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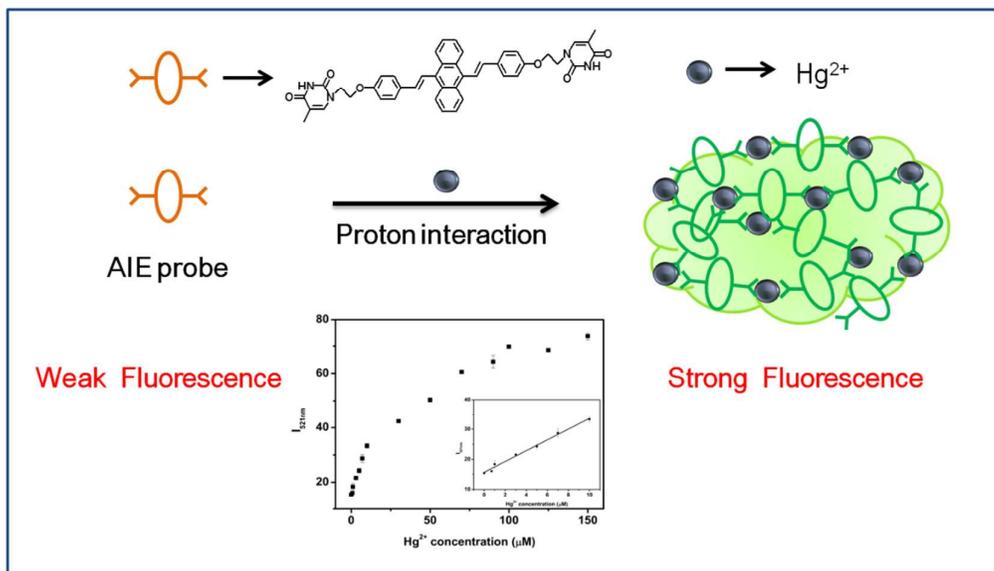
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A turn-on fluorescent probe was developed for the sensitive and selective sensing of  $\text{Hg}^{2+}$  based on aggregation-induced emission feature.



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## ARTICLE TYPE

# A sensitive and selective “turn-on” fluorescent probe for Hg<sup>2+</sup> based on thymine-Hg<sup>2+</sup>-thymine complex with aggregation-induced emission feature

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A fluorescent turn-on approach for the sensitive and selective sensing of Hg<sup>2+</sup> based on an aggregation-induced emission fluorescent molecule (DSA-T<sub>2</sub>) containing 9, 10-distyrylanthracene as a fluorophore and thymine as a Hg<sup>2+</sup> receptor, was developed. Under optimum conditions, a linear relationship (R<sub>2</sub>=0.9894) is obtained between the fluorescent intensity and the concentration of Hg<sup>2+</sup> from 7 × 10<sup>-7</sup> mol/L to 1 × 10<sup>-5</sup> mol/L. The theoretical detection limit of Hg<sup>2+</sup> is evaluated to be 3.4 × 10<sup>-7</sup> mol/L. And the selectivity towards Hg<sup>2+</sup> is good compared to other metal ions.

## 1. Introduction

Sensitive and selective chemosensors for heavy metal ions, such as Ag<sup>+</sup>, Hg<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>, have developed rapidly due to their considerable importance for environmental protection and human health [1-8]. Hg<sup>2+</sup> is known to be one severe environmental pollutant which can induce diseases of nausea, vomit, bellyache and renal damage. And after the absorption of aquatic microorganism, Hg<sup>2+</sup> can be transformed into methyl mercury and accumulated in the body through food cycle [9]. So, the investigation of Hg<sup>2+</sup> detection attracts more and more attention. There are several traditional methods to detect Hg<sup>2+</sup>, such as spectrophotometry, atomic emission spectrometry, atomic absorption spectrometry, atomic fluorescence spectroscopy. But they all have their own drawbacks. Spectrophotometry is sensitive but lacks the selectivity for Hg<sup>2+</sup> detection and is time-consuming. Atomic emission spectrometry is selective for Hg<sup>2+</sup> detection but quite expensive. Atomic absorption spectrometry is the most common way to detect Hg<sup>2+</sup> but has strict requirements on sample preparation and measurement instruments. Atomic fluorescence spectroscopy is an effective method due to its pretty low detection line, high sensitivity and selectivity for Hg<sup>2+</sup> detection, but its further applications on bioassay and bioimaging are limited because of aggregation-caused quenching (ACQ) effect [10-16]. Therefore, it is significant to explore new Hg<sup>2+</sup> detection approaches which are highly sensitive and selective, inexpensive and easily-processed.

Recently, the unique luminescent property of aggregation-induced emission (AIE) has proposed one alternative way for the detection of biomolecules and metal ions. Accordingly, a variety of molecules have been reported, including silole, tetraphenylethene, and their derivatives. They have shown good fluorescent efficiency to overcome the ACQ effect and displayed excellent “turn-on” character [17-18]. However there are few reports on fluorescent “turn-on” sensors for Hg<sup>2+</sup> detection [19].

One kind of TPE derivative with thymine groups was reported by D. Q. Zhang with a theoretical detection limit of 3.7 × 10<sup>-7</sup> mol/L and a detection range from 2 × 10<sup>-5</sup> mol/L to 2.14 × 10<sup>-4</sup> mol/L for Hg<sup>2+</sup> detection [20]. Meanwhile another kind of TPE derivative with quaternary ammonium salt groups was reported by B. Z. Tang based on the configurational change of DNA. The theoretical detection limit was 2.24 × 10<sup>-7</sup> mol/L and the detection range was from 6 × 10<sup>-7</sup> mol/L to 1 × 10<sup>-5</sup> mol/L for Hg<sup>2+</sup> detection [21]. There is thymine-Hg<sup>2+</sup>-thymine complex formation in the two reports due to the protonation of the third N of thymine groups through a imino proton-metal exchange process, where two imino protons were released upon thymine-Hg<sup>2+</sup>-thymine pairing [22].

In our previous research, we have developed a series of 9,10-distyrylanthracene (DSA) derivatives, which exhibited good AIE properties [23-28]. Our study indicates that the restricted intramolecular rotations between the 9,10-anthylene core and the vinylene segment are the origin of the AIE property [29].

In this study, we successfully achieved a turn-on fluorescent probe for Hg<sup>2+</sup> via a thymine-Hg<sup>2+</sup>-thymine complex [30] based on aggregation induced emission feature [17]. This probe (DSA-T<sub>2</sub>) contains 9, 10-distyrylanthracene as a fluorophore and thymine as a Hg<sup>2+</sup> receptor. It shows an excellent fluorescent enhancement behavior for Hg<sup>2+</sup> detection and a good selectivity towards Hg<sup>2+</sup> compared to other metal ions. Under optimum experiment conditions, it has a low theoretical detection limit of 3.4 × 10<sup>-7</sup> mol/L and a detection range from 7 × 10<sup>-7</sup> mol/L to 1.5 × 10<sup>-4</sup> mol/L.

## 2. Experimental

### 2.1 Materials

All reagents and starting materials were commercially available and were used without further purification. Anthracene (99%) was purchased from J&K Chemical Co. (China). 4-tert-

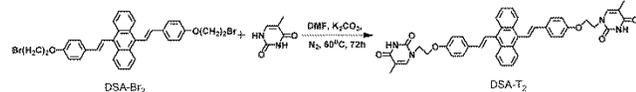
Butylbenzaldehyde was purchased from Alfa Aesar Co. (China). 4-Hydroxybenzaldehyde was purchased from Sinopharm Chemical Co. (China). 3,4-Dihydro-2H-pyran (99%) was purchased from Acros (U.S.A). 1,2-Dibromoethane was purchased from Aladdin Chemistry Co. (China). Thymine (>99.0%) was purchased as lyophilized white powder from Shanghai Yuanye Biology Co. (China). All other reagents were purchased as analytical grade from either Tianjin Fuyu Co. (China) or Beijing Chemical Reagent Co. (China). Dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF) were purified by fractional distillation before used as solvents.

## 2.2 Instrumentation

$^1\text{H}$  NMR spectra were recorded on Bruker AVANVE 600 MHz spectrometer at 298 K with deuterated DMSO as solvent and tetramethylsilane (TMS) as its internal standard. Time-of-flight mass spectra were recorded by a Kratos MALDI-TOF mass system. Fluorescence measurements were carried out with a Shimadzu RF-5301PC spectrophotometer. Transmission electron microscopy (TEM) images were recorded on a JEOL JEM-2100F electron microscopy.

## 2.3 Synthesis

As shown in Scheme 1, 9,10-Bis(4-(2-bromoethoxy)styryl)anthracen (DSA-Br<sub>2</sub>) and other compounds were prepared according to literature procedures [29]. A round bottomed flask (250 mL) equipped with a magnetic stirring bar was added with DSA-Br<sub>2</sub> (0.09 g, 0.15 mmol), thymine (0.08 g, 0.63 mmol), K<sub>2</sub>CO<sub>3</sub> (0.22 g, 1.60 mmol) and DMF (10 ml). The flask was then evacuated and charged with nitrogen. The solution was stirred at 60 °C for 72 h. After removing the organic solvents (DMF) with a rotary evaporator, the resultant precipitate was washed with H<sub>2</sub>O for a day and then washed with CHCl<sub>3</sub> for half a day by using a soxhlet extractor. After evaporating the residue, some yellow powder called DSA-T<sub>2</sub> (50 mg, 50% yield) was achieved.  $^1\text{H}$  NMR (600 MHz, DMSO-D<sub>6</sub>):  $\delta$  (TMS, ppm): 11.324 (s, 2H), 8.368-8.384 (m, 4H), 7.963-7.990 (d, J=16.2 Hz, 2H), 7.749-7.763 (d, J=8.4 Hz, 4H), 7.610 (m, 2H), 7.537-7.552 (m, 4H), 7.036-7.050 (d, J=8.4 Hz, 4H), 6.854-6.882 (d, J=16.8 Hz, 2H), 4.256 (t, 4H), 4.063 (t, 4H), 1.792 (s, 6H). MALDI/TOF MS calcd for DSA-T<sub>2</sub>: 718.28. Found: 718.185. Anal. calcd for DSA-T<sub>2</sub>: C, 73.52; H, 5.33; N, 7.79. Found: C, 73.50; H, 5.36; N, 7.76.



**Scheme 1.** Synthesis of Functionalized DSA-T<sub>2</sub>: 9,10-Bis(4-(2-(thymine ethoxy) styryl) anthracen).

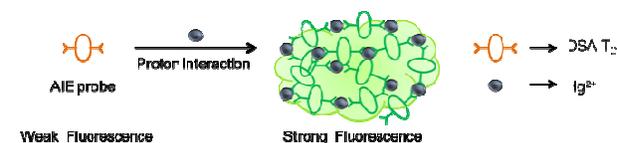
## 2.4 Fluorescence detection for Hg<sup>2+</sup>

The probe DSA-T<sub>2</sub> ( $1.16 \times 10^{-5}$  mol/L) was mixed in a CH<sub>3</sub>CN/water mixture (3:2, v/v). Then different volume of Hg<sup>2+</sup> solution ( $1 \times 10^{-4}$  mol/L) was added to pre-blended solution of the probe and carefully mixed (total volume =  $3 \times 10^{-4}$  L). The concentration range of Hg<sup>2+</sup> was from 0 to  $1.5 \times 10^{-4}$  mol/L.

## 3. Results and discussion

### 3.1 Sensing strategy

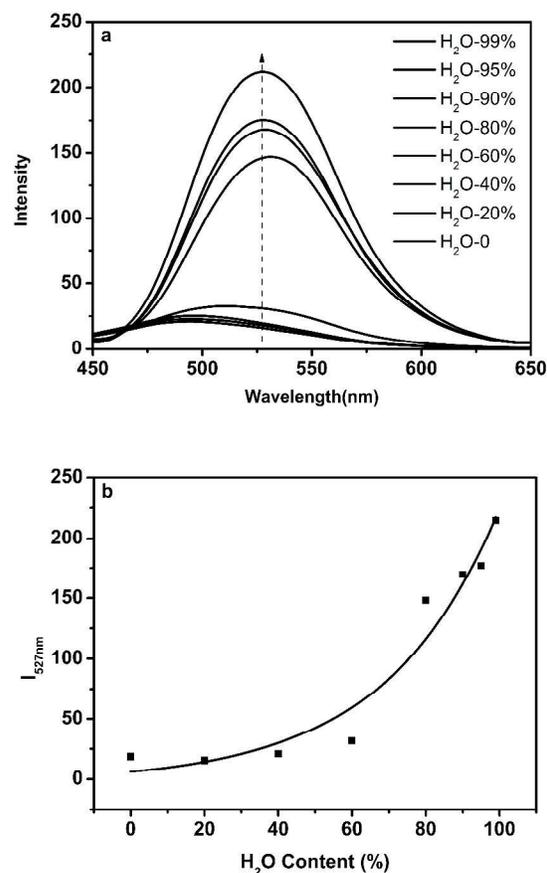
The design rationale for the Hg<sup>2+</sup> chemosensor is schematically illustrated in Scheme 2. DSA-T<sub>2</sub> exhibits weak fluorescence in its organic solvents like CH<sub>3</sub>CN and THF. After the addition of Hg(NO<sub>3</sub>)<sub>2</sub>, DSA-T<sub>2</sub> connects with Hg<sup>2+</sup> by the selective binding groups of thymine through the imino proton-metal exchange process [22]. It shows rather strong fluorescent emission after the aggregation of DSA-T<sub>2</sub> in the solution. Two imino protons of DSA-T<sub>2</sub> are released upon thymine-Hg<sup>2+</sup>-thymine pairing, which promotes the aggregation of DSA-T<sub>2</sub>. Thus, the aggregation structure of a coordination complex is formed, which limits the intramolecular rotation of DSA-T<sub>2</sub> and performs a fluorescent enhancement effect [29].



**Scheme 2.** Designing rationale for Hg<sup>2+</sup> chemosensor.

### 3.2 Aggregation-induced emission property of the probe

DSA-T<sub>2</sub> is soluble in organic solvents like CH<sub>3</sub>CN and THF, but insoluble in water. As shown in figure 1a, the emission of DSA-T<sub>2</sub> is weak in the CH<sub>3</sub>CN solution, but its fluorescent intensity increases with the addition of water.



**Fig. 1.** (a) Fluorescence spectra of DSA-T<sub>2</sub> ( $1.16 \times 10^{-5}$  mol/L) in CH<sub>3</sub>CN/H<sub>2</sub>O mixture,  $\lambda_{\text{ex}}=420$  nm. (b) Plot of the fluorescent intensity ( $I_{527\text{nm}}$ ) vs the water content.

As shown in figure 1b, when the water fraction reaches 60 %, the fluorescent intensity doesn't have an obvious increase. When the water fraction is larger than 60 %, the fluorescent intensity has a rapid increase. With the water fraction of 99 %, the fluorescent intensity is 10 times higher than that in pure CH<sub>3</sub>CN. In addition, the addition of water results in a bathochromic shift (from 493 nm to 527 nm) in the fluorescent spectra. This is because the addition of water will result in the aggregation of the probe, which limits the intramolecular rotation of DSA-T<sub>2</sub> and performs a fluorescent enhancement effect [29]. It proves that DSA-T<sub>2</sub> has the aggregation induced emission feature and it can be used as a fluorescent enhancement probe [18]. To investigate the aggregation morphology of the probe, we choose water fraction of 60 % as the matrix of DSA-T<sub>2</sub>. As shown in figure S2, transmission electron microscopy (TEM) image of DSA-T<sub>2</sub> performs as small particles with the size about 3nm. It suggests that at the water fraction of 60 %, a small amount of molecules aggregate. Therefore, a mixed solution with water fraction of 60 % is chosen for the following experiments.

### 3.3 Sensitivity of the probe

To study the sensitivity of the probe for Hg<sup>2+</sup> detection, the fluorescent changes of DSA-T<sub>2</sub> with different concentration of Hg<sup>2+</sup> was investigated. Figure 2 shows the fluorescent spectra of DSA-T<sub>2</sub> ( $\lambda_{\text{ex}} = 420 \text{ nm}$ ) with the presence of different concentration of Hg(NO<sub>3</sub>)<sub>2</sub> (from 0 to  $1.5 \times 10^{-4} \text{ mol/L}$ ) in CH<sub>3</sub>CN/H<sub>2</sub>O (3:2, v/v) mixture. When there is no Hg<sup>2+</sup> in the mixture, the emission of DSA-T<sub>2</sub> shows a weak intensity at the concentration of  $1.16 \times 10^{-5} \text{ mol/L}$ . With the increasing concentration of Hg<sup>2+</sup>, the fluorescent emission gradually increases, which is properly due to the formation of a coordination complex named thymine-Hg<sup>2+</sup>-thymine [22]. When the concentration of Hg<sup>2+</sup> reaches  $1 \times 10^{-4} \text{ mol/L}$ , the fluorescent intensity gets saturated and more addition of Hg<sup>2+</sup> can hardly increase the fluorescence. After the addition of a certain amount of Hg<sup>2+</sup>, the imino protons of DSA-T<sub>2</sub> are totally released upon thymine-Hg<sup>2+</sup>-thymine pairing and more addition of Hg<sup>2+</sup> can not further enhance the aggregation of DSA-T<sub>2</sub>. In addition, the addition of Hg<sup>2+</sup> results in a bathochromic shift (from 501 nm to 521 nm) in the fluorescent spectrum of coordination complex due to the aggregation of DSA-T<sub>2</sub>. The fluorescent intensity of DSA-T<sub>2</sub> is enhanced by 4-fold after the concentration of Hg<sup>2+</sup> reaches  $1.5 \times 10^{-4} \text{ mol/L}$ . The fluorescent intensity at 521 nm is linear (R<sup>2</sup> = 0.9894) with the concentration of Hg<sup>2+</sup> in the range from 0 to  $1 \times 10^{-5} \text{ mol/L}$ . Then the fluorescent intensity gradually increases as a parabola with the concentration of Hg<sup>2+</sup> in the range from  $1 \times 10^{-5} \text{ mol/L}$  to  $1.5 \times 10^{-4} \text{ mol/L}$ . At the emission wavelength of 521 nm, the fluorescent intensity at the concentration of  $1.5 \times 10^{-4} \text{ mol L}^{-1}$  is 4.8-fold higher than that without Hg<sup>2+</sup>. The concentration of Hg<sup>2+</sup> as low as  $7 \times 10^{-7} \text{ mol/L}$  can be detected through the fluorescent intensity change of the probe, which indicates the sensitivity of the fluorescent probe. The theoretical detection limit of the present approach at a signal-to-noise ratio (S/N) of 3 is measured to be nearly  $3.4 \times 10^{-7} \text{ mol/L}$ . And the detection range is from  $7 \times 10^{-7} \text{ mol/L}$  to  $1.5 \times 10^{-4} \text{ mol/L}$  for Hg<sup>2+</sup> detection.

### 3.4 Aggregate morphology of the probe

To demonstrate the aggregation of DSA-T<sub>2</sub> in the presence of

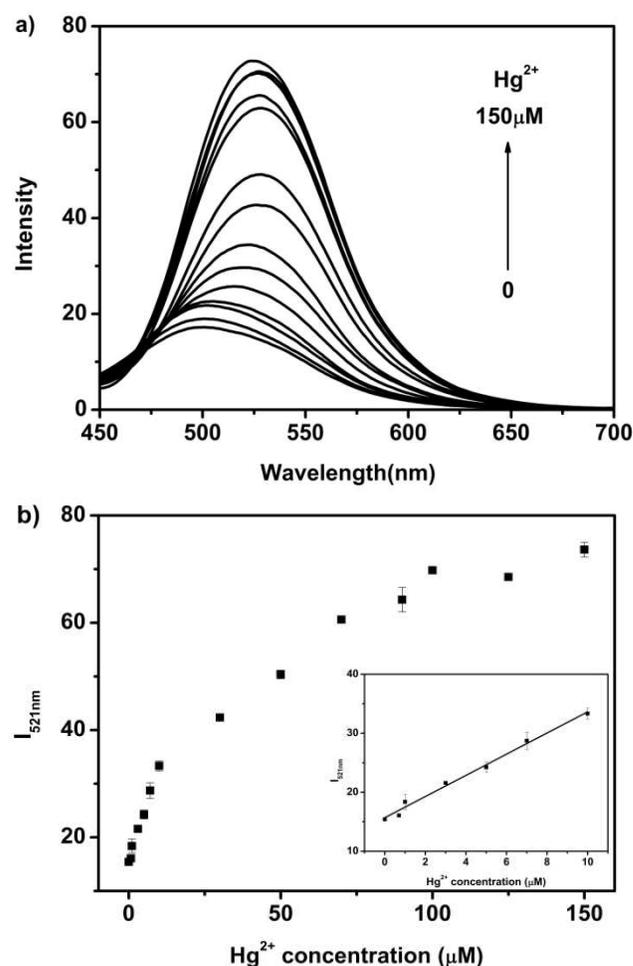


Fig. 2. (a) Fluorescence spectra of DSA-T<sub>2</sub> ( $1.16 \times 10^{-5} \text{ mol/L}$ ) in CH<sub>3</sub>CN/H<sub>2</sub>O (3:2, v/v) in the presence of increasing amounts of Hg<sup>2+</sup> (from 0 to  $1.5 \times 10^{-4} \text{ mol/L}$ ),  $\lambda_{\text{ex}}=420 \text{ nm}$ . (b) Plot of the fluorescent intensity ( $I_{521\text{nm}}$ ) vs the concentration of Hg<sup>2+</sup>.

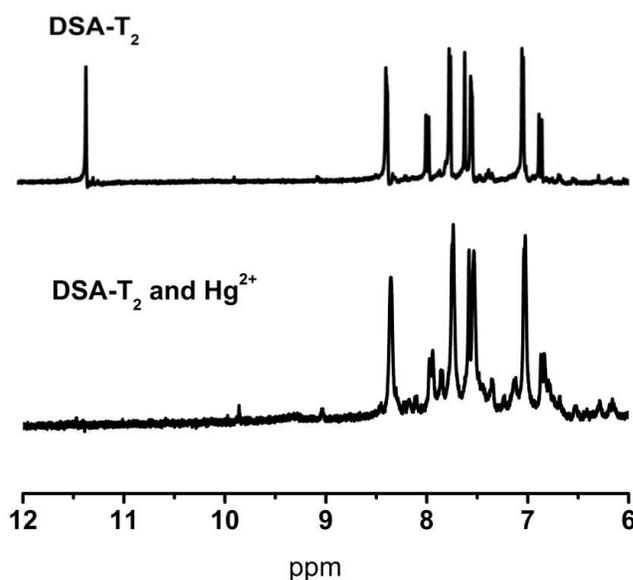


Fig. 3. (top) part of <sup>1</sup>H NMR spectrum of DSA-T<sub>2</sub> in DMSO-d<sub>6</sub> and (bottom) part of <sup>1</sup>H NMR spectrum of DSA-T<sub>2</sub> with the addition of Hg<sup>2+</sup> in DMSO-d<sub>6</sub>.

Hg<sup>2+</sup>, NMR spectra provide the evidence which explains the imino proton-metal exchange process [22]. <sup>1</sup>H NMR spectrum of DSA-T<sub>2</sub> in d-DMSO solvent (top) and <sup>1</sup>H NMR spectrum of DSA-T<sub>2</sub> mixed with Hg<sup>2+</sup> in d-DMSO solvent (bottom) are shown in figure 3. In the spectrum of DSA-T<sub>2</sub>, the single peak at 11.324 ppm represents the two imino hydrogen atoms of DSA-T<sub>2</sub>. With the addition of Hg<sup>2+</sup>, the single peak at 11.324 ppm disappears as a result of the protonation of DSA-T<sub>2</sub> [20]. The nitrogen atoms of DSA-T<sub>2</sub> have lone pair electrons and Hg<sup>2+</sup> is electron-deficient. In the presence of Hg<sup>2+</sup>, nitrogen atoms will attract Hg<sup>2+</sup> through the imino proton-metal exchange process. In this way, the imino hydrogen atoms will be released upon thymine-Hg<sup>2+</sup>-thymine pairing [22]. The result indicates that with the addition of Hg<sup>2+</sup>, the protons of DSA-T<sub>2</sub> has been released and a coordination complex has formed, which results in the aggregation of the probe.

To investigate the aggregate morphology of the coordination complex, transmission electron microscopy (TEM) image of the coordination complex was performed. Figure 4 shows the TEM image of DSA-T<sub>2</sub> with the addition of Hg<sup>2+</sup>. Because a small amount of molecules aggregate at the water fraction of 60 % (Figure S2), we choose a CH<sub>3</sub>CN/H<sub>2</sub>O (3:2, v/v) mixture as the matrix of the coordination complex. In the presence of Hg(NO<sub>3</sub>)<sub>2</sub> (1 × 10<sup>-4</sup> mol/L), the aggregation degree of DSA-T<sub>2</sub> increases and some deep colour dots appear. The deep colour dots properly represent Hg<sup>2+</sup>. This result is properly due to the imino proton-metal exchange process. The binding groups of thymine have the ability to contact Hg<sup>2+</sup> in the solution through the imino proton-metal exchange process [22]. DSA-T<sub>2</sub> possesses two thymine groups, thus the molecules can be connected with each other by thymine-Hg<sup>2+</sup>-thymine complex when form an aggregation structure. The aggregation will thus result in the restriction of intramolecular rotation [31]. In addition, the bathochromic shift of the fluorescent emission is observed and induced by the coordination of DSA-T<sub>2</sub> with Hg<sup>2+</sup>, which strengthens the intermolecular interactions between the molecules.

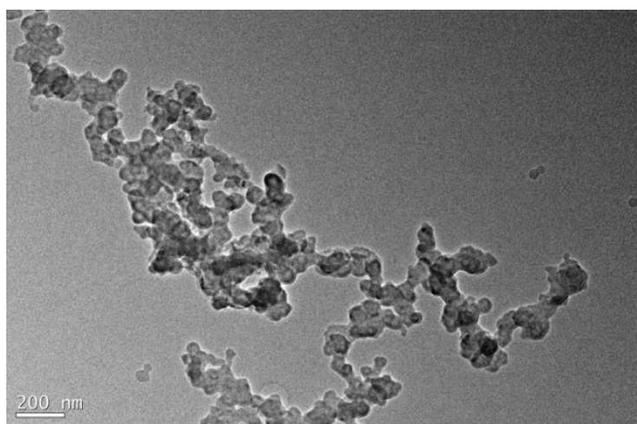


Fig. 4. TEM image of DSA-T<sub>2</sub> (1.16 × 10<sup>-5</sup> mol/L) in CH<sub>3</sub>CN/H<sub>2</sub>O (3:2, v/v) after the addition of Hg(NO<sub>3</sub>)<sub>2</sub> (1 × 10<sup>-4</sup> mol/L).

### 3.5 Specificity of the probe

To testify the selectivity of this probe towards Hg<sup>2+</sup> analysis, the fluorescent spectra of DSA-T<sub>2</sub> were performed in the presence of metal ions, such as Al<sup>3+</sup>, Ca<sup>2+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup>, Fe<sup>3+</sup>, K<sup>+</sup>, Li<sup>+</sup>, Mg<sup>2+</sup>,

Mn<sup>2+</sup>, Na<sup>+</sup>, Zn<sup>2+</sup> and Hg<sup>2+</sup>. Figure 5 shows the fluorescent spectra of DSA-T<sub>2</sub> at 521 nm in the presence of individual metal ion under the same experimental conditions. The notation I represents the fluorescent intensity of DSA-T<sub>2</sub> after the addition of different ion and the notation I<sub>0</sub> represents the fluorescent intensity of pure DSA-T<sub>2</sub>. It clearly indicates that among these metal ions, only Hg<sup>2+</sup> can induce a strong fluorescent emission at the wavelength of 521 nm and other metal ions can hardly enhance the fluorescent emission, which obviously proves that DSA-T<sub>2</sub> has an excellent selectivity for the specific detection of Hg<sup>2+</sup>. This is reasonable by considering the effective binding of thymine groups with Hg<sup>2+</sup>.

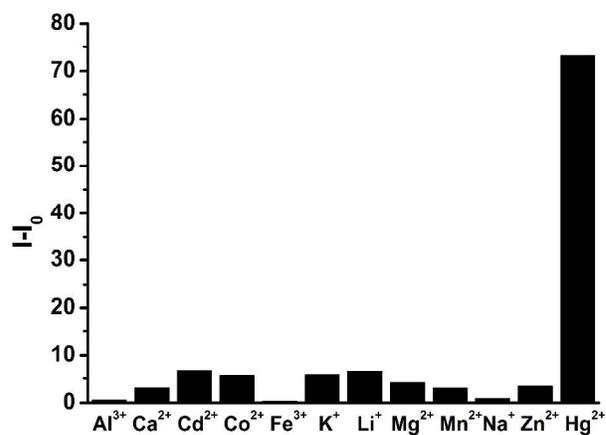


Fig. 5. Fluorescent intensity (I521 nm) of DSA-T<sub>2</sub> (1.16 × 10<sup>-5</sup> mol/L) in CH<sub>3</sub>CN/H<sub>2</sub>O (3:2, v/v) in the presence of the respective ions (7 × 10<sup>-5</sup> mol/L).

## 4. Conclusions

In summary, we have successfully achieved a fluorescence turn-on approach for the sensing of Hg<sup>2+</sup> via a thymine-Hg<sup>2+</sup>-thymine complex [30] based on an aggregation-induced emission fluorescent molecule containing 9,10-distyrylanthracene as a fluorophore and thymine as a Hg<sup>2+</sup> receptor. With the addition of water in the solution, it presents a fluorescent enhancement phenomenon due to the aggregation-induced emission property. Through the imino proton-metal exchange process, DSA-T<sub>2</sub> can connect with Hg<sup>2+</sup> and form a thymine-Hg<sup>2+</sup>-thymine complex. The formation of this complex results in the aggregation of molecules in the solution, which boosts the fluorescent enhancement effect. The theoretical detection limit of Hg<sup>2+</sup> can reach as low as 3.4 × 10<sup>-7</sup> mol/L and the detection range is from 7 × 10<sup>-7</sup> mol/L to 1.5 × 10<sup>-4</sup> mol/L. Given its easy operation, good sensitivity and good selectivity, this probe can endow it great promise in environmental monitoring. Our further research will focus on the water-solubility of this probe to make it probably used for bioimaging.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: [Scheme S1. Synthetic route to DSA-T<sub>2</sub>; Figure S1. (A) <sup>1</sup>H NMR spectrum of DSA-T<sub>2</sub> in DMSO-d<sub>6</sub> and (B) <sup>1</sup>H NMR spectrum of DSA-T<sub>2</sub> with the addition of Hg<sup>2+</sup> in DMSO-d<sub>6</sub>; Figure S2. TEM image of DSA-T<sub>2</sub> (1.16 × 10<sup>-5</sup> mol/L) in CH<sub>3</sub>CN/H<sub>2</sub>O (3:2, v/v) mixture]. See DOI: 10.1039/b000000x/

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