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Synthesis of novel diarylethene compounds containing two imidazole bridge units and tuning of their optical properties

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ABSTRACT

A novel series of symmetrical diarylethenes incorporating two imidazole bridge units and their *N*-methylated derivatives have been synthesized, and the products have been characterized by means of NMR and MS. Each of the compounds displays excellent photochromism and both “turn-off” and “turn-on” fluorescence properties upon UV/vis light irradiation in solution. It has been found that the electronic properties of substituents on the benzene ring, methylation of the N—H units on the two imidazole rings and Cu^{2+} have great effects on both the photochromic property and fluorescence property of these diarylethenes. The photophysical properties of these compounds can be easily tuned by varying the electronic properties of the substituents or by simple modification of the molecular structure, which provides a new strategy for the design of novel fluorescent diarylethene systems to be used as switches.

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1. Introduction

Photochromic diarylethene compounds have attracted much attention in recent years since the first report by Kellogg et al. [1] and the subsequent extensive studies by Irie and co-workers [2–6] on the photochromic properties of these systems. For practical applications, several attempts to modulate the photochromic properties of diarylethenes have recently been reported. Tian and co-workers [7–12] enhanced the photochromism of these molecules through their coordination to various metal cations. Irie et al. [13–15] modulated the photochromic properties of diarylethenes using intramolecular hydrogen bonds. Huang’s group [16,17] gated the spectral properties of diarylethenes by means of Lewis acid—base interaction between B and F^-. Among the diarylethene derivatives hitherto reported, diarylethenes with heterocyclic aryl groups, especially those bearing two thiophene or benzothiophene rings, are the most promising candidates by virtue of their excellent thermally irreversible property, remarkable fatigue resistance, and high sensitivity [3,7–22].

As a current key area of research for photochromic dithienylethenes is to develop novel structures with unique properties, an effective method is to modify the structure by functionalizing the group R in Fig. 1. Many studies on the photochromic properties of diarylethene derivatives have been focused on the substituent on the thiophene moiety [23–36]. Imidazole is a common scaffold and imidazole derivatives are important five-membered nitrogen-containing heterocyclic compounds that are widely used in many fields, such as medicine [37], ionic liquids [38], anion sensors [39,40], as well as electrical and optical materials [41–43]. Against this background, two substituted imidazole units were attached to the dithienylethene backbone in the hope of achieving novel structures with excellent photochromic properties, with a view to developing novel optical materials having potential applications. In the work described herein, several dithienylethenes bearing two imidazole units and their *N*-methylated derivatives have been synthesized and their photochromic and fluorescence properties have been investigated. It is demonstrated that the photophysical properties of these compounds can be easily tuned by introducing different substituents or by methylation of the N—H moieties on the two imidazole rings. Simultaneously, due to imidazole is an outstanding ligand, the effect of various metal ions on optical properties of all the diarylethene compounds will also be researched.

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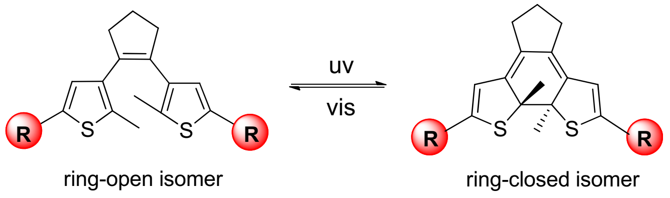

Fig. 1. Ring-opening and ring-closing photoisomerization of diarylethene.

2. Materials and methods

2.1. Experimental

General: All manipulations were carried out under an argon atmosphere by using standard Schlenk techniques, unless otherwise stated. DMF was dried with magnesum sulfate then distilled under vacuum. 1,2-Bis(5-formyl-2-methylthien-3-yl)cyclopentene (**1**) was prepared by literature methods [44]. Different substitutional benzil (**2**) except benzil were prepared by modified procedures of reported methods [45]. All other starting materials were obtained commercially as analytical-grade and used without further purification. The relative quantum yields were determined by comparing the reaction yield with the known yield of the compound 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene [46]. ^{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. UV–Vis spectra were obtained on U-3310 UV Spectrophotometer. Fluorescence spectra were taken on a Fluoromax-P luminescence spectrometer (HORIBA JOBIN YVON INC.).

2.2. Synthesis

2.2.1. Synthesis of dithienylethene with two imidazole units 3–6

Target compounds **3**–**6** were prepared according to the synthetic route presented in Fig. 2 by modified procedures of reported methods [47].

Synthesis of **3**: To a solution of ammonium acetate (1.2 g, 15.2 mmol) in refluxing glacial acetic acid (15 mL) was added **1** (0.30 g, 0.95 mmol) under an argon atmosphere at 120 °C, and it was refluxed for 2 h. Benzil (0.40 g, 0.95 mmol) was added to the reaction solution above and continue to reacted further for overnight. The reaction mixture was allowed to cool to room temperature, and then transferred to ice water (200 mL), carefully neutralized with a 10% sodium carbonate solution to a pH of 6.5–7.0. The formed precipitate was collected and the crude product was washed with water, the dried solid was recrystallized from methylene chloride to give an ivory-white solid (0.48 g) in a yield of 73%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.89 (s, 6H, CH_3), 2.04–2.08 (m, 2H, CH_2), 2.82 (t, $J = 7.2$ Hz, 4H, CH_2), 7.26–7.48 (m, 22H, Ar–H), 12.7 (s, 2H, N–H). MS (m/z): 696 $[M]^+$.

Synthesis of **4**: Compound **4** was prepared by an analogous method similar to that used for to **3** and was obtained as an ivory-white solid (0.46 g) in a yield 64%. ^{1}H NMR (600 MHz, DMSO-d_6): δ 1.89 (s, 6H, CH_3), 2.05–2.09 (m, 2H, CH_2), 2.27 (s, 6H, CH_3), 2.33 (s, 6H, CH_3), 2.83 (t, $J = 6.6$ Hz, 4H, CH_2), 7.09 (d, $J = 7.8$ Hz, 4H, Ar–H), 7.22 (d, $J = 7.2$ Hz, 4H, Ar–H), 7.33–7.37 (m, 8H, Ar–H), 7.49 (s, 2H, thiophene-H), 12.56 (s, 2H, N–H). MS (m/z): 753 $[M]^+$.

Synthesis of **5**: Compound **5** was prepared by an analogous method to **3** and obtained as an ivory-white solid (0.71 g) in a yield 91%. ^{1}H NMR (400 MHz, DMSO-d_6): ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.89 (s, 6H, CH_3), 2.05–2.09 (m, 2H, CH_2), 2.83 (t, $J = 7.2$ Hz, 4H, CH_2), 3.34 (s, 6H, OCH_3), 3.36 (s, 6H, OCH_3), 6.86 (d, $J = 8.4$ Hz, 4H, Ar–H), 6.99 (d, $J = 8.4$ Hz, 4H, Ar–H), 7.38 (t, 8H, Ar–H), 7.47 (s, 2H, thiophene-H), 12.50 (s, 2H, N–H). MS (m/z): 816 $[M]^+$.

Synthesis of **6**: Compound **6** was prepared by an analogous method to **3** and purified on a silica gel column with ethyl acetate/petroleum ether (1:1) to obtain a yellow-blue solid (0.52 g) in a yield 63%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.88 (s, 6H, CH_3), 2.04–2.08 (m, 2H, CH_2), 2.82 (t, $J = 7.2$ Hz, 4H, CH_2), 6.69–7.45 (m, 18H, Ar–H), 12.30 (s, 2H, N–H). MS (m/z): 869 $[M]^+$.

2.2.2. Synthesis of N-methylation derivatives **7**–**9**

Target compounds **7**–**9** were prepared according to the synthetic route presented in Fig. 2.

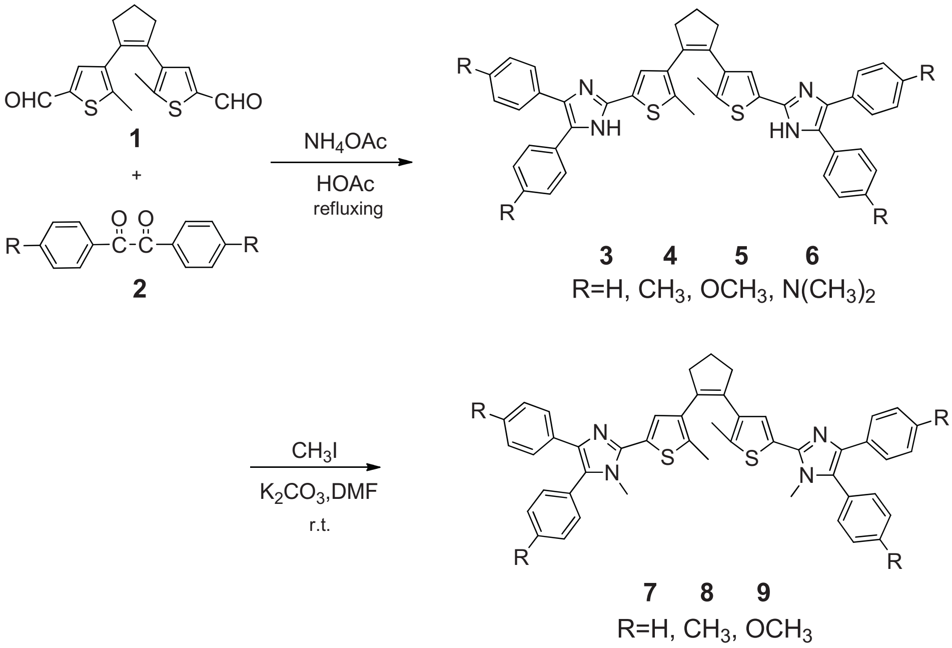

Fig. 2. Synthesis of dithienylethene with two imidazole units **3**–**6** and their derivatives **7**–**9**.

Table 1
Crystal data and structure refinement parameters for **7**.

	7
Empirical formula	$C_{47}H_{40}N_4S_2$
Formula weight	724.95
Temperature	298 (2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
a (Å)	9.6777 (13)
b (Å)	16.041 (2)
c (Å)	24.854 (3)
α (deg)	90
β (deg)	99.304 (3)
γ (deg)	90
Volume (Å^{-3})	3807.5 (9)
Z	4
Density (calculated)	1.265 Mg/m^3
Absorption coefficient	0.179 mm^{-1}
F (000)	1528
Crystal size	0.12 × 0.10 × 0.02 mm^3
Theta range for data collection	2.48–26.00
Index ranges	$-11 \leq h \leq 11$, $-19 \leq k \leq 19$, $-30 \leq l \leq 30$
Reflections collected	19896
Independent reflections	3755 [R (int) = 0.0928]
Completeness to theta = 26.00	100.0%
Absorption correction	None
Max. and min. transmission	0.9971 and 0.9788
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3755/0/242
Goodness-of-fit on F^2	1.045
Final R indices [$I > 2\text{sigma}(I)$]	$R1 = 0.0616$, w$R2 = 0.1289$
R indices (all data)	$R1 = 0.1084$, w$R2 = 0.1425$
Largest diff. peak and hole	0.279 and −0.225 e^{-3}

Synthesis of **7**: To a solution of **3** (0.35 g, 0.5 mmol) in *N*,*N*-dimethylformamide (10 mL) in the presence of potassium carbomate (0.28 g, 2 mmol) was added methyl iodide(0.12 mL, 2 mmol) under dark conditions for 12 h at room temperature. The reaction mixture was allowed to cool, transferred to about 100 mL of water. The formed precipitate was collected and the crude product was washed with water, the dried solid was redissolved in DCM. The solution was dried over sodium sulfate, then removed solvent under reduced pressure and purified on a silica gel column using petroleum ether / ethyl acetate(1:1) as the eluent to obtain the target compound as a grey solid (0.5g) in a yield of 42%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.13 (s, 6H, CH_3), 2.05–2.13 (m, 2H, CH_2), 2.87 (t, J = 7.2 Hz, 4H, CH_2), 3.47 (s, 6H, N–CH_3), 7.09 (s, 2H, thiophene-H), 7.03–7.47 (m, 20H, Ar–H). MS (m/z): 724 [M]$^+$.

Synthesis of **8**: Compound **8** was prepared by an analogous method to **7** and obtained as a grey solid (0.25 g) in a yield 64%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.12 (s, 6H, CH_3), 2.00–2.12 (m, 2H, CH_2), 2.27 (s, 6H, CH_3), 2.40 (s, 6H, CH_3), 2.86 (t, J = 6.4 Hz, 4H, CH_2), 3.44 (s, 6H, N–CH_3), 6.99 (d, J = 7.2 Hz, 4H, Ar–H), 7.06 (s, 2H, thiophene-H), 7.23 (d, J = 13.6 Hz, 4H, Ar–H), 7.37 (d, J = 7.2 Hz, 4H, Ar–H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.32 (s, CH_3), 21.13 (s, CH_3), 21.35 (s, CH_3), 23.03 (s, CH_2), 32.78 (s, CH_2), 38.17 (s, N–CH_3), 126.76, 127.30, 127.84, 128.66, 128.88, 129.64, 130.02, 130.69, 131.64, 134.78,135.69, 136.02,137.60, 138.29, 141.77 (s, thiophene, ethene, Ar). MS (m/z): 780 [M]$^+$.

Synthesis of **9**: Compound **9** was prepared by an analogous method to **7** and obtained as a grey solid (0.27 g) in a yield 65%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.12 (s, 6H, CH_3), 2.10–2.14 (m, 2H, CH_2), 2.85 (t, J = 7.2 Hz, 4H, CH_2), 3.43 (s, 6H, OCH_3), 3.74 (s, 6H, N–CH_3), 3.84 (s, 6H, N–CH_3), 6.74 (d, J = 8.8 Hz, 4H, Ar–H), 6.95 (d, J = 8.8 Hz, 4H, Ar–H), 7.05 (s, 2H, thiophene-H), 7.24 (d, J = 8.8 Hz, 4H, Ar–H), 7.41 (d, J = 8.8 Hz, 4H, Ar–H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.29 (s, CH_3), 23.01 (s, CH_2), 32.68 (s, CH_2), 38.12 (s, OCH_3), 55.05 (s, N–CH_3), 55.20 (s, N–CH_3), 113.36, 114.35, 122.94, 127.18, 127.29, 127.95, 128.93, 129.23, 132.13, 134.77, 135.93, 136.00, 137.33, 141.55, 158.03, 159.58 (s, thiophene, ethene, Ar). MS (m/z): 844 [M]$^+$.

2.3. Source of metal ions and preparation of mixtures containing metal ions and target ligands in DMF

All metal ions for binding experiments used acetate salts as sources except for Ca^{2+}, K^+, Fe^{3+} and Cd^{2+}, which were used as $CaCl_2$, KCl, $FeCl_3$, and $CdCl_2$ as sources. Metal ions in water were obtained by dissolution of the metal salts in water. Metal ions in water were added to the ligand solution in DMF by syringe, and then mixed round under dark conditions for overnight at room temperature.

2.4. Crystallographic details

Crystals suitable for X-ray diffraction were grown from a dichloromethane of solution **7** layered with hexane. A crystal with approximate dimensions of 0.12 × 0.10 × 0.02 mm^3 for **7** was mounted on a glass fiber for diffraction experiment. Intensity data were collected on a Nonius Kappa CCD diffractometer with Mo Kα

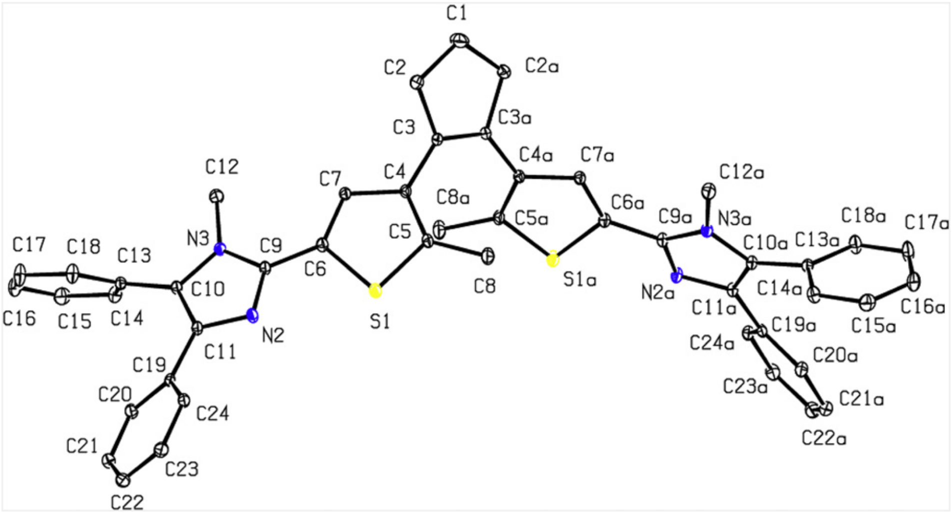

Fig. 3. Molecular structures of **7**. The H atoms have been omited for clarity.

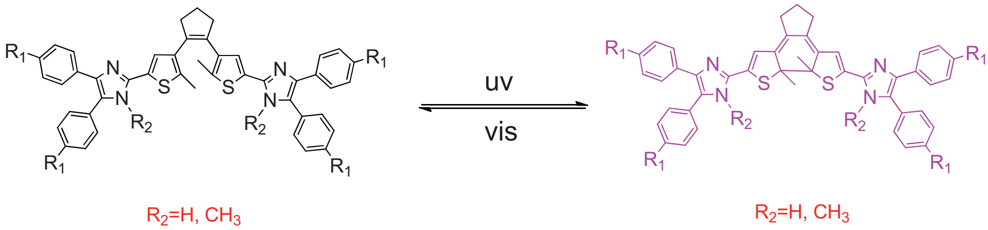

Fig. 4. Photochromism of diarylethenes **3**–**9**.

radiation (0.71073 Å) at 298 K. The structures were solved by a combination of direct methods (SHELXS-97) and Fourier difference techniques and refined by full-matrix least squares (SHELXL-97). All non-H atoms were refined anisotropically. The hydrogen atoms were placed in the ideal positions and refined as riding atoms. Crystallographic data for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplemental publication CCDC 781133. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: 544 0 1223 336 033 or e-mail: deposit@ccdc.cam.ac.uk).

3. Results and discussion

3.1. Discussion of the synthetic strategy

The target dithienylethenes with two imidazole units **3**–**6** were obtained by condensation reactions of 1,2-bis(5-formyl-2-methylthien-3-yl)cyclopentene (**1**) and differently substituted benzils (**2**) in the presence of excess ammonium acetate in moderate to good yields of 63–91% (Fig. 2). N-Methylation was achieved by treatment of **3**–**5** with iodomethane in the presence of potassium carbonate to give **7**–**9** in moderate yields of 42–64%. It was found that a 2:1 ratio of iodomethane to imidazoles **3**–**5** was needed because a greater excess of MeI could have led to the formation of salts, thereby reducing the yield of methylation products. Unfortunately, N-methylation of **6** was not successful, presumably because N-methylation of the *N*,*N*-dimethyl moiety is much easier than that of imidazole, resulting in the formation of a water-soluble quaternary ammonium salt. All of the target compounds were characterized by NMR and MS.

3.2. X-ray structures of **7**

The molecular structures of **7** was determined by X-ray crystallography. The crystallographic details are given in Table 1. The molecular structures of **7** is depicted in Fig. 3. The diarylethene **7** crystallizes with an approximate C_2 symmetry with the photoactive antiparallel conformation in the crystalline phase, which can undergo photocyclization [48]. The molecule includes five kinds of planar rings. The dihedral angle between the cyclopentene ring and the thiophene ring is 46.02° for S1/C4–C7, and that between the thiophene ring and the linked imidazole ring is 19.97°, and those between the imidazole ring and two linked benzene rings are 69.92° for C13–C18 and 33.58° for C19–C24. The intramolecular distance between the two reactive carbons (C5–C5a) is 3.559 Å, which is short enough for the cyclization reaction to take place as photochromic reactivity usually appears when the distance between the reactive carbon atoms is less than 4.2 Å [49].

3.3. Photochromic behavior

The photochromic behavior of diarylethenes **3**–**9** induced by photoirradiation in DMF was measured at room temperature. The synthesized diarylethenes undergo photoisomerization between **3o**–**9o** (ring-open isomer) and **3c**–**9c** (ring-closed isomer) upon alternating irradiation with UV light ($\lambda = 302$ nm) and visible light ($\lambda > 402$ nm), as illustrated in Fig. 4. As shown in Fig. 5A, the absorption maximum of compound **4** in DMF was observed at 336 nm ($\varepsilon = 5.23 \times 10^4$ L mol^{-1} cm^{-1}) as a result of a π–π^* transition [50]. This colorless solution turned purple and a new absorption band centered at 552 nm ($\varepsilon = 3.27 \times 10^4$ L mol^{-1} cm^{-1}) appeared when it was irradiated with 302 nm UV light, as a result of a ring-closure reaction to give the ring-closed isomer **4c**. In addition, a well-defined isosbestic point was observed at 361 nm. Upon irradiation with visible light ($\lambda > 402$ nm), the colored **4c** underwent a cycloreversion reaction to the initial colorless ring-opened isomer **4o**. Similar results were obtained when solutions of the other diarylethenes **3**, **5**–**9** in DMF were irradiated with UV/vis light.

The photochromic parameters of diarylethenes **3**–**9** are summarized in Table 2. These data show that different substituent

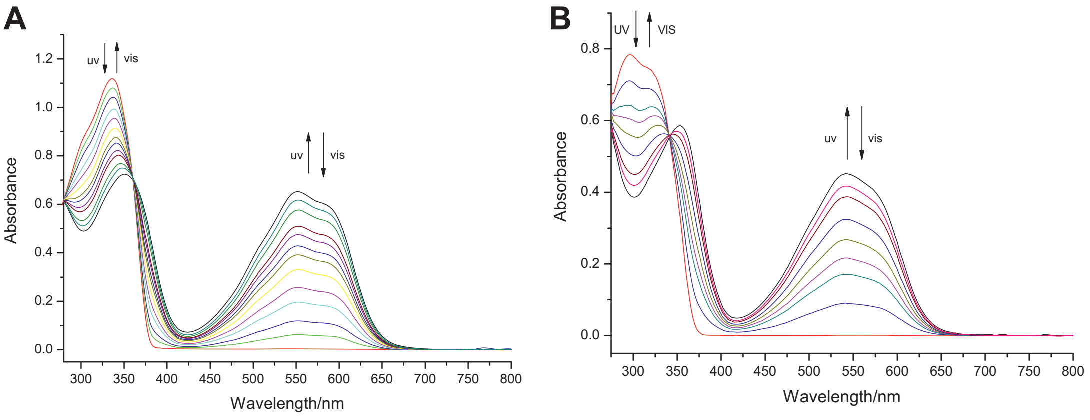

Fig. 5. Absorption spectral changes of diarylethene **4** and **8** by photoirradiation in DMF (2.0×10^{-5} mol/L) at room temperature. (A) spectral changes for **4**; (B) spectral changes for **8**.

Table 2
Absorption characteristics and photochromic quantum yields of **3**–**9** in DMF (2.0×10^{-5} mol/L).

Compound	λ_{max}^{Abs}/nm[a] ($\varepsilon \times 10^{-4}$)	λ_{max}^{Abs}/nm[b] ($\varepsilon \times 10^{-4}$)	Φ[c]	
	(Open)	(PSS)	ϕ_{o-c} (λ/nm)	ϕ_{c-o} (λ/nm)
3	334 (4.86)	550 (2.71)	0.559 (550)	0.0014 (334)
4	336 (5.23)	552 (3.27)	0.375 (552)	0.0011 (336)
5	340 (4.99)	554 (2.79)	0.510 (554)	0.00073 (256)
6	320 (5.39)	568 (3.43)	0.411 (568)	0.00034 (276)
7	296 (2.93)	542 (1.56)	0.580 (542)	0.0076 (296)
8	296 (2.90)	542 (2.26)	0.675 (542)	0.0055 (296)
9	292 (3.86)	544 (2.21)	0.726 (544)	0.0042 (292)

[a] Absorption maxima of open-ring isomers.
[b] Absorption maxima of closed-ring isomers.
[c] Quantum yields of open-ring (ϕ_{c-o}) and closed-ring isomers (ϕ_{o-c}), respectively.

Table 3
^{1}H NMR chemical shifts of opened and closed-ring isomers for **3**–**6**.

Compounds	δ_{Meo}	δ_{Mec}	δ_{Tho}	δ_{Thc}	Conversion
3	1.91	1.96	7.51	6.83	65%
4	1.90	2.02	7.48	6.83	72%
5	1.86	2.03	7.46	6.81	72%
6	1.89	1.99	7.45	6.78	45%

on the benzene ring and N-methylation of the imidazole ring have a remarkable effect on the photochromic properties of these diarylethenes, including the absorption maxima and quantum yields of the cyclization and cycloreversion reactions. For diarylethenes **6**, the absorption maxima of in the visible region of the ring-closed isomers are red-shifted compared with those of **3**–**5**. However, the absorption maxima of the ring-closed isomers of **7**–**9** are blue-shifted compared with those of **3**–**5**, which may be attributed to a reduction in the degree of conjugation after N-methylation of the imidazole rings. As shown in Table 2, the cyclization quantum yields of diarylethenes **3**–**9** are much higher than their respective cycloreversion quantum yields. The quantum yields of cyclization and cycloreversion reactions of diarylethenes **3**–**5** are much lower than those of diarylethenes **7**–**9**. This indicates that N-methylation of the two imidazole rings improves the quantum yields of cyclization and cycloreversion.

The photochromic behavior of the diarylethenes **3**–**6** was examined by means of NMR spectrometry. The ratios between the closed and open isomers at the photostationary state were measured from the ^{1}H NMR spectra. The characteristic shifts of their Me and thiophene groups were observed in the ^{1}H NMR spectra. Irradiation with UV light caused the appearance of a new set of singlets with the concomitant disappearance of the singlets of the original state. As shown in Fig. 6 and Table 3, the ^{1}H NMR signal of the methyl groups attached to the thiophene rings appeared at $\delta = 1.90$ ppm for **4o** and $\delta = 2.02$ ppm for **4c**, and the ^{1}H NMR signal of the protons attached to the thiophene rings appeared at $\delta = 7.48$ ppm for **4o** and $\delta = 6.83$ ppm for **4c**. Thus the chemical shift of the protons on the thiophene rings appeared at higher field compared to that in the case of **4o**, while the chemical shift of the methyl protons appeared at lower field. Similar shift changes have also been observed in the ^{1}H NMR spectra of other diarylethene compounds **3**, **5**, and **6**. The photocyclization yields of diarylethenes **3**–**6** was from 45% to 72% according to ^{1}H NMR analysis. Unfortunately, ^{1}H NMR Chemical Shifts and photocyclization yields of Opened and Closed-Ring Isomers for their *N*-methylated derivatives **7**–**9** cannot be obtained.

3.4. Fluorescence of the diarylethenes

The fluorescence change of diarylethenes **3**–**9** induced by photoirradiation in DMF was investigated at room temperature. As shown in Fig. 7A, upon excitation of **5** in DMF solution at an excitation wavelength of 335 nm, it exhibited emission at 413 nm, and a small fluorescence quantum yield ($\phi_f = 0.027$) was measured using quinoline sulfate ($\phi_f = 0.55$, in 0.1 M aqueous H_2SO_4) as a reference. The emission intensity of diarylethene **5** was rapidly decreased upon irradiation with 302 nm UV light. On reaching the photostationary state, the emission intensity of **5** was quenched by *ca*. 91%. Irradiation with visible light (λ >402 nm) regenerated the ring-opened isomer and restored the original emission spectrum. Similar results were obtained when solutions of the other diarylethenes **3**, **4**, and **6**–**9** in DMF were irradiated with UV/vis light. The corresponding fluorescence data of the other compounds are summarized in Table 4.

As shown in Table 4, Fig. 7C and D, different substituent on the benzene ring and N-methylation of the imidazole ring obviously affect the fluorescence property of these diarylethenes. As shown in Fig. 7C and Table 4, the emission bands of the ring-open isomers

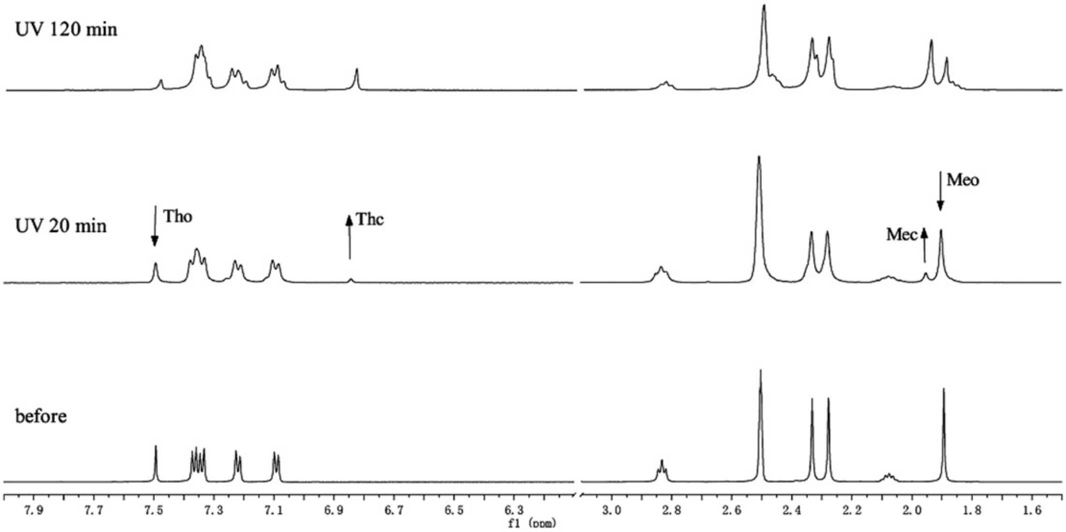

Fig. 6. ^{1}H NMR spectral changes of diarylethene **4** upon 302 nm light irradiation (observed in DMSO-d_6). (methyl and thiophene signal).

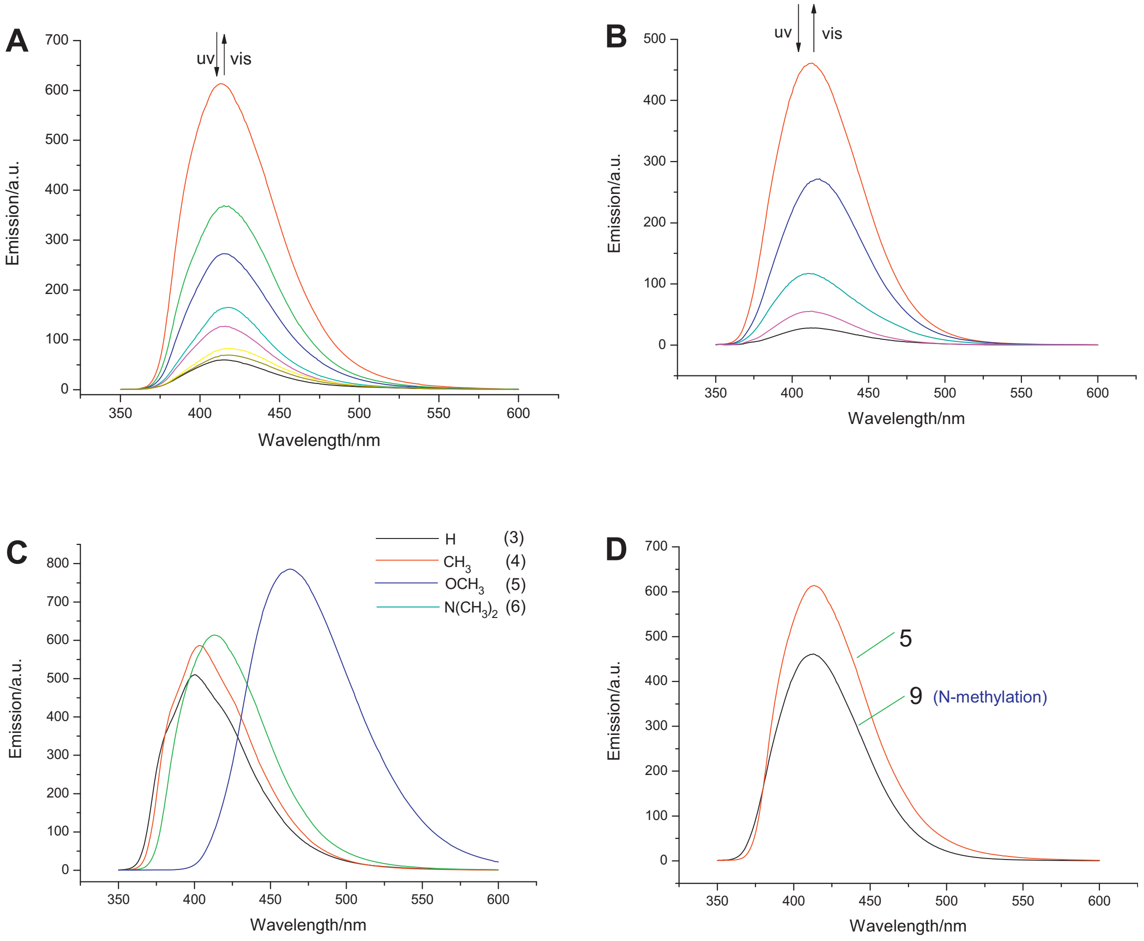

Fig. 7. Emission intensity changes of partial diarylethenes in DMF (2.0×10^{-5} mol/L) with UV/vis light irradiation ($\lambda_{ex} = 335$ nm). (A) spectral changes for **5**; (B) spectral changes for **9**; (C) fluorescence intensity of **3**–**6** before UV irradiation; (D) fluorescence intensity of **5** and **9** before UV irradiation.

exhibit significant red-shifts with increasing electron-donating ability of the substituents, and it was found that the fluorescence intensity was enhanced so that the fluorescence quantum yields of diarylethenes **3**–**6** gradually increased. However, the fluorescence of **9** was dramatically reduced upon N-methylation (Fig. 7D), which is in agreement with a previous literature report [51]. This may be mainly because the introduction of a methyl group at the *N*-position of the imidazole ring distorts the relative orientation of the thiophene and imidazole rings. The same effect was observed for the other *N*-methylated products.

3.5. Efect of metal ions on the optical properties

Both absorbance and fluorescence change of diarylethenes **3**–**9** induced by addition of various metal ions in DMF was investigated at room temperature. It was found that Cu^{2+} has an obvious effect on the optical properties of diarylethenes **3**–**6**, but no, or a very small, change in absorbance and emission was detected by binding with other metal ions (K^+, Ag^+, Ca^{2+}, Cu^{2+}, Mn^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Hg^{2+} and Fe^{3+}) under the same conditions.

For diarylethenes **4**, as shown in Figs. 5A and 8, the absorption maxima of the ring-open isomer of diarylethene **4** in the presence of Cu^{2+} (4 eq) was blue-shifted (26 nm) compared with that of free **4**, while its absorbance maxima of ring-closed isomer was

Table 4
Fluorescence data of diarylethene **3**–**9** in DMF ($\lambda_{ex} = 335$ nm).

Compound	λ_{em} (nm)	ϕ_f [a]	Rate of quenching (%)
3	400	0.018	89
4	403	0.019	90
5	413	0.027	91
6	462	0.032	93
7	399	0.011	74
8	401	0.011	90
9	412	0.020	94

[a] Fluorescence quantum yields of diarylethene **3**–**9** before uv irradiation.

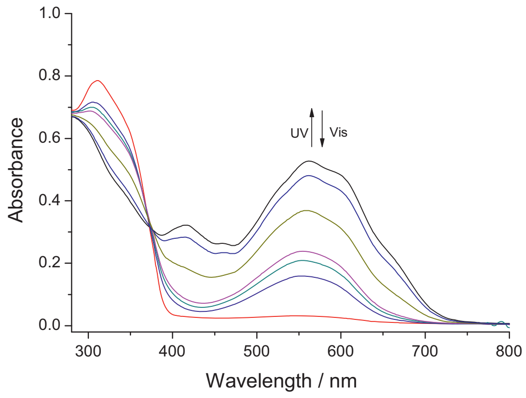

Fig. 8. Absorption changes of **4** in DMF binding with Cu^{2+} (4 eq).

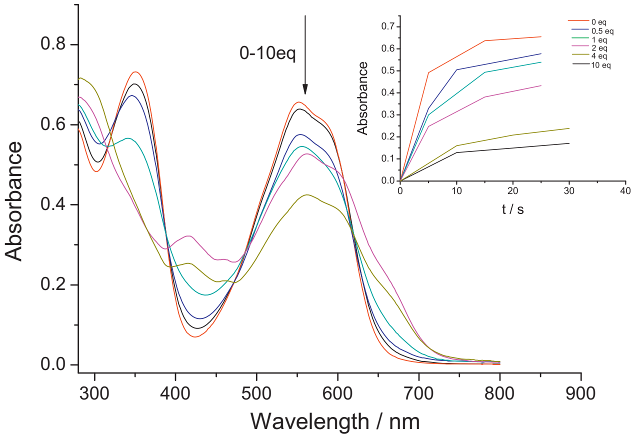

Fig. 9. UV–Vis absorption spectra of compound **4** (2 × 10−5 M) in DMF upon the addition of various amounts of Cu^{2+} (0, 0.5, 1, 2, 4, 10 eq) in PSS by light of 302 nm. Insert figure: relationship between the changes of the absorption maxima in the visible region and time of photocyclization by irradiation with 302 nm.

red-shifted (10 nm) compared with that of **4** in the absence of Cu^{2+}, which may be attributed to a change of conjugation degree of diarylethenes after binding Cu^{2+}. As shown in Fig. 9, upon the addition of varying amounts of Cu^{2+} (0–10 eq), the intensity of absorption maxima in the visible region weakened gradually; ring-closure quantum yield decreased from 0.375 to 0.144 and the responding rate on UV radiation droped off remarkably. It may be ascribed to the influence of the copper ion. It plays an important role in directing the steric course of the photocyclization reaction. Although it is difficult to predict the mechanism of how the imidazole units orient themselves around a metal ion in solution, it clearly decreased the photocyclization quantum yield. Because of the high binding affinity of imidazole with metal ions, the interconversion efficiency from the parallel to the anti-parallel configuration is strongly suppressed by Cu^{2+} complex.

As presented in Fig. 10, the emission at 403 nm band decreased significantly upon the addition of varying amounts of Cu^{2+} (0–10 eq), and the fluorescence quantum yield decreased from 0.019 to 0.0013 when the amount of Cu^{2+} was varied from 0 to 10 equivalents. The fluorescence quenching of **4** upon the addition of Cu^{2+} may result from ligand-to-metal charge transfer (LMCT), in which the electronic charge is transferred from the ligand towards the coordinating metal. A control experiment showed that the fluorescence of **4** was quenched slightly by water.

Similar results were obtained for other diarylethenes **3**, **5** and **6** containing imidazole units, but not found for *N*-methylated derivatives **7**–**9**. It may be because N–H of imidazole participated in coordinating to Cu^{2+}.

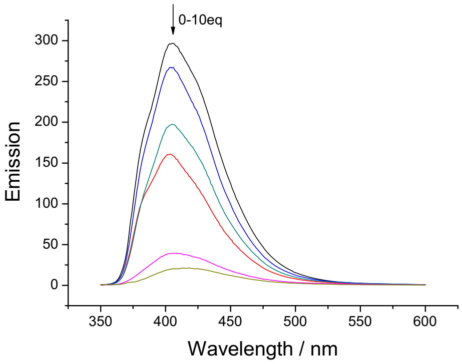

Fig. 10. Fluorescence response of **4** (2×10^{-5} M) in DMF upon the addition of various amounts of Cu^{2+} (0, 0.5, 1, 2, 4, 10 eq) before irradiation with 302 nm ($\lambda_{ex} = 335$ nm).

4. Conclusions

Seven symmetrical diarylethenes incorporating two imidazole bridge units have been synthesized. Their photochromic and fluorescence properties have been investigated. It has been demonstrated that the electronic properties of the substituent on the benzene ring, methylation of the N–H units on the two imidazole rings and Cu^{2+} have great effects on the photochromic property and fluorescence property of these diarylethenes.

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