Supporting Information

Pre-concentration and Energy Transfer Enable Efficient Luminescent Sensing of Transition Metal Ions by Metal-Organic Frameworks

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S1 General Information

Zirconium tetrachloride ($ZrCl_4$),2,2'-Bipyridine-5,5'-dicarboxylic acid (bpydc), Trifluoroacetic acid (CF_3COOH), Europium nitrate hexahydrate ($Eu(NO_3)_3•6H_2O$), N,N-Dimethylformamide (DMF) and all the perchlorates (Cd^{2+}, Ni^{2+}, Fe^{2+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, Mn^{2+} and Co^{2+}) were obtained from commercial sources. Other solvents were of reagent grade and used without further purification. HPLC grade methanol was used in the luminescent measurement of UiO-bpydc. Transmission electron microscopy (TEM) images were obtained on a Japanese JEOL Corporation TEM (JEM – 1400) at voltage of 100 kV. Thermogravimetric analysis (TGA) of UiO-bpydc was obtained on a SDTQ600 Thermal Analyzer. Thermogravimetric analysis (TGA) for Eu-bpydc were obtained on a TG60 Thermal Analyzer. The morphology was monitored by scanning electron microscopy (SEM, Hitachi S4800). X-ray powder diffraction patterns within the 2θ range of 5-50°were obtained on a Rigaku Ultima IV XRD using Cu Kα radiation with 15 mA and 30 kV. Single Crystal X-ray Diffraction data were taken on Oxford Gemini S Ultra X-ray single-crystal diffractometer using Mo Kα radiation (Eu-bpydc) and Agilent Supernova X-ray single-crystal diffractometer using Cu Kα radiation (Eu-bpydc-Cu(I)) at 100K. Fluorescence spectra were acquired on Hitachi F7000 fluorescence spectrometer with PMT Voltage 800V, 5.0nm ex/em slit width and 1200nm/min scan speed. The luminescence lifetimes of the samples were measured on the Horiba JY FLuoro Max-4 spectrophotometer.

S2 Experimental Details

Synthesis of $Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(bpydc)_{12}$ (UiO-bpydc).

UiO-bpydc was hydrothermally synthesized from a mixture of $ZrCl_4$ (30mg, 0.13mmol), 2,2'-Bipyridine-5,5'-dicarboxylic acid(30mg, 0.13mmol), CF_3COOH(60μL) and DMF(15mL) as reported in the literature.[1] The mixture was heated at 120℃ for 5 days. After cooling to room temperature, powdery samples were collected by centrifugation, before washing with DMF for several times. The powdery samples were then soaked in methanol to exchange the DMF molecule in the channel by methanol, and air-dried for storage.

Luminescence Quenching Experiments for UiO-bpydc.

5mg of the UiO-bpydc were added into 1mL of methanol and grounded to fine particles by a stir bar overnight. The white suspension was then diluted with methanol to 6μM based on the bpydc ligand. To obtain the luminescence quenching data, 3mL of the UiO-bpydc suspension was added to the quartz cuvette with stirring. The luminescent signal of the suspension was monitored for a while to ensure signal stability of the stirred suspension. After the signal stabilized, the average luminescent intensity was obtained by taking three parallel intensity

measurements. Methanol solutions of the metal salts $M(ClO_4)_x$ were then added to the cuvette. The average intensity was obtained for different metal ion concentrations. A Stern-Völmer plot of the luminescent quenching data was then used to calculate the Stern-Völmer constant, as a measurement of the sensing sensitivity. The luminescent quenching of a methanol solution of the bpydc ligand instead of MOF was performed in a similar manner.

Synthesis of Eu-bpydc.

Powdery samples of $Eu_2(bpydc)_3(H_2O)_3$ was synthesized from the mixture of ($Eu(NO_3)_3$•$6H_2O$) (146.4mg, 0.33mmol), 2,2'-Bipyridine-5,5'-dicarboxylic acid(145.2mg, 0.6mmol) and DMF(20mL) in the tube of microwave reactor. The mixture was heated at 150℃ for 15 minutes. After cooling to room temperature, powdery samples were collected by centrifugation after washing with DMF for several times.

Single crystal of Eu-bpydc [$Eu_2(bpydc)_3(H_2O)_3$] was synthesized following literature procedure.[2] A mixture of $Eu(NO_3)_3 \cdot 6H_2O$ (120.4mg, 0.27 mmol), 2,2'-Bipyridine-5,5'-dicarboxylic acid (99.2mg, 0.41mmol) and DMF (10 mL) was stirred at room temperature for one hour. The mixture was then placed in an autoclave and heated in a preheated oven at 120 °C for one day. Rod-shaped crystals were collected and washed with DMF.

The Cu^+-loaded single crystal Eu-bpydc-Cu(I) was prepared by soaking the Eu-bpydc crystals in acetonitrile solution of excess amount of $[CuOSO_2CF_3]_2 \cdot C_6H_6$. The crystal/solution mixture was sealed in a 10 mL Teflon-capped vial, free of oxygen, and was then allowed to react for 24 h at 55 °C. The obtained red crystals were washed with fresh acetonitrile several times, and were then used for single-crystal X-ray diffraction experiments.

Luminescence Quenching Experiments for Eu-bpydc.

2.69mg of the Eu-bpydc were added into 1mL of DMF and grounded to fine particles by a stir bar overnight. The white suspension was then diluted with DMF to 30μM based on the bpydc ligand. To obtain the luminescence quenching data, 3mL of the Eu-bpydc solution was added to the quartz cuvette with stirring. Luminescence quenching experiments were carried out in a similar fashion as that of the UiO-bpydc.

S3 Electron Microscopy (EM) Images

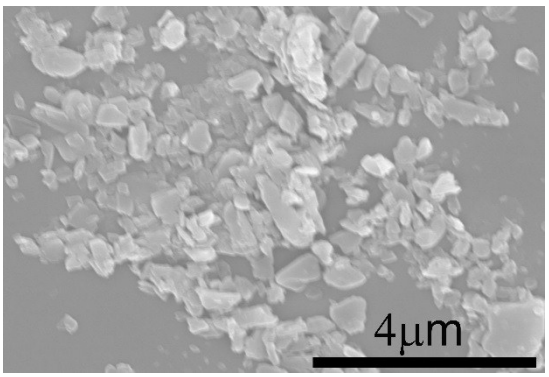

Figure S1.SEM image of the Eu-bpydc powerder

S4 Thermogravimetric Analysis (TGA) Plots

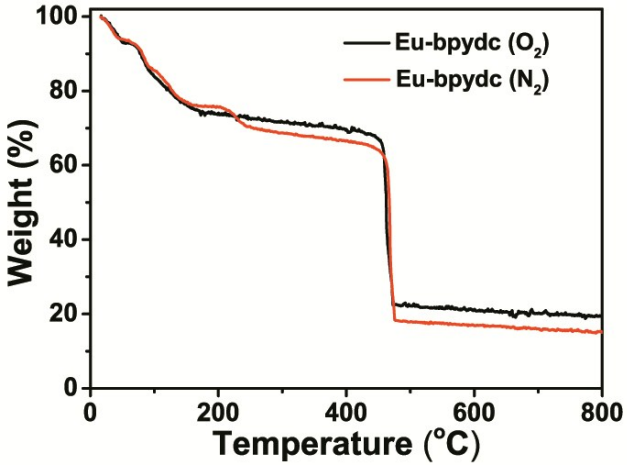

Figure S2.The TGA plot of the Eu-bpydc powder

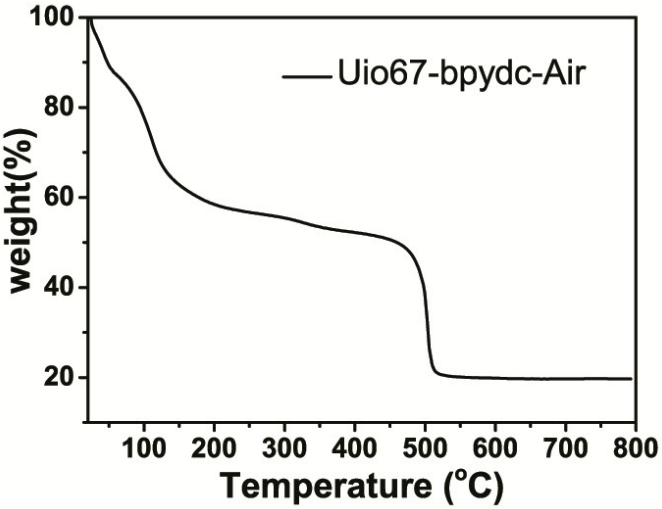

Figure S3. The TGA plot of UiO-bpydc

S5 (Powder X-ray Diffraction) PXRD Patterns

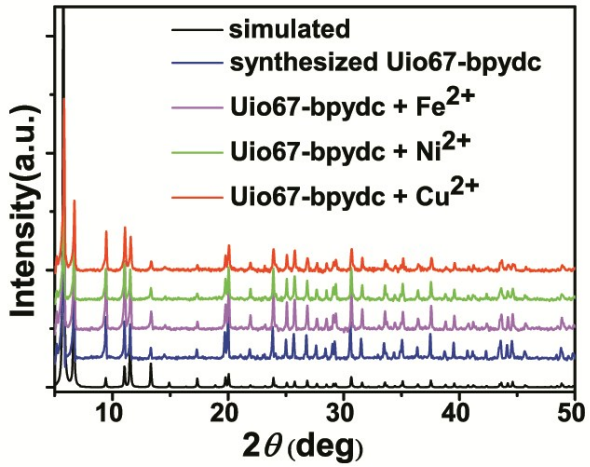

Figure S4. PXRD patterns for UiO-bpydc: simulated (black), as synthesized (blue) and after soaking in Fe^{2+}(pink),Ni^{2+}(green),Cu^{2+}(red) solutions.

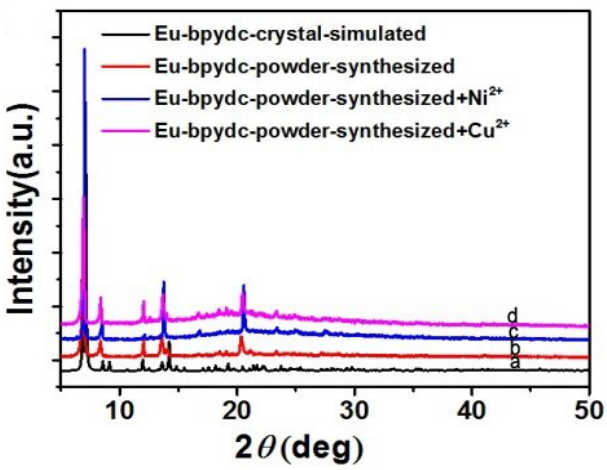

Figure S5. PXRD patterns of Eu-bpydc powder after soaking in DMF solutions of different metal ions.

S6 Fluorescence Spectra and UV-Vis、Fluorescence Quenching Data

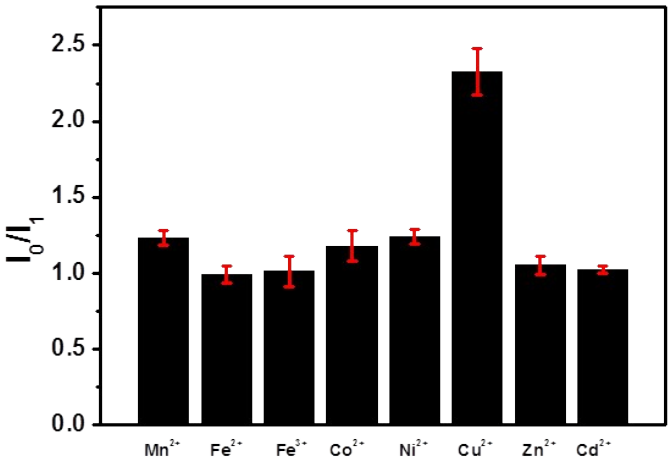

Figure S6. The luminescence quenching of Eu-bpydc in DMF solutions with different metals of H_2O

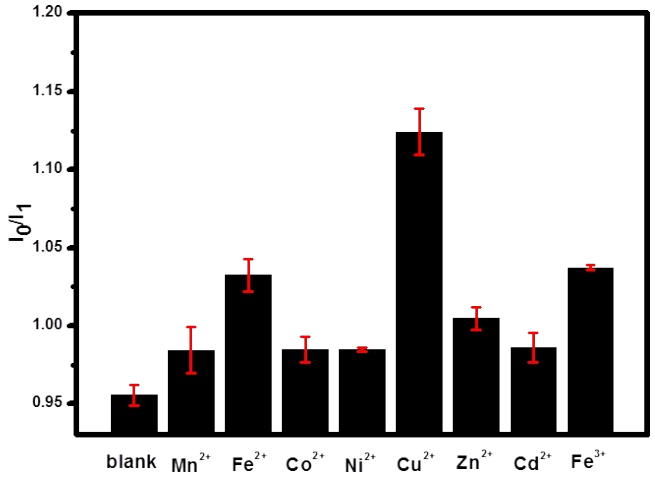

Figure S7.The fluorescence intensity of Eu-bpydc in MeOH solutions in the presence of different metal ions

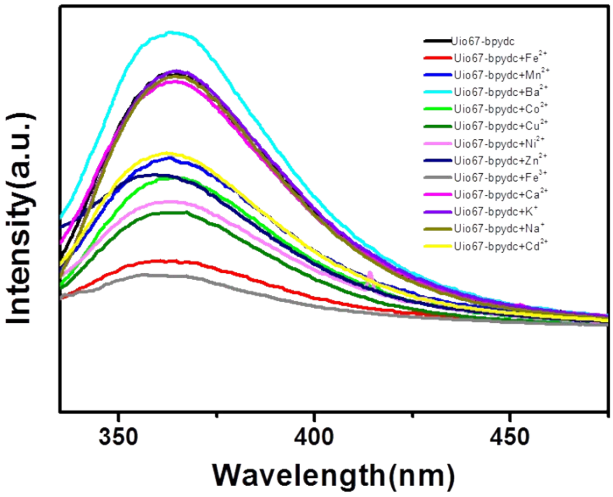

Figure S8. The effects of different metal ions on fluorescence intensities of UiO-bpydc in methanol.

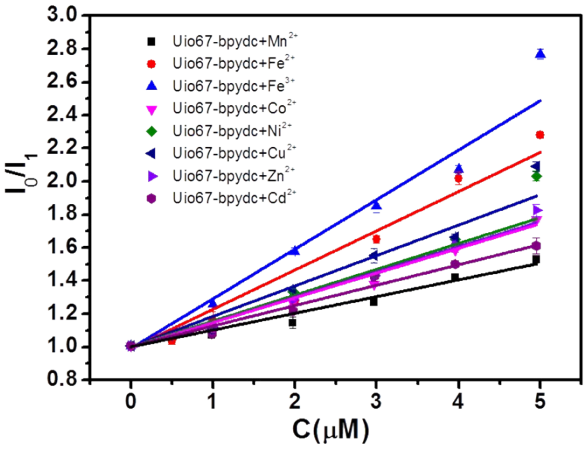

Figure S9. The comparison of UiO-bpydc fluorescence intensity on different concentrations of metal ions.

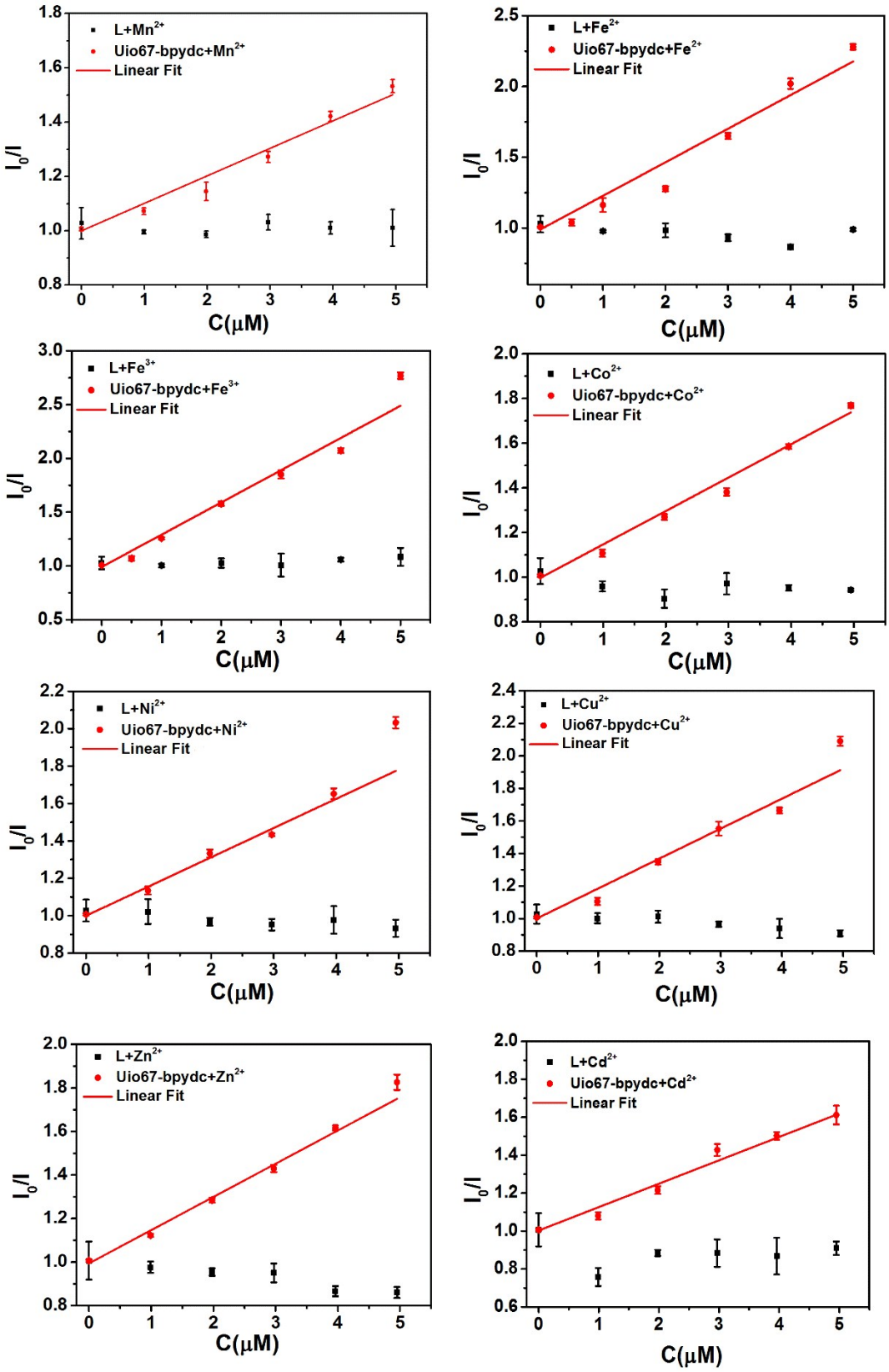

Figure S10. The dependence of UiO-bpydc fluorescence intensity on different concentrations of metal ions.

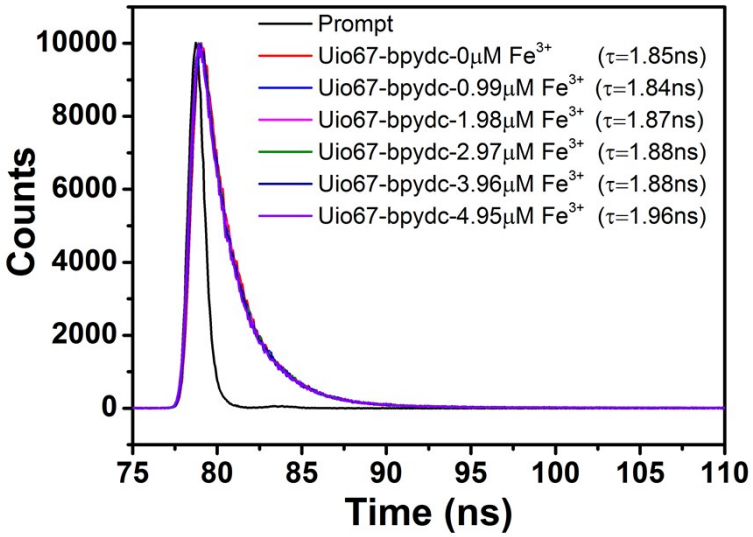

Figure S11. Time-resolved fluorescence decay traces of UiO-bpydc and UiO-bpydc with Fe^{3+}.

The time-resolved fluorescence exhibited a decay curve that can be fitted to bi-exponential decays $I(t) = A + B_1 e^{-t/\tau_1} + B_2 e^{-t/\tau_2}$ where A is a constant, and B_1 and B_2 are pre-exponential factors; τ_1 and τ_2 are fitted time constants of the decay. The weighted fluorescence lifetime was calculated according to $\tau = (B_1\tau_1^2+B_2\tau_2^2)/(B_1\tau_1+B_2\tau_2)$.

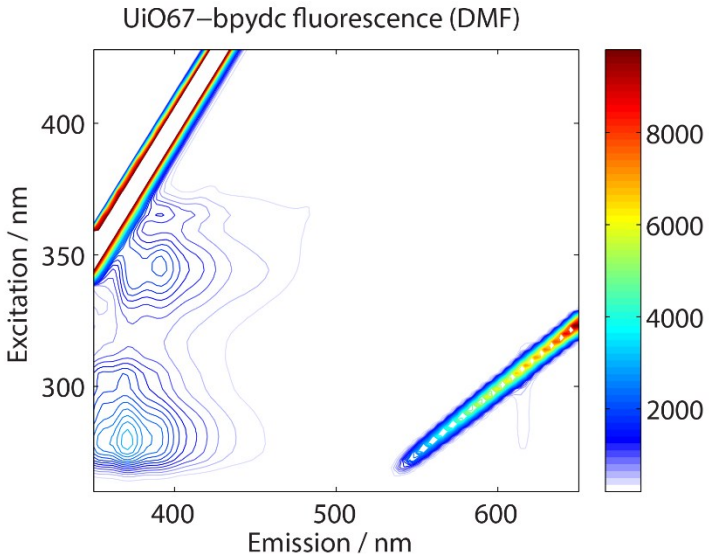

Figure S12. The 2D fluorescence of UiO-bpydc in DMF.

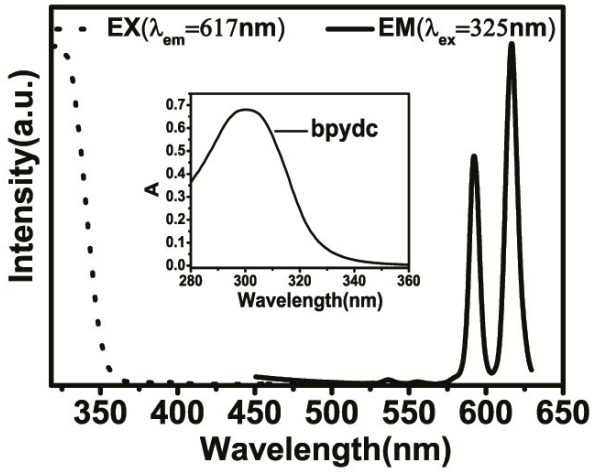

Figure S13. Fluorescence spectrum of Eu-bpydc in DMF.

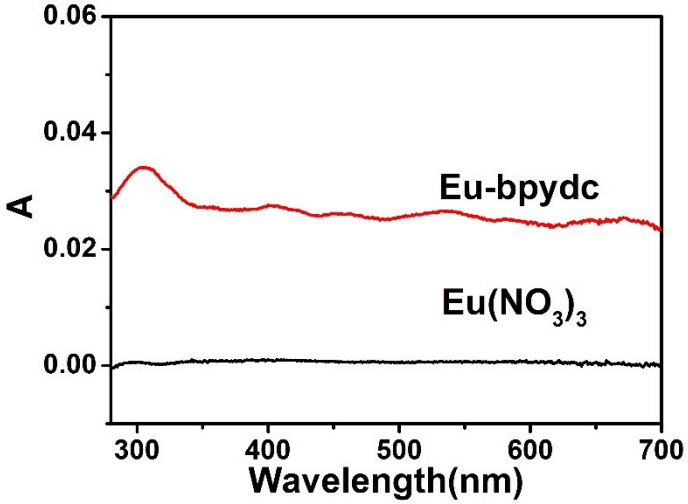

Figure S14.UV-Vis spectra of Eu^{3+}ions and Eu-bpydc powder in DMF (containing 20 μM Eu^{3+}ions, $\lambda_{MOF,max}$=306nm)

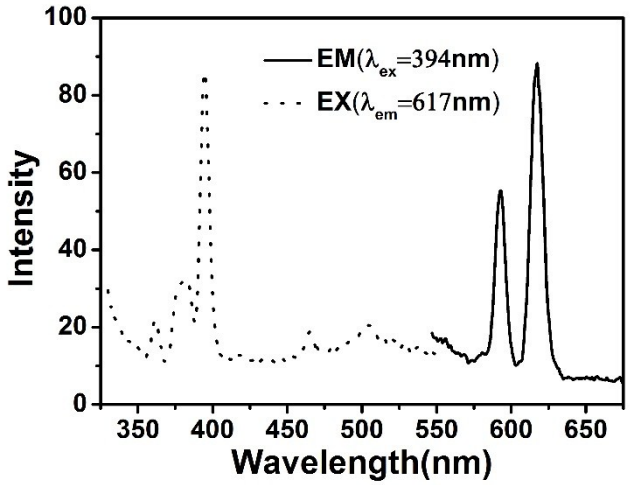

Figure S15.Fluorescence spectrum of $Eu(NO_3)_3$ in DMF (containing 200 μM Eu^{3+}ions).

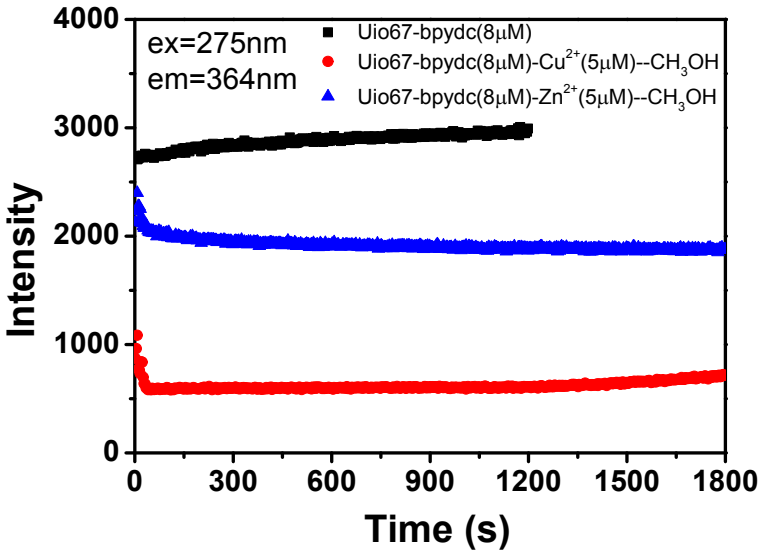

Figure S16. Time-dependent fluorescence intensity of UiO-bpydc in methanol with different metal ions.The signal reached equilibrium within one minute.

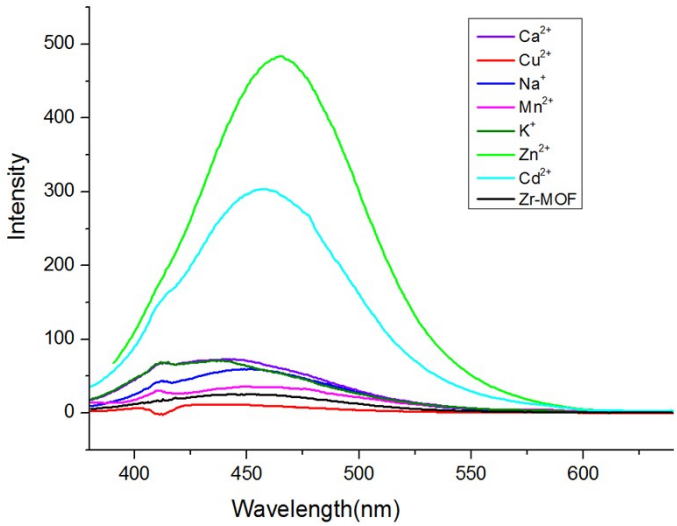

Figure S17. The effects of different metal ions on the fluorescence of UiO-bpydc in H_2O in the presence of 100 μM metal ions after equilibrium for 12 hours.

S7 Crystallographic Data and Structure Refinement Details

Table S1. Crystallographic Information for Eu-bpydc and Eu-bpydc-Cu(I)

Compound	Eu-bpydc	Eu-bpydc-Cu(I)

Empirical formula	$C_{36}Eu_2N_6O_{17}$	$C_{36}Cu_{1.02}Eu_2N_7O_{15}$
Formula weight	1092.34	1139.48
Temperature/K	100	100
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	26.238(2)	26.531(2)
b/Å	14.1876(15)	13.617(4)
c/Å	16.8586(11)	16.4067(19)
α/°	90	90
β/°	98.014(7)	98.040(11)
γ/°	90	90
Volume/Å^3	6214.3(9)	5869.1(19)
Z	4	4
ρ_{calc}g/cm^3	1.168	1.290
μ/mm^{-1}	2.052	15.990
F(000)	2080.0	2163.0
Crystal size/mm^3	0.4 × 0.1 × 0.1	0.4 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.796 to 50	10.102 to 131.192
Index ranges	-31 ≤ h ≤ 21, -16 ≤ k ≤ 15, -20 ≤ l ≤ 19	-29 ≤ h ≤ 9, -10 ≤ k ≤ 9, -19 ≤ l ≤ 17
Reflections collected	25407	4607
Independent reflections	10883 [R_{int} = 0.0843, R_{sigma} = 0.1336]	3528 [R_{int} = 0.0604, R_{sigma} = 0.1027]
Data/restraints/parameters	10883/0/550	3528/0/183
Goodness-of-fit on F^2	1.060	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0870, wR_2 = 0.2294	R_1 = 0.1266, wR_2 = 0.3030
Final R indexes [all data]	R_1 = 0.1507, wR_2 = 0.2762	R_1 = 0.1862, wR_2 = 0.3609

Reference

1. L. Li, S. Tang, C. Wang, X. Lv, M. Jiang, H. Wu and X. Zhao, *Chem. Commun.*, 2014, **50**, 2304-2307.

2. M. Gustafsson, J. Su, H. Yue, Q. Yao and X. Zou, *Crystal Growth & Design*, 2012, **12**, 3243-3249.