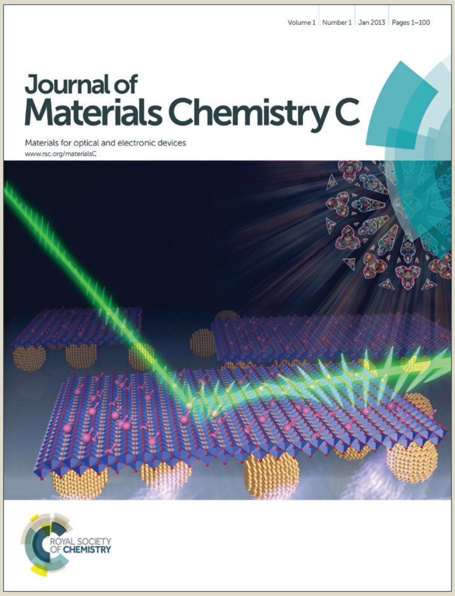
Journal of Materials Chemistry C

Accepted Manuscript



Journal of Materials Chemistry C

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Ion induced cycle opening of a diarylethene and its application on visual detection of Cu^{2+} and $Hg^{2+}$and keypad lock

Junjie He,[a] Jingxian He,[b] Tingting Wang[a] and Heping Zeng[a]*

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

A phenanthrene bridged photochromic diarylethene with two crown ethers as ion recognizing groups has been synthesized and characterized by single crystal X-ray diffraction. This material shows good photochromism and fatigue resistance. Only the closed form of this diarylethene derivative can form coordination complexes with Cu^{2+} and Hg^{2+} and at the same time, the combination of the photochromic material and metal ions would lead to the cycle opening of closed photochromic unit and color bleaching processes. This special property can be applied in visual detection of these two heavy metal ions not only in solution but also in solid state. The fluorescence of the diarylethene is sensitive to light, copper and mercury ions. As a result, a single molecular logic circuit was constructed by using the absorbance and fluorescence intensity at specific wavelength as outputs and appropriate combinational stimuli of UV/Vis light, Cu^{2+} and Hg^{2+} ions as inputs. Moreover, the fluorescence of it is sensitive to historical input signals. Based on this a key pad lock using three codes to open was fabricated.

Introduction

Photochromic materials(PMs) have attracted much attention in these years as their potential application in optical information storage media, biological probe, live cell imaging and Intelligent Stimuli-Responsive Materials[1-5]. Their color can be switched by alternative irradiation under UV or visible light[6-9]. The color changes of these materials are ascribed to the photo induced electronic structural changes of the molecules[10]. There are four main kinds of PMs including azobenzene, spiropyran, furylfulgide and diarylethene. Especially the diarylethene derivertives (DAEs) have become the "star molecules" due to their excellent thermal stability and fatigue resistance[11-15]. As a result of that, many photo-controllable ion or anion receptors based on DAEs were designed and synthesized. These materials mostly incorporated DAEs with various ion recognizing groups[16-19]. The ion/anion uptake and release can be controlled by irradiation with light at different wavelengths. These materials overcome some drawbacks of one-time use sensors, such as excluding the possibility of tailoring highly selective ligands that operate in competitive media[20].

To date, although numerous methods have been developed for the detection of toxic heavy metal ions, there are some limitations, such as tedious sample pretreatment, and requiring expensive equipment, etc[21]. In order to meet the needs of rapid and real-time detection of heavy metal ions with simple instruments, visual detection of heavy metal ions has attracted more and more attentions during the latest years since they can be perceived by naked eyes rather than expensive equipment[22-27]. Indubitably, distinct color of sensors before and after combination with metal ions is necessary for visual detection. Detection of Cu^{2+} and Hg^{2+} ions is of great importance as high levels of both ions in the environment have begun to negatively affect human health and agriculture[28-32]. In this work we designed and synthesized a DAE, which is incorporated crown ether as the ionic signal responsive group, **PBC** shown in Scheme 1. The phenanthrene bridge is the fluorophore of which the fluorescence is photocontrolable by alternating UV/Vis light irradiation. The fluorescence of this material can be affected by Cu^{2+} or Hg^{2+} ions. Surprisingly, the ions not only selectively combined with the closed- isomer, but also induced cycle opening and color bleaching of closed form of **PBC**. This special property facilitates us to fabricate a testing paper for visual detection of Cu^{2+} and Hg^{2+} ions.

DAEs also have many advantages for practical logic gates, which can function as binary switches and much more complex Boolean logic gates. These small molecules have captured worldwide interest since the original conception by de Silva[33]. Various interesting molecules with different function mimicking traditional logic gates have been designed, such as half-adder, half-subtractors, encoders, decoders, keypad locks, etc[34-39]. Till to date, even independent molecular logic gates have been cascaded by Akkaya, etal[40] to fabricate logic circuit with more complicated function. Molecular scale keypad lock (one kind of logic gates) is able to perform the function of circuits where the states of the output are not only sensitive to the present input combination, but also to the input history. In order to build molecular keypad locks, three or more input signals are required[41-43]. We constructed a molecular logic gate with Cu^{2+}, Hg^{2+} and UV light as three input signals, while the fluorescence and absorbance were two output signals. A key pad lock was fabricated based on the different outputs from various input orders.

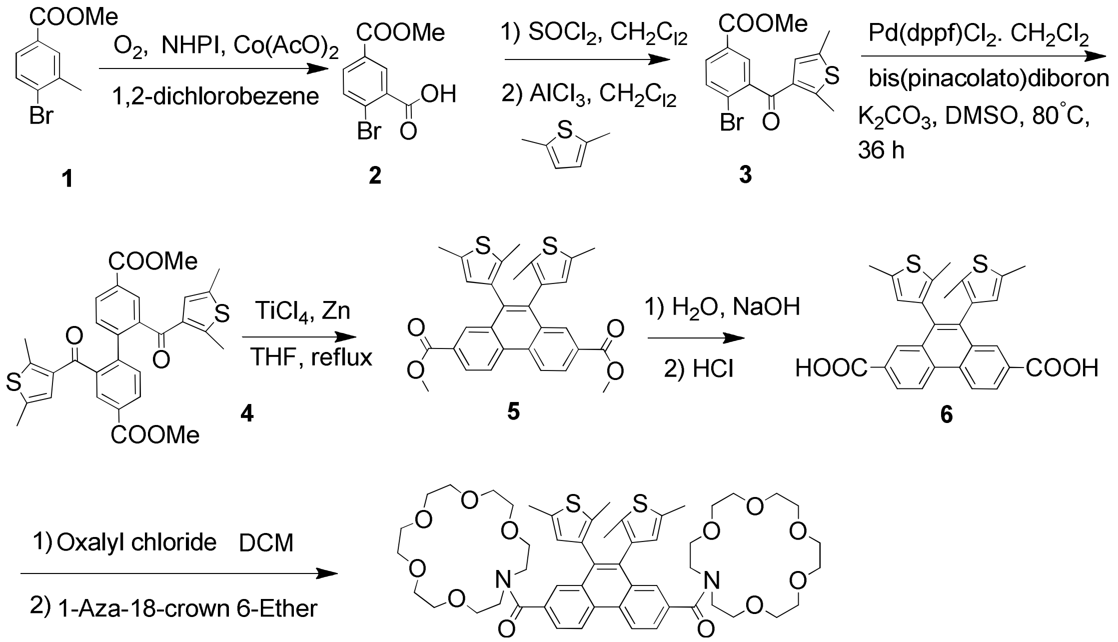
Experiments

General methods

Solvents used in photochemical measurements were spectroscopic grade and purified by distillation before use. 1-Aza-18-crown 6-Ether was purchased from Tokyo Chemical Industry Co. (TCI Shanghai). ^1H NMR and ^{13}C NMR spectra were recorded on a NMR spectrometer (Bruker-AVANCE-400, 400 MHz). Samples were dissolved in $CDCl_3$ or d^6-DMSO with tetramethylsilane as an internal standard. Mass spectra were measured with a mass spectrometer (Esquire HCT PLUS). Absorption and fluorescence spectra were measured with a Hitachi U-3010 absorption spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer, respectively. Photo irradiation was carried out using an USHIO 1 kW high-pressure mercury lamp as the light source. Monochromic light was obtained by passing the light through a band-pass filter ($\Delta\lambda 1/2$ = 15 nm).

Synthesis

The synthetic route for diarylethenes is shown in Scheme1. In order to obtain higher yield of product, we modified the synthesis method of phenanthrene-bridged diarylethenes in our previous research[44]. In order to introduce the crown ethers at the specific positions of phenanthrene, compound **1** was chosen as the key starting material. Friedel-craft reaction was applied to prepare ketone **3**. The acyl chloride and 2, 5- dimethylthiophene were stirred in dichloromethane under catalyzation of excess $AlCl_3$ to give **4** in yield of 51 %. McMurry coupling reaction had also been applied to prepare phenanthrene-bridged diarylethenes[45-48] however the yield of this step is relatively low. The structures of all compounds were confirmed by elemental analysis, MS, NMR, and IR spectroscopy.



Scheme 1

Synthesis of 2-bromo-5-(methoxycarbonyl)benzoic acid (2)

Oxidation of methyl 4-bromo-3-methylbenzoate was carried out according to reference[49]. Methyl 4-bromo-3-methylbenzoate (2.29 g, 10 mmol), N-hydroxy phthalimide (NHPI, 32.6 mg, 0.2 mmol), $Co(AcO)_2$ (124.5 mg, 0.7 mmol) and KBr (35.7 mg, 0.3 mmol) were dissolved in 6 ml 1, 2-dichlorobenzene in a three necked flask with a stirring bar. Then the mixture was stirred at 120 °C around 36 h, while oxygen was bubbled into the mixture. The color of the mixture would turn to dark green from pink. TLC was applied to monitor the reaction process. When the reaction completed, the mixture was cooled to room temperature. Then 50 ml $NaHCO_3$ aqueous solution (2 %) was added and stirred for a while. The mixture was extracted by ethyl acetate (3×50 ml) to exclude the 1, 2-dichlorobenzene. The aqueous layer was acidified by hydrochloric acid and extracted by ethyl acetate (3×50 ml). The organic extracts were combined, dried over Na_2SO_4 and concentrated by rotary evaporation and loaded onto a column of silica gel. The product was obtained by eluting cyclohexane, ethyl acetate, ethanol, acetic acid (60:20:20:0.05) and removal of the solvent. Yield 2.69 g (94 %). Mp 150-152 °C; ^1H NMR (400 MHz, DMSO) δ = 13.73 (s, 1H), 8.26 (s, 1H), 7.95 (d, J = 8.3 Hz, 1H), 7.90 (d, J = 8.3 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ = 166.37, 164.94, 134.73, 133.84, 132.52, 131.02, 129.01, 125.68, 52.53; ESI-MS: $[M+1]^+$ = 258.9; HR-MS: calcd for $C_9H_8BrO_4$, 258.9606; found, 258.9592.

Synthesis of methyl 4-bromo-3-(2,5-dimethylthiophene-3-carbonyl)benzoate(3)

2-bromo-5-(methoxycarbonyl)benzoic acid (9.93 g, 34 mmol) and 5 ml $SOCl_2$ were added in a flask containing 230 ml dichloride methane. The flask was equipped with a condenser and the mixture was refluxed for 4 h. The solvent and unreacted $SOCl_2$ were evaporated by rotary evaporator. The residual dark brown oil and 2, 5- dimethylthiophene (6.6 ml) were dissolved in 200 ml dichloride methane and the mixture was chilled in ice water. Then $AlCl_3$ (9.0 g, 68 mmol) was added in several portions with stirring. After that, the flask was sealed and the solution was stirred overnight. Ice water was slowly added into the flask to decompose the $AlCl_3$. The organic layer was collected and the aqueous phase was extracted with dichloride methane (3×100 ml). The organic extracts were combined, washed with dilute $NaHCO_3$ aqueous solution, dried over Na_2SO_4 and concentrated by rotary evaporation. The residual sticky liquid was dissolved in ethyl acetate. Colorless crystals were obtained by slowly evaporation of the solvent at room temperature. Yield 11.5 g (96 %). Mp 137-139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.98 (m, 2H), 7.73 (d, *J* = 8.2 Hz, 1H), 6.59 (s, 1H), 3.94 (s, 3H), 2.65 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 189.42, 165.78, 150.07, 142.91, 135.42, 134.77, 133.48, 131.47, 129.47, 129.23, 127.64, 124.41, 52.48, 15.87, 14.89; ESI-HRMS: calcd for $C_{15}H_{14}BrO_3S$, 352.9847; found, 352.9831.

Synthesis of dimethyl 2, 2'-bis(2,5-dimethylthiophene-3-carbonyl) biphenyl-4,4'-dicarboxylate(4)

This compound was synthesized with modified Brase's method[50]. 20 ml dry DMSO was added by a syringe into a three necked flask containing methyl 4-bromo-3-(2,5-dimethylthiophene-3-carbonyl)benzoate (3.28 g, 9.29 mmol), bis(pinacolato)diboron (1.18 g, 4.65 mmol), $PdCl_2$(dppf) (0.3 g, 4 mol %) and K_2CO_3 (3.85 g, 30 mmol) under an atmosphere of argon and the mixture was stirred and heated at 80 °C for 3 h. When the solution cooled to r.t., water was added and the mixture was extracted with ethyl acetate (3×150 ml). The organic extracts were combined, washed with water, dried over Na_2SO_4 and concentrated by rotary evaporation. Purification by chromatography (silica gel, Hexane:Ethylacetate / 24:1) yielded 2.3 g (92 %) of product **4** as a white powder. Mp 177-179 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.09 (d, J = 8.0 Hz, 2H), 8.09 (d, J = 8.0 Hz, 2H), 7.97 (s, 2H), 7.97 (s, 2H), 7.42 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 6.44 (s, 2H), 3.84 (s, 6H), 2.39 (s, 6H), 2.16 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 190.6, 166.2, 149.7, 144.2, 140.2, 135.2, 134.1, 131.4, 131.1, 129.6, 128.9, 128.4, 52.4, 15.7, 14.7; ESI-MS: $[M+Na]^+$=569.1; Anal. Calcd. for $C_{30}H_{26}O_6S_2$: C, 65.91; H, 4.79; Found: C, 65.78; H, 4.72.

Synthesis of dimethyl 9, 10-bis(2,5-dimethylthiophen-3-yl)phenanthrene-2,7-dicarboxylate(5)

The McMurry coupling was carried out to prepare **5**. Dry THF (30 mL) was placed in a dried 100 mL threenecked flask containing zinc dust (417.2 mg, 6.38 mmol). Under nitrogen protection and magnetic stirring 0.34 mL (3.07 mmol) of $TiC1_4$ was added with a syringe at 0 °C. The ice bath was removed, and 0.21 mL of pyridine was added, the solution turned completely black. A solution of 778 mg (1.42 mmol) of **4** in 30 mL of absolute THF was added within 20 min, and when the addition was complete the mixture was refluxed for 4 h. After cooling to room temperature, 60 mL of a dilute (10 %) aqueous K_2CO_3 solution was added and extracted with 100 mL of CH_2Cl_2. After two more extractions of the aqueous phase, the combined organic layers were dried with Na_2SO_4. Solvent removal provided a slightly yellow solid, which was purified by chromatography (silica gel, Hexane:Ethylacetate / 25:1) yielded 190 mg (0.37 mmol, 26 %) of product **5** as a white powder. Analytically pure sample of **5** were obtained by recrystallization from ethyl acetate. Mp 165-167 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.73 (d, J = 8.7 Hz, 2H), 8.32 (d, 2H), 8.18 (d, J = 8.7, 2H), 6.25 (d, 2H), 3.85 (d, 3H), 2.31 (d, 6H), 1.91 (d, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 167.1, 167.1, 135.4, 135.2, 134.8, 134.7, 134.3, 134.1, 133.6, 132.4, 132.4, 132.4, 132.2, 129.9, 129.7, 129.2, 129.1, 128.4, 127.2, 126.6, 123.5, 52.3, 15.2, 15.2, 14.1, 14.1; APCI-MS: $[M]^+$ =514.5; Anal. Calcd. for $C_{30}H_{26}O_4S_2$: C, C, 70.01; H, 5.09; Found: C, 69.86; H, 5.03.

Synthesis of 9, 10-bis(2,5-dimethylthiophen-3-yl)phenanthrene-2,7-dicarboxylic acid(6)

2 mL of NaOH aqueous solution(1 M) was added to a flask containing 10 mL THF solution of **5**(103.0 mg, 0.2 mmol). Then the mixture was stirred at 70 °C for 24 h. The solvent was removed in vacuo and the residue was dissolved in water (20 mL). The aqueous solution was refluxed for 1 h. The resulting solution was acidified with hydrochloric acid and extracted with ethyl acetate (3×20 mL). The combined organic extracts were then dried over Na_2SO_4 and the solvents evaporated to get product **6**(93 mg, 0.19 mmol, 96 %). Mp 282-284 °C; ^{1}H NMR (400 MHz, DMSO) δ = 9.11 (d, J = 8.8 Hz, 2H), 8.21 (m, J = 15.5 Hz, 4H), 6.51 (d, J = 5.4 Hz, 2H), 2.37 (s, 6H), 1.98 (s, 3H), 1.92 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ = 167.1, 134.8, 134.6, 134.6, 134.3, 134.1, 134.0, 133.2, 132.9, 131.9, 131.8, 131.5, 131.4, 129.9, 128.6, 128.6, 128.5, 127.4, 126.8, 126.7, 124.3, 124.3, 14.8, 13.6; ESI-MS: $[M-2]^-$=484.3; Anal. Calcd. for $C_{28}H_{22}O_4S_2$: C, 69.11; H, 4.56; Found: C, 69.02; H, 4.52.

Synthesis of PBC

9,10-bis(2,5-dimethylthiophen-3-yl)phenanthrene-2,7-dicarboxylic acid (61.7 mg, 61.7 mmol) and 10 ml dichloromethane was added in a dry flask with a magnetic stirring bar. Oxalyl chloride (0.05 ml) was dropped into the mixture following a drop of DMF. Four h later, the white solid disappeared and the solvent of the clear solution and unreacted oxalyl chloride were removed by rotary evaporation. The residual was dissolved in 10 ml dichloromethane. 1-Aza-18-crown 6-Ether (72 mg, 0.28 mmol) and Triethylamine were added to the mixture. The mixture was stirred under room temperature overnight. Water was added to the flask. The organic layer was separated and the water phase was extracted with dichloromethane. The organic extracts were combined, washed with water and dried over Na_2SO_4. Product(109 mg, 90 %) was obtained by chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.71 (d, *J* = 8.6 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.59 (s, 1H), 7.52 (s, 1H), 6.27 (d, *J* = 2.2 Hz, 2H), 3.67 – 3.03 (m, 48H), 2.30 (d, *J* = 2.9 Hz, 2H), 1.91 (d, *J* = 13.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.00, 135.34, 135.13, 134.96, 134.70, 134.25, 134.15, 133.71, 133.34, 131.66, 131.50, 130.00, 128.44, 127.17, 125.45, 125.34, 125.22, 123.26, 70.73, 70.58, 70.44, 69.76, 69.54, 15.20, 14.03; ESI-HR-MS: $[M+Na]^+$: calcd, 999.4111; found, 999.4095.

Results and discussion

Photochromism and fluorescence of PBC

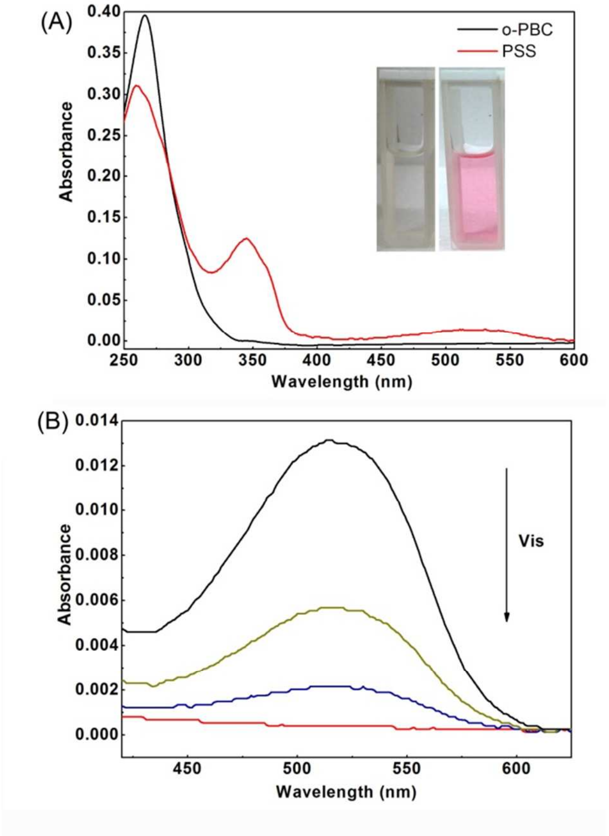


Fig. 1 Changes in absorption spectra and color of **PBC** by alternating irradiation with UV and visible light in acetonitrile(1.0×10^{-5} mol·L^{-1}) at room temperature: (A) absorption spectra and (inset) color change of **o-PBC** upon irradiation with UV light(254 nm), (B) absorption spectral changes of **c-PBC** upon irradiation with visible light(550 nm).

Fig. 1(A) shows the absorption spectral and color changes of **PBC** in acetonitrile (1.0×10^{-5} mol·L^{-1}) induced by alternating irradiation with UV and visible light. A strong absorption peak at 265 nm (ε_{max}=4.0×10^{4} mol^{-1} L cm^{-1}), which corresponds to a $\pi\rightarrow\pi^*$ transition, was observed. Upon irradiation with a UV light (254 nm), two new bands appeared at 344 and 550 nm respectively and the colorless solution turned to purple (see Fig.1(A) insert). The intensity of the new peaks progressively enhanced due to the photocyclization reaction from the open-ring isomer (**o-PBC**) to closed-ring isomer(**c-PBC**). After irradiation under UV light for 3 minutes, the color and the intensity of the new peaks did not change anymore. It indicated that the photostationary state (PSS) was reached. The red line in Fig. 1 (A) shows the absorption spectra of **PBC** in PSS. As **o-PBC** has no absorption peak at 550 nm, the absorbance at 550 nm was only contributed by **c-PBC** in the solution. Fig. 1(B) shows the evolution of absorption spectra of **PBC** solution in PSS while it was irradiated by 550 nm visible light. The intensity of the peak at 550 nm disappeared slowly and the purple solution turned colorless again due to the corresponding cycloreversion from **c-PBC** to **o-PBC**[51]. The coloration–decoloration cycles could be repeated more than 5 times with negligible degradation. The minor degradation should mainly be attributed to the unwanted isomerization during the cyclizing process[52].

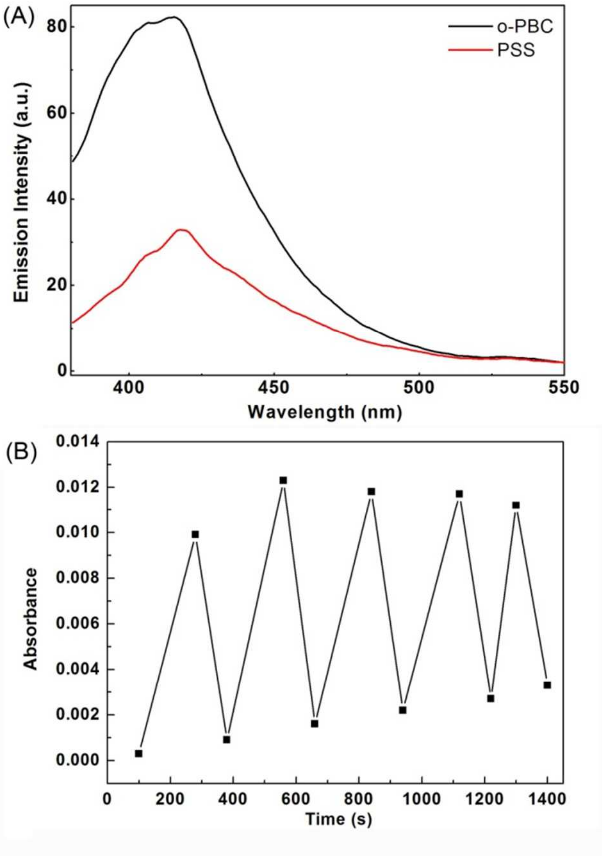


Fig. 2 (A) Fluorescent changes of **o-PBC** under 254 nm light irradiation (Excitation wavelength was 360 nm). (B) Fatigue resistance upon irradiation with alternation of 254 and 550 nm light in acetonitrile(1.0×10^{-5} mol·L^{-1}, monitoring wavelength is 530 nm).

When excited with 360 nm light, a sharp emission peak of **o-PBC** at 415 nm was obtained. After irradiation upon 254 nm UV light, the emission intensity decreased significantly by ca.60.0 %. The residual fluorescence in the photostationary state might be attributed to the existence of residual open-ring isomers with parallel conformation, as the phenanthrene bridge of the **c-PBC**, which was the fluorophore, would be twisted and couldn't emit light[53]. Utilization of the photoisomerization of diarylethene bridge as a fluorescence switch has been reported in the literature before[54]. However, we found the photochromic unit had non-destructive capability in our previous research as the photoluminescence and photoisomerization can be initiated by light of different wavelength[44].

Absorbance and fluorescence response to metal ions

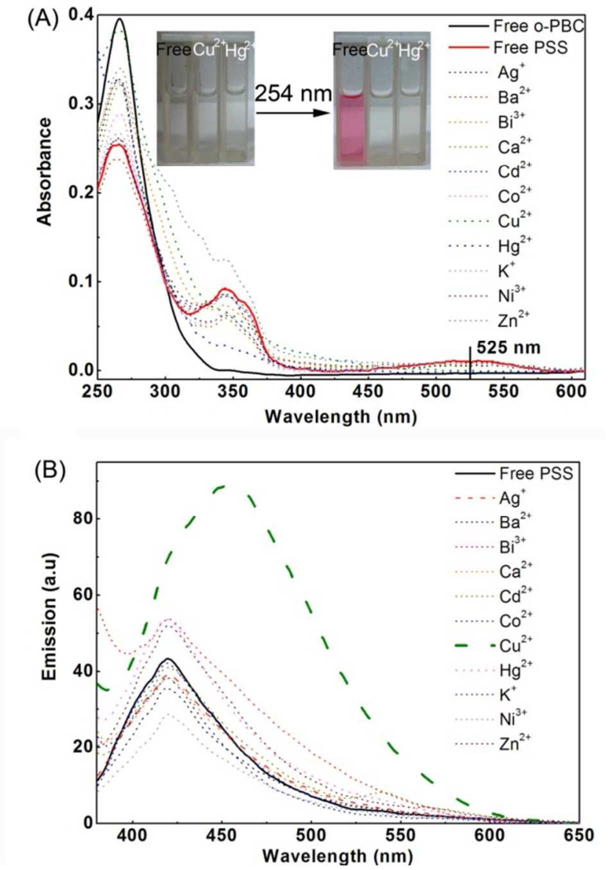


Fig. 3 (A) UV-Vis absorbtion spectra of **c-PBC** containing different metal ions (20 equiv.) acetonitrile solutions (1.0×10^{-5} mol·L^{-1}) at room temperature. The inset shows the color change of solutions containing copper or mercury ions before and after UV light irradiation. (B)Fluorescence spectra of solutions added different metal ions and irradiated by UV light.

When different metal ions were mixed into the acetonitrile solution of **o-PBC**, the absorption and photoluminescence spectra were investigated in detail. The solution of **o-PBC** remained colorless and there was no obvious change on the UV-Vis and fluorescence spectra before and after addition of various metal ions (Fig. S1, ESI). Then those solutions containing various ions were irradiated under 254 nm UV light for three minutes. Surprisingly, we found the solutions containing Cu^{2+} or Hg^{2+} ions did not show any color change and the new band at 550 nm did not appear like them of the free one and those added other metal ions (see Fig. 3 (A)). However, the fluorescent intensity of the solution containing copper ion enhanced impressively (Fig. S2, ESI). This new emission peak red-shifted 33 nm to 452 nm (see Fig. 3 (B)). It indicated that photo induced electron transfer between metal ion and organic ligand[55, 56].

Then a red solution of **PBC** in PSS was added Cu^{2+} or Hg^{2+} ions respectively. The red solution could also bleach immediately after adding Cu^{2+} or Hg^{2+} ions. These phenomena indicated that: 1) The existence of copper ion not only affected the photochromism, but also lead to the formation of some new substance with stronger luminescence; 2) As the spectra of open form of **PBC** had not been affected by adding ions, the new substance with stronger luminescence was formed by **c-PBC** and copper ion; 3) The **o-PBC** was insensitive to all metal ions tested, while the **c-PBC** could selectively coordinate to Cu^{2+} or Hg^{2+} ions and form colorless complexes; 4) It is also clear that the **c-PBC** shows good selectivity for transition-metal ions.

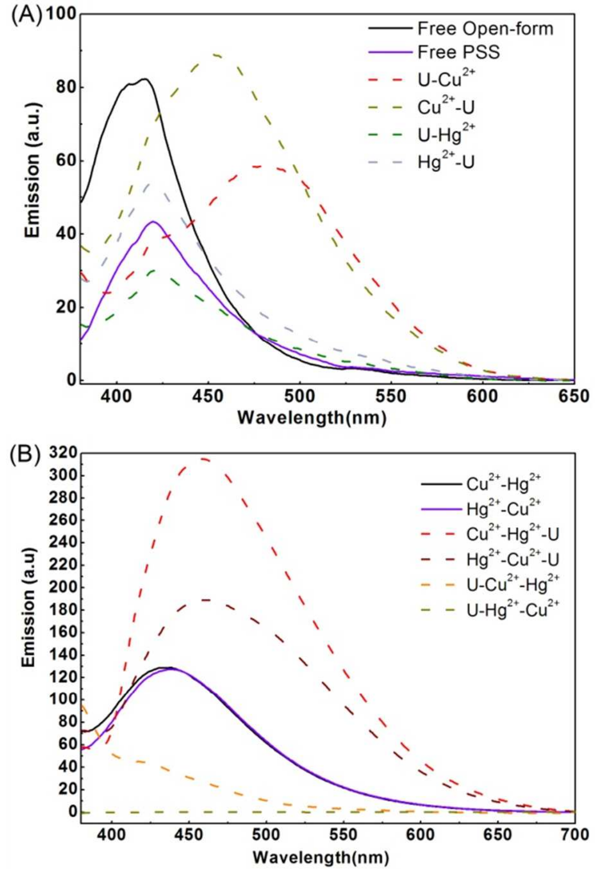


Fig. 4 (A) shows the fluorescence of **PBC** solution with different input order of single metal ion and UV light(U). (B) shows the fluorescence of **PBC** solution with different input order of UV light and the synergistic action of two metal ions on **PBC**.

In order to study the effect between the metal ions and **PBC**, fluorescent spectra were obtained under different conditions of which the orders of input signals are not same. In Fig. 4 (A), we realized that as long as copper ions were added in the **PBC** solution, the spectra would red shift. However, the order of UV light irradiation (U) and addition of metal ions also affected the results when irradiation time and sum concentration of metal ions were kept invariable. That means the existence of metal ions affected the photoreaction process, although stable complex could not form. The reason might be that the formation of new complex during photoreaction led to the equilibrium movement of photoreaction. In Fig. 4 (B), more spectra were shown under different combination of three input signals, Cu^{2+}, Hg^{2+} and UV irradiation. The solution showing the strongest fluorescence is that one which is obtained by adding 10 equiv. Cu^{2+}, 10 equiv. Hg^{2+} ions and final UV irradiation of **PBC** solution. Surprisingly, we found that the fluorescence of the solution obtained by irradiation of UV light, adding 10 equiv. Hg^{2+} and 10 equiv. Cu^{2+} was completely quenched.

Journal of Materials Chemistry C

Dynamic Article Links ▶

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

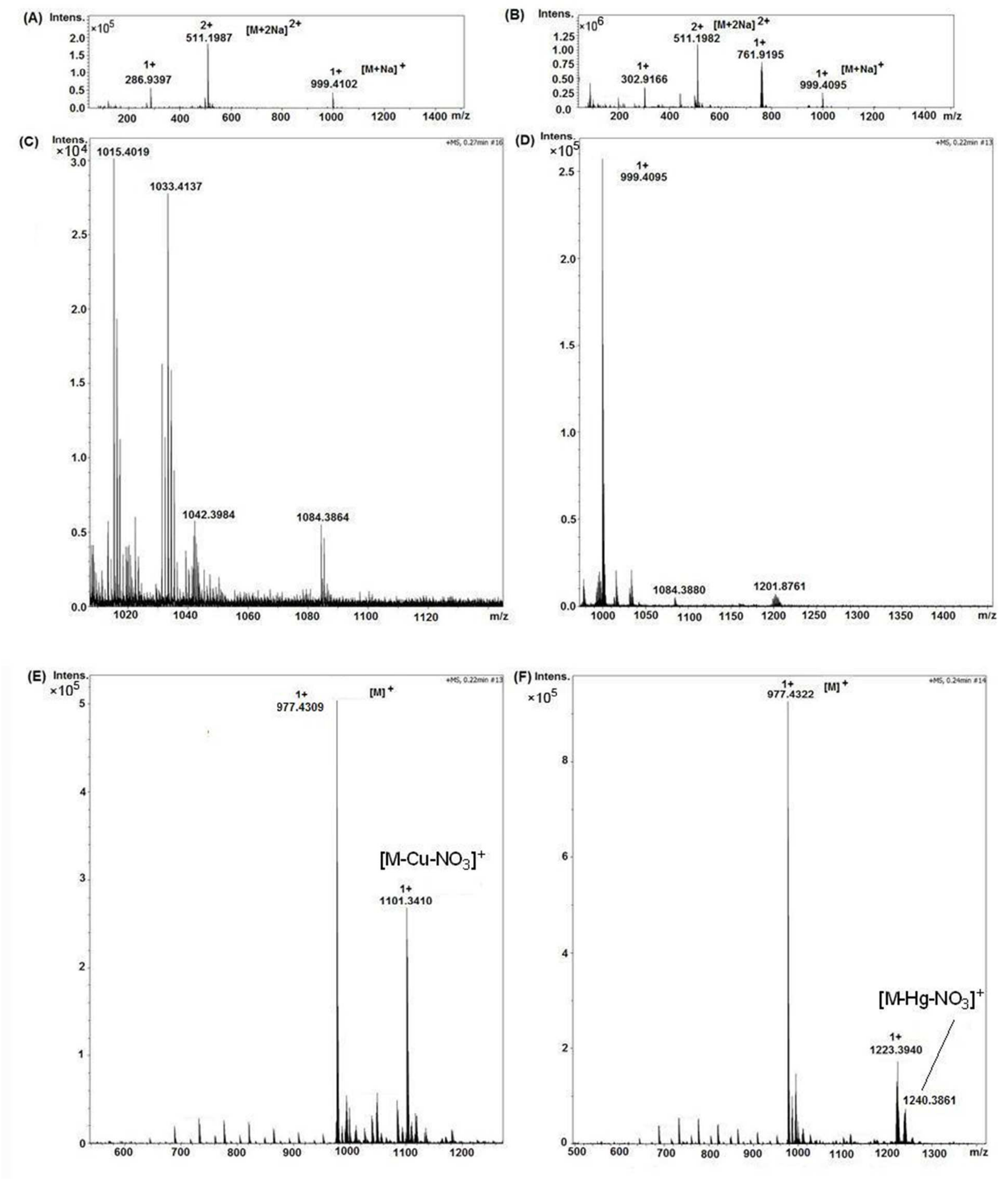


Fig. 5 (A) and (B) show the mass spectra of **o-PBC** added Cu^{2+} or Hg^{2+} in acetonitrile respectively. (C) and (D) show the magnified region of (A) and (B) over 1000 m/z. (E) and (F) show them of **c-PBC** added Cu^{2+} or Hg^{2+} in acetonitrile respectively. (The spectra were modified for clarity. M = PBC).

MS and ^{1}H NMR analysis were conducted to find out what happened between **c-PBC** and these metal ions. For the **o-PBC** solution, only molecular containing one or two sodium ion peaks of **PBC** were found at 999.4 or 511.2 m/z in MS spectra, no matter if Cu^{2+} or Hg^{2+} ions were added or not(Fig. 5(A) and (B)). In Fig. 5(C) and (D) which are the 10 times magnified region of (A) and (B) over 1000 m/z, no ion peak related to Cu^{2+} or Hg^{2+} ions was found. However, the molecular ion peak of **PBC-Cu-NO$_3$**[1101.3410 m/z, intens.= ×10^5] or **PBC-Hg-NO$_3$**[1240.3861 m/z, intens.= ×10^4] was found in HRMS for the **c-PBC** solution added Cu^{2+} or Hg^{2+} ions(Fig. 5(E)and(F)). It means that the binding ability of **o-PBC** for metal ions is lower than it of **c-PBC**. It is just complementary to the previous report in which 1, 2-bisthiophenyl perfluorocyclopentene was applied as photochromic unit[17]. In their case, the open isomer has stronger binding ability. This is mainly attributed to the increase of electronic density in the crown ether of the closed form due to the break of aromatic phenanthrene which is considered as an electron withdrawing group here. It is worth noting that although two aza-18-crown 6-ether groups attached to the phenanthrene bridge, the **c-PBC** could uptake only one metal ion.

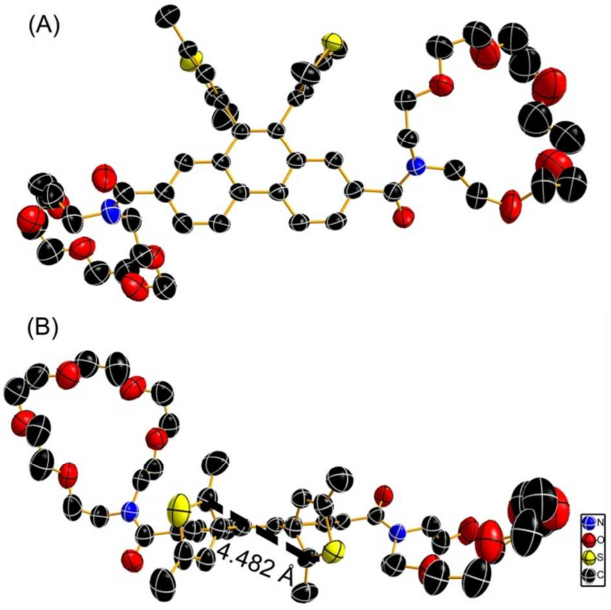


Fig. 6 Top view(A) and side view(B) of ORTEP drawing of **o-PBC** showing 50% probability displacement ellipsoids(hydrogen were omitted for clarity).

Fortunately, single crystal of **o-PBC** was obtained from its d^6-DMSO solution after all NMR measurement finished. Although the crystal for X-ray diffraction was obtained from a solution containing excessive Cu^{2+} ions, no Cu^{2+} ion was found in the structure(Fig. 6). It also confirmed that the **o-PBC** was not active to combine metal ions and form stable complex. Meanwhile, we realized that the molecule was not symmetrical as the unequal substitution of two crown ether groups to phenanthrene core. It is believed that the unequal substitution of two crown ether groups is the main reason why only one crown ether group can coordinate with metal ion, however which one is not sure.

The material did not show photochromism in the crystalline state(Fig. S3, ESI), as the distance between the reactive carbons of thiophene rings was 4.482 Å and out of reactive range[57, 58].

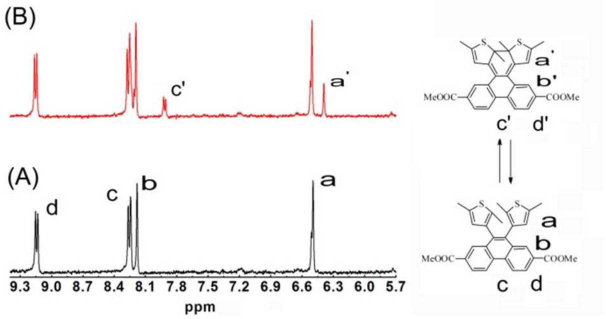


Fig. 7 ^{1}H NMR spectra of both open form(A) and PSS (B) of compound **4**.

As mentioned above, the red **PBC** solution in PSS would bleach after adding Cu^{2+} or Hg^{2+} ions respectively. It indicated that the closed photochromic unit might convert to its open form. ^{1}H NMR analysis revealed that both of the ions did lead to cycle opening of **PBC**. The ^{1}H NMR spectra of both open form and PSS state of compound **4** were provided for comparison(see Fig. 7). ^{1}H NMR signals of protons attached to aromatic cycles were designated. After irradiation by UV light, new signals at 6.39 and 7.92 ppm contributed by protons at 4-position of thiophene and phenanthrene respectively of closed form were observed. Meanwhile, the photoconversion ratio from open- to closed-ring isomers of **PBC** in PSS was calculated according to the integral of peaks contributed by thiophene rings of open and closed form, and the value was 21 %.

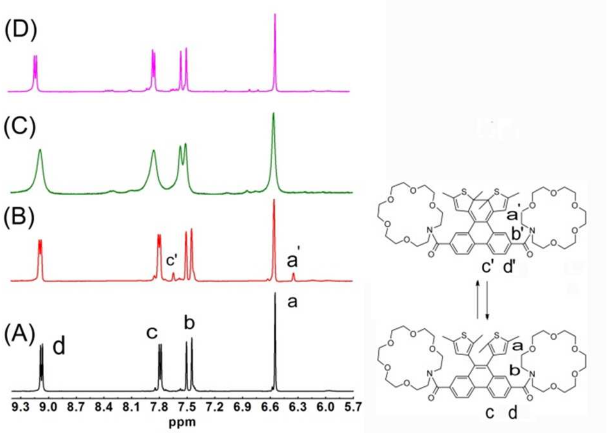
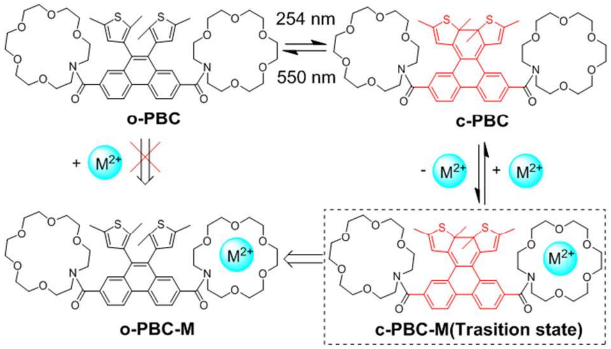


Fig. 8 ^{1}H NMR spectra of both open form(A) and PSS (B) of **PBC**. (C) and (D) show the spectra added 20 equiv. Cu^{2+} and Hg^{2+} ions respectively.

Similar ^{1}H NMR analysis was carried out to monitor the photochemical and ion induced bleaching process. The signal assignment could be found in Fig. 8 (A) for the **o-PBC**. Just like the reference compound **4**, new signals at 6.34 and 7.64 ppm, which were contributed by the proton a' and b' of **c-PBC**, were observed after 254 nm light irradiation (Fig. 8 (B)). It is worth noting that the introduction of crown ether decreased the photoconversion ratio from open- to closed-ring isomers of photochromic unit in the PSS to 8 %. The main reason probably is that the steric hindrance of crown ether prohibited the rotation of thiophene groups. In fact, the ratio between inactive parallel and active anti-parallel isomers of **o-PBC** did not change according to the integral area of two peaks around 7.5 ppm contributed by protons b of the two isomers (Fig. 8 (A)). Although the ratio of active isomer is 50 %, only 8 % open isomer cyclized under UV light irradiation. It means most of the materials are wasted and modification to improve photoconversion ratio is needed. Then the tested DMSO solutions in PSS were added 20 equv. Cu^{2+} and Hg^{2+} ions respectively. After a while, the red solutions bleached in the dark and their ^1H NMR spectra were tested again (Fig. 8 (C) and (D)). In both spectra, the signals from **c-PBC** (peaks a' and b' in Fig. 8 (B)) disappeared completely. It indicated that the closed photochromic unit reverted to its open form for the existence of these metal ions. To the best of our knowledge, this is the first example which the closed form of DAEs can transform to open form under ion existence beside visible light irradiation and thermal heat.



Scheme 2 Schematic representation of the cation uptake by compound **PBC** after its photoisomerization to **c-PBC** driven by irradiation with UV light ($M^{2+}= Cu^{2+}, Hg^{2+}$).

We presumed that the combination of **c-PBC** and metal ions with positive charge decreased the density of electronic cloud between the photoactive carbon atoms of thiophene rings of **c-PBC** and decreased the activation energy of the cycle opening process at ground state. In our experiment, the photostationary solution of **PBC** bleached almost simultaneously when the metal ions were added. We believe the existence of **c-PBC-M** as the transition state, although it was not detectable. Because the closing process of free **PBC** could not occur at ground state, the **c-PBC-M** converted to **o-PBC-M** smoothly at room temperature while the reversal process is forbidden. The combination and separation between **c-PBC** and metal ions are competition processes and will reach equilibrium. As long as there are enough specific metal ions, all **c-PBC** will convert to **o-PBC-M** finally. Scheme 2 illustrates the possible process of metal ion uptake by **PBC**.

In short summary, **c-PBC** can selectively combine with only one Cu^{2+} or Hg^{2+} ion, but **o-PBC** is inactive to all metal ions. The transition state, **c-PBC-M**, is not stable at room temperature and will transform to **o-PBC-M** quickly.

Application of diarylethene PBC in logic circuit

To simulate logic circuit with specific function on one molecule platform is interesting and of practical importance for information technology and biochemistry. In our case, a logic circuit was constructed with **PBC**, utilizing UV light irradiation and metal ions as the input signals. The outputs are designated as output-1 ($A > 0.01$) and output-2 ($I > 40$), respectively, where A is the absorbance at 550 nm and I is the value of fluorescence intensity at 480 nm. If the value of A or I locates in a specific range, the corresponding output is considered as the "1" state, otherwise, it is considered as the "0" state. Thus, according to the truth table (Table 1), a logic circuit with AND and NOT gates integrated within a single molecule is approached (Fig. 9 (A)).

Table 1 Truth table for the monomolecular circuit

Entry	Input-1 UV	Input-2 Cu^{2+}	Input-3 Hg^{2+}	Output-1 $A > 0.01$	Output-2 $I > 40$
1	0	0	0	0	0
2	0	1	0	0	0
3	0	0	1	0	0
4	0	1	1	0	0
5	1	0	0	1	0
6	1	1	0	0	1
7	1	0	1	0	0
8	1	1	1	0	0

Key pad locks are circuits where the outputs are not only sensitive to the present input combination, but also to the input history. As mentioned above, the fluorescent spectra of **PBC** solutions obtained by different orders of input signal were different. It facilitates us to fabricate a binary logic gate which can work as a key pad lock. Depending on the different combinations of three inputs (UV irradiation, Cu^{2+} and Hg^{2+} designated as ''U'', ''C'' and ''H'', respectively), compound **PBC** can switch between different fluorescence emission states ''On and Off''. Out of six possible input combinations i.e. UCH, UHC, CUH, CHU, HUC, HCU, only the CHU input combination (i.e. it is the password) gives birth to an instinct fluorescent output signal (intensity over 230 in Fig. S4, ESI). As illustrated in Fig. 9(B), when the sequence of three input keys CHU is inserted, the keypad lock ''opens'', corresponding to a strong fluorescent intensity at 530 nm. All other sequences (as wrong passwords), which give weak fluorescence signal outputs, fail to open the lock.

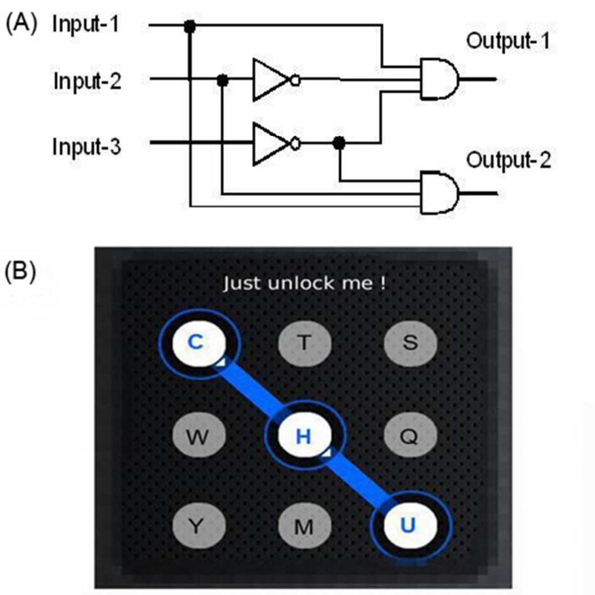


Fig. 9 (A) A logic circuit and (B) a fluorescence keypad lock with inputs of UV irradiation, Cu^{2+} and Hg^{2+}.

Visual detection of heavy metal ions in non-solution environment

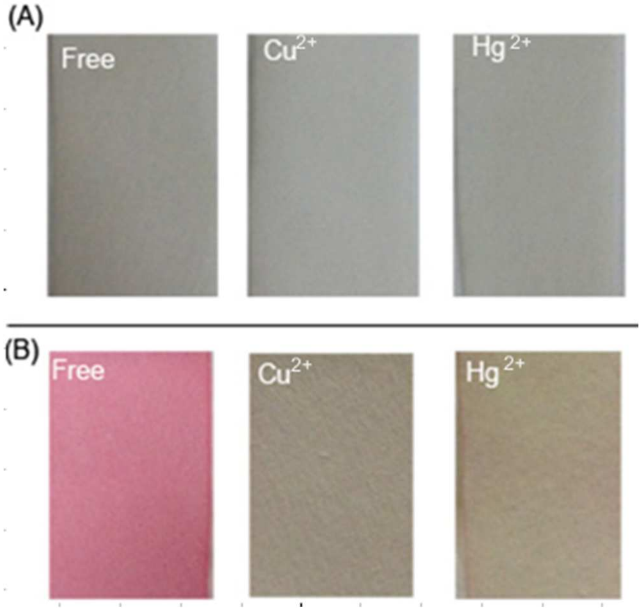


Fig. 10 Color change of testing paper before(A) and after(B) UV light activation. After UV irradiation, all papers were put in dark for 5 min.

Absolutely the **c-PBC** solution can be used to detect Cu^{2+} or Hg^{2+}, as **c-PBC** can selectively coordinate to these metal ions and show impressive color bleaching while it was not active to the other ions (Fig. 3(A)). Encouraged by the color bleaching phenomena of **PBC** in solution environment, we fabricated Cu^{2+} or Hg^{2+} test papers by immerging filter papers in acetonitrile solution of **PBC** (1×10^{-4} mol. L^{-1}). After evaporation of the solvent, they can be applied in visual detection of Cu^{2+} or Hg^{2+} ions in non-solution environment.

Two sheets of test paper were immerged into water solution containing Cu^{2+} or Hg^{2+} ions respectively while one remain free as reference. In Fig. 10(A), all of the three dried papers look the same before UV light activation. After activation by UV light, the color of three test papers turned purple, but when they were put into the dark no longer than 5 min, the purple color of the test paper which absorbed Cu^{2+} or Hg^{2+} ions bleached completely but the reference did not change (Fig. 10(B)). It is also worth noting that the bleaching process in solid state is slower than it in solution.

Conclusion

In conclusion, a novel phenanthrene bridged photochromic diarylethene with double crown ethers as ion recognizing groups has been synthesized and fully characterized. Its photochromic behavior and selectively interaction with Cu^{2+} or Hg^{2+} were investigated in detail. Only one crown ether of the closed isomer can selectively combine with specific metal ions (Cu^{2+} or Hg^{2+}) to form complexes. The combination also leads to the cycle opening of the photochromic unit and bleaching of the solution in photostationary state. This material not only could be applied to visual detection of Cu^{2+} and Hg^{2+} in solution, but also was found effective in a dry testing paper fabricated by emerging ordinary filter paper into its solution. The diarylethene shows excellent absorbance and fluorescent switching behaviors with distinctive color changes in response to three combinational inputs of UV, Cu^{2+} and Hg^{2+}. Based on this characteristic, a logic circuit was designed using the absorption and fluorescence intensity as the output signals with the inputs of UV, Cu^{2+} and Hg^{2+}. A key pad lock was fabricated as the historical input signals also affected the fluorescent intensity at specific wavelength. The results will be useful for information processing on the unimolecular platform with potential applications in visual detection toxic metal ions, data manipulation, as well as intelligent diagnostics. However, the low photoconversion ratio and slow bleaching speed in solid state need to optimize.

Acknowledgements

The authors acknowledge financial support from the National Natural Science Foundation of China (No. 21371060), the Pearl River in Guangzhou city of Nova of Science and Technology Special Funded Projects (No. 2014J2200047) and the research fund of the Key Laboratory of Fuel Cell Technology of Guangdong Province.

Notes and references

[a] *State Key Laboratory of Luminescent Materials and Devices, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China. E-mail: hpzeng@scut.edu.cn*
[b] *School of Physics and Technology, Yunnan University, Yunnan 650504, China. E-mail: jingxian_he@sina.com*

† Electronic Supplementary Information (ESI) available: Original IR, ^1H NMR, ^{13}C NMR and MS spectra. See DOI: 10.1039/b000000x/

‡ Crystallographic data for **PBC**. $C_{52}H_{68}N_2O_{12}S_2$, 977.20, triclinic, a= 8.8993(6)Å, b= 12.6608(11)Å, c= 24.2498(19)Å, α= 99.20°, β= 99.02°, γ=96.96°, U= 2633.6(4) $Å^3$, T= 298(2) K, space group *P-1*, Z= 2, ρ_{calcd}= 1.232 g cm^{-3}, μ(MoKα)= 0.162, 13431 reflections measured, 9133 unique

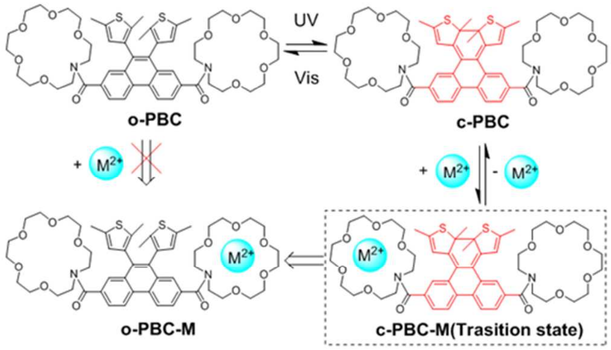
(Rint= 0.0871) which were used in all calculations. The final $wR(F_2)$ was 0.2596. CCDC 998583 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1. M. Irie, *Chem. Rev.*, 2000, **100**, 1685-1716.
2. H. Tian and S. Yang, *Chem. Soc. Rev.*, 2004, **33**, 85-97.
3. Q. Li, John Wiley & Sons Inc, New Jersey, 2013.
4. Y. Wang and Q. Li, *Adv. Mater.*, 2012, **24**, 1926-1945.
5. Y. N. Li, A. Urbas and Q. Li, *J. Org. Chem.*, 2011, **76**, 7148-7156.
6. K. Hakouk, O. Oms, A. Dolbecq, J. Marrot, A. Saad, P. Mialane, H. El Bekkachi, S. Jobic, P. Deniard and R. Dessapt, *J. Mater. Chem. C*, 2014, **2**, 1628-1641.
7. K. Rameshbabu, L. Zou, C. Kim, A. Urbas and Q. Li, *J. Mater. Chem.*, 2011, **21**, 15673-15677.
8. Y. N. Li, A. Urbas and Q. Li, *J. Am. Chem. Soc.*, 2012, **134**, 9573-9576.
9. Y. N. Li, C. M. Xue, M. F. Wang, A. Urbas and Q. Li, *Angew. Chem.-Int. Edit.*, 2013, **52**, 13703-13707.
10. P. L. Jacquemin, Y. Garcia and M. Devillers, *J. Mater. Chem. C*, 2014, **2**, 1815-1822.
11. M. Irie, *P. Jpn. Acad. B-Phys.*, 2010, **86**, 472-483.
12. M. Taguchi, T. Nakagawa, T. Nakashima and T. Kawai, *J. Mater. Chem.*, 2011, **21**, 17425-17432.
13. T. Tsujioka, *J. Mater. Chem.*, 2011, **21**, 12639-12643.
14. T. Tsujioka, *J. Mater. Chem. C*, 2014, **2**, 221-227.
15. Y. N. Li, M. F. Wang, A. Urbas and Q. Li, *J. Mater. Chem. C*, 2013, **1**, 3917-3923.
16. M. Takeshita, K. Uchida and M. Irie, *Chem. Commun.*, 1996, 1807-1808.
17. J. P. Malval, I. Gosse, J. P. Morand and R. Lapouyade, *J. Am. Chem. Soc.*, 2002, **124**, 904-905.
18. Z. G. Zhou, S. Z. Xiao, J. Xu, Z. Q. Liu, M. Shi, F. Y. Li, T. Yi and C. H. Huang, *Org. Lett.*, 2006, **8**, 3911-3914.
19. S. Jing, C. Zheng, S. Pu, C. Fan and G. Liu, *Dyes and Pigments*, 2014, **107**, 38-44.
20. M. Natali and S. Giordani, *Chem. Soc. Rev.*, 2012, **41**, 4010-4029.
21. Q. L. Xu, K. M. Lee, F. Wang and J. Yoon, *J. Mater. Chem.*, 2011, **21**, 15214-15217.
22. S. Z. Pu, T. F. Wang, G. Liu, W. J. Liu and S. Q. Cui, *Dyes and Pigments*, 2012, **94**, 416-422.
23. Z. Yao, Y. Yang, X. Chen, X. Hu, L. Zhang, L. Liu, Y. Zhao and H. C. Wu, *Anal Chem*, 2013, **85**, 5650-5653.
24. M. Zhang, H. N. Le, X. Q. Jiang and B. C. Ye, *Chem. Commun.*, 2013, **49**, 2133-2135.
25. L. He, V. L. L. So and J. H. Xin, *Sens. Actuators, B-Chem.*, 2014, **192**, 496-502.
26. L. J. Qu, C. X. Yin, F. J. Huo, J. B. Chao, Y. B. Zhang and F. Q. Cheng, *Sens. Actuators, B-Chem.*, 2014, **191**, 158-164.
27. S. Goswami, A. K. Das, A. K. Maity, A. Manna, K. Aich, S. Maity, P. Saha and T. K. Mandal, *Dalton T.*, 2014, **43**, 231-239.
28. D. H. Nies, *Appl. Microbiol. Biotechnol.*, 1999, **51**, 730-750.
29. D. W. Boening, *Chemosphere*, 2000, **40**, 1335-1351.
30. X. Guo, X. Qian and L. Jia, *J. Am. Chem. Soc.*, 2004, **126**, 2272-2273.
31. C. S. He, W. P. Zhu, Y. F. Xu, T. Chen and X. H. Qian, *Anal. Chim. Acta*, 2009, **651**, 227-233.
32. W. Lin, X. Cao, Y. Ding, L. Yuan and L. Long, *Chem. Commun.*, 2010, **46**, 3529-3531.
33. A. P. De Silva, H. Q. N. Gunaratne and C. P. Mccoy, *Nature*, 1993, **364**, 42-44.
34. A. Credi, *Angew. Chem.-Int. Edit.*, 2007, **46**, 5472-5475.
35. J. Andreasson and U. Pischel, *Chem. Soc. Rev.*, 2010, **39**, 174-188.
36. J. Andreasson, U. Pischel, S. D. Straight, T. A. Moore, A. L. Moore and D. Gust, *J. Am. Chem. Soc.*, 2011, **133**, 11641-11648.
37. S. J. Chen, Y. H. Yang, Y. Wu, H. Tian and W. H. Zhu, *J. Mater. Chem.*, 2012, **22**, 5486-5494.
38. J. J. Zhang, Q. Zou and H. Tian, *Adv. Mater.*, 2013, **25**, 378-399.
39. U. Pischel, J. Andreasson, D. Gust and V. F. Pais, *Chemphyschem*, 2013, **14**, 28-46.
40. E. T. Ecik, A. Atilgan, R. Guliyev, T. B. Uyar, A. Gumus and E. U. Akkaya, *Dalton T.*, 2014, **43**, 67-70.
41. C. H. Xu, W. Sun, C. Zhang, Y. C. Bai, C. J. Fang, W. T. Li, Y. Y. Huang and C. H. Yan, *Science in China Series B-Chemistry*, 2009, **52**, 700-714.
42. H. H. Liu, X. Zhang, Z. Gao and Y. Chen, *J. Phys. Chem. A*, 2012, **116**, 9900-9903.
43. S. Z. Pu, Z. P. Tong, G. Liu and R. J. Wang, *J. Mater. Chem. C*, 2013, **1**, 4726-4739.
44. J. J. He, T. T. Wang, S. X. Chen, R. P. Zheng, H. Y. Chen, J. Li and H. P. Zeng, *J. Photoch. Photobio. A*, 2014, **277**, 45-52.
45. J. E. McMurry, *Chem. Rev.*, 1989, **89**, 1513-1524.
46. A. Fürstner and B. Bogdanović, *Angew. Chem. Int. Ed.*, 1996, **35**, 2442-2469.
47. M. Ephritikhine, *Chem. Commun.*, 1998, 2549-2554.
48. M. Walko and B. L. Feringa, *Chem Commun*, 2007, 1745-1747.
49. F. Yang, J. Sun, R. Zheng, W. W. Qiu, J. Tang and M. Y. He, *Tetrahedron*, 2004, **60**, 1225-1228.
50. C. F. Nising, U. K. Schmid, M. Nieger and S. Brase, *J. Org. Chem.*, 2004, **69**, 6830-6833.
51. M. Irie and K. Uchida, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 985-996.
52. M. Irie, T. Lifka, K. Uchida, S. Kobatake and Y. Shindo, *Chem. Commun.*, 1999, 747-748.
53. T. Fukaminato, T. Sasaki, T. Kawai, N. Tamai and M. Irie, *J Am Chem Soc*, 2004, **126**, 14843-14849.
54. X. L. Meng, W. H. Zhu, Q. Zhang, Y. L. Feng, W. J. Tan and H. Tian, *J. Phys. Chem. B*, 2008, **112**, 15636-15645.
55. A. Yari and F. Papi, *Sens. Actuators, B-Chem.*, 2009, **138**, 467-473.
56. P. Ncube, R. W. Krause, D. T. Ndinteh and B. B. Mamba, *Water SA*, 2014, **40**, 175-182.
57. S. Kobatake, K. Uchida, E. Tsuchida and M. Irie, *Chem. Commun.*, 2002, 2804-2805.
58. A. Spangenberg, R. Metivier, J. Gonzalez, K. Nakatani, P. Yu, M. Giraud, A. Leaustic, R. Guillot, T. Uwada and T. Asahi, *Adv. Mater.*, 2009, **21**, 309-313.

Ion induced cycle opening of a diarylethene and its application on visual detection of Cu^{2+} and Hg^{2+} and keypad lock

Junjie He,[a] Jingxian He,[b] Tingting Wang[a] and Heping Zeng[a]*

We demonstrate a diarylethene of which the binding ability to specific metal ions depends on the state of photochromic unit. Only the closed form can combine with the metal ions, meanwhile the coordination would surprisingly induce cycle opening of photochromic unit and color bleaching process. These properties can be applied in detection of Cu^{2+} and Hg^{2+} ions and single molecular keypad lock.



M^{2+}=Cu^{2+}, Hg^{2+}