Theory of Primary Photoexcitations in Donor-Acceptor Copolymers

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Theory of primary photoexcitations in donor-acceptor copolymers

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We present a generic theory of primary photoexcitations in low bandgap donor-acceptor conjugated copolymers. Due to the combined effects of strong electron correlations and broken symmetry, there is considerable mixing between a charge-transfer exciton and an energetically proximate triplet-triplet state with overall spin singlet. The triplet-triplet state, optically forbidden in homopolymers, is allowed in donor-acceptor copolymers. For intermediate difference in electron affinities of the donor and the acceptor, the triplet-triplet state can have stronger oscillator strength than the charge-transfer exciton. We discuss the possibility of intramolecular singlet fission from the triplet-triplet state, and how such fission can be detected experimentally.

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The primary photophysical process in polymer solar cells is photoinduced charge transfer (PICT), whereby optical excitation at the junction between a donor conjugated polymer and acceptor molecules creates a CT exciton whose dissociation leads to charge carriers. The donor polymeric materials used to be homopolymers such as polythiophene which absorb in the visible range of the solar spectrum [1]. Homopolymers have recently been replaced by block copolymers whose repeat units consist of alternating donor (D) and acceptor (A) moieties [2–11]. This architecture reduces the optical gap drastically, and the DA copolymers absorb in the near infrared, where the largest fraction of the photons emitted by the sun lie. The power conversion efficiencies (PCEs) of organic solar cells with DA copolymers as donor materials have exceeded 10% [11], and there is strong interest in the development of structure-property correlations that will facilitate further enhancement of the PCE. Clearly, this requires precise understanding of the nature of the primary photoexcitations of DA copolymers.

Existing electronic structure calculations of DA copolymers are primarily based on the DFT approach or its time-dependent version (TD-DFT) [12–18]. The motivations behind these calculations have largely been to understand the localized versus delocalized character of the excited state reached by ground state absorption. Experimentally, DA copolymers exhibit a broad low energy (LE) absorption band at ∼ 700-800 nm and a higher energy (HE) absorption band at ∼ 400-450 nm [2–4]. There is agreement between the computational studies that the LE band is due to CT from D to A, and the HE band is a higher $\pi - \pi^*$ excitation.

Recent optical studies indicate that the above simple characterization of the LE band might be incomplete, and as in the homopolymers [19], electron correlations play a stronger role in the photophysics of the DA copolymers than envisaged within DFT approaches. Grancini et al. determined from ultrafast dynamics studies that the broad LE band in PCPDT-BT (see Supplemental Material [20] for the structures of this and other DA copolymers) is composed of *two* distinct absorptions [23, 24] centered at 725 nm and 650 nm. TD-DFT calculations assign these to the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ excitations, with however the oscillator strength of the second transition smaller by more than an order of magnitude [24]. Two transitions underlying the LE bands in copolymers with CPDT as the donor have been postulated also by Tautz et al. [25]. Huynh et al. have performed transient absorption study of the DA copolymer PTB7, with optical gap ∼ 1.6 eV [26]. With the pump energy at 1.55 eV these authors found two distinct photoinduced absorptions (PAs) with the same dynamics, PA_1 at 0.4 eV and PA_2 at 0.96 eV. This is in sharp contrast to homopolymers, where only PA_1, but not PA_2, is observed. Comparing against steady state PA measurements, Huynh et al. showed that, (a) PA_2 is not a polaron absorption, and (b) PA_2 overlaps strongly with PA from the lowest *triplet* exciton, PA_{T_1} [see Figs S2(a) and S2(b) in Supplemental Material [20]]. These authors have obtained nearly identical results for a different DA copolymer PDTP-DFBT [27]. Busby et al. have reported triplet exciton generation in picosecond (ps) time scale from transient absorption measurement of the DA copolymer PBTDO1 [28]. The transient absorption observed is the equivalent of the higher energy PA_2 absorption of Huynh et al. [26] [see Fig. 3 Ref. [28]]. No measurement in the low energy region corresponding to PA_1 was reported. The authors suggested that the triplets are generated by intramolecular singlet fission (iSF) of the optical CT exciton. SF is the process by which an optical singlet exciton dissociates into two triplet excitons with energies half or less than that of the singlet exciton, and is currently being intensively investigated, as a mechanism for doubling the number of photocarriers in organic solar cells [29]. Busby et al. noted the absence of iSF in PFTDO1, which has the same acceptor as PBTDO1 but a weaker donor [20], in spite of the singlet and triplet energies satisfying the condition for iSF. The authors concluded that iSF requires strong CT character of the LE excitation [28].

The above experimental results, in particular, the possibility of iSF indicate that the theoretical treatment of DA copolymers must incorporate electron correlation effects beyond TD-DFT. This is because iSF proceeds via a highly correlated two electron−two hole (2e-2h) triplet-triplet (TT) state, which is not captured by TD-DFT [30, 31]. Intramolecular TT states have been extensively discussed for linear polyenes, where the lowest TT state, the $2^1\mathrm{A}_g^-$ occurs below the optical $1^1\mathrm{B}_u^+$ state [32]; precise description of 2e-2h states here require configuration interaction (CI) calculations that include configurations quadruply excited from the Hartree-Fock (HF) ground state [32–35]. Unfortunately, the large and complex repeat units of the DA copolymers [20] preclude quadruple configuration interaction (QCI) calculations and many-body techniques such as the density matrix renormalization group. Furthermore, our goal is not to explain the behavior of individual DA copolymers, but to develop a broad theoretical framework within which structure-property correlations may be sought. We construct here an *effective* correlated-electron theory for DA copolymers that takes both these issues into consideration.

Generic theoretical models of π-conjugated homopolymers treat systems with aromatic groups or heteroatoms as *"dressed"* polyacetylenes [36–38], with modified carbon (C)−atom site energies [37] and C−C bond strengths [38]. The goal is to understand low energy excitations near the optical gap. Effective theories miss effects due to torsional motion of the aromatic groups, or high energy excitations involving molecular orbitals (MOs) localized on the aromatic groups. They do, however, capture the essential photophysics near the optical gap, which is determined almost entirely by excitations from the highest valence band to the lowest conduction band. We adopt the same approach here.

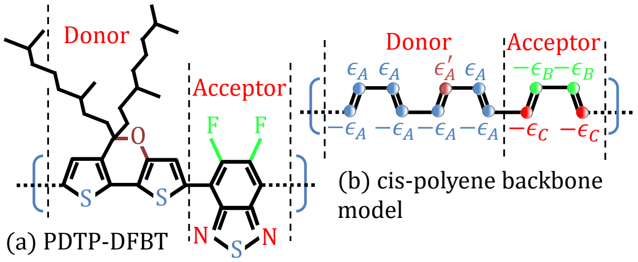

FIG. 1: (color online). (a) PDTP-DFBT monomer. (b) The effective cis-polyene with the same π-conjugation path as PDTP-DFBT. The C-atom site energies reflect the inductive effects of groups directly bonded to these atoms in PDTP-DFBT (see text).

We begin by developing an effective model for the DA copolymer PDTP-DFBT, which when blended with $\mathrm{PC_{71}BM}$ has given the highest PCE in tandem solar cells [7]. We will point out the generic nature of our theory later. The repeat unit of PDTP-DFBT is shown in Fig. 1(a). The effective model cis-polyene expected to mimic the behavior of PDTP-DFBT is shown in Fig. 1(b). The effective polyene has the same C-C π-conjugation path as the conjugated backbone of PDTP-DFBT, with C-atom site energies determined by the electron affinities of the groups bonded to them in PDTP-DFBT. We investigate the monomer and dimer of the effective cis-polyene within the Pariser−Parr−Pople (PPP) π-electron only Hamiltonian [39, 40],

$$H_{\mathrm{PPP}} = -\sum_{\langle ij\rangle\sigma} t_{ij}(\hat{c}_{i\sigma}^{\dagger}\hat{c}_{j\sigma} + \hat{c}_{j\sigma}^{\dagger}\hat{c}_{i\sigma}) + U\sum_{i}\hat{n}_{i\uparrow}\hat{n}_{i\downarrow} + \sum_{i<j} V_{ij}(\hat{n}_i - 1)(\hat{n}_j - 1) + \sum_{i}\epsilon_i\hat{n}_i\,, \qquad (1)$$

where $\hat{c}_{i\sigma}^{\dagger}$ creates a π-electron of spin σ on C atom i, $\hat{n}_{i\sigma} = \hat{c}_{i\sigma}^{\dagger}\hat{c}_{i\sigma}$ is the number of electrons with spin σ on C atom i, $\hat{n}_i = \sum_{\sigma}\hat{n}_{i\sigma}$ and ϵ_i the site energy. We use standard nearest neighbor hopping integrals $t_{ij} = 2.2$ (2.6) eV for single (double) C-C bonds. U is the Coulomb repulsion between two π electrons on the same C atom, and V_{ij} is the intersite Coulomb interaction. We parametrize the Coulomb interactions as $V_{ij} = U/\kappa\sqrt{1 + 0.6117R_{ij}^2}$, where R_{ij} is the distance in Å between C atoms i and j, and choose $U = 8$ eV, $\kappa = 2$ [41]. We have chosen fixed $\epsilon_{\mathrm{A}} = 0.5$ eV [37] and $\epsilon_{\mathrm{A}}' = 1.0$ eV, and larger ϵ_{B} and ϵ_{C} to reproduce the acceptor character of the DFBT group. We fix $\epsilon_{\mathrm{B}}/\epsilon_{\mathrm{C}} = 3/2$, but vary ϵ_{B} to simulate the variation of the extent of CT. In the following, nonzero ϵ_{B} implies that all other site energies are also nonzero.

In Fig. 2(a) we have shown the calculated highest occupied and lowest unoccupied HF MOs (HOMOs and LUMOs) for the D and A groups of the "bare" polyene ($\epsilon_{\mathrm{A}} = \epsilon_{\mathrm{A}}' = \epsilon_{\mathrm{B}} = \epsilon_{\mathrm{C}} = 0$). Fig. 2(b) shows the same for nonzero site energies which reproduce the DA character of the system at the HF level. Our calculations of ground and excited state absorptions go beyond HF, and use exact diagonalization (full CI) for the monomer and QCI for the dimer of Fig. 1(b). The C_{2v} and charge-conjugation symmetries of the bare polyene imply distinct one- and two-photon states, with $^1\mathrm{B}_1^+$ and $^1\mathrm{A}_1^-$ symmetries, respectively. Our calculated exact monomer energies of the $1^1\mathrm{B}_1^+$ (3.9 eV) and $2^1\mathrm{A}_1^-$ (3.0 eV) in the bare limit compare very favorably against the experimental gas phase energies [42] of the $1^1\mathrm{B}_u^+$ (3.65 eV) and $2^1\mathrm{A}_g^-$ (2.73 eV) in trans-dodecahexaene, allowing for the small differences expected between the cis and trans configurations, giving us confidence about our PPP parametrization.

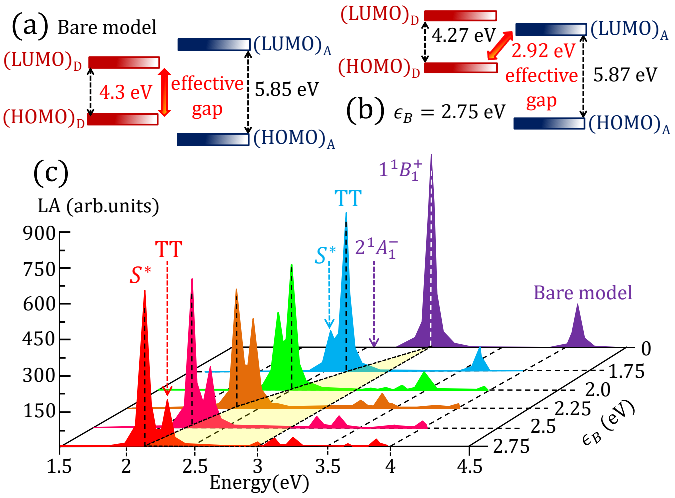

FIG. 2: (color online). PPP-HF HOMO and LUMO of the D and A segments of the monomer of Fig. 1(b) (a) for zero site energies, and (b) for nonzero site energies with $\epsilon_{\rm B} = 2.75$ eV. (c) Ground state absorption spectra of the dimer of Fig. 1(b) for a range of $\epsilon_{\rm B}$, calculated using QCI. The TT state continues to remain optically allowed up to $\epsilon_{\rm B} = 2.75$ eV.

TABLE I: QCI energies (in eV) of the two lowest singlet excited states versus twice the lowest triplet energy $E(\mathrm{T}_1)$, for the dimer of Fig. 1(b), as a function of $\epsilon_{\rm B}$. A TT state exists for all $\epsilon_{\rm B}$. For $\epsilon_{\rm B} > 1.75$ eV TT is at higher energy.

$\epsilon_{\rm B}$	S*	TT	$2\times E(\mathrm{T}_1)$
0 (bare model)	3.01 ($1^1\mathrm{B}_1^+$)	2.58 ($2^1\mathrm{A}_1^-$)	2.56
1	2.81	2.57	2.58
1.75	2.46	2.58	2.52
2	2.40	2.51	2.49
2.125	2.37	2.47	2.48
2.25	2.33	2.44	2.46
2.375	2.28	2.41	2.44
2.5	2.24	2.38	2.41
2.625	2.19	2.35	2.39
2.75	2.14	2.32	2.36

Fig. 2(c) shows our calculated QCI ground state absorption spectra for the dimer of Fig. 1(b) for increasing $\epsilon_{\rm B}$. For $\epsilon_{\rm B} = 0$ allowed absorption is to $1^1\mathrm{B}_1^+$ alone, which is of CT character. We will henceforth refer to the CT exciton as S*. The energy location of the dipole-forbidden $2^1\mathrm{A}_1^-$, which is a quantum-entangled TT state with nearly twice the energy of the lowest triplet exciton $E(\mathrm{T}_1)$ [32–34], is indicated in the figure. For nonzero $\epsilon_{\rm B}$, the C_{2v} symmetry is lost, and considerable configuration mixing occurs. Surprisingly, *in spite of strong configuration mixing, there always exists a TT state at energy* $\sim 2\times E(T_1)$. The decrease in energy of S* with $\epsilon_{\rm B}$ is expected from the HF calculation, but the more interesting result is the decrease in the energy difference between S* and TT and their crossing, when the TT is the higher energy state for $\epsilon_{\rm B} \geq 1.75$ eV. The TT has nonzero oscillator strength and there are two allowed absorptions. For a range of $\epsilon_{\rm B}$ the two absorptions have essentially merged, and their oscillator strengths are comparable. In the parameter range 1.75 eV$\leq \epsilon_{\rm B} \leq 2.125$ eV the TT state actually has larger oscillator strength. For still larger $\epsilon_{\rm B} > 2.25$ eV, the TT moves away from S* and its oscillator strength begins to decrease again. In Table I we have listed the energies of the S* and TT states as a function of $\epsilon_{\rm B}$, for comparison against $2\times E(\mathrm{T}_1)$. We will show below that these theoretical results, especially the intermediate coupling region, are of strong experimental relevance.

Although our calculations are for a specific dressed polyene, similar effective polyene models can be constructed for arbitrary DA copolymers. Indeed, instead of assigning multiple C−atom site energies, a single parameter that differentiates between atoms belonging to D and A groups would be sufficient to derive the generic model, within which the combined effects of electron correlations and broken symmetry give two optically accessible states, S* and TT. We have calculated excited state absorptions from S*, TT and T_1, hereafter $\mathrm{PA}_{\mathrm{S}*}$, $\mathrm{PA}_{\mathrm{TT}}$ and $\mathrm{PA}_{\mathrm{T}_1}$, respectively, for the dimer of Fig. 1(b) to understand the experimental transient and steady state PA measurements [26–28]. These theoretical results are shown in Fig 3, for several different $\epsilon_{\rm B}$. For comparison to the experimental PA spectra of different materials [26–28], we have normalized all PA energies by scaling against the optical gap of 1.55 eV in PDTP-DFBT. For small $\epsilon_{\rm B} \leq 1$ eV, the calculated and experimental [20, 26] $\mathrm{PA}_{\mathrm{TT}}$ spectra are conspicuously different. The calculated $\mathrm{PA}_{\mathrm{TT}}$ and $\mathrm{PA}_{\mathrm{T}_1}$ bands also occur at very different energies for small $\epsilon_{\rm B}$. Only for $\epsilon_{\rm B} \geq 1.75$ eV, the calculated $\mathrm{PA}_{\mathrm{TT}}$ resembles the experimental two-band transient $\mathrm{PA}_{\mathrm{TT}}$ shown in Supplemental Material, Fig. S2(a) [20, 26, 27]. In the region 1.75 eV $\leq \epsilon_{\rm B} \leq$ 2.25 eV in Fig. 2(c), the energy difference between S* and TT states for the dimer of Fig. 1(b) (corresponding to the two-unit oligomer of the PDTP-DFBT copolymer) is negligible (see Table I). This energy difference in the long chain limit will be vanishing relative to the C-C stretching frequency. The two optical states therefore lie within the "phonon bath" of the copolymer and will even be coupled by electron-phonon interactions ignored within our purely electronic model. Thus, experimental PA_1 is from both states but PA_2 is from TT alone (see also below). It is also worth noting that the two PA bands are correlated since they show the same dynamics and magnetic response [27].

Quantum chemical calculations of DA copolymers structurally related to PDTP-DFBT find the LUMO-LUMO offset to be nearly equal to and sometimes even larger than the HOMO-HOMO offset for copolymers with BT [12–18]. We report additional calculations for the model polyene in the Supplemental Material, where the

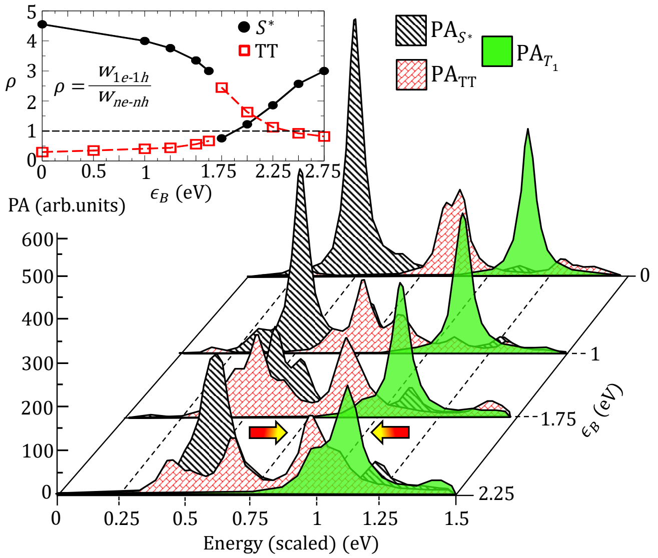

FIG. 3: (color online). Calculated $\mathrm{PA}_{\mathrm{S}^*}$, $\mathrm{PA}_{\mathrm{TT}}$ and $\mathrm{PA}_{\mathrm{T}_1}$ for the dimer of Fig. 1(b) for different ϵ_{B}. The arrows indicate nearly complete overlap between the higher energy component of $\mathrm{PA}_{\mathrm{TT}}$ and $\mathrm{PA}_{\mathrm{T}_1}$ at $\epsilon_{\mathrm{B}} = 2.25$ eV. The inset shows the ratio of the relative weights of 1e−1h and ne−nh (n> 1) excitations to the QCI wavefunctions of S* (circles) and TT (squares) states. The cross-over at $\epsilon_{\mathrm{B}} = 1.75$ eV is evident.

LUMO-LUMO and HOMO-HOMO offsets for the substituted polyene are nearly identical in magnitudes to those reported in Ref. [12]. The results of these calculations are nearly the same as in Figs. 2(c) and 3, showing very clearly that no generality is lost by particular choice of MO offsets. For each DA pair, there exist offsets where TT is optically allowed and PA_2 is close to $\mathrm{PA}_{\mathrm{T}_1}$. Conversely, two PAs, with PA_2 close to $\mathrm{PA}_{\mathrm{T}_1}$ require that S^* and TT be nearly degenerate. PA_1 is from both states and PA_2 is from higher energy state.

S^* and TT will occur as distinct absorptions in the polymeric limit if their natures are qualitatively different. The extent to which their wavefunctions of the optically allowed S^* and TT differ is therefore of interest. The QCI excited state wavefunctions are superpositions of excitations from the HF ground state. In the bare polyene limit the S^* state is predominantly 1e−1h whereas the TT has larger contributions from ne−nh excitations (n>1) [31, 34]. The inset of Fig. 3 shows the ratio ρ of the relative weights of 1e−1h versus ne−nh excitations in the S^* and TT states as a function of ϵ_{B}. The intermediate magnitude of ρ of the TT state at moderate ϵ_{B} is a signature of its partial CT character. In the theoretical literature, the discussion of the intramolecular TT state, the $2^1\mathrm{A}_g^-$, has been almost entirely in the context of polyenes [32–34] or polydiacetylenes [43]. Within valence bond theory, the dipole-forbidden character of the $2^1\mathrm{A}_g^-$ results from its covalent character [32–34]. The ionicity of the TT versus S^* are of interest here, in view of the dipole-allowed character of the TT state. One measure of the ionicity is $\langle n_{i,\uparrow} n_{i,\downarrow}\rangle$, the probability that the p_z-orbital of C-atom i is doubly occupied with electrons. Exact $\langle n_{i,\uparrow} n_{i,\downarrow}\rangle$ for the 12-atom monomer of Fig. 2(b) for both the S^* and TT states as a function of ϵ_{B} are shown in Fig. 4. The asymmetry of $\langle n_{i,\uparrow} n_{i,\downarrow}\rangle$ about the chain center is indicative of the CT character of S^*. There is little change of $\langle n_{i,\uparrow} n_{i,\downarrow}\rangle$ in S^* for this range of ϵ_{B}. In the TT state however, $\langle n_{i,\uparrow} n_{i,\downarrow}\rangle$ increases steeply with ϵ_{B} on the C-atoms constituting the acceptor (the C-atoms constituting the D group become positively charged, which is not measured by $\langle n_{i,\uparrow} n_{i,\downarrow}\rangle$). *Covalent character is thus not a requirement for a state to be TT, as is commonly presumed.* In addition to their ionicities, S^* and TT also differ in their bond orders, which are discussed in the Supplemental Material [20].

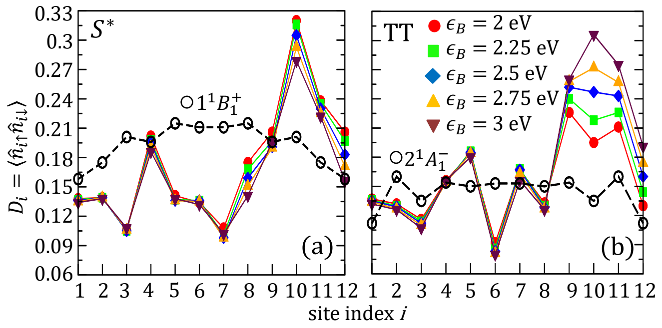

FIG. 4: (color online). Double occupancies by electrons of individual C-atom p_z orbitals of the monomer of Fig. 1(b), for different ϵ_{B}: (a) S^*, (b) TT. The results for $1^1\mathrm{B}_1^+$ and $2^1\mathrm{A}_1^-$ states of the bare polyene are given for comparison.

The peculiarities noted in ultrafast spectroscopic measurements of different DA copolymers [23, 24, 26–28] are all explained within our generic theory. Two close-lying ground state absorptions [23, 24] and two distinct transient PA bands, with strong overlap between PA_2 and $\mathrm{PA}_{\mathrm{T}_1}$ [20, 26, 27] simply require an optical TT state, [see Figs. 2(c) and 3], which in turn requires both strong electron correlations and broken spatial symmetry. The two peculiar observations of Busby et al. are: (i) absence of triplet generation in PFTDO1 with a weaker donor than PBTDO1, and (iii) ultrashort lifetimes of the triplets generated by photoexcitation: their lifetimes are four orders of magnitude shorter than the lifetimes of the triplets generated by sensitization. The explanations of these observations are as follows (i) Weak donor implies small ϵ_{B} in Figs. 2(c) and 3; in this case the TT state is not optically accessible and the apparent iSF is not expected. (ii) The short lifetimes of the triplets generated through photoexcitation are to be expected. Either the TT state does not undergo dissociation into individual T_1 at all, or the partially separated T_1 pairs recombine to the TT state.

In summary, the photophysics of DA copolymers indicate the combined effects of strong electron correlations and broken symmetry. In the single chain limit iSF leading to complete separation into individual triplet excitons is unlikely, although this can occur in an aggregate or at long times. Experimental verification of iSF would require the instrumental capability to perform transient PA experiments in the full frequency range covering both PA_1 and PA_2: the occurrence of a single PA band, as opposed to two, would indicate iSF. How the optically allowed character of TT in DA polymers influences PCEs of solar cells is an intriguing question and the topic of future research.

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