RSC Advances

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Cite this: *RSC Advances*, 2012, **2**, 4754–4758

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PAPER

Novel "turn-on" fluorescent chemodosimeters based on thioxanthen-9-thione for the selective detection of mercuric ions in aqueous media†

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Received 8th January 2012, Accepted 23rd February 2012
DOI: 10.1039/c2ra00048b

Two Hg^{2+}-selective chemodosimeters based on thioxanthen-9-thione (**DP-TXT** and **BDPA-TXT**) were synthesized and structurally characterized. The highly sensitive and selective chemodosimetric behaviors of thioxanthen-9-thione towards Hg^{2+} ions were investigated. Significant chromogenic and fluorogenic signaling occurred from the transformation of thioxanthen-9-thione to thioxanthen-9-one by Hg^{2+}-induced selective desulfurization. Both of the two probes exhibit excellent Hg^{2+}-specific fluorescence enhancement over various competitive cations in aqueous media.

Introduction

To date, fluorescence detection has become the dominant strategy for Hg^{2+} sensing owing to its operational simplicity, low cost, real time monitoring and high sensitivity.[1–6] Our increasing awareness of the deleterious effects of mercury exposure has sparked interest in the development of novel fluorescent probes for detecting Hg^{2+}. As known, there are a number of sophisticated systems for the optical detection of Hg^{2+} ions,[7–20] and many of the small molecule-derived fluorescence sensors for Hg^{2+} reported so far compose of two components: a recognition moiety containing nitrogen/sulfur atoms and a fluorophore that signals the change of absorption/fluorescence upon exposure to Hg^{2+}.[21–28] As a result, Hg^{2+}-triggered desulfurization and transformation of thioamide,[29,30] thiourea[31–33] and thione[34,35] have been successfully utilized. For instance, Czarnik *et al.* reported that a chemodosimeter based on thioamide substituted anthracene could give 56-fold fluorescence enhancement by Hg^{2+} addition.[36] However, in some cases interference from other metal ions can affect the selectivity, and only a handful of fluorescent sensors displayed good water solubility, so the search for readily accessible fluorescent Hg^{2+} probes with good water solubility as well as high sensitivity and selectivity is still a challenging task. Herein, we report two thioxanthen-9-thione derivatives, **DP-TXT** and **BDPA-TXT** (Scheme 1), can be used as highly sensitive and selective chemodosimeters for Hg^{2+} ions in aqueous media.

When the carbonyl group in thioxanthen-9-one was replaced by a thiocarbonyl group, there existed obvious fluorescence quenching which was attributed to the heavy atom effect and photo-induced electron transfer (PET) properties of S atoms.[35] Hence, we designed and synthesized two thioxanthen-9-thione based chemodosimeters. Addition of Hg^{2+} resulted in significant fluorescence enhancement by desulfurization of thione. For modification of the optical properties of compound **DP-TXO**, compound **BDPA-TXO** possessing diphenylamine group was synthesized *via* Buchwald–Hartwig amination (Scheme 2). As expected, compound **BDPA-TXO** exhibited a bathochromic-shift both in UV-vis and fluorescence spectra due to the enhanced intramolecular charge transfer (ICT) process.

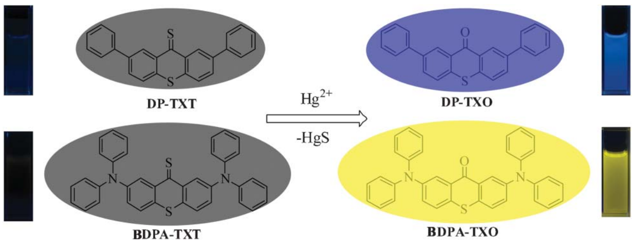
Experimental

Materials

Toluene and tetrahydrofuran (THF) were pre-dried over 4 Å molecular sieves and distilled under an argon atmosphere from sodium and benzophenone immediately prior to use. Unless otherwise stated, all reagents were obtained from commercial suppliers and were used without further purification.

Apparatus

^{1}H NMR and ^{13}C NMR spectra were recorded on Brucker AM-400 spectrometers. Chemical shifts were reported in ppm relative to a tetramethylsilane (TMS) standard in $CDCl_3$ or DMSO-d_6. Mass spectra (MS) were obtained on a Waters LCT Premier XE spectrometer. UV-vis absorption spectra were performed on a



Scheme 1 Fluorescence changes in the presence of Hg^{2+} and proposed sensing mechanism: desulfurization of **DP-TXT** and **BDPA-TXT** promoted by Hg^{2+}.

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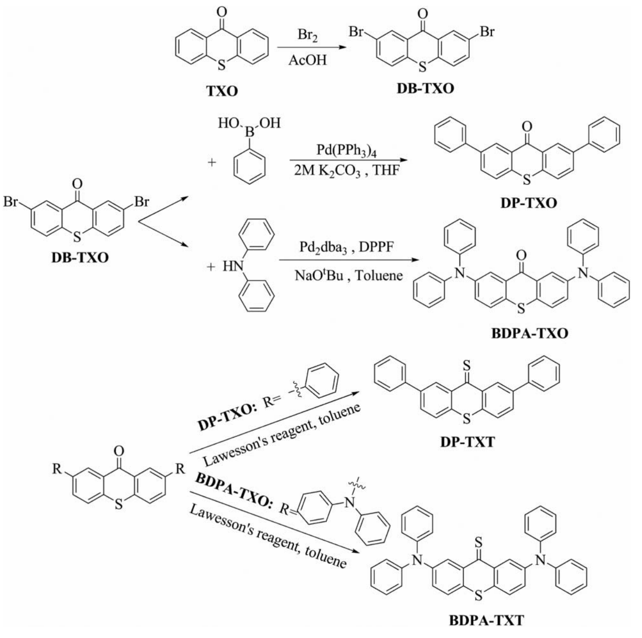
† Electronic Supplementary Information (ESI) available. See DOI: 10.1039/c2ra00048b/



Scheme 2 Synthesis of chemodosimeters **DP-TXT** and **BDPA-TXT**.

Varian Cray 500 spectrophotometer and fluorescence spectra were recorded on a Varian Cray Eclipse. Quantum yields of samples (1.0 × 10^{-5} M in aqueous media) were recorded on a Horiba Fluoromax-4 with a calibrated intergrating sphere system. The melting points were measured on an X4 Micro-melting point apparatus.

Synthesis of 2,7-dibromothioxanthen-9-one (DB-TXO)

To a solution of thioxanthone (5.0 g, 23.6 mmol) in glacial acetic acid (45 mL) was added bromine (10 mL) dropwise over 20 min. The solution was stirred continuously and heated at reflux temperature for 20 h, after which half of the solvent volume was removed by distillation. The reaction mixture was then allowed to cool then poured over crushed ice. The resulting yellow precipitate was collected by filtration and washed with saturated sodium bicarbonate, a 20% aqueous solution of sodium bisulfite, and finally with water. The solid was then dried under vacuum and recrystallized twice from toluene to afford a bright yellow solid (5.1 g, 13.9 mmol, yield: 59%). m.p. 263–266 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.47 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 8.74 (s, 2H). HR-MS (ESI): calculated for $C_{13}H_6Br_2OS$ $[M + H]^+$ 368.8584, found 368.8580.

Synthesis of 2,7-diphenylthioxanthen-9-one (DP-TXO)

Phenylboronic acid (0.54 g, 4.4 mmol) and compound **DB-TXO** (0.736 g, 2.0 mmol) were mixed in THF (15 mL). 10 mL of 2 M aqueous potassium carbonate solution was added, and the mixture was stirred with magnetic stirring. After added tetrakis(triphenylphsosphine)palladium (0.022 g, 0.02 mmol), the reaction solution was heated at reflux temperature for 12 h under the atmosphere of nitrogen. Then the mixture was cooled to room temperature, evaporated under reduced pressure and extracted with dichloromethane (3 × 10 mL). The organic portion was washed with brine and water, and then dried by anhydrous $MgSO_4$. The solvent was evaporated, and the residue was purified by column chromatography with petroleum ether–dichloromethane (2 : 1, v/v) as the eluent to afford a yellow solid (0.61 g, 1.7 mmol, yield: 85%). m.p. 200–203 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.41 (t, *J* = 7.4 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 4H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 7.8 Hz, 4H), 7.90 (dd, *J* = 8.4 Hz, 2H), 8.89 (d, *J* = 2.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 126.67, 127.14, 127.94, 129.04, 129.43, 131.10, 135.99, 139.41, 139.51, 180.02. HR-MS (ESI): calculated for $C_{25}H_{16}OS$ $[M + H]^+$ 365.1000, found 365.1000.

Synthesis of 2,7-diphenylthioxanthen-9-thione (DP-TXT)

Compound **DP-TXO** (0.364 g, 1.0 mmol) and Lawesson's reagent (0.405 g, 1.0 mmol) were dissolved in toluene (15 mL) in a 50 mL round-bottom flask. Then the reaction mixture was refluxed for 3 h under the atmosphere of nitrogen. The mixture was concentrated under vacuum, purified by silica gel column chromatography with petroleum ether/dichloromethane (3 : 1, v/v) as eluent to afford a tan solid (0.3 g, 0.8 mmol, yield: 80%). m.p. 210–212 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.40 (t, *J* = 7.3 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 4H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 7.3 Hz, 4H), 7.88 (dd, *J* = 8.3 Hz, 2H), 9.29 (d, *J* = 1.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 126.60, 127.21, 127.93, 129.03, 130.57, 130.77, 131.61, 137.70, 139.60,140.04, 210.73. HR-MS (ESI): calculated for $C_{25}H_{16}S_2$ $[M + H]^+$ 381.0772, found 381.0773.

Synthesis of 2,7-bis(diphenylamino)thioxanthen-9-one (BDPA-TXO)[37,38]

Tris(dibenzylideneacetone)dipalladium(0) (Pd_2dba_3) (0.055 g, 0.06 mmol) and 1,1′-bis(diphenylphosphino)ferrocene (DPPF) (0.066 g, 0.12 mmol) were dissolved in toluene under argon and degassed by two freeze-pump-thaw cycles. This activated catalyst was then added to a degassed mixture of compound **DB-TXO** (0.5 g, 1.36 mmol), diphenylamine (0.506 g, 2.99 mmol) and sodium *tert*-butoxide (NaO^tBu, 0.366 g, 3.81 mmol) in toluene. The mixture was stirred for 15 h at 90 °C. After the mixture was cooled to room temperature, the reaction was quenched by adding 5 mL of methanol, diluted with diethyl ether, and washed twice with brine and water, respectively. The combined aqueous phase was extracted twice with diethyl ether. The combined organic phase was then dried with $MgSO_4$, filtered, and the solvent evaporated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether–dichloromethane (2 : 1, v/v) as the eluent to afford a yellow solid (0.360 g, 0.66 mmol, yield: 49%). m.p. 250–251 °C. ^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm): 7.10 (d, *J* = 8.1 Hz, 8H), 7.14 (d, *J* = 7.4 Hz, 4H), 7.34–7.38 (m, 8H), 7.39 (d, *J* = 2.7 Hz, 2H), 7.75 (d, *J* = 8.8 Hz, 2H), 7.89 (d, *J* = 2.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 122.57, 123.59, 124.60, 126.89, 128.19, 129.52, 129.82, 130.24, 146.55, 147.16, 179.07. HR-MS (ESI): calculated for $C_{37}H_{26}N_2OS$ $[M + H]^+$ 547.1844, found 547.1847.

Synthesis of 2,7-bis(diphenylamino)thioxanthen-9-thione (BDPA-TXT)

Compound **BDPA-TXO** (0.109 g, 0.2 mmol) and Lawesson's reagent (0.081 g, 0.2 mmol) were dissolved in toluene (10 mL) in a 50 mL round-bottom flask. Then the reaction mixture was refluxed for 3 h under the atmosphere of nitrogen. The mixture was concentrated under vacuum, purified by silica gel column chromatography with petroleum ether–dichloromethane (1 : 1, v/v) as the eluent to afford a dark purple solid (0.086 g, 0.15 mmol, yield: 76%). m.p. 238–239 °C. ^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm): 7.10 (d, J = 7.5 Hz, 8H), 7.13 (d, J = 7.3 Hz, 4H), 7.35 (t, J = 8.2 Hz, 8H), 7.41 (d, J = 8.8 Hz, 2H), 7.81 (d, J = 8.8 Hz, 2H), 8.52 (d, J = 2.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 123.59, 124.56, 125.29, 125.83, 126.82, 127.80, 129.50, 138.34, 147.07, 208.16. HR-MS (ESI): calculated for $C_{37}H_{26}N_2S_2$ $[M + H]^+$ 563.1616, found 563.1615.

Results and discussion

Synthesis and characterization

The synthetic route of **DP-TXT** and **BDPA-TXT** is shown in Scheme 2. Bromination of thioxanthen-9-one was carried out according to literature procedures[39] to afford a bright yellow solid **DB-TXO** in 59% yield through recrystallization twice from toluene. It was necessary that one of the reagent bromines should be in large excess for a reaction time of 20 h. Buchwald–Hartwig amination proceeded under the conditions of Pd_2dba_3 (catalyst), DPPF (ligand), NaO^{t}Bu (base) and toluene solutions, and the catalyst and ligand were activated under argon and degassed by two freeze-pump-thaw cycles prior to the addition of other reagents. As for the thionation procedure, it was performed in refluxing toluene with Lawesson's reagent under an atmosphere of nitrogen. The structures of **DP-TXT**, **BDPA-TXT** and other intermediate products were confirmed by ^{1}H NMR, ^{13}C NMR, and ESI-MS (Fig. S1–S14 in the ESI†). As for the solvent choosing principles of **DP-TXT** and **BDPA-TXT** for the optical detection of Hg^{2+}, acetonitrile (CH_3CN) and dimethyl sulfoxide (DMSO) are both water-miscible and are low-toxicity organic solvents, so they provide opportunities for optical detection in aqueous media. What's more, **DP-TXT** and **BDPA-TXT** show good solubility in CH_3CN and DMSO, respectively.

Colorimetric response of chemodosimeters DP-TXT and BDPA-TXT

As shown in Fig. 1a and Fig. 2, among the various metal ions tested, only Hg^{2+} significantly affected the absorption behavior of **DP-TXT**. The absorption band was blue shifted from 487 nm to 397 nm with the addition of Hg^{2+} in $CH_3CN–H_2O$ (5 : 5, v/v). The solution color changed from orange to colorless, which allowed a naked-eye detection of Hg^{2+}. As for **BDPA-TXT**, the absorption band also exhibited a dramatic blue shift upon addition of Hg^{2+} in $DMSO–H_2O$ (9 : 1, v/v), and it displayed an obvious colorimetric response from purple to yellow (Fig. 1b and Fig. 3). All these results above suggest that chemodosimeters **DP-TXT** and **BDPA-TXT** can serve as "naked-eye" indicators for Hg^{2+}.

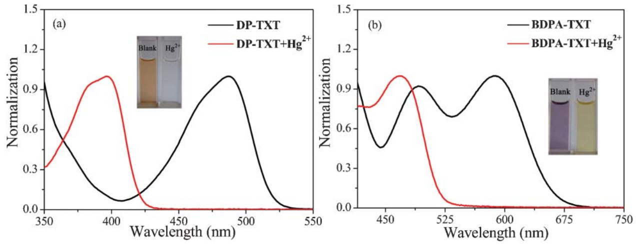


Fig. 1 (a) UV-vis spectra of **DP-TXT** in the absence (black line) and presence (red line) of Hg^{2+} in $CH_3CN–H_2O$ (5 : 5, v/v). Inset: Color change of **DP-TXT** upon addition of Hg^{2+}. (b) UV-vis spectra of **BDPA-TXT** in the absence (black line) and presence (red line) of Hg^{2+} in $DMSO–H_2O$ (9 : 1, v/v). Inset: Color change of **BDPA-TXT** upon addition of Hg^{2+}.

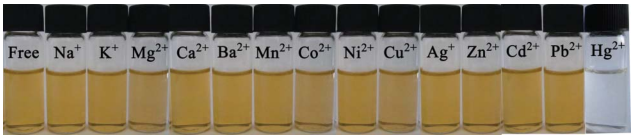


Fig. 2 Color changes of **DP-TXT** towards various metal ions.

Fluorescence spectra of chemodosimeter DP-TXT in the presence of Hg^{2+}

DP-TXT exhibited almost no emission centered on 460 nm in 50% aqueous acetonitrile. Upon interaction with Hg^{2+} ions, however, the fluorescence intensity at 460 nm increased 40-fold and the solution color under illumination with a UV lamp changed from dark to bright blue (Fig. 4), and the absolute fluorescence quantum yield varied dramatically from 1.3% to 21.7%. Furthermore, the fluorescence intensity as a function of Hg^{2+} concentration shows a near-linear relationship (Fig. S15 in the ESI†). As a consequence, the detection limit reached 21 nM.

The Hg^{2+}-selective signaling process of compound **DP-TXT** was also examined by ^{1}H NMR titration experiment (Fig. S16 in

Fig. 3 Color changes of **BDPA-TXT** towards various metal ions.

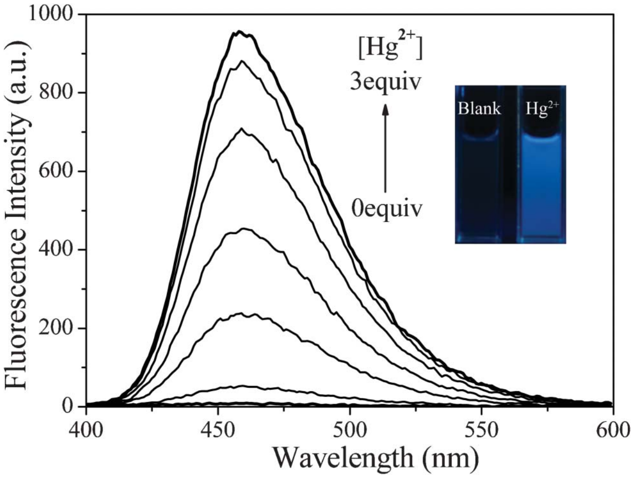


Fig. 4 Fluorescence spectra of **DP-TXT** (1.0×10^{-5} M) in the presence of Hg^{2+} ($0–3.0 \times 10^{-5}$ M) in $CH_3CN–H_2O$ (5 : 5, v/v), λ_{ex} = 309 nm. Inset: Fluorescence change of **DP-TXT** upon addition of Hg^{2+}.

the ESI†). Upon treatment of **DP-TXT** with 3 equiv. of Hg^{2+}, the resonances of **DP-TXT** were completely transformed to those of **DP-TXO**. As shown in Fig. S16,† the resonances of the thioxanthen-9-thione moiety were upfield shifted (from 9.29 to 8.89 ppm for the protons at the *ortho* position of the thiocarbonyl of **DP-TXT**), while the resonances for other protons did not significantly change. Analogous to **DP-TXT**, the peak of the protons at the *ortho* position of the thiocarbonyl of **BDPA-TXT** also upfield shifted from 8.52 to 7.89 ppm (Fig. S17 in the ESI†).

Fluorescence spectra of chemodosimeter BDPA-TXT in the presence of Hg^{2+}

The fluorescent changes of **BDPA-TXT** towards different concentrations of Hg^{2+} were also examined in DMSO–H_2O (9 : 1, v/v). Compared to **DP-TXT**, the addition of Hg^{2+} to **BDPA-TXT** revealed an emission band at 570 nm which bathochromically shifted 110 nm owing to the two diphenylamine moieties introducing as donor groups. A 43-fold fluorescent enhancement was obtained at 570 nm and the solution color varied from nearly dark to bright yellow by using hand-held UV light irradiation (Fig. 5). The absolute fluorescence quantum yields in the absence and presence of Hg^{2+} were measured to be 0.8% and 9.6%, respectively. The detection limit for Hg^{2+} with chemodosimeter **BDPA-TXT** was determined to be 75 nM (Fig. S18 in the ESI†).

Moreover, mass spectra demonstrated the proposed Hg^{2+}-induced conversion process by revealing a diagnostic peak at *m*/*z* = 547.1847 of **BDPA-TXO**, instead of the peak at *m*/*z* = 563.1615 that would be expected for the molecular ion of **BDPA-TXT** (Fig. S19 in the ESI†). HRMS (ESI) experiments for **DP-TXT** also confirmed the Hg^{2+}-triggered desulfurization process (Fig. S20 in the ESI†).

Selective fluorescence response of chemodosimeters DP-TXT and BDPA-TXT

The fluorescence responses of chemodosimeters **DP-TXT** and **BDPA-TXT** towards various other metal ions including alkali (Na^+, K^+), alkaline earth (Mg^{2+}, Ca^{2+}, Ba^{2+}), and transition-metal ions (Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ag^+, Zn^{2+}, Cd^{2+}, Pb^{2+}) were examined, and there is no significant influence on the emission color of **DP-TXT** except for Hg^{2+} (Fig. 6a and Fig. 7). Enhancing efficiency, defined as I/I_0 (I_0 and I represent the fluorescence intensity of **DP-TXT** in the absence and in the presence of metal ions at 460 nm, respectively), for Hg^{2+} was calculated to be more than 40, whereas the ratio of I/I_0 varied in a limited range from 0.97 (Cu^{2+}) to 1.29 (Ag^+) for the other metal ions (Fig. S21a in the ESI†).

Analogous to **DP-TXT**, no significant fluorescence changes of **BDPA-TXT** were observed in the presence of other metal ions in excess (Fig. 6b and Fig. 8). Addition of Ag^+ resulted in weak fluorescent enhancement at 570 nm because of its weak thiophile ability. The enhancing efficiency of **BDPA-TXT** remained constant (≈ 1) after addition of other surveyed metal ions except Ag^+ (6.28) and Hg^{2+} (43.41) (Fig. S21b in the ESI†).

Therefore, compounds **DP-TXT** and **BDPA-TXT** exhibited specific selectivity for Hg^{2+} over other examined metal ions in aqueous media.

Conclusions

In conclusion, two new fluorescent chemodosimeters based on thioxanthen-9-thione were developed for the selective detection of mercuric ions in aqueous media. Pronounced Hg^{2+}-selective fluorogenic signaling behaviors were observed: dark to bright blue, dark to bright yellow under illumination with a UV lamp, respectively. Between the two chemodosimeters, **DP-TXT**

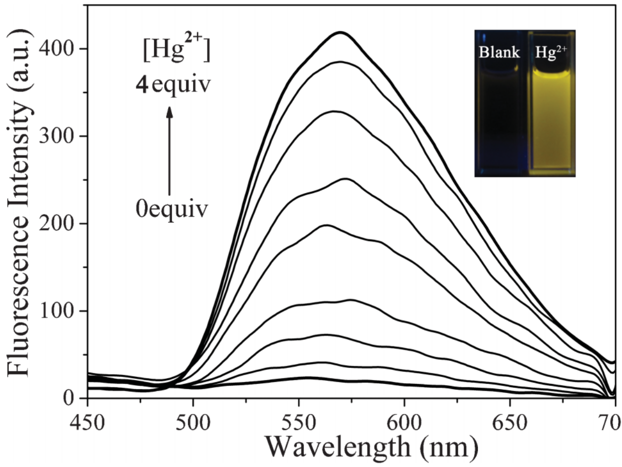


Fig. 5 Fluorescence spectra of **BDPA-TXT** (1.0×10^{-5} M) in the presence of Hg^{2+} (0–4.0×10^{-5} M) in DMSO–H_2O (9 : 1, v/v), λ_{ex} = 357 nm. Inset: Fluorescence change of **BDPA-TXT** upon addition of Hg^{2+}.

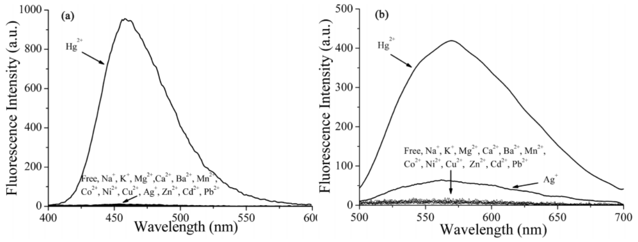


Fig. 6 (a) Fluorescence spectra of chemodosimeter **DP-TXT** towards various metal ions in CH_3CN–H_2O (5 : 5, v/v). [**DP-TXT**] = 1.0×10^{-5} M, [Hg^{2+}] = 3.0×10^{-5} M, [M^{n+}] = 1.0×10^{-4} M. (b) Fluorescence spectra of chemodosimeter **BDPA-TXT** towards various metal ions in DMSO–H_2O (9 : 1, v/v). [**BDPA-TXT**] = 1.0×10^{-5} M, [Hg^{2+}] = 4.0×10^{-5} M, [M^{n+}] = 1.0×10^{-4} M.

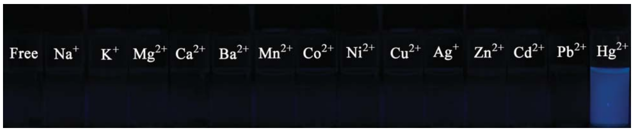


Fig. 7 Fluorescence images of **DP-TXT** towards various metal ions.

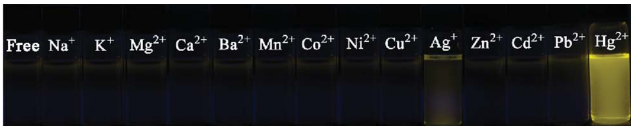


Fig. 8 Fluorescence images of **BDPA-TXT** towards various metal ions.

exhibits the better sensitivity and selectivity properties with a lower detection limit and less interference from other metal ions. The recognition mechanism is attributed to Hg^{2+}-triggered transformation of thioxanthen-9-thione to a thioxanthen-9-one derivative, and this kind of transformation could potentially be used for the design of other supramolecular systems that show sensitive and selective signaling behaviors for Hg^{2+} ions in aqueous environments. Furthermore, efforts will be focused on the sensing system's actual applicability, such as the feasibility of detecting real environmental samples in future research.

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