Journal of Materials Chemistry A

Accepted Manuscript

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Structural Variations to a Donor Polymer with Low Energy Losses

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Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Two regioregular narrow band gap conjugated polymers with a D'-A-D-A repeat unit architecture, namely PIFCF and PSFCF, were designed and synthesized. Both polymers contain strictly organized fluorobenzo[c][1,2,5]thiadiazole (FBT) orientations and different solubilizing side chains for solution processing. Compared to the previously reported asymmetric pyridyl-[2,1,3]thiadiazole (PT) based regioregular polymer, namely PIPCP, PIFCF and PSFCF exhibit wider band gaps, tighter π - π stacking, and improved hole mobilities. When incorporated into solar cells with fullerene acceptors, the $E_{\text{loss}} = E_g - eV_{\text{oc}}$ values of PIFCF and PSFCF devices are increased compared to solar cells based on PIPCP. Determination of E_{ct} in these solar cells reveals that, relative to PIPCP, PIFCF solar cells lose more energy from $E_g - E_{\text{ct}}$, and PSFCF solar cells lose more energy from both $E_g - E_{\text{ct}}$ and $E_{\text{ct}} - eV_{\text{oc}}$. The close structural relationship between PIPCP and PIFCF provides an excellent framework to establish molecular features that impact the relationship between E_g and E_{ct} . Theoretical calculations predict that E_{loss} of PIFCF:PC₆₁BM would be higher than in the case of PIPCP:PC₆₁BM, due to greater $E_g - E_{\text{ct}}$. These findings provide insight into the design of high performance, low voltage loss photovoltaic polymeric materials with desirable optoelectronic properties.

1. Introduction

Organic semiconductors based on conjugated polymers with regioregular molecular structures are attractive due to their ability to achieve a greater degree of interchain order, when compared to their less structurally precise counterparts.¹⁻² Studies of the widely investigated "classical" regioregular polymer poly(3-hexylthiophene-2,5-diyl) (P3HT) have demonstrated how controlling the orientation of monomers in the backbone translates to desirable modifications in the degree of crystallinity, charge transport, and overall organization in the thin film.³⁻⁵ The asymmetry in P3HT arises due to the absence of a mirror plane perpendicular to the thiophene plane, see Figure 1.

Recent work in the development of donor (electron rich)-acceptor (electron poor) (D-A) narrow bandgap conjugated polymers has demonstrated cases where controlling the orientation of asymmetric A units brings in improvements in relevant optoelectronic properties.⁶⁻¹¹ One case in point

involves the pyridyl-[2,1,3]thiadiazole (PT) fragment, see Figure 1, which exhibits a similar symmetry to that of 3-hexylthiophene. Introducing PT in a controlled fashion can allow one to achieve exceptional hole mobilities.¹² Müllen and collaborators also reported fluorobenzo[c][1,2,5]thiadiazole (FBT) based regioregular D-A polymers with enhanced solar cell power conversion efficiencies (PCE).¹³ More recently, our group reported on a donor polymer, PIPCP,¹⁴ see Figure 1, with a regiochemically precise set of D'-A-D-A repeat units. Notably, bulk heterojunction (BHJ) solar cells using PIPCP exhibit a relatively high open circuit voltage (V_{oc}) due to a low energy loss (here, E_{loss} is defined as $E_g - eV_{\text{oc}}$), when compared against a wide range of polymers with similar optical gaps (E_g).¹⁵⁻²⁸

Larger E_{loss} values due to exciton splitting driving force, charge transfer (CT) state binding energy, interfacial disorder, and recombination translate directly into lower PCEs.²⁹⁻³⁰ Compared to wide bandgap materials with high V_{oc} values,³¹⁻³⁵ narrow bandgap polymers facilitate light absorption up to

Figure 1. Asymmetric building blocks and polymer designs: (a) replacing PT with FBT; (b) replacing IDT with SIIDT.

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Electronic Supplementary Information (ESI) available: [The experimental details of synthesis of monomers and polymers, NOESY and NMR spectra, TGA and DSC curves, UV-vis, CV data, SCLC mobility measurements, GIWAXS data, solar cell device data, and TD-DFT calculations are available.]. See DOI: 10.1039/x0xx00000x

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near-IR energies, which can better match the solar radiation spectrum, leading to higher short-circuit current (J_{sc}) values. Narrow bandgap polymers with low E_{loss} therefore provide opportunities to maximize the performance of organic photovoltaic (OPV) devices.^{15,19,36-41} Unfortunately, although PIPCP-based solar cells have a low E_{loss} , the system has been limited due to a low fill factor (FF). For high performance OPVs, materials optimization requires a better understanding of the how molecular features impacts E_{loss} and FF .

In this contribution, we first describe the design of a new polymer structure related to PIPCP, namely PIFCF (Figure 1), in which we switch the PT units in PIPCP to FBT units in PIFCF. Furthermore, we exchanged the solubilizing side groups in the IDT unit in PIPCP and PIFCF to the less bulky SiIDT unit to make PSFCF. Both polymers serve as models to understand how subtle changes in molecular structure impact relevant optoelectronic properties and the resulting solar cell characteristics.⁴²

2. Results and Discussion

2.1 Preparation and Characterization of FBT Copolymers PIFCF and PSFCF

Relative to PT-based regioregular polymers, FBT-based analogs provide the opportunity to accentuate intermolecular arrangements via H...F hydrogen bonds⁴³⁻⁴⁵ and to avoid interfacial issues due to protonation of the pyridyl nitrogen atom in PT by acidic surfaces.⁴⁶⁻⁴⁸ It is also worth noting the difference between the reactivity of the dibromide precursors, namely 4,7-dibromo-5-fluorobenzo[c][1,2,5]thiadiazole (Br_2 FBT) and 4,7-dibromo-[1,2,5]thiadiazolo[3,4-c]pyridine (Br_2 PT). For Br_2 FBT, the Br meta to the fluorine substituent is more reactive toward transition metal-mediated cross coupling reactions.⁴⁹ In the case of Br_2 PT, one finds that the Br adjacent to the pyridyl N is more reactive.¹² As such, one finds opposite regioselectivity between Br_2 FBT and Br_2 PT. Like PIPCP, PIFCF and PSFCF are D'-A-D-A type copolymers; however, they contain FBT instead of PT for the A unit, which enables investigation of the aforementioned effects of the FBT substitution. For PSFCF, we further modified the solubilizing side groups on D' relative to PIFCF: benzo[1,2-b:4,5-b']bis(4,4'-dihexyl-4H-silolo[3,2-b]thiophene-2,2'-diyl) (SiIDT)⁴⁹ was introduced as D' because both the silicon bridge atom and the removal of bulky substituted phenyl groups was anticipated to improve polymer chain packing.⁵⁰⁻⁵¹

As shown in Scheme 1, compound 1 was synthesized in 60% yield via the Stille cross-coupling reaction.⁵² The regioselectivity of 1 was confirmed by 1H - 1H NOESY spectroscopy (Figure S1, ESI). PIFCF and PSFCF were obtained by polymerization of 1 with 2 and 1 with 3, respectively, using $Pd_2(dba)_3/P(o-tol)_3$ under conventional heating conditions. For PIFCF, after stirring at 110 °C for an hour, the mixture becomes viscous and difficult to stir. A similar protocol starting with 1 and 3 produced PSFCF. Interestingly, PSFCF showed higher solubility in chloroform and chlorobenzene at room temperature relative to PIFCF (Table 1). The number-average molecular weights (M_n) and dispersities ($\bar{D}$) were determined

Scheme 1. Molecular structures and synthetic access to PIFCF and PSFCF. (Red arrows are provided to highlight the orientation of the asymmetric FBT units.)

Table 1. Solubility, optical gap, electronic state energies, and SCLC hole mobility of PIPCP, PIFCF, and PSFCF.

	Solubility ^a (mg/mL)	E_g (eV)	IP^b (eV)	EA^b (eV)	μ_h ($cm^2V^{-1}s^{-1}$)
PIPCP	>20	1.47	5.26	3.79	1.1×10^{-4}
PIFCF	12	1.65	5.20	3.55	2.2×10^{-4}
PSFCF	>20	1.57	5.16	3.59	1.5×10^{-3}

^aThe concentration of a saturated solution in chloroform at 25 °C; ^b IP s (ionization potentials) were estimated from the onset of the oxidation peaks of cyclic voltammetry measurements; ⁵⁰ EA (electron affinity) values are evaluated as $IP - E_g$ (a procedure that neglects any exciton binding energy).

by gel permeation chromatography (PIFCF: $M_n = 17$ kDa, $\bar{D} = 1.8$; PSFCF: $M_n = 36$ kDa, $\bar{D} = 1.6$). We also intentionally synthesized a lower molecular weight batch of PSFCF ($M_n = 18$ kDa, $\bar{D} = 2.2$). Both PIFCF and PSFCF show good thermal stability under nitrogen, with 5% weight-loss temperatures at 414 °C and 408 °C for PIFCF and PSFCF, respectively (Figure S4, ESI). No thermal transitions were observed for either material by differential scanning calorimetry (DSC) in the range 30 - 300 °C (Figure S5, ESI).

2.2 UV-vis Absorption

Optical absorption spectra of PIFCF and PSFCF, compared to PIPCP, are shown in Figure 2. As shown in Figure 2a, all polymers in solution display π - π^* transition peaks around 400 nm while their lowest energy intramolecular charge transfer (ICT) optical transitions are in the 600-800 nm range. PIFCF displays *ca.* 70 nm blue-shifted absorption relative to PIPCP, consistent with FBT being a weaker acceptor relative to PT

Figure 2. Absorption spectra of polymers (a) in solution (0.01 mg/ml, in chloroform); (b) in thin films.

(and therefore having a smaller electron affinity (*EA*), *i.e.*, higher-lying LUMO).⁴⁶⁻⁴⁸ The SiIDT-based polymer PSFCF exhibits a 20 nm blue shift in absorption compared to the IDT-based polymer. Thin film absorption spectra are shown in Figure 2b. Consistent with the solution measurements, PIFCF and PSFCF have a blue-shifted absorption compared to PIPCP. In the solid state, however, PSFCF film absorption is more red-shifted compared to PIFCF. This phenomenon suggests that PSFCF exhibits more intimate interchain contacts relative to PIFCF. As determined by the onset of film absorption, the E_g of PSFCF and PIFCF is 1.57 eV and 1.65 eV, respectively, as summarized in Table 1.

2.3 Electrochemical Properties

Thin-film cyclic voltammetry (CV) measurements (Figure S8, ESI) were used to estimate the ionization potentials (*IP*s), using the oxidation onsets.⁵³⁻⁵⁴ The *E*_{as} were estimated by subtraction of E_g to the *IP* values (thus, neglecting the exciton binding energies, which can be expected to be similar for the three co-polymers). As summarized in Table 1, the PT-to-FBT substitution decreases the *IP* of PIFCF (*i.e.*, to a first approximation, destabilizes the HOMO) to 5.20 eV, from 5.26 eV for PIPCP. Substitution of SiIDT unit decreases the PSFCF *IP* even more, up to 5.16 eV. Using the optical gaps, the *E*_{as} are estimated as 3.55 eV and 3.59 eV for PIFCF and PSFCF, respectively. Though there is still considerable debate over the applicability and accuracy of CV measurements, with considerations such as the film morphology and its impact on the polarization effects,⁵⁵⁻⁵⁶ as well as polymer/electrode contact and the accurate determination of the onset, the *E*_{as} difference (0.20 - 0.24 eV) between the FBT-polymer analogues and PIPCP is significant enough to point at the influence of substituting PT to FBT. The CV measurements are also consistent with what has been concluded from the ICT peaks in the UV-vis measurement (*i.e.* PT is a stronger acceptor unit relative to FBT). Since achieving a small *EA* (donor) - *EA* (acceptor) offset is conducive to minimizing E_{loss} ,^{15, 39} the effect of destabilizing the LUMO energy levels of FBT analogues relative to PIPCP is expected to increase E_{loss} in fullerene-based devices.

2.4 GIWAXS and Charge-Carrier Transport of Neat Polymer Films

Hole mobilities of the polymers were calculated using the space-charge limited current (SCLC) model for hole-only devices with the configuration ITO/PEDOT:PSS/Polymer/Au (see Figure S9a, ESI).⁵⁷⁻⁵⁸ The pristine PIFCF film ($\mu = 2.2 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$) exhibits slightly improved hole mobility relative to PIPCP ($\mu = 1.1 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$).¹⁴ PSFCF exhibits a much improved hole mobility of $1.5 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, when compared to PIPCP. Improving charge carrier mobilities has been shown to increase the *FF* in simulations and in solar cells devices,⁵⁹⁻⁶⁰ and may reflect a better intrachain and interchain electronic coupling in the solid state.⁵⁰

Grazing incidence wide-angle X-ray scattering (GIWAXS) measurements were performed to investigate relevant for neat polymer films are provided in Figure 3. Similar to PIPCP, the FBT-analogue polymers have a face-on orientation, with

Figure 3. 2D-GIWAXS patterns of neat polymer thin films: (a) PIFCF, (b) PSFCF.

stronger reflection peaks in the out-of-plane direction at $q_z = 1.57 \text{ \AA}^{-1}$ and $q_z = 1.63 \text{ \AA}^{-1}$ for PIFCF and PSFCF, respectively, which corresponds to a “ π - π stacking” distance of 4.00 Å and 3.80 Å. These distances indicate tighter intermolecular contacts relative to PIPCP (4.30 Å),¹⁴ in good correlation with the hole mobilities. These data suggest that changing the bulky sidechains on the IDT unit in PIPCP and PIFCF was effective at allowing tighter interchain packing. Crystal correlation lengths (CCL) were calculated from Gaussian fitting of the “lamellar” and π -stacking diffraction peaks.⁶² We note that the determination of CCL does not directly correspond to crystallite size due to contributions to peak broadening from disorder; however, correlations between CCL and the PCE of devices incorporating these donor polymers may provide insight useful for further molecular design improvements. The CCLs of π -stacking peaks (Table S1, ESI) in the nominally out-of-plane direction were 1.5 nm for neat PIFCF and 2.6 nm for PSFCF, comparing to that of 1.2 nm for neat PIPCP, suggesting a higher degree of morphological order via the SiIDT substitution.

2.5 Photovoltaic Characteristics of PIFCF and PSFCF

The photovoltaic properties of PIFCF and PSFCF are summarized in Table 2 and in the SI. PIFCF was blended both with PC₆₁BM to allow for a direct comparison with previous work on PIPCP, and with PC₇₁BM. Device optimization for these blends is summarized in the ESI, including adjustments of solvents, additives, donor-acceptor blend ratio, and active layer thickness (see Table S2-S6, ESI). Optimal efficiencies, summarized in Table 2, were achieved using inverted devices, with a configuration of ITO/ZnO/active layer/MoO₃/Ag. Table 2 and Figure 4 summarize the photovoltaic performance of PIFCF and PSFCF, compared to PIPCP. PIFCF:PC₆₁BM blends at a ratio of 1:2 cast from chloroform without any thermal or additive treatment exhibit an best PCE of 2.9%. Fabricating devices with PIFCF:PC₇₁BM shows little change in solar cell performance. Note that solvent additive treatment and thermal annealing have negligible impact on the photovoltaic performance of PIFCF blends (see Table S2, ESI). In the case of PSFCF:PC₇₁BM, the weight ratios were also optimized at 1:2. PSFCF:PC₇₁BM blends cast from neat solvent without any treatment exhibited PCEs of ~3.1% (see Table S3, ESI). Further device optimization of PSFCF:PC₇₁BM showed improvements upon introduction 1,8-diiodooctane (DIO)^{48,63} as a solvent additive to the processing solvent, with a PCE of up to 8.0% (see Table S3 and S6, ESI).

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Table 2. Optimized devices based on PIPCP,¹⁶ PIFCF and PSFCF using an ITO/ZnO/Active layer/MoO₃/Ag structure.

Blend	V _{oc} (V)	J _{sc} (mA/cm ²)	FF	PCE ^a (%)	E _{loss} ^b (eV)
PIPCP:	0.90	14.8	0.51	6.9	0.52
PC ₆₁ BM	(0.89±0.01)	(14.0±0.1)	(0.51±0.02)	(6.4±0.3)	
PIFCF:	0.84	9.3	0.37	2.9	0.81
PC ₆₁ BM	(0.84±0.02)	(9.2±0.3)	(0.37±0.01)	(2.8±0.1)	
PIFCF:	0.83	7.9	0.43	2.8	0.82
PC ₇₁ BM	(0.83±0.02)	(7.8±0.2)	(0.43±0.02)	(2.7±0.1)	
PSFCF:	0.79	15.4	0.66	8.0	0.78
PC ₇₁ BM	(0.78±0.03)	(15.2±0.2)	(0.64±0.02)	(7.8±0.2)	

^a Average values obtained from 5 to 10 devices;^b E_{loss} = E_g - eV_{oc}, E_g was calculated for the onset of blend absorption. **Figure 4.** Optimal solar cell device (polymer:PC₇₁BM) characteristics: (a) J-V curves; (b) the corresponding EQE curves.

V_{oc} values of optimized PIFCF and PSFCF devices (0.83–0.84 V and 0.79 V, respectively) are significantly lower than PIPCP^{14,16} (0.89 V). From Table 2, one observes that the J_{sc} and FF of PIFCF-based solar cells are both low regardless of the fullerene, 7.9–9.3 mA/cm² and 43–37%, respectively. However, PSFCF:PC₇₁BM devices achieve improved FF (66%), compared to PIPCP:PC₆₁BM (51%), and a relatively high J_{sc} of 15.4 mA/cm². External quantum efficiency (EQE) curves are shown in Figure 4b. Note that there is no obvious molecular weight dependence on the PSC performance of PSFCF devices of different molecular weights (Table S5, ESI). Both PIFCF and PSFCF solar cells show a broad EQE response from 300 to 800 nm; the J_{sc} values calculated from integrating the EQE are in agreement (± 5%) with the J_{sc} obtained from the J-V measurements.

2.6 Charge Transfer State and Energy Loss in PIFCF and PSFCF Solar Cells.

The E_{loss} in PIPCP:PC₆₁BM is among the lowest obtained for a polymer/fullerene solar cell blend system with PCE > 6%. The analysis on PIPCP:PC₆₁BM revealed that the charge transfer state energy (E_{ct}) and polymer singlet (S₁) energy are very close, differing only by ≈ 50 meV, thereby reducing potential losses associated with formation of the charge transfer species.¹⁶ Note that the performance of PIPCP:PC₇₁BM is similar to PIPCP:PC₆₁BM, with a V_{oc} of 0.86 ± 0.01 eV¹⁴ and E_{loss} = 0.55 eV. However, as shown in Table 2, the E_{loss} values of both PIFCF and PSFCF solar cells are 0.82 eV and 0.78 eV, respectively, significantly higher than what was achieved with PIPCP (0.52 eV). In order to understand the increase in the E_{loss} values, we examined the different contributions that make up

the value. E_{loss} can be split into two contributions: E_g - E_{ct} can provide information about the energy losses due to energetic offsets for charge transfer, while E_{ct} - eV_{oc} is the result of potential losses due to charge recombination. To identify the source of the larger E_{loss} in the FBT polymers, we determined the E_{ct} values by using Marcus theory equations for reduced absorption (Equation 1) and reduced emission (Equation 2), fit simultaneously to EQE and electroluminescence (EL) spectra collected from solar cell devices.⁶⁴

$$E \times EQE_{pv}(E) = \frac{f}{\sqrt{4\pi\lambda kT}} \exp\left(\frac{-(E_{ct} + \lambda - E)^2}{4\lambda kT}\right) \quad (1)$$

$$\frac{EL_{pv}(E)}{E} = \frac{f}{\sqrt{4\pi\lambda kT}} \exp\left(\frac{-(E_{ct} - \lambda - E)^2}{4\lambda kT}\right) \quad (2)$$

In these equations: E is the photon energy; k is the Boltzmann constant; and T is the temperature. The fit parameters are: CT state energy, E_{ct}; the reorganization energy, λ; and a factor proportional to the number of CT states and the square of their coupling matrix with the ground state, f. The CT state is identified in EQE and EL measurements as absorption or emission at sub-bandgap energies. In the case of most solar cell blends studied to date, the shape of the blend EQE spectrum resembles the spectra of the neat materials, and decreases sharply at energies below the bandgap of the neat materials. The CT state is identified in log-scale EQE spectra as a shoulder at low energies which deviates from the sharp decrease as seen from the neat material EQE spectra.^{65,66} The EQE, EL and the corresponding fits and fit parameters are shown in Figure 5. For reference, the EQE spectra of the neat polymers and fullerenes are also provided in the figure. In general, we attribute photocurrent generation at energies that are below the bandgap of the polymer or fullerene as photocurrent generation from the CT state, with certain exceptions which will be discussed below. It is paramount that the fitting to obtain E_{ct} is done on both the EQE and the EL, instead of only the EQE, in order to reduce the degrees of freedom in the fits, especially for the case of PIPCP and PIFCF solar cells. The E_{ct} values obtained by this analysis are

Figure 5. EQE and EL spectra of (a) PIPCP:PC₆₁BM, (b) PIFCF:PC₆₁BM, (c) PSFCF:PC₇₁BM, and (d) PIFCF:PC₇₁BM devices. Dashed lines are the fit results using Equations 1 and 2, fit to the low-energy tail of the EQE and low-energy peak of the EL simultaneously. The light-colored spectra are the normalized EQE response of the neat polymers or fullerenes. The obtained fit parameters are reported for each blend.

summarized in Table 3 and a general layout of E_{loss} is provided in Figure 6.

Examination of Figure 5b reveals that PIFCF:PC₆₁BM shows significant charge generation at energies below the EQE response of the neat polymer or fullerene, while the characteristic signature (shoulder to the EQE) of the CT state is absent. At energies below 1.7 eV, the EQE spectrum of the solar cell blend deviates from the shape of the EQE of neat PIFCF or PC₆₁BM. This resembles the EQE of PIPCP:PC₆₁BM (Figure 5a), which also shows significant charge generation at sub-bandgap energies, and no obvious CT state shoulder in the EQE. A red-shift in the absorption, with no clear CT state shoulder, is not often observed for OPV systems.⁶⁴ However, similar phenomenon was observed in PIPCP:PC₆₁BM blends (Figure 5a), in which case we speculate that the red-shifted absorption results from morphological reorganization upon blending with PC₆₁BM, thus altering the absorption spectrum of PIPCP.¹⁶ The CT state absorption in PIPCP:PC₆₁BM is hidden within the absorption of PIPCP since E_g and E_{ct} are very close in energy for that blend. Similarly, it may be that PIFCF polymer chains undergo a morphological and energetic shift upon blending with PC₆₁BM or PC₇₁BM, resulting in the red-shifted absorption. Unlike PIPCP, however, the EQE of PIFCF is not indicative of a highly ordered system, as the absorption tail is very broad and does not follow an exponential dependence on photon energy.¹⁶ Therefore, it is probable that also in this case the CT state absorption is buried within the absorption of PIFCF.

Such spectral broadening significantly complicates determination of E_{ct} in PIFCF blends, as it is not possible to confidently identify a feature of CT state absorption alone. Therefore, we must use the EL spectra of the corresponding devices to confine the fitting parameters. However, the EL spectra of PIFCF (and PSFCF) blends present additional difficulties for an accurate fit to determine the E_{ct} . First, on the low-energy side, the EL spectra continue past the sensitivity limit of the Si detector used for these measurements. Second, the EL spectra are broadened towards high photon energies, indicating that the spectra may be composed of singlet emission in addition to CT state emission. In this case, only the low-energy side of the EL spectra would be relevant for determining the E_{ct} . For these reasons, we focus our fits on the low-energy side of the EL spectra. The spectral ranges of the EQE and EL spectra where the fit was done were chosen such that the fit to the low-energy EL and EQE were both optimized. We proceed with the analysis to establish estimates for E_{ct} values, while acknowledging these uncertainty in the fits.

The E_{loss} of PIFCF:PC₆₁BM solar cells (0.81 eV) is much higher than the E_{loss} of PIPCP:PC₆₁BM solar cells (0.52 eV). The reason the E_{loss} in PIFCF-based solar cells is greater lies in losses that can be attributed to charge-transfer losses, $E_g - E_{ct} = 0.30$ eV, compared to $E_g - E_{ct} = 0.05$ eV in PIPCP-based solar cells (see Table 3). The added loss due to $E_g - E_{ct}$ correlates well with the smaller EA (*i.e.*, destabilized LUMO level) of PIFCF compared to PIPCP (3.55 vs. 3.79 eV, see Table 1), indicating of losses due to energetic offsets. The differences between $E_g - E_{ct}$ values of PIPCP and PIFCF solar cells are also evaluated using density functional theory (DFT) calculations, as will be

elaborated below. It is interesting to note that the $E_{ct} - eV_{oc}$ of PIPCP- and PIFCF-based solar cells is low, at 0.51 eV for both.

In contrast to PIPCP and PIFCF, PSFCF-based solar cells show EQE spectra that track in shape the EQE response of the neat polymer and exhibits a clear (albeit small) shoulder in the low energy regime, which is characteristic of CT state contribution to the EQE. This is similar to what has been observed for other OPV blends.⁶⁵⁻⁶⁶ Nonetheless, PSFCF solar cells also have a larger E_{loss} (0.78 eV) when compared to PIPCP solar cells (0.51 eV). The larger E_{loss} in PSFCF solar cells is a result of a larger $E_g - E_{ct} = 0.19$ eV (charge transfer losses), as well as a larger $E_{ct} - eV_{oc} = 0.59$ eV (charge recombination losses). The EA of PSFCF (3.59 eV) is smaller compared to PIPCP (3.79 eV), correlating with the $E_g - E_{ct}$ differences. While there may be a larger-than-conventional uncertainty in the fits, given the unusual EQE and EL spectra of these blends, we wish to emphasize that the trends observed here are more dependent on the difference in E_g and eV_{oc} values, as the E_{ct} values are relatively close to each other (~0.6 eV difference). Even if one were to ignore the difference in E_{ct} values and treat them as within error of each other, the trend discussed above would still be the same.

Empirical observations have correlated $E_{ct} - eV_{oc} = 0.6 \pm 0.1$ eV,^{28,64-67} describing bimolecular recombination losses. These recombination losses can be further split into radiative and non-radiative recombination losses.⁶⁴ Non-radiative recombination has been identified as among the primary reasons that the V_{oc} in OPV devices has remained limited,⁶⁵ and until recently, little was understood about the nature of non-radiative recombination. However, a recent comprehensive study by Benduhn *et al.* has shown a clear correlation between E_{ct} and the magnitude of voltage loss due to non-radiative recombination, suggesting that the nature of the non-radiative losses may lie in the C-C bonds, intrinsic to organic semiconductors.²⁸ The losses due to $E_{ct} - eV_{oc}$ in the systems studied here fit within the empirical trend observed for all other studied OPV systems.

As an aside, we point out that while it may be tempting to tie the results in Table 3 back to the superior PCE of PSFCF relative to PIFCF, it is evident that the electronic state energies alone cannot account for the difference in device performance. PSFCF-based solar cells have superior FF and J_{sc} values compared to PIFCF-based solar cells. As illustrated by $E_g - E_{ct}$ in Table 3, this is not due to a superior driving force for charge transfer in PSFCF. It is noted that PSFCF blend film has greater absorbance relative to the PIFCF blend film (see Figure S7, ESI), which would affect the J_{sc} . Furthermore, hole mobility measurements of polymer:PC₇₁BM blend films show that PSFCF:PC₇₁BM blend ($\mu_h = 3.0 \times 10^{-4}$ cm²V⁻¹s⁻¹) exhibits a

Table 3. Energy level estimates for the OPV devices.

Device	E_g (eV)	eV_{oc} (eV)	E_{ct} (eV)	E_{loss} (eV)	$E_g - E_{ct}$ (eV)	$E_{ct} - eV_{oc}$ (eV)
PIPCP:PC ₆₁ BM	1.41	0.89	1.40	0.52	0.01	0.51
PIFCF:PC ₆₁ BM	1.65	0.84	1.35	0.81	0.30	0.51
PIFCF:PC ₇₁ BM	1.65	0.83	1.34	0.82	0.31	0.51
PSFCF:PC ₇₁ BM	1.57	0.79	1.38	0.78	0.19	0.59

Figure 6. Breakdown of the $E_{loss} = E_g - eV_{oc}$ in PIPCP:PC₆₁BM, PIFCF:PC₆₁BM, PIFCF:PC₇₁BM, and PSFCF:PC₇₁BM. E_{loss} is broken into $E_g - E_{ct}$ (dark shaded area) and $E_{ct} - eV_{oc}$ (light shaded area). We emphasize here the difficulty in accurately determining the E_{ct} values in these blends, as is discussed in the main text.

greater mobility relative to PIFCF:PC₇₁BM blend ($\mu_h = 8.9 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). Hole and electron transport are more balanced in PSFCF:PC₇₁BM ($\mu_e = 2.9 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) than PIFCF:PC₇₁BM ($\mu_e = 2.3 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) (see Figure S9b and S9c, ESI). Our current thinking is that the key for the enhanced FF and J_{sc} may lie in the improved charge carrier mobility of PSFCF (which may improve extraction vs. bimolecular recombination^{59,60}) or perhaps morphological details (see Figure S11, ESI) that may affect charge generation vs. geminate recombination, as well as transport.⁶⁸ According to the chemical design, it is likely that the bulky phenyl groups connecting the solubilizing chains to the IDT units in PIFCF and PIPCP disrupt close π - π interchain packing, reducing favourable intermolecular interactions for charge transport.^{51,69-70} Consistent with this idea is that the π - π stacking distance, determined by GIWAXS measurements, is 3.8 Å in PSFCF and 4.0 Å in PIFCF neat films (Figure 3), and 4.3 Å for PIPCP neat films (Figure S10, ESI).¹⁴

2.7 Time-Dependent Density Functional Theory Calculations

The close structural relationship between PIPCP and PIFCF, together with the differences in $E_g - E_{ct}$ values, provides an interesting case study on how molecular-scale features impact the energies of relevant electronic states. A number of initial polymer-fullerene configurations for PIFCF and PC₆₁BM were randomly generated by forming an interaction between the fullerene molecule and different locations on the polymer backbone fragment (Figure S14, ESI). These configurations were optimized at the ω B97X-D/6-31g(d,p) level. Time-dependent density functional theory (TD-DFT) calculations were carried out on the optimized geometries at the long-range corrected OT-PCM- ω B97X-D/6-31g(d,p) ($\epsilon = 3.5$) level of theory.⁷¹⁻⁷³ The calculations carried out for PIFCF are compared with the calculations previously performed on PIPCP and PC₆₁BM.¹⁷ Figure 7 shows the calculated energies for S_1 and E_{ct} in PIPCP:PC₆₁BM and PIFCF:PC₆₁BM.

TD-DFT calculations predict on average that the difference between the S_1 and E_{ct} excitation energies in PIPCP and PC₆₁BM is 27 meV, compared to an average difference of 234

Figure 7. Calculations of S_1 and E_{ct} excitation energies for (a) PIPCP:PC₆₁BM (adapted from reference 17) and (b) PIFCF:PC₆₁BM, at a range of different donor:acceptor configurations. The configurations are shown in the SI, Figure S14.

meV for PIFCF and PC₆₁BM. The differences in energies between S_1 and E_{ct} for the two donor:acceptor interactions (PIPCP:PC₆₁BM vs. PIFCF:PC₆₁BM) are in good agreement with the experimentally calculated $E_g - E_{ct}$, and contribute to the explanation for the larger E_{loss} in PIFCF:fullerene solar cells.

We further note that calculations on PIPCP:PC₆₁BM show that the electron in the excited E_{ct} state is shared between PC₆₁BM and PIPCP (while the hole remains on the polymer chain), and that at certain donor:acceptor configurations S_1 even appears to be lower in energy than E_{ct} .¹⁶ In contrast, such an energetic inversion of S_1 and E_{ct} is not observed for PIFCF:PC₆₁BM, and similarly the calculations for E_{ct} in this system show only marginal electron density on the polymer (Figure S15, ESI). The distribution of the electron density in the E_{ct} over both fullerene and polymer chain is a consequence of the very small energetic offset $E_g - E_{ct}$, which was characterized for that system both experimentally and by calculations, and of the strong electronic mixing between the two states.¹⁷

3. Conclusions

In conclusion, we report on the synthesis and characterization of two narrow optical gap conjugated polymers PIFCF (IDT-FBT-CPDT-FBT) and PSFCF (SiIDT-FBT-CPDT-FBT) that were designed to probe how structural variations influence the energy losses in organic solar cells. Their structures are based on the previously reported PIPCP (IDT-PT-CPDT-PT). Regioregular control over the precise orientation of the FBT fragments relative to the backbone vector was achieved by chemical selectivity of metal-mediated cross coupling reactions. Compared to the PT-based regioregular PIPCP, the weaker ICT in the FBT-analog polymers resulted in blue-shifted absorption spectra and smaller E_{As} . When compared to PIPCP, which demonstrated $E_{\text{loss}} = 0.52$ eV, the E_{loss} loss in FBT-based analogs increased to 0.82 eV and 0.79 eV for PIFCF and PSFCF based solar cells, respectively. Determination of the E_{ct} reveals that the greater E_{loss} in PIFCF solar cells is due to losses in $E_{\text{g}} - E_{\text{ct}} = 0.30$ eV, while the loss from $E_{\text{ct}} - eV_{\text{oc}} = 0.51$ eV is as low as in PIPCP:PC₆₁BM. This is not the case for PIFCF:PC₆₁BM. PSFCF based solar cells lose energy from $E_{\text{g}} - E_{\text{ct}} = 0.19$ eV, as well as $E_{\text{ct}} - eV_{\text{oc}} = 0.59$ eV. The losses due to $E_{\text{g}} - E_{\text{ct}}$ correlate well with the changes in the E_{A} of the donor polymers: $E_{\text{g}} - E_{\text{CT}} = 0.3, 0.19, 0.01$ eV, and $E_{\text{A}} = 3.55, 3.59, 3.79$ eV, for PIFCF, PSFCF, and PIPCP, respectively. The losses due to charge recombination ($E_{\text{ct}} - eV_{\text{oc}}$) for the polymers studied here follow the empirical trend observed for organic solar cells, $E_{\text{ct}} - eV_{\text{oc}} = 0.6 \pm 0.1$ eV. PIFCF and PIPCP are at the bottom of the distribution with $E_{\text{ct}} - eV_{\text{oc}} = 0.51$ eV, while PSFCF solar cells lose 0.58 eV to recombination losses. The greater loss due to $E_{\text{g}} - E_{\text{ct}}$ in PIFCF:PC₆₁BM is supported by theoretical calculations, which predict that on average, the $S_1 - E_{\text{ct}}$ in PIFCF:PC₆₁BM is 234 meV, while similar calculations on PIPCP:PC₆₁BM predict that $S_1 - E_{\text{ct}}$ is only 27 meV for PIPCP:PC₆₁BM. Depending on the molecular configuration between PIPCP and PC₆₁BM, the calculations also found that the electron density of the CT state is shared between PC₆₁BM and PIPCP.

Having available three structurally related regioregular donor polymers has therefore allowed us to dissect the different contributions to E_{loss} in OPV devices. $E_{\text{ct}} - eV_{\text{oc}}$ is low and similar between PIPCP and PIFCF, which may indicate a particular relationship with the IDT-A-CPDT-A structural combination. That the $E_{\text{g}} - E_{\text{ct}}$ contribution to the loss is lower in PIPCP vs. PIFCF reflects the lower electron affinity of PIPCP. The lower electron affinity of PIPCP compared to PIFCF may also explain the greater degree of shared electron density between the fullerene and the PT unit in the backbone of PIPCP.

Acknowledgements

J. Y. thanks the scholarship for China Scholarship Council (CSC), Collaborative Innovation Center of Suzhou Nano Science & Technology, the Priority Academic Program Development of Jiangsu Higher Education Institutions. Structural characterization efforts were supported by the National Science Foundation (DMR-1411240). Use of the Stanford Synchrotron Radiation Light source, SLAC National Accelerator

Laboratory, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515. N.A.R., T.-Q.N., and G.C.B. acknowledge support from the Department of the Navy, Office of Naval Research (Award Nos. N00014-14-1-0580 and N00014-16-1-25200). We would like to thank Kathryn O'Hara for her help with X-ray scattering data collection. Work at KAUST was funded through the KAUST Competitive Research Grant Program. M.K.R. and J.L.B. acknowledge the KAUST IT Research Computing Team and Supercomputing Laboratory for providing outstanding assistance as well as computational and storage resources.

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Table of Contents Graphic

Two regioregular narrow band gap conjugated polymers with a D'-A-D-A repeat unit architecture, namely PIFCF and PSFCF, were synthesized for PSC applications. Determination of E_{ct} in these solar cells reveals that, relative to PIPCP, PIFCF solar cells lose more energy from $E_g - E_{ctr}$ and PSFCF solar cells lose more energy from both $E_g - E_{ct}$ and $E_{ct} - eV_{oc}$.