

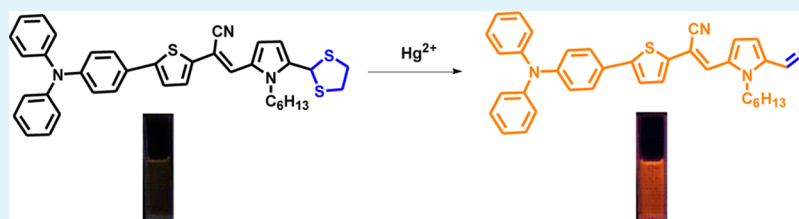
“Turn-On” Fluorescent Probe for Mercury(II): High Selectivity and Sensitivity and New Design Approach by the Adjustment of the π -Bridge

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S Supporting Information



ABSTRACT: By intelligent design, a new “turn-on” fluorescent probe (1-CN) was obtained based on the deprotection reaction of the dithioacetal promoted by Hg^{2+} ions, which could sense mercury ions sensitively and selectively, with the detection limit of 8×10^{-7} M. Thanks to the apparent turn-on signal, 1-CN has been successfully applied to rapidly detect trace amounts of mercury ions as test strips and cell image.

KEYWORDS: “turn-on” fluorescent probe, mercury ions, deprotection of thioacetals, structural modification, test strips, cell imaging

INTRODUCTION

Mercury ions (Hg^{2+}) is recognized as a detrimental neurological toxin, since they could block the groups containing sulphhydryl moieties (-SH) in enzymes and proteins.^{1–6} Once converted to methylmercury by bacteria in the environment, it will cause many different kinds of diseases in the central nervous system, brain, and kidney, as the result of the dysfunction of cells.^{7–12} In contrast to traditional analytical methods,^{13,14} including nuclear magnetic resonance (NMR), electron paramagnetic resonance (EPR), and atomic spectroscopy, with the limitation of complex instruments and procedures, those rapid and facile Hg^{2+} -sensing systems, such as colorimetric, fluorescent, and redox sensors, have been exploited with increasing interest, based on proteins,^{15–20} nucleic acids,^{21–23} DNAs,^{24–28} nanoparticles,^{29–32} conjugated polymers,^{33–38} and different small molecules.^{39–44} In particular, the chemodosimeter system according to a specific chemical reaction occurring in the target species and dosimeter molecule, is much more attractive, which exhibits the sensitive and selective signaling with negligible background. Actually, lots of fluorescent chemodosimeters have been reported for the selective detection of Hg^{2+} ions on the basis of the deprotection reaction of the dithioacetal promoted by Hg^{2+} ions.^{45–50} However, most of the fluorescent sensors were of the “turn-off” type, derived from the quenching nature of mercury ions,^{51,52} while most of the present “turn-on” ones suffered from the long response time (~ 0.5 h), relatively bad selectivity, or some other

shortcomings. Thus, the design of “turn-on” fluorescent sensors, which could probe mercury ions rapidly and selectively with high quantum yields, remains a challenge.

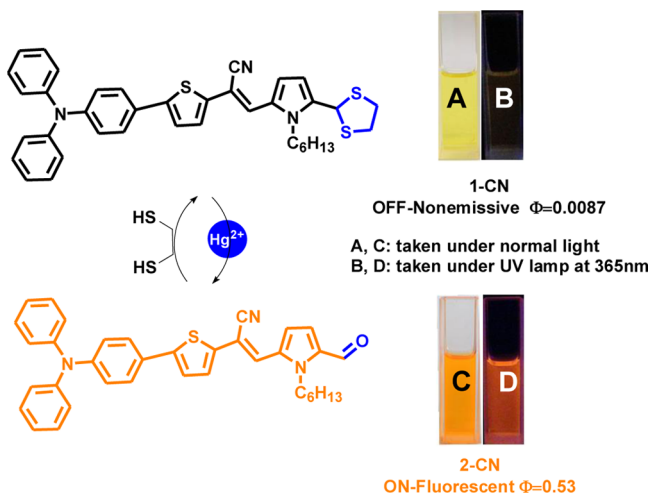
On the basis of the deprotection reaction of the dithioacetal promoted by Hg^{2+} ions, some chemodosimeters, with the donor- π -acceptor structure (D- π -A), were developed by Kim et al. and us,^{53–57} which exhibited a “turn-off”, ratiometric fluorescent changes or colorimetric response. According to this idea, Guo and co-workers have successfully obtained a “turn-on” one, but its quantum yield was too low (0.0053).⁵⁸ Considering that the fluorescent property of a D- π -A molecule was heavily dependent on its structure, some good “turn-on” probes should be achieved by carefully adjusting the molecular structure. Fortunately, by introducing a weak withdrawing cyano group on the π -bridge, we have constructed such a chemodosimeter (1-CN, Scheme 1), which was nonemissive with a very low quantum yield of 0.0087. Upon the addition of trace mercury ions, the resultant 2-CN gave a strong orange-red emission with much higher quantum yield of 0.53. For comparison, their analogues without cyano groups (1 and 2) were also prepared. Herein, we present their synthesis, characterization, sensing behavior, and practical applications in cell image and test strips in detail.

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Scheme 1. "Turn-On" Sensing Mechanism of 1-CN



MATERIALS AND INSTRUMENTATION

Dichloromethane, under an atmosphere of dry nitrogen, was first dried over CaH_2 and then distilled before use. Tetrahydrofuran (THF), under an atmosphere of dry nitrogen, was dried over K–Na alloy for several hours and then distilled before use. All inorganic salts ($\text{Hg}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{CdSO}_4 \cdot 2\text{H}_2\text{O}$, LiCl , KNO_3 , AgNO_3 , $\text{Ba}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, NaNO_3 , $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{MnSO}_4 \cdot 2\text{H}_2\text{O}$, and MgSO_4) were purchased and used without purification (Shanghai Chemical Reagent Co., Shanghai of China). All other reagents and solvents were of analytical grade, and they were purchased directly from Sigma-Aldrich Chemical Co. To get the aqueous solution (1×10^{-2} mol/L) of each inorganic salt, 1 mmol was weighted and dissolved in 10 mL of distilled water. The obtained stock solutions, before use, were diluted to required concentrations when needed.

The ^{13}C and ^1H NMR spectra were conducted, with tetramethylsilane (TMS; $\delta = 0$ ppm) as an internal standard, on a Varian Mercury 300 spectrometer. PerkinElmer-2 spectrometer was utilized to measure the FTIR spectra in the region of $3000\text{--}400\text{ cm}^{-1}$ by using NaCl pellets. UV/vis spectra could be conducted on a Shimadzu UV-2550 spectrometer, while photoluminescence (PL) spectra were measured on a fluorescence spectrophotometer (Hitachi F-4600). A Waters Micromass LCT Premier XE was used to record the high-resolution-electrospray ionization-time-of-flight (HR-ESI-TOF) mass spectra, and a CHI voltammetric analyzer was utilized to test CV in a three-electrode cell, in which the three electrodes were a Pt counter electrode, a Ag/AgCl reference electrode, and a glassy carbon working electrode. The scan rate was 10 mV s^{-1} , and 0.1 M tetrabutylammonium perchlorate (Alfa Aesar), in anhydrous dichloromethane, acted as the supporting electrolyte, and the experiments were conducted under an atmosphere of nitrogen. By means of an internal Fc^+/Fc standard, the obtained potential values versus the Ag/Ag $^+$ electrode could be converted to values in the reference to the saturated calomel electrode (SCE).

Synthesis of Compound 3a. Compound 6 (936 mg, 3 mmol) and compound 5 59 (538 mg, 3 mmol) were dissolved in THF (24 mL), then potassium tertbutoxide (505 mg, 4.5 mmol) was added at room temperature. The reaction mixture was stirred for 6 h at 25 °C. After removal of THF by a rotary evaporator, dichloromethane was added to dissolve the residue. Then, the resultant solution was washed with water for several times and dried over sodium sulfate. Finally, the obtained solid was isolated and purified by chromatography on silica gel, and in the process, the mixture of petroleum ether and ethyl acetate (25:1, v/v) was used as the eluent. Compound 3a was an orange oil (906 mg, 88%). ^1H NMR (300 MHz, CDCl_3) (ppm): 6.92–6.91 (d, 1H), 6.88–6.83 (d, 1H), 6.70–6.69 (d, 1H), 6.67–6.61

(d, 2H), 6.45–6.44 (d, 1H), 6.15–6.13 (t, 1H), 3.93–3.88 (t, 2H), 1.74–1.70 (t, 2H), 1.30–1.24 (t, 6H), 0.88–0.86 (d, 3H). ^{13}C NMR (75 MHz, CDCl_3) (ppm): 13.80, 22.30, 26.15, 31.16, 46.61, 106.71, 108.17, 109.21, 117.00, 117.79, 122.66, 124.66, 129.92, 130.14, 144.94.

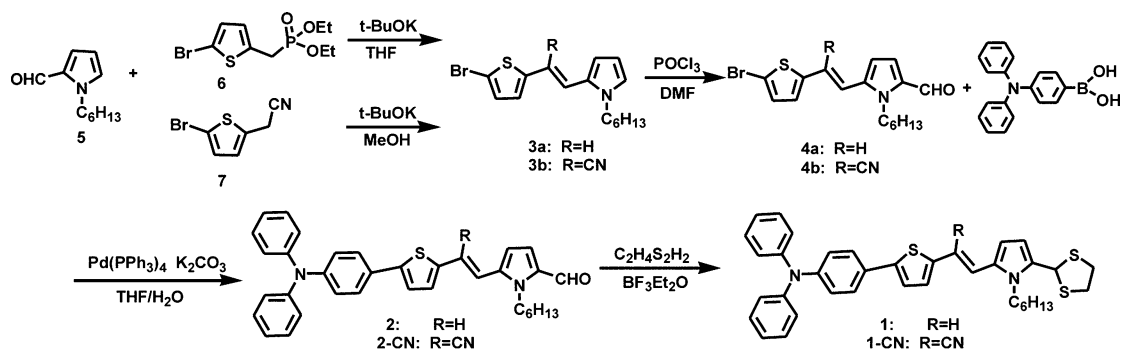
Synthesis of Compound 3b. Compound 7 60 (2.43 g, 12 mmol) and compound 5 (1.79 g, 10 mmol) were dissolved in methyl alcohol (30 mL), then potassium tertbutoxide (2.25 g, 20 mmol) was added at room temperature. The reaction mixture was stirred for 6 h at 25 °C. After removal of methyl alcohol by a rotary evaporator, dichloromethane was added to dissolve the residue. Then, the resultant solution was washed with water for several times and dried over sodium sulfate. Finally, the obtained solid was isolated and purified by chromatography on silica gel, and in the process, the mixture of petroleum ether and ethyl acetate (20:1, v/v) was used as the eluent. Compound 3b was a yellow oil (2.57, 70.7%). ^1H NMR (300 MHz, CDCl_3) (ppm): 7.41–7.42 (d, $J = 3.0$ Hz, 1H), 7.04 (s, 1H), 7.00 (s, 2H), 6.85–6.86 (d, $J = 3.0$ Hz, 1H), 6.29–6.31 (t, $J = 3.0$ Hz, 1H), 3.94–3.99 (t, $J = 9.0$ Hz, 2H), 1.73–1.75 (d, $J = 6.0$ Hz, 2H), 1.30 (s, 6H), 0.87–0.89 (d, $J = 6.0$ Hz, 3H).

Synthesis of Compound 4a. Compound 3a (671 mg, 2 mmol) was dissolved in $\text{ClCH}_2\text{CH}_2\text{Cl}$ (25 mL), then POCl_3 (613 mg, 4 mmol) in DMF (293 mg, 4 mmol) was added to the above mixture at 0 °C dropwise. After stirred for half an hour, the reacting temperature was raised to room temperature, then the reaction mixture was heated to 80 °C and stirred overnight. After this, the reaction was stopped. After cooling, the resultant reaction mixture was poured in the mixture of ice and water with stirring and later neutralized with K_2CO_3 . After filtration, the obtained solid was purified by column chromatography (silica gel). Petroleum ether/ethyl acetate (15:1, v/v) was used as the eluent to afford compound 4a as a yellow solid (481 mg, 66%). ^1H NMR (300 MHz, CDCl_3) (ppm): 9.46 (s, 1H), 7.13–7.08 (d, 1H), 6.98–6.97 (d, 1H), 6.91–6.89 (d, 1H), 6.84–6.83 (d, 1H), 6.68–6.63 (d, 1H), 6.52–6.50 (d, 1H), 4.44–4.39 (t, 2H), 1.72–1.68 (t, 2H), 1.31 (s, 6H), 0.90–0.86 (t, 3H). ^{13}C NMR (75 MHz, CDCl_3) (ppm): 14.16, 22.68, 26.31, 31.49, 45.05, 108.08, 112.35, 115.03, 124.84, 125.24, 127.43, 130.89, 132.30, 140.04, 143.81, 178.61.

Synthesis of Compound 4b. Compound 3b (1.53 g, 4.2 mmol) was dissolved in $\text{ClCH}_2\text{CH}_2\text{Cl}$ (20 mL), then POCl_3 (0.6 mL, 6.3 mmol) in DMF was slowly added to the above mixture at 0 °C dropwise. After stirring for half an hour, the reacting temperature was raised to room temperature, then the reaction mixture was heated to 80 °C and stirred overnight. After this, the reaction was stopped. After cooling, the resultant reaction mixture was poured in the mixture of ice and water with stirring and later neutralized with K_2CO_3 . After filtration, the obtained solid was purified by column chromatography (silica gel). Petroleum ether/dichloromethane (1/3, v/v) was used as the eluent to afford compound 4b as a yellow solid (1.65 g, 72%). ^1H NMR (300 MHz, CDCl_3) (ppm): 9.62 (s, 1H), 7.37–3.38 (d, $J = 3.0$ Hz, 1H), 7.14–7.15 (d, $J = 3.0$ Hz, 1H), 7.06–7.07 (d, $J = 3.0$ Hz, 1H), 7.01–7.02 (t, $J = 3.0$ Hz, 1H), 4.43–4.48 (t, $J = 6.0$ Hz, 2H), 1.70 (s, 2H), 1.32 (s, 6H), 0.89 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) (ppm): 14.13, 22.66, 26.36, 31.48, 31.77, 45.08, 105.67, 113.66, 113.97, 116.15, 124.68, 127.92, 131.50, 133.65, 134.73, 135.08, 140.20, 180.00.

Synthesis of Compound 2. Compound 4a (365 mg, 1 mmol), 4-(diphenyl-amino) phenylboronic acid (347 mg, 1.2 mmol), and K_2CO_3 (553 mg, 4 mmol) were added in the mixture of dry THF (20 mL) and degassed H_2O (5 mL), with the presence of $\text{Pd}(\text{PPh}_3)_4$ as catalyst. The resultant mixture was stirred at 80 °C overnight, then cooled to room temperature, and extracted several times by using CHCl_3 as the solvent. The chloroform layer was combined. Finally, the obtained solid was isolated and purified by chromatography on silica gel, and in the process, the mixture of petroleum ether and ethyl acetate (15:1, v/v) was used as the eluent. Compound 2 was a light yellow solid (516 mg, 97%). ^1H NMR (300 MHz, CDCl_3) (ppm): 9.45 (s, 1H), 7.48–7.45 (d, 2H), 7.30–7.23 (q, 4H), 7.20–7.17 (d, 1H), 7.13–7.11 (d, 5H), 7.07–7.03 (q, 6H), 6.92–6.90 (d, 1H), 6.75–6.70 (d, 1H), 6.53–6.52 (d, 1H), 4.47–4.42 (t, 2H), 1.73–1.71 (d, 2H), 1.32–1.23 (t, 6H), 0.90–0.88 (d, 2H). ^{13}C NMR (75 MHz, CDCl_3) (ppm): 14.27, 22.77, 26.43, 31.52, 45.19, 108.05, 113.98,

Scheme 2. Synthetic Route to 1 and 1-CN



121.86, 123.02, 123.52, 124.90, 125.69, 126.11, 126.67, 127.88, 129.04, 129.23, 129.60, 132.19, 140.71, 141.02, 144.43, 147.52, 147.89, 178.58. Anal. Calcd for $C_{35}H_{34}N_2OS$: C 79.21, H 6.46, N 5.28, O 3.01, S 6.04. Found: C 79.19, H 6.444, N 5.213, S 6.146. MS (ESI): m/z 530.23; found, 530.20.

Synthesis of Compound 1. Dry dichloromethane (12 mL) was added to dissolve compound 2 (265 mg, 0.5 mmol) and 1,2-ethanedithiol (94 mg, 1 mmol), under an atmosphere of dry argon, then $BF_3 \cdot Et_2O$ (36 mg, 0.25 mmol) was added as the Lewis acid. The resultant mixture was stirred for 3 h at 0 °C, then its pH value was adjusted to 8–9 by adding the aqueous solution of $NaHCO_3$ (0.1 mol/L). After this, dichloromethane was added to extract the organic compounds several times, and the dichloromethane layer was combined together. Finally, the obtained solid was isolated and purified by chromatography on silica gel, and in the process, the mixture of petroleum ether and ethyl acetate (25:1, v/v) was used as the eluent. Compound 1 was a brown solid (67 mg, 22%). 1H NMR (300 MHz, $CDCl_3$) (ppm): 0.90–0.92 (d, 3H), 1.43 (m, 4H), 1.78–1.83 (t, 4H), 3.35–3.49 (m, 4H), 3.52–3.56 (t, 2H), 5.70 (s, 1H), 6.52–6.54 (d, 1H), 7.06–7.16 (m, 11H), 7.20–7.21 (d, 1H), 7.28–7.34 (m, 4H), 7.43–7.46 (d, 3H). MS (ESI): m/z 606.22; found, 606.20.

Synthesis of Compound 2-CN. Compound 4b (265 mg, 0.68 mmol), 4-(diphenylamino) phenylboronic acid (303 mg, 0.82 mmol), and K_2CO_3 (376 mg, 2.72 mmol) were added in the mixture of dry THF (13 mL) and degassed H_2O (3 mL), with the presence of $Pd(PPh_3)_4$ as catalyst. The resultant mixture was stirred at 80 °C overnight, then cooled to room temperature, and extracted several times by using $CHCl_3$ as the solvent. The chloroform layer was combined. Finally, the obtained solid was isolated and purified by chromatography on silica gel, and in the process, the mixture of petroleum ether and dichloromethane (1:5, v/v) was used as the eluent. Compound 2-CN was a dark red solid (362 mg, 96%). 1H NMR (300 MHz, $CDCl_3$) (ppm): 0.88–0.90 (d, 3H), 1.33 (s, 6H), 1.73 (s, 2H), 4.46–4.50 (t, 2H), 7.01 (d, 1H), 7.05–7.10 (t, 4H), 7.12–7.14 (d, 5H), 7.18–7.20 (d, 1H), 7.29–7.31 (d, 4H), 7.33–7.35 (d, 1H), 7.36–7.38 (d, 1H), 7.44–7.47 (d, 2H), 9.61 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) (ppm): 14.59, 23.06, 26.76, 31.85, 32.08, 45.43, 107.13, 113.66, 116.95, 123.34, 123.57, 124.14, 125.43, 127.12, 129.67, 129.98, 133.76, 135.79, 137.45, 146.33, 147.62, 148.73, 180.17. HRMS (ESI-TOF): m/z calcd for $C_{36}H_{33}N_3OS$ [$M + H$] $^+$, 556.2423; found, 556.2427.

Synthesis of Compound 1-CN. Dry dichloromethane (8 mL) was added to dissolve compound 2-CN (278 mg, 0.5 mmol) and 1,2-ethanedithiol (95 mg, 1 mmol), under an atmosphere of dry argon, then $BF_3 \cdot Et_2O$ (36 mg, 0.25 mmol) was added as the Lewis acid. The resultant mixture was stirred for 3 h at 0 °C, then its pH value was adjusted to 8–9 by adding the aqueous solution of $NaHCO_3$ (0.1 mol/L). After this, dichloromethane was added to extract the organic compounds for several times, and the dichloromethane layer was combined together. Finally, the obtained solid was isolated and purified by chromatography on silica gel, and in the process, the mixture of petroleum ether and dichloromethane (3:2, v/v) was used as the eluent. Compound 1-CN was an orange solid (218 mg, 69%).

1H NMR (300 MHz, $CDCl_3$) (ppm): 0.90 (s, 3H), 1.37 (s, 6H), 1.77 (s, 2H), 3.31–3.40 (m, 2H), 3.42–3.50 (m, 2H), 4.01–4.06 (t, 2H), 5.70 (s, 1H), 6.51–6.53 (d, 1H), 7.05–7.07 (d, 6H), 7.11–7.14 (d, 2H), 7.19–7.20 (d, 1H), 7.27–7.30 (d, 4H), 7.32–7.34 (d, 1H), 7.42–7.45 (d, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) (ppm): 14.23, 22.73, 26.82, 31.51, 31.93, 39.59, 44.05, 47.68, 99.51, 111.61, 113.46, 117.74, 123.16, 123.44, 123.44, 123.54, 124.86, 125.55, 126.60, 126.88, 127.53, 128.91, 129.56, 130.04, 136.01, 138.48, 143.60, 147.44, 147.89. HRMS (ESI-TOF): m/z calcd for $C_{38}H_{37}N_3S_3$ [$M + H$] $^+$, 632.2228; found, 632.2230. Anal. Calcd for $C_{38}H_{37}N_3S_3$: C 72.23, H 5.90, N 6.65, S 15.22; found, C 71.81, H 5.601, N 6.624, S 14.86.

RESULTS AND DISCUSSION

Synthesis. The synthetic route is demonstrated in Scheme 2. Through the general Wittig reaction, Knoevenagel condensation reaction, Vilsmeier reaction, and the Suzuki coupling reaction, 2-CN was readily prepared and then converted into dithioacetals 1-CN through a straightforward reaction with ethanethiol. Following a similar procedure, the analogue molecules, 1 and 2, were also obtained. Compounds 2, 2-CN, 1, and 1-CN were easily soluble in acetone, dichloromethane, chloroform, and THF, etc. Different spectroscopic methods have been used to characterize the yielded compounds, and all of them gave satisfactory spectra data (Figure S1–S4 in the Supporting Information).

Table 1. Optical Data and Calculated Energy Levels of 1, 2, 1-CN, and 2-CN

	E_{HOMO} (eV)	E_{LUMO} (eV)	$\lambda_{max,abs}$ (nm)	PL λ_{max} (nm)	Φ_F (%)
2	−4.85	−1.94	425	518	17.1
1	−4.55	−1.49	356	450	31.9
2-CN	−5.05	−2.46	456	600	53.1
1-CN	−4.8	−1.97	445	535	0.87

As shown in Table 1 and Figure 1a, the maximum absorption wavelength of 2 red-shifted 69 nm, in comparison with that of the corresponding dithioacetal 1. After the introduction of cyano group, the UV–vis spectra of 1-CN and 2-CN exhibit a small additional absorption peak around 350 nm, corresponding to a higher energy band for the intramolecular charge transfer (ICT) of the conjugated π -electron systems possibly caused by the cyano group. Moreover, 1-CN shows a slight red-shift after protected by ethanethiol, indicating that the introduced cyano groups could reduce the electron transition energy from the ground state to the excited state.^{61–63} Upon excitation, 1-CN was nearly nonemissive, while others gave

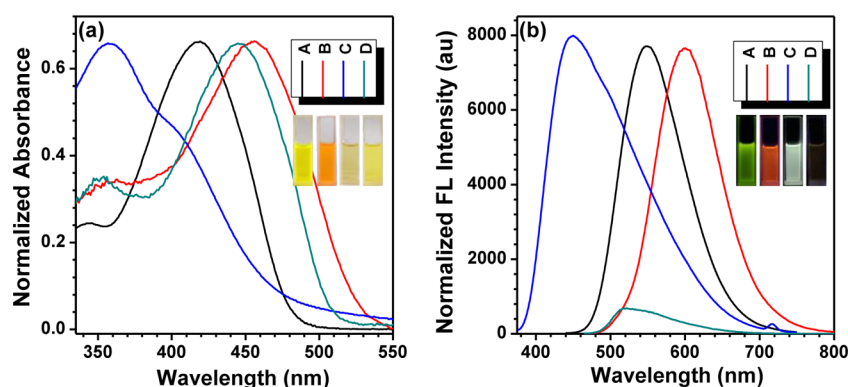


Figure 1. UV-vis absorption (a) and fluorescent emission (b) spectra and the corresponding photos of (A) 2, (B) 2-CN, (C) 1, and (D) 1-CN in THF.

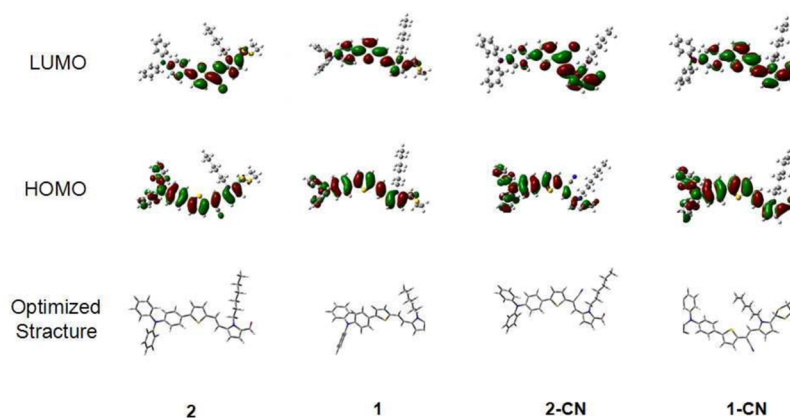


Figure 2. Frontier molecular orbitals optimized at the B3LYP/6-31G* level of theory and electronic cloud distribution of 1, 2, 1-CN, and 2-CN.

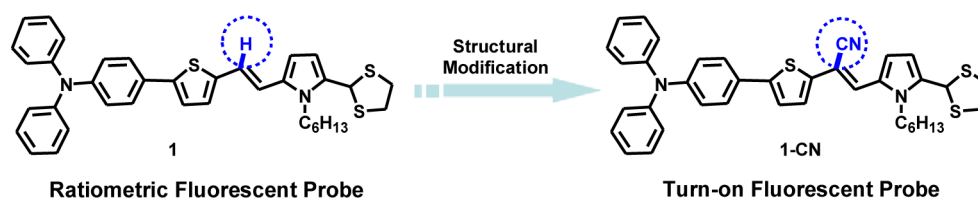


Figure 3. Structural modification strategy for different types of Hg^{2+} fluorescence probes.

strong emissions (Figure 1b). This was reasonable. The cyano group was bonded to the π -bridge, acting as a weaker acceptor. Thus, in 2-CN, the cyano group helped the aldehyde group contribute to the ICT process, leading to its much red-shifted emission (600 nm vs 518 nm of 2); however, in 1-CN, the cyano one was the only acceptor between the two donor parts (the pyrrole group should act as electron donor in 1-CN), possibly trapping the energy and quenching the emission.

To know more information about the molecular structure, by using the Gaussian 09 program DFT calculations for 1, 2, 1-CN, and 2-CN were carried out at the level of B3LYP/6-31G(d). As illustrated in Figure 2, the highest occupied molecular orbitals (HOMOs) of compounds 2 and 2-CN demonstrated similar distributions of the dispersed electron cloud over the entire molecules. The lowest unoccupied molecular orbital (LUMO) of compound 2 resided primarily on the aldehyde group, the electron-withdrawing one, which should be ascribed to the contribution of the π^* orbitals of the group of $-\text{CHO}$. However, in 2-CN, the electron clouds of the TPA moiety partially transferred to the cyano group at its

LUMO because of the strong electron-withdrawing ability of the cyano group. Thus, the differences in the electron cloud distributions of their LUMOs directly caused the different absorption and fluorescent properties. On the basis of the experimental results, the energy gaps of 2 and 2-CN between the HOMO and LUMO could be calculated, which were 2.91 and 2.58 eV, respectively. For 2-CN, the distribution between HOMO and LUMO was relatively well-separated. This indicated that there was substantial charge transfer from the donor to acceptor moieties, while 2-CN was excited. However, this was clearly prohibited for 1-CN, in which the cyano group acts as the electron acceptor, due to the shorter length of π -conjugation after the reaction with ethanethiol, resulting in much lower ICT efficiency in dithioacetal 1-CN. To investigate the electrochemical properties of these molecules, their cyclic voltammetry (CV) behaviors were also studied (Figure S5 in the Supporting Information), with the corresponding data summarized in Table S1 in the Supporting Information. For 2-CN and 1-CN, the corresponding energy gaps between HOMO and LUMO could be calculated, which were 2.58

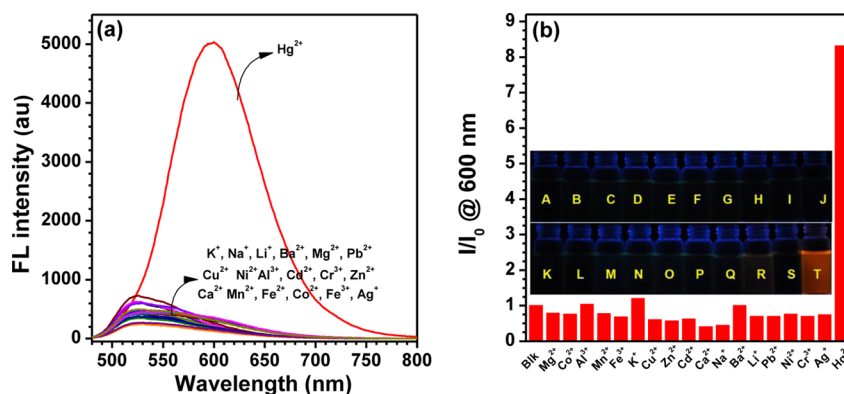


Figure 4. (a) Fluorescence emission response of 1-CN (10 μM) to various metal ions (10 μM). (b) Fluorescence emission response of 1-CN (10 μM) to various metal ions ($[\text{Hg}^{2+}]$, 10 μM ; other ions, 100 μM). Excited at 456 nm. Inset: Fluorescence photos of 1-CN, taken under UV light at 365 nm, in the presence of various metal ions. (A) K^+ ; (B) Na^+ ; (C) Li^+ ; (D) Ba^{2+} ; (E) Mg^{2+} ; (F) Pb^{2+} ; (G) Ca^{2+} ; (H) Mn^{2+} ; (I) Fe^{2+} ; (J) Co^{2+} ; (K) Fe^{3+} ; (L) Cu^{2+} ; (M) Ni^{2+} ; (N) Al^{3+} ; (O) Cd^{2+} ; (P) Cr^{3+} ; (Q) Zn^{2+} ; (R) Ag^+ ; (S) blank; and (T) Hg^{2+} .

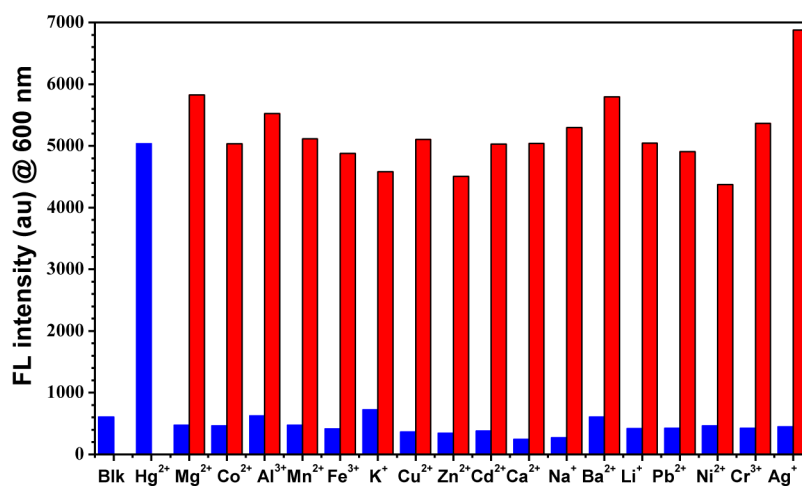


Figure 5. Fluorescence intensity at 600 nm of 1-CN (20 μM) upon addition of various metal ions (blue bar, 1-CN with other metals; red bar, 1-CN with Hg^{2+} (20 μM) and other metals (20 μM)).

and 2.81 eV respectively, in good accordance with the apparent redshift in both emission and absorption spectra of 2-CN, compared to those of 1-CN, regardless of the discrepancies between the calculation and experimental results.

Thus, the calculations and experimental results confirmed the importance of the cyano group, which created the much different fluorescent behavior of 1 and 1-CN. Actually, 1 acts as a ratiometric fluorescent probe for Hg^{2+} while 1-CN a “turn-on” one (Figure 3). That is to say, the introduction of the cyano group to the bridge might be a new approach to adjust the energy level of the whole molecule, ideally, directly leading to the design of “turn-on” probes from the original ratiometric fluorescent ones. However, much work is still needed to confirm this point.

Unlike the small changes in the UV–vis spectra of 1-CN upon the addition of mercury ions (Figure S6 in the Supporting Information), as shown in Figure S7 in the Supporting Information, the fluorescent intensity increased rapidly and reached equilibrium in 6 min, displaying a quick response to Hg^{2+} . Moreover, the photostability of 1 and 1-CN was investigated and the fluorescence intensity remained almost constant when excited at 456 nm for 1 h, which indicated that 1-CN was stable enough to be applied to track intracellular mercury ions by microscopic fluorescence imaging. Then, the fluorescence titration of 1-CN (10 μM) was conducted.

Possibly due to the relatively slow hydrolysis of the reaction intermediate b, in the initial titration stage, the fluorescence increase exhibits abrupt changes (Figures S8 and S9 in the Supporting Information).⁶⁴ The organomercury group could readily reattack the sulfonium moieties and promote the deprotection reaction to 2-CN, resulting in the quick response time upon the addition of increasing concentrations of Hg^{2+} . Furthermore, when increasing the concentrations of mercury ions to higher levels, the fluorescent emission spectra became more close to that of aldehyde 2-CN once reaching the titration equilibrium (Figure S8 in the Supporting Information). The final emission enhancement was about 101-fold, according to the emission intensity at 600 nm. Quantitatively, the Hg^{2+} -promoted deprotection reaction of 1-CN occurred from nonfluorescent ($\sqrt{\text{I}} = 0.0087$) to strongly orange fluorescent ($\sqrt{\text{I}} = 0.53$, 2-CN) with a 61-fold enhancement in the quantum yield. Moreover, it displayed a good linear relationship ranging from 0 to 10 μM of Hg^{2+} , and the detection limit was estimated to be 0.8 μM (Figure S10 in the Supporting Information) and three sets of parallel experiments were also conducted and the approximate error was calculated to be as low as 0.07 μM .

To verify the specificity, the fluorescence spectra of 1-CN were recorded, respectively, in the presence of other environmentally or physiologically important metal ions under identical conditions to the Hg^{2+} ion. As shown in Figure 4,

Hg²⁺ induced significant fluorescence changes, whereas no distinct fluorescence enhancements were observed upon the addition of other ions. Also, the fluorescence enhancement upon the addition of Hg²⁺ ions almost remained unchanged even after the addition of large amounts of other competitive metal ions, such as K⁺, Na⁺, Li⁺, Ba²⁺, Mg²⁺, Pb²⁺, Ca²⁺, Mn²⁺, Fe²⁺, Co²⁺, Fe³⁺, Cu²⁺, Ni²⁺, Al³⁺, Cd²⁺, Cr³⁺, and Zn²⁺, except Ag⁺ with a slight fluorescence enhancement. All these results demonstrated that 1-CN was able to sense Hg²⁺ via displaying the “turn-on” emission with high selectivity and would not be disturbed by a large excess of other metal ions (Figure 5).

The sensing mechanism of the deprotection reaction of dithioacetal 1-CN induced by Hg²⁺ was confirmed by FTIR studies. As shown in Figure S11 in the Supporting Information, the FTIR spectra of 1-CN in the presence of Hg²⁺ clearly showed that the characteristic stretching band for the aldehyde group appeared at 1657 cm⁻¹. Moreover, the spectra profiles were almost the same as that of 2-CN, indicating that 2-CN was regenerated from the reaction between 1-CN and Hg²⁺. To further confirm the formation of 2-CN from the reaction of 1-CN with Hg²⁺, the ¹H NMR spectra was recorded to monitor the Hg²⁺-promoted deprotection reaction (Figure 6). The

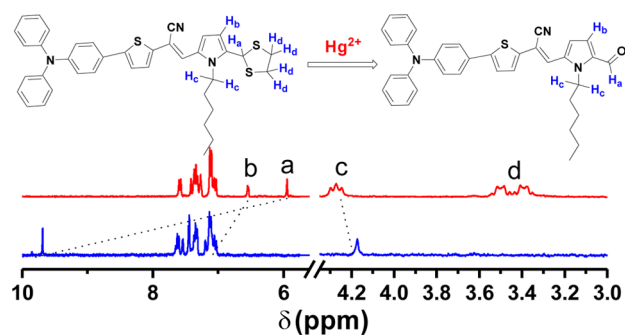


Figure 6. ¹H NMR spectra of 1-CN (the upper one with a red line) and 1-CN with 2 equiv of Hg²⁺ (the lower one with a blue line) conducted in CDCl₃.

signals at 3.37 and 3.48 ppm assigned to the methylene protons of the ethylene mercaptan, and the methine proton at 5.95 ppm in 1-CN, disappeared, while the resonance signal of the aldehyde proton appeared at 9.69 ppm. Also, the original signal of the proton b on the pyrrole ring at 6.54 ppm and the methylene proton centered at 4.27 ppm, shifted to 7.03 and 4.17 ppm, respectively. Similar proof could be found in their mass spectra. As shown in Figure S12 in the Supporting Information, a major peak of *m/z* 555.20, corresponding to 2-CN, was observed in the ESI-MS spectrum, upon the treatment of 1-CN with Hg²⁺. Thus, all these results confirmed the sensing mechanism of the deprotection reaction of dithioacetal triggered by Hg²⁺.

To investigate the practical application of 1-CN, a dilute solution of 1-CN (1 × 10⁻³ mol/L) was drop-coated on a silica gel plate. Once dipped into different aqueous solutions of mercury ions with different concentrations, these silica gel plates clearly demonstrated an apparent color change of emission from weak pale green to strong orange observed by a naked-eye under a UV lamp of 365 nm (Figure 7). Excitedly, a very low concentration of Hg²⁺ ions (1 × 10⁻⁵ mol/L) could be discerned. And importantly, these strips could be used for the detection of Hg²⁺ conveniently. The application of 1-CN to track intracellular Hg²⁺ levels was also investigated by scanning

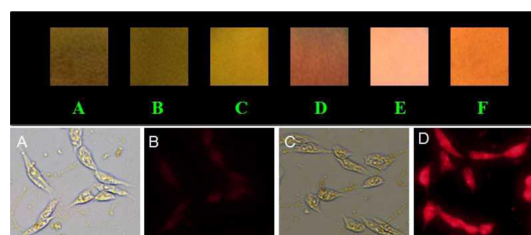


Figure 7. Fluorescence photos of 1-CN (1 × 10⁻³ mol/L) with different concentrations of Hg²⁺. The upper row: (A) free, (B) 1 × 10⁻⁶ mol/L, (C) 1 × 10⁻⁵ mol/L, (D) 1 × 10⁻⁴ mol/L, (E) 1 × 10⁻³ mol/L, and (F) 1 × 10⁻² mol/L. The lower row: scanning microscopic images of HepG2 cells: (A) bright-field image of cells incubated with 1-CN; (B) fluorescence image of cells incubated with 1-CN; (C) bright-field image of cells incubated with 1-CN, then with mercury ions; (D) fluorescence image of cells incubated with 1-CN, then with mercury ions. Size bar: 20 μm.

microscopy on the basis of its excellent sensing performance. At room temperature, HepG2 cells were incubated for 3 min with 1-CN (100 μM) in DMSO, then phosphate-buffered saline (PBS; 10 mM, pH 7.12) was used to wash the resultant cells three times. Through the observation under bright-field, it was confirmed that the cells were viable. As shown in Figure 7, HepG2 cells exhibited ignorable emission; however, once incubated with the solution of Hg(ClO₄)₂ (200 μM) for 0.5 h, the whole cell displayed remarkable fluorescence enhancement in the intracellular region. The images taken before and after the addition of the metal species demonstrated a distinct fluorescence change, inconsistent with the results observed in the solution, indicating that it was capable for 1-CN to penetrate the cell membrane; thus, 1-CN could be potentially utilized to image Hg²⁺ ions in living cells, with the switching-on fluorescent signal. Although the fluorescent enhancement was unsatisfactory when 1-CN was incubated in PBS (10% DMSO) owing to the poor solubility of 1-CN (Figure S13 in the Supporting Information), we will try to focus on the improvement of its solubility in our subsequent work.

CONCLUSIONS

In conclusion, a “turn-on” probe, 1-CN, was prepared based on the Hg²⁺-promoted deprotection reaction, coupled with the ICT mechanism. By the convenient introduction of a cyano group into the π-bridge, we have successfully realized the conversion of a normal ratiometric fluorescence probe (1) to another ideal turn-on one (1-CN), which exhibits distinct “turn-on” fluorescence enhancement for Hg²⁺ at a long wavelength region peaked at 600 nm with high selectivity and sensitivity, and could be utilized in practical applications as test strips and in cell image. The design idea reported here might provide a new avenue to develop new fluorescence “turn-on” probes for mercury ions. Also, by utilizing the strategy of the introduction of a weak withdrawing group to the π-bridge, other “turn-on” probes for other analytes might be further developed conveniently from the related ratiometric fluorescence ones with similar structure.

ASSOCIATED CONTENT

Supporting Information

NMR, MS, IR, fluorescence and absorption spectral data, and CV. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b01800.

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Notes

The authors declare no competing financial interest.

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