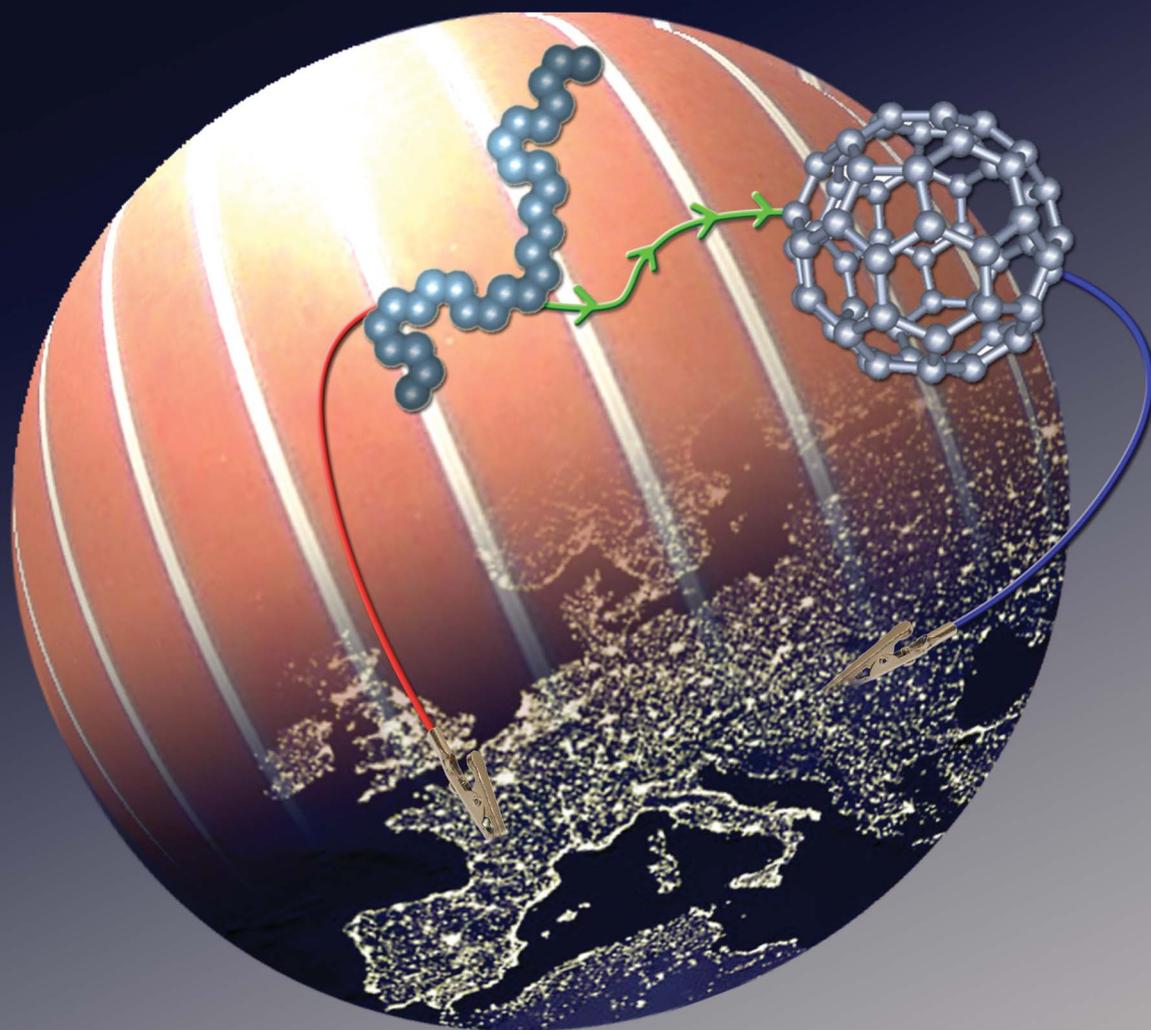


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FEATURE ARTICLE

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Sub-picosecond delocalization in the excited state of conjugated homopolymers and donor–acceptor copolymers

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In this feature article, we review and examine evidence that the primary photoexcited species in conjugated polymers is considerably delocalized. Localization occurs via a series of complex relaxation mechanisms on the <200 femtosecond time scale. We show that short-lived delocalization in the neutral excited state and charge separated state of bulk heterojunction blends might play an essential role in ensuring efficient formation of free charge carriers for photovoltaic applications. Finally, the additional parameter of intramolecular charge transfer character in the excited state of more recently developed donor–acceptor copolymers is discussed. Both delocalization and partial charge transfer reduce the binding of the electron and hole in photoexcited organic semiconductors and can help to overcome the bottleneck to macroscopic current generation in polymer solar cells.

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1 Introduction

Conjugated polymers are successful organic electronic materials, promising low-cost processing from solution together with light weight and flexibility.^{1–4} Applications include light-emitting diodes (OLEDs),^{5–10} field effect transistors (OFETs),^{11–15} lasers,^{16–20} photodetectors,^{21–25} sensors,^{26–29} and organic

photovoltaic (OPV) devices.^{30–34} Functioning is often based on processes that occur in the excited state, populated for example by optical absorption or electrical stimulus. These processes can be extremely fast. In polymer solar cells, photocurrent generation initiates from ultrafast charge separation (CS) in excited polymer:fullerene bulk heterojunction (BHJ) blends. CS components faster than 100 fs have been reported on numerous occasions.^{35–38} In order to fully exploit the potential of conjugated polymers and to allow their intelligent design for highly efficient devices, it is therefore essential to understand what happens in their excited state on the sub-picosecond time scale. Nevertheless, the nature of the primary photoexcitation, its ultrafast relaxation, as well as its dissociation into charges within pure polymers and at the fullerene interface is still not univocally elucidated. Here, longstanding and often conflicting paradigms will only be briefly discussed. We give priority to recent works, which shine new light on the problem, refresh existing theories and, in particular, outline the importance of short-lived delocalized states in conjugated macromolecular materials.

2 Classic conjugated homopolymers

It is largely the development of soluble and processible materials, such as functionalized poly(alkylthiophenes) and poly(phenylene vinylenes), that has initially led to the success of conjugated polymers in organic electronics.³⁹ Those classic homopolymers typically have a quite small repeat unit containing a single aromatic ring. The nature of their excited state has been extensively studied, but has also remained subject to considerable debate.⁴⁰ There are two main schools of thought. On the one hand, conjugated polymers have been treated as

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one-dimensional semiconductors, where mobile electrons and holes are directly photogenerated in energy bands and eventually localize into a bound exciton state.^{2,39,41} On the other hand, evidence exists for a more molecular approach, where the primary photoexcitation is already a bound exciton.^{42–44} In the present article, we will more neutrally use “excited state” as the terminology and show that its nature depends on both disorder and on the time scale at which it is observed.

2.1 The influence of disorder

The extent of disorder in the conjugated polymer chain determines the delocalization of the excited state and hence its more semiconductor-like or more molecular-like behaviour. Indeed, some of the early experimental support for the energy band description by Heeger *et al.* stems from the band-shape analysis of the absorption, emission and electro-absorption spectra of ordered, stretch-oriented MEH-PPV (poly(2-methoxy,5-(2'-ethylhexoxy)-*p*-phenylenevinylene)) chains.^{45–47} Also, Schott *et al.* have reported highly ordered polydiacetylene quantum wires (diluted in their monomer crystalline matrix), with quantum coherence reaching tens of micrometers.⁴⁸ This macroscopic delocalization of the excited state, limited only by chain length, was demonstrated by the interference of the emission from two spatially separated regions, using microscopic imaging spectroscopy. In such ordered cases, the one-dimensional semiconductor model might be justified, and has been successfully applied by Spano and Yamagata to theoretically describe the polydiacetylene spectra.⁴⁹ It should be mentioned, however, that the latter work also shows that the photophysical properties of ordered polydiacetylene are remarkably similar to linear J-aggregates of through-bond coupled repeat units, a concept that might more generally contribute to the excited state description of conjugated polymers, even in the presence of intermolecular interactions and disorder.⁵¹

Highly ordered conjugated polymers remain an exception. In most cases, disorder in the dissolved or solid-state materials prevents the delocalization of the excited state over the entire chain and breaks it into much smaller, more molecular-like chromophores of variable size (Fig. 1A).⁵⁰ This has been evidenced by Förster-type excitation energy transfer (EET) within the inhomogeneous distribution of chromophores on the picosecond to hundreds of picoseconds time scale (Fig. 1C). Multistep EET to sites with lower energy typically leads to a progressive red shift of the fluorescence spectrum, extensively studied by (site-selective) time-resolved emission measurements, often combined with Monte Carlo simulations.^{52–62} The individual chromophores within the polymer chain can be addressed with single molecule spectroscopy, yielding narrow fluorescence lines at low temperature.⁶³ Moreover, rotation of the excitation and/or emission polarization during the single molecule experiments allows relating the EET dynamics to polymer chain conformation,⁶⁴ and gaining insight into the shape (bent or straight) of the individual chromophores.⁶⁵ EET to well-defined quenching sites could even be directly visualized in super-resolution measurements.⁶⁴

2.2 Short-lived delocalized states

The nature of the excited state in conjugated polymers also depends on the time after absorption at which it is observed, so that treating it as a static species would be a strong oversimplification. We will show in the following that the early excited state probed with the typical 100–200 femtosecond time resolution of ultrafast laser experiments (before any Förster-type EET occurs) is already considerably different and more localized than the one directly following excitation.

Experimental evidence. There is extensive experimental evidence for relaxation processes occurring within tens to hundreds of femtoseconds in isolated polymer chains as well as in the solid state. Time-resolved emission spectra of P3HT (poly(3-hexylthiophene)) in chlorobenzene solution and in spin-cast thin films were recorded by Banerji *et al.* and are shown in Fig. 2A.⁶⁶ The time-resolution of the fluorescence up-conversion experiments was about 200 fs and the earliest measurable spectra at this time delay show clear signs that relaxation has already taken place before. Indeed, for solution and film, the spectral position of the 0.2 ps and the steady-state spectrum is quite close and strongly red-shifted compared to the absorption, indicating that <200 fs relaxation leads to a major fraction of the Stokes shift. The 0.2 ps emission is also narrower than the mirror image of the absorption spectrum, which points to either a different nature of the emitting state and/or to an ultrafast reduction of (conformational) inhomogeneity. Moreover, the earliest spectrum in a P3HT film is similar with 400 nm and 500 nm excitation, although respectively more amorphous and more H-aggregated regions of the materials are selectively excited at the two wavelengths.^{67,68} The ultrafast relaxation therefore either leads to migration of the photoexcitation from amorphous to crystalline polymer regions, or to conversion of amorphous to H-aggregated chains by conformational changes.

A commonly observed effect of <200 fs relaxation in the excited state of conjugated polymers is the ultrafast decay of anisotropy (loss of polarization memory) in time-resolved fluorescence and transient absorption (TA) measurements.^{69–73} The anisotropy decay curves measured by Banerji *et al.* in the previously mentioned fluorescence study of P3HT are shown in Fig. 2B.⁶⁶ It is obvious that the earliest measurable initial anisotropy at 0.2 ps is significantly below 0.4, the theoretical value expected in the absence of any relaxation. The ultrafast anisotropy decay is in this case unresolved. Differences in the initial anisotropy between film and solution and with excitation wavelength will be discussed below. Grage *et al.* could on the other hand directly observe an anisotropy decay component of only 40 fs for PTOPT (poly(3-(4-octylphenyl)-(2,2')-bithiophene)) thin films, using TA measurements with 10 fs resolution.⁷³ This was too fast to be explained by Förster EET. More evidence for ultrafast relaxation, this time in PPV (poly(*p*-phenylenevinylene)), comes from femtosecond wave packet interferometry, where the beating of the fluorescence from two-pulse excitation was damped in 130–150 fs.^{53,74} Finally, the decay of the peak shift in three-pulse photon echo (3-PEPS) experiments allows one to gain insight into the initial excited-state processes in conjugated polymers.^{75–78} In particular, Scholes *et al.* studied

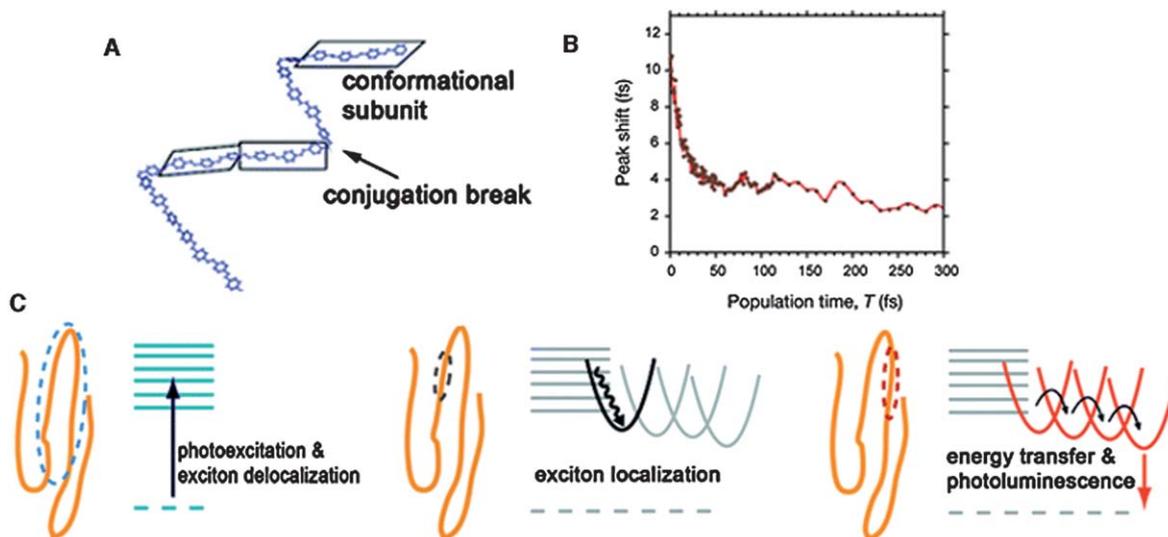


Fig. 1 (A) Part of a MEH-PPV chain disrupted into chromophores by conformational conjugation breaks according to the model by Scholes *et al.* (B) Three-pulse photon echo peak shift of dilute MEH-PPV in chlorobenzene as a function of population time. (C) Evolution of the polymer excited state in a single chain: there is initial delocalization, before the excited state localizes and finally hops between chromophores by EET. Adapted with permission from ref. 50. Copyright 2010 American Chemical Society. (B) was adapted in ref. 50 from ref. 75. Copyright (2005) by The American Physical Society.

MEH-PPV in different solutions and thin film, observing a characteristic ~ 50 fs peak shift decay component (Fig. 1B).^{75,76}

Origins of dynamic localization. It is now established that the origin of the <200 fs relaxation in conjugated polymers is somehow related to the evolution from an initially delocalized photoexcitation to a more localized state (Fig. 1C).⁵⁰ The relaxation of the short-lived delocalization is highly complex and originates from a number of entangled processes. Three main contributions to the dynamic localization have been identified by experimental and theoretical studies:

- Electronic relaxation to a more localized lowest-energy state through a manifold of delocalized states formed by coupling of the chromophoric units.
- Self-trapping of the electronic states caused by strong coupling to nuclear modes, *i.e.* localization caused by structural distortion on the polymer chain.
- Coherent excitation energy transfer between chromophore units in the intermediate coupling regime.

As discussed in the following, the precise interplay and relative importance of the three processes is still matter of some controversy. It depends to some extent on the nature of the investigated polymer (*e.g.* polythiophene or poly(*p*-phenylenevinylene), strength of coupling to nuclear modes, torsional freedom, chemical conjugation breaks) and on environmental effects such as disorder, medium (solution or film), and temperature.

Coupling of chromophoric units. Scholes *et al.* could describe the 3-PEPS data of MEH-PPV simultaneously with the homogeneous and inhomogeneous lineshape of the absorption and fluorescence spectra.^{50,75,76} In their model, chromophores along the polymer chain are formed by conformational conjugation breaks (disorder leading to inhomogeneity, Fig. 1A). The chromophores interact (*i.e.* their orbitals couple like in aggregates), giving rise to the collective delocalized states observed directly

after photoexcitation. The coupling can be intrachain (between adjacent chromophores) as well as interchain (when an isolated polymer chain bends or upon chain aggregation). The importance of interchain delocalization was evidenced by Herz *et al.* by comparing the ultrafast fluorescence depolarization in aggregated polydiphenylenevinyls (PDVs) to polymer chains isolated with a surrounding macrocycle or by complexation to an inert host polymer.⁷⁰ Both the experimental 3-PEPS data and the ultrafast decay of the TA anisotropy in MEH-PPV were modeled in polymer chains generated by a random growth algorithm with conformations obtained from molecular dynamics simulations (conjugation breaks every 2–12 repeat units).⁶⁹ A semiempirical Hartree–Fock method (INDO) together with single configuration interaction (SCI) allowed calculating the site energy of the chromophores and their coupling. It was found that the <50 fs component responsible for the TA depolarization and decay of the 3-PEPS signal can largely be explained by relaxation among the slightly delocalized states formed by coupled chromophores.

Coupling to nuclear modes. The conformation of a conjugated polymer directly after photoexcitation is the one of the ground state, because nuclei do not have time to move during the electronic transition (Born–Oppenheimer approximation). Therefore, structural relaxation to accommodate the electronic distribution of the excited state is expected. For example, conjugated polymers containing aromatic rings are typically torsionally disordered in the ground state, but tend to planarize in the excited state because the torsional potential is steeper.⁵⁰ This relaxation is largely responsible for the absence of mirror image symmetry and the large Stokes shift between the absorption and emission spectra of conjugated polymers and oligomers. The effects are much smaller in, for example, rigid ladder-type polymers, where torsional disorder is suppressed.⁷⁹ In the time-resolved emission spectra of P3HT shown in Fig. 2A,⁶⁶ there is a red shift of the

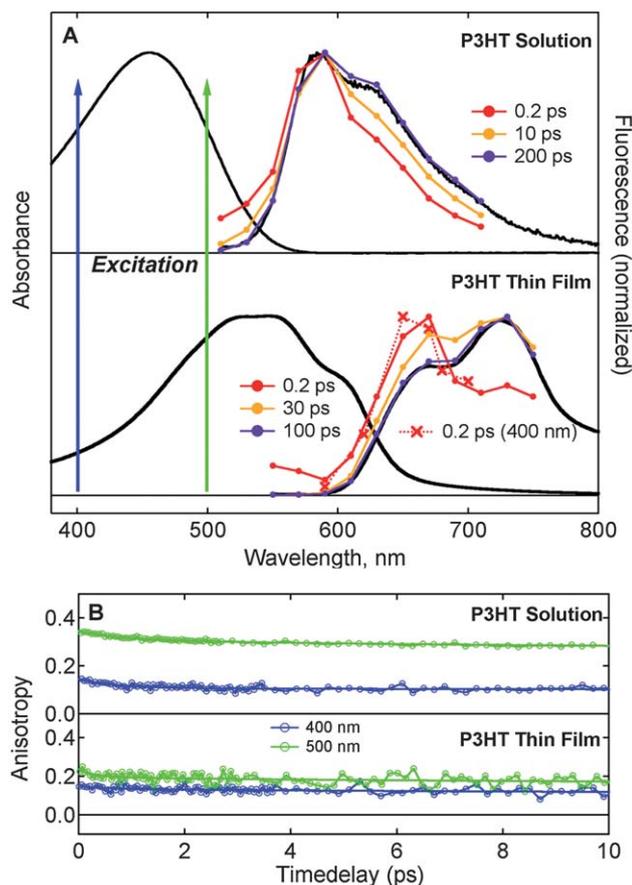


Fig. 2 (A) Steady-state spectra of P3HT in solution and in the solid state (in black), together with the normalized time-resolved emission spectra reconstructed from the fluorescence time profiles recorded after excitation at 500 nm (dots) and 400 nm (crosses). (B) Corresponding time-resolved fluorescence anisotropy recorded at the emission maximum with excitation at 400 nm (blue) and 500 nm (green). Adapted with permission from ref. 66. Copyright 2011 American Chemical Society.

emission spectrum between 0.2 ps and ~ 200 ps, ascribed to Förster EET between chromophores. In parallel, the vibronic structure of the emission spectra changes: the second vibrational shoulder in solution grows, while there is inversion of the two bands in the thin film. This is caused by relatively slow, large scale planarization of the polymer backbone.

On the ultrafast time scale (<200 fs), photoexcitation leads to structural relaxation of the bond-length alternation between double and single bonds and to local planarization. Typically, there is a transition from the benzoidal to the quinoidal structure of aromatic rings.² This ultrafast conformational change might be responsible for the <200 fs increase in homogeneity of the excited state observed for P3HT and shown in Fig. 2A (narrowing and excitation wavelength independence of the early emission spectrum).⁶⁶ It is mediated by two nuclear modes: a 0.18 eV C=C stretching vibration and a lower frequency ~ 0.016 eV torsion. Those modes also strongly couple to the electronic excited state.^{50,72,78} Therefore, the structural distortion at the centre of a chromophore caused by the nuclear relaxation contributes to the ultrafast localization effects in the excited state. This is known as self-trapping and occurs within the

period of the involved vibration (20–30 fs for C=C stretch, 160 fs for torsion).

It should be noted here that the picture of chromophores formed by disorder-induced conjugation breaks might be oversimplified and that coupling to nuclear modes can also contribute to segmenting the polymer chain into chromophores. Beenken and Pullerits showed through semiempirical quantum chemical calculations (ZINDO method) that kinks, torsions and *cis-trans* defects in a polythiophene chain do not necessarily disrupt the conjugation.⁸⁰ It was also pointed out that chromophores are not straight, but can be bent.⁶⁵ Barford *et al.* proposed an alternative interpretation of the chromophoric units (which they entitled “local exciton ground states”, LEGS) in PPV.^{81,82} The size (length-scale of localization) of the relaxed LEGS is not necessarily determined by conjugation breaks, but by the strength of coupling to nuclear modes. It is thus the self-trapping that breaks the polymer chain into localized chromophores. Higher energy states delocalize over several LEGS forming “quasi-extended excitons” (QEES). When QEES are excited at high energy, there is first a nonadiabatic conversion to unrelaxed LEGS (which can also be directly excited near the band edge). This causes already significant localization. The LEGS then become self-trapped, causing an additional localization to about 8 repeat units within 35 fs. This is only associated with the high-frequency C=C bond vibrations, which create a benzoid–quinoid distortion at the centre of the localization. According to this model, torsional modes play a smaller role in the self-trapping on the slower 100 fs time scale. However the initial torsional disorder determines the delocalization of the unrelaxed (vertical) LEGS. The model was validated by simulations using the Pariser–Parr–Pople–Peierls formalism, and later the more practical disordered Frenkel–Holstein model solved with the Ehrenfest approximation.

Delocalization and anisotropy decay. The simulations by Barford *et al.* also allowed them to predict that the extent of ultrafast depolarization in fluorescence experiments depends on the difference of localization between the initial state and the relaxed LEGS.^{81,82} Higher primary delocalization, for example due to excitation into higher energy states, should therefore lead to more loss of anisotropy. The ultrafast depolarization in conjugated polymers is complex and probably determined by the interplay of several effects described in previous paragraphs: dynamic conformational disorder, structural relaxation, excited-state localization and coherent EET. Nevertheless, the predictions of Barford *et al.* are at least qualitatively verified by experiment.

In the fluorescence anisotropy data shown for P3HT in Fig. 2B, the initial anisotropy is considerably lower with higher energy excitation at 400 nm compared to 500 nm excitation (0.15 *versus* 0.35 in solution, 0.15 *versus* 0.23 in the thin film), confirming that higher initial delocalization leads to more relaxation.⁶⁶ The effect is larger in solution than in the thin film, because the blue-shifted absorption spectrum allows excitation nearer to the band-gap at 500 nm. In the thin film, the generally lower initial anisotropy can be explained by higher excess energy at the two excitation wavelengths, and by an enhanced contribution of intermolecular coupling to the ultrafast

dynamics. The result is consistent with a TA study by Guo *et al.*, where the initial anisotropy in the excited-state absorption of regiorandom P3HT film was also found to be much higher upon 500 nm compared to 400 nm excitation.⁸³ Along the same lines, Milota *et al.* showed that the ultrafast (20–30 fs) decay of the 3-PEPS signal in MEH-PPV decelerates at lower excitation energy.⁷⁷ We note here that the lower initial anisotropy with higher energy excitation can also partially be caused by coupling of the first to the second electronic transition in P3HT, since Beenken and Pullerits theoretically demonstrated orthogonal transition dipole moments if the polymer chain is kinked or bent.⁸⁰

Higher initial delocalization and therefore a larger initial anisotropy loss can also be expected for fully conjugated polymer chains compared to samples with voluntarily introduced conjugation breaks. Indeed, Ruseckas *et al.* investigated the TA and fluorescence anisotropy decay of fully conjugated and partially conjugated MEH-PPV chains and observed that 50–90 fs decay occurred only in the fully conjugated sample (Fig. 3A), which also showed a larger red shift of the emission spectrum within 100 fs.⁷² This outlines that disrupting the coupling between the chromophores hinders initial delocalization (estimated to 14 repeat units in the fully conjugated sample) and therefore partially prevents the ultrafast relaxation. A similar

effect was observed for P3HT of different molecular weights in solution, where the initial anisotropy decreased for the high molecular weight sample, which might have higher initial delocalization and more conformational disorder (Fig. 3B).⁷¹

Coherent EET. In the model used by Scholes *et al.* for the 3-PEPS data (Fig. 1C), both the ultrafast electronic relaxation and the structural self-trapping were described as incoherent processes, mediated by random fluctuations of the bath and of the nuclei, respectively.^{75,76} The same authors showed later on that coherent processes also play a role on the <200 fs time scale, which might explain why conjugated polymers can have some semiconductor-like properties in spite of pronounced disorder.^{84,85} If chromophores along a polymer chain were weakly coupled, EET between them could only occur by the relatively slow, incoherent Förster mechanism. Strong coupling would imply complete delocalization. The situation is in fact in-between, in the intermediate coupling regime, mainly because nuclear modes perturb the delocalization. Here, partial delocalization allows quantum-assisted transport between the chromophores on the ~100 fs time scale, thus both excited state population and coherences move in concert. This is known as “coherent EET” and was experimentally demonstrated by a specifically designed experiment (two-time anisotropy decay, TTDA) combined with two-dimensional electronic spectroscopy. By comparison of MEH-PPV chains in different conformations (solution and nanoparticles), the mechanism was shown to be predominantly intrachain. Surprisingly long electronic coherences of 250 fs were found at room temperature. It was suggested that low frequency nuclear modes (for example torsions) that span more than one chromophore help to maintain the correlation of the energy gap fluctuations. By using two-color 3-PEPS at different probe wavelengths for dissolved P3HT, Blank and Wells confirmed that spectral correlation (even over 0.7 eV) is maintained during ultrafast relaxation.⁷⁸

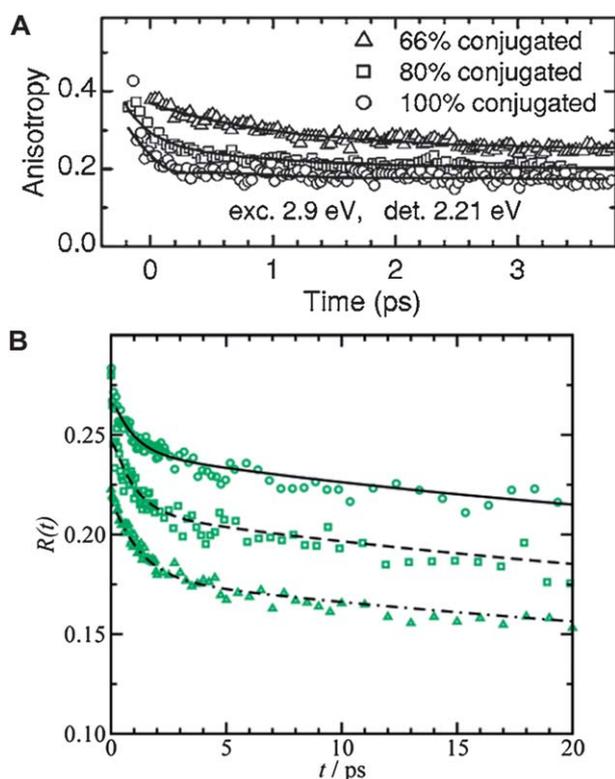


Fig. 3 (A) Fluorescence anisotropy decay of fully and partially conjugated MEH-PPV in solution, from ref. 72. Copyright (2005) by The American Physical Society. (B) Fluorescence anisotropy decay of P3HT in solution for different molecular weights ($M_n = 4.1$ kDa, 7.7 kDa and 13 kDa for circles, squares and triangles, respectively), with 2.64 eV excitation and for 2.18 eV emission, reprinted with permission from ref. 71. Copyright 2007 American Chemical Society.

2.3 Delocalization and charge carrier generation

Neat polymers. Until now, the discussion focused on neutral excited states. Charges have also been observed as a consequence of light absorption in neat conjugated polymers.^{44,86–99} The macroscopic yield that can be extracted as photocurrent is typically very low (<10%),⁹² although charge yield as high as 30% has been reported for thin films of semi-crystalline P3HT.¹⁰⁰ It is possible that more charges are present shortly after photoexcitation than at long time delays,⁸⁹ so that the measured yield depends on the method of its determination. Many mechanisms for the generation of intrachain and interchain charges have been put forward based on detailed spectroscopy and photocurrent studies. Those include direct interband excitation of mobile electrons and holes (semiconductor model),^{93–95,97,98} hot (vibrationally unrelaxed) exciton dissociation,^{89,96} charge generation facilitated by exciton–exciton annihilation,^{86,90,91,99} exciton splitting at impurities,¹⁰¹ polaron-pair formation by sequential excitation,^{91,92} and charge separation at amorphous–crystalline interfaces in P3HT.^{87,88} A detailed discussion is beyond the scope of the present manuscript. Nevertheless,

Heeger *et al.* reported “instantaneous” generation of charges in neat polymers on the <100–200 fs time scale and it seems established now that at least part of the charges appear on this ultrafast time scale.^{94,95,98} This is noteworthy in the current context, because it is so close to the time scale of excited state localization in conjugated polymers discussed here. We would therefore like to point out the importance to further examine the role played by the delocalized primary photoexcitation for charge generation in neat polymers.⁵⁰ We suggest that the electron and hole contributions of the excited state, less tightly bound during delocalization, might localize on different parts of the same chain or on neighbouring polymers. A branched pathway from the initially excited species can therefore lead to the formation of either neutral or charged states. The polaron (charge coupled to a local nuclear distortion) formation might be helped by some asymmetry in the system, such as an amorphous–crystalline interface or intramolecular charge transfer along the polymer chain, as will be discussed below.

Bulk heterojunction blends. In order to achieve significant macroscopic yield of photocurrent for organic photovoltaics, electron-donating conjugated polymers are mixed with an electron acceptor, typically a fullerene derivative.^{30,33,34} It is generally considered that phase segregated domains of about 10 nm are formed in the solid-state bulk heterojunction (BHJ) blend. After light absorption by the polymer, the ensuing excited state (exciton) diffuses to an interface and transfers an electron to the fullerene. Holes and electrons in the donor and acceptor phases are the result of this interfacial charge separation (CS); they are then transported to opposite electrodes.

This simple picture presents a significant discrepancy. Experimental evidence points to the appearance of charges in efficient BHJ blends within less than 100 fs.^{35–38} However, point-like excited state diffusion in 100 fs is limited to the 0.1–0.2 nm length scale, according to published exciton diffusion coefficients.^{102,103} We have also seen that hopping of the excited state by Förster EET typically occurs on the slower >1 ps time scale. The distance that an excited state can diffuse (0.1–0.2 nm) and the distance that it needs to diffuse (up to 10 nm) to reach a fullerene interface for ultrafast (<100 fs) CS thus need to be reconciled. Considering slower CS would resolve the discrepancy, but even if CS components of a few picoseconds have been measured for morphologies with large polymer domains, they are still too fast to be preceded by significant migration of a point-like excited state.^{35,104,105} A plausible explanation has been put forward by Durrant *et al.* for PBTTT (poly(2,5-bis(3-alkylthiophen-2-yl)thieno[3,2-*b*]thiophene)):fullerene blends.¹⁰⁶ This challenges the common view of BHJ morphology and the related 10 nm length scale. The fullerene is intimately mixed (intercalated) with the PBTTT, so that diffusion of the photoexcitation is no longer necessary. A separate, pure fullerene phase ensures efficient spatial charge separation and transport of electrons to the electrodes. It is possible that microstructures involving mixed polymer:fullerene domains can be generalized to more BHJ blends, consequent future investigation will be of high interest.

Independent of morphology, Banerji *et al.* have suggested an alternative mechanism to account for ultrafast CS in

organic solar cells.^{66,108,109} This invokes the initial delocalization of the excited state in conjugated polymers. CS faster than 100 fs might occur from the delocalized primary photoexcitation, before there is time for relaxation processes and dynamic localization. Given the larger spatial extent sampled at this point of time *via* delocalization, a fullerene interface can be reached on the ultrafast time scale, without significant point-like diffusion, possibly assisted by quantum transport such as coherent EET.^{84,85} Moreover, the binding energy of the electron and hole in the short-lived excited state is reduced by initial delocalization, and there is excess energy in the system, which can help CS. In summary, Förster-type diffusion of a localized and relaxed excited state is unlikely to be involved in the CS mechanism in polymer:fullerene BHJ blends, because it is too slow. The much debated concepts of exciton diffusion length and binding energy therefore may be less important for CS in polymer solar cells than has been commonly assumed. Delocalization of the primary photoexcitation and transport assisted by quantum effects offer a plausible explanation for the observation that provides the foundation for the entire field of BHJ solar cells: ultrafast photoinduced CS.

Delocalization not only of the neutral excited state, but also of the charges, might be essential in ensuring high solar cell efficiency. Indeed, simple CS between the polymer and fullerene is not sufficient to generate free charge carriers, because the electron and hole can still be Coulomb bound across the interface of the two phases. The existence of a bound intermediate charge transfer (CT) state, which evolves according to the Onsager–Braun model into free charges, has often been invoked.^{37,110–115} However, detailed TA measurements by Laquai *et al.* on several polymer:fullerene systems and spanning orders of magnitude in time (200 fs to 10 μ s) have led to the conclusion that free charge carriers are directly generated upon CS within 100 fs.^{35,104,116} Depending on the particular system and morphology, only a small fraction of charges is generated in the CT state and is lost to photocurrent generation by geminate recombination. The CT state is thus a trap, which cannot dissociate into free carriers.

Insight into the mechanism of direct free charge generation was provided by Bakulin *et al.*, who developed a pump–push photocurrent experiment.¹⁰⁷ It was found that CS at the acceptor interface in various polymer:fullerene and polymer–polymer blends leads to “hot” electronic CT_{*n*} states with considerable delocalization, *i.e.* band states populated before self-trapping to polarons. Long-range separated free charges are generated *via* the hot states within hundreds of femtoseconds (Fig. 4), so that reaching the delocalized states is the driving force to overcome Coulomb binding. Alternatively, relaxation of the charge pairs to the lowest-lying (localized) CT₀ state, followed by geminate recombination, can occur. In the experiment, a second IR “push” pulse was delivered to directly re-populate the delocalized CT_{*n*} states from the relaxed CT₀, giving the charges a second chance to dissociate. This led to the expected increase in photocurrent through enhanced free carrier generation, especially in poor photovoltaic systems with significant formation of the “lost” CT₀ charges. Complementary all-optical pump–push–probe measurements with

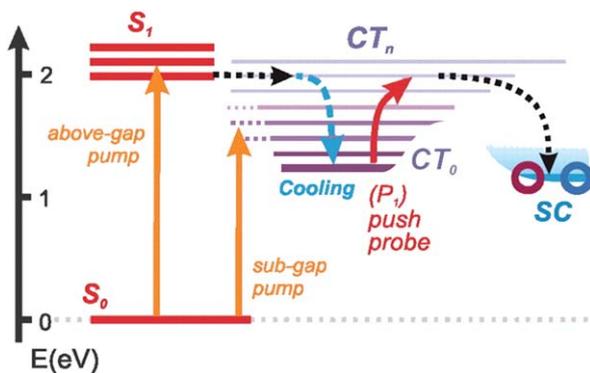


Fig. 4 Free energy state diagram of a typical OPV system according to the model developed by Bakulin *et al.* (from ref. 107; reprinted with permission from AAAS). The singlet state, charge transfer (CT) states (CT_0 = lowest-lying, CT_n = delocalized band states) and separated charges (SC) are shown. Solid arrows show optical transitions, and dashed arrows indicate energy and charge-transfer pathways involved in free charge generation.

polarization control confirmed the short lifetime (<1 ps) and enhanced mobility of the CT_n states. The past year has seen a lively discussion about the role of hot and delocalized CT states and excess energy in photocurrent generation.^{107,110,117–123} For example, a combined theoretical and TA study by Lanzani *et al.* directly evidenced the dissociation of neutral photoexcitations into hot interfacial CT states and consequently free charges.¹¹⁹ Carrier generation within tens of femtoseconds *via* delocalized states was enhanced by excitation into higher-lying singlet states (more excess energy). The role of excess energy was further explored by Durrant *et al.* in a polymer:fullerene system with very small driving force for CS.¹²³ Unlike in blends with a higher LUMO level offset between the donor and acceptor, excitation near the band edge in the present BHJ did not allow reaching the delocalized CT_n states, so that the photocurrent quantum yield was reduced and the yield of the bound CT_0 state enhanced.

A question that has hardly been raised in the literature is the precise origin of the delocalized CT states and their possible relationship with the delocalized primary neutral photoexcitation in conjugated polymers. The following model should be considered in future investigation: light absorption in the polymer phase of the BHJ blend populates a short-lived delocalized excited state, which reaches a fullerene interface on the ultrafast time scale assisted by quantum-mechanical transport. The delocalization is maintained during the <100 fs CS step and in the hot CT_n states. It ultimately favors the full dissociation of holes and electrons in the donor and acceptor phases, so that they can be extracted from the solar cell *via* the electrodes.

2.4 Take-home message

The take-home message of this first section of the article is that the primary photoexcitation in conjugated polymers is much more delocalized than the more relaxed excited state after 100–200 fs. Absorption therefore occurs in a larger segment of the polymer chain than is probed by emission. The short-lived delocalization in the neutral excited state and charge separated

state of bulk heterojunction blends might play an essential role in ensuring the efficient formation of free charge carriers for photovoltaic applications.

3 Donor–acceptor copolymers

As described above, the excited state properties of conjugated homopolymers with relatively simple aromatic repeat units have been extensively studied and are very complex. The need for higher efficiency in applications has driven the design of chemically more challenging materials. Alternating donor–acceptor copolymers enjoy success for ambipolar charge transport,^{14,124,125} and in highly efficient (7–8%) organic solar cells.^{31,126–128} Their large repeat unit consists of an electron-rich moiety (D) and an electron-poor moiety (A). Hybridization of the molecular orbitals from D and A leads to new transitions in the copolymer, and the quinoidal resonance form is stabilized by D–A alternation.^{129–132} As a consequence, the optical bandgap is reduced, allowing better harvesting of the solar spectrum for photovoltaic devices, especially in the near-infrared region. Compared to classic homopolymers, additional parameters need to be taken into account for D–A materials: dipole moments in the ground and excited states, as well as the change in this intramolecular charge transfer (ICT) character during relaxation. We will discuss how the notion of ICT (implying localization of charges in the excited state) reconciles with the short-lived delocalization expected in conjugated systems. Moreover, studies showing that D–A dipoles assist charge separation in neat polymers and bulk heterojunction blends will be presented.

3.1 Ultrafast excited-state processes

Relaxation in the excited state of D–A copolymers has been less investigated than in homopolymers, especially on the ultrafast <200 fs time scale of dynamic localization. Banerji *et al.* studied PCDTBT (poly[*N*-9'-hepta-decanyl-2,7-carbazole-*alt*-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)]) by fluorescence upconversion spectroscopy.¹⁰⁹ This polymer (shown in Fig. 5A) attracted attention in 2009 as the first D–A copolymer with high photovoltaic power conversion efficiency exceeding 6% (today, 7.2% can be achieved with this material).^{32,127,133,134} The steady-state absorption spectrum shows two broad bands ("camel back" shape), while there is a single, unstructured emission peak (Fig. 5A for thin film). The latter is red shifted compared to the time-resolved emission spectrum at 200 fs recorded with 500 nm excitation. This shift, together with a narrowing on the blue side, a slight broadening on the red side and a decay of intensity in the 600 nm region, is caused by relatively slow relaxation mechanisms (Förster EET, backbone planarization, Fig. 5A). The large fraction of the Stokes shift within the 200 fs experimental time resolution and initial loss of anisotropy to a value around 0.3 (Fig. 6B) evidence that ultrafast relaxation also takes place in PCDTBT, probably by similar localization mechanisms of the excited state as in classic homopolymers.

Interestingly, the relaxation is similar to that of higher energy excitation at 400 nm and the same initial anisotropy is

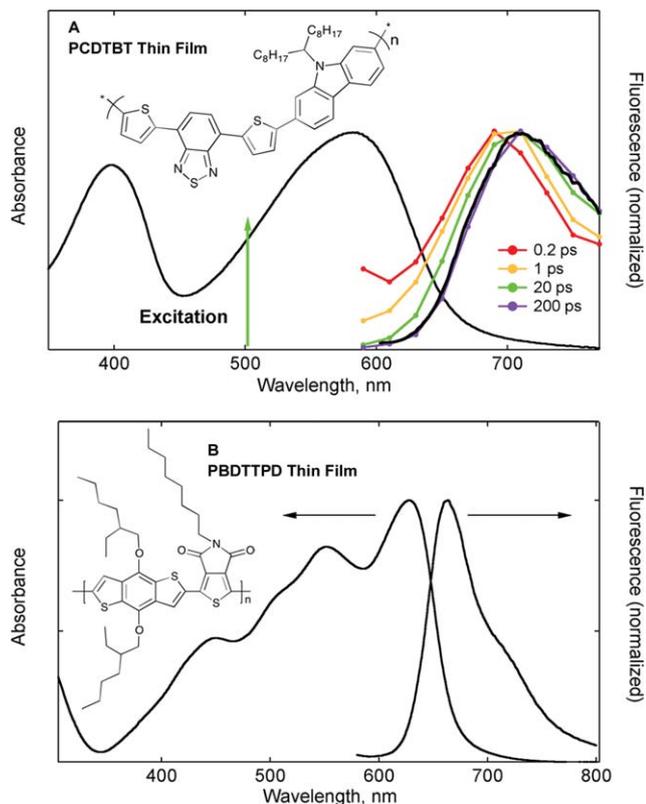


Fig. 5 (A) Steady-state spectra of PCDTBT thin film (in black), together with the normalized time-resolved emission spectra reconstructed from the fluorescence time profiles recorded after excitation at 500 nm (coloured curves). Adapted with permission from ref. 109. Copyright 2010 American Chemical Society. (B) Steady-state spectra of PBDTTPD thin film. Adapted with permission from ref. 135. Copyright 2012 American Chemical Society.

found as with 500 nm absorption (Fig. 6B), in clear contrast to P3HT (Fig. 2B). Light at 400 nm is absorbed into the second absorption band of PCDTBT, so that there is the additional complication of ultrafast internal conversion. This was studied in detail for another D–A copolymer by Lanzani *et al.* and is strongly intricate with torsional relaxation.¹³⁶ Exciting at different positions of the first absorption band in PCDTBT might be a better way to study the wavelength effect on ultrafast delocalization. Finally, the investigation by Banerji *et al.* revealed that not only are the steady-state spectra of PCDTBT very similar in film and solution, but also the emission dynamics and anisotropy during the first 10 ps (Fig. 6A and B).¹⁰⁹ This points to comparable chain conformation in solution and in the amorphous film. Considering that PCDTBT chains should be isolated in the dilute solution, the similar behaviour might also indicate that processes on the short time scale are essentially intrachain. If interchain processes should occur in solution (folding of a chain or aggregation of several chains), they resemble the ones in the thin film. The enhanced packing effects become evident in the solid state only after 10 ps. There is faster fluorescence decay (self-quenching) and complete loss of the polarization memory within 200 ps (Fig. 6), while significant anisotropy persists in solution (fewer transition dipole directions are sampled by more limited EET).

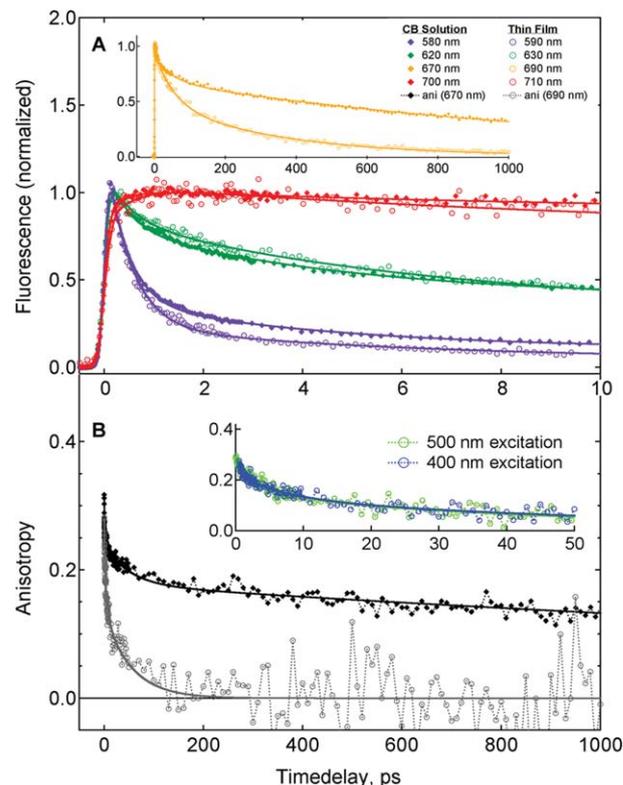


Fig. 6 (A) Fluorescence time profiles of PCDTBT in chlorobenzene solution and in the solid state, recorded at various emission wavelengths following excitation at 500 nm. (B) Corresponding anisotropy decay recorded at 670 nm (solution) or 690 nm (thin film). The inset compares the anisotropy in the thin film (at 610 nm) with 400 nm and 500 nm excitation. Adapted with permission from ref. 109. Copyright 2010 American Chemical Society.

3.2 Breaking down the problem

A useful strategy to study the detailed electronic structure of PCDTBT is to use the small molecule model compounds CB ((9-(heptadecan-9-yl)-9H-carbazole), dTBT (4,7-di-(2-thienyl)-2,1,3-benzothiadiazole) and CDTBT ((4-(5-(N-(9-heptadecanyl)carbazol-2-yl)thiophen-2-yl)-7-(5-phenylthiophen-2-yl)benzo[2,1,3]thiadiazole)), thus building blocks of the polymer chain.¹³⁷ The structure and steady-state spectra in solution are shown in Fig. 7A. While the shape of the CB spectra is clearly different, the typical “camel back” double absorption band together with the single unstructured emission band is present in dTBT, CDTBT and PCDTBT. This points to a strong influence of dTBT (already a donor–acceptor material with an electron-withdrawing benzothiadiazole, BT, flanked by two electron-donating thiophenes) on the properties of the PCDTBT polymer.

Quantum-chemical simulations are often used to understand and predict the properties of D–A copolymers.^{133,138–149} To afford reasonable computational time, model oligomers of a few repeat units are investigated and the results are extrapolated to account for the increased conjugation length of the polymers. The synthesis of the dTBT and CDTBT monomers allowed a more direct comparison between theory and experiment.^{137,150} The vertical absorption and emission transitions, calculated by TD-DFT at the M062X/6-31+G* level of theory

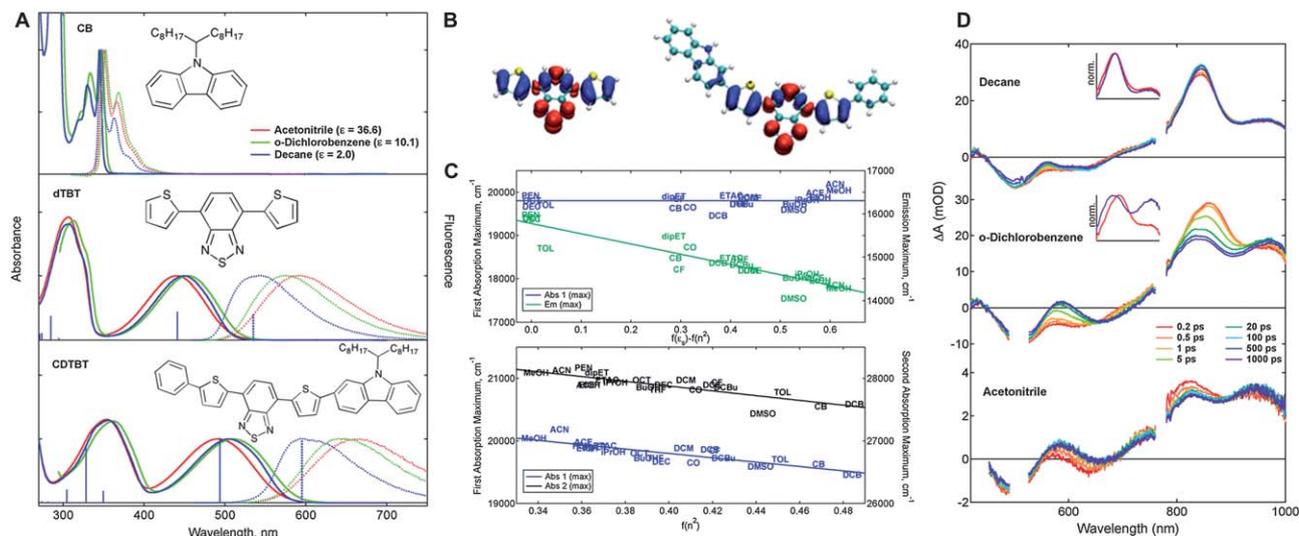


Fig. 7 (A) Molecular structure and steady-state spectra of the building blocks of PCDTBT in solvents of varying polarity. The gas-phase transitions calculated by TD-DFT (M062X/6-31+G*) are depicted as solid and dashed vertical blue lines for absorption and emission, respectively. (B) TD-DFT absorption transitions obtained for dTBT (left) and CDTBT (right). The difference between the first excited and ground state electron density calculated for vertical absorption is shown. (C) First absorption and emission maxima of CDTBT versus the Onsager polarity function [$f(\epsilon_s) - f(n^2)$] (top); first and second absorption maxima of CDTBT versus the Onsager function of the solvent refractive index $f(n^2)$ (bottom). (D) Transient absorption spectra of CDTBT in different solvents, recorded at various time delays following excitation at 510 nm. Panels A, B and D are adapted from ref. 150. Panel C is reproduced with permission from ref. 137. Copyright 2012 American Chemical Society.

following gas phase geometry optimization in the ground and excited state, are plotted as lines in Fig. 7A.¹⁵⁰ There is excellent agreement with the experimental spectra in non-polar decane (DEC, most comparable to gas phase). The electron density difference between ground and excited states for the $S_0 \rightarrow S_1$ transition, which dominates the first absorption band, is depicted in Fig. 7B for dTBT and CDTBT. The transition is similar in the two compounds and clearly has partial charge transfer character, since electrons are concentrated on the BT unit from a more delocalized HOMO orbital. It should be noted that the carbazole unit in CDTBT does not act as a localized donor with significant hole concentration in the excited state, it rather extends the conjugation of the backbone. Qualitatively very similar TD-DFT results were reported with other functionals (yielding often less good agreement with the experimental spectra), and for larger oligomers.^{137,138,140,142} There is consensus that absorption into the first band of PCDTBT leads to partial charge transfer.

The assignment of the second absorption band, which is generally present in co-polymers containing the dTBT unit, is less clear. It is often considered as a pure $\pi-\pi^*$ transition.¹⁴⁹ TD-DFT calculations on the CDTBT monomer predict several transitions in the vicinity of the second band (Fig. 7A), which are quite delocalized with some weak charge transfer components.^{137,142,150} The contribution of ICT to the higher absorption band of the PCDTBT polymer has recently been experimentally challenged.¹⁵¹ What seems to be established in any case is that the electron and hole distributions in the second band are more spread out over the entire repeat unit, rather than localized on the donor or acceptor unit. In agreement with this, resonance Raman spectroscopy on PCDTBT has shown an enhancement of all Raman peaks (donor and acceptor) with high energy excitation, while the modes on the

BT acceptor were more enhanced by excitation in the first band, due to electron concentration on this unit during ICT.¹³⁸

The transitions in each repeat unit couple together when they are linked to form the polymer. This leads to a reduction of the bandgap because the HOMO and LUMO levels become respectively destabilized and stabilized with increased conjugation length.¹⁴² Moreover, calculations on increasingly long oligomers of PCDTBT show that the density of states near the frontier orbitals increases upon polymerization, so that higher energy, more delocalized orbitals can be reached, leading to a more diffused nature of the excited state (up to 10 nm).¹³⁸ We note that the 0.2 eV red shift when going from the CDTBT repeat unit to the PCDTBT polymer is relatively small (Fig. 5A and 7A).¹³⁷ Indeed, the bandgap of PCDTBT is about 1.9 eV lower than the one of isolated BT. 75% of the bandgap is already reduced in dTBT, 15% more when CB is linked to dTBT to form the repeat unit, and only 10% more upon polymerization. The small polymerization effect is mainly ascribed to the large size of the repeat unit, which has already extended conjugation over five aromatic rings, so that saturation is reached more quickly when more units are added. The partial electron localization on the BT unit in the LUMO level might also prevent effective coupling of this orbital amongst monomers, and conjugation might be reduced by the (calculated) 26° twist angle between the CB and dTBT planes. Additional blue shift for a PCDTBT derivative with bulky side chains occurred upon increase of the twist angle.¹⁵²

3.3 Charge-transfer relaxation

Let us now discuss how ICT character intervenes in the relaxation of photoexcited D-A copolymers. Scholes *et al.* have

investigated the excited state evolution of dissolved PCDTBT and PBDTPD (poly(benzo[1,2-*b*:4,5-*b'*]dithiophene-*alt*-thieno[3,4-*c*]pyrrole)-4,6-dione, Fig. 5B) on the <1 ps time scale using two-dimensional electronic spectroscopy (2D-ES) with extremely high time resolution.¹⁵³ Only for PCDTBT, they observed an increase of dipole moment during relaxation, *i.e.* a <200 fs increase of ICT character and thus weakening of electron–hole correlation. Experimentally, this was seen as an inter-conversion between off-diagonal excited state absorption peaks in the two-dimensional spectra, assigned to states with weaker and stronger ICT character, respectively. Concomitantly, the ground state bleach shifted to the red, because the neighbouring polymer environment became more polar (dynamic Stark effect).

As a further support for charge transfer relaxation, the emission spectrum of PCDTBT was found to be more affected by solvent polarity than the absorption spectrum.¹⁵³ In contrast, the steady-state spectra of PBDTPD (also a D–A copolymer) did not depend on the solvent and no increase in ICT character was visible in the 2D-ES spectra. This can be rationalized by considering that ultrafast torsional relaxation in PCDTBT mediates the increase in the dipole moment by changing the coupling between the donor and acceptor units. According to quantum chemical calculations, PBDTPD is quite planar in the ground state (explaining the presence of vibrational structure in the absorption spectrum, Fig. 5B),¹⁴² so that little change in torsional conformation when going to the excited state is expected (as can be seen by the small Stokes shift). Hence, no charge transfer relaxation occurs and the excited state remains weakly polar. On the other hand, PCDTBT is twisted and has torsional disorder in the ground state. By selectively exciting more planar segments at the very band edge, the state with higher ICT character was directly reached, while excitation at the absorption maximum (more twisted chains) led to the above-mentioned charge transfer relaxation within 200 fs.

The significant phenomenon of charge transfer relaxation in PCDTBT reported by Scholes *et al.* is difficult to investigate in detail and using more conventional techniques, because of the limited polymer solubility and the experimentally rather inaccessible ~200 fs time scale.¹⁵³ Banerji *et al.* used the isolated repeat unit CDTBT to overcome those difficulties.¹⁵⁰ Not only is CDTBT soluble in most organic solvents, but relaxation is slowed down in a reduced density of states compared to the polymer. The solvatochromic behavior that Scholes *et al.* observed for PCDTBT was confirmed in the monomer, with a correlation of the emission maximum with solvent polarity (Fig. 7A and C). On the other hand, a plot of the first two absorption maxima revealed a linear dependence on the Onsager function of the refractive index but no correlation with the polarity function. Absorption is thus dominated by dispersion interactions. The lack of polarity effects can be explained by a small permanent dipole in the ground state (no ICT) and also indicates that the increase of ICT character predicted by TD-DFT upon absorption is rather moderate. In contrast, a strong dipole moment in the emitting state (10.1 Debye) was estimated from the slope of the emission polarity dependence, pointing to an increase of charge transfer during relaxation. The strong ICT character after relaxation is also confirmed by the fluorescence

quantum yield. This drops from 87% in DEC to 75% in *o*-dichlorobenzene (DCB) to 56% in acetonitrile (ACN), consistent with stabilization of partial charges, leading to a decreased overlap of the electron–hole distributions and hence to reduced oscillator strength of the transition. We note that the relatively high emission even in ACN confirms partial ICT in the relaxed excited state, not the formation of separate charges.

The charge transfer relaxation in CDTBT was directly visualized using femtosecond TA spectroscopy.¹⁵⁰ In non-polar DEC there was practically no evolution of the ground state bleach (GSB), stimulated emission (SE) and excited state absorption (ESA) features within the 1 ns window of the experiment, pointing to negligible relaxation (Fig. 7D). However, in the more polar solvents (DCB and ACN), there was a red shift of the SE and a concomitant transition of the ESA from the single peak also observed in DEC to a double-peaked feature. The spectral changes were ascribed to charge transfer relaxation in the excited state, from a moderately polar directly excited form to a relaxed form with pronounced ICT character, stabilized by solvent polarity. The time scale of the transition was slower in viscous DCB (biexponential with 3.5 ps and 22.4 ps time constants) than in non-viscous ACN (0.8 ps), thus closely following the solvation time reported for the two solvents.¹⁵⁴ Therefore, solvent rearrangements seem to dominate the charge transfer relaxation, although torsional relaxation (planarization) might also play a role, as shown by excited state geometry relaxation using TD-DFT calculations. In the ground state of CDTBT, the thiophenes are rotated by about 15° with respect to the BT unit, while the dihedral angle between the thiophene and carbazole is around 29°. Those angles respectively relax to ~0° and 16° in the emitting state.

The density of electronic and vibrational states in the PCDTBT polymer is much higher than in the monomer, and in this case Scholes *et al.* showed that torsions (not solvent) dominate the <200 fs charge transfer relaxation.¹⁵³ Unlike in the polymer, the relaxation in the CDTBT repeat unit had no dependence on excitation wavelength (within the first absorption band) and occurred similarly after excitation in the second band, following unresolved internal conversion.¹⁵⁰ Very interestingly, Banerji *et al.* observed the charge transfer relaxation in CDTBT also in the solid state (thin film) within only 1.2 ps, where neighboring molecules replace the solvent. This shows that the necessary intramolecular and intermolecular rearrangements are possible and fast, as well as that the environment is sufficiently polar. Moreover, there was in this case evidence for intermolecular delocalization and possibly for evolution from the partial intramolecular charges to separate charges between neighboring molecules (this is still under investigation).

3.4 Charges in D–A copolymers

There is recent experimental evidence that ICT character in the excited state of D–A copolymers promotes the formation of separate charges (polarons) within the polymer chain.^{155–157} The decreased overlap of the electron and hole distributions might also favor the generation of free charges in bulk heterojunction

blends.^{157–159} In addition to a low bandgap, this might explain the success of D–A copolymers in organic solar cells.

Scherf *et al.* identified polaron signatures in a series of D–A copolymers and P3HT by chemical doping.¹⁵⁶ They then investigated the formation of polaron pairs (more separated electrons and holes with weaker Coulomb attraction) in thin films of the neat polymers by femtosecond TA spectroscopy with near-IR probing. Both neutral excitons and polaron pairs were found to originate from the primary excited state within the 150 fs time resolution and they had uncorrelated dynamics. The yield of polaron pairs was estimated and was systematically higher in the co-polymers (up to 24%) than in P3HT. Moreover, polymers with stronger acceptor units or closer distance between the donor and acceptor (no thiophene between the two) formed more polaron pairs, which nevertheless also recombined faster on the <3 ps time scale. The authors concluded that short-lived polaron-pairs might be beneficial to separate charges in BHJ devices (by lowering the required LUMO offset with the fullerene), especially for intimately mixed morphologies. They noted nevertheless that too strong localization of the charge carriers on the donor or acceptor might cause fast recombination and poor mobility, which is a disadvantage for bulk heterojunctions with large polymer domains requiring diffusion and/or delocalization to reach an interface.

Along the same lines, Chen *et al.* investigated a series of D–A copolymers with alternating thieno[3,4-*b*]thiophene and benzodithiophene moieties and varying number/position of pendant fluorine atoms (PTBF series) in solution.¹⁵⁷ The calculated HOMO and LUMO levels of model tetramers were generally quite delocalized, with some concentration on the donor and acceptor end, respectively. Experimentally, intramolecular splitting of the neutral excited state, largely within the 160 fs time resolution, was observed. Interestingly, this occurred to two distinct non-sequential states: a more bound pseudo-charge-transfer (PCT) state and a fully charge-separated (CS) state, Fig. 8. Even if this partial or full charge separation occurred between entire fragments of the PTBF chains and not just between the localized donor and acceptor monomers, it seemed to be favored by stronger local ICT character (*i.e.* a larger difference in electronegativity between the donor and acceptor units). More importantly, a correlation between the ratio of CS/PCT branching in the polymers and the photovoltaic efficiency in corresponding polymer:fullerene bulk heterojunction devices was found, confirming the advantage of charge separation within a D–A polymer chain for device functioning. Yu *et al.* also explained the low photovoltaic efficiency in related copolymers by the absence of large ICT character during absorption.^{158,159} A clear dependence of photovoltaic efficiency on the calculated difference of the ground and excited state net dipole moments in the D–A repeat unit was found. This supports the picture that polarization in the excited state lowers the binding of the electron and hole, favoring faster and more complete charge separation at a BHJ interface and reducing geminate recombination.

We saw that delocalization also plays an essential role in the generation of free charge carriers. A delicate balance between the two effects must be achieved for high solar cell efficiency,

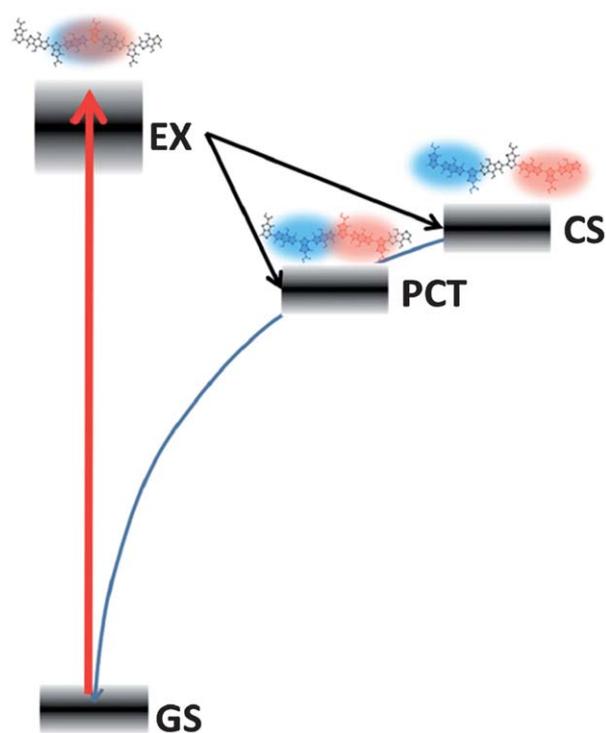


Fig. 8 Ultrafast dissociation of the neutral excited state (EX) to the pseudo-charge-transfer (PCT) state and charge-separated (CS) state observed by Chen *et al.* for PTBF polymers. Reprinted with permission from ref. 157. Copyright 2012 American Chemical Society.

and this depends on the case-to-case morphology of the system. We tentatively suggest that delocalization plays the main role in systems such as P3HT or PBDTTPD, where excited state ICT is less important. For PCDTBT, the primary photoexcitation is moderately polarized, but remains considerably delocalized. It is likely that the electron is transferred to the fullerene at this point, before charge transfer relaxation in the polymer phase occurs. In polymers such as the PTBF series, experimental evidence shows the essential role of intramolecular dipoles. Finally, extremely high electronegativity differences between the donor and acceptor can lead to very localized electrons and holes, which is possibly a disadvantage for solar cells. This might explain why PCDTBT performs better in solar cells compared to related carbazole copolymers with stronger electron acceptors, although higher efficiency was expected from their energy levels.¹³³

3.5 Take-home message

The development of conjugated donor–acceptor copolymers introduces new possibilities to control functionality for organic electronic applications through charge transfer character in the ground and excited states. A thorough understanding of intramolecular dipoles and their evolution during excited state relaxation is necessary in order to fully exploit this opportunity. This can be achieved by studying oligomeric model systems. Charge transfer character in D–A copolymers does not necessarily contradict delocalization by strongly localizing the

electron and hole distributions of the excited state on the acceptor and donor units. For example in PCDTBT, the HOMO level remains delocalized over the backbone. Additionally, delocalized states above the bandgap can be reached in the extended conjugated system. Initial delocalization in the excited state, as was discussed for homopolymers, can therefore also occur in D–A copolymers. Finally, given a good balance with delocalization effects, intramolecular charge transfer in the polymer lowers the binding of the electron and hole, which helps the generation of free charges in solar cells.

4 Conclusion

In summary, we have seen that the binding of the electron and hole in the excited state of organic semiconductors presents a bottleneck to the efficient generation of free charge carriers in solar cells. Two factors have been identified that help to overcome this setback: excited-state delocalization and donor–acceptor dipoles in the neat polymer phase. Both effects exist mainly on a very short (possibly sub-picosecond) time scale, but this is sufficient because charge transfer to a fullerene at an interface is also ultrafast. They reduce the overlap of the electron and hole distributions, thus favoring their full dissociation. Moreover, delocalization can help the excited state to reach an interface in the case of large polymer domains.

The essential role of delocalization and intramolecular dipoles has only started to transpire in the past year. Targeted research in the field is now required to gain full understanding of the effects and to optimize design rules for future materials with even higher efficiency in photovoltaic devices.

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