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Authors: Shengjian Liu, Yuliar Firdaus, Simil Thomas, Zhipeng Kan, Federico Cruciani, Sergei Lopatin, Jean-Luc M. Bredas, and Pierre M. Beaujuge

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# Isoindigo–3,4-Difluorothiophene Polymer Acceptors Yield "All-Polymer" BHJ Solar Cells with >7% Efficiency

Shengjian Liu,<sup>†,&</sup> Yuliar Firdaus,<sup>†,&</sup> Simil Thomas,<sup>‡</sup> Zhipeng Kan,<sup>†</sup> Federico Cruciani,<sup>†</sup> Sergei Lopatin,<sup>§</sup> Jean-Luc Bredas,<sup>‡</sup> and Pierre M. Beaujuge<sup>\*,†</sup>

**Abstract:** Poly(isoindigo–*alt*–3,4-difluorothiophene) (PIID[2F]T) analogues used as "*polymer acceptors*" in bulk-heterojunction (BHJ) solar cells achieve >7% efficiency when used in conjunction with the polymer donor PBFTAZ (model system; copolymer of benzo[1,2-*b*:4,5-*b*]dithiophene and 5,6-difluorobenzotriazole). Considering that most efficient polymer acceptor alternatives to fullerenes (e.g. PC<sub>61</sub>BM or its C<sub>71</sub> derivative) are based on perylenediimide or naphthalenediimide motifs thus far, branched alkyl-substituted PIID[2F]T polymers are particularly promising nonfullerene candidates for "all-polymer" BHJ solar cells.

In the early years of research on "all-polymer" bulk heterojunction (BHJ) solar cells (all-PSCs), devices made from blends of *n*-conjugated polymer donors and acceptors met with limited power conversion efficiencies (PCEs).<sup>1</sup> While in all-PSCs, polymer acceptors are used as alternatives to fullerenes (e.g. PC<sub>61</sub>BM or its C<sub>71</sub> analogue), the ability to concurrently achieve donor-acceptor networks with adequate domain sizes (within the lengthscale of exciton diffusion) and efficient charge transfer between the donor and acceptor counterparts is paramount. Therefore, only a few polymer acceptors have been shown to yield BHJ device PCEs >7% with polymer donors to date.<sup>2</sup> In comparison, PSCs composed of either a fullerene or a nonfullerene molecular acceptor can achieve PCEs >11%,3 although their lack of morphological stability and mechanical conformability remains a matter of examination at this time.<sup>4</sup> Meanwhile, polymer acceptors are more synthetically accessible than PCBM analogues and come with the perspective of lower synthetic costs in light of the more standard purification protocols followed.<sup>2</sup> In parallel, the tunability in their synthetic design can give access to specific optical and electronic properties (i.e., electron affinities (EAs), ionization potentials (IPs), spectral absorption, etc.) that are not readily accessible with fullerene acceptors.<sup>2</sup>

The active-layer material selection, choice of electron/holetransporting interlayers, and the device processing conditions in

[ <sup>&amp;</sup> ]	These authors contributed equally to this work.
[']	Dr. S. Liu, Dr. Y. Firdaus, Dr. Z. Kan, F. Cruciani, Prof. P. M.
	Beaujuge*
	Physical Science and Engineering Division, Solar & Photovoltaics
	Engineering Research Center (SPERC)
	King Abdullah University of Science and Technology (KAUST)
	Thuwal 23955-6900, Saudi Arabia.
	E-mail: pierre.beaujuge@kaust.edu.sa.
[ <sup>‡</sup> ]	Dr. S. Thomas, Prof. J.–L. Bredas
	School of Chemistry and Biochemistry, Center for Organic
	Photonics and Electronics (COPE)
	Georgia Institute of Technology
	Atlanta, Georgia 30332-0400, United States.
[ <sup>§</sup> ]	Dr. S. Lopatin
	King Abdullah University of Science and Technology (KAUST)
	Thuwal 23955-6900, Saudi Arabia.
	Supporting information for this article can be found under:
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all-PSCs are some important parameters that have received significant attention in recent years.<sup>2</sup> While a large part of that effort has been directed to extending the range of efficient polymer acceptors, analogues based on perylenediimide (PDI) and naphthalenediimide (NDI) motifs remain the most efficient thus far, achieving PCEs of 7%-9% in all-PSCs with selected polymer donors.<sup>2,4,5</sup> Polymer acceptors based on B←N bridged bipyridine (BNBP) represent another emerging class of promising fullerene alternatives that has recently been shown to reach PCEs of ca. 6%.<sup>6</sup> Several other acceptor motifs are being as diketopyrrolopyrrole,7a examined. such 2.1.3benzothiadiazole,7b and various nitrile (CN)-derived motifs;7c with reported PCEs in range of 1-4%. However, to date, polymer acceptor developments remain synthetically challenging, and the manifold of electron-deficient motifs and polymer acceptor candidates that can rival fullerenes for efficient BHJ solar cells with polymer donors remains modest. Thus, broadening the class of polymer acceptors for further examinations of the "allpolymer" BHJ concept is a critically important step to take in the improvement of device performance beyond currently reported PCEs.

Isoindigo (IID) motifs may serve as alternatives to their PDI and NDI counterparts.<sup>8,9</sup> These synthons have primarily been used in the design of low-bandgap polymer donors for BHJ solar cell<sup>8</sup> and thin-film transistor<sup>8a</sup> applications. Only few studies have discussed their possible use in the design of polymer acceptors, mainly because of the high-lying HOMO ("highest occupied molecular orbital"; i.e., low IP) that IID motifs tend to induce when incorporated in the polymer main-chain.<sup>9</sup> The two lactam moieties in IIDs impart their substantial electron-withdrawing character, and the various alkyl substituents that can be appended to the nitrogen sites provide a handle on solubility and polymer self-assembly.<sup>8</sup> Turning to polymer acceptor designs, systems incorporating IIDs should however include adequate electron-deficient co-monomers that can result in alternating sequences with sufficiently high IP and EA values (corresponding to low-lying HOMO and LUMO ("lowest unoccupied molecular orbital") energy levels) to be used as nonfullerene acceptors in BHJ solar cells.<sup>2,9,10</sup>

In this contribution, we report on a set of branched alkylsubstituted polymer acceptors composed of alternating IID<sup>8,9</sup> and 3,4-difluorothiophene [2F]T motifs,10 and show that the appropriately functionalized poly(isoindigo-alt-3,4difluorothiophene) analogue, namely PIID[2F]T (Figure 1a), can achieve PCEs as high as 7.3% in BHJ solar cells with PBFTAZ<sup>11</sup> as the polymer donor (model system; Figure 1b). PBFTAZ  $(E_{opt} \sim 1.9 \text{ eV})$  and PIID[2F]T  $(E_{opt} \sim 1.7 \text{ eV})$  provide spectral complementary across the UV-vis spectrum (300-750 nm), yielding high short-circuit current densities  $(J_{SC})$  of ca. 13.2 mA/cm<sup>2</sup> and some of the best open-circuit voltage (V<sub>oc</sub>) values (ca. 1.0 V) achieved thus far in single-cell BHJ devices. Given the extent of synthetic modularity known for IID motifs,8 adequately substituted PIID[2F]T analogues effectively broaden

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the class of systems with tunable electronic and optical spectra for all-PSCs with improved PCEs.



**Figure 1.** Chemical structures of (a) PIID[2F]T with various branched alkyl substituents (2BO, 2HD, and 2BO/2HD [2:1] in random sequences) and (b) PBFTAZ (model system). (c) Representations of the TD-DFT tuned- $\omega$ B97X-D natural transition orbitals (NTOs) with the largest contribution to the vertical S0-S1 transition for a IID[2F]T hexamer (bottom: hole NTO; top: electron NTO). (d) Superimposed thin-film UV-vis optical absorption spectra of PIID[2F]Ts and the polymer donor PBFTAZ (normalized).

Prior to synthesizing the PIID[2F]T analogues, density functional theory (DFT), at the  $\omega$ B97XD/6-31G(d,p) level of theory, was employed to probe the main-chain conformation and the extent of  $\pi$ -electron delocalization along the alternating IID and [2F]T motif sequences.12 Figure S2 gives the torsion potential energy surface as a function of rotation of the IID motif with respect to the [2F]T unit; two minima occur, corresponding to the anti/155° and syn/25° conformations. The syn/25° conformation slightly more stable than is the anti/155° conformations by some 0.5 kcal/mol (which is close to thermal energy at room temperature). Figure 1c depicts the time-dependent (TD) DFT tuned-wB97XD natural transition orbitals with the largest contribution to the vertical S<sub>0</sub>-S<sub>1</sub> transition for a IID[2F]T hexamer, with the excitation delocalized over ca. three repeat units (cf. additional details in SI). The offsets between the DFT-calculated IPs and EAs of the polymer donor PBFTAZ and the nonfullerene acceptor PIID[2F]T are found to be 0.37 eV and 0.57 eV (Figure S7), respectively; these results indicate that the polymers have appropriate energy band offsets to be used as donor and acceptor counterparts in BHJ solar cells.

The PIID[2F]Ts with various branched alkyl side-chains shown in Figure 1a (2-butyloctyl: 2BO, 2-hexyldecyl: 2HD, and 2BO/2HD [2:1] in random sequences) were synthesized via Stille cross-coupling polymerization (see experimental details in SI).<sup>10</sup> Here, we note that the relatively limited solubility of the 2BO derivative in common organic solvents made us first consider turning to the longer branched 2HD analogue. However, the higher branched 2HD analogue showing complete solubility in dichloromethane, we envisioned the random polymerization of the two motifs 2BO and 2HD in various stoichiometric ratios (details in SI). The 2BO/2HD [2:1] analogue proved to provide sufficient solubility in the common organic solvents used in BHJ active-layer processing steps. The thermal analyses in Figure S8 indicate that PIID[2F]T and PBFTAZ are thermally stable until ca. 400 °C and that no visible characteristic peak for glass transition, crystallization, or melting are observed in the range 25-250 °C. Hence, the polymers can be considered sufficiently stable to be subjected to post-processing thermal annealing in BHJ device optimization steps (detailed in later sections).

The normalized thin-film UV-vis absorption spectra of the PIID[2F]T analogues and that of the polymer donor PBFTAZ (model system; later used in the device study) are superimposed in Figure 1d. The PIID[2F]T derivatives have equivalent absorption spectra across the range 400-750 nm (peaking at ca. 624 nm) and optical gaps ( $E_{opt}$ ) of ~1.7 eV. The spectral absorption of PBFTAZ falls in the range 400-650 nm, where PIID[2F]T does not absorb as effectively -thus adding in complementarity, a substantial benefit in the optimization of BHJ solar cell efficiency. The IP of PIID[2F]T estimated by photoelectron spectroscopy in air (PESA) is ~5.6 eV, vs. ~4.8 eV for PBFTAZ (see Figure S12 and Table S3). These notably large IP values for PIID[2F]T are comparable to benchmark polymer acceptors such as N2200 (~5.7 eV estimated by PESA). From Figure S13, the electrochemically estimated IPs and EAs can be inferred as follows: ~6.2 eV for PIID[2F]T (vs. ~5.5 eV for PBFTAZ) and ~4.0 eV (vs. ~3.9 eV for PBFTAZ), respectively (results reported in Table S4). Here, it is worth noting that the EA estimate is 0.1 eV lower than that of the fullerene acceptor PCBM (4.1-4.2 eV) and slightly lower than those of PDI/NDIbased polymer acceptors.<sup>4-5</sup> The lower EA values inferred for PIID[2F]T should be conducive to high Voc values in BHJ solar cells (see below).

Thin-film BHJ solar cells with the inverted device configuration ITO/ZnO/PEOz/PBFTAZ:PIID[2F]T/MoO<sub>3</sub>/Ag (device area: 0.1 cm<sup>2</sup>) were fabricated and tested under AM1.5G solar illumination (100 mW/cm<sup>2</sup>). The devices with optimized PBFTAZ:PIID[2F]T blend ratios of 1:1 (wt/wt) were cast from hot chlorobenzene (CB; *ca.* 100 °C). Systematic device fabrication, optimization steps, and statistics are provided in the SI. As shown in Figure 2a and Table 1, optimized all-PSC devices made with the PIID[2F]T analogues appended with various substituents (2BO, 2HD, and 2BO/2HD) and the polymer donor PBFTAZ achieve very distinct performance characteristics. COMMUNICATION

While optimized BHJ devices made with PIID[2F]T(2BO) (limited solubility) reach promising  $J_{SC}$  and fill-factor (FF) values of ca.



**Figure 2.** (a) Characteristic *J*-*V* curves and (b) EQE and IQE spectra of optimized all-PSCs fabricated with the polymer donor PBFTAZ and the PIID[2F]T polymer acceptors (here named 2BO, 2HD, and 2BO/2HD). Integrated EQEs are in agreement (±0.6 mA/cm<sup>2</sup>; ±5%) with the  $J_{SC}$  values reported in Table 1.

Table 1. PV Performance of the PIID[2F]Ts Derivatives in Inverted BHJ Devices with the polymer donor PBFTAZ.  $^{\rm a,b}$ 

				Avg.	Max.
	$J_{ m sc}$	Voc	FF	PCE	PCE
Acceptor	[mA/cm <sup>2</sup> ]	[V]	[%]	[%]	[%]
2BO	9.3	0.99	50	4.4	4.6
2BO/2HD°	13.2	0.97	55	7.1	7.3
2HD	8.2	1.00	42	3.4	3.7
PC <sub>71</sub> BM	11.4	0.70	60	4.5	4.8

[a] Average values across >10 devices. [b] Device statistics in SI, Table S5. [c] Randomly substituted alkyl chains (2BO/2HD, 2:1).

9.3 mA/cm<sup>2</sup> and 50%, respectively, the same figures of merit obtained for devices made with PIID[2F]T(2HD) (the more soluble counterpart) remain relatively modest: ca. 8.2 mA/cm<sup>2</sup> and 42%. Overall, PCEs remain in the 3-5% range, in spite of the high Voc of 1.0 V achieved. Turning to optimized BHJ solar cells made with PIID[2F]T(2BO/2HD) (adequate solubility in CB), Table 1 shows markedly improved figures of merit, with a  $J_{SC}$  as high as 13.2 mA/cm<sup>2</sup>, a FF nearing 55%, and PCEs of up to 7.3% (avg. 7.1%) -representing a stark ca. twofold PCE improvement over devices made with the 2BO and 2HD derivatives. The Voc of 1.0 V - consistent with the reduced electrochemically-inferred EA estimates for PIID[2F]T compared to PC71BM (Table S4) - is 0.3 V greater than that of the control PC71BM-based devices with PBFTAZ (ca. 0.7 V; Table 1).<sup>11</sup> The higher  $J_{SC}$  values for the 2BO/2HD devices (13.2 mA/cm<sup>2</sup>) compared to those of the control PC<sub>71</sub>BM-based devices (11.4 mA/cm<sup>2</sup>) result in part from the more efficient spectral absorption of the all-PSC solar cells (PC71BM's absorption being limited to the short-wavelength region where the photon flux is only modest). Thus, importantly, all-PSCs based on 2BO/2HD achieve PCEs higher by ca. 50% relative to those of the PC71BM-based BHJ solar cells (max. 4.8%)

The external quantum efficiency (EQE) and internal quantum efficiency (IQE) spectra provided in Figure 2b are consistent with the trend in  $J_{SC}$  values described in Table 1. PIID[2F]T-based all-PSCs show prominent spectral contributions from both donor

and acceptor counterparts in the range 350-750 nm, the average IQE of *ca.* 73% (up to 77% at 570 nm) obtained with the



Figure 3. (a-c) Dark field STEM images of the optimized BHJ active layers and (d-f) corresponding EELS maps depicting the phase-separation patterns between donor-rich domains (green; PBFTAZ) and acceptor-rich domains (red; PIID[2F]T). (a,d: 2BO, b,e: 2BO/2HD and c,f: 2HD); see experimental details in SL.



Figure 4. Dark current density-voltage characteristics for (a) hole-only and (b) electron-only diodes made with optimized BHJ active layers composed of PBFTAZ and the PIID[2F]T polymer acceptors (2BO, 2HD, and 2BO/2HD). The experimental data are fitted using the SCLC model (solid lines; cf. details in the SI).

2BO/2HD derivative emphasizes the effectiveness of the photon-to-current conversion process. In comparison, the 2BOand 2HD-based devices averaging 50% IQE across the same wavelength range point to the existence of charge recombination and/or collection losses (analyses beyond the scope of this concise report).

Given the solubility differences observed between the PIID[2F]T analogues (stated in earlier sections), we turned to a systematic analysis of their phase-separation patterns with the polymer donor PBFTAZ across optimized BHJ active layers – using a combination of scanning transmission electron microscopy (STEM) and spatially resolved electron energy-loss spectroscopy (EELS) methods (see experimental details in SI).<sup>13</sup> Figure 3 shows three distinct donor-acceptor segregation patterns, with the most evidently "adequate" corresponding to that of optimized 2BO/2HD-based active layers: smaller domain sizes indicative of a higher degree of donor-acceptor mixing.

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Meanwhile, 2BO-based active layers show the characteristics of larger domains with lengthscales notably greater than expected **Table 2.** Space-Charge-Limited Current (SCLC) Carrier Mobility Estimates for Optimized BHJ Thin Films with PBFTAZ and PIID[2F]Ts.

	$\mu_{h}$	$\mu_{ m e}$	
Acceptor	[cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ]	[cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ]	$\mu_{ m h}/\mu_{ m e}$
2BO	3.9 × 10 <sup>-4</sup>	1.0 × 10 <sup>-5</sup>	39
2BO/2HD <sup>a</sup>	4.1 × 10 <sup>-4</sup>	2.9 × 10 <sup>-5</sup>	14
2HD	$1.3 \times 10^{-4}$	3.8 × 10 <sup>-6</sup>	34

[a] Randomly substituted alkyl chains (2BO/2HD, 2:1).

exciton diffusion limits (5-20 nm);<sup>13</sup> 2HD-based active layers are more finely mixed compared to 2BO/2HD-based films –in agreement with the higher PL quenching efficiency observed for 2HD-based films (see SI, Figure S19). Correlating with the distinct morphology patterns described in Figure 3, Figure 4 and Table 2 provide the hole ( $\mu_n$ ) and electron ( $\mu_e$ ) mobility characteristics and estimates determined by the space-chargelimited current (SCLC) approach (see experimental details in SI). In optimized 2BO/2HD active layers,  $\mu_h$  and  $\mu_e$  reach 4.1×10<sup>-4</sup> cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> and 2.9×10<sup>-5</sup> cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>, respectively.

In summary, we have shown that the nonfullerene PIID[2F]T polymer analogues ( $E_{opt}$ ~1.9 eV) used with the polymer donor PBFTAZ (model system;  $E_{opt}$ ~1.6 eV) can achieve PCEs >7% and some of the highest reported  $J_{SC}$  and  $V_{OC}$  values for all-PSCs (>13 mA/cm<sup>2</sup>, 1.0 V). Given that, to date, most efficient polymer acceptors are based on PDI or NDI motifs, branched alkyl-substituted PIID[2F]T alternatives to PC<sub>61</sub>BM (or its C<sub>71</sub> derivative) expand the class of efficient material systems for further developments of the "all-polymer" BHJ solar cell approach. The examination of other polymer donors will be of importance in future work with the nonfullerene PIID[2F]T polymer analogues.

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Poly(isoindigo–*alt*–3,4-difluorothiophene) (PIID[2F]T) analogues can serve as fullerene alternatives in *"all-polymer"* bulk heterojunction (BHJ) solar cells with efficiencies as high as 7.3%. Employing a wide-bandgap polymer donor (PBFTAZ; commonly used with fullerenes) yields some of the best  $V_{\rm OC}$  figures (*ca.* 1.0 V) reported to date for BHJ solar cells.

S. Liu,<sup>†,&</sup> Y. Firdaus,<sup>†,&</sup> S. Thomas,<sup>‡</sup> Z. Kan,<sup>†</sup> F. Cruciani,<sup>†</sup> S. Lopatin,<sup>§</sup> J.-L. Bredas,<sup>‡</sup> and P. M. Beaujuge<sup>\*,†</sup>

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