Supporting Information for

A Straightforward Method to Electron Transporting Conjugated Polymers

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Contents

1.1 General Experimental Methods	2
1.2 Polymer Acronyms	3
2. UV-Vis Spectra of Polymers in Chloroform	3
3. Redox Properties of Polymers	4
4. Wide Angle X-ray Spectroscopy of Polymers and Simulated	
Polymer Packing of PBTDV1	5
5. GPC Data	6
6. Frontier Energy Levels Comparison	7
7. Photocurrent transient of PBTDV1 and PBTDV2	8
8. Optimization of Synthesis Conditions for Compound 2	9
9. Optimization of Synthesis Conditions for PBTD2	10
10. Optimization of Synthesis Conditions for PBTDV1	11
11. Optimization of Synthesis Conditions for PBTDV2	11
12. Synthesis	
12.1. Monomer Synthesis	12
12.2. Polymer Synthesis	15
13. NMR Spectra	18

1.1. General Experimental Methods

All chemicals were purchased from commercial sources (Acros, Aldrich, Alfa Aesar, TCI, and Strem) and used without further purification, unless otherwise noted. THF was distilled from sodium-benzophenone ketyl. Common solvents were purchased from EMD (through VWR). Routine monitoring of reactions was carried out on glass-supported EMD silica gel 60 F_{254} TLC plates. Flash chromatography was performed using silica gel from Sorbent Technologies (Standard Grade, 60 Å, 32-63 µm). All ¹H and ¹³C {¹H} NMR spectra were recorded on a Bruker Avance400 spectrometer, unless otherwise noted. Chemical shifts and coupling constants (*J*) are reported in parts per million (δ) and Hertz, respectively. Deuterated solvents were obtained from Cambridge Isotope Laboratories, Inc. Chloroform-D (CDCl₃) contained 0.05% v/v tetramethylsilane (TMS) and chloroform-D peak was set to 7.26 ppm on all proton spectra. The ¹H NMR spectra of polymers were recorded in 1,1,2,2-tetrachloroethane-d2 at 100 °C and the sovlent peak was set at 6.0 ppm on all spectra.

Gel permeation chromatography (GPC), mass spectrometry, and WAXS were recorded in the NSF-sponsored Materials Research Science and Engineering Center on Polymers (MRSEC) at the University of Massachusetts Amherst. GPC analyses were performed on Agilent 1200 chloroform GPC and Agilent 1260 tetrahydrofuran GPC with polystyrene as a standard and toluene as the flow rate marker and RI detection mode. WAXS was recorded on Molecular Metrology Inc. (presently sold as Rigaku S-Max3000) instrument. Mass spectrometry was recorded on JEOL M Station JMS700. UV-Vis absorption spectra were measured with a Shimadzu UV 3600PC spectrometer Polymer-Based Materials Harvesting Solar Energy EFRC (Energy Frontier Research Center at the University of Massachusetts Amherst) laboratory. Stock solutions of polymers (c = 1 mg/10 mL) were prepared in spectrophotometric grade chloroform (Fisher, Optima). UV-Vis absorption spectra of polymer thin films were recorded by spin casting polymer solutions on to a glass plate. Cyclic voltammetry spectra were recorded using BAS CV-50 W instrument. The polymer solutions were drop cast on to a platinum working electrode and the spectra was recorded with tetrabutylammonium hexfluorophosphate as a supporting electrolyte (0.1M) in acetonitrile. The redox potentials were determined versus a Ag/Ag^+ reference electrode. The working and auxiliary electrodes were cleaned after each run. The HOMO and LUMO values were calculated using Fc/Fc⁺ as a reference. Time of flight (ToF)

measurements was done at room temperature under vacuum (10^{-2} Torr). A frequency doubled YAG laser (532 nm) was utilized as the pulsed excitation source and the photocurrent was measured across a 50 Ω resistor by a digitizing oscilloscope HP 54510B.

1.2 Polymer Acronyms:

P3HT: Poly(3-hexylthiophene)

PCPTDTBT: Poly[2,1,3-benzothiadiazole-4,7-diyl[4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2,6-diyl]] (see FigureS6 for chemical structure)

PBDTTT-CF: Poly[4,8-bis-substituted-benzo[1,2-b:4,5-b']dithiophene-2,6-diyl-alt-4substituted-thieno[3, 4-b]thiophene-2,6-diyl]-CF (see FigureS6 for chemical structure)

PBnDT-FTAZ: polymer of benzodithiophene and fluorinated analogue of benzotriazole (see FigureS6 for chemical structure)

F8BT: poly[(9,9-di-*n*-octylfluorenyl-2,7-diyl)-*alt*-(benzo[2,1,3]thiadiazol-4,8-diyl)]

1.2 PBTD1 PBTD2 PBTDV1 1.0 PBTDV2 0.8 Absorption (a.u) 0.6 0.4 0.2 0.0 400 600 300 500 700 800 Wavelength (nm)

2. UV-Vis Spectra of Polymers in Chloroform

Figure S1. UV-Vis absorption spectra of polymers in chloroform.

3. Redox Properties of Polymers



Figure S2. Cyclic voltammograms of polymer thin films.

	E ^{elec} (eV)	HOMO ^{elec} (eV)	LUMO ^{elec} (eV)
PBTD1	-	-	-2.93
PBTD2	2.93	-5.96	-3.03
PBTDV1	2.03	-5.45	-3.42
PBTDV2	1.79	-5.24	-3.45

PBTD1 showed no oxidation peak thus, HOMO^{elec} and LUMO^{opt} cannot be determined

4. Wide Angle X-ray Spectra of Polymer Thin Films and Simulated Polymer Packing of PBTDV1.



Figure S3. Wide Angle X-ray Spectra (WAXS) of polymer thin films.



Figure S4. Simulated (using Cerius 2) polymer packing of PBTDV1.

5. GPC Spectra of Polymers



Figure S5. GPC (THF) spectra of polymers with polystyrene standards.

6. Comparison of Frontier Energy Levels



Figure S6. Frontier energy levels of PBTDV1, PCBM, and various low band gap and high efficiency hole conducting polymers. The efficiencies shown here are with PCBM as electron conductor. The energy loss for charge transfer is minimum with PBTDV1 as an electron conductor compared to PCBM.

7. Photocurrent Transient of PBTDV1 and PBTDV2



Figure S7. Photocurrent transients of a) PBTDV1 and b) PBTDV2.

8. Optimization of Synthesis Conditions for Compound 2

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Reagent	Acid	Solvent	Temperature (°C)	Time (h)
NIS	H_2SO_4	DCM	RT	24
NIS	CF ₃ SO ₃ H	DCM	RT	12
I ₂	CH₃COOH	CHCl ₃	50	48
I ₂	H_2SO_4	CH ₃ COOH, H ₂ O	70	24
I ₂	$H_2SO_{4,}$ NaIO ₃	CH ₃ COOH, H ₂ O	110	24
I ₂	H ₂ SO ₄ , HIO ₃	CH ₃ COOH, H ₂ O	90	24
I ₂	H_2SO_4, H_5IO_6	CH ₃ COOH, H ₂ O	70	12

Table S1. Attempted iodinating conditions for compound 2.

All the reactions after the work up showed multiple spots on TLC and the crude NMR showed no product peak.

9. Optimization of Synthesis Conditions for PBTD2

Catalyst	Solvent	Base	Temeperature (^o C)	$\mathbf{M}_{\mathbf{w}}(\mathbf{KDa})^{\mathrm{a}}$
Pd(PPh ₃) ₄	NMP/ODCB	K ₂ CO ₃	90	2.7
Pd(OAc) ₂	NMP/ODCB	K ₂ CO ₃	90	2.8
$Pd(^{t}Bu_{3}P)_{2}$	NMP/ODCB	K ₂ CO ₃	90	3.5
Pd(PPh ₃) ₄	Toluene	K ₂ CO ₃	80	2.0
Pd(PPh ₃) ₄	Toluene	LiOH.H ₂ O	80	2.8
$Pd(^{t}Bu_{3}P)_{2}$	THF	LiOH.H ₂ O	60	3.5
$Pd(^{t}Bu_{3}P)_{2}$	ⁿ Bu ₂ O	LiOH.H ₂ O	110	15.7, 3.9, 2.5

 Table S2. Attempted polymerization conditions for PBTD2.

^aGPC (THF) with polystyrene standards

10. Optimization of Synthesis Conditions for PBTDV1

Catalyst	Solvent	Temeperature (^o C)	$\mathbf{M}_{\mathbf{w}} \left(\mathbf{KDa} \right)^{\mathbf{a}}$
Pd(PPh ₃) ₄	ODCB	110	2.0
Pd ₂ (dba) ₃ P(o-tol) ₃	СВ	110	-

 Table S3. Attempted polymerization conditions for PBTDV1.

^aGPC (CHCl₃) with polystyrene standards.

11. Optimization of Synthesis Conditions for PBTDV2

Table S4. Attempted polymerization conditions for PBTDV2.

Catalyst	Solvent	Temperature (°C)	$\mathbf{M}_{\mathbf{w}}(\mathbf{KDa})^{\mathrm{a}}$
Pd ₂ (dba) ₃ P(o-tol) ₃	NMP/ODCB	140	9.6
Pd(^t Bu ₃ P) ₂ , CuI	NMP/ODCB	130	3.6
Pd(^t Bu ₃ P) ₂ , CuI	ⁿ Bu ₂ O	100	3.5 ^b

^aGPC (THF) with polystyrene standards

^bGPC (CHCl₃) with polystyrene standards

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12. Experimental Procedures

12.1 Monomer Syntheses



Compound **1** is synthesized using established protocols.

1,2-bis(tetradecyloxy)benzene (4). ¹H NMR (CDCl₃): δ = 6.91 (s, 4H), 3.99-4.03 (t, *J* = 6.6 Hz, 4H), 1.88-1.81 (m, 4H), 1.52-1.15 (m, 44H), 0.94-0.90 (t, *J* = 6.6 Hz, 6H). ¹³C NMR (CDCl₃): δ = 149.3, 121.0, 114.1, 69.3, 32.0, 29.79, 29.75, 29.72, 29.53, 29.45, 29.43, 26.1, 22.8, 14.2.

1,2-dinitro-4,5-bis(tetradecyloxy)benzene (5). ¹H NMR (CDCl₃): δ = 7.29 (s, 2H), 4.10 (t, *J* = 6.5 Hz, 4H), 1.90-1.83 (m, 4H), 1.51-1.26 (m, 44H), 0.88 (t, *J* = 6.6 Hz, 6H). ¹³C NMR (CDCl₃): δ = 151.8, 136.4, 107.9, 70.2, 31.9, 29.73, 29.69, 29.60, 29.55, 29.40, 29.26, 28.72, 25.83, 22.71, 14.11.

5,6-bis(tetradecyloxy)benzo[*c*][**1,2,5]thiadiazole (7).** ¹H NMR (CDCl₃): δ = 7.13 (s, 2H), 4.09 (t, *J* = 6.5 Hz, 4H), 1.94-1.87 (m, 4H), 1.56-1.26 (m, 44H), 0.89-0.85 (m, 6H). ¹³C NMR (CDCl₃): δ = 154.1, 151.40, 98.4, 69.1, 31.9, 29.72, 29.68, 29.62, 29.4, 28.7, 26.0, 22.7, 14.1.

4,7-dibromo-5,6-bis(tetradecyloxy)benzo[*c*][**1,2,5]thiadiazole** (**1**). ¹H NMR (CDCl₃): δ = 4.16 (t, *J* = 6.6 Hz, 4H), 1.92-1.85 (m, 4H), 1.62-1.46 (m, 4H), 1.46-1.19 (m, 40H), 0.88 (t, *J* = 6.6 Hz, 6H). ¹³C NMR (CDCl₃): δ = 154.5, 150.4, 106.3, 75.2, 31.9, 30.3, 29.72, 29.70, 29.69, 29.65, 29.63, 29.45, 29.39, 26.0, 22.7, 14.1. LRMS (FAB+) Calculated for C34H58Br2N2O2S (M+H)⁺ 719.26; Found 719.2.



1,2-bis-octyloxy-benzene (8). To a solution of catechol (15 g, 0.136 mol) in DMF (75 mL) was added 1-bromooctane (0.34mol, 59.2 mL) and K₂CO₃ (56.5 g, 0.408 mol). The mixture was stirred at 100 °C under a nitrogen atmosphere for 48 hours. After cooling the mixture to room temperature (RT), 150 mL of water was added. The organic layer was separated and the aqueous layer was extracted with DCM. The organic layers were mixed and washed with sodium thiosulfate and brine solution. The combined organic phase was dried over Na₂SO₄. After filtration, the mixture was concentrated under vacuum. The residual DMF and 1-bromooctane were distilled out at 120 °C under reduced pressure (300 millitorr). The purification of the residue by silica gel chromatography (10:90 dichloromethane: hexanes) afforded **9** as colorless oil. Yield: 35.5 g (78%), colorless liquid.¹H NMR (CDCl₃): $\delta = 6.89$ (s, 4H), 3.99 (t, J = 6.6 Hz, 4H), 1.85-1.78 (m, 4H), 1.57-1.22 (m, 20H), 0.89 (t, J = 6.6 Hz, 6H). ¹³C NMR (CDCl₃): $\delta = 149.38$, 121.12, 114.23, 69.40, 31.98, 29.55, 29.49, 29.44, 26.20, 22.82, 14.24.

1,2-dinitro-4,5-bis-octyloxy-benzene (9). A two neck round-bottom flask containing dichloromethane (420 mL), acetic acid (420mL), and **8** (35 g, 0.104 mol) was cooled to 10 °C and

65% nitric acid (550 mL) was added drop wise. The mixture was allowed to warm to room temperature and stirred for 48 hours. After completion of the reaction, the reaction mixture was poured into ice-water and the dichloromethane layer separated. The water phase was extracted with dichloromethane. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated. The crude product was recrystallized from ethanol. Yield: 36 g (81%), yellow solid. ¹H NMR (CDCl₃): δ = 7.29 (s, 2H), 4.09 (t, *J* = 6.5 Hz, 4H), 1.90-1.82 (m, 4H), 1.51-1.28 (m, 20H), 0.88 (t, *J* = 6.6 Hz, 6H). ¹³C NMR (CDCl₃): δ = 151.93, 136.55, 108.01, 70.31, 31.87, 29.30, 28.81, 25.92, 22.75, 14.18.

4,5-bis(octoloxy)benzene-1,2-diaminium chloride (10). A mixture of **9** (10 g, 0.0235 mol), Sn(II)Cl₂ (0.188 mol, 42.5 g) in ethanol (350 mL), and conc. HCl (140 mL) were heated to 85 °C for overnight. The reaction mixture was cooled to room temperature and the product was filtered and washed with water and methanol. The product was finally dried at RT under a stream of argon and used directly (unstable). Yield: 21 g (quantitative yield), off-white solid.

5,6-bis-octyloxy-benzo[**1,2,5**]**thiadiazole** (**2**). To a mixture of **10** (17g, 38.85 mmol) and triethylamine (388.5 mmol, 55 mL) in 500mL dichloromethane, a solution of thionyl chloride (77.72 mmol, 5.67mL) in 80 mL dichloromethane was added slowly. The mixture was refluxed for 6 hours and the solution was cooled. The solution was then concentrated in vacuum followed by trituration in water. The mixture was stirred for 30 min and the product was filtered and reprecipitated from ethanol. The reprecipitated compound was purified by silica gel chromatography (4:96 EtOAc: hexanes) to afford **4** as off-white solid. Yield: 9.0 g (59 %). ¹H NMR (CDCl₃): δ = 7.13 (s, 2H), 4.09 (t, *J* = 6.5 Hz, 4H), 1.94-1.87 (m, 4H), 1.53-1.29 (m, 20H), 0.90-0.87 (m, 6H). ¹³C NMR (CDCl₃): δ = 154.29, 151.54, 98.55, 69.28, 31.95, 29.47, 29.41, 28.88, 26.16, 22.82, 14.25.

4,7-Diiodo-5,6-bis-octyloxy-benzo[**1,2,5**]**thiadiazole** (**3**). In a round bottom flask compound **2** (1g, 2.547 mmol), iodine (0.775g, 3.056 mmol), and PhI(OCOCF₃)₂ (1.31g, 3.056 mmol) were added along with 60 mL dichloromethane. The reaction mixture was refluxed for 5 h. After 5 h, the reaction was brought to room temperature and sodium thiosulphate solution (100mL) was added and stirred further for 1 h. Water (100mL) was added and the reaction mixture was extracted with DCM (4x50mL). The organic layer was washed with NaHCO₃ (100mL) and sat. NaCl (100mL) solution and dried over Na₂SO₄. The crude was purified by silica gel chromatography (40:60 DCM:

hexanes) to afford **2** as light yellow solid. Yield: 1.35g (82 %).¹H NMR (CDCl₃): $\delta = 4.12$ (t, J = 6.5 Hz, 4H), 1.94-1.87 (m, 4H), 1.58-1.30 (m, 20H), 0.91-0.87 (m, 6H). ¹³C NMR (CDCl₃): $\delta = 157.24$, 151.96, 82.80, 75.10, 31.99, 30.51, 29.59, 29.43, 26.28, 22.82, 14.26. HRMS (EI+) Calculated for C22H34I2N2O2S M⁺ 644.04; Found 644.043.

12.2 Polymer Syntheses

Polymer PBTD1

Compound 1 (250 mg, 0.347 mmol) was added to the Schlenk flask and taken into the glove box. Compound **BTD** and $Pd(^{t}Bu_{3}P)_{2}$ (17.7 mg, 0.0347 mmol) catalyst were added to the Schlenk flask inside the glove box. The solvents *n*-butyl ether (n-Bu₂O) and *ortho*-dichlorobenzene (ODCB) (1:1) were taken into another Schlenk flask and degassed thrice by freeze pump thaw technique. THF was also degassed thrice by freeze pump thaw technique. 4 mL of degassed n-Bu₂O and ODCB mixture was added to aliquat 336 (12 drops) under argon atmosphere and the solution was deoxygenated by bubbling argon into it for 30 minutes. This solution and the degassed THF were added to the Schlenk flask containing compound 1, compound 3, and catalyst under argon atmosphere. Deoxygenated aq.LiOH (2.6 mL) was also subsequently added to the Schlenk flask containing all other reagents and the Schlenk flask was immsered in to an oil bath preheated to 90 °C. The polymerization was carried out for 7 days maintaining the same temperature and the reaction mixture was precipitated in to methanol. The polymer was transferred to an extraction thimble and fractionated via Soxhlet extraction with MeOH, EtOAc, ether, and CHCl₃. The CHCl₃ fraction, after concentration under reduced pressure, afforded 170 mg of the polymer. The polymer isolated from the chloroform fraction was analyzed by GPC. The ¹H NMR spectrum of the polymer was recorded in 1,1,2,2-tetrachloroethane-d2 at 100 °C.

Polymer PBTD2

Compound **3** (404 mg, 0.626 mmol) was added to a Schlenk flask and taken into the glove box. Compound **BTD** and $Pd({}^{t}Bu_{3}P)_{2}$ (32.02mg, 0.0626 mmol) catalyst were added to the Schlenk flask inside the glove box. The solvents *n*-butyl ether (*n*-Bu₂O) and *ortho*-dichlorobenzene (ODCB) (1:1) were taken into another Schlenk flask and degassed thrice by freeze pump thaw technique. 12 mL of ${}^{n}Bu_{2}O$ and ODCB mixture was added to aliquat 336 (20 drops) under argon atmosphere and the solution was deoxygenated by bubbling argon into it for 30 minutes. This solution was added to the Schlenk flask containing compound **2**, compound **3**, and catalyst under argon atmosphere. Deoxygenated aq.LiOH (5 mL) was also subsequently added to the Schlenk flask containing all other reagents and the Schlenk flask was immsered in to an oil bath preheated to 110 °C. The polymerization was carried out for 8 days maintaining the same temperature and the reaction mixture was precipitated in to methanol. The polymer was transferred to an extraction thimble and fractionated via Soxhlet extraction with MeOH, EtOAc, and CHCl₃. The CHCl₃ fraction, after concentration under reduced pressure, afforded 90 mg of the polymer. The polymer isolated from the chloroform fraction was analyzed by GPC. The ¹H NMR spectrum of the polymer was recorded in 1,1,2,2-tetrachloroethane-d2 at 100 °C.

Polymer PBTDV 1

Compound **1** (80 mg, 0.113 mmol) was added to a Schlenk flask and the flask was taken into the glovebox. Pd(PPh₃)₄ (12.8mg, 0.0113 mmol) catalyst was added to the Schlenk flask inside the glove box. Toluene (3 mL) was taken into another Schlenk flask and degassed thrice by freeze pump thaw technique. Approximately 1 mL of the degassed Toluene was added to a Schlenk flask containing trans-1,2-bis(tri-n-butylstannyl)ethylene (67 mg, 0.113 mmol) and the solution was deoxygenated by bubbling argon into it for 30 minutes. This solution was added to the Schlenk flask containing compound **1** and Pd(PPh₃)₄ catalyst under argon atmosphere, followed by the addition of 2 mL of deoxygenated Toluene. The Schlenk flask was immsered in to an oil bath preheated to 90 °C. The polymerization was carried out for 5 days maintaining the same temperature and the reaction mixture was precipitated in to methanol. The polymer was transferred to an extraction thimble and fractionated via Soxhlet extraction with MeOH, acetone, and CHCl₃. The CHCl₃ fraction, after concentration under reduced pressure, afforded 60 mg of the polymer. The polymer isolated from the chloroform fraction was analyzed by GPC. The ¹H NMR spectrum of the polymer was recorded in 1,1,2,2-tetrachloroethane-d2 at 100 °C.

Polymer PBTDV2

Compound **3** (400mg, 0.620 mmol) was added to a Schlenk flask and the flask was taken into the glovebox. $Pd(PPh_3)_4$ (71.7 mg, 0.062 mmol) catalyst was added to the Schlenk flask inside the

glove box. N-methyl-2-pyrrolidone and 1,2-dichlorobenzene (20 mL (1:2 v/v)) were taken in another Schlenk flask and degassed by thrice by freeze pump thaw technique. Approximately 3 mL of degassed N-methyl-2-pyrrolidone and 1,2-dichlorobenzene sovlent mixture was added to the Schlenk flask containing trans-1,2-bis(tri-n-butylstannyl)ethylene (413mg, 0.6828 mmol) and the solution was deoxygenated by bubbling argon into it for 30 minutes. This solution was added to the Schlenk flask containing compound **2** and Pd(PPh₃)₄ catalyst under argon atmosphere, followed by the addition of the remaining 17 mL of degassed polymerization was carried out for 5 days maintaining the same temperature and the reaction mixture was precipitated in to methanol. The polymer was transferred to an extraction thimble and fractionated via Soxhlet extraction with MeOH, acetone, ethyl acetate, and CHCl₃. The CHCl₃ fraction, after concentration under reduced pressure, afforded 150 mg of the polymer. The polymer isolated from the chloroform fraction was analyzed by GPC. The ¹H NMR spectrum of the polymer was recorded in 1,1,2,2-tetrachloroethane-d2 at 100 °C.

13. NMR Spectra





















