Supplementary Material (ESI) for Dalton Transactions


**Supporting Information**

# Role of molar-ratio, temperature and solvent on the Zn/Cd 1,2,4-triazolate system with novel topological architectures

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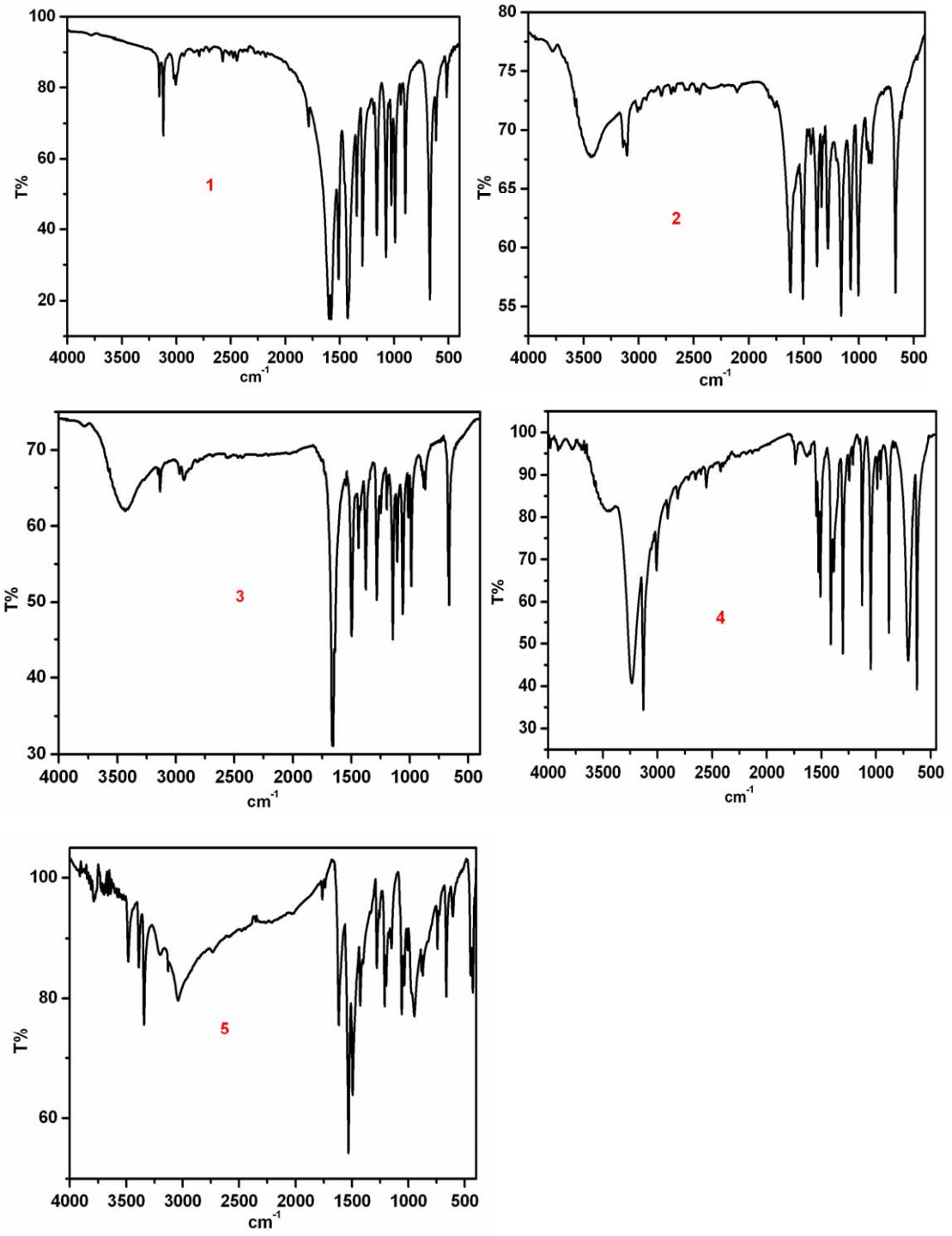


**Fig.S1** The IR spectra of complexes **1-5**.

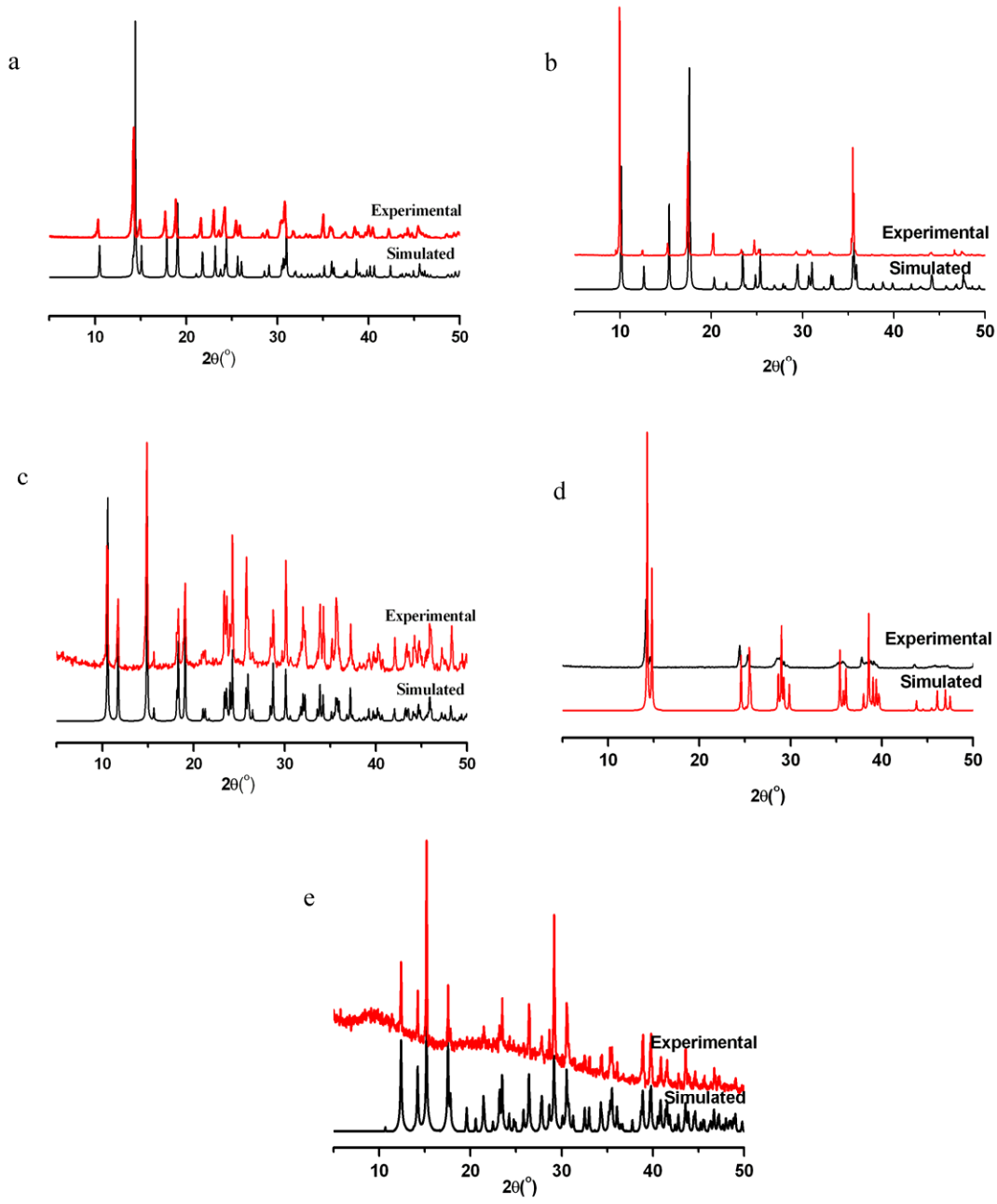


**Fig. S2** The simulated and experimental XRD diagrams of each compound in this work: (a)-**1**, (b)-**2**, (c)-**3**, (d)-**4** and (e)-**5**, red, experimental data, black, simulated from single-crystal X-ray data.

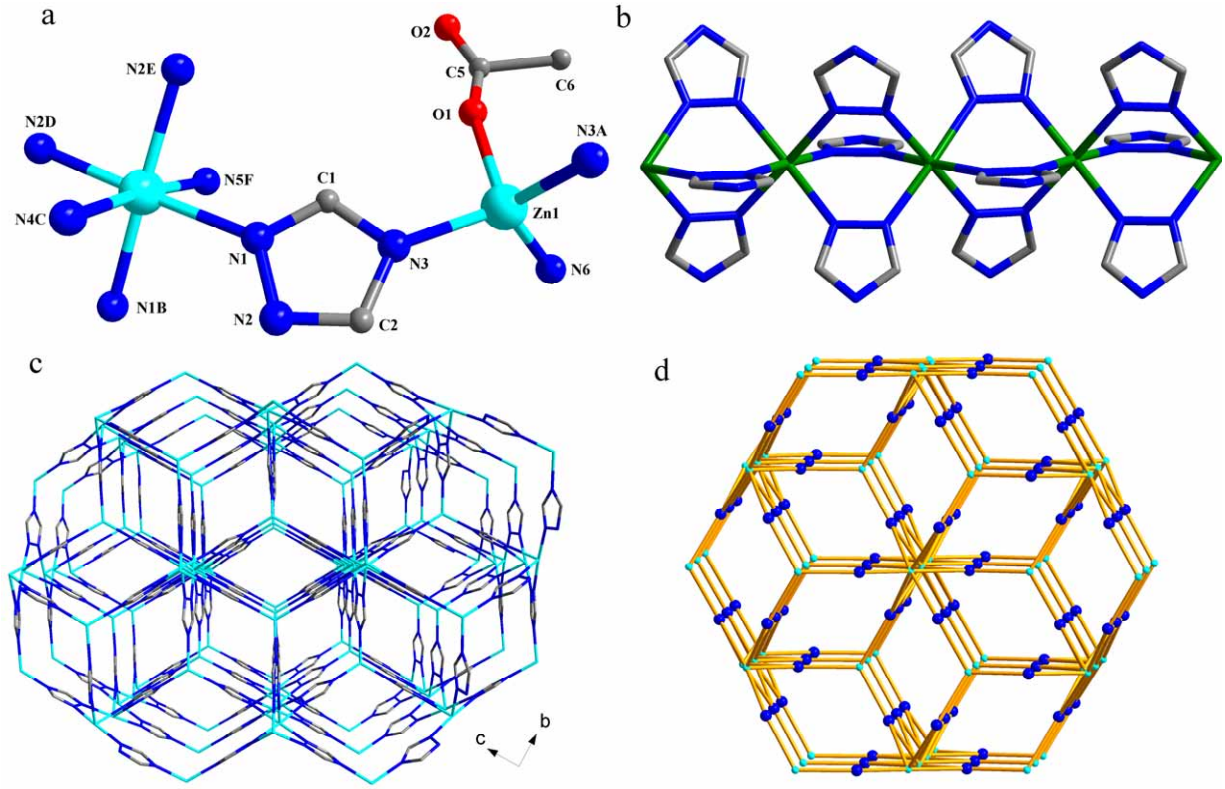


**Fig. S3** (a) Details of the coordination environments of Zn1 and Zn2 in complex **2**. Symmetry codes for generated atoms: A: x, -0.5 - y, z; B: x, 0.5 - y, z; C: 0.5 – x, -y, -0.5 + z; D: -0.5 + x, 0.5 – y, -0.5 – z; E: -0.5 + x, y, -0.5 – z; F: -x, 0.5 + y, -z. (b) 1D chain of $\{Zn(TAZ)_3\}_n^{n-}$ comprising Zn(2). (c) Perspective view of the 3D structure**,** acetate groups have been omitted for clarity. (d) Schematic representation of the 3D (3,6)-connected net.

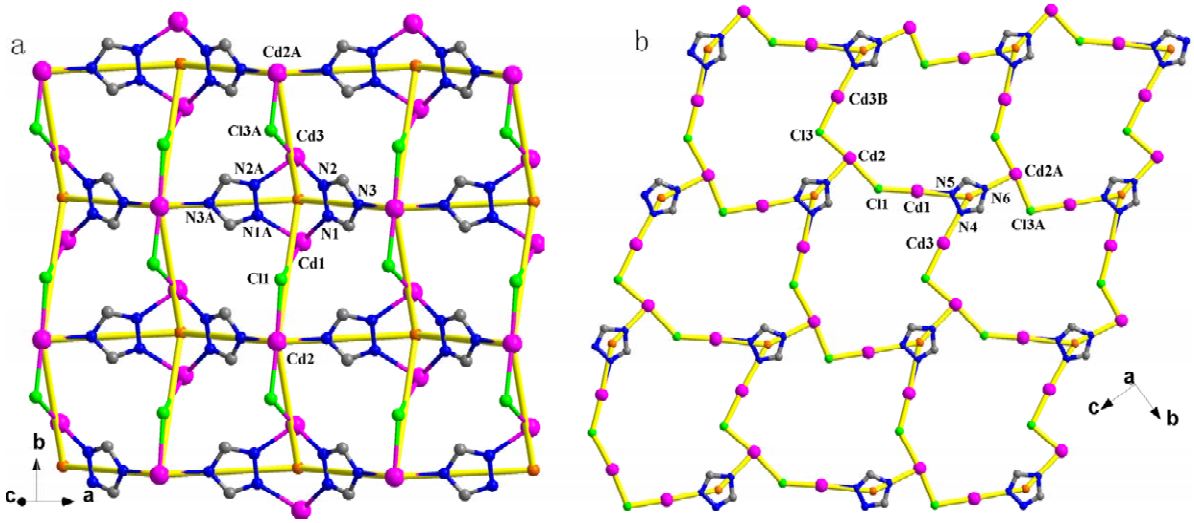


**Fig. S4** View of two types of 2D substructures of complex **3**: (a) 2D (4, 4) layer and (b) 2D layer based on macrocycle. Symmetry codes for generated atoms: (a) A: -2 - x, -y, -0.5 + z; B: x, -1 + y, z. (b) A: -2 – x, y, z; B: x, 1 + y, z.

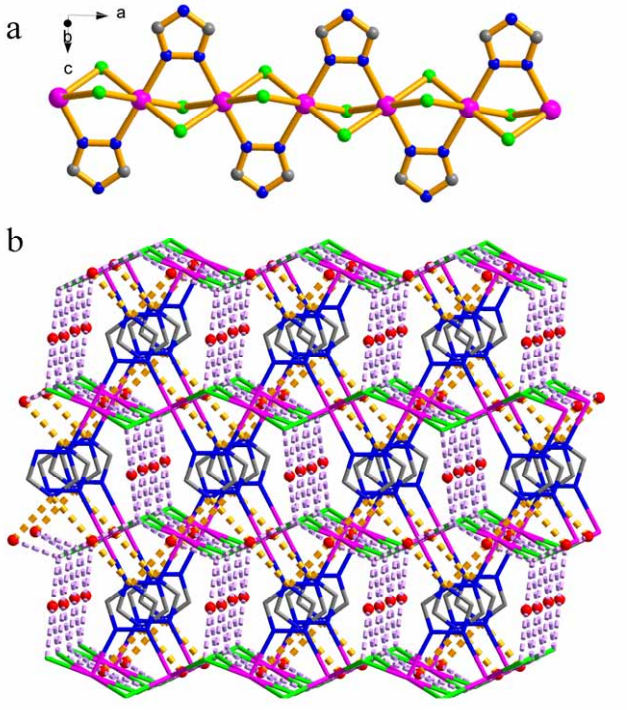


**Fig. S5** (a) Portion of the 1D tribridged $[Cd(TAZ)Cl_2]_n$ chain in **4**. (b) Perspective view of the 3D supramolecular architecture of **4**.

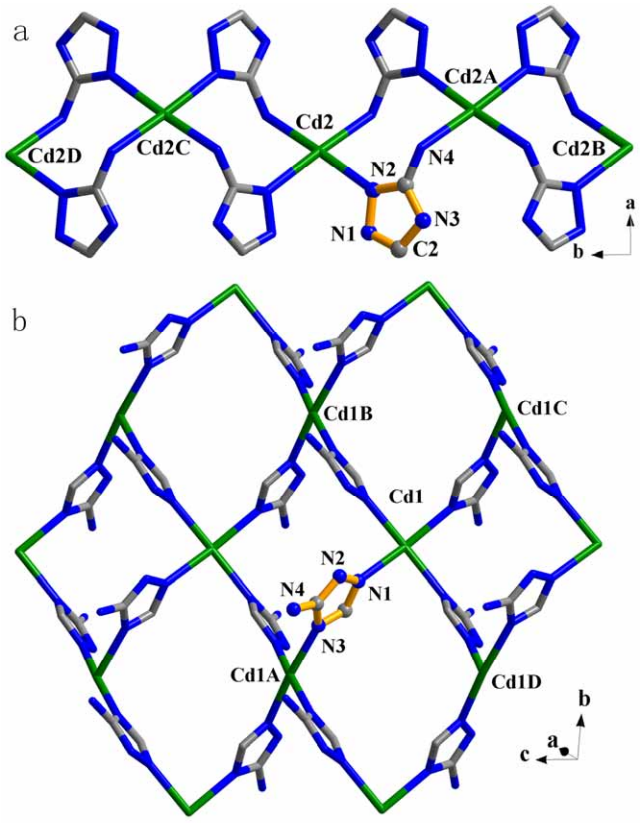


**Fig. S6** View of two structural motifs in **5** bridged by $\mu_4$-AmTAZ: (a) $\mu_4$-AmTAZ bridge Cd(2) into 1D double-bridged chain and (b) $\mu_4$-AmTAZ link Cd(1) into 2D (4,4) layer . Symmetry codes for generated atoms: (a) A: 1 - x, -0.5 + y, -z; B: x, -1 + y, z; C: 1 – x, 0.5 + y, -z; D: x, 1 + y, z. (b) A: 0.5 –x, -y, 0.5 + z; B: 0.5 –x, 1 - y, 0.5 + z; C: 0.5 –x, 1 - y, -0.5 + z; D: 0.5 –x, -y, -0.5 + z.

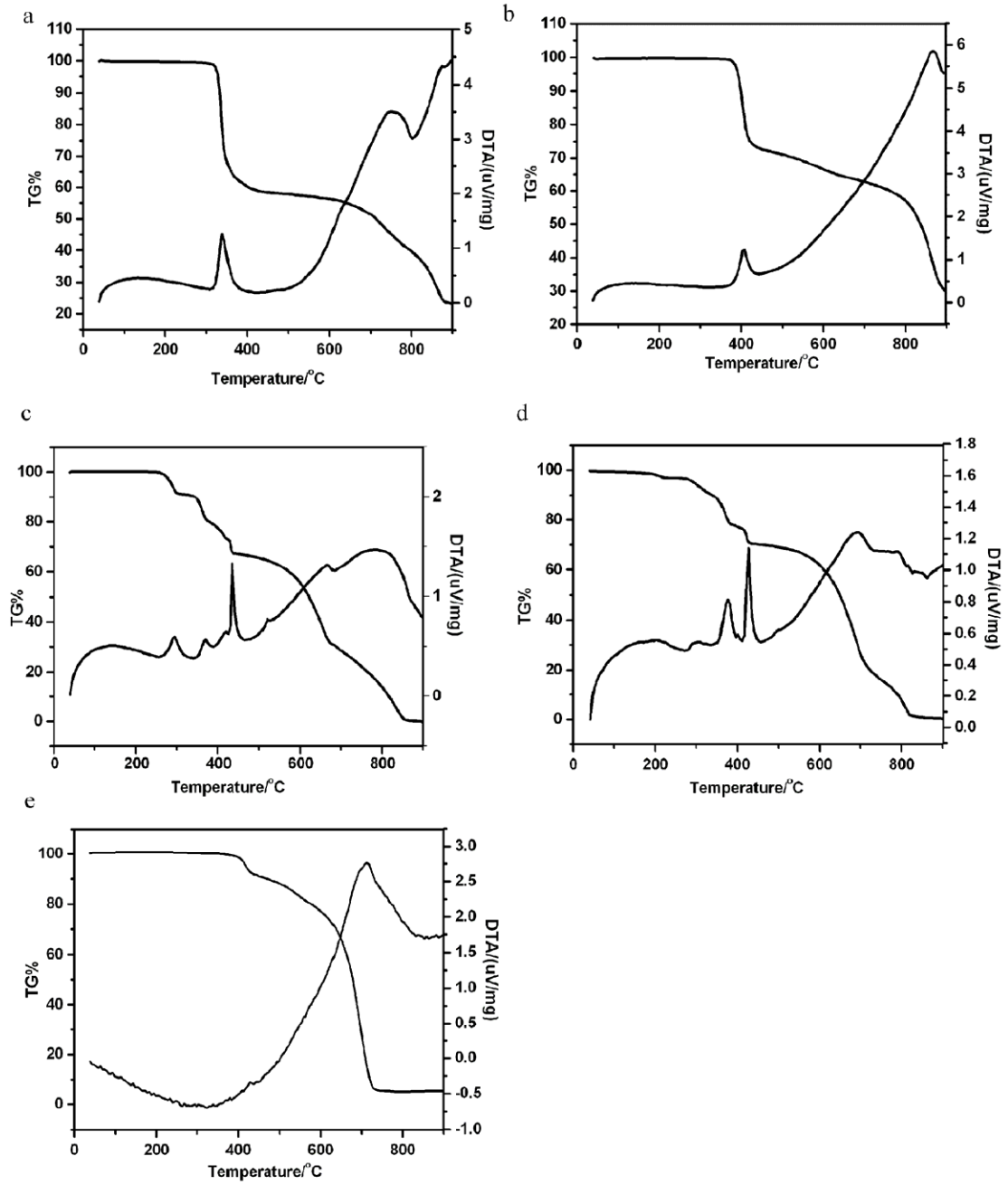


**Fig. S7** TG-DTA curves of complexes **1-5**: (a)-**1**, (b)-**2**, (c)-**3**, (d)-**4**, (e)-**5.**

**Table S1.** Crystal Data and Structure Refinements for Compounds **1-5**

| param | **1** | **2** | **3** | **4** | **5** |
|---|---|---|---|---|---|
| formula | $C_4H_5ZnN_3O_2$ | $C_8H_9Zn_2N_9O_2$ | $C_{12}H_{20}Cd_3Cl_3N_{11}O_2$ | $C_2H_5CdCl_2N_3O$ | $C_6H_9Cd_2ClN_{12}$ |
| fw | 192.50 | 394.02 | 793.97 | 270.40 | 509.52 |
| temp(*K*) | 293(2) | 293(2) | 293(2) | 293(2) | 293(2) |
| cryst syst | Orthorhombic | Orthorhombic | Orthorhombic | Orthorhombic | Orthorhombic |
| space group | *Pmn2₁* | *Pnma* | *Cmc2₁* | *Imma* | *Pnma* |
| *a* (Å) | 9.303(6) | 7.663(3) | 11.856(8) | 7.09(2) | 16.562(7) |
| *b* (Å) | 8.413(6) | 10.104(4) | 12.019(8) | 7.24(2) | 10.103(4) |
| *c* (Å) | 8.161(6) | 17.426(8) | 16.688(12) | 11.96(3) | 7.904(3) |
| *V* (Å$^3$) | 638.7(8) | 1349.2(10) | 2378(3) | 614(3) | 1322.5(9) |
| *Z* | 4 | 4 | 4 | 4 | 4 |
| $D_{calcd}$ (g cm$^{-3}$) | 2.002 | 1.940 | 2.218 | 2.903 | 2.559 |
| $\mu$ (mm$^{-1}$) | 3.778 | 3.575 | 3.029 | 4.334 | 3.432 |
| GOF | 1.031 | 1.107 | 1.072 | 1.093 | 1.079 |
| R1[a] ($I > 2\sigma(I)$) | 0.0276 | 0.0312 | 0.0418 | 0.0624 | 0.0254 |
| wR2[a] (all data) | 0.0645 | 0.0761 | 0.0956 | 0.2198 | 0.0592 |

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2)+(aP)^2+bP]$, where $P = [\max(F_o^2,0)+2F_c^2]/3$ for all data.

**Table S2.** Selected bond lengths (Å) and angles (°) for complexes **1-5**[a]

Complex **1**

| | | | |
|---|---|---|---|
| Zn(1)-O(2) | 1.923(4) | Zn(2)-N(1) | 2.124(3) |
| Zn(1)-O(4)#1 | 1.936(4) | Zn(2)-O(1)#4 | 2.140(4) |
| Zn(1)-N(3) | 2.020(3) | Zn(2)-N(2)#5 | 2.161(3) |
| Zn(1)-N(3)#2 | 2.020(3) | Zn(2)-N(2)#6 | 2.161(3) |
| Zn(2)-N(1)#3 | 2.124(3) | Zn(2)-O(3) | 2.201 (4) |
| O(2)-Zn(1)-O(4)#1 | 111.88(17) | | |
| O(2)-Zn(1)-N(3) | 108.99(11) | O(1)#4-Zn(2)-N(2)#5 | 92.52(11) |
| O(4)#1-Zn(1)-N(3) | 113.76(10) | N(1)-Zn(2)-N(2)#6 | 175.86(11) |
| O(2)-Zn(1)-N(3)#2 | 108.99(11) | N(1)#3-Zn(2)-N(2)#6 | 90.17(12) |
| O(4)#1-Zn(1)-N(3)#2 | 113.76(10) | O(1)#4-Zn(2)-N(2)#6 | 92.52(11) |
| N(3)-Zn(1)-N(3)#2 | 98.65(18) | N(2)#5-Zn(2)-N(2)#6 | 88.32(16) |
| N(1)-Zn(2)-N(1)#3 | 91.07(16) | N(1)-Zn(2)-O(3) | 87.34(11) |
| N(1)-Zn(2)-O(1)#4 | 91.40(11) | N(1)#3-Zn(2)-O(3) | 87.34(11) |
| N(1)#3-Zn(2)-O(1)#4 | 91.40(11) | O(1)#4-Zn(2)-O(3) | 178.21(14) |
| N(1)-Zn(2)-N(2)#5 | 90.17(12) | N(2)#5-Zn(2)-O(3) | 88.77(11) |
| N(1)#3-Zn(2)-N(2)#5 | 175.86(11) | N(2)#6-Zn(2)-O(3) | 88.77(11) |

Complex **2**

| | | | |
|---|---|---|---|
| Zn(1)-O(1) | 1.975(4) | Zn(2)-N(2)#3 | 2.153(2) |
| Zn(1)-N(6) | 1.990(3) | Zn(2)-N(2)#4 | 2.153(2) |
| Zn(1)-N(3)#1 | 1.994(2) | Zn(2)-N(1)#5 | 2.171(2) |
| Zn(1)-N(3) | 1.994(2) | Zn(2)-N(1) | 2.171(2) |
| Zn(2)-N(4)#2 | 2.130(3) | Zn(2)-N(5)#6 | 2.237(3) |
| O(1)-Zn(1)-N(6) | 105.11(16) | | |
| O(1)-Zn(1)-N(3)#1 | 100.93(9) | N(2)#4-Zn(2)-N(1)#5 | 89.15(9) |
| N(6)-Zn(1)-N(3)#1 | 115.86(8) | N(4)#2-Zn(2)-N(1) | 90.30(8) |
| O(1)-Zn(1)-N(3) | 100.93(9) | N(2)#3-Zn(2)-N(1) | 89.15(9) |
| N(6)-Zn(1)-N(3) | 115.86(8) | N(2)#4-Zn(2)-N(1) | 176.21(8) |

| | | | |
|---|---|---|---|
| N(3)#1-Zn(1)-N(3) | 114.97(13) | N(1)#5-Zn(2)-N(1) | 90.68(12) |
| N(4)#2-Zn(2)-N(2)#3 | 93.48(8) | N(4)#2-Zn(2)-N(5)#6 | 174.65(11) |
| N(4)#2-Zn(2)-N(2)#4 | 93.48(8) | N(2)#3-Zn(2)-N(5)#6 | 90.28(8) |
| N(2)#3-Zn(2)-N(2)#4 | 90.76(12) | N(2)#4-Zn(2)-N(5)#6 | 90.28(8) |
| N(4)#2-Zn(2)-N(1)#5 | 90.30(8) | N(1)#5-Zn(2)-N(5)#6 | 85.94(8) |
| N(2)#3-Zn(2)-N(1)#5 | 176.21(8) | N(1)-Zn(2)-N(5)#6 | 85.94(8) |
| | | Complex **3** | |
| Cd(1)-N(1) | 2.314(7) | Cd(2)-N(6)#4 | 2.281(10) |
| Cd(1)-N(1)#1 | 2.314(7) | Cd(2)-Cl(3) | 2.631(3) |
| Cd(1)-O(1) | 2.326(8) | Cd(2)-Cl(1) | 2.799(3) |
| Cd(1)-O(1)#1 | 2.326(8) | Cd(3)-N(2) | 2.251(7) |
| Cd(1)-N(5) | 2.350(10) | Cd(3)-N(2)#1 | 2.251(7) |
| Cd(1)-Cl(1) | 2.597(3) | Cd(3)-N(4) | 2.359(11) |
| Cd(2)-N(3)#2 | 2.258(7) | Cd(3)-Cl(2) | 2.481(3) |
| Cd(2)-N(3)#3 | 2.258(7) | Cd(3)-Cl(3)#5 | 2.658(4) |
| N(1)-Cd(1)-N(1)#1 | 100.6(3) | | |
| N(1)-Cd(1)-O(1) | 170.9(4) | N(3)#2-Cd(2)-Cl(3) | 97.69(16) |
| N(1)#1-Cd(1)-O(1) | 86.4(3) | N(3)#3-Cd(2)-Cl(3) | 97.69(16) |
| N(1)-Cd(1)-O(1)#1 | 86.4(3) | N(6)#4-Cd(2)-Cl(3) | 87.1(2) |
| N(1)#1-Cd(1)-O(1)#1 | 170.9(4) | N(3)#2-Cd(2)-Cl(1) | 84.02(15) |
| O(1)-Cd(1)-O(1)#1 | 86.0(6) | N(3)#3-Cd(2)-Cl(1) | 84.02(15) |
| N(1)-Cd(1)-N(5) | 87.1(2) | N(6)#4-Cd(2)-Cl(1) | 86.4(2) |
| N(1)#1-Cd(1)-N(5) | 87.1(2) | Cl(3)-Cd(2)-Cl(1) | 173.54(11) |
| O(1)-Cd(1)-N(5) | 87.6(3) | N(2)-Cd(3)-N(2)#1 | 102.1(4) |
| O(1)#1-Cd(1)-N(5) | 87.6(3) | N(2)-Cd(3)-N(4) | 91.1(2) |
| N(1)-Cd(1)-Cl(1) | 92.59(18) | N(2)#1-Cd(3)-N(4) | 91.1(2) |
| N(1)#1-Cd(1)-Cl(1) | 92.59(18) | N(2)-Cd(3)-Cl(2) | 128.89(18) |
| O(1)-Cd(1)-Cl(1) | 92.8(3) | N(2)#1-Cd(3)-Cl(2) | 128.89(18) |
| O(1)#1-Cd(1)-Cl(1) | 92.8(3) | N(4)-Cd(3)-Cl(2) | 91.0(2) |

| | | | |
|---|---|---|---|
| N(5)-Cd(1)-Cl(1) | 179.5(3) | N(2)-Cd(3)-Cl(3)#5 | 90.6(2) |
| N(3)#2-Cd(2)-N(3)#3 | 146.5(4) | N(2)#1-Cd(3)-Cl(3)#5 | 90.6(2) |
| N(3)#2-Cd(2)-N(6)#4 | 105.2(2) | N(4)-Cd(3)-Cl(3)#5 | 177.3(2) |
| N(3)#3-Cd(2)-N(6)#4 | 105.2(2) | Cl(2)-Cd(3)-Cl(3)#5 | 86.36(12) |

Complex **4**

| | | | |
|---|---|---|---|
| Cd(1)-N(1) | 2.296(10) | Cd(1)-Cl(1)#1 | 2.638(5) |
| Cd(1)-N(1)#1 | 2.296(10) | Cd(1)-Cl(1)#3 | 2.638(5) |
| Cd(1)-Cl(1)#2 | 2.638(5) | Cd(1)-Cl(1) | 2.638(5) |
| N(1)-Cd(1)-N(1)#1 | 180.0 | | |
| N(1)-Cd(1)-Cl(1)#2 | 91.8(2) | Cl(1)#2-Cd(1)-Cl(1)#3 | 180.0 |
| N(1)#1-Cd(1)-Cl(1)#2 | 88.2(2) | Cl(1)#1-Cd(1)-Cl(1)#3 | 95.9(2) |
| N(1)-Cd(1)-Cl(1)#1 | 91.8(2) | N(1)-Cd(1)-Cl(1) | 88.2(2) |
| N(1)#1-Cd(1)-Cl(1)#1 | 88.2(2) | N(1)#1-Cd(1)-Cl(1) | 91.8(2) |
| Cl(1)#2-Cd(1)-Cl(1)#1 | 84.1(2) | Cl(1)#2-Cd(1)-Cl(1) | 95.9(2) |
| N(1)-Cd(1)-Cl(1)#3 | 88.2(2) | Cl(1)#1-Cd(1)-Cl(1) | 180.00(17) |
| N(1)#1-Cd(1)-Cl(1)#3 | 91.8(2) | Cl(1)#3-Cd(1)-Cl(1) | 84.1(2) |

Complex **5**

| | | | |
|---|---|---|---|
| Cd(1)-N(7) | 2.309(4) | Cd(2)-N(6)#4 | 2.296(4) |
| Cd(1)-N(1)#1 | 2.330(3) | Cd(2)-N(2)#1 | 2.337(3) |
| Cd(1)-N(1) | 2.330(3) | Cd(2)-N(2) | 2.337(3) |
| Cd(1)-N(3)#2 | 2.348(3) | Cd(2)-N(4)#5 | 2.481(3) |
| Cd(1)-N(3)#3 | 2.348(3) | Cd(2)-N(4)#6 | 2.481(3) |
| Cd(1)-Cl(1) | 2.7622(15) | Cd(2)-Cl(1) | 2.6259(14) |
| N(7)-Cd(1)-N(1)#1 | 90.60 (11) | N(6)#4-Cd(2)-N(2)#1 | 91.02(10) |
| N(7)-Cd(1)-N(1) | 90.60(11) | N(6)#4-Cd(2)-N(2) | 91.02(10) |
| N(1)#1-Cd(1)-N(1) | 85.86(15) | N(2)#1-Cd(2)-N(2) | 95.94(14) |
| N(7)-Cd(1)-N(3)#2 | 96.85(10) | N(6)#4-Cd(2)-N(4)#5 | 100.07(10) |
| N(1)#1-Cd(1)-N(3)#2 | 171.68(10) | N(2)#1-Cd(2)-N(4)#5 | 87.19(10) |
| N(1)-Cd(1)-N(3)#2 | 90.34(10) | N(2)-Cd(2)-N(4)#5 | 168.44(10) |

| | | | |
|---|---|---|---|
| N(7)-Cd(1)-N(3)#3 | 96.85(10) | N(6)#4-Cd(2)-N(4)#6 | 100.07(10) |
| N(1)#1-Cd(1)-N(3)#3 | 90.34(11) | N(2)#1-Cd(2)-N(4)#6 | 168.44(10) |
| N(1)-Cd(1)-N(3)#3 | 171.68(10) | N(2)-Cd(2)-N(4)#6 | 87.19(10) |
| N(3)#2-Cd(1)-N(3)#3 | 92.44(14) | N(4)#5-Cd(2)-N(4)#6 | 87.65(15) |
| N(7)-Cd(1)-Cl(1) | 172.84(11) | N(6)#4-Cd(2)-Cl(1) | 178.47(11) |
| N(1)#1-Cd(1)-Cl(1) | 84.17(8) | N(2)#1-Cd(2)-Cl(1) | 87.96(7) |
| N(1)-Cd(1)-Cl(1) | 84.17(8) | N(2)-Cd(2)-Cl(1) | 87.96(7) |
| N(3)#2-Cd(1)-Cl(1) | 88.09(7) | N(4)#5-Cd(2)-Cl(1) | 81.02(7) |
| N(3)#3-Cd(1)-Cl(1) | 88.09(7) | N(4)#6-Cd(2)-Cl(1) | 81.02(7) |

[a] Symmetry codes: **1**: #1 -x+1/2, -y+2, z-1/2; #2 -x+1, y, z; #3 -x, y, z; #4 -x+1/2, -y+3, z+1/2; #5 x-1/2, -y+2, z+1/2; #6 -x+1/2, -y+2, z+1/2. **2**: #1 x, -y-1/2, z; #2 -x+1/2, -y, z-1/2; #3 x-1/2, y, -z-1/2; #4 x-1/2, -y+1/2, -z-1/2; #5 x, -y+1/2, z; #6 -x, -y, -z. **3**: #1 -x-2, y, z; #2 x-1/2, y-1/2, z; #3 -x-3/2, y-1/2, z; #4 -x-2, -y, z+1/2; #5 x, y+1, z. **4**: #1 -x-1/2, -y+1/2, z-1/2; #2 -x, -y+1/2, z; #3 x-1/2, y, -z-1/2.**5**: #1 x, -y+1/2, z; #2 -x+1/2, -y, z-1/2; #3 -x+1/2, y+1/2, z-1/2; #4 x+1/2, y, -z+1/2; #5 -x+1, y+1/2, -z; #6 -x+1, -y, -z.