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Smart lanthanide coordination polymer fluorescence probe for mercury(II) determination

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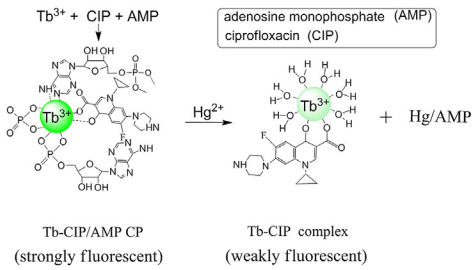
HIGHLIGHTS

- Lanthanide coordination polymer of Tb-CIP/AMP was synthesized via a simple self-assembly process.
- AMP was employed as a bifunctional molecule for both fluorescence sensitization and target recognition.
- Hypersensitive detection of Hg^{2+} was achieved based on time-resolved spectroscopy.

GRAPHICAL ABSTRACT



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ABSTRACT

Lanthanide coordination polymers (LCPs) have recently emerged as attractive biosensor materials due to their flexible components, high tailorable properties and unique luminescence features. In this work, we designed a smart LCP probe of Tb-CIP/AMP {(CIP, ciprofloxacin) (AMP, adenosine monophosphate)} for Hg^{2+} detection by using lanthanide ions as metal nodes, CIP as ligand molecule, and AMP as bridging linker and recognition unit. Tb-CIP/AMP emits strong green luminescence due to the inclusion of AMP, which withdraws the coordinated water molecules and shields Tb^{3+} from the quenching effect of O—H vibration in water molecules. The subsequent addition of Hg^{2+} into Tb-CIP/AMP can strongly quench the fluorescence because of the specific coordination interaction between AMP and Hg^{2+}. As a kind of Hg^{2+} nanosensor, the probe exhibited excellent selectivity for Hg^{2+} and high sensitivity with detection limit of 0.16 nM. In addition, the probe has long fluorescence lifetime up to millisecond and has been applied to detect Hg^{2+} in drinking water and human urine samples with satisfactory results. We envision that our strategy, in the future, could be extended to the designation of other LCP-based hypersensitive time-gated luminescence assays in biological media and biomedical imaging.

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1. Introduction

Coordination polymers constructed from metal ions and molecular bridging ligands have received huge attention due to their flexible structures and utilitarian properties [1–3]. As a class of fascinating hybrid materials, coordination polymers, compared with conventional organic or inorganic nanomaterials, possess many advantages, such as high level of structure tailorability, high loading capacity and size, morphology-dependent properties [4,5]. Furthermore, the variety of organic linkers, metal ions/clusters, and structural motifs affords an infinite array of possible combinations. Therefore, coordination polymers have the potential of a wider scope of applications. So far, they have been explored in diverse areas, such as gas storage/separations [5], drug delivery [6], heterogeneous catalysis [7] and luminescence sensing [8]. Of all these applications, sensing has been largely unexplored until recent several years. Several groups have reported their discoveries of coordination polymer-based fluorescence assays which aimed at the determination of chemical vapors and gases [9], organic solvents [10], and biological species [11,12]. Even so, the design and development of coordination polymer-based fluorescent sensors are still in the initial stage. Particularly, the improvement in the sensitivity and selectivity of coordination polymers to analytes especially in complicated biological medium remains a great challenge because the interferences from background and scattering fluorescence are hard to eliminate.

For sensing applications, lanthanide coordination polymers (LCPs) are more powerful candidates than transition-metal coordination polymers because the luminescence of lanthanide(III) coordination polymers probes is long-lived with large Stokes shifts and sharp emission profiles [13]. The long lifetime enables these LCPs to be easily used for the time-gated luminescence measurement to dispel the effect of the autofluorescence from biological tissues and matrices [14]. Currently, some LCPs have been used as fluorescent probes for the sensing of aromatic compounds [15], F- [16], and DMF vapor [17]. However, many LCP probes are conducted mainly in organic solution or gaseous phase owing to the use of water-insoluble and toxic organic molecules as bridging ligands. This hinders their sensing applications in aqueous solution, not to mention in biological matrix.

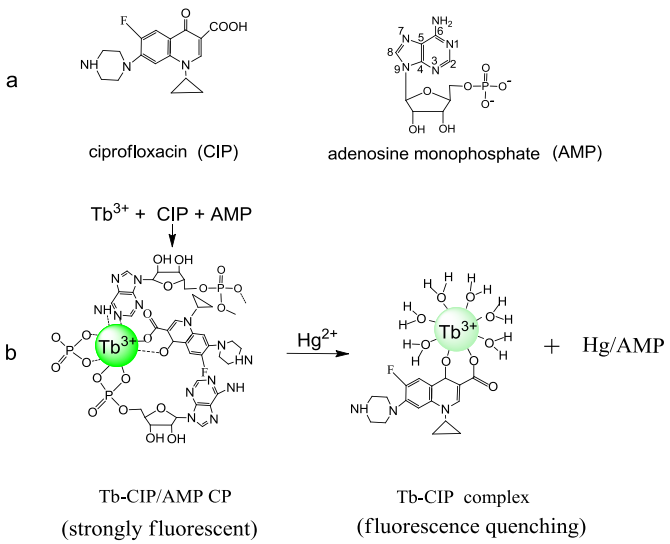
Mercury pollutant has become a serious and urgent global problem due to their potential to do great harm to the environment and the human health [18,19]. The water-soluble mercuric ion (Hg^{2+}) is one of the most stable inorganic forms of mercury, which is non-biodegradable and bioaccumulable through the food chain. Even at very low concentrations, it can damage brain, kidneys, and nervous system [20–22]. Therefore, high sensitive method for Hg^{2+} detection is really worth pursuing. Multiple approaches, such as atomic absorption spectrometry (AAS) [23], atomic emission spectrometry (AES) [24], inductively coupled plasma mass spectrometry (ICP-MS) [25] and electrochemistry [26] have been applied to detect Hg^{2+} with high sensitivity. However, these methods require expensive and sophisticated equipment and/or involve tedious sample preparation procedures prior to the analysis, which limits their applications greatly. In recent years, researchers have instead developed a number of optical colorimetric/fluorometric arrays for Hg^{2+} [27–34]. Colorimetric methods are rapid, simple without needing complicated analytical instruments and practicable for in-field analysis, yet they are susceptible to high ionic strength or other impurities in complicated application environments. Currently, various fluorescent probes including organic molecules and nano-materials have already been employed for the determination of Hg^{2+} with high sensitivity [29–34]. But certain drawbacks still exist. For example, organic molecules probes usually need to be prepared by laborious synthesis process; nanomaterial-based fluorescence assays often required complicated modification before the determination. More importantly, the fluorescence sensors are powerless against the autofluorescence from biological tissues and matrices when they are used in biological environments. To overcome the limitations of these methods, lanthanide fluorescence probes for Hg^{2+} are highly desirable because of their advantages of high sensitivity, easy preparation procedure and high anti-interference ability in complicated media. Nevertheless, few studies have centered on using LCPs probes for the detection of Hg^{2+}.

Herein, we attempt to design a time-gated luminescence probe based on LCP for Hg^{2+} detection in drinking water and human urine samples by combining the features of the long fluorescence life of lanthanide ions and high tailorable properties of coordination polymers. The LCP was composed of terbium ion (Tb^{3+}), ciprofloxacin (CIP), and adenosine monophosphate (AMP), i.e., Tb-CIP/AMP. The idea of the combination was based on the following facts. Single Tb^{3+} is almost non-fluorescent because of its low absorption coefficient, whose luminescence has to be sensitized by matched organic ligands as antenna molecules. CIP has been found to be able to coordinate to Tb^{3+} through O atoms of carbonyl group and/or carboxyl group for building Tb-CIP complex and absorb energy in the UV range to sensitize the emission of Tb^{3+} [35,36]. However, Tb-CIP complex displayed very weak fluorescence in aqueous solutions due to the quenching effect of hydroxyl (−OH) oscillators of the coordinated water molecules. Upon the adding of AMP, very interestingly, a network-structured LCP was constructed based on the self-assembly properties, rigid structure and multiple binding sites for metal ions of AMP, and a 20-fold fluorescence enhancement was observed due to the removal of coordination water molecules. Hg^{2+} has high affinity for AMP, which could destroy the hydrophobic environment of Tb^{3+} and weaken the fluorescence of Tb-CIP/AMP. Consequently, a highly selective and sensitive time-gated luminescence detection method for Hg^{2+} using LCP as sensing platform is expected to be established (Scheme 1).

2. Materials and methods

2.1. Chemicals and reagents

$Tb(NO_3)_3 \cdot 6H_2O$ (99.99%) and adenosine-5′-monophosphate disodium (AMP) were purchased from Aladdin Reagent Co. Ltd



Scheme 1. Chemical structures of CIP and AMP (a) and illustration of lanthanide coordination polymer probe of Tb-CIP/AMP for the detection of Hg^{2+} (b).

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(Shanghai, China). Mercury nitrate standard solution (30 mM) was from Beijing Zhongbiao Huawei Technology Co. Ltd. Metal salts ($AgNO_3$, $MgCl_2$, $Pb(NO_3)_2$, $CaCl_2$, $CdCl_2$, $FeCl_3$, $FeCl_2$, $CrCl_3$, $Ni(NO_3)_2$, $MnCl_2$, $CoCl_2$, NaCl, $Cu(NO_3)_2$) were purchased from Beijing Chemical Reagent Company. Ciprofloxacin hydrochloride and N-2-hydroxyethyl piperazine-N′-2-ethanesulfonic acid (HEPES) were obtained from Sangon Biotech Co. Ltd. (Shanghai, China). HEPES buffer (100 mM, pH 7.4) was prepared by dissolving HEPES in ultrapure water; 5 M NaOH was used to adjust pH to 7.4. Ultrapure water (18 MΩ cm, Milli-Q gradient system, Millipore) was used for the preparation of all aqueous solutions. The stock solutions of interfering ions (150 μM) were prepared by directly dissolving an appropriate amount of metal salts in HEPES buffer (100 mM, pH 7.4). Unless otherwise stated, all chemicals are of analytical reagent grade and were used without further purification.

2.2. Instruments and determinations

The morphology of coordination polymers were examined by scanning electron microscopy (SEM) (Oxford, UK) equipped with an energy dispersive X-ray spectrometer (EDS) detector. A D8 advance diffractometer (Bruker, Germany) was used for the collection of diffraction data useful for phase determination. An Avatar 360 FTIR spectrometer (Nicolet, USA) was used to record the Fourier transform infrared (FTIR) spectra with the KBr pellet technique. UV−visible absorption spectra were recorded on a Cary 60 UV−vis spectrophotometer (Agilent, USA). Fluorescence spectra were recorded on an LS55 luminescence spectrometer (PerkinElmer, UK) with a xenon lamp as excitation source. The detection solution was placed in a quartz micro cuvette with 100 μL capacity and 2 mm light path. The emission spectra of Tb^{3+} were monitored at 273 nm excitation wavelength. For the time resolved fluorescence spectra, the delay time of 0.05 ms and the gate time of 2 ms were used, respectively. The AAS measurement was carried out using a TAS-990 atomic absorption spectrophotometer equipped with GF-990 graphite furnace atomizer system. A mercury hollow-cathode lamp operated at 2.0 mA was used as radiation source. All the experiments were performed at room temperature. All error bars represent standard deviations from three repeated experiments.

2.3. Preparation of the coordination polymer of Tb-CIP/AMP

Tb-CIP/AMP was synthesized via a previously reported method [37,38]. The steps were as follows: 0.5 mL of $Tb(NO_3)_3$ aqueous solution (5 mM) and 1 mL of HEPES buffer (100 mM, pH 7.4) containing ciprofloxacin (2.5 mM) was mixed. To obtain Tb-CIP complex, the mixture solutions was incubated for 30 min at room temperature. Then, 1 mL of AMP disodium salt dissolved in HEPES buffer (100 mM, pH 7.4) (7.5 mM) was added into the obtained Tb-CIP complex solutions, white precipitate was formed immediately. After stirring for 3 h at room temperature, the white precipitate was collected by centrifugation at 12000 rpm for 5 min. The precipitate was washed with ultrapure water for several times to remove unreacted reactants. Finally, the obtained Tb-CIP/AMP precipitate was dispersed in 5 mL of HEPES buffer (100 mM, pH 7.4) to form a Tb-CIP/AMP suspension. For controls, the coordination polymers of Tb/AMP and Hg/AMP were also prepared according to the above conditions without the addition of CIP water solution. In addition, Tb-CIP complex (molar ratio, Tb: CIP = 1:3) was also prepared according to the literature method [39].

2.4. Fluorescence assay of Hg^{2+} in aqueous solution by Tb-CIP/AMP

Before testing, the original Tb-CIP/AMP suspension was diluted 30-folds. To check the response of Tb-CIP/AMP suspension for Hg^{2+}, different volumes of Hg^{2+} stock solutions (3 μM, 0.3 μM, 0.003 μM) and HEPES buffer (100 mM, pH 7.4) were added to 10 μL of Tb-CIP/AMP suspension to make a final Hg^{2+} concentrations of 0 nM, 0.16 nM, 1.5 nM, 4 nM, 20 nM, 30 nM, 40 nM, 70 nM, 200 nM, 700 nM, 1500 nM, respectively; The total volume was fixed at 100 μL by adjusting the amount of HEPES buffer (100 mM, pH 7.4). These mixed solutions reacted for 10 min under ultrasound at room temperature, and the corresponding fluorescence spectra were recorded by exciting at 273 nm. To test the selectivity of Tb-CIP/AMP suspension for Hg^{2+}, 1 μL of 150 μM stock solutions of these interference ions and 89 μL HEPES buffer (100 mM, pH 7.4) were added to 10 μL of Tb-CIP/AMP suspension. After being incubated for 10 min, the fluorescent intensities of the mixtures were measured under the same instrument conditions as that of the detection of Hg^{2+}. The blank solution was composed of 10 μL Tb-CIP/AMP suspension and HEPES buffer (100 mM, pH 7.4).

2.5. Determination of Hg^{2+} in drinking water

A series of samples of drinking water containing different concentrations of Hg^{2+} were prepared by "spiking" them with standard solutions of Hg^{2+}. Then, 10 μL of water samples containing Hg^{2+} were added to 90 μL of HEPES buffer (10 mM, pH 7.4) solutions containing 10 μL of Tb-CIP/AMP suspension, respectively. After being incubated for 10 min, the fluorescence intensities at 545 nm were recorded at an excitation wavelength of 273 nm.

2.6. Determination of Hg^{2+} in human urine samples

To check the practical applications of Tb-CIP/AMP in biofluid samples, we determined Hg^{2+} in human urine. Urine samples were obtained from healthy volunteers. To avoid the interferences of the thiol group in some compounds, 200 μL thiol-blocking reagent of N-ethylmaleimide (0.1 M) was added to 500 μL original urine samples, reacting for 2 h at 37 °C. A series of urine samples containing different concentrations of Hg^{2+} were prepared by spiking different volumes of Hg^{2+} stock solution. Then, to 10 μL Tb-CIP/AMP suspension, 40 μL HEPES buffer solutions (100 mM, pH = 7.4) and 50 μL urine samples with different concentrations of Hg^{2+} was added. After 10 min incubation at room temperature, their fluorescence intensities were recorded under the same conditions as above.

3. Results and discussion

3.1. Preparation, characterization of Tb-CIP/AMP and its response to Hg^{2+}

Tb-CIP/AMP was synthesized via the self-assembling of AMP with Tb-CIP complex in HEPES buffer (100 mM, pH 7.4) at room temperature. As controls, Tb/AMP and Hg/AMP were prepared by the self-assembly of AMP with metal ions. The morphology of Tb-CIP/AMP was examined by scanning electron microscopy (SEM). As shown in Fig. 1a, Tb-CIP/AMP is multiporous and network-structural, which displayed the same pattern as that of Tb-AMP (Fig. S1a). These results imply that Tb-AMP may construct the host framework of the coordination polymer and the incorporation of CIP does not affect the pattern of Tb-AMP. The selected area electron diffraction (SAED) image and X-ray diffraction (XRD) analysis of Tb-CIP/AMP revealed it is amorphous (Fig. S2 and Fig. S3). The chemical compositions were analyzed by an energy-dispersive X-ray (EDX) spectrograph. The peaks of Tb besides C, N, O, F, and P were observed in the spectra of Tb-CIP/AMP (Fig. S4a), indicating that Tb^{3+}, CIP, and AMP were all involved in the construction of Tb-CIP/AMP. To check the response of the probe to

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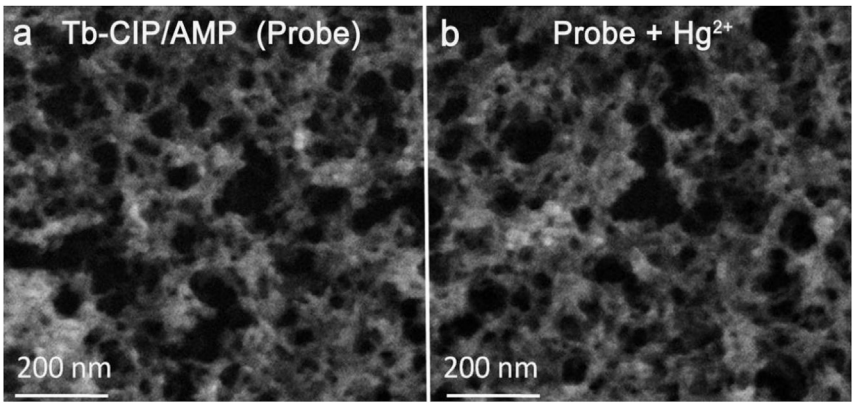

Fig. 1. SEM images of Tb-CIP/AMP probe (a) and Tb-CIP/AMP in the presence of Hg^{2+}(b).

Hg^{2+}, the morphology and the chemical compositions of Tb-CIP/AMP in the presence of Hg^{2+} were also tested. After the addition of Hg^{2+}, no obvious change was observed in their morphology (Fig. 1b). However, the chemical compositions of Tb-CIP/AMP varied distinctively. As can be seen from Fig. S4b, the peaks of C, N, O, P remained, and the peaks associated with Tb and F disappeared, whereas a new peak of Hg appeared. These results indicate that Hg^{2+} has displaced Tb^{3+} and reacted with the probe of Tb-CIP/AMP, forming a substance containing Hg and AMP. The substance exhibited the same morphology as Hg/AMP, as shown in Fig. S1b.

To prove the coordination of CIP and AMP with Tb^{3+}, we also conducted a FT-IR analysis. For pure CIP, the peaks at 1627 cm^{-1}, 1496 cm^{-1}, and 1387 cm^{-1} was assigned to the ν(C═O), νasym(-COO) and νsym(COO) stretching vibrations, respectively [40,41] (Fig. S5). In case of the spectrum of Tb-CIP/AMP, The C═O band shifted to 1613 cm^{-1}, two characteristic stretching bands associated with νasym(COO) and νsym(COO) shifted to 1551 cm^{-1} and 1389 cm^{-1}, respectively. These changes indicate that Tb^{3+} could coordinate with protonated carboxylate O and carbonyl groups [40,41]. In addition, compared with the spectrum of AMP, Tb-CIP/AMP showed some changes of C2—N1 stretching vibrations of adenine (1582 cm^{-1} to 1577 cm^{-1}), scissoring vibration of NH_2 (1656 cm^{-1} to 1645 cm^{-1}), and symmetric stretching bands of phosphate group (977 cm^{-1} to 994 cm^{-1}). These shifts confirmed that AMP bound to Tb^{3+} through its two phosphate groups, N1 and NH_2 sites, respectively. Based on these results, we speculate that both CIP and AMP were involved in the formation of the polymeric coordination network of Tb-CIP/AMP.

Fig. 2 displayed the luminescent behaviors of Tb-CIP complex, Tb-CIP/AMP and Tb-CIP/AMP in the presence of Hg^{2+} under time-resolved mode. Tb-CIP complex showed weak emission in water solution, which was attributed to the fluorescence quenching because of the coupling and energy transform between Tb excited state and O—H oscillators in coordinated water molecules [42]. However, the luminescence of Tb-CIP/AMP is approximately 20 times higher than that of Tb-CIP complex, indicating the fluorescence of Tb-CIP complexes were strongly enhanced after the involvement of AMP. And the fluorescence intensity of Tb-CIP/AMP is related to the molar ratios of Tb^{3+}, CIP and AMP. A molar ratio of 1: 1: 3 (Tb: CIP: AMP) produced the strongest fluorescence enhancement (Fig. S6). This enhancement can be attributed to the fact that AMP binds to Tb^{3+} at unsaturated coordination sites and withdraws water molecules, forming a hydrophobic environment inside Tb-CIP/AMP and minimizing the rate constant of nonradioactive deactivation caused by O—H vibration. Such a luminescence enhancement can also be explained by the changes of UV absorption spectra of Tb-CIP complex after the addition of AMP. As shown

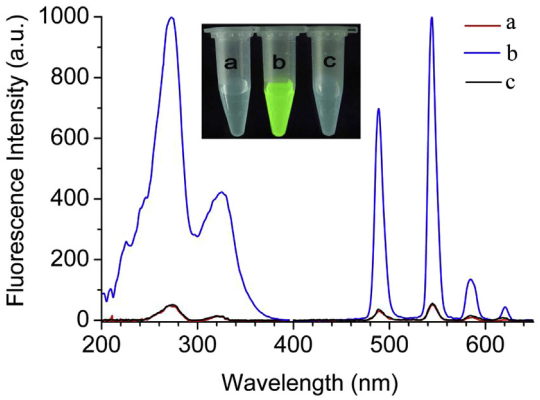

Fig. 2. Excitation and emission spectra of Tb-CIP complex (a), Tb-CIP/AMP (b), and Tb-CIP/AMP in the presence of Hg^{2+} (c). Inset is the change of fluorescence under a UV lamp.

in Fig. S7, Compared with the absorbance of Tb-CIP complex, the peak corresponds to the absorption of Tb-CIP complex at 273 nm within Tb-CIP/AMP distinctively increased. The strong absorption in the UV range could cause an efficient energy transfer from CIP to the emissive $^5D_4$ state of Tb^{3+} and sensitize the luminescence of Tb^{3+} ion effectively (Fig. 2). Hg^{2+} possesses much higher binding ability to AMP than other metal ions. Therefore, in the presence of Hg^{2+}, the hydrophobic environment of Tb^{3+} was destroyed because of the coordination of AMP with Hg^{2+}, accordingly, the luminescence of Tb-CIP/AMP was quenched effectively (Fig. 2). In addition, the characteristic emission peaks of Tb^{3+} at 489, 545, 585, and 625 nm can still be observed, even higher level of Hg^{2+} did not yet quench the green luminescence of Tb-CIP/AMP thoroughly (data were not given). The result indicates that the addition of Hg^{2+} does not affect the coordination between Tb^{3+} and CIP. This deduction can be confirmed by the blue mission at about 450 nm of free CIP under UV irradiation (Fig. S8).

The luminescence intensity of Tb-CIP/AMP is pH dependent, which reached a maximum value at pH 7.4 (Fig. S9). This may be a result of a collapse of network-structured Tb-CIP/AMP owing to the protonation of AMP in more acid or the formation of terbium hydrate in more basic solutions. The TEM image of Tb-CIP/AMP at pH = 4.0 (Fig. S10) confirmed that at strong acid media, network-structrual Tb-CIP-AMP has been broken up into fragments. In this work, therefore, the proposed assay for Hg^{2+} was conducted in HEPES buffer (100 mM, pH 7.4).

We also compared the change of the emission lifetime of Tb-CIP/

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AMP with that of Tb-CIP complex. As shown in Fig. 3, the luminescence lifetime of Tb-CIP/AMP is 0.857 ms, which is longer than that of Tb-CIP complex with 0.586 ms. The longer emission lifetime implies the replacement of coordinated water molecules by AMP and a decrease of radiationless decay of excited state Tb^{3+}. Because of the long luminescence lifetime, such prepared coordination polymer of Tb-CIP/AMP is well qualified as time-resolved fluorescence assay for applications in biological samples.

3.2. Fluorescence assay of Hg^{2+} by Tb-CIP/AMP

The fluorescence varieties of Tb-CIP/AMP to Hg^{2+} with different concentrations were shown in Fig. 4. The fluorescence of Tb-CIP/AMP was quenched gradually with the increase of Hg^{2+} concentrations. In the concentration range of 1.5–70 nM, there is a linear fluorescence response to Hg^{2+} (Inset of Fig. 4). The detection limits is about 0.16 nM (signal/noise ratio>3:1). The U.S. Environmental Protection Agency (EPA) has regulated a maximum permitted level of 10 nM Hg in drinking water [43]. According to this standard, our assay is more than enough for the determination of Hg^{2+} ions in drinking water. In addition, this detection sensitivity of Hg^{2+} ion is comparable with that of the conventional spectrophotometric methods with detection limit (DL) of (90 ng L^{-1}, 0.45 nM) [23], (0.75 μg L^{-1}, 3.7 nM) [24] and (12 ng L^{-1}, 0.06 nM) [25] and exceeds to that of the fluorescent sensors based on cytidine-stabilized gold nanoclusters (DL = 30 nM) [30], triethanolamine-capped CdSe quantum dots (DL = 1.9×10^{-7} mol L^{-1}, 190 nM) [31] and organic chemosensor of ferrier carbocyclization (DL = 0.15 μM, 150 nM) [32]. This results show that the method based on Tb-CIP/AMP probe is highly sensitive for Hg^{2+} sensing. As discussed above, the introduction of AMP can facilely react with Tb-CIP complex to form Tb-CIP/AMP CP and switch on the luminescence of Tb-CIP complex distinctively by excluding of the coordinating water molecules from Tb^{3+}, so we attributed the fluorescence quenching of Tb-CIP/AMP by Hg^{2+} to the strong interaction between Hg^{2+} and AMP, which broke the coordination bond between AMP and Tb^{3+}, leading water molecules to coordinate with Tb^{3+} again, and, hence, an O–H vibrational quenching.

3.3. Selectivity of Tb-CIP/AMP for the detection of Hg^{2+}

To investigate the selectivity of our assay, different kinds of species that may possibly be considered to interfere with the detection of Hg^{2+} were checked by observing their influences on the luminescence intensity of Tb-CIP/AMP (gray bars of Fig. 5).

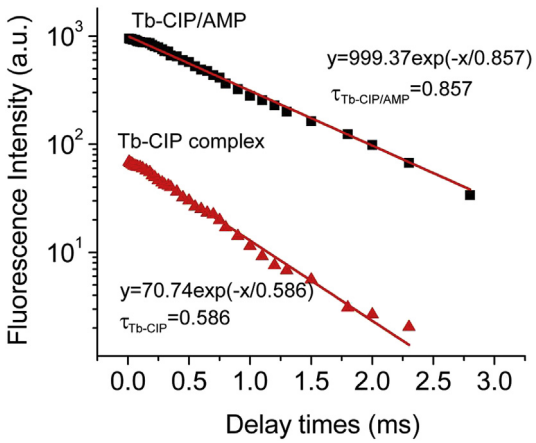

Fig. 3. Fluorescence lifetime of Tb-CIP and Tb-CIP/AMP in aqueous solution.

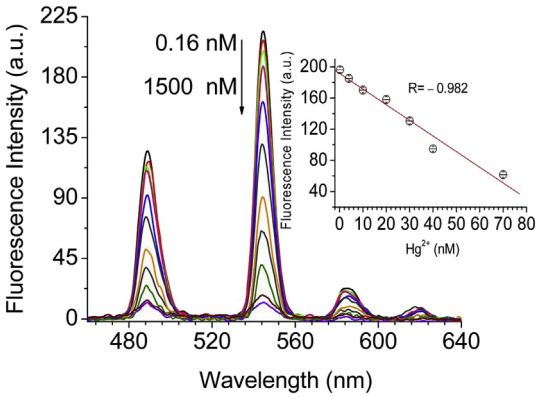

Fig. 4. Fluorescent spectra of Tb-CIP/AMP with the addition of different concentrations of Hg^{2+} (0 nM, 0.16 nM, 1.5 nM, 4 nM, 20 nM, 30 nM, 40 nM, 70 nM, 200 nM, 700 nM, 1500 nM) in HEPES buffer (pH = 7.4). (Inset is the linear relationship between the fluorescent intensity of Tb-CIP/AMP and the concentrations of Hg^{2+}).

Under identical conditions, only the addition of Hg^{2+} produced a distinctive fluorescence quenching; other metal ions (Mg^{2+}, Pb^{2+}, Ca^{2+}, Cd^{2+}, Fe^{3+}, Fe^{2+}, Cr^{3+}, Ni^{2+}, Mn^{2+}, Co^{2+}, Na^{+}, Cu^{2+}) have almost no effect on the fluorescence of Tb-CIP/AMP (<5%). The presence of Ag^{+} raised the luminescence intensity of Tb-CIP/AMP slightly probably due to the ability of Ag^{+} to sensitize the fluorescence of Tb^{3+} within Tb/AMP CP [44]. These results indicated that other metal ions did not interfere with the determination of Hg^{2+}. We attributed the high selectivity of Tb-CIP/AMP to the fact that the coordination ability of Hg^{2+} with N-containing ligand is higher than that of other interfering metal ions [45–47]. Furthermore, we also evaluated the anti-interference ability of Tb-CIP/AMP toward Hg^{2+} in the presence of Ag^{+}, Mg^{2+}, Pb^{2+}, Ca^{2+}, Cd^{2+}, Fe^{3+}, Fe^{2+}, Cr^{3+}, Ni^{2+}, Mn^{2+}, Co^{2+}, Na^{+} and Cu^{2+}, respectively. As shown in Fig. 5 (black bars), no obvious discrepancy was observed between fluorescence response of Tb-CIP/AMP to the mixture of Hg^{2+} with other background metal ions and that to the single metal ion. This result proved further that these background metal ions have no influence on the detection of Hg^{2+}.

3.4. Determination of Hg^{2+} in drinking water

Hg^{2+}, as the most stable form of inorganic mercury, in water samples, can be converted into hypertoxic methylmercury by microbial biomethylation, accumulating in fish, shrimp or other seafoods, then enters the human body through the food chain, causing brain damage as well as other chronic diseases. Therefore, it is

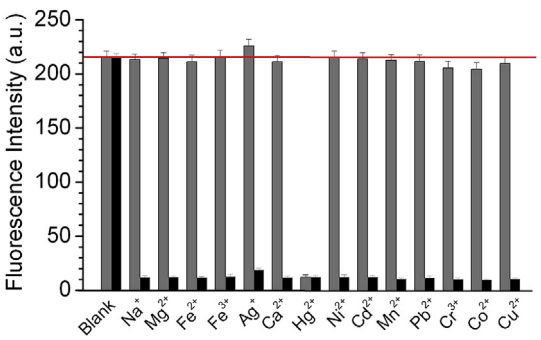

Fig. 5. Detection selectivity of Tb-CIP/AMP in the presence of 1.5 μM various metal ions. Gray bars represent the luminescence response after addition of single metal ion (1.5 μM); Black bars represent the luminescence response after addition of single metal ion (1.5 μM) and Hg^{2+} (1.5 μ M) together.

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Table 1
Determination of Hg^{2+} in drinking waters.

Sample	Spiked Hg^{2+} (nM)	Detected Hg^{2+} (nM)[a]	Recovery (%)
Drinking water 1	5.00 nM	5.26 ± 0.42	105.25
Drinking water 2	15.00 nM	14.88 ± 0.98	99.23
Drinking water 3	50.00 nM	48.56 ± 1.86	97.12

[a] Mean value (n = 3) ± standard deviation.

Table 2
Determination of Hg^{2+} in urine samples based on time-resolved fluorescence.

Urine samples	Current method				AAS method detected (nM)[a]
	Endogenous Hg^{2+}(nM)[a]	Added Hg^{2+}(nM)	Detected Hg^{2+}(nM)[a]	Recovery (%)	
Urine 1	3.49 ± 0.51	2.55	5.81 ± 0.81	96.2%	3.56 ± 0.35
Urine 2	5.89 ± 0.91	5.00	10.87 ± 1.79	99.8%	5.78 ± 0.81
Urine 3	12.35 ± 1.92	30.80	42.65 ± 2.88	98.8%	12.75 ± 1.59

[a] Mean value (n = 3) ± standard deviation.

important to check the level of inorganic Hg^{2+} in water samples. We apply the probe of Tb-CIP/AMP to detect trace Hg^{2+} in drinking water samples due to the low detection limit and high selectivity. As seen from Table 1, different concentrations of Hg^{2+} in drinking water samples were determined using Tb-CIP/AMP. The added standard Hg^{2+} can be accurately measured with good recoveries (more than 96%), indicating that there was no obvious systemic error of this method.

3.5. Determination of Hg^{2+} in urine samples based on time-resolved fluorescence

The long fluorescence lifetime of Tb-CIP/AMP prompted us to attempt using this material to detect Hg^{2+} in human urine based on time-resolved fluorescence. As shown in Fig. S11, the fluorescence intensity of Tb-CIP/AMP against the concentration of Hg^{2+} produced a linear correlation in the range of 2–60 nM (R = − 0.988). The detection limit is 2 nM on the basis of a signal-to-noise ratio of 3:1. The recoveries of urine samples containing different concentrations of Hg^{2+} are 96.2–98.8%, indicating a high precision and no obvious method error (Table 2). The results of Hg^{2+} determinations in urine samples were further confirmed by AAS method. The determination results using the two methods are basically consistent (Table 2). Urinary mercury level of healthy body has been reported to be below 20 μg/L (99.7 nM) [48]. Therefore, current method can satisfy the determination of Hg^{2+} in urine samples without the interference of background fluorescence based on time-resolved fluorimetry.

4. Conclusions

In summary, we reported a fluorescence assay for hypersensitive detection of Hg^{2+} in drinking water and human urine samples by using lanthanide coordination polymer of Tb-CIP/AMP as fluorescent probe. As a kind of sensing material for Hg^{2+} detection, compared with other reported luminescent probes, lanthanide coordination polymer of Tb-CIP/AMP possesses several desirable properties including simple preparation based on a self-assembly process and excellent water dispersion behavior. Moreover, the long-lived luminescence of Tb-CIP/AMP owing to the inclusion of trivalent lanthanide ions allows the probe to be favorably useful for the background-free time-gated luminescence detection for other biosamples.

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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.aca.2016.01.044.

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