
The Signatures of Intermolecular Interactions in PM6 and Y6 and their Role in High-Efficiency Solar Cells

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Abstract

The efficiency of organic solar cells is strongly influenced by the microscopic morphology and intermolecular interactions within the active layer. In particular, the donor–acceptor system PM6:Y6 has emerged as a benchmark material combination, yet the mechanisms by which molecular packing, electronic coupling, and the character of intermolecular interaction influence exciton and charge-generation dynamics are still not fully understood. This thesis investigates how aggregation and intermolecular coupling dictate the optoelectronic properties of PM6:Y6 and related Y-type acceptors by combining steady-state and transient optical spectroscopy, energy-resolved electrochemical impedance spectroscopy, and Franck–Condon analysis. The combination of PM6:Y6 serves as exemplary prototype for the wide range of available donor:acceptor combinations.

My investigations with temperature-dependent absorption and photoluminescence measurements reveal that both Y6 and its structural derivative N4 form distinct types of aggregates in solution. The aggregates differ in interaction strength and excitonic coupling. I find that Y6 predominantly adapts J-type interactions, while N4 initially forms H-like aggregates that gradually reorient toward more J-like configurations upon thermal annealing. These aggregation motifs persist in blend films and correlate with the differing photovoltaic efficiencies of PM6:Y6 and PM6:N4 devices. The spectroscopic identification of interacting and non-interacting molecular phases enables a quantitative deconvolution of their contributions in neat and blend films. This provides a direct link between molecular packing and energetic landscape.

With this insight I aimed to understand why charge-transfer (CT) state dissociation in PM6:Y6 is not thermally activated. To quantify the binding energy of the CT state, the density-of-states distributions of the HOMO and LUMO levels were determined using energy-resolved impedance spectroscopy. A surprisingly low CT binding energy of approximately 150 meV was found, which is far below the expected value for localized charges at a nanometer separation. This reduction arises from hole delocalization along the PM6 backbone and electron delocalization in aggregated Y6. As a result of this low binding energy, the dissociation yield is no longer controlled by the dissociation rate and hence becomes independent of thermal activation.

To further disentangle the exciton and charge generation dynamics of interacting and non-interacting Y6, I turned to pump-probe measurements. By controlling aggregation in dilute solution and correlating steady-state spectra with ultrafast transient absorption measurements, I could assign the characteristic spectral signatures of both phases unambiguously. Interacting Y6 exhibits exciton dynamics dominated by singlet–singlet annihilation (SSA) with lifetimes of

30–200 ps, whereas non-interacting Y6 shows a fluence-independent decay with a lifetime of about 1 ns. At longer delay times, a persistent spectral feature is identified as a polaronic state residing on interacting Y6. These findings support the notion of an ultrafast, Onsager-like autoionization mechanism in which delocalized excitons residing on aggregates can dissociate. The required excess energy for charge separation is either provided by the SSA process or by direct excitation with high energy photons. Nevertheless, the overall polaron yield remains moderate (approximately 8 %), consistent with other organic semiconductors. This contradicts current interpretations of particularly highly efficient dissociation pathways.

Together, the results of this thesis establish a comprehensive spectroscopic framework for understanding the charge photogeneration process in donor-acceptor blends consisting of interacting and non-interacting chromophores. My results elucidate how aggregation-dependent electronic coupling governs exciton delocalization, CT-state energetics, and, hence, charge generation pathways. These insights contribute to a deeper understanding of structure–property relationships in high-performance organic solar cells.

Deutsche Zusammenfassung

Die Effizienz organischer Solarzellen wird stark von der mikroskopischen Morphologie und den intermolekularen Wechselwirkungen innerhalb der aktiven Schicht beeinflusst. Insbesondere das Donor-Akzeptor-System PM6:Y6 hat sich als Referenzmaterialkombination herauskristallisiert, doch die Mechanismen, durch die Molekülpackung, elektronische Kopplung und die Art der intermolekularen Wechselwirkung die Dynamik der Exzitonen- und Ladungserzeugung beeinflussen, sind noch nicht vollständig verstanden. Diese Arbeit untersucht, wie Aggregation und intermolekulare Kopplung die optoelektronischen Eigenschaften von PM6:Y6 und verwandten Y-Type-Akzeptoren bestimmen, indem sie stationäre und transiente optische Spektroskopie, energieaufgelöste elektrochemische Impedanzspektroskopie und Franck-Condon-Analyse kombiniert. Die Kombination PM6:Y6 dient als exemplarischer Prototyp für die Vielzahl der verfügbaren Donor-Akzeptor-Kombinationen.

Temperaturabhängige Absorptions- und Photolumineszenzmessungen zeigen, dass sowohl Y6 als auch sein strukturelles Derivat N4 in Lösung unterschiedliche Arten von Aggregaten bilden. Die Aggregate unterscheiden sich in ihrer Wechselwirkungsstärke und ihrer Exzitonenkopplung. Ich finde, dass Y6 überwiegend J-Type-Wechselwirkungen annimmt, während N4 zunächst H-ähnliche Aggregate bildet, die sich bei thermischer Behandlung allmählich zu eher J-ähnlichen Konfigurationen umorientieren. Diese Aggregationsmotive bleiben in Blendfilmen bestehen und korrelieren mit den unterschiedlichen Wirkungsgraden von PM6:Y6- und PM6:N4 Solarzellen. Die spektroskopische Identifizierung von interagierenden und nicht-interagierenden molekularen Phasen ermöglicht eine quantitative Zerlegung ihrer Beiträge in reinen und Blendfilmen. Dies stellt einen direkten Zusammenhang zwischen molekularer Packung und energetischer Landschaft her.

Mit dieser Erkenntnis wollte ich herausfinden, warum die Dissoziation des Ladungstransferzustands (CT) in PM6:Y6 nicht thermisch aktiviert wird. Um die Bindungsenergie des CT Zustandes zu quantifizieren habe ich die Zustandsdichteverteilungen der HOMO- und LUMO-Niveaus mittels energieaufgelöster Impedanzspektroskopie bestimmt. Es wurde eine überraschend niedrige CT-Bindungsenergie von etwa 150 meV festgestellt, die weit unter dem erwarteten Wert für lokalisierte Ladungen bei einem Abstand im Nanometerbereich liegt. Diese Verringerung resultiert aus der Delokalisierung von Löchern entlang des PM6-Rückgrats und der Delokalisierung von Elektronen in aggregiertem Y6. Aufgrund dieser geringen Bindungsenergie wird die Dissoziationsausbeute nicht mehr von der Dissoziationsrate bestimmt und ist somit unabhängig von der thermischen Aktivierung.

Um die Dynamik der Exziton- und Ladungserzeugung bei wechselwirkendem und nicht wechselwirkendem Y6 weiter zu entwirren, habe ich auf Pump-Probe-Messungen zurückgegriffen. Durch kontrollierte Aggregation in verdünnter Lösung und die Korrelation von Steady-State-Spektren mit ultraschnellen transienten Absorptionsmessungen konnte ich die charakteristischen spektralen Signaturen beider Phasen eindeutig zugeordnen. Interagierendes Y6 zeigt eine Exzitodynamik, die von Singulett-Singulett-Annihilation (SSA) mit Lebensdauern von 30–200 ps dominiert wird, während nicht interagierendes Y6 einen fluenzunabhängigen Zerfall mit einer Lebenszeit von etwa 1 ns aufweist. Bei längeren Verzögerungszeiten wird ein langlebiges Spektralmerkmal als Polaronenzustand identifiziert, der auf interagierendem Y6 sitzt. Diese Ergebnisse stützen die Vorstellung eines ultraschnellen, Onsager-ähnlichen Autoionisationsmechanismus, bei dem delokalisierte Exzitonen auf Y6 Aggregaten dissoziieren können. Die für die Ladungstrennung erforderliche überschüssige Energie wird entweder durch den SSA-Prozess oder durch direkte Anregung mit hochenergetischen Photonen bereitgestellt. Die Polaronausbeute bleibt jedoch moderat (etwa 8 %), was mit anderen organischen Halbleitern übereinstimmt. Dies steht im Widerspruch zu derzeitigen Interpretationen von besonders hocheffizienter Excitonendissoziation.

Insgesamt liefern die Ergebnisse dieser Arbeit einen umfassenden spektroskopischen Rahmen für das Verständnis des Ladungserzeugungsprozesses in Donor-Akzeptor-Mischungen, die aus wechselwirkenden und nicht wechselwirkenden Chromophoren bestehen. Meine Ergebnisse erläutern, wie die aggregationsabhängige elektronische Kopplung die Delokalisierung von Exzitonen, die Energie des CT-Zustands und somit die Wege der Ladungserzeugung steuert. Diese Erkenntnisse tragen zu einem tieferen Verständnis der Struktur-Eigenschafts-Beziehungen in hocheffizienten organischen Solarzellen bei.

Declaration

I, Daniel Kroh, confirm that:

- This thesis comprises only my original work, except where indicated in the preface.
- Due acknowledgement has been made in the text to all other materials used.
- The thesis is less than 100,000 words in length exclusive of tables, bibliographies, and appendices.

Signature:

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Preface

Acknowledgments

The fact that this thesis exists in written form is thanks to the support of many people who accompanied me on this journey and encouraged me over the past years. I would like to take this opportunity to thank them.

First, I want to thank Prof. Anna Köhler, my supervisor on the German side. During my master's, she gave me the opportunity to spend several months in David Jones' group at the University of Melbourne, and later supported and encouraged me to embark on this Joint PhD. You also helped me regain focus whenever projects grew too large and I started to lose track. I am also deeply grateful to Heinz, who patiently shared his extensive knowledge and expertise, and with whom I had many productive and insightful discussions.

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Thank you.

Publications included in this thesis

Identifying the signatures of intermolecular interactions in blends of PM6 with Y6 and N4 using absorption spectroscopy

Daniel Kroh, Fabian Eller, Konstantin Schötz, Stefan Wedler, Lorena Perdigón-Toro, Guillaume Freychet, Qingya Wei, Maximilian Dörr, David Jones, Yingping Zou, Eva M. Herzig, Dieter Neher, Anna Köhler

in *Advanced Functional Materials*, 32 (44), 2205711, (2022)

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AK and DN initiated the project. **DK planned the experiments. DK prepared all samples, conducted all temperature-dependent steady-state absorption and photoluminescence experiments and analyzed the data** with support of SW and KS. SW and MD had carried out preliminary studies. QW synthesized the N4 molecule under the supervision of YZ. GF measured GIWAXS of the blend samples according to instructions by FE and EMH, and FE measured GIWAXS of the neat samples. FE performed the data analysis of all GIWAXS measurements under the supervision of EMH. FE, guided by EMH, provided a draft for the GIWAXS-section of the manuscript. DJ, LPT, DN, FE and EMH provided conceptual ideas regarding the interpretation of the film morphology. **DK outlined and wrote the manuscript.** AK edited the manuscript. All authors critically read the manuscript and commented on the manuscript. AK supervised the project. This paper constitutes **Chapter 6**.

An impedance study of the density of states distribution in blends of PM6:Y6 in relation to barrierless dissociation of CT states

Daniel Kroh, Stavros Athanasopoulos, Vojtech Nádaždy, Frank-Julian Kahle, Heinz Bässler, Anna Köhler

in *Advanced Functional Materials*, 34 (50), 2302520, (2024)

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DK and HB conceived the project together with AK. DK planned all experiments. DK prepared the samples for the IQE measurements and performed the experiment with assistance from FJK. VN prepared the samples for the ER-EIS experiments and performed ER-EIS measurements. **DK analyzed the IQE and ER-EIS data.** SA performed the kinetic Monte Carlo simulations. **DK interpreted all data and discussed the findings with HB and AK. DK, together with HB and SA wrote the manuscript.** AK revised and finalized the manuscript. All authors critically read and commented on the manuscript. AK supervised the project. This paper constitutes **Chapter 7**.

Disentangling polaron formation pathways in Y6 probing non-interacting and interacting chromophores via transient absorption spectroscopy

Daniel Kroh, Xinyue Xu, Trevor Smith, Anna Köhler

Unpublished material in preparation for publication but not yet submitted, including preprints

Preliminary author contributions statement.

DK conceived and planned the project together with AK, DK performed all measurements, collected, analyzed, and first interpreted the data. DK was supported by XX in measurement techniques and data processing. DK wrote a first draft of the manuscript. AK edited the manuscript. All authors critically read the manuscript and commented on the manuscript. AK and TS supervised the project.

This paper constitutes **Chapter 8**.

Contents

English Abstract	1
German Abstract	3
Declaration	5
Preface	7
Acknowledgments	7
Publications included in this thesis	9
1 Motivation	19
2 Fundamentals	23
2.1 From isolated to condensed phase	23
2.1.1 Franck-Condon principle	23
2.1.2 Optical signatures of environmental effects and intermolecular interactions	27
2.1.3 Aggregation in solution and in film	32
2.1.4 Morphology in condensed phase	35
2.2 State of the art OPV materials and their morphological properties	38
3 Experimental Methods	43
3.1 Temperature-dependent steady-state UV-VIS absorption and photoluminescence setup	43
3.2 Transient Absorption Spectroscopy	44
4 References	49
5 Overview of the thesis	67
6 Signatures of Intermolecular Interactions	69
7 DOS Distribution in Blends of PM6:Y6	101
8 Excitation Kinetics of interacting and non-interacting Y6	111
9 Conclusion and Outlook	167

Eidesstattliche Versicherung

171

List of Figures

1.1	OPV applications	19
1.2	Principle of an organic solar cell	20
1.3	Chemical structure of Y6 and PM6	21
1.4	Schematic of bulk hetero junction solar cell	22
2.1	Franck-Condon principle	24
2.2	Environmental influence on the ground and excited state of a chromophore . .	27
2.3	Impact of different solvent environments on Absorption and PL of Y6	28
2.4	Energy level modifications by H- and J- type interactions	30
2.5	Influence of morphology on the optical spectra	34
2.6	Spectral deconvolution of absorption and amission of interacting and non-interacting P3HT	36
2.7	Development of power conversion efficiencies for organic solar cells	39
2.8	Molecular packing of Y6	40
3.1	Home-built temperature-dependent absorption and PL setup	43
3.2	Principle of transient absorption spectroscopy	46
3.3	Transient absorption spectroscopy setup	47
5.1	Thesis Overview	67

List of abbreviations

A Acceptor

BHJ Bulk Heterojunction

C-C Core-to-Core

CCD Charge-Coupled Device

C-T Core-to-Terminal

cH Cyclohexane

CT Charge Transfer

D Donor

DFT Density Functional Theory

DOS Density of States

ER-EIS Energy-Resolved Electrochemical Impedance Spectroscopy

ES Excited State

ESA Excited-State Absorption

FC Franck-Condon

GIWAXS Grazing-Incidence Wide-Angle X-ray Scattering

GS Ground State

GSB Ground-State Bleach

HOMO Highest Occupied Molecular Orbital

InGaAs Indium Gallium Arsenide

IQE Internal Quantum Efficiency

LUMO Lowest Unoccupied Molecular Orbital

MD Molecular Dynamics

ND Neutral Density

NFA Non-Fullerene Acceptor

NIR Near-Infrared

OD Optical Density

OFET Organic Field-Effect Transistor

OLED Organic Light-Emitting Diode

OPV Organic Photovoltaic

OSC Organic Solar Cell

PCE Power Conversion Efficiency

PL Photoluminescence

SAXS Small-Angle X-ray Scattering

SE Stimulated Emission

TA Transient Absorption

TAS Transient Absorption Spectroscopy

THF Tetrahydrofuran

TRPL Time-Resolved Photoluminescence

T-T Terminal-to-Terminal

UV-VIS Ultraviolet-Visible

$\lambda/2$ **plate** Half-Wave Plate

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1 Motivation

The ability to tune the electronic, optical, thermal and mechanical properties through molecular design, makes organic semiconductors a versatile class of functional materials for a broad range of applications ranging from organic light-emitting diodes (OLEDs),^{1–6} organic field-effect transistors (OFETs),^{7–12} organic solar cells (OSCs),^{13–16} wearable sensors, and supercapacitors.^{17–19}

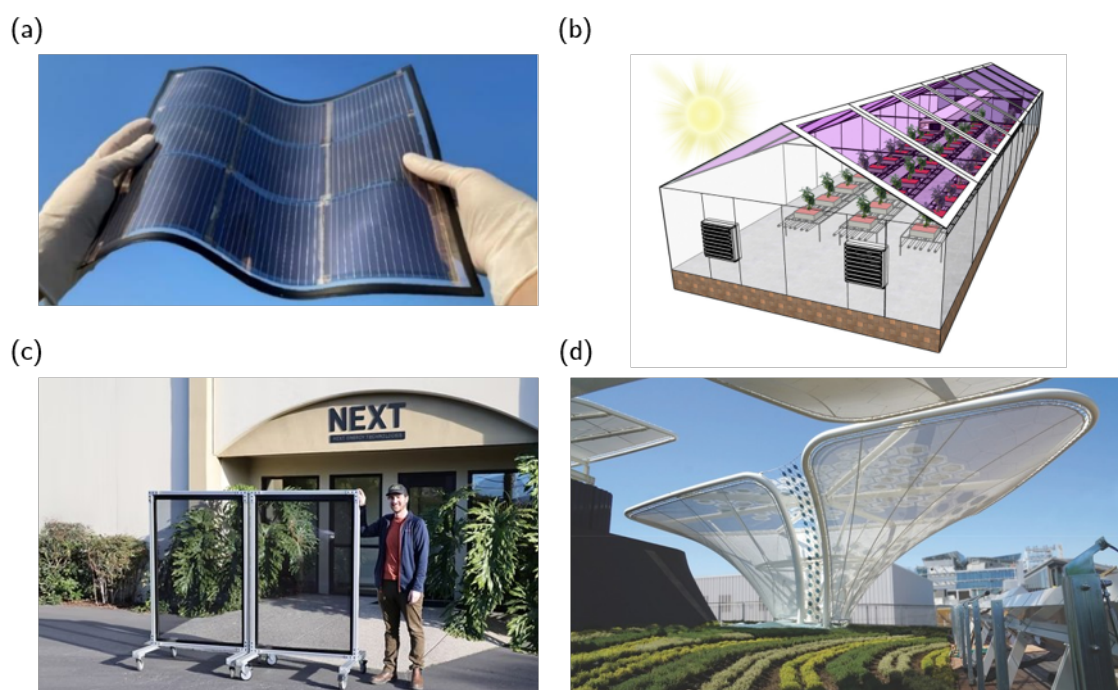


Figure 1.1: Examples of OPV applications. (a) Flexible OPV module, reproduced with permission.²⁰ (b) Conceptual model of a net-zero greenhouse featuring an OPV-integrated roof, reproduced with permission.²¹ (c) Transparent solar windows used as facades, canopies, or balustrades by NEXT Energy Technologies, reproduced with permission from NEXT. (d) Solar tree installation incorporating OPV modules as design elements at the Universal Exhibition Milan 2015. Image from Berny et al. with permission.²²

Devices based on organic semiconductors have developed over the years and have arrived in our everyday life. Especially OLED displays have become commercially relevant and can be found in various screen sizes in televisions and smartphones. Their lightweight and flexible nature has enabled the development of the latest generation of smartphones, known as foldables, which

rely on bendable OLED displays representing a paradigm shift in portable electronics. While OLEDs have already conquered the commercial market, OSCs are still in an earlier stage of commercialization, yet recently important milestones have been achieved. Most notably, the power conversion efficiencies (PCEs) of laboratory-scale devices have exceeded the 20 % mark,^{23–25} and also large scale efficiencies improved to 14.5 %.²⁶ Despite not yet reaching the PCEs of inorganic semiconductors for large-scale outdoor power generation, OSCs offer compelling advantages such as mechanical flexibility, semitransparency, color tunability, and a compatibility with roll-to-roll printing processes,^{22, 27–30} which allows for low-cost production. These properties, which distinguish organic from inorganic semiconductors, are already being used for novel applications. The integration of semi-transparent OPVs enables, for example, net-zero energy greenhouses,^{21, 31–33} flexible building-integrated photovoltaics, and large-scale transparent solar windows for energy-efficient urban planning.^{20, 34–39} (see Figure 1.1)

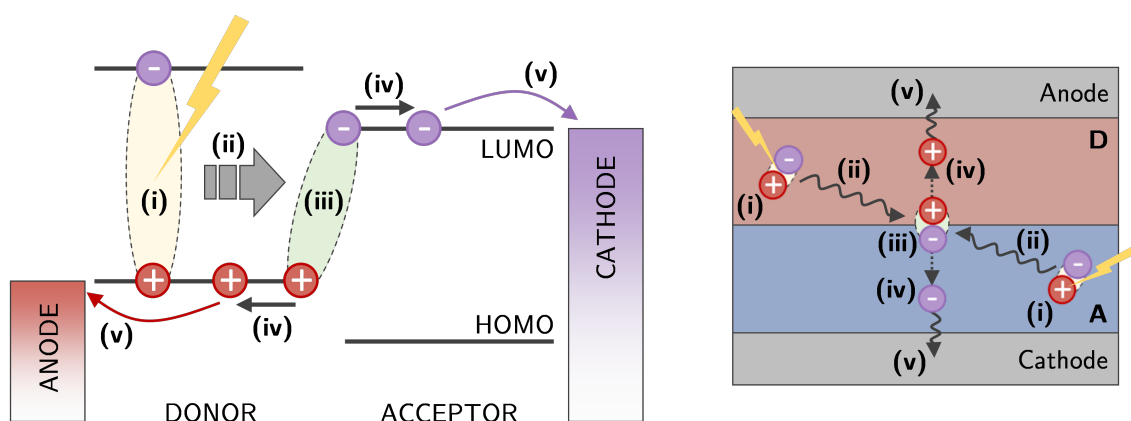


Figure 1.2: Schematic illustration of the operating principle of an organic solar cell, showing the molecular frontier orbitals (HOMO and LUMO) of the donor and acceptor materials together with the electrode work functions. The energy level alignment corresponds to open-circuit conditions. The text discusses the sequence of processes from exciton formation to charge generation. The schematic on the right depicts these processes for a donor–acceptor bilayer OPV architecture.

In contrast to inorganic semiconductors such as silicon, where light absorption leads to efficient generation of free charges, in thin films of organic semiconductors, absorption of photons results in strongly bound excitons.⁴⁰ Due to exciton binding energies significantly larger than the thermal energy at room temperature, simply sandwiching a layer of organic semiconductor between electrodes results in low efficiencies. To improve exciton dissociation, the active layer in an organic solar cell therefore consists of two components: an electron donor (D) and an electron acceptor (A) material. This active layer is sandwiched between electrodes, and additional functional interlayers serve to optimize electron and hole extraction. Figure 1.2 depicts the energy levels of the lowest unoccupied molecular orbital (LUMO) and highest occupied

molecular orbital (HOMO) for D and A compounds as well as the work function levels of the electrodes. Additionally, the stepwise processes from light absorption to charge extraction are indicated. First, the absorption of a photon leads to the creation of an exciton, typically dominantly in the D compound (i). The exciton is a tightly-bound electron-hole pair with close proximity and can be created anywhere in the bulk, so it must first diffuse to the D-A interface (ii). Here, the formation of an interfacial charge transfer (CT) state takes place as the electron transfers from the LUMO of the D to the LUMO of the A (iii). In current state-of-the-art materials, the A compound also takes part in the light harvesting process. In the case of exciton generation in the A material, the CT state forms through hole transfer from the A HOMO to the D HOMO. Further, the CT states need to dissociate into free charges. Usually, an electric field is applied to overcome the mutual Coulomb attraction of the electron-hole pair (iv). The free charges diffuse to the electrodes, where they are extracted from the device (v).

To develop an efficient organic solar cell, each step from light absorption to charge extraction needs to be optimized as each step contributes to the overall efficiency. However, most of these processes cannot be optimized individually, but are interconnected in some way. In recent years, it has become clear that the morphology of the active layer plays a crucial role.^{41–47} While intermixing of D and A domains increases the interface, beneficial for exciton dissociation, too much intermixing hinders the charge extraction due to lack of percolation paths for the charge carriers to move to the electrode. Further, the performance of OPVs does not only depend on the chemical and inherent electronic structure of the materials, but rather on the morphological organization. Intermolecular coupling and the resulting molecular conformations and arrangements in molecular aggregates directly govern exciton and charge mobilities, promote exciton delocalization and define the energetic landscape for charge generation.^{48–52}

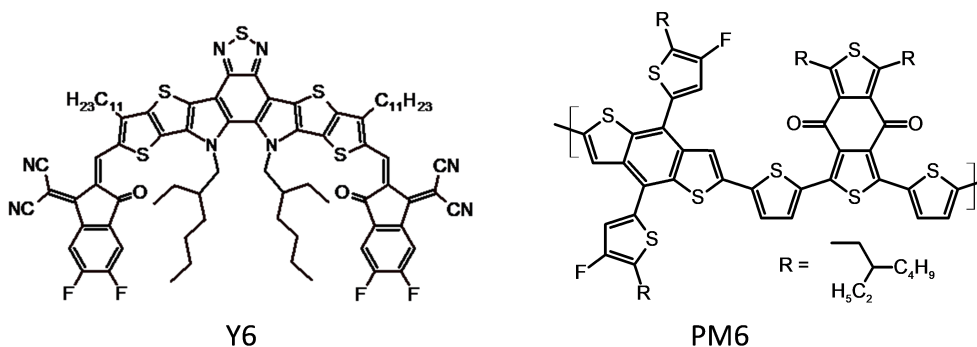


Figure 1.3: Chemical structure of Y6 and PM6.

This demonstrates the importance of a fundamental understanding of the structure-property relationship, which has recently attracted considerable attention in research, particularly with the introduction of current high-efficient OPV material systems. In earlier generations the

acceptor served mainly as a passive electron-accepting unit, while the newest generation of acceptors, so called Y-type acceptors, actively participate in the charge generation process. As the active layer of a bulk hetero-junction (BHJ) OPV consists of a mixture of domains characterized by short-range order and amorphous regions of both, donor and acceptor compounds, the task of disentangling structure-property relations becomes more and more complex. This thesis aims to first disentangle the spectroscopic signatures, character and dynamics of the non-interacting and interacting phase of state-of-the-art OPV materials focusing on the polymer electron donor PM6 and non-fullerene acceptor (NFA) Y6, which chemical structures are displayed in Figure 1.3. Further, I investigated the impact of aggregation on the opto-electronic properties, in the neat material as well as in the blend.

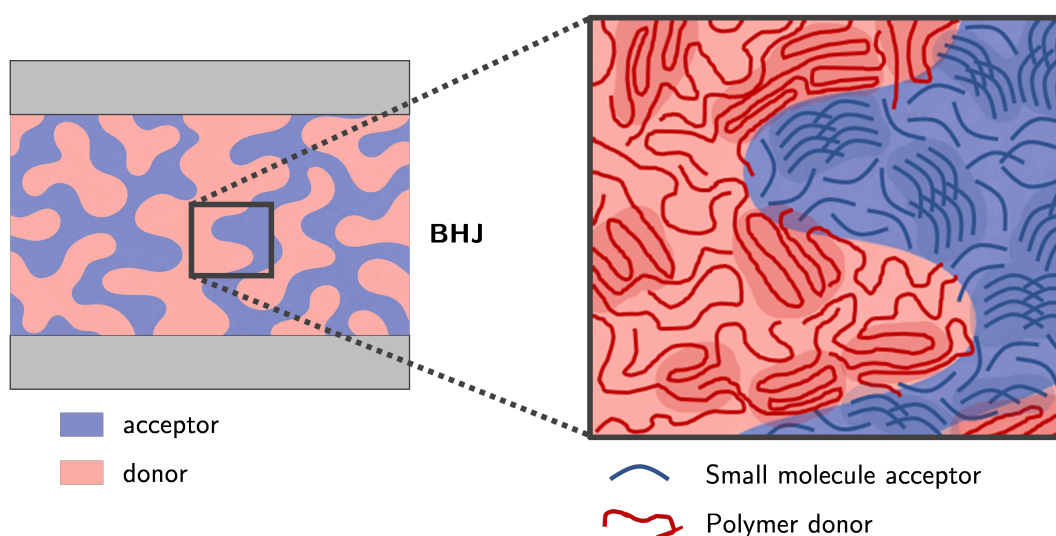


Figure 1.4: Schematic of a bulk hetero junction (BHJ) of a polymer electron donor (red) and molecular electron acceptor (blue) with loosely and tightly packed regions, respectively. The darker colors highlight domains where tight molecular packing allows for intermolecular interactions.

This thesis is structured in two main parts. Part I provides an overview of the current state of research, relevant theoretical background and concepts, and my own contributions. Chapter 2 introduces the fundamental theoretical concepts that enable conclusions to be drawn about local structural order using optical spectroscopy and summarizes the current state of research about Y6 and its derivatives. Chapter 3 describes the main methods and setups used for optical spectroscopy in this thesis. Chapter 5 presents my publications, that are incorporated in this thesis, and their contribution to the main research question. Finally, Part II contains reprints of the publications that constitute the core scientific contributions of this work.

2 Fundamentals

The electronic structure of a molecule and the transitions between its electronic states determine its fundamental photophysical behavior. As the shape and energetic positions of absorption and emission spectra are highly sensitive to both intra- and intermolecular interactions, optical spectroscopy is a powerful tool to investigate the influence of molecular interactions on excited-state energetics and dynamics. This chapter summarizes the key concepts required to describe and interpret optical spectra, from isolated molecules to condensed phase systems, as relevant for the analyses presented in this thesis. Further this chapter covers the morphological characteristics and their impact on the optoelectronic properties of state-of-the-art OPV materials focusing on the electron acceptor material Y6.

2.1 From isolated to condensed phase

2.1.1 Franck-Condon principle

Optical transitions in molecules are intrinsically coupled to nuclear motion. The nuclei vibrate about their equilibrium positions with characteristic frequency ω , giving vibrational energy levels $(n + 1/2)\hbar\omega$ for the vibrational quantum number n . Coupling between electronic transitions and these vibrations follow from the Born-Oppenheimer approximation, which exploits the large mass difference between electrons and nuclei. Electronic dynamics occur on much faster timescales than nuclear motion, so an electronic transition can be treated as occurring at fixed nuclear geometry. Under this separation the total wavefunction factorizes into independent electronic (Ψ_{el}), vibrational (Ψ_{vib}) and spin (Ψ_{spin}) contributions:^{53, 54}

$$\Psi_{\text{total}} = \Psi_{\text{el}} \Psi_{\text{spin}} \Psi_{\text{vib}} \quad (2.1)$$

By Fermi's golden rule the rate of an optical transition between an initial $|\Psi_i\rangle$ and a final state $|\Psi_f\rangle$ is proportional to the squared modulus of the transition dipole matrix element $|\mu|^2 = |\langle\Psi_f|e\hat{\mathbf{r}}|\Psi_i\rangle|^2$. The dipole operator $e\hat{\mathbf{r}}$ acts only on the electronic coordinates because electrons respond to the optical timescale, whereas the heavy nuclei and the spins do not. Consequently

the matrix element separates into electronic, vibrational and spin contributions:

$$|\mu|^2 = |\langle \Psi_{\text{el},f} | e\tilde{\mathbf{r}} | \Psi_{\text{el},i} \rangle|^2 \cdot |\langle \Psi_{\text{vib},f} | \Psi_{\text{vib},i} \rangle|^2 \cdot |\langle \Psi_{\text{spin},f} | \Psi_{\text{spin},i} \rangle|^2 \quad (2.2)$$

These three factors have distinct physical meanings and define the probability of an optical transition. The spin overlap $|\langle \Psi_{\text{spin},f} | \Psi_{\text{spin},i} \rangle|^2$ enforces spin selection rules and is nonzero only for transitions that conserve total spin. The electronic matrix element $|\langle \Psi_{\text{el},f} | e\tilde{\mathbf{r}} | \Psi_{\text{el},i} \rangle|^2$ determines whether a transition is allowed by electronic selection rules and sets the overall oscillator strength. The vibrational overlap $|\langle \Psi_{\text{vib},f} | \Psi_{\text{vib},i} \rangle|^2$, known as the Franck-Condon factor, controls the relative intensities of vibronic peaks and thus the detailed shape of absorption and emission spectra. The Franck-Condon factor is computed from the overlaps of vibrational wavefunctions expressed in the molecule's normal coordinates Q , and it quantifies how changes in nuclear configuration between electronic states distribute intensity among the vibronic transitions.

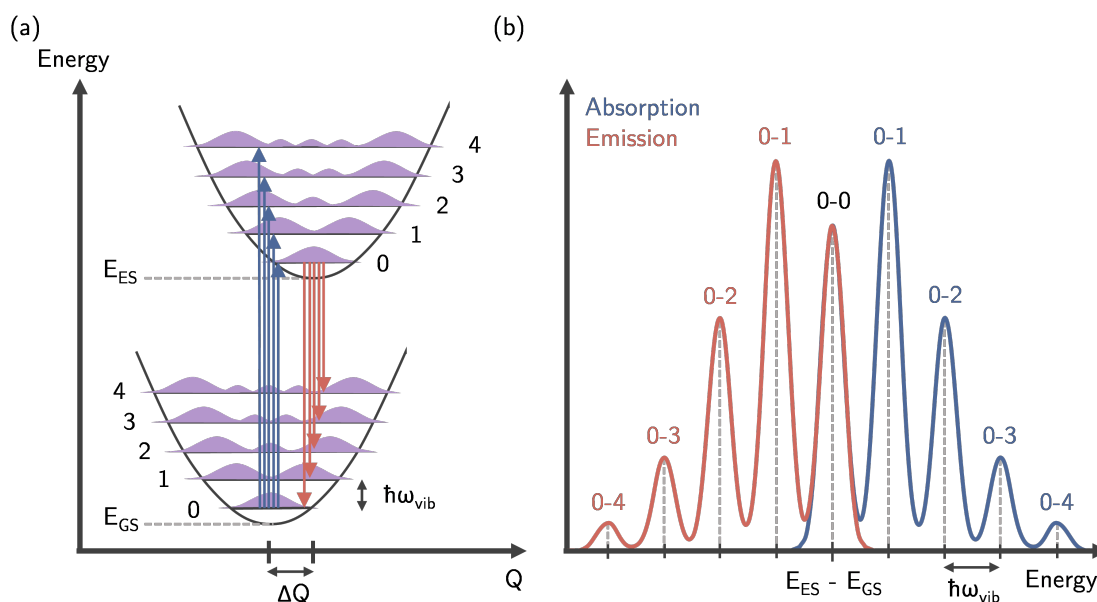


Figure 2.1: Illustration of the Franck–Condon principle. (a) Electronic potential-energy surfaces of the ground state (GS) and excited state (ES) along a generalized coordinate Q within the harmonic approximation. The GS and ES minima are displaced by ΔQ . The first five vibrational levels, separated by $\hbar\omega_{\text{vib}}$, are shown together with their probability densities (purple) for both states. Vertical arrows indicate electronic transitions: absorption in blue and emission in red. (b) Representative absorption and emission spectra arising from Franck–Condon transitions.

For most organic molecules the vibrational potential of both the electronic ground and excited states are well approximated by harmonic oscillators.⁵⁵ In this approximation the ground- and excited-state potential energy surfaces are represented by two harmonic wells that are displaced relative to one another by a coordinate shift ΔQ , while they share the same vibrational spacing

$\hbar\omega_{\text{vib}}$. Because typical vibrational quanta (on the order of 100-300 meV) exceed thermal energies at room temperature, optical absorption usually originates from the vibrational ground state ($n = 0$) of the electronic ground state.

Electronic excitation commonly promotes an electron into a less bonding (often antibonding) orbital, which reduces electron density between nuclei and increases the equilibrium bond length in the excited state. This leads to a displacement ΔQ of the potential energy surface of the excited state. Since nuclei are comparatively heavy and cannot follow the ultrafast oscillation of the optical field, the electronic transition is effectively instantaneous with respect to nuclear motion and therefore occurs vertically on the potential-energy diagram (Franck-Condon principle).^{40, 56} As a result, the probability of a given vibronic transition is governed by the overlap between the initial and final vibrational wavefunctions.

Figure 2.1 depicts the Franck-Condon principle for a two-level system consisting of a ground (GS) and excited state (ES) for a single vibrational mode.

For a single displaced harmonic mode the Franck-Condon factor for a transition from the ground-state 0^{th} vibrational level to the m^{th} vibrational level of the excited state follows a Poisson distribution,

$$I_{0 \rightarrow m} = \frac{S^m e^{-S}}{m!} \quad (2.3)$$

where the dimensionless Huang-Rhys parameter S quantifies the electron-phonon coupling and can be written as

$$S = \frac{1}{2}k \frac{\Delta Q^2}{\hbar\omega_{\text{vib}}} = \frac{1}{2}M\omega_{\text{vib}}^2 \frac{\Delta Q^2}{\hbar} \quad (2.4)$$

with effective mass M and force constant $k = M\omega_{\text{vib}}^2$ when $kT \ll \hbar\omega_{\text{vib}}$.⁵⁵ Physically, S corresponds to the average number of vibrational quanta involved in the optical transition. Relaxation to the excited-state equilibrium geometry after the vertical transition gives rise to the reorganization energy

$$\lambda = S\hbar\omega_{\text{vib}} \quad (2.5)$$

Absorption and photoluminescence spectra are constructed by summing the individual vibronic transitions weighted by their Franck-Condon factors and convolving with a line-shape function $\Gamma(E)$ that accounts for homogeneous and inhomogeneous broadening. For a single mode this yields the progression of peaks spaced by $\hbar\omega_{\text{vib}}$ about the 0-0 transition energy E_0 :

$$\frac{I_{\text{Abs}}(E)}{n(E) \cdot E} \propto \sum_{m \geq 0} \frac{S^m e^{-S}}{m!} \cdot \Gamma(E - (E_0 + m\hbar\omega_{\text{vib}})) \quad (2.6a)$$

$$\frac{I_{\text{PL}}(E)}{(n(E) \cdot E)^3} \propto \sum_{m \geq 0} \frac{S^m e^{-S}}{m!} \cdot \Gamma(E - (E_0 + m\hbar\omega_{\text{vib}})) \quad (2.6b)$$

where $n(E)$ is the refractive index at the photon energy E .

When the photon density of states in the surrounding medium (for example a solution) is taken into account, the Einstein coefficients introduce the prefactors $n(E) \cdot E$ for absorption and $(n(E) \cdot E)^3$ for spontaneous emission.^{57, 58} In dilute solutions, or when the emission band is well separated from the absorption band, the refractive index $n(E)$ varies only weakly with photon energy and can be approximated as constant. In real molecules multiple normal modes typically contribute, rather than a single dominant vibration. In that case the spectral expressions must include all contributing modes. For N vibrational modes with Huang-Rhys factors S_i and energies $\hbar\omega_{i,\text{vib}}$ the absorption and emission spectra are obtained by summing over all combinations $(m_1, \dots, m_N)$ of vibrational quanta, with each vibronic line weighted by the product $\prod_{i=1}^N \frac{S_i^{m_i} e^{-S_i}}{m_i!}$ and centered at energies shifted by $\sum_{i=1}^N m_i \hbar\omega_{i,\text{vib}}$:

$$\frac{I_{\text{Abs}}(E)}{n(E) \cdot E} \propto \sum_{(m_1, \dots, m_N)} \left\{ \left(\prod_{i=1}^N \frac{S_i^{m_i} e^{-S_i}}{m_i!} \right) \cdot \Gamma \left[E - \left(E_0 + \sum_{i=1}^N m_i \hbar\omega_{i,\text{vib}} \right) \right] \right\} \quad (2.7a)$$

$$\frac{I_{\text{PL}}(E)}{(n(E) \cdot E)^3} \propto \sum_{(m_1, \dots, m_N)} \left\{ \left(\prod_{i=1}^N \frac{S_i^{m_i} e^{-S_i}}{m_i!} \right) \cdot \Gamma \left[E - \left(E_0 + \sum_{i=1}^N m_i \hbar\omega_{i,\text{vib}} \right) \right] \right\} \quad (2.7b)$$

These displaced-oscillator expressions provide a compact, physically transparent description of the vibronic structure observed in the optical spectra of organic semiconductors and have been successfully applied to conjugated polymers and small organic molecules.^{51, 59–72}

2.1.2 Optical signatures of environmental effects and intermolecular interactions

The model discussed so far primarily describes the spectra of isolated molecules. However, in real systems organic molecules and polymers are typically studied as molecular assemblies, for example in the solid state or in solution. In the following, I address how the molecular environment and interactions with neighboring species influence optical spectra.

Effects arising from environmental polarization

Introducing a molecular environment generally leads to a redshift of both absorption and emission. This energetic shift originates from the permanent electric dipole moment of the chromophore (Figure 2.2). The dipole induces dipoles in adjacent molecules which stabilizes the system through electrostatic interactions. Consequently, the potential energy of the chromophore is lowered by the interaction energy of the dipoles. Because the excited-state dipole moment is typically larger than that of the ground state, the excited state experiences stronger stabilization, resulting in a reduced optical transition energy. This effect can be described by a simplified point-dipole model. The interaction energy between the chromophore dipole and the induced dipoles in the surrounding medium scales with the polarizability of the environment and decreases with the sixth power of the intermolecular separation. The model therefore predicts that environments with higher polarizability induce stronger stabilization and thus larger energetic redshifts.

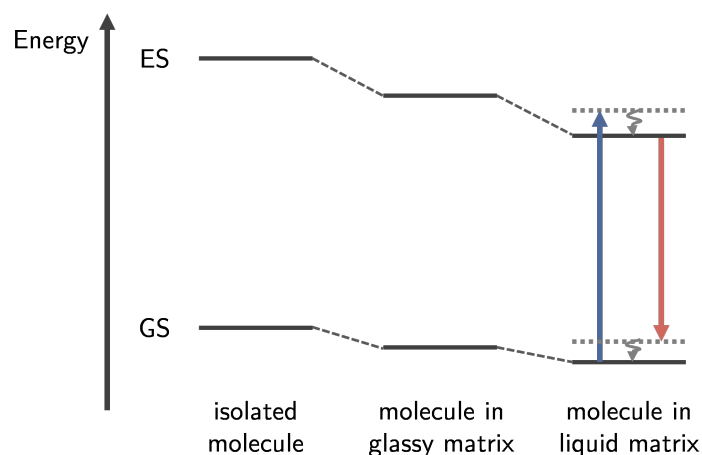


Figure 2.2: Schematic illustration of how the surrounding molecular environment modifies the ground (GS) and excited (ES) states of a chromophore as it transitions from an isolated molecule to a glassy or liquid molecular matrix.

The magnitude and nature of this stabilization depend on whether the chromophore is embedded in a glassy or liquid matrix. In a liquid matrix, such as a dilute solution, an additional

dynamic contribution occurs. Mobile solvent molecules can reorient to maximize the interaction energy and thereby minimize the total energy of the system.

Upon photon absorption, the electronic transition occurs on a timescale much faster than nuclear motion. Immediately after excitation, the chromophore and its environment therefore still retain the ground-state geometry. In terms of energy, this transition energy is comparable to that in a rigid, glassy matrix. However, the sudden change in dipole moment during excitation means that the solvent solvent dipoles are initially aligned in a configuration favorable for the ground state. Solvent reorganization then occurs on sub-picosecond to picosecond timescales, aligning the surrounding dipoles with the excited-state dipole moment. This relaxation stabilizes the excited state and dissipates energy as heat. Fluorescence subsequently originates from this relaxed excited state, leading to emission at lower energy than absorption. the resulting energy difference between absorption and emission is known as the Stokes Shift.

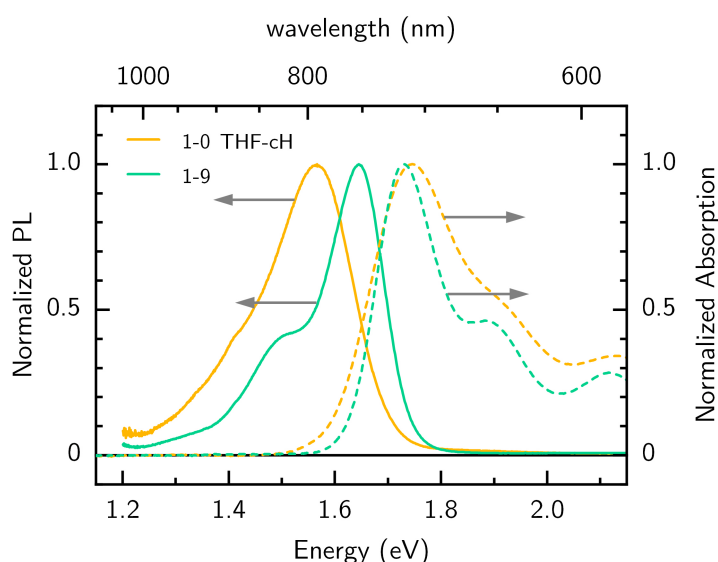


Figure 2.3: Normalized photoluminescence (solid lines) and absorption (dashed lines) spectra of Y6 in THF-cyclohexane solution with 1:0 (orange) and 1:9 (green) solvent ratio highlighting the effect of solvent polarity on the optical spectra, as THF is a polar and cyclohexane a non-polar solvent.

The degree of stabilization increases with the polarity of the environment, and consequently the Stokes shift becomes larger in more polar solvents. Thus, this also has an effect when using different solvents with different polarity. In Chapter 8, for example, I dissolved Y6 in the polar solvent THF and compared it with a mixture of THF and the non-polar solvent cyclohexane. Figure 2.3 shows the normalized steady-state absorption and emission spectra for Y6 in pure THF and a mixture of THF and cyclohexane in a ratio of 1:9. Y6 in polar THF (yellow lines) exhibits a significantly higher Stokes shift than in the nonpolar THF-cyclohexane mixture (green lines). This is because the dipoles of the THF molecules interact strongly with the dipole moment of Y6. In contrast, cyclohexane molecules do not have a permanent dipole

moment. Thus, they hardly “feel” the change in the electric field of Y6. Thus, the remaining energetic separation between absorption and emission comes from the internal reorganization in the Y6 molecule itself, according to equation 2.5. It is also noticeable that the line width of the spectrum of Y6 in THF is significantly broader than in the THF-cyclohexane mix. This is due to the inhomogeneous broadening. In the case of the polar solvent THF, the dipoles of the solvent are arranged statistically differently around the Y6 molecule. Thus, each Y6 molecule experiences a stronger or weaker local electric field. As a result, each individual molecule has a slightly different transition energy, which leads to a Gaussian spectral broadening. Since cyclohexane is nonpolar, each Y6 molecule experiences a similar energetic landscape of the environment, which leads to a comparatively narrower line width.

Effects due to electronic coupling - aggregation

The Franck-Condon model described above adequately captures the behavior of isolated molecules, including environmental effects. However, the situation becomes substantially more complex in molecular aggregates. When multiple molecules assemble through van der Waals interactions, the electronic coupling between their transition dipoles becomes a dominant factor. This coupling strongly modifies the electronic states and thus also the photophysical properties. Intermolecular interactions introduce shifts and splittings of molecular energy levels.

Kasha’s exciton model, developed in the 1960s using the point-dipole approximation, provided the foundational framework for describing such intermolecular interactions.^{73, 74} The underlying features of the model will now first be explained using the simplest model of an interacting dimer, before more complex arrangements are addressed.

A dimer composed of two identical molecules is described by the Hamiltonian $\tilde{H} = \tilde{H}_1 + \tilde{H}_2 + \tilde{V}_{12}$ with the Hamiltonians for the isolated molecules $\tilde{H}_1$ and $\tilde{H}_2$, and the interaction potential $\tilde{V}_{12}$. Solving the Schrödinger equation with the ground state wavefunction $\Psi_{\text{GS}} = \Psi_1 \Psi_2$ yields the ground state energy $E_{\text{GS}} = E_1 + E_2 + D$, with $D = \langle \Psi_1 \Psi_2 | V_{12} | \Psi_1 \Psi_2 \rangle$ accounting for the van-der-Waals interaction.

In the excited state of the dimer, the excitation cannot be assigned to a specific molecule. Analogous to the normal modes of two mechanical coupled pendula, the system forms symmetric and antisymmetric combinations of the monomer excitation as $\Psi_{\text{ES}\pm} = \frac{1}{\sqrt{2}} (\Psi_1^* \Psi_2 \pm \Psi_1 \Psi_2^*)$ with the star denoting the excited molecules. These states are split in energy according to $E_{\text{ES}\pm} = E_1 + E_2 + D \pm \beta$ with D the van-der-Waals interaction in the excited state and $\beta = \langle \Psi_1 \Psi_2 | V_{12} | \Psi_1 \Psi_2 \rangle$ the resonance interaction determining the splitting between the two energy levels of the excited state. The resulting transition energy of the dimer is $\Delta E_{\text{dimer}} = \Delta E_1 + \Delta D \pm \beta$ with $\Delta E_1 = E_1 - E_1$ is the monomer transition energy. In summary, the intermolecular distance r_{12} and the relative orientation to each other critically determine how the energy levels change with intermolecular interaction. Figure 2.4 illustrates these effects for a physical dimer with moderate resonance coupling (≈ 100 meV). Considering the intermolec-

ular orientation angle θ yields two limiting cases for the excited state and the resulting optical transitions.

J-Aggregates

In the case of $\theta = 0^\circ$, the dipoles are arranged in line. Here, the lower energy level $\Psi_{\text{ES}-}$ of the excited state shows a transition dipole that is twice as large as that of an isolated molecule. In contrast, the higher energy level $\Psi_{\text{ES}+}$ has a vanishing transition dipole. According to the selection rules both absorption and emission are dipole allowed from and to the energetically lower excited state level resulting in a reduced Stokes' shift. Compared to the isolated molecule, the transition energy is reduced leading to a red-shifted absorption and emission and increased radiative rates. The mechanism for this aggregate arrangement was discovered independently by Jelly and Scheibe and was thus named *J-aggregate* or *Scheibe-aggregate*.^{75–77}

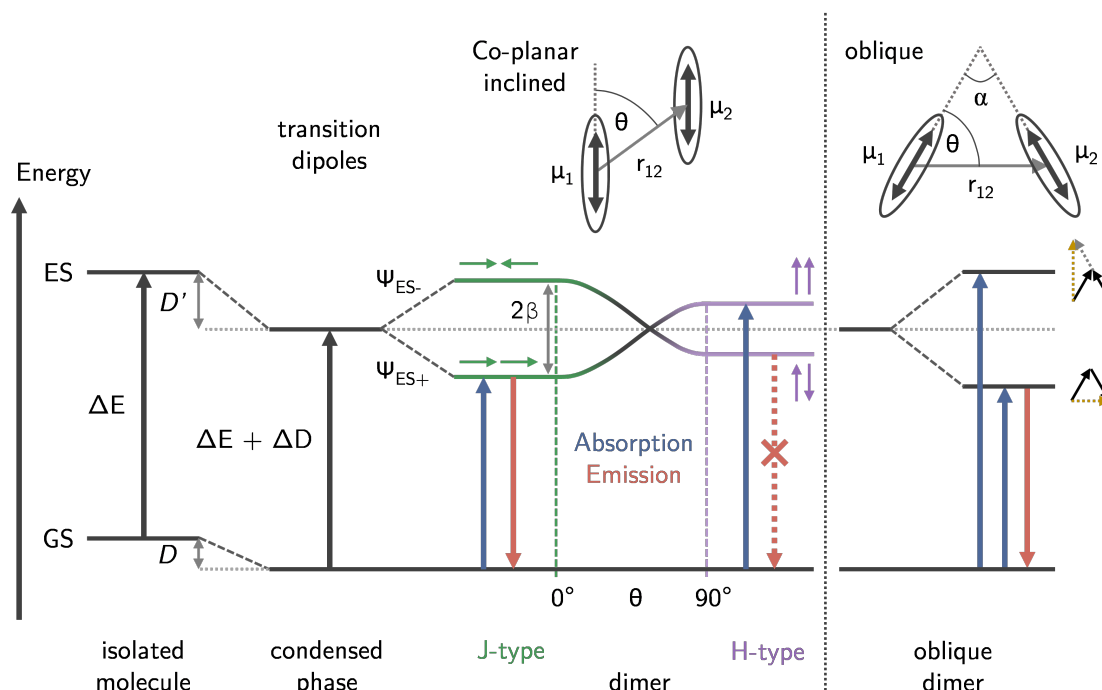


Figure 2.4: Schematic illustration of how intermolecular interactions modify energy levels and exciton splitting upon formation of a physical dimer in different geometric arrangements, including co-planar and oblique configurations. The angle θ denotes the orientation between the intermolecular distance vector r_{12} and the transition-dipole polarization axes. Small arrows indicate the relative dipole orientations associated with each split excitonic level. The crossover between H- and J-type coupling is shown for constant $|r_{12}|$ and increasing θ in the co-planar case, following Kasha's exciton model within the point-dipole approximation.⁷⁴ Exciton splitting for an oblique arrangement is illustrated for an arbitrary angle α between the molecular transition dipoles.

H-Aggregates

For $\theta = 90^\circ$, the dipoles are aligned side-by-side, forming an H-aggregate. Here, the energetic

ordering of the excited states is reversed compared to the J-aggregate with $\Psi_{\text{ES}+}$ being bright and $\Psi_{\text{ES}-}$ being dark. Absorption is blue-shifted, and after rapid relaxation to the dark state, emission is strongly suppressed. This leads to a strong reduction in the radiative rate and an increased Stokes shift. In real systems, perturbations such as finite temperature or static disorder partially relax the selection rules, enabling weak emission.

In real systems, molecular arrangements of dimers often also exhibit angles between $\theta = 0^\circ$ and 90° in the co-planar configuration or oblique angle between the dipoles. In these cases, both split energy levels of the excited state have finite transition moments, and thus absorption occurs in both states, as indicated in Figure 2.4.

A key prediction of Kasha's model is that the exciton splitting scales with the square of the transition dipole moment and inversely with the cube of the intermolecular separation r_{12} .⁷⁴ However, assigning aggregate type solely from spectral shifts can be misleading as the dispersion shift ΔD may dominate over the resonance interaction β . This could lead to a bathochromic shift, even for H-type interacting chromophores.

Excimers

For sufficiently strong coupling β , the intermolecular interaction can change the dimer geometry in the excited state in such a way that the intermolecular distances significantly reduce, that the potential of the dimer's ground state is non-bonding and repulsive. The resulting species, only stable in the excited state, is an excimer.⁴⁰ Excimers exhibit a broad, structureless emission and monomer-like absorption, as absorption occurs at large intermolecular separation. This behavior was first identified and reported by Förster in 1955,⁷⁸ and later extensively studied by Birks for pyrene derivatives.^{79–81} More recent work deals with excimers in molecular J- and H-aggregates.⁸²

Extending the concept of two interacting molecules to a linear chain consisting of N interacting chromophores with spacing α yields the Frenkel exciton picture.^{83, 84} The excited state splits into N levels. Similar to the dimer, the geometric arrangements as well as the extent of the intermolecular coupling determines the photophysical properties.

Vibronic Coupling and the Spano Model

Even though Kasha's model can describe the basic properties of interacting molecules, it neglects exciton-phonon coupling. Spano and co-workers developed a more comprehensive theoretical framework incorporating vibronic coupling, static and dynamic disorder, and excitonic interactions.^{85–88} Their approach expands the wavefunctions into one- and two-particle vibronic states. The one-particle state represents a molecular ensemble in the ground state with exactly one molecule in an excited state with vibronic excitations. In two-particle states, a molecule in the electronic ground state additionally exhibits a vibronic excitation.^{89, 90}

Although the full band structure is complex, the optical signatures are dominated by the 0-0 transition. Thus, the ratio of the 0-0 to 0-1 peak is a key indicator of the type of interaction. For J-aggregates, the 0-0 peak is enhanced in absorption with increasing exciton bandwidth and suppressed for H-aggregates. Perfect H-aggregates would not exhibit emission intensity of the 0-0 transition, though disorder and finite temperature relax this constraint. In comparison, the emission spectrum of J-aggregates shows a dominant 0-0 peak, which is reduced by static disorder and temperature. These effects modify the Franck-Condon expressions, which changes equations 2.6 and 2.7 as follows^{91, 92}

$$\frac{I_{\text{Abs}}(E)}{n(E) \cdot E} \propto \sum_{m \geq 0} \left(\frac{S^m e^{-S}}{m!} \right) \left(1 - \frac{W e^{-S}}{2\hbar\omega_{\text{vib}}} G_m \right) \Gamma(E - (E_0 + m\hbar\omega_{\text{vib}})) \quad (2.8a)$$

$$\frac{I_{\text{PL}}(E)}{(n(E) \cdot E)^3} \propto e^{-S} \alpha \Gamma(E - E_0) + \sum_{m \geq 0} \frac{S^m e^{-S}}{m!} \cdot \Gamma(E - (E_0 + m\hbar\omega_{\text{vib}})) \quad (2.8b)$$

with the exciton bandwidth W and the constant G_m that depends on m according to $G_m = \sum_{n \neq m} \frac{S^n}{n!(n-m)}$ for the absorption. For emission, the empirical factor α modifies the 0-0 transition intensity.⁹³

The above model with its extensions mainly accounts for intermolecular Coulomb interactions and thus mainly for negligible overlap of the molecular orbitals of neighboring molecules. When wavefunctions overlap becomes significant, short-range charge-transfer (CT) interactions arise. This significantly affects the nature of the excited state and thus also has a strong influence on the photophysical properties.^{94–97} These interactions are highly sensitive to molecular orientation and displacement, as wavefunctions may invert within a single aromatic ring. Spano and co-workers incorporated CT coupling into their theoretical framework.^{96, 98–100} The overall aggregate character (H- or J-type) results from the combined contributions of Coulombic and CT interactions. Notably, when the contributions of both have opposite sign with comparable magnitude, destructive interference can yield spectra resembling those of isolated molecules. Spano and co-workers also further extended this model to account for D-A polymers and D-A-D oligomers and polymers, which represent the structure of the current highest performing organic solar cell materials, including PM6 and Y6, among others.^{90, 101–105}

2.1.3 Aggregation in solution and in film

In addition to their optoelectronic properties, the morphological properties of organic semiconductors play a crucial role, as they exhibit a sensitive interplay. The molecular order and structure formation of π -conjugated chromophores, small molecules and polymers, are determined by a combination of thermodynamic and kinetic factors.^{106–116} Flory, Huggins, and

co-workers developed a mathematical framework to statistically describe small molecules and polymers and their conformations.^{117–119} Nowadays, conformations and aggregates of organic molecules and polymers are typically determined using a combination of DFT and molecular dynamics/Monte Carlo simulations. DFT is used to calculate torsion profiles and energetically favorable geometries. With this information, MD simulations can be used to simulate longer chains and multi-body systems such as solutions, melts, or films. From this, conformational distributions, aggregate forms, and supramolecular packings can be extracted.^{120–125} As described above, the spectral and, therefore, also the optoelectronic properties of isolated, non-interacting, and interacting molecules differ drastically. In a device based on organic semiconductors, its efficiency depends not only on the molecular structure of the individual molecule, but also specifically on the respective nano- and macrostructures.^{111, 126, 127} Thus, different morphologies can be achieved for the same material system under different film processing conditions. This determines whether the device exhibits poor or high performance.¹²⁸ The active layer in organic solar cells is typically a solution-processed thin film. In order to understand the final morphology and its relationship to the processing properties, one must first understand the aggregation behavior of the material in solution.^{129, 130} The following describes how aggregation can be induced in solution and how aggregation takes place in solution, and also discusses the different morphologies that can occur in thin films and the influence of different morphologies on optoelectronic properties.

Aggregate formation in solution

Two basic mechanisms can induce aggregation of π -conjugated polymers or small molecules in solution. One is through temperature reduction, and the other is through reduction of solvent quality. Both methods reduce the thermodynamic stability of dissolved chromophores and promote intermolecular interactions.

At high temperatures in good solvents, chromophore-solvent interactions and thermal motion predominate. As the solution cools, the interactions between polymer segments or small molecules become energetically more favorable than solvation. Chromophores begin to interact with each other and form aggregated, ordered structures through π - π interactions. The critical temperature at which the chromophore-chromophore interaction exceeds the chromophore-solvent interaction depends on both the solvent and the molecule/polymer itself. Panzer et al. and others investigated the temperature-dependent aggregation of different π -conjugated material classes by UV-Vis absorption and photoluminescence spectroscopy. They found that for all π -conjugated polymers and molecules, aggregate formation can be understood as an order-disorder transition.^{131–135} Across materials, they discovered that the aggregation of π -conjugated materials takes place in the following steps. Figure 2.5 shows these steps using the model polymer P3HT in tetrahydrofuran (THF). At high temperatures, when the polymer is well dissolved and in its random coil conformation, the absorption and emission spectra of P3HT are reasonably broad and unstructured. Upon cooling, the backbones of the individual

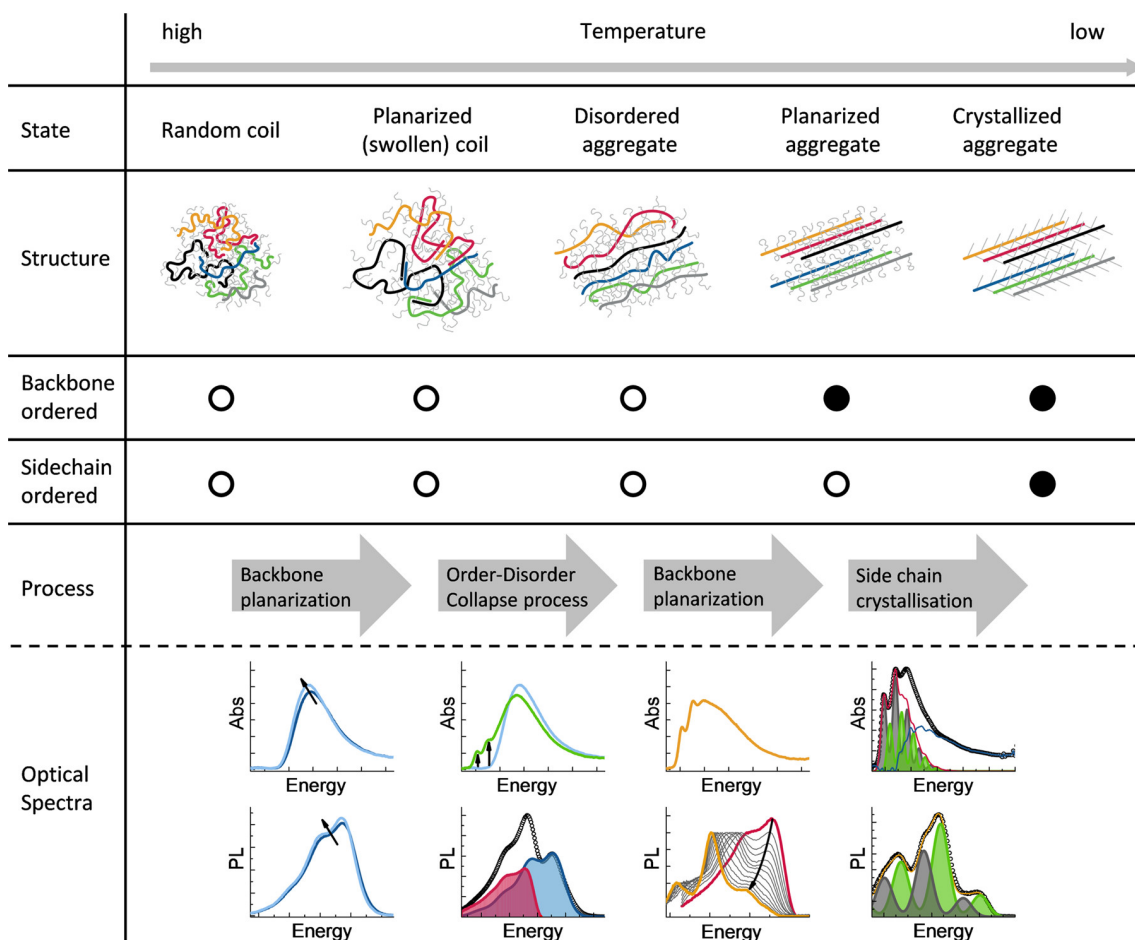


Figure 2.5: Schematic of the changes in morphology and optical spectra that occur upon temperature induced order-disorder transition of conjugated polymers in solution based on the model polymer P3HT. Reproduced with permission from Panzer et al.,¹³¹

polymer segments first planarize, leading to a swelling of the polymer coil and an extension in conjugation length. This increases the oscillator strength, which is noticeable through an increase in intensity of absorption and emission. Further cooling induces chromophore-chromophore interactions and the polymer backbones start to stack on top of each other and form aggregates, even though they are not fully planar yet. This leads to the occurrence and growth of the spectral features of interacting, aggregated P3HT in absorption and emission. Compared to the spectra of the random coil conformation, the aggregated phase exhibits vibronically structured spectra at lower energies. This disorder-order transition leads to an isosbestic point in the absorption spectra indicating a phase transition. At lower temperatures, more and more polymer segments aggregate, and the backbones in the aggregates become even more planar. In the case of P3HT, cooling below the melting point of THF to 5 K even leads to crystallization of the side chains, which results the observation of a new spectral progression in the absorption and emission for those crystallized aggregates. The optical spectra can be decomposed by using a Franck-Condon analysis using several Franck-Condon

progressions for each present phase (coiled and aggregated) of P3HT at all temperature steps. This allows the extraction of the fraction of aggregates in the polymer sample, as well as the degree of order and character of the intermolecular interaction that prevails in the aggregates. Also the step-wise aggregation allows important insights into the aggregation behavior of the compound in solution, which basically defines the morphology achieved during solution-based film processing. This method of controlled aggregation through temperature reduction does not only apply for polymers,^{64, 131, 132, 135–139} but also oligomers and small molecules.^{60, 64} In Chapter 6 I used this approach to induce controlled step-by-step aggregation of Y6, N4 and PM6 to investigate the spectral signatures and character of the interacting phase by steady-state spectroscopy.

Similarly, at constant temperature, adding a poor solvent to a chromophore in a good solvent reduces the overall solvent quality, thereby inducing aggregation. In a good solvent, the chromophore-solvent interactions are thermodynamically more favorable. The poor solvent reduces this interaction. The polymer chains collapse and start to aggregate due to increased polymer-polymer interactions (similar for small molecules). Thus, by changing the solvent ratio of a good and poor solvent, the aggregation of a chromophore can be controlled.^{60, 140} Both methods, cooling a solution or adding a poor solvent, can also be used to control aggregation and order in solution-processed thin films. Pre-aggregation of the chromophores in the solution prior to film formation plays a crucial role in the resulting film morphology.

2.1.4 Morphology in condensed phase

In condensed phases, such as thin films, organic semiconductors can exhibit domains with different morphologies. The stiffness and planar conformation of the π -conjugated backbone of many organic semiconductors enable an efficient aggregation, even for polymers. Organic molecules can exist in a disordered, amorphous configuration, with no or only weak intermolecular coupling, or in an aggregated phase in which molecules can stack due to their planar backbones.^{141–146} In condensed phases, aggregated domains can exhibit long-range order due to strong intermolecular coupling. Amorphous domains consist of flexible, disordered polymer chains, chain ends and chain foldings, or of molecules with a high freedom of rotation that prevents intermolecular coupling, in the case of small molecules. Furthermore, organic semiconductor materials can show local, short-distance order with liquid crystalline properties.^{130, 147–155}

Solution-processed thin films formed by spin-coating, slot-dye or blade coating, exhibit complex, mostly semi-crystalline morphologies. Here, the film formation process from a wet solution film to a condensed thin film is governed by the evaporation of the solvent. This means that with less solvent content in the still wet thin film, the chromophores become less and less mobile and are ultimately frozen in a non-equilibrium state. The semi-crystalline thin film then consists of non-interacting, less-ordered chromophore domains and ordered, interacting domains (aggregates). Note, that this is the crucial difference to single-crystal morphologies, which

form long-range crystalline structures through slow, controlled growth. As non-interacting and interacting/aggregated polymers and molecules exhibit different characteristic optical behavior, as discussed above, optical spectroscopy is a powerful tool to investigate the thin film composition. Panzer et al. spectroscopically probed the amorphous and aggregated phase of a P3HT film highlighting the different characteristic absorption and emission for the interacting (blue) and non-interacting (orange) chains, decomposed using a Franck-Condon analysis (see Figure 2.6).¹³⁶

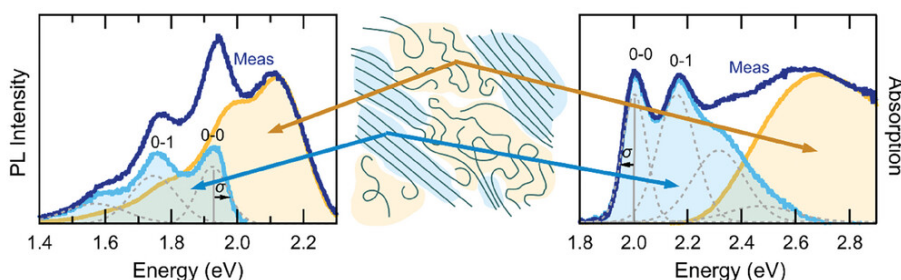


Figure 2.6: Absorption and PL spectra of P3HT in chloroform disentangled in contributions of disordered, amorphous (orange) and ordered, aggregated (blue) chains. Subtracting the absorption contribution of the disordered phase from the spectrum results in a remaining spectrum that can be assigned to predominantly aggregated, interacting chains. Fitting the resulting spectra with a Franck-Condon progression gives rise of peak ratios and linewidth. Reproduced from Panzer et al.,¹³⁶ licensed under CC BY 4.0.

Absorption probes both the regions of aggregated, interacting domains and the non-interacting, disordered regions without intermolecular coupling, as it provides more information about the ground state and the transitions from there to the excited state. Emission exhibits other information, since photoluminescence occurs after relaxation and energy transfer of the excited state.^{64, 156} In semi-crystalline films, exciton transfer occurs from higher energy states to energetically more favorable, usually more ordered areas in the energy landscape before emission takes place. Since the energy levels of interacting chromophores are energetically more favorable, ultra-fast exciton transfer takes place from the non-aggregated to the aggregated phase.^{116, 157, 158} Thus, in a semi-crystalline film with domain sizes in the order of the exciton diffusion length, emission is usually only observed from the energetically most favorable phase. If the domain size is larger than the exciton diffusion length, some excitons remain within their domain during their lifetime, and photoluminescence also occurs from there.^{159, 160} This provides information about domain sizes, intermixing, and exciton diffusion length. Thus, optical spectroscopy is a powerful tool to investigate both the ordered and disordered phases.

To obtain a comprehensive picture, it is nevertheless important to complement optical spectroscopy with other methods. While optical spectra provide important information about the nature of the interaction,^{67, 86, 132, 161} accurately determining the molecular conformation present is usually complex. Simulations, calculations, and scattering experiments help here.

Theory provides possible molecular conformations,^{120, 123} while scattering experiments—such as GIWAXS (Grazing-Incidence Wide-Angle X-ray Scattering) and SAXS (Small-Angle X-ray Scattering)—provide information about intermolecular distances, alignment, and domain sizes of ordered structures.^{111, 162} GIWAXS probes crystalline regions with long-range order, while SAXS gives information about the mesoscale structures such as domains and interfaces. In addition, time-resolved optical methods, such as TRPL (time-resolved photoluminescence) and TA (transient absorption), provide insights into the kinetics of exciton transfer.^{163, 164} It is essential to consider all these methods combined to obtain a comprehensive picture of the underlying morphology, as each one individually samples only part of the overall morphology.^{115, 130} The morphology of organic semiconductors, from molecular conformations to packing and domain structure, is the primary design parameter for the optoelectronic properties. The charge mobility is strongly dependent on the order of crystalline packings, π - π -stacking distances, and interconnectivity of domains.^{111, 130, 157, 165} However, the ultimate goal is not necessarily a high degree of crystallinity, but rather well-connected, ordered domains that allow for a continuous percolation path for charge carriers.^{157, 166–171} The molecular packing determines the energetic landscape, which defines the HOMO and LUMO level positions, which are decisive for the exciton dissociation. Additionally, the dissociation is effected by the intermolecular packing and the associated exciton delocalization. The delocalization over several interacting chromophore units increases the exciton mobility and enhances exciton dissociation due to lowered Coulomb binding energy.^{50, 172–175} The exciton diffusion length increases with coherence and order within domains up to several tens of nanometers, but is strongly reduced by deep trap states. In organic solar cells, the domain size is one of the critical factors for efficient charge separation. Domains on the order of the excitation diffusion length enable high efficiencies, while larger domains or strong intermixing of different phases annihilate charge separation.^{129, 176, 177}

Additionally, the molecular orientation relative to the substrate defines the anisotropy of charge transport.^{126, 178, 179} Face-on stacking, where the chromophore backbone stacks lie flat on the substrate, enables efficient vertical (perpendicular to the substrate plane) transport, more favorable for the geometry of a solar cell device. In contrast, edge-on stacking promotes lateral transport, which is beneficial for organic field-effect transistors (OFETs). Therefore, controlling and understanding morphology at all length scales, from molecular conformations and crystallinity to domain size and phase separation, is crucial for optoelectronic performance and the further design of highly efficient materials. To date, fine-tuning morphology, especially in solution-processed films, and understanding the morphology-property relationships remain key challenges.

2.2 State of the art OPV materials and their morphological properties

Over the last decade, the field of OPVs has undergone a transformative change, as reflected in both the material classes and the achieved device efficiencies. Previously, the field was dominated by homopolymer-donor:fullerene-acceptor systems. However, these systems exhibit some fundamental limitations. Fullerene acceptors exhibit weak absorption in the visible spectral range, as well as limited tunability of the electronic levels and a tendency towards excessive aggregation, leading to issues in long-term phase stability.^{146, 180, 181} On the other hand, homopolymers, such as the workhorse material P3HT, dominated as donor materials due to their good processability, moderate crystallinity, and commercial availability. However, homopolymers are strongly limited by moderate hole mobility and their broad optical bandwidth (~ 2.0 eV), meaning that most of the sun's spectrum remains unused. Additionally, homopolymers exhibit a pronounced exciton binding energy (~ 0.4 - 0.5 eV in P3HT), as the electron and hole reside on a single conjugated segment with limited delocalization. This leads to strong Coulomb attraction between electron and hole. The high binding energy hinders the exciton dissociation. As a result, systems such as P3HT:PCBM only achieve maximum efficiencies of 5%.^{40, 129, 143, 165, 182} In the case of donor materials, donor-acceptor (D-A) copolymers with alternating donor and acceptor units in the backbone were developed to address these limitations. The electrostatic interaction between the two units results in a reduced effective band gap and absorption that is significantly better matched to the solar spectrum. The D-A architecture also leads to stronger exciton delocalization. The HOMO orbitals reside on the donor and the LUMO orbitals on the acceptor, which leads to a greater spatial separation of electrons and holes already in the excited state. This lowers the effective exciton binding energy. The D-A structure also offers high tunability through variation of the individual donor and acceptor units as well as side chains. This allows adjustability of electronic levels and morphology to achieve optimal spectral absorption and charge separation.^{115, 183-189}

In terms of acceptor materials, PCBM (PC_{61}BM , PC_{71}BM) were the standard electron acceptor for decades due to their high electron mobility and isotropic charge transport.¹⁹⁰ However, the above mentioned limitations led to stagnation in device efficiencies. This was revolutionized in 2015 by the introduction of ITIC (indacenodithiophene-indanone)¹⁹¹ and the early A-D-A non-fullerene acceptors (NFAs), with a donor core and two acceptor end groups. In contrast to fullerenes, ITIC exhibits strong absorption in the spectral range of 500-750 nm. By modifying the end groups, it was possible to adjust the LUMO level, and the tendency to overaggregation was lower compared to fullerenes. This enabled device efficiencies of up to 13 % to be achieved in blends with polymer donors such as PBDB-T.^{171, 180, 181, 191-198}

In 2019, Y6 (BTP-4F), introduced by Yuan and co-workers, and other so-called Y-type NFAs set a new milestone.^{201, 202} Y-type acceptors feature a so-called A-DA'D-A architecture with an extended π -conjugated core (dithienothiophene(3,2-b)pyrrolobenzothiadiazole) with two

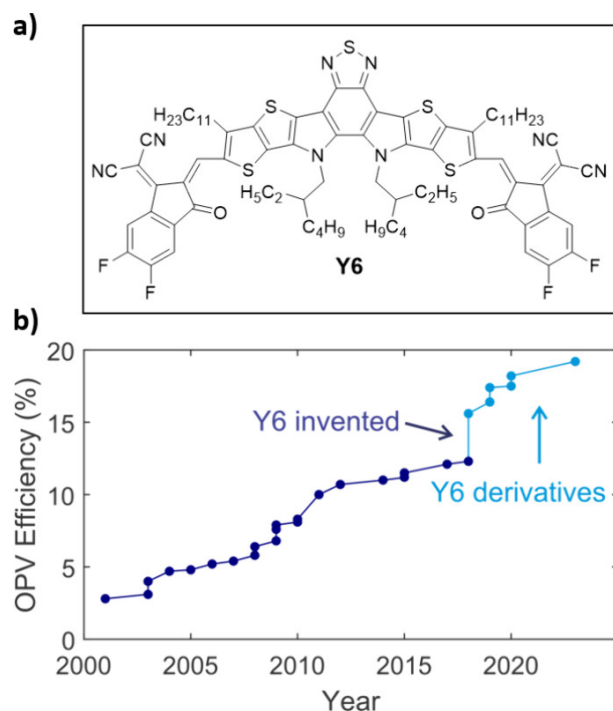


Figure 2.7: (a) Chemical structure of Y6. (b) Development of the highest confirmed PCEs for organic research cells over the years. Data from the National Renewable Energy Laboratory.¹⁹⁹ Reproduced from Hume et al.,²⁰⁰ licensed under CC BY 4.0.

acceptor end groups (2-(3-oxo-2,3-dihydroinden-1-ylidene)malononitrile). The curved, banana shape geometry allows for various conformations of π - π interactions. Absorption ranges from 600 nm to the NIR at around 1000 nm with an optical gap of approximately 1.33 eV.^{50, 171, 203} With the introduction of the Y-type NFAs, which exhibit even strong absorption in the NIR, the requirements for donor materials shifted again toward wide-bandgap donors ($E_g \sim 2.0$ eV) in order to complement the NFA absorption. This led to the development of PM6 (PBDB-TF), which exhibits complementary absorption to Y6 that the blend of the two materials covers the solar spectrum with strong absorption from 300-1000 nm. The HOMO level is adjusted to the LUMO level of Y6. Additionally, PM6 tends to be face-on oriented, which is favorable for the perpendicular transport required in the OPV device.^{192, 204–206}

Furthermore, the development of various Y6 derivatives has led to further improvement in the efficiencies of OPVs.^{158, 202, 207–209}

In this thesis I will discuss the special morphological properties of Y6 and their effect on opto-electronic properties. Y6 exhibits a unique A-DA'D-A architecture with an intrinsically molecular bending, which differs fundamentally from planar NFAs such as ITIC. The dihedral angle between the central units, approximately 20-30°, gives the molecule a characteristic banana shape. It has already been shown for other small molecules that deviations from a linear structure enable multiple dimer conformations and packing motifs.²¹⁰ In the case of Y6, it leads to multidirectional π - π interactions, including terminal-terminal (T-T), core-core (C-C), core-terminal (C-T), and mixed configurations (see Figure 2.8). The several possible geome-

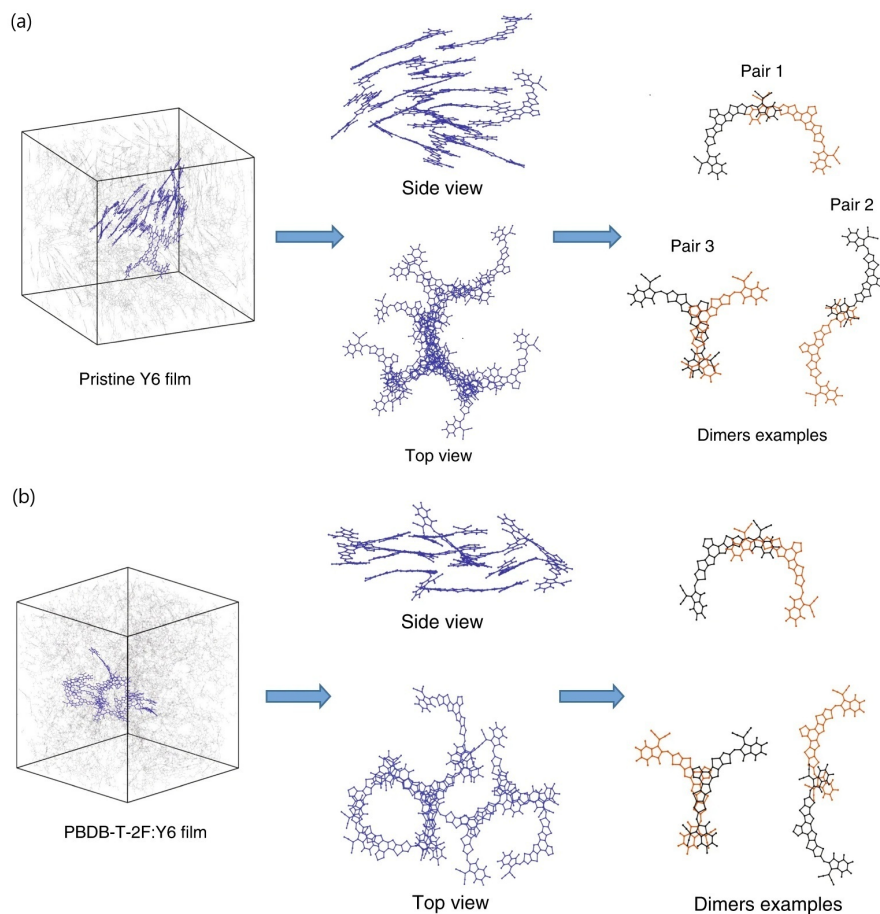


Figure 2.8: Illustration of the Y6 packing predicted from molecular-dynamic simulations in (a) pristine Y6 and (b) PBDB-T-2F:Y6 films. Reproduced from Zhang et al.,⁵⁰ licensed under CC BY 4.0.

tries allow for adaptation to different molecular environments (in pristine films and blend films with polymers), resulting in a remarkable morphological robustness.^{50, 171, 203, 211–214}

The dimer configurations of Y6 fundamentally define the optoelectronic properties and energetic landscape of Y6 pristine and blend films. Zhang and co-workers identified three characteristic dimer configurations that coexist in a 3D network from single crystal investigations, enabling an isotropic transport mobility.^{50, 215} Additionally, MD simulations revealed a variety of dimer configurations with different orientations and overlap patterns.¹⁷¹ In addition to simulations and studies on single crystals, it has been demonstrated that the different packing motifs of interacting Y6 in single crystals are also found in solution-processed pristine and blend films and can be manipulated by using different solvent additives during film processing.^{50, 51, 179, 216–218}

In aggregated, interacting Y6, the electron wavefunction delocalizes over several Y6 molecules in dimer clusters. This increases the electron-hole separation compared to the monomer/non-interacting Y6 and thus reduces the Coulomb binding energy. Thus, the electron and hole

are already spatially separated before reaching an interface to a donor, which facilitates exciton dissociation. The reduced binding energy allows exciton dissociation even at low donor-acceptor energy offsets.^{50, 172, 173, 204, 219, 220} This phenomenon also leads to an ongoing discussion in the community about whether efficient free charge generation also occurs in pristine Y6.^{51, 200, 204, 221–225}

There is broad agreement that excitons in interacting Y6 exhibit a mixed Frenkel-charge-transfer character. Both theoretical and spectroscopic studies indicate delocalization over several molecules, in some cases extending to up to six molecular units.^{50, 51, 175, 200, 220, 224, 226} However, there is no general consensus on the extent to which the electron and hole separate and dissociate into free charge carriers or remain Coulombically bound.^{200, 204, 221, 227} A major challenge in this context is the lack of a uniform interpretation of transient absorption spectra, as both the spectral signal assignments and the associated ultrafast kinetics remain debated, particularly on a sub-picosecond to picosecond time scale.^{158, 179, 224, 228, 229} Proposed mechanisms include rapid exciton transfer from non-interacting, weakly coupled Y6 domains (where the exciton cannot delocalize over several molecules) to interacting, tightly-packed Y6 domains,¹⁵⁸ as well as the formation of intermolecular CT states or free charge generation.^{221, 224} All these mechanisms occur on sub-picosecond to ps timescales and are absent in well-dissolved, non-interacting Y6, which highlights the crucial role of intermolecular interactions.^{51, 230} It is worth mentioning that some publications proposing a model including free-charge generation from sub-ps spectral evolution neglect that the Y6 solution-processed film not only exhibits strongly coupled, interacting Y6 domains (such as in a single crystal), but also domains of loosely packed, non-interacting Y6. In Chapter 6, I have identified the spectral signatures of non-interacting Y6 in pristine films. Guo and co-workers have further demonstrated the presence and exciton migration from the non-interacting to the interacting Y6 phase using temperature-dependent transient electroabsorption spectroscopy.¹⁵⁸ These results also demonstrate that the exciton transfer mechanism dominates the sub-ps/ps spectral kinetics in TA. However, further indications of intrinsic charge generation come from the relatively high PCEs, around 5%,^{222, 227, 231} although it remains under discussion whether exciton dissociation occurs in the bulk or predominantly at the interface with charge-transport layers. Regardless of whether Y6 primarily forms CT states or free charges, most interpretations agree that exciton dissociation does take place, albeit with an unresolved degree of charge separation.

In summary, the unique architecture and morphological properties of Y6 and its derivatives allow efficient exciton dissociation through reduced binding energies and strong intermolecular coupling. Although the detailed mechanisms, whether charge generation takes place in the bulk or at the interface, as well as the extent of the charge separation, remain fundamentally unresolved. Further advances in understanding requires phase-selective spectroscopic approaches to disentangle the contributions of the different morphological conformations of Y6 to charge generation and transport.

3 Experimental Methods

This chapter describes the two main experimental setups and methods employed in this thesis. In addition, Chapters 6–8 contain more details of other setups.

3.1 Temperature-dependent steady-state UV-VIS absorption and photoluminescence setup

A home-built temperature-dependent steady-state UV-VIS absorption and photoluminescence setup is used to investigate the aggregation behavior of organic semiconductors. As discussed in Chapter 2, the optical spectra give valuable information about the character of intermolecular interactions. Stepwise cooling of a dilute sample solution decreases solubility, inducing intermolecular interactions among the molecules/polymers, and allows for the controlled aggregation of the sample. A home-built setup can record the absorption and photoluminescence spectra in a temperature range from 5 K to 500 K. Figure 3.1 depicts the schematic of the setup.

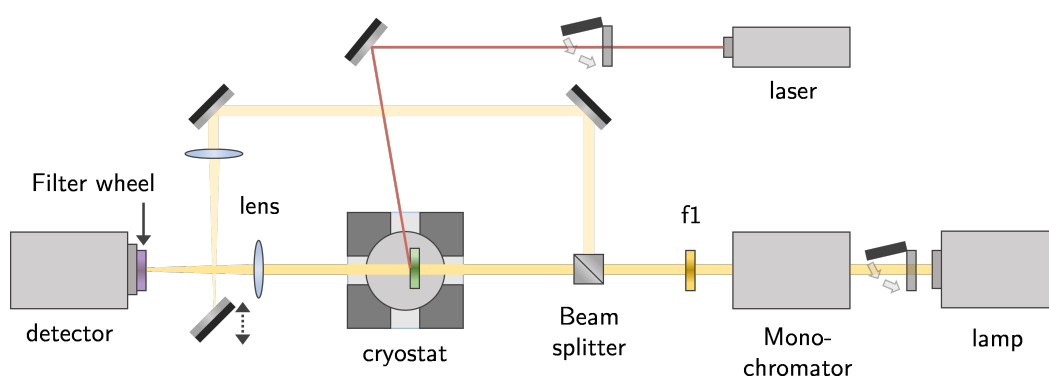


Figure 3.1: Schematic illustration of the home-built temperature-dependent steady-state absorption and photoluminescence setup.

The sample is located in an electrically heatable continuous flow cryostat by Oxford Instruments under a helium atmosphere. A temperature controller (Oxford Instruments ITC 502) regulates the helium gas flow and the electric heating to reach the desired temperature. A tungsten halogen lamp generates white light for absorption measurements. A monochromator reduces the initial intensity. This monochromator has no analytical function in this place and is used

in the 0th order mode. As the generated white light shows a more pronounced intensity in the red region of the spectrum compared to the blue, filter f1 is used to balance the white light intensity. An 80:20 beamsplitter divides the incident white light beam into a sample and calibration beam. The sample beam propagates straight through the sample before being focused onto the detector. The calibration beam ensures correction for possible variations in the intensity of the tungsten lamp. Thus, a calibration spectrum is captured immediately after each absorption measurement. Therefore, a mirror on a stepper motor can be moved into the beam in a way that it blocks the sample beam and reflects the focused calibration beam onto the detector. The detection system consists of a monochromator by Andor Technology (Shamrock SR303i) coupled to a CCD-camera by Oxford Instruments (Andor iDus DU420-OE) and a photo diode array (Andor iDus 490 InGaAs) to extend the spectral range into the NIR-range. A reference spectrum was taken before each measurement series. The actual corrected optical density (OD) of the sample is calculated by

$$OD = -\log \left(\frac{I_t}{I_r} \cdot \frac{I_{c,0}}{I_c} \right) \quad (3.1)$$

with the intensity of the transmitted sample beam I_t , the transmitted beam for the reference measurement I_r , the intensity of the calibration beam I_c , and the intensity of the calibration beam for the reference measurement $I_{c,0}$. To measure PL, the white light beam is blocked. Laser diodes with the desired operation wavelength excite the sample through a side window of the cryostat. The PL is captured by the same detection system as the absorption. A suitable filter in a filter wheel, before the monochromator, blocks any remaining intensity of the laser.

3.2 Transient Absorption Spectroscopy

Transient absorption spectroscopy (TAS), also known as pump-probe spectroscopy, is a spectroscopic technique used to study the time-resolved kinetics of ultrafast, photoinduced processes. The basic principle involves two laser pulses overlapping spatially at the sample position (see Figure 3.2a). One of the laser pulses excites the sample to an excited state, known as the pump pulse. The other laser pulse, typically of a broadband spectral nature to give spectral resolution as a function of wavelength λ , is used to interrogate the sample's transmission and is called the probe pulse. Chopping every second pump pulse out, by a mechanical chopper synchronized to the laser amplifier frequency, and comparing the probe signals with and without the pump pulse allows the change of absorbance ΔA of the sample, caused by the excitation from the pump pulse, to be determined. Varying the time delay between the pump and the probe pulses also enables the study of the time-dependent behavior of ΔA . Usually, the precise delay modulation between the pulses is realized with a high precision computer-controlled translation stage with corresponding temporal resolution on a sub-fs scale. This leads to a

two-dimensional dataset $\Delta A(\lambda, t)$, determined as

$$\Delta A(\lambda, t) = A(\lambda, t)_{\text{pump on}} - A(\lambda, t)_{\text{pump off}} \quad (3.2)$$

$A(\lambda, t)_{\text{pump off}}$ corresponds to the steady-state absorption spectrum of the sample, whereas $A(\lambda, t)_{\text{pump on}}$ also contains contributions from the excited state species of the sample. As the difference of the two signals is usually on a scale of 10^{-3} , it is important to constantly monitor both signals alternately throughout the experiment to correct for laser intensity fluctuations. In simple terms, a TA spectrum represents the difference in absorption between the excited-state species and the ground state as a function of the delay time after photoexcitation by the pump pulse. A TA signal usually consists of three different photophysical contributions (see Figure 3.2b).¹⁶³ Initially, the pump pulse excites the sample. The formed excited-state species may be further excited to higher lying excited states by the probe pulse. This results in an additional absorption signal, which is not present in the ground state, referred to as an excited-state absorption (ESA), and leads to a positive TA signal. The photoexcitation by the pump pulse depopulates the ground state. Thus, fewer photons can be absorbed at those wavelengths, resulting in a negative signal that resembles the steady-state absorption spectrum. This phenomenon is called ground-state bleach (GSB). A stimulated emission (SE) signal occurs when the photoexcited sample emits photons that are stimulated by the probe pulse. This process effectively increases the detected photon number and, thus, the transmission, appearing as a negative signal at the wavelength corresponding to the material's photoluminescence.

The kinetics of these signals give valuable information about the exciton dynamics with high temporal resolution on the scale of 200 fs. In general, the presence of a GSB signal at a specific delay time indicates that there is still some excited-state species that has not decayed to the ground state, but does not give information about the character of the excited state. The ESA signal is characteristic of the respective excited state from which the absorption occurs. As the energy levels and transition probabilities are molecule-specific, the ESA spectrum depends on the electronic character of the respective excited state. Thus, the ESA spectrum allows for the assignment of the excited-state species and the direct tracking of its population kinetics. Complementary to this, the SE signal characterizes the emissive states. These signals typically overlap, which complicates a straightforward assignment. Therefore, identifying the spectral characteristics of each phase within the sample in the steady-state spectra is key to deconvolute the spectral contributions in TA spectra.

For example, Figure 3.2c shows the TA spectrum of Y6 fully dissolved in tetrahydrofuran (THF) with a concentration of 0.02 g/l, excited with a 410 nm pump wavelength after 20 ps. Additionally, the normalized and inverse steady-state PL (dotted) and absorption (dashed) spectra of the sample are plotted. This allows us to assign the negative spectral progression with a minimum at about 1.75 eV and a shoulder at 1.90 eV to a GSB signal as it matches the steady-state absorption spectrum, and the negative signal at 1.55 eV to the SE signal as it

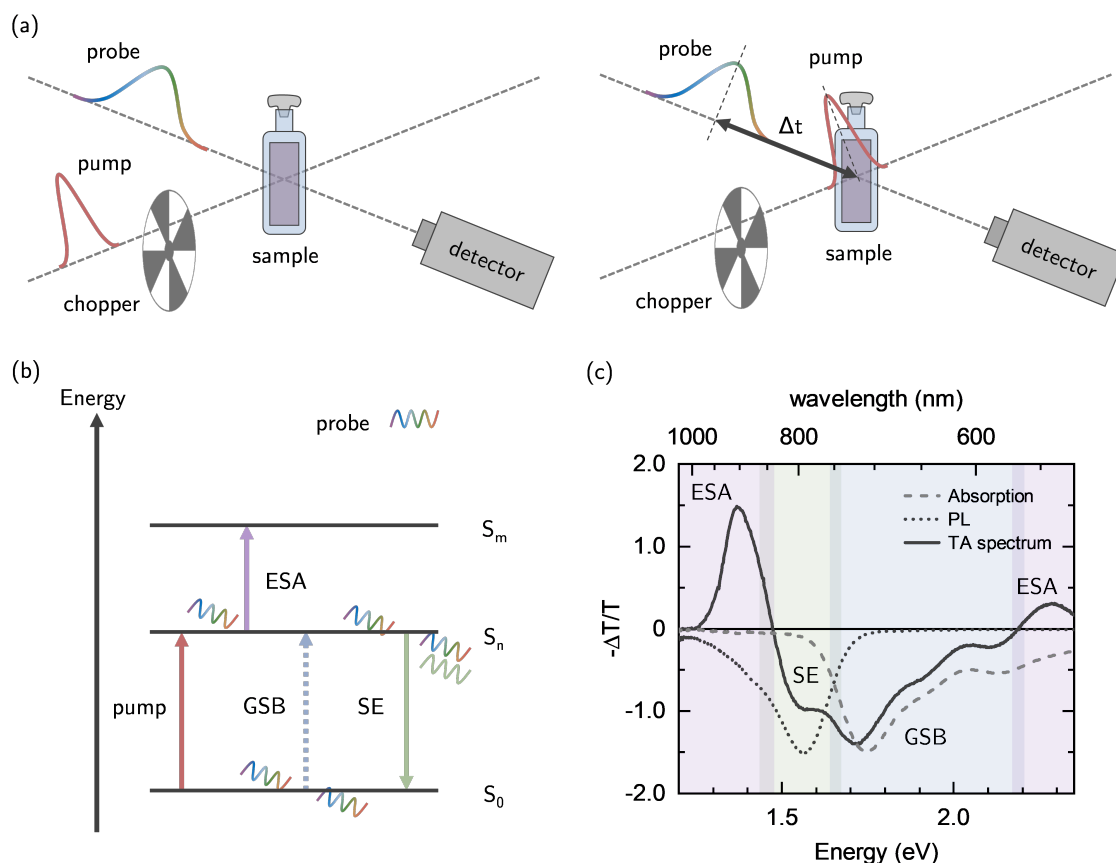


Figure 3.2: Schematic illustration (a) of the geometry of a pump-probe experiment, (b) of the possible signals detected during transient absorption spectroscopy. (c) Example of a transient absorption spectrum with additional steady-state absorption and emission spectrum to assign the origin of the different signals (ESA, SE, GSB), as indicated by different background. The shown spectrum is taken from Y6 in THF solution ($c = 0.02$ g/L) with a pump wavelength of 410 nm probed with 20 ps delay.

corresponds to the steady-state PL. Consequently, we can assign the positive signals to ESA signals. Note that at the negative and positive signals overlap, leading to deviations of the GSB (SE) signals and the steady-state absorption (PL) spectra.

Figure 3.3 displays the home-built femtosecond transient absorption setup used in this work, leaving out some mirrors and irises for simplification. A Yb:KGW femtosecond amplifier (Light Conversion, Pharos) serves as the primary light source with 180 fs pulses centered at 1030 nm at a repetition rate of 33 kHz. One output was used to generate a broadband probe beam. First, the beam goes through a collimating telescope. An optical delay line consisting of a quad-pass translation stage (Newport, DL325) allows for pump-probe delay times up to 7.5 ns. The probe beam then passes through a coarse delay stage to compensate for the different optical path lengths of the used pump line, respectively. A polarizing beamsplitter is used to control and stabilize the power of the fundamental before being focused onto a 2 mm sapphire

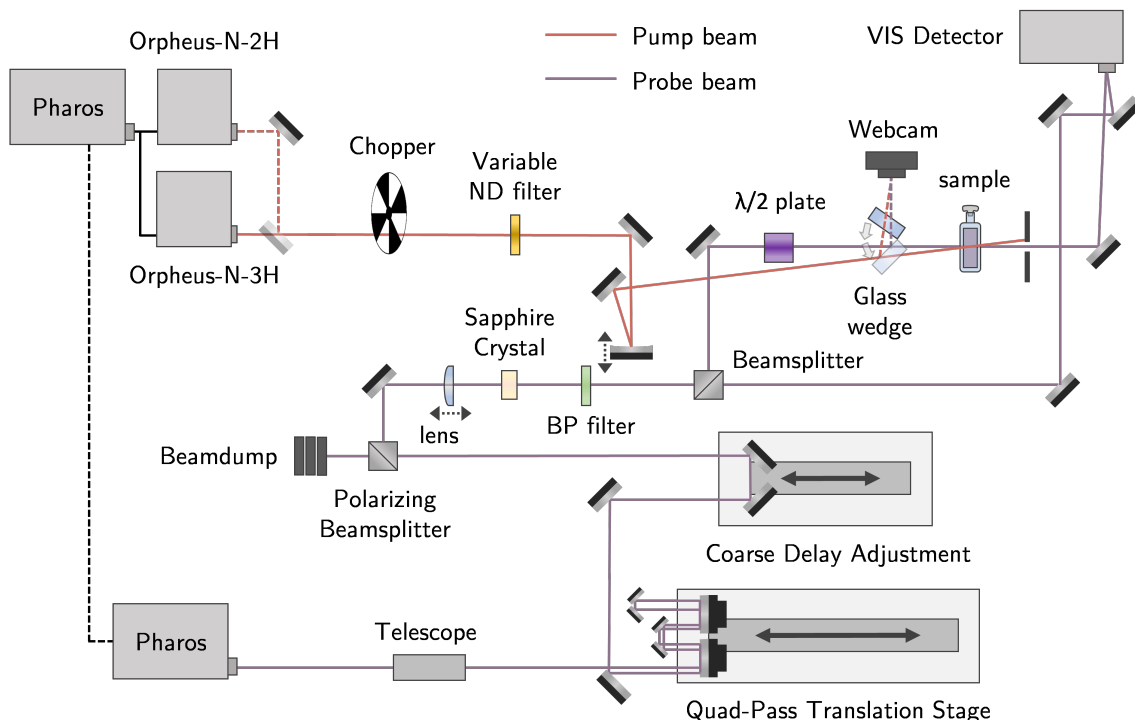


Figure 3.3: Schematic illustration of the home-built transient absorption spectroscopy setup. For simplification, only the essential components are depicted.

crystal for visible broadband generation. A bandpass filter blocks the remaining intensity of the fundamental. A 50:50 beamsplitter splits the beam into a sample and reference beam. Before hitting the sample, the beam passes through a $\lambda/2$ plate to maintain a relative pump-probe polarization at the magic angle (54.7°), thereby minimizing polarization biases. The sample and reference beam are then detected with a high-speed detector (EB Stresing, FLC3030) operating at the fundamental repetition rate (here 33 kHz) using a CCD camera. The second output of the 1030 nm output from the femtosecond amplifier was used to pump one of two non-collinear optical parametric amplifiers (Light Conversion, Orpheus-N-2H/Orpheus-N-3H), generating 30 fs excitation pulses centered at the desired pump wavelength. An optical chopper operating at 16.6 kHz modulated the excitation pulses to achieve an alternating pump-on/pump-off measurement. A variable ND filter allows for varying the pump-fluences before the beam is focused onto the sample. A flip-in glass wedge, combined with a webcam positioned directly before the sample, enables the determination of the spot sizes of the pump and probe beams. Throughout the measurement, the solution samples were constantly stirred.

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5 Overview of the thesis

This chapter provides an overview of the thesis, outlines the central research question, and explains how the individual projects and publications are interconnected. In addition, I highlight my specific contribution to each project and to the resulting scientific outputs.

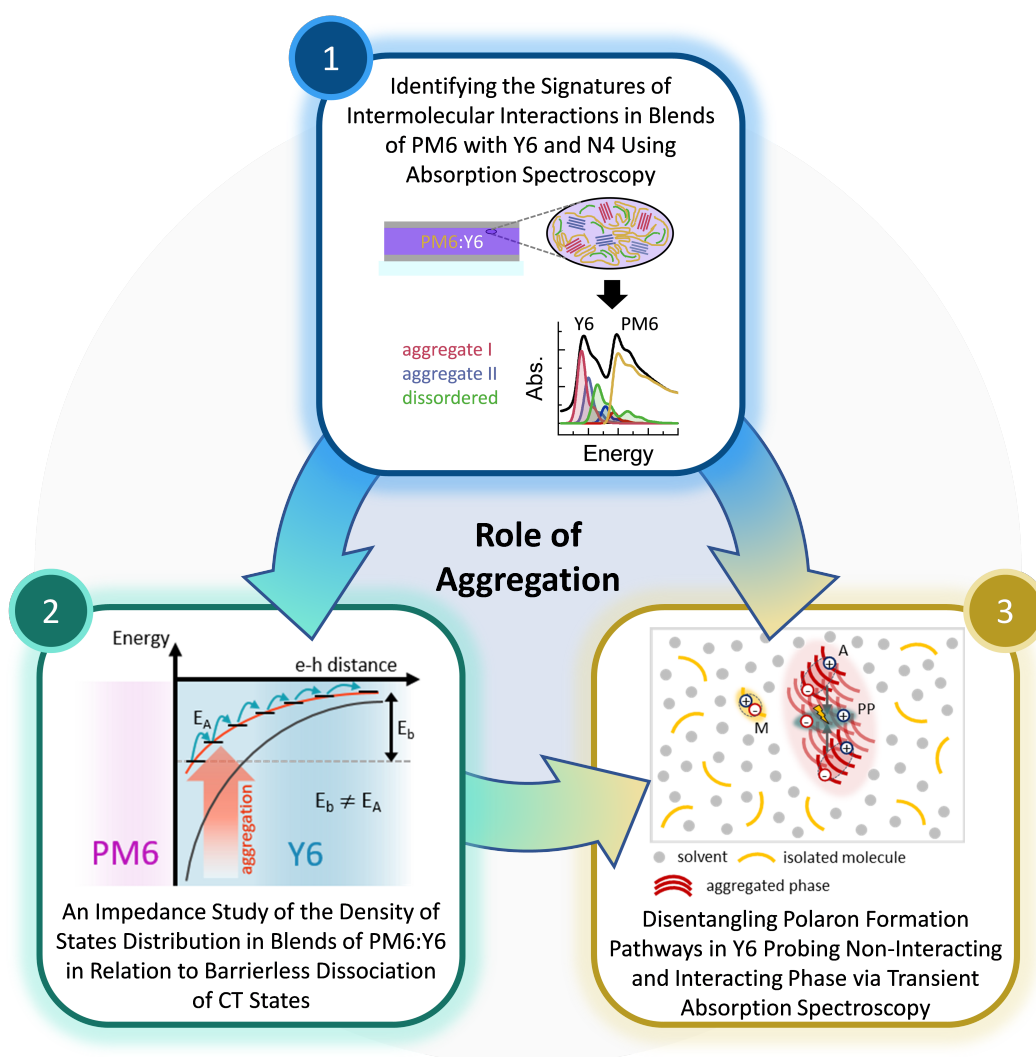


Figure 5.1: Overview of the research projects constituting the core of this thesis

The introduction of the polymer donor PM6 and the non-fullerene acceptor Y6 have significantly pushed the power conversion efficiencies of organic solar cells (OSCs) in recent years. Their exceptional performance is accompanied by a complex internal morphology consisting of a mixture of domains characterized by short-range order and amorphous regions containing a

blend of both materials. These domains together define the energetic landscape and optoelectronic properties. This dissertation aims to improve our understanding of how intermolecular interactions influence these properties in high-efficiency organic solar cell systems

The **first publication** (D. Kroh et al., *Adv. Funct. Mater.*, 32 (44), 2205711, 2022) focuses on identifying and assigning aggregate species in PM6, Y6 and N4 — an acceptor closely related to Y6, but with a more distant branching point in its side chain. Using temperature-dependent steady-state absorption and photoluminescence spectroscopy, we investigate the formation and nature of aggregation in these materials. For Y6 and N4, we observe two distinct types of aggregates with markedly different spectral characteristics. Through detailed Franck–Condon analysis, we identify these aggregate species in both neat and blend films with PM6, enabling spectral deconvolution into ordered and disordered components. PM6:Y6 films notably exhibit a stronger degree of aggregation, facilitating more efficient percolation pathways and superior charge transport and device performance compared to PM6:N4.

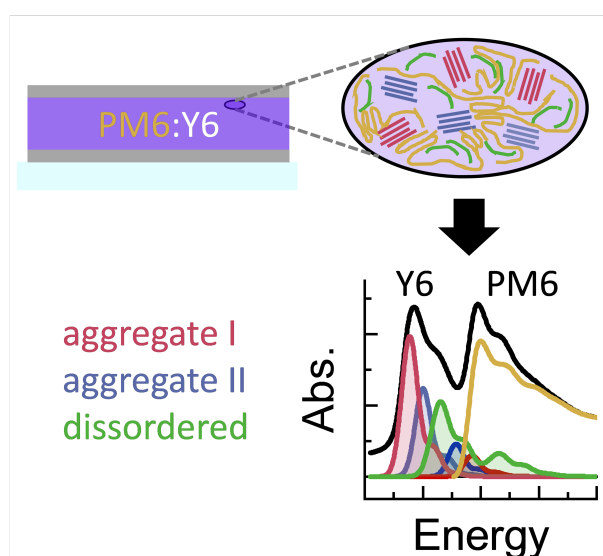
The **second publication** (D. Kroh et al., *Adv. Funct. Mater.*, 34 (50), 2302520, 2024) investigates the impact of aggregation on the energetic landscape and the binding energy of charge-transfer (CT) states in PM6:Y6 blends without a thermal barrier, motivated by the question of why CT states dissociate efficiently in these blends. Using energy resolved electrochemical impedance spectroscopy and intrinsic photoconductivity measurements, we determine the density of states (DOS) for the HOMO and LUMO levels of neat PM6, Y6 and the PM6:Y6 blend. We found a surprisingly low CT binding energy of 150 meV, which we attribute to hole delocalization along the polymer backbone and electron delocalization across multiple Y6 molecules within aggregates. A key insight from this study is also the distinction between the spectroscopically defined CT binding energy and the thermal activation energy of photocurrent generation.

The **third publication** addresses the challenge of identifying polaronic signatures in neat Y6 films. Previous transient absorption studies had reported polaron formation; however, due to the coexistence of disordered and ordered phases, as well as ultrafast exciton migration between them, it was difficult to assign signals to specific domains. To overcome this issue, we investigated the spectral signatures and excitation kinetics of the disordered and aggregated phases in isolation by inducing controlled aggregation in dilute solution. This approach enables us to deconvolute the spectra of both phases. We found that the aggregated phase exhibits a strong fluence-dependent decay, with lifetimes ranging from 30 to 200 ps. In contrast, the non-interacting species shows a fluence-independent decay around 1 ns. Additionally, we detect a long-lived species in the aggregated phase, which we attribute to polarons. These form in an Onsager-like autoionization manner. This provides valuable insight into the ultrafast photo-physics and charge-generation mechanisms of Y-type acceptors.

In summary, these three studies form a coherent body of work spanning the pathway from molecular aggregation to charge generation. A key finding was the clear identification of the spectral signatures of molecular interactions in Steady-state and transient absorption spectroscopy as well as their impact on excitonic kinetics. These insights not only clarify fundamental structure-function relationships but also support the targeted design of materials and morphologies for next-generation photovoltaic devices.

6

Identifying the Signatures of Intermolecular Interactions in Blends of PM6 with Y6 and N4 Using Absorption Spectroscopy



Author comment

This chapter incorporates the following publication: Daniel Kroh et al., "Identifying the Signatures of Intermolecular Interactions in Blends of PM6 with Y6 and N4 Using Absorption Spectroscopy", *Adv. Funct. Mater.*, 32, 2205711, **2022** ©2022 The Authors. Advanced Functional Materials published by Wiley-VCH GmbH

This publication sets the foundation of this thesis. Identifying the signatures of aggregation and being able to deconvolute the optical spectra was a breaking point to further investigate the optoelectronic behavior of interacting and non-interacting phases of organic semiconductors.

Identifying the Signatures of Intermolecular Interactions in Blends of PM6 with Y6 and N4 Using Absorption Spectroscopy

Daniel Kroh, Fabian Eller, Konstantin Schötz, Stefan Wedler, Lorena Perdigón-Toro, Guillaume Freychet, Qingya Wei, Maximilian Dörr, David Jones, Yingping Zou, Eva M. Herzig, Dieter Neher, and Anna Köhler*

In organic solar cells, the resulting device efficiency depends strongly on the local morphology and intermolecular interactions of the blend film. Optical spectroscopy was used to identify the spectral signatures of interacting chromophores in blend films of the donor polymer PM6 with two state-of-the-art nonfullerene acceptors, Y6 and N4, which differ merely in the branching point of the side chain. From temperature-dependent absorption and luminescence spectroscopy in solution, it is inferred that both acceptor materials form two types of aggregates that differ in their interaction energy. Y6 forms an aggregate with a predominant J-type character in solution, while for N4 molecules the interaction is predominantly in a H-like manner in solution and freshly spin-cast film, yet the molecules reorient with respect to each other with time or thermal annealing to adopt a more J-type interaction. The different aggregation behavior of the acceptor materials is also reflected in the blend films and accounts for the different solar cell efficiencies reported with the two blends.

1. Introduction

The efficiency of organic solar cells (OSCs) has remarkably improved within the last years to power conversion efficiencies surpassing 19% for single layer bulk-heterojunctions,^[1–13] and beyond 20% for tandem cells.^[14] This mainly results from the recent developments of nonfullerene acceptors (NFAs).^[15] The NFAs adjustability in energy levels, electronic structure, and harvesting long-wavelength absorption allowed for significant advances of the solar cell efficiency over that obtained in fullerene-based acceptor devices.^[15–19] This approach proved particularly successful when the so-called Y series acceptors, based on a general A–DA'D–A structure (A = acceptor moiety, D = donor moiety) and absorbing from 1.4 eV onward,

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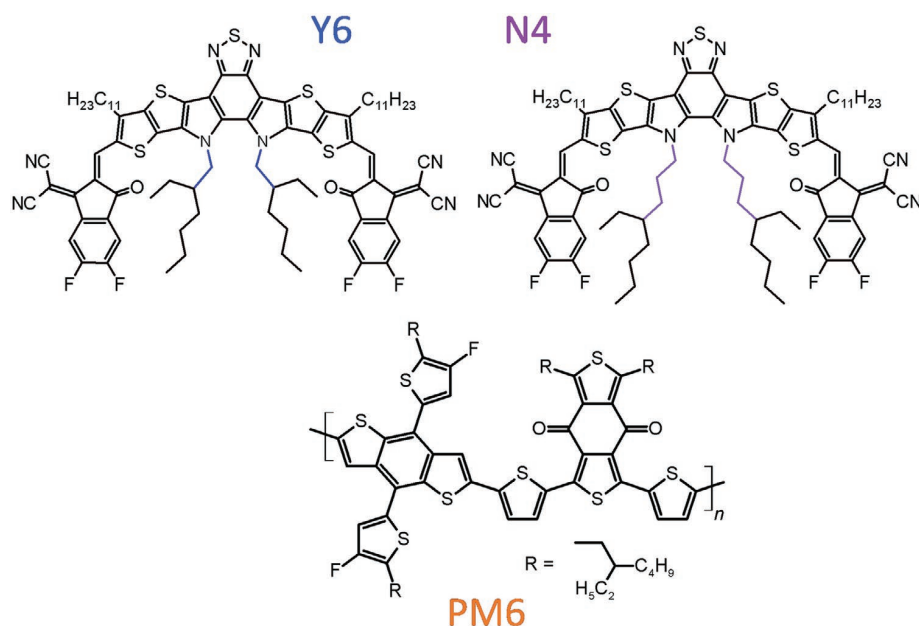


Figure 1. Chemical structures of Y6, N4, and PM6.

are combined with the polymer PM6 or related polymers (Figure 1).^[2–3,20–23] PM6 has a general D- π -A structure with an optical gap around 1.8 eV.

The outstanding performance of these Y-type acceptor materials especially blended with PM6 prompted many groups to dedicate significant effort to understanding the reason behind this. The observed dependence of the device performance on the processing conditions and blend composition suggested a strong role of the molecular arrangements and order in the blend film.^[24–27] This insight was further supported by the observation that side-chain modifications have a great impact on device performance. Side-chain modifications are well-known to alter the aggregation behavior and long-range order.^[23,25–26,28–40]

It is well-known that the performance of OSCs does not only depend on the material itself, but rather on the arrangement and orientation of individual molecules with respect to neighboring molecules. It is the local morphology and the resulting intermolecular interactions that control the energy levels as well as optical and electronic properties of the material, including the efficiency of exciton dissociation and charge extraction in a device.^[41–43] In consequence, the morphology of films with Y-type acceptors has been extensively studied by X-ray scattering. In single crystals, Y6 was found to form a “honeycomb” superstructure. Building blocks of this complex structure were identified in neat films of Y6 and in blend films made with Y6 and PM6. Molecular dynamics (MD) simulations and density functional theory (DFT) calculations allowed pinpointing dimer configurations that can make up these building blocks.^[7,44]

We complement these investigations on Y-type acceptors by identifying the associated intermolecular interactions using optical spectroscopy. This provides information about both, noninteracting and interacting chromophores not only in highly ordered but also in amorphous phases. Our aim is

to elucidate the presence and nature of such interactions in blend films of PM6 with two different Y-type acceptors. This requires first of all a clear identification of the optical signatures of intermolecular interactions in the neat materials. We therefore choose Y6 and N4 as electron acceptor materials (see Figure 1), which merely differ in the position of the branching point of the alkyl sidechains in the bay area of the molecule (2nd position branching for Y6, 4th position branching for N4).

It has been previously observed that both materials show differences in their long-range order, and thus, we expect concomitant differences in their aggregation behavior and intermolecular interactions that will help to understand the role of the backbone and sidechains.^[26,45] We are ultimately interested in blend films of PM6:Y6 and PM6:N4, which have previously been used by some of us to study the role of structural and energetic disorder on free charge recombination and open circuit voltage (V_{OC}).^[25] For this, we will first identify the signatures of intermolecular interactions that show in solutions upon cooling, which is a well-established approach.^[46–52] Cooling down the solution decreases the quality of the solvent. This induces interactions between the backbones of the sample molecules so that dimers or aggregates form. These interactions result in different absorption and photoluminescence spectra, which allows their identification and provides insight into the nature of the interactions.^[53–54] The spectral signatures of intermolecular interactions in solution will then be used to recognize interacting chromophores in the spectra of neat film of Y6, N4, and PM6, and subsequently in blend films of PM6:Y6 and PM6:N4, which are more complex as the spectra of the components superimpose.

For each of the acceptors, we assign the spectral signatures from two different types of interacting chromophores, one with a larger interaction energy and one with a smaller one, while

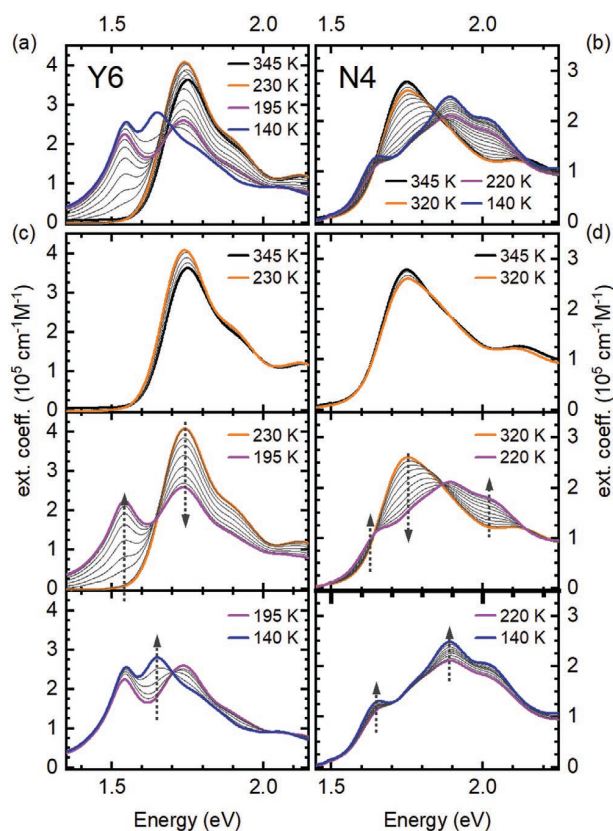


Figure 2. Absorption spectra of a) Y6 (left) and b) N4 (right) in MeTHF at a concentration of 0.15 mg mL^{-1} for different temperatures upon cooling from 345 to 140 K. Spectra taken at characteristic temperatures are drawn with colored solid lines and given in the legend. c,d) Spectra separated in three characteristic temperature ranges, respectively. Arrows indicate spectral changes in each temperature range.

there is only one type of interacting chromophores in the donor polymers PM6.

2. Results

2.1. Y6 and N4 in Solution

Figure 2 shows the absorption of Y6 and N4 in 2-Methyltetrahydrofuran (MeTHF) solution upon cooling from 345 to 140 K. A comparison of the full spectral evolution is shown in Figure 2a,b. Based on the spectral evolution of the absorption spectra upon cooling, we can group the spectra into three temperature ranges. These are displayed separately for clarity in Figure 2c,d. The corresponding emission spectra are shown in Figures S1 and S2 (Supporting Information). For Y6, the first characteristic temperature range is between 345 and 230 K (Figure 2b). At 345 K, the absorption spectrum has a peak centered at 1.75 eV and a shoulder at 2.90 eV. The linewidth, corresponding to a Gaussian linewidth with $\sigma = 72 \text{ meV}$, is characteristic for noninteracting molecules with a distribution of conformations in solution. Upon cooling, the first absorption

band increases slightly in intensity and shifts to lower energies by 10 meV. This behavior is indicative of an increase in conjugation due to a more planarized molecular backbone.^[46–49,51–52] An additional analysis of the emission spectra and decay times (see Figures S1–S3, Supporting Information) confirms that the electronic interactions between the molecules do not change down to 230 K.

The second characteristic temperature range is between 230 and 195 K. In this range, a new spectral feature in absorption appears at 1.54 eV. Concomitantly, the absorption band at 1.75 eV decreases in intensity, resulting in an isosbestic point at 1.64 eV. The appearance of an additional absorption feature, accompanied by an isosbestic point, indicates the transformation of one phase into another. This can be considered as a disorder–order transition with an onset temperature of $T_{\text{onset}} = 230 \text{ K}$, which is the first temperature upon cooling where signatures of aggregates can be observed.^[47–48,51–52] Evidently, individual solvated Y6 molecules start to interact electronically, thus forming physical aggregates. We further observe a rise in the baseline, which is characteristic for light scattering from small particles.

The lowest investigated temperature range between 195 and 140 K is shown on the bottom panel of Figure 2c. Below 190 K, there is another phase transition as evidenced by the emergence of a new peak at 1.65 eV, accompanied by a new isosbestic point at 1.70 eV. The observation of a second isosbestic point with $T_{\text{onset}} = 195 \text{ K}$ hints to the formation of a second type of aggregate. This is unusual for organic semiconducting materials in solution and has only been reported in a few cases.^[49,55] This phenomenon will be discussed further after analyzing the spectra in more detail.

The temperature-dependent spectral changes of N4 upon cooling from 345 to 140 K, i.e., the derivative that differs from Y6 merely in the branching point of the side-chains, are displayed in Figure 2b,d. Despite this subtle change, a different evolution with temperature compared to Y6 is readily obvious when comparing Figure 2a,b. For N4, the first characteristic temperature range is from 345 to 320 K. At 345 K, N4 still shows a similar absorption spectrum to Y6 with a maximum in absorption at 1.75 eV and a shoulder at 1.90 eV. However, in contrast to Y6, the intensity of the absorption band at 1.75 eV does not increase upon cooling but rather decreases. Notably, in the second temperature range, from about 320 K downward, we observe the appearance of additional absorption features at 1.66, at 1.89, and at 2.02 eV, and with two isosbestic points at 1.64 and 1.87 eV. Evidently, there is a phase transition of N4 with an onset temperature at around $T_{\text{onset}} = 320 \text{ K}$. In contrast to Y6, the new phase in N4 is not characterized merely by an obvious new peak at lower energy (1.66 eV), but also by an intense band at higher energy (1.89, 2.02 eV), which is a more unusual observation. We again take these features as indication for the presence of electronically interacting chromophores, such as physical aggregates. In the lowest investigated temperature range, when cooling below 220 K the new absorption features increase in intensity and become more structured, while the intensity of the original contribution at 1.75 eV remains constant. This suggests that the number of aggregates formed remains constant below 220 K, yet the molecules in the aggregates further optimize their geometry, e.g., by planarization.^[47,49,56] In contrast to

Y6, we do not observe the separate appearance of a different type of aggregate below 220 K. Upon heating, the same spectral features are obtained than upon cooling, albeit with a small temperature hysteresis (Figure S4, Supporting Information). We also measured the spectra in chloroform solution for the temperature range from 330 K (close to the boiling point of CF) down to 215 K (close to the melting point of CF), and observe the same trends as detailed in Figure S5 (Supporting Information).

2.2. Spectral Analysis

The temperature-dependent absorption measurements suggest the formation of electronically interacting chromophores when the solubility of the molecule in solution is sufficiently poor. To identify the optical signatures of the interacting chromophores and to disentangle them from the spectra of the noninteracting chromophores, we use Kasha's dimer model as a simple yet sufficient approximation. This is illustrated for reference in Figure 3, though we note that the number of interacting chromophores may be larger than two.^[57] As widely known, in this framework interactions between adjacent molecules lead to an energetic splitting of the excited state, with one energy level above and one below the energy of the excited state of the monomer (see Figure 3). In the case that the dispersion shift is negligible compared to the splitting of the energy levels, the latter are located symmetrically around the energy level of the excited state of the monomer.^[57,58] Frequently, the molecules arrange so that all oscillator strength lies in the transitions to the lower or upper of the two levels, which is referred to as H- or J-type dimers (or aggregates, if more than two molecules are involved), and then consideration of only one level for the interacting chromophores is sufficient. The special curved geometry of the Y-type acceptor molecules however allows for various mutual interaction possibilities and arrangements.^[7] We therefore explicitly consider both energy levels to model the absorption from one type of interacting chromophores.

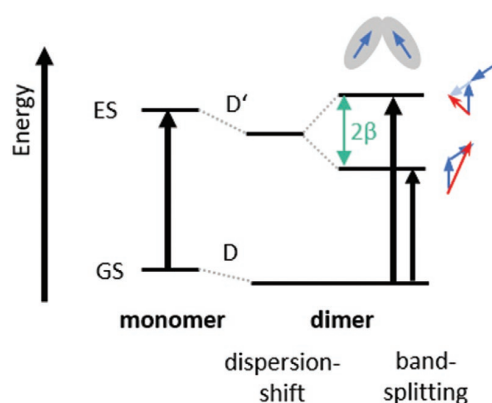


Figure 3. Oblique orientation of the dipoles of two molecules with the energy levels (GS: ground state, ES: excited state) for a monomer and the dimer, considering the dispersion shift $\Delta D = D - D'$ and the effect of the exchange energy β . The resulting transitions are displayed by the black arrows. The blue arrows indicate the transition dipoles of the corresponding molecules, the red arrows the total transition dipole moment.

Thus, to disentangle the different contributions to the absorption spectrum, we model the absorption spectra as a superposition of transitions, represented by Franck–Condon (FC) progressions. We first focus on the absorption spectra at a temperature just above the onset of the phase transition, where only noninteracting molecules prevail (i.e., at $T = 230$ K for Y6, at $T = 320$ K for N4). Based on Raman measurements of Y6,^[59] we use a single effective vibrational mode of $\hbar\omega = 162$ meV for both materials, Y6 and N4. This is justified since the two molecules only differ in the branching point of the alkyl side chains. We use one FC progression for the $S_0 \rightarrow S_1$ transition with a 0-0 energy of 1.74 eV and a second FC progression with the same Gaussian linewidth yet with a different Huang–Rhys parameter for the $S_0 \rightarrow S_2$ transition at about 2.15 eV. For both progressions, the Huang–Rhys parameter was optimized to best match the experimental spectra. The fit parameters are detailed in Table S1 and Figure S6 (Supporting Information).

We next considered the absorption spectra for Y6 at 230 and at 195 K, where we observed the additional absorption from interacting chromophores. To account for transitions to the two possible levels of one type of interacting chromophores, we add two further progressions, on redshifted and one blueshifted relative to the progression of the noninteracting molecules (marked by solid and dashed lines, respectively, in Figure 4). Even though we do not know whether the interacting chromophores are exactly two or maybe more molecules, we shall henceforth refer to them as aggregates in the implicit understanding that the limiting case of a dimer is included in this term. We constrain the two progressions pertaining to the lower and upper level of the aggregate to have the same dominant intramolecular effective vibrational mode of $\hbar\omega = 162$ meV as the noninteracting chromophores, yet since the aggregate may experience a narrower effective disorder, we allow the linewidth to differ from the noninteracting molecule. We further impose a symmetric splitting around the 0-0 energy of the noninteracting molecule, after accounting for a dispersion shift ΔD . It turns out that a satisfactory fit to the experimental data cannot be obtained by considering only one type of aggregate, as detailed further in c.f. Figure S7 (Supporting Information). Rather, a second type of aggregate needs to be included with low intensity. The same modeling approach was used for N4.

Figure 4 shows the spectral decomposition of the absorption spectra in solution of Y6 and N4 at two temperatures, respectively. Table 1 summarizes the Franck–Condon fit parameters for Y6 at 195 K and N4 at 220 K, i.e., 0-0 transition energy E_{00} , Gaussian linewidth parameter σ , Huang–Rhys parameter S_1 , vibrational energy $\hbar\omega$. Values for 140 K and for the S_2 transition of the noninteracting chromophores can be found in the Supporting Information. We name the aggregate with the larger energetic splitting *aggregate I* (colored in red in Figure 4) and the one with smaller splitting *aggregate II* (colored in blue). The indices LE and HE refer to the lower and higher energy level for each aggregate.

There are several noteworthy features. Table 1 allows us to derive the values for the dispersion shift ΔD and the interaction energy β simply by rewriting the 0-0 transition energies to the aggregate as $E_{00} = E_M + \Delta D \pm \beta$. The resulting values are summarized in Table 2, along with an indication of the intensity of the 0-0 transitions relative to that of the amorphous phase at

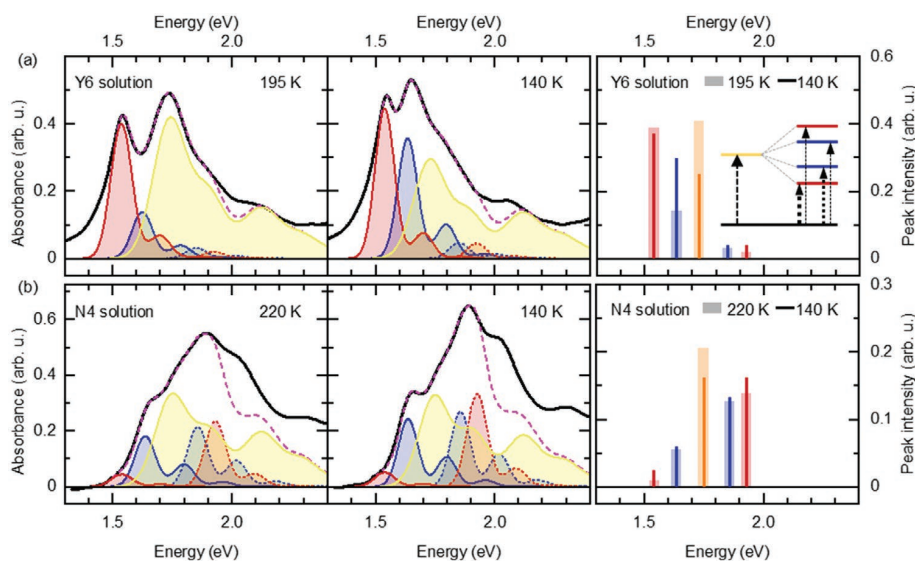


Figure 4. Spectral decomposition of the absorption spectra of a) Y6 and b) N4 in MeTHF solution at characteristic temperatures (195, 140 K for Y6 and 220, 140 K for N4) via a Franck–Condon Fit (detailed description in text). The disordered phase is colored in yellow, aggregate I in red and aggregate II in blue, each with their two progressions energetically below (solid line) and above (dashed line) the disordered phase. The global fit is displayed as pink dashed line. Additionally, we display the fractional intensity of each phase at 195/220 K as transparent bar and at 140 K as solid lines on the right side for both materials. A scheme of the underlying phenomenon of the energy level splitting is displayed in the top right graph.

195 K. The values for ΔD and β obtained for 140 K are almost identical except for the intensity of the transitions and can be found in the Supporting Information.

In summary, for Y6 we find that at 195 and at 140 K two different types of aggregates exist in the solution, in addition to the noninteracting chromophores. The absorption of aggregate I and aggregate II has some oscillator strength to both of the two split energy levels, yet the transition to the lower level dominates, akin to J-type aggregation. On the right side of Figure 4a, the associated intensities are displayed, normalized to sum up to one. The transparent bars show the intensities at 195 K, while the solid lines show the intensities at 140 K. At 195 K, the spectrum is dominated by comparable contributions from aggregate I and from noninteracting chromophores.

Table 1. The parameters for the FC-progressions used in Figure 4.

	Transition	E_{00} [eV]	σ [meV]	S_1	$\hbar\omega$ [meV]
Y6 in MeTHF 195 K	Noninteracting	1.74	69	0.43	162
	Agg. I, LE	1.54	44	0.15	162
	Agg. I, HE	1.92	44	0.15	162
	Agg. II, LE	1.62	44	0.26	162
	Agg. II, HE	1.85	44	0.26	162
N4 in MeTHF 220 K	Noninteracting	1.74	68	0.55	162
	Agg. I, LE	1.54	44	0.18	162
	Agg. I, HE	1.93	44	0.18	162
	Agg. II, LE	1.64	43	0.40	162
	Agg. II, HE	1.86	43	0.40	162

Upon cooling to 140 K, the contribution from noninteracting chromophores reduces further and concomitantly that from aggregate II increases, while the amount of aggregate I remains constant. Thus, below 195 K, a disorder–order transition takes place resulting almost without exception in the formation of aggregate II. Evidently, aggregate I has the stronger interaction energy and forms more readily even at a higher temperature, while aggregate II has a lower interaction energy and forms with less ease. As we performed the 140 K measurements on the same solution after the 195 K measurements, we cannot unambiguously distinguish whether aggregation II necessarily requires lower temperatures, i.e., a poorer solvent quality, or whether more time might already be sufficient for its formation.

Figure 4b shows the spectral decomposition of N4 in solution at 220 and 140 K with the corresponding intensities of the different species shown on the right side. We identify transitions to aggregates at about the same energetic positions as

Table 2. Dispersion shift, interaction energy, and fractional intensity for the aggregates in Y6 and N4 in MeTHF. The fractional intensity is shown for the low energy phase (LE) and high energy phase (HE) of the aggregates, respectively.

	ΔD [meV]	β [meV]	Fractional intensity	
			LE	HE
Y6, Noninteracting 195 K	–	–	0.41	
Y6, Agg. I at 195 K	–15	195	0.39	0.02
Y6, Agg. II at 195 K	–10	110	0.14	0.03
N4, Noninteracting 220 K			0.34	
N4, Agg. I at 220 K	–15	195	0.04	0.23
N4, Agg. II at 220 K	0	110	0.18	0.21

for Y6, and with similar interaction strength, yet with a clearly different intensity distribution. In contrast to Y6, at 220 K, the absorption of *aggregate I* (red) in N4 takes place mainly to the higher energy level, akin to a H-type aggregate, and the absorption to *aggregate II* (blue) takes place with almost equal intensity to both split energy levels.

Upon cooling down to 140 K, the distribution of oscillator strength remains nearly unchanged, except that the intensity of absorption from noninteracting chromophores reduces slightly relative to that from the aggregate. This very different distribution of oscillator strength in N4 compared to Y6 suggests that N4 forms dimers with similar interaction energy as Y6, yet with different relative orientations of the molecules. In simplified terms, one could associate the two aggregates in Y6 with a J-type character, and those in N4 with a more H-type character or oblique orientation of dipole moments. This assignment is consistent with the observed PL intensities (see the Supporting Information).

It is remarkable that this change in orientation of the interacting chromophores as well as the higher onset temperature of N4 is brought about merely by the change in the branching point of the side chain. In N4, the branching point is further away from the backbone than in Y6, reducing steric constraints for the mutual orientation of chromophore backbones and exposing the π -system. We speculate that this, first, increases the likelihood of π - π -stacking allowing for aggregation already at higher temperatures, and second permits a staggered backbone arrangement with partial overlap between donor and acceptor sites in N4, that may be precluded in Y6. The group of Brédas identified several dimer configurations by molecular dynamics simulations, either with more J-like or H-like character, which may correspond to the aggregate configurations observed with our spectroscopic analysis.^[7,44] This will be further discussed below. The observation of several aggregate types is not surprising in Y6 since a complex honeycomb structure has been previously confirmed, which consists of different dimer configurations.^[6–7,60]

2.3. Neat Y6 and N4 Films

Having identified the prevailing aggregates and their spectral characteristics in solution, the next step toward understanding the blend film composition is a spectral analysis of neat films for the acceptor materials, Y6 and N4. **Figure 5a,b** shows the absorption of Y6 and N4 films, spun from a solution of chloroform with 0.5% chloronaphthalene (CN) as-cast (ac, dotted lines) and after thermal annealing for 5 min at 90 °C (TA, blue and purple solid lines, respectively). These preparation conditions are well-known to achieve the best performances in solar cells made with blend films. For reference, the absorption in solution at 140 K is indicated as gray dotted line (sol.).

The first transition band of the neat, as-cast Y6 film has a dominant absorption peak at 1.55 eV with shoulders at 1.68 and 1.91 eV. Centered at 2.5 eV, a weak and structureless second transition band is evident. Annealing the neat Y6 film results in only small changes, where the low energy peak position slightly shifts to lower energies. Comparing the film spectra with the absorption in MeTHF solution at 140 K, it is evident that the observed peak at 1.55 eV and the shoulder at 1.68 eV of the films coincide with the energetic position of the peaks

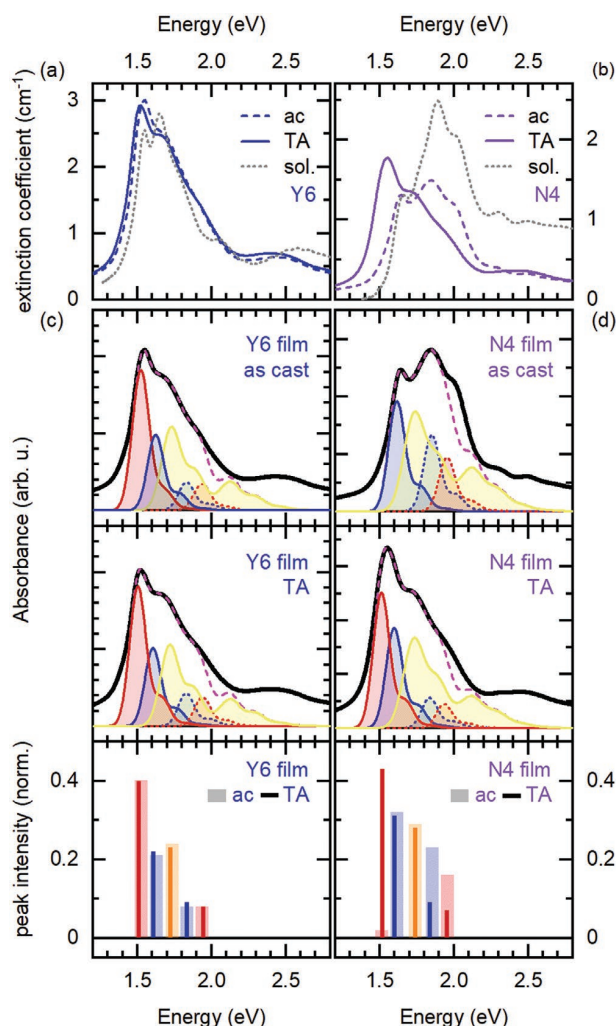


Figure 5. Absorption spectra of as-cast (dashed line) and thermally annealed (solid line) films of a) Y6 and b) N4. Additionally, the absorption in solution at 140 K is depicted (gray, dotted line), respectively. Spectral decomposition of the absorption spectra of the as-cast (top) and thermal annealed (middle) films of c) Y6 and d) N4 via a Franck-Condon Fit (detailed description in text). The disordered phase is colored in yellow, *aggregate I* in red and *aggregate II* in blue, each with their two progressions energetically below (solid line) and above (dashed line) the disordered phase. The global fit is displayed as pink dashed line. For a better comparison, we depict the peak intensity of each phase according to the spectral decomposition of the as-cast (transparent bar) and TA (solid line) film in one graph on the bottom.

of both aggregate types observed in solution, though the peak intensities differ slightly. For N4, the peak positions in the as-cast film also coincide with those in MeTHF at 140 K, yet the relative peak intensities differ strongly. Furthermore, and also in contrast to Y6, the absorption spectrum of the neat N4 film changes drastically in shape and position by thermal annealing, with a dominant lower energy peak emerging. As a result, the annealed N4 film appears similar to the spectrum of the Y6 film. Qualitatively the same spectral change is observed in N4 when, instead of annealing, the as-cast film is left to rest

Table 3. The parameters for the FC-progressions used in Figure 4.

	Phase ^{a)}	E_{00} [eV]	σ [meV]	S_1	$\hbar\omega$ [meV]
Y6 film as-cast	Noninteracting	1.73	64	0.42	162
	Agg. I, LE	1.52	57	0.13	162
	Agg. I, HE	1.93	57	0.13	162
	Agg. II, LE	1.62	55	0.20	162
	Agg. II, HE	1.83	55	0.20	162
N4 film as-cast	Noninteracting	1.73	70	0.48	162
	Agg. I, LE	1.51	55	0.18	162
	Agg. I, HE	1.95	55	0.18	162
	Agg. II, LE	1.61	55	0.20	162
	Agg. II, HE	1.85	55	0.20	162

^{a)}The FC-parameters for the TA films are very similar to the as-cast films for both, Y6 and N4, and can be found in the Supporting Information.

and measured again after 3 months (see Figure S8, Supporting Information). We point out that the extinction coefficient of the annealed Y6 film is almost twice the value of the annealed N4 film. Thus, the difference in the absorption of Y6 and N4 in the film is manifested in two features, that is an overall lower intensity of the N4 absorption, which is not present in solution, and a significant change in shape and position after annealing.

Figure 5c,d shows the spectral decompositions of the neat films, as-cast and thermal annealed, using the same approach as for the spectra in solution. For Y6, we find aggregates with similar energetic positions, Huang–Rhys parameters, coupling strength and even relative intensities in the as-cast or TA films as in solution, as detailed in Tables 3 and 4. Only the linewidth of the aggregates in the film is increased from roughly $\sigma = 44$ meV to $\sigma = 56$ meV when going from solution to film. This testifies that during film formation with the given preparation conditions, Y6 forms the same aggregates as in solution upon cooling. For N4, we also find two types of aggregates, at approximately the same energetic positions as in solution and as in Y6, and with similar Huang–Rhys factors. Even coupling strength and the change in linewidth from solution to film are similar to Y6. The feature that causes the strikingly different absorption in N4 is the different distribution of oscillator strength. Comparing the as-cast film to the MeTHF solution, we see a lesser contribution of the higher aggregate levels, a stronger contribution of the lower level of aggregate II, and, most prominently, a nearly complete absence of the lower level of aggregate I. Upon annealing, this level acquires significant oscillator strength, while that of the upper aggregate levels reduces, so that the distribution of oscillator strength is now closer to the case in Y6. Evidently, annealing N4 causes a significant reorientation of molecules with respect to each other toward a geometry that supports more J-type aggregation.

In summary, upon film formation we observe the formation of aggregates with similar energy levels as in solution. However, we find an overall lower absorption strength in the N4 film compared to the Y6 film, and we observe the signature of a significant change in geometric orientation between individual molecules after annealing. After annealing, the very similar

Table 4. Dispersion shift and interaction energy for the aggregates in Y6 and N4 in film.

		ΔD [meV]	β [meV]	Fractional intensity ^{a)}	
				LE	HE
Y6, as cast	Noninteracting	–	–	0.24	
	Agg. I	–5	205	0.40	0.08
	Agg. II	–5	105	0.21	0.08
Y6, TA	Noninteracting	–	–	0.23	
	Agg. I	+5	220	0.40	0.08
	Agg. II	+10	115	0.22	0.09
N4, as-cast	Noninteracting			0.29	
	Agg. I	–	215	0.0	0.16
	Agg. II	–5	120	0.32	0.23
N4, TA	Noninteracting			0.28	
	Agg. I	–5	215	0.43	0.07
	Agg. II	–15	120	0.31	0.09

^{a)}Intensities normalized so that intensities of all phases add up to 1 in the respective as-cast film.

spectra of Y6 and N4 suggest a similar orientation between molecules.

These findings can be compared against results obtained from grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements. Figure 6a shows the 2D maps of the scattering patterns of N4 and Y6 films on silicon, as-cast and after thermal annealing, respectively. Reference measurements on glass, confirming the analogous behavior of the examined materials on both substrate types, can be found in the Supporting Information. Both N4 films, as-cast and thermally annealed, show intensity at around $1.8 \text{ \AA}^{-1}$ predominantly in horizontal (q_{xy}) direction. This is indicative for π – π stacking with an edge-on orientation to the substrate. In contrast, the Y6 film shows intensity at around $1.8 \text{ \AA}^{-1}$ in vertical (q_z) direction, indicating a π – π stacking in face-on orientation consistent with previous publications.^[2,6,25,61] This difference in backbone orientation between N4 and Y6 accounts for the higher absorption intensity of Y6. Since the transition dipole moment is in the plane of the molecules, more intense absorption is possible for the predominant face-on orientation of Y6 compared to the edge on orientation of N4. The scattering images show no changes in the fundamental orientation upon thermal annealing.

The nature of nanostructure of the aggregates, as obtained from the low q -values, also differs between Y6 and N4 films. The horizontal and vertical cuts at low q -values are shown in Figure 6b. For the Y6 as-cast film we observe multiple clearly defined peaks at 0.22, 0.34, and $0.44 \text{ \AA}^{-1}$ in horizontal direction and at 0.52 and $0.62 \text{ \AA}^{-1}$ in vertical direction. This suggests a sample containing a complex structure. Upon annealing, only the peak intensities slightly change, which can also arise from small differences of the film thickness. The as-cast N4 film, in contrast, shows only one peak in this q range at $0.32 \text{ \AA}^{-1}$

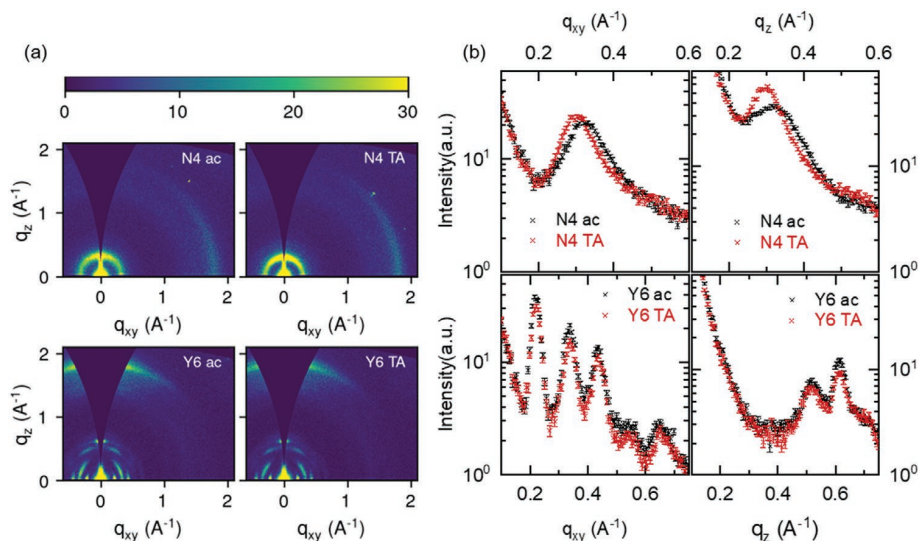


Figure 6. a) 2D-GIWAXS images of N4 (top) and Y6 (bottom) films, as-cast (left) and after thermal annealing (right) measured on Si substrates. b) Horizontal (left) and vertical (right) line cuts of the as-cast and thermal annealed films of N4 (top) and Y6 (bottom).

in horizontal and vertical direction. Hence, there is less pronounced order in as-cast films of N4 compared to Y6 which shows a clear superstructure beyond single molecules. Upon thermal annealing, we observe a significant change in the scattering pattern of N4. The main peak shifts to smaller q -values with a peak at $0.30 \text{ \AA}^{-1}$ in both directions. This shift is accompanied by an intensity gain in vertical direction, indicating an increase in the preferred orientation. The change in peak position and intensity suggests a significant adjustment of the nanostructure including an increase of the lattice parameter.

Evidently, the shift to smaller q_z values upon annealing N4 correlates with the redistribution of oscillator strength to the lower aggregate levels, and thus a reorientation of the transition dipole moments. However, as displayed in Figure 5, after annealing, the films of N4 and Y6 are characterized by very similar intermolecular electronic interaction, that is two kinds of predominantly J-like aggregates, in addition to a disordered phase, while they still differ significantly in their nanostructure, as demonstrated by the strikingly different GIWAXS data (Figure 6b). The difference in the formed nanostructures in N4 is even more striking when considering that N4 has aggregates in solution already at room temperature at the start of film formation, so that extended structures could potentially form during the entire drying process. But even in the dried film the structural order is not as well defined for N4 as for Y6 as observed by scattering. This method includes the investigation of structural order beyond individual molecules in contrast to spectroscopy. The Y6 nanostructure shows smaller peak width in the scattering data due to larger coherence lengths which can be translated to a molecular ordering with a range of almost 20 nm, while it is only about 7 nm for N4. This well-defined honeycomb nanostructure occurs during film formation, although Y6 at room temperature does not yet show signatures of aggregation in solution. We speculate that on the one hand, the longer side chains of N4 allow for an easier aggregation of

individual molecules, however, on the other hand these longer side chains also induce steric hindrance such that larger complex nanostructures cannot be formed.

2.4. Aggregation of PM6 in Solution and Film

Having considered the optical and GIWAXS signatures of the acceptor materials, we now investigate the aggregation behavior of the electron donor material PM6. Figure 7 shows the temperature-dependent evolution of the PL and absorption spectra of PM6 in oDCB at a concentration of 0.25 mg mL^{-1} upon cooling from 450 to 270 K. Here, PM6 follows the typical behavior of a conjugated polymer that aggregates upon cooling in solution. It displays an initial redshift upon cooling, followed by the appearance of a lower energy absorption, and a final sharpening of the vibrational structure at lower temperature, here 270 K. The PL intensity reduces as the aggregate absorption grows, which points toward a more H-like character.^[47–48,50–51] Thus, PM6 undergoes a disorder–order transition with an onset temperature at $T_{\text{onset}} = 420 \text{ K}$, i.e., well above room temperature. Above 420 K PM6 has only noninteracting chains. The PL spectrum is broad, which is typical for donor–acceptor polymers.^[62–63] The spectral shape of the PL spectrum from the interacting chains corresponds to the spectra obtained at 270 K. For the absorption spectrum of the interacting chains, the contribution from the noninteracting chains needs to be subtracted (see the Supporting Information).^[49,64] This implies that PM6 is one of the frequently used donor polymers that already contain aggregates in room temperature solution, a feature that has an impact on the resulting morphology in the thin film.^[50–51] For applications such as solar cells, the amount of PM6 aggregates in room temperature solution can be modified through the usual parameters such as choice of solvent, temperature, molecular weight, polydispersity, and other approaches.^[48,65–74]

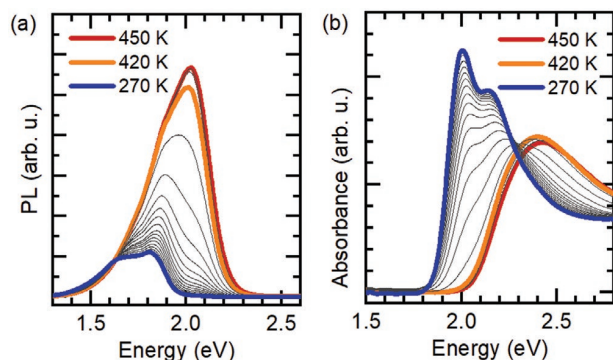


Figure 7. PL a) and absorption b) spectra of PM6 in oDCB at a concentration of 0.25 mg mL^{-1} upon cooling from 450 to 270 K in 10 K-steps. Spectra taken at characteristic temperatures are drawn with colored solid lines and given in the legend.

2.5. Blend Films

With the knowledge of the optical signatures of aggregates in Y6, N4, and PM6, we can now attempt to identify which species exist in blends of PM6:Y6 and PM6:N4. Solar cells made with such blends have previously been compared by Perdigón-Toro et al. They find a higher solar cell efficiency in the PM6:Y6 film, which is mainly a result of a higher open-circuit voltage V_{OC} . Perdigón-Toro et al. attributed this to a lower energetic disorder and higher phase purity in PM6:Y6. Temperature-dependent recombination studies revealed that free charge recombination is merely between a Gaussian-shaped highest occupied molecular orbital (HOMO) of the donor and a Gaussian-type lowest unoccupied molecular orbital (LUMO) density of states (DOS) of the acceptor in PM6:Y6, whereas recombination in PM6:N4 involves a wider Gaussian width of the acceptor LUMO and, in

addition, an exponential tail in the HOMO DOS, causing a significant decrease of the resulting V_{OC} .^[25]

In our work, we use blend films, prepared under the same conditions as Perdigón-Toro et al. and focus on the question how these blends differ regarding their content and nature of aggregated species. We use thermally annealed blend films with a material ratio of 1:1.2 for PM6:Y6 and 1:1.25 for PM6:N4 spun from chloroform with 0.5%/V CN as solvent additive. The absorption of the blend films is shown in Figure 8a. For both blend films, we observe two distinct absorption bands around 1.5 eV and around 2.0 eV, respectively, which are due to the absorption of the electron acceptor and the PM6, respectively. The absorption of N4 in the blend appears shifted to slightly higher energies compared to Y6. This suggests differences of the aggregation behavior between the acceptor compounds. The absorption of PM6 looks similar for both films, except for a slight difference in intensity, which may result from the slightly different material mixing ratios.

We can perform a spectral decomposition of the blend absorption by employing the parameters obtained from the Franck–Condon analysis of the neat films. It turns out that all values for the FC progression in Y6 and N4 are nearly identical in the blend and in the thermally annealed neat films (see the Supporting Information). For Y6, this is consistent with the results of molecular dynamics (MD) simulations, which show that the molecular packing of pristine Y6 is largely maintained in the blends.^[7] Differences occur only in the oscillator strength of the aggregates' components and their contribution relative to the noninteracting chains. The fractional intensities of the different aggregate levels are shown in Figure 8b.

The most obvious difference in the PM6:Y6 film is a higher contribution of the J-like aggregates relative to the noninteracting chains, and a particularly strong contribution of *aggregate I* (red). This feature has much less intensity in the PM6:N4 film, which accounts for the apparent blueshift of the spectrum.

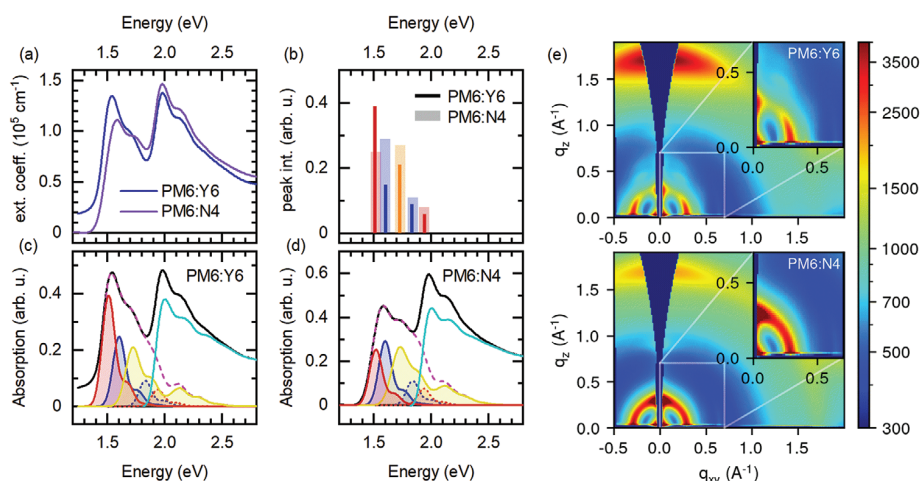


Figure 8. Absorption of TA blend films of a) PM6:Y6 (1:1.2) and PM6:N4 (1:1.25). b) Fractional intensities of the several phases of the acceptor compound in PM6:Y6 (solid line) and PM6:N4 (transparent bars) as obtained from the c,d) spectral decomposition of the absorption spectra of the blend films into a disordered phase of the acceptor compounds Y6 and N4 (dark yellow). The two acceptor aggregated phases (red, blue) with their low energy (solid line) and high energy (dotted line) progressions are shown respectively for N4 and Y6. The absorption contributed to PM6 is drawn with a turquoise line. e) 2D-GIWAXS images of PM6:Y6 (top) and PM6:N4 (bottom) measured on Si substrates. The inset shows a magnification of the low q -range (marked by the white square).

The higher degree of aggregation of Y6 in the blend film and the higher amount of *aggregate I* correlates to the better overall performance of the PM6:Y6 organic solar cell device than PM6:N4, which will be discussed below. The higher contribution of aggregates in the PM6:Y6 film is further consistent with GIWAXS measurements in the PM6:Y6 blend which show signatures of nanostructures arising from Y6 molecules, in contrast to the PM6:N4 film,^[25] as illustrated by the GIWAXS data shown in Figure 8e. Several connected Y6 molecules are required to form such superstructures.

3. Discussion

In recent years, many studies focused on unveiling the structural and morphological properties of Y-type NFA materials and their impact on the photophysical properties when blended with electron donors, such as PM6. For example, X-ray scattering revealed that Y6 and some of its derivatives form a complex “honeycomb” structure in single crystals.^[6–8,60,75] Molecular dynamics simulations show that pristine films of Y6 contain building blocks of this honeycomb structure, which are largely maintained when blended with PM6.^[7,44] Extracted from these simulations, four dimer configurations have been identified with different orientations of the molecular core (C) and terminal (T), as illustrated in Figure 9.

We put our results in context with the structures reported by Kupgan et al.^[44] For all samples in our study, we observe two aggregates, which differ in the interaction energy β and the distribution of the oscillator strength into the two levels. It is tempting to associate the dimers with the larger molecular overlap, i.e., CT–CT and CC–TT with the aggregates I that have a β just above 200 meV (c.f. Table 4), and the dimers with the smaller molecular overlap, such as TT and CT with aggregates II where β takes about half that value. The extent of the molecular overlap in the CC–TT arrangement appears to be similar

to the one in the CT–CT configuration. By visual inspection, it is reasonable to expect the transition dipole moments for CC–TT to align in a parallel fashion thus yielding a predominant H-type character, whereas the more sequential alignment in CT–CT will result in a J-type nature. In this framework, the observed reorientation and change from H-like to J-like character of aggregate I during the thermal annealing of the N4 neat film would correspond to a reorientation from the CC–TT to the CT–CT configuration. In Y6, the formation of a CC–TT orientation seems to be inhibited by the closer position of the side-chain branching to the backbone and its associated steric demand, while it is enabled by the more remote branching point in N4. This conclusion also fits to the observed scattering pattern. Previous spectroscopic and molecular dynamics studies on other D–A-type molecules revealed that for banana shaped molecules, like the shape of the Y-family, there are different pathways for dimer formation that lead to structures with CT–CT or CC–TT character. Which pathway is accessible depends on the steric demand of the sidechains.^[46,76]

The different branching point of the sidechain in N4 compared to Y6 can also account for the higher onset temperature of aggregate formation in MeTHF solution. Less steric hindrance of the sidechains enables electronic interaction of the backbones already at higher temperatures for N4, so that aggregation can occur. This is consistent with the observations by Lei et al. that moving the branching point away from a backbone results in stronger π -stacking interactions.^[77] We consider that this higher onset temperature for aggregation is also the cause for the different orientation of the aggregates toward the substrate that we observe by GIWAXS measurements. We found an edge-on orientation for N4 and face-on for Y6, in accordance with earlier reports.^[26] The higher onset temperature for aggregation, above room temperature, leads to the presence of aggregates already in solution prior to the film formation. Thereby, the π - π -interactions are already saturated to a certain degree, and the ability of the π -system to interact with the

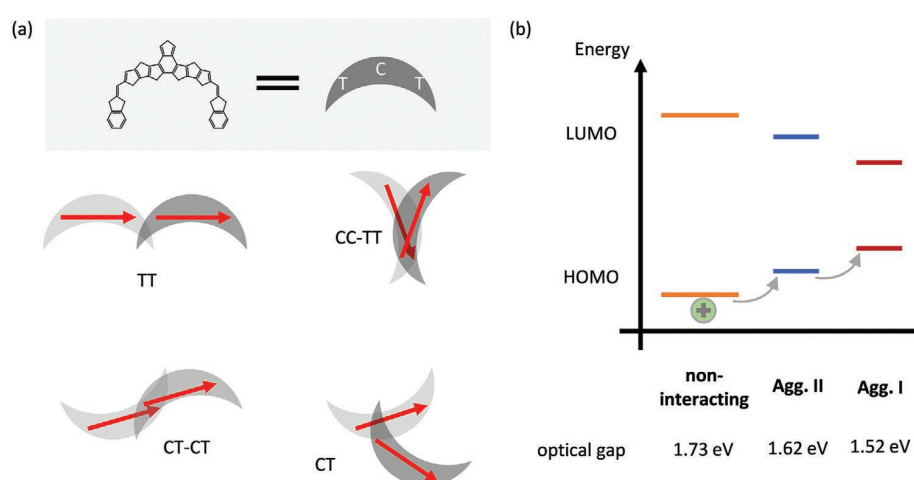


Figure 9. a) Schematic dimer configurations with interactions between the molecular core (C) and terminal (T) in different orientations as suggested by Kupgan et al. on the basis of MD simulations, along with our expected orientation of the transition dipole moments (red arrows). After.^[44] b) Schematic illustrating possible positions of HOMO/LUMO levels of aggregate I and II in a qualitative manner.

substrate is reduced. Consequently, preferably the side chains interact with the substrate, leading to a predominant edge-on orientation. In contrast, Y6 with a clearly lower onset temperature ($T_{\text{onset}} = 230$ K) is well dissolved until shortly prior to the complete evaporation of the solvent. Thereby, the π -system of the molecules can interact with the substrate unimpeded, resulting in a face-on orientation.

By influencing the short-range order in neat films, we also expect the sidechains to have an influence on the solar cell performance of blends with PM6. Both PM6 blend films with Y6 and N4 are reported to show excellent power conversion efficiencies. However, the Y6 based devices exceed the performance of devices with N4.^[25] Perdigón-Toro et al. attributed this to the unfavorable molecular edge-on orientation in the PM6:N4 blend, causing a reduced mobility. More importantly, the PM6:N4 blend was shown to exhibit a larger energetic disorder, in part with an exponential tail of trap states, which was shown to be the main reason for the smaller V_{OC} in PM6:N4 devices compared with PM6:Y6.^[25–26]

We find that the absorption spectra of PM6:Y6 contain a higher fraction of interacting chromophores than PM6:N4, and among them a particularly dominant proportion of aggregate I. While we do not know the HOMO and LUMO levels for Aggregate I and Aggregate II relative to those of the non-interacting molecules, their lower optical gap suggests a concomitant HOMO destabilization and LUMO stabilization. Consequently, charges will predominantly relax toward interacting chromophores of Aggregate I. (c.f. Figure 9) From the results of Perdigón-Toro we conclude that the number and distribution of Aggregate I-type chromophores in PM6:Y6 is sufficient to support a good percolation path for the charge carriers. In contrast, either the fraction or the distribution (or both) of Aggregate I-type chromophores in the PM6:N4 blend is such that transport is disrupted, with Aggregate I-type chromophores providing trap states for electrons. We consider that the long-range Coulomb potential fluctuations due to the presence of trapped negative charges lead to an nearly exponential tail in the HOMO DOS.^[54,78–79] We therefore conclude that the distribution of Aggregate I-type chromophores is responsible for the differences in the density of states (DOS) suggested by Perdigón-Toro et al., and the concomitant differences in solar cell performance.

We finally consider the effect of the different molecular packing in the two blends on the V_{OC} , which is found to be systematically lower in the PM6:N4 system.^[25–26] It was shown that free charge recombination in PM6:Y6 proceeds almost entirely through the CT state^[80] and we expect the same situation for the PM6:N4 blend. Then, the V_{OC} is determined by the energy, energetic disorder, and decay rate of the CT state.^[81] Unfortunately, the CT state absorption and emission is nearly hidden under the strong NFA exciton in both systems;^[25,80] therefore these properties are not attainable from optical spectroscopy. It has, however, been shown that the CT properties are largely linked to the energy, aggregation, and orientation of the molecules forming the CT states.^[82] As we point out earlier, the most obvious difference in the optical spectra is a higher contribution of the J-like aggregates in the PM6:Y6 film compared to the noninteracting chains but also the PM6:N4 blend. In addition, the GIWAXS measurements in the PM6:Y6 blend show

signatures of nanostructures arising from Y6 molecules, which require aggregates of several Y6 molecules to be present. Our GIWAXS results further reveal a more isotropic molecular orientation of the constituents in the PM6:N4 blend. In combination of these effects, we expect a larger energetic disorder of the CT state in the PM6:N4 blend, which will translate into a faster nonradiative decay and a smaller V_{OC} .^[83]

4. Conclusion

In this study, we identify and analyze the intermolecular interactions in Y series NFAs, and the role of the side chain branching point in the formation of aggregates, in highly efficient blend systems by optical spectroscopy in combination with a Franck–Condon analysis. For this, we used the well-established Y-type acceptors Y6, with 2nd position branching of the alkyl side-chains, and N4 (4th position branching), and combine these with the donor polymer PM6. PM6 shows a distinct aggregate formation in films as well as in solution with an aggregate onset temperature well above the room temperature. The two acceptor molecules are found to form two aggregate types, though with clearly different nature. Y6 forms two J-like aggregates with different interaction energies, which can also be observed in blend films with PM6. In contrast, N4 forms aggregates with more H-like character as the further branching point of the side chains enables a more parallel stacking due to less steric hinderance. Upon thermal annealing or for longer storage time, this H-character converts into a J-like character, which can be traced back to a molecular reorientation, in accordance with GIWAXS measurements. In the thermally annealed blend films with PM6, the aggregates of both acceptor materials show similar character, though the proportions of the aggregates differ. The PM6:Y6 blend contains a significant higher amount of the acceptor aggregate with higher interaction energy. This dominant absorption of acceptor aggregate correlates with good transport properties and low energetic disorder in the corresponding solar cells.^[25] This is not the case for the N4 phase in the PM6:N4 blend. There, an even distribution of the two types of aggregates and an overall lower contribution correlates with the appearance of an exponential tail in the DOS of the PM6 HOMO, consistent with the classical picture of DOS broadening by counter-charges on trapped isolated lower energy sites. In this way, the modification of the aggregation behavior through the slight extension of the side chain in the acceptor N4 causes a substantial change in the electronic structure of the donor PM6, with strong impact on the solar cell performance.

5. Experimental Section

The electron acceptor Y6 and the donor polymer PM6 were purchased by “1-material.” N4 was synthesized as described.^[26] For temperature-dependent solution measurements, N4 and Y6 at 0.15 mg mL^{−1} in MeTHF were dissolved. This corresponds to a molar concentration of about 1×10^{-4} mol L^{−1} for both materials. PM6 was dissolved in ortho-dichlorobenzene (ODB) at a concentration of 0.25 mg mL^{−1}. The solutions were stirred for at least 1 h at 50 °C to ensure complete dissolution of the materials. Temperature-dependent absorption and

emission measurements were carried out using a home-built setup. The solutions were filled in a 1 mm fused silica cuvette and placed in a temperature controlled continuous flow helium cryostat by Oxford Instruments. After reaching each temperature step of the measurement, waited for 15 min to ensure a fully equilibrated system before taking the measurement. The lowest accessible temperature was determined by the glass transition temperature of MeTHF, i.e., 137 K. A tungsten lamp is used as light source for absorption measurements. For emission measurements, a 405 nm continuous wave diode laser from Coherent was used to excite the PM6 samples and a 659 nm continuous wave diode laser for the Y6 and N4 samples. A spectrograph Andor Shamrock SR303i coupled to a CCD camera (Andor iDus 420) functions as detection system.

For neat film samples, solutions of neat Y6 and of neat N4 in chloroform at 12 mg mL⁻¹, and of neat PM6 in chlorobenzene at 8 mg mL⁻¹ were prepared. Solutions of blends with PM6:Y6 in weight ratios of 1:1.2, and of PM6:N4 (weight ratio 1:1.25) were prepared in chloroform at a total concentration of 16 mg mL⁻¹. All solutions were mixed with 0.5% chloronaphthalene (CN) and then stirred for at least 2 h at 50 °C. All films were prepared by spin-casting the solution in a glovebox with nitrogen atmosphere at room temperature with 1000 rpm. Thermal annealing (TA) was conducted at 90 °C for 5 min. UV–vis absorption spectra of films at room temperature were captured with a Cary 5000 UV–vis spectrometer.

GIWAXS on neat films coated on silicon substrates was performed in vacuum at RT on a laboratory system at the University of Bayreuth (Xeuss 3.0, Xenocs SAS, Grenoble, France) with a Cu K α source ($\lambda = 1.54$ Å), a Dectris EIGER 2R 1 m detector, and a sample-to-detector distance of 52.5 mm. Scattering experiments were carried out on silicon substrates due to decreased scattering background compared to glass. Figure S9 (Supporting Information) shows the GIWAXS data on glass for comparison. The presented q -profiles are cake cuts covering an azimuthal angle of 70°–110° for the cuts in the vertical direction and 0°–20° as well as 160°–180° for the cuts in the horizontal direction. The 2D GIWAXS measurements on blend films were performed on PEDOT:PSS (poly(3,4-ethylenedioxythiophene) polystyrene sulfonate) coated silicon substrates in vacuum at RT at the Soft Matter Interfaces beamline (12-ID) at the National Synchrotron Lightsource II (NSLS-II) at Brookhaven National Laboratory ($\lambda = 0.77$ Å), with a Dectris Pilatus200KW detector with a sample-to-detector distance of 275 mm at different rotational angles. These measurements are averages over 6 positions on the sample each measured for 20 s to reduce effects due to inhomogeneities. Changes in intensity profiles with time were tested and no beam damage was determined for 20 s of exposure.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

charge-transfer states, Frank–Condon analysis, morphology, organic solar cells

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Supporting Information

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Identifying the Signatures of Intermolecular Interactions
in Blends of PM6 with Y6 and N4 Using Absorption
Spectroscopy

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Supporting Information

Identifying the signatures of intermolecular interactions in blends of PM6 with Y6 and N4 using absorption spectroscopy

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Y6 in mTHF – emission and TCSPC

Figure S1 shows the corresponding emission spectra of Y6 in mTHF solution (left), displayed in the same temperature ranges as the absorption (right).

In the high temperature range, the shape of the emission spectra resembles a mirror image of the absorption spectra. However, while the absorption increases only moderately, the emission rises strongly, reaching its maximum at 250 K (solid black line) and then decreasing slightly to 230 K. This is accompanied by a slight bathochromic shift.

The increase in emission intensity far exceeds the increase in absorption. Evidently, there is a mechanism that increases the photoluminescence quantum yield, $\Phi = k_r/(k_r + k_{nr})$ with the radiative transition rate k_r and non-radiative transition rate k_{nr} . To establish whether k_r increases, or whether k_{nr} decreases, we measured the photoluminescence transients at 345 K, 295 K and 250 K, which gave mono-exponential decays with lifetimes of 386 ps, 1.0 ns, and 1.4 ns, respectively (see Figure S2). Evaluating the relative changes in Φ and τ lifetime shows that k_r remains unchanged implying that k_{nr} reduces upon decreasing the temperature, most likely by freezing out thermal deactivation through rotations between the Y6-core and the acceptor arms. The constant value of k_r implies that electronic interactions between the molecules in solution do not change down to 230 K. Consequently, Y6 remains completely in the disordered phase down to 230 K

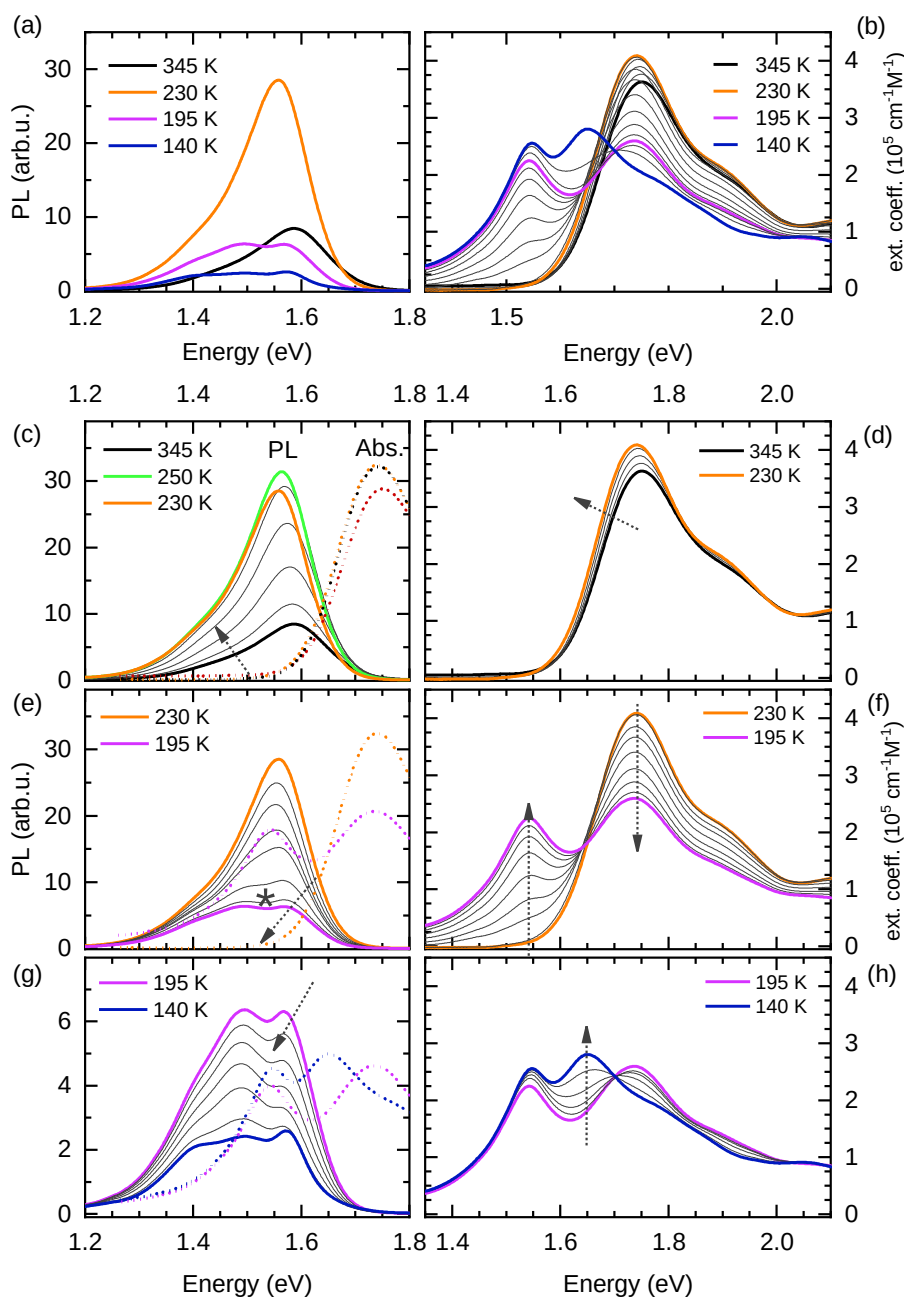


Figure S1: PL (a,c,e,g) and absorption (b,d,f,h) spectra of Y6 in mTHF at a concentration of 0.15 mg/ml for different temperatures upon cooling from (a,b) 345 K to 140 K. Spectra taken at characteristic temperatures are drawn with colored solid lines and given in the legend. Spectra are shown (c,d) between 345 K and 230 K in steps of 20K, (e,f) between 230 K and 195 K in steps of 5 K, and (g,h) between 195 K and 140 K in steps of 10 K. In the absorption spectra at characteristic temperatures outside the ranges are shown with dashed lines. In the PL spectra the absorption spectra at specific temperatures are additionally drawn in dotted lines.

N4 in mTHF – emission

Figure S2 shows the corresponding emission spectra of N4 in mTHF solution (left), displayed in the same temperature ranges as the absorption (right). The absorption spectra are described and discussed in the manuscript.

At 345 K, the PL spectrum is broad and a mirror image of the absorption spectrum with a peak at 1.58 eV. In the high temperature range, the PL slightly increases and the peak shifts to lower energies, implying an increase in oscillator strength by planarization of the molecules. Upon cooling below 320 K, the overall intensity strongly decreases at 1.58 eV, resulting in a spectrum with a peak at 1.40 eV at 220 K, while the absorption reveals that aggregate formation takes place in this temperature range. Further cooling to 140 K slightly increases the PL intensity and the spectrum shifts to lower energies, while the intensity at 1.58 eV goes down to zero. This is consistent with the observation, that in this temperature range the aggregates phase planarizes, which enhances the PLQY and enhances the energy transfer from the disordered phase to the aggregated phase. Thus, at 140 K, we only observe emission from the aggregated phase.

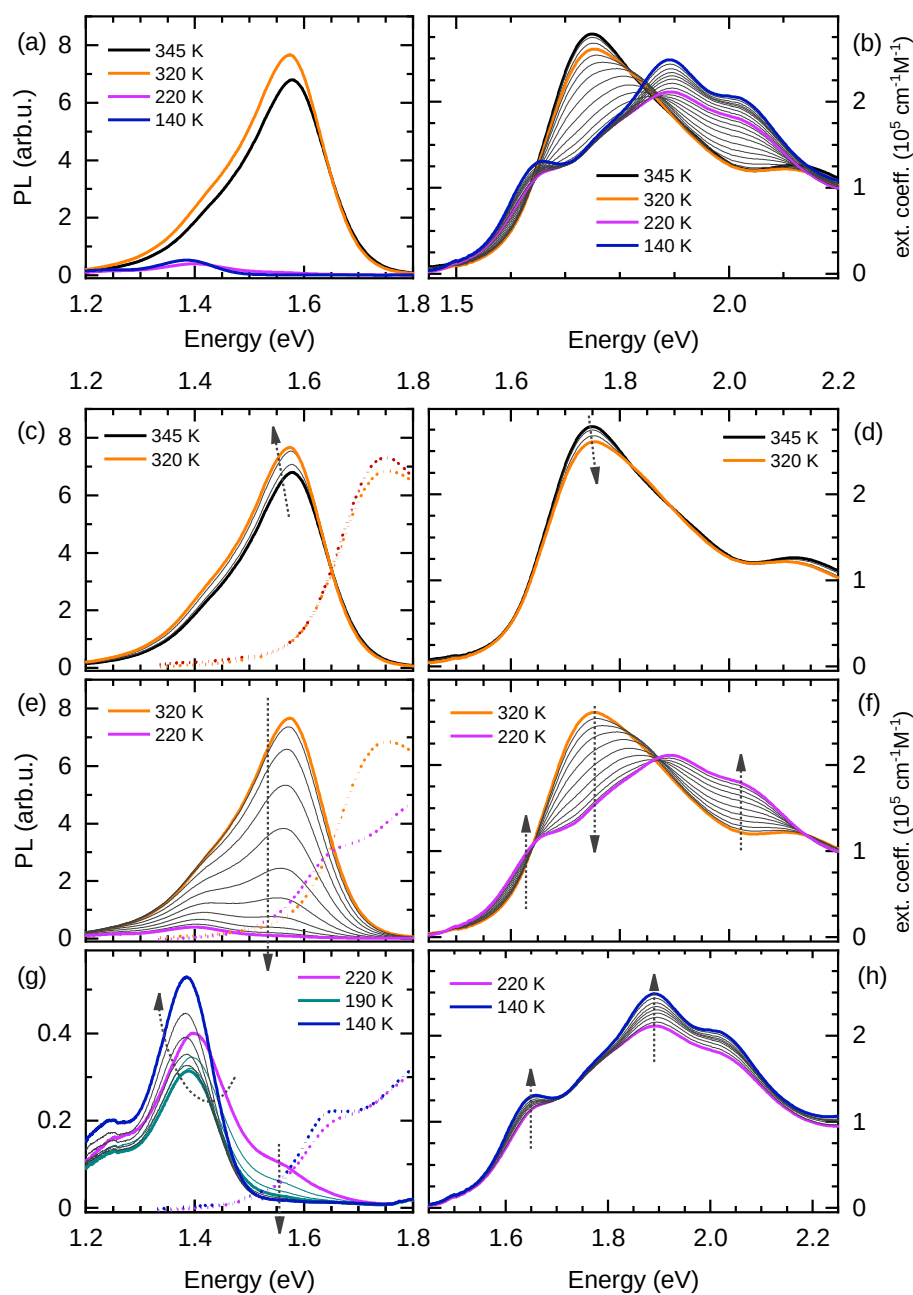


Figure S2: PL (a,c,e,g) and absorption (b,d,f,h) spectra of N4 in mTHF for different temperatures upon cooling from (a,b) 345 K to 140 K at a concentration of 0.15 mg/ml. Spectra taken at characteristic temperatures are drawn with colored solid lines and given in the legend. Spectra are shown (c,d) between 345 K and 320 K, (e,f) between 320 K and 220 K, and (g,h) between 220 K and 140 K in steps of 10 K. In the absorption spectra at characteristic temperatures outside the ranges are shown with dashed lines. In the PL spectra the absorption spectra at specific temperatures are additionally drawn in dashed lines.

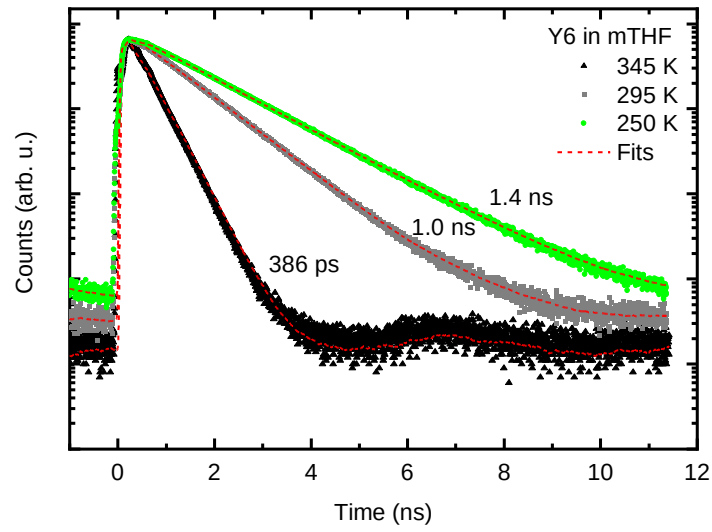


Figure S3: TCSPC measurements of Y6 in mTHF solution at 345 K, 295 K and 250 K with monoexponential decays with lifetimes of 386 ps, 1.0 ns, and 1.4 ns, respectively.

PLQY calculation:

$$\Phi = k_r * \tau$$

$$\frac{\Phi_{345K}}{\Phi_{250K}} = \frac{8.6}{31.4} = 0.27 \text{ (PL Peak intensity)}$$

$$\frac{\tau_{345K}}{\tau_{250K}} = \frac{386}{1434} = 0.27 \text{ (PL life - times)}$$

$$\Phi_{345K} = 0.27 \Phi_{250K}$$

$$k_r^{345K} * \tau^{345K} = 0.27 k_r^{250K} * \tau^{250K} \text{ with life - times}$$

$$k_r^{345K} = k_r^{250K}$$

Heating process of Y6 and N4 in mTHF solution

Figure S4 shows the absorption spectra during the heating process of Y6 and N4 in mTHF solution. Compared to the cooling process, the absorption spectra show a slight hysteresis. From 140 K to 170 K, we identify an isosbestic point at 1.73 eV accompanied by a decrease of the peak intensity at 1.65 eV and increase at 1.75 eV, indicating a dissolution of *aggregate II*. Between 170 K and 220 K we have a transition range, where the intensity below 1.73 eV decreases, which indicates a dissolution of both aggregated phases. Above 220 K we identify another isosbestic point at 1.65 eV accompanied by a decrease of the peak intensity at 1.53 eV and a strong increase of the intensity at 1.75 eV, which indicates a re-transformation of *aggregate I* to non-interacting, disordered molecules. Thus, the heating process shows a slight hysteresis, which in a temperature-delayed manner.

In contrast, the absorption spectra of the heating process of N4 in mTHF shows almost no hysteresis compared to the cooling process.

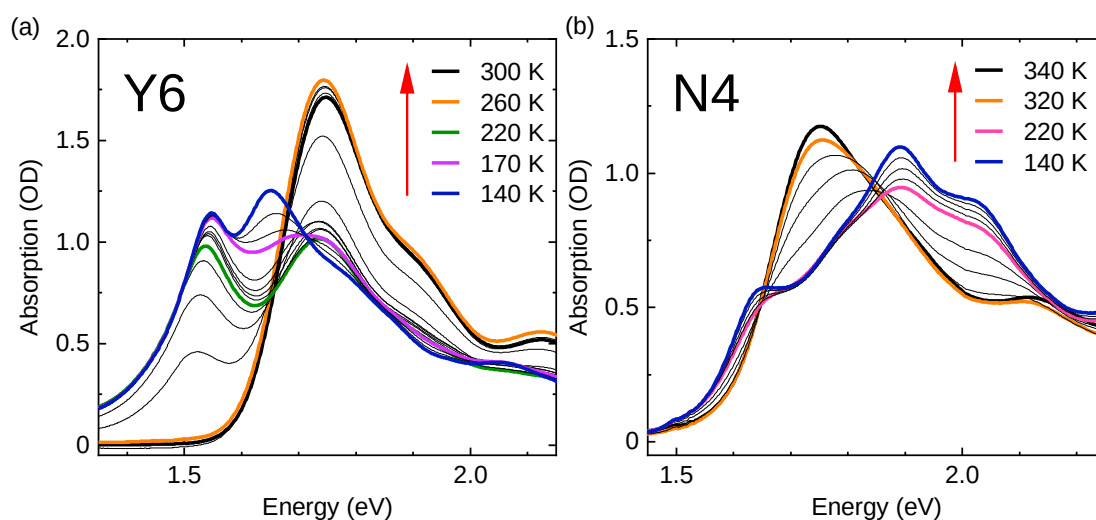


Figure S4: Absorption spectra of (a) Y6 in mTHF solution at a concentration of 0.2 mg/ml upon heating from 140 K (blue) to 300 K (black) in 10 K steps and (b) N4 in mTHF solution at a concentration of 0.2 mg/mL upon heating from 140 K (blue) to 340 K (black) in 20 K steps.

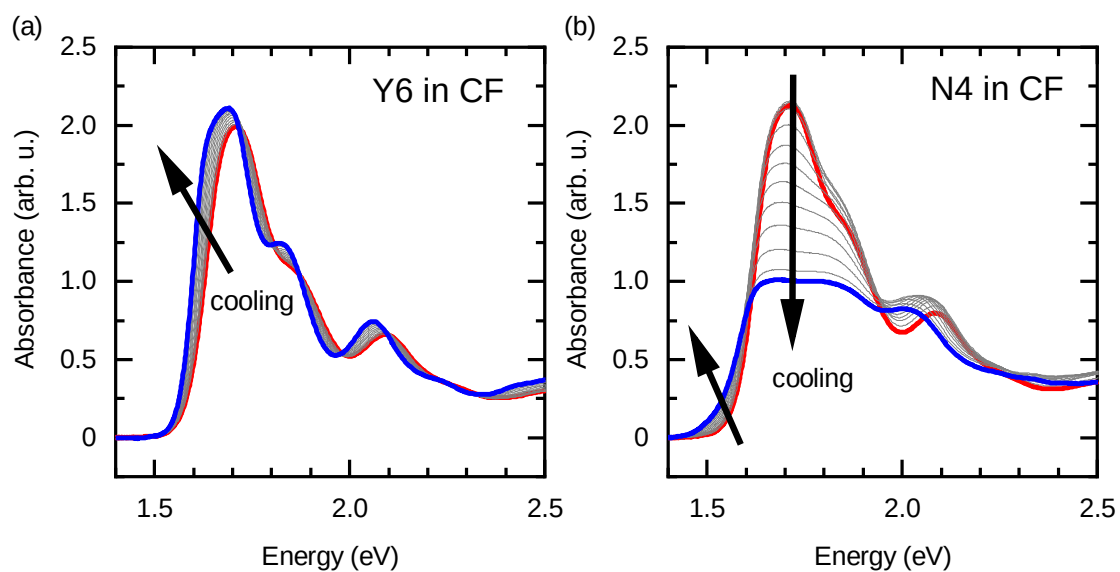


Figure S5: Absorption spectra of (a) Y6 and (b) N4 in CF solution at a concentration of 0.2 mg/ml upon cooling from 330 K (red) to 215 K (blue) in 10 K steps from 330 K to 220 K and the lowest measured temperature 215 K. Arrows indicate spectral changes upon cooling.

Franck-Condon analysis

Figure S6 shows the Franck-Condon fit for the absorption of Y6 in mTHF at 230 K, which we assign to the spectrum of the non-interacting conformation. Therefore, we used an effective mode of 162 eV to fit the $S_0 \rightarrow S_1$ transition with an E_{00} at 1.73 eV. We assign the peak at 2.13 eV to the $S_0 \rightarrow S_2$ transition and thus fitted it with a new progression with the same effective mode, but adjusted Huang-Rhys parameter. The values for the fits to the $S_0 \rightarrow S_2$ transition of the non-interacting conformations are shown in Table S1. For all other FC fits, the values of the $S_0 \rightarrow S_2$ transition are kept constant as well as the intensity ratio of $S_0 \rightarrow S_1$ to $S_0 \rightarrow S_2$.

Table S1: The parameters for the FC-progressions used for the non-interacting conformation of Y6 at 230 K

	transition	E_{00} (eV)	σ (meV)	S_1	$\hbar\omega$ (meV)
Y6 in mTHF 230 K	non-interacting, $S_0 \rightarrow S_1$	1.73	69	0.43	162
	non-interacting, $S_0 \rightarrow S_1$	2.13	72	0.50	162

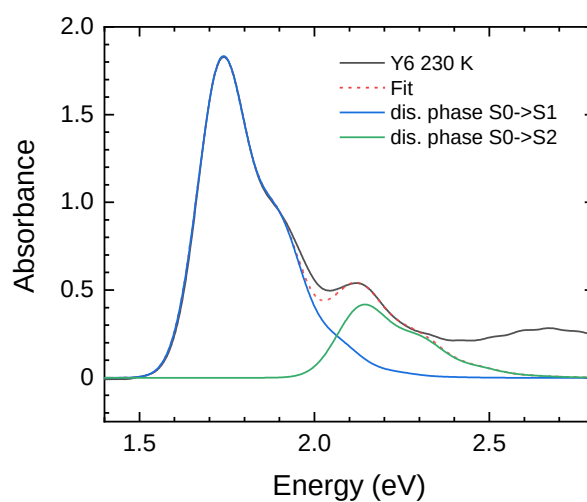


Figure S6: Absorption spectrum of Y6 in mTHF at 230 K with Franck-Condon fit with a progression at 1.73 eV fit with an effective mode at 162 meV to fit the $S_0 \rightarrow S_1$ transition and a second progression at 2.13 eV with an effective mode of 162 meV to fit the $S_0 \rightarrow S_2$ transition. The spectrum has been used as “monomer-phase” to decompose absorption spectra at lower temperatures, where spectral signatures of aggregate absorption appears.

Franck-Condon Fit: Y6 at 195 K in mTHF solution

Figure S7 shows a Franck-Condon Fit of the absorption spectrum of Y6 in mTHF solution at 195 K using a monomer/disordered phase and only one aggregate species. The peak at about 1.54 eV limits the linewidth of the aggregated phase (red) leading to a deviation of the global fit (red, dashed line) and the absorption spectrum at around 1.62 eV. Thus, we used a second aggregated phase to fit the absorption as described in the manuscript.

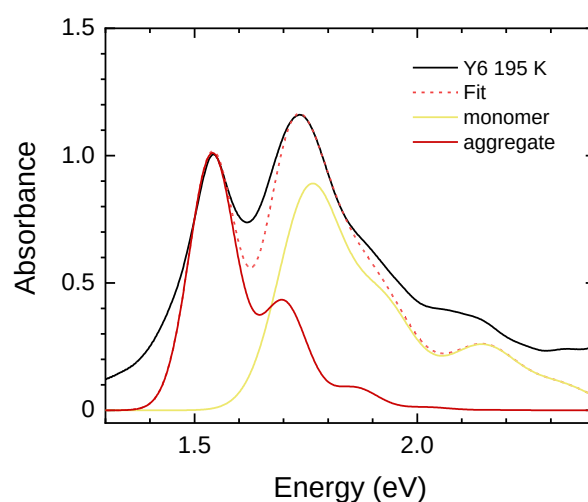


Figure S7: Absorption spectrum of Y6 in mTHF at 195 K with a Franck-Condon global fit (red dashed line) with a monomer phase (yellow) and only one aggregated phase (red).

N4 film after 3 months

Figure S8 shows the absorption spectra of the same N4 films, as-cast and thermally annealed, after 3 months. The spectrum of the thermally annealed film does not undergo spectral changes and only decreases a slightly in intensity. The spectrum of the as-cast N4 film has changed over time and almost resembles the spectrum of the thermal annealed film. Thus, giving the system of the as-cast film time results in a change of the morphology to the thermodynamic more stable morphology present in the TA films.

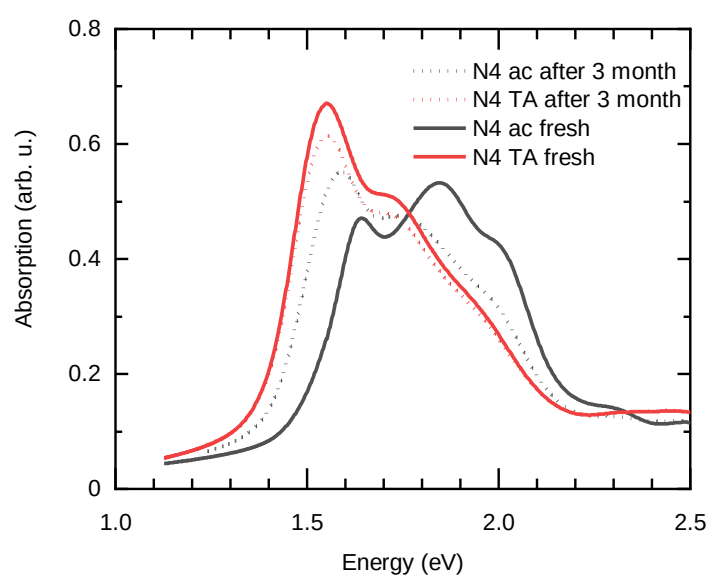


Figure S8: Absorption spectra of neat N4 films as-cast (black lines) and after thermal annealing (red lines), fresh after processing (solid lines) and 3 month later (dotted lines)

GIWAXS data of N4 films on glass

Figure S9 shows the comparison between GIWAXS measurements of N4 films, as-cast and after thermal annealing, on glass and silicon (Si) substrates. The 2D-maps are shown in Figure S9a,b and the corresponding horizontal and vertical cuts in Figure S8c,d, respectively. Comparing the 2D maps, the data on glass show a strongly increased intensity at q -values around $1.75 \text{ \AA}^{-1}$, which originates from the scattering background of the glass substrate. The scattering pattern of the lamellar stacking at lower q -values is almost identical, which can also be seen in the horizontal and vertical cuts. Additionally, the data on glass substrates show the same trend upon thermal annealing as on silicon. The scattering pattern shifts to lower q -values indicating a significant reorientation. Consequently, we observe the same scattering behaviour of N4 on glass and Si substrates. Thus, we assume, that a comparison of the GIWAXS data on Si (due to its decreased scattering background) with the absorption data on glass substrates is meaningful.

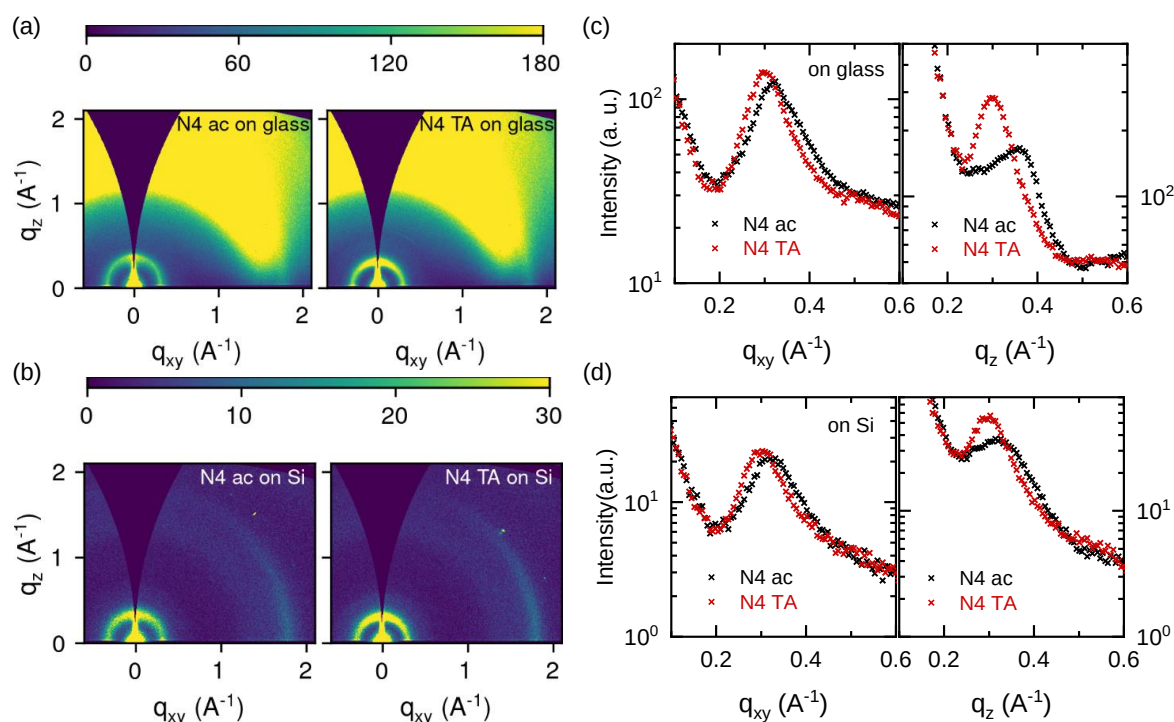


Figure S9: 2D-GIWAXS images of N4 films measured (a) on glass substrates and (b) on silicon substrates (Si), as-cast (ac) and after thermal annealing (TA). (c,d) Horizontal (left) and vertical (right) line cuts of the as-cast and thermally annealed films of N4 on (c) glass substrates and on (d) Si substrates, respectively.

Spectral decomposition of PM6 in solution and film

Fig. S10a,b show the temperature dependent PL and absorption spectra of PM6 in oDCB in a temperature range from 450 K to 270 K in 10 K steps. The spectral evolution is discussed in the manuscript. Additionally, a spectral decomposition into an aggregated and disordered phase of the absorption spectra of PM6 in solution at 270 K is shown in Fig. S10c and of a neat film in Fig. S10d. For the spectral decomposition we took the absorption spectrum at 420 K, which is right above the critical temperature and thus the absorption spectrum of the pure disordered phase, and scaled it to the absorption spectra at 270 K in solution and the neat film, respectively. Then we subtract the spectrum of the disordered phase resulting in the aggregate absorption (dashed lines). We scaled the spectrum of the disordered phase (orange) a bit below the absorption spectra, as in reality the absorption of the aggregate will not go down to zero at about 2.4 eV. This is a good approach to estimate the absorption spectra of the aggregated phase in solution and film. (REF, REICHI) For both, solution at 270 K and film, we find a similar pronounced aggregate absorption with a 0-0-peak at 2.00 eV and a shoulder at 2.13 eV.

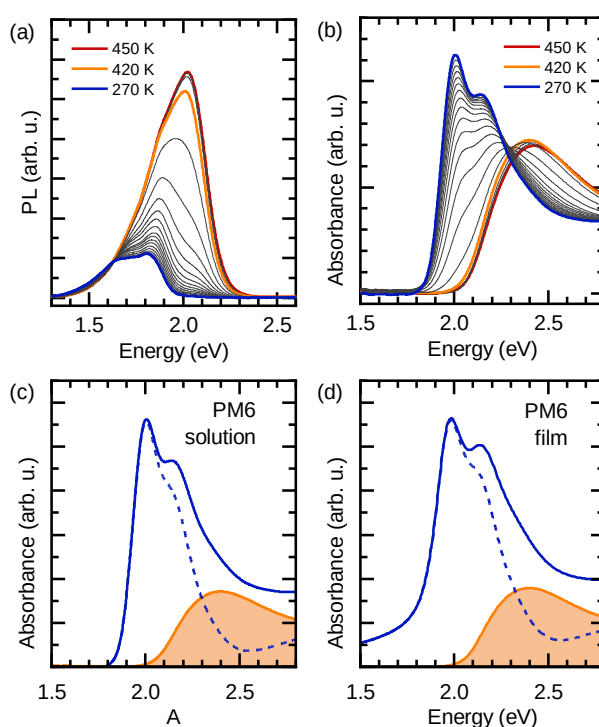


Figure S10: PL (a) and absorption (b) spectra of PM6 in oDCB at a concentration of 0.25 mg/ml. Spectra taken at characteristic temperatures are drawn with colored solid lines and given in the legend. Decomposition of absorption spectra into aggregated (dashed blue line) and disordered (orange area) phase (c) in solution at 270 K and (d) in a neat PM6 film.

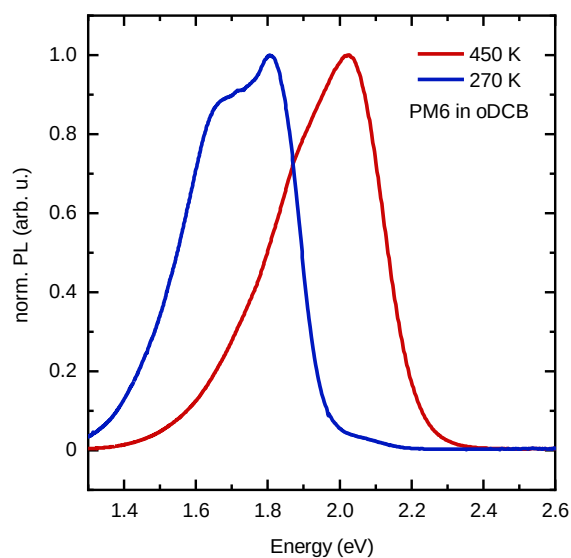


Figure S11: PL spectra of PM6 in oDCB at a concentration of 0.25 mg/ml at 450 K and 270 K normalized to their maxima.

Assuming, that the PM6 chains are fully solvated at 450 K, we assign the PL spectrum at 450 K with a maximum at 2.02 eV to the disordered phase. Upon cooling, the intensity at 2.02 eV decreases, while starting from 420 K spectral signatures of aggregation appear in absorption. The red-shifted PL at 270 K shows almost no intensity at 2.02 eV and we thus assign this PL spectrum to the aggregated phase of PM6 (see Figure S11).

Franck-Condon analysis parameters:

Table S2 shows the Franck-Condon fit parameters of the spectral decomposition of the electron acceptor materials Y6 and N4 in solution, neat films and blend films with PM6 according to Figure 3, Figure 4 and Figure 7.

Table S2: Fitting parameters of the Franck-Condon analysis for the decomposition of the absorption spectra of the electron acceptors Y6 and N4 in mTHF solution, in as-cast and TA films and in blend films with PM6; with the energetic position of the 0-0 transition E_{00} , the linewidth σ , the Huang-Rhys parameter S_1 and the effective vibrational mode $\hbar\omega$.

Y6 in mTHF	transition	E_{00} (eV)	σ (meV)	S_1	$\hbar\omega$ (meV)
195 K	non-interacting	1.74	68.6	0.43	162
	Agg. I, LE	1.54	44.4	0.15	162
	Agg. I, HE	1.92	44.4	0.15	162
	Agg. II, LE	1.62	43.5	0.26	162
	Agg. II, HE	1.85	43.5	0.26	162
140 K	non-interacting	1.74	66.8	0.43	162
	Agg. I, LE	1.54	40.6	0.15	162
	Agg. I, HE	1.92	40.6	0.15	162
	Agg. II, LE	1.63	41.3	0.26	162
	Agg. II, HE	1.85	41.3	0.26	162
N4 in mTHF	transition	E_{00} (eV)	σ (meV)	S_1	$\hbar\omega$ (meV)
220 K	non-interacting	1.74	67.9	0.55	162
	Agg. I, LE	1.54	44.2	0.18	162
	Agg. I, HE	1.93	44.2	0.18	162
	Agg. II, LE	1.64	43.0	0.40	162
	Agg. II, HE	1.86	43.0	0.40	162
140 K	non-interacting	1.74	64.1	0.55	162
	Agg. I, LE	1.54	42.6	0.18	162
	Agg. I, HE	1.93	42.6	0.18	162
	Agg. II, LE	1.64	40.5	0.40	162
	Agg. II, HE	1.86	40.5	0.40	162

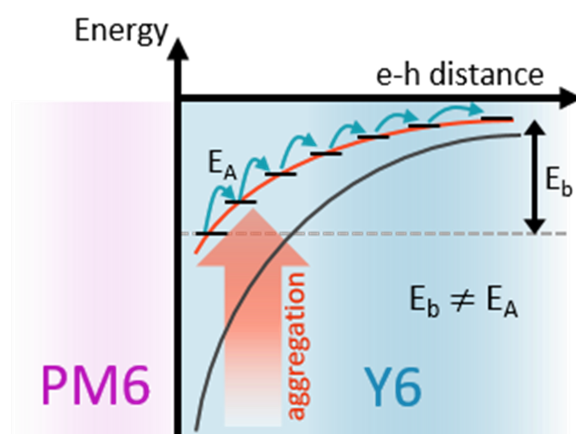
Y6 film	transition	E_{00} (eV)	σ (meV)	S_1	$\hbar\omega$ (meV)
as-cast	non-interacting	1.73	64.1	0.42	162
	Agg. I, LE	1.52	57.2	0.13	162
	Agg. I, HE	1.93	57.2	0.13	162
	Agg. II, LE	1.62	54.7	0.20	162
	Agg. II, HE	1.83	54.7	0.20	162
TA	non-interacting.	1.72	62.1	0.42	162
	Agg. I, LE	1.50	55.1	0.18	162
	Agg. I, HE	1.94	55.1	0.18	162
	Agg. II, LE	1.60	54.0	0.20	162
	Agg. II, HE	1.83	54.0	0.20	162

N4 film	transition	E_{00} (eV)	σ (meV)	S_1	$\hbar\omega$ (meV)
as-cast	non-interacting	1.73	70.2	0.48	162
	Agg. I, LE	1.51	55.1	0.18	162
	Agg. I, HE	1.95	55.1	0.18	162
	Agg. II, LE	1.61	55.3	0.20	162
	Agg. II, HE	1.85	55.3	0.20	162
TA	non-interacting	1.73	69.7	0.48	162
	Agg. I, LE	1.51	55.1	0.18	162
	Agg. I, HE	1.93	55.1	0.18	162
	Agg. II, LE	1.60	55.3	0.20	162
	Agg. II, HE	1.84	55.3	0.20	162

Blend films	transition	E_{00} (eV)	σ (meV)	S_1	$\hbar\omega$ (meV)
PM6:Y6	non-interacting	1.72	62.1	0.42	162
	Agg. I, LE	1.51	55.0	0.19	162
	Agg. I, HE	1.94	55.0	0.19	162
	Agg. II, LE	1.60	54.0	0.20	162
	Agg. II, HE	1.83	54.0	0.20	162
PM6:N4	non-interacting	1.72	69.7	0.48	162
	Agg. I, LE	1.52	55.1	0.18	162
	Agg. I, HE	1.93	55.1	0.18	162
	Agg. II, LE	1.60	55.3	0.20	162
	Agg. II, HE	1.84	55.3	0.20	162

7

An Impedance Study of the Density of States Distribution in Blends of PM6:Y6 in Relation to Barrierless Dissociation of CT States



Author comment

This chapter incorporates the following publication: Daniel Kroh et al., "An Impedance Study of the Density of States Distribution in Blends of PM6:Y6 in Relation to Barrierless Dissociation of CT States", *Adv. Funct. Mater.*, 34, 2302520, 2024 ©2023 The Authors. Advanced Functional Materials published by Wiley-VCH GmbH

This publication was motivated by earlier findings from the group of Prof. Dieter Neher, who observed that optically generated charge-transfer states in PM6:Y6 solar cells dissociate with almost no thermal activation. Although this phenomenon was experimentally well established, its origin remained unclear. To address this open question, a detailed understanding of the energetic landscape within PM6:Y6 blend films was required. In this work, we approached this challenge by employing energy-resolved electrochemical impedance spectroscopy to determine the density-of-states distributions of the donor and acceptor materials, ultimately leading to the insights presented in the following publication.

RESEARCH ARTICLE

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An Impedance Study of the Density of States Distribution in Blends of PM6:Y6 in Relation to Barrierless Dissociation of CT States

Daniel Kroh, Stavros Athanasopoulos, Vojtech Nádaždy, Frank-Julian Kahle, Heinz Bässler, and Anna Köhler*

In an endeavor to understand why the dissociation of charge-transfer (CT) states in a PM6:Y6 solar-cell is not a thermally activated process, measurements of energy-resolved impedance as well as of intrinsic photoconduction are employed. This study determines the density of states distributions of the pertinent HOMO and LUMO states and obtains a Coulomb binding energy ($E_{b,CT}$) of ≈ 150 meV. This is 250 meV lower than the value expected for a pair of localized charges with 1 nm separation. The reason is that the hole is delocalized in the polymer and the electron is shared among Y6 molecules forming a J-like aggregate. There are two key reasons why this binding energy of the CT state is not reflected in the temperature dependence of the photocurrent of PM6:Y6-diode: i) The e–h dissociation in a disordered system is a multi-step process whose activation energy is principally different from the binding energy of the CT state and can be substantially less than $E_{b,CT}$, and ii) since dissociation of the CT state competes with its intrinsic decay, the dissociation yield saturates once the rate of dissociation grossly exceeds the rate of intrinsic decay. This study argues that these conditions are met in a PM6:Y6-solar cell.

1. Introduction

Blending the polymeric donor material PM6 with the monomeric acceptor Y6 is the basis for an unusually efficient solar cell, yet it is open to discussion why this cell is so efficient.^[1–6] One reason is that the optical gap is as low as 1.45 eV and both components have high oscillator strengths. Therefore, more light is absorbed in a PM6:Y6 solar cell than in a cell with PCBM as an acceptor. It is less obvious, though, why almost no thermal energy is needed to dissociate to optically generated charge transfer states (CT).^[7] The CT state ought to be Coulomb bound but obviously, it is bound only very weakly. One reason is related to the polymeric nature of the donor that favors delocalization of the hole and, concomitantly, reduces the binding energy of the CT state.^[7–10] The morphology of the blend and static disorder also contributes

favorably to CT dissociation.^[9] Recently, it has been suggested that the quadrupole of the Y6 molecule increases the dissociation yield because it gives rise to a repulsive term of the potential energy of a charged donor–acceptor pair.^[7,11] To verify these conjectures requires detailed knowledge of the energetic landscape of a PM6:Y6 blend, which is difficult to determine experimentally. While conventional photoemission is a suitable method to determine the HOMO level, inverse photoemission is experimentally demanding and in principle unsuitable for exploring the LUMO-structure of a two-component system. In order to overcome the latter problem, Neusser et al.^[12] conducted a spectro-electrochemical study to determine the HOMO and LUMO levels in the neat films of PM6 and Y6 as well as their blends with particular emphasis on the film-morphology. While this technique can locate the level-positions, it is inadequate to map the pertinent density of states distributions. For this reason, we resort to energy resolved electrochemical impedance spectroscopy (ER-EIS) to determine the density of the states (DOS) distribution of PM6 and Y6 films and the PM6:Y6 blend.^[13–15] The blend we used was prepared as described by Perdigon-Toro et al.^[16] and also used in our previous study, where we investigated the role of order on the open-circuit voltage in solar cells.^[1] In particular, we used the same batch of PM6 as in Refs. [16] and [1], and dissolved it with Y6 (from the same supplier, 1-Material Inc.) in CHCl₃ to a total

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concentration of 16 mg mL⁻¹ with a 1.0–1.2 weight ratio and 0.5% CN (v/v, CN/ CHCl₃) as additive. Complementary, we also measure the action spectrum of intrinsic photoconduction in order to determine the electrical gap of neat PM6 and Y6 films.

It turns out that the ER-EIS spectrum of a PM6:Y6 blend is basically a superposition of HOMO and LUMO features of the parent components indicating that blending does not give rise to additional states. It yields a binding energy of the CT state of ≈150 meV. This value is consistent with earlier studies,^[16,17] yet unusually low as compared with an expected Coulomb energy of ≈400 meV. In recent studies,^[1,18] we used an analysis of absorption and PL-spectra in combination with grazing incidence wide angle x-ray scattering (GIWAXS) measurements to associate the presence of J-like aggregates with the high solar cell quantum yields reported by Perdigo-Toro et al.^[16] In the study presented here, we shall now argue further that the low binding energy of the CT state is a consequence of the formation of these J-type aggregates. It implies that the electron in the acceptor-phase is delocalized among two molecules. This lowers the Coulomb energy of the CT state beyond the contribution of hole delocalization in the PM6 polymer.

An important aspect of the current study is the question whether or not the spectroscopically determined binding energy of a CT state ($E_{b,CT}$) is identical to the activation energy of the photocurrent in a PM6:Y6-blend. Supported by kinetic argument and simulations using an analytical hopping model we shall argue that both energies are principally different. While $E_{b,CT}$ is a spectroscopically defined quantity, the thermal activation energy is not, because CT dissociation is a multi-step rate process that depends on the topology and dimensionality of the system, and therefore the activation energy is lower than the binding energy of the CT-state. After all, we shall stress that the yield of CT-dissociation is determined by the trade-off between the rate of escape process and the rate of its intrinsic decay to the ground state. If CT dissociation is fast compared to intrinsic decay, its yield is unity regardless of how much energy an individual jump of a charge carrier in the course of dissociation may cost. This is an important, yet often overlooked argument in the discussion on the activation energy of CT-dissociation.

2. Results

2.1. Photoconduction

Before embarking into ER-EIS experiments, we shall first report on experiments of photoconduction on neat films of only one material. They rest upon the autoionization concept of a molecular solid. Upon generating singlet excitons in a biased neat molecular solid one usually observes a photocurrent. It is mainly of extrinsic nature because singlet excitons do not have enough energy to dissociate and originates from exciton dissociation at an electrode or an impurity^[19] or by bimolecular annihilation of excitons. However, above a threshold energy a higher excited vibronic state can overcome the Coulombic binding energy of a singlet exciton and can autoionize. This gives rise to a superimposed intrinsic photocurrent. The threshold energy for this process defines the electrical bandgap E_g , i.e., the separation between the valence and the conduction states of the system, as compared to the optical gap. The difference between the electrical and the op-

tical gap is the binding energy of the singlet exciton. Pope et al.^[20] and Braun et al.^[21] were pioneers in this research. In the course of our endeavor to characterize the optical properties of conjugated polymers, we drew upon those classic ideas and measured the action spectrum of the photocurrent of the ladder-type poly-para-phenylene (MeLPPP) in order to discriminate between intrinsic and extrinsic photoconduction.^[22] It turned out that there is a threshold energy of 3.8 ± 0.1 eV above back to which the photocurrent increases sharply. More recently, we measured the impedance spectra of the material and we found that the HOMO–LUMO gap, E_g , is 3.72 eV Bässler et al.^[15] This agreement proves that both methods to determine E_g are internally consistent.

Single layer devices for external quantum efficiency (EQE) measurements using Y6 and PM6 were fabricated on structured ITO-coated glass substrates. As a hole transport layer, a 15 nm thick layer of MoO₃ on top of the ITO was used. The Y6 layer was spun from chloroform solution (10 mg mL⁻¹), the PM6 layer from chlorobenzene solution (10 mg mL⁻¹), both with a thickness of 100 nm. Last, a 100 nm thick aluminum cathode was evaporated. EQE measurements were performed using a Keithley 236 source-measure-unit under monochromatic illumination from a 450 W tungsten lamp (Osram). All EQE spectra were recorded under short-circuit conditions. For the measurement, the sample was kept in a sample holder under vacuum at room temperature.

We calculated the internal quantum efficiency (IQE) using the absorption profiles we obtained via the transfer matrix algorithm. These calculations were performed using the code provided free of charge by McGehee and coworkers.^[23] The values for the real (n) and imaginary part (k) of the refractive index for glass, ITO and Al were taken from the library provided by McGehee. For MoO₃ we used the values from the free online library RefractiveIndex.INFO.^[24] For PM6 and Y6, we followed the approach presented by McGehee and coworkers. Thus, we used the refractive index $n(\lambda)$ for Y6 and PM6, determined by Kerremans and coworkers^[25] and only measured the absorption coefficient of the respective materials from which we then calculated the k -values according to $k = \lambda \alpha / 4\pi$, where λ is the wavelength of the incident light and α is the absorption-coefficient.^[23]

In Figure 1 we show the absorption spectra as well as the IQE spectra of PM6 (Figure 1a) and Y6 (Figure 1b). The onset of the IQE spectra coincides with the absorption threshold. With increasing photon energy, the IQE spectra saturate (IQE_{sat}) yet above a certain threshold the photocurrent increases again. We associate this increase of the intrinsic photocurrent with autoionization of higher excited states. At even higher energies, e.g., at 3.2 eV for PM6 and 2.6 eV for Y6, we notice a reduced increase or even decrease. Evidently, there are other decay channels for the singlet exciton opening up that compete with autoionization, such as conceivably pathways related to singlet fission or other processes. To determine the electrical gap E_g we plot the $(IQE(h\nu) - IQE_{sat})^{1/2}$ versus $h\nu$ (Figure 1c,d). This is an empirical way to quantify the increase of the number of intrinsically generated charge carriers as a function of the excess photon energy because the number of charges that escape from their Coulomb funnel increases approximately quadratically with their excess energy.^[26] This procedure yields the HOMO–LUMO gaps, i.e., the electrical gaps, E_g (PM6) = 2.51 eV (±0.10 eV) and E_g (Y6) = 1.77 eV (±0.10 eV)

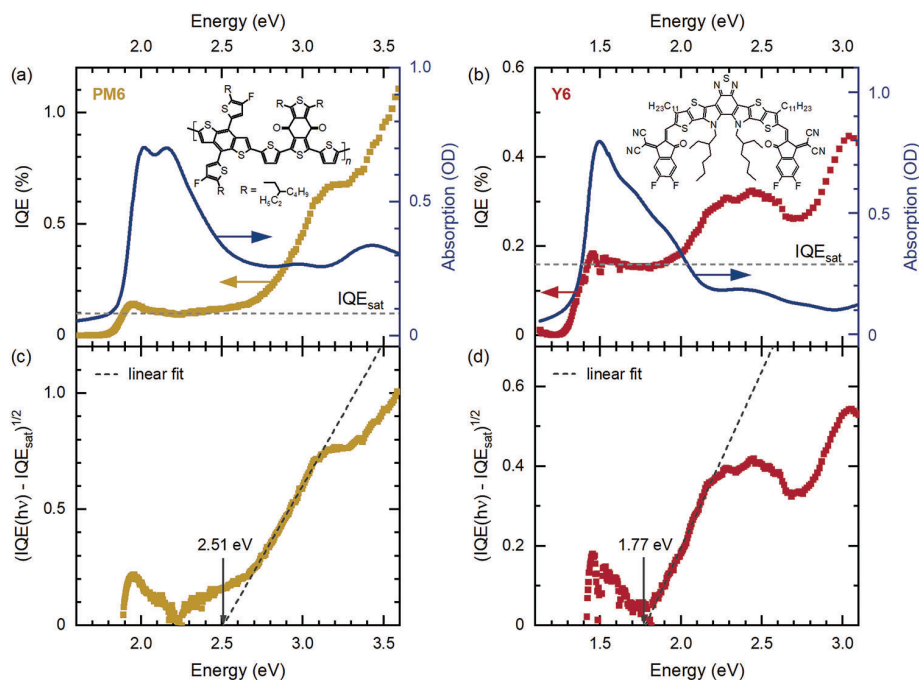


Figure 1. Internal quantum efficiency (IQE) spectra for a) PM6-only and b) Y6-only device under short-circuit conditions with its absorption on the right axis and the material structure on the top. Plot of the square root of $IQE(h\nu) - IQE_{sat}$ versus $h\nu$ with a linear fit to determine the electrical gap E_g for c) PM6-only and d) Y6-only devices.

2.2. Impedance Spectroscopy (ER-EIS)

ER-EIS is a spectroscopic technique to map the density of states (DOS) distribution of an organic solid in contact with an electrolyte via a redox-reaction. It is an elaborate version of conventional cyclic voltammetry used to determine ionization potentials and electron affinities of organic materials in solution. In brief, an organic film is deposited onto a conductive substrate, e.g., an ITO covered glass or doped Si, and immersed into an electrolyte with an Ag/AgCl reference and a Pt auxiliary wire electrode. Between film and the electrolyte, a Helmholtz layer is established. Experimentally, one measures the charge transfer resistance at the interface between the electrolyte and the organic semiconductor by superimposing a periodic perturbation of the applied potential. Reversible charge transfer from ions of the electrolyte to the semiconductor will occur once the applied voltage compensates the difference between those states and gives rise to the real component of the measured impedance. Since the interfacial resistance depends on the number of the available states at the semiconductors surface, a scan of the resistance as a function of the applied voltage will translate into the distribution of HOMO and LUMO states of the semiconductor. For more information on the ER-EIS technique see Refs. [13–15].

In the present experiments, thin films, typically 100 nm thick, were deposited onto a tin-oxide (ITO) covered glass plate. Y6 films were spin-coated from chloroform solution (16 mg mL⁻¹), PM6 from chlorobenzene solution (10 mg mL⁻¹), and PM6:Y6-blends (1:1.2 ratio) from chloroform solution (16 mg mL⁻¹).

Figure 2a shows the ER-EIS spectrum of a PM6 film, i.e., the density of states distributions (DOS) of HOMO and LUMO

states. The tails of both DOSs are perfect Gaussians distributions with standard deviations $\sigma_H = 100$ meV and $\sigma_L = 43$ meV, respectively. The maxima of the HOMO and LUMO distributions are at -5.82 and -3.32 eV, respectively. It implies an electrical gap E_g (PM6) of 2.50 eV. This is in agreement with the threshold for intrinsic photoconduction (2.51 ± 0.10 eV) but is by 0.25 eV higher than the value inferred from spectral voltammetry (2.25 eV).^[12] The most likely reason for this discrepancy is that in the latter technique the level position is inferred from the onset of the feature in the voltammetry-spectrum. A broad HOMO distribution—as measured for a neat PM6 film ($\sigma = 100$ meV) can therefore translate into an erroneously lower HOMO level and, thus, to a lower value of E_g .

Interpreting the ER-EIS spectrum of an Y6 film is less straightforward because Y6 tends to crystallize^[1,18,27–31] and the morphology of the film depends somewhat on the choice of the solvent and processing conditions.^[29,32–37] GIWAXS measurements have shown that our Y6 films exhibit long-range order that is distinctly different from the ordered regions characterized by π – π stacking between chains that prevail in PM6.^[1,18] The spectrum shown in Figure 2a indicates that from -6.2 to -5.0 eV the HOMO-DOS decays smoothly except for a superimposed local maximum at -5.99 eV. The LUMO feature is a spike at -4.34 eV, accompanied by a weak shoulder at lower energies. Beyond -4.34 eV there is a broad local maximum followed by another local maximum at -3.0 eV. It is straightforward to assume that the LUMO spectrum is related to the film morphology. Temperature-dependent absorption spectra on Y6 in solution and on Y6 films show that Y6 forms aggregates with predominate J-like character embedded in an amorphous phase.^[18] It is straightforward to associate

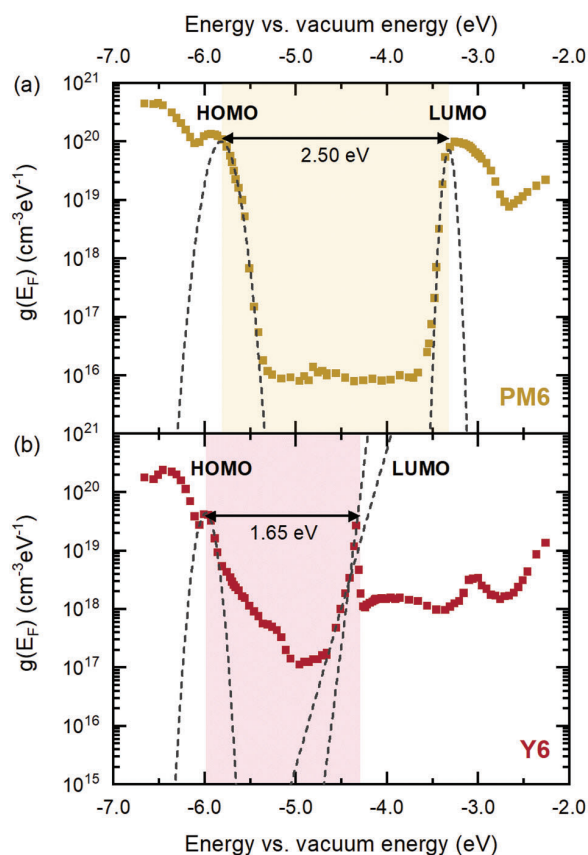


Figure 2. The DOS function $g(E_F)$ for HOMO and LUMO states of a) PM6 and b) Y6 film inferred from ER-EIS measurements. The dashed lines indicate Gaussian and exponential fits. The arrows indicate the energetic HOMO–LUMO gap.

the spike of the LUMO feature in an Y6 film to LUMO states of well-ordered crystallites and the broad feature beyond -4.20 eV to the amorphous phase. The weak tail associated with central spike we associate with states at the grain boundaries of the crystallites. Alam et al.^[38] noticed a similar spike at -4.3 eV in ER-EIS spectra of donor–acceptor blends with ITIC, an acceptor that is chemically similar to Y6. They associated it with a Fano resonance between a local and a continuum of states. We conjecture that the spike is a characteristic signature of well-ordered aggregates. The following results of PM6:Y6 blends will support this reasoning. Taking the HOMO feature at -5.99 eV and the LUMO-spike at -4.34 eV we end up with an electrical gap E_g of 1.65 eV for Y6. This is in excellent agreement with the value of 1.64 eV inferred from spectral voltammetry^[12] and in fair agreement with the threshold energy for intrinsic photoconduction (1.77 eV $\pm$ 0.10 eV).

The key experimental result of this study is the ER-EIS spectrum of the PM6:Y6 blend, shown in the bottom of Figure 3. To illustrate more clearly the changes that occur upon blending we include in Figure 3a also the spectra of the single materials. The spectrum of the blend is basically the sum of the spectrum of the components albeit with characteristic modifications: i) In the blend the unusually high density of states within the forbidden

zone of the Y6 spectrum has vanished. This suggests that the states within the forbidden zone are in some way related to grain boundaries between the crystallites in the neat Y6 film that are eliminated upon blending with PM6. ii) The HOMO spectrum of the blend is entirely dominated by that of the donor PM6 and the Gaussian width is diminished from 100 meV of the neat film to 74 meV in excellent agreement with literature.^[1] iii) In the blend, the LUMO spectrum of Y6 is shifted by ≈ 100 meV. Such an effect was already noticed in the course of our earlier study on MeLPPP:PCBM cells and can be attributed to different dielectric screening on the blend with respect to neat films or to interfacial dipoles.^[39] iv) Both the spike and the associated tail below 4 eV are weakly broadened. Obviously, blending decreases the structural order within the crystalline domains and at the grain boundaries and the LUMO features acquire Gaussian shapes with standard deviations of 60 meV (crystallites) and 100 meV (tail states). This disorder-controlled line-broadening indicates that the sharp LUMO feature should not be assigned to a Fano resonance.^[38] v) The electrical gap between the centers of the HOMO features of PM6 and the boundary and central crystallite LUMO features of Y6 are 1.44 and 1.59 eV, respectively. vi) The LUMO feature on the PM6 spectrum and the second LUMO feature of Y6 are amalgamated.

3. Discussion

Interpreting the binding energies of singlet excitons in neat PM6 and Y6 films appears to be straightforward. The difference between the electrical gap of 2.50 eV of a PM6 film and the $0-0$ -transition of S_1-S_0 transition at 1.90 eV yields an electrical gap of 0.60 eV. Identifying it with the Coulomb energy of a pair of point-like charges in a dielectric medium with a dielectric constant of 3.5 translates into an on-chain e–h pair with a separation of 0.7 nm. For a Y6 film we find that the electrical gap is 1.65 eV and the origin of the S_1-S_0 transition is 1.40 eV. This yields a binding energy of a pair of point-like charges of 0.25 eV and translates into an unusually large e–h separation of 1.6 nm. The likely reason is that since Y6 molecules form J-like aggregates the charges can delocalize among the pair partners (vide infra).

The observation that the ER-EIS spectrum of a PM6:Y6 blend is basically a superposition of the HOMO and LUMO DOS distributions of the components with only marginal shift (<100 meV) proves that blending does neither create new states nor modifies their energetic positions appreciably. Obviously, the quadrupole moment of the Y6 molecule does not alter the HOMO or LUMO levels noticeably when a donor–acceptor pair is formed.

Upon optical excitation of a PM6:Y6 blend singlet excitons are created either in Y6 domains or via energy transfer from PM6 to Y6. Some excitons are lost by fluorescence from Y6 domains, but their majority migrates to the domain boundaries at which holes are transferred to a PM6 chains thereby generating CT states. Their energy is difficult to measure because the CT emission is weak and overlaps with the residual fluorescence of Y6. By subtracting the photoluminescence from the electroluminescence of a PM6:Y6 diode, Perdigon-Toro et al.^[16] came up with a CT emission spectrum with a peak at 1.15 eV with origin at 1.30 eV. When we subtract the value of the CT origin from our value of 1.44 eV for the difference between the centers of the HOMO and LUMO

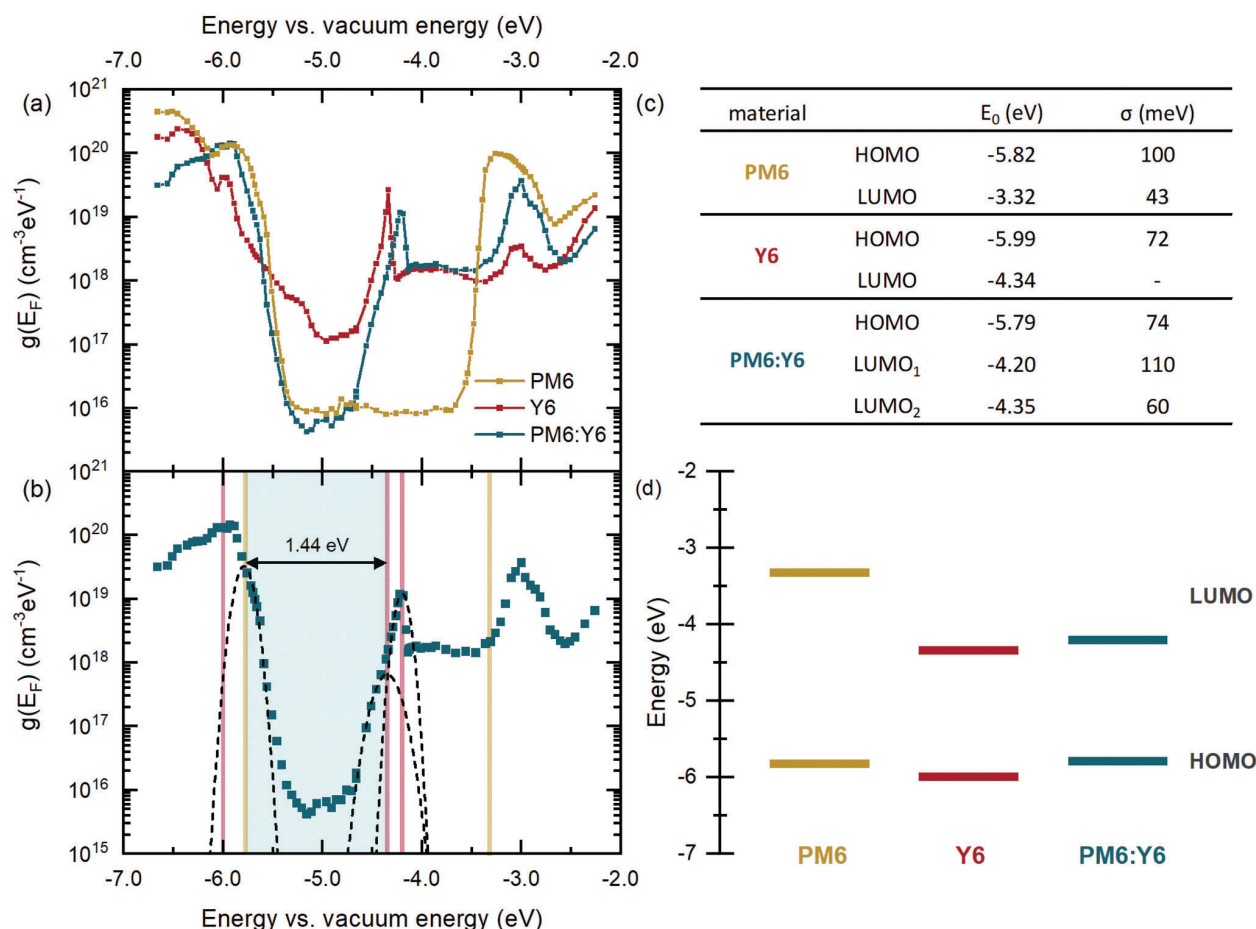


Figure 3. a) The DOS function $g(E_F)$ for HOMO and LUMO states of a PM6, Y6 and PM6:Y6 film inferred from ER-EIS measurements. b) $g(E_F)$ for a PM6:Y6 blend film inferred by ER-EIS. The dashed lines indicate Gaussian fits. The arrow indicates the energetic HOMO–LUMO gap. The vertical lines indicate the energetic positions of the HOMO and LUMO levels of a neat PM6 (yellow) and Y6 (red) film, respectively. c) Table with energetic position E_0 and linewidth σ of DOSs of HOMO and LUMO from PM6, Y6 and PM6:Y6 films. d) Energy scheme of HOMO and LUMO positions for PM6, Y6 and PM6:Y6 film as inferred by ER-EIS measurements.

gap of the blend inferred from the ER-EIS spectrum we arrive at a binding energy of ≈ 150 meV for the CT state. Considering that the estimated Coulomb energy of a pair of point-like charges with intra-pair separation of 1 nm in a medium with a dielectric constant of 3.5 is 410 meV, it is obvious that the spectroscopically determined binding energy of the CT state is significantly reduced. Recalling that the binding energy of a singlet exciton in a neat Y6 (vide supra) is also unusually low we conjecture that both observations have a common origin, namely the delocalization of the electron within an Y6 dimer and the delocalization of the hole in the polymer.

In order to check this conjecture we calculated the Coulombic binding energy of an electron-hole pair with an intra-pair separation of 1 nm embedded in a medium with a dielectric constant of 3.5 as a function of electron-hole separation employing the effective mass model for the hole in the polymer developed earlier.^[40] It involves solving the 1D Schrödinger equation for the hole in the presence of the potential created by an electron that is either localized on a single site or delocalized between two units (1/2 e on

two sites), three units (1/3 e on three sites), or four units (1/4 e on four sites), respectively, with the electron sites being perpendicular to the axis of the chain that carries the hole on the polymeric PM6 donor. Delocalization of the hole is taken into account via its effective mass. We find that for an e–h-pair with charge separation 1 nm, in which the electron is localized on a single site and the hole is delocalized on the polymer with a relative effective mass of 0.1, the binding energy $E_{b,CT}$ is 0.25 eV (Figure 4). Replacing a monomeric acceptor by a J-like dimer with a center of mass separation of 1.5 nm, reduces $E_{b,CT}$ to ≈ 150 meV, which is consistent with the spectroscopically determined CT-state-energy. This simple reasoning demonstrates that dimerization of the acceptor combined with hole-delocalization of the in the polymer lowers the binding energy of a CT state, yet it does not explain why the measured thermal activation energy for photo-dissociation in a PM6:Y6 blend is as low as 6 meV.^[7]

To solve this puzzle, one has to consider that CT dissociation is a kinetically determined process in which recombination of the CT state, quantified by the rate constant k_{rec} , and dissociation,

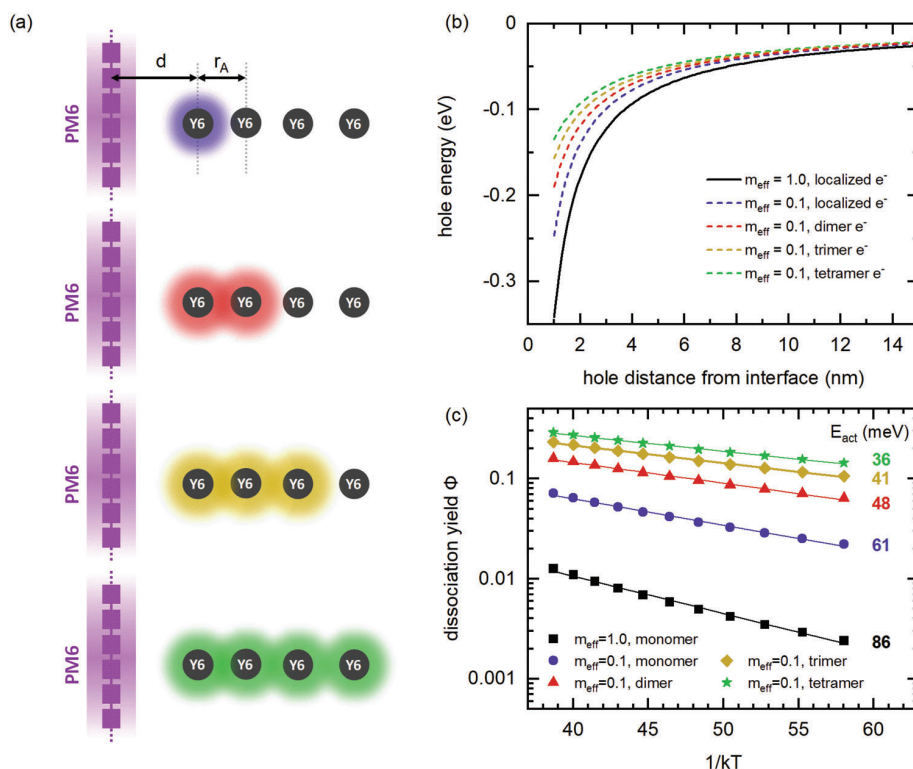


Figure 4. a) Schematic illustrating the geometry between the donor polymer segment (purple squares) and the acceptor molecule (circles) for the case where the electron is extended over one, two, three, and four molecules. Here, r_A is the intra-pair separation and d is the distance between the center-of-mass of the wavefunctions for electron and hole, b) Coulomb potential and c) Dissociation yield, for the hole on the donor polymer segment for the case of a localized hole on the donor and an electron localized on a single acceptor molecule (black), and for the cases of a delocalized hole on the donor ($m_{eff} = 0.1$) and the electron extended over one, two, three, and four acceptor molecules as indicated in the legend.

quantified by rate constant k_{diss} are competing processes. The k_{diss} is the product of a prefactor rate $k_{diss,0}$ and a Boltzmann factor, $k_{diss} = k_{diss,0} \exp(-E_{b,CT}/kT)$ with $E_{b,CT}$ being the Coulomb energy of the CT state. The dissociation yield is $\phi = k_{diss}/(k_{diss} + k_{rec})$. Suppose that $k_{rec} \gg k_{diss}$, for instance, because recombination is controlled by charge carrier hopping among nearest neighbor molecules. In this case the yield is $\phi = (k_{diss,0}/k_{rec}) \exp(-E_{b,CT}/kT)$, i.e. the temperature dependence of ϕ is Arrhenius-like and the activation energy is $E_{b,CT}$. An example is geminate pair recombination of electron-hole pairs tractable in terms of Onsager's 1938 formalism.^[41] In the opposite case, $k_{diss} \gg k_{rec}$, the yield approaches unity. Although the individual dissociation event does cost thermal energy, the overall yield is, in this case, independent of temperature because the activated dissociation event is completed before the CT state could decay intrinsically. Obviously, the temperature dependence of photo-dissociation then does not reflect the true binding energy of the CT state and can, indeed, be negligible.

We will substantiate this reasoning in terms of an analytical hopping model.^[49] We will start with the simplest case and consider a 1D random walk of an electron in an array of statistically disordered hopping sites with a standard deviation of 100 meV in the presence of a stationary hole on a polymer chain characterized by a relative effective mass of either 1 or 0.1. When the electron approaches its sibling, it can form a CT state whose life-

time is considered to be 3000 times the pre-factor rate constant (ν_0) for the activated motion of the hole, e.g., $\tau_{CT} = 30$ ns and $k_{diss,0} = 10^{11} \text{ s}^{-1}$. In the simulations, we assume that the electric field is $5 \times 10^4 \text{ V cm}^{-1}$ and $\epsilon = 3.5$. The result of the simulations is shown in Figure 4c. Intuitively, it is astonishing that even for case of $m_{eff} = 1$ the activation energy for dissociation is only 86 meV although the Coulomb energy is 350 meV (Figure 4b). This is a signature of the great impact moderate disorder has on the escape process of an e-h pair.^[1,49,50] Note also that the activation energy for CT-dissociation is principally different from the binding energy of the CT state because its escape from the Coulomb potential is not a one step process but rather a multi-step random walk, yet the simulated activation energy for CT dissociation is still finite, contrary with experiment. The reason is that in the simulations of Figure 4, the hole is considered to remain stationary, contrary to the experiment. In earlier, more detailed kMC simulations^[9] the case of bipolar transport had been this limitation has been taken care of. They showed that the inclusion of bipolar transport does increase the dissociation yield considerably. The reason is that when both partners of an e-h pair separated by the phase boundary are both mobile, the probability to meet and form a CT state is greatly reduced and geminate recombination is greatly reduced. In efficient organic solar cells geminate pair recombination is, in fact, negligible.^[1] The activation energy further decreases when the hole is

delocalized along the polymer chain and, in addition, when the electron is shared among the partners of an aggregate. In fact, wavefunction delocalization in Y6 dimers has been reported to facilitate charge separation in blends^[42–44] while the role of vibronic coupling,^[45] hot exciton dissociation,^[46] and entropy^[47] have also been acknowledged to contribute to charge separation in donor–acceptor systems. In an earlier publication, we have shown that although dimensionality and entropic effects increase the overall separation yield, they do not influence the activation energy for charge separation.^[9] Moreover, experiments and simulations have shown that efficient charge separation occurs mainly through cold charge transfer states.^[48,49]

4. Conclusion

Employing energy-resolved impedance spectroscopy, we determined the distribution of hole and electron transporting states in neat films of PM6 and Y6, as well as their blends. It turns out that the HOMO and LUMO spectrum of the blend is basically the superposition of the spectra of the components. No additional features are formed upon blending, only defect-related features in the spectra of neat Y6 film are eliminated. From the analysis of the ER-EIS combined with published photoluminescence spectra of PM6:Y6 blends, we find that the binding energy of the CT state of ≈ 150 meV, i.e., 250 meV lower than the Coulomb binding energy expected for an isolated, localized e–h-pair with 1 nm separation. The reason is that the hole is delocalized on the polymer chain and the electron is shared among two or more molecules because Y6 forms J-like aggregates, yet dissociating a CT state should cost thermal energy, contrary with experiment.

To solve this question, one must consider that the yield of CT state dissociation is determined by the competition between intrinsic recombination of the CT state, associated with rate constant $k_{\text{rec}} = 1/\tau$, τ being the lifetime of the CT state, and its dissociation with rate constant k_{diss} . There are several reasons why in a PM6:Y6 solar cell the condition $k_{\text{diss}} \gg k_{\text{rec}}$ is fulfilled and, therefore, virtually all CT states dissociate under short circuit conditions. The cell is a blend of a well-ordered polymeric donor and an acceptor that tends to form domains in which the elements are electronically J-like coupled dimers. This ensures electronic delocalization in both the donor and the acceptor phase, which reduces the Coulomb attraction of the CT pair. Further advantages are that the charge carrier mobilities are moderately high ($> \approx 10^{-4}$ cm² Vs⁻¹) and the aggregates in Y6 arrange to crystallites that allow for percolation pathways. This ensures that the electron of the CT exciton can quickly diffuse away from its sibling at the phase boundary and has very little chance to recombine geminately with it. The existence of a quadrupole of Y6 may also contribute to preventing geminate recombination.^[7] Overall, the combination of energetic disorder, the existence of percolation pathways, hole delocalization along the PM6 backbone, and electron delocalization enabled by aggregation of Y6 molecules allows for highly efficient barrierless CT state dissociation.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

aggregates, exciton dissociation, organic solar cell

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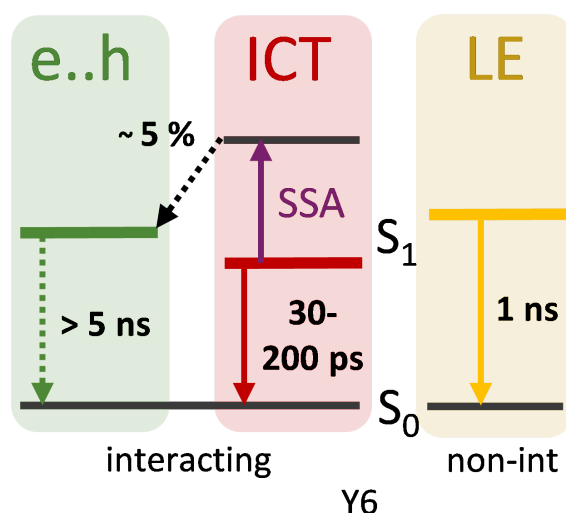
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8

Disentangling Polaron Formation Pathways in Y6 Probing Non-Interacting and Interacting Chromophores via Transient Absorption Spectroscopy



Author comment

This chapter contains a pre-print of a manuscript that will be submitted shortly after the completion of this thesis. It builds directly on the work presented in Chapter 6, where the optical signatures of interacting and non-interacting Y6 were identified under steady-state conditions. All experiments for that study were carried out in the group of Prof. Anna Köhler at the University of Bayreuth.

A natural continuation of this work was to investigate how these two Y6 phases differ in their exciton dynamics. I am particularly grateful for the opportunity provided by the Joint PhD program, which enabled me to perform the transient absorption measurements in the group of Prof. Trevor Smith at the University of Melbourne. This collaborative framework made it possible to combine steady-state and ultrafast spectroscopy across both research environments, ultimately allowing a comprehensive analysis of interacting and non-interacting Y6.

Disentangling polaron formation pathways in Y6 by probing non-interacting and interacting Chromophores via transient absorption spectroscopy

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Abstract

In highly efficient organic solar cells, the optoelectronic properties of the non-fullerene acceptor Y6 are governed by the molecular packing of non-interacting and interacting molecules. In this study, steady-state and transient absorption spectroscopy are employed to disentangle the spectral signatures and excited-state dynamics of interacting and non-interacting Y6 in solution and thin films. By controlling aggregation in dilute solution, localized Frenkel-type excitons on non-interacting Y6 and intermolecular charge-transfer (ICT) excitons on aggregated Y6 are selectively identified. The ICT excitons exhibit strongly fluence-dependent lifetimes (30–200 ps) governed by singlet–singlet annihilation, whereas localized excitons decay monoexponentially on a nanosecond timescale. Furthermore, long-lived polaronic states are observed to form on aggregated Y6 within tens of picoseconds and persist into the nanosecond regime. Comparison with thin-film measurements reveals similar processes with an additional ultrafast energy transfer from non-interacting chromophores to aggregated domains. These results establish a consistent framework for assigning transient absorption features in Y6 and demonstrate that in neat films of Y6, polaron formation arises from an Onsager-like autoionization process of delocalized excitons in interacting domains with moderate yield. This provides central insight into charge-generation mechanisms in Y6-based photovoltaic systems.

1. Introduction:

The non-fullerene acceptor Y6 has emerged as a key material in the development of high performance organic solar cells (OSCs),^[1–4] enabling record power conversion efficiencies up to 19.3% in single junction devices.^[5] Since its introduction in 2019, Y6 has remained a central focus of research, particularly regarding the interplay between molecular packing, solid-state morphology, and optoelectronic properties.^[6–16] A detailed understanding of how microscopic structural order affects electronic coupling, exciton dynamics, and charge formation processes remains essential for further progress in organic photovoltaics.

Y-type molecules such as Y6 can exhibit an unusual crystalline architecture characterized by long-range 3D honeycomb-like packing motifs with various intermolecular configurations.^[7,12,13,17–21] This highly ordered arrangement leads to strong intermolecular interactions and exciton delocalization over several molecular units which is often invoked to explain their exceptional performance.^[22] There is ample evidence that the optoelectronic properties are highly sensitive to intermolecular interactions.^[8,12,19,23–28] Consequently, much effort has been devoted towards understanding how these structural motifs influence photophysical behavior. However, interpretations are often derived from single-crystal measurements, which may not directly translate to the semi-crystalline morphologies of solution-processed thin films.

It is worth recalling that spin-cast films of organic semiconductors can contain multiple structural phases.^[20,29–35] In single crystals, molecules approach thermodynamic equilibrium during growth and can planarize sufficiently to maximize intermolecular coupling. Spin-casting, however, induces rapid solvent evaporation, driving molecules into close proximity on sub-second timescales and leading to kinetically trapped semi-crystalline or amorphous morphologies. In a spin-cast film, some molecules or molecular units may be only loosely packed. As they do not interact electronically with adjacent molecules, we refer to them as forming a phase of non-interacting molecules. Other molecules may be more tightly packed and exhibit strong intermolecular coupling. We refer to them as forming an aggregated phase or as interacting molecules.

In previous work,^[30] we distinguished between these two phases, domains with non-interacting molecules where excitons remain localized on individual molecules, and domains

with aggregated, interacting molecules, characterized by face-on π - π -stacking, where strong intermolecular coupling enables exciton delocalization over multiple Y6 units. The latter exhibit reduced exciton-vibration coupling leading to slower non-radiative decays compared to the former.^[11] In Y6 both experimental and theoretical studies indicate that the delocalization facilitates charge separation in neat Y6 films even in the absence of external fields.^[7,11,21,22,36–38] This special property distinguishes Y6 and other Y-type acceptors from previous generations of electron acceptors. The delocalization in tightly packed Y6 has also been shown to stabilize charge transfer states at donor-acceptor interfaces in bulk heterojunctions and promote exciton dissociation.^[29,39–44] However, the microscopic mechanism of polaron formation in neat Y6 remains unresolved and widely debated.^[7,28,36,41,43,45–49]

Transient absorption spectroscopy (TAS) is a central experimental technique for probing exciton and polaron dynamics in organic semiconductors, yet studies on neat Y6 films have yielded divergent interpretations of the transient absorption (TA) features.^[36,37,41,43,45,46,50] Reports variously attribute the sub-picosecond decay of the singlet exciton excited state absorption (ESA) to ultrafast free-charge generation^[45] or the formation of polaron pairs in kinetic equilibrium with delocalized excitons.^[36] More recent work, based on temperature-dependent transient electro-absorption measurements, proposes that this decay instead reflects exciton migration between non-interacting and interacting Y6 domains.^[29]

We suggest that these discrepancies partially stem from analyses that focus predominantly on aggregated molecules while neglecting the coexistence of non-interacting species. The relative fractions of both phases can vary between samples, yet both need to be considered when analyzing TA spectra of thin films. However, disentangling their spectral contributions is challenging due to the strong overlap of positive (excited-state absorption) and negative (ground-state bleach, stimulated emission) features arising from each phase. Clear spectral assignment and a robust understanding of the decay pathways within each phase are therefore essential for correctly describing the photophysics of Y6.

In this work, we isolate and characterize the photophysical response of each phase independently, under conditions that preclude interphase exciton migration. By correlating the steady-state spectra and ultrafast TA spectral signatures with controlled aggregation in dilute solution, we unambiguously assign the TA features associated with both the interacting

and non-interacting Y6. These assignments establish a reliable framework for interpreting TA spectra in neat Y6 films, where spectral congestion and interphase energy transfer would otherwise obscure the origin of individual signals. Our results thereby provide new insights into the mechanism of polaron formation in neat Y6.

2. Results:

2.1. Steady-State Absorption and PL

It is necessary to understand the steady-state absorption spectra to identify and deconvolute the overlapping excited-state absorption (ESA), ground state bleach (GSB) and stimulated emission (SE) features in the TA signals. Previously, we have identified the signatures of non-interacting and electronically interacting Y6 molecules by analyzing the absorption in solution, neat films and blends with PM6.^[30] In neat films, we observe spectral features from both electronically interacting Y6 molecules (such as dimers or tightly packed aggregates with short-range order) and from isolated, non-interacting molecules, indicating the coexistence of more ordered domains and regions with looser packing or higher disorder. We found that these interactions are highly sensitive to solvent quality and processing conditions.

In our previous work, we have varied the effective solubility of the solvent by changing the temperature, yet in this study we are interested in room temperature TA measurements in solutions. We have achieved this by controlling the formation of aggregates in dilute solution by mixing good and poor solvents. We used the polar solvent tetrahydrofuran (THF, $\epsilon_r=7.6$) and non-polar solvent cyclo-hexane (cH, $\epsilon_r=2.0$) as good and poor solvent, respectively. Compared to thin film measurements, solution measurements preclude long-range exciton migration and thus reduce difficulties in interpretation of the time-resolved spectra.

First, we identify the spectral signatures of non-interacting and interacting Y6 molecules in the solvent mixtures. Figure 1 shows the steady-state photoluminescence (PL) and absorption spectra of Y6 in THF:cH solution with increasing amount of the poor solvent (ratios of 1:0, 1:9, 1:19, and 1:49). To preserve the spectral linewidth over the large spectral range investigated, all spectra in this work are displayed as a function of energy in the unit of eV (see Figure S1-S 3 for the spectra on a wavelength axis).

Focusing on the absorption spectra, the 1:0 sample shows one absorption band with a peak at 1.75 eV, a shoulder at 1.91 eV, and a Gaussian linewidth of 69 meV (Figure S4), along with a second band at ~ 2.14 eV. These two bands correspond to the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions of well-dissolved Y6 without intermolecular interactions. Consistent with the terminology used by, for example, Guo *et al.* and Giannini *et al.*,^[29,36] we refer to them as Frenkel-type

localized excited states (LE excitons) and we show their signatures in orange throughout this study.

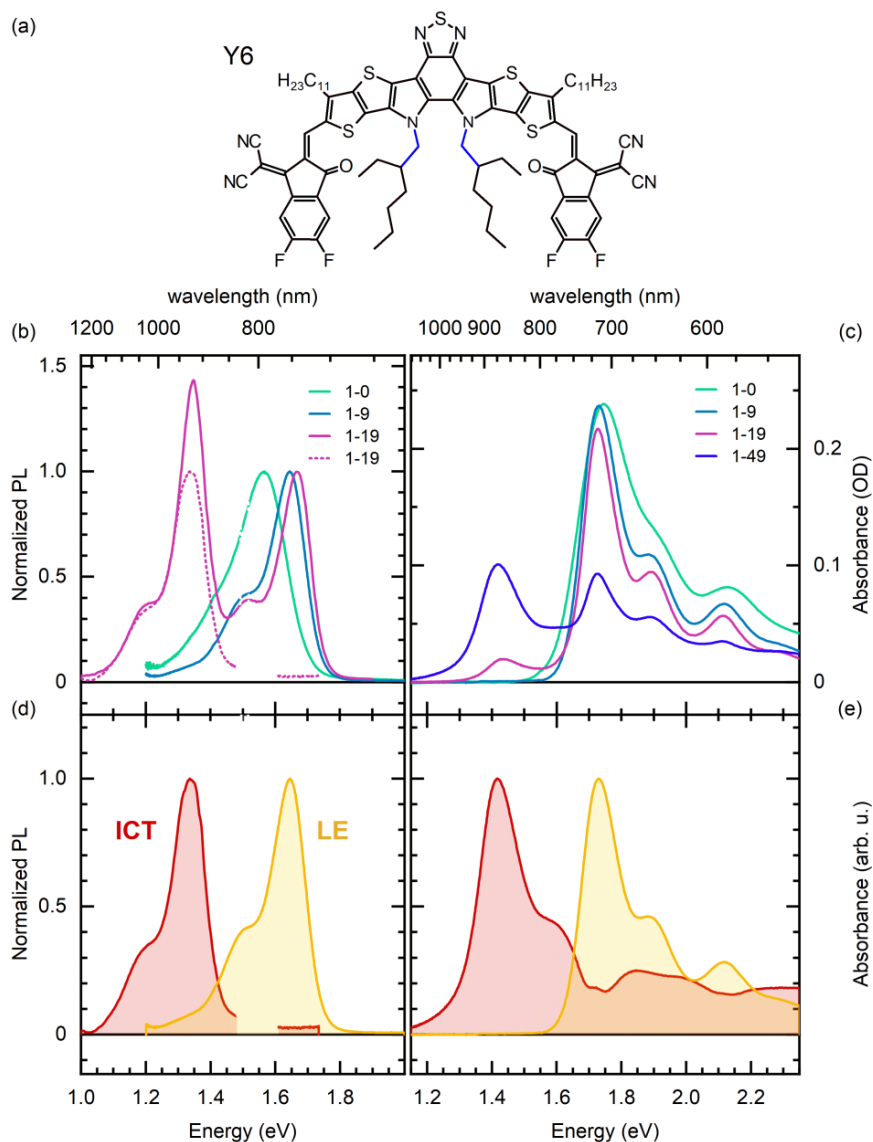


Figure 1. (a) Molecular structure of Y6. (b) Steady-state PL and (c) absorption spectra of Y6 in THF:CH solvent mixtures with ratios from 1:0 to 1:49. Solid lines display PL with excitation at 410 nm, dotted line (1:19 mixture) with excitation at 820 nm. (d) PL attributed to the LE and ICT exciton and (e) Absorption spectra for non-interacting and interacting Y6 derived by appropriate subtraction.

The 1:9 sample exhibits a similar spectrum (1.73 eV peak, 1.89 eV shoulder, 2.12 eV S_2 peak) but with a significantly reduced Gaussian linewidth of 51 meV. The PL spectra show analogous trends: the 1:0 sample emits at 1.57 eV with a shoulder at 1.40 eV, whereas the 1:9 emission

is spectrally narrower. Furthermore, it is blue shifted by about 80 meV. This hypsochromic shift and narrowing in a less polar solvent result from solvatochromism: polar solvents induce broadening via inhomogeneous solvation and excited-state stabilization, while non-polar environments lack such stabilization, leading to higher-energy emission.^[51,52]

The absorption spectrum of the 1:19 sample shows a new feature at 1.44 eV, while the signatures from non-interacting Y6 molecules remain largely unchanged yet reduce in intensity. This new feature corresponds to aggregate-related absorption (displayed in red consistently throughout this work, Figure 1e). The formation of aggregates with tightly packed structures allows for the excited state to delocalize over several Y6 molecules, and to adopt a more pronounced charge-transfer (CT) character, and is assigned to an intermolecular charge-transfer (ICT) state.^[22,29,36,41] Increasing the cyclohexane ratio further enhances the band attributed to the aggregate and subsequently, the absorption intensity of non-interacting molecules decreases. The aggregate peak also redshifts to 1.42 eV implying greater stabilization by exciton delocalization. Notably, this aggregate absorption lies ~ 100 meV lower than the Y6 aggregates in 2-Methyltetrahydrofuran (mTHF) and in films reported previously.^[30] Selectively exciting the ICT state in the 1:19 sample using 820 nm reveals the pure ICT emission in the PL spectra featuring a peak at 1.35 eV and a shoulder at 1.20 eV. PL from the LE state (1.67 eV peak, 1.52 eV shoulder) is observed for excitation with 410 nm.

The clear identification of the LE and ICT bands in the absorption and PL spectra allows us to spectrally disentangle the two contributions by appropriate subtraction (as described in Figure S5).^[32–35,53] The resulting spectra for the LE and ICT states are given in Figures 1d and e for reference. This decomposition enables the unambiguous assignment of GSB, SE, and ESA features in the TA spectra.

2.2. Transient absorption spectroscopy of non-interacting and aggregated Y6

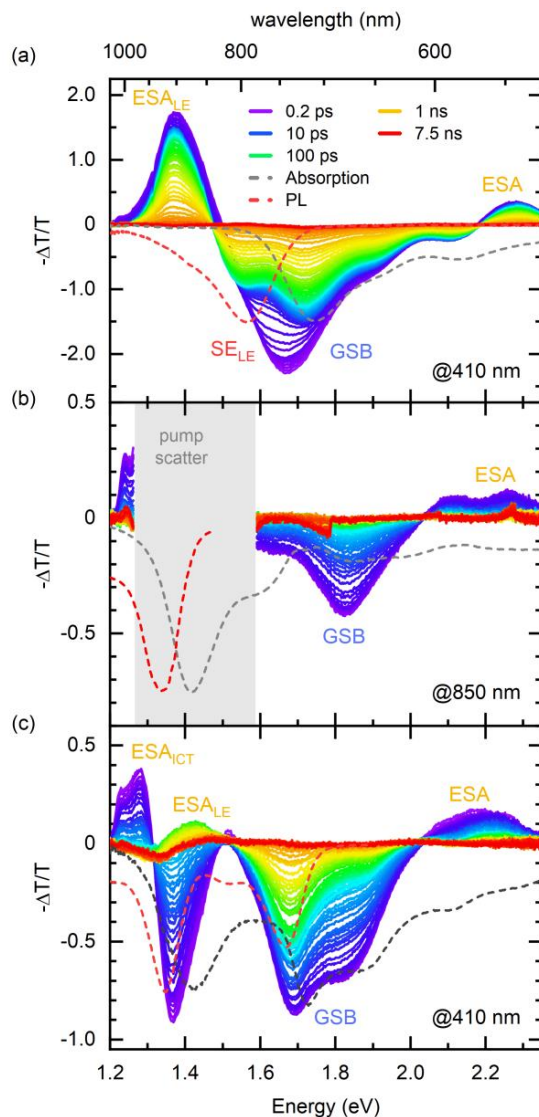


Figure 2. Transient absorption spectra of Y6 in THF:CH solvent mixture with ratios of (a) 1:0 with pump at 410 nm to excite only non-interacting Y6 molecules, (b) 1:49 with 850 nm pump to excite only Y6 aggregates, (c) 1:49 with pump at 410 nm to excite both, non-interacting and interacting Y6 molecules. When exciting with the 850 nm pump beam, pump scattering prevents meaningful interpretation of the data in the range from 1.28 eV to 1.58 eV. For easier assignment of the signals, the inverted steady-state PL (red dashed line) and absorption (grey dashed line) spectra are also shown with arbitrary normalization.

To identify the spectral signatures and dynamics of the non-interacting and interacting Y6 molecules, we conducted TA spectroscopy using three excitation conditions, i.e. (i) we probe non-interacting Y6 molecules by pumping the 1:0 sample at 410 nm, (ii) we investigate

aggregated Y6 molecules by pumping the 1:49 sample at 850 nm, and (iii) we probe both the non-interacting and the interacting Y6 molecules by pumping the 1:49 sample at 410 nm.

The corresponding TA spectra are shown in Figure 2, and the 2D contour plots (0.2 ps–7.5 ns) in Figure 3. The panel arrangement in Figure 2 (and in Figure 3 for the temporal evolution) is arranged to enable straightforward comparison across spectra and dynamics.

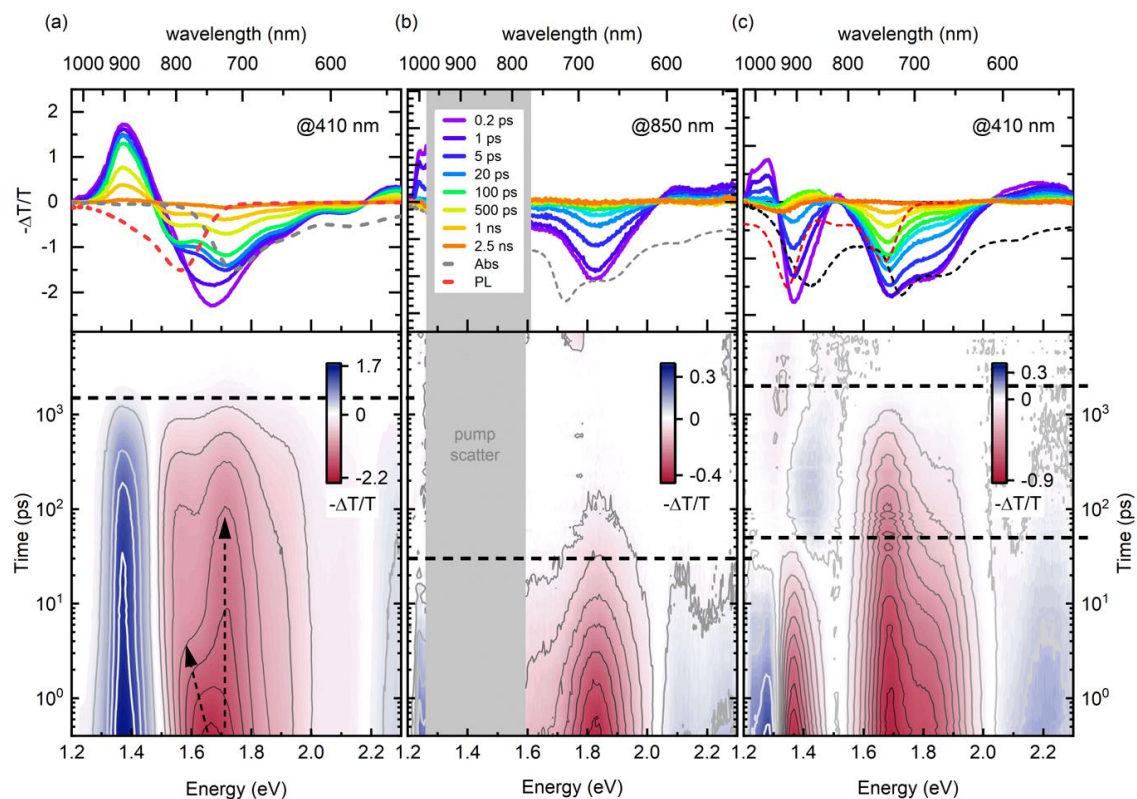


Figure 3. Transient absorption spectra of Y6 in THF:CH mix with ratios of (a) 1:0 with pump at 410 nm to probe only non-interacting Y6 molecules, (b) 1:49 with 850 nm pump to probe only aggregated Y6, (c) 1:49 with pump at 410 nm to probe both non-interacting and interacting Y6, plotted as a 2D map. When exciting with the 850 nm pump beam, pump scattering prevents meaningful interpretation of the data in the range from 1.28 eV to 1.58 eV. The black, dashed lines indicate the time scales for the decay of the main signals of the non-interacting and aggregated phase, respectively.

(i) (Part a in Figures 2 and 3) At 0.2 ps, the TA spectrum shows two positive ESA signals (1.37 eV, 2.28 eV) and negative features at 1.67 eV, 1.88 eV, and 2.11 eV. Comparing to the steady-state spectra shown inverted by dashed lines, the negative bands at 1.88 eV and

2.11 eV were assigned to GSB. The peak at 1.67 eV results from the overlap of the broad GSB (0-0 at 1.74 eV) and SE (0-0 at 1.56 eV). Within the first 10 ps, the SE shifts from about 1.63 eV to 1.55 eV due to solvation relaxation in the polar solvent, while the GSB features remain unshifted. In less polar mixtures this shift is correspondingly reduced. (see Figure S6-8 for deconvolution in different solvent mixtures and more details on the solvation shift). Our interpretation is consistent with previous work by Natsuda *et al.* and Hao *et al.*^[54,55] Both ESA signals originate from the LE exciton of dissolved Y6. Furthermore, from 10 ps to 1 ns, ESA, SE, and GSB decay monoexponentially with time constant $\tau = 0.8$ ns without further spectral changes (Figure S6), implying that the LE to ground state transition dominates these decays. From 4 ns onwards, no signatures from the LE population are persistent, but a small residual GSB remains (Figure S9). This has previously been assigned to the long-lived triplet by quenching experiments.^[54] Overall, for the non-interacting Y6 molecules in solution, we observed three processes on different timescales: first, a SE redshift from solvation ($\sim$ ps); second, the decay of the LE singlet state ($\sim$ 1 ns); and finally the observation of the long-lived LE triplet state.

(ii) (Part b in Figures 2 and 3) The aggregated Y6 molecules exhibit different TA signals from the dissolved Y6 molecules. At 0.2 ps, the spectrum consists of a negative GSB signal at 1.83 eV, one ESA signal at 1.24 eV and a second ESA with a double peak at 2.12 eV and 2.26 eV; the expected GSB/SE below $\sim$ 1.6 eV is obscured by pump scatter. All observed spectral features can be assigned to the ICT state, as only aggregates are excited at 850 nm, which is supported by their identical decay kinetics (see Figure S10). Notably, all ICT-related signals decay within 50 ps, roughly twenty times faster than the LE-state decay in non-interacting Y6.

(iii) (Part c in Figures 2 and 3) At 0.2 ps, the spectrum contains negative signals from both the interacting and the non-interacting Y6 molecules. Comparing to the steady-state spectra, we identify the SE/GSB near 1.37 eV as arising from the aggregated Y6 and the SE/GSB around 1.69 eV (shoulder 1.82 eV) from a superposition of LE and ICT state. The positive feature at 1.28 eV corresponds to the ICT state ESA, while the broader ESA region near 2.1 eV reflects overlap of absorption features from both the LE and the ICT states. By 50 ps (horizontal dashed line in Figure 3c), the features from the ICT state (ESA at 1.28 eV, GSB/SE around 1.37 eV, GSB at 1.85 eV, and parts of the 2.1 eV ESA) have decayed significantly, leaving mainly signal from

the LE state on non-interacting Y6 except for the LE ESA band at about 1.4 eV which is significantly different from the measurements on the isolated non-interacting Y6. Between 0.2 ps and 100 ps, the absence of a distinct LE ESA feature can be attributed to its overlap with the ICT-related SE/GSB. After 100 ps, once the ICT state has fully decayed, this explanation no longer holds. Instead, the LE ESA seems to be masked by a weak negative signal centered around 1.3 eV, which becomes increasingly pronounced at longer delay times, reaching a maximum around 2 ns at which point the LE contributions have also vanished. Plots highlighting the different time regimes separately are available in the SI (Figure S11 and S12).

2.3. Insights into the short exciton lifetimes in the interacting Y6 molecules

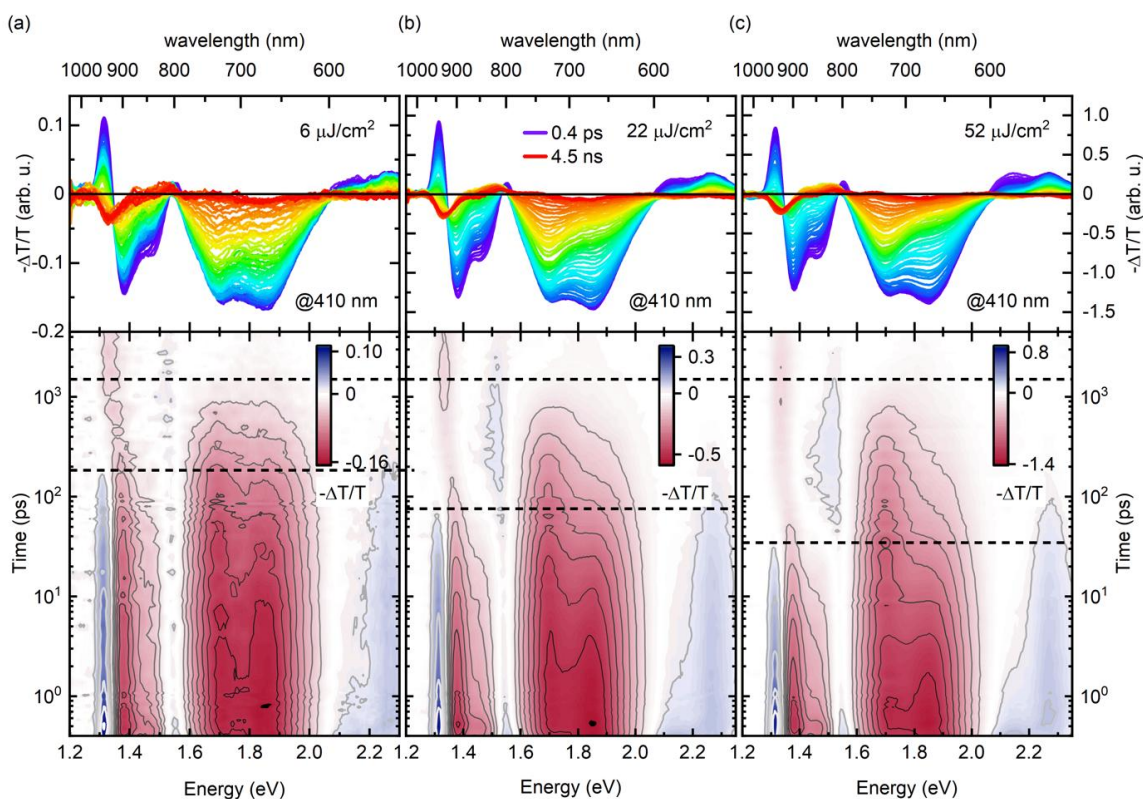


Figure 4. Pump-fluence dependent transient absorption spectra and 2D contour plot of Y6 in THF:CH mix with ratios of 1:19 with pump at 410 nm at (a) $6 \mu\text{J}/\text{cm}^2$, (b) $22 \mu\text{J}/\text{cm}^2$ and (c) $52 \mu\text{J}/\text{cm}^2$. The black dashed lines in the contour plots indicate characteristic timescales for the decay of the non-interacting and aggregated Y6.

To understand why the ICT excitons in the aggregated Y6 molecules decay much faster than the LE excitons in the non-interacting Y6, we performed pump-fluence-dependent TA measurements on both species using 410 nm excitation ($3\text{--}52 \mu\text{J cm}^{-2}$). Figure 4 shows

representative kinetics for 3 different pump fluences (results with other pump fluences are shown in Figure S13 and S14). Across all fluences, the spectral shape matches the superimposed features from both species shown in Figure 2c. However, the temporal behavior differs markedly. Signals attributed to the ICT state in aggregated Y6, such as the ESA at 1.31 eV and the GSB features near 1.4 eV and 1.9 eV, decay faster with increasing pump fluence, while the lifetime of the LE state in non-interacting Y6 remains at ~ 1 ns, independent of pump fluence. This is indicated by the horizontal dashed lines in Figure 4.

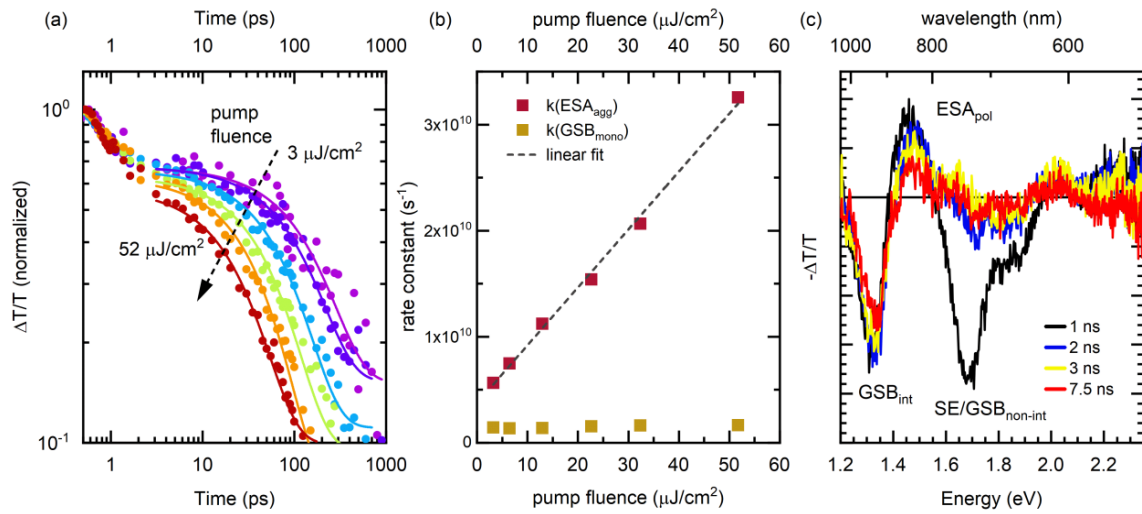


Figure 5. (a) Normalized TA decay kinetics of the characteristic ICT state ESA (at 1.31 eV) of Y6 in THF:CH (1-19) solution at different pump-fluences ranging from 3 $\mu\text{J}/\text{cm}^2$ to 52 $\mu\text{J}/\text{cm}^2$, fitted with a mono-exponential decay from 3 ps to later times. (b) Extracted decay rates of the aggregated (purple) and non-interacting (yellow) Y6 molecules as a function of the pump-fluence. (c) Transient absorption spectra of Y6 in THF:CH (1-49) after 1 ns.

The ESA at 1.31 eV, which characterizes the ICT state, can be analyzed with mono-exponential fits after 3 ps (Figure 5a). The resulting lifetimes give rate constants that increase linearly with pump fluence as shown in Figure 5b. This linear dependence indicates a dominant bimolecular decay pathway, in this case singlet-singlet annihilation (SSA) from the ICT excitons. The domains of tightly packed Y6 molecules that support ICT excitons appear to be large enough to host multiple mobile, delocalized ICT excitons, allowing exciton-exciton annihilation to occur. Indeed, while the freshly prepared solutions were clear during our measurements, we observed that the material precipitated from solution after a few hours upon standing (in the 1:19 and 1:49 samples), implying ongoing growth of crystallites. In contrast to the ICT state, the LE state exhibits a fluence-independent decay rate of

$\sim 1.5 \times 10^9 \text{ s}^{-1}$ as determined from the decay of the GSB (at 1.74 eV), confirming an intrinsic monomolecular decay channel.

To summarize the findings up to this point, ICT excitons in aggregated Y6 undergo SSA on a 30–180 ps timescale, as inferred from their strongly fluence-dependent lifetimes. In contrast, non-interacting Y6 displays intrinsic ~ 1 ns decay of LE excitons. The long-lived signal from 2 ns on will be addressed in the next section.

Figure 5c shows the transient spectra from 1 ns onwards. At this delay, the ground-state bleach (GSB) at 1.75 eV and the excited-state absorption (ESA) at 1.45 eV indicate that a fraction of localized LE singlet states remains on non-interacting Y6 molecules. By 2 ns, this GSB has vanished, the ESA has moved to 1.53 eV, and the spectrum is dominated by a pronounced negative feature at 1.33 eV, which is already present at times as early as 50 ps (see Figure S11). This feature corresponds to the GSB associated with the tail of the density of states (DOS) of interacting Y6 species (cf. Figures 1d and 2c), commonly associated with well-conjugated, delocalized π -systems. This suggests that species residing on aggregated Y6 molecules form very rapidly (< 50 ps) and persist for a long duration of time (> 7 ns).

Two likely candidates for such long-lived species are triplet excitons and polarons. We rule out triplets because the very fast appearance of this signal would require an intersystem crossing rate greater than $2 \times 10^{10} \text{ s}^{-1}$ which is an implausibly high value for rigid, tightly packed organic chromophores in aggregated environments. We therefore assign the long-lived GSB to polarons located on interacting Y6 molecules. This assignment is further supported by the ESA we observed simultaneously at 1.53 eV. In polymer:Y6 blends, an ESA signal at 1.5 eV (800 nm) has indeed been attributed to Y6 polarons by Giannini *et al.* and others.^[36,41,56] (see Figure S15).

2.4. Proposed model

Our results lead to the following model for exciton dynamics for Y6 molecules in solution (Figure 6). In good solvents, Y6 molecules do not interact electronically, so that photoexcitation above 1.7 eV generates local excited (LE) states with a pump-fluence-independent singlet lifetime of approximately 1 ns. In samples containing a higher fraction of non-polar solvent, tightly packed Y6 aggregates form. 410 nm photoexcitation generates not only LE excitons on well-dissolved non-interacting Y6 molecules but also ICT excitons on interacting Y6 units. The ICT exciton lifetime is governed by fluence-dependent SSA with ICT lifetimes between 30 and 200 ps. Furthermore, we observe a small fraction of long-lived polarons ($e...h$) on interacting Y6. These polarons are generated within 50 ps. We speculate that these polarons result from an Onsager-like autoionization process from a higher state accessed either by SSA or direct high-energy excitation on the interacting Y6.

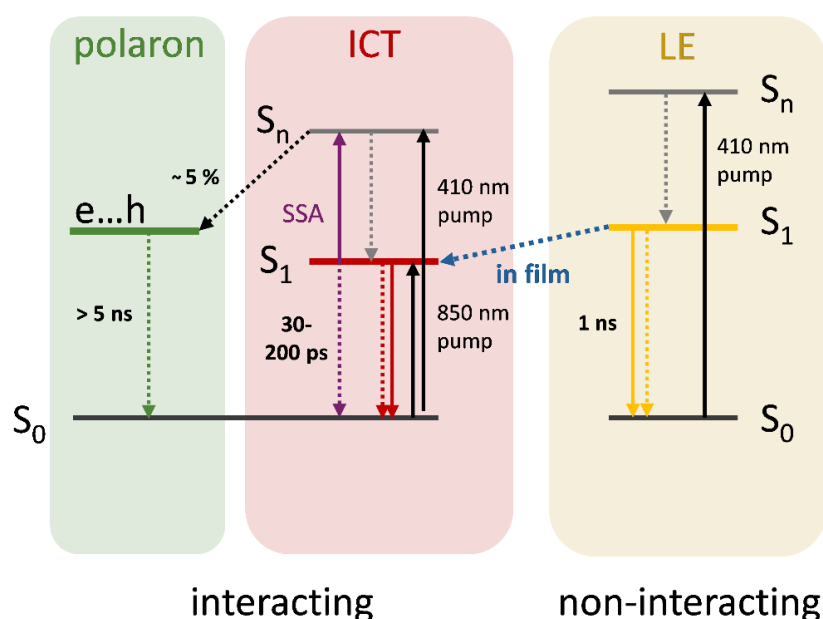


Figure 6. Schematic energy diagram of the excited state dynamics in our solutions containing non-interacting Y6 (right panel) and interacting Y6 (left panel). Solid lines show absorption or radiative transitions; dashed lines indicate non-radiative transitions. Lifetimes are indicated for all states. The blue arrow indicates the additional energy transfer from LE to ICT states which takes place in films.

In fact, the intensity of the polaron signal after 2 ns for excitation with 410 nm depends on the excitation fluence to the power of 0.81 (Figure S16) indicates a mixed bimolecular (SSA)

and monomolecular (direct excitation) formation pathway. An approximate polaron formation yield of $\approx 8\%$ is obtained by comparing the GSB intensity of ICT states at 0.2 ps with the GSB intensity associated with long-lived polarons at 2 ns (Figure S17). This value agrees well with the low EQE reported for neat Y6 films, thus further supporting our model of polaron generation on interacting Y6.^[40,48]

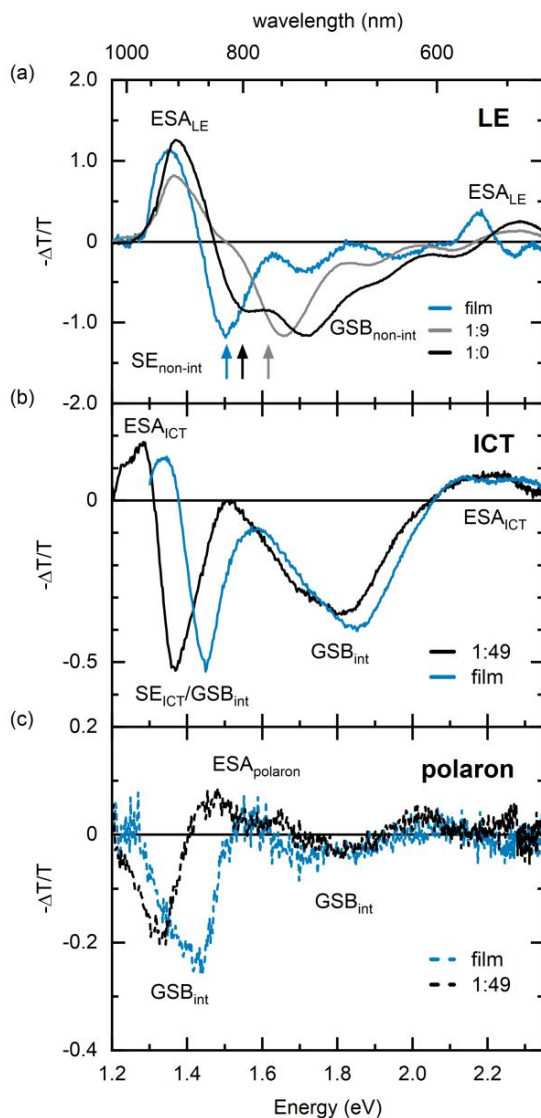


Figure 7. Comparison of the isolated TA spectra for Y6 film (blue) and solution (black) of the (a) LE, (b) ICT and (c) polaron signatures. The LE state signatures in solution are displayed for polar (1:0 THF:CH mixture) and non-polar (1:9) environment. The vertical lines in (a) indicate the positions of the SE signals which depend on the polarity.

The TA signatures of LE excitons, ICT excitons, and polarons in solution can be isolated from the data (Figure 7). The LE TA spectrum is extracted from the 1:0 and 1:9 THF:CH samples in

which Y6 is well dissolved and show no signs of intermolecular interactions. The spectra taken at 50 ps when solvent relaxation is completed so that the spectra evolve no further with time, are shown in Figure S6-7. As a result of the stronger solvent relaxation in the more polar 1:0 sample, the linewidths of all features and the Stokes' shift between SE and GSB are broadened, while SE and GSB merge to a single peak in the less polar 1:9 sample.

A representative polaron TA spectrum can be obtained from the most aggregated 1:49 sample at 3 ns, where the ICT and LE state have largely decayed. We also use the TA data from the 1:49 sample to isolate the ICT spectrum. We exploit the different lifetimes of LE (~ 1 ns) and ICT ($\tau = 40$ ps). At early times (2.5 ps), the spectrum has contributions from both, LE and ICT, while at later times (50 ps) the LE contribution dominates. Hence, the difference between the two spectra yields the ICT spectrum. By comparing the ICT TA spectrum to the measurement that selectively probe ICT states in aggregates by 850 nm excitation, we further validate the spectral subtraction approach (see Figure S12).

Knowing the LE, ICT and polaron TA signatures in solution allows us to identify the corresponding signatures in thin films. Y6 films were spin-cast from chloroform solution and TA measured at 410 nm excitation (Figure 8).

At 0.2 ps the TA spectrum shows two ESA bands (1.33 and 2.20 eV), a combined GSB/SE peak at 1.47 eV, and GSB shoulders at 1.70 and 1.85 eV. Within the first 2 ps the ESA feature at 1.33 eV decays strongly, the 1.47 eV feature red-shifts, and the 1.70 eV shoulder diminishes. From 2–50 ps the spectral shape remains constant while its amplitude decreases. From 100 ps on this component has largely decayed, leaving a long-lived (>4 ns) spectrum with GSB features at 1.42 and 1.80 eV and an ESA at 1.55 eV. Figure 8b shows the 1.33 eV ESA kinetics at two pump fluences (5 and 40 $\mu\text{J cm}^{-2}$). The intensity drops rapidly in the first 2 ps followed by monoexponential decay with lifetimes of 190 ps and 40 ps for 5 $\mu\text{J cm}^{-2}$ and 40 $\mu\text{J cm}^{-2}$, respectively.

The detailed analysis of these spectra at two pump fluences is provided in the SI (Figure S18). In essence, SSA and polaron formation occur in interacting Y6 molecules, analogous to the solution study. A blue shift of the ESA and SE/GSB at low energy causes the ICT ESA at 1.38 eV to overlap with the ESA of LE excitons, complicating the spectral assignment. Thus, characterizing the individual species in solution is essential for reliable interpretation of the

neat-film and blend spectra. However, in addition, energy transfer from LE to ICT states take place on a sub-picosecond time scale (400 fs, Figure 8b), as observed before by others.^[29,57,58] Consequently, the thin film spectra are soon dominated by the ICT state and polaron residing on the aggregates, while initial contributions from the LE states on non-interacting chromophores are more difficult to discern. The lifetimes for LE states, ICT states and polaron are again very distinctively separated by different evolution timescales, i.e. sub-ps to ps range, 40-200 ps and exceeding 5 ns, for those species, respectively. This allows us to separate the associated spectra analogous to the case in solution.

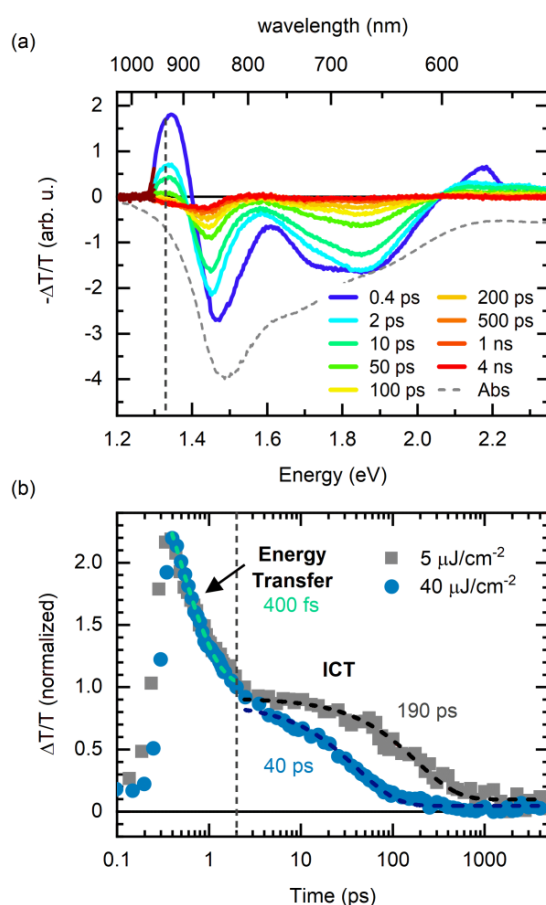


Figure 8. (a) Transient absorption spectra of a neat Y6 film with pump at 410 nm at $40 \mu\text{J}/\text{cm}^2$. The spectral region up to 1.3 eV is masked due to insufficient intensity in that spectral region of the pump pulse in that measurement. (b) TA kinetics of the ESA signal from a neat Y6 film at 1.33 eV (indicated with a dashed line in (a)) at pump-fluences of $5 \mu\text{J}/\text{cm}^2$ and $40 \mu\text{J}/\text{cm}^2$. The kinetics are fitted from 2 ps on with mono-exponentials (dashed lines).

The polaron TA spectrum in the film is given by the TA signal obtained at 4 ns, when the LE and ICT state have decayed. Similarly, the signal at 10 ps is representative for the ICT TA. To extract the LE state signature, we compare spectra recorded before (at 0.4 ps) and after (2 ps) energy transfer (c.f. Figure S19). These thin film TA spectra are compared with the solution TA spectra in Figure 7a-c to assign the TA features. Given the different local environments in both sets of samples (as explained in the next paragraph), solution and film agree well, thereby validating our approach.

The difference between film and solution can be rationalized as follows: The LE state TA signatures in film, derived from the small residual population between 0.4 ps and 2.0 ps, closely resemble those observed in polar environments in solution (ESA near 1.38 eV and 2.20 eV, SE around 1.50 eV, and GSB near 1.73 eV) This seems reasonable for compound made up of distinct donor and acceptor units.^[59]

The ICT spectra obtained in solution (1:49) and in film agree well in spectral shape. However, the GSB/SE near 1.4 eV and the ESA near 1.3 eV are at lower energies in solution than in the film, consistent with the lower energy of the steady-state absorption (Figure S20). In solution, aggregates can evolve slowly to adopt optimized, extended and well-packed arrangements with long effective conjugation length. This will result in red-shifted absorption and emission spectra. In contrast, spin-cast films from chloroform dry rapidly with kinetically limited molecular reorganization. This is likely to result in less extended aggregates with concomitantly reduced effective conjugation length and hence higher CT-state energies. This interpretation is consistent with calculations by Akram *et al.* showing that the energy of CT-like states decreases as delocalization extends over multiple Y6 units.^[22] The same argument pertains to the position of the GSB and ESA in the TA of the polarons residing on the aggregates.

Overall, our data suggests that in neat films of Y6, the same processes occur as in well-solvated solution samples, with additional ultrafast ($\tau = 400$ fs) energy transfer from the non-interacting Y6 to aggregated, interacting Y6. With the clear identification of LE state, ICT state and polaron TA signatures in film and solution, our results offer a consistent framework for understanding the photophysics of Y6. This motivates a closer examination of prior literature, where different interpretations of polaron formation and exciton dynamics have been proposed.

2.5. Discussion

Due to the exceptional power conversion yields obtained in organic solar cells with Y6-type non-fullerene-acceptors, there is an ongoing discussion on whether free polarons are already formed efficiently in neat domains of Y6 in blends, and concomitantly also in neat Y6 films.^[28,36,41,45,46,60] Giannini *et al.* and Price *et al.* both investigated the TA behavior of neat Y6 films and interpreted their spectra to indicate ultra-fast polaron formation with high yields up to about 70 %, substantially higher than the ~8 % yield we have observed.^[36,45] A significant difference in their model compared to ours is that they do not consider possible domains of loosely packed, non-interacting Y6 molecules. This leads to a different interpretation in the decrease of the ESA signal at about 1.4 eV on the ps timescale.

The observed TA signal arises from absorption by photogenerated LE and ICT states. The LE component decays within 2 ps due to ultrafast energy transfer to ICT states. The remaining signal after 2 ps is attributed to ICT excitons on aggregates, which subsequently undergo annihilation to produce polarons with an approximate yield of 8 % (Figure S21) within 10s to 100s of ps.

The works by Giannini *et al.* and Price *et al.*, in contrast, presume that all photogenerated states prevail on interacting Y6. Hence, the fast (< 2 ps) initial decay of the 1.4 eV ESA is interpreted as the decay of the excited state into polarons. Consequently, the signal remaining after 2 ps is *not* attributed to ICT excitons, but rather to polarons. Because this species dominates the film population after 2 ps, it is interpreted as evidence for a high polaron yield. (Figure S22)

Furthermore, the fluence-dependent annihilation process, assigned to SSA on aggregates leading to polarons in our model, is attributed to fluence-dependent non-radiative polaron recombination in the model by Giannini *et al.* and Price *et al.*, with a concomitantly short polaron lifetime of a few hundred picoseconds. However, such a short polaron lifetime is at variance with the findings by Saglamkaya *et al.* and Ham *et al.*, who both investigate neat Y6 films and observe polarons with lifetimes of tens of nanoseconds and with yields that increase with the fraction of aggregates present.^[46,61] Their work is in line with our finding of polarons that form on aggregates in the picosecond scale and extend well into the nanosecond range.

Moreover, our observation of polaron formation in aggregates by an Onsager-type autoionization with a yield of $\sim 8\%$ in solution and films is consistent with the observed quantum efficiencies of a few per cent in neat Y6 single layer solar cells.^[40,48] Our value is also consistent with typical polaron formation yields measured in neat films of conjugated polymers containing aggregates.^[57,58,62–75] In some of these works, the intermolecular interaction and exciton delocalization were clearly identified as key factor enabling polaron formation, for example by Herrmann *et al.* and by Tautz *et al.*^[72–76] This conclusion is also consistent with low quantum efficiency measurements on neat Y6 films.^[40,48]

Support for our interpretation of a fast, initial LE to ICT state energy transfer can also be found in the site-selective excitation data presented in Fig. 5 of Giannini *et al.*^[36] (Figure S23) When films were excited at 1.3 eV, i.e. at the tail of the aggregate absorption, and well below the absorption of non-interacting Y6, the fast (< 2 ps) decay of the 1.4 eV ESA feature is absent. This is also consistent with the observations from Guo *et al.* who investigated the ultrafast energy transfer from LE to ICT states in Y6 by temperature dependent transient electro absorption spectroscopy.^[29]

3. Conclusion

In this study, we investigate spectral signatures and kinetics of non-interacting and interacting Y6 molecules with TAS in dilute solutions and thin films by comparing with steady-state absorption and PL spectra. This can be used as a tool to analyze the spectra and kinetics of neat and blend films with Y6, where several overlapping signals complicate the assignment. We find that the exciton dynamics in the interacting molecules are dominated by a SSA with lifetimes ranging from 30-200 ps depending on the excitation density. In contrast, the excitons in the non-interacting molecules exhibit a fluence-independent mono-exponential decay of approximately 1 ns. At longer delay times, we detect a persistent spectral signature that we assign to a polaronic state residing on the aggregated and interacting Y6 molecules. Our results indicate a ultrafast charge separation mechanism according to an Onsager-like autoionization. For the polaron formation, the delocalization of the exciton over several molecules of interacting Y6 is needed. The required excess energy to overcome the Coulomb binding energy can either come from the SSA process or by direct excitation with high energy

photons. Nevertheless, the polaron formation process remains moderate with a yield of about 8 %, comparably with previous studies on other OSC materials. Our results highlight the importance to consider both interacting and non-interacting Y6 molecules to obtain a complete understanding of charge generation. This consideration is especially critical in thin films, where rapid energy transfer between these species can occur. The necessity to take into account both aggregated and non-aggregated molecules extends beyond Y6 to a broader class of rigid donor–acceptor compounds, which are prone to aggregation yet widely used in organic solar cells.

4. Experimental details

Y6 was purchased from “1-Material, Canada”. For the transient absorption measurements, Y6 was dissolved at 0.02 mg mL^{-1} (corresponding to a molar concentration of about $1 \times 10^{-5} \text{ mol L}^{-1}$) in mixtures of tetrahydrofuran (THF) and cyclohexane (cH) with ratios of 1:0, 1:9, 1:19 and 1:49. The solutions were stirred for at least 1 h at 50°C . Y6 films were spin-cast from a 12 mg mL^{-1} chloroform solution at 1000 rpm and afterwards thermally annealed at 90°C for 5 min. Steady-state absorption measurements performed using a Varian Carry 5000 UV-vis spectrometer (Agilent). Steady-state PL measurements were carried out using a home-built setup: The solutions were filled in a 10 mm fused silica cuvette. A 405 nm and 820 nm continuous wave diode laser were used to excite, the non-interacting Y6, aggregated Y6 or both. A spectrograph (Andor Shamrock SR303i) coupled to a CCD camera (Andor iDus 420) extended with a photo diode array (Andor iDus 490 InGaAs) to enhance in the NIR-range were used as detection system.

For femtosecond TA measurements, a custom-built spectrometer was used. Two synchronized Yb:KGW femtosecond amplifiers seeded by a shared oscillator (Light Conversion, Pharos Duo), which generate 1030 nm pulses with $100 \mu\text{W}$ and 180 fs duration function as primary light sources. The repetition rate of the amplifiers is 100 kHz but was reduced to lower frequency as required. The pump pulses centered at either 410 nm and 850 nm with 30 fs duration were generated by a noncollinear optical parametric amplifier (Light Conversion, Orpheus-N-2H) pumped by one femtosecond amplifier. A broadband VIS-NIR probe pulse was generated by focusing the output of the second femtosecond amplifier onto a 2 mm sapphire crystal. A computer-controlled delay line (Newport, DL325) enabled pump-probe optical delays in the range of -10 ps to 7 ns. A high-speed prism-and CCD camera-based spectrometer (Entwicklungsbüro Stressing GmbH, FLC3030, CCD camera, 50 kHz maximum frame rate) was used to acquire spectra from each pulse. The polarization of the pump and probe beams were held at the magic angle (54.7°) for all measurements. The solutions were filled in a 2 mm quartz cuvette and were continuously stirred during the measurements. The TA measurements were performed at a laser repetition rate of 33 kHz, with the pump modulated by optical chopper (310CD, SciTech Instruments) at half the probe frequency.

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SUPPORTING INFORMATION

Disentangling polaron formation pathways in Y6 probing non-interacting and interacting chromophores via transient absorption spectroscopy

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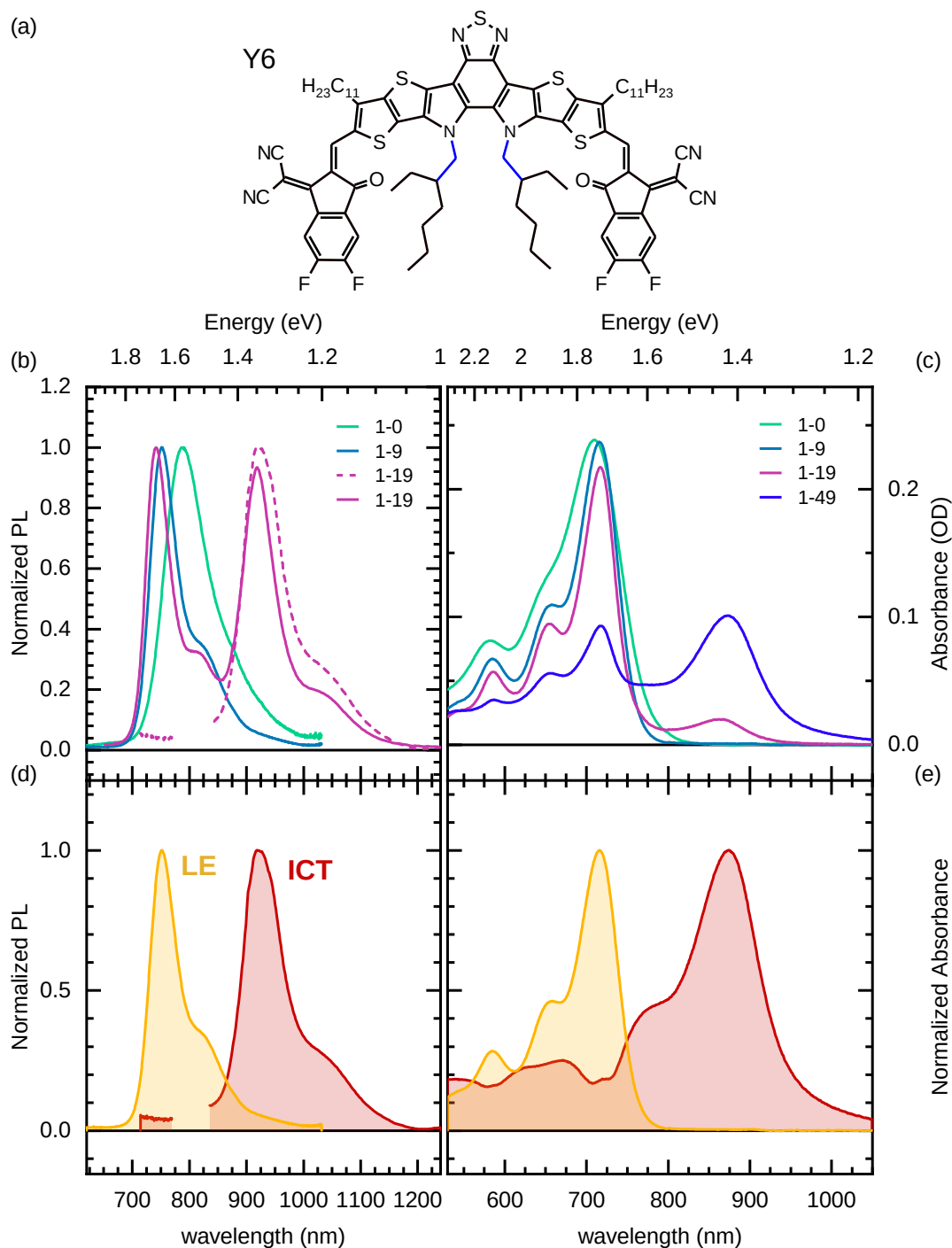


Figure S1: (a) Molecular structure of Y6. (b) Steady-state photoluminescence and (c) absorption spectra (linear on wavelength scale) of Y6 in THF:CH solvent mixtures with ratios from 1:0 to 1:49. Solid lines in PL with excitation at 410nm, dotted line (1:19 mixture) with excitation at 820 nm. (d) Normalized PL and (e) Absorption spectra for the LE and ICT state derived by appropriate subtraction.

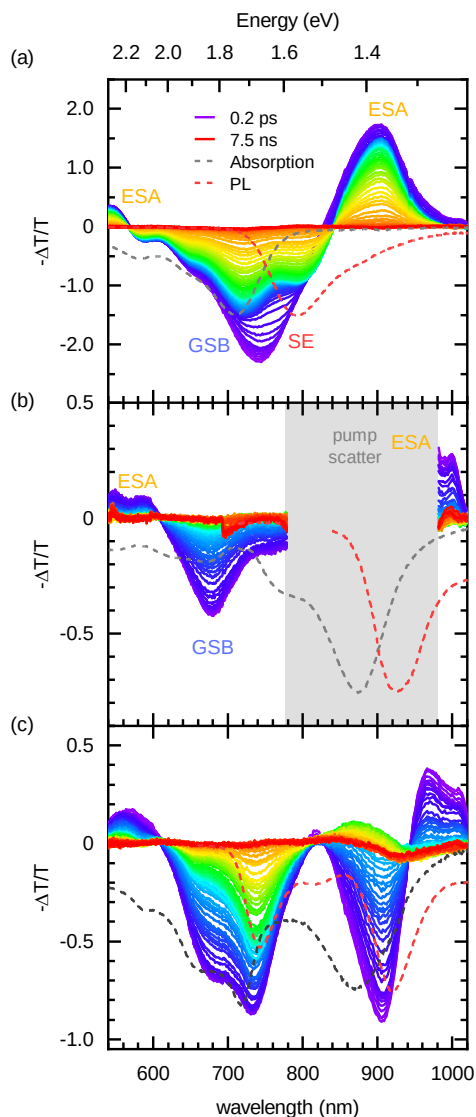


Figure S2: Transient absorption spectra (linear on wavelength scale) of Y6 in THF:cH mixed solvent with ratios of (a) 1:0 with pump at 410 nm to probe only the non-interacting phase of Y6, (b) 1:49 with 850 nm pump to probe only the aggregated phase of Y6, (c) 1:49 with pump at 410 nm to probe both phases. When exciting with the 850 nm pump beam, pump scattering prevents meaningful interpretation of the data in the range from 1.28 eV to 1.58 eV. For easier assignment of the signals, the inverted steady-state PL (red dashed line) and absorption (grey dashed line) spectra are also shown with arbitrary normalization.

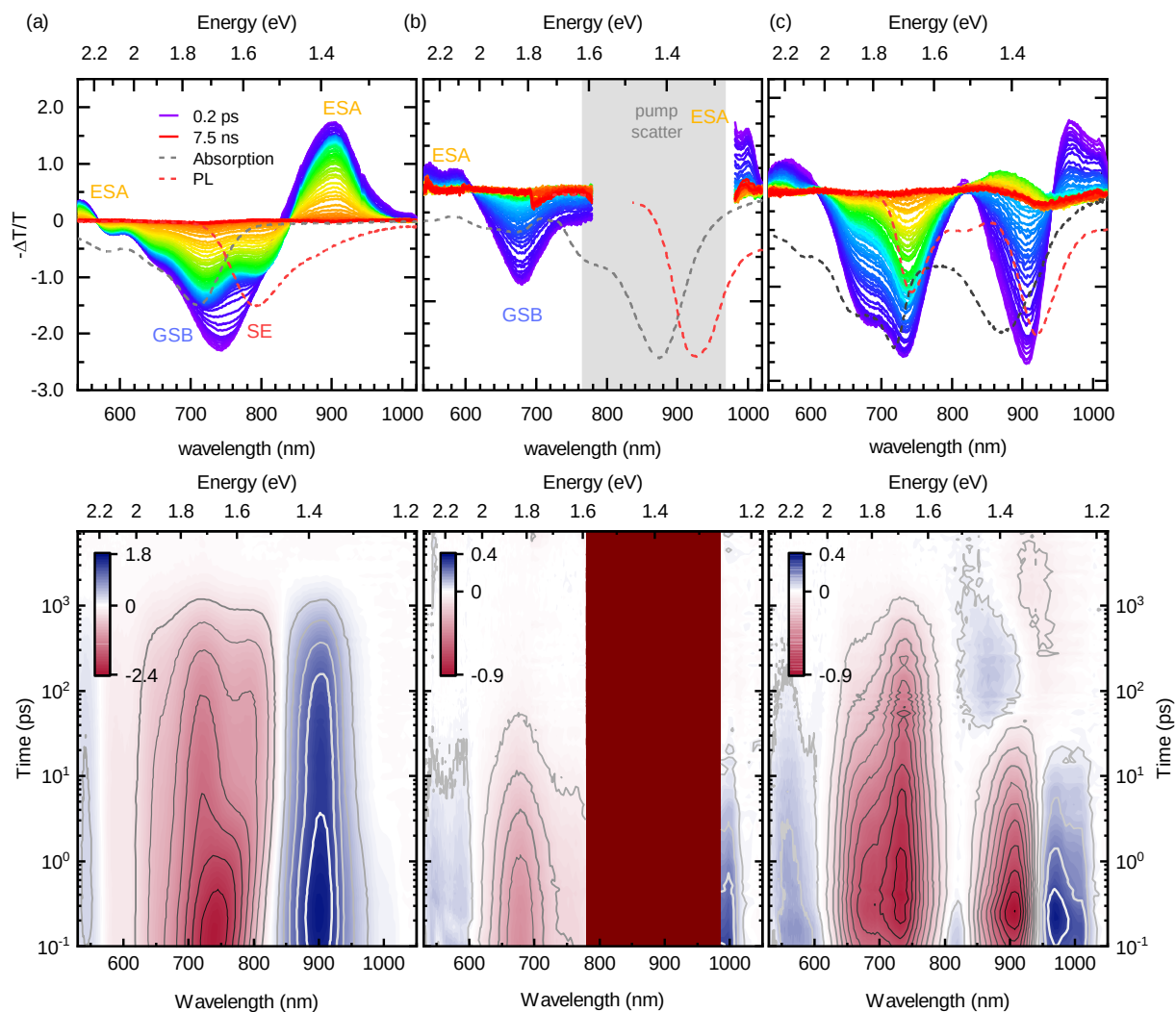


Figure S3: Transient absorption spectra (linear on wavelength scale) of Y6 in THF:CH mixed solvent with ratios of (a) 1:0 with pump at 410 nm to probe only the non-interacting phase of Y6, (b) 1:49 with 850 nm pump to probe only the aggregated phase of Y6, (c) 1:49 with pump at 410 nm to probe both phases, plotted as a 2D map. When exciting with the 850 nm pump beam, pump scattering prevents meaningful interpretation of the data in the range from 1.28 eV to 1.58 eV. The black, dashed lines indicate the time scales for the decay of the main signals of the non-interacting and aggregated phase, respectively.

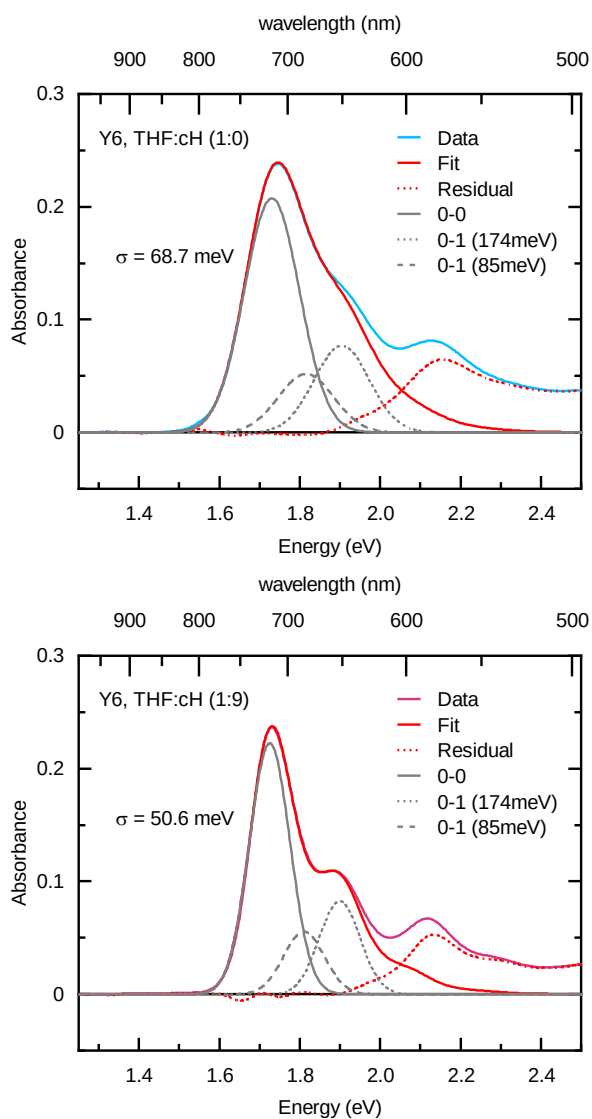


Figure S4: Franck-Condon fit of the S1 state of the non-interacting phase of Y6 in solvent mixture of THF:cH with (a) 1:0 and (b) 1:9 ratio, with two vibrational modes (174 meV and 85 meV).

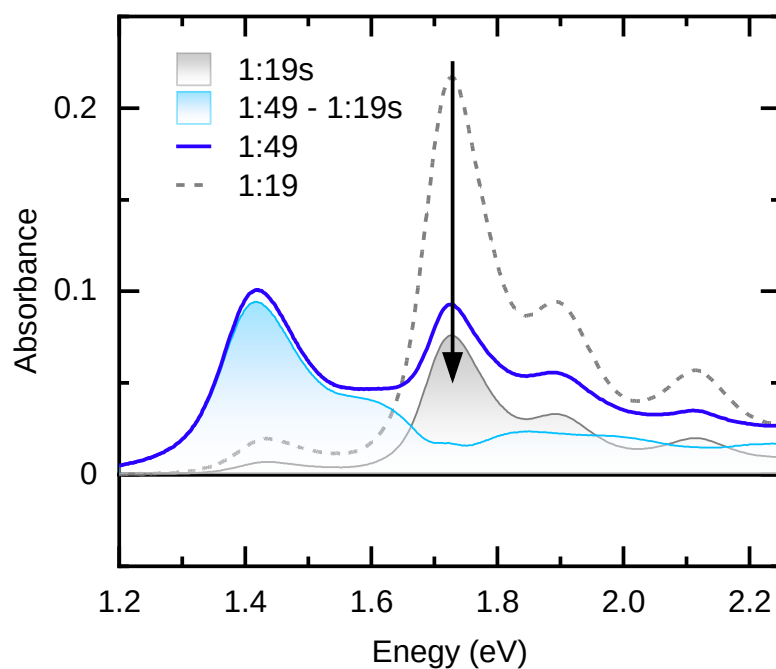


Figure S5: Demonstration of the deconvolution of absorption spectra of Y6 in THF:CH (1:49) solution (blue solid line) to receive the absorption contribution of the interacting Y6 (light blue). Therefore, the absorption spectrum of Y6 in 1:19 solvent ratio, with dominantly non-interacting Y6 and only minor signs of aggregation, is scaled appropriately (indicated by black arrow). Subtracting the latter spectrum from the 1:49 spectrum gives a good estimation of the absorption spectrum of interacting Y6. Note, that even though this method gives a good estimation of the aggregate absorption in the sample, the absorption intensity, particularly around the peak of the scaled absorption spectrum (of non-interacting molecules) may have slight deviations.

Details on the solvation shift of LE state in non-interacting Y6

First, we display the TA spectra of Y6 in the pure THF solution (1:0) normalized to the 1.90 eV, associated with the GSB signal, where no ESA or SE overlaps. We observe no spectral changes between 10 ps and 1 ns. Prior to 10 ps, the spectrum in the range of 1.6 eV is evolving.

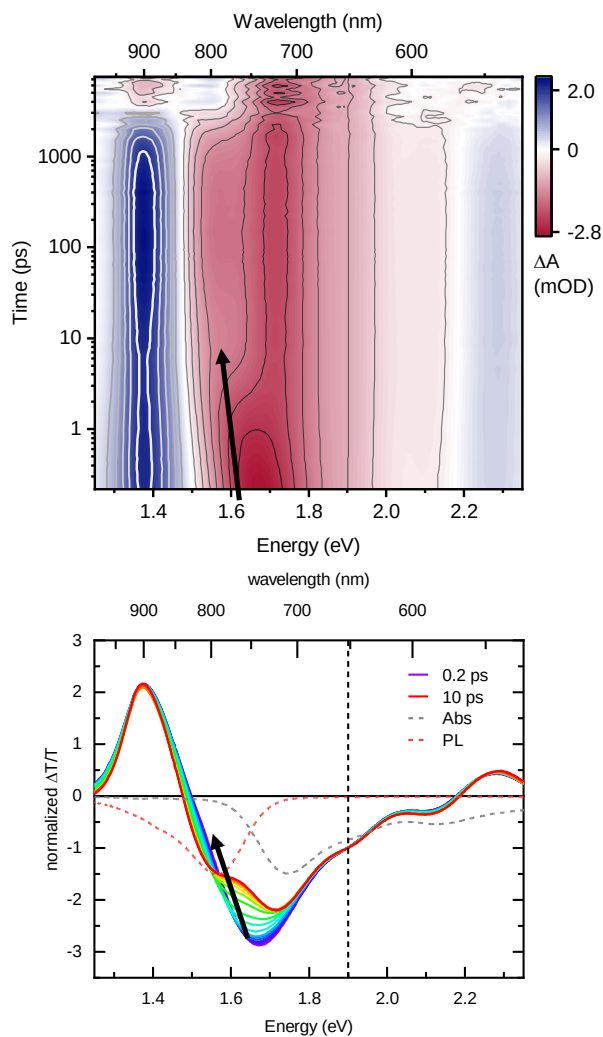


Figure S6: Transient absorption spectra of Y6 in THF, 0.02 g/l, @410nm, normalized to GSB signal at 1.90eV as there are the no overlapping components of the SE and the ESA features. Plotted in different time ranges from 0.2ps-10ps; 50ps-1000ps; 1ns-7ns.

The minimum at 1.65 eV evolves into two minima within the first 10 ps due to an energetic shift of the stimulated emission signal to lower energies.

Transient absorption spectra of Y6 in THF:cH (1:9) solvent mix

Compared to the transient absorption spectra of Y6 in pure THF (polar), in the less polar solvent environment (1:9) the SE shifts a lot less after photoexcitation (indicated by the arrow) leading only to a minor shift of the minimum of the TA spectra in the first ps and thus, to a decreased Stokes-shift.

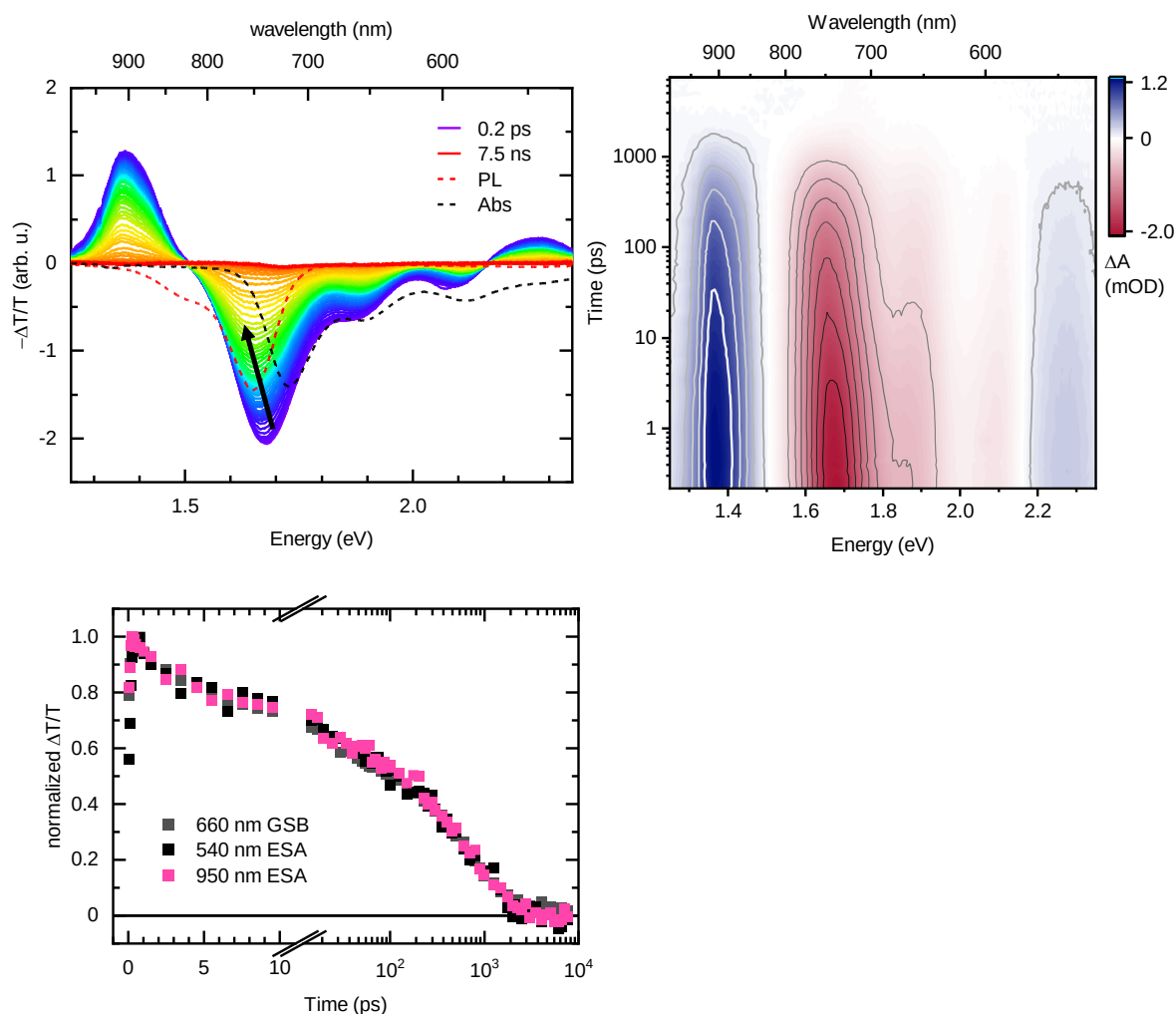


Figure S7: Top: Transient absorption spectra and 2D map of Y6 in THF:cH (1:9) with concentration of 0.02 g/l, excited @410nm, from 0.2 ps to 7.5 ns. Additionally, the steady-state absorption and PL are plotted in dashed lines. Bottom: Normalized evolution of the TA signals at specific wavelength.

Demonstration of the impact of solvation shift of SE

Taking the steady state absorption and PL as GSB and SE signals, respectively, and the overlap of both signals as the resulting, expected TA signal. Shifting the SE signal in two steps by 50 meV each results in an initial single peak (purple) that evolves into a double peak (green) as soon as the SE signal shifts far enough to the red.

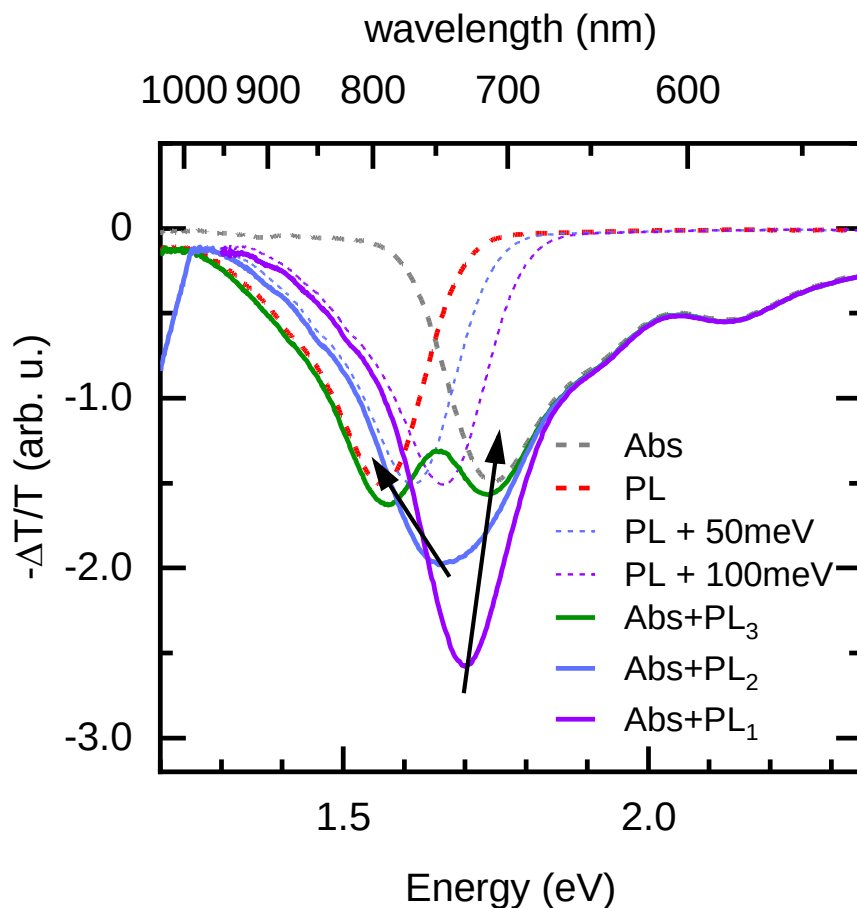


Figure S8: Demonstration of the impact of the shift of the SE signal on the transient absorption spectra. The dashed lines display the inverted, normalized absorption (grey) and PL (red) spectra of Y6 in THF solution. The solid lines represent the superposition of the inverted absorption and PL spectra corresponding to an overlapping SE and GSB signal in transient absorption spectra. Shifting the PL signal over 100 meV (thin purple and blue dashed line) leads to a spectral evolution from a single peak (purple solid line) to a double peak (green solid line) as observed in our transient absorption spectra.

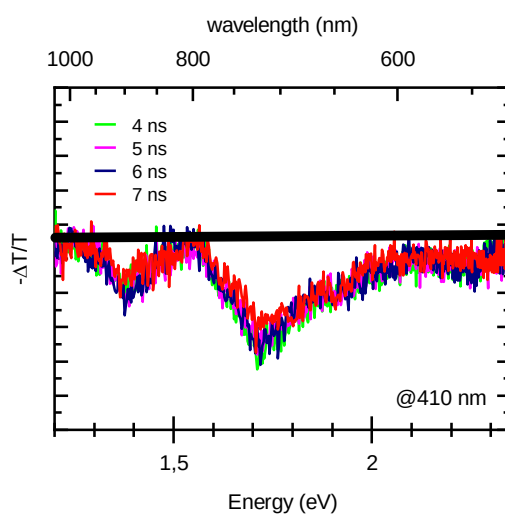


Figure S9: Transient absorption spectra of Y6 in THF with pump at 410 nm to probe only the non-interacting phase of Y6 at long time delays (4 ns to 7 ns), assigned to the signatures of a triplet exciton residing on a non-interacting Y6 molecules.

ICT exciton decay under 850 nm pump excitation

From 0.6 ps on, all signals (ESAs at 1.26 eV and 2.12 eV and GSB around 1.87 eV) decay monoexponentially with the same lifetime. Thus, all signals can be assigned to the same excited species, in this case the ICT exciton.

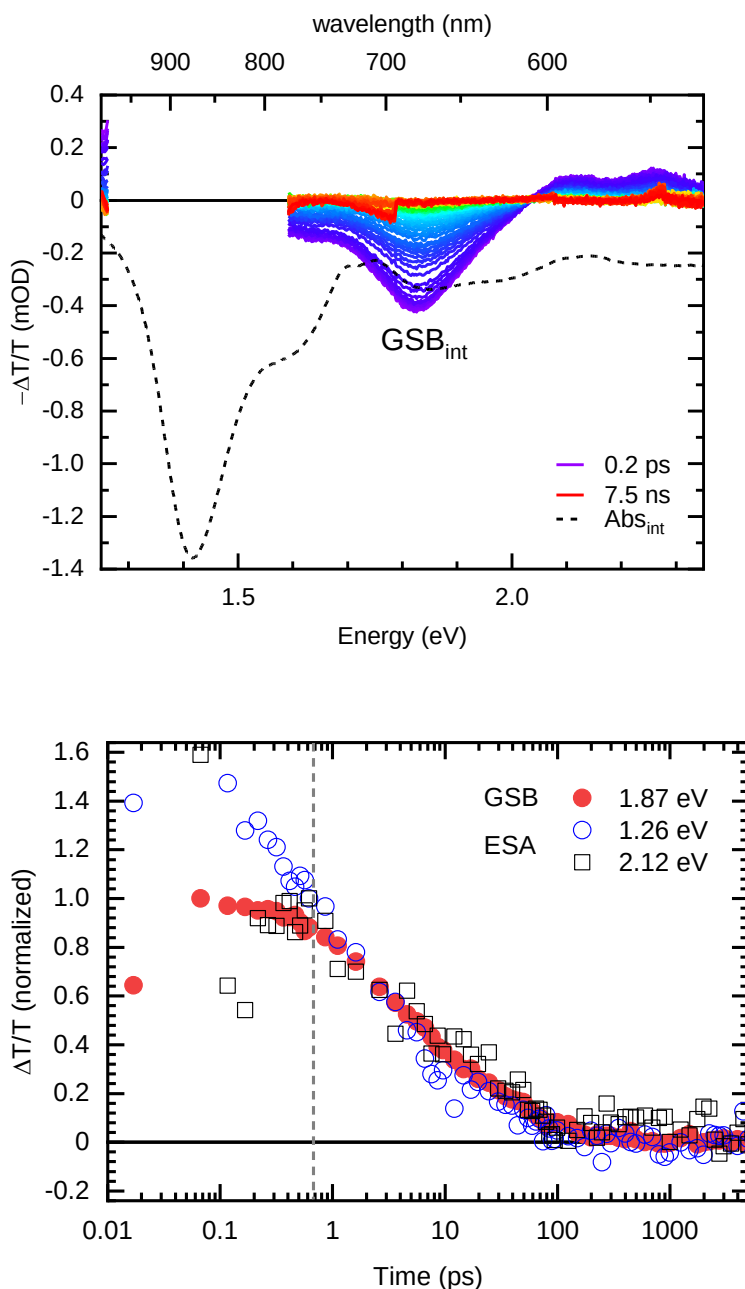


Figure S10: Top: Transient absorption spectra of Y6 in THF:CH (1:49) with pump at 850 nm to probe only the aggregated phase of Y6. The dashed grey line displays the steady-state absorption of interacting Y6 for reference. Bottom: Kinetics of the transient absorption spectra at 1.87 eV (GSB), 1.26 eV (ESA) and 2.12 eV (ESA) normalized to the intensity at 0.6 ps.

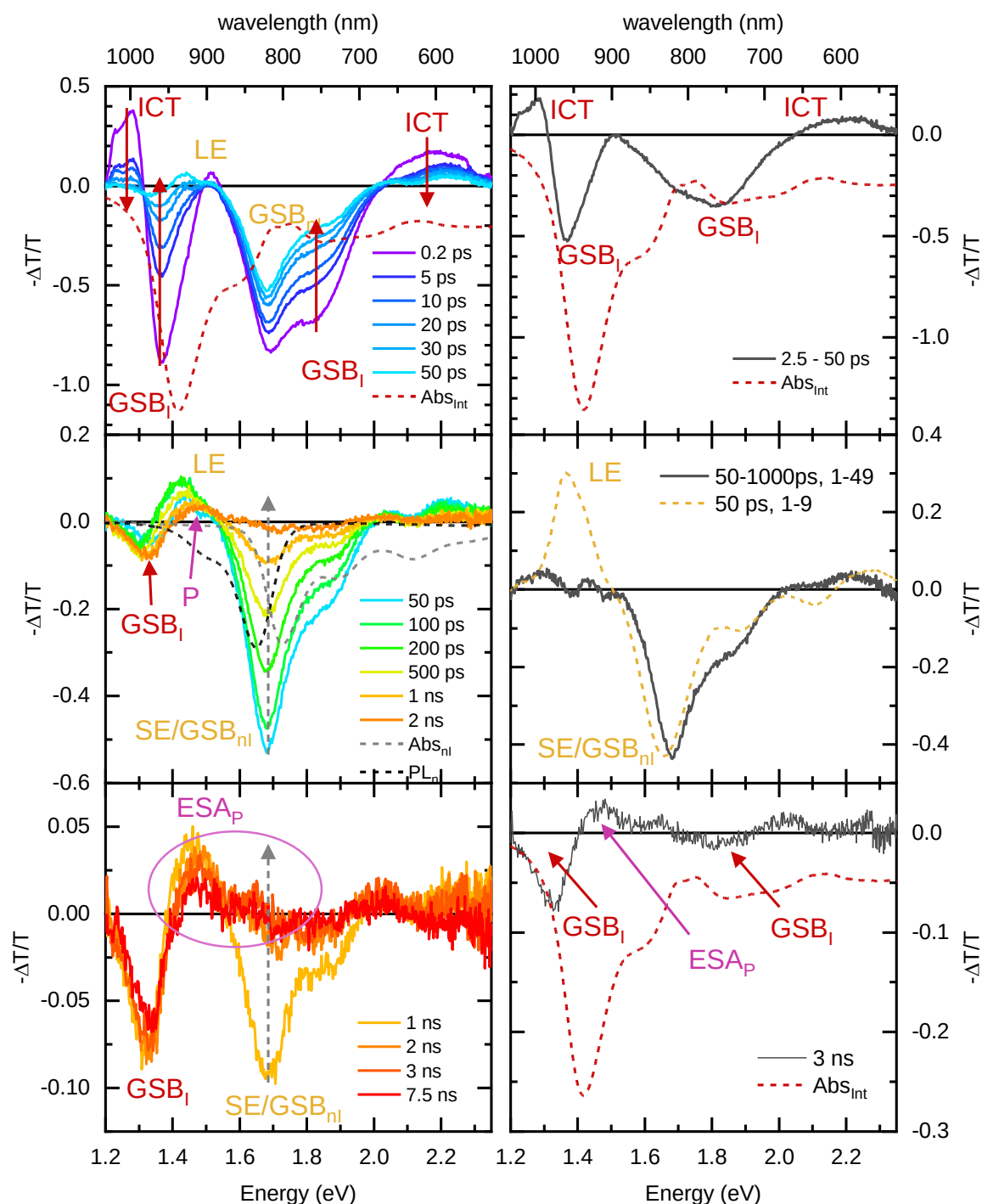


Figure S11: Left: Transient absorption spectra of Y6 in THF:CH (1:49) solution excited at 410 nm highlighting the different time regimes separately. The arrows indicate spectral evolutions and the signals are labeled with indices “nl” for non-interacting (yellow) and “I” for interacting (red) Y6. The inverted absorption and PL spectra are shown respectively for reference. Right: Difference of the of initial and final transient absorption spectra in the time regime, respectively. In the first time regime up to 50 ps this “difference” spectrum corresponds mainly to the spectrum of the ICT state as the other species (LE and polaron)

decay on a much longer time scale. The spectrum in the second time-regime (from 50 ps to 1 ns) mainly resembles the transient absorption signals of LE states on non-interacting Y6. The only difference is a strongly suppressed ESA absorption around 1.4 eV (see yellow dashed line for reference), which results from the ongoing overlapping negative features of the ICT and polaron species over the whole time-range. The spectrum at the bottom right is the TA spectrum at 3 ns which resembles the signatures of polarons on Y6 as both, LE and ICT excitons, have completely decayed.

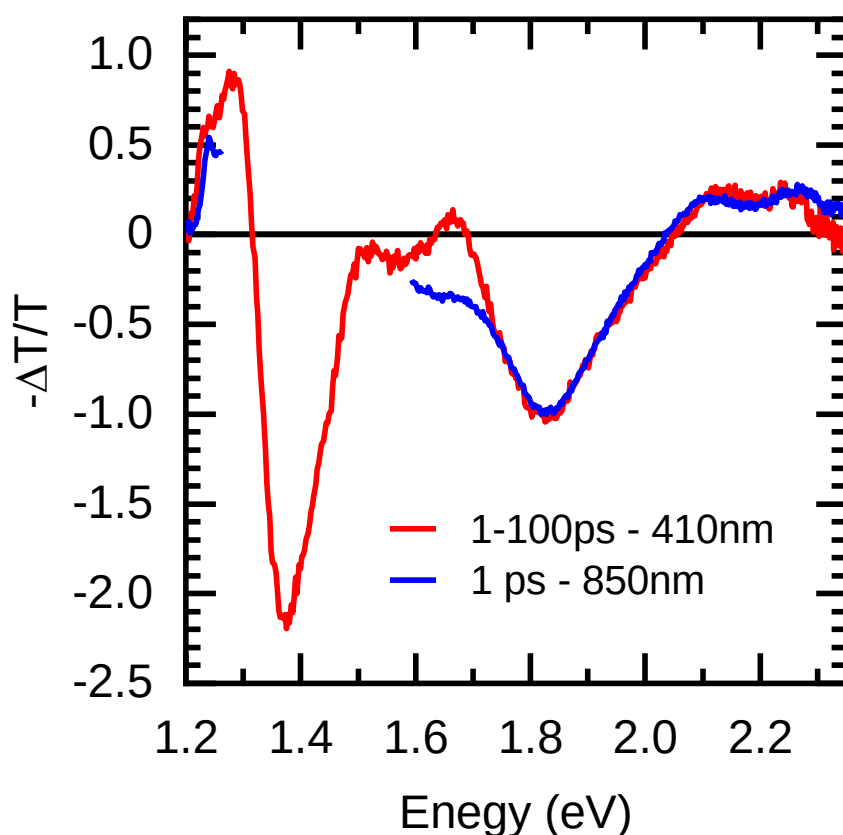


Figure S12: Comparison of the transient absorption spectrum of the ICT exciton in interacting Y6 when selectively exciting aggregated Y6 with 850 nm pump (blue) in THF:cH (1:49) solution and the disentangled spectrum associated with the ICT exciton from the measurement exciting both, non-interacting and interacting Y6, in THF:cH (1:49) with 410 nm pump. The disentangled spectrum (red) is the “difference” spectrum from 1 ps and 100 ps similar to the spectrum in Figure S11-top-right. Both spectra (blue and red) coincide verifying that spectral deconvolution is meaningful.

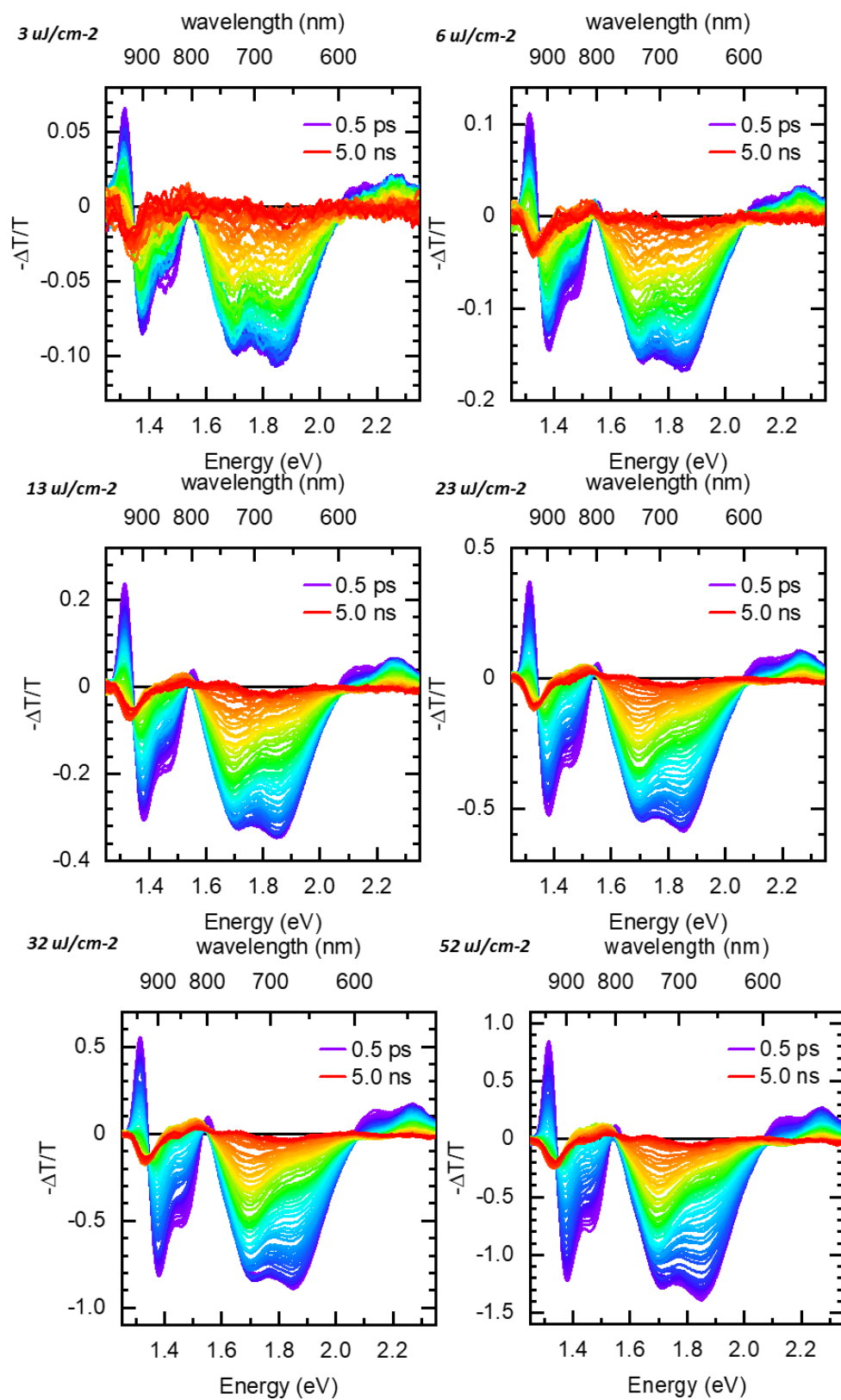


Figure S13: Pump-power dependent transient absorption spectra of Y6 in THF:CH (1:49) solution with 410 nm pump at several pump powers.

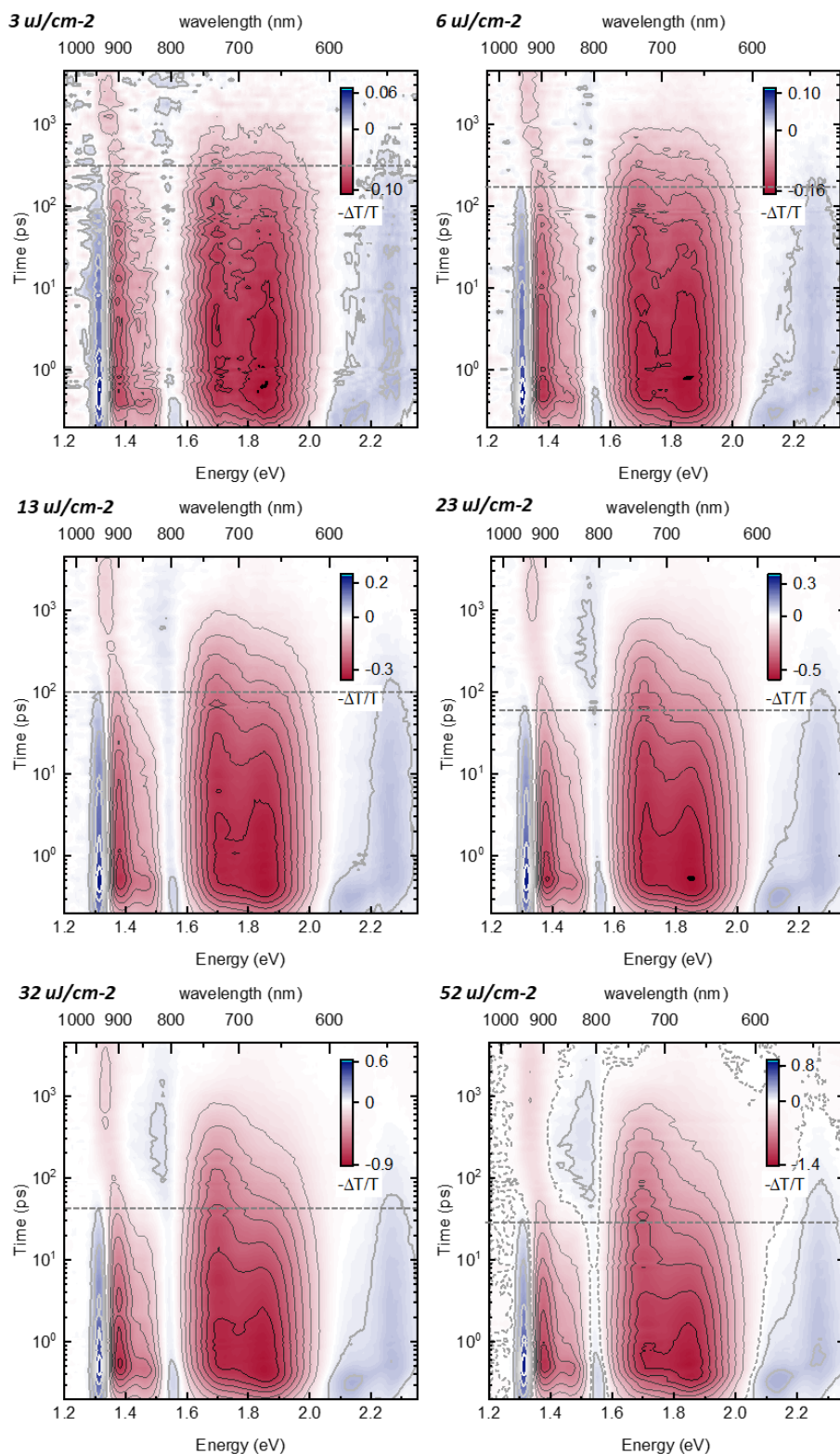


Figure S14: 2D plots of pump-power dependent transient absorption spectra of Y6 in THF:CH (1:49) solution with 410 nm pump at several pump powers as in Figure S13. The dashed horizontal lines indicate the decreasing lifetime of the ICT associated signals with increasing pump-fluence.

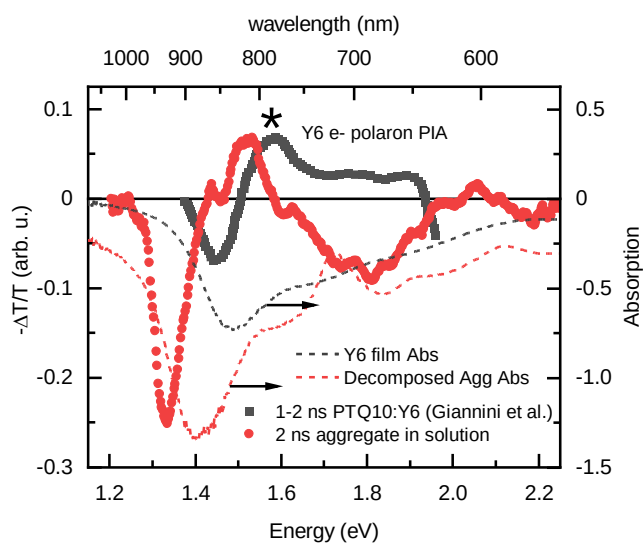


Figure S15: TA spectrum of PTQ10:Y6 blend film at 1-2 ns (black dots) replotted from Giannini et al.^[1], and converted to energy scale where they assigned the ESA (marked with star) at about 800 nm to the absorption of an electron polaron on Y6, as they observe this signal after blending Y6 with several electron donor materials. TA spectrum of Y6 in THF:CH (1:19) solution, excited at 410 nm at 2 ns (red dots). We also assign the ESA to the polaron absorption residing on interacting Y6, with the difference between the TA spectra stemming from the red-shifted GSB signal from the interacting Y6 in the non-polar environment in the THF:CH (1:19) solution. Therefore, compare the inverse steady-state absorption spectra (dashed lines) of the film (black) and the solution (red).

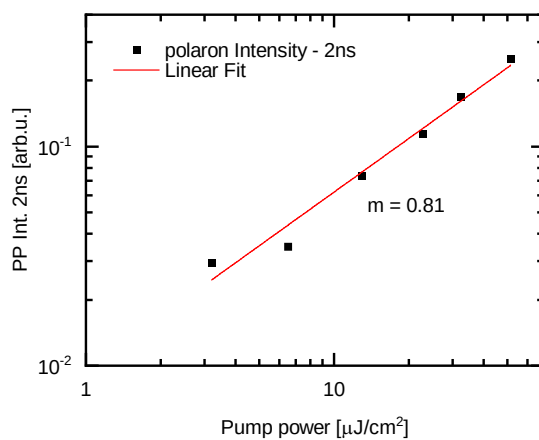


Figure S16: Pump power dependent intensity of polaron PiA signal after 2 ns, extracted from transient absorption spectra of Y6 in THF:CH (1:19) solution, excited at @410 nm. Thus, the pump pulse excites both, the non-interacting and interacting phase of Y6. The intensities are fitted with a linear progression with a slope of $m = 0.81$.

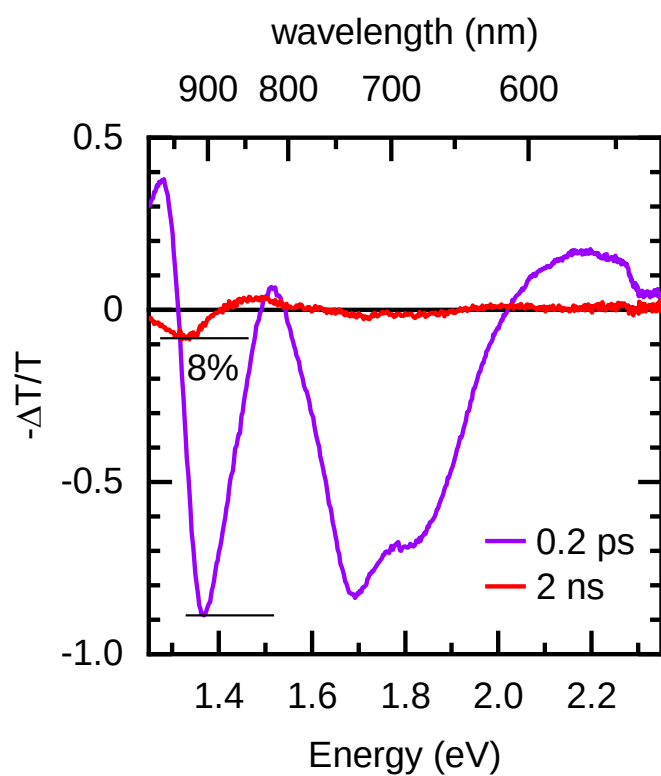


Figure S17: TA spectra of Y6 in THF:cH (1:49) solution with 410 nm at 0.2 ps and 2 ns delay. Comparing the GSB signal around 1.35 eV at the two time delays can be used to estimate the polaron yield to about 8 %.

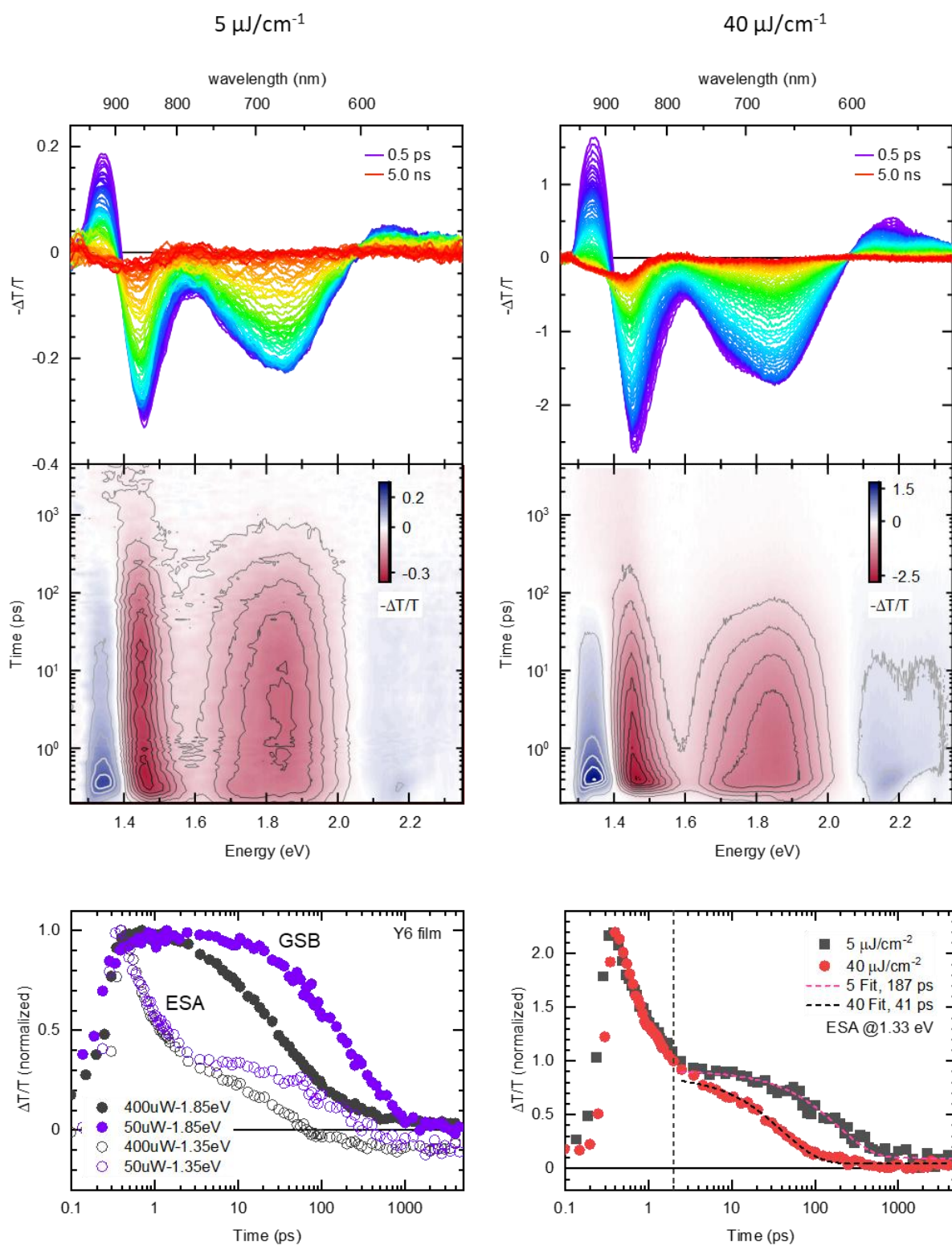


Figure S18: Top: TA spectra of Y6 films at 5 and 40 $\mu\text{J}/\text{cm}^2$ pump fluence. Bottom: Comparison of GSB and ESA kinetics of the two pump fluences with mono-exponential fits or the ESA signal at 1.33 eV from 2 ps to longer times.

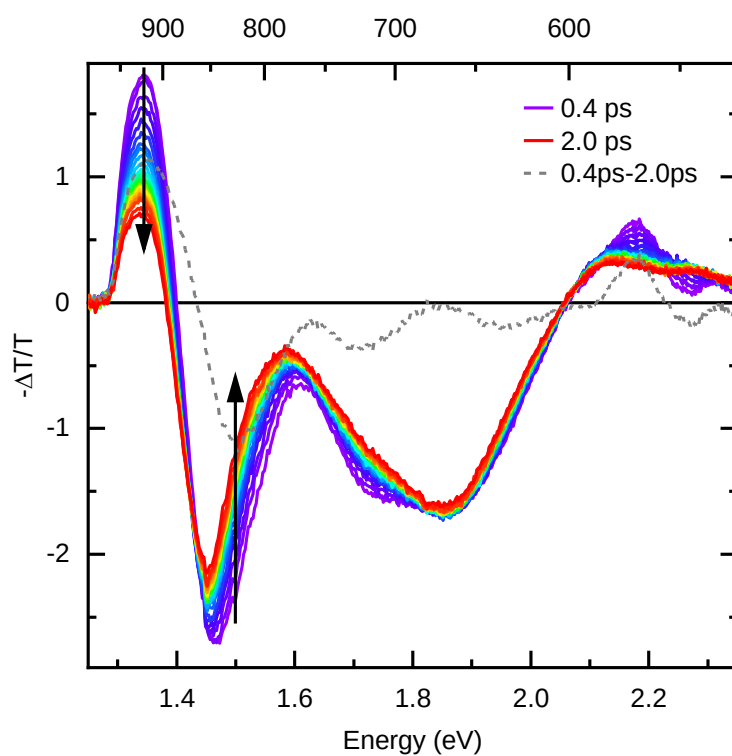


Figure S19: Y6 film, LE extraction.

At very short delays both non-interacting and interacting Y6 molecules are excited, so the early spectrum represents a superposition of LE and ICT features. As energy transfer proceeds, the relative ICT contribution increases, while the LE signatures vanish. The difference spectrum between 0.4 ps and 2 ps is therefore representative of the LE spectrum.

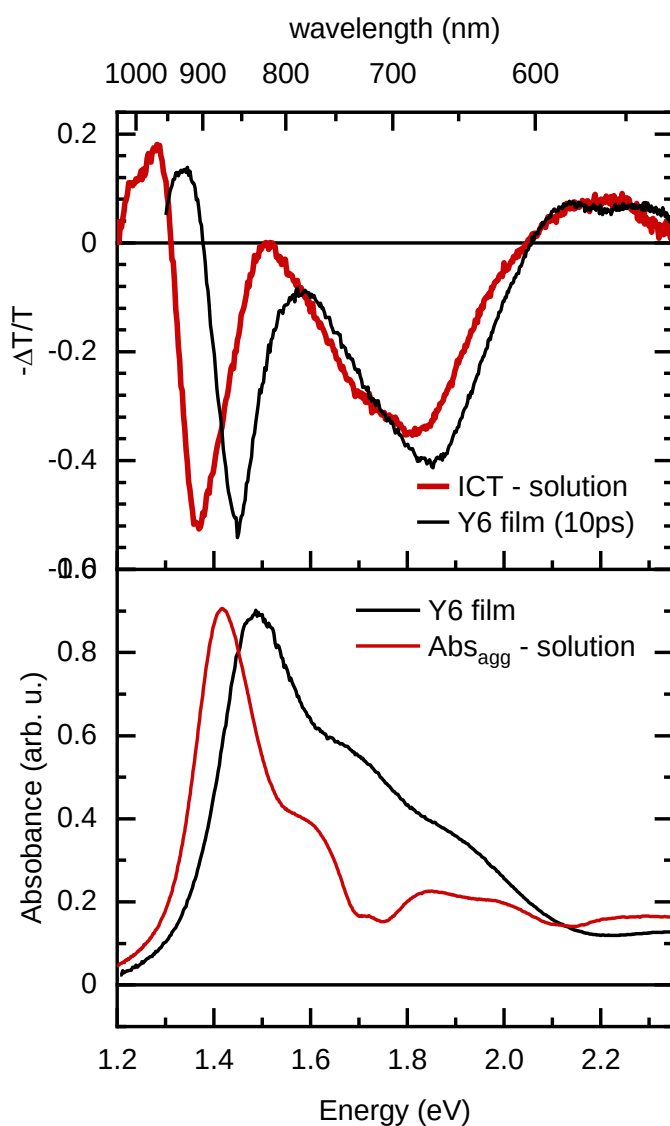


Figure S20: Top: Transient absorption spectrum of the ICT state of Y6 in solution, as shown and described in Figure 6b and the transient absorption spectrum of the neat Y6 film after 10 ps (410 nm pump) for comparison. Bottom: steady-state absorption of interacting Y6 in THF:CH (1:49) solution and the absorption of the neat Y6 film.

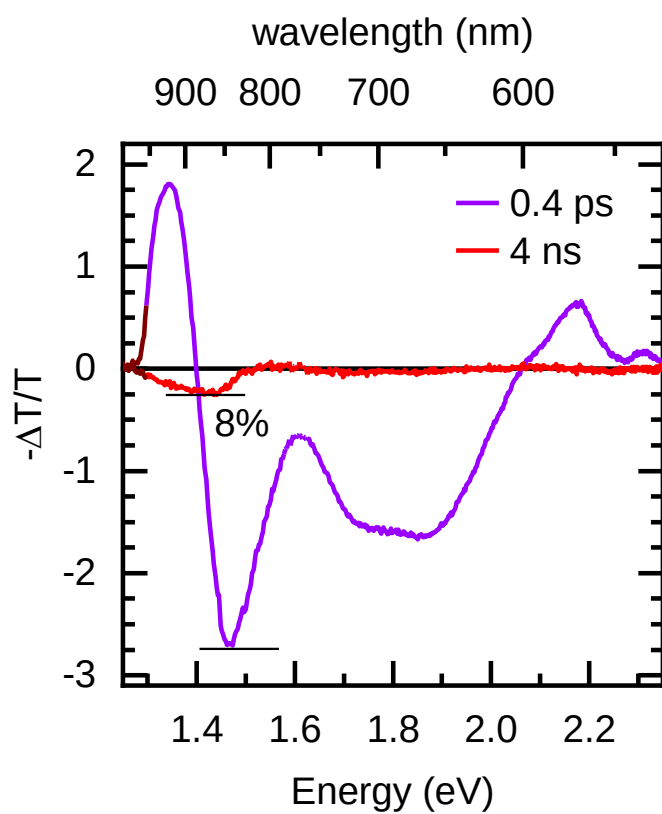


Figure S21: TA spectra of neat Y6 film with 410 nm at 0.4 ps and 4 ns delay. Comparing the GSB signal around 1.4 eV can be used to estimate the polaron yield to about 8 %.

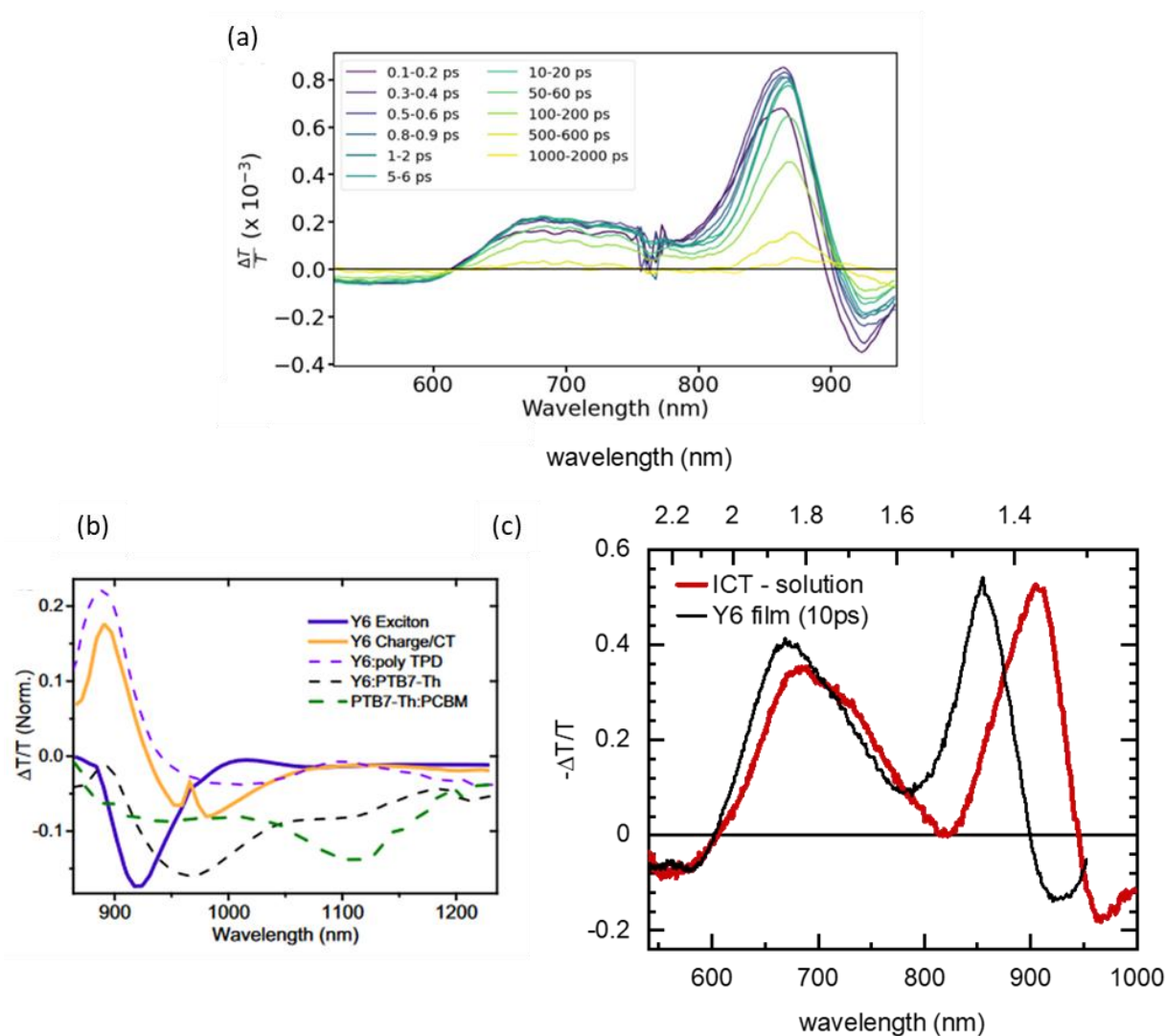


Figure S22: Comparison of TA spectra of Y6 films from (a) Giannini et al.^[1] (licensed under CC BY 4.0) and (b) Price et al.^[2] (licensed under CC BY 4.0) with (c) our TA spectra of ICT species in solution and the TA spectrum of the film after 10 ps.

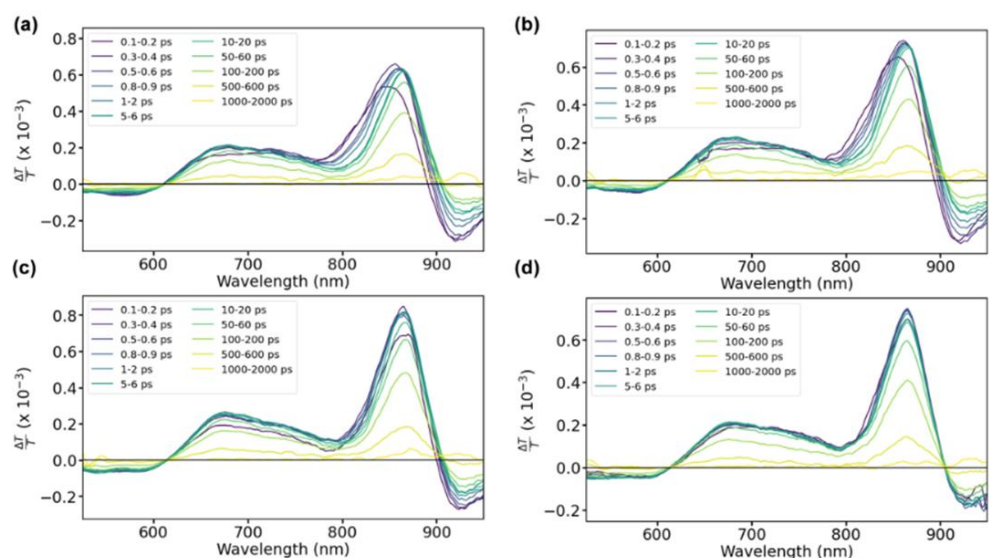


FIG. 5

Excitation-dependent Y6 100 wt% thin-film visible probe ps-TAS spectra at (a) fluence = $2.26 \mu\text{J cm}^{-2}$ ($\lambda_{\text{pump}} = 500 \text{ nm}$), (b) fluence = $1.38 \mu\text{J cm}^{-2}$ ($\lambda_{\text{pump}} = 650 \text{ nm}$), (c) fluence = $0.98 \mu\text{J cm}^{-2}$ ($\lambda_{\text{pump}} = 870 \text{ nm}$), (d) fluence = $19.5 \mu\text{J cm}^{-2}$ ($\lambda_{\text{pump}} = 950 \text{ nm}$).

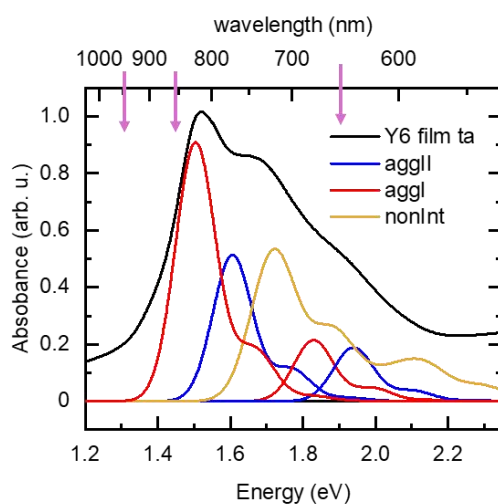


Figure S23: Pump-wavelength dependent TA spectra of neat Y6 film from Giannini et al.^[1] (licensed under CC BY 4.0) Comparison with different the absorption attributed to aggregates and non-interacting phase in a Y6 film from Kroh et al.^[3] (licensed under CC BY 4.0)

9 Conclusion and Outlook

This thesis investigated how molecular aggregation and intermolecular coupling govern the optoelectronic properties of the state-of-the-art OPV material system PM6:Y6. By combining steady-state and transient absorption spectroscopy, energy-resolved electrochemical impedance spectroscopy, and Franck-Condon analysis, I systematically disentangled and identified the key spectral signatures, energetic landscape, and exciton and charge-generation dynamics associated with interacting and non-interacting molecules. These insights clarify the role of intermolecular interactions in defining the optoelectronic properties of prototypical donor-acceptor systems.

In Chapter 6, I identified the characteristic spectral fingerprints of intermolecular coupling in Y6, its close derivative N4, and the donor PM6 in dilute solution. Multiple aggregate conformations of the Y-type acceptors were resolved and shown to coexist in both neat and blend films. A detailed Franck-Condon analysis enabled quantitative spectral deconvolution of interacting and non-interacting molecular phases in neat and blend films. To the best of my knowledge, this was the first spectroscopic deconvolution in Y6-based films. These results demonstrate that the nature and amount of aggregates in Y-type acceptors are highly sensitive to side-chain configurations and thermal post-treatment. Moreover, PM6 already exhibits pronounced aggregation in common processing solvents at room temperature, which must be considered in the context of film formation and morphology control. The developed deconvolution approach thus provides a powerful spectroscopic tool to directly probe morphological composition, which influences the energetic landscape and exciton dynamics in organic semiconductors.

Chapter 7 expanded these insights by investigating the impact of aggregation on the energetic landscape and the binding energy of CT states in PM6:Y6 blends using ER-EIS to determine the DOS distributions for the HOMO and LUMO levels. A remarkably low CT binding energy of approximately 150 meV was found, attributed to hole delocalization along the PM6 backbone and electron delocalization across multiple Y6 molecules within aggregates. The results further highlight the distinction between spectroscopically determined CT binding energies and the thermal activation energies relevant for photocurrent generation.

In Chapter 8, transient absorption spectroscopy probing the non-interacting and interacting Y6 domains separately in dilute solution, allowed the analysis of their intrinsic exciton kinetics without exciton energy transfer from one phase to another. By correlating transient absorption spectra with steady-state absorption and PL, the distinct spectral signatures of both phases were clearly identified and assigned. The unambiguous spectral separation resolves long-standing ambiguities in interpretation of transient absorption data of Y6-based films, where the coexistence of multiple morphological phases was often overlooked or insufficiently accounted for.

The exciton dynamics of the two phases differ fundamentally. Interacting Y6 exhibits ultrafast exciton decay dominated by singlet-singlet annihilation, with lifetimes ranging from 30-200 fs depending on the pump fluence. In contrast, non-interacting Y6 shows a fluence-independent monoexponential decay of approximately 1 ns. At longer delay times, a persistent spectral signature is observed and assigned to a polaronic state residing on interacting Y6. These findings support an ultrafast charge-separation mechanism consistent with Onsager-like autoionization, enabled by exciton delocalization across several Y6 molecules. The excess energy required to overcome the Coulomb barrier can originate either from the SSA process or from direct excitation with high-energy photons. Despite this pathway, the overall polaron yield remains moderate at around 8%, comparable to values reported for other organic semiconductors, which contradicts current interpretations of high-efficient exciton dissociation. Our results highlight the importance to consider both interacting and non interacting Y6 molecules to obtain a complete understanding of charge generation. This consideration is especially critical in thin films, where rapid energy transfer between these species can occur. The necessity to take into account both aggregated and non-aggregated molecules extends beyond Y6 to a broader class of rigid donor-acceptor compounds, which are prone to aggregation yet widely used in organic solar cells.

Beyond the spectroscopic insights gained in the individual chapters, this thesis demonstrates that the optoelectronic performance of PM6:Y6 is fundamentally dictated by its nanoscale morphology. The balance between aggregated and non-aggregated chromophores, their packing motifs, and their spatial arrangement collectively shape the exciton kinetics and charge generation pathways. Crucially, these functional properties do not arise from the molecular structures alone but from the specific molecular organization established during solution processing. Consequently, parameters such as solvent environment, drying kinetics, and thermal annealing become important tuning points for aggregation behavior and, ultimately, device efficiency. The findings of this work therefore underscore that morphology control is as crucial as molecular design in the development of high-performance organic semiconductors.

Overall, this work provides a comprehensive spectroscopic framework to distinguish and characterize the signatures, characteristics and kinetics of non-interacting and interacting chromophores in PM6:Y6. This distinction is particularly relevant for solution-processed OPV films, which inherently exhibit a heterogeneous morphology composed of tightly packed, interacting domains and loosely packed, amorphous regions. The ability to disentangle these coexisting phases enables a more accurate interpretation of exciton and charge-generation pathways and offers a methodology generalizable for studying structure-function relationships in solution-processed organic semiconductors.

Outlook

The spectral assignment and deconvolution techniques developed in this thesis open new pathways for disentangling overlapping kinetic processes in transient absorption spectra of complex organic semiconductor systems. Applying these methods to systems with controlled aggregation or intentionally amorphous morphology will provide insight into how distinct aggregate conformations influence energy-level alignment and charge generation efficiency.

Beyond PM6:Y6, the presented experimental and analytical approaches in this thesis are trans-

ferable to other organic semiconductors, including non-OPV applications. By linking molecular packing motifs to optoelectronic performance, these insights can contribute to the formulation of design rules for next-generation high-efficiency organic semiconductors.

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