

The Importance of End Groups for Solution-Processed Small-Molecule Bulk-Heterojunction Photovoltaic Cells

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End groups in small-molecule photovoltaic materials are important owing to their strong influence on molecular stability, solubility, energy levels, and aggregation behaviors. In this work, a series of donor–acceptor pentads $(D_2-A-D_1-A-D_2)$ were designed and synthesized, aiming to investigate the effect of the end groups on the materials properties and photovoltaic device performance. These molecules share identical central $A-D_1-A$ triads (with benzodithiophene as D_1 and 6-car-

Introduction

Conjugated small molecules can be precisely purified and characterized by standard laboratory techniques with high batchto-batch reproducibility, which is advantageous in large-scale application of organic photovoltaics (OPV) compared with conjugated polymers.^[1] Small molecules as donor materials in bulk heterojunction (BHJ) devices should meet several requirements: they must (1) have sufficient environmental stability, (2) harvest as many photons as possible, (3) have appropriate energy levels, and (4) possess sufficiently high charge-carrier mobility. Intensive investigations on polymeric donors give some valuable guidelines to achieve these goals with small molecules. For example: (1) the donor-acceptor (D-A) alternating structure is an effective way to decrease the energy-gap;^[2] (2) 2D conjugated structures are promising for broad absorption and high charge-carrier mobility values;^[3] (3) extending backbones is favorable for improving film quality,^[4] and (4) branched alkyl side chains are more effective in improving solubility than straight carbon chains, although the latter has the beneficial effect of improving close molecular packing.^[5] Following these guidelines, many excellent conjugated small molecules were developed,^[6] leading to power conversion efficiency (PCE) values of up to 10.1 %.^[7]

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bonyl-thieno[3,4-*b*]thiophene as A), but with various D_2 end groups composed of alkyl-substituted thiophene (T), thieno[3,2-*b*]thiophene (TT), and 2,2'-bithiophene (BT). The results indicate a relationship between conjugated segment/alkyl chain length of the end groups and the photovoltaic performance, which contributes to the evolving molecular design principles for high efficiency organic solar cells.

In comparison with high molecular weight polymers, end groups in oligomeric small molecules naturally play a much more important role.^[8] They not only determine the stability of molecules, but also affect the energy-level properties and the self-assembly behaviors, which are all related directly to device performance. Therefore, we designed and synthesized a series of conjugated small molecules with a common central unit and different end groups. They are namely M1, M2, M3-C8, M3-C6, and M3-C4, as shown in Figure 1. Their identical central core is an acceptor-donor-acceptor (A-D₁-A) alternating structure, with a 2D benzodithiophene (2D-BDT) as D1 and (thieno[3,4-b]thiophene-2-yl)-2-ethylhexan-1-one (TT-C) as A. On both ends of the central $A-D_1-A$ structure, varied end groups were installed. A systematic study of end groups was carried out to explore the relationship between the molecular properties and end groups. Upon going from M1 to M2 to M3-C8, the end groups are thiophene (T), thieno[3,2-b]thiophene (TT), and 2,2'-bithiophene (BT), all decorated with n-octyl chains on the terminal site. The comparison of M1, M2, and M3-C8 should reveal the effect of the conjugated segment length of the end groups. Next, to gain understanding of the effect of the length of terminal alkyl chains, we considered the series M3-C8, M3-C6 up to M3-C4, all with identical conjugated pentads, but varied alkyl chains of n-octyl, n-hexyl, and n-butyl, respectively. From the results of photovoltaic studies of these five compounds, we found that the aromatic unit length of the D₂ end group can strongly influence the thermal stability, energy levels, and molecular packing, with measured PCEs ranging from 1.1% for M1 to 3.7% for M2 to 5.2% for M3-C8. From the M3 series, we see no effect of terminal alkyl chain length on thermal stability or the energy levels, but minor difference on phase separation of the active layer contributing to an increase in the PCE to 5.5% for M3-C6 and 6.0% for M3-C4.



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Figure 1. Molecular structures of M1, M2, M3-C8, M3-C6, and M3-C4.

Results and Discussion

M1, **M2**, and **M3-C8** all contain a 2D-BDT segment as D₁, TT-C as A, and varied T, TT, or BT as D₂, respectively. The 2D-BDT core was selected considering its large conjugation plane and excellent solubility.^[6d,c] TT-C was chosen as it was shown to be very effective for lowering the energy gap and imparting superior performance in polymer materials.^[10,11] Three end units based on *n*-octyl-subsituted thiophene derivatives with weakly electron donating effects were introduced to extend the conjugated backbone. Because the terminal α -proton of the thiophene end groups would be a site of instability, *n*-octyl chains were implanted to make the molecules stable as well as to improve solubility and modify packing.

The D₂-A-D₁-A-D₂ pentads were synthesized according to Scheme 1. First, thiophene derivatives 1, 3, or 6 were deprotonated with *n*-butyllithium in ultra-dry THF solution, followed by quenching with trialkyltin chlorides at 0°C, which afforded products 2, 4, and 7, respectively. The key intermediate 10 was prepared under Stille coupling conditions from 9 and an excess of 8 in toluene at 80°C with a yield of 60%. Finally the three target molecules M1, M2, and M3-C8 were synthesized through hetero-coupling reaction between dibromo 10 and compounds 2, 4, or 7 using tetrakis(triphenylphosphine)palladium [Pd(PPh₃)₄] mediated reactions in toluene at 110°C. Good yields (60-70%) were obtained after purifying using silica-gel column chromatography and preparative-gel permeation chromatography (GPC). Synthetic details are available in the Supporting Information. The structures and purities of all final targets were unambiguously characterized with MALDI-TOF mass spectrometry, ¹H and ¹³C NMR spectroscopy, and elemental analysis. All molecules show good solubility in common organic solvents, such as dichloromethane, chloroform, toluene, chlorobenzene, and dichlorobenzene.

As the acceptor building block **8** is asymmetric, its regio selective Stille coupling with the **9** could lead to three possible

constitutionally isomeric A–D₁–A triad cores **10**, **11**, and **12** (Scheme 1).^[1b,12] Fortunately, a single isomer (**10**) could be isolated in good yield, as confirmed by ¹H NMR and ¹H–¹H 2D NOESY-NMR spectroscopy (Figure 2). The structure was confirmed as follows: First, the ¹H NMR spectrum contains only four aromatic proton signals (Figure S2 in the Supporting Information), which excludes the lower symmetry compound **12** with its six unique aromatic protons. Next, in the ¹H–¹H 2D NOESY-NMR spectrum, coupling is observed that indicates the proximity of H1 to H2 and H3, thus eliminating **11** and confirming **10** as the isolated triad. Although the coupling of 2D-BDT (**9**) and TT-C (**8**) was widely reported in polymers, here it is the first applied to prove the construction and symmetry of the A–D–A oligomer **10**^[3,9,10,13]

The thermal behavior of materials can be one of the most important considerations for real applications. The thermal properties of **M1**, **M2**, and **M3-C8** were investigated using thermogravimetric analysis (TGA, Figure S3a) and differential scanning calorimetry (DSC, Figure S4). As shown in Figure S3, all three molecules exhibited good thermal stability up to 370°C under nitrogen at a heating rate of 10° C min⁻¹. DSC analysis for the three molecules revealed phase-transition peaks at 148, 233, and 162°C for **M1**, **M2**, and **M3-C8**, respectively.

Harvesting of photons is the precondition to utilize solar energy. The UV/Vis absorption spectra of **M1**, **M2**, and **M3-C8** in chloroform and in thin films are shown in Figure 3. In solution, the molecules exhibit broad absorption in the visible region from 350–700 nm with a peak maximum at ~570 nm. With an increase of the conjugated segment length of the end group, the peak shifts from 560 nm for **M1**, to 572 nm for **M2**, and to 578 nm for **M3-C8**. Along with conjugated segment length increase, extinction coefficients (ε) increase from 57000 m⁻¹ cm⁻¹ for **M1** to ~78000 m⁻¹ cm⁻¹ for **M2** and **M3-C8**. Films on quartz plates used for UV/Vis absorption spectroscopy measurements were prepared by spin coating from chloroform solutions of **M1**, **M2**, and **M3-C8** (10 mg mL⁻¹). In



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Scheme 1. Synthetic routes of M1, M2, and M3-C8.



Figure 2. ¹H-¹H 2D NOESY-NMR spectroscopy of compound 10.

comparison with the absorption spectra in solution, the absorption bands of all three compounds are broader and redshifted in the solid state. The broadening and red-shifting of the absorption bands in the films are usually ascribed to the formation of aggregates or ordered π - π stacking, which are helpful for improving charge-carrier mobility of the resulting films. In film, **M1** exhibits an absorption maximum at about 656 nm, which is red-shifted by approximately 96 nm compared to its solution spectrum. **M2** and **M3-C8** in film also displayed bathochromic absorption peaks at about 667 and 681 nm, respectively. From the onset of the thin film absorption, the optical energy gaps were estimated to be 1.7, 1.7, and 1.6 eV for **M1**, **M2**, and **M3-C8**, respectively. The optical properties of the molecules are summarized in Table 1. It is





Figure 3. UV/Vis absorption spectra of M1, M2, and M3-C8.

Table 1. Optical and electrochemical data for M1, M2, and M3-C8.										
Material	$\lambda^{ m sol}_{ m max}$ [nm] ^[a]	ε [M ⁻¹ cm ⁻¹]	$\lambda_{\scriptscriptstyle max}^{\sf film} \ [{\sf nm}]^{[b]}$	E_{g}^{opt} [eV] ^[c]	$E_{\rm HOMO}^{\rm CV}$ [eV] ^[d]	E_{LUMO}^{CV} [eV] ^[d]	E ^{cv} [eV] ^[e]			
M1	560	57000	603;656	1.7	-5.2	-3.2	2.0			
M2	572	77000	610;667	1.7	-5.0	-3.2	1.8			
M3-C8	578	78000	626;681	1.6	-5.0	-3.2	1.8			

[a] Measured on 10^{-5} M solutions in chloroform. [b] Samples were spin coated on quartz plates. [c] Estimated from the long wavelength onset of the thin-film absorption. [d] CV values are referenced to Ag/Ag⁺. Fc/Fc⁺ was used as an external reference ($E_{1/2}^{Fc/Fc^+} = 0.38$ V vs. Ag/Ag⁺, $E_{HOMO} = -4.80$ eV). [e] $E_g^{CV} = E_{LUMO} - E_{HOMO}$.

worth noting that a polymer (**PBDTTT-C-T**) reported by Hou et al.^[9] with donor and acceptor units identical to those in this work, had a thin-film absorption profile (maxima at 631 and 692 nm and an optical gap of approximately 1.58 eV)^[9] nearly equal to **M3-C8**. This result indicates that, by adopting larger conjugated end groups, the absorption of small molecules can be improved to behave as well as polymeric materials.

Appropriate energy levels are a key factor to realize the conversion from light-to-electrical energy. The electrochemical properties of **M1**, **M2**, and **M3-C8** were investigated by cyclic voltammetry in solution (CV, Figure 4). For calibration, the redox potential of the ferrocene/ferrocenium (Fc/Fc⁺, φ_{Fc/Fc^+})



Figure 4. CV traces of M1, M2, and M3-C8 in CH_2CI_2 (1×10⁻³ M) with 0.1 M Bu_4NPF_6 as the supporting electrolyte measured at a scan rate of 50 mV s⁻¹.

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redox couple was measured under the same conditions, and is located at 0.38 V versus the Ag/Ag⁺ electrode. If the absolute energy level of Fc/Fc^+ is set at -4.8 eV relative to vacuum, the energy levels of the HOMO and LUMO could be estimated by the following equations: E_{HOMO} (eV) = - ($\varphi_{\text{ox}} - \varphi_{\text{Fc/Fc}^+} + 4.8$); $E_{
m LUMO}$ (eV) = –($\varphi_{
m red}$ – $\varphi_{
m Fc/Fc^+}$ + 4.8), where $\varphi_{
m ox}$ and $\varphi_{
m red}$ are the oxidation and reduction potentials versus Ag/Ag⁺, respectively. The HOMO and LUMO energies were estimated to be -5.2and -3.2 eV for M1, -5.0 and -3.2 eV for M2, and -5.0 and -3.2 eV for M3-C8, respectively. The changes in end groups show little effect on the LUMO values for these molecules. The similarities of LUMO values originate from the identical acceptor units, whereas varying HOMO energies arise from the different electron-donating properties of the end groups. From the most simplistic viewpoint, extended conjugation leads to HOMO destabilization (shallower HOMO energies) as was observed here for M2 and M3-C8. The estimated energy levels of the three molecules and [6,6]-phenyl-C71-butyric acid methyl ester (PC₇₁BM) are summarized in Figure S5. Here, it was apparent that the LUMO levels of all three donating molecules are approximately 0.8 eV above that of PC71BM. This value is sufficient to produce exciton dissociation in the interlayer between donor and PC₇₁BM.

XRD was used to investigate the packing of the molecules in solid films. Films of **M1**, **M2**, and **M3-C8** were spin-coated from chloroform solutions onto silica substrates. As shown in Figure 5, the pure **M1-**, **M2-** and **M3-C8**-based films displayed a single sharp reflection peak (100) at low diffraction angles at 2θ of 4.6°, 4.2°, and 4.7°, respectively, indicating their strong molecular packing.^[6c]



Figure 5. The XRD profiles of M1, M2, and M3-C8.

To investigate the effect of the end groups on photovoltaic performance, single layer BHJ photovoltaic cells based on the three molecules as the donor component and $PC_{71}BM$ as the acceptor material were fabricated with an ITO/PEDOT:PSS/ **MX**:PC₇₁BM/Al architecture (see the Supporting Information for details). The photovoltaic data were collected under AM1.5G at 100 mW cm⁻². To obtain improved device performance, the device fabrication conditions were optimized to D/A ratios of 3:1 and an active layer thickness of 100 nm without annealing (see the Supporting Information for details). The current–





Figure 6. *J*–*V* characteristics of BHJ devices fabricated using **M1**, **M2**, and **M3-C8** as the donor and PC₇₁BM as the acceptor measured under AM1.5G illumination (100 mW cm⁻²) and in the dark. These devices were made with D/A ratios of 3:1 without processing additives or thermal annealing.

voltage (J-V) curves for the resulting devices are shown in Figure 6. The optimized PCEs are 1.1, 3.7, and 5.2% for **M1**, **M2**, and **M3-C8** (average over 20 devices), respectively. To make a clear comparison, the corresponding results are listed in Table 2.

Table 2. Photovoltaic properties of BHJ solar cells based on M1, M2, M3-C8, M3-C6, or M3-C4 with PC71BM.										
Donor	V _{oc} ^[a] [V]	لا ^{ر (a, b)} [mA cm ⁻²]	$J_{\rm SC}^{\rm EQE^{[c]}}$ [mA cm ⁻²]	FF ^[a] [%]	PCE ^[a] [%]					
M1 M2 M3-C8 M3-C6 M3-C4	$\begin{array}{c} 0.87 \pm 0.01 \\ 0.87 \pm 0.01 \\ 0.84 \pm 0.01 \\ 0.82 \pm 0.01 \\ 0.78 \pm 0.01 \end{array}$	$\begin{array}{c} 2.66 \pm 0.03 \\ 8.60 \pm 0.13 \\ 10.83 \pm 0.21 \\ 12.73 \pm 0.13 \\ 13.92 \pm 0.05 \end{array}$	2.4 8.9 10.1 11.7 12.9	$\begin{array}{c} 47.4 \pm 0.50 \\ 50.0 \pm 0.30 \\ 57.2 \pm 1.08 \\ 53.3 \pm 0.40 \\ 55.0 \pm 0.76 \end{array}$	$\begin{array}{c} 1.11 \pm 0.03 \\ 3.70 \pm 0.10 \\ 5.20 \pm 0.09 \\ 5.50 \pm 0.04 \\ 6.00 \pm 0.08 \end{array}$					
[a] Average value and standard deviation based on the measurement of 20 duplicate devices under simulated AM 1.5 G illumination (100 mW cm ⁻²). [b] Calculated from the $J-V$ curve. [c] Calculated from the EQE spectrum.										

The open circuit voltages (V_{oc}) were estimated from the J–V curves to be 0.87, 0.87, and 0.84 V for M1, M2, and M3-C8, respectively. As the $V_{\rm OC}$ can be estimated by the gap between the LUMO of PC71BM and the HOMO of the donor, the results also indicated this the trend (i.e., M2 and M3-C8 had lower HOMOs than that of M1, and thus the photovoltaic devices of M2 and M3-C8 exhibited higher $V_{\rm OC}$.^[14] The short-circuit current densities (J_{SC}) determined from the J–V curves were 2.66, 8.60 and 10.83 mA cm⁻² for M1, M2, and M3-C8, respectively. The variation in J_{SC} is consistent with the trend of incident photon-to-current efficiency (IPCE) and hole mobility values, as discussed below. In this case, M1 yielded the weakest IPCE and lowest hole mobility; therefore, M1 also exhibited the lowest J_{sc}. On the contrary, M3-C8 gave a highest IPCE and hole mobility and it achieved highest J_{sc} in this series. Combined with a fill factor (FF) of 47% for M1, 50% for M2, and 57% for M3**C8**, an increase in the PCEs was demonstrated from **M1**, to **M2** to **M3-C8**. It is worth noting that the variation in end groups caused only a slight difference in the molecular properties (e.g., UV/Vis absorption and electrochemistry as observed by CV), but remarkable changes in efficiency were observed in the photovoltaic performance.

Figure 7 shows the IPCE response of the three molecules based on optimal device conditions. Because of the main contribution of the IPCE originating from the donor absorption,



Figure 7. IPCE of the corresponding devices.

M2 and **M3-C8** show broader and stronger absorption than **M1** in the 300–750 nm range, leading to an increased IPCE response in this region. The integral current density is an evaluation of the devices ability to harvest photons and transfer charges. The integral currents of **M1**, **M2**, and **M3-C8** are 2.38, 8.95, 10.06 mA cm⁻², respectively, which is in agreement with the photovoltaic test results.

To gain some insight in the differences in J_{SC} , hole mobility values were measured using the space-charge limited current (SCLC) method and found to be 2.79×10^{-5} , 1.13×10^{-4} , and 1.25×10^{-4} cm²V⁻¹S⁻¹ for **M1**, **M2**, and **M3-C8**, respectively. It would appear that hole mobility values indeed increase as a function of the conjugated-segment length of the end groups, as longer conjugated end groups facilitate to extend delocalization and increase intermolecular electron hopping.

To further understand the device performance, the morphology of three blend layers were investigated by AFM. As shown in Figure 8, the height images show obvious differences in morphologies with root mean square (RMS) roughnesses of 1.69, 0.82, and 0.95 nm for the **M1**, **M2**, and **M3-C8** active layers, respectively. The **M1**/PC₇₁BM layer shows the roughest surface among the three blend layers. From their phase images, it can be seen that the blend films of **M2**/PC₇₁BM and **M3-C8**/PC₇₁BM show nano-scale phase separation with desirable domain sizes around 20 nm, whereas the blend film of **M1**/PC₇₁BM shows less desirable, larger domain sizes around 100 nm. In contrast, the proper phase separation in blended films of **M3-C8**/PC₇₁BM is favorable for the production and collection of charges from excitons, leading to a good IPCE response, high hole mobility, and large PCE values.



Figure 8. AFM height images of active layer blends: (a) $M1/PC_{71}BM$ (3:1), (c) $M2/PC_{71}BM$ (3:1), and (e) $M3-C8/PC_{71}BM$ (3:1). AFM phase images of active layer blends: (b) $M1/PC_{71}BM$ (3:1), (d) $M2/PC_{71}BM$ (3:1), and (f) $M3-C8/PC_{71}BM$ (3:1).

The effect of length of terminal alkyl chains

The alkyl chains attached to these molecules also are an important factor for material performance, as they can influence the active layer phase separation behavior. To investigate the effect of length of substituents on the device performance, two analogues of M3-C8 were prepared with shorter terminal alkyl chains and denoted M3-C6 and M3-C4 (Figure 1). Their chemical nomenclature and synthetic details are reported in the Supporting Information. The conjugated pentad structure of M3-C8 was chosen as it demonstrated the best performance in preliminary studies.

The basic physical properties, including UV/Vis, TGA, and CV spectra are shown in Figure S6. Owing to their identical backbone structure, the **M3** series show similar thermal stability, as well as (opto)electronic properties. The optical and electrochemical properties of **M3** are summarized in Table 1. DSC revealed a regular transition point rise as the terminal alkyl chains shorten, with peak temperatures at 203, 223, and 258 °C for **M3-C8**, **M3-C6**, and **M3-C4** respectively (Figure 9). This is a very clear trend of increasing thermal stability of the room-temperature phase with decreasing the length of terminal alkyl chain.



Figure 9. DSC curves of M3-C8, M3-C6, and M3-C4.

AM 1.5 G illumination (100 mW cm⁻²) and in the dark.

10

5

0

-5

-10

-15

0.0

0.2

0.4

Voltage (V)

Figure 10. *J–V* characteristics of BHJ devices fabricated using **M3-C8**, **M3-C6**, and **M3-C4** as the donor and PC₇₁BM as the acceptor measured under

2 Current density (mA/cm)

slightly, but the J_{SC} increased markedly. With no apparent change trend in FF, it seems that the increase in J_{SC} is the main driving force for the growing PCE values of 5.2, 5.5, and 6.0% for **M3-C8**, **M3-C6**, and **M3-C4**, respectively. Furthermore, their IPCE (Figure S7) profiles are nearly identical, but the integral is increasing as the terminal alkyl chain length decreases, with integral currents of 10.1, 11.7, and 12.9 mA cm⁻² for **M3-C8**, **M3-C6**, and **M3-C4**, respectively. In AFM height images of the **M3**-based active layers, all show quite smooth surfaces. From the height image, a RMS of 0.82, 0.71, and 0.63 nm for **M3-C8**, **M3-C6**, and **M3-C4** can be estimated, respectively (Figure 11), which indicates that the **M3-C4**-based active layer presents the most favorable phase separation. Therefore, terminal butyl chains are more appropriate than hexyl and octyl

The photovoltaic performances of **M3-C8**, **M3-C6**, and **M3-C4** were investigated in the same fashion as described above. Their *J–V* curves are shown in Figure 10 and their PCE data are

collected in Table 2. From the J-V curves, it was observed that

as the terminal alkyl chains became shorter, the $V_{\rm OC}$ decreased

M3-C4 illumination +

M3-C8 illumination—↔ M3-C8 dark M3-C6 illumination—↔ M3-C6 dark

– M3-C4 dark

0.6

0.8

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Figure 11. AFM height images of active layer blends: (a) M3-C8/PC₇₁BM (3:1), (c) M3-C6/PC₇₁BM (3:1), and (e) M3-C4/PC₇₁BM (3:1). AFM phase images of active layer blends: (b) M3-C8/PC₇₁BM (3:1), (d) M3-C6/PC₇₁BM (3:1), and (f) M3-C4/PC₇₁BM (3:1).

chains for these conjugated cores, owing to more efficient molecular packing and thus more efficient intermolecular charge transport.

Conclusions

Three novel D_2 -A- D_1 -A- D_2 -type conjugated small molecules with varying donor (D₂) end groups, M1, M2, and M3-C8, were synthesized and applied in solar cells as the donor materials. As the D₂ end groups were varied in conjugated length from thiophene to thieno[3,2-b]thiophene to 2,2'-bithiophene, the average device performance dramatically increased from 1.1 to 3.7 to 5.2%. Focusing on the highest performing D_2 -A- D_1 -A-D₂ pentad, we found the terminal alkyl chain length could further improve the device performance. When the alkyl chains were shortened from *n*-octyl to *n*-hexyl to *n*-butyl the PCE increased from 5.2 to 5.5 to 6.0%. This result shows that the extended conjugated length of the end groups in a small molecule donor can effectively adjust the molecular energy levels and aggregation behaviors of the active layer, thereby improving the device performance. Moreover, the optimized alkyl chain length of the end groups can further improve the PCE while maintaining molecular thermal stability and energy level positions. This study should contribute to the growing understanding of the subtle demands of designing small molecules for OPV, where both the nature of the π system and the solubilizing side chains are critical.

Experimental Section

Materials and methods. All reactions were carried out under argon atmosphere with the use of standard Schlenk techniques. 2,6-Bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (9) was prepared according the reported method.^{3c} 1-(4,6-Dibromothieno[3,2-c]thiophen-2-yl)-2-ethylhexan-1-one (8) was purchased from Solarmer Energy, Inc. and used as received. Other starting materials were purchased from Alfa-Aesar and Sigma–Aldrich and used without further purification.

¹H and ¹³C NMR spectra were recorded on a Bruker DRX 250 or Bruker DRX 850. MALDI-TOF mass spectrometry was performed on

a Bruker Reflex II-TOF Spectrometer using a 337 nm nitrogen laser with TCNQ as matrix. UV/Vis absorption spectra were collected on a PerkinElmer Lambda 9 spectrophotometer at room temperature. CV measurements were carried out on a computer-controlled GSTAT₁₂ in a three-electrode cell in a dichloromethane solution of tetrabutylammoniumhexafluorophosphate (Bu₄NPF₆, 0.1 м) with a scan rate of 50 mV s⁻¹ at room temperature. A Pt wire, a silver wire, and a glassy carbon electrode were used as counter electrode, reference electrode, and working electrode, respectively. DSC was carried out with a Mettler DSC 30 with a heating rate of 10 Kmin⁻¹ from 25 to 250 $^{\circ}$ C. TGA was carried out on a Mettler 500 thermo gravimetry analyzer. AFM experiments were performed on a Bruker VeecoMultiMode 8 atomic force microscope. Film XRD was performed on a theta-theta Philips PW 1820 Kristalloflex diffractometer with a graphite-monochromatized $Cu_{\kappa_{\alpha}}$ X-ray beam $(\lambda = 1.5418 \text{ Å})$ hitting the thin film. The diffraction patterns were recorded in the 2θ range from 0 to 30° .

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