Supporting Information

A Series of inorganic–organic hybrid cadmium borates with novel Cd-centred $[Cd@B_{14}O_{20}(OH)_6]^{2-}$ clusters

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Table S1. Selected bond length ranges (Å) of compounds **1-4**.

Compound	1	2	3	4
Cd-N	2.296(2)-2.296(2)	2.274(7)-2.274(7)	2.292(2)-2.292(2)	2.232(2)-2.232(2)
Cd-O	2.3494(18)-2.366(2)	2.346(4)-2.373(4)	2.3733(18)-2.382(2)	2.3532(18)-2.3789(17)
$B(1)_{\Delta}$-O	1.353(3)-1.385(3)	1.349(7)-1.383(7)	1.344(4)-1.395(4)	1.354(4)-1.387(4)
$B(2)_{T}$-O	1.424(3)-1.527(3)	1.419(7)-1.524(7)	1.442(3)-1.533(3)	1.435(3)-1.523(3)
$B(3)_{\Delta}$-O	1.352(3)-1.378(3)	1.348(7)-1.396(7)	1.352(4)-1.371(3)	1.350(3)-1.374(4)
$B(4)_{\Delta}$-O	1.353(3)-1.385(3)	1.358(7)-1.362(7)	1.354(4)-1.373(3)	1.353(3)-1.373(4)
$B(5)_{\Delta}$-O	1.352(4)-1.373(4)	1.346(7)-1.389(7)	1.340(3)-1.395(3)	1.349(4)-1.389(3)
$B(6)_{\Delta}$-O	1.355(3)-1.379(3)	1.351(7)-1.374(7)	1.356(4)-1.378(4)	1.357(3)-1.374(3)
$B(7)_{T}$-O	1.419(3)-1.526(3)	1.425(6)-1.520(7)	1.439(3)-1.524(3)	1.426(3)-1.527(3)

Table S2. Details of hydrogen bonds data of compounds **1-4**.

Interaction	D-H(Å)	H...A (Å)	D...A (Å)	<DHA (°)
Compound **1**				
N1-H1D...O11(#1)	0.89	2.01	2.878(4)	165.5
N1-H1D...O12(#1)	0.89	2.55	3.221(3)	132.2
N1-H1E...O4(#2)	0.89	2.04	2.910(3)	164.4
N1-H1F...O3	0.89	1.99	2.767(3)	145.5
O4-H4A...O7(#3)	0.82	1.93	2.748(3)	174.8
O3-H3A...O10(#1)	0.82	1.87	2.679(3)	171.4
O2-H2A...O13(#4)	0.82	1.91	2.714(3)	166.5
Compound **2**				
O1-H1A...O9(#1)	0.82	1.9	2.705(5)	165.8
O2-H2A...O12(#2)	0.82	1.88	2.687(5)	169.8
O3-H3A...O11(#3)	0.82	1.96	2.777(5)	173.4
N2-H2C...O8(#2)	0.89	1.98	2.866(7)	170.6
N2-H2C...O13(#2)	0.89	2.57	3.190(7)	126.9
N2-H2D...O3(#4)	0.89	2.07	2.912(6)	157.9
N2-H2E...O2	0.89	1.94	2.775(6)	155.3
Compound **3**				
O1-H1B...O6(#1)	0.85	2.53	3.384(3)	179.9
O2-H2D...O11(#2)	0.82	2.1	2.806(3)	144.6
O11-H11A...O4(#3)	0.82	1.95	2.751(3)	164.3
N2-H2B...O9(#4)	0.86	1.78	2.629(3)	169.6
N2-H2B...O7(#4)	0.86	2.65	3.174(3)	120.5
Compound **4**				
O2-H2B...O7(#1)	0.82	2	2.739(3)	149.4
O3-H3F...O1(#2)	0.82	1.8	2.594(3)	162.9
O3-H3F...O10(#2)	0.82	2.68	3.102(3)	113.9
O5-H5C...O12(#3)	0.82	2	2.808(3)	168.8
N3-H3C...O10(#4)	0.89	2.43	3.053(3)	127.5
N3-H3D...O3(#3)	0.89	2.03	2.884(3)	159.1
N3-H3E...O7(#5)	0.89	2.44	3.095(3)	131.0

Symmetry codes: For **1**: (#1) -*x*+1, *y*+1/2, -*z*+1/2; (#2) -*x*+2, *y*+1/2, -*z*+1/2; (#3) -*x*+1, *y*-1/2, -*z*+1/2; (#4) *x*-1, *y*, z. For **2**: (#1) *x*-1, *y*, *z*; (#2) -*x*+1, *y*+1/2, -*z*+1/2; (#3) -*x*+1, *y*-1/2, -*z*+1/2; (#4) -*x*+2, *y*+1/2, -*z*+1/2. For **3**: (#1) -*x*-1, *y*-1/2, -*z*+1/2; (#2) -*x*-2, -*y*, -*z*; (#3) *x*-1, *y*, *z*; (#4) -*x*-1, *y*-1/2, -*z*+1/2. For **4**: (#1) -*x*+1, -*y*+2, -*z*; (#2) *x*-1, *y*, *z*; (#3) -*x*+1, -*y*+1, -*z*; (#4) -*x*+2, -*y*+1, -*z*; (#5) *x*+1, *y*-1, *z*.

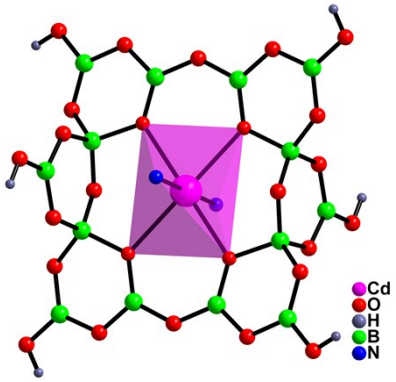

Figure S1. The fundamental building block of $[N_2Cd@B_{14}O_{20}(OH)_6]$ of compounds **1-4**.

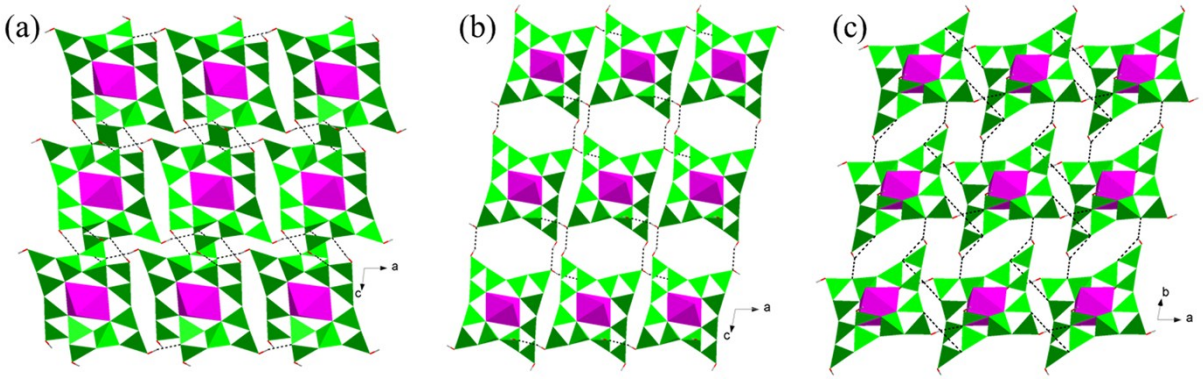

Figure S2. View of the layer of (a) **1** with two types narrow 8-MRs in the *ac* plane, (b) **3** with quasi-hexagonal and narrow 8-MRs in the *ac* plane, and (c) **4** with two types 6-MR in the *ab* plane.

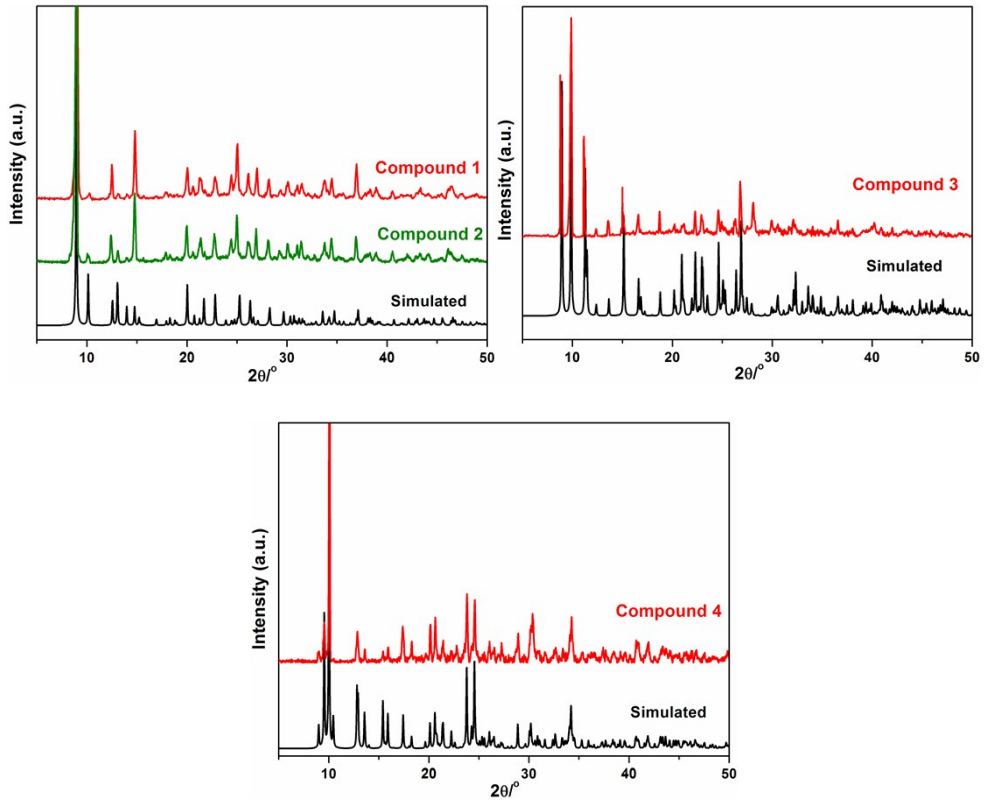

Figure S3. Simulated and experimental powder XRD patterns of compounds **1-4**.

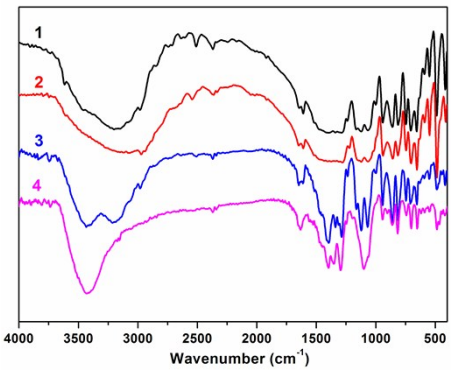

Figure S4. IR spectra of compounds **1-4**.

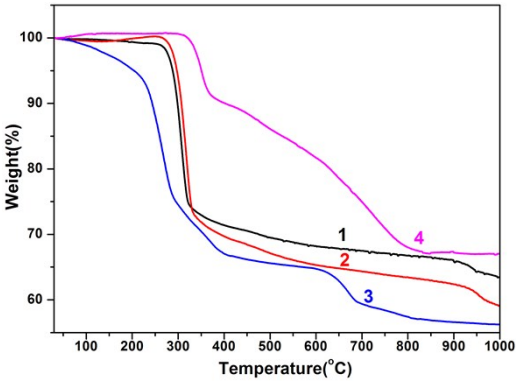

Figure S5. TG curves of compounds **1-4**.