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## *Poly(Pyridinium Phenylene)s: Water-Soluble N-Type Polymers*

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# Poly(Pyridinium Phenylene)s: Water Soluble N-Type Polymers

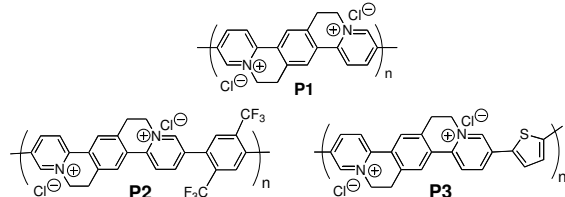
Daisuke Izuhara and Timothy M. Swager\*

Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139

RECEIVED DATE (automatically inserted by publisher); E-mail: tswager@mit.edu

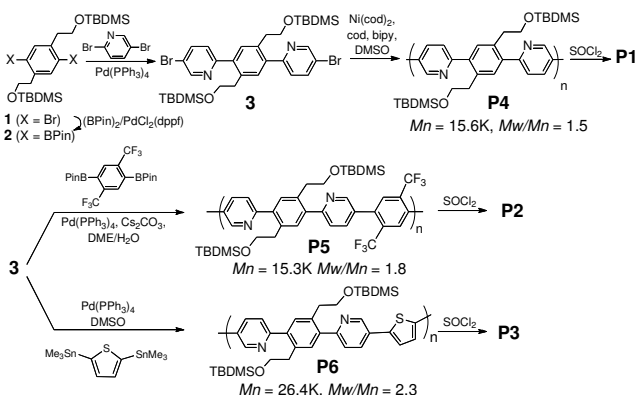
Conjugated polymer semiconductors can be fabricated over large areas by low-cost solution processing and hence offer economic advantages in the production of photovoltaic cells,<sup>1</sup> light emitting diodes,<sup>2</sup> and field-effect transistors.<sup>3</sup> Although many varieties of high performance p-type polymers are available,<sup>4</sup> stable processable n-type polymers remain largely elusive.<sup>5</sup> Few studies have been reported concerning heterojunctions between p/n-type polymers for photovoltaic cells,<sup>6</sup> mainly due to the limited high electron affinity (EA) n-type polymers, and the polymer photovoltaic devices have focused heavily on acceptor molecules, such as methanofullerene phenyl-C<sub>61</sub>-butyric-acid-methyl-ester (PCBM, EA = 4.2 eV).<sup>1b</sup> Access to conjugated high electron affinity polymers remains a critical challenge and one of the most successful strategies has been the construction of conjugated polymers based upon N-heterocyclic electron-deficient aromatics.<sup>5a,7</sup> However, development of nitrogen-containing polyheterocycles with high electron affinities and solubility in common solvents has met limited success.<sup>8</sup>

We report herein the syntheses and electron-accepting properties of a new class of water-solution processable n-type conjugated polymers (**P1**, **P2**, **P3**) with pyridinium-phenylene units that exhibit reversible electroactivity, useful electron affinities, and high electrical conductivity. In these materials the electron-deficient pyridinium rings are produced by an intramolecular cyclization that provides low LUMO energies and a relatively planar structure for extended  $\pi$ -electron delocalization. We further demonstrate electron transfer quenching in bilayer donor/accepter polymers heterojunctions<sup>8-9</sup> with the well-known p-type material, poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene-vinylene) (MEH-PPV).<sup>10</sup>



Scheme 1 shows the synthetic routes to **P1** and copolymers **P2** and **P3**. We first synthesize a pyridyl precursor-polymer that is then subjected to intramolecular nucleophilic substitution reactions to form the pyridinium rings. A symmetrical monomer **3** provides a head-to-head skeleton that was expected to display reversible viologen-like redox behavior.<sup>11</sup> The boronation of 2,5-bis(2-(*tert*-butyldimethylsilyloxy)ethyl)-1,4-benzenedibromide (**1**) gives the corresponding diboronic acid bis(pinacol) ester (**2**). Head-to-head monomer **3**, 1,4-bis[2-(5-bromopyridyl)]-2,5-bis(2-(*tert*-butyl dimethylsilyloxy)ethyl) benzene, was synthesized by regioselective Suzuki coupling of **2** with 2,5-dibromopyridine in 58% yield. Yamamoto, Suzuki, and Stille coupling polymerizations yielded high-molecular-weight siloxyethyl-substituted poly(pyridine phenylene)s, **P4**, **P5**, and **P6**, in 65-95%

**Scheme 1.** Synthetic Routes to **P1**, **P2**, and **P3**.



**Table 1.** Optical and Electrochemical Properties of **P1**, **P2** and **P3**.

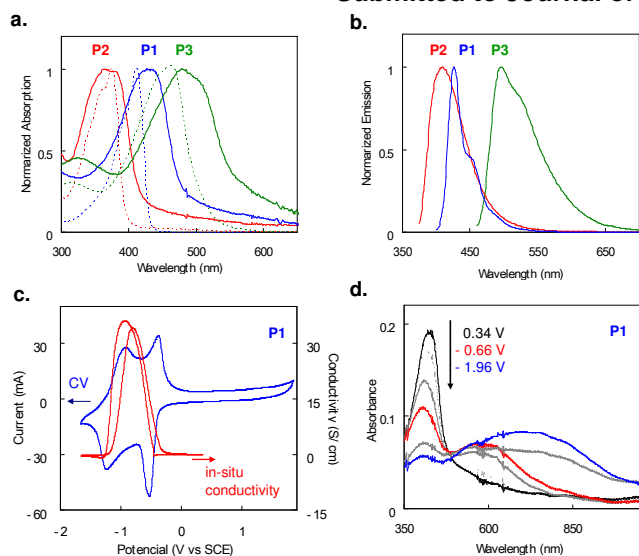
polymer	$\lambda_{\text{max}}$ (nm)	$\lambda_{\text{onset}}$ (nm)	$E_g^a$ (eV)	$E_{\text{red}}^b$ (V)	$E_{\text{onset}}^b$ (V)	EA <sup>c</sup> (eV)	IP <sup>d</sup> (eV)
<b>P1</b>	431	485	2.56	-0.56, -1.27	-0.40	4.00	6.56
<b>P2</b>	376	420	2.95	-0.71, -0.90	-0.50	3.90	6.85
<b>P3</b>	483	575	2.16	-0.59, -0.99	-0.26	4.14	6.30

<sup>a</sup>  $E_g$ : Band gap estimated from the band edge ( $\lambda_{\text{onset}}$ ) of the absorption spectra. <sup>b</sup>  $E_{\text{red}}$ ,  $E_{\text{onset}}$ : Formal and onset reduction potentials (vs SCE). <sup>c</sup> EA: Electron affinity obtained based on EA =  $E_{\text{onset}} + 4.4$  (eV). <sup>d</sup> IP: Ionization potential calculated from IP = EA +  $E_g$  (eV). <sup>e</sup>

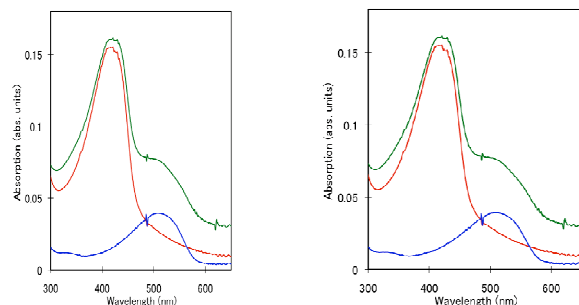
yield.<sup>12</sup> All the precursor polymers were soluble in common organic solvents (e.g. CHCl<sub>3</sub>, THF) and thionyl chloride induced quaternization cyclization gave polyelectrolytes **P1**, **P2**, and **P3**.<sup>13</sup> The polyelectrolytes are only soluble in highly polar solvents, such as water and methanol, and this feature allows for the facile formation of multi-layer polymer structures by simple spin-coating on top of polymers with orthogonal solubilities.

The absorption and emission spectra of **P1**, **P2**, and **P3** (Figure 1a-b) are significantly red-shifted relative to their respective precursors.<sup>12</sup> This is attributed to the two ethylene bridges enforcing a planar conformation of the bis-pyridinium-phenylene segment. Thin films of **P3** displayed the smallest  $E_g$  (2.16 eV) as a result of the donor-accepter type structure as well as less steric hindrance.

The electron affinities (EA) of **P1**, **P2**, and **P3** are estimated at 3.90-4.14 eV from the onset reduction potential in cyclic voltammetry (CV) (Table 1).<sup>12,14</sup> Interestingly, the EA values are higher than those estimated in the same method for most conventional polyheterocycles,<sup>7a</sup> and are comparable to well known electron transporters PCBM (4.2 eV)<sup>1b</sup> or polybenzimidazobenzophenanthroline (BBL) (4.0 eV).<sup>8</sup>



**Figure 1.** (a) UV-vis absorption spectra of **P1-3**; thin films (continuous line), water or methanol solutions (dashed line). (b) PL emission spectra of **P1-3** in water or methanol solutions. (c) Cyclic voltammogram, in-situ conductivity measurement, and (d) Spectroelectrochemistry of **P1** thin film.



**Figure 2.** (left) UV-vis absorption and (right) PL emission spectra ( $\lambda_{\text{ex}} = 507$  nm) of thin films of MEH-PPV, **P1**, and a bilayer of MEH-PPV/**P1**.

Additionally, **P1**, **P2**, and **P3** exhibit reversible electrochemical behavior as revealed in Figure 1c for **P1**. The in-situ conductivity measurements of **P1** thin films (Figure 1c) on interdigitated microelectrodes reveal a narrow window of high conductivity ( $\sigma_{\text{max}} = 36$  S/cm at  $-0.96$  V).<sup>15</sup> Conductivity measurements on thin films of **P1** were made difficult by the need to reduce with THF solutions of  $\text{Na}^+$ -naphthalide. Less than optimal redox states and decreased film quality from the solvent exposure, resulted in  $\sigma = 1.1$  S/cm, which lower than our *in situ* determination. The maximum *in situ* conductivities of **P3** ( $\sigma_{\text{max}} = 160$  S/cm) rivals values observed of well-known p-type poly(3-alkyl thiophene)s and **P2** exhibits  $\sigma_{\text{max}} = 9$  S/cm. The *in situ* conductivity profile indicates that the ‘mixed valence’ state is conductive and that the neutral (fully reduced) material is insulating.<sup>12</sup> We investigated the reduction of **P1** thin films deposited onto ITO-coated glass electrodes by spectroelectrochemistry (Figure 1d). The absorption spectra show a decrease of the original band-gap transition and the build-up of intra-gap energy states, which matches well to negative polaron-bipolaron model for charge delocalized  $\pi$ -platforms.<sup>16</sup>

Optical absorption and photoluminescence (PL) spectra of thin films of MEH-PPV, **P1**, and a MEH-PPV/**P1** bilayer are shown in Figure 2. It is noteworthy that high quality bilayer films can be obtained by coating a water solution of **P1** on the top of a MEH-PPV thin film prepared from the chloroform solution, since MEH-

PPV neither dissolves nor swells in water. The absorption spectrum of bilayer heterojunction is a superposition of those of the two polymer layers, indicating no detectable ground state interaction at the heterojunction interface. Figure 2b shows how the characteristic PL emission spectrum of MEH-PPV ( $\lambda_{\text{em}} = 585$  nm,  $\lambda_{\text{excitation}} = 507$  nm) is strongly quenched (93%) in the bilayer structure with **P1** layer (40 nm). These results clearly indicate that the electron transfer occurs from the MEH-PPV (EA/IP = 2.9/5.1 eV)<sup>8,10</sup> to the **P1** (EA/IP = 4.0/6.6 eV). Preliminary studies on bilayer organic photovoltaic devices between **P1** and poly(3-hexyl thiophene) gave large open circuit voltages ( $V_{\text{oc}} = 1.2$  V) but low short circuit currents ( $7 \mu\text{A}/\text{cm}^2$ ). Field effect transistor devices of **P1** were investigated in air and n-type behaviors with mobilities of  $0.24 \text{ cm}^2/\text{Vs}$  at gate voltages of 5-15V and  $3.4 \text{ cm}^2/\text{Vs}$  for gate voltages of 15-20V were observed (Figure S10). Significant experimentation is needed to understand the role of counterions in these applications.

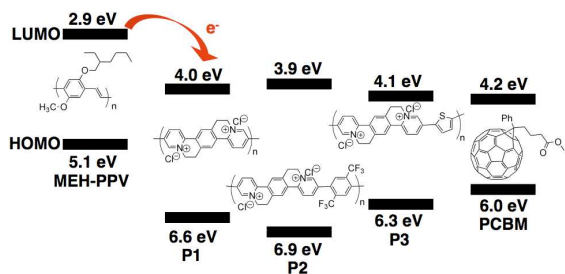
In conclusion, we report a promising class of water and/or methanol soluble electron-accepting (n-type) conjugated polymers. These materials display high EAs, reversible redox behavior, high conductivities, good electron mobilities, and efficient quenching of acceptor polymers.

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**Supporting Information Available:** Experimental details and characterization of the products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Abstract: Poly(pyridinium phenylene) conjugated polymers are synthesized by a cross-coupling and cyclization sequence. These polyelectrolytes are freely soluble in water and display high degrees of electroactivity. When reduced (n-doped) these materials display *in situ* conductivities as high as 160 S/cm. The high conductivity is attributed to the planar structure that is enforced by the cyclic structures of the polymer. The electron affinities are compared to PCBM, a C<sub>60</sub> based n-type material. We find that these polymers undergo excited state electron transfer reactions with other donor conjugated polymers and hence may find utility in photovoltaic devices.

## Poly(Pyridinium Phenylene)s: Water Soluble N-Type Polymers

Daisuke Izuhara and Timothy M. Swager\*

Department of Chemistry, Massachusetts Institute of Technology,  
77 Massachusetts Avenue, Cambridge, Massachusetts 02139

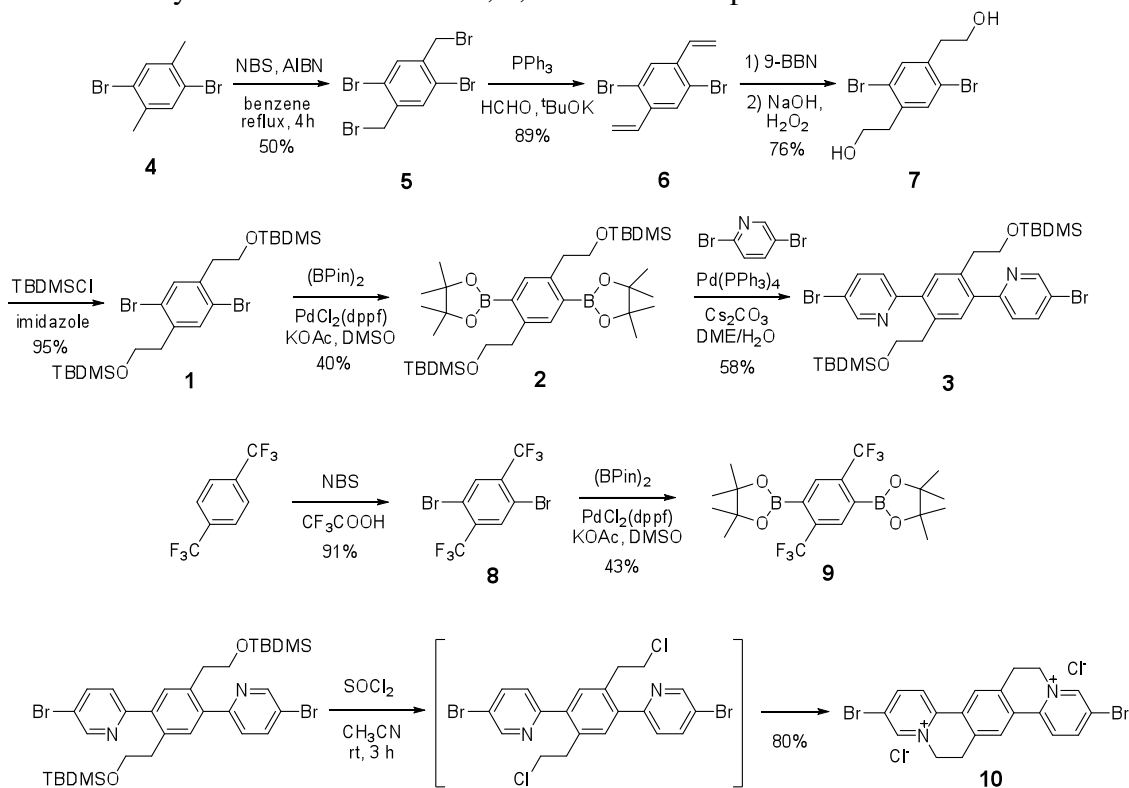
[tswager@mit.edu](mailto:tswager@mit.edu)

**General:** All air and water sensitive synthetic manipulations were performed under an argon atmosphere using standard Schlenk techniques. 1,4-Dibromo-2,5-bis(bromomethyl)benzene (**5** in Scheme S1),<sup>1</sup> 1,4-Dibromo-2,5-divinylbenzene (**6**),<sup>1</sup> and 1,4-dibromo-2,5-bis(trifluoromethyl)benzene (**8**),<sup>2</sup> and 2,5-bis(trimethylstannyl)thiophene<sup>3</sup> were prepared according to literature methods. Anhydrous dichloromethane, acetonitrile, and tetrahydrofuran were obtained using a solvent purification system (Innovative Technologies). All other chemicals were of reagent grade and used as received. Column chromatography was performed using ultra pure silica gel (SILIYCYCLE, 40~63  $\mu\text{m}$ ). NMR spectra were obtained on a Varian Mercury-300 spectrometer, and all chemical shifts are referenced to residual  $\text{CHCl}_3$ . High-resolution mass spectra were obtained at the MIT Department of Chemistry Instrumentation Facility (DCIF) on a Bruker Daltonics APEX II3 Tesla FT-ICR-MS. Polymer molecular weights and polydispersity indexes were estimated by gel permeation chromatography (GPC) using a HP series 1100 GPC system. Polystyrene standards were used for calibration, and tetrahydrofuran (THF) was used as the eluent at a flow rate of 1.0 mL/min. Fluorescence spectra were measured on a SPEX Fluorolog- $\tau$ 3 fluorimeter (model FL-321, 450 W Xenon lamp), the excitation wavelength used to obtain the fluorescence spectra corresponded to the absorption maxima in each case. Ultraviolet-visible absorption spectra were measured with an Agilent 8453 diode array spectrophotometer and corrected for background signal.

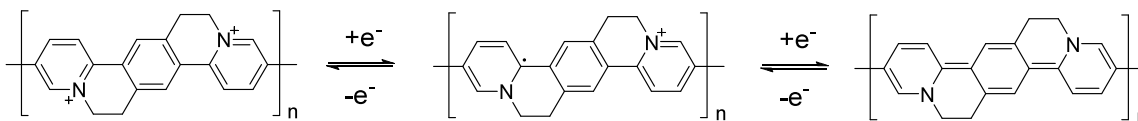
All electrochemical measurements were made with an AUTOLAB PGSTAT 20 potentiostat (Eco Chemie) using a quasi-internal Ag wire reference electrode (BioAnalytical Systems) submersed in 0.01 M  $\text{AgNO}_3$ /0.1 M  $n\text{-Bu}_4\text{NPF}_6$  in anhydrous MeCN. Typical CVs were recorded using platinum button electrodes or indium tin oxide (ITO) coated glass electrodes as the working electrode and a platinum coil counter electrode. The ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) redox couple was used as an external reference. Spectroelectrochemistry was performed under ambient laboratory conditions on polymer films cast onto ITO coated glass electrodes. The films were placed in a quartz cuvette in the path of the light source along with counter and reference electrodes as used above. In-situ conductivity measurements were carried out by using 5  $\mu\text{m}$  interdigitated microelectrodes as working electrodes. Films were cast on interdigitated microelectrodes for conductivity studies by applying a cyclic potential. *In situ* conductivity measurements were carried out at a scan rate of 5 mV/s with a 40 mV offset potential between the two

working electrodes. Film thickness was determined with a Veeco Dektak 6M STYLUS PROFILER. The conductivity ( $\sigma$ ) was then calculated by the equation  $\sigma = (i_D/V_D)(D/nTL)$ , where  $i_D$  is the drain current,  $V_D$  is the offset potential, and  $T$  is the polymer thickness; with a 5  $\mu\text{m}$  gap,  $D$ ;  $n = 99$  gaps; and 0.5 cm electrode length,  $L$ . The conductivity was then calculated from the value of the drain current by applying geometrical factors and also corrected with a known material, poly(3-octylthiophene) (230 S/cm).

**Scheme S1.** Syntheses of monomers **3**, **9**, and model compound **10**.



**Scheme S2.** Redox behaviors of **P1**.



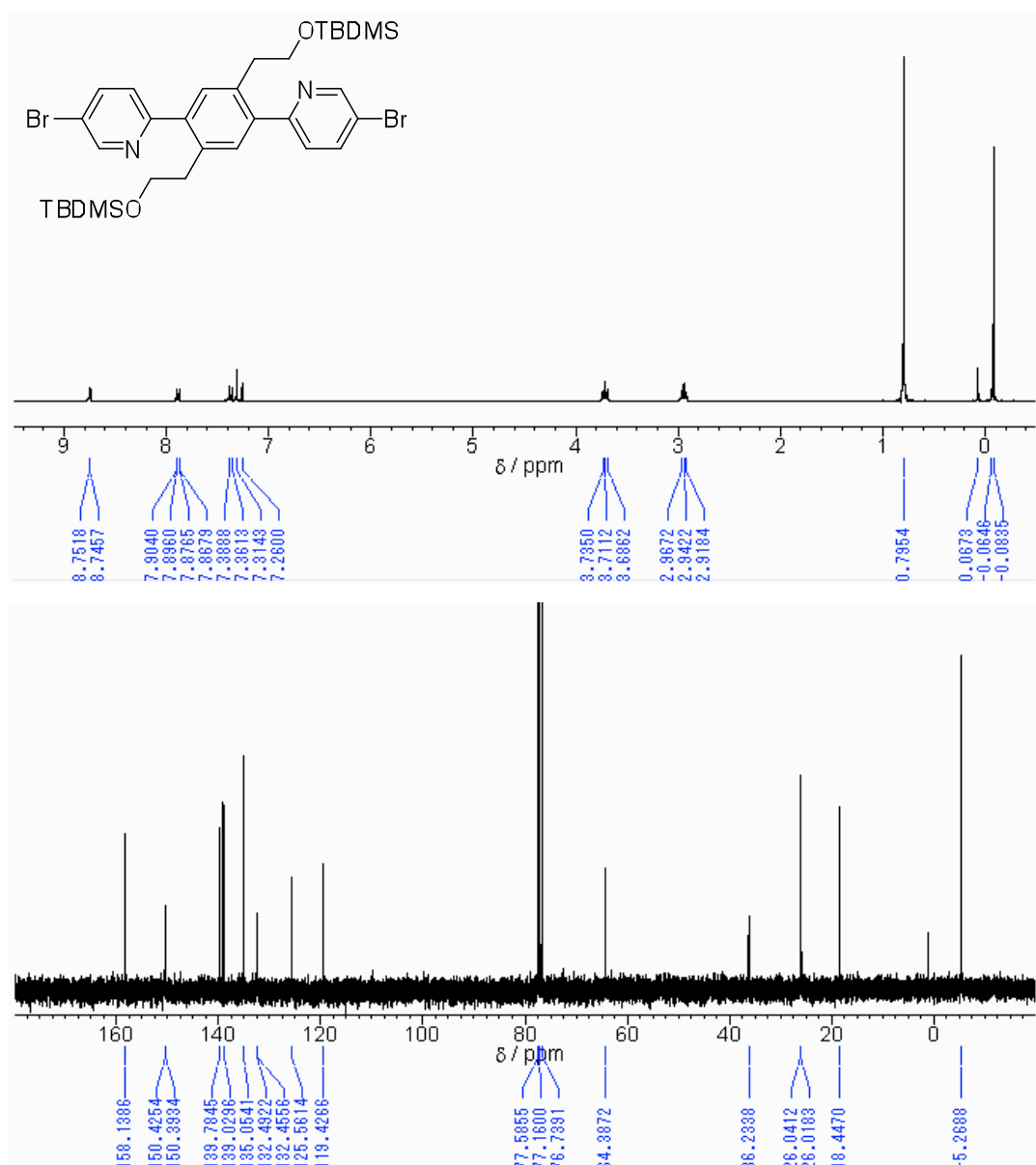
**2,2'-(2,5-dibromo-1,4-phenylene)diethanol (7):** 9-BBN (0.5 M in THF, 145 mL, 72.5 mmol) was added dropwise over 30 min to a stirred and cooled (0 °C) solution of 1,4-dibromo-2,5-divinylbenzene (8.68 g, 30.1 mmol) in THF (125 mL). The ice bath was removed, and stirring was continued for 10 h. The mixture was cooled to 0 °C and quenched by dropwise addition of MeOH (50 mL). Aqueous NaOH (2 M, 250 mL) and 30% H<sub>2</sub>O<sub>2</sub> (50 mL) were poured into the stirred mixture. Stirring was continued for 2 h, and the mixture was extracted with Et<sub>2</sub>O. The combined organic extracts were washed with brine, dried (Na<sub>2</sub>SO<sub>4</sub>), and the solvent was evaporated. The crude product was purified through column chromatography (silica gel, hexane/EtOAc=3/1) to give compound **7** as a white solid (7.66 g, 76%). M.p. 135-136°C. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>): δ 2.80 (t, *J* = 6.8 Hz, 4H), 3.58 (q, *J* = 6.8 Hz, 4H), 4.77 (t, *J* = 5.3 Hz, 2H), 7.55 (s, 2H). <sup>13</sup>C NMR (75 MHz, DMSO-d<sub>6</sub>): δ 38.2, 60.0, 122.8, 134.6, 138.5. HR-MS (ESI): calcd for C<sub>10</sub>H<sub>12</sub>Br<sub>2</sub>O<sub>2</sub> 344.9096 [M+Na]<sup>+</sup>; found 344.9094.

**(2,2'-(2,5-dibromo-1,4-phenylene)bis(ethane-2,1-diyl))bis(oxy)bis(*tert*-butyldimethylsilane) (1):** Compound **7** (4.22 g, 13 mmol) was dissolved in 12 mL of DMF and treated with imidazole (3.54 g, 52 mmol, 4.0 equiv.) and TBDMSCl (4.7 g, 31.2 mmol, 2.4 equiv) at 0 °C. The reaction solution was warmed to rt and stirred for 24 h and then diluted with CH<sub>2</sub>Cl<sub>2</sub>. This mixture was washed with water and brine. The organic phase was dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated in vacuo to give compound **1** as a white solid (6.82 g, 95%). M.p. 50-51°C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ -0.03 (s, 12H), 0.87 (s, 18H), 2.89 (t, *J* = 6.8 Hz, 4H), 3.79 (t, *J* = 6.8 Hz, 4H), 7.43 (s, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ -5.3, 18.4, 26.0, 38.9, 62.2, 123.1, 135.3, 138.3. HR-MS (ESI): calcd for C<sub>22</sub>H<sub>40</sub>Br<sub>2</sub>O<sub>2</sub>Si<sub>2</sub> 573.0826 [M+Na]<sup>+</sup>; found 573.0835.

**(2,2'-(2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-phenylene)bis(ethane-2,1-diyl))bis(oxy)bis(*tert*-butyldimethylsilane) (2):** Compound **1** (2.21 g, 4.0 mmol), pinacoldiboron ester (3.05 g, 12 mmol), KOAc (2.36 g, 24 mmol), and PdCl<sub>2</sub>(dppf) (196 mg, 0.24 mmol) were dissolved in DMSO (40 mL) under argon atmosphere. The mixture was heated at 80 °C for 24 h, cooled and then diluted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed with water and brine, and then dried (Na<sub>2</sub>SO<sub>4</sub>), and the solvent was evaporated. The crude product was purified through column chromatography (silica gel, hexane/EtOAc=8/1). Recrystallization from hexane gave compound **2** as a white solid (1.03 g, 40%). M.p. 133-134°C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ -0.02 (s, 12H), 0.87 (s, 18H), 1.33 (s, 24H), 3.08 (t, *J* = 7.5 Hz, 4H), 3.73 (t, *J* = 7.5 Hz, 4H), 7.62 (s, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ -5.1, 18.5, 25.0, 26.2, 38.9, 65.7, 83.6, 137.9, 138.1, 142.1. HR-MS (ESI): calcd for C<sub>34</sub>H<sub>64</sub>B<sub>2</sub>O<sub>6</sub>Si<sub>2</sub> 669.4346 [M+Na]<sup>+</sup>; found 669.4351.

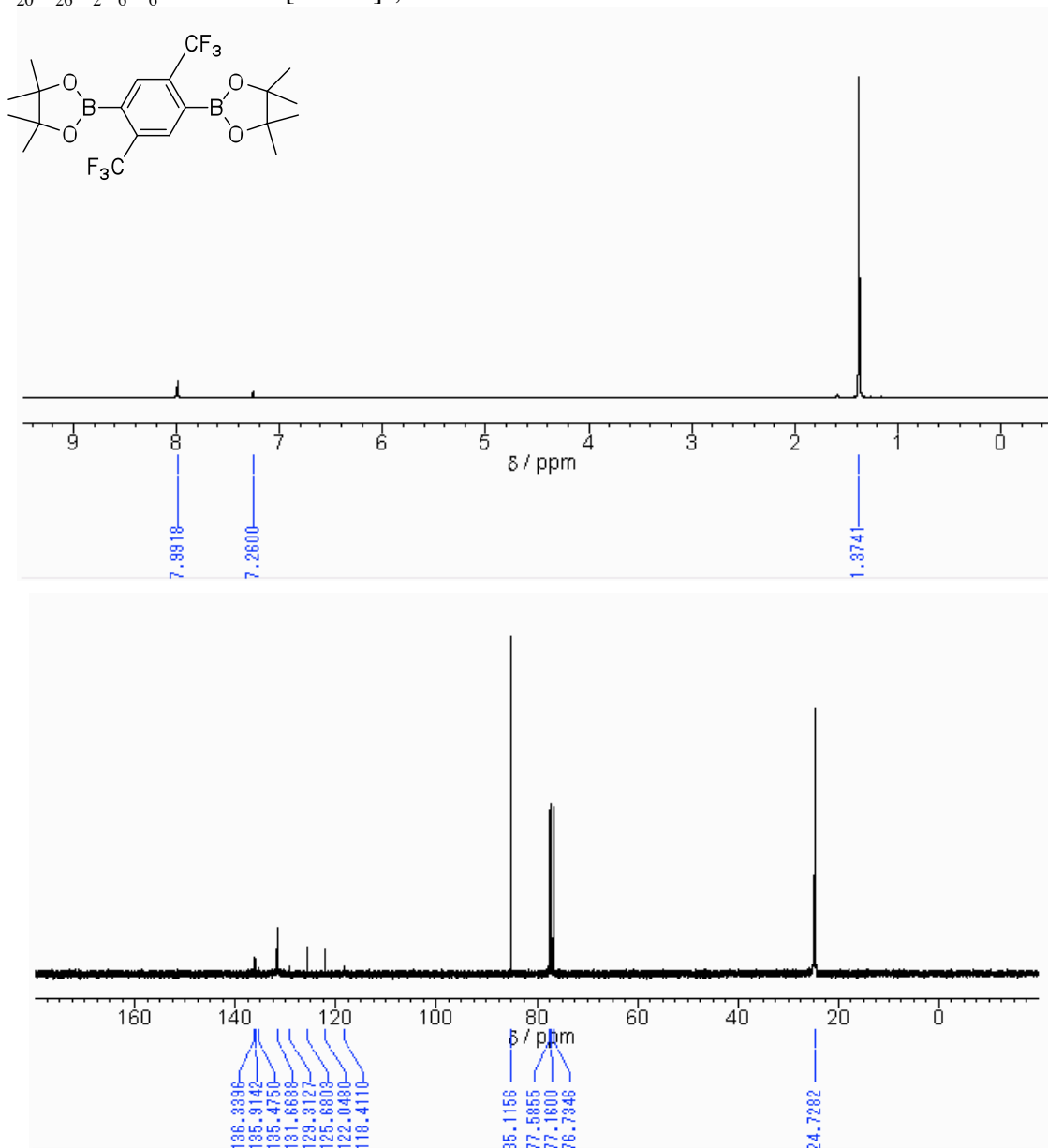


**6,6'-(2,5-bis(2-(*tert*-butyldimethylsilyloxy)ethyl)-1,4-phenylene)bis(3-bromopyridine) (3):** Compound **2** (517 mg, 0.8 mmol), 2,5-dibromopyridine (758 mg, 3.2 mmol), CsCO<sub>3</sub> (1.30 g, 4.0 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (92 mg, 0.08 mmol) were dissolved in DME/H<sub>2</sub>O (8/4 mL) under argon atmosphere. The mixture was heated at 100 °C for 24 h, cooled and then diluted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed with water and brine, and then dried (Na<sub>2</sub>SO<sub>4</sub>), and the solvent was evaporated. Recrystallization from DME gave compound **3** as a white solid (328 mg, 58%). M.p. 140-142°C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ -0.08 (s, 12H), 0.80 (s, 18H), 2.94 (t, *J* = 7.5 Hz, 4H), 3.71 (t, *J* = 7.5 Hz, 4H), 7.31 (s, 2H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.89 (dd, *J* = 8.3 Hz, *J* = 2.5 Hz, 2H), 8.75 (d, *J* = 1.8 Hz, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ -5.3, 18.4, 26.0, 26.1, 36.2, 64.4, 119.4, 125.6, 132.5, 135.1, 139.0, 139.8, 150.4, 158.1. HR-MS (ESI): calcd for C<sub>32</sub>H<sub>46</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>Si<sub>2</sub> 705.1537 [M+H]<sup>+</sup>; found 705.1505.



**Figure S1.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of monomer **3** in CDCl<sub>3</sub>.

**2,2'-(2,5-bis(trifluoromethyl)-1,4-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (9):** 1,4-dibromo-2,5-bis(trifluoromethyl)benzene **8** (2.23 g, 6.0 mmol), pinacoldiboron ester (4.57 g, 18 mmol), KOAc (3.53 g, 36 mmol), and PdCl<sub>2</sub>(dppf) (490 mg, 0.6 mmol) were dissolved in DMSO (40 mL) under argon atmosphere. The mixture was heated at 80 °C for 24 h, cooled and then diluted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed with water and brine, and then dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated. The crude product was purified through column chromatography (silica gel, hexane/EtOAc=8/1). Recrystallization from hexane gave compound **9** as a white solid (1.20 g, 43%). M.p. 211-212°C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 1.37 (s, 24H), 7.99 (s, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 24.7, 85.1, 123.9, 131.6, 131.7, 136.1. HR-MS (ESI): calcd for C<sub>20</sub>H<sub>26</sub>B<sub>2</sub>F<sub>6</sub>O<sub>6</sub> 489.1835 [M+Na]<sup>+</sup>; found 489.1827.

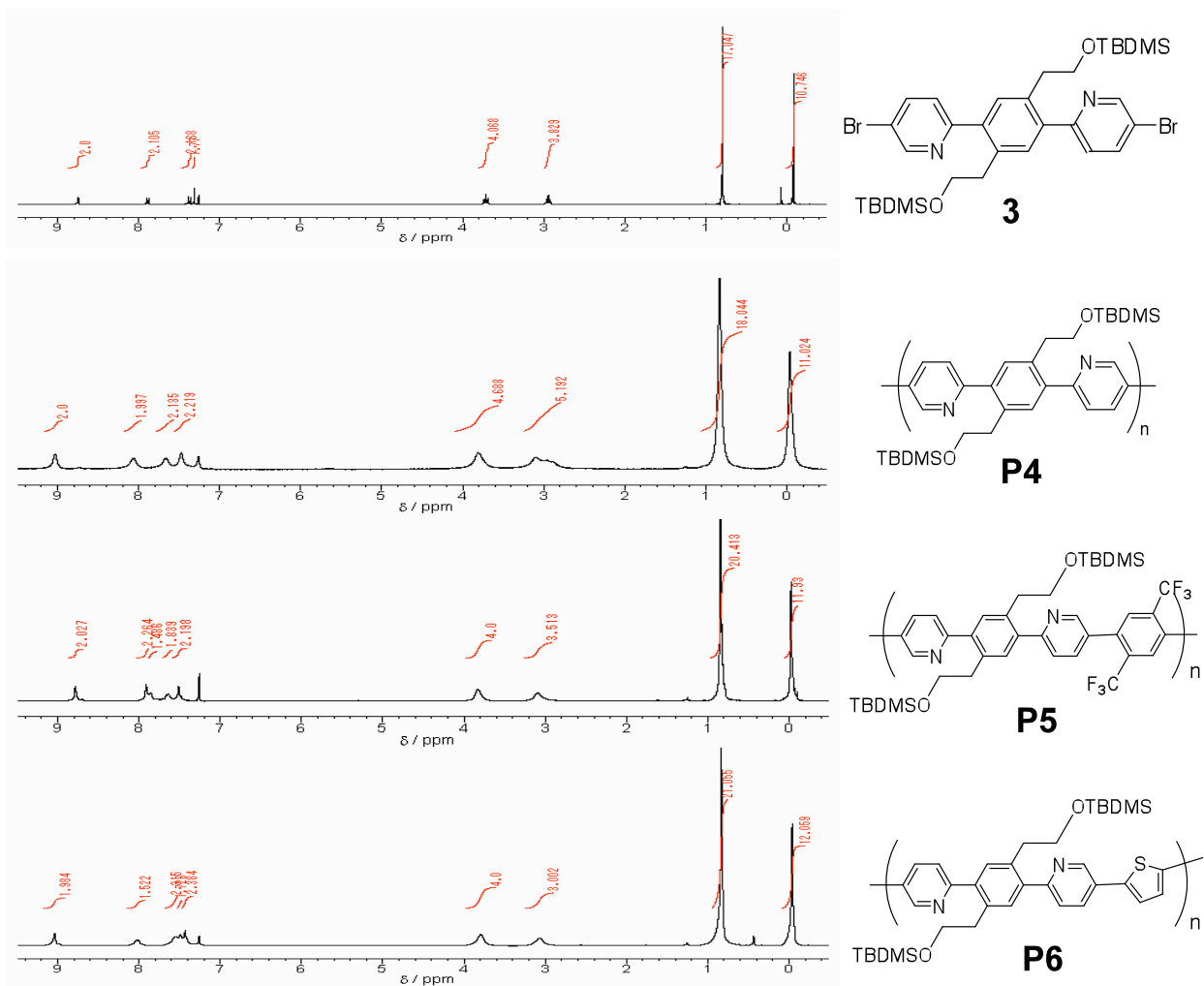


**Figure S2.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of monomer **9** in CDCl<sub>3</sub>.

**Siloxyethyl-substituted poly(pyridine phenylene) P4:** A solution of **3** (49 mg, 0.07 mmol), bis(1,5-cyclooctadiene)nickel (0) (23 mg, 0.084 mmol), 1,5-cyclooctadiene (10  $\mu$ L, 0.084 mmol), and 2,2'-bipyridine (13 mg, 0.084 mmol) in 2 mL of anhydrous DMSO was stirred for 24 h at 60 °C under argon. The reaction mixture was cooled to room temperature, and precipitated into methanol. The precipitate was collected by centrifugation, dried, dissolved in chloroform, and then re-precipitated from methanol. The resulting pale yellow precipitate was collected by centrifugation and dried (65% yield).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  -0.04 (s, 12H), 0.83 (s, 18H), 3.10 (br, 4H), 3.81 (br, 4H), 7.47 (br, 2H), 7.66 (br, 2H), 8.07 (br, 2H), 9.03 (br, 2H).

**Siloxyethyl-substituted poly(pyridine phenylene) copolymer P5:** A solution of **3** (28 mg, 0.04 mmol), **9** (19 mg, 0.04 mmol),  $\text{Pd(PPh}_3)_4$  (2.3 mg, 0.002 mmol), and  $\text{Cs}_2\text{CO}_3$  (65 mg, 0.2 mmol) in 2/1 mL of DME and water was stirred for 24 h at 100 °C under argon. The reaction mixture was cooled to room temperature, and precipitated into methanol. The precipitate was collected by centrifugation, dried, dissolved in chloroform, and then re-precipitated from methanol. The resulting pale yellow precipitate was collected by centrifugation and dried (92% yield).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  -0.02 (s, 12H), 0.84 (s, 18H), 3.10 (br, 4H), 3.83 (br, 4H), 7.51 (s, 2H), 7.65 (br, 2H), 7.85 (br, 2H), 7.91 (s, 2H), 8.78 (s, 2H).

**Siloxyethyl-substituted poly(pyridine phenylene) copolymer P6:** A solution of **3** (28 mg, 0.04 mmol), 2,5-bis(trimethylstannyl) thiophene (16 mg, 0.04 mmol), and  $\text{Pd(PPh}_3)_4$  (2.3 mg, 0.002 mmol) in 2 mL of DMSO was stirred for 24 h at 90 °C under argon. The reaction mixture was cooled to room temperature, and precipitated into methanol. The precipitate was collected by centrifugation, dried, dissolved in chloroform, and then re-precipitated from methanol. The resulting yellow precipitate was collected by centrifugation and dried (95% yield).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  -0.04 (s, 12H), 0.83 (s, 18H), 3.07 (br, 4H), 3.79 (br, 4H), 7.43 (s, 2H), 7.49 (br, 2H), 7.54 (br, 2H), 8.03 (br, 2H), 9.04 (s, 2H).



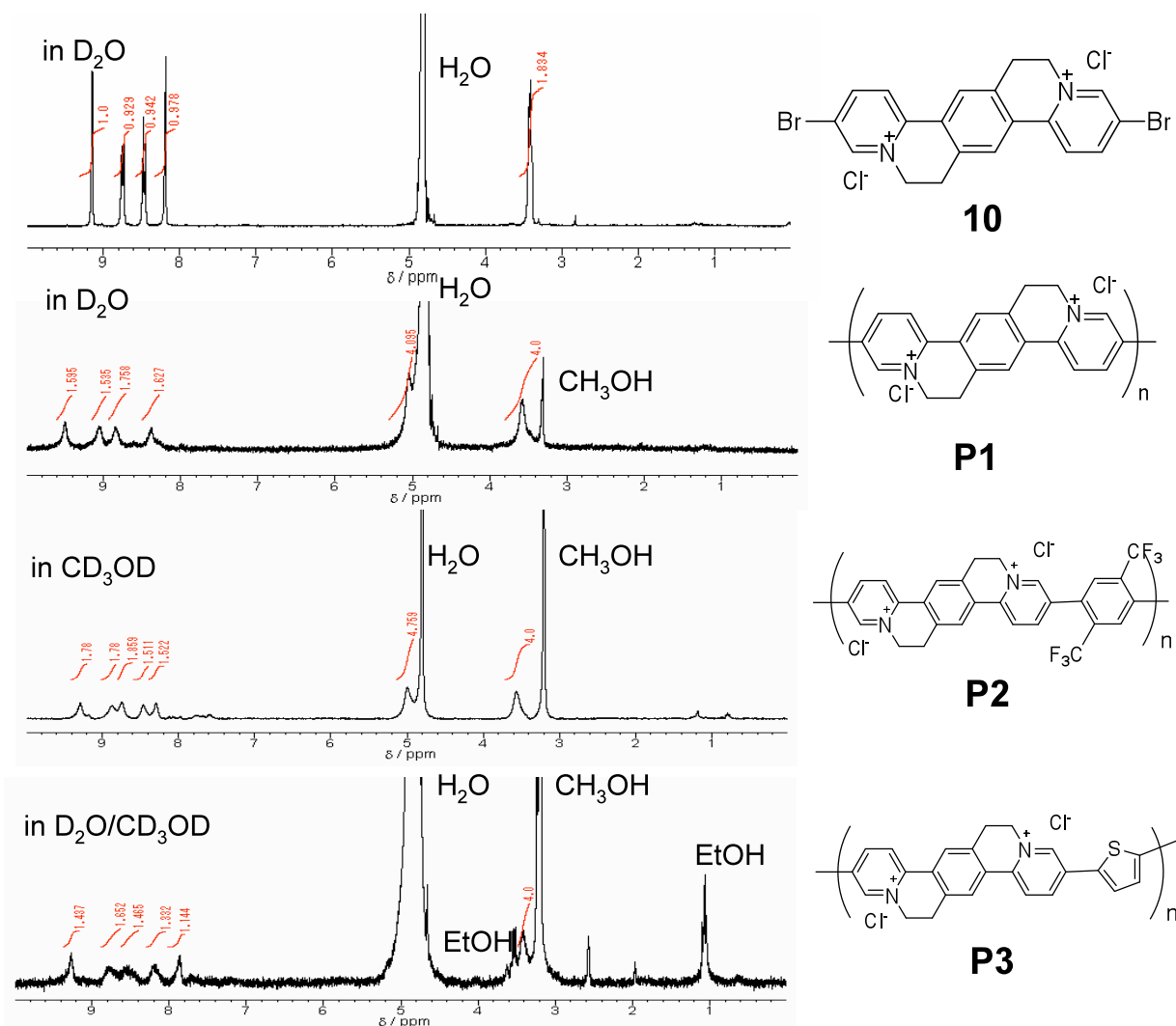
**Figure S3.**  $^1\text{H}$  NMR spectra of monomer **3** and polymers **P4-6** in  $\text{CDCl}_3$ .

**Cyclization of 3 by the reaction with thionyl chloride:** To a solution of **3** (20 mg, 0.028 mmol) in 3 mL of acetonitrile,  $\text{SOCl}_2$  (0.6 mL) was added and the mixture was stirred at room temperature for 3 hours. The resulting solution was evaporated. Recrystallization from methanol and water gave model compound **10** as a pale yellow solid (80%).  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  3.41 (t,  $J$  = 6.6 Hz, 4H), 4.85 (t, 4H), 8.18 (s, 2H), 8.45 (d,  $J$  = 8.8 Hz, 2H), 8.74 (d,  $J$  = 8.9 Hz, 2H), 9.14 (s, 2H). HR-MS (ESI): calcd for  $\text{C}_{20}\text{H}_{16}\text{Br}_2\text{Cl}_2\text{N}_2$  220.9835  $[\text{M}-2\text{Cl}]^{2+}$ ; found 220.9838.

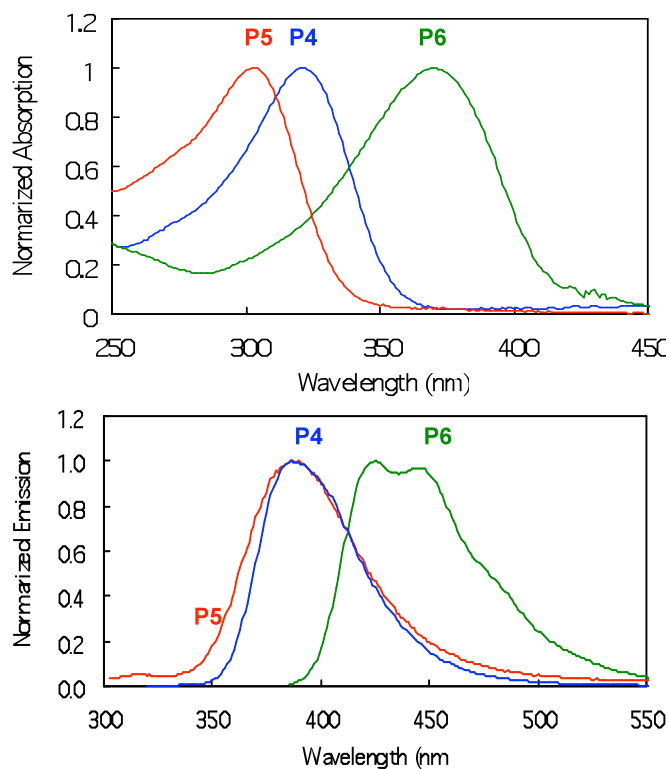
**Ethylene-bridged poly(pyridinium phenylene) P1:** To a solution of **P4** (24 mg, 0.044 mmol) in 5 mL of acetonitrile,  $\text{SOCl}_2$  (1.0 mL) was added and the mixture was stirred at room temperature for 24 hours. The solution was evaporated, and then the resulting solid was washed with methanol and DMF to give polymer **P1** as a yellow solid (98%).  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  3.57 (br, 4H), 5.04 (br, 4H), 8.37 (br, 2H), 8.84 (br, 2H), 9.06 (br, 2H), 9.50 (br, 2H).

**Phenylene-linked poly(pyridinium phenylene) copolymer P2:** To a solution of **P5** (24 mg, 0.031 mmol) in 5 mL of acetonitrile,  $\text{SOCl}_2$  (1.0 mL) was added and the mixture was stirred at room temperature for 24 hours. The solution was evaporated, and then the resulting solid was dissolved in methanol, and then re-precipitated and washed with hexane/ethanol to give polymer **P2** as a yellow solid (85%).  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  3.56 (br, 4H), 4.99 (br, 4H), 8.29 (br, 2H), 8.46 (br, 2H), 8.74 (br, 2H), 8.87 (br, 2H), 9.29 (br, 2H).

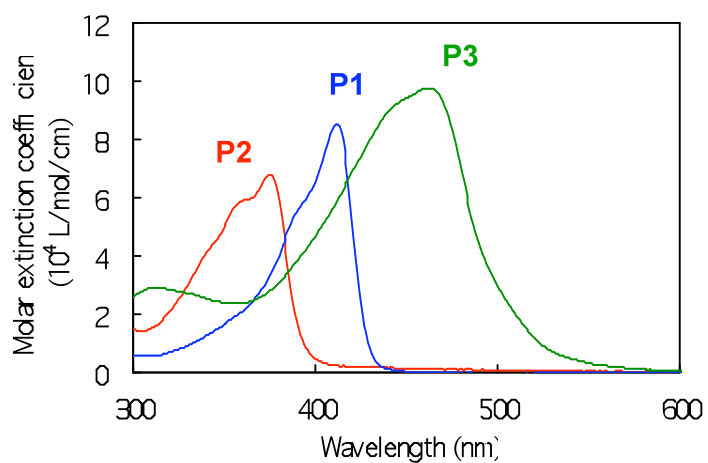
**Thiophene-linked poly(pyridinium phenylene) copolymer P3:** To a solution of **P6** (24 mg, 0.038 mmol) in 5 mL of acetonitrile,  $\text{SOCl}_2$  (1.0 mL) was added and the mixture was stirred at room temperature for 24 hours. The solution was evaporated, and then the resulting solid was dissolved in methanol, and then re-precipitated and washed with hexane/ethanol to give polymer **P3** as a red solid (99%).  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{OD}/\text{D}_2\text{O}$ ):  $\delta$  3.42 (br, 4H), 7.86 (br, 2H), 8.19 (br, 2H), 8.52 (br, 2H), 8.78 (br, 2H), 9.26 (br, 2H).



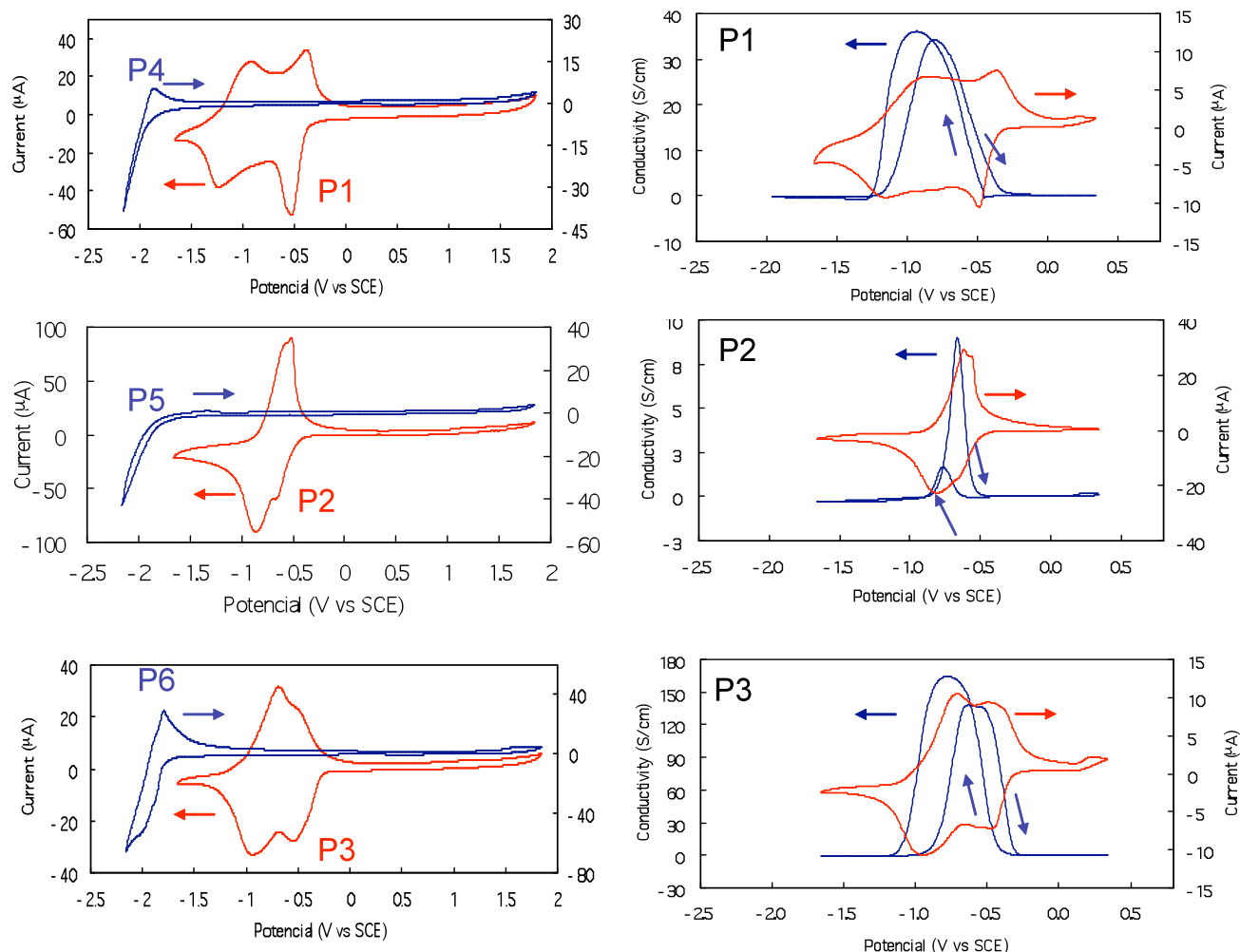
**Figure S4.**  $^1\text{H}$  NMR spectra of compound **10** and polymers **P1-3** in  $\text{D}_2\text{O}$  or  $\text{CD}_3\text{OD}$ .



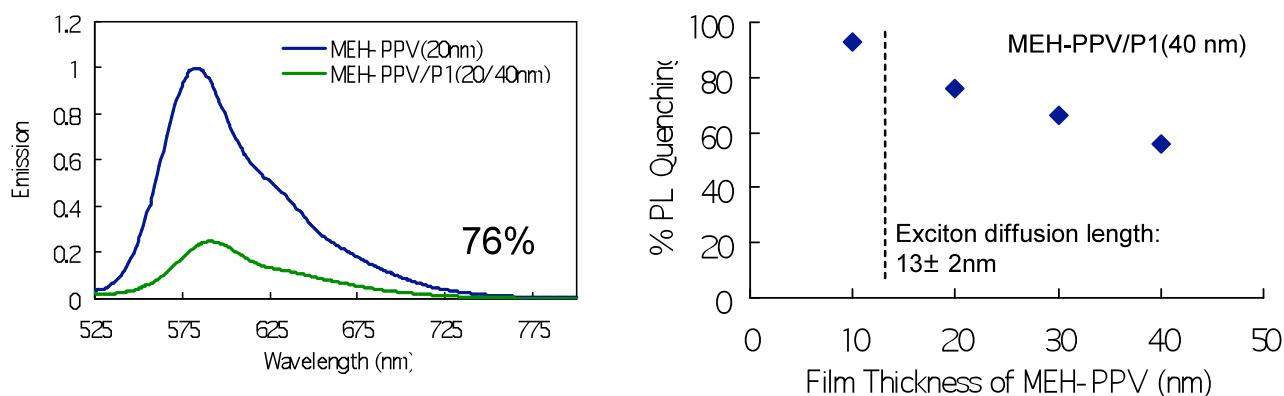
**Figure S5.** UV-vis absorption and PL emission spectra of **P4-6** in THF.



**Figure S6.** UV-Vis absorption spectra (axis molar extinction coefficients per repeating unit) of **P1-3** in water or methanol solutions.

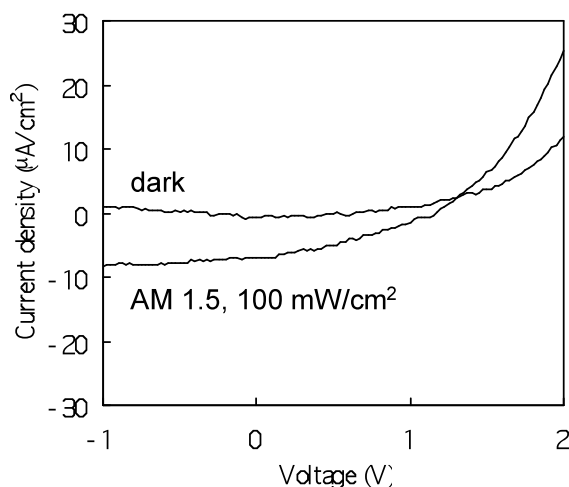


**Figure S7.** Cyclic voltammogram (left) and in-situ conductivity measurement (right) of **P1-6** thin films.



**Figure S8.** PL emission spectra ( $\lambda_{\text{ex}} = 507 \text{ nm}$ ) (left) single layer MEH-PPV and bilayer MEH-PPV/**P1** thin films, and film thickness dependence (right) of PL quenching.

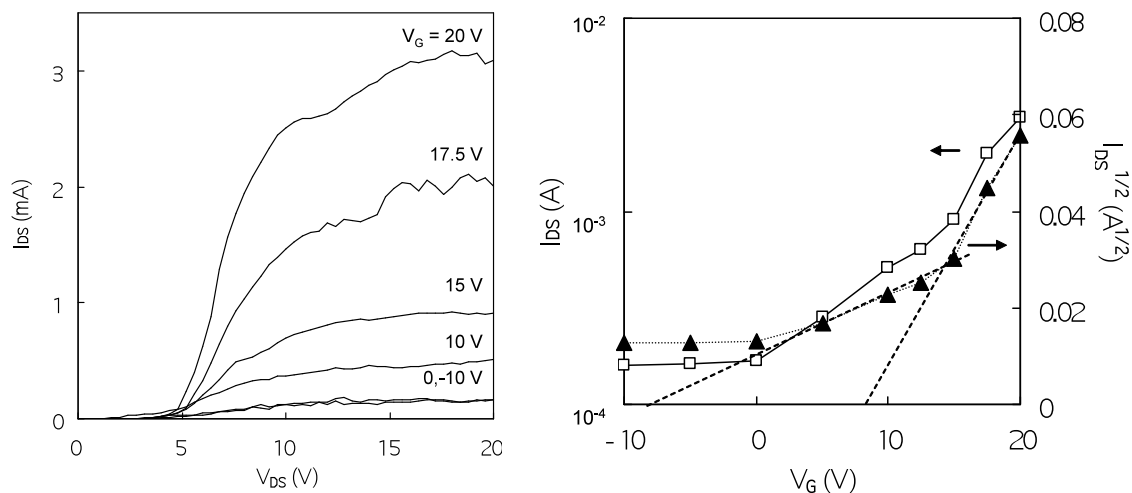
**Fabrication and characterization of polymer solar cells:** The bilayer heterojunction solar cells were fabricated with a structure of ITO/PEDOT:PSS/P3HT(50 nm)/**P1**(50 nm)/Al. The ITO glass was pre-cleaned and modified by a thin layer of PEDOT:PSS (Bayer) which was spin-coated from a PEDOT:PSS aqueous solution on the ITO substrate. P3HT thin films were spin coated from a chloroform solution. On top of the resulting P3HT thin film a layer of **P1** was spin coated from 2,2,2-trifluoroethanol solution, followed by drying at 80 °C for 30 min. Then the metal cathode Al (65 nm) was deposited on the polymer layer by vacuum evaporation. The effective area of one cell was 1 mm<sup>2</sup>. Under the illumination of an AM 1.5 solar simulator (100 mW/cm<sup>2</sup>), the bilayer heterojunction device exhibits an open circuit voltage (V<sub>oc</sub>) of 1.2 V, a short-circuit current density (J<sub>sc</sub>) of 7 μA/cm<sup>2</sup>, and a fill factor (FF) of 0.32. The power conversion efficiency (PCE) is 0.003%.



**Figure S9.** Current–voltage characteristics of a device with the structure ITO/PEDOT:PSS/P3HT(50 nm)/**P1**(50 nm)/Al in the dark and under the illumination of an AM 1.5 solar simulator, 100 mW/cm<sup>2</sup>.

**Fabrication and characterization of field effect transistors:** Field effect transistors were fabricated in the bottom gate, bottom contact configuration on heavily n-doped silicon substrates as the gate and a thermally grown 230 nm SiO<sub>2</sub> as the dielectric insulator (Fraunhofer). The source and drain electrodes were patterned on the SiO<sub>2</sub> by lift-off technique of 10 nm of ITO and 30 nm of gold. The channel lengths (L) were 2.5, 5, 10, and 20 μm, and the channel width (W) was 10 mm. Prior to polymer deposition, the surface of the devices were treated with UV/ozone irradiation for 10 min and subsequently 1,1,1,3,3,3-hexamethyldisilazane (HMDS) vapor. The devices were then cleaned with acetone and isopropanol. The polymer films were deposited by spin-coating 6 mg/mL 2,2,2-trifluoroethanol solution of **P1**. The mobility (μ) was extracted from the saturation regime at V<sub>DS</sub> = 20 V using the slope of the line drawn through the linear part of an I<sub>DS</sub><sup>1/2</sup> vs V<sub>G</sub> plot, where V<sub>G</sub>, V<sub>DS</sub> and I<sub>DS</sub> are the gate voltage, drain-source voltage and current, respectively, from the equation I<sub>DS</sub> = (W/2L)μC<sub>i</sub>(V<sub>G</sub> - V<sub>T</sub>)<sup>2</sup>. Electron field-effect mobility of 3.4 cm<sup>2</sup>/Vs was extracted in the saturation region (V<sub>G</sub> = 15–20 V), with a low threshold voltage of ca. 8.4 V and a current on/off ratio 20.





**Figure S10.** Current-voltage characteristics ( $I_{DS}$  vs  $V_{DS}$ ) at several values of the gate voltage ( $V_G$ ) (left) and  $(I_{DS})^{1/2}$  vs  $V_G$  plots at  $V_{DS}$  of 20 V (right) for a bottom contact device with  $W = 10$  mm,  $L = 10$   $\mu$ m, and 100 nm of **P1**.

#### References for the Supporting Information.

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