Supporting Information

Four uncommon nanocage-based Ln-MOFs: highly selective luminescent sensing for Cu^{2+} ion and selective CO_2 capture

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Materials and Measurements. All reagents and solvents were commercially available and were used without further purification. Infrared spectra were obtained in KBr discs on a Nicolet Avatar 360 FTIR spectrometer in the 400-4000 cm^{-1} region. Photoluminescence analyses were performed on an Edinburgh FLS55 luminescence spectrometer. Elemental analyses (C, H and N) were performed with a Perkin Elmer 2400C Elemental Analyzer. Thermalgravimetric analyses (TGA) were carried out in nitrogen stream using a Netzsch TG209F3 equipment at a heating rate of 5°C/min. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 ADVANCE X-ray powder diffractometer (Cu Kα, 1.5418 Å). All the gas sorption isotherms were measured by using a ASAP 2020M adsorption equipment.

Photoluminescence Measurements. The photoluminescence and decay lifetime of **1-Eu** and **1-Tb** were investigated in the solid state at room temperature. For the experiments of sensing metal ions, **1-Eu** powder (5 mg) was immersed in DMF solutions containing 10^{-2} M of $M(NO_3)_x$ (M = Na^+, K^+, Mg^{2+}, Ca^{2+}, Zn^{2+}, Cd^{2+}, Mn^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, In^{3+}, or Tb^{3+}) as well as the same way used for the sensing in mixed metal ions (the concentration of 10^{-2} M for Cu^{2+} ion and 10^{-1} M for other metal ions). Before photoluminescence measurements, the suspensions were oscillated for 30 min using ultrasonic waves to ensure uniform dispersion. For the titration experiments of Cu^{2+} ion, **1-Eu** powder (5 mg) was immersed in DMF or DMF solutions contain other metal ions with the dropped addition of different concentrations of Cu^{2+} in DMF.

Sorption Measurements. The activated samples were prepared by soaking the as-synthesized samples in CH_3OH for two days, then in CH_2Cl_2 for three days and subsequent heating at 120 °C in a quartz tube under high vacuum for 10 h to remove the free DMF and H_2O molecules prior to measurements.

Synthesis of $[H_2N(CH_3)_2][Eu_3(L)_2(HCOO)_2(DMF)_2(H_2O)]\cdot 2DMF\cdot 20(H_2O)$ (1-Eu). A mixture of H_4L (12.22 mg, 0.03 mmol) and $Eu(NO_3)_3\cdot 6H_2O$ (44.60 mg, 0.10 mmol) was dissolved in DMF (2 mL) in a screw-capped vial. After two drops of HNO_3 (63%, aq.) and 0.1 mL of H_2O were added to the mixture, the vial was capped and placed in an oven at 105 ºC for 12 h. The resulting single crystals were washed with DMF three times to give **1-Eu**. The yield was ~27.1 mg (87.4% based on H_4L). Anal. Calc. for $C_{58}H_{98}Eu_3N_7O_{45}$: C, 33.66; H, 4.77; N, 4.74. Found: C, 33.39; H, 4.62; N, 4.81%. IR (KBr, cm^{-1}): 3402(s), 2933(m), 2492(w), 2322(w), 2026(w), 1662(m), 1435(w), 1327(m), 1279(m), 1253(m), 1179(s), 1102(s), 1062(m), 930(m), 860(m), 783(s), 719(s), 657(s), 529(m).

Synthesis of $[H_2N(CH_3)_2][Ln_3(L)_2(HCOO)_2(DMF)_2(H_2O)]\cdot 2DMF\cdot X(H_2O)$ (Ln = Tb, Gd and Dy; X = 20 for 1-Tb; X = 18 for 1-Gd and 1-Dy). With $Tb(NO_3)_3\cdot 6H_2O$ (45.30 mg), $Gd(NO_3)_3\cdot 6H_2O$ (45.14 mg), and $Dy(NO_3)_3\cdot 6H_2O$ (45.66 mg) using otherwise identical procedures, **1-Tb**, **1-Gd**, and **1-Dy** were obtained respectively. **1-Tb**: Yield: ~24.0 mg (76.6% based on H_4L), Anal. Calc. for $C_{58}H_{98}Tb_3N_7O_{45}$: C, 33.33; H, 4.73; N, 4.69. Found: C, 33.46; H, 4.59; N, 4.72%. IR (KBr, cm^{-1}): 3418(s), 2932(m), 2492(w), 2322(w), 2025(w), 1547(m), 1389(w), 1323(m), 1280(m), 1252(m), 1179(s), 1100(s), 1062(m), 930(m), 860(m), 783(s), 719(s), 657(s), 529(m). **1-Gd**: Yield: ~25.2 mg (82.1% based on H_4L), Anal. Calc. for $C_{58}H_{94}Gd_3N_7O_{43}$: C, 34.00; H, 4.62; N, 4.79. Found: C, 33.43; H, 4.76; N, 4.83%. IR (KBr, cm^{-1}): 3404(s), 2933(m), 2493(w), 2318(w), 2026(w), 1662(m), 1435(w), 1325(m), 1280(m), 1252(m), 1179(s), 1102(s), 1062(m), 930(m), 861(m), 783(s), 720(s), 657(s), 529(m). **1-Dy**: Yield: ~22.9 mg (73.9% based on H_4L), Anal. Calc. for $C_{58}H_{94}Dy_3N_7O_{43}$: C, 33.74; H, 4.59; N, 4.75. Found: C, 33.57; H, 4.36; N, 4.69%. IR (KBr, cm^{-1}): 3421(s), 2932(m), 2479(w), 2321(w), 2026(w), 1660(m), 1436(w), 1322(m), 1279(m), 1253(m), 1180(s), 1104(s), 1060(m), 930(m), 862(m), 781(s), 720(s), 657(s), 543(m).

Crystallography. The diffraction data were collected at 295(2) and 100(2) K for **1-Eu** and **1-Gd**,

respectively, with a Bruker-AXS SMART CCD area detector diffractometer using ω rotation scans with a scanwidth of 0.3º and Mo Kα radiation (λ = 0.71073 Å). Absorption corrections were carried out utilizing SADABS routine.[1] The structures were solved by direct methods and refined using the *SHELXTL 97* software.[2] Atoms were located from iterative examination of difference F-maps following least squares refinements of the earlier models. All the atoms except hydrogen atoms, which were fixed at calculated positions and refined by using a riding mode, were refined anisotropically until full convergence was achieved. The large voids in the structure allow for considerable flexing and uncertainty in the positions of the framework atoms and this is evidenced in large atomic displacement parameters for many of the pyridine carbons, nitrogens from ligand. It was necessary to constrain or restrain a number of bond lengths and angles in the structure in order get a stable refinement and chemically reasonable model. All carbon and nitrogen atoms from pyridine were restrained to have similar ADP's as their neighbors with simu and delu command in the refinement. The large cage of the unit was occupied by extremely electron density, which could be assigned to be $H_2N(Me)_2$ countercations and free solvent molecules. Because these guest solvents in the crystal is highly disordered and impossible to refine using conventional discrete-atom models, the SQUEEZE[3] subroutine of the PLATON software suite was applied to remove the scattering from the highly disordered solvent molecules, and sets of solvent-free diffraction intensities were produced.

The structures of **1-Tb** and **1-Dy** were not measured by single crystal X-ray diffraction, however, which are isostructural with **1-Eu** and **1-Gd**, confirmed by the same crystal shapes and very similar power X-ray diffraction patterns in **Fig. S3**.

The final formulas for the complexes were determined by combining single crystal structures, IR, elemental microanalysis and TGA data.

Crystal data for **1-Eu**: $C_{50}N_4O_{23}H_{36}Eu_3$, M = 1516.71, Cubic Im-3, $a = b = c$ = 37.9826(10) Å, V = 54797(2) Å^3. Z = 24, Dc = 1.103 g cm^{-3}, μ = 2.086 mm^{-1}, R_{int} = 0.0534, final R_1 = 0.1332, wR_2 = 0.3266 for 9417 unique reflections (I ≥ 2σ), S = 1.036. Crystal data for **1-Gd**: $C_{50}N_4O_{23}H_{36}Gd_3$, M = 1532.58, Cubic Im-3, $a = b = c$ = 37.9569(9) Å, V = 54686(2) Å^3. Z = 24, Dc = 1.117 g cm^{-3}, μ = 2.209 mm^{-1}, R_{int} = 0.0676, final R_1 = 0.1306, wR_2 = 0.4069 for 9389 unique reflections (I ≥ 2σ), S = 1.947. CCDC-998805 and 998812 contains the crystallographic data of **1-Eu** and **1-Gd** for this paper.

References

1) Bruker. *SADABS*, *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconson, USA, 2002.

2) 2 G. M. Sheldrick, *SHELXL-97, program for the refinement of the crystal structures*. University of Göttingen, Germany, 1997.

3) Spek, A. L. *Acta Crystallogr., Sect. A*, 1990, 46, C34.

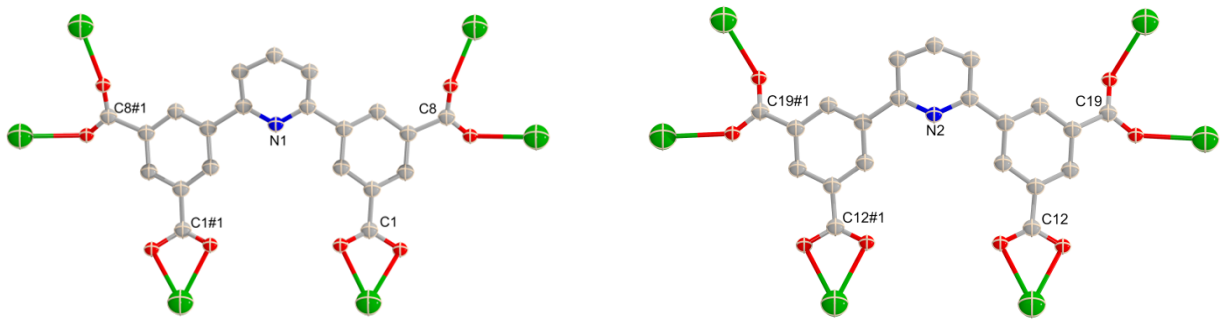

Fig. S1 The bridging fashions of the carboxylate groups of two different L^{4-} in **1-Eu**. Symmetry codes: #1 x, 2-y, z.

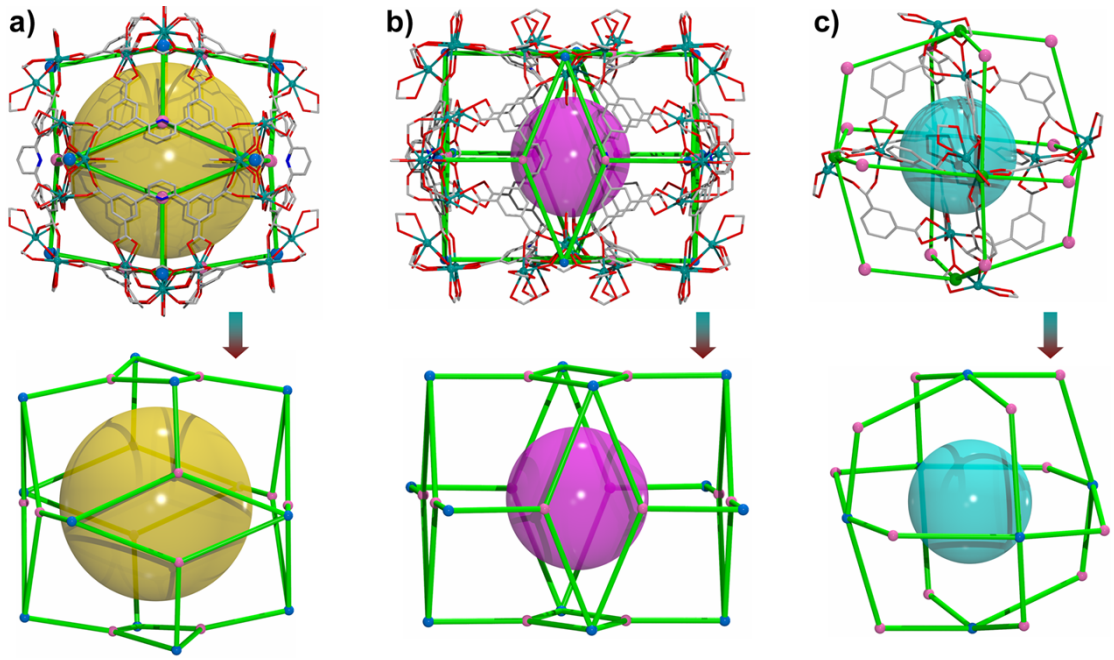

Fig. S2 Three kinds of nanocages in **1-Eu**: a) cage **A**, b) cage **B**, c) cage **C**, and their simplified nets.

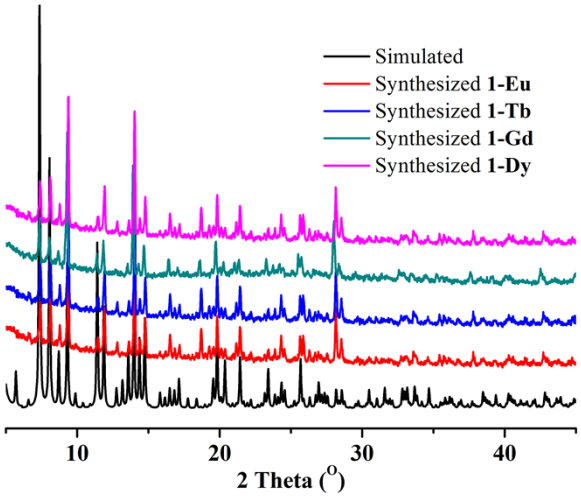

Fig. S3 PXRD patterns of **1-Eu** simulated from the X-ray single-crystal structure and as-synthesized samples of **1-Eu**, **1-Tb**, **1-Gd** and **1-Dy**. The very similar PXRD patters confirmed the isostructural frameworks of four complexes.

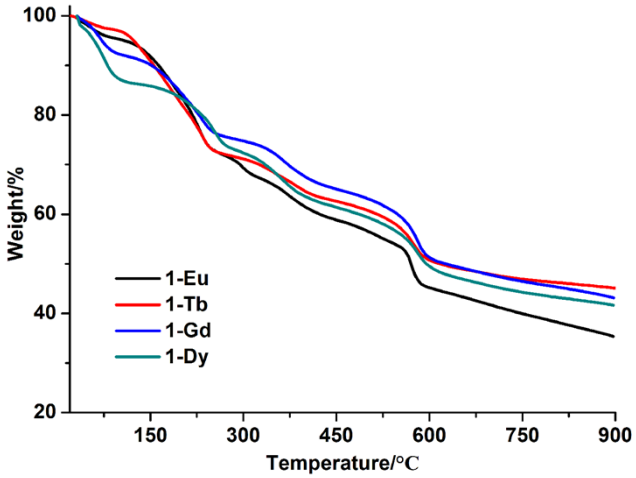

Fig. S4 TGA plots of **1-Ln** under N_2 environment. TGA plots of **1-Ln** reveal similar weight loss processes, which lose all guest solvents below around 235−250 ºC. For **1-Eu**, a total weight loss of 24.6% at 32−235 ºC, corresponding to the loss of 2DMF and $20H_2O$ guest molecules per formula unit (calc. 24.5%). For **1-Tb**, a total weight loss of 24.7% at 32−235 ºC, corresponding to the loss of 2DMF and $20H_2O$ guest molecules per formula unit (calc. 24.2%). For **1-Gd**, a total weight loss of 23.1% at 32−246 ºC, corresponding to the loss of 2DMF and $18H_2O$ guest molecules per formula unit (calc. 22.9%). For **1-Dy**, a total weight loss of 22.7% at 32−250 ºC, corresponding to the loss of 2DMF and $18H_2O$ guest molecules per formula unit (calc. 22.8%), the further releases of aqua and DMF ligands. Above 320−390 ºC, these frameworks begin to collapse with the loss of other organic molecules.

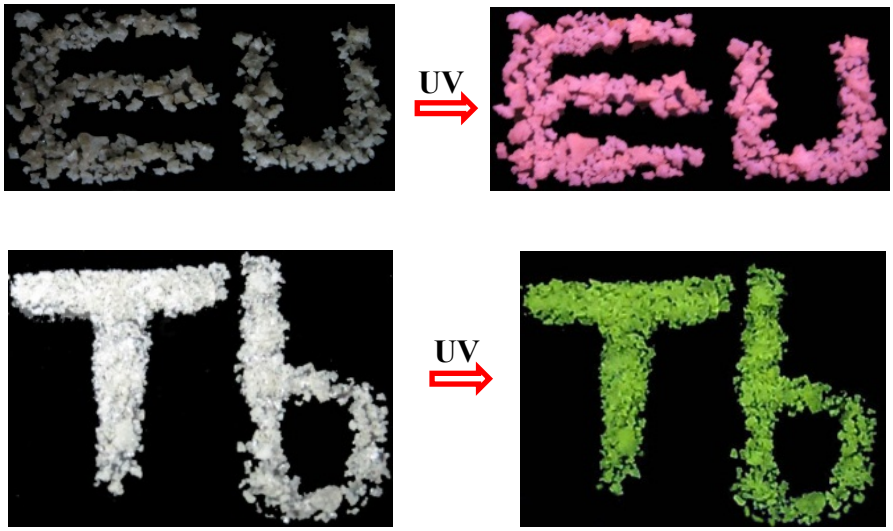

Fig. S5 The snapshots of **1-Eu** and **1-Tb** under UV light (365 nm).

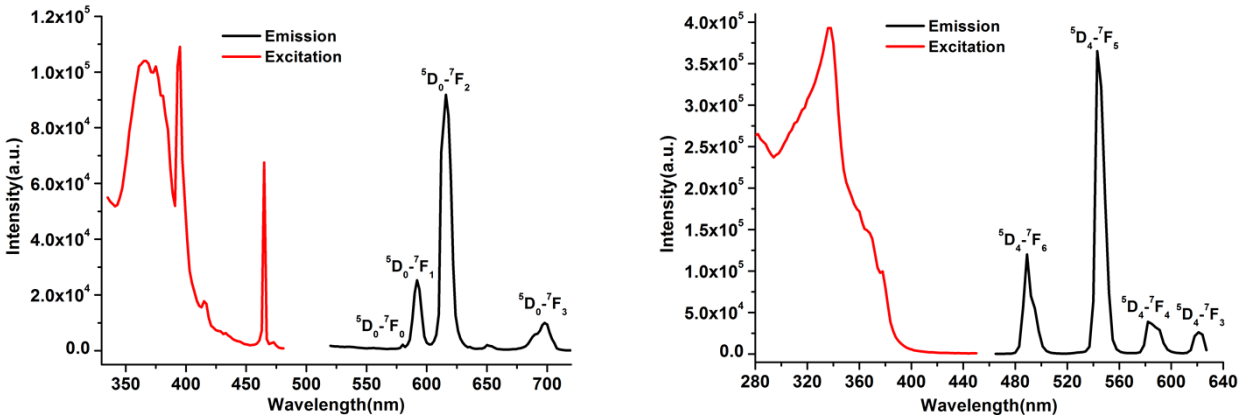

Fig. S6 The excitation and emission spectra of **1-Eu** (left) and **1-Tb** (right).

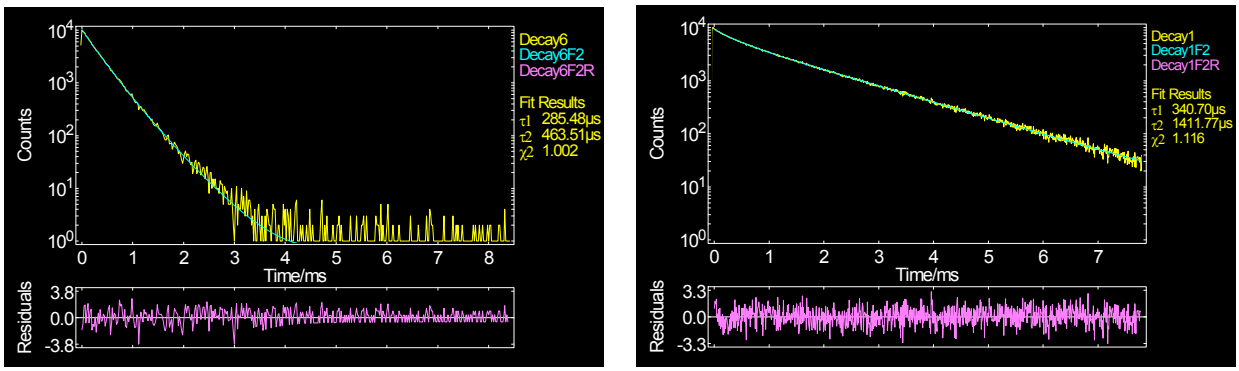

Fig. S7 The luminescence decays of **1-Eu** (left) and **1-Tb** (right) monitored at corresponding excitation/emission maxima.

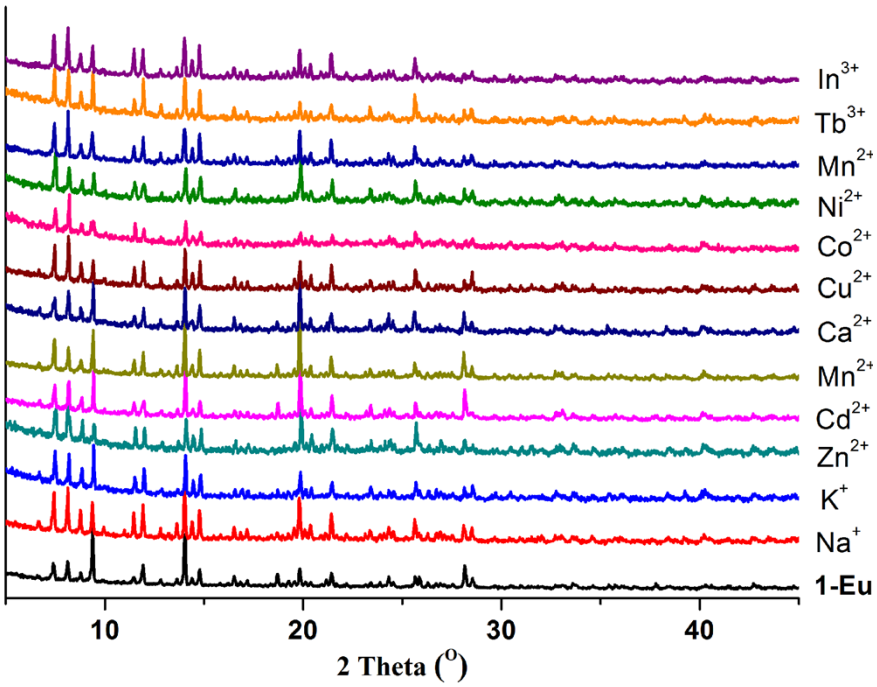

Fig. S8 The PXRD patterns of **1-Eu** treated by different $M(NO_3)x$ (M = Na^+, K^+, Mg^{2+}, Ca^{2+}, Zn^{2+}, Cd^{2+}, Mn^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, $Tb^{3+}$and In^{3+}) DMF solutions. Based on the XRD patterns, **1-Eu** retains its framework after immersed in DMF solution containing different metal ions.

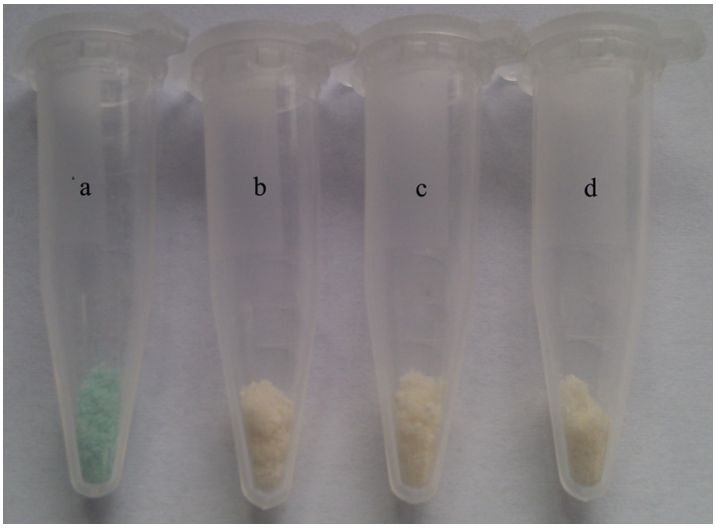

Fig. S9 Photographs of crystals of **1-Eu** soaked in DMF solution containing $M(NO_3)_2$ with 10^{-1} M, a) Cu^{2+}, b) Co^{2+}, c) Ni^{2+}, d) Mn^{2+} for 24 h, indicating selective color changes for Cu^{2+}.

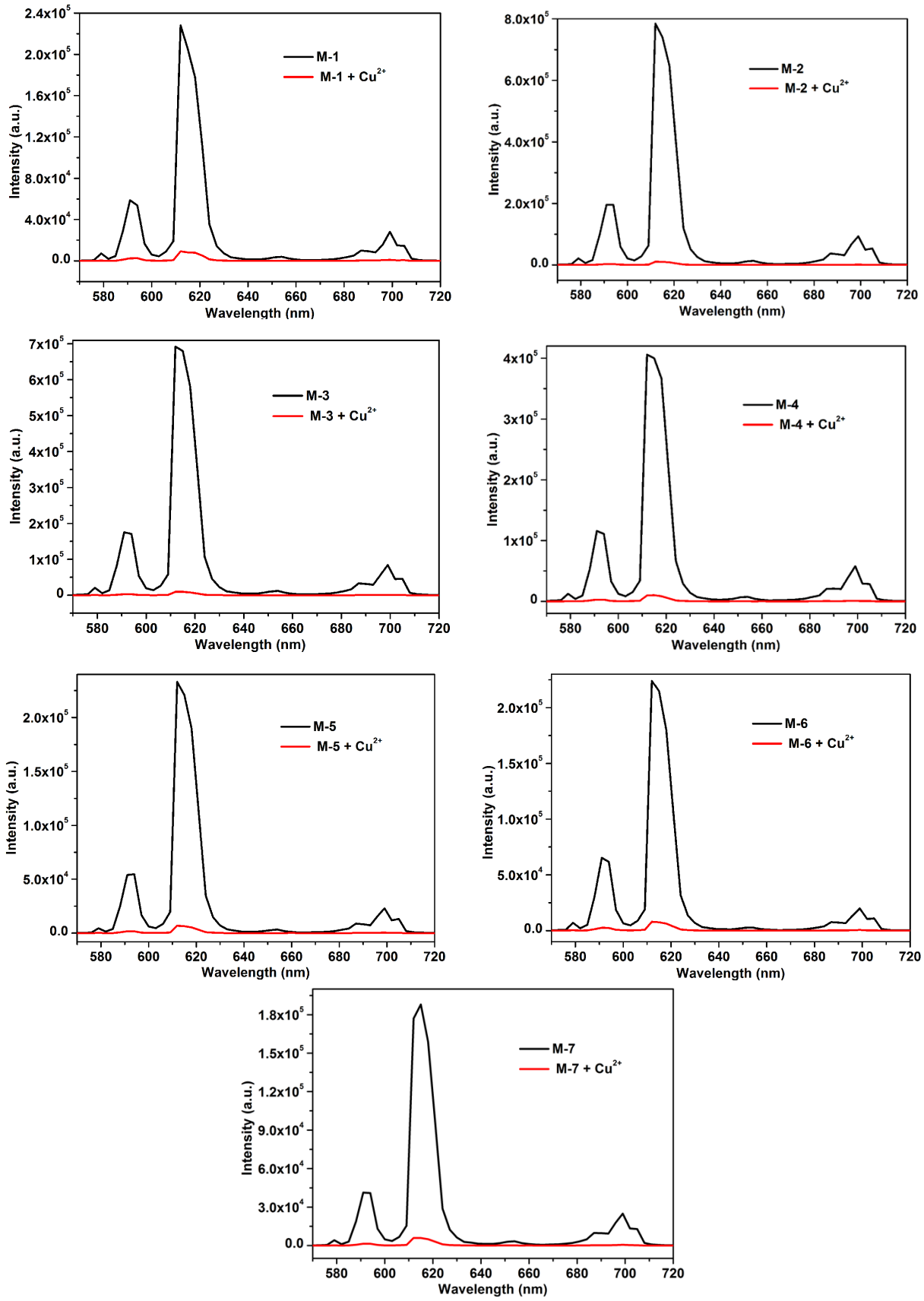

Fig. S10 The luminescence spectra of **1-Eu** in DMF with different mixed metal ions (10^{-1} M) in the absence (black) and presence (red) of Cu^{2+} ion (10^{-2} M). M-1: **1-Eu**, M-2: **1-Eu** + Na^{+}/Mg^{2+}/Ca^{2+}, M3: **1-Eu** + Mg^{2+}/Ca^{2+}, M4: **1-Eu** + Zn^{2+}/Cd^{2+}, M5: **1-Eu** + Co^{2+}/Ni^{2+}, M6: **1-Eu** + Zn^{2+}/Cd^{2+}/Ni^{2+}, M-7: **1-Eu** + Zn^{2+}/Cd^{2+}/Co^{2+}.

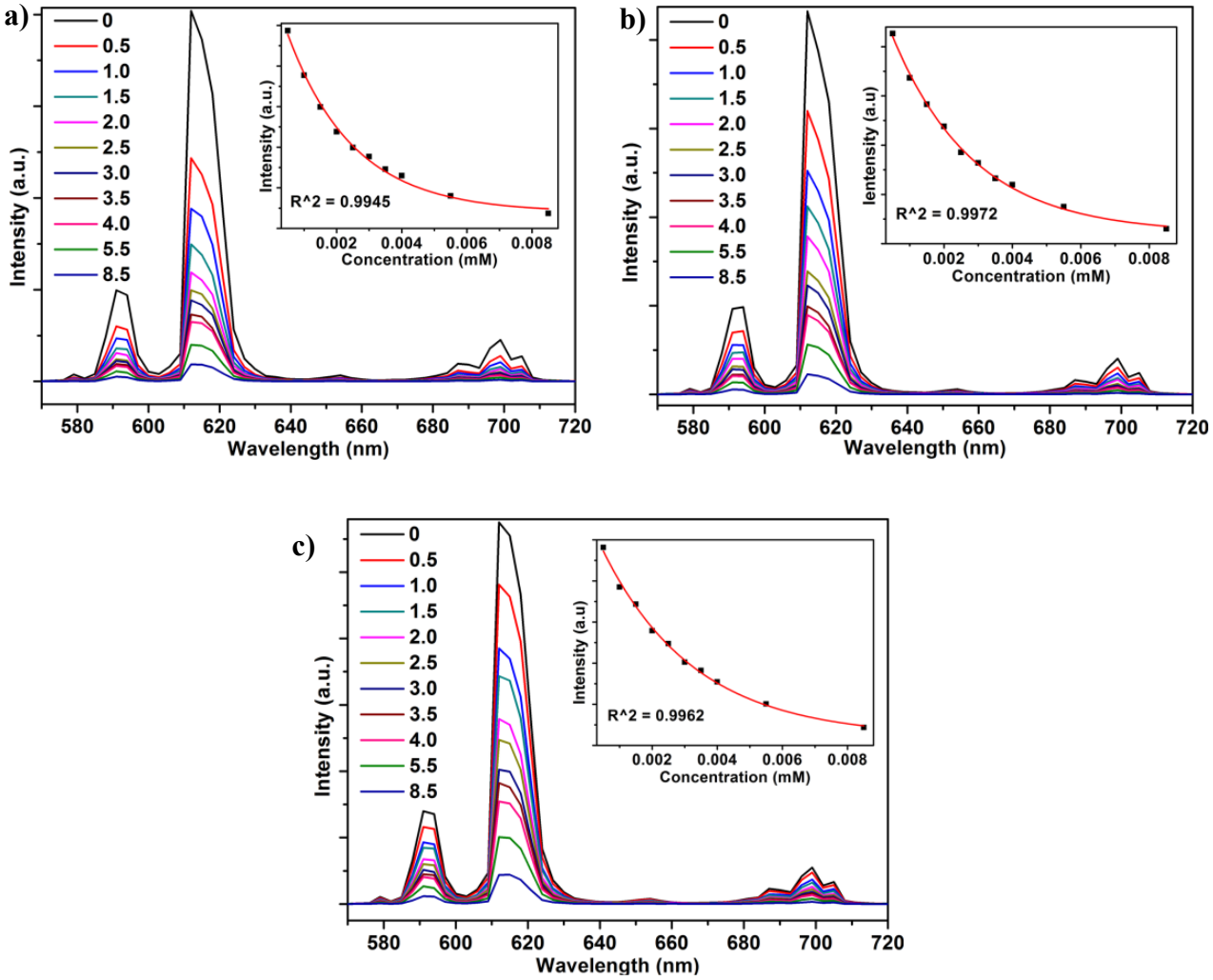

Fig. S11 The luminescence spectra of **1-Eu** in mixed metal ions (10^{-1} M) a) $Na^{+}/Mg^{2+}/Ca^{2+}$, b) Co^{2+}/Ni^{2+} and c) $Zn^{2+}/Co^{2+}/Ni^{2+}$ in the presence of different amounts of Cu^{2+} (mM). Inset: the fitted plot of intensity versus Cu^{2+} ion concentration.

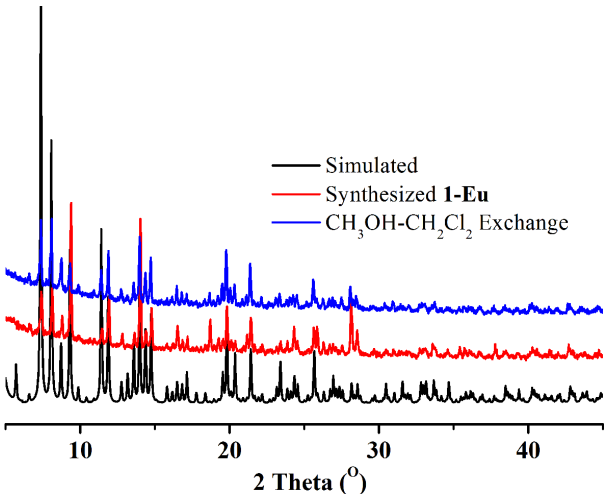

Fig. S12 PXRD patterns of **1-Eu** simulated from the X-ray single-crystal structure, as-synthesized and CH_3OH-CH_2Cl_2 exchanged samples.

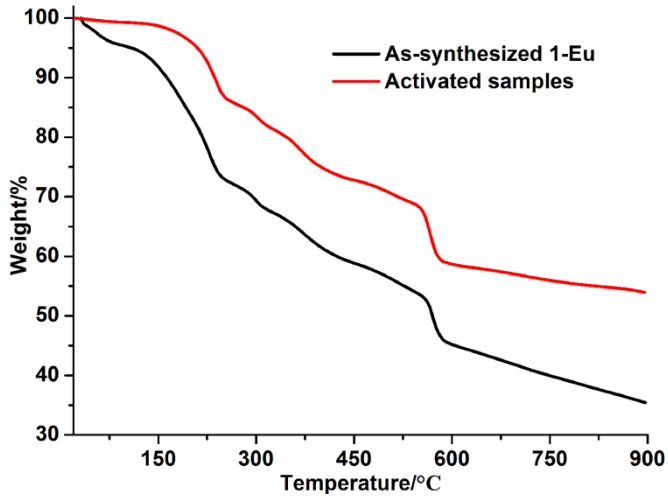

Fig. S13 TGA plots of the as-synthesized and activated samples of **1-Eu**.

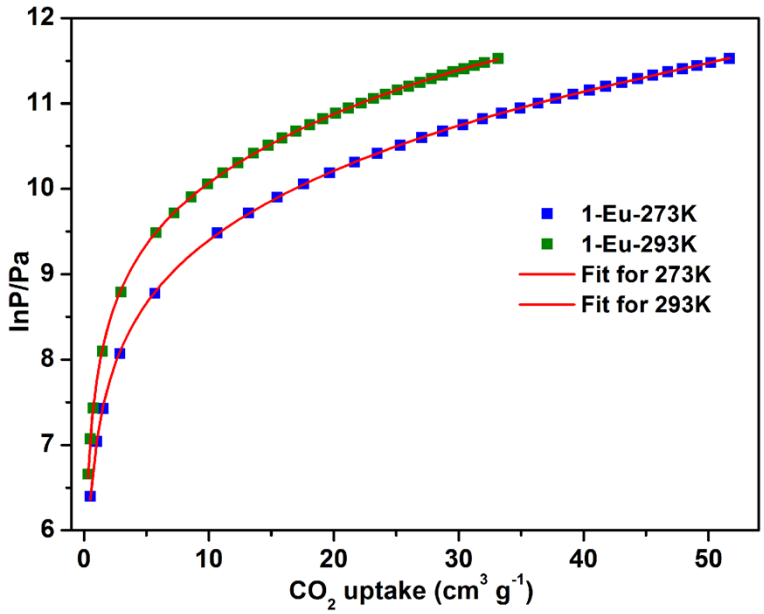

Fig. S14 Virial analysis of the CO_2 sorption data for **1-Eu**. (a0 = -2846.45706 ± 39.61158, a1 = 25.93085 ± 11.35286, a2 = -1.20980 ± 0.78418, a3 = 0.01919 ± 0.01509, a4 = 0.00004 ± 0.00001, b0 = 17.45728 ± 0.13924, b1 = -0.09435 ± 0.03964, b2 = 0.00517 ± 0.00272, b3 = -0.00008 ± 0.00005, Chi^2 = 0.00013, R^2 = 0.99992.)

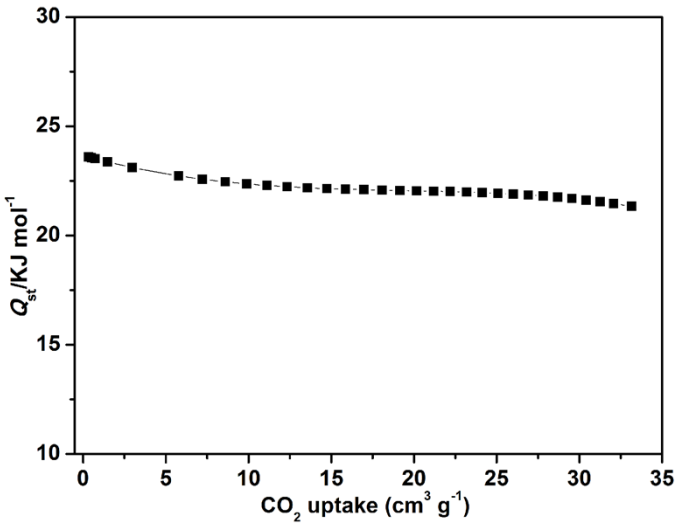

Fig. S15 Heat of CO_2 adsorption for **1-Eu** estimated by the virial equation.

Table S1. Quenching effect coefficients (K_{sv}) of different metal ions on the luminescence intensity of metal-ion-incorporated **1-Eu**, calculated by Stern–Volmer equation: $I_0/I = 1+K_{sv}[M]$, in which the values I_0 and I are the luminescent intensity of metal-ion-free **1-Eu** in DMF and metal-ion-incorporated **1-Eu** in DMF, respectively, [M] is the molar concentration of metal ion, and K_{sv} is the quenching effect coefficient of metal ion (see reference *Angew. Chem. Int. Ed.*, 2009, **48**, 500). The results were shown below.

Metal ion	K_{sv} [M^{-1}]
Ca^{2+}	-64
Tb^{3+}	-63
Mg^{2+}	-57
Zn^{2+}	-54
In^{3+}	-49
Cd^{2+}	-40
Mn^{2+}	-33
Ni^{2+}	-30
Co^{2+}	-19
Na^{+}	-9
K^{+}	1
Cu^{2+}	2.35×10^3

Table S2. Quenching effect coefficients (K_{sv}) of Cu^{2+} ion (10^{-2} M) in **1-Eu** and mixed metal ions (10^{-1} M) systems.

Mixed metal ions	K_{sv} [M^{-1}]
$Na^{+}/Mg^{2+}/Ca^{2+}$	7.31×10^{3}
Mg^{2+}/Ca^{2+}	7.12×10^{3}
Zn^{2+}/Cd^{2+}	4.17×10^{3}
Co^{2+}/Ni^{2+}	3.32×10^{3}
$Zn^{2+}/Cd^{2+}/Ni^{2+}$	2.75×10^{3}
$Zn^{2+}/Cd^{2+}/Co^{2+}$	2.89×10^{3}