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A Novel Co-crystallization Molecular Ferroelectric Induced by Ordering of Sulphate Anions and Hydrogen Atoms

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Table S1 Crystal data and structure refinement for **1**

Complex	**1-a**	**1-b**
Empirical formula	$C_{26}H_{22}CuN_4O_6S$	$C_{13}H_{11}Cu_{0.5}N_2O_3S_{0.5}$
Formula weight	582.08	291.04
Temperature	173.15 K	293(2) K
Crystal system	Monoclinic	Monoclinic
Space group	*Cc*	*C2/c*
a (Å)	17.674(9)	17.6404(14)
b (Å)	11.958(5)	12.0146(8)
c (Å)	13.124(7)	13.1577(9)
α (deg)	90	90
β (deg)	120.998(7)	120.947(7)
γ (deg)	90	90
V (Å³)	2378(2)	2391.7(3)
Dcalca /M gm⁻³	1.626	1.617
Z	4	8
μ (mm-1)	1.060	1.053
F(000)	1196	1196
Data / restraints / parameters	5374/2/344	2346 / 6 / 185
GOF	1.036	1.082
R1[I > 2σ(I)]	R_1 = 0.0354, wR_2 = 0.0769	R_1 = 0.0462, wR_2 = 0.0889
wR2 (all data)	R_1 = 0.0376, wR_2 = 0.0783	R_1 = 0.0551, wR_2 = 0.0941
△ρmax / △ρmin (eÅ⁻³)	0.40 /-0.38	1.486 / -1.106

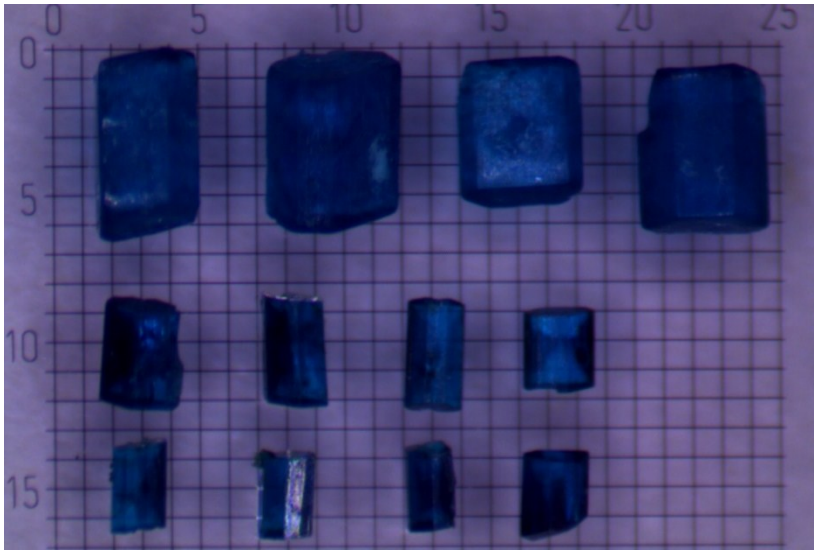

Figure S1 the blue block crystals for **1** obtained by hydrothermal synthesis

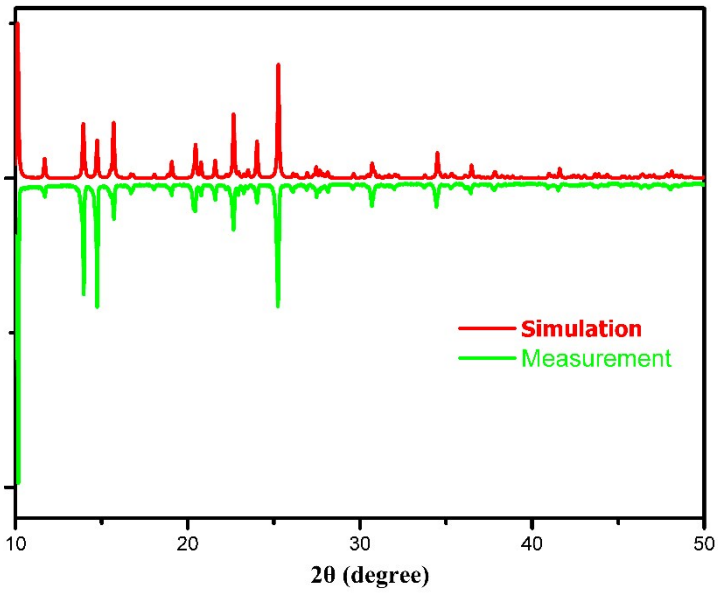

Figure S2 Powder XRD patterns of (Fit) the simulation based on the single crystal analysis of **1-b**, (Measurement) the as-synthesized sample at room temperature

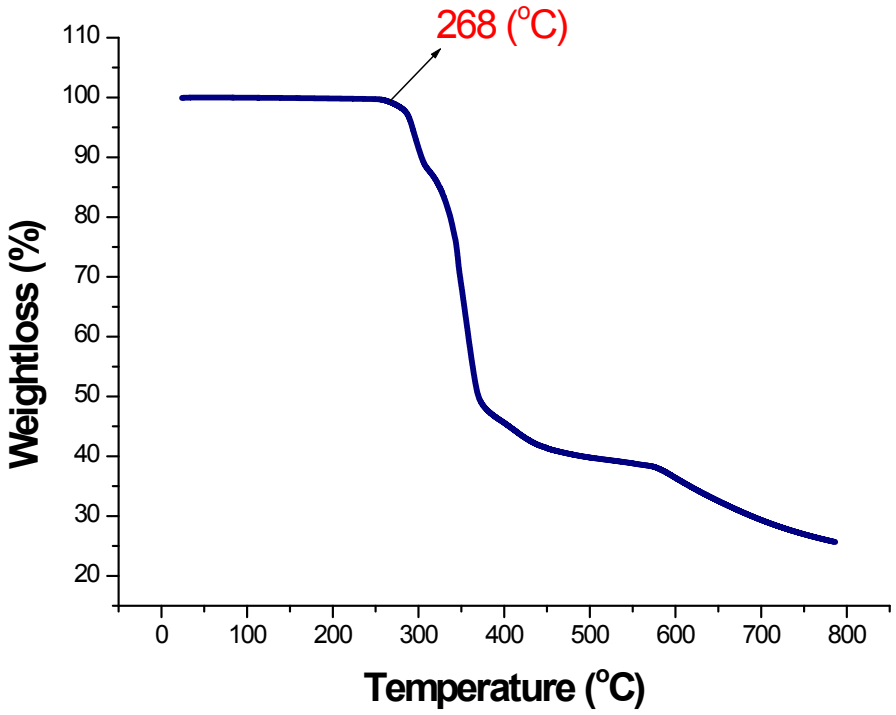

Figure S3 the thermo-gravimetric analysis (TGA) curve for **1**

Table S2 Bond lengths [Å] and angles [°] for **1**

1-a

Bond lengths

Cu1 O1	1.979(3)	C9 C10	1.426(7)
Cu1 N4	1.997(4)	C10 N2	1.323(7)
Cu1 N2	2.012(4)	C11 N2	1.357(6)
Cu1 N3	2.066(4)	C11 C12	1.442(6)
Cu1 N1	2.167(4)	C12 N1	1.356(5)
S1 O2	1.464(3)	C13 N4	1.340(6)
S1 O3	1.479(3)	C13 C14	1.374(7)
S1 O4	1.481(3)	C14 C15	1.388(8)
S1 O1	1.501(3)	C15 C16	1.420(7)
O5 C26	1.420(6)	C16 C24	1.391(6)
O6 C25	1.421(6)	C16 C17	1.444(7)
C1 N1	1.332(6)	C17 C18	1.353(7)
C1 C2	1.414(7)	C18 C19	1.434(7)
C2 C3	1.360(7)	C19 C20	1.406(7)
C3 C5	1.422(7)	C19 C23	1.406(7)
C4 C6	1.369(7)	C20 C21	1.372(7)
C4 C5	1.425(7)	C21 C22	1.395(7)
C5 C12	1.406(7)	C22 N3	1.344(6)

C6 C7	1.432(7)	C23 N3	1.366(6)
C7 C8	1.413(7)	C23 C24	1.442(7)
C7 C11	1.415(6)	C24 N4	1.365(6)
C8 C9	1.362(8)	C25 C26	1.486(7)

Bond angles

O1 Cu1 N4	90.88(13)	C5 C12 C11	119.6(4)
O1 Cu1 N2	97.14(14)	N4 C13 C14	122.6(5)
N4 Cu1 N2	170.95(12)	C13 C14 C15	120.1(5)
O1 Cu1 N3	143.34(14)	C14 C15 C16	118.7(5)
N4 Cu1 N3	81.50(16)	C24 C16 C15	117.2(4)
N2 Cu1 N3	94.41(16)	C24 C16 C17	118.9(4)
O1 Cu1 N1	104.09(13)	C15 C16 C17	123.9(4)
N4 Cu1 N1	93.47(15)	C18 C17 C16	120.5(4)
N2 Cu1 N1	80.53(16)	C17 C18 C19	121.9(5)
N3 Cu1 N1	112.10(11)	C20 C19 C23	116.8(4)
O2 S1 O3	110.72(18)	C20 C19 C18	124.7(5)
O2 S1 O4	110.70(17)	C23 C19 C18	118.6(4)
O3 S1 O4	109.63(16)	C21 C20 C19	119.7(5)
O2 S1 O1	109.43(17)	C20 C21 C22	119.8(5)
O3 S1 O1	109.27(18)	N3 C22 C21	122.7(4)
O4 S1 O1	107.01(18)	N3 C23 C19	123.9(4)
S1 O1 Cu1	128.73(18)	N3 C23 C24	116.5(4)
N1 C1 C2	121.8(4)	C19 C23 C24	119.6(4)
C3 C2 C1	120.1(4)	N4 C24 C16	123.4(4)
C2 C3 C5	119.2(5)	N4 C24 C23	116.1(4)
C6 C4 C5	120.7(5)	C16 C24 C23	120.5(4)
C12 C5 C3	117.0(4)	O6 C25 C26	114.3(5)
C12 C5 C4	120.1(4)	O5 C26 C25	113.4(5)
C3 C5 C4	122.9(5)	C1 N1 C12	118.6(4)
C4 C6 C7	120.6(4)	C1 N1 Cu1	131.5(3)
C8 C7 C11	116.9(5)	C12 N1 Cu1	109.8(3)
C8 C7 C6	123.3(5)	C10 N2 C11	119.1(4)
C11 C7 C6	119.8(4)	C10 N2 Cu1	126.6(4)
C9 C8 C7	120.2(5)	C11 N2 Cu1	114.2(3)
C8 C9 C10	119.0(5)	C22 N3 C23	117.1(4)
N2 C10 C9	122.1(5)	C22 N3 Cu1	131.2(3)
N2 C11 C7	122.6(4)	C23 N3 Cu1	111.7(3)
N2 C11 C12	118.2(4)	C13 N4 C24	117.9(4)
C7 C11 C12	119.2(4)	C13 N4 Cu1	127.8(3)
N1 C12 C5	123.2(4)	C24 N4 Cu1	114.1(3)

N1 C12 C11	117.2(4)		

1-b

Bond lengths

Cu(1)-O(1')	1.945(3)	Cu(1)-N(2)	1.9983(18)
Cu(1)-N(2)#1	1.9983(18)	Cu(1)-N(1)#1	2.1183(13)
Cu(1)-N(1)	2.1183(13)	S(1)-O(1')#1	1.411(3)
S(1)-O(1')	1.411(3)	S(1)-O(2)#1	1.4179(16)
S(1)-O(2)	1.4179(16)		

Bond angles

O(1')-Cu(1)-O(1')#1	37.12(13)	O(1')-Cu(1)-N(2)	96.67(11)
O(1')#1-Cu(1)-N(2)	92.22(12)	O(1')-Cu(1)-N(2)#1	92.22(12)
O(1')#1-Cu(1)-N(2)#1	96.67(11)	N(2)-Cu(1)-N(2)#1	170.63(10)
O(1')-Cu(1)-N(1)#1	142.07(8)	O(1')#1-Cu(1)-N(1)#1	106.29(8)
N(2)-Cu(1)-N(1)#1	93.78(6)	N(2)#1-Cu(1)-N(1)#1	80.90(6)
O(1')-Cu(1)-N(1)	106.29(8)	O(1')#1-Cu(1)-N(1)	142.07(8)
N(2)-Cu(1)-N(1)	80.90(6)	N(2)#1-Cu(1)-N(1)	93.78(6)
N(1)#1-Cu(1)-N(1)	111.34(8)	O(1')#1-S(1)-O(1')	52.04(19)
O(1')#1-S(1)-O(2)#1	134.32(16)	O(1')-S(1)-O(2)#1	105.49(13)
O(1')#1-S(1)-O(2)	105.49(13)	O(1')-S(1)-O(2)	134.32(16)
O(2)#1-S(1)-O(2)	115.00(15)	O(1')#1-S(1)-O(1)	100.51(17)
O(1')-S(1)-O(1)	61.78(17)	O(2)#1-S(1)-O(1)	99.29(11)
O(2)-S(1)-O(1)	90.70(12)	O(1')#1-S(1)-O(1)#1	61.78(17)
O(1')-S(1)-O(1)#1	100.51(17)	O(2)#1-S(1)-O(1)#1	90.70(12)
O(2)-S(1)-O(1)#1	99.29(11)	O(1)-S(1)-O(1)#1	161.4(2)

Table S3 Hydrogen bonds parameters of **1**

D-H···A	D-H	H···A	D···A	∠D-H···A
1-a				
O(6)-H(6B)···O(4)	0.84	1.92	2.764(5)	177
O(5)-H(5A)···O(3)	0.84	1.96	2.792(5)	170
1-b				
O(3)-H(3A)···O(2)#3	0.82	1.973	2.790(3)	172.9

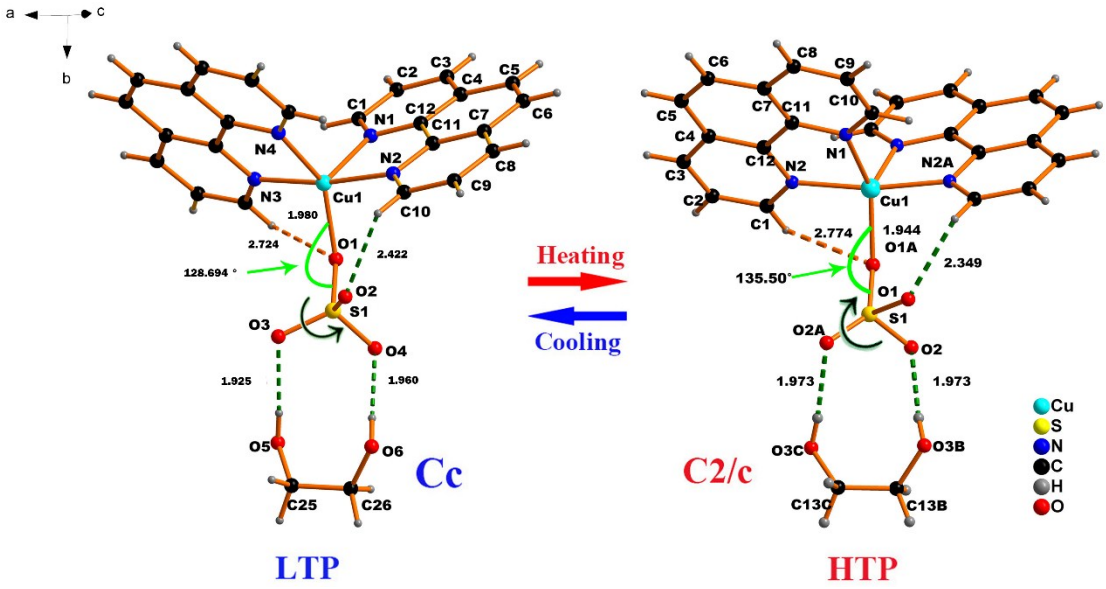

Figure S4(a) **Figure S4(b)**

Figure S4 (a) the crystal structure of **1-a** shows ordered sulfate ions, unsymmetrical motion hydrogen atoms and canted angles of (Cu1-O1-S1) at 100 K; (b) the crystal structure of **1-b** shows disordered sulfate ions and symmetrical motion hydrogen atoms at 293K. Symmetry codes: (A) 1-x, y, 0.5-z; (B) 1+x, y, z; (C) 0.5+x, 0.5+y, z; (D) 1.5-x, 0.5+y, 0.5-z.