Electronic Supplementary Material (ESI) for CrystEngComm.


**Table S1** Crystallographic Data for **1-3**

| | **1** | **2** | **3** |
|---|---|---|---|
| Empirical formula | $C_{16}H_{10}CdN_6O_7$ | $C_{16}H_{10}N_6O_7Zn$ | $C_{16}H_{10}CuN_6O_7$ |
| fw | 510.70 | 463.67 | 461.84 |
| cryst syst | Monoclinic | Orthorhombic | Orthorhombic |
| *a* (Å) | 17.3051(5) | 7.8558(3) | 7.838(3) |
| *b* (Å) | 8.1682(2) | 13.5861(5) | 30.941(7) |
| *c* (Å) | 12.9742(4) | 31.5006(14) | 13.665(8) |
| $\alpha$ (°) | 90 | 90 | 90 |
| $\beta$ (°) | 108.332(3) | 90 | 90 |
| $\gamma$ (°) | 90 | 90 | 90 |
| *V* (Å$^3$) | 1740.85(9) | 3362.1(2) | 3314(2) |
| space Group | $P2_1/c$ | *P*bca | *P*bca |
| *Z* value | 4 | 8 | 8 |
| $\rho$ calc. (g/cm$^3$) | 1.949 | 1.832 | 1.851 |
| $\mu$ (mm$^{-1}$) | 1.313 | 1.522 | 1.380 |
| temp(K) | 298(2) | 298(2) | 298(2) |
| Data / restraints / parameters | 3556 / 0 / 271 | 3139 / 0 / 271 | 3078 / 30 / 299 |
| FinalRindics [I>2sigma(I)]: *R; $R_w$* | 0.0293; 0.0595 | 0.0401; 0.0926 | 0.1007; 0.2553 |

[a] $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. $wR2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$

**Table S2** Crystallographic Data for **4-6**

| | **4** | **5** | **6** |
|---|---|---|---|
| Empirical formula | $C_{32}H_{20}CdCl_2N_8O_{10}$ | $C_{32}H_{20}Cl_2CuN_8O_{10}$ | $C_{17}H_{11}CdCl_3N_6O_7$ |
| fw | 843.86 | 811.00 | 630.07 |
| cryst syst | Monoclinic | Trigonal | Monoclinic |
| *a* (Å) | 26.783(3) | 30.6123(10) | 9.5455(4) |
| *b* (Å) | 10.9091(10) | 30.6123(10) | 13.8394(6) |
| *c* (Å) | 28.532(4) | 29.4707(12) | 17.2740(8) |
| $\alpha$ (°) | 90 | 90 | 90 |

| | | | |
|---|---|---|---|
| $\beta$ (°) | 145.631(6) | 90 | 102.492(4) |
| $\gamma$ (°) | 90 | 120 | 90 |
| $V$ (Å$^3$) | 4706.1(9) | 23917.4(15) | 2 2227.93(17) |
| space Group | $C2/c$ | $R$-3 | $P2_1/n$ |
| $Z$ value | 4 | 18 | 4 |
| $\rho$ calc. (g/cm$^3$) | 1.191 | 1.014 | 1.878 |
| μ (mm$^{-1}$) | 0.626 | 0.557 | 1.393 |
| temp(K) | 103(4) | 108(11) | 298(2) |
| Data / restraints / parameters | 4811 / 21 / 244 | 10855 / 0 / 481 | 4151 / 0 / 307 |
| Final R indics [I>2sigma(I)]: *R;* | 0.1037; 0.2998 | 0.1114; 0.3184 | 0.0341; 0.0638 |

[a] $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. $wR2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$

**Table S3** Hydrogen bonds for **4** [Å and °]

| D-H…A | d(D-H) | d(H…A) | d(D…A) | ∠(DHA) |
|---|---|---|---|---|
| C(13)-H(13)…O(2)[3] | 0.93 | 2.34 | 3.043(14) | 131.8 |
| C(16)-H(16)…O(1) | 0.93 | 2.43 | 2.788(10) | 102.5 |
| C(9)-H(9) …O(3)[2] | 0.93 | 2.60 | 3.299(19) | 132.0 |
| C(9)-H(9) …O(2) | 0.93 | 2.56 | 3.442(15) | 159.0 |

Symmetry transformations used to generate equivalent atoms:
[2]-X, +Y, 1/2-Z; [3]1/2-X, -1/2+Y, 1/2-Z

**Table S4** Hydrogen bonds for **5** [Å and °]

| D-H…A | d(D-H) | d(H…A) | d(D…A) | ∠(DHA) |
|---|---|---|---|---|
| C(29)-H(29)…O(6)[1] | 0.93 | 2.57 | 3.357(8) | 142.1 |

Symmetry transformations used to generate equivalent atoms:
[1] 2/3-Y+X, 1/3+X, 1/3-Z

**Table S5**. The result of "TOPOS 4.0 professional".

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**5**:C32 H20 Cl2 Cu N8 O10

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Topology for Cu1

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Atom Cu1 links by bridge ligands and has

| Common vertex with | | | | | R(A-A) | |
|---|---|---|---|---|---|---|
| Cu 2 | 0.1667 | 0.8333 | 0.3333 | ( 0 1 0) | 10.110A | 1 |
| Cu 2 | -0.1667 | 0.1667 | 0.6667 | ( 0 0 1) | 10.110A | 1 |
| Cu 2 | 0.1667 | 0.3333 | 0.3333 | ( 0 0 0) | 10.110A | 1 |
| Cu 2 | -0.1667 | 0.6667 | 0.6667 | ( 0 1 1) | 10.110A | 1 |

Topology for Cu2

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Atom Cu2 links by bridge ligands and has

| Common vertex with | | | | | R(A-A) | |
|---|---|---|---|---|---|---|
| Cu 1 | 0.3333 | 0.1667 | 0.1667 | ( 0 0 0) | 10.110A | 1 |
| Cu 1 | 0.0000 | 0.5000 | 0.5000 | ( 0 0 0) | 10.110A | 1 |
| Cu 1 | -0.1667 | 0.1667 | 0.1667 | (-1-1 0) | 10.110A | 1 |
| Cu 1 | 0.5000 | 0.5000 | 0.5000 | ( 1 1 0) | 10.110A | 1 |

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Structural group analysis

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Structural group No 1

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Structure consists of 3D framework with Cu

Coordination sequences

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| Cu1: | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Num | 4 | 12 | 28 | 50 | 76 | 110 | 148 | 194 | 244 | 302 |
| Cum | 5 | 17 | 45 | 95 | 171 | 281 | 429 | 623 | 867 | 1169 |

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Cu2: 1 2 3 4 5 6 7 8 9 10

Num 4 12 28 50 76 110 148 194 244 302

Cum 5 17 45 95 171 281 429 623 867 1169

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TD10=1169

Vertex symbols for selected sublattice

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Cu1 Point symbol:{6^4.8^2}

Extended point symbol:[6(2).6(2).6(2).6(2).8(6).8(6)]

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Cu2 Point symbol:{6^4.8^2}

Extended point symbol:[6(2).6(2).6(2).6(2).8(6).8(6)]

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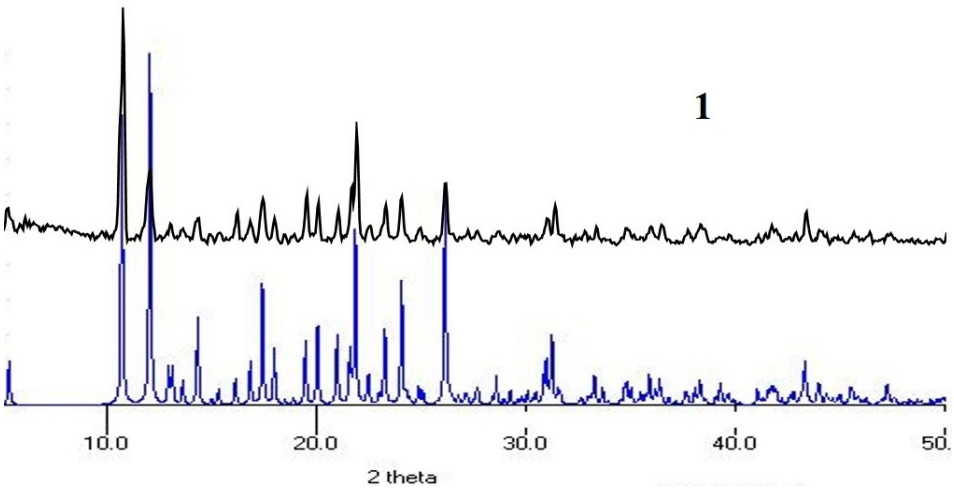
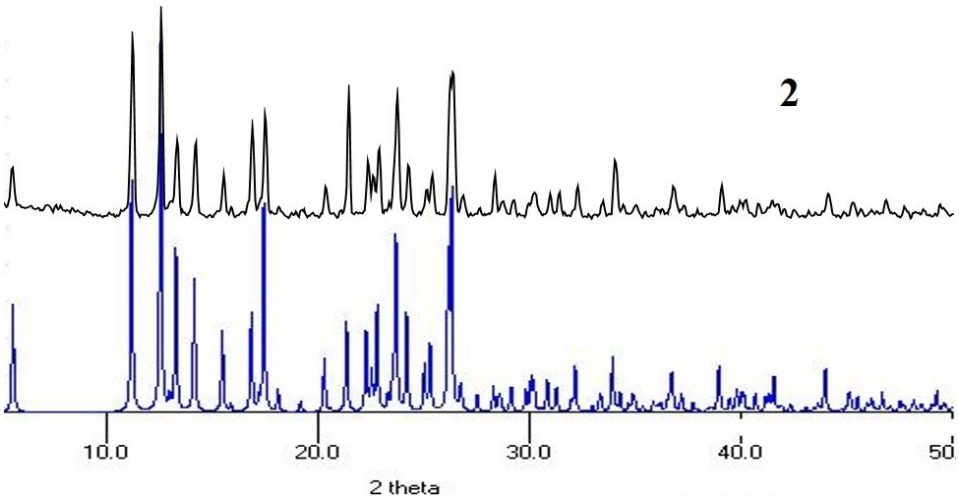
Point symbol for net: {6^4.8^2}

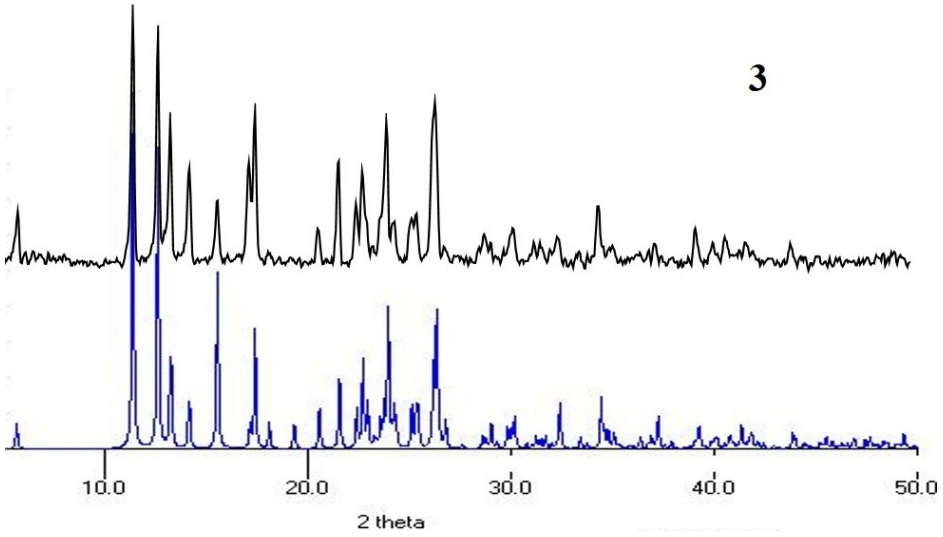
4-c net; uninodal net

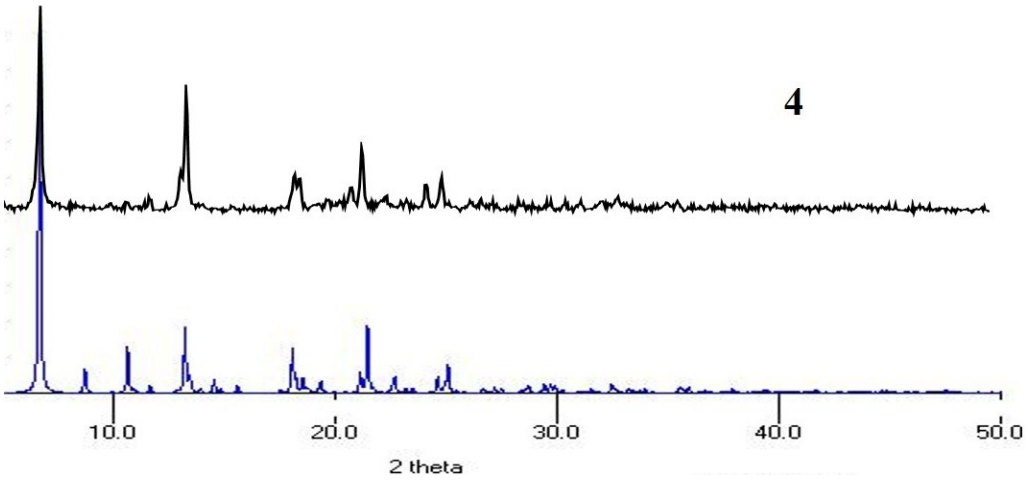
Topological type: nbo NbO; 4/6/c2; sqc35 (topos&RCSR.ttd) {6^4.8^2} - VS [6(2).6(2).6(2).6(2).8(2).8(2)] (73689 types in 11 databases)

Elapsed time: 10.74 sec.




2
10.0
20.0
30.0
40.0
50
2 theta


3
10.0
20.0
30.0
40.0
50.0
2 theta


4
10.0
20.0
30.0
40.0
50.0
2 theta

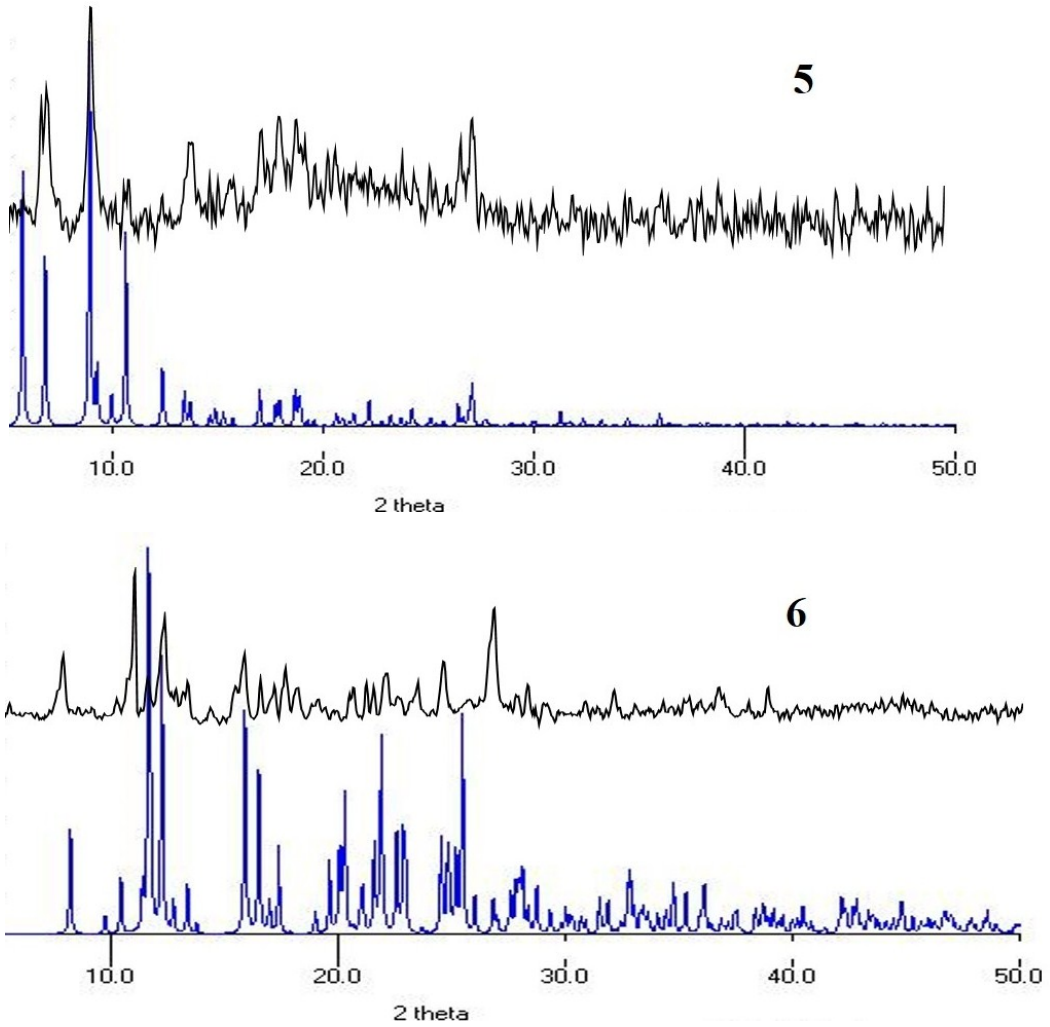
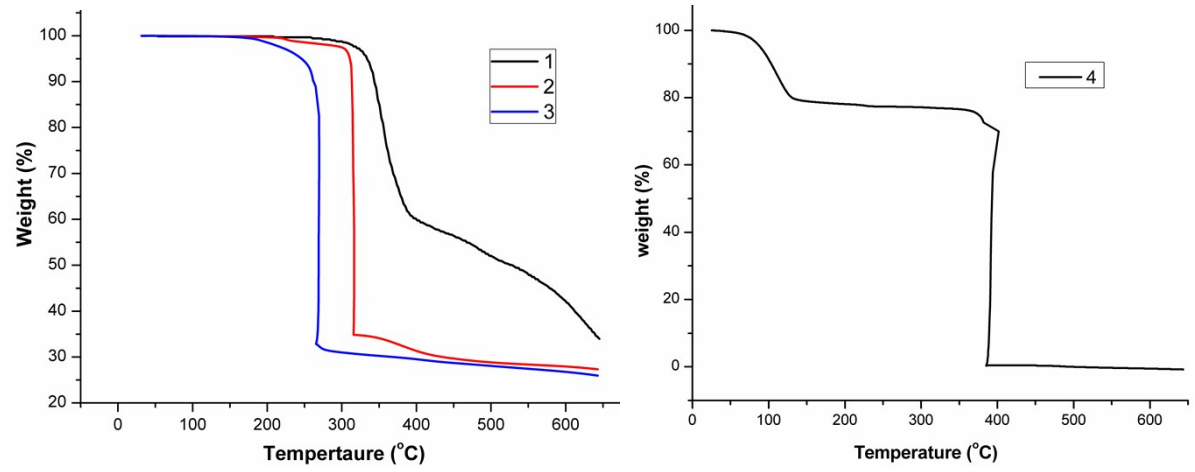



Fig. S1 Simulated (blue) and experimental (black) powder X-ray diffraction (PXRD) patterns of **1–6.**



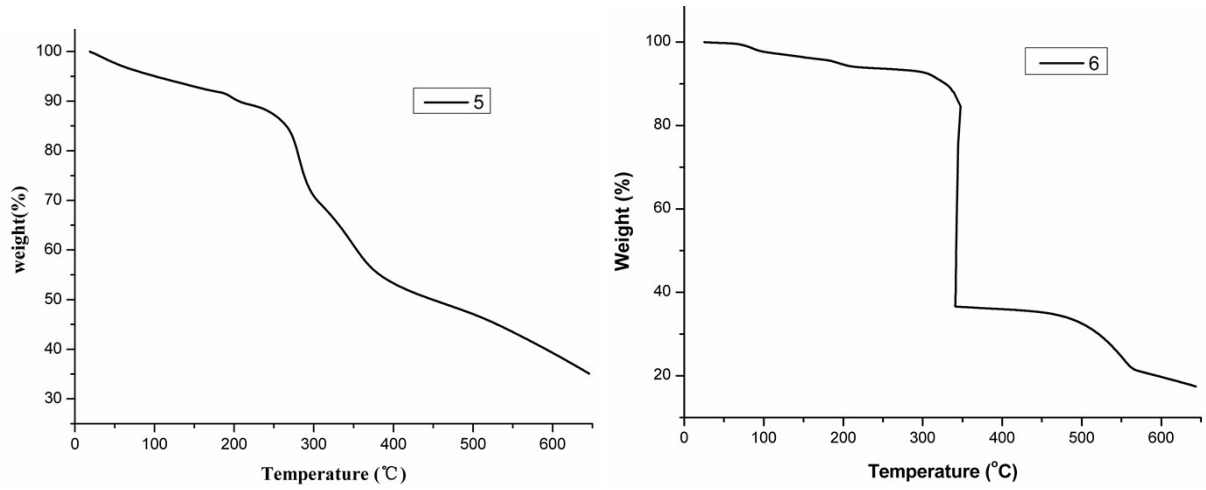



Fig. S2 TGA curves of **1–6.**

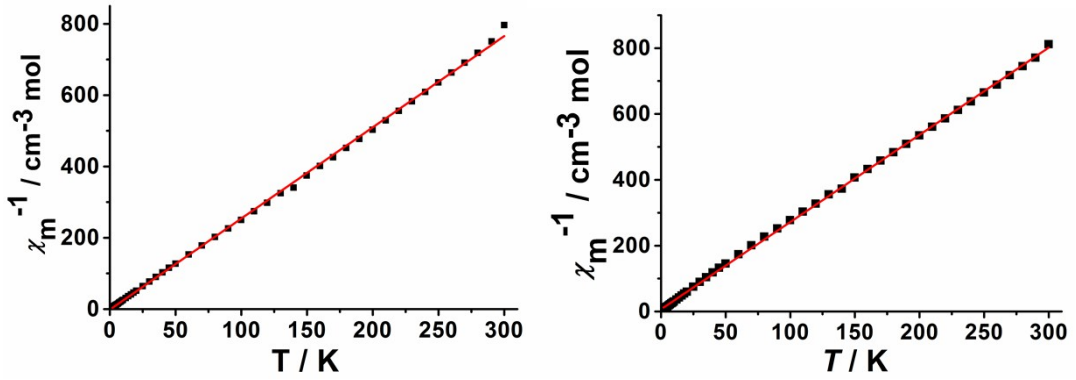



Figure S3. Temperature dependence of $\chi_M^{-1}$ values of of **3** (left) and **5** (right) in the temperature range of 2-300 K under 1000 Oe field. Solid lines represent the fitting data.