One-dimensional channel-structured Eu-MOF for sensing of small organic molecules and Cu^{2+} ion

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Scheme S1 The basic synthetic route to the ligand of FBPT.

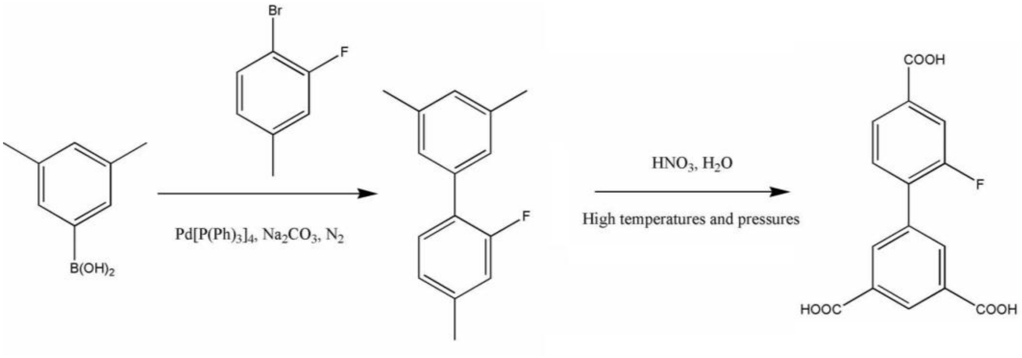

Figure S1 The ^{1}H NMR (400 MHz, DMSO-d^6) spectra for the ligand of FBPT.

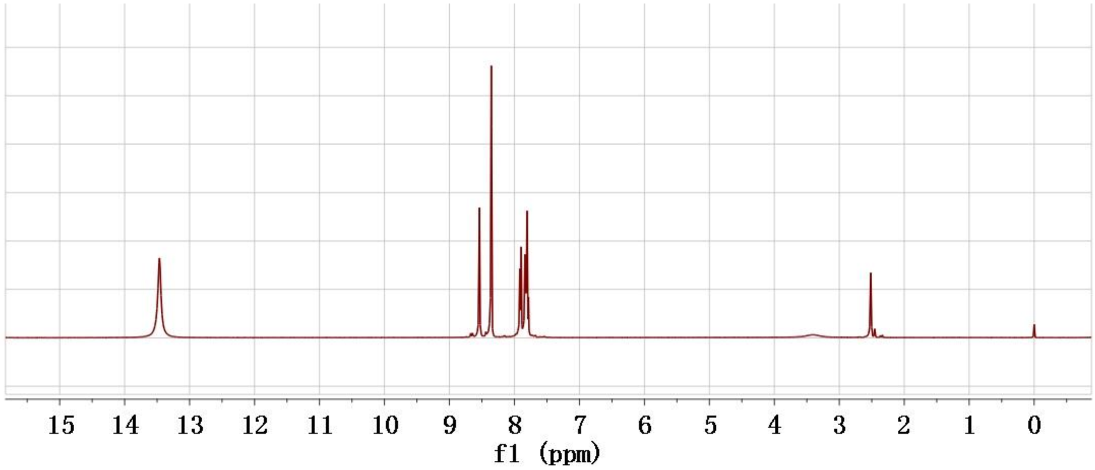

Figure S2 The excitation and emission spectra of **EuL** (left) and **TbL** (right) in the solution of DMF. The excitation and emission spectra were obtained with a HITACHIF-4500 spectrophotometer equipped with a 150 W xenon lamp as the excitation source.

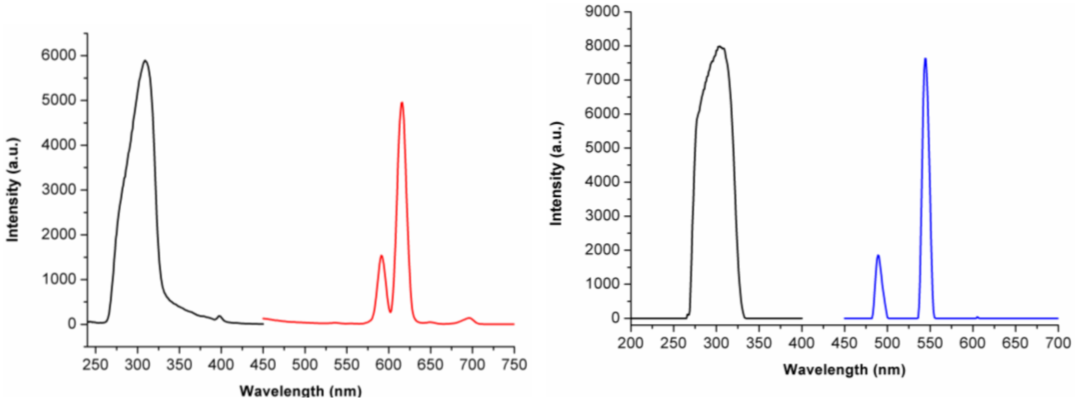

Figure S3 N_2 absorption and desorption curves for **EuL**. Nitrogen sorption experiments were carried out on a Quantachrome Autosorb Automated Gas Sorption System. Prior to the N_2 isotherm measurements at 77 K, the crystals of **EuL** were immersed in dry methanol for 3 days in a 25 mL glass bottle with three times renewal of the methanol repeatedly every day. Then, the sample (287 mg) was outgassed at 120 ºC for 24h.

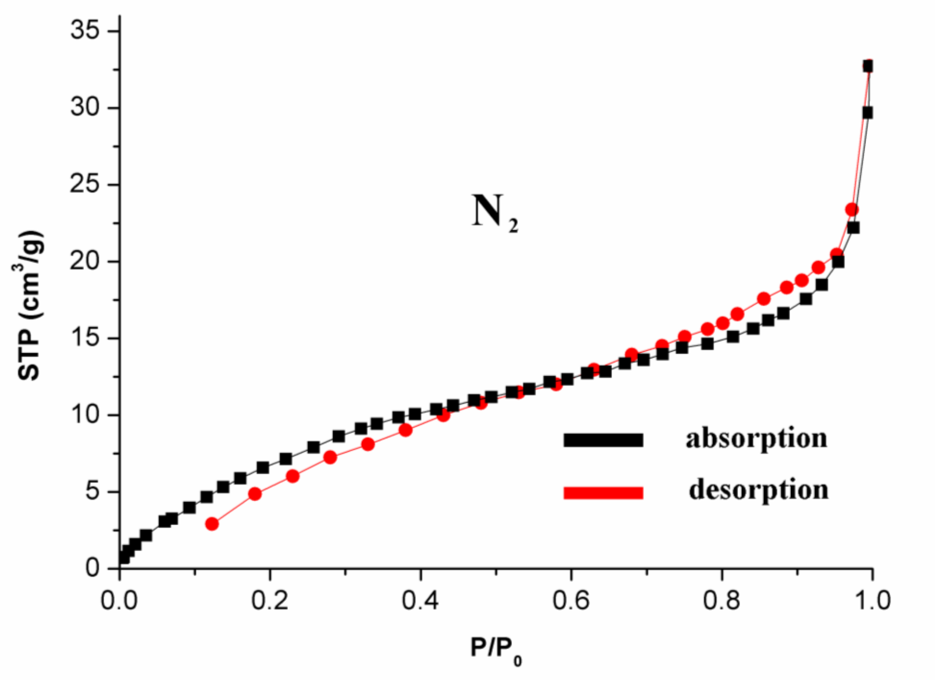

Figure S4 H_2 absorption and desorption curves for **EuL**. The H_2 gas sorption experiment of **EuL** was recorded on the analyzer as same as N_2.

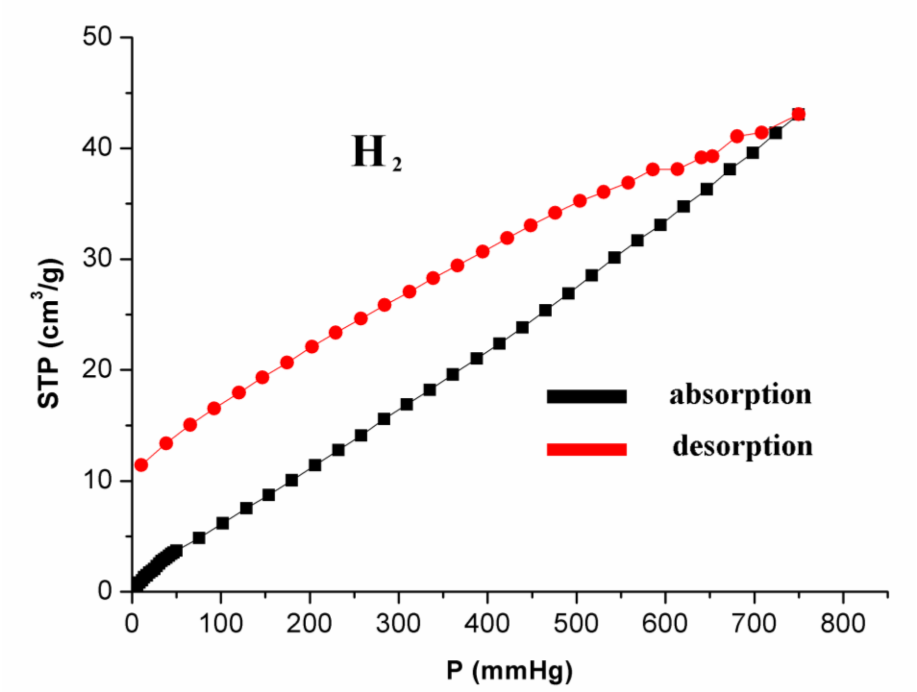

Figure S5 TG curves of solid I_2 and I_2-incorporated **EuL**. To get I_2-incorporated **EuL**, the outgassed sample of **EuL** was immersed in dry hexane solution with the concentration of I_2 in 0.1 mol/L for 3 days. Finally, the fresh sample was washed by hexane for 4-6 times to remove the I_2 on the surface of sample. The two samples were measured under air atmosphere from room temperature to 400 °C. There is a complete weight loss observed before 126 ºC for solid I_2. Quite significantly, the TG curve of I_2-incorporated **EuL** shows a hysteresis for the loss of the iodine as the solid I_2 molecules were not completely released until the temperature was 207 ºC, hinting that the I_2 molecules have entered the framework.

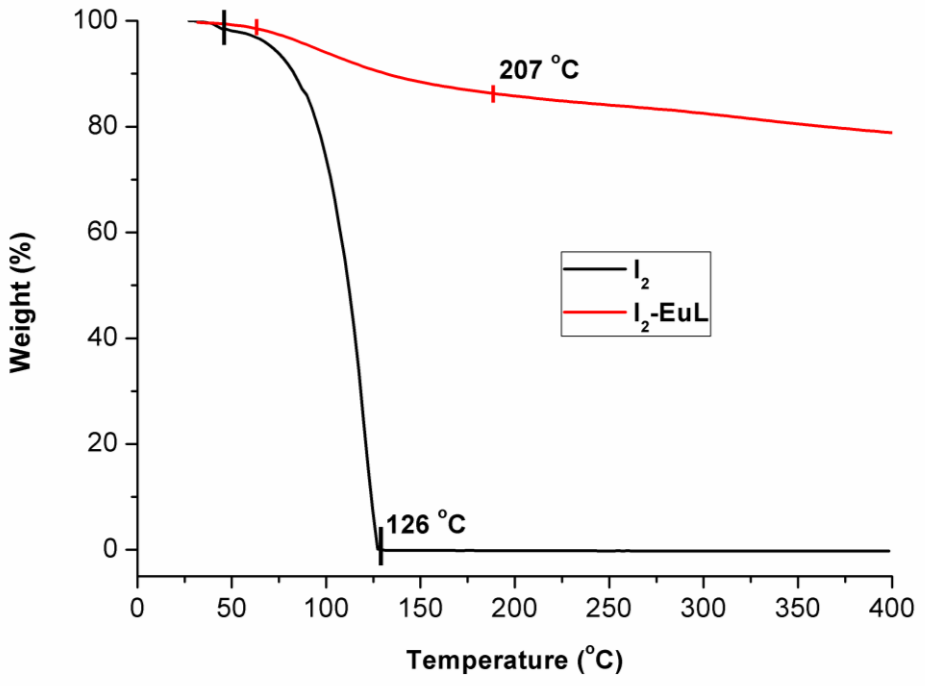

Figure S6 The XRD curves for the representative samples: a) the simulated curve; b) the sample immersed in I_2 (I_2-**EuL**); c) acetone-**EuL**; d) 1-phenylethanone-**EuL**; e) benzaldehyde-**EuL**; f) $Cu(NO_3)_2$-**EuL**. XRD patterns were performed on a D8 Focus (Bruker) diffractometer with Cu-Ka radiation Field-emission (λ = 0.15405 nm, continuous, 40 kV, 40 mA, increment 0.02°).

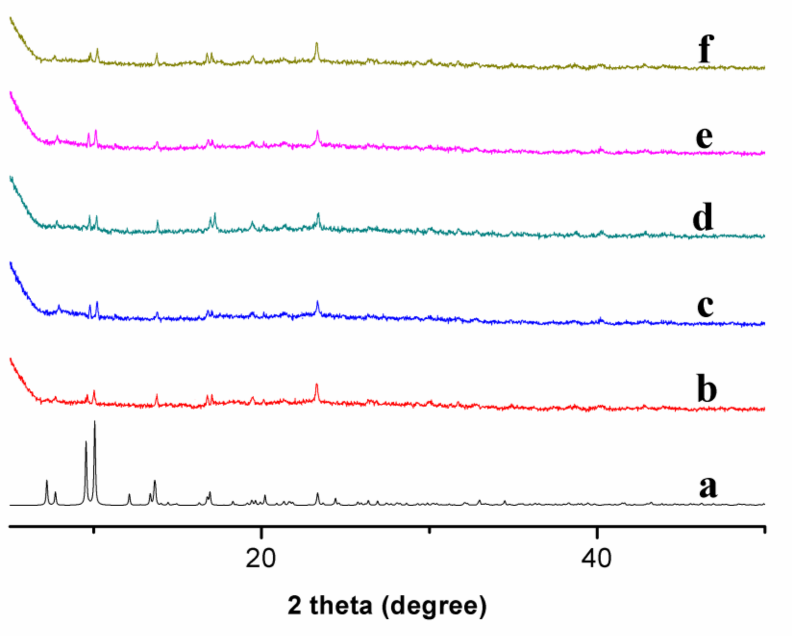

Figure S7 The luminescence relative intensity (the luminescence intensity of acetone-incorporated **EuL**/acetone-free **EuL**·DMF at 616 nm) of the **EuL** DMF suspension as a function of acetone content.

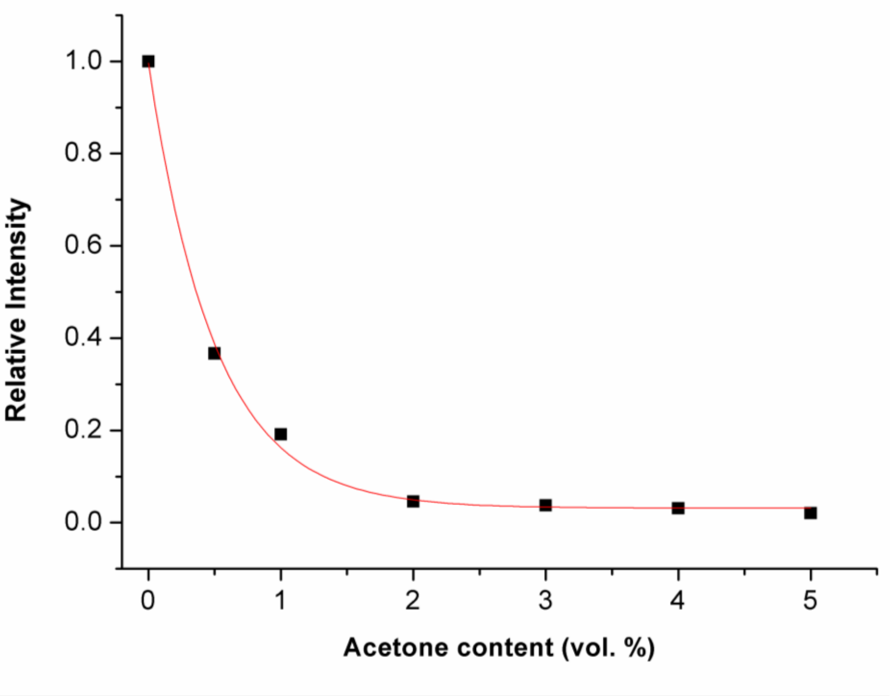

Figure S8 The luminescence lifetime curve for **EuL**.

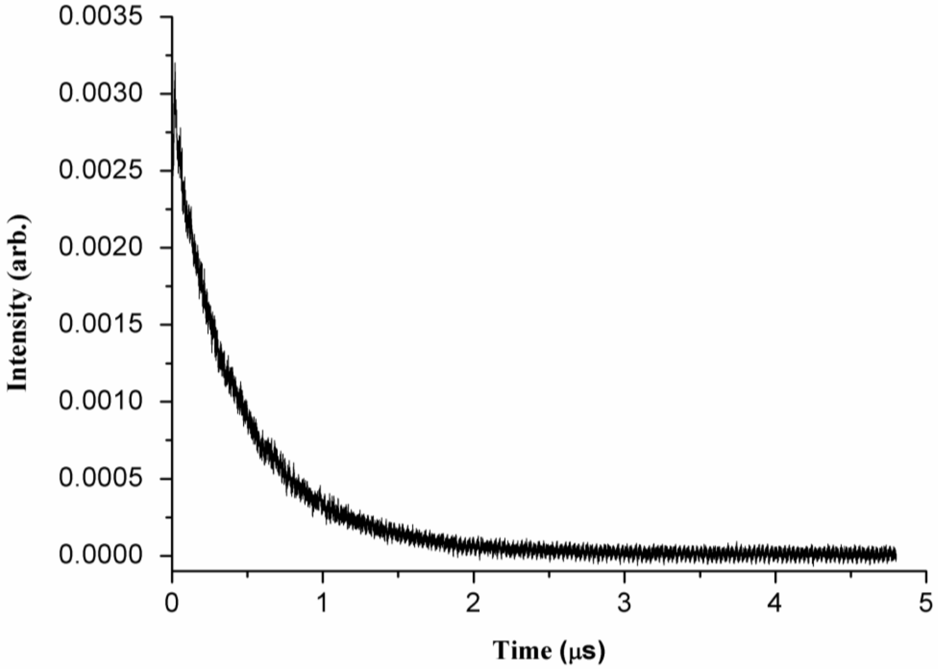

Figure S9 The relationship between relative intensity (the luminescence intensity of **EuL** DMF immediate / initial emulsion) and time at 616 nm.

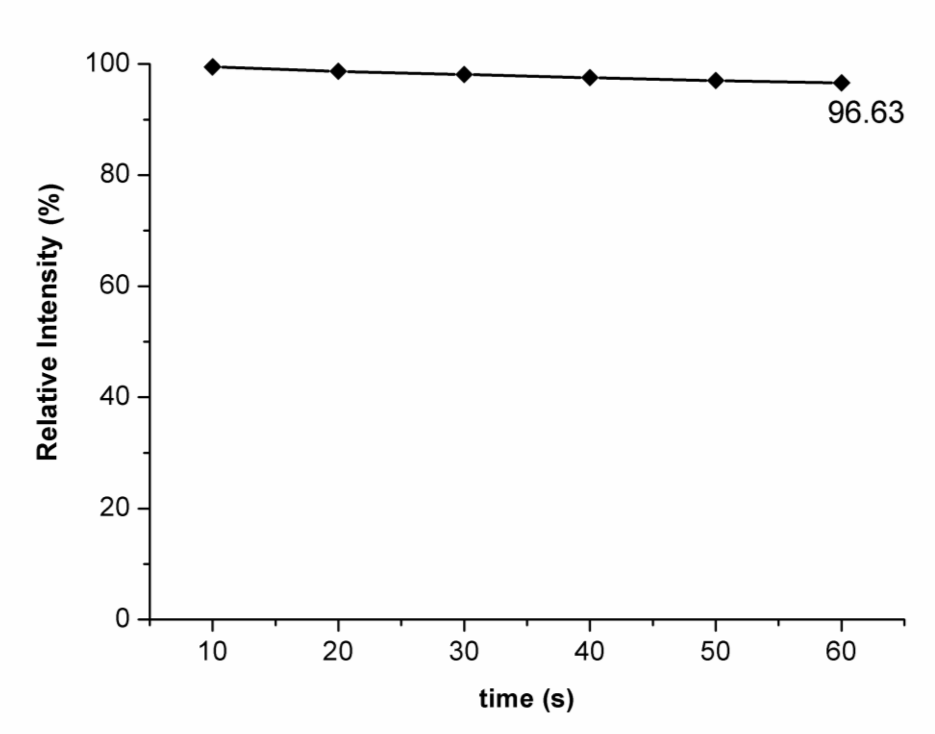

Figure S10 Comparison of the luminescence intensity of the $^5D_0 \rightarrow {}^7F_2$ transition of **EuL** exchanging with 0.01 M DMF solution of different organic molecules and metal ions.

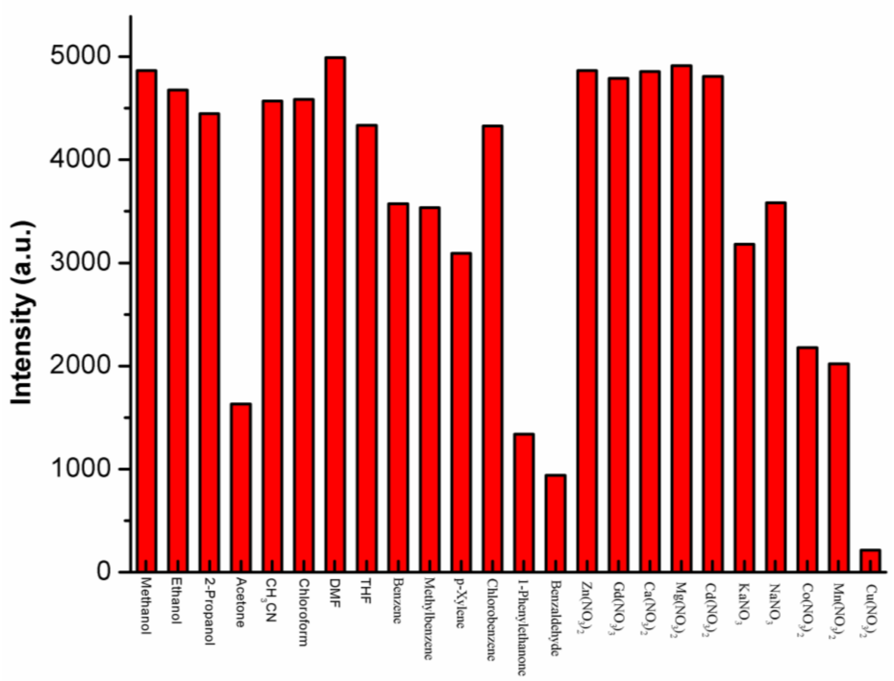

Figure S11 The PL spectra of **EuL** in Cu(NO$_3$)$_2$ DMF solution at low concentrations. As shown below, the **EuL** also has good performance in sensing Cu^{2+} when the concentration of Cu^{2+} is 10^{-6} M.

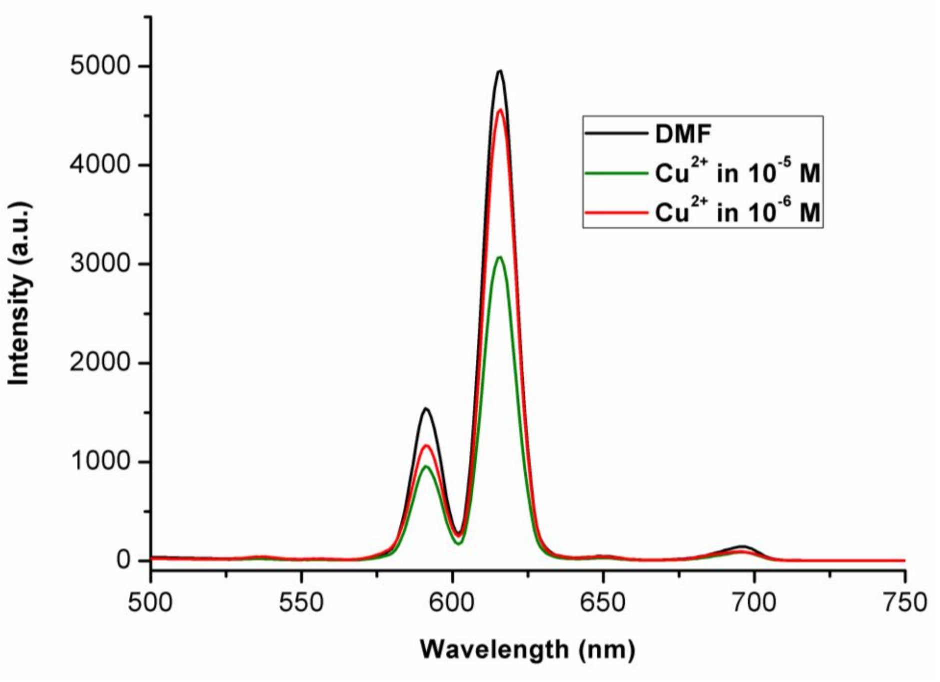

Figure S12 Stern-Volmer plots for the quenching of **EuL** by acetone. For acetone molecules, the quenching effect has been rationalized by the Stern-Volmer equation: $I_0/I = 1 + K_{sv}\,[M]$.[1] In the equation, the values I_0 and I are the luminescence intensity of acetone-free **EuL**·DMF and acetone-incorporated **EuL**, respectively, $[M]$ is the molar concentration of the acetone, and K_{sv} is the quenching effect coefficient of the acetone. To measure the luminescence intensity, acetone molecules are dissolved in DMF. As shown below, the K_{sv} value is 58.5 L/mol for acetone, indicating that acetone molecules have good quenching effect on the luminescence intensity of **EuL**.

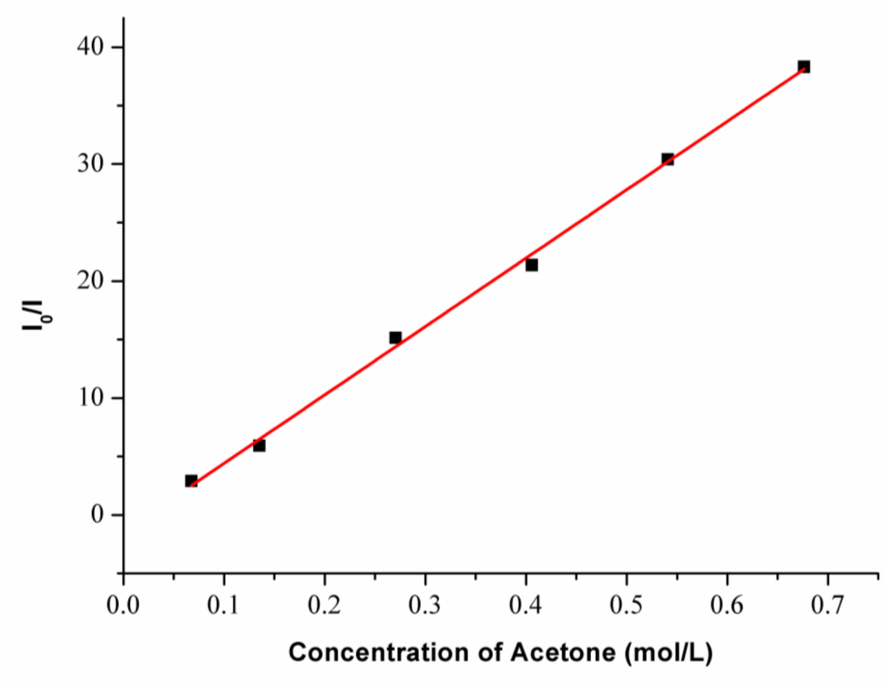

Figure S13 The energy-dispersive X-ray spectroscopy (EDS) line scan across a single crystal of Cu^{2+}-incorporated **EuL** for Cu. To verify Cu^{2+} into the pores, EDS line scan of Cu was employed. According to reported literatures,[2] equal-height EDS line-scan signals represent that the measuring element was evenly distributed in the three-dimension sample, while the signals of EDS line scan will be saddle-pattern with low central portion and two high edges if the measured element is distributed in the outer layer of the sample, because the edge of the sample contains higher surface area than the central portion when they have an equal volume (left-down figure). As shown in the right-down figure, the line scan for the single crystal of Cu^{2+}-incorporated **EuL** shows that the Cu signals are approximately equal in height, being not in accordance with typical surface adsorption, and suggesting that the Cu^{2+} ions have entered the pores of **EuL**.

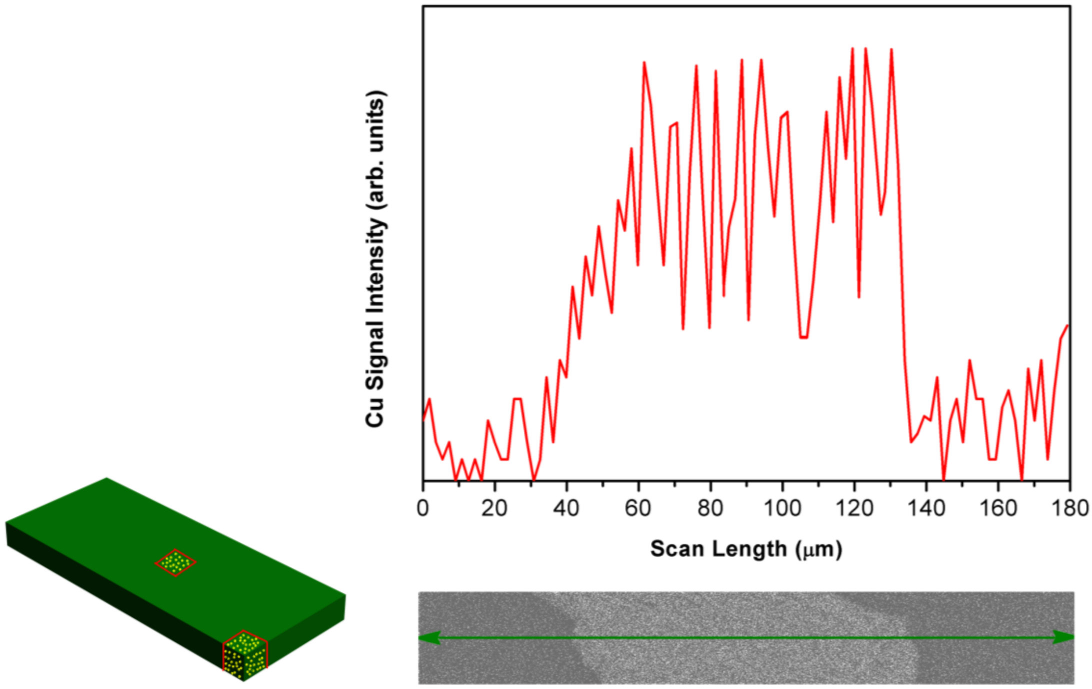

Table S1 The intensity ratios (R=I_2/I_1) between the $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transitions for **EuL** in different solvent molecules and metal ions. It is known that the transition $^5D_0 \rightarrow ^7F_1$ belongs to a magnetic dipolar transition that is insensitive to the surrounding environment of the Eu^{3+} ions, whereas $^5D_0 \rightarrow ^7F_2$ is an electric dipolar transition, and the relative intensity ratio (R) of $^5D_0 \rightarrow ^7F_1$ to $^5D_0 \rightarrow ^7F_2$ can indicate how far the local environment of the Eu^{3+} ions is centrosymmetric.[3] As calculated, the R values of samples are slightly different. Compared to the pure sample of **EuL**, chloroform has the greatest influence on the local environment of the Eu^{3+} ions.

	I_1 (intensity of $^5D_0 \rightarrow ^7F_1$)	I_2 (intensity of $^5D_0 \rightarrow ^7F_2$)	R ($R = I_2/I_1$)
methanol	741	3824	5.16
ethanol	785	3025	3.85
2-propanol	436	2282	5.23
acetone	93	331	3.55
acetonitrile	546	2543	4.65
chloroform	422	2708	6.41
DMF	1565	4960	3.17
THF	575	2048	3.56
benzene	197	957	4.85
methylbenzene	195	909	4.66
p-xylene	152	670	4.41
chlorobenzene	435	2514	5.77
1-phenylethanone	47	206	4.37
benzaldehyde	34	135	3.96
Zn^{2+}	1553	4910	3.16
Gd^{3+}	1542	4867	3.15
Ca^{2+}	1584	4894	3.09
Mg^{2+}	1538	4923	3.20
Cd^{2+}	1454	4871	3.35
K^+	1041	3581	3.44
Na^+	894	3112	3.48
Co^{3+}	509	2096	4.11
Mn^{2+}	523	2020	3.86
Cu^{2+}	54	193	3.55
Pure **EuL**	271	828	3.06

Table S2 The intensity ratios (R) between the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions for acetone-incorporated **EuL** in different quantities of acetone. As shown below, the R values of samples with different doping quantities of acetone did not change on the whole, even up to 10 vol%. Besides, the XRD patterns of five different samples also state that there is no formation of new complexes during the addition of the quencher. The possible reason for the high capacity of doping acetone may be attributed to the special structure of this material.

Sample name	The quantity of acetone (vol%)	R ($R = I_2/I_1$)
1	0.1	3.13
2	1	3.41
3	2	3.36
4	5	3.47
5	10	3.62

References:

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(2) a) F. Wang, R. R. Deng, J. Wang, Q. X. Wang, Y. Han, H. M. Zhu, X. Y. Chen and X. G. Liu, *Nat. Mater.*, 2011, **10**, 968. b) K. A. Abel, J. C. Boyer, C. M. Andrei and F. C. J. M. van Veggel, *J. Phys. Chem. Lett.*, 2011, **2**, 18.

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