Supplementary Information

Oxozinc Carboxylates: A Predesigned Platform for Modelling Prototypical Zn-MOFs' Reactivity Toward Water and Donor Solvents

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Experimental Section

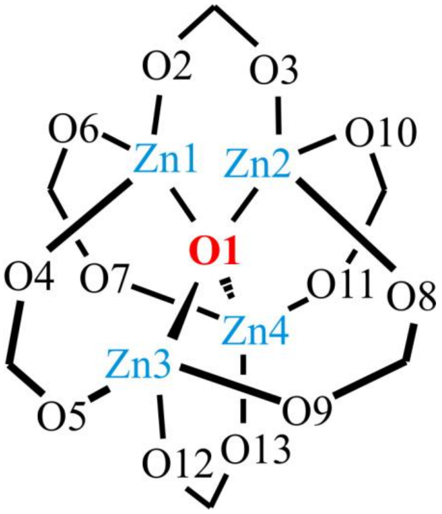
General Remarks

All manipulations were conducted under a nitrogen atmosphere by using standard Schlenk techniques. All other reagents were purchased from commercial vendors. Solvents were dried and distilled prior to use. Redistilled water was degassed carefully by six freeze-pump-thaw cycles before use. NMR spectra were acquired on Varian Mercury 400 Spectrometer. The infrared spectra were recorded on a FT-IR Perkin-Elmer System 2000 spectrometer.

Synthesis of 2: Degassed H_2O (18 µL, 1.00 mmol) was added dropwise to a suspension of **1** (1,004 g, 1.00 mmol) in THF (10 mL) and stirred for further 4h. Compound **2** was obtained as colourless crystals after crystallization from THF/hexane mixture at 4°C; isolated yield ca. 84 %. Elemental analysis (%) calcd for $C_{54}H_{56}O_{17}Zn_4$ (sample dried in vacuo for 10h): C 50.50, H 3.65; found: C 50.67, H 3.86; ^{1}H NMR ($CDCl_3$, 400.10 MHz, 298 K): δ = 1.85 (m, 12H; -CH_{2THF}), 2.78 (s, 2H, H_2O), 3.75 (m, 12H; -OCH_{2THF}) 7.41 (m, 12H, Ar), 7.52 (m, 6H, Ar), 8.22 ppm (m, 12H, Ar).

Synthesis of 3: $ZnEt_2$ (0.492 g, 4.00 mmol) was added dropwise to a suspension of 9-antracenecarboxylic acid (1.33 g, 6.00 mmol) in THF (10 mL) at –78°C. After 4h, degassed water (18 µL, 1.00 mmol) was added, and the solution was stirred for an additional 20 h. Yellow cubic crystals were isolated by crystallization from a THF solution at -20 ºC; isolated yield ca. 89%. Elemental analysis (%) calcd for $C_{102}H_{78}O_{16}Zn_4$: C 67.29, H 4.28; found: C 67.42, H 4.39; ^{1}H NMR ($CDCl_3$, 400.10 MHz, 298 K): δ = 1.84 (m, 12H; CH_{2THF}), 3.74 (m, 12H; OCH_{2THF}), 7.14 - 8.48 ppm (m, 54H, Ar).

Table S1. Comparison of selected Bond Lengths (Å) in $[Zn_4O]^{6+}$ core for **1, 2, 3** and MOF-5.

Bond	**1**	**2**	**3**	**MOF-5[1]**	**MOF-5[2]**	**Projection of the $[Zn_4O]^{6+}$ core of the compounds under considerations coordinated by six bridging carboxylate**
O1-Zn1	1.950(6)	2.027(4)	1.999(6)	1.960(2)	1.9409(8)	
O1-Zn2	1.936(6)	1.925(5)	1.986(6)	1.959(6)	1.9409(8)	
O1-Zn3	1.950(6)	1.932(4)	1.917(6)	1.959(2)	1.9409(8)	
O1-Zn4	1.936(6)	1.921(4)	1.923(5)	1.959(2)	1.9409(8)	
Zn1-O2	1.950(8)	2.118(4)	2.028(6)	1.948(4)	1.922(4)	
Zn1-O4	1.935(8)	2.114(4)	2.035(7)	1.944(3)	1.922(4)	
Zn1-O6	1.929(8)	2.067(4)	2.075(6)	1.944(3)	1.922(4)	
Zn2-O3	1.949(8)	1.939(5)	2.042(6)	1.952(4)	1.922(4)	
Zn2-O8	1.941(8)	1.950(4)	2.035(6)	1.951(3)	1.922(4)	
Zn2-O10	1.945(8)	1.977(5)	2.042(6)	1.951(3)	1.922(4)	
Zn3-O5	1.935(8)	1.925(4)	1.929(7)	1.944(4)	1.922(4)	
Zn3-O9	1.929(8)	1.962(5)	1.942(6)	1.948(4)	1.922(4)	
Zn3-O12	1.950(8)	1.989(5)	1.977(6)	1.944(4)	1.922(4)	
Zn4-O7	1.941(8)	1.942(4)	1.939(7)	1.944(4)	1.922(4)	
Zn4-O11	1.945(8)	1.984(5)	1.941(7)	1.948(4)	1.922(4)	
Zn4-O13	1.949(8)	1.980(5)	1.989(6)	1.944(4)	1.922(4)	

X-Ray Crystallography

Data were collected using the 'oil drop technique' to mount crystals on a Nonius Kappa-CCD equipped with an Oxford Cryostream low-temperature device. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Powder X-ray diffraction

Powder XRD data were collected on a Siemens D5005 diffractometer (Bruker AXS). Measurements employed Ni-filtered Cu Kα radiation of a copper sealed tube charged with 40kV voltage and 40mA current and Bragg-Brentano geometry with beam divergence of 1 deg. in the scattering plane. Diffraction patterns were measured in the range of 5-70 degrees of scattering angle by step scanning with step of 0.02 degree.

Crystal data for 2, $C_{54}H_{56}O_{17}Zn_4$: M = 1238.55, crystal dimensions 0.42 × 0.30 × 0.20 mm^3, monoclinic, space group P 21/c (no. 14), a = 23.1389(9) Å, b = 11.6701(5) Å c = 24.0951(5) Å, β = 117.427(2) °, U = 5775.1(4) $Å^3$, Z = 4, F(000) = 2544, D_c = 1.424 g m^3, T = 100(2)K, μ(Mo-Kα) = 1.707 mm^{-1}, Nonius Kappa-CCD diffractometer, θ_{max} = 21.97 °, 7042 unique reflections. The structure was solved by direct methods using the SHELXS97[3] program and was refined by full matrix least–squares on F^2 using the program SHELXL97.[4] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced at geometrically idealized coordinates with a fixed isotropic displacement parameter equal to 1.2. Refinement converged at $R1$ = 0.0814, $wR2$ = 0.1161 for all data and 692 parameters ($R1$ = 0.0541, $wR2$ = 0.1051 for 5152 reflections with $I_o > 2\sigma(I_o)$). The goodness-of-fit on F^2 was equal 1.034. A weighting scheme $w = [\sigma^2(F_o^2 + (0.0418P)^2 + 3.1964P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the final stage of refinement. The residual electron density = + 0.47 /- 0.43 $eÅ^{-3}$. The structure contained molecules of THF. The THF molecules appear to be highly disordered and it was difficult to model their positions and distribution reliably. Therefore, the SQUEEZE function of PLATON (van der Sluis & Spek, 1990; Spek, 2001) was used to eliminate the contribution of the electron density in the solvent region from the intensity data. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. **CCDC- 830651**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

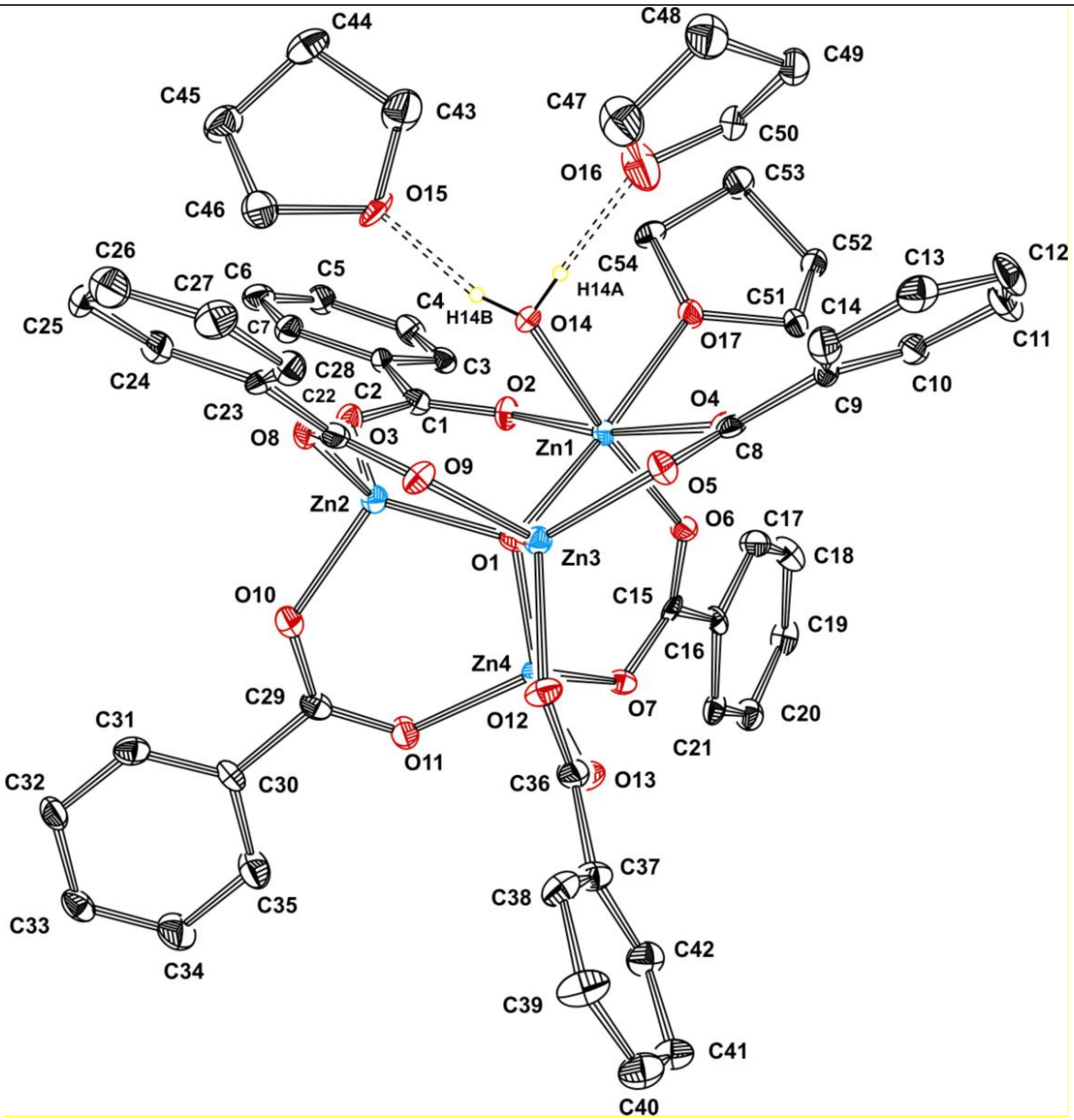


Figure S1. ORTEP diagram of molecular structure of **2** with thermal ellipsoids set at 30% probability; hydrogen atoms have been omitted for clarity

Table S2. Selected Bond Lengths (Å) and Angles (deg) for Compound **2**.

Zn1 – O1	2.027(4)
Zn1 – O2	2.118(4)
Zn1 – O4	2.114(4)
Zn1 – O6	2.067(4)
Zn1 – O14	2.102(5)
Zn1 – O17	2.183(4)
Zn2 – O1	1.925(5)
Zn2 – O3	1.939(5)
Zn2 – O8	1.950(4)
Zn2 – O10	1.977(5)
Zn3 – O1	1.932(4)
Zn3 – O5	1.925(4)

Zn3 – O9	1.962(5)
Zn3 – O12	1.989(5)
Zn4 – O1	1.921(4)
Zn4 – O7	1.942(4)
Zn4 – O11	1.984(5)
Zn4 – O13	1.980(5)
O14 – H14A···O16	2.669(7)
O14 – H14B···O15	2.727(2)

Zn1 – O1 – Zn2	109.1(2)
Zn1 – O1 – Zn3	110.0(2)
Zn1 – O1 – Zn4	113.7(2)
Zn2 – O1 – Zn3	104.6(2)
Zn2 – O1 – Zn4	109.9(2)
Zn3 – O1 – Zn4	109.1(2)
O1 – Zn1 –O2	94.13(17)
O1 – Zn1 – O4	98.11(17)
O1 – Zn1 –O6	97.82(17)
O1 – Zn1 –O14	87.94(19)
O1 – Zn1 – O17	175.91(18)
O1 – Zn2 – O3	115.29(19)
O1 – Zn2 – O8	115.38(19)
O1 – Zn2 – O10	109.78(19)
O1 – Zn3 – O5	118.0(2)
O1 – Zn3 – O9	113.7(2)
O1 – Zn3 – O12	108.58(18)
O1 – Zn4 – O7	116.79(19)
O1 – Zn4 – O11	110.5(2)
O1 – Zn4 – O13	113.16(18)
O14 – Zn1 – O17	88.07(19)
O14 – Zn1 – O2	91.51(19)
O14 – Zn1 – O4	87.53(19)
O14 – Zn1 – O6	174.22(19)
O2 – Zn1 – O17	85.06(17)
O2 – Zn1 – O4	167.68(18)
O2 – Zn1 – O6	87.64(18)
O8 – Zn2 – O3	109.0(2)
O8 – Zn2 – O10	101.99(19)
O3 – Zn2 – O10	109.78(19)
O5 – Zn3 – O9	103.41(19)
O5 – Zn3 – O12	108.2(2)
O9 – Zn3 – O12	104.02(19)
O7 – Zn4 – O11	106.64(19)
O7 – Zn4 – O13	106.79(19)
O11 – Zn4 – O13	101.7(2)
O14 – H14A···O16	178.17
O14 – H14B···O15	161.03

Crystal data for 3, $C_{102}H_{78}O_{16}Zn_4$: M = 1821.21, crystal dimensions 0.42 × 0.30 × 0.20 mm^3, triclinic, space group P –1 (no. 2), a = 14.302(3) Å, b = 14.733(3) Å c = 23.048(5) Å, α = 103.534(14) °, β = 98.096(8) °, γ = 105.510(16) °, U = 4441.1(18) $Å^3$, Z = 2, F(000) = 1876, D_c = 1.362 g m^3, T = 100(2)K, μ(Mo-Kα) = 1.134 mm^{-1}, Nonius Kappa-CCD diffractometer, θ_{max} = 21.97 °, 9746 unique reflections. The structure was solved by direct methods using the SHELXS97 program and was refined by full matrix least–squares on F^2 using the program SHELXL97. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced at geometrically idealized coordinates with a fixed isotropic displacement parameter equal to 1.2. Refinement converged at $R1$ = 0.1084, $wR2$ = 0.1822 for all data and 1118 parameters, restraints 29 ($R1$ = 0.0672, $wR2$ = 0.1588 for 6049 reflections with $I_o > 2\sigma(I_o)$). The goodness-of-fit on F^2 was equal 1.047. A weighting scheme $w = [\sigma^2(F_o^2 + (0.0418P)^2 + 3.1964P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the final stage of refinement. The residual electron density = + 0.49 /- 0.52 e$Å^{-3}$. The structure contained molecules of THF. The THF molecules appear to be highly disordered and it was difficult to model their positions and distribution reliably. Therefore, the SQUEEZE function of PLATON (van der Sluis & Spek, 1990; Spek, 2001) was used to eliminate the contribution of the electron density in the solvent region from the intensity data.

To improve the geometrical parameters, ultimately restrained instructions DFIX and SIMU were applied in the refinement. Disorder and/or high thermal motion were noted, usually associated with THF molecule. Of particular note were the observations of two positions of each of the carbons [C96-C97] in the THF molecule (in a 2.5 : 1 ratio).

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. **CCDC- 830650**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

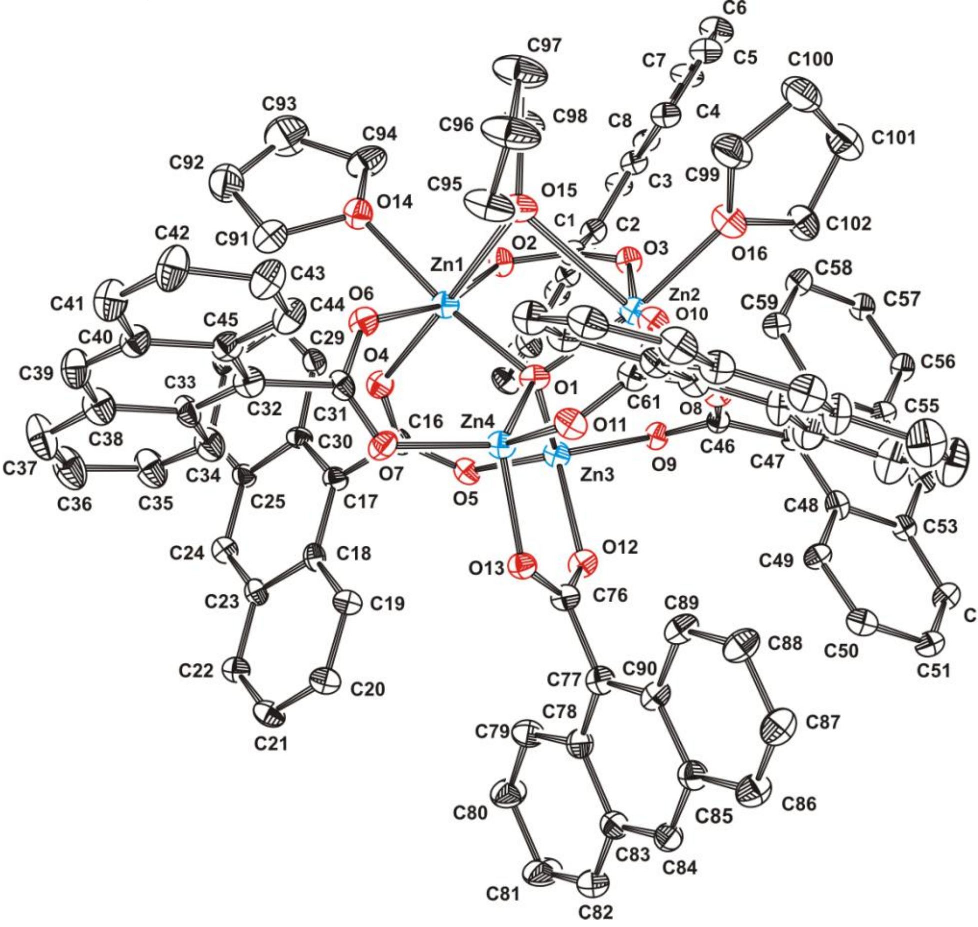


Figure S2. ORTEP diagram of molecular structure of **3** with thermal ellipsoids set at 30% probability; hydrogen atoms have been omitted for clarity.

Table S3. Selected Bond Lengths (Å) and Angles (deg) for Compound **3**.

Zn1 – O1	1.997(6)
Zn1 – O2	2.030(6)
Zn1 – O4	2.034(7)
Zn1 – O6	2.075(6)
Zn1 – O14	2.158(7)
Zn1 – O15	2.431(7)
Zn2 – O1	1.987(6)
Zn2 – O3	2.042(6)
Zn2 – O8	2.036(6)
Zn2 – O10	2.043(6)
Zn2 – O15	2.587(8)
Zn2 – O16	2.139(8)
Zn3 – O1	1.916(5)
Zn3 – O5	1.927(7)
Zn3 – O9	1.943(6)
Zn3 – O12	1.978(6)
Zn4 – O1	1.923(5)
Zn4 – O7	1.938(7)
Zn4 – O11	1.941(7)
Zn4 – O13	1.988(6)
Zn1 – O1 – Zn2	108.2(3)
Zn1 – O1 – Zn3	110.5(2)
Zn1 – O1 – Zn4	110.7(3)
Zn2 – O1 – Zn3	107.6(3)
Zn2 – O1 – Zn4	115.8(3)
Zn3 – O1 – Zn4	103.8(3)
Zn1 – O15 – Zn2	80.0(2)
O1 – Zn1 –O2	97.0(2)
O1 – Zn1– O4	99.3(3)
O1 – Zn1 – O6	98.4(2)
O1 – Zn1 – O14	171.3(3)
O1 – Zn1 – O15	81.0(2)
O1 – Zn2 – O3	96.0(2)
O1 – Zn2 – O8	99.5(3)
O1 – Zn2 – O10	99.5(2)
O1 – Zn2 – O15	77.3(2)
O1 – Zn2 – O16	170.2(3)
O1 – Zn3 – O5	111.8(3)
O1 – Zn3 – O9	113.0(3)
O1 – Zn3 – O12	113.8(2)
O1 – Zn4 – O7	118.4(3)
O1 – Zn4 – O11	111.7(3)
O1 – Zn4 – O13	114.5(2)

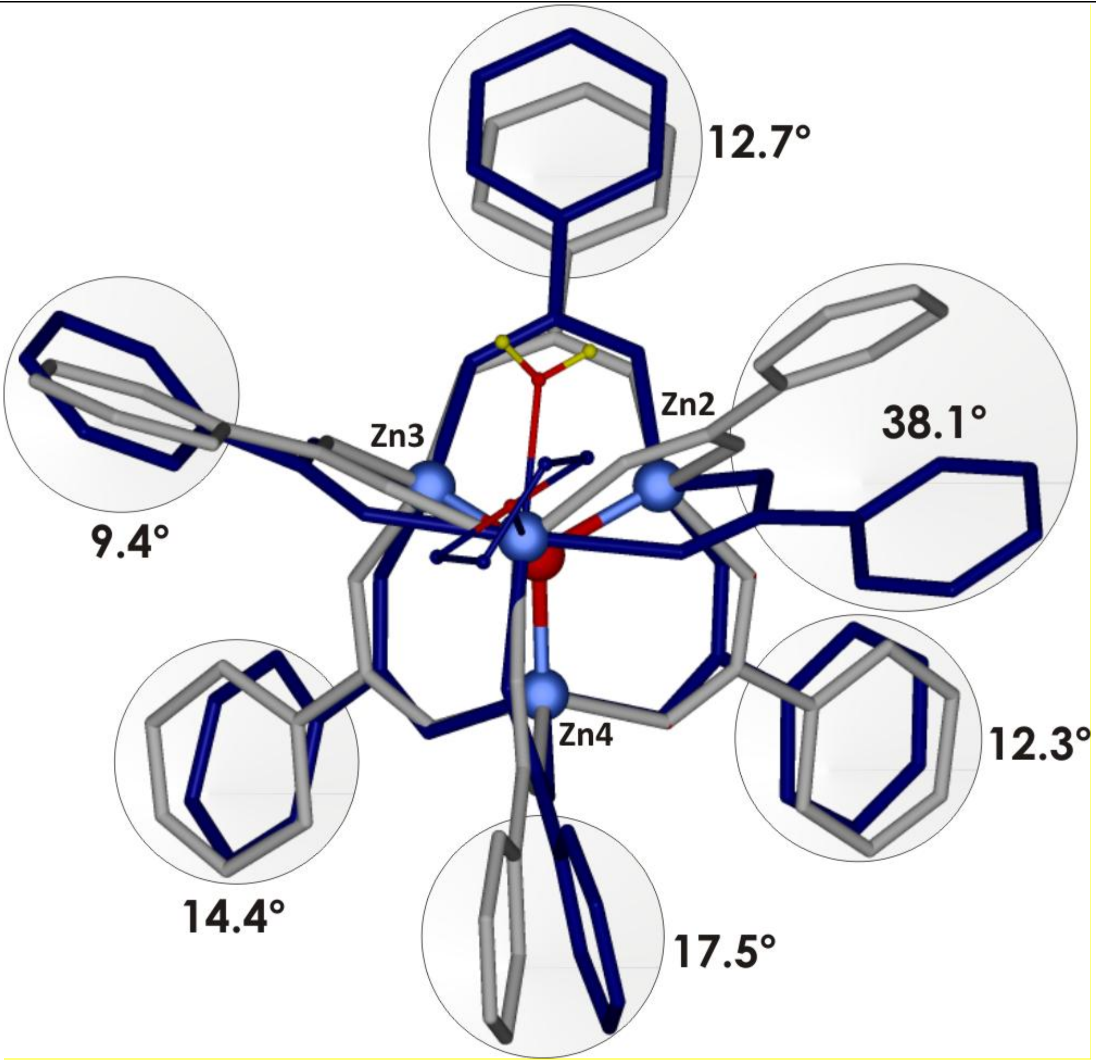


Figure S3. Overlay of the molecular structures of **1** (gray) and **2** (blue) showing the effect of the coordinated H_2O and THF molecules on the the prototypical Zn-MOF core; the measure of ligand distortion is defined as a dihedral angle between carboxylate groups' planes of benzoate ligands in **1** and **2**.

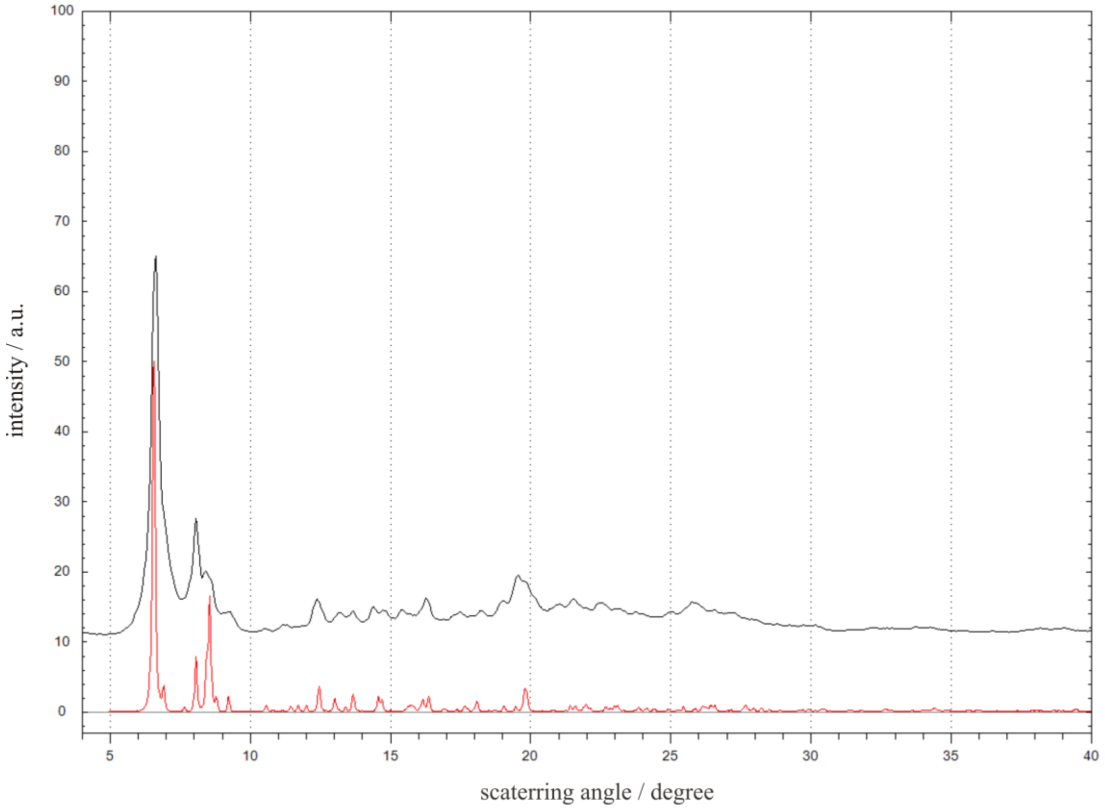


Figure S4. The PXRD patterns calculated from single crystal reflection data for **2** (red line) and for as synthesized **2** (black line)

We were unable to obtain good quality PXRD pattern for the bulk phase of **2** at ambient conditions, however single crystal XRD measurements for several crystals obtained from the same batch of **2** provided the same unit cell parameters.

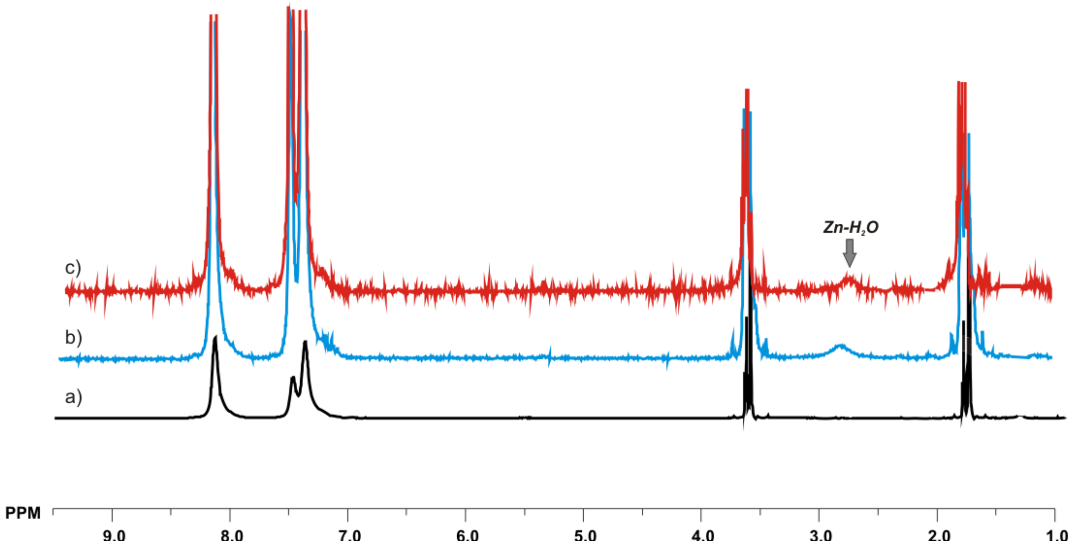


Figure S5. ^{1}H NMR spectrum for a) **1**, b) **2**, c) post-reaction mixture of **2** in THF-D_8

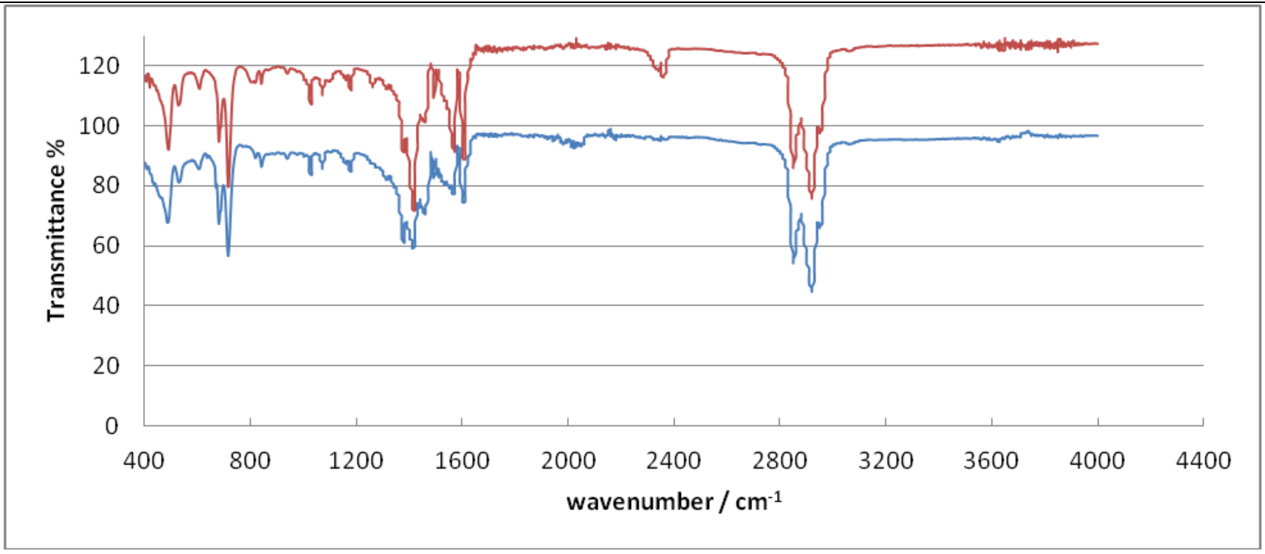


Figure S6. IR spectrum for **1** (blue) and post-reaction mixture of **2** (red).

References

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[1] J. Hafizovic, M. Bjorgen, U. Olsbye, P. D. C. Dietzel, S. Bordiga, C. Prestipino, C. Lamberti and K. P. Lillerud *J. Am. Chem. Soc.*, 2007, **129**, 3612-3620.

[2] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Science*, 2002, **295**, 469-472.

[3] SHELXS-97, Program for Structure Solution: G. M. Sheldrick, *Acta Crystallogr.*, Sect. A 1990, **46**, 467.

[4] G. M. Sheldrick, SHELXL-97, Program for Structure Refinement, Universität Göttingen, 1997.