Dyes and Pigments 94 (2012) 416–422

Contents lists available at SciVerse ScienceDirect

Dyes and Pigments

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

A new photoinduced fluorescent switch based on a photochromic diarylethene with a rhodamine fluorophore

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ARTICLE INFO

Article history:
Received 22 November 2011
Received in revised form
14 February 2012
Accepted 16 February 2012
Available online 23 February 2012

Keywords:
Fluorescence switch
Photochromism
Diarylethene
Rhodamine fluorophore
FRET
Cation recognition

ABSTRACT

A new photoinduced fluorescent switch based on a photochromic diarylethene with a rhodamine fluorophore has been successfully explored. The target compound exhibits excellent photochromism with good fatigue-resistance upon photo-irradiation. Upon addition of Cr(III), the color of the diarylethene turns from colorless to pink accompanied with a 300-fold increase in fluorescence emission intensity in methanol. In the presence of Cr(III), an efficient FRET process from the rhodamine moiety (FRET donor) to the closed-ring diarylethene moiety (FRET acceptor) occurs upon UV light stimuli, and its emission intensity can be recovered upon irradiation with visible light. Also, the ability of the compound to detect metal ions has been evaluated by monitoring the changes of emission intensity in methanol. Amongst the tested metal ions, only Cr(III), Al(III) and Fe(III) are efficiently detected. The result indicates that the diarylethene can selectively recognize Cr(III) with significant color and fluorescence changes.

1. Introduction

Metal ions play a fundamental role in a wide range of chemical and biological processes. A number of efforts have been made in the development of effective fluorescent probes based on ion-induced changes in fluorescence. Such probes are particularly attractive due to their instantaneous response, visual simplicity, and high sensitivity [1–5]. Trivalent chromium, Cr(III), is an essential component of a balanced human and animal diet [6]. Chromium can cause disturbances in the glucose levels and lipid metabolism, and lead to a variety of diseases, including diabetes [7] and cardiovascular problems [8]. In addition, chromium is an environmental pollutant and its build-up due to various industrial and agricultural activities is a matter of concern [9]. Thus, great importance is attached to developing chemical sensors that are capable of detecting the presence of chromium ions in environmental and biological samples. Due to its simplicity, the selective fluorimetric detection of Cr(III) has great advantages over other detection techniques such as electrochemical [10] and potentiometric [11]. Paramagnetic Cr(III) is described as one of the most efficient fluorescence quenchers among the transition-metal ions, which renders it difficult to develop a Cr(III) turn-on sensor. In the last few years considerable effort has been directed towards the development of fluorescence probes for the detection of paramagnetic species [12–15].

Rhodamine B is extensively used as a chemosensor because of its high absorption coefficient, high fluorescent quantum yield and excitation within visible wavelengths [16]. Furthermore, it can also undergo equilibrium between the colorless spirolactam (no fluorescence) form and the red open-ring form (strong fluorescence). Therefore rhodamine-based dyes are excellent off/on type fluorescence probes for various species [17]. So far, several successful attempts have been made to develop selective fluorescent sensors based on rhodamine for Cu(II) [18], Pb(II) [19], and Zn(II) [20], and some fluorescent probes for Cr(III) based on rhodamine have also been developed [21–26].

Photochromic diarylethenes are attractive because of their excellent thermal stability, remarkable fatigue-resistance, rapid response and dual-control fluorescence switches. In particular the construction of controllable fluorescent molecular switches has been a growing interest [27–30]. Upon irradiation with UV light, the emission intensity of diarylethene in a photostationary state was quenched to some extent due to the formation of its non-fluorescence ring-closed isomer. So a multi-control functional molecule may be constructed by connecting fluorophores to a photochromic diarylethene. The fluorescent behavior of fluorophore-photochromic dyads can be regulated on the basis of energy transfer. The photoinduced and reversible interconversion of the diarylethene can control the intramolecular transfer of the

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doi:10.1016/j.dyepig.2012.02.012

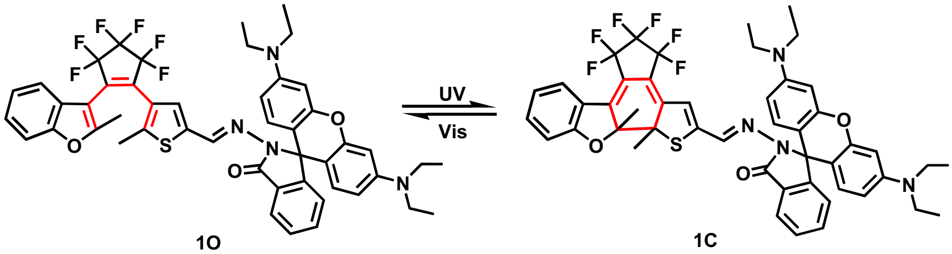

Fig. 1. Photochromism of diarylethene **1**.

excitation energy of the fluorophore from one component to the other [31]. Back irradiation of the appropriate wavelength of visible light regenerated the open-ring isomer of diarylethene and duplicated the original emission spectra.

Recently, Zheng et al. reported a dual-control molecular switch based on photochromic hexahydrogencyclopentene bearing two rhodamine units and proposed an integrated logic circuit at the molecular level [32]. Our group reported fluorescent molecular switches based on photochromic perfluorocyclopentenes bearing a rhodamine unit [33,34]. Tian et al. reported some new chemsensors based on photochromic perhydrogencyclopentene in response to ions such as Hg(II), F(I) [35], Cu(II) [36] and Al(III) [37]. Compared with photochromic perhydrogencyclopentene, the chemsensors based on photochromic perfluorocyclopentene had advantages in stability, sensitivity, and fatigue-resistance. But until now, there are only a few publications concerning the controllable fluorescent chemsensors for cation recognition based on hybrid perfluorocyclopentene with a rhodamine fluorophore [34]. In this work, a new photochromic diarylethene with a rhodamine fluorophore was explored and its controllable fluorescent switching characteristic was discussed. The photochromism of the diarylethene is shown in Fig. 1.

2. Experiments

2.1. General

NMR spectra were recorded on a Bruker AV400 (400 MHz) spectrometer with $CDCl_3$ as the solvent and tetramethylsilane as an internal standard. Melting points were measured on a WRS-1B melting point apparatus. UV–vis spectra were recorded on a PerkinElmer Lambda 900 spectrometer. The IR spectra were generated on a Bruker Vertex-70 spectrometer using KBr pallets. Elemental analyses were determined with a PE CHN 2400 analyzer. Photoirradiation was carried out with an SHG-200 UV lamp, a CX-21 ultraviolet fluorescence analysis cabinet, and a BMH-250 visible lamp. Radiation of appropriate wavelength was isolated by different light filters. Luminescence spectra were measured on a Hitachi 4500 fluorescence spectrophotometer. All solvents were of analytical grade and purified by distillation before use. Other reagents were used as received without further purification.

3. Results and discussion

3.1. Synthesis

The synthetic route to obtain the target compound is shown in Fig. 2. First, the mono-substituted (2-methyl-3-benzofuranyl)perfluorocyclopentene (**3**) was synthesized by the similar method reported by Yamaguchi and Irie [38]. 3-Bromo-2-methyl-5-(1,3-dioxolane)thiophene (**4**) [39] was lithiated and coupled with **3** and then directly hydrolyzed to give diarylethene **2O**. Finally, the target compound **1O** was prepared by the condensation reaction of diarylethene **2O** with rhodamine B hydrazine (**5**) [34]. The structures of diarylethenes **1O** and **2O** were confirmed by elemental analysis, NMR, and IR.

3.1.1. *1-(2-Methyl-3-benzofuranyl)-2-(2-methyl-5-formyl-3-thienyl)perfluorocyclopentene (**2O**)*

Compound **4** (0.60 g, 2.64 mmol) in anhydrous THF (60 mL) was added dropwise to a 2.5 mol/L n-BuLi/hexane solution (1.05 mL) at 195 K under an argon atmosphere. Stirring was continued for 30 min, THF (15 mL) containing compound **3** (0.86 g, 2.65 mmol) was slowly added to the reaction mixture at 195 K and stirred for 2 h at this low temperature. Then, the reaction was allowed to slowly warm to the room temperature and quenched by water.

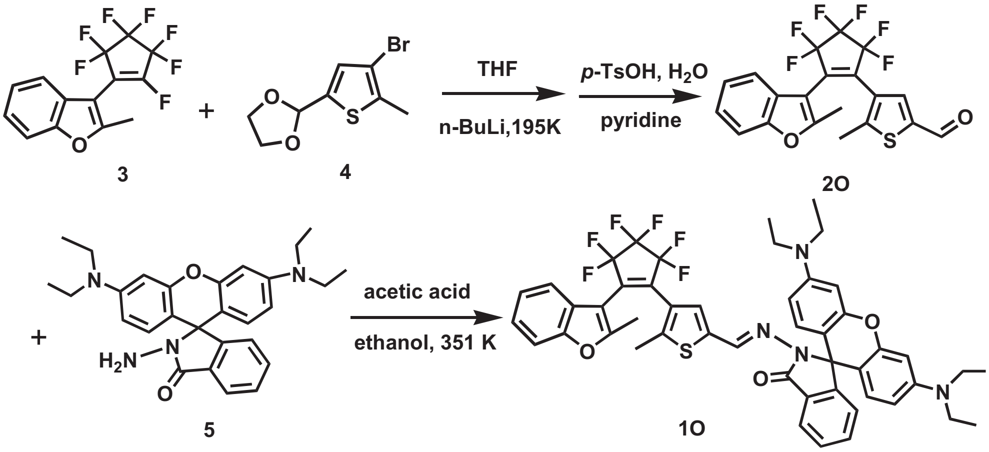

Fig. 2. Synthetic route for diarylethene **1O**.

After being extracted with ether (3 × 30 mL) and evaporated in vacuo, the crude product was directly hydrolyzed in the presence of pyridine and p-toluenesulfonic acid in acetone/water. The mixture was extracted with ether. The organic layer was collected and dried over $MgSO_4$, filtered and evaporated. The crude compound was purified by column chromatography on silica gel using petroleum/ethyl acetate (v/v = 6/1) as the eluent to give diarylethene **2O** (0.45 g, 39% yield) as a colorless solid. M.p. 100.2–101.6 °C; IR (KBr, ν, cm^{-1}): 752, 798, 839, 894, 925, 987, 1058, 1126, 1193, 1271, 1338, 1458, 1543, 1681, 2856,2922; ^1H NMR ($CDCl_3$, 400 MHz, TMS), δ (ppm): 2.07 (s, 3H, $-CH_3$), 2.46 (s, 3H, $-CH_3$), 7.21–7.31 (m, 2H, phenyl-H) 7.42–7.45 (m, 2H, phenyl-H), 7.81 (s, 1H, thienyl-H), 9.88 (s, 1H, -CHO); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): 13.36, 22.02, 29.56, 32.91, 111.23, 119.80, 123.80, 125.28, 136.27, 141.85, 154.25, 155.94, 158.43, 182.04; Anal. Calcd. for $C_{20}H_{12}F_6O_2S$: Calcd C, 55.82; H, 2.81. Found C, 56.02; H, 2.82.

3.1.2. 1-[2-Methyl-3-benzofuranyl]-2-[2-methyl-5-(rhodamine B hydrazine-schiff base-yl)-3-thienyl]perfluorocyclopentene (*1O*)

To a solution containing compound **2O** (0.40 g, 0.93 mmol) and compound **5** (0.46 g, 1.07 mmol) in ethanol (50 mL) was added acetic acid (0.02 equiv). The mixture was stirred at 351 K and the reaction was detected by TLC plate. After stirring 48 h at 351 K, it was cooled to room temperature and washed with dilute $NaHCO_3$ solution. After being extracted with chloroform (3 × 30 mL), dried using anhydrous magnesium sulfate, filtered, and evaporated, the crude product was purified by column chromatography on silica gel using petroleum/ethyl acetate (4:1) as the eluent to give diarylethene **1O** (0.34 g, 47% yield) as a black solid. M.p. 125.2–126.1 °C; IR (KBr, ν, cm^{-1}): 752, 786, 956, 1008, 1074, 1120, 1191, 1220, 1267, 1305, 1516, 1548, 1616, 1691, 2929, 2968; ^1H NMR ($CDCl_3$, 400 MHz, TMS), δ (ppm): 1.15 (t, 12H, $-CH_3$), 1.99 (s, 3H, $-CH_3$), 2.05 (s, 3H, $-CH_3$), 3.34 (t, 8H, $-CH_2$) 6.24–6.27 (m, 2H, phenyl-H), 6.44–6.50 (m, 4H, phenyl-H), 7.06(s, 1H, thienyl-H), 7.13–7.18 (m, 2H, phenyl-H) 7.38–7.44 (m, 2H, phenyl-H), 7.46–7.52 (m, 2H, phenyl-H), 7.92 (s, 2H, phenyl-H), 8.87 (s, 1H, -CH=N); ^{13}C NMR ($CDCl_3$, 400 MHz, TMS), δ (ppm): 10.67, 14.04, 14.73, 44.45, 68.17, 98.59, 105.21, 111.24, 119.94, 123.38, 123.61, 123.84, 124.02, 126.36, 128.05, 128.47, 128.85, 130.90, 133.35, 139.78, 150.95, 153.48, 154.15, 155.98, 164.29; Anal. Calcd. for $C_{48}H_{42}F_6N_4O_3S$: Calcd C, 66.35; H, 4.87; N, 6.45. Found C, 66.71; H, 4.82; N, 6.33.

3.2. Photochromic behaviors

Fig. 3 shows the changes in the absorption spectra and color of diarylethenes **1** and **2** in methanol (2.0×10^{-5} mol L^{-1}) induced by alternating irradiation with UV and visible light. The absorption maximum of **1O** is observed at 321 nm (ε, 3.60×10^4 L mol^{-1} cm^{-1}) in methanol. Upon irradiation with 297 nm light, a new visible absorption band centered at 555 nm (ε, 8.47×10^3 L mol^{-1} cm^{-1}) appeared while the original peak at 321 nm decreased due to the formation of the closed-ring isomer **1C**; this change in absorption was manifested in the colorless solution becoming violet. The violet colored solution returned colorless by irradiation with visible light ($\lambda > 500$ nm) because the closed-ring isomer of **1O** returned to the initial state **1O**. The coloration–decoloration cycles could be repeated more than 30 times and a clear isosbestic point was observed at 350 nm. The thermal stability of open- and closed-ring isomers of diarylethene **1** was examined in methanol both at room temperature and at 337 K. Upon storing a solution of diarylethene **1** in the dark and then exposing it to air for more than 90 days at room temperature, no changes in the UV/vis spectra of diarylethene **1** were observed. At 337 K, diarylethene **1** also showed good thermal stability for more than 8 h. In order to validate the difference before and after the introduction of the rhodamine dye moiety into the diarylethene, the photochromic behavior of the parent diarylethene **2O** was studied under the same measurement conditions (Fig. 3B). The absorption maximum of the open-ring isomer **2O** was observed at 252 nm (ε, 5.50×10^4 L mol^{-1} cm^{-1}) and that of the closed-ring isomer **2C** induced by the irradiation of UV light was observed at 544 nm (ε, 1.69×10^4 L mol^{-1} cm^{-1}) in methanol. Accordingly, the color of this solution changes from colorless to purple (Fig. 3C). When arrived at the photostationary state, the isosbestic point of diarylethene **2** was observed at 307 nm. Therefore, apparent differences exist between the photochromic properties of diarylethene **1** and the unsubstituted parent

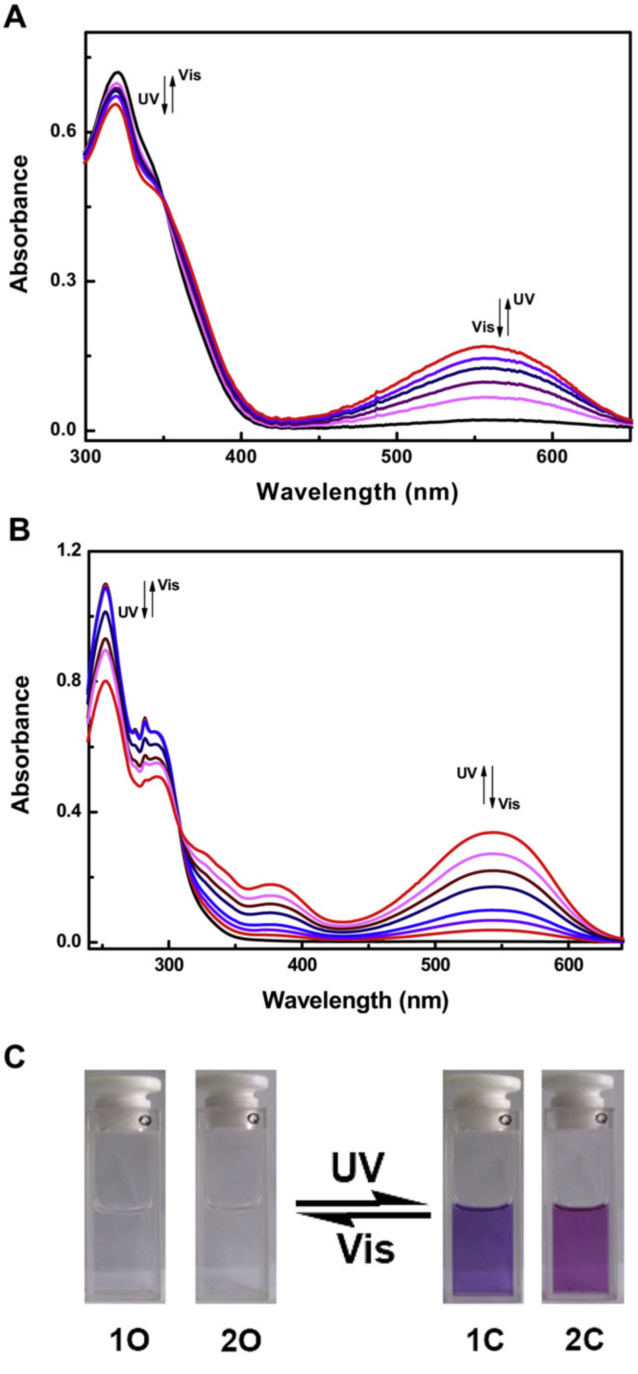

Fig. 3. Absorption spectra and color changes of diarylethenes **1** and **2** by alternating irradiation with UV and visible light in methanol (2.0×10^{-5} mol L^{-1}) at room temperature: (A) spectral changes for **1**; (B) spectral changes for **2**; (C) color changes for **1** and **2**.

2. The result indicates that diarylethene **1** exhibits a smaller molar absorption coefficient in either the open- or closed-ring isomers than those of **2**, while displays a longer absorption maxima in both open- and closed-ring isomers than those of **2**. The strong bathochromic shift may be attributed to the substituent effect induced by the rhodamine unit, and the analogous observations have been extensively reported [40–44]. The result was completely contrary to that of the analog diarylethene bearing two thiophene rings whose molar absorption coefficient in either the open-ring isomer or closed-ring isomer was much larger than that of its unsubstituted parent diarylethene [33].

3.3. *Optical spectral changes of diarylethene **1O** with response to Cr(III)*

The structure of diarylethene **1O** was composed of a photochromic unit and a rhodamine dye. Actually, rhodamine derivatives can change the colorless spirolactam form to the red amide form stimulated by protons or metal ions, and the two isomers show completely different optical properties. Therefore, the spectral changes of **1O** stimulated by metal ions can be expected. In this section, the UV/vis absorption and fluorescence changes of diarylethene **1O** with respond to Cr(III) were investigated by spectral analysis. The absorption spectra of **1O** in methanol (2.0×10^{-5} mol L^{-1}) were recorded at room temperature and $Cr(NO)_39H_2O$ was used as the Cr(III) source. The absorbance change of **1O** after addition of 0–240 μM Cr(III) is shown in Fig. 4. In methanol, the absorption maximum of **1O** is observed at 320 nm. When titrating trace amount of Cr(III) into the solution containing diarylethene **1O**, a new visible absorption band peaked at 556 nm appeared due to the formation of the open-ring amide form of Rhodamine B Schiff base [34,45]; this change in absorption was manifested in the colorless solution becoming pink within 1 s (inset graph in Fig. 4). The absorbance at the maximum wavelength (556 nm) was dramatically increased with the increase of titration amounts of Cr(III). When the amount of Cr(III) was larger than 240 μM, the absorbance achieved the maximum and remained unchanged. That is to say, diarylethene **1O** can exhibit a notable change in its absorption spectrum and color when the amount of Cr(III) is in the range of 0–240 μM, suggesting that it has high sensitivity towards Cr(III) [21,24]. Therefore, the notable and fast color changes in **1O** in methanol solution upon addition of Cr(III) indicated that it could be potentially becoming a sensitive visual indicator for Cr(III) [22].

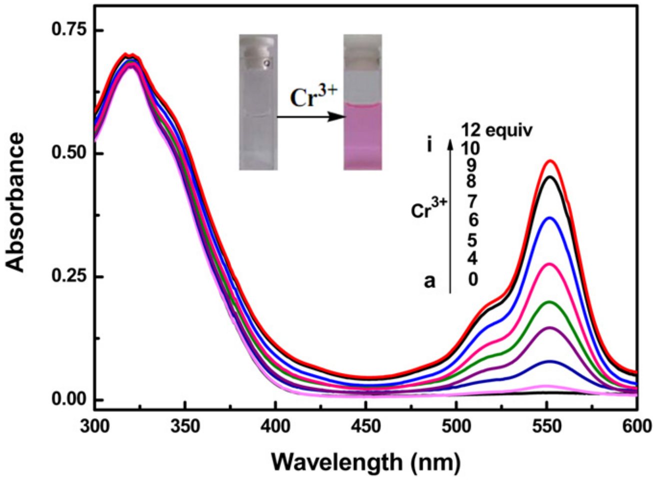

Fig. 4. Absorption spectra changes of diarylethene **1O** by stimulation of Cr(III) in methanol (*a*→*i*): 0, 80, 100, 120, 140, 160, 180, 200, 240 μM. Inset: color of **1O** before and after addition of 12 equiv Cr(III).

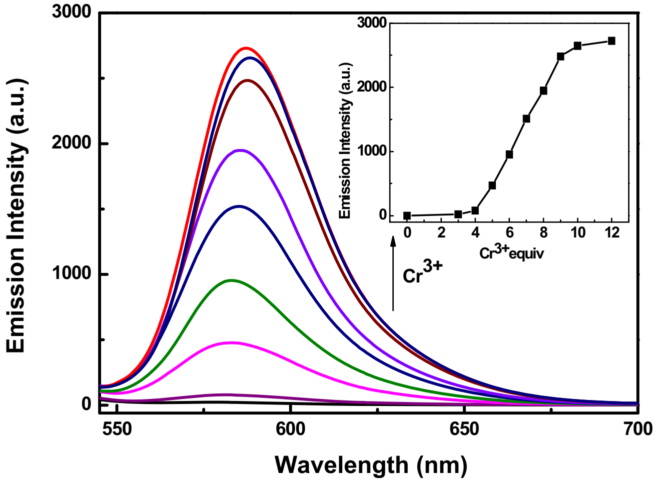

Fig. 5. Emission intensity changes of **1O** in methanol (2.0×10^{-5} mol L^{-1}) solution by stimulation Cr(III) when excited at 520 nm. Inset: curve of emission intensity at 585 nm of **1O** upon addition of different equiv Cr(III).

The enhancement effect of various amounts of Cr(III) on the fluorescence of diarylethene **1O** was examined at the excitation wavelength of 520 nm and at room temperature. Fig. 5 shows the emission intensity changes with addition of Cr(III). When titrating Cr(III) into the methanol solution containing diarylethene **1O** ($C = 2 \times 10^{-5}$ mol L^{-1}), a remarkable fluorescence enhancement (FE) was observed with the increase of the amounts of Cr(III). The emission intensity at 585 nm increased by approximately 300-fold when Cr(III) concentration increased from 0 to 12 equivalents, and remained unchanged with further titration. The fluorescence quantum yield in solution was 0.29 when Rhodamine B ($\Phi = 0.50$) in methanol [46] was used as a reference, suggesting that the diarylethene **1O** was an excellent "turn-on" probe for Cr(III). The inset of Fig. 5 depicts the effect of Cr(III) concentration on the fluorescent emission intensity of **1O** at 585 nm, which significantly increased as the amount of Cr(III) concentration rose from 0 to 240 μM. The result indicated that the fluorescent emission intensity of **1O** as a function of the concentration of Cr(III) showed a good linearity when the amount of Cr(III) was in the range of 60–180 μM. This phenomenon could be potentially used as a colorimetric fluorescent probe for Cr(III) [17].

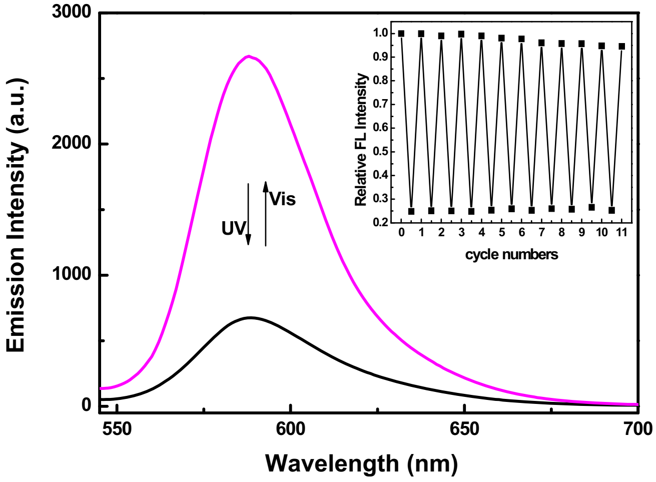

Fig. 6. Emission intensity changes of diarylethene **1** in methanol (2.0×10^{-5} mol L^{-1}) in the presence of 12 equiv Cr(III) upon irradiation with UV and visible light at room temperature when excited at 520 m. Inset: fluorescent switch cycles of **1** in the presence of 12 equiv Cr(III) upon alternating irradiation with UV and visible light.

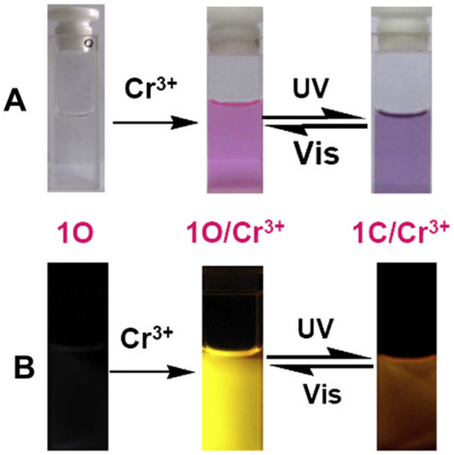

Fig. 7. Changes in color (A) and fluorescence (B) of diarylethene **1** by stimulation of Cr(III) and light in methanol.

3.4. *Photoinduced fluorescent switch of diarylethene* ***1O*** *with response to Cr(III)*

Generally, diarylethene derivatives undergo a reversible transformation from the open-ring isomer to the closed-ring isomer upon irradiation with UV light and are accompanied by a decrease of fluorescent emission intensity; the inverse process from the closed-ring isomer to the open-ring isomer can be accomplished by the irradiation of visible light with appropriate wavelength and the fluorescent intensity recovers to the initial state. This characteristic is usually used to design the fluorescent controllable switch by assembling photochromic diarylethene with fluorophore dye [29]. Fig. 6 shows the fluorescent emission intensity changes of diarylethene **1** in the presence of 12 equiv Cr(III) upon alternating irradiation with UV and visible light in methanol at room temperature. The result shows that the fluorescent emission diarylethene **1** in the presence of 12 equiv Cr(III) can be modulated reversibly upon alternating irradiation with UV and visible light. Under in the presence of 240 μM Cr(III), diarylethene **1O** exhibits a strong fluorescent emission at 585 nm in methanol, which is ascribed to the formation of the open-ring rhodamine amide. The emission intensity is heavily dependent on the status of the diarylethene, whether in open-ring form or closed-ring form. Upon irradiation with UV light, the photocyclization reaction is performed on the diarylethene unit and the emission intensity at 585 nm significantly quenched along with the increasing UV irradiation time due to the formation of the non-fluorescent closed-ring isomer **1C**. When arrived at the photostationary state, the emission intensity of **1C** was quenched to only 25% of its original intensity. The residual fluorescence in the photostationary state may be attributed to the incomplete cyclization reaction and the existence of parallel conformations [47]. The inset of Fig. 6 depicts the "off" and "on" states of the regulable fluorescent switch cycles of **1** in the presence of 12 equiv Cr(III) upon altering irradiation with UV and visible light at room temperature. The result indicated that the fluorescent switch cycles could be repeated more than 11 times with less than 5% degradation of the emission intensity, suggesting that the fluorescent switch had potentially good stability and fatigue-resistance.

Fig. 7 shows the colorimetric and fluorescence changes of diarylethene **1** by stimulation of Cr(III) and light in methanol. After addition of 12 equiv Cr(III) into the methanol solution containing diarylethene **1O**, it induced a visible color change from colorless to pink, as well as an effective fluorescence change from colorless to bright yellow. Upon irradiation with UV light, the color of this solution turned from pink to violet, and the fluorescence changed from bright yellow to dark yellow. Certainly, the color and the fluorescence diarylethene **1** could return its original state upon irradiation with visible light. Such fluorescence quenching may be attributed to the efficient intermolecular fluorescence resonance energy transfer (FRET) from the open-ring rhodamine amide (energy donor) to the closed-ring diarylethene (energy receptor). The FRET process requires that the characteristic absorption band of the acceptor overlaps the emission of the donor and a link distance between the acceptor fluorophore and the donor fluorophore is in the range of 1–10 nm [48,49]. Because the emission band of the open-ring rhodamine unit (550–650 nm) overlaps entirely with the absorption band of the closed-ring isomer **1C** (450–650 nm), the FRET process occurs easily between the diarylethene moiety and the rhodamine unit stimulated by UV light (Fig. 8). Compared with the reported analogs [33,34,36], diarylethene **1** has the most well-matched condition to produce an efficient FRET process. Therefore, diarylethene **1** may emerge as the most promising candidate for constructing the reversible and photo-controllable fluorescent switch in biological technology [50–52].

In order to discuss the selectivity of diarylethene **1O** with response to Cr(III), other metal ions including alkali, alkaline earth, and transition-metal ions were separately added into the methanol solution containing diarylethene **1O** under the same experimental condition. Fig. 9 shows the emission intensity of **1O** at 585 nm in methanol in the presence of respective metal cations at room temperature when excited at 520 nm. The results revealed that **1O** responded to various metal ions with different selectivity and possessed an excellent selectivity for Cr(III), Al(III), and Fe(III). As depicted in Fig. 9, it could be easily seen that its emission intensity was essentially not influenced by addition of 12 equiv of Na(I), K(I), Mg(II), Mn(II), Sr(II), Ba(II), Zn(II), Ni(II), Cd(II), Ca(II) and Co(II), and very weakly influenced by Hg(II), Pb(II) and Cu(II). However, the

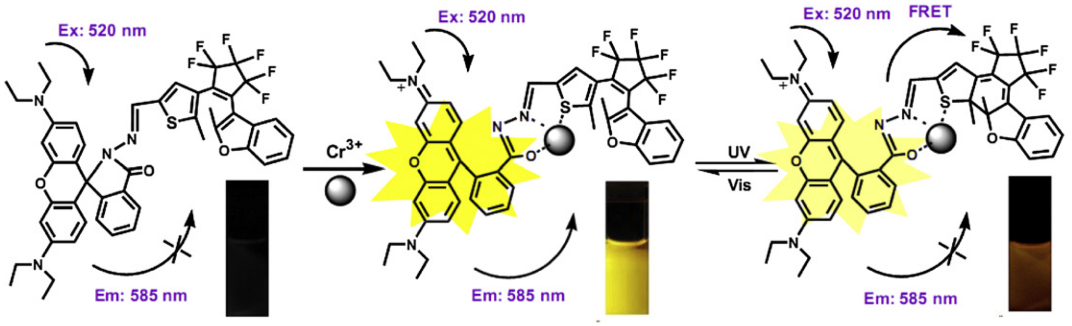

Fig. 8. Proposed mechanism of the emission intensity changes for **1O** in the presence of Cr(III) by photo-irradiation.

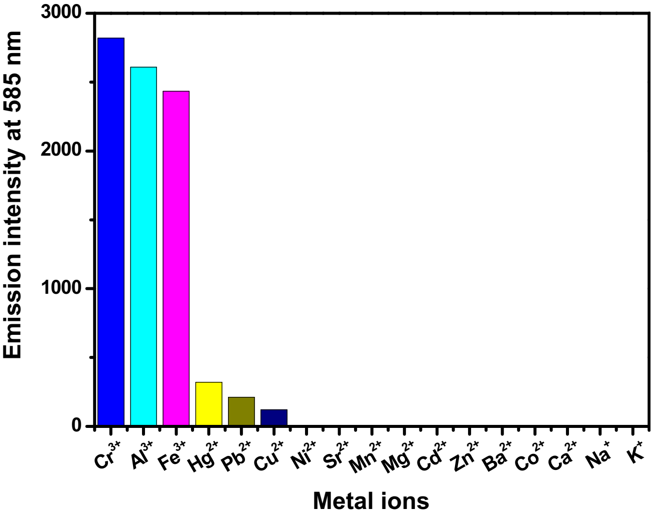

Fig. 9. Emission intensity of **1O** at 585 nm in methanol (2.0×10^{-5} mol L^{-1}) in the presence of respective metal cations (12 equiv) at room temperature, excited at 520 nm.

emission intensity increased significantly after the addition of Cr(III), Al(III), or Fe(III). The results indicated that diarylethene **1** was only selective toward Cr(III) cations with the exception of Al(III) and Fe(III). As has been observed for most of the reported chemosensors based on the rhodamine spirolactam skeleton [53–55], the fluorescence enhancement of **1O** may be induced by the ring-opening mechanism of the rhodamine spirolactam moiety, which is resulted from the chelation of the rhodamine moiety of **1O** binding with Cr(III), Al(III), or Fe(III).

4. Conclusion

In conclusion, the photophysical ability of a Rhodamine B hydrazine-Schiff base terminated photochromic diarylethene to determinate cations in methanol was investigated. The results revealed that only Cr(III), Al(III) and Fe(III) could be efficiently detected. In the presence of Cr(III), the color and fluorescence of the target compound could be effectively modulated upon alternating irradiation with UV and visible light. Therefore, it could be able to act as a multi-addressable fluorescent switch and be potentially employed as a fundamental element of an optical device stimulated by cations and light. The concept presented here may be helpful for the construction of more miniaturized molecular level devices with multiple functions.

Acknowledgements

This work was supported by Program for the NSFC of China (20962008, 21162011), the Project of Jiangxi Academic and Technological leader (2009DD00100), the project of Jiangxi Excellent Science and Technology Innovation Team (20113BCB24023), and the Project of the Science Funds of Jiangxi Education Office (GJJ09646, GJJ11026).

References

[1] Desvergne JP, Czarnik AW. Chemosensors of ion and molecule recognition. Anal Chem 1997;496:245–76.

[2] Leigh DA, Morales MAF, Perez EM, Wong JKY, Saiz CG, Slawin AMZ, et al. Patterning through controlled submolecular motion: rotaxane-based switches and logic gates that function in solution and polymer films. Angew Chem Int Ed 2005;44:3062–7.

[3] Valeur B, Leray I. Design principles of fluorescent molecular sensors for cation recognition. Coord Chem Rev 2000;205:3–40.

[4] Rurack K. Flipping the light switch "on" – the design of sensor molecules that show cation-induced fluorescence enhancement with heavy and transition metal ions. Spectrochim Acta A 2001;57:2161–95.

[5] Amendola V, Fabbrizzi L, Forti F, Licchelli M, Mangano C, Pallavicini P, et al. Light emitting molecular devices based on transition metals. Coord Chem Rev 2006;250:273–99.

[6] Mertz W, Schwarz K. Impaired intravenous glucose tolerance as an early sign of dietary necrotic liver degeneration. Arch Biochem Biophys 1955;58:504–6.

[7] Arakawa H, Ahmad R, Naoui M, Tajmir-Riahi HA. A comparative study of calf thymus DNA binding to Cr(III) and Cr(VI) ions. Evidence for the guanine N-7-chromium-phosphate chelate formation. J Biol Chem 2000;275: 10,150–10,153.

[8] Anderson RA. Chromium, trace elements in human and animal nutrition. New York: Academic Press; 1987.

[9] Adel MZ, Norman T. Chromium in the environment: factors affecting biological remediation. Plant Soil 2003;249:139–56.

[10] Singh AK, Singh R, Saxena P. Tetraazacyclohexadeca macrocyclic ligand as a neutral carrier in a Cr ion-selective electrode. Sensors 2004;4:187–95.

[11] Hassan SSM, EL-Shahawi MS, Othman AM, Mosaad MAA. Potentiometric rhodamine-B based membrane sensor for the selective determination of chromium ions in waste water. Anal Sci 2005;21:673–8.

[12] Rurack K, Kollmannsberger M, Resch-Genger U, Daub JA. Selective and sensitive fluoroionophore for Hg(II), Ag(I), and Cu(II) with virtually decoupled fluorophore and receptor units. J Am Chem Soc 2000;122:968–9.

[13] Royzen M, Dai Z, Canary WJ. Ratiometric displacement approach to Cu(II) sensing by fluorescence. J Am Chem Soc 2005;127:1612–3.

[14] Banthia S, Samanta A. A new strategy for ratiometric fluorescence detection of transition metal ions. J Phys Chem B 2006;110:6437–40.

[15] Sankaran NB, Banthia S, Das A, Samanta A. Fluorescence signaling of transition metal ions: a new approach. New J Chem 2002;26:1529–31.

[16] Zhao Y, Sun Y, Lv X, Liu YL, Chen ML, Guo W. Rhodamine-based chemosensor for Hg^{2+} in aqueous solution with a broad pH range and its application in live cell imaging. Org Biomol Chem 2010;8:4143–7.

[17] Yang YK, Yook KJ, Tae J. A rhodamine-based fluorescent and colorimetric chemodosimeter for the rapid detection of Hg^{2+} ions in aqueous media. J Am Chem Soc 2005;127:16760–1.

[18] Xiang Y, Tong A, Jin P, Ju Y. New fluorescent rhodamine hydrazone chemosensor for Cu(II) with high selectivity and sensitivity. Org Lett 2006;8: 2863–6.

[19] Kwon JY, Jang YJ, Lee YJ, Kim KM, Seo MS, Nam W, et al. A highly selective fluorescent chemosensor for Pb^{2+}. J Am Chem Soc 2005;127:10107–11.

[20] Hiromi S, Kenjiro H, Yasuteru U, Takuya T, Tetsuo N. Design and synthesis of a novel fluorescence probe for Zn^{2+} based on the spirolactam ring-opening process of rhodamine derivatives. Bioorg Med Chem 2011;19:1072–8.

[21] Huang KW, Hong Y, Zhou ZG, Yu MX, Li FY, Gao X, et al. Multi-signal chemosensor for Cr^{3+} and its application in bioimaging. Org Lett 2008;10: 2557–60.

[22] Zhou ZG, Yu MX, Yang H, Huang KW, Li FU, Yi T, et al. FRET-based sensor for imaging Chromium(III) in living cells. Chem Commun 2008;7:3387–9.

[23] Mao J, Wang L, Dou W, Tang X, Yan Y, Liu W. Tuning the selectivity of two chemosensors to Fe(III) and Cr(III). Org Lett 2007;9:4567–70.

[24] Mao J, He Q, Liu W. An "off–on" fluorescence probe for chromium(III) ion determination in aqueous solution. Anal Bioanal Chem 2010;396: 1197–203.

[25] Hu XY, Zhang XL, He GJ, He C, Duan CY. A FRET approach for luminescence sensing Cr^{3+} in aqueous solution and living cells through functionalizing glutathione and glucose moieties. Tetrahedron 2011;67:1091–5.

[26] Weerasinghe AJ, Schmiesing C, Sinn E. Highly sensitive and selective reversible sensor for the detection of highly sensitive and selective reversible sensor for the detection of Cr^{3+}. Tetrahedron Lett 2009;50:6407–10.

[27] Liu HH, Chen Y. Construction of multi-level fluorescent switch using photochromic diarylethene and fluorescent dye. Dyes Pigm 2011;89:212–6.

[28] Murse S, Teramoto M, Furukawa H. Photochemically induced fluorescence control with intermolecular energy transfer from a fluorescent dye to a photochromic diarylethene in a polymer film. Macromolecules 2003;36: 964–6.

[29] Pu SZ, Jiang DH, Liu WJ, Liu G, Cui SQ. Multi-addressable molecular switches based on photochromic diarylethenes bearing a rhodamine unit. J Mater Chem 2012;22:3517–26.

[30] Norsten TB, Branda NR. Photoregulation of fluorescence in a porphyrinic dithienylethene photochrome. J Am Chem Soc 2001;123:1784–5.

[31] Cusido J, Deniz E, Raymo FM. Fluorescent switches based on photochromic compounds. Eur J Org Chem 2009;2009:2031–45.

[32] 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.

[33] Liu WJ, Pu SZ, Cui SQ, Liu G, Fan CB. A proton and optic dual-control molecular switch based on diarylethene bearing a rhodamine unit. Tetrahedron 2011; 67:4236–42.

[34] Liu WJ, Pu SZ, Jiang DH, Cui SQ, Liu G, Fan CB. Fluorescent probes for Al(III) and Cr(III) based on a combination of a photochromic diarylethene and a fluorescent rhodamine moiety. Microchimica Acta 2011;174:329–36.

[35] Zou Q, Jin JY, Xu B, Ding L, Tian H. New photochromic chemosensors for Hg^{2+} and F^-. Tetrahedron 2011;67:915–21.
[36] Zhang JJ, Tan WJ, Meng XL, Tian H. Softmimic gear-shift with a multi-stimulus modified diarylethene. J Mater Chem 2009;19:5726–9.
[37] Ren JQ, Tian H. Thermally stable merocyanine form of photochromic spiropyran with aluminum ion as a reversible photo-driven sensor in aqueous solution. Sensors 2007;7:3166–78.
[38] Yamaguchi T, Irie M. Photochromism of bis(2-alkyl-1-benzofuran-3-yl) perfluorocyclopentene derivatives. J Org Chem 2005;70:10,323–10,328.
[39] Zheng CH, Pu SZ, Xu JK, Luo MB, Huang DC, Shen L. Synthesis and the effect of alkyl chain length on optoelectronic properties of diarylethene derivatives. Tetrahedron 2007;63:5437–49.
[40] Pu SZ, Li M, Liu G, Le ZG. Syntheses and substituent effects on the properties of unsymmetrical photochromic diarylethenes bearing a benzothiophene unit. Aust J Chem 2009;62:464–74.
[41] 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.
[42] Pu SZ, Yan PJ, Liu G, Miao WJ, Liu WJ. New photochromic diarylethenes bearing a pyridine moiety. Tetrahedron Lett 2011;52:143–7.
[43] Pu SZ, Li H, Liu G, Liu WJ. Photochromism of new diarylethenes bearing both thiazole and benzene moieties. Tetrahedron Lett 2010;51:3575–9.
[44] Pu SZ, Zheng CH, Le ZG, Liu G, Fan CB. Substituent effects on the properties of photochromic diarylethenes. Tetrahedron 2008;64:2576–85.
[45] Quang DT, Wu JS, Luyen ND, Duong TN, Dan D, Bao NC, et al. Rhodamine-derived Schiff base for the selective determination of mercuric ions in water media. Spectrochim Acta A 2011;78:753–6.
[46] Bindhu CV, Harilal SS. Effect of the excitation source on the quantum-yield measurements of rhodamine B laser dye studied using thermal-lens technique. Anal Sci 2001;17:141–4.
[47] Fan CB, Pu SZ, Liu G, Yang TS. Substituent position effect on the properties of new unsymmetrical isomeric diarylethenes having a chlorine atom. J Photochem Photobiol A 2008;197:415–25.
[48] Giordano L, Jovin TM, Irie M, Jares-Erijman EA. Diheteroarylethenes as thermally stable photo-switchable acceptors in photochromic fluorescence resonance energy transfer (pcFRET). J Am Chem Soc 2002;124:7481–9.
[49] Lu HC, Schöps O, Woggon U, Niemeyer CM. Self-assembled donor comprising quantum dots and fluorescent proteins for long-range fluorescence resonance energy transfer. J Am Chem Soc 2008;130:4815–27.
[50] Zhu MQ, Zhang GF, Chong L, Aldred MP, Chang E, Drezek RA, et al. Reversible two-photon photo switching and two-photon imaging of immunofunctionalized nanparticles targeted to cancer cells. J Am Chem Soc 2010;133:365–72.
[51] Zou Y, Yi T, Xiao SZ, Li FY, Li CY, Gao X, et al. Amphiphilic diarylethene as a photoswitchable probe for imaging living cells. J Am Chem Soc 2008;130:15750–1.
[52] Piao XJ, Zou Y, Wu JC, Li CY, Yi T. Multiresponsive switchable diarylethene and its application in bioimaging. Org Lett 2009;11:3818–21.
[53] Yang H, Zhou ZG, Huang KW, Yu MX, Li FY, Yi T, et al. Multisignaling optical-electrochemical sensor for Hg^{2+} based on rhodamine derivative with ferrocene units. Org Lett 2007;9:4729–32.
[54] Ko SK, Yang YK, Tae J, Shin I. In vivo monitoring of mercury ions using a rhodamine-based molecular probe. J Am Chem Soc 2006;128:14150–5.
[55] Xiang Y, Tong A. A new rhodamine-based chemosensor exhibiting selective Fe(III)-amplified fluorescence. Org Lett 2006;8:1549–52.