# Supporting Information

## Evaluation of Structural Transformation in 2D Metal–Organic Frameworks Based on 4,4'-Sulfonyldibenzoate Linker: Microwave-Assisted Solvothermal Synthesis, Characterization and Applications

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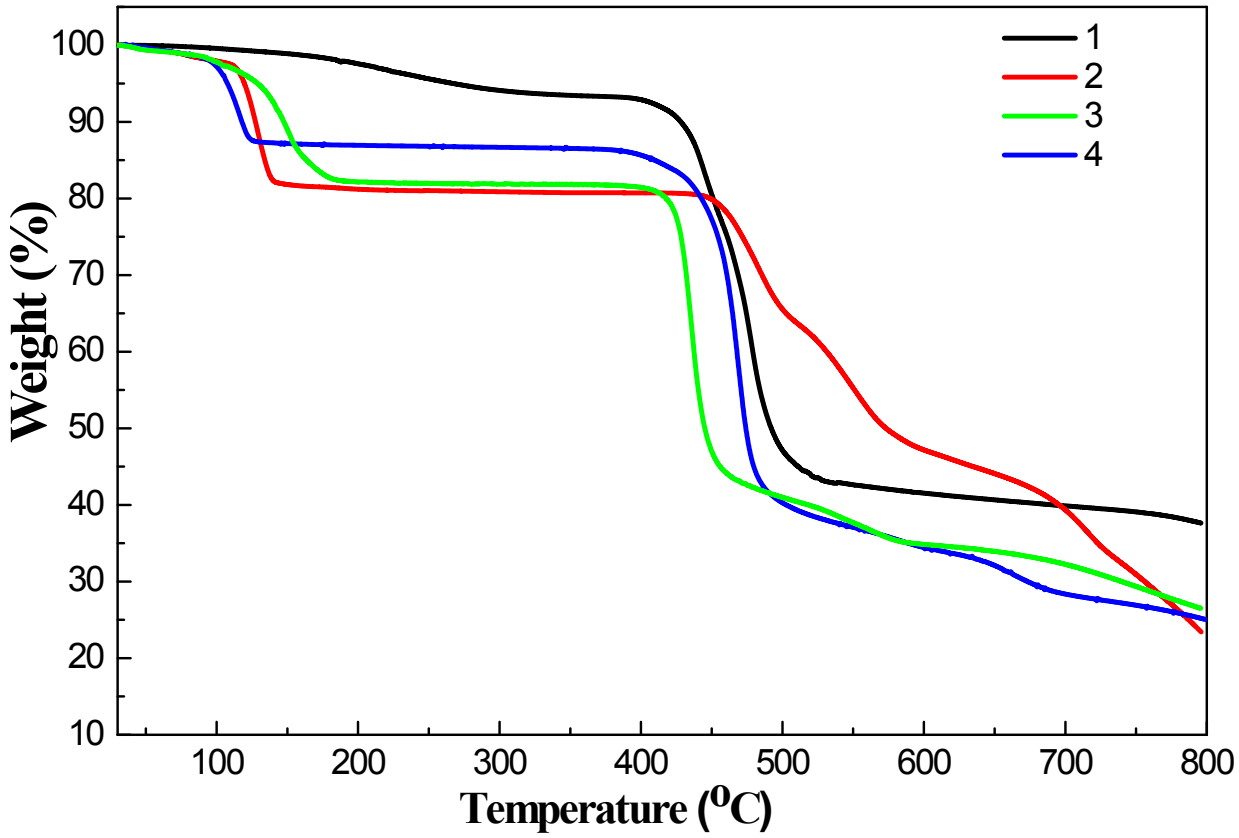


Figure S1. The TGA curves for the compounds **1**-**4**.

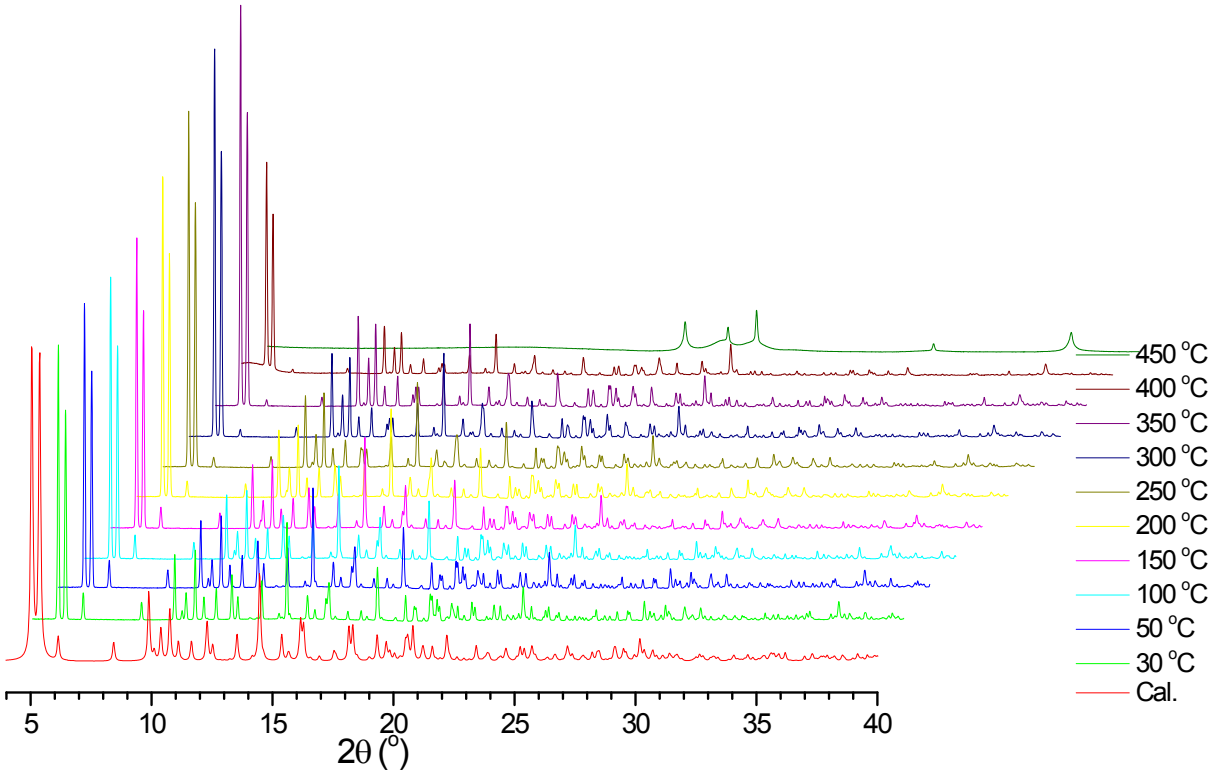


Figure S2. Varied temperatures powder XRD patterns of **1**.

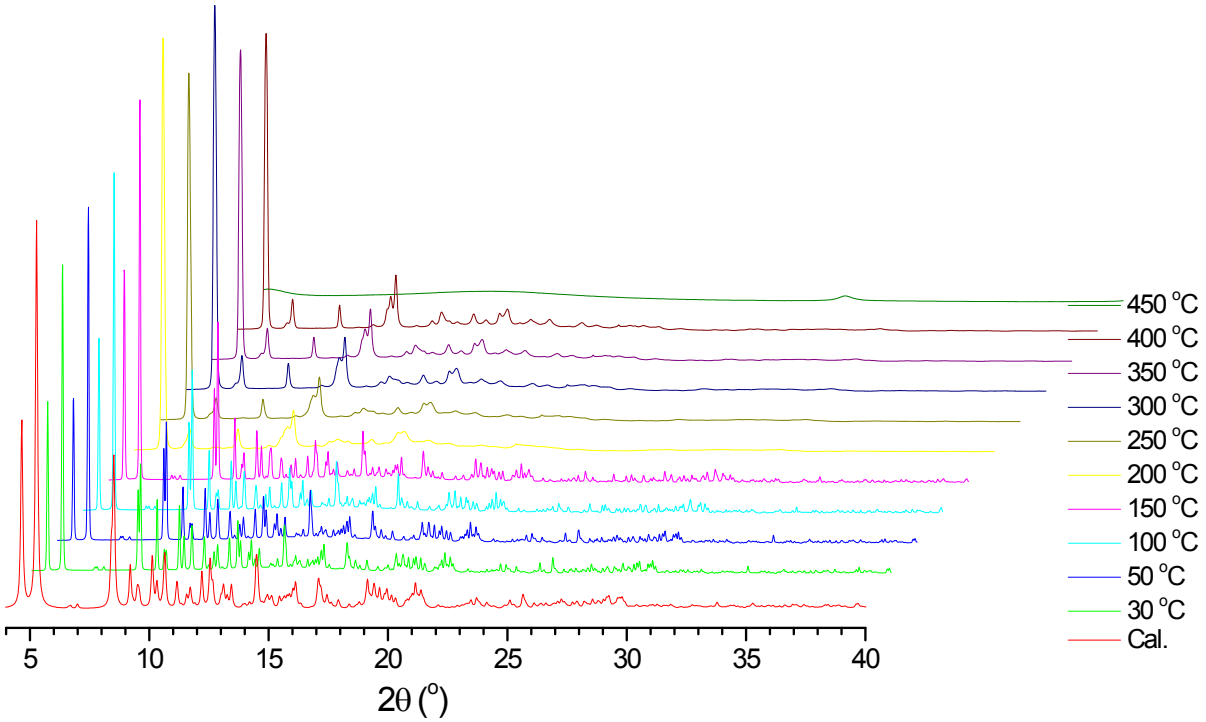


Figure S3. Varied temperatures powder XRD patterns of **2**.

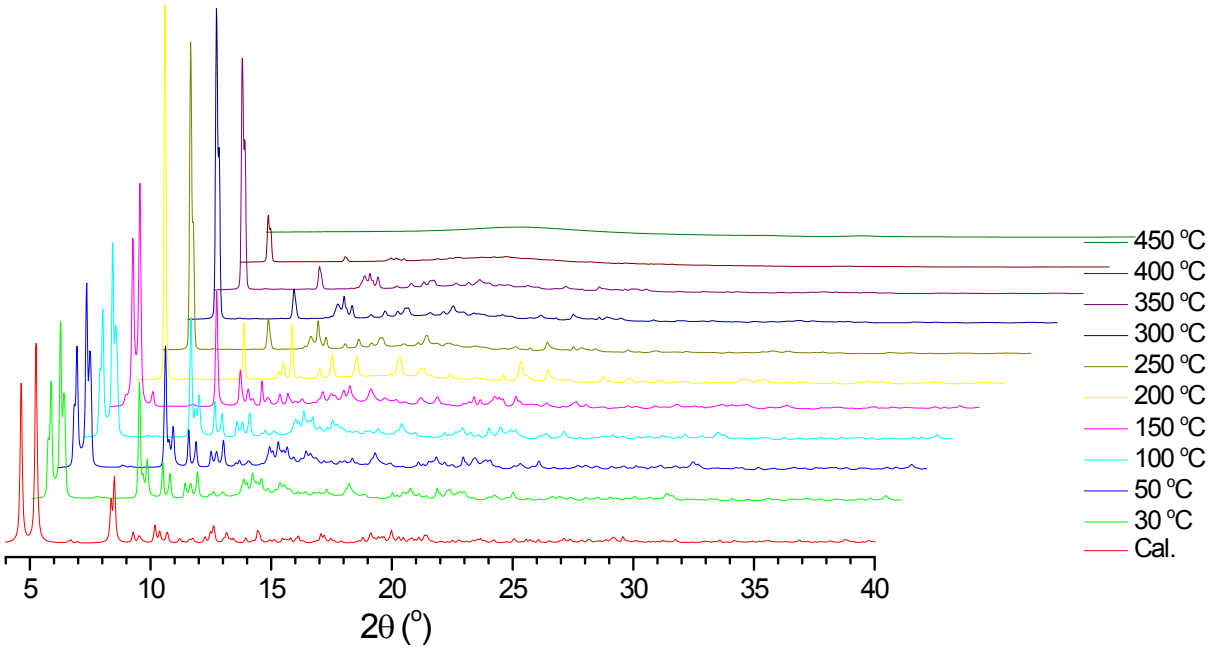


Figure S4. Varied temperatures powder XRD patterns of **3**.

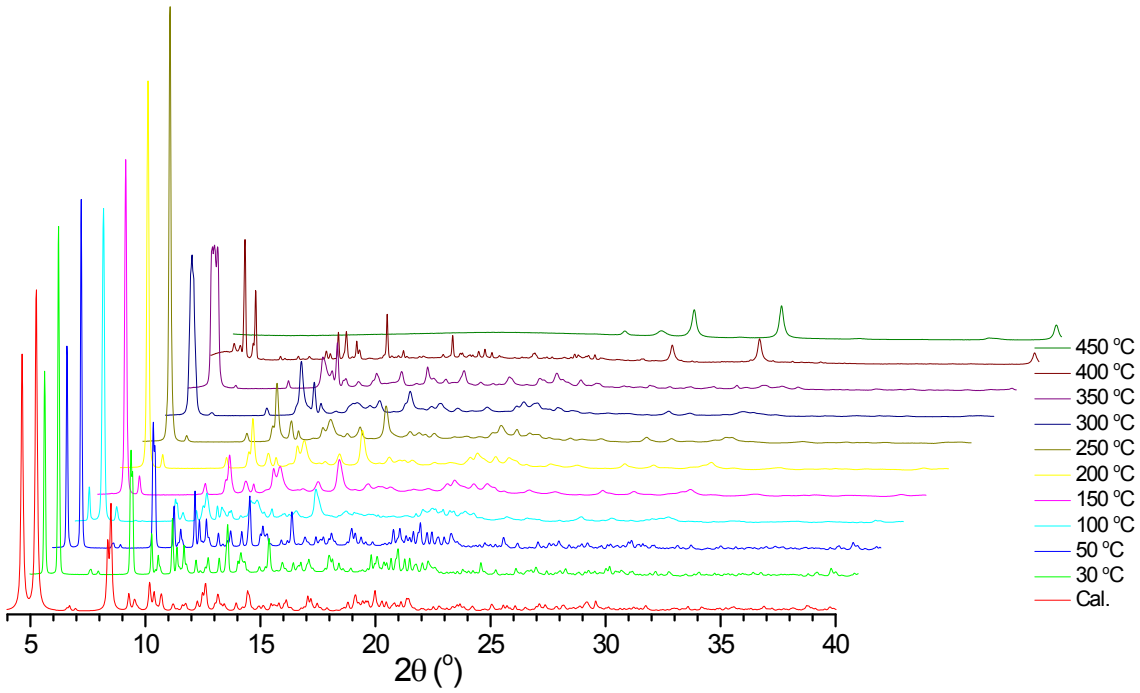


Figure S5. Varied temperatures powder XRD patterns of **4**.

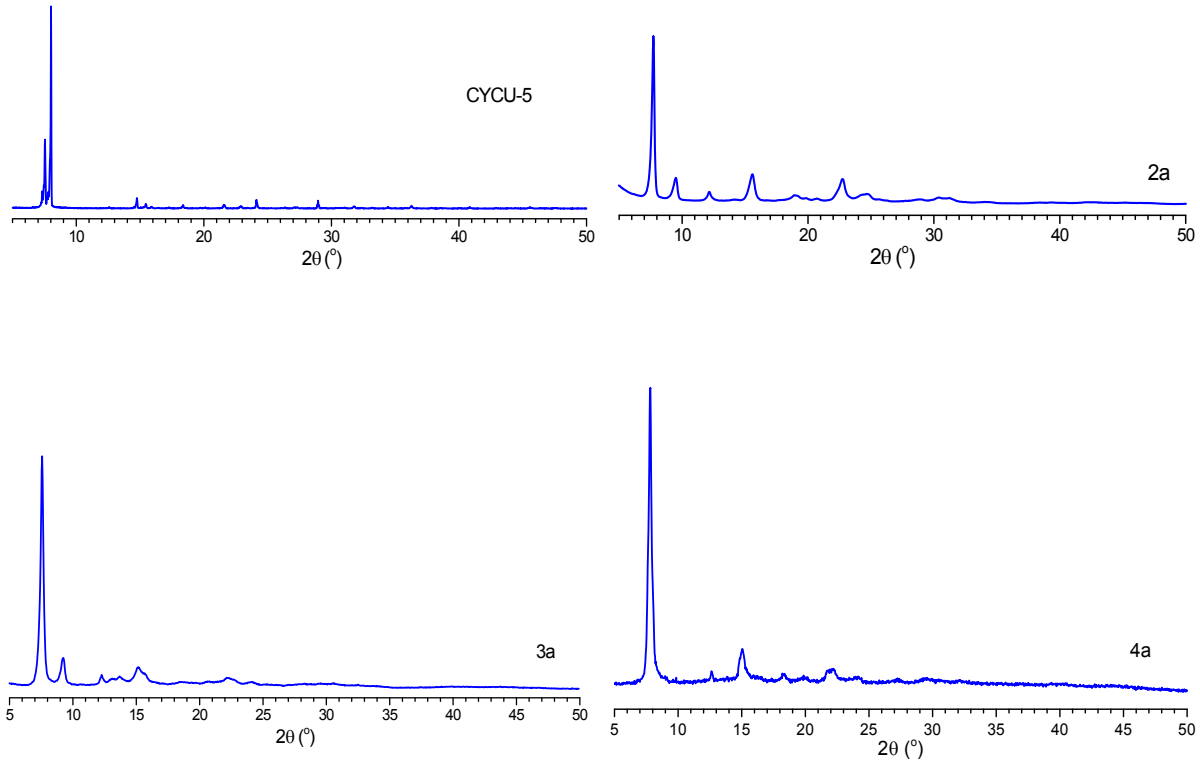


Figure S6. Powder XRD patterns of the samples after gas sorption measurements.

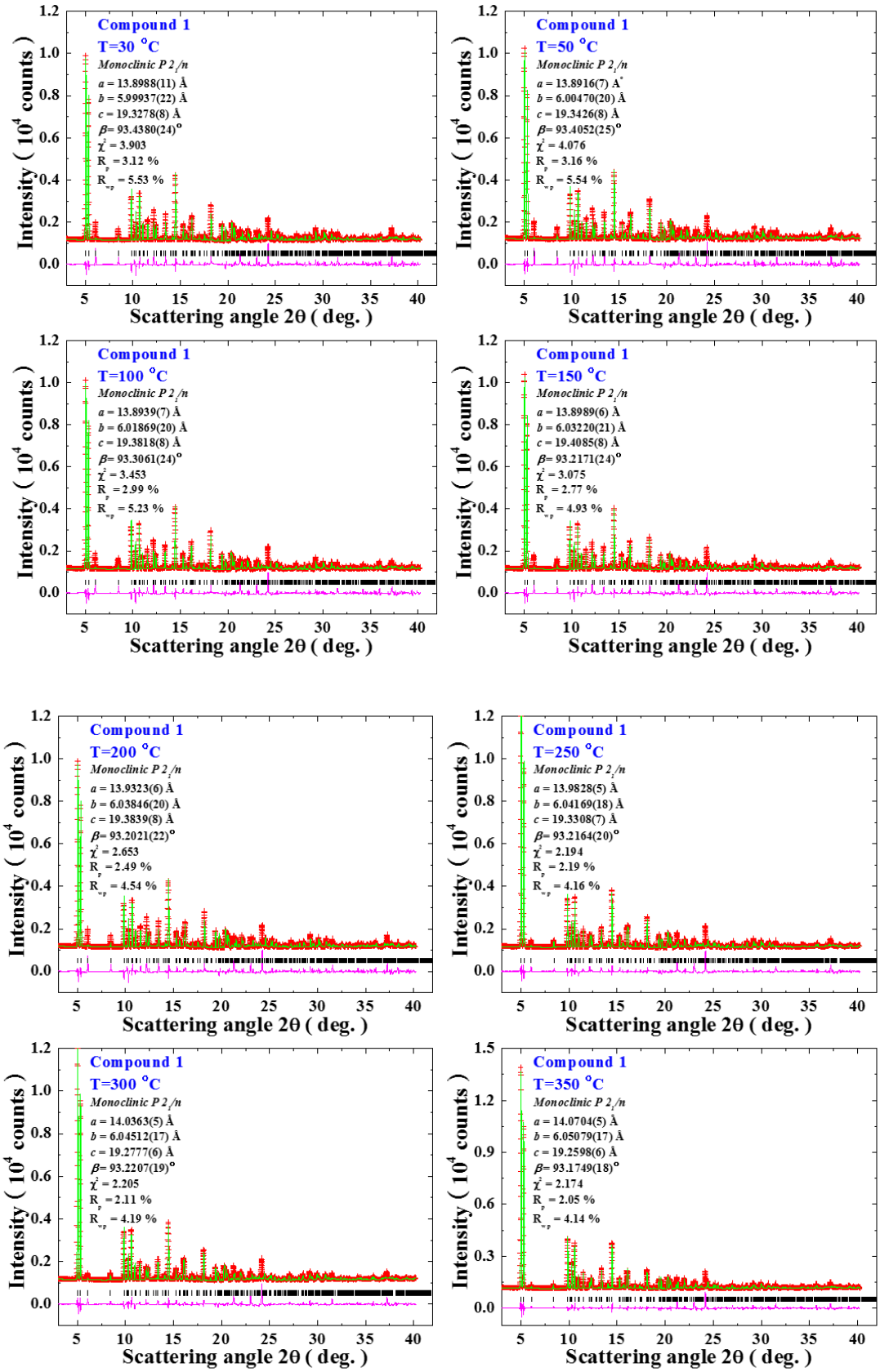


Figure S7-1. Rietveld profile fits to synchrotron powder X-ray data for **1** as a function of temperature. The measured values are in red, the calculated intensity is in green and the difference plot is in pink color.

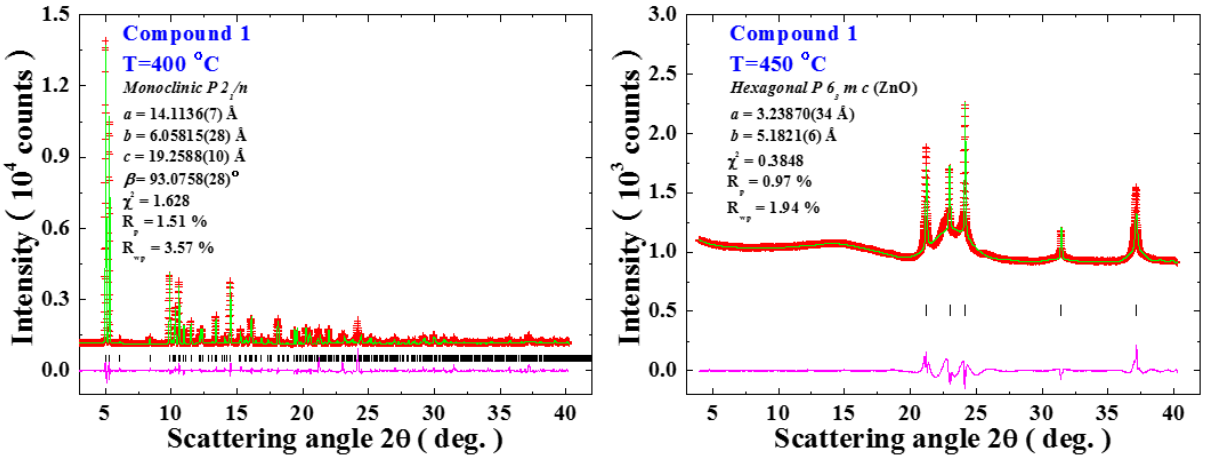


Figure S7-2. Rietveld profile fits to synchrotron powder X-ray data for **1** as a function of temperature. The measured values are in red, the calculated intensity is in green and the difference plot is in pink color.

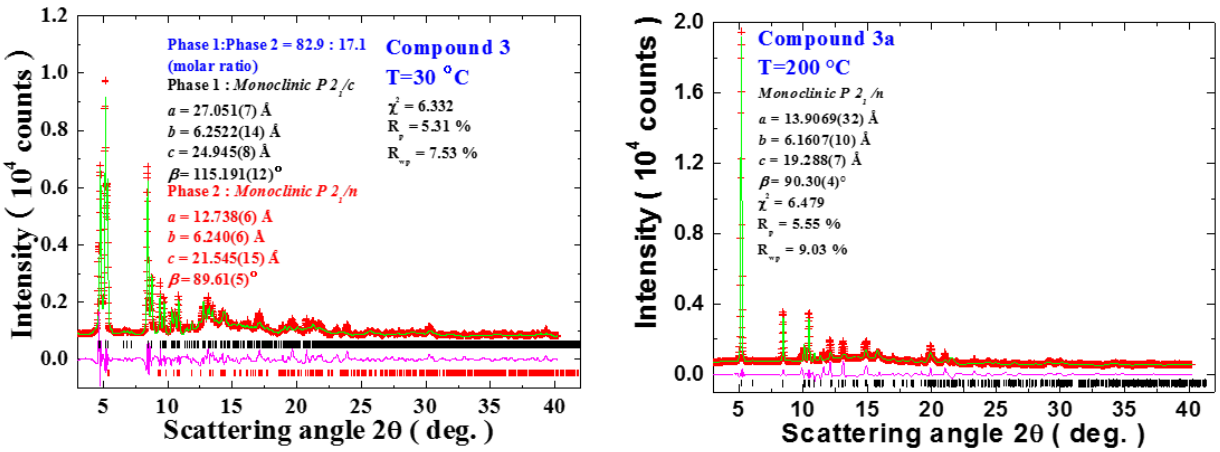


Figure S8. Rietveld profile fits to synchrotron powder X-ray data for **3** at 303 and 473 K. The measured values are in red, the calculated intensity is in green and the difference plot is in pink color.

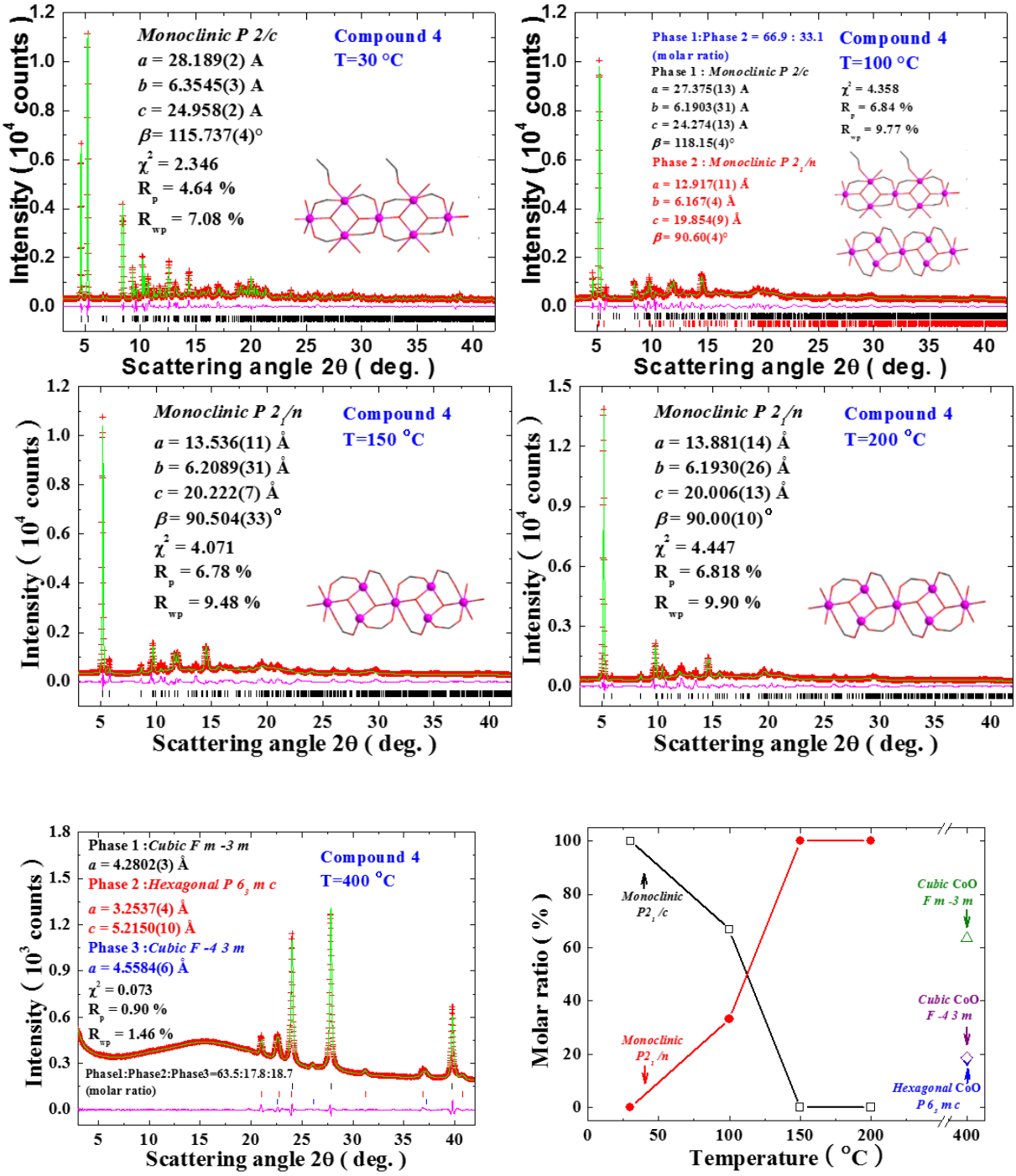


Figure S9. Rietveld profile fits to synchrotron powder X-ray data for **4** as a function of temperature. The measured values are in red, the calculated intensity is in green and the difference plot is in pink color.

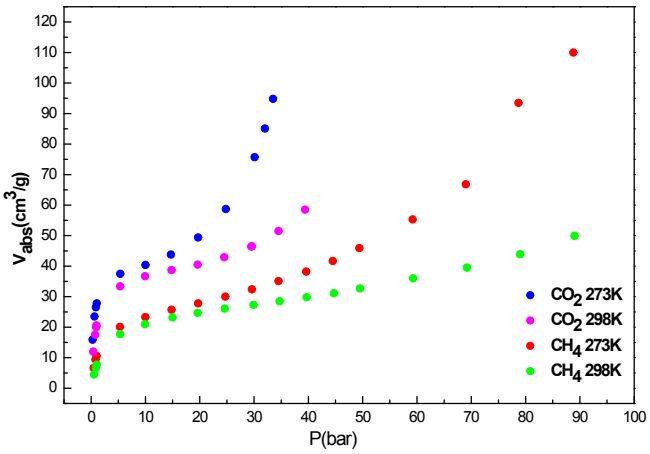


Figure S10. The high pressure $CO_2$ and $CH_4$ adsorption isotherms of **CYCU-5** at 273 and 298 K.

**Table S1**. Selected bond lengths (Å).

| | | | |
|---|---|---|---|
| | | **1** | |
| Zn(1)-O(7)#1 | 2.027(3) | Zn(1)-O(7) | 2.027(3) |
| Zn(1)-O(2) | 2.080(3) | Zn(1)-O(2)#1 | 2.080(3) |
| Zn(1)-O(3) | 2.170(3) | Zn(1)-O(3)#1 | 2.170(3) |
| Zn(2)-O(4) | 1.909(3) | Zn(2)-O(1) | 1.927(3) |
| Zn(2)-O(7) | 1.965(3) | Zn(2)-O(7)#2 | 2.003(3) |
| | | **CYCU-5** | |
| Zn(1)-O(1) | 2.032(15) | Zn(1)-O(1)#1 | 2.032(15) |
| Zn(1)-O(7)#2 | 2.080(14) | Zn(1)-O(7)#3 | 2.080(14) |
| Zn(1)-O(3)#4 | 2.180(16) | Zn(1)-O(3)#5 | 2.180(16) |
| Zn(2)-O(2) | 1.904(16) | Zn(2)-O(6)#2 | 1.918(15) |
| Zn(2)-O(1) | 1.971(14) | Zn(2)-O(1)#4 | 2.002(15) |
| | | **2** | |
| Mg(1)-O(1) | 2.054(2) | Mg(1)-O(2) | 2.063(2) |
| Mg(1)-O(5) | 2.079(2) | Mg(1)-O(4) | 2.095(2) |
| Mg(1)-O(3) | 2.115(2) | Mg(1)-O(6) | 2.124(2) |
| Mg(2)-O(1) | 2.049(2) | Mg(2)-O(2) | 2.057(2) |
| Mg(2)-O(9) | 2.083 (2) | Mg(2)-O(8) | 2.090(2) |
| Mg(2)-O(10) | 2.099(2) | Mg(2)-O(7) | 2.109(2) |
| Mg(3)-O(2) | 2.057(2) | Mg(3)-O(2) | 2.058(1) |
| Mg(3)-O(12) | 2.077(2) | Mg(3)-O(4) | 2.087(11) |
| Mg(3)-O(13) | 2.109(2) | Mg(3)-O(6) | 2.119(14) |
| | | **5** | |
| Mn(1)-O(3) | 2.085(3) | Mn(1)-O(4)#1 | 2.109(3) |
| Mn(1)-O(1S) | 2.166(3) | Mn(1)-O(1)#1 | 2.178(2) |
| Mn(1)-O(2) | 2.239(3) | Mn(1)-O(1) | 2.369(3) |
| | | **6** | |
| Mn(1)-O(1)#1 | 2.126(2) | Mn(1)-O(2) | 2.162(2) |
| Mn(1)-O(4)#2 | 2.166(2) | Mn(1)-O(3)#3 | 2.195(2) |
| Mn(1)-O(1S) | 2.198(3) | Mn(1)-O(3)#4 | 2.284(2) |

Symmetry transformations used to generate equivalent atoms: for **1** #1 -x+1,-y+1,-z+1, #2 -x+1,-y+2,-z+1; for **CYCU-5**, #1 -x+1,-y+1,-z+1, #2 -x,-y+2,-z+1, #3 x+1,y-1,z, #4 -x+1,-y+2,-z+1, #5 x,y-1,z; for **5**, #1 -x+3/2,y-1/2,-z+1/2, #2 -x+1/2,y-1/2,-z+1/2; for **6**, #1 -x+1,-y+1,-z, #2 x-1,y-1,z-1, #3 -x+2,-y+2,-z+1, #4 x,y-1,z-1;.

**Table S2.** Hydrogen Bonding Distance (Å) and Angle (°) Data.

| D — H ··· A | d(H···A) | d(D···A) | ∠DHA | Symmetry Code |
|---|---|---|---|---|
| | | **1** | | |
| O(7)-H(7)...O(6)# | 1.98 | 2.815(4) | 155.8 | x+1/2,-y+3/2,z-1/2 |
| | | **CYCU-5** | | |
| O(7)-H(7)...O(6)# | 2.00 | 2.851(2) | 157.0 | x+1/2,-y+3/2,z-1/2 |
| | | **2** | | |
| O(3)-H(3B)...O(18) | 2.06 | 2.894(3) | 168.1 | -x+2,-y,-z+1 |
| O(3)-H(3C)...O(9) | 1.92 | 2.760(3) | 167.1 | x,y-1,z |
| O(6)-H(6B)...O(17) | 2.32 | 3.070(3) | 148.1 | -x+2,-y,-z+1 |
| O(6)-H(6C)...O(8) | 2.00 | 2.832(3) | 165.5 | |
| O(13)-H(13B)...O(16) | 2.09 | 2.860(3) | 150.1 | -x+1,-y,-z+1 |
| O(13)-H(13C)...O(10) | 1.92 | 2.758(3) | 168.3 | x,y-1,z |
| O(14)-H(14A)...O(7) | 2.09 | 2.722(3) | 130.6 | |
| O(1W)-H(1WA)...O(11) | 2.20 | 2.758(9) | 123.5 | |
| O(1W)-H(1WB)...O(3W) | 2.37 | 3.175(13) | 158.8 | x,y-1,z |
| O(2W)-H(2WA)...O(12) | 2.28 | 2.906(11) | 130.5 | |
| O(2W)-H(2WB)...O(4W) | 2.26 | 3.11(2) | 173.8 | |

**Table S3.** TGA weight loss data for the compounds **1**-**4**.

| Compound | Weight loss | |
|---|---|---|
| | Observed | Calculated |
| **1** | 6% at 300 ºC | 5.2% for EtOH |
| **2** | 18.1% at150 ºC | 16.8% for 6.5$H_2O$ and EtOH |
| **3** | 17.8% at 190 ºC | 15.4% for 6.5$H_2O$ and EtOH |
| **4** | 12.8% at 140 ºC | 15.3% for 6.5$H_2O$ and EtOH |

**Table S4-1**. Crystallographic details of **1** as a function of temperature, as determined from synchrotron powder X-Ray data.

| | **1**-303K | **1**-323K | **1**-373K | **1**-423K |
|---|---|---|---|---|
| Chemical formula | $C_{28}H_{18}Zn_3O_{14}S_2$ | $C_{28}H_{18}Zn_3O_{14}S_2$ | $C_{28}H_{18}Zn_3O_{14}S_2$ | $C_{28}H_{18}Zn_3O_{14}S_2$ |
| Formula weight | 833.8 | 833.8 | 833.8 | 833.8 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Temperature (K) | 303 | 323 | 373 | 423 |
| Space group | $P2_1/n$ | $P2_1/n$ | $P2_1/n$ | $P2_1/n$ |
| $a$ (Å) | 13.8988(11) | 13.8916(7) | 13.8939(7) | 13.8989(6) |
| $b$ (Å) | 5.9994(2) | 6.0047(2) | 6.0187(2) | 6.0322(2) |
| $c$ (Å) | 19.3278(8) | 19.3426(8) | 19.3818(8) | 19.4085(8) |
| $\beta$ (°) | 93.4380(24) | 93.4052(25) | 93.3061(24) | 93.2171(24) |
| $V$ (Å$^3$) | 1608.73(1) | 1610.61(1) | 1618.07(1) | 1624.66(1) |
| $Z$ | 2 | 2 | 2 | 2 |
| Radiation (Å) | 1.0332 | 1.0332 | 1.0332 | 1.0332 |
| $\chi^2$ | 3.903 | 4.076 | 3.453 | 3.075 |
| $R_p$ (%) | 3.12 | 3.16 | 2.99 | 2.77 |
| $R_{wp}$ (%) | 5.53 | 5.54 | 5.23 | 4.93 |

**Table S4-2**. Crystallographic details of **1** as a function of temperature, as determined from synchrotron powder X-Ray data.

| | **1**-473K | **1**-523K | **1**-573K | **1**-623K | **1**-673K |
|---|---|---|---|---|---|
| Chemical formula | $C_{28}H_{18}Zn_3O_{14}S_2$ | $C_{28}H_{18}Zn_3O_{14}S_2$ | $C_{28}H_{18}Zn_3O_{14}S_2$ | $C_{28}H_{18}Zn_3O_{14}S_2$ | $C_{28}H_{18}Zn_3O_{14}S_2$ |
| Formula weight | 833.8 | 833.8 | 833.8 | 833.8 | 833.8 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Temperature (K) | 473 | 523 | 573 | 623 | 673 |
| Space group | $P2_1/n$ | $P2_1/n$ | $P2_1/n$ | $P2_1/n$ | $P2_1/n$ |
| $a$ (Å) | 13.9323(6) | 13.9828(5) | 14.0363(5) | 14.0704(5) | 14.1136(7) |
| $b$ (Å) | 6.0385(2) | 6.0417(2) | 6.0451(2) | 6.0508(2) | 6.0582(2) |
| $c$ (Å) | 19.3839(8) | 19.3308(7) | 19.2777(6) | 19.2598(6) | 19.2588(10) |
| $\beta$ (°) | 93.2021(22) | 93.2164(20) | 93.2207(19) | 93.1749(18) | 93.0758(28) |
| $V$ (Å$^3$) | 1628.22(1) | 1630.49(1) | 1633.14(1) | 1637.2(1) | 1644.3(1) |
| $Z$ | 2 | 2 | 2 | 2 | 2 |
| Radiation (Å) | 1.0332 | 1.0332 | 1.0332 | 1.0332 | 1.0332 |
| $\chi^2$ | 2.653 | 2.194 | 2.205 | 2.174 | 1.618 |
| $R_p$ (%) | 2.49 | 2.19 | 2.11 | 2.05 | 1.51 |
| $R_{wp}$ (%) | 4.54 | 4.16 | 4.19 | 4.14 | 3.57 |

**Table S5**. Crystallographic details of **4** as a function of temperature, as determined from synchrotron powder X-Ray data.

| | **4**-303K | **4**-373K (67 %) | **4**-373K (33 %) | **4**-423K | **4**-473K |
|---|---|---|---|---|---|
| Chemical formula | $C_{30}H_{29}Co_3O_{18}S_2$ | $C_{28}H_{18}Mg_3O_{14}S_2$ | $C_{28}H_{18}Mg_3O_{14}S_2$ | $C_{28}H_{18}Ni_3O_{14}S_2$ | $C_{28}H_{18}Co_3O_{14}S_2$ |
| Formula weight | 917.88 | 917.88 | 818.8 | 818.8 | 818.8 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Temperature (K) | 303 | 373 | 373 | 423 | 473 |
| Space group | *P2/c* | *P2/c* | $P2_1/n$ | $P2_1/n$ | $P2_1/n$ |
| *a* (Å) | 28.1888(19) | 27.375(13) | 12.917(11) | 13.536(11) | 13.881(14) |
| *b* (Å) | 6.3545(3) | 6.1903(31) | 6.167(4) | 6.2089(31) | 6.1930(26) |
| *c* (Å) | 24.9584(15) | 24.274(13) | 19.854(9) | 20.222(7) | 20.006(13) |
| $\beta$ (°) | 115.737(4) | 118.15(4) | 90.60(4) | 90.504(33) | 90.0(1) |
| *V* (Å$^3$) | 4027.2(4) | 3626.9(34) | 1581.5(18) | 1699.5(17) | 1719.82(219) |
| *Z* | 4 | 4 | 2 | 2 | 2 |
| Radiation (Å) | 1.0332 | 1.0332 | 1.0332 | 1.0332 | 1.0332 |
| $\chi^2$ | 2.346 | 4.358 | 4.358 | 4.071 | 4.447 |
| $R_p$ (%) | 4.64 | 6.84 | 6.84 | 6.78 | 6.818 |
| $R_{wp}$ (%) | 7.08 | 9.77 | 9.77 | 9.48 | 9.90 |

Table S6. Selective bond length and distance of **1** as a function of temperature, as determined from synchrotron powder X-Ray data.

| | 303K | 323K | 423K | 473K | 523K | 623K |
|---|---|---|---|---|---|---|
| Zn1—O1 | 2.0189 | 2.0205 | 2.0292 | 2.0307 | 2.0310 | 2.0328 |
| Zn1—O1 | 2.0189 | 2.0205 | 2.0292 | 2.0307 | 2.0310 | 2.0328 |
| Zn1—O7$^{i}$ | 2.0571 | 2.0569 | 2.0582 | 2.0593 | 2.0605 | 2.0628 |
| Zn1—O7 | 2.0571 | 2.0569 | 2.0582 | 2.0593 | 2.0605 | 2.0628 |
| Zn1—O3$^{ii}$ | 2.1627 | 2.1634 | 2.1710 | 2.1730 | 2.1746 | 2.1798 |
| Zn1—O3 | 2.1627 | 2.1634 | 2.1710 | 2.1730 | 2.1746 | 2.1798 |
| Zn2···Zn2 | 2.8577 | 2.8569 | 2.8615 | 2.8679 | 2.8770 | 2.8938 |
| **Zn2—O2** | **1.8949** | **1.8963** | **1.9045** | **1.9044** | **1.9025** | **1.9016** |
| Zn2—O1 | 1.9474 | 1.9471 | 1.9498 | 1.9534 | 1.9583 | 1.9670 |
| Zn2—O1 | 1.9894 | 1.9906 | 1.9984 | 2.0003 | 2.0014 | 2.0052 |
| Zn2—O6 | 1.8963 | 1.8961 | 1.8978 | 1.8993 | 1.9012 | 1.9047 |
| S1—O5 | 1.4212 | 1.4225 | 1.429 | 1.4305 | 1.4312 | 1.4333 |
| **S1—O4** | **1.4319** | **1.4331** | **1.439** | **1.4384** | **1.436** | **1.4334** |
| S1—C5 | 1.7486 | 1.7486 | 1.7533 | 1.7563 | 1.7600 | 1.7677 |
| S1—C8 | 1.7555 | 1.7554 | 1.7566 | 1.7576 | 1.7588 | 1.7610 |
| O2—C1 | 1.2599 | 1.2610 | 1.2667 | 1.2680 | 1.2687 | 1.2706 |
| **O1···O4** | **2.8313** | **2.8331** | **2.8415** | **2.8387** | **2.8326** | **2.8243** |

Symmetry codes: (i) $x+1, y-1, z$; (ii) $x, y-1, z$.

Table S7. Selective bond length and distance of **3** and **4** as a function of temperature, as determined from synchrotron powder X-Ray data.

| | **2**-473K | **3**-303K | **3**-473K | **4**-373K | **4**-423K | **4**-473K |
|---|---|---|---|---|---|---|
| M1—O1 | 2.0317(15) | 2.1127(16) | 2.0614(3) | 2.0698(12) | 2.0875(9) | 2.0797(8) |
| M1—O1 | 2.0317(15) | 2.1127(16) | 2.0614(3) | 2.0698(12) | 2.0875(9) | 2.0797(8) |
| M1—O7$^{i}$ | 1.9972(17) | 2.0346(12) | 2.0090(7) | 1.9744(11) | 2.0329(10) | 2.0375(20) |
| M1—O7 | 1.9972(17) | 2.0346(12) | 2.0090(7) | 1.9744(11) | 2.0329(10) | 2.0375(20) |
| M1—O3$^{ii}$ | 2.2540(21) | 2.2557(13) | 2.2225(9) | 2.1598(13) | 2.2341(12) | 2.2624(24) |
| M1—O3 | 2.2540(21) | 2.2557(13) | 2.2225(9) | 2.1598(13) | 2.2341(12) | 2.2624(24) |
| M2···M2 | 2.985(4) | 2.7151(14) | 2.9003(8) | 2.7136(22) | 2.8377(22) | 2.9076(30) |
| **M2—O2** | **1.9288(13)** | **2.0642(11)** | **1.9392(6)** | **1.9457(8)** | **1.9883(7)** | **1.9881(15)** |
| M2—O1 | 1.9729(20) | 1.8541(8) | 1.9487(4) | 1.8621(11) | 1.9235(11) | 1.9501(14) |
| M2—O1 | 2.0517(14) | 2.0792(10) | 2.0440(5) | 2.0110(9) | 2.0588(8) | 2.0727(15) |
| M2—O6 | 1.8586(15) | 1.8618(10) | 1.8642(6) | 1.8220(10) | 1.8748(9) | 1.8840(17) |
| S1—O5 | 1.4408(12) | 1.4790(13) | 1.4594(2) | 1.4609(9) | 1.4711(7) | 1.4673(6) |
| **S1—O4** | **1.4242(9)** | **1.5700(9)** | **1.4501(4)** | **1.4770(5)** | **1.4998(4)** | **1.4890(7)** |
| S1—C5 | 1.8308(21) | 1.7395(9) | 1.7912(6) | 1.7057(12) | 1.7722(11) | 1.8070(19) |
| S1—C8 | 1.7074(14) | 1.7354(10) | 1.7169(6) | 1.6866(9) | 1.7359(8) | 1.7401(17) |
| O2—C1 | 1.2778(10) | 1.3105(12) | 1.2938(2) | 1.2944(8) | 1.3038(6) | 1.3009(5) |
| **O1···O4** | **2.7425(22)** | **3.0913(20)** | **2.8111(9)** | **2.8798(12)** | **2.9311(9)** | **2.9013(18)** |

Symmetry codes: (i) $x+1, y-1, z$; (ii) $x, y-1, z$.

M = Mg (**2a**), Ni(**3a**), Co(**4a**).