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Fluorescent and Colorimetric Probes for Mercury(II): Tunable Structures of Electron Donor and π-Conjugated Bridge

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Abstract: A new series of intramolecular-charge-transfer (ICT) molecules (compounds **1**, **2**, and **3**) were synthesized by attaching various electron-donating thiophenes groups to a triphenylamine backbone with an aldehyde group as the electron acceptor. Based on the protection reaction between ethanethiol and aldehyde, the corresponding dithioacetals (compounds **S1**, **S2**, and **S3**) were prepared to serve as novel colorimetric and fluorescent chemosensors for Hg^{2+} ions. Also, compound **S1** was further utilized to construct the chemical-reaction-based conjugated polymer probe (**PS1**) towards Hg^{2+} ions. In the presence of as little as 10 nM Hg^{2+}, compound **PS1** displayed an apparent change in the fluorescent intensity. The sensing processes were revealed to be mediated by ICT, as confirmed by time-dependent DFT calculations. Furthermore, compound **S1** was successfully applied to microscopic imaging for the detection of Hg^{2+} in HeLa cells with ratiometric fluorescent methods.

Keywords: charge transfer · colorimetry · fluorescence · mercury · sensors

Introduction

In recent years, the development of artificial detectors for the sensing and recognition of environmentally and biologically toxic metal ions has been actively investigated.[1] In this regard, the detection of mercury ions are especially important because both elemental and ionic mercury can be converted by bacteria in the environment into methyl mercury, which subsequently bioaccumulates through the food chain.[2] Thus, methods for selective and sensitive detection of mercury species have received a great deal of attention lately.[3] Thanks to the great efforts of scientists, a number of Hg^{2+} sensors have been developed with good performance, for example, redox, colorimetric, and fluorescent Hg^{2+} sensors by using proteins,[4] nucleic acids,[5] DNAs,[6] nanoparticles,[7] and several types of small molecules[8] as Hg^{2+} acceptors. In particular, the detection of mercury ions based on a specific chemical reaction between the sensor molecule and target species is a rapidly growing area owing to its high selectivity.[9] Indeed, many fluorescent chemodosimeters for Hg^{2+} ion selective detection have been designed on the basis of the mercury desulfurization reaction.[10] However, several significant challenges still exist in this field. For example, to drive these desulfurization reactions to completion, it is often necessary to use either elevated temperatures or excess quantities of Hg^{2+}. Herein, based on our previous work,[11] we report a series of new probes of Hg^{2+} ions with high sensitivity and selectivity based on the Hg^{2+}-promoted deprotection reaction of the dithioacetal; all of the probes displayed efficient chromo- and fluorogenic signaling towards Hg^{2+} ions at room temperature.

As we know, thiophenes are ideal building blocks to provide the basis for the synthesis of conjugated π systems for the following reasons: 1) the enormous and attractive potential of structural variation, which allows tuning of the electronic properties over a wide range; 2) their outstanding chemical and physical properties; and 3) the high polarizability of sulfur atoms in thiophene rings leads to a stabilization of the conjugated chain and to excellent charge-transport properties, which are one of the most crucial assets for applications in molecular design.[12]

With such considerations at the forefront, a new series of intramolecular-charge-transfer (ICT) molecules (compounds **1**, **2** and **3**; Scheme 1) were synthesized by attaching various electron-donating thiophenes groups to a triphenylamine backbone (**T1**) with an aldehyde group as the fixed electron acceptor. Based on the triphenylamine backbone, the ethylenedioxythiophene and thiophene moieties were introduced to enhance the efficiency of the donor to benefit the delocalization of the whole chromophore in compounds **1** and **2**, respectively (Scheme 1a and b). Then, we linked bithiophene moieties to the backbone to extend the length of π conjugation to prepare compound **3** (Scheme 1c). Based on the protection reaction between ethanethiol and aldehyde, the corresponding dithioacetals (compounds **S1**, **S2**, and **S3**)

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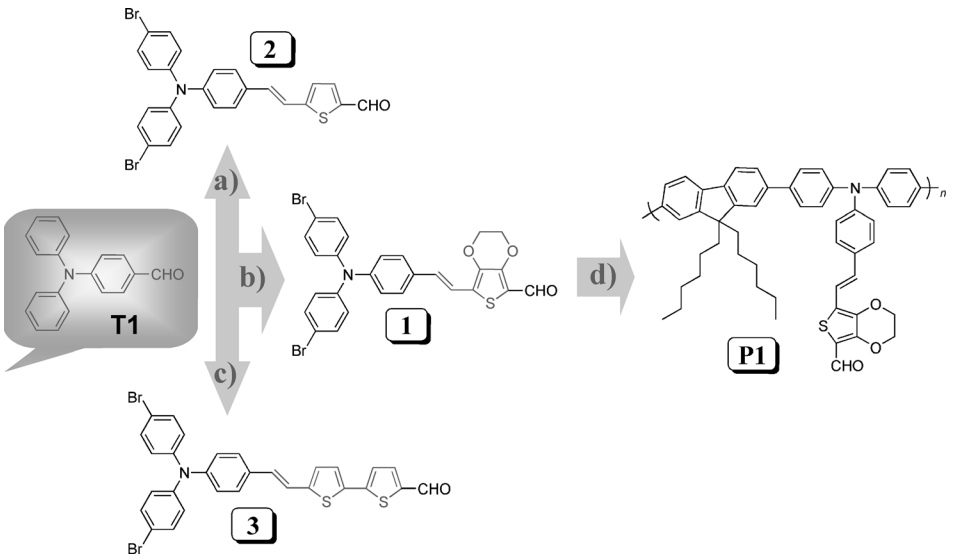


Scheme 1. Structures of the new series of ICT molecules: a) and b) to enhance the efficiency of the donor; c) to extend the length of π-conjugation; d) to construct the conjugated polymer probe.

were prepared to serve as novel dual-channel chemosensors for Hg^{2+} ions. Also, compound **1** was introduced into the conjugated polymer backbone (**P1**; Scheme 1 d) and further utilized to construct the chemical-reaction-based conjugated polymer probe (**PS1**) towards Hg^{2+} ions. Taking advantage of the distinct Hg^{2+}-promoted deprotection reaction of the dithioacetal, all of the probes displayed efficient chromo- and fluorogenic signaling towards Hg^{2+} ions at room temperature. Herein, we describe the synthesis and spectroscopic evaluation of all of the dual-channel chemsensors in detail.

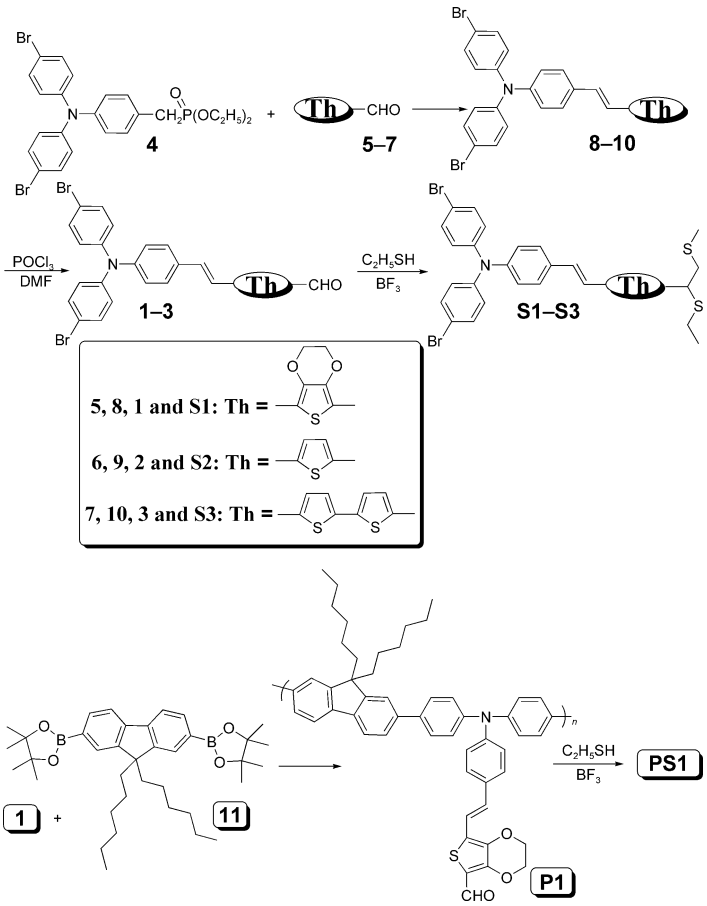
Results and Discussion

Synthesis and structural characterization: The general synthetic procedure is given in Scheme 2. The Wittig reaction of 2-formylthiophene and derivatives (**5**, **6**, or **7**) with diethyl {[4-(diphenylamino)benzyl]triphenyl}phosphonate (**4**) gave the corresponding triphenylamine vinyl thiophenes (**8**, **9**, or **10**). The followed Vilsmeier reaction of **8**, **9**, or **10** yielded the corresponding aldehyde **1**, **2**, or **3**, which was readily converted into dithioacetals **S1**, **S2**, or **S3** through a straightforward protection reaction between ethanethiol and aldehyde. By the Suzuki coupling reactions between **1** and **11**, compound **P1** was prepared and converted into dithioacetal **PS1** by the protection reaction of ethanethiol and aldehyde **P1**.

Compounds **S1**–**S3** exhibited good solubility in common organic solvents, such as chloroform, acetone, dichloromethane, and THF. Compound **PS1** exhibited good solubility in THF. They were characterized by spectroscopic methods and all gave satisfactory spectral data (see the Experimental Section).

The UV/Vis absorption maxima (λ_{abs}) and the maximum wavelength of fluorescent emission (λ_{em}) for the new ICT molecules in THF are summarized in Table 1. Different absorption and emission behavior of the aldehydes and resulting dithioacetals demonstrated changes in the electronic properties before and after the protection reaction between mercaptan and aldehydes, leading to different ICT efficiencies.

Hg^{2+} sensing properties: As demonstrated by the results given in Table 1, the maximum emission wavelength of **1** centered at about 525 nm. After the protection reaction, the maximum emission wavelength of the resulting dithioacetal **S1** shifted to 440 nm; the UV/Vis absorption maximum wavelength shifted from 422 to 385 nm. This indicated that, after the protection reaction of



Scheme 2. General procedure for the synthesis of **S1**–**S3** and **PS1**.

Table 1. Optical data for the sensor molecules.

	λ_{abs} [nm]	λ_{em} [nm]
1	422	525
2	353	538
3	354	580
P1	438	564
S1	385	440
S2	310	448
S3	310	497
PS1	393	462

the aldehyde, the electronic property of the aldehyde group changed, resulting in different fluorescent behavior due to different ICT efficiency. Then, we added Hg^{2+} ions to a dilute solution of dithioacetal **S1** and investigated its response to Hg^{2+} ions in THF in detail.

As shown in Figure 1, upon treatment with Hg^{2+} ions, the emission intensity of dithioacetal **S1** at 440 nm decreased immediately with the fluorescent intensity at 525 nm increasing. When the concentration of Hg^{2+} ions became higher, the emission spectra were more close to that of aldehyde **1** (emission maximum centered at about 525 nm). To see the sensing process more visually, we compared the intensities at different wavelengths, 525 and 440 nm; the obtained experimental results are summarized in Figure S1 in the Supporting Information. In fact, the fluorescence change for the solution of dithioacetal **S1** before and after the addition of Hg^{2+} ions could be easily distinguished by the naked eye (from blue to green), as shown in the inset of Figure 1. Furthermore, the fluorescent properties of dithioacetal **S1** at different concentrations (100 and 1 μM) towards Hg^{2+} ions were studied carefully to test the reproducibility of the sensing behavior of dithioacetal **S1** for Hg^{2+} ions, as demonstrated in Figures S2 and S3 in the Supporting Information. At a concentration of 1 μM, the fluorescent intensity of **S1** changed even at concentrations of Hg^{2+} ions as low as 2×10^{-6} mol L^{-1} (Figure S3 in the Supporting Information); this makes dithioacetal **S1** a highly sensitive ratiometric fluorescent probe for the detection of Hg^{2+}.

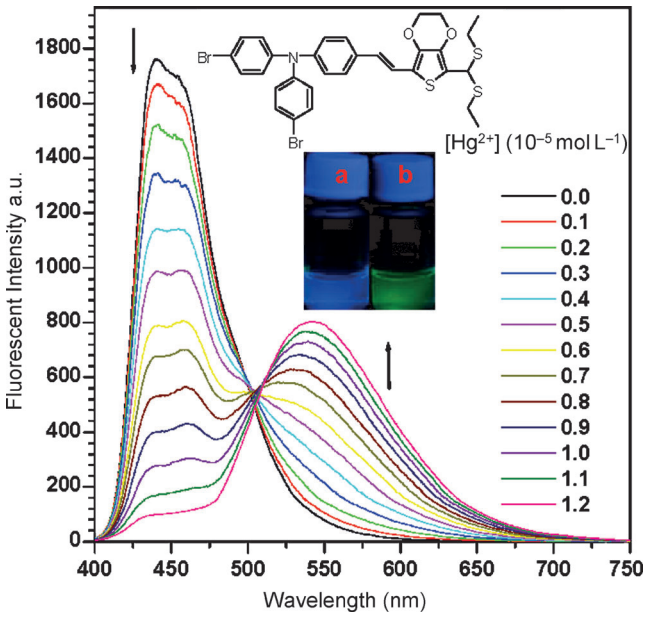


Figure 1. Fluorescent emission spectra of **S1** (10 μM) in the presence of increasing concentrations of Hg^{2+}. Inset: Fluorescence photograph of **S1** (10 μM; a), **S1**+Hg^{2+} (20 μM; b).

To evaluate the specific nature of dithioacetal **S1** towards Hg^{2+} ions, the influence of added trace water and other metal ions were investigated. As shown in Figure S4 in the Supporting Information, the intensity was nearly unchanged even upon the addition of relatively large amounts of water (50 μL), indicating this would not affect the results of the titration experiment. Figure 2 shows that, except slight influence from Fe^{3+}, for all other metal ions, including Mg^{2+}, Mn^{2+}, Zn^{2+}, Ni^{2+}, Pb^{2+}, Ba^{2+}, Ca^{2+}, Co^{2+}, Al^{3+}, Cu^{2+}, Cd^{2+}, Cr^{3+}, Fe^{2+}, Li^{+}, Na^{+}, and K^{+}, there were nearly no changes in the fluorescence spectra observed upon the addition of metal ions with concentrations of 50 μM, indicating that our probe had a selective response towards Hg^{2+} over other metal ions. As demonstrated by the images given in the inset of Figure 2, different sensing behavior could be easily seen by the naked eye under a normal UV lamp, realizing our thought of the design of new chemosensors towards Hg^{2+} ions based on the ITC mechanism and the Hg^{2+}-promoted deprotection reaction of dithioacetals.

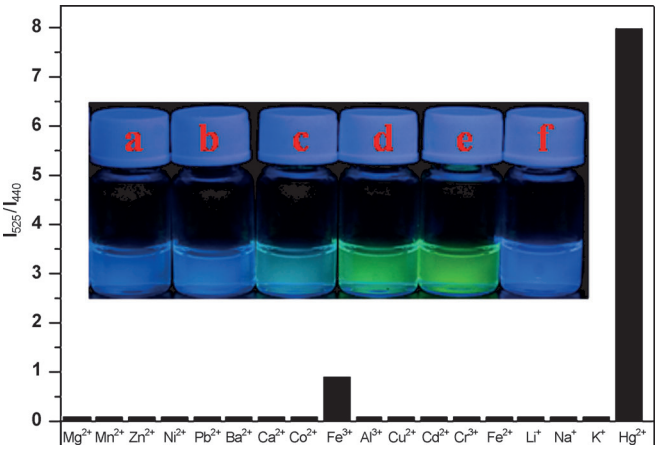


Figure 2. Fluorescence responses of **S1** (10 μM) to various metal ions ([Hg^{2+}]: 12 μM; other ions: 50 μM) in THF. Inset: Fluorescence photograph of **S1** (10 μM; a), **S1**+Hg^{2+} (2 μM; b), **S1**+Hg^{2+} (5 μM; c), **S1**+Hg^{2+} (10 μM; d), **S1**+Hg^{2+} (20 μM; e), and **S1**+a mixture of other metal ions (10 μM; f).

Recently, colorimetric sensors have been especially promising because the color change can be easily observed by the naked eye, thus less work and no equipment are required. Therefore, the colorimetric behavior of **S1** was also investigated under the same conditions. As shown in Figure 3, the apparent change in the absorption could be induced only upon the addition of Hg^{2+} ions, even at concentrations as low as 15 μM. With increasing Hg^{2+} concentrations, the typi-

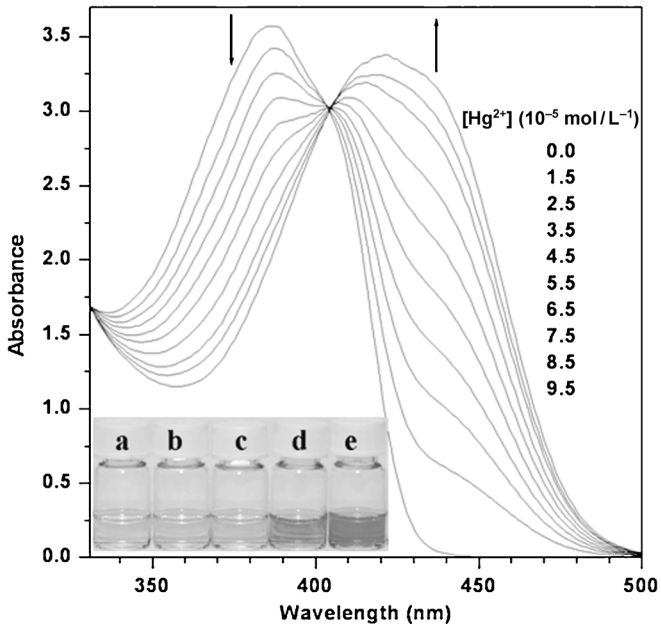


Figure 3. UV/Vis spectra of **S1** (10 μM) in the presence of increasing concentrations of Hg^{2+}. Inset: Photograph of **S1** (100 μM; a), **S1**+Hg^{2+} (5 μM; b), **S1**+Hg^{2+} (10 μM; c), **S1**+Hg^{2+} (50 μM; d), and **S1**+Hg^{2+} (100 μM; e).

cal strong absorption band of **S1** at 385 nm gradually decreased along with the appearance of a new absorption band centered at 422 nm, which was responsible for the color change (from colorless to yellow) and perceptible to the naked eye (the inset of Figure 3). Usually, the response time of the chemical-reaction-based sensor system was relatively slow; therefore, the reaction rate might have affected the experimental results. As a result, some time was needed to complete the reaction. However, in our case, both the fluorescent and colorimetric changes for the solution of dithioacetal **S1** occurred immediately upon the addition of Hg^{2+} ions by the virtue of the thiophilic properties of mercury.

As we reported previously,[11] although being less thiophilic than Hg^{2+} ions, Ag^{+} could also promote the deprotection reactions. Herein, we also investigated the sensing behavior of dithioacetal **S1** towards silver ions. As shown in Figures S5 and S6 in the Supporting Information, upon the addition of silver ions, the fluorescent and UV/Vis absorption spectra underwent the same changes as those observed in the case of Hg^{2+} titration experiments. The obtained results were unexpected, but important because dithioacetal **S1** could also be regarded as a good probe towards Ag^{+} ions, since it is also necessary to detect Ag^{+} ions due to strong toxicity towards humans and our environment.[13] The IR spectra of dithioacetal **S1** before and after the addition of Hg^{2+} and Ag^{+} ions could give some proof of this transformation. As shown in Figure S7 in the Supporting Information, no absorption peak centered at about 1665 cm^{-1} was observed in the IR spectrum of dithioacetal **S1**, in accordance with the absence of aldehyde groups. But after the addition of Hg^{2+} or Ag^{+} ions, a typical absorption peak of aldehyde groups at 1665 cm^{-1} appeared in the IR spectrum as a result of the reaction between **S1** and Hg^{2+} or Ag^{+} ions, and this spectrum was nearly the same as that of aldehyde **1**, proving the successful deprotection reaction of dithioacetal **S1**. All of the above experimental results suggested that our probe displayed both efficient fluoro- and chromogenic signaling towards Hg^{2+} ions and could serve as novel dual-channel chemosensors for Hg^{2+} ions.

To check the above experimental results from another aspect, we further designed and synthesized two other dithioacetals, compounds **S2** and **S3**, with similar molecular structures as dithioacetal **S1** (Scheme 2), in which the previous ethylenedioxythiophene moieties were replaced by thiophene and bithiophene ones, respectively. Figures S8–S24 in the Supporting Information demonstrated the fluorescent and colorimetric behavior of dithioacetals **S2** and **S3** in the presence and absence of Hg^{2+} and Ag^{+} ions. Similar to **S1**, dithioacetals **S2** and **S3** could give response to Hg^{2+} ions with relatively good performances. The IR spectra in Figures S14 and S24 in the Supporting Information also give some evidence about this transformation. Thus, the obtained experimental results for dithioacetals **S2** and **S3**, on one hand, further proved our idea for the development of good chemosensors towards Hg^{2+} ions, on the other hand, the results indicated that, after optimizing the structural design, more Hg^{2+} ions chemosensors with better performances could be obtained by using the Hg^{2+}-promoted deprotection reaction coupled with the ICT mechanism.

To date, conjugated polymers (CPs) have often been used as the optical platforms in sensitive chemical and biological sensors[14] because they exhibited signal amplification along the whole polymer backbone through the molecular wire effect. Due to this fact, interest in the development of conjugated polymeric sensors for the detection of Hg^{2+} ions increased and the reported examples demonstrated good performance.[15] Thus, we wondered that if it was possible to further increase the detecting sensitivity towards Hg^{2+} ions by introducing compound **1** to the backbone of CPs (**P1**). From this point, we designed and prepared a CP probe, **PS1**, through a similar synthetic procedure to those for dithioacetals **S1**–**S3** (Scheme 2).

Then, we tried to add Hg^{2+} to a dilute solution of **PS1** (Figures S25–S33 in the Supporting Information). Similarly to **S1**, the dilute solution of **PS1** also showed a ratiometric fluorescence response (Figure 4). With increasing concentrations of Hg^{2+}, the typical strong emission band of **PS1** at 462 nm gradually decreased along with the appearance of a new emission band centered at 564 nm, which was responsible for the fluorescent color change and was perceptible to the naked eye under a normal UV lamp. By comparing the fluorescent intensity of **PS1** (1 μM) and **S1** (1 μM) in the presence of different concentrations of Hg^{2+}, it was clear that **PS1** had a much higher sensitivity towards Hg^{2+} than **S1**. As shown in Figure 4 and Figure S3a in the Supporting Information, with the same concentrations of Hg^{2+} ions (1.6 μM), the fluorescent intensity of **PS1** at 462 nm decreased by 52% of the original one, whereas that of **S1** at

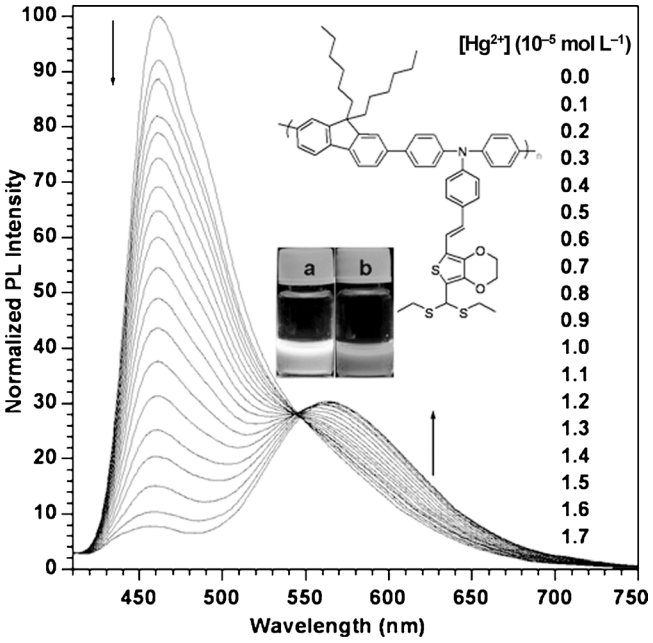


Figure 4. Fluorescent emission spectra of **PS1** (1 μM) in the presence of increasing concentrations of Hg^{2+}. Inset: Fluorescence photograph of **PS1** (10 μM; a) and **PS1**+Hg^{2+} (2 μM; b).

440 nm decreased by only 15%. Furthermore, compound **PS1** still responded to Hg^{2+} ions with a concentration of 0.1 μM, whereas **S1** did not. From Figure S27 in the Supporting Information, the detection limit of **PS1** towards Hg^{2+} could be determined as 10 nM, which was much lower than that of **S1** (2 μM; Figure S3 in the Supporting Information). All of the results indicated that the molecular wire effect of the CPs did work and offered the CPs excellent sensing performances relative to the corresponding monomer, **S1**. From the UV/Vis spectra (Figures S31 and S32 in the Supporting Information), it was confirmed that the Hg^{2+}-promoted deprotection reaction of dithioacetal **PS1** occurred as expected. The possible influence of water and the Hg^{2+} ion selective nature of **PS1** were also investigated carefully. Similar to dithioacetal **S1**, additional water did not cause big changes in the fluorescent intensity (Figure S32 in the Supporting Information), which would be negligible. However, compound **PS1** could still give a response to Ag^{+} ions (Figures S28 and S31 in the Supporting Information), although other metal ions had little effect on its sensing behavior towards Hg^{2+} ions (Figure S33 in the Supporting Information). These results further confirmed the phenomena observed above, and demonstrated that the probes reported herein were dual ones for both Hg^{2+} and Ag^{+} ions.

Theoretical calculations: To get an insight into the molecular structure and the different fluorescence and absorption behavior before and after the protection/deprotection reaction, DFT calculations were carried out at the B3LYP/6-31G(d) level by using the Gaussian 09 program.[16] The calculated HOMOs and LUMOs of compounds **1**–**3**, **S1**–**S3** and **T1** are illustrated in Figure 5. The HOMOs of compounds

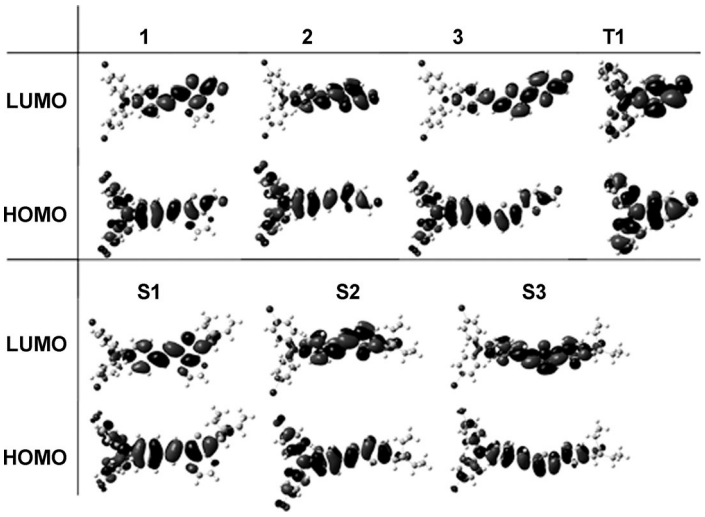


Figure 5. Frontier molecular orbitals optimized at the B3LYP/6-31G* level of theory.

1–**3** primarily resided on the electron-donating triphenylamine and the conjugated thiophene rings with low coefficients on the electron-withdrawing aldehyde group. The LUMOs were mainly located on the electron-withdrawing aldehyde groups due to the contribution of the π^* orbitals of the aldehyde group to the LUMOs of compounds **1**–**3.** Thus, the relatively well-separated distribution between HOMO and LUMO indicated substantial charge transfer from the donor moiety to the acceptor one when the molecules were excited. In terms of compound **T1**, the separation between HOMO and LUMO was not so clear, relative to **1**–**3**, resulting in lower ICT efficiency. Therefore, the extent of ICT can be enhanced by extending the length of π conjugation or by using a stronger donor. This result supported our prior hypothesis that the introduction of ethylenedioxythiophene and thiophene moieties enhanced the efficiency of the donor and benefitted charge transfer of the whole chromophore.

Cyclic voltammetry (CV) was employed to estimate the HOMO and LUMO energy levels of the sensor molecules. The CV curves are shown in Figure S34 in the Supporting Information, with the corresponding data summarized in Table 2. All reported potentials were calibrated against the ferrocene/ferrocenium (Fc/Fc^{+}) couple, which was used as

Table 2. Electrochemical properties of sensor molecules.[a]

	HOMO[b] [eV]	LUMO [eV]	E_g^{opt}
1	−5.20 (−5.20)	−2.62 (−2.21)	2.58 (2.99)
2	−5.27 (−5.35)	−2.73 (−2.45)	2.53 (2.90)
3	−5.18 (−5.21)	−2.73 (−2.59)	2.45 (2.62)
T1	−5.44 (−5.34)	−1.79 (−1.47)	3.65 (3.87)
S1	−5.04 (−4.92)	−2.14 (−1.67)	2.90 (3.25)
S2	−5.04 (−5.11)	−2.11 (−1.83)	2.93 (3.28)
S3	−5.06 (−5.00)	−2.34 (−2.11)	2.72 (2.89)

[a] The corresponding calculated values are given in parentheses for comparison. [b] HOMO = $-(E_{ox}^{onset}+4.71)$ eV, LUMO = E_g^{opt} + HOMO. The optical band gap (E_g^{opt}) was obtained from the empirical formula $E_g = 1240/\lambda_{edge}$.

the internal standard. The HOMO levels were obtained corresponding to the initial onset oxidation potential of the chromophores, according to the empirical equation $(E)_{HOMO} = -(E_{ox}^{onset} + 4.71)$ eV, and their LUMO energies were estimated from the optical band gaps and HOMO energies. Furthermore, we could still obtain some information from Table 2, although there were some discrepancies existed between the calculation and experimental results. Taking **1** and **S1**, for example, the corresponding energy gaps between HOMO and LUMO were calculated to be 2.99 and 3.25 eV for **1** and **S1**, respectively, which were in agreement with the remarkable redshift in both luminescence and absorption spectra of **1** compared with that of **S1**, leading to the different optical behaviors before and after the addition of Hg^{2+} ions. Similar results could be obtained from the experimental values. This was reasonable. From the LUMOs, it was clear that ICT took place through a conjugated bridge between the electron donor moieties and aldehyde groups in compounds **1**–**3**, whereas this was clearly prohibited in dithioacetals **S1**–**S3** due to the saturated bridge (−C−S−) after the reaction with ethanethiol.

Cell imaging: The application of probe **S1** to track intracellular Hg^{2+} levels was also investigated by scanning microscopy. As shown in Figure 6, the **S1**-loaded cells showed intracellular fluorescence at an emission channel collected at wavelengths longer than 455 nm, indicating that probe **S1** could penetrate the cell membrane and potentially be used for imaging of Hg^{2+} in living cells and in vivo. When the cells were treated with a 200 μM aqueous solution of $Hg(ClO)_2$ for 30 min, followed by subsequent staining with **S1** (100 μM, 0.5 h), and then washing three times with phosphate-buffered saline (PBS; 10 mM, pH 7.12), the intensity of the emission collected at the wavelength longer than 455 nm decreased, whereas the intensity of the emission collected at wavelengths longer than 520 nm increased. Accordingly, the green and blue fluorescence images of **S1** and **S1**+Hg^{2+} were monitored and the mean green to blue intensities (FG/FB) were found in ratios of 0.36 and 6.09, respectively. These were consistent with the observations in titration experiments and demonstrated that probe **S1** could readily detect the Hg^{2+} ions in cells with ratiometric fluorescent methods.

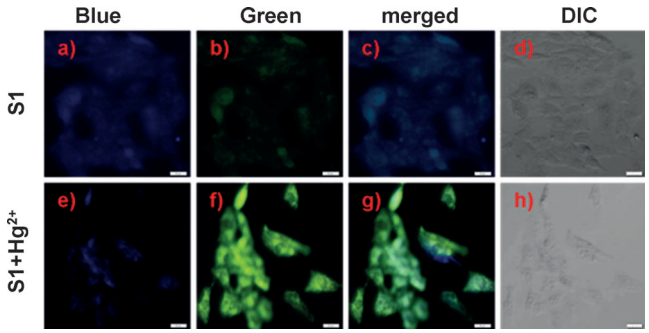


Figure 6. Scanning microscopic images of HeLa cells incubated with **S1** and **S1** upon treatment of Hg^{2+}.

By taking advantage of the distinct Hg^{2+}-promoted deprotection reaction of the dithioacetal, all of the probes displayed efficient chromo- and fluorogenic signaling towards Hg^{2+} ions at room temperature. Moreover, more Hg^{2+} ion chemosensors with better performances could be obtained by simply adjusting and optimizing the chemical structure.

Conclusion

A series of ICT molecules (compounds **1**, **2**, **3**, and **P1**) were synthesized by attaching various electron-donating thiophenes groups to a triphenylamine backbone with an aldehyde group as the electron acceptor. Based on the protection reaction between ethanethiol and aldehyde, the corresponding dithioacetals (compound **S1**, **S2**, **S3**, and **PS1**) were prepared to serve as novel dual-channel chemosensors for Hg^{2+} ions. All probes displayed high sensitivity and selectivity for Hg^{2+} with respect to several common alkali, alkaline earth, and transition-metal ions. In addition, DFT calculations were carried out at the B3LYP/6-31G(d) level to investigate different fluorescence and absorption behavior before and after the addition of Hg^{2+} ions. Probe **S1** was successfully applied to the microscopic imaging for detection of Hg^{2+} in HeLa cells with ratiometric fluorescent methods.

Experimental Section

Materials and instrumentations: The ^1H and ^{13}C NMR spectra were measured on a Varian Mercury300 spectrometer with tetramethylsilane (TMS; $\delta = 0$ ppm) as an internal standard. The FTIR spectra were recorded on a PerkinElmer-2 spectrometer in the region of 3000–400 cm^{-1} on NaCl pellets. UV/Vis spectra were obtained by using a Shimadzu UV-2550 spectrometer. Photoluminescence spectra were performed on a Hitachi F-4500 fluorescence spectrophotometer. Gel permeation chromatography (GPC) was used to determine the molecular weights of the polymers. GPC analysis was performed on an Agilent 1100 series HPLC system and a G1362A refractive index detector. Polystyrene standards were used as calibration standards for GPC. THF was used as an eluent and the flow rate was 1.0 mL min^{-1}. HR-ESI-TOF mass spectra were recorded on a Waters Micromass LCT Premier XE. CV was carried out on a CHI voltammetric analyzer in a three-electrode cell with a Pt counter electrode, a Ag/AgCl reference electrode, and a glassy carbon working electrode at a scan rate of 10 mV s^{-1} with 0.1 M tetrabutylammonium perchlorate (purchased from Alfa Aesar) as the supporting electrolyte in anhydrous dichloromethane purged with nitrogen. The potential values obtained in reference to the Ag/Ag^+ electrode were converted to values versus the saturated calomel electrode (SCE) by means of an internal Fc^+/Fc standard. Fluorescence cell imaging was performed with an OLYMPUS IX71 scanning microscope. Emission of **S1**-loaded cells was collected at 400–410 nm and 460–490 nm for blue and green channels, respectively. The data for ratio fluorescence imaging were analyzed by using software package provided by OLYMPUS instruments. Immediately before the experiments, cells were washed with PBS and then incubated with 100 μM **S1** in PBS/DMSO (10/1, v/v) for 30 min. Cell imaging was then carried out after washing the cells with PBS. Dichloromethane was dried over and distilled from CaH_2 under an atmosphere of dry nitrogen. THF was dried over and distilled from K–Na alloy under an atmosphere

of dry nitrogen. All other reagents were used as purchased. Compounds **4**, **5**–**7**, and **11** were synthesized according to literature procedures.[17]

General procedure for the synthesis of compounds 1–3: Compound **8**, **9**, or **10** (1 equiv) was dissolved in $ClCH_2CH_2Cl$ then $POCl_3$ (2.7 equiv) in DMF was added dropwise to the mixture at 0°C. After the temperature rose to room temperature, the reaction was heated to 45°C. After cooling, the mixture was poured in an ice bath with stirring and later neutralized with sodium carbonate. The solution was filtered and the crude product was purified by column chromatography on silica gel to afford the resulting powder.

Synthesis of 1: Compound **8** (1.14 g, 2.0 mmol), DMF (1 mL, 13.0 mmol), $POCl_3$ (0.5 mL, 5.35 mmol), and $ClCH_2CH_2Cl$ (50 mL) were used in the general procedure. Petroleum ether/$CHCl_3$ (1:1, v/v) was used as the eluent to obtain **1** as a salmon pink powder (1.00 g, 83.7%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.89 (s, 1H; -CHO), 7.38–7.35 (m, 8H; Ar-H), 7.05–7.01 (m, 2H; -CH=CH-), 6.98–6.95 (m, 4H; Ar-H), 4.38–4.37 ppm (m, 4H; $-CH_2-CH_2-$); ^{13}C NMR ($CDCl_3$): δ = 179.5, 148.9, 147.3, 146.2, 138.7, 132.7, 131.4, 131.0, 128.6, 128.2, 126.2, 123.7, 116.5, 116.3, 115.5, 65.6, 64.8 ppm.

Synthesis of 2: Compound **9** (0.51 g, 1.0 mmol), DMF (0.5 mL, 6.5 mmol), $POCl_3$ (0.25 mL, 2.7 mmol), and $ClCH_2CH_2Cl$ (25 mL) were used in the general procedure. Petroleum ether/$CHCl_3$ (1:1, v/v) was used as the eluent to obtain **2** as an orange–red powder (0.30 g, 56%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.87 (s, 1H; -CHO), 7.67 (d, 1H; Ar-H), 7.40–7.38 (m, 6H; Ar-H), 7.13 (d, 1H; Ar-H), 7.11 (d, 2H; -CH=CH-), 7.03 (d, 2H; Ar-H), 6.98–7.01 ppm (m, 4H; Ar-H); ^{13}C NMR ($CDCl_3$): δ = 186.5, 156. 8, 151.4, 149.9, 145.3, 141.4, 136.6, 136.2, 134.7, 132.1, 130.2, 130.1, 127.5, 123.6, 120.4 ppm.

Synthesis of 3: Compound **10** (0.59 g, 1.0 mmol), DMF (1 mL, 13.0 mmol), $POCl_3$ (0.37 mL, 4.04 mmol), and $ClCH_2CH_2Cl$ (50 mL) were used in the general procedure. Petroleum ether/$CHCl_3$ (1:2, v/v) was used as the eluent to obtain **3** as a salmon pink powder (0.36 g, 58%).^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.86 (s, 1H; -CHO), 7.68–7.67 (m, 2H; Ar-H), 7.38–7.35 (m, 6H; Ar-H), 7.25–7.23 (m, 2H; $-CH_2-$),7.06–6.92 ppm (m, 8H; Ar-H); ^{13}C NMR ($CDCl_3$): δ = 182.7, 146.3, 137.7, 132.7, 129.3, 127.8, 127.3, 126.1, 124.0, 120.2, 116.3 ppm.

General procedure for the synthesis of compounds S1–S3: Under an atmosphere of argon, compound **1**, **2**, or **3** (1 equiv) and ethanethiol (2.5 equiv) were dissolved in dry dichloromethane with $BF_3{\cdot}Et_2O$ (3 equiv) as the Lewis acid. After being stirred at 0°C overnight, 0.1 mol L^{-1} aqueous $NaHCO_3$ was added to adjust the pH value of the solution to 8–9. The final product was extracted with diethyl ether and purified by column chromatography to afford the target compounds.

Synthesis of S1: Compound **1** (0.122 g, 0.2 mmol), ethanethiol (0.037 mL, 0.5 mmol), $BF_3{\cdot}Et_2O$ (0.072 mL, 0.6 mmol), and CH_2Cl_2 (10 mL) were used in the general procedure. Petroleum ether/$CHCl_3$ (1:1, v/v) was used as the eluent to obtain **S1** as a yellow solid (0.12 g, 86.7%).^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29–7.19 (m, 8H; Ar-H), 6.92–6.87 (m, 6H; Ar-H), 5.25 (s, 1H; -CH-), 4.20 (brs, 4H; $-CH_2-CH_2-$), 2.64–2.59 (m, 4H; $-CH_2-$), 1.21 ppm (t, 6H; $-CH_3$); ^{13}C NMR ($CDCl_3$): δ = 146.5, 138.4, 132.6, 127.4, 125.8, 124.4, 117.1, 115.9, 65.1, 43.0, 26.9, 14.5 ppm: HRMS (ESI-TOF): *m*/*z* calcd for $C_{31}H_{29}Br_2NO_2S_3$ $[M+H]^+$: 701.9805; found: 701.9826.

Synthesis of S2: Compound **2** (0.18 g, 0.2 mmol), ethanethiol (0.037 mL, 0.5 mmol), $BF_3{\cdot}Et_2O$ (0.072 mL, 0.6 mmol), and CH_2Cl_2 (10 mL) were used in the general procedure. Petroleum ether/$CHCl_3$ (1:1, v/v) was used as the eluent to obtain **S1** as a yellow solid (0.05 g, 40.7%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47–7.41 (m, 4H; Ar-H), 7.31–7.28 (m, 4H; Ar-H), 6.95–6.87 (m, 8H; Ar-H), 4.84 (s, 1H; -CH-), 2.63–2.60 (m, 4H; $-CH_2-$), 1.25–1.18 ppm (m, 6H; $-CH_3$); ^{13}C NMR ($CDCl_3$): δ = 146.7, 146.2, 139.3, 138.8, 133.2, 132.7, 127.6, 126.0, 125.3, 124.6, 117.2, 115.5, 65.3, 42.6, 26.5; HRMS (ESI-TOF): *m*/*z* calcd for $C_{29}H_{27}Br_2NS_3$ $[M+H]^+$: 643.9751; found: 643.9739.

Synthesis of S3: Compound **3** (0.062 g, 0.1 mmol), ethanethiol (0.02 mL, 0.25 mmol), $BF_3{\cdot}Et_2O$ (0.036 mL, 0.3 mmol), and CH_2Cl_2 (5 mL) were used in the general procedure. Petroleum ether/$CHCl_3$ (1:1, v/v) was used as the eluent to obtain **S1** as a yellow solid (0.025 g, 34.7%).^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39–7.38 (m, 4H; Ar-H), 7.38–7.36 (m, 2H; Ar-H), 7.34–7.30 (m, 4H; Ar-H), 7.08–6.98 (m, 8H; Ar-H), 4.92 (s, 1H; -CH-), 2.76–2.56 (m, 4H; $-CH_2-$), 1.36–1.26 (m, 6H; $-CH_3$); ^{13}C NMR ($CDCl_3$): δ = 145.7, 144.2, 137.3, 135.6, 132.0, 130.6, 126.7, 126.0, 125.6, 124.1, 121.0, 120.5, 119.7, 117.6, 113.7, 109.5, 60.3, 40.6, 21.1 ppm; HRMS (ESI-TOF): *m*/*z* calcd for $C_{33}H_{29}Br_2NS_4$ $[M+H]^+$: 725.9628; found: 725.9655.

Synthesis of P1: Compound **1** (179.2 mg, 0.3 mmol) and **11** (175.93 mg, 0.3 mmol) were placed in a round-bottomed flask. A mixture of a 1.5 M aqueous solution of K_2CO_3 (2 mL) and toluene (11 mL) were added to the flask and the reaction mixture was degassed. The mixture was heated at reflux with vigorous stirring for 3 d under a nitrogen atmosphere. After the mixture was cooled to room temperature, it was poured into methanol (200 mL). The precipitated material was recovered by filtration through a funnel. The resulting solid material was washed with acetone to remove oligomers and catalyst residues. Compound **P1** was obtained as a yellow solid (0.151 g, 65.2%). M_n = 5000, M_w = 7400, M_w/M_n = 1.48 (GPC, polystyrene calibration); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.89 (s, 1H; -CHO), 7.76 (brs, 4H, Ar-H), 7.65 (brs, 8H, Ar-H), 7.41 (brs, 4H, Ar-H), 7.19 (brs, 2H, Ar-H), 7.10 (brs, 2H, Ar-H), 4.38 (brs, 4H, $-CH_2-$), 2.05 (brs, 4H, $-CH_2-$), 1.25 (brs, 4H, $-CH_2-$), 1.07 (brs, 12H, $-CH_3$), 0.76 ppm (brs, 6H, $-CH_3$).

Synthesis of PS1: Under an atmosphere of argon, compound P**1** (0.04 g, 0.05 mmol) and ethanethiol (0.02 mL, 0.25 mmol) were dissolved in dry THF (3 mL) with $BF_3{\cdot}Et_2O$ (0.036 mL, 0.3 mmol) as the Lewis acid. After being stirred at 0°C overnight, the resulting mixture was then poured into methanol (200 mL). The precipitate was collected by filtration and then washed with methanol and acetone three times to remove oligomers. Compound **PS1** was obtained as a yellow solid (0.035 g, 79.5%). M_n = 6400, M_w = 10000, M_w/M_n = 1.56 (GPC, polystyrene calibration); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74 (brs, 6H, Ar-H), 7.58 (brs, 4H, Ar-H), 7.25 (brs, 2H, Ar-H), 7.05 (brs, 4H, Ar-H), 6.78 (brs, 2H, Ar-H), 6.66 (brs, 2H, Ar-H), 5.31 (s, 1H, -CH-),4.38 (brs, 8H, $-CH_2-$), 2.68 (brs, 4H, $-CH_2-$), 2.15 (brs, 8H, $-CH_2-$), 1.61 (brs, 6H, $-CH_2-$), 1.24 (brs, 6H, $-CH_3$), 0.86 ppm (brs, 6H, $-CH_3$).

Preparation of solutions of metal ions: Each inorganic salt (1 mmol; $NaNO_3$, KNO_3, LiCl, $Ba(NO_3)_2$, $AgNO_3$, $Cr(NO_3)_3{\cdot}9H_2O$, $CoCl_2{\cdot}6H_2O$, $Ca(NO_3)_2{\cdot}4H_2O$, $Pb(NO_3)_2$, $Ni(NO_3)_2{\cdot}6H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, $MnSO_4{\cdot}2H_2O$, $CdSO_4){\cdot}8H_2O$, $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$, $MgSO_4$, or $Hg(ClO_4)_2{\cdot}3H_2O$) was dissolved in distilled water (10 mL) to afford a 1×10^{-1} mol L^{-1} aqueous solution. The stock solutions were diluted to desired concentrations with water when required.

Fluorescence titration of S1–S3 or PS1 with Hg^{2+} ions: A solution of **S1**–**S3** or **PS1** (1×10^{-5} mol L^{-1}) was prepared in THF. The solution of Hg^{2+} (1×10^{-3} mol L^{-1}) was prepared in distilled water. A solution of **S1**–**S3** or **PS1** (3.0 mL) was placed in a quartz cell (10.0 mm width) and the fluorescence spectrum was recorded. The Hg^{2+} ion solution was introduced in portions and fluorescence intensity changes were recorded at room temperature each time.

Fluorescence intensity changes of S1–S3 or PS1 with different metal ions: A solution of **S1–S3** or **PS1** (1×10^{-5} mol L^{-1}) was prepared in THF. The solutions of metal ions (1×10^{-1} mol L^{-1}) were prepared in distilled water. A solution of **S1**–**S3** or **PS1** (3.0 mL) was placed in a quartz cell (10.0 mm width) and the fluorescence spectrum was recorded. Different ion solutions were introduced and the changes of the fluorescence intensity were recorded at room temperature each time.

UV absorption changes of S1–S3 or PS1 by Hg^{2+} ions: A solution of **S1**–**S3** or **PS1** (1.0×10^{-5} mol L^{-1}) was prepared in THF. The solution of Hg^{2+} (1×10^{-3} mol L^{-1}) was prepared in distilled water. A solution of **S1**–**S3** or **PS1** (3.0 mL) was placed in a quartz cell (10.0 mm width) and the absorption spectrum was recorded. The Hg^{2+} ion solution was introduced in portions and absorption changes were recorded at room temperature each time.

UV absorption changes of S1–S3 or PS1 by different metal ions: A solution of **S1**–**S3** or **PS1** (1×10^{-5} mol L^{-1}) was prepared in THF. The solutions of metal ions (1×10^{-1} mol L^{-1}) were prepared in distilled water. A solution of **S1**–**S3** or **PS1** (3.0 mL) was placed in a quartz cell (10.0 mm

width) and the absorption spectrum was recorded. Different ion solutions were introduced and the changes of the absorption changes were recorded at room temperature each time.

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