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Supporting information

Polyrotaxane-like metal-organic framework showing luminescent sensing of Eu^{3+} cation and proton conductivity

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Table S1. Selected bond lengths (Å) and bond angles (°)

Bond lengths (Å)			
Cd(1)-O(4)	2.246(3)	Cd(1)-O(12)#1	2.558(3)
Cd(1)-O(13)#1	2.270(3)	Cd(2)-O(15)#2	2.303(3)
Cd(1)-O(5)	2.387(3)	Cd(2)-O(7)	2.359(3)
Cd(1)-O(6)	2.415(3)	Cd(2)-O(8)	2.171(3)
Cd(1)-O(1)	2.419(4)	Cd(2)-O(11)#2	2.428(3)
Cd(1)-O(14)	2.541(3)		
Bond angles (°)			
O(4)-Cd(1)-O(13)#3	133.19(13)	O(1)-Cd(1)-O(14)	80.16(15)
O(4)-Cd(1)-O(5)	96.31(13)	O(6)-Cd(1)-O(14)	86.00(11)
O(13)#3-Cd(1)-O(5)	92.56(14)	O(4)-Cd(1)-O(12)#3	80.49(11)
O(4)-Cd(1)-O(1)	115.14(15)	O(13)#3-Cd(1)-O(12)#3	53.29(12)
O(13)#3-Cd(1)-O(1)	90.43(15)	O(5)-Cd(1)-O(12)#3	91.83(12)
O(5)-Cd(1)-O(1)	132.66(13)	O(1)-Cd(1)-O(12)#3	126.13(14)
O(4)-Cd(1)-O(6)	130.68(11)	O(6)-Cd(1)-O(12)#3	131.62(11)
O(13)#3-Cd(1)-O(6)	90.95(12)	O(14)-Cd(1)-O(12)#3	134.17(11)
O(5)-Cd(1)-O(6)	54.33(10)	O(8)-Cd(2)-O(7)	80.88(14)
O(1)-Cd(1)-O(6)	78.40(13)	O(15)#4-Cd(2)-O(7)	85.42(13)
O(4)-Cd(1)-O(14)	53.68(12)	O(8)-Cd(2)-O(11)#4	105.03(14)
O(13)#3-Cd(1)-O(14)	170.51(14)	O(15)#4-Cd(2)-O(11)#4	55.56(13)
O(5)-Cd(1)-O(14)	92.95(15)	O(7)-Cd(2)-O(11)#4	138.37(13)

Symmetry transformations used to generate equivalent atoms: #1= x,-y+2,z-1/2; #2 = x,-y-1,z-1/2; #3 =x,-y+2,z+1/2; #4= x,-y-1,z+1/2;

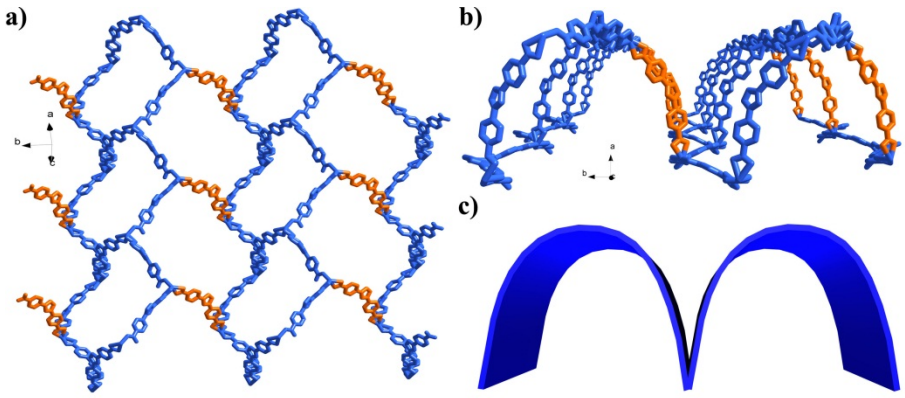


Fig. S1 a) and b) The loop-like chains are bridged by L^- to form a 2D infinite bow-shaped (6,3) layer. C) schematic representation of the 2D infinite bow-shaped (6,3) layer.

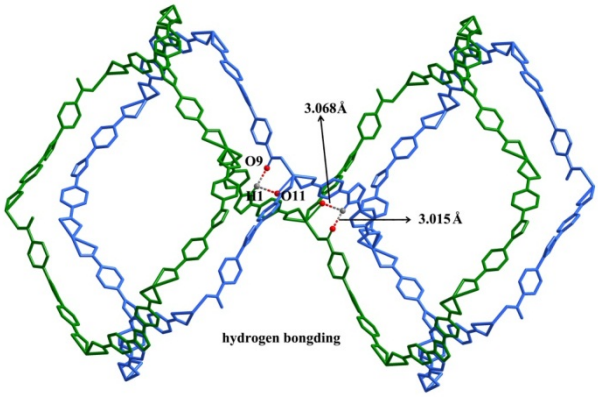
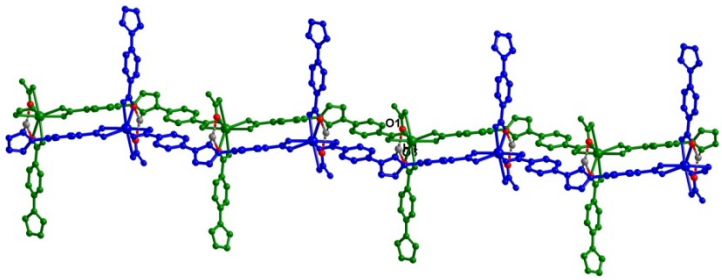
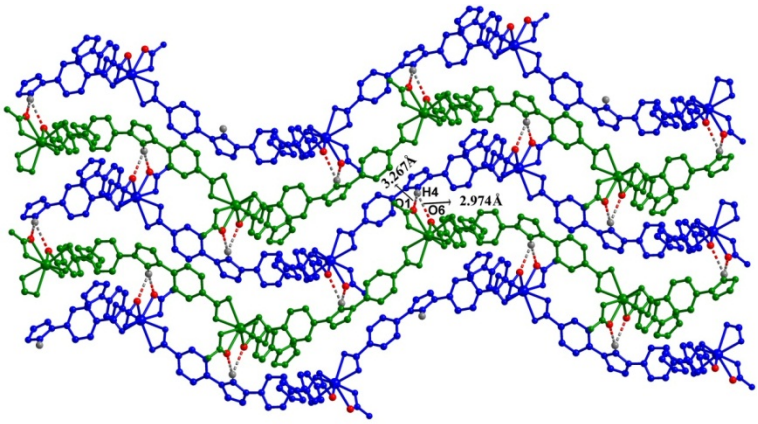


Fig. S2 The strong hydrogen bonding (C-H···O = 3.015-3.068 Å) between the oxygen atoms belong to the $[Cd_6L_6]$ 6-membered ring from one 3-fold interpenetration network and the highly acidic methylene hydrogen of the imidazolium moiety of the ligand rod from another 3-fold interpenetration network.



(a)



(b)

Fig. S3 (a) The interdigitated model in **1**. (b) The strong hydrogen bonding (C-H···O = 2.345-2.630 Å) in the interdigitated model in **1.**

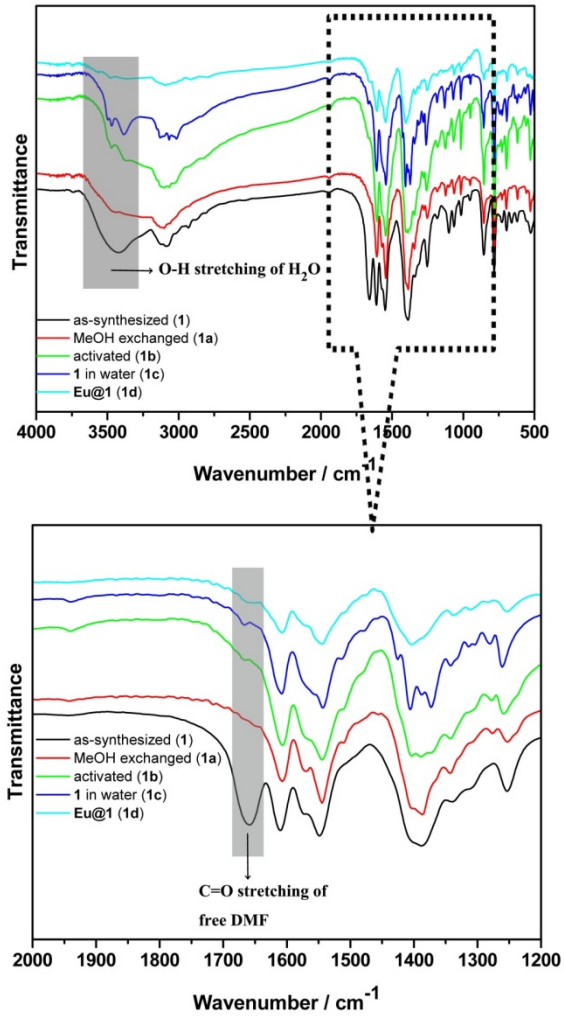


Fig. S4 Infrared spectrum of fresh **1,** MeOH-exchanged (**1a**), activated (**1b**), **1** in water (**1c**), and **Eu@1** (**1d**). The broad peak at 3421 cm^{-1} in the IR spectrum of **1** indicates the presence of water molecules in the structure. Sharp peaks at 1658 and 1610 cm^{-1} ascribe to CO stretching vibrations of the free and coordinated dimethylformamide molecules, respectively, inside the channels. Another sharp peak at 1388 cm^{-1} appears due to the presence of coordinated nitrate anions. The complete removal of the free DMF and H_2O molecules was verified by the disappearance of the vibration at 1658 cm^{-1} and 3421 cm^{-1} in **1a** and **1b**, respectively. Interestingly, when fresh samples of **1** were immersed in 0.3 mol / L DMF solution of $Eu(NO_3)_3$ for 5 days to get **Eu@1,** the IR spectrum of **Eu@1** shows scarcely any free DMF and H_2O molecules in it.

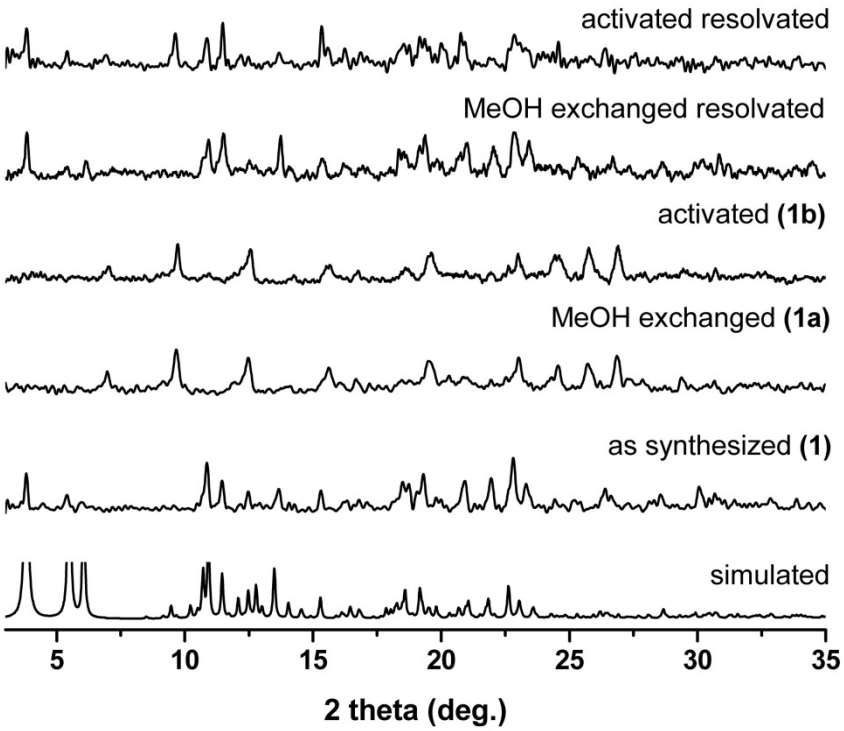


Fig. S5 PXRD profiles of as-synthesized (**1**), MeOH-exchanged (**1a**), activated (**1b**), and resolvated samples.

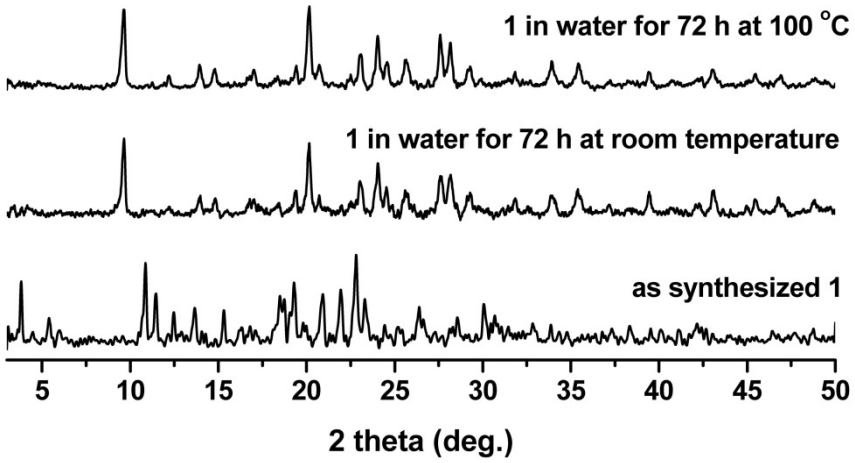


Fig. S6 PXRD profiles of as-synthesized samples and the as-synthesized samples in water under different conditions.

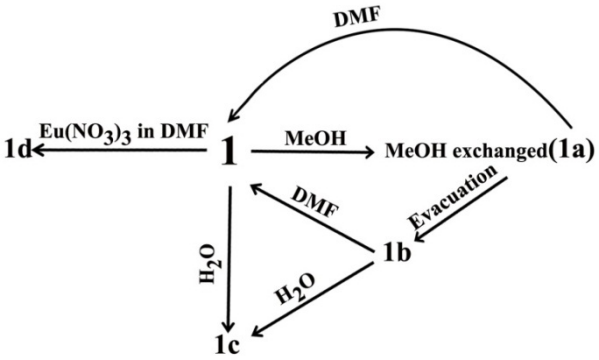
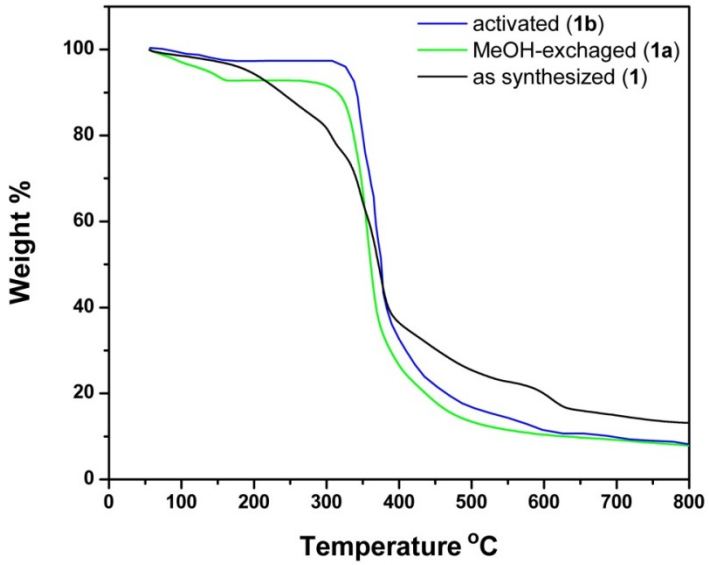
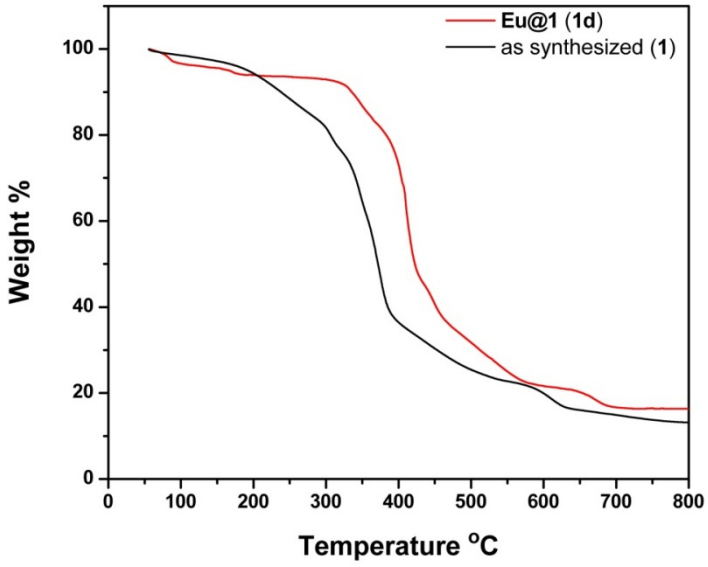


Fig. S7 The phase transformation during different process.



(a)



(b)

Fig. S8 (a) TGA curves of compound **1**, MeOH-exchanged samples (**1a**), and activated samples of **1b**. (b) TGA curves of compound **1** and samples of **Eu@1** (**1d**).

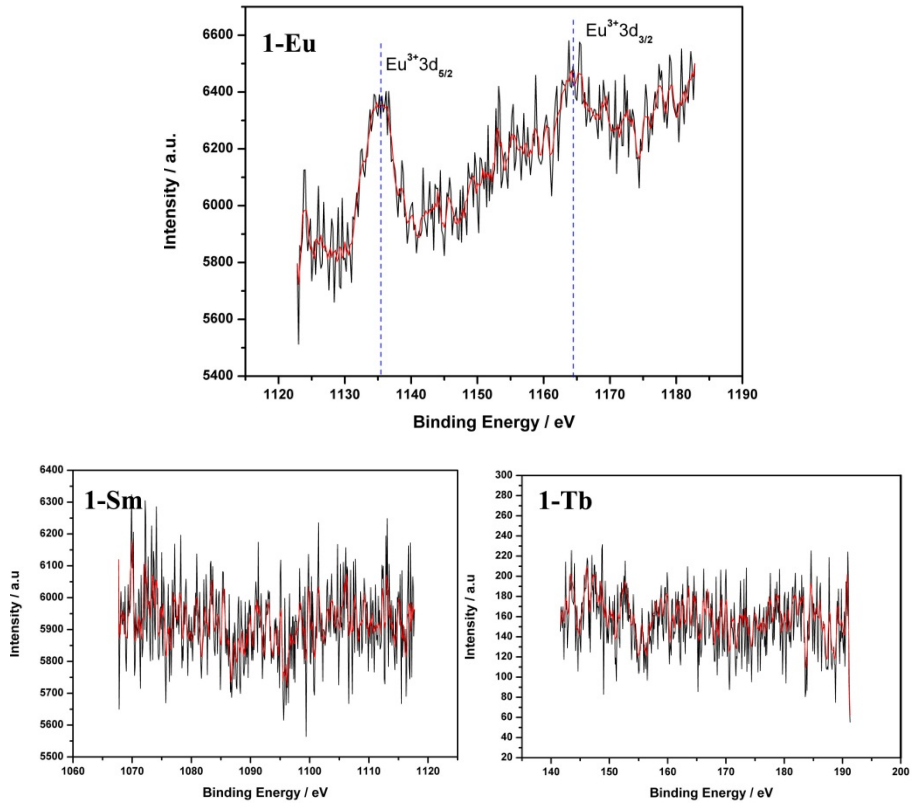


Fig. S9 Eu 3d, Sm 3d, Tb 4d XPS spectra for 1-Eu, 1-Sm, 1-Tb, respectively. **1-Ln^{3+}** represents the samples which were immersed in 0.3 mol / L DMF solution of nitrate salts of Ln^{3+} cations for 5 days. In the XPS spectrum of **1-Eu**, the peaks at 1135.2 eV and 1165.1 eV are assigned to the Eu 3d5/2 and Eu 3d3/2, respectively. But for **1-Sm** and **1-Tb**, no peaks for Sm 3d and Tb 4d are found.

Table S2. ICP analysis for the samples which were immersed in 0.3 mol / L DMF solution of nitrate salts of Ln^{3+} cations for 5 days

ICP	1-Eu	1-Tb	1-Sm	1-Dy
Cd	19.81%	20.97%	20.95%	21.00%
Ln	2.95%	0	0	0
Ln:Cd(wt:wt)	0.15:1	0	0	0
Ln:Cd(molar:molar)	0.11:1	0	0	0

1-Ln^{3+} represents the samples which were immersed in 0.3 mol / L DMF solution of nitrate salts of Ln^{3+} cations for 5 days.

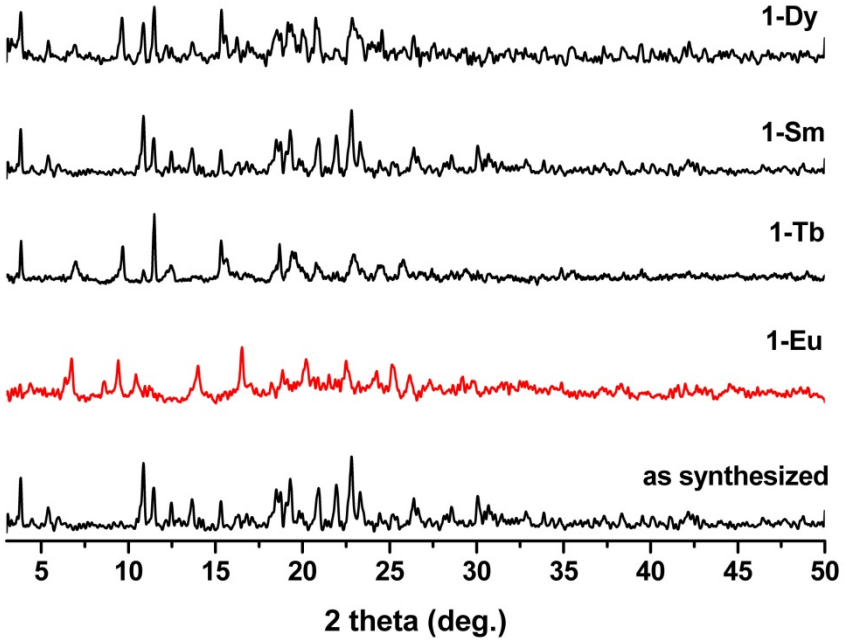


Fig. S10 PXRD profiles of as-synthesized samples and **1-Ln** samples which were soaked in 0.3 mol / L DMF solution of nitrate salts of Ln^{3+} cations for 5 days.

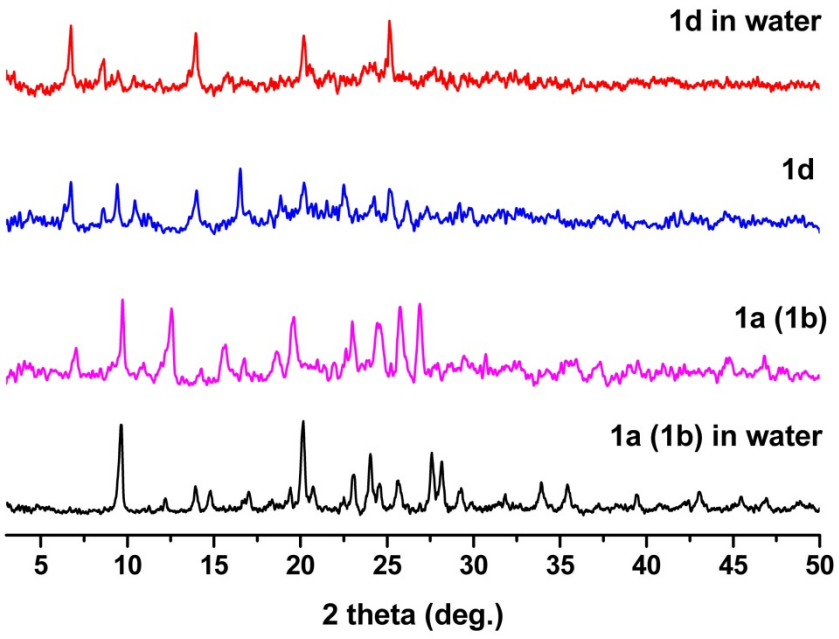
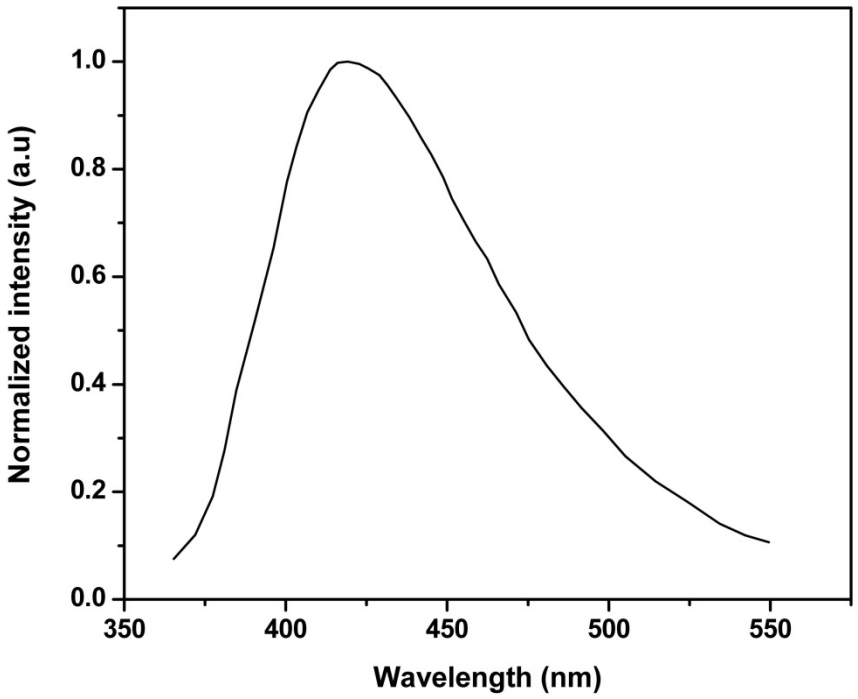
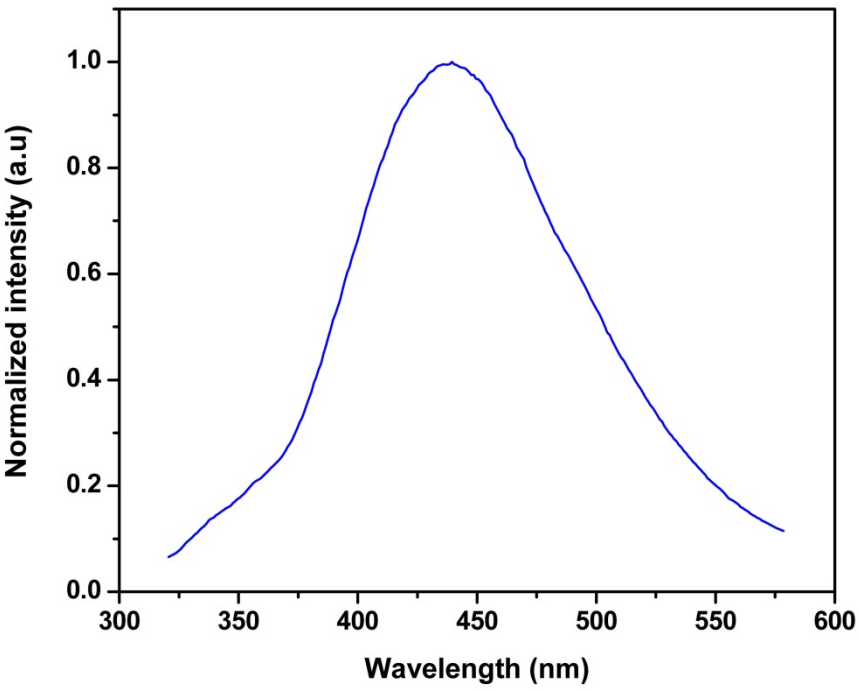


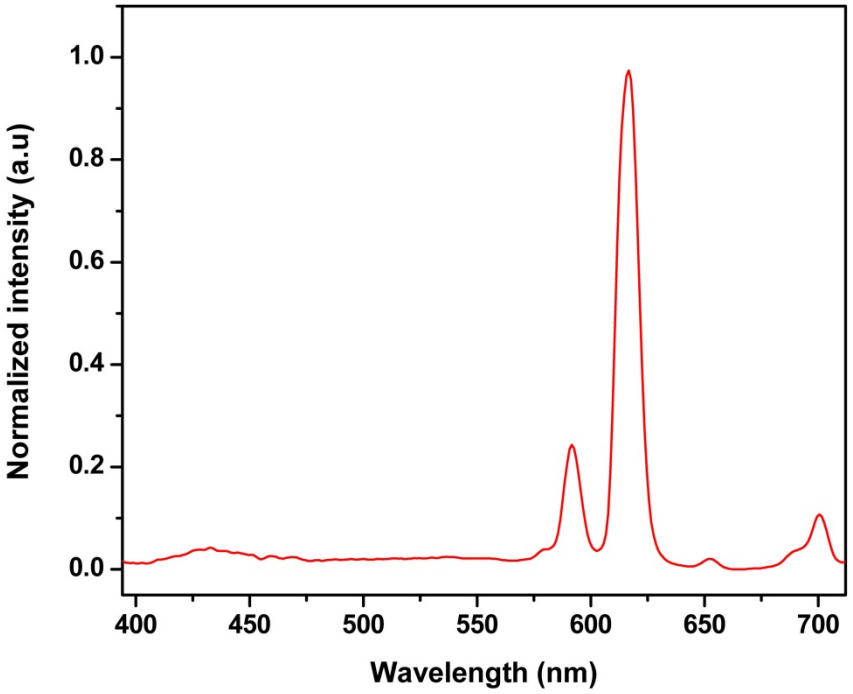
Fig. S11 PXRD profiles of MeOH-exchanged (**1a**) samples, desolvated samples (**1b**), samples of **1a** or **1b** in water, samples of **Eu@1** (**1d**), and samples of **1d** in water.


Normalized intensity (a.u)
1.0
0.8
0.6
0.4
0.2
0.0
350
400
450
500
550
Wavelength (nm)

(a)

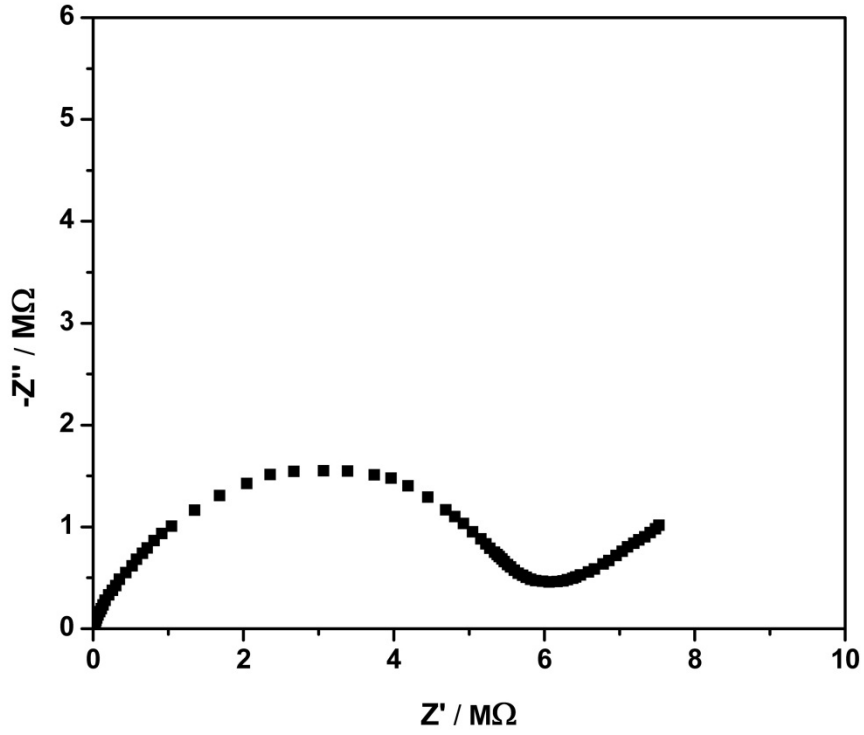

Normalized intensity (a.u)
1.0
0.8
0.6
0.4
0.2
0.0
300
350
400
450
500
550
600
Wavelength (nm)

(b)

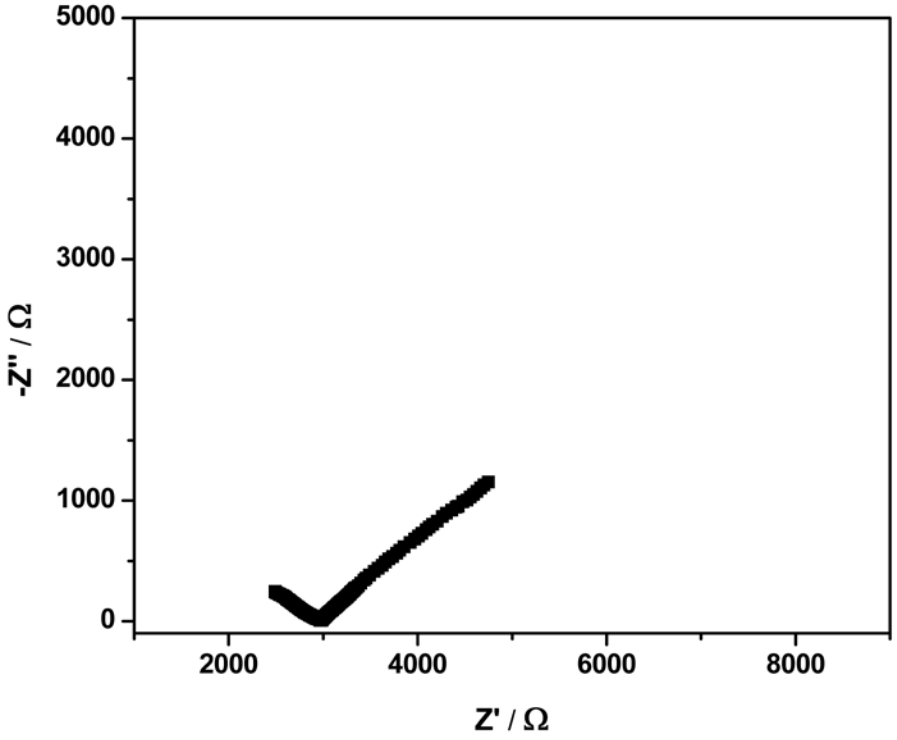


(c)

Fig. S12 (a) Solid-state photoluminescent spectra of $H_2L^+Cl^-$ (λ_{ex} = 340 nm and λ_{em} = 420 nm). (b) Solid-state photoluminescent spectra of **1** (λ_{ex} = 340 nm and λ_{em} = 438 nm). (c) The visible emission spectra of **Eu@ 1** with λ_{ex} = 340 nm in DMF.



(a)



(b)

Fig. S13 Some of the Nyquist plots for **1** at 298 K under different relative humidity (a) 40 % (b) 98 %.