CHEMISTRY OF MATERIALS

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# Carbazole-Based Ladder-Type Heptacylic Arene with Aliphatic Side Chains Leading to Enhanced Efficiency of Organic Photovoltaics

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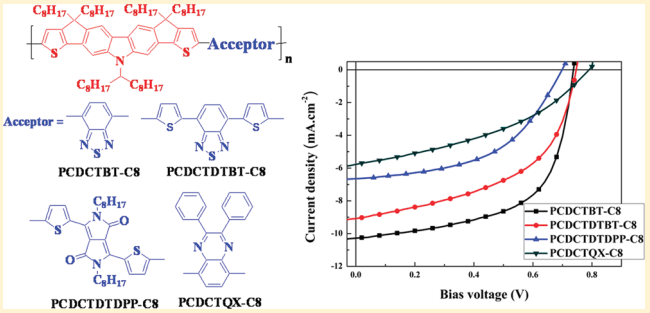
Supporting Information

**ABSTRACT:** By utilizing Friedel−Crafts cyclization, we have successfully designed and synthesized a ladder-type heptacyclic carbazole-dicyclopentathiophene (**CDCT-C8**) unit in which two outer thiophene subunits are covalently fastened to the central 2,7-carbazole core. The nitrogen-directing effect of the carbazole unit facilitates the intramolecular cyclization and thereby suppresses the acid-induced dehydration, allowing us to incorporate two octyl side chains on the cyclopentadiene rings in good chemical yield. The distannyl-**CDCT-C8** building block was copolymerized with benzothiadiazole (**BT**), dithienylbenzothiadiazole (**DTBT**), dithienyldiketopyrrolopyrrole (**DTDPP**) and quinoxaline (**QX**) units by Stille polymerization to afford four alternating donor−acceptor copolymers, **PCDCTBT-C8**, **PCDCTDTBT-C8**, **PCDCTDTDPP-C8** and **PCDCTQX-C8**, respectively. The device based on the **PCDCTBT-C8**:$PC_{71}BM$ (1:3 in wt%) blend exhibited a $V_{oc}$ of 0.74 V, a $J_{sc}$ of 10.3 mA/cm$^2$, a FF of 60%, delivering an impressive PCE of 4.6%. This value represents one of the best performances among carbazole-based conjugated polymers in the literatures. The corresponding **PCDCTBT-C8**:$PC_{71}BM$ blend showed a high hole mobility of $1.2 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$, which is in good agreement with its high current density and fill factor. This improved performance is associated with the modification of the aliphatic side chains on the **CDCT** structure to optimize the interchain interactions for enhanced charge transporting. The devices based on **PCDCTDTBT-C8**, **PCDCTDTDPP-C8** and **PCDCTQX-C8** polymers also displayed promising efficiencies of 3.5%, 2.4%, and 1.8%, respectively.




**KEYWORDS:** Friedel−Crafts cyclization, carbazole, ladder-type, polymerization, organic photovoltaics

## INTRODUCTION

Over the past few years, tremendous research effort has been made on all-solution processed bulk-heterojunction polymer solar cells (PSCs) in order to realize low-cost, lightweight, large-area and flexible photovoltaic devices.[1] To achieve high efficiency of PSCs, the most critical challenge at the molecular level is to develop the p-type conjugated polymers that possess (1) sufficient solubility to guarantee solution processability and miscibility with an n-type material, (2) low band gap (LBG) for strong and broad absorption spectrum to capture more solar photons and (3) high hole mobility for efficient charge transport. The general approach to produce a LBG polymer is to incorporate electron-rich donor and electron-deficient acceptor segments along the conjugated polymer backbone. Based on these polymers, researchers have made a breakthrough in fabricating PSC devices with PCEs over 5%.[2] Planarization of polyaromatic system facilitates $\pi$-electron delocalization and elongates effective conjugation length, providing another effective way to reduce the band gap.[3] Moreover, coplanar geometries and rigid structures can suppress the rotational disorder around interannular single bonds and lower the reorganization energy, which in turn enhances the intrinsic charge mobility.[4] Tricyclic 2,7-carbazole[5] unit is an ideal electron-rich building block to construct donor−acceptor polymers because its derivatives exhibit deep-lying HOMO energy levels and good hole-transporting properties which are crucial prerequisites to achieve high open-circuit voltages ($V_{oc}$) and short circuit currents ($J_{sc}$), respectively. Poly(2,7-carbazole-*alt*-dithienylbenzothiadiazole) (**PCDTBT**) has been shown to act as a superior p-type photoactive material for the application in PSCs (Scheme 1).[5] Inspired by the skeletons of the **PCDTBT** polymers, for the first time, we have successfully utilized a facile Friedel-Craft cyclization to develop a novel carbazole-based coplanar $\pi$-conjugated system, carbazole-dicyclopentathiophene (**CDCT**), where the 3-positon of two outer thiophenes are covalently connected with the 3,6-position of central carbazole cores by a sp$^3$-hybridized carbon bridge (Scheme 1).[6] By copolymerizing this heptacyclic structure with electron-deficient benzothiadizole unit, an alternating poly(carbazole-dicyclopentathiophene-*alt*-benzothiadiazole) (**PCDCTBT**) was synthesized.[6] The two cyclopentadiene rings embedded in the **CDCT** structure allows for introducing four 4-(2-ethylhexoxy)phenyl groups to guarantee solubility and

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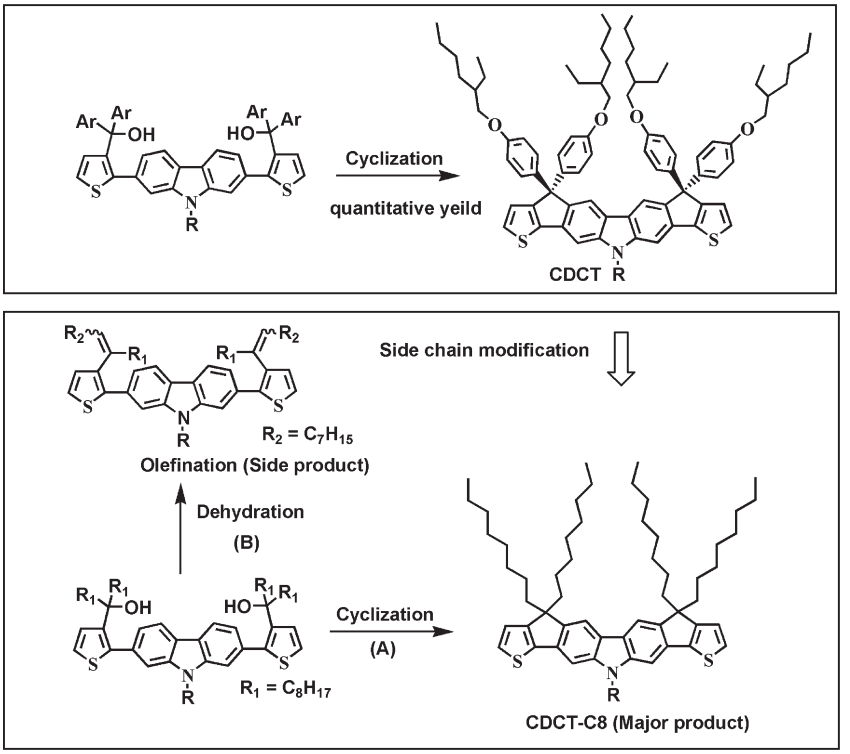
**Scheme 1. Modification of the Side Chain on the CP Rings of the Heptacyclic Structure**




processing capability of the resulting polymer. The PSC utilizing this polymer achieved a promising PCE of 3.7%. In addition to intrinsic properties at molecular level, intermolecular interactions between polymers in the solid state play an important role in determining nanomorphological properties such as crystallinity, phase behavior and miscibility between different components. Appropriate interchain $\pi-\pi$ stacking could lead to many advantageous characteristics of the conjugated polymers including enhanced absorption intensity, reduced optical band gap, and improved charge mobility. Manipulation of structural features (i.e., length, bulkiness, rigidity or chirality) of the solubilizing groups on the polyaromatic backbone is a straightforward way to control the intermolecular self-assembly.[7] For example, **PTPTBT**, functionalized with two 4-hexylphenyl groups on the carbon atom of the CP ring, shows amorphous nature and moderate charge mobility in the solid state,[8] whereas its analogous polymer with two octyl groups on the carbon bridge exhibits crystalline nature with high hole mobility.[9] Similarly, the bulky and rigid ethylhexoxyphenyl groups sticking out of the coplanar backbone of **CDCT** will suppress the intermolecular interaction, making the **PCDCTBT** polymer highly amorphous. To tailor the intermolecular interaction for optimizing bulk properties, it is promising to modify the molecular structure of **CDCT** by replacing the branch ethylhexoxyphenyl groups on the CP rings with more flexible aliphatic groups. However, in contrast to aryl substituents, introducing two long aliphatic side chains on the CP ring embedded in an arene system by intramolecular Friedel-Craft alkylation is synthetically challenging and has not been successful so far. Usually, a three-step acylation-reduction-alkylation sequence is required to incorporate two aliphatic side chains.[10] We found that a competing dehydration reaction of the tertiary alcohol would readily occur to generate the olefination product (Path B in Scheme 1), thus prohibiting the intramolecular cyclization under the acidic Friedel-Craft condition. Encouragingly, in our substrate, the nitrogen-directing effect in the carbazole strongly facilitates the electrophilic aromatic substitution at the 3, 6-position of the carbazole (Path A). This advantage enables us to successfully incorporate four octyl side chains onto the **CDCT** core in good yield by using our designed synthetic pathway (**CDCT-C8** in Scheme 1).

In order to further modulate and optimize the electronic and optical properties, exploration of different electron-deficient units incorporated into **CDCT**-based polymeric backbone is highly desirable. Benzothiadiazole (**BT**)[11] and quinoxaline (**QX**)[12] units are the widely used electron-deficient units introduced in the D−A copolymers due to their suitable electron affinity and easy synthesis. In addition, diketopyrrolopyrrole (**DPP**) unit has also emerged as a useful acceptor unit because of its planar conjugated bicyclic structure and strong electron-withdrawing nature of polar amide group.[13] On the basis of the modified **CDCT-C8** as the core structure, we have successfully synthesized four D−A copolymers, poly(carbazole-dicyclopentathiophene-*alt*-benzothiadiazole) (**PCDCTBT-C8**), poly(carbazole-dicyclopentathiophene-*alt*-dithienylbenzothiadiazole) (**PCDCTDTBT-C8**), poly(carbazole-dicyclopentathiophene-*alt*-dithienyldiketopyrrolopyrrole) (**PCDCTDTDPP-C8**), and ploy(carbazole-dicyclopentathiophene-*alt*-quinoxaline) (**PCDCTQX-C8**) (Scheme 2). The synthesis, characterization and photovoltaic applications of these polymers will be discussed.

## RESULTS AND DISCUSSION

**Synthesis and Characterization.** The synthetic route of the **CDCT-C8** monomer **6** is depicted in the Scheme 3. Double nucleophilic addition of the freshly prepared *n*-octyl magnesium bromide to the ester groups of **3** led to the formation of tertiary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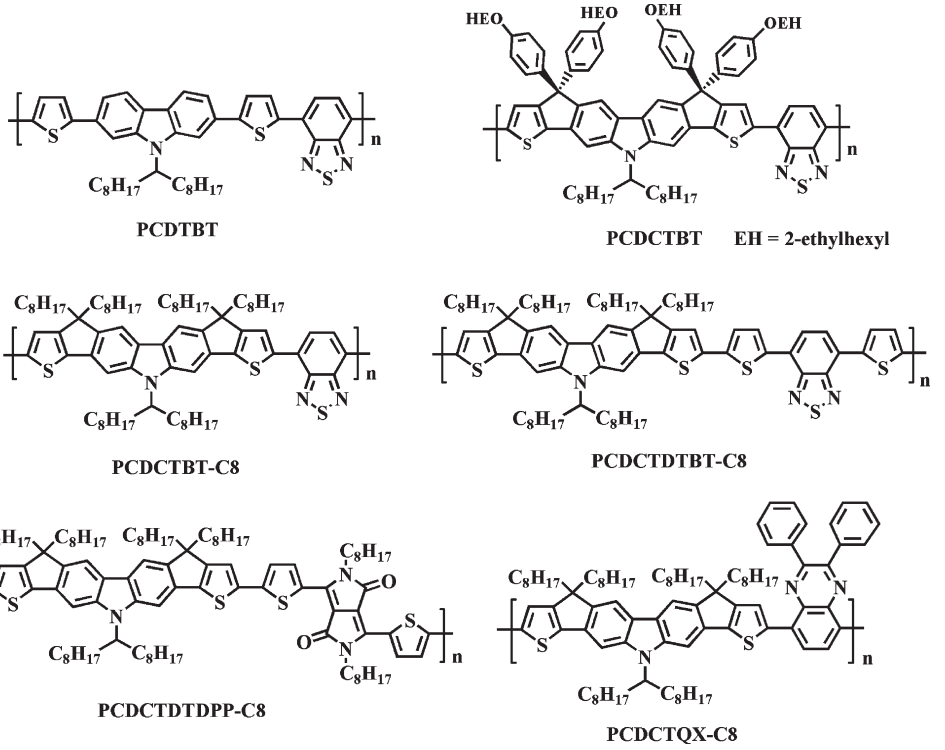
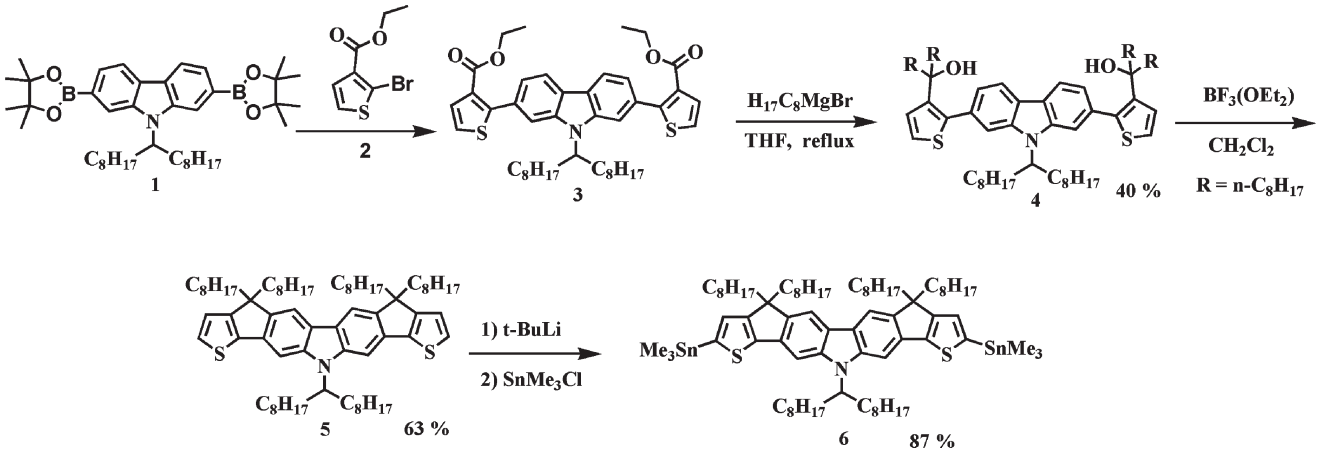
**Scheme 2. Chemical Structures of Carbazole-Based Donor−Acceptor Polymers**




**Scheme 3. Synthetic Route of the CDCT Monomer with Octyl Side Chains**




alcohol **4**. Compound **4** was subjected to intramolecular annulation through Lewis acid-mediated Friedel−Crafts reaction to furnish the multifused heptacyclic arene **5** in good yield of 63%. It should be noted that in this step, small amount of dehydration product was also obtained. Compound **5** can be efficiently lithiated by *t*-butyllithium through deprotonation followed by reacting with trimethyltin chloride to afford the distannyl **6**. Monomer **6** was copolymerized with 4,7-dibromo-2,1,3-benzothiadiazole **7**, 4,7-bis-(5-bromo-2-thienyl)-2,1,3-benzothiadiazole **8**, 3,6-bis(5-bromothiophen-2-yl)-2,5-bisoctylpyrrolo[3,4-*c*] pyrrole-1,4-dione **9** or 5,8-dibromo-2,3-diphenylquinoxaline **10**, by Stille coupling to give **PCDCTBT-C8** ($M_n$ = 38.1 kDa, PDI = 1.60), **PCDCTDTBT-C8** ($M_n$ = 14.1 kDa, PDI = 2.17), **PCDCTDTDPP-C8** ($M_n$ = 18.0 kDa, PDI = 1.12) and **PCDCTQX-C8** ($M_n$ = 5.6 kDa, PDI = 2.53), respectively (Scheme 4). The structures of the polymers were determined with NMR spectroscopy. All the polymers show excellent solubilities in common organic solvents, such as chloroform, toluene, dichlorobenzene, due to the five alkyl chains flanked on both sides of the **CDCT** heptacyclic arene.

**Thermal Properties.** The thermal stability of the polymers was analyzed by thermogravimetric analysis (TGA). **PCDCTBT-C8**, **PCDCTDTBT-C8**, **PCDCTQX-C8** and **PCDCTDTDPP-C8** exhibited sufficiently high decomposition temperatures ($T_d$) of 422 °C, 456 °C, 419 and 417 °C, respectively (Table 1 and Supporting Information Figure S1). Thermal properties of the polymers were determined by differential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**Scheme 4. Stille Polymerization towards the CDCT-C8-based Donor−Acceptor Polymers**

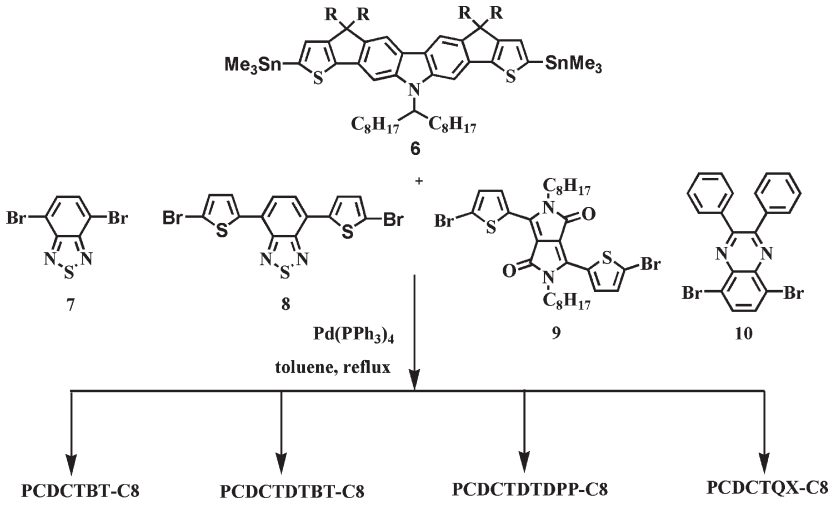


**Table 1. Summary of the Intrinsic Properties of the Polymers**

| | | | | | | | $\lambda_{max}$ (nm) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| polymer | Mn (kDa) | PDI | $T_{g\,z}$ (°C) | $T_d$ (°C) | $T_m$ (°C) | $E_g^{opt}$ (eV) (Film) | toluene | film | HOMO (eV) | LUMO[a] (eV) |
| **PCDCTBT-C8** | 38.1 | 1.60 | 139 | 422 | NA | 1.64 | 419<br>630 | 425<br>645 | −5.31 | −3.67 |
| **PCDCTDTBT-C8** | 14.1 | 2.17 | 105 | 456 | NA | 1.66 | 441<br>585 | 441<br>599 | −5.31 | −3.65 |
| **PCDCTDTDPP-C8** | 18.0 | 1.12 | 52 | 417 | 98 | 1.37 | 406<br>705 | 414<br>708 | −5.24 | −3.87 |
| **PCDCTQX-C8** | 5.6 | 2.53 | 81 | 419 | 101 | 1.72 | 419<br>578 | 414<br>585 | −5.25 | −3.53 |

[a] LUMO = HOMO − $E_g^{opt}$.

scanning calorimetry (DSC) (Table 1 and Supporting Information Figure S2). All of the polymers showed a glass transition temperature. **PCDCTBT-C8** and **PCDCTDTBT-C8** have smaller free volume and thus exhibited higher $T_g$ at 139 and 105 °C, respectively, compared to **PCDCTDTDPP-C8** and **PCDCTQX-C8** ($T_g$ at 52 and 81 °C, respectively) with the acceptors functionalized with alkyl chains or phenyl rings. In addition, **PCDCTDTDPP-C8** and **PCDCTQX-C8** showed a melting point at 98 and 101 °C, respectively, presumably due to the high planarity of the backbone.

**Optical Properties.** All of the copolymers exhibited two characteristic bands in the absorption spectra (Figure 1). The shorter wavelength absorbance comes from the $\pi-\pi^*$ transition of the heptacyclic units, while the lower energy band is attributed to the intramolecular charge transfer (ICT) between the electron-rich and the electron-deficient segments. Compared to the absorption spectrum in the solution state, **PCDCTBT-C8** showed not only a bathochromic shift but also broadening of the ICT band in the solid state. Note that the absorption spectrum of **PCDCTBT** with 4-(2-ethylhexoxy)phenyl side chains remained essentially unchanged in both the solution and solid state.[6] Furthermore, compared to **PCDCTBT** showing the absorption maxima at 412 and 607 nm in the thin film, **PCDCTBT-C8** exhibited bathochromic shifts of the absorption maxima at 425 and 645 nm. These phenomena clearly indicate that the aliphatic side chains indeed are capable of enhancing interchain $\pi-\pi$ stacking interactions effectively in the solid state (Figure 1). **PCDCTDTDPP-C8** exhibited the absorption maximum of the ICT band at 708 nm in the thin film followed by **PCDCTBT-C8** at 645 nm, **PCDCTDTBT-C8** at 599 nm and **PCDCTQX-C8** at 585 nm (Table 1). The optical band-gaps ($E_g^{opt}$) deduced from the absorption edges of the thin film spectra are in the following order: **PCDCTQX-C8** (1.72 eV) > **PCDCTDTBT-C8** (1.66 eV) > **PCDCTBT-C8** (1.64 eV) > **PCDCTDTDPP-C8** (1.37 eV) (Table 1). The difference of their $\lambda_{max}$ as well as $E_g^{opt}$ points out that the acceptor strength is in the order: **DPP** > **BT** > **QX**. Compared to **PCDCTBT-C8**, **PCDCTDTBT-C8** with two additional thiophene rings in the repeating unit showed the red-shifted $\pi-\pi^*$ transition band due to the longer conjugated length. However, this modification also results in a blue-shift of the ICT band due to the weaker donor−acceptor interaction. It is also worthy to note that the intensities of the shorter wavelength bands of four polymers in the solid state are apparently stronger


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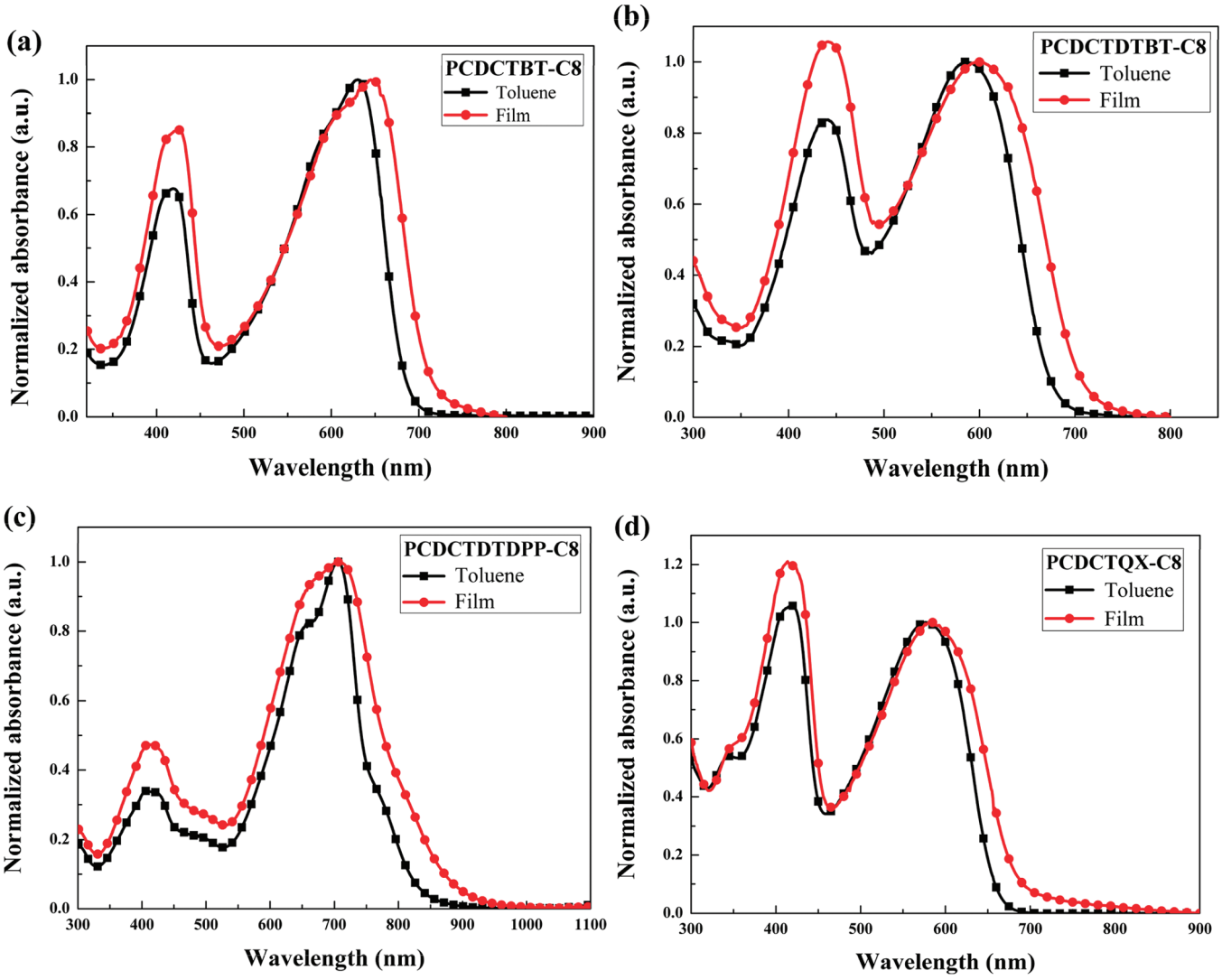


**Figure 1.** Normalized absorption spectra of **PCDCTBT-C8** (a), **PCDCTDTBT-C8** (b), **PCDCTDTDPP-C8** (c), and **PCDCTQX-C8** (d) in the toluene solution and the solid state.

than these in the solution state, which also suggests that the coplanar heptacyclic units increase their extinction coefficient in the solid state.

**Electrochemical Properties.** Cyclic voltammetry (CV) was employed to examine the electrochemical properties and evaluate the HOMO levels of the polymers (Table 1 and Figure 2). All of these polymers showed stable and reversible process in the oxidative scans. The HOMO levels being estimated to be −5.31, −5.31, −5.24 ,and −5.25 eV for **PCDCTBT-C8**, **PCDCTDTBT-C8**, **PCDCTDTDPP-C8**, and **PCDCTQX-C8** are at ideal range to ensure better air-stability and greater attainable $V_{oc}$ in the final device. The LUMO energy levels were approximately estimated by subtracting the band gap values from the corresponding HOMO levels. The influence of the electron acceptors on the absorption ICT band totally reflects the position of LUMO levels (−3.87 eV for **PCDCTDTDPP-C8**, −3.67 eV for **PCDCTBT-C8**, - 3.65 eV for **PCDCTDTBT-C8**, and −3.53 eV for **PCDCTQX-C8**), indicating that the LUMO energy levels are mainly determined by the electron acceptors. The LUMO energy levels of the polymers are above the LUMO level of the $PC_{71}BM$ acceptor to ensure energetically favorable electron transfer.[14]

**Photovoltaic and Hole-mobility Characteristics.** Bulk heterojunction photovoltaic cells were fabricated by spin-coating the blends from *o*-DCB solutions at various polymer-to-$PC_{71}BM$ ratios on the basis of ITO/PEDOT:PSS/polymer:$PC_{71}BM$/Ca/Al configuration and their performances were measured under a simulated AM 1.5 G illumination of 100 mW/cm$^2$. The asymmetric $PC_{71}BM$ was used due to its stronger light absorption in the visible region than that of $PC_{61}BM$.[15] In addition, to evaluate the hole mobility in the blending active layer, hole-only devices (ITO/PEDOT:PSS/polymer:$PC_{71}BM$/Au) were fabricated. The characterization data are summarized in Table 2 and the $J-V$ curves of these polymers are shown in Figure 3. The blend ratio of the active layers shown in the Table 2 is the result of the optimized conditions for the devices. The device based on the **PCDCTBT-C8**:$PC_{71}BM$ (1:3 in wt%) blend exhibited a $V_{oc}$ of 0.74 V, a $J_{sc}$ of 10.3 mA/cm$^2$, a FF of 60%, delivering an impressive PCE of 4.6%. This value represents not only a ca. 24% enhancement in efficiency compared to the devices based on the **PCDCTBT** (PCE = 3.7%) and **PCDTBT** (PCE = 3.6%)[5e] but also one of the best performances among carbazole-based conjugated polymers in the literatures. The **PCDCTBT-C8**:$PC_{71}BM$ (1:3 in wt%) composite also showed very high hole


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mobility of $1.2 \times 10^{-3}$ cm$^2$ $V^{-1}$ s$^{-1}$, which is in good agreement with its high current density and fill factor. This improvement is highly associated with the modification of the side chains on the **CDCT** structure to optimize the interchain interactions for enhanced charge transporting. The device based on **PCDCTDTBT-C8** with two additional thiophene rings also showed a high PCE of 3.5% with a $V_{oc}$ of 0.74, a $J_{sc}$ of 9.2 cm$^2$ $V^{-1}$ s$^{-1}$, a FF of 52%. Compared to **PCDCTBT-C8** and **PCDCTDTBT-C8**, the device based on **PCDCTDTDPP-C8** exhibited slightly lower $V_{oc}$ of 0.7 V and $J_{sc}$ of 6.7 mA/cm$^2$ because of the highest HOMO level (−5.24 eV) and lowest LUMO level (−3.87 eV) of **PCDCTDTDPP-C8**, respectively, leading to a moderate PCE of 2.4%. The device based on **PCDCTQ-C8** exhibited the relatively lower PCE of 1.8% due to its smallest $J_{sc}$ of 5.8 mA/cm$^2$. This result can be attributed to the lower hole mobility of $1.5 \times 10^{-5}$ cm$^2$ $V^{-1}$ s$^{-1}$ in **PCDCTQX-C8**/$PC_{71}BM$ blend (1:2, w/w).

## CONCLUSION

We have successfully designed and synthesized a ladder-type carbazole-dicyclopentathiophene (**CDCT-C8**) unit with rigid and coplanar backbone. The nitrogen-directing effect of the carbazole unit facilitates the intramolecular Friedel−Crafts cyclization and thereby suppresses the acid-induced dehydration, allowing us to incorporate two aliphatic octyl side chains on the cyclopentadiene rings in good chemical yield. The distannyl-**CDCT-C8** building block was copolymerized with electron-deficient benzothiadiazole (**BT**), dithienylbenzothiadiazole (**DTBT**), dithienyldiketopyrrolopyrrole (**DTDPP**) and quinoxaline (**QX**) units by Stille polymerization to afford four alternating donor−acceptor copolymers, **PCDCTBT-C8**, **PCDCTDTBT-C8**, **PCDCTDTDPP-C8**, and **PCDCTQX-C8**, respectively. Compared to **PCDCTBT** using 4-(2-ethylhexoxy)phenyl moieties as the side chains, **PCDCTBT-C8** exhibits a broadening and bathochromic shift absorption spectrum as well as smaller optical band gap due to the enhanced intermolecular interaction in the solid state. Through such a simple and straightforward engineering of molecular structures, the device based on the **PCDCTBT-C8**:$PC_{71}BM$ (1:3 in wt%) blend performed a $V_{oc}$ of 0.74 V, a $J_{sc}$ of 10.3 mA/cm$^2$, a FF of 60%, delivering an impressive PCE of 4.6%. The corresponding **PCDCTBT-C8**:$PC_{71}BM$ blend also showed a high hole mobility of $1.2 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$, leading to the high current density and fill factor. The improved performance is associated with the modification of the aliphatic side chains on the **CDCT** structure to optimize the interchain interactions for enhanced charge transporting.

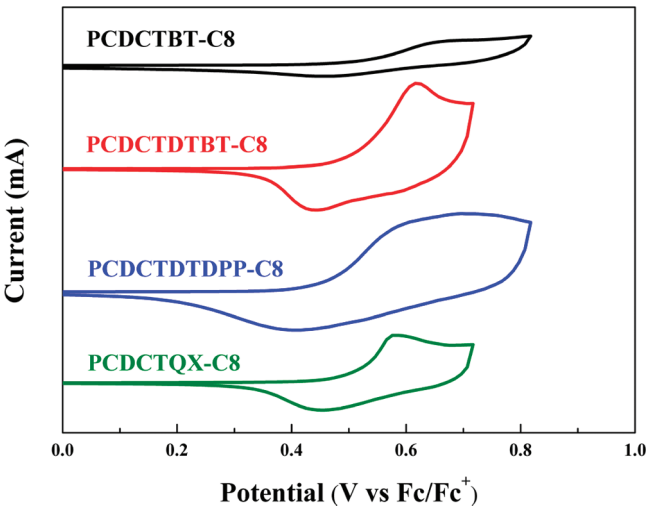


**Figure 2.** Cyclic voltammograms of **PCDCTBT-C8**, **PCDCTDTBT-C8**, **PCDCTDTDPP-C8**, and **PCDCTQX-C8** in the thin film at a scan rate of 30 mV/s.

## EXPERIMENTAL SECTION

**General Measurement and Characterization.** All chemicals are purchased from Aldrich or Acros and used as received unless otherwise specified. $^1$H and $^{13}$C NMR spectra were measured using a Varian 300 MHz instrument spectrometer. Fourier transform infrared spectroscopy (FTIR) was measured on a Perkin-Elmer One Instrument by preparing KBr Pellets. Differential scanning calorimeter (DSC) was measured on a TA Q200 Instrument and thermogravimetric analysis (TGA) was recorded on a Perkin-Elmer Pyris under nitrogen atmosphere at a heating rate of 10 °C/min. Absorption spectra were collected on a HP8453 UV−vis spectrophotometer. The molecular weight of polymers were measured by the GPC method on a Viscotek VE2001GPC, and polystyrene was used as the standard (THF as the eluent). The electrochemical cyclic voltammetry

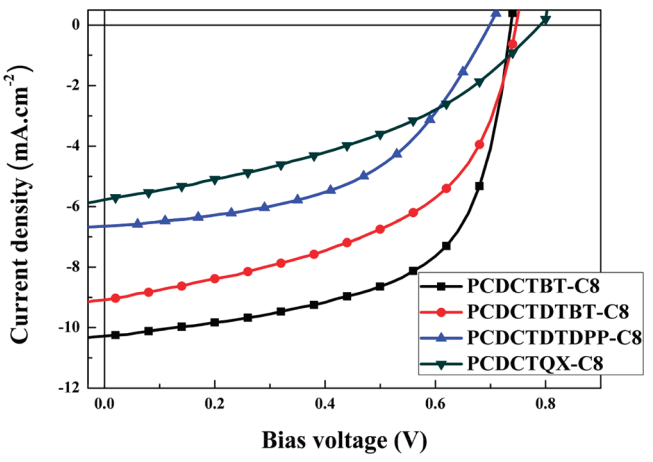


**Figure 3.** Current density−voltage characteristics of ITO/PEDOT:PSS/polymer:$PC_{71}BM$/Ca/Al devices under illumination of AM 1.5 G at 100 mW/cm$^2$.

**Table 2. Hole Mobilities and Photovoltaic Characteristics**

| polymer | blend ratio with $PC_{71}BM$ | $\mu_h$[a] (cm$^2$ V$^{-1}$ s$^{-1}$) | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | FF (%) | PCE (%) |
|---|---|---|---|---|---|---|
| **PCDCTBT-C8** | 1:3 | $1.2 \times 10^{-3}$ | 0.74 | 10.3 | 60 | 4.59 |
| **PCDCTDTBT-C8** | 1:3 | $7.6 \times 10^{-4}$ | 0.74 | 9.2 | 52 | 3.53 |
| **PCDCTDTDPP-C8** | 1:1 | $4.4 \times 10^{-4}$ | 0.70 | 6.7 | 50 | 2.35 |
| **PCDCTQX-C8** | 1:2 | $1.5 \times 10^{-5}$ | 0.78 | 5.8 | 40 | 1.80 |
| **PCDCTBT**[b] | 1:2 | $4.0 \times 10^{-4}$ | 0.80 | 10.7 | 43 | 3.70 |

[a] Hole mobility of the blends determined by space-charge limit current (SCLC). [b] Device data from ref 6.


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(CV) was conducted on a Autolab ADC 164. A Carbon glass coated with a thin polymer film was used as the working electrode and standard calomel electrode as the reference electrode, whereas 0.1 M tetrabutylammonium tetrafluoroborate ($Bu_4NBF_4$) in acetonitrile was the electrolyte. CV curves were calibrated using ferrocence as the standard, whose oxidation potential is set at −4.8 eV with respect to zero vacuum level. The HOMO energy levels were obtained from the equation HOMO = $-(E_{ox}^{onset} - E_{(ferrocene)}^{onset} + 4.8)$ eV. The LUMO levels of polymer were obtained from the equation LUMO = $-(E_{red}^{onset} - E_{(ferrocene)}^{onset} + 4.8)$ eV.

**Device Fabrication.** ITO/Glass substrates were ultrasonically cleaned sequentially in detergent, water, acetone and *iso*-propanol (IPA). The cleaned substrates were covered by a 30 nm thick layer of PEDOT:PSS (Clevios P provided by Stark) by spin coating . After annealing in air at 200 °C for 10 min, the samples were cooled to room temperature. Polymers were dissolved in *o*-dichlorobenzene (ODCB) (10 mg/mL) and $PC_{71}BM$ (purchased from Nano-C) was added (20 mg/mL). The solution was then heated at 100 °C for 30 min and stirred overnight at room temperature. Prior to deposition, the solution were filtered (1 $\mu$m filters) and the substrates were transferred in a glovebox. The solution of polymer:$PC_{71}BM$ was then spin coated to form the active layer (90 nm). All the polymer films except **PCDCTDTDPP-C8** were thermally annealed at 140 °C for 15 min. The cathode made of calcium (35 nm thick) and aluminum (100 nm thick) was sequentially evaporated through a shadow mask under high vacuum ($<10^{-6}$ Torr). Each sample consists of four independent pixels defined by an active area of 0.04 $cm^2$. Finally, the devices were encapsulated and characterized in air. In order to investigate the hole mobilities of the different polymer films, unipolar devices have been prepared following the same procedure except that the Ca/Al cathode is replaced by evaporated gold (40 nm). The hole mobilities were calculated according to space charge limited current theory (SCLC). The *J*−*V* curves were fitted according to the following equation:

$$J = \frac{9}{8}\varepsilon\mu\frac{V^2}{L^3}$$

Where $\varepsilon$ is the permittivity of the polymer, $\mu$ is the hole mobility and *L* is the film thickness.

**Synthesis of Compound 4.** To a solution of compound **3**[6] (3.0 g, 4.2 mmol) in dry THF (20 mL) was added dropwise n-octyl magnesium bromide which was freshly prepared by reacting 1-bromooctane (6.49 g, 33.6 mmol) with magnesium turnings (0.9 g, 37.0 mmol). The reaction mixture was refluxed at 70 °C for 16 h and then quenched with water, followed by extraction with diethyl ether (50 mL × 3) and water (100 mL). The collected organic layer was dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 30/1) to give a orange sticky product **4** (1.8 g, 40%). $^1$H NMR ($CDCl_3$, 300 MHz): 0.79−0.88 (m, 18 H), 1.07−1.37 (m, 72 H), 1.63−1.74 (m, 8 H), 1.79 (s, 2 H), 1.85−1.93 (m, 2 H), 2.21−2.25 (m, 2 H), 4.47−4.51 (m, 1 H), 7.10 (d, *J* = 5.1 Hz, 2 H), 7.24 (d, *J* = 5.1 Hz, 2 H), 7.28 (br, 2 H), 7.43 (br, 1 H), 7.63 (br, 1 H), 8.05 (t, *J* = 8.4 Hz, 2 H); $^{13}$C NMR ($CDCl_3$, 75 MHz): 14.20, 14.25, 22.75, 22.81, 23.61, 23.95, 27.12, 29.35, 29.49, 29.53, 29.57, 29.79, 29.84, 30.19, 30.43, 31.93, 32.04, 33.93, 39.44, 43.47, 56.88, 78.32, 111.39, 114.06, 119.63, 119.90, 121.82, 122.10, 122.88, 123.48, 128.18, 132.31, 132.82, 138.18, 138.37, 138.54, 141.91, 143.01 (Multiple carbon peaks result from phenomenon of atropisomerism[5a]); IR (KBr) 3600, 2954, 2924, 2855, 1626, 1600, 1456, 1377, 1327, 1241, 1194, 1137, 1065, 1001, 804, 722, 677, 564 $cm^{-1}$; MS (FAB, $C_{71}H_{115}NO_2S_2$): calcd, 1078.81; found, 1079; elemental analysis (%) Calcd, for $C_{71}H_{115}NO_2S_2$: C, 79.05; H, 10.74; N, 1.3. Found: C, 79.15; H, 10.32; N, 1.47.

**Synthesis of Compound 5.** To a solution of compound **4** (1.8 g, 1.67 mmol) in dichloromethane (50 mL) was added borontrifluoride diethyletherate (5.4 mL). The reaction mixture was stirred for 10 h at room temperature and then was extracted with dichloromethane (50 mL × 4) and water (100 mL). The collected organic layer was dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/diethyl ether, v/v, 50/1) to give a orange sticky product **5** (1.1 g, 63%). $^1$H NMR ($CDCl_3$, 300 MHz): 0.77−0.82 (m, 18 H), 0.85−0.90 (m, 12 H), 1.12−1.25 (m, 60 H), 1.87−2.05 (m, 10 H), 2.27−2.31 (m, 2 H), 4.54−4.55 (m, 1 H), 6.99 (d, *J* = 4.8 Hz, 2 H), 7.28 (d, *J* = 4.8 Hz, 2 H), 7.34 (br s, 1 H), 7.47 (br s, 1 H), 7.89 (s, 1 H), 7.92 (s, 1 H). (two set of singlets result from phenomenon of atropisomerism[5a]); $^{13}$C NMR ($CDCl_3$, 75 MHz): 14.17, 22.73, 24.53, 27.19, 29.33, 29.45, 29.49, 29.61, 30.35, 31.90, 31.94, 33.90, 39.94, 53.22, 56.84, 99.14, 101.81, 113.36, 113.74, 120.45, 122.05, 126.37, 135.69, 136.12, 138.59, 142.11, 145.37, 156.00 (Multiple carbon peaks result from phenomenon of atropisomerism[5a]); IR (KBr) 3064, 2950, 2925, 2852, 1655, 1629, 1602, 1465, 1342, 1204, 1085, 918, 872, 721, 666, 546 $cm^{-1}$; MS (FAB, $C_{71}H_{111}NS_2$): calcd, 1042.78; found, 1043; elemental analysis (%) Calcd, for $C_{71}H_{111}NS_2$: C, 81.78; H, 10.73; N, 1.34. Found: C, 81.56; H, 10.42; N, 1.49.

**Synthesis of Compound 6.** To a solution of **5** (1.12 g, 1.07 mmol) in dry THF (20 mL) was added a 1.6 M solution of *t*-BuLi in hexane (5.4 mL, 8.64 mmol) dropwise at −78 °C. After stirring at −78 °C for 30 min, 1.0 M solution of chlorotrimethylstannane in THF (13 mL, 13 mmol) was introduced by syringe to the solution. The mixture solution was warmed up to room temperature and stirred for 15 h. The mixture solution was quenched with water and extracted with diethyl ether (50 mL × 3) and water (50 mL). After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/$Et_3N$, v/v, 50/1) to give a light orange sticky product **6** (1.28 g, 87%). $^1$H NMR ($CDCl_3$,300 MHz): 0.41 (s, 18 H), 0.77−0.82 (m, 18 H), 0.95−0.97 (m, 8 H), 1.13−1.28 (m, 64 H), 1.86−2.07 (m, 10 H), 2.27−2.30 (m, 2 H), 4.52−4.56 (m, 1 H), 7.02 (s, 2 H), 7.32 (br s, 1 H), 7.46 (br s, 1 H), 7.88 (s, 1 H), 7.91 (s, 1 H) (two sets of singlets result from phenomenon of atropisomerism[5a]); IR (KBr) 3046, 2954, 2924, 2852, 1670, 1626, 1611, 1465, 1376, 1343, 1310, 1213, 1082, 950, 872, 838, 770, 721, 532 $cm^{-1}$; MS (FAB, $C_{77}H_{127}NS_2Sn_2$): calcd, 1368.39; found, 1369.

**Synthesis of PCDCTBT-C8.** To a solution of dry and deoxygenated toluene (13 mL) was introduced **6** (0.6 g, 0.438 mmol), 4,7-dibromo-2,1,3-benzothiadiazole **7** (128.8 mg, 0.438 mmol), and $Pd(PPh_3)_4$ (25.3 mg, 0.022 mmol). The reaction mixture was refluxed at 120 °C for 72 h. The solution was dropwise added into methanol. The precipitate was collected by filtration and washed by Soxhlet extraction with hexane sequentially for two days. The product was redissolved in THF. The Pd-thiol gel (Silicycle Inc.) was added to above THF solution to remove the residual Pd catalyst. After filtration and removal of the solvent, the polymer was redissolved in THF again and added into methanol to reprecipitate. The purified polymer was collected by filtration and dried under vacuum for 1 day to give dark violet solid (200 mg, yield 39%, $M_n$ = 38.1 kDa, PDI = 1.60). $^1$H NMR ($CDCl_3$, 300 MHz): 0.77−0.81 (m, 18 H), 1.61 (br, 72 H), 2.04−2.34 (m, 12 H), 4.61 (br, 1 H), 7.46 (br, 1 H), 7.60 (br, 1 H), 8.00 (br, 4 H), 8.07−8.11 (br, 2 H); IR (KBr) 2952, 2923, 2851, 1717, 1628, 1599, 1486, 1459, 1341, 1250, 1216, 1171, 1080, 828, 671, 554 $cm^{-1}$.

**Synthesis of PCDCTDTBT-C8.** To a solution of dry and deoxygenated toluene (14 mL) was introduced **6** (0.684 g, 0.499 mmol), 4,7-bis(5-bromo-2-thienyl)-2,1,3-benzothiadiazole **8** (228.8 mg, 0.499 mmol), and $Pd(PPh_3)_4$ (28.8 mg, 0.025 mmol). The reaction mixture was refluxed at 120 °C for 72 h. The solution was dropwise added into methanol. The precipitate was collected by filtration and washed by Soxhlet extraction with hexane/acetone (1/3, v/v) sequentially for two days. The product was redissolved in THF. The Pd-thiol gel (Silicycle Inc.) was added to above THF solution to remove the residual Pd catalyst. After filtration and removal of the solvent, the polymer was redissolved in THF again and added into methanol to reprecipitate. The purified polymer was collected by filtration and dried under vacuum for

1 day to give dark violet solid (580 mg, yield 87%, $M_n$ = 14.1 kDa, PDI = 2.17). $^1$H NMR ($CDCl_3$, 300 MHz): 0.78−0.82 (m, 18 H), 1.16 (br, 72 H), 2.02 (br, 10 H), 2.30 (br, 2 H), 4.59 (br, 1 H), 7.34 (br, 4 H), 7.49 (br, 2 H), 7.91 (br, 4 H), 8.08 (br, 2 H); IR (KBr) 3066, 2922, 2849, 1650, 1628, 1604, 1482, 1458, 1424, 1340, 1212, 1128, 1040, 915, 873, 830, 795, 690, 547 cm$^{-1}$.

**Synthesis of PCDCTDTDPP-C8.** To a solution of dry and deoxygenated toluene (22 mL) was introduced **6** (1.071 g, 0.782 mmol), 3, 6-bis(5-bromothiophen-2-yl)-2,5-bisoctylpyrrolo[3,4-*c*] pyrrole-1,4- dione **9**[13] (533.8 mg, 0.782 mmol), and $Pd(PPh_3)_4$ (45.2 mg, 0.039 mmol). The reaction mixture was refluxed at 120 °C for 72 h. The solution was dropwise added into methanol. The precipitate was collected by filtration and washed by Soxhlet extraction with hexane/acetone (2/3, v/v) sequentially for two days. The product was redissolved in THF. The Pd-thiol gel (Silicycle Inc.) was added to above THF solution to remove the residual Pd catalyst. After filtration and removal of the solvent, the polymer was redissolved in THF again and added into methanol to reprecipitate. The purified polymer was collected by filtration and dried under vacuum for 1 day to give black solid (700 mg, yield 57%, $M_n$ = 18.0 kDa, PDI = 1.12). $^1$H NMR ($CDCl_3$, 300 MHz): 0.80−0.90 (m, 24 H), 1.16−1.32 (m, 92 H), 1.82 (br, 4 H), 2.03 (br, 8 H), 2.31 (br, 4 H), 4.16 (br, 4 H), 4.56 (br, 1 H), 7.39 (br, 4 H), 7.49 (br, 2 H), 7.91 (br, 2 H), 8.94 (br, 2 H); IR (KBr) 3070, 2952, 2922, 2850, 1662, 1555, 1528, 1498, 1460, 1412, 1341, 1214, 1099, 1081, 1050, 873, 834, 807, 731, 552 cm$^{-1}$.

**Synthesis of PCDCTQX-C8.** To a solution of dry and deoxygenated toluene (14 mL) was introduced **6** (0.671 g, 0.490 mmol), 5,8-dibromo-2,3-diphenylquinoxaline **10**[12] (215.4 mg, 0.490 mmol), and $Pd(PPh_3)_4$ (28.3 mg, 0.024 mmol). The reaction mixture was refluxed at 120 °C for 72 h. The solution was dropwise added into methanol. The precipitate was collected by filtration and washed by Soxhlet extraction with hexane/acetone (2/3, v/v) sequentially for two days. The product was redissolved in THF. The Pd-thiol gel (Silicycle Inc.) was added to above THF solution to remove the residual Pd catalyst. After filtration and removal of the solvent, the polymer was redissolved in THF again and added into methanol to reprecipitate. The purified polymer was collected by filtration and dried under vacuum for 1 day to give black solid (150 mg, yield 23%, $M_n$ = 5.6 kDa, PDI = 2.53). $^1$H NMR ($CDCl_3$, 300 MHz): 0.79 (br, 18 H), 1.16 (br, 72 H), 2.03 (br, 10 H), 2.36 (br, 2 H), 4.61 (br, 1 H), 7.47 (br, 6 H), 7.58 (br, 1 H), 7.72 (br, 1 H), 7.80−8.01 (m, 8 H), 8.21 (br, 2 H); IR (KBr) 3060, 2952, 2922, 2850, 1656, 1604, 1562, 1459, 1376, 1339, 1215, 1174, 1108, 1023, 965, 917, 873, 829, 767, 694, 537 cm$^{-1}$.

## ■ ASSOCIATED CONTENT

**Supporting Information.** TGA, DSC, and NMR spectra of the new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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