Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Calixarene-based coordination cage as efficient luminescent sensor for Fe^{3+}, MnO_4^-, NB in aqueous medium

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S1. Materials and Methods

p-tert-Butyltetrathiacalix[4]arene (H_4TC4A) was synthesized by the literature method[S1], other reagents are purchased from commercial sources and used directly. FT-IR spectra was obtained in the range of 400-4000 cm^{-1} on a BRUKER-EQUINOX-55 IR spectrophotometer with KBr pellets. TGA measurements were performed using a Rigaku Thermo plus TG8120. Powder X-ray diffraction (pXRD) measurement was investigated by MSALXD3 X-ray diffractometer (Beijing Puxi General Instrument Co. Ltd, Beijing, China) with Cu *Kα* (λ = 0.15406 nm), scan rate at 8°/min from 5° to 50°.

S2. Single-crystal X-ray diffraction

The intensity data of **SWU-2** was recorded on a Bruker D8 VENTURE system with Mo-*Kα* radiation (λ = 0.71073 Å). The crystal structure was solved by means of Direct Methods and refined employing full-matrix least squares on F^2 (SHELXTL-2018)[S2]. The high R_1 and wR_2 factor of compound **SWU-2** might be due to the weak high-angle diffractions and the disorder of *p-tert*-butyl atoms. It was not possible to model the disordered solvent molecules appropriately even with the low temperature data obtained at about 150 K. The diffraction data were treated by the "SQUEEZE" method as implemented in PLATON[S3] to remove the contributions of the highly disordered solvent molecules. The SQUEEZE results for both structures are listed below. The detailed crystallographic data and structure refinement parameters for **SWU-2** (CCDC 2217047) are summarized in Table S1. Selected bond lengths (Å) and angles (°) for **SWU-2** are given in Table S2. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

Table S1 Crystal data and structure refinement for **SWU-2**.

Complex	**SWU-2**
Formula	$C_{312}H_{300}Mg_{24}O_{78}S_{24}$
Mr	6650.38
Crystal system	tetragonal
space group	*I4/m*
a (Å)	26.170(5)
b (Å)	26.170(5)
c (Å)	43.516(14)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
Volume(Å^3)	29802(15)
Z	2
Temperature(K)	150(2)
Dc(g/cm^3)	0.740
μ(mm^{-1})	0.229
Reflections collected	125648
Unique data (R_{int})	0.0649
GOF on F^2	1.300
R_1[a] [$I>2\sigma(I)$]	0.0754
wR_2[b]	0.2406

[a]$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; [b]$wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

Table S2. Selected bond distances (Å) and angles (deg) for **SWU-2**.

Bond lengths (Å)			
Mg1-O$^{\#1}$	2.004(2)	Mg1-O1	2.003(2)
Mg1-O4$^{\#1}$	2.016(2)	Mg1-O5	2.015(2)
Mg1-O11	2.2432(15)	Mg1-S1	2.7706(14)
Mg2-O3	2.007(2)	Mg2-O3$^{\#3}$	2.007(2)
Mg2-O7$^{\#3}$	2.014(2)	Mg2-S4	2.7608(17)
Mg2-O12$^{\#2}$	2.253(3)	Mg3-O2$^{\#4}$	2.009(2)
Mg3-O2$^{\#1}$	2.009(2)	Mg3-S2$^{\#1}$	2.7091(18)
Mg3-O8$^{\#3}$	2.015(2)	Mg3-O8	2.015(2)
Mg3-O12	2.265(3)	Mg4-O2$^{\#4}$	2.008(2)
Mg4-O3$^{\#4}$	2.006(2)	Mg4-O6$^{\#1}$	2.023(2)
Mg4-O9	2.006(2)	Mg4-O12	2.2257(14)
Mg4-S3$^{\#4}$	2.7854(13)		
Symmetry transformations used to generate equivalent atoms: #1: 1-Y, +X, +Z; #2: +Y, 1-X, 1-Z; #3: +X,+Y,1-Z; #4: 1-Y,+X,1-Z.			
Bond angles (°)			
O1-Mg1-S1	75.93(7)	O1$^{\#1}$-Mg1-S1	75.65(7)
O1-Mg1-O1$^{\#1}$	93.18(13)	O1-Mg1-O4$^{\#1}$	175.58(11)
O1$^{\#1}$-Mg1-O4$^{\#1}$	90.38(10)	O1$^{\#1}$-Mg1-O5	175.01(11)
O1-Mg1-O5	90.70(10)	O1$^{\#1}$-Mg1-O11	82.34(9)
O1-Mg1-O11	82.35(9)	O4$^{\#1}$-Mg1-S1	102.46(8)
O4$^{\#1}$-Mg1-O5	85.60(10)	O4$^{\#1}$-Mg1-O11	100.74(10)
O5-Mg1-S4	102.31(8)	O5-Mg1-O11	101.29(10)
O11-Mg1-S1	147.90(10)	O3-Mg2-S4	76.05(6)
O3$^{\#3}$-Mg2-S4	76.05(6)	O3-Mg2-O3$^{\#3}$	93.87(13)
O3$^{\#3}$-Mg2-O7$^{\#3}$	175.08(10)	O3-Mg2-O7$^{\#3}$	90.27(9)
O3-Mg2-O7	175.08(10)	O3$^{\#4}$-Mg2-O7	90.28(9)
O3-Mg2-O12$^{\#2}$	82.14(8)	O3$^{\#3}$-Mg2-O12$^{\#2}$	82.14(8)
O7$^{\#3}$-Mg2-S4	102.45(8)	O7-Mg2-S4	102.45(8)
O7-Mg2-O7$^{\#3}$	85.47(13)	O7-Mg2-O12$^{\#2}$	101.07(9)
O7$^{\#3}$-Mg2-O12$^{\#2}$	101.07(9)	O12$^{\#2}$-Mg2-S4	147.77(8)
O2$^{\#4}$-Mg3-S2$^{\#1}$	75.36(6)	O2$^{\#1}$-Mg3-S2$^{\#1}$	75.36(6)
O2$^{\#4}$-Mg3-O2$^{\#1}$	94.09(13)	O2$^{\#4}$-Mg3-O12	81.77(8)
O2$^{\#1}$-Mg3-O12	81.77(8)	O8-Mg3-S2$^{\#1}$	104.93(8)
O8$^{\#3}$-Mg3-S2$^{\#1}$	104.93(8)	O8$^{\#3}$-Mg3-O2$^{\#1}$	90.43(9)
O8$^{\#3}$-Mg3-O2$^{\#4}$	175.38(10)	O8-Mg3-O2$^{\#1}$	175.38(10)
O8-Mg3-O2$^{\#4}$	90.43(9)	O8-Mg3-O8$^{\#3}$	85.03(12)
O8$^{\#3}$-Mg3-O12	99.86(9)	O8-Mg3-O12	99.86(9)
O12-Mg3-S2$^{\#1}$	146.11(9)	O2$^{\#4}$-Mg4-S3$^{\#4}$	75.72(6)
O2$^{\#4}$-Mg4-O6$^{\#1}$	174.15(10)	O2$^{\#4}$-Mg4-O9	90.31(9)
O2$^{\#4}$-Mg4-O12	82.78(9)	O3$^{\#4}$-Mg4-S3$^{\#4}$	74.86(6)

O3$^{\#4}$-Mg4-O2$^{\#4}$	94.22(9)	O3$^{\#4}$-Mg4-O6$^{\#1}$	90.13(9)
O3$^{\#4}$-Mg4-O9	174.31(10)	O3$^{\#4}$-Mg4-O12	82.86(9)
O6$^{\#1}$-Mg4-S3$^{\#4}$	101.74(7)	O6$^{\#1}$-Mg4-O12	101.66(10)
O9-Mg4-S3$^{\#4}$	103.01(8)	O9-Mg4-O6$^{\#1}$	85.21(9)
O9-Mg4-O12	101.16(10)	O12-Mg4-S3$^{\#4}$	147.50(7)
Symmetry transformations used to generate equivalent atoms: #1: 1-Y, +X, +Z; #2: +Y, 1-X, 1-Z; #3: +X, +Y, 1-Z; #4: 1-Y, +X, 1-Z.			

SQUEEZE RESULTS for **SWU-2**

```
# Note: Data are Listed for all Voids in the P1 Unit Cell
# i.e. Centre of Gravity, Solvent Accessible Volume,
# Recovered number of Electrons in the Void and
# Details about the Squeezed Material
loop_
   _platon_squeeze_void_nr
   _platon_squeeze_void_average_x
   _platon_squeeze_void_average_y
   _platon_squeeze_void_average_z
   _platon_squeeze_void_volume
   _platon_squeeze_void_count_electrons
   _platon_squeeze_void_content
    1   0.000   0.000   0.000      662        200 ' '
    2   0.489   0.000 -0.001    13615       2885 ' '
    3   0.000   0.000   0.500     1140        266 ' '
    4   0.500   0.500   0.000     1140        266 ' '
    5   0.500   0.500   0.500      662        200 ' '
```

SQUEEZE gives 3817 electrons per unit cell in **SWU-2**, which can be assigned to the contributions of the disordered species in the voids. For there is two formula unit per cell, each formula would contain 1908.5 e^- for the disordered solvent molecules. So 1908.5 e^- correspond to about106 CH_3OH (18 e^-) molecules or 47 DMF (40 e^-) molecules. When all the results of SQUEEZE and TG are considered, the appropriate chemical formula can be proposed as $\{Mg_{24}(TC4A)_6(BTC)_8(H_2O)_6\}\cdot 106CH_3OH$ or $\{Mg_{24}(TC4A)_6(BTC)_8(H_2O)_6\}\cdot 46DMF$.

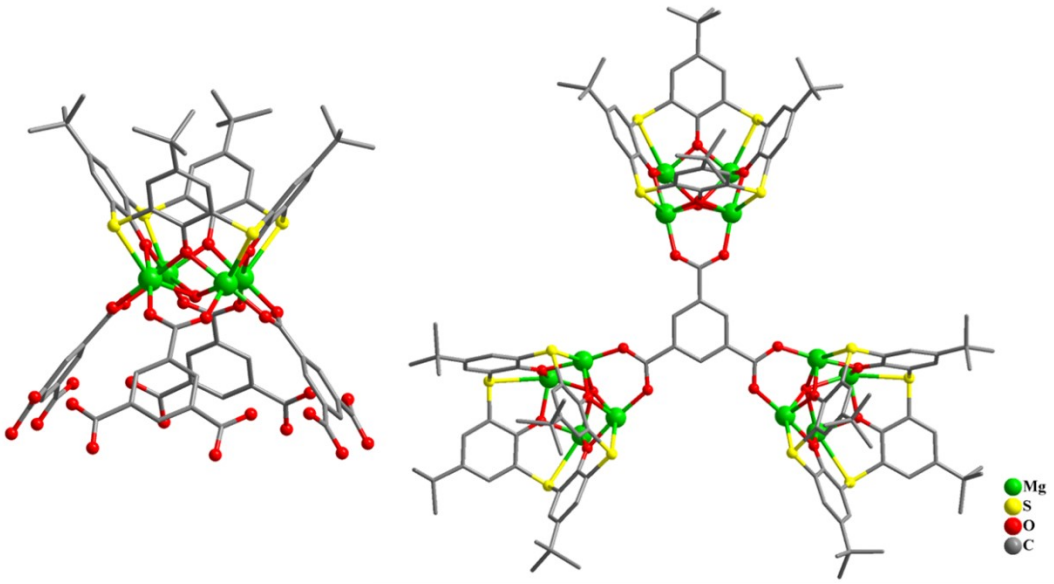

Fig. S1 Co4-TC4A SBUs and BTC coordination environment in **SWU-2**.

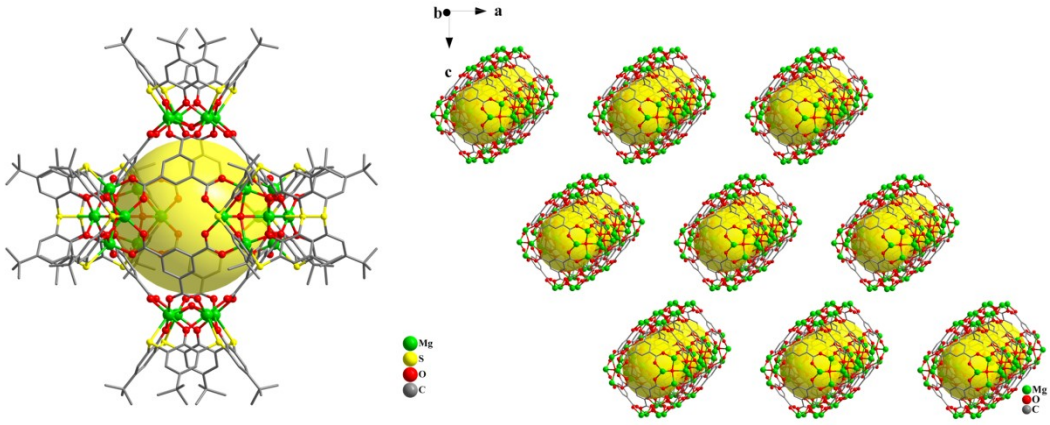

Fig. S2 Molecular structure of **SWU-2** and packing diagram of the nanocages. (The calixarene molecules are omitted for clarity.)

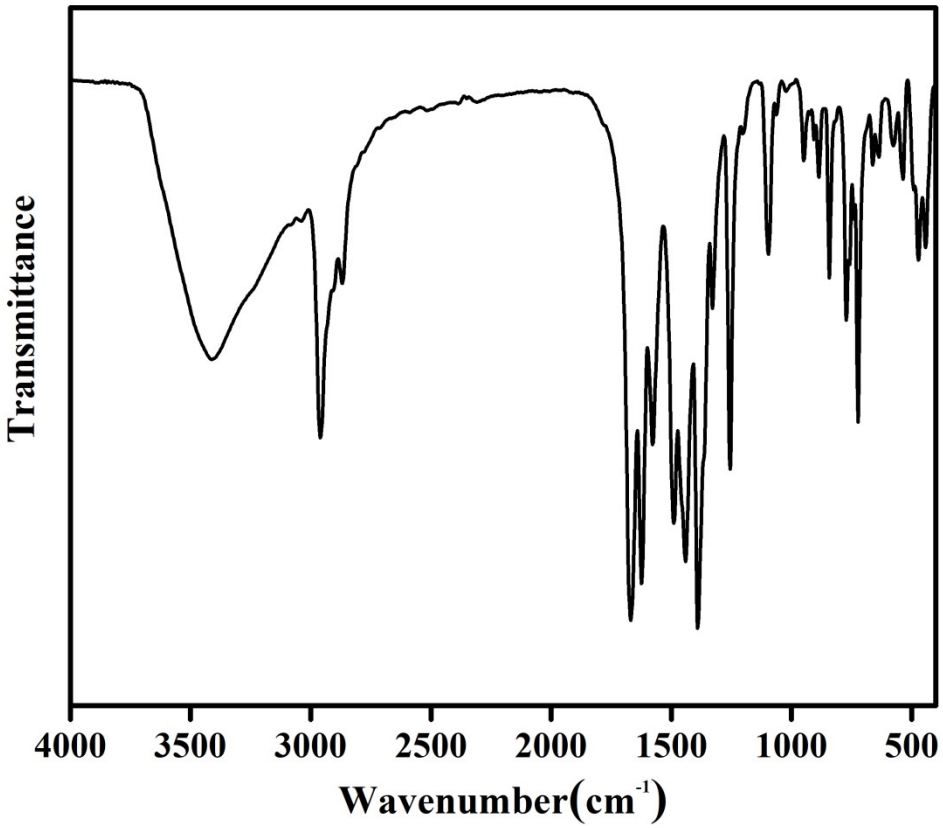

Fig. S3 FT-IR spectra of **SWU-2**.

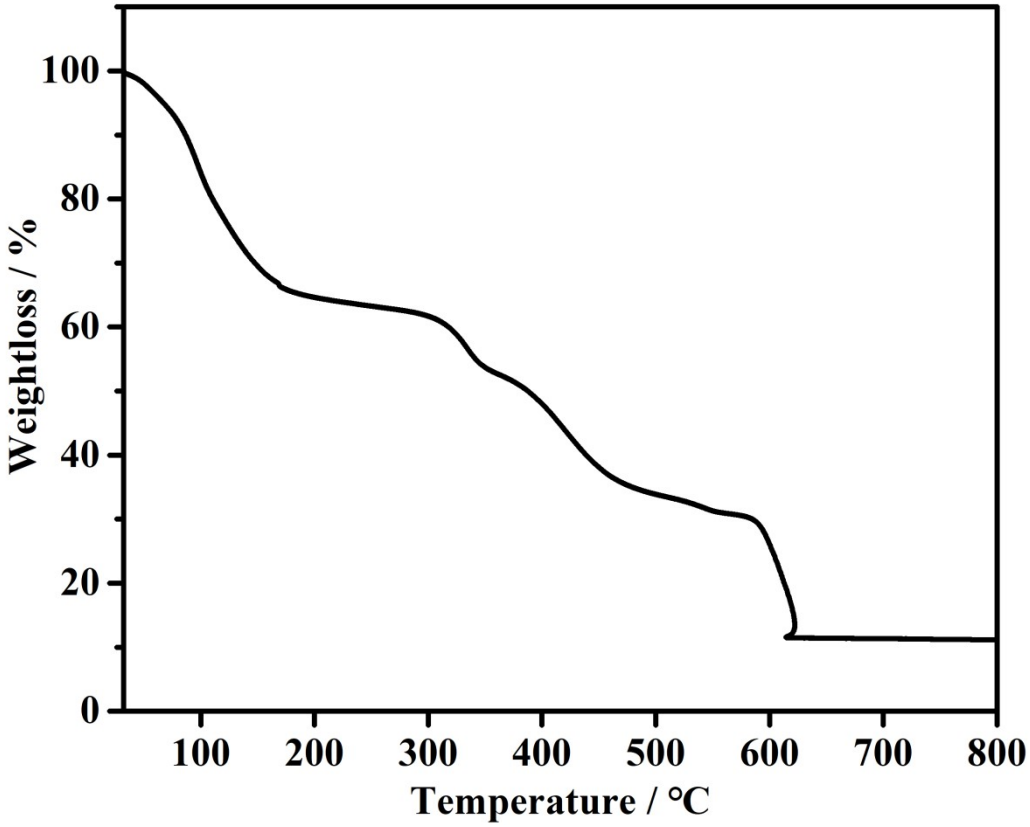

Fig. S4 The TG curves of the compound **SWU-2**.

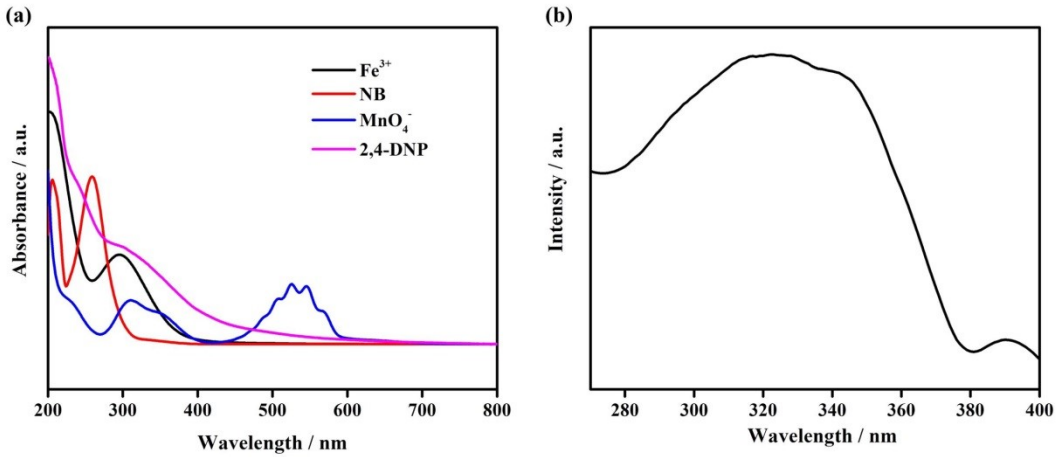

Fig. S5 (a) The UV-Vis absorption spectra of the solutions of Fe^{3+}, MnO_4^-, NB and 2,4-DNP; (b) The excitation spectra for **SWU-2**.

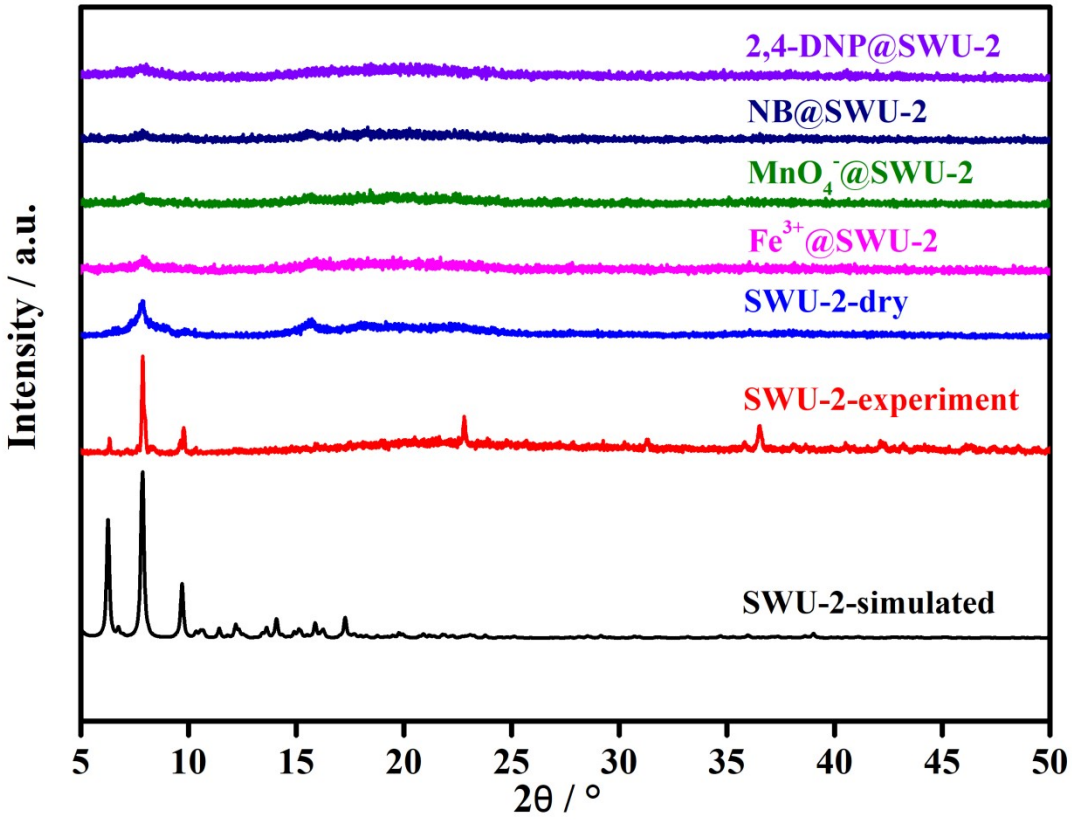

Fig. S6 Power X-ray diffraction patterns of **SWU-2** after soaking in different solutions.

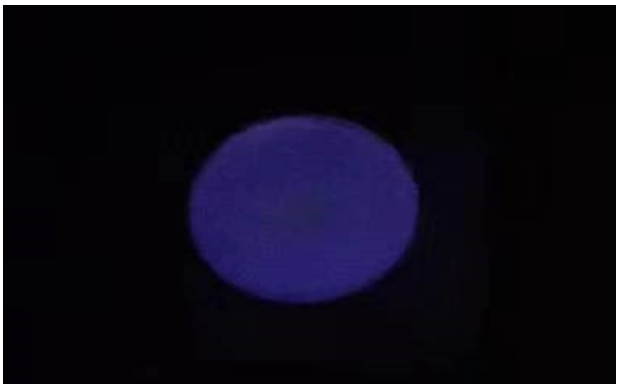

Fig. S7 The blue light of **SWU-2** at UV 245 nm.

Table S3 Comparison of the values of K_{sv} for Fe^{3+} in this work with those of some previously reported compounds for sensing Fe^{3+} ion.

Analyte	Material	Solution	LOD	K_{sv}	Ref
Fe^{3+}	$\{Mg_{24}(TC4A)_6(BTC)_4(H_2O)_6\}$	Water	2.65 μM	3.08×10^4 M^{-1}	This work
Fe^{3+}	$[Cd_2(1,6\text{-NDS})_2(bbimb)_3(H_2O)_4]\cdot2H_2O$	Water	1.80×10^{-4} M	1.01×10^4 M^{-1}	S4
	$[Zn(1,6\text{-NDS})(bbimb)_{1.5}]\cdot2H_2O$		1.76×10^{-4} M	7.17×10^3 M^{-1}	
Fe^{3+}	$[Tb_4(TATB)_2]$	Water	4.84 μM	—	S5
Fe^{3+}	HCAA@UiO-66	Water	4.87 μM	—	S6
Fe^{3+}	$[Cd(BIM)_2Cl_2]_n$	Water	21.5 μM	9.59×10^3 M^{-1}	S7

bbimb = 1,4-bis(benzoimidazol-1-yl)butane; H_3TATB = 4,4',4''-(1,3,5-triazine-2,4,6-triyl)tribenzoic acid; HCAA = 7-hydroxycoumarin-4-acetic acid; BIM = *bis*(XXXmidazole-1-yl)methane.

Table S4 Comparison of the values of K_{sv} for MnO_4^- in this work with those of some previously reported compounds for sensing MnO_4^- ion.

Analyte	Material	Solution	LOD	K_{sv}	Ref
MnO_4^-	$\{Mg_{24}(TC4A)_6(BTC)_4(H_2O)_6\}$	Water	1.73 μM	4.72×10^4 M^{-1}	This work
MnO_4^-	$[Cd_2(L)_2(Bda)(NO_3)H_2O]\cdot2H_2O$	Water	4.70 μM	5.6×10^3 M^{-1}	S8
MnO_4^-	$[Cd_3(L^{Me})(H_2O)]\cdot DMF\cdot3H_2O$	Water	3.50 μM	2.67×10^4 M^{-1}	S9
MnO_4^-	$Sm_8(HDBA)_6\cdot H_2O$	Water	2.26 μM	—	S10

Bda = Succinic acid; L = 3,5-bis-(triazol-1-yl)-benzoic acid; L^{Me} = 1,3,5-tris(dimethyl-isophthalate-1-ethynyl); H_5DBA = 3,5-di(2′,4′-dicarboxylphenyl)benzoic acid.

Table S5 Comparison of the values of K_{sv} for NB in this work with those of some previously reported compounds for sensing NB.

Analyte	Material	Solution	LOD	K_{sv}	Ref
NB	$\{Mg_{24}(TC4A)_6(BTC)_4(H_2O)_6\}$	Water	1.10 μM	7.45×10^4 M^{-1}	This work
NB	$\{[Eu_4(INO)_5(\mu_3\text{-}OH)_2Cl_4(H_2O)]\cdot(NO_3)\cdot(H_2O)_5\}_n$	Water	80.0 μM	0.30×10^3 M^{-1}	S11

Table S6 Comparison of the values of K_{sv} for 2,4-DNP in this work with those of some previously reported compounds for sensing 2,4-DNP.

Analyte	Material	Solution	LOD	K_{sv}	Ref
2,4-DNP	$\{Mg_{24}(TC4A)_6(BTC)_4(H_2O)_6\}$	Water	2.06 μM	3.98×10^4 M^{-1}	This work
2,4-DNP	$\{[Eu_4(INO)_5(\mu_3\text{-}OH)_2Cl_4(H_2O)]\cdot(NO_3)\cdot(H_2O)_5\}_n$	Water	2.87 μM	5.11×10^3 M^{-1}	S12

Notes and References

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