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Distinct contiguous versus separated triplet-pair multiexcitons in an intramolecular singlet fission chromophore

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We show from many-body quantum mechanical calculations that there occur structurally distinct triplet-pair eigenstates in the intramolecular singlet fission (iSF) compound pentacene-tetracene-pentacene. Triplet excitons occupy neigboring pentacene and tetracene monomers in the higher energy doubly degenerate triplet-triplet multiexcitons, and terminal pentacene chromophores in the lower energy multiexciton. The lowest energy multiexciton is reached by ultrafast triplet migration within the triplet-triplet manifold, a result with profound implication for the design of superior iSF compounds.

Electron correlation effects on the optoelectronic properties of carbon-based π-conjugated systems have been of continuous and intense interest [1–4]. One consequence of strong π-electron correlation is the occurrence of the two electron-two hole (2e-2h) bound spin triplet-pair state $^m(T_1T_1)$ energetically below the one electron-one hole (1e-1h) optical spin-singlet state in long linear conjugated polyenes [5] and polyacenes [6, 7] (here and in what follows T_1 is the lowest triplet exciton, and m the overall spin multiplicity). This energy ordering is of direct relevance to singlet fission (SF), a spin-allowed photophysical process involving the internal conversion of the optically accessible spin-singlet exciton to the optically dark $^1(T_1T_1)$ state [8–13]. The possibility of circumventing the Shockley-Queisser limit to photoconductivity [14] in organic solar cells has been the driver of the field. In systems with small triplet-triplet binding energy E_b, defined as $2\times E(T_1)$ - $E(^1(T_1T_1))$, where $E(T_1)$ and $E(^1(T_1T_1))$ are the energies of the lowest free triplet and the triplet-triplet multiexciton, $^m(T_1T_1)$ will undergo dissociation to two free triplets T_1. In principle, each triplet can donate an electron to an acceptor molecule in a donor-acceptor heterostructure, thereby doubling the photoconductivity [8–13].

Until recently research on SF was largely limited to *inter*molecular SF (xSF), in which the triplet excitons constituting the $^1(T_1T_1)$ occupy chromophore monomers that are not bonded covalently [8–13]. SF being a multichromophore process requires moderate to strong "through space" coupling between the chromophore monomers in this case, which in turn places stringent morphological requirements for the chromophore composite, thereby limiting the classes of materials available for xSF. The focus of SF research consequently shifted to *intra*molecular SF (iSF), in which the chromophore monomers are either directly covalently bonded or are linked covalently via bridge molecules [15–38]. Based on ultrafast spectroscopic measurements that found excited state absorptions (ESAs) at triplet absorption energies of the terminal chromophore molecules in the visible wavelength region it was initially believed that iSF led to rapid generation of free triplets. Following theoretical research that demonstrated that the bound $^1(T_1T_1)$ had *additional* ESA in the IR over and above ESA in the visible [39, 40], and experimental observations of this additional ESA [41, 42] it is now accepted that while iSF may lead to rapid $^1(T_1T_1)$ generation, quantitative dissociation to free triplets is rare.

Successful implementation of iSF in organic photovoltaics will require fast $^1(T_1T_1)$ generation as well as its fast dissociation to free triplets, overcoming competing photophysical processes that include triplet recombination. This requirement poses serious theoretical and experimental challenges, as fast $^1(T_1T_1)$ generation necessarily requires strong effective electronic coupling between the chromophore components occupied by the individual triplet excitations of the $^1(T_1T_1)$ wavefunction [26, 43, 44]. The latter in turn leads to strong E_b, which slows down and even prevents triplet dissociation. Recent iSF research has therefore focused on the search for appropriate chromophore-bridge molecule combination that can solve the riddle of fast $^1(T_1T_1)$ generation yet small E_b. From a theoretical perspective this requires, (i) precise understanding of $^1(T_1T_1)$ wavefunction, (ii) the dependence of the triplet-triplet entanglement on the structure of the bridge molecule, (iii) the mechanism of $^1(T_1T_1)$ formation, and (iv) the mechanism of spin dephasing. Simply increasing the length of the bridge molecule is not an optimal solution; even as that reduces E_b it also slows $^1(T_1T_1)$ generation [31]. The $^1(T_1T_1)$ has therefore been the focus of several recent reviews [45, 46].

An ingenious advance in the design of iSF compounds with ultrafast $^1(T_1T_1)$ generation (in few ps) yet long lifetime (hundreds of ns) was achieved recently by Pun *et al.* [26]. The authors synthesized and tested a series of iSF compounds **P-Tn-P**, where **P**, **T** and **n** refer to terminal pentacene chromophores, linker tetracene molecules and the number of linker molecules, respectively (see Fig. 1). According to the authors, initial pho-

toexcitation at pentacene singlet exciton energy creates a localized excitation on a terminal **P** monomer, which undergoes rapid conversion to a contiguous triplet-triplet pair $^1(T_{1[P]}T_{1[T]})$, where $T_{1[P]}$ and $T_{1[T]}$ refer to lowest triplets on **P** and **T**, respectively. The difference in the triplet energies of **T** and **P** monomers ($\sim$ 0.3 eV) then drives triplet migration and transition from contiguous triplets to the lowest energy triplet-pair $^1(T_{1[P]}T_{1[P]})$ in which the triplets occupy only the terminal pentacenes. This conclusion was reached from observation of transient ESA in the IR due to $^1(T_{1[P]}T_{1[T]})$ almost immediately after photoexcitation, and the rapid disappearance of this ESA (in 3.0 ps and 5.3 ps in $n = 2$ and $n = 3$, respectively) followed by $^1(T_{1[P]}T_{1[P]})$ generation [26]. The physical separation between the triplets and uphill recombination are behind the long $^1(T_{1[P]}T_{1[P]})$ lifetime [26].

The experimental results are exciting, as they for the first time suggest that triplet separation can occur by *downhill* triplet migration. Theoretical evidence for distinct phase-coherent high energy $^1(T_{1[P]}T_{1[T]})$ and low energy $^1(T_{1[P]}T_{1[P]})$ that would be required for the proposed triplet migration scheme [26], as opposed to quantum mechanical superpositions, currently does not exist. There are multiple reasons ons for pursuing complete theoretical understanding of this claim, as we briefly discuss. First, weakly phase-coherent physically separated triplet-triplet $^1(T_1 \cdots T_1)$ has also been suggested in the context of xSF [42, 46–51]. Within the proposed scenario there, the weakly bound multiexciton is reached from the strongly bound $^1(T_1T_1)$ in an *uphill* process, which requires overcoming the binding energy of the nearest neighbor triplet-pair. Convincing theoretical evidence for such a $^1(T_1 \cdots T_1)$ state in xSF is lacking. In the present case, whether or not triplet migration is the mechanism behind $^1(T_{1[P]}T_{1[P]})$ generation in the $n = 1$ chromophore **P-T-P** is a particularly challenging issue. The authors of reference 26 were unable to measure the decay time of $^1(T_{1[P]}T_{1[T]})$ in this case, which could be due to either too rapid generation of $^1(T_{1[P]}T_{1[P]})$ via triplet migration, or a different triplet-triplet generation mechanism dominating in the single bridge molecule case. In structurally related compounds with a single bridge moleculex **P**-β-**P**, β = benzene (**B**), naphthalene (**N**) and anthracene (**A**) triplets in the lowest triplet-triplet $^1(T_1T_1)$ do occupy the terminal **P** chromophores only, but the $^1(T_1T_1)$ in these are reached via virtual charge-transfer (CT) excitation between the terminal pentacene chromophore themselves, effectively bypassing the bridge molecules [52]. Taken together, these observations suggest that the mechanism of iSF in these closely related compounds changes with the length of the bridge molecule. Clear understanding of the roles of interchromophore CT versus triplet migration, as functions of electron correlation and bridge molecule length will be essential to establish triplet migration as the dominant pathway to the lowest triplet-triplet in **P-Tn-P**.

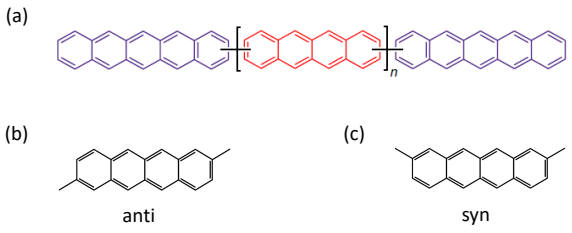


FIG. 1. (Color online) (a) Schematic structure of the **P-Tn-P** compounds investigated experimentally [26]. (b) *Anti-* versus (c) *syn-* linkages investigated here for the **n=1** molecule.

In what follows we present the results of detailed quantum many-body calculations of the excited state electronic structures of the **n**=1 compound **P-T-P**, focusing not only on the triplet-triplet states, but also on the mechanism of their generation. Determining precise energy orderings of the different multiexciton triplet-triplets, relative to the 1e-1h optical exciton is essential for arriving at the correct conclusions here. This in turn requires incorporation of configuration interaction with up to quadruple excitations, which is out of scope of quantum chemical approaches based on the time-dependent density functional theory (TDDFT), and beyond the capability of more sophisticated approaches such as coupled-cluster singles and doubles (CCSD) for systems containing more than about 14-20 electrons [45, 53], because of the explosion in the number of quadruples with system size. Computations based on restricted active spaces (RAS, usually consisting of 4 electrons on 4 molecular orbitals) [20, 21, 50] are not useful in this case. We are unaware of RAS-based calculations of $^1(T_1T_1)$ for iSF chromophores with large bridge molecules. Our calculations are based on the π-electron only Pariser-Parr-Pople (PPP) Hamiltonian [54, 55], which has a long history of application to π-conjugated carbon(C)-based systems [1–4],

$$H = \sum_{\langle ij\rangle,\sigma} t_{ij}(c^\dagger_{i\sigma}c_{j\sigma} + c^\dagger_{j\sigma}c_{i\sigma}) + U\sum_i n_{i\uparrow}n_{i\downarrow} + \sum_{i<j} V_{ij}(n_i - 1)(n_j - 1) \quad (1)$$

Here $c^\dagger_{i\sigma}$ creates an electron with spin σ on the p_z orbital of C-atom i, $n_{i\sigma} = c^\dagger_{i\sigma}c_{i\sigma}$ is the number of electrons with spin σ on atom i, and $n_i = \sum_\sigma n_{i\sigma}$ is the total number of electrons on the atom. t_{ij} are nearest neighbor electron hopping integrals, U the Coulomb repulsion between two electrons occupying the p_z orbital of the same C-atom, and V_{ij} is long range Coulomb interaction. The parameters are taken from our previous applications of the model to acene monomers and dimers [39, 40, 52]. We have chosen peripheral and internal bond lengths for the acene monomers to be (1.40 Å) and (1.46

Å), respectively, and the corresponding t_{ij} as -2.4 and -2.2 eV, respectively [39, 40]. We have assumed the molecules to be planar for simplicity, with the interunit bond length 1.46 Å and the corresponding hopping integral -2.2 eV, respectively. Monomer rotation effect can be taken into consideration by reducing the interunit t_{ij} by a multiplicative factor of $cos\theta$, where θ is the dihedral angle [56]. Explicit calculations have confirmed that physical conclusions are not altered substantively by ignoring rotation effects [39]. We use the screened Ohno parameterization for the long range Coulomb repulsion, $V_{ij} = U/\kappa\sqrt{1 + 0.6117R_{ij}^2}$, where R_{ij} is the distance in Å between C-atoms i and j and κ is an effective dielectric constant [57]. The Coulomb parameter for C-atoms U (7.7 eV) and the dielectric constant κ (1.3) are chosen based on fitting monomer energetics [39, 40].

Our calculations are done within the diagrammatic molecular exciton basis to obtain physical pictorial descriptions of eigenstates [39, 40, 52]. Accurate determinations of energy orderings and correlated wavefunction of the $^1(T_1T_1)$ excited states demand inclusion of high order correlation effects. We use the multiple reference singles and doubles configuration interaction (MRSDCI) procedure that incorporates CI with dominant memh excited configurations (m=1-4) [58, 59]. What distinguishes the MRSDCI procedure from other electron-correlation methodologies is that it treats the ground and the excited-state wave functions on the same footing, while accounting for their multi-reference character. The calculations are done over exciton basis active spaces of 22-26 localized molecular orbitals (8-10 MOs for each **P** monomer and 6-8 per **T** monomer. Details of the MRSDCI procedure using the exciton basis are given in the Supplemental Material (SM), S.1 [60](see also reference [1] therein). Energy convergence required MRSDCI matrices of dimensions several times 10^6 (Table I, SM).

In Fig. 2(a) we have shown the calculated ground state optical absorption spectra for *anti*- and *syn*-**P-T-P**, constructed using Lorentzians with the calculated energy differences and wavefunctions as input parameters, and uniform linewidth of 0.05 eV. The absorption spectra of Fig. 2(a) are different from those for **P-B-P**, **P-N-P** and **P-A-P** in two important ways. First, the CT absorption in **P-T-P** occurs at energy higher than the localized monomeric absorptions of both the terminal pentacene and the linker tetracene, in contrast to **P-B-P, P-N-P and P-A-P** where CT absorption is either to a state that occurs below the localized bridge molecule exciton (**P-B-P** and **P-N-P**) or to a state that exhibits significant configuration mixing with the bridge exciton (**P-A-P**). The latter is the the criterion for bridge resonance [52] within correlated-electron theory. Second, the nearly equal strengths of the CT absorptions for *anti*- and *syn*-**P-T-P** is also in contrast to that in β = **B**, **N** and **A**, where the CT absorption occurs only for *anti* connectivity in **P-B-P** and **P-N-P**, and is stronger for *anti*-**P-A-P** than in *syn*-**P-A-P** [52]. The difference between *anti* versus *syn* connectivities there is ascribed to the tendency to electron-correlation driven antiferromagnetic spin-coupling between electrons on nearest neighbor C-atoms, which promotes selective stronger direct CT between the terminal pentacenes for *anti* connectivity. The exciton-basis allows precise characterizations of the final states of the absorption bands as excitations localized on the monomer molecules versus CT. Detailed examinations of the exciton basis CT eigenstates indicated one-to-one correspondence between iSF rate and the (a) strength of the dipole coupling between the ground state and the CT eigenstate and (b) strong contribution to the CT eigenstate by the configuration with direct CT coupling between the terminal **P** chromophores. The constructive (destructive) quantum interference leading to strong (vanishing to weaker) CT absorption in *anti* (*syn*) β = **B, N, A** compounds is direct evidence for

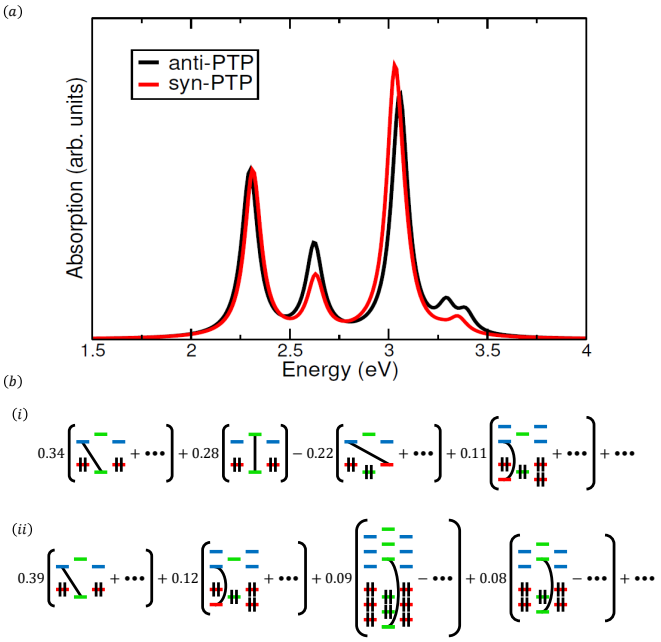


FIG. 2. (Color online) (a) Ground state absorption spectra of *anti* and *syn*-**P-T-P** (see text). The two lower energy bands correspond to **P** and **T** monomer absorptions, the highest energy band is due to intermonomer CT. (b) Normalized exciton basis wavefunctions that contribute most strongly to the CT absorption band in (i) *anti*- and (ii) *syn*-**P-T-P**. The outer (inner) horizontal bars correspond to bonding and antibonding MOs of **P** (bonding and antibonding MOs of **T**(see S.1 [60]). Bonding (antibonding) MOs not shown are fully occupied (empty). Straight or curved lines connecting the MOs denote spin-singlet coupling between singly-occupied MOs. Ellipses correspond to additional configurations related by mirror-plane and charge-conjugation symmetries. See also S.2 [60]

CT-mediated iSF [52].

We show in Figs. 2(b)(i) and (ii) the most dominant exciton basis contributions to the CT eigenstates with the largest dipole couplings to the ground states in *anti*- and *syn*-**P-T-P**. In strong contrast to **P-B-P**, **P-N-P** and **P-A-P**, the relative weight of the configuration with direct CT coupling between the terminal **P** chromophores is noticeably smaller than that of configurations with CT between **P** and **T** (see (i)), or is vanishingly small (see (ii)). Additional CT states also contribute to the very strong CT band in Fig. 2(a). The energies, dipole couplings to the ground states and the dominant exciton basis contributions to all these states are shown in supplementary Table I [60]. The relative weights of configurations with direct CT between the **P** monomers are smaller than that of configurations with CT between **P** and **T**, or are vanishingly small in every case. Dominant CT in all these wavefunctions is between nearest neighbor **P** and **T** monomers, as in PT dimer [40], suggesting already that CT-mediation here will generate contiguous triplet-triplet ${}^1(T_{1[P]}T_{1[T]})$ but not ${}^1(\mathrm{T}_{1[P]}\mathrm{T}_{1[P]})$ with distant triplets.

CT wavefunctions of symmetric iSF molecules occur as nearly degenerate pairs with even and odd parity symmetries. Ground state absorption is to the odd parity CT eigenstate and provides only indirect information about CT-mediated SF. The CT process directly relevant for SF is the virtual excitation from the optical singlet to the even parity CT excitation [8, 61, 62], which has sometimes been referred to as the superexchange mechanism. Dominant contributions to the final states of the strongest dipole-allowed CT excitations from the optical exciton localized on pentacene are shown in Figs. 3(a) and (b). Supplementary Table II gives the normalized contributions to the final states of all wavefunctions to which ESAs from the optical singlets are expected, and the dipole couplings between the initial and final eigenstates [60]. Once again, CT between the terminal **P** molecules is significantly smaller than that between **P** and **T**. Taken together, Figs. 2 and 3 give clear evidence

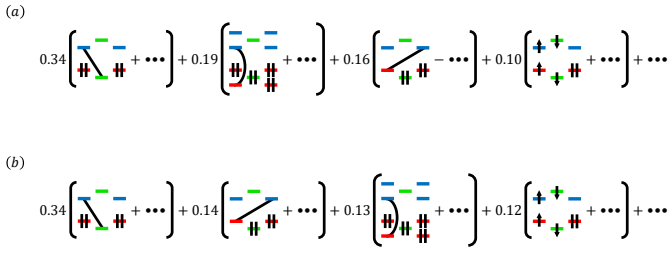


FIG. 3. (Color online) Normalized wavefunctions of CT eigenstates to which ESAs from the optical spin singlet state are the strongest, for (a) *anti* and (b) *syn*-connectivity. The last many-electron configuration in both cases is a contiguous triplet-triplet with total spin zero (see Fig. 4).

that ${}^1(T_{1[P]}T_{1[P]})$ is not generated in a single-step CT-mediated process. Additionally, the last many-electron configurations in both Fig. 3(a) and (b) are ${}^1(\mathrm{T}_{1[T]}\mathrm{T}_{1[P]})$ (see below), which is a direct demonstration of the superexchange mechanism involving neigboring monomers.

We have calculated model-exact energies and wavefunctions of the lowest triplet-triplet eigenstates of **P-T-P**. The lowest of these, ${}^1(\mathrm{T}_{1[P]}\mathrm{T}_{1[P]})$, occurs energetically below the optical exciton, while doubly degenerate higher energy ${}^1(\mathrm{T}_{1[P]}\mathrm{T}_{1[T]})$ and ${}^1(\mathrm{T}_{1[T]}\mathrm{T}_{1[P]})$ states occur immediately above the optical exciton (2.4 eV versus 2.3 eV). The wavefunctions are shown in Figs 4(a)-(c). Triplet excitations in ${}^1(\mathrm{T}_{1[P]}\mathrm{T}_{1[P]})$ are localized entirely on the terminal pentacenes. Higher energy triplet-triplet eigenstates consist entirely of even and odd linear combinations of ${}^1(\mathrm{T}_{1[P]}\mathrm{T}_{1[T]})$ and ${}^1(\mathrm{T}_{1[T]}\mathrm{T}_{1[P]})$. Fig. 4 shows only the largest contributions to the multiexciton eigenstates. We have examined upto 15 higher order quadruple excitations in each case, with normalized coefficients down to 0.03. Even these higher order excitations are strictly localized either on nearest neighbor monomers or on distant monomers, but not both in the same eigenstate. It is now interesting to go back to Fig. 3: the admixing between the first and last terms in the two wavefunctions here give indirect proof of the hypothesis that initial triple-triplet multiexciton generation occurs via virtual excitation of the CT eigenstate dipole-coupled to the optical singlet [8, 61, 62].

Free triplet generation from the bound triplet-triplet is preceded by spin mixing between overall spin singlet ($m = 1$), triplet ($m = 3$) and quintet ($m = 5$) multiexcitons [63, 64]. In Table I we have given the calculated $m = 1$ and $m = 5$ energies of ${}^m(\mathrm{T}_{1[P]}\mathrm{T}_{1[P]})$ and ${}^m(\mathrm{T}_{1[P]}\mathrm{T}_{1[T]})$. Δ_s between the quintet and singlet spin states in the contiguous triplet-pair ${}^m(\mathrm{T}_{1[P]}\mathrm{T}_{1[T]})$ is large compared to room temperature, explaining the downhill triplet migration from this state over spin dephasing [26].

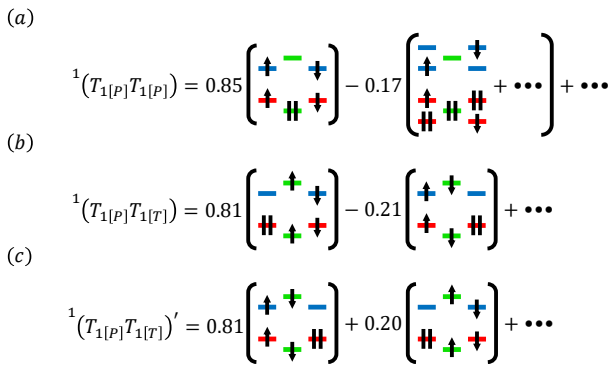


FIG. 4. (Color online) Normalized wavefunctions of (a) ${}^1[\mathrm{T}_{1P}\mathrm{T}_{1P}]$, (b) and (c) ${}^1[\mathrm{T}_{1P}\mathrm{T}_{1T}]$ states in *anti*-**P-T-P**. Intramonomer excitations are spin triplet, with the overall spin of the configuration zero. The corresponding wavefunctions for *syn*-**P-T-P** are nearly identical and are not shown.

Fast thermally-induced mixing between the spin states is however expected in $^m(T_{1[P]}T_{1[P]})$. The larger distance between the triplet excitons occupying the terminal pentacenes in $\mathbf{n} > 1$ **P-Tn-P** would lead to even smaller Δ_s, explaining the very long lifetimes of the triplet-triplet in these [26].

TABLE I. Calculated energies (in eV) of $^m(T_{1[P]}T_{1[T]})$ and $^m(T_{1[P]}T_{1[P]})$ for **P-T-P**, $m = 1$ and 5, for *anti-* and *syn-*connectivities. The calculated energy of the pentacene singlet exciton is 2.3 eV. Δ_s is the calculated spin gap (in eV) between $m = 5$ and $m = 1$.

connectivity	multiexciton	$E(m=1)$	$E(m=5)$	Δ_s
anti	$^m(T_{[1P]}T_{[1T]})$	2.42	2.46	0.040
	$^m(T_{[1P]}T_{[1P]})$	2.04	2.05	0.005
syn	$^m(T_{[1P]}T_{[1T]})$	2.44	2.47	0.040
	$^m(T_{[1P]}T_{[1P]})$	2.04	2.04	0.0003

In summary, there indeed occur distinct triplet-triplet eigenstates in **P-T-P** (therefore in **P-Tn-P**) with triplets occurring on neigboring versus distant acene monomers. Our theoretical work therefore justifies the hypothesis made in Ref. [26]. With pentacene as the terminal chromophore and acenes shorter than tetracene as the bridge molecule, the bridge optical singlets as well as triplets have signifiantly higher energies than the terminal chromophore pentacene's optical singlet. Our calculations reported here show that with longer bridge molecule tetracene, the contiguous triplet-triplet $^1(T_{1[P]}T_{1[T]})$ occurs below the lowest CT state (see Fig. 2(a) and Table I). The iSF process occurs in two steps now. First there occurs almost instantaneous nearest neighbor CT-mediated generation of contiguous triplet-triplet (see Fig. 3), which is nearly isoenergetic with the optical exciton. The relatively large energy difference between $^1(T_{1[P]}T_{1[T]})$ and $^1(T_{1[P]}T_{1[P]})$ (Table I) then ensures ultrafast decay from the former to the latter, viz., downhill triplet migration as envisioned in [26]. Recombination is uphill and therefore slow to nearly noneixtent [26].

Our theoretical demonstration of distinct higher energy contiguous and lower energy separated $^1(T_1T_1)$ goes a long way towards overcoming a major hurdle in the field of SF: for the first time a "formula" is established that will lead to rapid generation of triplet-triplet followed by downhill triplet migration and separation. In principle all long-chain iSF compounds in which the contiguous triplet-triplet is isoenergetic or slightly lower in energy than the singlet exciton of the terminal monomers will exhibit this feature. Ingenious synthesis of iSF compounds containing heteroatoms in which lattice distortion follows generation of triplet pairs on terminal monomers can lead to even longer recombination times than already achieved in **P-Tn-P** [26]. We expect many applications of the basic concept as well as trial use of some of the newly generated chrompohores in the construction of trial solar cells on the laboratory scale.

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