Electronic Supplementary Material (ESI) for CrystEngComm.


# Supporting Information

Switchable dielectric phase transition originating from disorder-order transformation and distortion in $\{[(C_4H_4N_2)Co(H_2O)_4]SO_4\cdot 2H_2O\}_n$

Table S1 Selected bond lengths (Å) and bond angles (°) for compound **1** at 296 K and 100 K.

| | | | |
|---|---|---|---|
| **296K** | | | |
| Co1−O1W | 2.099(2) | Co1−O2W | 2.038(2) |
| Co1−O2WA | 2.201(2) | Co1−O1WA | 2.099(2) |
| Co1−N1 | 2.038(2) | Co1−N1A | 2.201(2) |
| S1−O4B | 1.385(7) | S1−O1B | 1.430(8) |
| S1−O1 | 1.430(8) | S1−O2 | 1.528(5) |
| S1−O2B | 1.528(5) | S1−O3 | 1.471(4) |
| S1−O4 | 1.385(7) | N1−C1 | 1.329(4) |
| N1−C2 | 1.332(4) | C1−C2C | 1.384(4) |
| O1W−Co1−O2W | 91.31(9) | O1W−Co1−N1 | 87.37(8) |
| O1W−Co1−O1WA | 180 | O1−Co1−O2WA | 88.69(9) |
| O1W−Co1−N1A | 92.63(8) | O2W−Co1−N1 | 87.02(8) |
| O1WA−Co1−O2W | 88.69(9) | O2W−Co1−O2WA | 180 |
| O2W−Co1−N1A | 92.98(8) | O1W_b−Co1−N1 | 92.63(8) |
| O2WA−Co1−N1 | 92.98(8) | N1−Co1−N1A | 180 |
| O1WA−Co1−O2WA | 91.31(9) | O1−S1−O1B | 152.6(5) |
| O1−S1−O2 | 105.2(4) | O1−S1−O2B | 62.9(4) |
| O1A−S1−O2 | 62.9(4) | O1B−S1−O2B | 105.2(4) |
| O1−S1−O3 | 103.7(4) | O1B−S1−O3 | 103.7(4) |
| O1−S1−O4A | 51.6(5) | O1B−S1−O4 | 51.6(5) |
| O1−S1−O4 | 118.4(5) | O1B−S1−O4B | 118.4(5) |
| O2−S1−O2A | 131.8(3) | O2B−S1−O3 | 114.1(2) |
| O2−S1−O3 | 114.1(2) | O2−S1−O4 | 107.9(4) |
| O2B−S1−O4 | 56.2(4) | O2−S1−O4B | 56.2(4) |
| O2B−S1−O4A | 107.9(4) | O3−S1−O4B | 107.8(3) |
| O4−S1−O4A | 144.4(5) | Co1−N1−C1 | 124.4(2) |
| Co1−N1−C1 | 124.4(2) | C1−N1−C2 | 116.3(3) |
| C1−N1−C2 | 116.3(3) | Co1−N1−C2 | 119.3(2) |
| Co1−N1−C2 | 119.3(2) | N1−C1−C2C | 121.7(3) |
| N1−C1−C2C | 121.7(3) | N1−C2−C1C | 122.0(3) |
| N1−C2−C1C | 122.0(3) | | |
| **100K** | | | |
| Co1−O1W | 2.1120(9) | Co1−O2W | 2.0314(10) |
| Co1−O3W | 2.0915(9) | Co1−O4W | 2.0468(9) |
| Co1−N1 | 2.1898(12) | Co1−N2 | 2.1966(12) |
| S1−O1 | 1.4689(10) | S1−O2 | 1.4751(10) |
| S1−O3 | 1.4787(11) | S1−O4 | 1.4726(11) |
| N1−C1 | 1.3432(17) | N1−C2 | 1.3405(17) |
| N2−C3 | 1.3409(17) | N2−C4 | 1.3440(17) |
| C1−C2A | 1.3850(19) | C3−C4B | 1.3877(19) |
| O1W−Co1−O2W | 92.37(4) | O1W−Co1−O3W | 178.84(4) |
| O1W−Co1−O4W | 88.96(4) | O1W−Co1−N1 | 92.09(4) |
| O1W−Co1−N2 | 86.22(4) | O2W−Co1−O3W | 88.67(4) |
| O2W−Co1−O4W | 178.65(4) | O2W−Co1−N1 | 92.98(4) |
| O2W−Co1−N2 | 85.71(4) | O3W−Co1−O4W | 90.00(4) |

| | | | |
|---|---|---|---|
| O3W−Co1−N1 | 87.33(4) | O3W−Co1−N2 | 94.38(4) |
| O4W−Co1−N1 | 86.73(4) | O3W−Co1−N2 | 94.38(4) |
| O4W−Co1−N1 | 86.73(4) | O4W−Co1−N2 | 94.62(4) |
| N1−Co1−N2 | 177.82(4) | O1−S1−O3 | 108.11(6) |
| O1−S1−O4 | 110.43(6) | O2−S1−O3 | 109.38(6) |
| O2−S1−O4 | 108.92(6) | O3−S1−O4 | 108.78(6) |
| O1−S1−O2 | 111.18(6) | Co1−N1−C1 | 119.19(9) |
| Co1−N1−C2 | 124.21(9) | C1−N1−C2 | 116.60(11) |
| C3−N2−C4 | 116.52(11) | Co1−N2−C4 | 117.92(9) |
| Co1−N2−C3 | 125.56(9) | N1−C1−C2A | 121.34(12) |
| N1−C2−C1A | 122.06(12) | N2−C3−C4B | 121.80(12) |
| N2−C4−C3B | 121.68(12) | | |

Symmetry transformations of RTP used to generate equivalent atoms: A = -x, 1-y, 1-z; B = -1-x, y, 1/2-z; C = 1/2-x, 3/2-y, 1-z.

Symmetry transformations of LTP used to generate equivalent atoms: A = -x, 1-y, -z; B = 1-x, -y, -z.

Table S2 Hydrogen bonds for compound **1** at 296 K and 100 K.

| **296 K** | | | | |
|---|---|---|---|---|
| D−H···A | d(D−H) | d(H···A) | d(D···A) | ∠(DHA) |
| O1W−H1WB···O2 | 0.86 | 1.93 | 2.709(6) | 151 |
| O1W−H1WB···O4[a] | 0.86 | 2 | 2.709(7) | 139 |
| O1W−H1WA···O3W[b] | 0.86 | 1.93 | 2.780(3) | 170 |
| O2W−H2WA···O3W | 0.86 | 1.96 | 2.717(4) | 145 |
| O2W−H2WB···O3[c] | 0.87 | 1.75 | 2.593(4) | 162 |
| O3W−H3WB···O1[d] | 0.79 | 1.86 | 2.630(9) | 164 |
| O3W−H3WB···O2[e] | 0.79 | 2.05 | 2.759(7) | 149 |
| O3W−H3WA···O1[f] | 0.95 | 1.86 | 2.812(8) | 177 |
| O3W−H3WA···O4[g] | 0.95 | 2.11 | 2.949(8) | 147 |
| **100 K** | | | | |
| O1W−H1WB···O2[a] | 0.82 | 1.9 | 2.7013(13) | 165 |
| O1W−H1WA···O5W[b] | 0.79 | 1.98 | 2.7641(13) | 175 |
| O2W−H2WB···O6W[c] | 0.82 | 1.93 | 2.7063(14) | 158 |
| O2W−H2WA···O3[c] | 0.8 | 1.82 | 2.6156(14) | 168 |
| O3W−H3WB···O6W | 0.82 | 1.96 | 2.7797(13) | 174 |
| O3W−H3WA···O4 | 0.8 | 1.92 | 2.7149(14) | 175 |
| O4W−H4WB···O5W[d] | 0.82 | 1.91 | 2.7178(14) | 170 |
| O4W H4WA···O3[e] | 0.74 | 1.9 | 2.6271(13) | 173 |
| O5W−H5WB···O1[f] | 0.83 | 1.82 | 2.6532(14) | 173 |
| O5W−H5WA···O2[g] | 0.82 | 2.02 | 2.8302(14) | 168 |
| O6W−H6WB···O1[c] | 0.82 | 1.99 | 2.8120(14) | 177 |
| O6W−H6WA···O4[h] | 0.84 | 1.9 | 2.7162(14) | 161 |
| C3−H3A···O3[e] | 0.93 | 2.58 | 3.1953(17) | 124 |

Symmetry transformations(296 K): a = -1-x, y, 1/2-z; b = -1/2+x, 1/2+y, z; c = 1/2+x, -1/2+y, z; d = 1+x, y, z; e = -x, y, 1/2-z; f = -x, 1-y, 1-z; g = 1+x, 1-y, 1/2+z.

Symmetry transformations(100 K): a = -1+x, 1/2-y, -1/2+z; b =x, 1/2-y, -1/2+z; c = 1-x, 1-y, -z; d = -x, -1/2+y, 1/2-z; e = 1-x, -1/2+y, 1/2-z; f = 1-x, 1/2+y, 1/2-z; g = 1-x, 1-y, 1-z; h = 1-x, 1/2+y, 1/2-z.

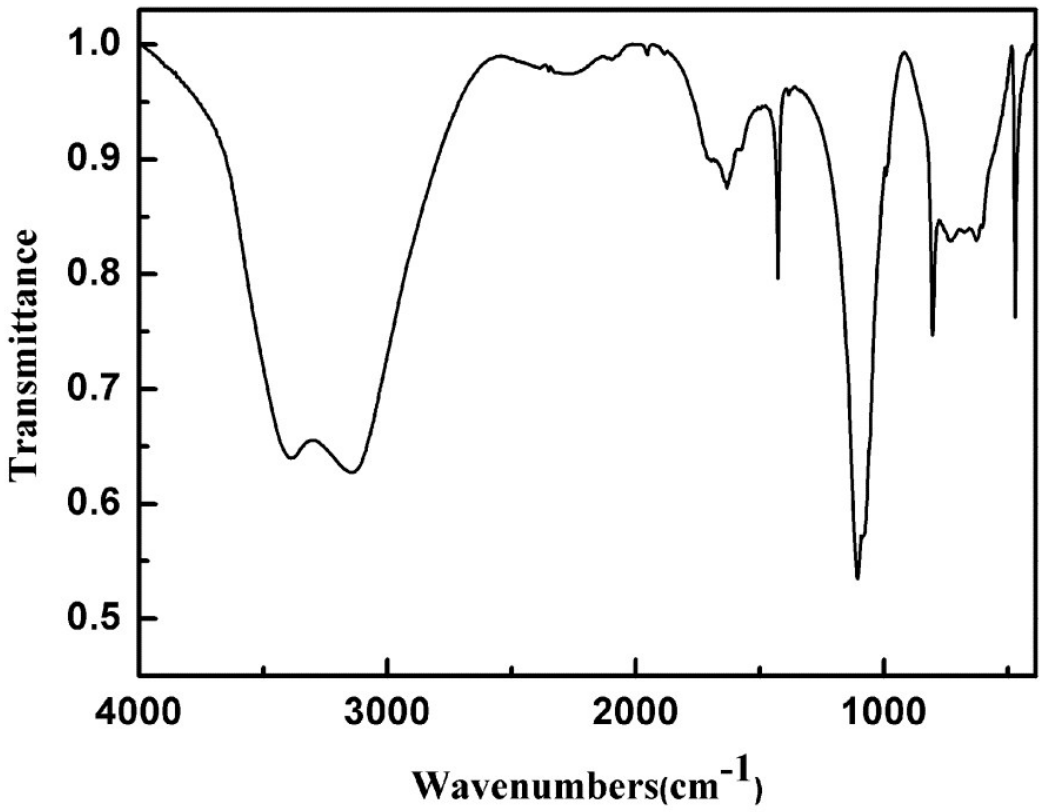


Figure S1 IR spectrum of compound **1.**

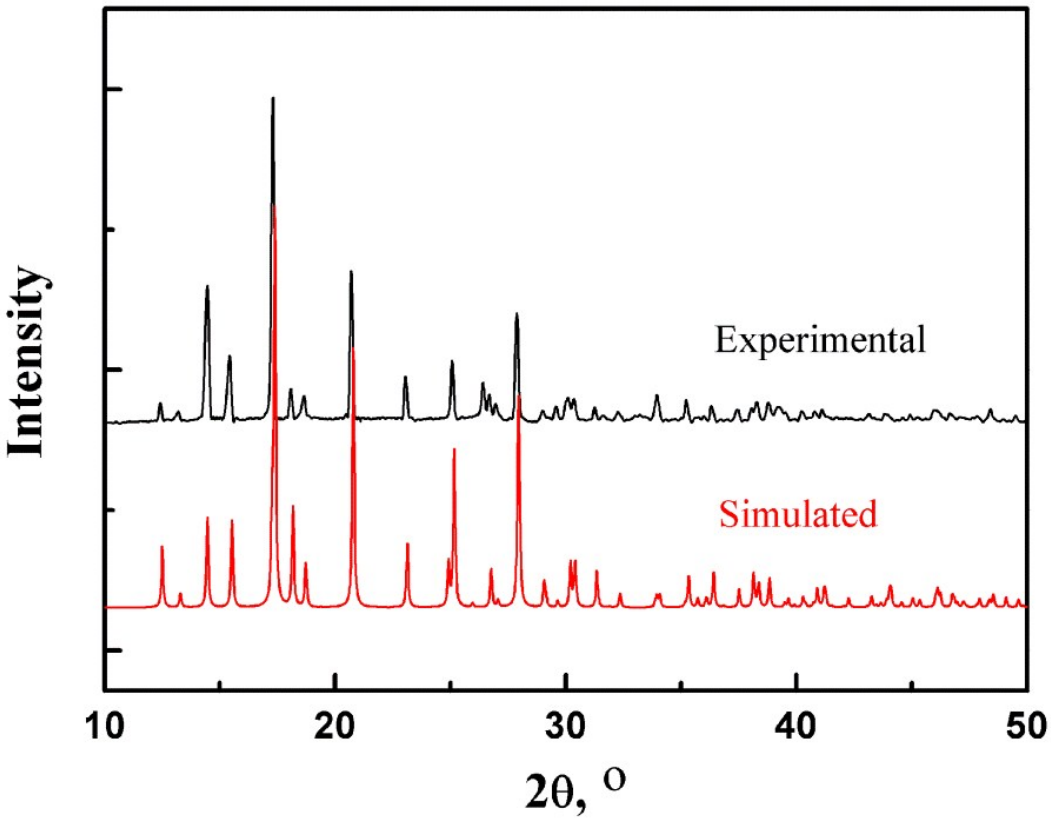


Figure S2 PXRD pattern of compound **1**.

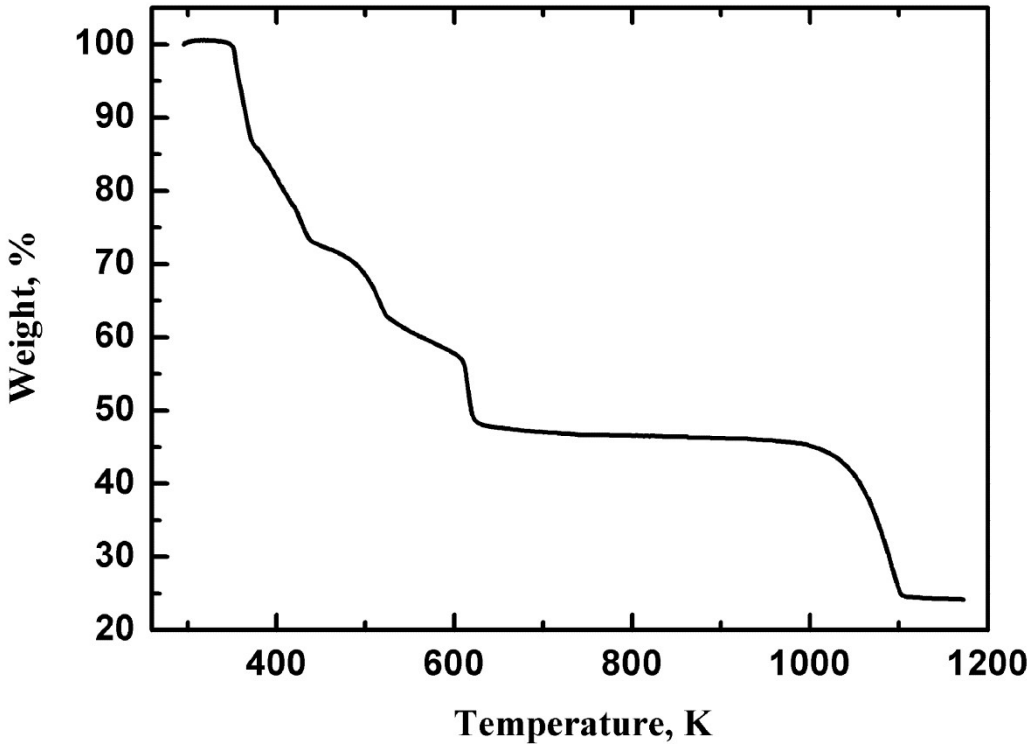


Figure S3 The TG curves of compound **1** in flowing air with a heating rate of 10 K/min.

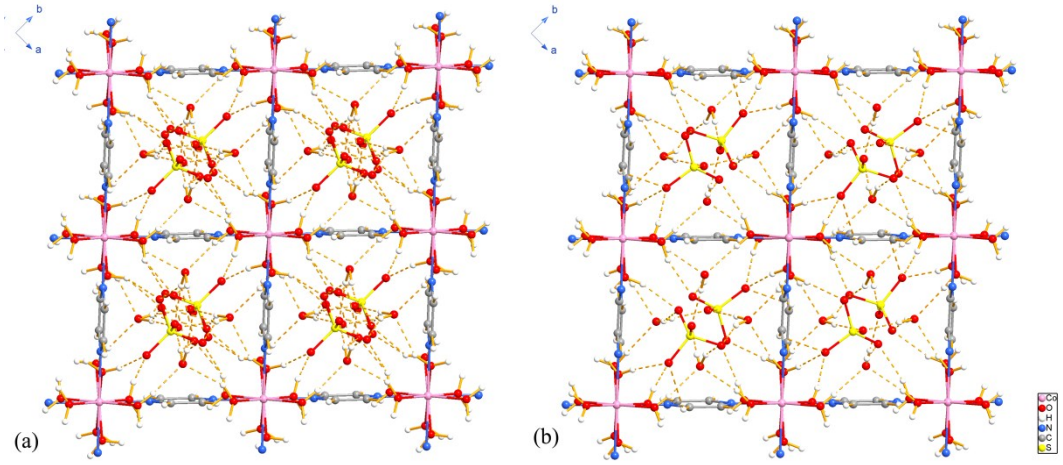


Figure S4 The packing diagrams of compound **1** at (a) 296 K and (b) 100K.