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# Modulating the Exciton Dissociation Rate Up to More Than 2 Orders of Magnitude by Controlling the Alignment of LUMO+1 in Organic Photovoltaics

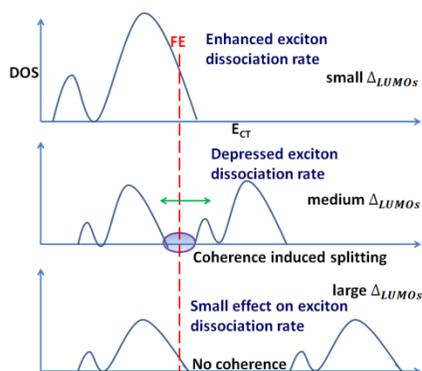
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**ABSTRACT:** *Efficient organic solar cells require a high yield of exciton dissociation. Nowadays, in organic photovoltaic community it is generally believed that for a donor/acceptor (D/A) pair in non-fullerene acceptor blends only the lowest charge transfer (CT) state of participates in the exciton dynamics and consequently the role of a second CT (CT<sub>2</sub>) state of a non-fullerene D/A dimer is completely neglected. Here, we investigate the possibility of having more than one CT state below the first optically bright Frenkel exciton (FE) state for common molecular D/A pairs and the role of the CT<sub>2</sub> state in the exciton dissociation process. It is shown to be very common for a D/A pair to have two CT states locating below FE state and we reveal that the position of CT<sub>2</sub> can remarkably modulate the exciton dissociation rate up to more than 2 orders of magnitude. Thus, controlling the alignment of CT<sub>2</sub> is suggested as a promising rule for designing new D/A heterojunctions.*

## TOC GRAPHICS



**KEYWORDS:** organic solar cell; non-fullerene acceptor; exciton dissociation; charge separation

## ■ INTRODUCTION

The nature of electronic excited states in organic semiconductors, governing the dynamics of excitation energy transfer and/or exciton dissociation, is an important ingredient in understanding the fundamental mechanism of organic photovoltaics (OPVs).[1–8] With the rapidly growing interests in OPVs in both scientific and industrial communities, theoretical modeling of the electronic structure of excitons and their accompanying dynamics has been widely implemented and now plays an important role in interpreting the elementary processes or designing new materials.[5–17] Due to the large size of the system, the theoretical investigations are mainly based on simplified models with the common assumption that only the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of each molecule participate in the exciton dynamics within the donor (D)/acceptor (A) heterojunction, i.e. one initially photo-excited Frenkel exciton (FE) can convert to a charge transfer (CT) excited state where the hole occupies the HOMO of the donor (or a linear combination of HOMOs of many donors) and the electron occupies the LUMO of the acceptor (or a linear combination of LUMOs in case of many acceptors). These CT states evolve into free electrons and holes with a mechanism that is still controversial [18–32]. The idea that only the lowest CT state (CT<sub>1</sub>) dominated by the HOMO(D) to LUMO(A) transition is accessible through the internal conversion process from the FE state is very useful for giving qualitative descriptions of exciton dynamics in many cases but sometimes it may be too simplified for quantitative predictions especially when one considers the relatively dense energy levels of frontier orbitals in medium to large sized  $\pi$ -conjugated molecules and also the structural versatility of chemical substances. For example, it is well-known that the fullerene (C<sub>60</sub>) molecule has three degenerate LUMOs due to

its high symmetry and accordingly the dimer complex of any donor molecule and one fullerene molecule will have three nearly degenerate lowest CT states. Then the charge separation efficiency can be expected to be much enhanced because it will be the sum of the contributions by three CT states. Recent work by Liu and Troisi [33] verified that slightly lifted LUMO/LUMO+1 degeneracy in the fullerene derivatives can further increase the charge separation rate by more than one order of magnitude instead of only three times because the slightly lifted LUMO/LUMO+1 degeneracy can decrease the Gibbs free energy of the charge separation. However, whether such kind of 2nd CT state ( $CT_2$ ) or other higher CT states locating below the dipole allowed FE state can exist in other general D/A pairs with non-fullerene organic small electron-acceptor molecules is still unknown. (Please note that  $CT_1$ ,  $CT_2$  and other CT states in this paper are specified for a two-molecule system (a D/A pair). They do not have the usual meanings as the electronic excited states in large D/A heterojunction aggregates in other literatures.) If the answer is affirmative, it may provide further elements to explain why some donor-acceptor pairs are more efficient than others: an energetically accessible  $CT_2$  state from FE state can not only enhance the charge transfer rate but also provide multiple exciton dissociation channels and then, accordingly, improve the charge separation efficiency as illustrated in the scheme of Figure 1.

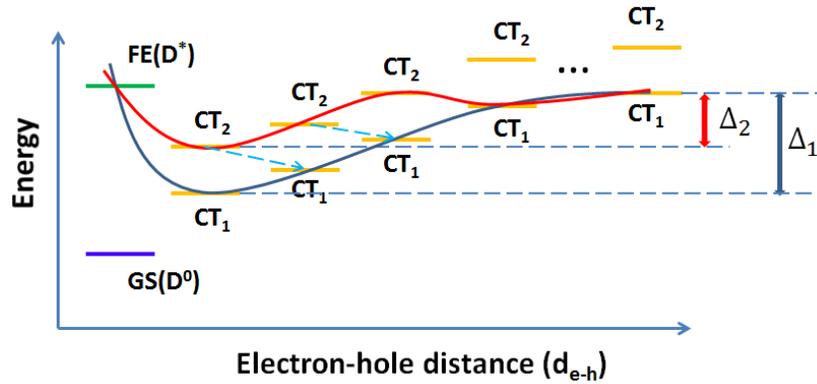


Figure 1: Schematics of the possible new channel (red lines) for photo-induced electron migration.

The aim of this work is therefore to answer the following two questions by virtue of quantum chemical calculations in conjugation with phenomenological models: i) can more than one CT states be energetically lower than the FE state for general non-fullerene D/A pairs? ii) can the exciton dissociation efficiency in OPVs be modulated by tuning the energy difference between  $CT_1$  and  $CT_2$ ? The outline of this study is as follows. In Sec. II, computational methods are introduced; in Sec. III, we studied the electronic structures of several widely used non-fullerene electron donor and acceptor molecules (as illustrated in Figure 2a) as well as their D/A dimers by quantum chemical calculations and we found that  $CT_2$  locating below the dipole allowed local exciton state can exist in not only nearly-degenerate fullerene-based systems but also, and maybe surprisingly, in some commonly used D/A pairs; in Sec. IV, we investigated the influence of the  $CT_2$  position on the exciton dissociation through a phenomenological models and different limits for the expression of the exciton dissociation rate. Some conclusions are given in simulations, and we revealed the exciton dissociation rate can be modulated up to more than 2 orders of magnitude; and finally, our results are summarized and concluded in Sec. V.

## ■ METHODS

**Quantum chemical calculations.** We calculated the electronic structures of selected representative non-fullerene electron donor and acceptor molecules by density functional theory (DFT) at their optimized neutral ground geometries. In order to avoid possible underestimation of fundamental gap and the energy of CT excited states by conventional DFT functionals, here we adopted the range-separated  $\omega$ B97X-D functional [34] with polarized Pople basis set 6-31G(d). For each of selected D/A pairs, we optimized the neutral ground state (GS) geometry by  $\omega$ B97X-D/6-31G(d) and then performed excited state electronic structure calculation at this GS geometry with time-dependent density functional theory (TDDFT) [35, 36]. The excited state nature (local excitation or charge-transfer character) was investigated by natural transition orbital [37] analysis. (see supporting information, Figure S1) Comparisons with results by other hybrid or range-separated density functionals and experimental observations of two representative molecules indicated that our scheme can give at least qualitatively correct estimation of the relative positions of frontier MO levels and the excitation energies for such small to medium sized conjugated molecules. (see supporting information, Table SI). All the quantum chemical calculations in this work were performed using Gaussian09 D.01 software package [38].

**Calculation of exciton dissociation rate.** For the purpose of evaluating the role of more CT states on the exciton dissociation efficiency in organic photovoltaics we considered two phenomenological models corresponding to two extreme situations: incoherent localized model and coherent delocalized model, which should capture the essential physics of the exciton dissociation process. In the first incoherent localized model we assume that the exciton dissociate into the CT state where hole and electron are adjacent (bound hole-electron pair) and we use Marcus theory [39] of charge transfer reaction to evaluate the charge separation rate increase due to the presence of the additional acceptor state. In the opposite limit when the Frenkel excitation

separates in the coherent delocalized charges we use a model that only takes into account the electronic degrees of freedom and describe the charge dissociation process as the irreversible transfer from a Frenkel state to the manifold of charge separated states degenerate with the original Frenkel state. In this limit a Fermi Golden rule expression can be applied.

## ■ CAN CT<sub>2</sub> LOCATE BELOW FE FOR NON-FULLERENE D/A PAIRS?

### Frontier MOs of representative molecules.

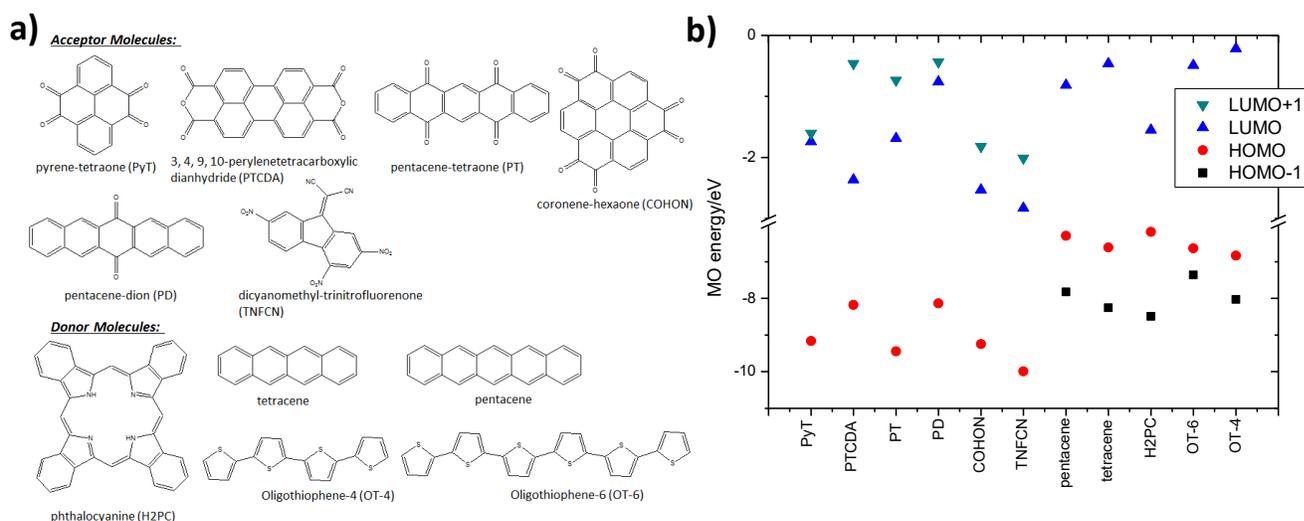


Figure 2: a) Selected electron donor and acceptor molecules studied in this work; b) frontier molecular orbital energy.

A low LUMO+1 energy of a acceptor molecule or a high HOMO-1 energy of a donor molecule may lead to low energy CT<sub>2</sub> state, as a low energy transition of HOMO(D)→LUMO+1(A) or HOMO-1(D) →LUMO(A) can be expected under these circumstance. Figure 2b reports the energies of the frontier MOs of selected representative electron donor and acceptor molecules listed in Figure 2a. As can be seen from Figure 2b, the investigated acceptor molecules in this

work do not have LUMO/LUMO+1 degeneracy and their energy difference is quite variable for different molecules, ranging from 0.14 eV for PyT to 1.91 eV for PTCDA. Similarly, the investigated donor molecules in this work do not have HOMO-1/HOMO degeneracy and their energy difference is also quite variable for different molecules, ranging from 0.72 eV for OT-6 to 2.31 eV for H2PC. Another important observation is that in many non-fullerene electron-acceptor molecules both LUMO and LUMO+1 are energetically lower than the LUMO of donor molecules and also in many donor molecules both HOMO and HOMO-1 are energetically higher than the HOMO of acceptor molecules. These facts imply that CT<sub>2</sub> may be located below the FE in many D/A heterojunctions.

**How frequently a CT<sub>2</sub> can be located energetically below FE in D/A pairs.** To estimate this frequency, we considered all 16 possibilities of constructing D/A dimer complexes from 4 widely used electron-donor molecules (pentacene, tetracene, H2PC and OT-6) and 4 popular non-fullerene electron-acceptor molecules (PyT, PT, COHON, TNFCN). The energy differences between CT<sub>2</sub> and FE state ( $\Delta_{CT_2-FE}$ ) for all these 16 D/A pairs are listed in Table I. Half (8) of all 16 pairs were found to have a negative  $\Delta_{CT_2-FE}$ . Therefore, not all D/A pairs have a CT<sub>2</sub> state which is energetically lower than FE, but this does happen quite often in many general D/A pairs suggesting that the presence of low lying CT<sub>2</sub> is one of the interface characteristics to be considered when different D/A pairs are considered.

TABLE I: Energy difference between CT<sub>2</sub> and CT<sub>1</sub> or the dipole allowed FE state in units of eV for various D/A dimers at their ground state optimized geometries. (The number before slash corresponds to  $\Delta_{CT_2-CT_1}$  and the number after slash corresponds to  $\Delta_{CT_2-FE}$ .)

	PyT	PT	COHON	TNFCN
pentacene	0.31/-0.36	0.98/0.75	0.50/0.12	0.80/-0.19
tetracene	0.16/-0.53	0.80/0.20	0.69/-0.31	0.92/-0.39
H2PC	0.22/0.47	1.12/1.26	0.71/0.49	0.76/0.33
OT-6	0.17/-0.56	0.76/0.02	0.47/-0.61	0.87/-0.55

The energy gaps between LUMO and LUMO+1 ( $\Delta_{LUMOs}$ ) for the four acceptor molecule (PyT, PT, COHON and TNFCN) are 0.14, 0.95, 0.71 and 0.82 eV respectively, and those between HOMO-1 and HOMO ( $\Delta_{HOMOs}$ ) for the four donor molecules (pentacene, tetracene, H2PC and OT-6) are 1.53, 1.65, 2.31 and 0.72 eV. Therefore, in most D/A pairs  $\Delta_{LUMOs}$  is much smaller than  $\Delta_{HOMOs}$ , which can also be found from Figure 2b, and accordingly a low energy CT<sub>2</sub> in many cases may be mainly contributed by a transition of HOMO(D)→LUMO+1(A). Figure 3 illustrates the relationship between  $\Delta_{LUMOs}$  of the acceptor molecule and  $\Delta_{CT_2-CT_1}$  for 16 selected D/A pairs. The quasi-linear relationship between  $\Delta_{LUMOs}$  and  $\Delta_{CT_2-CT_1}$  implies that the relative position of the two CT states is mainly determined by the energetic levels of the acceptor molecule and  $\Delta_{LUMOs}$  can be used as a rough estimation of  $\Delta_{CT_2-CT_1}$ .

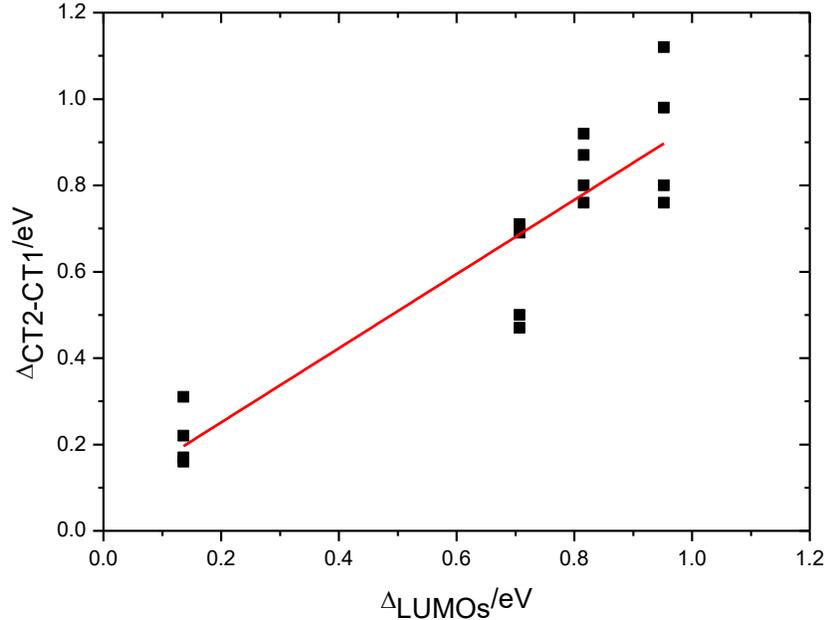


Figure 3: Relationship between  $\Delta_{LUMOs}$  of the acceptor molecule and the energy difference between CT<sub>2</sub> and CT<sub>1</sub> ( $\Delta_{CT2-CT1}$ ) for 16 D/A pairs.

**Effect of the intermolecular distance on the excited state energy level alignment.** It is well-known that the energy of CT states depends on the e-h distance, i.e., the intermolecular distance  $R$  between the donor and acceptor molecules. Therefore here we further examined the  $R$  dependence of the excitation energy of CT and local FE states for two selected D/A pairs (pentacene/PyT and tetracene/COHON) and the results were presented in Figure 4. It is shown that the energy of FE decreases slowly with the increasing intermolecular distance  $R$  while the CT<sub>1</sub> and CT<sub>2</sub> energies increase with  $R$  due to the weakening of e-h binding. For both dimers, CT<sub>1</sub> and CT<sub>2</sub> lie below FE when  $R$  is less than 4.5 or 5 Å. It should be noticed that the equilibrium intermolecular distance  $R$  for the ground state (GS) is around 3.5 Å for both dimers. Therefore, the two CT excited states are energetically accessible from the dipole allowed local FE state in

some general D/A dimer systems like pentacene/PyT and tetracene/COHON around their equilibrium GS geometries as we have shown in Table I. If the dielectric screening effect of the bulk materials (the relative permittivity of organic donor and acceptor molecules is usually around 2~4) is further considered, one can expect an additional stabilization of the CT states with respect to the FE state, increasing the likelihood of CT<sub>2</sub> being lower than FE and the range of donor-acceptor distance where this happens. It can be also noticed from Figure 3 that the energy gap between CT<sub>1</sub> and CT<sub>2</sub> does not change much with the varying intermolecular distance, indicating that the relative position of the two CT states is mainly determined by the energetic levels of the acceptor molecule, not much dependent on the intermolecular couplings.

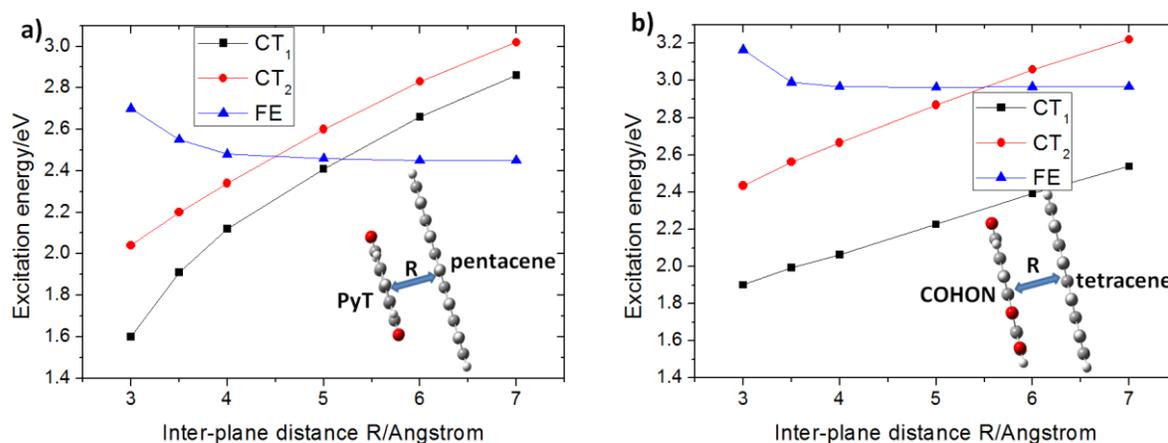


Figure 4: Dependence of the CT and local FE excited states on center-to-center intermolecular distance for (a) a pentacene/PyT dimer and (b) a tetracene/COHON dimer.

### Effect of excited state geometry relaxation on the excited state energy level alignment.

Organic electron donor or acceptor molecule may undergo geometrical reorganization within its specified new electronic state in slow incoherent hopping transport of the charge or exciton.[40,

41] The re-evaluation of the energy level alignment under relaxed geometries of different electronic states is therefore highly necessary. In this work we performed geometry optimizations for all three electronic states (GS, CT<sub>1</sub> and CT<sub>2</sub>) of the two dimers and also illustrated the energy level alignment of these states at different optimized geometries in Fig. 5. We found that for both dimers the intermolecular distance for CT<sub>1</sub> and CT<sub>2</sub> is slightly shorter than that for GS. Such slightly reduced intermolecular distance in CT<sub>1</sub> and CT<sub>2</sub> can decrease the e-h separation for which the energies of CT<sub>1</sub> and CT<sub>2</sub> can be lowered, and also increase the electronic couplings between neighboring molecules for which the FE energy can be also reduced. More importantly, it is evident that both CT<sub>1</sub> and CT<sub>2</sub> are always energetically lower than FE state in all three different optimized geometries of both pentacene/PyT and tetracene/COHON dimers. This verifies that more than one CT excited state can be energetically accessible from the FE state for a D/A pair during the realistic photo-induced electron transfer process even with the consideration of molecular geometry reorganization.

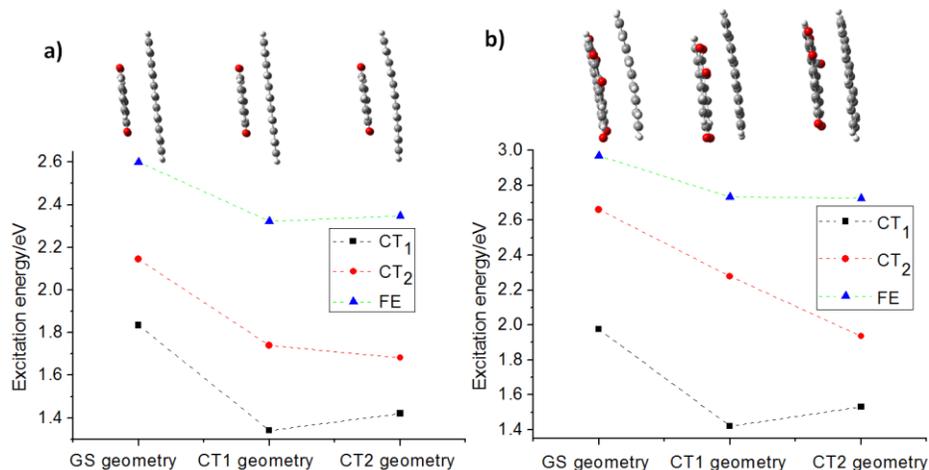


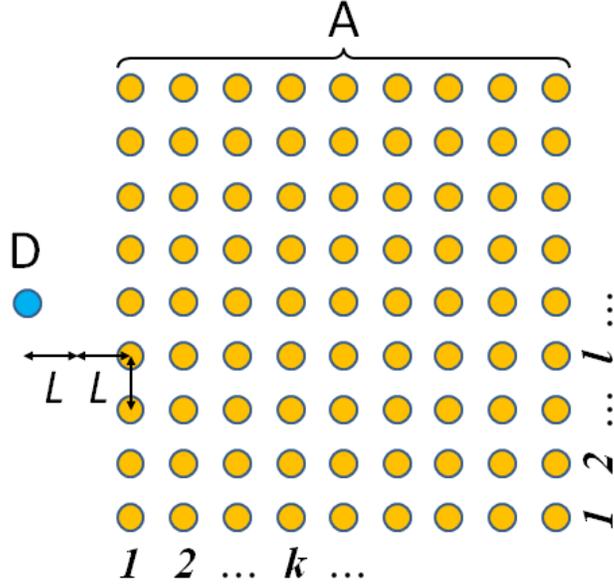
Figure 5: Energy level alignment of CT<sub>1</sub>, CT<sub>2</sub> and FE states of the pentacene/PyT dimer (a) and the tetracene/COHON dimer (b) at optimized geometries for different electronic states.

## ■ ROLE OF CT<sub>2</sub> STATE IN EXCITON DISSOCIATIONS

For the purpose of evaluating the role of more CT states on the exciton dissociation efficiency in organic photovoltaics we studied the phenomenological model illustrated in Figure 6 (and a variant discussed below), which should capture the essential physics of the exciton dissociation process. We started by considering a single donor molecule, coupled to a square aggregate of  $9 \times 9$  acceptor molecules with lattice unit  $L$  (results are similar for larger aggregates). The Frenkel exciton is initially localized on the donor and we assume that there are two available LUMOs on each of the acceptors separated by an energy  $\Delta_{LUMOs}$ . The dissociation of the Frenkel exciton generates states that are linear combination of the charge transfer states  $|kl, \alpha\rangle$  where the index  $k$  and  $l$  indicate the position of the acceptor molecule (see Figure 6) and the index  $\alpha$  indicates transfer to the LUMO ( $\alpha=1$ ) or the LUMO+1 ( $\alpha=2$ ). The Hamiltonian can be written as:

$$\hat{H}_{CT} = \sum_{kl, \alpha} -\frac{C}{r_{kl,D}} |kl, \alpha\rangle\langle kl, \alpha| + \sum_{kl} \Delta_{LUMOs} |kl, 2\rangle\langle kl, 2| + \sum_{\alpha\alpha'} \sum_{\{kl, k'l'\}} V |kl, \alpha\rangle\langle k'l', \alpha'| \quad (1)$$

The first term represents the Coulombic hole-electron attraction, where  $r_{kl,D}$  is the distance between donor and acceptor in units of  $L$ . The constant  $C$  is set to 0.96 eV, corresponding to lattice distance  $L=5 \text{ \AA}$  and relative dielectric constant 3. The second term indicates the additional energy needed to transfer the electron to the LUMO+1 orbital instead of the LUMO. The last term represents the coupling between CT states. The summation  $\{kl, k'l'\}$  is limited to nearest neighbour sites. We present here the results with a unique coupling parameters between CT states ( $V=0.1 \text{ eV}$ ) as more general models, where this coupling is different between different type of CT states, yield similar results.



**Figure 6.** Schematics of the model system considered to study the rate of exciton dissociation.

The DOS generated by the Hamiltonian above is depicted in Figure 7 and displays, expectedly, two well-separated CT band for large values of  $\Delta_{LUMOs}$  that approach each other until merging when  $\Delta_{LUMOs}$  is reduced down to  $\sim 1$  eV. The lowest energy of an isolated hole and electron are the zero of the energy scale. The model Hamiltonian in eq. (1) does not include the effect of disorder. However it was noted [Vazquez, Troisi, *PHYS. REV. B* 88, 205304, 2013] that plausible values of disorder do not affect appreciably the shape of the DOS which is dominated by the magnitude of the transfer integral and the Coulombic term (the latter being typically one order of magnitude larger than the disorder). Disorder does affect exciton localization and dynamics (not relevant for this model, where we consider a donor at a fixed position) and the hole and electron dynamics following the charge dissociation.

We assume that the Frenkel state is only coupled, via a matrix element  $V_{DA}$ , to the CT configurations obtained by transferring an electron to the closer acceptor (either LUMO or LUMO+1 orbital), i.e. to the states  $|15,1\rangle$  and  $|15,2\rangle$  in the  $9\times 9$  cluster. The perturbation that couples the Frenkel state with the CT manifold can be written as

$$\hat{V}_{DA} = V_{DA}(|\Psi_{FE}\rangle\langle 15,1| + |\Psi_{FE}\rangle\langle 15,2|) + h.c. \quad (2)$$

This allows a simple evaluation of the coupling  $V_{m,FE}$  between any CT state  $\Psi_{CT}^{(m)}$  and the Frenkel state as  $V_{m,FE} = V_{DA} \left( \langle 15,1 | \Psi_{CT}^{(m)} \rangle + \langle 15,2 | \Psi_{CT}^{(m)} \rangle \right)$ . We set the energy of the Frenkel state to  $E_{FE}=0.1$  eV, i.e. slightly above the energy of isolated hole and electron, and indicate the energy of the CT states as  $E_{CT}^{(m)}$ . The coupling  $V_{m,FE}$  is larger in CT states where the electron is closer to the hole (donor). To analyze the dependence of this coupling with the energy we can introduce the following quantity

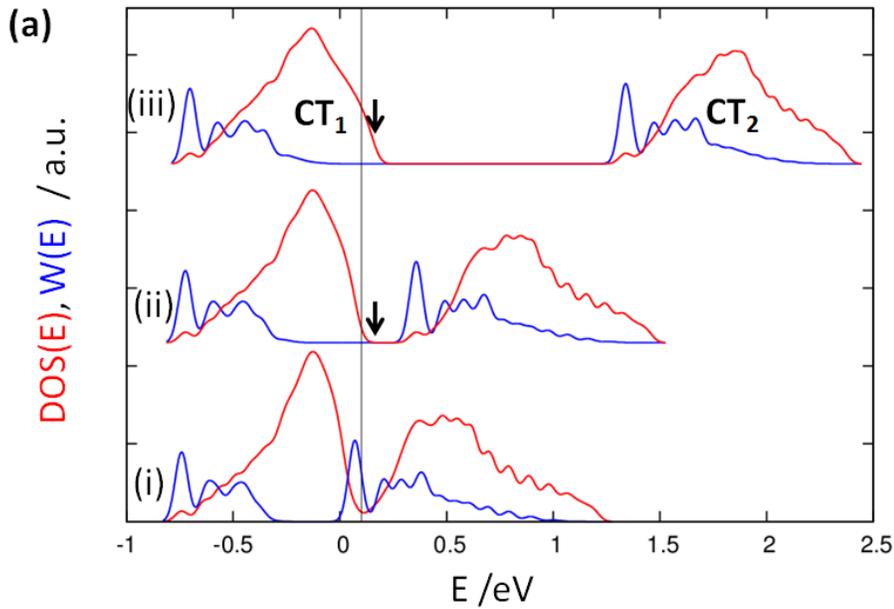
$$W(E) = \sum_m |V_{m,FE}|^2 \delta(E_{CT}^{(m)} - E) / |V_{DA}|^2 \quad (3)$$

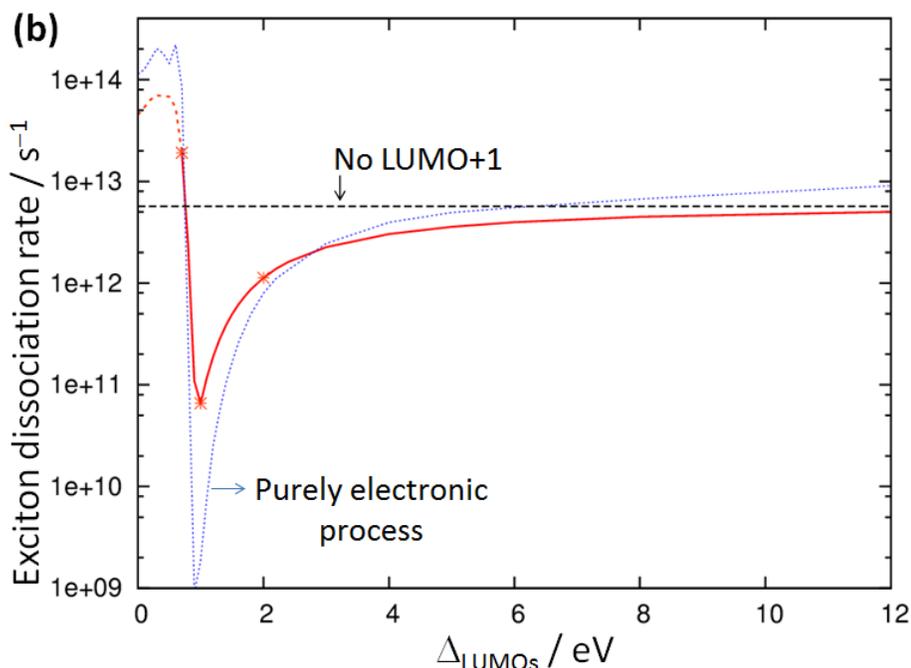
which is essentially a density of the CT states weighted by the strength of the coupling with the Frenkel state. This function, also reported in Figure 7, shows clear maxima at the lower energy edge of the two CT bands, i.e. the energy region where the CT states are more “bound”, with a closer hole-electron distance.

Finally, for the evaluation of the exciton dissociation rate we follow two different routes to better illustrate the nature of the charge dissociation process. We can initially assume that the dissociation rate is the sum of all dissociation rates toward any of the final CT states, each expressed by a Marcus rate equation (the validity of this approach is discussed below):

$$k_{ED} = \sum_m \frac{2\pi}{\hbar} \frac{|V_{m,FE}|^2}{(4\pi\lambda_m k_B T)^{1/2}} \exp \left[ -\frac{(E_{CT}^{(m)} - E_{FE} + \lambda_m)^2}{4\lambda_m k_B T} \right] \quad (4)$$

The reorganization energy  $\lambda_m$ , following ref. [12], is reduced for more delocalized CT states and can be parameterized as  $\lambda_m = \lambda_0 \left( \frac{1}{2} + \frac{1}{2IPR_m} \right)$ , where  $IPR_m$  is the inverse participation ratio of the CT states [12] (a measure of delocalization) and  $\lambda_0$  is the reorganization energy for a system formed by a single donor an acceptor, here set to 0.25 eV [12]. The computed rates, evaluated at  $k_B T = 0.025$  eV, are reported in Figure 7b as a function of the parameter  $\Delta_{LUMOs}$ .





**Figure 7.** a) Red curve: density of CT states for  $\Delta_{LUMOs} = 0.7$  (i), 1.0 (ii), 2.0 (iii) eV. Blue curve: function  $W(E)$ , defined in eq. 3, proportional to the squared coupling between FE and CT states (multiplied by 25 to improve visualization). The vertical line is the energy of the Frenkel exciton. b) Red curve: Exciton dissociation rate as a function of the energy difference between LUMO and LUMO+1 computed from eq. 4. The dashed portion of this curve corresponds to a region where the rate is possibly too fast for the adopted model to be valid. The dashed horizontal line is the reference value in the absence of a LUMO+1 state. The dotted line is the exciton dissociation rate computed from the Fermi golden rule neglecting polaronic effects (eq. 5, with delta function approximated by a normalized Gaussian with standard deviation 0.05 eV).

When  $\Delta_{LUMOs}$  is large, its value becomes irrelevant and the charge dissociation rate is similar to that of a system with only one accessible LUMO per molecule. For  $\Delta_{LUMOs} < 1$  eV, an order of magnitude enhancement of the charge dissociation rate is observed, due to the resonance

between the Frenkel exciton energy and the lowest CT state formed by a charge transfer to the nearest LUMO+1 orbital. Slightly less obvious is the explanation of the sharp decrease in exciton dissociation rate for  $\Delta_{LUMOs} \sim 1$  eV. In this region there are two CT bands, close but non-overlapping. The CT<sub>2</sub> band is not resonant with the Frenkel exciton and the dissociation proceeds toward the high energy states of the CT<sub>1</sub> band. The vicinity of the CT<sub>2</sub> band however modifies the DOS of the CT<sub>1</sub> band pushing the high energy states in the CT<sub>1</sub> toward lower energies and off resonance with respect to the Frenkel exciton. This effect is highlighted in Figure 7a where two arrows indicate the energy region where the CT<sub>1</sub> DOS is pushed at lower energy by the vicinity of the CT<sub>2</sub> band. In this situation, corresponding to  $\Delta_{LUMOs} \sim 1$  eV for the current model parameters, the exciton dissociation rate is reduced by more than one order of magnitude with respect to the reference situation of no LUMO+1 orbital present. The combination of these enhancing and decreasing effects suggests that the positioning of the LUMO+1 orbital can modulate the exciton dissociation rate by more than 2 order of magnitudes, a very remarkable observation considering that this parameter is essentially ignored in all qualitative descriptions of charge dissociation.

The supporting information reports the results of an analogous model where also the hole can be delocalized over many donors, which yields similar qualitative results and confirms that the assumption of a localized hole is not critical for the described phenomenon to take place. As originally noted in ref.[Troisi\_Faraday], when eq. 2 is used for delocalized states (of both donors and acceptors) the reorganization energy vanishes and the rate expression approaches the limit of the Fermi golden rule:

$$k_{ED}(\lambda_m \rightarrow 0) = \sum_m \frac{2\pi}{\hbar} |V_{m,FE}|^2 \delta(E_{CT}^{(m)} - E_{FE}) \quad (5)$$

This is the situation where the molecular vibrations do not play any role and the process is a purely electronic one. A successful description of the exciton dissociation in terms of purely electronic states was achieved for example in [*Gelinas, Science 2014 cited*]. This implies that eq. 4 has a broader range of validity than standard Marcus rate expression for the hopping between two electronic states. In the presence of a continuum of electronic states, the total rate (which can possibly be even in the ultrafast range), results from the sum of many vanishing individual rates for which Marcus expression is valid. It is instructive to consider the rate computed from eq. 5 to illustrate the results of a system where nuclear modes can be frozen, in a model reminiscent of the Newns-Anderson model [*DM, Newns, Phys Rev 178 (1969) 1123*]. The results are rather close to that computed from eq. 4 confirming that the charge dissociation process is dominated by the purely electronic degrees of freedom[DOI: 10.1039/C4CP01791A]. Moreover, the main feature described in this paper, namely the strong dependence of the dissociation rate on the LUMO+1 position, is not determined by the approximations introduced to include the electron-phonon coupling in eq. 4. Still, for exciton dissociation rates exceeding  $10^{13} \text{ s}^{-1}$ , it may be desirable to replace the theory used here with a description of a coherent dynamics within the CT manifold, which is however outside the scope of this paper.

The presence of low energy LUMO+1 is a well-known feature of all fullerene derivatives used as electron acceptors, which remain the most efficient electron acceptors to date. There is an ongoing effort to replace fullerene derivatives with other molecules and it is interesting to see whether the best non-fullerene acceptors share with fullerenes the property of having low energy LUMO+1 orbital. A survey of the recent literature suggests that this might be the case. The recently synthesized perylene diimide (PDI) dimer (namely Bis-PDI-T-EG) [42] was reported to

have a high PCE of 4.03% (the highest among non-fullerene acceptors at the time of publication), but it has very close LUMO energy with its monomeric counterpart PDI 1 (-3.84 eV vs. -3.74 eV) and quite different PCE value (4.03% vs. 0.13%). Our calculation found that Bis-PDI-T-EG has a very small energy gap between LUMO and LUMO+1 (0.02 eV) while PDI 1 has a considerably higher LUMO+1 (1.67 eV). Therefore, our model can nicely explain this new experimental phenomenon because we have revealed that the positioning of the LUMO+1 orbital can significantly influence exciton dissociation rate. The high efficiency acceptor described above is part of a promising family of acceptors reviewed in [*Mater. Horiz.*, 2014,1, 470-488] and based on dimers (and trimers) of the PDI moiety, which naturally possess low lying LUMO+1 (and LUMO+2) orbitals. Another very recently proposed acceptor, a Zn(II) complex based on azadipyrromethene [DOI: 10.1002/adma.201400647] displays PCE of 4.1% and possesses a computed gap between LUMO and LUMO+1 of just 0.06 eV. The available molecular acceptors with PCE larger than 3% are still too few to conclude that the correct positioning of the LUMO+1 is a general “rule” for high efficiency acceptors (and surely there are other important characteristics that acceptor molecules must have) but the survey of the literature seems to support the proposed model so far.

## CONCLUSION

In summary, we have first shown that it is very common in molecular donor-acceptor pairs to find two CT states energetically below the first optically bright state. Then we have shown that the position of the second CT state can modulate the exciton dissociation rate up to more than 2

orders of magnitude. ~~This provides a new guiding principle for the design of novel organic solar cells with further enhanced PCEs.~~

Herein we only focused on the possibilities to have CT<sub>2</sub> energetically lower than FE in many non-fullerene D/A pairs, but actually one can also expect that even CT<sub>3</sub> or other higher CT states will locate below FE in some special systems. For example, trimer structure with weak linkages between monomer units is possible to have close LUMO, LUMO+1 and LUMO+2 and the consequent small energy gaps between CT<sub>1</sub>, CT<sub>2</sub> and CT<sub>3</sub>. More significant modulation behavior of exciton dissociation rate by tuning both CT<sub>2</sub> and CT<sub>3</sub> positions is therefore highly expected. ~~This is not the scope of this work but obviously further detailed explorations by both theories and experiments along this direction are highly desired in the near future.~~ It should be of course remembered that OPV devices are extremely complex and it will never be possible to build two devices which differ only for the energy position of the second CT state. On the other hand, the presented model and the available data in literature indicate that the alignment of CT<sub>2</sub> state should be included among the guiding principles for the design of novel organic solar cell with enhanced PCE.

#### ASSOCIATED CONTENT

**Supporting Information.** Natural transition orbital analysis of different excited states. Effect of quantum chemical method on the accuracy of calculated energy levels. Phenomenological model including the delocalization over the HOMO orbitals. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## Notes

The authors declare no competing financial interests.

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