Supporting Information

Tetra-Fe(III) and deca-Mn(III) metallacrown built from bis-salicylhydrazide ligand: synthesis, structures and magnetic properties

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Comment S1: Materials and characterization for complexes 1-4.

C, H, N elemental analyses were performed on an Elementar Vario MICRO E III analyzer. IR spectra were recorded as KBr pellets on a Perkin Elmer spectrometer. Ultraviolet spectra were recorded using a Shimadzu UV-3600 Spectrophotometer. TGA was performed on a NETZSCH STA 449C thermo-gravimetric analyzer in flowing N_2 with a heating rate of 10 ^oC min^{-1}. Powder X-ray diffraction patterns (PXRD) were acquired on a D8 Advance X-ray diffractometer operating at 40 kV and 40 mA with Cu Kα radiation (λ = 1.5406 Å). Single crystal X-ray data were collected using BRUKER APEX DUO CCD diffractometer with Mo-Kα radiation (λ = 0.71073 Å). Magnetic moments were recorded using a Quantum Design MPMS SQUID magnetometer over the temperature range 5 to 300K. The magnetic data were collected in an applied field of 0.2 T and corrected for diamagnetism using a Pascal's constants according to a reference[1].

The cyclic voltammetry (CV) studies were perfomed on an electrochemical workstation (CHI 660, Shanghai CH Instruments Co., China) in a single compartment cell with three-electrode cofiguration, which consisted of working electrode, a platinum gauze as auxiliary electrode, and Ag/Ag^+ (0.01 M $AgNO_3$ in 0.1 M tetrabutylammonium hexafluorophosphate–MeCN) as reference electrode. The reference electrode was stabilized in a glass tube with a Luggin capillary, which was filling with corresponding catholyte. CV measurements in nitrogen gas-saturated electrolyte were taken between -1.5 V and 1.5 V vs. Ag/Ag^+ at a sweep rate 100 $mV{\cdot}s^{-1}$. Prior to experiments, all the metal electrodes (0.5 cm×0.5 cm) were polished with fine sand paper and then were sonicated in acetone for 10 min, followed by washing with water and ethanol, and finally dried in N_2 atmosphere.

Comment S2: Syntheses of complexes 1-4.

Synthesis of H_6PentaCShz

5-Chloro salicylic acid hydrazide (7.63g, 0.041mol), glutaryl chloride (3.21g, 0.019mol) and pyridine (0.057mol) were dissolved in DMF (50mL) and stirred for two hours at 50^{o}C. A white precipitate was obtained after slowly warming the solution up to room temperature. This was filtered off and rinsed with chloroform and diethyl ether and dried at 100^{o}C in an oven (Yield: 5.15g, 57.8%). *Anal./Calcd.* for $C_{19}H_{18}N_4O_6Cl_2$: C 48.63; H 3.87; N 11.94. Found: C 48.65; H 3.90; N 12.00. ^{1}HNMR(DMSO-d_6) δ(ppm)：11.91 (s,2H; $_{-ph-}$OH), 10.54 (s,2H; $_{-phCO-}$NH-), 10.26 (s, 2H; -NH$_{-COCH2-}$), 8.89 (d,2H; $_{o-ph}$CH), 7.89-7.90 (m,2H; $_{p-ph}$CH), 6.99-7.01(m, 2H; $_{m-Ph}$CH), 1.84-2.26 (s,6H; -$CH_2CH_2CH_2$-); ^{13}CNMR (DMSO-d_6) δ(ppm): 170.81 ($_{-NH-}$CO-$_{CH2-}$)，165.51 ($_{-Ph-}$CO-$_{NH}$), 157.668 ($_{-Ph}$C$_{-OH}$), 135.91 ($_{.Ph}$C), 128.46 ($_{o-Ph}$C), 119.69 ($_{m-Ph}$C), 117.05 (PhC-CO-), 110.33(m-PhC), 32.80 ($_{-CO-}$$CH_{2-CH2-}$), 21.46 ($_{-COCH2-}$ CH_2-); IR (KBr pellet, cm^{-1}): υ_{N-H},3224(b); υ_{O-H}, 3348(s), broad; $\upsilon_{C=O}$,1634(s); $\upsilon_{C=N}$,1585(s); $_{C-N}$,1353(s); υ($_{=C-C=C-}$)phenolic,1224(vs).

Synthesis of H_6PentaBShz

H_6PentaBShz was prepared in a similar method to ligand H_6PentaCShz except for the amount of the 5-Bromo salicyclic acid hydrazide (9.712g, 0.042mol). (Yield: 6.4g, 72%). *Anal./Calcd.* for $C_{19}H_{18}N_4O_6Br_2$: C 40.88; H 3.25; N 10.04. Found: C 40.85; H 3.50; N 10.07.

^{1}HNMR(DMSO-d_6), δ(ppm): 11.9 (s,2H;$_{\text{-ph-}}$OH), 10.57 (s,2H; $_{\text{-phCO}}$-NH-), 10.29 (s,2H; -NH-$_{\text{COCH2-}}$) 8.024 (d,2H;$_{\text{o-ph}}$CH), 7.59-7.60 (m,2H; $_{\text{p-ph}}$CH), 6.93-6.96 (m, 2H; $_{\text{m-Ph}}$CH) 1.62-2.25 (s,6H;-$CH_2CH_2CH_2$-); ^{13}CNMR (DMSO-d_6) δ(ppm): 170.52($_{\text{-NH-}}$CO-$_{\text{CH2-}}$), 164.99 ($_{\text{-Ph-}}$CO-$_{\text{NH-}}$), 157.784 ($_{\text{-Ph}}$C$_{\text{-OH}}$), 136.40 ($_{\text{p-}}$Ph$_{\text{C}}$), δ131.058 ($_{\text{o-Ph}}$C), 119.72($_{\text{m-Ph}}$C), 117.247(PhC-CO-), 110.28(m-PhC), 33.91 ($_{\text{-CO-}}$$CH_2$-$_{\text{CH2-}}$), 25.22 ($_{\text{-COCH2-}}$$CH_2$-); IR (KBr pellet,cm^{-1}): $\upsilon_{\text{N-H}}$, 3409(b); $\upsilon_{\text{O-H}}$, 3319(s), broad; $\upsilon_{\text{C=O}}$, 1631(s); $\upsilon_{\text{C=N}}$, 1582(s); $\upsilon_{\text{C-N}}$, 1368(s); $\upsilon_{\text{=C-C=C-(phenolic)}}$, 1483(vs).

Synthesis of $[Fe_4(PentaCShz)_2(H_2O)_4]\cdot 8DMF$ (1)

H_6PentaCShz (0.0469g, 0.1 mmol) was dissolved in 20.0mL DMF firstly, to which $FeCl_3$ (0.0324 g, 0.2 mmol) was then added slowly. And then ten drops of pyridine were added into the solution to adjust the pH value to be ca. 7.0. The mixed solution was stirred for two hours at room temperature and the resulted solution was filtered. The filtrate was standing for two weeks at ambient temperature. Crystals suitable for X-ray diffraction experiment were obtained at the bottom of the vessel. (Yield: 56.6mg, 62%). *Anal./Calcd*. for $Fe_4C_{62}H_{88}N_{16}O_{24}Cl_4$ (M_r=1806.68): C 41.22; H 4.91; N 12.40. Found: C 40.80; H 4.96; N 12.28. IR (KBr pellet, cm^{-1}): 3439(m,br), 2928(w), 1654(vs), 1597(w), 553(s), 1508(vs), 1420(m), 1404(vs), 1370(vs), 1307(w), 1249(w), 1098(w), 920(w), 829(w), 808(w), 773(w), 728(m), 703(w), 667(w)cm^{-1}.

Synthesis of $[Fe_4(PentaBShz)_2(H_2O)_4]\cdot 8DMF$ (2)

Compound 2 was prepared in an analogous procedure to 1 except for the amount of the H_6PentaBShz (0.0558g, 0.1 mmol). (Yield: 47.2mg, 48%). *Anal./Calcd*. for $Fe_4C_{62}H_{88}N_{16}O_{24}Br_4$ (M_r=1984.52): C 37.52; H 4.47; N 11.29. Found: C 36.85; H 4.58; N 11.08. IR(KBr,pellet,cm^{-1}): 3454(m,br), 2368(w), 1870(w), 1845(w), 1831(w), 1793(w), 1773(w), 1735(w), 1718(w), 1701(w), 1685(w), 1654(w), 1591(m), 1550(vs), 1507(vs), 1458(w), 1420(vs), 1404(w), 1369(w), 1330(w), 1304(w),1249(w), 1116(w), 1016(w), 915(w), 829(w), 774(w), 710(w), 669(w), 659(w), 622(w), 607(w),541(w),431(w).

Synthesis of $[Mn_{10}(PentaCShz)_5(DMF)_4\cdot(Py)_2\cdot(H_2O)_4]$ (3)

Compound 3 was prepared in an analogous procedure to 1 except for the amount of the H_6PentaCShz (0.0469g, 0.1 mmol) and $Mn(OAc)_2\cdot 4H_2O$ (0.049 g, 0.2 mmol) . (Yield: 71.4mg, 30% . Note, the squeezed DMF solvent molecules were taken into account in the formula weight). *Anal./Calcd*. for $Mn_{10}C_{174}H_{235}N_{41}O_{56}Cl_{10}$ (M_r=4693.75): C 44.53; H 5.11; N 12.32. Found: C 44.42; H 4.76; N 11.44. IR(KBr , pellet, cm^{-1}): 3440(m,br), 2931(w), 1657(vs), 1600(s), 1557(vs) 1513(vs), 1426(vs), 1382(vs), 1360(vs), 1303(s) ,1268(m), 1247(m), 1151(m), 1103(m), 1001(w), 897(w), 857(w), 825(w), 799(w), 768(w), 734(s), 698(w), 641(m), 560(w), 540(w), 448(w).

Synthesis of $[Mn_{10}(PentaBShz)_5(DMF)_4\cdot(Py)_2\cdot(H_2O)_4]$ (4)

Compound 3 was prepared in an analogous procedure to 1 except for the amount of the H_6PentaBShz (0.0558g, 0.1 mmol) and $Mn(OAc)_2\cdot 4H_2O$ (0.049 g, 0.2 mmol) . (Yield: 78.3mg, 28% Note, the squeezed DMF solvent molecules were taken into account in the formula weight). *Anal./Calcd*. for $Mn_{10}C_{193}H_{278}N_{46}O_{62}Br_{10}$ (M_r=5570.57): C 41.52; H 5.02; N 11.54. Found: C 40.07; H 4.16; N 10.12. IR(KBr,pellet,cm^{-1}): 3439(m,br), 2929(w), 1656(vs), 1595(vs), 1556(vs),

1509(vs), 1425(vs), 1379(vs), 1307(vs), 1268(vs), 1104(m), 1001(w), 910(w), 857(m), 823(w), 767(m), 715(m), 671(m), 629(m), 558(w), 534(w).

The larger deviations between the theoretical and found values for elemental analysis in 3-4 should be due to the losing of some crystallized molecules as for their easily deteriorating natures at room temperature.

Comment S3: X-ray crystallography for complexes 1-4.

Single-crystal X-ray data for complexes 1–4 were collected on an Bruker Apex (II) Duo diffractometer using graphite monochromated Mo-Ka (λ=0.71073 Å) radiation at 150K. Empirical absorption correction was applied. The structures were solved by direct methods and refined by the full-matrix least-squares methods on F^2 using the SHELX-97 software[2]. All non-hydrogen atoms were refined anisotropically. All of the hydrogen atoms were placed in the calculated positions. The crystal data and structure refinements for H_2L and complexes 1–4 are summarized in Table S1. The solvent molecules are seriously disordered although the crystal was determined at 150K. Then the contributions of these solvent molecules are taken into account using the SQUEEZE/PLATON program[3].

For **1**, due to some untreated disorders of atoms in DMF solvent (C11/C12/N3, C14/C15/N4/C16), some slightly abnormal thermal factors were resulted in which do not affect the discussion of the crystal structure. Hydrogen atoms bonded to water molecules were initially found from the difference maps and then be constrained to be at their indicative positions with the O-H distance of 0.82Å and $U_{iso}(H)=1.5U_{eq}(O)$.

For **2**, these two DMF solvent (C1S/C2S/N1S/C3S/O1S, C1T/C2T/N1T/C3T/O1T) are both disordered over two sites. They are refined with the final site occupancies of 0.84(1):0.16(1) and 0.60(1):0.40(1) for the major and minor components, respectively. In the refinement, the commands 'DFIX', 'DANG', 'EDAP', 'FLAT' and 'ISOR' were used to restrain some bond distances, angles and some thermal factors, etc. Similar to the treatment of water hydrogen atoms, hydrogen atoms bonded to water O4 atom were initially found from the difference maps and then be constrained to be at their ideal positions with the O-H distance of 0.82Å and $U_{iso}(H)=1.5U_{eq}(O)$.

For **3**, although the crystals selected were determined at 150K, the non-coordinated solvent molecules could not be modelled by discrete atoms due to the weak diffraction ability of the crystal selected for x-ray experiment. Then, in the final structural refinement a PLATON/SQUEEZE treatment was employed to take into account the diffraction contribution of the solvent molecules and, thereby, to produce a set of solvent-free diffraction intensities.[2] The reported refinements are of the guest-free structures using the *.hkp files. The SQUEEZE calculations showed a total solvent accessible area volume of 4898.9 $Å^3$ in **3** and the residual electron density amounted to 1526 e per unit cell, corresponding to nearly 38.2 molecules of DMF (about nineteen DMF molecules per asymmetric unit), i.e. every

$[Mn_{10}(PentaCShz)_5(DMF)_4\cdot(Py)_2\cdot(H_2O)_4]$ unit was distributed 19 DMF molecules. The suitable formula of e should be $[Mn_{10}(PentaCShz)_5(DMF)_4\cdot(Py)_2\cdot(H_2O)_4]\cdot(DMF)_{19}$. And some related items in the cif file such as D_{calc}, F(000) and formula weight should consider this. For the coordinated DMF (C1U/C2U/N1U/C3U/O1U, C1V/C2V/N1V/C3V/O1V, C1W/C2W/N1W/C3W/O1W and C1X/C2X/N1X/C3X/O1X) and pyridine (C1S/C2S/C3S/C4S/C5S/N1S and C1T/C2T/C3T/C4T/C5T/N1T) molecules, the thermal factors are indicative of medium disorder and then some commands 'DFIX', 'DANG', 'SADI', 'ISOR' and 'FLAT' were used to restrain some bond distances, angels and thermal factors. The positions of water hydrogen atoms were calculated by using PLATON[3].

For **4**, the crystal was tested and refined in a similar way. In the final structural refinement a PLATON/SQUEEZE treatment was employed to give a total solvent accessible area volume of 4263.7 $Å^3$ in **3** and the residual electron density amounted to 1879.7 e per unit cell, corresponding to nearly 48 molecules of DMF (about 24 DMF molecules per asymmetric unit), i.e. every $[Mn_{10}(PentaCShz)_5(DMF)_4\cdot(Py)_2\cdot(H_2O)_4]$ unit was distributed 24 DMF molecules. Also in the refinement, similar commands to that in 3 have applied.

Table S1 A Cambridge Structural Database (CSD) search based on the [M-N-N]-containing metallacrown structural unit.

No.	Refcode	Space group	a	b	c	α	β	γ	V	Nuclearity	Substitue R
1	AFOGOR	P-1	11.5	14.0	15.8	111.4	90.6	105.6	2253.6	**6 Co**	NH_2
2	AFOGUX	P-1	10.2	13.0	15.0	85.2	85.6	68.2	1830.6	**6 Co**	H
3	AFOHAE	$P2_1/n$	13.3	19.3	16.3	90.0	108.3	90.0	3950.4	**6 Co**	Methyl
4	AFOHEI	P-1	11.8	14.5	16.5	65.2	73.9	74.9	2416.4	**6 Co**	Eethyl
5	BEYSIJ	C2/c	30.3	15.5	26.9	90.0	121.9	90.0	10716.4	**6 Fe**	Methyl
6	BEYSOP	$P2_1/c$	15.0	14.4	22.8	90.0	106.4	90.0	4741.5	**6 Fe**	Methyl
7	BULVIO	P-1	13.6	15.6	16.4	97.9	107.1	112.3	2943.0	**6 Fe**	(Z)3-methoxy-3-oxoprop-1-enyl
8	CEGKUV	R-3c	17.3	17.3	52.4	90.0	90.0	120.0	13512.5	**6 Mn**	Methyl
9	COVBUL	$P6_3$	27.8	27.8	26.5	90.0	90.0	120.0	17746.7	**15 Mn**	2-phenyl-acetylenyl
10	ECAFUJ	P-1	10.2	13.0	14.9	85.2	85.3	67.8	1822.8	**6 Co**	H
11	ECAGAQ	P-1	22.9	17.6	14.4	89.9	109.1	89.9	5488.6	**6 Fe**	Methyl
12	ECAGEU	R-3	17.9	17.9	32.8	90.0	90.0	120.0	9118.5	**6 Fe**	Eethyl

13	ECAGIY	C2/c	28.6	16.1	28.3	90.0	118.7	90.0	11383.2	**6 Fe**	n-Pentyl
14	ECAGOE	$P2_1$	18.1	13.6	34.3	90.0	94.8	90.0	8423.1	**6 Ga**	H
15	ECAGUK	P-1	10.8	15.3	15.9	115.4	93.6	102.3	2283.7	**6 Ga**	Methyl
16	ECAHAR	$P2_1/c$	14.5	17.0	21.6	90.0	103.3	90.0	5169.1	**6 Ga**	Eethyl
17	ECAHEV	P-1	14.7	15.4	20.1	70.3	74.1	74.8	4037.1	**6 Ga**	n-undecyl
18	EGETAM	P-1	26.7	28.3	30.1	92.1	94.3	108.3	21413.4	**16 Mn**	Biphenyl
19	EGETEQ	$P2_1$	35.4	24.5	36.8	90.0	110.9	90.0	29757.9	**20 Mn**	2,2-diphenylethyl
20	FATKER	$I4_1/a$	41.4	41.4	17.8	90.0	90.0	90.0	30480.3	**6 Mn**	n-undecyl
21	FATKIV	R-3	51.7	51.7	20.4	90.0	90.0	120.0	47036.1	**6 Mn**	n-heptyl
22	FEPTOK	R-3	30.2	30.2	9.3	90.0	90.0	120.0	7371.3	**6 Mn**	Methyl
23	FUZVOM	P-3	25.4	25.4	14.7	90.0	90.0	120.0	8202.9	**6 Fe**	Eethyl
24	GOMHAS	R-3	32.0	32.0	10.8	90.0	90.0	120.0	9539.4	**6 Mn**	Methyl
25	GUJDOF	P-1	20.5	21.0	21.8	61.3	67.0	80.4	7556.8	**8 Mn**	Isopropyl
26	GUJGIC	Ia-3	27.3	27.3	27.3	90.0	90.0	90.0	20377.7	**6 Mn**	Methyl
27	HEPPIC	$P4_2/n$	39.3	39.3	17.8	90.0	90.0	90.0	27514.4	**20 Mn**	(E)-styryl
28	HILWEE	P-1	10.0	15.1	15.6	112.1	106.6	100.0	1989.8	**6 Mn**	Eethyl
29	HULPOU	R-3	18.0	18.0	28.9	90.0	90.0	120.0	8112.8	**6 Mn**	Eethyl
30	IFARUC	$P2_1/n$	16.0	19.5	16.2	90.0	118.2	90.0	4446.0	**6 Fe**	Methyl
31	IJAJIN	$P2_1/n$	16.3	20.9	17.7	90.0	100.7	90.0	5908.5	**6 Fe**	Eethyl
32	IJAKAG	P-1	20.2	22.0	22.1	60.9	73.5	74.1	8142.6	**8 Mn**	Eethyl
33	IPEBUB	P-1	9.4	14.1	14.2	85.0	82.8	74.0	1782.0	**6 Cr**	Methyl
34	IXUCUZ	P-1	20.0	20.3	20.6	77.8	66.1	66.3	6995.2	**8 Fe**	Isopropyl
35	KADQUD	P-1	13.6	15.6	16.4	96.9	107.2	112.7	2941.7	**6 Fe**	(Z)3-methoxy-3-oxoprop-1-enyl
36	KEMQID	$P2_1/n$	20.6	13.5	20.7	90.0	95.3	90.0	5730.4	**6 Mn**	Methyl

37	KENDUD	$P4_2/n$	27.0	27.0	18.8	90.0	90.0	90.0	13721.4	**12 Mn**	cyclohexenyl
38	KENFAL	$P4_2/n$	27.2	27.2	18.9	90.0	90.0	90.0	13974.6	**12 Mn**	cyclohexenyl
39	KENFEP	$P4_2/n$	27.1	27.1	18.9	90.0	90.0	90.0	13859.3	**12 Mn**	cyclohexenyl
40	KIGPAS	$P2_1/n$	16.5	15.4	21.0	90.0	103.9	90.0	5177.8	**6 Mn**	Eethyl
41	KUPKUC	P-1	15.3	15.8	16.3	111.2	95.8	115.6	3137.4	**6 Fe**	(Z)3-methoxy-3-oxoprop-1-enyl
42	KUWRIE	Pa-3	21.5	21.5	21.5	90.0	90.0	90.0	9899.6	**6 Fe**	Methyl
43	LIFGEN	P-1	13.1	16.9	17.0	66.4	74.4	74.8	3275.8	**6 Fe**	Methyl
44	LIFWED	P-1	12.2	14.9	14.9	70.6	78.1	72.7	2420.1	**6 Fe**	Methyl
45	LIFWIH	R-3c	17.0	17.0	62.2	90.0	90.0	120.0	15581.2	**6 Mn**	Methyl
46	MEGFIN	$I4_1/a$	40.4	40.4	17.8	90.0	90.0	90.0	29004.6	**6 Mn**	Methyl
47	MONBEX	P-1	18.2	19.8	23.1	75.0	69.1	79.2	7433.1	**8 Mn**	prop-1-en-2-yl
48	MONBIB	P-1	16.2	16.7	26.5	80.1	76.9	68.2	6492.5	**6 Mn**	Benzyl
49	MOPLAF	C2/c	30.7	14.2	25.3	90.0	118.9	90.0	9634.0	**6 Fe**	3-methoxy-3-oxoprop-1-enyl
50	NARCIU	P-1	14.5	14.8	27.1	85.5	89.1	73.2	5524.0	**6 Fe**	4-methoxy-4-oxobutyl
51	NAZPUB	P-1	13.1	16.9	17.0	66.4	74.4	74.8	3275.8	**6 Fe**	Methyl
52	NETWUF	P-1	12.8	15.3	17.5	69.1	71.8	76.6	2997.8	**6 Mn**	Methyl
53	NETXAM	P-1	15.6	20.3	21.5	99.6	106.7	101.3	6236.6	**10 Mn**	Phenyl
54	NITGON	$P2_1/n$	16.9	27.3	16.9	90.0	107.1	90.0	7481.6	**6 Ga**	(E)-styryl
55	NITGUT	P4/n	39.1	39.1	14.6	90.0	90.0	90.0	22287.5	**16 Mn**	(E)-styryl
56	NOLJII	R-3	29.0	29.0	26.7	90.0	90.0	120.0	19524.1	**12 Mn**	2,6-dimethoxyphenyl
57	OPOFEF	C2/c	64.0	14.4	29.5	90.0	108.5	90.0	25708.4	**6 Mn**	Ethyl
58	OYURAC	P-1	14.8	18.7	22.0	83.3	73.0	89.1	5759.4	**10 Mn**	4-isopropyl-Phenyl
59	PORTIA	P-1	14.7	21.6	22.5	64.8	76.6	82.2	6285.1	**12 Mn**	(E)-but-1-enyl
60	PORTOG	$P2_1/n$	14.5	14.7	62.9	90.0	92.3	90.0	13364.4	**8 Mn**	(E)-but-1-enyl

61	PORTUM	P-1	15.5	19.1	28.0	109.8	94.7	102.4	7499.1	**8 Mn**	(E)-but-1-enyl
62	QEVBAU	P-1	14.5	18.2	21.4	76.6	74.2	86.0	5286.9	**10 Mn**	Phenyl
63	QEVBEY	P-1	14.7	18.9	21.1	71.2	77.1	84.8	5406.0	**10 Fe**	Phenyl
64	QISDEC	Cc	49.3	19.9	36.6	90.0	127.1	90.0	28660.0	**6 Ga**	Cyclopentyl
65	QOJQEL	P-1	12.9	14.6	16.0	63.9	73.8	76.5	2565.7	**6 Mn**	Methyl
66	QOJQIP	P-1	13.0	14.7	16.2	110.6	94.9	109.4	2672.3	**6 Mn**	Ethyl
67	QOJQOV	P-1	14.7	15.7	16.2	61.7	81.5	75.8	3189.5	**6 Mn**	n-pentyl
68	QOJQUB	P-1	16.4	28.1	28.6	118.8	93.7	100.9	11185.0	**6 Mn**	n-hexanyl
69	SAKSIH	R-3	23.7	23.7	38.3	90.0	90.0	120.0	18626.6	**12 Mn**	(E)-but-1-enyl
70	SATVAL	R-3	18.2	18.2	31.9	90.0	90.0	120.0	9146.9	**6 Mn**	2-Methylpropyl
71	SATVEP	P-1	14.5	15.1	16.0	62.1	81.7	85.7	3048.3	**6 Mn**	Benzyl
72	SATVIT	P-1	20.2	23.6	36.4	91.4	100.8	111.0	15815.0	**8 Mn**	Isopropyl
73	SATVOZ	C2/c	39.0	20.7	28.1	90.0	118.2	90.0	20041.8	**10 Mn**	Isobutyl
74	SATVUF	$P2_1/n$	21.4	25.1	22.8	90.0	108.6	90.0	11645.3	**10 Mn**	t-butyl
75	SATWAM	R-3c	18.4	18.4	64.8	90.0	90.0	120.0	19002.6	**6 Mn**	2,2-dimethyl propyl
76	SAZPAL	C2/c	39.2	20.5	28.3	90.0	118.8	90.0	19913.1	**10 Mn**	Isobutyl
77	SEKKOJ	R-3c	16.3	16.3	64.1	90.0	90.0	120.0	14721.3	**6 Mn**	Methyl
78	SULRUN	P-1	11.0	17.0	17.1	64.5	86.8	71.3	2715.5	**6 Mn**	Ethyl
79	TARKEE	P-1	12.2	14.9	15.0	69.7	78.0	73.3	2423.2	**6 Fe**	Methyl
80	UJOSUH	R-3	24.8	24.8	11.3	90.0	90.0	120.0	6000.5	**6 Mn**	Methyl
81	UJOTAO	R-3	26.6	26.6	23.3	90.0	90.0	120.0	14307.3	**6 Mn**	Methyl
82	UWEJEM	$P2_1/c$	13.0	28.2	34.7	90.0	99.8	90.0	12561.0	**10 Mn**	cyclohexenyl
83	VIYFEP	P-1	18.2	18.3	23.4	94.3	106.2	119.5	6292.1	**6 Fe**	ethenyl
84	VUHGOV	C2/c	16.7	28.7	23.7	90.0	100.2	90.0	11148.3	**6 Mn**	Ethyl

85	VUHGUB	P4/ncc	27.0	27.0	29.2	90.0	90.0	90.0	21237.3	**8 Mn**	Ethyl
86	WUFWOK	P-1	16.4	17.0	21.6	67.8	87.1	63.9	4928.5	**6 Mn**	Methyl
87	XAKYUE	$I4_1/a$	40.6	40.6	17.6	90.0	90.0	90.0	29086.1	**6 Mn**	Ethyl
88	XAKZAL	$I4_1/a$	40.7	40.7	17.5	90.0	90.0	90.0	28937.4	**6 Mn**	n-pentyl
89	XAKZEP	$I4_1/a$	39.9	39.9	17.8	90.0	90.0	90.0	28188.6	**6 Mn**	Methyl
90	XAKZIT	$I4_1/a$	39.9	39.9	18.0	90.0	90.0	90.0	28731.8	**6 Mn**	Methyl
91	XAKZOZ	$I4_1/a$	40.2	40.2	17.8	90.0	90.0	90.0	28734.5	**6 Mn**	Methyl
92	XAKZUF	$I4_1/a$	40.7	40.7	17.5	90.0	90.0	90.0	28948.4	**6 Mn**	Ethyl
93	XALBAO	$I4_1/a$	40.4	40.4	17.6	90.0	90.0	90.0	28638.1	**6 Mn**	Ethyl
94	XALBES	$I4_1/a$	40.3	40.3	17.6	90.0	90.0	90.0	28592.9	**6 Mn**	Ethyl
95	XALBIW	$I4_1/a$	40.7	40.7	17.6	90.0	90.0	90.0	29020.5	**6 Mn**	Ethyl
96	XALBOC	$I4_1/a$	40.5	40.5	17.6	90.0	90.0	90.0	28935.6	**6 Mn**	Ethyl
97	XALBUI	$I4_1/a$	40.4	40.4	17.8	90.0	90.0	90.0	29111.1	**6 Mn**	Ethyl
98	XALCAP	$I4_1/a$	40.6	40.6	17.4	90.0	90.0	90.0	28716.0	**6 Mn**	Ethyl
99	XALCET	$I4_1/a$	41.0	41.0	17.2	90.0	90.0	90.0	28867.1	**6 Mn**	Ethyl
100	XALCIX	$I4_1/a$	40.9	40.9	17.3	90.0	90.0	90.0	28939.7	**6 Mn**	n-pentyl
101	XALCOD	$I4_1/a$	40.9	40.9	17.5	90.0	90.0	90.0	29212.1	**6 Mn**	n-pentyl
102	XALCUJ	$I4_1/a$	40.9	40.9	17.4	90.0	90.0	90.0	29104.2	**6 Mn**	n-pentyl
103	XALDAQ	$I4_1/a$	40.8	40.8	17.4	90.0	90.0	90.0	29023.3	**6 Mn**	n-pentyl
104	XALDEU	$I4_1/a$	40.7	40.7	17.2	90.0	90.0	90.0	28481.5	**6 Mn**	n-pentyl
105	XALDIY	$I4_1/a$	40.7	40.7	17.4	90.0	90.0	90.0	28698.0	**6 Mn**	n-pentyl
106	XALDOE	$I4_1/a$	40.9	40.9	17.5	90.0	90.0	90.0	29234.4	**6 Mn**	n-pentyl
107	YIGDUO	P-1	12.8	15.3	17.7	68.7	70.7	76.0	3018.6	**6 Mn**	Methyl
108	YUMGUJ	R-3	32.3	32.3	11.3	90.0	90.0	120.0	10211.2	**6 Mn**	Methyl

Table S2 Crystal parameters of compound 1-4.

Complex	1	2	3	4
Formula	$C_{62}H_{88}Cl_4Fe_4N_{16}O_{24}$	$C_{62}H_{88}Br_4Fe_4N_{16}O_{24}$	$C_{117}H_{106}Cl_{10}Mn_{10}N_{26}O_{38}$	$C_{100}H_{65}Br_{10}Mn_{10}N_{21}O_{39}$
Formula weight	1806.68	1984.52	3388.17	3832.77
Temperature(K)	150(2)	150(2)	150(2)	150(2)
Crystsyst	Tetragonal	Tetragonal	Triclinic	Triclinic
Space group	$I4_1/a$	$I4_1/a$	$P\bar{1}$	$P\bar{1}$
a(Å)	26.284(3)	26.292(5)	20.032(3)	20.239(9)
b(Å)	26.284(3)	26.292(5)	21.900(3)	21.285(9)
c(Å)	12.9228(15)	12.959(2)	27.421(4)	26.335(11)
α(°)	90°	90°	113.261(2)	113.598(6)
β(°)	90°	90°	92.344(3)	91.571(7)
γ(°)	90°	90°	96.129(2)	95.727(6)
V(Å^3)	8928(2)	8958(3)	10943(2)	10316(8)
Z	4	4	2	2
μ (mm^{-1})	0.830	2.492	0.728	2.585
GOF on F^2	1.035	1.011	1.028	1.234
Final R indices [I＞2σ(I)]	R_1 = 0.0603	$R1$ = 0.0577	R_1 = 0.0706	R_1 = 0.0989
	wR_2 = 0.1735	wR_2 = 0.1470	wR_2 = 0.1595	wR_2 = 0.2351

Table S3 Some selected bond lengths (Å) and angles (°) in 1-4.

Compound **1**

Fe1-O1	1.897(3)	Fe1-N1	2.053(3)
Fe1-O2$^{\#1}$	2.034(3)	Fe1-O4	2.055(3)
Fe1-O3	2.043(3)	Fe1-N2$^{\#1}$	2.110(4)
O1-Fe1-O2$^{\#1}$	114.80(13)	O3-Fe1-O4	87.63(14)
O1-Fe1-O3	159.59(13)	N1-Fe1-O4	102.71(14)
O2$^{\#1}$-Fe1-O3	85.21(12)	O1-Fe1-N2$^{\#1}$	97.53(15)
O1-Fe1-N1	85.88(13)	O2$^{\#1}$-Fe1-N2$^{\#1}$	75.55(13)
O2$^{\#1}$-Fe1-N1	158.15(13)	O3-Fe1-N2$^{\#1}$	91.15(13)
O3-Fe1-N1	74.87(13)	N1-Fe1-N2$^{\#1}$	95.65(13)
O1-Fe1-O4	90.11(15)	O4-Fe1-N2$^{\#1}$	160.58(14)

Symmetry code: #1： 5/4 - *y*, *x* - 3/4, 1/4 – *z*.

Compound **2**

Fe1-O1$^{\#1}$	1.893(3)	Fe1-O4	2.049(3)
Fe1-O2	2.036(3)	Fe1-N1$^{\#1}$	2.056(3)
Fe1-O3$^{\#1}$	2.038(3)	Fe1-N2	2.113(3)
O1-Fe1-O2$^{\#1}$	114.80(13)	O3-Fe1-O4	87.63(14)
O1-Fe1-O3	159.59(13)	N1-Fe1-O4	102.71(14)

$O2^{\#1}$-Fe1-O3	85.21(12)	O1-Fe1-N2#1	97.53(15)
O1-Fe1-N1	85.88(13)	$O2^{\#1}$-Fe1-$N2^{\#1}$	75.55(13)
$O2^{\#1}$-Fe1-N1	158.15(13)	O3-Fe1-$N2^{\#1}$	91.15(13)
O3-Fe1-N1	74.87(13)	N1-Fe1-$N2^{\#1}$	95.65(13)

Symmetry code: #1：5/4 - *y*, *x* - 3/4, 1/4 – *z*.

Compound **3**

Mn1-O1A	1.859(4)	Mn6-O6A	1.850(4)
Mn1-O3A	1.895(4)	Mn6-O4A	1.886(4)
Mn1-N1A	1.950(5)	Mn6-N4A	1.944(4)
Mn1-O5B	1.969(4)	Mn6-O5D	1.983(4)
Mn1-N3B	2.231(5)	Mn6-N3D	2.247(5)
Mn1-N1S	2.276(4)	Mn6-N1T	2.292(5)
Mn2-O6B	1.850(3)	Mn7-O6D	1.876(4)
Mn2-O4B	1.943(4)	Mn7-O4D	1.935(4)
Mn2-N4B	1.949(4)	Mn7-N4D	1.950(5)
Mn2-O2C	1.982(3)	Mn7-O5E	1.954(4)
Mn2-O1F	2.197(4)	Mn7-O3F	2.209(4)
Mn2-N2C	2.271(5)	Mn7-N3E	2.279(5)
Mn3-O1C	1.864(4)	Mn8-O6E	1.879(4)
Mn3-N1C	1.923(4)	Mn8-O4E	1.922(4)
Mn3-O3C	1.931(3)	Mn8-N4E	1.931(5)
Mn3-O2B	1.958(4)	Mn8-O2D	1.958(4)
Mn3-O2F	2.265(4)	Mn8-O4F	2.238(5)
Mn3-N2B	2.313(5)	Mn8-N2D	2.315(5)
Mn4-O1B	1.842(4)	Mn9-O1D	1.850(4)
Mn4-O3B	1.919(4)	Mn9-O3D	1.917(4)
Mn4-N1B	1.950(4)	Mn9-N1D	1.938(5)
Mn4-O5C	1.970(4)	Mn9-O2E	1.962(4)
Mn4-O1U	2.275(5)	Mn9-O1V	2.226(6)
Mn4-N3C	2.295(4)	Mn9-N2E	2.312(5)
Mn5-O6C	1.855(4)	Mn10-O1E	1.862(4)
Mn5-N4C	1.931(4)	Mn10-O3E	1.925(4)
Mn5-O4C	1.932(3)	Mn10-N1E	1.926(5)
Mn5-O5A	1.949(4)	Mn10-O2A	1.947(4)
Mn5-O1X	2.288(4)	Mn10-O1W	2.306(4)
Mn5-N3A	2.410(5)	Mn10-N2A	2.393(4)
O1A-Mn1-O3A	171.52(19)	O6A-Mn6-O4A	171.26(19)
O1A-Mn1-N1A	91.6(2)	O6A-Mn6-N4A	92.2(2)
O3A-Mn1-N1A	79.87(19)	O4A-Mn6-N4A	79.06(18)
O1A-Mn1-O5B	93.16(19)	O6A-Mn6-O5D	92.46(19)
O3A-Mn1-O5B	95.33(17)	O4A-Mn6-O5D	96.26(17)
N1A-Mn1-O5B	175.2(2)	N4A-Mn6-O5D	175.32(18)

O1A-Mn1-N3B	92.99(18)	O6A-Mn6-N3D	92.65(18)
O3A-Mn1-N3B	89.40(15)	O4A-Mn6-N3D	89.17(16)
N1A-Mn1-N3B	105.45(18)	N4A-Mn6-N3D	104.76(18)
O5B-Mn1-N3B	74.69(16)	O5D-Mn6-N3D	74.72(17)
O1A-Mn1-N1S	90.2(2)	O6A-Mn6-N1T	89.8(2)
O3A-Mn1-N1S	90.11(18)	O4A-Mn6-N1T	91.22(18)
N1A-Mn1-N1S	92.65(19)	N4A-Mn6-N1T	93.68(18)
O5B-Mn1-N1S	86.95(17)	O5D-Mn6-N1T	86.64(18)
N3B-Mn1-N1S	161.50(19)	N3D-Mn6-N1T	161.28(19)
O6B-Mn2-O4B	169.82(16)	O6D-Mn7-O4D	170.03(18)
O6B-Mn2-N4B	90.05(17)	O6D-Mn7-N4D	89.9(2)
O4B-Mn2-N4B	80.05(17)	O4D-Mn7-N4D	80.30(18)
O6B-Mn2-O2C	100.88(15)	O6D-Mn7-O5E	100.66(18)
O4B-Mn2-O2C	88.87(16)	O4D-Mn7-O5E	89.02(17)
N4B-Mn2-O2C	168.53(17)	N4D-Mn7-O5E	169.19(19)
O6B-Mn2-O1F	91.17(16)	O6D-Mn7-O3F	91.02(19)
O4B-Mn2-O1F	92.15(16)	O4D-Mn7-O3F	91.80(17)
N4B-Mn2-O1F	95.67(16)	N4D-Mn7-O3F	94.66(18)
O2C-Mn2-O1F	87.63(15)	O5E-Mn7-O3F	87.32(18)
O6B-Mn2-N2C	92.59(16)	O6D-Mn7-N3E	92.38(18)
O4B-Mn2-N2C	87.16(15)	O4D-Mn7-N3E	87.73(16)
N4B-Mn2-N2C	101.73(17)	N4D-Mn7-N3E	102.19(18)
O2C-Mn2-N2C	74.56(15)	O5E-Mn7-N3E	75.49(17)
O1F-Mn2-N2C	162.19(15)	O3F-Mn7-N3E	162.81(17)
O1C-Mn3-N1C	90.23(18)	O6E-Mn8-O4E	169.76(19)
O1C-Mn3-O3C	169.45(17)	O6E-Mn8-N4E	89.9(2)
N1C-Mn3-O3C	79.23(17)	O4E-Mn8-N4E	79.9(2)
O1C-Mn3-O2B	98.55(16)	O6E-Mn8-O2D	98.31(17)
N1C-Mn3-O2B	170.78(17)	O4E-Mn8-O2D	91.91(18)
O3C-Mn3-O2B	92.01(16)	N4E-Mn8-O2D	171.49(19)
O1C-Mn3-O2F	91.49(19)	O6E-Mn8-O4F	91.8(2)
N1C-Mn3-O2F	96.85(18)	O4E-Mn8-O4F	89.31(19)
O3C-Mn3-O2F	89.31(17)	N4E-Mn8-O4F	95.62(19)
O2B-Mn3-O2F	85.80(17)	O2D-Mn8-O4F	86.42(19)
O1C-Mn3-N2B	98.57(16)	O6E-Mn8-N2D	98.47(18)
N1C-Mn3-N2B	102.61(18)	O4E-Mn8-N2D	83.86(16)
O3C-Mn3-N2B	84.36(15)	N4E-Mn8-N2D	102.89(19)
O2B-Mn3-N2B	73.41(17)	O2D-Mn8-N2D	73.79(17)
O2F-Mn3-N2B	157.98(18)	O4F-Mn8-N2D	158.8(2)
O1B-Mn4-O3B	170.62(17)	O1D-Mn9-O3D	170.34(18)
O1B-Mn4-N1B	90.50(19)	O1D-Mn9-N1D	89.9(2)
O3B-Mn4-N1B	80.13(18)	O3D-Mn9-N1D	80.49(19)
O1B-Mn4-O5C	92.50(17)	O1D-Mn9-O2E	92.68(17)
O3B-Mn4-O5C	96.88(16)	O3D-Mn9-O2E	96.91(16)

N1B-Mn4-O5C	176.93(19)	N1D-Mn9-O2E	177.4(2)
O1B-Mn4-O1U	92.26(19)	O1D-Mn9-O1V	91.9(2)
O3B-Mn4-O1U	88.17(17)	O3D-Mn9-O1V	90.02(19)
N1B-Mn4-O1U	94.70(16)	N1D-Mn9-O1V	94.08(19)
O5C-Mn4-O1U	85.83(16)	O2E-Mn9-O1V	86.12(18)
O1B-Mn4-N3C	92.50(17)	O1D-Mn9-N2E	91.74(18)
O3B-Mn4-N3C	90.33(15)	O3D-Mn9-N2E	89.76(15)
N1B-Mn4-N3C	105.11(16)	N1D-Mn9-N2E	105.79(19)
O5C-Mn4-N3C	74.13(15)	O2E-Mn9-N2E	73.86(17)
O1U-Mn4-N3C	159.58(16)	O1V-Mn9-N2E	159.80(18)
O6C-Mn5-N4C	90.29(17)	O1E-Mn10-O3E	169.15(18)
O6C-Mn5-O4C	169.45(15)	O1E-Mn10-N1E	90.9(2)
N4C-Mn5-O4C	80.11(16)	O3E-Mn10-N1E	79.10(18)
O6C-Mn5-O5A	96.14(16)	O1E-Mn10-O2A	96.96(18)
N4C-Mn5-O5A	167.29(17)	O3E-Mn10-O2A	93.67(17)
O4C-Mn5-O5A	94.13(15)	N1E-Mn10-O2A	166.14(18)
O6C-Mn5-O1X	97.81(16)	O1E-Mn10-O1W	98.26(16)
N4C-Mn5-O1X	88.88(16)	O3E-Mn10-O1W	85.49(15)

Compound **4**			
Mn1-O3A	1.852(12)	Mn6-O6A	1.843(13)
Mn1-O1A	1.912(12)	Mn6-O4A	1.867(12)
Mn1-N1A	1.929(17)	Mn6-N4A	1.947(13)
Mn1-O5B	1.937(15)	Mn6-O5D	2.027(12)
Mn1-N1S	2.199(16)	Mn6-N3D	2.242(16)
Mn1-N3B	2.216(16)	Mn6-N1T	2.248(11)
Mn2-O6B	1.857(13)	Mn7-O6D	1.921(14)
Mn2-O2C	1.956(10)	Mn7-O5E	1.945(12)
Mn2-O4B	1.964(13)	Mn7-N4D	1.949(17)
Mn2-N4B	1.964(15)	Mn7-O4D	1.957(11)
Mn2-O1F	2.190(12)	Mn7-O3F	2.112(13)
Mn2-N2C	2.341(17)	Mn7-N3E	2.217(17)
Mn3-O1C	1.858(10)	Mn8-O6E	1.899(11)
Mn3-O3C	1.901(11)	Mn8-N4E	1.909(15)
Mn3-N1C	1.905(15)	Mn8-O2D	1.932(12)
Mn3-O2B	1.933(10)	Mn8-O4E	1.940(13)
Mn3-O2F	2.225(11)	Mn8-O4F	2.171(13)
Mn3-N2B	2.271(15)	Mn8-N2D	2.254(14)
Mn4-O1B	1.833(11)	Mn9-O1D	1.844(12)
Mn4-O3B	1.919(10)	Mn9-O3D	1.917(11)
Mn4-N1B	1.973(13)	Mn9-O2E	1.942(11)
Mn4-O5C	1.993(11)	Mn9-N1D	1.971(14)
Mn4-O1U	2.264(16)	Mn9-O1V	2.237(15)

Mn4-N3C	2.267(16)	Mn9-N2E	2.267(15)
Mn5-O6C	1.854(11)	Mn10-O1E	1.820(12)
Mn5-N4C	1.897(13)	Mn10-N1E	1.895(14)
Mn5-O4C	1.906(10)	Mn10-O3E	1.946(11)
Mn5-O5A	1.911(11)	Mn10-O2A	1.982(13)
Mn5-O1X	2.303(12)	Mn10-O1W	2.218(13)
Mn5-N3A	2.327(13)	Mn10-N2A	2.346(16)
O3A-Mn1-O1A	171.1(6)	O4C-Mn5-N3A	91.8(5)
O3A-Mn1-N1A	83.0(7)	O5A-Mn5-N3A	73.0(5)
O1A-Mn1-N1A	88.1(7)	O1X-Mn5-N3A	154.7(5)
O3A-Mn1-O5B	94.2(6)	O6A-Mn6-O4A	171.8(6)
O1A-Mn1-O5B	94.7(6)	O6A-Mn6-N4A	93.8(6)
N1A-Mn1-O5B	176.6(7)	O4A-Mn6-N4A	78.2(6)
O3A-Mn1-N1S	93.3(7)	O6A-Mn6-O5D	92.2(6)
O1A-Mn1-N1S	87.8(7)	O4A-Mn6-O5D	95.9(5)
N1A-Mn1-N1S	95.5(7)	N4A-Mn6-O5D	174.0(5)
O5B-Mn1-N1S	86.6(6)	O6A-Mn6-N3D	91.2(6)
O3A-Mn1-N3B	88.4(5)	O4A-Mn6-N3D	92.0(5)
O1A-Mn1-N3B	93.4(5)	N4A-Mn6-N3D	104.6(6)
N1A-Mn1-N3B	102.9(7)	O5D-Mn6-N3D	74.5(6)
O5B-Mn1-N3B	75.0(6)	O6A-Mn6-N1T	88.3(5)
N1S-Mn1-N3B	161.6(7)	O4A-Mn6-N1T	91.3(5)
O3A-Mn1-C8A	26.4(5)	N4A-Mn6-N1T	95.2(5)
O1A-Mn1-C8A	144.7(7)	O5D-Mn6-N1T	85.7(5)
N1A-Mn1-C8A	56.6(7)	N3D-Mn6-N1T	160.2(6)
O5B-Mn1-C8A	120.5(6)	O6D-Mn7-O5E	97.9(6)
N1S-Mn1-C8A	96.5(7)	O6D-Mn7-N4D	91.7(7)
N3B-Mn1-C8A	93.1(5)	O5E-Mn7-N4D	169.7(7)
O6B-Mn2-O2C	100.9(5)	O6D-Mn7-O4D	172.4(6)
O6B-Mn2-O4B	170.6(5)	O5E-Mn7-O4D	89.0(5)
O2C-Mn2-O4B	88.0(5)	N4D-Mn7-O4D	81.2(6)
O6B-Mn2-N4B	89.2(7)	O6D-Mn7-O3F	91.4(6)
O2C-Mn2-N4B	169.2(7)	O5E-Mn7-O3F	88.5(5)
O4B-Mn2-N4B	81.7(7)	N4D-Mn7-O3F	95.2(6)
O6B-Mn2-O1F	89.5(5)	O4D-Mn7-O3F	92.0(5)
O2C-Mn2-O1F	91.3(5)	O6D-Mn7-N3E	92.5(6)
O4B-Mn2-O1F	93.2(5)	O5E-Mn7-N3E	74.0(5)
N4B-Mn2-O1F	92.5(5)	N4D-Mn7-N3E	101.9(6)
O6B-Mn2-N2C	93.7(5)	O4D-Mn7-N3E	86.2(5)
O2C-Mn2-N2C	74.0(5)	O3F-Mn7-N3E	162.4(6)
O4B-Mn2-N2C	85.9(5)	O6E-Mn8-N4E	91.4(6)
N4B-Mn2-N2C	102.0(6)	O6E-Mn8-O2D	98.1(5)
O1F-Mn2-N2C	165.2(5)	N4E-Mn8-O2D	170.4(6)
O1C-Mn3-O3C	169.9(5)	O6E-Mn8-O4E	170.9(6)

O1C-Mn3-N1C	90.1(6)	N4E-Mn8-O4E	79.6(7)
O3C-Mn3-N1C	80.1(6)	O2D-Mn8-O4E	90.8(6)
O1C-Mn3-O2B	100.4(5)	O6E-Mn8-O4F	92.7(5)
O3C-Mn3-O2B	89.5(5)	N4E-Mn8-O4F	97.5(6)
N1C-Mn3-O2B	169.5(5)	O2D-Mn8-O4F	83.9(6)
O1C-Mn3-O2F	91.6(5)	O4E-Mn8-O4F	90.3(5)
O3C-Mn3-O2F	91.7(5)	O6E-Mn8-N2D	96.8(5)
N1C-Mn3-O2F	97.4(6)	N4E-Mn8-N2D	105.5(6)
O2B-Mn3-O2F	83.3(4)	O2D-Mn8-N2D	71.8(5)
O1C-Mn3-N2B	97.5(5)	O4E-Mn8-N2D	84.0(5)
O3C-Mn3-N2B	82.7(5)	O4F-Mn8-N2D	154.9(6)
N1C-Mn3-N2B	102.4(6)	O1D-Mn9-O3D	170.5(5)
O2B-Mn3-N2B	75.5(5)	O1D-Mn9-O2E	92.4(5)
O2F-Mn3-N2B	158.1(5)	O3D-Mn9-O2E	97.1(5)
O1B-Mn4-O3B	171.5(5)	O1D-Mn9-N1D	90.9(6)
O1B-Mn4-N1B	91.0(5)	O3D-Mn9-N1D	79.6(5)
O3B-Mn4-N1B	80.7(5)	O2E-Mn9-N1D	176.6(6)
O1B-Mn4-O5C	91.6(5)	O1D-Mn9-O1V	96.3(6)
O3B-Mn4-O5C	96.7(5)	O3D-Mn9-O1V	84.2(5)
N1B-Mn4-O5C	177.4(6)	O2E-Mn9-O1V	86.9(5)
O1B-Mn4-O1U	91.4(5)	N1D-Mn9-O1V	92.9(6)
O3B-Mn4-O1U	87.7(5)	O1D-Mn9-N2E	93.4(6)
N1B-Mn4-O1U	96.0(5)	O3D-Mn9-N2E	89.1(5)
O5C-Mn4-O1U	83.6(5)	O2E-Mn9-N2E	75.2(5)
O1B-Mn4-N3C	92.8(5)	N1D-Mn9-N2E	104.5(6)
O3B-Mn4-N3C	91.0(5)	O1V-Mn9-N2E	160.0(5)
N1B-Mn4-N3C	104.3(6)	O1E-Mn10-N1E	91.8(6)
O5C-Mn4-N3C	75.8(6)	O1E-Mn10-O3E	169.2(5)
O1U-Mn4-N3C	159.1(5)	N1E-Mn10-O3E	80.4(6)
O6C-Mn5-N4C	91.4(5)	O1E-Mn10-O2A	96.8(6)
O6C-Mn5-O4C	168.8(5)	N1E-Mn10-O2A	166.5(6)
N4C-Mn5-O4C	79.1(5)	O3E-Mn10-O2A	92.3(5)
O6C-Mn5-O5A	97.3(5)	O1E-Mn10-O1W	97.4(5)
N4C-Mn5-O5A	166.0(5)	N1E-Mn10-O1W	86.7(6)
O4C-Mn5-O5A	93.2(5)	O3E-Mn10-O1W	89.7(5)
O6C-Mn5-O1X	95.0(5)	O2A-Mn10-O1W	81.9(5)
N4C-Mn5-O1X	86.6(5)	O1E-Mn10-N2A	89.3(5)
O4C-Mn5-O1X	90.5(4)	N1E-Mn10-N2A	118.6(6)
O5A-Mn5-O1X	81.7(5)	O3E-Mn10-N2A	87.9(5)
O6C-Mn5-N3A	87.4(5)	O2A-Mn10-N2A	72.1(6)
N4C-Mn5-N3A	118.6(5)	O1W-Mn10-N2A	153.8(6)

Table S4 Hydrogen-bonding parameters of 1-2 (Å, °).

D−H…A	$d_{D\text{-}H}$	$d_{H\ldots A}$	$d_{D\ldots A}$	<(DHA)
		Complex **1**		
O4−H4A…O5	0.82	1.83	2.634(6)	168.6
O4−H4B…O6$^{\#1}$	0.82	1.88	2.680(13)	165.7
		Complex **2**		
O4−H4A…O1S	0.82	1.86	2.663(8)	164.2
O4−H34B…O1T'$^{\#1}$	0.82	1.88	2.662(19)	160.3

Symmetry codes: #1 = 5/4 - *y*, *x* - 3/4, 1/4 - *z* in **1**; #1=5/4 - *y*, *x* + 1/4, 1/4 – *z* in **2**.

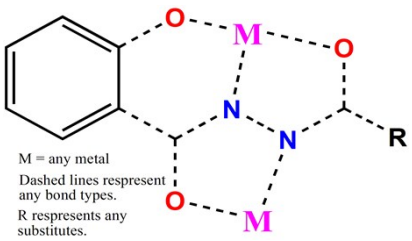

Fig. S1 The indexing structural unit used in the CSD search for metallacrowns.

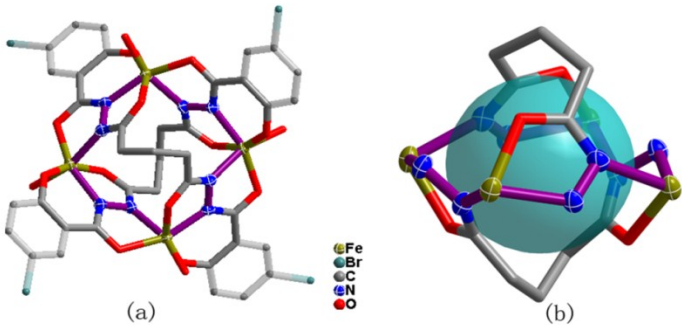

Fig. S2 (a) The structure of compound 2 without solution molecules and (b) the tetrahedron inside.

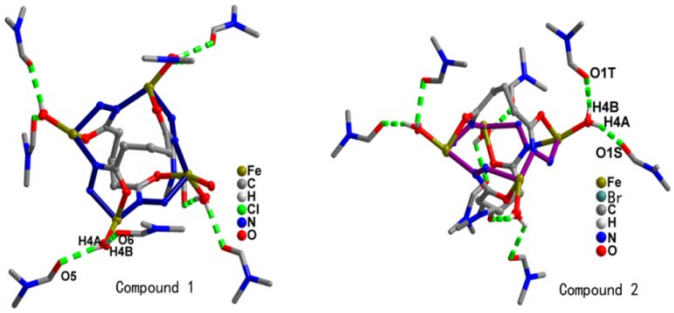

Fig. S3 The hydrogen bonds between four coordinated water and eight lattice solvent molecules DMF.

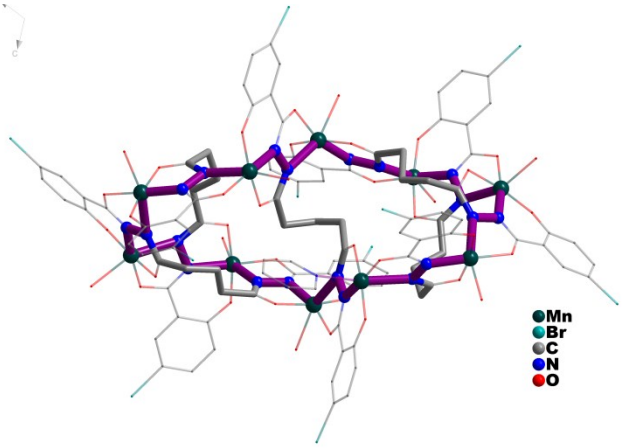

Fig. S4 The structure of compound 4 without hydrogen atoms and solvent molecules.

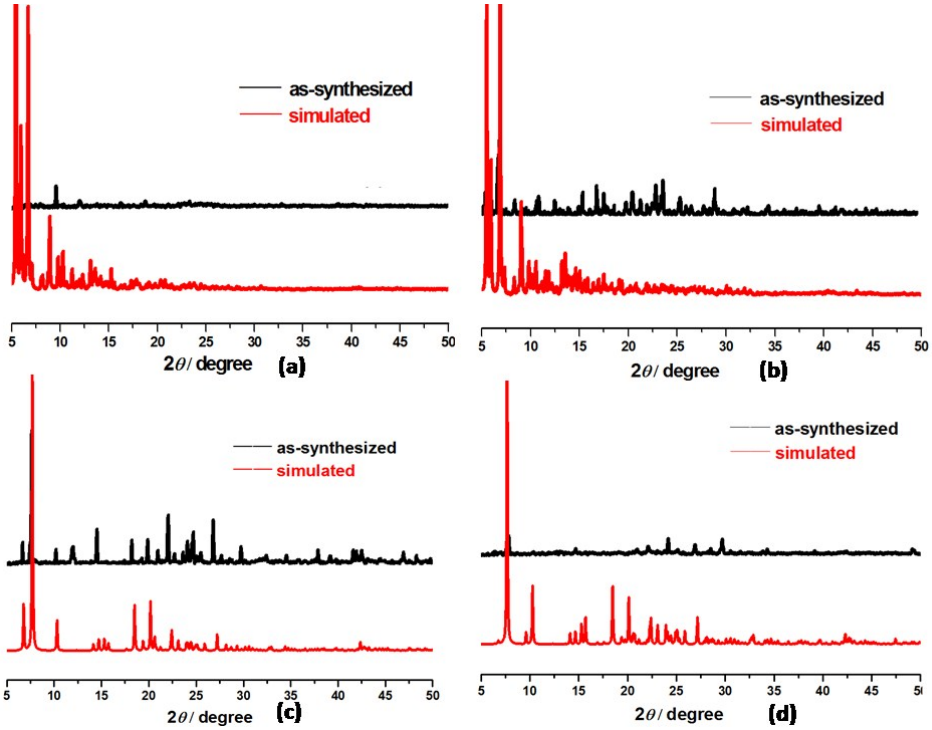

Fig. S5 The theoretical and experimental PXRD of compounds 1 for (a), 2 for (b), 3 for (c) and 4 for (d).

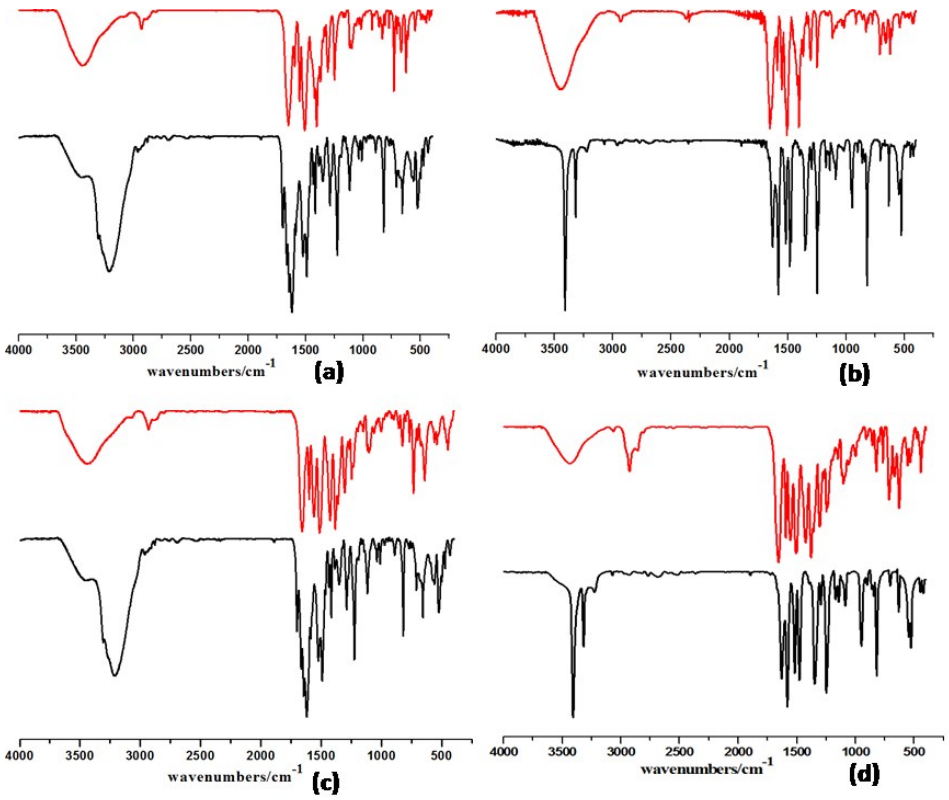

Fig. S6 The IR spectra of compound 1 for (a), 2 for (b), 3 for (c), 4 for (d) (red) and ligands (black).

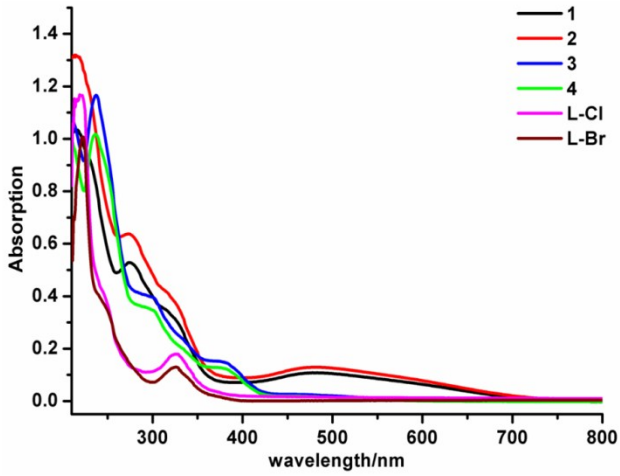

Fig. S7 The UV spectra of compound 1-4 and the relative ligands.

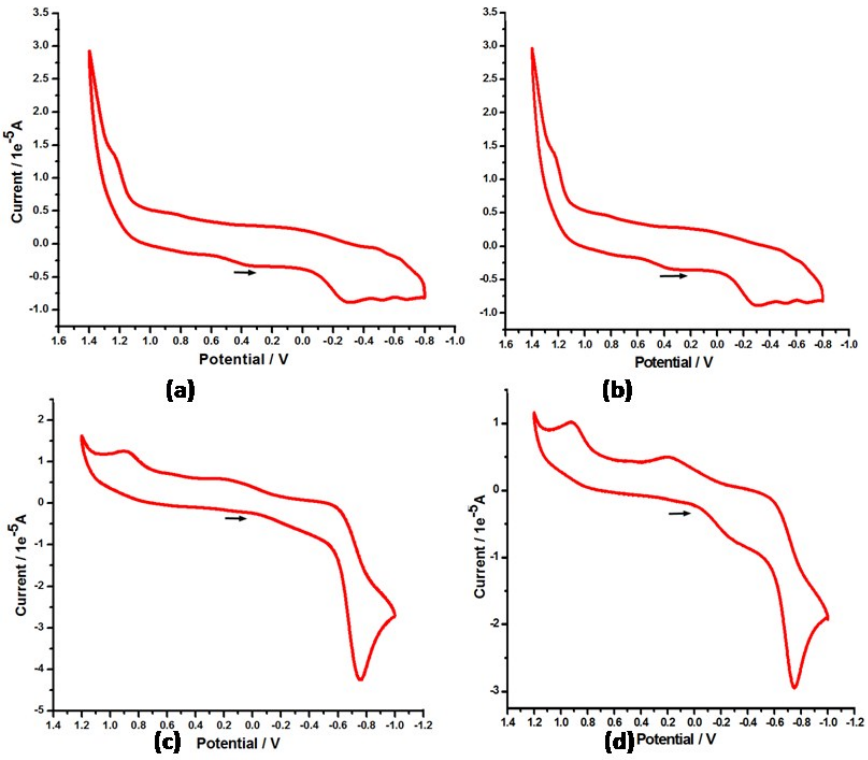

Fig. S8 Cyclic voltammetry (CV) of compound 1 for (a), 2 for (b), 3 for (c) and 4 for (d) in DMF.

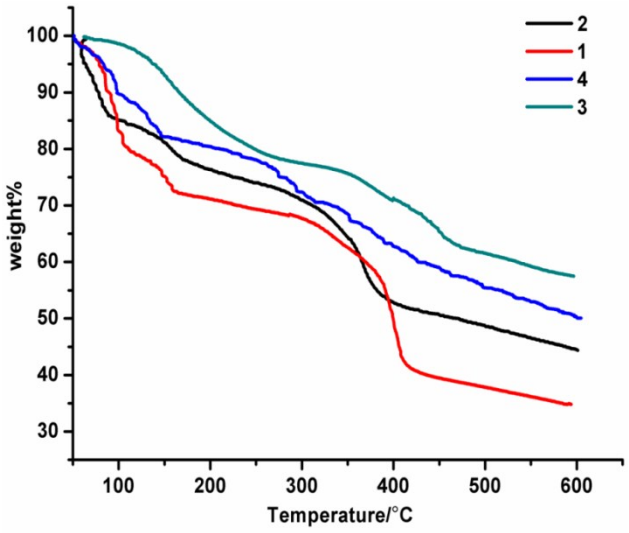

Fig. S9 Thermal gravimetric of compounds 1-4.

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2. (a) Sheldrick, G. M. A short history of SHELX. *Acta Crystallogr*. *Sect*. *A* **2008**, *64*, 112; (b) Sheldrick, G. M. Program for solution of crystal structures, *University of Göttingen*, **2014**.

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