Dyes and Pigments 92 (2012) 961–966

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Imidazole-based dithienylethenes as a selective chemosensors for iron(III) ions

Shuyuan Huang, Ziyong Li, Sisi Li, Jun Yin*, Shenghua Liu*

Key Laboratory of Pesticide and Chemical Biology, Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, PR China

ARTICLE INFO

Article history:
Received 23 June 2011
Received in revised form
1 August 2011
Accepted 3 August 2011
Available online 10 August 2011

Keywords:
Dithienylethene
Imidazole
Molecular recognition
Photochromism
Fluorescence
Iron(III) ions

ABSTRACT

Four novel imidazole-based dithienylethenes have been successfully synthesized in good yields. Their structures have been confirmed by NMR spectrometry, mass spectrometry, and elemental analyses. UV/Vis absorption spectra indicated that these dithienylethenes can easily isomerize between the open-ring and closed-ring isomers upon irradiation with UV or visible light in solution, and that the respective closed-ring isomers show decreased fluorescence properties compared with the open-ring isomers. Moreover, the open-ring and closed-ring isomers display high selectivity toward Fe^{3+}, such that the addition of Fe^{3+} obviously suppresses their fluorescence intensity.

1. Introduction

Photochromic dithienylethenes are considered to be among the most promising systems for applications in optical memory media and switching devices due to their excellent photochromic properties coupled with thermal stability, fatigue resistance, and sensitivity [1–7]. Cyclopentenes and derivatives bearing thiophene substituents attached via their 2- and 3-positions have been extensively investigated [8–11]. Therefore, current research interest is focused on the introduction of heterocycles to obtain novel photochromic materials with excellent properties. Imidazole as a building block has been widely used in many fields, such as biology [12], medicine [13], ionic liquids [14] as well as electronic and optical materials [15–17] due to its biological activity and available sites for further functionalization. Furthermore, the imidazole moiety has also been widely applied in supramolecular chemistry. For example, the imidazole NH has been used as a hydrogen-bond donor in anion sensors [18–23]. Moreover, imidazole shows excellent coordinative abilities toward metal ions [24–31], so imidazole derivatives have also been applied in environmental monitoring, industrial process control, metalloneurochemistry, and biomedical diagnostics [32–34].

Therefore, the imidazole ring has been incorporated into the photochromic dithienylethene unit with a view to optimizing the photochromism and giving rise to some novel properties. There have been some recent reports in the field of dithienylethenes. For example, Huang et al. and others have reported imidazole-substituted thiophene cyclopentenes [35–37]. Recently, we also synthesized a series of imidazole-substituted thiophene cyclopentenes [26,38]. At the same time, the imidazole ring has also been used as a bridging unit in substituting the cyclopentene ring [39]. As mentioned in the introduction, the imidazole moiety has been widely used in chemosensors. However, there have been few investigations concerning the use of imidazole-based dithienylethenes as chemosensors. In the present work, we have designed and synthesized four dithienylethenes incorporating imidazole and *N*-methylated imidazole bridging units (Scheme 1), and have investigated the photochromic and fluorescence properties of their open-ring and closed-ring isomers. Furthermore, we have also investigated the effects of metal ions. These studies have revealed that: 1) the respective closed-ring isomers show decreased fluorescence properties compared with their open-ring isomers, 2) the respective open-ring and closed-ring isomers show an obvious decrease in fluorescence when iron (III) ions are added.

2. Experimental

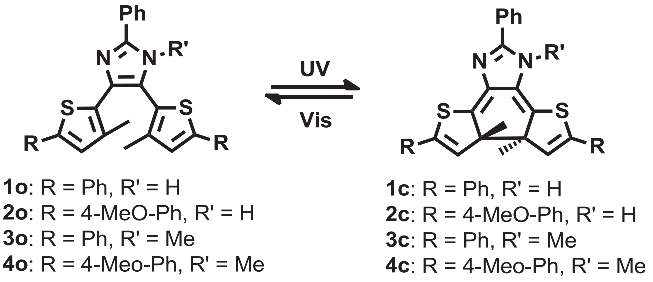
2.1. General procedures

All manipulations were carried out under an argon atmosphere by using standard Schlenk techniques, unless otherwise stated. All

---

* Corresponding authors. Tel./fax: +86 27 67867725.
E-mail addresses: yinj@mail.ccnu.edu.cn (J. Yin), chshliu@mail.ccnu.edu.cn (S. Liu).

0143-7208/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2011.08.005



Scheme 1. The molecular structures of dithienylethenes **1**–**4**.

reagents and starting materials were obtained from commercial suppliers and used without further purification. DMF was dried with magnesium sulfate then distilled under vacuum. Column chromatography was performed on silica gel (200–300 mesh). ^{1}H and ^{13}C NMR spectra were collected on American Varian Mercury Plus 400 spectrometer (400 MHz) or 600 MHz. ^{1}H and ^{13}C NMR chemical shifts are relative to TMS. Elemental analyses (C, H, N) were performed by the Microanalytical Services, College of Chemistry, CCNU. Electron impact ionization (EI) mass spectra were carried on Trace MS 2000. UV–Vis spectra were obtained on U-3310 UV Spectrophotometer. Fluorescence spectra were taken on a Fluoromax-P luminescence spectrometer (HORIBA JOBIN YVON INC.). Diketone **60** was prepared by literature methods [40]. Target compounds **1**–**4** were prepared according to the synthetic route presented in Scheme 2 by modified procedures of reported methods [41,42].

*2.2. Synthesis of dithienylethene-based complexes **1**–**4**, **7**–**9***

*2.2.1. Synthesis of **1** and **2***

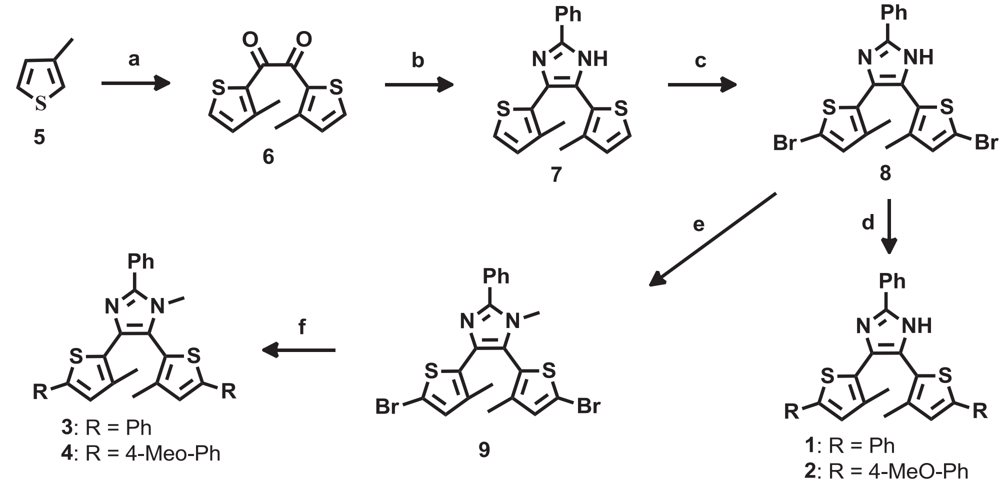
To a suspension of **8** (148 mg, 0.3 mmol), $Pd(PPh_3)_4$ (69 mg, 0.06 mmol) and K_2CO_3 (42 mg, 0.3 mmol) in a stirred solution of toluene (12 mL), ethanol (6 mL) and water (2 mL), phenylboric acid (109 mg, 0.9 mmol) or 4-methoxylphenylboric acid (136 mg, 0.9 mmol) was added under nitrogen atmosphere. The mixture was heated to reflux for 8 h. After cooling to room temperature, cold water (10 mL) was carefully added to the reaction mixture and the water layer was extracted with DCM (3 × 20 mL). The combined organic layers were dried (Na_2SO_4) before the solvent was removed in vacuo. Chromatography of the residue on silica gel (petroleum ether/DCM = 1:2, v/v) afforded the compound **1** as white solid (79 mg, 54%) and the compound **2** as yellow solid (95 mg, 60%). Compound **1**: ^{1}H NMR (400 MHz, DMSO): δ ppm = 2.03 (s, 6H, CH_3), 7.35 (d, $J = 4$ Hz, 2H, thiophene-H), 7.48–7.62 (m, 13H, Ar-H), 8.07 (d, $J = 8$ Hz, 2H, Ar-H), 13.01(s, 1H, NH). ^{13}C NMR (100 MHz, DMSO): δ ppm = 14.65, 120.61, 121.23, 123.14, 124.04, 124.95, 125.25, 128.82, 129.14, 131.81, 132.78, 149.46. MS (m/z): 488.04 (M^+). Anal. Calcd for $C_{31}H_{24}N_2S_2$: C, 76.19; H, 4.95; N, 5.73; S, 13.12. Found: C, 76.15; H, 4.83; N, 5.71, S, 13.16. Compound **2**: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 1.99 (s, 6H, CH_3), 3.82 (s, 6H, OCH_3), 6.88–6.90 (m, 4H, Ar-H), 6.96 (s, 2H, thiophene-H), 7.25–7.50 (m, 7H, Ar-H), 7.91 (d, $J = 8$ Hz, 2H, Ar-H), 9.47 (s, 1H, N-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm = 14.88, 55.37, 114.28, 121.47, 123.74, 125.31, 126.78, 128.88, 128.97, 129.64, 146.44, 159.01. MS (m/z): 548.09 (M^+). Anal. Calcd for $C_{33}H_{28}N_2O_2S_2$: C, 72.23; H, 5.14; N, 5.11; S, 11.69. Found: C, 72.03; H, 5.02; N, 5.13; S, 11.72.

*2.2.2. Synthesis of **3** and **4***

This synthesis was similar to the synthesis of **1** and **2**, using the compound **9** instead of **8**. Compound **3**: Yield, 70%. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 2.06 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 3.65 (s, 3H, N-CH_3), 7.05 (s, 1H, Ar-H), 7.21 (s, 2H, thiophene-H), 7.25–7.63 (m, 12H, Ar-H), 7.78 (d, $J = 8$ Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm = 14.85, 15.13, 33.25, 109.66, 115.52, 119.39, 123.32, 124.17, 125.30, 125.50, 125.77, 126.49, 126.90, 127.74, 128.51, 128.64, 128.88, 129.12, 130.27, 130.43, 133.83, 134.52, 135.80, 140.55, 141.81, 145.48, 148.62. MS (m/z): 502.07 (M^+). Anal. Calcd for $C_{32}H_{26}N_2S_2$: C, 76.46; H, 5.21; N, 5.57; S, 12.76. Found: C, 76.25; H, 5.09; N, 5.23, S; 12.79. Compound **4**: Yield, 79%. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 2.04 (s, 3H, CH_3), 2.16 (s, 3H, CH_3), 3.65 (s, 3H, N-CH_3), 3.80 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 6.85 (s, 1H, thiophene-H), 6.87 (s, 1H, thiophene-H), 6.91–6.93 (t, $J = 4$ Hz, 3H, Ar-H), 7.09 (s, 1H, Ar-H), 7.45–7.56 (m, 7H, Ar-H), 7.78 (d, $J = 8$ Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.85, 15.12, 29.66, 33.24, 55.31, 114.03, 114.23, 123.11, 123.31, 125.47, 126.57, 126.74, 126.79, 127.50, 128.48, 128.80, 128.88, 130.49, 135.68, 140.47, 141.71, 145.39, 148.47, 158.73, 159.32. MS (m/z): 562.05 (M^+). Anal. Calcd for $C_{34}H_{30}N_2O_2S_2$: C, 72.57; H, 5.37; N, 4.98; S, 11.44. Found: C, 72.36; H, 5.49; N, 4.96; S, 11.47.

*2.2.3. Synthesis of **7***

A mixture of ammonium acetate (3.1 g, 40 mmol) and benzaldehyde (0.53 g, 5 mmol) was refluxed for 1 h in acetic acid (25 mL)



Scheme 2. Regents and conditions: (a) oxalyl chloride, aluminium trichloride, CS_2, 53%; (b) benzaldehyde, ammonium acetate, acetic acid, 63%; (c) NBS, acetic acid, benzene, 81%; (d) phenylboric acid or 4-methoxylphenylboric acid, $Pd(PPh_3)_4$, potassium carbonate, toluene, water, ethanol, 60%; (e) methyl iodide, potassium carbonate, DMF, 82%. (f) phenylboric acid or 4-methoxylphenylboric acid, $Pd(PPh_3)_4$, potassium carbonate, toluene, water, ethanol, 79%.

under nitrogen atmosphere. Then the compound **6** (1.25 g, 5 mmol) was added and the mixture was further refluxed overnight. The mixture was poured into cold water (50 mL), neutralized with 10% aq. Na_2CO_3 and extracted with DCM (3 × 20 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was removed in vacuum. The compound was purified by column chromatography (petroleum ether/ethyl acetate = 20:1, v/v) to yield (1.06 g, 63%) of a white solid. ^1H NMR (400 MHz, $CDCl_3$): δ ppm = 1.92 (s, 6H, CH_3), 6.80 (d, $J = 4$ Hz, 2H, thiophene-H), 7.19 (d, $J = 8$ Hz, 2H, thiophene-H), 7.35–7.38 (m, 3H, Ar-H), 7.86 (d, $J = 4$ Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm = 14.39, 109.84, 124.99, 125.38, 125.92, 126.23, 128.78, 128.89, 129.48, 130.10, 136.28, 146.59. MS (m/z): 336.00 (M^+). Anal. Calcd for $C_{19}H_{16}N_2S_2$: C, 67.82; H, 4.79; N, 8.33; S, 19.06. Found: C, 67.68; H, 4.68; N, 8.31; S, 19.11.

2.2.4. Synthesis of **8**

7 (2 g, 6 mmol) was suspended in a stirred solution of benzene (50 mL) and acetic acid (50 mL). Subsequently NBS (2.24 g, 12.6 mmol) was added and the solid material dissolved. The reaction mixture was refluxed for 4 h. After cooling, the mixture was poured into 3 M aq. NaOH solution (100 mL) and yellow precipitate was formed immediately. The solid was collected by filtration, washed with water and dried under vacuum to give the compound **8** in 81% yield. ^1H NMR (400 MHz, $CDCl_3$): δ ppm = 2.00 (s, 6H, CH_3), 6.82 (s, 2H, thiophene-H), 7.39–7.45 (m,3H, Ar-H), 7.87 (d, $J = 4$ Hz, 2H, Ar). ^{13}C NMR (100 MHz, DMSO): δ ppm = 14.34, 111.44, 125.27, 128.81, 129.63, 132.11, 133.27, 133.89, 134.33, 134.63, 135.10, 135.60, 146.67. MS (m/z): 493.99 (M^+). Anal. Calcd for $C_{19}H_{14}Br_2N_2S_2$: C, 46.17; H, 2.85; N, 5.67; S, 12.97. Found: C, 46.11; H, 2.79; N, 5.66; S, 12.99.

2.2.5. Synthesis of **9**

A mixture of **8** (2.85 g, 4 mmol), and K_2CO_3 (1.6 g, 8 mmol) in dry DMF (100 mL) was stirred for 0.5 h at room temperature. Subsequently CH_3I (1.64 g, 8 mmol) was added and the mixture was further stirred overnight at room temperature. Then the reaction mixture was poured into ice water (100 mL), yellow precipitate was formed. After filtering, washed with H_2O and dry under vacuum, the compound **9** was obtained in 82% yield. ^1H NMR (400 MHz, $CDCl_3$): δ ppm = 1.98 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 3.53 (s, 3H, N-CH_3), 6.74 (s, 1H, thiophene-H), 6.93 (s, 1H, thiophene-H), 7.24–7.48 (m, 3H, Ar-H), 7.70 (d, $J = 8$ Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm = 14.49, 14.97, 32.96, 110.30, 114.07, 121.98, 125.97, 128.48, 128.71, 128.94, 130.10, 131.69, 132.68, 132.93, 135.49, 135.61, 140.60, 148.67. MS (m/z): 507.78 (M^+). Anal. Calcd for $C_{20}H_{16}Br_2N_2S_2$: C, 47.26; H, 3.17; N, 5.51; S, 12.62. Found: C, 47.12; H, 3.23; N, 5.66; S; 12.65.

3. Results and discussion

3.1. General synthetic procedure of **1**–**4**, **7**–**9**

The synthetic route to the target compounds (**1**–**4**) is shown in Scheme 2. In our target compounds, two thiophene rings are attached to the imidazole moiety via their 2-positions, and the π-conjugation is extended by benzene or 4-methoxybenzene rings, which were appended by Suzuki coupling reactions. The imidazole unit was obtained in 63% yield by condensation of diketone **6** and benzaldehyde in the presence of ammonium acetate in acetic acid under nitrogen atmosphere. After bromination with NBS, compound **8** was obtained in high yield. The target dithienylethenes **1** and **2** were synthesized by palladium-catalyzed Suzuki coupling reactions. However, they showed very poor solubility, which was consistent with observations in previous literature reports [26,38]. Therefore, the NH of the imidazole ring was methylated with CH_3I in the presence of K_2CO_3 in DMF under nitrogen atmosphere to obtain the dithienylethenes **3** and **4**, which showed perfect solubility due to this modification of the imidazole ring. All of the dithienylethenes were characterized by standard analytical techniques, such as NMR, mass spectrometry, and elemental analysis (see the Supporting Information).

3.2. Photochromic and fluorescent properties

The absorption spectra of each of the compounds were measured at room temperature from 1.0×10^{-5} mol/L solutions. As shown in Fig. 1a, the absorption maxima of compounds **1o** and **2o** were observed at 328 nm and 326 nm ($\varepsilon = 1.81 \times 10^4$ and 2.48×10^4 L mol^{-1} cm^{-1}, respectively), which were considered to correspond to a π–π* transition [43]. After *N*-methylation of the imidazole ring, the absorptions of compounds **3o** and **4o** showed slight blue-shifts compared with compounds **1o** and **2o** possibly due to the decrease of the conjugated degree after *N*-methylation on the imidazole rings, which was in well agreement with our previous report [26]. Fig. 1b shows the changes in the absorption of compound **2** (1.0×10^{-5} mol/L in CH_2Cl_2) upon irradiation with UV light ($\lambda = 302$ nm). In general, the absorption of the ring-open isomer at a shorter wavelength (326 nm) decreased, while the absorption of the ring-closed isomer at a longer wavelength (505 nm) increased, since π-electrons delocalized and extended to the two thiophene rings [44]. Upon irradiation with visible light ($\lambda > 402$ nm), the **2c** underwent a cycloreversion reaction to thering-opened isomer **2o**. The corresponding *N*-methylated compound **4** behaved similarly to compound **2**. As shown in Fig. 1c, a new absorption band appeared at 510 nm owing to the formation of the ring-closed isomer upon irradiation with UV light. The isomerization properties of the other synthesized compounds upon irradiation with UV and visible light were also investigated and showed similar changes (see Figures S1 and S2 in the Supporting Information). According to these data, we found that compounds **1**–**4** showed similar photochromic properties. The absorption characteristics and the quantum yields of open-ring ($\varphi_{c\text{-}o}$) and closed-ring isomers ($\varphi_{o\text{-}c}$) of the compounds were summarized in Table 1.

Subsequently, their fluorescence spectra were obtained in CH_2Cl_2 at room temperature. According to the data (Table 1), compound **1o** exhibited an obvious fluorescence emission at 456 nm. However, upon irradiation with 254 nm UV light, the fluorescence intensity was quenched by *ca.* 76% as the ring-open isomer **1o** was converted into the ring-closed isomer **1c**, as depicted in Fig. 2a. Similar results were obtained when compounds **2o**, **3o**, and **4o** were irradiated with UV light (Fig. 2b; Figures S3 and S4 in the Supporting Information). Furthermore, we found that the fluorescence intensities of the *N*-methylated dithienylethenes **3o** and **4o** were higher than those of the corresponding non-methylated dithienylethenes **1o** and **2o**. In addition, the fluorescence quantum yields which were measured using quinoline sulfate ($\varphi_f = 0.55$, in 0.1 M aqueous H_2SO_4) as a reference of diarylethenes **3** and **4** were found to be higher than those of diarylethenes **1** and **2**, which indicated that *N*-methylation of the imidazole ring improves the fluorescence quantum yields. The photochromic parameters of the synthesized compounds are summarized in Table 1.

3.3. Fluorescence probe for Fe^{3+}

Subsequently, we investigated the changes in the fluorescence properties of the open- and closed-ring forms in acetonitrile at 2.0×10^{-5} mol/L at room temperature when metal ions were added. As shown in Fig. 3a, the fluorescence intensity of compound

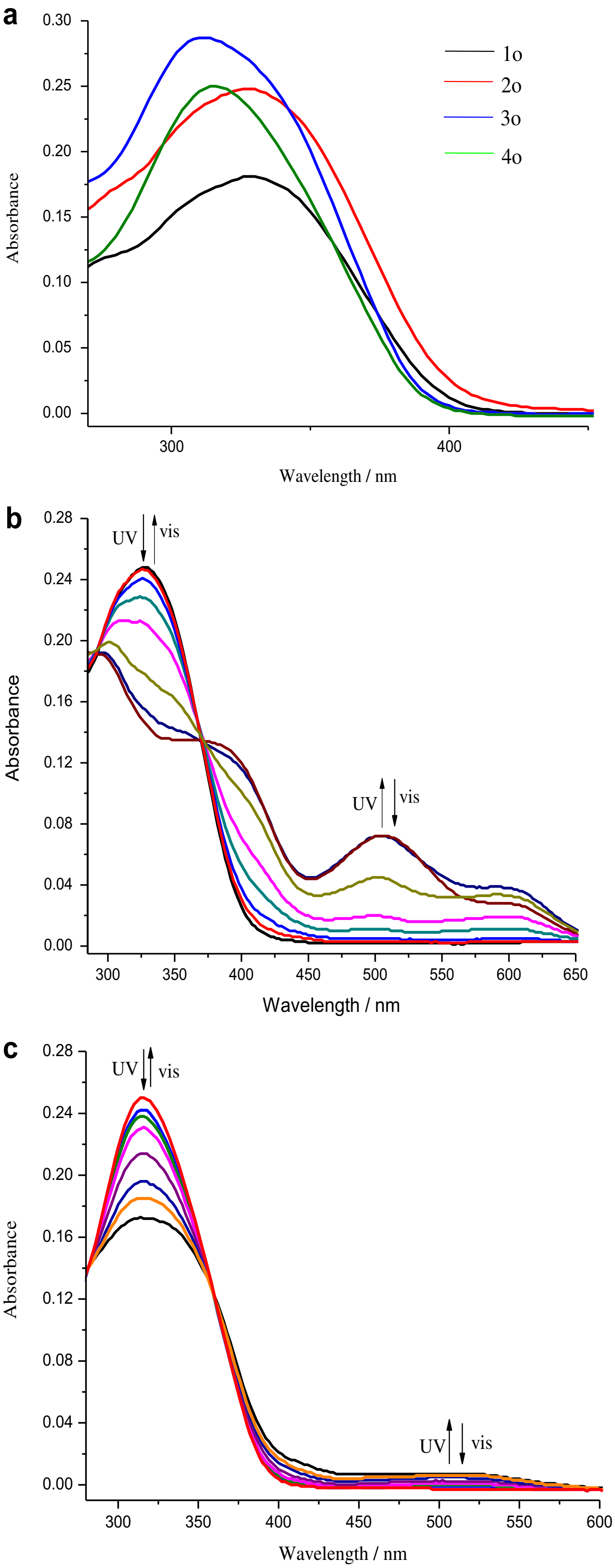


Fig. 1. (a) Absorption spectra of dithienylethenes **1**–**4**. Absorption spectral changes of compound **2** (b) and **4** (c) by photoirradiation in CH_2Cl_2 (1.0×10^{-5} mol/L) at room temperature.

Table 1
Absorption and fluorescence characteristics of dithienylethenes **1**–**4** in DCM (1.0×10^{-5} mol/L).

Compound	λ_{max}^{Abs}/nm[a] ($\varepsilon \times 10^4$/ L mol^{-1} cm^{-1})	λ_{max}^{Abs}/nm[b] ($\varepsilon \times 10^4$/ L mol^{-1} cm^{-1})	Φ[c]		λ_{max}^{Abs}/nm[d] (Φ[e])
	(Open)	(PSS)	$\varphi_{o\text{-}c}$ (λ/nm)	$\varphi_{c\text{-}o}$ (λ/nm)	
1	328(1.81)	548(0.13)	0.082(548)	0.0024(328)	456(0.04)
2	326(2.48)	504(0.72)	0.405(504)	0.0019(326)	456(0.04)
3	312(2.87)	424(0.33)	0.179(424)	0.0022(312)	458(0.06)
4	316(2.50)	528(0.07)	0.193(528)	0.0017(316)	457(0.11)

[a] Absorption maxima of open-ring isomers.
[b] Absorption maxima of closed-ring isomers.
[c] Quantum yields of open-ring ($\varphi_{c\text{-}o}$) and closed-ring isomers ($\varphi_{o\text{-}c}$), respectively.
[d] Emission maxima of fluorescence.
[e] Quantum yields of fluorescence.

3o decreased significantly in the presence of Fe^{3+} ions, while other metal ions (such as K^+, Ca^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}, Cd^{2+} and Hg^{2+}) did not exert such a quenching effect on the fluorescence under the same conditions. This result suggests that this compound displays remarkable "turn-off" fluorescence, and shows high selectivity toward Fe^{3+} among the various metal ions

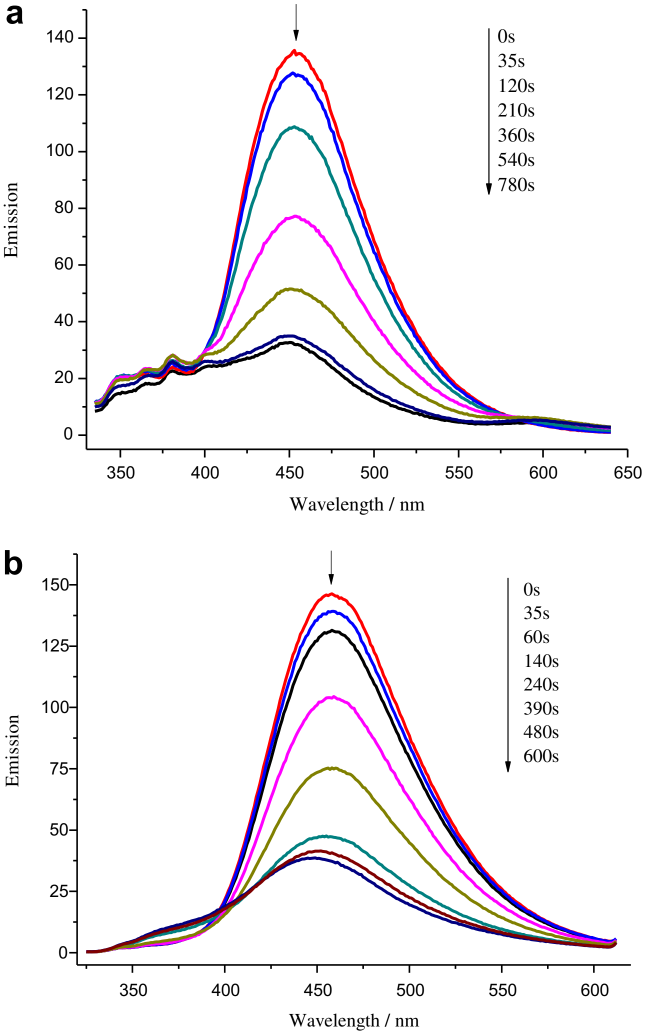


Fig. 2. Emission intensity changes of compounds **1** ($\lambda_{ex} = 328$ nm) (a) and **3** ($\lambda_{ex} = 312$ nm) (b) in CH_2Cl_2 (1.0×10^{-5} mol/L) with UV light irradiation.

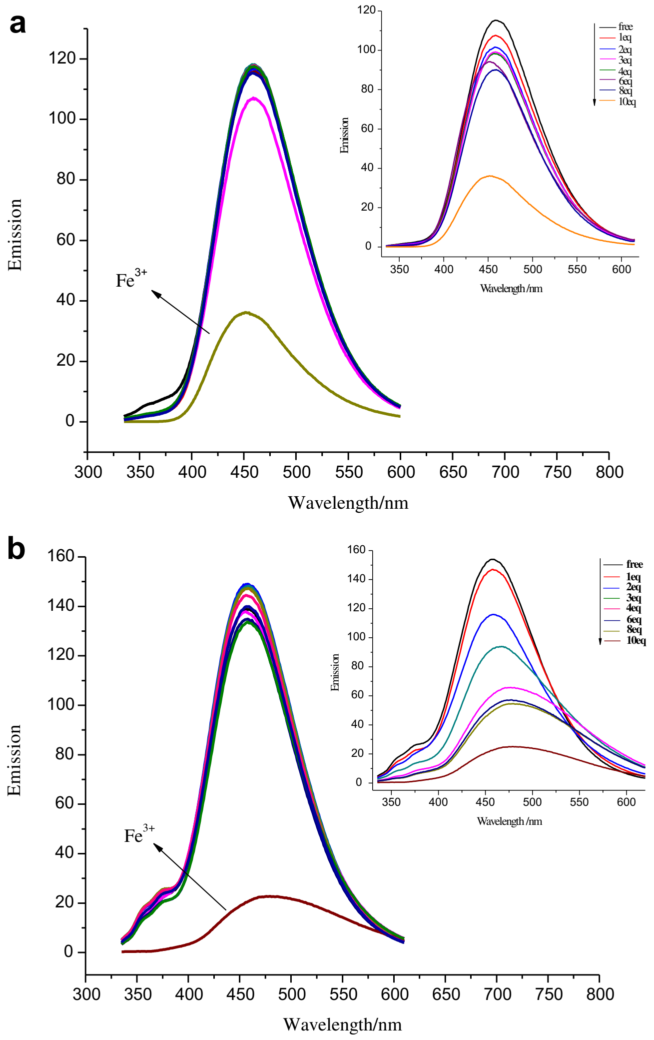


Fig. 3. Fluorescence responses of **3o** (a) and **4o** (b) in the presence of different metal ions (K^+, Ca^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Hg^{2+}, Fe^{2+} and Fe^{3+}) in acetonitrile/water solution (100:1, v/v, 10 equiv.); (Inset) Fluorescence response changes by the addition of Fe^{3+} from 0 to 10 equiv.

tested. A similar phenomenon was also observed in the fluorescence spectra of the other open-ring isomers **1o**, **2o**, and **4o** (see Fig. 3b; Figures S5 and S6 in the Supporting Information). The results indicated that the respective open-ring isomers can be used as highly selective chemosensors for Fe^{3+} ions. The fluorescence quenching of compounds **1**–**4** upon the addition of Fe^{3+} may result from ligand-to-metal charge transfer (LMCT), in which the electronic charge is transferred from the ligand toward the coordinating metal [26]. The electron donor of compounds was the nitrogen atoms on the imidazole rings. The coordination with Fe^{3+} decreased its electron donating ability, which resulted that the electron transfer from the nitrogen atom to the imidazole p-system was hindered. Moreover, we found that the addition of Fe^{3+} ions resulted in slight shifts of the fluorescence spectra compared with the free open-ring isomers. Subsequently, we investigated the effects of metal ions toward the closed-ring isomers, in which the closed-ring isomers were obtained by irradiating the solution of compounds **1**–**4** in CH_2Cl_2 with UV light, till the photostationary state was reached. After removing the solvent, the closed-ring isomers **1c**–**4c** were obtained by purification using TLC silica gel plates. The changes in the fluorescence properties of the closed-ring forms in acetonitrile were performed under the same conduction when metal ions were added. The results display that these closed-ring isomers exhibit a quenching effects on the fluorescence in the presence of Fe^{3+} ions. As shown in Fig. 4, Figures S11 and S12 (see Supporting Information), they show high selectivity toward Fe^{3+} among the various metal ions tested as well as the ring-open isomers. Subsequently, we investigated the influence of pH values on the rate of quenching of **2o** in the presence of Fe^{3+}. As shown in Supporting Information, when the pH values of systems were higher than 9.0, the rate of quenching obviously decreases. Similar results were also observed when other compounds were investigated (Figures S13–S16 in the Supporting Information).

Fluorescence intensity changes are usually described in terms of the decrease factor (DF), which is calculated from the fluorescence intensities of the chemosensor without (F_0) or with metal ions (F). According to these data (Figures S7–S10, S17–S20 in the Supporting Information), we found that all of the open-ring and closed-ring isomers displayed highly selective binding of Fe^{3+} ions.

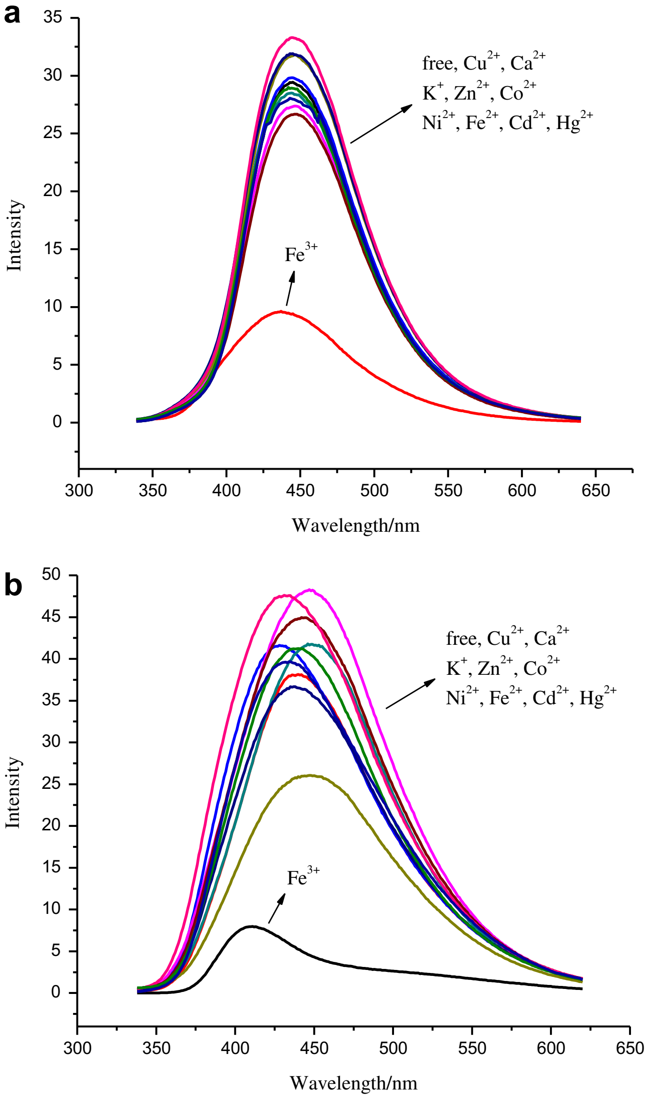


Fig. 4. Fluorescence responses of **1c** (a) and **2c** (b) in the presence of different metal ions (K^+, Ca^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Hg^{2+}, Fe^{2+} and Fe^{3+}) in acetonitrile/water solution (100:1, v/v, 10 equiv.).

4. Conclusion

Four novel imidazole-based dithienylethenes have been successfully synthesized in good yields. UV/Vis absorption spectra indicated that these dithienylethenes can easily isomerize between the open-ring and closed-ring isomers upon irradiation with UV or visible light in solution, and that the respective closed-ring isomers show decreased fluorescence properties compared with the open-ring isomers. Moreover, the respective open-ring and closed-ring isomers display high selectivity toward Fe^{3+}, such that the addition of Fe^{3+} obviously decreases their fluorescence intensities. In this respect, our research provides a basis for the future construction of multifunctional molecular architectures as well as switchable chemosensors.

Acknowledgments

The authors acknowledge financial support from National Natural Science Foundation of China (Nos. 2072039, 20931006, 21072070) and Program for Changjiang Scholars and Innovative Research Team in University (No. IRT0953).

Appendix. Supplementary material

Supplementary data related to this article can be found online at doi:10.1016/j.dyepig.2011.08.005.

References

[1] Irie M. Diarylethenes for memories and switches. Chem Rev 2000;100:1685–716.
[2] Kobatake S, Imao S, Yamashiro Y, Terakawa Y. Photoswitching of an alcohol-sensitive photochromic diarylethene. Tetrahedron Lett 2011;52:1905–8.
[3] Tian H, Yang SJ. Recent progresses on diarylethene based photochromic switches. Chem Soc Rev 2004;33:85–97.
[4] Tian H, Feng YL. Next step of photochromic switches. J Mater Chem 2008;18:1617–22.
[5] Bianco A, Bertarelli C, Rabolt JF, Zerbi G. Diarylethenes with electroactive substituents: a theoretical study to understand the effect on the IR spectrum and a simple way to read optical memory in the mid-IR. Chem Mater 2005;17:869–74.
[6] Majumdar D, Lee HM, Kim J, Kim KS. Photoswitch and nonlinear optical switch: theoretical studies on 1,2-bis-(3-thienyl)-ethene derivatives. J Chem Phys 1999;111:5866–72.
[7] Shim S, Joo T, Bae SC, Kim KS, Kim E. Ring opening dynamics of a photochromic diarylethene derivative in solution. J Phys Chem A 2003;107:8106–10.
[8] Nakatsuji S. Recent progress toward the exploitation of organic radical compounds with photo-responsive magnetic properties. Chem Soc Rev 2004;33:348–53.
[9] Pu SZ, Li H, Liu G, Liu WJ, Cui SQ, Fan CB. Synthesis and the effects of substitution upon photochromic diarylethenes bearing an isoxazole moiety. Tetrahedron 2011;67:1438–47.
[10] Irie M, Kobatake S, Horichi M. Reversible surface morphology changes of a photochromic diarylethene single crystal by photoirradiation. Science 2001;291:1769–72.
[11] Zheng HY, Zhou WD, Yuan MJ, Yin XD, Zuo ZC, Ouyang CB, et al. Optic and proton dual-control of the fluorescence of rhodamine based on photochromic diarylethene: mimicking the performance of an integrated logic gate. Tetrahedron Lett 2009;50:1588–92.
[12] Bando T, Sugiyama H. Synthesis and biological properties of sequence-specific DNA-alkylating pyrrole–imidazole polyamides. Acc Chem Res 2006;39:935–44.
[13] Bellina F, Cauteruccio S, Montib S, Rossi R. Novel imidazole-based combretastatin A-4 analogues: evaluation of their in vitro antitumor activity and molecular modeling study of their binding to the colchicine site of tubulin. Bioorg Med Chem Lett 2006;16:5757–62.
[14] Peter W, Wilhelm K. Ionic liquids—new "solutions" for transition metal catalysis. Angew Chem Int Ed 2000;39:3772–89.
[15] Bellina F, Cauteruccio S, Rossi RS. Synthesis and biological activity of vicinal diaryl-substituted 1H-imidazoles. Tetrahedron 2007;63:4571–624.
[16] Park S, Kwon OH, Kim S, Park S, Choi MG, Cha M, et al. Imidazole-based excited-state intramolecular proton-transfer materials: synthesis and amplified spontaneous emission from a large single crystal. J Am Chem Soc 2005;127:10070–4.
[17] Sun YF, Cui YP. The synthesis, structure and spectroscopic properties of novel oxazolone-, pyrazolone- and pyrazoline-containing heterocycle chromophores. Dyes Pigm 2009;81:27–34.
[18] Yoon J, Kim SK, Singh NJ, Kim KS. Imidazolium receptors for the recognition of anions. Chem Soc Rev 2006;35:355–60.
[19] Xu Z, Kim SK, Yoon J. Revisit to imidazolium receptors for the recognition of anions: highlighted research during 2006–2009. Chem Soc Rev 2010;39:1457–66.
[20] Caltagirone C, Gale PA. Anion receptor chemistry: highlights from 2007. Chem Soc Rev 2009;38:520–63.
[21] Singh NJ, Jun EJ, Chellappan K, Thangadurai D, Chandran RP, Hwang I, et al. Quinoxaline–imidazolium receptors for unique sensing of pyrophosphate and acetate by charge transfer. Org Lett 2007;9:485–8.
[22] Ihm H, Yun S, Kim HG, Kim JK, Kim KS. Tripodal nitro-imidazolium receptor for anion binding driven by (C-H)$^{+}$—X- hydrogen bonds. Org Lett 2002;4:2897–900.
[23] Chellappan K, Singh NJ, Hwang I-C, Lee JW, Kim KS. A Calix[4]imidazolium[2] pyridine as an anion receptor. Angew Chem Int Ed 2005;44:2899–903.
[24] Sundberg RJ, Martin RB. Interactions of histidine and other imidazole derivatives with transition metal ions in chemical and biological systems. Chem Rev 1974;74:471–517.
[25] Liu H, Chen Y. A bifunctional metal probe with independent signal outputs and regulable detection limits. Eur J Org Chem 2009;30:5261–5.
[26] Li ZY, Lin Y, Xia JL, Zhang H, Fan FY, Zeng QB, et al. Synthesis of novel diarylethene compounds containing two imidazole bridge units and tuning of their optical properties. Dyes Pigm 2011;90:245–52.
[27] Chen BZ, Wang MZ, Wu YQ, Tian H. Reversible near-infrared fluorescence switch by novel photochromic unsymmetrical-phthalocyanine hybrids based on bisthienylethene. Chem Commun; 2002:1060–1.
[28] Qin B, Yao RX, Zhao XL, Tian H. Enhanced photochromism of 1,2-dithienylcyclopentene complexes with metal ion. Org Biomol Chem 2003;1:2187–91.
[29] Tian H, Qin B, Yao RX, Zhao XL, Yang SJ. A single photochromic molecular switch with four optical outputs probing four inputs. Adv Mater 2003;15:2104–7.
[30] Tchouka H, Meetsma A, Browne W. Spectroscopic and magnetic properties of a series of μ-cyano bridged bimetallic compounds of the type M^{II}–NC–Fe^{III} (M = Mn, Co, and Zn) using the building block [Fe^{III}(CN)5imidazole]$^{2-}$. Inorg Chem 2010;49:10557–70.
[31] Ikuko K, Yuri M, Yukinari S, Naohide M, Toshio N, Masaaki K. Spontaneous resolution induced by self-organization of chiral self-complementary cobalt(III) complexes with achiral tripod-type ligands containing three imidazole groups. J Am Chem Soc 2002;124:629–40.
[32] Lim MH, Lippard SJ. Metal-based turn-on fluorescent probes for sensing nitric oxide. Acc Chem Res 2007;40:41–51.
[33] Jiang P, Guo Z. Fluorescent detection of zinc in biological systems: recent development on the design of chemosensors and biosensors. Chem Rev 2004;248:205–29.
[34] Gao J, Gu H, Xu B. Multifunctional magnetic nanoparticles: design, synthesis, and biomedical applications. Acc Chem Res 2009;42:1097–107.
[35] Xiao SZ, Yi T, Zhou YF, Zhao Q, Li FY, Huang CH. Multi-state molecular switches based on dithienylperfluorocyclopentene and imidazo [4,5-f] [1,10] phenanthroline. Tetrahedron 2006;62:10072–8.
[36] Lee PH-M, Ko C-C, Zhu NY, Yam VW-W. Metal coordination-assisted near-infrared photochromic behavior: a large perturbation on absorption wavelength properties of N, N-donor ligands containing diarylethene derivatives by coordination to the rhenium(I) metal center. J Am Chem Soc 2007;129:6058–9.
[37] Yam VW-W, Lee JK-W, Ko C-C, Zhu NY. Photochromic diarylethene-containing ionic liquids and N-heterocyclic carbenes. J Am Chem Soc 2009;131:912–3.
[38] Yuan JJ, Li ZY, Hu M, Li SS, Huang SY, Yin J, et al. Synthesis and photochromic properties of imidazole-based diarylethenes. Photochem Photobiol 2011;10:587–91.
[39] Liu H, Chen Y. The photochromism and fluorescence of diarylethenes with a imidazole bridge unit: a strategy for the design of turn-on fluorescent diarylethene system. J Phys Chem A 2009;113:5550–3.
[40] Cantalupo SA, Crundwell G. 1,2-Bis(3-methyl-2-thienyl)ethane-1,2-dione. Acta Crystallogr E Struct 2005;E61:o3079–80.
[41] Lucas LN, Jong JJ, vanEsch JH, Kellogy RM, Feringa BL. Syntheses of dithienylcyclopentene optical molecular switches. Eur J Org Chem 2003;2003:155–6.
[42] Eseda AO, Li W, Gao R, Zhang M, Hao X, Liang T, et al. Syntheses, structures, and fluorescent properties of 2-(1h-imidazol-2-yl)phenols and their neutral Zn(II) complexes. Inorg Chem 2009;48:9133–46.
[43] Li ZX, Liao LY, Sun W, Xu CH, Zhang C, Fang CJ. Reconfigurable cascade circuit in a photo- and chemical-switchable fluorescent diarylethene derivative. J Phys Chem C 2008;112:5190–6.
[44] Li XC, Tian H. One-step synthesis and photochromic properties of a stable triangle terthiophene. Tetrahedron Lett 2005;46:5409–12.