**Supplementary Information**

# Metal-organic frameworks with pyridyl- and carboxylate-containing ligand: syntheses, structures and properties

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**Table S1.** Selected bond lengths (Å) and angles (°) for complexes **1 - 6**

| **1**[a] | | | |
|---|---|---|---|
| Mn(1)-O(31)#1 | 2.3032(17) | Mn(1)-O(51)#2 | 2.1041(18) |
| Mn(1)-O(32)#1 | 2.2609(18) | Mn(1)-O(52)#3 | 2.1014(18) |
| Mn(1)-O(2) | 2.236(2) | Mn(1)-N(11) | 2.267(2) |
| | | | |
| O(2)-Mn(1)-O(32)#1 | 84.66(7) | O(2)-Mn(1)-N(11) | 172.18(8) |
| O(2)-Mn(1)-O(51)#2 | 92.25(8) | O(32)#1-Mn(1)-O(51)#2 | 153.22(7) |
| O(2)-Mn(1)-O(52)#3 | 87.78(9) | O(32)#1-Mn(1)-O(52)#3 | 94.02(7) |
| O(2)-Mn(1)-O(31)#1 | 84.74(7) | O(52)#3-Mn(1)-N(11) | 91.00(8) |
| O(31)#1-Mn(1)-N(11) | 92.68(7) | O(32)#1-Mn(1)-N(11) | 87.72(7) |

| | | | |
|---|---|---|---|
| O(51)#2-Mn(1)-N(11) | 95.35(8) | O(31)#1-Mn(1)-O(52)#3 | 151.16(7) |
| O(51)#2-Mn(1)-O(52)#3 | 112.47(7) | O(31)#1-Mn(1)-O(32)#1 | 57.60(6) |
| O(31)#1-Mn(1)-O(51)#2 | 95.65(7) | | |

**2**[b]

| | | | |
|---|---|---|---|
| Mn(1)-O(1) | 2.1867(17) | Mn(1)-N(2)#1 | 2.2729(19) |
| Mn(1)-O(3)#2 | 2.3734(17) | Mn(1)-O(1W) | 2.1592(18) |
| Mn(1)-O(4)#2 | 2.2814(17) | Mn(1)-O(2W) | 2.1631(19) |
| | | | |
| O(1)-Mn(1)-O(1W) | 98.70(7) | O(1)-Mn(1)-O(2W) | 86.84(7) |
| O(1)-Mn(1)-O(3)#2 | 136.29(6) | O(1)-Mn(1)-O(4)#2 | 81.59(6) |
| O(1)-Mn(1)-N(2)#1 | 136.45(7) | O(1W)-Mn(1)-O(2W) | 171.53(7) |
| O(1W)-Mn(1)-O(3)#2 | 92.53(7) | O(1W)-Mn(1)-O(4)#2 | 91.63(7) |
| O(1W)-Mn(1)-N(2)#1 | 85.10(7) | O(2W)-Mn(1)-O(3)#2 | 87.78(8) |
| O(2W)-Mn(1)-O(4)#2 | 95.53(7) | O(2W)-Mn(1)-N(2)#1 | 86.48(7) |
| O(3)#2-Mn(1)-O(4)#2 | 55.85(6) | O(3)#2-Mn(1)-N(2)#1 | 86.33(6) |
| O(4)#2-Mn(1)-N(2)#1 | 141.91(7) | | |

**3**[c]

| | | | |
|---|---|---|---|
| Co(1)-O(1W) | 2.143(2) | Co(1)-O(2) | 2.056(2) |
| Co(1)-O(4)#1 | 2.014(2) | Co(1)-N(2)#2 | 2.125(3) |
| Co(1)-O(3)#3 | 2.106(2) | Co(1)-O(1) | 2.320(2) |
| | | | |
| O(4)#1-Co(1)-O(2) | 159.62(9) | O(4)#1-Co(1)-O(3)#3 | 89.79(9) |
| O(2)-Co(1)-O(3)#3 | 94.42(9) | O(4)#1-Co(1)-N(2)#2 | 106.73(9) |
| O(2)-Co(1)-N(2)#2 | 92.83(9) | O(3)#3-Co(1)-N(2)#2 | 94.39(9) |
| O(4)#1-Co(1)-O(1W) | 85.57(9) | O(2)-Co(1)-O(1W) | 88.24(9) |
| O(3)#3-Co(1)-O(1W) | 173.13(8) | N(2)#2-Co(1)-O(1W) | 91.80(10) |
| O(4)#1-Co(1)-O(1) | 100.67(8) | O(2)-Co(1)-O(1) | 59.68(8) |
| O(3)#3-Co(1)-O(1) | 87.80(9) | N(2)#2-Co(1)-O(1) | 152.51(9) |
| O(1W)-Co(1)-O(1) | 88.08(9) | | |

**4**[d]

| | | | |
|---|---|---|---|
| Co(1)-O(1) | 1.9791(18) | Co(1)-N(3) | 2.159(2) |
| Co(1)-N(2)#1 | 2.151(2) | Co(1)-O(4)#2 | 2.0001(18) |
| Co(1)-O(3)#3 | 2.0004(18) | | |
| | | | |
| O(1)-Co(1)-N(3) | 87.64(8) | O(1)-Co(1)-N(2)#1 | 87.03(8) |
| O(1)-Co(1)-O(4)#2 | 127.73(8) | O(1)-Co(1)-O(3)#3 | 111.01(8) |
| N(2)#1-Co(1)-N(3) | 172.21(8) | O(4)#2-Co(1)-N(3) | 88.66(8) |
| O(3)#3-Co(1)-N(3) | 88.19(8) | O(4)#2-Co(1)-N(2)#1 | 99.10(8) |
| O(3)#3-Co(1)-N(2)#1 | 88.41(8) | O(3)#3-Co(1)-O(4)#2 | 120.95(8) |
| | | $5^{e}$ | |
| Co(1)-O(4)#1 | 2.047(3) | Co(1)-O(1) | 2.117(2) |
| Co(1)-O(2) | 2.326(3) | Co(1)-O(1W) | 2.116(3) |
| Co(1)-N(3) | 2.101(3) | Co(1)-N(2)#2 | 2.126(3) |
| | | | |
| O(4)#1-Co(1)-N(3) | 92.20(11) | O(4)#1-Co(1)-O(1) | 109.56(9) |
| N(3)-Co(1)-O(1) | 88.67(11) | O(4)#1-Co(1)-O(1W) | 90.20(10) |
| N(3)-Co(1)-O(1W) | 175.82(10) | O(1)-Co(1)-O(1W) | 87.30(10) |
| O(4)#1-Co(1)-N(2)#2 | 96.27(10) | N(3)-Co(1)-N(2)#2 | 94.93(12) |
| O(1)-Co(1)-N(2)#2 | 153.78(11) | O(1W)-Co(1)-N(2)#2 | 88.21(11) |
| O(4)#1-Co(1)-O(2) | 168.18(8) | N(3)-Co(1)-O(2) | 87.83(10) |
| O(1)-Co(1)-O(2) | 58.63(8) | O(1W)-Co(1)-O(2) | 89.12(9) |
| N(2)#2-Co(1)-O(2) | 95.49(10) | | |
| | | $6^{f}$ | |
| Cu(1)-O(2) | 1.9550(17) | Cu(1)-O(31) | 1.9975(14) |
| Cu(1)-N(21) | 1.9617(19) | Cu(1)-N(11)#1 | 2.1438(17) |
| Cu(1)-O(51)#2 | 2.1022(15) | | |
| | | | |
| O(2)-Cu(1)-O(31) | 88.35(7) | O(2)-Cu(1)-N(21) | 175.43(7) |
| O(2)-Cu(1)-N(11)#1 | 89.66(7) | O(2)-Cu(1)-O(51)#2 | 88.60(6) |
| O(31)-Cu(1)-N(21) | 88.47(7) | O(31)-Cu(1)-N(11)#1 | 135.48(6) |

| | | | |
|---|---|---|---|
| O(31)-Cu(1)-O(51)#2 | 129.83(6) | N(11)#1-Cu(1)-N(21) | 94.91(7) |
| O(51)#2-Cu(1)-N(21) | 90.92(7) | O(51)#2-Cu(1)-N(11)#1 | 94.55(6) |

[a]Symmetry transformations used to generate equivalent atoms: #1: x+1/2, y-1/2, -z+1/2, #2: x+1/2, y+1/2, -z+1/2, #3: -x+1/2, -y+1/2, z+1/2.

[b]Symmetry transformations used to generate equivalent atoms: #1: x, y, -1+z, #2: x, -1+y, z.

[c]Symmetry transformations used to generate equivalent atoms: #1: x, 1+y, z #2: 1+x, 1+y, -1+z #3: 1-x, 1-y, 1-z.

[d]Symmetry transformations used to generate equivalent atoms: #1: -1+x ,-1+y, -1+z, #2: x, -1+y, z #3: 1-x, 1-y, -z.

[e]Symmetry transformations used to generate equivalent atoms: #1: 1-x, -1/2+y, 3/2-z #2: -1+x, y, -1+z.

[f]Symmetry transformations used to generate equivalent atoms: #1: 1+x, y, 1+z #2: 1-x, -1/2+y, 1/2-z.

Table S2 Distance [Å] and angles [°] of hydrogen bonding for complexes **1 - 6**[a]

| D-H···A | Distance (D···A) | Angle (D-H-A) |
|---|---|---|
| **1** | | |
| N(1)-H(1)···O(31)$^{\#1}$ | 2.904(3) | 157 |
| C(12)-H(5)···O(4) | 3.201(5) | 138 |
| C(16)-H(8)···O(2)$^{\#2}$ | 3.398(4) | 144 |
| C(16)-H(8)···O(52)$^{\#3}$ | 3.365(4) | 144 |
| C(23)-H(14)···O(1)$^{\#4}$ | 3.306(5) | 142 |
| **2** | | |
| N(1)-H(1)···O(4W)$^{\#5}$ | 2.886(3) | 166 |
| O(1W)-H(1WB)···O(2)$^{\#6}$ | 2.714(3) | 157 |
| O(1W)-H(1WA)···O(5W) | 2.785(3) | 152 |
| O(2W)-H(2WB)···O(3)$^{\#7}$ | 2.730(3) | 152 |
| O(2W)-H(2WA)···O(5W)$^{\#8}$ | 2.833(3) | 152 |
| O(4W)-H(4WA)···O(6W) | 2.860(4) | 179 |
| O(4W)-H(4WB)···O(1) | 2.899(3) | 179 |
| O(3W)-H(3WB)···(O4)$^{\#9}$ | 2.864(4) | 178 |
| O(5W)-H(5WA)···O(1W) | 2.785(3) | 177 |
| **3** | | |
| O(1W)-H(1WA)···O(3W)$^{\#10}$ | 2.785(4) | 166 |
| O(2W)-H(2WA)···O(1)$^{\#11}$ | 2.829(4) | 177 |
| O(2W)-H(2WB)···O(1W) | 2.732(4) | 177 |
| O(3W)-H(3WA)···O(1W)$^{\#12}$ | 2.785(4) | 165 |
| O(3W)-H(3WB)···O(1) | 2.873(4) | 165 |
| **4** | | |
| N(1)-H(1)···O(2)$^{\#13}$ | 2.893(3) | 163 |
| C(3)-H(3)···O(2)$^{\#13}$ | 3.192(3) | 142 |
| C(5)-H(5)···O(5) | 2.803(3) | 122 |
| C(10)-H(10)···O(2)$^{\#13}$ | 3.284(4) | 158 |
| C(11)-H(11)···O(3)$^{\#14}$ | 3.228(4) | 138 |

| | | |
|---|---|---|
| C(16)-H(16)···O(5)$^{\#15}$ | 3.055(4) | 122 |
| **5** | | |
| O(1W)-H(1WB)···O(2)$^{\#16}$ | 2.760(4) | 164 |
| O(1W)-H(1WA)···O(2W)$^{\#17}$ | 2.712(4) | 164 |
| O(2W)-H(2WA)···O(3)$^{\#18}$ | 2.718(4) | 168 |
| O(2W)-H(2WB)···O(5)$^{\#16}$ | 3.050(5) | 169 |
| **6** | | |
| O(2)-H(2)···O(3) | 2.662(3) | 169 |
| O(2)-H(3)···O(32)$^{\#19}$ | 2.671(2) | 168 |
| O(3)-H(4)···O(1)$^{\#20}$ | 2.974(3) | 153 |
| O(3)-H(5)···O(52)$^{\#19}$ | 2.701(3) | 163 |
| N(22)-H(14)···O(31)$^{21}$ | 3.187(3) | 145 |
| N(22)-H(14)···O(52)$^{\#22}$ | 3.061(3) | 132 |

[a]Symmetry transformation used to generate equivalent atoms: #1 = 1/2-x, -1/2+y, z. #2 1-x, 1-y, 1-z. #3 1/2+x, 1/2+y, 1/2-z. #4 1/2+x, 1/2-y, 1-z. #5 1-x, 2-y, 1-z, #6 1-x, 2-y, -z, #7 2-x, 2-y, -z, #8 1+x, y, z. #9 x, -1+y, z. #10 1+x, y, z. #11 1-x, 1-y, 2-z. #12 -1+x, y, z. #13 1-x, 1-y, 1-z. #14 1+x, y, 1+z. #15 x, -1+y, z. #16 1-x, 1-y, 1-z. #17 1-x, -1/2+y, 1/2-z. #18 x, 3/2-y, -1/2+z. #19 1-x, 1-y, 1-z. #20 x, 1/2-y, 1/2+z. #21 1+x, y, z. #22 2-x, -1/2+y, 1/2-z.

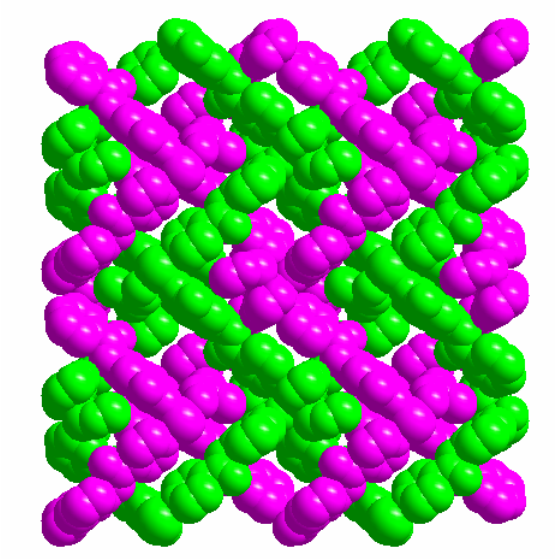


Figure S1. Space-filling representation of the two-fold interpenetrated net with free DMF molecule omitted for clarity in **1**.

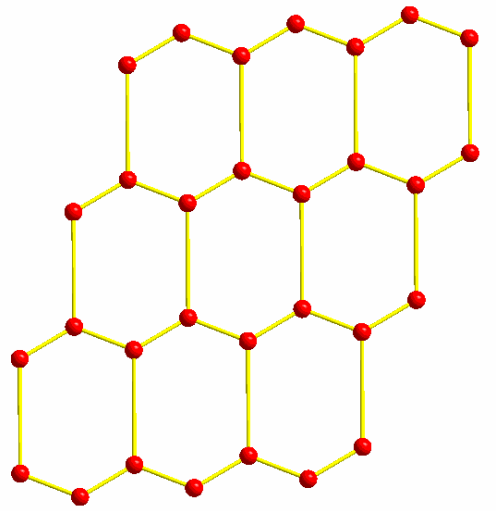


Figure S2. Simplified 2D network of **2** with (6, 3) topology.

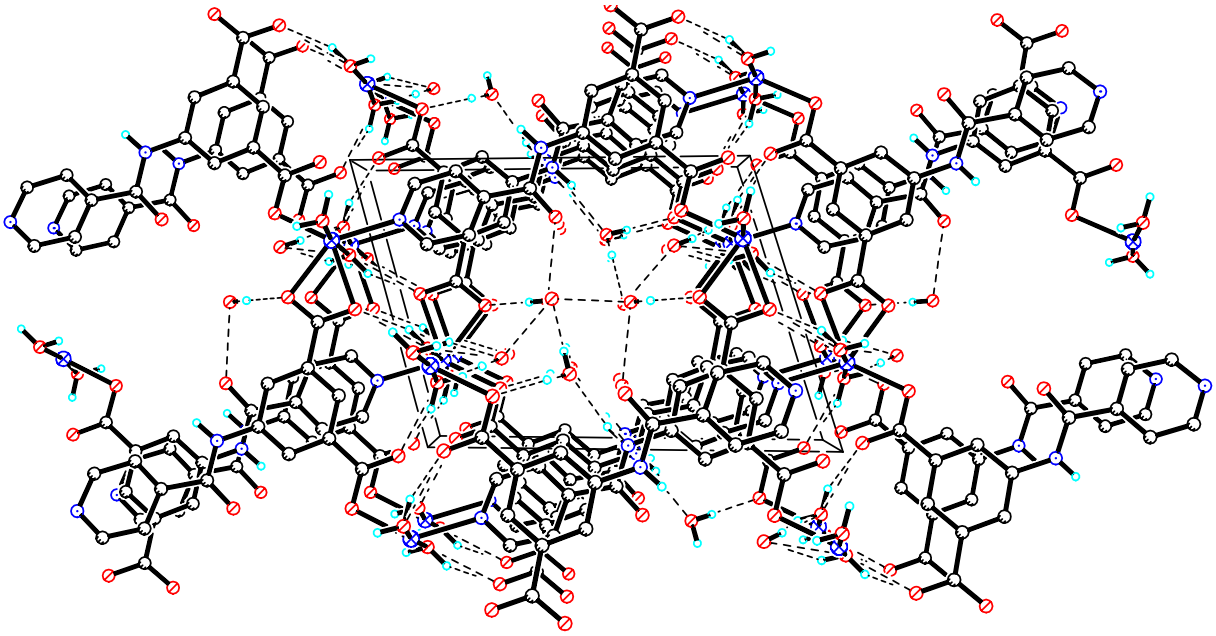


Figure S3. 3D structure of **2** with hydrogen bonds indicated by dashed lines.

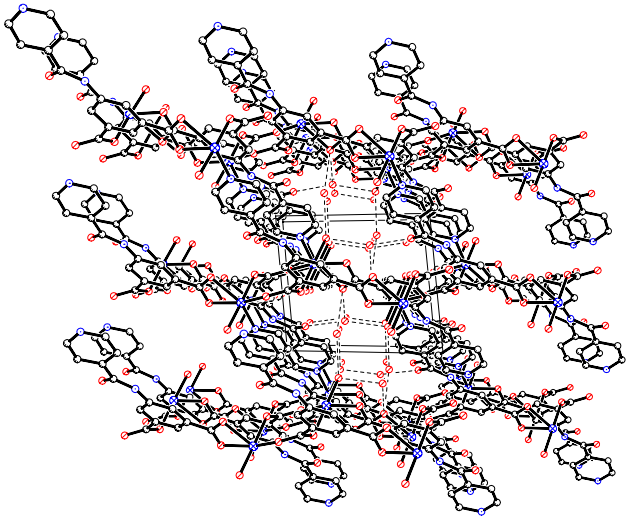


Figure S4. 3D packing structure of **3** with hydrogen bonds indicated by dashed lines.

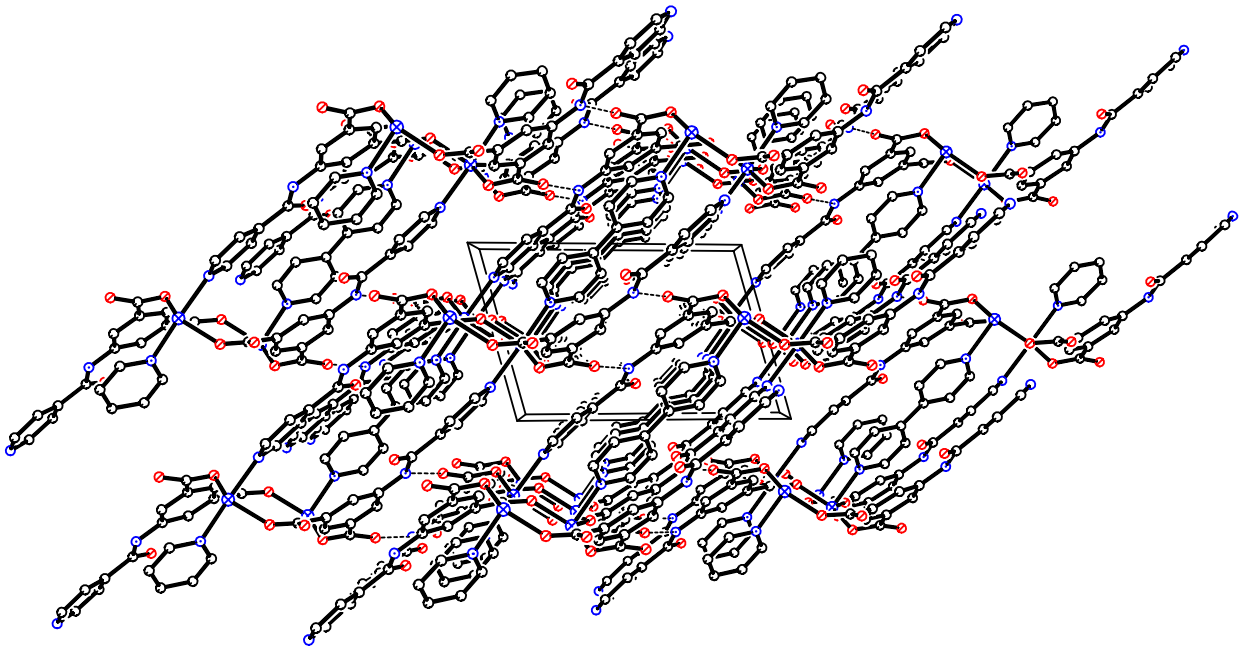
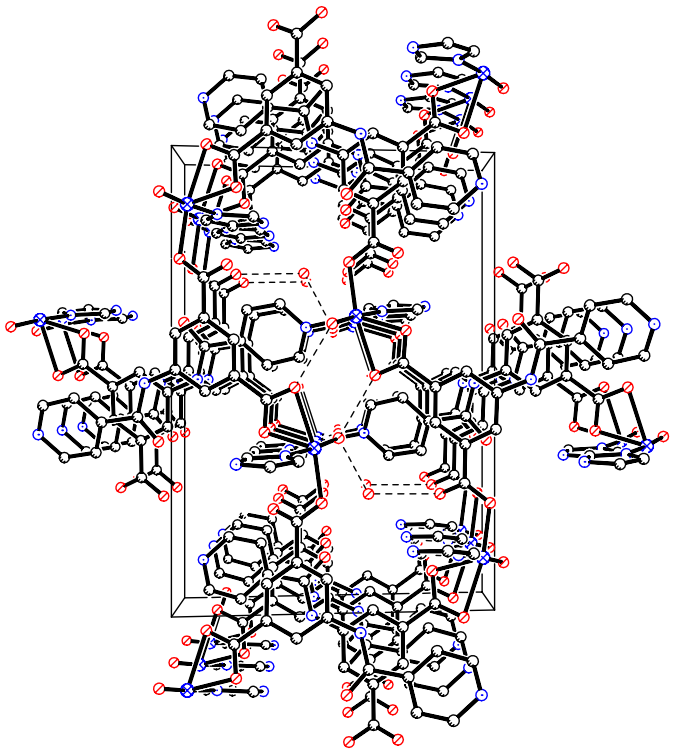
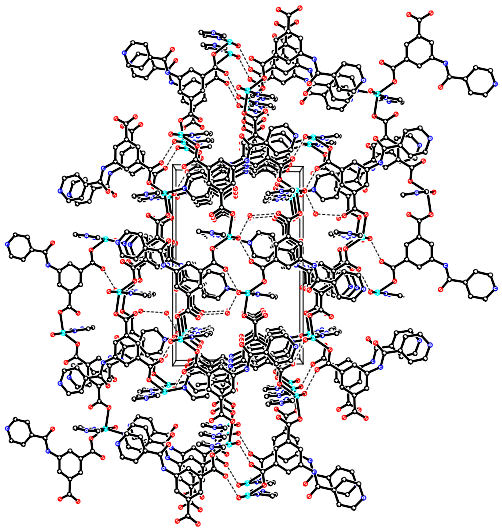


Figure S5. 3D packing structure of **4** with hydrogen bonds indicated by dashed lines.



(a)



(b)

Figure S6. 3D packing structures of **5** (a) and **6** (b) with hydrogen bonds indicated by dashed lines.

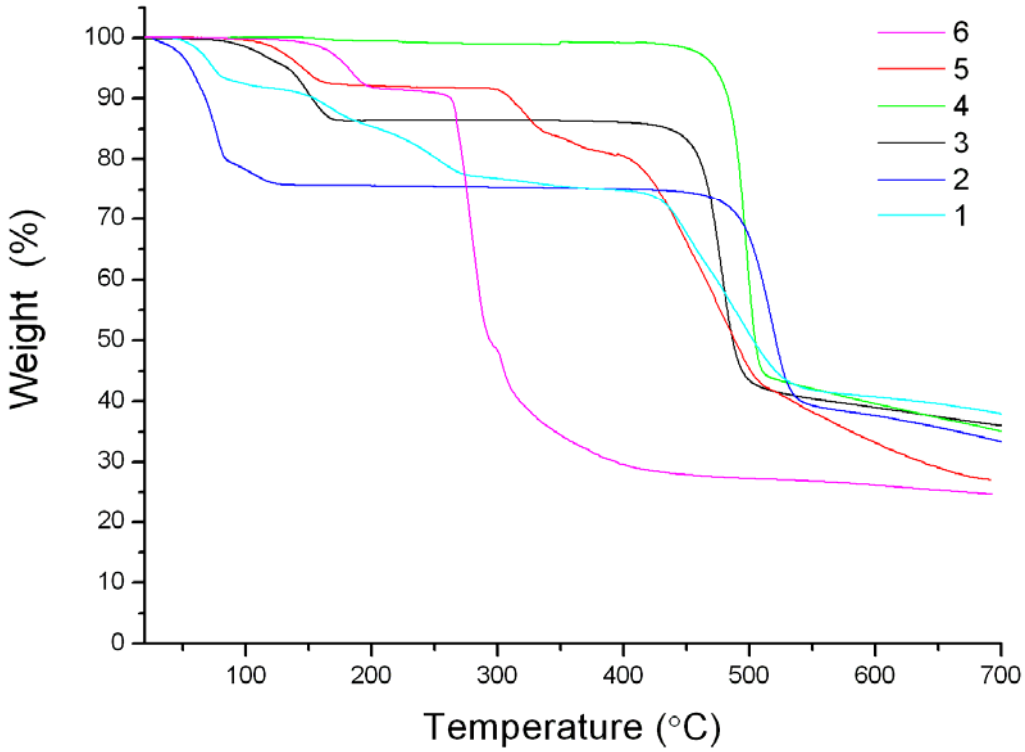
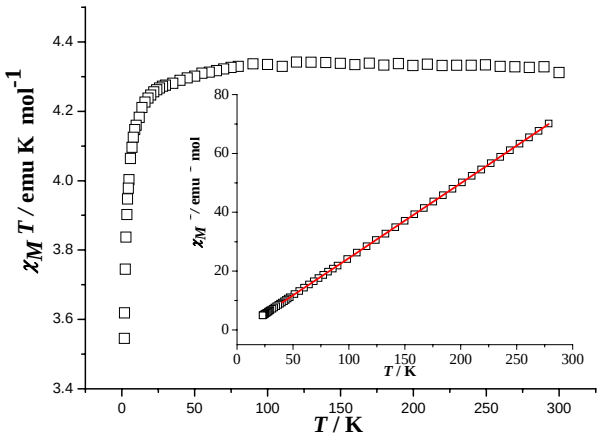
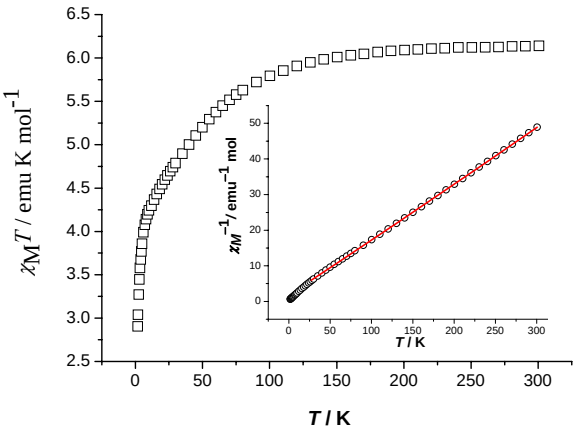


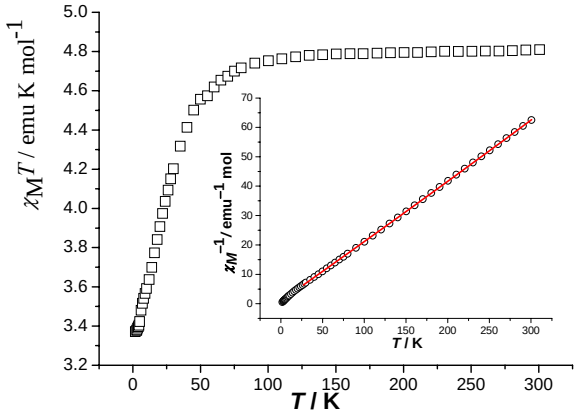

Figure S7. The TG curves of compounds **1** - **6**.


χM T / emu K mol-1
T / K
χM -1 / emu - 1 mol
T / K

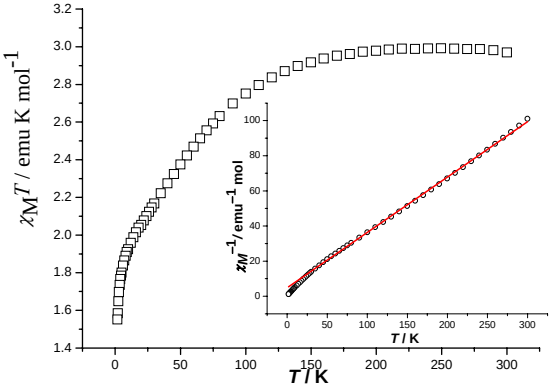
(a)


χM T / emu K mol-1
T / K
χM -1 / emu-1 mol
T / K

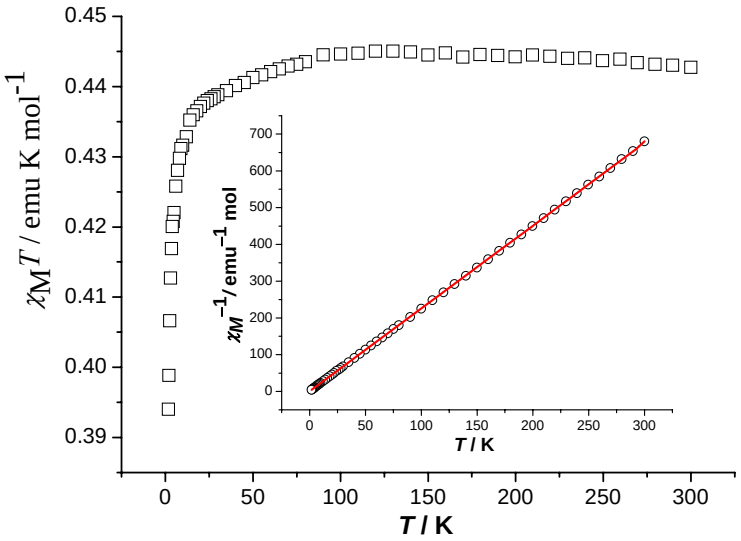
(b)


χM T / emu K mol-1
T / K
χM -1 / emu-1 mol
T / K

(c)


χM T / emu K mol-1
T / K
χM -1 / emu-1 mol
T / K

(d)




(e)

Figure S8 Temperature dependence of $\chi_M T$ and $\chi_M^{-1}$ for **2 - 6**. The red solid line shows the Curie-Weiss fitting.

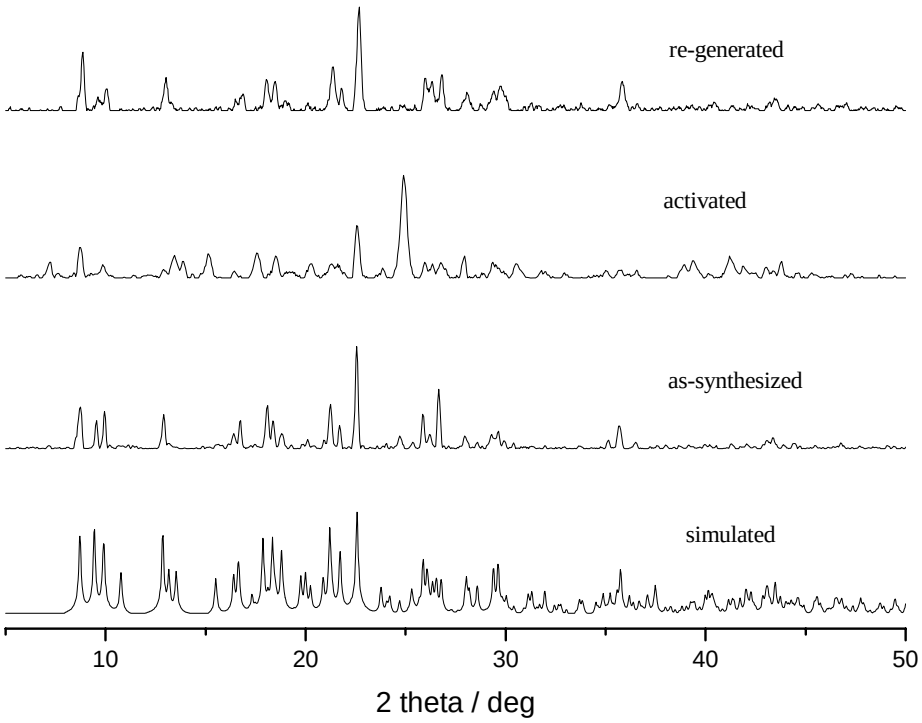



Figure S9. The powder X-ray diffraction patterns of compound **1.**

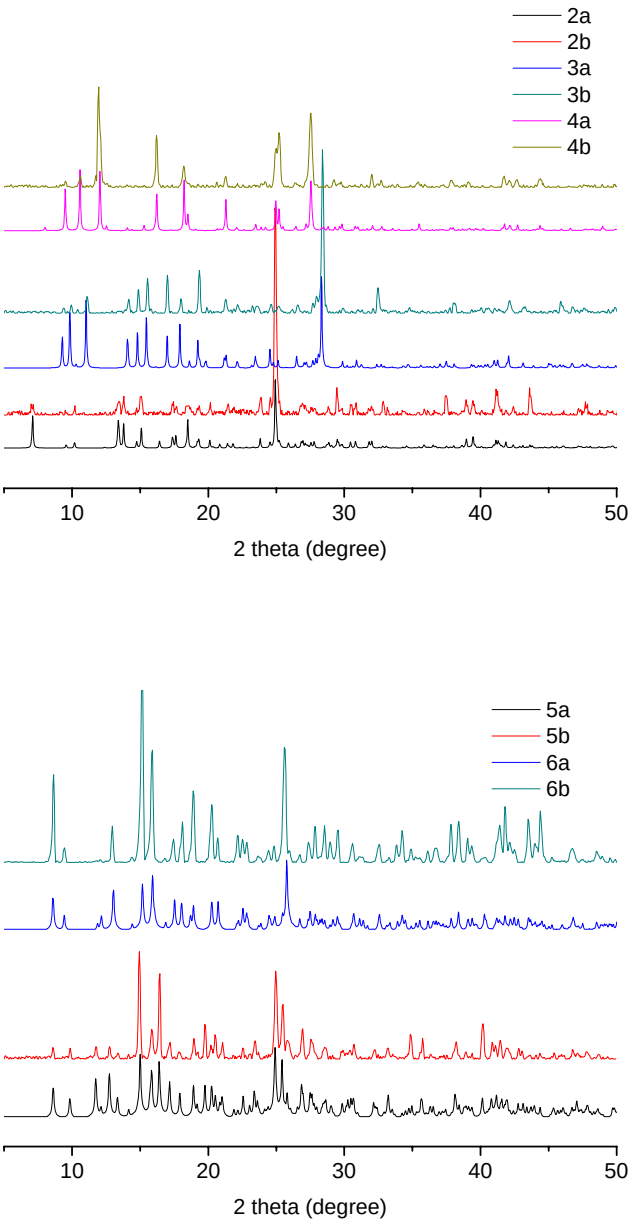



Figure S10. The powder X-ray diffraction patterns of compounds **2** – **6**: a – simulated; b – as-synthesized.