Ladder-Type Nonacyclic Structure Consisting of Alternate Thiophene and Benzene Units for Efficient Conventional and Inverted Organic Photovoltaics

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ABSTRACT: A ladder-type nonacyclic thienyl-phenylene-thienylene-phenylene-thienyl TPTPT unit, consisting of alternate interfused thiophene and benzene units, is designed and synthesized. This multifused distannyl-TPTPT monomer was polymerized with two electron-deficient acceptors, 4,7-dibromo-2,1,3-benzothiadiazole BT and 5,8-dibromo-2,3-diphenylquinoxaline QX monomers, by Stille coupling reaction to afford two alternating donor–acceptor copolymers, PTPTPTB and PTPPTQX, respectively. Because of the covalent planarization of the conjugated framework, PTPTPTB simultaneously possess excellent solubilities for solution-processability, low bandgaps with suitable position of HOMO/LUMO energy levels, and high hole mobilities. The devices based on the PTPTPTB/PC71BM blend not only showed a promising PCE of 5.3% with conventional configuration but also achieved a high PCE of 5.9% with inverted configuration. This value is among the highest performance from the inverted solar cells incorporating a donor–acceptor low bandgap polymer.

KEYWORDS: ladder-type structure, organic photovoltaics, alternating copolymer

INTRODUCTION

Research on excitonic solar cells using organic p-type (donor) and n-type (acceptor) semiconductors has attracted tremendous scientific and industrial interest in recent years. The most critical challenge at molecular level is to translate excellent microscopic properties of photoactive materials into optimal macroscopic device characteristics. Donor–acceptor (D–A) polymers incorporating tricyclic 2,7-fluorene unit have shown to possess deep-lying HOMO energy levels that are an important prerequisite to guarantee greater open-circuit voltages ($V_{oc}$). Nevertheless, because of high aromatic stabilization energy of the benzene rings, fluorine-based polymers exhibit relatively large optical band gaps (>2 eV) that restrict their absorption ability and, thus, result in insufficient photocurrents. 4H-cyclopentadithiophene (CPDT) appears to be another attractive thiophene-based tricyclic analogue. CPDT-based D–A polymers have shown narrower optical bandgaps and higher hole mobilities, yielding very high short-circuit currents ($J_{sc}$). Unfortunately, the resulting devices deliver only moderate $V_{oc}$ values (<0.65 V). Development of a new donor moiety that can extract the advantages of benzene-based fluorene and thiophene-based CPDT units may overcome the trade-off between $J_{sc}$ and $V_{oc}$. Chemical planarization by covalently fastening adjacent aromatic units in the polymeric backbone can facilitate π-electron delocalization and increase effective conjugation length. Moreover, such rigidification also suppresses the rotational disorder around interannular single bonds and lowers the reorganization energy, which in turn enhances the intrinsic charge mobility. On the basis of the aforementioned consideration, integration of alternate thiophene and benzene units into a coplanar entity with forced rigidification becomes a novel molecular design. Pentacyclic fused indacenodithiophene (IDT) unit exemplifies a successful system in this category. The devices utilizing the IDT-based D–A polymers have shown superior photovoltaic performance. The other pentacyclic arrangement system is the fused diindenothiophene (DIDT) with highly planar structure. We recently reported a DIDT-based alternating copolymer poly((DIDT-alt-dithienylbenzothiadiazole) (PDIDTDTBT) and its corresponding device has shown a moderate power conversion efficiency (PCE) of 1.65% (Figure 1). If the 3,7-position of the DIDT units in PDIDTDTBT are covalently rigidified with the 3-position of two adjacent thiophene rings by a carbon bridge, an alternate thienyl-phenylene-thienylene-phenylene-thienyl (TPTPT) nonacyclic building block with forced coplanarity will be emerged (Figure 1). Compared to DIDT, TPTPT unit may exhibit improved optical and electronic properties due to the higher thiophene content and extended coplanarity of the conjugated backbone. In this research, we report the synthesis of the distannyl-TPTPT monomer which is copolymerized with 4,7-dibromo-2,1,3-benzothiadiazole BT and 5,8-dibromo-2,3-diphenylquinoxaline QX acceptor monomers to afford two alternating D–A copolymers poly(TPTPT-alt-benzothiadiazole-)}
zole (PTPTPTBT) and poly(TPTPT-alt-quinoxaline) (PTPTPTQX), respectively (Figure 1). Bulk-heterojunction (BHJ) solar cells incorporating these polymers have shown promising photovoltaic performance in both conventional and inverted architectures.

**RESULTS AND DISCUSSION**

**Synthesis.** The synthetic route toward Sn-TPTPT monomer is depicted in Scheme 1. Suzuki coupling of 2,8-diboronic ester DIDT (1) with ethyl 2-bromothiophene-3-carboxylate yielded compound 2. Double nucleophilic addition of the ester groups in 2 by (4-octyloxy)phenyl magnesium bromide led to the formation of benzylic alcohols in 3 which was subjected to intramolecular Friedel–Crafts cyclization under acidic condition to furnish the nonacyclic arene TPTPT in a high yield of 81%. It is noteworthy that the reaction sites occur regioselectively at 3,7-position of DIDT unit. TPTPT can be efficiently lithiated by t-butyllithium followed by quenching with trimethyltin chloride to afford the distannyl Sn-TPTPT in a moderate yield of 62%. 2,7-dibromo-2,1,3-benzothiadiazole (BT) and 5,8-dibromo-2,3-diphenylquinoxaline (QX) were copolymerized with the donor Sn-TPTPT by Stille coupling to afford PTPTPTBT ($M_n = 30 \text{ kDa}, \text{PDI} = 1.69$) and PTPTPTQX ($M_n = 34 \text{ kDa}, \text{PDI} = 1.60$), respectively.

These copolymers purified by successive precipitation and Soxhlet extraction showed narrow molecular weight distributions with polydispersity index below 1.7. The resulting copolymers flanked with eight side chains on TPTPT showed excellent solubilities in common organic solvents, such as chloroform, toluene, chlorobenzene, and 1,2-dichlorobenzene.

**Thermal Properties.** Thermal stability of PTPTPTBT and PTPTPTQX was analyzed by thermal gravimetric analysis (TGA). The decomposition temperatures ($T_d$) of PTPTPTBT and PTPTPTQX are located at 389 and 409 °C (Figure 2), indicating sufficient thermal stabilities for PSCs applications. From the DSC measurement, both of the polymers showed neither glass transition temperature nor melting point, suggesting that these copolymers tend to be amorphous (Table 1).

**Optical Properties.** The optical properties of the polymers are shown in Table 2. Both of PTPTPTBT and PTPTPTQX...
exhibited two distinct bands in the absorption spectra (Figure 3). One band at shorter wavelengths region is due to localized $\pi-\pi^*$ transitions and the other band at longer wavelengths is attributed to intramolecular charge transfer (ICT). Compared to PTPTPTQX showing the absorption maxima at 452 and 593 nm in the thin film, PTPTPTBT exhibited a similar absorption maximum at 452 nm but a bathochromic shift of the ICT band at 639 nm. In addition, the optical band gaps ($E_{\text{g opt}}$) deduced from the absorption edges of thin film spectra are determined to be 1.73 eV (715 nm) for PTPTPTBT and 1.80 eV (688 nm) for PTPTPTQX. These results indicate that accepting strength of BT is stronger than that of QX unit. It should be emphasized that PTPTPTBT showed significantly red-shifted absorption maximum in comparison with its corresponding nonfused PDIDTDTBT analogue (444 vs 415 nm for the localized transition and 628 vs 544 nm for the ICT transition in chloroform solution), demonstrating that the effective conjugated length of the coplanar donor is increased and electron coupling between the rigidified donor and the acceptor units is substantially enhanced. Note that the intensities of the shorter wavelength bands of the polymer in the solid state are apparently stronger than those in the solution state, which also suggests that the rigid and coplanar nonacyclic units can enhance their light absorption ability in the solid state.

Theoretical Calculations. To further understand the effect of covalent planarization on the molecular structures and properties, we performed theoretical calculations by density functional theory at the level of B3LYP/6-31G(d). One repeating units TPTPTBT and DIDTDTBT were used as simplified models for simulation of PTPTPTBT and PDIDTDTBT copolymers, respectively. All the side-chain substituents were replaced with methyl groups for simplicity. The optimized structures for TPTPTBT and DIDTDTBT are shown in Figure 4. The strategy to sew-up C64/C65 and C61/C62 of DIDTDTBT effectively planarizes the whole molecule (TPTPTBT), in which the dihedral angels $\phi(C42-C43-C44-C45)$ and $\phi(C55-C54-C60-C61)$ are zero. For comparison, the corresponding angles in DIDTDTBT are $\phi(C64-C25-C24-C65)$ = 26.6° and $\phi(C62-C34-C39-C61)$ = 23.6°. Furthermore, such ring-fusion also makes impact on the coplanarity between the BT and the neighboring thiophene rings: the dihedral angles between these two...
structural motifs are $\phi(C40-C41-C49-C50) = 7.32^\circ$ for DIDTDTBT and $\phi(C62-C63-C71-C72) = 0.07^\circ$ for TPTPTBT.

The frontier orbitals of the model compound TPTPTBT were also shown in Figure 5. The electron density of the HOMO for TPTPTBT is homogeneously distributed along the nonacyclic donor unit, whereas the electron density of the LUMO is redistributed to the BT acceptor unit. Such an electronic redistribution shows a pronounced intramolecular charge separation between donor and acceptor after excitation. The energy of HOMO–LUMO transition for TPTPTBT is calculated to be 631 nm, which is in good agreement with its experimental absorption maximum (628 nm in chloroform).

Electrochemical Properties. Cyclic voltammetry (CV) was employed to examine the electrochemical properties and evaluate the HOMO and LUMO levels of the polymer (Figure 6 and Table 3). Both polymers showed a stable and reversible p-doing and n-doping processes, which are important prerequisites for p-type semiconductor materials. The HOMO energy levels being estimated to be $-5.24$ eV for PTPTPTBT and $-5.21$ eV for PTPTPTQX are in an ideal range to ensure better air-stability and greater attainable $V_{oc}$ in the final device. The LUMO energy levels are approximately located at $-3.38$ eV for PTPTPTBT and $-3.30$ eV for PTPTPTQX, which are higher than the LUMO level of the PC$_{71}$BM acceptor ($-3.8$ eV) to ensure energetically favorable electron transfer. This can be unambiguously evidenced by the complete photoluminescence quenching in the film of the PTPTPTBT/PC$_{71}$BM (1:4, w/w) and PTPTPTQX/PC$_{71}$BM (1:2, w/w) blends (Figure 7).

Photovoltaic and Hole-Mobility Characteristics. Despite the amorphous nature in thin films, PTPTPTBT and PTPTPTQX showed good hole transporting properties because of their rigid and coplanar structures. Hole-only
PTPTPTBT/PC71BM at excitation wavelength of 628 nm, PTPTPTQX and PTPTPTQX/PC71BM (1/2, w/w) at excitation wavelength of 593 nm in the thin film.

devices (ITO/PEDOT:PSS/polymer/Au) were fabricated to estimate the intrinsic hole mobilities of these polymers by means of the space-charge limit current (SCLC) theory. PTPTPTBT and PTPTPTQX exhibited higher hole mobilities of $5.1 \times 10^{-4} \text{ cm}^2/(\text{V s})$ and $3.7 \times 10^{-4} \text{ cm}^2/(\text{V s})$, respectively, compared to PDITIDTBT with $1 \times 10^{-4} \text{ cm}^2/(\text{V s})$. On the basis of ITO/PEDOT:PSS/polymer:PC71BM/Ca/Al configuration, bulk heterojunction solar cells were fabricated and characterized under simulated 100 mW cm$^{-2}$ AM 1.5 G illumination. The current density–voltage characteristics of the devices, the corresponding external quantum efficiency (EQE) for both the conventional and inverted solar cells was measured under illumination of monochromatic light (Figure 8). The $J_{sc}$ calculated from integration of the EQE with an AM 1.5 G reference spectrum agrees well with the $J_{sc}$ obtained from the $J$–$V$ measurements.

### CONCLUSIONS

In summary, we have successfully synthesized a nonacylic distannyl-TPTPT unit that consists of alternate thiophene and benzene units fused by four embedded cyclopentadienyl rings. PTPTPTQX copolymers incorporating this rigidified and coplanar TPTPT units simultaneously possess excellent solubilities for solution-processability, low bandgaps with suitable position of HOMO/LUMO energy levels, and high hole mobilities, leading to promising PCEs of 4.1 and 5.3%, respectively. Most significantly, the PTPTPTQX/PC71BM-based device with inverted architecture achieved an impressively high PCE of 5.9%. This value is among the highest
efficiency ever reported for the inverted solar cells incorporating a D–A type LBG polymer. We envisage that further improvement of device performance is achievable by optimizing the processing conditions.

**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 Varian 300 MHz instrument spectrometer. The molecular weight of polymers was measured by the GPC method (Viscotek VE2001GPC), and polystyrene was used as the standard (THF as the eluent). Differential scanning calorimeter (DSC) was measured on TA Q200 Instrument and thermal gravimetric analysis (TGA) was recorded on Perkin-Elmer Pyris under a nitrogen atmosphere at a heating rate of 10 °C/min. Absorption spectra were taken on a HP8453 UV–vis spectrophotometer. The electrochemical cyclic voltammetry was conducted on a CH instruments electrochemical analyzer. A carbon glass coated with a thin polymer film was used as the working electrode and an Ag/AgCl as the reference electrode, whereas 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) in acetonitrile was the electrolyte. CV curves were calibrated using ferrocene as the standard, whose HOMO is set at $−4.8$ eV with respect to zero vacuum level. The HOMO energy levels were obtained from the equation HOMO = $E_{\text{ox}}^{\text{ onset}} − E_{\text{Fc}}^{\text{red}} + 4.8$ eV. The LUMO levels of polymer were obtained from the equation LUMO = $E_{\text{red}}^{\text{ onset}} − E_{\text{Fc}}^{\text{ox}} + 4.8$ eV. Surface images were measured by Veeco di-Innova Atomic Force Microscope.

Fabrication and Characterization of BHJ Devices. ITO/Glass substrates were ultrasonically cleaned sequentially in detergent, water, acetone and isopropyl alcohol. Then, the substrates were covered by a 30 nm thick layer of PEDOT:PSS (Clevios P provided by H. C. Stark) by spin coating. After annealing in air at 150 °C during 30 min, the samples were cooled down to rt. Polymers were dissolved in ortho-dichlorobenzene (ODCB) (0.47 wt.%) and PC$_{71}$BM (purchased from Nano-C) was added to reach the desired ratio. The solution was then heated at 110 °C and stirred overnight. Prior to deposition, the solution was filtrated through a 0.45 μm filter and the substrates were transferred in a glovebox. The photoactive layer was then spin coated at different spin coating speed in order to tune its thickness. After drying, the samples were annealed during 15 min. The detailed processing parameters (spin coating speed; annealing temperature) are shown as follows: PTPTPTBT/PC$_{71}$BM (700 rpm; 150 °C) and PTPTPTQX/PC$_{71}$BM (700 rpm; 150 °C). The cathode made of calcium (35 nm thick) and aluminum (100 nm thick) was evaporated through a shadow mask under high vacuum (<1 × 10$^{-3}$ Torr). Each device is constituted of 4 pixels defined by an active area of 0.04 cm$^2$.

Hole-Only Devices. To investigate the respective hole mobility of the different copolymer films, we have prepared unipolar devices following the same procedure except that the active layer is made of pure polymer and the Ca/Al cathode is replaced by evaporated gold (40 nm). The hole mobilities were calculated according to space

**Table 4. Hole Mobilities and Photovoltaic Characteristics**

<table>
<thead>
<tr>
<th>copolymer</th>
<th>polymer:PC$_{71}$BM wt% ratio</th>
<th>mobility (cm$^2$/V s)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTPTPTBT</td>
<td>1:4</td>
<td>$5.1 \times 10^{-4}$</td>
<td>0.76</td>
<td>11.4 (11.2)</td>
<td>61</td>
<td>5.3</td>
</tr>
<tr>
<td>PTPTPTBT</td>
<td>1:4</td>
<td>$12.1 \times 10^{-4}$</td>
<td>0.76</td>
<td>64</td>
<td>5.9</td>
<td></td>
</tr>
<tr>
<td>PTPTPTQX</td>
<td>1:2</td>
<td>$3.7 \times 10^{-4}$</td>
<td>0.74</td>
<td>9.0 (9.1)</td>
<td>61</td>
<td>4.1</td>
</tr>
<tr>
<td>PTPTPTQX</td>
<td>1:2</td>
<td>10.2 (9.6)</td>
<td>0.74</td>
<td>62</td>
<td>4.7</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Conventional device structure: ITO/PEDOT:PSS/copolymer:PC$_{71}$BM/Ca/Al. $^b$Inverted device structure: ITO/ZnO/C-PCBSD/copolymer:PC$_{71}$BM/PEDOT:PSS/Ag. $^c$Calculated from the EQE spectrum.

Figure 9. AFM height (left) and phase images (right) of the surface of PTPTPTBT/PC$_{71}$BM (1:4, w/w) blend (10.0 μm × 10.0 μm). The surface roughness is estimated to be 0.4 nm.
charge limited current theory (SCLC). The $J = V^2/L$ curves were fitted according to the following equation

$$J = \frac{9}{8} \varepsilon_0 \mu \frac{V^2}{L^2}$$

Where $\varepsilon$ is the dielectric permittivity of the polymer, $\mu$ is the hole mobility, and $L$ is the film thickness (distance between the two electrodes).

**Synthesis of Compound 2.** To a 50 mL round-bottom flask was introduced 1 (2.20 g, 2.29 mmol), ethyl 2-bromothiophene-3-carboxylate (1.24 g, 5.27 mmol), Pd[PPh4]2 (0.265 g, 0.23 mmol), K2CO3 (1.90 g, 13.75 mmol), and Aliquat 336 (0.23 g, 0.57 mmol) in a solution of degassed toluene (17 mL) and degassed H2O (3.5 mL). The mixture was heated to 90 °C under nitrogen for 72 h. The reaction solution was extracted with ethyl acetate (300 mL × 3) and water (150 mL). The combined organic layer was dried over MgSO4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 20/1) and then recrystallized from hexane to give a light yellow solid (2.07 g, 81%); $\delta$ (d, $J = 5.6$ Hz, 2 H), 7.16 (d, $J = 9.0$ Hz, 8 H), 7.09 (d, $J = 5.6$ Hz, 2 H), 6.94 (s, 2 H), 6.84 (d, $J = 9.0$ Hz, 8 H), 6.41 (d, $J = 5.6$ Hz, 2 H), 3.97 (t, $J = 6.5$ Hz, 8 H), 3.07 (s, 2 H), 1.95–1.60 (m, 16 H), 1.55–0.40 (m, 112 H). 13C NMR (CDCl3, 75 MHz): $\delta$ 163.4, 152.0, 151.6, 149.9, 149.8, 139.3, 130.0, 128.8, 128.1, 123.6, 123.5, 117.3, 60.4, 55.6, 40.2, 31.8, 30.3, 29.6, 29.5, 24.2, 22.6, 14.2, 14.0; MS (FAB, C64H88O4S3): calcd, 1017.58; found, 1017.58, 1017.60.

**Synthesis of Compound 3.** A Grignard reagent was prepared by the following procedure. To a suspension of magnesmum turnings (0.8 g, 33.3 mmol) and 3–4 drops of 1,2-diobromoethane in dry THF (20 mL) was slowly added 1-bromo-4-(octyloxy)benzene (8.56 g, 30.0 mmol) dropwise and stirred for 1 h. To a solution of 2 (0.80 g, 0.79 mmol) in dry THF (20 mL) under nitrogen was added freshly prepared 4-(octyloxy)benzyl magnesium bromide (20 mL) dropwise at −78 °C. The reaction solution was heated at reflux for 16 h. The reaction solution was extracted with ethyl acetate (150 mL × 3) and water (100 mL). The combined organic layer was dried over MgSO4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 100/1) to a yellow oil (3 g, 17.85%). 1H NMR (CDCl3, 300 MHz): $\delta$ 7.24 (d, $J = 9.0$ Hz, 2 H), 7.17 (d, $J = 9.0$ Hz, 2 H), 7.16 (d, $J = 9.0$ Hz, 8 H), 7.09 (d, $J = 5.6$ Hz, 2 H), 6.94 (s, 2 H), 6.84 (d, $J = 9.0$ Hz, 8 H), 6.41 (d, $J = 5.6$ Hz, 2 H), 3.97 (t, $J = 6.5$ Hz, 8 H), 3.07 (s, 2 H), 1.95–1.60 (m, 16 H), 1.55–0.40 (m, 112 H). 13C NMR (CDCl3, 75 MHz): $\delta$ 152.0, 151.6, 149.9, 149.8, 139.3, 130.0, 128.8, 128.1, 123.6, 123.5, 117.3, 60.4, 55.6, 40.2, 31.8, 30.3, 29.6, 29.5, 24.2, 22.6, 14.2, 14.0; MS (FAB, C64H88O4S3): calcd, 1017.58; found, 1017.58.

**Synthesis of TPTPT.** To a 15 mL round-bottom flask was introduced Sn-TPTPT (145.4 mg, 0.07 mmol), 4,7-dibromo-2,1,3-benzothiadiazole BT (20.6 mg, 0.07 mmol), Pd(dba)2 (3.2 mg, 0.0035 mmol), tri(o-tolyl)phosphine (6.8 mg, 0.022 mmol), and dry chlorobenzene (3 mL). The mixture was then degassed by bubbling nitrogen for 10 min at room temperature. The reaction was then added into the microwave reactor and reacted for 45 min under 270 W. To end-cap the resulting polymer, we added triethyl(tiophen-2-yl)stannane (13.1 mg, 0.035 mmol) into the mixture solution and reacted it for 10 min under 270 W. Finally, 2-bromothiophene (6.2 mg, 0.038 mmol) was added to the mixture solution and reacted for 10 min under 270 W. The solution was then added into methanol dropwise. The precipitate was collected by filtration and washed by Soxhlet extraction with acetone, hexane, and chloroform sequentially for one week. The Pd-thiol gel (Silicyc Inc.) and Pd-TAAcOH were added to above chloroform solution to remove the residual Pd catalyst and Sn metal. After filtration and removal of the solvent, the polymer was redissolved in chloroform again and added into methanol to precipitate. The purified polymer was collected by filtration and dried under vacuum for 1 day to give a dark-green fiber-like solid (215 mg, 62%, $M_2 = 30,000$, PDI = 1.69). 1H NMR (CDCl3, 300 MHz): $\delta$ 8.00–8.50 (m, 2 H), 7.75–7.80 (m, 2 H), 7.50–7.70 (m, 4 H), 7.25–7.15 (m, 8 H), 6.90–6.70 (m, 8 H), 4.00–3.80 (m, 8H), 1.85–1.60 (m, 16H), 1.50–1.00 (m, 8 H), 0.90–0.70 (m, 24 H).

**Synthesis of PTPTPTQX.** To a 15 mL round-bottom flask was introduced Sn-TPTPT (259.7 mg, 0.13 mmol), 5,8-dibromo-2,3-diphenylquinoline QX (56 mg, 0.13 mmol), Pd(dba)2 (4.7 mg, 0.0051 mmol), tri(o-tolyl)phosphine (12.4 mg, 0.041 mmol) and dry chlorobenzene (5 mL). The mixture was then degassed by bubbling nitrogen for 10 min at room temperature. The reaction solution was then added into the microwave reactor and reacted for 45 min under 270 W. To end-cap the resulting polymer, we added tributyl(tiophen-2-yl)stannane (23.8 mg, 0.064 mmol) into the mixture solution and reacted for 10 min under 270 W. The solution was then added into methanol dropwise. The precipitate was collected by filtration and washed by Soxhlet extraction with acetone, hexane, and chloroform sequentially for one week. The Pd-thiol gel (Silicyc Inc.) and Pd-TAAcOH were added to above chloroform solution to remove the residual Pd catalyst and Sn metal. After filtration and removal of the solvent, the polymer was redissolved in chloroform again and added into methanol to precipitate. The purified polymer was collected by filtration and dried under vacuum for 1 day to give a dark-green fiber-like solid (215 mg, 62%, $M_2 = 30,000$, PDI = 1.69). 1H NMR (CDCl3, 300 MHz): $\delta$ 8.00–8.50 (m, 2 H), 7.75–7.80 (m, 2 H), 7.50–7.70 (m, 4 H), 7.25–7.15 (m, 8 H), 6.90–6.70 (m, 8 H), 4.00–3.80 (m, 8H), 1.85–1.60 (m, 16H), 1.50–1.00 (m, 8 H), 0.90–0.70 (m, 24 H).

**ASSOCIATED CONTENT**

Supporting Information

1H and 13C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.
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