Supplemental files

Two cluster-based metal-organic frameworks with selective detection of Hg^{2+} ion and magnetic properties

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Contents:

Materials and Methods

All reagents and solvents were of commercial origin and used without further purification. The ligand L was synthesized according to the literature[1]. $Mn(BF_4)_2{\cdot}4H_2O$ were synthesized by the reaction of $MnCO_3$ and HBF_4. A Bruker Apex Smart APEX II X-ray single crystal diffractometer was used to collect the X-ray crystallographic data. Elemental analyses of C, H and N were performed on a Perkin-Elmer 240C Elemental Analyzer. Powder X-ray diffraction (PXRD) were recorded on a Bruker D8 diffractometer equipped with monochromatized Cu-Kα (λ = 1.5418 Å) radiation at room temperature with a scan speed of 5°/min. IR spectra were recorded with a NICOLET iS50 FT-IR spectrometer with KBr pellets in the range of 4000 to 400 cm^{-1}. The direct current magnetic data were measured at temperature between 2.0 and 300 K on MPMS-XL7 SQUID magnetometer. Experimental susceptibilities were corrected for the diamagnetism estimated Pascal's tables and for sample holder by previous calibration. Fluorescence emission spectra were investigated on a Perkin

Elmer LS55 fluorescence luminescence spectrophotometer under the same measurement conditions. Thermogravimetric analyses (TGA) were carried out on an STA 449-F5 analyzer under N_2 atmosphere at a heating rate of 10 °C·min^{-1} from room temperature to 800 °C. XPS was performed by utilizing an apparatus (Thermo Scientific, K-Alpha) with an Al Ka X-ray source.

Table S1 Selected bond lengths (Å) and bond angles (°) in **1-2**

1					
Cd(1)-Br(1)	3.0151(12)	Cd(1)-Br(1)#1	3.0152(12)	Cd(1)-Br(1)#2	3.0152(12)
Cd(2)-N(1)	2.302(7)	Cd(2)-N(4)#4	2.367(7)	Cd(2)-N(6)#5	2.304(7)
Cd(1)-Br(1)#3	3.0152(12)	Cd(1)-Br(3)	2.461(2)	Cd(1)-Br(3)#3	2.461(2)
Cd(2)-Br(1)	2.7454(13)	Cd(2)-Br(2)	2.5525(14)		
Br(1)-Cd(1)-Br(1)#2	177.48(4)	Br(1)-Cd(1)-Br(1)#3	90.027(1)	Br(1)#2-Cd(1)-Br(1)#1	90.028(1)
Br(1)#2-Cd(1)-Br(1)#3	90.028(1)	Br(1)-Cd(1)-Br(1)#1	90.029(1)	Br(1)#1-Cd(1)-Br(1)#3	177.48(4)
Br(3)#3-Cd(1)-Br(1)	88.742(19)	Br(3)#3-Cd(1)-Br(1)#3	91.258(19)	Br(3)-Cd(1)-Br(1)#1	88.742(19)
Br(3)-Cd(1)-Br(1)#2	91.258(19)	Br(3)-Cd(1)-Br(1)	91.258(19)	Br(3)#3-Cd(1)-Br(1)#2	88.742(19)
Br(3)-Cd(1)-Br(1)#3	88.742(19)	Br(3)#3-Cd(1)-Br(1)#1	91.258(19)	Br(3)-Cd(1)-Br(3)#3	180.0
Br(2)-Cd(2)-Br(1)	117.99(5)	N(1)-Cd(2)-Br(1) N(1)-	85.87(18)	N(1)-Cd(2)-Br(2) N(4)#4-	107.77(19)
N(1)-Cd(2)-N(4)#4	81.2(3)	Cd(2)-N(6)#5	141.6(3)	Cd(2)-Br(1) N(6)#5-	142.78(19)
N(4)#4-Cd(2)-Br(2)	99.19(19)	N(6)#5-Cd(2)-Br(1)	86.41(18)	Cd(2)-Br(2)	109.0(2)

Symmetry codes: #1 -y+1/2, x, -z-1/2 #2 -x+1/2,-y+1/2,z #3 y,-x+1/2,-z-1/2 #4 -x+1,-y,-z #5 x,y,z-1 #6 x,y,z+1

2					
Mn(1)-O(1)#3	2.172(2)	Mn(1)-O(1)#5	2.172(2)	Mn(1)-N(1)	2.224(7)
Mn(1)-O(1)#4	2.172(2)	Mn(1)-O(2)	2.0810(8)	O(2)-Mn(1)#6	2.0811(9)
Mn(1)-O(1)	2.172(2)				
O(1)-Mn(1)-O(1)#5	91.79(15)	O(1)#4-Mn(1)-O(1)#	91.79(15)	O(1)#5-Mn(1)-O(1)#3	88.08(15)
O(1)-Mn(1)-O(1)#4	88.08(15)	O(1)#5-Mn(1)-O(1)#	176.26(14)	O(1)-Mn(1)-O(1)#3	176.26(14)
O(1)-Mn(1)-N(1)	94.7(4)	O(1)#4-Mn(1)-N(1)	85.2(4)	O(1)#5-Mn(1)-N(1)	91.1(4)
O(1)#3-Mn(1)-N(1)	81.5(4)	O(2)-Mn(1)-O(1)#3	91.87(7)	O(2)-Mn(1)-O(1)#5	91.87(1)
O(2)-Mn(1)-O(1)#4	91.87(7)	O(2)-Mn(1)-O(1)	91.87(7)	O(2)-Mn(1)-N(1)	72.7(3)
Mn(1)#7-O(2)-Mn(1)	120.001(1)	Mn(1)#8-O(2)-Mn(1)	119.999(1)	Mn(1)#8-O(2)-Mn(1)#7	120.0

Symmetry codes: #1 -y+1,-x+1,z #2 y,x,-z #3 -x+y,y,-z+1/2 #4 -x+y,y,z #5 x,y,-z+1/2 #6 -y,-x,z #7 -y+1,x-y+1,z #8 -x+y,-x+1,-z+1/2

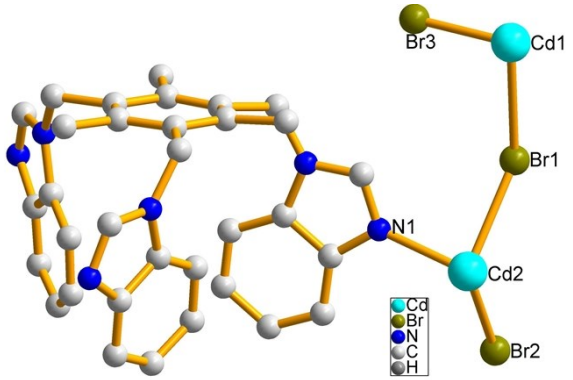

Fig. S1. The asymmetric unit of compound **1** showing the clearly resolved ligand L; atom Cd1 is at site with crystallographically-imposed $\bar{4}$ symmetry while Br3 lies on the twofold axis which also passes through Cd1.

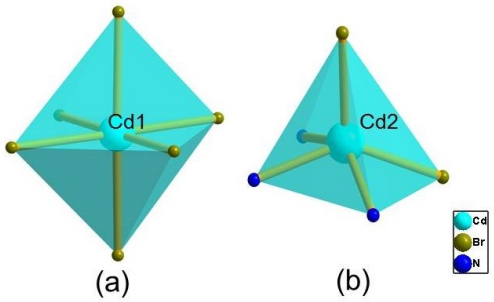

Fig. S2 Coordination modes of Cd1 and Cd2 in **1**.

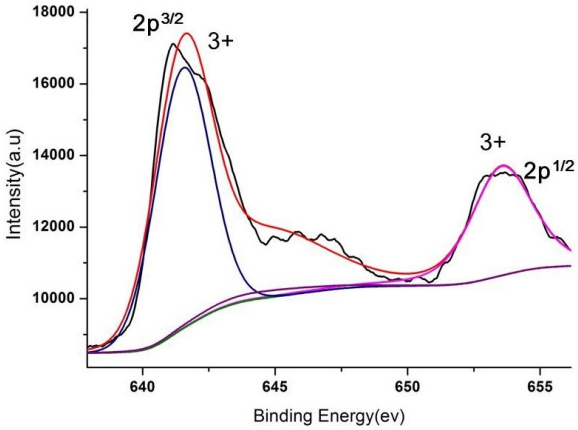

Fig. S3 The XPS for Mn^{III} ions of compound **2**.

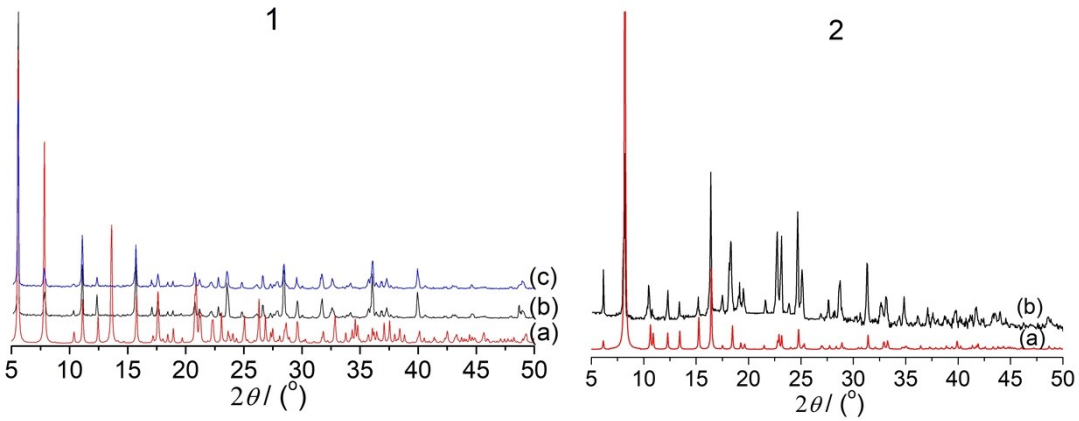

Fig. S4 Powder XRD patterns for **1** and **2**, (a) simulated, (b) as-synthesized, (c) after the sensing experiments.

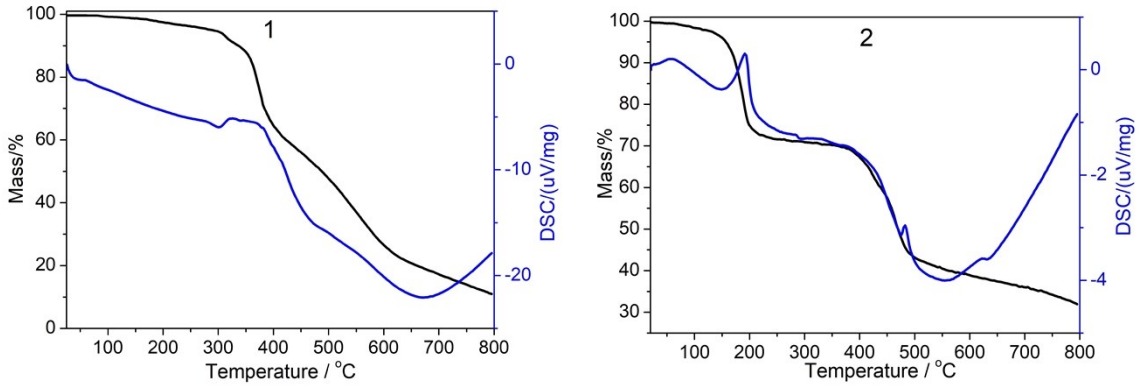

Fig. S5 TGA-DSC curves of **1** and **2** under nitrogen.

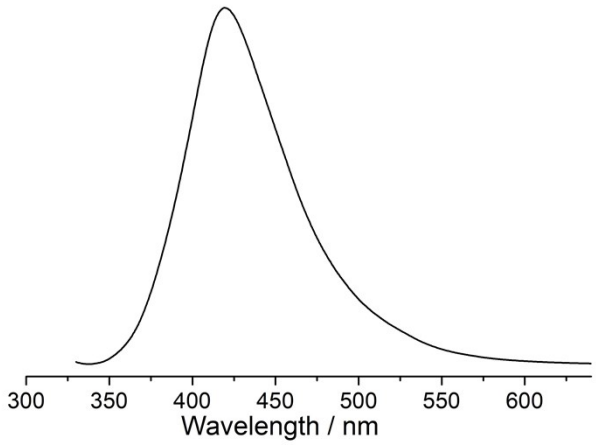

Fig. S6 The fluorescence spectra of **1** in DMSO at room temperature.

Reference

1. C. Y. Su, Y. P. Cai, C. L. Chen, M. D. Smith, W. Kaim and H. C. Zur Loye, *J. Am. Chem. Soc.*, 2003, **125**, 8595-8613.