

VISIBLE AND NEAR-INFRARED CHIROPTICAL GELS CONTAINING ELECTROCHROMIC ANTHRAQUINONE IMIDE GROUPS*

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Abstract A cholesterol-based organogelator bearing an anthraquinone imide (AQI) group was synthesized and characterized. It self-assembled into chiral gels in acetonitrile at low concentrations, which displayed a combination of electrochromic and chiroptical properties. Upon electrochemical reduction at -700 mV, the gel exhibited new absorption bands at around 820 nm corresponding to $\pi^*-\pi^*$ (SOMO $\rightarrow$ LUMO) transitions of the radical anion of AQI and strong negative Cotton effects in the same spectral region. With further reduction at -1000 mV, a new CD band with a negative Cotton effect in the range from 500 nm to 800 nm appeared concomitant with the variation of absorption spectrum. Thus, with the use of electrochromic AQI chromophore as a switch-responsive unit and the stable gel of compound *N*-[3 β -cholest-5-en-3-yl *N*-(2-aminoethyl) carbamate] anthraquinone-2,3-dicarboxylic imide as a chiral scaffold, a redox-triggered chiroptical switch operating in visible and near-infrared region was realized.

Keywords: Near-infrared; Chiroptical switch; Organogel; Gelator; Cholesterol; Anthraquinone imide.

INTRODUCTION

Recently, there has been a considerable trend in the area of low molecular weight organogelators (LMWGs) from just construction of new fibrous morphology to the design of novel functional materials^[1]. Cholesterol-based gelators represent one of the most extensively studied functional LMWGs^[2–10]. The cholesterol moieties tend to form tightly packed column stacks, which are considered to be the origin of the gel fiber formation. Due to their inherent chirality, these column stacks usually exhibit a helical structure. Consequently, the chromophores which are covalently-appended at 3-position of the cholesterol moiety are arranged in an ordered and helical fashion^[11]. The controlled ordering and orientation of chromophores in cholesterol-based organogels afford promising functions, such as photo-responsive, metal-responsive, proton-responsive, luminescence and so on^[1–9]. However, little attention has been paid to electrochromic and chiroptical switching phenomena in organogel systems.

Chiroptical switches whose chiral properties can be reversibly modulated within the UV-Vis spectral region by external stimuli have been designed and well studied^[12–17]. As near-infrared (NIR) light sources (*e.g.*, light-emitting diodes) become readily commercially available and are widely used in photonics, NIR molecular switches have an increasing potential to find applications in optical recording, thermal display, optical

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communication and medical area^[18, 19]. Given that chiroptical properties depend on both absorption properties and dissymmetric spatial orientation of chromophores^[17, 20], NIR chiroptical switching properties are expected upon electron oxidation/reduction, when NIR electrochromic (EC) dyes are introduced at 3-position of the cholesterol moiety in organogels.

Previously, we prepared chiroptical switching material in organogels formed by sugar-appended naphthalene diimides, which exhibited reversible changes in circular dichroism in the visible and NIR spectral region^[17]. Owing to the rigidity and planarity of naphthalene ring, the sugar-appended naphthalene diimides tended to precipitate in most solvents, and formed gels only in *n*-butanol. However, the resulting gels were not stable and gradually decomposed after one day. Moreover, more molecules are desired to understand the structure-property relationship of chiroptical switches based on asymmetric supramolecular structures. We herein put forward a new design of NIR chiroptical switches based on anthraquinone imide (AQI) bearing cholesterol groups, in which the AQI core and cholesterol moieties are connected with urethane linkages. AQIs are typical NIR electrochromic chromophores^[21, 22] and less planar than naphthalene rings. The gel-forming ability of the cholesterol moieties, together with the flexible linkages, makes AQIs to pack in an ordered way, which can afford NIR chiroptical switching properties upon electron reduction in chiral organogels.

EXPERIMENTAL

General Method

The ¹H-NMR and ¹³C-NMR spectra were measured using a Bruker-400 or a Varian 300 FR-NMR spectrometer at ambient temperature. Chemical shifts (δ) of ¹H-NMR spectra were reported in parts per million downfield from tetramethylsilane (TMS); and chemical shifts (δ) of ¹³C-NMR spectra were recorded from the solvent resonance employed as the internal standard. Melting points were determined by an SGW-X-4 melting instrument. Mass spectra were recorded on a Bruker Apex IV FTMS mass spectrometer. Elemental analyses were performed on an Elementar Vario EL instrument.

Images of TEM were recorded on a JEM-200CX transmission electron microscope at 120 kV, and images of optical microscopy were taken by using a Leica DML polarized light optical microscope. For TEM and optical microscopy measurements, the xerogels were directly put on the clean copper grid and glass substrate, respectively.

The UV/Vis/NIR absorption spectra were recorded on a Lambda 900 Perkin-Elmer spectrophotometer and circular dichroism spectra were recorded on a JASCO P-1030 (Japan) spectropolarimeter. Cyclic voltammograms (CV) were performed on a BAS 100 or a CHI 630C electrochemical workstation. For the cyclic voltammograms (CV) experiment, solutions were made in anhydrous CH₂Cl₂ containing 0.1 mol/L tetra-*n*-butylammonium perchlorate (TBAP) and were degassed with nitrogen for 30 min before measurements. Glass carbon working electrode, platinum counter electrode and silver pseudoreference electrode were used together, all the potentials were corrected using ferrocene/ferrocenium (Fc/Fc⁺) and reported relative to normal hydrogen electrode (NHE).

The OTTLE cell and the redox potentials were chosen according to the CV data. Spectroelectrochemical studies of films were performed using a quartz cuvette cell, which contained two ITO glass plates stick to each other, one was coated with thin films of gels of *N*-[3 β -cholest-5-en-3-yl] *N*-(2-aminoethyl) carbamate] anthraquinone-2,3-dicarboxylic imide (**1**) and used as working electrode, another was used to avoid the leakage of films; and also a silver pseudoreference electrode and a platinum counter electrode were in the same quartz cell. The electrolyte solution was CH₃CN (0.1 mol/L TBAP), and the redox potentials were selected according to the CV results.

Synthesis and Characterization

Preparation of 2,3-dimethylantraquinone (**4a**)

Aluminum chloride (63.0 g, 0.47 mol) was added to a solution of phthalic anhydride (29.6 g, 0.2 mol) in *o*-xylene (500 mL). The mixture was refluxed for 4 h and then cooled to room temperature. The cooled HCl

solution (2 mol/L, 400 mL) was added into the solution. The resulting mixture was stirred for 2 h, taken up in ether and extracted with 2 mol/L NaOH. The aqueous solution was washed with ether and acidified to pH = 2 with cold concentrated HCl. 34 g solid was collected by filtration and washed with water. After drying, 30 g white solid was obtained, which were then dissolved in concentrated sulfuric acid (200 mL). The solution was warmed gradually to 110°C over 30 min, kept at this temperature for 4 h and then poured onto ice (400 g). 17 g precipitated gray powder was collected by filtration in the yield of 35%. There is isomer 1,2-dimethylantraquinone in the product, but it will be purified in the next reaction step. m.p. 179–180°C. ¹H-NMR (300 MHz, CDCl₃, δ): 8.28 (q, 2H, ph-H), 8.02 (s, 2H, ph-H), 7.78 (q, 2H, ph-H), 2.42 (s, 6H, —CH₃). ¹³C-NMR (75 MHz, CDCl₃, δ): 183.27, 144.03, 133.80, 133.68, 131.51, 128.16, 127.04, 20.19. MS: calculated for C₁₆H₁₂O₂: 236.08373 m/z, found 237.09107 [M+H]⁺. Anal. Calcd for C₁₆H₁₂O₂: C, 81.34; H, 5.12. Found: C, 81.23; H, 5.14.

Preparation of anthraquinone-2,3-dicarboxylic anhydride (2a)

4a (5 g, 21 mmol) was dissolved in 54 mL concentrated sulfuric acid. The mixture was slowly added into 200 mL of water. The resulting white suspension was heated to 95°C, then 32 g (0.2 mol) KMnO₄ was added as several portions during 4 h. The mixture was heated for another 30 min, and then cooled to room temperature. Excessive oxalic acid was added until the color of solution changed from black to light yellow. The solid was filtrated, washed with water and then added into 50 mL of ammonia water. The mixture was filtrated again and the filtrate was acidified by dilute HCl to pH = 2. 2.3 g precipitate thus formed was recrystallized from acetic acid to afford 0.3 g (1 mmol) of light yellow solid with the yield of 4.7%.

The above yellow solid (0.3 g) and 20 mL acetic anhydride were added into a 50 mL round bottom flask. The mixture was heated until all the solid was dissolved and kept reflux for another 30 min. Then it was cooled to room temperature and 0.3 g green-yellow solid was produced. The solid was filtrated and washed with acetic anhydride. 0.23 g (0.7 mmol) light yellow solid was obtained through sublimation with the yield of 70%. Due to the poor solubility, compound **2a** was not characterized by ¹³C-NMR. m.p. 209–210°C. ¹H-NMR (300 MHz, DMSO, δ): 8.37 (s, 2H, *J* = 6.0 Hz, ph-H), 8.26 (q, 2H, *J*₁ = 3.3 Hz, *J*₂ = 4.2 Hz, *J*₃ = 11.4 Hz, ph-H), 7.98 (q, 2H, *J*₁ = 3.6 Hz, *J*₂ = 4.2 Hz, *J*₃ = 11.4 Hz, ph-H). MS: calculated for C₁₆H₆O₅: 278.02152 m/z, found 279.02912 [M+H]⁺. Anal. Calcd for C₁₆H₆O₅: C, 69.07; H, 2.17. Found: C, 69.05; H, 2.18.

Preparation of 3β-cholest-5-en-3-yl N-(2-aminoethyl) carbamate (2b)

To a solution of ethylenediamine (16.7 mL, 250 mmol) in dry toluene (200 mL) was added portionwise toluene solution of cholesteryl chloroformate (0.1 mol/L, 50 mL) for 30 min at 0°C under nitrogen atmosphere, and the solution was stirred at room temperature for 16 h. The reaction mixture was washed with water, dried over anhydrous magnesium sulfate and evaporated in vacuo to dryness. The residue was dissolved in dichloromethane (20 mL), and then methanol (20 mL) was added. The suspension thus formed was filtered off to remove the biscarbamate, and the filtrate was evaporated in vacuo to give **2b** as a white solid 0.8 g (2 mmol) with the yield of 40%. m.p. 166–168°C. ¹H-NMR (300 MHz, CDCl₃, δ): 5.38 (d, 1H, *J* = 3.6 Hz, CH=C), 4.89–5.10 (m, 1H, NHCOO), 4.40–4.59 (m, 1H, OCH), 3.24 (q, 2H, *J* = 3.6 Hz, NH₂CH₂), 2.82 (t, 2H, NH₂CH₂), 2.21–2.42 (m, 2H), 1.75–2.06 (m, 5H), 0.95–1.66 (m, 23 H, CH and NH), 0.91 (d, 3H, Me), 0.83 (d, 6H, Me), 1.01 (s, 3H, Me), 0.68 (s, 3H, Me). ¹³C-NMR (75 MHz, CDCl₃, δ): 156.393, 139.708, 122.363, 74.167, 56.577, 56.055, 49.883, 43.282, 42.199, 39.639, 39.413, 36.440, 36.090, 35.714, 28.141, 28.086, 27.900, 24.186, 23.764, 22.739, 22.477, 20.947, 19.249, 18.623, 11.761. MS: calculated for C₃₀H₅₂N₂O₂: 472.40288 m/z, found 473.41054 [M+H]⁺. Anal. Calcd for C₃₀H₅₂N₂O₂: C, 76.22; H, 11.09; N, 5.93. Found: C, 75.39; H, 10.62; N, 5.46.

Preparation of N-[3β-cholest-5-en-3-yl N-(2-aminoethyl) carbamate] anthraquinone-2,3-dicarboxylic imide (1)
2b (0.25 g, 0.53 mmol) and anhydrous DMF (10 mL) were added into a 50 mL, three-necked flask. Under Ar atmosphere, **2a** (0.13g, 0.43 mmol) was added. The mixture was stirred for 2 h until all the solid was dissolved at room temperature, then it was heated to reflux. After 24 h, the mixture was allowed to cool to room temperature and poured into 100 mL of water. The solid thus produced was filtrated and washed with water to

afford 0.45 g yellow-green solid. The crude product was purified by column chromatography (silica gel, $\text{CH}_2\text{Cl}_2/\text{EtOAc} = 1:1$). Yellow solid ($R_f = 0.6$) was collected and further purified by recrystallization from toluene to yield the product 0.31 g (0.4 mmol) with the yield of 93%. m.p. 230–231°C. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ): 8.79 (s, 2H, ph-H), 8.37 (q, 2H, $J = 2.7$ Hz, ph-H), 7.88 (q, 2H, $J = 2.7$ Hz, ph-H), 5.19 (d, 1H, $\text{CH} = \text{C}$), 4.85–4.95 (m, 1H, NHCOO), 4.25–4.35 (m, 1H, OCH), 3.93 (t, 2H, NH_2CH_2), 3.50 (q, 2H, $J = 11.7$ Hz, CH_2NHCOO), 2.14 (d, 2H $J = 5.4$ Hz), 1.96 (d, 1H), 1.65–1.85 (m, 4 H), 1.15–1.65 (m, 16H), 0.95–1.17 (m, 8H), 0.95 (d, 3H, Me), 0.88 (d, 3H, Me), 0.86 (d, 3H, Me), 0.85 (d, 3H, Me), 0.65 (s, 3H, Me). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3 , δ): 181.50, 166.66, 156.32, 139.66, 138.09, 135.83, 134.92, 133.09, 127.75, 122.73, 122.52, 56.66, 56.14, 49.96, 42.30, 39.72, 39.53, 36.51, 36.19, 35.79, 31.82, 28.22, 28.02, 24.27, 23.84, 22.82, 22.57, 21.00, 19.27, 18.72, 11.85. MS: calculated for $\text{C}_{46}\text{H}_{56}\text{N}_2\text{O}_6$: 733.42166 m/z, found 734.42054 $[\text{M}+\text{H}]^+$. Anal. Calcd for $\text{C}_{46}\text{H}_{56}\text{N}_2\text{O}_6 \cdot 12\text{H}_2\text{O}$: C, 58.17; H, 8.43; N, 2.95. Found: C, 57.92; H, 7.72; N, 2.88.

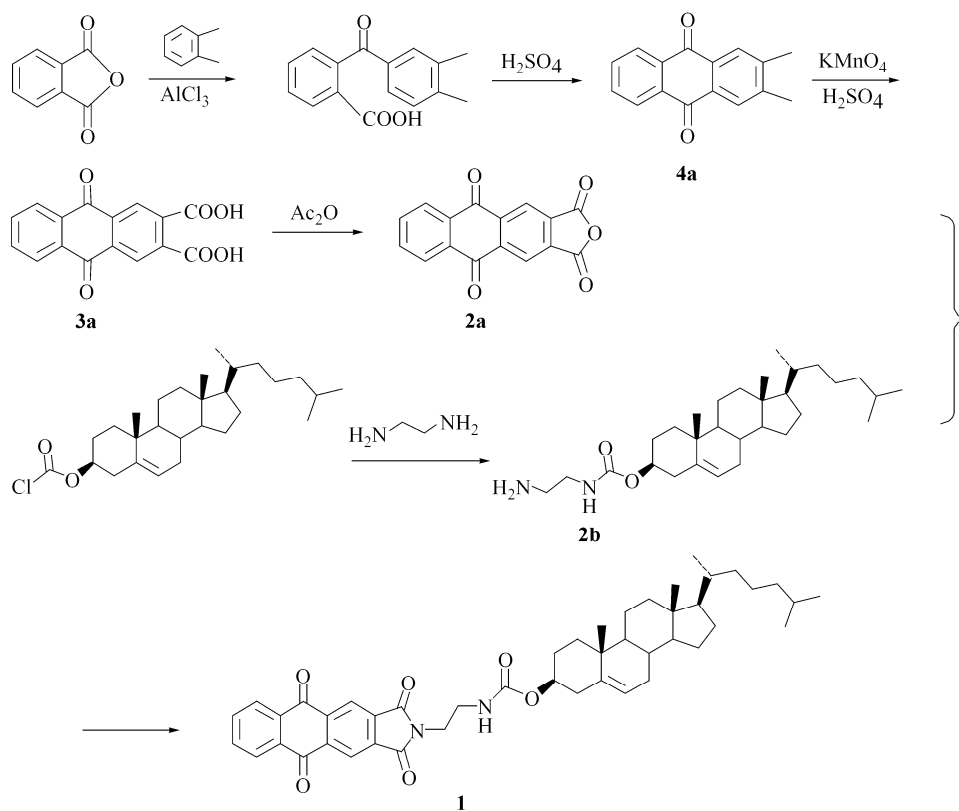
Gelation Test

The gelation test was carried out as follows. Compound **1** (20.0 mg) and 1.0 mL of the solvent were placed into a capped test tube. The mixture was heated until the compound was dissolved completely. The solution was allowed to cool to room temperature. Gelation was determined by the absence of flow of the solvent when the tube was inverted. To measure the critical gelation concentration (CGC), 100 μL of solvent was added each time until the concentration was insufficient for forming a stable gel.

RESULTS AND DISCUSSION

Synthesis and Characterization

For the synthesis of anthraquinone imide^[1], the important immediate, anthraquinone-2,3-dicarboxylic anhydride (**2a**), was first prepared *via* a multi-step synthetic route as illustrated in Scheme 1^[21,22]. Friedel-Crafts acylation



Scheme 1 Synthetic route of compound **1**

of *o*-xylene with phthalic anhydride in the presence of anhydrous aluminum chloride, followed by ring closure reaction using sulfuric acid afforded 2,3-dimethylantraquinones (**4a**), which was then oxidized by KMnO_4 in an acidic solution and refluxed in acetic anhydride to afford anhydride **2a**. Before imidization reaction, flexible ethylene linker was introduced into the cholesterol moiety (**2b**) by the reaction of cholesterol chloroformate with ethylenediamine^[2], in order to improve the gelling ability of AQIs (Scheme 1). The chemical structures and purities of all intermediates and target molecule were verified by elemental analysis, melting point characterization, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ and ESI HRMS. All the data agreed well with the expected structures except for **2b**. The chemical structure of the compound **2b** has been verified by $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ and ESI HRMS. However, when elemental analysis was run, the results were changing every minute probably due to the moisture absorption.

Gelation Properties

Compound **1** formed gels in glycol (0.4 wt%), *n*-butanol (1.8 wt%), acetonitrile (1.8 wt%) and ethyl acetate (0.3 wt%) at room temperature, and all of them were stable and could last for at least one month. Further insight into the aggregation behaviors of **1** in the gel was obtained by UV-Vis and CD measurements. The UV-Vis spectrum of the gel film of **1** formed in acetonitrile (about 10–20 μm in thickness) displayed a broad peak from 240 nm to 350 nm due to the π - π^* transition of the anthraquinone moiety (Fig. 1). Chromophore aggregation was clearly present in the gel because of the broader absorption bands compared to the sharp peaks at 230, 260 and 330 nm for **1** in dilute solution (Fig. 2).

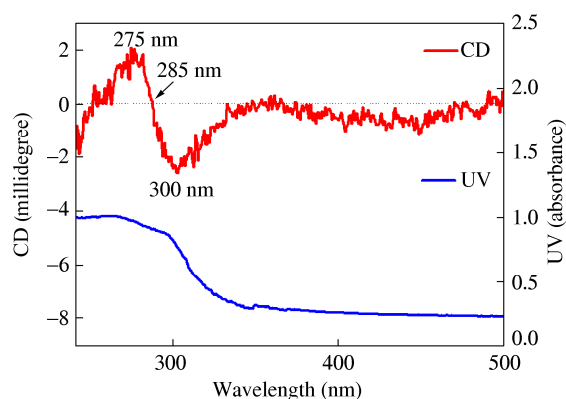


Fig. 1 Absorption and circular dichroism spectra of the gels of **1** formed in acetonitrile ($c = 0.6$ wt%) at 25°C

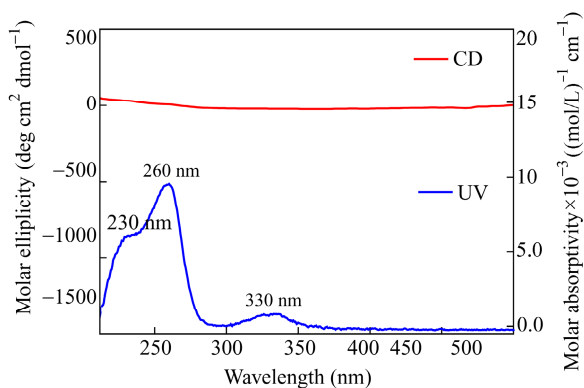


Fig. 2 Absorption and circular dichroism spectra of **1** ($c = 0.001$ wt%) in acetonitrile at 25°C

The CD spectrum of the film of gels exhibited an exciton-coupled bisignate signal, being first a negative Cotton effect (λ_{max} 300 nm) followed by a positive Cotton effect (λ_{max} 275 nm). The $\lambda(\theta = 0)$ value (285 nm) was comparable with the corresponding absorption (Fig. 1); while no CD signal was observed in the same region when **1** was fully dissolved (Fig. 2). This indicated that with the aid of the cholesterol groups, chiral supramolecular assembly of AQIs maybe formed during gelation^[10]. It was also proved by CD measurements upon cooling as shown in Fig. 3. During the formation of partial-gels of **1** in acetonitrile upon cooling, Cotton effects from 240 nm to 350 nm corresponding to the absorption of AQIs appeared and gradually increased.

To obtain a visual image of the gels of **1** formed in acetonitrile, the xerogel sample was subjected to transmission electron microscopy (TEM) and optical microscopy. TEM and optical microscopy images of an unstained xerogel of **1** (0.8 wt %) revealed fibrous structure with diameters of *ca.* 1–2 μm and lengths up to tens of microns (Fig. 4). However, the chirality at molecular level didn't transfer to the high order assemblies, and as a result one dimensional helical structure was not revealed by electron microscopy and optical microscopy.

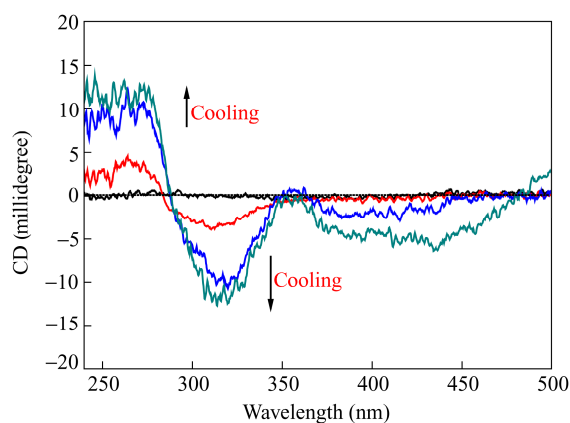


Fig. 3 Variation of CD spectra of **1** in acetonitrile upon cooling ($c = 0.2$ wt%) in 0.5 cm cylindrical quartz cell

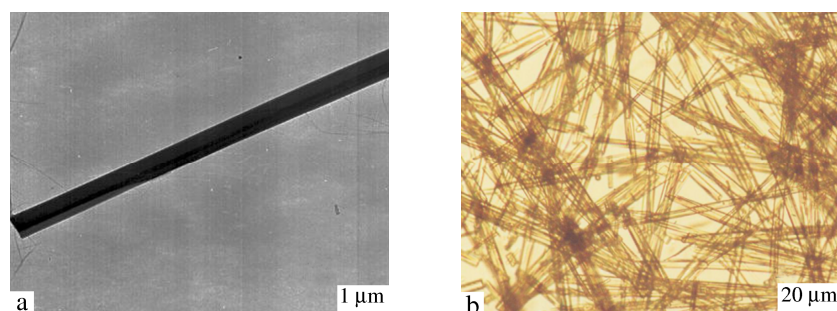


Fig. 4 (a) TEM image and (b) optical microphotograph of the xerogel prepared from **1** in acetonitrile ($c = 0.8$ wt%)

Electrochemical and Electrochromic Studies in Solution

The redox property of **1** was investigated using cyclic voltammetry (CV) in dichloromethane containing 0.1 mol/L tetra-*n*-butylammonium perchlorate (TBAP). Two reversible reductions at -0.64 and -1.07 V, respectively were observed (Fig. 5). The first reduction corresponded to the formation of radical anions, while the second reduction related to the formation of dianions^[21, 22].

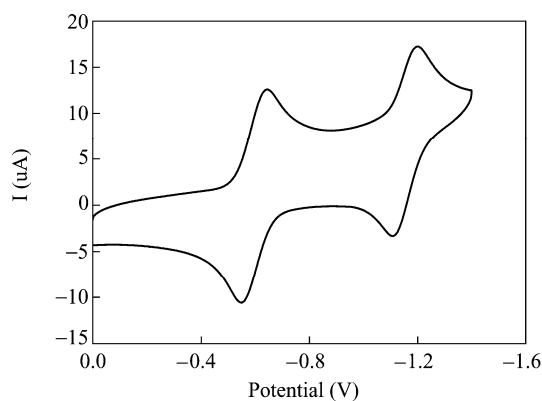


Fig. 5 Cyclic voltammograms of **1** (10^{-3} mol/L) in CH_2Cl_2 containing 0.1 mol/L TBAP

The electrochromic property of **1** in dichloromethane was then characterized using an OTTE cell^[3]. Compound **1** in dilute solution absorbed at 230, 260 and 330 nm, respectively. Upon one-electron reduction to radical anion at -700 mV, as shown in Fig. 6, intense NIR absorptions appeared in the range of 600–1200 nm with the maximal absorption at 820 nm. These NIR absorptions can be attributed to $\pi^*-\pi^*$ (SOMO $\rightarrow$ LUMO) transitions of the radical anions of AQIs. Further reduction to the dianionic state was achieved by applying a voltage of -1000 mV, and the color of solution changed from brown to purple. As the NIR absorption of radical anions disappeared, new absorption band centered at 600 nm appeared and gradually increased^[21, 22].

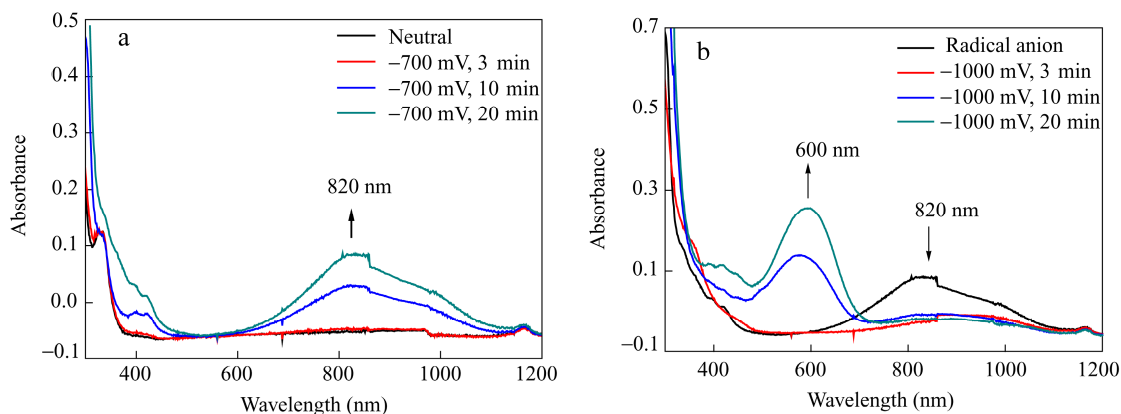


Fig. 6 Spectroelectrochemistry of **1** (10^{-3} mol/L) in CH_2Cl_2 containing 0.1 mol/L TBAP

Electrochromic and Chiroptical Switching of Gels

When a thin and light yellow gel film of **1** formed in acetonitrile was cast on ITO glasses and subjected to -700 mV reduction in a quartz cell, it turned to light brown in color, typical for the radical anion of AQIs. The NIR absorption bands of the reduced film appeared in the same region as in dilute solution, which had a maximal absorption around 820 nm and a shoulder around 1000 nm. Unlike the naphthalene diimides^[23], there was no new absorbance beyond 1200 nm, which is caused by the “optical conducting band” between molecules. Further reduction at -1000 mV yielded the purple colored dianionic film with strong absorbance from 500 nm to 900 nm, which centered around 700 nm, as shown in Fig. 7.

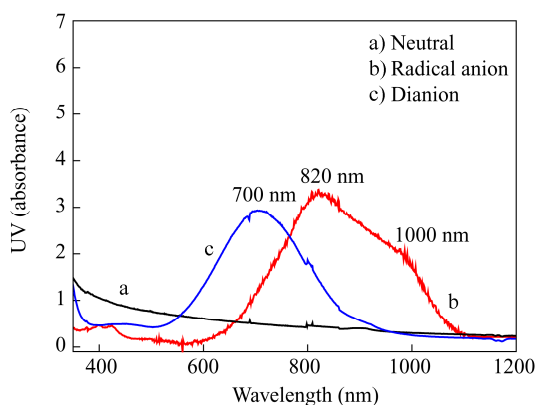


Fig. 7 UV-Vis-NIR spectra of film of gels of **1** in its neutral, radical anionic and dianionic states

Transformation between the redox states in the gels was reversible, and optical modulation at 820 nm could be achieved with stepping potentials between $+0.2$ V (neutral) and -0.7 V (radical anion), as shown in Fig. 8.

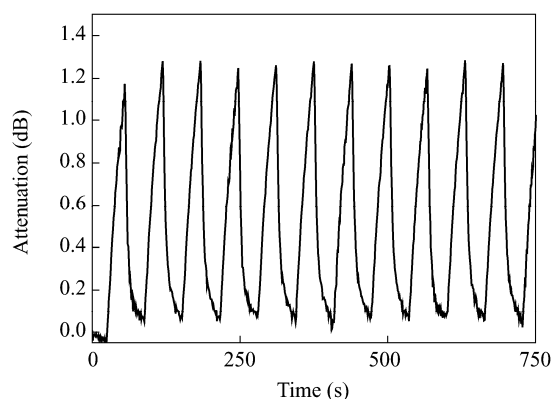


Fig. 8 Changes in optical transmission of film of gels of **1** at 820 nm over time with stepping potentials between -0.7 V and $+0.2$ V

Since the gels of **1** possessed distinct absorption properties in three states, its chiroptical property was expected to vary remarkably with redox state. Thus thin casting films of gels of **1** on ITO glasses were also subjected to CD measurements upon electrochemical process. After reduction at -700 mV, the film exhibited strong negative Cotton effects from 600 nm to 800 nm (Fig. 9), corresponding to the NIR absorption of radical anions. Due to the sensitivity limit of our CD instrument, CD signals were too weak compared to noise to be characterized. Rotating the sample caused no discernible changes in CD spectrum, indicating the absence of influence of linear dichroism. Upon further reduction to the dianionic state at -1000 mV, the CD signals blue shifted to 500 nm, with the maximal absorption around 720 nm, concomitant with the variation of absorption spectra in Fig. 7. Regarding the chiroptical switching ability, CD signals at 790 nm can be reversibly modulated between neutral and reduced states by applying the potential between $+0.2$ V (neutral) and -0.7 V (radical anion), as shown in Fig. 10.

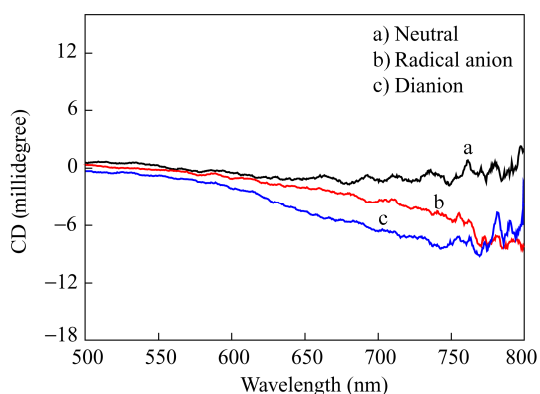


Fig. 9 CD spectra of film of gels of **1** in its neutral, radical anionic and dianionic states

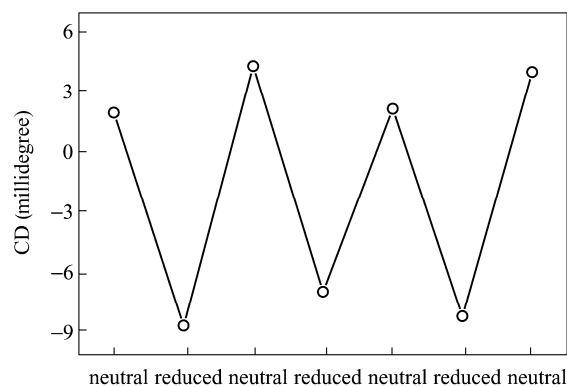


Fig. 10 Changes in CD spectrum of film of gels of **1** at 790 nm between the neutral (Neutral) and radical anion (Reduced) states during redox cycles

CONCLUSIONS

We have prepared an NIR chiroptical switching material based on an anthraquinone imide bearing cholesterol. As a result of the chiral packing of electrochromic chromophores within the chiral gels, this material exhibits obvious change in the absorption and CD spectra in Vis-NIR region. Additionally, this supramolecular approach by using gels as a chiral scaffold and EC molecule as a switching trigger is an effective way to prepare chiroptical switching material in a wide spectral region.

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