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New photochromic chemosensors for Hg^{2+} and F^-

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Two new chemosensors (**1a** and **1b**) based on photochromic dithienylcyclopentene were designed and synthesized, and their spectral behaviors toward various metal ions and anions were investigated in detail. Compounds show excellent optical properties and distinguish Hg^{2+} and F^- in CH_3CN. Job's plot reveals that the presence of Hg^{2+} induces the formation of a 1:1 complex between **1a** or **1b** and Hg^{2+}. From the spectral responses and ^1H NMR analysis, the deprotonation of the thioamide protons is proposed to explain the sensing mechanism for **1a** and **1b** toward F^-. It is found that **1a** and **1b** exhibit ring-opening and ring-closing photoisomerization with UV–vis light irradiation. Furthermore, their photochromic properties can be modulated by Hg^{2+} and F^- ions. Moreover, **1a** and **1b** in photostationary states become promising sensors for Hg^{2+} and F^- with high selectivity.

1. Introduction

Recently, considerable efforts have been devoted to the development of sensitive and selective sensors, which are capable of detecting Hg^{2+} and F^- ions in an inexpensive, convenient, accurate, quantitative, and rapid manner.[1–9] It is still a challenge to design and synthesize multi-functional sensors for sensing Hg^{2+} and F^- ions with excellent properties. Mercury and its derivatives are extensively used in industry and owing to the grisly immunotoxic, genotoxic, and neurotoxic effects, they pose threats to environment and public health.[10,11] Among them, inorganic mercury species can damage the brain, heart, kidney, stomach, and intestines.[12,13] On the other hand, fluoride ion is one of the most significant anions due to its pivotal role in the health, medical, and environmental sciences.[14,15] Furthermore, fluoride ion is also associated with nerve gases, in the analysis of drinking water, and the refinement of uranium used in nuclear weapon manufacture. Thus, due to diversity of their functions, both beneficial and otherwise, the detection of mercury and fluoride ions has received increasing attention in recent years.

Photochromic compounds including diarylethenes, fulguides, spiropyrans have been intensively investigated for several decades from both the fundamental and practical points of view for their numerous potential applications as optical devices. In particular, diarylethene derivatives attract strong interest for photo-electronic applications, such as erasable-memory media, photo-optical switching, display, and photo-drive actuators owing to their excellent thermal-stability, remarkable fatigue-resistance, rapid response, and fairly high photocyclization quantum yields.[16–18] Upon photo-irradiation, diarylethene derivatives can undergo photochromic cyclization/cycloreversion reactions accompanied by global changes of the bulk materials characteristics, such as UV–vis absorption spectra, fluorescence spectra. Among these diarylethene compounds reported, unsymmetrical diarylethenes exhibited good optical and electrochemical performances because of their special structures.[19,20] For the practical applications, several attempts to modulate the photochromic property of diarylethene derivatives by ions have been reported.[21–25]

In this context, we reported a convenient synthesis of two novel compounds, **1a** and **1b** shown in Scheme 1, containing dithienylcyclopentene as a photochromic bridging unit that integrates fluorophore with thiosemicarbazone to form a donor-bridge-acceptor system. There are several novelty and merits in the design of these compounds. (1) Compounds **1a** and **1b** possess unsymmetric molecular architecture. The incorporated bridge of the dithienylcyclopentene is conjugated to the donor–acceptor system, assuming good photochromism with considerable sensing ability. The known dithienylcyclopentene based photochromic compounds usually bear symmetric subunits on the both ends. (2) Thiosemicarbazone is an outstanding candidate as multiple interaction sites for constructing sensing system. It was widely used ionophore chelated with Hg^{2+}.[26–28] As a part of thiosemicarbazone, the thioamide has often been used as the binding group for the detection of anions especially F^-.[29,30] (3) As a photoswitchable unit, dithienylcyclopentene is regarded as a suitable candidate to impart functionality in these donor–acceptor systems.[18,31] Dithienylcyclopentene (BTE)

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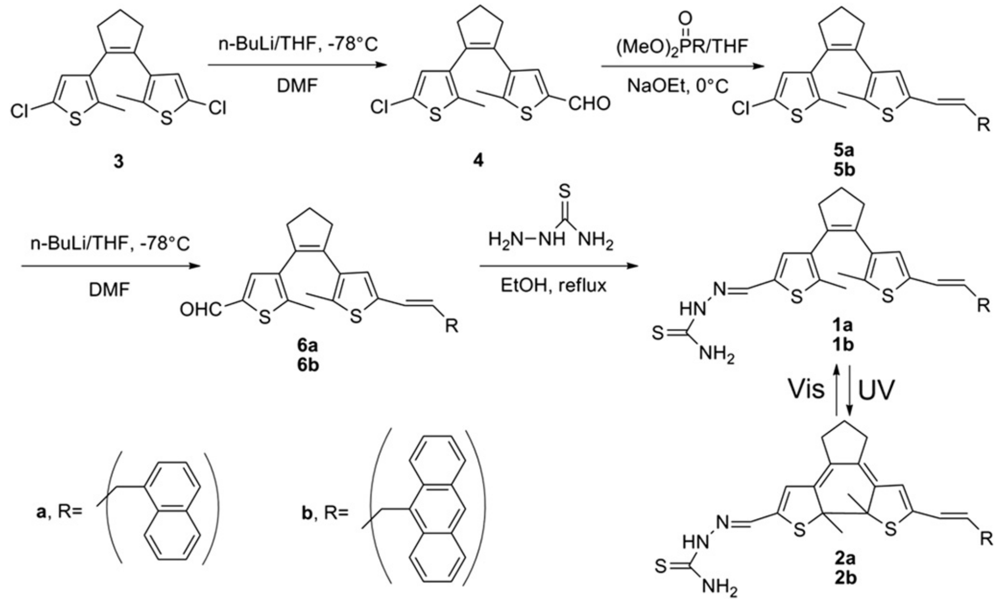

Scheme 1. Synthetic routine of photochromic chemosensors **1a** and **1b**.

makes **1a** and **1b** become fluorescent photochromic compounds and the absorption spectra of **2a** and **2b** (**1a** and **1b** in the photostationary state) are modulated by Hg^{2+} and F^- with sensitivity and selectivity, respectively.

2. Results and discussion

The syntheses of compounds **1a** and **1b** were given in Scheme 1. The structures of **1a**, **1b** and other intermediate products were confirmed by ^{1}H NMR, ^{13}C NMR, and HRMS (Figs. S8–28).

2.1. Photochromic properties of 1a and 1b

Under alternative illumination with ultraviolet and visible light, **1a** and **1b** exhibited photochromic properties in the solutions. Fig. 1 and Fig. S1 show the absorption and fluorescence spectra of the open forms (**1a** and **1b**) and closed forms (**2a** and **2b**) in CH_3CN, respectively. As seen from Fig. 1, upon irradiation with the light of 254 nm, a new absorption band centered at 600 nm appeared with the increase of irradiation time till the photostationary state (PSS) was reached meanwhile the fluorescence of **1a** was quenched completely, corresponding to the color change of the solution from colorless to blue, and indicating the formation of the closed isomer (**2a**). The fluorescence quenching by the closed form is attributed to the efficient energy transfer from the excited fluorophore core to the attached closed-ring BTE unit that has lower energy level.[32] Upon irradiation with visible light, the blue solution was bleached back to colorless solution, and the open-ring isomer (**1a**) was formed.

Analogous to **1a**, a new absorption band at 580 nm appeared and the fluorescence intensity decreased were also observed in the spectra of **1b** except more time (ca. 25 min, Fig. S1) required and the yellow solution turned to green upon irradiation with UV light (254 nm). The spectral and color changes were ascribed to the formation of **2b**.

In a sense, the energy transfer between the donor and acceptor units could be redirected by photochemical isomerization of the central 'switching' unit. In the open form, the BTE acted as a photophysically innocent bridging unit. In the closed form BTE acted to quench the emission of the fluorophore, thereby it modulated the luminescence output of the fluorophore unit.

2.2. Optical characteristics of 1a and 1b and their Hg^{2+} sensing abilities

The binding properties of **1a** and **1b** with Hg^{2+} were investigated by UV–vis absorption and fluorescence spectroscopy. In CH_3CN solution, **1a** and **1b** displayed a main absorption band at 350 nm and 348 nm. Addition of Hg^{2+} induced that the 350 nm band for **1a** and the 348 nm band for **1b** decreased significantly

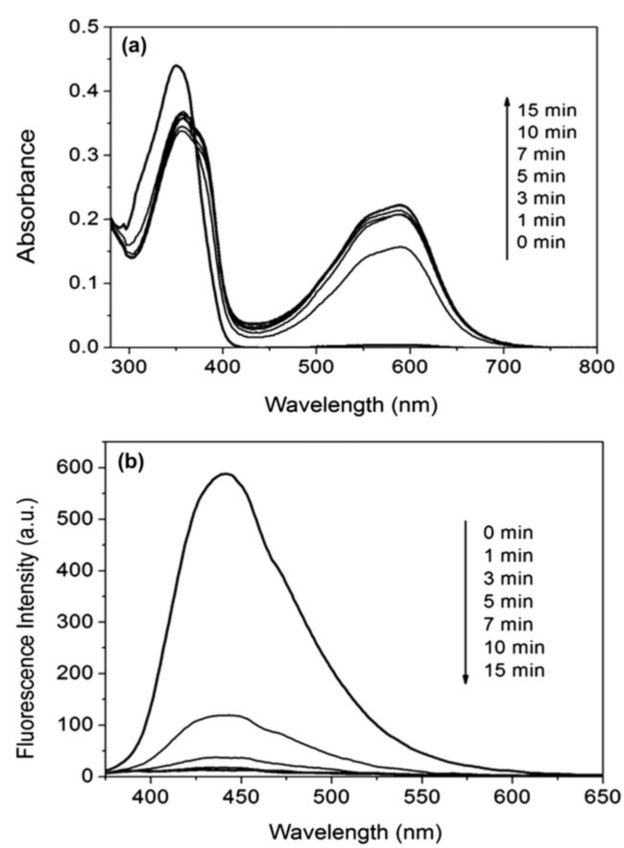

Fig. 1. Absorption changes (a) and fluorescence changes (b) of **1a** in CH_3CN (1.0×10^{-5} M) upon irradiation with 254 nm light.

along with a bathochromic shift about 9 nm from 350 nm to 359 nm for **1a** and a bathochromic shift about 21 nm from 348 nm to 369 nm for **1b** (Fig. 2a and Fig. S2a). An isosbestic point at 368 nm for **1a** and 365 nm for **1b** throughout the titration was attributed to the formation of **1a**–Hg^{2+} complex and **1b**–Hg^{2+} complex. Meanwhile the fluorescence of **1a** and **1b** was considerably quenched by Hg^{2+} (Fig. 2b and Fig. S2b).

metal ions at 442 nm and 511 nm, respectively) were measured upon the addition of 15 different metal ions. As depicted in Fig. 4a, **1a** showed complexation with some metal ions with high concentrations, such as Pb^{2+}, Cd^{2+}, Cu^{2+}, but no significant fluorescence change of **1a** occurred in the presence of these metal ions. These results demonstrated that compound **1a** exhibited specific selectivity for Hg^{2+} over other examined metal ions in CH_3CN

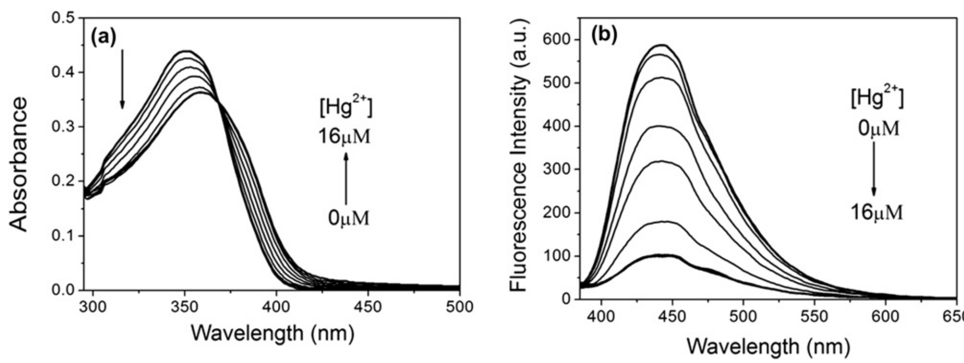

Fig. 2. (a) UV–vis spectra of **1a** (1.0×10^{-5} M) and Hg^{2+} ($0–1.6\times10^{-5}$ M) in CH_3CN at 25 °C. (b) Fluorescence titration of **1a** (1.0×10^{-5} M) with Hg^{2+} ($0–1.6\times10^{-5}$ M) in CH_3CN at 25 °C, λ_{ex}=350 nm.

By plotting the changes of **1a** in the absorbance intensity at 350 nm as a function of Hg^{2+} concentration, the curve was obtained and as shown in Fig. S3, it suggested a 1:1 binding mode between **1a** and Hg^{2+}. To gain an insight into the stoichiometry of the **1a**–Hg^{2+} complex, the method of continuous variations (Job's plot) was used (Fig. 3). As expected, when the molar fraction of **1a** was 0.50, the absorbance value approached a maximum, which demonstrated the formation of a 1:1 complex between **1a** and Hg^{2+}. From spectral changes of **1b**, it was plausible that **1b** also formed a 1:1 complex with Hg^{2+}. The detection limits valued as three times of the standard deviation of the background noise for Hg^{2+} with **1a** and **1b** were, respectively, estimated to be 1.0×10^{-6} M and 7.0×10^{-7} M under the present conditions, pointing to the high detection sensitivities.

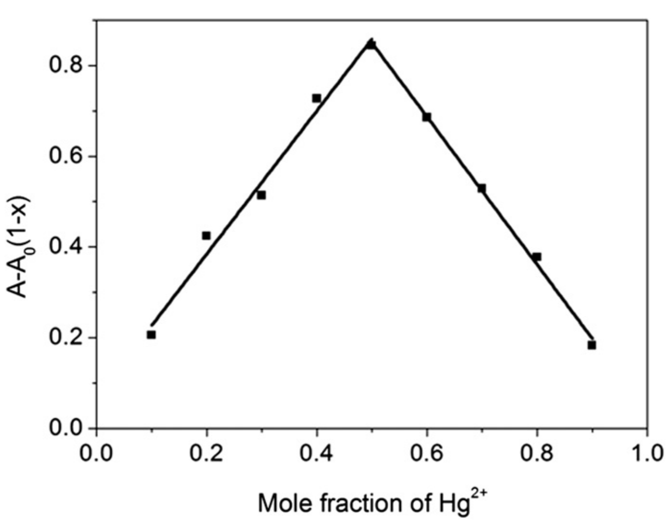

Fig. 3. Job's plot of **1a** and Hg^{2+}, A and A_0 are the absorbance value at 350 nm of **1a** in the presence and absence of Hg^{2+}, respectively, the total concentration of **1a** and Hg^{2+} is 1.0×10^{-4} M in CH_3CN at 25 °C.

An important feature of the sensor is its high selectivity toward analyte over other competitive species. The changes in the reduced ratio of fluorescence intensity $(I_0-I)/I_0$ (I and I_0 represent the fluorescence intensity of **1a** and **1b** in the presence and absence of

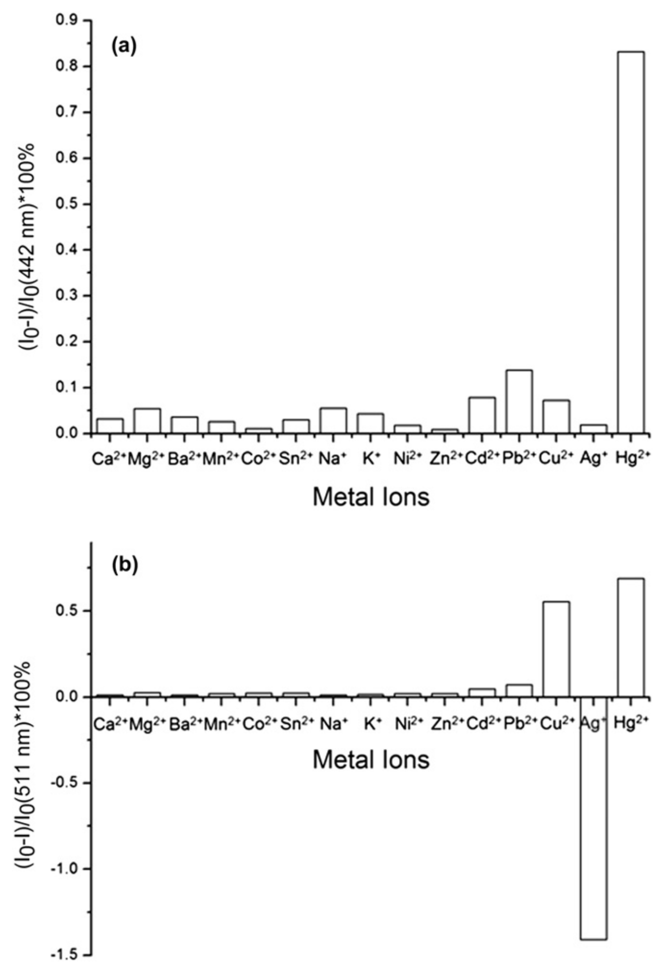

Fig. 4. Fluorescence intensity changes ($(I-I_0)/I_0\times100\%$) of **1a** (a) and **1b** (b) in the presence of various metal ions. [**1a**]=1.0×10^{-5} M, [**1b**]=1.0×10^{-5} M, [Hg^{2+}]=1.2×10^{-5} M, [Cu^{2+}]=2.0×10^{-5} M, [Ag^{+}]=2.0×10^{-5} M, [M^{n+}]=1.0×10^{-4} M in CH_3CN at 25 °C. Each spectrum was acquired 10 min after metal ions addition.

solution. Fig. 4b showed that **1b** response to Hg^{2+} was affected by 2 equiv of Cu^{2+} and surprisingly it was easy to distinguish Ag^{+}, which resulted in fluorescent enhancement from other metal ions. If the interference of Cu^{2+} was eliminated in advance, **1b** could be served as a fluorescent sensor for the detection of Hg^{2+} and Ag^{+}.

2.3. Optical characteristics of 1a and 1b and their F^{-} sensing abilities

In addition to cation binding properties, the sensing properties of **1a** and **1b** toward different anions (F^{-}, Cl^{-}, Br^{-}, I^{-}, NO_3^{-}, HSO_4^{-}, $H_2PO_4^{-}$, Ac^{-}, ClO_4^{-}) using tetrabutylammoniums counter cation were also investigated. Addition of F^{-} to the solution of **1a** induced that the 350 nm band decreased along with a bathochromic shift about 8 nm from 350 nm to 358 nm with an isosbestic point at 368 nm (Fig. 5a). With the addition of F^{-} (Fig. S4a), the UV–vis absorption of **1b** at 348 nm was diminished, whilst new peaks at 389 nm appeared with an isosbestic point at 366 nm. The fluorescence intensity of **1a** and **1b** was decreased with the increasing F^{-} concentration, meanwhile the spectral shape kept unchanged (Fig. 5b and Fig. S4b). The significant changes of the UV–vis and fluorescence spectra of **1a** and **1b** upon titration with F^{-} were attributed to the deprotonation of the thioamide protons, which resulted in the formation of an anion.

To elucidate the intermolecular interactions between compound **1a** and fluorine ion, ^{1}H NMR titration experiments were also carried out in $CDCl_3$ (Fig. 6). Upon the addition of 1 equiv F^{-}, the disappearance of thioamide N–H (δ=9.05) and H–N–H (δ=7.09) signals occured as a result of the deprotonation by F^{-}. In the meanwhile, large downfield shift of imine proton (Ha) was observed and there was no appreciable change in the chemical shift of imine proton with progressive addition of F^{-}. This would be due to the through bond effect of the hydrogen bond.[29] With the addition of F^{-} (1–10 equiv), the signal for proton (Hb) of thiophene, which attached to thiosemicarbazone shifted upfield gradually. These indicated that a structural change of **1a** could influence both the imide as well as thiophene protons.

The fluorescence intensity changes ($(I-I_0)/I_0\times100\%$) of **1a** and **1b** upon addition of anions were listed in Table S1. No remarkable fluorescence intensity changes were observed even in the presence of larger excess of hundred equivalents of the corresponding anions, which suggested the high selectivity of compounds **1a** and **1b** to F^{-} over other examined anions investigated.

2.4. Modulation of the photochromic properties of 2a and 2b by Hg^{2+} and F^{-}

The modulation of spectral properties of **2a** and **2b** upon addition of Hg^{2+} and F^{-} was recorded by UV–vis techniques. Fig. 7

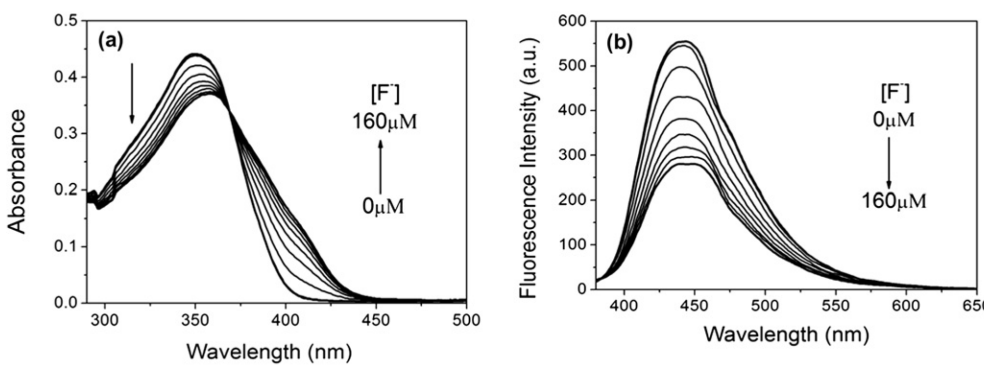

Fig. 5. (a) UV–vis spectra of **1a** (1.0×10^{-5} M) and F^{-} ($0–1.6\times10^{-4}$ M) in CH_3CN at 25 °C. (b) Fluorescence titration of **1a** (1.0×10^{-5} M) with F^{-} ($0–1.6\times10^{-4}$ M) in CH_3CN at 25 °C, λ_{ex}=350 nm.

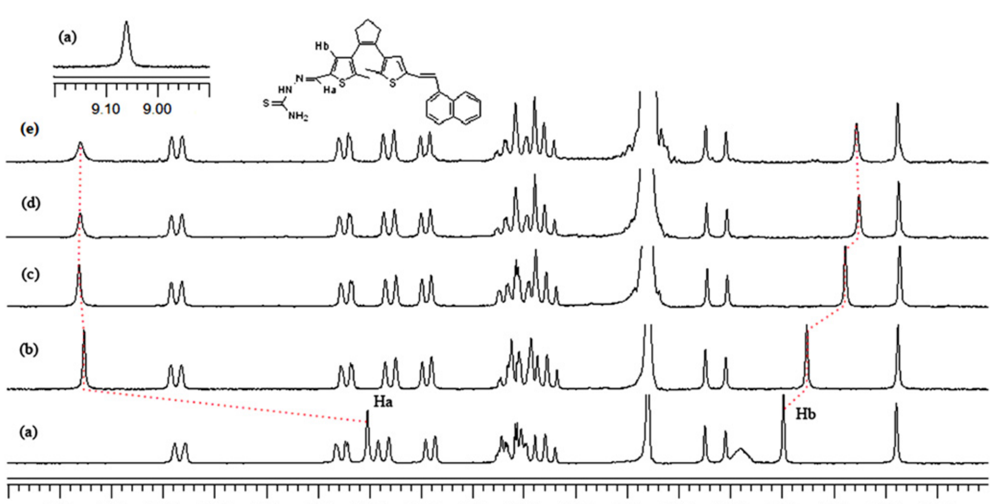

Fig. 6. Partial ^{1}H NMR (400 MHz) titrations of **1a** (5×10^{-3} M) in $CDCl_3$ at 25 °C with F^{-} (a) none; (b) 1 equiv; (c) 5 equiv; (d) 10 equiv; (e) 15 equiv.

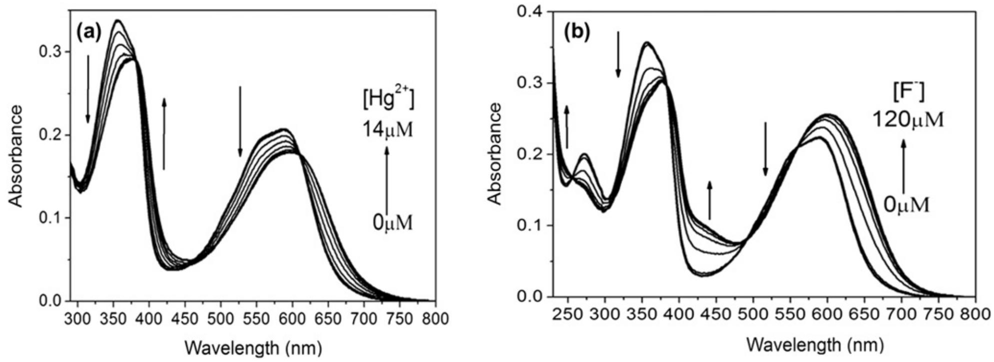

Fig. 7. Changes in UV–vis spectra of **2a** (1.0×10^{-5} M) upon addition of (a) Hg^{2+} ($0–1.4\times10^{-5}$ M) and (b) F^- ($0–1.2\times10^{-4}$ M) in CH_3CN at 25 °C.

displayed the changes in UV–vis absorption spectra of **2a** in CH_3CN solution with the addition of Hg^{2+} and F^-, respectively. Upon addition of 1.4 equiv of Hg^{2+}, the absorption maxima of **2a** were red-shifted from 583 nm to 600 nm indicating **2a**–Hg^{2+} complex formation. When 12 equiv of F^- were added to the solutions, the 583 nm band increased significantly along with a bathochromic shift about 18 nm. It demonstrated that F^- gave rise to the deprotonation of the thioamide proton.

Similarly, as presented in Fig. S5, the addition of increasing amounts of Hg^{2+} (0–1.2 equiv) to the solution of **2b** in CH_3CN resulted in decrease in absorption band at 570 nm and formation of new red-shifted absorption band at 588 nm. The presence of F^- induced the intensity of the absorption band at 570 nm increasing gradually accompanied with a bathochromic shift about 19 nm.

We also tested the absorption response of **2a** and **2b** to other metal ions such as Ca^{2+}, Mg^{2+}, Ba^{2+}, Mn^{2+}, Co^{2+}, Sn^{2+}, Na^+, K^+, Ni^+, Zn^{2+}, Cd^{2+}, Fe^{3+}, Pb^{2+}, Cu^{2+}, Ag^+ besides Hg^{2+} and as depicted in Fig. S6, no significant bathochromic shift of absorption maxima for **2a** and **2b** occurred in the presence of these metal ions except Hg^{2+}. Additionally, the selectivity of **2a** and **2b** toward different anions (F^-, Cl^-, Br^-, I^-, NO_3^-, HSO_4^-, $H_2PO_4^-$, Ac^-, ClO_4^-) using tetrabutylammoniums counter cation were investigated. It could be seen from Fig. S7 that only upon addition of F^- induced significant absorption changes of **2a** and **2b**. In generally, **2a** and **2b** could effectively detect Hg^{2+} and F^- in the presence of other common interfering metal ions and anions.

3. Conclusions

In summary, two structurally special yet efficient chemosensors, which own thiosemicarbazone as the recognition moiety coupled to naphthalene or anthracene through the dithienylcyclopentene acting as a bridging unit have been developed for sensing Hg^{2+} and F^- ions. Compounds **1a** and **1b** in ring-open form may be considered as potential bifunctional fluorescent sensors for Hg^{2+} and F^-. In addition, their spectral properties in ring-closed form (**2a** and **2b**) can be modulated by Hg^{2+} and F^-, respectively. The results provide a useful design strategy for developing the multi-functional sensor with photochromism.

4. Experimental

4.1. Materials and instrumentations

The synthesis of 1,2-bis(5-chloro-2-methyl-3-thienyl) cyclopentene (compound **3** shown in Scheme 1) was based on the literature method.[32,33] *n*-Butyl lithium (2.5 M solution in hexane) was purchased from Sigma–Aldrich and used without further purification. Other starting materials were commercially available and purified before use. All other reagents were of analytical purity and used without further treatment.

^{1}H NMR and ^{13}C NMR spectra in $CDCl_3$ were recorded on Brucker AM-400 spectrometers with tetramethylsilane (TMS) as the internal standard. Mass spectra (MS) were recorded on EI mass spectroscopy and ESI mass spectroscopy. UV–vis absorption spectra were performed on a Varian Cray 500 spectrophotometer and fluorescence spectra were recorded on a Varian Cray Eclipse fluorescence spectrophotometer; both spectrophotometers were standardized.

4.2. Synthesis of 1-(5-chloro-2-methyl-3-thienyl)-2-(5-formyl-2-methyl-3-thienyl)cyclopentene (4)

1,2-Bis(5-chloro-2-methylthien-3-yl)cyclopentene (1.645 g, 5 mmol) was dissolved in anhydrous THF (15 mL) and *n*-butyl lithium (2.00 mL of 2.5 M solution in hexane) was added dropwise under nitrogen at −78 °C using a syringe. The mixture was stirred for 30 min at −78 °C and then the reaction mixture was quenched with anhydrous dimethylformamide (1.93 mL). The mixture was stirred for an addition hour at room temperature, before it was poured into HCl (2 M, 15 mL). The mixture was extracted with ether. The organic layer was dried over $MgSO_4$, filtrated, and concentrated. The residue was purified by column chromatography (silica gel, CH_2Cl_2/petroleum ether 1:4) to give the compound **4** (0.97 g, 60.2%) as a red oil; ^{1}H NMR (400 MHz, $CDC1_3$) 1.84 (3H, s, $-CH_3$), 2.09 (5H, m, $-CH_3$, and $-CH_2-$), 2.77 (4H, m, $-CH_2-$), 6.57 (1H, s, thiophene-H), 7.43 (1H, s, thiophene-H), 9.74 (1H, s, −CHO); ^{13}C NMR (100 MHz, $CDCl_3$) 13.1, 14.4, 21.8, 37.3, 37.4, 124.6, 125.5, 132.3, 132.8, 133.5, 134.6, 136.4, 136.8, 138.9, 145.5, 181.5; HRMS (EI^+): M^+, found 322.0251. $C_{16}H_{15}ClOS_2$ requires 322.0253.

4.3. Synthesis of 1-(5-chloro-2-methyl-3-thienyl)-2-(5-(naphthalen-1-yl)vinyl- 2-methyl-3-thienyl)cyclopentene (5a)

A mixture of 1-chloromethyl naphthalene (0.624 g, 3.53 mmol) and trimethyl phosphite (0.875 g, 7.06 mmol) was refluxed under stirring for 5 h then concentrated under reduced pressure. After cooling to 0 °C, the solution of compound **4** (0.950 g, 2.95 mmol) and anhydrous THF (25 mL) was added under nitrogen using a syringe. Then sodium ethoxide (0.401 g, 5.90 mmol) was slowly added. The reaction mixture was stirred for an addition hour at 0 °C, before it was poured into icy water (150 mL). The mixture was extracted with ether. The organic layer was dried over $MgSO_4$, filtrated, and concentrated. The residue was purified by column chromatography (silica gel, petroleum ether) to give the compound **5a** (0.55 g, 41.8%) as a red oil; ^{1}H NMR (400 MHz, $CDC1_3$) 1.90 (3H, s, $-CH_3$), 2.00 (5H, m, $-CH_3$, and $-CH_2-$), 2.76 (4H, m, $-CH_2-$), 6.62 (1H, s, thiophene-H), 6.77 (1H, s, thiophene-H), 7.12 (1H, d, *J*

15.6 Hz, −CH=CH−), 7.48 (4H, m, naphthalene-H), 7.67 (1H, d, *J* 7.2 Hz, −CH=CH−), 7.75 (1H, d, *J* 8.0 Hz, naphthalene-H), 7.84 (1H, d, *J* 6.4 Hz, naphthalene-H), 8.17 (1H, d, *J* 8.0 Hz, naphthalene-H); ^{13}C NMR (100 MHz, $CDCl_3$) 14.3, 14.7, 22.9, 38.4, 38.5, 123.1, 123.7, 124.0, 124.7, 125.1, 125.7, 125.9, 126.1, 126.9, 127.7, 127.9, 128.6, 131.2, 133.3, 133.8, 133.9, 134.5, 134.6, 135.1, 135.2, 136.0, 139.1; HRMS (EI$^+$): M$^+$, found 446.0920. $C_{27}H_{23}ClS_2$ requires 446.0930.

4.4. Synthesis of 1-(5-formyl-2-methyl-3-thienyl)-2-(5-(naphthalen-1-yl)vinyl-2-methyl-3-thienyl)cyclopentene (6a)

Compound **5a** (0.420 g, 0.94 mmol) was dissolved in anhydrous THF (8 mL) and *n*-butyl lithium (0.49 mL of 2.5 M solution in hexane) was added dropwise under nitrogen at −78 °C using a syringe. The mixture was stirred for 30 min at −78 °C and then the reaction mixture was quenched with anhydrous dimethylformamide (0.22 mL). The mixture was stirred for an addition hour at room temperature, before it was poured into HCl (2 M, 10 mL). The mixture was extracted with ether. The organic layer was dried over $MgSO_4$, filtrated, and concentrated. The residue was purified by column chromatography (silica gel, CH_2Cl_2/petroleum ether 1:4) to give the compound **6a** (0.21 g, 50.8%) as a blue solid; ^{1}H NMR (400 MHz, $CDC1_3$) 1.96 (3H, s, $-CH_3$), 2.11 (5H, m, $-CH_3$, and $-CH_2-$), 2.82 (4H, m, $-CH_2-$), 6.77 (1H, s, thiophene-H), 7.12 (1H, d, *J* 16.0 Hz, −CH=CH−), 7.49 (5H, m, naphthalene-H, and thiophene-H), 7.68 (1H, d, *J* 7.2 Hz, −CH=CH−), 7.77 (1H, d, *J* 8.4 Hz, naphthalene-H), 7.85 (1H, d, *J* 7.6 Hz, naphthalene-H), 8.16 (1H, d, *J* 8.0 Hz, naphthalene-H), 9.75 (1H, s, −CHO); ^{13}C NMR (100 MHz, $CDCl_3$) 14.6, 15.6, 23.0, 29.7, 38.3, 38.5, 123.2, 123.6, 124.3, 124.5, 125.7, 125.9, 126.1, 127.4, 128.0, 128.6, 131.2, 133.2, 133.8, 134.5, 135.7, 136.3, 137.8, 138.1, 139.4, 139.8, 146.7, 182.6; HRMS (EI$^+$): M$^+$, found 440.1268. $C_{28}H_{24}OS_2$ requires 440.1269.

4.5. Synthesis of 1-(5-hydrazinecaibothioamide-2-methyl-3-thienyl)-2-(5-(naphthalen-1-yl)vinyl-2-methyl-3-thienyl) cyclopentene (1a)

A mixture of compound **6a** (0.100 g, 0.227 mmol) with thiosemibazide (0.021 g, 0.227 mmol) in ethanol (1.5 mL) was refluxed for 4 h. After cooling to room temperature, the green precipitates were collected by filtration and washed with cold ethanol. The crude product was purified by column chromatography (silica gel, CH_2Cl_2) to give the compound **1a** (0.082 g, 70.4%) as a green solid; ^{1}H NMR (400 MHz, $CDC1_3$) 1.98 (3H, s, $-CH_3$), 2.05 (5H, m, $-CH_3$, and $-CH_2-$), 2.80 (4H, m, $-CH_2-$), 6.78 (1H, s, thiophene-H), 7.00 (1H,s, thiophene-H), 7.09 (2H, s, $-NH_2$), 7.13 (1H, d, *J* 15.6 Hz, −CH=CH−), 7.49 (4H, m, naphthalene-H), 7.68 (1H, d, *J* 7.6 Hz, −CH=CH−), 7.77 (1H, d, *J* 8.0 Hz, naphthalene-H), 7.80 (1H, s, −CH=N−), 7.86 (1H, d, *J* 8.0 Hz, naphthalene-H), 8.17 (1H, d, *J* 8.0 Hz, naphthalene-H), 9.05 (1H, s, −NH−); ^{13}C NMR (100 MHz, $CDCl_3$) 14.6, 14.9, 22.9, 38.3, 38.4, 123.1, 123.6, 124.1, 124.6, 125.7, 125.8, 126.1, 127.6, 127.9, 128.6, 131.1, 132.9, 133.5, 133.7, 134.4, 134.5, 135.4, 135.9, 136.8, 138.8, 139.2, 139.5, 177.5; HRMS (ESI$^+$): MH$^+$, found 514.1468. $C_{29}H_{28}N_3S_3$ requires 514.1445.

4.6. Synthesis of 1-(5-chloro-2-methyl-3-thienyl)-2-(5-(anthracen-1-yl)vinyl-2-methyl-3-thienyl)cyclopentene (5b)

A mixture of 9-chloromethyl anthracene (0.717 g, 3.16 mmol) and trimethyl phosphite (0.784 g, 6.32 mmol) was refluxed under stirring for 7 h then concentrated under reduced pressure. After cooling to 0 °C, the solution of compound **4** (0.850 g, 2.64 mmol) and anhydrous THF (25 mL) was added under nitrogen using a syringe. Then sodium ethoxide (0.359 g, 5.28 mmol) was slowly added. The reaction mixture was stirred for an addition hour at 0 °C, before it was poured into icy water (120 mL). The mixture was extracted with ether. The organic layer was dried over $MgSO_4$, filtrated, and concentrated. The residue was purified by column chromatography (silica gel, petroleum ether) to give the compound **5b** (0.55 g, 41.8%) as a yellow solid; ^{1}H NMR (400 MHz, $CDC1_3$) 1.98 (3H, s, $-CH_3$), 2.04 (5H, m, $-CH_3$, and $-CH_2-$), 2.78 (4H, m, $-CH_2-$), 6.64 (1H, s, thiophene-H), 6.80 (1H, s, thiophene-H), 6.94 (1H, d, *J* 16.0 Hz, −CH=CH−), 7.47 (4H, m, anthracene-H), 7.59 (1H, d, *J* 16.4 Hz, −CH=CH−), 8.00 (2H, dd, *J* 6.4 Hz, anthracene-H), 8.35 (2H, dd, *J* 6.8 Hz, anthracene-H), 8.38 (1H, s, anthracene-H); ^{13}C NMR (100 MHz, $CDCl_3$) 14.4, 14.7, 22.9, 29.7, 38.4, 38.5, 123.1, 125.1, 125.2, 125.5, 126.0, 126.4, 126.9, 127.7, 128.7, 129.7, 130.4, 131.5, 132.3, 133.3, 133.9, 134.7, 135.1, 135.2, 136.0, 138.6; HRMS (EI$^+$): M$^+$, found 496.1070. $C_{31}H_{25}ClS_2$ requires 496.1086.

4.7. Synthesis of 1-(5-formyl-2-methyl-3-thienyl)-2-(5-(anthracen-1-yl)vinyl-2-methyl-3-thienyl)cyclopentene (6b)

Compound **5b** (0.520 g, 1.05 mmol) was dissolved in anhydrous THF (8 mL) and *n*-butyl lithium (0.54 mL of 2.5 M solution in hexane) was added dropwise under nitrogen at −78 °C using a syringe. The mixture was stirred for 30 min at −78 °C and then the reaction mixture was quenched with anhydrous dimethylformamide (0.41 mL). The mixture was stirred for an addition hour at room temperature, before it was poured into HCl (2 M, 12 mL). The mixture was extracted with ether. The organic layer was dried over $MgSO_4$, filtrated, and concentrated. The residue was purified by column chromatography (silica gel, CH_2Cl_2/petroleum ether 1:4) to give the compound **6b** (0.19 g, 36.9%) as a yellow solid; ^{1}H NMR (400 MHz, $CDC1_3$) 1.99 (3H, s, $-CH_3$), 2.11 (2H, m, $-CH_2-$), 2.18 (3H, s, $-CH_3$), 2.84 (4H, m, $-CH_2-$), 6.80 (1H, s, thiophene-H), 6.93 (1H, d, *J* 16.4 Hz, −CH=CH−), 7.48 (5H, m, anthracene-H, and thiophene-H), 7.60 (1H, d, *J* 16.4 Hz, −CH=CH−), 8.01 (2H, dd, *J* 6.4 Hz, anthracene-H), 8.33 (2H, dd, *J* 6.8 Hz, anthracene-H), 8.39 (1H, s, anthracene-H), 9.78 (1H, s, −CHO); ^{13}C NMR (100 MHz, $CDCl_3$) 14.6, 15.7, 23.0, 38.4, 38.6, 123.5, 125.2, 125.6, 125.9, 126.6, 127.5, 128.8, 129.7, 130.3, 131.5, 132.1, 133.3, 134.6, 135.7, 136.3, 137.8, 138.1, 139.0, 139.9, 146.6, 182.6; HRMS (EI$^+$): M$^+$, found 490.1413. $C_{32}H_{26}OS_2$ requires 490.1425.

4.8. Synthesis of 1-(5-hydrazinecaibothioamide-2-methyl-3-thienyl)-2-(5-(anthracen-9-yl)vinyl-2-methyl-3-thienyl) cyclopentene (1b)

A mixture of compound **6b** (0.089 g, 0.182 mmol) with thiosemibazide (0.017 g, 0.182 mmol) in ethanol (1.5 mL) was refluxed for 5 h. After cooling to room temperature, the yellow precipitates were collected by filtration and washed with cold ethanol. The crude product was purified by column chromatography (silica gel, CH_2Cl_2) to give the compound **1b** (0.051 g, 49.9%) as a yellow solid; ^{1}H NMR (400 MHz, $CDC1_3$) 2.01 (3H, s, $-CH_3$), 2.10 (5H, m, $-CH_3$, and $-CH_2-$), 2.81 (4H, m, $-CH_2-$), 6.79 (1H, s, thiophene-H), 6.93 (1H, d, *J* 16.0 Hz, −CH=CH−), 7.01 (1H,s, thiophene-H), 7.09 (2H, s, $-NH_2$), 7.48 (4H, m, anthracene-H), 7.59 (1H, d, *J* 16.0 Hz, −CH=CH−), 7.81 (1H, s, −CH=N−), 8.01 (2H, dd, *J* 6.4 Hz, anthracene-H), 8.33 (2H, dd, *J* 6.4 Hz, anthracene-H), 8.39 (1H, s, anthracene-H), 9.05 (1H, s, −NH−); ^{13}C NMR (100 MHz, $CDCl_3$) 14.7, 15.0, 23.0, 38.4, 38.5, 123.2, 125.2, 125.5, 126.0, 126.5, 127.7, 128.7, 129.7, 130.4, 131.5, 132.2, 133.0, 133.6, 133.8, 134.6, 135.4, 136.0, 136.8, 138.7, 139.0, 139.4, 177.4; HRMS (ESI$^+$): MH$^+$, found 564.1601. $C_{33}H_{30}N_3S_3$ requires 564.1602.

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Supplementary data

Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.12.019. These data include MOL files and InChIKeys of the most important compounds described in this article.

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