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D. Beljonne[1,2], H. Yamagata[3], J.L. Brédas[2], F.C. Spano[3], Y. Olivier[1]

[1]Laboratory for Chemistry of Novel Materials, University of Mons, Place du Parc 20, 7000 Mons (Belgium)

[2]School of Chemistry and Biochemistry and Center for Organic Photonics and Electronics, Georgia Institute of Technology, Atlanta, Georgia 30332-0400, USA

[3]Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122, USA

Abstract: Quantum-chemical calculations are combined to a model Frenkel-Holstein Hamiltonian to assess the nature of the lowest electronic excitations in the pentacene crystal. We show that admixture of charge-transfer excitations into the lowest singlet excited states form the origin of the Davydov splitting and mediate instantaneous singlet exciton fission by direct optical excitation of coherently coupled single and double exciton states, in agreement with recent experiments.

Singlet fission (SF) is a spin conserving process that generates two triplet excitons out of a singlet. Though this process has been documented as early as the late sixties[i], it has recently regained interest due to the potential of SF to overcome the so-called Shockley-Queisser limit of ~31% in organic solar cells[ii]. This can be achieved by converting high-energy photons that would otherwise contribute to waste heat into free charge carriers in adequately designed organic photovoltaic (PV) cells. For instance, bilayer PV devices capitalizing on SF of singlets in pentacene followed by triplet ionization at the interface with low band gap quantum dots have been recently reported[iii]. Similarly, SF has been exploited in nanostructured organic solar cells comprising tetracene, copper phtalocyanine, and C_{60}[iv].

Much work has been devoted to rationalizing the mechanistic aspects of SF in organics. Smith and Michl[v] have proposed to classify SF pathways according to different classes of chromophores. Among these, class-I chromophores have their lowest singlet molecular excited state dominated by a HOMO-to-LUMO single excitation. While this is apparently the case of pentacene, the second excited state (presumably close in energy) that predominantly displays double hole-double electron origin has been conjectured to result in fission into two local triplets initially residing on different parts of the same molecule[vi]. Yet, there is compelling evidence that SF is enhanced in the solid state[vii] (we note SF has been observed in both polycrystalline and amorphous pentacene films[viii]); thus a purely single-molecule origin is in fact unlikely. Considering that the overall process is of *intermolecular* origin and exoenergetic (S_1 energy larger than twice the T_1 energy), class-I chromophores can undergo efficient SF through a direct two-electron quantum-mechanical coupling or, alternatively, via a sequential process involving an intermediate charge-transfer (CT) state[iv,ix,x]. In addition to such events that rely on *electronic* interactions between adjacent molecules, surface hopping driven by *nonadiabatic* coupling between the potential energy surfaces has also been suggested as a major contributor to SF in oligoacene crystals[xi].

We note that from *ab initio* quantum-chemical calculations on pentacene clusters, it has been argued that the lowest adiabatic excited states have vanishing contributions from charge-transfer excitations[xi,xii]. As the generation of triplets from SF in pentacene is ultrafast (~80 fs)[xiii], a two-step incoherent process is unlikely, which would then *a priori* rule out a CT-mediated mechanism. We demonstrate here that CT configurations do play a major role in the photophysics of pentacene single crystals and seed a direct pathway to SF. On the one hand (in line with our earlier findings[xiv]), extensive quantum-chemical calculations and phenomenological models underline how CT excitations shape the *sign and magnitude* of the Davydov splitting in pentacene. On the other hand, single and multiple Frenkel excitations are shown to interact *directly* through their admixture with CT excitations; as a result, optical excitation can potentially generate coherently coupled pairs of such states, as observed in the femtosecond nonlinear spectroscopy work of Chan *et al* [xv].

We start with the analysis of the Davydov splitting (DS) in pentacene single crystals. As detailed in Reference[xiv], excellent agreement with the experimental absorption spectra is obtained when including charge-transfer configurations in addition to Frenkel excitations (FE) in a phenomenological Holstein model. Within a simple model where a single Frenkel S_1 excited state per molecule is retained and a monoclinic unit cell supporting two sub-lattices is assumed, the symmetric and antisymmetric combinations of the S_1 molecular states, say FE^{aa} and FE^{bb} (where the superscripts refer to localization of the excitation on molecule a or b), yield two excitonic bands, FE^+ and FE^-, respectively. Quantum-chemical calculations based on FE states[xiv] yield a symmetric *b*-polarized Davydov component at a higher energy than its antisymmetric counterpart and a negative DS value. Importantly, when CT excitations are considered, there occurs a reversal in the ordering of the lowest excited states. This can be understood as follows. As in the case of the Frenkel states, the two sub-lattices give rise to symmetric and antisymmetric combinations (CT^+ and CT^-, respectively) of the nearest neighbor charge-transfer excitations (CT^{ab} and CT^{ba}, where superscripts *ij* denote hole on molecule *i* and electron on molecule *j*). Since pentacene is a direct gap semiconductor, the hole-hole and electron-electron resonance integrals mixing Frenkel and charge-transfer excitations have comparable magnitude but opposite signs; this results in a much larger interaction of CT excitations (using either a localized or symmetry-adapted basis set) with the symmetric FE^+ state that pushes the *b*-polarized transition below the *a*-polarized transition and yields a positive DS, in *quantitative* agreement with experiment (*vide infra*).

INDO/SCI[xvi] calculations have been performed on the unit cell of the pentacene crystal and the electron-hole wavefunctions partitioned into local and charge-transfer contributions. The admixture of CT in the lowest eigenstates of a pentacene dimer depends on the relative energetic positions of the diabatic CT configurations, which can be tuned via the functional form of the INDO electron-electron potential and its distance dependence. Fig. 1a demonstrates that the DS splitting between the lowest two excited states directly comes from admixture with the CT excitations, as the sign and magnitude of the DS correlate with the amount of CT. We note that this picture holds when including double electronic excitations in the framework of a size-consistent CCSD approach[xvii], see Fig. 1a. Similarly, the DS increases when decreasing the intermolecular distances between the non-equivalent molecules (along the C-C intermolecular distance, see[xi]), as a result of both lower CT diabatic state energies and larger electronic coupling matrix elements (transfer integrals) with localized excitations, see supporting information.

Though the comparison with an electronic dimer model should be considered with caution (as the DS will also be affected by vibronic coupling and the presence of four nearest neighbors in the crystal), the experimental DS value in pentacene of *ca* 1000-1100 cm^{-1} [xviii] is reproduced only by INDO/SCI[CCSD] dimer calculations where the use of screened electron-electron interactions results in the lowest electronic excited state including as much as 50% CT character; this is in agreement not only with our earlier estimate[xiv] but also with recent electron-energy loss investigations[xix] and is consistent with earlier theoretical studies[xx]. The results of TD-DFT calculations performed using a range of density functionals bracket the experimental value, see supporting information. We note that the ωB97XD functional adopted in[xi] gives rise to a DS that is ~40% too small compared to experiment; this is in line with our interpretation above based on CT admixture as this functional has been shown to yield too high charge-transfer excitation energies, thereby resulting in a reduced mixing with localized excitations and hence a (too) small DS.

We now address the singlet fission process from a general mechanistic standpoint in order to examine the possible role of CT excitations. For simplicity, we focus on two molecules *a* and *b*, each described by a two-level (*H*=HOMO, *L*=LUMO) system. Working in a localized basis set, the CT pair with cation on *a* and anion on *b* (*i.e.*, CT^{ab}) can couple to both a single molecular excitation localized on *a* and a doubly excited configuration where two electrons are simultaneously excited on both molecules via the following one-electron resonance integrals, see Fig. 2:

$$\begin{aligned}\left\langle CT^{ab}\middle|\hat{\mathrm{H}}\middle|FE^{aa}\right\rangle &= \left\langle H_a \rightarrow L_b\middle|\hat{\mathrm{H}}\middle|H_a \rightarrow L_a\right\rangle \sim \left\langle L_b\middle|\hat{t}\middle|L_a\right\rangle = l_b l_a;\\ \left\langle CT^{ba}\middle|\hat{\mathrm{H}}\middle|FE^{aa}\right\rangle &= \left\langle H_b \rightarrow L_a\middle|\hat{\mathrm{H}}\middle|H_a \rightarrow L_a\right\rangle \sim -\left\langle H_b\middle|\hat{t}\middle|H_a\right\rangle = -h_b h_a\end{aligned} \qquad [1]$$

$$\begin{aligned}\left\langle CT^{ab}\middle|\hat{\mathrm{H}}\middle|FE^{bb}\right\rangle &= \left\langle H_a \rightarrow L_b\middle|\hat{\mathrm{H}}\middle|H_b \rightarrow L_b\right\rangle \sim -\left\langle H_a\middle|\hat{t}\middle|H_b\right\rangle = -h_a h_b;\\ \left\langle CT^{ba}\middle|\mathrm{H}\middle|FE^{bb}\right\rangle &= \left\langle H_b \rightarrow L_a\middle|\hat{\mathrm{H}}\middle|H_b \rightarrow L_b\right\rangle \sim \left\langle L_a\middle|\hat{t}\middle|L_b\right\rangle = l_a l_b\end{aligned} \qquad [2]$$

$$\begin{aligned}\left\langle CT^{ab}\middle|\hat{\mathrm{H}}\middle|TT\right\rangle &= \left\langle H_a \rightarrow L_b\middle|\hat{\mathrm{H}}\middle|H_a H_b \rightarrow L_a L_b\right\rangle \sim \sqrt{\frac{3}{2}}\left\langle H_b\middle|\hat{t}\middle|L_a\right\rangle = \sqrt{\frac{3}{2}}h_b l_a;\\ \left\langle CT^{ba}\middle|\hat{\mathrm{H}}\middle|TT\right\rangle &= \left\langle H_b \rightarrow L_a\middle|\hat{\mathrm{H}}\middle|H_a H_b \rightarrow L_a L_b\right\rangle \sim \sqrt{\frac{3}{2}}\left\langle H_a\middle|\hat{t}\middle|L_b\right\rangle = \sqrt{\frac{3}{2}}h_a l_b\end{aligned} \qquad [3]$$

where $\left|H_{a(b)} \rightarrow L_{b(a)}\right\rangle$, $\left|H_{a(b)} \rightarrow L_{a(b)}\right\rangle$, and $\left|H_a H_b \rightarrow L_a L_b\right\rangle$ denote spin-adapted (singlet) charge-transfer, single Frenkel and double Frenkel (or triplet pair) excitations, respectively. The complete expression of the matrix elements can be found in[v]. These include additional two-electron repulsion integrals, namely between single and double excitations, which are usually smaller (a few meV in the case of a slip-stacked configuration of isobenzofuran molecules) than the one-electron transfer integrals above (up to one hundred meV in the herringbone dimer of pentacene, Table 1). In a perturbative scheme, the molecular single and double excitations are thus expected to mix together through their CT component, albeit only to second order. In the most general case, it is difficult to predict whether the CT-mediated second-order effect will be dominant over the first-order two-electron coupling mechanism proposed by Michl and co-workers[xxi]. For large Frenkel-CT mixing as found in pentacene, however, perturbation theory breaks down and the exact eigenstates of the system are superposition states with (similar) weights from the five configurations above fixed by their relative energies and the off-diagonal electronic matrix elements. Recent nonlinear optical measurements performed on thin crystalline pentacene films have demonstrated that the primary species generated by a resonant optical excitation pulse are in fact coherent superposition states with equal weights from single and multiple excitons, which suggests large (in)direct couplings[xv]; these states then subsequently dephase to produce free triplet pairs.

From these mechanistic considerations,[xxii] CT pairs thus appear to provide the link between single and multiple exciton states in pentacene. It is, however, important to bear in mind that, if we switch from the localized representation of Eq. [1-3] to a symmetry-adapted basis set, the relevant matrix elements now involve the FE$^+$, FE$^-$, CT$^+$, CT$^-$ and triplet pair (TT) wavefunctions and the electronic Hamiltonian matrix reads:

$$H = \begin{pmatrix} E_{FE^+} & l_a l_b - h_a h_b & 0 & 0 & 0 \\ l_a l_b - h_a h_b & E_{CT^+} & 0 & 0 & \frac{\sqrt{3}}{2}(h_a l_b + h_b l_a) \\ 0 & 0 & E_{FE^-} & l_a l_b + h_a h_b & 0 \\ 0 & 0 & l_a l_b + h_a h_b & E_{CT^-} & \frac{\sqrt{3}}{2}(h_a l_b - h_b l_a) \\ 0 & \frac{\sqrt{3}}{2}(h_a l_b + h_b l_a) & 0 & \frac{\sqrt{3}}{2}(h_a l_b - h_b l_a) & E_{TT} \end{pmatrix} \qquad [4]$$

where $E_{CT}^+ = E_{CT}^- = E_{CT}^{ab} = E_{CT}^{ba}$ (we neglect the weak coupling between charge-transfer excitations) and $E_{FE}^+ - E_{FE}^- = 2V_{Cb}$ with V_{Cb} the long-range Coulomb interaction between the localized Frenkel molecular excitations. As discussed above, the DFT-calculated $l_a l_b$ and $h_a h_b$ transfer integrals have opposite signs and similar absolute values, so that much larger couplings are obtained among the *symmetric* components of the CT and FE excitations, which brings the correct ordering of the lowest eigenstates and a positive DS, *vide supra*. Likewise, $h_a l_b$ and $h_b l_a$ are comparable yet opposite in sign, such that it is now the *antisymmetric* component of the CT excitation that is expected to mix more strongly with the triplet-triplet pair. Thus, in the limiting case that $l_a l_b = - h_a h_b$ and $h_a l_b = - h_b l_a$, the CT-mediated electronic coupling between single and double excitations is strictly zero due to cancellation effects, *i.e.*, FE and TT do not mix.

This result can be tested by carrying out supermolecular calculations including at least single and double electronic excitations. INDO/CCSD transition energies computed for the pentacene dimer in the unit cell are plotted versus intermolecular separation in Fig. 1b. The corresponding excited states can be unambiguously assigned as single and double excitations from a detailed analysis of their wavefunctions. At the crystal equilibrium distance of ~5.6Å, the TT pair is calculated to be located about 0.05 eV below the lowest Frenkel-CT mixed state. In[xv], it was inferred that single and multiple exciton states are energetically resonant at time zero after the excitation pulse. The relative positioning of these states turns out to be very sensitive to the electron-electron potential used in the INDO/CCSD calculations and the relative positioning of the molecules, which precludes a quantitative assessment. To drive the system towards the energetic degeneracy suggested by the experimental data, we have considered the situation where the intermolecular separation is reduced in order to bring the symmetric single exciton down in energy (owing to its CT character). Most interestingly, the electronic wavefunctions of the lowest eigenstates are found to change markedly at shorter distances and to mix substantially; this is best appreciated from a consideration of the corresponding oscillator strengths, Fig. 1c. While the double exciton state is dark at large separations (as expected from the one-electron character of the dipole operator), it acquires increasing absorption cross-section with decreasing distance via intensity borrowing from the single exciton states. At a distance of 5.4Å, single and double excitations come in pairs with similar weights in the total eigenfunctions, thereby displaying similar transition dipoles. This feature is fully consistent with the experimental observation of simultaneous generation of single and multiple exciton states[xv].

Because the results reported in Fig. 1 refer to adiabatic states obtained by diagonalizing the full INDO/CCSD Hamiltonian in a large electronic configurational basis, a two-state coupling matrix element between single and double excitons, W, cannot be extracted from such calculations. However, it can be argued that W should not be larger than the (in)homogeneous linewidth of the pentacene absorption spectrum so that the reshuffling in optical cross-section from FE to TT states ends up being smeared out by the spectral broadening. Still, W should be large enough that the oscillator strength is almost equally shared between the two excited states in the INDO/CCSD dimer calculations. As suggested by the analysis above, a non-zero W value implies relaxing either: (i) the assumption of equal amplitude for the intermolecular hole-hole versus electron-electron, and hole-electron versus electron-hole transfer integrals; at the DFT level, this asymmetry amounts to about 10% at 5.6 Å and increases up to 15% at 5.3 Å, Table S1; and/or (ii) the strict degeneracy in the energy of the charge-transfer excitations; in the dimer, the herringbone arrangement of the pentacene molecules drives an energy splitting between CT pairs where the hole and electron localized over the two molecules are swapped, *i.e.*, CT^{ab} and CT^{ba} have distinct energies mainly because of charge-quadrupole interactions[xxiii]. Both scenarios would favor local CT^{ab} and CT^{ba} excitations over delocalized CT^{+} and CT^{-} pairs and result in an efficient mixing between single and double (triplet-triplet) excitations as seen in Fig. 1c (since the relevant matrix elements are now given by Eqs.1-3).

We have investigated this feature further by considering a Frenkel-Holstein model augmented with exciton-vibrational couplings to CT (periodic boundary conditions are applied using an 300x300x1(axbxc) unit cell and five exciton bands are included, see supporting information. All energy terms in the Hamiltonian have been set according to experimental data (*e.g.*, reorganization energies for Frenkel excitons and charge carriers, CT excitation energies) or correlated quantum-chemical calculations (namely INDO/CCSD excitonic couplings, DFT transfer integrals). The optical absorption spectrum for pentacene is shown in Fig.3 alongside the experimental spectra of Sebastian *et al.*[xxiv] and Hinderhofer *et al.*[xxv]. The very good agreement between experiment and theory across a spectral range of ~1 eV brings confidence that the model captures the essential photophysics of pentacene films. We stress that slightly different combinations of diabatic CT energies and transfer integrals lead to similar spectra, hence there is some flexibility in the parameter space that reproduces the experimental optical spectra. Yet, these combinations all yield a *unique* CT ratio in the lowest optically allowed eigenstate of about 45-50%, in excellent agreement with the supermolecular dimer calculations discussed above.

Finally, we have included double hole – double electron excitations (TT pairs) in the basis set of the Frenkel-Holstein model. The expression of the full Hamiltonian is cumbersome and detailed in supporting information. The electronic matrix elements between CT, single and double excitations coincide with the dimer Hamiltonian in Eq. 4. The E_{TT} energy has been set to be 0.17eV below the singlet S_1 energy, resulting in *adiabatic* single and double excitons that are almost degenerate (this henceforth ensures an exothermic energy close to the experimental value of ~0.11eV[xv] when the optically generated adiabatic excitons collapse into diabatic states, namely upon conversion from ME to ME' in[xv]). Starting from the DFT calculated resonance integrals in Eq. 4, we first averaged the couplings enforcing both electron-hole and inversion symmetry and then introduced disparity factors δ1 for the CT energies: $\delta 1 = \left(E(CT^{ab}) - E(CT^{ba})\right)/2$ and $\delta 2$ for the matrix elements: $\delta 2 = \left(h_a l_b + h_b l_a\right)/2 = \left(l_a l_b + h_a h_b\right)/2$. In the parameter space investigated ($-200\text{cm}^{-1} < \delta 1, \delta 2 < 200\text{cm}^{-1}$), the optical spectra remain virtually unchanged when the symmetry in the CT energies and/or electronic couplings is lifted, see supporting information. However, as predicted from the INDO/CCSD dimer calculations and anticipated from the analysis of the use of localized versus delocalized CT pairs, non-zero $\delta 2$ and, to a lesser degree, $\delta 1$ values of ~100cm^{-1} are enough to split almost equally the oscillator strength between single and double exciton states, Fig. 3c. Note that, in this range of disparity factors, the effective coupling, $|W|$, between the triplet pair and the symmetric Frenkel-CT exciton is predicted to peak to a value of ~900 cm^{-1} at ($\delta 1, \delta 2$)=(200,-200) cm^{-1}, see supporting information.

To conclude, our modeling provides strong support to the case that the admixture of charge-transfer excitations by up to 50% to the lowest singlet excitons in crystalline pentacene is the main contributor to the Davydov splitting in this material. One-electron resonance integrals of a similar nature and magnitude couple the CT to the triplet pair configurations, thereby providing the mechanism for *simultaneous* generation of single and multiple excitons in pentacene. Though this mechanism likely applies to other organic conjugated materials, it should be stressed that: (i) the instantaneous formation of a coherent superposition of single and multiple exciton states upon light absorption in pentacene is, at least partly, a result of their very close excitation energies; and (ii) in molecular materials where this resonance condition is not met, admixture of CT contributions into the lowest singlet excitons should still yield electronic couplings with double exciton states on the order of a fraction of the resonance integrals $h_i l_j$ (~100 meV); these should translate into fast SF rates, yet via a two-step process[xxvi]: optical absorption into a mixed Frenkel-CT state followed by conversion into two triplet excitations. We further note that the latter scenario is consistent with the excimer pathway proposed both in polycrystalline pentacene[xxvii] and in concentrated solutions of a pentacene derivative[xxviii], as excimers imply excitations with a significant fraction of CT character. Clearly, the timescales for singlet fission are expected to vary by orders of magnitude, going from ultra-fast (sub-ps) in single crystals to slow (ns) in solution (where diffusion is the rate limiting step). The calculations presented here demonstrate that the one-electron matrix elements mediating admixture of CT configurations into singlet and triplet-triplet excitons are simultaneously large in the herringbone configuration of pentacene; we are now extending these simulations to assess how both couplings vary in the configurational space explored by molecules in (dis)ordered solid and liquid environments (such as, *e.g.*, stacked and slip-stacked configurations).[v]

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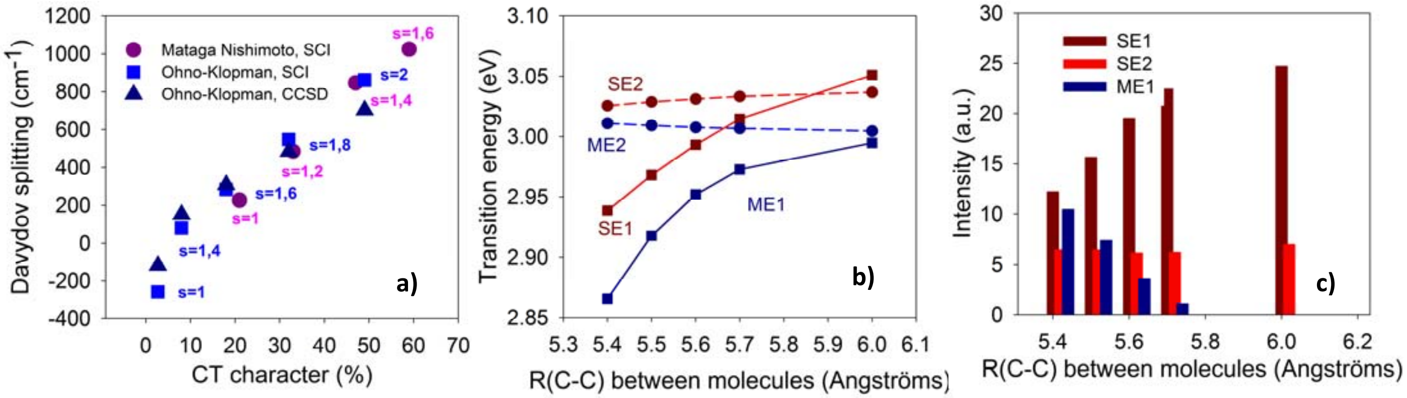

Fig. 1. **(a)** Davydov splitting calculated at the INDO/SCI and INDO/CCSD levels versus the charge-transfer character in the lowest eigenstate of a pentacene unit cell dimer. The results are shown for two different electron-electron potentials V(r) and using different screening factors s, with $V_{scr}(r)=V(r*s)$. **(b)** INDO/CCSD (s=1.4) transition energies to the lowest three singlet excited states of the pentacene unit cell dimer versus intermolecular separation. SE1 and SE2 denote single exciton states (their energy difference is the DS) and ME1 is a double exciton state. **(c)** Relative intensities (squared transition dipole moment) for the lowest three electronic transitions in Fig.1b. Note the strong intensity borrowing from SE1 to ME1 at short distances.

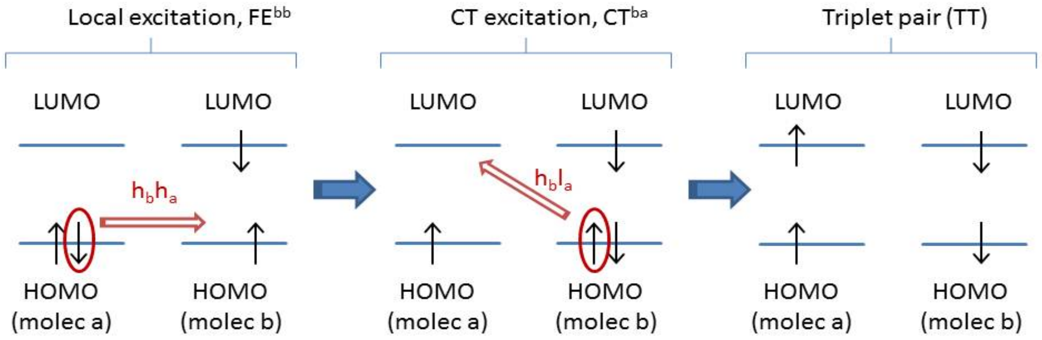

Fig. 2. Schematic one-electron energy diagram showing single Frenkel, charge-transfer and triplet pair excitations in a localized representation of a molecular dimer {a,b}. The labels in red refer to the resonance integrals coupling these electronic configurations, see text.

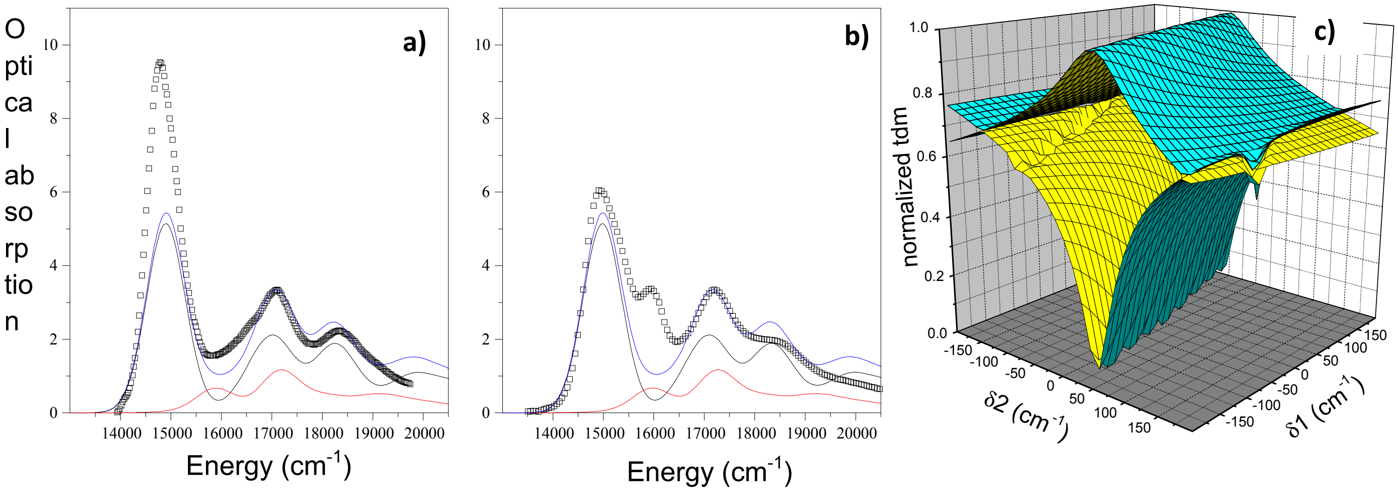

Fig. 3.: Calculated absorption spectra along with experiment spectra (□) of **(a)** Sebastian *et al*. [xxiv] and **(b)** Hinderhofer *et al.*[xxv] The black and red curves represent respectively ∥*b* and ⊥*b* polarized spectra and the blue curves represent unpolarized spectra. Experiment and the calculated spectra are normalized and aligned at the 0-1 peak. Calculation details are given in supporting information. **(c)** Transition dipole moment (tdm) as a function of the disparities in CT energies (δ1) and matrix elements (δ2). The top surface represents the highest tdm among the coupled FE/TT states while the bottom surface represents second largest tdm. Note that at (0, 0), there is no tdm sharing between the FE and the TT states due to cancellation effects.

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[i] R.E. Merrifield, J. Chem. Phys. 48, 4318 (1968).

[ii] W. Shockley, H. J. Queisser, J. Appl. Phys. 32, 510 (1961).

[iii] B. Ehrler, M.W.B. Wilson, A. Rao, R.H. Friend, N.C. Greenham, Nano Lett. 12, 1053 (2012).

[iv] P. J. Jadhav, A. Mohanty, J. Sussman, J. Lee, M. A. Baldo, Nano Lett. 11, 1495 (2011).

[v] M.B. Smith, J. Michl, Chem. Rev. 110, 6891 (2010).

[vi] P. Zimmerman, Z. Zhang, C. Musgrave, Nature Chem. 2, 648 (2010).

[vii] A.M. Müller, Y.A. Avlasevich, W.W. Schoeller, K. Müllen, C. J. Bardeen, J. Am. Chem. Soc. 129, 14240 (2007).

[viii] S.T. Roberts, R.E. McAnally, J.N. Mastron, D.H. Webber, M.T. Whited, R.L. Brutchey, M.E. Thompson, S.E. Bradforth, J. Am. Chem. Soc.134, 6388 (2012).

[ix] E.C. Greyson, J. Vura-Weis, J. Michl, M. A. Ratner, J. Phys. Chem. B 114, 14168 (2010).

[x] P.E. Teichen, J.D. Eaves, J. Phys. Chem. B 116, 11473 (2012).

[xi] P.M. Zimmerman, F. Bell, D. Casanova, M.J. Head-Gordon, J. Am. Chem. Soc. 133, 19944 (2011).

[xii] Note that if CT excitations come in pairs, CT^{ab} and CT^{ba}, with equal weight, the overall state dipole of the resulting adiabatic state will necessarily vanish, which does not mean that CT and Frenkel excitons do not mix.

[xiii] M.W.B. Wilson, A. Rao, J. Clark, R.S.S. Kumar, D. Brida, G. Cerullo, R.H. Friend, J. Am. Chem. Soc. 133, 11830 (2011).

[xiv] H. Yamagata, J. Norton, E. Hontz, Y. Olivier, D. Beljonne, J.L. Brédas, R.J.J. Silbey, J. Chem. Phys. 134, 204703 (2011).

[xv] W.-L. Chan, M. Ligges, A. Jailaubekov, L. Kaake, L. Miaja-Avila, X.-Y. Zhu, Science 334, 1541 (2011).

[xvi] J. Ridley, M. Zerner, Theoret. Chim. Acta 134, 111 (1973).

[xvii] Z. Shuai and J. L. Brédas, Phys. Rev. B 62, 15452 (2000).

[xviii] A. F. Prikhotko, L.I. Tsikora, Optics and Spectoscopy 25, 242 (1968); V. Zanker, J. Preuss, Zeitschrift Fur Angewandte Physik 27, 363 (1969).

[xix] F. Anger, J.O. Ossó, U. Heinemeyer, K. Broch, R. Scholz, A. Gerlach, F. Schreiber, J. Chem. Phys. 136, 054701 (2012).

[xx] M.L. Tiago, J.E. Northrup, S.G. Louie, Phys. Rev. B 67, 115212 (2003).

[xxi] J. C. Johnson, A. J. Nozik, J. Michl, J. Am. Chem. Soc. 132, 16302 (2010).

[xxii] See also M. Chandross, Y, Shimoi, S. Mazumdar, Phys. Rev. B, 59, 4822 (1999).

[xxiii] D. Beljonne, J. Cornil, L. Muccioli, C. Zannoni, J.L. Brédas, F. Castet, Chem. Mat. 23 , 591 (2011).

[xxiv] L. Sebastian, G. Weiserand, H. Bassler, Chem. Phys. 61, 125 (1981).

[xxv] A. Hinderhofer, U. Heinemeyer, A. Gerlach, S. Kowarik, R. M. J. Jacobs, Y. Sakamoto, T. Suzuki, F. Schreiber, J. Chem. Phys. 127, 194705 (2007).

[xxvi] A similar CT-mediated mechanism has been recently proposed in T.C. Berkelbach, M.S. Hybertsen and D.R. Reichman, J. Chem. Phys. 138, 114103 (2013).

[xxvii] H. Marciniak, I. Pugliesi, B. Nickel, S. Lochbrunner, Phys. Rev. B 79, 235318 (2009).

[xxviii] B. Walker, A.J. Musser and R.H. Friend, private discussion.