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## ARTICLE

# Photoactive rare earth complexes for fluorescent tuning and sensing cations ( $\text{Fe}^{3+}$ ) and anions ( $\text{Cr}_2\text{O}_7^{2-}$ )

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A series of photoactive rare earth complexes have been synthesized hydrothermally with two kinds of organic ligands, adenine and biphenyl-4,4'-dicarboxylic acid, which is formulated as RE/Ad/BPDC (RE = Y, Eu, Tb, Sm, Dy). The multi-color can be tuned and the fluorescent sensing properties of these materials are studied in details. Especially  $\text{Y}_{0.99}\text{Eu}_{0.01}/\text{Ad}/\text{BPDC}$  system has selective fluorescent quenching effect for  $\text{Fe}^{3+}$  and  $\text{Cr}_2\text{O}_7^{2-}$ .

## Introduction

Coordination compounds, including coordination polymers with repeating coordination entities extending in 1, 2, or 3 dimensions, have attracted much attention for their potentials and advantages as inorganic-organic hybrid materials.<sup>1</sup> The variety of metal ions, organic linkers, and structural motifs affords an essentially infinite number of possible combinations. Up to now, these materials have shown their potential applications in making luminescent thin film,<sup>2</sup> biological imaging,<sup>3</sup> organic light emitting diode,<sup>4</sup> chemical sensors<sup>5</sup> and so on. The luminescent properties of coordination compounds are very sensitive to their structural characteristics, coordination environment, and their interactions with guest species. This endows coordination compounds with inherent advantage in luminescent sensing, especially for the rare earth coordination complexes. However, because of poor light absorption abilities of trivalent rare earth ion, it is difficult to utilize these ions directly although they have sharp emissions, high color purity and relatively long luminescence lifetimes.<sup>6</sup> This problem can be overcome by coupling species that can participate in energy transfer processes, known as "antenna effect".<sup>7</sup> Organic ligands in rare earth coordination complexes can absorb the light and transfer energy to rare earth ions and then luminescence is generated.

Recently, these rare earth coordination compounds have unlimited potentials as chemical sensors, detecting cations,<sup>8</sup> anions,<sup>9</sup> small molecules,<sup>10</sup> pH value<sup>8b,11</sup> and temperature.<sup>12</sup> Among cations, sensing  $\text{Fe}^{3+}$  is a hotlight of this area because that  $\text{Fe}^{3+}$  ion is one of the essential elements for humans and living organisms, involved in biochemical processes and biological systems.<sup>13</sup> It is of great significance in life science, environment and chemistry research. For anions, several articles about sensing of  $\text{Cr}_2\text{O}_7^{2-}$  have been reported<sup>14</sup>. As is known, highly toxic hexavalent chromium ion can lead to respiratory disease, gastrointestinal disease, skin lesions and can cause cancer. Therefore, the identification and quantification of these ions are significantly important.

Among rare earth ions, compounds based on ytterbium ions are often used as matrices for traditional luminescent material, while others, such as  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ ,  $\text{Sm}^{3+}$  and  $\text{Dy}^{3+}$  ions, act as vital activators. Herein, in this study, adenine was chosen as a biomolecular ligand and biphenyl-4,4'-dicarboxylic acid (BPDC) was introduced as an organic ligand together with rare earth ions (RE = Y, Eu, Tb, Sm, Dy) in dimethylformamide (DMF) to yield a series rare earth complexes, RE/Ad/BPDC. As synthesized RE/Ad/BPDC was used to study their luminescence properties which shows the selected ligands could effectively sensitize the luminescence of rare earth ions, especially  $\text{Eu}^{3+}$  ions. Moreover, a series of Eu-functionalized material ( $\text{Y}_{1-x}\text{Eu}_x/\text{Ad}/\text{BPDC}$ ) was selected to detect sensing properties. Particularly,  $\text{Y}_{0.99}\text{Eu}_{0.01}/\text{Ad}/\text{BPDC}$  has selective fluorescent quenching effect for  $\text{Fe}^{3+}$  and  $\text{Cr}_2\text{O}_7^{2-}$ .

## Experimental section

**Chemicals.** Chemicals were purchased from commercial sources. All solvent were analytical grade and without further purification.  $\text{RE}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ , adenine, biphenyl-4,4'-dicarboxylic acid and N, N-Dimethylformamide (DMF) were used to synthesize ternary rare earth complexes.  $\text{RE}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  (RE = Y, Eu, Tb, Sm and Dy) were obtained by dissolving corresponding oxide in nitric acid, followed by evaporation and vacuum drying. Adenine (Adamas-beta) and biphenyl-4,4'-dicarboxylic acid (Adamas-beta) were used as received. Ultrapure water and ethanol were used throughout all experiment.

**Synthesis of rare earth complexes with adenine and biphenyl-4,4-dicarboxylic acid.** Adenine (0.125 mmol), biphenyl-4,4-dicarboxylic acid (BPDC) (0.125 mmol),  $\text{RE}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  (0.125 mmol), DMF (13.5 mL), and water (1 mL) were added to a Teflon-lined autoclave, heated at 150 °C for 24 h, and then cooled to room temperature naturally. The material was collected, washed with DMF (5 mL  $\times$  3), and dried under vacuum (24 h). Elemental analysis data: Anal (%) for  $\text{C}_{19}\text{H}_{18}\text{O}_6\text{NY}$ : C 51.09, H 3.91, N 3.03; Calcd (%) for  $\text{C}_{19}\text{H}_{18}\text{O}_6\text{NEu}$ : C 45.05, H 3.37, N 2.55;

Calcd (%): C 44.89, H 3.57, N 2.76. Anal (%) for  $C_{19}H_{18}O_6NSm$ : C 45.20, H 3.40, N 2.56; Calcd (%): C 45.04, H 3.58, N 2.76. Anal (%) for  $C_{19}H_{18}O_6NTb$ : C 44.15, H 3.39, N 2.50; Calcd (%): C 44.29, H 3.52, N 2.72. Anal (%) for  $C_{19}H_{18}O_6NDy$ : C 44.11, H 3.35, N 2.57; Calcd (%): C 43.98, H 3.50, N 2.70. The above data suggest the composition of these lanthanide coordination polymers are predicted to be  $RE(Ad)(BPDC)\cdot 2H_2O$  ( $RE/Ad/BPDC$ , Ad = adeninate, BPDC = biphenyl-4,4'-dicarboxylate).

**Synthesis of mixed rare earth complexes with adenine and biphenyl-4,4'-dicarboxylic acid.** Take an example of  $Y_{1-x}Eu_x/Ad/BPDC$  to illuminate how to produce mixed rare earth complexes. The mixed rare earth materials could be readily synthesized by varying the original molar ratios of  $Eu(NO_3)_3\cdot xH_2O$  to  $Y(NO_3)_3\cdot xH_2O$  through the same synthetic procedures. All the materials are denoted as corresponding rare earth elements.

**Physical characterization.** Fourier transform infrared spectra (FTIR) were measured with KBr pellets from 4000 to 400  $cm^{-1}$  using a Nexus 912AO446 infrared spectrum radiometer. X-ray powder diffraction patterns (XRD) were collected using a Bruker Focus D8 at 40 kV, 40 mA for Cu-K $\alpha$  with a scan speed of 0.30 sec/step and a step size of 0.02  $^\circ$ ; the data were collected within 2 $\theta$  range of 3-50  $^\circ$ . Scanning electron microscope (SEM) images were obtained with a Hitachi S-4800.

**Luminescent measurements.** The luminescence spectra were recorded on an Edinburgh FL920 phosphorimeter using a 450W xenon lamp as excitation source. The outer luminescent quantum efficiency was determined using an integrating sphere from Edinburgh FLS920 phosphorimeter.

**Sensing.**<sup>15</sup> We detected  $Y_{0.99}Eu_{0.01}/Ad/BPDC$  sensing of metal ions and anion ions aqueous solution. The suspensions of samples were prepared by introducing each sample (5 mg) as a powder into different solvents (3.0 mL) and then were vigorously agitated using ultrasound. Aqueous solutions of  $Al^{3+}$ ,  $Cd^{2+}$ ,  $Cu^{2+}$ ,  $Co^{2+}$ ,  $Mn^{2+}$ ,  $Ni^{2+}$ ,  $Hg^{2+}$ ,  $Fe^{3+}$  were prepared from chlorate salts;  $Ag^+$ ,  $Cr^{3+}$ ,  $Pb^{2+}$  were prepared from nitrate salts. The material was immersed in various metal ions aqueous solution for luminescence studies, which concentrations were all controlled of  $1.0\times 10^{-2}$  M. The same concentration was controlled when detecting anion sensing. Aqueous solutions of  $NO_3^-$ ,  $Br^-$ ,  $Cl^-$ ,  $F^-$ ,  $I^-$ ,  $CrO_4^{2-}$ ,  $Cr_2O_7^{2-}$  were prepared from potassium salts and  $SO_4^{2-}$  was from sodium salt.

**Stern–Volmer equation:**

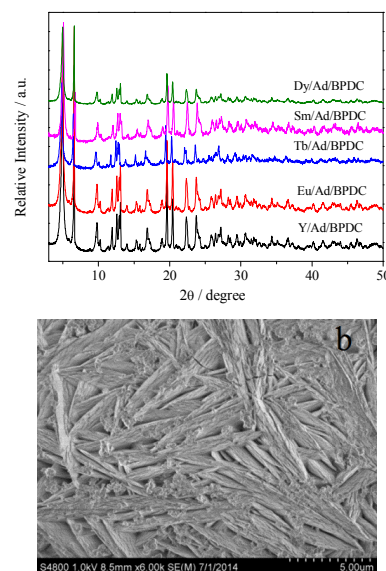
$$\frac{I_0}{I} = 1 + K_{SV} [M]$$

$I_0$  and  $I$  are the fluorescent intensity before and after the incorporation of metal ion, respectively.  $[M]$  is molar concentration of metal ion.  $K_{SV}$  is the coefficient of quenching. The reduction of fluorescent intensity is proportional to ion concentration.  $K_{SV}$  can be calculated via fluorescent data.<sup>16</sup>

## Results and discussion

A series of isostructural rare earth complexes,  $RE/Ad/BPDC$  (Ad = adenine; RE = Y, Eu, Tb, Sm, Dy; BPDC = biphenyl-4,4'-dicarboxylic acid) were hydrothermally synthesized by the reaction of adenine and BPDC with  $Ln(NO_3)_3$  at 150  $^\circ C$  for 24 h. As is

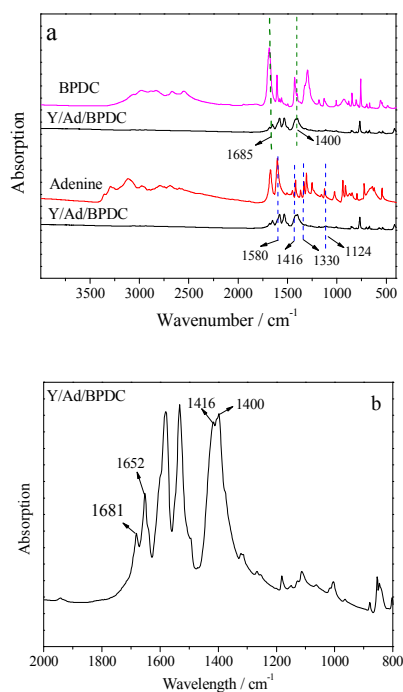
reported by Rosi's group<sup>17</sup>, adenine is one of nucleobases that constitute nucleic acids. The characteristics of adenine includes that it is rigid, has accessible nitrogen and oxygen electron lone pairs and has multiple possible metal binding modes, making it an ideal building block for constructing metal-organic complexes.<sup>18</sup> Besides, the aromatic polycarboxylates in conjunction with rare earth metals which possess high and variable coordination numbers and flexible coordination geometries, leading to the formation of the exotic molecular architectures.<sup>19</sup> In the view of these advantages, adenine and biphenyl-4,4'-dicarboxylic acid were selected as the ligands. The X-ray diffraction patterns (Figure 1a) and corresponding FT-IR spectroscopy (Figure S2) suggest that this series materials are isostructural. Unlike transition metal ions, rare earth ions have similar ionic radius and coordinate environment. In a result, the XRD spectra will show similarity between each material.<sup>20</sup> The morphology of Y is shaped like leaf with the dimension in the range of 5 $\mu m$  from SEM image (Figure 1b). The X-ray diffraction patterns of above ternary yttrium complex and binary Y complex of BPDC (Figure S3) are totally different from each other which can prove the coordinative role adenine played in these complexes.



**Figure 1** PXRD pattern of  $RE/Ad/BPDC$  materials (a) and SEM image of  $RE/Ad/BPDC$  (b)

To discern the coordination interaction between  $RE/Ad/BPDC$ , adenine (Figure S1a) and BPDC (Figure S1b), an FT-IR analysis is conducted in Figure 2. Shifts in wavenumbers of C4N9 stretching vibrations ( $1418\text{ cm}^{-1}$  shifts to  $1416\text{ cm}^{-1}$ ) and ring stretching vibrations ( $1603\text{ cm}^{-1}$  shifted to  $1580\text{ cm}^{-1}$ ) of adenine are observed while the C2N3 stretching vibrations, C5N7 stretching vibrations and N9H deformation vibrations disappear. All of these suggest coordination interactions between rare earth ions and adenine, which indicating that adenine could offer multiple metal-binding sites for the coordination of rare earth ions. In addition, by comparison to BPDC, three characteristic peaks of benzene ring stretching vibrations ( $1600\sim 1500\text{ cm}^{-1}$ ) remain after reaction. The asymmetric vibrations ( $1685\text{ cm}^{-1}$ ) of carboxylate ions and its symmetric vibrations ( $1427\text{ cm}^{-1}$ ) have changed simultaneously, proving the

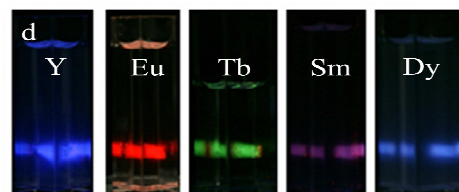
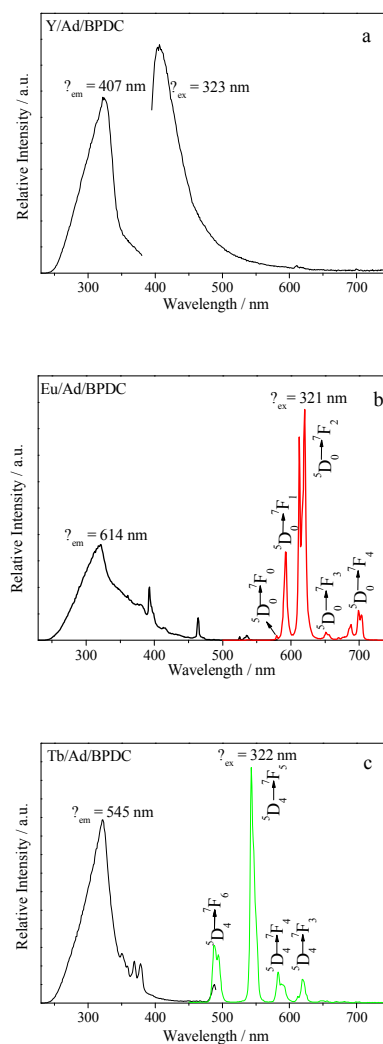
carboxyl groups have coordinated with rare earth ions successfully.<sup>21</sup> Details of wave numbers of FT-IR are listed in Table S1. The inferred structure of these series rare earth complexes is shown in Figure S4.



**Figure 2** (a) FT-IR spectra of adenine, BPDC and RE/Ad/BPDC, (b) the enlarged view of (a) from 2000 to 800  $\text{cm}^{-1}$

The emission and excitation spectra of adenine, BPDC ligands and RE/Ad/BPDC measured at room temperature for the powder samples (Figure S5 and Figure 3). The free BPDC ligand exhibits excitation at 335 nm and emission at 412 nm which is presumably due to  $\pi \rightarrow \pi^*$  electron transitions while the excitation and emission of adenine are 346 nm and 411 nm respectively (Figure S5). The emission of Y is at 407 nm, under the excitation at 323 nm (Figure 3a). The emission of Eu exhibits very strong characteristic transitions ( ${}^5D_0 \rightarrow {}^7F_J, J = 0-4$ ) of  $\text{Eu}^{3+}$  at 594, 614, 650, and 699 nm (Figure 3b), while Tb displays the characteristic transitions ( ${}^5D_4 \rightarrow {}^7F_J, J = 6-3$ ) of  $\text{Tb}^{3+}$  at 491, 545, 585, and 622 nm (Figure 3c). The excitation spectrum of europium compounds is obtained by monitoring the emission wavelength at 614 nm, which is dominated by a broad band centered at about 321 nm and two sharp lines, assigned to the  ${}^7F_0 \rightarrow {}^5D_2$  (at 463 nm) and  ${}^7F_0 \rightarrow {}^5L_6$  (at 394 nm). It indicates the antenna effect<sup>7</sup> occurs, which means that energy migration takes place upon ligand absorption, followed by intersystem crossing  $S_1 \rightarrow T_1$  and antenna  $T_1 \rightarrow f$  transfer, and then generating  $f \rightarrow f$  emissions of  $\text{Eu}^{3+}$  cation. Under the same excitation, Sm exhibits both the blue-shifted emission of the two ligands at about 407 nm and the characteristic transitions ( ${}^4G_{5/2} \rightarrow {}^6H_J, J = 5/2, 7/2, 9/2, 11/2$ ) of  $\text{Sm}^{3+}$  at 561, 596, 644 and 703 nm, respectively (Figure S6). Because of the week emission of  $\text{Sm}^{3+}$ , some disturbing peaks can be observed in the emission spectra, which also exist in dysprosium complex material while excited at 306 nm. The Dy displays its characteristic transitions ( ${}^4F_{9/2} \rightarrow {}^6H_J, J = 15/2, 13/2$ ) at 482, 573 nm

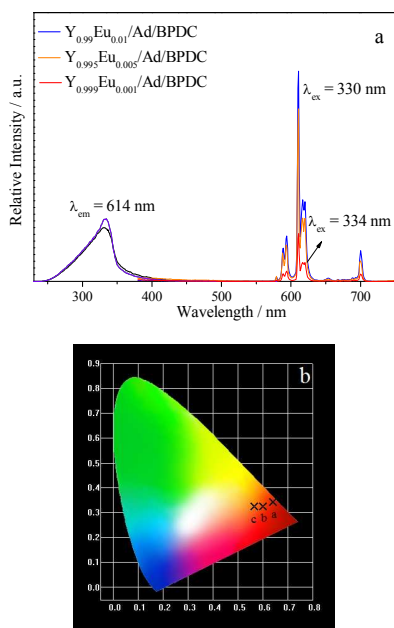
(Figure S7). The other reason for the weak emission is that the selected ligands are not suitable for sensitizing samarium and dysprosium. Under characteristic excitation of each material, various colours can be obtained such as blue for Y, red for Eu, green for Tb, purple for Sm and blue for Dy. (Figure 3d)



**Figure 3** The excitation and emission spectra of Y (a), Eu (b), Tb (c) and the corresponding luminescent pictures under xenon lamp (d)

A series of mixed rare earth compounds were straightforwardly synthesized in which different types of rare earth ions of variable molar ratios can be incorporated into the ytterbium matrices. A small amount of  $\text{Eu}^{3+}$  is doped into Y to achieve  $\text{Y}_{1-x}\text{Eu}_x/\text{Ad}/\text{BPDC}$  for exploring their luminescent properties. In Figure 4a, the intensity of characteristic emission of  $\text{Eu}^{3+}$  ( $\lambda_{\text{ex}} = 330$  nm and 334 nm) is strengthened with increasing the amount of  $\text{Eu}^{3+}$  from 0.01% to 1%, meanwhile the colour of the emission changed from pale red to dark

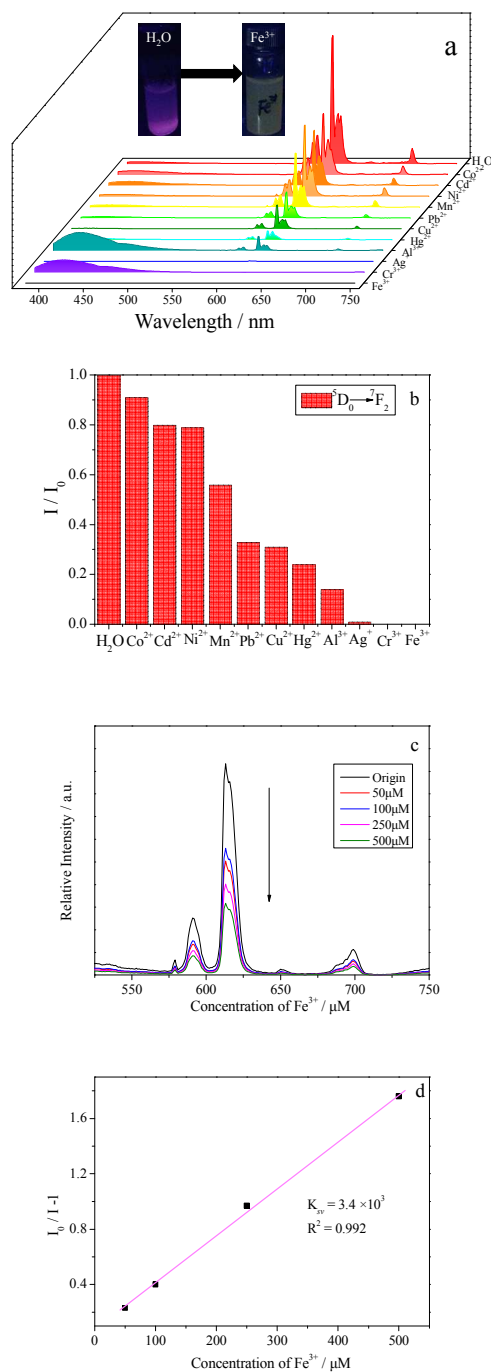
red which could be visually observed in the corresponding CIE chromaticity diagram (Figure 4b). Under excited at 351 or 349 nm which belongs to excitation of adenine and BPDC ligands, the characteristic emission of  $\text{Eu}^{3+}$  also can be observed (Figure S8). This implies that the coordination complexes could effectively sensitize  $\text{Eu}^{3+}$  ion.



**Figure 4** The excitation and emission spectra of  $\text{Y}_{1-x}\text{Eu}_x$  ( $x = 0.01, 0.005$  and  $0.0001$ ) (a) and the CIE chromaticity diagram of  $\text{Y}_{1-x}\text{Eu}_x$ , a for  $\text{Y}_{0.99}\text{Eu}_{0.01}$ , b for  $\text{Y}_{0.995}\text{Eu}_{0.005}$ , c for  $\text{Y}_{0.999}\text{Eu}_{0.001}$  (b).

$\text{Y}_{0.99}\text{Eu}_{0.01}/\text{Ad}/\text{BPDC}$  was selected and suspended in different metal ions aqueous solutions and anions aqueous solutions to examine the potential for sensing of metal ions and anions. The luminescent responses for sensing metal ions including  $\text{Al}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ag}^+$ ,  $\text{Cr}^{3+}$ ,  $\text{Pb}^{2+}$ , are shown in Figure 5a,5b and the quenching coefficient  $K_{sv}$  is shown in Table S2. The results reveal that metal ions show different degrees of quenching effects on the luminescence intensity. The quenching effects of  $\text{Ag}^+$ ,  $\text{Cr}^{3+}$  and  $\text{Fe}^{3+}$  are pronounced, especially the  $\text{Fe}^{3+}$  ions. With quenching effect increasing, the emission intensity at 614 nm is gradually decreasing. Therefore, the emission colours are gradually changing from red to pink under UV light. Specially, unlike other cations,  $\text{Al}^{3+}$  and  $\text{Cr}^{3+}$  only quench the emission of  $\text{Eu}^{3+}$  while the ligand-centered emission around 409 nm remains, which induce the samples' colours in these two solutions are blue under UV light (Figure S9). Differently, the emission colour of  $\text{Fe}^{3+}$  is dark under UV light because it can not only quench the emission of  $\text{Eu}^{3+}$  but also cause the emission of ligands quenched (Figure 5a inset). These results indicate that  $\text{Y}_{0.99}\text{Eu}_{0.01}/\text{Ad}/\text{BPDC}$  can selectively sense  $\text{Fe}^{3+}$ . For better understanding the quenching response of  $\text{Y}_{0.99}\text{Eu}_{0.01}$  to  $\text{Fe}^{3+}$  cations, the sample were suspended in several different concentrations of  $\text{Fe}^{3+}$  aqueous solutions. As demonstrated in Figure 5c, the emission intensity of  $\text{Y}_{0.99}\text{Eu}_{0.01}/\text{Ad}/\text{BPDC}$  declines sharply with the concentration of  $\text{Fe}^{3+}$  increasing from 0 to 0.5 mM. And Figure 5d displays the corresponding  $K_{sv}$  curve with  $\text{Fe}^{3+}$ , the

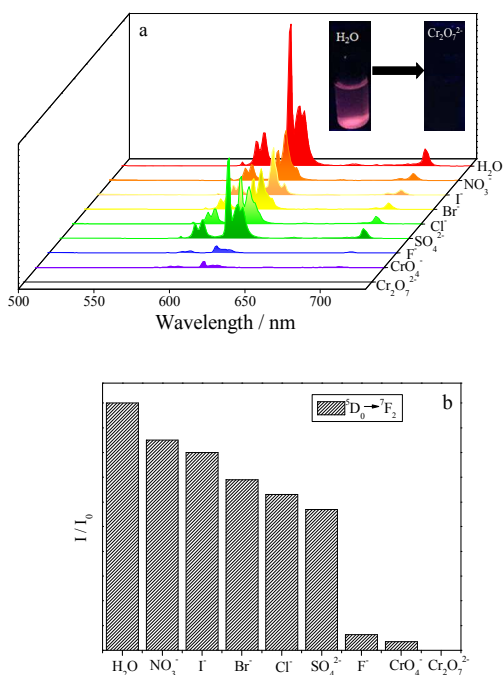
value of which is calculated as  $3.4 \times 10^3$ . The linear correlation coefficients ( $R^2$ ) is 0.992, suggesting the quenching effect of  $\text{Fe}^{3+}$  to  $\text{Y}_{0.99}\text{Eu}_{0.01}/\text{Ad}/\text{BPDC}$  fits the Stern-Volmer model well.



**Figure 5** (a) PL spectra of  $\text{Y}_{0.99}\text{Eu}_{0.01}/\text{Ad}/\text{BPDC}$  dispersed into different metal ions aqueous solutions ( $10^{-2} \text{ mol}\cdot\text{L}^{-1}$ ) when excited at 324 nm and the inset shows the process from the original aqueous to that in the  $\text{Fe}^{3+}$  aqueous solution, the color from red to dark; (b) the luminescent intensity of the  ${}^3\text{D}_0 \rightarrow {}^7\text{F}_2$  transition of  $\text{Y}_{0.99}\text{Eu}_{0.01}/\text{Ad}/\text{BPDC}$  interacting with different metalions; (c) emission spectra of  $\text{Y}_{0.99}\text{Eu}_{0.01}/\text{Ad}/\text{BPDC}$  in various concentrations of  $\text{Fe}^{3+}$  under excitation at 317 nm; (d)  $K_{sv}$  curve between  $I_0/I$  with the concentration of  $\text{Fe}^{3+}$ .

Simultaneously, various anions are selected to carry out the anion-sensing function in aqueous solutions (anion =  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,

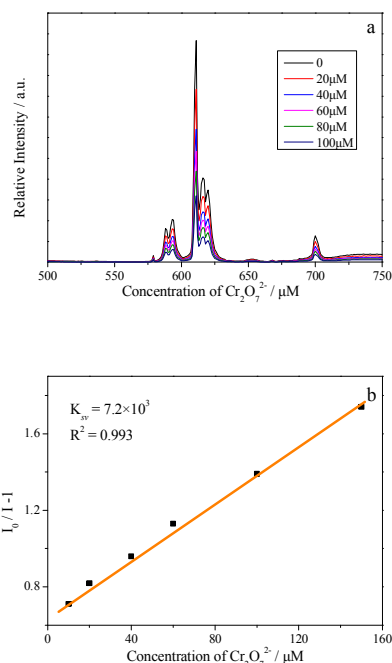
Br<sup>-</sup>, Cl<sup>-</sup>, F<sup>-</sup>, I<sup>-</sup>, CrO<sub>4</sub><sup>2-</sup>, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>). The luminescent measurements illustrate that the difference of anions has a great influence on the luminescent intensity of Y<sub>0.99</sub>Eu<sub>0.01</sub>/Ad/BPDC. The obtained emission spectra and bar diagrams based on the relative emission intensities are depicted in Figure 6a and 6b. To a certain extent, the other anions have a certain effect on Eu<sup>3+</sup> and make the luminescence of Eu<sup>3+</sup> much weaker. Remarkably, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> has the largest quenching effect on the luminescent emission. The inset in Figure 6a shows the colour changing from red in original aqueous to dark in Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> solution under the irradiation of UV light of 365 nm, completely quenching the <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> of Eu<sup>3+</sup>. Quantitatively, the value of K<sub>sv</sub> in Table 1 consists with the phenomenon as well. The colour changes in different anions aqueous under UV-light irradiation at 365 nm are shown in Figure S10.



**Figure 6** (a) PL spectra of Y<sub>0.99</sub>Eu<sub>0.01</sub>/Ad/BPDC dispersed into different anions aqueous solutions (10<sup>-2</sup> mol·L<sup>-1</sup>) when excited at 324 nm, and the inset showing the quenching effect from aqueous to Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, the color from red to dark, (b) the bar diagrams based on the relative emission intensity of <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> transition

**Table 1** Quenching effect coefficients (K<sub>sv</sub>) of different metal ions on the luminescent intensity of anion-incorporated Y<sub>0.99</sub>Eu<sub>0.01</sub>/Ad/BPDC

Anions	K <sub>sv</sub> [mol·L <sup>-1</sup> ]
NO <sub>3</sub> <sup>-</sup>	18
I <sup>-</sup>	25
Br <sup>-</sup>	44
Cl <sup>-</sup>	57
SO <sub>4</sub> <sup>2-</sup>	76
F <sup>-</sup>	1497
CrO <sub>4</sub> <sup>2-</sup>	2738
Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup>	150211



**Figure 7** (a) Concentration-dependent luminescent emission of Y<sub>0.99</sub>Eu<sub>0.01</sub>/Ad/BPDC in the presence of various concentrations of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, (b) the K<sub>sv</sub> curve between I<sub>0</sub>/I with the concentration of dichromate ion.

To study further, we also examined the quenching effect of Y<sub>0.99</sub>Eu<sub>0.01</sub>/Ad/BPDC with various concentrations of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> ranging from 0 – 10<sup>-4</sup> mol·L<sup>-1</sup>. The concentration-dependent luminescence measurements were also carried out. In Figure 7a, the luminescent intensity of Eu<sup>3+</sup> decreases gradually while the concentration of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> increasing. From the K<sub>sv</sub> curve in Figure 7b, it is clearly that when the concentration ranging from 0 to 10<sup>-4</sup> mol·L<sup>-1</sup>, there is a linear relationship between Y<sub>0.99</sub>Eu<sub>0.01</sub>/Ad/BPDC with dichromate ion. K<sub>sv</sub> value is calculated as 7.2×10<sup>3</sup>, displaying a strong quenching effect on the selected sample. Additionally, a good linear relationship can be obtained with the coefficients, 0.993.

## Conclusions

In summary, we have researched a series of photoactive rare earth complexes (RE = Y, Eu, Tb, Sm and Dy) based on two organic ligands including adenine and biphenyl-4,4'-dicarboxylic acid. Luminescence studies reveal that they all belong to the luminescence materials system with broad excitation band in the visible light region. The fluorescence spectra show the characteristic emission of each Ln<sup>3+</sup>, among which the ligands can effectively sensitize the luminescence of Eu<sup>3+</sup>. Furthermore, the mixed rare earth complexes were selected to explore their potential for sensing metal ions and anions. The sample of Y<sub>0.99</sub>Eu<sub>0.01</sub>/Ad/BPDC performs highly selective and sensitive luminescence sensor for Fe<sup>3+</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> and the luminescence in each ion aqueous has quenched immediately from red to dark.

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### Notes and references

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