous lines indicate fits as $\log\langle x^2 \rangle = D + \log(t)$, where the free parameter D is the diffusion coefficient.

Figure S6 presents the dynamics of the SSA and STA annihilation coefficients (using either an approximate Miller-Abrahams or a Marcus energy dependence), which are $\propto t^{-0.5}$ for all values of σ_g . The disorder strength rather plays out as a (small) vertical scale factor. This behaviour is consistent with the way energy disorder is introduced in the model: because the energy-dependent factor $\Phi(\Delta E)$ depends solely on the energy difference between the initial and final site, it affects by the same amount the energy transfer rates for EEA and exciton diffusion between any two sites, hence leaving the average annihilation:diffusion probability ratio unchanged.

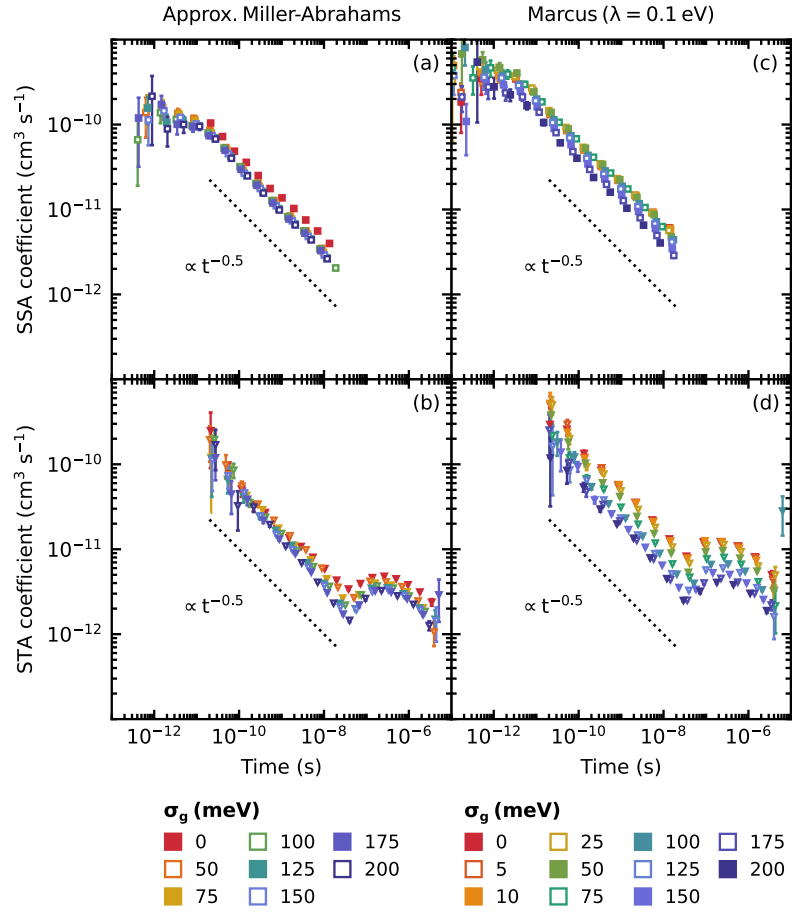


Figure S6. Annihilation coefficients for (a,c) SSA and (b,d) TTA as a function of time, parametric against the energetic disorder parameter σ_g , using either (a,b) an approximate Miller-Abrahams or (c,d) Marcus energy dependence. The black dotted lines indicate a $\propto t^{-0.5}$ time dependence. SSA (STA) rates are not shown for $t \geq 10^{-8}$ s ($t \leq 10^{-11}$ s) due to large statistical noise.

S4. Relationship between the exciton radial distribution function and the annihilation coefficients

We can relate the macroscopic annihilation coefficients $k_{XYA}(r)$ to the spin-specific RDF $g_{XY}(r, t)$ and the corresponding microscopic energy transfer rates $\xi(r)$ (neglecting the energy dependence for simplicity) as:

$$k_{XYA}^{\text{continuum}}(t) \propto \int_a^{+\infty} \xi(r) \cdot g_{XY}(r, t) \cdot 4\pi r^2 dr \quad (\text{S3})$$

where a is the closest approach distance. Equivalently, on a lattice:

$$k_{XYA}^{\text{lattice}}(t) \propto \sum_i \xi(r_i) \cdot g_{XY}(r_i, t) \cdot n(r_i) \quad (\text{S4})$$

where additionally $n(r_i)$ is the number of sites at a distance r_i from the origin [$n(r_i) \approx 4\pi r_i^2$ for large r_i]. For simplicity, for $\xi(r)$ we take Equation 2 with $\Phi(\Delta E) = 1$.

Figure S7 shows that, even in this simplified treatment Equation S4 can reproduce both the time evolution of the SSA (Figure S7a) and STA (Figure S7b) coefficients calculated from kMC data, including the “bump” in the STA rate at long delay times. Similar observations hold for the steady-state SSA (Figure S7c) and STA (Figure S7d) coefficients. The $\Phi(\Delta E)$ prefactor that we neglected in Equation S4 effectively results in a multiplicative constant on the calculated annihilation coefficients. Discrepancies can be attributed to noise in the RDF when the singlet or triplet population is small.

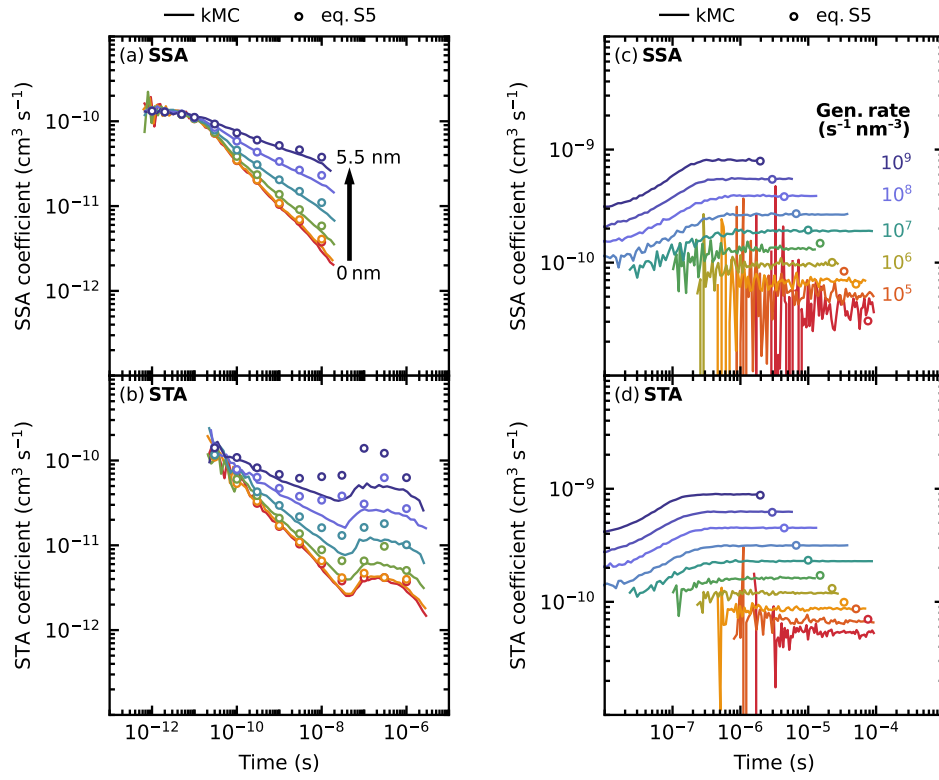


Figure S7. (a,c) SSA and (b,d) STA annihilation coefficients as a function of time, for (a,b) systems under pulsed excitation, parametric against the Förster radius for singlet energy transfer $R_{0,\text{STR}} = 0, 0.5, 1.5, 2.5, 3.5, 4.5, 5.5 \text{ nm}$, and (c,d) system under continuous irradiation with the indicated singlet generation rates (note that steady-state is reached after $\sim 10^{-7} \text{ s}$). (Symbols) Annihilation coefficients calculated with Equation 6 of the main text, (Symbols) coefficients calculated according to Equation S4. The kMC data in panels (a,b) correspond to the data in Figure 4 and of the main text.

S5. Effect of the (reverse) intersystem crossing

TADF systems are able “gather” dark triplet excitons and reconvert them into emissive singlet excitons via reverse intersystem crossing (rISC). Significant singlet and triplet populations then coexist for much longer than the natural singlet lifetime, leading to the coexistence and competition of different spin-dependent annihilation mechanisms. In this section, we will observe some consequences of this extended coexistence.

In Figure S8 we compare the transient annihilation coefficients for two systems which only differ in the values of k_{ISC} and k_{rISC} . Specifically, we take one system where the photophysical parameters are as indicated in Table I (Figure S8a), and one where the intersystem crossing and rISC rates (k_{ISC} and k_{rISC}) are ten times higher (Figure S8b). The dynamics of SSA and STA coefficients are unaffected, except for the “bump” in the STA coefficients, appearing at ~ 300 ns for the “default” parameter set and at ~ 30 ns for the system with faster ISC and RISC. Evidently the cause of this “bump” does not lie in the exciton density or diffusivity, but rather in the regeneration of singlets via rISC. Note that average-rate models, e.g. formulas based on the Smoluchowski equation, cannot capture this feature. Vice versa, it can be well reproduced by considering the radial distribution function, as shown in the previous Section S4. We conclude that the RDF implicitly includes the effect of the photophysical spin-flip rates.

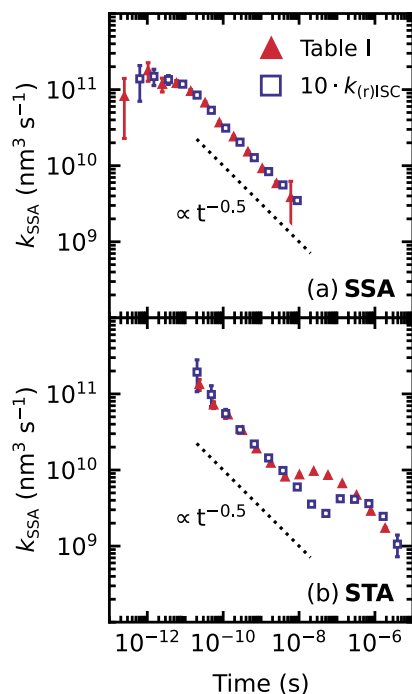


Figure S8. Annihilation coefficients as a function of time for (c) SSA and (d) STA a system with photophysical rates as indicated in Table I (red triangles) or with ten times higher ISC and rISC rates (blue squares). The black dotted lines indicate a $t^{-0.5}$ time dependence.

S6. Effect of the interplay between SSA and STA

In the main body of this publication, we have elected to work in the special case with equal Förster radii for singlet-singlet and singlet-triplet annihilation, $R_{0,SSA} = R_{0,STA} = 3.5$ nm. This allowed to approximate the radial distribution functions $g_{SS}(r, t) \approx g_{ST}(r, t) \approx g(r, t)$ (see Section S2). This near-equivalence holds because the spatial correlation of exciton positions is determined by the occurrence of singlet annihilation events, and singlet excitons are annihilated equally by singlet and triplet excitons. Additionally, triplet diffusion is negligible on the SSA and STA timescales, so that the near-equivalence holds until very long delay times.

To understand how the interplay between SSA and STA changes when $R_{0,SSA} \neq R_{0,STA}$, we have carried out additional simulations for systems with $R_{0,STA} = 1.5$ nm and $R_{0,SSA}$ ranging from 0.5 nm to 5.5 nm, with other parameters as listed in Table I of the main text. Despite the very large statistics gathered for these systems, g_{SS} and g_{ST} are inherently very noisy when either population is scarce. Rather than reporting the RDF themselves, in Figure S9 we show the evolution in time of the “midpoint” $r_{0.5}(t)$ of the RDF, defined such that $g(r_{0.5}, t) = 0.5$. To find the midpoint, we interpolate the time-dependent RDF to get a continuous function (rather than the discrete data points corresponding to lattice distances $r = 1, \sqrt{2}, \sqrt{3}, 2, \dots$ nm). Because the minimum exciton-exciton distance in our simulation is the lattice step $a = 1$ nm, we cannot resolve shorter distances.

We suggest the following reading of Figure S9: a midpoint closer to 1 nm (intersite distance) indicates that the RDF does not decay significantly in time. Vice versa, a midpoint at large distance indicates a fast decay of the RDF in time. Figure S9 shows that, for $R_{0,SSA} = R_{0,STA}$ (green hexagons), the midpoints of g_{SS} and g_{ST} coincide, indicating that the two functions fall off comparably fast, as we argued in the beginning. Understandably, for $R_{0,SSA} > R_{0,STA}$, g_{SS} falls off faster than g_{ST} , and vice versa. Note that, for different values of $R_{0,SSA}$, the midpoints of g_{ST} do not overlap, even though $R_{0,STA}$ itself is constant. Rather, a faster decay of g_{SS} induces a faster decay of g_{ST} as well. This stems from the fact that, in transient PL, triplet excitons are generated by ISC from singlet excitons. If $R_{0,SSA} > R_{0,STA}$, SSA imposes a correlation between the positions of singlet excitons before ISC can happen and, by the time triplets are generated, they are already farther apart than they would be through STA or TTA alone. Differently, when $R_{0,SSA} < R_{0,STA}$, STA the decay of the RDF, hence the g_{ST} midpoints correspond and virtually no correlation develops between the singlet positions.

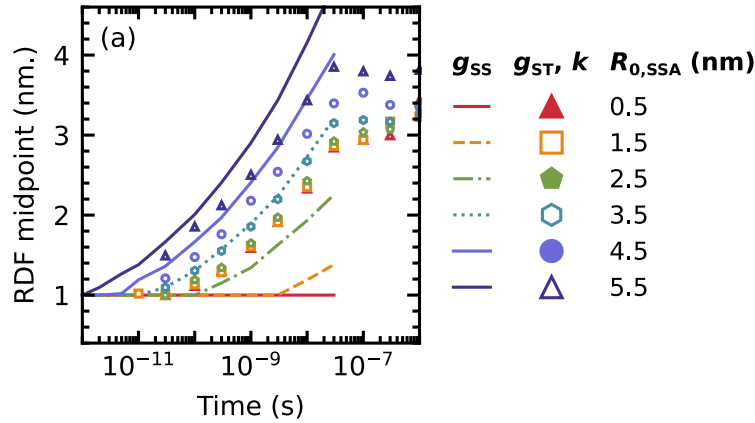


Figure S9. Midpoint of the radial distribution function g_{SS} (lines) and g_{ST} (symbols) as a function of time, parametric against the SSA Förster radius $R_{0,SSA}$. To avoid visual clutter, those data points for which the relative uncertainty on the RDF exceeds 10% are not displayed.

The fact that SSA and STA compete with and influence each other appears even more clearly from the dynamics of the annihilation coefficients. Figure S10b,c displays the coefficients for SSA (Figure S10b) and STA (Figure S10c) as a function of time, parametric against $R_{0,SSA}$ at fixed $R_{0,STA} = 3.5$ nm. At decreasing $R_{0,SSA}$, the SSA coefficient decreases in magnitude and, for $R_{0,STA} \leq 2.5$ nm, appears constant at early times. This effective time-independence is the result of $g_{SS}(r, t) \approx 1$, as no correlation between singlet positions develops. We can be sure this is an effect of negligible correlation, rather than the exciton diffusion compensating for the local depletion of excitons, as the dynamics of the SSA coefficient is identical if diffusion is disabled (Figure S11). More interestingly, at increasing $R_{0,SSA}$, the SSA coefficient also decreases. This decrease cannot simply relate to the (on average) lower triplet density for increasing $R_{0,SSA}$, as we have shown in the main text (Figure 7) that the annihilation coefficients do not depend on the exciton density. Rather, the reasoning is the same as above: because SSA produces a correlation between the positions of singlet exciton before the onset of ISC, once a sizable triplet population has developed, the average singlet-triplet distance is larger than it would be due to STA alone. In experimental terms, this direct interplay between SSA and STA – where the faster process determines the spatial distribution of both exciton species – means that annihilation coefficients extracted for a material may change when changing the microscopic annihilation parameters, e.g. shifting the emission spectrum by changing the host, hence affecting all Förster-mediated processes.

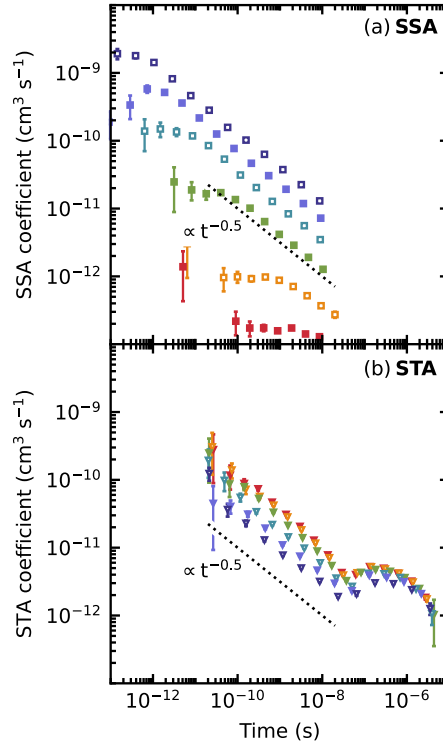


Figure S10. Annihilation coefficients for (a) SSA and (b) STA as a function of time, parametric against the SSA Förster radius $R_{0,\text{SSA}}$. The black dotted lines indicate a $\propto t^{-0.5}$ time dependence. SSA (STA) rates are not shown for $t \geq 10^{-8}$ s ($t \leq 10^{-11}$ s) due to large statistical noise.

S7. Further simulation results

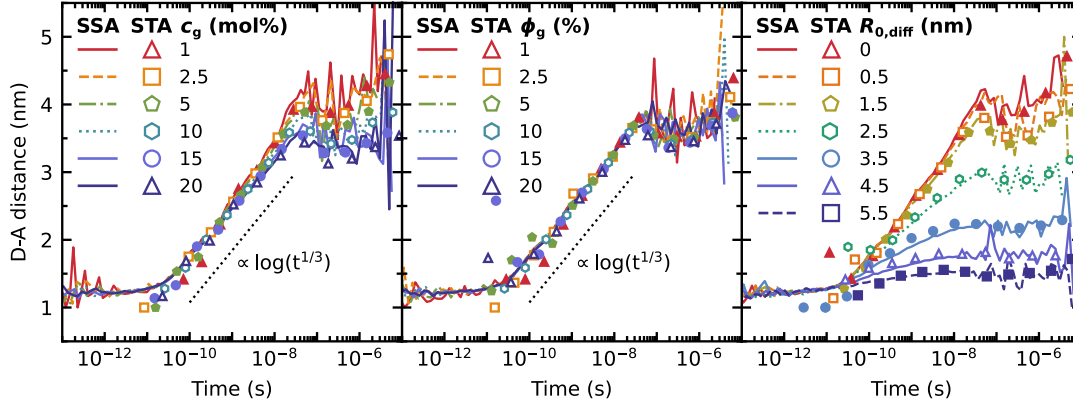


Figure S11. Average annihilation distance. Average exciton-exciton annihilation distance for SSA (lines) and STA (markers) as a function of time, parametric as (a) the guest concentration c , (b) the fraction of initially excited guest sites ϕ , and (c) the Förster radius for singlet diffusion $R_{0,STR}$. Default values for these parameters (i.e., when not indicated) are $c_g = 10$ mol%, $\phi_g = 10\%$, $R_{0,diff} = 1.5$ nm, and $R_{0,SSA} = R_{0,STA} = 3.5$ nm. The other parameters are as indicated in Table I of the main text.

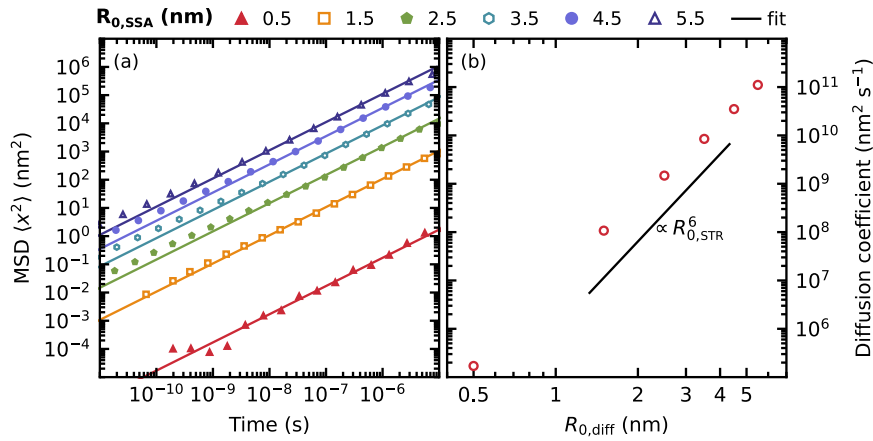


Figure S12. (a) Mean squared displacement (MSD, $\langle x^2 \rangle$) as a function of time, parametric against the Förster radius for singlet energy transfer $R_{0,STR}$. Continuous lines indicate fits to $\log\langle x^2 \rangle = D + \log(t)$, where the free parameter D is the diffusion coefficient. (b) Extracted diffusion coefficients as a function of $R_{0,STR}$, the black line indicates a $\propto (R_{0,STR})^6$ dependence.

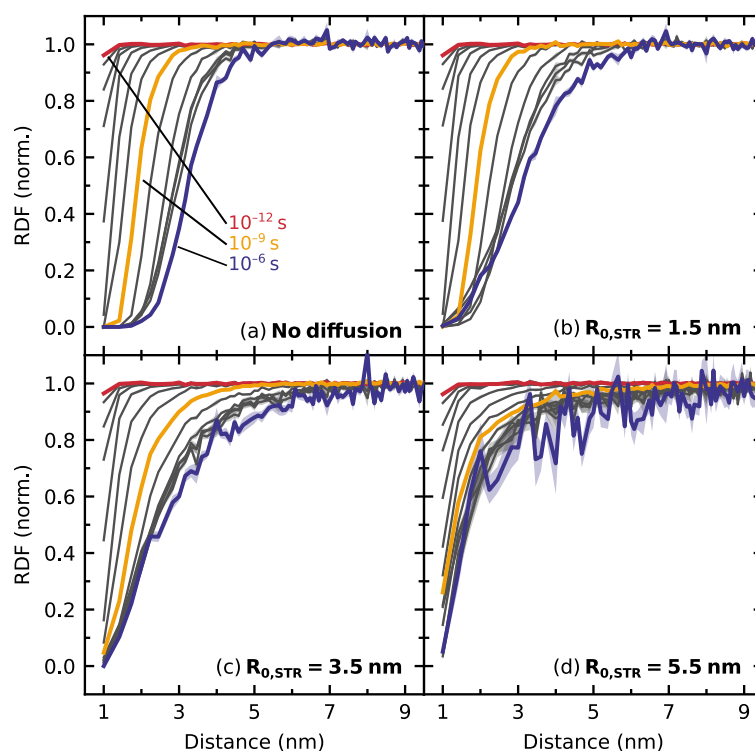


Figure S13. Cumulative radial distribution function $g(x, t)$ as a function of the exciton-exciton separation distance, parametric against time, for systems with varying Förster radii for singlet diffusion. All other parameters are as listed in Table I of the main text.

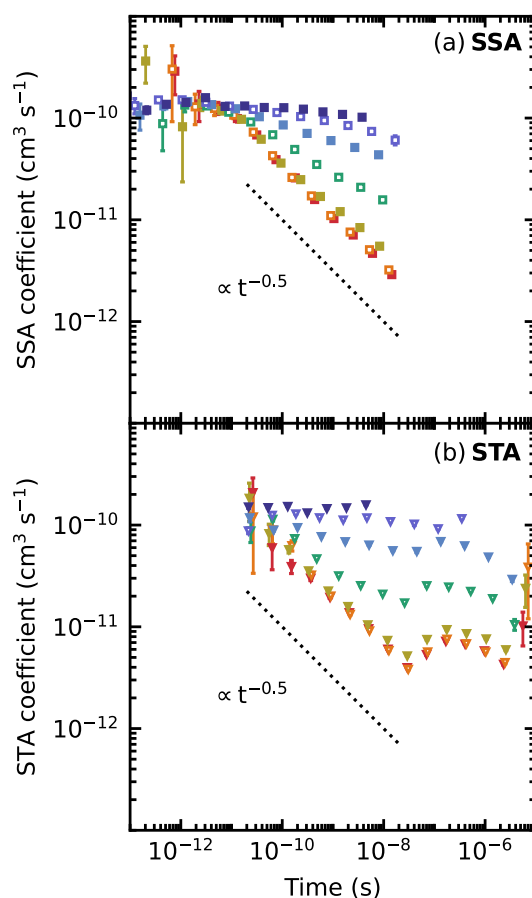


Figure S14. Annihilation coefficients for (a) singlet-singlet annihilation and (b) singlet-triplet annihilation as a function of time, parametric against the Förster radius for singlet exciton transfer $R_{0,\text{STR}}$ in a neat guest system ($c = 100\%$). All other parameters are as indicated in Table I of the main text. SSA (STA) rates are not shown for $t \geq 2 \cdot 10^{-8}$ s ($t \leq 10^{-11}$ s) due to large statistical noise. The black dashed line indicates a $t^{-0.5}$ dependence against time.

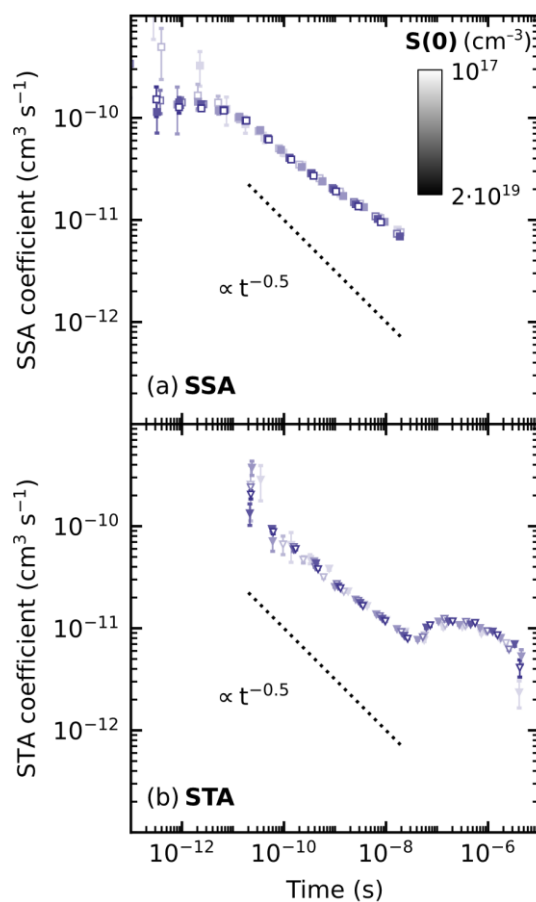


Figure S15. Annihilation coefficients for (a) singlet-singlet annihilation and (b) singlet-triplet annihilation as a function of time, parametric against the initial exciton density (colour gradient) in a host:10 mol% guest system with a Förster radius for singlet energy transfer $R_{0,\text{STR}} = 3.5$ nm. All other parameters are as indicated in Table I of the main text. SSA (STA) rates are not shown for $t \geq 10^{-8}$ s ($t \leq 10^{-11}$ s) due to large statistical noise. The black dashed line indicates a $\propto t^{-0.5}$ dependence against time.

Conclusions and outlook

In this thesis, we employed kinetic Monte Carlo simulations to connect molecular-scale processes to device-level performances, providing both mechanistic insight and practical guidance for improving the efficiency and stability of OLED devices.

Our results demonstrate that OLED performances depend not only on the intrinsic properties of the constituent materials, but also on morphological aspects. Namely, the nanoscale structure of organic-organic interfaces can influence the spatial distribution of charge carriers and excitons within the device. Although this redistribution does not appear to directly affect the device efficiency, focusing charge transport and high-energy exciton loss processes on a limited number of molecules may favour localised material degradation. Future work should assess the impact of such heterogeneous degradation on the device lifetime.

Beyond morphology, the alignment of the frontier orbital energy levels between the active layer components can also play a crucial role in determining the device efficiency. For hyperfluorescent devices, we identified the conversion of local excitons on the terminal emitter to dark intermolecular charge-transfer states as major loss mechanism. Further analysis led to the determination of directly applicable criteria for the choice of materials, in order to minimise such losses and improve the device efficiency.

Differently, bright charge-transfer states can play a beneficial role. For example, co-hosts capable of emission from the charge-transfer states are at the base of high efficiency devices. More fundamentally, emission from the charge-transfer state represents a direct link between spectroscopic observations and charge transport processes. We related the spectral diffusion of the charge-transfer state emission spectrum to the relaxation dynamics of charge carriers in an energetically disordered medium, and proposed a comprehensive framework able to bring together multiple experimental observations. Future work should increase the range of applicability of this model by including processes such as energy transfer from charge transfer states and bimolecular loss processes involving such states.

In fact, bimolecular processes such as exciton-exciton annihilation and exciton-polaron quenching represent some of the primary factors limiting OLED efficiency. In particular, exciton-exciton annihilation is often quantified through power-dependent transient photoluminescence measurements, prior to device applications. Despite the apparent simplicity of the measurement, our kinetic Monte Carlo simulations reveal a complex microscopic interplay between the spatially inhomogeneous depletion of the exciton population caused by annihilation and the homogenising effect of exciton diffusion. These findings highlight the importance of accounting for microscopic spatial heterogeneity when interpreting experimental measurements and extracting material parameters.

Overall, this thesis advances the organic electronics field by elucidating some factors that affect the dynamics of charge carriers and excitons in organic amorphous semiconductors, hence the efficiency of organic light emitting devices. Our work demonstrates the importance of considering the dynamics of charge and exciton phenomena at the microscopic scale, as enabled by kinetic Monte Carlo simulations. The resulting framework offers a powerful basis for the rational design of future OLED materials and architectures.

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Full list of publications

Publications included in this thesis

1. Giacomo Cotelli[‡], Engin Torun, Stefano Gottardi, and Anna Köhler. *Simulation of charge and exciton dynamics across nanostructured rough interfaces in Organic Light Emitting Devices*. In: Physical Review B 112.3 (July 2025), p. 035307. DOI: 10.1103/36kq-7pvt.
2. Rishabh Saxena[‡], Giacomo Cotelli[‡], Kleitos Stavrou, Engin Torun, Larissa G. Franca, Andrew P. Monkman, Stefano Gottardi, and Anna Köhler. *Sweet spot of energy-level alignment in hyperfluorescent organic light-emitting diodes*. In: Physical Review Applied 24.2 (Aug. 2025), p. 024064. DOI: 10.1103/k967-sr56.
3. Giacomo Cotelli[‡], Anna Köhler, and Reinder Coehoorn. *Spectral diffusion due to charge carrier relaxation of intermolecular charge-transfer states in donor:acceptor blends of disordered organic semiconductors*. Under review for Physical Review Applied.
4. Giacomo Cotelli[‡] and Anna Köhler. *The rates are not what they seem: understanding the time dependence of exciton-exciton annihilation “constants” in a TADF system*. Ready for submission.

Publications not included in this thesis

1. Christian McDonald[‡], Hiroki Tomita, Giacomo Cotelli, Louka L. Brüll, Nanno G. de Rooij, Lucas R. L. Norg, and Reinder Coehoorn. *Large-scale determination of frontier orbital energies of disordered small-molecule organic semiconductors using exciplex emission spectra*. In: Advanced Materials (May 2026), DOI: 10.1002/adma.73113.
2. Andrea Delledonne[‡], Guillem Vargas-Nadal[‡], Giacomo Cotelli, Nora Ventosa, Mariana Köber, and Cristina Sissa. *Quatsomes as versatile fluorescent nanocarriers: stable Eosin Y loading and FRET with a membrane dye*. In: Nanoscale Advances (May 2026), DOI: 10.1039/d6na00124f.

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E ora... **poof**

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puf

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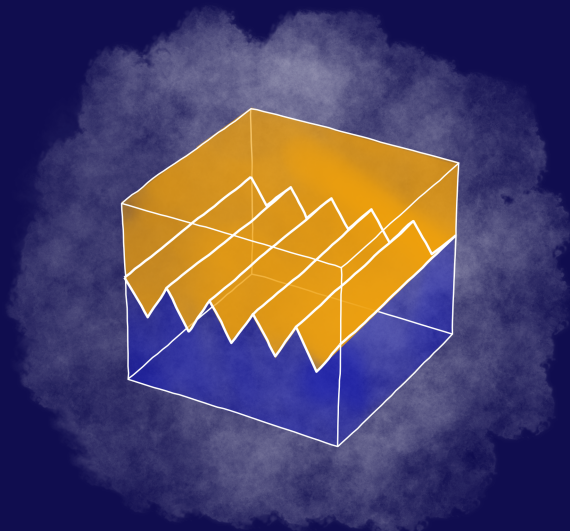
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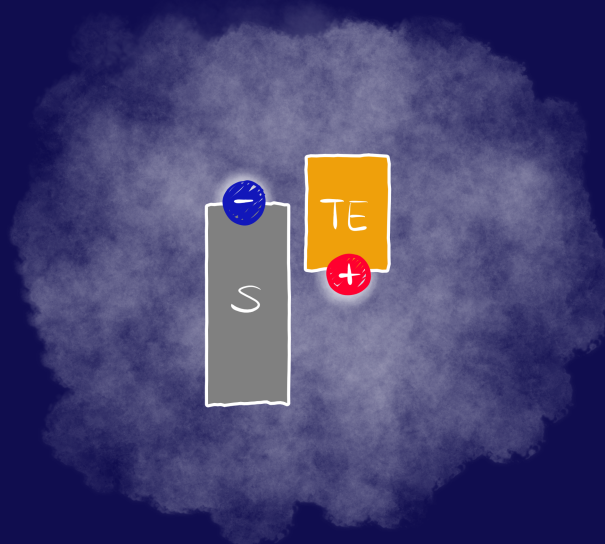
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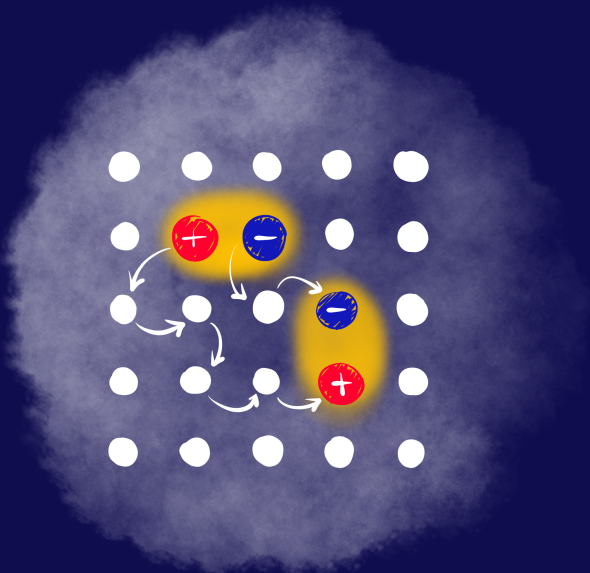
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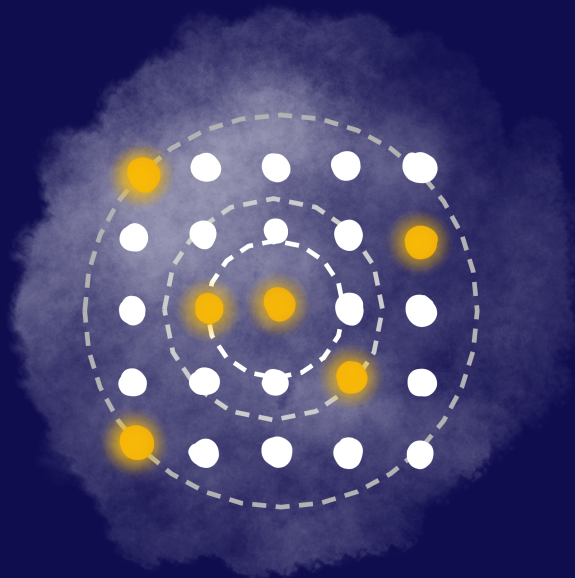
Rough interfaces



Hyperfluorescent OLEDs



Charge-transfer state emission



Exciton-exciton annihilation



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