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

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Poly(Pyrindium Phenylene): Water Soluble N-Type Polymers

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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, light emitting diodes, and field-effect transistors. Although many varieties of high performance p-type polymers are available, stable processable n-type polymers remain largely elusive. Few studies have been reported concerning heterojunctions between p/n-type polymers for photovoltaic cells, 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-C₆₁-butryric-acid-methyl-ester (PCBM, EA = 4.2 eV). 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. However, development of nitrogen-containing polycyclic systems with high electron affinities and solubility in common solvents has met limited success.

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 π-electron delocalization. We further demonstrate electron transfer quenching in bilayer donor/accepter polymers heterojunctions with the well-known p-type material, poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene-vinylene) (MEH-PPV).

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 is able to display reversible viologen-like redox behavior. The boronation of 2,5-bis(2-(tert-butyldimethylsilyloxy)ethyl)-1,4-benzenediiodobromide (I) gives the corresponding diboron 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 siloxyl-substituted poly(pyridine phenylene), P₄, P₅, and P₆, in 65-95% yield. All the precursor polymers were soluble in common organic solvents (e.g. CHCl₃, THF) and thionyl chloride induced quaternization cyclization gave polyelectrolytes P₁, P₂, and P₃.

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. 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 Eₘ (2.16 eV) as a result of the donor-acceptor 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). Interestingly, the EA values are higher than those estimated in the same method for most conventional polycyclic systems, and are comparable to well known electron transporters PCBM (4.2 eV) or polybenzimidazobenzophenanthroline (BBL) (4.0 eV).

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

<table>
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<tr>
<th>polymer</th>
<th>λmax (nm)</th>
<th>λonset (nm)</th>
<th>Eₐ (eV)</th>
<th>Ered (V)</th>
<th>Eonset (V)</th>
<th>EA (eV)</th>
<th>IP (eV)</th>
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<tr>
<td>P₁</td>
<td>431</td>
<td>485</td>
<td>2.56</td>
<td>-0.56</td>
<td>-1.27</td>
<td>-0.40</td>
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<td>P₂</td>
<td>376</td>
<td>420</td>
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<td>-0.50</td>
<td>3.90</td>
</tr>
<tr>
<td>P₃</td>
<td>483</td>
<td>575</td>
<td>2.16</td>
<td>-0.59</td>
<td>-0.99</td>
<td>-0.26</td>
<td>4.14</td>
</tr>
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**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 (λ_{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 (σ_{max} = 36 S/cm at -0.96 V).\(^{15}\) Conductivity measurements on thin films of P1 were made difficult by the need to reduce with THF solutions of Na-naphthalide. Less than optimal redox states and maximum σ_{max} exhibited in-situ conductivity 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 (λ_{em} = 585 nm, λ_{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)\(^{12}\) 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_{OC} = 1.2 V) but low short circuit currents (7 μA/cm\(^2\)). Field effect transistor devices of P1 were investigated in air and n-type behaviors with mobilities of 0.24 cm\(^2\)/Vs at gate voltages of -15V and 3.4 cm\(^2\)/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.

**Acknowledgement.** This work was supported by the National Science Foundation DMR-0706408 and TORAY Industries. The authors thank Dr. Changsik Song and Dr. Moon-Ho Ham for technical discussions.

**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](http://pubs.acs.org).

**References**

9. (a) Michaelis, M.; Hill, E. S. J. Gen. Physiol., 1933, 16, 459. (b) See the Supporting Information.
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 \textit{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\textsubscript{60} 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.
Supporting Information for

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

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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), 1,4-Dibromo-2,5-divinylbenzene (6), and 1,4-dibromo-2,5-bis(trifluoromethyl)benzene (8), and 2,5-bis(trimethylstannyl)thiophene 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 (SILICYCLE, 40–63 μm). NMR spectra were obtained on a Varian Mercury-300 spectrometer, and all chemical shifts are referenced to residual CHCl₃. High-resolution mass spectra were obtained at the MIT Department of Chemistry Instrumentation Facility (DCIF) on a Bruker Daltronics APEX II 3 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-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 AgNO₃/0.1 M n-Bu₄NPF₆ 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/ferroconium (Fc/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 μm 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 µm 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.**

\[
\left[ \begin{array}{c}
\text{N} \\
\text{N}
\end{array} \right]_n \xrightarrow{+e^-} \left[ \begin{array}{c}
\text{N} \\
\text{N}
\end{array} \right]_n \xleftarrow{-e^-} \left[ \begin{array}{c}
\text{N} \\
\text{N}
\end{array} \right]_n
\]

*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% H₂O₂ (50 mL) were poured into the stirred mixture. Stirring was continued for 2 h, and the mixture was extracted with Et₂O. The combined organic extracts were washed with brine, dried (Na₂SO₄), 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. ¹H NMR (300 MHz, DMSO-d₆): 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). ¹³C NMR (75 MHz, DMSO-d₆): δ 38.2, 60.0, 122.8, 134.6, 138.5. HR-MS (ESI): calcld for C₇₆H₇₂Br₂O₂ 344.9094 [M+Na]⁺; found 344.9094.

*2,2'-*(2,5-dibromo-1,4-phenylene)bis(ethane-2,1-diyl))bis(oxy)bis(tert-butyl dimethylsilane) (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 CH₂Cl₂. This mixture was washed with water and brine. The organic phase was dried (Na₂SO₄), and evaporated in vacuo to give compound 1 as a white solid (6.82 g, 95%). M.p. 50-51°C. ¹H NMR (300 MHz, CDCl₃): 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). ¹³C NMR (75 MHz, CDCl₃): δ -5.3, 18.4, 26.0, 38.9, 62.2, 123.1, 135.3, 138.3. HR-MS (ESI): calcld for C₂₂H₄₀Br₂O₂Si₂ 573.0826 [M+Na]⁺; 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-butyl dimethylsilane) (2):* Compound 1 (2.21 g, 4.0 mmol), pinacoldiboron ester (3.05 g, 12 mmol), KOAc (2.36 g, 24 mmol), and PdCl₂(dpdpf) (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 CH₂Cl₂. The organic layer was washed with water and brine, and then dried (Na₂SO₄), 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. ¹H NMR (300 MHz, CDCl₃): 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). ¹³C NMR (75 MHz, CDCl₃): δ -5.1, 18.5, 25.0, 26.2, 38.9, 65.7, 83.6, 137.9, 138.1, 142.1. HR-MS (ESI): calcld for C₃₄H₄₆B₂O₆Si₂ 669.4346 [M+Na]⁺; found 669.4351.
6,6’-(2,5-bis(2-(tert-butyldimethylsilyloxy)ethyl)-1,4-phenylene)bis(3-bromo pyridine) (3): Compound 2 (517 mg, 0.8 mmol), 2,5-dibromopyridine (758 mg, 3.2 mmol), CsCO₃ (1.30 g, 4.0 mmol), and Pd(PPh₃)₄ (92 mg, 0.08 mmol) were dissolved in DME/H₂O (8/4 mL) under argon atmosphere. The mixture was heated at 100 °C for 24 h, cooled and then diluted with CH₂Cl₂. The organic layer was washed with water and brine, and then dried (Na₂SO₄), and the solvent was evaporated. Recrystallization from DME gave compound 3 as a white solid (328 mg, 58%). M.p. 140-142°C. ¹H NMR (300 MHz, CDCl₃): 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). ¹³C NMR (75 MHz, CDCl₃): 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 C₃₂H₄₆Br₂N₂O₂Si₂ 705.1537 [M+H]+; found 705.1505.

Figure S1. ¹H and ¹³C NMR spectra of monomer 3 in CDCl₃.
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 PdCl₂(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 CH₂Cl₂. The organic layer was washed with water and brine, and then dried (Na₂SO₄), 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. 

H NMR (300 MHz, CDCl₃): δ 1.37 (s, 24H), 7.99 (s, 2H). 

13C NMR (75 MHz, CDCl₃): δ 24.7, 85.1, 123.9, 131.6, 131.7, 136.1. 

HR-MS (ESI): calcd for C₂₀H₂₆B₂F₆O₆ 489.1835 [M+Na]+; found 489.1827.

Figure S2. ¹H and ¹³C NMR spectra of monomer 9 in CDCl₃.
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 µL, 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). \(^1\)H NMR (300 MHz, 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), Pd(PPh\(_3\))\(_4\) (2.3 mg, 0.002 mmol), and Cs\(_2\)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). \(^1\)H NMR (300 MHz, 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 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). \(^1\)H NMR (300 MHz, 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).
Cyclization of 3 by the reaction with thionyl chloride: To a solution of 3 (20 mg, 0.028 mmol) in 3 mL of acetonitrile, SOCl₂ (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%). ¹H NMR (300 MHz, D₂O): δ 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 C₂₀H₁₆Br₂Cl₂N₂ 220.9835 [M-2Cl]⁺; found 220.9838.

Ethylene-bridged poly(pyridinium phenylene) P1: To a solution of P4 (24 mg, 0.044 mmol) in 5 mL of acetonitrile, SOCl₂ (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%). ¹H NMR (300 MHz, D₂O): δ 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, SOCl₂ (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%). 

\[ ^1H \text{ NMR (300 MHz, CD}_3\text{OD): } \delta 3.56 \text{ (br, 4H), 4.99 (br, 4H), 8.29 (br, 2H), 8.46 (br, 2H), 8.74 (br, 2H), 8.87 (br, 2H), 9.29 (br, 2H).} \]

Thiophene-linked poly(pyridinium phenylene) copolymer P3: To a solution of P6 (24 mg, 0.038 mmol) in 5 mL of acetonitrile, SOCl₂ (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%). 

\[ ^1H \text{ NMR (300 MHz, CD}_3\text{OD/D}_2\text{O): } \delta 3.42 \text{ (br, 4H), 7.86 (br, 2H), 8.19 (br, 2H), 8.52 (br, 2H), 8.78 (br, 2H), 9.26 (br, 2H).} \]

Figure S4. 

Figure S4. 

$^1$H NMR spectra of compound 10 and polymers P1-3 in D$_2$O or CD$_3$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 ($\lambda_{ex} = 507$ 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 mm². Under the illumination of an AM 1.5 solar simulator (100 mW/cm²), the bilayer heterojunction device exhibits an open circuit voltage (Voc) of 1.2 V, a short-circuit current density (Jsc) of 7 µA/cm², and a fill factor (FF) of 0.32. The power conversion efficiency (PCE) is 0.003%.

![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/cm².](image)

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/cm².

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 SiO₂ as the dielectric insulator (Fraunhofer). The source and drain electrodes were patterned on the SiO₂ 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_DS = 20 V using the slope of the line drawn through the linear part of an I_DS vs V_G plot, where V_G, V_DS and I_DS are the gate voltage, drain-source voltage and current, respectively, from the equation I_DS = (W/2L)µC_i(V_G-V_T)^2. Electron field-effect mobility of 3.4 cm²/Vs was extracted in the saturation region (V_G =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, $L = 10$ µm, and 100 nm of P1.

References for the Supporting Information.