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Prominent Bathochromic Shift Effect of Indole-Containing Diarylethene Derivatives

Hong-Bo Cheng, Yao-Dong Huang, Lina Zhao, Xu Li and Hai-Chen Wu*

The potential implication of photochromic materials with absorption and reactivity in the near-infrared region is far-reaching. In this work, three novel bisindole-containing diarylethene derivatives 1o–3o have been successfully synthesized and their photochromic behaviours exhibit strong bathochromic shift effect compared with bisbenzothiophene diarylethene 4o. These new bisindole-diarylethene compounds 1o–3o are highly sensitive to photo-stimuli both in solution and in poly(methyl methacrylate) films. Besides, 1o–3o exhibit excellent reversible fluorescence switching behavior modulated by optical stimuli.

1. Introduction

Photochromic materials have attracted a great deal of interest because their photoisomerization can be used to develop photochemically controllable materials for novel photoswitching devices and optical data storage.¹ Photochromic compounds with absorption and reactivity in the near-infrared (NIR) region can enhance the semiconductor diode laser susceptibility for applications in optical memory storage.² Among various photochromic compounds, diarylethene derivatives (DAEs) are the most promising optically responsive compounds in photochemistry and materials science owing to their reversible transformations between ring-open and ring-closed conformations that have markedly different optical and electronic properties.³ To achieve NIR-absorption in DAEs, one commonly used method is to augment the π-conjugation of the thiophene moiety. But, this approach often requires laborious syntheses and suffers from the convergence limit of the bathochromic shift effect.⁴ Therefore, different attempts have been made to construct diarylethene derivatives with NIR absorptions. Yam and co-workers reported an innovative way of achieving NIR photochrome behaviour through metal-coordination-assisted planarization of the extended π-conjugated system in dithienylethene.⁵ Recently, Tian and coworkers constructed two NIR photochromic systems by introducing electron-donating (D) and electron-accepting moieties (A) to DAEs, whose fluorescence performance can be modulated by cyanide anion.⁶ Diarylenes containing thiophene moieties have been intensively investigated.⁷ Compared with thiophene, indole ring has higher electron density that may have potential influence on the photochromic performance of DAEs. However, bisindole-containing diarylenes have rarely been exploited to construct NIR photochromic systems so far.

Herein, we described the design and syntheses of three bisindole diarylperfluorocyclopentenes 1o–3o as well as the reference compound bisbenzothiophene diarylethene 4o (Scheme 1), and investigated their photochromic behavior and photophysical properties. The compounds 1o–3o form molecular switches that undergo light-induced cyclization and decyclization reactions. We introduced perfluorocyclopentene to DAEs 1o–3o as the central ethene linker because of its resistance to fatigue.⁸ Interestingly, 1o–3o exhibited prominent bathochromic shift effect to the NIR region compared with the reference compound 4o.

Scheme 1. Photoisomerization of 1o–3o and the reference compound 4o.
2. Results and Discussion

Synthesis

The syntheses of photochromic diarylethenes 1o–3o are illustrated in Scheme 2. The open diarylethen 1o and open diarylethen 3o were prepared in 52–55% yield by lithiation of 3-bromo-5-methoxy-1,2-dimethyl-1H-indole (5) and 3-bromo-1,2-dimethyl-1H-indole (6) followed by the addition of 0.5 equivalent octafluorocyclopentene. The open diarylethen 2o was synthesized by lithiation of 3-bromo-1,2-dimethyl-1H-indole (6) followed by the addition of 5-methoxy-1,2-dimethyl-3-(perfluorocyclopent-1-enyl)-1H-indole (7). The compounds were characterised by NMR spectroscopy, mass spectroscopy, and X-ray crystallographic analysis. (see Supporting Information Figures S1–S9).

![Scheme 2. Syntheses of compounds 1o–3o.](image)

X-ray crystallographic study

The single crystals of 1o were acquired by slow evaporation from an ethyl acetate/hexane (1:1, v/v) solution at room temperature for a week. Single-crystal X-ray diffraction measurements reveal that 1o crystallize in the monoclinic space group $P2_1/n$. The X-ray crystallographic data are listed in Table S1. As shown in Figure 1, the structure of 1o exclusively adopts the antiparallel conformations, which are in sharp contrast to the solution-phase behavior, where the antiparallel and parallel conformers coexist. The distance between the photocyclizing carbon atoms C8 and C24 is 3.768 Å.

The crystals of 1o would 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. Torsion angles between indole and hexafluorocyclopentene rings are -47.3° (C6-C7-C12-C13) and -56.2° (C15-C16-C17-C18). Interestingly, 1o also shows photochromic reactivity in the crystalline state. Upon irradiation with 365 nm light, the pale crystals of 1o turned blue, and the blue color faded after irradiation with visible light (Figure 2).

Molecular packing arrangements of 1o were shown in Figure 3. In the crystal, the intermolecular C-H-F and C-H-O interactions are clearly noticed. Fluorine atoms F2 and F3 of the hexafluorocyclopentene ring serve as the acceptors for hydrogen atoms H5 and H2 of the indole ring of the adjacent molecule, respectively. Oxygen atom O1 serves as acceptor for hydrogen atom H3 of the neighbouring molecule. Consequently, a 3D supramolecular network was formed via hydrogen-bonding interactions in 1o (C(2)--H(2)--F(3), 3.467(2) Å, 173°; C(3)--H(3)--O(1), 3.403(2) Å, 154°; C(5)--H(5)--F(2), 3.083(2) Å, 132°).

Photochromic Behaviour

The backbones of DAEs 1o–3o could switch between colorless open forms and colored closed forms by alternated irradiation with UV and visible light. The spectral changes of bisindole-containing 1o–3o and reference compound 4o in hexane exposed to UV light are shown in Figures S10 and
The photochromic properties of DAEs 1o–4o in toluene are similar to those in hexane (Figure 4). Upon 365 nm UV light irradiation, the spectral changes of 1o–4o in toluene are shown in Figure S4. The absorption showed evident bathochromic shift effect with the increase in the polarity of solvents. The photo-generated closed-ring isomers 1c–4c have their absorption maxima at 638, 620, 593 and 523 nm, respectively. As shown in Table 1, the absorption maxima of closed-ring isomers 1c–4c underwent an obvious solvent-induced red shift of 26, 26, 21, and 9 nm, respectively. Moreover, the thermal stability of closed-ring isomer 1c was investigated by UV/vis spectroscopy at an elevated temperature of 45°C. The signal of thermal ring opening was hardly observed for at least 270 min upon monitoring at 638, 466 and 350 nm (Figure 5). We also examined the fatigue resistance properties of 1o–3o upon alternating UV and visible-light irradiation. As shown in Figure S13, the cycles could be repeated many times without any significant degradation in toluene. The quantum yields of 1o–3o are summarized in Table S3 (Supporting Information). The photocyclization quantum yields ($\Phi_{o\rightarrow c}$) for active conformers were determined to be 0.28 for 1o, 0.20 for 2o and 0.25 for 3o.

### Table 1. The UV-vis absorption maxima of compounds 1o–4o in hexane and toluene before and after irradiation with 365 nm light at 25 °C (0–2 min).

<table>
<thead>
<tr>
<th>compounds</th>
<th>Hexane</th>
<th>Toluene</th>
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<tbody>
<tr>
<td></td>
<td>$\lambda_{\text{max}}$ (open)</td>
<td>$\lambda_{\text{max}}$ (closed)</td>
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<tr>
<td>1o</td>
<td>277 nm</td>
<td>612 nm</td>
</tr>
<tr>
<td>2o</td>
<td>280 nm</td>
<td>594 nm</td>
</tr>
<tr>
<td>3o</td>
<td>279 nm</td>
<td>572 nm</td>
</tr>
<tr>
<td>4o</td>
<td>266 nm</td>
<td>514 nm</td>
</tr>
</tbody>
</table>

Figure 4 UV-vis spectral changes of (a) 1o, (b) 2o, (c) 3o and (d) 4o upon UV light (365 nm) irradiation in toluene at 25 °C (0–2 min).

Table 1. Upon irradiation with 365 nm UV-light, the initially colorless solutions of compounds 1o–4o display a strong coloration and the photo-generated closed-ring isomers have their absorption maxima at 612, 594, 572 and 514 nm, respectively. Compared with reference compound 4o, compounds 1o–3o showed strong bathochromic shift effect (~98 nm for 1o, ~80 nm for 2o and ~58 nm for 3o) upon UV light irradiation. Once switched to visible light irradiation, the bluish color disappeared and the absorption peaks of the open-ring forms were restored. The stronger bathochromic shift of 1c compared with 2c and 3c is probably due to substituent effects. This observation confirmed that indole and its derivatives can play a crucial role in constructing NIR-responsive photochromic materials.
of a new absorption band in the visible light range, with 1c, 2c and 3c having their maxima at 649, 628 and 600 nm, respectively. The absorption maxima of closed-ring isomers 1e–3e underwent an obvious red shift of 11, 8 and 7 ppm compared with the absorption maxima of these compounds in toluene. This observation further confirmed that altering the electronic properties of the heteroaryl moieties is an efficient approach to fine-tune the spectral profiles of these photochromic materials.

The bisindole-containing DAEs 1o–3o underwent light-induced cyclization and decyclization reactions and show excellent photochromic properties accompanied with efficient quenching of fluorescence emission by the closed form of the diarylethene moiety. These features allow them to behave as reversible optical molecular switches. We believe the results presented here will provide a new perspective for the design of NIR-sensitive molecular machines and smart materials.

3. Conclusions

In summary, we have designed and synthesized three bisindole diarylethene derivatives 1o–3o and their photochromic behaviors show prominent red shift to the NIR region compared with the reference compound 4o. The photophysical and photochromic properties of 1o–3o were comprehensively investigated by UV/vis, fluorescence spectra and X-ray crystallographic analysis. Compared with 2o and 3o, 1o exhibits stronger red shift both in solution and in PMMA under UV irradiation probably due to the substituent effect. Moreover, 1o–3o undergo light-induced cyclization and decyclization reactions and show excellent photochromic properties accompanied with efficient quenching of fluorescence emission by the closed form of the diarylethene moiety. These features allow them to behave as reversible optical molecular switches. We believe the results presented here will provide a new perspective for the design of NIR-sensitive molecular machines and smart materials.

4. Experimental

Instrumentation

All the commercial reagents unless otherwise annotated were purchased from Sigma Aldrich, Alfa Aesar and were used without further purification. 3,3’-(perfluorocyclopent-1-ene-1,2-diy|bis(2-methylbenzo[b]thiophene) (4o), 3-bromo-5-methoxy-1,2-dimethyl-1H-indole (5), 3-bromo-1,2-dimethyl-1H-indole (6) and 5-methoxy-1,2-dimethyl-3-(perfluorocyclopent-1-eyl)-1H-indole (7) were prepared according to the literatures procedure. The optical
switch experiments were carried out using a photochemical reaction apparatus with a 500W 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) on a Varian Cary Eclipse equipped with a Varian Cary single-cell Peltier accessory to control the temperature. The method preparation of PMMA Film: photochromic materials 10-30 dissolved in 3 ml of chloroform. The solution was filtered using membranes and added PMMA in the solution stirring until the PMMA was resolved. The solution was spin-coated on a glass substrate with a spin rate of 2000 rpm. The coated film was dried in a vacuum oven to give transparent and homogeneous film.

Preparation of Compound 1o:

n-Butyllithium (2.4 M in hexane, 15.6 mmol, 6.5 mL) was added dropwise to a stirred solution of 3-bromo-5-methoxy-1,2-dimethyl-1H-indole 5 (3.04 g, 12 mmol) in 100 mL of THF at −78 °C under a nitrogen atmosphere. After 60 min, a solution of compound perfluorocyclopentene (1.27 g, 6 mmol) in 20 mL of THF was added dropwise to the reaction mixture. The reaction mixture was stirred for 1 hour at −78 °C, then allowed to warm up to room temperature, and stirred for additional 16 h. After addition of 100 mL of water, THF was removed under reduced pressure, and the residue was extracted with CH2Cl2 (3 × 30 mL). The combined organic phases were dried over MgSO4, filtered and evaporated in vacuo and chromatographed with silica gel. Elution with a 1:15 acetic ether/hexane mixture afforded 1o as yellow crystals (1.63 g, 52%). Mp: 244-245 °C; 1H NMR (400 MHz CDCl3) δ 6.97-6.95 (d, J = 9.5 Hz, 2H), 6.88 (s, 2H) 6.69-6.67 (d, J = 8.2 Hz, 2H), 3.15 (s, 6H) 3.37 (s, 6H); 13C NMR (100 MHz CDCl3) δ 151.7, 138.2, 138.0, 120.5, 119.5, 119.3, 118.5, 118.4, 107.9, 100.3, 28.1, 10.4; HRMS (ESI) m/z [M+ H]+ calecd for C25H24F2N2O2 478.1600, found 478.1594. IR (KBr) v: 3051, 2918, 1542, 1475, 1329, 1269, 1233, 1179, 1181, 1087, 1040, 1001, 969, 849, 822, 802, 743, 554 cm⁻¹.

Preparation of Compound 2o:

n-Butyllithium (2.4 M in hexane, 15.6 mmol, 6.5 mL) was added dropwise to a stirred solution of 3-bromo-1,2-dimethyl-1H-indole 6 (2.69 g, 12 mmol) in 100 mL of THF at −78 °C under a nitrogen atmosphere. After 60 min, a solution of compound perfluorocyclopentene (1.27 g, 6 mmol) in 20 mL of THF was added dropwise to the reaction mixture. The reaction mixture was stirred for 1 hour at −78 °C, then allowed to warm up to room temperature, and stirred for additional 16 h. After addition of 100 mL of water, THF was removed under reduced pressure, and the residue was extracted with CH2Cl2 (3 × 30 mL). The combined organic phases were dried over MgSO4, filtered and evaporated in vacuo and chromatographed with silica gel. Elution with a 1:15 acetic ether/hexane mixture afforded 2o as yellow crystals (2.95 g, 50%). Mp: 237-238°C; 1H NMR (400 MHz CDCl3) δ 7.71-7.69 (d, J = 7.7 Hz, 1H) 7.15-7.14 (d, J = 3.8 Hz, 1H) 7.11-7.08 (dd, J1,J2 = 4.4 Hz, J1,J3 = 8.0 Hz, 1H) 7.02-6.99 (d, J = 8.8 Hz, 1H) 6.83 (s, 1H) 6.73-6.71 (d, J = 8.7 Hz, 1H) 3.49 (s, 3H) 3.44 (s, 3H) 3.41 (s, 3H) 2.01 (s, 3H) 1.84 (s, 3H); 13C NMR (100 MHz CDCl3) δ 247.9, 154.6, 138.1, 137.9, 136.9, 131.9, 126.2, 126.1, 121.6, 120.6, 119.9, 119.6, 119.6, 111.5, 109.6, 108.9, 101.7, 101.2, 55.5, 29.8, 29.7, 11.7, 11.3; HRMS (ESI) m/z [M+H]+ calecd for C25H23F2N2O2 493.1715, found 493.1700. IR (KBr) v: 3686, 2948, 1619, 1539, 1488, 1438, 1338, 1272, 1218, 1181, 1159, 1119, 1042, 975, 839, 813, 798, 764, 744, 554 cm⁻¹.

Preparation of Compound 3o:

-n-Butyllithium (2.4 M in hexane, 15.6 mmol, 6.5 mL) was added dropwise to a stirred solution of 3-bromo-1,2-dimethyl-1H-indole 6 (2.69 g, 12 mmol) in 100 mL of THF at −78 °C under a nitrogen atmosphere. After 60 min, a solution of compound perfluorocyclopentene (1.27 g, 6 mmol) in 20 mL of THF was added dropwise to the reaction mixture. The reaction mixture was stirred for 1 hour at −78 °C, then allowed to warm up to room temperature, and stirred for additional 16 h. After addition of 100 mL of water, THF was removed under reduced pressure, and the residue was extracted with CH2Cl2 (3 × 30 mL). The combined organic phases were dried over MgSO4, filtered and evaporated in vacuo and chromatographed with silica gel. Elution with a 1:15 acetic ether/hexane mixture afforded 3o as yellow crystals (1.52 g, 55%). Mp: 222-223 °C; 1H NMR (400 MHz CDCl3) δ 7.64-7.62 (d, J = 7.7 Hz, 2H), 7.19-7.14 (dd, J1,J2 = 7.5 Hz, J1,J3 = 13.8 Hz, 4H) 7.11-7.09 (d, J = 7.3 Hz, 2H) 3.49 (s, 6H) 1.89 (s, 3H); 13C NMR (100 MHz CDCl3) δ 136.6, 135.787, 125.1, 120.5, 119.5, 118.5, 118.5, 118.4, 107.9, 100.3, 28.8, 10.4; HRMS (ESI) m/z [M+H]+ calecd for C25H23F2N2O2 463.1609, found 463.1594. IR (KBr) v: 3051, 2918, 1542, 1475, 1329, 1269, 1233, 1179, 1117, 1087, 1040, 1001, 969, 849, 822, 802, 743, 554 cm⁻¹.

Molecular Orbital Calculation Method

In this study, we use spin-unrestricted density functional theory (DFT) method for the molecular orbital calculations. Simulations are carried out through an effective core potentials method within the Perdew, Burke and Ernzerhof (PBE) of general gradient approximations (GGA) exchange-correction functional approximation as implemented in the DMOl3 program package in the Materials Studio of Accelrys Inc. The basis set is chosen as DND. The real-space global orbital cutoff radius quality is set as high as possible. Fully relaxed geometries are obtained by optimizing all atomic positions until the energy convergence tolerance, force convergence tolerance and displacement convergence tolerance are less than 1×10⁻⁵ Ha, 0.002 Ha and 0.005 Å, respectively.

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