# CHEMISTRY OF MATERIALS

# Self-Organizing Mesomorphic Diketopyrrolopyrrole Derivatives for Efficient Solution-Processed Organic Solar Cells

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Supporting Information

**ABSTRACT:** We describe the synthesis, self-organization, and photovoltaic properties of diketopyrrolopyrrole (DPP)-based mesomorphic small-molecule materials, 3,6-bis{5-(4alkylphenyl)thiophen-2-yl}-2,5-di(2-ethylhexyl)-pyrrolo[3,4-c]pyrrole-1,4-diones (DPP-TP6 and DPP-TP12), which have strong visible absorption characteristics. The effects of varying terminal alkyl chains on the self-assembling properties and photovoltaic device performances have been studied. With the appropriate ratio of the lengths of the alkyl chains to its rigid DPP core, DPP-TP6 exhibits liquid-crystalline properties and forms well-developed nanostructured bulk heterojunction



(BHJ) architectures with a fullerene derivative (PC71BM). Organic solar cells (OSCs) employing BHJ DPP-TP6:PC71BM films show a power conversion efficiency as high as 4.3% with a high open-circuit voltage of 0.93 V and a fill factor of 0.55. These results demonstrate that liquid-crystalline organization to direct molecular self-assembly is a promising strategy for fabricating high-performance solution-processed small-molecule OSCs.

**KEYWORDS:** organic solar cells, diketopyrrolopyrrole, bulk heterojunction, self-organization, liquid crystals

# INTRODUCTION

Organic solar cells (OSCs) are drawing considerable interest for the great promise as a next-generation clean and renewable energy source.<sup>1,2</sup> To date, intensive research efforts have focused on developing dye-sensitized solar cells,<sup>3</sup> low-bandgap polymer/fullerene bulk heterojunction (BHJ) solar cells,<sup>1a</sup> and vacuum-deposited small-molecule solar cells.<sup>5</sup> Recently, solution-processed small-molecule OSCs<sup>1f-i,6,7</sup> have been emerging as an attractive alternative to widely studied polymeric counterparts, offering several promising advantages such as monodispersity and well-defined structure, easy purification, and less batch-to-batch variation (better reproducibility). Indeed, high power conversion efficiencies (PCEs) exceeding 6% have been accomplished thus far for smallmolecule BHJ OSCs,<sup>6a-d</sup> approaching those with conjugated polymers. However, overall performance of solution-processed small-molecule devices still lags behind alternative sources. In most cases, the small molecular system suffers from inferior film quality and interconnectivity in the active layer because of their intrinsic crystallization, which results in low device fill factors.

Because of the relatively large exciton binding energy (e.g., 0.3 eV) and short exciton diffusion length (e.g., 10-20 nm) in organic semiconductors, a large donor/acceptor (D/A) interfacial area should be required for efficient exciton

dissociation and charge carrier transport in BHJ OSCs.<sup>8</sup> However, if the scale of the phase-segregated domains in the BHJ layer is smaller than the Coulomb capture radius, it will increase the geminate or bimolecular recombination probability.<sup>8a</sup> Therefore, the design of suitable donor molecules, which are capable of forming nanoscale ordered structures and overall optimum film morphologies, is a prerequisite for highperformance BHJ OSCs. Our intention here is to utilize selforganization of liquid-crystalline (LC) molecules9 for the fabrication of well-ordered BHJ architectures in small-molecule OSCs, to achieve better photovoltaic efficiencies. A few researches have been conducted on tuning the active layer morphology by using LC donor molecules.<sup>10</sup> As a platform to explore this approach, we have designed and synthesized simple diketopyrrolopyrrole (DPP)-based small molecules, DPP-TP6 and DPP-TP12 (Scheme 1), since the incorporation of multiple flexible chains into the rigid  $\pi$ -conjugated DPP core can provide highly light-absorbing donor materials forming LC ordering. Various DPP-based small molecules<sup>7</sup> and polymeric materials<sup>4b,11</sup> have been developed to render high charge carrier

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#### Scheme 1. Synthesis of DPP-Based Donor Molecules<sup>a</sup>



"Reaction conditions: (i) 1-bromo-2-ethylhexane, K<sub>2</sub>CO<sub>3</sub>, DMF; (ii) NBS, CHCl<sub>3</sub>; (iii) 2-(4-alkylphenyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane, K<sub>2</sub>CO<sub>3</sub>, Pd(PPh<sub>3</sub>)<sub>4</sub>, THF/H<sub>2</sub>O.

mobility and photovoltaic properties. Nguyen and co-workers reported DPP-containing small-molecule donors that achieved up to 4.8% power conversion efficiencies (PCEs) with [6,6]-phenyl- $C_{71}$ -butyric acid methyl ester (PC<sub>71</sub>BM) in solution-processed BHJ devices.<sup>7a,b</sup>

In this study, we investigate the optoelectronic and selforganizing properties of **DPP-TP6** and **DPP-TP12**, as well as their performance as donor materials in solution-processed OSCs. Furthermore, we here demonstrate that the formation of well-developed nanostructured domains through LC organization has a drastic impact on the photovoltaic properties.

#### RESULTS AND DISCUSSION

Synthesis and Characterization. DPP-TP6 and DPP-TP12 were synthesized from dithienyl-DPP precursor (1),<sup>12</sup> using palladium-catalyzed Suzuki-Miyaura cross-coupling reactions (see Experimental Section and the Supporting Information for details). To make donor molecules with a deeper highest occupied molecular orbital (HOMO) level suitable for OSC applications, the phenylthiophene-appended DPP was designed as the low bandgap  $\pi$ -conjugated core and was tethered with multiple alkyl chains, which enhance solubility and film-forming properties. The chemical structures of the final products were ascertained by NMR spectroscopy, matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry, and elemental analysis after purification. As expected, DPP-TP6 and DPP-TP12 are soluble in common organic solvents such as CHCl<sub>3</sub>, THF, toluene, and chlorobenzene.

Thermogravimetric analysis (TGA) indicates that **DPP-TP6** and **DPP-TP12** possess high thermal stability with a 5% weight loss temperature ( $T_d$ ) greater than 360 °C under N<sub>2</sub> atmosphere (Supporting Information, Figure S1). Thermal behavior of these compounds have been further studied by differential scanning calorimetry (DSC). As shown in Figure 1, **DPP-TP6** with hexyl terminal chains exhibits two endothermic peaks at 117 and 170 °C upon heating, corresponding to LC mesophase and isotropic phase transitions, respectively.<sup>13</sup> In **DPP-TP12**, the introduction of dodecyl chains on both terminals results in a decrease of the isotropization temperature to 128 °C and the LC mesophase disappears.

**Optical Properties.** The UV/vis absorption spectrum of **DPP-TP6** in CHCl<sub>3</sub> solution presents an absorption peak  $(\lambda_{max})$  at 602 nm (Figure 2a), which corresponds to the  $\pi - \pi^*$  (HOMO  $\rightarrow$  LUMO) transition. The structured absorption is likely intrinsic to a single molecule with restricted intramolecular motion. Compared with dilute solutions, a spin-



Figure 1. DSC thermograms of DPP-TP6 and DPP-TP12 at 5  $^{\circ}\mathrm{C}$  min  $^{-1}$ 



Figure 2. (a) UV/vis absorption spectra of DPP-TP6 in  $CHCl_3$  solution and an as-spun thin film. (b) Photoelectron yield spectrum of a DPP-TP6 thin film.

coated thin film of **DPP-TP6** exhibits a red-shifted  $\lambda_{max}$  at 637 nm with a large maximum absorption coefficient of 4.7 × 10<sup>4</sup> cm<sup>-1</sup>, and a distinct subpeak at 581 nm. The red-shift of the lowest vibronic band in the solid state originates from *J*-type aggregation,<sup>13</sup> because of the excitonic coupling between the transition dipoles of adjacent molecules. The absorption bands thus extend from 500 nm to a lower energy level of ~700 nm in the thin films of **DPP-TP6** and **DPP-TP12**, and their optical bandgap is estimated to be 1.8 eV from the absorption edge.

The HOMO energy levels of **DPP-TP6** and **DPP-TP12** in the thin films have been determined to be approximately -5.5eV by photoelectron yield spectroscopy (Figure 2b). The lowlying HOMO levels and sufficient LUMO offsets (>0.6 eV), allow these materials to serve as electron donors in combination with PC<sub>71</sub>BM as an acceptor material, which has HOMO and LUMO levels of -6.1 and -4.3 eV, respectively. The optical data of **DPP-TP6** and **DPP-TP12** are summarized in Table 1.

To clarify how the thermotropic LC behavior can affect the molecular assembly and optoelectronic properties, the

#### Table 1. Optical Properties of DPP-Based Materials

absorption	$\lambda_{\max}$ (nm)			
solution <sup>a</sup>	film <sup>b</sup>	HOMO <sup>c</sup> (eV)	LUMO <sup>d</sup> (eV)	${\mathop{E_{g}}\limits^{d}}$ (eV)
602, 563	637, 581	-5.50	-3.69	1.81
603, 563	651, 592	-5.48	-3.68	1.80
	absorption solution <sup>a</sup> 602, 563 603, 563	absorption λ <sub>max</sub> (nm) solution <sup>a</sup> film <sup>b</sup> 602, 563 637, 581 603, 563 651, 592	$\begin{array}{c} \mbox{absorption } \lambda_{\max} \ (nm) \\ \mbox{solution}^{a} \ \ film^{b} \\ 602, 563 \ \ 637, 581 \\ 603, 563 \ \ 651, 592 \\ \end{array} \begin{array}{c} -5.50 \\ -5.48 \end{array}$	$\begin{array}{c} \mbox{absorption } \lambda_{max} \ (nm) \\ \mbox{solution}^{a} \ \ film^{b} \\ 602, 563 \\ 603, 563 \\ 651, 592 \\ \ \ -5.48 \\ \ \ \ -3.68 \end{array} \begin{array}{c} \mbox{LUMO}^{d} \\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ $

<sup>*a*</sup>In CHCl<sub>3</sub> solution at 10<sup>-4</sup> M. <sup>*b*</sup>Spin-coated thin film (ca. 100 nm). <sup>*c*</sup>Determined by photoelectron yield spectroscopy. <sup>*d*</sup>LUMO = HOMO +  $E_{g'}$  in which the optical energy gap,  $E_{g'}$  was derived from the absorption onset of the thin film.

absorption spectra of **DPP-TP6**:PC<sub>71</sub>BM and **DPP-TP12**:PC<sub>71</sub>BM (1:1, w/w) blend films have been measured by varying the thermal annealing temperatures (Figure 3). The



Figure 3. Changes in absorption spectra of (a) DPP-TP6: $PC_{71}BM$  (1:1, w/w) and (b) DPP-TP12: $PC_{71}BM$  (1:1, w/w) blend thin films upon thermal annealing.

blend films were deposited by spin-coating from CHCl<sub>3</sub> solutions, with a donor concentration of 7-8% (w/v). It should be noted that the absorption coefficient of the Jaggregation band at ~640 nm observed for the as-cast DPP-TP6:PC71BM film steadily decreases and at the same time a new absorption band centered around 540 nm emerges, as the annealing temperature increases to 140 °C (Figure 3a). This hypsochromic shift of the absorption band is the defining characteristic of H-type aggregation.<sup>14</sup> Therefore, upon thermal treatment, the J-aggregates composed of the DPP-TP6 molecules eventually transform into the thermodynamically favored H-aggregates, accompanied by specific stacking changes within the thin film. Very similar spectral changes have been observed for pristine DPP-TP6 thin films as a function of annealing temperature (Supporting Information, Figures S2 and S3). This thermo-responsive reorganization behavior for DPP-TP6 is in accordance with the appearance of the LC state from 117 °C upon heating (Figure 1), in which the DPP-TP6 molecules retain at least some mobility. However, for DPP-TP12:PC71BM films, the initial peak position and absorption intensity do not change significantly by thermal annealing (Figure 3b), suggesting that the DPP-TP12 molecules with longer dodecyl chains predominantly form slipped-stacking Jaggregates in the thin films over a wide range of temperatures. The difference in the terminal chain length has a strong impact on the mesomorphism and self-organizing behavior of the donor molecules in both the neat and the BHJ thin films.

**Solar Cell Performance.** Solution-processed BHJ solar cells have been fabricated using **DPP-TP6** and **DPP-TP12** as an electron donor and  $PC_{71}BM$  as an acceptor with a standard device structure (Figure 4): ITO/PEDOT:PSS (40 nm)/ donor:PC<sub>71</sub>BM blend (90–120 nm)/LiF (1 nm)/Al (100 nm).



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**Figure 4.** Energy-level diagram of BHJ solar cells based on **DPP**-**TP**:PC<sub>71</sub>BM layer and the calculated HOMO/LUMO distributions of the  $\pi$ -conjugated core of the donor molecules.

Various donor:PC<sub>71</sub>BM blend ratios (1:1, 1.5:1, and 2:1, w/w), film thickness, and postdeposition thermal annealing have been examined. Table 2 summarizes the photovoltaic parameters of representative BHJ devices obtained under AM 1.5G illumination at an intensity of 100 mW cm<sup>-2</sup>. These devices provide reasonably high open-circuit voltages ( $V_{oc}$ ) of ~0.93 V, regardless of the D/A weight ratio, which is attributed to a large difference (~1.2 eV) between the HOMO level of the donors and the lowest unoccupied molecular orbital (LUMO) level of the PC<sub>71</sub>BM acceptor<sup>15</sup> (Figure 4).

Figure 5a depicts the current density-voltage (J-V)characteristics of as-cast and annealed DPP-TP6:PC71BM (1:1, w/w) BHJ solar cells. The optimized device based on the **DPP-TP6**:PC<sub>71</sub>BM layer with annealing at 140 °C, exhibits a short-circuit current density  $(I_{sc})$  of 8.4 mA cm<sup>-2</sup>,  $V_{oc}$  of 0.93 V, and a fill factor (FF) of 0.55, yielding a power conversion efficiency (PCE) of 4.3% (Table 2); whereas the as-cast device gives a much lower PCE of 2.6%. It can be found that for DPP-TP6-based devices, thermo-responsive LC molecular organization improves J<sub>sc</sub> and FF, significantly increasing device efficiencies. The substantial increases in  $J_{sc}$  and FF should be attributed to the reduction of series resistance  $(R_s)$  and the increase of shunt resistance  $(R_{\rm sh})$  of the devices, upon the LC phase transition in the active layer. From a physical point of view, R<sub>s</sub> is associated with the conductivity of the semiconductors, and thus the carrier mobility in the active layer; while  $R_{\rm sh}$  is related to the loss of charge carriers via recombination and leakage.<sup>8</sup> Indeed, the dark *I-V* curves of the devices (inset of Figure 5a) reveals the effective suppression of the leakage current under low biases after thermal annealing, indicating improved diode characteristics. Similar enhancement in the PCEs upon thermal annealing has been attained for other DPP-TP6:PC71BM blend ratios as well (Table 2). When the DPP-TP6:PC71BM blend ratios are changed to 1.5:1 and 2:1, the  $J_{sc}$  tends to decrease gradually and the  $V_{oc}$  remains relatively constant (Supporting Information, Figure S4).

To address the origin of the enhanced device performances, we have measured the incident photon-to-current conversion efficiency (IPCE) spectra for the **DPP-TP6**-based BHJ devices (Figure 5b). With annealing at 140 °C, a pronounced enhancement in photoresponses ranging from 350 to 600 nm, corresponding to the superposition of the absorption of *H*-aggregated **DPP-TP6** and PC<sub>71</sub>BM molecules, can be observed. The IPCE reaches the maximum value at ~70%, which is considerably high for small-molecule BHJ solar cells, implying highly efficient charge extraction. In contrast, negligible enhancement of the device performances (PCE = 1.1% to

	Table	2.	Photovo	ltaic	Parameters	for	Solution-	Processed	BHJ	Solar	Cells"
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donor	D/A ratio (w/w)	thickness (nm)	annealing temp. (°C)	$J_{\rm sc}  ({\rm mA/cm^2})$	$V_{\rm oc}$ (V)	FF (%)	PCE (%)	$R_{\rm s}~(\Omega~{\rm cm}^2)$	$R_{\rm sh}~(\Omega~{\rm cm}^2)$
DPP-TP6	1:1	112	as-spun	$7.51 \pm 0.26$	0.92	$38 \pm 1$	$2.6 \pm 0.1$	18.9	566
	1:1	107	140	$8.27 \pm 0.10$	0.93	54 ± 1	$4.2 \pm 0.1$	9.1	773
	1.5:1	114	as-spun	$6.65 \pm 0.26$	0.91	36 ± 2	$2.1 \pm 0.2$	12.8	238
	1.5:1	94	140	$7.28 \pm 0.08$	0.93	$51 \pm 1$	$3.5 \pm 0.1$	12.1	1426
	2:1	112	as-spun	$7.04 \pm 0.47$	0.91	$32 \pm 1$	$2.0 \pm 0.2$	36.0	213
	2:1	101	140	$6.24 \pm 0.10$	0.94	$50 \pm 1$	$3.0 \pm 0.1$	17.2	967
DPP-TP12	1:1	97	as-spun	$3.86 \pm 0.11$	0.91	$31 \pm 2$	$1.1 \pm 0.1$	69.4	352
	1:1	108	120	$3.73 \pm 0.17$	0.93	$35 \pm 1$	$1.2 \pm 0.1$	85.1	451

<sup>*a*</sup>Device structure: ITO/PEDOT:PSS/donor:PC<sub>71</sub>BM blend/LiF/Al, with 4 mm<sup>2</sup> illuminated areas. All devices were characterized under the standard AM 1.5G 1 Sun test conditions. Power conversion efficiencies (PCEs) were derived from the equation: PCE =  $(J_{sc} \times V_{oc} \times FF)/P_0$ , where  $J_{sc}$  = short-circuit current density,  $V_{oc}$  = open-circuit voltage, FF = fill factor, and  $P_0$  = incident light intensity. Series resistance ( $R_s$ ) and shunt resistance ( $R_{sh}$ ) were estimated from the reverse slopes of the J-V curves at zero current and at zero voltage, respectively.



**Figure 5.** (a) J-V characteristics under one sun illumination (inset: dark J-V curves) and (b) IPCE spectra for BHJ solar cells based on **DPP-TP6**:PC<sub>71</sub>BM (1:1, w/w) blend as-cast and after thermal annealing at 140 °C for 10 min.

1.2%) has been observed for **DPP-TP12**:PC<sub>71</sub>BM devices even after annealing (Supporting Information, Figure S5). Despite the similarities in molecular structures and physical properties, the non-LC **DPP-TP12** molecules are unable to reorganize into an appropriate chromophore packing structure upon heating, resulting in a relatively low device performance (Table 2).

Thin Film Morphology and Structures. To gain deeper insight into the variation in the photovoltaic properties of DPP-TP6:PC<sub>71</sub>BM BHJ devices by LC organization, the active layer morphologies have been analyzed using polarizing optical microscopy (POM) and atomic force microscopy (AFM), as shown in Figure 6. The morphology of the active material in the BHJ solar cells significantly affects the device performance. With increasing annealing temperature, the POM images indicate the emergence of highly birefringent LC domains with sizes over several tens of micrometers (Figure 6a–c), implying the spontaneous formation of well-organized crystallites within the blend films.



**Figure 6.** Polarizing optical micrographs (left panels) and AMF height images (right panels) of **DPP-TP6**:PC<sub>71</sub>BM (1:1, w/w) films on ITO-coated glass substrates: (a, d) as-spun and after thermal annealing at (b, e) 120 °C and (c, f) 140 °C for 10 min. The scan size for the AFM images is  $5 \times 5 \mu$ m.

The AFM image of the as-cast DPP-TP6:PC71BM blend film exhibits a small-grained (100-200 nm in size) macrophaseseparated morphology, with a root-mean-square (RMS) roughness of 12.6 nm (Figure 6d); whereas the pure DPP-TP6 neat film has a smooth surface (RMS = 1.0 nm, Supporting Information, Figure S6). This coarse surface structure of the blend films is ascribed to the low entropy of mixing between DPP-TP6 and PC71BM during the spincoating process. After thermal annealing at 140 °C, the protruding edges merge into larger homogeneous domains (approximately tens of micrometers in size), and the surface morphology of the composite blend film becomes smoother with a surface roughness of around 4 nm (Figure 6e, f). The obvious trend of such morphological changes by LC organization is also observed for other blend ratios. We infer that thermal annealing allows the LC DPP-TP6 and PC71BM molecules to diffuse and reorganize into thermodynamically favorable nanoscale interpenetrating networks in the active layer. Since the exciton diffusion length of organic materials is generally about 10-20 nm,8 the well-developed interpenetrat-

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ing nanostructures with enlarged interfacial D/A areas should be beneficial to effective exciton dissociation and charge transport in the BHJ layer. In contrast, for the non-LC **DPP-TP12**:PC<sub>71</sub>BM blends the grains are not interconnected and the surface morphology of the films is coarse even after thermal annealing (Supporting Information, Figure S7). There is weaker molecular ordering within the blend films owing to the lack of LC characteristics, which agrees with the lower photovoltaic properties of **DPP-TP12**, compared with those of **DPP-TP6**.

X-ray diffraction (XRD) studies clearly manifest the enhancement of molecular ordering within the **DPP-TP6**:PC<sub>71</sub>BM blend films by LC organization (Figure 7). The



Figure 7. Out-of-plane XRD patterns of DPP-TP6:PC<sub>71</sub>BM (1:1, w/w) films on ITO-coated glass substrates: (a) as-spun and after thermal annealing at (b) 120 °C and (c) 140 °C for 10 min. The peak with a \* denotes reflection from ITO.

as-cast DPP-TP6:PC<sub>71</sub>BM (1:1, w/w) film only shows a weak broad scattering at  $2\theta = 5.8^{\circ}$ , corresponding to a *d*-spacing of 1.52 nm, which originates from very small crystalline domains of DPP-TP6. Once the thin film is annealed to 120 °C, an additional reflection peak appears at  $6.7^{\circ}$  (d = 1.32 nm). Further annealing at 140 °C leads to a steep increase of the intensity of the latter peak, as a result of the formation of Haggregates in the LC mesophase. The size of the DPP-TP6 crystallites (D) can be estimated from the full width at halfmaximum (fwhm) of the respective XRD peaks using Scherrer's equation<sup>16</sup>  $D = (K\lambda)/(\beta \cos \theta)$ , where K is the shape factor (normally assumed to be 0.89),  $\lambda$  is the incident X-ray wavelength,  $\beta$  is the fwhm in radians of the XRD peak, and  $\theta$  is the diffraction angle. Apparently, the average size of the crystallites of DPP-TP6 increases from 1.0 nm for the as-spun to 32 nm for the annealed DPP-TP6:PC71BM films.

This observation allows us to correlate the morphology of the active layer with the resulting photovoltaic properties. The larger size of the crystallites corresponds to a larger D/A segregation in the composite films. This nanostructured texture provides better percolation pathways for the generated charge carriers, which would be reflected in larger  $J_{sc}$  and FF of the annealed **DPP-TP6**:PC<sub>71</sub>BM device. Molecular dynamics (MD) simulations have been performed on the **DPP**-**TP6**:PC<sub>71</sub>BM (1:1, w/w) system with a constant temperature at 140  $^{\circ}$ C, as displayed in Figure 8 (see also Supporting



**Figure 8.** MD snapshot of **DPP-TP6**:PC<sub>71</sub>BM (1:1, w/w) blend at 140 °C, after 50 ns. Atoms belonging to PC<sub>71</sub>BM, the **DPP-TP6** conjugated backbone, and the alkyl chains are colored blue, pink, and gray, respectively. A movie file in the Supporting Information reveals the 360° view of the three-dimensional structure of the binary blend.

Information). The simulation cell contains 160 molecules of **DPP-TP6** and 128 molecules of PC<sub>71</sub>BM, and the cell size is around (x, y, z) = (6.6 nm, 6.6 nm, 8.5 nm) at the equilibrated state. It is observed that the **DPP-TP6** molecules repel the PC<sub>71</sub>BM molecules to form a stable phase-segregated structure after proper relaxation. The formation of zigzag layers of PC<sub>71</sub>BM agglomerates can be discerned, which is similar to the single-crystal structure of PCBM.<sup>17</sup>

Charge Carrier Mobilities. As the enhancement in photovoltaic properties can also be related to facile charge transport and collection, the impact of LC organization on charge carrier mobilities of the semiconductor materials has been assessed in organic field-effect transistors (OFETs). Topcontact bottom-gate OFETs have been fabricated by employing pure DPP-TP6 and blended DPP-TP6:PC<sub>71</sub>BM (1:1, w/w) materials. The carrier mobilities are obtained from the sourcedrain current versus gate voltage  $(I_D \text{ vs } V_G)$  plots in wellresolved saturation regions (Figure 9). As-cast films of the pristine **DPP-TP6** exhibit a hole mobility of  $7.0 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup>  $s^{-1}$ . After thermal annealing at 140 °C, the hole mobility of **DPP-TP6** increases to  $4.2 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> (Figure 9a). Thermal annealing results in a higher degree of crystallinity of the DPP-TP6 molecules (cf. Figures 6 and 7), which is manifested in increased hole mobilities. We have further investigated the hole mobility of the annealed DPP-TP6 film by means of the space-charge-limited current (SCLC) method.<sup>18</sup> The SCLC hole mobility is  $2-4 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> (Supporting Information, Figure S8), which is coincident with that obtained with the OFET, in spite of the difference in the charge transport lengths between SCLC (ca. 300 nm) and OFET devices (50  $\mu$ m). However, it has been found that the hole mobility of DPP-TP6 decreases to approximately 10<sup>-5</sup>  $cm^2 V^{-1} s^{-1}$  when mixed with PC<sub>71</sub>BM in a 1:1 (w/w) ratio, which is about 2 orders of magnitude lower with respect to the pristine DPP-TP6 after annealing.



**Figure 9.** Source–drain current  $(I_D)$  and  $I_D^{-1/2}$  vs gate voltage  $(V_G)$  plots of OFETs based on (a) pure **DPP-TP6** film with annealing at 140 °C for p-type operation and (b) **DPP-TP6**:PC<sub>71</sub>BM (1:1, w/w) blend film with annealing at 140 °C for n-type operation. Insets: POM images of each device (scale bar: 100  $\mu$ m). Channel length (*L*) and width (*W*) were 50 and 2000  $\mu$ m, respectively.

Likewise, the electron mobilities show a pronounced dependence on thermal annealing. The OFETs based on asspun **DPP-TP6**:PC<sub>71</sub>BM films without annealing exhibits a low electron mobility of  $1.6 \times 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, and after annealing at 140 °C, the electron mobility abruptly increases to  $1.1 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> (Figure 9b). These results suggest that the enhancement of photovoltaic properties for the BHJ **DPP-TP6**:PC<sub>71</sub>BM films is ascribable in part to the improved hole and electron transport. However, the electron and hole mobilities still differ by approximately 2 orders of magnitude in the **DPP-TP6**:PC<sub>71</sub>BM BHJ architectures. Therefore, higher photovoltaic performance could be achieved if one can further improve the hole mobility of the LC donor materials.

# CONCLUSIONS

We have synthesized and characterized solution-processable diketopyrrolopyrrole-based photovoltaic molecules, DPP-TP6 and DPP-TP12, that show an intense absorption in the visible region from 400 to 700 nm, with a small optical bandgap of 1.8 eV and a deep HOMO level of -5.5 eV. The use of these molecules as electron donors has been demonstrated in solution-processed BHJ solar cells with PC71BM as the electron acceptor. We have investigated the effect of LC properties on photovoltaic performance of the BHJ devices based on DPP-TP6:PC71BM and DPP-TP12:PC71BM films, in which the molecular packing and thin film morphologies are strongly affected by the length of the terminal alkyl chains. The  $J_{sc}$  and FF have increased significantly for the DPP-TP6-based devices through the LC organization process, and the best-performing device has generated a high PCE of 4.3% with a  $V_{oc}$  of 0.93 V,  $J_{\rm sc}$  of 8.4 mA cm<sup>-2</sup>, and FF of 0.55 without use of any additives. The induction of LC characteristics to direct molecular selfassembly represents an effective strategy for designing donor molecules. It is anticipated that further enhancement of photovoltaic performances could be realized by a combination of fine structural tuning of DPP-based materials and precise control of their LC organization processing. Further studies along this line are underway.

#### EXPERIMENTAL SECTION

**Synthesis of DPP-TP6.** To a stirred solution of 3,6-bis(5-bromothiophen-2-yl)-2,5-di(2-ethylhexyl)-pyrrolo[3,4-c]pyrrole-1,4-diones (1.10 g, 1.61 mmol) and 2-(4-hexylphenyl)-4,4,5,5-tetramethyl[1,3,2]dioxaborolane (0.98 g, 3.38 mmol) in dry tetrahydrofuran

(THF, 80 mL) were added  $Pd(PPh_3)_4$  (0.075 g, 0.064 mmol) and aqueous K<sub>2</sub>CO<sub>3</sub> (2.0 M, 5 mL; N<sub>2</sub> bubbled before use). The mixture was vigorously stirred for 24 h at 55 °C. After cooling to room temperature, the reaction mixture was poured into water, and then extracted with CHCl<sub>3</sub>. The combined organic layers were washed with water, and dried over anhydrous MgSO4. After filtration and evaporation, the crude product was purified by column chromatographically (SiO<sub>2</sub>, eluent =  $CHCl_3$ ), recrystallized from  $CHCl_3/$ methanol, and dried under vacuum to afford a dark violet solid. This compound was further purified by recycling preparative gel permeation chromatography (GPC) prior to use (yield = 0.71 g, 52%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.97 (d, J = 4.5 Hz, 2H), 7.59 (d, J = 8.0 Hz, 4H), 7.43 (d, J = 4.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 4H), 4.13-4.04 (m, 4H), 2.64 (t, J = 7.8 Hz, 4H), 1.97–1.93 (m, 2H), 1.67–1.61 (m, 4H), 1.41–1.26 (m, 28H), 0.93–0.89 (m, 18H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 161.80, 150.00, 144.14, 139.90, 136.85, 130.70, 129.22, 128.40, 126.08, 124.03, 108.11, 46.02, 39.27, 35.77, 31.73, 31.30, 30.40, 28.97, 28.61, 23.75, 23.13, 22.61, 14.09, 14.07 10.62. MS (MALDI-TOF): m/z 844.50  $[M]^+$ . Anal. Calcd (%) for  $C_{54}H_{72}N_2O_2S_2{:}$  C, 76.73; H, 8.59; N, 3.31; found: C, 76.65; H, 8.63; N, 3.32.

Synthesis of DPP-TP12. This compound was prepared in a fashion similar to DPP-TP6, using 3,6-bis(5-bromothiophen-2-yl)-2,5di(2-ethylhexyl)-pyrrolo[3,4-*c*]pyrrole-1,4-diones (0.97 g, 1.42 mmol), 2-(4-dodecylphenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (1.11 g, 2.98 mmol), and  $Pd(PPh_3)_4$  (0.066 g, 0.057 mmol). The product was purified by column chromatography (SiO<sub>2</sub>, eluent =  $CHCl_3$ ) and recycling preparative GPC to give a dark purple solid (yield =1.23 g, 85%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.97 (d, J = 4.0 Hz, 2H), 7.59 (d, J = 8.5 Hz, 4H), 7.43 (d, J = 4.0 Hz, 2H), 7.23 (d, J = 8.0 Hz, 4H),4.13-4.03 (m, 4H), 2.64 (t, J = 7.8 Hz, 4H), 1.97-1.92 (m, 2H), 1.67-1.60 (m, 4H), 1.43-1.26 (m, 52H), 0.93-0.85 (m, 18H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>2</sub>): δ 161.78, 149.98, 144.13, 139.87, 136.85, 130.68, 129.21, 128.39, 126.07, 124.02, 108.09, 46.01, 39.27, 35.77, 31.93, 31.34, 30.41, 29.67, 29.65, 29.60, 29.51, 29.36, 29.30, 28.60, 23.74, 23.13, 22.70, 14.11, 14.07, 10.61. MS (MALDI-TOF): m/z 1012.65  $[M]^+$ . Anal. Calcd (%) for  $C_{66}H_{96}N_2O_2S_2$ : C, 78.21; H, 9.55; N, 2.76; found: C, 78.20; H, 9.45; N, 2.71.

OSC Device Fabrication and Measurements. Prepatterned ITO-coated glass substrates were cleansed sequentially by sonicating in detergent solution, deionized water, acetone, and isopropanol for 10 min each, and were then subjected to UV/ozone treatment for 15 min. A thin layer (~40 nm) of PEDOT:PSS (Clevios P VP Al 4083) was spin-coated onto the precleaned ITO substrate at 2000 rpm for 60 s, and then baked at 150 °C for 10 min under air. The photoactive layer was deposited by spin-cast (1000 rpm for 60 s) from a CHCl<sub>3</sub> solution containing 7-8 mg/mL of a donor and a respective amount of PC<sub>71</sub>BM, after passing through a 0.45  $\mu$ m poly(tetrafluoroethylene) filter. The thickness of the active layers was 90-120 nm, measured with a Dektak profilometer. Finally, a 1-nm thick LiF and 100-nm thick Al layers were thermally evaporated on top of the active layer under high vacuum, through a shadow mask defining an active device area of 0.04 cm<sup>2</sup>. The current density-voltage (I-V) curves of photovoltaic devices were measured using a Keithley 2400 source measure unit in air under AM 1.5G solar illumination at 100 mW cm<sup>-2</sup> (1 sun) using a Bunko-keiki SRO-25GD solar simulator and IPEC measurement system, calibrated with a standard Si solar cell.

**OFET Device Fabrication and Measurements.** OFET devices were fabricated in a top-contact configuration on heavily doped n-type Si wafers with 300-nm thick thermally grown SiO<sub>2</sub>. The SiO<sub>2</sub>/Si substrates were pretreated with a piranha solution at 90 °C for 0.5 h, and then copiously cleaned with sonication in deionized water, acetone, and isopropanol for 10 min each, followed by UV/ozone treatment for 15 min. An organic semiconductor layer was spin-coated onto the substrate from a CHCl<sub>3</sub> solution with a donor concentration of 4% (w/v), at 1000 rpm for 60 s under N<sub>2</sub> atmosphere. The devices were completed by evaporating 50-nm thick Au (or Al) source and drain electrodes through a shadow mask, where the source–drain channel length (*L*) and width (*W*) were 50 and 2000  $\mu$ m, respectively. Current–voltage characteristics of the OFETs were measured using an

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Agilent B1500A semiconductor parameter analyzer under an inert atmosphere at room temperature. Field-effect mobilities ( $\mu$ ) were calculated in the saturation regime of the  $I_{\rm D}$  using the following equation:  $I_{\rm D} = (W/2L)\mu C_{\rm i}(V_{\rm G} - V_{\rm th})^2$ , where  $I_{\rm D}$  is the source–drain current,  $C_{\rm i}$  is the capacitance per unit area of the gate dielectric (11.5 nF/cm<sup>2</sup>),  $V_{\rm G}$  is the gate voltage, and  $V_{\rm th}$  is the threshold voltage.

# ASSOCIATED CONTENT

#### **S** Supporting Information

Experimental details, additional data and spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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