Direct and Energy-Transfer Mediated Charge Transfer State Formation and Recombination in Triangulene-Spacer-Perylenediimide Multichromophores: Lessons for Photovoltaic Applications

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ABSTRACT: We study dynamics of primary photoexcitations in three symmetric donor-spacer-acceptor-spacer-donor (D-S-A-S-D) multichromophores with increasing oligophenylene spacer length, following selective donor or acceptor excitation. Energy levels of the donor and acceptor moieties are tailored to facilitate splitting of the excited state into a lower-lying charge transfer (CT) state, mimicking the functionality of a donor-acceptor interface for charge generation, and thus resulting in long-lived charge separation. Ultrafast electronic energy transfer (EET) from the donor followed by fast hole (back)transfer from the acceptor populates the molecules' CT states. However, the charge transfer efficiency is found to be close to unity independent of the donor or acceptor photoexcitation. The ratio of charge transfer and recombination rates, which reflects the population of CT states, increases with the oligophenylene spacer length for both, direct hole transfer and hole-transfer following EET, boosting the population of CT states under continuous excitation. We observe the population of high-lying 'dark' excited states following energy transfer from the donor to the acceptor. The 'dark' states successively undergo charge transfer and form CT states of higher energy, with decreased recombination rates, while maintaining the high charge generation efficiency. Changes in charge transfer reaction rates are rationalized within the Marcus theory, with driving forces and reorganization energies evaluated by density functional theory and polarizable continuum models. The present study demonstrates the importance of energetically higher-lying states, which cannot be directly photoexcited, yet are accessible through energy transfer from local excited states. Similar processes are anticipated in other donor-acceptor systems, which allow for both energy and charge transfer processes, such as bulk heterojunctions of polymer and small molecule donor / non-fullerene acceptor typically used in photovoltaic systems.

INTRODUCTION

Photoinduced electronic energy transfer (EET) and charge transfer (CT) processes are of key interest in photosynthesis,¹⁻³ photocatalysis,⁴⁻⁵ organic light emitting diodes,⁶⁻⁷ organic photovoltaic cells,⁸⁻¹⁴ and many related photophysical phenomena where long-distance charge separation is essential.¹⁵⁻¹⁹ These processes are, however, rather intricate already in simple molecular donor-acceptor type dyads,²⁰⁻²² where EET can proceed via the CT state, enabling fast energy transfer between the donor and the acceptor units even with orthogonal transition dipoles.²³ Moreover, Förster or Redfield theories, which are successful in describing long-range EET, cannot rationalize it in small molecular dyads with large electronic couplings between the states.²⁴⁻²⁶ The situation is even more complex in symmetric donor-acceptor-donor (DAD), or acceptor-

donor-acceptor (ADA) triads, where also the symmetry of the charge transfer state (quadrupolar versus dipolar) depends on the strength of the electronic coupling between donor and acceptor units and stabilization by the environment.²⁷⁻²⁸ The molecular structure can therefore be used to control the charge transfer mechanism by, e.g., varying the length of the conjugated spacer, thereby controlling the coupling between the donor and acceptor in the multichromophor.¹⁶

The precise mechanism of charge transfer and separation in donor-acceptor systems as nowadays used in organic solar cells is still a matter of debate. In this regard, an open question is the optimum distance between donor and acceptor that ensures complete charge transfer and separation, while simultaneously suppressing charge-transfer state (geminate) recombination. Donor-spacer-acceptor molecules with varying spacer lengths between the donor and acceptor moieties are

ideal test systems, as they allow to study the effect of donor-acceptor separation without the complexity of intermolecular interaction typical for a bulk heterojunction or even single-component OSCs.²⁹⁻³²

Previous works demonstrate that increasing the donor-acceptor spatial separation slows down charge generation and recombination due to a distance-dependent superexchange charge tunneling mechanism. Furthermore, it has been shown that a transition to a weakly distance-dependent charge transport regime is possible at increased donor-acceptor separation. This mechanism corresponds to a thermally-activated charge hopping process between spacer units.^{15-16, 33-35} Gorczak et al.³⁶ observed the same distance-dependent behavior for hole transfer, while the electron transfer process was faster and distance-independent. They explained the imbalance of the two processes by differences in delocalization of the initial excitations. Intramolecular energy transfer was also investigated in donor-spacer-acceptor systems and shown to be distance-dependent.³⁷ Kölle et al.³⁸ studied charge and energy transfer processes in PDI dyads through polyyne spacers with varying length. However, up to now an in-depth study revealing the effect of energy transfer on the efficiency of sequential charge generation has not been presented.

More specifically, with the recent development of non-fullerene acceptors,³⁹⁻⁴⁷ energy transfer competing with charge transfer between the donor and acceptor moieties has to be considered as well.⁴⁸⁻⁴⁹ Again, molecular DA systems can be tailored to have both energy and charge transfer, depending on the energetics of the donor and acceptor building blocks, in turn allowing to study both processes in one molecular system.⁵⁰⁻⁵² A better understanding of the photophysics in a well-controlled DA multichromophore could help to further fine-tune the efficiency boost brought to the OSC field by non-fullerene acceptors.

Of particular interest in charge transfer systems such as OSCs is the ratio of two rates, the rate of intramolecular generation of a charge transfer (CT) state to its non-radiative recombination rate, $k_{(e^* \rightarrow ct)}/k_{(ct \rightarrow g)}$. Indeed, in the stationary case and as long as we can neglect electron back-transfer from the CT to the primary excited state and the recombination of the primary excited state itself, $p_{(e^*)}k_{(e^* \rightarrow ct)} = p_{(ct)}k_{(ct \rightarrow g)}$, where $p_{(e^*)}$ is the population of molecules in the primary excited state and $p_{(ct)}$ is the population of molecules in the charge transfer state. This ratio is effectively a measure of the charge generation efficiency irrespective if the process is an electron transfer, hole transfer, or hole (back)transfer after energy transfer (two-step process). Since the internal quantum efficiency is proportional to $p_{(ct)}/p_{(e^*)}$, we can improve the total efficiency of the solar cell by increasing this ratio, e.g., by varying the distance between the electron donor and acceptor.

Though both rates are expected to decrease with the spacer length, it is difficult to predict whether their ratio decreases or increases with the length. Furthermore, the rates could be different for direct hole-transfer or sequential energy and hole transfer from the donor to the acceptor, if other electronic or vibronic states are involved. To address these questions, we designed and synthesized a series of symmetric donor-spacer-

acceptor-spacer-donor model arrays with different oligophenylene spacer length, varying from one up to four phenylene groups, as depicted in Figure 1. All molecules are comprised of a perylene-diimide (PDI⁵³) electron acceptor. In addition to varying the spacer length, the donor strength is altered as well. Precisely, the PDI acceptor is either linked to two triangulene (N-heterotriangulene: dimethylmethylene-bridged triphenylamines) or two thiotriangulene (NS-heterotriangulene: dimethylmethylene- and thio-bridged triphenylamines) electron donating donor moieties. Both triangulene donor units, namely the N-heterotriangulene (T) and NS-heterotriangulene (TT), resemble triphenylamine, a common building block used in organic semiconductors as electron donor and / or charge (hole) transport moiety. We note that the thiotriangulene's reduction potential is about 100 meV higher (closer to the vacuum level) than that of triangulene itself. Compared to triphenylamine, the triangulene (and heterotriangulene) structures are more planar due to the bridging carbon (or sulphur) atoms, in turn allowing closer intermolecular packing and thereby facilitating charge transport. The (thio)triangulene donor is spatially separated from the electron acceptor PDI by oligophenylene spacers of different length: TT-Ph-PDI has one phenylene, while T-(Ph)₂-PDI and T-(Ph)₄-PDI employ two and four para-oligophenylenes as spacer units, respectively. Although the individual phenylene rings are conjugated, experimentally measured absorption spectra as well as density functional calculations show that the large twisting angle between successive rings interrupts the conjugation between the donor and acceptor units. Using ultrafast transient absorption (TA) spectroscopy we investigate the effects of increasing spacer length on the generation and recombination rates of intramolecular CT states following photoexcitation of either the acceptor or donor by monitoring the spectral evolution of the primary photoexcitation (local exciton) and intramolecular CT states in diluted dichloromethane (DCM) solutions. We apply multivariate curve resolution-alternating least square (MCR-ALS)⁵⁴ to separate the component-associated spectra and dynamics of singlet excitons and intramolecular CT states and to accurately determine the hole and electron transfer rates and CT state lifetimes.

Figure 1. Chemical structures of donor-spacer-acceptor-spacer-donor arrays used in this study (**TT-Ph-PDI**, **T-(Ph)₂-PDI**, and **T-(Ph)₄-PDI**) as well as two donor moieties (triangulene and thiotriangulene). PDI core (acceptor) is highlighted in red.

RESULTS AND DISCUSSION

Synthetic Procedures.

TT-Ph-PDI, **T-(Ph)₂-PDI**, and **T-(Ph)₄-PDI** were synthesized according to the synthetic concepts used for rylene-based multi-chromophores.⁵⁵⁻⁵⁶ Scheme 1 and Scheme 2 depict the three

separate steps: synthesis of 1) donor moieties, 2) acceptor units, and 3) coupling of donor and acceptor units.

The functionalized donor subunit, triangulene **4**, was obtained via stoichiometric bisfunctionalization of N-heterotriangulene **1** with N-bromosuccinimide (NBS). Subsequent Suzuki-Miyaura coupling with 4-(methylthio)phenylboronic acid pinacol ester and an additional NBS bromination yielded the final building block **4** as a colorless powder. The other donor moiety, heterotriangulene **11** is a newly designed molecule. Its synthesis was based on the synthetic method used for **1**. The inclusion of the sulfur atom into the conjugated backbone of the triarylamine was achieved by utilizing readily available phenothiazine **6** as starting material. Compound **6** was reacted with dimethyl-2-bromoisophthalate under Ullmann conditions yielding the diester **7**. Subsequent Grignard-reaction and acid-catalyzed intramolecular cyclization afforded the targeted donor building block **9**. Due to the reduced symmetry when comparing **9** and **1**, a selective mono-bromination could be achieved in the “para”-position in regards to the sulfur atom yielding **10** with 94%. Subsequent borylation by Pd-catalyzed reaction led to **11** as a yellow powder.

The synthesis of acceptor units for all three investigated sequences started with dibromo-PDI **13**. Donor building-block **11** was directly coupled to **13** via the Suzuki-Miyaura coupling, furnishing **TT-Ph-PDI** in 49%. Incorporation of the solubilizing terphenylene spacer was achieved through a borylation/cross-coupling/borylation cascade reaction using 1,4-dibromo-2,5-diocetylbenzene. The final Suzuki-Miyaura heterocoupling between **16** and triangulene **4** led to the targeted dyad **T-(Ph)₂-PDI**. In the case of **T-(Ph)₄-PDI**, the terphenylene spacer **12** was applied, followed by the coupling between **17** and **4**. More detailed synthetic procedures and molecular characterization are provided in Supplementary Note 1.

Scheme 1. i) N-Bromosuccinimide (NBS), CHCl_3 , 0 °C, 72%; ii) 1,4-dioxane, K_2CO_3 , $\text{Pd}(\text{PPh}_3)_4$, 90 °C, 4 h, 87%; iii) CHCl_3/THF (10:1), NBS, 0 °C, 3 h, 76%; iv) CuI , Cu , K_2CO_3 , Ph_2O , 180 °C, 2 d, 65%; v) MeMgBr or MeMgI , toluene/ Et_2O , no purification; vi) H_3PO_4 , RT, overnight, 43% over two steps; vii) NBS, CHCl_3 , -10 °C to 0 °C, 1 h, overnight, 95%; viii) bis(pinacolato)diboron (B_2PIN_2), DMF, KOAc, $\text{Pd}(\text{dppf})_2\text{Cl}_2$, 85 °C, 3 h, 68%.

Scheme 2. i) **12**, K₂CO₃, Pd(PPh₃)₄, toluene/water/EtOH, 85 °C, overnight; 49%; ii) B₂PIN₂, 1,4-dioxane, KOAc, Pd(dppf)₂Cl₂, 85 °C, 5 h, 42%; iii) toluene/water/ethanol, K₂CO₃, Pd(PPh₃)₄, 85 °C, 8 h, 81%; iv) B₂PIN₂, 1,4-dioxane, KOAc, Pd(dppf)₂Cl₂, 85 °C, 12 h, 68%; v) **4**, toluene/water/Aliquat336, 18-crown-6, K₂CO₃, Pd(PPh₃)₄, 85 °C, 2 h, 60%; vi) K₂CO₃, Pd(PPh₃)₄, toluene/water/EtOH, 85 °C, overnight, 54%; vii) K₂CO₃, Pd(PPh₃)₄, toluene/water/Aliquat 336, 85 °C, overnight, 14%.

Electronic Properties

The results of cyclic voltammetry (CV) measurements of multichromophores as well as the neat triangulene donor and PDI acceptor moieties are summarized in Figure 2 (cyclic voltammograms are shown in Supplementary Note 2). Reduction potentials of the three tryads are due to the (thio)triangulene unit. A difference in the oxidation potential of about 100 meV between the neat thiotriangulene and triangulene is observed, which translates to a difference of about 50 meV in the title compounds (donor-acceptor tryads). The oxidation potential is due to the PDI core, and does not change with the spacer length. Density functional theory (DFT) calculations further support this: the highest occupied molecular orbital (HOMO) is localized on the triangulenes/thiotriangulenes, while the lowest unoccupied molecular orbital (LUMO) is localized on PDI, as shown in Figure 2 for the compound with the shortest spacer. While CV measurements and DFT calculations confirm the donor-acceptor nature of the molecules, no ground state CT formation, i.e., reduction of perylene diimide / oxidation of (thio)triangulene, is observed in dichloromethane.

Figure 2. Reduction (red) and oxidation (blue) potentials as extracted from cyclic voltammetry. Localization of the highest occupied (HOMO, red) and lowest unoccupied (LUMO, blue) orbitals shown for **TT-Ph-PDI** indicates that the conjugation between the donor and acceptor units is indeed broken already for the shortest spacer. Calculations are performed at the m062x/6-31g(d) level of theory using implicit solvent (dichloromethane, DCM).

Steady-State Optical Characterization

UV-Vis absorption and steady-state photoluminescence (PL) spectra were recorded in dichloromethane (DCM) at concentrations of 10^{-5} mol/L. As shown in Figure 3, the absorption of the D-A complexes clearly resembles the signatures of its donor and acceptor moieties. The 0-0, 0-1, and 0-2 vibronic bands of PDI can be seen at 528 nm, 492 nm, and 460 nm, while the higher energy absorption bands (wavelengths below 400 nm) clearly resemble the absorption of the (thio)triangulene molecules (black lines). However, notable differences also exist between the absorption of different DA dyads: in **TT-Ph-PDI**, the high energy absorption is red-shifted compared to that of thiotriangulene, while no such shift can be seen in **T-(Ph)₂-PDI** and **T-(Ph)₄-PDI**. In addition, the intensity of the first high energy absorption peak at around 370 nm increases with the spacer length. An increase and/or red shift of absorption with spacer length in D-spacer-A type molecules has been reported previously^{37, 57-58} and can be explained by the delocalization of the orbitals across the spacer. This is further supported by TD-DFT calculations: The natural transition orbitals of several lowest energy optical transitions in thiotriangulene, triangulene, **TT-Ph-PDI** and **T-(Ph)₂-PDI** are also shown in Figure 3. In all DA molecules, the first ‘bright’ excited state (denoted as A, state 1 of **TT-Ph-PDI** in Figure 3) corresponds to the first excited state of PDI. The charge transfer state with an electron localized on the PDI and a hole on a triangulene has a lower energy (in DCM), but is dark due to the broken conjugation by the spacer between the donor and acceptor blocks. Note that the electronic decoupling of the donor and acceptor is due to a bridging unit with two methyl groups, which lock its orthogonal orientation with respect to the acceptor. Hence, the acceptor is very well decoupled from the bridge and hence from the donor. The entire list of the first ten excited states, their energies, oscillator strengths, and natural transition orbitals is given in Supplementary Note 4. The second bright excited state (denoted as B and C in Figure 3) originates from the donor, triangulene. Again, a small red shift with respect to the triangulene itself is due to wavefunction delocalization over the spacer. In the case of **T-(Ph)₂-PDI** and **T-(Ph)₄-PDI**, peak C (states 7 and 8, respectively) corresponds to the lowest energy absorption of the triangulene (peak 3, state 1 of triangulene). Peak B of **TT-Ph-PDI** corresponds to an excited state, which is practically non-absorbing in thiotriangulene (state 2 is responsible for the shoulder 1 of the absorption). In **TT-Ph-PDI** this state redshifts and becomes optically active due to the extension over the spacer (state 9 of **TT-Ph-PDI**). Since each DA dyad has two triangulenes, its molar extinction is doubled in the 300-400 nm spectral region of the DA dyad. For the same reason, all excited states corresponding to triangulene are doubly degenerate. Overall, none of the ten lowest energy excited states of the DA molecules extends over both the PDI and triangulene blocks,

indicating a strong decoupling due to the out-of-plane twist of the spacer unit. Such conjugation breaking,⁵⁹⁻⁶¹ together with the alignment of the energy levels of the first optically active and charge transfer states, makes these systems very much alike to donor/acceptor pairs at heterojunction interfaces of organic solar cells. A clear advantage of D-A-D tryads is that the DA intermolecular distance is (chemically) controlled, greatly simplifying the analysis of the electro-optical processes.

The steady-state fluorescence spectra were measured by exciting the PDI core at 490 nm. The emission spectra, shown in Figure 3 (dashed-dotted line), are similar for all three molecules, mirroring the absorption spectrum of the PDI. The fluorescence quantum yields are, however, very low. Since previous studies showed that PDI monomers in solution have a fluorescence quantum yield close to one,⁶² we can already anticipate that the PDI excitation is converted to a ‘dark’ state in competition to its fluorescent decay.

Figure 3. UV-Vis absorption spectra (solid lines) and fluorescence (dashed-dotted lines) of **TT-Ph-PDI** (blue) and thiotriangulene, **T-(Ph)₂-PDI** (red) and triangulene, and **T-(Ph)₄-PDI** (green) and triangulene measured in dilute solutions, together with the natural transition orbitals of **TT-Ph-PDI**, **T-(Ph)₂-PDI**, and the individual triangulene molecules. First ten orbitals for all compounds are shown in the Supporting Information.

Excited and Charge Transfer State Dynamics

To further investigate the fate of the PDI excited state, transient absorption (TA) spectra of a dilute solution of **TT-Ph-PDI** (10^{-5} mol/L in DCM) were recorded for delay times in the ps-ns range after selective excitation of the PDI at 490 nm. The TA spectra, shown in Figure 4a, consist of three main features assigned by comparison with independent reference measurements from other spectroscopy techniques, shown in Figure 4b. First, from 2.32 to 3.0 eV, a positive differential transmission signal matching the steady-state UV-Vis absorption of PDI (solid line) is attributed to the ground state bleach (GSB) of the acceptor part of the molecule. Second, between 1.85 and 2.30 eV, a positive TA signal is observed only at early time delays and ties to the PL emission obtained by steady-state PL (dotted line) experiments. Thus, these bands are assigned to stimulated emission (SE). Third, below 1.9 eV, a negative signal due to excited state absorption (ESA) is observed.

The evolution of the TA spectra reveals that a transition occurs between two states. These two states are observed by monitoring the spectral region of SE, shown in Figure 4c. Here, we focus on this spectral region as it shows a clear and fast transition. We first observe the initial SE signal including the 0-1 and 0-2 PDI vibronic peaks of emission from PDI excitons. These peaks decay fast within the first 8 ps, and evolve to a broad negative ESA signal, which is significantly longer-lived. The TA kinetics of SE and ESA regions are compared in Figure 4d and clearly show different dynamics. We assign the positive SE signal to the primary photoexcitation, i.e., PDI excitons, since the SE signal reflects the population of PDI excitons as seen in Figure 4b. The negative longer-lived ESA signal is assigned to absorption from intramolecular CT states, as the spectral signatures of these long-lived bands match those of PDI anions. The spectrum of PDI anions, measured by photo-induced absorption (PIA) and presented in Figure 4b, clearly exhibits the same ESA bands at 1.3, 1.5, and 1.68 eV as the ESA observed in TA after a few picoseconds (after the decay of PDI excitons). We therefore conclude that the observed evolution of the TA spectra can be attributed to hole transfer from the photoexcited PDI to the thiotriangulene (see Supplementary Note 6 for more details about the extraction of the PIA spectrum).

Figure 4. (a) Transient absorption (TA) spectra of TT-Ph-PDI in

solution (10^{-5} mol/L) photo-excited at 490 nm (excitation density $53 \mu\text{J}/\text{cm}^2$) (b) Reconstruction of TA spectra using UV-Vis absorption (solid line), PL emission (dotted line) and PIA spectrum of poly(3-hexylthiophene):PDI (dashed-dotted line). (c) Spectral evolution from SE to ESA in TT-Ph-PDI. (d) TA kinetics of SE region (integrated between 1.9 and 2.13 eV) and ESA region (integrated between 1.25 and 1.75 eV).

We de-convoluted the TA spectra dynamics into PDI excitons and intramolecular CT-states using multivariate curve resolution (MCR) analysis as explained in the Supplementary Note 7. The component spectra of the MCR analysis match the previously reported spectra of PDI* (excitons) and PDI anions, supporting that two states are observed.^{15, 36, 63} MCR analysis confirms that we observe two dominating processes upon PDI excitation: hole transfer from the PDI excited state [a^*] to the thiotriangulene, forming the charge transfer [ct] state, and the charge transfer state decay back to the ground state. To extract the charge transfer and charge recombination rates, we used a minimalistic set of rate equations^{21, 64} for a three-state system, depicted in Figure 5. We omitted back-transfer of the hole from thiotriangulene to PDI, since the ionization energy offsets between thiotriangulene and PDI are larger than 0.5 eV, that is, well above the thermal activation energy.⁶⁵ The fluorescence decay of PDI chromophores was also neglected, since the PDI fluorescence decay rate in dichloromethane is of the order of $\sim 2.5 \times 10^8 \text{s}^{-1}$,^{62, 66} thus well below the sub-100 ps exciton decay predicted by our MCR analysis. To this end, the forward hole-transfer rates and recombination rates of CT-states were obtained by applying a global fit on the MCR output dynamics using the solution of the rate equations as explained in the Supplementary Note 20.

Figure 5. Four state model used to fit the experimental data. $k_{a^* \rightarrow g}$ and $k_{ct \rightarrow g}$ are the decay rates of excited singlet and CT states to the ground state, $k_{a^* \rightarrow ct}$ is the hole-transfer rate from the PDI to the

triangulene block, and $k_{d^* \rightarrow a^*}$ is the energy transfer rate from the donor to the acceptor (PDI) and is only present if donor is excited.

Figure 6 shows the experimentally determined population dynamics of PDI excitons and CT states in all three model tryads, together with their fits. The CT state generation and recombination rates, as well as their ratios, are summarized in Table 1. In organic solar cells, donor and acceptor absorption spectra can complement each other, thereby helping to harvest a larger part of the solar spectrum. To gain more insight into the role of the donor excitation on the processes occurring at the DA interface, we performed also TA measurements following excitation of the donor at 355 nm. Analysis of the TA spectra presented in Supplementary Note 8 clearly indicates that an additional process takes place upon donor excitation, and can be assigned to the energy transfer from the excited donor to the PDI core.⁶⁷ To extract the charge transfer and charge recombination rates, we additionally took into account the energy transfer process, as illustrated in Figure 5. The corresponding fit of the output of the MCR analysis is shown in Figure 6. The rates of energy and hole transfer, as well as charge recombination are summarized in Table 1. As expected, the energy transfer rate from $T^*(\text{Ph})_4\text{-PDI}$ to $T(\text{Ph})_4\text{-PDI}^*$ is smaller than from $T^*(\text{Ph})_2\text{-PDI}$ to $T(\text{Ph})_2\text{-PDI}^*$, since the donor and acceptor are further apart in $T(\text{Ph})_4\text{-PDI}$. However, the ratio of the rates does not obey the Förster rate expression, $k \sim d^{-6}$, since the donor and the acceptor are too close to each other to justify the dipole-dipole interaction approximation (this would theoretically amount to a ratio of $\sim (27/19)^6 \approx 6$ as compared to $217/105 \sim 2$ observed experimentally). The ultrafast energy transfer in **TT-Ph-PDI** is a first

indication that in this multichromophore tryad Dexter-type energy transfer takes place. This conclusion is further supported by DFT calculations, which demonstrate that the donor orbitals are partially delocalized over the spacer unit closest to them, resulting in a partial direct overlap between the donor and acceptor orbitals participating in the energy transfer reaction.

Figure 6. Population of PDI excitons (black circles), triangulene excitons (orange rectangles) and intramolecular CT-states (blue triangles for **TT-Ph-PDI**, red triangles for **T-(Ph)₂-PDI** and green triangles for **T-(Ph)₄-PDI**) upon acceptor excitation (D-S-A*) and upon donor excitation (D*-S-A). Dynamics of thiotriangulene excitons in **TT*-Ph-PDI** are not shown, since their decay is much faster than the temporal resolution of our TA setup. Global fits of equations explained in Supplementary Note 20 are shown as solid lines. The observed initial rise of the CT state population is due to the excitation laser pulse.

Table 1. Energy transfer, generation and recombination rates of intramolecular CT-states determined by fitting the population dynamics of MCR outputs. D-S-A* solutions were photo-excited at 490 nm. D*-S-A solutions were photo-excited at 355 nm. Energy transfer, charge generation and recombination rates are extracted by fitting the population dynamics of MCR outputs.

Excitation	Energy transfer $k_{d^* \rightarrow a^*}$ [$\times 10^9 \text{s}^{-1}$]	Generation $k_{a^* \rightarrow ct}$ [$\times 10^9 \text{s}^{-1}$]	Recombination $k_{ct \rightarrow g}$ [$\times 10^9 \text{s}^{-1}$]	$\frac{k_{a^* \rightarrow ct}}{k_{ct \rightarrow g}}$
TT-Ph-PDI*	-	416 ± 12	99 ± 3	4.2
T-(Ph) ₂ -PDI*	-	62 ± 0.6	4.0 ± 0.04	15.5
T-(Ph) ₄ -PDI*	-	23 ± 0.2	0.11 ± 0.001	209
TT*-Ph-PDI	> 10000	187 ± 4	47 ± 1.1	4.0
T*(Ph) ₂ -PDI	217 ± 5	50.3 ± 1	3.8 ± 0.07	13.2
T*(Ph) ₄ -PDI	105 ± 2	17.3 ± 0.3	0.07 ± 0.003	247

Discussions

Several remarkable observations can be made by comparing the dynamics of CT state formation and recombination upon donor and acceptor excitation of the tryads studied here. When the donor is excited, the population of CT states in **TT-Ph-PDI** reaches its maximum at around 10 ps and decays to

zero at around 200 ps. When the acceptor is excited, these values are much smaller, ca 5 ps and 50 ps, respectively, resulting in much higher CT state generation and recombination rates in **TT-Ph-PDI*** as compared to **TT*-Ph-PDI**. This is surprising: in all three multichromophores fast energy transfer takes place, effectively converting D*-S-A into D-S-A* prior the CT state formation and recombination. In fact, in **T-(Ph)₂-PDI** and **T-(Ph)₄-**

PDI the CT state formation and recombination rates are practically unaffected by the type of the initial excitations. We excluded degradation by UV (355 nm) laser exposure as a reason for varying rates in TT*-Ph-PDI compared to TT-Ph-PDI* by re-measuring the same sample with 490 nm excitation (Figure S14) after UV exposure. Hence, the only remaining explanation of this observation is that the energy of the first excited state of the donor (thiotriangulene, TT) is comparable (slightly above, see Supplementary Note 4) to the second excited state of the acceptor (PDI). The second excited state of PDI is, however, a dark state. Consequently, Förster-type energy transfer to this state is not possible but, because of the short spacer of **TT-Ph-PDI**, Dexter-type energy transfer to the second excited state can still take place. An immediate implication is that the second CT state can be populated and recombine to the ground state, however, now with different generation and recombination rates compared to those observed after the direct excitation of the PDI. This can potentially impact the performance of OPV devices, where exciton conversion into a higher-lying CT state can boost the subsequent transition of the CT to charge separated states, and needs to be considered in donor-acceptor systems, in which one or both of the components have higher-lying dark states. However, the ratio of charge generation/recombination rates for both TT-Ph-PDI* and TT*-Ph-PDI excitation are the same (see Table 1), implying that populating higher-lying dark states does not affect the charge generation efficiency. We note that PDI is an often-used building block in the design of novel non-fullerene acceptors, thus similar phenomena may occur in OPV blends that use materials based on PDIs.

To rationalize the dependence of the rates on the spacer length, we employ the Marcus expression for the charge transfer rate,

$$k_{ET} = \frac{2\pi}{h\sqrt{4\pi\lambda k_B T}} J^2 \exp\left[-\frac{(\lambda + \Delta G)^2}{4\lambda k_B T}\right],$$

where ΔG is the driving force, or the free energy difference between the states, J is the electronic coupling element, and λ is the reorganization energy. For **TT-Ph-PDI**, for example, the calculations predict for the CT to ground state transition a driving force of $\Delta G_{ct \rightarrow g} = 1.04$ eV and a reorganization energy $\lambda_{ct \rightarrow g} = 1.03$ eV. For the a^* to CT state transition, we obtain $\Delta G_{a^* \rightarrow ct} = 0.003$ eV, $\lambda_{a^* \rightarrow ct} = 0.063$ eV. Correspondingly, the ratio of Boltzmann prefactors in the rate is 0.54, indicating that the ratio of the HOMO/HOMO to HOMO/LUMO electronic coupling is of the order of 10, since the experimentally measured rate ratio for **TT-Ph-PDI** is ~ 4.2 .

Figure 7. Semi-logarithmic plot of the charge generation rate (blue squares) and charge recombination rate (red circles) as a function of the donor-acceptor distance. Centers of mass of the corresponding units are used to quantify their separations. Inset: Semi-logarithmic plot of the ratio of the generation rate, k_G , and the recombination rate k_R , as a function of the donor-acceptor distance.

The calculations show that the driving force for the excited (a^*) to CT state slightly increases with the spacer length, and so does the reorganization energy. The overall reaction barrier, $(\lambda + \Delta G)^2/4\lambda$, slightly decreases. We can therefore conclude that the main reason for the decrease of the CT state generation rate, given in Table 1 and displayed in Figure 7, is the decrease of the electronic coupling between the donor and acceptor units. For the CT to the ground state reaction, the driving force decreases and reorganization energy increases with the spacer length. Hence, the CT state recombination slowdown is affected by both the increasing barrier and decreasing electronic coupling. This explains an exponential increase of the ratio of the generation and recombination rates, which is presented in the inset of Figure 7.

CONCLUSIONS

The photophysical studies of properly designed donor-spacer-acceptor-spacer-donor systems offer important implications for donor-acceptor heterojunction interfaces and organic photovoltaics in general. Firstly, a somehow controversial conclusion is that a longer spacer between the donor and acceptor blocks is beneficial for populating charge transfer states, in spite of the slowing down of the CT state generation. This effect can be used in a bulk heterojunction cell. Indeed, more efficient molecular CT state generation as compared to recombination reduces overall geminate recombination in a photovoltaic device.⁶⁸ In addition, larger donor-acceptor separations lead to smaller Coulomb binding energies of CT states and hence facilitate formation of charge separated states from charge transfer states, enabling CT state splitting even in a single-component OSC, as reported recently.⁶⁹⁻⁷⁰ Chemically, this can be realized by shielding groups participating in the charge transfer state formation. Care, however, should be taken, since steric shielding might also reduce charge mobility in pristine mesophases.

Secondly, energy transfer between the (electron) donor and (electron) acceptor can even take place, if the donor emission and the acceptor absorption spectra overlap, or spatial separations between the donor and acceptor are small. For bulk heterojunction OPV, energy transfer provides an additional degree of freedom in designing the energy level offsets. Indeed, efficient splitting of an excited state requires sizable offsets between ionization energies (acceptor excitation) or electron affinities (donor excitation). If efficient energy transfer takes place, say from the donor to the acceptor, then the only requirement is to have a large offset of the ionization energy, since the acceptor is solely responsible for splitting the excited states.

Thirdly, it appears that the short-range Dexter-type energy transfer can involve higher excited (and, consequently, CT) states, if the spectra of the donor and acceptor are complementary. The higher-lying excited states are assumed to be 'dark' states, which contribute to CT state formation. In fact, this concept could be explored further in novel donor – acceptor systems, and used to our advantage, since energetically higher CT states can provide larger driving forces for the CT to charge-separated state reactions and hence reduce both geminate and non-geminate recombination.

EXPERIMENTAL METHODS

Transient Absorption (TA) Spectroscopy

TA spectroscopy was carried out using a homebuilt pump–probe setup. Two different configurations of the setup were used for either short delay, namely 100 fs to 8 ns experiments, or long delay, namely 1 ns to 100 μ s delays, as described below: The output of a titanium:sapphire amplifier (Coherent LEGEND DUO, 4.5 mJ, 3 kHz, 100 fs) was split into three beams (2, 1, and 1.5 mJ). Two of them were used to separately pump two optical parametric amplifiers (OPA) (Light Conversion TOPAS Prime). TOPAS 1 generates tunable 490 nm in addition to 710 pump pulses, subsequently frequency doubled to 355 nm with a 2 mm thick barium metaborate (BBO) crystal, while TOPAS 2 generates signal (1300 nm) and idler (2000 nm) only. For measuring TA in the visible range, we used 1300 nm (signal) of TOPAS 2 to produce white-light super continuum from 350 to 1100 nm. For short delay TA measurements, TOPAS 1 was used to generate pump pulses, while the probe pathway length to the sample was kept constant at $\approx$ 5 m between the output of TOPAS 1 and the sample. The pump pathway length was varied between 5.12 and 2.6 m with a broadband retroreflector mounted on an automated mechanical delay stage (Newport linear stage IMS600CCHA controlled by a Newport XPS motion controller), thereby generating delays between pump and probe from $-$ 400 ps to 8 ns. For the 1 ns to 300 μ s delay (long delay) TA measurement, the same probe white-light supercontinuum was used as for the 100 fs to 8 ns delays. Here the excitation light (pump pulse) was provided by an actively Q-switched Nd:YVO₄ laser (InnoLas piccolo AOT) frequency-doubled to provide pulses at 532 nm. The pump laser was triggered by an electronic delay generator (Stanford Research Systems DG535), itself triggered by the transistor–transistor logic (TTL) sync from the Legend DUO, allowing control of the delay between pump and probe with a jitter of roughly

100 ps. Pump and probe beams were focused on the sample which was kept under a dynamic vacuum of <10 –5 mbar. The transmitted fraction of the white light was guided to a custom-made prism spectrograph (Entwicklungsbüro Stresing) where it was dispersed by a prism onto a 1024 pixel negative channel metal oxide semiconductor (NMOS) linear image sensor (Hamamatsu S8381-512) and a 512 pixel complementary metal-oxide-semiconductor (CMOS) linear image sensor (Hamamatsu G11608-512DA). The probe pulse repetition rate was 3 kHz, while the excitation pulses were mechanically chopped to 1.5 kHz (100 fs to 8 ns delays) or directly generated at 1.5 kHz frequency (1 ns to 300 μ s delays), while the detector array was read out at 3 kHz. Adjacent diode readings corresponding to the transmission of the sample after excitation and in the absence of an excitation pulse were used to calculate $\Delta T/T$. Measurements were averaged over several thousand shots to obtain a good signal-to-noise ratio.

Multivariate Curve Resolution Alternating Least Squares (MCR-ALS) Analysis

To separate the TA spectra and determine the spectral weight of each component, MCR-ALS analysis^{71–72} was applied to an augmented matrix comprised of TA data at different excitation fluence. Singular value decomposition (SVD) was applied to estimate the number of components present in the data matrix. One constraint was applied to the analysis that is non-negativity of concentration.

Theoretical Calculations

Ground state geometries were optimized using the m062x range-separated functional and the 6-311g(d) basis set. All optimizations were performed in the implicit solvent (dichloromethane) using the IEFPCM model. Absorption spectra were calculated at the same level of theory using non-equilibrium solvation model (PISALR) in which only the electronic relaxation is taken into account. All calculations were performed using the GAUSSIAN 09 package.

Averaged vertical excitation energies were calculated using the m062x range-separated functional and the 6-311g(d) basis set. Polarizable continuum model^{73–75} was used to account for the solvent stabilization. All calculations were performed using the GAUSSIAN09 package.

To evaluate (ensemble-averaged) vertical excitation energies, we used the polarizable continuum model (PCM).^{73–75} We first performed geometry optimizations in the g, ct, and a* states at the m062x/6-31g(d) level of theory using DCM as an implicit solvent, saved the optimized solvent state, and then evaluated the excited state energies of other states in the saved (nonequilibrium) solvation shells.

Driving forces and reorganization energies were calculated using the m062x range-separated functional and the 6-311g(d) basis set, and are summarized in Supplementary Note 9. Polarizable continuum model^{73–75} was used to account for the solvent stabilization. All calculations were performed using the GAUSSIAN09 package.⁷⁶

ASSOCIATED CONTENT

Supporting Information. Details of synthesis, cyclic voltammetry, UV-Vis spectrum, TD-DFT calculation details, MCR-ALS analysis, and TA spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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TOC image caption: Although a longer spacer between the donor and acceptor slows down both generation and recombination rates of the charge transfer state, their ratio increases, which is beneficial for charge transfer.