

Theory of Primary Photoexcitations in Donor-Acceptor Copolymers

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We present a generic theory of primary photoexcitations in low band gap donor-acceptor conjugated copolymers. Because of 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 an overall spin singlet. The triplet-triplet state, optically forbidden in homopolymers, is allowed in donor-acceptor copolymers. For an intermediate difference in electron affinities of the donor and the acceptor, the triplet-triplet state can have a 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, whereby optical excitation at the junction between a donor conjugated polymer and acceptor molecules creates a charge transfer (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 Homopolymers have recently been replaced by block copolymers whose repeat units consist of alternating donor (*D*) and acceptor (*A*) moieties [2–11].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 density-functional theory (DFT) approach or its time-dependent version (TD-DFT) [12–18]. The motivations behind these calculations have largely been to understand the localized vs 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 π - π^* 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 the Supplemental Material [20] for the structures of this and other *DA* copolymers) is composed of *two* distinct absorptions [23,24] centered at 725 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 a transient absorption study of the *DA* copolymer PTB7, with an 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, PA₁ at 0.4 eV and PA₂ at 0.96 eV. This is in sharp contrast to homopolymers, where only PA₁, not PA₂, is observed. Comparing against steady state PA measurements, Huynh *et al.* showed that (a) PA₂ is not a polaron absorption and (b) PA₂ overlaps strongly with PA from the lowest *triplet* exciton, PA_{T₁} [see Figs. S2(a) and S2(b) in the 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 a picosecond time scale from a transient absorption measurement of the *DA* copolymer PBTDO1 [28]. The transient absorption observed is the equivalent of the higher energy PA₂ absorption of Huynh *et al.* [26] (see Fig. 3 in Ref. [28]). No measurement in the low energy region corresponding to PA₁ 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 it 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 the 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, $2^1A_g^-$, occurs below the optical $1^1B_u^+$ state [32]; a precise description of $2e$ - $2h$ states here requires 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 rather 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 of 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 the 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.

We begin by developing an effective model for the *DA* copolymer PDTP-DFBT, which when blended with PC₇₁BM 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 the C-atom site energies determined by the electron affinities of the groups bonded to them in PDTP-DFBT. We investigate the

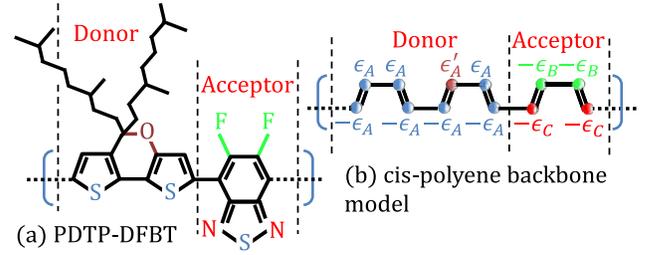


FIG. 1 (color online). (a) PDTP-DFBT monomer. (b) The effective cis-polyene with the same π conjugation path as PDTP-DFBT. The C-atom site energies reflect the inductive effects of groups directly bonded to these atoms in PDTP-DFBT (see the text).

monomer and the dimer of the effective cis-polyene within the Pariser-Parr-Pople (PPP) π -electron-only Hamiltonian [39,40],

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

where $\hat{c}_{i\sigma}^\dagger$ creates a π electron of spin σ on the 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 the 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 angstroms between C atoms i and j , and choose $U = 8$ eV, $\kappa = 2$ [41]. We have chosen fixed $\epsilon_A = 0.5$ eV [37] and $\epsilon'_A = 1.0$ eV and larger ϵ_B and ϵ_C to reproduce the acceptor character of the DFBT group. We fix $\epsilon_B/\epsilon_C = 3/2$ 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 ($\epsilon_A = \epsilon'_A = \epsilon_B = \epsilon_C = 0$). Figure 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 they 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 $1^1B_1^+$ and $1^1A_1^-$ symmetries, respectively. Our calculated exact monomer energies of the $1^1B_1^+$ (3.9 eV) and $2^1A_1^-$ (3.0 eV) in the bare limit compare very favorably against the experimental gas phase energies [42] of the $1^1B_u^+$ (3.65 eV) and $2^1A_g^-$ (2.73 eV) in

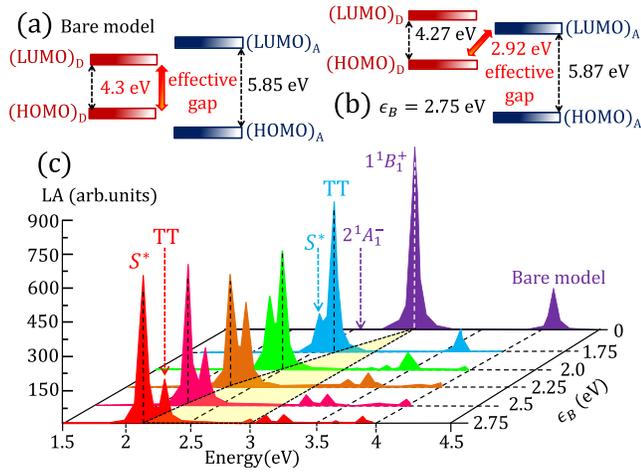


FIG. 2 (color online). PPP-HF HOMO and LUMO of the D and A segments of the monomer of Fig. 1(b) (a) for zero site energies and (b) for nonzero site energies with $\epsilon_B = 2.75$ eV. (c) Ground state absorption spectra of the dimer of Fig. 1(b) for a range of ϵ_B , calculated using QCI. The TT state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

trans-dodecahexaene, allowing for the small differences expected between the cis- and trans-configurations, giving us confidence in our PPP parametrization.

Figure 2(c) shows our calculated QCI ground state absorption spectra for the dimer of Fig. 1(b) for increasing ϵ_B . For $\epsilon_B = 0$, the allowed absorption is to $1^1B_1^+$ alone, which is of CT character. We will henceforth refer to the CT exciton as S^* . The energy location of the dipole-forbidden $2^1A_1^-$, which is a quantum-entangled TT state with nearly twice the energy of the lowest triplet exciton $E(T_1)$ [32–34], is indicated in the figure. For nonzero ϵ_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 ϵ_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 $\epsilon_B \geq 1.75$ eV. The TT has nonzero oscillator strength and there are two allowed absorptions. For a range of ϵ_B the two absorptions have essentially merged, and their oscillator strengths are comparable. In the parameter range $1.75 \text{ eV} \leq \epsilon_B \leq 2.125$ eV, the TT state actually has a larger oscillator strength. For still larger $\epsilon_B > 2.25$ 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 ϵ_B , for comparison against $2 \times E(T_1)$. 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

TABLE I. QCI energies (in eV) of the two lowest singlet excited states vs twice the lowest triplet energy $E(T_1)$, for the dimer of Fig. 1(b), as a function of ϵ_B . A TT state exists for all ϵ_B 's. For $\epsilon_B > 1.75$ eV, TT is at higher energy.

ϵ_B	S^*	TT	$2 \times E(T_1)$
0 (bare model)	3.01 ($1^1B_1^+$)	2.58 ($2^1A_1^-$)	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

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 PA_{S^*} , PA_{TT} and PA_{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 ϵ_B 's. For comparison to the experimental PA spectra of different materials [26–28],

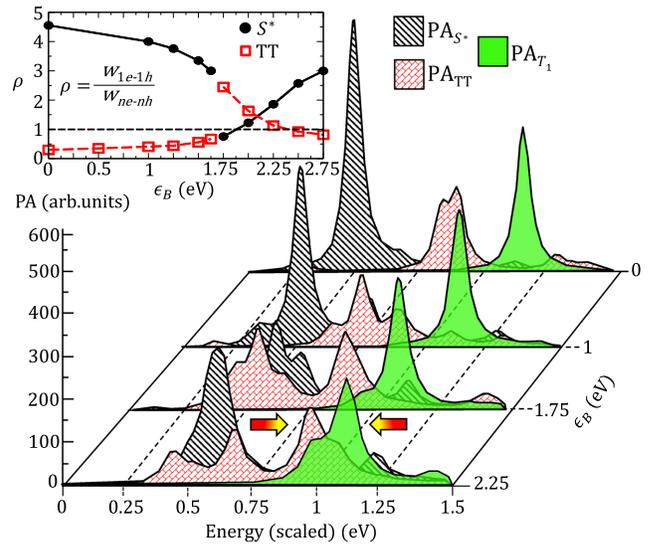


FIG. 3 (color online). Calculated PA_{S^*} , PA_{TT} and PA_{T_1} for the dimer of Fig. 1(b) for different ϵ_B 's. The arrows indicate a nearly complete overlap between the higher energy component of PA_{TT} and PA_{T_1} at $\epsilon_B = 2.25$ eV. (Inset) The ratio of the relative weights of $1e-1h$ and $ne-nh$ ($n > 1$) excitations to the QCI wave functions of S^* (circles) and TT (squares) states. The crossover at $\epsilon_B = 1.75$ eV is evident.

we have normalized all PA energies by scaling against the optical gap of 1.55 eV in PDTP-DFBT. For small $\epsilon_B \leq 1$ eV, the calculated and experimental [20,26] PA_{TT} spectra are conspicuously different. The calculated PA_{TT} and PA_{T_1} bands also occur at very different energies for small ϵ_B 's. Only, for $\epsilon_B \geq 1.75$ eV, the calculated PA_{TT} resembles the experimental two-band transient PA_{TT} shown in Fig. S2(a) of the Supplemental Material [20,26,27]. In the region $1.75 \text{ eV} \leq \epsilon_B \leq 2.25 \text{ eV}$ in Fig. 2(c), the energy difference between the 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 [20], where the LUMO-LUMO and HOMO-HOMO offsets for the substituted polyene are nearly identical in magnitude 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 the particular choice of MO offsets. For each DA pair, there exist offsets where TT is optically allowed and PA_2 is close to PA_{T_1} . Conversely, two PAs, with PA_2 close to PA_{T_1} require that S^* and TT be nearly degenerate. PA_1 is from both states and PA_2 is from the 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 the wave functions of the optically allowed S^* and TT differ is therefore of interest. The QCI excited state wave functions are superpositions of excitations from the HF ground state. In the bare polyene limit the S^* state is predominantly a $1e-1h$ one, whereas the TT has larger contributions from the $ne-nh$ 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 a moderate ϵ_B is a signature of its partial CT character. In the theoretical literature, the discussion of the intramolecular TT state, the $2^1A_g^-$, has been almost entirely in the context of polyenes [32–34] or polydiacetylenes [43]. Within valence bond theory, the dipole-forbidden character of the $2^1A_g^-$ results from its covalent character [32–34]. The ionicity of the TT vs S^* are of

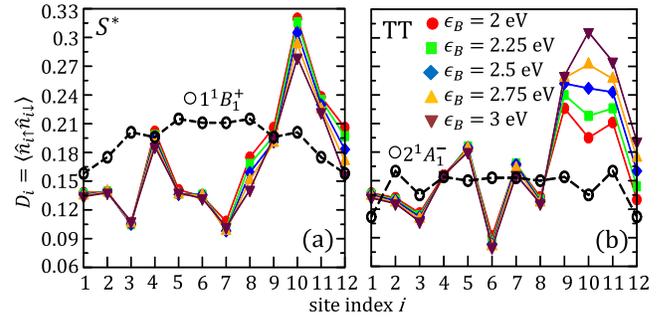


FIG. 4 (color online). Double occupancies by electrons of individual C-atom p_z orbitals of the monomer of Fig. 1(b) for different ϵ_B 's: (a) S^* , (b) TT. The results for the $1^1B_1^+$ and $2^1A_1^-$ states of the bare polyene are given for comparison.

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 $\langle n_{i,\uparrow} n_{i,\downarrow} \rangle$'s 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].

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 PA_{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 PBTD01 and (ii) ultrashort lifetimes of the triplets generated by photoexcitation: their lifetimes are 4 orders of magnitude shorter than the lifetimes of the triplets generated by sensitization. The explanations for these observations are as follows. (i) A weak donor implies a 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 PA₁ and PA₂: 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 the PCEs of solar cells is an intriguing question and a topic for future research.

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