Electronic Supplementary Information

Crystal structures and ferroelectric properties of homochiral metal organic frameworks constructed from a single chiral ligand

Xuebin Xu, Meiying Liu and Zhiliang Liu*

Inner Mongolia Key Laboratory of Chemistry and Physics of Rare Earth Materials, School of Chemistry and Chemical Engineering, Inner Mongolia University, Hohhot 010021, China. *Corresponding author.

Fax/ Tel: +86-471-4992261

E-mail addresses: cezlliu@imu.edu.cn (Z. L. Liu)

1. Crystal Data Collection and Refinement

Crystallographic data were collected at a temperature of 293(2) K on a Bruker Apex II CCD diffractometer with graphite mono chromated Mo-K_a radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined using Olex2 suite of programs. All non-hydrogen atoms were refinement anisotropically. The H atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms. CCDC 1936599 and 1936602 contained the supplementary crystallographic data for this paper. In case of Co-MOF-1, there is two water molecules (from electron density map, TG and Elemental analyses) present in the lattice of unit cell (Figure S1b).

1.1 Crystallographic structural parameters of MOFs

Table S1. Crystallographic structural parameters of Co-MOF-1 and Co-MOF-2

Co-MOFs	1	2
Empirical formula	$C_{28}H_{34}CoN_4O_8$	$C_{28}H_{28}CoN_4O_5$
Formula weight	613.537	559.47
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic
space group	*P* 1	*P* 2_1
a	6.2526(4) Å	6.3218(7) Å
b	9.2824(6) Å	24.686(3) Å
c	13.0984(8) Å	9.3234(11) Å
a	82.2450(10) °	90 °
β	80.4760(10) °	100.936(2) °
γ	81.3350(10) °	90 °
Volume	736.45(8) $Å^3$	1428.6(3) $Å^3$
Z	1	2
Calculated density	1.383 Mg/m^3	1.301 Mg/m^3
Absorption coefficient	0.637 mm^{-1}	0.643 mm^{-1}
F(000)	321.527	582.0
Theta range for data collection	1.59 to 28.34 °	1.650 to 28.400 °
Reflections collected	10247	20232
Independent reflections	7177 [*R*(int) = 0.0147]	7133 [*R*(int) = 0.0203]
Completeness to theta = 25.242°	99.9 %	100 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	7177 / 8 / 359	7133 / 672 / 635
Goodness-of-fit on F^2	0.9666	1.068
Flack parameter	-0.023(11)	0.021(4)
Final *R* indices [I>2sigma(I)]	R_1 = 0.0225, wR_2 = 0.0523	R_1 = 0.0337, wR_2 = 0.0909
R indices (all data)	R_1 = 0.0232, wR_2 = 0.0526	R_1 = 0.0355, wR_2 = 0.0920
Largest diff. peak and hole	0.1913 and -0.1790 e. $Å^{-3}$	0.437 and -0.287 e. $Å^{-3}$

1.2 Selected distances and angles (deg) for Co-MOFs-1 and Co-MOF-2

Table S2. Selected bond lengths (Å) and angles (º) for Co-MOF-1

Bond distances (Å)		Bond angles (º)	
Co1–O1	2.0728(12)	O1–Co1–O2	88.55(5)
Co1–O2	2.1945(13)	O1–Co1–O3	167.46(5)
Co1–O3	2.0386(12)	O2–Co1–O3	88.17(5)
Co1–N1	2.1388(14)	O1–Co1–N1	99.42(5)
Co1–N2	2.1901(15)	O1–Co1–N2	91.66(6)
Co1–N3	2.1991(13)	O1–Co1–N3	77.94(5)
		N1–Co1–N2	86.68(6)
		N1–Co1–N3	177.35(7)
		N2–Co1–N3	93.28(5)

Table S3. Selected bond lengths (Å) and angles (º) for Co-MOF-2

Bond distances (Å)		Bond angles (º)	
Co1–O1	2.010(3)	O1–Co1–O2	87.50(9)
Co1–O2	2.078(2)	O1–Co1–O3	175.40(7)
Co1–O3	2.102(2)	O2–Co1–O3	89.48(10)
Co1–N1	2.199(13)	O1–Co1–N1	82.00(6)
Co1–N2	2.159(12)	O1–Co1–N2	92.30(11)
Co1–N3	2.200(2)	O1–Co1–N3	90.00(6)
		N1–Co1–N2	95.30(10)
		N1–Co1–N3	172.50(6)
		N2–Co1–N3	85.10(11)

Table S4. Hydrogen bonding parameters for Co-MOF-1

D-H···A	d(D-H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<D-H···A (˚)
O(5)-H(5B)···O(4)[#]	0.85	1.76	2.59	163.30

Symmetry operations: [#] x,y,z+1.

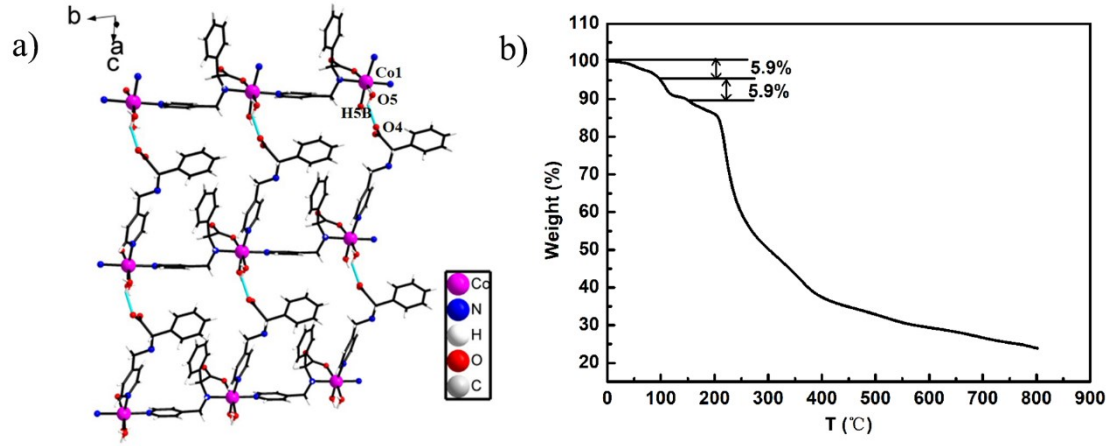

Figure S1. (a) View of 2D arrangement via O–H···O weak interactions for Co-MOF-1 (view along

a-axis); (b) TG curves of Co-MOF-1.

2. Ferroelectric Studies

2.1 The point electric charge model calculated saturation spontaneous polarization for Co-MOF-2.

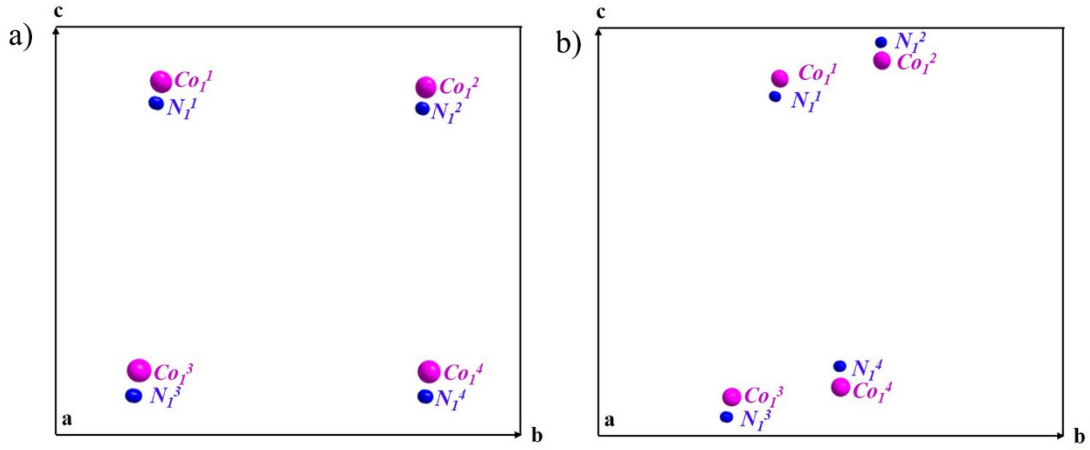

Figure S2. Project of the coordinate positions of the Co(II) and N atoms in the unit cell of Co-MOF-2 (assumed the positive charge and the negative charge reside on the protonated N atoms and Co atoms, respectively).

Table S5. Coordinates of the point electric charges in Co-MOF-2

Atoms	Coordinate		Central coordinate
Co	Co_1^1 (0.4366, 0.5988, 0.8879)	Co_1^2 (0.4366, 0.4012, 0.8879)	(0.4366, 0.5, 0.5)
	Co_1^3 (0.4366, 0.5988, 0.1122)	Co_1^4 (0.4366, 0.4012, 0.1121)	
N	N_1^1 (0.4083, 0.6090, 0.6507)	N_1^2 (0.4083, 0.3910, 0.6507)	(0.4083, 0.5, 0.5)
	N_1^3 (0.4083, 0.6090, 0.3493)	N_1^4 (0.4083, 0.3910, 0.3493)	

The molecular dipole moment (μ) and P_s were calculated using the point electric charge model. We select a unit cell and make an assumption that the center of positive and negative charge is on the central Co(II) atom. The values of μ and P_s along its polar *a*-axis in the unit cell can be estimated as following:

$$\mu = \left(qCo_1 rCo_1 + qN_1 rN_1\right) \times 2 \times a$$
$$= [(0.4366 \times e) + (-0.4083 \times e)] \times 2 \times a$$
$$= 0.0283 \times 1.6 \times 10^{-19} \times 2 \times 6.3218 \times 10^{-10}\,C \bullet m$$
$$\approx 5.725 \times 10^{-30}\,C \bullet m$$

Thus,

$$P_s = 5.725 \times 10^{-30}\,C \bullet m / V = 5.725 \times 10^{-30}\,C \bullet m / 1428.6 \times 10^{-30}\,m^3$$
$$\approx 0.40\ \mu C / cm^2$$

If the polar direction is b-axis, and the estimated P_s value for Co-MOF-2 is 0.56

$\mu C \cdot cm^{-2}$.

2.2 Leakage current of ferroelectric hysteresis loop of Co-MOFs

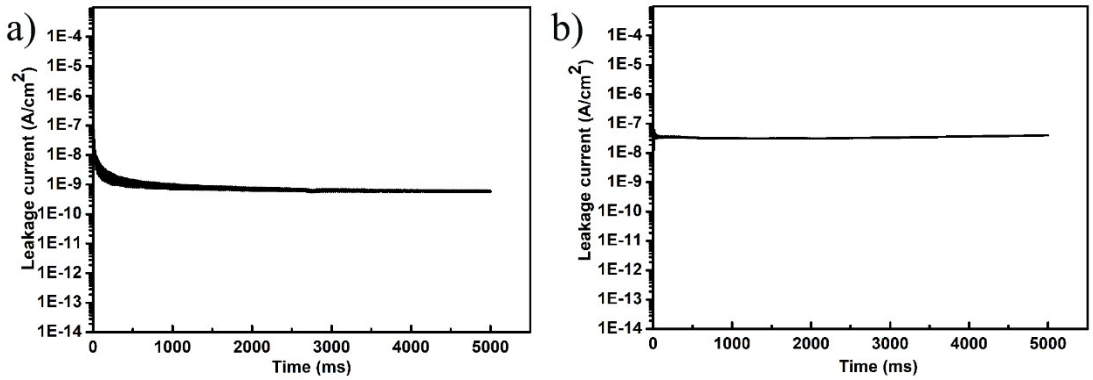

Figure S3. The leakage current of Co-MOF-1 (a) and Co-MOF-2 (b) recorded under 900 V.

2.3 Dielectric property and thermal behavior of Co-MOF-2

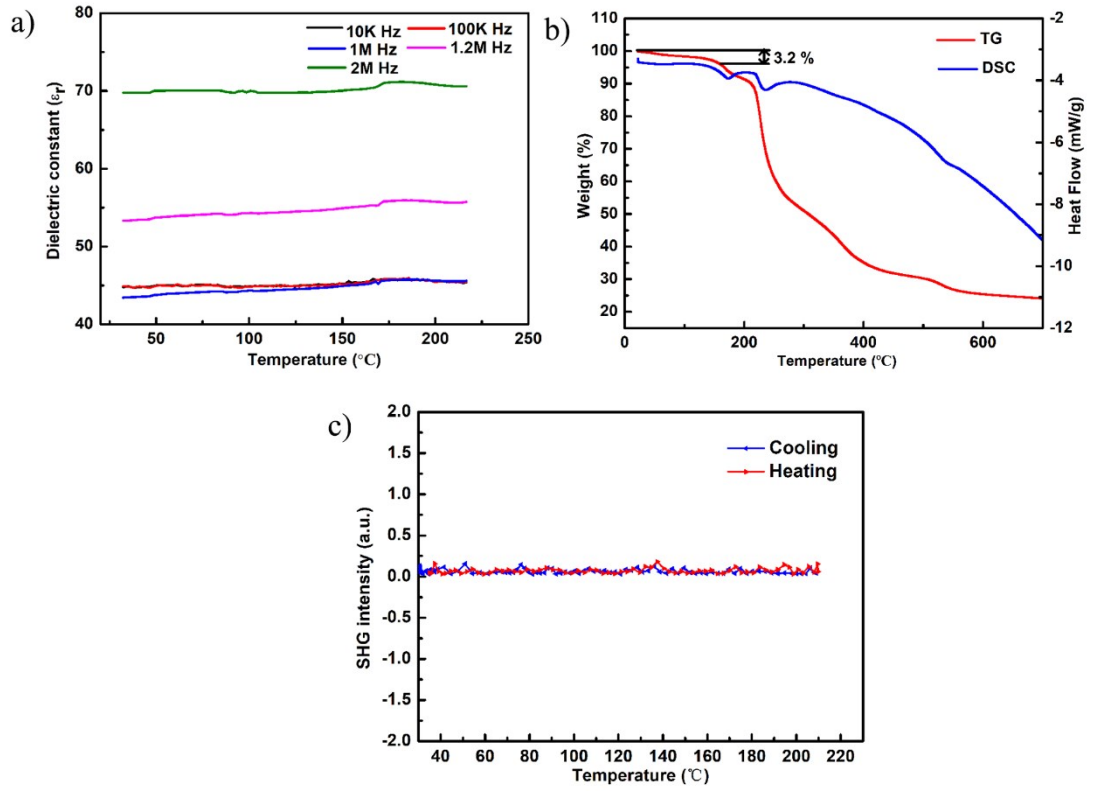

Figure S4. (a) Dielectric constant of Co-MOF-2, (b) DSC curves and TG curves of Co-MOF-2, (c) Temperature-dependent SHG effect of Co-MOF-2.