SUPPORTING INFORMATION

A microporous europium–organic framework anchored with open -COOH groups for selective cation sensing**

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Table of Content

S1. Materials and Methods

1.1. Materials and Instruments.

Reactions were carried out in 25 ml Teflon-lined autoclave under autogenous pressure. All the reactants are of reagent-grade quality and used as commercially purchased without further purification. The power X-ray diffraction patterns (PXRD) were collected by a Bruker D8 Advance using Cu Kα radiation (λ = 0.154 nm). Single gas adsorption measurements were performed in the Accelerated Surface Area and Porosimetry 2020 (ASAP2020) System, in which **BMM-7** was determined in a clean ultra high vacuum system and the N_2 sorption measurement was performed at 77 K. Elemental analyses for C, H, N were carried out on a German Elementary Vario EL III instrument. Thermogravimetric analyses were recorded on a NETZSCH STA 449C unit at a heating rate of 10 $^{o}C\cdot$ min^{-1} under flowing nitrogen atmosphere. Scanning transmission electron microscopy (STEM) and energy dispersive X-ray spectroscopy (EDS) analyses were carried out under JEOL JEM-2100F microscope operating at an accelerating voltage of 200 kV. Fluorescent spectra were measured on an Edinburgh Instruments analyzer model FLS920 with 450W xenon light.

1.2. Synthesis of $[Eu_2(BPTC)(H_2BPTC)(DMF)_4]\bullet 4DMF\bullet 10H_2O$ (BMM-7)

A mixture of $Eu(NO_3)_3$ (0.10 mmol, 45 mg) and H_4BPTC (0.10 mmol, 33 mg, H_3BPTC = Biphenyl-3,3',5,5'-tetracarboxylic acid) in the solvent of N,N'-Dimethylformamide (DMF, 5 mL) with an additional drop of HNO_3 (0.1 ml, 65 wt %) was sealed in a 25 ml autoclave, which was heated at 150 ^{o}C for 4 days, and cooled gradually to room temperature in 1 day. After washed by fresh DMF and ethanol solvent in turn, the colorless crystals were obtained in *ca*. ~50% yield based on the organic ligand. Elemental analysis was calculated for **BMM-7**: C, 39.03%; H, 5.26%; N, 6.50%.. Found: C, 38.84%; H, 5.49%; N, 6.29%. The phase purity of the sample is confirmed by PXRD (Figure S4). Moreover, the as-synthesized crystals and the Cu(II)-trapped **BMM-7** sample (**Cu^{2+}-BMM-7**) have also been confirmed by EDX and the elemental mapping in main article, respectively.

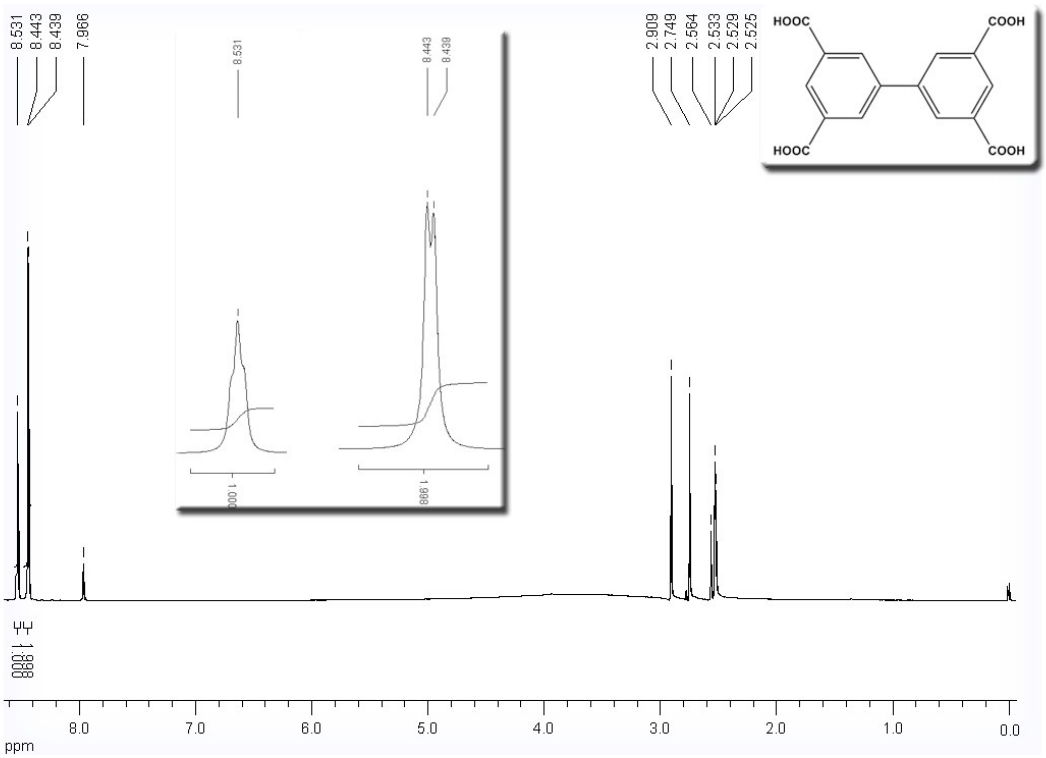


Figure S1. ^{1}H-NMR spectrum of the H_4BPTC ligand was measured in DMSO-d_6.

1.3. Single-Crystal X-ray Crystallography

The structure data of **BMM-7** were collected on a SuperNova, Dual, Cu at zero, Atlas diffractometer. The crystal was kept at 100 K during data collection. By Using Olex2,[S1] the structure was solved with the ShelXS[S2] structure solution program using Direct Methods and refined with the ShelXL[S3] refinement package using Least Squares minimisation. Crystallographic data and structure refinement parameters for this single crystal are listed in Table S1 below. In the meantime, we have also applied PLATON/SQUEEZE[S4] to calculate the contribution to the diffraction from the solvent region and thereby produced a set of solvent-free diffraction intensities. The final formulae were calculated from the SQUEEZE results combined with elemental analysis data and TGA data. The solvent-squeezed structure was denoted as **BMM-7-Squeezed**. More details on the crystallographic studies as well as atomic displacement parameters are given in Supporting Information as CIF files. Crystallographic data for the structure reported in this paper has been deposited. The following crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the

deposition number (CCDC No.) 1496638 and 1496639 for **BMM-7** and **BMM-7-Squeezed**, respectively. These data can be obtained free of charge via *www.ccdc.cam.ac.uk/data_request/ cif.*

Table S1. Summary of Crystal Data and Refinement Results

Items	**BMM-7**	**BMM-7-Squeezed**
formula	$EuC_{28}N_4O_{12}H_{35}$	$EuC_{22}N_2O_{10}H_{20}$
M	771.56	624.36
crystal system	Triclinic	Triclinic
space group	*P-1* (#. 2)	*P-1* (#. 2)
a (Å)	10.4640(4)	10.4702(4)
b (Å)	12.0162(5)	12.0131(5)
c (Å)	13.1846(5)	13.1765(6)
α (°)	83.780(3)	83.827(4)
β (°)	86.014(3)	85.920(4)
γ (°)	75.659(4)	75.686(4)
V (Å^3)	1595.12(11)	1594.86(12)
T (K)	173 (2)	173 (2)
Z	2	2
F(000)	780	618
R_{int}	0.0350	0.0292
R_1 (I>2σ(I))	0.0305	0.0278
wR_2	0.0672	0.0725
Goof	1.036	1.044
CCDC number	1496638	1496639

BMM *denotes Bifunctional Method Material; More details see CIF files.*

S2. Additional X-ray Crystal Structural Figures

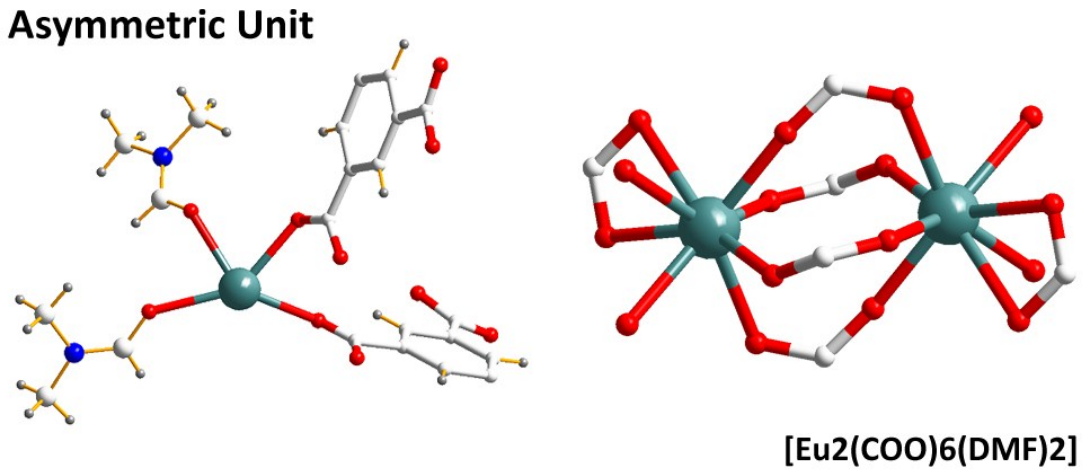


Figure S2. Asymmetric unit and secondary building unit for **BMM-7**, respectively.

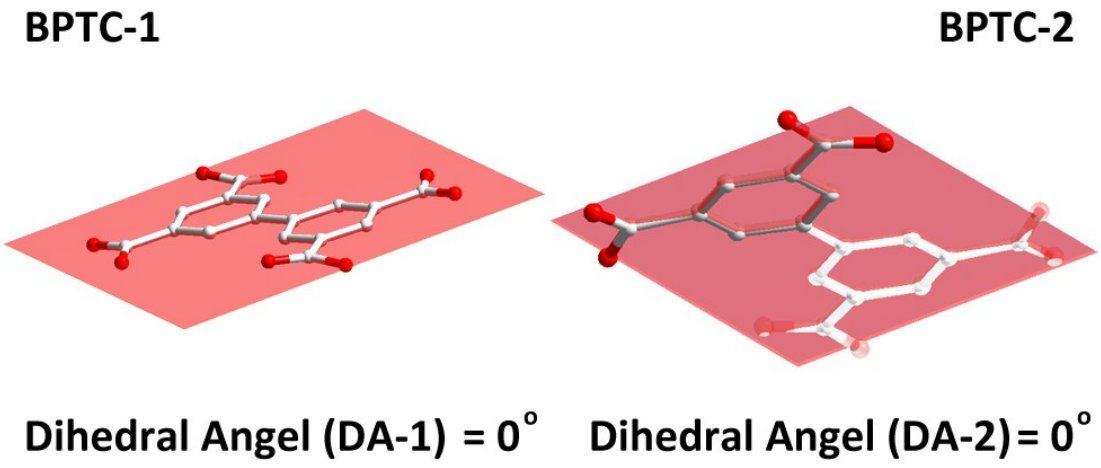


Figure S3. The dihedral angels of BPTC-1 and BPTC-2 in the **BMM-7**, and their values are 0^{O}.

S3. Topological Analysis Results by TOPOS 4.0

1:C22 H20 Eu N2 O10 (**BMM-7**)

Topology for BPTC-1

BPTC-1 links by bridge ligands and has

Common vertex with					R(A-A)	
SBU	0.0000	0.5000	0.5000	(0 0 0)	6.924A	1
SBU	1.0000	-0.5000	0.5000	(1-1 0)	6.924A	1
SBU	1.0000	0.5000	0.5000	(1 0 0)	8.890A	1
SBU	0.0000	-0.5000	0.5000	(0-1 0)	8.890A	1
BPTC-1	0.5000	0.0000	-0.5000	(0 0-1)	13.177A	1
BPTC-1	0.5000	0.0000	1.5000	(0 0 1)	13.177A	1

Topology for SBU

SBU [$Eu_2(COO)_6(DMF)_2$] links by bridge ligands and has

Common vertex with					R(A-A)	
BPTC-1	0.5000	0.0000	0.5000	(0 0 0)	6.924A	1
BPTC-1	-0.5000	1.0000	0.5000	(-1 1 0)	6.924A	1
BPTC-1	-0.5000	0.0000	0.5000	(-1 0 0)	8.890A	1
BPTC-1	0.5000	1.0000	0.5000	(0 1 0)	8.890A	1

Structure consists of 3D framework with Eu-BPTC

Coordination sequences

BPTC-1:	1	2	3	4	5	6	7	8	9	10
Num	6	18	38	66	102	146	198	258	326	402
Cum	7	25	63	129	231	377	575	833	1159	1561

SBU:	1	2	3	4	5	6	7	8	9	10
Num	4	16	38	66	102	146	198	258	326	402
Cum	5	21	59	125	227	373	571	829	1155	1557

TD10=1559

Vertex symbols for selected sublattice

BPTC-1 Point (Schlafli) symbol:{4^4.6^10.8}

Extended point symbol:[4.4.4.4.6(2).6(2).6(5).6(5).6(5).6(5).6(5).6(5).6(5).6(5).8(20)]

SBU Point (Schlafli) symbol:{4^4.6^2}

Extended point symbol:[4.4.4.4.6(4).6(4)]

Point (Schlafli) symbol for net: {4^4.6^10.8}{4^4.6^2}

4,6-c net with stoichiometry (4-c)(6-c); 2-nodal net

Topological type: **fsc**

S4. PXRD and TGA data

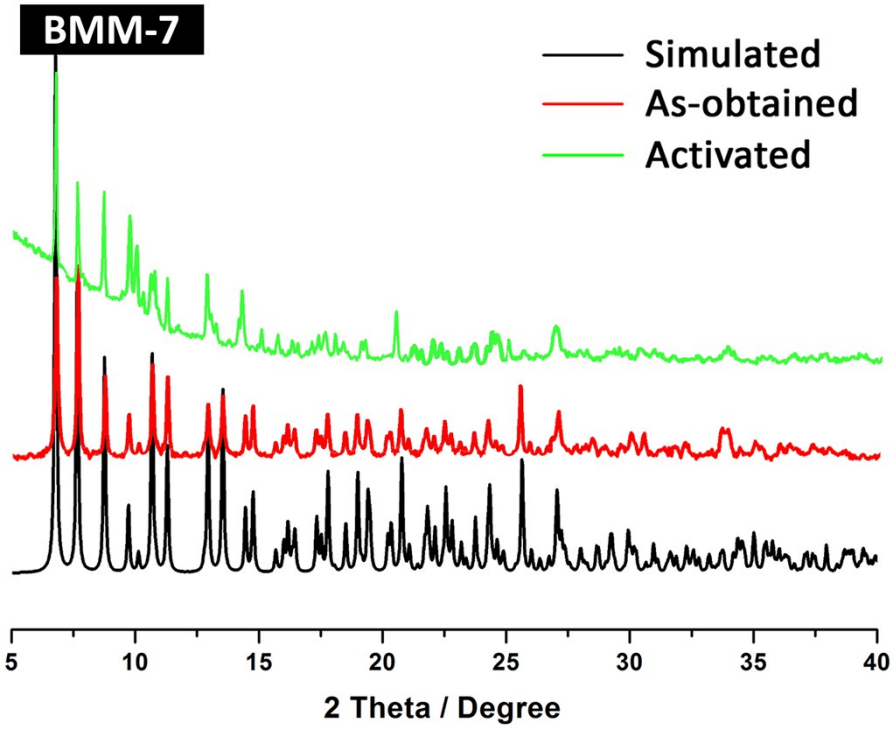


Figure S4. PXRD patterns of crystalline materials used in the manuscript: simulated from the crystallographic information file (black); from the as-prepared sample (red); from the desolvated sample by thermal activation (green).

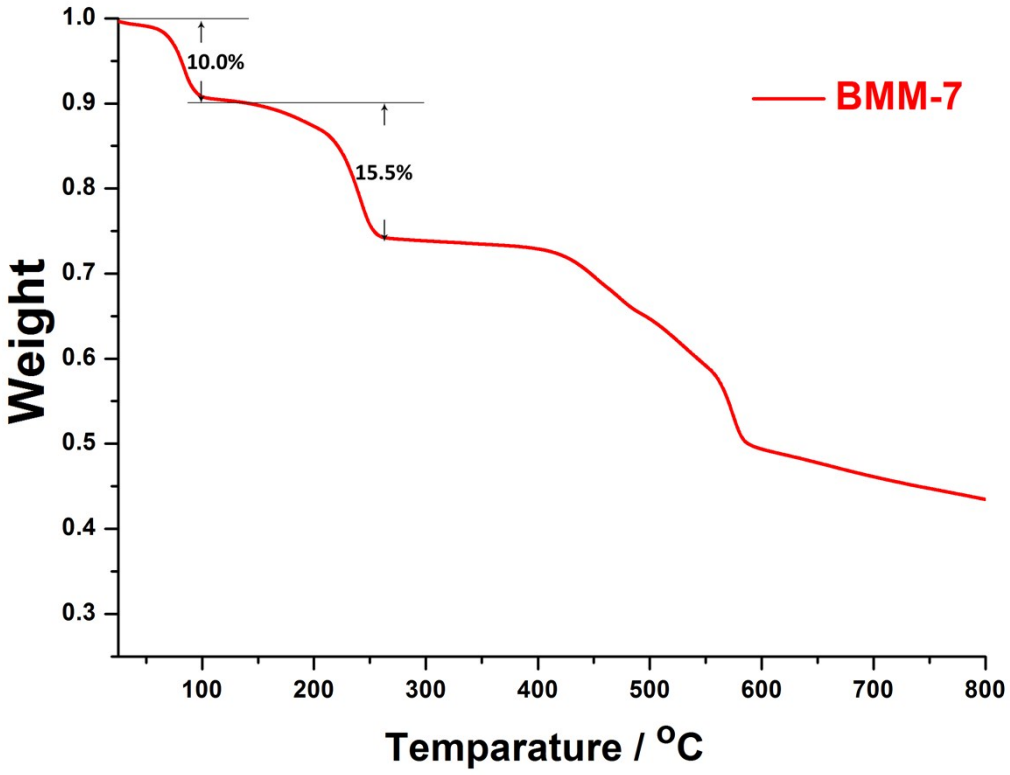


Figure S5. TGA curves for **BMM-7**.

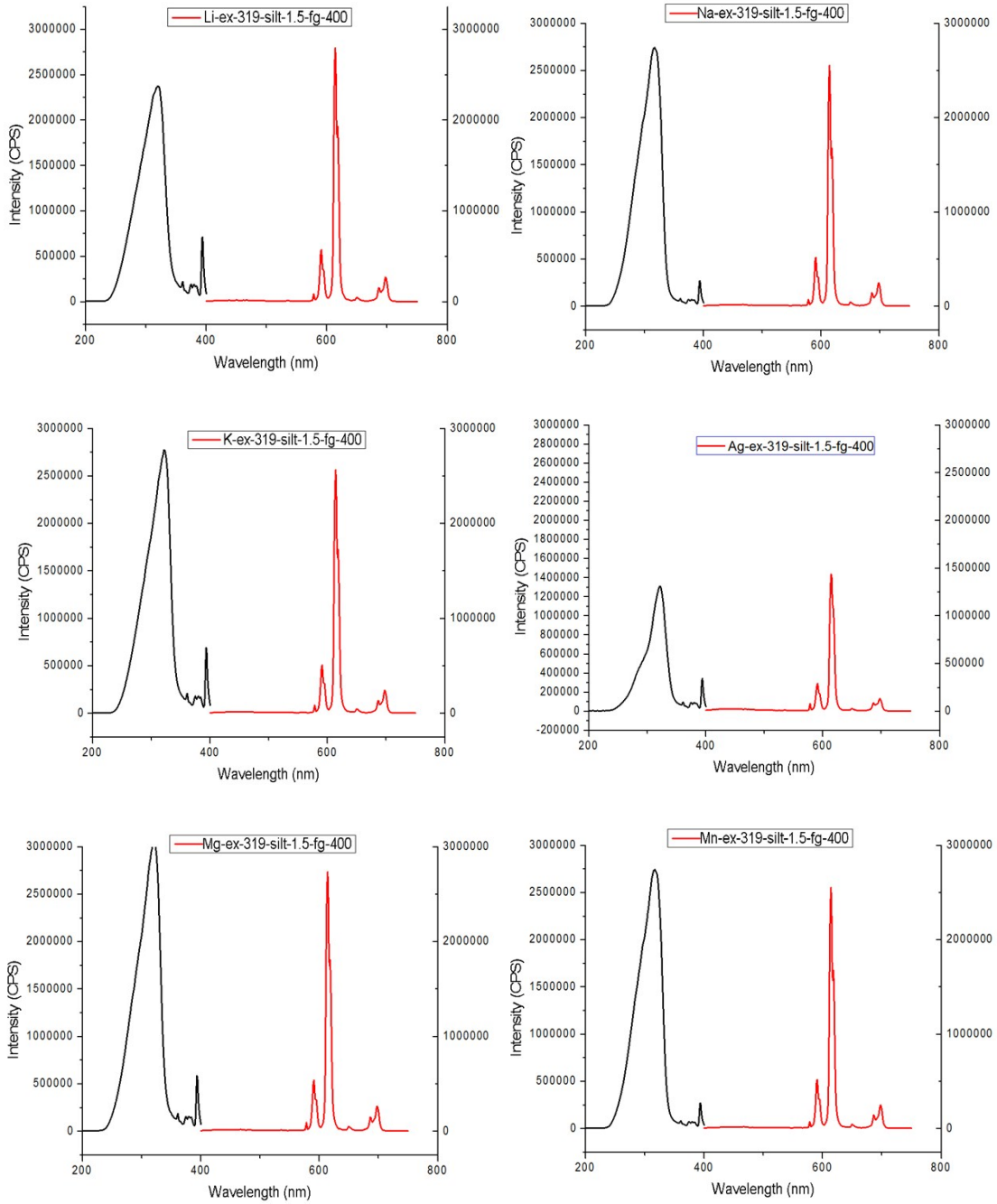
The thermogravimetric analysis (TGA) was carried out on polycrystalline samples of BMM-7 in the temperature range from 25 to 800 °C in the flowing N2 atmosphere with a heating rate of 5 °C min^{-1} (plz see Fig. S5 on Page S7).

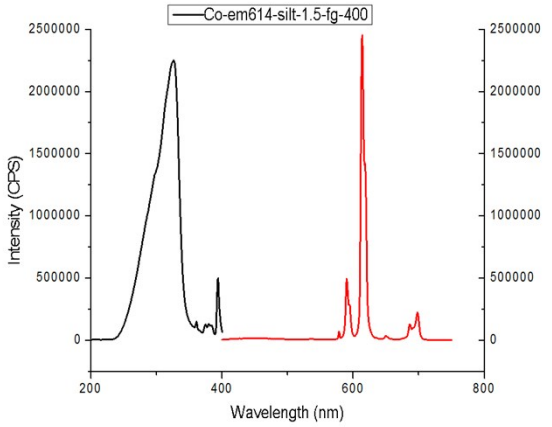
At the beginning, BMM-7 displays a weight loss of 10.0% (cal. 10.45%) at the temperature of 100 °C, which corresponds to the loss of guest uncoordinated water molecules.

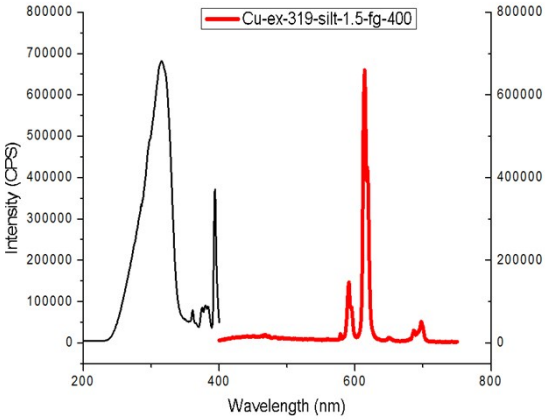
After that, it turns out to be a continuous weight loss of 15.5% (cal. 15.6%) in the temperature range of 100-260 °C, which is attributed to the departure of uncoordinated DMF molecules in the microporous channels. The terminally coordinated DMF molecules are not going to decompose at this point.

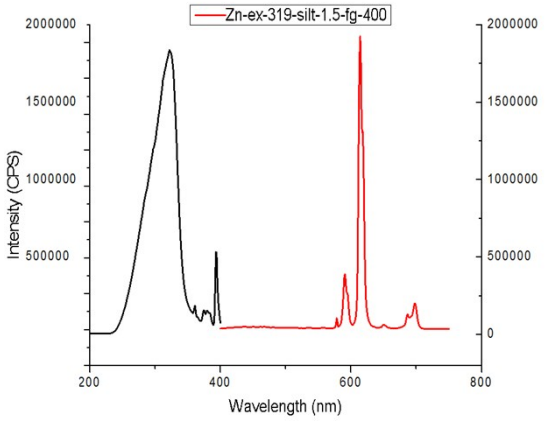
Finally, with the increasing temperature, the main framework of BMM-7 is starting to collapse, and the coordination bonds between Eu(III) centres and ligands is going to break down, the BPTC ligands and DMF molecules are going to deteriorate seriously, which is presented in TGA cures with a continuous weight loss until 850 ^{o}C.

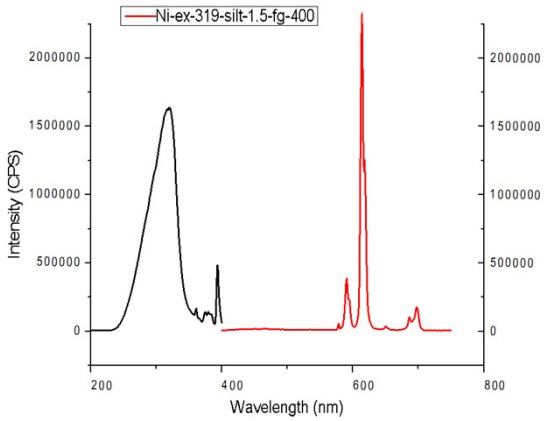
S5. Excitation and Emission Curves for Different M^{n+}-BMM-7 Samples

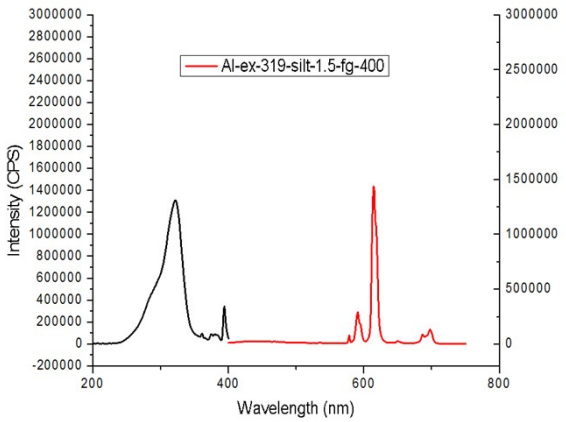


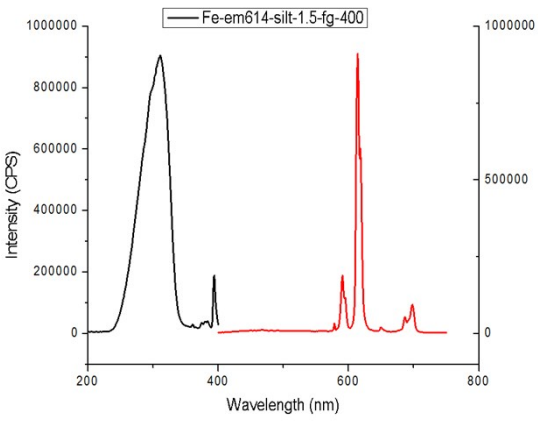

Co-em614-silt-1.5-fg-400
Intensity (CPS)
Wavelength (nm)


Cu-ex-319-silt-1.5-fg-400
Intensity (CPS)
Wavelength (nm)


Zn-ex-319-silt-1.5-fg-400
Intensity (CPS)
Wavelength (nm)


Ni-ex-319-silt-1.5-fg-400
Intensity (CPS)
Wavelength (nm)


Al-ex-319-silt-1.5-fg-400
Intensity (CPS)
Wavelength (nm)


Fe-em614-silt-1.5-fg-400
Intensity (CPS)
Wavelength (nm)

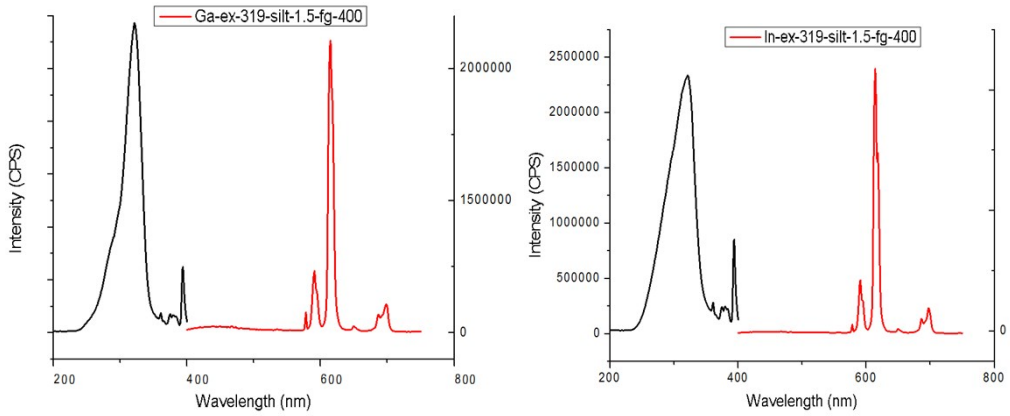


Figure S6 (a) The excitation (black, λ_{em} =614 nm) and emission spectra (red, λ_{ex} = 319 nm) of **M^{n+}-BMM-7**, solid state samples at room temperature. And the metal ions are Li^{+}, Na^{+}, K^{+}, Ag^{+}, Mg^{2+}, Mn^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Al^{3+}, Fe^{3+}, Ga^{3+}, In^{3+}, respectively (from top left to bottom right)

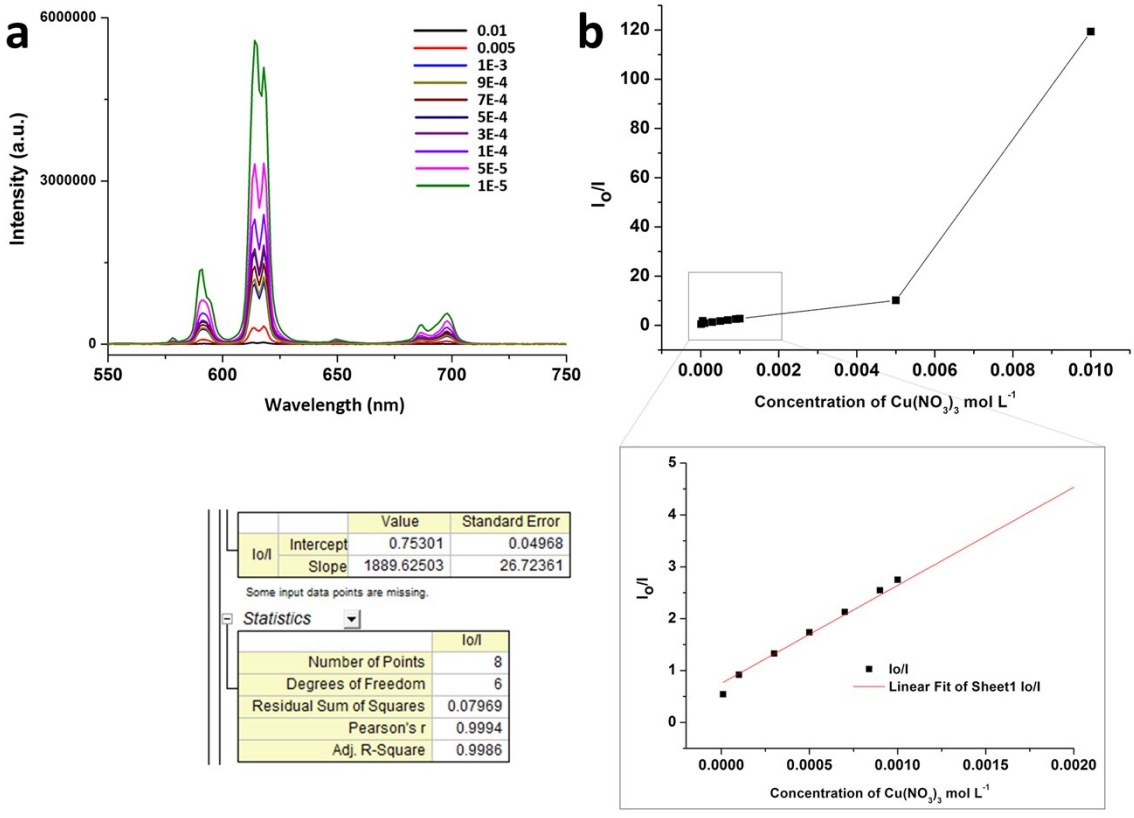


Figure S7 (a) Luminescence intensity of BMM-7 suspension with different concentrations of $Cu(NO_3)_2$. (b) and (c) Stern-Volmer plot with the fitting factors.

First, in order to determine the linear range and limit of detection for the sensitivity of Cu(II) cations, the compound was dispersed in ethanol solutions with varying concentrations of Cu(II) ions. As presented in Fig. 4 on Page 4 in the main

article, the luminescence intensity at 614 nm of Eu(III) ions is decreased obviously as the concentration of copper ions increase gradually, and BMM-7 shows nearly no emission when the concentration of Cu(II) cations increases to 0.01 mol L^{-1}.

With the increasing concentration of Cu(III) ions, the emission intensity of EtOH-suspended stock solution of BMM-7 decreased gradually in the concentration range of 10^{-5} to 10^{-2} mol L^{-1} (Fig. 7a). What should be emphasized here is that in the concentration range of 10^{-4} to 10^{-3} mol L^{-1}, a good linear correlation (R^2 = 0.9986) between the quenching efficiency and the amount of Cu(II) was observed (Fig. 7b), despite the I_o/I curve cannot severely fit linearly under the high concentration (> 0.01 mol $L^{-1)}$.

Second, the quenching effect can be verified by the quenching effect coefficient (Ksv), based on the luminescent data, which is calculated according to the Stern-Volmer equation:

$$I_o/I = 1 + K_{sv}[M]$$

in which the values of I_o and I are the luminescent intensity of metal-ion-free and metal-ion-incorporated BBM-7 in alcoholic solutions, respectively. [M] is the molar concentration of metal ion. As listed in Table S2 as blow, Cu(II) ions show the highest value of 360.7 M^{-1}, indicating that Cu(II) ions have the most distinct quenching effect on the luminescent intensity of BMM-7.

Table. S2 Quenching effect coefficients (Ksv) of different metal ions on the luminescence intensity of metal-ion-incorporated BMM-7.

Metal ion	$^5D_0 - {}^7F_2$	K_{sv}
Li^+	2798220	8.6
Na^+	2.665290	14.0
K^+	2568190	18.4
Ag^+	1787720	70.0
Mg^{2+}	2735630	11.1
Mn^{2+}	2554300	19.0
Co^{2+}	2454730	23.8
Cu^{2+}	**659800**	**360.7**
Zn^{2+}	1918200	58.5
Ni^{2+}	1893290	60.5
Al^{3+}	1638000	85.6
Fe^{3+}	1502010	102.3
Ga^{3+}	2070130	46.8
In^{3+}	2398700	26.7

S6. N_2 isotherms of non-activated and activated BMM-7

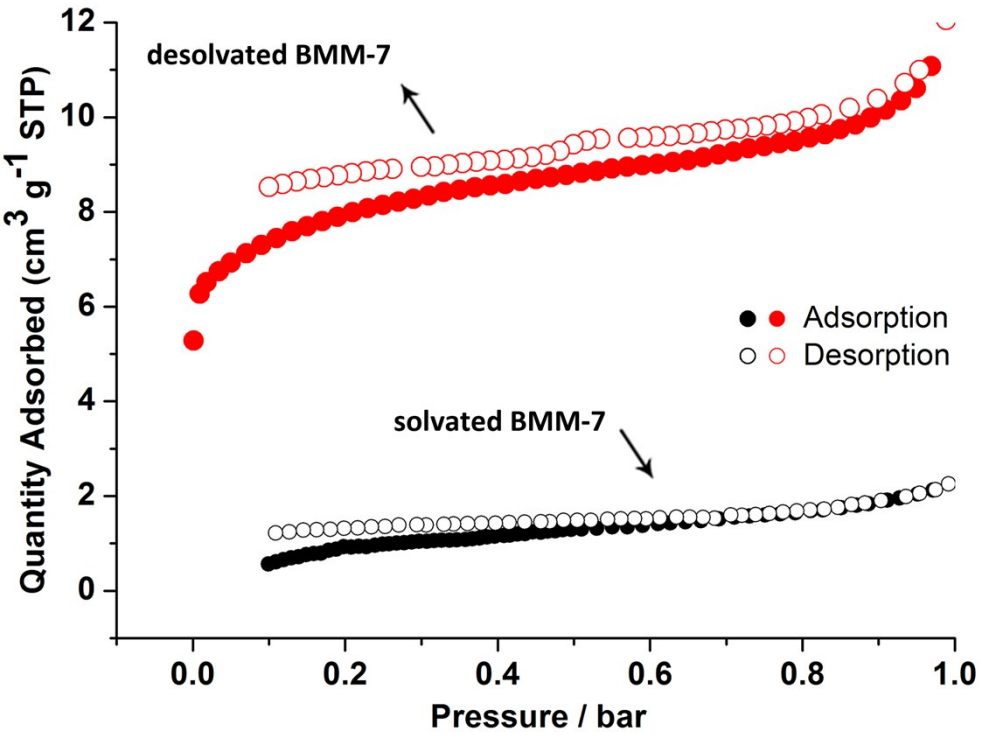


Figure S8 The Experimental nitrogen adsorption (closed) and desorption (open) isotherms at 77 K for BMM-7.

S7 References.

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[S2] SHELXS, G.M. Sheldrick, *Acta Cryst*. **2008**, *A64*, 112.

[S3] SHELXL, G.M. Sheldrick, *Acta Cryst*. **2008**, *A64*, 112.

[S4] (a) A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7; (b) P. v.d. Sluis and A. L. Spek, *Acta Crystallogr., Sect. A*, **1990**, *46*, 194.