

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

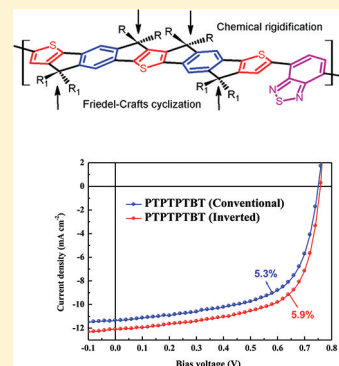
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Supporting Information

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, PTPPTBT and PTPPTQX, respectively. Because of the covalent planarization of the conjugated framework, PTPPTBT 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 PTPPTBT/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.¹ The most critical challenge at molecular level is to translate excellent microscopic properties of photoactive materials into optimal macroscopic device characteristics.² 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}).³ Nevertheless, because of high aromatic stabilization energy of the benzene rings, fluorene-based polymers exhibit relatively large optical band gaps (>2 eV) that restrict their absorption ability and, thus, result in insufficient photocurrents. 4*H*-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}).⁴ 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.⁵ 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.⁶ 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.⁷ 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).⁸ 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*-benzothia-

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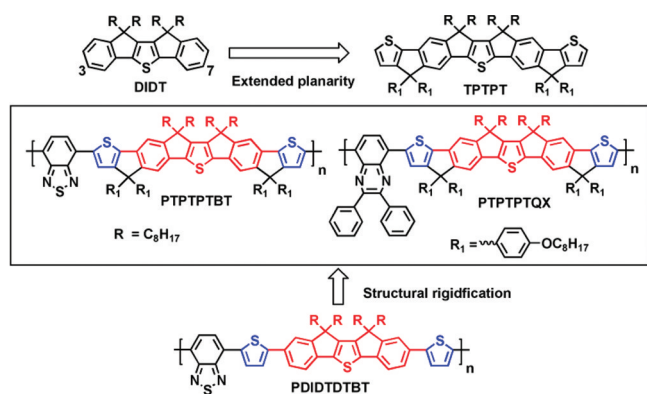


Figure 1. Chemical structure of DIDT and TPTPT units, fused PTPTPTBT, PTPTPTQX copolymers, and nonfused PDDIDTBT.

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

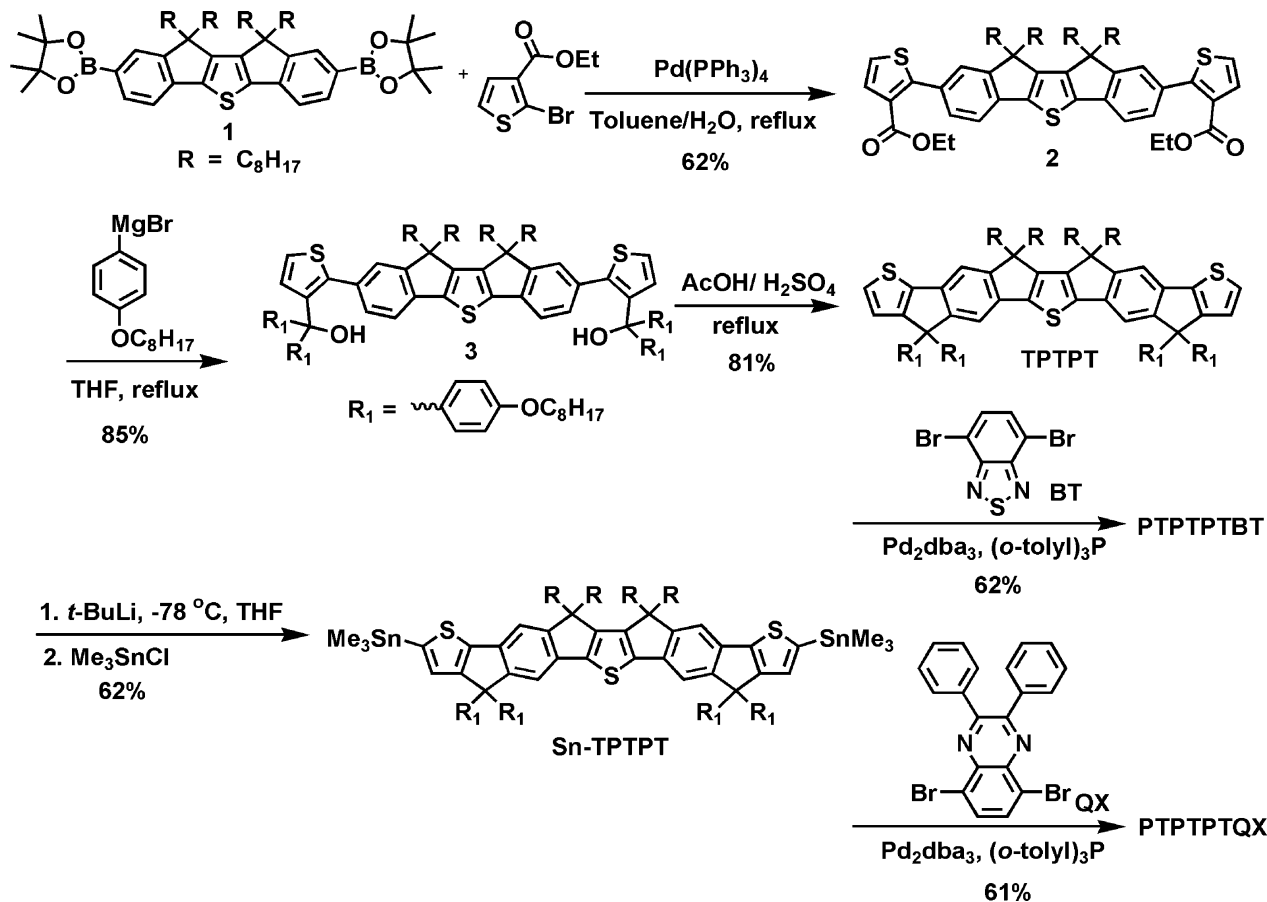
the formation of benzylic alcohols in 3 which was subjected to intramolecular Friedel–Crafts cyclization under acidic condition to furnish the nonacyclic arene TPTPT in a high yield of 81%. It is noteworthy that the reaction sites occur regioselectively at 3,7-position of DIDT unit. TPTPT can be efficiently 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 ($M_n = 30$ kDa, PDI = 1.69) and PTPTPTQX ($M_n = 34$ kDa, PDI = 1.60), respectively.

These copolymers purified by successive reprecipitation 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

Scheme 1. Synthetic Route of the Sn-TPTPT Monomer Leading to the Targeted PTPTPTBT and PTPTPTQX Copolymers



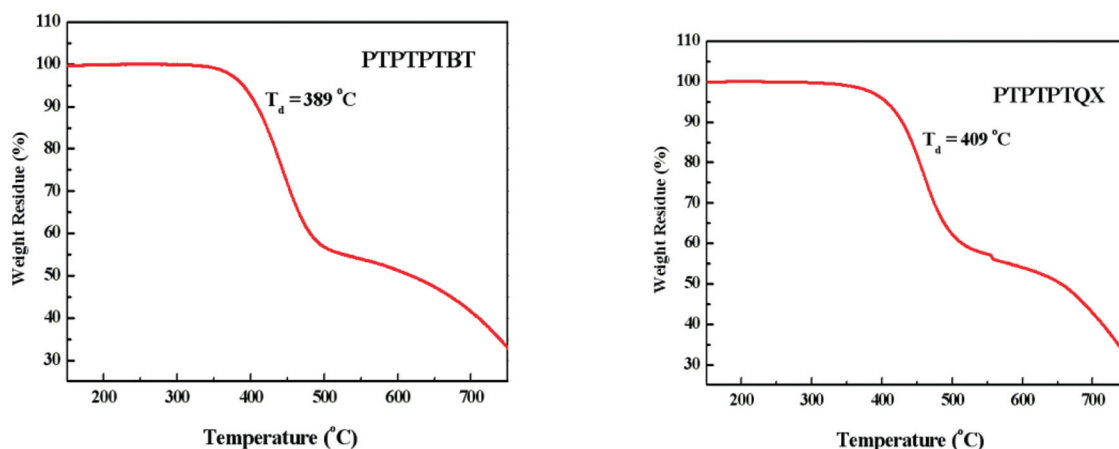


Figure 2. Thermogravimetric analysis (TGA) of PTPPTBT and PTPPTQX.

Table 1. Molecular Weights and Thermal Properties of Polymers

copolymer	M_w	M_n	PDI	T_g (°C)	T_d (°C) ^a
PTPPTBT	50700	30000	1.69		389
PTPPTQX	54400	34000	1.60		409

^bDecomposition temperature (5% weight loss) measured by TGA.

Table 2. Optical Properties of the Copolymers

polymer	chloroform solution			thin film		
	λ_{\max} (nm)	λ_{onset} (nm)	E_g^{opt} (eV)	λ_{\max} (nm)	λ_{onset} (nm)	E_g^{opt} (eV)
PTPPTBT	444, 628	713	1.74	452, 639	715	1.73
PTPPTQX	449, 593	674	1.84	452, 593	688	1.80

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 PTPPTQX showing the absorption maxima at 452 and 593 nm in the thin film, PTPPTBT 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_g^{opt}) deduced from the absorption edges of thin film spectra are determined to be 1.73 eV (715 nm) for PTPPTBT and 1.80 eV (688 nm) for PTPPTQX. These results indicate that accepting strength of BT is stronger than that of QX unit. It

should be emphasized that PTPPTBT showed significantly red-shifted absorption maximum in comparison with its corresponding nonfused PDIDDTBT 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 DIDDTBT were used as simplified models for simulation of PTPPTBT and PDIDDTBT copolymers, respectively. All the side-chain substituents were replaced with methyl groups for simplicity. The optimized structures for TPTPTBT and DIDDTBT are shown in Figure 4. The strategy to sew-up C64/C65 and C61/C62 of DIDDTBT effectively planarizes the whole molecule (TPTPTBT), in which the dihedral angles $\varphi(\text{C42}-\text{C43}-\text{C44}-\text{C45})$ and $\varphi(\text{C55}-\text{C54}-\text{C60}-\text{C61})$ are zero. For comparison, the corresponding angles in DIDDTBT are $\varphi(\text{C64}-\text{C25}-\text{C24}-\text{C65}) = 26.6^\circ$ and $\varphi(\text{C62}-\text{C34}-\text{C39}-\text{C61}) = 23.6^\circ$. Furthermore, such ring-fusion also makes impact on the coplanarity between the BT and the neighboring thiophene rings: the dihedral angles between these two

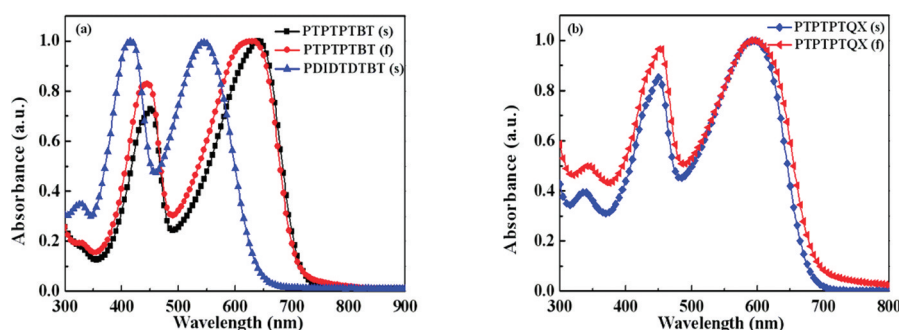


Figure 3. Normalized absorption spectra of (a) PTPPTBT and (b) PTPPTQX in the chloroform solution and the solid state. Absorption spectrum of PDIDDTBT in chloroform is included in (a) for comparison.

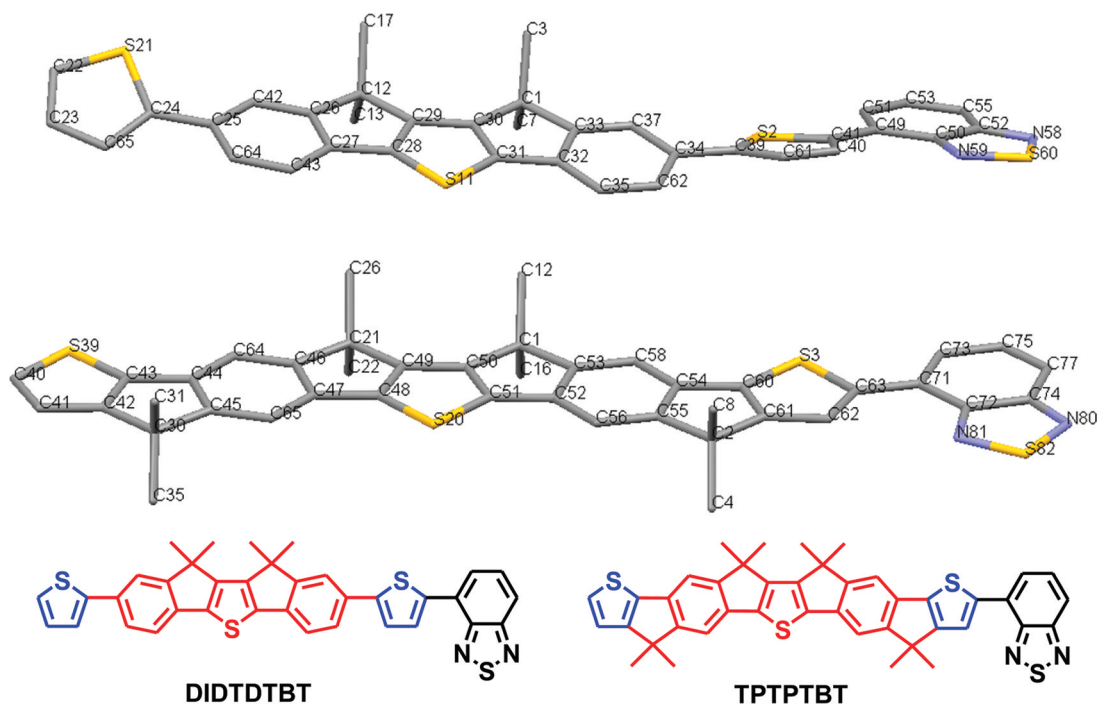


Figure 4. Optimized conformations for the structure of DIDTDTBT (top) and TPTPTBT (bottom), respectively, at the level of B3LYP/6-31G(d). Yellow: sulfur; blue: nitrogen; and gray: carbon; hydrogens are omitted for clarity.

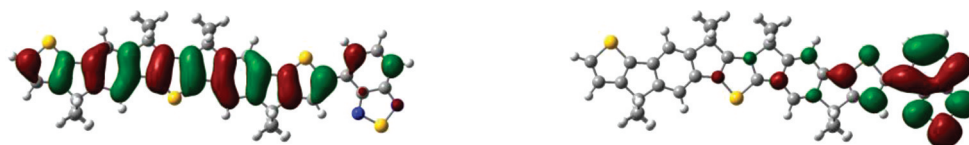


Figure 5. Wave functions of the HOMO (left) and LUMO (right) orbitals of the TPTPTBT calculated at the level of B3LYP/6-31G (d,p).

structural motifs are $\varphi(\text{C40-C41-C49-C50}) = 7.32^\circ$ for DIDTDTBT and $\varphi(\text{C62-C63-C71-C72}) = 0.07^\circ$ 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-doping 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 TPTPTBT 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 TPTPTBT and -3.30 eV for PTPTPTQX, which are higher than the LUMO level of the PC₇₁BM 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

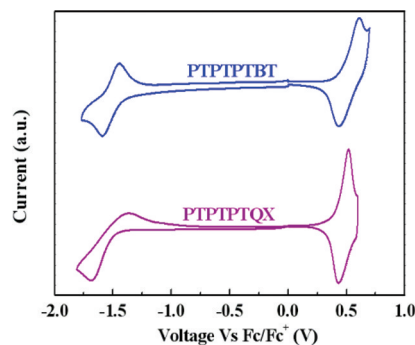


Figure 6. Cyclic voltammograms of TPTPTBT and PTPTPTQX in the thin film at a scan rate of 80 mV s^{-1} .

Table 3. Electrochemical Properties of the Polymers

copolymer	$E_{ox}^{onset}(\text{V})$	$E_{red}^{onset}(\text{V})$	HOMO (eV)	LUMO ^{el} (eV)	E_g^{el} (eV)
TPTPTBT	0.44	-1.42	-5.24	-3.38	1.86
PTPTPTQX	0.41	-1.50	-5.21	-3.30	1.91

TPTPTBT/PC₇₁BM (1:4, w/w) and PTPTPTQX/PC₇₁BM (1:2, w/w) blends (Figure 7).

Photovoltaic and Hole-Mobility Characteristics. Despite the amorphous nature in thin films, TPTPTBT and PTPTPTQX showed good hole transporting properties because of their rigid and coplanar structures. Hole-only

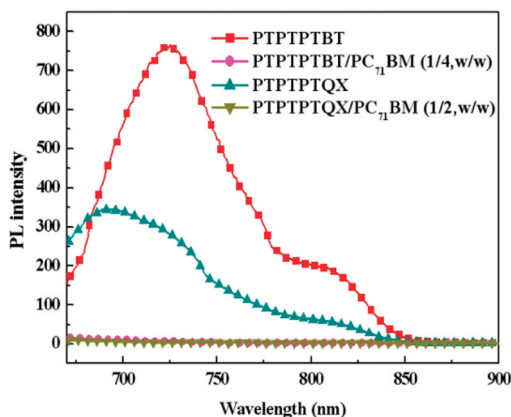


Figure 7. Emission spectra of PTPPTBT, PTPPTBT/PC₇₁BM at excitation wavelength of 628 nm, PTPPTQX and PTPPTQX/PC₇₁BM (1/2, w/w) at excitation wavelength of 593 nm in the thin film.

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. PTPPTBT and PTPPTQX 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 PDITDTBT 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 are shown in Figure 8 and the device parameters are summarized in Table 4. The preliminary device based on PTPPTQX/PC₇₁BM (1:2, w/w) blend exhibited a V_{oc} of 0.74 V, a J_{sc} of 9.0 mA/cm^2 , a FF of 61% and a high PCE of 4.1%. More encouragingly, the device using PTPPTBT/PC₇₁BM (1:4, w/w) blend delivered superior performance with a J_{sc} of 11.4 mA/cm^2 , a V_{oc} of 0.76 V, a FF of 61%, and an exceptional PCE of 5.3%, which dramatically outperforms the device based on the nonfused PDITDTBT/PC₇₁BM (1:2, w/w) blend by 3-fold. ($V_{oc} = 0.7 \text{ V}$, $J_{sc} = 5.30 \text{ mA/cm}^2$, FF = 44%, and a PCE of 1.65%).⁷ This result reveals that the nonacyclic TPTPT unit having rigid and extended coplanar conjugated system indeed improves all the device characteristics.

The morphology of thin film was evaluated by atomic force microscopy (Figure 9). The image of the PTPPTBT/PC₇₁BM (1:4, w/w) blend showed a very smooth surface and

small phase separation domains, suggesting its good morphological properties for efficient charge separation and transport.

BHJ devices with inverted architecture are known to possess much improved long-term stability compared to conventional structure. However, PCEs of P3HT/PCBM-based inverted PSCs are mostly in the range of ca. 2–4%, which is inferior to that of conventional PSCs.⁹ Therefore, recent research of inverted solar cells is mainly devoted to device engineering and interfacial modification. The utilization of low bandgap (LBG) conjugated polymers other than P3HT as p-type photoactive materials is only sporadically explored.¹⁰ It is highly desirable to evaluate the new copolymers in the application of inverted solar cells. The inverted devices were fabricated based on the configuration of ITO/ZnO/C-PCBSD/copolymer:PC₇₁BM/PEDOT:PSS/Ag where a cross-linked PC₆₁BM derivative, [6,6]-phenyl-C₆₁-butyric styryl dendron ester (C-PCBSD) was used as an interlayer.¹¹ Encouragingly, the inverted device using PTPPTQX/PC₇₁BM (1:2, w/w) blend delivered an enhanced PCE of 4.7%. Similarly, the device incorporating PTPPTBT/PC₇₁BM (1:4, w/w) blend further achieved a high PCE of 5.9% with $J_{sc} = 12.10 \text{ mA/cm}^2$, $V_{oc} = 0.76 \text{ V}$ and FF = 64%. This performance outperforms not only the P3HT/PC₆₁BM-based device under the identical device configuration (PCE = 4.4%)¹¹ but also an inverted tandem cell (PCE = 5.1%) combining P3HT and poly[bis(2-ethylhexyl)dithienosilole]-*alt*-(2,1,3-benzothiadiazole)] (PSBTBT) as the photoactive materials.¹² To confirm the accuracy of the measurements 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 nonacyclic distannyl-TPTPT unit that consists of alternate thiophene and benzene units fused by four embedded cyclopentadienyl rings. PTPPTBT and PTPPTQX 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 PTPPTBT/PC₇₁BM-based device with inverted architecture achieved an impressively high PCE of 5.9%. This value is among the highest

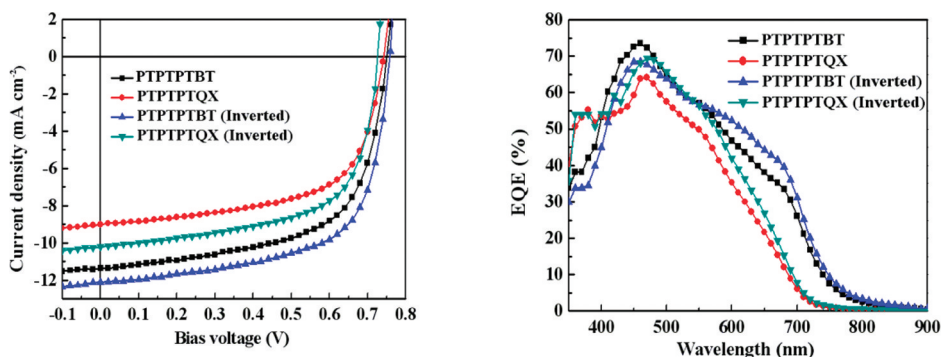


Figure 8. Current density–voltage characteristics (left) and EQE spectra (right) of the conventional devices (ITO/PEDOT:PSS/polymer:PC₇₁BM/Ca/Al) and inverted devices (ITO/ZnO/C-PCBSD/polymer:PC₇₁BM/PEDOT:PSS/Ag) devices under illumination of AM 1.5 G, 100 mW cm^{-2} .

Table 4. Hole Mobilities and Photovoltaic Characteristics

copolymer	polymer:PC ₇₁ BM wt% ratio	mobility (cm ² /V s)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
PTPTPTBT ^a	1:4	5.1 × 10 ⁻⁴	0.76	11.4 (11.2) ^c	61	5.3
PTPTPTBT ^b	1:4		0.76	12.1 (11.6) ^c	64	5.9
PTPTPTQX ^a	1:2	3.7 × 10 ⁻⁴	0.74	9.0 (9.1) ^c	61	4.1
PTPTPTQX ^b	1:2		0.74	10.2 (9.6) ^c	62	4.7

^aConventional device structure: ITO/PEDOT:PSS/copolymer:PC₇₁BM/Ca/Al. ^bInverted device structure: ITO/ZnO/C-PCBSD/copolymer:PC₇₁BM/PEDOT:PSS/Ag. ^cCalculated from the EQE spectrum.

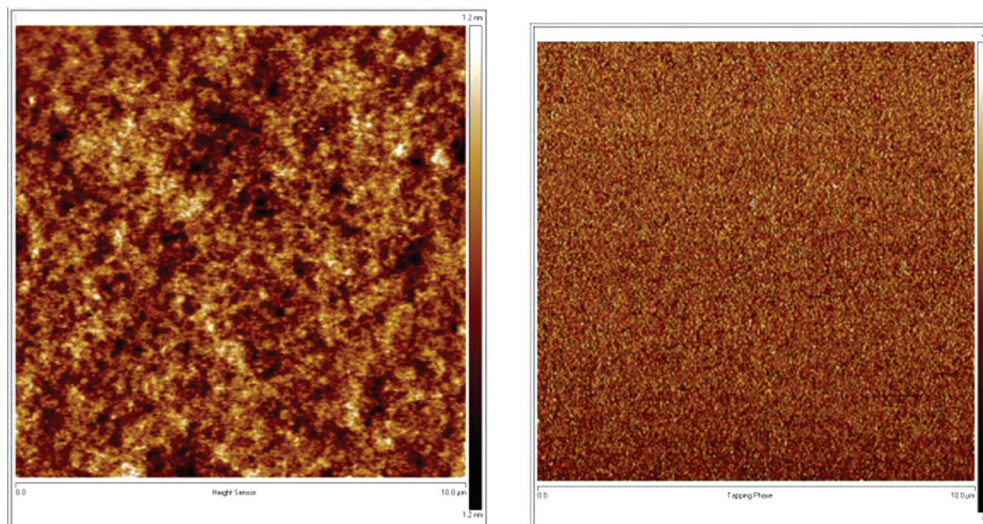


Figure 9. AFM height (left) and phase images (right) of the surface of PTPTPTBT/PC₇₁BM (1:4, w/w) blend (10.0 μm × 10.0 μm). The surface roughness is estimated to be 0.4 nm.

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. ¹H and ¹³C 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 (TBAPF₆) 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_{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. 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 PC₇₁BM (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/PC₇₁BM (700 rpm; 150 °C) and PTPTPTQX/PC₇₁BM (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 × 10⁻⁶ Torr). Each device is constituted of 4 pixels defined by an active area of 0.04 cm². Finally, the devices were encapsulated and *I*–*V* curves were measured in air.

For the inverted architecture, a ZnO precursor solution, consisting of 157 mg mL⁻¹ zinc acetate dehydrate in 96% 2-methoxy ethanol and 4% ethanalamine, was spin coated onto ITO-coated glass, followed by thermal annealing in air at 300 °C for 10 min to crystallize the film (thickness = ca. 50 nm). Subsequently, PCBSD solution (5 mg mL⁻¹ in *ortho*-dichlorobenzene) was spin coated onto the ZnO layer and the as-cast film was heated at 180 °C for 10 min for thermal cross-linking (thickness = 10 nm). The same process for the active layer in the conventional architecture was used for the inverted devices. The PEDOT:PSS solution diluted with equal volume of isopropyl alcohol and 0.2 wt % of Triton X-100 nonionic surfactant, was then spin coated on top of the active layer, followed by thermal annealing at 120 °C for 10 min (thickness = 60 nm). A silver top electrode (thickness = ca. 150 nm) was then thermally evaporated to complete the inverted device.

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

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 ε is the dielectric permittivity of the polymer, μ 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(PPh₃)₄ (0.265 g, 0.23 mmol), K₂CO₃ (1.90 g, 13.75 mmol), and Aliquant 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** (2.07 g, 62%); mp: 110 °C; ¹H NMR (CDCl₃, 300 MHz): δ 7.52 (d, J = 5.6 Hz, 2 H), 7.51–7.30 (m, 6 H), 3.17–3.58 (m, 4 H), 7.23 (d, J = 5.6 Hz, 2 H), 4.20 (q, J = 7.2 Hz, 4 H), 2.09 (t, J = 8.1 Hz, 8 H), 1.40–0.96 (m, 54 H), 0.82 (t, J = 13.4 Hz, 12 H); ¹³C NMR (CDCl₃, 75 MHz): δ 163.4, 152.0, 151.6, 149.9, 144.8, 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.

Synthesis of Compound 3. A Grignard reagent was prepared by the following procedure. To a suspension of magnesium turnings (0.8 g, 33.3 mmol) and 3–4 drops of 1,2-dibromoethane 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)benzene 1-magnesium bromide (20 mL, 7.9 mmol) dropwise at room temperature. The resulting mixture 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 give a yellow oil **3** (1.17 g, 85%); ¹H NMR (CDCl₃, 300 MHz): δ 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 = 5.1 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): δ 158.2, 152.5, 149.7, 144.5, 144.1, 140.7, 139.2, 138.8, 131.5, 131.0, 128.9, 123.1, 122.2, 117.9, 113.7, 80.4, 68.0, 55.4, 39.9, 31.9, 31.8, 30.2, 29.7, 29.5, 29.4, 29.3, 29.26, 26.1, 24.1, 22.7, 22.6, 14.1, 14.05. MS (FAB, C₁₁₆H₁₆₄O₆S₃): calcd, 1750.73; found, 1751.

Synthesis of TPTPT. To a solution of **3** (2.00 g, 1.14 mmol) in boiling acetic acid (116 mL) was added conc. sulfuric acid (3.5 mL) in one portion. The resulting solution was stirred for 18 h at 95 °C and then was extracted with ethyl acetate (500 mL × 3) and water (250 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 give an orange oil **TPTPT** (1.58 g, 81%); ¹H NMR (d₈-THF, 300 MHz): δ 7.45 (s, 2 H), 7.34 (d, J = 4.8 Hz, 2H), 7.33 (s, 2 H), 7.12 (d, J = 8.7 Hz, 8H), 6.99 (d, J = 4.8 Hz, 2H), 6.72 (d, J = 8.7 Hz, 8 H), 3.87 (t, J = 6.0 Hz, 8 H), 2.3–2.1 (m, 8 H), 1.50–0.95 (m, 96 H), 0.90–0.70 (m, 24 H). ¹³C NMR (CDCl₃, 75 MHz): δ 157.9, 155.9, 153.2, 152.2, 148.9, 144.6, 141.3, 137.1, 137.0, 134.3, 129.0, 126.9, 123.0, 115.8, 114.1, 113.1, 67.9, 61.8, 55.1, 40.5, 31.9, 31.85, 31.8, 30.3, 29.7, 29.5, 29.3, 29.29, 29.2, 26.0, 24.2, 22.6, 14.1, 14.0. MS (FAB, C₁₁₆H₁₆₀O₄S₃): calcd, 1714.70; found, 1715.

Synthesis of Sn-TPTPT. To a solution of **TPTPT** (1.60 g, 0.93 mmol) in dry THF (28 mL) was added 1.6 M solution of *t*-BuLi in hexane (1.8 mL, 2.80 mmol) dropwise at –78 °C. After stirring at –78 °C for 1 h, 1.0 M solution of chlorotrimethylstannane in THF (3.7

mL, 3.73 mmol) was introduced dropwise by syringe to the solution. The mixture solution was quenched with water and extracted with hexane (300 mL × 3) and water (100 mL). The combined organic layer was dried over MgSO₄. After removal of the solvent under reduced pressure, Sn-TPTPT (1.18 g, 62%) was obtained as an orange oil and used without further purification; ¹H NMR (CDCl₃, 300 MHz): δ 7.29 (s, 2 H), 7.27 (s, 2H), 7.21 (d, J = 8.7 Hz, 8 H), 7.06 (s, 2 H), 6.81 (d, J = 8.7 Hz, 8 H), 3.94 (t, J = 6.3 Hz, 8 H), 2.20–2.00 (m, 8 H), 1.85–1.70 (m, 8 H), 1.50–0.60 (m, 112 H), 0.40 (s, 18 H). ¹³C NMR (CDCl₃, 75 MHz): 157.8, 153.5, 152.1, 148.8, 147.3, 144.5, 140.5, 137.2, 136.9, 134.1, 130.5, 129.1, 129.0, 115.8, 114.0, 113.2, 67.8, 61.3, 55.0, 40.4, 35.7, 31.8, 31.7, 30.3, 29.6, 29.4, 29.3, 29.2, 26.0, 24.2, 22.6, 14.06, 14.03, –8.0. Elemental anal. Calcd (%) for C₁₂₂H₁₇₆O₄S₃Sn₂: C, 71.82; H, 8.69. Found: C, 71.67; H, 8.78.

Synthesis of PTPTPTBT. 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), Pd₂(dba)₃ (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 round-bottom flask was placed into the microwave reactor and reacted for 45 min under 270 W. To end-cap the resulting polymer, we added tributyl(thiophen-2-yl)stannane (13.1 mg, 0.035 mmol) to 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 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 (Silicycle 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 reprecipitate. 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_n = 30 000, PDI = 1.69). ¹H NMR (CDCl₃, 300 MHz): δ 8.20–8.00 (m, 2 H), 7.95–7.80 (m, 2 H), 7.50–7.30 (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, 88 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-diphenylquinoxaline **QX** (56 mg, 0.13 mmol), Pd₂(dba)₃ (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 round-bottom flask was placed into the microwave reactor and reacted for 45 min under 270 W. To end-cap the resulting polymer, tributyl(thiophen-2-yl)stannane (23.8 mg, 0.064 mmol) was added to the mixture solution and reacted for 10 min under 270 W. Finally, 2-bromothiophene (11.2 mg, 0.069 mmol) was added to the mixture solution and reacted for 10 min under 270 W. The solution was 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 (Silicycle 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 reprecipitate. The purified polymer was collected by filtration and dried under vacuum for 1 day to give a dark-green fiberlike solid (155 mg, 61%, M_n = 34 000, PDI = 1.60). ¹H NMR (CDCl₃, 300 MHz): δ 8.10–8.00 (m, 2H), 7.95–7.85 (m, 2H), 7.80–7.70 (m, 4H), 7.55–7.30 (m, 10H), 7.20–7.00 (m, 8H), 6.90–6.70 (m, 8H), 4.00–3.80 (m, 8H), 1.85–1.65 (m, 16H), 1.50–1.00 (m, 88 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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