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Near-Infrared Photochromic Diarylethenes Based on the Changes in the π-Conjugated System and the Electronic Properties of the Heteroaryl Moieties

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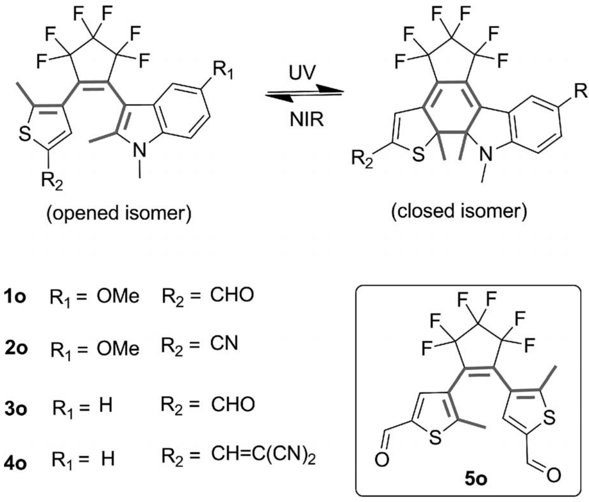
It is very challenging to construct photochromic materials with absorption and reactivity in the near-infrared (NIR) spectral region. Herein, four unsymmetrical diarylethene derivatives **1o**–**4o**, which contain both indole and thiophene moieties, have been successfully synthesized, and their photochromic behaviors have been shifted to the NIR region. These newly developed NIR photochromic materials are highly sensitive and responsive to photostimuli both in solution and in poly(methyl methacrylate) films. It has been shown that **1o**–**4o** exhibit remarkable UV/Vis and fluorescence spectral changes, allowing them to behave as reversible optical molecular switches in the NIR region.

Introduction

Research on photochromic materials has received much attention because of the materials′ potential application to optical data storage and optoelectronic devices.[1] Due to excellent thermally irreversible photochromic behavior and outstanding fatigue resistance properties, diarylethene derivatives (DAEs) are the most promising optically responsive compounds among photochromic compounds.[2] To enhance the susceptibility of optical memory storage, photochromic compounds with absorption and reactivity in the near-infrared (NIR) region are highly desirable.[3] Recently, a few research groups have developed a series of NIR photochromic materials, including introducing transition metal and borane complexes[4] to the aromatic heterocyclic chromophore of diarylethenes. When two naphthopyran entities were joined through a dithienylethene bridge, a triphotochromic system resulted in an absorption behavior reaching far into NIR region.[5] However, to design and synthesize NIR-responsive photochromic materials remains a challenge. Extending the π-conjugation of DAEs and introducing organic donor–acceptor (D–π–A) chromophores are important and efficient in shifting the absorption maxima to the NIR region.[6]

In this work, we describe the design and synthesis of four NIR-responsive unsymmetrical diarylperfluorocyclopentenes bearing both indole and thiophene moieties, **1o**–**4o**, and the reference compound **5o** (Scheme 1). Their photophysical, X-ray crystallographic, and photochromic behaviors were investigated in detail. These photochromic compounds **1o**–**4o** underwent a reversible pericyclic reaction, generating closed and opened isomers by irradiation with light in the UV and NIR regions. We introduced the indole chromophore in **1o**–**4o** to enhance electron transport properties in order to facilitate low-energy intramolecular charge transfer (CT) from electron-donor indole units to the powerful electron-accepting chromophores of the photochromic switches. We also introduced the thermally stable thiophene chromophore to our unsymmetrical DAEs using perfluorocyclopentene as the central ethene linker because of its resistance to fatigue.



Scheme 1. Photoisomerization of **1o**–**4o** and the reference compound **5o**.

Results and Discussion

Synthesis

The syntheses of **1o**–**4o** are shown in Scheme 2. The target unsymmetrical DAEs **1o** and **3o** were prepared in 55–

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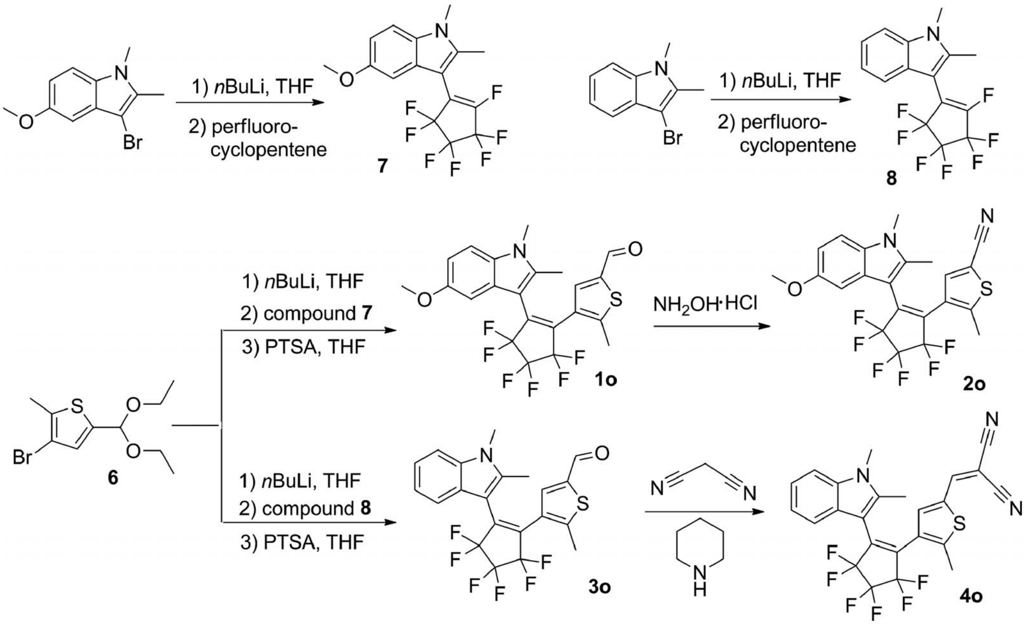

Scheme 2. Synthesis of compounds **1o**–**4o**.

60% yield by condensation between the 3-bromothiophene derivatives and the perfluorocyclopentene-substituted indole.[7] Compound **2o** was synthesized from **1o** by reaction with hydroxylamine hydrochloride (yield, 60%). Compound **4o** was prepared in 63% yield by the reaction of **3o** with malononitrile under basic conditions. The structures were identified by NMR spectroscopy, HRMS spectra, and X-ray crystallographic analysis (see Supporting Information Figures S1–S8).

X-ray Crystallographic Study

Single crystals of **1o**, **3o** and **7** were obtained by slow evaporation from an ethyl acetate/hexane solution. Final structural conformations of **1o**, **3o** and **7** were provided by X-ray crystallographic analysis. Their structural features are shown in Figure 1, and packing diagrams are shown in Figure 2. As shown in Figure 2, they exclusively adopt the antiparallel conformations, which are in sharp contrast to the

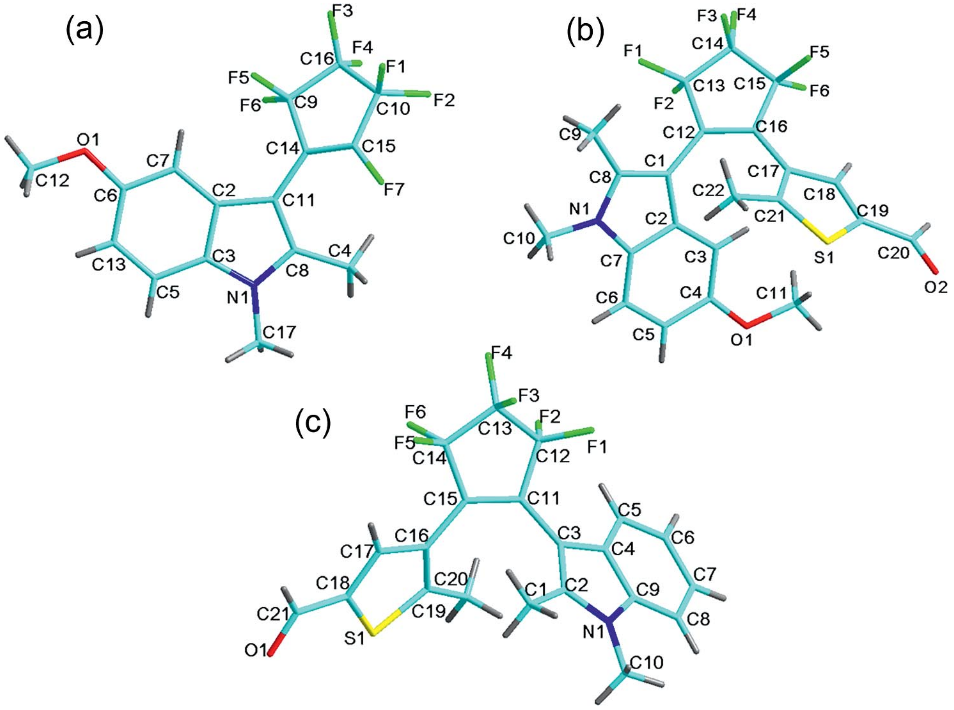

Figure 1. Crystal structures of (a) **7**, (b) **1o**, and (c) **3o**.

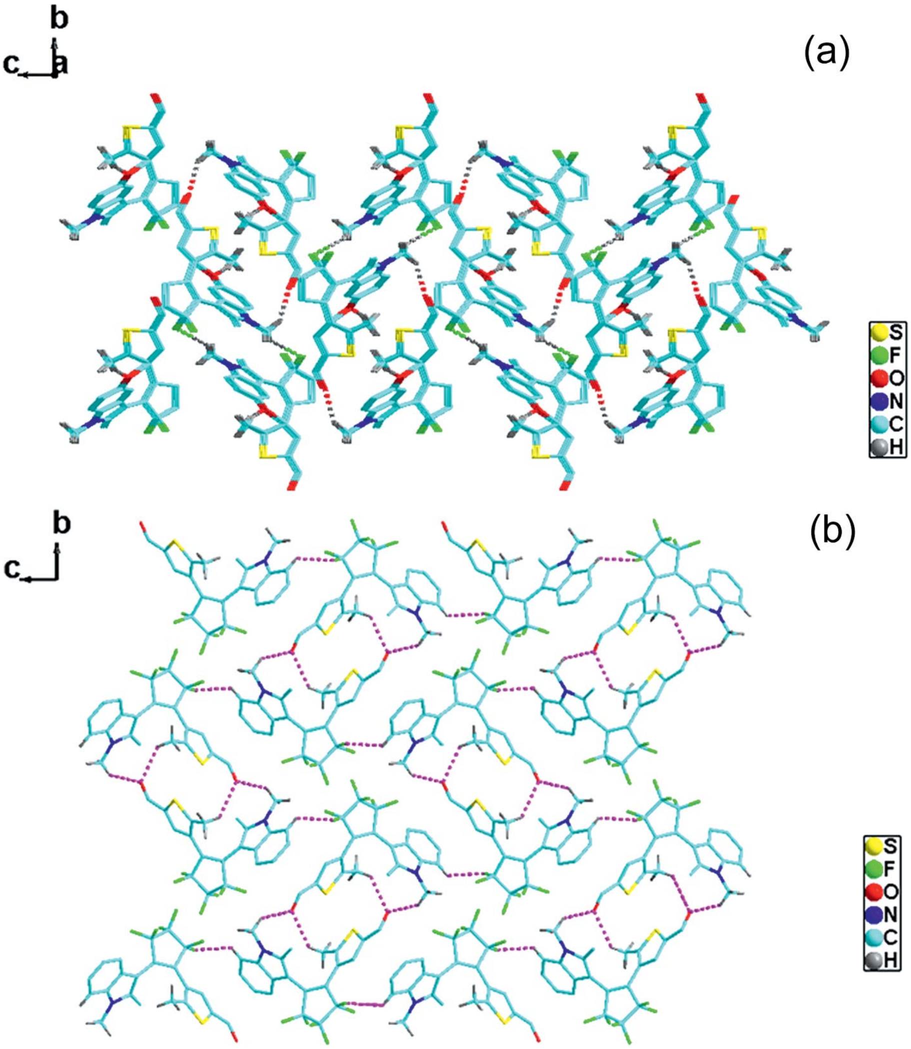

Figure 2. Molecular packing diagrams of (a) **1o** and (b) **3o**.

solution-phase behavior, where the antiparallel and parallel conformers coexist. Moreover, the 3D supermolecular framework and 2D layers are formed by the hydrogen-bonding interactions in **1o** and **3o**. The distance between the photocyclizing carbon atoms (C8···C21 for **1o**, C2···C19 for **3o**) is 4.369 Å and 3.597 Å, respectively. The crystals of **3o** show photochromic effect upon irradiation with UV light because photochromic reactivity usually appears when the distance between the reactive C atoms is less than 4.2 Å and the molecule is fixed in an antiparallel mode.[8]

Photochromic Behaviour

The spectral changes of **1o**–**5o** in hexane exposed to UV light are shown in Figures S1 (in the Supporting Information) and Table 1. Upon irradiation with UV light, the initially colorless solutions of compounds **1o**–**4o** display a strong coloration (Figure S9, Figure S10). The photogenerated closed-ring isomers have their absorption maxima at 675, 650, 630 and 720 nm, respectively. Upon NIR light irradiation ($\lambda > 600$ nm) the dark blue color disappeared and the absorption bands of the open-ring forms were restored. On the other hand, the differences in their spectral properties are attributed to the heteroaryl substituents, which alter the electronic properties of the switches. Compound **3c** exhibited its maximum at 630 nm, whereas the maximum of **1c** is located at 675 nm. The bathochromic shift of **1c** is due to a relative increase of electron density in the indole moiety caused by the electron-donating methoxy substituents. Moreover, compared with compound **3o**, compound **4o** showed a strong bathochromic shift (ca. 92 nm) upon UV irradiation. This observation confirmed that ex-

Table 1. The UV/Vis absorption maxima of compounds **1o**–**4o** in hexane, toluene and poly(methyl metharcrylate) (PMMA) before and after irradiation with 365 nm light at 25 °C (0–2 min).

	Hexane λ_{max} [nm]	Toluene λ_{max} [nm]	PMMA λ_{max} [nm]
1o	675	702	728
2o	650	672	680
3o	630	653	660
4o	722	748	754
5o	605	608	612

tending the π-conjugation of DAEs and introducing organic D–π–A chromophores are efficient approaches to shifting the absorption maxima to longer wavelengths.

The spectral and the color changes upon UV light irradiation of **1o**–**4o** in toluene are shown in Figure 3 and Figure 4. The absorption spectra showed a strong bathochromic shift with the increase in the polarity of solvents. The photogenerated closed-ring isomers have their absorption maxima at 702, 672, 653 and 748 nm, respectively. As discerned from Table 1, the absorption maxima of closed-ring isomers **1c**–**4c** underwent an obvious solvent-induced shift of 27, 22, 23, and 28 ppm, respectively. Of particular note, NIR photochromic materials **1**–**4** could be repeatedly transformed between the ring-open and ring-closed forms by alternate UV and NIR-light irradiation without any apparent degradation (Figure S11). Moreover, **1o**–**4o** displayed excellent photochromic performance in poly(methyl methacrylate) (PMMA), as well as in solution (Figure 5). Irradiation with UV light triggered the emergence of a broad absorption band in the NIR range, with **1c** and **2c** having their maxima at 728 and 680 nm, whereas the maxima of **3c**, **4c** were located at 660 and 754 nm.

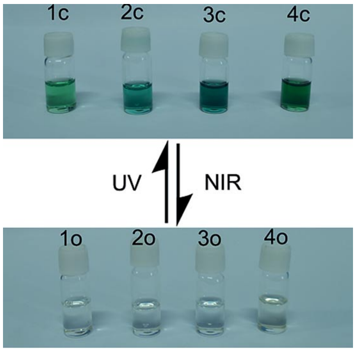

Figure 3. Photographic images of **1o**–**4o** upon alternating UV and NIR-light irradiation in toluene at 25 °C.

The absorption maxima of closed-ring isomers **1c**–**4c** underwent an obvious redshift of 26, 8, 7, and 6 ppm in PMMA films compared with solutions of these compounds in toluene. The bathochromic shift of **4c** is due to a relative increase of the π-conjugation and a relative decrease of electron density in the thiophene moiety caused by the electron-withdrawing malononitrile substituents. This illustrates the possibility of fine-tuning the spectral profile of these molecular switches by changing the electronic properties of the heteroaryl moieties.[9] Significantly, **1o**–**4o** underwent an obvious redshift compared with the reference compound **5o** both in solution and in PMMA under UV irradiation. Moreover, upon irradiation with NIR light (>600 nm), the absorption bands of the open-ring forms of **1o**–**4o** were restored (Figure S12, S13). These observations indicate these compounds can revert to the colorless open form even in PMMA film.

It is well documented that distinct differences in NMR signals between the opened isomers and the closed isomers of DAEs at both high-and low-field could be observed.[9c] As shown in Figure 6, for example, the methyl hydrogens

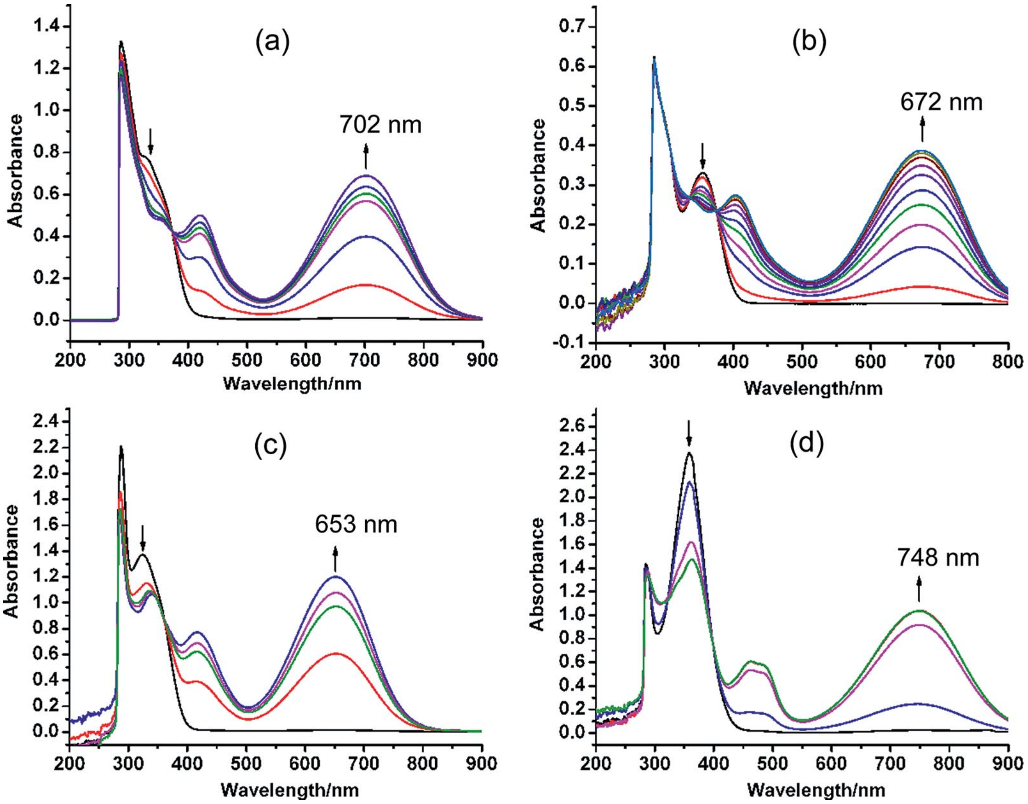

Figure 4. UV/Vis spectral changes of (a) **1o**, (b) **2o**, (c) **3o** and (d) **4o** upon UV-light irradiation in toluene at 25 °C (0–2 min).

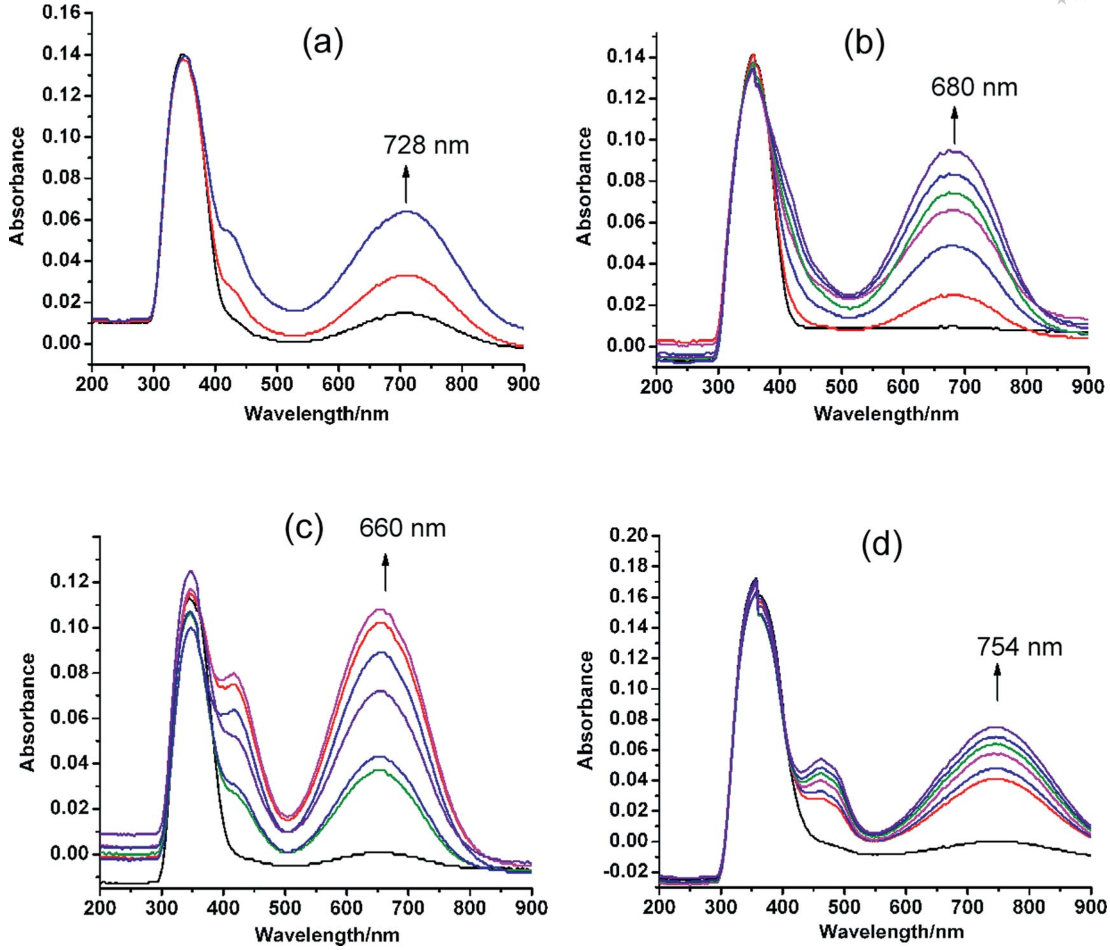

Figure 5. UV/Vis spectral changes of a poly(methyl methacrylate) (PMMA) film loaded at 2 wt.-% with (a) **1o**, (b) **2o**, (c) **3o** and (d) **4o** at 25 °C (0–2 min) after irradiation with 365 nm light.

(H^1 and H^2) at the reactive carbon in **2o** give two single peaks at δ = 1.99 and 1.86 ppm, respectively. Upon irradiation with UV light, two new peaks appear at δ = 1.68 and 1.64 ppm, corresponding to the methyl protons of **2c**. On the other hand, in contrast with the H^3 and H^4 signals (3.80 and 3.63 ppm) in **2o**, the signals of $H^{3'}$ and $H^{4'}$ in **2c** are shifted upfield to 3.78 and 2.71 ppm, respectively. Additionally, the protons H^5 located on the thiophene moiety undergo a significant upfield shift by 0.62 ppm.

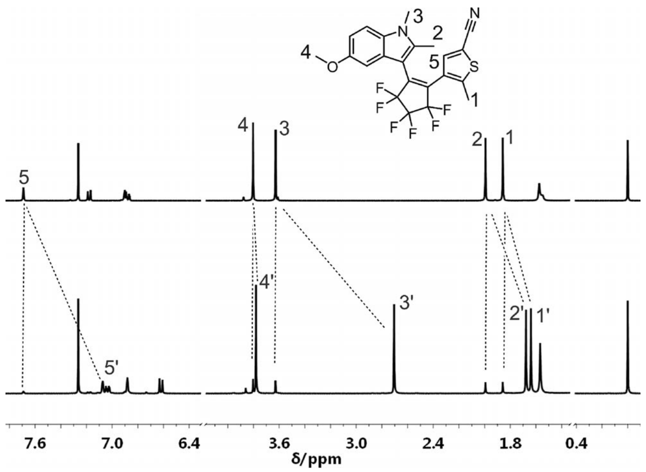

Figure 6. Changes in the ^1H NMR signals of **2o** upon UV irradiation in $CDCl_3$ solution.

The photocyclization process of **3o** was also examined by ^1H NMR spectroscopy. Upon irradiation at 365 nm (Figure 7), the methyl hydrogens H^1 and H^2 at the reactive carbon in **3o** were shifted upfield ($\Delta\delta$ = –0.20 and –0.32 ppm, respectively), while the protons H^4 located on the thiophene moiety in **3o** was shifted downfield ($\Delta\delta$ = 0.04 ppm). In addition, the methyl hydrogens H^3 located on the indole portion of **3o** shifted downfield after photocyclization. These changes in NMR signals might be ascribed to the great changes in the chemical environment upon photochromic reaction. Moreover, the conversion yields from opened-form to closed-form were determined to be 86.1% for **2** and 85.9% for **3** by ^1H NMR (Table S2). These observations jointly indicate that the unsymmetrical DAEs **2o** and **3o** exhibited excellent photochromic performance.

The fluorescence properties of unsymmetrical DAEs can also be modulated by their photochromism. As discerned

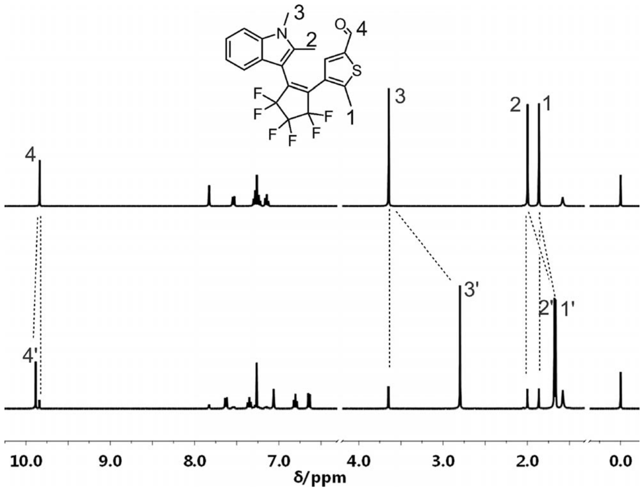

Figure 7. Changes in the ^{1}H NMR signals of **3o** upon UV irradiation in $CDCl_3$ solution.

from Figure 8a, upon excitation at the isosbestic point of 375 nm, **1o** exhibits an intense fluorescence at ca. 470 nm. Upon irradiation at UV (365 nm), an obvious fluorescence quenching was observed on account of the resulting closed form (**1c**). When reaching the photostationary state (PSS), the fluorescence intensity of **1o** decreased by about 88 %. On the other hand, upon excitation at the isosbestic point of 350 nm, **3o** exhibited an intense fluorescence at ca. 461 nm. Moreover, when **3o** was exposed to 365 nm UV light, the fluorescence intensity maximum decreased ca. 80 % (Figure 8, b). However, after NIR-light ($\lambda > 600$ nm) irradiation for 10 min, the fluorescence intensity of **1o** and **3o** were totally recovered.

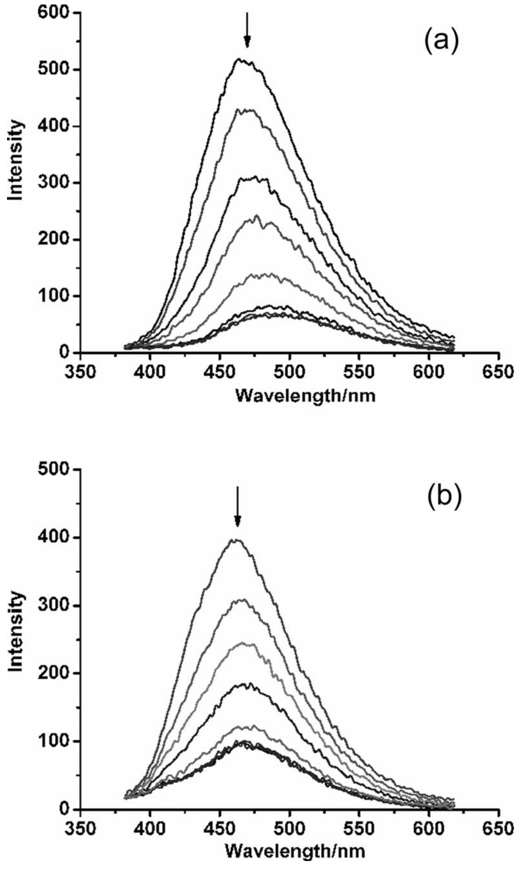

Figure 8. Fluorescence spectral changes of (a) **1o** and (b) **3o** (2.0×10^{-5} M) upon 365 nm light irradiation in toluene at 25 °C (0–2 min).

Conclusions

In summary, we have designed and synthesized four unsymmetrical diarylethene derivatives, **1o**–**4o**, which contain both indole and thiophene moieties, and their photochromic behaviors have been shifted to the NIR region. These compounds form molecular switches that undergo light-induced cyclization and decylization reversion reactions. Moreover, their photophysical and photochromic properties were comprehensively investigated by NMR, UV/Vis, fluorescence spectral and X-ray crystallographic analysis. These newly developed NIR photochromic materials showed good photochromism both in solution and in PMMA films. Compared with the reference compound **5o**, the absorbance maxima of **1o**–**4o** were dramatically redshifted both in solution and in PMMA under UV irradiation. Significantly, **4o** underwent an obvious redshift compared with **1o**–**3o** both in solution and in PMMA under UV irradiation. The bathochromic shift may be due to a relative increase of the π-conjugation and a relative decrease of the electron density in the thiophene moiety. We have shown that this can be exploited to generate switches with distinct spectral properties by changing the electronic properties of the heteroaryl moieties. Further exploration of such switches could be useful for the development of more sophisticated and functional NIR-sensitive optoelectronic devices.

Experimental Section

Instrumentation: All chemicals were commercially available unless stated otherwise. 4,4′-(Perfluorocyclopent-1-ene-1,2-diyl)bis(5-methylthiophene-2-carbaldehyde) (**5o**),[10] 3-bromo-5-(diethoxymethyl)-2-methylthiophene (**6**),[11] 5-methoxy-1,2-dimethyl-3-(perfluorocyclopent-1-enyl)-1*H*-indole (**7**)[1d] and 1,2-dimethyl-3-(perfluorocyclopent-1-enyl)-1*H*-indole (**8**)[7] were prepared according to the literature procedures. NMR spectra were recorded with a Varian Mercury VX400 instrument. The optical switch experiments were carried out using a photochemical reaction apparatus with a 500 W Hg lamp. UV/Vis spectra were recorded with a Shimadzu UV-3600 spectrophotometer equipped with a PTC-348WI temperature controller. Steady-state fluorescence spectra were recorded in a conventional quartz cell (light path 10 mm) with a Varian Cary Eclipse instrument equipped with a Varian Cary single-cell Peltier accessory to control the temperature.

4-[3,3,4,4,5,5-Hexafluoro-2-(5-methoxy-1,2-dimethyl-1*H*-indol-3-yl)cyclopent-1-enyl]-5-methylthiophene-2-carbaldehyde (1o): *n*-Butyllithium (2.4 M in hexane, 15.6 mmol, 6.5 mL) was added dropwise to a stirred solution of compound **6** (3.35 g, 12 mmol) in THF (100 mL) at –78 °C under a nitrogen atmosphere. After 60 min, the reaction mixture was transferred to a Schlenk tube containing a solution of compound **7** (4.38 g, 12 mmol) in THF (20 mL). The reaction mixture was stirred for 1 h at –78 °C, then warmed to room temperature, and stirred for an additional 16 h. After the addition of water (200 mL), the THF was removed under reduced pressure, and the residue was extracted with CH_2Cl_2 (3× 30 mL). The combined organic phases were dried with $MgSO_4$, filtered and the solvents were evaporated in vacuo. The residue was extracted with 50 mL of THF. Then *p*-toluenesulfonic acid (PTSA) (0.23 g, 1.2 mmol) and a few drops of water were added. The reaction mixture was stirred for 24 h at 45 °C. The THF was removed under reduced pressure, and then water (100 mL) was added, and the residue was extracted with CH_2Cl_2 (3× 30 mL). The combined organic phases were dried with $MgSO_4$, filtered and the solvents evaporated in vacuo. The residue was purified by chromatography over silica gel. Elution with an ethyl acetate/pentane (1:12) mixture afforded **1o** as yellow crystals (2.83 g, 50%); m.p. 158–159 °C. ^{1}H NMR (400 MHz $CDCl_3$): δ = 9.77 (s, 1 H), 7.77 (s, 1 H), 7.11–7.09 (d, J = 8.9 Hz, 1 H), 6.90 (s, 1 H), 6.82–6.80 (d, J = 9.8 Hz, 1 H), 3.73 (s, 3 H), 3.54 (s, 3 H), 1.91 (s, 3 H), 1.80 (s, 3 H) ppm. ^{13}C NMR (100 MHz $CDCl_3$): δ = 181.2, 154.2, 150.7, 140.2, 137.2, 135.8, 131.2, 126.6, 124.7, 111.0, 109.0, 100.6, 100.5, 99.4, 54.7, 29.2, 28.7, 14.7, 10.6 ppm. HRMS (ESI) m/z [M + H]$^+$ calcd. for $C_{22}H_{17}F_6NO_2S^+$ 474.0948, found 474.0957.

4-[3,3,4,4,5,5-Hexafluoro-2-(5-methoxy-1,2-dimethyl-1*H*-indol-3-yl)cyclopent-1-enyl]-5-methylthiophene-2-carbonitrile (2o): Compound **1o** (1.2 g, 2.5 mmol) was added to a mixture of ethanol (100 mL), $NH_2OH{\cdot}HCl$ (0.35 g, 5.06 mmol), and aqueous $NaHCO_3$ (10%, 3.3 mL), and the resulting mixture was stirred for 2 h at room temperature. The solvent was removed in vacuo, acetic anhydride (20 mL) was added to the residue, and the solution was heated for 24 h at 100 °C. The reaction mixture was cooled to room temperature, and water (50 mL) was added, followed by aqueous $NaHCO_3$ (10%, 5.0 mL). To the resulting aqueous mixture were added ether (40 mL) and saturated aqueous sodium hydrogen carbonate (100 mL), and the organic layer was separated. The organic phase was dried with $MgSO_4$, filtered and the solvents evaporated in vacuo. The residue was purified by chromatography over silica gel. Elution with a 1:15 ethyl acetate/pentane mixture afforded **2o** as yellow crystals (0.7 g, 60%); m.p. 150–151 °C. ^{1}H NMR (400 MHz $CDCl_3$): δ = 7.68 (s, 1 H), 7.18–7.16 (d, J = 8.7 Hz, 1 H), 6.89 (s, 1 H), 6.87–6.86 (d, J = 8.9 Hz, 1 H), 3.79 (s, 3 H), 3.62 (s, 3 H),1.99 (s, 3 H), 1.86 (s, 3 H) ppm. ^{13}C NMR (100 MHz $CDCl_3$): δ = 155.3, 148.5, 138.3, 137.8, 132.3, 127.1, 125.6, 113.4, 112.1, 110.2, 107.6, 101.4, 100.2, 55.7, 30.2, 14.9, 11.6 ppm. HRMS (ESI): calcd. for $C_{22}H_{17}F_6N_2OS^+$ [M + H]$^+$ 471.0966; found 471.0955.

4-[2-(1,2-Dimethyl-1*H*-indol-3-yl)-3,3,4,4,5,5-hexafluorocyclopent-1-enyl]-5-methylthiophene-2-carbaldehyde (3o): *n*-Butyllithium (2.4 M in hexane, 15.6 mmol, 6.5 mL) was added dropwise to a stirred solution of compound **6** (3.35 g, 12 mmol) in THF (100 mL) at –78 °C under a nitrogen atmosphere. After 60 min, the reaction mixture was transferred to a Schlenk tube containing a solution of compound **7** (4.04 g, 12 mmol) in THF (20 mL). The reaction mixture was stirred for 1 h at –78 °C, then warmed to room temperature, and stirred for an additional 16 h. THF was removed under reduced pressure, then water (200 mL) was added, and the residue was extracted with CH_2Cl_2 (3× 30 mL). The combined organic phases were dried with $MgSO_4$, filtered, and the solvents were evaporated in vacuo. The residue was extracted with THF (50 mL). *p*-Toluenesulfonic acid (PTSA, 0.23 g, 1.2 mmol) and a few drops of water were added. The reaction mixture was stirred for 24 h at 45 °C. The THF was removed under reduced pressure, and then water (100 mL) was added, and the residue was extracted with CH_2Cl_2 (3× 30 mL). The combined organic phases were dried with $MgSO_4$, filtered and the solvents were evaporated in vacuo. The residue was purified by chromatography over silica gel. Elution with a 1:12 ethyl acetate/pentane mixture afforded **3o** as yellow crystals (2.92 g, 55%); m.p. 162–163 °C. ^{1}H NMR (400 MHz $CDCl_3$): δ = 9.84 (s, 1 H), 7.82 (s, 1 H), 7.55–7.53 (d, J = 8.0 Hz, 1 H), 7.29–7.28 (d, J = 8.1 Hz, 1 H), 7.24–7.22 (d, J = 8.3 Hz, 1 H), 7.16–7.12 (t, J = 7.5 Hz, 1 H), 3.64 (s, 3 H), 2.00 (s, 3 H), 1.87 (s, 3 H) ppm. ^{13}C NMR (100 MHz $CDCl_3$): δ = 182.2, 151.6, 141.3, 137.9, 137.1, 136.9, 127.5, 125.3, 122.3, 121.3, 119.3, 109.4, 100.6, 77.4, 77.0, 76.8, 30.0, 15.6, 11.4 ppm. HRMS (ESI): calcd. for $C_{21}H_{15}F_6NOS^+$ [M + H]$^+$ 444.0851; found 444.0855.

2-({4-[2-(1,2-Dimethyl-1*H*-indol-3-yl)-3,3,4,4,5,5-hexafluorocyclopent-1-enyl]-5-methylthiophen-2-yl}methylene)malononitrile (4o): Compound **3o** (0.91 g, 2.0 mmol) was added to a mixture of tetrahydrofuran (100 mL), malononitrile (0.14 g, 2.1 mmol), and piperidine (0.5 mL), and the resulting mixture was heated for 24 h at 65 °C. The solvent was removed in vacuo, and then water (100 mL) was added. The residue was extracted with CH_2Cl_2 (3× 30 mL), and the combined organic phases were dried with $MgSO_4$, filtered and the solvents evaporated in vacuo. The crude product was purified by chromatography over silica gel. Elution with a 1:9 ethyl acetate/pentane mixture afforded **4o** as grey crystals (0.63 g, 63%), m.p. 194–195 °C. ^{1}H NMR (400 MHz $CDCl_3$): δ = 7.80 (s, 1 H). 7.76 (s, 1 H), 7.52–7.49 (d, J = 7.9 Hz, 1 H), 7.35–7.33 (d, J = 8.1 Hz, 1 H), 7.28–7.26 (d, J = 8.1 Hz, 1 H), 7.19–7.15 (t, J = 7.4 Hz, 3 H), 3.69 (s, 3 H), 2.06 (s, 3 H), 1.97 (s, 3 H) ppm. ^{13}C NMR (100 MHz $CDCl_3$): δ = 152.4, 149.3, 138.3, 136.9, 136.2, 131.8, 127.2, 124.1, 121.5, 120.4, 118.2, 111.8, 108.5, 99.4, 29.1, 14.6, 10.5 ppm. HRMS (ESI): calcd. for $C_{24}H_{15}F_6N_3S^+$ [M + H]$^+$ 492.0964; found 492.0962.

Supporting Information (see footnote on the first page of this article): NMR spectra, absorption spectra and crystallographic data of NIR-sensitive diarylethene derivatives.

Acknowledgments

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