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Synthesis of diarylethene derivatives containing various heterocycles and tuning of light-emitting properties in a turn-on fluorescent diarylethene system

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ABSTRACT

A novel series of diarylethenes incorporating different heterocycles and their N-methylated derivatives have been synthesized, and the products have been characterized by means of NMR, MS and elemental analysis. Each of the compounds displays photochromism and “turn-on” fluorescence properties upon irradiation with UV light. It has been found that both the nature of the heterocycle attached to the imidazole ring and methylation of the imidazole ring greatly affect the optical properties. The light-emitting properties can be easily tuned from blue light-emitting to yellow light-emitting fluorescence by varying the nature of the heterocycle or by simple modification of structures, which provides a new strategy for the design of novel fluorescent switches. Moreover, Cu^{2+} , Hg^{2+} , and Fe^{3+} greatly affect the fluorescence properties of diarylethene **4** in the photostationary state, so that these systems might be deployed in a novel molecular sensor for the detection of such cations by fluorescence recognition.

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1. Introduction

Photochromism is a reversible transformation between two isomers with different absorption spectra caused by alternating irradiation with UV and visible light. The design and synthesis of novel photochromic molecules is a “hotspot” research area because of their potential application in photonic devices, such as in memory media and optical switching [1]. Photochromic compounds, such as spiropyrans [2], azobenzene [3], fulgides [4], and diarylethenes [5], have been extensively investigated. Among these various types of photochromic compounds, diarylethenes with heterocyclic aryl groups, especially those bearing two thiophene or benzothiophene rings, are the most promising candidates for technological applications by virtue of their excellent thermally irreversible properties, remarkable fatigue resistance, and high sensitivity [6–21].

Fluorescent photochromic diarylethenes have attracted considerable attention during recent years in that they can be used to fabricate promising optoelectronic devices such as molecular switches [22] and optical memories [23]. In most instances [24], such systems show turn-off fluorescence upon irradiation with UV light: ring-open isomers exhibit fluorescence, but the fluorescence is quenched following photocyclization of diarylethenes, with the

ring-closed isomers showing little or no fluorescence due to efficient energy transfer between the excited fluorescent chromophore group and the ring-closed diarylethene fragment [25]. However, instances of turn-on fluorescence of photochromic diarylethene systems upon irradiation with UV light are rather rare [26]. This interesting turn-on fluorescence system is anticipated to be of great significance in the field of the design and application of novel optoelectronic devices. Therefore, we have been inspired to further investigate the turn-on fluorescence of diarylethenes. In the work described in this paper, various heterocycles (furan, thiophene, pyrrole) have been appended to imidazole rings and slightly modified in the molecular structures. This was undertaken in the hope of achieving novel diarylethene systems with excellent photochromic and light-emitting properties, with a view to developing novel optical materials having potential applications. Simultaneously, since imidazole and the attached heterocycles (such as furan, pyrrole, and so on) are excellent ligands, the effects of various metal ions on the optical properties of the respective diarylethene compounds have also been investigated.

2. Materials and methods

2.1. Experimental

General: All manipulations were carried out under an argon atmosphere by using standard Schlenk techniques, unless

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otherwise stated. DMF was dried with magnesium sulfate then distilled under vacuum. 1,2-Bis(5-chloro-2-methylthiophen-3-yl)ethane-1,2-dione (**1**) was prepared by literature methods [26]. 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 [27]. ^1H and ^{13}C NMR spectra were collected on American Varian Mercury Plus 400 spectrometer (400 MHz) or 600 MHz ^1H 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 imidazole unit 2–5

Target compounds **2–5** were prepared according to the synthetic route presented in Fig. 1 by modified procedures of reported methods [28].

2.2.1.1. Synthesis of 2. To a solution of ammonium acetate (1.2×10^{-3} kg, 16×10^{-3} mol) in refluxing glacial acetic acid (1.5×10^{-5} m³) was added furan-2-carbaldehyde (0.20×10^{-3} kg, 2.0×10^{-3} mol) under an argon atmosphere at 120 °C, and it was refluxed for 2 h. 1,2-Bis(5-chloro-2-methylthiophen-3-yl)ethane-1,2-dione (**1**) (0.64×10^{-3} kg, 2.0×10^{-3} mol) was added to the reaction solution above and continue to react further for overnight. The reaction mixture was allowed to cool to room temperature, and then transferred to ice water (2.0×10^{-4} m³), 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 redissolved in DCM. Then dried over sodium sulfate, unon removed of solvent under reduced pressure and purified on a silica gel column using petroleum ether/ethyl acetate (4:1) as the eluent to obtain the target compound as a yellow powder in a yield of 63%. m. p.: 266–267 °C. ^1H NMR (400 MHz, DMSO): δ 2.00 (s, 3H, CH₃), 2.13 (s, 3H, CH₃), 6.64, 6.91, 7.80 (s, 3H, furan-H), 6.82, 7.07 (s, 2H, thiophene-H), 12.84 (s, 1H, –NH). IR (KBr, cm^{−1}): 3443, 3117, 2913, 2850, 1634, 1569, 1542, 1438, 1393, 1275, 1198, 1124, 1069, 1012, 954, 833, 729, 516. MS (*m/z*): 394 [M]⁺. Anal. Calcd for C₁₇H₁₂Cl₂N₂OS₂: C, 51.65; H, 3.06; N, 7.09. Found: C, 51.35; H, 3.36; N, 6.83.

2.2.1.2. Synthesis of 3. Compound **3** was prepared by an analogous method similar to that used for **2** and was obtained as an ivory-white solid in a yield 80%. m. p.: 271–273 °C. ^1H NMR (400 MHz,

DMSO): δ 1.99 (s, 3H, CH₃), 2.14 (s, 3H, CH₃), 7.13, 7.55, 7.61 (s, 3H, thiophene-H), 6.81, 7.10 (s, 2H, thiophene-H), 12.81 (s, 1H, –NH). IR (KBr, cm^{−1}): 3442, 3123, 1569, 1536, 1418, 1266, 1194, 1121, 1069, 995, 954, 864, 830, 772, 691, 621, 562, 517. MS (*m/z*): 410 [M]⁺. Anal. Calcd for C₁₇H₁₂Cl₂N₂S₃: C, 49.63; H, 2.94; N, 6.81. Found: C, 49.49; H, 3.18; N, 6.90.

2.2.1.3. Synthesis of 4. Compound **4** was prepared by an analogous method to **2** and obtained as a light yellow solid in a yield 67%. m. p.: 280–281 °C. ^1H NMR (600 MHz, DMSO): δ 2.00 (s, 3H, CH₃), 2.16 (s, 3H, CH₃), 6.80, 6.82, 7.07 (s, 3H, pyrrole-H), 6.11, 6.61 (s, 2H, thiophene-H), 11.31 (s, 1H, pyrrole-NH), 12.31 (s, 1H, –NH). IR (KBr, cm^{−1}): 3431, 3127, 2961, 2922, 1616, 1569, 1506, 1457, 1382, 1261, 1121, 1069, 1013, 955, 865, 830, 723, 562, 539, 517. MS (*m/z*): 393 [M]⁺. Anal. Calcd for C₁₇H₁₃Cl₂N₃S₂: C, 51.78; H, 3.32; N, 10.66. Found: C, 51.99; H, 3.07; N, 10.79.

2.2.1.4. Synthesis of 5. Compound **5** were prepared according to procedures of reported methods [26].

2.2.2. Synthesis of *N*-methylation derivatives 6–9

Target compounds **6–9** were prepared according to the synthetic route presented in Fig. 1.

2.2.2.1. Synthesis of 6. To a solution of **2** (0.20×10^{-3} kg, 0.5×10^{-3} mol) in *N,N*-dimethylformamide (1.0×10^{-5} m³) in the presence of potassium carbonate (0.14×10^{-3} kg, 1.0×10^{-3} mol) was added methyl iodide (6.0×10^{-8} m³, 1.0×10^{-3} mol) under dark conditions for 12 h at room temperature. The reaction mixture was allowed to cool, transferred to about 1.0×10^{-4} m³ of water. The formed precipitate was collected and the crude product was washed with water, the dried solid was redissolved in DCM. Then dried over sodium sulfate, unon removed of solvent under reduced pressure and purified on a silica gel column using petroleum ether/ethyl acetate (5:1) as the eluent to obtain the target compound as a yellow solid in a yield of 90%. m. p.: 148–150 °C. ^1H NMR (400 MHz, CDCl₃): δ 2.02 (s, 3H, CH₃), 2.22 (s, 3H, CH₃), 3.69 (s, 3H, N–CH₃), 6.54 (s, 1H, furan-H), 6.67, 6.73 (s, 2H, thiophene-H), 6.92 (d, *J* = 3.6 Hz 1H, furan-H), 7.54 (s, 1H, furan-H). ^{13}C NMR (100 MHz, CDCl₃): δ 13.81 (s, CH₃), 14.13 (s, CH₃), 32.65 (s, N–CH₃), 109.87, 111.52, 124.43, 124.95, 125.78, 126.86, 127.21, 127.34, 130.61, 134.44, 135.56, 138.69, 139.66, 142.74, 145.69 (s, thiophene, ethene, furan). IR (KBr, cm^{−1}): 3443, 3090, 2919, 2448, 1714, 1570, 1456, 1433, 1386, 1262, 1121, 1070, 1008, 955, 864, 830, 808, 732, 517. MS (*m/z*): 408 [M]⁺. Anal. Calcd for C₁₈H₁₄Cl₂N₂OS₂: C, 52.81; H, 3.45; N, 6.84. Found: C, 52.71; H, 3.37; N, 6.92.

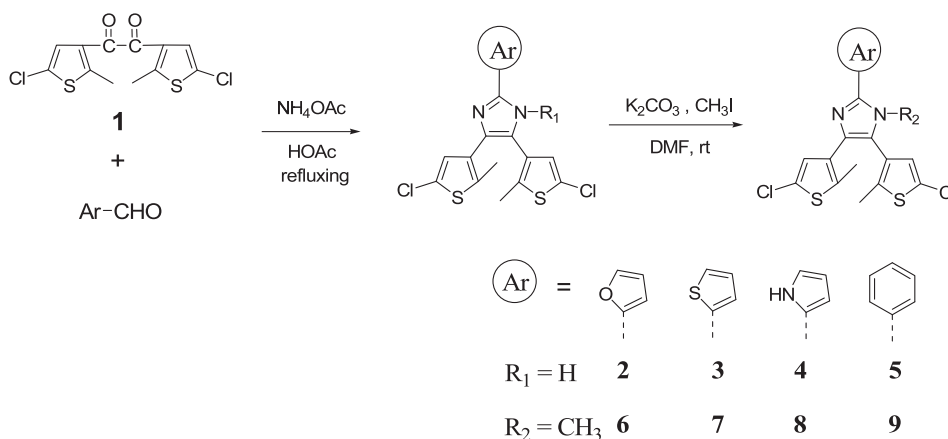


Fig. 1. Synthesis of dithienylethenes with an imidazole bridge unit **2–5** and their derivatives **6–9**.

2.2.2.2. Synthesis of 7. Compound **3** was prepared by an analogous method to **6** and obtained as a yellow solid in a yield 86%. m. p.: 139–140 °C. ^1H NMR (400 MHz, CDCl_3): δ 2.02 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 3.64 (s, 3H, $\text{N}-\text{CH}_3$), 6.64, 6.75 (s, 2H, thiophene-H), 7.13 (t, $J = 4.4$ Hz 1H, thiophene-H), 7.40 (d, 2H, thiophene-H). ^{13}C NMR (100 MHz, CDCl_3): δ 13.85 (s, CH_3), 14.22 (s, CH_3), 32.84 (s, $\text{N}-\text{CH}_3$), 124.70, 124.86, 125.86, 125.93, 126.76, 126.86, 127.02, 127.25, 127.49, 130.46, 132.94, 134.42, 135.38, 138.64, 142.43 (s, thiophene, ethene). IR (KBr, cm^{-1}): 3442, 3086, 2921, 2853, 1646, 1569, 1506, 1448, 1418, 1391, 1261, 1122, 1069, 989, 954, 840, 822, 796, 696, 517. MS (m/z): 424 $[\text{M}]^+$. Anal. Calcd for $\text{C}_{18}\text{H}_{14}\text{Cl}_2\text{N}_2\text{S}_3$: C, 50.82; H, 3.32; N, 6.58. Found: C, 50.75; H, 3.35; N, 6.45.

2.2.2.3. Synthesis of 8. Compound **8** was prepared by an analogous method to **6** and obtained as a yellow solid in a yield 83%. m. p.: 194–196 °C. ^1H NMR (400 MHz, CDCl_3): δ 1.99 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 3.62 (s, 3H, $\text{N}-\text{CH}_3$), 6.21, 6.49, 6.66 (s, 3H, pyrrole-H), 6.54, 6.74 (s, 2H, thiophene-H), 10.93 (s, 1H, pyrrole-NH). ^{13}C NMR (100 MHz, CDCl_3): δ 13.71 (s, CH_3), 14.03 (s, CH_3), 32.60 (s, $\text{N}-\text{CH}_3$), 107.61, 109.16, 119.83, 121.80, 123.64, 124.93, 125.96, 126.74, 127.09, 127.35, 130.70, 134.07, 138.38, 142.45 (s, thiophene, ethene, pyrrole). IR (KBr, cm^{-1}): 3444, 3274, 3126, 2915, 2446, 1591, 1512, 1452, 1381, 1265, 1202, 1122, 1069, 954, 835, 727, 517. MS (m/z): 407 $[\text{M}]^+$. Anal. Calcd for $\text{C}_{18}\text{H}_{15}\text{Cl}_2\text{N}_3\text{S}_2$: C, 52.94; H, 3.70; N, 10.29. Found: C, 53.17; H, 4.04; N, 10.57.

2.2.2.4. Synthesis of 9. Compound **9** was prepared by an analogous method to **6** and obtained as a yellow solid in a yield 81%. m. p.: 140–143 °C. ^1H NMR (600 MHz, CDCl_3): δ 2.04 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 3.55 (s, 3H, $\text{N}-\text{CH}_3$), 6.68, 6.79 (s, 2H, thiophene-H), 7.43 (t, $J = 7.2$ Hz 1H, Ar-H), 7.48 (t, $J = 7.2$ Hz 2H, Ar-H), 7.71 (d, $J = 7.2$ Hz 2H, Ar-H). ^{13}C NMR (150 MHz, CDCl_3): δ 13.90 (s, CH_3), 14.27 (s, CH_3), 33.12 (s, $\text{N}-\text{CH}_3$), 124.74, 124.85, 126.35, 126.78, 127.18, 127.28, 128.56, 128.74, 128.83, 130.46, 130.86, 134.17, 135.30, 1138.40, 148.03 (s, thiophene, ethene, Ar). IR (KBr, cm^{-1}): 3445, 3083, 2924, 2853, 1744, 1563, 1536, 1518, 1461, 1434, 1382, 1261, 1201, 1136, 1070, 1002, 953, 840, 772, 703, 517. MS (m/z): 418 $[\text{M}]^+$. Anal. Calcd for $\text{C}_{20}\text{H}_{16}\text{Cl}_2\text{N}_2\text{S}_2$: C, 57.28; H, 3.85; N, 6.68. Found: C, 57.41; H, 4.01; N, 6.53.

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

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 at room temperature.

2.4. Crystallographic details

Crystals suitable for X-ray diffraction were grown from a dichloromethane of solution **2** and **8** layered with hexane. Two crystals with approximate dimensions of $0.16 \times 0.05 \times 0.02 \text{ mm}^3$ for **2** and $0.25 \times 0.20 \times 0.10 \text{ mm}^3$ for **8** were mounted on a glass fiber for diffraction experiment. Intensity data were collected on a Nonius Kappa CCD diffractometer with Mo $\text{K}\alpha$ radiation (0.71073 \AA) 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

797035 & 797036. 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 bearing imidazole unit, **2–5**, were obtained by condensation reactions of 1,2-bis(5-chloro-2-methylthiophen-3-yl)ethane-1,2-dione (**1**) and the appropriate aromatic aldehydes in the presence of excess ammonium acetate in moderate yields of 63–80% (Fig. 1). *N*-Methylation was achieved by treatment of **2–5** with iodomethane in the presence of potassium carbonate to give **6–9** in good yields of 81–93%. A 2:1 ratio of iodomethane to imidazoles **2–5** was found to be optimal because a greater excess could have led to the formation of salts, thereby reducing the yield of methylation products. All of the target compounds were characterized by NMR, MS, and elemental analysis.

3.2. X-ray structures of 2 and 8

The molecular structures of **2** and **8** were determined by X-ray crystallography. The crystallographic details are given in Table 1, and the molecular structures are depicted in Fig. 2. Diarylethene **2** crystallized in the photoactive antiparallel conformation, which can undergo photocyclization, while diarylethene **8** crystallized in the photoactive parallel conformation, which cannot undergo photocyclization in the crystalline phase [29]. The dihedral angle between the heterocycle ring and the imidazole ring is 17.12° in **2** and 9.97° in **8**. The intramolecular distance between the two reactive carbons in **2** is 3.645 \AA , which is sufficiently short for the cyclization reaction to take place, as photochromic activity usually appears when the distance between the reactive carbon atoms is less than 4.2 \AA [30]. However, the intramolecular distance between the two reactive carbons in **8** is 4.964 \AA , which is too long for the cyclization reaction to take place in the crystalline phase.

3.3. Photochromic behavior

The photochromic behavior of diarylethenes **2–9** induced by photoirradiation in acetonitrile was measured at room

Table 1
Crystal data and structure refinement parameters for **2** and **8**.

	2	8
Formula	$\text{C}_{17}\text{H}_{12}\text{Cl}_2\text{N}_2\text{O}_2\text{S}_2$	$\text{C}_{18}\text{H}_{15}\text{Cl}_2\text{N}_3\text{S}_2$
Formula weight	395.31	408.35
Temperature (K)	298 (2)	298 (2)
Wavelength (\AA)	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic
Space group	Pbca	C2/c
a (\AA)	23.002 (7)	37.0221 (6)
b (\AA)	9.485 (3)	6.68640 (8)
c (\AA)	32.142 (10)	16.5693 (3)
β (deg)	90	111.463 (2)
Volume (\AA^3)	7013 (4)	3817.21 (11)
Z	16	4
D_{cal} (Mg/m^3)	1.498	1.421
F (000)	3232	1680
Crystal size (mm^3)	$0.16 \times 0.05 \times 0.02$	$0.25 \times 0.20 \times 0.10$
Goodness-of-fit on F^2	1.042	0.916
Final R indices [$I > 2\sigma(I)$]		
R ₁	0.0765	0.0461
wR ₂	0.1650	0.1070
R indices (all data)		
R ₁	0.1219	0.0844
wR ₂	0.1849	0.1186

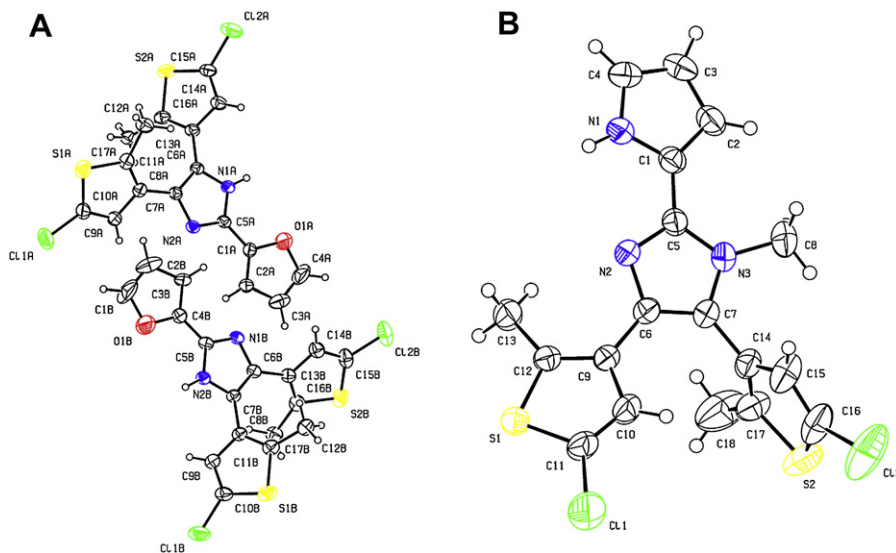


Fig. 2. Molecular structures of 2(A) and 8(B). The H atoms have been omitted for clarity.

temperature. The synthesized diarylethenes undergo photoisomerization between **2o–9o** (ring-open isomers) and **2c–9c** (ring-closed isomers) upon alternating irradiation with UV light ($\lambda = 302$ nm) and visible light ($\lambda > 402$ nm). As shown in Fig. 3A, the absorption maximum of compound **4** in acetonitrile was observed at 294 nm ($\epsilon = 2.34 \times 10^4$ L mol⁻¹ cm⁻¹) as a result of a $\pi-\pi^*$ transition [31]. This colorless solution turned pink and a new absorption band centered at 564 nm ($\epsilon = 1.03 \times 10^4$ L mol⁻¹ cm⁻¹) appeared when it was irradiated with UV light of wavelength 302 nm, as a result of a ring-closure reaction to give the isomer **4c**. In addition, a well-defined isosbestic point was observed at 316 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 **2**, **3**, and **5–9** in acetonitrile were irradiated with UV–Vis light.

The photochromic parameters of diarylethenes **2–9** are summarized in Table 2. These data show that the nature of the heterocycle attached to the imidazole ring and methylation of the N–H unit on the imidazole ring have great effects on the photochromic properties of these diarylethenes, including the absorption maxima and quantum yields of the cyclization and cycloreversion

reactions. For diarylethenes **5**, the absorption maxima in the visible region of the ring-closed isomers are blue-shifted compared with those of **2–4**, which indicates that the heterocycle attached to the imidazole ring contributes to increasing the conjugation of the whole molecule compared with a benzene ring. However, the absorption maxima of the ring-closed isomers of **6–9** are red-shifted compared with those of **2–5**, which may be attributed to an increase in the degree of conjugation after *N*-methylation of the imidazole rings, while the absorption maxima of their corresponding ring-open isomers are blue-shifted compared to those of **2–5**. The molar absorption coefficients of both the open-ring isomer and the closed-ring isomer of **5** are the smallest; while those of **3** are the biggest. However, for their *N*-methylated derivatives the molar absorption coefficients of both the open-ring isomer and the closed-ring isomer of **9** are the smallest. It indicates that the benzene ring linked to the imidazole ring decrease the molar absorption coefficient compared with a heterocycle. As shown in Table 2, the cyclization quantum yields of diarylethenes **2–9** are much higher than their respective cycloreversion quantum yields. The quantum yields of cyclization and cycloreversion reactions of diarylethenes **2–5** are much lower than those of their corresponding *N*-methylated derivatives **6–9**. This indicates that

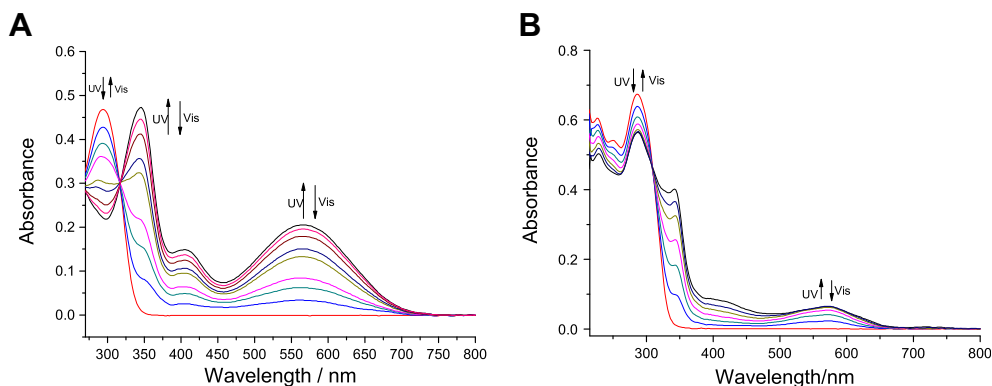


Fig. 3. Absorption spectral changes of diarylethenes **4** and **8** by photoirradiation in acetonitrile (2.0×10^{-5} mol/L) at room temperature. (A) spectral changes for **4**; (B) spectral changes for **8**.

Table 2

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

Compound	$\lambda_{\text{max}}^{\text{Abs}}/\text{nm}$ ($\epsilon \times 10^{-4}$) (Open) ^a	$\lambda_{\text{max}}^{\text{Abs}}/\text{nm}$ ($\epsilon \times 10^{-4}$) (PPS) ^b	Φ^c	
			$\phi_{\text{o-c}}$ (λ/nm)	$\phi_{\text{c-o}}$ (λ/nm)
2	296 (1.98)	536 (0.58)	0.280 (536)	0.0009 (296)
3	312 (2.45)	534 (1.37)	0.356 (534)	0.0004 (312)
4	294 (2.34)	564 (1.03)	0.164 (564)	0.0003 (294)
5	298 (1.86)	516 (0.50)	0.222 (516)	0.0013 (298)
6	288 (1.94)	588 (0.20)	0.719 (588)	0.0015 (288)
7	304 (1.45)	574 (0.27)	0.700 (574)	0.0019 (296)
8	286 (3.37)	572 (0.32)	0.366 (572)	0.0008 (286)
9	282 (1.21)	574 (0.16)	0.317 (574)	0.0023 (282)

^a Absorption maxima of open-ring isomers.

^b Absorption maxima of closed-ring isomers.

^c Quantum yields of open-ring ($\phi_{\text{c-o}}$) and closed-ring isomers ($\phi_{\text{o-c}}$), respectively.

N-methylation of the imidazole ring enhances the quantum yields of cyclization and cycloreversion, which is in agreement with our previous research work [32].

3.4. Fluorescence of the diarylethenes

The fluorescence change of diarylethenes **2–9** induced by photoirradiation in acetonitrile was investigated at room temperature. As shown in Fig. 4A, upon excitation of **4** in acetonitrile solution at an excitation wavelength of 375 nm, it exhibited a weak emission at 450 nm. Diarylethene **4** displayed strong yellow-emitting fluorescence at 548 nm upon irradiation with UV light of wavelength 302 nm. On reaching the photostationary state (PSS), the emission intensity of **4** was enhanced by ca. 98%, and a small fluorescence quantum yield ($\phi_{\text{f}} = 0.059$) was measured using quinoline sulfate ($\phi_{\text{f}} = 0.55$, in 0.1 M aqueous H_2SO_4) as a reference. Similar results were obtained when solutions of the other diarylethenes **2**, **3**, and **5–9** in acetonitrile were irradiated with UV light.

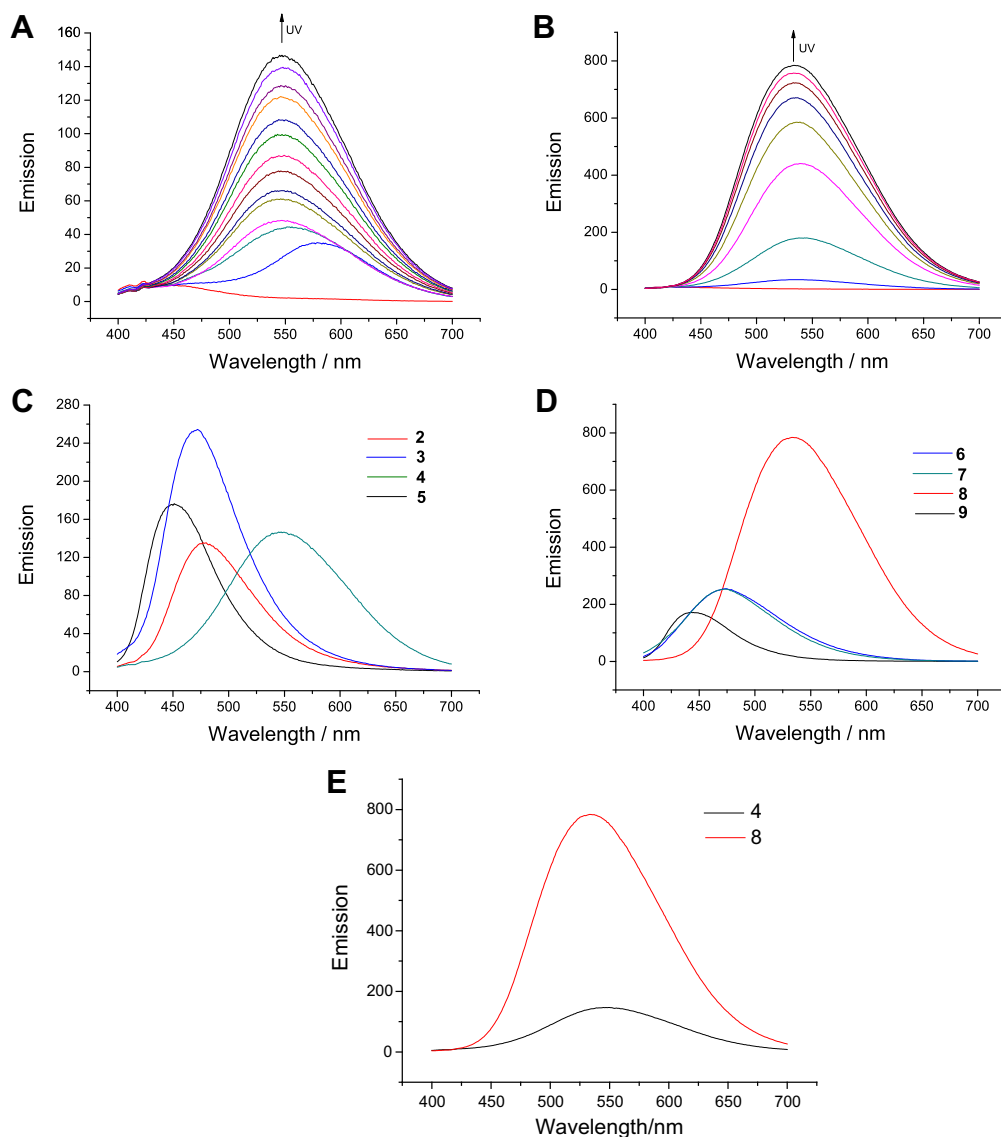


Fig. 4. Emission intensity changes of partial diarylethenes in acetonitrile (2.0×10^{-5} mol/L) with UV light irradiation ($\lambda_{\text{ex}} = 375$ nm). (A) emission spectral changes for **4**; (B) emission spectral changes for **8**; (C) fluorescence intensity of **2–5** in PSS; (D) fluorescence intensity of **6–9** in PSS; (E) fluorescence intensity of **4** and **8** in PSS.

Table 3
Fluorescence data of diarylethene **2–9** in acetonitrile ($\lambda_{\text{ex}} = 375$ nm).

Compound	λ_{em} (nm)	ϕ_f^a	Enhancement rate (%) ^b
2	478	0.011	88
3	472	0.059	99
4	548	0.059	98
5	450	0.044	97
6	475	0.195	90
7	470	0.181	99
8	534	0.496	99
9	443	0.101	98

^a Fluorescence quantum yields of diarylethene **2–9** in PSS.

^b Enhancement rate (%) = $F(\text{PSS}) - F(\text{initial}) / F(\text{PSS})$.

The corresponding fluorescence data of the other compounds are summarized in Table 3.

As shown in Table 3 and Fig. 4C–E, the nature of the heterocycle attached to the imidazole ring and methylation of the N–H unit on the imidazole ring also exerted obvious effects on the fluorescence performances of these diarylethenes, principally their emission maxima and fluorescence quantum yields. Moreover, as shown in Fig. 5, the light-emitting properties of these compounds could be easily tuned from blue light-emitting to yellow light-emitting fluorescence by varying the nature of the heterocycle or by simple modification of the molecular structure. Compared to **9**, these heterocycle-derivatized compounds show emissions that are red-shifted by 27–105 nm both before and after *N*-methylation of the imidazole ring. Emission at longer wavelengths is beneficial for fluorescence analysis, especially fluorescence bioimaging [33]. Simultaneously, it was found that the fluorescence intensities and fluorescence quantum yields of diarylethenes **6–9** were obviously increased after *N*-methylation of the imidazole ring in diarylethenes **2–5**, which is at variance with a previous literature report [34].

3.5. Effects of metal ions on the optical properties

Both the absorbance and fluorescence changes of diarylethenes **2–9** induced by the addition of various metal ions in acetonitrile were investigated at room temperature. It was found that Cu^{2+} , Hg^{2+} , and Fe^{3+} had obvious effects on the optical properties of diarylethenes **4**, but little, if any, changes in absorbance and emission were detected upon the binding of other metal ions (K^+ , Ag^+ , Ca^{2+} , Mn^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} , and Cd^{2+}) under the same conditions.

For diarylethene **4**, as shown in Figs. S1–S5, the absorption maximum (510 nm) of the ring-open isomer of **4** in the presence of Cu^{2+} was red-shifted compared with that of free **4** (294 nm) before irradiation with UV light. Accordingly, the color of the solution immediately changed from colorless to purple-red upon the addition of Cu^{2+} , which may be attributed to a change in the degree of conjugation of the diarylethene after binding Cu^{2+} . Meanwhile, the absorbance maximum of diarylethene **4** after irradiation with UV

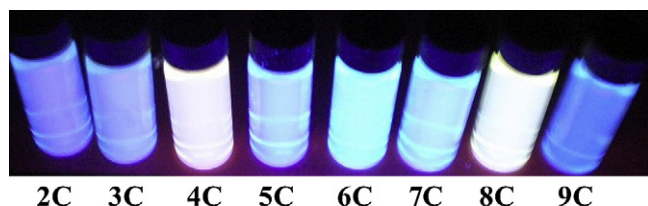


Fig. 5. Fluorescent light-emitting changes of diarylethenes **2–9** by photoirradiation in acetonitrile (2.0×10^{-5} mol/L) at room temperature.

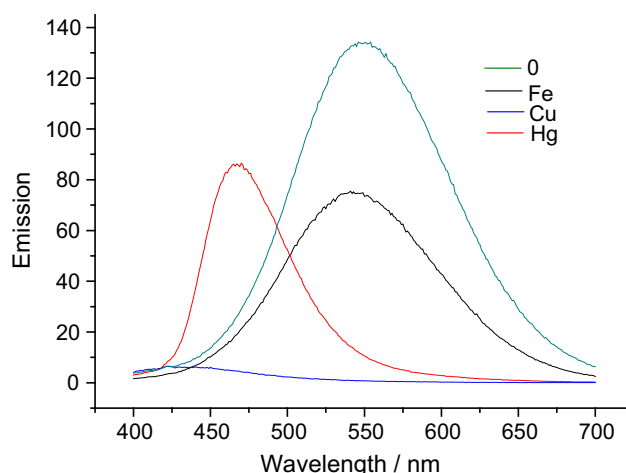


Fig. 6. Fluorescence response of **4** (2×10^{-5} M) in acetonitrile upon the addition of Cu^{2+} , Hg^{2+} and Fe^{3+} (8×10^{-5} M) in PSS by light of 302 nm ($\lambda_{\text{ex}} = 335$ nm).

light was fundamentally invariable compared with that of **4** before irradiation with UV light in the presence of Cu^{2+} . The absorption maximum (320 nm) of the ring-open isomer of diarylethene **4** in the presence of Hg^{2+} was red-shifted compared with that of free **4** (294 nm) before irradiation with UV light, while the photochromic activity of diarylethene **4** was completely inhibited after binding Hg^{2+} . The UV–Vis spectrum of diarylethene **4** displayed three absorption maxima in the presence of Fe^{3+} at 238, 310, and 360 nm, possibly due to iron(III) oxidizing an N–H group of the imidazole or pyrrole. Although it is difficult to predict the manner in which the imidazole and pyrrole units will orient themselves around a metal ion in solution, it clearly affected the photochromic properties of diarylethene **4** due to the high binding affinities of imidazole and pyrrole towards metal ions.

As presented in Fig. 6, the emission intensity of diarylethene **4** at 548 nm in the PSS decreased significantly upon the addition of Fe^{3+} , and the fluorescence quantum yield decreased from 0.059 to 0.026. Moreover, the fluorescence of compound **4** in the PSS was completely quenched in the presence of Cu^{2+} . The fluorescence quenching of **4** upon the addition of Fe^{3+} and Cu^{2+} may result from ligand-to-metal charge transfer (LMCT). The emission maximum of diarylethene **4** in the presence of Hg^{2+} was blue-shifted (467 nm) compared with that of free **4** (548 nm) in the PSS, and the corresponding fluorescence emission immediately changed from strong yellow-emitting to green-emitting fluorescence upon the addition of Hg^{2+} . However, similar results were not obtained for the other diarylethenes **2**, **3**, and **5–9**.

4. Conclusions

A novel series of diarylethenes incorporating different heterocycles (furan, thiophene, pyrrole) and their *N*-methylated derivatives have been synthesized. Their photochromic and fluorescence properties have been investigated. Each of the compounds displays excellent photochromism and “turn-on” fluorescence properties upon irradiation with UV light in solution. It has been found that the nature of the heterocycle attached to the imidazole ring and methylation of the N–H units on the imidazole ring exert great effects on both the photochromic and fluorescent properties of these diarylethenes. The light-emitting properties of these compounds can be easily tuned from blue light-emitting to yellow light-emitting fluorescence by varying the nature of the heterocycle or by simple modification of the molecular structure. It was found

that Cu^{2+} , Hg^{2+} , and Fe^{3+} have great effects on the fluorescence properties of diarylethenes **4** in the PPS. This provides a promising approach for the design of novel molecular sensors that might be used for the detection of Cu^{2+} and Hg^{2+} by fluorescence recognition.

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Appendix. Supporting information

Supplementary data related to this article can be found online at doi:10.1016/j.dyepig.2011.01.008.

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