# Supporting Information

## Design, Structural Diversity and Properties of Novel Zwitterionic Metal-Organic Frameworks

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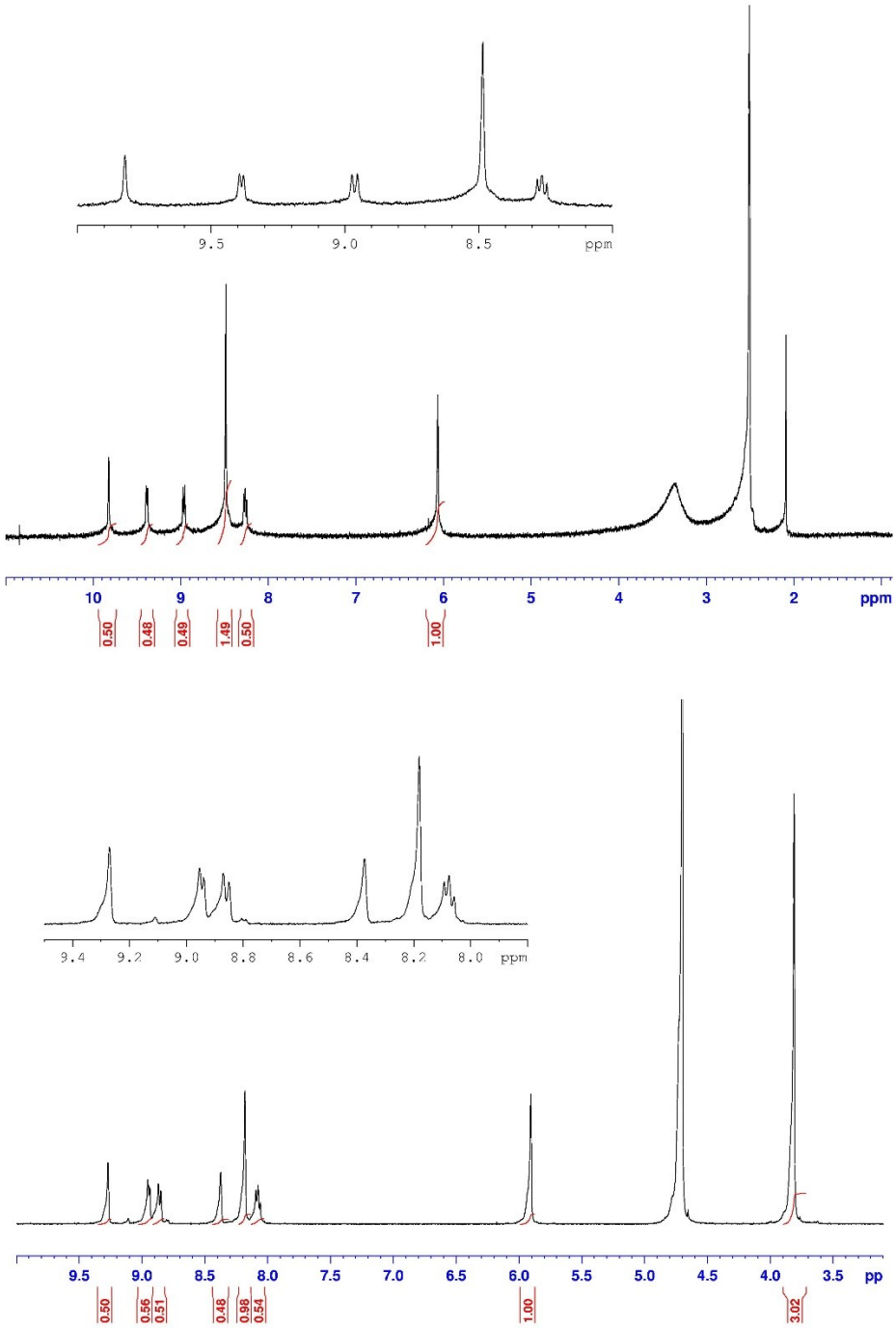


**Figure S1.** $^{1}$H NMR of **$Me_2$HL1** in $D_2O$ (top) and **H3L1** in DMSO (bottom).

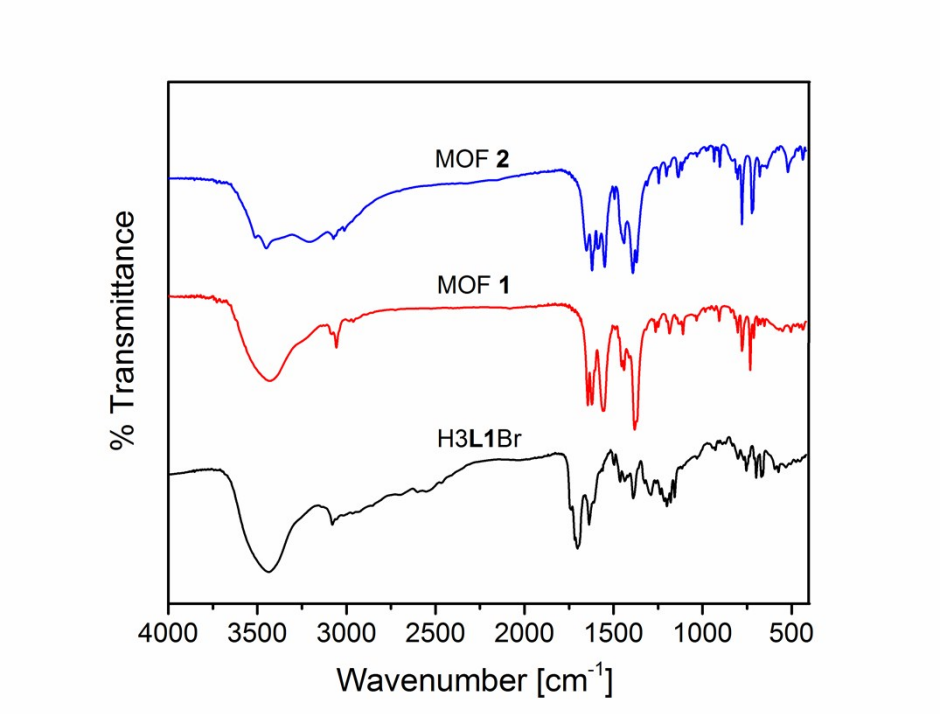


**Figure S2.** IR data of **H3L1** (black), MOF **1** (red) and **2** (blue).

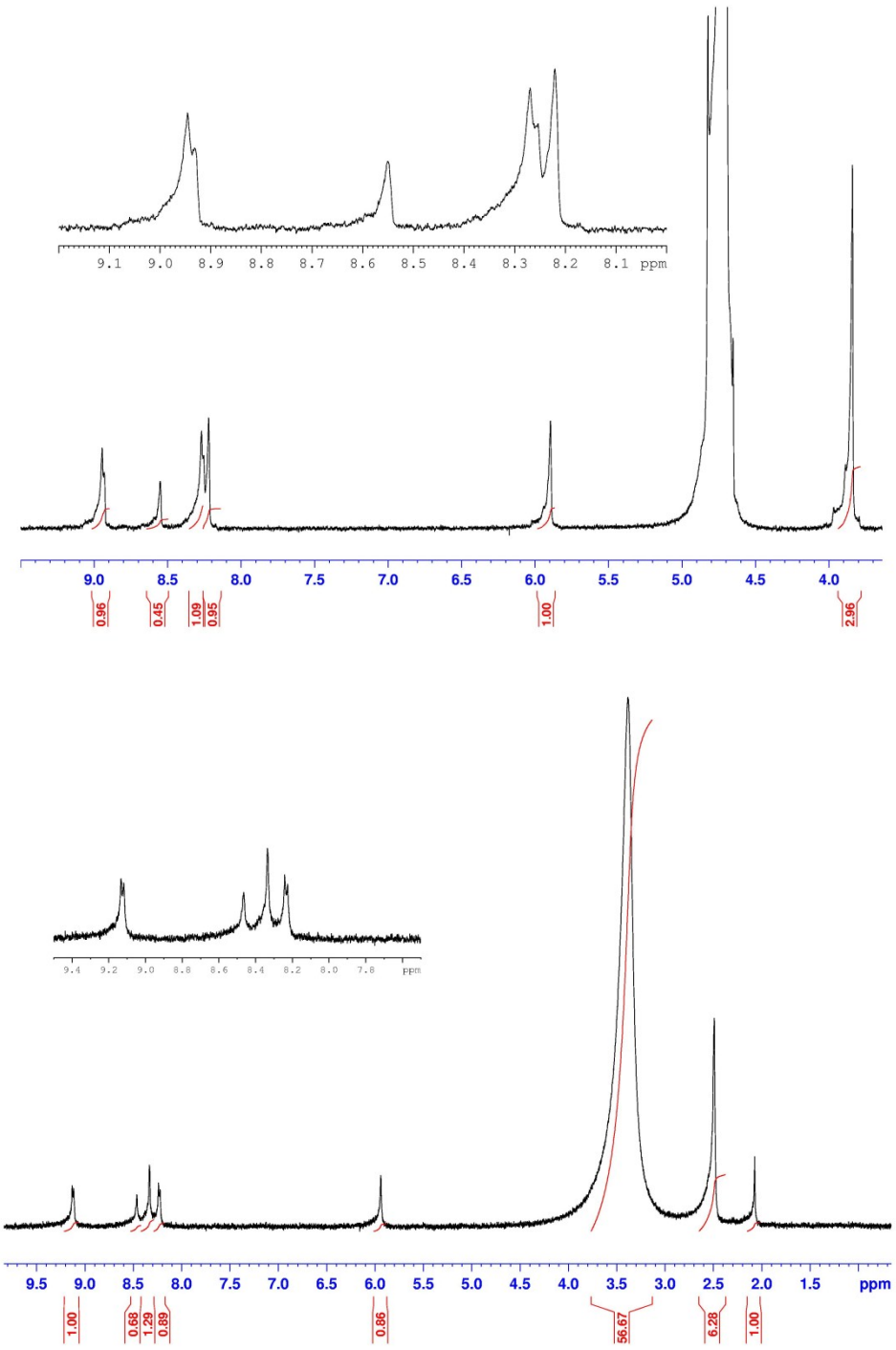


**Figure S3.** $^{1}$H NMR of **$Me_2$HL2** in $D_2O$ (top) and **H3L2** in DMSO (bottom).

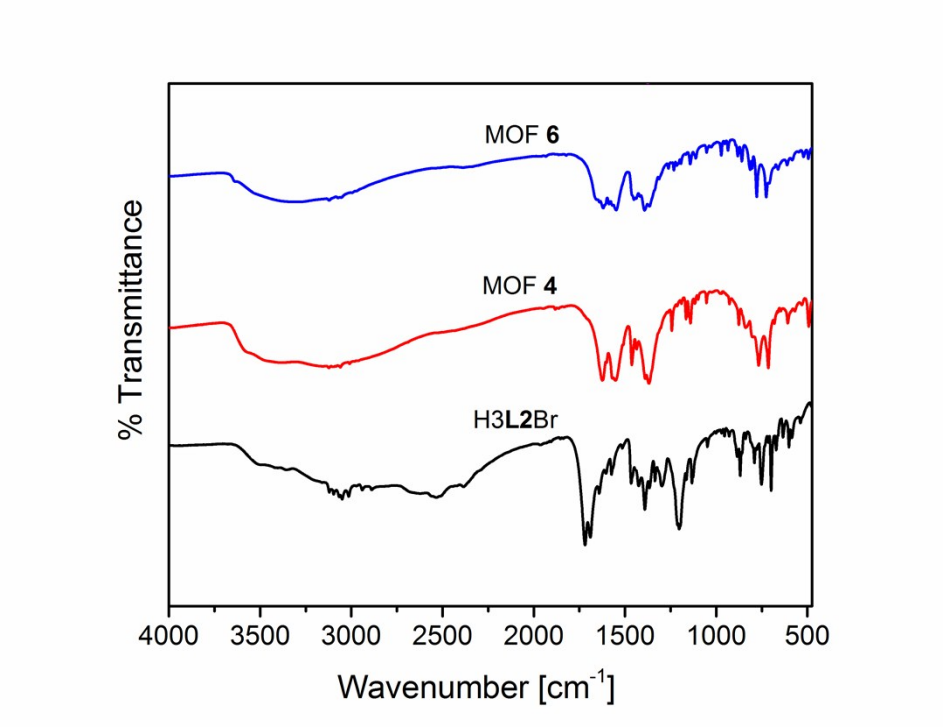


**Figure S4.** IR data of **H3L2** (black), MOF **4** (red), and **6** (blue).

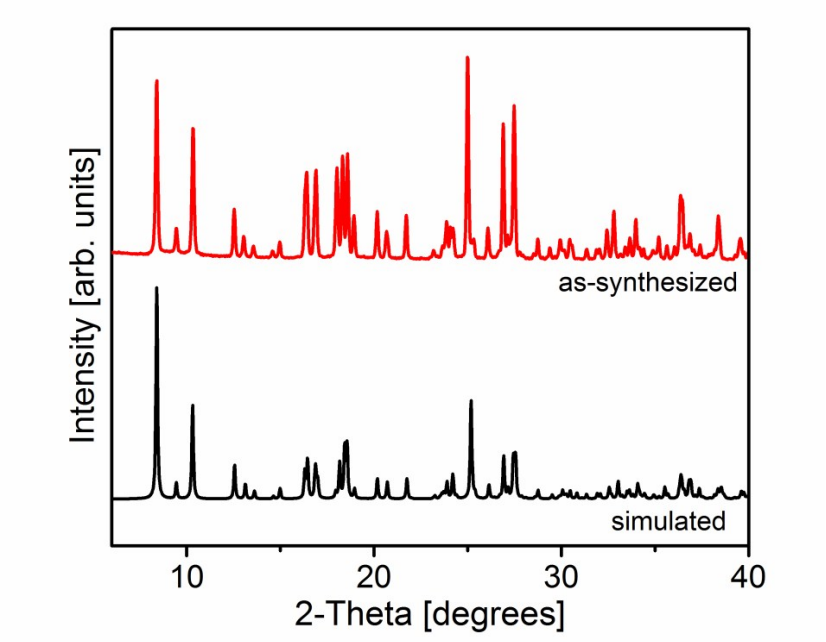


**Figure S5.** Powder X-ray diffraction patterns for simulated (black) and as-synthesized (red) forms of **1**.

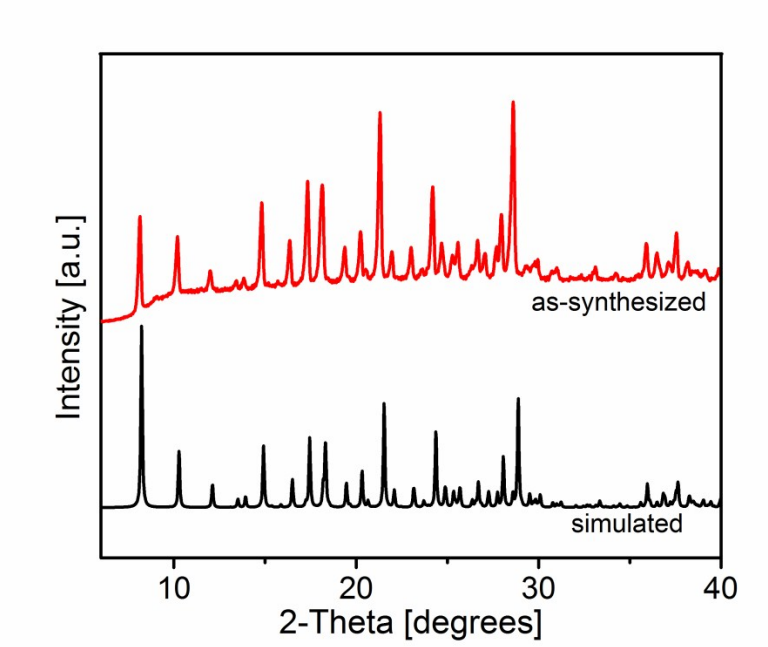


**Figure S6.** Powder X-ray diffraction patterns for simulated (black) and as-synthesized (red) forms of **2**.

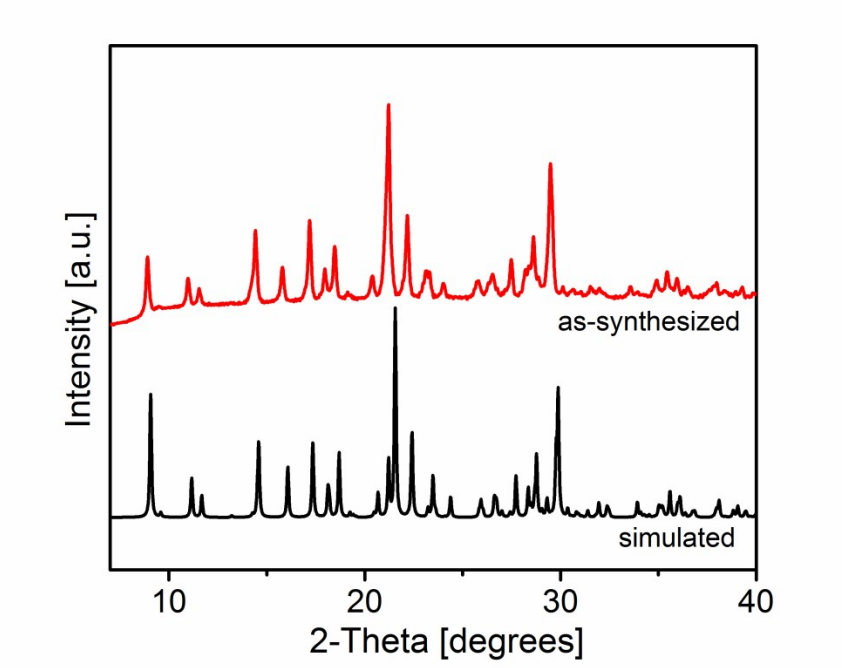


**Figure S7.** Powder X-ray diffraction patterns for simulated (black) and as-synthesized (red) forms of **4**.

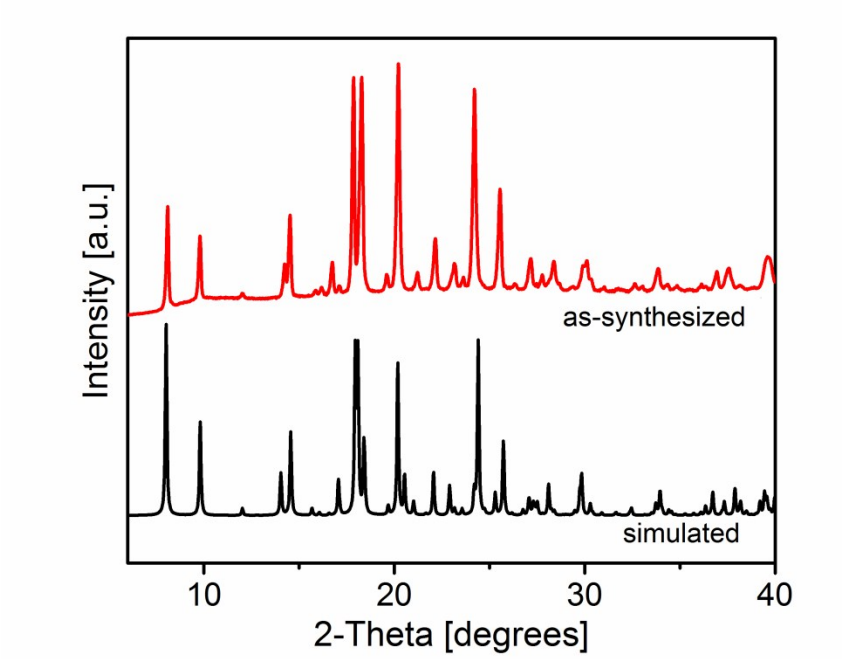


**Figure S8.** Powder X-ray diffraction patterns for simulated (black) and as-synthesized (red) forms of **6.**

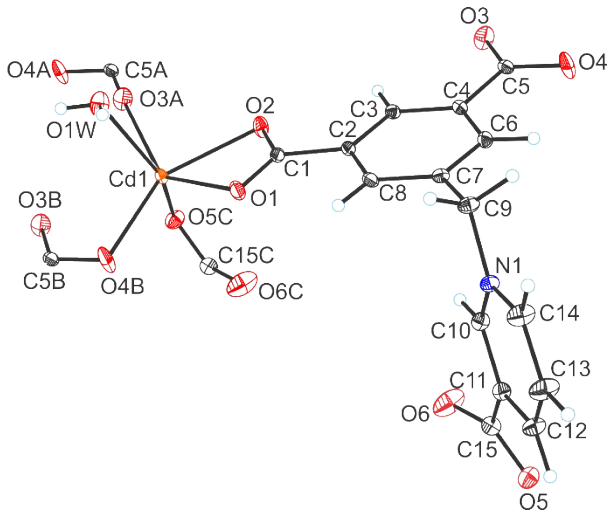


**Figure S9.** Crystal structure of **1** with view of coordination sphere of Cd(II) cation with displacement ellipsoids drawn at 30% probability level. Selected atoms are labelled. Symmetry codes: A = -x + 1, -y + 1, -z; B = x, y -1, z; C = -x + 1, -y + 1, -z +1.

**Table S1**. Selected bond lengths [Å] and angles [deg] in **1**.

| | | | | | |
|---|---|---|---|---|---|
| Cd1-O5 | 2.2706(14) | O4A-Cd1-O2C | 97.53(5) | O4A-Cd1-O3B | 128.92(5) |
| Cd1-O4A | 2.2761(14) | O3B-Cd1-O2c | 137.67(5) | O2C-Cd1-O1C | 55.85(5) |
| Cd1-O3B | 2.3082(14) | O5-Cd1-O1W | 92.29(5) | O1W-Cd1-O1C | 86.00(5) |
| Cd1-O2C | 2.3201(13) | O4A-Cd1-O1W | 85.53(6) | O5-Cd1-C1C | 111.63(5) |
| Cd1-O1W | 2.3879(14) | O3B-Cd1-O1W | 74.60(5) | O4A-Cd1-C1C | 10.9.92(5) |
| Cd1-O1C | 2.4017(13) | O2C-Cd1-O1W | 98.85(5) | O3C-Cd1-C1C | 117.98(5) |
| Cd1-C1C | 2.6892(17) | O5-Cd1-O1C | 124.04(5) | O2C-Cd1-C1C | 28.09(5) |
| O5-Cd1-O4A | 98.98(6) | O4A-Cd1-O1C | 82.79(5) | O1W-Cd1-C1C | 94.31(5) |
| O5-Cd1-O3B | 79.68(5) | O3B-Cd1-O1C | 139.83(5) | O1C-Cd1-C1C | 27.86(5) |

Symmetry transformations used to generate equivalent atoms:
A = -x + 1, -y + 2, -z + 1; B = x, y, z + 1; C = -x + 1, -y + 1, -z + 1

**Table S2**. Bond lengths [Å] and angles [deg] of hydrogen bonding interactions in **1**.

| **D–H** | ***d*(H···A) [Å]** | **<DHA [deg]** | ***d*(D···A) [Å]** | **A** |
|---|---|---|---|---|
| C9-H9A | 2.272 | 155.99 | 3.201 | O2 [ x-1, y, z ] |
| C13-H13 | 2.299 | 163.77 | 3.222 | O6 [ x-1, y, z ] |
| O1W-H1WA | 1.940 | 163.52 | 2.755 | O5 [ -x+1, -y+2, -z+2 ] |
| O1W-H1WB | 2.152 | 156.11 | 2.940 | O4 [ x+1, y, z+1 ] |
| O2W-H2WA | 2.349 | 156.32 | 3.136 | O4 [ x-1, y, z ] |
| O3W-H3WA | 1.944 | 144.32 | 2.672 | O2W |
| O3W-H3WB | 2.436 | 148.25 | 3.181 | O1W [ x-1, y, z-1 ] |

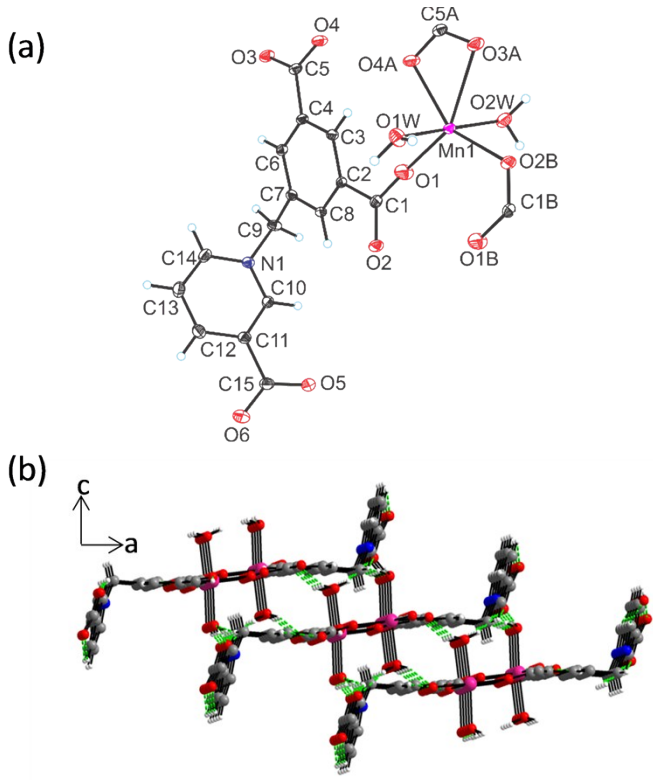


**Figure S10.** (a) Crystal structure of **2** with view of coordination sphere of Mn(II) cation with displacement ellipsoids drawn at the 30% probability level. Selected atoms are labelled. Symmetry code: A = -x + 2, -y + 1, -z + 2; B = -x + 2, -y + 2, -z + 2; (b) Perspective view of **2** along *b*-axis showing intermolecular hydrogen bonding interactions stabilizing the framework, dashed green lines indicate the hydrogen bonding interactions.

**Table S3**. Selected bond lengths [Å] and angles [deg] in **2**.

| | | | | | |
|---|---|---|---|---|---|
| Mn1-O1 | 2.0734(10) | O1-Mn1-O1W | 90.75(4) | O4B-Mn1-O3B | 56.89(3) |
| Mn1-O2A | 2.1085(9) | O2A-Mn1-O1W | 87.15(4) | O1W-Mn1-O3B | 91.40(3) |
| Mn1-O4B | 2.2038(9) | O4B-Mn1-O1W | 91.85(4) | O2W-Mn1-O3B | 86.13(3) |
| Mn1-O1W | 2.2073(10) | O1-Mn1-O2W | 94.14(4) | O1-Mn1-C5B | 120.91(4) |
| Mn1-O2W | 2.2123(10) | O2A-Mn1-O2W | 87.45(4) | O2A-Mn1-C5B | 119.41(4) |
| Mn1-O3B | 2.4172(9) | O4B-Mn1-O2W | 91.35(4) | O4B-Mn1-C5B | 28.35(4) |
| Mn1-C5B | 2.6399(12) | O1W-Mn1-O2W | 174.04(4) | O1W-Mn1-C5B | 92.76(4) |
| O1-Mn1-O2A | 119.67(4) | O1-Mn1-O3B | 149.49(4) | O2W-Mn1-C5B | 87.67(4) |
| O1-Mn1-O4B | 92.62(4) | O2A-Mn1-O3B | 90.84(3) | O3B-Mn1-C5B | 28.57(4) |

Symmetry transformations used to generate equivalent atoms:
A = -x + 2, -y + 2, -z + 2; B = -x + 2, -y + 1, -z + 2

**Table S4.** Bond lengths [Å] and angles [deg] of hydrogen bonding interactions in **2**.

| D–H | *d*(H···A) [Å] | <DHA [deg] | *d*(D···A) [Å] | A |
|---|---|---|---|---|
| O1W-H1WB | 1.808 | 174.46 | 2.669 | O4 [ -x+3, -y+2, -z+2 ] |
| O2W-H2WA | 2.023 | 162.24 | 2.864 | O4 [ x-1, y+1, z ] |
| O2W-H2WB | 1.842 | 164.26 | 2.690 | O6 [ x-1, y, z ] |
| O3W-H3WA | 2.164 | 143.46 | 2.892 | O4 [ -x+3, -y+1, -z+3 ] |
| O3W-H3WB | 1.905 | 165.66 | 2.737 | O5 |
| C9-H9A | 2.308 | 169.30 | 3.266 | O1W [ -x+3, -y+1, -z+2] |
| C9-H9B | 2.648 | 122.31 | 3.271 | O3 [ x+1, y, z ] |
| C14-H14 | 2.288 | 145.28 | 3.098 | O3W [ x, y-1, z ] |
| C13-H13 | 2.576 | 153.17 | 3.431 | O2 [ -x+3, -y+1, -z+3 ] |

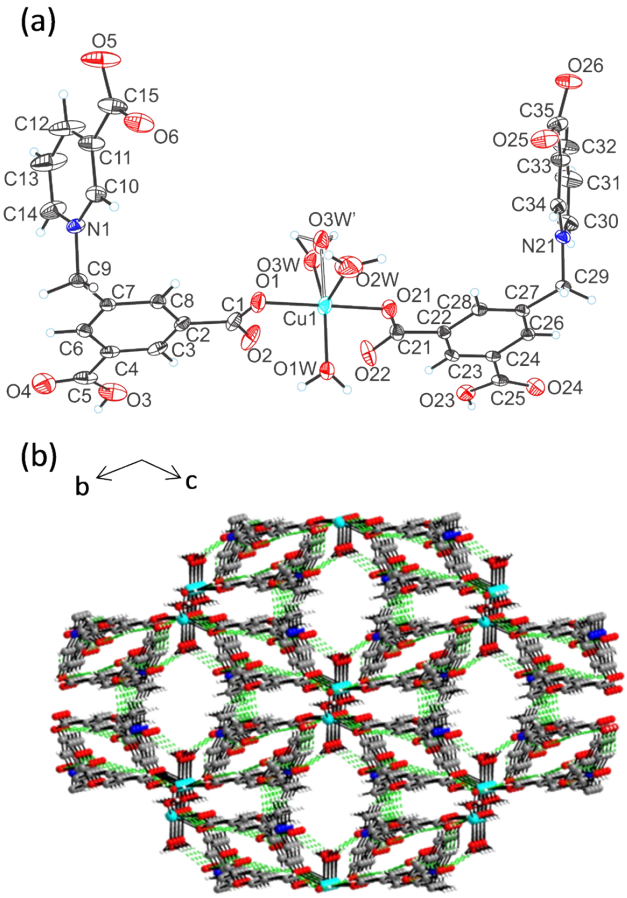


**Figure S11.** (a) Crystal structure of **3** with view of the coordination sphere of the Cu(II) cation with displacement ellipsoids drawn at the 30% probability level. Selected atoms are labelled; (b) Crystal packing view along *a*-axis. Green lines indicate the hydrogen bonding interactions present.

**Table S5**. Selected bond lengths [Å] and angles [deg] in **3**.

| | | | | | |
|---|---|---|---|---|---|
| Cu1-O21 | 1.9378(14) | O21-Cu1-O3W' | 90.29(11) | O1-Cu1-O2W | 93.26(8) |
| Cu1-O1 | 1.9499(14) | O1-Cu1-O3W' | 89.49(11) | O1W-Cu1-O2W | 95.71(8) |
| Cu1-O1W | 1.9878(15) | O1W-Cu1-O3W' | 177.72(12) | O3W'-Cu1-O2W | 83.05(14) |
| Cu1-O3W' | 2.007(4) | O21-Cu1-O3W | 90.58(11) | O3W-Cu1-O2W | 109.90(15) |
| Cu1-O3W | 2.030(4) | O1-Cu1-O3W | 88.61(11) | O21-Cu1-O1W | 91.58(6) |
| Cu1-O2W | 2.230(2) | O1W-Cu1-O3W | 154.36(14) | O1-Cu1-O1W | 88.67(6) |
| O21-Cu1-O1 | 178.64(7) | O21-Cu1-O2W | 88.05(7) | | |

**Table S6**. Bond lengths [Å] and angles [deg] of hydrogen bonding interactions in **3**.

| **D–H** | ***d*(H···A) [Å]** | **<DHA [deg]** | ***d*(D···A) [Å]** | **A** |
|---|---|---|---|---|
| O3-H3 | 1.681 | 160.81 | 2.489 | O5 [ x, y, z+1 ] |
| O23-H23 | 1.691 | 170.16 | 2.523 | O26 [ x, y, z+1 ] |
| C29-H29A | 2.472 | 152.73 | 3.382 | O6 [ -x+2, -y+2, -z ] |
| O1W-H1WA | 1.819 | 168.50 | 2.647 | O22 [ -x+2, -y+2, -z+1 ] |
| O1W-H1W B | 1.849 | 161.57 | 2.659 | O2 [ -x+2, -y+2, -z+1 ] |
| O3W-H3WA | 1.901 | 138.19 | 2.685 | O24 [ -x+2, -y+3, -z+1 ] |
| O3W'-H3WA | 1.901 | 157.92 | 2.698 | O24 [ -x+2, -y+3, -z+1 ] |
| O3W-H3WB | 2.046 | 127.48 | 2.776 | O4 [ -x+3, -y+2, -z+1 ] |
| O3W'-H3WB | 2.046 | 170.80 | 2.878 | O4 [ -x+3, -y+2, -z+1 ] |

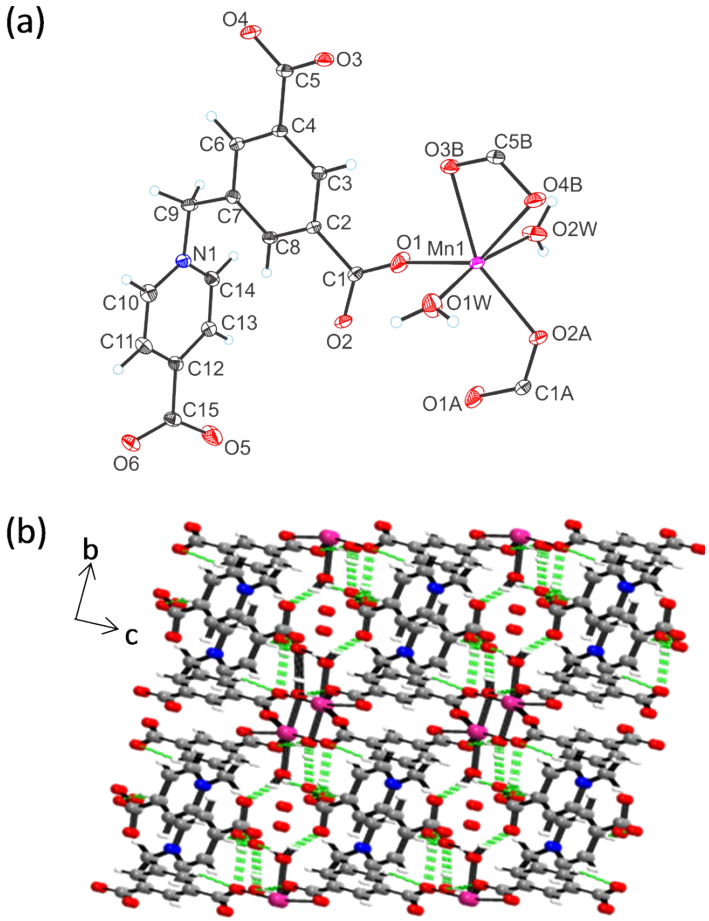


**Figure S12.** (a) Crystal structure of **4** with view of the coordination sphere of the Mn(II) cation with displacement ellipsoids drawn at the 30% probability level. Selected atoms are labelled. Symmetry code: A = - x, - y, - z; B = - x, - y, - z + 1; (b) Perspective view of ZW MOF **4** along the crystallographic *a*-axis. Green lines indicate the hydrogen bonding interactions prevalent.

**Table S7**. Selected bond lengths [Å] and angles [deg] in **4**.

| | | | |
|---|---|---|---|
| Mn1-O1 | 2.1203(11) | O1-Mn1-O2A | 122.94(4) |
| Mn1-O2A | 2.1310(10) | C1-O1-Mn1 | 165.65(11) |
| Mn1-O3 | 2.2512(14) | O3-Mn1-C5 | 92.18(4) |
| Mn1-O4 | 2.3254(15) | O4-Mn1-C | 88.64(18) |
| Mn1-O1W | 2.1623(11) | O1W-Mn1-O2W | 167.81(11) |
| Mn1-O2W | 2.170(10) | O2W-Mn1-O1W | 167.81(11) |

Symmetry transformations used to generate equivalent atoms:
A = -x, -y, -z

**Table S8**. Bond lengths [Å] and angles [deg] of hydrogen bonding interactions in **4.**

| D–H | *d*(H···A) [Å] | <DHA [deg] | *d*(D···A) [Å] | A |
|---|---|---|---|---|
| O1W-H1WB | 1.942 | 175.41 | 2.780 | O4 [ x+1, y, z-1 ] |
| O1W-H1WA | 1.887 | 177.65 | 2.726 | O5 [ x+1, y, z ] |
| O2W-H2WA | 1.861 | 164.10 | 2.678 | O6 [ x+1, y+1, z ] |
| O2W-H2WB | 1.918 | 161.14 | 2.726 | O5 [ -x-1, -y, -z ] |
| O4W-H4WB | 2.137 | 156.02 | 2.953 | O2 |
| O4W-H4WB’ | 2.551 | 127.93 | 3.161 | O2W [ -x, -y, -z ] |

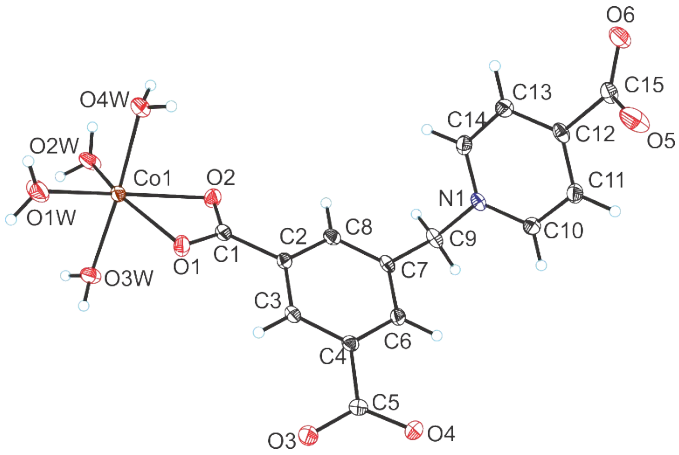


**Figure S13.** Crystal structure of **5** with view of the coordination sphere of the Co(II) cation with displacement ellipsoids drawn at the 30% probability level. Selected atoms are labelled.

**Table S9**. Selected bond lengths [Å] and angles [deg] in **5**.

| | | | | | |
|---|---|---|---|---|---|
| Co1-O1 | 2.0951(11) | O2-Co1-C1 | 30.32(4) | O1-Co1-O4W | 96.75(4) |
| Co1-O2 | 2.2461(10) | O1W-Co1-O1 | 106.95(5) | O2W-Co1-C1 | 122.95(5) |
| Co1-C1 | 2.4990(14) | O1W-Co1-O2 | 165.95(5) | O2W-Co1-O3W | 83.96(4) |
| Co1-O1W | 2.0205(12) | O1W-Co1-C1 | 137.03(5) | O2W-Co1-O4W | 94.73(4) |
| Co1-O2W | 2.0233(11) | O1W-Co1-O2W | 99.83(6) | O3W-Co1-O2 | 97.59(4) |
| Co1-O3W | 2.1296(10) | O1W-Co1-O3W | 88.78(4) | O3W-Co1-C1 | 91.60(4) |
| Co1-O4W | 2.1132(10) | O1W-Co1-O4W | 87.84(4) | O4W-Co1-O2 | 86.13(4) |
| O1-Co1-O2 | 60.73(4) | O2W-Co1-O1 | 151.16(5) | O4W-Co1-C1 | 92.17(4) |
| O1-Co1-C1 | 30.42(4) | O2W-Co1-O2 | 93.89(4) | O4W-Co1-O3W | 176.12(4) |

**Table S10**. Bond lengths [Å] and angles [deg] of hydrogen bonding interactions in **5**.

| D–H | *d*(H···A) [Å] | <DHA [deg] | *d*(D···A) [Å] | A |
|---|---|---|---|---|
| O1W-H1WA | 1.845 | 179.09 | 2.685 | O5W |
| O1W-H1WB | 1.911 | 172.27 | 2.745 | O4 [ x+1, y, z ] |
| O2W-H2WA | 1.900 | 143.45 | 2.623 | O6 [ x+1, -y+5/2, z +1/2] |
| O3W-H3WA | 1.875 | 167.66 | 2.701 | O5 [ -x+1, -y+2, -z +1] |
| O3W-H3WB | 1.964 | 171.79 | 2.798 | O5 [ x+1, -y+3/2, z +1/2] |
| O4W-H4WA | 2.066 | 159.42 | 2.868 | O4 [ -x+1, -y+2, -z +1] |
| O4W-H4WB | 1.868 | 175.39 | 2.706 | O5 [ x+1, -y+5/2, z +1/2] |
| O5W-H5WA | 2.029 | 174.87 | 2.867 | O2 [ -x, y+1/2, -z +3/2] |
| O5W-H5WB | 2.202 | 151.60 | 2.968 | O2W [ x, -y+3/2, z -1/2] |

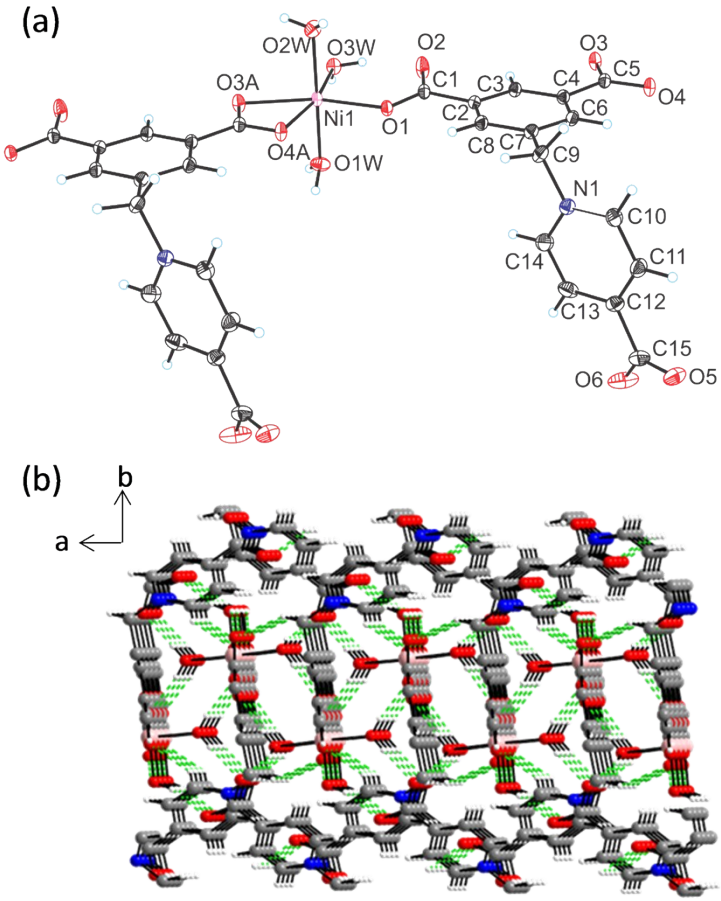


**Figure S14.** (a) Crystal structure of **6** with view of the coordination sphere of the Ni(II) cation with displacement ellipsoids drawn at the 30% probability level. Selected atoms are labelled. Symmetry code: A = x, y, z + 1; (b) Perspective view of ZW MOF **6** along the crystallographic *a*-axis. Green lines indicate the hydrogen bonding interactions prevalent.

**Table S11**. Selected bond lengths [Å] and angles [deg] in **6**.

| | | | | | |
|---|---|---|---|---|---|
| Ni1-O1 | 2.086(16) | O1-Ni1-C5A | 127.53(7) | O1W-Ni1-O2W | 178.11(7) |
| Ni1-O3A | 2.1560(17) | O1-Ni1-O1W | 90.01(7) | O2W-Ni1-O3A | 90.49(7) |
| Ni1-O4A | 2.0828(17) | O1-Ni1-O2W | 90.95(7) | O2W-Ni1-O4A | 91.50(7) |
| Ni1-C5A | 2.448(2) | O1-Ni1-O3W | 97.10(7) | O2W-Ni1-C5A | 91.51(7) |
| Ni1-O1W | 2.0420(17) | O4A-Ni1-O3A | 62.38(6) | O3W-Ni1-O3A | 104.17(7) |
| Ni1-O2W | 2.0648(17) | O4A-Ni1-C5A | 31.18(7) | O3W-Ni1-O4A | 135.37(7) |
| Ni1-O3W | 2.0347(16) | O1W-Ni1-O3A | 89.22(7) | O3W-Ni1-C5A | 90.90(7) |
| O1-Ni1-O3A | 158.73(6) | O1W-Ni1-O4A | 90.01(7) | O3W-Ni1-O1W | 87.37(7) |
| O1-Ni1-O4A | 96.37(6) | O1W-Ni1-C5A | 89.20(7) | O3W-Ni1-O2W | 125.04(16) |

Symmetry transformations used to generate equivalent atoms:
A = x, y, z + 1

**Table S12**. Bond lengths [Å] and angles [deg] of hydrogen bonding interactions in **6**.

| **D–H** | ***d*(H···A) [Å]** | **<DHA [deg]** | ***d*(D···A) [Å]** | **A** |
|---|---|---|---|---|
| C9-H9A | 2.464 | 145.90 | 3.331 | O2 [ -x, -y+2, -z-1 ] |
| C9-H9B | 2.555 | 155.28 | 3.479 | O5 [ x-1/2, -y+5/2, z+1/2 ] |
| C10-H10 | 2.576 | 117.23 | 3.127 | O6 [ x-1, y, z ] |
| C14-H14 | 2.385 | 140.77 | 3.178 | O3 [ -x-1, -y+2, -z-1 ] |
| O1W-H1WA | 1.989 | 169.35 | 2.819 | O1 [ -x-1, -y+2, -z ] |
| O1W-H1WB | 1.892 | 167.94 | 2.719 | O5 [ -x-3/2, y-1/2, -z-1/2 ] |
| O2W-H2WA | 1.884 | 177.61 | 2.723 | O4 [ -x, -y+2, -z-1 ] |
| O2W-H2WB | 2.064 | 157.77 | 2.859 | O5 [ -x-1/2, y-1/2, -z-1/2 ] |
| O3W-H3WA | 1.874 | 164.17 | 2.693 | O6 [ -x+3/2, y-1/2, -z-1/2 ] |
| O3W-H3WB | 1.874 | 145.38 | 2.610 | O2 |

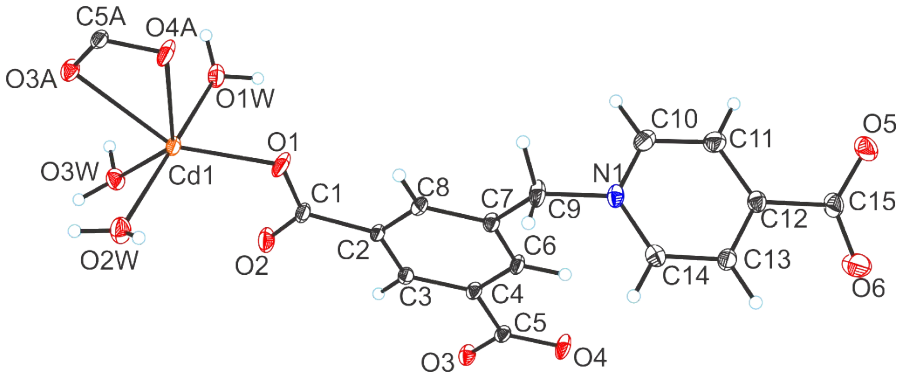


**Figure S15.** Crystal structure of **7** with view of the coordination sphere of the Cd(II) cation with displacement ellipsoids drawn at the 30% probability level. Selected atoms are labelled. Symmetry code: A = x, y - 1, z.

**Table S13**. Selected bond lengths [Å] and angles [deg] in **7**.

| | | | | | |
|---|---|---|---|---|---|
| Cd1-O1 | 2.2305(11) | O1-Cd1-O4A | 83.67(4) | O2W-Cd1-O3A | 87.54(4) |
| Cd1-O3A | 2.4446(10) | O1-Cd1-O1W | 90.89(4) | O2W-Cd1-O4A | 93.37(4) |
| Cd1-O4A | 2.4222(11) | O1-Cd1-O2W | 93.49(4) | O2W-Cd1-O1W | 172.16(4) |
| Cd1-O1W | 2.2812(11) | O1-Cd1-O3W | 136.48(4) | O2W-Cd1-O3W | 92.78(4) |
| Cd1-O2W | 2.2642(11) | O4A-Cd1-O3A | 53.65(3) | O3W-Cd1-O3A | 86.01(4) |
| Cd1-O3W | 2.2796(11) | O1W-Cd1-O3A | 93.66(4) | O3W-Cd1-O4A | 138.79(4) |
| O1-Cd1-O3A | 137.25(4) | O1W-Cd1-O4A | 93.58(4) | O3W-Cd1-O1W | 79.58(4) |

Symmetry transformations used to generate equivalent atoms:
A = x, y - 1, z

**Table S14.** Bond lengths [Å] and angles [deg] of hydrogen bonding interactions in **7**.

| **D–H** | ***d*(H···A) [Å]** | **<DHA [deg]** | ***d*(D···A) [Å]** | **A** |
|---|---|---|---|---|
| O1W-H1WA | 2.625 | 133.48 | 3.260 | O6 [ -x+1, -y+1, -z+1 ] |
| O1W-H1WB | 2.007 | 148.80 | 2.760 | O6 [ x-1, y-1, z ] |
| O2W-H2WA | 1.900 | 169.83 | 2.731 | O6W [ -x+1, -y, -z ] |
| O2W-H2WB | 1.914 | 173.26 | 2.749 | O4 [ -x+1, -y+1, -z ] |
| O3W-H3WA | 1.857 | 168.53 | 2.686 | O3 [ -x, -y+1, -z ] |
| O3W-H3WB | 1.929 | 169.00 | 2.758 | O6W [ x-1, y, z ] |
| O5W-H5WA | 2.428 | 150.19 | 3.185 | O6 [ -x+1, -y+1, -z+1 ] |
| O5W-H5WA | 2.233 | 114.60 | 2.693 | O4W' |
| O5W-H5WB | 1.978 | 162.47 | 2.790 | O1 |
| O6W-H6WA | 1.844 | 172.12 | 2.718 | O6 [ x, y-1, z ] |
| O6W-H6WB | 1.864 | 169.43 | 2.694 | O5W |

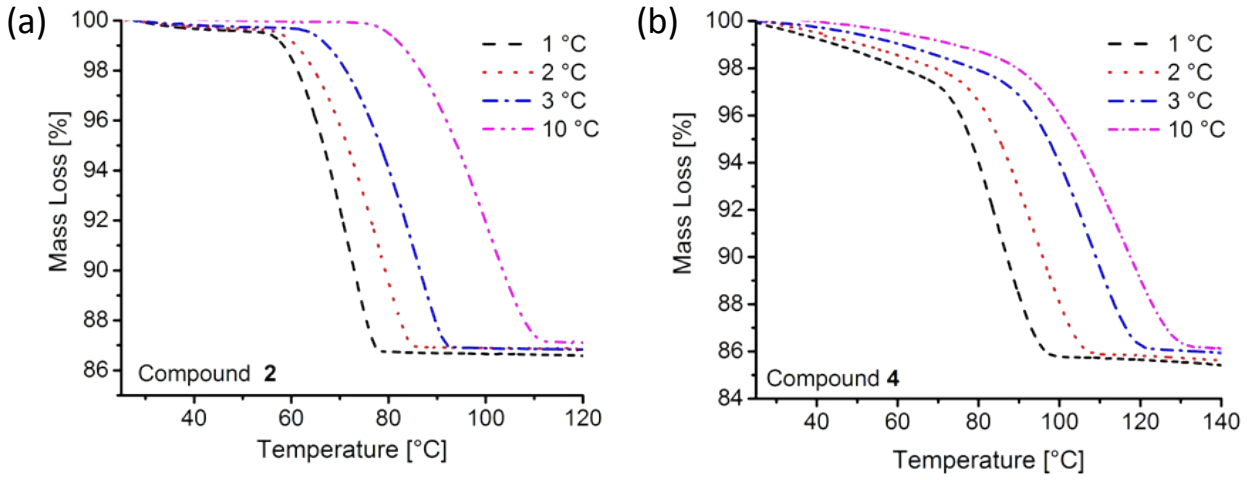


**Figure S16.** Heating rate dependent TGA curves for compounds (a) **2** and (b) **4.**

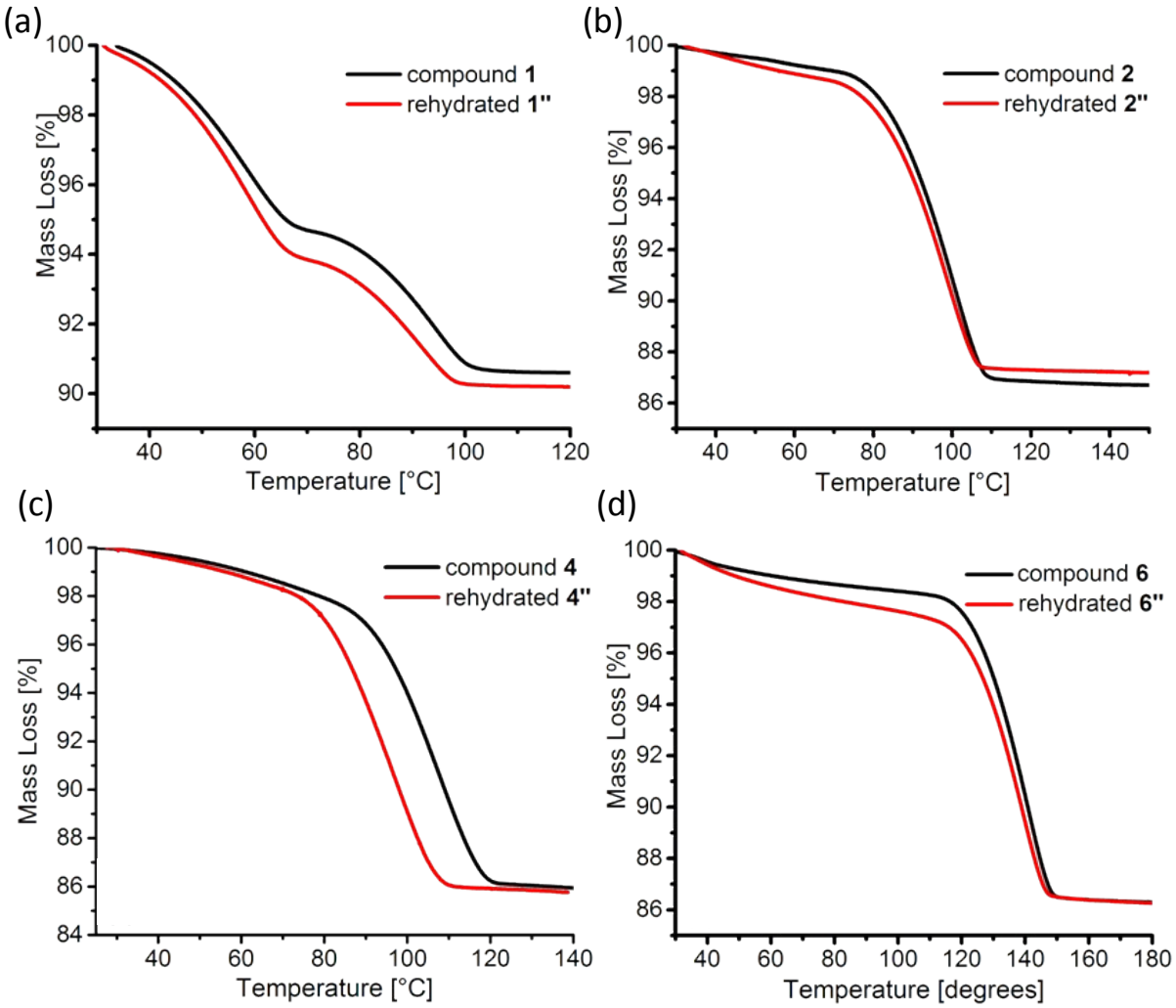


**Figure S17.** TGA curves of the rehydrated compounds (a) **1**, (b) **2**, (c) **4** and (d) **6** compared with their pristine analogues.

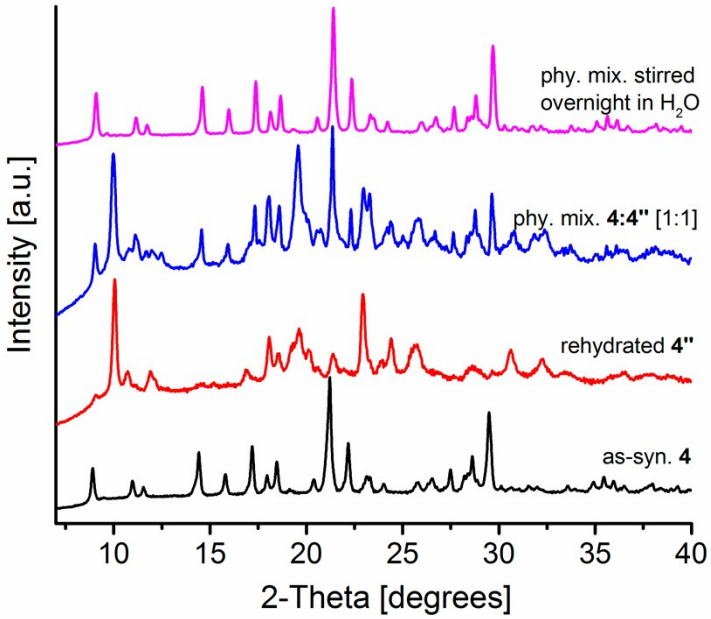


**Figure S18.** Powder X-ray diffraction patterns for as-synthesized **4** (black), rehydrated **4''** (red), physical mixture of **4** and **4''** [1:1] (blue) and physical mixture stirred in water overnight (majenta).