Electronic Supplementary Information (ESI)

pH-Dependent cobalt(II) frameworks with mixed 3,3',5,5'-tetra(1H-imidazol-1-yl)-1,1'-biphenyl and 1,3,5-benzenetricarboxylate ligands: synthesis, structure and sorption property†

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Materials and methods

All commercially available chemicals and solvents are of reagent grade and were used as received without further purification. Elemental analyses for C, H, and N were performed on a Perkin-Elmer 240C Elemental Analyzer at the analysis centre of Nanjing University. Thermogravimetric analyses (TGA) were performed on a simultaneous SDT 2960 thermal analyzer under nitrogen atmosphere with a heating rate of 10 ℃ min^{-1}. FT-IR spectra were recorded in the range of 400 - 4000 cm^{-1} on a Bruker Vector22 FT-IR spectrophotometer using KBr pellets. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 Advance X-ray diffractometer using Cu-Kα radiation (λ = 1.5418 Å), in which the X-ray tube was operated at 40 kV and 40 mA. Solid-state UV-vis diffusion reflectance spectra were obtained at room temperature on a Shimadzu UV-3600 double monochromator spectrophotometer, and $BaSO_4$ was used as a 100% reflectance standard for all samples. Sorption experiments were carried out on a Belsorp-max volumetric gas sorption instrument.

Table S1 Selected Bond Lengths (Å) and Angles (deg) for Complexes **1** - **3**.[a]

1			
Co(1)-O(1)	2.066(3)	Co(1)-O(3)	2.070(3)
Co(1)-N(22)#1	2.094(3)	Co(1)-N(12)	2.098(3)
Co(1)-O(4)#2	2.132(3)	Co(1)-O(2)	2.189(2)
O(1)-Co(1)-O(3)	173.58(11)	O(1)-Co(1)-N(22)#1	90.41(12)
O(1)-Co(1)-N(12)	96.46(12)	N(22)#1-Co(1)-N(12)	90.94(13)
N(12)-Co(1)-O(4)#2	83.92(11)	N(22)#1-Co(1)-O(2)	88.31(11)
O(4)#2-Co(1)-O(2)	96.76(9)	O(3)-Co(1)-O(4)#2	88.38(11)
2			
Co(1)-O(1)	1.956(2)	Co(1)-O(5)#1	1.956(3)
Co(1)-N(6)#2	2.013(3)	Co(1)-N(1)	2.037(3)
Co(2)-O(4)	2.083(3)	Co(2)-O(4)#3	2.083(3)
Co(2)-N(4)#4	2.084(3)	Co(2)-N(4)#5	2.084(3)
Co(2)-O(3)	2.226(3)	Co(2)-O(3)#3	2.226(3)
O(1)-Co(1)-O(5)#1	123.76(12)	O(1)-Co(1)-N(6)#2	101.23(12)
O(5)#1-Co(1)-N(6)#2	118.48(13)	O(1)-Co(1)-N(1)	104.13(12)
O(5)#1-Co(1)-N(1)	102.72(13)	N(6)#2-Co(1)-N(1)	104.21(12)
O(4)-Co(2)-O(4)#3	178.13(18)	O(4)-Co(2)-N(4)#4	93.04(13)
O(4)-Co(2)-N(4)#5	88.21(12)	N(4)#4-Co(2)-N(4)#5	96.1(2)
O(4)-Co(2)-O(3)	60.06(11)	O(4)#3-Co(2)-O(3)	118.49(13)
N(4)#4-Co(2)-O(3)#3	147.26(12)	O(3)-Co(2)-O(3)#3	94.88(16)
3			
Co(1)-N(32)	2.140(3)	Co(1)-N(12)	2.186(3)

Co(1)-O(5)#1	2.088(3)	Co(1)-O(4)#2	2.109(3)
Co(1)-O(7)	2.029(3)	Co(1)-O(8)	2.304(3)
Co(2)-O(7)	2.014(3)	Co(2)-O(6)#1	2.059(2)
Co(2)-O(2)	2.064(3)	Co(2)-N(22)#3	2.113(3)
Co(2)-N(42)#4	2.162(3)	Co(2)-O(9)	2.312(5)
O(7)-Co(1)-O(5)#1	99.34(11)	O(5)#4-Co(1)-O(4)#2	90.48(10)
O(7)-Co(1)-O(4)#2	169.94(11)	O(5)#1-Co(1)-N(32)	89.93(11)
O(5)#1-Co(1)-N(12)	88.61(11)	N(32)-Co(1)-O(8)	91.91(12)
N(12)-Co(1)-O(8)	89.48(12)	N(32)-Co(1)-N(12)	177.92(12)
N(32)-Co(1)-O(7)	91.11(12)	N(32)-Co(1)-O(4)#2	91.09(11)
N(12)-Co(1)-O(7)	90.60(12)	N(12)-Co(1)-O(4)#2	87.44(12)
O(7)-Co(1)-O(8)	83.28(11)	O(5)#1-Co(1)-O(8)	176.77(11)
O(4)#2-Co(1)-O(8)	86.83(11)	O(6)#1-Co(2)-O(2)	89.57(11)
O(7)-Co(2)-N(22)#3	94.29(12)	O(2)-Co(2)-N(22)#3	88.13(11)
O(7)-Co(2)-N(42)#4	91.39(12)	O(2)-Co(2)-N(42)#4	85.30(12)
O(7)-Co(2)-O(9)	76.49(17)	O(2)-Co(2)-O(9)	91.27(17)
O(7)-Co(2)-O(6)#1	102.63(11)	O(7)-Co(2)-O(2)	167.43(12)
O(6)#1-Co(2)-O(9)	178.81(16)	O(6)#1-Co(2)-N(22)#3	92.43(11)
O(6)#1-Co(2)-N(42)#4	90.96(12)	N(42)#4-Co(2)-O(9)	88.27(16)
N(22)#3-Co(2)-O(9)	88.43(15)	N(22)#3-Co(2)-N(42)#4	172.59(12)

[a] Symmetry transformations used to generate equivalent atoms: #1 *x*,*y*+1,*z*; #2 -*x*+1,*y*,-*z*+1/2 for **1**; #1 -*x*+1/2,*y*+1/2,-*z*+5/2; #2 *x*+1/2,*y*+1/2,*z*; #3 -*x*+1,*y*,-*z*+5/2; #4 *x*+1/2,*y*-1/2,*z*; #5 -*x*+1/2,*y*-1/2,-*z*+5/2 for **2**; #1 -*x*+1/2,*y*,*z*+1/2; #2 *x*,*y*,*z*+1; #3 -*x*+1,*y*+1/2, -*z*+1/2; #4 -*x*+1,*y*-1/2,-*z*+1/2 for **3**.

Table S2 Hydrogen bonding data for complexes **1** - **2**.[a]

D–H ··A	d(D ··A) (Å)	∠D–H ··A ( )
1		
O(1)–H(1A) ··O(7)#1	2.949(5)	138
O(1)–H(1A) ··O(8)#1	3.027(4)	155
O(1)–H(1B) ··O(4)#2	2.773(4)	175
O(2)–H(2A) ··O(7)#3	2.714(4)	167
O(6)–H(6A) ··O(6)#4	2.501(5)	168
C(201)–H(201) ··O(8)#1	3.428(6)	153
C(202)–H(202) ··O(5)#4	3.420(6)	163
2		
C(10)–H(10) ··O(1)#1	3.332(5)	146
C(18)–H(18) ··O(2W)#2	3.244(8)	149
C(19)–H(19) ··O(4)#3	2.846(5)	118
C(21)–H(21) ··O(1W)#4	3.333(11)	160

[a] Symmetry transformations used to generate equivalent atoms: #1 1-*x*,*y*,1/2-*z*; #2 *x*,1-*y*,1/2+*z*; #3 *x*,*1*+*y*,*z*; #4 -*x*,-*y*,-*z* for **1**. #1 1/2-*x*,1/2-*y*,2-*z*; #2 *x*,*y*,*1*+*z*; #3 1/2-*x*,1/2+*y*,5/2-*z*; #4 -*x*,*y*,3/2-*z* for **2**.

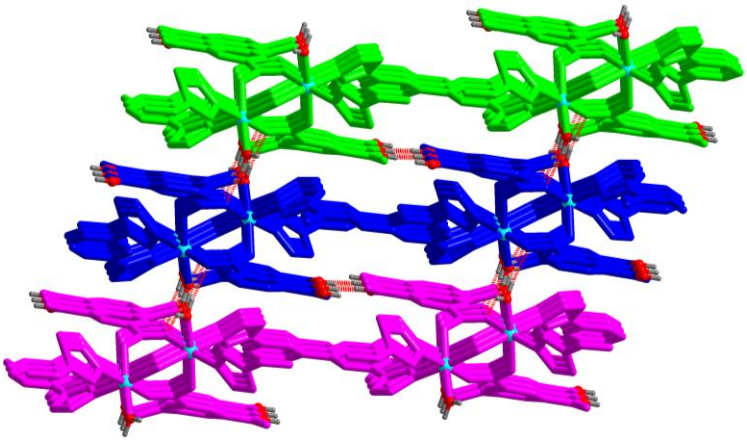


Fig. S1 The 3D supramolecular structure of **1** constructed from layer linked by hydrogen bonds indicated by the red dashed lines: different colours indicate the different layers.

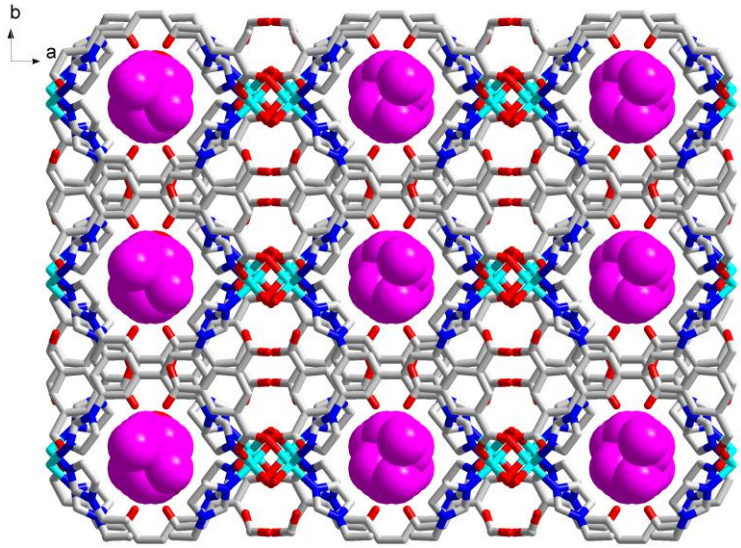


Fig. S2 Crystal packing diagram of **1** with free waters shown in space-filling mode.

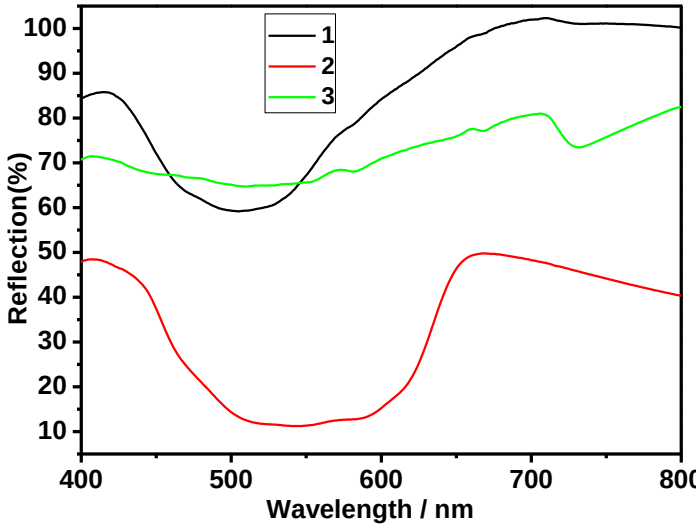


Fig. S3 UV-vis spectra of complexes **1 - 3** in the solid state at room temperature.

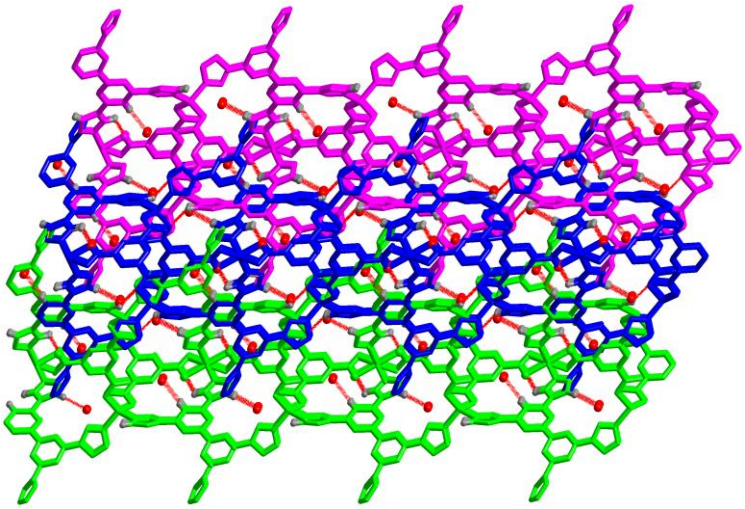


Fig. S4 The 3D supramolecular structure of **2** with hydrogen bonds indicated by red dashed lines: different colours indicate the different layers.

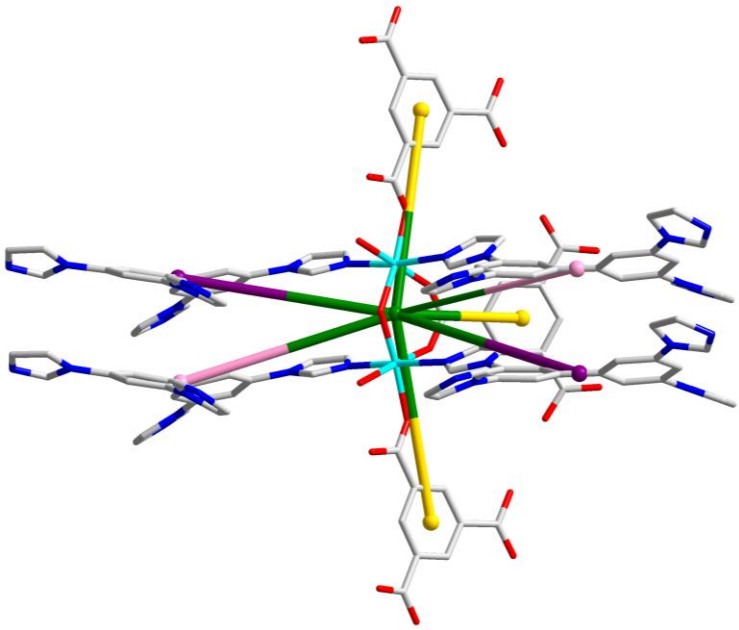
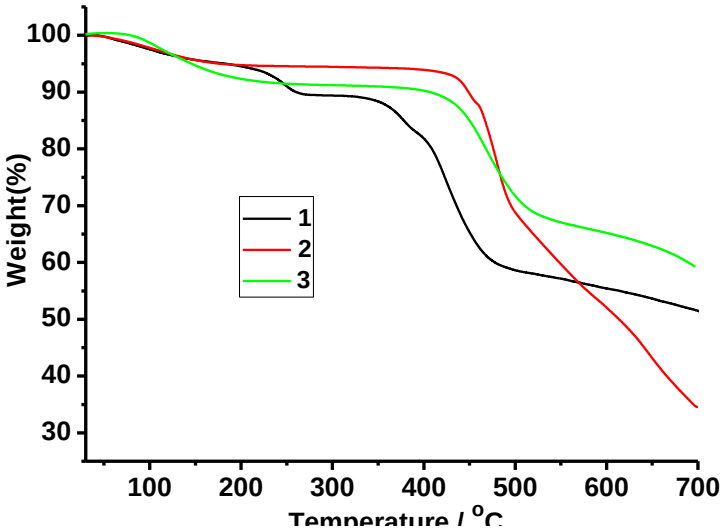
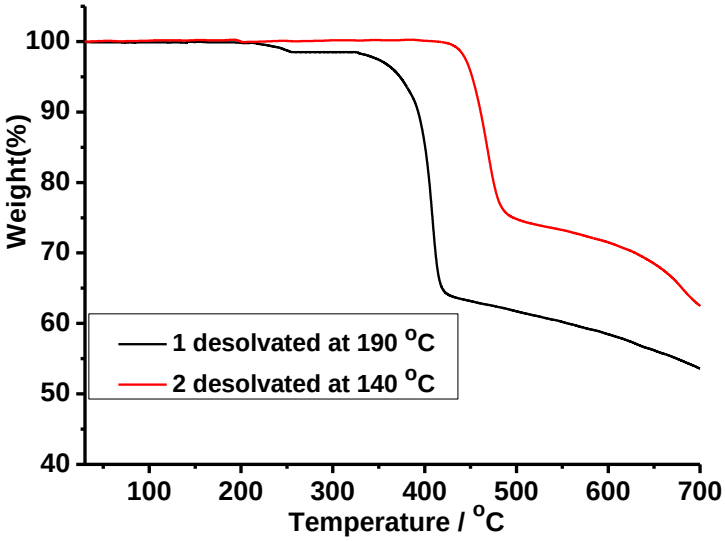


Fig. S5 The seven-node of [Co_2(μ_2-OH)(OCO)] binuclear subunit in **3**.



(A)



(B)

Fig. S6 TGA curves for complexes **1- 3** (A), samples **1'** and **2'** (B).

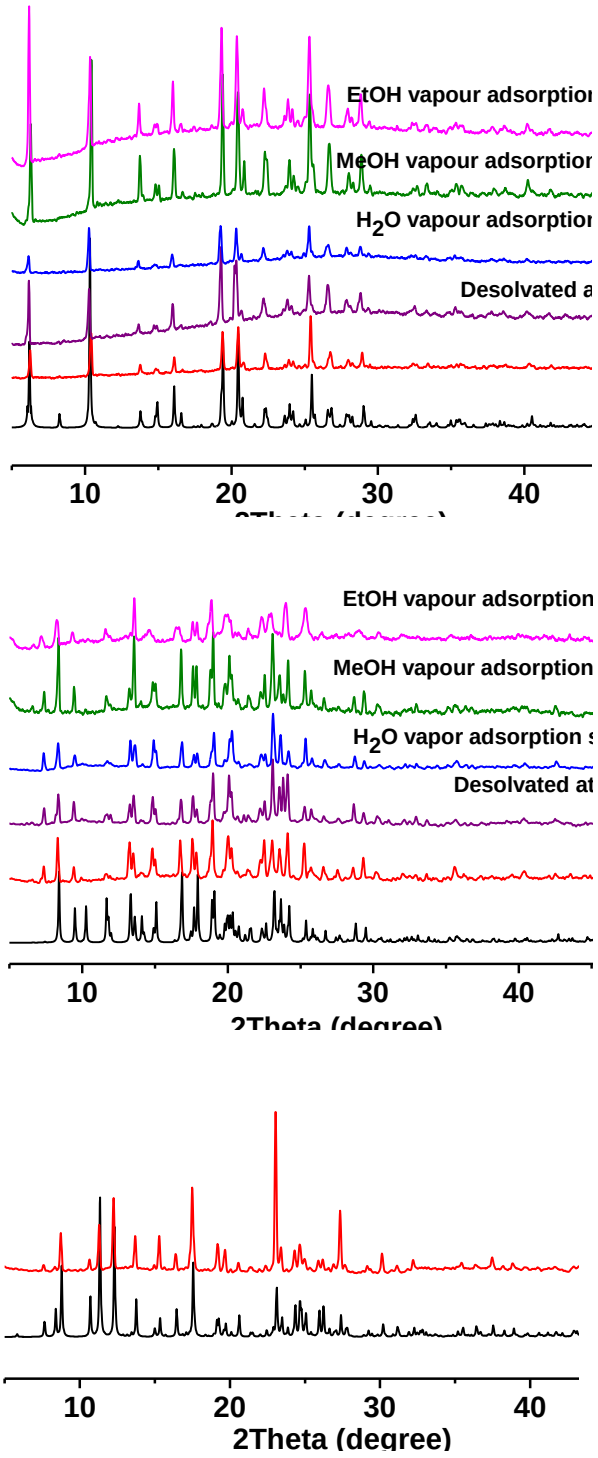


Fig. S7 The PXRD patterns of complexes **1** - **3** under different conditions: a - simulated; b - as-synthesized.