Optical switching and fluorescence modulation properties of photochromic dithienylethene derivatives

Huiyuan Hu [a,b], Manzhou Zhu [a,*], Xiangming Meng [a], Zhiping Zhang [a], Kai Wei [a], Qingxiang Guo [a,*]

[a] *Department of Chemistry, University of Science and Technology of China, Hefei 230026, China*
[b] *Department of Applied Chemistry, Shenzhen University, Shenzhen 518060, China*

Abstract

Fluorescent photoswitching molecules in which photochromic diarylethene with terpyridine units (tpy) attached via a phenylene linker to the thiophene rings were synthesized. Both compounds exhibited pronounced photochromic properties. Irradiation of the open form of compounds **1** and **2** with UV light resulted in immediate photocyclization to the blue closed form; the colorless open forms could be regenerated by irradiation with visible light. In terms of potential use for optical data storage and readout, compounds **1** and **2** display fluorescence discrimination between their open and closed form. This fluorescence switching could be the basis of a nondestructive readout method. And the complexation of these two compounds with metal ions was also studied. It is amazing to find the addition of Zn^{2+} lead the emission wavelengths of **2a** red shift up to 105 nm. This unique phenomenon makes the compound **2a**, a candidate for the chemical sensor for zinc.
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Keywords: Diarylethene; Photochromism; Fluorescence switching; Metal ions

1. Introduction

Concurrent with the rapid development of modern science and technology, materials for fast and high density data storage are in high demand. The information is expected to be processed at molecular or atomic-scales with response times ultimately within nanosecond or picosecond levels. Organic photochromic materials have shown to be one of the most promising of memory media that meet such demands. Among various types of photochromic compounds, diarylethenes with attached thiophene rings are regarded as the most promising classes of photochromic materials [1]. The important features of this class of molecules are the good fatigue resistance, fairly high photocyclization quantum yields, high reversibility of the forward and reverse photo processes triggered by irradiation with light of different wavelengths and thermal stability of the products [2]. Moreover, it has recently been found that some diarylethenes having thiophene or benzothiophene rings undergo photochromic reactions even in the single-crystalline phase [3].

For practical applications to optical memory, nondestructive readout capability is indispensable. When the recorded information is read out by light that electronically excites the photochromic compounds the information is lost during the reading process [4]. As a consequence, much activity is presently being directed towards the design of systems with nondestructive readout capability. Although some alternatives have already been proposed [5], further development of new systems is warranted. Several ways to achieve a nondestructive readout have been suggested, such as locking the system in one state [6], or observing changes in optical rotation [7,8], refractive index [9], emission [10–13], or infrared absorption [4].

Fluorescent photochromic materials attract strong interest for their possible applications in optical memory as well as in fluorescent probes. In particular fluorescent diarylethenes, which show reversible change in fluorescence intensity with photochromic reaction, are useful for the nondestructive optical readout system. Although many diarylethene derivatives have been reported, compounds which exhibit strong fluorescent emission are rare [14–17].

R: H2C—⟨phenyl-terpyridine⟩
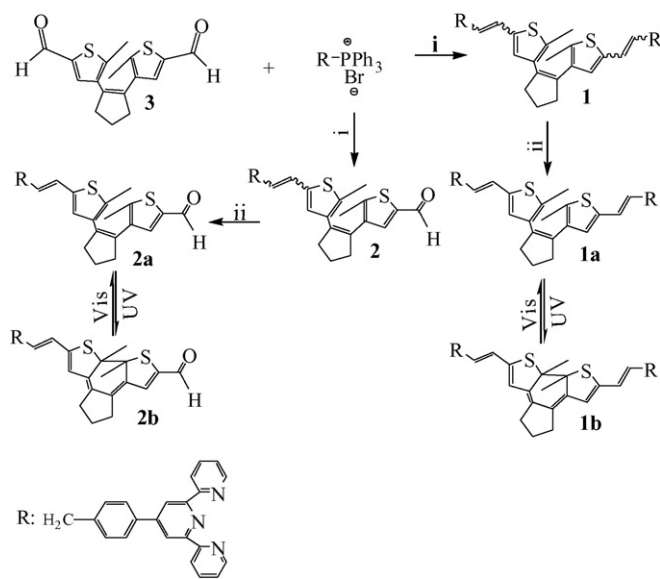
i) t-BuOK, CH2Cl2, rt, 2h; ii)I2, toluene, reflux, 12h

Scheme 1.

Furthermore, we now observed properties of the two discrete states upon irradiation are average behavior of the bulk systems. In other words, under normal conditions there exists a vast number of molecules in the system, the experimental data gradually change upon photoirradiation because the open/closed form ratio changes. The performance is not a real "switching" in the literal sense of the word. If we can detect the photochromic reaction at the single molecular level, real digital photoswitching is anticipated. For the observation, it is indispensable to prepare a photochromic molecule, which changes the fluorescence intensity along with the photochromic reaction and has high photostability. Green fluorescence protein is the only example that exhibits the optically induced switching of fluorescence at room temperature [18]. There are only a few artificial fluorescent photochromic molecules that can be applied to the single-molecule experiment [19]. It is required to newly design and synthesize robust fluorescent photochromic or photoswitching molecules.

Hence the fluorescent photoswitching molecules in which photochromic diarylethene with terpyridine units attached via a phenylene linker to the thiophene rings were synthesized (Scheme 1). And we performed a detailed study of their photochromic properties in solution.

2. Experimental

2.1. Synthesis

2.1.1. General methods

All the reactions were carried under N$_2$ atmosphere. In the case of photochromic complexes, reactions and further purifications were carried out protected from light with aluminium foil. Starting materials were commercially available and were used without further purification. The 4-(2-(5-formyl-2-methylthiophen-3-yl) cyclopent-1-enyl)-5-methylthiophene-2-

carbaldehyde (**3**) was synthesized from the known 1, 2-bis(5-chloro-2-methyl-3-thienyl)-cyclopentene according to literature [20]. And the 2-(6-(pyridin-2-yl)-4-p-tolylpyridin-2-yl)pyridine (**4**) was also synthesized according to literature [21]. The terpyridine was brominated by NBS in CCl$_4$ before the triphenylphosphonium was added to obtain the salt.

^{1}H NMR and ^{13}C NMR were recorded with a Bruker DMX-300 spectrometer, CDCl$_3$ as solvent and chemical shift was given in ppm downfield from TMS. Mass spectra were detected by Finnigan LCQ Advantage Max instrument. Elemental analysis was performed on a Perkin-Elmer 240C analytical instrument. The melting point was measured by WRS-2A melting point apparatus.

2.1.2. Synthesis of 2-(4-(4-((E)-2-(4-(2-(5-((E)-4-(2,6-di(pyridin-2-yl)pyridin-4-yl)styryl)-2-methylthiophen-3-yl)cyclopent-1-enyl)-5-methylthiophen-2-yl)vinyl)phenyl)-6-(pyridin-2-yl)pyridin-2-yl)pyridine (1a) and (E)-4-(2-(5-(4-(2,6-di(pyridin-2-yl)pyridin-4-yl)styryl)-2-methylthiophen-3-yl)cyclopent-1-enyl)-5-methylthiophene-2-carbaldehyde (2a)

A mixture of dialdehyde **3** (0.2 g, 0.63 mmol), (4-terpyridinephenyl) triphenyl-phosphonium bromide (1.0 g, 1.5 mmol) and t-BuOK (0.17 g, 1.5 mmol) in CH$_2$Cl$_2$ (30 ml) were stirred at room temperature for 1 h under N$_2$. A saturated aqueous NH$_4$Cl solution (20 ml) was then added. The aqueous layer was extracted twice with CH$_2$Cl$_2$ (10 ml × 2). The combined organic layer was washed with water and dried over MgSO$_4$. The residue was evaporated to dryness. Column chromatography (SiO$_2$, petroleum ether/acetic acetate/acetone/ammonia solution = 10:4:1:0.15) gave **1** (0.26 g, 0.28 mmol) and **2** (0.11 g, 0.18 mmol), respectively, as an E:Z isomer mixture. The mixture obtained after chromatography purification was directly isomerized as follows: a solution of the E:Z mixture and I$_2$ (1.0 mg) in toluene was refluxed for 12 h and then cooled to room temperature. The resulting toluene solution was washed with an aqueous 0.3 M Na$_2$S$_2$O$_3$ solution and water, dried over MgSO$_4$ and evaporated to dryness. Column chromatography (SiO$_2$, petroleum ether/acetic acetate/acetone/ammonia solution = 10:4:1:0.15) gave corresponding E isomers **1a** and **2a**.

1a: Mp, 152.8 °C. ^{1}H NMR (CDCl$_3$, 300 MHz) δ: 8.74 (m, 8H), 8.68 (d, 4H, J = 7.7 Hz), 7.91 (m, 8H), 7.58 (d, 4H, J = 7.9 Hz), 7.36 (m, 4H), 7.23 (d, 2H, J = 16.1 Hz), 6.83 (d, 4H, J = 13.2 Hz), 2.84 (t, 4H, J$_1$ = 6.9 Hz, J$_2$ = 7.3 Hz), 2.10 (m, 2H), 1.92 (s, 6H). ^{13}C NMR (CDCl$_3$, 75 Hz) δ: 156.4, 156.0, 149.7, 149.2, 138.6, 138.1, 136.9, 136.4, 134.6, 133.4, 132.2, 132.1, 132.0, 128.6, 128.5, 128.1, 127.6, 126.7, 126.4, 123.9, 123.0, 121.4, 118.5, 38.6, 23.0, 14.8; MS m/z 927.57 (M$^+$). Anal. calcd. for C$_{61}$H$_{46}$N$_6$S$_2$: C, 79.02; H, 5.00; N, 9.06; S, 6.92. Found: C, 79.67; H, 4.93; N, 9.02; S, 6.38.

2a: Mp, 96 °C. ^{1}H NMR (CDCl$_3$, 300 MHz) δ: 9.75 (s, 1H), 8.75 (m, 4H), 8.69 (d, 2H, J = 7.9 Hz), 7.91 (m, 4H), 7.57 (d, 2H, J = 8.2 Hz), 7.41 (s, 1H), 7.39 (m, 2H), 7.19 (d, 1H, J = 16.0 Hz), 6.83 (d, 2H, J = 19.0 Hz), 2.84 (t, 4H, J$_1$ = 7.2 Hz, J$_2$ = 7.4 Hz), 2.12 (m, 5H), 1.94 (s, 3H). ^{13}C NMR (CDCl$_3$, 75 Hz) δ: 182.6,

156.1, 149.7, 149.2, 146.7, 140.0, 139.2, 138.1, 138.0, 137.8, 137.3, 136.9, 136.3, 135.8, 134.8, 133.3, 127.7, 127.6, 126.9, 126.8, 123.9, 122.7, 121.5, 118.6, 38.6, 23.0, 15.6, 14.5; MS m/z 621.19 (M^+). Anal. calcd. for $C_{39}H_{31}N_3OS_2$: C, 75.33; H, 5.03; N, 6.76; S, 10.31. Found: C, 74.85; H, 5.12; N, 6.76; S, 10.53.

2.2. Spectroscopic measurements

Solvents used in the photochemical measurements were purified by distillation before use. Steady-state absorption spectra were measured with an UV–vis spectrophotometer (Perkin-Elmer lambda 45). Fluorescence emission spectra were conducted on a CRT970 fluorescence spectrophotometer. The excitation slit width was set at 2.0 nm. UV irradiations were carried out using a standard lamps used for visualizing TLC plates. For visible irradiation, light from 200 W mercury lamp was passed through a 480 nm high-pass filter and the samples were placed in a quartz chamber maintained at room temperature (RT). The quantum yields of cyclization and cycloreversion reactions were determined by using furyl flugide as a reference [22].

3. Results and discussion

3.1. Molecular design of fluorescent photochromic molecules

Photochromic diarylethene and terpyridine units were attached via a phenylene spacer group. The phenyl-substituted 2,2′:6′,2″-terpyridine (tpy) was employed as the fluorescent unit, because of its high fluorescence quantum yield, good thermal and chemical stability. Furthermore, the ring nitrogens of pyridine could serve as multiple interaction sites, and form stable coordination and hydrogen-bonded complexes with various metal ions and molecules. They have been widely used as ligands for transition metal cations and building blocks in supramolecular chemistry [23].

Both the compounds **1** and **2** were obtained in good yields (63 and 74%, respectively) by stirring the starting photochromic compound with triphenylphosphonium salt in dichloromethane at room temperature. As the Wittig reaction of triphenylphosphonium salt with aldehyde affords mixtures of (Z)- and (E)-alkenes nonsterospecifically, **1** and **2** were obtained as mixture of trans–trans isomers enriched with the corresponding cis–trans and cis–cis analogues. Both compounds required isomerization of the reaction mixture to the all-trans isomers **1a** and **2a** via reflux in toluene, containing a catalytic trace of iodine. The all-trans isomers were obtained in ~30% yield. The good solubility of these two compounds allowed monitoring of this aspect by high-resolution NMR. In particular, the signals of the vinylic protons of **1** and **2** were a series of peaks between δ 6.85 and 6.62. After the isomerization, the vinylic protons changed to a doublet peak at δ 6.83 with ^3J value of 13 and 19 Hz, respectively, related to the trans–trans configuration. Moreover, the ^1H NMR spectra recorded after completion of the isomerization reaction is much simpler than that of the starting isomeric

mixture. The structures of both compounds were also confirmed by ^{13}C NMR and mass spectroscopy.

3.2. Absorption spectra

The UV/vis spectra of the open and closed forms of compounds **1a** and **2a** are consistent with the remarkable photochromism demonstrated for diarylethenes of this type. Both compounds show similar absorption band at around 360 nm corresponds to the $S_0 \rightarrow S_1$ (^1IL) transition localized on the photochromic unit, while the shoulder at 270 nm involves the $\pi \rightarrow \pi^*$ transition of the tpy ligands. Irradiation of cyclohexane solution of these two compounds at 365 nm results in an immediate increase in the absorption in the visible spectral region and a visual change in color from colorless to blue due to the appearance of the ring-closed isomer. The cyclization forces the system into a more planar isomer, thereby increasing the conjugation and lowering the energy of the $S_0 \rightarrow S_1$ transition of the photochromic unit [24]. As can be seen in Fig. 1, the tpy intraligand transitions are not effected by the cyclization of the central unit, while the $S_0 \rightarrow S_1$ absorption maximum of the dithienylethene moiety shifts from 360 to 610 nm for compound **1**. The reverse reaction is triggered by visible light since the closed form has a strong absorption in the 450–750 nm region (Fig. 1). Subsequent irradiation of the sample with visible light of wavelengths > 480 nm resulted in a clean reconversion into the colorless open state.
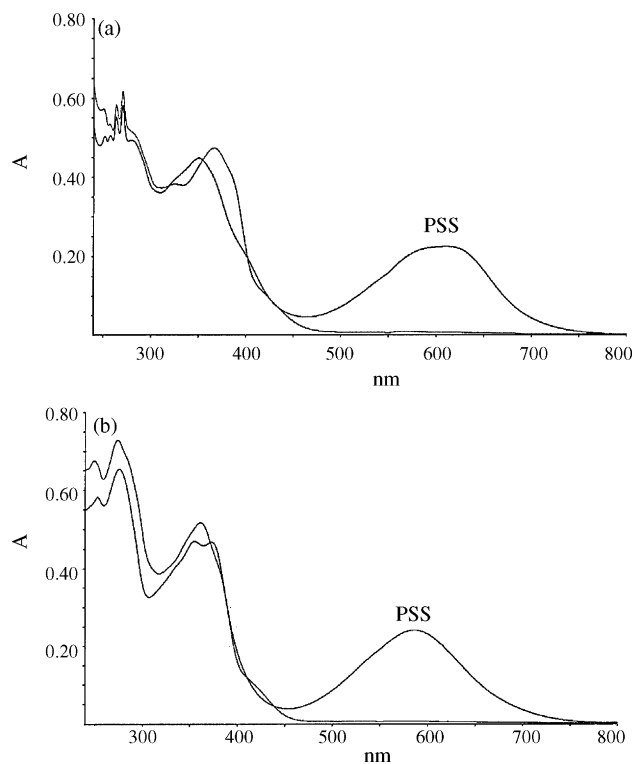

Fig. 1. UV/vis absorption spectra of **1a** (a) and **2a** (b) at open and photostationary state (PSS). All spectra were measured in cyclohexane solution. The PSS were obtained by irradiating solutions of **1a** and **2a** with 365 nm light until no spectral changes were observed.

Table 1
^{1}H NMR chemical shift data before and after irradiation

Compound[a]	δ		
	Thio-H	Cyclopentene-H	Thio-Me
1a	7.23 (d)	2.84 (t), 2.10 (m)	2.00 (s)
1b	6.15 (s)	2.50 (t), 1.94 (m)	2.00 (s)
2a	7.47 (s), 7.19 (d)	2.84 (t), 2.12 (m)	2.10 (s) 1.94 (s)
2b	7.16 (s), 6.13 (s)	2.54 (m), 1.97 (m)	2.02 (s), 1.99 (s)

[a] 300 MHz, CDCl$_3$ as solvent (δ in ppm).

Comparison of the observed spectra shifts of the absorption maxima of the mono and disubstituted compounds confirms the extended π conjugation across the central DTE unit in the closed isomers. In the case of the open isomers, where the π conjugation across the central DTE unit is interrupted (actually it is cross-conjugated), the positions of the absorption maxima of the mono and disubstituted compounds in the UV region are approximately the same. In contrast, for the closed isomers, the π conjugation across the closed central unit is evident from the significant shift of the absorption maxima in the visible spectral region of the disubstituted compounds compared to the mono-substituted ones. It quite agrees with the red shift ($\Delta\lambda = 25$ nm) of the absorption maximum of **1b** compared to **2b**.

The photocyclization of dithienylethenes is not always quantitative since, at a certain moment, equilibrium is established between the two photoactive forms. The photostationary state (PSS) can be analyzed with other spectroscopic tools to determine the exact ratio between the open and closed forms. The most straightforward method is ^{1}H NMR spectroscopy that permits comparison of the relative intensities of selected proton signals. Irradiation of the ring-open isomer solution with UV light resulted in the decrease and eventual disappearance of the signals in the NMR spectrum (Table 1) of the open isomer and the appearance of a new series of peaks corresponding to the closed form. At the photostationary state, no trace of the open compound could be detected, corresponding to a conversion of greater than 95%.

The open isomer of dithienylethene derivatives may exist as two conformers. The so-called parallel (p) and antiparallel (a-p) conforms are obtained from the planar, closed isomers by con and disrotatory rotations of the thiophene rings and have the local symmetry of C_s and C_2, respectively. According to the Woodward-Hoffmann rule, only the a-p conformer may undergo the ring-closure reaction. The high conversion ratio of
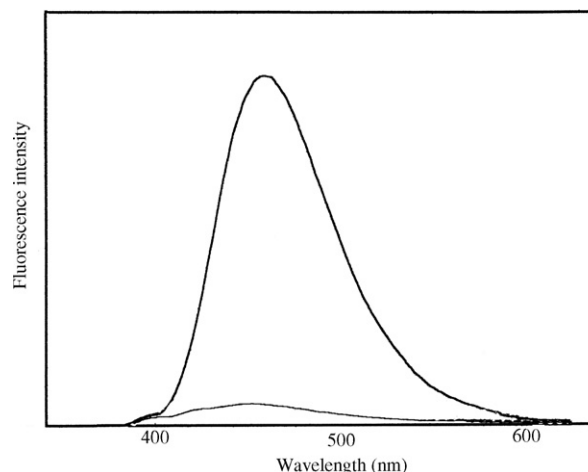

Fig. 2. Fluorescence spectra of **1a** and the photostationary state (excitation wavelength = 365 nm).

the compound shows the evidence of the high population of a-p conformer. To evaluate the relative population of the two conformers, the structure was optimized by the PM3 method and the single-point energy was calculated by B31YP/6-31G* method. This energy was corrected with the zero point energy calculated at PM3 level to generate the energy of the species at 0 K. The differences between the heat of formation of the two conforms are 3.67 and 10.78 kcal/mol for **1a** and **2a**, respectively. Neglecting entropy differences and correlations due to differences in salvation energy, the Boltzmann population of both conformers, ρ_p and ρ_{a-p}, are determined as $\rho_p \approx 1\%$ and $\rho_{a-p} \approx 99\%$ for compound **1a**, while for compound **2a** $\rho_p \approx 0.01\%$ and $\rho_{a-p} \approx 99.99\%$. It is fit well with the ^{1}H NMR data. And the relatively high cyclization quantum yields of both compounds (Table 2) were also proved it.

3.3. Switching of fluorescence

Fig. 2 shows the fluorescence spectral change of **1a** in a dichloromethane solution upon irradiation with UV light. The fluorescence maximum was observed at 466 nm. Upon irradiation with 365 nm light, the fluorescence intensity decreased and the emission was scarcely observed in the photostationary state. Similar fluorescence intensity changes upon irradiation with 365 nm light were also observed for **2a**. The fluorescence quantum yields of **1a** and **2a** by irradiation with 365 nm light

Table 2
Spectral data of compounds **1** and **2**

Compounds	λ_{abs} (nm)[a]	λ_{fluo} (nm)[b]	$\Phi_{o \to c}$	$\Phi_{c \to o}$	Φ_{fluo}[c]
1a	263, 270, 365	467	0.68	–	5.29×10^{-2}
1b	263, 270, 349, 610	–	–	0.015	3.75×10^{-3d}
2a	249, 273, 361	458	0.76	–	2.78×10^{-2}
2b	252, 275, 354, 372, 585	–	–	0.023	2.59×10^{-3d}

[a] In cyclohexane.

[b] In dichloromethane.

[c] Quinine sulfate was used as the standard ($\Phi = 0.546$ in 1.0N H$_2$SO$_4$, $\lambda_{ex} = 365$ nm [27]).

[d] Fluorescence quantum yield were measured at PSS.

were measured and summarized in Table 2. The higher quantum yield of 5.29×10^{-2} was observed for **1a**.

The strong fluorescence quench in **1b** is attributed to the efficient energy transfer from the excited terpyridine moiety to the closed-ring dithienylethene unit. Because the fluorescence spectrum of **1a** well overlaps the absorption spectrum of the closed-ring form of the diarylethene unit, the fluorescence is efficiently quenched when the diarylethene unit converts from the open- to closed-ring form. The fluorescence intensity gradually decreased in proportion to the conversion from **1a** to **1b**. At the photostationary state, the fluorescence intensity decreased to 3% of the initial intensity. Since **1b** was almost nonfluorescent, this result is in good agreement with the ^{1}H NMR data. Upon irradiation with >480 nm light, the fluorescence again returned to the original intensity by inchmeal.

The large fluorescence intensity change between the open- and closed-ring isomers makes it possible to use the change as the readout signal. When the fluorescence can be detected without influencing the ratio of the two isomers, the readout method becomes nondestructive. When the irradiation was performed with a narrow range of the excitation wavelength, the cycloreversion reaction was very slow. Although the system has no perfect performance of nondestructive readout, a very large number of fluorescence reading can, in principle, be performed before significant change takes place.

3.4. Coordination with metal ions

Terpyridine has ring nitrogens serving as multiple interaction sites, and can form stable coordination complexes with various metal ions. The luminescence of some transition metal complexes of terpyridines is well established including application to chemical sensing [25,26]. On the other hand, terpyridine ligands themselves have generally not been considered for use as fluorescent sensors, possibly owing to an expected lack of selectivity and perhaps also to the fact that few terpyridines are strongly emissive at wavelengths other than in the UV, with short-wavelength excitation being required.

We added ethanolic solution of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+} to the solution of ligands in 1:1 molar ratio (ligand:metal ion). The influence of metal ions was studied by the UV/vis absorption spectra (Fig. 3). All the spectroscopic data were listed in Table 3. For both compounds, the addition of metal ions causes big changes in the spectroscopic properties compared to the free ligand. For the metal coordination, an absorption band due to a singlet metal-to-ligand charge-transfer transition (^{1}MLCT) is presented at a lower energy than the $S_0 \approx S_1$ transition of the photochromic unit in the open state. It is noteworthy that a very weak absorption band between 550 and 700 nm was appeared for **2a** along with the addition of metal ions. This new band makes the mixture a visual change in color from colorless to light yellow.

The photochromic properties of the mixed solution were also studied. For compound **2a**, the addition of metal ions has no evident effect on the photochromic reaction. And the same happens when the addition of Pb^{2+} to the solution of **1a**. While after the addition of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} to the solution
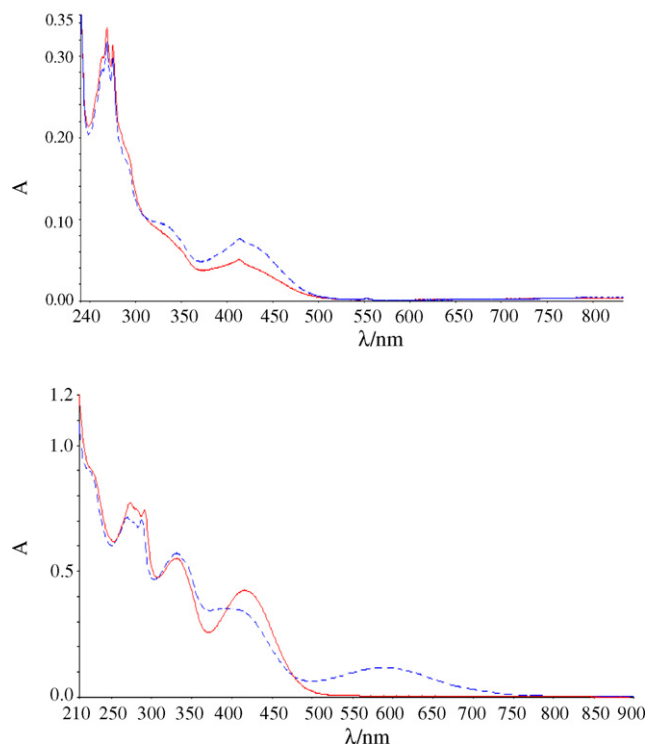

Fig. 3. Typical UV/vis spectra of metal complexes of the ligands: **1a** + Cu^{2+} (—), **1b** + Cu^{2+} (- - -) (upper); **2a** + Cu^{2+} (—), **2b** + Cu^{2+} (- - -) (lower).

of **1a**, irradiating the mixture with UV light caused no obvious change in solution color (Fig. 3). It means no absorption band was appeared in the visible region during the photochromic process. Since terpyridines are well known to form 2:1 complexes with transition metal ions, the complexation of **1a** with transition metal ions may form a linear chain structure in which the photochromic center probably distorted from the reaction plane. So the photochromic properties of the mixture differ from the free ligand.

In the presence of the tpy ligand, fluorescence quenching of both compounds **1a** and **2a** were observed for ethanolic solution containing several different metal ions (Table 4). Quenching is observed for Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} cations in solution. In the case of Cu^{2+}, the fluorescence is quenching and the emission undergoes a red-shift of up to 90 nm with the addition of the transition metal ions. It is surprisingly to find that the addition
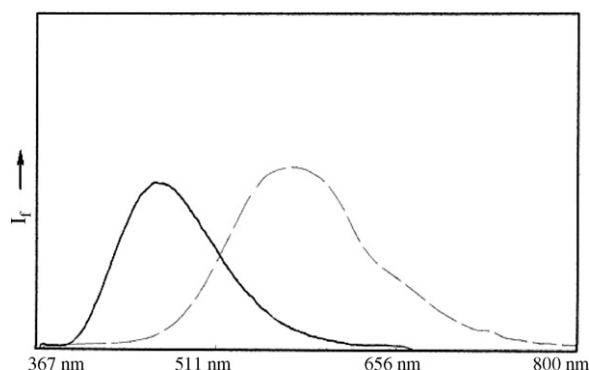

Fig. 4. Fluorescence spectra of **2a** (—) and **2a** + Zn^{2+} (- - -).

Table 3
UV/vis absorption maxima and absorption molar coefficients of the investigated photochromic metal complexes in their open and closed forms[a]

Compounds[b]	λ_{max} (nm) (ε_{max} ($\times 10^4$ M^{-1} cm^{-1}))
1a	257 (0.75), 263 (0.83), 270 (0.98), 275 (0.94), 363 (0.24)
1b	254 (0.79), 260 (0.75), 265 (0.91), 272 (0.87), 344 (0.36), 609 (0.20)
1a + Mn^{2+}	265 (1.17), 272 (1.07), 286 (0.66), 389 (0.25)
1b + Mn^{2+}	268 (1.13), 275 (1.03), 286 (0.66), 289 (0.60), 386 (0.30), 594 (0.07)
1a + Co^{2+}	268 (1.10), 275 (1.00), 289 (0.63), 326 (sh, 0.43), 404 (0.23)
1b + Co^{2+}	268 (1.30), 275 (1.21), 289 (0.72), 326 (sh, 0.54), 414 (0.38)
1a + Ni^{2+}	268 (0.97), 275 (0.93), 285 (0.54), 324 (sh, 0.36), 401 (0.23)
1b + Ni^{2+}	268 (1.00), 275 (0.94), 285 (0.51), 327 (0.41), 406 (0.38)
1a + Cu^{2+}	268 (1.67), 275 (1.57), 413 (0.26)
1b + Cu^{2+}	268 (1.13), 275 (1.49), 333 (sh, 0.40), 413 (0.38)
1a + Zn^{2+}	263 (0.58), 268 (0.73), 275 (0.64), 289 (0.19), 325 (0.15), 402 (0.09)
1b + Zn^{2+}	263 (0.62), 268 (0.76), 275 (0.67), 289 (0.20), 329 (0.16), 401 (0.12)
1a + Pb^{2+}	265 (1.21), 272 (1.07), 287 (sh, 0.56), 380 (0.22)
1b + Pb^{2+}	269 (1.06), 276 (0.93), 344 (0.49), 624 (0.22)
2a	251 (3.09), 278 (3.70), 363 (2.85)
2b	255 (2.80), 280 (3.48), 368 (2.43), 590 (0.84)
2a + Mn^{2+}	239 (2.83), 288 (3.43), 320 (sh, 2.33), 387 (2.33)
2b + Mn^{2+}	233 (3.07), 287 (3.40), 328 (sh, 2.47), 369 (1.99), 587 (0.82)
2a + Co^{2+}	288 (3.57), 321 (2.74), 401 (2.19)
2b + Co^{2+}	289 (3.45), 325 (2.82), 382 (sh, 1.87), 592 (0.52)
2a + Ni^{2+}	281 (3.70), 323 (2.74), 405 (2.21)
2b + Ni^{2+}	285 (3.35), 329 (2.72), 398 (1.89), 592 (0.56)
2a + Cu^{2+}	273 (3.86), 291 (3.72), 331 (2.77), 416 (2.13)
2b + Cu^{2+}	269 (3.58), 288 (3.51), 331 (2.86), 408 (sh, 1.74), 590 (0.59)
2a + Zn^{2+}	239 (2.87), 288 (3.48), 326 (2.61), 400 (2.19)
2b + Zn^{2+}	235 (1.44), 288 (2.87), 340 (sh, 2.64), 375 (sh, 1.92), 592 (0.97)
2a + Pb^{2+}	243 (3.26), 281 (3.66), 368 (2.46)
2b + Pb^{2+}	282 (3.20), 360 (sh, 2.52), 591 (1.36)

[a] PSS mixture.
[b] All the measurements were carried out in ethanol solution, the concentration of both ligands is 2×10^{-5} M, the concentration of metal ions added for **1a** and **2a** are 4×10^{-5}, 2×10^{-5} M, respectively.

of Zn^{2+} lead to a large shift to longer wavelengths for compound **2a** (Fig. 4). Since a large number of cellular functions have been identified for zinc over the past decade, probes of cellular Zn^{2+} concentration are of interesting interest [27]. Thus, the unique

Table 4
Fluorescence data of the metal complexes

Compounds[a]	λ_{em} (nm) (I_f/I_0[b])	Compounds[a]	λ_{em} (nm) (I_f/I_0[b])
1a	471 (1.00)	**2a**	465 (1.00)
1a + Mn^{2+}	–[c]	**2a** + Mn^{2+}	465 (0.18)
1a + Co^{2+}	–[c]	**2a** + Co^{2+}	–[c]
1b + Ni^{2+}	–[c]	**2b** + Ni^{2+}	–[c]
1a + Cu^{2+}	555[d] (0.08)	**2a** + Cu^{2+}	555[d] (0.12)
1a + Zn^{2+}	570 (0.15)	**2a** + Zn^{2+}	570 (1.09)
1a + Pb^{2+}	484 (0.40)	**2a** + Pb^{2+}	465 (0.81)

[a] All the measurements were carried out in ethanol solution using $\lambda_{ex} = 365$ nm, the concentration of both ligands is 2×10^{-5} M, the concentration of metal ions added for **1a** and **2a** are 4×10^{-5}, 2×10^{-5} M, respectively.
[b] I_0 refer to the original fluorescence intensity of the free ligands without the metal ions.
[c] Not detected.
[d] $\lambda_{ex} = 390$ nm.

responses of **2a** to Zn^{2+} lighten the design of potential sensory system for zinc, although a water-soluble analogue would be required in order to allow use in physiological studies.

4. Conclusion

Diarylethene having a fluorescent phenyl-substituted 2,2′:6′,2″-terpyridine chromophore **1a** and **2a** were synthesized. Both compounds underwent reversible photocyclization reactions by alternate irradiation with UV ($\lambda = 365$ nm) and a visible ($\lambda > 480$ nm) light. The fluorescence intensity also reversibly changed with the photochromic reactions. The fluorescence quantum yields of the open-ring isomers are 5.29×10^{-2} and 2.78×10^{-2}. Furthermore, the fluorescence discrimination between the open and closed form of **1a** and **2a** could be the basis of a nondestructive readout method. The effects of the metal ions were also studied in ethanolic solution. The emission wavelengths red-shift of **2a** induced by the addition of Zn^{2+} make itself a candidate of chemical sensor for zinc ions.

References

[1] T. He, S. Yang, J. Chem. Soc. Rev. 33 (2004) 85.
[2] M. Irie, Chem. Rev. 100 (2000) 1685.
[3] (a) M. Irie, K. Uchida, T. Eriguchi, H. Tsuzuki, Chem. Lett. (1995) 899;
(b) S. Kobatake, T. Yamada, K. Uchida, N. Kato, M. Irie, J. Am. Chem. Soc. 121 (1999) 2380;
(c) S. Kobatake, M. Yamada, T. Yamada, M. Irie, J. Am. Chem. Soc. 121 (1999) 8450;
(d) T. Yamada, S. Kobatake, M. Irie, J. Am. Chem. Soc. 122 (2000) 1589;
(e) M. Irie, T. Lifka, S. Kobatake, N. Kato, J. Am. Chem. Soc. 122 (2000) 4871;
(f) T. Kodani, K. Matsuda, T. Yamada, S. Kobatake, M. Irie, J. Am. Chem. Soc. 122 (2000) 9631;
(g) T. Yamada, S. Kobatake, M. Irie, Bull. Chem. Soc. Jpn. 73 (2000) 2179;
(h) K. Shibata, K. Muto, S. Kobatake, M. Irie, J. Phys. Chem. A 106 (2002) 209;
(i) S. Kobatake, K. Uchida, E. Tsuchida, M. Irie, J. Chem. Soc. Chem. Commun. (2002) 2804.
[4] K. Uchida, M. Saito, A. Murakami, S. Nakamura, M. Irie, Adv. Mater. 15 (2003) 121.
[5] (a) S.H. Kawai, S.L. Gilat, J.-M. Lehn, J. Chem. Soc. Chem. Commun. (1994) 1011;
(b) G.M. Tsivgoulis, J.-M. Lehn, Angew. Chem. Int. Ed. Engl. 34 (1995) 1119;
(c) A. Fernaández-Acebes, J.-M. Lehn, Adv. Mater. 10 (1998) 1519;
(d) M. Irie, K. Sakemura, M. Okinaka, K. Uchida, J. Org. Chem. 60 (1995) 8305;
(e) M. Hanazawa, R. Sumiya, Y. Horikawa, M. Irie, J. Chem. Soc. Chem. Commun. (1992) 206;
(f) M. Irie, O. Miyatake, K. Uchida, J. Am. Chem. Soc. 114 (1992) 8715.
[6] S.H. Kawai, S.L. Gilat, R. Ponsinet, J.M. Lehn, Chem. Eur. J. 1 (1995) 285.
[7] T. Yamaguchi, K. Uchida, M. Irie, J. Am. Chem. Soc. 119 (1997) 6066.
[8] A. Fernández-Acebes, Chirality 12 (2000) 149.
[9] N. Tanio, M. Irie, J. Jpn. J. Appl. Phys. 33 (1994) 1550.
[10] A.J. Myles, N.R. Branda, Adv. Funct. Mater. 12 (2002) 167.
[11] K. Yagi, C.F. Soong, M. Irie, J. Org. Chem. 66 (2001) 5419.

[12] T.B. Norsten, N.R. Branda, J. Am. Chem. Soc. 123 (2001) 1784.

[13] H. Cho, E. Kim, Macromolecules 35 (2002) 8684.

[14] G.M. Tsivgoulius, J.-M. Lehn, Chem. Eur. J. 2 (1996) 1399.

[15] M. Takeshita, M. Irie, Chem. Lett. (1998) 1123.

[16] A. Fernández-Acebes, J.-M. Lehn, Chem. Eur. J. 5 (1999) 3285.

[17] J. Ern, A.T. Benz, H.-D. Martin, S. Mukamel, S. Tretiak, K. Tsyganenko, K. Kuldova, H.P. Trommsdorff, C. Kryschi, J. Phys. Chem. A 105 (2001) 1741.

[18] R.M. Dickson, A.B. Cubitt, R.Y. Tsien, W.E. Moerner, Nature 388 (1997) 355.

[19] M. Irie, T. Fukaminato, T. Sasaki, N. Tamai, T. Kawai, Nature 420 (2002) 759.

[20] L.N. Lucas, J. van Esch, R.M. Kellogg, B.L. Feringa, Chem. Commun. (1998) 2313.

[21] B. Farlow, T.A. Nile, J.L. Walsh, Polyhedron 12 (1993) 2891.

[22] (a) Y. Yokoyama, Y. Kurita, J. Synth. Org. Chem. Jpn. 49 (1991) 364;
(b) H.G. Hellar, J.R. Langan, J. Chem. Soc. Perkin Trans. 2 (1981) 341.

[23] (a) D.S. Lawrence, T. Jiang, M. Levett, Chem. Rev. 95 (1995) 2229;
(b) J.-P. Collin, P. Gaviña, V. Heitz, J.-P. Sauvage, Eur. J. Inorg. Chem. (1998) 1.

[24] J. Ern, A.T. Bens, H.-D. Matin, S. Mukamel, D. Schmid, S. Tretiak, E. Tsiper, C. Kryschi, Chem. Phys. 246 (1999) 115.

[25] (a) F. Barigelletti, L. Flamigni, M. Guardigli, J.-P. Sauvage, J.-P. Collin, A. Sour, Chem. Commun. (1996) 1329;
(b) F. Barigelletti, L. Flamigni, G. Calogero, L. Hammarström, J.-P. Sauvage, J.-P. Collin, Chem. Commun. (1996) 2334.

[26] (a) M. Licini, J.A.G. Williams, Chem. Commun. (1999) 1943;
(b) W. Goodall, J.A.G. Williams, J. Chem. Soc. Dalton Trans. (2000) 2893.

[27] S.C. Burdette, S.J. Lippard, Coord. Chem. Rev. 333 (2000) 216.