Assembly of {Co_{14}} nanoclusters from adenine-modified Co_4-thiacalix[4]arene units

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Additional figures

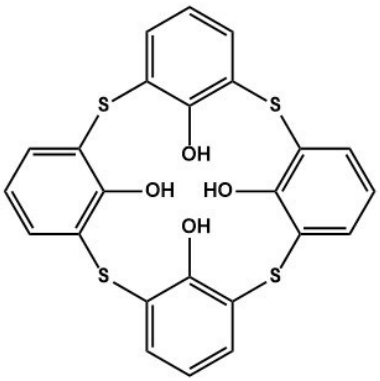

Figure S1. The structure of H_4T4A.

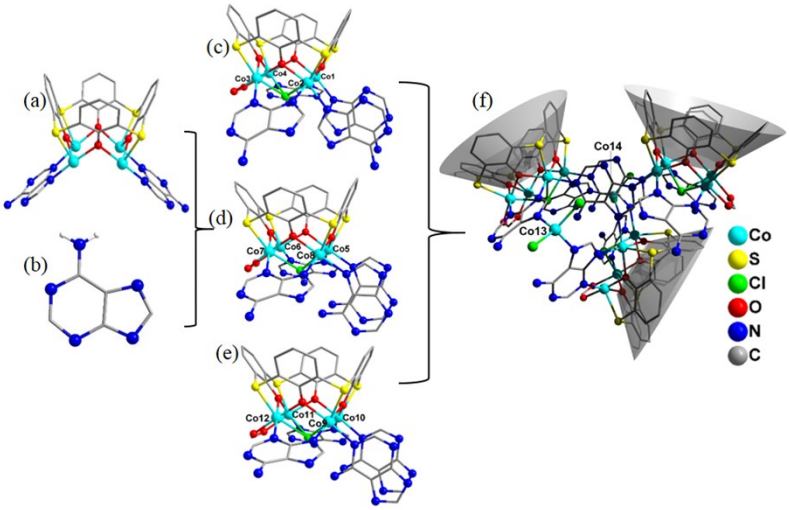

Figure S2. The assembly of **Co_{14}α**: (a) the adenine-functionalized Co_4-T4A secondary building unit (SBU); (b) adenine ligand; (c), (d), (e) the asymmetric units; (f) the crystal structure of **Co_{14}α**.

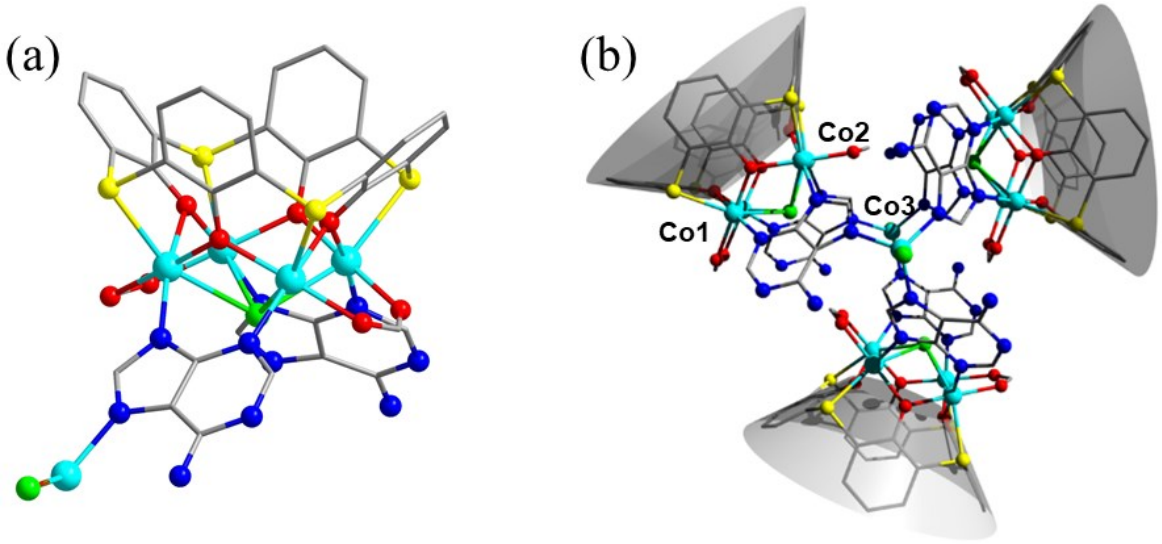

Figure S3. (a) The asymmetric unit of and (b) the crystal structure of **Co_{14}β**.

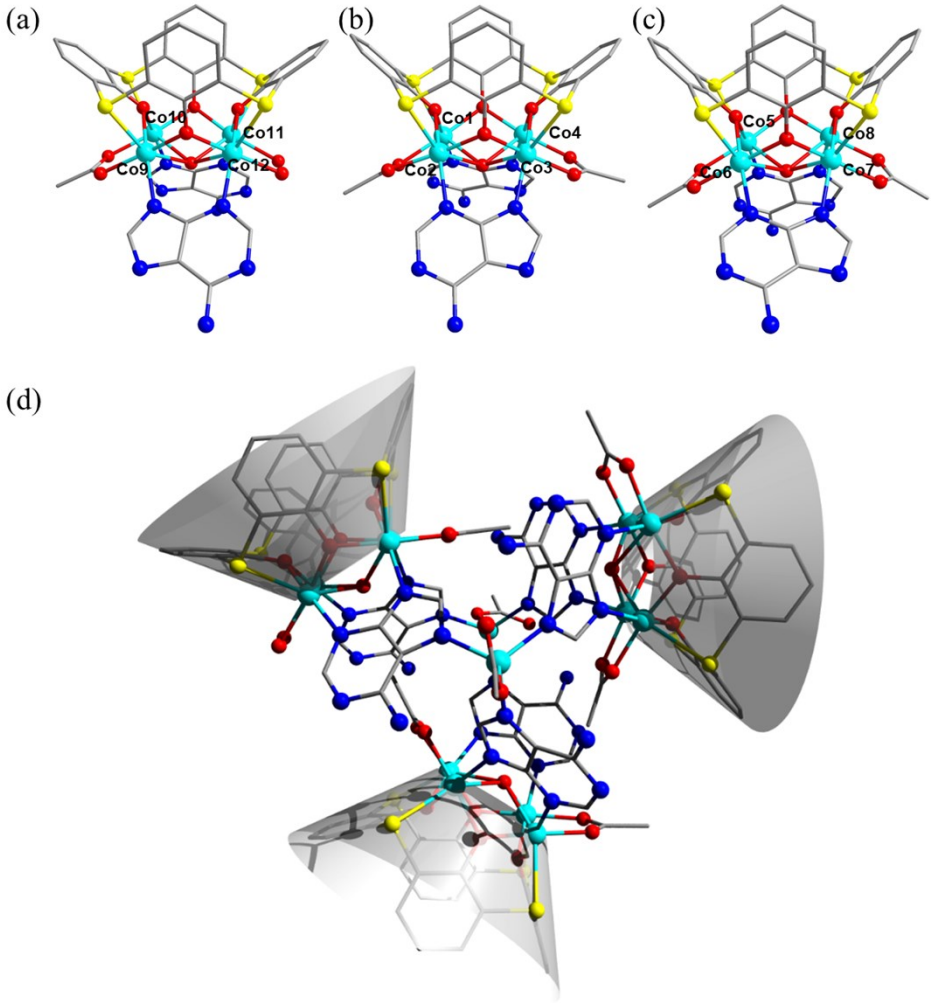

Figure S4. (a,b,c) Three adenine-functionalized Co_4-T4A SBUs and (d) the crystal structure of **Co_{14}γ**.

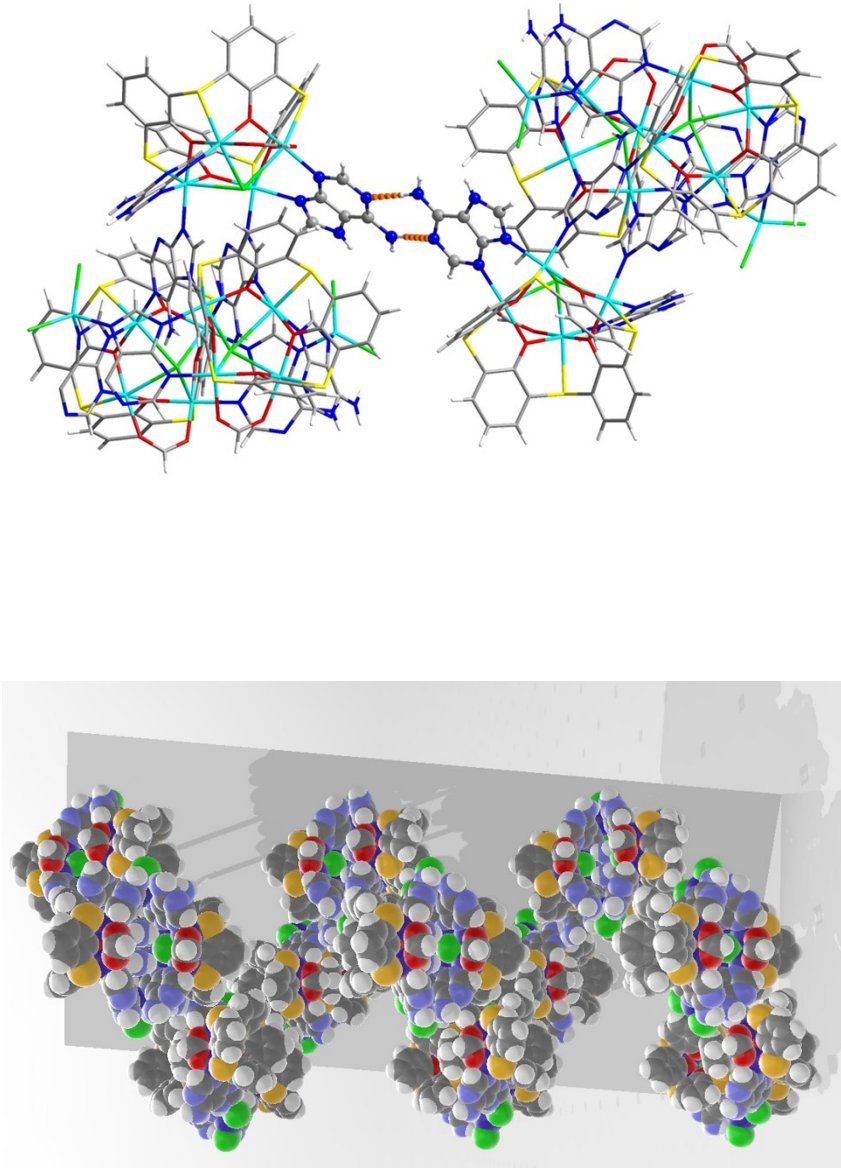

Figure S5. The intermolecular hydrogen bonds N-H…N (up) and right-hand helical chain alone *c* axis (down) in **Co_{14}α**

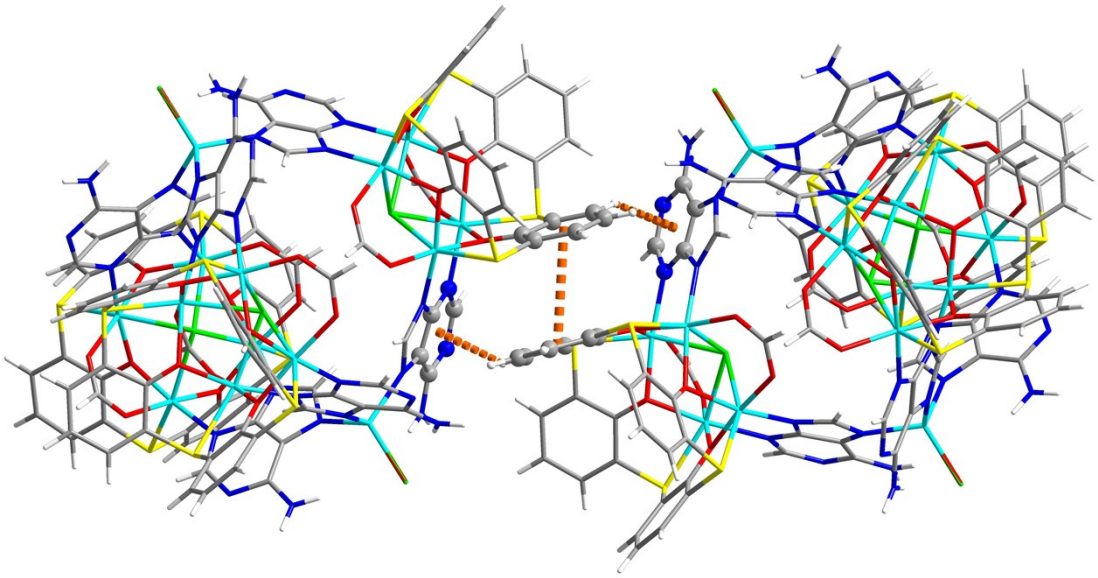

Figure S6. The intercluster CH…π and face-to-face π…π interactions in **Co_{14}β**.

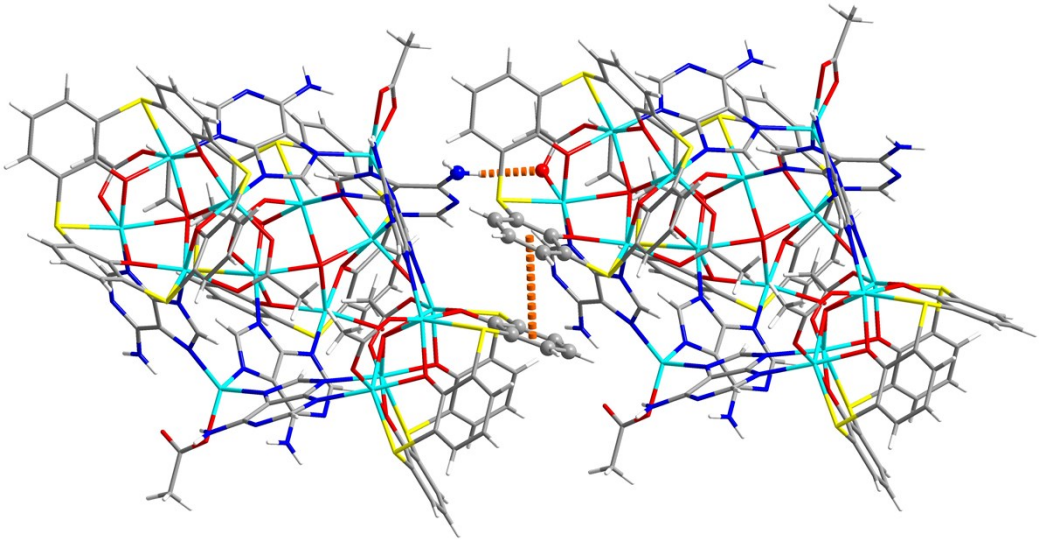

Figure S7. The intermolecular hydrogen bond N-H…O and face-to-face π…π interactions in **Co_{14}γ**.

PXRD measurements

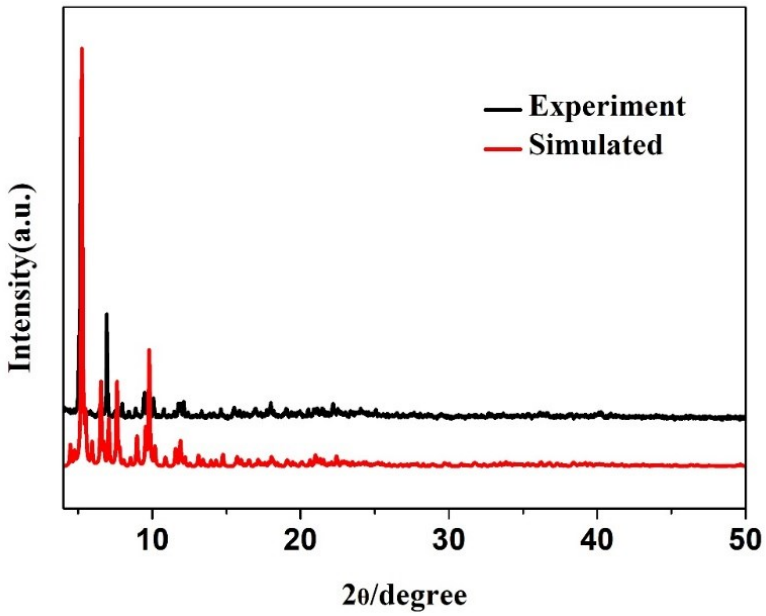

Figure S8. PXRD of the compound **$Co_{14}\alpha$**.

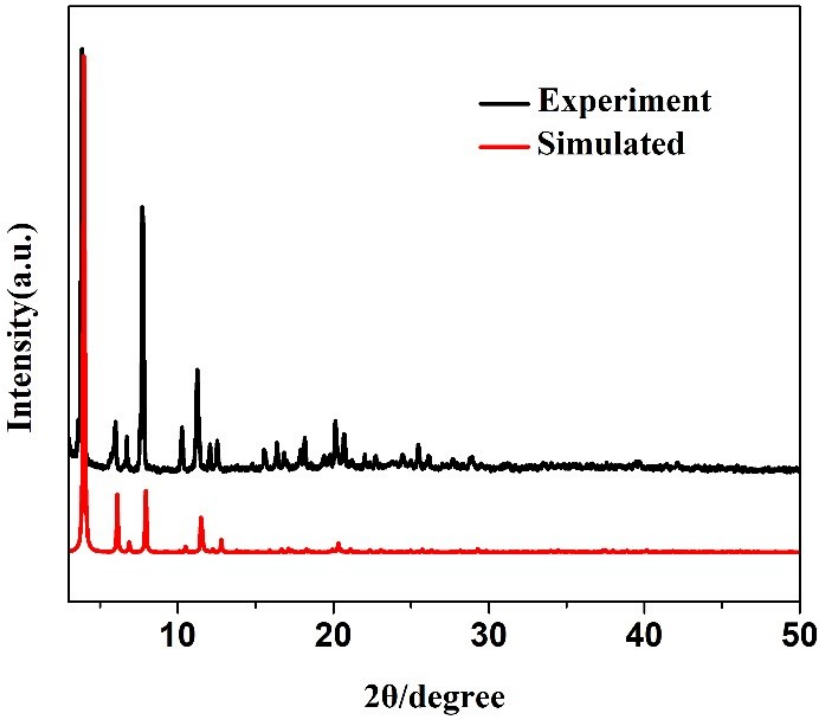

Figure S9. PXRD of compound **$Co_{14}\beta$**.

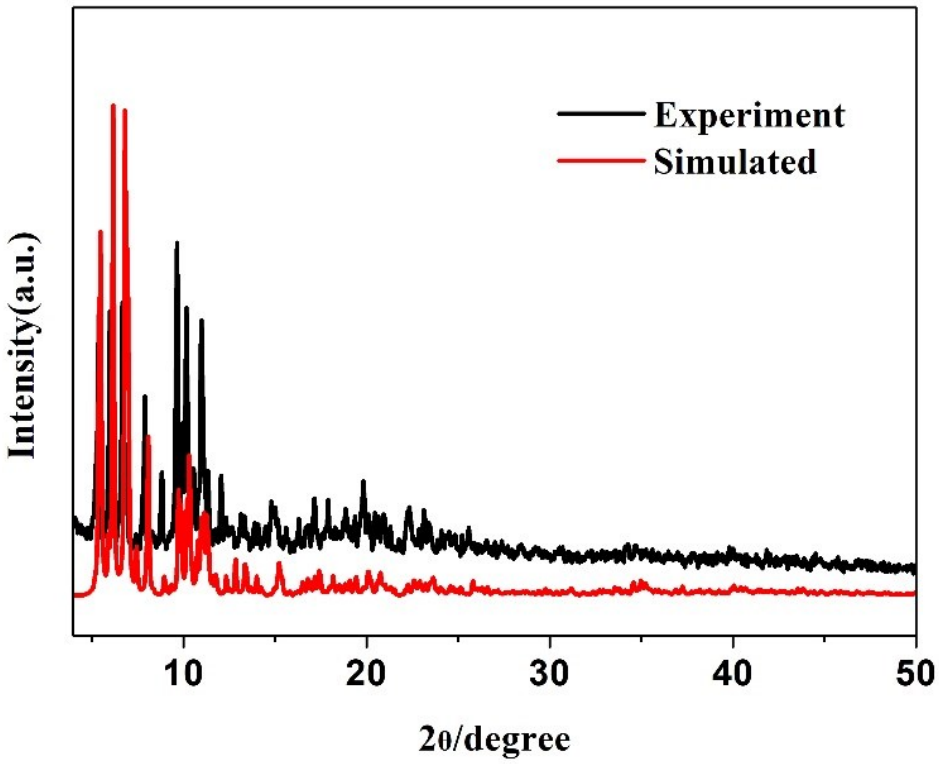

Figure S10. PXRD of compound **$Co_{14}\gamma$**.

The experimental PXRD patterns of the three compounds are consistent with the simulation results derived from the single crystal X-ray data, confirming the phase purity of the samples.

TGA experiments

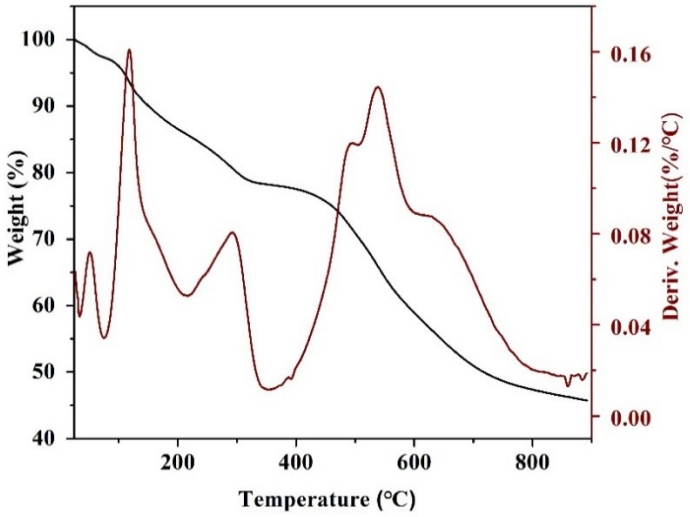

Figure S11. The TGA curves of **$Co_{14}\alpha$** recorded in high pure N_2 (99.999%) at 20 mL/min with heating rate of 10 °C /min.

In the TGA plot of **$Co_{14}\alpha$**, the weight loss is ca. 20% from the beginning to 300 °C corresponding to loss solvent molecules in the lattice and weakly coordinated molecules (eg. CH_3OH, H_2O, DMF).

From 300 °C to 450 °C, the weight decreases slowly. Further weight loss deceases sharply which can be assigned to the decompose of thiacalix[4]arene and adenine ligands. After 800°C, the TGA map reached a relatively slow weight loss area. Finally, a dark black deposition product was observed at 900 °C.

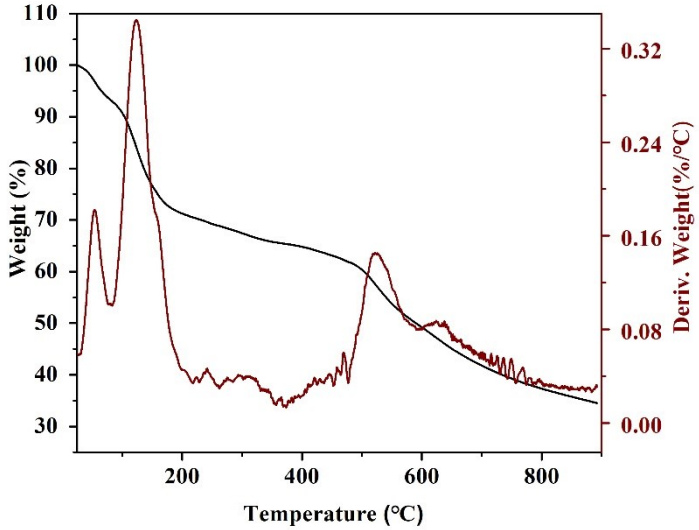

Figure S12. The TGA curves of **$Co_{14}\beta$** recorded in high pure N_2 (99.999%) at 20 mL/min with heating rate of 10 °C /min.

In the TGA plot of **$Co_{14}\beta$**, the weight loss is ca. 30% from the beginning to 200 °C corresponding to loss solvent molecules in the lattice and weakly coordinated molecules (eg. CH_3OH, H_2O, DMF). From 200 °C to 500 °C, the weight decreases slowly. Further weight loss deceases sharply which can be assigned to the decompose of thiacalix[4]arene and adenine ligands. After 800 °C, the TGA map reached a relatively slow weight loss area. Finally, a dark black deposition product was observed at 900 °C.

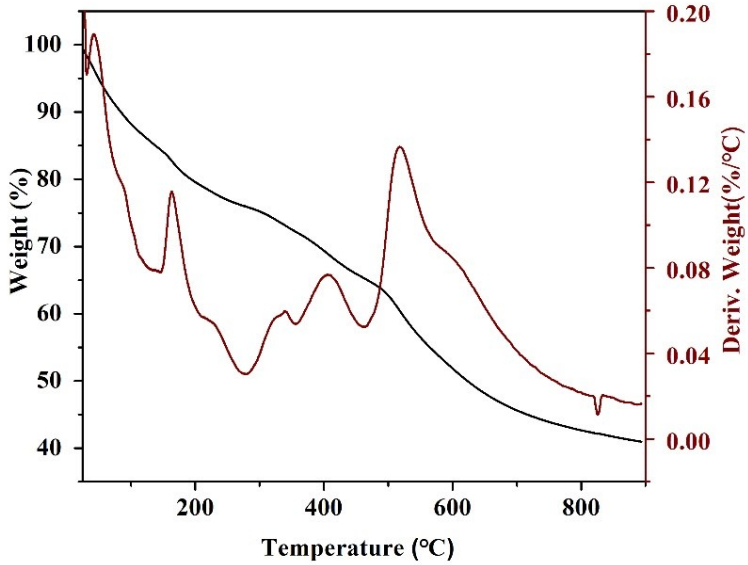

Figure S13. The TGA curves of **$Co_{14}\gamma$** recorded in high pure N_2 (99.999%) at 20 mL/min with heating rate of 10 °C /min.

In the TGA plot of **$Co_{14}\gamma$**, the weight loss is ca. 20% from the beginning to 200 °C corresponding to loss solvent molecules in the lattice and weakly coordinated molecules (eg.CH_3OH, H_2O, DMF). From 300 °C to 500 °C, the weight decreases slowly. Further weight loss deceases sharply which

can be assigned to the decompose of thiacalix[4]arene and adenine ligands. After 800 °C, the TGA map reached a relatively slow weight loss area. Finally, a dark black deposition product was observed at 900 °C.

FTIR spectra

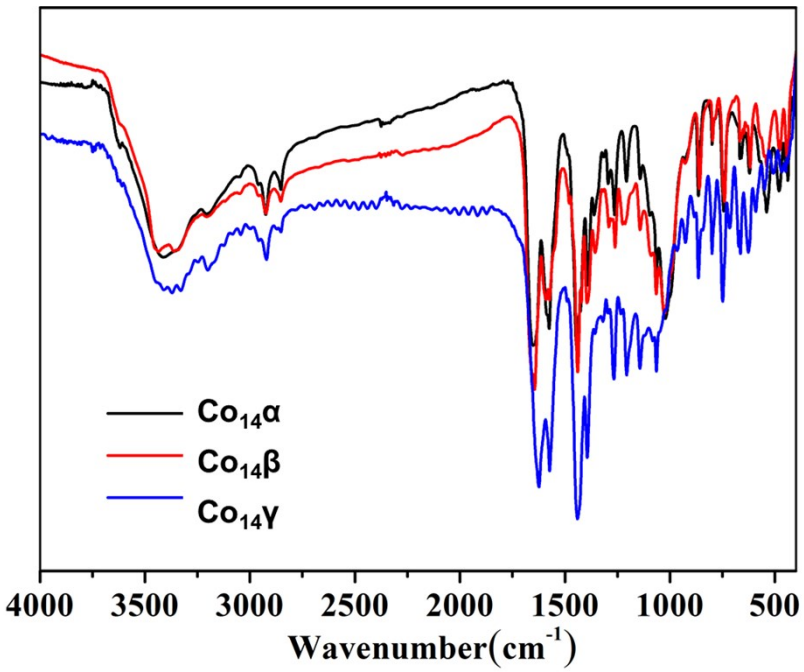

Figure S14. FTIR spectra of **Co_{14}α, Co_{14}β** and **Co_{14}γ,** ν_s (-NH) = 3618cm^{-1}, ν_{as} (-NH) =3411cm^{-1}, ν (-C=C) & ν (-C=N) = 1650cm^{-1}, 1445cm^{-1}.

Solid-state UV-vis light absorption

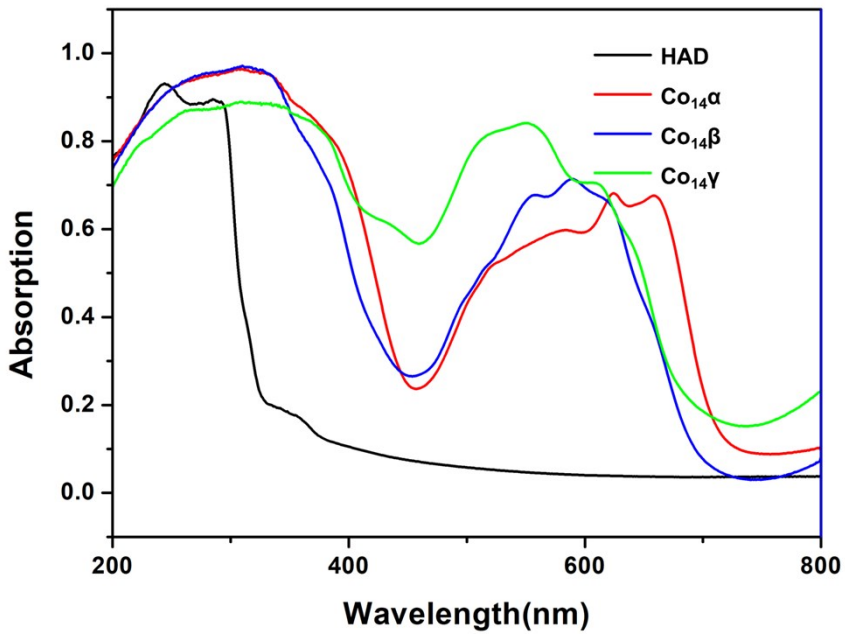

Figure S15. The photos pictures (up) and solid-state UV-vis absorption for **$Co_{14}\alpha$**, **$Co_{14}\beta$** and **$Co_{14}\gamma$ (**HAD supplied for comparison**)**.

Table S1. Selected bond distances (Å) and BVS calculations for **Co_4**, **$Co_{14}\alpha$**, **$Co_{14}\beta$** and **$Co_{14}\gamma$**

Co_4							
Band	Distance	r	Valu	Band	Distance	r	Value
Co(1)-O(1)	2.0029(19)	1.69	0.432	Co(3)-O(3)	2.024(6)	1.69	0.449
Co(1)-O(6)	2.022(2)	1.69	0.410	Co(3)-O(2)	2.037(6)	1.69	0.410
Co(1)-O(4)	2.048(2)	1.69	0.382	Co(3)-O(8)	2.114(7)	1.69	0.408
Co(1)-N(1)	2.069(2)	1.84	0.539	Co(3)-N(6)	2.127(8)	1.84	0.474
Co(1)-S(1)	2.5401(9)	2.06	0.273	Co(3)-S(3)	2.514(3)	2.06	0.280

Co(1)-Cl(1)	2.6660(9)	2.01	0.170	Co(3)-Cl(1)	2.684(3)	2.01	0.204
valence			2.205	valence			2.225
Co(2)-O(1)	1.9886(19)	1.69	0.449	Co(4)-O(3)	2.002(2)	1.69	0.433
Co(2)-O(2)	2.025(2)	1.69	0.407	Co(4)-O(4)	2.010(2)	1.69	0.423
Co(2)-O(7)	2.054(2)	1.69	0.376	Co(4)-O(5)	2.027(2)	1.69	0.404
Co(2)-N(2)	2.075(2)	1.84	0.530	Co(4)-N(7)	2.116(2)	1.84	0.474
Co(2)-S(2)	2.5417(9)	2.06	0.272	Co(4)-S(4)	2.5605(9)	2.06	0.259
Co(2)-Cl(1)	2.6419(8)	2.01	0.181	Co(4)-Cl(1)	2.6304(8)	2.01	0.187
valence			2.214	valence			2.180
$Co_{14}\alpha$							
Band	Distance	r	Valu	Band	Distance	r	Value
Co(1)-O(4)	2.015(5)	1.69	0.418	Co(8)-O(8)	2.032(5)	1.69	0.399
Co(1)-O(1)	2.016(5)	1.69	0.417	Co(8)-O(7)	2.031(4)	1.69	0.400
Co(1)-N(1)	2.032(7)	1.84	0.595	Co(8)-N(7)	2.112(6)	1.84	0.479
Co(1)-N(11)	2.123(6)	1.84	0.465	Co(8)-N(26)	2.130(6)	1.84	0.457
Co(1)-S(1)	2.460(2)	2.06	0.339	Co(8)-S(8)	2.513(2)	2.06	0.294
				Co(8)-Cl(2)	2.683(2)	2.01	0.162
valence			2.234	valence			2.191
Co(2)-O(1)	2.012(5)	1.69	0.421	Co(9)-O(9)	2.020(5)	1.69	0.412
Co(2)-O(2)	2.015(5)	1.69	0.418	Co(9)-O(12)	2.037(5)	1.69	0.394
Co(2)-N(6)	2.083(7)	1.84	0.519	Co(9)-N(31)	2.093(7)	1.84	0.505
Co(2)-N(16)	2.162(7)	1.84	0.419	Co(9)-N(4)	2.117(7)	1.84	0.473
Co(2)-S(2)	2.470(2)	2.06	0.330	Co(9)-S(9)	2.518(2)	2.06	0.290
Co(2)-Cl(1)	2.729(2)	2.01	0.143	Co(9)-Cl(3)	2.695(2)	2.01	0.157
valence			2.250	valence			2.230
Co(3)-O(3)	1.997(5)	1.69	0.439	Co(10)-O(9)	2.020(5)	1.69	0.412
Co(3)-O(2)	2.001(5)	1.69	0.434	Co(10)-O(10)	2.029(6)	1.69	0.402
Co(3)-O(14)	2.037(6)	1.69	0.394	Co(10)-N(36)	2.103(7)	1.84	0.491
Co(3)-N(18)	2.097(7)	1.84	0.499	Co(10)-N(9)	2.131(7)	1.84	0.455
Co(3)-S(3)	2.545(2)	2.06	0.270	Co(10)-S(12)	2.500(2)	2.06	0.304
Co(3)-Cl(1)	2.625(2)	2.01	0.190	Co(10)-Cl(3)	2.673(2)	2.01	0.167
valence			2.225	valence			2.232
Co(4)-O(3)	1.988(5)	1.69	0.449	Co(11)-O(10)	1.995(6)	1.69	0.441
Co(4)-O(4)	2.014(5)	1.69	0.419	Co(11)-O(11)	2.013(6)	1.69	0.420
Co(4)-O(13)	2.037(5)	1.69	0.394	Co(11)-O(17)	2.033(7)	1.69	0.398
Co(4)-N(13)	2.090(6)	1.84	0.509	Co(11)-N(38)	2.098(8)	1.84	0.498
Co(4)-S(4)	2.517(2)	2.06	0.291	Co(11)-S(11)	2.499(3)	2.06	0.305
Co(4)-Cl(1)	2.604(2)	2.01	0.201	Co(11)-Cl(3)	2.734(3)	2.01	0.141
valence			2.262	valence			2.203
Co(5)-O(8)	2.016(5)	1.69	0.417	Co(12)-O(11)	1.986(6)	1.69	0.452
Co(5)-O(5)	2.043(5)	1.69	0.387	Co(12)-O(12)	2.016(6)	1.69	0.417
Co(5)-N(21)	2.078(6)	1.84	0.526	Co(12)-O(18)	2.046(8)	1.69	0.384
Co(5)-N(2)	2.112(6)	1.84	0.479	Co(12)-N(33)	2.077(8)	1.84	0.527
Co(5)-S(5)	2.520(2)	2.06	0.288	Co(12)-S(10)	2.494(3)	2.06	0.309
Co(5)-Cl(2)	2.649(2)	2.01	0.178	Co(12)-Cl(3)	2.704(2)	2.01	0.153
valence			2.275	valence			2.242

Co(6)-O(6)	1.972(5)	1.69	0.469	Co(13)-N(27)	1.987(6)	1.84	0.672
Co(6)-O(5)	2.008(5)	1.69	0.426	Co(13)-N(37)	2.023(8)	1.84	0.610
Co(6)-O(16)	2.061(6)	1.69	0.369	Co(13)-Cl(4)	2.256(2)	2.01	0.514
Co(6)-N(23)	2.055(7)	1.84	0.559	Co(13)-Cl(5)	2.267(3)	2.01	0.499
Co(6)-S(6)	2.495(2)	2.06	0.309				
valence			2.132	valence			2.296
Band	Distance	r	Valu	Band	Distance	r	Value
Co(7)-O(6)	1.964(5)	1.69	0.479	Co(14)-N(32)	2.028(8)	1.84	0.602
Co(7)-O(7)	2.002(5)	1.69	0.433	Co(14)-N(22)	2.025(7)	1.84	0.607
Co(7)-O(15)	2.060(6)	1.69	0.370	Co(14)-Cl(7)	2.244(3)	2.01	0.531
Co(7)-N(28)	2.070(6)	1.84	0.537	Co(14)-Cl(6)	2.250(3)	2.01	0.523
Co(7)-S(7)	2.485(2)	2.06	0.317				
Co(7)-Cl(2)	2.715(2)	2.01	0.149				
valence			2.285	valence			2.262
$Co_{14}\beta$							
Band	Distance	r	Valu	Band	Distance	r	Value
Co(1)-O(2)	1.974(6)	1.69	0.467	Co(3)-N(2)	1.992(6)	1.84	0.663
Co(1)-O(4)	2.025(7)	1.69	0.407	Co(3)-N(2)	1.992(6)	1.84	0.663
Co(1)-O(1)	2.031(6)	1.69	0.400	Co(3)-N(2)	1.992(6)	1.84	0.663
Co(1)-N(4)	2.087(7)	1.84	0.513	Co(3)-O(6)	2.20(13)	1.69	0.253
Co(1)-S(1)	2.516(3)	2.06	0.292	Co(3)-Cl(2)	2.22(5)	2.01	0.567
Co(1)-Cl(1)	2.585(2)	2.01	0.211				
valence			2.289	valence			2.810
Co(2)-O(2)	2.003(6)	1.69	0.431				
Co(2)-O(5)	2.017(6)	1.69	0.415				
Co(2)-O(3)	2.048(6)	1.69	0.382				
Co(2)-N(1)	2.075(6)	1.84	0.530				
Co(2)-S(2)	2.543(2)	2.06	0.271				
Co(2)-Cl(1)	2.633(3)	2.01	0.186				
valence			2.216	valence			
$Co_{14}\gamma$							
Band	Distance	r	Valu	Band	Distance	r	Value
Co(1)-O(4)	1.981(4)	1.69	0.458	Co(8)-O(8)	1.986(4)	1.69	0.452
Co(1)-O(1)	2.041(4)	1.69	0.389	Co(8)-O(20)	2.040(5)	1.69	0.390
Co(1)-O(13)	2.064(4)	1.69	0.366	Co(8)-S(8)	2.573(2)	2.06	0.250
Co(1)-N(1)	2.121(5)	1.84	0.468	Co(8)-O(7)	2.018(4)	1.69	0.414
Co(1)-O(29)	2.262(4)	1.69	0.214	Co(8)-N(12)	2.074(5)	1.84	0.531
Co(1)-S(1)	2.5762(18)	2.06	0.248				
valence			2.143	valence			2.038
Co(2)-O(2)	1.991(4)	1.69	0.446	Co(9)-O(12)	1.995(5)	1.69	0.441
Co(2)-O(1)	2.018(4)	1.69	0.414	Co(9)-O(21)	2.054(5)	1.69	0.376
Co(2)-O(14)	2.072(4)	1.69	0.358	Co(9)-O(31)	2.283(4)	1.69	0.202
Co(2)-N(6)	2.102(5)	1.84	0.493	Co(9)-O(9))	2.044(4)	1.69	0.386
Co(2)-S(2)	2.5758(18)	2.06	0.248	Co(9)-N(21)	2.077(5)	1.84	0.527
				Co(9)-S(9)	2.626(2)	2.06	0.217
valence			1.959	valence			2.149

Co(3)-O(2)	1.994(4)	1.69	0.442	Co(10)-O(10)	1.992(5)	1.69	0.444
Co(3)-O(15)	2.037(5)	1.69	0.394	Co(10)-O(9)	2.040(5)	1.69	0.390
Co(3)-O(3)	2.047(4)	1.69	0.383	Co(10)-O(31)	2.358(5)	1.69	0.165
Co(3)-O(29)	2.322(7)	1.69	0.182	Co(10)-O(22)	2.030(5)	1.69	0.401
Co(3)-N(9)	2.106(5)	1.84	0.487	Co(10)-N(26)	2.099(6)	1.84	0.497
Co(3)-S(3)	2.6175(19)	2.06	0.222	Co(10)-S(10)	2.612(2)	2.06	0.225
valence			2.107	valence			2.123
Co(4)-O(3)	2.009(4)	1.69	0.425	Co(11)-O(10)	1.995(5)	1.69	0.441
Co(4)-O(4)	1.978(4)	1.69	0.462	Co(11)-O(23)	2.128(8)	1.69	0.308
Co(4)-O(16)	2.027(4)	1.69	0.404	Co(11)-O(31)	2.240(4)	1.69	0.227
Co(4)-O(29)	2.367(4)	1.69	0.161	Co(11)-O(11)	2.044(5)	1.69	0.386
Co(4)-N(2)	2.057(5)	1.84	0.556	Co(11)-N(27)	2.148(6)	1.84	0.435
Co(4)-S(4)	2.6215(19)	2.06	0.219	Co(11)-S(11)	2.616(2)	2.06	0.223
valence			2.227	valence			2.020
Co(5)-O(8)	1.999(4)	1.69	0.436	Co(12)-O(12)	1.981(5)	1.69	0.458
Co(5)-O(17)	2.059(5)	1.69	0.371	Co(12)-O(24)	2.090(7)	1.69	0.341
Co(5)-O(30)	2.257(4)	1.69	0.217	Co(12)-S(12)	2.569(2)	2.06	0.253
Co(5)-O(5)	2.032(4)	1.69	0.399	Co(12)-O(11)	2.035(5)	1.69	0.396
Co(5)-N(11)	2.120(5)	1.84	0.469	Co(12)-N(24)	2.118(6)	1.84	0.472
Co(5)-S(5)	2.6300(19)	2.06	0.214				
valence			2.107	valence			1.919
Co(6)-O(6)	1.985(5)	1.69	0.453	Co(13)-O(25)	1.935(5)	1.69	0.519
Co(6)-O(5)	2.017(4)	1.69	0.415	Co(13)-N(8)	1.992(5)	1.84	0.663
Co(6)-O(30)	2.363(4)	1.69	0.163	Co(13)-N(29)	2.021(5)	1.84	0.613
Co(6)-O(18)	2.013(5)	1.69	0.420	Co(13)-N(18)	2.008(5)	1.84	0.635
Co(6)-N(16)	2.094(5)	1.84	0.503				
Co(6)-S(6)	2.5736(19)	2.06	0.250				
valence			2.204	valence			2.430
Co(7)-O(6)	1.987(4)	1.69	0.451	Co(14)-O(27)	1.941(6)	1.69	0.510
Co(7)-O(19)	2.043(5)	1.69	0.387	Co(14)-N(3)	2.008(5)	1.84	0.635
Co(7)-O(30)	2.253(4)	1.69	0.220	Co(14)-N(22)	2.011(5)	1.84	0.630
Co(7)-O(7)	2.012(4)	1.69	0.421	Co(14)-N(13)	2.008(5)	1.84	0.635
Co(7)-N(19)	2.083(5)	1.84	0.519				
Co(7)-S(7)	2.637(2)	2.06	0.210				
valence			2.207	valence			2.410

BVS calculations reveal that all the cobalt atoms in these four metal clusters are dvalent.