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Citation: Izuhara, Daisuke, and Timothy M. Swager. "Bispyridinium-phenylene-based Copolymers: Low Band Gap N-type Alternating Copolymers." *Journal of Materials Chemistry* 21.11 (2011): 3579.

As Published: <http://dx.doi.org/10.1039/c0jm02530e>

Publisher: Royal Society of Chemistry

Persistent URL: <http://hdl.handle.net/1721.1/74524>

Version: Author's final manuscript: final author's manuscript post peer review, without publisher's formatting or copy editing

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Bispyridinium-Phenylene-Based Copolymers: Low Band Gap N-Type Alternating Copolymers

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Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X

First published on the web Xth XXXXXXXXX 200X

DOI: 10.1039/b000000x

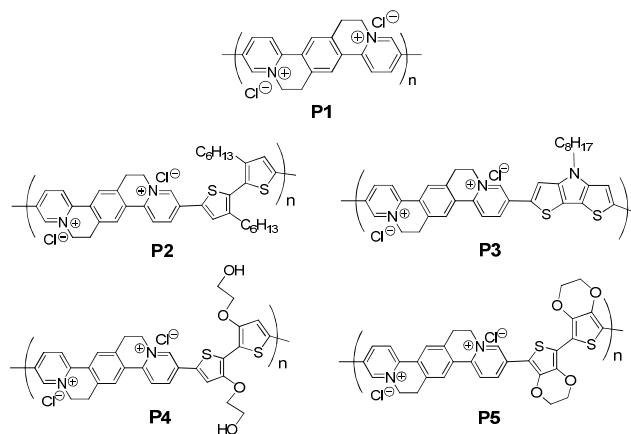
Bispyridinium-phenylene-based conjugated donor-acceptor copolymers were synthesized by a Stille cross-coupling and cyclization sequence. These polyelectrolytes are freely soluble in organic solvents and display broad optical absorption bands that extend into the near-infrared region. They show ambipolar redox properties with high electron affinities (LUMO levels) of 3.9–4.0 eV as well as high degrees of electroactivity. When reduced (n-doped) these materials display in situ conductivities as high as 180 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 C₆₀ based n-type material and hence may find utility in photovoltaic devices.

Introduction

Conjugated polymer semiconductors continue to attract considerable attention for applications in optoelectronic and electrochemical devices, such as photovoltaic cells,¹ light emitting diodes,² sensors,³ electrochromics,⁴ and field-effect transistors.⁵ Plastic materials can offer great advantages for the creation of flexible and light-weight devices that can be fabricated in large area formats by low-cost solution processing techniques. For applications, the electron-donating or electron-accepting properties of the conjugated polymers are of crucial importance. Although many varieties of high performance p-type (electron donor) polymers and ambipolar polymers are available,⁶ stable processable n-type polymers with high electron affinities (c.a. 4 eV) are not in abundance.⁷ Relatively few studies have been reported concerning heterojunctions between p/n-type polymers for photovoltaic cells,⁸ mainly due to the limited n-type polymers with the necessary high electron affinity (EA). As a result the majority of organic polymer photovoltaic devices have employed fullerene acceptor molecules, such as methanofullerene phenyl-C₆₁-butyric-acid-methyl-ester (PCBM, EA = 4.2 eV).¹ A major drawback of fullerene derivatives is their weak absorption in the visible and near-infrared regions and hence highly absorbing n-type polymers are an attractive goal. Achievement of conjugated high electron affinity polymers remains a critical challenge and one of the most successful strategies has been the construction of conjugated polymers incorporating N-heterocyclic electron-deficient aromatics.^{7,9} However, development of nitrogen-containing polyheterocycles with high electron affinities and solubility in common solvents has met limited success.¹⁰

Recently, we have reported on a new class of water and/or alcohol soluble electron-accepting (n-type) conjugated polymers (**P1**) with bispyridinium-phenylene units.¹¹ In these materials, the electron-deficient pyridinium rings were produced by an intramolecular cyclization to produce low

LUMO energies and a relatively planar structure for extended π -electron delocalization. These materials displayed high EAs, reversible redox behavior, high conductivities, good electron mobilities, and efficient quenching of donor polymers. In this present work, we have built upon these initial designs to create conjugated donor-acceptor semiconductive copolymers (**P2–P5**) with bispyridinium-phenylene units as the electron acceptor comonomer. We have systematically modulated of the intramolecular charge transfer (ICT) interactions by choice of electron donor (D) units with the pyridinium-phenylene electron acceptor (A) units. The donor-acceptor copolymers (**P3–5**) exhibiting strong ICT have broad absorption bands that extend into the near-IR region, and ambipolar redox properties with large electron affinities (3.9–4.0 eV).



Experimental

Instrumentation

NMR spectra were obtained on a Varian Mercury-300 spectrometer, and all chemical shifts are referenced to residual solvent peaks. 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- τ 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 an internal Ag wire quasi-reference electrode (BioAnalytical Systems) submerged in 0.01 M AgNO₃/0.1 M tetrabutylammonium hexafluorophosphate (*n*-Bu₄NPF₆) in anhydrous CH₃CN or anhydrous CH₂Cl₂. Typical cyclic voltammograms were recorded using platinum button electrodes as the working electrode and a platinum coil counter electrode. The ferrocene/ferrocenium (Fc/Fc⁺) redox couple was used as an external reference. In-situ conductivity measurements were carried out by using interdigitated microelectrodes (5 μ m gaps) as working electrodes. The polymer films were deposited in air by dropcasting the polymer solutions on interdigitated microelectrodes. 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 (σ) 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 μ 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).

Materials

1,4-bis[2-(5-bromopyridyl)]-2,5-bis(2-(*tert*-butyldimethylsilyloxy)ethyl)benzene (**3**), TBDMS-protected poly(bispyridyl phenylene) (**P6**), and ethylene-bridged poly(bispyridinium phenylene) (**P1**) were synthesized according to the previous paper.¹¹ 5,5'-bis(trimethylstannyl)-3,3'-dihexyl-2,2'-bithiophene (**4**),¹² 2,6-di(trimethylstannyl)-*N*-(1-octyl)dithieno[3,2-*b*:2',3'-*d*]pyrrole (**5**),¹³ THP-protected 5,5'-di(trimethylstannyl)-3,3'-bis(2-hydroxyethoxy)-2,2'-bithiophene (**6**),¹⁴ 5,5'-bis(trimethylstannyl)-2,2'-bis(3,4-ethylenedioxythiophene) (**7**)¹⁵ were also prepared according to literature methods. Anhydrous dichloromethane, acetonitrile, and tetrahydrofuran were obtained using a solvent purification system (Innovative Technologies). Anhydrous DMSO was purchased from Aldrich as Sure-Seal Bottles and used as received. Tetrabutylammonium hexafluorophosphate was recrystallized in ethanol prior to use. All other chemicals were of reagent grade and used as received. Column chromatography was performed using ultra pure silica gel (SILYCYCLE, 40~63 μ m).

General procedure for siloxyethyl-substituted bispyridyl-phenylene-based copolymers. Copolymer P7

A solution of **3** (71 mg, 0.1 mmol), **4** (66 mg, 0.1 mmol), and Pd(PPh₃)₄ (5.8 mg, 0.005 mmol) in 5 mL of THF was stirred for 24 h at 75 °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 reprecipitated from methanol. The resulting yellow precipitate was collected by centrifugation and dried (92% yield). ¹H NMR (300 MHz, CDCl₃): δ -0.05 (s, 12H), 0.82 (s, 18H), 0.88 (br, 6H), 1.30 (br, 12H), 1.67 (br, 4H), 2.64 (br, 4H), 3.04 (br, 4H), 3.77 (br, 4H), 7.33 (s, 2H), 7.41 (br, 2H), 7.50 (br, 2H), 7.94 (s, 2H), 8.97 (s, 2H).

Copolymer P8

P8 was synthesized by the polymerization of **3** with **5** to yield an orange precipitate (90% yield). ¹H NMR (300 MHz, CDCl₃): δ -0.04 (s, 12H), 0.83 (s, 18H), 0.88 (br, 3H), 1.28 (br, 10H), 1.98 (br, 2H), 3.07 (br, 4H), 3.79 (br, 4H), 4.29 (br, 2H), 7.38 (s, 2H), 7.42 (br, 2H), 7.51 (br, 2H), 7.98 (s, 2H), 9.03 (s, 2H).

Copolymer P9

P9 was synthesized by the polymerization of **3** with **6** to yield an orange precipitate (91% yield). ¹H NMR (300 MHz, CDCl₃): δ -0.05 (s, 12H), 0.82 (s, 18H), 1.57-1.89 (br, 12H), 3.05 (br, 4H), 3.60 (br, 2H), 3.77 (br, 4H), 3.97 (br, 4H), 4.22 (br, 2H), 4.46 (br, 4H), 4.83 (br, 2H), 7.29 (s, 2H), 7.40 (br, 2H), 7.49 (br, 2H), 7.93 (br, 2H), 8.96 (s, 2H).

Copolymer P10

P10 was synthesized by the polymerization of **3** with **7** to yield an orange precipitate (55% yield). ¹H NMR (300 MHz, CDCl₃): δ -0.07 (s, 12H), 0.82 (s, 18H), 3.05 (br, 4H), 3.75 (br, 4H), 4.46 (br, 4H), 4.50 (br, 4H), 7.38 (s, 2H), 7.46 (br, 2H), 8.09 (br, 2H), 9.08 (s, 2H).

General procedure for ethylene-bridged poly(bispyridinium-phenylene bithiophene) copolymers. Copolymer P2

To a solution of **P7** (50 mg, 0.057 mmol) in 10 mL of CHCl₃, SOCl₂ (2.0 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 red solid (95% yield). ¹H NMR (300 MHz, CD₃OD): δ 0.89 (br, 6H), 1.32 (br, 12H), 1.72 (br, 4H), 2.72 (br, 4H), 3.58 (br, 4H), 5.01 (br, 4H), 7.98 (br, 2H), 8.43 (br, 2H), 8.79 (br, 2H), 8.89 (br, 2H), 9.49 (br, 2H).

Copolymer P3

P3 was synthesized by the reaction of **P8** with SOCl₂ to yield a violet blue precipitate (90% yield). ¹H NMR (300 MHz, DMSO-*d*₆): δ 0.83 (br, 3H), 1.23 (br, 10H), 1.98 (br, 2H), 3.46 (br, 4H), 4.07 (br, 2H), 4.92 (br, 4H), 7.68 (br, 2H), 7.82 (br, 2H), 8.35 (br, 2H), 8.93 (br, 2H), 9.49 (br, 2H).

Copolymer P4

P4 was synthesized by the reaction of **P9** with SOCl₂ to yield a violet blue precipitate (91% yield). ¹H NMR (300 MHz, DMSO-*d*₆): δ 3.48 (br, 4H), 4.21 (br, 4H), 4.66 (br, 4H), 4.93

(br, 4H), 8.18 (s, 2H), 8.46 (br, 2H), 8.80 (br, 2H), 8.91 (br, 2H), 9.49 (br, 2H).

Copolymer P5

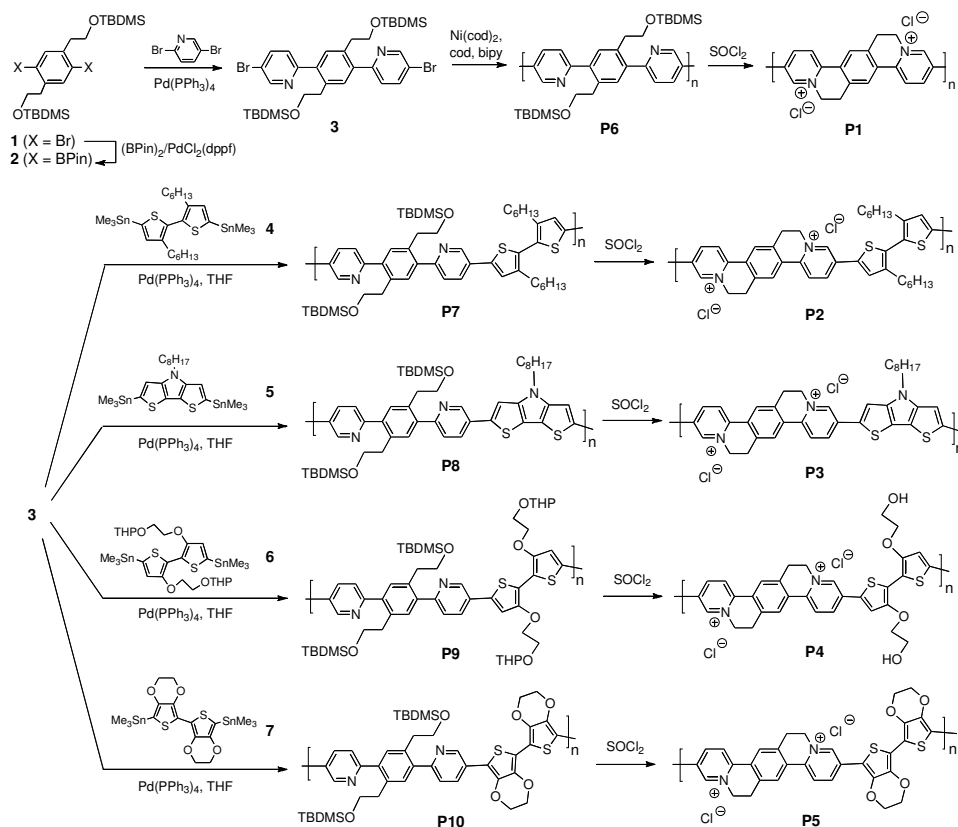
P5 was synthesized by the reaction of **P10** with SOCl_2 to yield a violet blue precipitate (88% yield). ^1H NMR (300 MHz, DMSO-d_6): δ 3.42 (br, 4H), 4.60 (br, 8H), 4.95 (br, 4H), 8.39 (s, 2H), 8.71 (br, 2H), 9.03 (br, 2H), 9.59 (br, 2H).

Results and discussion

Synthesis and characterization

Scheme 1 shows the synthetic routes to the homopolymer **P1** and the alternating copolymers **P2-5**.¹¹ A pyridyl precursor-polymer is initially synthesized and is then transformed via an intramolecular nucleophilic substitution pathway to the target polymers having acceptor pyridinium rings. The symmetrical monomer **3** provides a head-to-head bispyridinium-phenylene-based skeleton, which as expected displays reversible viologen-like redox behavior in the cyclized form.¹⁶ This material is prepared by regioselective Suzuki coupling of **2** with 2,5-dibromopyridine in 58% yield. Starting material **2** prepared by the boronation of 2,5-bis(2-*tert*-butyldimethylsilyloxy)ethyl)-1,4-benzenedibromide (**1**). Yamamoto and Stille coupling copolymerizations of electron donor monomers with **3** yielded high-molecular-weight siloxyethyl-substituted poly(bispyridyl phenylene)s, **P6-10**, in 55-92% yield. All the precursor polymers were soluble in common organic solvents (e.g. CHCl_3 , THF) and thionyl chloride induced quaternizative cyclization gave polyelectrolytes **P1-5**.¹⁷ Although the polyelectrolytes **P1-2**

are only soluble in highly polar solvents, such as water and methanol, the copolymers **P3-5** containing stronger donor groups are soluble in aprotic polar solvents, such as DMF and DMSO, but are only partially soluble in methanol. The weight average molecular weights (M_w) of **P6-10** were determined by GPC and found to be 7000-26,900 with a polydispersity index (M_w/M_n) of 1.4-2.2 (Table 1). The assignment of the molecular structures of the copolymers were supported by ^1H NMR spectra. The ^1H NMR spectra of the precursor copolymers **P7-10** and cyclized polyelectrolytes **P2-5** were in agreement with their structures, as shown in Figure S1-2 (See the Supporting Information). The singlet resonances at 8.96-9.08 ppm in the spectra of **P7-10** and at 9.49-9.59 ppm in the spectra of **P2-5**, are assigned to the two protons (labeled "d" in Figure S1-2) adjacent to the nitrogen atoms in the pyridine or pyridinium rings, were observed. The resonances at 7.29-7.98 ppm in the spectra of **P7-9** and at 7.68-8.93 ppm in the spectra of **P2-4**, are assigned to the two protons in the thiophene rings (labeled "e" in Figure S1-2), the two protons in the phenylene ring (labeled "a" in Figure S1-2), and the other four protons in the pyridine or pyridinium rings (labeled "b, c" in Figure S1-2). The resonances at 7.38-8.09 ppm in the spectrum of **P10** and at 8.39-9.03 ppm in the spectrum of **P5** also correspond to the two protons in the phenylene ring and the other four protons in the pyridine or pyridinium rings. The peaks in the range 0.8-5.0 ppm arise from alkyl groups in the copolymers **P7-10** and **P2-5**, and the large two singlet peaks at -0.77-0.83 ppm, corresponding to the TBDMS groups, were observed only in the precursor copolymers **P7-10**.



Scheme 1 Synthetic Routes to P1-5.

Optical properties

An essential component for improving the efficiency of photovoltaic cells is to match the absorption spectra of the photovoltaic materials with the solar spectrum that extends from 350 to 1500 nm with a maximum photon flux at around 700 nm. Therefore, conjugated polymers with broad absorption bandwidths and strong absorbance are desirable for photovoltaic cells.

The optical absorption and emission spectra of the precursor homopolymer **P6** and the bithiophene-based precursor copolymers **P7-10** in dilute chloroform solution are shown in Figure 1a-b. As compared to homopolymer **P6**, 3,3'-dihexyl-2,2'-bithiophene-based copolymer **P7** displayed 30nm red shift as a result of the enhanced delocalization of the thiophene unit over the more aromatic pyridyl and phenylene units. Furthermore, the solution absorption spectra of *N*-(1-octyl)dithieno[3,2-*b*:2',3'-*d*]pyrrole-based copolymer **P8**, with an absorption maximum (λ_{\max}) at 423 nm, 3,3'-bis(2-hydroxyethoxy)-2,2'-bithiophene-based copolymer **P9** ($\lambda_{\max} = 435$ nm), and 2,2'-bis(3,4-ethylenedioxythiophene)-based copolymer **P10** ($\lambda_{\max} = 428, 448$ nm), are broadened and red-shifted compared to that of **P7** ($\lambda_{\max} = 352$ nm). In the chain structures of **P8-10**, the *N*-alkyldithienopyrrole, bis(alkyloxy)-bithiophene, or bis(alkylenedioxythiophene) moiety are much more electron-rich units compared to dialkylbithiophene of **P7**, resulting in the ICT effects.

Figure 1c-d demonstrates the optical absorption spectra of dilute water or DMF solutions and thin films of pyridinium-based copolymers **P1-5**. The optical properties of the homopolymer **P1** and the donor-acceptor alternating copolymers **P2-5** are also summarized in Table 1. The absorption spectra of **P1-5** are significantly red-shifted relative to their respective precursors. This is attributed to the two ethylene bridges enforcing a planar conformation of the bispyridinium-phenylene segment and inserting the electronic accepting pyridiniums. The thin film absorption spectra are generally similar in shape to those in dilute solutions. The solutions of **P3-5** with the stronger donor units have very broad absorption bands that extend into the near-infrared region with a λ_{\max} at 632 nm for **P3**, 700 nm for **P4**, and 600 nm for **P5**. Their optical band gap (E_g^{opt}) derived from the absorption edge of the thin film spectra was 1.6 eV for **P3** and 1.4 eV for **P4-5** (Table 1). Insertion of bispyridinium-phenylene segment into the repeating structure of poly(**5**), poly(**6**), or poly(**7**) has a significant effect on their E_g^{opt} (1.55-1.80 eV),^{13,18} and among them **P5** with the most electron-rich bis(3,4-ethylenedioxythiophene) units has the strongest ICT interaction, and the smallest optical band gap, 1.1 eV, which is much smaller than that of homopolymer **P1** (2.6 eV).¹¹ **P2** had weak emission bands with peaks at 442 nm in dilute DMF solution, but all of the **P3-5** have no detectable emission in solutions and thin films.

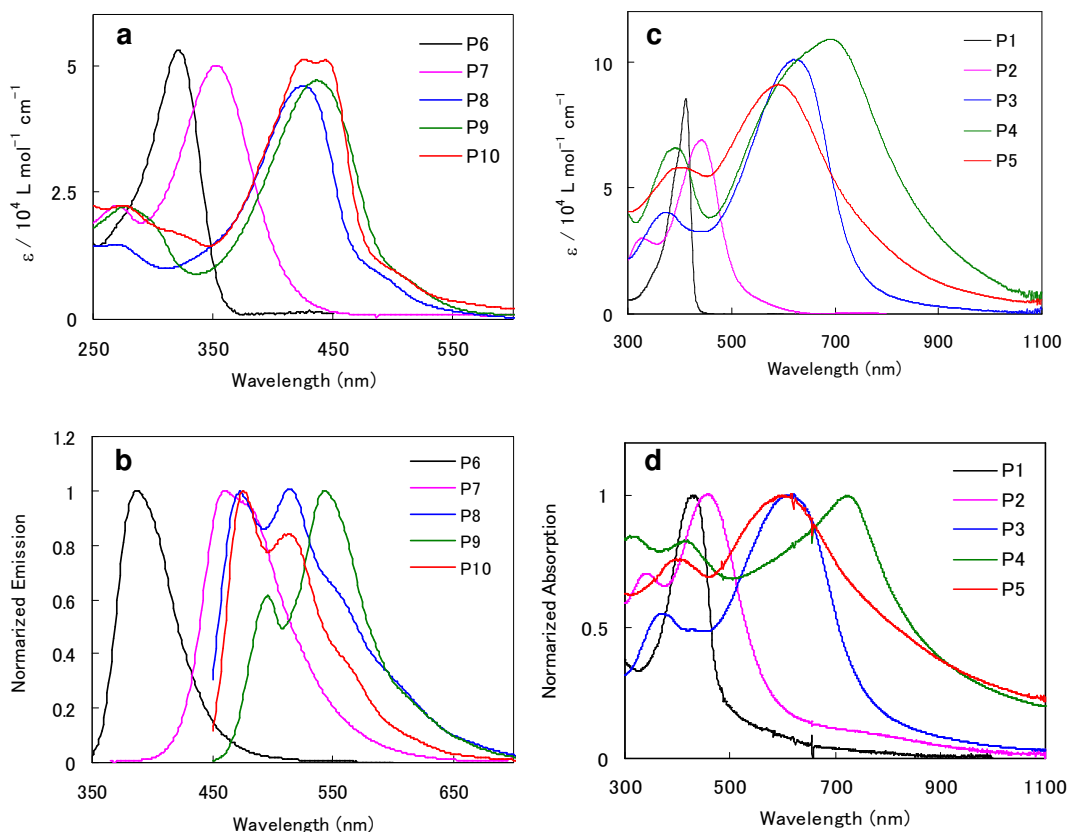


Figure 1 (a) UV-vis absorption spectra and (b) PL emission spectra of **P6-10** in CHCl_3 solutions. (c) UV-vis absorption spectra of **P1-P5** in water (**P1**) or DMF solutions (**P2-P5**) and (d) as the thin films on glass substrates.

| polymer | Mn | Mw/Mn | λ_{max} (nm) | λ_{onset} (nm) | $E_{\text{g}}^{\text{opt a}}$ (eV) | $E_{\text{red}}^{\text{b}}$ (V) | $E_{\text{red}}^{\text{onset b}}$ (V) | E_{ox}^{b} (V) | $E_{\text{ox}}^{\text{onset b}}$ (V) | $E_{\text{g}}^{\text{el c}}$ (eV) | EA ^d (eV) | IP ^e (eV) |
|-----------|-------|-------|--------------------------------|----------------------------------|---------------------------------------|------------------------------------|--|-----------------------------------|---|--------------------------------------|-------------------------|-------------------------|
| P1 | 15600 | 1.5 | 431 | 485 | 2.6 | -0.56, -1.27 | -0.40 | - | - | - | 4.0 | 6.6 |
| P2 | 26700 | 1.9 | 462 | 620 | 2.0 | -0.71, -0.90 | -0.55 | - | - | - | 3.9 | 5.9 |
| P3 | 26900 | 2.2 | 615 | 787 | 1.6 | -0.90, -1.25 | -0.42 | 1.33 | 0.98 | 1.4 | 4.0 | 5.4 |
| P4 | 12700 | 1.7 | 730 | 885 | 1.4 | -0.92, -1.25 | -0.42 | 1.14 | 0.77 | 1.2 | 4.0 | 5.2 |
| P5 | 7000 | 1.4 | 608 | 900 | 1.4 | -0.99, -1.27 | -0.51 | 0.72, 1.13 | 0.27 | 0.8 | 3.9 | 4.7 |

Table 1 Optical and electrochemical properties of **P1-5**. ^a $E_{\text{g}}^{\text{opt}}$: Optical band gap estimated from the band edge (λ_{onset}) of the absorption spectra. ^b E_{red} , $E_{\text{red}}^{\text{onset}}$, E_{ox} , $E_{\text{ox}}^{\text{onset}}$: Formal and onset reduction and formal and onset oxidation potentials (vs SCE). ^c E_{g}^{el} : Electrochemical band gap estimated from the onset reduction and oxidation potentials. ^d EA: Electron affinity obtained based on $\text{EA} = E_{\text{red}}^{\text{onset}} + 4.4$ (eV). ^e IP: Ionization potential calculated from $\text{IP} = \text{EA} + E_{\text{g}}^{\text{opt}}$ for **P1-2** and $\text{IP} = E_{\text{ox}}^{\text{onset}} + 4.4$ (eV) for **P3-5** (eV).

10 Electrochemical properties

The oxidation and reduction potentials of thin films of pyridinium-based conjugated D-A copolymers **P2-5** and their respective precursors **P6-10** were determined by cyclic voltammetry in CH_2Cl_2 or CH_3CN (vs SCE), as shown in Figure 2a-f and Table 1. The reduction potentials of **P2-5** are significantly more positive relative to **P6-10** as expected with the introduction of the highly electron-withdrawing pyridinium rings. All of the pyridinium copolymers **P2-5** showed two reversible viologen-like redox behavior, and among them **P3-5** displayed reversible ambipolar redox properties as evident from the areas and close proximity of the anodic and cathodic peaks. The oxidation wave was observed in the cyclic voltammogram of **P3-5** at the formal potentials between 0.72 and 1.33 V, whereas no oxidation wave was observed for **P2** with weaker electron-donating groups. Also **P2-5** exhibited two similar potential reductions ranging from -0.99 to -0.71 V. The onset reduction and oxidation potentials of the polyelectrolytes **P2-5** were from -0.55 to -0.42 V and from 0.27 to 0.98 V (vs. SCE), respectively, from which we estimated an electron affinity (EA, LUMO level) of 3.9 to 4.0 eV ($\text{EA} = E_{\text{red}}^{\text{onset}} + 4.4$) and an ionization potentials (IP, HOMO level) of 4.7 to 5.9 eV ($\text{IP} = E_{\text{ox}}^{\text{onset}} + 4.4$).¹⁹ Interestingly, the EA values are higher than those estimated in the same method for most conventional polyheterocycles,⁹ and are comparable to well known electron transporters PCBM (4.2 eV)¹ or BBL (4.0 eV),¹⁰ as well as homopolymer **P1** (4.0 eV).¹¹ The lower band gap values of **P3-5** compared to those of the homopolymers **P1** are due to the strong ICT exhibited

by these D-A alternating copolymers.

An electrochemically reversible charge trapping behavior was observed in the CVs of **P4** and **P5** (Fig. 4c and 4e). Scanning the reductive and oxidative regions separately also results in reversible redox behavior, as shown in Fig. 4d and 4f. In the case of **P4**, the cyclic voltammogram shows six peaks A-F in the potential range between -1.5 and 1.1 V (vs. SCE, Fig. 4c). The position of peak A corresponds to the reported oxidation potential of bis(alkyloxy)-bithiophene moiety, and the positions of the C-F and D-E couples roughly agree with the doping and undoping potentials of poly(bispyridinium phenylene) **P1**. In the range from -0.5 to 1.1 V, only the A-B couple is observed, whereas scanning in the range -1.5 to 0 V gives rise only to the C-F and D-E couples (Fig. 4d). These observations indicate that the A-B couple is mainly related to the oxidation and re-reduction of the bithiophene units, whereas the C-F and D-E couples are related to the reduction and oxidation of the bispyridinium-phenylene units. Similar charge trapping phenomena have been observed in other thiophene- or $\text{Ru}(\text{bpy})_3$ -based polymers wherein thiophenes are connected adjacent to metal-bound pyridyl groups.²⁰ The unusually large potential difference between the A and B peaks suggests the occurrence of a particular chemical interaction (possibly a weak σ -bond or π -bond) after the oxidation of the thiophene ring. The electrochemical band gap ($E_{\text{g}}^{\text{el}} = \text{IP} - \text{EA}$) was determined from Fig. 4d and 4f to be 1.4 eV for **P3**, 1.2 eV for **P4**, and 0.8 eV for **P5**, which are 0.1-0.3 eV larger than the optically determined ones ($E_{\text{g}}^{\text{opt}} = 1.1-1.6$ eV).

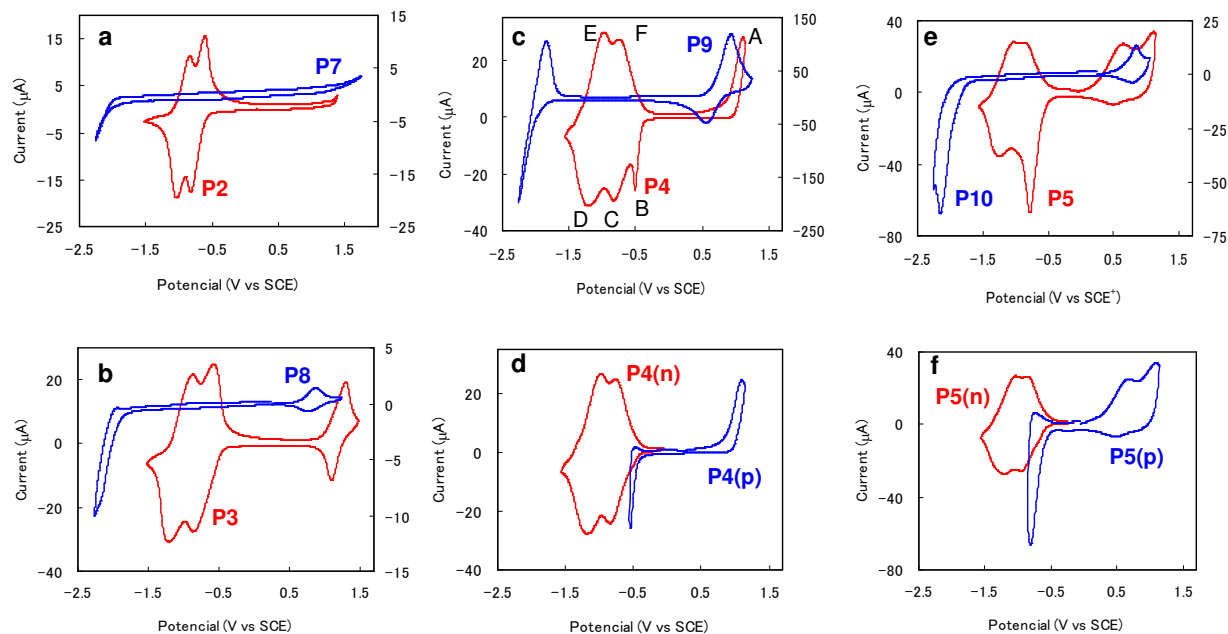


Figure 2 Cyclic voltammograms of drop-cast films of **P2-5** and **P6-10** on a Pt button electrode in CH_2Cl_2 or CH_3CN with 0.1 M TBAPF₆ as a supporting electrolyte.

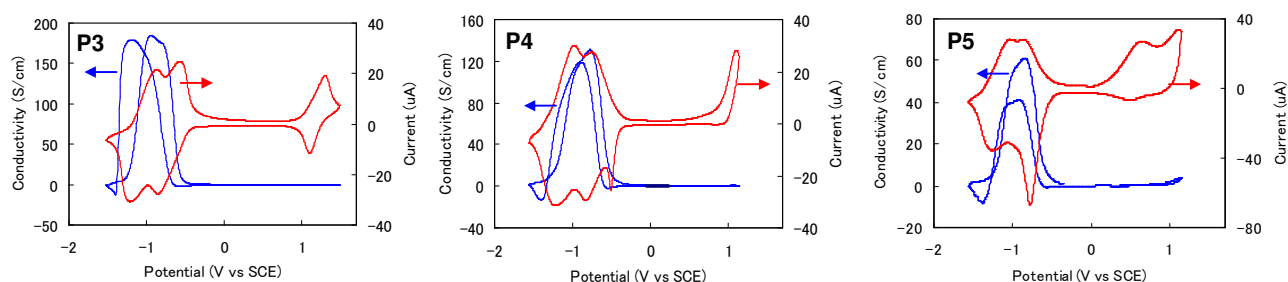


Figure 3 In-situ conductivity measurement of drop-cast films of **P3-5** on interdigitated Pt microelectrodes with 5 μm gaps in CH_2Cl_2 or CH_3CN with 0.1 M TBAPF₆ as a supporting electrolyte.

In-situ conductivity measurement

In-situ conductivity measurements of **P3-5** thin films were made using interdigitated microelectrodes and reveal a narrow window of high conductivity²¹ as shown in Figure 3. Additionally their in-situ conductance measurements are consistent with doping processes observed by cyclic voltammetry. The maximum *in situ* conductivities of **P3** ($\sigma_{\text{max}} = 183 \text{ S/cm}$), **P4** ($\sigma_{\text{max}} = 130 \text{ S/cm}$), and **P5** ($\sigma_{\text{max}} = 60 \text{ S/cm}$) rival values observed of well-known p-type poly(3-alkylthiophene)s. Although the cyclic voltammetry results showed clear ambipolar redox properties, measurable p-type conductivities were not observed in any of the copolymer semiconductors. The narrow window of the *in situ* conductivity profile indicates that the mixed redox state is conductive and that the neutral (fully reduced) material is insulating, as similar to homopolymer **P1**.

Conclusion

We have synthesized new electron-accepting low band gap conjugated polymers, **P3**, **P4**, and **P5** by a Stille cross-coupling and cyclization sequence. These polyelectrolytes are freely soluble in organic solvents and display broad optical absorption bands that extend into the near-infrared region. These materials have high electron affinities (LUMO levels) of 3.9-4.0 eV, reversible ambipolar redox behavior, charge trapping behavior, and high conductivities as high as 180 S/cm when reduced. The combination of these properties qualifies **P3**, **P4**, and **P5** as promising n-type polymer semiconductors for printable electronic applications and all-polymer solar cells.

Acknowledgments

This work was supported by the National Science Foundation DMR-0706408. The authors thank Dr. Changsik Song for technical discussions and TORAY Industries, Inc. for partial financial support.

Notes

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References and notes

- 1 S. Gunes, H. Neugebauer, N. S. Sariciftci, *Chem. Rev.*, 2007, **107**, 1324.; B. C. Thompson, J. M. J. Frechét, *Angew. Chem., Int. Ed.*, 2008, **47**, 58.
- 2 A. Kraft, A. C. Grimsdale, A. B. Holmes, *Angew. Chem., Int. Ed.*, 1998, **37**, 402.
- 3 *Electrochromism: Fundamentals and Applications*, P. M. S. Monk, R. J. Mortimer, D. R. Rosseinsky, Eds., VCH:Weinheim, 1995.; S. A. Sapp, G. A. Sotzing, J. R. Reynolds, *Chem. Mater.*, 1998, **10**, 2101.
- 4 T. M. Swager, *Acc. Chem. Res.*, 1998, **31**, 201.; D. T. McQuade, A. E. Pullen, T. M. Swager, *Chem. Rev.*, 2000, **100**, 2537.
- 5 S. Allard, M. Forster, B. Souharce, H. Thiem, U. Scherf, *Angew. Chem., Int. Ed.*, 2008, **47**, 4070.; A. R. Murphy, J. M. J. Frechét, *Chem. Rev.*, 2007, **107**, 1066.
- 6 R. D. McCullough, *Adv. Mater.*, **1998**, *10*, 93.; I. McCulloch, M. Heeney, C. Bailey, K. Genevicius, I. MacDonald, 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.; H. Usta, G. Lu, A. Facchetti, T. J. Marks, *J. Am. Chem. Soc.*, 2006, **128**, 9034.
- 7 A. Babel, S. A. Jenekhe, *J. Am. Chem. Soc.*, 2003, **125**, 13656.; X. Zhan, Z. Tan, B. Domercq, Z. An, X. Zhang, S. Barlow, Y. Li, D. Zhu, B. Kippelen, S. R. Marder, *J. Am. Chem. Soc.*, 2007, **129**, 7246.; J. A. Letizia, M. R. Salata, C. M. Tribout, A. Facchetti, M. A. Ratner, T. J. Marks, *J. Am. Chem. Soc.*, 2008, **130**, 9679.; H. Usta, A. Facchetti, T. J. Marks, *J. Am. Chem. Soc.*, 2008, **130**, 8580.
- 8 M. Granstrom, K. Petritsch, A. C. Arias, A. Lux, M. R. Andersson, R. H. Friend, *Nature (London)*, 1998, **395**, 257.; S. A. Jenekhe, S. Yi, *Appl. Phys. Lett.*, 2000, **77**, 2635.; T. Kietzke, D. A. M. Egbe, H-H. Hrhold, D. Neher, *Macromolecules*, 2006, **39**, 4018.
- 9 A. P. Kulkarni, C. J. Tonzola, A. Babel, S. A. Jenekhe, *Chem. Mater.*, 2004, **16**, 4556, and references therein.; Y. Zhu, C-T. Yen, S. A. Jenekhe, W-C. Chen, *Macromol. Rapid Commun.*, 2004, **25**, 1829.
- 10 While EA 4.0 eV has been reported for BBL, it is noteworthy that BBL was processed by strong acid, rather than common solvents; M. Alam, S. A. Jenekhe, *Chem. Mater.*, 2004, **16**, 4647.
- 11 D. Izuhara, T. M. Swager, *J. Am. Chem. Soc.*, 2009, **131**, 17724.
- 12 X. Guo, M. D. Watson, *Org. Lett.*, 2008, **10**, 5333.
- 13 G. Koeckelberghs, L. D. Cremer, A. Persoons, T. Verbiest, *Macromolecules*, 2007, **40**, 4173.
- 14 M. J. Marsella, R. J. Newland, P. J. Carroll, T. M. Swager, *J. Am. Chem. Soc.*, 1995, **117**, 9842.
- 15 A. K. Mohanakrishnan, A. Hucke, M. A. Lyon, M. V. Lakshmikantham, M. P. Cava, *Tetrahedron*, 1999, **55**, 11745.
- 16 M. Michaelis, E. S. J. Hill, *Gen. Physiol.*, 1933, **16**, 859.
- 17 S-W. Zhang, T. M. Swager, *J. Am. Chem. Soc.*, 2003, **125**, 3420.
- 18 R. Cloutier, M. Leclerc, *J. Chem. Soc., Chem. Commun.*, 1991, 1194.; S. Akoudad, J. Roncali, *Synth. Met.*, 1998, **93**, 111.
- 19 Y. Li, J. Ding, M. Day, Y. Tao, J. Lu, M. D'iorio, *Chem. Mater.*, 2004, **16**, 2165.
- 20 G. Zotti, G. Schiavon, S. Zecchin, *Synth. Met.*, 1995, **72**, 275.; S. S. Zhu, R. P. Kingsborough, T. M. Swager, *J. Mater. Chem.*, 1999, **9**, 2123.; Z. Zhou, T. Maruyama, T. Kanbara, T. Ikeda, K. Ichimura, T. Yamamoto, K. Tokudab, *J. Chem. Soc., Chem. Commun.*, 1991, 1210.
- 21 G. P. Kittlesen, H. S. White, M. S. Wrighton, *J. Am. Chem. Soc.*, 1984, **106**, 7389.

Bispyridinium-Phenylene-Based Copolymers: Low Band Gap N-Type Alternating Copolymers

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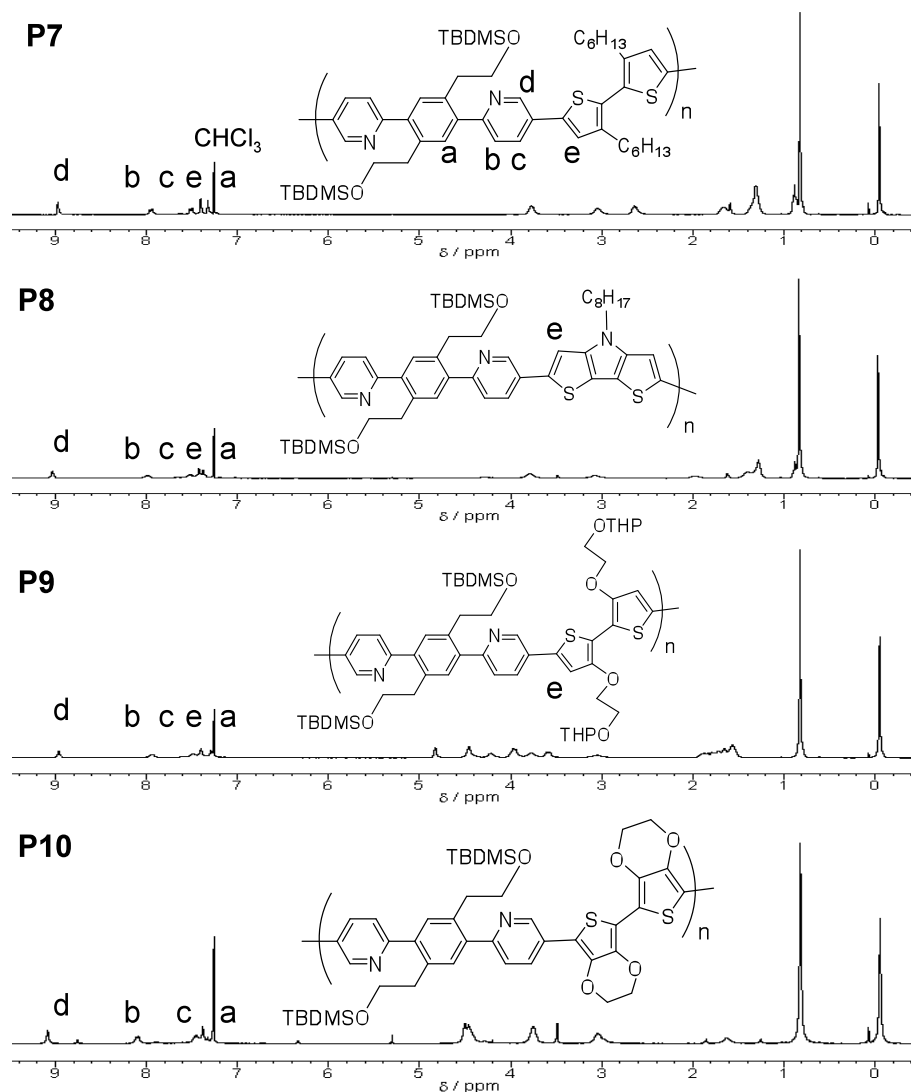


Figure S1. ^1H NMR spectra of **P7-10** in CDCl_3 .

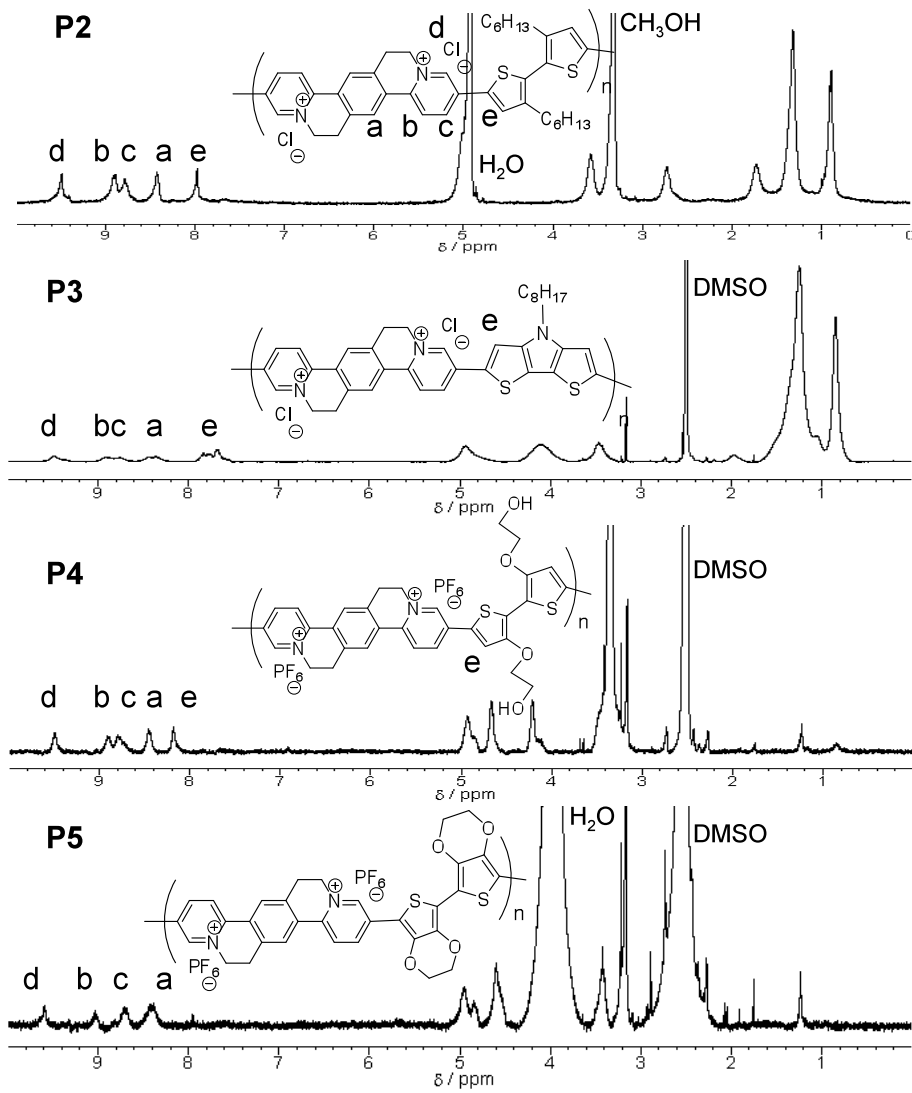


Figure S2. ^1H NMR spectra of **P2-5** in CD_3OD , DMSO-d_6 or $\text{DMSO-d}_6/\text{D}_2\text{O}$.