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Supporting Information For

NbO lattice MOFs based on M(II) and ditopic pyridyl substituted diketonate ligands: structure, encapsulation and guest-driven luminescent property

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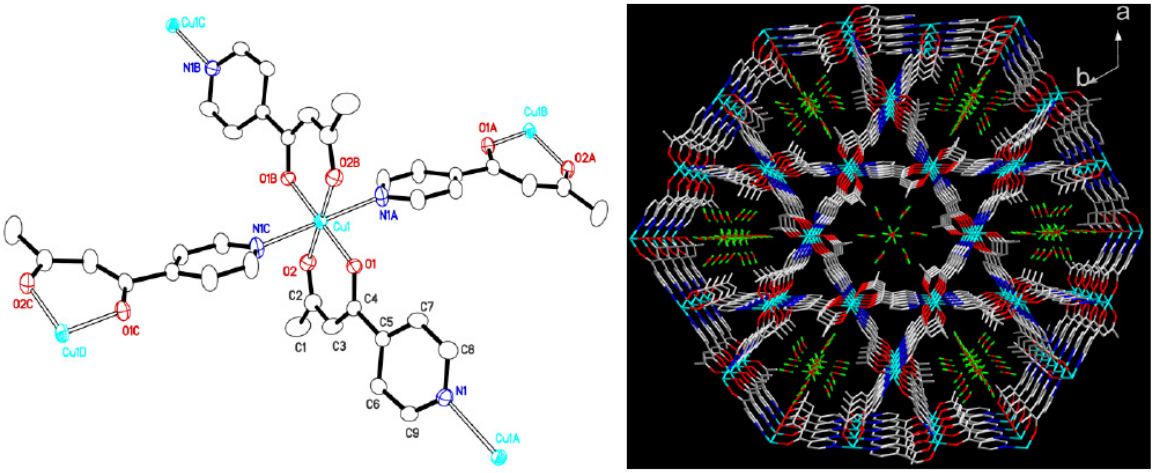

Fig. S1 ORTEP figure (left) of **1** (**1'**) and its crystal packing pattern (right).

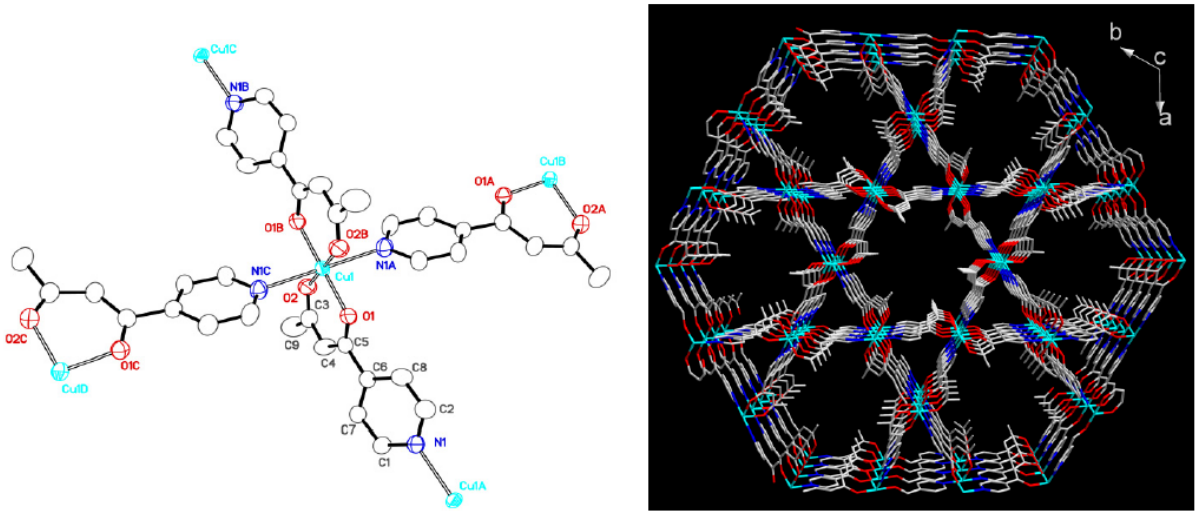

Fig. S2 ORTEP figure (left) of **2** and its crystal packing pattern (right).

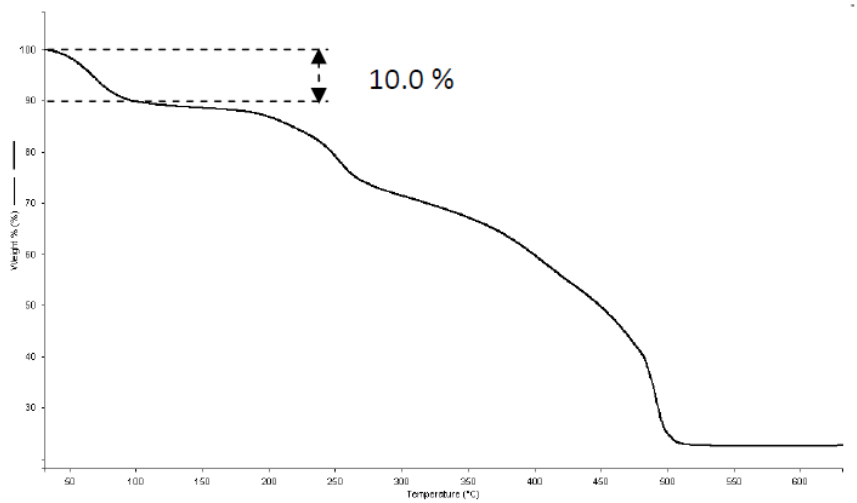

Fig. S3 TGA trace of **1**. The observed water mass loss was 10.0 % and the calculated water mass loss was 8.6 %.

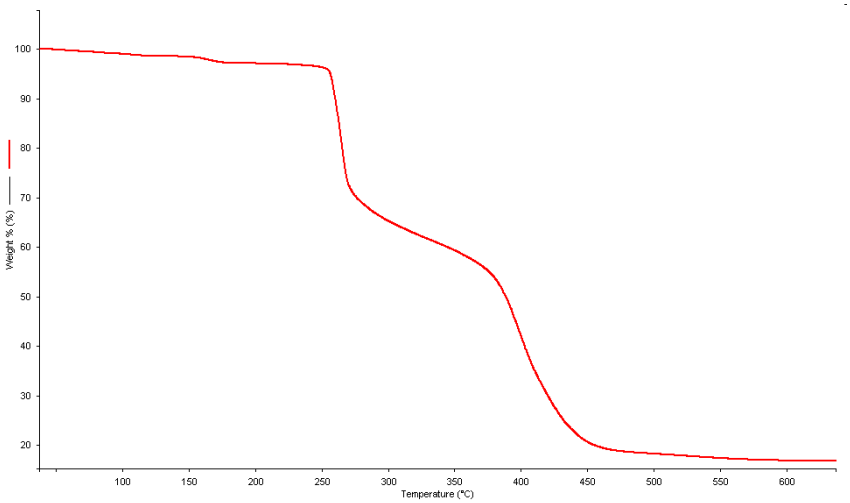

Fig. S4 TGA trace of **2**. No water guest mass loss was detected.

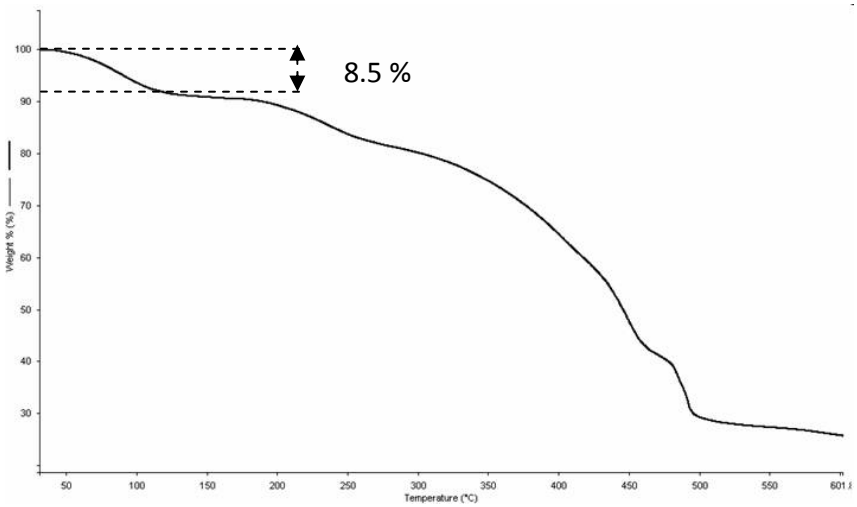

Fig. S5 TGA trace of **1'**. The observed water mass loss was 8.5 % and the calculated water mass loss was 8.6 %.

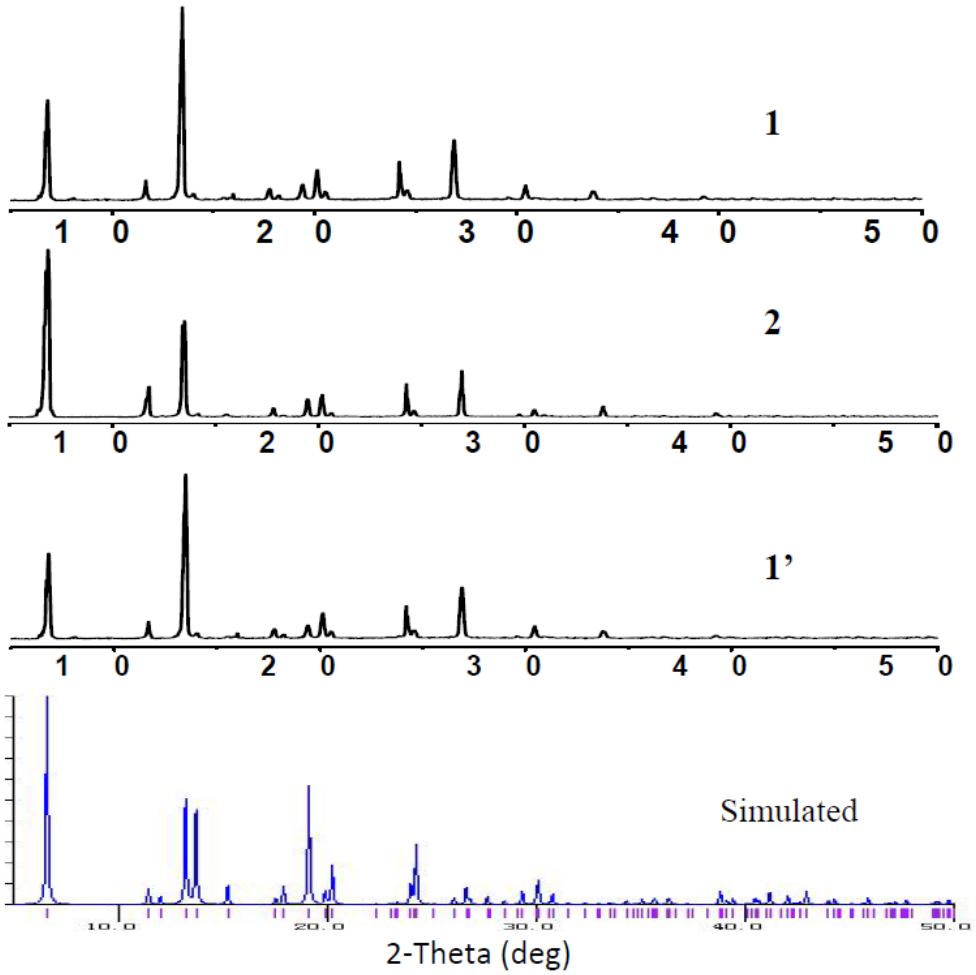

Fig. S6 XRPD patterns of **1**, **2** and regenerated **1'** are identical to the simulated one.

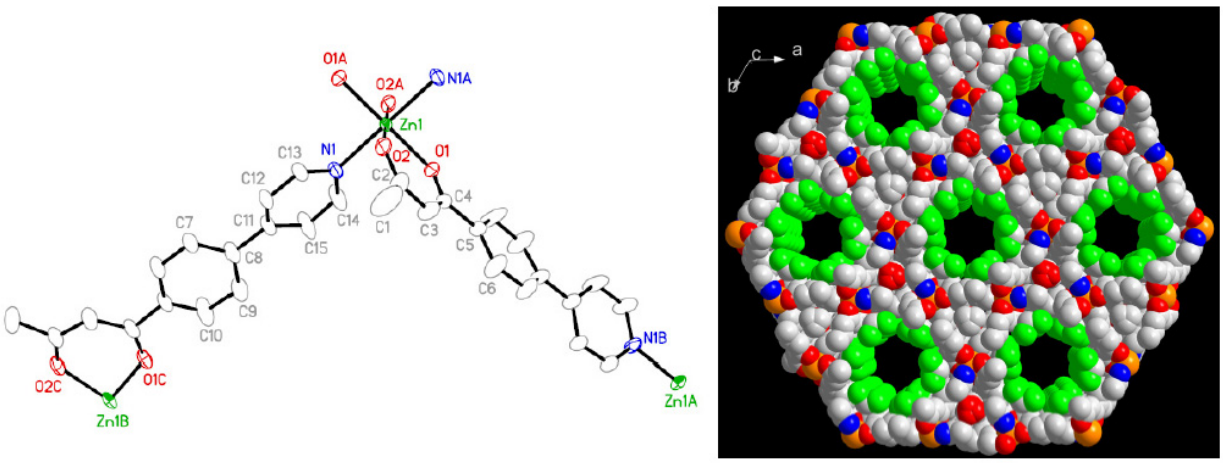

Fig. S7 The ORTEP figure (left) and space-filling diagram of **3**.

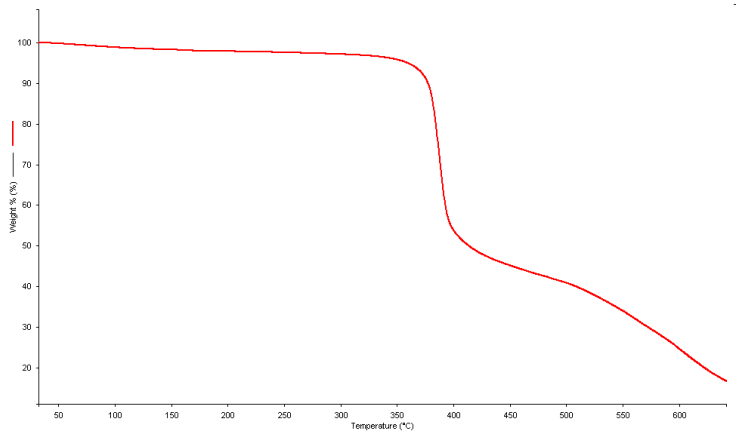

Fig. S8 TGA trace of desolvated **3**. No guest solvent mass loss was detected.

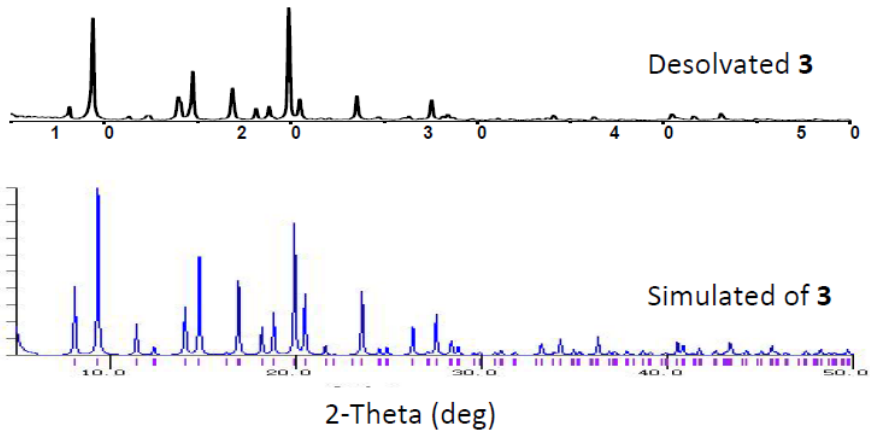

Fig. S9 XRPD pattern on desolvated sample of **3** is identical to that of calculated one.

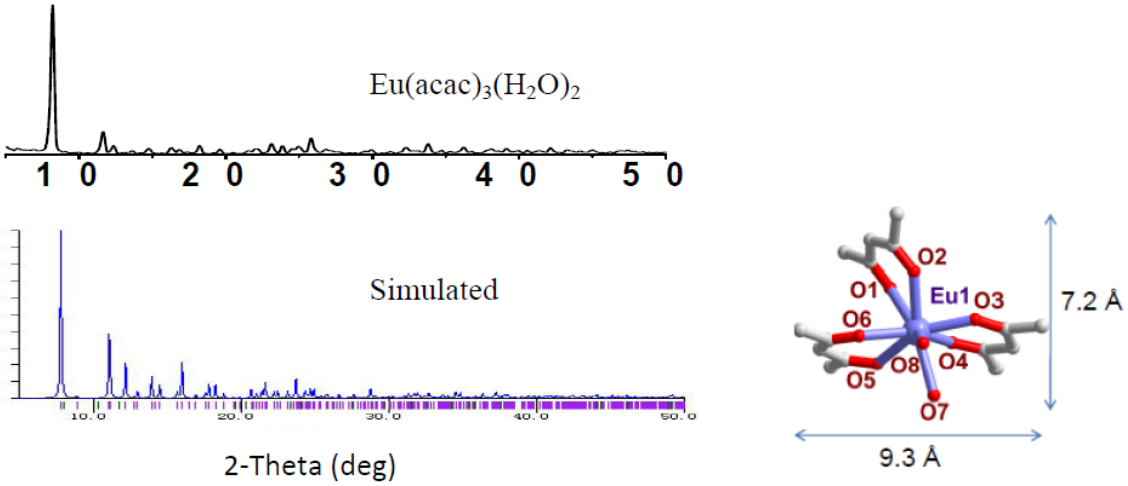

Fig. S10 XRPD pattern on $Eu(acac)_3(H_2O)_2$ which is used for guest encapsulation is identical to that of calculated one. The single-crystal structure of $Eu(acac)_3(H_2O)_2$ is shown (right).

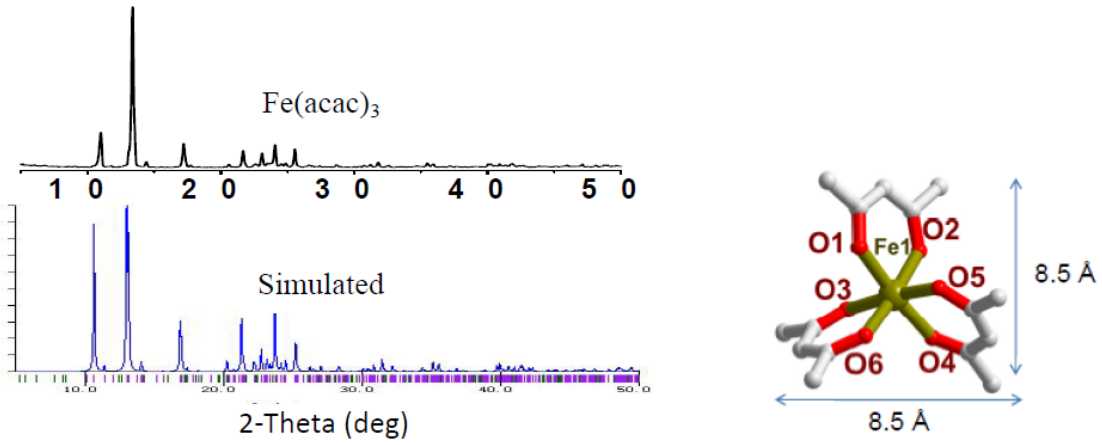

Fig. S11 XRPD pattern on $Fe(acac)_3$ which is used for guest encapsulation is identical to that of calculated one. The single-crystal structure of $Fe(acac)_3$ is shown (right).

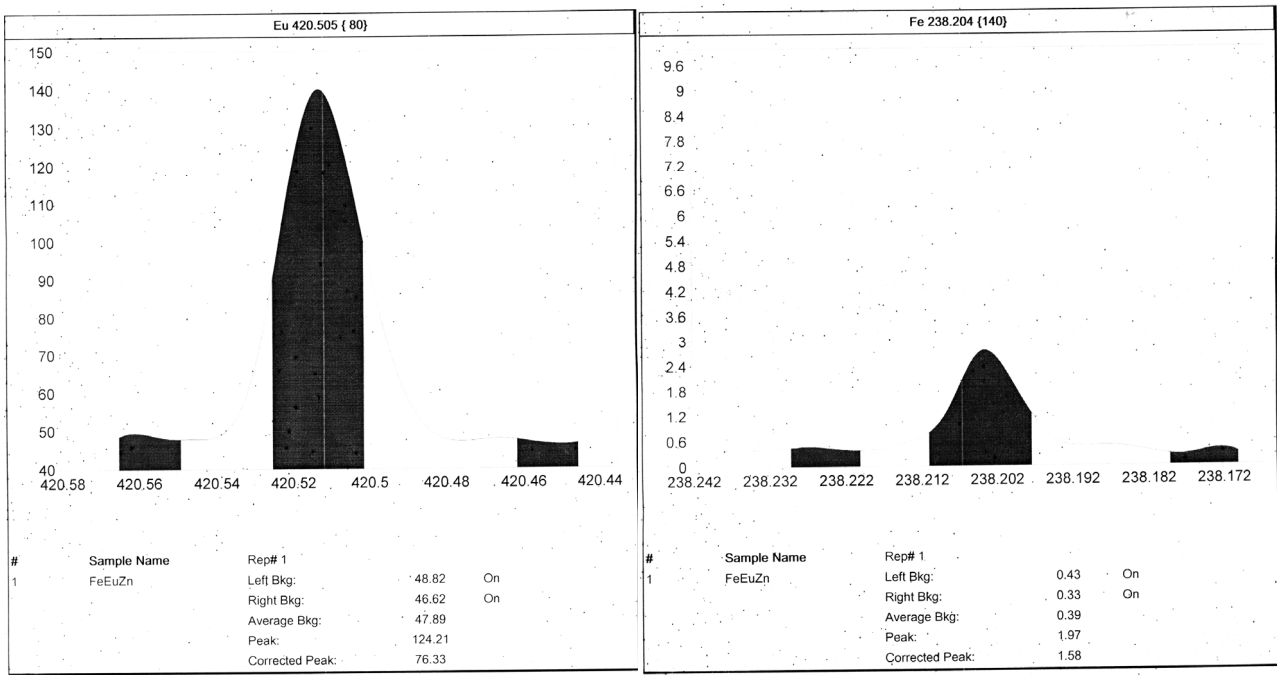

Fig. S12 The ICP-LC measurement indicate that the doped amount of Fe(III) and Eu(III) in Zn(**L2**)$_2$ are 0.36 and 0.30 %, respectively, after 0.013Eu(acac)$_3$⊂Zn (**L2**)$_2$ **(5)** was immersed in a CH_2Cl_2/MeOH (15 : 1, v/v) mixed solvent system of $Fe(acac)_3$ (5×10^{-3} mol/L) for 2 hours, indicating the formation of 0.036Fe(acac)$_3$/0.011Eu(acac)$_3$(H_2O)$_2$⊂Zn(**L2**)$_2$ (**6**).

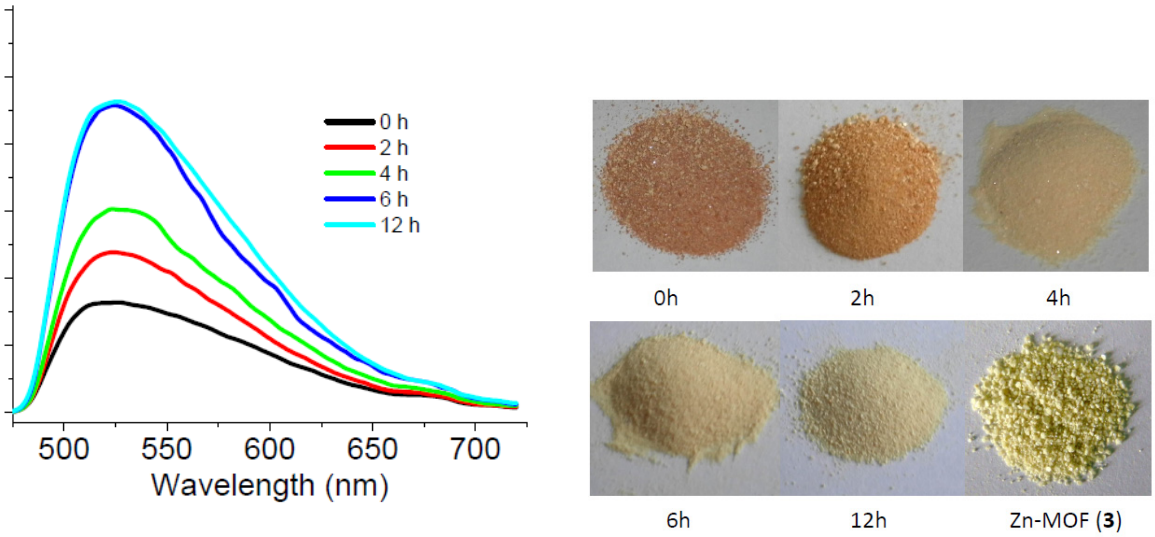

Fig. S13 Left: The emission spectra obtained by immersing $Fe(acac)_3 \subset Zn(\mathbf{L2})_2$ (**4**) in MeOH at 2h, 4h, 6h and 12h. The emission intensity of **3** increases by degrees as the time going on, which indicates that the Fe-acac guest can be extracted by MeOH. Right: Photographs showing the visual color change of bulk samples of $Fe(acac)_3 \subset Zn(\mathbf{L2})_2$ (**4**) after immersing in MeOH at different time points.

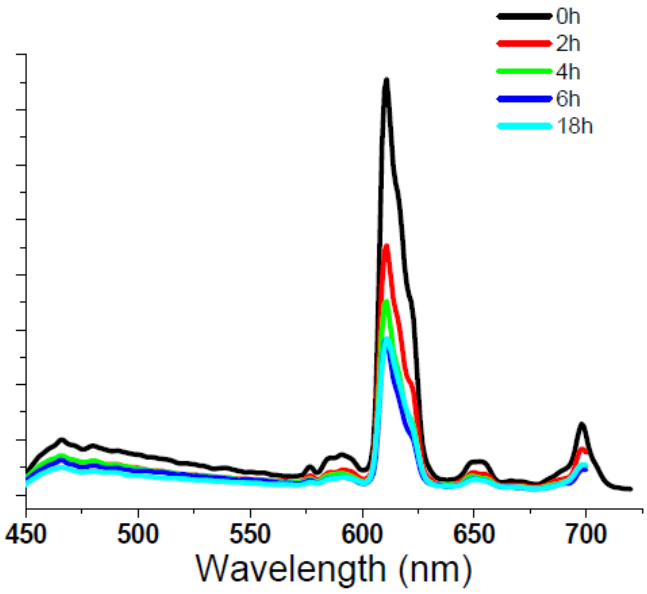

Fig. S14 The emission spectra obtained by immersing $Eu(acac)_3(H_2O)_2 \subset Zn(\mathbf{L2})_2$ (**5**) in MeOH at 2h, 4h, 6h and 18h. The Eu(III) emission intensity decreased by degrees as the time going on, which indicates that the Eu-acac guest can be extracted by MeOH.

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Experimental Section. Infrared (IR) samples were prepared as KBr pellets, and spectra were obtained in the 400-4000 cm^{-1} range using a Perkin-Elmer 1600 FTIR spectrometer. Elemental analyses were performed on a Perkin-Elmer Model 2400 analyzer. All fluorescence measurements were carried out on a Cary Eclipse Spectrofluorimeter (Varian, Australia) equipped with a xenon lamp and quartz carrier at room temperature. Thermogravimetric analyses were carried out using a TA Instrument SDT 2960 simultaneous DTA-TGA under flowing nitrogen at a heating rate of 10°C/min. ICP-LC and ICP-MS were performed on IRIS Interpid II XSP and NU AttoM, respectively.

Synthesis of 1. A solution of HL1 (13 mg, 0.08 mmol) and $CuBF_4$ (8.0 mg, 0.04 mmol) in THF/MeOH (8 mL) was left for about one week at room temperature, and bright green crystals (16 mg) were obtained. Yield, 76 %. IR (KBr pellet, cm^{-1}): 3424(m), 3045(m), 2922(m), 1597(s), 1550(s), 1516(s), 1486(s), 1452(s), 1398(s), 1319(m), 1284(m), 1210(m), 1062(m), 1006(m), 850(m), 771(s), 692(m). Elemental analysis (%) calcd. for $C_{54}H_{62}Cu_3N_6O_{19}$: C 50.24, H 4.80, N 6.51; Found: C 50.20, H 4.93, N 6.90.

Synthesis of 2. The crystals of **1** were left for 6 days at room temperature to generate desolvated crystals of 2 in quantitative yield. IR(KBr pellet cm^{-1}): 3442(m), 3045(m), 1597(s), 1550(s), 1516 (s), 1488(s), 1452(s), 1400(s), 1320(m), 1285(m), 1211(m), 1063(m), 1007(m), 851(m), 771(m), 694(m). Elemental analysis (%) calcd. for $C_{54}H_{48}Cu_3N_6O_{12}$: C 55.68, H 4.12, N 7.21; Found: C 55.63, H 4.35, N 7.24.

Synthesis of 1'. The crystals of **2** were immersed in mother liquor for 12 hours at room temperature to regenerate crystals of **1** in quantitative yield. IR (KBr pellet, cm^{-1}): 3426(m), 3045(m), 2922(m), 1597(s), 1550(s), 1516(s), 1486(s), 1452(s), 1398(s), 1319(m), 1285(m), 1211(m), 1062(m), 1006(m),

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850(m), 771(s), 692(m). Elemental analysis (%) calcd. for $C_{54}H_{62}Cu_3N_6O_{19}$: C 50.24, H 4.80, N 6.51; Found: C 50.34, H 4.97, N 6.89.

Synthesis of 3. A solution of $Zn(OAc)_2$ (2.4 mg, 0.01 mmol) in MeOH (1 mL) was layered onto a solution of **HL2** (4.8 mg, 0.02 mmol) in CH_2Cl_2 (2 mL). The solutions were left for about 3 days at room temperature, and light yellow crystals were obtained. Yield, 80 %. IR (KBr pellet, cm^{-1}): 3423 (w), 1590 (s), 1564 (s), 1506 (s), 1486 (s), 1411 (s), 1287 (m), 1220 (m), 1007 (m), 852 (m), 823 (m), 772 (s). Elemental analysis(%) calcd for $C_{30}H_{24}N_2O_4Zn$ (desolvated): C 66.50, H 4.43, N 5.17; Found: C 66.83, H 4.92, N 4.94.

Single-crystal analysis. For **1** (**1'**) and **2**, X-ray intensity data were measured at 293 K on a Bruker SMART APEX CCD-based diffractometer (Mo Kα radiation, λ = 0.71073 Å). The raw frame data were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects using SAINT.[1] Corrections for incident and diffracted beam absorption effects were applied using SADABS.[1] None of the crystals showed evidence of crystal decay during data collection. All structures were solved by a combination of direct methods and difference Fourier syntheses and refined against F^2 by the full-matrix least squares technique. Crystal data, data collection parameters, and refinement statistics are listed in Table S1-3. For **3**, systematic absences in the intensity data were consistent with the space group P-3. The structure was solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix least-squares against F^2, using the SHELXTL software package.[1] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to refined atoms were placed in geometrically idealized positions and refined using a riding model, half a CH_2Cl_2 and one MeOH molecular was refined as disordered over two orientations , The ADPs of Cl_4, Cl3 and C9 were restrained to be isotropic within a standard

deviation of 0.005 Å^2, the ADPs of C2, C3, C4, O1 and O2 were restrained to be same within a standard deviation of 0.005 Å , the ADPs of C7, C8, C9 and C10 were also restrained to be same within a standard deviation of 0.005 Å, the ADPs of C11, C12, C13, C14, C15 and N1 were restrained to be same within a standard deviation of 0.005 Å. In total 57 restraints (SHELX DFIX, DELU) were used in modeling the disorder. At this point, some electron density peaks were observed in the voids in the 3D framework. SQUEEZE / PLATON[2] was used to account for that. The program calculated a solvent accessible void volume of 523.9 Å^3 corresponding to 208 e$^-$/cell. The contribution of these disordered species was then removed from the structure factor calculations. The tabulated F(000), MW and density reflect known species only. Crystal data, data collection parameters, and refinement statistics are listed in Table S4. The single crystals of **4** and **5** were also obtained. When all guest species are treated with SQUEEZE / PLATON. For Fe(acac)$_3$⊂Zn(**L2**)$_2$ (**4**), the cell volume was 6320.8(11) Å^3, the guest species accessible void volume was 2941.7 Å^3, and electron count / cell is 1275. For Eu(acac)$_3$⊂Zn(**L2**)$_2$ (**5**), the cell volume was 3143.7(11) Å^3, the guest species accessible void volume is 1456.8 Å^3, and electron count / cell is 633. So there must be some heavier species more than solvent molecules in channel void due to the significant electron density peaks. We think that the heavier species are those extremely small amounts of Iron(III) 2,4-pentanedionate and Europlum(III) 2,4-pentanedionate. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no CCDC 833167, 833168, 833169 and 833170. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Table S1. Crystal data and structure refinement for **1.**

Identification code	**1**
Empirical formula	C54 H62 Cu3 N6 O19
Formula weight	1289.72
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Rhombohedral, R-3
Unit cell dimensions	a = 26.718(5) A alpha = 90 deg.
	b = 26.718(5) A beta = 90 deg.
	c = 7.7553(19) A gamma = 120 deg.
Volume	4794.3(17) A^3
Z, Calculated density	3, 1.340 Mg/m^3
Absorption coefficient	1.060 mm^-1
F(000)	2001
Crystal size	0.50 x 0.10 x 0.08 mm
Theta range for data collection	2.64 to 25.00 deg.
Limiting indices	-17<=h<=31, -31<=k<=29, -9<=l<=9
Reflections collected / unique	8105 / 1877 [R(int) = 0.0430]
Completeness to theta = 25.00	99.9 %
Absorption correction	None
Max. and min. transmission	0.9200 and 0.6194
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1877 / 6 / 121
Goodness-of-fit on F^2	1.039
Final R indices [I>2sigma(I)]	R1 = 0.0460, wR2 = 0.1160
R indices (all data)	R1 = 0.0576, wR2 = 0.1236
Largest diff. peak and hole	0.504 and -0.390 e.A^-3

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Table S2. Crystal data and structure refinement for **2.**

Identification code	**2**
Empirical formula	C54 H48 Cu3 N6 O12
Formula weight	1163.60
Temperature	298(2) K
Wavelength	0.71073 A
Crystal system, space group	Rhombohedral, R-3
Unit cell dimensions	a = 26.473(4) A alpha = 90 deg.
	b = 26.473(4) A beta = 90 deg.
	c = 7.635(2) A gamma = 120 deg.
Volume	4633.8(17) A^3
Z, Calculated density	3, 1.251 Mg/m^3
Absorption coefficient	1.081 mm^-1
F(000)	1791
Crystal size	0.35 x 0.10 x 0.06 mm
Theta range for data collection	2.67 to 25.48 deg.
Limiting indices	-32<=h<=31, -19<=k<=32, -9<=l<=9
Reflections collected / unique	8103 / 1915 [R(int) = 0.0546]
Completeness to theta = 25.48	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9380 and 0.7034
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1915 / 0 / 116
Goodness-of-fit on F^2	0.985
Final R indices [I>2sigma(I)]	R1 = 0.0513, wR2 = 0.1146
R indices (all data)	R1 = 0.0827, wR2 = 0.1293
Largest diff. peak and hole	0.389 and -0.185 e.A^-3

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Table S3. Crystal data and structure refinement for **1'.**

Identification code	**1'**
Empirical formula	C54 H62 Cu3 N6 O19
Formula weight	1289.72
Temperature	298(2) K
Wavelength	0.71073 A
Crystal system, space group	Trigonal, R-3
Unit cell dimensions	a = 26.642(4) A alpha = 90 deg.
	b = 26.642(4) A beta = 90 deg.
	c = 7.741(2) A gamma = 120 deg.
Volume	4758.3(16) A^3
Z, Calculated density	3, 1.350 Mg/m^3
Absorption coefficient	1.068 mm^-1
F(000)	2001
Crystal size	0.15 x 0.13 x 0.10 mm
Theta range for data collection	2.78 to 25.50 deg.
Limiting indices	-32<=h<=28, -27<=k<=32, -9<=l<=7
Reflections collected / unique	7504 / 1953 [R(int) = 0.0675]
Completeness to theta = 25.50	98.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9007 and 0.8563
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1953 / 0 / 121
Goodness-of-fit on F^2	0.936
Final R indices [I>2sigma(I)]	R1 = 0.0463, wR2 = 0.1159
R indices (all data)	R1 = 0.0670, wR2 = 0.1225
Largest diff. peak and hole	0.787 and -0.347 e.A^-3

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Table S4. Crystal data and structure refinement for **3.**

Identification code	**3**
Empirical formula	$C_{31.67}H_{28.67}Cl_2N_2O_{4.67}Zn$
Formula weight	648.17
Temperature	173(2) K
Wavelength	0.71073 A
Crystal system, space group	Trigonal, P-3
Unit cell dimensions	a = 21.746(2) A alpha = 90 deg.
	b = 21.746(2) A beta = 90 deg.
	c = 7.7165(16) A gamma = 120 deg.
Volume	3160.1(8) A^3
Z, Calculated density	3, 1.022 Mg/m^3
Absorption coefficient	0.739 mm^-1
F(000)	1002
Crystal size	0.40 x 0.35 x 0.30 mm
Theta range for data collection	1.08 to 25.58 deg.
Limiting indices	-26<=h<=22, -20<=k<=26, -8<=l<=9
Reflections collected / unique	16720 / 3984 [R(int) = 0.0451]
Completeness to theta = 25.58	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8086 and 0.7563
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3984 / 57 / 246
Goodness-of-fit on F^2	1.046
Final R indices [I>2sigma(I)]	R1 = 0.0721, wR2 = 0.2117
R indices (all data)	R1 = 0.0851, wR2 = 0.2219
Largest diff. peak and hole	0.841 and -0.493 e.A^-3

References

(1) Sheldrick, G. M. SHELXTL Version 5.12; Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 1997.

(2) Spek, A. L. PLATON, A Multipurpose Crystallographic Tool. University of Utrecht, Utrecht, the Netherlands, 1998.