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Effect of structure on the solubility and photovoltaic properties of bis-diketopyrrolopyrrole molecules[†]

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Four structurally related molecules consisting of two diketopyrrolopyrrole (DPP) units linked via a terthiophene aromatic π -bridge were synthesized and blended with [70]PCBM in solution-processed small-molecule organic solar cells. The four bis-DPP molecules possess nearly identical optical band gaps and energy levels, but their solubility differs significantly. The processing conditions, such as the solvent, processing additive, and total concentration, have a significant effect on the device performance. The bis-DPP derivative with the lowest solubility gives the highest power conversion efficiency (PCE) of 4.6% when blended with [70]PCBM, compared to 3.6–4.0% for the other three. The results show that subtle changes and tailoring of the molecular structure can strongly affect the solubility and, in turn, the processing conditions leading to the optimized device performance and its ultimate PCE.

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I. Introduction

Bulk heterojunction solar cells comprising blends of lightabsorbing, semiconducting organic donor materials and fullerene acceptors have attracted significant interest in the last decade. Both semiconducting conjugated molecules and polymers are widely explored to enhance the photovoltaic response. Simultaneous optimization of optical band gap (E_g) , charge carrier mobility, crystallinity, and micro-morphology has resulted in power conversion efficiencies (PCEs) of 8-9%¹ for polymers and 6-8%²⁻⁴ for small molecules in solution-processed organic solar cells (OSCs). Small-molecules can be beneficial for OSCs because of the well-defined chemical structures and the more rigorous purification that can be achieved compared to semiconducting polymers.5 However, their relatively short conjugated backbone reduces the tendency to form interpenetrating networks and mixed morphologies when blended with fullerene derivatives.⁶ Furthermore, the limited conjugated length makes that charge transport in these materials is primarily intermolecular and has a negligible intrachain contribution compared to polymers. Overcoming these obstacles is necessary to decrease geminate and non-geminate charge recombination in small molecule OSCs that cause low photocurrent and low fill factors (FF), and to further increase the PCE.⁷

Recently, using small conjugated molecules that incorporate electron donating and electron deficient moieties with overall extended conjugation has shown to be a promising strategy to improve the PCE of OSCs.^{2,3,8} This design motif can be used to lower the optical band gap to absorb near-infrared light, while the long aromatic backbone produces a tendency to crystallize and aggregate, assisting the formation of favorable morphologies for high PCEs.

Conjugated polymers based on diketopyrrolopyrrole (DPP) units have been successfully applied in high mobility field effect transistors (FETs)9-11 and OSCs.12-15 Due to their strong electronwithdrawing ability, the DPP units can afford absorption in the near infrared (NIR) region up to 1000 nm and their polar lactam rings provide a high tendency to form semicrystalline structures. Likewise, linear and star-shaped DPP-based small molecules have been explored for organic solar cells.16-40 Among the large variety of molecules that have been studied, structures that incorporate two DPP units connected via aromatic π -bridges are attracting attention. The bis-DPP design allows for introducing extended planar aromatic π -bridges to provide good charge mobility and to enable manipulation of the energy offset between electron rich and electron deficient groups to control voltage and charge transfer to the fullerene acceptor, respectively. To date bis-DPPs afford PCEs of 4.2%,33 4.4%,35 5.3%,36 and 5.8%,38 which are among the highest for DPP-based small molecule solar cells.

In this paper, we describe the effect of small changes in the chemical structure of bis-DPPs in which the two electron deficient DPP moieties are separated by an aromatic conjugated terthiophene oligomer and end-capped with 2-(thiophen-2-yl)benzo[*b*]thiophene or 2-(thiophen-2-yl)benzofuran (Fig. 1).

The four bis-DPP molecules have very similar optical and electrochemical properties, but the optimized conditions for processing into OSCs are largely different due to a different solubility. We demonstrate that the processing conditions, such as the solvent, processing additive, and concentration, have a large effect on the device performance. BT-TDPP with the lowest

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solubility gives the highest PCE of 4.6% when spin coated from 1,1,2,2-tetrachloroethane (TCE) solution, while the other bis-DPP molecules give lower PCEs of 3.6–4.0%.

II. Results and discussion

Synthesis

The route for the bis-DPP molecules is shown in Scheme 1. The two key precursors, 2 and 3, were synthesized by Suzuki crosscoupling of 3,6-bis(5-bromo-2-thienyl)-2,5-dihydro-2,5-di(2'ethylhexyl)-pyrrolo-[3,4-c]pyrrolo-1,4-dione (1) with benzo[b]thiophene-2 and benzofuran-2 boronic acid pinacol esters, respectively. The relatively low yield in these reactions is due to the formation of bis-substituted products, which are easily removed by column chromatography. The DPP molecules were readily obtained from 2 or 3 by Stille cross-coupling with the appropriate 2,5-bis(trimethylstannyl)thiophene. The four bis-DPP molecules were purified by recrystallization from toluene. BT-TDPP and BF-TDPP with a central thiophene ring are poorly soluble in chloroform at room temperature ($<1 \text{ mg ml}^{-1}$), but can be dissolved (>10 mg ml⁻¹) in 1,1,2,2-tetrachloroethane (TCE) at 90 °C. In contrast, BT-DMTDPP and BF-MDTDPP with a central 3,4-dimethylthiophene ring are easily soluble in chloroform (>10 mg ml⁻¹). The solubility of the four bis-DPP molecules increases as: BT-TDPP < BF-TDPP < BT-DMTDPP < BF-DMTDPP. The increased solubility of the furan containing DPP-molecules as compared to their thiophene analogues is consistent with earlier observations. Higher solubility has been

found for oligofurans compared to oligothiophenes,41,42 and for DPP molecules and polymers that contain furan rings instead of thiophene rings.^{32,43} The influence of the solubility on the performance of the organic solar cells will be addressed in the following sections. The bis-DPP molecules with benzo[b]thiophene units give a higher melting temperature (T_m) and crystallization temperature (T_c) as determined by differential scanning calorimetry (DSC) than the corresponding benzofurans (Table 1 and ESI[†] Fig. S1). This difference matches with previous results on furan vs. thiophene derivatives.^{32,42} The higher solubility and lower melting temperature of the furan derivatives cannot be directly linked to the intermolecular π - π stacking distance, because in crystals of conjugated furan compounds this distance is smaller than that of the corresponding thiophene analogue.^{32,41} Introducing methyl groups on the central thiophene increases $T_{\rm m}$ and $T_{\rm c}$ (Table 1). The heat of crystallization (ΔH_c) calculated from the DSC thermograms (Table 1) is higher for the benzo b thiophenes than for the corresponding benzofurans. The molecules with the central 3,4-dimethylthiophene ring have a higher ΔH_c than those with an unsubstituted central thiophene ring. Hence, ΔH_c and T_c correlate, but there is no simple relationship between ΔH_c or T_c and solubility.

Optical and electrochemical properties

The UV-vis-NIR absorption spectra of the bis-DPP molecules dissolved in chloroform and in thin solid state films are shown in Fig. 2 and the data are summarized in Table 1. The effect of benzo[b]thiophene or benzofuran on the long-wavelength onset of absorption in chloroform is minimal, but the introduction of two methyl groups on the central thiophene ring results in a ~ 20 nm blue shift of the absorption maximum. This can be explained by a small reduction of the conjugation because of a reduced planarity introduced when the centre thiophene ring bears two methyl groups. Compared to the bis-DPPs in solution, their absorption in solid films is red-shifted by 70–100 nm, indicating aggregation. The similar optical absorption spectra of the four bis-DPP molecules give the possibility to determine and compare the effects of other properties than the optical band gap on the photovoltaic performance. Compared to the



Scheme 1 Synthesis of four bis-DPP based molecules. (i) Pd(PPh₃)₄/K₂CO₃ (aq.)/Aliquat 336 in toluene at 115 °C. (ii) Pd(PPh₃)₄ in toluene at 115 °C. (iii) Pd₂(dba)₃/PPh₃ in toluene –DMF (10 : 1, v/v) at 115 °C.

 Table 1
 Optical and thermal properties of the bis-DPP molecules

	CHCl ₃ solution			Film					
Molecule	$\lambda_{\text{peak}} \left(\text{nm} \right)$	$\lambda_{onset} (nm)$	$E_{\rm g}^{ m sol}\left({ m eV} ight)$	$\lambda_{\mathrm{peak}}\left(\mathrm{nm} ight)$	$\lambda_{onset} (nm)$	$E_{\mathrm{g}}^{\mathrm{film}}\left(\mathrm{eV}\right)$	$T_{\rm m}$ (°C) $T_{\rm c}$	$T_{\rm c}$ (°C)	$\Delta H_{\rm c} \left({ m J g}^{-1} ight)$
BT-TDPP	664	745	1.66	691, 753	821	1.51	258	225	38.3
BF-TDPP	664	748	1.66	634, 755	838	1.48	215	171	20.9
BT-DMTDPP	645	736	1.68	697, 761	837	1.48	281	255	42.3
BF-DMTDPP	647	739	1.68	698, 761	838	1.48	251	208	35.1



Fig. 2 UV-vis-NIR absorption spectra of the bis-DPP molecules in $CHCl_3$ solution (solid lines) and in solid state films (dashed lines).



Fig. 3 Cyclic voltammograms of the bis-DPP molecules in *o*-DCB. Potential *vs.* Fc/Fc⁺.

optical band gaps of 1.72 eV and 1.75 eV for the molecules $DPP(T-TB)_2$ and $DPP(T-BFT)_2$ with one DPP unit,³² the bis-DPP molecules BT-TDPP and BF-TDPP have lower energy band gaps of 1.51 eV and 1.48 eV (Table 1).

The HOMO and LUMO energy levels of the bis-DPPs have been assessed using cyclic voltammetry. In an *o*-DCB electrolyte each bis-DPP shows two chemically reversible one-electron oxidation waves of the central terthiophene and two chemically reversible two-electron reduction waves of the two DDPs (Fig. 3). The molecules have very similar first oxidation (+0.15 to +0.18 V) and first reduction (-1.49 to -1.53 V) potentials (Table 2), although the bis-DPPs with the central 3,4-dimethylthiophene have a slightly higher lying LUMO. The electrochemical band gaps in *o*-DCB (1.63 to 1.69 eV, Table 2) are consistent with the optical band gaps in chloroform (1.66 to 1.68 eV, Table 1). The Paper

offset (α) between the LUMO of the bis-DPPs and the LUMO of [70]PCBM varies in the range of 0.41–0.46 eV. Such a difference is generally considered sufficient for photoinduced electron transfer.

Photovoltaic properties

The bis-DPP molecules were blended with [70]PCBM and used as photoactive layers in photovoltaic devices, sandwiched between the transparent ITO/PEDOT:PSS front and the reflecting LiF/Al back electrodes. The photoactive layers comprising the bis-DPPs and [70]PCBM were carefully optimized with respect to the donor/acceptor ratio, processing solvent, use of additive, layer thickness, spin coating speed, and total concentration. A more detailed description on the influence of the various processing conditions on the device performance can be found in the ESI (Tables S1-S4[†]). Generally, the blends based on BT-TDPP or BF-TDPP with [70]PCBM (1:1, w/w) give the best performance when processed from TCE at 90 °C. For these layers the use of the high boiling point processing additive 1,8-diiodooctane (DIO) has a detrimental effect on the device performance (Table 3 for BF-TDPP and ESI† Table S1 for BT-TDPP). Atomic force microscopy (AFM) indicates a higher root mean square (rms) surface roughness (R_{q}) when DIO is used (Fig. 4 and Table 3). The higher surface roughness coincides with a lower short-circuit current density (J_{sc}) and PCE (Table 3). A similar result has also been found for the BT-TDPP:[70]PCBM blend system (ESI[†] Fig. S2 and Table S1). The active layers from BT-DMTDPP and BF-DMTDPP can be processed from chloroform solution at room temperature, and the DIO content has less influence on the device performance (ESI[†] Tables S3 and S4).

The optimized processing conditions and photovoltaic performance for four bis-DPP[70]PCBM blends are summarized in Table 4. The solar cells based on BT-TDPP and BF-TDPP reach PCEs of 4.6% and 4.0%. Both molecules gave

Table 2 Electrochemical properties of the bis-DPP molecules									
Molecule	$E_{\mathrm{red}}^{a}(\mathrm{V})$	$E_{\mathrm{ox}}^{a}(\mathbf{V})$	$E_{\mathrm{g}}^{\mathrm{CV}}\left(\mathrm{eV}\right)$	$\alpha^{b}(\mathbf{V})$					
BT-TDPP	-1.49	0.18	1.67	0.42					
BF-TDPP BT-DMTDPP	$-1.48 \\ -1.51$	0.15 0.17	1.63 1.68	$\begin{array}{c} 0.41 \\ 0.44 \end{array}$					
BF-DMTDPP	-1.53	0.16	1.69	0.46					

^{*a*} Versus Fc/Fc⁺. ^{*b*} $\alpha = E_{red}([70]PCBM) - E_{red}$, with $E_{red}([70]PCBM) = -1.07 \nu s$. Fc/Fc⁺.⁴⁴

Table 3 Effect of DIO on BF-TDPP:[70]PCBM (1 : 1) solar cells

Solvent	$J_{\rm sc}^{\ a}$ (mA cm ⁻²)	$V_{ m oc}\left({ m V} ight)$	FF	PCE^{a} (%)	$R_{\rm q}({\rm nm})$
TCE	10.4	0.67	0.58	4.0	1.11
TCE:DIO 0.2%	6.5	0.58	0.59	2.2	7.38
TCE:DIO 0.5%	8.4	0.61	0.58	2.9	2.69
TCE:DIO 1%	6.8	0.72	0.50	2.5	6.27
TCE:DIO 2.5%	5.6	0.73	0.49	2.0	10.50

 $^aJ_{\rm sc}$ was calculated by integrating the EQE spectrum with the AM1.5G spectrum.



Fig. 4 AFM height images (size 3 μ m × 3 μ m) of blend films of BF-TDPP:[70]-PCBM (1 : 1 w/w) spin coated from TCE at 90 °C with different amounts of DIO added. (a) 0% DIO, (b) 0.2% DIO, (c) 0.5% DIO, (d) 1.0% DIO and (e) 2.5% DIO. Height scales are (a) 20 nm, (b) 50 nm, (c) 30 nm, (d) 50 nm, and (e) 70 nm.

similar $V_{\rm oc}$ and FF, but for BT-TDPP the $J_{\rm sc}$ of 11.9 mA cm⁻² and external quantum efficiency (EQE) of 0.50 are somewhat higher compared to $J_{\rm sc} = 10.4$ mA cm⁻² and EQE = 0.47 for BF-TDPP (Fig. 5b). BT-DMTDPP and BF-DMTDPP, with a central 3,4-dimethylthiophene, are sufficiently soluble to spin coat blends with [70]PCBM from chloroform, resulting in optimized PCEs of 3.5% for BT-DMTDPP and 3.8% for BF-DMTDPP when a small amount of DIO (0.2 vol%) is used. For the optimized cells, $J_{\rm sc}$ and $V_{\rm oc}$ are similar, but BF-DMTDPP provides a slightly higher FF. Compared to the molecules with thiophene as the central unit, molecules with 3,4-dimethylthiophene give higher $V_{\rm oc}$. We note that the photovoltaic devices from 3,4-dimethylthiophene-based molecules with [70]PCBM processed from TCE solution at 90 °C gave a dramatically reduced performance as a result of significant drop in J_{sc} and FF (Table 4, Fig. 5c and d).

Table 4 lists the photon energy loss, defined as $E_{\rm g} - eV_{\rm oc}$, and the EQE for the optimized bis-DPP solar cells. For BT-TDPP:[70]-PCBM with the highest PCE, $E_{\rm g} - eV_{\rm oc} = 0.82$ eV and EQE = 50%. The best bis-DPP based cell reported in the literature to date (PCE = 5.8%) has a similar photon-energy loss (0.81 eV) but a significantly higher EQE = 69%.³⁸ Hence, for the cells listed in Table 4, the EQE and photocurrent are limiting the device performance most.

The different performance of solar cells for the bis-DPP molecules was further analyzed by AFM (Fig. 6). The active layers of BT-TDPP and BF-TDPP with [70]PCBM have a surface roughness of $R_q = 0.94$ nm and $R_q = 1.11$ nm that is higher than $R_{\rm q} = 0.51$ nm and $R_{\rm q} = 0.49$ nm for the BT-DMTDPP and BF-DMTDPP blends with [70]PCBM prepared from chloroform with 0.2% DIO. This indicates increased phase separation. The blends of BT-DMTDPP and BF-DMTDPP with [70]PCBM spin coated from TCE give similarly low surface roughness ($R_{q} =$ 0.41 nm and $R_q = 0.48$ nm). The almost absent surface corrugation in blends of BT-DMTDPP or BF-DMTDPP with [70]PCBM suggests a finer mixing. Finer mixing generally prevents interfacial charge-transfer states that are formed upon photoexcitation to separate into free electrons and holes and enhances the possibility of geminate charge recombination.44 The *I-V* characteristics, shown in Fig. 5c, of the BT-DMTDPP and BF-DMTDPP blends with [70]PCBM spin coated from TCE show that the photocurrent is strongly field-dependent, but that under a negative bias of -1 V, the current densities are very similar to the more efficient devices shown in Fig. 5b. This is consistent with the suggestion that charge-separation from initially formed charge-transfer states is limiting the device performance and causes the low FF. Further investigation of the blend films by transmission electron microscopy (TEM) (ESI⁺, Fig. S3) reveals clear fibrillar structures in the BF-TDPP:[70]-PCBM blends, but provides little contrast for the other blends. The TEM results are consistent with the intimate mixing inferred from AFM, but do not give much more detailed information.

From the results on the four bis-DPP molecules, we conclude that it is important to carefully optimize the solvent composition for structurally similar molecules with different solubilities. Solubility directly influences the phase segregation and the extent of blending in the mixed films and thereby the performance in solar cells.

Table 4 Characteristics of optimized solar cells of bis-DPP molecules with [70]PCBM									
Molecule	Solvent	<i>d</i> (nm)	$J_{\rm sc}^{\ a} ({\rm mA \ cm}^{-2})$	$V_{\rm oc}$ (V)	FF	PCE^{a} (%)	EQE _{max}	$R_{\rm q}$ (nm)	$E_{\rm g}-eV_{ m oc}~({ m eV})$
BT-TDPP	TCE	80	11.9	0.69	0.57	4.6	0.50	0.94	0.82
BF-TDPP	TCE	95	10.4	0.67	0.58	4.0	0.47	1.11	0.81
BT-DMTDPP	TCE	85	7.0	0.79	0.33	1.8	0.29	0.41	0.69
	$CHCl_3:DIO^b$	90	10.6	0.73	0.45	3.5	0.43	0.51	0.75
BF-DMTDPP	TCE	100	7.2	0.78	0.34	1.9	0.29	0.48	0.70
	$CHCl_3:DIO^b$	100	10.3	0.71	0.52	3.8	0.40	0.49	0.77

 $^{a}J_{sc}$ was calculated by integrating the EQE spectrum with the AM1.5G spectrum. b 0.2 vol% DIO.



Fig. 5 (a) *J–V* characteristics in the dark (dashed lines) and under white light illumination (solid lines) of optimized solar cells of the bis-DPP molecules with [70]PCBM. (b) EQE of the optimized devices. (c) *J–V* characteristics in the dark (dashed lines) and under white light illumination (solid lines) of BT-DMTDPP and BF-DMTDPP spin coated from TCE with [70]PCBM. (d) EQE of BT-DMTDPP and BF-DMTDPP spin coated from TCE.



Table 5 Effect of concentration on the solar cell performance of BT-TDPP:[70]-PCBM (1:1)

Concentration ^{a} (mg ml ⁻¹)	$J_{ m sc}^{b}$ (mA cm ⁻²)	$V_{\rm oc}$ (V)	FF	PCE^{b} (%)	$R_{\rm q}~({\rm nm})$
10		0.55			a
12	9.9	0.66	0.52	3.4	3.05
14	10.6	0.68	0.55	4.0	2.16
16	11.9	0.69	0.57	4.6	0.94
18	12.3	0.69	0.53	4.5	1.36
20	12.2	0.70	0.54	4.6	1.11

 a Concentration of BT-TDPP in TCE. $^bJ_{\rm sc}$ was calculated by integrating the EQE spectrum with the AM1.5G spectrum. The thickness for the active layers is $\sim\!90$ nm.

Fig. 6 AFM height images (size 3 μ m × 3 μ m) of the optimized blend films of: (a) BT-TDPP and (b) BF-TDPP with [70]PCBM spin coated from TCE at 90 °C. (c) BT-DMTDPP and (d) BF-DMTDPP with [70]PCBM spin coated from chloroform with 0.2% DIO at room temperature. (e) BT-DMTDPP and (f) BT-DMTDPP with [70]-PCBM spin coated from TCE at 90 °C. The vertical height scale is 20 nm for all images.

Influence of concentration on device performance

In our investigation, we found that the concentration of the BT-TDPP:[70]PCBM solution has a strong influence on the device performance as shown in Table 5. When increasing the concentration of BT-TDPP from 12 to 16 mg ml⁻¹, the PCE

increases from 3.4% to 4.6%. Higher concentrations do not further increase the PCE. AFM reveals that by increasing the concentration of solutions, the surface roughness is reduced (Fig. 7). The possible explanation for this effect of concentration is that high spin rates are needed at higher concentration to obtain the same optimized thickness. Higher spin rates reduce the drying time and reduce the time available for aggregation and crystallization to occur, such that molecules with poor solubility give a better mixed morphology.⁴⁵ For the BF-TDPP:[70]PCBM blend, the concentration dependence is less pronounced (ESI† Table S2).



Fig. 7 AFM height images (size 3 μ m × 3 μ m) of the optimized blend films of BT-TDPP:[70]PCBM (1 : 1 w/w) spin coated from TCE at 90 °C with different concentrations of BT-TDPP, (a) 12 mg ml⁻¹, (b) 14 mg ml⁻¹, (c) 16 mg ml⁻¹, (d) 18 mg ml⁻¹ and (e) 20 mg ml⁻¹. The vertical height scale is 20 nm for all images.

III. Conclusions

Four structurally similar bis-diketopyrrolopyrrole-terthiophene derivatives end-capped with benzo[b]thiophene or benzofuran were synthesized and incorporated into solution processed solar cells with [70]PCBM to give PCE up to 4.6%. The four bis-DPP molecules possess nearly identical low energy optical absorption bands and energy levels, but their solubility is very different. Detailed optimization of the processing conditions of the blend films under various conditions reveals that the photovoltaic performance is strongly dependent on the solvent, temperature, additive, and concentration of solutions used for spin coating. Under carefully adjusted processing conditions, the PCEs obtained for the four bis-DPP derivatives can be optimized to a fairly limited range between 3.6% and 4.6%, but the highest PCE is obtained for the derivative with the lowest solubility. The results show that fairly small structural changes in the molecular structure can strongly affect solubility and that the solubility is an important parameter in making efficient blend layers and improving the photovoltaic performance.

IV. Experimental section

Materials and measurements

All synthetic procedures were performed under an argon atmosphere. Commercial chemicals were used as received. Dry solvents were distilled over 4 Å molecular sieves. [70]PCBM (purity ~95%) were purchased from Solenne BV. 3,6-Bis(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (1)¹⁷ and 2,5-bis(trimethylstannyl)-3,4-dimethylthiophene⁴⁶ were synthesized according to literature procedures.

¹H-NMR and ¹³C-NMR spectra were recorded at 400 MHz and 100 MHz on a VARIAN mercury spectrometer with CDCl₃ as the solvent and tetramethylsilane (TMS) as the internal standard. Electronic spectra were recorded on a Perkin Elmer Lambda 900 UV-vis-NIR spectrophotometer. Differential scanning calorimetry (DSC) was performed on a TA instruments calorimeter at a heating rate of 10 °C min⁻¹. The second heating DSC scans are reported for all DPP-molecules. Cyclic voltammetry was conducted with a scan rate of 0.1 V s⁻¹ under an inert atmosphere with 1 M tetrabutylammonium hexa-fluorophosphate in *o*-DCB as the electrolyte. The working electrode was a platinum disk and the counter electrode was a silver electrode. The concentration of the sample in the electrolyte was approximately 1 mM, based on monomers. Fc/Fc⁺ was used as an internal standard.

Photovoltaic devices were prepared by spin coating poly-(ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Clevios P, VP AI 4083) onto pre-cleaned, patterned indium tin oxide (ITO) substrates (14 Ω per square) (Naranjo Substrates). The photoactive layers were deposited by spin coating a 1,1,2,2tetrachloroethane (TCE) or chloroform solution containing the molecules and [70]PCBM with a 1:1 (w/w) ratio and the appropriate amount of 1,8-diiodooctane (DIO). Solution, substrates, and pipettes were heated to 90 °C for hot spin coating. LiF (1 nm) and Al (100 nm) were deposited by vacuum evaporation at ${\sim}2 \times 10^{-7}$ mbar as the back electrode. The high boiling point solvents (TCE and DIO) can be removed in this high vacuum. The active area of the cells was 0.09 or 0.16 cm² and no size dependence was found between these two dimensions. J–V characteristics were measured under $\sim 100 \text{ mW cm}^{-2}$ white light from a tungsten-halogen lamp filtered by a Schott GG385 UV filter and a Hoya LB 120 daylight filter, using a Keithley 2400 source meter. Short-circuit current densities under AM1.5G conditions were estimated from the spectral response and convolution with the solar spectrum. The spectral response was measured under simulated 1 sun operation conditions using bias light from a 532 nm solid state laser (Edmund Optics). Light from a 50 W tungsten-halogen lamp (Osram64610) was used as probe light and modulated with a mechanical chopper before passing the monochromator (Oriel, Cornerstone 130) to select the wavelength. The response was recorded as the voltage over a 50 resistance, using a lock-in amplifier (Stanford Research Systems SR 830). A calibrated Si cell was used as the reference. The device was kept behind a quartz window in a nitrogen filled container. The thickness of the active layers in the photovoltaic devices was measured on a Veeco Dektak 150 profilometer.

3-(5-(Benzo[*b*]thiophen-2-yl)thiophen-2-yl)-6-(5bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (2)

To a solution of 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-ethyl-hexyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (1) (1.62 g, 2.37 mmol) and 2-(benzo[*b*]thiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.62 g, 2.37 mmol) in toluene (25 ml) was added 2 M K₂CO₃ solution in H₂O (5 ml) and 1 drop of Aliquat 336. Ar₂ was bubbled through the solution for 15 minutes. Pd(PPh₃)₄ (0.11 g, 0.095 mmol) was added and the reaction solution was heated to 115 °C for 18 hours. After completion CHCl₃ was added and the solution was removed *in vacuo*. The residue was chromatographed on a SiO₂ plug using

heptane–CH₂Cl₂ (1 : 1, v/v) as the eluent. After recrystallization from ethanol, product 2 was obtained as a dark solid (0.62 g, 35%). ¹H NMR δ (ppm): 8.95 (d, 1H), 8.65 (d, 1H), 7.79 (m, 2H), 7.56 (s, 1H), 7.44 (d, 1H), 7.37 (m, 2H), 7.23 (d, 1H), 4.05 (d, 2H), 3.96 (d, 2H), 1.92 (b, 1H), 1.85 (b, 1H), 1.33 (m, 16H), 0.90 (m, 12H). ¹³C NMR δ (ppm): 161.57, 161.32, 142.79, 140.09, 140.04, 139.63, 138.73, 136.76, 135.74, 135.17, 131.39, 131.25, 129.01, 126.00, 125.30, 125.02, 123.86, 122.21, 121.21, 118.70, 108.30, 108.25, 45.99, 39.26, 39.11, 30.17, 28.53, 28.32, 23.68, 23.57, 23.11, 23.03, 14.08, 14.02, 10.55, 10.48. MS (MALDI): calculated: 735.86, found: 736.18 (M⁺).

3-(5-(Benzofuran-2-yl)thiophen-2-yl)-6-(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (3)

To a solution of 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (1) (0.75 g, 1.099 mmol) and 2-(benzofuran-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.27 g, 1.099 mmol) in toluene (25 ml) was added 2 M K₂CO₃ solution in H₂O (3 ml) and 1 drop of Aliquat 336. Ar₂ was bubbled through the solution for 15 minutes. Then $Pd(PPh_3)_4$ (50 mg, 0.044 mmol) was added and the reaction solution was heated to 115 °C for 18 hours. After completion CHCl₃ was added and the solution was washed with H2O, dried over MgSO₄, and filtered and the solvent was removed *in vacuo*. The residue was chromatographed on a SiO₂ plug using heptane : CH_2Cl_2 (1 : 1, v/v) as the eluent. After precipitation from MeOH, product 3 was obtained as a black solid (185 mg, 23%). ¹H NMR δ (ppm): 8.99 (d, 1H), 8.66 (d, 1H), 7.60 (d, 1H), 7.56 (m, 2H), 7.33 (m, 2H), 7.23 (d, 1H), 7.07 (s, 1H), 4.07 (d, 2H), 3.97 (d, 2H), 1.89 (b, 2H), 1.32 (m, 16H), 0.90 (m, 12H). 13 C NMR δ (ppm): 161.58, 161.35, 154.95, 140.15, 138.76, 138.14, 136.67, 135.19, 131.44, 131.25, 129.36, 128.83, 125.42, 123.53, 121.19, 118.83, 111.26, 108.33, 103.73, 46.02, 39.22, 39.11, 30.30, 30.17, 28.49, 28.32, 23.63, 23.57, 23.08, 23.04, 14.06, 14.02, 10.51, 10.48. MS (MALDI): calculated: 719.79, found: 720.20 (M⁺).

BT-TDPP

A solution of 2 (70 mg, 0.095 mmol) and 2,5-bis(trimethylstannyl)thiophene (19.1 mg, 0.047 mmol) in toluene (3 ml) was bubbled with Ar₂ for 30 minutes. Then Pd(PPh₃)₄ (4.4 mg, 0.0038 mmol) was added and the reaction solution was heated to 115 °C for 18 hours. After completion CHCl₃ was added and the solution was precipitated in acetone. Several recrystallizations from toluene were performed to obtain the pure product BT-TDPP as a purple solid (50 mg, 77%). ¹H NMR δ (ppm): 8.96 (d, 2H), 8.93 (d, 2H), 7.72 (m, 4H), 7.42 (s, 2H), 7.31 (d, 2H), 7.30 (m, 4H), 7.20 (d, 2H), 7.18 (s, 2H), 4.01 (m, 8H), 1.91 (b, 4H), 1.31 (m, 32H), 0.94 (m, 24H). MS (MALDI): calculated: 1394.03, found: 1392.49 (M⁺).

BF-TDPP

A solution of 3 (65.7 mg, 0.091 mmol) and 2,5-bis(trimethylstannyl)thiophene (18.5 mg, 0.0452 mmol) in toluene (4 ml) was bubbled with Ar for 30 minutes. Then $Pd(PPh_3)_4$ (4.2 mg, 0.00365 mmol) was added and the reaction solution was heated to 115 °C for 18 hours. After completion CHCl₃ was added and the solution was precipitated in acetone. Several recrystallizations from toluene were performed to obtain the pure product BF-TDPP as a dark purple solid (30 mg, 49%). ¹H NMR δ (ppm): 8.97 (d, 2H), 8.95 (d, 2H), 7.46 (m, 4H), 7.42 (s, 2H), 7.28 (d, 2H), 7.17 (m, 4H), 7.17 (d, 2H), 6.90 (s, 2H), 4.02 (m, 8H), 1.92 (b, 4H), 1.31 (m, 32H), 0.93 (m, 24H). MS (MALDI): calculated: 1361.90, found: 1360.55 (M⁺).

BT-DMTDPP

A solution of 2 (60 mg, 0.082 mmol), 2,5-bis(trimethylstannyl)-3,4-dimethylthiophene (17.5 mg, 0.04 mmol) and PPh₃ (2.57 mg, 0.0098 mmol) in toluene (3 ml) and DMF (0.3 ml) was bubbled with Ar for 15 minutes. Then Pd₂(dba)₃ (2.24 mg, 0.0024 mmol) was added and the reaction solution was heated to 115 °C for 18 hours. After completion CHCl₃ was added and the solution was precipitated in acetone. Several recrystallizations from toluene were performed to obtain the pure product BT-DMTDPP as a purple solid (31 mg, 55%). ¹H NMR δ (ppm): 9.07 (d, 2H), 8.94 (d, 2H), 7.75 (m, 4H), 7.51 (s, 2H), 7.39 (d, 2H), 7.35 (m, 4H), 7.32 (d, 2H), 4.06 (m, 8H), 2.42 (s, 6H), 1.94 (b, 4H), 1.37 (m, 32H), 0.91 (m, 24H). MS (MALDI): calculated: 1422.09, found: 1420.53 (M⁺).

BF-DMTDPP

A solution of 3 (60 mg, 0.083 mmol), 2,5-bis(trimethylstannyl)-3,4-dimethylthiophene (17.9 mg, 0.041 mmol) and PPh₃ (2.62 mg, 0.01 mmol) in toluene (3 ml) and DMF (0.3 ml) was bubbled with Ar₂ for 15 minutes. Then Pd₂(dba)₃ (2.3 mg, 0.0025 mmol) was added and the reaction solution was heated to 115 °C for 18 hours. After completion CHCl₃ was added and the solution was precipitated into acetone. Several recrystallizations from toluene were performed to obtain the pure product BF-DMTDPP as a purple solid (31 mg, 55%). ¹H NMR δ (ppm): 9.07 (d, 2H), 8.99 (d, 2H), 7.58 (d, 2H), 7.52 (m, 4H), 7.34 (d, 2H), 7.25 (m, 4H), 7.04 (s, 2H), 4.08 (m, 8H), 2.43 (s, 6H), 1.95 (b, 4H), 1.39 (m, 32H), 0.91 (m, 24H). MS (MALDI): calculated: 1389.96, found: 1388.57 (M⁺).

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Notes and references

- 1 Z. He, C. Zhong, S. Su, M. Xu, H. Wu and Y. Cao, *Nat. Photonics*, 2012, **6**, 591–595.
- 2 Y. M. Sun, G. C. Welch, W. L. Leong, C. J. Takacs, G. C. Bazan and A. J. Heeger, *Nat. Mater.*, 2011, **11**, 44–48.

- 3 J. Y. Zhou, X. J. Wan, Y. S. Liu, Y. Zuo, Z. Li, G. R. He, G. K. Long, W. Ni, C. X. Li, X. C. Su and Y. S. Chen, *J. Am. Chem. Soc.*, 2012, **134**, 16345–16351.
- 4 A. K. K. Kyaw, D. H. Wang, V. Gupta, J. Zhang, S. Chand, G. C. Bazan and A. J. Heeger, *Adv. Mater.*, 2013, 25, 2397–2402.
- 5 A. Mishra and P. Bäuerle, Angew. Chem., Int. Ed., 2012, 51, 2020–2067.
- 6 X. Yang, S. C. Veenstra, W. J. H. Verhees, M. M. Wienk, R. A. J. Janssen, J. M. Kroon, M. A. J. Michels and J. Loos, *Nano Lett.*, 2005, 5, 579–583.
- 7 D. Credgington, F. C. Jamieson, B. Walker, T. Q. Nguyen and J. R. Durrant, *Adv. Mater.*, 2012, **24**, 2135–2141.
- 8 X. F. Liu, Y. M. Su, L. A. Perez, W. Wen, M. F. Toney,
 A. J. Heeger and G. C. Bazan, *J. Am. Chem. Soc.*, 2012, 134, 20609–20612.
- 9 C. B. Nielsen, M. Turbiez and I. McCulloch, *Adv. Mater.*, 2013, 25, 1859–1880.
- 10 J. Lee, A. R. Han, J. Kim, Y. Kim, J. H. Oh and C. Yang, *J. Am. Chem. Soc.*, 2012, **134**, 20713–20721.
- 11 H. Chen, Y. Guo, G. Yu, Y. Zhao, J. Zhang, D. Gao, H. Liu and Y. Liu, *Adv. Mater.*, 2012, **24**, 4589.
- 12 L. T. Dou, J. B. You, J. Yang, C. C. Chen, Y. J. He, S. Murase, T. Moriarty, K. Emery, G. Li and Y. Yang, *Nat. Photonics*, 2012, **6**, 180–185.
- 13 L. Dou, W.-H. Chang, J. Gao, C.-C. Chen, J. You and Y. Yang, *Adv. Mater.*, 2013, **25**, 825–831.
- 14 W. W. Li, K. H. Hendriks, W. S. C. Roelofs, Y. Kim, M. M. Wienk and R. A. J. Janssen, *Adv. Mater.*, 2013, 25, 3182–3186.
- 15 W. W. Li, A. Furlan, K. H. Hendriks, M. M. Wienk and R. A. J. Janssen, *J. Am. Chem. Soc.*, 2013, **135**, 5529–5532.
- 16 B. Tamayo, B. Walker and T.-Q. Nguyen, *J. Phys. Chem. C*, 2008, **112**, 11545–11551.
- 17 B. Walker, A. B. Tamayo, X.-D. Dang, P. Zalar, J. H. Seo, A. Garcia, M. Tantiwiwat and T.-Q. Nguyen, Adv. Funct. Mater., 2009, 19, 3063–3069.
- 18 A. B. Tamayo, X.-D. Dang, B. Walker, J. Seo, T. Kent and T.-Q. Nguyen, *Appl. Phys. Lett.*, 2009, 94, 103301.
- 19 P. Sonar, G.-M. Ng, T. T. Lin, A. Dodabalapur and Z.-K. Chen, J. Mater. Chem., 2010, 20, 3626–3636.
- 20 S. Loser, C. J. Bruns, H. Miyauchi, R. C. Ortiz, A. Facchetti,
 S. I. Stupp and T. J. Marks, *J. Am. Chem. Soc.*, 2011, 133(21), 8142–8145.
- 21 O. P. Lee, A. T. Yiu, P. M. Beaujuge, C. H. Woo, T. W. Holcombe, J. E. Millstone, J. D. Douglas, M. S. Chen and J. M. J. Fréchet, *Adv. Mater.*, 2011, 23, 5359–5363.
- 22 S. Loser, H. Miyauchi, J. W. Hennek, J. Smith, C. Huang, A. Facchetti and T. J. Marks, *Chem. Commun.*, 2012, **48**, 8511–8513.
- 23 P.-L. T. Boudreault, J. W. Hennek, S. Loser, R. P. Ortiz,
 B. J. Eckstein, A. Facchetti and T. J. Marks, *Chem. Mater.*,
 2012, 24, 2929–2942.
- 24 B.-S. Jeong, H. Choi, N. Cho, H. M. Ko, W. Lim, K. Song, J. K. Lee and J. Ko, *Sol. Energy Mater. Sol. Cells*, 2011, 95, 1731–1740.

- 25 Y. Zhang, X.-D. Dang, C. Kim and T.-Q. Nguyen, *Adv. Energy Mater.*, 2011, 1, 610–617.
- 26 J. Mei, K. R. Graham, R. Stadler, S. P. Tiwari, H. Cheun, J. Shim, M. Yoshi, C. Nuckolls, B. Kippelen, R. K. Castellano and J. R. Reynolds, *Chem. Mater.*, 2011, 23, 2285–2288.
- 27 W. Kylberg, P. Sonar, J. Heier, J.-N. Tisserant, C. Müller,
 F. Nüesch, Z.-L. Chen, A. Dodabalapur, S. Yoon and
 R. Hany, *Energy Environ. Sci.*, 2011, 4, 3617–3624.
- 28 D. Sahu, C.-H. Tsai, H.-Y. Wei, K.-C. Ho, F.-C. Chang and C.-W. Chu, *J. Mater. Chem.*, 2012, 22, 7945–7953.
- 29 E. Ripaud, D. Demeter, T. Rousseau, E. Boucard-Cétol, M. Allain, R. Po, P. Leriche and J. Roncali, *Dyes Pigm.*, 2012, 95, 126–133.
- 30 J. W. Lee, Y. S. Choi and W. H. Jo, *Org. Electron.*, 2012, **13**, 3060–3066.
- 31 Y. Liu, X. Du, Z. Xiao, J. Cao, S. Tan, Q. Zuo and L. Ding, *Synth. Met.*, 2012, **162**, 1665–1671.
- 32 J. H. Liu, B. Walker, A. Tamayo, Y. Zhang and T. Q. Nguyen, *Adv. Funct. Mater.*, 2013, 23, 47–56.
- 33 B. Walker, J. Liu, C. Kim, G. C. Welch, J. K. Park, J. Lin, P. Zalar, C. M. Proctor, J. H. Seo, G. C. Bazan and T.-Q. Nguyen, *Energy Environ. Sci.*, 2013, 6, 952–962.
- 34 C. M. Proctor, C. Kim, D. Neher and T.-Q. Nguyen, *Adv. Funct. Mater.*, 2013, **23**, 3584–3594.
- 35 Y. S. Choi and W. H. Jo, *Org. Electron.*, 2013, **14**, 1621–1628.
- 36 J. Huang, C. Zhan, X. Zhang, Y. Zhao, Z. Lu, H. Jia, B. Jiang, J. Ye, S. Zhang, A. Tang, Y. Liu, Q. Pei and J. Yao, ACS Appl. Mater. Interfaces, 2013, 5, 2033–2039.
- 37 A. Tang, L. Li, Z. Lu, J. Huang, H. Jia, C. Zhan, Z. Tan, Y. Li and J. Yao, *J. Mater. Chem. A*, 2013, 1, 5747–5757.
- 38 Y. Lin, L. Ma, Y. Li, Y. Liu, D. Zhu and X. Zhan, *Adv. Energy Mater.*, 2013, 3, 1166–1170.
- 39 J.-Y. Pan, L.-J. Zuo, X.-L. Hu, W.-F. Fu, M.-R. Chen, L. Fu, X. Gu, H.-Q. Shi, M.-M. Shi, H.-Y. Li and H.-Z. Chen, ACS Appl. Mater. Interfaces, 2013, 5, 972–980.
- 40 H. Wang, F. Liu, L. Bu, J. Gao, C. Wang, W. Wei and T. P. Russell, *Adv. Mater.*, 2013, DOI: 10.1002/ adma.201302848.
- 41 O. Gidron, Y. Diskin-Posner and M. Bendikov, *J. Am. Chem. Soc.*, 2010, **132**, 2148–2149.
- 42 Y. Miyata, T. Nishinaga and K. Komatsu, *J. Org. Chem.*, 2005, **70**, 1147–1153.
- 43 A. T. Yiu, P. M. Beaujuge, O. P. Lee, C. H. Woo, M. F. Toney and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 2012, **134**, 2180–2185.
- 44 D. Veldman, Ö. İpek, S. C. J. Meskers, J. Sweelssen, M. M. Koetse, S. C. Veenstra, J. M. Kroon, S. S. van Bavel, J. Loos and R. A. J. Janssen, *J. Am. Chem. Soc.*, 2008, 130, 7721–7735.
- 45 L. J. Lindgren, F. L. Zhang, M. Andersson, S. Barrau, S. Hellström, W. Mammo, E. Perzon, O. Inganäs and M. R. Andersson, *Chem. Mater.*, 2009, **21**, 3491–3502.
- 46 H. Ziehlke, R. Fitzner, C. Koerner, R. Gresser, E. Reinold,
 P. Bäuerle, K. Leo and M. K. Riede, *J. Phys. Chem. A*, 2011, 115, 8437–8446.