Macromolecules **2008**, *41*, 7805−7811

Synthesis and Redox-Driven Chiroptically Switching Properties of Viologen-Containing Optically Active Polymer with Main-Chain Axial Chirality

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Received July 1, 2008; Revised Manuscript Received August 29, 2008

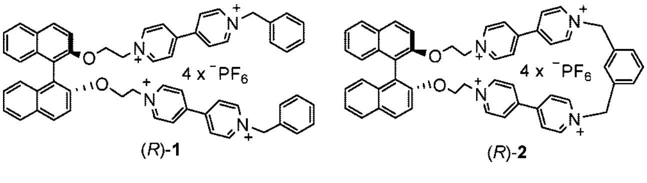
ABSTRACT: A novel type of redox-based chiroptically switching polymer was prepared by grafting electrochromic viologens onto side chains of a 1,1′-binaphthyl-6,6′-diyl-based optically active conjugated polymer. The resulting polymer exhibited much larger mean residue optical rotation ($[m]_D^{20} = -3308°$) than the molar rotation of the corresponding model compound (*R*)-BBEBPP ($[\phi]_D^{20} = +384°$) and an intense negative CD signal in the absorption band of the polymer backbone, indicating a secondary chirality of the main chain. The viologen-grafting ratio was determined to be ∼50% by proton NMR and thermogravimetric analysis, which corresponds to a predominant polymer structure with one viologen on each repeat unit. Due to the presence of viologen groups, the polymer exhibited a distinctive color change from light yellow to dark blue upon electrochemical or chemical reduction of cationic viologens (V^{2+}) to radical cations ($V^{+\bullet}$). Correspondingly, the CD spectrum of **P4** ($V^{+\bullet}$) showed two new positive Cotton effects in the absorption bands of $V^{+\bullet}$ at 404 and 520 nm. In comparison with the small molecular model compound that exhibited stronger negative Cotton effects in absorption bands of $V^{+\bullet}$, **P4** ($V^{+\bullet}$) has a quite different CD pattern, which was attributed to a different exciton coupling mechanism between the two. By taking advantage of the pronounced changes in the CD spectrum of **P4** before and after reduction (e.g., $[\theta]$ from measuring nearly 0 to 1.2×10^4 deg cm^2 dmol^{-1} at 404 nm or 5.9×10^3 deg cm^2 dmol^{-1} at 520 nm), redox-driven chiroptically switching properties of **P4** was probed in a DMF solution using tin as the reducing agent. After five redox cycles, no deterioration of the sample solution was observed and good reversibility in CD signals was demonstrated.

Introduction

Optically active polymers have been the subject of intense studies in past decades due to their potential applications in enantiomer separation and asymmetric catalysis.[1−3] Interest arises mainly from their unique chiral structures (e.g., helix) that resemble those of naturally occurring materials (e.g., proteins, nucleic acids, and amino acids) characterized by high performance in molecular recognition and catalytic activity. In comparison, however, utilization of the most intrinsic and unique optical properties derived from chiral structures, i.e., chiroptical properties including circular birefringence (or optical rotation, OR) and circular dichroism (CD), have been underexplored to a great extent in terms of their potential photonic applications. From a functionality point of view, both OR and CD can be used for manipulation of polarization of light and may function as optical rotators or waveplates. Currently, predominant polarization elements are based on inorganic materials (e.g., quartz) that have poor processability and are typically used in the form of plates or prisms. Given that a precise control of polarization of light is critical for optimal performance of many optical systems and there is an increasing demand for photonic integrations, it is desirable to develop highly efficient optically active polymers for polarization manipulation applications.[4] On one hand, the good processability of organic polymers allows for easy fabrication of the polymers into optical thin films or waveguides that can be integrated with very large scale semiconductor integrations; on the other hand, the responsive properties of optically active materials to external stimuli (e.g., light and electric field) may allow for active control of polarization of light.[5−7]

To be successfully used as polarization materials, optically active polymers with large chiroptical properties at application wavelengths and pronounced stimuli-responsive chiroptical properties are highly desired. Although previous theoretical studies and recently developed computational techniques have enabled some accurate prediction of chiroptical properties of compounds with well-defined structures,[8,9] it appears challenging in design and synthesis of materials with very large chiroptical properties at long wavelengths, e.g., the near-infrared communication wavelengths at 1300 or 1550 nm, due to the optical rotatory dispersion and difficulties in achieving optimal dissymmetric geometric arrangements of chromophores. Toward optically active materials with large chiroptical properties, we recently established an unambiguous structural model correlating the magnitude of chiroptical properties with the spatial arrangements of electrochromic chromophores, i.e., viologens.[10] According to the model, a novel type of redox-driven chiroptical switching molecules having axially dissymmetric 1,1′-binaphthyl-2,2′-diyl as the chiral source [i.e., (*R*)-**1** and (*R*)-**2**, Chart 1] and exhibiting large NIR chiroptical properties {e.g., $[\theta]_{750\ \mathrm{nm}} = -8.44 \times 10^4$ deg cm^2 dmol^{-1} and $[\alpha]_{1500\ \mathrm{nm}} = -235°$} were first demonstrated.[10] However, according to structural

Chart 1



(*R*)-**1** (*R*)-**2**

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10.1021/ma8014646 CCC: $40.75

modeling results the geometric arrangements of viologens in (*R*)-**1** and (*R*)-**2** are not yet close to optimization, indicating room for further enhancing the chiroptical properties through rational structural design.

Optically active polymers with secondary chiral structures (such as main-chain chirality) are known to exhibit pronounced chiroptical amplification effects.[1,3,11] This is manifested by the much larger OR of the polymers than those of the corresponding monomers or repeat units. In the hope of taking advantage of the chiroptical amplification effect and preparing materials with large chiroptical properties as well as good thin-film processability, herein, we designed and prepared a novel type of optically active conjugated polymer containing 1,1′-binaphthyls in the backbone and viologens in the side chains. Chiroptical studies revealed an enhanced OR at the sodium D line and an intense CD signal associated with backbone absorptions, indicating formation of main-chain chiral conformation. Due to the presence of electrochromic viologens at the side chains, the polymer exhibited distinctive and reversible color changes upon redox cycles between cationic viologens and radical cations. Consequently, a pronounced redox-driven chiroptically switching behavior was observed for the polymer at the absorption wavelengths of radical cations.

Experimental Section

Materials. (*R*)-1,1′-Binaphthyl-2,2′-diol {$[\alpha]_D^{20} = +34°$, (c = 1.0, THF); 99% ee} (Lianyungang Chiral Chem. Ltd.) and 4,4′-bipyridine (Jinan Liming Technology Corp.) were purchased and used as received. (*R*)-6,6′-Dibromo-2,2′-dihydroxy-1,1′-binaphthyl {(*R*)-DDB, $[\alpha]_D^{20} = -89.0°$ (c = 0.2, $CHCl_3$); lit. $[\alpha]_D^{20} = -97.8°$ (c = 0.1, $CHCl_3$)},[12] (*R*)-6,6′-dibromo-2,2′-bis(2-hydroxyethoxy)-1,1′-binaphthyl {(*R*)-DBB, $[\alpha]_D^{20} = -49.3°$ (c = 0.3, THF); lit. $[\alpha]_D^{20} = -43.8°$ (c = 0.3, THF)},[12] {(*R*)-2,2′-bis(2-bromoethyloxy)-1,1′-binaphthyl (*R*)-BEB, $[\alpha]_D^{20} = 44.3°$ (c = 0.28, THF); lit. $[\alpha]_D^{20} = 45.6°$ (c = 0.296, THF)},[13] 9,9-dioctylfluorene-2,7-bis(trimethyleneborate) (DFBT),[14] 1-propyl-4,4′-pyridinium bromine (PPB, mp 188−189 °C),[15] and tetrakis(triphenylphosphine) palladium [$Pd(PPh_3)_4$][16] were prepared according to literature methods. *N*,*N*′-Dimethylformamide (DMF) and acetonitrile (MeCN) were purchased from Beijing Chemical Reagents Co. and distilled from phosphorus pentoxide and calcium hydride, respectively, before use. All other chemicals and reagents were purchased from Beijing Chemical Reagents Co. and used as received.

(*R*)-6,6′-Dibromo-2,2′-bis(2-bromoethyloxy)-1,1′-binaphthyl [(*R*)-BBEB]. A solution of (*R*)-BEB (3.0 g, 6.0 mmol) in dichloromethane (50 mL) was cooled in an dry ice/acetone bath to −78 °C. Under magnetic stirring, bromine (0.8 mL, 2.5 g, 16 mmol) in dichloromethane (10 mL) was dropped into the solution in 20 min. After stirring at −78 °C for 3 h, the reaction solution was allowed to warm to room temperature and stirred overnight. An aqueous solution of sodium bisulfite (10%, 80 mL) was added to the solution, and the mixture was stirred until the bromine color disappeared. The organic phase was separated in a separatory funnel, washed with a saturated aqueous sodium chloride solution, and dried over anhydrous magnesium sulfate. After filtration to remove the magnesium sulfate, the filtrate was concentrated on a rotary evaporator to ca. 5 mL and then subjected to silica-gel column chromatography (eluent ethyl acetate/ligroin = 1/3, v/v, R_f = 0.7) to give a viscous liquid that solidified upon standing at room temperature for 10 days: 3.4 g (85% yield); mp 158−159 °C; $[\alpha]_D^{20} = +6.0°$ (c = 0.4, DMF); ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (2H, d, J = 1.8 Hz), 7.88 (2H, d, J = 8.8 Hz), 7.41 (2H, d, J = 8.8 Hz), 7.29 (2H, dd, J = 8.8 Hz, 1.8 Hz), 6.95 (2H, d, J = 8.8 Hz), 4.19−4.27 (4H, m), 3.22−3.27 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) 153.7, 132.4, 130.7, 129.9, 128.9, 127.0, 120.3, 118.0, 116.8, 69.6, 29.0; ESI-MS (m/z) 681 [M + Na^+].

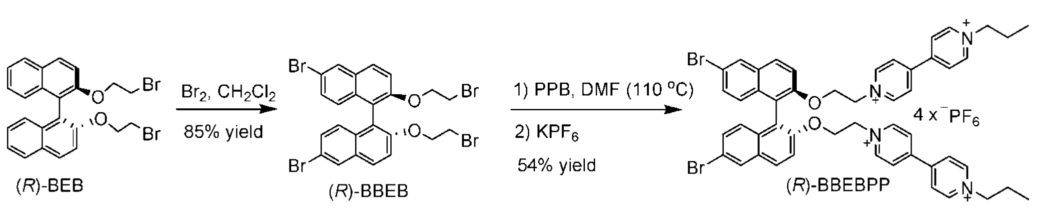
(*R*)-6,6′-Dibromo-2,2′-bis[2-(1′-propyl-4,4′-bipyridinium-1-yl)-ethyl-1-oxy]-1,1′-binaphthyl Tetrahexafluorophosphate [(*R*)-BBEBPP]. A mixture solution of (*R*)-BBEB (0.30 g, 0.44 mmol) and PPB (0.30 g, 1.07 mmol) in DMF (5 mL) was heated to 100 °C and stirred under nitrogen for 24 h. After cooling to room temperature, the solution was concentrated to ca. 1 mL under reduced pressure and acetonitrile (15 mL) was added to precipitate the product. Filtration was performed to collect the precipitates, which were thoroughly washed with acetronitrile and then redissolved in distilled water (5 mL). To the resulting aqueous solution was added potassium hexafluorophosphate until saturation. The pale-yellow precipitate was collected by filtration, washed with distilled water, and dried under vacuum (~1 mmHg) at 60 °C: 0.53 g (54% yield); mp 214 − 217 °C; $[\alpha]_D^{20} = +26.0°$ ($[\phi]_D^{20} = +383.8°$) (c = 0.4, DMF); ^1H NMR (400 MHz, $CDCl_3$) δ 9.47 (4H, d, J = 6.9 Hz), 8.76 (4H, d, J = 6.9 Hz), 8.70 (4H, d, J = 6.9 Hz), 8.19 (4H, d, J = 6.9 Hz), 8.02 (2H, d, J = 9.2 Hz), 7.83 (2H, d, J = 2.0 Hz), 7.68 (2H, d, J = 9.2 Hz), 6.98 (2H, dd, J = 9.0 Hz, 2.2 Hz), 6.26 (2H, d, J = 9.2 Hz), 4.84−4.96 (4H, m), 4.72−4.75 (6H, m), 4.51−4.53 (2H, m), 2.04−2.10 (4H, m), 1.00 (6H, t, J = 7.4 Hz, 7.4 Hz); ^{13}C NMR (100 MHz, DMSO-d_6) δ 152.8, 147.3, 147.2, 146.11, 145.4, 130.9, 129.9, 129.4, 129.2, 126.4, 126.0, 124.8, 118.0, 116.9, 67.3, 62.0, 59.5, 24.5, 20.4; ESI-MS (m/z) 1331 [M − PF_6^-].

Synthesis of Polymers. P1. A 150 mL three-neck round-bottomed flask equipped with a condenser and a magnetic stirring bar was charged with 9,9-dioctylfluorene-2,7-bis(trimethyleneborate) (DFBT) (1.0492 g, 1.8789 mmol), (*R*)-DBB (1.0000 g, 1.8789 mmol), anhydrous potassium carbonate (5.20 g, 37.6 mmol), and $Pd(PPh_3)_4$ (0.075 g, 0.065 mmol). The flask was purged with argon for 20 min before degassed tetrahydrofuran (30 mL) and degassed distilled water (30 mL) were added through a syringe. The resulting mixture solution was then heated to 95 °C and magnetically stirred for 48 h. After cooling to room temperature, the mixture solution was poured into a separatory funnel, where the organic phase was separated and the water phase was washed with dichloromethane (3 × 10 mL). The organic phases were combined and concentrated on a rotary evaporator to ca. 15 mL, which was then precipitated into methanol (300 mL). The resulting pale yellow solid was collected by filtration, washed thoroughly with methanol, and dried in vacuo at 60 °C to give the polymer product (1.34 g, 65% yield): $M_n = 4.4 \times 10^4$, PDI = 1.62 (GPC); $[\alpha]_D^{20} = -462.0°$ ($[m]_D^{20} = -3516°$) (c = 0.4, DMF); ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (2H, s), 8.09 (2H, d, J = 9.1 Hz), 7.78 (2H, d, J = 7.8 Hz), 7.61−7.68 (6H, m), 7.51 (2H, d, J = 9.1 Hz), 7.28 (2H, d, J = 8.8 Hz), 4.27−2.29 (2H, m), 4.10 (2H, m), 3.62 (4H, m), 2.54 (2H, t, J = 6.4 Hz, 6.4 Hz), 2.04 (4H, br s), 1.04−1.15 (20H, m), 0.72−0.75 (10H, m); IR (KBr, cm^{-1}) 3427, 1639, 1537, 1505, 1450, 842, 559; T_g = 227 °C (DSC, nitrogen); $T_{d,onset}$ = 384 °C (TGA, nitrogen).

P2. To a solution of **P1** (0.50 g, 0.66 mmol) and triethylamine (0.29 g, 2.86 mmol) in dichloromethane (20 mL) at 0 °C was added methylsulfonyl chloride (0.41 g, 3.6 mmol). The reaction solution was allowed to warm to room temperature and stirred overnight. The resulting yellow solution was washed in a separatory funnel with distilled water (3 × 10 mL), concentrated by rotary evaporation to ca. 10 mL, and then precipitated into methanol (200 mL) to give a pale-yellow solid, which was collected by filtration, washed thoroughly with methanol, and dried in vacuo at 60 °C (0.49 g, 83% yield): $[\alpha]_D^{20} = -341.5°$ ($[m]_D^{20} = -3128°$) (c = 0.4, DMF); ^1H NMR (400 MHz, $CDCl_3$) δ 8.16 (2H, s), 8.10 (2H, d, J = 9.1 Hz), 7.80 (2H, d, J = 8.0 Hz), 7.61−7.67 (6H, m), 7.49 (2H, d, J = 9.1 Hz), 7.25 (2H, d, J = 8.0 Hz), 4.33 (6H, br s), 4.24−4.26 (2H, m), 2.27 (6H, s), 2.05 (4H, br s), 1.05−1.15 (20H, m), 0.72−0.76 (10H, m); T_g = not detectable (DSC, nitrogen); $T_{d,onset}$ = 232 °C (TGA, nitrogen). The sulfonation yield is estimated to be 100% from the ^1H NMR spectrum.

P3. A solution of **P2** (0.20 g, 0.22 mmol) and potassium iodide (0.20 g, 1.20 mmol) in anhydrous DMF (4 mL) was heated under nitrogen to 80 °C and stirred for 24 h. After cooling to room temperature, the reaction solution was poured into methanol (80 mL). The resulting precipitate was collected by filtration, washed thoroughly with a mixture of methanol and distilled water (20 mL, v/v, 1/1), and vaccuum dried at 60 °C to give the white product 0.20 g (94% yield): ^1H NMR (300 MHz, $CDCl_3$) δ 8.17 (2H, s),

Scheme 1. Synthesis of (*R*)-BBEBPP



8.07 (2H, d, $J = 6.0$ Hz), 7.77 (2H, br s), 7.60−7.65 (6H, m), 7.46 (2H, d, $J = 6.0$ Hz), 7.26 (overlapped with CDCl$_3$), 4.23−4.27 (4H, m), 3.08 (4H, br s), 2.04 (4H, br s), 1.05 (20H, br s), 0.74 (10H, br s); T_g = not detectable (DSC, nitrogen); $T_{d,onset} = 241$ °C (TGA, nitrogen). The iodization yield is estimated to be 100% from the ^{1}H NMR spectrum.

P4. A solution of **P2** (0.10 g, 0.11 mmol) and potassium iodide (0.07 g, 0.42 mmol) in DMF (5 mL) was heated to 80 °C and stirred for 24 h. BPP (0.076 g, 0.27 mmol) in DMF (1.5 mL) was added, and the solution was heated to 100 °C and stirred for another 48 h. The solution was cooled to room temperature and poured into methanol (150 mL) to give a light yellow powder, which was collected by filtration, washed thoroughly with methanol and distilled water, and dried in vacuo at 60 °C to give a purple-colored product (0.10 g, 72% yield): $[\alpha]_D^{20} = -263.0°$ ($[m]_D^{20} = -3308°$) ($c = 0.4$, DMF); IR (KBr, cm^{-1}) 2923, 2854, 1665, 1592, 1474, 1339, 1243, 1084, 1048, 950, 887, 814; T_g = not detectable (DSC, nitrogen); $T_{d,onset} = 189$ °C (TGA, nitrogen). The viologen-grafting ratio is estimated to be 50% from ^{1}H NMR analysis.

General Characterization Methods. ^{1}H NMR spectra were recorded on a Bruker ARX 400 MHz spectrometer using tetramethylsilane as an internal standard. The chemical shifts are reported in ppm. IR spectra were recorded on a Nicolet Magna 750 Fourier transform infrared spectrometer. Gel permeation chromatographic (GPC) measurements were performed with a Waters 2410 refractive index detector at room temperature. Tetrahydrofuran was used as the eluent with a flow rate of 1.0 mL/min. All GPC data were calibrated with linear polystyrene standards. Thermogravimetric analysis (TGA) was performed on a TA Q600 instrument at a heating rate of 10 °C/min in nitrogen. Differential scanning calorimetry (DSC) was recorded with a Perkin-Elmer Pyris I DSC in nitrogen. UV−vis absorption spectra were recorded with a Varian Cary 1E spectrometer. Photoluminescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. Optical rotations were measured at 20 °C using a Jasco model P-1030 polarimeter. Circular dichroic spectra were recorded on a Jasco J-810 spectropolarimeter.

Cyclic voltammetry (CV) was conducted using a CHI 600C voltammetric analyzer. The experiments were performed at room temperature in DMF solutions containing 0.1 M tetrabutylammonium perchlorate (NBu$_4$ClO$_4$) as the supporting electrolyte at a scan speed of 50 mV/s. The working electrode was a glassy carbon disk (diameter 2 mm, freshly polished) for voltammetry. A platinum stick (1 mm thick) was used as the counter electrode. The reference electrode was AgCl/Ag. All potentials reported here are potentials measured versus the AgCl/Ag electrode.

Redox-Based UV−vis and CD Spectroscopy. Redox-based spectroscopic measurements were made chemically using an OTTLE-type quartz cell with an optical path length of 1 mm and in nitrogen-saturated DMF. A soldering tin-attached Pt grid of size 6 × 20 mm^2 and 800 mesh/cm^2 was used as the reducing agent. During experiments, the soldering tin together with the Pt grid was immersed into the solution and the reduction occurred on the surfaces of both the tin particle and the Pt grid. Oxidation of reduced sample solutions was readily done by shaking the cell in air.

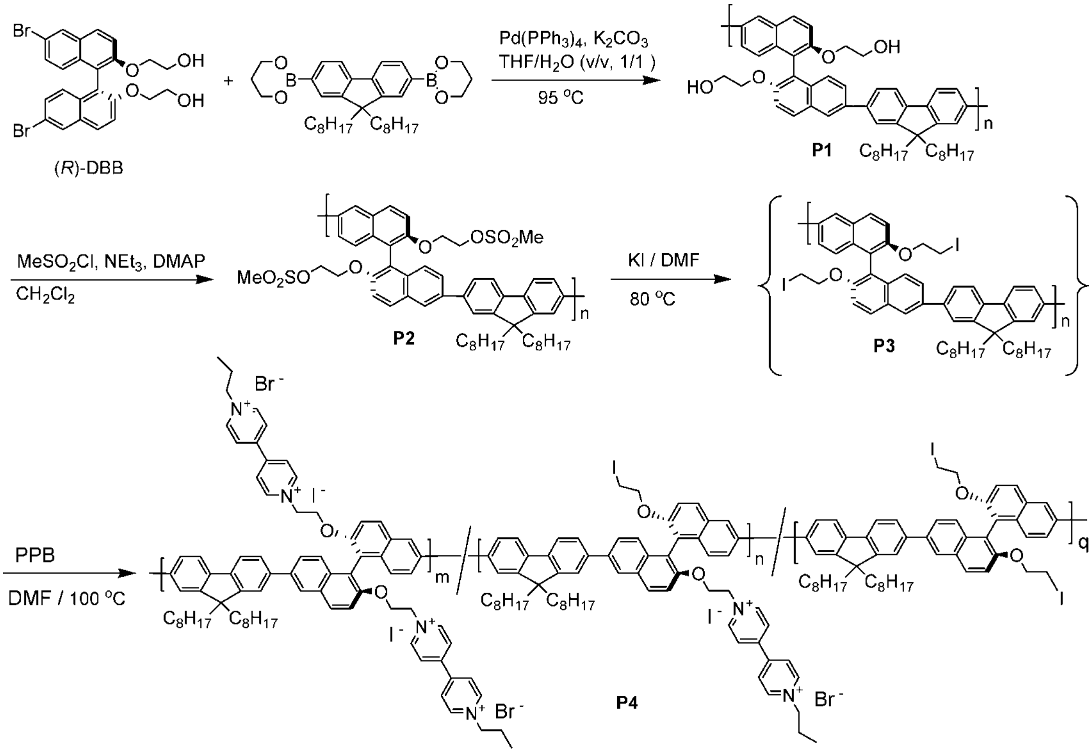
Results and Discussion

Synthesis. 1,1′-Binaphthyl (BN)-based chiral conjugated polymers have been extensively studied by Pu et al.[3] for their potential use in asymmetric synthesis and chiral recognition. Most polymers in their study exhibited secondary chirality (e.g., major groove with cisoid conformation[3a]) due to the rigid main-chain structure as well as the strong twisting power of BN at both the 2,2′ and the 6,6′ positions. In our study, the axial dissymmetry of BN at both the 2,2′ and the 6,6′ positions is utilized. On one hand, electrochromic chromophores, i.e., viologens, are introduced to the 2,2′ positions to allow for a vicinal dissymmetric spatial arrangement of viologens so that large chiroptical switching due to the electrochromism of viologens can be achieved;[10] on the other hand, polymerization at the 6,6′ positions would induce a secondary chiral conformation of the polymer main chain, which may impose a chiral environment for viologens from adjacent repeat units, allowing for additional asymmetric electronic interaction between viologens.

To prepare 1,1′-binaphthyl-based optically active polymer bearing viologens in the side chains viologen-containing 6,6′-bibromo-1,1′-binaphthyl monomer, i.e., (*R*)-6,6′-bibromo-2,2′-bis[2-(1′-propyl-4,4′-bipyridinium-1-yl)ethoxy]-1,1′-binaphthyl tetrabromide [(*R*)-BBEBPP], was first prepared by the quarternization reaction between PPB and (*R*)-BBEB that was in turn prepared by the bromination reaction of (*R*)-BEB using bromine (Scheme 1). However, direct polymerization of (*R*)-BBEBPP with 9,9-dioctylfluorene-2,7-bis(trimethyleneborate) (DFBT) via the Pd-catalyzed Suzuki coupling reaction was unsuccessful due to the liability of viologen to bases such as potassium carbonate, sodium hydroxide, and sodium bicarbonate. Thus, (*R*)-6,6-bibromo-2,2′-bis(2-hydroxyl ethoxy)-1,1′-binaphthyl [(*R*)-DBB] was prepared according to the literature method[12] and polymerized with DFBT to first yield a high molecular weight, hydroxyl-containing optically active polymer **P1** ($M_n = 4.4 \times 10^4$, DP ≈ 58), which was subsequentially methylsulfonated (**P2**), iodinated (**P3**), and reacted with PPB to give the viologen-containing optically active polymer **P4** (Scheme 2). Chemical structures of the resulting polymers **P1−3** were confirmed by NMR and IR spectroscopies, according to which the methylsulfonation and iodination efficiency of **P2** and **P3**, respectively, was determined to be 100% (see Supporting Information, Figures S1−S3).

Since the iodinated polymer **P3** exhibited poor solubility after it was isolated and dried, synthesis of **P4** was carried out via a one-pot synthetic method, that is **P2** was first reacted with potassium iodide to produce **P3** that without separation further reacted with PPB to give the target polymer at a moderately high yield of 72%. The ^{1}H NMR spectrum of **P4** clearly shows peaks associated with viologen protons (Figure 1), indicating successful grafting of viologens. Different from **P1−3** whose ^{1}H NMR spectra showed relatively well-resolved resonant peaks, **P4** showed much broadening of all the NMR peaks, suggesting a high viologen grafting ratio and a pronounced shielding effect of it to the backbone. By comparison between the integral of all the aromatic protons (I_A) and the integral of the aliphatic protons on the fluorene units and on viologens (I_F) ($I_A/I_F = 29/50 = 0.6$), a viologen grafting ratio of ~50%, i.e., there is on average one viologen on each repeat unit (calcd $I_A/I_F = 0.6$), was estimated.

Scheme 2. Synthesis of Optically Active Polymer P4



Thermal Properties. Thermal properties of the resulting polymers, i.e., **P1**, **P2**, and **P4**, were characterized by TGA and DSC. From Figure 2 it can be seen that the hydroxyl-containing polymer **P1** exhibited very good thermal stability up to 380 °C in nitrogen, while the methylsulfonated polymer **P2** and viologen-containing polymer **P4** showed lower on-set temperatures for decomposition (i.e., $T_d = 232$ °C for **P2** and 189 °C for **P4**). Both **P2** and **P4** exhibited a two-stage decomposition process with the second decomposition occurring at around 380 °C, where **P1** starts to decompose. In the first decomposition stage (e.g., at 380 °C) **P2** showed a weight loss of 20 wt %, attributable to loss of methylsulfonate groups (calcd wt % = 20%). Similarly, **P4** exhibited a weight loss of 28 wt % at 380 °C, which should be attributable to decomposition of viologen groups.[17] On the basis of such a weight loss, a viologen-grafting ratio of 42% was derived, which is a bit lower than the result of NMR analysis. DSC investigations found a high glass-transition temperature (T_g) of 227 °C for **P1**. **P2** and **P4** exhibited no T_g before their thermal decomposition temperatures at around 200 °C.

UV–vis and Photoluminescent Properties. The solubility of the resulting optically active polymers **P1–4** was tested in different solvents. **P1** and **P2** exhibited good solubility in common organic solvents such as tetrahydrofuran, chloroform, and DMF, while **P3** showed only partial solubility in these

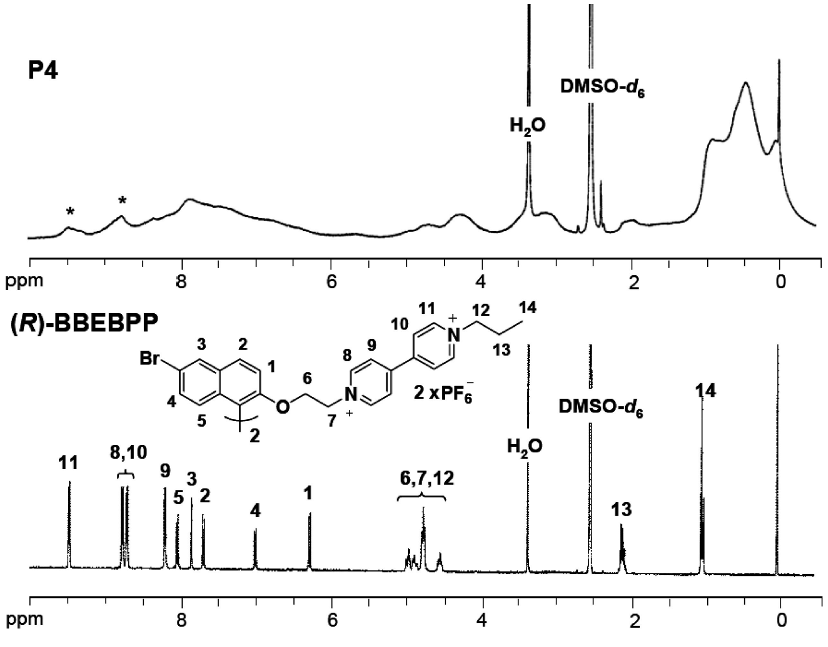


Figure 1. ^{1}H NMR (400 MHz) spectra of (*R*)-BBEBPP and polymer **P4** in DMSO-d_6.

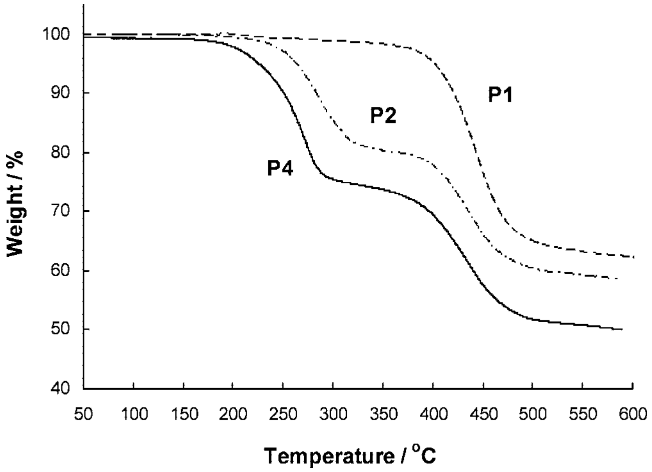


Figure 2. TGA curves of **P1**, **P2**, and **P4** in nitrogen. The heating rate is 10 °C/min.

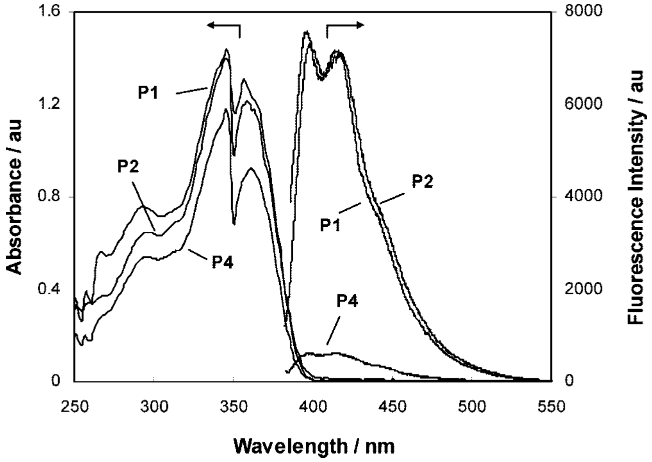


Figure 3. UV−vis absorption and photoluminescent spectra of **P1**, **P2**, and **P4** in DMF. The solution concentrations were the same at 3.0 × 10^{-5} M. The emission spectra were recorded at an excitation wavelength of 310 nm.

solvents after drying. After introduction of viologens to the side chains, **P4** appeared to be insoluble in chloroform and THF but readily soluble in polar aprotic solvents such DMF and *N*,*N*-dimethylacetamide. **P4** in DMF can be easily spin cast into thin films. Figure 3 displays the UV−vis absorption spectra of **P1**, **P2**, and **P4** in DMF solution. All of them show very similar UV−vis absorptions in the spectral range of 300−400 nm with two maximal absorptions (λ_{max}) at ca. 346 and 360 nm. In comparison with monomers, i.e., DBB (λ_{max} = 226 nm) and DFBT (λ_{max} = 316 nm), distinctive red shifts in absorption (>30 nm) were observed for these polymers due to the more extended conjugated structure of the repeat units. Similarly, a red shift in photoluminescence was also observed for **P1** and **P2** (λ_{em} = 399 and 417 nm) relative to those of DBB (λ_{em} = 366 nm) and DFBT (λ_{em} = 336 nm). **P4** shows a very similar photoluminescent spectrum with those of **P1** and **P2** but with a pronounced quenching effect due to introduction of electron-deficient viologen groups. A photoinduced intramolecular electron transfer from the fluorescent polymer backbone to viologen was believed to be responsible for such a quenching.[18] Although a mixture of **P2** and 1,1′-dipropyl 4,4′-bipyridine (1:1, wt/wt) in DMF solution also showed a decrease in the intensity of photoluminescence, the quenching was much less effective (see Supporting Information, Figure S4).

Redox-Based UV−vis Spectroscopy. The redox properties of **P4** were first investigated in DMF solution by cyclic voltammetry (CV). As shown in Figure 4, two redox processes were found at $E_{1/2}$ = −0.30 and −0.84 V in the first redox scan, corresponding to the single-electron reduction processes of viologen from the double cationic (V^{2+}) state to the radical cation (or violene, $V^{+\bullet}$) state and from the violene state to the neutral semiquinone (V) state, respectively.[19] In comparison with the redox pattern of (*R*)-**1** ($E_{1/2}$ = −0.40 and −0.85 V),[10] **P4** exhibited a lower potential for the first reduction and a comparable potential for the second reduction. The readiness in reduction of **P4** to the violene state is apparent in that the polymer changed color from light yellow to dark purple during the vacuum drying process. In contrast to (*R*)-**1**, which has good redox reversibility,[10] the redox processes of **P4** appear to be poorly reversible during the CV measurements, as evidenced by the disappearance of the first reduction peak in the subsequent redox scans. Since yellow precipitate was observed on the working electrode after the CV measurement, which can be slowly redissolved into the solution upon standing for a long period of time (e.g., 2 days), the irreversibility of the redox properties may be accounted for by the poor solubility of the polymer with viologens in the semiquinone state in DMF. Due to precipitation of the polymer on the working electrode, effective reduction of cationic viologens in the solution was depressed.

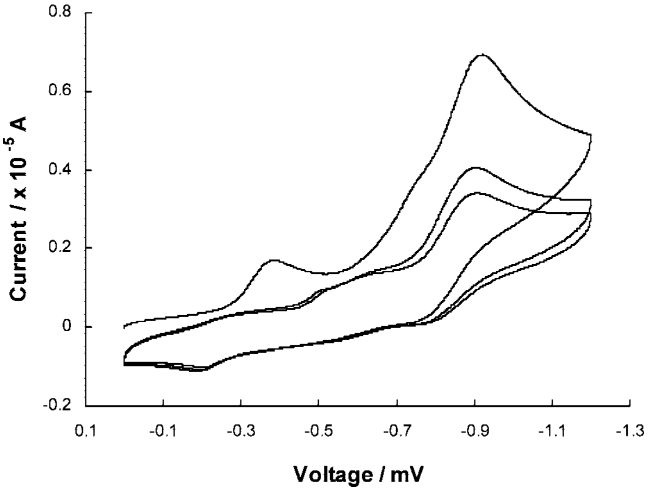


Figure 4. Cyclic voltammogram of **P4** in 0.1 M Bu_4NClO_4/DMF solution ($c = 1.5 \times 10^{-4}$ M) with a scan speed of 50 mV/s: working electrode, glassy carbon; counter electrode, Pt wire; reference electrode, AgCl/Ag.

UV−vis spectroelectrochemistry of **P4** in Bu_4NClO_4/DMF at a reducing potential of −0.5 V was also unsuccessful due to an unavoidable over reduction of viologens to the semiquinone state and precipitation of the polymer. To overcome this problem, chemical reduction of **P4** (V^{2+}) to the violene state ($V^{+\bullet}$) was conducted. In the study both zinc powders and tin particles were found to be effective in reducing the light yellow **P4** in DMF solution to the dark blue violenes. However, due to the low diffusion rate of high M_w **P4** ($V^{+\bullet}$) in an undisturbed solution, the blue color of violenes was confined within a small area around the reducing agents, which hampered direct spectroscopic measurements of the solution. To improve the vertical color uniformity within the cell and increase the contact area of the reducing agent with the solution, herein, an inert Pt grid bearing soldering tin was used as the reducing agent. During the experiment the Pt grid together with the soldering tin was immersed into the solution and the color change of the solution occurred on both surfaces of the tin particle and the Pt grid. Figure 5 shows the redox-based chromic behavior of **P4** in DMF solution. Upon reduction to the violenes, **P4** exhibited a drastic color change from light yellow to dark blue accompanied by

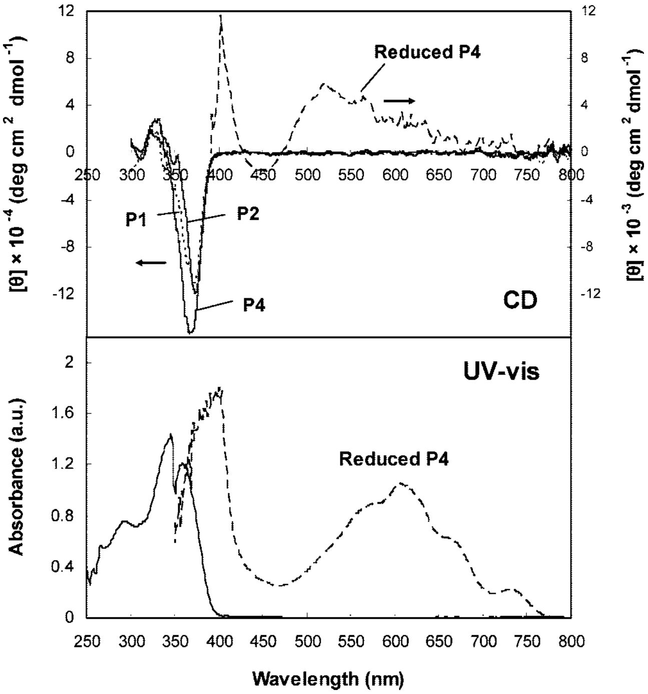


Figure 5. UV−vis (bottom) and CD (top) spectroelectrochemistry of **P4** in DMF ($c = 10$ mg/mL). The chemical reduction was carried out by immersing a Pt grid soldered with a tin particle into nitrogen-saturated solution for 2 h. The mean molar ellipticity per repeat unit ([θ]) of reduced **P4** is calculated using a concentration estimated from the UV−vis absorbance of reduced **P4** solution and the known extinction coefficients of violene.[19a] The CD spectra of **P1** and **P2** in DMF solutions are also shown in the top figure.

the appearance of two new strong absorption bands at around 394 and 604 nm. No obvious absorption band at 537 nm due to epimerization of violenes was observed for **P4**. In contrast to (*R*)-**1**, which changed color of solution rapidly (e.g., in minutes) upon chemical reduction using soldering tin on Pt grid,[10] **P4** in DMF took more than 1 h (e.g., 1.5−2 h) to change from light yellow to dark blue. This can be attributed to the slow diffusion rate of high M_w polymer chains. Indeed, it was observed in our study that when low M_w **P4** (e.g., $M_n \approx 5000$) was subjected to chemical reduction, the color change took less time, 15−30 min.

Chiroptical Properties. Given the nearly insurmountable barrier to rotation about the σ bond of 1,1′-binaphthyl-2,2′-diyls,[20] no racemization of the chiral binaphthyl units in the polymer backbones should be expected during preparation. In comparison with the specific rotations of monomers {e.g. $[\alpha]_D^{20} = +26.0°$ for (*R*)-BBEBPP and −49.3° for (*R*)-DBB}, all polymers (i.e., **P1**, **P2**, and **P4**) exhibited much larger $[\alpha]_D^{20}$ in the range from −260° to −460°, suggesting a chiral conformation of the polymer main chain. To further confirm the main-chain chirality of the polymers, mean molar optical rotations per repeat unit ($[m]_D^T$, deg cm^2 mol^{-1}) were calculated and compared with molar rotations of (*R*)-BBEBPP and (*R*)-DBB. As expected, the polymers **P1**, **P2**, and **P4** exhibited similar $[m]_D^T$ values in the range from −3128° to −3516°, which are significantly larger than the molar rotations of (*R*)-BBEBPP ($[\phi]_D = +383.8°$) and (*R*)-DBB ($[\phi]_D = -263°$). Meanwhile, circular dichroism (CD) investigations of **P1**, **P2**, and **P4** in DMF solutions also revealed similar strong CD signals ($[\theta] = -1.1$ to -1.5×10^5 deg cm^2 dmol^{-1}) in the main-chain absorption band (i.e., 300−400 nm) (Figure 5), confirming a secondary chirality of the polymers. Given the *R* configuration of 1,1′-binaphthyls and the negative Cotton effect at ca. 370 nm, a major-groove cisoid main-chain conformation was assigned to the polymers.[3a]

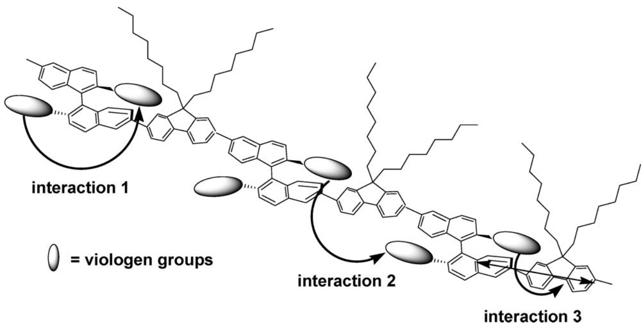


Figure 6. Illustration of possible electronic interactions contributing to the CD signals of **P4** in the 400 and 600 nm absorption bands.

Figure 5 also shows the CD spectrum of **P4** after chemical reduction to the violene state. In comparison with the CD spectrum of **P4** before reduction, two new positive CD bands corresponding to violene absorptions at around 404 and 520 nm were observed with mean residue ellipticities per repeat unit ([θ]) being 1.2×10^4 and 5.9×10^3 deg cm^2 dmol^{-1}, respectively. Rotatory strengths (*R*) of these two CD bands were calculated according to the Rosenfeld equation,[8c] which are $R = 8.83 \times 10^{-40}$ cgs at 520 nm and $R = 3.11 \times 10^{-40}$ cgs at 404 nm. In contrast to (*R*)-**1**, which showed strong negative CD signals at 420 nm ($[\theta] = -8.67 \times 10^4$ deg cm^2 dmol^{-1}) and 600 nm ($[\theta] = -2.40 \times 10^4$ deg cm^2 dmol^{-1}), **P4** exhibits weaker CD signals with opposite sign, indicating a different exciton coupling mechanism. Figure 6 illustrates three possible interchromophoric interactions contributing to the CD signals: (1) viologen−viologen interactions within a single repeat unit; (2) viologen−viologen interactions from adjacent repeat units; and (3) viologen−polymer backbone interactions. Given that the viologen-grafting ratio is about 50% and each repeat unit contains only one viologen on average, interactions 2 and 3 may play the major role in yielding the CD signals of **P4**. A nonoptimized spatial arrangement of viologens from adjacent repeat units and the mismatch of energy levels between the polymer backbone ($\lambda_{max} = 346$ and 360 nm) and violene ($\lambda_{max} = 394$ and 601 nm) may be used to account for the different CD spectrum of **P4** from that of (*R*)-**1**.

Chiroptically Switching Property. Although the CD signals of **P4** ($V^{+\bullet}$) are weaker than those of (*R*)-**1** ($V^{+\bullet}$), they are comparable with many other optically active systems such as polyacetylenes[21] and polyisocyanates.[22] In particular, the pronounced changes in CD signals between nearly zero for **P4** (V^{2+}) to 1.2×10^4 deg cm^2 dmol^{-1} at 404 nm or 5.9×10^3 deg cm^2 dmol^{-1} at 520 nm for **P4** ($V^{+\bullet}$) justify the good potential of **P4** as redox-based chiroptical switches once the CD signals can be efficiently modulated. The redox-driven chiroptically switching properties of **P4** were investigated in DMF solution. Figure 7 shows the CD spectra of **P4** that was chemically reduced to the violene state ($V^{+\bullet}$), oxidized back to the double cationic state (V^{2+}), and rereduced to the violene state. Both the first and second reductions were effected by immersing a Pt grid bearing a soldering tin particle into nitrogen-saturated sample solution for 2 h. Oxidation was done by shaking the sample cell in the air. From the figure it can be seen that the CD signals associated with violene absorptions became distinctive upon first reduction, completely disappeared after oxidation, and regenerated upon second reduction. The CD spectrum reproduced from the second reduction agrees well with that from the first reduction, indicating a good switching property. Figure 8 shows the reversible changes in the CD signal at 520 nm upon multiple redox cycles. No deterioration of the sample solution (e.g., precipitation) or CD signals was observed after five redox cycles.

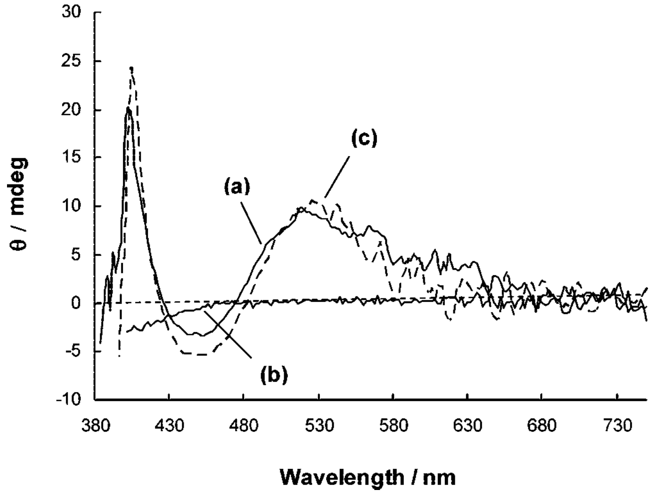


Figure 7. CD spectral changes of **P4** upon redox cycle: (a) first reduction and (c) second reduction of **P4** solution in DMF ($c = 10$ mg/mL) carried out by immersing a Pt grid soldered with a tin particle into nitrogen-saturated solution for 2 h; (b) oxidation of the reduced **P3** by shaking the cell in air.

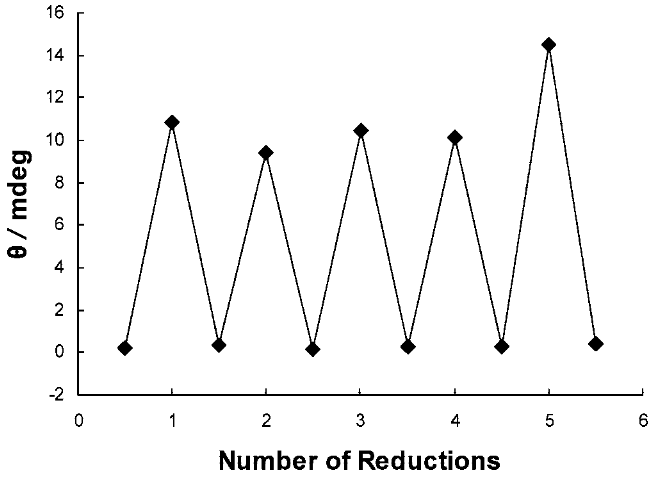


Figure 8. Redox-based chiroptical switching of **P4** in CD signals at 520 nm. For each redox cycle reduction of **P4** solution in DMF ($c = 10$ mg/mL) was accomplished by immersing a Pt grid soldered with a tin particle into nitrogen-saturated solution for 2 h. Oxidation of reduced **P4** was done by shaking the cell in air.

Conclusion

A novel type of redox-based chiroptically switching polymer containing axially dissymmetric 1,1′-binaphthyls in the backbone and electrochromic viologens in the side chain was designed and prepared. The polymer exhibited significantly larger optical rotation than the monomer and a strong negative Cotton effect at the main-chain absorption band, indicating the secondary chirality of the polymer (i.e., major-groove cisoid main-chain conformation). Redox-based spectroscopic studies showed that the polymer changed color distinctively upon chemical reduction to violenes. Two new positive CD bands associated with violene absorptions were observed for the polymer, which can be reversibly switched in magnitude between one measuring nearly zero to moderately intense signals (e.g., 1.2×10^4 deg cm^2 dmol^{-1} at 404 nm or 5.9×10^3 deg cm ^{2} dmol^{-1} at 520 nm) upon redox cycles. Different from our expectation that introduction of viologens into a polymer with main-chain axial chirality would lead to enhanced chiroptical properties relative to those of model compound (*R*)-**1**, **P4** exhibited some weaker CD signals. The lack of strong viologen−viologen interactions due to the low viologen-grafting ratio (i.e., ~50%) and the weak viologen−backbone interactions are believed to be accountable for such an unexpected chiroptical property.

Acknowledgment. N.S. is thankful to Prof. Q. Zhou for constructive discussions. We are thankful for the financial support from the National Natural Science Foundation of China (grant no. 20774002) and the SRF for ROCS, SEM.

Supporting Information Available: ^{1}H NMR (400 MHz) spectra of polymers **P1**, **P2**, and **P3**; photoluminescent spectra of mixtures of **P2** and 1,1′-dipropyl-4,4′-bipyridinium bromide. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA8014646