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Dithienosilole-Based Small-Molecule Organic Solar Cells with an Efficiency over 8%: Investigation of the Relationship between the Molecular Structure and Photovoltaic Performance

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Supporting Information

ABSTRACT: Two new acceptor—donor—acceptor (A-D-A) small molecules with 2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']-dithiophene (DTC) and (4,4'-bis(2-ethylhexyl) dithieno[3,2-b:2',3'-d]silole)–2,6-diyl (DTS) as the central building block unit and 3-ethyl-rhodanine as the end-capping groups have been designed and synthesized. The influence of the bridging atoms on the optical, electrochemical properties, packing properties, morphology, and device performance of these two molecules was systematically investigated. Although with only the difference of one atom on the central core units, the two molecules showed great different properties such as film absorption, molecular packing,



and charge transport properties. The optimized device based on molecule DR3TDTS exhibited a power conversion efficiency (PCE) of >8%.

1. INTRODUCTION

Bulk heterojunction (BHJ) organic photovoltaic cells (OPVs) have been considered to be one of the promising photovoltaic technologies, because of their advantages of low cost, lightweight, solution processability, and flexibility.¹⁻⁴ In the past decade, great attention has been paid to the design strategy of polymer and small molecule donor materials, including finely tuning conjugated polymer backbones, rationally changing the side chains, and suitably varying the substituents.^{5–12} Currently, power conversion efficiencies (PCEs) over 10% have been achieved for single junction organic solar cells using the BHJ device structure.¹³⁻¹⁸ For high-performance donor materials, several criteria must be met, i.e., strong absorption, suitable energy levels, high hole mobility, good solubility, and filmforming property. Besides, morphology of the BHJ blend film plays an important role in device performance, and a bicontinuous network of phase separated donor-acceptor morphology with length scale commensurating with exciton diffusion length would be ideal to harvest sunlight and generate high PCEs. Although some morphological control methods could tune the phase separation scale, 19-25 the initial morphology formation of the blend film, and the tunability of the morphology are largely determined by the donor intrinsic packing modes, miscibility, and phase separation with acceptor materials. Therefore, the property of donor materials is crucial for achieving ideal morphology and high-performance OPVs. Even minor changes in the chemical structure of the donor materials could cause large changes in their properties, thus leading to large difference in film morphology and device performance.

Two frequently used electron-donating units in the design of donor materials share a similar backbone: 2,6-(4,4-bis(2ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']-dithiophene (DTC) and (4,4'-bis(2-ethylhexyl) dithieno[3,2-b:2',3'-d]silole)-2,6diyl (DTS), respectively, with carbon and silicon as the bridge atoms. The influence of changing the bridge atom from carbon to silicon on the device performance has been well-studied in polymer-based OPVs.^{26–30} However, studies on the corresponding counterparts of small-molecule-based OPVs have received little attention.^{31,32} For rational design of highperformance donor molecules, a systematic investigation on the effect of changing a specific atom of a molecule on optoelectronic properties, molecular packing mode, and the morphology of the blend films, and further understanding the

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Scheme 1. Synthesis Routes of DR3TDTC and DR3TDTS



relationships between the chemical structure of donor materials and device performance are of high importance. Furthermore, with the advantages of small molecules including defined but versatile chemical structures (thus, easier energy level control), mobility tuning, and less batch-to-batch variation, 33-36 it is believed that small molecules are a good choice for investigating the structure-performance relationships.

Herein, we designed and synthesized two analogous small molecules, named DR3TDTC and DR3TDTS, with DTC and DTS as the central units, respectively (Scheme 1), with only the single one bridging atom difference. The influence of such small difference on the optical, electrochemical properties, packing properties, morphology and device performance of these two molecules were systematically investigated. Although the molecular structures of these two compounds were essentially the same, a large difference in their OPV performance was observed. The optimized device based on DR3TDTS exhibited a high PCE of 8.02%, while the device based on DR3TDTC only showed a low PCE of 0.75%. Our study demonstrates that such a small change in the central bridge atom could cause significant changes in the molecular packing/crystallization, which is closely correlated to the phase separation of donor and acceptor in the BHJ blend films and, thus, is crucial for the formation of the film morphology and their OPV performance.

2. RESULTS AND DISCUSSION

2.1. Thermal and Optical Properties. Thermogravimetric analyses (TGA) indicates that both of DR3TDTC and DR3TDTS exhibit good thermal stability up to 350 °C under N₂ atmosphere (see Figure S1 in the Supporting Information). The solution and normalized thin-film absorption spectra of DR3TDTC and DR3TDTS are presented in Figure 1a. DR3TDTC-diluted chloroform solutions show a maximum absorption peak at 529 nm, with a maximal absorption



Figure 1. (a) UV-vis absorption spectra of DR3TDTC and DR3TDTS chloroform solutions and as-cast films. (b) Cyclic voltammograms of DR3TDTC and DR3TDTS dichloromethane solutions with 0.1 mol L^{-1} Bu₄NPF₆ and a scan rate of 100 mV s⁻¹.

coefficient of $8.79 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. DR3TDTS exhibits similar absorption at 527 nm in solution, with a higher maximal coefficient of 9.46 \times 10⁴ M⁻¹ cm⁻¹. In the solid state,

Table 1. Optica	l and E	Electrochen	nical Data	of DR	3TDTC	and	DR3TI	DTS
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compound	$\lambda_{\rm max,sol} \ [{\rm nm}]$	$\varepsilon_{\rm sol} \; [{\rm M}^{-1} \; {\rm cm}^{-1}]$	$\lambda_{\max, \mathrm{film}}$ [nm]	$E_{\rm g}^{\rm opt, film} [{\rm eV}]$	ionization potential, IP $[eV]^a$	electron affinity, EA $[eV]^a$
DR3TDTC	529	8.79×10^{4}	579	1.71	4.93	3.27
DR3TDTS	527	9.46×10^{4}	610	1.66	4.94	3.28
^a As measured by	y cyclic voltamm	etry.				

DR3TDTC film displays an absorption peak at 579 nm, which is red-shifted by ~50 nm, relative to the solution absorption. DR3TDTS shows a much more red-shifted maximum absorption peak at 610 nm, and an obvious vibronic shoulder at 675 nm, indicating an effective intermolecular interactions between the molecule backbones.^{37,38} The optical band gaps of DR3TDTC and DR3TDTS are estimated to be 1.71 and 1.66 eV from the onset of the film absorption spectra, respectively.

2.2. Electrochemical Properties. The electrochemical properties of DR3TDTC and DR3TDTS were investigated by cyclic voltammetry (CV) in a dichloromethane solution. Ferrocene/ferrocenium of the (Fc/Fc^+) redox couple (4.8 eV below the vacuum level) was used as the internal calibration. Note that the reference value of 4.80 eV neglects the system-dependent variations in polarization energies between solution and solid state for the same materials. In many instances, the solid-state values of ionization potential (IP) and electron affinity (EA) are approximated experimentally via cyclic voltammetry measurements of the oxidation and reduction potentials carried out in solution.³⁹ Therefore, the IP values of the molecules in this work were estimated from the onset of the oxidation peak (vs the saturated calomel electrode (SCE)) in the cyclic voltammogram calculated using the equation

$$IP = e[E_{ox} - E(Fc/Fc^{+}) + 4.80]$$

and the EA values of the molecules were estimated from the onset reduction peak (vs SCE) in the cyclic voltammogram calculated by the equation 40,41

$$EA = e[E_{red} - E(Fc/Fc^{+}) + 4.80]$$

The estimated IP values are 4.93 and 4.94 eV for DR3TDTC and DR3TDTS, respectively. The estimated EA values are 3.27 and 3.28 eV for DR3TDTC and DR3TDTS, respectively. Some important optical and electrochemical properties of the two molecules are listed in Table 1.

2.3. Photovoltaic Performance. BHJ organic solar cells were fabricated using DR3TDTC and DR3TDTS as the electron donor materials and [6,6]-phenyl-C71-butyric acid methyl ester ($PC_{71}BM$) as the electron acceptor material with a device structure of glass/ITO/PEDOT:PSS/donor:acceptor/ ETL-1/Al, using the conventional solution spin-coating process, and tested under AM 1.5G illumination at an intensity of 100 mW cm⁻². ETL-1,⁴² which is used as the interfacial layer for cathodes, is a methanol-soluble fullerene surfactant developed by Jen et al., and its structure is shown in Figure S2 in the Supporting Information. The optimum current density vs voltage (J-V) curves with a donor: acceptor ratio of 1:0.8 (w/w) are shown in Figure 2, with more performance data under various conditions detailed in Table S1 in the Supporting Information. The device based on the DR3TDTC:PC71BM blend film without any post-treatment showed a PCE of 0.72% with an open-circuit voltage (V_{oc}) of 0.86 V, a poor short-circuit current (J_{sc}) of 2.63 mA cm⁻², and a low fill factor (FF) of 0.32. The device based on DR3TDTS without post-treatment showed values of PCE = 1.84%, V_{oc} = 0.86 V, $J_{sc} = 5.78$ mA cm⁻², and FF = 0.37. The similar V_{oc}



Figure 2. (a) Typical J-V curves of DR3TDTC:PC₇₁BM (1:0.8, w/w) and DR3TDTS:PC₇₁BM (1:0.8, w/w) with different treatments. (b) EQE spectra of DR3TDTC:PC₇₁BM and DR3TDTS:PC₇₁BM blend films with different treatments. (c) Normalized EQE spectra of DR3TDTC:PC₇₁BM and DR3TDTS:PC₇₁BM blend films with different treatments.

values could be attributed to the similar IP values of the two donor molecules. The low $J_{\rm sc}$ and FF values of the devices are attributed to the unoptimized morphology of the photovoltaic layers, which could be seen from the atomic force microscopy (AFM) and transmission electron microscopy (TEM) images and will be discussed below. In our previous work, we used a simple two-step annealing (TSA) approach that combined thermal annealing and solvent vapor annealing to tune the morphology of the active layer.⁴³ Herein, the same approach

donor	$V_{\rm oc}^{\ c} \ [V]$	$J_{\rm sc}^{\ c} \left[{\rm mA} {\rm cm}^{-2} \right]$	fill factor, FF ^c	PCE [%] ^{<i>c</i>,<i>d</i>}	thickness [nm]
DR3TDTC ^a	0.86 ± 0.01	2.54 ± 0.09	0.31 ± 0.01	$0.67 \pm 0.05 \ (0.72)$	108
DR3TDTC ^b	0.85 ± 0.01	2.74 ± 0.12	0.30 ± 0.01	$0.71 \pm 0.04 \ (0.75)$	107
DR3TDTS ^a	0.86 ± 0.01	5.62 ± 0.16	0.36 ± 0.01	$1.77 \pm 0.07 (1.84)$	110
DR3TDTS ^b	0.82 ± 0.01	13.67 ± 0.30	0.69 ± 0.01	$7.80 \pm 0.22 \ (8.02)$	110
^{<i>a</i>} Without post-treatment. ^{<i>b</i>} With TSA treatment. ^{<i>c</i>} Average values from 30 devices. ^{<i>d</i>} The best PCE values are shown in parentheses.					

Table 2. Current Density-Voltage Characteristics of the OPV Devices Based on DR3TDTC and DR3TDTS

was also employed in the device optimization. The device based on DR3TDTS:PC₇₁BM with TSA treatment showed significantly improved $J_{\rm sc}$ value of 13.97 mA cm⁻² and FF = 0.70, thus resulting in a significantly higher PCE of 8.02% (with an average PCE of 7.80%), which is among the highest values for dithienosilole-based organic solar cells. However, for the DR3TDTC-based device, TSA treatment had surprisingly little impact on the OPV performance with values of $V_{\rm oc}$ = 0.85 V, $J_{\rm sc}$ = 2.86 mA cm⁻², FF = 0.31, and PCE = 0.75%. (See Table 2.) Some other methods, such as the use of additives, were also used to tune the morphology of the DR3TDTC:PC₇₁BM blend films, and the devices all showed similar poor PCEs (<0.6%).

The external quantum efficiency (EQE) curves of the devices are shown in Figure 2b. As shown in Figure 2b, without posttreatment, the devices fabricated with both DR3TDTS:PC₇₁BM and DR3TDTC:PC₇₁BM blend films showed relatively low EQE, with maximum values of <30%. After TSA treatment, the EQE of the device based on DR3TDTS:PC₇₁BM was significantly improved with the maximum value of 68% and over 60% across the range of 475–665 nm, while the EQE of the device based on DR3TDTC:PC₇₁BM hardly changed. As illustrated from the normalized EQE curves in Figure 2c, the EQE spectra of the DR3TDTS-based devices without and with TSA treatment exhibited a red shift of ~30 nm and ~100 nm, respectively, in comparison with those of the DR3TDTC-based devices.

2.4. Light Absorption and Charge Transport Property. To further understand the high performance of the DR3TDTS-based device, the absorption and charge transport properties of the blend films were investigated. As shown in Figure 3, compared with the DR3TDTC:PC₇₁BM blend films, the DR3TDTS:PC₇₁BM blend films with and without TSA all show red-shifted absorption, which is consistent with the red shift of the EQE spectrum. In addition, the blend films of both two compounds exhibit much blue-shifted absorption peak compared with the pure donor films (see Figure 1a and Table



Figure 3. Ultraviolet–visible light (UV-vis) absorption spectra of DR3TDTC: $PC_{71}BM$ and DR3TDTS: $PC_{71}BM$ blend films with different treatments.

1), indicating that the addition of $PC_{71}BM$ disrupts the intermolecular packing of the donor molecules. After TSA treatment, the absorption peak of the DR3TDTS:PC71BM blend film is red-shifted by \sim 50 nm, relative to the film without any treatment, and exhibits an increasing shoulder peak at ~680 nm. These suggest that better molecular packing is formed for DR3TDTS after TSA treatment. In contrast, the case of DR3TDTC is completely different: the absorption of the DR3TDTC:PC71BM blend film with TSA treatment is similar to that without TSA. The hole mobilities of the two molecules were measured by the space charge limited current (SCLC) method (see Figures S3 and S4 in the Supporting Information) and the average mobility values are calculated over more than 10 devices. For the devices without any treatment, the hole mobilities are 7.04 (\pm 0.70) × 10⁻⁵ cm² V⁻¹ s⁻¹ for the DR3TDTC blend film and 9.97 (± 0.80) $\times 10^{-5}$ cm² V⁻¹ s⁻¹ for the DR3TDTS blend film, respectively. After TSA treatment, the hole mobilities are improved to 7.50 (\pm $(0.65) \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for the DR3TDTC blend film and $4.35(\pm 0.60) \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for the DR3TDTS blend film, respectively. For the devices without any treatment, the electron mobilities are 3.22 $(\pm~0.50)\times10^{-5}~\text{cm}^2~V^{-1}~\text{s}^{-1}$ for the DR3TDTC blend film and 6.92 (± 0.60) \times $10^{-5}~cm^2~V^{-1}~s^{-1}$ for the DR3TDTS blend film, respectively. After TSA treatment, the electron mobility increases significantly to 3.45 $(\pm 0.45) \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for the DR3TDTS blend film, while the mobility for the DR3TDTC blend film is 3.56 (\pm 0.55) \times 10⁻⁵ cm² V⁻¹ s⁻¹, with little change. The much improved and more balanced hole and electron mobilities of the DR3TDTS blend films after TSA treatment could promote charge transport and reduce charge recombination, thus leading to better device performance.

2.5. Film Microstructure and Morphology Analysis. To investigate the effect of the bridge atom on the molecular ordering at solid state, the microstructures of the films were characterized by X-ray diffraction (XRD) and grazing-incidence wide-angle X-ray scattering (GIWAXS). As shown in Figure S5 in the Supporting Information, the DR3TDTS neat film showed a strong (100) diffraction peak at $2\theta = 5.09^{\circ}$, while the DR3TDTC film showed no clear (100) diffraction, indicating a poor molecular packing behavior. The GIWAXS results of the blend films are shown in Figure 4. For the DR3TDTS:PC₇₁BM blend film without post-treatment, (100) reflection along the q_z direction was observed at 0.33 $Å^{-1}$, corresponding to an interchain distance of 19.0 Å. After TSA treatment, multiple higher-order (h00) reflections along the q_z -direction were observed for the DR3TDTS:PC71BM film, indicative of the long-range order and crystallinity in the blend film. In addition, the DR3TDTS:PC71BM blend film with TSA treatment showed a (010) reflection at 1.70 Å⁻¹, corresponding to $\pi - \pi$ stacking distances of 3.69 Å. DR3TDTS showed more-intensive (010) reflection along the q_z -direction than that along the q_{xy} . indicating a preferred face-on orientation. The preferred faceon orientation of the DR3TDTS:PC71BM blend film with TSA





Figure 4. GIWAXS images of (a, b) DR3TDTC:PC₇₁BM (1:0.8, w/w) and (c, d) DR3TDTS:PC₇₁BM (1:0.8, w/w) blend films from CHCl₃. (Panels a and c show the blend films without post-treatment; panels b and d shows the blend films with TSA treatment.) (e) Out-of-plane line cuts of GIWAXS patterns for the blend films.

treatment, facilitating charge transport, which is consistent with its higher J_{sc} and FF. However, both of the DR3TDTC:PC₇₁BM blend films with and without TSA showed only weak (100) peaks, indicating much less longrange ordered packing. The GIWAXS results demonstrate that TSA treatment is effective for improving the packing and orientation of DR3TDTS, but has little impact on those of DR3TDTC.

From the AFM images shown in Figure S4, the root-meansquare (RMS) roughness values are 0.26 and 0.37 nm for the DR3TDTC:PC₇₁BM and DR3TDTS:PC₇₁BM blend films without any treatment, respectively. After TSA treatment, the RMS roughness is 0.38 nm for DR3TDTC:PC₇₁BM and 0.66 nm for DR3TDTS:PC₇₁BM, indicating that all of the blend films are smooth with high quality. Transmission electron microscopy (TEM) studies (Figure 5) show that the morphologies of the blend films for these two compounds are quite different. Without post-treatment, both DR3TDTC:PC₇₁BM and DR3TDTS:PC₇₁BM blend films show no obvious phase separation of the donor and the acceptor, which could be harmful for charge transport, thus leading to low $J_{\rm sc}$ and FF. After TSA treatment, the DR3TDTC:PC₇₁BM blend film still shows no clear phase separation, which could be due to the poor packing properties of DR3TDTC. For the DR3TDTS:PC₇₁BM blend film with TSA treatment, the films exhibits a homogeneous interpenetrating network with a domain size of 20–30 nm, comparable to the exciton diffusion length.^{44,45} The excellent morphology of the DR3TDTS:PC₇₁BM blend film with TSA could increase exciton dissociation and charge transport efficiency and reduce charge carriers recombination, thus, the high $J_{\rm sc}$ and FF values.

Resonant soft X-ray scattering (RSoXS) were taken to investigate the phase aggregation of the blend films. As shown in Figure 5, the DR3TDTS:PC71BM blend film with TSA treatment show an interference ($q = 0.0146 \text{ A}^{-1}$, where q is the scattering vector) corresponding to a domain center-to-center distance of 43 nm. For DR3TDTS:PC71BM without TSA and DR3TDTS:PC71BM without (and with) TSA, no significant interference is observed, indicating no clear phase separation in these blend films. These results are consistent with the morphological results from TEM studies. These morphology information together with GIWAXS results demonstrate that (1) suitable donor-acceptor phase separation is one of the prerequisites for highly efficient OPV devices and (2) TSA treatment could redistribute the donor and acceptor phases in the DR3TDTS:PC71BM blend film to form optimal phase separation by promoting DR3TDTS crystallization. However, the TSA treatment does not work for the DR3TDTC:PC₇₁BM system, which might be due to some intrinsic packing property that needs to be investigated further.

The surprisingly significant difference in morphology and device performance of these two molecules must be attributed to the change of bridging atoms. Compared to DR3TDTC, the larger Si atom and the longer C–Si bond in the central donor unit of DR3TDTS could reduce the interaction of the bulk alkyl side chains, thus reducing the steric hindrance, leading to the formation of strong π – π interactions between the molecule backbones. The higher-ordered packing and better orientation of DR3TDTS at solid state could promote better optical absorption, higher mobility, and the formation of suitable phase separation when blended with PC₇₁BM. Therefore, the devices based on DR3TDTS exhibit outstanding photovoltaic performance with a PCE over 8%, while devices based on DR3TDTC show a poor PCE of <1%.

3. CONCLUSION

In conclusion, we synthesized two new small molecules with DTC and DTS as the central building block units, respectively. Although with only the difference of one atom on the central core units, the two molecules showed great different properties such as film absorption, molecular packing, and charge transport properties. DR3TDTS with a Si atom in the central core showed more favorable absorption and packing behavior than DR3TDTC with a C atom in the central core. The optimized devices based on DR3TDTS with TSA treatment exhibited a PCE over 8%, while a PCE below 1% was obtained for the DR3TDTC-based device. Morphology investigation demonstrated that the higher PCE of the DR3TDTS-based device was mainly ascribed to the suitable phase separation with a domain size of 20–30 nm after TSA treatment. The results



Figure 5. TEM images of (a, b) DR3TDTC:PC₇₁BM (1:0.8, w/w) and (c, d) DR3TDTS:PC₇₁BM (1:0.8, w/w) blend films. (Panels a and c show the blend films without post-treatment; panels b and d shows the blend films with TSA treatment.) (e) Resonant soft X-ray scattering (RSoXS) profiles of DR3TDTC:PC₇₁BM and DR3TDTS:PC₇₁ BM films without post-treatment and with TSA treatment.

indicate that delicate molecule design is still one of the fundamental tasks for achieving high-performance small-molecule-based OPVs.

4. EXPERIMENTAL SECTION

4.1. Synthesis. All reactions and manipulations were carried under an argon atmosphere using standard Schlenk techniques. All starting materials were purchased from commercial suppliers and used without further purification. The synthesis routes of DR3TDTC and DR3TDTS are shown in Scheme 1, with details described in the Supporting Information. Compounds 5-bromo-3,3-dioctyl-2,2':5,2"terthiophene-2-carbaldehyde (1), 4,4'-bis(2-ethylhexyl)-2,6-bis-(trimethylstannyl)-4H-cyclopenta [2,1-b:3,4-b']-dithiophene (2), and 4,4'-bis(2-ethylhexyl)-2,6-bis(trimethylstannyl)-dithieno[3,2-b:2',3'd]silole) (3) were synthesized according to the literature. $^{26,46-48}$ The intermediates of dialdehyde DCHO3TDTC and DCHO3TDTS 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, DR3TDTC and DR3TDTS, were then prepared by Knoevenagel condensation of DCHO3TDTC and DCHO3TDTS with 3-ethyl-rhodanine, respectively.

4.2. Measurements and Instruments. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were performed on a Bruker Autoflex III instrument. Thermogravimetric analysis (TGA) was performed using a Netzsch Model STA 409PC instrument under purified nitrogen gas flow with a heating rate of 10 °C min⁻¹. ¹H nuclear magnetic resonance (NMR) spectra were obtained using a Bruker Model AV400 spectrometer. UV-vis spectra were obtained with a JASCO Model V-570 spectrophotometer. X-ray diffraction (XRD) experiments were performed on a Bruker Model D8 FOCUS X-ray diffractometer with Cu K α radiation (λ = 1.5406 Å) at a generator voltage of 40 kV and a current of 40 mA. Atomic force microscopy (AFM) investigation was performed using a Bruker MultiMode 8 system in "tapping" mode. Transmission electron microscopy (TEM) was performed on a Philips Technical G² F20 system at 200 kV. Cyclic voltammetry (CV) experiments were performed with a Model LK98B II microcomputer-based electrochemical analyzer in dichloromethane solutions. All CV measurements were carried out at room temperature with a conventional threeelectrode 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 argon 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.

Mobility was measured via the space charge limited current (SCLC) method by taking the dark current density in the range of 0-6 V and fitting the results to a space-charge-limited form, where SCLC 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), V is the internal voltage of the device ($V = V_{\rm appl} - V_{\rm bi}$), $V_{\rm appl}$ is the applied voltage to the device, and $V_{\rm bi}$ is the built-in voltage due to the relative work function difference of the two electrodes.

The current density–voltage (J-V) characteristics of photovoltaic devices were obtained by a Keithley 2400 source-measure unit. The photocurrent was measured under illumination with simulated 100 mW cm⁻² AM1.5G irradiation using a xenon-lamp-based solar simulator [Oriel 96000 (AM1.5G)] in an argon-filled glovebox. Simulator irradiance was characterized using a calibrated spectrometer, and the illumination intensity was set using a certified silicon diode. The external quantum efficiency (EQE) value of the encapsulated device was obtained with a halogen-tungsten lamp, monochromator, optical chopper, and lock-in amplifier in air, and the photon flux was determined using a calibrated silicon photodiode.

4.3. Fabrication of Organic Solar Cells. The photovoltaic devices were fabricated with a structure of glass/ITO/PEDOT:PSS/ donor:acceptor/ETL-1/Al. The ITO-coated glass substrates were cleaned subsequently by ultrasonic treatment in detergent, deionized water, acetone, and isopropyl alcohol under ultrasonication for 15 min each solvent and then dried by a nitrogen flow. A thin layer of PEDOT:PSS (Baytron P VP AI 4083, filtered at 0.45 µm) was spincoated (3000 rpm, ca. 40 nm thick) onto the ITO surface. After being baked at 150 °C for 20 min, the substrates were transferred into an argon-filled glovebox. The active layer then was spin-coated from donor (10 mg/mL):PC71BM blend chloroform solution with different ratios at 1700 rpm for 20 s. Thermal annealing was carried out on a digitally controlled hot plate at 100 °C for 10 min after active layer spin coating in an argon-filled glovebox. Then, the films was placed in a glass petri dish containing 150 μ L of chloroform for solvent vapor annealing for 1 min. Subsequently, ETL-1 solution (1 mg/mL) was spin-coated on top of the active layers. Finally, a 50-nm-thick Al layer was deposited on ETL-1 film under high vacuum ($< 2 \times 10^{-4}$ Pa). The thickness of active layers was measured using Dektak 150 profilometer. The effective area of each cell was 4 mm² defined by masks for the solar cell devices discussed in this work.

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.5b02616.

Detailed synthetic procedures and characterization data for the new compounds and additional experimental results (PDF)

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Notes

The authors declare no competing financial interest.

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