Supporting information

A Tubular Europium-Organic Framework Exhibiting Selective Sensing of Fe³⁺ and Al³⁺ Upon Mixed Metal Ions

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(1) Experimental Procedures

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. ¹H NMR spectra was measured on a Bruker AVANCE-400 NMR Spectrometer. Elemental analyses (C, H, N) were obtained on a PerkinElmer 240 elemental analyzer. The thermogravimetric analysis (TGA) for 1 was carried out between room temperature and 600 °C in a static N₂ with a heating rate of 10°C/min. Photoluminescence spectra were measured on a Hitachi F-7000 Fluorescence Spectrophotometer. X-ray powder diffractions were measured on a Panalytical X-Pert pro diffractometer with Cu-K α radiation.

(2) Preparation of H4BTMIPA



Scheme 1. Synthesis of H4BTMIPA.

Preparation of H4BTMIPA. Into a 250 ml round bottomed flask fitted with stirrer, thermometer, and reflux condenser were introduced 3.3 g of 91% paraformaldehyde and 25 g of 88% formic acid. The mixture was heated to 80 °C and stirred until the paraformaldehyde was dissolved. To the mixture was rapidly added 36 g of mesitylene, and the mixture was stirred under reflux for 6 hours. On cooling to room temperature, a large amount of colorless crystalline powder formed. The solid was collected by filtration and washed by stirring with 50ml benzene. This slurry of solid in benzene was filtered and sucked dry on a buchner funnel, to obtain the colorless crystals B 22.6 g (60%). ¹H NMR (CDCl3): 6.8 (2H, CH), 4.0(1H, CH2), 2.2 (3H, CH3), 2.1(6H, CH3).

To a mixture of B (18.9 g; 0.075 mol), paraformaldehyde (10.0 g; 0.33 mol), and 50 mL of glacial acetic acid was added 40 mL of a 45 wt% HBr/acetic acid solution rapidly. The mixture was kept for 12 h at 95 °C and then poured into 100 mL of water. The product was filtered off and dried in vacuum, to obtain a white solid C (43 g, 92%). ¹H NMR (CDCl3): 4.6 (4H, CH2), 4.2 (1H, CH2), 2.4 (3H, CH3), 2.1 (6H, CH3).

A mixture of C (2.65 g, 4.16 mmol), anhydrous sodium acetate (2.6 g, 31 mmol), and glacial acetic acid (52 mL) was heated in a sealed tube at 130-140 $^{\circ}$ C overnight. The resulting heterogeneous mixture was cooled to room temperature, transferred to a flask, and the solvent was evaporated to dryness under reduced pressure. The resulting white solid was partitioned between water (100 mL) and CH2Cl2 (100 mL). The separated organic layer was successively washed with a saturated aqueous sodium bicarbonate (100 mL) and water (50 mL). The collected organic layer was dried with anhydrous sodium sulfate and the solvent was evaporated to dryness. The resulting white solid was recrystallized from methanol to give D (1.96 g, 87%) as long white needles. ¹H NMR (CDCl3): 5.2 (4H, CH2), 4.2 (1H, CH2), 2.4 (3H, CH2), 2.2 (3H, CH3), 2.1(6H, CH3).

A mixture of D (1.96 g, 3.6 mmol), and lithium hydroxide hydrate (0.80 g, 19.2 mmol)

in reagent grade ethanol (60 mL) was stirred under reflux overnight. The resulting heterogeneous reaction mixture was cooled to room temperature and evaporated to dryness. The resulting white solid was suspended in cold water (120 mL), filtered, and washed with water (48 mL), dried under heating to 150 $^{\circ}$ C in vacuo to provide E (1.2 g, 90%) as a white solid. ¹H NMR ([*d*6]DMSO): 4.6 (2H, CH₂), 4.4 (4H, CH₂), 4.1 (1H, OH) 2.4 (3H, CH₃), 2.1 (6H, CH₃).

A suspension of E (1.2 g, 3.2 mmol) in reagent grade acetone (50 mL) was treated dropwise with Jones reagent (14 mL, 38.5 mmol CrO₃) at 4 oC. The mixture was stirred for 20 min at 4 °C, 20 min at room temperature, and 5 min at 30 °C.The resulting green heterogeneous mixture was poured into cold water (150 mL) and extracted with diethyl ether (3×50 mL). The combined organic fractions were extracted with water (50 mL), separated, dried with anhydrous sodium sulfate, and the solvent was evaporated under reduced pressure. The resulting gray solid was recrystallized from acetonitrile to afford F as a white solid (0.56 g, 41%). ¹H NMR ([*d*6]DMSO): 13.2 (2H, CO₂H), 4.1(1H, CH₂), 2.2 (3H, CH₃), 2.1(6H, CH₃).

Synthesis of 1. Complex 1 was obtained in a typical procedure. A mixture of Eu(NO3)3•6H2O (0.15 mmol), H4BTMIPA (0.10 mmol), DMF (2 mL), and H2O (3 mL) was placed in a Teflon reactor (20 mL) and heated at 140 °C for three days. The mixture was gradually cooled to room temperature in 600 minutes to obtain crystals suitable for single crystal X-ray structure determination. (Yield: 50%). Elemental analysis (%) for 1: Calcd: C 47.62, H 5.75, N 2.22; Found: C 46.98, H 5.51, N 2.26.

Preparation of the test plate. Referring to the method of the preparation of silica gel plate, an appropriate amount of powder (ca. 20 mg) of 1 was added to a 0.5 ml 0.5% aqueous of carboxymethylcellulose sodium (CMC) and stirred into suspension. The resulting suspension was added dropwise and tiled on a clean glass plate (1.5×4.5 cm2), then dried in air to obtain the test plate.

(3) Crystal structure determination of 1.

Single-crystal X-ray diffraction was performed using a Bruker Apex II CCD diffractometer equipped with a fine-focus sealed-tube X-ray source ($Mo_{K\alpha}$ radiation, graphite monochromated). Structures were solved by direct methods using SHELXTL and were refined by full-matrix least-squares on F^2 using SHELX-97. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles.

Crystal data for 1: C₂₅H₃₆NO₁₂Eu, M = 694.51, monoclinic, a = 8.9760(7) Å, b = 25.7636(19) Å, c = 11.8280(9) Å, $\beta = 90.3230(10)^\circ$, V = 2735.2(4) Å³, T = 298 K, space group P2(1)/n, Z = 4, $\rho=1.6766$ g/cm³, F(000)=1392, $\mu=2.357$ mm⁻¹, 15938 reflection measured, 4802 unique (R_{int}=0.0537), final R₁=0.0366, wR₂=0.0970 for all data. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Center with CCDC Number: 942215 for **1**

(4) The possible mechanism for enhancement and quenching of the emission intensity:

The luminescence enhancement and quenching mechanism may be attributed to the presence of simultaneous dynamic and static process (Figure S8[†]). The dynamic process mechanism was governed by the collisional encounters between the anionic framework and the cations. The static quenching mechanism may be due to the formation of new bonds between the anionic framework and the cations. Considering the channel diameter of complex 1, it is possible for metal ions to exist in the channel steadily. The metal ions may bind to sites on the inner surface of the channels. In the structure of 1, the carboxylic oxygen atoms inside of the channel, the coordinated water molecules located on Eu³⁺, and the water molecules in the channel can create a favorable coordination environment for metal ions. For the dynamic process, the interattraction between the metal ions and anionic framework will make the charge move directionally which strengthen the energy transition from the organic ligands to Eu³⁺. For the static process, The bonding of the metal ions to the organic ligands will

change the energy level of the excited state of ligand, which makes the energy match between the excited states of ligands and Eu³⁺ longer, and results in a less efficient energy transition from the organic ligands to Eu³⁺. For Al³⁺, the dynamic mechanism is in dominant position and result in the fluoresence enhancement. For Fe³⁺, the static mechanism is in dominant position because the interactions between transition-metal ions and organic ligands quench the S1 state of organic ligands by d-d electron transfer of transition-metal ions, annihilating subsequent energy transfer onto the lanthanide ions. ^{S1-S3}

(4) Figure S1: A 1D stitching needle-like ladder in 1



(5) Figure S2: A view of 3D-structure of 1 with hydrogen bonds







Figure S3: Excitation (dashed, $\lambda em = 617$ nm) and emission spectra (solid, $\lambda_{ex} = 395$ nm) of 1, solid sample.

(7)



Figure S4: Comparison of the photoluminescence intensity of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition (617 nm) of 1 at different times for Al³⁺ (a) and Fe³⁺ (b) (10-3 M), and in different concentrations of Al³⁺ (c) and Fe³⁺ (d) one day in dmf solution.

(8) Figure S5: XRD spectrum of 1



Figure S6: IR spectrum of 1



Figure S7: TGA curve of 1. Thermogravimetric analysis (TGA) reveals that complex 1 can be stable up to 235 °C. The first weight loss of 5.2 % from 30 to 70 °C corresponds to the loss of two uncoordinated water molecules (calcd: 5.7%). The second weight loss of 5.2 % from 95 to 165 °C corresponds to the loss of two coordinated water molecules (calcd: 5.7 %). There is no weight loss from 165 to 235 °C, and after 235 °C, 1 starts to decompose.



(9)



Figure S8: After adding different concentrations of acetylacetone (acac) which can chelate the free Al^{3+}/Fe^{3+} ions in emulsions into Eu-DMF emulsions containing 1.0×10^{-3} M Al^{3+}/Fe^{3+} ions, the luminescence intensity is weaked for both of them indicate the enhance effect of dynamic mechanism. The luminescence intensity lower than Eu-MOF without metal ions at last for Al^{3+} and the fluoresence quenching for Fe^{3+} indicate that the the quench effect of static mechanism and the the dynamic mechanism is in dominant position for Al^{3+} while the static mechanism is in dominant position for Fe^{3+} .



Figure S9: Luminescence spectra of the filtrate of 1 (0.002 M) after immersed in 5ml DMF solution in the presence of different Al^{3+} concentrations (excited at 395 nm) for 3 days. With the Al^{3+} concentration increasing to 0.001M, the exchange between $[H_2N(CH_3)_2]^+$ and Fe^{3+}/Al^{3+} is complete and the cation exchange between Eu^{3+} and Al^{3+} increases, which result in collapsing of 1 and the intensities of the characteristic emissions of Eu^{3+} ion in the filtrate increase.



Figure S10: The pictures of 1 (0.002 M) in 5ml DMF in the presence of different concentrations of Al^{3+} after 3 days under the irradiation of UV light of 365 nm. With the Al^{3+} concentrations increasing, the colors changed from red to colorless (clear solution), indicating the exchange between Eu³⁺ and Al^{3+} increases to result in the collapse of the framework completely.



Figure S11: Luminescence spectra of the filtrate of 1 (0.002 M) after immersed in 5ml DMF solution in the presence of 0.001M different metal ions (excited at 395 nm). For the Cd^{2+} and Ca^{2+} -loaded samples, there are no characteristic emissions of Eu^{3+} ion in the filtrates, whereas the characteristic emissions of Eu^{3+} are observed for Fe³⁺ – and Al³⁺-loaded samples. These results indicate the special properties of Fe³⁺/Al³⁺ for 1.



Figure S12: Left: the optical images of the test plates soaked in 5ml DMF in the presence of different concentrations of Fe^{3+} ions after 5 minutes under the irradiation of UV light of 365 nm. Right: the image of the test plate before immersion into dmf solution under daylight.



Figure S13: Optical images of the test plates immersed in 5ml H_2O in the presence of different concentrations of Fe^{3+} ions after 5 minutes under the irradiation of UV light of 365 nm.



Figure S14: Powder X-ray diffraction profiles of 1, as-synthesized and after immersed in different metal ions for 3 days. Based on the XRD patterns, complex 1 retains its framework after immersed in dmf solution containing different metal ions.



Figure S15: The EDS of the solid samples obtained by centrifugal separation of the emulsion of 1 in DMF containing Cd^{2+} , Tb^{3+} , Fe^{3+} , Al^{3+} , washing with water, and drying in air.

Acquire Date:	22 00 2012	5:01 nm		Somelo Tuno:	A 13+
Acquire Date:	23-00-2013	5.01 pn	1	Sample Type:	Als
Elem	Avg	1	Units	Stddev	%RSD
AI3082	4.716		ppm	0.0165	0.3508
Eu3819	184.2		ppm	1.2815	0.6956
2					
Acquire Date:	23-00-2013	5:03 pr	n	Sample Type:	Fe ³⁺
Elem	Avg		Units	Stddev	%RSD
Eu3819	195.1		ppm	0.2751	0.1411
Fe2382	9.152		ppm	0.1513	1.6534
Acquire Date:	07-00-2013	5:40 p	m	Sample Type	: Cd ²⁺
Acquire Date:	07-⊒⊒-2013 A	5:40 p vg	m Units	Sample Type Stddev	c Cd²⁺ %RSD
Acquire Date: Elem Cd2265	07-□□-2013 A 5.5	5:40 p vg 94	m Units ppm	Sample Type Stddev .000	: Cd ²⁺ %RSD .0000
Acquire Date: Elem Cd2265 Eu3819	07-□□-2013 A 5.5 144	5:40 p vg 94 4.7	m Units ppm ppm	Sample Type Stddev .000 .0	: Cd²⁺ %RSD .0000 .0000
Acquire Date: Elem Cd2265 Eu3819 4	07-□□-2013 A 5.5 144	5:40 p vg 94 4.7	m Units ppm ppm	Sample Type Stddev .000 .0	: Cd ²⁺ %RSD .0000 .0000
Acquire Date: Elem Cd2265 Eu3819 4 Acquire Date:	07-□□-2013 A 5.5 144 : 07-□□-2013	5:40 p vg 94 4.7 5:43 p	m Units ppm ppm	Sample Type Stddev .000 .0 Sample Type	:: Cd ²⁺ <u>%RSD</u> .0000 .0000 e: Na ⁺
Acquire Date: Elem Cd2265 Eu3819 4 Acquire Date: Elem	07-00-2013 A 5.5 144 : 07-00-2013 A	5:40 p vg 94 4.7 5:43 p vg	m Units ppm ppm m Units	Sample Type <u>Stddev</u> .000 .0 Sample Type Stddev	:: Cd ² * <u>%RSD</u> .0000 .0000 e: Na* <u>%RSD</u>
Acquire Date: Elem Cd2265 Eu3819 4 Acquire Date: Elem Na5895	07-0-2013 A 5.5 144 : 07-0-2013 A 1.9	5:40 p vg 94 4.7 5:43 p vg 987	m <u>Units</u> ppm ppm m <u>Units</u> ppm	Sample Type Stddev .000 .0 Sample Type Stddev .000	:: Cd ²⁺ .0000 .0000 :: Na ⁺ <u>%RSD</u> .0000
Acquire Date: Elem Cd2265 Eu3819 4 Acquire Date: Elem Na5895 Eu3819	07-00-2013 A 5.5 144 : 07-00-2013 A 1.9 15	5:40 p vg 94 4.7 5:43 p vg 187 3.9	m <u>Units</u> ppm ppm m <u>Units</u> ppm ppm	Sample Type Stddev .000 .0 Sample Type Stddev .000 .0	:: Cd ²⁺ .0000 .0000 :: Na ⁺ .0000 .0000

Figure S16: The ICP date for 1 after immersed in dmf solution containing Fe^{3+} and Al^{3+} (0.001 M), respectively, for 7 days, which showed the molar ratio of Al:Eu is about 14.4%, Fe:Eu is about 12.73%, Cd:Eu is about 5.23% and Na:Eu is about 8.53%.



Figure S17: The solid-state luminescent spectrums of solid samples obtained by centrifugal separation of the emulsion of 1 in DMF containing 0.001 M/L Al^{3+} and Fe^{3+} .



Figure S18: The luminescence lifetime for Eu-MOF in DMF is 365.15 μ s and after exchanging with Al³⁺/Fe³⁺ are 979.74 and 318.39 μ s respectively. (The symbol curves are the experimental lifetime decay curves and the solid line curves are the first order exponential decay curves).



Figure S19: The picture of an emulsion of 1 (0.002 M) in 5ml DMF in the presence of 0.001 M different metal ions after 3 days under the irradiation of UV light of 365 nm.



Figure S20: Emission spectra of an emulsion of 1 (0.002 M) in 5ml DMF in the presence of 0.001 M different metal ions after 3 days (excited at 395 nm).



Figure S21: (a) The time-denpedent luminescence spectra of an emulsion of 1 (0.002 M) in 5ml DMF in the presence of 0.001M Al³⁺ ions (excited at 395 nm).



(b) The time-denpedent luminescence spectra of an emulsion of 1 (0.002 M) in DMF in the presence of 0.001M Fe^{3+} ions (excited at 395 nm).



(c) Emission spectra of an emulsion of 1 (0.002 M) in 5ml DMF in the presence of different concentrations of Al^{3+} ions (excited at 395 nm).



(d) Emission spectra of an emulsion of 1 (0.002 M) in 5ml DMF in the presence of different concentrations of Fe^{3+} ions (excited at 395 nm).

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