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# Triplet Formation by Charge Recombination in Thin Film Blends of Perylene Red and Pyrene: Developing a Target Model for the Photophysics of Organic Photovoltaic Materials

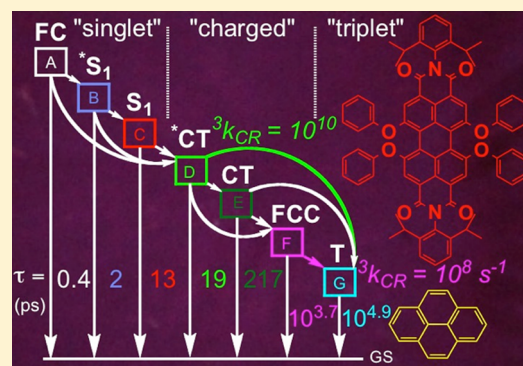
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## Supporting Information

**ABSTRACT:** Photoinduced charge separation in a mixture of Perylene Red (*N,N'*-bis(2,6-di-isopropylphenyl)-1,6,7,12-tetraphenoxyperylene-3,4:9,10-tetracarboxylic acid bis-imide) and pyrene, organized in thin solid film on quartz, was studied by means of steady-state absorption and emission spectroscopy and by femtosecond transient absorption spectroscopy. Steady state spectroscopy shows substantial interaction between the two chromophores in the ground and excited states. Luminescence quenching indicates charge transfer interaction. Global and target analysis of the transient absorption data indicates a complex photophysical behavior with the formation of long-lived charges (free charge carriers) and of a triplet excited state species (with rates of  $\sim 10.4 \times 10^9$  and  $72.1 \times 10^6$  s<sup>-1</sup>) via charge recombination pathways from charged states. A generally applicable target model for the analysis of photophysical data of photovoltaic blends is developed.



## INTRODUCTION

Thin films containing organic chromophores that are able to conduct charges are very important in relatively new industries directed at the production of (opto)electronic devices based on organic materials, such as electronic paper, photovoltaic cells, field effect transistors, and light-emitting diodes. These activities are aimed at product development, for example, printable electronics for ultrathin televisions, walls that can be lit up, and lightweight solar cells that can be rolled up. In principle, such devices can be inexpensive when produced by roll-to-roll printing of conductive inks on plastic films. With further advances in productivity, reliability, and related cost, printed electronics can become cheaper than silicon-based electronics.<sup>1</sup>

Besides chromophores such as fullerene adducts (for example, PCBM) and conducting polymers (for example, P3HT),<sup>2</sup> perylene-bis(dicarboximides) (PDIs) are also part of this new industrial development (for example, (bis-CN)-bay-substituted PDI compounds with fluoro-alkyl substituents on the imide nitrogens in OFETs).<sup>3</sup> It should be noted that the first organic solar cell developed by Tang in 1986 contained a perylene dye (3,4:9,10-perylene tetracarboxylic bis-(benzimidazole)) and a copper phthalocyanine in a two-layer device with  $\sim 1\%$  efficiency.<sup>4</sup>

Perylene-bis(dicarboximides) are extremely stable organic dyes, of which the chemistry has been explored in many directions and applied in many fields. Early applications range

from car paints, hair-treatment compositions, and active conducting components in photocopying devices to laser dyes.<sup>5</sup> The electron accepting abilities of perylene-bis-(dicarboximides) (PDIs) make them interesting components for electron transfer systems<sup>6</sup> and for application in optoelectronic devices.<sup>7</sup> Several early examples have been reported where perylene dyes are the n-type material in organic solar cells.<sup>4</sup> As they are the best n-type organic semiconductors available to date with high charge carrier mobilities,<sup>8</sup> PDI dyes are used and studied in xerography,<sup>9</sup> organic field-effect transistors (OFETs),<sup>3,10</sup> organic light-emitting diodes (OLEDs),<sup>11</sup> and organic photovoltaic (OPV) devices using, for example, a PDI/hexabenzocoronene<sup>5b</sup> or a PDI/polymer blend.<sup>12</sup>

Langhals, Würthner, Müllen, and Wasielewski have contributed strongly to the development of PDI derivatives as one of the most useful classes of chromophores.<sup>13,14</sup> Quite diverse electronic and optical properties can be incorporated into the PDI chromophore by introducing proper substituents in the so-called bay positions. The tetra-substituted chloro, fluoro, or phenoxy as well as the bisubstituted bromo, fluoro, cyano, phenoxy, and pyrrolidino bay-substituted PDIs are available, as

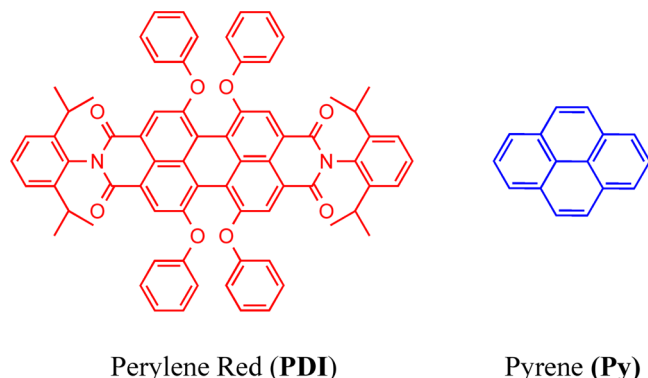
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are the core unsubstituted derivatives. Scheme 1 shows the structure of Perylene Red that has phenoxy groups in the bay

**Scheme 1. Molecular Structures of Perylene Red (PDI) (*N,N'*-Bis(2,6-diisopropylphenyl)-1,6,7,12-tetraphenoxy-perylene-3,4:9,10-tetracarboxylic Acid Bis-imide) and of Pyrene (Py)**



region. Thus, a broad section of the visible spectrum can be utilized for light-harvesting purposes. Crystallographic structures of most PDI derivatives substituted at the bay region are characterized by a twist of the carbon framework resulting from repulsion and steric effects among the substituents.<sup>15</sup>

PDI systems are often applied in artificial systems for photoinduced electron and/or energy transfer processes. Electro-active units such as fluorenone and anthraquinone,<sup>16</sup> tetrathiafulvalene,<sup>17</sup> pyrene,<sup>18</sup> oligothiophene,<sup>19</sup> zinc phthalocyanine,<sup>20</sup> 3,4-ethylenedioxy thiophene,<sup>21</sup> zinc porphyrin,<sup>22</sup> hexaazatriphenylenes,<sup>23</sup> anthracene dendrimers,<sup>24</sup> perylenemoinimide,<sup>25</sup> tetraboron-dipyrrin,<sup>26</sup> and poly(fluorene-*alt*-phenylene)<sup>27</sup> were connected to the PDI dye.

Stimulated by these facts, we have studied the photophysics of doped thin films of perylene bisimides. As a first representative, we took Perylene Red as the chromophore and as the dopant we chose pyrene (see Scheme 1), a textbook chromophore that we previously applied as an energy and electron donating bay substituent in photoactive molecular squares. Ultrafast energy and electron transfer cascades in a multichromophoric light-harvesting molecular square of nanometric dimensions containing Perylene Red and pyrene as chromophores (in solution) were reported by us.<sup>18</sup>

We thus present a study of thin films on quartz containing Perylene Red (PDI) (*N,N'*-bis(2,6-diisopropylphenyl)-1,6,7,12-tetraphenoxy-perylene-3,4:9,10-tetracarboxylic acid bis-imide) as the chromophore and mixed films containing both Perylene Red (PDI) and pyrene (Py). The thin films were studied with steady state UV–vis absorption and emission spectroscopy as well as femtosecond transient absorption spectroscopy. We show ground state interaction and emission quenching by charge transfer and present a new target model, describing the fs-TA data, which has general applicability to organic photovoltaic materials. A target model for the analysis of photophysical data of thin film blends is developed in which three singlet excited state species and three charged excited state species play a role. If a local triplet state is present below the charged states (like in the blend studied here), a seventh state (a triplet) can come into play.

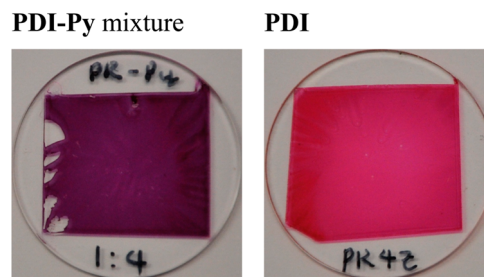
The aim of this work is twofold: First, we want to give a detailed description of the photophysical properties of a thin

film blend containing Perylene Red as the acceptor and pyrene as the electron donor. Second, and most importantly, we want to show the organic photovoltaic research community that the extensive data analysis methods for time-resolved spectroscopic data, that have been used intensively by biophysicists such as Rienk van Grondelle to model the photophysics of biological photosystems, can be very useful to give more insight and a much more detailed and accurate description of the photophysics of organic photovoltaic materials. A target model is developed of which the basis is suitable to describe other (more important) photovoltaic blends. The choice of perylene bisimide and pyrene as chromophores is based on our experience with these types of chromophores in molecular systems in solution that we studied in the past.<sup>18,28</sup> We do not envisage this particular chromophore combination to have great importance in the future for the practical application as materials for organic photovoltaics. The combination of perylenebisimides and pyrene as co-components in bulk heterojunctions has been applied<sup>29</sup> in organic solar cells and has yielded a power conversion efficiency of 3.17%.

## RESULTS AND DISCUSSION

Scheme 1 presents the structures of the compounds. Mixtures of Perylene Red and pyrene in a 1:4 molar ratio were used as before.<sup>18</sup>

The photos of the samples (Figure 1) and optical microscopy show that the spin-coated thin films display a good

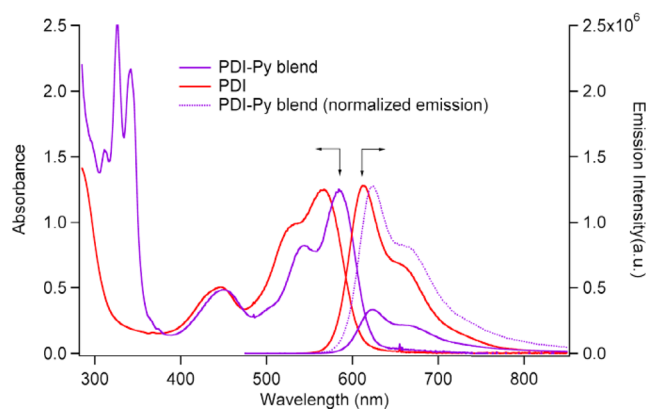


**Figure 1.** Photos of the thin films of a mixture of Perylene Red and pyrene (PDI–Py, left) and of pure Perylene Red (PDI, right;  $\approx$  actual size).

homogeneity in the center ( $1 \times 1 \text{ cm}^2$ ) of the substrate. The thickness of the thin films was estimated to be  $\approx 70 \text{ nm}$  (see the Supporting Information).<sup>3,30,31</sup>

The color of the PDI–Py film is significantly different from that of the PDI layer, whereas that of the corresponding solutions is very similar. The color of the samples changes from reddish pink (PDI) to dark purple (PDI–Py). The change in color can be explained by the interaction between PDI and Py, which was also observed in the UV–vis absorption and emission spectra.

**UV–vis Absorption and Emission Spectroscopy.** The UV–vis absorption spectrum (Figure 2) of the blend shows maxima at 311, 326, 342, 450, 544, and 585 nm. The first three peaks are characteristic of the pyrene chromophores, and the latter three belong to the PDI (slightly red-shifted relative to the values in solution (444, 535, 575 nm, see the Supporting Information, Figure S1) and relative to the pure PDI thin film (with maxima at 446, 531 (sh), and 565 nm)). It is also clear that the blend exhibits a more pronounced PDI vibrational fine structure. The absorption bands at  $\sim 535$  and  $\sim 575 \text{ nm}$  correspond to the  $S_0 \rightarrow S_1$  transition, whereas the band in the



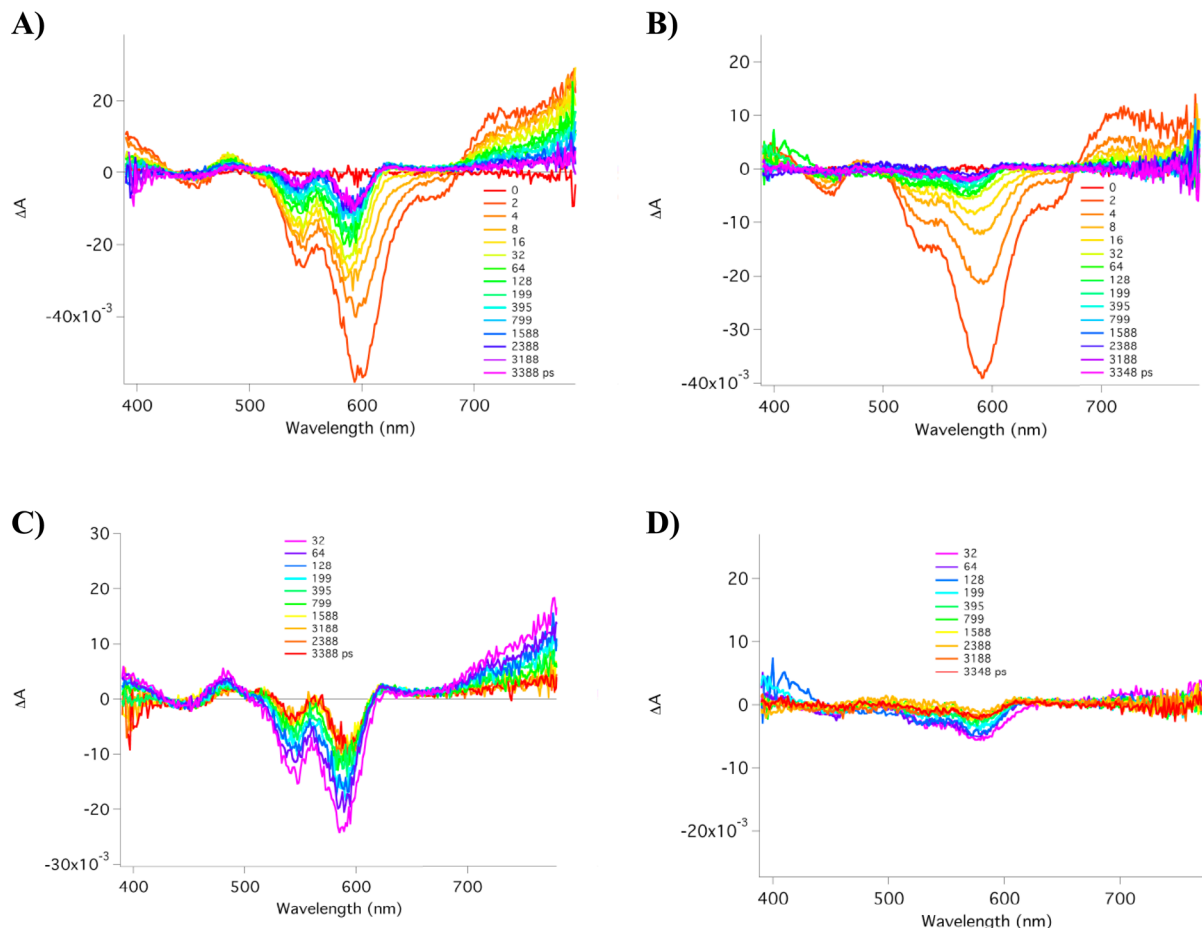
**Figure 2.** Absorption and emission spectra ( $\lambda_{\text{ex}} = 465 \text{ nm}$ ) of the thin films of Perylene Red (PDI) and the mixture of Perylene Red and pyrene (PDI-Py, 1:4 molar concentration ratio). The normalized emission spectrum of the PDI-Py mixture is shown as a dotted purple line. The absorption spectrum of PDI was multiplied by 1.25 for clarity.

400–480 nm region is assigned to the  $S_0 \rightarrow S_2$  transition. These bands are typical for Perylene Red derivatives.<sup>32</sup> Spin-coated films of (non-liquid-crystalline) perylene bisimides (prepared at room temperature and without annealing) are

often amorphous.<sup>33</sup> A highly ordered structure can only be obtained either from high temperature annealing or self-organization of dyes under the influence of solvent vapor annealing.<sup>30,33,34</sup> The twist angle (about  $30^\circ$ ) between the two naphthalene units of PDI can also play a role, reducing the  $\pi$ - $\pi$  stacking distance, as well as the 2,6-di-isopropylphenyl attachment at the imide nitrogen.<sup>14,35</sup>

The absorption spectrum of the pure PDI thin film displays some minor differences as compared to the perylene bisimide in solution (see the Supporting Information, Figure S1). A slight increase in intensity of the band at 530 nm and a small blue shift (8 nm) of the  $S_0 \rightarrow S_1$  transition is observed, indicating the presence of a dimer-like or H-type aggregate species. This change is very similar to the phenomena observed for a calix[4]arene containing two Perylene Red groups as substituents, in nonpolar solvent, studied in ref 28h. The hypsochromic shift of the PDI film indicates the dominance of H-type aggregates<sup>36,37,28i</sup> in Perylene Red layers.

The presence of Py in the film shifts the PDI absorption band to longer wavelengths, indicating interactions of Py and PDI in the solid state. In the mixed films,  $\pi$ - $\pi$  interactions between PDI and Py can occur, which generally result in a red shift. In dichloromethane solution, no perturbation of the PDI spectrum by Py is observed (see the Supporting Information, Figure S1).<sup>18</sup>



**Figure 3.** fs-TA spectra ( $\lambda_{\text{ex}} = 550 \text{ nm}$ , fluence =  $25 \mu\text{J}/\text{cm}^2$ ) of (A and C) the PDI-Py film and (B and D) the PDI thin film. In parts C and D, the spectra on the longer time scale are given, showing more clearly the differences on the long time scale between the two samples. The absorbance of the samples at 550 nm was 0.80 and 0.74, respectively. The scaling of part D has been adapted for better comparison. See the Supporting Information (Figure S3) for selected spectra at specific times with a fit from target analysis of PDI-Py.



Emission maxima are also shifted, to 624 nm for the blend and to 612 nm for the **PDI** film (relative to 610 nm<sup>32a</sup> observed for a **PDI** solution as well as a solution of the mixture of **PDI** and **Py**, see Figure S2 in the Supporting Information). The relative quenching effect on the **PDI** emission of the **Py** chromophore in the thin films was calculated by comparing the emission intensity (corrected for absorption factor) of the **PDI–Py** layer to the corresponding **PDI** layer to be a factor of 5× (implying that the emission is quenched for 80%).

From the absorption and emission spectroscopy, we can deduce the following: the change in color and absorption maxima show that there is substantial  $\pi$ – $\pi$  interaction between most **PDI** molecules and pyrene. The substantial (but not complete) quenching indicates that some domains are present where **PDI** molecules do not have a **Py** neighbor molecule. To get more insight into the interaction between **PDI** and **Py** in the solid state, we carried out femtosecond transient absorption measurements of **PDI** and **PDI–Py** thin films.

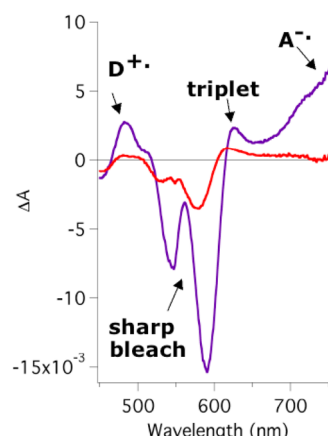
**Femtosecond Transient Absorption (fs-TA) Spectroscopy.** Figure 3 shows transient absorption (fs-TA) spectra of **PDI–Py** and **PDI** at the probe delays indicated, upon 550 nm excitation.

Four important differences between the two data sets can be observed: (1) for the **PDI–Py** blend, a greater absorption signal is observed between 700 and (sloping up toward) 800 nm [the radical anion (or negative polaron) region]<sup>18,28m–o,38</sup> especially at longer time scales; (2) the **PDI** ground state bleaching signals at 450, 540, and 590 nm pertain for much longer and are stronger (and sharper) in the **PDI–Py** blend (indicating longer-lived states); (3) at the longer time scales, an  $\sim$ 620 nm band is observed for both samples. These observations are in accordance with photoinduced electron transfer (charge transfer state formation) occurring in the blend, leading to long-lived charges (free charge carriers), and to triplet state formation<sup>28f,j,k,39</sup> (620 nm band). The sharp ground state bleaching agrees with the UV–vis absorption spectra. The radical cation (or positive polaron) gives a weak signal and is observed at  $\sim$ 470 nm.<sup>28n,40</sup>

Figure 4 compares the long-lived species observed in the two samples. If we take the intensity of the 615 and 625 nm bands, at the long time scale, as representative for the amount of triplet state formation, it indicates that in the blend 2.6 times more triplet is formed than in the pure **PDI** film. Since 80% of the **PDI** emission is quenched, there is a maximum of 20% of the surface that contains a **PDI** phase. Thus, in the blend, we would expect 5 times less triplet state formation (from **PDI** only domains). This clearly indicates that the main part of the triplet state formation in the blend has occurred via charged states (i.e., triplet formation by charge recombination, see later). The absolute triplet quantum yields are estimated to be 0.19 for the **PDI–Py** blend and 0.07 for the **PDI** film (see later).

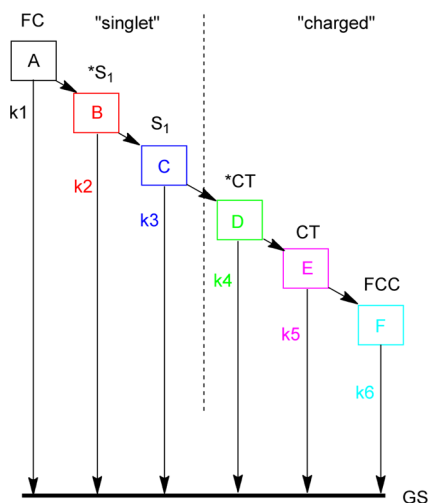
**Global and Target Analysis Model for Photovoltaic Blends.** The previous sections show that emission quenching occurs and that charges are generated in the **PDI–Py** blends. An advanced data analysis method<sup>41–43</sup> was applied to the femtosecond transient absorption data matrices in order to extract as much as possible detail about the photophysical processes in these films (see p S17 of the Supporting Information for a short description of the data analysis method).

As a general starting point for the global and target analysis of femtosecond transient absorption data sets of organic photovoltaic blends, we use a scheme that contains six excited



**Figure 4.** Comparison of the integrated spectra (100 ps to 3.6 ns) of the **PDI–Py** blend (in violet) and the pure **PDI** film (in red), exemplifying the larger amount of triplet state formation (at 620 nm), sharp ground state bleaching (at 580 nm), and negative polarons (radical anions,  $A^{\bullet-}$ , at 750 nm) and positive polarons (radical cations,  $D^{\bullet+}$ , at 470 nm) in the blend (corrected for absorption factor). The charge transfer states and the free charge carriers contain the spectral features of  $D^{\bullet+}$  and  $A^{\bullet-}$ .

state species (see Figure 5) within the first 3 ns after excitation. Since the bulk heterojunction consists of phase-separated



**Figure 5.** Basis of the general target model scheme for an organic photovoltaic blend. It is a global sequential model with decay to the ground state for every intermediate. Each species can have its own spectrum, branching factors, and total decay rate. Introducing branching from specific upper states to specific lower states with branching factors finalizes the model (for example, from “hot  $S_1$ ” to “hot CT”). FC = Franck–Condon excited state;  $*S_1$  = hot singlet state;  $S_1$  = relaxed singlet excited state;  $*CT$  = hot charge transfer state; CT = relaxed charge transfer state; FCC = free charge carriers, GS = ground state.

domains of a two-component blend, it is a strongly heterogeneous system where populations of similar excited state species play a role. Many molecular conformations, orientations, and environments of the electron donating and electron accepting components and their interfaces will be present in the thin films.

These six excited state species are the following: (1) A Franck–Condon excited state (FC): this is the first ultra-short-

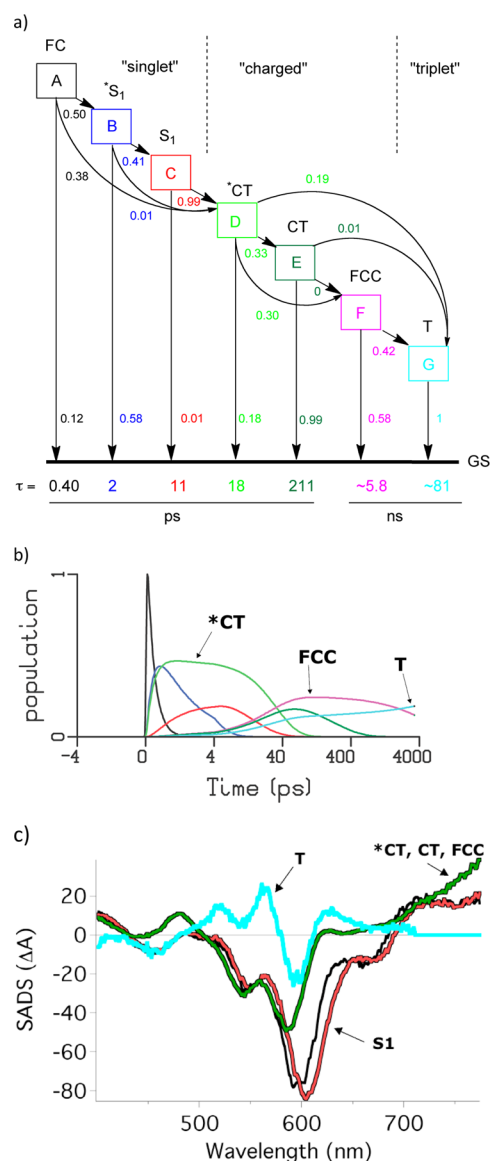
lived species that can be observed. (2) A hot singlet state ( $*S_1$ ) evolves that represents a vibrationally hot version of the relaxed excited singlet state, or an upper excited singlet state. Hot and upper excited singlet states can play a role in charge separation in molecular systems. We have shown that in solution, in a molecular square containing 20 chromophores, the  $S_2$  state of a donor molecule can result in direct charge transfer, giving already 10% of the total charge separation yield (see ref 18b and for a similar example ref 44). Hot singlets that are not quenched can result in the formation of relaxed singlets (3). All three singlet excited state species (FC,  $*S_1$ ,  $S_1$ ) can give rise to the formation of charged states.

Three charged excited state species can be formed: a hot charge transfer state ( $*CT$ ), a relaxed charge transfer state (CT), and free charge carriers (FCC).

Recent work by Friend et al. has shown the crucial importance of the hot charge transfer state by using the pump–push photocurrent technique.<sup>45</sup> It has to be noted that the hot CT state (which we can also call the geminate polaron pair) is not a vibrationally hot CT state but mainly a collection of higher lying CT states within the CT density of states. The relaxed CT state is the lowest collection of CT states present within the heterogeneous blend. It has become more and more apparent in recent years that the relaxed charge transfer state, a coulomb bound electron–hole pair, has its own intrinsic decay pathways that can be similar to events occurring in molecular systems in solution.<sup>46</sup> Besides charge transfer emission (red-shifted structure-less emission bands that represent the radiative process occurring upon charge recombination to the ground state), charge recombination to a local triplet state excited state is another decay process that this relaxed charge transfer state can undergo. The FCC are negative charges (radical anions or negative polarons) and positive charges (radical cations or positive polarons) that have escaped each others' Coulomb influence. The six species described here shortly are all well described in the 2010 review<sup>46</sup> by Clarke and Durrant but have, to our knowledge, not been incorporated into a single target analysis scheme before.

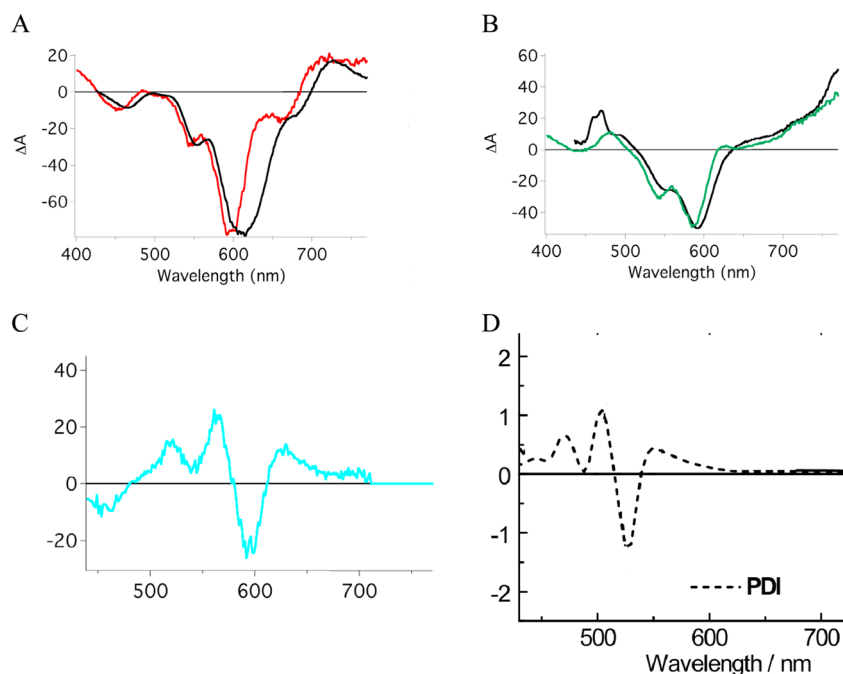
Figure 5 shows these six species in a simple scheme that can be used as a starting point, in which every state can convert into the next one and can also decay to the ground state. This scheme is a basic sequential global analysis scheme, in which the decay channels to the ground state are added. Converting this scheme into a target model requires the introduction of branching: for example, allowing conversion from the FC and  $*S_1$  to the hot charge transfer state ( $*CT$ ) represents the ultrafast charge generation. As can be concluded from the work<sup>45</sup> of Bakulin and Friend, the  $*CT$  can lead to the formation of free charge carriers. Whereas the scheme in Figure 5 can be considered unbiased, a target model implies that branching channels are allowed to occur within the data analysis, and as such require arguments and decisions. It is important to note that, in the work of Friend et al. on PCBM–P3HT mixtures on working devices under flat band conditions, two singlet excited state species were observed.<sup>47</sup> This is in agreement with our model suggested here. The first ultra-short-lived excited state species that can be obtained after dispersion correction and the determination of the coherent artifact, we call the FC state and assume it has singlet excited state character.

The main outcome of the target analysis for the PDI–Py blend is presented in Figure 6. Next to the most important time constants, we obtain the so-called species associated difference



**Figure 6.** (a) Target analysis scheme. Every species is characterized by one lifetime ( $\tau$ ) and two to four branching factors. Branching factors are indicated in the color of the species (for all rates, see the Supporting Information). Non-geminate charge recombination to the triplet is the transition from FCC to T. Geminate charge recombination to the triplet from  $*CT$  and CT to T. (b) Populations of states from the target analysis. Key: Franck–Condon (FC) state = black, hot  $S_1$  ( $*S_1$ ) = blue,  $S_1$  = red, hot charge transfer state ( $*CT$ ) = light green, charge transfer state (CT) = dark green, free charge carriers (FCC) = magenta, triplet (T) = cyan. The time axis is linear from  $-4$  until  $4$  ps, relative to the location of the IRF maximum, and logarithmic thereafter. For the three “charged species” (CT,  $*CT$ , and FCC) as well as for the  $S_1$  and  $*S_1$  species, spectral equivalence was imposed. The decay times are as follows: FC state = black = 400 fs; hot  $S_1$  = red = 2 ps;  $S_1$  = blue = 11 ps;  $*CT$  = light green = 18 ps, CT = dark green = 211 ps; FCC = magenta  $\approx$  5.8 ns; triplet = cyan  $\approx$  81 ns. The latter two are beyond the limit of our experiment and can be considered as long-lived. (c) Results of the target analysis showing the species associated difference spectra (SADS) of the Franck–Condon state (black), the hot or relaxed singlet state (red), hot charge transfer state  $*CT$ /charge transfer state CT/free charge carriers FCC, (green) and the triplet state (cyan).

spectra (SADS). These are the spectra belonging to specific species that play a role in the light induced processes. In order



**Figure 7.** Comparison of the SADS from Figure 6 (with the same color coding) with published spectra (depicted in black). (A) Relaxed singlet state (SADS of  $^*S1$  and  $S1$  in red) compared with singlet excited state absorption of reference molecular square consisting of four PDI units in solution; (B) SADS of  $^*CT$ ,  $CT$ , and  $FCC$  (in green) compared with molecular charge transfer state of pyrene substituted PDI molecular square in solution; (C) SADS of triplet excited state (in cyan blue) observed in thin solid film compared to (D) a molecular triplet of a PDI chromophore (without bay substituents) observed in solution. Part D is reprinted with permission from *J. Phys. Chem. A* **2008**, *112*, 5846–5857. Copyright 2008 American Chemical Society.

to describe the matrix of time-resolved spectra appropriately, we need three species with “singlet” character, three species with charges, and one triplet state.

For the blend of **PDI–Py**, we have to assume spectral equivalence for the  $^*CT$ ,  $CT$ , and  $FCC$  species in order to resolve the triplet. The lifetimes of the three species, however, are different. Spectrally, the charged species in the film (in green in Figure 6) are strikingly similar to the molecularly defined charge transfer state in solution of the molecular square with similar components (see ref 18b and Figure 7B).

From our previous studies<sup>18,28</sup> of various molecular systems in solution, we can use the spectral fingerprints of excited states to assign the species associated difference spectra reported here for the thin film blend. Figure 7 displays three SADS from Figure 6 together with the spectra obtained for molecular species in solution that we published previously. From the comparison of the spectra of the molecular squares studied by us in 2005,<sup>18b</sup> it is clear that the singlet excited state (Figure 7A) and the charged states (Figure 7B) have the right spectral features and excellent similarity is obtained between the species observed in the thin film blend and molecular excited states observed in solution.

Phenomenologically, the spectral development we see in the thin film blend is reminiscent of the spectral changes we observed for triplet state formation on PDI chromophores for the  $C_{60}$ –PDI dyad (with four chloro-atoms in the bay positions) that we studied in 2006.<sup>28f</sup> In this case, singlet–singlet energy transfer (from PDI to  $C_{60}$ ) was followed by triplet–triplet energy transfer from the attached  $C_{60}$  unit to the PDI unit. As was first reported in 1987 by Ford and Kamat,<sup>39</sup> the “true triplet–triplet absorption spectrum” of PDI chromophores (corrected for the ground state bleaching) is a broad positive absorption band between  $\sim 400$  and  $\sim 600$  nm.

The (negative) ground state bleaching bands modify the appearance strongly, and the particular ground state bleaching (which is correlated to the  $S_0 \rightarrow S_1$  absorption bands) of the various PDI chromophores (with or without bay substituents) now becomes an important factor.

In Figure 7C and D, the triplet SADS obtained in this study is compared to the observed triplet–triplet absorption spectrum of a “bare” PDI chromophore (without substituents in the bay position) in solution from our 2008 study.<sup>28k</sup> This PDI triplet spectrum (Figure 7D) shows an excellent resemblance to the triplet observed here (Figure 7C) in the solid state (red-shifted about 70 nm). Clearly, the true triplet–triplet absorption as well as the ground state bleaching bands in the blend is red-shifted in similar magnitude as compared to the unsubstituted PDI chromophore in solution. The longest wavelength absorption band of the phenoxy substituted PDI in the thin film used here (at 585 nm) is indeed red-shifted as compared to the unsubstituted PDI in solution (absorbing at 532 nm) used for Figure 7D.

As discussed before, we cannot separate the spectral information on the hot and relaxed CT states in this blend (see Figure 6), but by assuming spectral equivalence (for  $^*CT$ ,  $CT$ , and  $FCC$  species), we are able to obtain a well-structured spectrum for the long-lived triplet excited state that is formed mainly from the charged states. The triplet quantum yield can be determined by using the product of the branching factors in the scheme in Figure 6a (summing up for the different formation pathways). This gives  $\Phi_T = 0.19$  for the **PDI–Py** blend.

Interestingly, we have been able to make a spectral distinction between the hot CT state, the relaxed CT state, and the free charge carriers in an optimally annealed PCBM–P3HT blend (see Figures S4 and S5 in the Supporting

Information) by using an adapted target model analysis that contains six states and no triplet formation by charge recombination. Especially the enhanced structure observed in the ground state bleaching signals of the P3HT polarons observed at 550–620 nm is in good agreement with charge moving in time from more amorphous regions toward more ordered polymer domains which have an enhanced charge mobility.<sup>48</sup> Such enhanced structure in the ground state bleaching signals has been previously reported for neat P3HT upon red-edge excitation of annealed neat polymer films leading to excited singlet state formation. The selective ground state bleaching of the ordered polymer domains by red-edge excitation of neat polymer films<sup>49</sup> (see also Figure S6, Supporting Information) observed by Riedle et al. agrees very well with the ground state bleaching of the long-lived charges in the PCBM–P3HT blend reported here. In our analysis results, the hot and relaxed CT states do not contain this enhanced fine structure in the ground state bleaching signals.

For the **PDI–Py** blend, however, we have to assume spectral equivalence of the hot CT, relaxed CT, and FCC in the target model in order to be able to obtain information about the triplet state formation.

The global target analysis of the pure **PDI** film (without donor) is characterized by five excited state species, three of which have mainly singlet character but different lifetimes. One of the SADS has excimeric nature, and one is a triplet. Similar observations were made for molecular dimeric species.<sup>28k,l</sup> The long-lived SADS has clear triplet state character (see p S19 of the Supporting Information).

**Driving Force.** We can estimate the driving force for electron transfer between the components in the blends from spectroscopic and electrochemical data. Using  $E_{\text{ox}} = +1.4$  V vs SCE and  $E_{\text{red}} = -0.4$  V vs SCE and the singlet state energy  $E_{00} = 2.07$  eV results in a driving force of  $-0.21$  eV (in a dielectric medium with  $\epsilon = 4.7$  and a close contact of 7 Å and ionic radii of 3 Å). This indicates a charge transfer state with an energy of 1.86 eV, which is well above the triplet state (located at 1.2 eV).

## CONCLUSION

Our work shows that triplet formation by geminate and non-geminate charge recombination is occurring in thin film blends that contain Perylene Red as the electron accepting phase and pyrene as the electron donating phase. fs-TA spectra of blends of **PDI** and the electron donor (pyrene) show a typical fingerprint of the triplet state localized on the **PDI** (next to long-lived free charge carriers). Spectral and kinetic analysis shows that this triplet formation by charge recombination occurs mainly with a rate of  $\sim 10.4 \times 10^9 \text{ s}^{-1}$  and through a complex sequence of events and forms from the charged states. In agreement with recent work<sup>31</sup> of Ramanan et al., we see that the four phenoxy groups in the bay position result in films that maintain a lot of the “molecule-like” behavior (i.e., similar to that for molecules in solution). **PDI** aggregation is thereby prevented, and charge generation is promoted. In that work, a competition between singlet fission and charge transfer is found, next to triplet formation by charge recombination to a triplet localized on the pentacene chromophores that is below that of the **PDI** dyes.

Within the field of molecular electron donor–acceptor systems studied in solution, triplet formation by geminate charge recombination has been identified as an important decay channel of the CT state more than a decade ago, as well as in

recent works.<sup>50–53</sup> In 2009, Veldman et al. reviewed triplet formation by charge recombination in organic solar cell materials.<sup>54</sup> Since then, triplet formation by charge recombination has been reported in diketopyrrolopyrrole based conjugated polymer–PCBM blends,<sup>55</sup> in PCPDTBT:PCBM solar cells (and it is influenced by morphology),<sup>56</sup> in smectic films of a donor–acceptor–donor triad containing oligothiophene and perylene bisimide,<sup>57</sup> as well as in phthalocyanine–PCBM blends.<sup>58</sup>

Triplet formation by charge recombination is a general phenomenon that has to be considered. The triplet energy level of new (low band gap) materials for organic solar cell applications has to be taken into account in the molecular design phase. For this singlet–triplet gap engineering, the old “rules of thumb” of Michl<sup>59</sup> as well as modern calculation methods are available. Further studies are needed to probe the effects of, for example, ratios, donor strength, and acceptor character on these types of thin film blends. Similar charge recombination as observed in the **PDI–Py** films can occur in photovoltaic devices containing **PDI**-type chromophores if energetics allows.<sup>54</sup>

Within this study, we have developed a generally applicable target model for the analysis of time-resolved photophysical data of organic photovoltaic blends. This model contains six excited state species, three singlet and three charged species, in which any upper excited state species can be converted into any lower excited state species. If an excited triplet state level is present below the charged states, this seventh state plays an important role in the photophysics of the blends, especially through triplet formation by geminate and non-geminate charge recombination.

Our current focus is on the application of this target model to the photophysical data of diketopyrrolopyrrole based low-band-gap polymer/PCBM thin film blends with two different morphologies and correlated power conversion efficiencies.<sup>55,60</sup>

## ASSOCIATED CONTENT

### Supporting Information

Figures S1–S6, samples and preparation, spectroscopy setups used, UV–vis spectra in solution, layer thickness, global and target analysis of **PDI** and of **PDI–Py** films, and global and target analysis of PCBM/P3HT thin film blend. 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 interest.

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