FULL PAPER

Thieno[3,4-c]pyrrole-4,6-dione-Based Small Molecules for Highly Efficient Solution-Processed Organic Solar Cells

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Abstract: Two small molecules named BT-TPD and TBDT-TTPD with a thieno[3,4-c]pyrrole-4,6-dione (TPD) unit were designed and synthesized for solution-processed bulk-heterojunction solar cells. Their thermal, electrochemical, optical, charge-transport, and photovoltaic characteristics were investigated. These compounds exhibit strong absorption at 460–560 nm and low highest occupied molecular orbital

Keywords: bulk heterojunction • charge transfer • energy conversion • solar cells • small molecules

Introduction

Organic solar cells (OSCs) with bulk heterojunction (BHJ) architectures have attracted significant interest as sources of renewable energy, largely as a result of their advantages, which include low cost, low weight, and high mechanical flexibility.^[1-4] Until recently, 8–9% power conversion efficiencies (PCEs) for polymer-based solar cells have been achieved by enormous efforts in active layer, device structure, and fabricating techniques.^[5-7] Small-molecule organic solar cells (SMOSCs) are emerging because of their easier synthesis, less batch-to-batch variation, and more reproducible solar cell performances.^[8-10] Consequently, peak photovoltaic efficiencies above 8% have been obtained by using solution-processed small molecules.^[11] However, their overall efficiency is low relative to that of their polymer counter-

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levels (-5.36 eV). Field-effect hole mobilities of these compounds are 1.7- $7.7 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. Small-molecule organic solar cells based on blends of these donor molecules and a acceptor display power conversion efficiencies as high as 4.62 % under the illumination of AM 1.5G, 100 mW cm⁻².

parts. As such, the investigation into the design and development of SMOSCs has not received as much interest as the investigation into polymer solar cells. Therefore, various techniques for polymer-based solar cells can be applied to SMOSCs to increase their efficiency. Furthermore, research on active-layer materials, especially donor materials, is essential because these are a key factor for high PCEs of small-molecule photovoltaic devices. To address this issue, we designed new small molecules with simple and symmetric D-A alternating structures (D=donor, A=acceptor) based on thieno [3,4-c] pyrrole-4,6-dione (TPD). We postulated that the planar character of TPD would be beneficial for π -electron delocalization once incorporated into various conjugated molecule units.^[12,13] Its relatively strong electronwithdrawing nature facilitates low-lying highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels, which are desired to increase the open circuit voltage (V_{oc}) in OSCs.^[14] Finally, alkyl side chains were introduced on the pyrrole ring to improve the solubility and processability of the molecules.^[15] Ma et al. reported a PCE of 6.1% from an alternating TPD copolymer by using benzodithiophene as the donor and thienopyrrole-4,6-dione as the acceptor.^[16] Tao and co-workers achieved a PCE of 7.3% from an alternating copolymer by using 4,4-bis(2-ethylhexyl)-dithieno[3,2-b:2',3'-d]silole and N-octylthieno[3,4-c]pyrrole-4,6-dione (PDTSTPD) composed of dithienosilole and thienopyrrole-4,6-dione.^[17] Despite their remarkable performances in polymeric solar cells, TPD-containing small molecules are rarely employed for applications in organic photovoltaic devices. Herein, we report the syntheses and BHJ solar-cell performances of TPD-containing solution-processed small molecules. We designed two compounds with distinct molecular structures. The first was the (1,3-bis(5'-hexyl-2,2'-bithiophen-5-yl)-5-octyl-4H-thieno-[3,4-c]pyrrole-4,6(5H)-dione (BT-TPD) small molecule containing a D-A-D structural motif with a thiophene-capped

TPD as the core acceptor unit. The other was a 4-[5-(2ethyl-hexyl)-thiophen-2-yl]-8-[5-(2-ethyl-hexyl)-thiophen-2yl]-2,6-bis-11-[5-octyl-1,3-di-thiophen-2-yl-thieno[3,4-c]pyrrole-4,6-dionyl]-1,5-dithia-s-indacene (TBDT-TTPD) small molecule bearing an A-D-A architecture, and it was composed of a benzodithiophene (BDT) core donor unit and thiophene-bridged TPD acceptor arm units. We hypothesized that incorporation of the BDT donor unit as the core in TBDT-TTPD would result in enhanced π conjugation, increased absorption, and improved charge-transfer ability of the small molecules as a consequence of its rigid character.^[18] These small molecule donors exhibited thermal stability, excellent solubility in organic solvents, and strong optical absorption properties in the near-infrared region.

BT-TPD 100 TBDT-TTPD 80 Weight (%) 60 40 20 0 800 100 200 300 400 500 600 700 Temperature (°C)

Figure 1. TGA thermograms of BT-TPD and TBDT-TTPD.



Results and Discussion

The general synthetic routes to the monomers and small molecules are outlined in Scheme 1. BT-TPD and TBDT-TTPD were obtained as red and dark red solids, respective-



Scheme 1. Synthesis route to BT-TPD and TBDT-TTPD.

ly, by Stille coupling of 1,3-dibromo-5-octyl-4*H*-thieno[3,4*c*]pyrrole-4,6-(5*H*)-dione with 5-trimethylstannyl-5'-hexyl-2,2'-bithiophene and of 2,6-bis(trimethyltin)-4,8-bis[5-(2-ethylhexyl)thiophene-2-yl]benzo[1,2-*b*:4,5]dithiophene with 1-(5-bromothiophen-2-yl)-5-octyl-3-(thiophen-2-yl)-4*H*-thieno-[3,4*c*]pyrrole-4,6-(5*H*)-dione, respectively. The structures and purities of BT-TPD and TBDT-TTPD were confirmed by ¹H NMR spectroscopy and mass spectrometry. The small molecules show good solubility at room temperature in organic solvents such as *o*-dichlorobenzene, chloroform, chlorobenzene, and THF. The thermal properties of BT-TPD and TBDT-TTPD were investigated by thermogravimetric analysis (TGA) (Figure 1). TGA revealed onset decomposition temperatures (T_d) of BT-TPD and TBDT-TTPD with 5% weight loss of 442 and 457°C, respectively. This result con-

chlorobenzene solution with a concentration of $1 \times 10^{-4}\,\text{m}$ and b) as spin-coated films.

firmed that both compounds are highly stable and suitable for OSC fabrication and evaluation.

The optical properties of the chlorobenzene solutions and thin films of small molecules were investigated by UV/Vis absorption spectroscopy, as shown in Figure 2 and summarized in Table 1. In chlorobenzene $(1 \times 10^{-4} \text{ M}, \text{ Figure 2 a})$, the BT-TPD solution showed a main absorption band at 463 nm, whereas the main absorption band for TBDT-TTPD was redshifted to 488 nm and contained a shoulder at 517 nm as a result of the higher degree of intramolecular charge-transfer transitions (ICTs) resulting from the core BDT units.^[19] Moreover, the molar extinction coefficient (ε_{max}) of TBDT-TTPD (24120 LM⁻¹ cm⁻¹) appears to be larger than that of BT-TPD (15780 LM⁻¹ cm⁻¹), which indi-

Table 1. Photophysical properties of small-molecule compounds.

Small molecule	T_{d} [°C] ^[a]	$\varepsilon_{\rm max}/10^3 \ [{ m M}^{-1}{ m cm}^{-1}]^{[{ m b}]}$	λ _{max} [nm] solution	λ _{max} [nm] film	E_{g}^{opt} [eV] ^[c]	HOMO [eV]	LUMO[eV]
BT-TPD	442	15.780	463	448	2.19	-5.36	-3.17
TBDT-TTPD	457	24.120	488	524, 570	1.97	-5.36	-3.39

cates that TBDT-TTPD can absorb more photons.^[20] In comparison to their absorption spectra in dilute solution, the high-energy band (λ_{max} =448 nm) observed for BT-TPD in a thin solid film is slightly blueshifted and broadened to 566 nm. This is likely the result of various aggregation patterns of the BT-TPD molecules by combination of H- and Jtypes.^[21,22] The absorption spectrum of TBDT-TTPD as a thin film is bathochromically shifted and exhibits absorption bands at 524 and 570 nm, which thus indicates effective π - π stacking between the backbones of the molecules.^[23] The optical band gaps of BT-TPD and TBDT-TTPD were estimated from the onsets to be 2.19 and 1.97 eV, respectively. This indicates that TBDT-TTPD with long push-pull interaction has a stronger ICT effect than BT-TPD, and this leads to a smaller band gap, which is useful for increasing the short circuit current in SMOSCs. Cyclic voltammetry (CV) was employed to investigate the oxidation behaviors of BT-TPD and TBDT-TTPD by using a platinum counter electrode in an acetonitrile solution containing $0.1 \text{ mol } \text{L}^{-1}$ Bu_4NPF_6 with a scan rate of 50 mV s⁻¹ (Figure 3a). The onset oxidation potential for both small molecules was 0.96 V versus Ag/Ag⁺. The corresponding HOMO energy



Figure 3. a) Cyclic voltammograms of BT-TPD and TBDT-TTPD as thin films and b) the HOMO and LUMO energy levels of the small molecules and PCBMs.

level for both BT-TPD and TBDT-TTPD was estimated to be -5.36 eV (Table 1) by using the ferrocene reference value of -4.4 eV below the vacuum level.^[24] The LUMO levels were determined to be -3.17

and -3.39 eV, respectively, by using the calculated HOMO value and the optical band gaps. All synthesized small molecules not only have suitable HOMO energy levels to ensure a high value of $V_{\rm oc}$ (>0.8 V) in small-molecule solar cell applications, but their LUMO energies are approximately 0.9 eV above the energy levels of the LUMOs (-4.3 eV) of [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) n-type acceptors, which generates a driving force for energetically favorable electron transfer (see Figure 3b).^[25,26]

High hole mobility (μ_h) is a basic requirement for effective photovoltaic active donors to ensure effective chargecarrier transport to the electrodes and to reduce photocurrent loss in OSCs. To measure the hole mobility of the small molecules, organic field effect transistor (OFET) devices with a top-contact configuration were fabricated onto octyltrichlorosilane (OTS-8)-modified Si/SiO₂ substrates. As shown in Figure 4 and Table 2, OFET devices composed of BT-TPD and TBDT-TTPD exhibited p-channel transfer characteristics.



Figure 4. Typical transfer curves for BT-TPD and TBDT-TTPD devices.

Table 2. Device performance of solution-processed OFETs on BT-TPD and TBDT-TTPD.

Material	Mobility $[cm^2V^{-1}s^{-1}]$	$I_{\rm on}/I_{\rm off}$	$V_{ m th}$ [V]	SS [V decade ⁻¹]
BT-TPD	$\begin{array}{c} 1.72 \times 10^{-3} \\ 7.71 \times 10^{-3} \end{array}$	3.08×10^{5}	-12.7	0.558
TBDT-TTPD		2.11×10^{7}	-5.28	0.536

The field-effect hole mobility of BT-TPD was measured to be $1.72 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, and a slightly higher hole mobility of $7.71 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ was observed in the TBDT-TTPD-based device. This is a considerably high hole mobility for solution-processed small-molecule donors.^[27,28] The higher hole mobility of TBDT-TTPD-based devices relative to that of BT-TPD-based devices may be due to the shorter

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 π - π stacking distances and the better quality of the films on OTS-treated Si/SiO₂ substrates (see Figure S11, Supporting Information), which leads to enhanced charge-transporting properties.^[29] To demonstrate the reliability of those values, we also tested the hole mobility of the small molecule in blended films by using the space charge limited current (SCLC)(model (see the Supporting Information). The hole mobility trends were similarly shown for field-effect hole mobility and hole mobility in blended films. The hole mobility (μ_h) of BT-TPD was measured to be 9.28× $10^{-9} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for blends of BT-TPD/PC₇₁BM (PC₇₁BM= [6,6]-phenyl-C₇₁-butyric acid methyl ester)(, and a higher hole mobility of $8.87 \times 10^{-8} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ was exhibited in the TBDT-TTPD/PC $_{61}$ BM film. The difference in the hole mobility values is one order of magnitude, which also indicates that the hole-transporting abilities of TBDT-TTPD enable high hole mobility in blended films.^[30] The photovoltaic characteristics of small molecules were investigated by using the conventional structure of ITO/PEDOT/PSS/BT-TPD and TBDT-TTPD/PCBM/LiF/Al. To optimize the photovoltaic conditions, devices with different small molecule/acceptor weight ratios, fullerene derivative (PC61BM and PC71BM), solvent, and thermal annealing (from 100 to 160°C) were examined (detailed photovoltaic data are presented in the Supporting Information). First, the blend ratio was an important factor that influenced the device performance; therefore, we carefully tuned the blend ratio from 1:0.4 to 1:2 (w/w), A weight ratio of 1:2 for the active layers displayed the best performance for BT-TPD/PC₆₁BM, whereas the device having a weight ratio of 1:1 TBDT-TTPD/PC₆₁BM displayed optimal performance properties. Devices using a different solvent (i.e., chloroform) and fullerene (i.e., PC71BM) were also fabricated and compared at the optimized blend weight ratios of BT-TPD/PC61BM and TBDT-TTPD/PC₆₁BM. The results demonstrated that the best processing conditions involved the use of chlorobenzene as the solvent for both BT-TPD- and TBDT-TTPDbased devices. However, after changing the electron acceptor from PC₆₁BM to PC₇₁BM, a higher PCE was obtained for BT-TPD, whereas a lower PCE was obtained for TBDT-TTPD. Finally, post-treatment with thermal annealing was investigated to further enhance device performance. Thermal annealing has been proven to be an efficient and easy treatment to improve the morphology of active films. Herein, we introduced an optimal annealing temperature, and enhanced device performance was observed. Figure 5a shows the key photocurrent density voltage curves under illumination of AM 1.5G at 100 mW cm⁻², and the corresponding performance parameters are summarized in Table 3.

All devices achieved relatively high values of V_{oc} above 0.8 V, which is consistent with a low HOMO energy level (-5.36 eV).^[31] The BT-TPD and TBDT-TTPD small molecules cast from chlorobenzene without thermal annealing treatment showed a PCE of 1.16 and 3.90%, respectively. However, device performance dramatically changed after post-thermal annealing. We obtained a PCE of 1.43 and



Figure 5. a) Current–voltage characteristics of BHJ devices based on BT-TPD/PC₇₁BM (1:2 w/w) (—) and TBDT-TTPD /PC₆₁BM (1:1 w/w) (—) under illumination of AM 1.5 G, 100 mW cm⁻². b) EQE spectra of the corresponding devices.

Table 3. Device performance parameters for BHJ solar cells based on BT-TPD and TBDT-TTPD.

Small molecule / PCBM (w/ w)	Conditions	$V_{\rm oc}$ [V]	$J_{\rm sc}$ [mA cm ⁻²]	FF [%]	PCE [%]
BT-TPD/PC71BM (1:2)	as-cast	0.94	5.3	23.1	1.16
BT-TPD/PC ₇₁ BM (1:2)	annealed 160	0.84	6.2	27.5	1.43
TBDT-TTPD/PC ₆₁ BM $(1:1)$	as-cast	0.87	7.9	56.6	3.90
TBDT-TTPD/PC ₆₁ BM (1:1)	annealed 120	0.97	9.1	52.0	4.62

4.62% for BT-TPD and TBDT-TTPD at 160 and 120°C, respectively. The change in the PCE was mainly due to the improved short circuit current density (J_{sc}) (from 5.3 to 6.2 mW cm⁻² for BT-TPD and from 7.9 to 9.1 mW cm⁻² for TBDT-TTPD) and change properties such as film morphology and nanostructure order, which will be discussed below. Relative to that observed in the TBDT-TTPD-based devices, the smaller value of J_{sc} resulting from the slightly larger band gap, smaller hole mobility, and smaller fill factor (FF) translated into a lower PCE in the BT-TPD-based solar cell devices. The external quantum efficiency (EQE) spectra of these devices are shown in Figure 5b. The shapes of the EQE curves for the devices based on small-molecule/PCBM are similar to those of their absorption spectra, and this indicates that most of the absorbed photons of the small mole-

cules contribute to the generation of the photocurrent. The higher and broader coverage of the EQE for both the annealed BT-TPD/PC₇₁BM (1:2 w/w) and TBDT-TTPD/PC₆₁BM (1:1 w/w) devices led to considerable increases in the $J_{\rm sc}$ values.^[32] The BT-TPD/PC₇₁BM device exhibited a maximum EQE of approximately 40% at 413 nm, whereas the maximum EQE for the TBDT-TTPD/PC₆₁BM-based device was approximately 50% at 430 nm. These results support that the photocurrent in the TBDT-TTPD/PC₇₁BM-based cell is 1.5 times higher than that in the BT-TPD/PC₇₁BM-based cell. As the performances of the solar cell devices were closely associated with the nanomorphology of the active layer, we investigated the film morphology of the as-cast and annealed blended films by tapping mode atomic force microscopy (AFM), as shown in Figure 6. For the BT-TPD/



Figure 6. AFM height images of a) as-cast BT-TPD/PC₇₁BM, b) BT-TPD/PC₇₁BM annealed at 160 °C with a blend ratio of 1:2 w/w, c) as-cast TBDT-TTPD/PC₆₁BM, d) TBDT-TTPD/PC₆₁BM annealed at 120 °C with a blend ratio of 1:1 w/w.

 $PC_{71}BM$ film with a blend ratio of 1:2 and annealed at 160 °C, a root-mean-square (rms) roughness (1.64 nm) smaller than that found for the as-cast BT-TPD/PC₇₁BM film was observed, as was a clearly ordered network, which could explain the higher FF and photocurrent values. The relatively smooth active layer surface could reduce the charge recombination by evenly distributed morphological features as well as defect-free contact with the metal cathode, which would lead to increased FF values.^[33,34]

A network of the small-molecule crystals is formed with the ordered structure, which acts as an effective charge transporter. The formation of a crystal network therefore enhances charge transport, which thereby increases the current density.^[35] In the TBDT-TTPD/PC₆₁BM (1:1 w/w) annealed film at 120 °C, increased phase aggregation and roughness (from 0.52 to 0.85 nm) were observed relative to that observed in the as-cast TBDT-TTPD/PC₆₁BM film. The higher aggregation and the larger roughness of the annealed TBDT-TTPD/PC₆₁BM film are indicative of a more highly ordered structure, which indicates more efficient charge separation in the OSCs. (The FF value in the TBDT-TTPD/ PC61BM annealed film decreases as a result of an increase in the rms roughness.) A film surface with higher roughness and aggregation is also beneficial to internal light scattering and enhances light absorption.^[36] All of this results in a higher J_{sc} value and increased efficiency of the annealed TBDT-TTPD device relative to the as-cast TBDT-TTPD device. The increase in the PCE after annealing in conjugation with the AFM results suggests that thermal annealing causes a change in the distribution and/or a reorganization of the components in the blend. To probe the distribution of small-molecule/PCBM blended films in the bulk before and after thermal annealing, 2D grazing incidence X-ray diffraction (GIXD) analysis measurements were performed. The results of these experiments are shown in Figure 7.



Figure 7. GIXD patterns for blended BT-TPD/PC₇₁BM films a) as-cast and b) annealed at 160 °C; c) TBDT-TTPD/PC₆₁BM as-cast film; d) TBDT-TTPD/PC₆₁BM film annealed at 120 °C for 10 min.

To obtain GIXD patterns of blended films, small-molecule/PCBM films were prepared on a Si/PEDOT/PSS substrate by the spin-coating method. As shown in Figure 7, for the BT-TPD/PC₇₁BM as-cast film, no distinct diffraction peaks can be assigned to BT-TPD, which indicates that the majority of the small-molecule fraction has entered an amorphous state.^[37] Upon heating a BT-TPD/PC₇₁BM film to 160 °C, however, at which point BT-TPD starts to self-assemble, the intensity of the reflection dramatically increased with random orientation. In the as-cast TBDT-TTPD/ PC₆₁BM film, a distinct reflection was detected in the out-of plane direction at $q_z = 0.375$ Å⁻¹ (d = 1.67 nm), whereas a strong second-order peak was observed along the nominal direction in the film annealed at 120 °C. This implies the im-

proved order in the crystallites.^[38] This result suggests that the improvement in the PCE of the device observed upon thermally annealing may be ultimately attributed to substantially ordered donor domains. Comparison of the ordering structures of BT-TPD and TBDT-TTPD was also performed by using out-of-plane and in-plane X-ray diffraction (XRD, Figure S18). In both the BT-TPD/PC71BM and TBDT-TTPD/PC₆₁BM blend films, the diffraction patterns for outof-plane and in-plane directions were consistent with the 2D-GIXD results. All two-blend films were shown to have stronger crystalline diffraction peaks and a longer range ordering in the annealed films. For the BT-TPD/PC71BM blend film, the lamellar ($2\theta = 2.99^\circ$) and weak π - π stacking $(2\theta = 13.37^{\circ})$ peaks appear in out-of-plane and in-plane patterns, respectively. The corresponding interlayer d spacing and $\pi - \pi$ intermolecular stacking distance were 20.53 and 4.60 Å, respectively. In the TBDT-TTPD/PC₆₁BM film, crystalline diffraction peaks $(2\theta = 3.48^\circ, d \text{ spacing} = 17.63 \text{ Å})$ with second-order diffraction and a strong π - π in-plane peak ($2\theta = 17.45^{\circ}$, $\pi - \pi$ stacking distance = 3.53 Å) were observed. These findings indicate that the TBDT-TTPD film is composed of higher-order TBDT-TTPD crystallites and that is has a stronger packing structure with a shorter intermolecular distance.^[39] The dominant long-range ordering and shorter π - π stacking of TBDT-TTPD in the blend film allows efficient charge transport, which would explain why devices based on TBDT-TTPD showed higher hole mobility and an almost twofold higher PCE than those based on the less-ordered BT-TPD structure.

Conclusions

In conclusion, two novel small molecules, that is, BT-TPD and TBDT-TTPD, bearing TPD units as acceptor building blocks were designed and synthesized. The two small molecules show excellent thermal stability, strong absorption, relatively low HOMO levels, and high hole mobility. SMOSCs based on the blend of small-molecule/PCBM (1:1 or 1:2 w/ w) exhibit PCEs of 1.16-3.90% without any post-treatment. Increased PCEs were achieved for both BT-TPD- and TBDT-TTPD-based devices after thermal annealing, and the highest PCE of 4.6% with a notable V_{oc} of 0.97 V, J_{sc} of 9.1 mA cm⁻², and FF of 52.0% was obtained from the TBDT-TTPD-based solar cell. The PCE of >4.6% is among the highest reported for fully solution-processed photovoltaic devices based on the TPD motif. This work demonstrates that these small molecules based on the TPD moiety offer a good strategy for the development of novel photovoltaic small-molecule-based donor materials with high values of $J_{\rm sc}$ and $V_{\rm oc}$ for high-efficiency OSCs.

Experimental Section

General methods

All chemicals were purchased from Aldrich and Alpha: DMF, THF, NBS, nBuLi, toluene Pd(PPh₃)₂Cl₂, and trimethyltin chloride were used without further purification. ¹H NMR spectra were recorded by using a BrukerAM-200 spectrometer. ¹³C NMR spectra were recorded with a Bruker Advance-300 spectrometer. HRMS (EI) spectra were performed with a high-resolution GC mass spectrometer with LabRAM HR800 UV. MS (MALDI-TOF/TOF) spectra were performed with a high-resolution MALDI-TOF/TOF mass spectrometer with a Voyager DE-STR. Thermal analyses were performed with a TA TGA 2100 thermogravimetric analyzer under a nitrogen atmosphere at a rate of 10°Cmin⁻¹. UV/Vis absorption spectra were determined by using a Carry 5000 UV/Vis-near-IR double-beam spectrophotometer. Cyclic voltammetry (CV) was performed by using a PowerLab/AD instrument model system in 0.1 M solution of tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in anhydrous acetonitrile as supporting electrolyte at a scan rate of 50 mV s⁻¹. A glassy carbon disk (≈ 0.05 cm²) coated with a thin small molecule film, an Ag/AgNO3 electrode, and a platinum wire were used as the working electrode, reference electrode, and counter electrode, respectively. An atomic force microscope (Multimode IIIa, Digital Instruments) was used to obtain surface images of the active layer blended small molecules with PCBM. 2D Grazing incident X-ray diffraction (GIXD) was performed for structural analysis at the 9 A beamline at the Pohang Accelerator Laboratory (PAL). The measurements were performed with a sample-to-detector distance of 231.761 mm. Data were typically collected for 10 s by using an X-ray radiation source of $\lambda = 1.1189$ nm with a 2D charge-coupled detector (CCD) (Roper Scientific, Trenton, NJ, USA). The samples were mounted on a home-built z axis goniometer equipped with a vacuum chamber. The incidence angle a_i for the X-ray beam was set to 0.17°, which was intermediate between the critical angles of the films and the substrate ($a_{c.f}$ and $a_{c.s}$). X-ray diffraction (XRD) was also performed by using the 5 A beamline (wavelength = 1.071 Å) at the PAL.

OFET device fabrication and characterization

Top-contact organic field-effect transistors (OFETs) composed of BT-TPD and TBDT-TTPD were fabricated on a common gate of highly ndoped silicon with a 300 nm thick thermally grown SiO₂ dielectric layer. Before substrates were modified with octyltrichlorosilane (OTS-8), a piranha solution was used to clean the organic residues of silicon substrates; the surfaces were ozone treated for 20 min. Cleaned substrates were modified with hydrophobic OTS-8 from a toluene solution for 60 min at room temperature, and films of semiconducting materials were spin coated at 6000 rpm from 0.7 wt % toluene solutions with a thickness of 50 nm. Gold source and drain electrodes of the OFETs based on BT-TPD and TBDT-TTPD were evaporated on top of the semiconductor layers (80 nm). For all measurements, we used channel lengths of 50 μ m and channel widths of 2000 μ m. The electrical characteristics of the OFETs were measured in air by using both Keithley 2400 and 236 source/measure units.

Fabrication and characterization of the photovoltaic cells

The organic photovoltaic devices were fabricated on prepatterned ITO (indium tin oxide) glass substrates with the structure of glass/ITO/ PEDOT/PSS/small molecule/PCBM/LiF/Al (a 0.09 cm² active layer). The ITO-coated glass substrates were first cleaned with detergent, deionized water, acetone, and isopropyl alcohol by ultrasonication. UV/ozone treatment of the cleaned ITO substrates was then performed at room temperature for 30 min. PEDOT/PSS (Bay P VP AI 4083, Bayer AG) was spin coated at 4000 rpm for 60 s onto the ITO glass with a thickness of 30–40 nm after filtration by using a 0.45 μ m PVDF filter. A blend of BT-TPD or TBDT-TTPD and PC₇₁BM or PC₆₁BM with different weight ratios (from 1:0.4 to 1:2 w/w) was solubilized overnight in chlorobenzene or chloroform at a total concentration of 40 mg mL⁻¹. The blended solutions were spin coated at 1200 rpm for 60 s (thickness \approx 70–90 nm) on the top of the PEDOT/PSS layer and annealed at various temperatures for 15 min on a hot plate in the glove box. The LiF and Al cathodes were thermally deposited to thickness of 0.8 and 100 nm, respectively, onto the surface of the active layer. The current versus voltage (J-V) characteristics of each device without encapsulation were measured in the dark and under an ambient condition AM 1.5G illumination of 100 mV cm⁻² produced by an Oriel 1 KW solar simulator with respect to a reference cell PVM 132 calibrated at the National Renewable Energy Laboratory. The external quantum efficiency (EQE) spectra were obtained by using a photomodulation spectroscopic setup (model Merlin, Oriel), a calibrated Si UV detector, and a SR570 low-noise current amplifier.

Hole and electron mobility measurements

Hole- or electron-only devices were fabricated by using the ITO/ PEDOT/PSS/small molecule/PCBM/Au and Al/small molecule/PCBM/Al architectures, respectively. The mobility was extracted by fitting the current-voltage curves by using the Mott–Curney relationship [space charge limited current, Eq. (1)]:

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_h \frac{V^2}{L^3} \tag{1}$$

in which J is the current density, L is the film thickness of the active layer, $\mu_{\rm h}$ is the hole mobility, $\varepsilon_{\rm r}$ is the relative dielectric constant of the transport medium, ε_{θ} is the permittivity of free space, V is the internal voltage in the device, and $V=V_{\rm appl}-V_{\rm r}-V_{\rm bi}$, for which $V_{\rm appl}$ is the applied voltage to the device, $V_{\rm r}$ is the voltage drop resulting from contact resistance and series resistance across the electrodes, and $V_{\rm bi}$ is the built-in voltage arising from the relative work function difference of the two electrodes. The value of $V_{\rm bi}$ can be determined from the transition between the ohmic region and the SCLC region.

Synthesis of the monomers and small molecules

5-Hexyl-2,2'-bithiophene (2a), 4.8-dehydrobenzo[1,2-b:4,5-b']dithiophene-4,8-dione (5a), and 5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (1a) were synthesized by following literature procedures:^[40-42] A detailed synthesis scheme is presented in the Supporting information.

1,3-Dibromo-5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (1b)

Compound **1a** (4.90 g, 18.49 mmol) was dissolved in concentrated sulfuric acid (27.6 mL) and trifluoroacetic acid (92.4 mL). *N*-Bromosuccinimide (9.87 g, 55.47 mmol) was added in one portion, and the reaction mixture was stirred at room temperature overnight. The brown solution was then diluted with water (500 mL) and extracted with dichloromethane. The organic phase was dried with anhydrous magnesium sulfate and concentrate d to afford the crude product as orange crystals. Purification by column chromatography (silica gel, dichloromethane/hexane=1:1) followed by recrystallization (aqueous ethanol) gave **1b** (6.41 g, 15.16 mmol, 82%) as white crystals. M.p. 104–105°C (760 torr, 1 torr=0.13 kPa). ¹H NMR (300 MHz, CDCl₃): δ =3.60 (t, 2H), 1.62 (q, 2H), 1.31 (m, 10H), 0.89 ppm (t, 3H).

5-Trimethylstannyl-5'-hexyl-2, 2'-bithiophene (2b)

A solution of *n*BuLi (2.5 M in hexanes, 5.56 mL, 13.92 mmol) was added dropwise over a period of 30 min to a solution of **2a** (3.00 g, 12.00 mmol) in THF (60 mL). The reaction mixture was stirred at 50 °C for 2 h and then cooled down to -78 °C. The solution was stirred for 12 h. All volatile components were removed under high vacuum, and the residue was taken up in toluene (15 mL). A solution of trimethyltin chloride (2.98 g, 15.00 mmol) in THF (400 ml) was then added slowly. The mixture was first stirred at -78 °C for 3 h and then for an additional 12 h at ambient temperature. Quenching with aqueous NH₄Cl solution and extraction of the organic layer with ether gave a black oily material upon evaporation

of the solvents. Distillation at 140 °C under high vacuum (10–2 torr) gave **2b** (2.87 g, 6.96 mmol, 58%) as a colorless liquid. ¹H NMR (300 MHz, CDCl₃): δ =7.28 (d, 1H), 7.14 (d, 1H), 7.01 (d, 1H), 6.71 (d, 1H), 2.83 (t, 2H), 1.70 (m, 2H), 1.37 (m, 6H), 0.95 (t, 3H), 0.43 ppm (t, 9H).

5-Octyl-1,3-di(thiophen-2-yl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (3)

Compound **1b** (7.50 g, 17.73 mmol) and trimethyl(thiophen-2-yl)stannane (16.53 g, 44.32 mmol) were dissolved in toluene (300 mL) in a pressure tube. The solution was degassed by a nitrogen flow for 30 min. Then, Pd-(PPh₃)₂Cl₂ (0.37 g, 0.53 mmol) was added into the solution. The tube was capped and heated to 110 °C overnight. The mixture was extracted with dichloromethane. The combined organic layer was dried with anhydrous MgSO₄. After removing the solvent, the residue was purified by column chromatography (silica gel, hexane/dichloromethane = 4:1). Recrystallization (hexanes) afforded **3** (4.88 g, 11.34 mmol, 64%) as a yellow solid. ¹H NMR (300 MHz, CDCl₃): δ =8.00 (s, 2H), 7.45 (s, 2H), 7.15 (t, 2H), 3.68(t, 2H), 1.72 (m, 2H), 1.32 (m, 10H), 0.88 ppm (t, 3H).

1-(5-Bromothiophen-2-yl)-5-octyl-3-(thiophen-2-yl)-4H-thieno[3,4c]pyrrole-4,6(5H)-dione (**4**)

N-Bromosuccinimide(2.27 g, 12.79 mmol) was added dropwise over a period of 60 min to a solution of **3** (5.50 g, 12.79 mmol) in DMF (100 mL) and CHCl₃ (100 mL). After 2 h, the reaction mixture was poured into water and extracted three times with chloroform. The organic phase was combined and dried with anhydrous magnesium sulfate. After removal of the solvent, the crude product was purified by column chromatography (dichloromethane/hexane = 1:4). Recrystallization (hexanes) afforded **4** (3.44 g, 6.78 mmol, 53%) as a yellow solid. ¹H NMR (300 MHz, DMSO): δ =7.99 (s, 1H), 7.83 (s, 1H), 7.70 (t, 1H), 7.35 (d, 1H), 7.24(d, 1H), 3.51(t, 2H), 1.50 (s, 2H), 1.27 (m, 10H), 0.84 ppm (m, 3H).

4,8-Bis[5-(2-ethylhexyl)thiophen-2-yl]benzo[1,2-b;4,5-b']dithiophene (5b)

A dry, three-necked, 250 mL, nitrogen-purged flask was charged with a mixture of ethylhexylthiophene (9.34 g, 47.67 mmol) in THF (100 mL). At 0 °C, *n*BuLi (2.5 M in hexane, 19.06 mL, 47.67 mmol) was added dropwise over 30 min. The mixture was then warmed to 50 °C and stirred for 2 h. Compound **5a** (5.00 g, 22.70 mmol) was added to the reaction mixture, which was then stirred for 1.5 h at 50 °C. After cooling the reaction mixture to ambient temperature, SnCl₂·2H₂O (7.69 g, 34.05 mmol) in HCl (10%, 10 mL) was added, and the mixture was stirred for an additional 2 h. It was subsequently poured into ice water and extracted with diethyl ether. The combined extract was dried with anhydrous MgSO₄ and then concentrated. The crude product was purified by column chromatography (silica gel, petroleum ether) to give pure **5b** (9.07 g, 15.56 mmol, 69%) as a pale-yellow solid.¹H NMR (300 MHz, CDCl₃): δ =7.70 (d, 2H), 7.49 (d, 2H), 7.38 (d, 2H), 6.92 (d, 2H), 2.94 (d, 4H), 1.79 (m, 2H), 1.57–1.34 (br, 16H), 0.99–0.92 ppm (m, 12H).

2,6-Bis(trimethyltin)-4,8-bis[5-(2-ethylhexyl)thiophen-2-yl]benzo[1,2-b:4,5-b']dithiophene (**5c**)

In a dry, two-necked, 50 mL, nitrogen-purged flask, **5b** (1.00 g, 1.72 mmol) was dissolved in anhydrous THF (15 mL). The solution was cooled to 0°C, and a solution of *n*BuLi (2.5 m in hexane, 1.38 mL, 3.45 mmol) was added dropwise with stirring. The reaction mixture was then stirred for 2 h at room temperature. Next, the reaction mixture was cooled to 0°C and chlorotrimethylstannane (0.68 g, 3.45 mmol) was added in one portion. The reaction mixture was stirred at 0°C for 30 min and then warmed to room temperature over 2 h. Subsequently, the reaction mixture was quenched by the addition of distilled water (10 mL), and then the mixture was dried with anhydrous MgSO₄ and concentrated to obtain a yellow viscous crude product. Further purification by recrystallization (ethanol) afforded pure **5c** (1.12 g, 72%) as a yellow solid.

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¹H NMR (300 MHz, CDCl₃): δ = 7.70 (s, 2H), 7.32 (d, 2H), 6.91 (d, 2H), 2.90 (d, 4H), 1.56–1.37 (br, 18H), 0.97 (m, 12H), 0.50 ppm (t, 18H).

1,3-Bis(5'-hexyl-2,2'-bithiophen-5-yl)-5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (BT-TPD)

Compounds 2 (1.97 g, 4.77 mmol) and 7 (1.01 g, 2.38 mmol) were dissolved in dry THF (40 mL), and the solution was degassed with N₂ for 10 min. Then, Pd(PPh₃)₂L₂ (0.05 g, 0.07 mmol) was added. The mixture was stirred at 100 °C overnight under a nitrogen atmosphere. The reaction mixture was poured into water and extracted three times with chloroform. The organic phase was combined and dried with anhydrous magnesium sulfate. After removal of the solvent, the crude product was purified by column chromatography (chloroform/hexane=1:1). Recrystallization (hexanes) afforded BT-TPD (0.96 g, 1.26 mmol, 53%) as a red solid. ¹H NMR (300 MHz, CDCl₃): δ = 7.92 (d, 2H), 7.11 (d, 4H), 6.73 (d, 2H), 3.68 (t, 2H), 2.82 (t, 4H), 1.68 (m, 6H), 1.43–1.25 (br, 22H), 0.89 ppm (t, 9H). ¹³C NMR (500 MHz, CDCl₃): δ = 163.0, 147.4, 141.8, 136.3, 134.1, 131.1, 130.7, 128.5, 125.5, 125.0, 124.3, 39.0, 38.2, 32.1, 31.9, 31.8, 30.6, 29.6, 29.5, 29.1, 28.9, 27.3, 23.0, 22.9, 14.4 ppm. HRMS (EI): *m*/*z*: calcd for C₄₂H₅₁NO₂S₅: 761.252 [*M*⁺]; found: 765.25.

4-[5-(2-Ethylhexyl)thiophen-2-yl]-8-[5-(2-ethylhexyl)thiophen-2-yl]-2,6bis-11-[5-octyl-1,3-dithiophen-2-yl-thieno[3,4-c]pyrrole-4,6-dionyl]-1,5dithia-s-indacene (TBDT-TTPD)

Compounds 5 (0.89 g, 0.98 mmol) and 9 (1.00 g, 1.96 mmol) were dissolved in dry toluene (30 mL), and the solution was degassed with nitrogen for 10 min. Then, $Pd(PPh_3)_2Cl_2$ (0.02 g, 0.03 mmol) was added. The mixture was stirred at 100 °C overnight under a nitrogen atmosphere. The reaction mixture was poured into water and extracted three times with chloroform. The organic phase was combined and dried with anhydrous magnesium sulfate. The residue was purified by column chromatography (silica gel, hexane/dichloromethane=1:1), which was followed by recrystallization (hexanes) to give TBDT-TTPD (0.49 g, 0.34 mmol, 35%) as a dark red solid. ¹H NMR (300 MHz, CDCl₃): $\delta = 8.01$ (d, 2H), 7.91 (d, 2H), 7.66 (s, 2H), 7.44 (t, 2H), 7.32(d, 2H), 7.24 (d, 2H), 7.13 (d, 2H), 6.97 (d, 2H), 3.66 (t, 4H), 2.95 (t, 4H), 1.70 (br, 8H), 1.57-1.29 (br, 34H), 1.07–0.87 ppm (m, 18H). ¹³C NMR (500 MHz, CDCl₃): δ = 162.7, 162.6, 146.2, 140.6, 139.6, 137.4, 136.9, 135.9, 135.6, 132.9, 132.7, 132.2, $130.9,\ 130.2,\ 128.8,\ 128.7,\ 128.6,\ 128.4,\ 126.1,\ 125.9,\ 125.6,\ 123.6,\ 120.3,$ 41.8, 38.9, 34.8, 33.0, 32.2, 29.6, 29.4, 28.8, 27.5, 27.4, 26.2, 23.5, 23.0, 14.7, 14.4, 11.4 ppm. MS (MALDI-TOF/TOF): calcd for $C_{78}H_{84}N_2O_4S_{10}{\rm :}$ 1432.364; found: 1432.36

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