

What controls triplet exciton transfer in organic semiconductors?

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Dexter-type triplet transfer is a phenomenon that is ubiquitous in the field of molecular electronics, and that takes place at the interface of chemistry, physics and biology. It may be considered as a correlated transfer of two charges, and thus, models originally developed for charge transfer may be applied to describe triplet transfer. In dilute fluid solutions, triplet transfer from a donor to an acceptor is well-understood and it has been described in terms of Marcus theory, *i.e.* taking into account distortions in the molecule and its surroundings. In amorphous thin films, that are used for organic semiconductor applications, the effects of energetic disorder prevail, and they need to be considered for an appropriate description of triplet energy transfer. We present here an overview on recent experimental and theoretical work concerning a unified description of triplet energy transfer.

Introduction

Organic semiconductors combine the opto-electronic properties of a semiconductor with the mechanical properties of a plastic. The ability to absorb light, emit light and to transport charges is united with material parameters such as

flexibility, light weight and robustness and the advantages of solution or vapor processability. This opens the path to both new fabrication technologies for semiconductor devices such as ink-jet printing, vapor-jet printing or reel-to-reel coating, and to novel applications.¹ For example, ultra-thin displays based on organic light-emitting diodes (OLEDs) or very thin, robust E-readers employing organic field-effect transistors (OFETs) are already commercially available, while

possible products such as lighting windows, lighting wallpaper and flexible solar cell sheets are being currently examined by industry. On the route to applications, some of the general ideas and concepts for semiconductor applications are inspired from the long and successful tradition of inorganic semiconductors. However, in order to correctly interpret, predict and improve opto-electronic behavior in devices like OLEDs, organic solar cells and OFETs,

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on charge transport and on the spectroscopy of conjugated polymers.

one needs to be aware of some of the fundamental differences in the underlying physics between an inorganic crystalline semiconductor and an amorphous film of an organic semiconductor.

In a semiconductor such as crystalline silicon, atomic orbitals are strongly coupled by covalent interactions resulting in wide bands that delocalize over the entire crystal and that support a band transport of charges. In contrast, amorphous films of molecular or polymeric organic semiconductors are held together by weak van der Waals interactions that couple the molecular orbitals of neighboring sites only weakly. In addition, a molecule distorts when a charge is placed on it, and this vibronic coupling alters its energy. The combination of weak electronic coupling between molecules, strong vibronic coupling on the molecule and the energetic disorder inherent to an amorphous film results in localized molecular orbitals from which transport can only proceed by hopping. This is even the case along a chain of a non-crystalline semiconducting polymer, where orbital delocalization due to the stronger electronic coupling between repeat units is limited by disorder.

A further significant difference between inorganic and organic semiconductors consists in the polarizability of the orbitals. In a crystalline inorganic semiconductor, an additional positive or negative charge carrier is screened effectively by an easy readjustment of the surrounding charge density. Quantitatively, this is expressed through a high dielectric constant of about 12–13. The more localized orbitals in an organic semiconductor result in a much smaller dielectric constant of 3–4, so that the coulomb attraction from an additional charge carrier is reduced less. As a consequence, positive and negative charge carriers in organic semiconductors form strongly bound electron–hole pairs, *i.e.* excitons, where the two charge carriers are coulombically bound with a binding energy in the range of 0.4–1.0 eV,² and where their spin-parallel and spin-antiparallel combinations are energetically separated by an exchange energy in the same range, *i.e.* 0.4–1.0 eV.^{3–5} These excitons are the dominant species formed when light is absorbed, for example after illumination of an organic solar cell, or when electrons and holes combine after

injection from electrodes into the semiconductor of an OLED. The photo-physics of excitons therefore governs the device performance. In contrast in a crystalline bulk inorganic semiconductor, excitons are of little significance to applications, since the high dielectric screening in inorganic semiconductor reduces their binding and exchange energy to values in the range of a few meV, which is less or equal to the thermal energy at room temperature and implies that bound electron–hole pairs do not exist at room temperature.

So, in contrast to the band transport of free charge carriers that underlies the traditional textbook semiconductor physics, organic semiconductors are characterized by an incoherent hopping transport of charges and excitons. In terms of the molecular orbitals, an exciton can be considered comprising essentially an additional electron in the lowest unoccupied molecular orbital (LUMO) and only one (instead of two) electron in the highest occupied molecular orbital (HOMO) (Fig. 1).⁶ If the spins of the two electrons are antiparallel, radiative recombination from this spin-singlet excited state to the spin-singlet ground state can take place readily giving rise to fluorescence. In contrast, emission from the spin parallel combination can only take place as phosphorescence when a spin-flip occurs. This can happen due to a quantum-mechanical perturbation such as the spin–orbit coupling induced by heavy metals or, to a lesser degree, by out-of-plane vibrations. The spin parallel

combination can occur in three quantum-mechanically possible orientations making this a triplet state. While in semiconducting polymers, recombination of charges in an OLED to form an exciton may take place with different efficiencies for the spin singlet and spin triplet combination,^{7,8} in molecular films, exciton formation takes place without consideration of their respective spin, yielding three times as many triplet excitons than singlet excitons.^{3,9} To enable strong room temperature phosphorescence from this high fraction of triplet states, organometallic complexes are typically employed as emitting semiconductors, usually in combination with organic molecules particularly suited for charge transport.^{10–12} If such phosphorescent OLEDs are to be utilized for the desired lighting applications outlined above, high excitation densities are required. The associated high triplet density, however, causes some of these triplets to diffuse into other triplets or charges, which quenches the emission and thus reduces the overall power conversion efficiency of the OLED.^{13,14} To prevent this and to enable highly efficient OLEDs, the parameters governing triplet diffusion therefore need to be understood. Properly managed, the diffusion of triplets can even be employed for the non-resonant upconversion of low energy incident red light into high energy blue emission.^{15–17} This triplet upconversion may be used towards efficient fluorescent OLEDs or for biomedical applications such as photodynamic therapy.

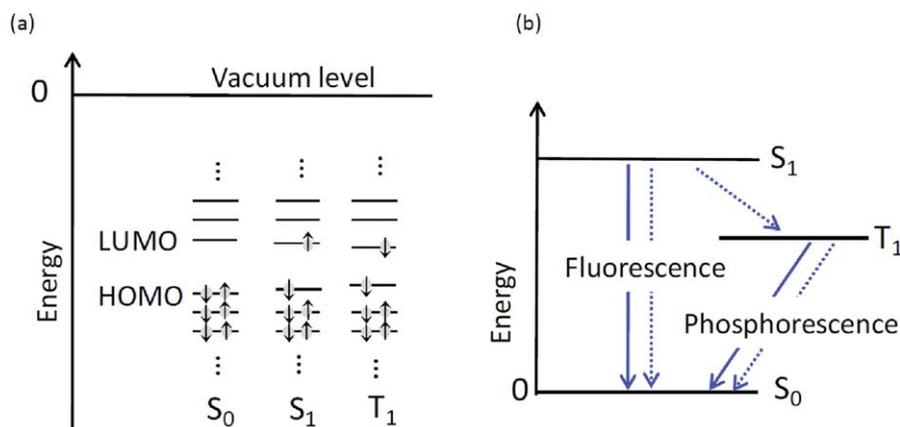


Fig. 1 Schematic of the first singlet and triplet excited states S_1 and T_1 in terms of (a) the configuration of molecular orbitals, with arrows indicating the electron spin, and (b) the resulting S_1 and T_1 excited state energies relative to the ground state S_0 . The radiative and non-radiative decay paths are indicated as solid and dotted line, respectively. In (a), we only display one representative spin configuration for each of the excited states.

Models for electron transfer

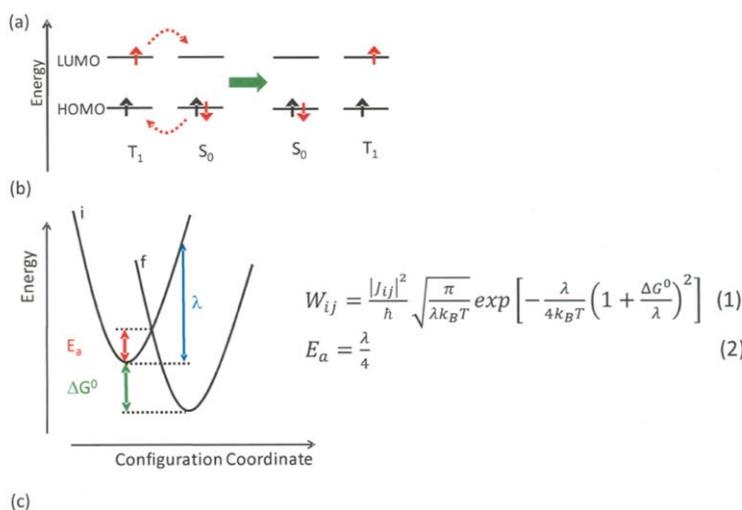
Triplet transfer is well understood for individual molecules in solutions, and it is commonly treated as quantum-mechanical Dexter-type energy transfer. However, in order to advance the solid state applications mentioned above, we need to understand how triplet exciton diffusion depends on parameters of the amorphous molecular film. These

parameters pertain to the above mentioned vibronic coupling and its dependence on oligomer length, the energetic disorder inherent to amorphous films, and the coupling between molecules and along polymer chains mediated by wavefunction overlap. To this end, it is useful to consider Dexter-type triplet transfer as a correlated transfer of two electrons, and then to apply and adapt concepts that have proven successful to

describe electron transfer in organic molecules. One such model that has found widespread application in particular in the field of chemistry and biology, and whose development was awarded with a Nobel prize is Marcus' theory.^{18–20} Concepts and equations relating to triplet energy transfer are summarized in Fig. 2.

The basic idea of classical Marcus theory for electron transfer between identical molecules can be summarized as follows: the system as a whole, *i.e.* the electron donating molecule, the accepting molecule and the solvent, proceeds from configurations near the donor equilibrium to the acceptor equilibrium. The associated difference in potential energy is the reorganization energy λ .^{20–22} Electron transfer occurs at the intersection for both potential energy curves. Thermal fluctuations are needed for the system to reach the intersection. Fluctuations in the vibrational coordinates need to be considered when equilibrium bond lengths or angles change between the initial and final state of donor or acceptor. In addition, fluctuations in the orientational coordinates of the solvent molecules are particularly important in polar solvents. The rate constant for electron transfer then depends on the probability of reaching the intersection (giving rise to an exponential factor with an activation energy), a frequency for crossing attempts (*e.g.* collision frequency), and the probability for crossing the surface (such as the transmission coefficient). In a semi-classical approach, starting with Fermi's golden rule, the collision frequency and transmission coefficient are implicitly included in the electronic coupling J .

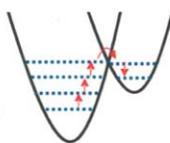
When donor and acceptor differ in equilibrium energy, this needs to be included in the activation energy through the term ΔG^0 (see Fig. 2b). While highly successful in many cases, the classical approach is somewhat oversimplified. In particular for large energy differences between the initial and final site and at low temperatures, a quantum chemical approach, explicitly including high-frequency modes as pioneered by Levich and Jortner,^{23–25} is needed to give quantitative results that are in good agreement with experiments.^{26–28} The corresponding mathematical equation for the rate constant of electron transfer is often referred to as Marcus–Levich–Jortner expression.^{20,21}



High Temperature - Multi-phonon hopping → „Marcus“ expression

$$W_{ij} = \frac{J_0^2 \exp(-2\frac{r_{ij}}{L})}{h} \sqrt{\frac{\pi}{4E_a k_B T}} \exp\left[-\frac{E_a}{k_B T} - \frac{\epsilon_j - \epsilon_i}{2k_B T} - \frac{(\epsilon_j - \epsilon_i)^2}{16E_a k_B T}\right] \quad (3a)$$

$$W_e = \frac{J_0^2 \exp(-2\frac{a}{L})}{h} \sqrt{\frac{\pi}{4E_a k_B T}} \exp\left[-\frac{E_a}{k_B T} - \frac{1}{8}\left(\frac{\sigma}{k_B T}\right)^2\right] \quad (4a)$$



Low Temperature – Single phonon-assisted tunneling → „Miller-Abrahams“ expression

$$W_{ij} = \nu_0 \exp\left(-2\frac{r_{ij}}{L}\right) \times \begin{cases} \exp\left(-\frac{\epsilon_j - \epsilon_i}{k_B T}\right), & \epsilon_j \geq \epsilon_i \\ 1, & \epsilon_j < \epsilon_i \end{cases} \quad (3b)$$

$$W_e = \nu_0 \exp\left(-2\frac{a}{L}\right) \exp\left[-\frac{1}{2}\left(\frac{\sigma}{k_B T}\right)^2\right] \quad (4b)$$

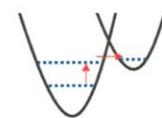


Fig. 2 Dexter-type triplet energy transfer. (a) Representation of the triplet transfer mechanism as a correlated electron transfer. (b) Representation of the triplet transfer as a Marcus-type process, showing the potential energy of the entire system before (i) and after (f) the transfer as a function of generalized configuration coordinates. Transfer requires an activation by $E_a = \lambda/4$ due to the geometric reorganization energy λ needed by the system. An energy difference ΔG^0 between the equilibrium potential energy before and after transfer also affects the transfer rate W_{ij} from molecule i to molecule j , given in eqn (1). J_{ij} is the electronic coupling between the two molecules i and j . (c) Energy transfer rates W_{ij} (eqn (3)) in a representation of discrete molecular energies ϵ_i, ϵ_j and, as W_e (eqn (4)), in a representation only referring to the variance σ of the distribution of the molecular energies. In the high temperature limit, for $\hbar\omega \ll k_B T$, eqn (3a) and (4a) describe a Marcus-type process where thermal excitation of low-energy vibrations makes crossing at the intersection possible, as illustrated. For $k_B T \ll \hbar\omega$, a tunneling process between the initial and final potential energy curves occurs, with a single vibration providing the energy difference between the potential energy minima, yielding Miller–Abrahams-type eqn (3b) and (4b). J_0 and ν_0 relate to the electronic coupling, r_{ij} and a relate to intermolecular distance.

To a scientist with a background in physics, classical Marcus theory appears mathematically as the high-temperature limit of Holstein's small polaron theory.^{29,30} In contrast to Marcus, who treated electron transfer between individual molecules in solution, Holstein considered electron transfer in a molecular crystal. The presence of a negative charge distorts the crystal lattice in its immediate vicinity, rendering the electron into a polaron, *i.e.* a charge that drags a lattice distortion with it. Holstein found polaron transport at high temperature to proceed by a temperature-activated hopping process, akin to the Marcus transfer process, while at low temperature, when lattice vibrations (phonons) are no longer available to promote the hopping, a tunneling process and band-like transport occur. High and low temperatures always refer to whether thermal energy is large or small compared to vibrational energies. When the crystal is not perfect, and in particular for amorphous films, the energy levels of adjacent molecules differ due to spatial fluctuations in the dielectric polarization of the surrounding. This energetic disorder prevents the formation of a band, and the tunneling process requires some activation energy, usually provided by a single phonon. The corresponding modified low-temperature expression is also known as Miller–Abrahams-equation. The equations based on the Holstein small polaron model are listed and illustrated in Fig. 2c.

When analyzing the transport of charges in an amorphous film of organic semiconductor such as the molecular films use in an OLED, the contributions due to distortions (polaronic effects) were found to be of lesser importance, and the effects due to energetic disorder are largely controlling the transport.^{31–34} It is worth noting that electron transfer in amorphous films does not take place in either extreme regime of the Holstein small polaron model, *i.e.* dominated entirely by (high temperature) Marcus-like multiphonon hopping due to polaronic effects or dominated entirely by (low temperature) Miller–Abrahams-like single-phonon tunneling due to disorder. Rather, electron transfer in organic films seems to occur in an intermediate region comprising both effects, polaronic and disorder, yet with a stronger emphasis on

the disorder contribution. As we shall demonstrate later, the same comprehensive property applies to triplet transfer, albeit with a stronger weight on the polaronic part.

Triplet transfer as correlated electron transfer

Having detailed different approaches to electron transfer, we now turn to the description of triplet transfer as a correlated double-charge transfer.³⁵ Dominant contributions to such a transfer mechanism are provided by both a two-electron transfer between the triplet donating molecule and the triplet accepting molecule (“direct exciton resonance interaction”) and two equivalent one-electron transfer processes mediated by charge-transfer configurations (“through-configuration excitons resonance interactions”).³⁶ If the transfer of a triplet is approximated as a simultaneous transfer of two charges, the triplet transfer rate should be approximately equal to or, when the differences in molecular reorganization energy are taken into account, slightly smaller than the product of the transfer rates for the electron and hole comprising the exciton. This is indeed what is found experimentally. For example, for the organic host material CBP (4,4'-bis(*N*-carbazolyl)-2,2'-biphenyl) widely used in OLEDs, a charge diffusivity of about $3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ can be derived, consistent with a triplet diffusivity of $1.4 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$.³ Charge diffusion coefficients in organic molecular crystals also match with the values obtained for the diffusivity of triplets. These findings for amorphous films and crystals are consistent with earlier reports by Closs and coworkers for molecules in solution.^{37,38} They could also demonstrate that the rate for triplet transfer is roughly proportional to the product of the rate for electron transfer and hole transfer, provided that the differences in reorganization energy are taken into account.³⁸

When treating triplet transfer in a framework of double charge transfer, one needs to contemplate which charge transfer model is appropriate to the particular situation. Closs and coworkers considered donor molecules based on biphenyl or benzophenonyl combined *via* a spacer with naphthyl acceptor molecules in solution. They were able to

successfully model the dependence of the triplet transfer rate on the temperature and on the energy difference between donor and acceptor, by using the quantum mechanical Marcus–Levich–Jortner expression.^{26,27} Their investigations involve donors and acceptors with large energy differences comprising the Marcus inverted regime, where the quantum mechanical corrections become essential.²⁸ For thin films of an organometallic Pt-monomer and corresponding Pt-polymer (*trans*-[Pt(PBu₃)₂-C≡C-C₆H₄-C≡C-]_{*n*}) that show very little energetic disorder, Sudha Devi and coworkers found semiclassical Marcus theory sufficient to describe the temperature dependence of the triplet transfer rate in a satisfactory manner.³⁹ Due to the low energetic disorder of these particular compounds, donor and acceptor site energies could be treated as isoenergetic. A more general approach to the temperature dependent transfer rate that allows for a statistical variation between donor and acceptor energies was subsequently developed theoretically by Fishchuk on the basis of Holstein's theory and verified experimentally by Hoffmann *et al.*^{40,41} Hoffmann used a series of poly(*p*-phenylene) type polymers that were chemically modified to allow for different degrees of phenyl ring torsions, thus altering the degree of conformational freedom and associated energetic disorder while keeping the general nature of the chemical backbone. The three publications^{39–41} form a coherent entity that is complemented by a more detailed investigation on the effect of disorder on triplet diffusion.⁴²

In this body of work, *i.e.* ref. 39–41, the temperature dependence of the triplet transfer rate is monitored by measuring the triplet excited state lifetime. Radiative decay and intrinsic non-radiative decay by internal conversion are considered as largely temperature-independent. The triplet lifetime is taken to be affected only by temperature-activated diffusion to quenching sites such as other triplets or defects, so that the temperature-induced change in lifetime reflects the change in diffusion rate. The so-obtained temperature dependence for the triplet diffusion rate, shown in Fig. 3 for poly(*p*-phenylene) based polymers, is interpreted qualitatively in a Holstein/Marcus based picture. The weak temperature

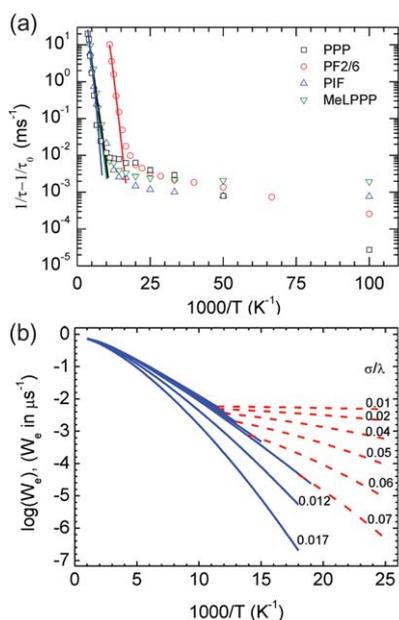


Fig. 3 The dependence of the triplet transfer rate on inverse temperature. (a) Experimentally measured triplet diffusion rate (in terms of the difference between the phosphorescence decay rates at 10 K and at the measurement temperature) for a series of poly(*p*-phenylene)-type polymers with increasing degree of energetic disorder from MeLPPP to PPP. The solid lines are fits to eqn (4a) in Fig. 2. After ref. 41. (b) Theoretically predicted triplet transfer rate for different values of energetic disorder σ compared to the molecular reorganization energy λ . The solid lines are based on simulations of eqn (4a) in Fig. 2, the dashed lines are based on eqn (4b). After ref. 40

dependence observed at cryogenic temperatures is attributed to a Miller–Abrahams like tunneling process, and the strongly temperature dependent diffusion observed above a transition temperature is assigned to a hopping process that is assisted by inter- or intramolecular vibrations.

The influence of molecular distortion

The work reported in ref. 39–41 introduces two novel aspects to the description of triplet energy transfer. First, it is shown that for a comprehensive description of triplet transfer, the effects of energetic disorder need to be included as will be portrayed further below. We take the variance σ of energy distribution for the triplet excited states as a quantitative measure for the degree of energetic

disorder. Second, it is demonstrated that the activation energy for triplet transfer above the transition temperature can be derived from an analysis of the phosphorescence spectrum. This activation energy (see eqn (4) in Fig. 2) comprises a contribution due to the change in the molecular geometry, *i.e.* the reorganization energy λ (with $\lambda = 4E_a$), and a contribution due to statistical differences in the energies of the initial and final sites, *i.e.* energetic disorder, expressed through the statistical variance σ . In rigid amorphous films, in contrast to solutions, contributions from changes in the polarization of the surrounding medium upon energy transfer tend to be comparatively small, and are therefore neglected. To understand the relationship between the molecular reorganization energy and the phosphorescence spectra, it is useful to consider a hypothetical set of molecules that are of identical energy (see Fig. 4). Molecule *i* will be initially in a triplet excited state, with an associated triplet excited state geometry, while all other molecules will be in a ground state geometry. After the transfer, molecule *i* has assumed the ground state geometry, while a triplet accepting molecule *j* will be in the triplet excited state geometry. The total reorganization energy needed for this process is thus the energy for one

molecule to get from a triplet excited state geometry to a ground state geometry, and *vice versa*. The same configurational change takes place after optical transitions, *i.e.* in the processes of phosphorescence and, hypothetically, absorption. For optical transitions, normal vibrational modes of high-energy efficiently promote the associated conformational change, and this is manifested in the vibrational structure of the absorption and emission band. The energy associated with the change in molecular geometry upon triplet transfer can be inferred when, for example, the phosphorescence is deconvoluted in the normal modes partaking in the optical transition through a so-called Franck–Condon analysis. For one molecule, the geometric relaxation energy is given by $E = \sum h\omega_i S_i$, where ω_i is the frequency of the normal mode *i*, and S_i the Huang–Rhys factor that is related to the intensity of the 0–*n* transition of that mode by $I_{0-n} = S^n e^{-S}/n!$. As two molecules are involved, a triplet donating one and a triplet accepting one, this needs to be doubled to obtain the entire reorganization energy λ .³⁹ When considering Fig. 2 for the case of isoenergetic transfer (*i.e.* $\Delta G^0 = 0$), and remembering the basic mathematics of a parabola, one notices that the activation energy due to the

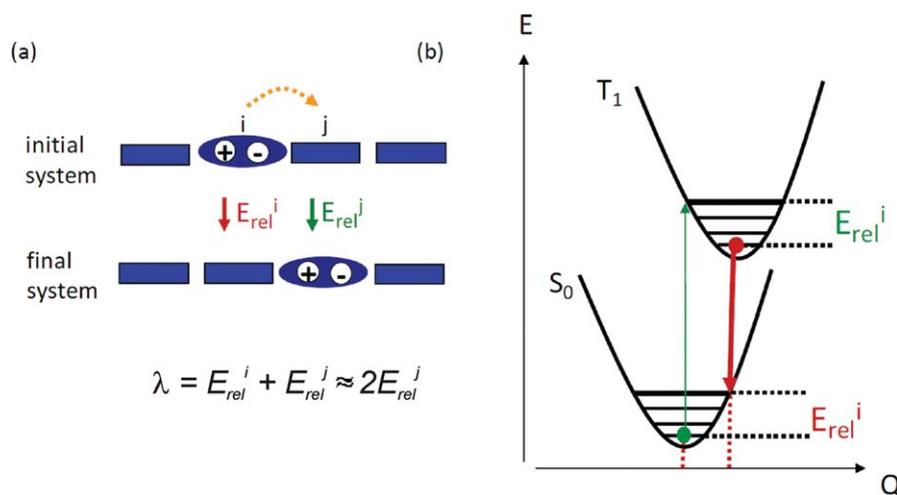


Fig. 4 Deriving the molecular reorganization energy λ for the triplet transfer process. (a) A system comprising four identical molecules, sketched as blue objects, with molecule *i* initially in the triplet excited state and thus in an excited state geometry. After the transfer of the triplet to molecule *j*, molecule *i* is in the ground state geometry while molecule *j* has assumed the excited state geometry. The total reorganization energy is composed of the relaxation energy E_{rel}^i associated with the change of molecule *i* from excited state geometry to ground state geometry, and of the energy E_{rel}^j for the inverse geometry change in molecule *j*. The same changes in geometry were to take place after vertical optical transitions. This is indicated in (b) which shows the potential energy of molecule *i* in the triplet excited state T_1 and the ground state S_0 as a function of configuration coordinates.

conformational change, *i.e.* the energy difference to the crossing point of both parabolas, is a quarter of the reorganization energy λ . The contribution of energetic disorder to the activation energy can also be inferred from the optical spectra. The variance σ is simply taken from the linewidth of the 0–0 vibrational transition. Due to the statistical nature of the energetic variation, the linewidth is broadened to a Gaussian shape, so that its full width half maximum (FWHM) relates to σ as $\text{FWHM} = 2\sqrt{2\ln(2)}\sigma$.

Experimentally, the activation energies thus derived from the analysis of the phosphorescence spectra have been found to be in good agreement with the values obtained from fitting the temperature dependence of the triplet diffusion rate. They were verified first for the Pt-monomer and Pt-polymer where disorder was neglected, and subsequently for the poly(*p*-phenylene) polymers and oligomers with variable degrees of disorder.^{39,41} This concurrence is remarkable, given that the overall approach is rather simple and can still be refined.

From a theoretical point of view it may be worthwhile to consider briefly whether the use of an optically derived reorganization energy is appropriate to describe the temperature dependence of the transfer process. The reorganization energy arises from a configurational change in the triplet donating molecule and the triplet accepting molecule upon energy transfer, *i.e.* a real change in bond lengths and angles. The quantity of the reorganization energy is derived from an analysis of the emission spectrum that is based on high-energy normal modes such as C=C stretching vibrations at about 1600 cm^{-1} (200 meV). However, we note that these are *not* the modes promoting the triplet transfer process. Only 10^{-4} to 10^{-5} of them are excited at room temperature. The more likely supply of the necessary energy is from low-energy modes that may be of intra- or intermolecular nature. For example, for poly(*p*-phenylene)-based polymers⁴¹ and for poly(phenylene ethynylene)-based polymers,^{43,44} the onset of temperature activated triplet transfer takes place around 100 K, corresponding to a thermal energy of 70 cm^{-1} . The frequencies for ring-torsional modes in poly(*p*-phenylene) oligomers from biphenyl to sexiphenyl have been observed through terahertz spectroscopy

by Johnston *et al.* in the range of 67.4–76.5 cm^{-1} ,⁴⁵ consistent with quantum chemical calculations by Karabunarliev that place them in the range of 61–84 cm^{-1} .⁴⁶ The promotion of triplet transfer along a polymer chain by modes like these low-energy ring-torsional modes is thus conceivable, in agreement with experimental results on electron transfer.²⁸ Overall, the activation energies found experimentally for triplet transfer are in the range of 50–150 meV (400–1200 cm^{-1}), while the available thermal energy ranges from 25 meV at room temperature to 9 meV at 100 K (200–70 cm^{-1}). Thus, while the high-frequency modes visible in the phosphorescent spectra provide a convenient means to estimate the activation energy needed for triplet transfer, we consider that this energy is actually provided through thermal excitation of low-energy vibrations, at least when considering triplet transfer that is only weakly exoergic.

Estimating the activation energy for triplet transfer from the size of the vibrational sidebands in the optical spectra is convenient. Taking a phosphorescence spectrum and looking at the respective size of the vibrational sidepeaks compared to the 0–0 vibrational transition is a relatively fast method, even suited for materials screening, in contrast to a temperature dependent measurement of triplet lifetimes. This approach suggests that triplet transfer between rigid molecules requires less activation energy than between flexible ones. For comparison, when considering electron transfer in weakly exoergic donor–spacer–acceptor type molecules, Miller, Closs and coworkers found an 8-fold increase in the electron transfer rate when replacing 4-biphenyl as donor with the more rigid 2-(9,9'-dimethyl)fluorene.²⁸ Furthermore, in comparison to oligomers, the geometric distortion associated with a triplet state on a polymer is small due to the larger excited state wavefunction delocalization. Consistent with this, the activation energy for polymers is lower than in oligomers.⁴¹ In addition, the electronic coupling for the triplet transfer is strong along a polymer chain due to good wavefunction overlap, so a low activation energy combines with strong coupling. This is not the case between short oligomers. The implication of this for the design of efficient OLEDs is

obvious. If triplet diffusion is to be suppressed, as desired for phosphorescent OLEDs, flexible molecules and short oligomers are to be used. In contrast if one aims at a strong triplet diffusion as for triplet upconversion applications, rigid polymers are a suitable choice. For charge transfer, it is not possible to experimentally determine the difference in molecular geometry before and after transfer by optical means. Incidentally, this has not refrained the theoretician Hopfield to employ the fictional spectral distribution associated with an electron removal or addition process to demonstrate the analogy between the mathematical treatment of Förster-type energy transfer and charge transfer.⁴⁷

The influence of energetic disorder

We now consider in more detail the second novel aspect that recent work introduced to the description of triplet transfer.⁴⁰ In the first paper³⁹ out of the series on “Triplet energy transfer in conjugated polymers”,^{39–41} Sudha Devi and coworkers could afford to neglect any effects due to energetic disorder since the compounds investigated had very narrow linewidth, implying low disorder. However, as mentioned in the Introduction and detailed elsewhere,³ a statistical variation of ground and excited state energies is a property inherent to amorphous films of organic semiconductors, and this energetic disorder needs to be included for a comprehensive description of its photophysical processes. Expressions allowing for different energies of initial and final site are of course already available by Marcus or Holstein, yet they involve the exact energies of each molecule involved. This is of little practical value for a macroscopic amorphous film where only the statistical distribution of molecular energies may be determined experimentally. Consequently, in the second paper of the series,⁴⁰ Fishchuk used a mean field approach^{48,49} to transform Emin’s formulation⁵⁰ of Holstein’s equations,³⁰ given as eqn (3) in Fig. 2, from an explicit dependence on site energies ϵ to a dependence on the variance σ of an energy distribution, displayed as eqn (4) in Fig. 2.

The beauty of theory is that it allows straightforward access to parameters that

are available through experiment only with significant effort. In the case of triplet transfer, the dependence of the transfer rate on the relative influences of geometric distortion and energetic disorder can now be studied. The key result is displayed in Fig. 3, where the temperature-dependent triplet transfer rates are shown for different values of the reorganization energy λ and the disorder parameter σ . In the high temperature regime, where transfer proceeds by multiphonon activated hopping à la Marcus, the effects of disorder consist merely in a small increase of the activation energy, and an accompanied slight deviation from the linear slope in the Arrhenius plot. This is confirmed experimentally in the third paper of the series, where the contribution to the activation energy by molecular distortion and energetic disorder are determined explicitly for the series of poly(*p*-phenylene)-derivatives.⁴¹ For small oligomers, where configurational changes are large upon excitation, disorder contributes less than 10% to the total room temperature activation energy. Geometric distortions are reduced while disorder increases in polymers, and so the disorder contribution to the room temperature triplet activation energy raises up to 35% for the most disordered polymer investigated.

Since the disorder contribution to the effective activation energy is inversely proportional to temperature, it becomes more significant when temperatures are lowered. In fact, in the low temperature regime, where transfer takes place by tunneling between the potential energy curves instead of crossing at their intersection, the effects of disorder are pronounced. Tunneling cannot occur when the initial site has a lower ground state energy than the final one, and a thermally excited vibration is essential to overcome this energy difference. As just one vibration is usually sufficient, this is referred to as single-phonon assisted tunneling, single phonon hopping or Miller–Abrahams-tunneling.⁵¹ Accordingly, Fishchuk's expression predicts a strong temperature dependence of the tunneling process as a consequence of energetic disorder. When the variance of the energetic disorder reaches about 0.07 of the reorganization energy, the regimes of multiphonon hopping and single-phonon assisted tunneling can no longer

be discerned. The transition from the tunneling to the hopping regime, predicted by Holstein for small polaron transfer, is difficult to detect for charge transfer in amorphous organic films. The result by Fishchuk clarifies why this cannot be observed within the temperature range relevant for charge transfer studies. For a charge in organic semiconductors such as poly(fluorene), typical values for the disorder have been determined to be around 130 meV while, on the basis of mobility measurements, an upper limit of 200 meV has been estimated for the reorganization energy λ . The low molecular distortion results from the fact that the wavefunction of a single charge delocalizes well over the entire molecule or a significant part of a polymer backbone. The high disorder arises since a charge reacts sensitively to variations in the dielectric polarization of its surroundings. In contrast, the energy of a molecule in a charge-neutral triplet excited state varies less with the spatial fluctuations in the polarization of its environment, and the small extent of the electron–hole pair comprising the triplet enforces strong molecular distortions. The different dependences of triplet transfer and charge transfer on the polarization of the surrounding have already been commented on in the 1960s by Singh and coworkers⁵² and later on by Closs and coworkers,³⁷ who, for this very reason, advocated the study of triplet transfer as a preferred way to learn about electronic coupling in electron transfer.

Experimentally, the strong dependence of triplet transfer on disorder at low temperatures is manifested in several ways. For example, when the temperature is lowered from room temperature to 10 K, the steady-state phosphorescence from a film of disordered semiconductor polymers first shifts to lower energies into the red spectral range until it moves back to higher energies in the blue.^{42,53} The initial bathochromic shift is well understood and documented.⁵⁴ In an amorphous film of organic semiconductors, excited states diffuse during their lifetime, thus sampling a number of molecules with a statistically broadened energy distribution. Hopping takes place in an energetic downward direction and, by thermal excitation, also in an energetic upward direction. In thermal equilibrium, the occupation of molecular sites will be

governed by a Boltzmann statistics, resulting in a temperature-dependent equilibrium energy for the excitations in the amorphous film. The hypsochromic shift observed for triplet diffusion in disordered films at lower temperatures, however, portrays an aspect that is a clear signature of disorder. It can be explained by considering that molecules with an energy corresponding to the very low-energy thermal equilibrium value may be well spread out spatially, as they form the tail of the statistical distribution. Diffusion to such molecules will therefore require detours *via* sites of higher energy. Triplet diffusion at low temperature now proceeds by thermally activated tunneling between immediately neighboring molecules (in contrast to singlet exciton diffusion where an individual step can bridge over several molecules). When the variance of the energy distribution is large, some diffusion steps may require activation energies that become increasingly improbable as the temperature is lowered. Consequently, the energetic relaxation process is kinetically frozen, even though the energetically lower equilibrium value is not reached, and the triplet excited state emits from the higher energy molecule on which it became stuck. Mathematically speaking, the excitation gets trapped in a local energy minimum instead of reaching the global minimum due to a lack of activation energy to overcome the barrier separating them.^{55,56} With reducing temperature, this occurs at increasingly higher energy sites, resulting in the observed hypsochromic shift.⁴²

At low temperature, the distribution of energetic sites accessible to a triplet exciton is thus smaller than the entire energetic distribution that is present in the film. When comparing the temperature dependence of the triplet diffusion rate predicted by Fishchuk with the experimentally measured values in the low temperature regime (Fig. 3), one observes a qualitative agreement, confirming the general approach. The more disordered the polymer, the steeper and less Arrhenius-like is the slope. However, when fitting the observed data quantitatively to the respective equation by Fishchuk (eqn (4b) in Fig. 2), one obtains a value for the disorder parameter σ that is far below the one obtained from the fit in the high-temperature regime or from the optical spectra. This is a result of the fact that, at

low temperature, thermal equilibrium is not reached so that the triplet can only access a more narrow energy distribution. The theory by Fishchuk presumes thermal equilibrium is reached (*i.e.* the triplets arrive at the very low-energy sites of the distribution) and therefore predicts a much lower diffusion rate. The formulation of a suitable non-equilibrium theory would be a worthwhile challenge for a gifted theoretician.

Rothe and Monkman studied this phenomenon of frustrated triplet transfer in a complementary way.⁵⁷ Instead of considering temperature dependent steady state spectra, they employed time dependent phosphorescence spectroscopy. The fact that triplet excitations tend to migrate towards the states at the bottom of the energetic distribution implies that the emission spectra must bear out a bathochromic shift also as a function of time. However, this shift is slowed down if the energetic relaxation process is kinetically hindered, *i.e.* frustrated, at low temperatures. Experiments on the phosphorescence of poly(fluorene) are in accordance with earlier theory by Movaghar *et al.* applied to glassy benzophenone,⁵⁶ and prove that the phenomenon is disorder controlled.

Summary and outlook

Overall, our understanding of what controls the process of triplet transfer has grown significantly over the last few years. Recent work has given some insight into the underlying photophysics.^{39–42} Analogous to earlier approaches by Closs and coworkers on molecules in solution,^{26,37,38} triplet transfer in amorphous organic semiconductor films has been described as a correlated electron transfer. A model capturing the essential physics has been developed on the basis of Holstein's small polaron theory.⁴⁰ This model includes both effects due to changes in the molecular geometry upon triplet transfer and effects that arise from the energy distribution of molecular states in an amorphous solid. It was demonstrated that, in contrast to charge transfer, the activation energy for triplet transfer can be inferred from an analysis of the phosphorescence spectra.^{39,41} At high temperatures, triplet transfer was found to proceed by a multiphonon

hopping process where the activation energy arises largely from the changes in molecular configurations. In contrast at low temperatures, triplets were found to transfer by a single-phonon assisted tunneling process. This regime is governed by the effects of energetic disorder.⁴² The model developed can explain why the transition from tunneling to hopping can be observed with ease for triplets yet not for charges. On a more practical note, the model allows to predict which materials will have high or low activation energies for triplet diffusion, and this will help the design of efficient organic semiconductor devices such as OLEDs for lighting application.

While this is a significant advance in our comprehension of triplet transfer in amorphous solids, there are still challenges remaining. The approach taken is phenomenological and based on a semiclassical picture. The experimental data suggest this works with reasonable quantitative agreement in the high-temperature regime for the case where energy differences between initial and final site are small. Quantitative though not qualitative discrepancies between the theoretical model and experimental data are found in the low-temperature regime. This has been attributed to the fact that the theory is formulated for a thermal equilibrium situation that is not reached experimentally at low temperatures. A suitable non-equilibrium theory for this range is clearly desirable.

Furthermore, in the high-temperature regime, the classical Marcus-type expression used may no longer be sufficient when there are large energy differences involved in the transfer. Deviations between the semiclassical and the quantum-mechanical treatment are small when initial and final sites have the same energy, yet they become significant for strongly exoergic processes, for example in the Marcus inverted regime.^{27,28} This can be the case when considering triplet transfer in an OLED that proceeds from a charge-transporting host molecule to a guest emitter complex.

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References

- 1 S. R. Forrest, *Nature*, 2004, **428**, 911.
- 2 H. Bässler, M. Gailberger, R. F. Mahrt, J. M. Oberski and S. Weiser, *Synth. Met.*, 1992, **49–50**, 341.
- 3 A. Köhler and H. Bässler, *Mater. Sci. Eng., R*, 2009, **66**, 71–109.
- 4 G. D. Scholes and G. Rumbles, *Nat. Mater.*, 2006, **5**, 683.
- 5 To be technically precise, the energetic separation of 0.4–1.0 eV between the spin-parallel and spin-antiparallel electron combination corresponds to twice the value of the exchange integral.
- 6 This simple picture of one-electron states is of course only an approximation. Due to the low dielectric constant in organic semiconductors, electron correlation effects such as configuration interactions are significant and need to be considered for a more realistic and quantitative quantum mechanical treatment. However, to capture the general idea, the picture of an exciton consisting of essentially an additional electron in the LUMO and a missing one in the HOMO is appropriate.
- 7 J. S. Wilson, A. S. Dhoot, A. J. A. B. Seeley, M. S. Khan, A. Köhler and R. H. Friend, *Nature*, 2001, **413**, 828–831.
- 8 M. Wohlgenannt, K. Tandon, S. Mazumdar, S. Ramasesha and Z. V. Vardeny, *Nature*, 2001, **409**, 494–497.
- 9 M. A. Baldo, D. F. O'Brien, M. E. Thompson and S. R. Forrest, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1999, **60**, 14422–14428.
- 10 Y. R. Sun, N. C. Giebink, H. Kanno, B. W. Ma, M. E. Thompson and S. R. Forrest, *Nature*, 2006, **440**, 908–912.
- 11 S. Reineke, F. Lindner, G. Schwartz, N. Seidler, K. Walzer, B. Lussem and K. Leo, *Nature*, 2009, **459**, 234–U116.
- 12 G. Schwartz, S. Reineke, T. C. Rosenow, K. Walzer and K. Leo, *Adv. Funct. Mater.*, 2009, **19**, 1319–1333.
- 13 S. Reineke, G. Schwartz, K. Walzer and K. Leo, *Appl. Phys. Lett.*, 2007, **91**, 123508.
- 14 N. C. Giebink and S. R. Forrest, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, **77**, 235215.
- 15 F. Laquai, G. Wegner, C. Im, A. Busing and S. Heun, *J. Chem. Phys.*, 2005, **123**, 074902.
- 16 S. Balushev, P. E. Keivanidis, G. Wegner, J. Jacob, A. C. Grimsdale, K. Müllen, T. Miteva, A. Yasuda and G. Nelles, *Appl. Phys. Lett.*, 2005, **86**, 061904.
- 17 A. Monguzzi, R. Tubino and F. Meinardi, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, **77**, 155122.
- 18 R. A. Marcus, *J. Chem. Phys.*, 1956, **24**, 966–978.
- 19 R. A. Marcus, *Rev. Mod. Phys.*, 1993, **65**, 599–610.
- 20 R. A. Marcus and N. Sutin, *Biochim. Biophys. Acta*, 1985, **811**, 265–322.
- 21 J. L. Bredas, D. Beljonne, V. Coropceanu and J. Cornil, *Chem. Rev.*, 2004, **104**, 4971–5003.
- 22 V. Coropceanu, J. Cornil, D. A. da Silva, Y. Olivier, R. Silbey and J. L. Bredas, *Chem. Rev.*, 2007, **107**, 926–952.
- 23 J. Jortner, *J. Phys. Chem.*, 1976, **64**, 4860–4867.

- 24 N. R. Kestner, J. Logan and J. Jortner, *J. Phys. Chem.*, 1974, **78**, 2148–2166.
- 25 V. G. Levich, *Adv. Electrochem. Electrochem. Eng.*, 1966, **4**, 249–371.
- 26 N. Liang, J. R. Miller and G. L. Closs, *J. Am. Chem. Soc.*, 1990, **112**, 5353–5354.
- 27 M. E. Sigman and G. L. Closs, *J. Phys. Chem.*, 1991, **95**, 5012–5017.
- 28 J. R. Miller, B. Pavlatos, R. Bal and G. L. Closs, *J. Phys. Chem.*, 1995, **99**, 6923–6925.
- 29 T. Holstein, *Ann. Phys. (Amsterdam, Neth.)*, 1959, **8**, 325–342.
- 30 T. Holstein, *Ann. Phys. (Amsterdam, Neth.)*, 1959, **8**, 343–389.
- 31 V. M. Kenkre and D. H. Dunlap, *Philos. Mag. B*, 1992, **65**, 831–841.
- 32 H. Bässler, *Phys. Status Solidi B*, 1993, **175**, 15–56.
- 33 V. I. Arkhipov, I. I. Fishchuk, A. Kadashchuk and H. Bässler, *Photophysics of Molecular Materials*, ed. G. Lanzani, Wiley, Weinheim, 2006, pp. 261–358.
- 34 S. L. M. van Mensfoort, S. I. E. Vulto, R. A. J. Janssen and R. Coehoorn, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, **78**, 085208.
- 35 M. Klessinger and J. Michl, *Excited States and Photochemistry of Organic Molecules*, VCH Publishers, New York, 1995.
- 36 R. D. Harcourt, G. D. Scholes and K. P. Ghiggino, *J. Chem. Phys.*, 1994, **101**, 10521.
- 37 G. L. Closs, P. Piotrowiak, J. M. MacInnis and G. R. Fleming, *J. Am. Chem. Soc.*, 1988, **110**, 2652–2653.
- 38 G. L. Closs, M. D. Johnson, J. R. Miller and P. Piotrowiak, *J. Am. Chem. Soc.*, 1989, **111**, 3751–3753.
- 39 L. Sudha Devi, M. K. Al-Suti, C. Dosche, M. S. Khan, R. H. Friend and A. Köhler, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, **78**, 045210.
- 40 I. I. Fishchuk, A. Kadashchuk, L. Sudha Devi, P. Heremans, H. Bässler and A. Köhler, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, **78**, 045211.
- 41 S. T. Hoffmann, E. Scheler, J. M. Koenen, M. Forster, U. Scherf, P. Strohriegl, H. Bassler and A. Köhler, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2010, **81**, 165208.
- 42 S. T. Hoffmann, H. Bassler, J. M. Koenen, M. Forster, U. Scherf, E. Scheler, P. Strohriegl and A. Köhler, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2010, **81**, 115103.
- 43 K. S. Schanze, E. E. Silverman and X. M. Zhao, *J. Phys. Chem. B*, 2005, **109**, 18451–18459.
- 44 K. Glusac, M. E. Kose, H. Jiang and K. S. Schanze, *J. Phys. Chem. B*, 2007, **111**, 929–940.
- 45 M. B. Johnston, L. M. Herz, A. L. T. Khan, A. Köhler, A. G. Davies and E. H. Linfield, *Chem. Phys. Lett.*, 2003, **377**, 256–262.
- 46 S. Karabunarliev, E. R. Bittner and M. Baumgarten, *J. Chem. Phys.*, 2001, **114**, 5863–5870.
- 47 J. J. Hopfield, *Proc. Natl. Acad. Sci. U. S. A.*, 1974, **71**, 3640–3644.
- 48 I. I. Fishchuk, A. Kadashchuk, H. Bässler and S. Nespurek, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2003, **67**, 224303.
- 49 I. I. Fishchuk, D. Hertel, H. Bässler and A. K. Kadashchuk, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2002, **65**, 125201.
- 50 D. Emin, *Adv. Phys.*, 1975, **24**, 305–348.
- 51 A. Miller and E. Abrahams, *Phys. Rev.*, 1960, **120**, 745–755.
- 52 S. Singh, W. J. Jones, W. Siebrand, B. P. Stoichef and W. G. Schneide, *J. Chem. Phys.*, 1965, **42**, 330.
- 53 C. Rothe and A. Monkman, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2002, **65**, 073201.
- 54 B. Movaghar, M. Grunewald, B. Ries, H. Bässler and D. Wurtz, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1986, **33**, 5545.
- 55 B. Movaghar, B. Ries and M. Grunewald, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1986, **34**, 5574–5582.
- 56 R. Richert, H. Bässler, B. Ries, B. Movaghar and M. Grunewald, *Philos. Mag. Lett.*, 1989, **59**, 95.
- 57 C. Rothe and A. P. Monkman, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2003, **68**, 075208.