Electronic Supplementary Information

Alkaline cations directed structural diversity of cubic-cage-based cobalt(II) metal-organic frameworks: from *pcu* to *bct* net

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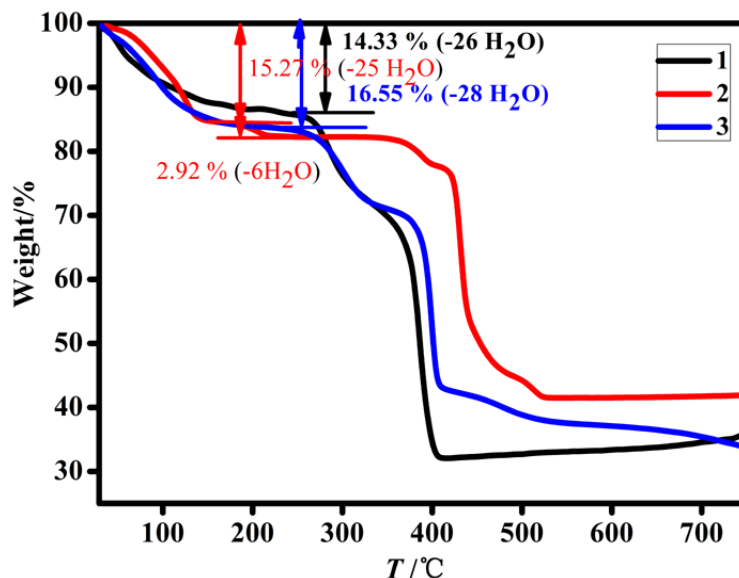
1. Thermogravimetric analysis

Fig. S1. The thermal gravimetric analysis (TGA) data of **1-3.**

The TGA curve shows a weight loss of 14.33% for **1** during the first major step before 250 °C, corresponding to the removal of twenty uncoordinated water molecules and six coordinated water molecules (Calculated: 14.23%). After the losses of all water molecules, no weight loss is observed, indicating the decomposition of **1**. The TGA curve shows a weight loss of 15.27% for **2** during the first major step before 145 °C, corresponding to the removal of twenty-five uncoordinated water molecules (Calculated: 15.13%). After the losses of all uncoordinated water molecules, another weight loss of 2.92% is observed at 240 °C, corresponding to the removal of six coordinated water molecules (Calculated: 3.63%). The framework is stable up to 340 ℃ until decomposition. The TGA curve shows a weight loss of 16.55% for **3** during the first major step before 235 °C, corresponding to the removal of twenty-six uncoordinated water molecules and two coordinated water molecules (Calculated: 16.27%). After the losses of all water molecules, no weight loss is observed, indicating the decomposition of **3**
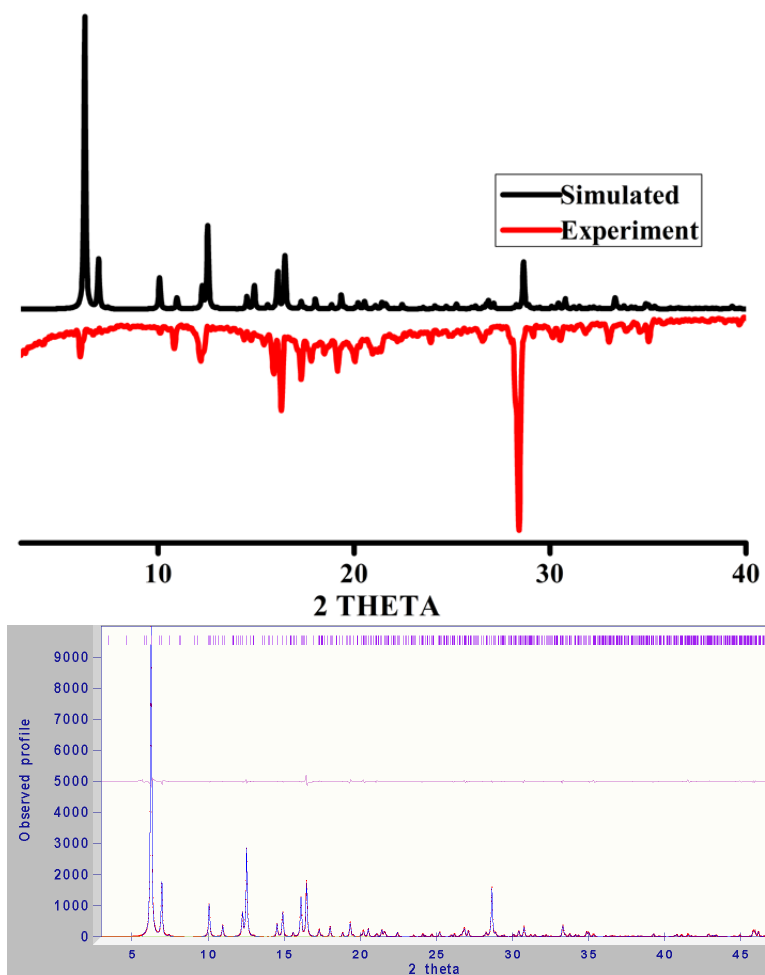
2. Power X-Ray diffraction

Fig. S2. Comparison of the experimental PXRD pattern of as-synthesized **1** with the one simulated from its single crystal structure (top); Room temperature X-ray diffraction pattern of of **1** fitted using the Pawley method (bottom).

Fig. S3. Comparison of the experimental PXRD pattern of as-synthesized **2** with the one simulated from its single crystal structure (top); Room temperature X-ray diffraction pattern of **2** fitted using the Pawley method (bottom).
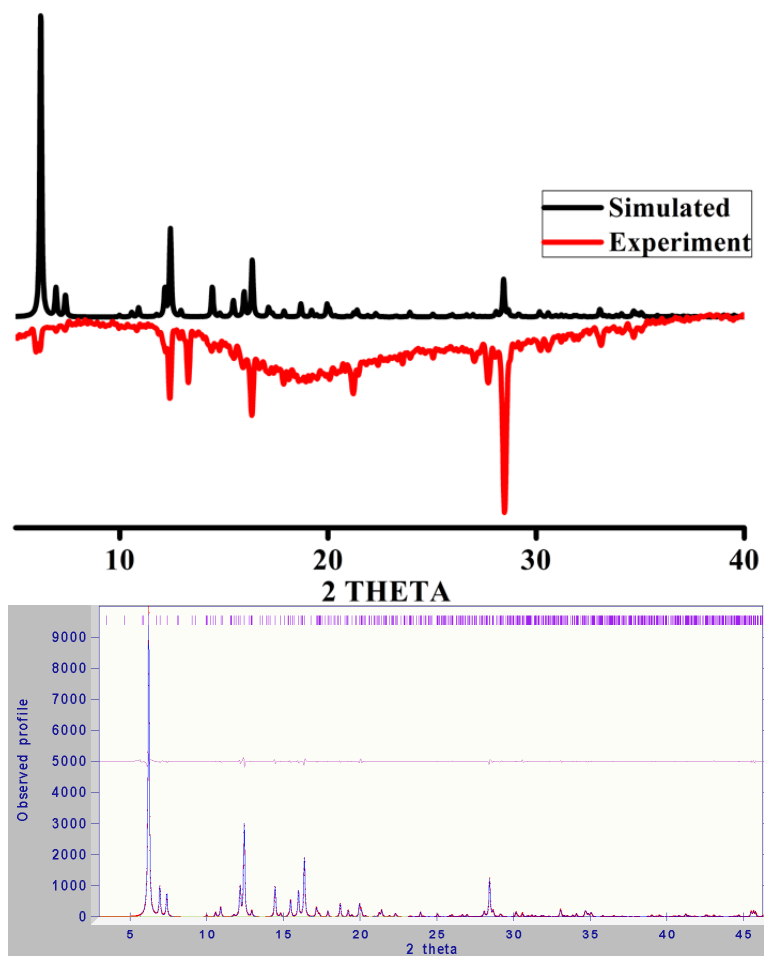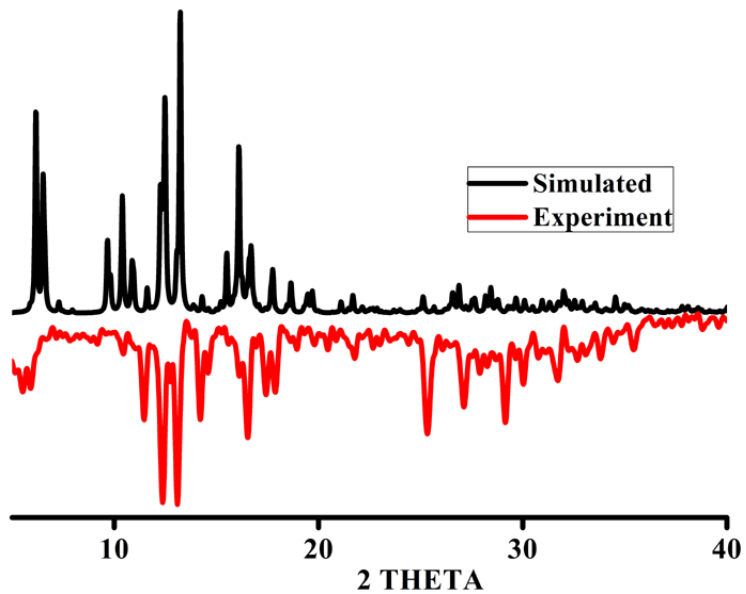
Fig. S4. Comparison of the experimental PXRD pattern of as-synthesized **3** with the one simulated from its single crystal structure.
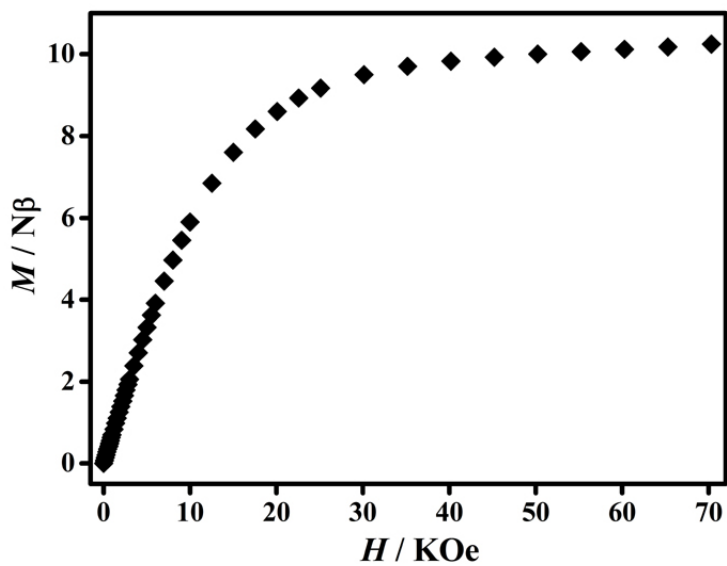
3. Magnetism Measurements

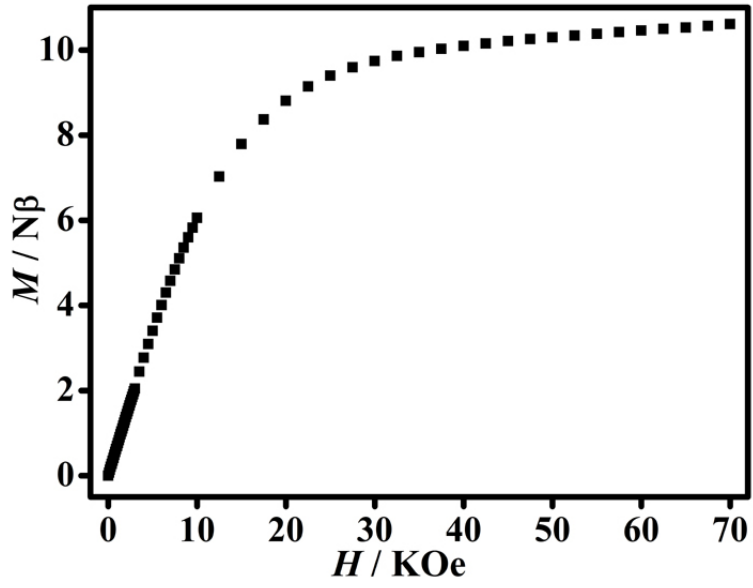**Fig. S5.** Field dependence of magnetizations for **1** at 2 K

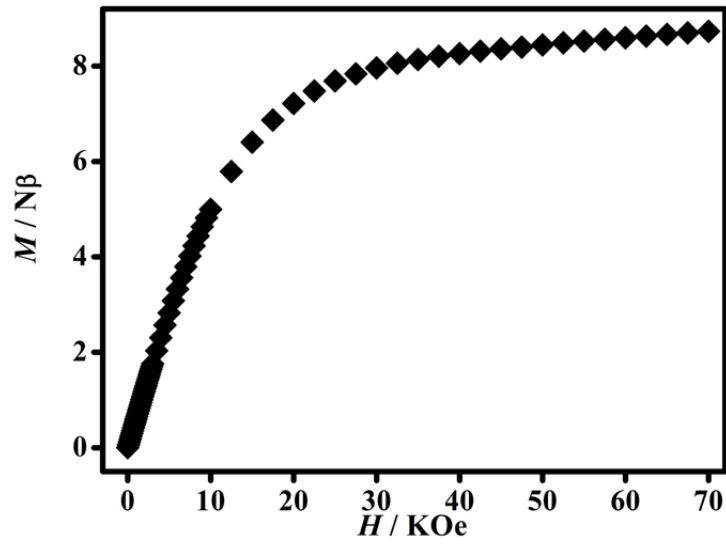**Fig. S6.** Field dependence of magnetizations for **2** at 2 K.

Fig. S7. Field dependence of magnetizations for **3** at 2 K.

4. BVS Calculations

The bond valence sum (BVS) calculations have been carried out based on BVS model.[1]

Table S1. Bond valence values for cobalt centers in **1-3**.

Bond type	Bond distance / Å	Bond valence	Bond valence sum
		1	
Co(1)-O(1)#1	2.016(3)	0.409	2.298 for Co1
Co(1)-O(1)#2	2.016(3)	0.409	
Co(1)-O(1)	2.016(3)	0.409	
Co(1)-N(1)#1	2.031(4)	0.357	
Co(1)-N(1)#2	2.031(4)	0.357	
Co(1)-N(1)	2.031(4)	0.357	
Co(2)-O(8)#3	1.996(4)	0.431	2.421 for Co2
Co(2)-N(4)	2.004(4)	0.384	
Co(2)-N(3)	1.997(4)	0.391	
Co(2)-O(4)	2.004(3)	0.422	
Co(2)-N(6)#3	2.016(5)	0.372	
Co(2)-O(5)	2.006(4)	0.420	
Co(3)-O(9) #4	2.048(3)	0.374	2.243 for Co3
Co(3)-O(9) #5	2.048(3)	0.374	
Co(3)-O(9) #6	2.048(3)	0.374	
Co(3)-O(9) #7	2.048(3)	0.374	
Co(3)-O(9) #8	2.048(3)	0.374	
Co(3)-O(9)	2.048(3)	0.374	
		2	
Co(1)-O(1)	2.010(3)	0.415	2.332 for Co1
Co(1)-O(1)#1	2.010(3)	0.415	
Co(1)-O(1)#2	2.010(3)	0.415	
Co(1)-N(1)#1	2.026(4)	0.362	
Co(1)-N(1)#2	2.026(4)	0.362	
Co(1)-N(1)	2.026(4)	0.362	
Co(2)-O(5)	2.002(4)	0.425	2.334 for Co2
Co(2)-O(4)	2.016(3)	0.409	
Co(2)-O(8)#3	2.016(4)	0.409	
Co(2)-N(6)#3	2.019(5)	0.369	
Co(2)-N(4)	2.025(5)	0.363	
Co(2)-N(3)	2.028(4)	0.360	
Co(3)-O(9)	2.062(3)	0.361	2.166 for Co3
Co(3)-O(9)#5	2.062(3)	0.361	
Co(3)-O(9)#6	2.062(3)	0.361	
Co(3)-O(9)#4	2.062(3)	0.361	
Co(3)-O(9)#7	2.062(3)	0.361	
Co(3)-O(9)#8	2.062(3)	0.361	
		3	
Co(1)-N(3)	1.976(6)	0.414	2.477 for Co1
Co(1)-O(4)	1.984(5)	0.446	

Co(1)-O(5)	1.992(5)	0.436
Co(1)-N(7)	1.987(7)	0.402
Co(1)-O(9)	2.017(5)	0.408
Co(1)-N(4)	2.017(6)	0.371
Co(2)-N(18)#2	1.988(6)	0.401	2.389 for Co2
Co(2)-O(2)#2	2.004(5)	0.422
Co(2)-N(1)#2	2.007(6)	0.381
Co(2)-O(24)#2	2.011(5)	0.414
Co(2)-O(16)	2.013(4)	0.412
Co(2)-N(12)	2.030(5)	0.358
Co(3)-N(9)	1.988(7)	0.401	2.393 for Co3
Co(3)-O(17)	2.002(6)	0.425
Co(3)-O(13)	2.010(5)	0.415
Co(3)-N(10)	2.009(5)	0.379
Co(3)-O(12)	2.022(5)	0.402
Co(3)-N(13)	2.017(6)	0.371
Co(4)-O(20)	1.971(7)	0.462	2.447 for Co4
Co(4)-N(16)	1.996(7)	0.393
Co(4)-O(21)	1.998(5)	0.429
Co(4)-N(15)	2.013(6)	0.375
Co(4)-N(6)#2	2.005(7)	0.383
Co(4)-O(7)#2	2.019(5)	0.405

Symmetry transformations used to generate equivalent atoms:

For **1**: #1: -x+y+1,-x+2,z, #2: -y+2,x-y+1,z, #3: y,x-y+1,-z+1, #4: x-y,x,-z+1, #5: -x+y,-x,z #6: -y,x-y,z, #7: y,-x+y,-z+1, #8: -x,-y,-z+1, #9: x-y+2/3,-y+4/3,-z+5/6;

For **2**: #1: -x+y+1,-x+2,z, #2: -y+2,x-y+1,z, #3: y,-x+y+1,-z+1, #4: x-y,x,-z+1, #5: -x+y,-x,z, #6: -y,x-y,z, #7: y,-x+y,-z+1, #8: -x,-y,-z+1, #9: x-y+2/3,-y+4/3,-z+5/6;

For **3**: #1: -x+1,y,-z+1/2, #2: -x+3/2,-y+3/2,-z+1.

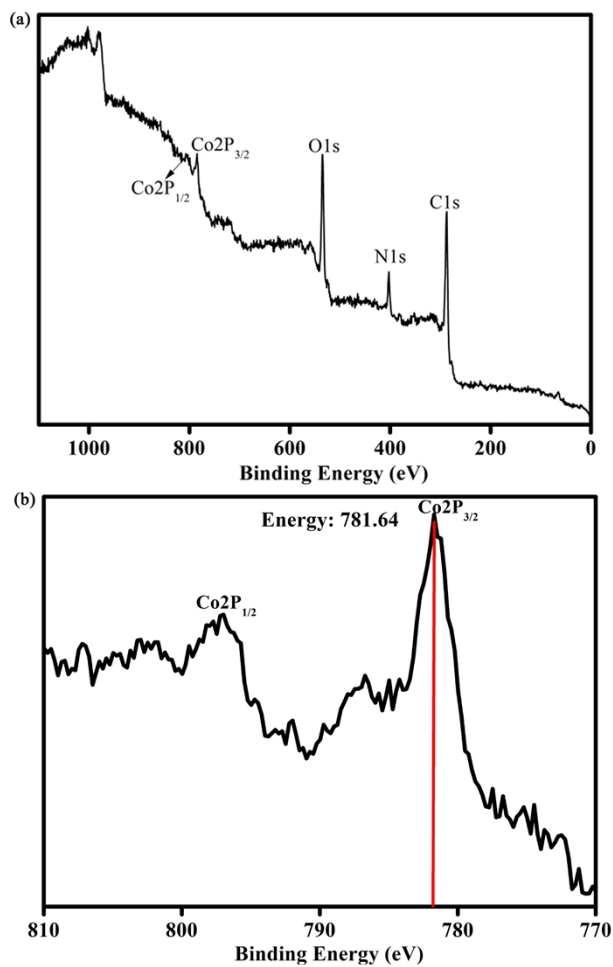## 5. X-ray Photoelectron Spectroscopy

Fig. S8. (a) X-ray photoelectron spectroscopy (XPS) of **1**; (b) XPS of the Co 2*p* level in **1**.
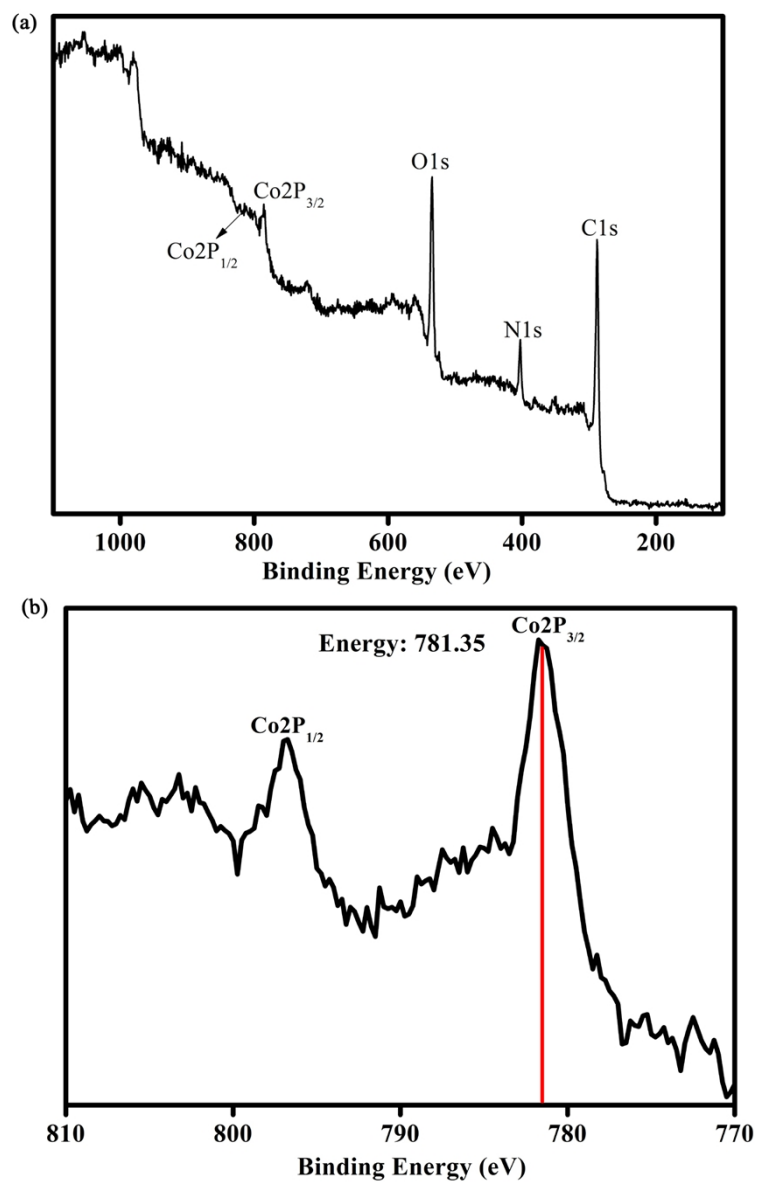
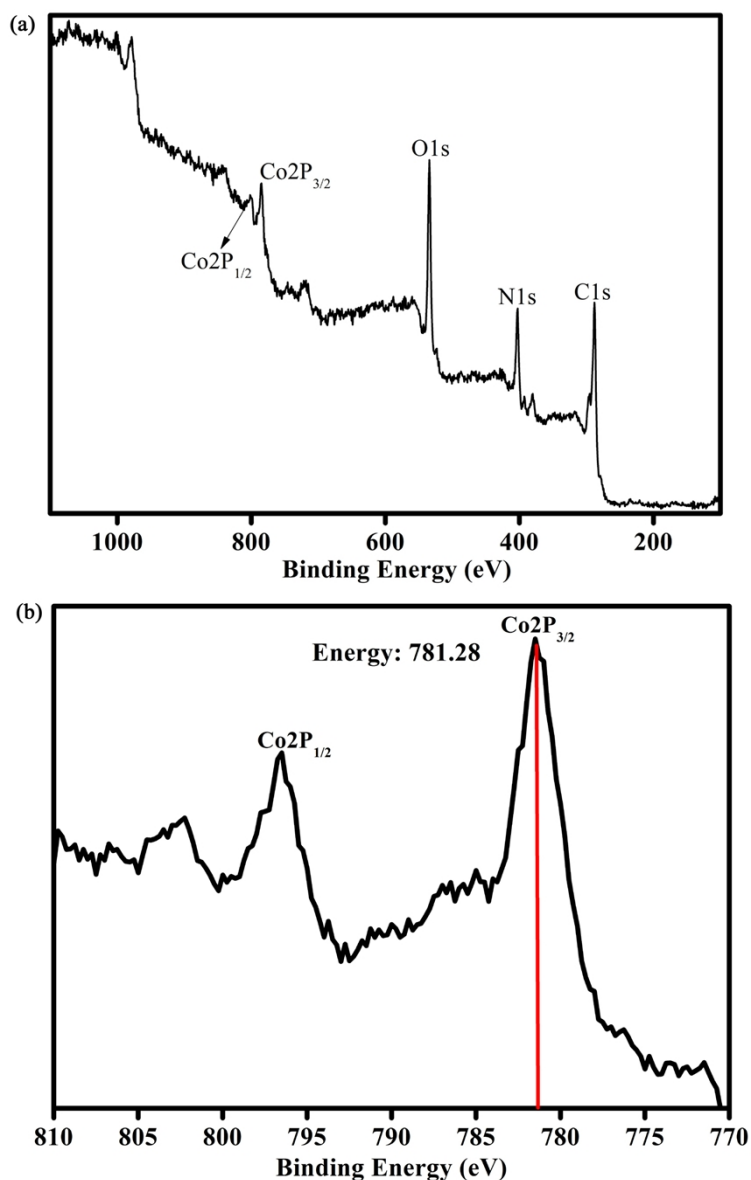Fig. S9. (a) X-ray photoelectron spectroscopy (XPS) of **2**; (b) XPS of the Co 2*p* level in **2**.

Fig. S10. (a) X-ray photoelectron spectroscopy (XPS) of **3**; (b) XPS of the Co 2*p* level in **3**.

The characteristic peaks of $Co^{3+}2P_{3/2}$ level of 779.2-779.6 ev with 15.1 eV splitting in **1-3** are not observed.[2] Instead, the Co2p spectrum with shake-up levels agreed well with the known Co^{2+} complexes.[3] These results indicate that all cobalt ions are divalent in **1-3**.

1. I. D. Brown, *The Chemical Bond in Inorganic Chemistry: The Bond Valence Model*, published by Oxford University Press, 2002, database available at http://www.iucr.org/resources/data/data-sets/bond-valence-parameters

2. S. H. Xiang, X. T. Wu, J. J. Zhang, R. B. Fu, S. M. Hu and X. D. Zhang, *J. Am. Chem. Soc.*, 2005, **127**, 16352.

3. (a) J. H. Burness, J. G. Dillard and L. T. Taylor, *J. Am. Chem. Soc.*, 1975, 6080; (b) J. Y. Zou, W. Shi, N. Xu, L. L. Li, J. K. Tang, H. L. Gao, J. Z. Cui and P. Cheng, *Chem. Commun.*, 2013, **49**, 8226.