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### Reaction-based AIEE-active conjugated polymer as fluorescent turn on probe for mercury ions with good sensing performance



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<i>Keywords:</i> Aggregation induced emission enhancement Conjugated polymer Chemodosimeter Mercury ions Fluorescence probe	Based on $Hg^{2+}$ -promoted deprotection reaction of thioketal, a type of thioketal decorated conjugated polymer ( <b>PTS</b> ) with the feature of aggregation induced emission enhancement (AIEE) was successfully synthesized as fluorescent turn on probe for $Hg^{2+}$ . With the introduction of trace aqueous $Hg^{2+}$ , fluorescence of <b>PTS</b> in THF- $H_2O$ mixture (water fraction of 98%) exhibited significant enhancement. The response was very fast with good selectivity towards $Hg^{2+}$ due to the specific chemical reaction. Other common metal ions (Ag <sup>+</sup> , Cr <sup>3+</sup> , Al <sup>3+</sup> , Fe <sup>3+</sup> , Ca <sup>2+</sup> , Ni <sup>2+</sup> , Co <sup>2+</sup> , Pb <sup>2+</sup> , Cu <sup>2+</sup> , Zn <sup>2+</sup> , Mg <sup>2+</sup> , Fe <sup>2+</sup> , Mn <sup>2+</sup> , Cd <sup>2+</sup> , Ba <sup>2+</sup> , Li <sup>+</sup> , Na <sup>+</sup> and K <sup>+</sup> ) gave nearly no disturbance to the sensing process. Furthermore, the detection limit of $Hg^{2+}$ reached 2.3 × 10 <sup>-7</sup> mol L <sup>-1</sup> for this sensing system.

#### 1. Introduction

Mercury ions are one of the most toxic heavy metal ions, have many adverse effects on the endocrine system, immune system and nervous system of organisms [1–3]. Even more seriously, some lower organisms can transform inorganic mercury into methylmercury, a potent neurotoxin for central nervous system, the harmful influence will dramatically increase [4-6]. Moreover, the mercury pollutant will be stored in animal tissues rather than excreted, the concentration may be very high in animals that at the top of the food chain. Thus, global mercury pollution from human activities and nature has become a serious threat to living beings and environment [7,8]. It is urgent to develop convenient methods for selective and sensitive detection of mercury ions. Traditional analytical methods include atomic absorption spectrometry, inductively coupled plasma mass spectroscopy, and chromatography. Whereas, most of them are incapable to meet the requirement of easyto-use detection due to complicated sample pretreatment and expensive instruments. Great efforts have been invested in developing straightforward methods, such as colorimetric, fluorescent and electrochemical probes. Among these methods, fluorescence-based probe has appeared as a powerful tool to detect mercury ions, due to its simple operation, high sensitivity and low-cost [9-13]. In the past several years, various fluorescent mercury ions probes based on polymers [14-18] or small organic molecules [19-28] have been developed. Compared to small molecular probes, probes based on fluorescent conjugated polymers

(CPs) have displayed huge superiority in detection sensitivity owing to their large delocalized molecular structures with unique signal amplification effect [29–31].

Recently, Tang and coworkers have found that some organic molecule was weak emissive in solution but strongly emissive in aggregated state [32,33]. These aggregation induced emission enhancement (AIEE) luminogens exhibited many advantages, such as intrinsic strong emission in aggregated state, good photobleaching-resistance and high sensitivity when used as fluorescent probes [34–40]. Since then, lots of turn on fluorescent Hg<sup>2+</sup> chemosensors based on AIEE small molecules have been successfully constructed [41–46].

To achieve high selectivity, fluorescent mercury ions probes based on specific chemical reactions have been developed [47–54]. In previous work, we have designed a novel AIEE-active fluorescent small molecular probe **TPE-S** towards mercury ions based on the  $Hg^{2+}$ -promoted deprotection reaction of mercaptal (Chart S1 and S2) [55]. The nitrobenzene moieties in **TPE-S** was highly twisted, so the nitro group was close to the fluorophore (tetraphenylethylene, TPE), quenching its fluorescence emission. While the nitro group in **TPE-O** was far from the TPE moiety, weakening the quenching effect (the crystal structures seen Chart S1). Thus, once triggered by  $Hg^{2+}$ , the conversion of **TPE-S** to **TPE-O** could give a turn on signal output. However, the fluorescence intensity and fluorescence enhancement value of this sensor were very limited, regardless of its high selectivity (Inset photos in Chart S1).

In this work, taking advantage of the excellent fluorescence

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Fig. 1. Chemical structure and the  $Hg^{2+}$  sensing



amplification effect of CPs, **TPE-S** was copolymerized with fluorene moieties to construct a new conjugated polymer of **PTS** with the aim of obtaining better sensing performance. So far, the AIEE-active conjugated polymers as fluorescence turn on probes for  $Hg^{2+}$  are very rare [56–59]. The chemical structure and the sensing process of **PTS** are shown in Fig. 1. In fact, **PTS** emits very weak fluorescence in THF-H<sub>2</sub>O mixtures with the water fraction of 98%. After the addition of trace  $Hg^{2+}$  ions to **PTS**, the deprotection reaction happened immediately, accompanying with the emission becomes dramatically strong. Other metal ions (Ag<sup>+</sup>, Cr<sup>3+</sup>, Al<sup>3+</sup>, Fe<sup>3+</sup>, Ca<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Mg<sup>2+</sup>, Fe<sup>2+</sup>, Mn<sup>2+</sup>, Cd<sup>2+</sup>, Ba<sup>2+</sup>, Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup>) gave nearly no disturbance to the sensing process. Herein, we present the synthesis, characterization, sensing behavior of **PTS** in detail.

#### 2. Experimental

#### 2.1. Material

Tetrahydrofuran (THF) was dried over and distilled from K-Na alloy under an atmosphere of dry nitrogen. Dichloromethane (DCM) was dried over and distilled from  $CaH_2$ . The solutions of various metal ions were prepared by double distilled water. Compounds **1** and **3** were synthesized according to previous literatures [60,61]. All other reagents were used as received without further purification.

# 2.2. Synthesis of 1-(4-(2,2-bis(4-bromophenyl)-1-phenylvinyl)phenyl)-2-(4-nitrophenyl)ethanone (2)

SOCl<sub>2</sub> (1 mL) was added to a solution of 2-(4-nitrophenyl)acetic acid (0.181 g, 1 mmol) in nitrobenzene (10 mL) and stirred at 60 °C overnight. Excess SOCl<sub>2</sub> was stripped off under vacuum at room temperature. Compound 1 (0.490 g, 1 mmol) was added to the resultant solution with an ice bath under nitrogen atmosphere, then  $AlCl_3$  (0.133 g, 1 mmol) was added. After 4 h, the reaction mixture was extracted with DCM for several times, the organic layer was combined and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the DCM solvent, the crude product was purified by column chromatography using PE (petroleum ether)-EA (ethyl acetate) (10:1, V/V) as eluent to afford a pale-vellow solid (0.451 g, 69%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 8.22 (d, J = 8.7, 2H, ArH), 7.79 (d, J = 8.7, 2H, ArH), 7.42 (d, J = 8.7, 3H, ArH), 7.24 (m, 2H, ArH), 7.16 (m, 6H, ArH), 6.98 (br, 2H, ArH), 6.88 (d, J = 7.2, 4H, ArH), 4.35 (s, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 195.3, 148.8, 147.0, 142.1, 142.0, 141.4, 140.8, 140.2, 134.2, 133.0, 132.8, 132.8, 131.6, 131.4, 131.2, 131.0, 130.6, 128.1, 128.0, 127.3, 123.6, 121.3, 121.1, 44.8. MS (EI), m/z [M<sup>+</sup>]: 653.4, calcd: 653.1. Anal. calcd for C34H23Br2NO3: C 62.50, H 3.55, N 2.14; found: C 62.81, H 3.66, N 2.08.

# 2.3. Synthesis of poly[1-(4-(2-(4-(9,9-dihexyl-7-methyl-9H-fluoren-2-yl) phenyl)-1-phenyl-2-p-tolylvinyl)phenyl)-2-(4-nitrophenyl)ethanone] (**PTO**)

A mixture of compound **2** and compound **3** (1.00 equiv),  $K_2CO_3$  (20.00 equiv), tetrakis (triphenylphosphine) palladium (Pd(PPh<sub>3</sub>)<sub>4</sub>) (5 mol %) and THF/H<sub>2</sub>O (2:1 in volume), was charged with argon. The reaction was stirred under reflux for 2 days. Then, the reaction mixture was filtered through a cotton filter, the filtrate was collected. After the

solvent was removed under vacuum, the residue was dissolved in a bit of chloroform, added dropwise into 200 mL of methanol through a cotton filter, the precipitates were collected by filtration. Then, the polymer was washed with methanol and dried to a constant weight. Yellow solid was obtained in 75% yield.  $M_w = 11240$ ;  $M_w/M_n = 1.74$ . <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 8.20 (d, J = 7.2, 2H, ArH), 7.82 (m, 4H, ArH), 7.55 (m, 11H, ArH), 7.19 (br, 10H, ArH), 4.35 (s, 2H), 2.00 (br, 4H), 1.03 (br, 12H), 0.74 (br, 10H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 195.4, 151.6, 149.9, 146.9, 143.3, 142.1, 142.0, 139.8, 139.1, 133.8, 131.8, 131.7, 131.3, 130.6, 129.0, 128.0, 126.5, 126.3, 125.8, 123.6, 121.0, 120.0, 55.2, 44.7, 40.4, 32.0, 29.6, 23.7, 22.5, 14.0.

process of PTS.

#### 2.4. Synthesis of poly[2-(4-(2-(4-(9,9-dihexyl-9H-fluoren-2-yl)phenyl)-1,2-diphenylvinyl)phenyl)-2-(4-nitrobenzyl)-1,3-dithiolane] (PTS)

PTO (1.00 equiv) and 1, 2-ethanedithiol (3.00 equiv) were dissolved in dry dichloromethane (10 mL), then BF3 Et2O (6.00 equiv) as the Lewis acid was added, stirring at room temperature for 2 days. Then, the reaction mixture was filtered through a cotton filter, the filtrate was collected. After the solvent was removed, the residue was dissolved in a bit of chloroform, added dropwise into 300 mL of methanol through a cotton filter, the precipitates were collected by filtration. Then, the polymer was washed with methanol and dried to a constant weight. Yellow solid was obtained in 62% yield.  $M_w = 12835$ ;  $M_w/M_n = 1.69$ . <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 8.00 (d, J = 7.2, 2H, ArH), 7.70 (br, 2H, ArH), 7.55 (m, 8H, ArH), 7.24 (m, 15H, ArH), 3.58 (s, 2H), 3.30 (m, 4H), 1.97 (br, 4H), 1.03 (br, 12H), 0.74 (br, 10H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm): 151.6, 151.5, 146.8, 144.6, 143.5, 143.2, 142.7, 142.4, 141.7, 140.5, 140.3, 140.1, 140.0, 139.5, 139.4, 139.3, 139.1, 132.0, 131.89, 131.8, 131.4, 130.9, 128.7, 128.4, 127.8, 127.1, 126.7, 126.6, 126.2, 125.9, 125.8, 122.4, 120.9, 120.0, 119.9, 55.1, 52.4, 40.4, 39.2, 31.4, 29.6, 23.7, 22.5, 13.9.

#### 2.5. Preparation of the solutions of various metal ions

One millimole of inorganic salt: Hg(ClO<sub>4</sub>)<sub>2</sub>:3H<sub>2</sub>O, AgNO<sub>3</sub>, Cr (NO<sub>3</sub>)<sub>3</sub>:9H<sub>2</sub>O, Al(NO<sub>3</sub>)<sub>3</sub> 9H<sub>2</sub>O, Fe(NO<sub>3</sub>)<sub>3</sub>:9H<sub>2</sub>O, CoCl<sub>2</sub>:6H<sub>2</sub>O, Ca (NO<sub>3</sub>)<sub>2</sub>:4H<sub>2</sub>O, Ba(NO<sub>3</sub>)<sub>2</sub>, Pb(NO<sub>3</sub>)<sub>2</sub>, Ni(NO<sub>3</sub>)<sub>2</sub>:6H<sub>2</sub>O, Zn(NO<sub>3</sub>)<sub>2</sub>:6H<sub>2</sub>O, Cu (NO<sub>3</sub>)<sub>2</sub>:3H<sub>2</sub>O, MnSO<sub>4</sub>:H<sub>2</sub>O, Cd(NO<sub>3</sub>)<sub>2</sub>:4H<sub>2</sub>O, Mg(ClO<sub>4</sub>)<sub>2</sub>, Fe(SO<sub>4</sub>)<sub>2</sub>:7H<sub>2</sub>O, KNO<sub>3</sub>, NaNO<sub>3</sub> and LiNO<sub>3</sub> was dissolved in double distilled water (10 mL) to afford  $1 \times 10^{-1}$  mol/L aqueous solution, respectively. The stock solutions were diluted to desired concentrations with double distilled water when needed.

#### 2.6. Fluorescence intensity changes of PTS with different metal ions

A solution of **PTS** ( $1 \times 10^{-3}$  mol/L) in THF was prepared. Different metal ions ( $1 \times 10^{-1}$  mol/L,  $4.5 \,\mu$ L) were added to the solution of **PTS** (60  $\mu$ L) in a quartz tube respectively, then distilled water was added to help the formation of aggregation state (with water fraction of 98%). The resultant solutions (3 mL) were placed in a quartz cell (10.0 mm width), and the changes of the fluorescence intensity were recorded at room temperature each time (excitation wavelength 368 nm).



Scheme 1. Synthetic pathway of probe PTS.

#### 2.7. Instrumentation

<sup>1</sup>H and <sup>13</sup>C NMR spectroscopy was conducted with a Varian Mercury 300 or Bruker ARX400 spectrometer using tetramethylsilane (TMS;  $\delta = 0$  ppm) as internal standard. EI-MS spectra were recorded with a Finnigan PRACE mass spectrometer. Elemental analyses (EA) were performed by a CARLOERBA-1106 by a micro-elemental analyzer. Gel permeation chromatography (GPC) was performed on an Agilent 1100 series HPLC system and a G1362A refractive index detector. Polystyrene standards were used as calibration standards for GPC. The Fourier transform infrared (FTIR) spectra were recorded on a PerkinElmer-2 spectrometer in the region of 4000–400 cm<sup>-1</sup>. UV/Vis spectra were obtained by using a Shimadzu UV-2550 spectrometer. Photoluminescence spectra were performed on a Hitachi F-4500 fluorescence spectrophotometer.

#### 3. Results and discussion

#### 3.1. Synthesis and characterization

The synthetic procedure of the polymers is shown in Scheme 1. Compounds 1 and 3 were synthesized according to previous literatures [60,61]. Compound 2 was synthesized by the acylation reaction between 1 and 2-(4-nitrophenyl) acetyl chloride. The precursor polymer **PTO** was prepared by the palladium-catalyzed Suzuki coupling reaction between 2 and 3. Then, the target polymer **PTS** was synthesized by the protection reaction between **PTO** and 1, 2-ethanedithiol. All these final products and intermediates were fully verified by <sup>1</sup>H and <sup>13</sup>C NMR (Figs. S3–S8), mass spectrometry, elemental analysis, GPC and Fourier transform infrared spectra.

The <sup>1</sup>H NMR spectra of **PTS** and **PTO** are shown in Fig. 2. After the protection reaction between **PTO** and 1, 2-ethanedithiol, the singlet at 4.35 ppm assigned to the methylene (Ha in **PTO**) attached to carbonyl group shifted from 4.35 to 3.58 ppm (Ha' in **PTS**) as the result of the transformation of the carbonyl group to thioketal group. Meanwhile, the multiplet at the range of 3.33–3.21 ppm assigned to the methylene (-SCH<sub>2</sub>CH<sub>2</sub>S-, Hb in **PTS**) attached to the sulfur atoms appeared. Moreover, great changes had also taken place in aromatic areas after the protection reaction. The hydrogen atoms ratio between Ha' and Hb in **PTS** was 1:2 confirming that carbonyl groups in **PTO** have been completely reacted with 1, 2-ethanedithiol (Fig. S7). The <sup>13</sup>C NMR spectra of **PTO** and **PTS** are shown in Fig. S6 and Fig. S8. After incorporation with thiol, the obvious signal shift at 195.39 ppm for carbon of the carbonyl group in **PTO** was disappeared in that of **PTS**.

#### 3.2. UV-vis absorption spectra

The UV/Vis absorption spectra of PTS and PTO are shown in Fig. S1. The dilute solution of PTO and PTS in THF were colorless with maximum absorption wavelength ( $\lambda_{max}$ ) at about 355 and 353 nm, respectively. As presented in the textbook of basic organic chemistry, the ketones could be transformed to enols in the presence of chemical base [62-64]. Thus, after the addition of *t*-BuOK to the solution of **PTO** in THF, the ketone-enol isomerization reaction occurred with a new absorption peak ( $\lambda_{max} = 569 \text{ nm}$ ) appeared. At the same condition, the addition of t-BuOK to PTS caused nearly no changes due to the absence of the methyl ketone group. However, when *t*-BuOK was added to the solution of  $PTS + Hg^{2+}$ , the ketone-enol isomerization reaction occurred immediately, with an apparent color change from colorless to red purple, and a new absorption peak ( $\lambda_{max} = 569 \text{ nm}$ ) appeared (Fig. S1b). Therefore,  $Hg^{2+}$  could promote the deprotection reaction of mercaptal very well, and caused the followed ketone-enol isomerization with the aid of *t*-BuOK.

#### 3.3. AIEE properties

PTO and PTS have good solubility in common organic solvents, such as dichloromethane, chloroform and THF, but insoluble in water. THF (good solvent) and H<sub>2</sub>O (poor solvent) were chosen as the solvent pair for their miscibility. As shown in Fig. 3, Photoluminescence (PL) spectra of PTO and PTS were measured in THF-H<sub>2</sub>O mixtures with different water fractions  $(f_w)$  to investigate their AIEE properties. Their dilute solution in pure THF showed weak emission. Upon the addition of water, the aggregates of these two polymers were formed step by step. Their PL intensity gradually increased with the increase of the water fraction in the mixture solvents, exhibiting the obvious AIEE phenomenon. As to PTO, the highest PL intensity was achieved when  $f_{\rm w}$  = 98%. As shown in the inset photos, its THF solution emitted weak light, but strong emissions were observed with  $f_w = 98\%$  (Fig. 3a). However, as to PTO, the PL intensity declined swiftly, even lower than that of its pure THF solution, when the water fraction was higher than 90% (Fig. 3b). Precipitates were formed and could be observed by naked eyes when  $f_w = 98\%$ , which would induce a decrease of the efficient concentration of fluorophores during the PL measurement. Thus, the fluorescence decline should be caused by the occurrence of amorphous aggregates and the quick formation of precipitate due to the introduction of large amount of water [65-68]. On the other hand, Yin et al. have demonstrated that fluorescence of dyes could be significantly quenched through efficient energy transfer from TPE to an additional fluorophore (via a non-conjugated linkage) [69]. Similarly, as mentioned above, the nitrobenzene moieties in TPE-S were highly twisted and close to TPE, quenching its fluorescence. Thus, molecular structure,



Fig. 2. <sup>1</sup>H NMR spectra of PTO and PTS (in CDCl<sub>3</sub>), the solvent peaks are marked with asterisks.

such as nitrobenzene moieties in the polymer could be another reason that quenched the fluorescence of **PTS**. Thus, once triggered by  $Hg^{2+}$ , the conversion of **PTS** (weak PL intensity) to **PTO** (high PL intensity) inTHF-H<sub>2</sub>O mixture (V<sub>THF</sub>/V<sub>water</sub> = 2/98), could give out the fluorescent turn on signal, to report the presence of  $Hg^{2+}$ .

### 3.4. $Hg^{2+}$ sensing properties

The PL spectra of **PTS** in the presence of  $Hg^{2+}$  ions at different concentrations are shown in Fig. 4. Upon the addition of  $Hg^{2+}$  ions, then water was added for the formation of aggregation state. The emission peak ( $\lambda_{em}$ ) of **PTS** gradually enhanced and slight red-shift with the increasing concentration of  $Hg^{2+}$ . And an emission enhancement of about 11.3-fold at 520 nm was observed until the concentration of  $Hg^{2+}$  reached to  $1.5 \times 10^{-4}$  M (Fig. 4a). In sharp contrast, fluorescence of **PTS** exhibited significant enhancement after the addition of  $Hg^{2+}$  ions, accompanying with the quantum yield of **PTS** increased from 0.64% to 7.67%. Under a normal UV lamp, the remarkable PL enhancement could be visually observed by the naked eyes (Inset photos in Fig. 4a). Also, there was a good linear relationship between the intensity change and the concentration of  $Hg^{2+}$  ions at both low and high concentration (Fig. 4b). Values of I/I<sub>0</sub> possess a good linear relationship

with the concentration of Hg<sup>2+</sup> ranging from 5 to 30  $\mu$ M (R<sup>2</sup> = 0.992, inset in Fig. 4b). The detection limit of Hg<sup>2+</sup> could be evaluated to be 2.3 × 10<sup>-7</sup> M (S/N = 3). In addition, as shown in Fig. S2, the Hg<sup>2+</sup>-promoted deprotection reaction of **PTS** occurred quickly within 5 min.

To evaluate the specificity of **PTS** towards  $Hg^{2+}$ , the influence of various common metal ions were investigated in parallel under the same conditions. Thus, various metal ions  $(Hg^{2+}, Ag^+, Cr^{3+}, Al^{3+}, Fe^{3+}, Ca^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+}, Cd^{2+}, Ba^{2+}, Li^+, Na^+ and K^+)$  were added to the solution of **PTS**. As shown in Fig. 5, only  $Hg^{2+}$  ions could led the remarkable PL enhancement, other metal ions brought slight influence on the PL intensity, indicating the specific chemical reactions between **PTS** and  $Hg^{2+}$ . This result is reasonable due to the strong affinity between  $Hg^{2+}$  and thioketal groups in **PTS**. The high selectivity of **PTS** towards  $Hg^{2+}$  could be further confirmed by the competition experiments. To the solution of **PTS** with one of the competitive metal ions was added  $Hg^{2+}$  subsequently, the fluorescence was still turn-on rapidly (Fig. 6), illustrating the nice anti-interference and excellent selectivity of **PTS** towards  $Hg^{2+}$ .

#### 3.5. Mechanism of the sensing process

This probe was designed according to the Hg<sup>2+</sup>-promoted



Fig. 3. PL spectra of PTO (A) and PTS (B) in THF-H<sub>2</sub>O mixtures (20 µM) with different water fractions. Inset: Photos of luminogens in THF/H<sub>2</sub>O mixtures taken under the illumination of a 365 nm UV lamp.



Fig. 4. (A) PL spectra of PTS ( $20 \mu$ M) in the presence of different amounts of Hg<sup>2+</sup>, excited at 368 nm in THF-H<sub>2</sub>O mixtures with the water fraction of 98%. Inset: corresponding fluorescence photos of PTS before and after reacted with Hg<sup>2+</sup> ( $1.5 \times 10^{-4}$  M). (B) PL enhancement values (I/I<sub>0</sub>) versus Hg<sup>2+</sup> concentration, the plots for Hg<sup>2+</sup> are shown as an inset.



Fig. 5. (A) PL spectra of PTS ( $20 \mu$ M) in the presence of various metal ions ( $1.5 \times 10^{-4}$  M) excited at 368 nm in THF-H<sub>2</sub>O mixtures with the water fraction of 98%. (B) Corresponding fluorescence responses of PTS to various metal ions.



Fig. 6. Fluorescence spectra profiles of PTS (20  $\mu$ M) in the presence of various metal ions ( $1.5 \times 10^{-4}$  M, black line), followed by added Hg<sup>2+</sup> ( $1.5 \times 10^{-4}$  M, red line), in THF/H<sub>2</sub>O (2/98, v/v) solution. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

deprotection reaction of thioketal, transforming **PTS** to **PTO** in the presence of  $Hg^{2+}$ . FTIR spectrum was used to confirm the sensing mechanism. As shown in Fig. 7, there was a very strong absorption peak at about 1686 cm<sup>-1</sup> in **PTO**, corresponding to the stretching vibration of the carbonyl group (C=O), which has completely disappeared in **PTS**, for the absence of carbonyl group (carbonyl group was transformed to thioketal). After the addition of  $Hg^{2+}$  ions, the typical absorption peak of carbonyl group at 1686 cm<sup>-1</sup> appeared (**PTS** +  $Hg^{2+}$ ), indicating the successful deprotection reaction of **PTS** and the formation of **PTO**.

#### 4. Conclusion

In conclusion, considering **TPE-S** has good performance towards  $Hg^{2+}$ , it was utilized to design a conjugated polymer probe **PTS** with the aim to enhance the fluorescence signal. Due to the signal amplification effect of conjugated polymer, a fluorescent turn on probe for aqueous  $Hg^{2+}$  with good sensing performance was realized. Once triggered by mercury ions, remarkable PL enhancement could be visually observed by naked eyes. The response was very fast with good selectivity towards  $Hg^{2+}$  due to the specific chemical reaction. Other metal ions (Ag<sup>+</sup>, Cr<sup>3+</sup>, Al<sup>3+</sup>, Fe<sup>3+</sup>, Ca<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>,



Fig. 7. IR spectra of PTO, PTS and the reaction product of PTS with Hg<sup>2+</sup>.

 $Zn^{2+}$ ,  $Mg^{2+}$ ,  $Fe^{2+}$ ,  $Mn^{2+}$ ,  $Cd^{2+}$ ,  $Ba^{2+}$ ,  $Li^+$ ,  $Na^+$  and  $K^+$ ) gave nearly no disturbance to the sensing process. Furthermore, the sensitivity of this probe was satisfied with the detection limit as low as  $2.3 \times 10^{-7}$  M.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx. doi.org/10.1016/j.dyepig.2018.03.060.

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