Supporting Information

Self-assembly, crystal structures and properties of metal-3,4,5-tris(carboxymethoxy)benzoic acid frameworks based on polynuclear metal-hydroxyl clusters (M = Zn, Co)

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1. Preparation of 3,4,5-tris(carboxymethoxy)benzoic acid (H_4TCBA). To 50 mL of water suspension of 3,4,5-trihydroxybenzoic acid (0.1 mol) was added NaOH (0.6 mol) at ambient temperature. After the reaction mixture became clear, a 50 mL solution of $ClCH_2COOH$ (0.3 mol) was added dropwisely at ca. 90 °C with vigorous stirring. After continuing the reaction for 5h, the resulting mixture was acidified with HCl to pH 2–3 and a gray product precipitated, then was filtered off, washed with 3×10 mL of deionized H_2O, and air-dried. Yield 89%. MS (ESI^-) m/z (M-H) 343.04. Anal. Calcd: C, 45.36; H, 3.51. Found: C, 45.72; H, 3.79. Mp: 296-297 °C. Main IR frequencies: 3483, 1708, 1500, 1419, 1331, 1139, 1030, 871, 771 cm^{-1}. ^1H NMR (DMSO-d_6, 400MHz) δ: 4.60 (s, 6H, CH_2), 7.15 (s, 2H, ArH).

Table S1 Selected bond lengths (Å) for complexes **1**–**3**

1			
Zn(1)–O(11)$^{\#1}$	2.068(2)	Zn(1)–O(11)$^{\#2}$	2.068(2)
Zn(1)–O(12)	2.100(1)	Zn(1)–O(12)$^{\#3}$	2.100(1)
Zn(1)–O(16)	2.115(2)	Zn(1)–O(16)$^{\#3}$	2.115(2)
Zn(2)–O(2)	2.031(1)	Zn(2)–O(8)$^{\#4}$	2.087(2)
Zn(2)–O(10)$^{\#2}$	2.096(1)	Zn(2)–O(12)	2.055(1)
Zn(2)–O(13)	2.213(1)	Zn(2)–O(14)	2.234(1)
Zn(3)–O(1)	2.061(2)	Zn(3)–O(4)$^{\#5}$	1.965(2)
Zn(3)–O(12)	1.987(1)	Zn(3)–O(15)	2.011(2)
2			
Zn(1)–O(7)	2.086(1)	Zn(1)–O(7)$^{\#1}$	2.086(1)
Zn(1)–O(12)	2.079(1)	Zn(1)–O(12)$^{\#1}$	2.079(1)
Zn(1)–O(13)	2.215(1)	Zn(1)–O(13)$^{\#1}$	2.215(1)
Zn(2)–O(1)$^{\#2}$	1.930(1)	Zn(2)–O(3)	2.401(1)
Zn(2)–O(5)	2.042(1)	Zn(2)–O(6)	2.484(1)
Zn(2)–O(7)	1.998(1)	Zn(2)–O(12)	2.099(1)
Zn(3)–O(2)$^{\#2}$	1.984(1)	Zn(3)–O(4)$^{\#3}$	1.972(2)
Zn(3)–O(11)$^{\#4}$	1.974(2)	Zn(3)–O(12)	1.982(1)
3			
Co(1)–O(4)$^{\#1}$	2.069(2)	Co(1)–O(8)$^{\#2}$	2.251(2)
Co(1)–O(11)$^{\#3}$	2.083(2)	Co(1)–O(12)	2.097(2)
Co(1)–O(13)$^{\#4}$	2.043(2)	Co(1)–O(17)	2.158(2)
Co(2)–O(1)	2.042(2)	Co(2)–O(5)$^{\#1}$	2.132(2)
Co(2)–O(8)$^{\#2}$	2.129(2)	Co(2)–O(12)	2.031(2)
Co(2)–O(14)	2.102(2)	Co(2)–O(15)	2.120(2)

Co(3)–O(2)	2.049(2)	Co(3)–O(10)$^{\#3}$	2.136(2)
Co(3)–O(12)	2.073(2)	Co(3)–O(13)	2.064(2)
Co(3)–O(13)$^{\#4}$	2.124(2)	Co(3)–O(16)	2.107(2)

Symmetry operation: **For 1**, #1 –*x* + 1, –*y*, –*z*; #2 *x*, *y*, *z* + 1; #3 –*x* + 1, –y, –*z* + 1; #4 –*x*, –*y* + 1, –*z*; #5 *x*, *y* – 1, *z*; **For 2**, #1 –*x*, –*y* + 1, –*z* + 1; #2 –*x* + 1, *y* + 1/2, –*z* + 1/2; #3 –*x* + 1, –*y* + 1, –*z* + 1; #4 –*x*, *y* + 1/2, –*z* + 1/2; **For 3**, #1 *x*, *y* + 1, *z*; #2 –*x* + 1, –*y* + 1, –*z* + 2; #3 *x*, *y*, *z* – 1; #4 –*x* + 1, –*y* + 1, –*z* + 1.

Table S2 Hydrogen bonding geometry (Å and °) for complexes **1**–**3**

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
1				
O(12)–H(12)···O(7)$^{\#1}$	0.82	2.22	2.988(2)	157.0
O(14)–H(3W)···O(9)$^{\#1}$	0.82	2.26	2.923(2)	138.5
O(14)–H(4W)···O(13)$^{\#2}$	0.82	2.05	2.814(2)	154.8
O(14)–H(4W)···O(10)$^{\#1}$	0.82	2.31	2.844(2)	122.9
O(15)–H(5W)···O(7)$^{\#1}$	0.83	2.23	2.936(2)	143.4
O(15)–H(6W)···O(5)$^{\#1}$	0.82	1.94	2.761(2)	174.2
O(16)–H(7W)···O(8)$^{\#3}$	0.82	1.90	2.712(2)	173.1
O(16)–H(8W)···O(7)$^{\#4}$	0.83	1.82	2.633(2)	165.0
#1 –*x* + 1, –*y* + 1, –*z*; #2 –*x* + 1, –*y* + 1 , –*z* + 1; #3 –*x*, –*y* + 1, –*z*; #4 *x*, *y* – 1, *z* + 1.				
2				
O(12)–H(12)···O(8)$^{\#1}$	0.82	2.45	3.023(2)	127.6
O(13)–H(1W)···O(5)$^{\#1}$	0.83	2.47	2.966(2)	119.4
O(13)–H(1W)···O(2)$^{\#2}$	0.83	2.47	3.170(3)	142.7
O(13)–H(2W)···O(11)$^{\#3}$	0.83	2.17	2.981(3)	167.4
#1 –*x*, –*y* + 1, –*z* + 1; #2 –*x*, *y* + 1/2, –*z* + 1/2; #3 *x*, –*y* + 3/2, *z* + 1/2.				
3				
O(12)–H(12)···O(7)$^{\#1}$	0.82	2.44	3.184(3)	151.7
O(13)–H(13)···O(10)$^{\#2}$	0.82	2.36	2.781(3)	112.7
O(14)–H(1W)···O(15)$^{\#3}$	0.82	1.95	2.729(3)	158.9
O(14)–H(2W)···O(9)$^{\#4}$	0.83	1.87	2.609(6)	147.9
O(15)–H(3W)···O(3)$^{\#5}$	0.84	2.37	2.872(3)	118.9
O(15)–H(3W)···O(5)$^{\#5}$	0.84	1.98	2.733(3)	149.6
O(15)–H(4W)···O(6)$^{\#5}$	0.82	1.93	2.746(2)	169.9
O(16)–H(6W)···O(6)$^{\#5}$	0.83	2.29	3.081(3)	161.2
O(16)–H(6W)···O(9)$^{\#5}$	0.83	2.36	2.953(3)	129.0
O(17)–H(7W)···O(7)$^{\#4}$	0.82	2.12	2.863(3)	150.4
O(17)–H(8W)···O(18)$^{\#6}$	0.82	2.20	2.935(4)	147.9
O(19)–H(12W)···O(18)$^{\#7}$	0.83	2.04	2.709(9)	136.7
#1 –*x* + 2, –*y* + 1, –*z* + 2; #2 *x*, *y*, *z* – 1; #3 –*x* + 2, –*y* + 2, –*z* + 2; #4 –*x* + 1, –*y* + 1, –*z* + 2; #5 –*x* + 2, –*y* + 1, –*z* + 2; #6 –*x* + 1, –*y* + 2, –*z* + 1; #7 –*x* + 1, –*y* + 1, –*z* + 1.				

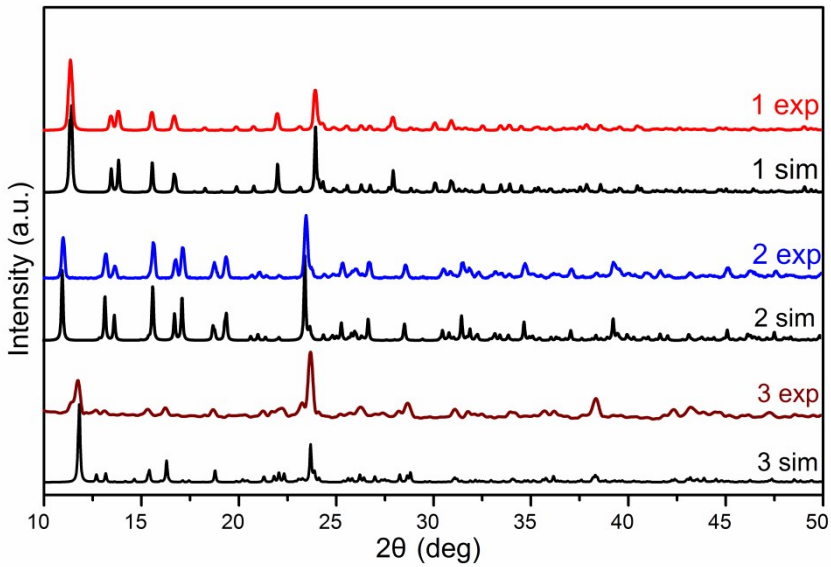

Fig. S1 Simulated and experimental PXRD patterns of **1**–**3**.

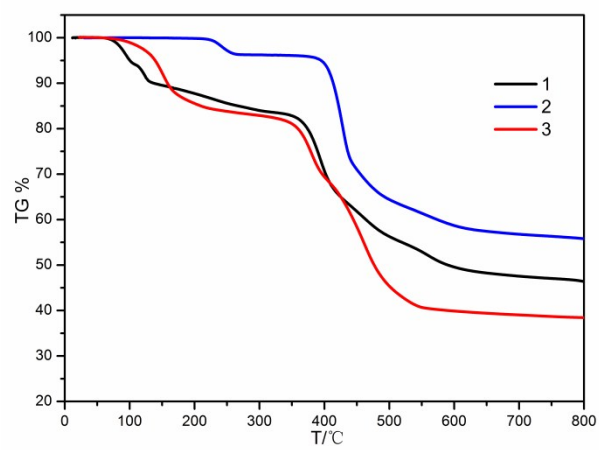

Fig. S2 TGA curves of complexes **1**–**3**.