

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

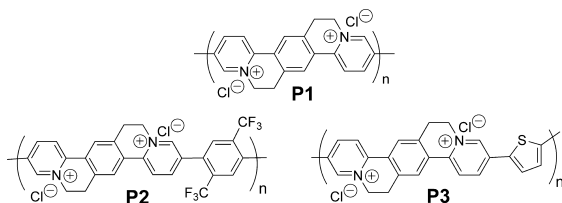
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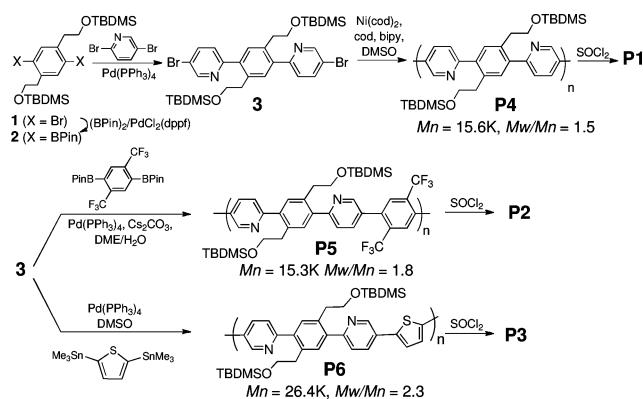
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Conjugated polymer semiconductors can be fabricated over large areas by low-cost solution processing and hence offer economic advantages in the production of photovoltaic cells,¹ light emitting diodes,² and field-effect transistors.³ Although many varieties of high performance p-type polymers are available,⁴ stable processable n-type polymers remain largely elusive.⁵ Few studies have been reported concerning heterojunctions between p/n-type polymers for photovoltaic cells,⁶ 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-butyric-acid-methyl-ester (PCBM, EA = 4.2 eV).^{1b} 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.^{5a,7} However, development of nitrogen-containing polyheterocycles with high electron affinities and solubility in common solvents has met limited success.⁸

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/acceptor polymer heterojunctions^{8,9} with the well-known p-type material, poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene-vinylene) (MEH-PPV).¹⁰



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.¹¹ 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*-butyldimethylsilyloxy)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% yield.¹² All the precursor

Scheme 1. Synthetic Routes to **P1**, **P2**, and **P3**Table 1. Optical and Electrochemical Properties of **P1**, **P2**, and **P3**

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

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

polymers were soluble in common organic solvents (e.g., CHCl₃, THF), and thionyl chloride induced quaternization gave polyelectrolytes **P1**, **P2**, and **P3**.¹³ The polyelectrolytes are only soluble in highly polar solvents, such as water and methanol, and this feature allows for the facile formation of multilayer 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.¹² 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–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).^{12,14} Interestingly, the EA values are higher than those estimated in the same method for most conventional polyheterocycles^{7a} and are comparable to well-known electron transporter PCBM (4.2 eV)^{1b} or polybenzimidazobenzophenanthroline (BBL) (4.0 eV).⁸ 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).¹⁵ Conductivity measurements on thin films of **P1** were made difficult by the need

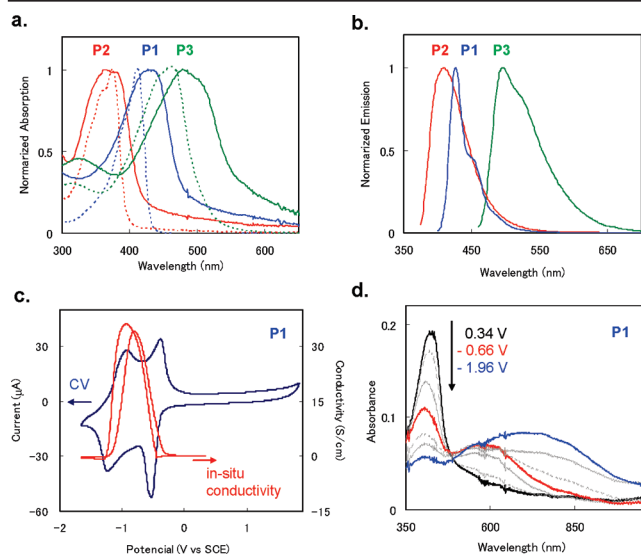


Figure 1. (a) UV-vis absorption spectra of **P1–3**; thin films (continuous line), water or methanol solutions (dashed line). (b) PL emission spectra of **P1–3** in water or methanol solutions. (c) Cyclic voltammogram, *in situ* conductivity measurement. (d) Spectroelectrochemistry of **P1** thin film.

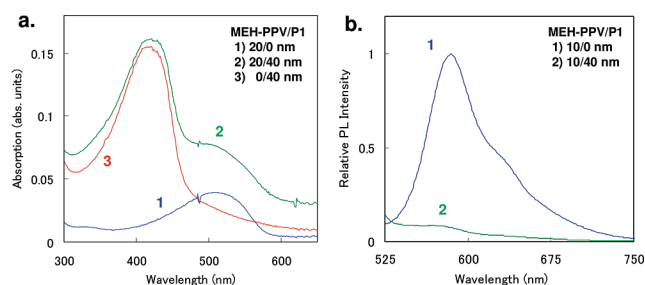


Figure 2. (a) UV-vis absorption and (b) PL emission spectra ($\lambda_{\text{ex}} = 507$ nm) of thin films of MEH-PPV, **P1**, and a bilayer of MEH-PPV/**P1**.

to reduce with THF solutions of Na^+ -naphthalide. Less than optimal redox states and decreased film quality from the solvent exposure resulted in $\sigma = 1.1$ S/cm, which is 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.¹² 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 buildup of intragap energy states, which matches well to the negative polaron–bipolaron model for charge delocalized π -platforms.¹⁶

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 an 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 charac-

teristic PL emission spectrum of MEH-PPV ($\lambda_{\text{em}} = 585$ nm, $\lambda_{\text{ex}} = 507$ nm) is strongly quenched (93%) in the bilayer structure with the **P1** layer (40 nm). These results clearly indicate that the electron transfer occurs from the MEH-PPV (EA/IP = 2.9/5.1 eV)^{8,10} 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 $0.24 \text{ cm}^2/(\text{V s})$ at gate voltages of 5–15 V and $3.4 \text{ cm}^2/(\text{V s})$ for gate voltages of 15–20 V 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 donor 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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