

Electronic supplementary information

Three resorcin[4]arene-based complexes with Cu(II)-exchange characters and fluorescence sensing POM in aqueous solution

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Experimental section

The ligand H₄L was prepared by reported procedures.^{1,2} All the reagents and solvents for synthesis were purchased from commercial sources and used without further purify.

Physical measurements. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm⁻¹ on a Mattson Alpha-Centauri spectrometer. Microanalyses of C, H, and N for the compounds were obtained using a Perkin–Elmer 2400CHN elemental analyzer. The powder X-ray diffraction (PXRD) patterns of the samples were collected on a Rigaku Dmax 2000 X-ray diffractometer with graphite monochromatized Cu K_α radiation ($\lambda = 0.154$ nm) and 2θ ranging from 5 to 50° at room temperature. Thermogravimetric analyses were performed on a Perkin-Elmer TG-7 analyzer heated from room temperature to 600°C under nitrogen gas. Inductively coupled plasma (ICP) analysis was performed on a Leeman Labs Prodigy inductively coupled plasma-optical atomic emission spectrometer (ICP-AES). The photoluminescent property was measured on a FLSP920 Edinburgh Fluorescence Spectrometer at room temperature.

Synthesis of [Cd₃L(H₂L)(H₂O)]·2DMF·11.5H₂O (1): A mixture of H₄L (0.028 g, 0.03

mmol), Cd(CH₃COO)₂·2H₂O (0.016 g, 0.06 mmol), DMF (4 mL) and H₂O (4 mL) was placed in a Teflon reactor (15 mL). The mixture was heated at 110 °C for 3 days and then cooled to room temperature gradually. Pale yellow colorless crystals were obtained in a 41% yield. Anal. calcd for C₁₀₂H₁₃₁O_{47.5}N₂Cd₃ (*Mr* = 2482.35): C, 49.35; H, 5.32; N, 1.13. Found: C, 49.81; H, 5.43; N, 1.10. IR data (KBr, cm⁻¹): 3648(w), 3422(m), 2930(w), 1664(s), 1556(s), 1457(m), 1429(s), 1332(w), 1302(w), 1239(w), 1152(w), 1087(m), 1020(w), 976(s), 925(w), 786(w), 735(w), 680(w), 666(w), 588(w), 502(w).

Synthesis of [Zn₄L₂(H₂O)₄]·2DMF·10H₂O (2): The mixture of H₄L (0.028 g, 0.03 mmol), Zn(CH₃COO)₂·2H₂O (0.013 g, 0.06 mmol), DMF (4 mL), and H₂O (4 mL) was placed in a Teflon reactor (15 mL) and heated at 100 °C for 3 days. Then it was gradually cooled to room temperature. Pale yellow crystals were harvest in a 44% yield. Anal. calcd for C₁₀₂H₁₃₀O₄₈N₂Zn₄ (*Mr* = 2413.74): C, 50.75; H, 5.43; N, 1.16. Found: C, 50.41; H, 5.51; N, 1.20. IR data (KBr, cm⁻¹): 3422(m), 2929(m), 1663(s), 1548(s), 1507(m), 1457(s), 1429(s), 1337(w), 1302(m), 1242(m), 1152(w), 1086(s), 1019(m), 976(s), 810(w), 787(w), 738(w), 682(w), 665(w), 588(w), 498(w).

Synthesis of [Mn₉L₄(HCOO)₂(H₂O)₁₂(DMF)₂]·2DMF·10H₂O (3): The preparation of **3** was similar to that of **2** except that Mn(CH₃COO)₂·2H₂O (0.016 g) was utilized in place of Zn(CH₃COO)₂·2H₂O. Pale yellow crystal products were isolated in a 35% yield. Anal. calcd for C₂₀₆H₂₅₀O₉₄N₄Mn₉ (*Mr* = 4780.60): C, 51.76; H, 5.27; N, 1.17. Found: C, 51.40; H, 5.45; N, 1.23. IR data (KBr, cm⁻¹): 3410(m), 2927(m), 1685(m), 1659(s), 1554(s), 1459(s), 1427(s), 1362(m), 1334(m), 1300(m), 1239(m), 1205(w), 1151(w), 1086(s), 1020(m), 974(s), 806(w), 785(w), 681(w), 641(w), 586(w), 499(w).

X-ray crystallography

An Oxford Diffraction Gemini R CCD with graphite-monochromated Mo-K α radiation for compounds **1** and **3** (λ = 0.071 nm) and Cu-K α radiation for compound **2** (λ = 0.154 nm) was used to collect single-crystal X-ray diffraction data at 293 K. A multiscan technique was used to perform absorption corrections. The structures were solved by the direct method.³ The full-matrix least squares techniques using the SHELXL-97 program within WINGX were used to refine all non-hydrogen atoms. In **1**, Cd₂ is split over two sites with the total of occupancy of 0.5. The free water molecules (O2W, O4W, O5W, O6W, O7W, O8W, O9W and O10W) are

disordered by symmetry. For **2**, the guest solvent atoms could not be resolved by point atom observations due to disorder. Hence, the PLATON squeeze procedure was performed. For **3**, Zn2, Zn3, O3W, O9 and O16 atoms are split over two sites with the total of occupancy of 1, respectively.

References

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- 2 A. G. Millar, A. C. Oehlschlager and J. W. Wong, *J. Org. Chem.*, 1983, **48**, 4404.
- 3 (a) G. M. Sheldrick, *SHELXS-97, Programs for X-ray Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997; (b) G. M. Sheldrick, *SHELXL-97, Programs for X-ray Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997; (c) L. J. Farrugia, *WINGX, A Windows Program for Crystal Structure Analysis*, University of Glasgow, Glasgow, UK, 1988.

Table S1 Selected bond distances (Å) and angles (°) for **1**.

Cd(1)-O(1)	2.212(1)	Cd(1)-O(1W)	2.289(3)
Cd(1)-O(5)	2.342(1)	Cd(1)-O(7) ^{#1}	2.364(1)
Cd(1)-O(3)	2.387(1)	Cd(1)-O(6)	2.397(1)
Cd(1)-O(2)	2.629(1)	Cd(2)-O(3) ^{#2}	2.146(1)
Cd(2)-O(3)	2.146(1)	Cd(2)-O(5)	2.386(1)
Cd(2)-O(5) ^{#2}	2.386(1)	Cd(2)-O(4) ^{#2}	2.569(1)
Cd(2)-O(4)	2.569(1)	O(1)-Cd(1)-O(1W)	86.7(6)
O(1)-Cd(1)-O(5)	163.7(5)	O(1W)-Cd(1)-O(5)	82.1(6)
O(1)-Cd(1)-O(7) ^{#1}	103.0(5)	O(1W)-Cd(1)-O(7) ^{#1}	170.3(6)
O(5)-Cd(1)-O(7) ^{#1}	88.2(6)	O(1)-Cd(1)-O(3)	98.4(4)
O(1W)-Cd(1)-O(3)	96.1(9)	O(5)-Cd(1)-O(3)	71.2(5)
O(7) ^{#1} -Cd(1)-O(3)	81.9(8)	O(1)-Cd(1)-O(6)	138.6(4)
O(1W)-Cd(1)-O(6)	87.9(7)	O(5)-Cd(1)-O(6)	53.0(5)
O(7) ^{#1} -Cd(1)-O(6)	85.2(6)	O(3)-Cd(1)-O(6)	123.0(4)

O(1)-Cd(1)-O(2)	53.0(4)	O(1W)-Cd(1)-O(2)	92.8(8)
O(5)-Cd(1)-O(2)	139.1(5)	O(7) ^{#1} -Cd(1)-O(2)	93.6(7)
O(3)-Cd(1)-O(2)	149.5(4)	O(6)-Cd(1)-O(2)	86.4(4)
O(3) ^{#2} -Cd(2)-O(3)	173.1(1)	O(3) ^{#2} -Cd(2)-O(5)	101.5(6)
O(3)-Cd(2)-O(5)	74.6(5)	O(5)-Cd(2)-O(5) ^{#2}	113.7(8)
O(3) ^{#2} -Cd(2)-O(4) ^{#2}	51.7(6)	O(3)-Cd(2)-O(4) ^{#2}	131.9(6)
O(5)-Cd(2)-O(4) ^{#2}	80.9(5)	O(5) ^{#2} -Cd(2)-O(4) ^{#2}	126.3(5)
O(3) ^{#2} -Cd(2)-O(4)	131.9(6)	O(3)-Cd(2)-O(4)	51.7(6)
O(5)-Cd(2)-O(4)	126.3(5)	O(5) ^{#2} -Cd(2)-O(4)	80.9(5)
O(4) ^{#2} -Cd(2)-O(4)	133.3(9)		

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

Table S2 Selected bond distances (Å) and angles (°) for **2**.

Zn(1)- O(12)	1.938(1)	Zn(1)-O(1W)	1.98(2)
Zn(1)-O(9) ^{#2}	2.692	Zn(1)-O(10) ^{#2}	1.924(1)
Zn(1)-O(2) ^{#2}	1.974(1)	Zn(2)-O(11)	1.979(1)
Zn(2)-O(1)	2.050(1)	Zn(2)-O(2W)	2.17(2)
Zn(2)-O(3) ^{#2}	1.957(1)	Zn(2)-O(4) ^{#2}	2.298(1)
Zn(3)-O(6) ^{#4}	1.892(1)	Zn(3)-O(14) ^{#3}	1.968(1)
Zn(3)-O(8)	2.099(1)	Zn(3)-O(3W)	2.17(4)
Zn(3)- O(5) ^{#4}	2.683	Zn(4)-O(13) ^{#1}	2.011(9)
Zn(4)-O(15) ^{#3}	2.030(1)	Zn(4)-O(16) ^{#3}	2.408(1)
Zn(4)- O(4W)	2.04(2)	Zn(4)- O(7)	1.983(1)
O(10) ^{#2} -Zn(1)-O(12)	118.9(5)	O(10) ^{#2} -Zn(1)-O(2) ^{#2}	132.0(5)
O(12)-Zn(1)-O(2) ^{#2}	100.9(6)	O(10) ^{#2} -Zn(1)-O(1W)	101.8(9)
O(12)-Zn(1)-O(1W)	95.7(10)	O(2) ^{#2} -Zn(1)-O(1W)	99.6(8)
O(3) ^{#2} -Zn(2)-O(11)	135.8(5)	O(11)-Zn(2)-O(1)	95.0(5)

O(3) ^{#2} -Zn(2)-O(2W)	56.1(6)	O(11)-Zn(2)-O(2W)	103.6(8)
O(1)-Zn(2)-O(2W)	94.9(7)	O(3) ^{#2} -Zn(2)-O(4) ^{#2}	56.1(6)
O(11)-Zn(2)-O(4) ^{#2}	105.5(7)	O(1)-Zn(2)-O(4) ^{#2}	95.2(5)
O(2W)-Zn(2)-O(4) ^{#2}	148.1(8)	O(6) ^{#4} -Zn(3)-O(14) ^{#3}	133.2(6)
O(6) ^{#4} -Zn(3)-O(8)	122.0(6)	O(14) ^{#3} -Zn(3)-O(8)	94.2(6)
O(6) ^{#4} -Zn(3)-O(3W)	99.2(1)	O(14) ^{#3} -Zn(3)-O(3W)	100.0(1)
O(8)-Zn(3)-O(3W)	103.3(1)	O(7)-Zn(4)-O(13) ^{#1}	95.7(5)
O(7)-Zn(4)-O(15) ^{#3}	135.9(6)	O(13) ^{#1} -Zn(4)-O(15) ^{#3}	123.4(6)
O(7)-Zn(4)-O(4W)	98.9(9)	O(13) ^{#1} -Zn(4)-O(4W)	101.4(9)
O(15) ^{#3} -Zn(4)-O(4W)	92.9(8)	O(7)-Zn(4)-O(16) ^{#3}	104.8(5)
O(13) ^{#1} -Zn(4)-O(16) ^{#3}	101.1(5)	O(15) ^{#3} -Zn(4)-O(16) ^{#3}	52.4(6)
O(4W)-Zn(4)-O(16) ^{#3}	145.2(6)		

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

Table S3 Selected bond distances (Å) and angles (°) for **3**.

Mn(1)-O(10)	2.128(4)	Mn(1)-O(1)	2.130(4)
Mn(1)-O(1W)	2.213(4)	Mn(2)-O(3W)	2.075(5)
Mn(2)-O(2)	2.112(5)	Mn(2)-O(16) ^{#2}	2.133(5)
Mn(2)-O(10)	2.186(4)	Mn(2)-O(2W)	2.223(8)
Mn(2)-O(9)	2.284(5)	Mn(3)-O(3)	2.090(5)
Mn(3)-O(15) ^{#2}	2.102(5)	Mn(3)-O(3W)	2.155(6)
Mn(3)-O(7) ^{#2}	2.229(5)	Mn(3)-O(4W)	2.280(7)
Mn(3)-O(13) ^{#2}	2.473(6)	Mn(4)-O(13) ^{#2}	2.120(5)
Mn(4)-O(7) ^{#2}	2.158(5)	Mn(4)-O(12) ^{#2}	2.164(5)
Mn(4)-O(5W)	2.164(4)	Mn(4)-O(4)	2.223(4)
Mn(4)-O(6) ^{#3}	2.257(5)	Mn(5)-O(7W)	2.131(9)
Mn(5)-O(8W)	2.179(7)	Mn(5)-O(4)	2.187(4)
Mn(5)-O(6W)	2.226(9)	Mn(5)-O(11) ^{#3}	2.255(6)

Mn(5)-O(6) ^{#3}	2.269(4)	O(10) ^{#1} -Mn(1)-O(1)	91.07(1)
O(10)-Mn(1)-O(1)	88.93(1)	O(10) ^{#1} -Mn(1)-O(1W)	87.48(1)
O(10)-Mn(1)-O(1W)	92.52(1)	O(1)-Mn(1)-O(1W)	88.9(2)
O(1) ^{#1} -Mn(1)-O(1W)	91.1(2)	O(3W)-Mn(2)-O(2)	100.1(2)
O(3W)-Mn(2)-O(16) ^{#2}	99.1(2)	O(2)-Mn(2)-O(16) ^{#2}	86.7(2)
O(16) ^{#2} -Mn(2)-O(10)	86.57(1)	O(3W)-Mn(2)-O(2W)	90.3(4)
O(2)-Mn(2)-O(2W)	86.8(3)	O(16) ^{#2} -Mn(2)-O(2W)	169.3(3)
O(10)-Mn(2)-O(2W)	86.1(3)	O(3W)-Mn(2)-O(9)	103.6(2)
O(2)-Mn(2)-O(9)	155.01(1)	O(16) ^{#2} -Mn(2)-O(9)	97.3(2)
O(10)-Mn(2)-O(9)	57.22(1)	O(2W)-Mn(2)-O(9)	85.3(3)
O(3)-Mn(3)-O(15) ^{#2}	170.9(2)	O(3)-Mn(3)-O(3W)	90.0(2)
O(15) ^{#2} -Mn(3)-O(3W)	99.0(2)	O(3)-Mn(3)-O(7) ^{#2}	81.5(2)
O(15) ^{#2} -Mn(3)-O(7) ^{#2}	90.97(1)	O(3W)-Mn(3)-O(7) ^{#2}	152.8(2)
O(3)-Mn(3)-O(4W)	89.5(2)	O(15) ^{#2} -Mn(3)-O(4W)	90.3(2)
O(3W)-Mn(3)-O(4W)	82.7(2)	O(7) ^{#2} -Mn(3)-O(4W)	122.7(2)
O(3)-Mn(3)-O(13) ^{#2}	84.4(2)	O(15) ^{#2} -Mn(3)-O(13) ^{#2}	98.15(1)
O(3W)-Mn(3)-O(13) ^{#2}	82.4(2)	O(7) ^{#2} -Mn(3)-O(13) ^{#2}	71.09(1)
O(4W)-Mn(3)-O(13) ^{#2}	163.9(2)	O(13) ^{#2} -Mn(4)-O(7) ^{#2}	79.67(1)
O(13) ^{#2} -Mn(4)-O(12) ^{#2}	89.01(1)	O(7) ^{#2} -Mn(4)-O(12) ^{#2}	93.5(2)
O(13) ^{#2} -Mn(4)-O(5W)	174.7(2)	O(7) ^{#2} -Mn(4)-O(5W)	95.12(1)
O(12) ^{#2} -Mn(4)-O(5W)	90.24(1)	O(13) ^{#2} -Mn(4)-O(4)	100.12(1)
O(7) ^{#2} -Mn(4)-O(4)	92.84(1)	O(12) ^{#2} -Mn(4)-O(4)	169.68(1)
O(5W)-Mn(4)-O(4)	81.11(1)	O(13) ^{#2} -Mn(4)-O(6) ^{#3}	97.73(1)
O(7) ^{#2} -Mn(4)-O(6) ^{#3}	169.24(1)	O(12) ^{#2} -Mn(4)-O(6) ^{#3}	96.87(1)
O(5W)-Mn(4)-O(6) ^{#3}	87.59(1)	O(4)-Mn(4)-O(6) ^{#3}	77.27(1)
O(7W)-Mn(5)-O(8W)	89.5(3)	O(7W)-Mn(5)-O(4)	170.5(3)
O(8W)-Mn(5)-O(4)	99.9(2)	O(7W)-Mn(5)-O(6W)	95.8(5)
O(8W)-Mn(5)-O(6W)	98.0(3)	O(4)-Mn(5)-O(6W)	81.3(3)
O(7W)-Mn(5)-O(11) ^{#3}	92.5(4)	O(8W)-Mn(5)-O(11) ^{#3}	87.5(3)

O(4)-Mn(5)-O(11) ^{#3}	89.58(1)	O(6W)-Mn(5)-O(11) ^{#3}	170.0(4)
O(7W)-Mn(5)-O(6) ^{#3}	93.0(3)	O(8W)-Mn(5)-O(6) ^{#3}	175.7(2)
O(4)-Mn(5)-O(6) ^{#3}	77.74(1)	O(6W)-Mn(5)-O(6) ^{#3}	85.2(3)
O(11) ^{#3} -Mn(5)-O(6) ^{#3}	88.92(1)		

Symmetry transformations used to generate equivalent atoms: ^{#1} -x, -y+2, -z+1; ^{#2} x-1, y, z; ^{#3} -x, -y+2, -z; ^{#4} x+1, y, z.

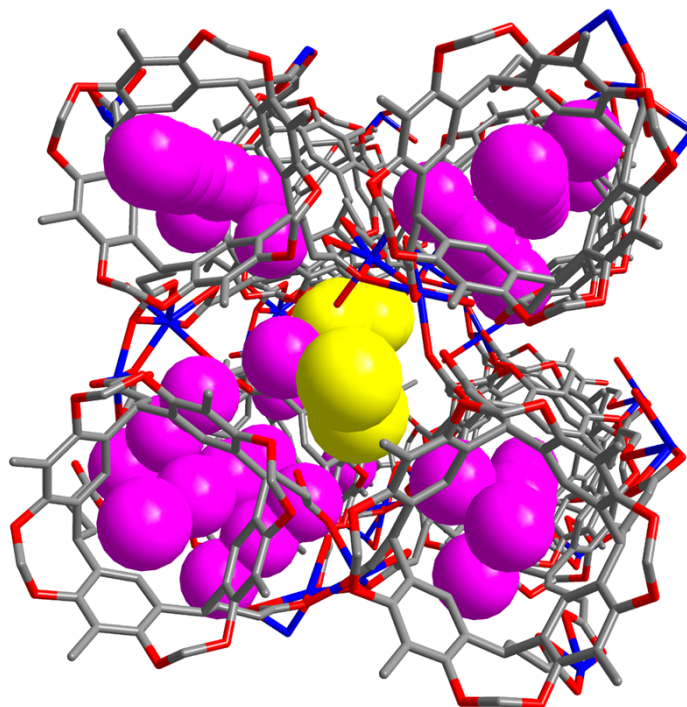


Fig. S1 View of the channels of **1** on the top of cavities of the resorcin[4]arenes (pink and yellow balls represent water and DMF molecules respectively).

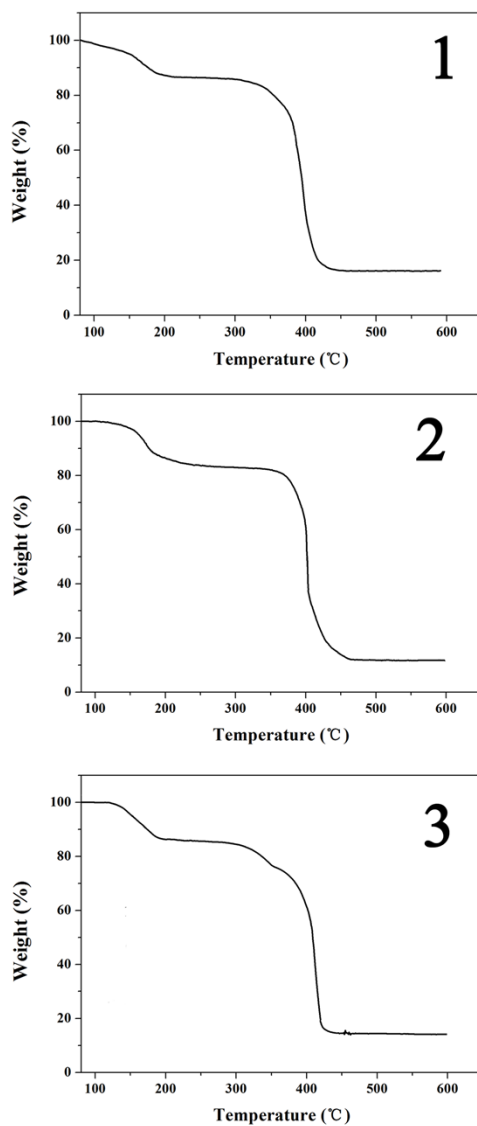


Fig. S2 Thermogravimetric curves of 1-3.

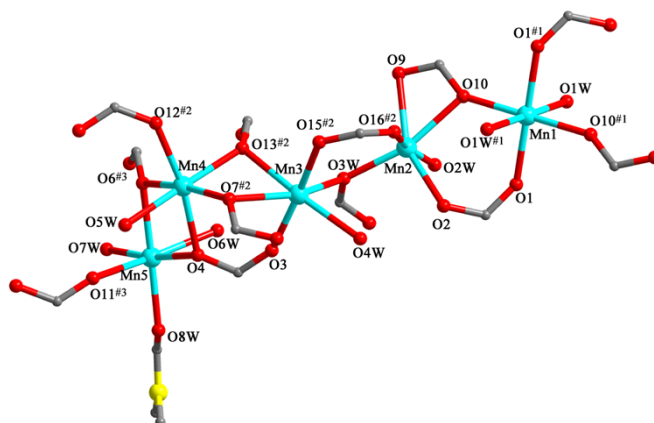


Fig. S3 Coordination environments of Mn(II) atoms in 3. Symmetry codes: #1 $-x, -y+2, -z+1$; #2 $x-1, y, z$; #3 $-x, -y+2, -z$; #4 $x+1, y, z$.

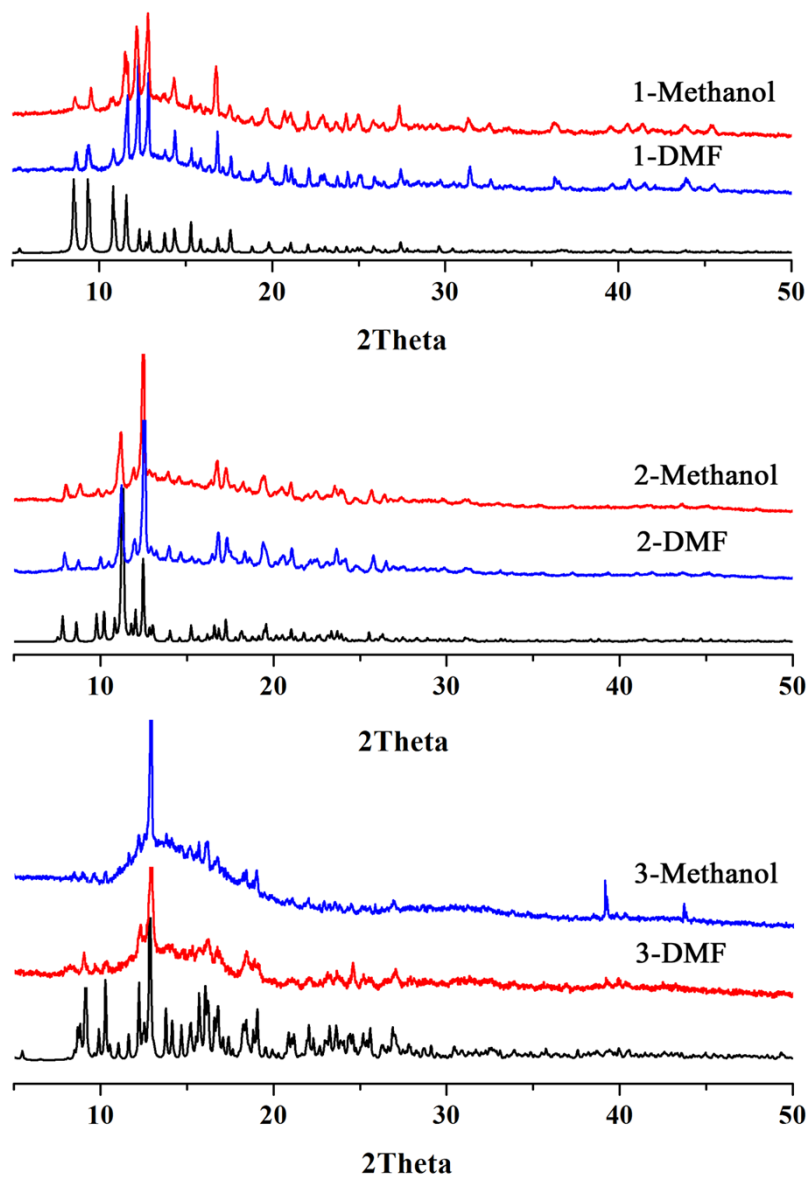


Fig. S4 PXR D patterns of **1-3** immersed in methanol (blue) and DMF (red) after one week.

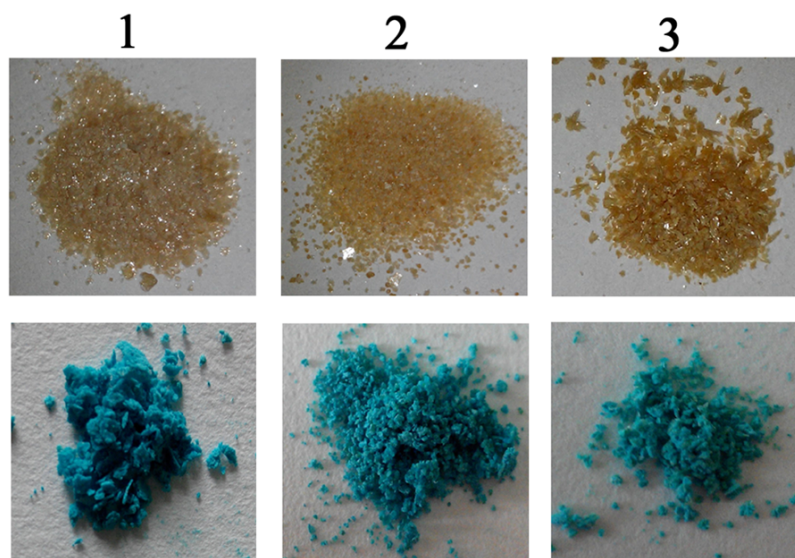


Fig. S5 The photographs of **1-3** (up) and Cu^{2+} -exchanged samples **1a-3a** (down).

It is a pity that good-enough X-ray crystallographic data were not collected because of efflorescence of the samples. We can only obtain the cell parameters of **1a-3a**. Nevertheless, by comparing the data, we can see that the cell parameters of **1a-3a** were similar to their parent structures, respectively (Table S4).

Table S4 Comparison of the crystal data of **1-1a**, **2-2a** and **3-3a**.

	1	1a	2	2a	3	3a
a (Å)	22.9973(4)	22.91(4)	17.6923(7)	17.45(12)	11.8811(6)	11.87(6)
b (Å)	22.9973(4)	23.02(4)	15.6746(7)	15.86(11)	20.9902(14)	21.06(6)
c (Å)	22.5955(7)	22.644(17)	42.5940(11)	42.51(19)	21.3711(11)	21.42(3)
)			
α (°)	90	90	90	90	79.558(5)	79.64(18)
β (°)	90	90	90	90	81.534(4)	81.2(2)
γ (°)	90	90	90	90	86.360(5)	86.9(3)
V (Å ³)	11950.2(6)	11940(17)	11812.2(8)	11768(1)	5180.6(5)	5196(30)

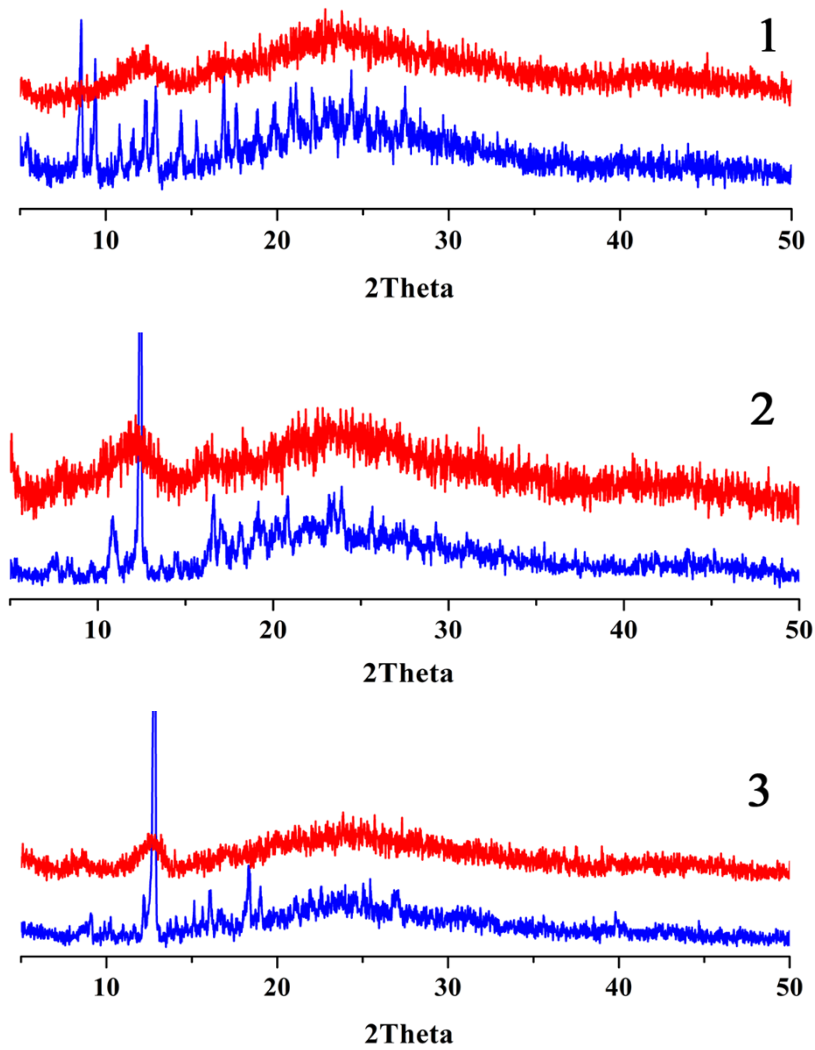


Fig. S6 PXR D patterns: experimental (blue) and Cu(II) exchanged samples with the soaking time of 140, 140 and 200 minutes for **1-3**, respectively (red).

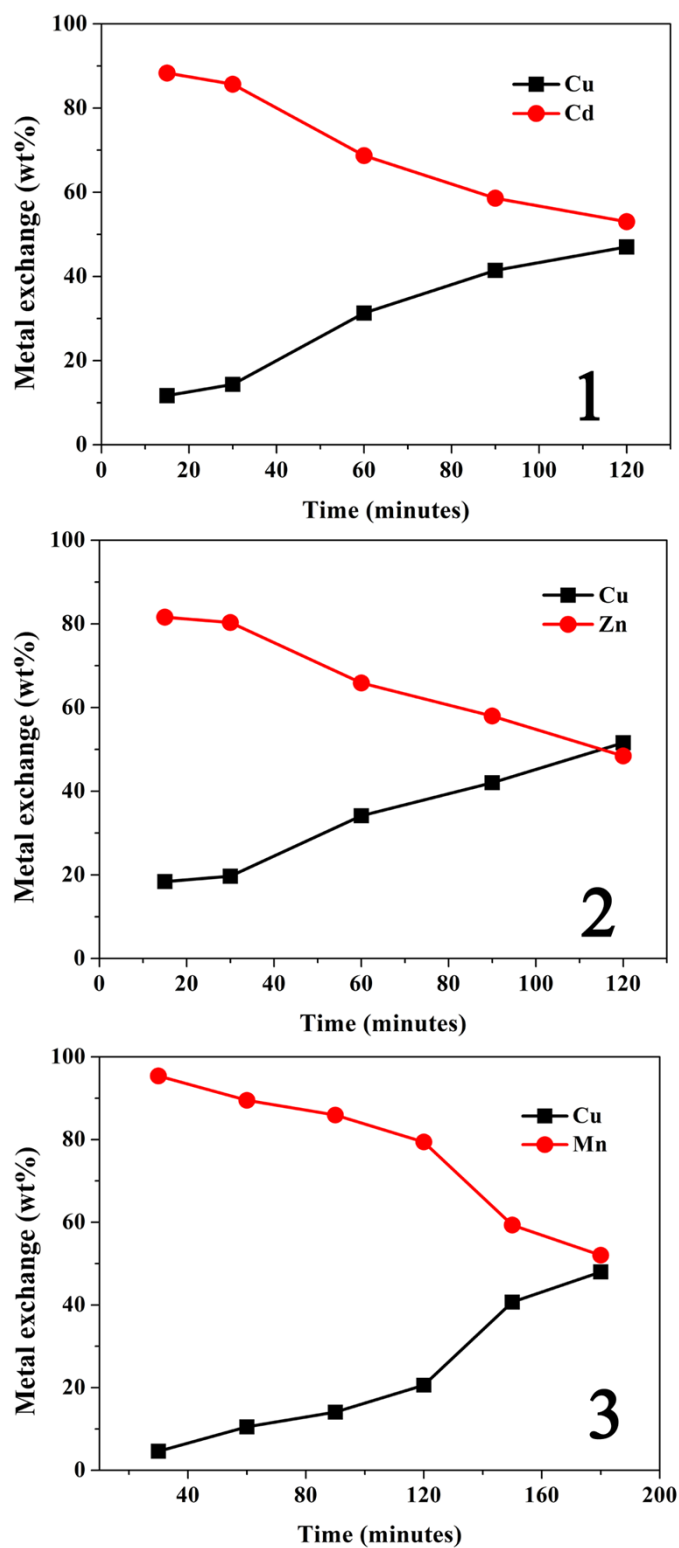


Fig. S7 Time-dependent ICP data for the metal composition during the Cu(II) ion exchanging for 1-3.