Journal of
Materials Chemistry B

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Nucleotide/Tb^{3+} coordination polymer as luminescent nanosensor: synthesis and sensing iron (II) in human serum

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Abstract

Metal organic coordination polymers have emerged as a new class of functional nanomaterials because of their flexible components and diverse architectures. Here, we report the synthesis of a luminescent sensing nucleotide/Tb^{3+} coordination polymer by the self-assembly of biomolecule nucleotide, lanthanide ion and functional ligand 1, 10-phenanthroline. Due to the incorporation of 1, 10-phenanthroline as both a sensitizer and a recognition unit, the luminescence of this coordination polymer was enhanced 32 times, and exhibited excellent selectivity and sensitivity to iron ion (II). This coordination polymer containing Tb^{3+} ion has a long luminescence lifetime up to millisecond, and was applied to detect Fe^{2+} ion in human serum by time-resolved fluorimetry. The detection limit is as low as 30 nM. The results demonstrate that metal organic coordination polymers have great potential in constructing specific nanosensors through their component and structural flexibility, and could provide new chemical sensing ways for ions /molecules.

Keywords: Terbium coordination polymer, fluorescence, phenanthroline, iron ion, human serum

1. Introduction

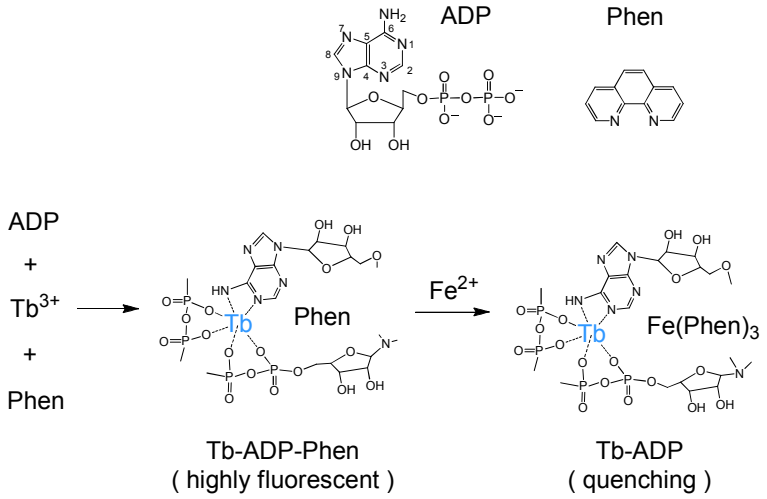
Metal organic coordination polymers (MOCPs), consisted of metal ion as node and organic ligand as linker, have rapidly grown into a fascinating new class of functional materials.[1,2,3] Because the variety of metal ions, organic linkers, and structural motifs affords an essentially infinite number of possible combinations, MOCPs have a great flexibility in structures and components. The rich variety of MOCPs has showed important applications in separation and purification processes, catalysis, release systems, smart materials.[4,5] The flexible structures and components of MOCPs are also expected to lead to applications in chemical sensing of molecules or ions. Recently, some fluorescent MOCPs have been employed to detect high explosives in the gas phase and metal ions and anions in organic solution. [6-11]. However, these sensings of MOCPs are conducted mainly by means of the size exclusion of porous surface and analyte-induced structural distortion,[10] and occurred in organic solution or gaseous phase. Less work about sensing in aqueous solution has been reported. On the other hand, the adsorption-based size exclusion is not an ideal sensing mode for a given molecule/ion due to non-exclusive interaction. MOCPs with a special interacting structure for analytes are of better sensing selectivity. Such integrative MOCPs often need be constructed from initial molecule/ion building blocks. It is still a challenge designing and fabricating a MOCP with specific sensing function directly through the assembly of molecule/ion building blocks.

As an essential trace element of human body, iron ion and iron-containing proteins play a vital role in many biological processes including oxygen transport, DNA synthesis and cell proliferation.[12] A deficient or excessive ingestion may cause the loss of some physiological functions and diseases including iron-deficiency anemia[13] and ovulatory infertility.[14] Recently, iron

ion has been reported to be involved in the pathogenesis of Alzheimer's disease.[15] To understand the mechanisms of these diseases and biochemical processes of iron ion, sensitive and accurate detection for iron ion in the body is highly desirable. Some detection methods for iron ion have been reported. These methods include spectrophotometry,[16,17] atomic absorption **s**pectrometry (AAS),[18,19] inductively coupled plasma mass spectrometry (ICP–MS)[20] and luminescent flow injection methods.[21] However, they are mostly equipment-complicated, destructive and non-real-time methods. Fluorescence methods would be more desirable due to their rapid detection and high sensitivity at trace levels. Recently, some reaction-based fluorescent reagents[22,23] and nanomaterial-based sensors[24-26] including gold nanoclusters, quantum dots and metal-organic framework have been developed for the determination of iron. However, reaction-based fluorescent methods must utilize fluorescent organic reagents with special structures, which often need to be prepared by complicated organic syntheses. Nanomaterial-based sensors usually need to be modified by interactional groups/molecules with analytes.

In this work, we constructed a luminescent nucleotide/Tb^{3+} coordination polymer with recognition function to Fe^{2+} ion by means of the component flexibility of coordination polymers. Trivalent terbium ions are of excellent fluorescent features such as large Stokes shift (>150 nm), sharp emission (<10 nm full width at half maximum), long fluorescence lifetime (up to millisecond). The long lifetime, permitting the use of time-gating techniques to separate the signal from fluorescent background, is particularly advantageous to the bioassays with autofluorescence. However, the luminescence of Tb^{3+} is weak due to its low absorption coefficient, which has to be improved by a sensitization of appropriate antenna ligand. Nucleotide molecules have self-assembly properties and good biocompatibility. Phenanthroline (Phen) have often been used

as the second ligand to form ternary luminescent lanthanide complexes,[27,28] also as a specific reagent of Fe^{2+} used in the spectrophotometric determinations.[16,17] The absorption of Phen in the UV range could sensitize the luminescence of Tb^{3+} ion. Hence, the combination of nucleotide, Tb^{3+} ion and Phen in the solid frame of coordination polymer would provide a new sensing way for Fe^{2+} as Scheme 1.



Scheme 1. Schematic diagram of Tb-ADP-Phen coordination polymer for sensing Fe^{2+}.

2. Results and discussion

2.1. Preparation and fluorescence characteristics of Tb-ADP-Phen CP

Tb-ADP-Phen CP was prepared by the self-assembling of ADP, Tb^{3+} and Phen in aqueous solution. Tb-ADP, as a control, was also prepared under the same conditions except the addition of Phen solution. Transmission electron microscopy (TEM) images showed that Tb-ADP-Phen is the same network-structure as Tb-ADP (Figure 1). The selected area electron diffraction (SAED) revealed that Tb-ADP-Phen is amorphous (Figure S1). This indicates that the incorporation of Phen does not affect the pattern of Tb-ADP. Even in the presence of Fe^{2+}, the pattern of

Tb-ADP-Phen is still no change, implying that Tb-ADP may construct the framework of this coordination polymer.

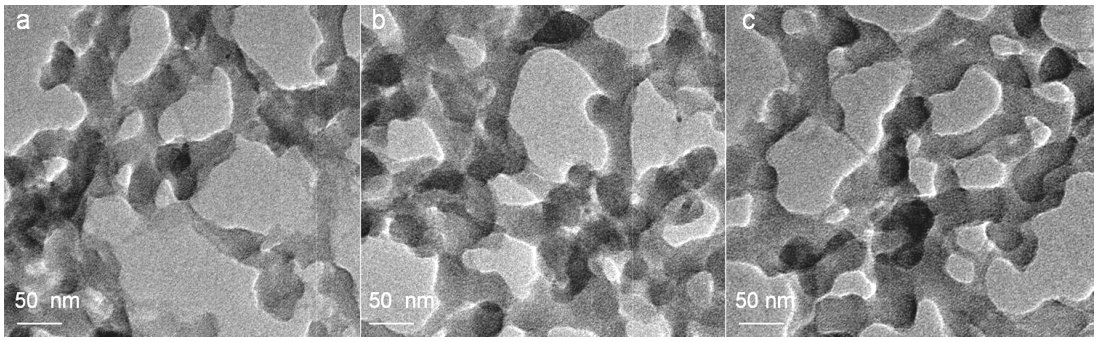


Figure 1. TEM images of Tb-ADP (a), Tb-ADP-Phen (b) and Tb-ADP-Phen in the presence of Fe^{2+} (c).

To understand the coordination of AMP and Phen with Tb^{3+} ion, we conducted FTIR analyses. Figure 2 is the FTIR spectra of ADP, Tb-ADP and Tb-DPA-Phen. Compared with ADP, Tb-ADP showed the shifts of stretching bands of PO_3^{3-} group (975 to 997 cm^{-1} and 923 to 937 cm^{-1}), adenine (1584 to 1577 cm^{-1}) and a new stretching band of N-H bond at 1689 cm^{-1}. These changes indicate that Tb^{3+} could coordinate with two phosphate groups, N1 and NH_2 sites of ADP, respectively. [29] For Phen molecule, the N atoms with lone electron pair are the only sites that offer coordination with transition metal ions. Tb-ADP-Phen has a band shift of C=N bond of Phen from 1563 to1547 cm^{-1}, indicating that Phen joined to coordinate with Tb^{3+} ion through its N atoms. [30]

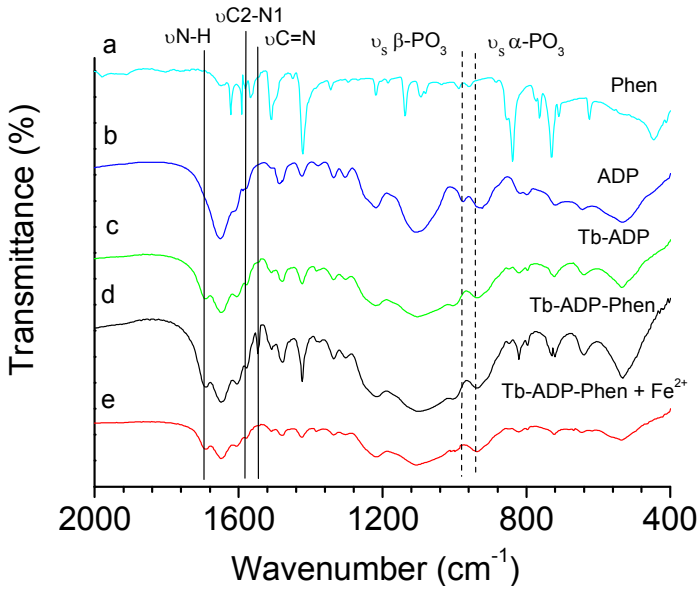


Figure 2. FTIR spectra of Phen (a), ADP (b), Tb-ADP (c), Tb-ADP-Phen (d) and Tb-ADP-Phen in the presence of Fe^{2+} (e). υ: stretching vibration; υ_s: symmetric stretching.

We investigated the fluorescence characteristics of Tb-ADP-Phen. As shown in Figure 3, Tb-ADP is weakly fluorescent, however, the fluorescence of Tb-ADP-Phen showed approximately 32 times higher than that of Tb-ADP (Figure. 3b). The peaks at 488, 545, 584, and 619 nm are the typical emission of Tb^{3+} ion, arising from its electronic excited state $^5D_4$ to multiple ground-states ^7F_J (J = 6 to 3), respectively.[31] This indicates that the fluorescence of Tb^{3+} ion was strongly enhanced by the sensitization of Phen. We attribute this enhancement to the fact that 1) Phen with chromophoric group can act as antenna molecule to Tb^{3+} ion due to the matching of energy transfer from triplet excited state of Phen (22132 cm^{-1}) to excited state of Tb^{3+} (20430 cm^{-1})[32,33] and 2) the hydrophobic environment inside Tb-ADP-Phen CP avoided the fluorescence quenching arising from water molecules. To confirm the deduction, we prepared Tb-ADP CP and Tb-Phen complex in anhydrous ethanol. As shown in Figure S2, the fluorescence intensities of Tb-ADP CP and Tb-Phen complex prepared in anhydrous ethanol are

much stronger than that in water. The emission of Tb-Phen complex in anhydrous ethanol was enhanced approximately 22 times, indicating that the exclusion of water molecule has a great effect on the fluorescence of Tb-ADP-Phen CP, and mainly on the sensitization of Phen to Tb^{3+} ion.

The molar ratios of Tb and Phen in the synthesis have an influence on the fluorescence of Tb-ADP-Phen. When the molar ratio of Tb^{3+} to Phen is 1:1, the fluorescence of Tb-ADP-Phen reached to maximum value (Figure S3). In addition, the fluorescence of Tb-ADP-Phen was pH-dependent. At about pH 7.4, there is a maximum fluorescence value (Fig. S4). This may be a result of the dissociation of Tb-ADP-Phen CP caused by the protonation of ADP in more acidic media and the formation of terbium hydrate in more basic media.

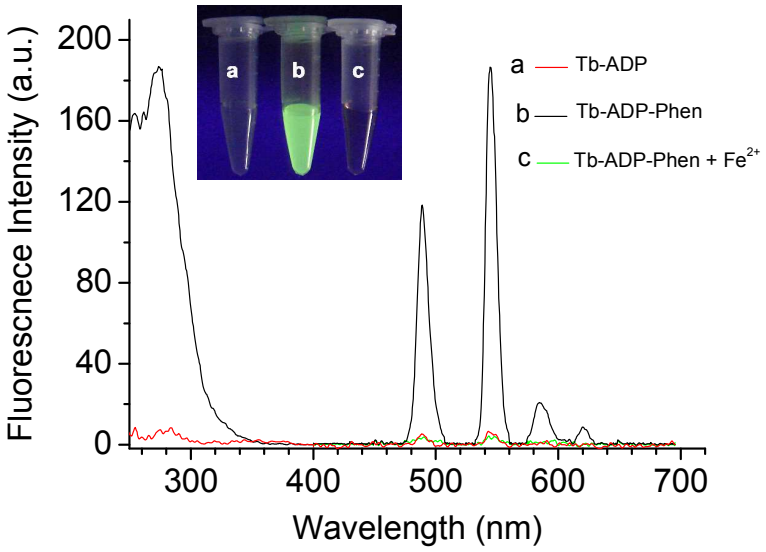


Figure 3. Emission spectra of Tb-ADP (a), Tb-ADP-Phen (b) and Tb-ADP-Phen in the presence of Fe^{2+} (20 μM) under a 275-nm exciting light. Inset is the corresponding colors of them under a common UV lamp.

We also investigated the fluorescence lifetime of Tb-ADP-Phen CP. As shown in Figure 4, the

emission lifetime of Tb-ADP-Phen is approximately 1.042 ms, which is longer than that of Tb-ADP with 0.962 ms. This agrees with that addition of ligands or encapsulation of the lanthanide leads to longer emission lifetimes due to the reduction of nonradiative deactivation through the O-H vibrations of water molecules. Furthermore, the radiation of Tb-ADP-Phen CP is very stable, no obvious change in the fluorescence intensity was observed for at least 30 days (Figure S5). The excellent photostability and long lifetime of Tb-ADP-Phen CP indicates that Tb-ADP-Phen has a good potential in time-resolved fluorescence assays.

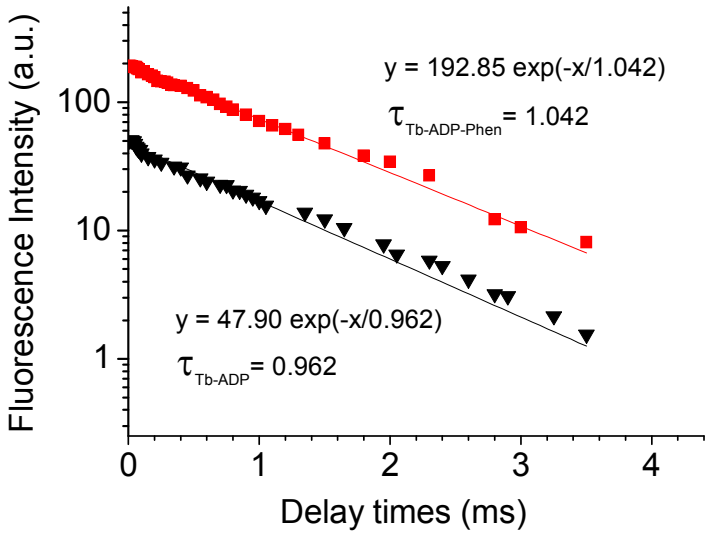


Figure 4. Fluorescence lifetime of Tb-ADP and Tb-ADP-Phen in aqueous solution.

2.2. Fluorescent response of Tb-ADP-Phen to Fe^{2+} in aqueous solution

In the presence of Fe^{2+}, the fluorescence of Tb-ADP-Phen was strongly quenched. Approximately 30 nM Fe^{2+} can produce an obvious reduction of fluorescence (signal/noise ratio>3:1) (Figure 5). The fluorescence intensity of Tb-ADP-Phen was gradually decreased with the increase of Fe^{2+} concentration, and there is a good linear correlation in the concentration

ranges of 30 nM–3 μM Fe^{2+} (Inset of Figure 5). The detection limit is approximately 30 nM on the basis of a signal-to-noise ratio of 3:1. This detection limit (DL) of Fe^{2+} ion is comparable with that of the conventional spectrophotometric methods with 2 ppM (2 μM)[16] and 18 μgL^{-1} (321 nM)[17] and much lower than that of the fluorescent nanosensors based on proline-modified gold nanoclusters (DL=2.0 μM)[24], semiconducting polymer dots (DL=18 μM)[25] and metal-organic framework (DL=0.9 μM)[26]. This showed that the method of Tb-ADP-Phen CP is highly sensitive to Fe^{2+} ion. We attributed the fluorescence quenching of Tb-ADP-Phen by Fe^{2+} to the formation of $Fe(Phen)_3$ complex due to a higher stability of $Fe(Phen)_3$ than $Tb(Phen)_3$.[34,35] The formation of $Fe(Phen)_3$ complex is supported by the spectroscopic data. As shown in Figure 2, the peak at 1547 cm^{-1} associated with C=N in Tb-ADP-Phen disappeared in the presence of Fe^{2+}, suggesting that the coordination between Phen and Tb^{3+} was destroyed. Figure 3 is the UV-vis spectra of Fe-Phen complex, Tb-ADP-Phen CP and Tb-ADP-Phen CP in the presence of Fe^{2+}. Phen has an absorption peak at 265 nm. Nucleotide ADP has a maximum absorption at 260 nm. Tb-ADP-Phen showed a remarkable increase in absorption at 265 nm, indicating that the absorption of Phen, not ADP, plays a main role in antenna-ligand-sensitized luminescence. In the presence of Fe^{2+}, Tb-ADP-Phen exhibited a new peak at 512 nm. The position of this new peak is in agreement with the characteristic absorption of $Fe(Phen)_3$ complex, confirming the formation of $Fe(Phen)_3$ complex. In addition, the complex of $Fe(Phen)_3$ possess a broad UV-vis absorption peak in the range of 360 nm-580 nm, which overlaps the maximum emission of Tb-ADP-Phen at 545 nm (Figure S6). Therefore, the absorption of $Fe(Phen)_3$ complex to the emission of Tb-ADP-Phen further led to the fluorescence quenching of Tb-ADP-Phen (Figure S7).

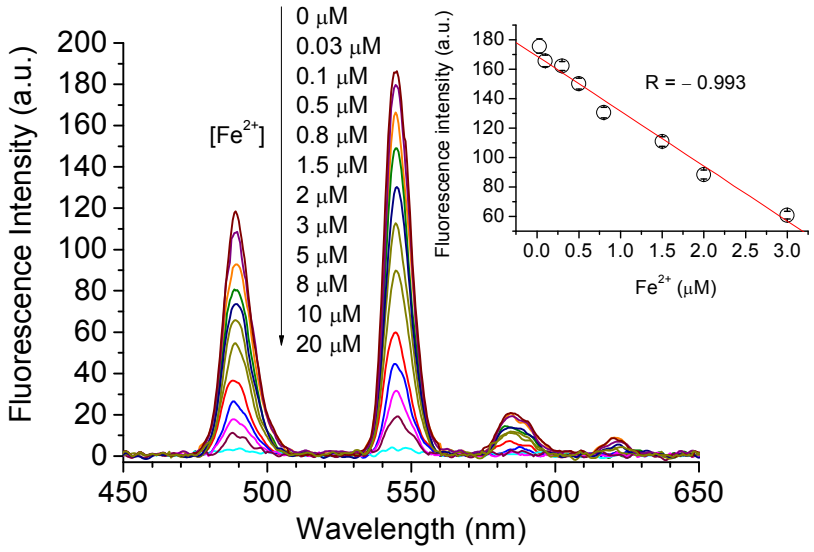


Figure 5. Fluorescence quenching of Tb-ADP-Phen CP in the presence of Fe^{2+} in HEPES buffer (100 mM, pH 7.4). Inset is the linear relationship between the fluorescence intensity of Tb-ADP-Phen CP and the concentration of Fe^{2+}.

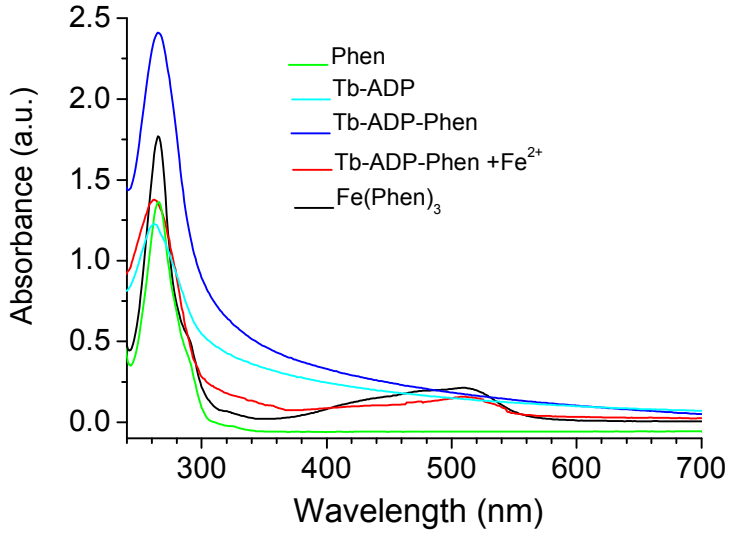


Figure 6. UV-vis spectra of Tb-ADP, Tb-ADP-Phen, Tb-ADP-Phen in the presence of Fe^{2+} (20 μM), Phen (50 μM) and $Fe(Phen)_3$ complex (20 μM) in NaAc-HAc buffer (100 mM, pH 5.0).

2.3. Selectivity of fluorescent response of Tb-ADP-Phen to Fe^{2+}

We tested the fluorescence quenching of Tb-ADP-Phen CP in the presence of common metal ions as interferents. As shown in Figure 7, under identical conditions, only the addition of Fe^{2+} produced a great fluorescence quenching; other metal ions (Ca^{2+}, Ag^{+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Cr^{6+}, Cr^{3+}, Mg^{2+}, Ba^{2+}) have almost no effect on the fluorescence of Tb-ADP-Phen (<5%) except Hg^{2+} and Cu^{2+} ions. When we added the masking reagent Na-DMPS and $NH_2OH{\cdot}HCl$, the interference of Hg^{2+} and Cu^{2+} ions can be eliminated effectively. These results indicated that Tb-ADP-Phen has a highly selective fluorescence response to Fe^{2+}. The selective fluorescence quenching of Tb-ADP-Phen by Fe^{2+} could be attributed to two factors: 1) Phen itself is a exclusive chromogenic agent for Fe^{2+}, which has been widely used for the analysis of Fe^{2+}, and has a specific binding ability to Fe^{2+};[36] 2) Only the produced $Fe(Phen)_3$ can significantly quench the fluorescence of Tb-ADP-Phen due to the overlap of the UV-vis absorption of $Fe(Phen)_3$ with the maximum emission of Tb-ADP-Phen.

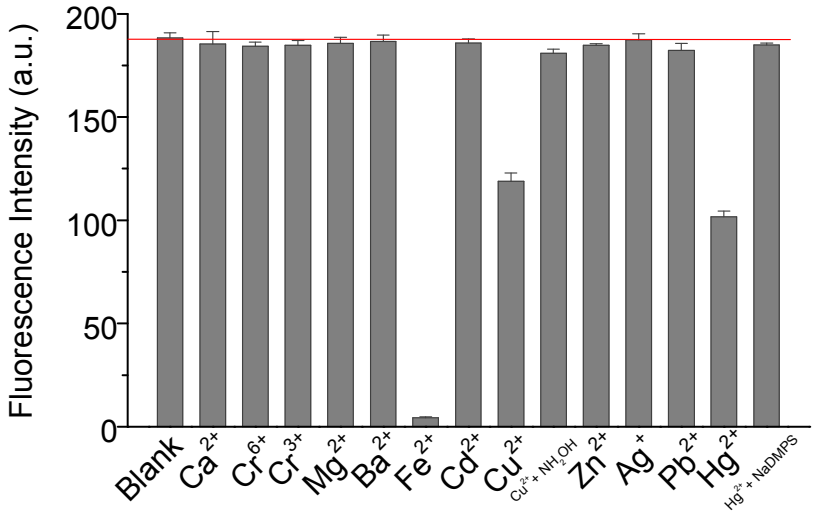


Figure 7. Selectivity of the determination of Fe^{2+} by Tb-ADP-Phen-based method. The concentrations of interfering metal ions are 20 μM.

2.4. Determination of Fe^{2+} and total iron in human serum by time-resolved fluorimetry

The long fluorescence lifetime of Tb-ADP-Phen CP inspired us to apply this material to detect Fe^{2+} ion in human serum by time-resolved fluorimetry. The iron in serum has been widely used to evaluate the current iron level in human body.[37] Because of the existence of autofluorescence from biocomponents, conventional dye-based fluorescence methods are often disturbed when biosamples such as serum are detected. The fluorescent intensity of Tb-ADP-Phen at 545 nm against the concentration of Fe^{2+} produced a linear correlation in the range of 80 nM–6 μM (R= –0.992) (Figure 8). The lowest detectable concentration of Fe^{2+} in serum is approximately 80 nM on the basis of a signal-to-noise ratio of 3:1. The normal level of Fe^{2+} in the serum of healthy body is approximately 11 to 29 μM.[38] Therefore, current method can not only satisfy the determination of Fe^{2+} but also effectively eliminate the interference of non-specific autofluorescence. We further measured the concentrations of total iron in human serum through the addition of reducing reagent hydroxylamine hydrochloride which reduces Fe^{3+} to Fe^{2+}. Table 1 showed the results for the determination of the total amount of Fe^{2+} and Fe^{3+}. The recoveries ranging from 96 to 104% indicated that this method has a good accuracy and no obvious system error.

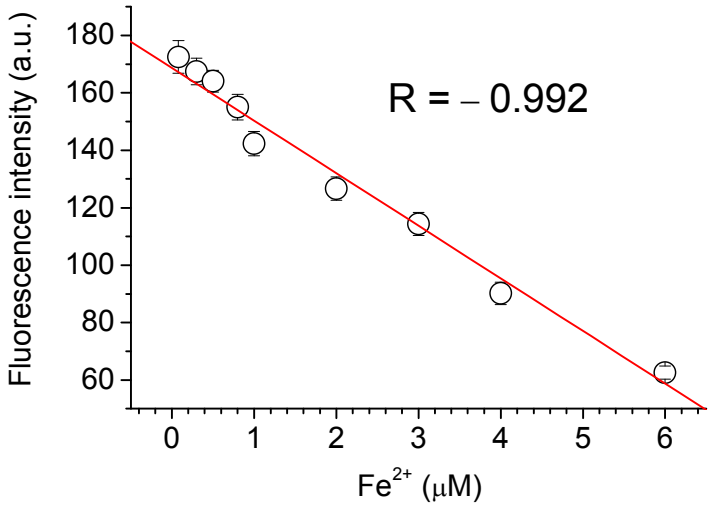


Figure 8. Determination of Fe^{2+} in human serum by Tb-ADP-Phen-based method.

Table 1. Determination of total iron in human serum samples

Sample	Added Fe^{2+} (μM)	Added Fe^{3+} (μM)	Detected total iron (μM)[a]	Recovery (%)	RSD (%)[b]
Serum sample 1	1.00 μM	1.00 μM	2.08 ± 0.05	104.00	2.50
Serum sample 2	1.00 μM	3.00 μM	4.15 ± 0.09	103.75	2.25
Serum sample 3	4.00 μM	2.00 μM	5.79 ± 0.15	96.50	2.50

a: mean value (n=3) ± standard deviation; b: relative standard deviation.

3. Conclusions

We prepared a kind of luminescent lanthanide CP with sensing function through the self-assembly of nucleotide molecule, Tb^{3+} ion and phenanthroline. The participation of ligand phenanthroline with sensitizing and recognition functions not only greatly enhanced the luminescence of the CP but also endowed the CP with high selectivity due to its specific binding ability to Fe^{2+} ion. This lanthanide CP has good optical stability and long luminescence lifetime,

was successfully applied to the determination of iron ion in human serum. Unlike most sensors that depend on extra recognition molecule to obtain selective function, this integrative nanosensor can directly response the existence of analytes. We hope that present strategy assembling the sensing materials with high selectivity by means of the component flexibility of CPs is helpful to the development of new types of nanosensors.

4. Experimental details

4.1. Chemicals and solutions

$Tb(NO_3)_3 \cdot 6H_2O$ (99.99%) was purchased from Rewin Rare Earth Metal Materials Co. Ltd. Metal salts ($CaCl_2$, $AgNO_3$, $ZnCl_2$, $CuCl_2$, $Pb(NO_3)_2$, $K_2Cr_2O_7$, $Cd(NO_3)_2$, $CrCl_3 \cdot 6H_2O$, $FeCl_3$, $FeCl_2$, $Hg(NO_3)_2$, $MgCl_2$, $BaCl_2$) were purchased from Nanjing Chemical Reagents Co. Ltd. Adenosine-5'-diphosphate disodium (ADP), sodium dimercaptosulfonate (Na-DMPS), 1,10-phenathroline (Phen), N-2-hydroxyethyl piperazine-N'-2-ethanesulfonic acid (HEPES), acetic acid (HAc) and hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) were obtained from Sangon Biotech (Shanghai) Co. Ltd. HEPES buffer (100 mM, pH 7.4) was prepared by dissolving 2.383 g HEPES in 100 mL of ultrapure water; 10 M NaOH was used to adjust pH to 7.4. NaAc-HAc buffer (100 mM, pH 5.0) was prepared by dissolving 1.36 g of NaAc in 100 mL of ultrapure water; acetic acid was used to adjust pH to 5.0. Ultrapure water (18 MΩ cm; Milli-Q, Millipore) was used for the preparation of all aqueous solutions. The stock solutions of interfering ions (2.0 mM) were prepared by directly dissolving 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.

4.2. Instruments and determinations

The morphology of coordination polymers were examined by transmission electron microscopy (TEM) (JEM-2100, Japan). Fourier transform infrared (FTIR) spectra were recorded with an Avatar 360 FTIR spectrometer (Nicolet, USA). UV-visible absorption spectra were recorded with a UV-3150 spectrophotometer (Shimadzu, Japan). 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 275-nm excitation wavelength was used for the emission spectra. A delay time of 0.05 ms and a gate time of 2 ms were used. Excitation spectra were recorded by observing the emission intensity of Tb^{3+} at 545 nm. For the emission lifetime, the fluorescence intensities at 545 nm were recorded under different delay times and fitted with an exponential function. All the experiments were performed at room temperature. All error bars represent standard deviations from three repeated experiments.

4.3. Preparation of Tb-ADP and Tb-ADP-Phen CPs

Tb-ADP and Tb-ADP-Phen coordination polymers were synthesized according to the reported methods.[39,40] For the preparation of Tb-ADP, typically, 1 mL of $Tb(NO_3)_3$ aqueous solution (3 mM) was added to 1 mL of ADP disodium salt water solution (3 mM), After stirring 3 h at room temperature, the product was collected by centrifugation at 10000 rpm for 20 min. To remove unreacted reactants, we washed the precipitate with ultrapure water for several times. The obtained Tb-ADP (0.9 mg, dry weight) was dispersed in 2 mL of HEPES buffer (100 mM, pH 7.4)

to form a Tb-ADP suspension. For the preparation of Tb-ADP-Phen, 2 mL of phen aqueous solution (1.5 mM) was added 2 mL of prepared Tb-ADP above, the other procedures were the same as the preparation of Tb-ADP. Finally, Tb-ADP-Phen CP (2.4 mg, dry weight) was dispersed in 2 mL of HEPES buffer (100 mM, pH 7.4) to form a Tb-ADP-Phen suspension.

4.4. Response of Tb-ADP-Phen CP to Fe^{2+} in aqueous solution

For the detection of Fe^{2+} in aqueous solution, Tb-ADP-Phen suspension (1.2 mg/mL) was diluted 4-fold before using. To 10 μL of Tb-ADP-Phen suspension (w/v, 0.3 mg/mL), different volumes of Fe^{2+} solution and HEPES buffer (100 mM, pH 7.4) were added to make a final Fe^{2+} concentration of 0, 0.03, 0.1, 0.5, 0.8, 1.5, 2, 3, 5, 8, 10 and 20 μM, respectively. The total volume is 100 μL. These mixed solutions were incubated for 20 min at room temperature. Then the variations in the fluorescence of Tb-ADP-Phen at 545 nm were recorded at 275 nm excitation wavelength. For the selectivity tests, 1 μL of 2 mM stock solutions of metal ion were added to 10 μL of Tb-ADP-Phen suspension, then certain volumes of HEPES buffer was added to the suspension till the total volume reached to 100 μL, respectively. After reacting for 20 min, the fluorescence intensities of the mixtures at 545 nm were measured under the excitation of 275 nm. The blank solution was composed of 10 μL of Tb-ADP-Phen suspension and 90 μL of HEPES buffer (100 mM, pH 7.4).

4.5. Determination of Fe^{2+} and total iron in human serum

Human serum was collected from healthy volunteers of Hospital of Southeast University. A series of serum samples containing different concentrations of Fe^{2+} were prepared by spiking

different volumes of Fe^{2+} stock solution. To 60 μL of HEPES buffer (10 mM, pH 7.4) solutions, 10 μL of Tb-ADP-Phen (0.3 mg/mL) suspension, 10 μL of Na-DMPS (300 μM) and 20 μL of serum samples containing different concentrations of Fe^{2+} were added, respectively. After incubated for 20 min, the fluorescence intensities at 545 nm were recorded under a 275 nm excitation wavelength. For the determination of total iron, 1 μL of $NH_2OH{\cdot}HCl$ (0.1g/L) was added to 99 μL of serum sample containing different concentrations of Fe^{3+} and Fe^{2+}. After the redox reaction was lasted for 30 min, the fluorescence determination was conducted under the same conditions.

Acknowledgements

This work was supported by the National Natural Science Foundation of China with the grant number of 60671014 and 20775012.

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