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Small Molecules with Asymmetric 4-Alkyl-8alkoxybenzo[1,2-b:4,5-b']dithiophene as the Central Unit for High-Performance Solar Cells with High Fill Factors

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Supporting Information



ABSTRACT: A small molecule named DRBDTCO based on benzo[1,2-*b*:4,5-*b*'] dithiophene (BDT) with an asymmetric side chain and its dimer, *d*DRBDTCO, with the octamethylene connector were designed and synthesized as donor materials for solution-processed bulk heterojunction solar cells. The optimized power conversion efficiency of a DRBDTCO-based device was 8.18% under AM 1.5 G irradiation (100 mW cm⁻²), which is higher than that of its *d*DRBDTCO-based device. Both molecule-based devices exhibited high fill factors of >73%, which are attributed to their optimized morphologies with a feature size of 15–20 nm, highly efficient charge collection, less bimolecular recombination, and well-balanced charge transport properties. The results demonstrate that the asymmetric BDT unit could be a promising building block for donor materials with high efficiencies and high fill factors.

1. INTRODUCTION

Solution-processed organic photovoltaic cells (OPVs) are of prime interest as a promising next-generation green technology because of their advantages, including their solution processability, low cost, light weight, and flexibility.^{1,2} Through great efforts,^{3–8} the power conversion efficiencies (PCEs) of OPVs have exceeded 10% in single-junction devices in the past few years.^{9–18} Small/oligomer-like molecule-based OPVs, as an important part of OPVs, have made great strides with encouraging PCEs of >10%.^{19–21} Benzo[1,2-*b*:4,5-*b'*]-dithiophene (BDT) derivative units are among the most widely used electron-donating blocks with high performance for polymer-based^{22,23} and small molecule-based^{24–28} bulk heterojunction (BHJ) solar cells, such as PTB7²⁹ and PTB7-Th,³⁰ DR3TSBDT,²⁰ DR3TBDTTT,³¹ and DR3TBDTTF.³² This is due to the structural symmetry and planarity as well as the rigid

fused aromatic system of the BDT unit, which can enhance electron delocalization and intermolecular interactions and thus improve charge transport.^{33–35} In addition, with weak electron donating ability, BDT is favored for maintaining a low highest occupied molecular orbital (HOMO) energy level for the resulting materials incorporating it, which is beneficial for obtaining a high open-circuit voltage ($V_{\rm oc}$) in the photovoltaic devices.^{36,37}

Among the high-performance materials containing BDT building blocks, the substituted groups at positions 4 and 8 of BDT, including alkyl, alkoxyl, and aryl, are normally the same to form symmetric BDT units, and the asymmetric structure of

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Figure 1. Chemical structures of DR3TBDT, DR3TDOBDT, DRBDTCO, and dDRBDTCO.





BDT (*a*-BDT) with different substitutes at positions 4 and 8 has been rarely explored in OPVs.^{38,39} Shin et al. have replaced one alkoxyl side chain of dialkoxy-BDT with the alkyl chain and synthesized a new polymer with a deep HOMO energy level because of its poorer electron donating ability of the alkyl chain.³⁸ The OPV device of the polymer showed a PCE higher than that of its analogue with symmetric dialkoxy-BDTs. The result demonstrates that the asymmetric BDT unit might be a

promising building block for the design of new highperformance OPV materials. On the other hand, as a competitive alternative with advantages such as well-defined structures and therefore less batch to batch variation, easier structure control, etc., small or oligomer-like molecule-based OPVs have attracted a great deal of attention, and breakthrough results have been achieved in recent years. It is worth noting that small or oligomer-like molecules with defined structures can provide more reliable analyses of the relationship between the chemical structure and their properties and device performance.^{40–47} Also currently, most of the small molecule donor materials have symmetric structures, and few studies have been performed on the small molecules with asymmetric chemical structures, especially asymmetric BDT units at positions 4 and 8.

In our previous work, we have reported several symmetric BDT-based small molecules. For example, DR3TBDT consisted of central symmetric bis(*O*-alkyl) BDT with a PCE of 7.38%.⁴⁸ Through the optimization of electron transport layers, the PCE of the DR3TBDT-based device was enhanced to 8.30%.⁴⁹ Another small molecule DR3TDOBDT with symmetric dioctyl-substituted BDT as the central building block has also been investigated, and this small molecule-based device offered a high PCE of 8.26%, with a $V_{\rm oc}$ of 0.94 V, a $J_{\rm sc}$ of 12.56 mA cm⁻², and a fill factor (FF) of 70%.⁵⁰ The two material-based devices achieved high $V_{\rm oc}$ and FF values. As indicated above, currently all small molecules with PCEs of >8% have symmetric chemical structures.

With these, in this work, we have designed an asymmetric molecule, DRBDTCO (Figure 1). Meanwhile, another molecule, dDRBDTCO, still with overall symmetry but an asymmetric building BDT block linked by a flexible linker has also been designed for comparison. For better comparison, the octamethylene linker was chosen as it has the same length as its counterpart symmetric molecules shown in Figure 1. The asymmetrical molecule DRBDTCO has wider and stronger optical absorption in the active layer, and thus J_{sc} and PCE values higher than those of dDRBDTCO. On the other hand, the dimer molecule dDRBDTCO has a blue-shifted and lower absorption, probably because the flexible linkage of octamethylene disrupted the order of backbones. Interestingly, however, devices based on both of these materials have high FF values of >73%, which were attributed to the optimized feature domain size of 15-20 nm, highly efficient charge collection, less bimolecular recombination, and well-balanced charge transport properties. With this, a higher PCE of 8.18% for DRBDTCO-based devices was achieved, which is comparable with that of its symmetric analogue molecule DR3TBDT and DR3TDOBDT. These results indicate that using such asymmetric building blocks for OPV might also be a promising strategy for designing high-performance OPV materials.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization. Figure 1 shows the chemical structures of the target molecules DRBDTCO and dDRBDTCO. The synthetic routes are shown in Scheme 1. The *a*-BDT unit was prepared using the procedure described in the literature.³⁸ The target molecules were synthesized via the Stille coupling and Knoevenagel condensation from the central units. The alkyl chain on the end caps of dDRBDTCO is noctyl, which is used to ensure the target molecule has good solubility in common organic solvents, such as chloroform, chlorobenzene, etc. The two compounds were purified by conventional chromatography with silica gel and provided for device fabrication after recrystallization from chloroform and hexane. Under a nitrogen atmosphere, the onset temperature with 5% weight loss by thermogravimetric analysis (TGA) was >370 °C for these two molecules (Figure S1), which indicates that the thermal stability of these molecules is adequate for application in OPVs. Clearing melting temperatures (T_m) upon heating and recrystallization points (T_{cr}) upon cooling are

observed via differential scanning calorimetry (DSC) analysis (Figure S2) of the two molecules, indicating some degree of crystallinity,⁵¹ which is consistent with the analysis by grazing incidence X-ray diffraction (GIXD) as discussed below.

2.2. Optical Absorption and Electrochemical Proper-ties. The ultraviolet–visible (UV–vis) absorption spectra of these two molecules in a diluted chloroform solution and thin film are shown in Figure 2. Although DRBDTCO shows a



Figure 2. (a) Ultraviolet-visible (UV-vis) absorption spectra of DRBDTCO and *d*DRBDTCO in diluted chloroform solutions. (b) UV-vis absorption spectra of DRBDTCO and *d*DRBDTCO films. (c) Cyclic voltammograms of DRBDTCO and *d*DRBDTCO in dichloromethane solutions.

maximal absorption (λ_{max}) peak at 504 nm compared with that at 524 nm for *d*DRBDTCO, it has a larger maximal absorption coefficient of 53.2 L g⁻¹ cm⁻¹ in solution. From solution to solid state, DRBDTCO exhibits a significant red shift and an absorption wider and stronger than that of *d*DRBDTCO. The obvious vibronic shoulder peak at 627 nm for DRBDTCO indicates effective $\pi - \pi$ stacking between the molecular backbones, but *d*DRBDTCO merely shows a slight shoulder

Table 1	l. 0	ptical	and	Electrochemical	Data	of	DRBDTC	CO	and	dDRBD	тсо
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	UV-vis				CV			
molecule	$\lambda_{\rm max, sol} \ ({\rm nm})$	$\varepsilon (L g^{-1} cm^{-1})$	$\lambda_{ m max, film} (m nm)$	$E_{\rm g}^{\rm opt}$ (eV)	HOMO (eV)	LUMO (eV)	$E_{\rm g}^{\rm cv}$ (eV)	
<i>d</i> DRBDTCO	524	44.5	566	1.80	-5.02	-3.30	1.72	
DRBDTCO	504	53.2	583, 627	1.73	-4.94	-3.30	1.62	
DR3TBDT ^a	508	46.8	583	1.74	-5.02	-3.27	1.75	
DR3TDOBDT ^b	511	45.0	583	1.79	-5.08	-3.27	1.81	
^{<i>a</i>} Data from ref 48. ^{<i>b</i>} Data from ref 50.								

Table 2. Average Photovoltaic Performance of DRBDTCO- and dDRBDTCO-Based Devices^a

molecule	$V_{\rm oc}$ (V)	$J_{\rm sc}~({\rm mA~cm^{-2}})$	FF	PCE (%)	$J_{\rm sc}^{\rm cal}$ (mA cm ⁻²)
dDRBDTCO ^b	$0.88 \pm 0.01 \ (0.89)$	$10.62 \pm 0.26 (10.88)$	$0.72 \pm 0.01 \ (0.73)$	$6.73 \pm 0.25 (7.07)$	10.61
DRBDTCO ^c	$0.86 \pm 0.01 \ (0.87)$	$12.31 \pm 0.23 (12.54)$	$0.74 \pm 0.01 \ (0.75)$	$7.83 \pm 0.27 \ (8.18)$	12.50
DR3TBDT ^d	0.92	12.92	0.70	8.32	12.19
DR3TDOBDT ^e	0.94	12.56	0.70	8.26	12.07

^{*a*}The best results are provided in parentheses. ^{*b*}With CS₂ solvent vapor annealing for 90 s. ^{*c*}With a 1:1 (v/v) mixed solvent of THF and CS₂ vapor annealing for 90 s. ^{*d*}OPV data for DR3TBDT from ref 49. ^{*e*}OPV data for DR3TDOBDT from ref 50.

peak at 620 nm, indicating a relatively weak $\pi-\pi$ stacking between the molecular backbones in contrast to that of DRBDTCO possibly because of the flexible linker group. These results are consistent with the GIXD results of the pure film as discussed blow. The optical band gap of DRBDTCO is 1.73 eV, estimated from the onset absorption of the as-cast pure film absorption, which is smaller than that of *d*DRBDTCO (1.80 eV).

Cyclic voltammetry (CV) was used to verify the energy levels of the two molecules, which are based on the oxidation and reduction onset potentials internally calibrated using the ferrocene/ferrocenium (Fc/Fc⁺) redox couple (-4.8 eV below the vacuum level).⁵² As shown in cyclic voltammograms (Figure 2c), the HOMO energy levels and lowest unoccupied molecular orbital (LUMO) energy levels of DRBDTCO are -4.94 and -3.30 eV, respectively. The values for *d*DRBDTCO are -5.02 and -3.30 eV, respectively. The electrochemical band gaps of DRBDTCO and *d*DRBDTCO are 1.64 and 1.72 eV, respectively.

The optical and electrochemical data of DRBDTCO and *d*DRBDTCO presented above together with those data of the symmetric molecules DR3TBDT and DR3TDOBDT for comparison are listed in Table 1. From Table 1, it can be seen that the introduction of asymmetric side chains into the BDT unit only slightly affects the absorption and electrochemical properties of A–D–A small molecules.

2.3. Photovoltaic Properties. Solution-processed BHJ devices with a conventional ITO/PSS:PEDOT/small molecules:PC₇₁BM/ETL-1⁵³/Al device configuration were fabricated to demonstrate the potential of these two small molecules as electron donors in organic solar cells. The details of device fabrication, measurements, and optimization procedures are described in the Experimental Section and Supporting Information. Without any treatment, dDRBDTCO:PC71BM [1:1 (w/w)] devices gave a low PCE of 2.20%, with a V_{oc} of 0.93 V, a J_{sc} of 5.70 mA cm⁻², and a FF of 42%. After solvent vapor annealing (SVA) treatment, the PCE was sharply improved to 7.07%, with a $V_{\rm oc}$ of 0.89 V, a $J_{\rm sc}$ of 10.88 mA cm⁻², and a FF of 73% (Table 2). As for DRBDTCO, a moderate PCE of 4.88% was achieved for the as-cast devices. Through systematic SVA treatment (Figures S7-S10), the maximal PCEs of DRBDTCO-based devices reached 8.18%,

with an outstanding FF of 75%, a V_{oc} of 0.87 V, and a J_{sc} of 12.54 mA cm⁻² (Figure 3).



Figure 3. Current density-voltage (J-V) characteristics of both devices without treatment and with SVA treatment.

The photovoltaic parameters of the optimized DR3TBDTand DR3TDOBDT-based devices are summarized in Table 2 for comparison. As one can see, the overall $J_{\rm sc}$ is the determining factor leading to the lower PCE of dDRBDTCO-based devices compared with that of DRBDTCO. This might be because *d*DRBDTCO has relatively poorer absorption, a lower internal quantum efficiency (IQE) (Figure S11), and a lower photoinduced charge transfer efficiency (Figure S12). The lower V_{oc} of the asymmetric DRBDTCO-based device compared with the value of the device based on symmetric molecules is consistent with its higher HOMO energy level, but the asymmetric molecule DRBDTCO gave a J_{sc} similar to that of the symmetric molecules. It is worth noting that DRBDTCO-based devices exhibit excellent FFs (\leq 75%), benefiting from the good morphology of DRBDTCO and its high charge carrier mobilities as discussed below.

To investigate the difference between the performances of two asymmetric molecule-based devices, the UV-vis absorption spectrum of the blend films and the external quantum efficiency (EQE) spectra of the optimized devices were measured and are plotted in Figure 4. From Figure 4a, it can be clearly seen that the absorption intensity of the



Figure 4. (a) UV-vis absorption spectra of DRBDTCO: $PC_{71}BM$ and $dDRBDTCO:PC_{71}BM$ blends with SVA treatment. (b) EQE curves of the optimized DRBDTCO- and dDRBDTCO-based devices.

DRBDTCO:PC71BM film is markedly higher than that of the dDRBDTCO:PC₇₁BM film, which favors a higher J_{sc} for the DRBDTCO-based device. There are clear shoulder peaks at ~620 nm for both films, which are related to the ordered molecular packing. Figure 4b displays the EQE curves of the best devices, and photocurrent responses from 300 to 730 nm are observed for both molecule-based devices. Obviously, the EQE values of the DRBDTCO-based device are >70% across the range of 410-570 nm and significantly higher than that of the dDRBDTCO-based device from 380 to 730 nm, indicating that the photoelectron conversion process of the DRBDTCObased device is more efficient. The calculated J_{sc} values from the EQE curves are 10.61 and 12.49 mA cm^{-2} for the best dDRBDTCO and DRBDTCO devices, respectively, which have a 3–5% mismatch compared with the J_{sc} values obtained from their J-V curves. Furthermore, IQE is used to judge the effective power conversion efficiency of the active layer, which is calculated from the measured effective absorption of the active layer and the EQE. As shown in Figure S11, the IQE for the DRBDTCO-based device is higher than that of dDRBDTCO in the range from 400 to 650 nm, indicating that the charge separation and collection processes of DRBDTCO-based devices are more efficient than those of the dDRBDTCO-based devices.54,55

To improve our understanding of the high performance and the remarkable FFs of two asymmetric molecule-based devices, the relationship between the photocurrent density $(J_{\rm ph})$ and effective voltage $(V_{\rm eff})$ for the devices was studied. The photocurrent is defined as $J_{\rm ph} = J_{\rm L} - J_{\rm D}$, where $J_{\rm L}$ and $J_{\rm D}$ are the current density under illumination and in the dark, respectively. For $V_{\rm eff} = V_0 - V_a$, V_0 is the voltage at which $J_{\rm ph}$ = 0 and $V_{\rm a}$ is the applied voltage.^{52,56} The photocurrent and normalized photocurrent $(J_{\rm ph}/J_{\rm sat})$ where $J_{\rm sat}$ is the saturated photocurrent) versus V_{eff} curves are plotted in Figure 5. It can be seen from Figure 5a that both J_{ph} values can reach saturation



Figure 5. (a) Photocurrent densities and (b) charge collection efficiencies vs effective voltage $(J_{\rm ph}-V_{\rm eff})$ characteristics for both optimal devices.

(13.04 and 11.39 mA cm⁻² for DRBDTCO and *d*DRBDTCO, respectively) when effective voltage $V_{\rm eff}$ arrives at a relatively low voltage of 2 V. These data suggest that the photogenerated excitons are dissociated into free charge carriers and charge carriers are collected at the electrodes very efficiently, with little geminate or bimolecular recombination; thus, high FFs are achieved. Under short-circuit conditions, both $J_{\rm ph}/J_{\rm sat}$ ratios reach 95%, suggesting high exciton dissociation efficiencies for the two molecule-based devices, but at the maximal power output point, although recombination will be strongly competing with carrier extraction, the $J_{\rm ph}/J_{\rm sat}$ of DRBDTCO:PC71BM-based devices (86%) is slightly higher than that of *d*DRBDTCO:PC71BM-based devices (84%), indicating a higher charge collection efficiency and less bimolecular recombination for DRBDTCO-based devices.^{57,58} The lower $J_{\rm ph}/J_{\rm sat}$ (81.95%)⁵⁰ at the maximal power output point should be responsible for the relatively lower FF of DR3TBDT-based devices. The photoluminescence (PL) spectra (Figure S12) showed that blending DRBDTCO with $PC_{71}BM$ led to almost complete fluorescence quenching (95%) of DRBDTCO, indicating effective photoinduced charge transfer between DRBDTCO and PC71BM in the active layer. However, the level of PL quenching (86%) in the dDRBDTCO:PC71BM active layer is lower than that of DRBDTCO. Thus, it is possible that fewer excitons are quenched in the *d*DRBDTCO:PC₇₁BM blend, therefore giving a lower J_{sc} ⁵⁹ These results are consistent with the overall performance as shown in Table 2 and indicate that the dimer

molecule *d*DRBDTCO with a flexible linker might not be a good strategy for achieving a high-performance molecule.

2.4. Morphology and Mobility. To investigate the reasons for their high FFs and the difference in their EQEs for these two molecules of DRBDTCO and *d*DRBDTCO, morphological characteristics of their optimal active layers were studied by transmission electron microscopy (TEM) and tapping-mode atomic force microscopy (AFM). From the AFM images (Figure 6a,b), both blend films exhibit a uniform



Figure 6. Tapping-mode AFM height images of (a) DRBDTCO:PC₇₁BM blend films and (b) dDRBDTCO:PC₇₁BM blend films. TEM images of (c) DRBDTCO:PC₇₁BM blend films and (d) dDRBDTCO:PC₇₁BM blend films with SVA treatment. The scale bars are 200 nm.

and smooth surface morphology with root-mean-square (rms) surface roughness values of 0.46 and 0.89 nm for *d*DRBDTCO and DRBDTCO, respectively. The film of DR3TDOBDT blended with $PC_{71}BM$ also possesses a small rms surface roughness of 1.06 nm,⁴⁹ compared with the rms surface roughness of 4.38 nm for the DR3TBDT: $PC_{71}BM$ film.⁵⁰ As shown in panels c and d of Figure 6, both blend films of DRBDTCO and *d*DRBDTCO exhibit good phase separation with a 15–20 nm domain size and a bicontinuous interpenetrating network, supporting their high FFs.⁶⁰ The less ordered fibrillar structure of the DR3TBDT: $PC_{71}BM$ (Figure S13) blend film should contribute to its lower FF compared with that of the asymmetric DRBDTCO-based devices.

Structural orders of both molecules in pure and blend films were also characterized by GIXD measurement (Table 3). Outof-plane and in-plane line cuts of GIXD of blend films are presented in Figure 7. As shown in Figure 7a, the as-cast DRBDTCO film showed obvious (h00) reflections in the outof-plane direction and complementary (010) reflection appearing in the in-plane direction, suggesting an edge-on

Table 3. Morphological Data from Out-of-Plane GIXD

		(100	(010)		
blend	(A ⁻¹)	d (Å)	crystal size (Å)	(A^{-1})	d (Å)
DRBDTCO:PC71BM	0.332	18.9	149	1.75	3.59
dDRBDTCO:PC71BM	0.311	20.2	121	1.73	3.63

orientation relative to the substrate. However, dDRBDTCO showed broad angle spreading (h00) and azimuthally independent (010) reflections. After SVA treatment (Figure S14), the (010) of dDRBDTCO is only oriented along the q_{xy} direction with a reduced amorphous scattering ring, indicating a preferred edge-on orientation. Under the as-cast and optimal conditions, dDRBDTCO exhibited less crystallinity than DRBDTCO did. This result may be related to the long and flexible octamethylene bridge in dDRBDTCO.

For their optimal blend films, similar obvious (h00) reflections could be observed, indicative of a long-range order and lateral packing of the backbones. The (100) peak in the out-of-plane direction of DRBDTCO is located at 0.332 Å⁻¹, which is larger than that of dDRBDTCO (0.311 Å⁻¹), corresponding to their alkyl–alkyl distances of 18.9 and 20.2 Å, respectively. The crystallite orientation of both molecules transforms from edge-on in pure film to face-on in optimal blend films, which are beneficial for exciton diffusion and charge transport. The (010) peaks for DRBDTCO and dDRBDTCO were located at 1.75 and 1.73 Å⁻¹, respectively, representing $\pi-\pi$ stacking distances of 3.59 and 3.63 Å, respectively. These results indicate that the flexible link in dDRBDTCO indeed interrupts its packing in the solid state.

Charge transport properties of holes and electrons are also playing important roles in the photovoltaic performance of devices. The mobilities of the optimized devices were measured by the space charge limited current (SCLC) method (Figure S15) with ITO/PEDOT:PSS/ITO/PEDOT/small molecules:PC71BM/Au and Al/small molecules:PC71BM/Al device structures for hole and electron mobilities, respectively. The hole and electron mobilities for DRBDTCO-based optimal devices are 6.5×10^{-4} and 4.7×10^{-4} cm² V⁻¹ s⁻¹, respectively. For the best dDRBDTCO-based device, the hole and electron mobilities are 5.9×10^{-4} and 3.9×10^{-4} cm² V⁻¹ s⁻¹, respectively, which are slightly lower than those for DRBDTCO-based devices because of the larger $\pi - \pi$ stacking distance of dDRBDTCO as indicated above. The relatively higher and more balanced electron/hole mobilities of DRBDTCO:PC71BM and dDRBDTCO:PC71BM blend films are believed to contribute to the higher FFs of their devices compared with those of the DR3TBDT:PC71BM-based⁴⁹ and DR3TDOBDT:PC71BM-based⁵⁰ devices.⁶¹

3. CONCLUSION

In summary, we have designed and synthesized two new small molecule donor materials, DRBDTCO and dDRBDTCO, which contain a central asymmetric BDT unit and a flexible octamethylene linking unit, respectively. The solution-processed OPVs based on these two molecules exhibit high performance and outstanding FFs (>73%), which were ascribed to their ordered molecular packing, preferable morphologies with a feature size of around 15-20 nm, and more balanced charge transport abilities. The better performance of DRBDTCO with one a-BDT central unit is believed to be due to its relatively better absorption and the higher IQE of the active layer. Considering the similarity of the structure of DRBDTCO to that of DR3TBDT and to that of DR3TDOBDT, both of which have symmetric central BDT building blocks, its lower V_{oc} is surprising, but its better FF and maintained relatively high J_{sc} are still encouraging. Overall, the dimer molecule with a flexible linker connected to the asymmetric BDT unit seems not to work well. With these results, it would be worth exploring other BDT-based



Figure 7. GIXD patterns for pure films of (a) DRBDTCO and (b) dDRBDTCO and (c) DRBDTCO:PC₇₁BM and (d) dDRBDTCO:PC₇₁BM blend films. (e) Out-of-plane line cuts and (f) in-plane line cuts of the GIXD patterns for the blend films.

molecules with asymmetric conjugated side chains or more rigid linking units for a better packed morphology and higher performance and an in-depth understanding of the relationship between structures and performance.

4. EXPERIMENTAL SECTION

4.1. Materials. All reactions and manipulations were performed under an argon atmosphere with the use of standard Schlenk tube techniques. All starting materials were used as purchased from commercial sources unless stated otherwise. ETL-1 was purchased from Lumtec. PC71BM was purchased from American Dye Source. The synthetic routes of DRBDTCO and dDRBDTCO are shown in Scheme 1, with details described in the Supporting Information. Compounds 8-octylbenzo[1,2-b:4,5-b']dithiophen-4-ol (1), [4-octyl-8-(octyloxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl]bis (tributylstannane) (3b), and 5"-bromo-3,3"-dioctyl[2,2':5',2"-terthiophene]-5carbaldehyde (4) were synthesized according to the procedures described in the literature. The intermediates of dialdehyde DCHOBDTCO and quaternary aldehyde TCHOBDTCO were synthesized from Stille coupling in refluxing toluene for 24 h under an argon atmosphere in the presence of $Pd(PPh_3)_4$ as the catalyst. The target molecules, DRBDTCO and dDRBDTCO, were then prepared by Knoevenagel condensation of DCHOBDTCO and TCHOBDTCO with 3-ethyl-rhodanine and 3-octyl-rhodanine, respectively.

4.2. Measurements and Instruments. The 1 H and 13 C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV400 spectrometer. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF) was performed on a Bruker Autoflex III LRF200-CID instrument. Thermogravimetric analysis (TGA) was performed on a NETZSCH STA 409PC instrument under a purified nitrogen gas flow with a heating rate of 10 °C min⁻¹. Differential scanning calorimetry (DSC) was performed using a DSC Q100 V9.0 Build 275 analyzer under a purified nitrogen gas flow with a heating rate of 10 °C min⁻¹. UV-vis spectra were recorded with a JASCO V-570 spectrophotometer. Cyclic voltammetry (CV) experiments were performed with a LK98B II microcomputer-based electrochemical analyzer. All CV measurements were taken at room temperature with a conventional three-electrode configuration employing a glassy carbon electrode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a Pt wire as the counter electrode. Dichloromethane was distilled from calcium hydride under dry nitrogen immediately prior to use. Tetrabutylammonium phosphorus hexafluoride (Bu₄NPF₆, 0.1 M) in

dichloromethane was used as the supporting electrolyte, and the scan rate was 100 mV s⁻¹. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels were calculated from the onset oxidation potential and the onset reduction potential, using the equations $E_{\text{HOMO}} = -(4.80 + E^{\text{ox}}_{\text{onset}})$ and $E_{\text{LUMO}} = -(4.80 + E^{\text{re}}_{\text{onset}})$.

Atomic force microscopy (AFM) was performed using Multimode 8 atomic force microscope in tapping mode. The transmission electron microscopy (TEM) investigation was performed on a Philips Technical G² F20 instrument at 200 kV. The specimen for TEM measurement was prepared by spin-casting the blend solution on an ITO/PEDOT:PSS substrate, then floating the film on a water surface, and transferring the film to TEM grids. Grazing incidence X-ray scattering characterization of the thin films was performed at beamline 7.3.3 of Lawrence Berkeley National Laboratory. The scattering signal was recorded on a two-dimensional detector (Pilatus 1M) with a pixel size of 172 $\mu{\rm m},$ on a 91 \times 1043 array. The X-ray energy is 10 keV. The samples were ~ 15 mm long in the direction of the beam path, and the detector was located 320 mm from the sample center (distance calibrated using a silver behenet standard). An incidence angle of 0.18° was chosen, which gave the optimized signal-to-background ratio. Thin film samples were prepared on PEDOT:PSS-covered silicon wafers to match the device conditions. The data were processed and analyzed using the Nika software package.

Space charge limited current (SCLC) mobility was measured using an ITO/PEDOT:PSS/donor:PC₇₁BM/Au diode configuration for hole by taking the dark current density in the range of 0-7 V and fitting the results to a space charge limited form, where the SCLC equation is described by

$$J = \frac{9\varepsilon_0 \varepsilon_r \mu_0 V^2}{8L^3} \exp\left(0.89\beta \sqrt{\frac{V}{L}}\right)$$

where J is the current density, L is the film thickness of the active layer, μ_0 is the hole mobility, ε_r is the relative dielectric constant of the transport medium, ε_0 is the permittivity of free space (8.85 × 10⁻¹² F m⁻¹), and V is the internal voltage in the device (= $V_{appl} - V_{bi'}$ where V_{appl} is the voltage applied to the device and V_{bi} is the built-in voltage due to the relative work function difference of the two electrodes).

4.3. Measurement and Characterization of Devices. The devices were fabricated with a glass/ITO/PEDOT:PSS/do-nor:PC₇₁BM/ETL-1/Al structure. The ITO-coated glass substrates were cleaned by ultrasonic treatment in detergent, deionized water, acetone, and isopropyl alcohol under ultrasonication for 15 min each

and subsequently dried with a nitrogen flow. A thin layer (40 nm) of PEDOT:PSS (Clevios P VP AI 4083, filtered at 0.45 μ m) was spin-cast on top of precleaned ITO substrates and annealed in air at 150 °C for 10 min. Subsequently, the active layer was spin-coated from blend chloroform solutions of donors and PC₇₁BM. Then ETL-1 dissolved in methanol was spin-coated. Finally, a 60 nm Al layer was deposited under high vacuum (<2 × 10⁻⁴ Pa). The effective areas of cells were 4 mm² defined by shadow masks. The current density–voltage (*J*–*V*) curves of photovoltaic devices were obtained with a Keithley 2400 source-measure unit. The photocurrent was measured under illumination-simulated 100 mW cm⁻² AM 1.5G irradiation using a SAN-EI XES-70S1 solar simulator, calibrated with a standard Si solar cell. The average PCE was obtained using 15 devices under the same conditions. External quantum efficiencies were measured using a Stanford Research Systems SR810 lock-in amplifier.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemma-ter.7b00642.

Characterization data for the new compounds, thermogravimetric analysis, differential scanning calorimetry, cyclic voltammogram, internal quantum efficiency, photoluminescence spectra, J-V characteristics of SCLC, NMR spectra, mass spectra, and other device data (PDF)

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Notes

The authors declare no competing financial interest.

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