Macromolecular Probe Based on a Ni\textsuperscript{II}/Tb\textsuperscript{III} Coordination Polymer for Sensitive Recognition of Human Serum Albumin (HSA) and MnO\textsubscript{4}\textsuperscript{−}

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Supporting Information

ABSTRACT: Reported here are the design and fluorescence characters of a Ni\textsuperscript{II}/Tb\textsuperscript{III} polymer, [Tb\textsubscript{2}Ni\textsubscript{3}(HCAM\textsubscript{6})(H\textsubscript{2}O\textsubscript{12})\textsubscript{n}] (1) (H\textsubscript{2}CAM = chelidamic acid). Under physiological conditions, the binding of biocompatible water soluble 1 to human serum albumin (HSA) was studied by spectroscopy techniques, which revealed that 1 could inherit the fluorescent light of HSA in a static quencher course and change the HSA second-level structure. The marked enhancement in 1 and its fluorescence intensity provide conclusive evidence that 1 can play the role of a “turn-on” sensor for recognition and detection of HSA in other biological interferents with a $K_{sv}$ value of $7.68 \times 10^4$ M$^{-1}$ and a detection limit of 0.14 μM. Luminescence experiments show that 1 has high selectivity and sensitivity to MnO\textsubscript{4} in other anions. Its quenching efficiency ($K_{sv}$) is $5.54 \times 10^3$ M$^{-1}$, and the detection limit is 0.29 μM.

1. INTRODUCTION

Nowadays, environmental pollution is a serious threat to biodiversity and people’s health, many of which are documented in prior contaminants by the U.S. Environmental Protection Agency (EPA); in particular, MnO\textsubscript{4} has received widespread attention.\textsuperscript{1} Some analytical techniques such as atomic absorption spectroscopy, ion chromatography, electrophoresis, and fluorescence determination have been used for the detection of MnO\textsubscript{4}.\textsuperscript{2,3} However, the detection accuracy and rate of these methods are not satisfactory. Therefore, there is an urgent need for new detectors with high sensitivity, good regeneration, and chemical stability. Polymers are a unique kind of porous crystalline materials, which have been widely studied for their application in gas separation/storage,\textsuperscript{4,5} luminescence,\textsuperscript{6,7} sensing,\textsuperscript{8} catalysis,\textsuperscript{9,10} and magnetism.\textsuperscript{11,12} Especially, they can be used for selective detection of environmental contaminants.\textsuperscript{13,14} Polymers may be an ideal new material for detecting MnO\textsubscript{4} ions.

It is well known that human serum albumin (HSA) can interact with several metabolites and drugs in vivo, thereby changing its pharmacokinetics and pharmacodynamics characteristics and further affecting its distribution and activity toward biological targets.\textsuperscript{15,16} Due to the complexity of biosystems, selective testing of HSA probes is an important research object in biomedical analyses. In this work, we are interested in the selectivity of HSA to BSA. BSA and HSA have 70% biological similarity.\textsuperscript{17,18} Therefore, it is very important to study the probes to distinguish the two similar proteins. Most of the reported fluorescent probes for serum albumin detection showed that the selectivity of the probes to HSA was lower than that of BSA, and their detection limit was above 30 mg/L.\textsuperscript{20-24} Most of the fluorescent probes reported are fluorescence quenching mechanisms.\textsuperscript{25} For all we know, a few fluorescent probes that have been reported via fluorescence enhancement may be “turn-on” mechanisms.\textsuperscript{26,27} Designing and synthesizing “turn-on” sensors is a challenging task, because there are several factors involved in the fluorescence process.

In this work, a new heterometallic 2D coordination polymer (CP) [Tb\textsubscript{2}Ni\textsubscript{3}(HCAM\textsubscript{6})(H\textsubscript{2}O\textsubscript{12})\textsubscript{n}] is synthesized under hydrothermal conditions. Powder X-ray diffraction (PXRD) study shows that 1 is a pure substance. CD, UV, and fluorescence spectra were used to study the binding mode of 1–HSA. The affinity constants of 1–HSA interaction and the changes of HSA secondary structure were obtained. This CP can discriminatingly detect HSA in the solution state. Interactions between HSA and 1 lead to “turn-on” fluorescence, with a $K_{sv}$ value of $7.68 \times 10^4$ M$^{-1}$ and a detection limit of 0.14 μM. In addition, 1 has a high selectivity.

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for MnO$_4^-$, with a $K_w$ value of $5.54 \times 10^{-3}$ M$^{-1}$ and a detection limit of 0.29 $\mu$M.

2. EXPERIMENTAL SECTION

2.1. General Methods and Materials. CT DNA, HSA, BSA, 1× TBS buffer solution, and amino acids are used as chromatographic reagents, and other reagents are of analytical grade. The solvents used in this study were purified by standard methods. Milli-Q water was used in all experiments. CT DNA reserve was prepared with 5 mM Tris-HCl/NaCl buffer (pH 7.4), I was prepared with Milli-Q water, and HSA was prepared with 1× TBS buffer (pH 7.4). All the solutions are refrigerated in a 4 °C refrigerator and used within 3 d.

Elemental analyses (H, N, and C) were measured on a PerkinElmer analyzer (model 240). The infrared spectrum of was measured at a heating rate of 10 K min$^{-1}$ with a NETSCH STA409PC thermal analyzer. The emission spectra of I in water solution were detected by a Spex Fluorog-2 spectrofluorimeter (model F111, Spex Industries, Edison, NJ, USA). The spectrometer uses a 450 W xenon lamp (XBO 450W/1, Osram, Germany) as the excitation light source and a 950 V photomultiplier tube (R928, Hamamatsu, Japan) as the detector. The slit, increment, and integration time of excitation and emission monochromator are set to 1 mm, 1 nm, and 1 s, respectively. All spectral data were obtained by a SPEX DM 3000F spectrometer computer. Luminescent sensing and fluorescence spectra upon the addition of various different cations or ions were performed on a Cary 300 spectrophotometer with a 150 W xenon lamp as the excitation source.

2.2. Synthesis of [Nb$_3$Ni$_6$(HCAM)$_2$]$_4$O$_{12}$I$_8$ (1). I was obtained by one-pot synthesis from Nb$_2$O$_5$ (0.04 mmol, 0.014 g), NiCl$_2$ (0.12 mmol, 0.028 g), H$_2$CDA (0.24 mmol, 0.043 g), and triethylenamine at pH = 3.0 in 15 mL of water. The reactants were placed in a 25 mL reactor, and the reaction mixture was heated to 180 °C under self-generated pressure for 96 h and cooled to normal atmospheric temperature at a rate of 1.5 °C/h.

One week later, light green rod-like-shaped crystals suitable for X-ray analysis were obtained, which was filtered and washed with H$_2$O (3 × 5 mL) and diethyl ether (3 × 5 mL) (yield: 280. mg, 39%). Elemental analysis (%): calc for C$_{42}$H$_{42}$N$_{10}$O$_{16}$I$_8$: C, 28.08; H, 2.36; N, 4.68. Found: C, 27.83; H, 2.57; N, 4.51. IR (KBr) $\nu$ (cm$^{-1}$): 3380.62 (vs), 2931.7 (s), 1608.56 (vs), 1562.56 (vs), 1416.99 (vs), 1331.53 (s), 1120.78 (s), 1028.23 (s), 978.01 (m), 860.03 (m), 739.48 (m), 543.25 (s).

2.3. Fluorescence Measurements. Using HSA as the model protein, the protein binding was studied by fluorescence quenching titration in 1× TBS buffer (pH 7.4). The fluorescence spectra at 273 and 298 K were measured at a $\lambda_{ex} = 280$ or 293 nm when the concentration of I was gradually increased to 3.8 $\mu$M in 6 $\mu$M HSA solution. The effect of HSA on the fluorescence of I was measured at a fixed concentration of $10^{-4}$ M ($\lambda_{ex} = 280$ nm), and the binding strength was calculated according to the change of emission curve.

2.4. CD Spectra. The CD spectra of HSA (1.2 $\mu$M) before and after adding different concentrations of I (2.4, 4.8, and 7.2 $\mu$M) were measured in the range of 190–250 nm.

2.5. UV Absorption Spectra. UV absorption spectra were measured in 1× TBS buffer (pH 7.4), maintaining a constant concentration of HSA (10 $\mu$M) and gradually increasing the concentration of I (0–4.6 $\mu$M). The same concentration of I was used as the reference solution to eliminate the influence of the absorbance of polymer I itself. Before testing the spectra, each sample was mixed for 10 min.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Spectroscopic Measurements. In this study, the heterometallic 2D CP was synthesized by one-pot hydrothermal synthetic approaches. It is noteworthy that hydrothermal synthesis is a commonly used method in a previous study.28 In the process of synthesizing 2D CPs, water plays an important role as the solvent of CPs, which is conducive to the formation of single crystals. In addition, another common strategy reported for the synthesis of 3d/4f CPs is to use simple compounds as ligands; however, this strategy rarely yields multidimensional polymers.29 From the point of view of polymer synthesis, it is meaningful to obtain 3d/4f two-dimensional CPs. For example, the degree of protonation of H$_2$CAM ligands depends on the synthesis conditions, where the ligand is separated into HCAM$^2$−. In addition, the ligand of H$_2$CAM satisfies the condition of binding 3d and 4f cations simultaneously—3d/4f metal centers within the asymmetric unit in 1 (Ni$^{II}$/Tb$^{III}$). The above-mentioned synthetic methodology used water as the solvent. The structure in 1 is characterized by presenting a covalent 2D CP without lattice H$_2$O molecules.

In the synthesis, it is noteworthy that water as the solvent is very important in the crystallization process; otherwise, the polymer crystals cannot be obtained. It is obvious that the synthesis method in this experiment is effective for obtaining 3d/4f heterogeneous metal CPs.

Figure S1 shows the crystal powder X-ray diffraction (PXRD) patterns of 1. Compared with the calculated pattern of X-ray single-crystal data simulation, the line sharpness and peak position are consistent with the simulated PXRD pattern. The results show that the structure of the sample is the same as the X-ray single-crystal data. As depicted in Figure S2a, Fourier transform infrared (FT-IR) spectra show that 1 is dominated by a broad band and an intermediate frequency band at 3380.62 cm$^{-1}$ designated as characteristic absorption peaks (\(\nu_{\text{COO}}\)) of coordination water molecules.30 The absence of absorption peaks at about 1700 cm$^{-1}$ indicates complete deprotonation of carboxyl groups. The coordination mode of carboxylic acid with metal ions was inferred by measuring the difference (\(\Delta\nu = \nu_{\text{COO}} - \nu_{\text{COO}}\)) of the complexes.31 The vibrations of \(\nu_{\text{COO}}\) (COO$^-$) and \(\nu_{\text{COO}}\) (COO$^2$) are at 1608.56 and 1562.56 cm$^{-1}$ and 1416.99 and 1331.53 cm$^{-1}$, respectively, for 1, which show that CAM plays an important role in both monodentate and bidentate motifs.32 The results of FT-IR spectra are consistent with those of X-ray single-crystal analysis. Thermogravimetric analyses were measured to determine divergent temperatures of solvent molecules in pores for thermal stabilities of 1, and the result was carried out from 25 to 800 °C (Figure S3). For 1, the first weight loss of 13.1% in the range of 50–100 °C, consistent with the corresponding calculated value of 12.02%, is due to the loss of hydrogen. The second weight loss above 100 °C is attributed to the
decomposition of 1. Similar phenomena have been reported.33 The samples were heated for 8 h at different temperatures, and the corresponding PXRD diagrams were determined. As shown in Figure S4, when heated above 160 °C, all coordination water molecules are removed and the framework collapses.

3.2. Crystal Structure Description. The structure of 1 was characterized by X-ray single-crystal diffraction analysis. Crystallographic data is given in Table S1. Table S2 lists the main bond lengths and angles. When we studied H$_2$CDA and Ni/Tb metal ions, an isomorphous 1 was isolated. The results
of the single-crystal structure show that 1 is a trigonal crystal system (space group R3) and is found to be an extended 2D CP, with Ni1II and Tb1III centers within the asymmetric units.

In 1, an elementary entity contains two Tb1III ions, three Ni1II ions, six partly deprotonated HCAM2– ligands, and a dozen end-coordinated water molecules (O6 and O7). The coordination around the Ni1II center may be best described as a bit twisted octahedron, with double oxygen atoms O(2)s from the carboxyl groups, and the Ni–O bond length was 2.023(3) Å; the bond lengths of other four oxygen atoms O(7)s and O(6)s of H2O and Ni–O were 2.031(4) and 2.052(3) Å, respectively, as depicted in Figure 1a. The Tb1III ion in the structure is nine-coordinated TbN3O6 with three nitrogen atoms N(1)s were from the pyridyl ring, and the Tb–N bond length was 2.495(3) Å. The bond angles of O–Tb–O ranged between 77.43(10)° and 147.03(8)°, and those of O–Tb–N ranged between 63.19(9)° and 140.04(9)°, which are within the range of H2O, CaM polymers for intramolecular ferromagnetic phenomena and/or fluorescence properties. One HCAM2– ligand connects one Tb1III ion and one Ni1II ion. Each Tb1III ion was coordinated by three HCAM2– ligands. One-dimensional zigzag chains were linked by HCAM2– ligands and Ni1II and Tb1III ions (Figure 1b).

The carboxyl groups are connected to Ni1II ions in the adjacent one-dimensional zigzag chain to form a two-dimensional surface, which is characterized by the Tb1III···Ni1II cycle, with Tb···Ni, Tb···Tb, and Ni···Ni distances (5.624, 11.250, and 7.166 Å, respectively) in the cycle, as shown in Figure 1c.

The coordination mode of HCAM2– can be found in Scheme 1b. The HCAM2– tetradentate ligand connects two metal centers (Tb1III/Ni1II). One HCAM2– links one Tb1III ion by O(1), O(3), and N(1), while O(2) from the carboxyl group bonded to Ni1I in 1. The shortest Tb1III···Ni1II distance through the HCAM2– anion is 5.624 Å

3.3. Fluorescence Characteristics of 1. Aromatic compounds and the complexes have attracted attention due to their unique fluorescence properties. Characteristic emission peaks for the free ligand H2CAM appear at approximately 442 and 470 nm, which are due to π*–π and/or π*–π transitions, as shown in Figure S5. Figure 2 shows that emission spectra of Tb1III ions in H2O are very weak.

Figure 2. FL spectra in the solution state in aqueous solution. λex = 280 nm: 1, Tb(NO3)3; 2, CP 1. Conditions: Tb(NO3)3, 1.0 × 10−3 M; CP 1, 1.0 × 10−3 M.

Compared with Tb1III ions, 1 shows strong emission bands with λem = 280 nm. This result indicates that intramolecular energy is transferred from H2CAM to Tb1III. Characteristic emission peaks of Tb1III appear at 488, 546, 584, and 624 nm, which are assigned to 5D4 → 7F5, 5D4 → 7F4, 5D4 → 7F3, and 5D4 → 7F2, respectively. Due to the coordination effect in 1, energy transfer is more likely to occur, which greatly reduces the loss of nonradioactive energy, which can increase the flow strength of Tb1III by several times; therefore, the fluorescence efficiency of Tb1III increases several times.

The stability of CP 1 was studied with the sample soaked in aqueous solution for 12 h, filtered, and dried in a vacuum oven. The samples are characterized by XRD patterns (Figure 3a); PXRD patterns of the desolvated 1 suspended in aqueous solution are in good agreement with the calculation graph from the single-crystal data. The results show that the 2D frame of 1 is stable in H2O. On the other hand, as shown in Figure 3b, the strength of the characteristic peaks at ≈546 nm is almost unchanged, indicating that 1 can maintain good fluorescence stability within 12 h, so CP 1 could be used as a polymer for fluorescence detection in H2O solution.

3.4. Effect of HSA on 1 Fluorescence Spectra. In this work, 1 was used as a fluorescent probe to detect common biological reagents. The specific experimental method is that the crystal material of 1 is ground into a powder sample and prepared into a suspension under physiological conditions. The fluorescence spectrum is then tested immediately with a biological reagent solution containing HSA. As shown in Figure 4A, when combined with other biomolecules, the emission spectrum of 1 has little or very weak change, and the results show that probe 1 can selectively detect HSA. As a fluorescent reagent, the strongest emission peak of 1 is at ≈546 nm in an excited wavelength of 280 nm. Figure 4B shows the effect of [HSA] on the fluorescence of 1. As the concentration of HSA increased, the emission intensity of 1 increased gradually, and no shift in emission wavelength was detected. The insertion of chromophores into HSA makes the conjugate structure of chromophores more stable and reduces the rotation of fluorescent groups, thus limiting the vibration inactivation, which is regarded as an important reason for fluorescence enhancement of 1. Figure 4C shows the luminescence intensity of linear enhancement with [HSA] from 3.0 to 9.0 μM. Figure 4D shows the influence of [HSA]...
on the luminescence intensity of I, according to the formula \( I_0/I = 1 + K_{sv}[\text{HSA}] \), where \( I \) and \( I_0 \) are the fluorescence intensity after and before adding HSA, respectively, \([\text{HSA}]\) is the concentration of HSA, and \( K_{sv} \) is the rate constant; the value of \( K_{sv} \) is \( 7.68 \times 10^4 \text{ M}^{-1} \), which indicates that the effect of HSA on the fluorescence intensity of I is relatively strong. The fluorescence detection limit of the reaction was calculated (detection limit = \( 3\sigma/k \)), and its value was \( 0.14 \pm 0.016 \mu\text{M} \) (\( S/N = 3 \)). The results show that I can be used as a fluorescent probe for identifying and detecting HSA. However, this bioprobe gave a detection limit that is lower than the reported detection limit of HSA (as low as 8.6 nM). As far as we are concerned, little work has been done to identify and detect HSA using polymers as fluorescent probes, in particular “turn on” effect on the luminescence intensity.

Figure 3. (a) PXRD patterns of I (black, calculated; red, experimental; blue, 12 h after immersion in water). (b) Fluorescence spectra of I after soaking in water for 0 and 12 h.

Figure 4. (A) Luminous intensity of I upon the addition of different biological interferents at 546 nm. [I] = \( 10^{-4} \text{ M} \); [biological interferents] = 10 \( \mu\text{M} \). (B) Luminescence spectra of I in different [HSA] solutions. (C) Comparison of luminous intensity of I under different [HSA] solutions. (D) \( I_0/I \) vs [HSA] plot.
We also studied the detection of HSA in the presence of various biological interferents (Figure S6). The test conditions were that the total concentration of HSA was 12 μM and that of biological interferents was 48 μM. The results showed that HSA on 1 still had a significant “turn on” luminescence effect in the presence of 16 biological interfering agents, indicating that the detection of 1 to HSA was not interfered by other biological substances, such as BSA, CT DNA, l-histidine, etc.

3.5. Effect of 1 on HSA Fluorescence. Tryptophan and tyrosine are amino acids related to the fluorescence of HSA. Both tryptophan and tyrosine emit fluorescence at 280 nm. However, only tryptophan emits fluorescence at 293 nm. Figure 5 shows the effect of 1 on HSA fluorescence. With the increase of [1], the fluorescence intensity of HSA (55% at λex = 280 nm; 78% at λex = 293 nm) increased steadily, accompanied by blue shifts of 5 and 4 nm, indicating that tryptophan and tyrosine were involved in the 1−HSA interaction process. This may be a result of the interaction between the ligand and the rigid aryl group.

To further understand the fluorescence enhancement nature of the 1−HSA system, the fluorescence data at 273 and 298 K were analyzed by Stern−Volmer equation:47,48

\[
\frac{I_0}{I} = 1 + K_{sv}[1] = 1 + k_q \tau_0[1],
\]

\[\tau_0 = 3.53 \times 10^{-9} \text{s}\] (Figure 6). The values of \(K_{sv}\) and \(k_q\) are listed in Table 1 according to the Stern−Volmer curves of \(I_0/I\) versus [1] at two temperatures. The data show that there is a significant difference in the value of \(K_{sv}\) under two wavelengths of excitation, indicating that Tyr residues participate in the interaction between HSA and 1. The obtained \(k_q\) values (≈10^13 M^-1 s^-1) is much higher than the maximum diffusion collision rate and biopolymer (≈2.0 × 10^10 M^-1 s^-1),49 indicating that fluorescence enhancement between HSA and 1 is likely to occur via a static mechanism.

The concentration effect of 1 on the structure of HSA protein was performed by circular dichroism (CD). The CD spectrum of HSA consists of two negative bands in the far UV region and is used to study the characteristics of the protein α-helix structure. Figure 7 shows that the two negative bands at 211 and 223 nm were observed to decrease steadily and in the presence of shift in CDmax, indicating that fluorescence enhancement between HSA and 1 is likely to occur via a static mechanism.

Figure 5. Fluorescence spectra of HSA (6 μM) with 0.0, 1.0, 1.5, 2.4, 3.0, 3.4, and 3.8 μM 1 (curves 1−7) at (A) λex = 280 nm and (B) λex = 293 nm at 298 K.

Figure 6. Fluorescence Stern−Volmer plots of 1−HSA at 273 and 298 K (λex = 280 and 293 nm).

Figure 7. CD spectra of 1.2 μM HSA with 0.0 μM 1 (black), 2.4 μM 1 (red), 4.8 μM 1 (green), and 7.2 μM 1 (blue) at 298 K.

Table 1. Thermodynamic and Bonding Parameters of 1−HSA Interaction at 273 and 298 K

| \(\lambda_{ex}\) (nm) | \(T\) (K) | \(10^{13} k_q (M^{-1} s^{-1})\) | \(10^3 K_{sv} (M^{-1})\) | \(R^a\) |
|-------------------|---------|-------------------------------|---------------------|-------|
| 293 | 298 | 2.61 | 0.923 | 0.998 |
| 293 | 298 | 3.51 | 1.24 | 0.994 |
| 280 | 273 | 3.17 | 1.12 | 0.996 |
| 293 | 273 | 3.88 | 1.37 | 0.997 |

\(^a\)R is the linear correlation coefficient.
In order to investigate the changes of HSA protein structure, the UV absorption spectrum of HSA was determined at different amounts of 1. Figure 8 shows that there is an absorption peak at 220 nm assigned to the $n \rightarrow \pi^*$ transition and that at 280 nm is attributed to the $\pi \rightarrow \pi^*$ transition of aromatic rings in aromatic amino acids. The absorption of HSA at 220 nm decreases and redshifts (6.2 nm) with the addition of 1. This may be due to the specific interaction between 1 and HSA, which destroys the $\alpha$-helix structure. At the same time, the absorption intensity at 280 nm did not change, indicating that there was no $\pi \rightarrow \pi$ interaction between 1 and HSA. Excluding the $\pi \rightarrow \pi$ stacking interaction between 1 and proteins, hydrogen bonding played a major role in the $1 \cdots$ HSA interaction because the carboxyl groups, phenolic hydroxyl groups, and coordination $\text{H}_2\text{O}$ existed in the 2D polymer. In addition, van der Waals forces were also involved.

3.6. Fluorescence Effect of $\text{MnO}_4^-$ on 1. To solve the environmental problems of water pollution, people showed a great interest in the specific detection of various pollutants in effluent. Due to the widespread application of $\text{MnO}_4^-$ in the industry and research experiments, it has caused water pollution; the new material for detecting $\text{MnO}_4^-$ has become a new research hotspot, so we have also studied the fluorescence reaction of different anions (10$^{-4}$ M) such as $\text{OH}^-$, $\text{Cl}^-$, $\text{Br}^-$, $\Gamma$, $\text{SO}_4^{2-}$, $\text{SO}_3^{2-}$, $\text{SCN}^-$, $\text{Ac}^-$, $\text{HCO}_3^-$, and $\text{CO}_3^{2-}$.

Figure 9a shows that only the $\text{MnO}_4^-$ ion exhibited obvious fluorescence quenching, while other anions had minor effects. In addition, in order to explore the fluorescence effect of 1 as a $\text{MnO}_4^-$ probe, the liquid luminescence spectrum of 1 was studied at different concentrations (25–150 $\mu$M) of $\text{MnO}_4^-$, as shown in Figure 9b. The data show that the fluorescence intensity of 1 decreases linearly with increasing $[\text{MnO}_4^-]$ in the range of 25 to 150 $\mu$M, as shown in Figure 9c. Further studying the correlation between quenching results and $[\text{MnO}_4^-]$, the graph of $I_0/I$ versus $\text{MnO}_4^-$ concentration...
should be based on the formula \( I_0/I = 1 + K_{sv}[\text{MnO}_4^-] \). In Figure 9d, a fine linear relation is showed \((R = 0.99259)\). According to the above equation, the value of \( K_{sv} \) can be calculated by the slope as \( 5.4 \times 10^3 \text{ L/mol}^{-1} \), indicating that \( \text{MnO}_4^- \) has a high fluorescence quenching efficiency during fluorescence emission of \( I \). The detection limit of \( I \) as a fluorescent chemosensor for \( \text{MnO}_4^- \) was calculated; the value was determined to be \( 0.29 \pm 0.04 \mu M \) \((S/N = 3)\). A high quenching efficiency and a low detection limit indicate that \( I \) can be used as a luminescent probe to detect \( \text{MnO}_4^- \). We also explored the detection of \( \text{MnO}_4^- \) in the presence of several mixed anions (Figure S7). The experimental conditions were that the total concentration of \( \text{MnO}_4^- \) was \( 9 \times 10^{-4} \text{ M} \) and that of anions was \( 3 \times 10^{-3} \text{ M} \). The results indicated that \( \text{MnO}_4^- \) had a significant “turn off” effect on fluorescence intensity and that the \( \text{MnO}_4^- \) anion could be selectively detected by \( I \) from anions such as \( \text{OH}^- \), \( \text{Cl}^- \), \( \text{Br}^- \), \( \Gamma \), \( \text{SO}_4^{2-} \), \( \text{SO}_3^{2-} \), \( \text{SCN}^- \), \( \text{Ac}^- \), \( \text{HCO}_3^- \), and \( \text{CO}_3^{2-} \) and was not affected.

We tried to explore the mechanism of fluorescence detection as follows: (1) The PXRD pattern of \( I \) is consistent with that calculated by single-crystal X-ray analysis, which indicates that the two-dimensional structure of \( I \) is stable (Figure 10a). (2) In the infrared spectrum of \( 1-\text{MnO}_4^- \), the characteristic peak of \( \text{MnO}_4^- \) at \( 892 \text{ cm}^{-1} \) indicates the existence of \( \text{MnO}_4^- \) in the two-dimensional structure of \( I \). In addition, the color of the solid sample after immersion in \( \text{KMnO}_4 \) aqueous solution was observed to have changed in both UV and ordinary light, which also confirmed that \( \text{MnO}_4^- \) was diffused into the two-dimensional structure of \( I \) (Figure 10b). (3) The EDS spectrum also supported the presence of Mn on \( I \) immersed in \( \text{KMnO}_4 \) solutions for 24 h (Figure 11). (4) Only the fluorescence intensity has changed (no bandshift) (Figure S8). In summary, \( I \) can selectively detect \( \text{MnO}_4^- \) ions by fluorescence quenching mechanism “turn off” effect. It is generally believed that when the added analyte spreads to the microporous frame of the polymer, it effectively absorbs the energy of the excited state of the excitation light and/or organic connectors, while upon reducing energy transfer to \( \text{Tb}^{III} \), the polymer’s luminous radiation will be greatly reduced.52−54 The reported polymer as a fluorescent probe for the specific detection of \( \text{MnO}_4^- \) ion contaminants is still rare. Among them is \{[\text{Ba}_3\text{La}_0.5(L_3)_2.5(\text{H}_2\text{O})_3(\text{DMF})]_n \} \_x \ (L = p\text{-terphenyl-3,4','5-tricarboxylic acid; DMF = dimethylformamide}) \_x \) with \( K_{sv} = 7.73 \times 10^3 \text{ M}^{-1} \) and detection limit = 0.28 \( \mu M \).55 Another example is tyloxapol with a detection limit of 0.392 \( \mu M \text{MnO}_4^- \).57 Therefore, \( I \) is a

![Figure 10. (a) PXRD patterns for as-synthesized \( I \) (black line); the samples of \( I \) immersed in \( \text{MnO}_4^- (10^{-4} \text{ M}) \) aqueous solutions for 24 h (red line). (b) Color of sample \( I \) dipped in \( \text{KMnO}_4 \) solution using normal light and UV lamp.](image-url)

![Figure 11. Elemental analysis by EDS of \( I-\text{MnO}_4^- \).](image-url)
rare example of a new type of luminescent probe for detecting MnO₄⁻ in aqueous solution.

4. CONCLUSIONS

In this work, we used a one-pot hydrothermal synthetic method to synthesize a two-dimensional TbⅢ/NiⅡ metal-based CP as a good candidate for neutrality sensing because the ligand moiety is a π-conjugated and water-soluble/stable fluorophore. An investigation of sensing properties reveals that CPs can be used as a fluorescent detector to detect MnO₄⁻ ions in water. Moreover, it can discriminately detect HSA in aqueous media through the “turn-on” fluorescence process. The difference in the response of CPs to HSA and BSA indicates that the probe has certain selectivity and can specifically detect these two similar proteins. As far as we know, this is a rare CP based on TbⅢ/NiⅡ as a multiresponse fluorescent detector for MnO₄⁻ and HSA. Under physiological conditions, the binding properties of 1–HSA were comprehensively studied, and the results showed that a static mechanism is involved in a specific interaction between HSA and CPs. CD and UV analyses show that the α-helix content of HSA is reduced and its structure is destroyed.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b03326.

Crystal data and structure refinements and selected bond lengths and angles for CP 1, simulated powder X-ray diffraction patterns and experimental powder X-ray diffraction patterns of 1, FT-IR spectra for 1 and 1–MnO₄⁻, thermogravimetric curve of 1, PXRD patterns of 1 at different temperatures (120 °C (red line), 160 °C (blue line), 180 °C (orange line)) and the simulated one calculated from the single-crystal structure analysis (black line), excitation spectrum of H₃CAM in the solution state at λex = 280 nm, fluorescence intensity of 1 (green) dispersed in water upon the addition of different biological interferents (red) and subsequent addition of HSA (black), fluorescence intensity of 1 (black) dispersed in water upon the addition of different anions (red) and subsequent addition of MnO₄⁻ (green), and luminescence spectra of 1 under different [MnO₄⁻] solutions (PDF)

X-ray crystal details for 1 (CIF)

Accession Codes
CCDC 1832291 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif by emailing data_request@ccdc.cam.ac.uk or by contacting The Cambridge Crystallographic Data Centre (12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033).

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Notes
The authors declare no competing financial interest.

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