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# A new thiosemicarbazone fluorescent probe based on 9,9'bianthracene for Hg<sup>2+</sup> and Ag<sup>+</sup>

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**ABSTRACT:** A new 9,9'-bianthracene-based thiosemicarbazone (**D1**) has been successfully synthesized and utilized for chemosensors. The properties of **D1** were systematically investigated by UV–Vis, fluorescence titration and theoretical calculations. As a result, **D1** exhibits a characteristic fluorescence quenching phenomenon in the presence of  $Hg^{2+}$  or  $Ag^+$  compared to other metal cations (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ba<sup>2+</sup>, Al<sup>3+</sup>, Zn<sup>2+</sup>, Fe<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup> and Mn<sup>2+</sup>). The detection limits of  $Hg^{2+}$  and  $Ag^+$  reach  $6.62 \times 10^{-7}$  M and  $1.99 \times 10^{-5}$  M, respectively. This is mainly attributed to the  $Hg^{2+}$  (or  $Ag^+$ ) forms a stable five-membered ring with the N atom in Schiff base C=N and the S atom in thiourea. The results suggest that the probe **D1** is a promising candidate for chemosensors in aqueous media due to its highly selectivity for  $Hg^{2+}$  and  $Ag^+$ .

Keywords: Fluorescent probe, Thiosemicarbazone, 9,9'-Bianthracene, Hg2+ and Ag+

### 1. Introduction

As important industrial raw materials, mercury and silver have an irreplaceable role in the modern chemical industry [1-3], especially in the fields of chloralkali industry, goldmining, pharmaceutical industry, photographic imaging technology, catalytic technology, semiconductors and so on [4-6].

However, with the development of industry, their pollution problems have become increasingly prominent, which poses a serious threat to human health and the earth's ecosystem. Excessive exposure to mercury and its derivatives can cause serious heart diseases, as well as disorders of the brain, kidney and central nervous system [7-13]. In addition, silver ions can also inactivate the sulphur-containing enzymes in the human body and interact with active substances such as amines, imidazoles, and carboxylic acids [14], resulting in various diseases. What is even more worrying is that they can also be enriched in living organisms through the food chain, which will seriously threaten human health [6, 15-17]. For these reasons, it is highly imperative to develop methods for rapid detection of  $Hg^{2+}$  and  $Ag^+$ .

So far, many methods such as atomic absorption spectrometry [18], inductively coupled plasma mass spectrometry [19], atomic emission spectroscopy [20], cyclic voltammetry [21], extraction spectrophotometry and fluorescence probes [22, 23] have been used for rapid detection of  $Hg^{2+}$  and  $Ag^+$ . Among these reported methods, fluorescence probes have drawn increasing attention owing to their advantages of high sensitivity and excellent selectivity, low detection limit, convenience, cheapness and quickness etc. Although many fluorescence probes for  $Hg^{2+}$  [5, 12, 24-31] and  $Ag^+$ [23, 32-42] detection have been reported, there are still few studies on the simultaneous detection of these ions by a single probe. Due to the suitable bandwidth, high fluorescence quantum efficiency and good thermal stability, 9,9'-bianthracene has been widely used in blue light materials. However, as far as we know, fluorescent probes based on 9,9'-bianthracene for  $Hg^{2+}$  or  $Ag^+$  detection have not been reported. Considering the special spatial structure where the two anthracene rings are perpendicular to each other, this helps to reduce the aggregation of molecules derived from the

intermolecular  $\pi$ - $\pi$  interactions as well as to maintain the stability of fluorescence, so the 9,9'bianthracene was selected as the fluorophore group. Besides, based on the excellent properties exhibited in the detection of Hg<sup>2+</sup> [43-52] and Ag<sup>+</sup> [53-55], thiosemicarbazone was selected as the recognition group. Finally, we designed and synthesized a new 9,9'-bianthracene based fluorescent probe (**D1**) for the selective detection of Hg<sup>2+</sup> and Ag<sup>+</sup>. Its absorption spectra, fluorescence emission spectrum and sensing behavior have been investigated in detail.

#### 2. Experimental section

#### 2.1. Apparatus

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance 600 MHz spectrometer in CDCl<sub>3</sub> or DMSO with tetramethylsilane as inner reference. The absorption and emission spectra in *N*,*N*dimethylformamide solution were measured at room temperature on a SHIMADZU UV-3600 Plus spectrophotometer and Hitachi F-4600 fluorescence spectrophotometer. HRMS data were recorded on a Finnigan MAT 95 XP mass spectrometer (Thermo Electron Corporation).

#### 2.2. Reagents

THF was distilled under an argon atmosphere over sodium metal for complete dryness. Other reagents were purchased from commercial sources and used without further purification. All inorganic salts solutions of KNO<sub>3</sub>, Na(OAc)<sub>2</sub>, Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, ZnSO<sub>4</sub>·7H<sub>2</sub>O, FeSO<sub>4</sub>, Pb(NO<sub>3</sub>)<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, HgCl<sub>2</sub>, AgNO<sub>3</sub>, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, NiSO<sub>4</sub>·6H<sub>2</sub>O, MnSO<sub>4</sub>·H<sub>2</sub>O and Ba(NO<sub>3</sub>)<sub>2</sub> were dissolved in distilled water and respective solutions were prepared. The solutions of anions (Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, CH<sub>3</sub>COO<sup>-</sup>, SCN<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, SO<sub>3</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup> and NO<sub>3</sub><sup>-</sup>) were prepared from their Na<sup>+</sup> or K<sup>+</sup> salts. The solution of **D1** was prepared

in DMF.

#### 2.3. Syntheses

#### 2.3.1. Synthesis of 4,4'-([9,9'-bianthracene]-10,10'-diyl)dibenzaldehyde (4):

To a mixture of 10,10-dibromo-9,9-bianthracene (0.948 g, 1.85 mmol), 4-formylphenylboronic acid (0.696 g, 4.64 mmol), and tetrakis(triphenylphosphine)palladium (0) (0.214 g, 0.185 mmol) in THF (50 mL), 2 M potassium carbonate aqueous solution (10 mL, 20 mmol) was added. The mixture was stirred and heated to reflux under argon for 24 h. After the mixture was cooled to ambient temperature, the reaction mixture was poured into water and extracted with DCM for three times. The combined extracts were washed with brine, dried over anhydrous MgSO<sub>4</sub>, and then filtered. Evaporation of the solvent was carried out under reduced pressure. Crude product was purified by chromatography on silica gel using petroleum ether/dichloromethane/ethyl acetate (40/20/1, v/v) as eluent and dried under vacuum to afford a yellow solid in 90% yield (936 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 10.27 (s, 2H, -CHO), 8.23 (d, *J* = 7.8 Hz, 4H, ArH), 7.85 (d, *J* = 7.8 Hz, 4H, ArH), 7.75 (d, *J* = 9 Hz, 4H, ArH), 7.39–7.36 (m, 4H, ArH), 7.26 (d, *J* = 8.4 Hz, 4H, ArH), 7.21–7.19 (m, 4H, ArH). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 192.17, 146.10, 136.37, 135.96, 134.12, 132.46, 131.39, 130.06, 129.78, 127.28, 126.78, 125.94. HRMS (ESI, m/z): [M + H]<sup>+</sup> calcd for [C<sub>42</sub>H<sub>27</sub>O<sub>2</sub>]<sup>+</sup>: 563.2006, found: 563.2053.

2.3.2. Synthesis of (2E,2'E)-2,2'-(([9,9'-bianthracene]-10,10'-diylbis(4,1-phenylene))bis(methanylylidene))bis(hydrazine-1-carbothioamide) (**D1**):

4,4'-([9,9'-Bianthracene]-10,10'-diyl)dibenzaldehyde (**4**) (0.281 g, 0.5 mmol), thiosemicarbazide (0.091 g, 1.0 mmol) and 25 mL ethanol were added to round-bottom flask. Then glacial acetic acid

(0.5 mL) was added to the flask. The reaction mixture was stirred at room temperature for 48 h. The precipitates were collected by centrifugation. The pure product was obtained by repeatedly washing with dichloromethane and centrifugation, as a yellow solid in 74.3% yield (263 mg). The solubility of **D1** was DMF > DMSO > THF > CH<sub>3</sub>CN in different solvents. <sup>1</sup>H NMR (600 MHz, DMSO)  $\delta$  ppm 11.55 (s, 2H, N–<u>NH</u>–C=S), 8.26 (s, 4H, –NH<sub>2</sub>), 8.13–8.12 (m, 6H, CH=N and ArH), 7.71–7.63 (m, 8H, ArH), 7.39–7.37 (m, 4H, ArH), 7.22–7.20 (m, 4H, ArH), 7.04 (d, *J* = 8.4 Hz, 4H, ArH). <sup>13</sup>C NMR (150 MHz, DMSO)  $\delta$  ppm 178.10, 141.94, 139.64, 137.03, 133.87, 132.69, 131.47, 130.65, 129.33, 127.60, 126.72, 126.37, 126.10, 125.84. HRMS (ESI, m/z): [M + H]<sup>+</sup> calcd for [C<sub>44</sub>H<sub>33</sub>N<sub>6</sub>S<sub>2</sub>]<sup>+</sup>: 709.2208, found: 709.2180.

### 3. Results and discussion

#### 3.1. Synthesis and characterization

The synthesis route of (2*E*,2'*E*)-2,2'-(([9,9'-bianthracene]-10,10'-diylbis(4,1-phenylene))bis(met-hanylylidene))bis(hydrazine-1-carbothioamide) (**D1**) has been exhibited in Scheme 1. The intermediate compound 10,10'-dibromo-9,9'-bianthracene (**3**) was synthesized from compound anthraquinone according to the same procedure as reported literature [56]. The fluorescence probe **D1** was synthesized by the condensation reaction of 4,4'-([9,9'-bianthracene]-10,10'-diyl) dibenzaldehyde (**4**) and thiosemicarbazide. All structures were confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR and HRMS analyses (Fig. S1–S5).

### Scheme 1.

### 3.2. Optical properties of **D1**

3.2.1. Optimization of experimental conditions

In order to get the best selectivity of fluorescence probe **D1**, further experiments must be carried out in order to establish detection environmental conditions. According to the solubility trend of **D1**, DMF was selected as the solvent. Fig. S6 displays optical properties of **D1** with different ratio of DMF and water. With the fraction of DMF in mixtures less than 90%, the fluorescence intensity of D1 decreases significantly. Therefore, the mixture of DMF/H<sub>2</sub>O (9/1, v/v) was selected as the optimized solvent systems for further detection experiments. Optical responses of D1 ( $5.0 \times 10^{-6}$ M) toward multifarious metal ions and anions were investigated in the medium. D1 has a strong characteristic fluorescence emission peak at 454 nm originated from 9,9'-bianthracene. Obvious fluorescence quenching of **D1** can be observed in the presence of Cu<sup>2+</sup>, Hg<sup>2+</sup>, Ag<sup>+</sup>, Cd<sup>2+</sup>, and the quenching degrees caused by  $Ag^+$ ,  $Hg^{2+}$  and  $Cu^{2+}$  are much higher than that brought by  $Cd^{2+}$  (Fig. S7a). All of anions don't bring obvious influence to the emission of D1 (Fig. S7b). Interestingly, the fluorescence quenching by Cu<sup>2+</sup> can be blocked by adjusting the pH value of probing medium to 3.0 (through the introduction of HNO<sub>3</sub>), but fluorescence quenching by  $Hg^{2+}$  and  $Ag^{+}$  do not seem to be influenced by the alteration of pH (Fig. S8). We believe that this may be due to the strong interaction between **D1** and  $Hg^{2+}$  or  $Ag^+$  which is not easily affected by the protonation of amino groups, and can form a stable chelate structure. It is interesting that the case of  $Cu^{2+}$  is just the opposite. The higher pH value in the **D1** solution, the better deprotonation of the amino group and therefore promoting the binding of **D1** to  $Cu^{2+}$  which resulting in the fluorescence quenching. Correspondingly, as the pH decreases, the N atom of C=N and the -NH<sub>2</sub> become more and more difficult to deprotonate. It makes the binding of **D1** and Cu<sup>2+</sup> gradually weakened and eventually leads to the fluorescence quenching not occurring. Based on these results, D1 can be used as a

fluorescent probe for  $Hg^{2+}$  and  $Ag^{+}$  as well as DMF/H<sub>2</sub>O (V/V, 9/1) (pH = 3.0) is selected as the testing medium for the further experiments.

### Fig. 1.

#### Fig. 2.

#### 3.2.2. Selectivity over metal ions

Selectivity of **D1** to multifarious metal ions have been investigated by UV–Vis absorption and fluorescence emission spectroscopy at room temperature in DMF/H<sub>2</sub>O (9/1, v/v, pH = 3.0). The addition of Hg<sup>2+</sup> and Ag<sup>+</sup> (10 eq.) make obvious changes in the UV–Vis absorption spectra and the fluorescence spectra. Meanwhile, other metal cations such as K<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Al<sup>3+</sup>, Zn<sup>2+</sup>, Fe<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup>, Mn<sup>2+</sup> and Ba<sup>2+</sup> do not show significant impact (see Fig.1 and 2). The absorption spectra of **D1** shows characteristic absorption of the anthracene group ( $\lambda_{max} = 360, 381$ and 403 nm), respectively, which can be ascribed to the superposition of the absorption generated by the  $\pi$ – $\pi$ \* transition and the aromatic ring vibration transition. With the addition of Hg<sup>2+</sup> or Ag<sup>+</sup>, the absorption peaks at 328 nm attributed to the  $\pi$ – $\pi$ \* transition of C=N exhibit a blue shift and a significant decrease, indicating that Hg<sup>2+</sup> or Ag<sup>+</sup> reacts with the thiosemicarbazide group to form a stable complex.

### 3.3. Titration experiment of **D1** toward $Hg^{2+}$

In order to further understand the binding affinity of **D1** and  $Hg^{2+}$ , titration experiment was carried out (Fig.3). With the addition of incremental  $Hg^{2+}$  (0–10 eq.) to the solution of **D1**, the absorption spectra at 328 nm and fluorescence intensity of **D1**– $Hg^{2+}$  solution at 456 nm decreased gradually (Fig. 3a-3b). Corresponding calibration curve of the fluorescence is presented in Fig.3c as a function of the Hg<sup>2+</sup> concentration. The detection limit (LOD) of **D1** for Hg<sup>2+</sup> is calculated to be as low as  $6.62 \times 10^{-7}$  M based on  $3\sigma$  criteria [57].

Fluorescence competition experiments in **D1** solution were conducted in the presence of 10 eq. of various other metal ions and  $Hg^{2+}$  (Fig. 4). The results suggest that the presence of other metal ions brings insignificant interference to the detection of  $Hg^{2+}$ , which means that the fluorescence probe **D1** has an excellent selectivity towards  $Hg^{2+}$ .

#### Fig. 3.

#### **Fig. 4**.

### 3.4. Titration experiment of D1 toward $Ag^+$

Ag<sup>+</sup> titration experiment of fluorescence probe **D1** was carried out similarly to Hg<sup>2+</sup> (Fig.5). The results are similar to Hg<sup>2+</sup> (Fig. 5a-5b). The detection limit (LOD) of **D1** for Ag<sup>+</sup> is calculated from the plot of emission intensity change (Fig. 5c) and it is calculated as  $1.99 \times 10^{-5}$  M based on  $3\sigma$  criteria. It can be seen that the detection sensitivity of **D1** to Ag<sup>+</sup> is slightly lower than that of **D1** to Hg<sup>2+</sup>.

Furtherly, competitive experiments with  $Ag^+$  and other ions have also been completed. Similarly, the presence of other metal ions does not significantly interfere with the detection of  $Ag^+$  (Fig. 6). Schiff base **D1** displayed an excellent selectivity towards  $Ag^+$ , the emission at 456 nm decreases and an intense peak at 332 nm (Fig. 7) is formed, which may be attributed to the coordination of  $Ag^+$  with heteroatoms resulting in a weaker electron donating ability and intramolecular charge transfer capability.

#### Fig. 5.

#### **Fig. 6.**

### Fig. 7.

### 3.5. Recognition mechanism

In order to confirm the complexation of the Schiff base D1 with  $Hg^{2+}$  (or  $Ag^{+}$ ), the job curve of the probe **D1** and  $Hg^{2+}$  (or  $Ag^+$ ) coordination was made in the experiment. The total concentration of probe D1 and Hg<sup>2+</sup> (or Ag<sup>+</sup>) is fixed to 100 µmol/L, and the fluorescence intensities were recorded by varying the mole ratio of  $Hg^{2+}$  (or  $Ag^{+}$ ). The result indicates the stoichiometry ratio between D1 and Hg<sup>2+</sup> (or Ag<sup>+</sup>) is 1:2 (Fig. S9), which can be further verified by the experimental data from fluorescent titration, namely, by the extended Benesi-Hildebrand equation [58-60] based on 1:2 and a linear correlation coefficient of 0.99 can be obtained (Fig. S10). The complexing constants between D1–Hg<sup>2+</sup> and D1–Ag<sup>+</sup> have also been calculated to be  $2.29 \times 10^{10}$  M<sup>-2</sup> and  $5.36 \times 10^{8}$  M<sup>-2</sup> according extended Benesi-Hildebrand equation below: to the is shown

$$\frac{1}{I_0 - I} = \frac{1}{K_a (I_0 - I_{\min}) [M^{n+}]^2} + \frac{1}{I_0 - I_{\min}}$$

In the formula, I<sub>0</sub> and I represent the fluorescence intensity of the absence and presence of Hg<sup>2+</sup> (or Ag <sup>+</sup>), I<sub>min</sub> represents the minimum of the fluorescence intensity, K<sub>a</sub> is the complexing constant. Energy level of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) play an important role in studying the photoelectric properties of organic conjugated molecules. To insight into the geometrical and electronic distribution of **D1**, density functional theory (DFT) calculations were performed with Gaussian 09 program using B3LYP/6-31G(d) level. As shown in Fig.8, the HOMO is distributed mainly on 9,9'-bianthracene, the LUMO spreads around the linkage between thiosemicarbazide and bianthracene. HOMO–LUMO excitation

partly moves the electron density distribution from 9,9'-bianthracene unit to the thiosemicarbazide unit, thus leading to weak fluorescence. The energy gap between HOMO and LUMO is calculated to be 3.39 eV.

#### Fig. 8.

Based on the above experimental results, we believe that the fluorescence quenching phenomenon is mainly due to the fact that  $Hg^{2+}$  (or  $Ag^+$ ) forms a stable five-membered ring with the S atom and the N atom of C=N in **D1**. The corresponding possible mechanism is graphically depicted in Scheme

2.

### Scheme 2.

#### 4. Conclusion

In summary, a new fluorescence probe (**D1**) employing 9,9'-bianthracene and thiosemicarbazone as skeletons has been designed and synthesized successfully. The results show that  $Hg^{2+}$  or  $Ag^+$  can cause fluorescence quenching of **D1** in DMF/H<sub>2</sub>O (9/1, v/v) (pH = 3.0) solution, which indicates that **D1** can be used to qualitatively detect the presence of these two metal ions, especially, **D1** has high selectivity and sensitivity towards to  $Hg^{2+}$ . When  $Ag^+$  is absent, the  $Hg^{2+}$  content can be quantitatively detected, and the detection limit is as low as  $6.62 \times 10^{-7}$  M; when  $Ag^+$  is present,  $Hg^{2+}$ can also be determined by adding a masking agent. This work clearly demonstrates that the presented probe **D1** possess the unique optical response to  $Hg^{2+}$  and  $Ag^+$ , which provides an alternative direction for the development of fluorescent probes of high selectivity and stability to  $Hg^{2+}$  and  $Ag^+$  in aqueous phase.

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#### **Figure Captions**

Scheme 1. The synthesis route of fluorescent probe D1

**Fig. 1.** UV–Vis absorption spectra of **D1** ( $\sim 5 \times 10^{-6}$  M) upon addition of 10 eq. of various metal ions in DMF/H<sub>2</sub>O (9/1, V/V, pH = 3.0).

**Fig. 2.** Fluorescence emission spectra of **D1** ( $\sim 5 \times 10^{-6}$  M) upon addition of 10 eq. of various metal ions in DMF/H<sub>2</sub>O (9/1, V/V, pH = 3.0) ( $\lambda_{ex}$ : 330 nm). Inset: fluorescence color change of the solution

of **D1** and **D1** induced by  $Hg^{2+}$  or  $Ag^{+}$  under a portable UV lamp (365 nm).

**Fig. 3.** UV–Vis (a) and fluorescence (b) titration spectra of **D1** (~5 × 10<sup>-6</sup> M) in DMF/H<sub>2</sub>O (9/1, V/V, pH = 3.0) with various concentrations of Hg<sup>2+</sup>, and the linear relationship between I<sub>0</sub>/I and [Hg<sup>2+</sup>] (c) (Inset is the corresponding enlarged region with [Hg<sup>2+</sup>] from 5 × 10<sup>-7</sup> to 20 × 10<sup>-6</sup> M) ( $\lambda_{ex}$ : 330 nm).

**Fig. 4.** Fluorescent intensity ratio (I/I<sub>0</sub>) of the competition experiments between Hg<sup>2+</sup> and other metal ions in DMF/H<sub>2</sub>O (9/1, V/V, pH = 3.0) solution with an emission of 456 nm ( $\lambda_{ex}$ : 330 nm).

Fig. 5. UV–Vis (a) and fluorescence (b) titration spectra of D1 ( $\sim$ 5 × 10<sup>-6</sup> M) in DMF/H<sub>2</sub>O (9/1,

V/V, pH = 3.0) with various concentrations of  $Ag^+$ , and the linear relationship between I<sub>0</sub>/I and [ $Ag^+$ ]

(c) (Inset is the corresponding enlarged region with [Ag<sup>+</sup>] from  $3 \times 10^{-5}$  to  $5 \times 10^{-5}$  M) ( $\lambda_{ex}$ : 330 nm).

**Fig. 6.** Fluorescent intensity ratio (I/I<sub>0</sub>) of the competition experiments between Ag<sup>+</sup> and other metal ions in DMF/H<sub>2</sub>O (9/1, V/V, pH = 3.0) solution with an emission of 456 nm ( $\lambda_{ex}$ : 330 nm).

**Fig. 7.** Fluorescence emission spectra of **D1** ( $\sim 5 \times 10^{-6}$  M) in DMF/H<sub>2</sub>O (9/1, V/V, pH = 3.0) upon addition of 10 eq. of Hg<sup>2+</sup> and Ag<sup>+</sup>.

**Fig. 8.** Isodensity surface plots of the HOMO-1, HOMO, LUMO and LUMO+1 of **D1** (isodensity value = 0.02).

Scheme 2. The proposed mechanism of D1 toward  $Hg^{2+}$  (or  $Ag^{+}$ ).

Highlights

- A 9,9'-bianthracene-based fluorescent probe (D1) with special spatial structure has been designed and synthesized.
- The probe D1 is highly selective in sensing Hg<sup>2+</sup> and Ag<sup>+</sup> with minimal influence from other common metals.
- "Turn-off" fluorescence alterations of D1 are observed upon the addition of Hg<sup>2+</sup> or Ag<sup>+</sup> in the aqueous medium.
- 4. The detection limits of Hg^+ and Ag^+ reach  $\sim$  0.66  $\mu M$  and 19.9  $\mu M,$  respectively.

CER MAR



Figure 1



Figure 2



Figure 3



Figure 4



Figure 5



Figure 6



Figure 7



