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Ring-fusion as a perylenediimide dimer design concept for high-performance non-fullerene organic photovoltaic acceptors†

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A series of perylenediimide (PDI) dimers are evaluated as acceptors for organic photovoltaic (OPV) cells. The materials are characterized using a wide variety of physical and computational techniques. These dimers are first linked at the bay position of each PDI molecule via an aromatic spacer; subsequent photocyclization affords ring-fused dimers. Thus, photocyclization of the thiophene-linked dimer 2,5-bis-[*N,N'*-bis-perylenediimide-1-yl]-thiophene (T1) affords the twisted acceptor [2,3-*b*:2',3'-*d*]-bis-[*N,N'*-bis-perylenediimide-1,12-yl]-thiophene (T2), while photocyclization of the thienothiophene-linked dimer, 2,5-bis-[*N,N'*-bis-perylenediimide-1-yl]-thienothiophene (TT1) affords the planar acceptor [2,3-*b*:2',3'-*d*]-bis-[*N,N'*-bis-perylenediimide-1,12-yl]-thienothiophene (TT2). Furthermore, a dimer linked by a phenylene group, 1,4-bis-[*N,N'*-bis-perylenediimide-1-yl]-benzene (Ph1), can be selectively photocyclized to form either the twisted dimer, [1,2:3,4]-bis-[*N,N'*-bis-perylenediimide-1,12-yl]-benzene (Ph1a) or the planar dimer [1,2:4,5]-bis-[*N,N'*-bis-perylenediimide-1,12-yl]-benzene (Ph2b). Ring-fusion results in increased electronic coupling between the PDI units, and increased space-charge limited thin film electron mobility. While charge transport is efficient in bulk-heterojunction blends of each dimer with the polymeric donor PBDTT-FTTE, in the case of the twisted dimers ring fusion leads to a significant decrease in geminate recombination, hence increased OPV photocurrent density and power conversion efficiency. This effect is not observed in planar dimers where ring fusion leads to increased crystallinity and excimer formation, decreased photocurrent density, and decreased power conversion efficiency. These results argue that ring fusion is an effective approach to increasing OPV bulk-heterojunction charge carrier generation efficiency in PDI dimers as long as they remain relatively amorphous, thereby suppressing excimer formation and coulombically trapped charge transfer states.

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Introduction

Organic photovoltaic (OPV) devices offer a potential avenue for inexpensive, mechanically flexible, and environmentally friendly solar energy conversion.^{1–10} The most efficient OPV active layers are based on blending an electron donating material with an electron accepting material to form a phase-separated bulk-heterojunction (BHJ) structure, although both

bilayer and single component active layer organic devices have also been demonstrated.^{11–16} By far the most heavily used acceptor materials in BHJ devices are fullerene derivatives due to their exceptional charge transport properties. Devices based on fullerenes have achieved internal quantum efficiencies near 100%, and fill factors near 80%.^{12,17,18} Fullerenes, however, are expensive to synthesize, difficult to modify, and air-sensitive, limiting their large-scale applicability/manufacturability.^{19,20} Because of these challenges, much recent OPV research has shifted towards developing efficient non-fullerene acceptors.^{21–31} One of the most successful and widespread classes of non-fullerene acceptors are derivatives of perylenediimide (PDIs). PDIs are attractive alternatives to fullerenes since they have electron affinities comparable to those of fullerenes, can have high n-type mobilities, are inexpensive to synthesize, strongly absorb visible light, and are straightforward to chemically modify, affording diverse electronic properties and solid-state morphologies.^{32–37}

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reduce computational time and the required optimization space. Geometry optimizations were followed by single-point energy calculations at the TDDFT/B3LYP/DZVP/COSMO level of the theory to determine ground state orbital energies and excited state transition energies from the ground state and anion state in the linear response regime. All energies and geometries for these species can be found in the ESI.†

EPR hyperfine coupling constants for the phenyl-containing species were computed by performing geometry optimization of the anion state (charge = -1 , multiplicity = 2) with an unrestricted Kohn–Sham (UKS) wavefunction at the B3LYP/EPR-II/COSMO level of theory, followed by a single point calculation of the isotropic and dipolar contributions to the hyperfine coupling tensor for each atom. All EPR calculations used tight convergence criteria (TIGHTSCF, Grid5, Finalgrid6).⁷⁰ The results of the EPR hyperfine coupling constant calculations can be found in Table S1.†

Using a recently developed computational methodology,⁵⁸ the bulk charge transport network properties of all PDI acceptor materials were screened, yielding calculated values of the Kirchoff transport index characterizing the strength and robustness of the charge transport networks formed by aggregates of the present PDI-acceptors. The results for these indices are provided in the ESI (Table S2†).

Grazing incidence wide angle X-ray scattering (GIWAXS)

Grazing incidence X-ray scattering (GIWAXS) measurements were carried out at Beamline 8-ID-E of the Advanced Photon Source at Argonne National Laboratory. Correlation lengths were calculated using a modified Scherrer analysis after fitting the lamellar scattering peaks in the horizontal and vertical linecuts.⁷¹ Detailed experimental and data analysis procedures have been reported previously.⁴⁰

Femtosecond transient absorption (fsTA) spectroscopy

Low-fluence fsTA spectra were collected using 25 nJ, 100 fs pump pulses focused to a spot size of 1 mm and operating at a 100 kHz repetition rate in order to minimize excitation density, hence to avoid exciton annihilation. All samples were excited at 525 nm, and details of the transient absorption instrumentation and experimental methodology have been reported previously.⁷²

Results and discussion

Materials synthesis

The present new PDI acceptors were synthesized according to a common strategy (Scheme 1). In each case, the unfused precursor structure was synthesized using Pd-catalyzed cross-coupling of brominated PDI with the appropriate aromatic core to give **T1**, **TT1**, and **Ph1**. **T1** and **TT1** were then photocyclized under oxidative conditions to afford **T2** and **TT2**, respectively. In these cases, photocyclization results in one possible isomer, but in the case of **Ph1** both a linear and a twisted product are possible. Thus, pure isomers of **Ph2a** and **Ph2b** were prepared from their corresponding anhydrides, **S2a** and **S2b**, which were

synthesized according to a published literature procedure where photocyclization is carried out under O_2 , to produce the twisted isomer, or N_2 followed by oxidation with DDQ, to produce the linear isomer.⁶⁶ Direct photocyclization of **Ph1** under conditions analogous to the photocyclization of **TT1** and **T1** was found to result predominantly in the formation of **Ph2a**, which was not isolated using this method because the use of the ester intermediate allowed for simpler purification.

Electronic structure and transport

Compared to an unsubstituted PDI, the solution phase optical absorption spectra of unfused structures **T1**, **TT1**, and **Ph1** are broadened and red-shifted. Upon ring fusion, the vibronic structure of the absorption sharpens and shifts to a higher energy for **T2**, **Ph2a**, and **TT2**. The absorption spectrum of **Ph2b** however shifts to lower energy and the transition is split resulting in several sharp peaks (Fig. 1a–c). The sharpening of the vibronic structure in solution is likely a result of added rigidity in the ring fused structures. When analyzed as thin films, the absorption spectra are broadened and, in the cases of **Ph2a**, **Ph2b**, and **TT2**, a new red-shifted shoulder appears (Fig. 1d–f). It is worth noting that the relative differences between the solution spectra and the film spectra are much more pronounced in the cases of **Ph2b**, and **TT2** than in the cases of **T2**, and **Ph2a**. This suggests that the intramolecular coupling is much weaker in the twisted structures than in the planar structures, consistent with previously reported data for fused PDI dimers.^{31,49} In **PBDTT-FTTE:PDI** blend films, the absorption of the polymer donor is observed above 600 nm while the acceptors absorb most strongly below 600 nm. This results in a broad absorption profile where the blend films absorb strongly across the entire visible spectrum. For the most part, the absorbances of the individual donor and acceptor components in the blend films are unchanged, resulting in absorption spectra which resemble the sum of the spectra of the individual components; however in the case of **T1** and **T2** the polymer absorbance is red-shifted by about 20 nm in the blend, suggesting the presence of a charge transfer (CT) interaction (Fig. 1d).

The reduction potentials of each molecule were measured electrochemically and used to estimate the LUMO levels of the acceptors (Fig. 2, Table 1). In all cases, ring fusion leads to a more negative reduction potential of between 30 mV (**Ph2b**) and 150 mV (**TT2**), consistent with increased coupling to the electron rich linker, and a larger shift in LUMO is observed for more electron rich linkers. While the first and second reductions of the unfused PDI dimers are separated by only 30–60 mV, this separation increases in the fused dimers to around 100 mV, further indicating increased coupling between the PDI molecules (Table 1).

SCLC electron carrier mobilities were measured for films of each acceptor blended with **PBDTT-FTTE** (Table 1). In each case, ring fusion results in 3–4× increase in electron mobility, suggesting the π – π electronic connectivity of neighboring molecules increases as a result of ring fusion, enabling easier flow of charge carriers, consistent with previous reports on **T2**.³¹ The





Scheme 1 Synthesis of PDI dimers. (a) Pd(PPh₃), toluene, (84–90%) (b) *hν*, toluene, air (84–88%) (c) CH₂Cl₂, I₂, air, *hν* (d) (1) toluene, I₂, *hν*, N₂ (2) DDQ (e) ClSO₃H (65–78% over 2 steps) (f) imidazole, 1-pentylhexyl.

electronic connectivity of the neighboring molecules is additionally supported by our computation of the corresponding Kirchoff transport indices (\mathcal{K}_T , see ESI†). In all cases, ring fusion leads to increased connectivity with a more significant enhancement for the planar fused dimers than in the twisted dimers (Table 1). This is consistent with the measured SCLC mobilities, providing an explanation for the observed trend and suggesting that the fused structures are more capable of forming connected charge transport networks than the unfused structures.

PDI electronic coupling

As discussed above, ring fusion results in splitting of the first and second reduction potentials of the PDI dimers and increased SCLC mobility, indicating increased electronic coupling between the individual PDI cores in the fused structures. To further investigate this effect, **Ph1**, **Ph2a**, and **Ph2b** were chemically reduced using cobaltocene and the resulting radical anions were investigated using EPR and optical

spectroscopy (Fig. 3). The EPR spectra of all three dimeric anions exhibit linewidths and ¹⁴N hyperfine coupling constants that are approximately one-half those observed for the monomeric PDI anion, suggesting that the unpaired electron is either fully delocalized or rapidly hopping between PDIs in all three dimeric systems on the timescale of the experiment (ns).⁷⁰ The principal difference in the EPR spectra is the strong coupling between the unpaired spin and the bridge protons in the fused structures, with ¹H hyperfine coupling constants of $a_H = 1.00$ MHz for **Ph2a**, and $a_H = 2.44$ MHz for **Ph2b**, while the unpaired spin is only weakly coupled to the bridge in **Ph1** ($a_H = 0.24$ MHz). These coupling constants are in agreement with computed values (Table S1†) and indicate that there is significant radical anion electron density on the bridge in the fused structures but not in the unfused structure. The electron density on the bridge in the fused structures suggests that the electron may be truly delocalized in the fused structures rather than simply hopping between the individual PDIs.



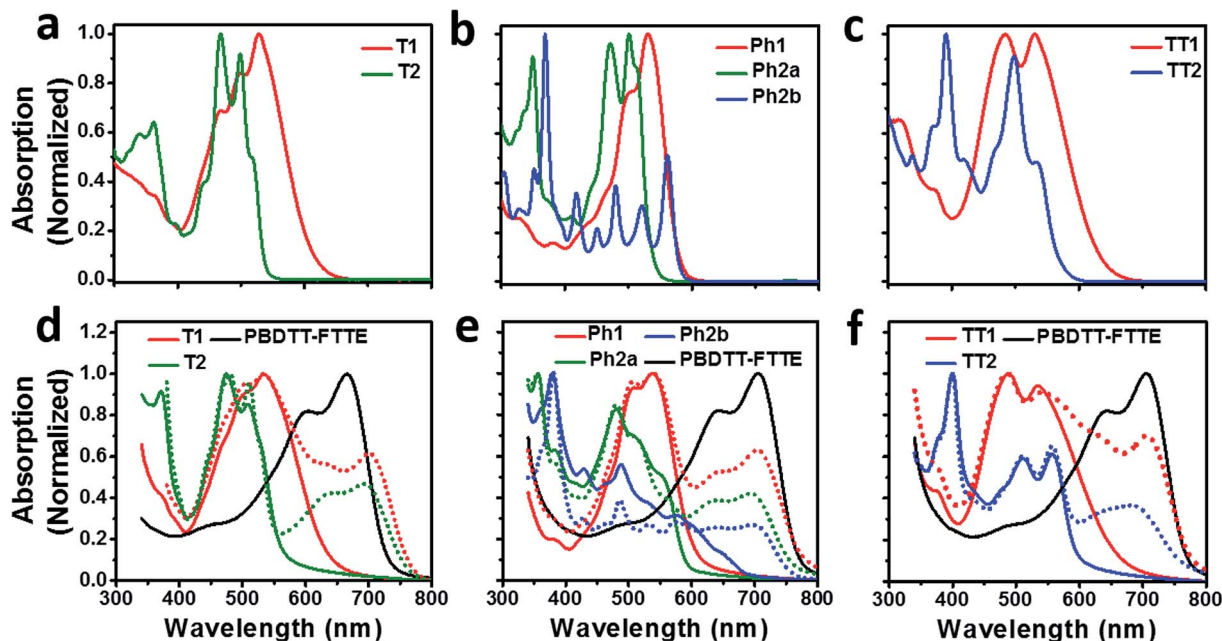


Fig. 1 Optical absorption spectra of the PDI acceptors in solution (a–c) and as thin films, and donor polymer PBDTT-FTTE as a thin film (d–f solid lines). Absorption spectra of blend films cast from chloroform are indicated by the dotted lines (d–f).

The optical absorbance spectra of the anions (Fig. 3) show that, when compared to the monomeric PDI radical anion (700, 795, and 955 nm),⁷³ **Ph1** is slightly red-shifted with absorption peaks at 724, 811, and 981 nm. These peak positions are similar to those observed for an anion hopping between adjacent monomeric PDIs in a solution aggregate.⁷⁰ In the case of **Ph2a**, the anion absorption peaks are blue-shifted to 682, 773, and 910 nm and broadened relative to those of **Ph1**, while in **Ph2b** the anion features are very broad. Broadening of the anion features in **Ph2a** and **Ph2b** is suggestive of increased anion delocalization.⁷⁴

OPV device fabrication and evaluation

OPV devices were fabricated from each PDI acceptor using an inverted architecture (ITO/ZnO/active layer/MoO₃/Ag) and PBDTT-FTTE as the donor material. The optimized device parameters are summarized in Table 2. The performance of

devices based on non-planar fused structures **T2** and **Ph2a** is significantly enhanced *versus* those based on unfused structures **T1**, **TT1**, and **Ph1**, although the performance is somewhat lower than that reported for a blend of **T2** with the same polymer.³¹ This is likely due to the fact that the active layers in the devices studied were thinner leading to incomplete absorption in the film (Fig. S2†). In contrast, devices based on planar fused structures (**Ph2b** and **TT2**) have inferior performance. The *J*-*V* plots (Fig. 4a–c) show that the observed trends in PCEs reflect variations in short circuit current (*J*_{SC}) and fill factor (FF). The open circuit voltages (*V*_{OC}) of the materials vary predictably with variations in the acceptor LUMO levels in that there is only a slight enhancement in *V*_{OC} for the fused structures. For dimeric PDIs **T2** and **Ph2a**, an increase in both FF and *J*_{SC} is observed, while a decrease in both parameters is observed for **Ph2b** and **TT2**. The increased FF is consistent with the increased SCLC mobility of the non-planar fused structures (Table 1), however, a similar increase in SCLC mobility is also observed

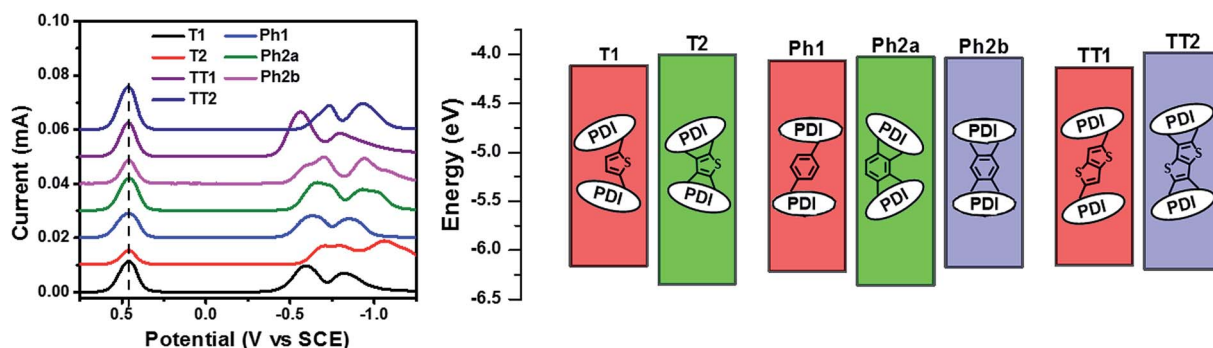


Fig. 2 DPV profiles (left) and energy levels (right) of the present PDI acceptor molecules.



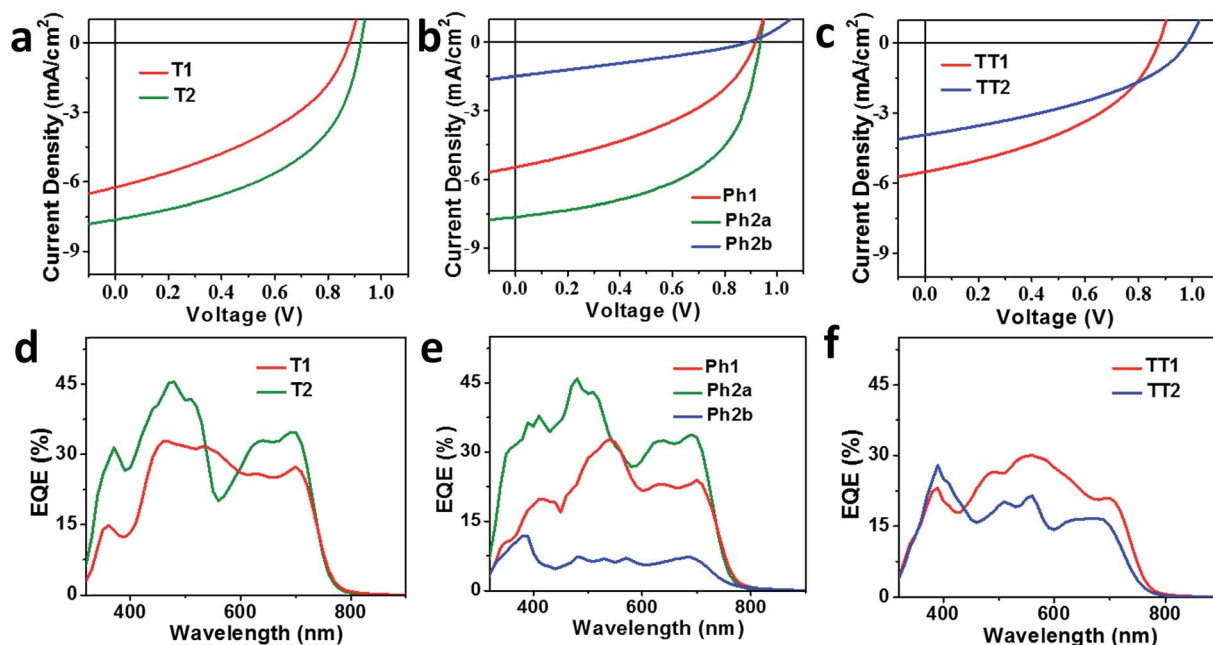


Fig. 4 J - V curves (a–c) and EQE spectra (d–f) of OPV devices based on T1 and T2 (a and d), Ph1, Ph2a, and Ph2b (b and e), and TT1 and TT2 (c and f) blended with the donor polymer PBDTT-FTTE.

be easily seen in the GIWAXS scattering images of the pristine acceptor films (Fig. S4†). The scattering patterns for the unfused structures have no noticeable peaks, and the scattering is mostly unchanged in **Ph2a** and **T2**, but in the case of the planar dimers, **Ph2b** and **TT2**, intense crystalline peaks are clearly

visible. Scherrer analysis of the GIWAXS linecuts supports this argument showing that the average correlation length is small in **T1**, **Ph1** and **TT1**, on the order of 2–5 nm. The correlation lengths increase slightly in the twisted dimers **T2** and **Ph2a**, to 3–8 nm, but increase much more significantly in the planar

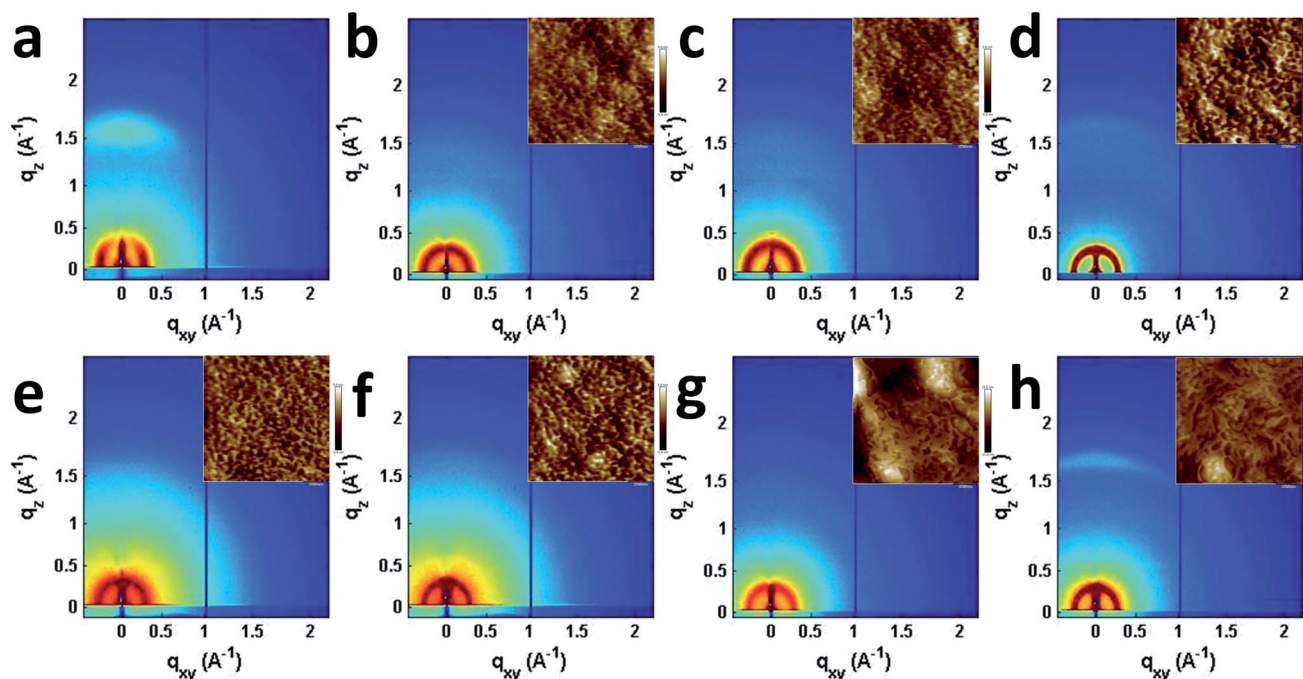


Fig. 5 GIWAXS images of pristine PBDTT-FTTE (a), PBDTT-FTTE:Ph1 (b), PBDTT-FTTE:Ph2a (c), PBDTT-FTTE:Ph2b (d), PBDTT-FTTE:T1 (e), PBDTT-FTTE:T2 (f), PBDTT-FTTE:TT1 (g), and PBDTT-FTTE:TT2 (h) films. AFM images of the blend films are shown in the insets and enlarged versions are available in Fig. S3.† All films were spin-coated on Si/SiO₂ from chloroform with 1 wt% DIO.



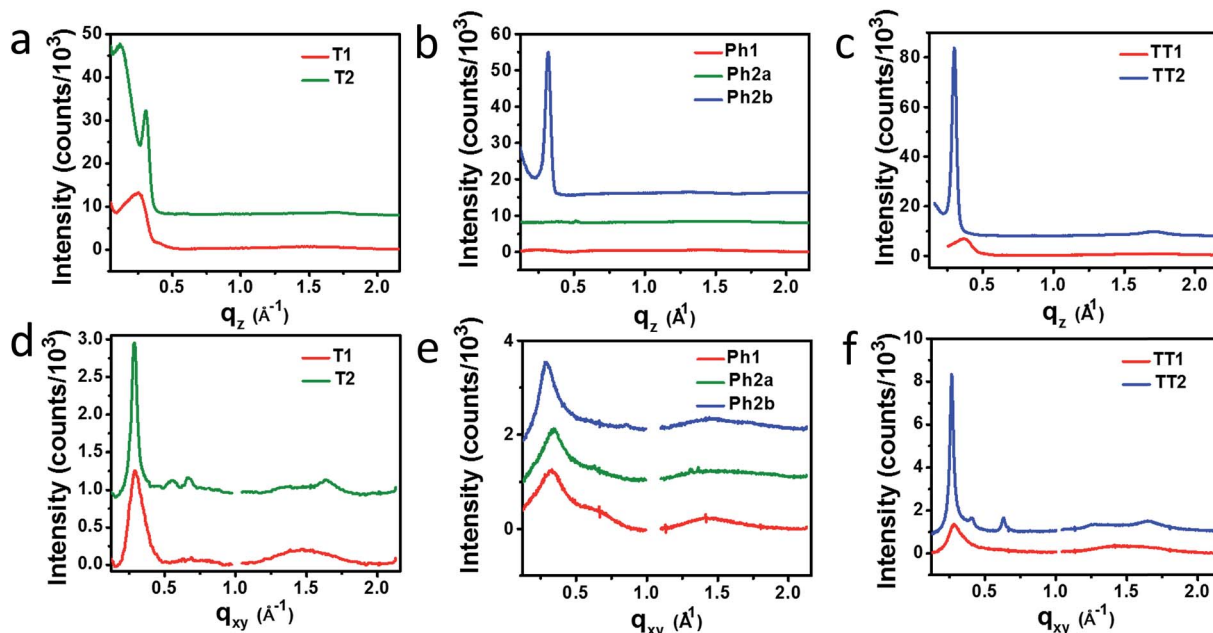


Fig. 6 Vertical (a–c) and horizontal (d–f) GIWAXS linecuts of PBDTT-FTTE:T1 and PBDTT-FTTE:T2, (a and d) PBDTT-FTTE:Ph1, PBDTT-FTTE:Ph2a, and PBDTT-FTTE:Ph2b (b and e), and PBDTT-FTTE:TT1 and PBDTT-FTTE:TT2 (c and f).

dimers, ranging from 11–18 nm (Table S2†). The high degree of crystallinity observed for the planar fused dimers likely contributes to the decreased PV efficiency of devices using these materials since crystallinity in PDIs has been associated previously with excimer formation and excessive phase segregation.^{80,81} Additionally, there is a strong end-on orientation preference for **Ph2b**, indicated by the relative intensity of the lamellar scattering peak in the out-of-plane linecut relative to the in-plane linecut, which has been shown to be detrimental to OPV performance because of the anisotropic nature of charge transport in PDIs.⁸²

Charge separation and recombination dynamics

Photoluminescence (PL) spectra (Fig. S6†) show that there is significant excimer formation in **Ph2b** films but not in **TT2** films, despite the fact that both are crystalline materials. These results can explain why a more significant decrease in PV performance is observed for devices based on **Ph2b**. Despite this observed excimer formation, blends of all seven materials show that PL is quenched by greater than 95%, suggesting that charge transfer is nearly quantitative, although **Ph2b** shows the lowest degree of quenching, and excimer states are generally not highly emissive,⁸³ so it is conceivable that charge transfer is less

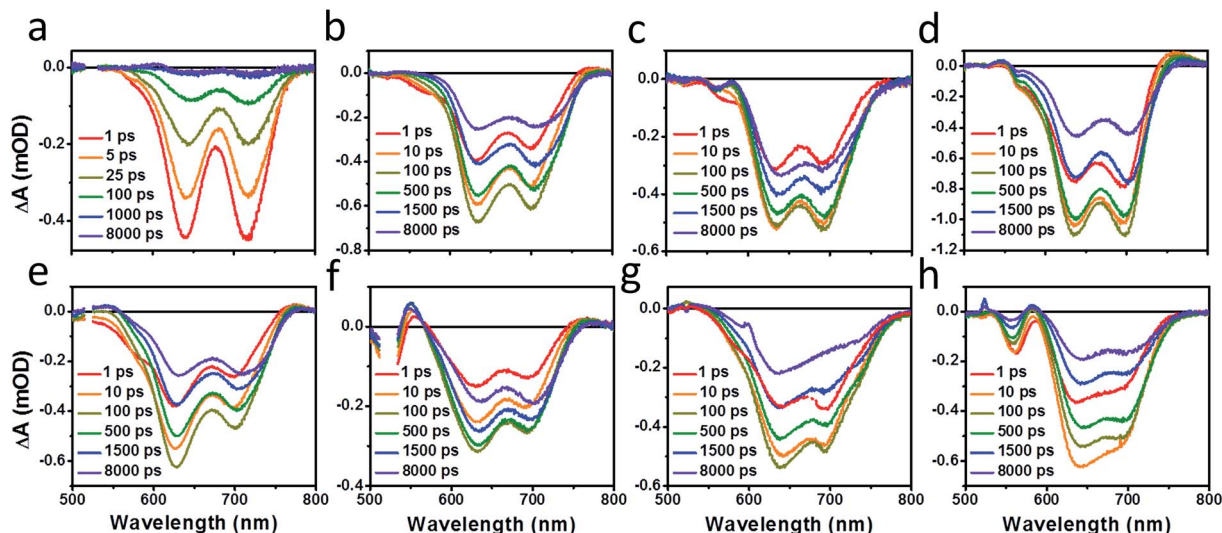


Fig. 7 fsTA film spectra of pristine PBDTT-FTTE (a), PBDTT-FTTE:Ph1 (b), PBDTT-FTTE:Ph2a (c), PBDTT-FTTE:Ph2b (d), PBDTT-FTTE:T1 (e), PBDTT-FTTE:T2 (f), PBDTT-FTTE:TT1 (g), and PBDTT-FTTE:TT2 (h).



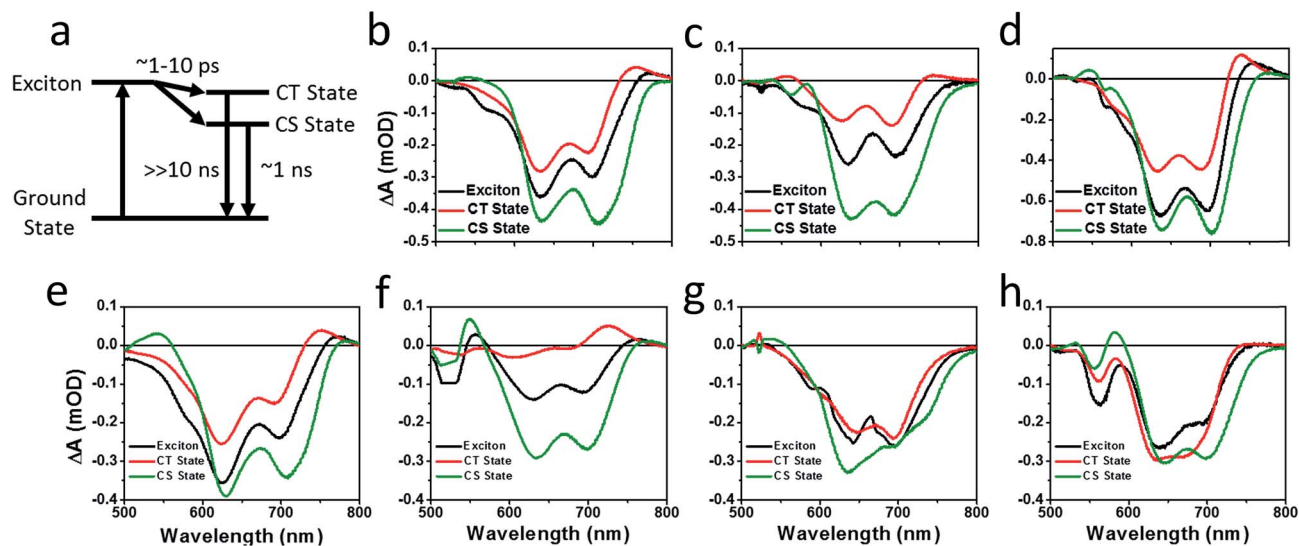


Fig. 8 Species associated spectra obtained by fitting the fsTA spectra of PBDTT-FTTE:Ph1 (b), PBDTT-FTTE:Ph2a (c), PBDTT-FTTE:Ph2b (d), PBDTT-FTTE:T1 (e), PBDTT-FTTE:T2 (f), PBDTT-FTTE:TT1 (g), PBDTT-FTTE:TT2 (h), to a model (a) in which the exciton forms either a trapped state (CT state), which rapidly decays to the ground state, or dissociates into free carriers (CS state), which recombine slowly.

efficient in this case. The high yields of charge transfer suggest that the increased OPV performance upon ring fusion for the non-planar dimers and the more modest performance for the planar dimers most likely results from differences in charge recombination dynamics and possibly charge collection.

The charge separation and recombination dynamics of the present PDI systems were further investigated using femto-second transient absorption (fsTA) spectroscopy. The transient spectra of the blend films and of pristine PBDTT-FTTE are shown in Fig. 7, while transient spectra of the pristine PDI dimers can be found in the ESI (Fig. S3[†]). The fsTA spectral features of the blends are dominated by the polymer bleach between 550 and 750 nm resulting in the spectra of the blends looking similar with slight changes at lower wavelengths resulting from changes in the PDI absorption. The (fsTA) spectra of the blends can be fit within experimental error (Fig. S5[†]) to a model where an exciton state undergoes electron transfer in 1–10 ps to either a CT state, which then undergoes geminate recombination in ~ 1 ns, or dissociates forming a fully charge separated (CS) state which does not recombine on the timescale of the experiment (Fig. 8a). This model must be treated as a pragmatic approximation since it does not distinguish between excitons on the PDI acceptor and excitons on the donor polymer and also does not account for energy transfer. In addition, this model does not account for the possibility of carriers in the trapped CT state dissociating into free carriers. However, the utility and value of this model can be seen from the fact that it is able to fit all seven data sets with a high degree of accuracy (Fig. S5[†]).

Results from fitting the fsTA spectra are shown in Fig. 8. The spectra are fits of the 2D dataset according to the model (Fig. 8a) and represent the exciton (shown in black), CT (shown in red), and CS (shown in green) states and are normalized to reflect their relative populations.

Since the polymer bleach feature dominates the spectra, the relative yields of the CT state and the CS state can be estimated by comparing their intensities between 600 and 700 nm. All three unfused systems are similar with a slightly higher yield of the CS state *versus* the CT state (Fig. 8b, e and g). In blends of the non-planar fused dimers T2 and Ph2, the yields of free carriers increase dramatically and are large compared to the yield of trapped carriers, suggesting that there is little geminate recombination in these systems (Fig. 8b and f). In marked contrast, blends of the planar fused dimers exhibit increased geminate recombination relative to the non-planar fused dimers and, in the case of TT2, even more geminate recombination than in the unfused TT1, convincingly explaining why there is a decrease in PCE for BHJ films of TT2 relative to TT1. These trends in geminate recombination are best explained by two mechanisms. In the fused structures, the individual PDI molecules are more tightly coupled, with the increased delocalization facilitating free carrier formation. In the case of Ph2b and TT2, this benefit is potentially offset by the fact that planar acceptors are capable of packing tightly with the polymer donor, resulting in higher coulombic binding energies and therefore a greater likelihood of forming a trapped CT state.^{84,85} When combined with the increased crystallinity and excimer formation in Ph2b and TT2, this increase in geminate recombination likely explains the observed trend in performance.

Conclusions

Ring fusion is found to increase the electronic coupling between PDI acceptor molecules, resulting in increased electron mobilities and increased LUMO energies. While the increased LUMO energy leads to increased V_{OC} for PBDTT-FTTE-based BHJ OPVs based on ring-fused dimeric acceptors, the major changes in device performance reflect changes in FF and J_{SC} . Although AFM indicates the absence of large domains in blends



- 74 T. van der Boom, R. T. Hayes, Y. Zhao, P. J. Bushard, E. A. Weiss and M. R. Wasielewski, *J. Am. Chem. Soc.*, 2002, **124**, 9582–9590.
- 75 G. Ren, E. Ahmed and S. A. Jenekhe, *Adv. Energy Mater.*, 2011, **1**, 946–953.
- 76 A. Sharenko, D. Gehrig, F. Laquai and T.-Q. Nguyen, *Chem. Mater.*, 2014, **26**, 4109–4118.
- 77 J. M. Szarko, J. Guo, Y. Liang, B. Lee, B. S. Rolczynski, J. Strzalka, T. Xu, S. Loser, T. J. Marks and L. Yu, *Adv. Mater.*, 2010, **22**, 5468–5472.
- 78 N. Zhou, H. Lin, S. J. Lou, X. Yu, P. Guo, E. F. Manley, S. Loser, P. Hartnett, H. Huang and M. R. Wasielewski, *Adv. Energy Mater.*, 2014, **4**, 1300785–1300793.
- 79 H. Li, T. Earmme, S. Subramanian and S. A. Jenekhe, *Adv. Energy Mater.*, 2015, **5**, 1402041–1402050.
- 80 J. J. Dittmer, E. A. Marseglia and R. H. Friend, *Adv. Mater.*, 2000, **12**, 1270–1274.
- 81 C. Li and H. Wonneberger, *Adv. Mater.*, 2012, **24**, 613–636.
- 82 I. P. Murray, S. J. Lou, L. J. Cote, S. Loser, C. J. Kadleck, T. Xu, J. M. Szarko, B. S. Rolczynski, J. E. Johns and J. Huang, *J. Phys. Chem. Lett.*, 2011, **2**, 3006–3012.
- 83 E. A. Margulies, L. E. Shoer, S. W. Eaton and M. R. Wasielewski, *Phys. Chem. Chem. Phys.*, 2014, **16**, 23735–23742.
- 84 J. M. Hodgkiss, A. R. Campbell, R. A. Marsh, A. Rao, S. Albert-Seifried and R. H. Friend, *Phys. Rev. Lett.*, 2010, **104**, 177701.
- 85 T. W. Holcombe, J. E. Norton, J. Rivnay, C. H. Woo, L. Goris, C. Piliago, G. Griffini, A. Sellinger, J.-L. Brédas, A. Salleo and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 2011, **133**, 12106–12114.

