Chem. Mater. **2008,** *20,* 6163–6168

Near-Infrared Electrochromic and Chiroptical Switching Materials: Design, Synthesis, and Characterization of Chiral Organogels Containing Stacked Naphthalene Diimide Chromophores

Jia Zheng,[†] Wenqiang Qiao,[†] Xinhua Wan,[*,†] Jian Ping Gao,[‡] and Zhi Yuan Wang[*,‡]

Beijing National Laboratory for Molecular Sciences, Key Laboratory of Polymer Chemistry and Physics of the Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, 202 Chengfu Road, Beijing 100871, China and Department of Chemistry, Carleton University, 1125 Colonel By Drive, Ottawa, Ontario, Canada K1S 5B6

Received May 29, 2008. Revised Manuscript Received July 12, 2008

Chiroptical switching materials in the visible and near-infrared spectral regions have been realized using a low molecular weight gel as a chiral scaffold and electrochromic chromophores as a stimulus-responsive trigger and operate as a result of the change in the electronic states of the chromophores within the chiral gel. *N*,*N*′-Bis(4-phenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside)-1,4,5,8-naphthalenetetracarboxylic diimide, synthesized by imidization of 1,4,5,8-naphthalenetetracarboxylic dianhydride with a sugar-bearing amine, can form stable chiral gels at room temperature. The redox-active gels exhibited reversible and drastic changes in circular dichroism in the visible and near-infrared spectral region between the three redox states (neutral, radical anion, dianion) of the naphthalene diimide chromophore. A large circular dichroism at 1310−1550 nm was induced when the stacked naphthalene diimide chromophores in the chiral gels were reduced to the radical anion state.

Introduction

Modulation of chiroptical properties can be achieved by changing the structure or/and electronic state of a single chiral molecule or the structure of a chiral supramolecular assembly.[1−11] A variety of chiral molecules that can undergo chiroptical changes under external stimuli have been designed and well studied. In a chiral supramolecular system, noncovalent interactions between chiral moieties are utilized in construction of chiral environments and the bonded or entrapped achiral chromophores could display the induced circular dichroism (CD) at wavelengths corresponding to their absorptions. To date, chiroptical switching has been achieved within the UV−vis spectral region but rarely beyond 1000 nm.[1,2,8−11] The ability of controlling the optical activity of a chiral material in the near-infrared (NIR) spectral region, especially within a biowindow (800−1300 nm) and telecom window (1310−1550 nm), have potential applications in biological sensing, optical communication, and data storage. As near-infrared light-emitting diodes (such as gallium aluminum arsenide and indium phosphide diode lasers) have been widely used as a light source and near-infrared light can penetrate deeper into the materials without much interference, chiroptical switches in the near-infrared region can offer a great deal of flexibility in signal detection and an opportunity for innovations in photonics.

Naphthlene diimides (NDI) are known to be electrochromic and undergo electrically reversible color change between the three redox states (neutral, radical anion, and dianion).[12−14] Recently, it has been demonstrated that the stacked NDI,

---

[*] To whom correspondence should be addressed. E-mail: waynewang@carleton.ca; xhwan@pku.edu.cn.

[†] Peking University.

[‡] Carleton University.

(1) (a) Feringa, B. L. *Molecular Switches*; Wiley-VCH: Weinheim, 2001. (b) Feringa, B. L.; van Delden, R. A.; Koumura, N.; Geertsema, E. M. *Chem. Rev.* **2000**, *100*, 1789–1816. (c) Feringa, B. L. *Acc. Chem. Res.* **2001**, *34*, 504–513. (d) Green, M. M.; Cheon, K.-S.; Yang, S.-Y.; Park, J.-W.; Swansburg, S.; Liu, W. *Acc. Chem. Res.* **2001**, *34*, 672–680.

(2) (a) Zahn, S.; Canary, J. W. *J. Am. Chem. Soc.* **2002**, *124*, 9204–9211. (b) Barcena, H. S.; Liu, B.; Mirkin, M. V.; Canary, J. W. *Inorg. Chem.* **2005**, *44*, 7652–7660. (c) Barcena, H. S.; Holmes, A. E.; Canary, J. W. *Org. Lett.* **2003**, *5*, 709–711. (d) Mori, T.; Grimme, S.; Inoue, Y. *J. Org. Chem.* **2007**, *72*, 6998–7010.

(3) (a) Nishida, J.-I.; Suzuki, T.; Ohkita, M.; Tsuji, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 3251–3254. (b) Deng, J.; Song, N. H.; Zhou, Q. F.; Su, Z. X. *Org. Lett.* **2007**, *9*, 5393–5396.

(4) (a) Wang, C.; Zhu, L. Y.; Xiang, J. F.; Yu, Y. X.; Zhang, D. Q.; Shuai, Z. G.; Zhu, D. B. *J. Org. Chem.* **2007**, *72*, 4306–4312. (b) Zhou, Y. C.; Zhang, D. Q.; Zhu, L. Y.; Shuai, Z. G.; Zhu, D. B. *J. Org. Chem.* **2006**, *71*, 2123–2130.

(5) (a) Beer, G.; Niederalt, C.; Grimme, S.; Daub, J. *Angew. Chem., Int. Ed.* **2000**, *39*, 3252–3255. (b) Mori, T.; Inoue, Y. *J. Phys. Chem. A.* **2005**, *109*, 2728–2740.

(6) (a) Todd, E. K.; Wang, S.; Wan, X. H.; Wang, Z. Y. *Tetrahedron Lett.* **2005**, *46*, 587–590. (b) Wang, Z. Y.; Todd, E. K.; Meng, X. S.; Gao, J. P. *J. Am. Chem. Soc.* **2005**, *127*, 11552–11553.

(7) Gomar-Nadal, E.; Veciana, J.; Rovira, C.; Amabilino, D. B. *Adv. Mater.* **2005**, *17*, 2095–2098.

(8) (a) de Jong, J. J. D.; Lucas, L. N.; Kellogg, R. M.; van Esch, J. H.; Feringa, B. L. *Science* **2004**, *304*, 278–281. (b) van Delden, R. A.; Mecca, T.; Rosini, C.; Feringa, B. L. *Chem. Eur. J.* **2004**, *10*, 61–70.

(9) (a) Goto, H.; Yashima, E. *J. Am. Chem. Soc.* **2002**, *124*, 7943–7949. (b) Guo, P. Z.; Zhang, L.; Liu, M. H. *Adv. Mater.* **2006**, *18*, 177–180.

(10) (a) Kim, M.-J.; Yoo, S.-J.; Kim, D.-Y. *Adv. Funct. Mater.* **2006**, *16*, 2089–2094. (b) Mammana, A.; D'Urso, A.; Lauceri, R.; Purrello, R. *J. Am. Chem. Soc.* **2007**, *129*, 8062–8063.

(11) Li, Y. G.; Wang, T. Y.; Liu, M. H. *Soft Matter* **2007**, *3*, 1312–1317.

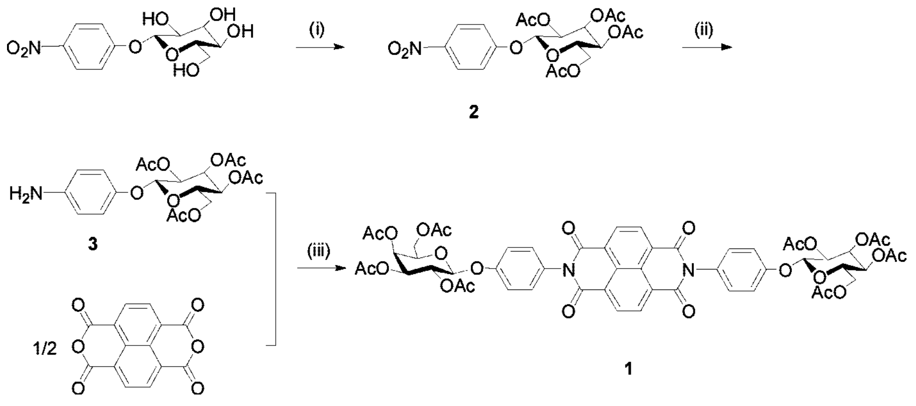
(12) Mortimer, R. J. *Chem. Soc. Rev.* **1997**, *26*, 147–156.

(13) Mackinnon, S. M.; Wang, Z. Y. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3467–3475.

(14) (a) Miller, L. L.; Mann, K. R. *Acc. Chem. Res.* **1996**, *29*, 417–423. (b) Penneau, J.-F.; Stallman, B. J.; Kasai, P. H.; Miller, L. L. *Chem. Mater.* **1991**, *3*, 791–796. (c) Miller, L. L.; Duan, R. G.; Hong, Y. L.; Tabakovic, I. *Chem. Mater.* **1995**, *7*, 1552–1557. (d) Miller, L. L.; Zhong, C.-J.; Kasai, P. *J. Am. Chem. Soc.* **1993**, *115*, 5982–5990.

10.1021/cm8014644 CCC: $40.75

Scheme 1. Synthesis of NDI Derivative 1[a]



[a] (i) Ac_2O, pyridine, rt, 24 h; (ii) H_2, 10% Pd/C, ethanol:CH_2Cl_2 = 4:1, rt, 24 h; (iii) *m*-cresol, 200 °C, 4 h.

upon reduction, display an "optical conduction band" in the NIR region (e.g., around 1500 nm), arising from excitation of π electrons along the stacks.[14] Conceivably, by having NDI molecules stacked asymmetrically in a chiral assembly, the induced CD and other chiroptical properties can be expected in the visible and NIR regions and readily modulated between the bistable redox states.[15]

Low molecular weight organogels (LMWG) formed in various solvents have complex fibrous structures. The origin of gel formation is considered to be one-dimensional alignment of gelator molecules, supported by multiple noncovalent interactions.[16−19] It is well documented that LMWG containing chirality-inducing groups, such as saccharide,[17] cholesterol,[18] and chiral urea groups,[19] are able to form chiral supramolecular structures through van der Waals interactions and/or hydrogen-bonding interactions. As a result, Cotton effects corresponding to the absorption bands of chromophores within the chiral assembly can be revealed by circular dichroism spectroscopy.[17−19] Thus, by incorporating electrochromic NDI chromophores into a chiral organogel assembly, an electrically switchable chiroptical material can display the induced NIR CD bands if the NDI chromophore within the chiral supramolecular assembly becomes NIR absorbing.

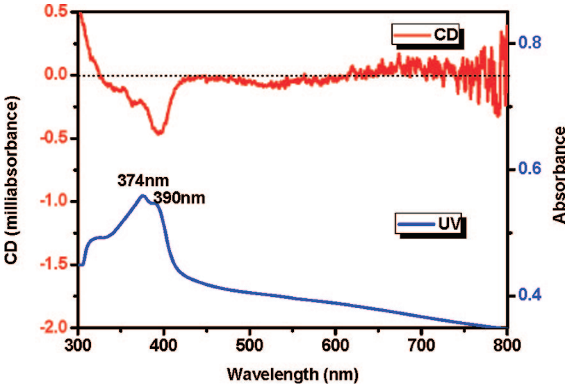


Figure 1. Absorption and circular dichroism spectra of the gels of **1** in *n*-butanol (*c* = 1.23 wt %).

Accordingly, an NDI derivative bearing two sugar groups (**1**, Scheme 1) was synthesized by imidization of 1,4,5,8-naphthalenetetracarboxylic dianhydride with the sugar-bearing amine, and its aggregation behavior was studied. The switching behaviors of the gel of **1** in the visible and near-infrared spectral regions were investigated by absorption and circular dichroism spectroscopy in conjunction with the electrochemical method.

Experimental Section

Materials. 4-Nitrophenyl-β-D-glucopyranoside was purchased from Acros and tetra-*n*-butylammonium perchlorate (TBAP) from Fluka. CH_3CN was dried with P_2O_5 and distilled before electrochemical experiment. Pyridine was dried with KOH and distilled before use. Other chemicals were purchased from Aldrich Canada Inc. and Beijing Chemical Reagents Co. and used as received.

Measurements. The ^1H NMR and ^{13}C NMR spectra were measured using Bruker-400 or Varian 300 FR-NMR spectrometers. Chemical shifts (δ) are reported in parts per million (ppm) downfield from tetramethylsilane. MS spectra were determined with BEFLEX III for MALDI-TOF MS. Elemental analyses were performed on an Elementar Vario EL instrument.

Images of optical microscopy and polarization optical microscopy (POM) were taken using a Leica DML polarized light optical microscope. Transmission electron microscopy (TEM) images were recorded on a JEM-200CX transmission electron microscope at 160 kV, and scanning electron microscopy (SEM) images were taken with a JEOLJSM-6700F field emission scanning microscope. Xerogels of **1** were made by slow evaporation at low temperature under reduced pressure. For optical microscopy and POM measurements, the xerogels were directly put on the clean glass substrate; for SEM measurements, samples on glass substrates were sputtered with gold before experiment; for TEM measurements, xerogels were first dispersed in *n*-hexane, followed by addition of one drop of the suspension onto the copper grid.

---

(15) (a) Elliot, C. *The Molecular Basis of Optical Activity: Optical Rotatory Dispersion and Circular Dichroism*; John Wiley: New York, 1979. (b) Harada, N.; Nakanishi, K. *Circular Dichroic Spectroscopy-Exciton Coupling in Organic Stereochemistry*; University Science Books: Mill Valley, CA, 1983. (c) Eyring, H.; Liu, H.-C.; Caldwell, D. *Chem. Rev.* **1968**, *68*, 525–540.

(16) (a) Weiss, R. G.; George, M. *Acc. Chem. Res.* **2006**, *39*, 489–497. (b) Ishi-i, T.; Shinkai, S. *Top. Curr. Chem.* **2005**, *258*, 119–160. (c) Ajayaghosh, A.; Praveen, V. K. *Acc. Chem. Res.* **2007**, *40*, 644–656.

(17) (a) Kobayashi, H.; Friggeri, A.; Koumoto, K.; Amaike, M.; Shinkai, S.; Reinhoudt, D. N. *Org. Lett.* **2002**, *4*, 4, 1423–1426. (b) Tamaru, S.-I.; Nakamura, M.; Takeuchi, M.; Shinkai, S. *Org. Lett.* **2001**, *3*, 3631–3634.

(18) Ajayaghosh, A.; Vijayakumar, C.; Varghese, R.; Ceorge, S. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 456–460.

(19) Tamaru, S.-I.; Uchino, S.-Y.; Takeuchi, M.; Ikeda, M.; Hatano, T.; Shinkai, S. *Tetrahedron Lett.* **2002**, *43*, 3751–3755.

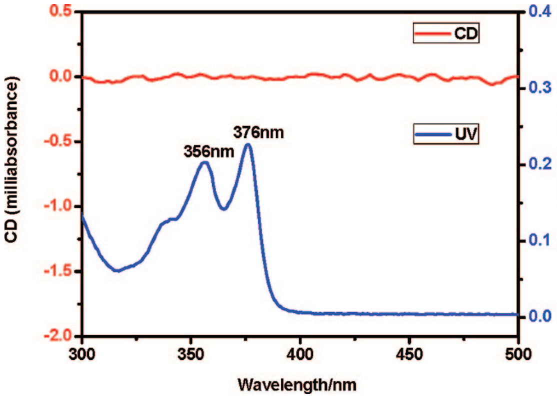


Figure 2. Absorption and circular dichroism spectra of **1** in CH_3CN (c = 8.31×10^{-6} M).

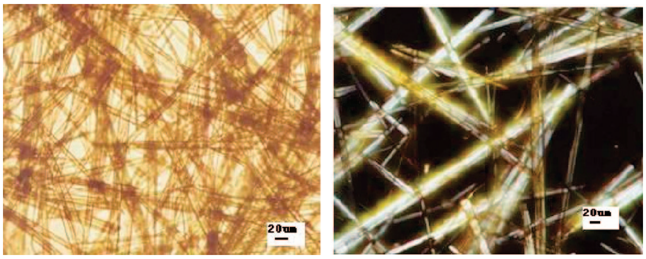


Figure 3. Optical microscopy (left) and POM (right) images of the xerogel prepared from **1** in *n*-butanol (c = 1.23 wt %).

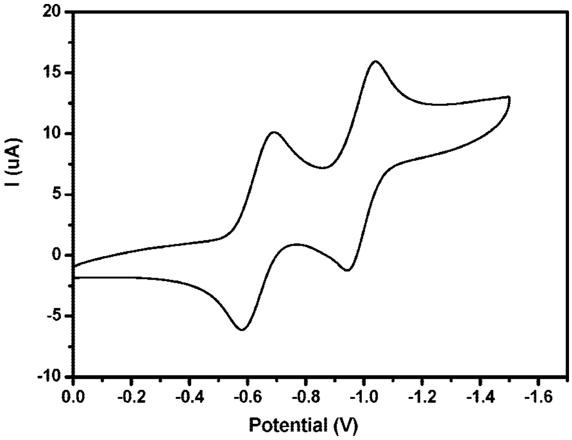


Figure 4. Cyclic voltammogram of **1** (10^{-3} M) in CH_3CN containing 0.1 M TBAP.

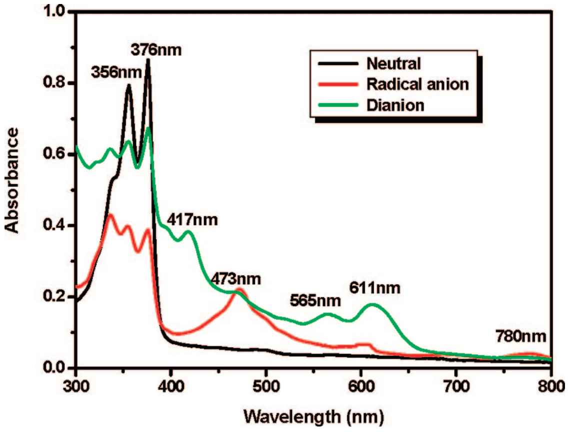


Figure 5. UV−vis−NIR spectra of **1** (10^{-3} M) in CH_3CN containing 0.1 M TBAP in its neutral, radical anionic, and dianionic states.

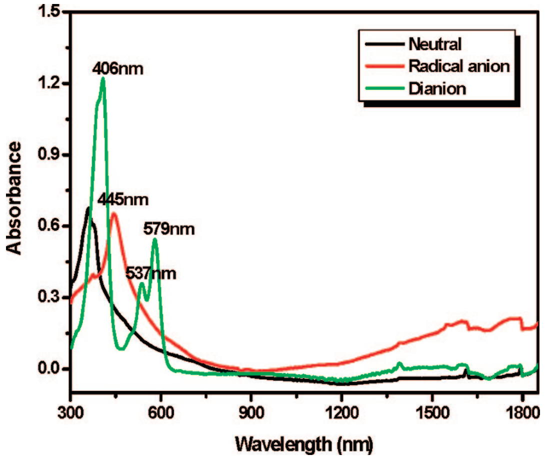


Figure 6. UV−vis−NIR spectra of films of gels of **1** in its neutral, radical anionic, and dianionic states.

The UV−vis−NIR absorption spectra were recorded on a Lambda 900 Perkin-Elmer spectrophotometer. Circular dichroism (CD) spectra were recorded on an Olis DSM 17 spectropolarimeter with either a PMT (200−900 nm) or a InGaAs (800−1650 nm) detector. The measurement parameters using the PMT detector were set as follows: number of increments = 300; bandwidth = 2 nm; integration time is a function of voltage. Each measurement involved baseline correction; the measurement parameters using InGaAs detector were set as follows: number of increments = 200; bandwidth = 5 nm; integration time = 0.1 s. Each measurement involved baseline correction and was taken as an average of 10 single scans. When measuring the changes of CD spectra at 1550 nm against repeated redox cycles, to avoid the interference of noise the data were collected for 1 min (about 116 signals) after the electrochemical reaction was complete and then averaged.

Cyclic voltammograms (CV) and other electrochemical experiments were performed on a BAS 100 electrochemical workstation. For the CV experiment, solutions of **1** were made in anhydrous CH_3CN containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) and degassed with nitrogen for 30 min before measurements. A glass carbon working electrode, platinum counter electrode, and silver pseudoreference electrode were used together; all potentials were corrected using ferrocene/ferrocenium (Fc/Fc^+) and reported relative to NHE.

The spectroelectrochemical measurements of solutions of **1** were performed in an optical transparent thin layer cell (OTTLE)[20] using the same solutions as for CV, and the redox potentials were chosen according to the results of CV.

Spectroelectrochemical studies of the gels were performed in a quartz cuvette cell, which contained an ITO glass plate coated with thin films of gels of **1**, a silver pseudoreference electrode, and a platinum counter electrode. D_2O containing 0.1 M NaCl was used as the electrolyte solution to avoid the overtone absorptions of OH in near-infrared region. The redox potentials were also the same as the CV results.

Sample Preparation. For electrochromic study, thin films of the gels of **1** were prepared by casting from hot *n*-butanol solution ([**1**] = 0.5 wt %) on the preheated ITO glasses (80 °C) and then cooled to room temperature under a nitrogen atmosphere.

Synthesis. *4-Nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranoside (**2**).* The procedures reported in the literature were modified as follows:[21] A solution of (4-nitrophenyl)-β-D-glucopyranoside (1.0 g, 3.3 mmol) in dry pyridine/Ac_2O (10:1 v/v, 275 mL) was stirred

---

(20) Kejecik, M.; Danek, M.; Hartl, F. *J. Electroanal. Chem.* **1991**, *317*, 179–187.

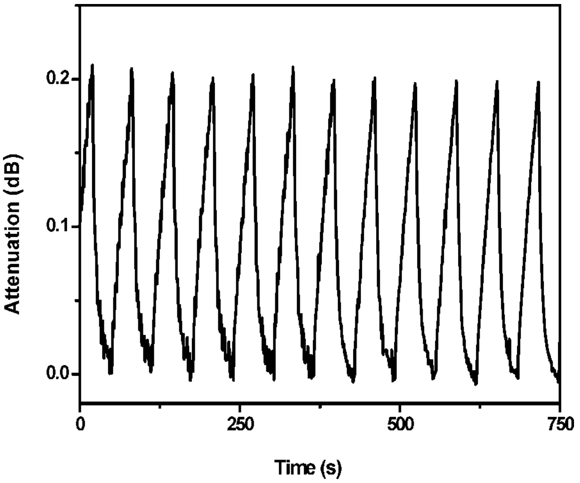


Figure 7. Changes in optical transmission of films of gels of **1** at 1550 nm over time with stepping potentials between −0.7 and +0.2 V.

at room temperature for 24 h. The yellow mixture was poured into saturated aqueous $NaHCO_3$ (250 mL), and the aqueous layer was extracted with $CHCl_3$ (3 × 25 mL). The organic layers were combined, dried over $MgSO_4$, and evaporated in vacuum to afford brown viscous solid. The solid was poured into dilute HCl (50 mL) while stirring; lots of white solids appeared. The solids were collected by filtration, washed by water until pH 7, and dried to yield **2** as a white solid (1.3 g, 86% yield). $R_f = 0.6$ (CH_2Cl_2/PE, 1/1). ^1H NMR (300 MHz, $CDCl_3$, ppm): δ 8.22 (d, 2H, −NCC*H*CHCO−), 7.08 (d, 2H, −NCCHC*H*CO−), 5.28−5.38 (m, 2H), 5.04−5.26 (m, 2H), 4.22−4.32 (q, 1H), 4.14−4.22 (q, 1H), 3.90−4.02 (m, 1H), 2.02−2.12 (q, 12H, CH_3COO−).

*4-Aminophenyl-2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranoside (**3**).* The procedures reported in the literature were modified as follows:[22] Pd/C (10%, 0.1 g) was added to a solution of **2** (1.3 g, 3 mmol) in 400 mL of ethanol/CH_2Cl_2 (4:1 v/v) at room temperature under nitrogen atmosphere for about 0.5 h, then stirring under a hydrogen atmosphere for 24 h. The mixture was filtered and evaporated in vacuum to afford a brown oily solid. The crude product was purified by flash chromatography, eluting with solvent (CH_2Cl_2/EtOAc, 5:1 v/v, $R_f = 0.7$). Yellow solids (1.1 g, 90% yield) were collected and dried. ^1H NMR (300 MHz, $CDCl_3$, ppm): δ 6.83 (d, 2H, −NCC*H*CHCO−), 6.65 (d, 2H, −NCCHC*H*CO−), 5.08−5.36 (m, 3H), 4.86−4.96 (d, 1H), 4.22−4.38 (q, 1H), 4.10−4.22 (q, 1H), 3.72−3.84 (m, 1H), 3.02−3.80 (br, 2H, −NH_2), 2.02−2.12 (m, 12H, CH_3COO−).

N,N′*-Bis(4-phenyl-2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranoside)-1,4,5,8-naphthalenetetracarboxylic Diimide (**1**).* The naphthalene derivatives were synthesized following a procedure that was slightly modified from that described previously for similar naphthalene derivatives.[6] Diimde **1** was obtained by condensation of 1,4,5,8-naphthalenetetracarboxylic dianhydride (0.107 g, 0.4 mmol) and **3** (0.37 g, 0.85 mmol) in 25 mL of *m*-cresol containing 3 drops of isoquinoline. The solution was stirred at 200 °C for 12 h under a nitrogen atmosphere. The red solution was poured into water (100 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The organic layers were combined, dried over $MgSO_4$, and evaporated in vacuum to afford a red oil solid. The crude product was purified by flash chromatography, eluting with solvent (CH_2Cl_2/EtOAc, 2:3 v/v, $R_f = 0.7$). Yellow solid was collected and further purified by recrystallization from toluene to yield the product (0.3 g, 65% yield). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 8.86 (s, 4H, naph-H), 7.30 (d, 4H, −NCC*H*CHCO−), 7.21 (d, 4H, −NCCHC*H*CO−), 5.31−5.36 (m, 4H), 5.19−5.25 (m, 4H), 4.30−4.36 (q, 2H), 4.18−4.23 (q, 2H), 3.91−3.95 (m, 2H), 2.05−2.11 (q, 24H, CH_3COO−). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 170.61, 170.26, 169.41, 169.32, 163.01, 157.11, 131.53, 129.73, 129.38, 127.16, 126.98, 117.85, 98.88, 72.69, 72.13, 71.10, 68.19, 61.89, 20.73, 20.69, 20.65, 20.62. MS (MALDI-TOF): calcd for $C_{54}H_{50}N_2O_{24}$, 1110 *m/z*; found 1133 $[M + Na]^+$, 1149 $[M + K]^+$. Anal. Calcd for $C_{54}H_{50}N_2O_{24}$: C, 58.38; H, 4.54; N, 2.52. Found: C, 58.39; H, 4.55; N, 2.47.

Results and Discussion

Gelation Study. The gelation test was carried out as follows. Compound **1** (20.0 mg) and 1.0 mL of the solvent were placed in a capped test tube, and 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 to form a stable gel. By this treatment **1** was insoluble in most solvents (water, *n*-hexane, cyclohexane, toluene, *p*-xylene, ethyl acetate, etc.). It swelled in glycol and *n*-heptanol but was not dissolved into these solvents even at reflux temperature. In contrast, it was well dissolved in DMF and acetonitrile. Among the solvents tested, **1** can form stable gels at 1.23 wt % in *n*-butanol at room temperature (see Supporting Information).

The aggregation behavior and optical activity of the gel of **1** were examined by UV−vis and CD spectroscopic means. The absorption spectrum of the gel film (about 10−20 μm) displays two peaks at 374 and 390 nm due to the naphthalene moiety (Figure 1). Typical J-type chromophore aggregation is clearly present in the gel because of the broader and bathochromically shifted absorption bands compared to the sharp peaks at 356 and 376 nm for **1** in homogeneous solution (Figure 2, 1 cm quartz cell).[23] The CD spectrum exhibits negative CD bands at 374 and 390 nm (Figure 1), while no CD signal is observed in the same region when **1** is fully dissolved (Figure 2). This indicates that with the aid of the saccharide groups, chiral supramolecular assembly is formed during gelation and induces the chirality of the NDI aggregates, as previously studied.[17] The similar change of UV−vis and CD spectra as described above can also be observed in sol−gel transformation of **1** in *n*-butanol upon changing temperature, and the CD signals at 374 and 390 nm can be switched on and off during a heating−cooling cycle (see Supporting Information).

To obtain a visual image of the *n*-butanol gel of **1**, the xerogel sample was subjected to optical microscopy analysis. Optical microscopic images as well as POM images (Figure 3) of an unstained xerogel of **1** (1.23 wt %) revealed an entangled network consisting of fibrous structure with diameters of ca. 2−4 um and lengths up to tens of mi-

---

(21) Benltifa, M.; Vidal, S.; Fenet, B.; Msaddek, M.; Goekjian, P. G.; Praly, J.-P.; Brunyánszki, A.; Docsa, T.; Gergely, P. *Eur. J. Org. Chem.* **2006**, *4242*, 4256.

(22) Sung, C.-H.; Kung, L.-R.; Hsu, C.-S.; Lin, T.-F.; Ho, R.-M. *Chem. Mater.* **2006**, *18*, 352–359.

(23) (a) Kasha, M. *Radiat. Res.* **1963**, *20*, 55–70. (b) Kasha, M. In *Spectroscopy of the Excited State*; Di Bartolo, B., Ed.; Plenum Press: New York, 1976.

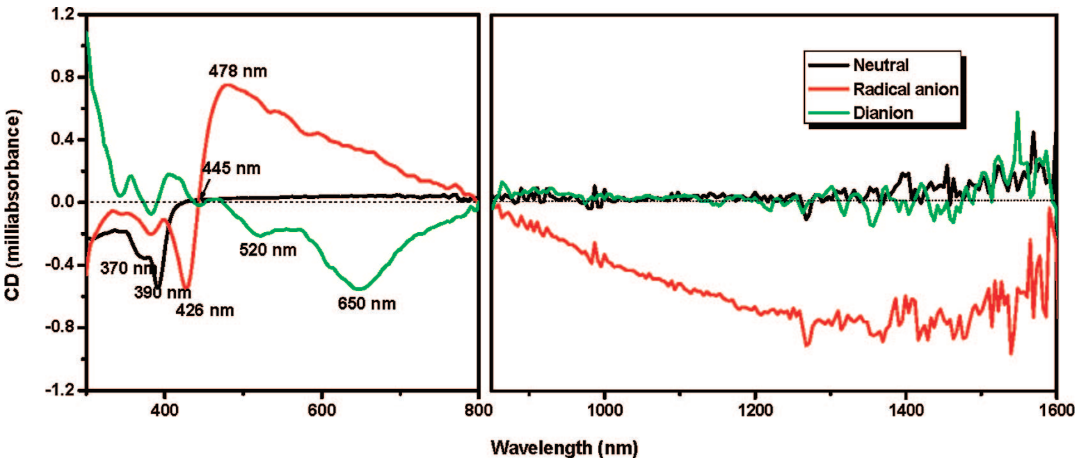


Figure 8. CD spectra of films of gels of **1** in its neutral, radical anionic, and dianionic states.

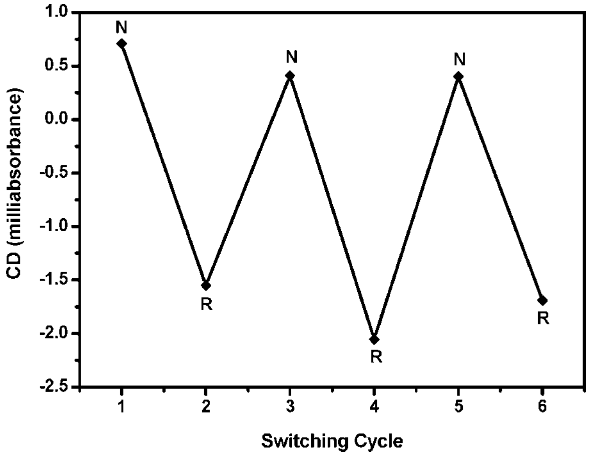


Figure 9. Changes in CD spectra of films of gels of **1** at 1550 nm between the neutral (N) and radical anion (R) states during repeated redox cycles.

crometers (also see TEM and SEM images in the Supporting Information). The fiber shows a birefringence character, which indicates a high degree of molecular ordering structure is developed in these aggregates according to the POM results.

Electrochemical and Electrochromic Studies in Solution. The electrochemical properties of **1** were examined using cyclic voltammetry (CV) in CH_3CN containing 0.1 M TBAP. Figure 4 shows that the imide groups undergo two reversible one-electron reductions, which occurred at −0.56 and −1.00 V. This suggests that the two imides behave individually. The first reduction corresponds to formation of radical anions, and the second reduction relates to formation of dianions.[14]

The electrochromic properties of **1** were studied using an OTTLE cell[20] in CH_3CN (Figure 5), similar to previous studies.[14] Compound **1** in CH_3CN absorbs at 356 and 376 nm. Upon electrochemical reduction to the radical anions, drastic changes in absorption took place with the appearance of one band at 780 nm and another intense band at 473 nm. There is no other absorption at longer wavelengths (above 800 nm). Further reduction to the dianioic state was achieved by applying a voltage of −1000 mV. The color of solution changed from brown to purple, and the new species had absorptions at 565 and 611 nm and a strong band at 417 nm, which was blue shifted relative to the radical anion.

Electrochromic Studies and Switching of Gels. The gel film also undergoes two reversible one-electron reductions at −0.56 and −1.00 V, identical to those for **1** in solution. When a thin gel film of **1** casted on ITO glass was subjected to −0.56 V reduction in a quartz cell, it turned light brown in color, typical for the radical anion of NDI. The visible absorption bands of the reduced film shifted to 445 nm, while a new broad band around 1500−1600 nm appeared (Figure 6, radical anionic state), which was not observed in the spectrum of the radical anion of **1** in solution (Figure 5, radical anionic state). Previous work demonstrated that radical anions of NDI could form π-stacked aggregates in poor solvents or films, and an optical conduction band in the NIR region could arise from excitation of π electrons along the chromophore stacks.[14] Stacking of radical anions in gel is therefore confirmed by the presence of this distinct NIR absorption band. Further reduction at −1.0 V yields the purple-colored dianions of NDI in gel with a strong band at 406 nm and others at 537 and 579 nm (Figure 6, dianionic state).

Studies on optical switching were also performed. Transformation between three redox states in the gel was electrochemically reversible, and optical modulation at 1550 nm was achieved with stepping potentials between +0.2 (neutral) and −0.7 V (radical anion) (Figure 7).

Chiroptical Studies and Switching of Gels. Considering the three distinct and reversible optical properties that gels of **1** possess, chiroptical properties of the three states should be totally different. Thus, thin cast films of gel samples on ITO glass were subjected to CD measurements upon redox switching. When reduced to the radical anionic and dianionc states, the CD spectra of the gel film of **1** changed significantly within the vis−NIR spectral region.

After reduction at −0.56 V, an exciton-coupled bisignate signal appeared,[15] being first a positive Cotton effect (λ_{max} 478 nm), followed by a negative Cotton effect curve (λ_{max} = 426 nm). The $\lambda_{\theta=0}$ value at 445 nm is comparable with that of the corresponding radical anion absorption at 445 nm. More strikingly, an intense negative Cotton effect curve around 1550 nm emerged, corresponding to the NIR absorption of the aggregated radical anion species (Figure 8, radical anion trace). As expected, upon further reduction to the dianionic state at −1.0 V, the CD signal in the NIR region vanished, while two negative CD bands around 520 and 650 nm appeared, concomitant with the corresponding variation in absorption.

Regarding the chiroptical switching ability, it is quite remarkable for the gel of **1** to display the switchable CD signals in a wide spectral region. In addition to the modulation of CD signals at 426 and 478 nm (see Supporting Information), the chiroptical switching at 1550 nm (Figure 9) can be achieved by applying the potential between +0.2 (neutral) and −0.7 V (radical anion).

It is also remarkable for the gel of **1** at its radical anion state to display an intense CD signal at the wavelengths of 1300−1550 nm (red trace in Figure 8). It is known that chromophores, with the assistance of a chiralilty-inducing group during the gelation process, could stack into a one-dimensional column in a one-handed helically twisted fashion.[17−19] Thus, the NDI chromophores in **1** are likely to pack into one-handed helical columns in various lengths, induced by the sugar moieties attached to the NDI terminals. Since the chiral assembly is apparently preserved during the redox cycle, the broad NIR absorption band should be due to excitation of π electrons along the helically stacked NDI radical anions, which in turn results in a large NIR CD signal. To our knowledge, this represents the first example of an electron-induced NIR supramolecular chiroptical switch that works as a result of the changes in the electronic states of the chromophores rather than the structure of the chiral assembly.

Conclusion

A new type of NIR chiroptical switching materials based on electrochromic chromophore-containing organogels has been demonstrated. Due to formation of the helically stacked electrochromic dyes within a chiral supramolecular assembly, when electrochemically reduced to the radical anionic and dianionic states, this chiral gel exhibits reversible and drastic changes in absorption and CD spectra over a wide range, in particular in the NIR region (e.g., 1310−1550 nm). Given a great flexibility in control of the supramolecular assembly and a wide selection of available visible−NIR electrochromic molecules, a variety of electron-induced chiroptical switching materials operational over a wide spectral range can be envisioned.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Research Council of Canada, the National Natural Science Foundation of China (Nos. 20674001, 20325415), the Research Fund for Doctoral Program of Higher Education of MOE (No. 20060001029), and the China Scholarship Council (No. 2007100285).

Supporting Information Available: Photos, TEM and SEM images of gels of **1**, variations of absorption and CD spectra of gels of **1** under different temperatures, and electrochromic and chiroptical switching of the gels of **1** in the visible region. This material is available free of charge via the Internet at http://pubs.acs.org.

CM8014644