Electronic Supplementary Material (ESI) for Chemical Communications


# Electronic Supplementary Information (ESI)

## $Ag^+$-enhanced fluorescence of lanthanide/nucleotide coordination polymer and $Ag^+$ sensing

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## Experimental section

### 1. Chemicals and reagents

Terbium nitrate (99.99%) was purchased from Baotou Rewin Rare Earth Metal Materials Co., Ltd; Metal salts ($AgNO_3$, NaCl, KCl, $CaCl_2$, $MgCl_2$, $Pb(NO_3)_2$, $CdCl_2$, $FeCl_3$, $FeCl_2$, $NiCl_2$, $CoCl_2$, $MnCl_2$, $CrCl_2$ and $CuCl_2$) were purchased from Sinopharm Chemical Reagent Company. Mercury (II) nitrate was from Beijing Zhongbiao Huawei Technology Company. Mercury (I) nitrate was from Adamas-beta Reagent Company. Adenosine-5'-monophosphate disodium and N-2-Hydroxyethyl piperazine-N'-2-ethanesulfonic acid (HEPES) were obtained from Sangon Biotech (Shanghai) Co., Ltd.; HEPES buffer (100 mM, pH 7.4) was prepared by dissolving appropriate amounts of HEPES in water and adjusting to pH 7.4 with concentrated NaOH. Ultrapure water (18 MΩcm; Milli-Q, Millipore) was used for the preparation of all aqueous solutions. Unless otherwise stated, all chemicals are of analytical reagent grade and were used without further purification.

**2. Instruments**

The morphology of coordination polymer prepared was observed by transmission electron microscopy (TEM) (JEM-2100, Japan). Fluorescence spectra and emission intensity 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 lightpath. The 270-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 fluorescent intensities at 545nm were recorded under different delay times and fitted with an exponential function. UV-visible absorption spectra were recorded with a UV-3150 spectrophotometer (Shimadzu, Japan) at room temperature. Fourier Transform infrared spectra (FTIR) were recorded with Avatar 360 FTIR spectrometer (Nicolet, USA). All the experiments were performed at room temperature.

**3. Preparation of nucleotide/lanthanide coordination polymer**

The nucleotide/lanthanide coordination polymer was prepared as the previous method [1]. Typically, l mL of $Tb(NO_3)_3$ aqueous solution (10 mM) was added to 1 mL of AMP disodium salt solution (10 mM) which was dissolved in HEPES buffer (100 mM, pH 7.4), white precipitate was formed immediately. After stirring 3 h at room temperature, the white precipitate was collected by centrifugation at 14000 rpm for 10 min. To remove unreacted reactants, the precipitate was washed three times with water. Finally, the precipitate (approximately 0.0172 g in dry) was dispersed in 1 mL of pure water to form a AMP/Tb suspension and stored in 4℃ for the use.

**4. Preparation of test solution and $Ag^+$-induced fluorescence enhancement of AMP/Tb**

10 mM stock solutions of interference ions were prepared by dissolving $AgNO_3$, NaCl, KCl, $CaCl_2$, $MgCl_2$, $Pb(NO_3)_2$, $CdCl_2$, $Hg(NO_3)_2$, $FeCl_3$, $FeCl_2$, $NiCl_2$, $CoCl_2$, $CrCl_2$ and $CuCl_2$ in water, respectively. For the $Ag^+$-induced fluorescence enhancement, different concentrations of $AgNO_3$ solution in the range of 0-100 μM were added to 5 μL of AMP/Tb suspension; the total volume is 100 μL. The mixture was shaken well and standed for 2 min at room temperature before recording

the spectra. For the experiments of selectivity, 1 μL of 10 mM stock solutions of these interference ions were added to 5 μL AMP-Tb suspension, pure water was added to the mixture till the total volume reached to 100 μL, respectively. After reacting for 2 min at room temperature, the fluorescent intensities of these mixtures at 545 nm were measured on the spectrofluorometer at a 270-nm excitation wavelength. For the effect of pH on the fluorescence enhancement, AMP/Tb suspension without and with 80 μM $Ag^+$ were added to HEPES buffer in the pH range of 3.0-11, respectively. The fluorescent intensities of these mixtures at 545 nm were examined after incubating for 30 min at room temperature. The stability of AMP/Tb in aqueous solution was tested by recording the fluorescent intensities of AMP/Tb stored at room temperature for 1-30 days in the absence or presence of 80 μM $Ag^+$.

**5. Detection of $Ag^+$ in water sample**

The crude water samples were filtered through 0.2 μm microfiltration membrane (Whatman) before detection. A series of water samples containing $Ag^+$ were prepared by "spiking" them with standard solutions of $Ag^+$. These water samples were added to 5 μl AMP/Tb solutions, respectively, and incubated for 2 min. The fluorescent intensities at 545 nm were recorded under a 270-nm excitation wavelength.

**References**

[1] R. Nishiyabu, N. Hashimoto, T. Cho, K. Watanabe, T. Yasunaga, A. Endo, K. Kaneko, T. Niidome, M. Murata and C. Adachi, *J. Am. Chem. Soc.* **2009**, *131*, 2151-2158.

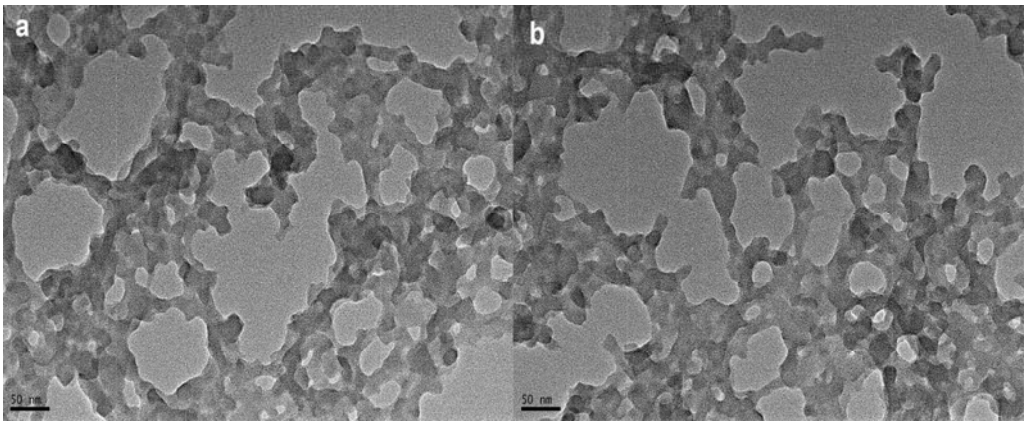


Figure S1. TEM images of AMP/Tb in aqueous solution before (a) and after (b) the addition of

$Ag^{+}$.

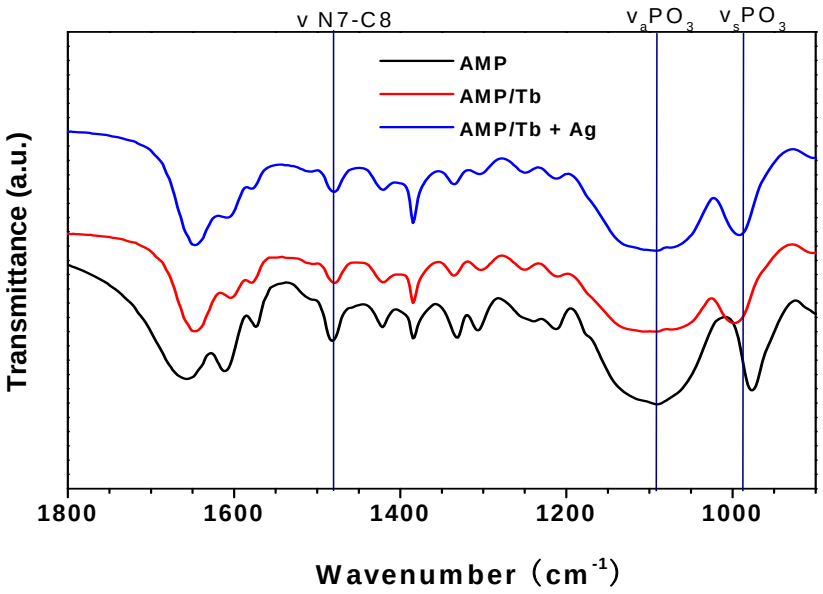


Figure S2. FTIR spectra of AMP, AMP/Tb in the absence and presence of $Ag^{+}$.

For AMP, the C-N stretching vibrations of adenine at 1481 $cm^{-1}$ and two characteristic antisymmetric and symmetric stretching bands associated with the phosphate group at 967 and 1088 $cm^{-1}$, were observed. Upon binding to $Tb^{3+}$, these bands shift to 1478, 996 and 1090 $cm^{-1}$, respectively. The changes of the wavenumbers of phosphate and C-N stretching vibrations of adenine result from the coordination of AMP to Tb. In the presence of $Ag^{+}$, on the other hand, the wavenumbers of C-N stretching vibrations shift from 1478 to 1480 $cm^{-1}$, symmetric and antisymmetric stretching of phosphate shit from 996 to 992 $cm^{-1}$ and from 1090 to 1093 $cm^{-1}$, respectively. These results further confirm that both of phosphate and nucleobase moieties in AMP are involved in the formation of coordination network, and the added $Ag^{+}$ coordinate with the nucleobase.

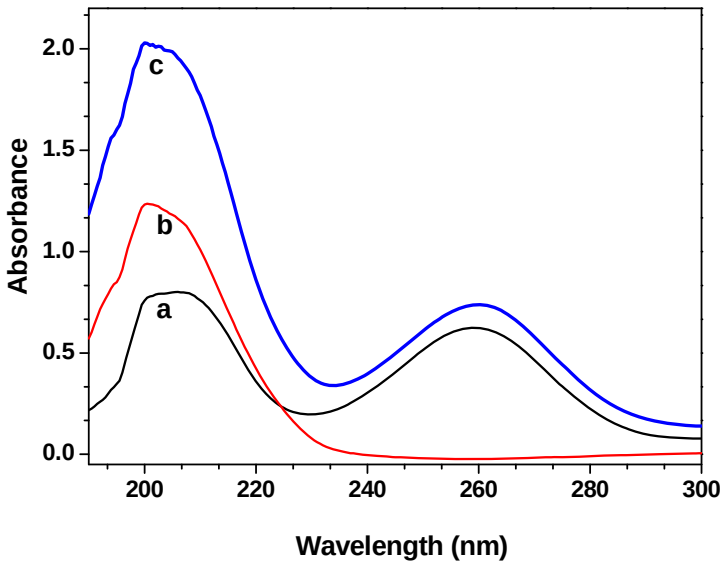


Figure S3. Absorption spectra of (a) AMP/Tb in aqueous solution, (b) 70μM $Ag^+$ solution, (c) AMP/Tb solution containing 70μM $Ag^+$.

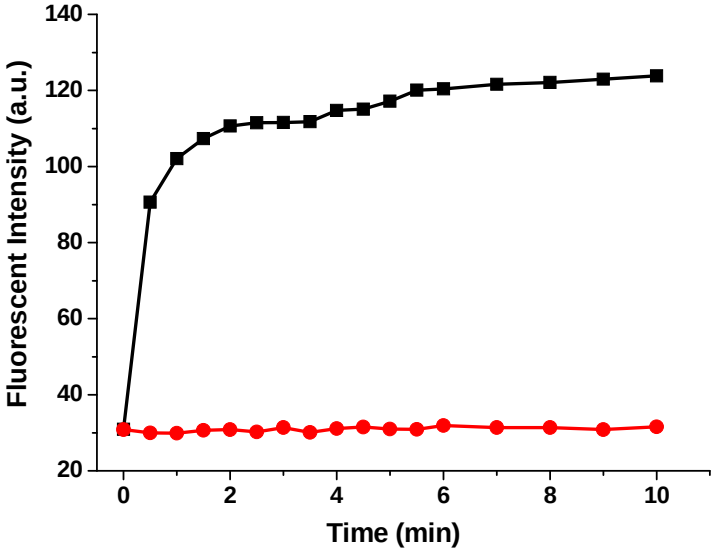


Figure S4. Effect of interaction time on fluorescence intensity of AMP/Tb solution in the absence (red) and presence (black) of 80 μM $Ag^+$. (Ex. 270 nm; Em. 545 nm).

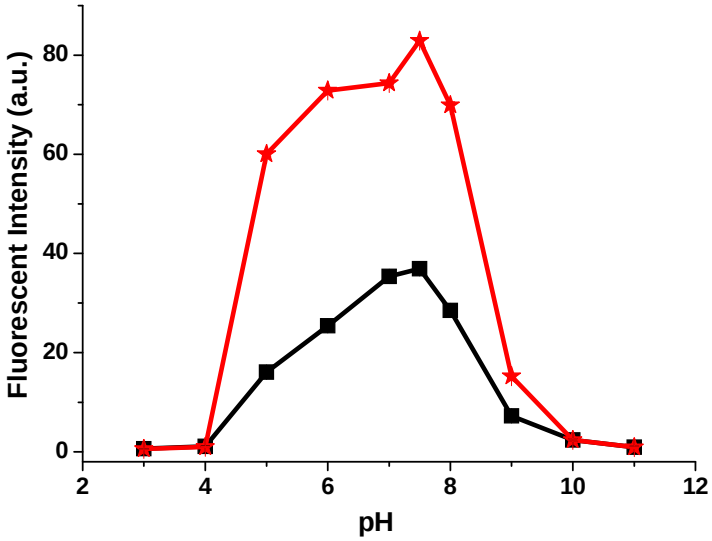


Figure S5. Effect of pH on fluorescent intensity at 545 nm of AMP/Tb (black) and AMP/Tb + 80μM $Ag^{+}$ (red) in 100 mM HEPES buffer.

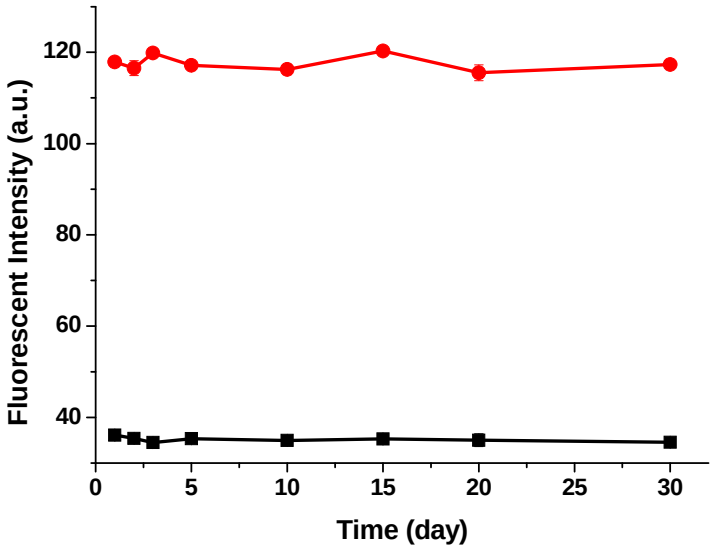


Figure S6. Stability of fluorescent intensity (at 545 nm) of AMP/Tb solution in the absence (black) and presence (red) of 80 μM $Ag^{+}$ in 30 days.

**Table S1.** Determination of $Ag^+$ in water samples

| Sample | Spiked $Ag^+$ (μM) | Detected $Ag^+$ (μM) | Recovery (%) |
|---|---|---|---|
| Lake water 1 | 0 | undetected | N/A |
| Lake water 2 | 0.08 | 0.079 | 99.53 |
| Lake water 3 | 50 | 48.61 | 97.21 |
| Lake water 4 | 100 | 98.59 | 98.59 |
| Tap water 1 | 0 | undetected | N/A |
| Tap water 2 | 0.08 | 0.082 | 102.85 |
| Tap water 3 | 50 | 49.39 | 98.78 |
| Tap water 4 | 100 | 100.08 | 100.08 |