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Electrically-Driven Chiroptical Switches Based on Axially Dissymmetric 1,1′-Binaphthyl and Electrochromic Viologens: Synthesis and Optical Properties

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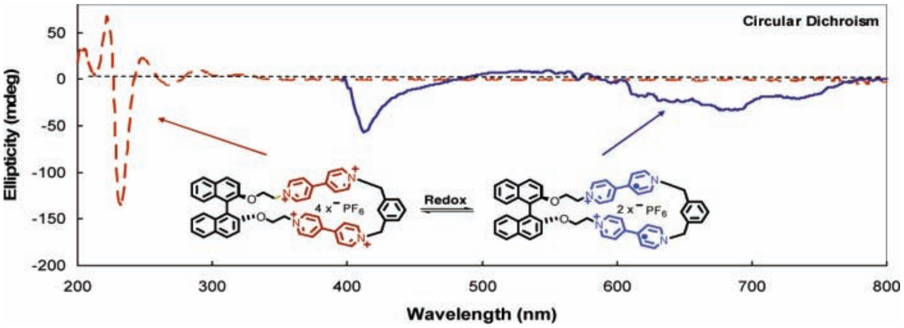
ABSTRACT



A novel redox type of chiral molecular switch based on axially dissymmetric 1,1′-binaphthyl and electrochromic 4,4′-bipyridinium exhibits drastic changes in absorption and circular dichroism spectra upon electrochemical redox reaction and is fully characterized for the electrically driven chiroptical switching properties.

Chiroptical switches refer to a class of chiral materials whose chiroptical properties (e.g., circular birefringence and circular dichroism) can be reversibly modulated under external stimuli such as light irradiation, heat, pH, chemicals, and electric fields.[1−4] Due to the uniqueness of the chiroptical properties, chiroptical switching materials are expected to find niched polarization-related photonics applications such as data storage, optical switches, and light modulators. To date, chiroptical switches triggered by photoisomerization or photochromism have been extensively explored due to

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the readiness in operation and the well-documented photoisomerizable systems such as azobenzenes, diarylethenes, spiropyrenes, fulgides, and overcrowded alkenes.[1,5] In contrast, electrically driven chiroptical switches based on the electrochromism of chiral systems are relatively less known,[4] although the drastic changes in absorption for electrochromic systems[6] may be utilized to achieve efficient chiroptical switches.

Herein, we present a novel type of electrically driven, chiroptical switching molecules (*R*)-**1** and (*R*)-**2** based on the axially dissymmetric 1,1′-binaphthyl and the electrochromic 4,4′-bipyridinium (or viologen). Such chiral molecules are designed to take advantage of the strong chiral force of 1,1′-binaphthyl-2,2′-diyls[7] and the well-studied electrochromic behavior of viologens.[6,8,9] (*R*)-**1** and (*R*)-**2** differ from each other in terms of the open-ring and the cyclic configuration. Given that chiroptical properties depend on both absorption properties and dissymmetric spatial arrangement (e.g., distance and orientation) of interacting chromophores,[10,11] different chiroptical switching properties are expected for (*R*)-**1** and (*R*)-**2**.

The synthesis of (*R*)-**1** and (*R*)-**2** was accomplished by reacting benzyl bromide and 1,3-dibromomethyl benzene, respectively, with (*R*)-BEBP that was in turn prepared by the reaction between (*R*)-2,2′-dibromoethyloxy-1,1′-binaphthyl [(*R*)-BEB][12] and 4,4′-bipyridine (Scheme 1, see Supporting Information). The counter anions of (*R*)-**1** and (*R*)-**2** were exchanged from bromide to hexafluorophosphate to achieve a good organosolubility such as in acetonitrile and *N*,*N*′-dimethylformamide (DMF). Both (*R*)-**1** and (*R*)-**2** were obtained as light-yellow powders. No melting point was detected for them below 250 °C. The chemical structures of (*R*)-**1** and (*R*)-**2** were confirmed by ^{1}H NMR, ^{13}C NMR, and mass spectroscopy (see Supporting Information).

Scheme 1. Synthesis of Chiral Molecules (*R*)-**1** and (*R*)-**2**

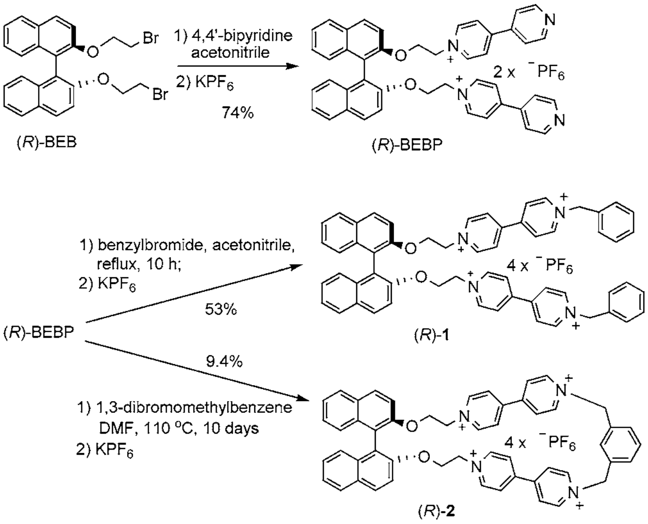

Figure 1 shows the UV−vis absorption spectra of (*R*)-BEB, (*R*)-**1**, and (*R*)-**2** in acetonitrile. For comparison, the absorption spectrum of 1,1′-dipropyl-4,4′-bipyridinium salt of hexafluorophosphate (BPP) in acetonitrile is also displayed. From the figure it can be clearly seen that the UV−vis absorptions of (*R*)-**1** and (*R*)-**2** are mainly composed of the absorptions of constituting components, i.e., (*R*)-BEB at 229 nm and BPP at 267 nm. A weak absorption at 400 nm was observed for BPP, (*R*)-**1**, and (*R*)-**2** and may be attributed to the presence of a slight amount of radical cations (or violenes, the semireduced state of viologen) resulting from the photoinduced electron transfer of samples during the UV−vis measurements or sample storage. A diffused absorption band in the range of 360−530 nm was discernible for (*R*)-**1** and (*R*)-**2** but absent in the spectra of (*R*)-BEB and BPP. An intramolecular charge transfer from the binaphthyl to the viologens may account for such an absorption behavior.[13]

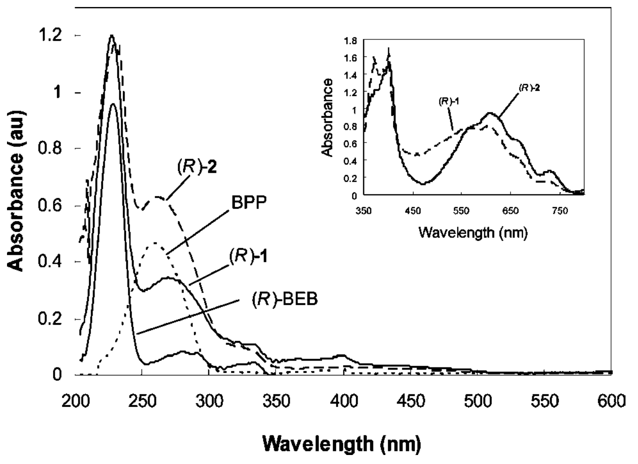

Figure 1. UV−vis absorption spectra of (*R*)-**1**, (*R*)-**2**, (*R*)-BEB, and BPP in acetonitrile. The solution concentrations were in the range of $1-3 \times 10^{-4}$ M. The intensities were adjusted for a better comparison. (Inset) UV−vis absorption spectra of (*R*)-**1** and (*R*)-**2** in DMF after electrochemical reduction to the violene states.

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The redox properties of (*R*)-**1** and (*R*)-**2** were investigated in DMF solution by cyclic voltammetry. Since both (*R*)-**1** and (*R*)-**2** contain two viologen units and each viologen units can undergo a two-step reduction, a total of four steps in reduction, each involving a one-electron process, may be expected. Figure 2 shows the cyclic voltammograms of (*R*)-**1** and (*R*)-**2**. Only two redox processes at $E_{1/2} = -0.40$ and -0.85 V were found for the open-ring tetracation (*R*)-**1**, comparable to the redox pattern of BPP, suggesting that the two viologens behave individually and do not interact with each other to a great extent. In contrast, the cyclic tetracation (*R*)-**2** exhibited three redox processes at $E_{1/2} = -0.37$, -0.74, and -0.86 V, with the first reduction that corresponds to the reduction to the double radical cation state occurring more easily by 30 mV than that for (*R*)-**1**. The second and the third reductions, corresponding to the reductions to the radical cation−neutral and neutral−neutral state, respectively, differ from each other by about 120 mV. Given the similar chemical constitutions of (*R*)-**1** and (*R*)-**2**, such a different redox pattern can be attributed to the intramolecular interactions between the two viologens in (*R*)-**2**, which contribute to the stabilization of radical cations and the radical cation−neutral state. Hünig et al.[9] and Stoddart et al.[8] observed similar redox patterns for their cyclophanes containing two viologen units.

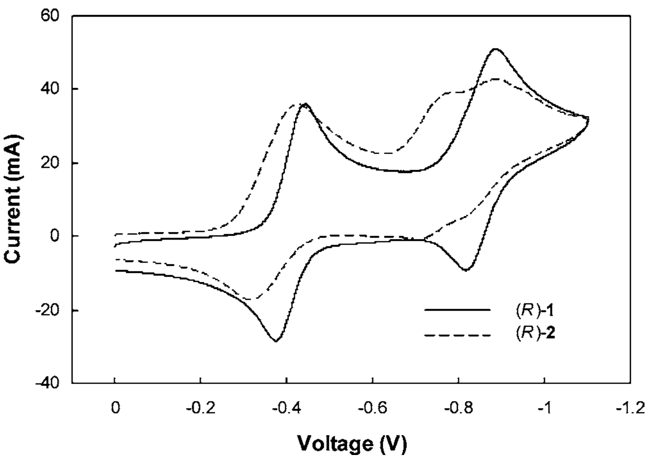

Figure 2. Cyclic voltammograms of (*R*)-**1** and (*R*)-**2** measured in 0.1 M Bu_4NClO_4/DMF. Working electrode: glassy carbon; counter electrode: Pt wire; reference electrode: AgCl/Ag.

The electrochromic properties of (*R*)-**1** and (*R*)-**2** were examined by UV−vis spectroscopy in DMF solutions (Figure 1, inset). Upon electrochemical reduction to the radical cations, drastic changes in absorption took place with the appearance of two strong absorption bands at around 402 ($\epsilon = 41800$) and 610 nm ($\epsilon = 13900$).[14] The same change in absorption can also be readily achieved by bubbling nitrogen slowly into the solution or by adding reducing agents such as zinc powders or tin particles. Since chiroptical properties of a chiral molecule (e.g., optical rotation dispersion and circular dichroism) depend greatly on the absorption properties,[10,11] such a drastic change in absorption is expected to lead to a significant change in chiroptical properties once the viologens are placed dissymetrically in proximity, such as in the case of (*R*)-**1** and (*R*)-**2**. Hünig et al.[9] studied in detail the pimerization of violenes in different systems and ascribed pimerized violenes to an absorption at 537 nm. In our study, no obvious pimerization of violenes in cyclic (*R*)-**2** was observed. In contrast, intermolecular pimerization of violenes occurred for (*R*)-**1** at a high concentration of radical cations, as evidenced by a blue shift of the maximum absorption from 610 to 548 nm that took place for the low-energy band as the electrochemical reduction of (*R*)-**1** ($c = 0.28$ mM) lengthened to over 3 min (see Supporting Information).

The chiroptical properties of (*R*)-**1** and (*R*)-**2** were examined using a polarimeter and a CD spectrometer. (*R*)-**1** has an optical rotation of $[\alpha]_D = -39.5°$ (0.4, MeCN), whereas (*R*)-**2** has an opposite sign of the optical rotation of $[\alpha]_D = +55.0°$ (0.4, MeCN). An effort to measure the optical rotation of the violenes of (*R*)-**1** and (*R*)-**2** failed due to the strong absorption at the measurement wavelengths (i.e., 365−598 nm). As shown in the CD spectrum (Figure 3), (*R*)-**1** exhibited a strong exciton couplet centered at 227 nm ($[\theta] = 5.0 \times 10^5$ deg·cm^2/dmol), corresponding to the binaphthyl unit, and a relatively weak exciton couplet at 268 nm ($[\theta] = 4.2 \times 10^4$ deg·cm^2/dmol, inset of Figure 3), corresponding to the absorption of viologens. (*R*)-**2** exhibited a similar pattern of the CD spectrum, but with very different intensities. The CD intensities of (*R*)-**2** at the binaphthyl and the viologen absorption regions are about 12 and 20 times, respectively, higher than those for (*R*)-**1**. From the Kirkwood's coupled oscillator model,[11] it is known that the intensity of CD signals depends greatly on the dissymmetric spatial arrangement of interacting chromophores, in particular

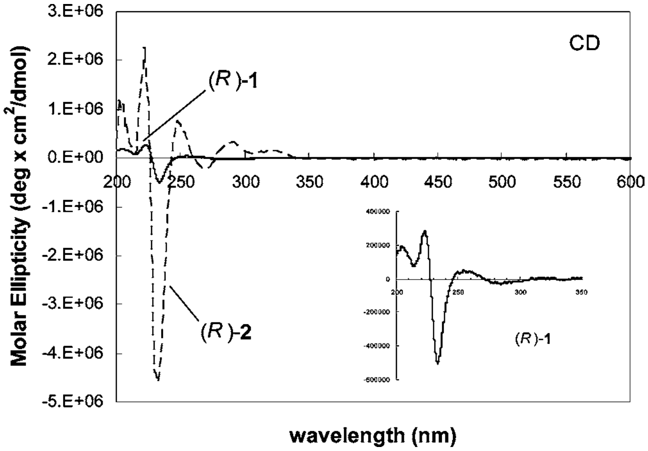

Figure 3. CD spectra of (*R*)-**1** and (*R*)-**2** in acetonitrile. (Inset) Enlarged CD spectrum of (*R*)-**1**.

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on the distance and the relative twisting angles between chromophores. Thus, the differences in the CD spectrum between (*R*)-**1** and (*R*)-**2** could be attributed to a more appropriate positioning of viologen moieties in (*R*)-**2** due to the rigid cyclic structure.

Upon electrochemical reduction of (*R*)-**1** and (*R*)-**2** at a potential of −0.5 V to the violenes, two new CD bands appeared at the positions similar to the absorption bands at 400 and 600 nm, respectively (Figure 4). As the reduction time extended, the intensity of these CD signals increased due to the increase of violene concentration. In comparison between (*R*)-**1** and (*R*)-**2**, the latter exhibited much stronger CD signals than the former at the same reduction time, presumably due to a more favorable dissymmetric arrangement of violenes. Considering that the magnitude of signal change is one of the important factors for switching applications, the cyclic tetracation (*R*)-**2** appears to be superior than the open-ring (*R*)-**1** for use as chiroptical switches.

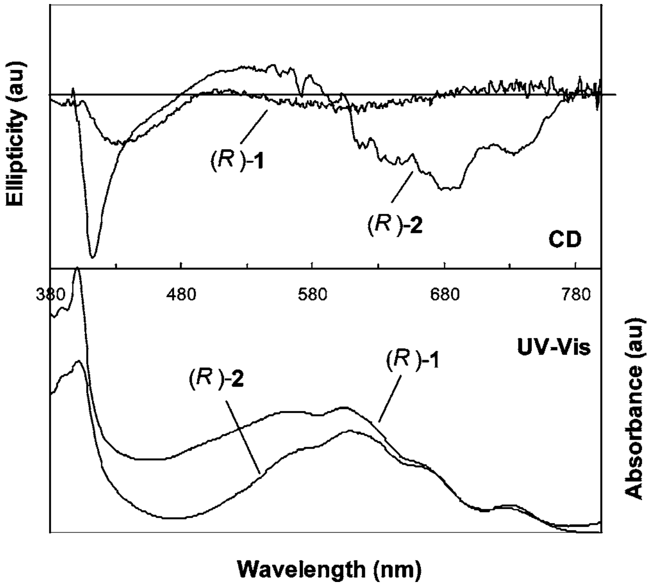

Figure 4. CD and UV−vis absorption spectra of radical cations of (*R*)-**1** and (*R*)-**2** obtained by electrochemical reduction in 0.1 M Bu_4NClO_4/DMF. The concentrations of sample solutions were around 2.8 mM. Working electrode: Pt grid; counter electrode: Pt wire (0.5 mm diameter); reference electrode: AgCl/Ag.

The electrically driven chiroptical switching property of (*R*)-**2** was demonstrated in DMF solution. As shown in Figure 5, the reduction of (*R*)-**2** to the violene by applying a voltage of −0.5 V for 5 s led to a deep blue color accompanied by the appearance of two new CD bands at around 400 and 660 nm. When the resulting blue solution was disturbed by shaking in the air, the original light-yellow color recovered, and the CD signals disappeared. Reapplication of the negative voltage (−0.7 V, 1 min) to the cell regenerated the blue color as well as the CD signals at the low-energy bands. These results indicate that it is possible to modulate the chiroptical properties of the resulting new chiral systems by applying a bias voltage and monitoring the CD signals in the visible region, e.g., at 400 and 660 nm.

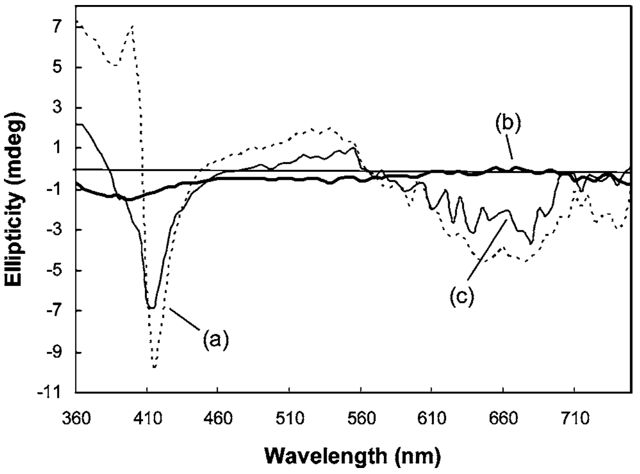

Figure 5. Demonstration of electrochemical switching of CD signals of (*R*)-**2** in 0.1 M Bu_4NClO_4/DMF. (a) First reduction at −0.5 V for 5 s; (b) tetracation recovered by shaking the cell in the air; (c) second reduction at −0.7 V for 1 min.

In summary, novel types of chiroptical switching molecules based on axially dissymmetric 1,1′-binaphthyl and electrochromic viologens were prepared and characterized. These compounds exhibited reversible, drastic changes in their absorption and CD spectra when electrochemically reduced to the violene state. The readiness in reading out the chiroptical changes between the two redox states in the visible region (e.g., from $[\theta] \approx 0$ deg·cm^2/dmol for the tetracation state to $[\theta] \approx -1.6 \times 10^5$ deg·cm^2/dmol[15] for the double radical cation state at 660 nm) demonstrates a high potential for electrically driven chiroptical switches.

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Supporting Information Available: Synthetic procedures and characterization data for (*R*)-**1** and (*R*)-**2**; time dependence of UV−vis spectroelectrochemistry of (*R*)-**1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[15] Molar ellipticity caculated for (*R*)-**2** that was reduced in 0.1 M Bu_4NClO_4/DMF solution for 57 s at a potential of −0.5 V. The concentration of the double radical cation in the solution was estimated from the UV−vis absorptions of the sample at 402 nm and 610 nm and by using the extincition coefficients reported in reference 14.