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Terbium-Based Coordination Polymer Nanoparticles for Detection of Ciprofloxacin in Tablets and Biological Fluids

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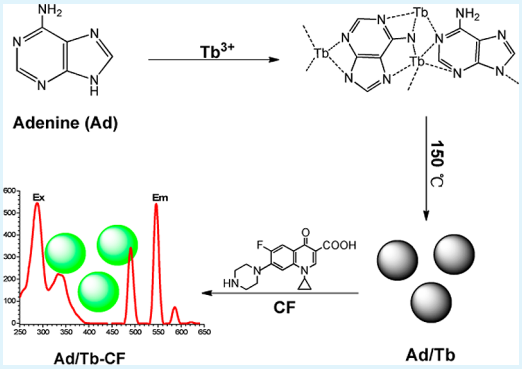
Supporting Information

ABSTRACT: The metal−organic coordination polymers with tunable structures and properties have been rapidly emerging as very important functional materials. In this work, we prepared terbium (Tb^{3+})-based coordination polymer nanoparticles (CPNPs) by employing adenine (Ad) as bridging ligands. The CPNPs was further used as a receptor reagent for ciprofloxacin (CF) detection in aqueous solution. Addition of CF induces a typical emission of Tb^{3+} due to the formation of Ad/Tb-CF complex and the sensitization of CF. The fluorescent intensity of Tb^{3+} was enhanced linearly with increasing the CF concentration from 60 nM to 14 μM. The detection limit for CF in aqueous solution is 60 nM. The Ad/Tb CPNPs was successfully applied to detect CF in tablet and urine samples and showed a satisfactory result. Compared with other methods, the proposed method is advantageous because that it provides a very simple strategy for CF detection, which does not require complicated sample pretreatment processes or special reaction media. The proposed strategy could be contributed to expand the potential applications of lanthanide coordination polymers in biological and environmental fields.



KEYWORDS: *terbium ion, adenine, coordination polymer nanoparticles, receptor reagent, fluorescence, ciprofloxacin*

INTRODUCTION

In recent years, metal−organic coordination polymers have been rapidly emerging as very important functional materials. Up to now, the applications of the coordination polymers have been exploited in many areas, such as heterogeneous catalysis,[1,2] sensing,[3,4] gas storage,[5,6] imaging,[7,8] and drug delivery.[9,10] In contrast to pure organic or inorganic materials, the limitless choices of metal ions and organic ligands afford the coordination polymers with different morphologies and physicochemical properties, and consequently they would have the potential to show promise for diverse applications.[11] Nevertheless, rational designs of functional coordination polymers are still in an immature primary stage. Trivalent lanthanide ions (Ln^{3+}) are in favor of the construction of the coordination polymers since they possess the properties of larger radius, versatile coordination geometry, and high affinity to the molecules containing negatively charged oxygen or oxygen−nitrogen hybridization.[12,13] Compared with molecular lanthanide compounds or inorganic nanocrystals, the lanthanide coordination polymers not only show excellent performances in mechanical properties, thermal stability and processability,[14] but also provide an interesting platform for assembling and modulating lanthanide ions and organic ligands in a solid framework. Particularly, the unique emission behaviors of lanthanide coordination polymers, including large Storks shift, high quantum yields, and long lifetime, make them attractive for the construction of optical devices and tunable luminescent sensors as well as probes for biological and chemical species. Therefore, new chemical sensing ways would be provided with the regulation of their luminescent properties. In fact, some lanthanide coordination polymers have recently been successfully employed for the sensing of metal ions,[15,16] anions,[17,18] and small molecules.[19,20] However, these sensing reactions of lanthanide coordination polymers mainly conducted in organic solution, less work about in aqueous solution has been reported.[21]

In the previous work, we constructed a lanthanide coordination polymer with fluorescent sensing function from initial building blocks.[22] Because of the fluorescence of this lanthanide coordination polymer can be modulated by Hg^{2+} through a process of photoinduced electron transfer, a sensor for detection of Hg^{2+} in aqueous solution has been developed. In spite of this, the application of lanthanide coordination polymers as receptor reagents for direct sensing of small molecules remains to be further studied. It is well-known that the coordination of aromatic compounds allowed $\pi-\pi^*$ transition with Ln^{3+} can compensate the defect of low molar absorption coefficients of Ln^{3+} itself, and sensitizing the fluorescence of Ln^{3+}. This principle has been widely applied in the Ln^{3+}-based fluorescent assays. However, most of the

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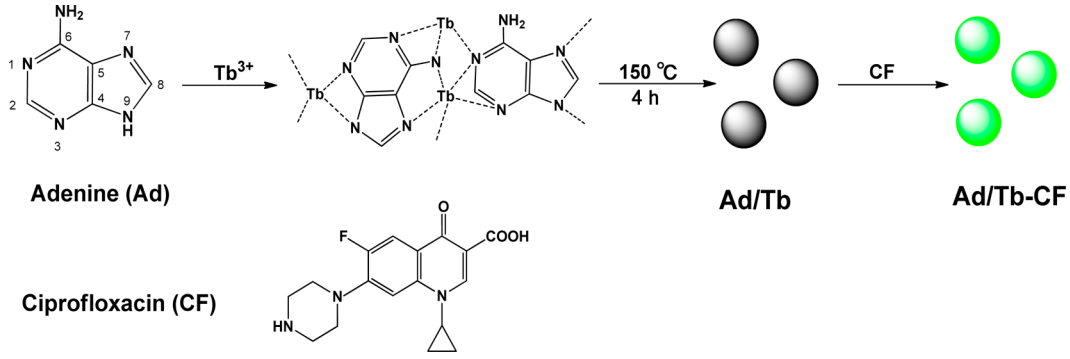
Scheme 1. Illustration of Ad/Tb CPNPs for Detection of CF



fluorescent assays limited in the using of molecular lanthanide compounds as fluorescent probes. Therefore, the development of new Ln^{3+}-based materials used as receptor regents for ultrasensitive fluorescent assays has been a hot topic, especially nanoscaled functional materials.

Ciprofloxacin (CF), as a third-generation synthetic fluoroquinolone antibiotic, has been widely used in medical clinical practice because of its relatively low side effects. CF has a broad-spectrum of activity against Gram-positive and Gram-negative bacteria and can treat the infections caused by the bacteria that single or multiple resistant to other antibiotics.[23] However, increasing evidence shows that CF can induce DNA damage[24] and may cause severe liver damage[25] and hematuria.[26] Currently, various methods have been developed to determine the level of CF, such as spectrophotometry,[27] spectrofluorimetry,[28,29] flow-injection with chemiluminescence detection,[23,30] and high performance liquid chromatography (HPLC).[31,32] Still, most of the above methods are time-consuming owing to the requirement of expensive and sophisticated instruments and have limited sensitivity or selectivity. Fluorescent detection for CF could be an ideal means because it has high sensitivity and does not require complicated procedures for sample pretreatment. In particular, Ln^{3+}-sensitized fluorescent detection is favorable for CF detection.[28] The long wavelength emission and long fluorescent lifetimes of Ln^{3+} can eliminate efficiently scattering interference and background fluorescence.[12] Nevertheless, the Ln^{3+}-based fluorescent methods for CF detection are often performed in conjunction with separating techniques, and the reports on using lanthanide fluorescent probes for direct detection of CF are relatively rare.

In this work, we attempt to employ adenine (Ad) as bridging ligand and Tb^{3+} as metal node to construct coordination polymer nanoparticles (CPNPs), denoted as Ad/Tb CPNPs, and utilize the CPNPs with highly tailorable property as a receptor reagent for the detection of CF. Ad is an attractive building block for the construction of metal−organic coordination polymers owing to its rich metal binding sites and rigid molecular structure.[33] However, the Ad/Tb CPNPs displayed almost no fluorescence because of the small molar absorption coefficient of Tb^{3+} (Scheme 1). As a derivative of 4-quinolone-3-carboxylic acid, CF can coordinate with Tb^{3+} through its carboxylate and keto oxygen atoms and sensitize Tb^{3+} emission via a process of intramolecular energy transfer.[30] With the addition of CF, therefore, the Ad/Tb CPNPs may produce desired fluorescence.

EXPERIMENTAL SECTION

Chemicals and Solutions. All chemicals were of analytical grade purity, obtained from commercial sources, and used as received. Terbium nitrate hexahydrate ($Tb(NO_3)_3{\cdot}6H_2O$, 99.99%) and N-2-hydroxyethyl piperazine-N′-2-ethanesulfonic acid (HEPES) were obtained from Ruike Rare Earth Metallurgy and Functional Materials Co., Ltd. (Baotou, China) and Sangon Biotech Co., Ltd. (Shanghai, China), respectively. Adenine, metal salts (KNO_3, $NaNO_3$, $CaCl_2$, KCl, NaCl, and $MgCl_2$), ciprofloxacin, ascorbic acid, starch, glucose, lactose, fructose, and sucrose were purchased from Sinopharm Chemical Reagent Company (Shanghai, China). A 100 mM of HEPES buffer was obtained by dissolving HEPES (11.915 g) in 450 mL of ultrapure water (18 MΩ, Millpore, USA), and NaOH (10 M) was used adjust the solution to pH 7.5, and finally making up the volume to 500 mL.

Characterization. The morphology of CPNPs was examined by a SU8020 field-emission scanning electron microscopy (FE-SEM, Hitachi, Japan) equipped with an energy-dispersive spectra (EDS) detector. The measurement of excitation and emission spectra was performed on PerkinElmer LS55 spectrofluorometer (PerkinElmer, U.K.). The delay time and gate time were set at 0.05 and 2 ms, respectively. The emission spectra were monitored using a 288 nm excitation wavelength, while the excitation spectra were recorded at an emission wavelength of 545 nm. Lambda35 spectrophotometer (PerkinElmer, U.K.) and Avatar 360 FTIR spectrometer (Nicolet, USA) were employed to record the UV−visible absorption spectra and Fourier transform infrared spectra (FTIR), respectively.

Preparation of Ad/Tb CPNPs. The Ad/Tb CPNPs were synthesized based on the previous report.[22] Briefly, 2 mL of $Tb(NO_3)_3$ dissolved in ulptrapure water (40 mM) was added dropwise into a mixture containing 2 mL of 20 mM Ad aqueous solution and 8 mL of N,N-dimethylformamide (DMF) with vigorous stirring. Ultrapure water (0.5 mL) was used to make up the final volume to 12.5 mL. The mixture was first reacted for 30 min at room temperature in a Teflon-lined stainless steel vessel (20 mL), and then transferred to an oven for reacting 4 h at 150 °C. The products were collected by centrifugation (13 000 rpm, 10 min) after cooling to room temperature and washed three times with absolute ethanol to remove unreacted reactants. Finally, a CPNP suspension was prepared by dispersing the as-prepared precipitate in ultrapure water (2 mL).

Determination of CF in Aqueous Solution. All experiments were performed at room temperature and the diluted Ad/Tb CPNPs suspension (50-folds) was used in all fluorescent studies. For quantization of CF concentration in aqueous solution, various amounts of CF were first added to the mixture of Ad/Tb CPNPs suspension (5 μL) and HEPES buffer and incubated for 15 min, respectively. The final volume of the reaction solution is 100 μL and the final concentrations of CF in the reaction solutions are in the range of 0 to 20 μM. Then, the emission spectra at 288 nm excitation of these reaction solutions were measured. Same procedures were used for the interference study of substances (KNO_3, $NaNO_3$, $CaCl_2$, KCl, NaCl, $MgCl_2$, ascorbic acid, starch, glucose, lactose, fructose, and sucrose). The final concentrations of these substances are 10 μM. For

the experiment of pH effect, the mixture containing 5 μL of Ad/Tb CPNP suspension and 16 μL of CF (100 mM) was added to HEPES buffer pH from 2 to 12 and incubated for 15 min. These mixtures were then transferred into quartz cell and measured their fluorescent spectra, respectively.

Determination of CF in Urine Samples. Drug-free human urine samples, which obtained from healthy adult volunteer, were used for the detection of CF in urine samples. Different amounts of CF standard solutions were added to 100-folds diluted urine samples to prepare spiked urine samples. The final CF concentrations in spiked urine samples ranged from 0 to 20 μM. Then, Ad/Tb CPNPs suspension (5 μL) was added to the spiked urine samples, and ultrapure water was used to make up the final volume of the reaction solutions to 100 μL. After a 15 min incubation, the fluorescent spectra of these reaction solutions were examined.

Determination of CF in Tablets. A tablet containing 250 mg of CF was obtained from hospital and used to determine CF concentration in tablets. First, five weighted tablets were finely powdered and a part of tablet powders with equal weight (0.25 g) was transferred to a beaker. The powders were then dissolved in ultrapure water and a filter operation based on ordinary filter paper was performed to separate CF from the tablet solution. The filtrate was collected and diluted with ultrapure water to prepare tablet samples with final expected CF concentration from to 1 to 20 μM. Finally, the CF concentrations in the as-prepared table samples were determined by using same procedures mentioned above.

RESULTS AND DISCUSSION

Unlike synthetic organic ligands, natural biomolecules with diverse chemical structures are mostly water-soluble and can provide multiple nodes for the binding of metal ions. Besides, the biomolecules also possess the intrinsic property of self-assembly. So, some new characteristics would be bestowed on the coordination polymers using biomolecules as bridging ligands.[33,34] Here, a Tb^{3+}-based CPNPs was prepared by employing Ad as bridging ligand, which is one of nucleobases and has been used to build meta-organic coordination polymers in recent years.[35−38] The morphology of the Ad/Tb CPNPs was measured by FE-SEM. Figure 1 displayed that the Ad/Tb

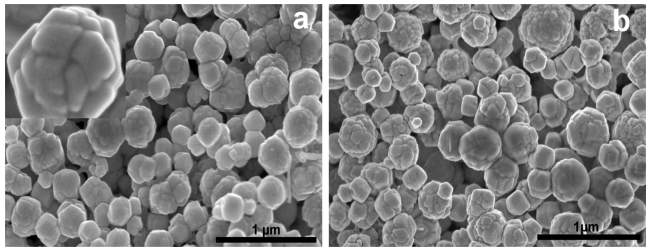


Figure 1. SEM images of Ad/Tb CPNPs in the absence (a) and presence (b) of CF.

CPNPs are spherical and have average sizes of 290 ± 50 nm. After the addition of CF, the structure of Ad/Tb CPNPs remains unchanged. These prepared Ad/Tb CPNPs are amorphous structures (data not shown). To further characterize the chemical compositions and structures of the Ad/Tb CPNPs, their energy-dispersed spectrum (EDS) and FTIR were analyzed, respectively. As shown in Figure S1 in the Supporting Information, the EDS peaks corresponding to Tb^{3+}, C, N, and O can be observed, indicating the existences of Tb^{3+} and Ad in the CPNPs. The FTIR spectrum changes of Ad/Tb CPNPs as compared with pure Ad reveal that the formation of Ad/Tb CPNPs is resulted from the coordination of Ad with Tb^{3+} (see Figure S2 in the Supporting Information). Moreover, we investigated the fluorescent characteristics of Ad/Tb CPNPs. It can be seen from Figure 2 that the Ad/Tb

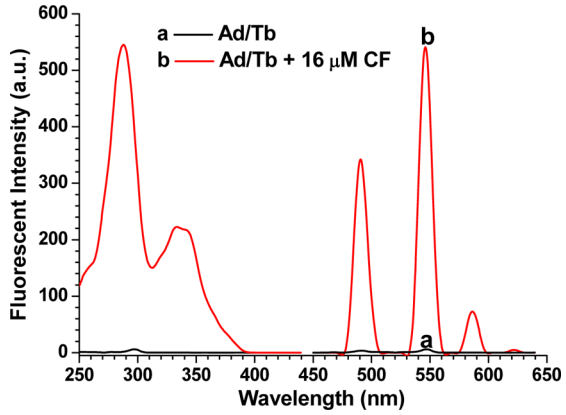


Figure 2. Excitation and emission spectra of Ad/Tb CPNPs in the (a) absence and (b) presence of 16 μM CF. The emission spectra of Ad/Td CPNPs in the absence and presence of CF were recorded at 260 and 288 nm excitation wavelengths, respectively.

CPNPs itself exhibited no fluorescence, which is attributed to that the molar absorption coefficient of Tb^{3+} is very small. With the addition of CF, however, a typical emission of Tb^{3+} with peaks at 490, 545, 584, and 620 nm was observed. These peaks can be assigned to $^5D_4$ to ^7F_j (j = 3−6) electronic transitions of Tb^{3+}.[12] Among these peaks, the emission at 545 nm is much stronger. The Tb^{3+} emission may be arisen from the formation of Ad/Tb-CF complex through the coordination of CF with Tb^{3+} on the surface of Ad/Tb CPNPs and the sensitization of CF. It is also noteworthy that the intrinsic fluorescence of CF was not observed. This suggests that the background fluorescence of CF can be eliminated effectively under time-resolved fluorescence mode, which is beneficial to use Ad/Tb CPNPs as a fluorescence probe for the detection of CF in biological samples.

To confirm the chemical coordination between the Ad/Tb CPNPs and CF, we measured the FTIR spectra of pure CF, Ad/Tb CPNPs alone and Ad/Tb CPNPs coexisted with CF. Compared with Ad/Tb CPNPs alone, a new peak at 1623 cm^{-1} was found from Ad/Tb CPNPs coexisted with CF (Figure 3). This new peak can be assigned to COO^- asymmetric stretching vibration of CF, which is a characteristic peak of CF-metal ion complex,[39] indicating the coordination of CF with Ad/Tb CPNPs. Besides, the disappearance of COO^- symmetric stretching vibration peak of CF at 1380 cm^{-1} and the shifts of CF in C═O (from 1443 to 1471 cm^{-1}) and COO^- symmetric stretching vibrations (from 1312 to 1340 cm^{-1}) were observed. The FTIR spectra changes of CF reflect that the formation of Ad/Tb-CF complex is resulted from the coordination of carboxylic acid group and ketone group of CF with Tb^{3+} on the surface of Ad/Tb CPNPs.[39,40] Apart from FTIR analysis, the absorption spectra changes of Ad/Tb CPNPs coexisted with CF were also examined due to that the binding of aromatic ligands with allowed $\pi-\pi^*$ transition with Ln^{3+} usually leads to the changes of their absorption peaks.[41] As shown in Figure 4, the free CF exhibits two maximum absorption peaks at 270 and 335 nm, respectively. When the CF was added to the Ad/Tb CPNPs suspension, however, the absorption peak at 270 nm was red-shifted to 276 nm and the peak at 335 nm was blue-shifted to 317 nm, respectively. The

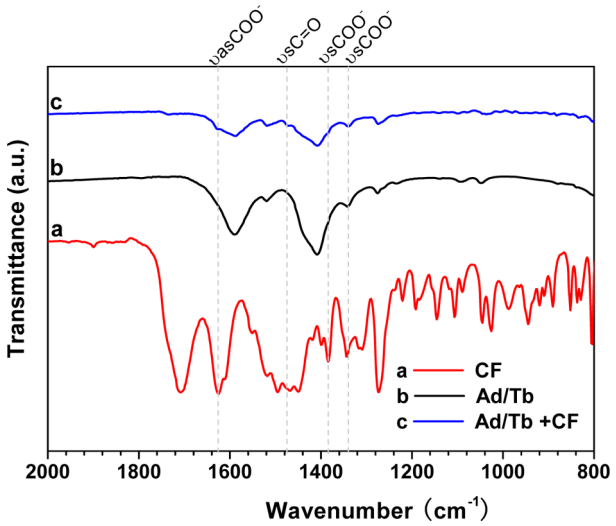


Figure 3. FTIR spectra of (a) CF, (b) Ad/Tb CPNPs alone, and (c) Ad/Tb CPNPs with the addition of CF. The νas and νs represent asymmetric stretching vibration and symmetric stretching vibration, respectively.

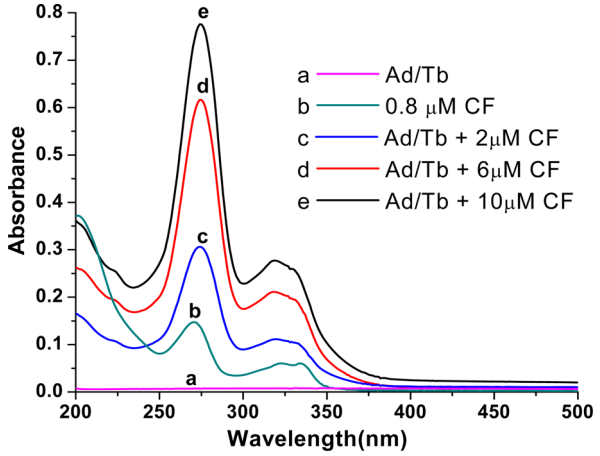


Figure 4. Absorption spectra of (a) Ad/Tb CPNPs, (b) CF, and (c–e) Ad/Tb CPNPs upon the addition of various concentrations of CF.

absorption spectra changes of CF further support the occurrence of chemical coordination between CF and Tb^{3+} on the surface of Ad/Tb CPNPs.[28] Moreover, we investigated the fluorescent behaviors of Ad/Tb CPNPs in the dispersed and separated states. As seen from Figure S3 in the Supporting Information, a green fluorescence can be observed from Ad/Tb CPNPs suspension coexisted with CF. After the Ad/Tb CPNPs suspension coexisted with CF was centrifuged, however, only the precipitate of the suspension showed a green fluorescence, and no fluorescence was observed from the supernatant. The results suggest that the CF was not adsorbed onto the external surface of the Ad/Tb CPNPs but participated in the coordination of Tb^{3+}, which results in the formation of Ad/Tb-CF complex.

Upon the addition of CF, the fluorescent intensity of Ad/Tb CPNPs was enhanced significantly and reached a plateau after 15 min (see Figure S4 in the Supporting Information). Thus, an incubation time of 15 min was used in further studies. In addition, the fluorescence of Ad/Tb-CF complex was seriously affected by the pH of reaction media (Figure 5). The fluorescent intensity of Ad/Tb-CF complex enhanced with

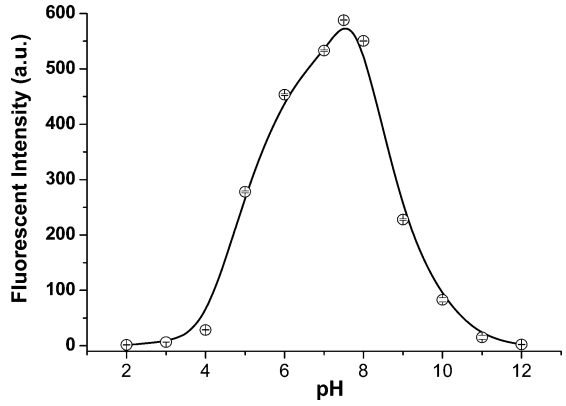


Figure 5. Effect of pH of reaction media on the fluorescence intensity of Ad/Tb CPNPs at 545 nm in the presence of 16 μM CF (Ad/Tb-CF complex).

the increase of the pH from 2 to 7.5, and the highest fluorescent enhancement was observed at pH 7.5. The fluorescent enhancement may be attributed to the deprotonation of the Ad and CF in neutral environment, which is helpful to the formation of Ad/Tb-CF complex. However, a gradually decrease in the fluorescent intensity of Ad/Tb-CF complex was observed when the pH value was more than 7.5. The fluorescence quenching behavior under strong basic condition might be ascribed to the formation of terbium hydroxide precipitation and the disassembly of the Ad/Tb CPNPs. Moreover, the fluorescent response of Ad/Tb CPNPs to CF remains unchanged for at least 30 days (see Figure S5 in the Supporting Information), which reflects that the fluorescent stability of Ad/Tb CPNPs is very excellent. Therefore, the Ad/Tb CPNPs as a fluorescent material may have wide potential in the development of biosensors.

To quantitative analysis CF using Ad/Tb CPNPs as a fluorescent probe, the fluorescence of the Ad/Tb CPNP coexisted with various concentrations of CF were measured. From Figure 6, we can found that the fluorescent intensities of Ad/Tb CPNPs enhanced with gradually increasing the CF concentration. The fluorescent intensities of Ad/Tb CPNPs displayed a linear correlation to CF concentration from 60 nM to 14 μM. The detection limit (DL) for CF in aqueous solution

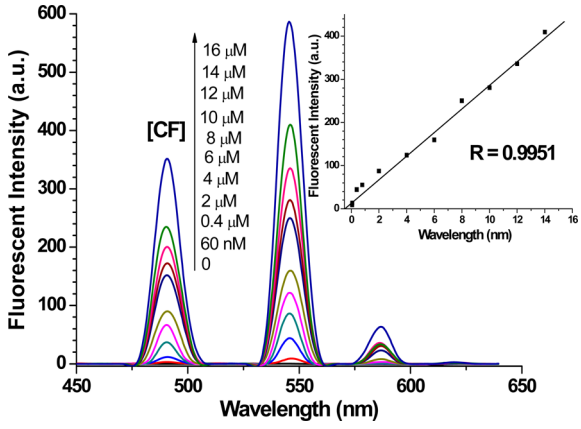


Figure 6. Fluorescent responses of Ad/Tb CPNPs upon the addition of various concentrations of CF (0, 60 nM, and 0.4, 2, 4, 6, 8, 10, 12, 14, and 16 μM). The inset is the plot of the fluorescent intensity of Tb^{3+} recorded at 545 nm vs CF concentration.

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is 60 nM (3σ), which is comparable with that of methods-based flow-injection enhanced chemiluminescence (DL = 12 nM)[23] and Tb^{3+} involved chemiluminescence (DL = 10 nM),[30] and much lower (four times) than those of previously reported methods that carried out in micellar environment (DL = 270 nM).[28] However, the methods performed in conjunction with separating techniques showed higher detection sensitivities as compared with the proposed method in the work.[42,43] In spite of this, the distinct advantage of the presented method is that it provides a simpler and faster detection procedure, which does not require complicated sample pretreatment processes. Furthermore, the Ad/Tb CPNPs as a kind of nanomaterials also offer the advantage of recognition ability of multiple molecules because of their high surface-to-volume ratio as compared with molecular lanthanide compounds.

We next investigated the selectivity of the Ad/Tb CPNPs for CF detection by testing the fluorescent response of Ad/Tb CPNPs to these substances that may exist in biological fluids or use as excipients to accelerate drug absorbing. In this work, the substances including metal ions (Na^+, K^+, Ca^{2+}, Mg^{2+}), anions (NO_3^- and Cl^-), starch, ascorbic acid (AA), glucose, lactose, fructose, and sucrose were selected as interferences because that they can coordinate with CF or Tb^{3+} and accordingly affect the fluorescence of Ad/Tb CPNPs.[44,45] The fluorescent responses of Ad/Tb CPNPs to these interferences were shown in Figure.7. The results exhibited that only CF can

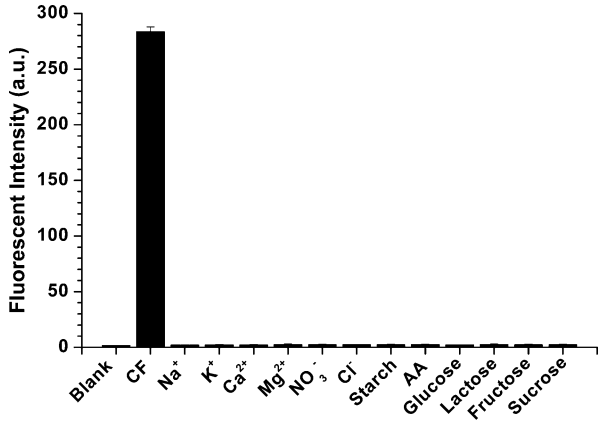

Figure 7. Fluorescent responses of Ad/Tb CPNPs to CF (10 μM) and interferential substances (10 μM).

cause an obvious enhancement in the fluorescence of Ad/Tb CPNPs, whereas the existences of the interferences displayed no influences on the fluorescence of Ad/Tb CPNPs. Even the concentrations of the interferences were increased to 1 mM, the fluorescence of Ad/Tb CPNPs still remained "OFF" state. The results suggest that the influences from these foreign substances are negligible, and Ad/Tb CPNPs appears to be useful for selective sensing of CF.

To explore the practical application of Ad/Tb CPNPs, we measured the levels of CF in tablet and spiked urine samples. After the tablet powders with known amounts of CF were dissolved in water, the as-prepared solution was filtered. The diluted filtrates were then analyzed using the proposed fluorescent method. For the detection of CF in urine samples, a standard addition method was used. Table S1 in the Supporting Information showed the results of Ad/Tb CPNPs as fluorescent probe for detection CF in tablet and urine. The recoveries of CF in tablet samples were between 99.47 and 103.4%, whereas those between 99.19 and 103.71% were obtained for urine samples. The relative standard deviations (RSD, n = 3) are all less than 0.83%. The results indicate that the detection of CF in tablet and urine samples by using Ad/Tb CPNPs as fluorescent probe showed good recovery and precision.

CONCLUSION

In summary, a Tb^{3+}-based CPNPs has been constructed by using biomolecule Ad as bridging ligands. This Ad/Tb CPNPs was further employed as a receptor reagent to direct detection of CF in aqueous solution. Because CF can transfer its absorbed energy to Tb^{3+} and sensitize the fluorescence of Tb^{3+}, a typical Tb^{3+} emission can be observed after the coordination of CF with Tb^{3+} on the surface of Ad/Tb CPNPs. The fluorescent intensity of Tb^{3+} was enhanced linearly with the CF concentration from 60 nM to 14 μM. The detection limit for CF in aqueous solution is 60 nM. The detection based on Ad/Tb CPNPs exhibits the advantages of direct and fast detection procedure, simple sample pretreatment processes and excellent stability and selectivity. The levels of CF in tablet and urine samples can be measured accurately by using the Ad/Tb CPNPs as a fluorescent probe. The proposed strategy might provide a new platform for the design and application of fluorescent sensors based on lanthanide coordination polymers.

ASSOCIATED CONTENT

Supporting Information

Figure S1–S5 and Table S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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