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ARTICLE

A molecular structure and crystallization correlation study of pyromellitic diimide-based conjugated copolymers

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Three pyromellitic diimide(PMDI)-based polymers—poly(pyromellitic diimide-co-bithiophene) [poly(PMDI-BTh)], poly(pyromellitic diimide-co-tetrathiophene) [poly(PMDI-TTh)], and poly(pyromellitic diimide-co-benzodithio- phene) [poly(PMDI-BDTTh)]—are synthesized to study the influence of different thiophene-containing electron-donating groups on the crystallizability of PMDI-based conjugated polymers. Computer simulation using Density Functional Theory (DFT) [Gaussian B3LYP/6–31 + G(d,p)] indicates that poly(PMDI-BDTTh) has a more planar molecular structure than the other two copolymers. Powder XRD diffraction experiment of the poly(PMDI-BDTTh) shows a diffraction peak at about $2\theta = 6.0°$, but no diffraction peak occurs for poly(PMDI-BTh) and poly(PMDI-TTh). Although PMDI is a planar structure that is favorable for the molecular aggregation, a comonomer with planar structure seems to be very crucial in order to synthesize a crystallizable push–pull-type PMDI-based conjugated copolymer.

KEYWORDS

crystallinity, molecular structure, pyromellitic diimide

1 | INTRODUCTION

Organic electronics such as organic light emitting diodes (OLED), polymeric light emitting diodes (PLED), organic photovoltaics (OPV), organic field-effect transistor (OFET), and many others have attracted much attention in the past few decades. Compared to materials used in inorganic-based devices such as inorganic LED, Si-based photovoltaics, and FET, the carrier mobility of organic semiconductors is usually lower than those of the corresponding inorganic semiconductors, which limit the further development of related organic electronics.[1,2]

Researchers have been trying to synthesize advanced organic semiconductors that have high carrier mobility[2] for organic electronic applications. In the area of OPV, many advanced semiconducting polymers have been developed recently. However, for the purpose of energy level alignment, push–pull-type conjugated copolymers are usually synthesized instead of homopolymers. Because of the electron-donating and electron-withdrawing moieties within the copolymers, very often, amorphous copolymers are obtained instead of semicrystalline polymers.

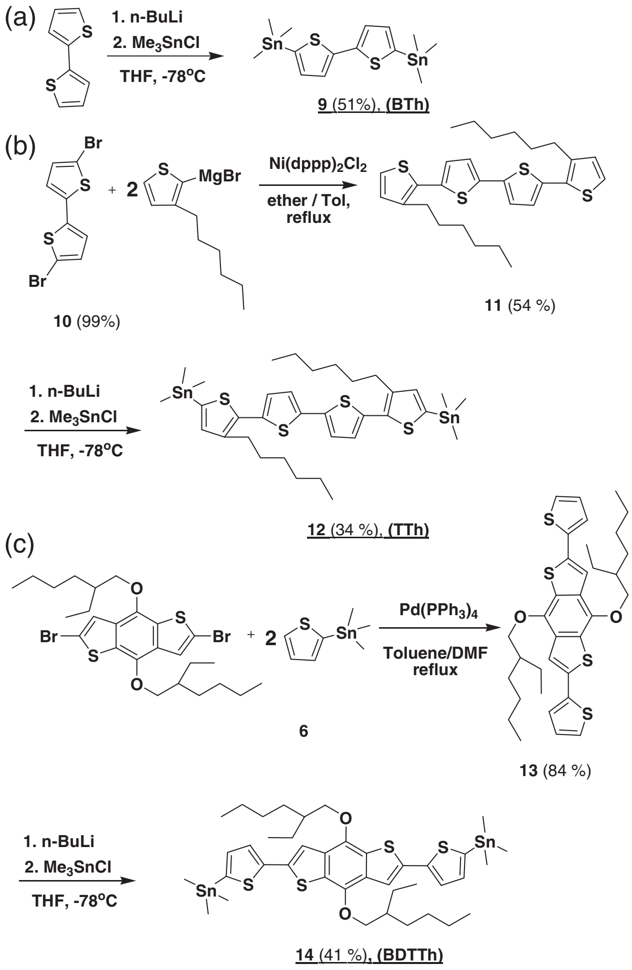
Theoretically, semicrystalline conjugated polymers can be synthesized with the following characteristics: (a) polymers with high regioregularity,[3] (b) polymers with high polarity functional groups,[4–10] (c) polymers with long alkyl side chains that will cause side-chain crystallinity, and[11–13] (d) high planarity backbone with strong π–π interaction.[14–21] Researchers have found improved carrier mobility for crystallizable semiconducting polymer such as P3HT. Carrier mobility increases as the regioregularity of P3HT increases. However, the absorption spectrum of P3HT limits the performance of the resulting OPV device. For semicrystalline conjugated polymers such as pBCN and PffBT4T-2OD, molecular structures are not fully symmetric. Polar functional group and long side chains are required to induce crystallization of the conjugated polymers. In this study, a pyromelittic diimide-based donor–acceptor copolymer model system is designed. A highly planar symmetric electron-withdrawing moiety pyromellitic diimide (PMDI,

8) is copolymerized with three molecularly symmetric thiophene-containing electron-donating monomers—bithiophene (BTh, **9**), tetrathiophene (TTh, **12**), and benzodithiophene (BDTTh, **14**)—to evaluate how comonomers affect the crystallization behavior of the corresponding conjugated copolymers.

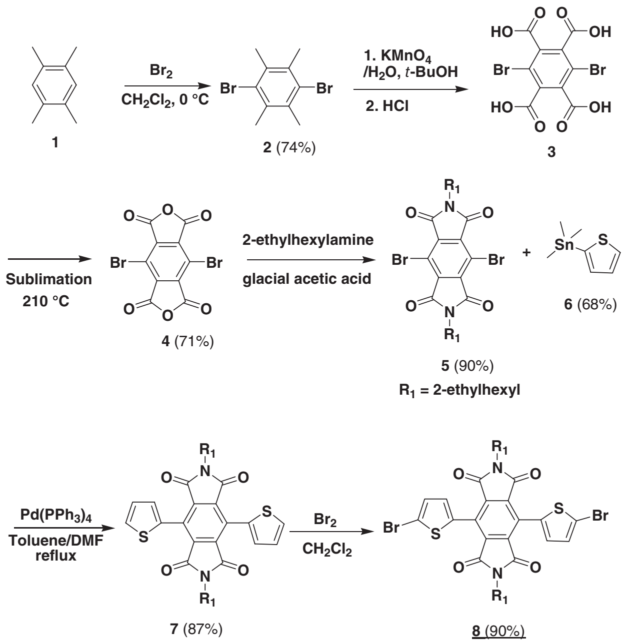
2 | RESULTS AND DISCUSSION

To synthesize the three PMDI-based conjugated polymers, an electron-withdrawing core PMDI (**8**) was synthesized to copolymerize with three thiophene-containing moieties—BTh (**9**), TTh (**12**), and BDTTh (**14**). Monomer **8** was synthesized by a modified procedure of Chi (Scheme 1).[22] Dibromo-tetracarboxylic acid benzene (**3**) was sublimed to dibromo-pyromellitic dianhydride (**4**) following by imidization with 2-ethylhexyl amine to obtain dibromo-pyromellitic diimide (**5**). Compound (**5**) underwent a Still-coupling reaction with trimethyltin thiophene (**6**) followed by bromination to obtain electron-withdrawing core **8**. Three thiophene-containing comonomers—compound **9, 12, and 14**—were synthesized following the procedures described in Scheme 2. To increase the solubility of compound **12** and **14**, dialkyl and dialkoxyl side chains were added to the main cores, respectively. The electron-withdrawing core **8** was reacted with comonomers **9**, **12**, and **14** to obtain the final conjugated copolymers poly(PMDI-BTh) (**P1**), poly(PMDI-TTh) (**P2**), and poly(PMDI-BDTTh) (**P3**), respectively (Scheme 3). **P1**, **P2**, and **P3** were subjected to soxhlation using methanol, hexane, and chloroform before final precipitation.

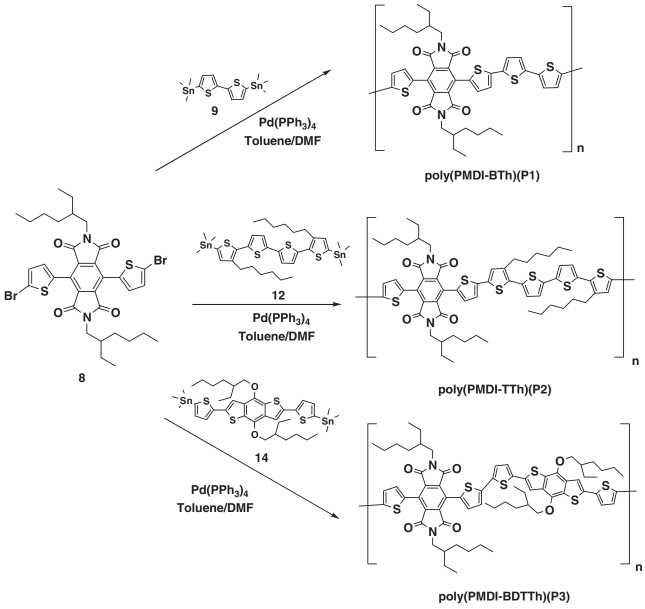
The thermal stability of **P1**, **P2**, and **P3** are shown in Figure 1. All three conjugated copolymers show high thermal stability above 350°C (Figure 1). Decomposition of **P1**



SCHEME 2 Synthetic routes of compound **9, 12, 14**



SCHEME 1 Synthetic routes of the compound **8**



SCHEME 3 Synthetic routes of polymers poly(PMDI- BTh), poly(PMDI-TTh), and poly(PMDI-BDTTh)

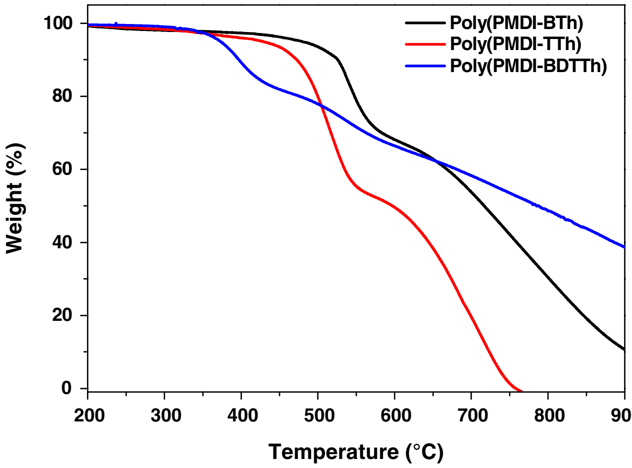


FIGURE 1 Thermogravimetric diagrams of poly(PMDI- BTh), poly(PMDI-TTh), and poly(PMDI- BDTTh)

at 479°C is attributed to the loss of 2-ethylhexyl group attached to the imide group (calculated: 29.4%; experimental: 29.3%).[22] Both **P2** and **P3** demonstrate two stages decomposition. The first stage in **P2** originates from the loss of the hexyl group attached to the thiophene. The first stage in **P3** is caused by the loss of alkoxyl group attached to the BDT moiety.[23] The second stage in **P2** and **P3** is the same as that of **P1**, which is attributed to the loss of the 2-ethylhexyl group. Differential Scanning Calorimeter (DSC) measurement shows the T_g of **P2** to be around 110°C (Figure S20, Supporting information). Because of backbone rigidity of **P1** and **P3**, glass transition of both polymers cannot be clearly measured. Molecular weight and polydispersity index are listed in Table 1. All three copolymers have number-averaged molecular weight around 20,000.

PMDI is a very strong electron-withdrawing moiety with symmetric structure. Conjugated copolymers synthesized with the PMDI core usually have low-lying HOMO value.[24,25] With electron-donating comonomers such as bithiophene (BTh) and tetrathiophene (TTh), highest occupied molecular orbital (HOMO) of **P1** and **P2** can be as low as −5.59 and −5.58 eV (Table 2), respectively. With a more planar comonomer bis(thiophene)benzodithiophene (BDTTh), HOMO of **P3** increases to −5.36 eV. Although thiophene is a good electron-donating unit, twisting between two thiophene units lowers the conjugation length of the final copolymers. As shown in Table 2, the band gap of **P1** is 2.13 eV. With extended thiophene units (TTh), the band gap of **P2** decreases to 2.06 eV. Replacing the TTh with a BDTTh comonomer, no major change in band gap is observed. Although extended electron-donating moieties such as TTh and BDTTh have been added to copolymerize with PMDI core (**8**), absorption $\lambda_{\max}$ of **P2** and **P3** are both relatively short (Figure 2). The maximal absorption wavelengths of **P2** (485 nm) and **P3** (491 nm) are somewhat red-shifted when compared with that of **P1**. The strong electron-withdrawing capability of PMDI will possibly prevent PMDI from being a good electron-withdrawing core in the synthesis of push–pull-type donor polymers.

TABLE 1 Molecular weight and decomposition temperature of poly(PMDI-BTh) (**P1**), poly(PMDI-TTh) (**P2**), and poly(PMDI-BDTTh) (**P3**)

	M_n (kDa)	M_w (kDa)	PDI	T_d (°C)
P1	25.4	83.3	3.28	479
P2	18.5	40.4	3.88	428
P3	22.1	46.9	2.10	373

TABLE 2 Optical properties and energy levels of poly(PMDI-BTh) (**P1**),poly(PMDI-TTh) (**P2**), and poly(PMDI-BDTTh) (**P3**)

	$\lambda_{\max,\mathrm{sol}}$ (nm)	$\lambda_{\max,\mathrm{film}}$ (nm)	$\lambda_{\mathrm{onset,film}}$ (nm)	HOMO (eV)	LUMO (eV)	E_g^{opt} (eV)
P1	455	477	582	−5.59	−3.46	2.13
P2	454	485	602	−5.58	−3.52	2.06
P3	467	491	605	−5.36	−3.31	2.05

PMDI is a very planar core; however, copolymers synthesized with PMDI core are not all crystallizable. as shown in Figure 3. P3 shows a diffraction peak at $2\Theta = 6.1,^{\circ}$indicating the existence of crystalline domains. However, when copolymerized with BTH (**9**) AND TTH (**12**), the resulting copolymers P1 and P2 are both not crystallizable. No characteristic peaks are found in these two copolymers (Figure 3). BTH (**9**) and TTH (**12**) are both good electron-donating moieties and are used in many syntheses of donor polymers. Although both have symmetrical molecular structures, twisting between two thiophene units results in noncoplanar molecules. The dihedral angle between two PMDI cores in P1 is about 46.95° (Figure 4). The dihedral angle significantly decreases to 29.37° when replacing BTH (**9**) with BDTTH (**14**). The more planar molecular structure allows P3 to aggregate together and form crystallites. With an extended structure to BTH (**9**), TTH (**12**) copolymerizes with PMDI and forms a curving molecular structure that hinders P2 from crystallization. It seems that a planar comonomer is beneficial to the molecular aggregation of PMDI-based copolymers

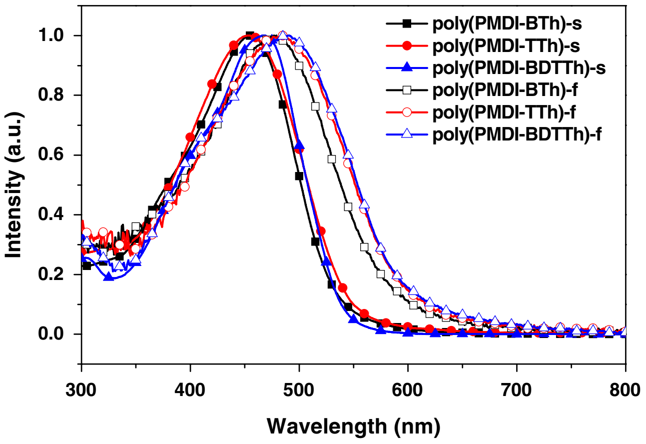


FIGURE 2 Absorption spectra of poly(PMDI-BTh), poly(PMDI-TTh), poly(PMDI-BDTTh) in solution (-s) ($CHCl_3$) and in films (-f)

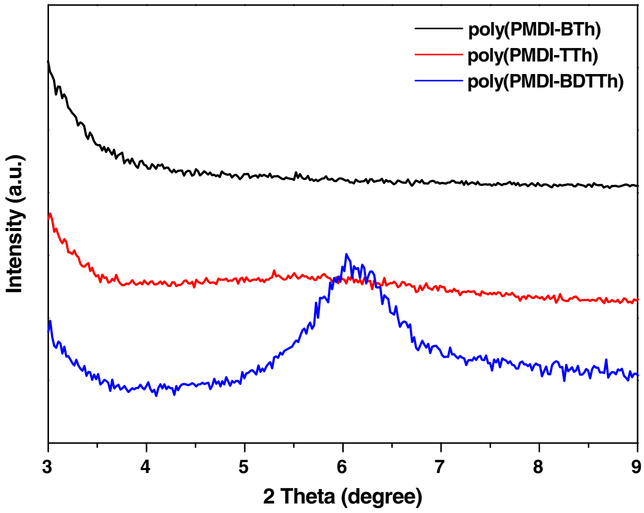


FIGURE 3 XRD diffraction of poly(PMDI-BTh), poly- (PMDI-TTh), and poly(PMDI-BDTTh) on Si

3 | EXPERIMENTAL

3.1 | General

All chemicals are of reagent grade and are used without further purification; 2,6-Dibromo-4,8-di(2-ethylhexyl oxy)-benzo[1,2-b:4,5-b′]dithiophene was purchased from Lumtec Technology, Taiwan, and also used without further purification.

FT-IR spectra were recorded using a Perkin Elmer Spectrum100 spectrometer. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Bruker AC-300 MHz NMR spectrometer. Mass spectra were reported with ion mass/charge (m/z) ratios as values in atomic mass units using a Finnigan MAT95XL Mass Spectrometry. A Shimadzu UV-3101 Double Beam Spectrophotometer was used to measure absorption spectra. Thermogravimetric Analysis (TGA) was carried out with a Versa Thermo HS system. Molecular weights of polymers were determined by a Viscotek DM400/LR40 Gel Permeation Chromatography (GPC) using standard polystyrene. HOMO energy levels were determined using a RKI Photoelectron Spectroscopy Model AC-2. XRD analysis was recorded by a Bruker D2 Phaser diffractometer on silicon wafer substrate.

3.2 | Synthesis

3.2.1 | 1,4-Dibromo-2,3,5,6-tetramethylbenzene (2)

The chemicals 1,2,4,5-tetramethylbenzene (25 g, 0.19 mol) and CH_2Cl_2 were mixed in a round-bottom flask. The mixture was cooled to 0°C, and Br_2 solution (24 mL Br_2 in 100 mL CH_2Cl_2) was added to the mixture dropwise. The mixture was refluxed for 1.5 hr. White precipitate forms after cooling back to room temperature. The white solid was filtered and washed with distilled water thoroughly. It was dried in vacuum overnight. Compound **2** was obtained as a white solid (40.3 g, 74%). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 2.48 (s, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 135.1, 128.2, 22.4.

3.2.2 | 3,6-Dibromopyromellitic dianhydride (4)

1,4-Dibromo-2,3,5,6-tetramethylbenzene **2** (8.760 g, 30 mmol) was mixed with water (100 mL), *t*-BuOH (100 mL), and celite (40 g) in a three-neck round-bottom flask; 40.3 g $KMnO_4$ (255 mmol) was added in portions within 30 min. The mixture was reacted at 95°C for 13 hr. After cooling to 80°C, ethanol was added slowly to the mixture. The mixture was filtered, and the filtrate was neutralized by $HCl_{(aq).}$ Solvent was removed under vacuum, and the solid was stirred in acetone overnight. The acetone solution was filtered and dried under vacuum. White solid **3** was obtained. Then, crude compound **3** was sublimated at 210°C under vacuum (10^{-2} mmHg); 8.02 g of Yellow solid **4** was collected (71%) and used without further purification. ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm: no signals; ^{13}C NMR (75 MHz, DMSO-d_6) δ ppm: 166.3, 137.6, 115.5.

3.2.3 | 4,8-Dibromo-2,6-bis(2-ethylhexyl)pyrrolo[3,4-f] isoindole-1,3,5,7(2H,6H)-tetraone (5)

Compound **4** (5.16 g, 13.7 mmol), 2-ethylhexyl- amine (3.90 g, 30.2 mmol), and glacial acetic acid (50 mL) were mixed in a round-bottom flask. The mixture was refluxed

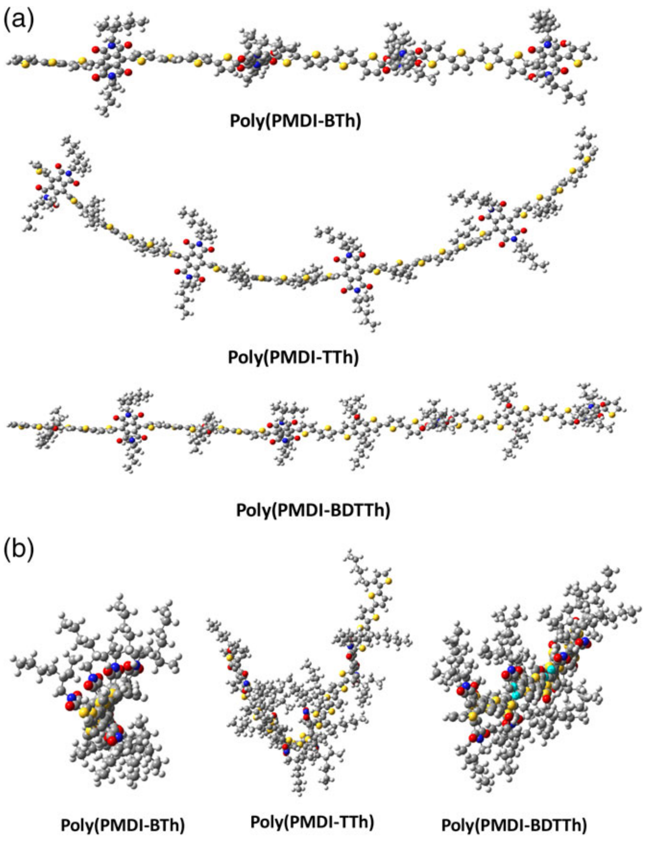


FIGURE 4 Molecular simulation of poly(PMDI-BTh), poly(PMDI-TTh), and poly(PMDI-BDTTh) using Gaussian DFT calculation [B3LYP/6–31 + G (d,p)] (a) side view; (b) front view (about 45° tilting angle)

for 13.5 hr and cooled to room temperature. It was added to methanol in a beaker, and white solid was collected by filtration. The white solid was dried, and the high purity compound **5** was collected (7.02 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 3.63 (d, 4H), 1.83 (m, 2H), 1.32 (m, 16H), 0.92 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* ppm: 163.8, 136.2, 114.2, 42.9, 38.3, 30.6, 28.6, 23.9, 23.0, 14.1, 10.4.

3.2.4 | **Trimethyl(thiophen-2-yl)stannane** (6)

Thiophene (15.1 g, 0.18 mol) was dissolved in ether (100 mL) in a three-neck round-bottom flask and cooled to 0°C. *n*-Butyllithium (72 mL, 0.18 mol) was added dropwise to the thiophene solution until all n-butyllithium was used up. The reaction was warmed to room temperature gradually and stirred for 3 hr. Trimethyltin chloride (35.0 g in 100 mL ether, 17.6 mol) was added to the above solution and stirred overnight. The reaction mixture was quenched with distilled water (100 mL × 2) and filtered. Filtrate was extracted with saturated NaCl solution (100 mL), and the organic layer was dried over anhydrous $MgSO_4$. After removing the solvent, the residue was purified by flash column (silica gel, hexanes). Transparent liquid **6** (30.16 g, 68%) was obtained. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 7.65 (dd, 1H), 7.26 (dd, 1H), 7.22 (dd, 1H), 0.37 (s, 9H).

3.2.5 | **2,6-Bis(2-ethylhexyl)-4,8-di(thiophen-2-yl)pyrrolo[3,4-f]isoindole-1,3,5,7(2H,6H)-tetraone** (7)

Compound **5** (0.598 g, 1 mmol), trimethyl(thiophen-2-yl) stannane (**6**) (0.755 g, 3.0 mmol), and tetrakis(triphenylphosphine) palladium (231 mg, 10 mol%) were mixed with 15 mL anhydrous toluene and 3 mL dimethylformamide under nitrogen in a three-necked round-bottom flask. The solution was refluxed under nitrogen at 120 °C for 18 hr and poured into 100 mL water after cooling to room temperature. It was extracted with CH_2Cl_2 (50 mL × 2). The CH_2Cl_2 portion was extracted with distilled water (100 mL × 2), saturated NaCl solution (100 mL), and dried over anhydrous $MgSO_{4(s)}$ After removing solvent under vacuum, the residue was purified by flash column (silica gel, CH_2Cl_2:hexanes = 3:2) and recrystallized from CH_2Cl_2/hexanes. The yellow solid **7** (0.528 g, 87%) was obtained. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 7.65 (dd, 2H), 7.27 (m, 4H), 3.51 (d, 4H),1.79 (m, 2H), 1.28 (m, 16H), 0.87 (t, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* ppm: 165.2, 135.3, 130.9, 130.1, 129.9, 128.3, 127.0, 42.7, 38.1, 30.6, 28.5, 24.0, 23.1, 14.1, 10.5.FTIR (KBr, υ cm^{-1}): 3053, 2982, 2684, 2516, 2410, 2303, 1767, 1717, 1550, 1421, 1396, 1262, 1158, 895, 751, 723, 706. HRMS: calcd. for $C_{34}H_{40}N_2O_4S_2$ 604.2429; found 604.2439.

3.2.6 | **4,8-Bis(5-bromothiophen-2-yl)-2,6-bis(2-ethylhexyl) pyrrolo[3,4-f]isoindole-1,3,5,7(2H,6H)-tetraone** (8)

N-Bromosuccinimide (0.34 g, 1.9 mmol) was added to a solution of **7** (0.528 g, 0.87 mmol) in acetic acid (25 mL) and CH_2Cl_2 (10 mL) at room temperature and stirred overnight. Another portion of N-bromosuccinimide (0.34 g, 1.9 mmol) was added and stirred for 3 hr. The solution was extracted with distilled water (50 mL × 2) and saturated NaCl solution (50 mL). The organic layer was dried over filtered anhydrous $MgSO_4$. After removing the solvent, the residue was purified by recrystallization in CH_2Cl_2/Hexanes. Yellow solid **8** (0.6 g, 90%) was obtained. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 7.17 (d, 2H), 7.02 (d, 2H), 3.50 (d, 4H), 1.76 (m, 2H), 1.26 (m, 16H), 0.86 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* ppm: 165.2, 135.3, 130.9, 130.1, 129.9, 128.3, 127.0, 42.8, 38.1, 30.6, 28.5, 24.0, 23.1, 14.1, 10.5. FITR (KBr, υ cm^{-1}): 3154, 3048, 2982, 2304, 2253, 1793, 1717, 1644, 1603, 1555, 1467, 1421, 1381, 1264, 1166, 1095, 910, 728. HRMS: calcd. for $C_{34}H_{38}Br_2N_2O_4S_2$ 760.0640; found 760.0635.

3.2.7 | **5,5′-Bis(trimethylstannyl)-2,2′-bithiophene** (9)

A solution of 2′2-bithiophene (1.0 g, 6.01 mmol) in dry THF (50 mL) was cooled to −78°C. *n*-BuLi (2.5 M in THF, 13.3 mmol) was added dropwise and stirred at −78°C for 1.5 hr; 13.3 mL Trimethyltin chloride (1 M in THF, 13.3 mmol) was added slowly to the reaction solution and stirred at room temperature overnight. Saturated $NH_4Cl_{(aq)}$ and ethyl acetate were mixed with the reaction solution. The organic layer was washed with water and dried over $MgSO_{4(s)}$. White solid was obtained after removing solvent and recrystallized from methanol. White solid compound **9** was obtained. Yield: 1.5 g (51%). ^{1}H NMR (300 MHz, $CDCl_3$) *δ* ppm: 7.28 (d, 2H), 7.08 (d, 2H), 0.38 (s, 18H).

3.2.8 | **5,5′-Dibromo-2,2′-bithiophene** (10)

N-Bromosuccinimide (4.48 g, 25 mmol) was added slowly at room temperature to a solution of 2,2′-bithiophene (2.0 g, 12 mmol) in acetic acid (60 mL) and stirred overnight. The reaction solution was poured into cold water (200 mL) and filtered. The filtered solid was washed by distilled water thoroughly and dried under reduced pressure. White solid **10** was collected (3.84 g, 99%). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 6.96 (d, 2H), 6.85 (d, 2H).

3.2.9 | **3,3‴-Dihexyl-2,2′:5′,2″:5″,2‴-quaterthiophene** (11)

A total of 0.52 g magnesium (21.2 mmol) was added to a 250 -mL three-neck round-bottom flask containing 40 mL dry ether and 0.3 mL 1,2-dibromoethane. The solution was heated slowly until the reaction started; 2-Bromo-3-hexylthiophene (3.72 mL, 18.7 mmol) was then added to the reaction dropwise and refluxed for 2 h; 5,5′-Dibromo-2,2′-bithiophene (2.63 g, 8 mmol) and [1,3-bis(diphenyl phosphino)-propane]dichloro- nickel(II) (65.2 mg, 0.12 mmol) were added to the other three-neck round-bottom flask containing toluene (60 mL) and ether (40 mL). The 3-hexylthiophene Grignard reagent prepared from the first part was added dropwise to the toluene/ether solution and refluxed overnight. Additional ether and distilled water were added to the reaction solution after cooling to room temperature. The organic phase was extracted with distilled water repeatedly. It was then washed with 100 mL saturated NaCl solution. The organic layer was dried over anhydrous $MgSO_4$, and the solvent was removed after filtering. After removing the solvent under vacuum, the residue was purified by flash column (silica gel, hexanes). Yellow oil **11** (2.16 g, 54%) was obtained. ^1H NMR (300 MHz, $CDCl_3$) δ ppm: 7.18 (d, 2H), 7.13 (d, 2H), 7.02 (d, 2H), 6.94 (d, 2H), 2.78 (m, 4H), 1.64 (m, 4H), 1.33 (m, 12H), 0.89 (m, 6H).

3.2.10 | (3,3‴-Dihexyl-[2,2′:5′,2″:5″,2‴-quaterthiophene]-5,5‴-diyl)bis(trimethyl-stannane) (12)

Compound **11** (2.16 g, 4.34 mmol) was mixed with THF (100 mL) in a three-neck round-bottom flask and cooled to −78°C. *n*-Butyllithium (10.8 mL, 26.99 mmol) was added dropwise and stirred for 3 hr. The temperature of the solution was returned to room temperature after adding 27.9 mL trimethyltin chloride (1 M in THF, 27.9 mmol) to round-bottom flask. The reaction mixture was stirred overnight and extracted with distilled water (100 mL × 2). The organic layer was dried over anhydrous $MgSO_4$. After removing solvent under vacuum, the residue was purified by recrystallization (CH_2Cl_2/MeOH). Light yellow solid **12** (1.224 g, 34%) was obtained. ^1H NMR (300 MHz, $CDCl_3$) δ ppm: 7.12 (m, 2H), 7.00 (m, 4H), 2.79 (m, 4H), 1.66 (m, 4H), 1.35 (m, 12H), 0.89 (m, 6H), 0.38 (s, 18H).

3.2.11 | 4,8-Bis((2-ethylhexyl)oxy)-2,6-di(thiophen-2-yl)benzo[1,2-b:4,5-b′]dithiophene (13)

2,6-Dibromo-4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b′]dithiophene (0.497 g, 0.82 mmol), compound **6** (0.51 g, 2.47 mmol), $Pd(PPh_3)_4$ (47 mg, 0.041 mmol), toluene (10 mL), and DMF (2 mL) were added to a three-neck round-bottom flask. The reaction mixture was degassed and refluxed for 42 hr. The reaction mixture was filtered through Celite and washed with ether. The filtrate was dried under reduced pressure, and yellow solid was washed with methanol. High purity yellow solid **13** (0.421 g, 84%) was obtained. ^1H NMR (300 MHz, $CDCl_3$) δ ppm: 7.49 (s, 2H), 7.32 (m, 4H), 7.10 (m, 2H), 4.18 (d, 4H), 1.62 (m, 18H), 1.04 (t, 6H), 0.96 (m, 6H).

3.2.12 | (5,5′-(4,8-Bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl)bis(thio-phene-5,2-diyl))bis(trimethylstannane) (14)

Compound **13** (1.96 g, 3.2 mmol) was mixed with THF (60 mL) in a three-neck round-bottom flask and cooled to −78°C. *n*-Butyllithium (7.68 mL, 19.2 mmol) was added dropwise and stirred for 3 hr. The temperature was returned to room temperature after adding 19.9 mL trimethyltin chloride (1 M in THF, 19.9 mmol) and stirred overnight. The reaction mixture was extracted with distilled water (100 mL × 2), and the organic layer was dried over anhydrous $CaCl_2$. The solution was filtered and dried under vacuum. Yellow precipitate was obtained and washed with methanol. Yellow solid **14** (1.24 g, 41%) was obtained. ^1H NMR (300 MHz, $CDCl_3$) δ ppm: 7.48 (s, 2H), 7.42 (d, 2H), 7.15 (d, 2H), 4.18 (d, 4H), 1.63 (m, 18H), 1.04 (t, 6H), 0.97 (m, 6H), 0.42 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 144.1, 143.0, 139.3, 136.6, 136.1, 132.5, 129.3, 126.5, 116.0, 76.1, 40.8, 30.6, 29.3, 24.0, 23.3, 14.3, 11.5, −8.1. HRMS: calcd. for $C_{40}H_{58}O_2S_4Sn_2$ 938.1364; found 938.1385.

3.2.13 | Poly(PMDI-BTh)

Compound **8** (0.5 g, 0.656 mmol), compound **9** (0.32 g, 0.656 mmol), and $Pd(PPh_3)_4$ (30 mg, 4 mol%) were added to a round-bottom flask containing 75 mL toluene and 25 mL DMF. The reaction mixtures were degassed and refluxed for 10 days; 0.05 mL Trimethyl- (thiophen-2-yl) stannane (0.08 mmol) was added after 10 days and reacted for 5 hr followed by the addition of 0.14 mL 2-bromothiophene (1.39 mmol) and reacted overnight. Polymer was precipitated in methanol and filtered. The filtered polymer was soxhlated with methanol, hexanes, and $CHCl_3$ in sequence. The $CHCl_3$ portion was dried under vacuum, and dark red solid **P1** (0.5 g, 99%) was obtained. ^1H NMR (300 MHz, $CDCl_3$) δ ppm: 7.25 (m, 8H), 3.52 (m, 4H), 1.80 (m, 2H), 1.27 (m, 18H), 0.87 (m, 12H). FTIR (υ cm^{-1}): 2956, 2930, 2870, 1767, 1715, 1464, 1437, 1397, 1358, 1086, 795, 767. Gel permeation chromatography (GPC) (THF at 25°C): $M_n = 25.4$ kDa; $M_w = 83.3$ kDa.

3.2.14 | Poly(PMDI-TTh)

Compound **8** (0.1 g, 0.13 mmol), compound **12** (0.11 g, 0.13 mmol), and $Pd(PPh_3)_4$ (6.1 mg, 4 mol%) were added to a round-bottom flask with 15 mL toluene and 5 mL DMF. The reaction mixtures were degassed and refluxed for 10 days; 0.05 mL Trimethyl(thiophen-2-yl) stannane (0.08 mmol) was added after 10 days and reacted for 5 hr followed by the addition of 0.14 mL 2-bromothiophene (1.39 mmol) and reacted overnight. Polymer was precipitated in methanol and filtered. The filtered polymer was soxhlated with methanol, hexanes, and $CHCl_3$, and the $CHCl_3$ was dried under vacuum. Dark red solid **P2** (0.14 g, 97%) was obtained. ^1H NMR (300 MHz, $CDCl_3$) δ ppm: 7.15 (m, 10H), 3.53 (m, 4H), 2.80 (m, 4H), 1.74 (m, 2H), 1.34 (m, 32H), 0.89 (m, 18H). FTIR (υ cm^{-1}): 3069, 2954, 2928, 2857, 1768, 1715, 1465, 1396, 1361, 1170, 1087, 1034, 1017, 830, 797, 768, 754. Gel permeation chromatography (GPC) (THF at 25°C): $M_n = 18.5$ kDa; $M_w = 40.4$ kDa.

3.2.15 | Poly(PMDI-BDTTh)

Compound **8** (0.1 g, 0.13 mmol), compound **14** (0.12 g, 0.13 mmol), and $Pd(PPh_3)_4$ (6.1 mg, 4 mol%) were mixed with 15 mL toluene and 5 mL DMF in a round-bottom flask. It was degassed and refluxed for 10 days; 0.05 mL

Trimethyl-(thiophen-2-yl)stannane (0.08 mmol) was added after 10 days and reacted for 5 hr followed by the addition of 0.14 mL 2-bromothiophene (1.39 mmol) and reacted overnight. Dark red precipitate was obtained after dropping the solution into methanol. The polymer was filtered and soxhlated with methanol, hexanes, and $CHCl_3$. The $CHCl_3$ solution was dried, and **P3** (0.159 g, 99%) was obtained. ^1H NMR (300 MHz, $CDCl_3$) δ ppm: 7.39 (m, 9H), 4.21 (m, 4H), 3.53 (m, 4H), 1.46 (m, 60H), 1.34 (m, 32H), 0.89 (m, 18H). FTIR (υ cm^{-1}): 2954, 2923, 2854, 1767, 1715, 1457, 1432, 1394, 1355, 1264, 1218, 1166, 1084, 1034, 792, 767. Gel permeation chromatography (GPC) (THF at 25°C): $M_n = 22.1$ kDa; $M_w = 46.9$ kDa.

4 | CONCLUSIONS

Three PMDI-based conjugated copolymers were synthesized. Although PMDI is a planar core that is feasible for synthesizing crystallizable conjugated copolymers, the selection of comonomer seems to also be very important. In this study, a planar electron-donating core, BDTTh, copolymerizes with PMDI and produces a crystallizable polymer—poly(PMDI-BDTTh). With extended thiophene units (BTh and TTh), twisting between two thiophene units results in curving or rotation of the polymer backbone, which is not favorable for the crystallization.

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REFERENCES

[1] S. Seki, A. Saeki, T. Sakurai, D. Sakamaki, *Phys. Chem. Chem. Phys.* **2014**, *16*, 11093.

[2] C. Liu, K. Wang, X. Gong, A. J. Heeger, *Chem. Soc. Rev.* **2016**, *45*, 4825.

[3] Y. Kim, S. Cook, S. Tuladhar, S. Choulis, J. Nelson, J. R. Durrant, D. D. C. Bradley, M. Giles, I. McCulloch, C.-S. Ha, M. Ree, *Nat. Mater.* **2006**, *5*, 197.

[4] K. Reichenbächer, H. I. Süss, J. Hulliger, *Chem. Soc. Rev.* **2005**, *34*, 22.

[5] J. W. Jo, S. Bae, F. Liu, T. P. Russell, W. H. Jo, *Adv. Funct. Mater.* **2015**, *25*, 120.

[6] S. C. Price, A. C. Stuart, L. Yang, H. Zhou, W. You, *J. Am. Chem. Soc.* **2011**, *133*, 4625.

[7] L. Yang, J. R. Tumbleston, H. Zhou, H. Ade, W. You, *Energy Environ. Sci.* **2013**, *6*, 316.

[8] H. J. Son, W. Wang, T. Xu, Y. Liang, Y. Wu, G. Li, L. Yu, *J. Am. Chem. Soc.* **2011**, *133*, 1885.

[9] A. C. Stuart, J. R. Tumbleston, H. Zhou, W. Li, S. Liu, H. Ade, W. You, *J. Am. Chem. Soc.* **2013**, *135*, 1806.

[10] H.-Y. Chen, J.-L. Wu, C.-T. Chen, *Chem. Commun.* **2012**, *48*, 1012.

[11] W. P. Hsu, K. Levon, K. S. Ho, A. S. Myerson, T. K. Kwei, *Macromolecules* **1993**, *26*, 1318.

[12] Y. Liu, J. Zhao, Z. Li, C. Mu, W. Ma, H. Hu, K. Jiang, H. Lin, H. Ade, H. Yan, *Nat. Commun.* **2014**, *5*, 5293.

[13] I. McCulloch, M. Heeney, C. Bailey, K. Genevicius, I. McDonald, M. Shkunov, D. Sparrowe, S. Tierney, R. Wagner, W. Zhang, M. L. Chabinyc, R. J. Kline, M. D. McGehee, M. F. Toney, *Nat. Mater.* **2006**, *5*, 328.

[14] K. Kranthiraja, K. Gunasekar, W. Cho, M. Song, Y. G. Park, J. Y. Lee, Y. Shin, I. N. Kang, A. Kim, H. Kim, B. Kim, S. H. Jin, *Macromolecules* **2014**, *47*, 7060.

[15] W. S. Yoon, D. W. Kim, J. M. Park, I. Cho, O. K. Kwon, D. R. Whang, J. H. Kim, J. H. Park, S. Y. Park, *Macromolecules* **2016**, *49*, 8489.

[16] Y. Lin, F. Zhao, Y. Wu, K. Chen, Y. Xia, G. Li, S. K. Prasad, J. Zhu, L. Huo, H. Bin, Z. G. Zhang, X. Guo, M. Zhang, Y. Sun, F. Gao, Z. Wei, W. Ma, C. Wang, J. Hodgkiss, Z. Bo, O. Inganäs, Y. Li, X. Zhan, *Adv. Mater.* **2017**, *29*, 1604155.

[17] Y. Lin, Q. He, F. Zhao, L. Huo, J. Mai, X. Lu, C. J. Su, T. Li, J. Wang, J. Zhu, Y. Sun, C. Wang, X. Zhan, *J. Am. Chem. Soc.* **2016**, *138*, 2973.

[18] Y. Lin, J. Wang, Z. G. Zhang, H. Bai, Y. Li, D. Zhu, X. Zhan, *Adv. Mater.* **2015**, *27*, 1170.

[19] Y. Lin, Z. G. Zhang, H. Bai, J. Wang, Y. Yao, Y. Li, D. Zhu, X. Zhan, *Energy Environ. Sci.* **2015**, *8*, 610.

[20] Y. Wu, H. Bai, Z. Wang, P. Cheng, S. Zhu, Y. Wang, W. Ma, X. Zhan, *Energy Environ. Sci.* **2015**, *8*, 3215.

[21] S. Holliday, R. S. Ashraf, C. B. Nielsen, M. Kirkus, J. A. Röhr, C. H. Tan, E. Collado-Fregoso, A. C. Knall, J. R. Durrant, J. Nelson, I. McCulloch, *J. Am. Chem. Soc.* **2015**, *137*, 898.

[22] J. Shao, J. Chang, G. Dai, C. Chi, *J. Polym. Sci. A* **2014**, *52*, 2454.

[23] G. Dai, J. Chang, C. Chi, *J. Mater. Chem.* **2012**, *22*, 21201.

[24] X. Guo, M. D. Watson, *Macromolecules* **2011**, *44*, 6711.

[25] X. Zhou, Y. Gao, X. Y. Wang, Z. H. Guo, J. Y. Wang, J. Pei, *Asian J. Org. Chem.* **2014**, *3*, 209.

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