Two new three-dimensional metal-organic frameworks with 4-connected diamondoid and unusual (6,16)-connected net topologies based on planar tetranuclear squares as secondary building units

SongLiang Cai, ShengRun Zheng*, Jun Fan, Rong-Hua Zeng, Wei-Guang Zhang*

School of Chemistry and Environment, South China Normal University, Guangzhou, 510006, P. R. China. E-mail: zhengsr@scnu.edu.cn, wgzhang@scnu.edu.cn; Fax:+86-20-39347768

Supporting information

Table S**1** Selected bond lengths [Å] and angles[°] for the compounds **1**-**2**.[a]

Compound **1**			
Co(1)-O(3)	2.059(3)	Co(1)-O(2W)	2.154(4)
Co(1)-O(1)	2.081(3)	Co(2)-O(2)#3	2.036(4)
Co(1)-N(1)	2.133(4)	Co(2)-O(4)	2.038(4)
Co(1)-O(1W)	2.149(4)	Co(2)-O(3W)	2.141(6)
Co(1)-N(2)	2.152(4)	Co(2)-O(4W)	2.162(6)
O(3)-Co(1)-O(1)	169.82(15)	N(1)-Co(1)-O(2W)	95.28(17)
O(3)-Co(1)-N(1)	106.66(16)	O(1W)-Co(1)-O(2W)	85.83(16)
O(1)-Co(1)-N(1)	78.08(14)	N(2)-Co(1)-O(2W)	160.01(16)
O(3)-Co(1)-O(1W)	91.34(15)	O(2)#3-Co(2)-O(2)#1	92.1(2)
O(1)-Co(1)-O(1W)	84.01(14)	O(2)#3-Co(2)-O(4)	177.66(15)
N(1)-Co(1)-O(1W)	161.98(15)	O(2)#3-Co(2)-O(4)#2	86.50(15)
O(3)-Co(1)-N(2)	77.33(14)	O(4)-Co(2)-O(4)#2	94.8(2)
O(1)-Co(1)-N(2)	111.65(16)	O(2)#3-Co(2)-O(3W)	91.64(18)
N(1)-Co(1)-N(2)	94.37(17)	O(4)-Co(2)-O(3W)	90.31(18)
O(1W)-Co(1)-N(2)	90.36(15)	O(2)#3-Co(2)-O(4W)	88.69(17)
O(3)-Co(1)-O(2W)	83.14(15)	O(4)-Co(2)-O(4W)	89.37(17)
O(1)-Co(1)-O(2W)	87.49(16)	O(3W)-Co(2)-O(4W)	179.5(3)
Compound **2**			
Mn(1)-O(8)#1	2.148(5)	Mn(2)-N(2)	2.208(5)

Mn(1)-O(5)	2.152(5)	Mn(3)-O(2)	1.983(8)
Mn(1)-O(1)	2.173(5)	Mn(3)-O(7)#4	2.018(8)
Mn(1)-N(3)	2.215(5)	Mn(3)-O(3)	2.023(6)
Mn(1)-N(4)#1	2.238(5)	Mn(3)-O(6)#4	2.031(6)
Mn(1)-N(1)	2.267(5)	Mn(3)-O(2W)	2.451(15)
Mn(2)-O(4)	2.205(4)	Mn(3)-O(1W)	2.477(16)
O(4)-Mn(2)-N(2)	74.55(17)	O(7)#4-Mn(3)-O(6)#4	91.3(3)
O(4)#2-Mn(2)-N(2)	160.3(2)	O(3)-Mn(3)-O(6)#4	92.8(2)
O(4)#3-Mn(2)-N(2)	90.8(2)	O(2)-Mn(3)-O(2W)	92.8(4)
O(4)#3-Mn(2)-N(2)#3	74.55(17)	O(7)#4-Mn(3)-O(2W)	82.2(5)
O(4)-Mn(2)-N(2)#2	90.8(2)	O(3)-Mn(3)-O(2W)	97.1(4)
O(4)#2-Mn(2)-N(2)#2	74.55(17)	O(6)#4-Mn(3)-O(2W)	75.4(4)
O(4)#3-Mn(2)-N(2)#2	160.3(2)	O(2)-Mn(3)-O(1W)	98.9(5)
N(2)-Mn(2)-N(2)#2	106.97(15)	O(7)#4-Mn(3)-O(1W)	92.2(5)
O(2)-Mn(3)-O(7)#4	83.6(3)	O(3)-Mn(3)-O(1W)	89.4(5)
O(2)-Mn(3)-O(3)	92.0(3)	O(6)#4-Mn(3)-O(1W)	92.5(5)
O(7)#4-Mn(3)-O(3)	175.5(3)	O(2W)-Mn(3)-O(1W)	166.4(5)
O(2)-Mn(3)-O(6)#4	167.7(4)		

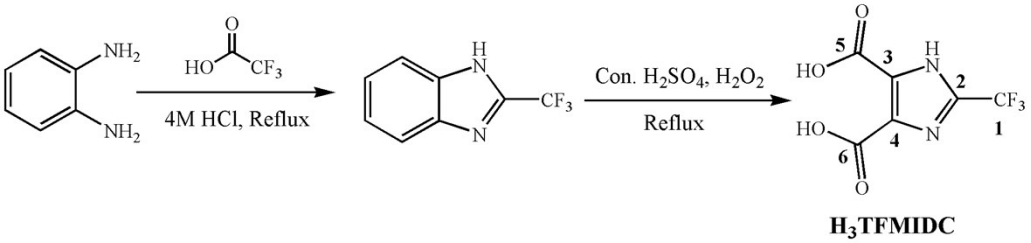
[a]Symmetry transformations used to generate equivalentatoms: #1 y – 1/4, –x + 3/4, z + 1/4; #2 –x + 1, y, z; #3 –y + 5/4, –x + 3/4, z + 1/4 for compound **1**; #1 –x + 1/4, –z + 3/4, y – 1/4; #2 –z, x + 1/2, –y + 1/2; #3 y – 1/2, –z + 1/2, –x; #4 z, –x+1, –y + 1/2 for compound **2**.

Table S**2** Structural comparison of coordination compounds containing tetranuclear square $[M_4L_4]$ SBUs.[b]

Compounds	Type of Ligand L	Coordination modes of Ligand L	Type of configurations of $[M_4L_4]$ SBUs	Four dihedral angles between each imidazole ring plane and tetranuclear square $[M_4L_4]$ plane	Dimension
$\{[Co_4(HIDC)_4(bpy)_4]\cdot 14H_2O\}_n$[10c]	H_3IDC	μ_2-*k*N,O:*k*N',O'	Tpye **I**	5.85, 89.35, 5.85, 89.35°	0D
$\{[Co_5(IDC)_2(HIDC)_2(phen)_4(H_2O)_2]\cdot 12H_2O\}_n$[10c]	H_3IDC	μ_2-*k*N,O:*k*N',O' and μ_3-*k*N,O:*k*N',O':*k*O'',O'''	Tpye **I**	0.86, 86.81, 0.86, 86.81°	1D
$\{[Co_4(HIDC)_4(pda)_4]\cdot 28H_2O\}_n$[10d]	H_3IDC	μ_2-*k*N,O:*k*N',O'	Tpye **II**	84.61, 84.61, 84.61, 84.61°	0D
$\{Na_2[Co_4(IDC)_4(bpy)_4]\cdot 12H_2O\}_n$[10e]	H_3IDC	μ_3-*k*N,O:*k*N',O':*k*O'',O'''	Tpye **I**	6.24, 89.99, 6.24, 89.99°	1D
$\{[Ni_4(HEIDC)_4(H_2O)_8]\cdot 2H_2O\}_n$[10a]	H_3EIDC	μ_2-*k*N,O:*k*N',O'	Tpye **II**	85.09, 85.09, 85.09, 85.09°	0D
$[Cd(HEIDC)(bix)_{0.5}(H_2O)]_n$[10f]	H_3EIDC	μ_2-*k*N,O:*k*N',O'	Tpye **II**	76.38, 76.38, 76.38, 76.38°	2D
$\{[Cd_4(HPIDC)_4(H_2O)_8]\cdot 2H_2O\}_n$[10b]	H_3PIDC	μ_2-*k*N,O:*k*N',O'	Tpye **II**	78.32, 85.60, 78.32, 85.60°	0D
$\{[Cd_4(HPIDC)_4(py)_8]\cdot 10H_2O\}_n$[10b]	H_3PIDC	μ_2-*k*N,O:*k*N',O'	Tpye **II**	80.20, 80.23, 80.20, 80.23°	0D
Compound **1** in this work	$H_3TFMIDC$	μ_3-*k*N,O:*k*N',O':*k*O'',O'''	Tpye **II**	69.91, 71.22, 69.91, 71.22°	3D
Compound **2** in this work	$H_3TFMIDC$	μ_3-*k*N,O:*k*N',O':*k*O'',O'''	Tpye **II**	72.00, 72.18, 72.00, 72.18°	3D

[b]H_3EIDC = 2-ethyl-1*H*-imidazole-4,5-dicarboxylic acid; H_3PIDC = 2-Propyl-1*H*-imidazole-4,5-dicarboxylic acid; bpy = 2,2'-bipyridine; phen = 1,10-phenanthroline; bix = 1,4-bis(imidazol-1-ylmethyl)benzene; pda = 1,2-propanediamine; py = pyridine. References 10a – 10f are given in the main text.

Scheme S**1** Synthetic route of ligand H_3TFMIDC



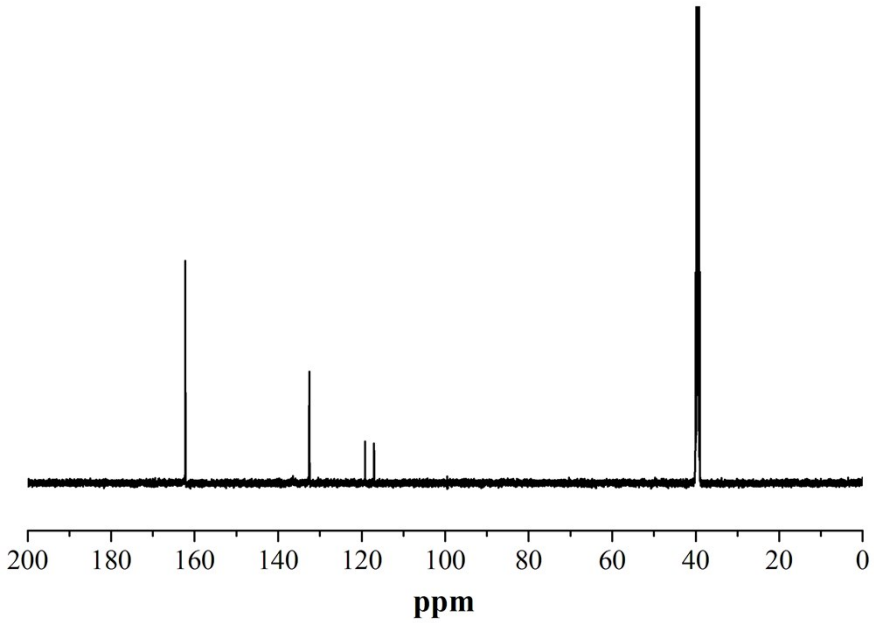


Figure S**1.** ^{13}C NMR spectrum measured in DMSO-d_6 of ligand H_3TFMIDC

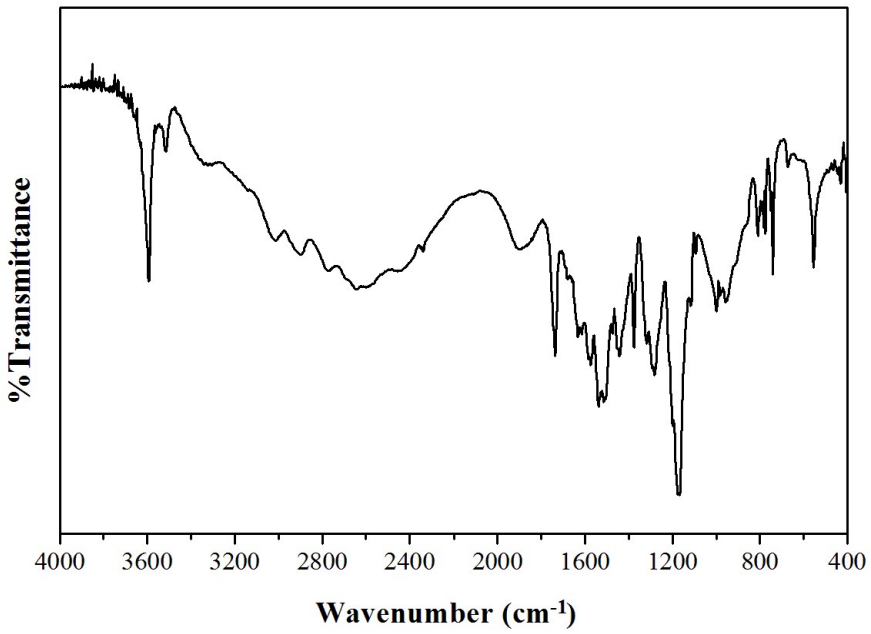


Figure S**2**. FT-IR spectrum of ligand H_3TFMIDC

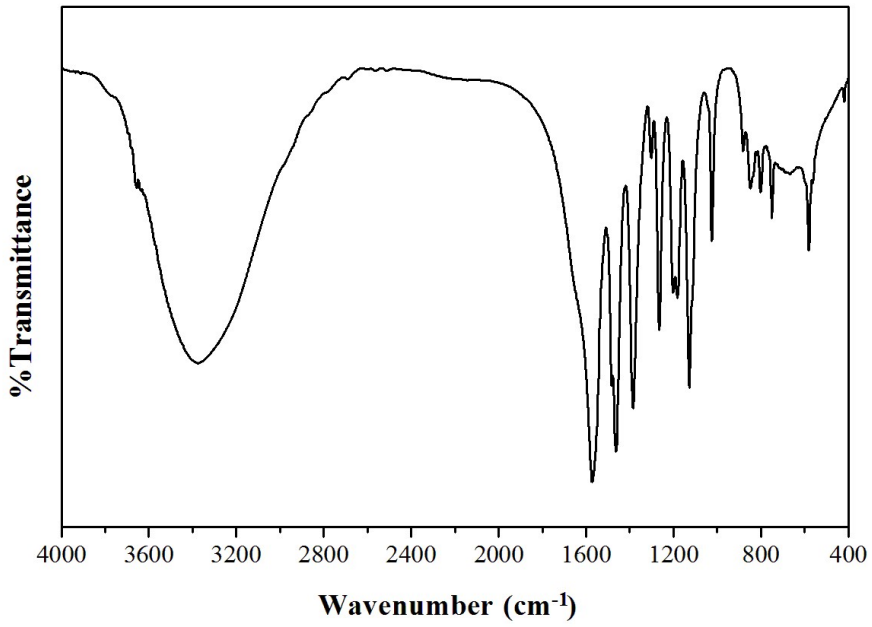


Figure S**3**. FT-IR spectrum of compound **1**.

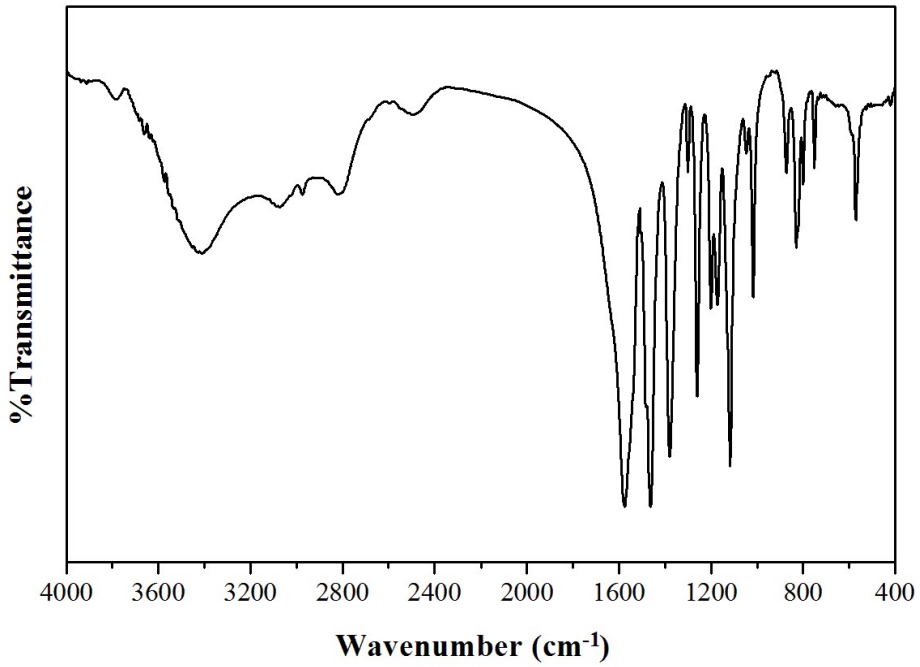


Figure S**4**. FT-IR spectrum of compound **2**.

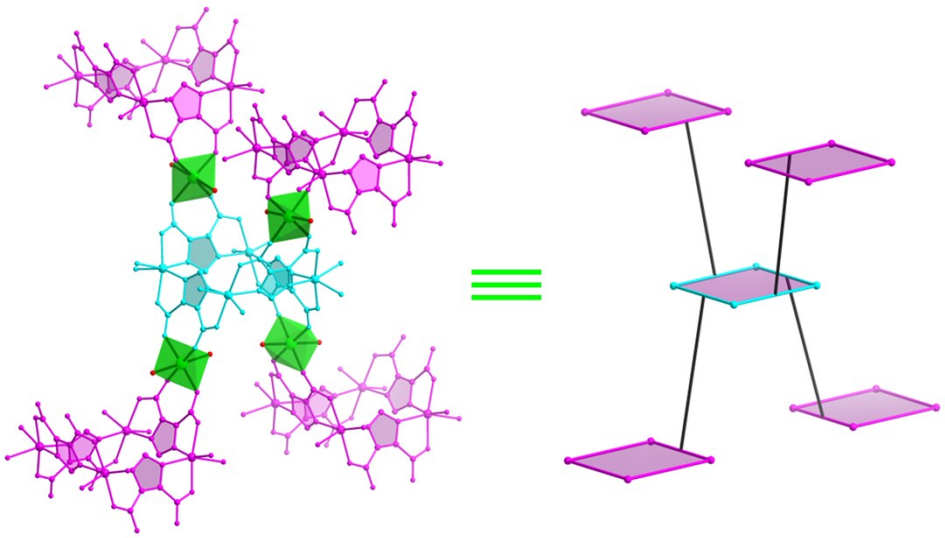


Figure S**5**. The four-connected square $[Co_4(TFMIDC)_4]$ SBU in **1**.

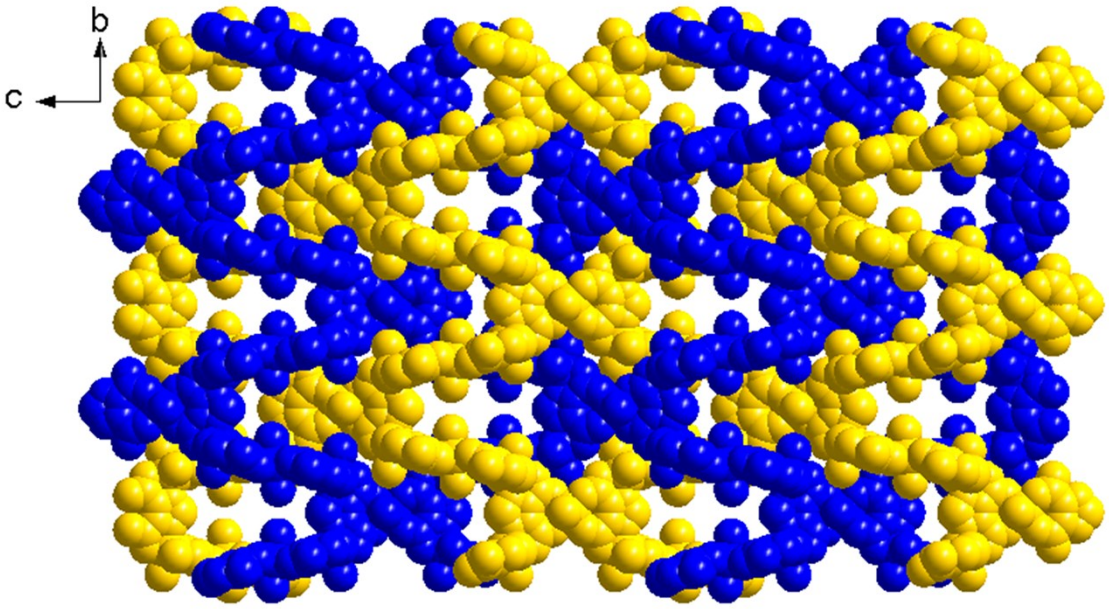


Figure S**6**. The 3D two-folded interpenetrated diamondoid framework of **1** discriminated by colors.

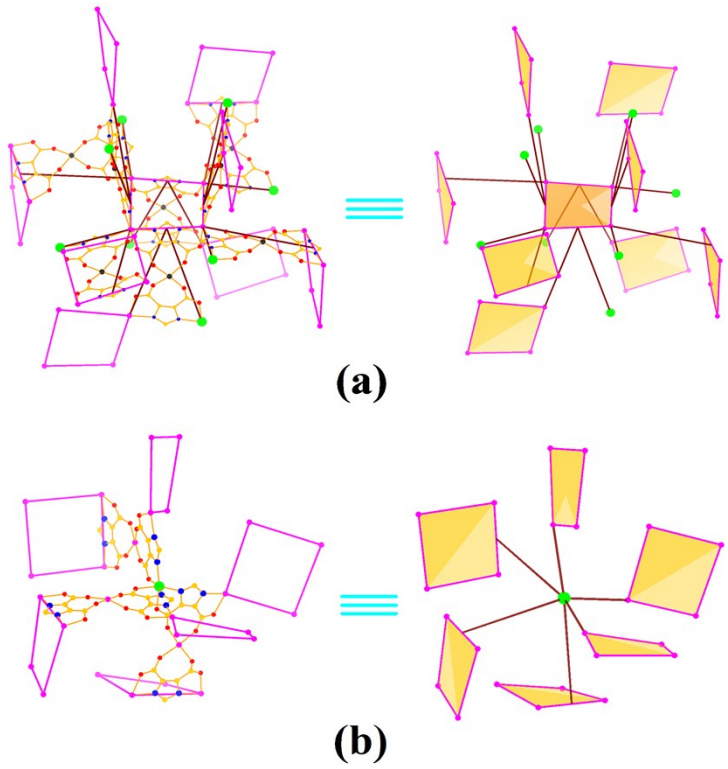


Figure S**7.** Schematic representation for the16-connected tetranuclear square SBU (a) and 6-connected Mn2 ion (b) in **2**.

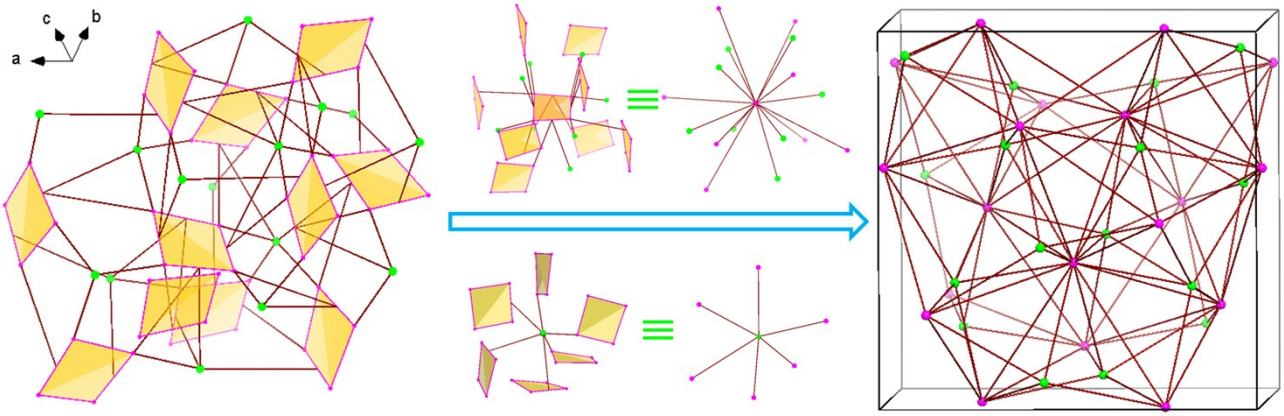


Figure S**8**. Views of the defined 16-connected and 6-connected nodes, as well as the whole topological net of compound **2**.

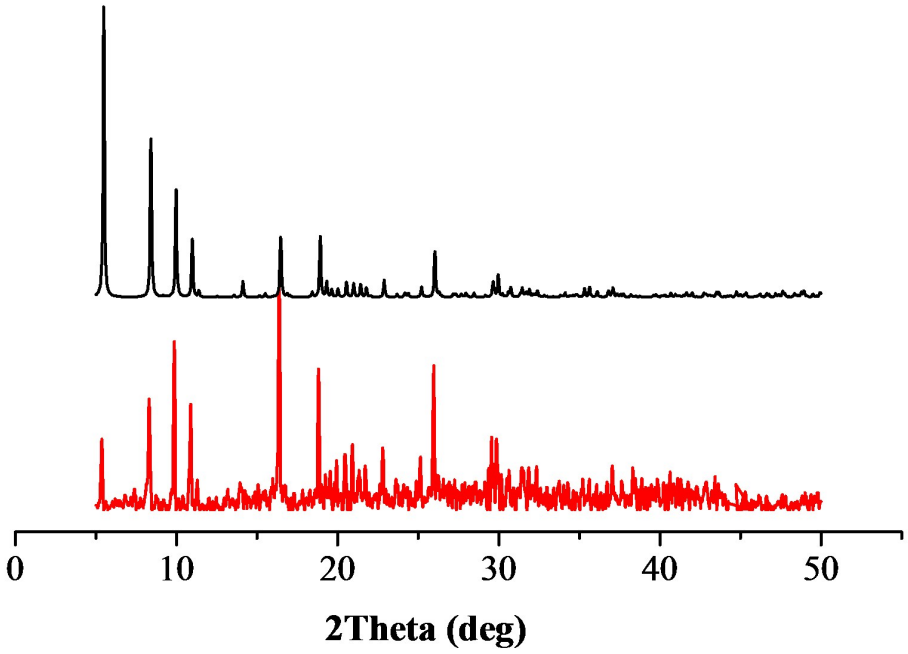


Figure S**9** The simulated X-ray powder diffraction patterns (black) and the measured one (red) of compound **1**.

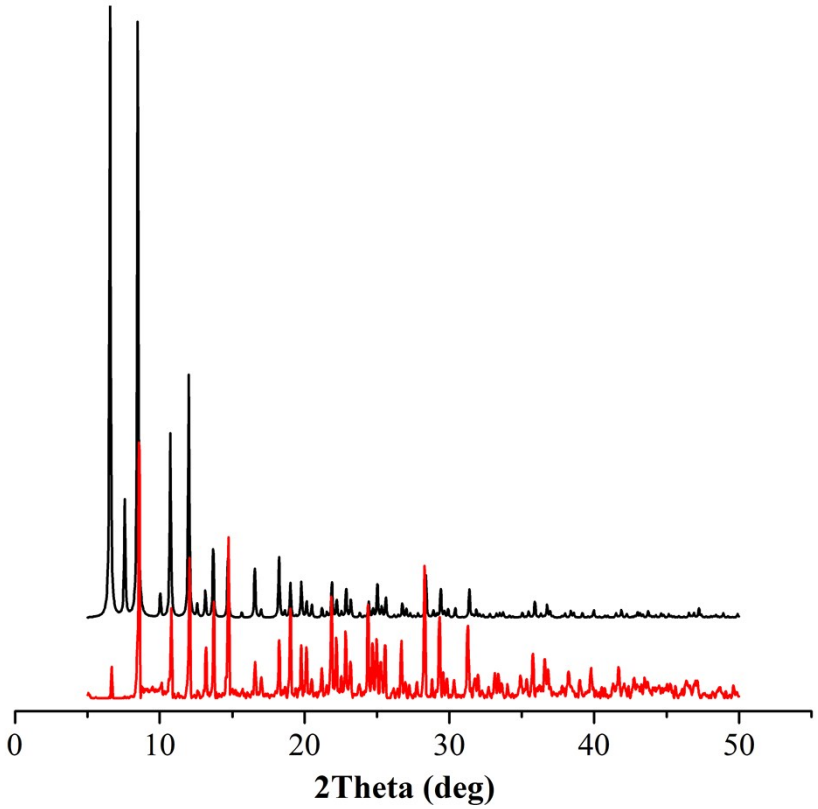


Figure S**10** The simulated X-ray powder diffraction patterns (black line) and the measured one (red line) of compound **2**.

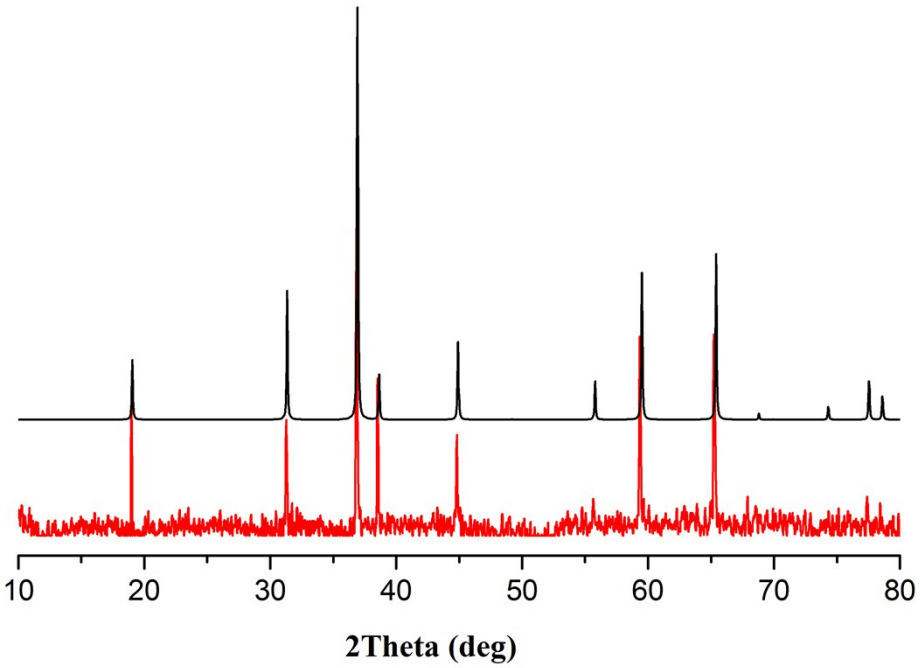


Figure S**11** The simulated X-ray powder diffraction patterns of cubic Co_3O_4 (black line, JCPDS card no. 43-1003) and the measured one (red line) of the residue after thermal decomposition of compound **1**.

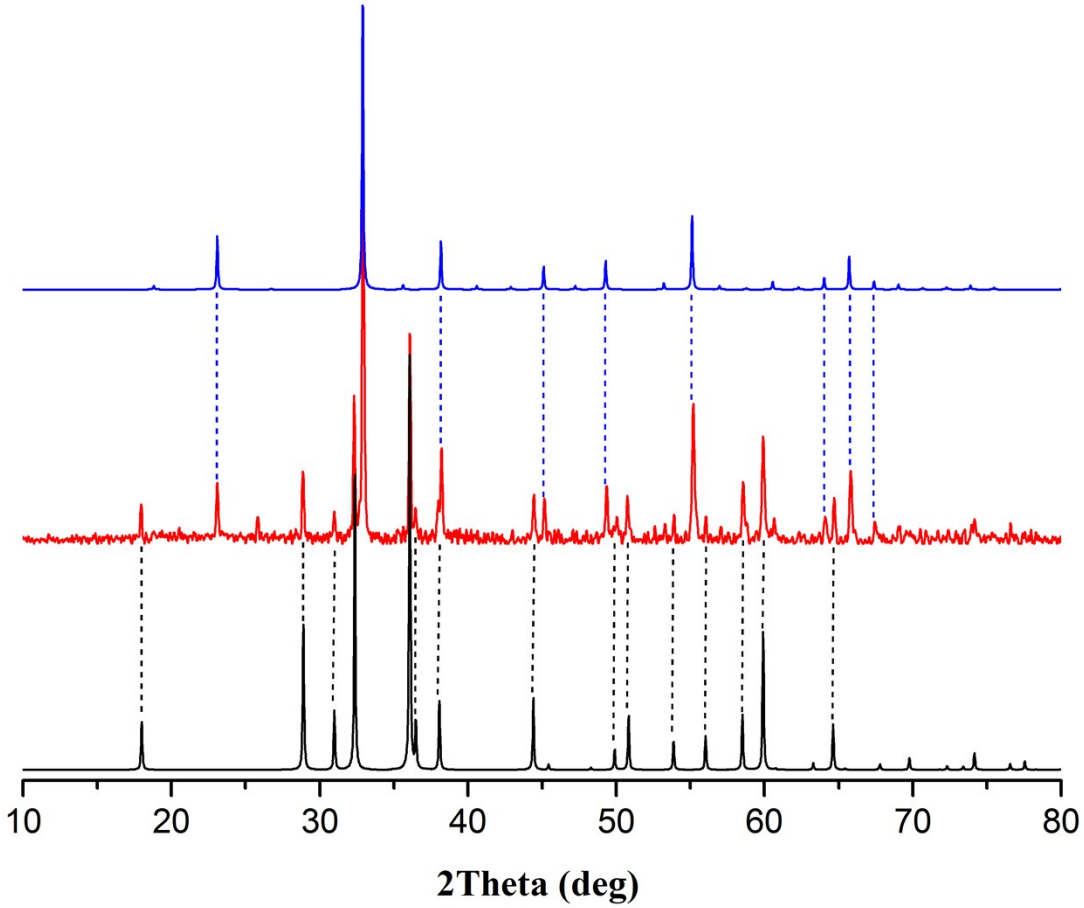


Figure S**12** The simulated X-ray powder diffraction patterns of cubic Mn_2O_3 (blue line, JCPDS card no. 41-1442), and tetragonal Mn_3O_4 (black line, JCPDS card no. 24-0734), as well as the measured one (red line) of the residue after thermal decomposition of compound **2**.