Ionothermal Synthesis, Structure, Magnetism-Structure Relation of two Biphenyltetracarboxylic acid-based Metal-Organic Frameworks:

Wen-xian Chen, Li Tan, Qiu-ping Liu, Gen-rong Qiang, Gui-lin Zhuang*

[a] Institute of Industrial Catalysis, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou, People's Republic of China, 310032. Fax: (+86)571-88871037 Tel: (+86)571-88871037. Email: glzhuang@zjut.edu.cn.

1. Experimental

All the reagents were of commercial origin without further purification. The C, H, and N element analyses were performed by use of a CE instruments EA 1110 elemental analyzer. The infrared spectra were measured on a Nicolet AVATAR FT-IR360 Spectrophotometer with pressed KBr pellets. The X-ray powder diffractometry (XRPD) study was performed on Panalytical X-Pert pro diffractometer with Cu-Ka radiation. TGA curves were prepared on a SDT Q600 Thermal Analyzer. The Co/Na ratio was determined in a Thermo Elemental Atomic absorption spectrophotometer. Magnetic measurements were performed by a Quantum Design MPMS superconducting quantum interference device (SQUID).

Single crystals having suitable dimensions for compounds **1-2** were used for data collection using a CrysAlis CCD diffractometer (Xcalibur, Eos, Gemini ultra) at 298 K equipped with Enhance (Mo) X-ray Source (λ = 0.71073 Å). Integration and cell refinement was carried out using CrysAlis RED. The absorption correction was performed by multi-scan method using SCALE3 ABSPACK scaling algorithm. All Corrections were made for Lorentz and polarization effects. The molecular structures were solved by direct methods (SHELXL-86/SHELXL-97) and refinement by full-matrix least-squares on F^2 (SHELXS-97). Crystal data and selective bond length and bond angle of compounds **1-2** are given in Table S1 and S2.

Table S1 Crystallographic Data and Details of Data Collection and Refinement for 1-4

Compound	**1**	**2**
Formula	$C_{58}H_{43}N_2O_{28}Na_5Co_3$	$C_{26}H_{24}N_2O_{10}Mn_2$
Mr	1507.68	634.35
Crystal system	Orthorhombic	Monoclinic
Space group	*Fddd*	*C2/c*
a/Å	25.655(5)	30.577(6)
b/Å	28.561(6)	13.818(3)
c/Å	32.001(6)	16.241(3)
α/°	90	90
β/°	90	115.81(3)
γ/°	90	90
V /Å^3	23448(8)	6177.5(2)
Z	16	8
D_{calcd} /g·cm^{-3}	1.708	1.065
μ /mm^{-1}	0.973	0.852
No. of data/parameter	5024/442	6053/273
θ range/°	3.14-24.99	3.06-26.00
Obs reflns	3952	3557
R_1 *[I>2σ(I)]*[a]	0.0792	0.0757
wR_2 (all data)[b]	0.2367	0.2750

[a] $R_1 = \sum||F_O| - |F_C||/\sum|F_O|$ [b] $wR_2 = \{\sum[w(F_O^2 - F_C^2)^2]/\sum[w(F_O^2)^2]\}^{1/2}$

Table S2 selective bond length and bond angle of 1 and 2.

Compound **1**					
Co1-O1	1.926(4)	O1-Co1-O5	105.79(18)	O6-Na1-O2$^{\#9}$	117.30(18)
Co1-O5	1.952(4)	O1-Co1-O12$^{\#1}$	131.18(19)	O6-Na1-O3$^{\#12}$	92.7(3)
Co1-O12$^{\#1}$	1.962(4)	O5-Co1-O12$^{\#1}$	94.90(15)	O2$^{\#9}$-Na1-O3$^{\#12}$	145.8(2)
Co1-O10	1.985(4)	O1-Co1-O10	98.02(17)	O6-Na1-O8$^{\#12}$	128.31(16)
Co2-O7	1.974(5)	O5-Co1-O10	126.65(15)	O2$^{\#9}$-Na1-O8$^{\#12}$	78.70(13)
Co2-O7$^{\#2}$	1.974(5)	O12#1-Co1-O10	104.13(15)	O6-Na1-O7$^{\#4}$	143.92(17)
Co2-O3	2.306(11)	O7-Co2-O7$^{\#2}$	122.8(3)	O2$^{\#9}$-Na1-O7$^{\#4}$	90.15(15)
Co2-O3$^{\#2}$	2.306(11)	O7-Co2-O3	89.1(2)	O3$^{\#12}$-Na1-O7$^{\#4}$	71.4(2)
Co2-O4	2.416(5)	O7$^{\#2}$-Co2-O3	98.9(3)	O8$^{\#12}$-Na1-O7$^{\#4}$	77.20(13)
Co2-O4$^{\#2}$	2.416(5)	O7-Co2-O3$^{\#2}$	98.9(3)	O4$^{\#9}$-Na2-O4	162.6(5)
Na5-O8$^{\#5}$	2.681(4)	O7$^{\#2}$-Co2-O3$^{\#2}$	89.1(2)	O4$^{\#9}$-Na2-O4$^{\#2}$	106.8(4)
Na5-O8$^{\#6}$	2.681(4)	O3-Co2-O3$^{\#2}$	163.3(4)	O4-Na2-O4$^{\#2}$	75.9(5)
Na5-O2	2.698(5)	O8$^{\#5}$-Na5-O8$^{\#6}$	83.97(18)	O4$^{\#9}$-Na2-O4$^{\#10}$	75.9(5)
Na5-O2$^{\#7}$	2.698(5)	O8$^{\#5}$- Na5-O2	91.52(13)	O4-Na2-O4#10	106.8(4)
Na5-O11$^{\#1}$	2.733(4)	O8$^{\#6}$- Na5-O2	80.25(14)	O4$^{\#2}$-Na2-O4$^{\#10}$	162.6(5)
Na5-O11$^{\#3}$	2.733(4)	O8$^{\#5}$- Na5-O2$^{\#7}$	80.25(14)	O4$^{\#9}$-Na2-O13	73.3(3)
Na1-O2$^{\#9}$	2.616(5)	O8$^{\#6}$- Na5-O2$^{\#7}$	91.52(13)	O4-Na2-O13	89.3(3)

Na1-O3$^{\#12}$	2.703(10)	O2- Na5-O2$^{\#7}$	169.10(12)	O4$^{\#2}$-Na2-O13	102.4(3)
Na1-O8$^{\#12}$	2.845(5)	O8$^{\#5}$- Na5-O11$^{\#1}$	171.70(12)	O4$^{\#10}$-Na2-O13	94.8(4)
Na1-O7$^{\#4}$	2.875(6)	O2- Na5-O11$^{\#1}$	95.74(13)	O9$^{\#13}$-Na3-O9	144.9(2)
Na2-O4$^{\#9}$	2.323(5)	O2- Na5-O11$^{\#3}$	93.05(13)	O9$^{\#13}$-Na3-O9$^{\#7}$	101.0(3)
Na2-O4$^{\#2}$	2.323(5)	Na3-O9$^{\#7}$	2.360(4)	O9-Na3-O9$^{\#7}$	89.6(2)
Na2-O4$^{\#10}$	2.323(5)	Na3-O9$^{\#14}$	2.360(4)	O9-Na3-O9$^{\#14}$	101.0(3)
Na2-O13	2.781(18)	Na4-O11$^{\#16}$	2.337(4)	O11$^{\#16}$-Na4-O11	90.1(2)
Na2-O13$^{\#10}$	2.781(18)	Na4-O10$^{\#12}$	2.422(4)	O11-Na4-O10#^{12}	112.14(14)
Na2-O13$^{\#2}$	2.781(18)	Na4-O10#1	2.422(4)	O11-Na4-O10$^{\#1}$	82.22(13)
Na2-O13$^{\#9}$	2.781(18)	Na4-O9$^{\#12}$	2.721(5)	O11-Na4-O9$^{\#12}$	155.60(14)
Na3-O9$^{\#13}$	2.360(4)	Na4-O9$^{\#1}$	2.721(5)	O11-Na4-O9$^{\#1}$	102.01(13)

Symmetrical Code： #1 -x+3/2,-y,-z-1/2 #2 -x+7/4,-y+3/4,z #3 x-1/4,y+1/4,-z-1/2 #4 -x+2,-y+1/2,-z-1/2 #5 x-1/4,-y+1/2,z+1/4 #6 -x+3/2,y-1/4,z+1/4 #7 -x+5/4,-y+1/4,z #9 -x+7/4,y,-z-1/4 #10 x,-y+3/4,-z-1/4 #12 x+1/4,y-1/4,-z-1/2 #13 -x+5/4,y,-z-3/4 #14 x,-y+1/4,-z-3/4 #16 -x+7/4,-y-1/4,z

Compound **2**

Mn1-O5$^{\#1}$	2.122(4)	O5$^{\#1}$-Mn1-O8$^{\#2}$	91.99(16)	O7$^{\#2}$-Mn2-O4	120.7(2)
Mn1-O8$^{\#2}$	2.124(4)	O5$^{\#1}$-Mn1-O3	84.54(17)	O7$^{\#2}$-Mn2-O6$^{\#3}$	141.9(2)
Mn1-O3	2.199(5)	O8$^{\#2}$-Mn1-O3	96.06(17)	O4-Mn2-O6$^{\#3}$	97.24(15)
Mn1-O1$^{\#3}$	2.218(4)	O5$^{\#1}$-Mn1-O1$^{\#3}$	121.63(15)	O7$^{\#2}$-Mn2-O10$^{\#4}$	85.09(18)
Mn1-O9	2.224(5)	O8$^{\#2}$-Mn1-O1$^{\#3}$	146.05(15)	O4-Mn2-O10$^{\#4}$	90.47(17)
Mn1-O2$^{\#3}$	2.511(4)	O3-Mn1-O1#3	83.73(18)	O6$^{\#3}$-Mn2-O10$^{\#4}$	91.56(16)
Mn2-O7$^{\#2}$	2.032(4)	O5$^{\#1}$-Mn1-O9	94.67(17)	O7$^{\#2}$-Mn2-O2$^{\#3}$	89.81(16)
Mn2-O4	2.112(4)	O8$^{\#2}$-Mn1-O9	92.38(17)	O4-Mn2-O2$^{\#3}$	87.26(15)
Mn2-O6$^{\#3}$	2.128(4)	O1$^{\#3}$-Mn1-O9	89.57(17)	O6$^{\#3}$-Mn2-O2$^{\#3}$	95.95(15)
Mn2-O10$^{\#4}$	2.144(4)	O5$^{\#1}$-Mn1-O2$^{\#3}$	170.29(15)	O10$^{\#4}$-Mn2-O2$^{\#3}$	172.38(16)
Mn2-O2$^{\#3}$	2.215(4)	O8$^{\#2}$-Mn1-O2$^{\#3}$	91.21(14)	O9-Mn1-O2$^{\#3}$	94.36(16)
O3-Mn1-O9	171.55(16)	O3-Mn1-O2$^{\#3}$	86.01(14)	O1$^{\#3}$-Mn1-O2$^{\#3}$	54.86(12)

Symmetrical Code： #1 -x+2,y,-z+5/2 #2 x+1/2,-y+1/2,z+1/2 #3 -x+2,-y+1,-z+3 #4 x,-y+1,z+1/2

2. QMC simulation details

Algorithm of our fitting Program: The quantum Monte Carlo calculations were performed by our fitting program, where we call LOOP module of ALPS and utilize five parameters (J, g, zJ and TIP) to further fit the experimental result by use of exhaustive-iterative method. The corresponding formulas were shown in Eq(1)-Eq(4). The running procedure of our program is presented in the Figure S1. In following description, we exhibit fitting process of one J: In the beginning, the range of five parameters (J, g, zJ and TIP) were respectively set to that: [J_1: J_2], [g_1: g_2], [TIP_1:

TIP_2], [zJ_1: zJ_2], and the step sizes were set to ΔJ, Δg, ΔTIP and ΔzJ. Until the running is over, the best parameters (R_b, J_b, g_b, TIP_b, zJ_b) were obtained.

$$\chi_u = \frac{1}{NT}\left\langle \left(\sum_{i=1}^{N} S_i^z \right)^2 \right\rangle \quad \text{Eq(1)}$$

where uniform magnetic susceptibility χ_u is dimensionless.

Convert uniform magnetic susceptibility to χ_T (cm^3mol^{-1})

$$\chi_T(cm^3mol^{-1}) = Ag^2\chi_u \quad \text{Eq(2)}$$

where g is Landég-factor and A is unit constant.

Import zJ and TIP factor to χ_T , as bellows:

$$\chi_T'(cm^3mol^{-1}) = \frac{(\chi_T + TIP)}{1 + \frac{zJ(\chi_T + TIP)}{0.1303g^2}} \quad \text{Eq(3)}$$

The reliability factor R is obtained by

$$R = \frac{\sum(\chi_T'T - \chi_{obs}T)^2}{\sum(\chi_{obs}T)^2} \quad \text{Eq(4)}$$

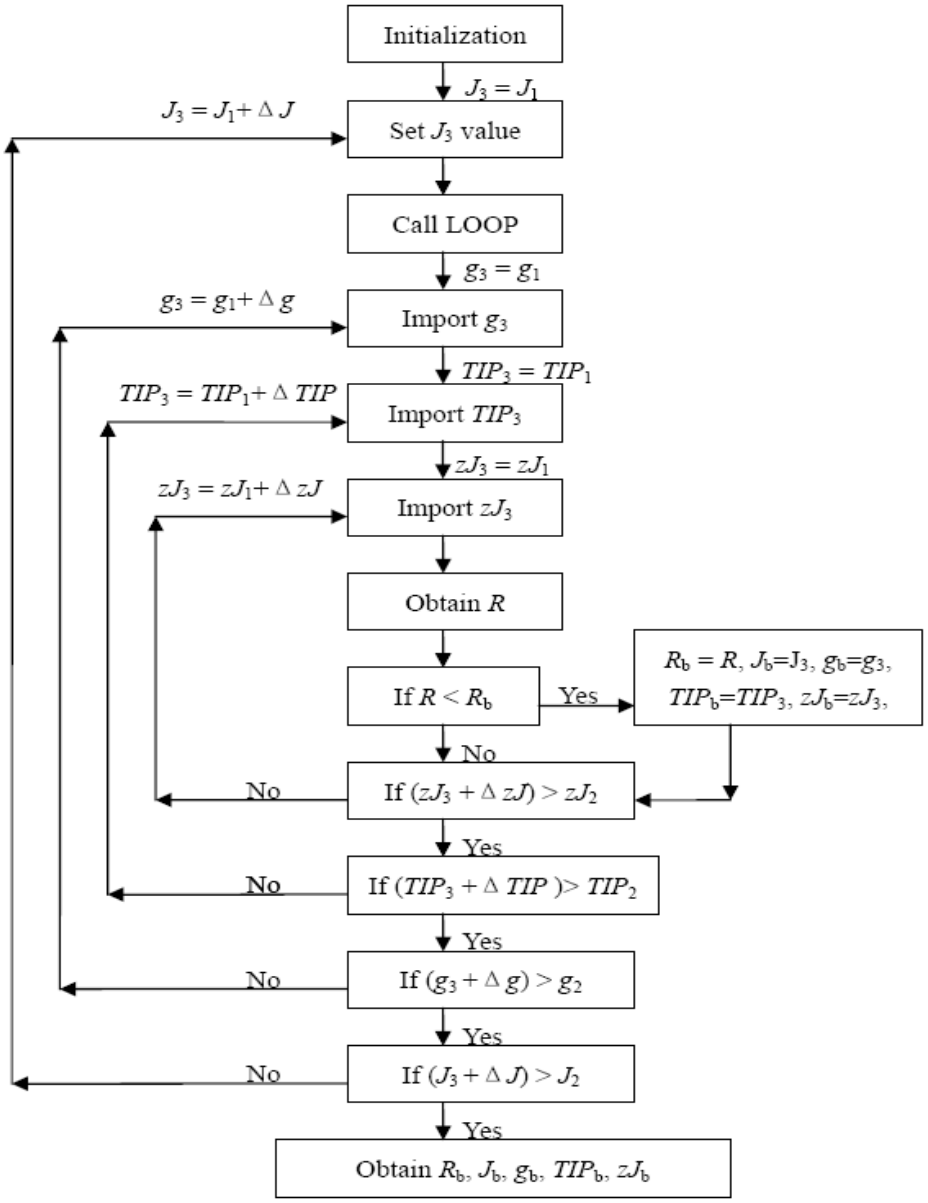

Figure S1 the running procedure of our program.

3. Structure of 1

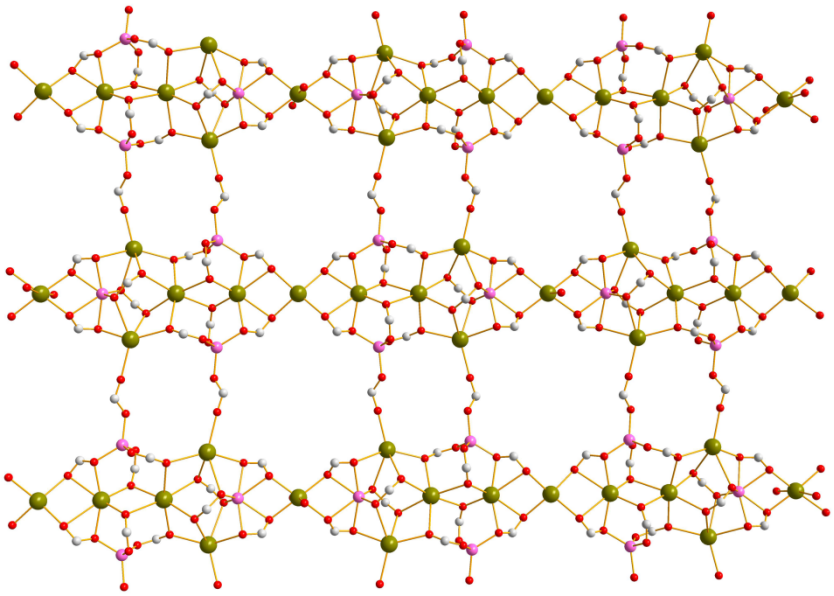

Fig. S2 three dimensional Co_3Na_6 –based framework in **1**.

4. Magnetic Properties of compounds 1 and 2.

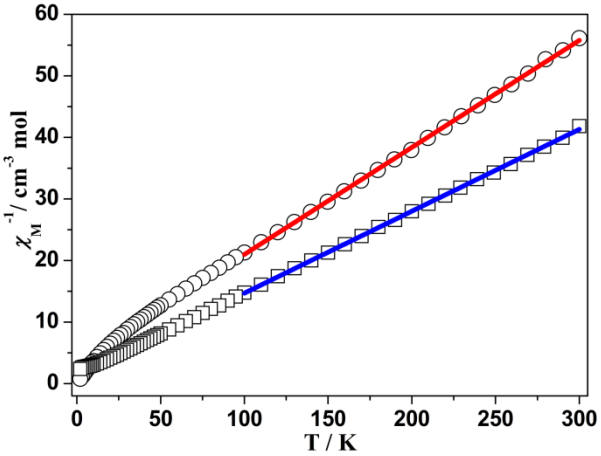

Fig. S3 χ_m^{-1} *vs* T plots of **1**(○) and **2**(□); linear fitting over the range of 100K-300K of **1**(red solid line), **2**(blue solid line).

6. PXRD of compounds 1 and 2.

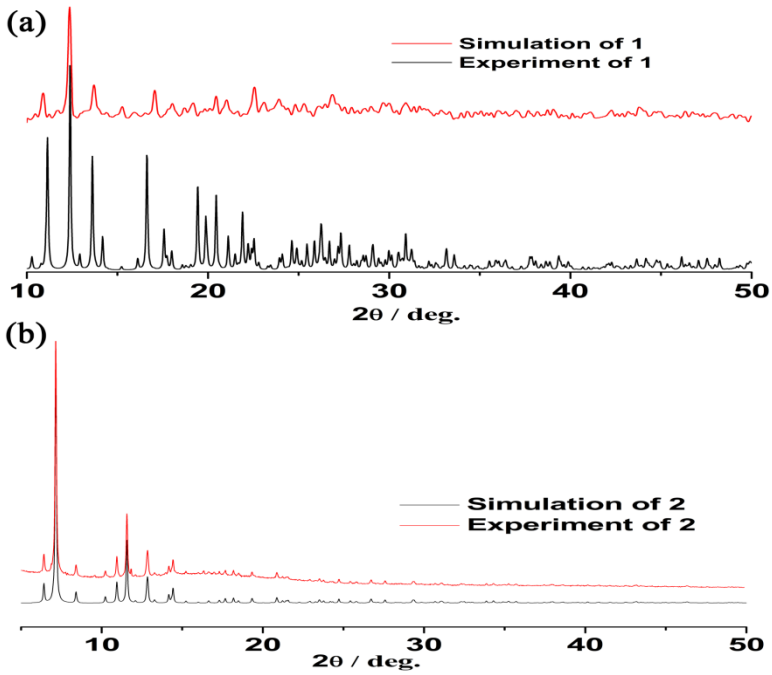

Fig. S4 Experimental and theoretical PXRD of **1** and **2**.