Electronic Supplementary Material (ESI) for CrystEngComm.


# Electronic Supplementary Information

# for

# A series of entangled MOFs constructed from flexible dipyridyl piperazine and rigid dicarboxylate: interpenetration, self-penetration and polycatenation

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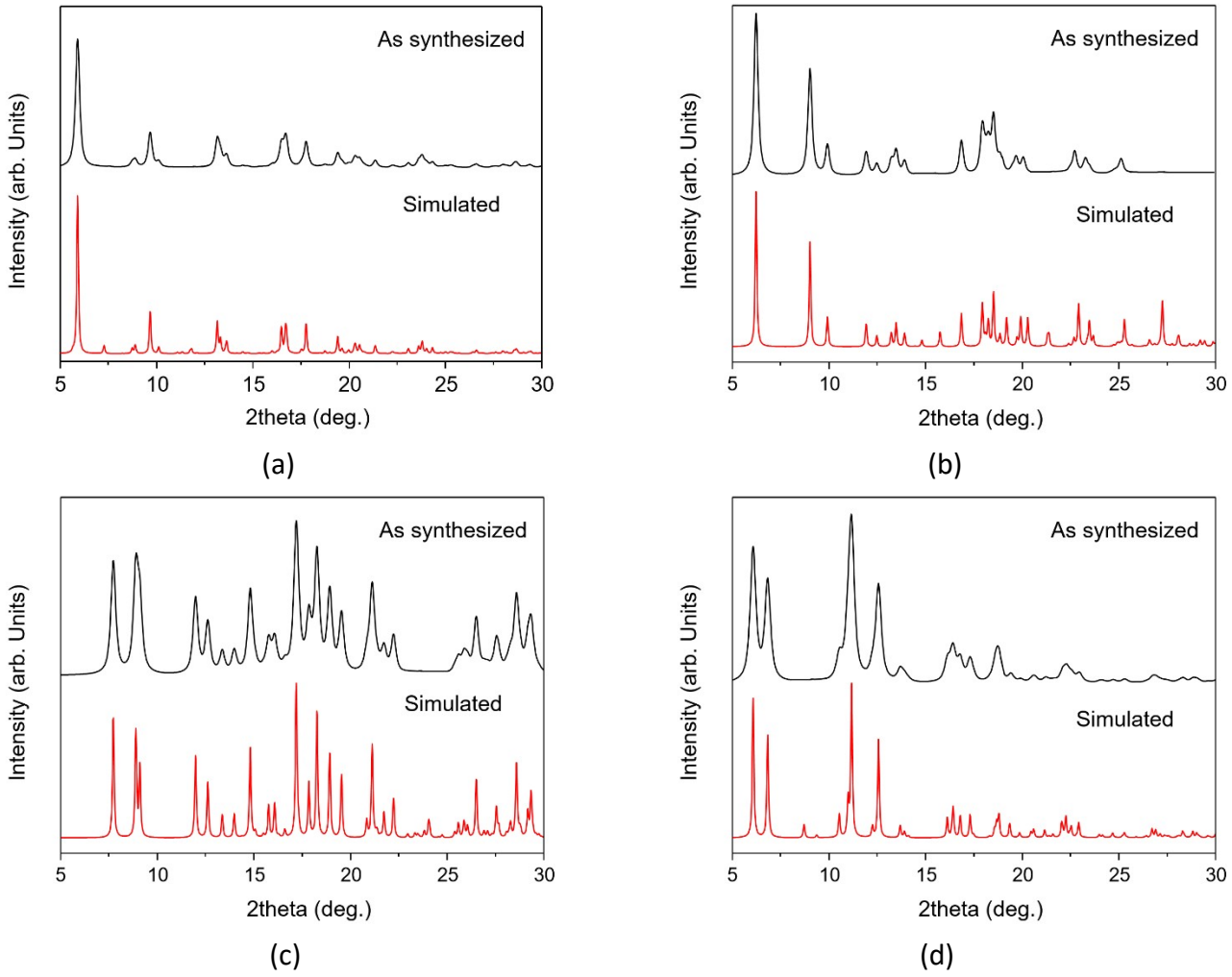



**Fig. S1** PXRD patterns of (a) **1**, (b) **2**, (c) **3** and (d) **4**.

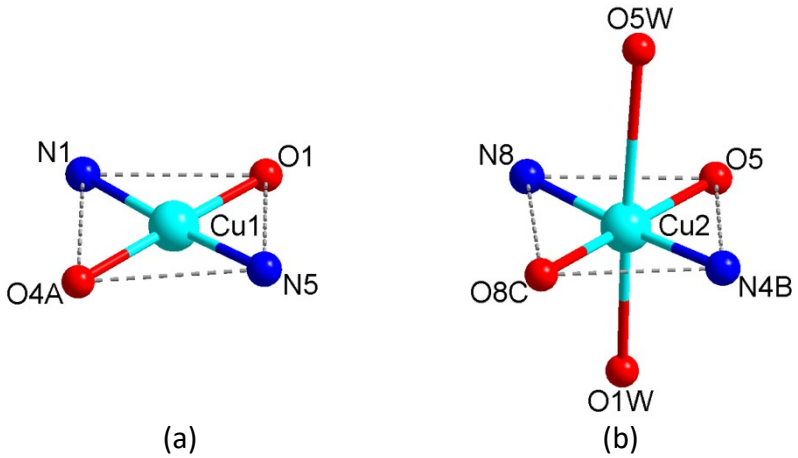
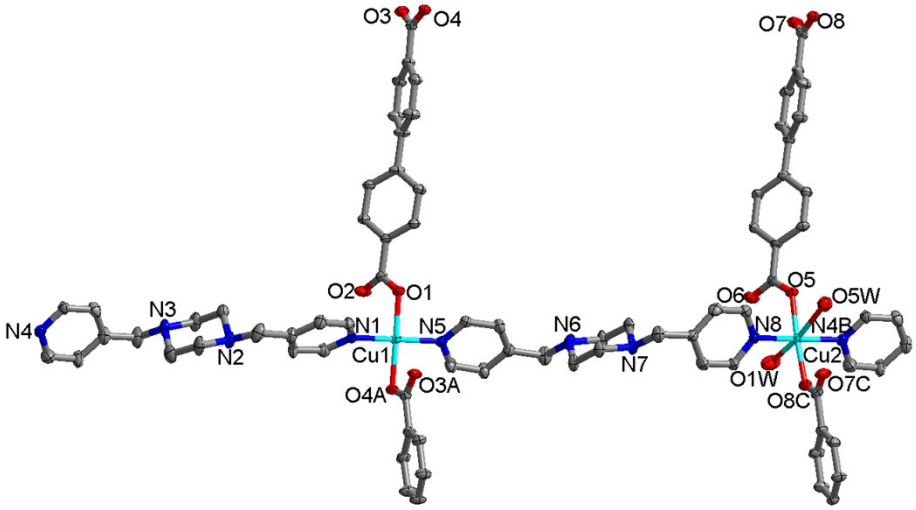
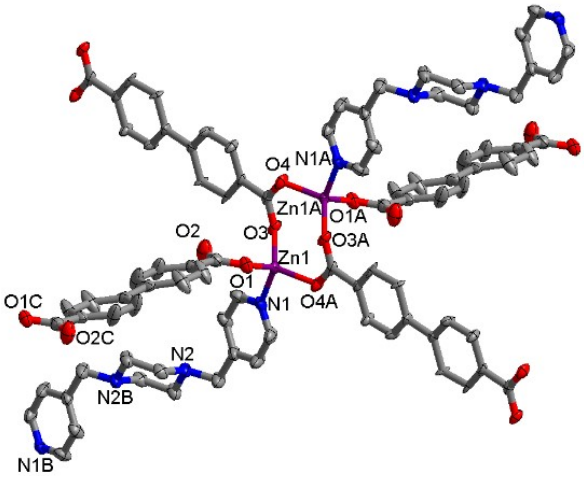


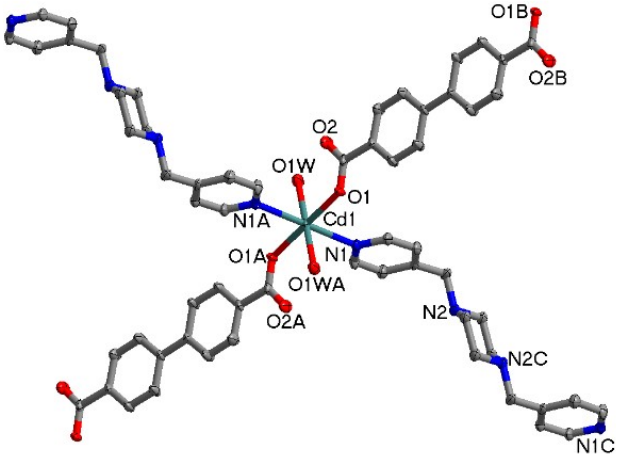

**Fig. S2** Local coordination geometries of (a) Cu1 (square planar) and (b) Cu2 (elongated octahedral) atoms in **1**.



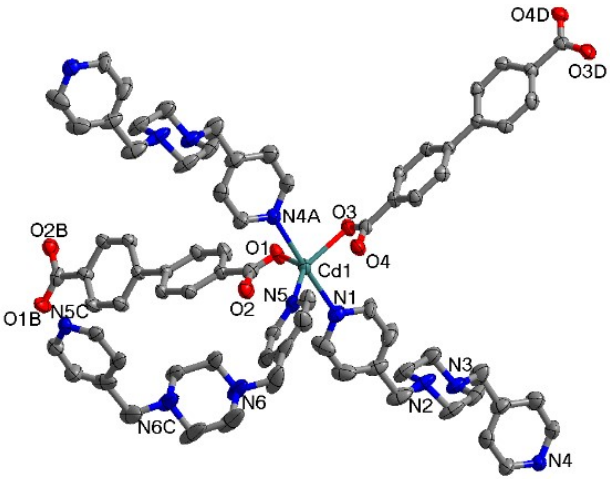

(a)




(b)




(c)




(d)

**Fig. S3** Thermal ellipsoid plot (30% probability) of the crystal structures for (a) **1**, (b) **2**, (c) **3** and (d) **4**.

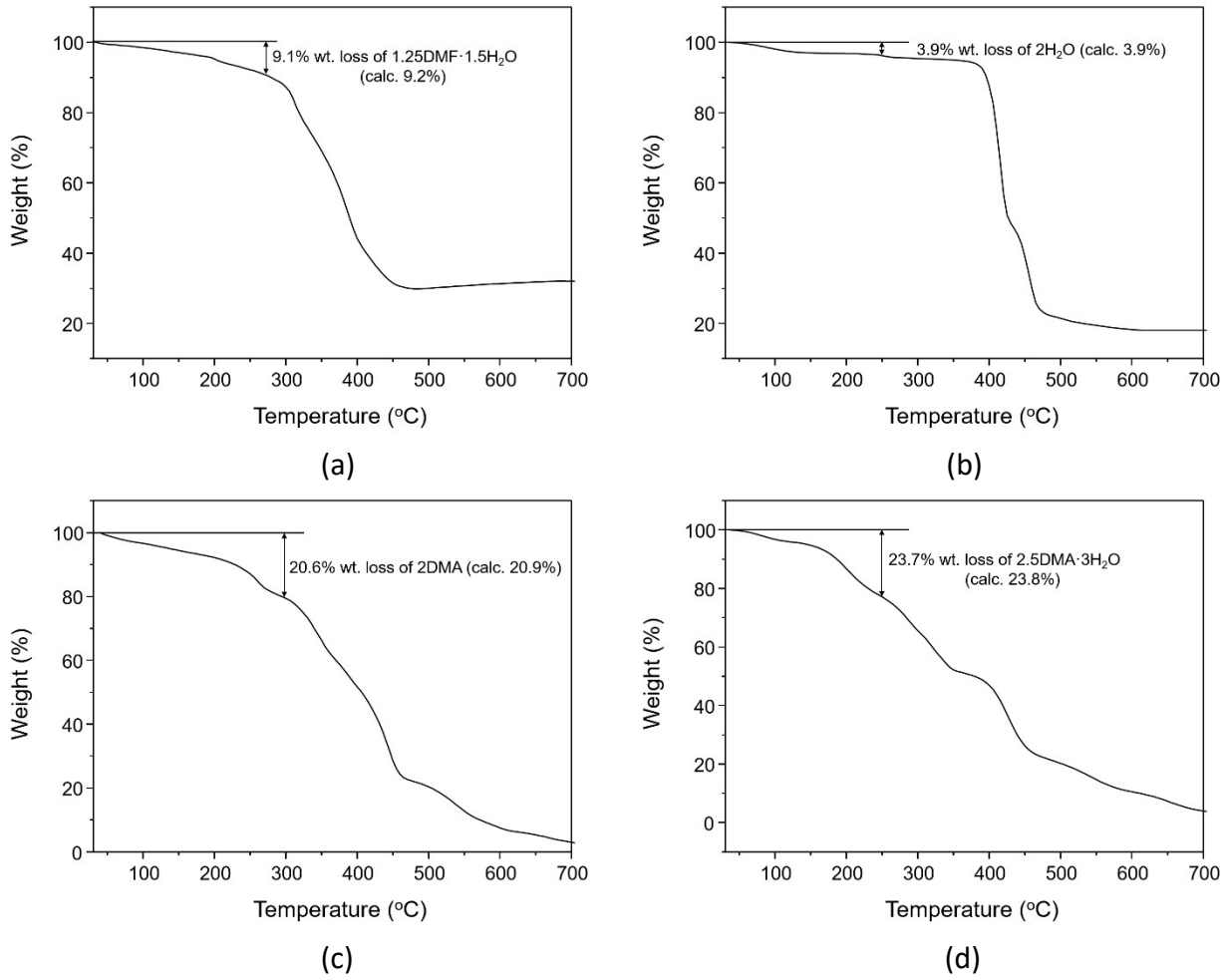



**Fig. S4** TGA curves for (a) **1**, (b) **2**, (c) **3** and (d) **4**.

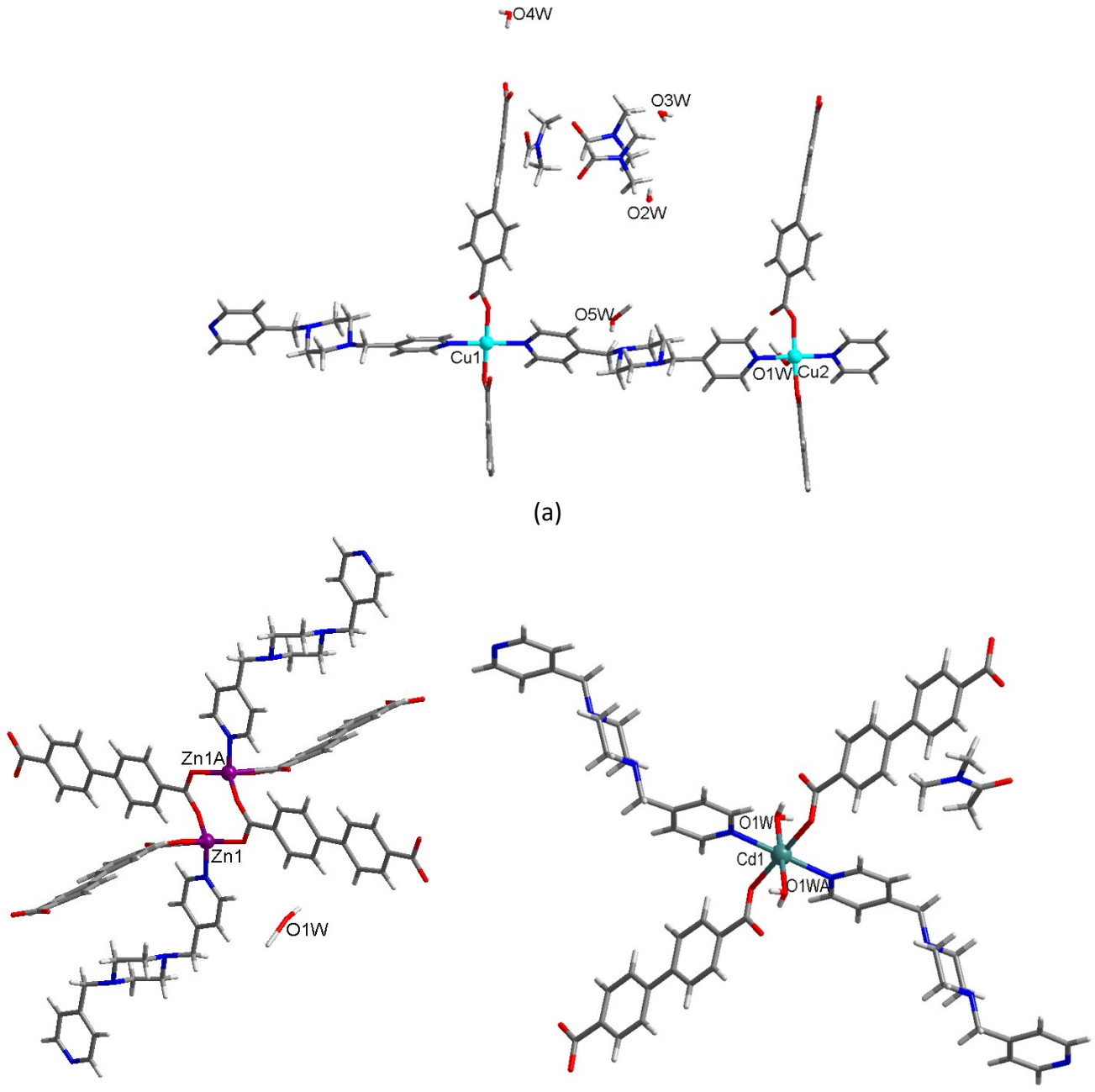



**Fig. S5** The coordination environments of the metal centres for (a) **1**, (b) **2** and (c) **3**. The hydrogen atoms of the water molecules were obtained using the HSite from *TopospPro* Program.[S1]

## Reference

S1. V. A. Blatov, A. P. Shevchenko and D. M. Proserpio*, Cryst. Growth Des.*, 2014, **14**, 3576-3586. (see also http://topospro.com)

**Table S1** Crystallographic data and structure refinement for **1**-**4**

| | **1** | **2** | **3** | **4** |
|---|---|---|---|---|
| formula | $C_{255}H_{287}Cu_8N_{37}O_{51}$ | $C_{22}H_{20}N_2O_5Zn$ | $C_{38}H_{50}CdN_6O_8$ | $C_{38}H_{38}CdN_6O_4$ |
| formula weight | 5194.52 | 457.77 | 831.24 | 755.14 |
| temperature, K | 173(2) | 173(2) | 173(2) | 173(2) |
| crystal system | Orthorhombic | Triclinic | Triclinic | Trigonal |
| space group | $P2_12_12_1$ | $P$-1 | $P$-1 | $P3_22_1$ |
| $a$ (Å) | 18.2794(5) | 7.0781(2) | 7.664(4) | 16.7798(6) |
| $b$ (Å) | 29.9253(8) | 10.5603(2) | 10.968(6) | 16.7798(6) |
| $c$ (Å) | 13.2838(3) | 14.5209(3 | 12.971(6) | 28.3067(12) |
| α (°) | 90 | 77.6050(10) | 114.880(18) | 90 |
| $\beta$ (°) | 90 | 84.3170(10) | 99.231(18) | 90 |
| γ (°) | 90 | 70.9640(10) | 97.47(2) | 120 |
| $V$ (Å$^3$) | 7266.5(3) | 1001.63(4) | 952.3(9) | 6902.3(6) |
| $Z$ | 1 | 2 | 1 | 6 |
| $D_{calc}$(g/cm$^3$) | 1.187 | 1.518 | 1.449 | 1.090 |
| $\mu$ (mm$^{-1}$) | 0.646 | 1.263 | 0.633 | 0.512 |
| $2\theta_{max}$ (°) | 52 | 52 | 52 | 52 |
| reflections collected | 51292 | 16713 | 9842 | 76624 |
| independent reflns | 14279 [$R_{int}$ = 0.0858] | 3924 [$R_{int}$ = 0.0362] | 3413 [$R_{int}$ = 0.0357] | 9030 [$R_{int}$ = 0.1048] |
| goodness-of-fit on $F^2$ | 1.031 | 1.059 | 1.156 | 1.029 |
| $R_1$, $wR_2$ [$I$> 2$\sigma$($I$)] | 0.0721, 0.1883 | 0.0353, 0.0771 | 0.0882, 0.2321 | 0.0453, 0.0965 |
| $R_1$, $wR_2$ (all data) | 0.1149, 0.2160 | 0.0435, 0.0808 | 0.1353, 0.3098 | 0.0756, 0.1071 |

**Table S2** Selected bond lengths (Å) and bond angles (°) for **1**

| | | | |
|---|---|---|---|
| Cu1-N1 | 1.991(6) | Cu1-N5 | 2.015(7) |
| Cu1-O1 | 1.917(5) | Cu1-O4A | 1.999(5) |
| Cu2-N4B | 2.005(7) | Cu2-N8 | 2.011(7) |
| Cu2-O5 | 1.949(5) | Cu2-O8C | 1.956(6) |
| Cu2-O1W | 2.448(8) | Cu2-O5W | 2.896(7) |
| O1-Cu1-N1 | 90.4(3) | O1-Cu1-O4A | 178.7(3) |
| N1-Cu1-O4A | 89.4(3) | O1-Cu1-N5 | 89.8(3) |
| N1-Cu1-N5 | 175.5(3) | O4A-Cu1-N5 | 90.5(3) |
| O5-Cu2-O8C | 176.4(3) | O5-Cu2-N8 | 92.6(3) |
| O8C-Cu2-N8 | 90.3(3) | O5-Cu2-N4B | 88.8(3) |
| O8C-Cu2-N4B | 88.2(3) | N8-Cu2-N4B | 174.1(3) |
| O5-Cu2-O1W | 94.7(3) | O8C-Cu2-O1W | 87.2(3) |
| N8-Cu2-O1W | 94.8(3) | N4B-Cu2-O1W | 90.8(3) |
| O5-Cu2-O5W | 79.6(2) | O8C-Cu2-O5W | 98.5(3) |
| N8-Cu2-O5W | 83.8(3) | N4B-Cu2-O5W | 90.8(3) |
| O1W-Cu2-O5W | 174.0(2) | | |

Symmetry operations: (A) -x-1, y-1/2, -z+1/2; (B) x+1, y, z+2; (C) –x+2, y-1/2, -z+5/2

**Table S3** Selected bond lengths (Å) and bond angles (°) for **2**

| | | | |
|---|---|---|---|
| Zn1-N1 | 2.019(2) | Zn1-O1 | 1.9349(19) |
| Zn1-O3 | 1.9423(17) | Zn1-O4A | 1.9548(17) |
| O1-Zn1-N1 | 113.11(8) | O3-Zn1-N1 | 103.28(8) |
| O4A-Zn1-N1 | 104.52(8) | O1-Zn1-O3 | 114.47(8) |
| O1-Zn1-O4A | 102.69(8) | O3-Zn1-O4A | 118.41(8) |

Symmetry operations: (A) -x, -y+1, -z+1

**Table S4** Selected bond lengths (Å) and bond angles (°) for **3**

| | | | |
|---|---|---|---|
| Cd1-N1 | 2.381(9) | Cd1-O1 | 2.286(7) |
| Cd1-O1W | 2.326(8) | | |
| O1-Cd1-O1A | 180.0 | O1-Cd1-O1WA | 88.0(3) |
| O1A-Cd1-O1WA | 92.0(3) | O1-Cd1-O1W | 92.0(3) |
| O1A-Cd1-O1W | 88.0(3) | O1WA-Cd1-O1W | 180.0 |
| O1-Cd1-N1 | 86.9(3) | O1A-Cd1-N1 | 93.1(3) |
| O1WA-Cd1-N1 | 84.1(3) | O1W-Cd1-N1 | 95.9(3) |
| O1-Cd1-N1A | 93.1(3) | O1A-Cd1-N1A | 86.9(3) |
| O1WA-Cd1-N1A | 95.9(3) | O1W-Cd1-N1A | 84.1(3) |
| N1-Cd1-N1A | 180.0(5) | | |

Symmetry operations: (A) -x+2, -y+2, -z

**Table S5** Selected bond lengths (Å) and bond angles (°) for **4**

| | | | |
|---|---|---|---|
| Cd1-N1 | 2.365(6) | Cd1-N4A | 2.357(6) |
| Cd1-N5 | 2.350(6) | Cd1-O1 | 2.296(4) |
| Cd1-O3 | 2.333(4) | Cd1-O4 | 2.454(4) |
| O1-Cd1-O3 | 87.21(16) | O1-Cd1-N5 | 136.56(18) |
| O3-Cd1-N5 | 136.20(18) | O1-Cd1-N4A | 90.3(2) |
| O3-Cd1-N4A | 89.8(2) | N5-Cd1-N4A | 88.9(2) |
| O1-Cd1-N1 | 86.50(19) | O3-Cd1-N1 | 86.7(2) |
| N5-Cd1-N1 | 95.7(2) | N4A-Cd1-N1 | 175.4(2) |
| O1-Cd1-O4 | 141.43(17) | O3-Cd1-O4 | 54.45(16) |
| N5-Cd1-O4 | 81.93(18) | N4A-Cd1-O4 | 93.32(19) |
| N1-Cd1-O4 | 87.14(18) | | |

Symmetry operations: (A) x, y+1, z