

**Effect of the structural disorder of T-shaped triazolyl-based coordination network compounds on the pore size and stability**

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**Methods**

Elemental analyses for C, H, and N were performed on a Perkin-Elmer 240C Elemental Analyzer. Thermogravimetric analyses (TGA) were performed on a simultaneous SDT 2960 thermal analyzer under nitrogen with a heating rate of 10 °C min<sup>-1</sup>. FT-IR spectra were recorded in the range of 400 - 4000 cm<sup>-1</sup> on a Bruker Vector22 FT-IR spectrophotometer using KBr pellets. Power X-ray diffraction (PXRD) patterns were measured on a Shimadzu XRD-6000 X-ray diffractometer with Cu K $\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) radiation at room temperature. The gas sorption isotherms were collected on a Belsorp-Max surface area and pore size analyzer under ultrahigh vacuum in a clean system, with a diaphragm and turbo pumping system. Ultrahigh-purity-grade (> 99.999%) N<sub>2</sub> and He gases were applied in adsorption measurements. The experimental temperatures were maintained by liquid nitrogen (77 K).

**Table S1** Selected bond lengths [Å] and angles [°] for Zn-CNC and Co-CNC.<sup>a</sup>

Zn-CNC			
Zn(1)–O(3) <sup>#1</sup>	1.992(10)	Zn(1)–O(1)	2.035(9)
Zn(1)–O(2) <sup>#2</sup>	2.039(10)	Zn(1)–N(12) <sup>#3</sup>	2.048(9)
Zn(1)–O(4) <sup>#4</sup>	2.070(12)	Zn(1B)–O(4B) <sup>#1</sup>	2.01(4)
Zn(1B)–O(1B) <sup>#5</sup>	2.02(5)	Zn(1B)–O(3B) <sup>#6</sup>	2.07(5)
Zn(1B)–O(2B)	2.15(3)	Zn(1B)–N(13) <sup>#7</sup>	2.152(11)
O(3) <sup>#1</sup> –Zn(1)–O(1)	90.2(4)	O(1)–Zn(1)–O(2) <sup>#2</sup>	157.2(4)
O(3) <sup>#1</sup> –Zn(1)–O(2) <sup>#2</sup>	89.5(4)	O(3) <sup>#1</sup> –Zn(1)–N(12) <sup>#3</sup>	104.1(4)
O(2) <sup>#2</sup> –Zn(1)–N(12) <sup>#3</sup>	96.7(4)	O(1)–Zn(1)–N(12) <sup>#3</sup>	105.5(4)
O(1)–Zn(1)–O(4) <sup>#4</sup>	88.8(4)	O(3) <sup>#1</sup> –Zn(1)–O(4) <sup>#4</sup>	156.9(4)
O(2) <sup>#2</sup> –Zn(1)–O(4) <sup>#4</sup>	82.6(5)	N(12) <sup>#3</sup> –Zn(1)–O(4) <sup>#4</sup>	98.4(4)
O(4B) <sup>#1</sup> –Zn(1B)–O(1B) <sup>#5</sup>	90.4(18)	O(4B) <sup>#1</sup> –Zn(1B)–O(3B) <sup>#6</sup>	152.8(18)
O(1B) <sup>#5</sup> –Zn(1B)–O(3B) <sup>#6</sup>	93(2)	O(4B) <sup>#1</sup> –Zn(1B)–O(2B)	68.3(15)
O(1B) <sup>#5</sup> –Zn(1B)–O(2B)	148.6(17)	O(3B) <sup>#6</sup> –Zn(1B)–O(2B)	96.0(19)
O(4B) <sup>#1</sup> –Zn(1B)–N(13) <sup>#7</sup>	98.8(9)	O(1B) <sup>#5</sup> –Zn(1B)–N(13) <sup>#7</sup>	103.2(15)
O(3B) <sup>#6</sup> –Zn(1B)–N(13) <sup>#7</sup>	106.4(12)	O(2B)–Zn(1B)–N(13) <sup>#7</sup>	102.6(8)
Co-CNC			
Co(1)–O(2) <sup>#1</sup>	2.021(7)	Co(1)–O(3) <sup>#2</sup>	2.023(7)
Co(1)–O(1)	2.036(6)	Co(1)–N(12) <sup>#4</sup>	2.057(6)
Co(1)–O(4) <sup>#3</sup>	2.038(7)	Co(1B)–O(3B) <sup>#2</sup>	2.027(15)
Co(1B)–O(1B)	2.036(17)	Co(1B)–O(2B) <sup>#5</sup>	2.037(16)
Co(1B)–O(4B) <sup>#6</sup>	2.083(16)	Co(1B)–N(13) <sup>#7</sup>	2.120(7)
O(3) <sup>#2</sup> –Co(1)–O(1)	89.1(3)	O(2) <sup>#1</sup> –Co(1)–O(1)	161.3(3)
O(2) <sup>#1</sup> –Co(1)–O(3) <sup>#2</sup>	92.4(3)	O(1)–Co(1)–O(4) <sup>#3</sup>	83.7(3)
O(1)–Co(1)–N(12) <sup>#4</sup>	91.4(3)	O(2) <sup>#1</sup> –Co(1)–O(4) <sup>#3</sup>	89.1(3)
O(3) <sup>#2</sup> –Co(1)–O(4) <sup>#3</sup>	161.3(3)	O(2) <sup>#1</sup> –Co(1)–N(12) <sup>#4</sup>	106.2(3)
O(4) <sup>#3</sup> –Co(1)–N(12) <sup>#4</sup>	93.3(3)	O(3) <sup>#2</sup> –Co(1)–N(12) <sup>#4</sup>	104.2(3)
O(3B) <sup>#2</sup> –Co(1B)–O(1B)	89.4(7)	O(3B) <sup>#2</sup> –Co(1B)–O(2B) <sup>#5</sup>	92.2(8)
O(1B)–Co(1B)–O(2B) <sup>#5</sup>	159.0(7)	O(3B) <sup>#2</sup> –Co(1B)–O(4B) <sup>#6</sup>	158.0(8)

O(1B)–Co(1B)–O(4B) <sup>#6</sup>	80.8(7)	O(2B) <sup>#5</sup> –Co(1B)–O(4B) <sup>#6</sup>	90.2(8)
O(3B) <sup>#2</sup> –Co(1B)–N(13) <sup>#7</sup>	102.8(6)	O(1B)–Co(1B)–N(13) <sup>#7</sup>	92.1(5)
O(2B) <sup>#5</sup> –Co(1B)–N(13) <sup>#7</sup>	107.9(6)	O(4B) <sup>#6</sup> –Co(1B)–N(13) <sup>#7</sup>	97.3(6)

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<sup>a</sup>Symmetry transformations used to generate equivalent atoms: #1  $x, -y + 3/2, z - 1/2$ ; #2  $-x + 2, -y + 2, -z + 1$ ; #3  $x + 1, y, z$ ; #4  $-x + 2, y + 1/2, -z + 3/2$ ; #5  $-x + 2, -y + 1, -z + 1$ ; #6  $-x + 2, y - 1/2, -z + 3/2$ ; #7  $-x + 1, -y + 1, -z + 1$  for Zn-CNC; #1  $-x, -y + 1, -z + 1$ ; #2  $-x, y - 1/2, -z + 1/2$ ; #3  $x, -y + 3/2, z + 1/2$ ; #4  $-x + 1, -y + 1, -z + 1$ ; #5  $-x, -y + 1, -z$ ; #6  $x, -y + 3/2, z - 1/2$ ; #7  $-x + 1, y - 1/2, -z + 1/2$  for Co-CNC.

**Table S2** Comparison of crystal data for Zn-CNC, Co-CNC, L<sub>triaz</sub>-Mn, L<sub>triaz</sub>-Cu, and L<sub>triaz</sub>-Zn.

	Zn-CNC	Co-CNC	L <sub>triaz</sub> -Mn <sup>1</sup>	L <sub>triaz</sub> -Cu <sup>2</sup>	L <sub>triaz</sub> -Cu <sup>3</sup>	L <sub>triaz</sub> -Cu <sup>4</sup>	L <sub>triaz</sub> -Zn <sup>5</sup>
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P2<sub>1</sub>/c</i>	<i>P2<sub>1</sub>/c</i>	<i>P2<sub>1</sub>/c</i>	<i>P2<sub>1</sub>/c</i>	<i>P2<sub>1</sub>/c</i>	<i>P2<sub>1</sub>/c</i>	<i>P2<sub>1</sub>/c</i>
<i>a</i> /Å	10.939(4)	10.977(5)	11.214(11)	10.884(5)	10.9121(3)	10.968(2)	10.9484(3)
<i>b</i> /Å	12.157(5)	11.819(4)	12.585(13)	12.049(6)	11.8420(3)	12.2031(14)	12.1060(4)
<i>c</i> /Å	14.450(6)	14.682(5)	14.447(15)	14.338(7)	14.5557(5)	14.366(2)	14.7728(5)
$\beta$ /°	110.232(14)	109.648(14)	110.125(15)	109.552(7)	109.471(3)	110.304(13)	109.791(3)
Volume /Å <sup>3</sup>	1803.0(13)	1793.9(12)	1914(3)	1772.0(15)	1773.35(10)	1803.3(5)	1842.35(10)
<i>Z</i>	4	4	4	4	4	4	4
solvent-accessible area /Å <sup>3</sup>	350.4	363.1	905.5	741.8	742.0	741.5	846.3
solvent-accessible area per unit cell volume /%	19.4	20.2	47.3	41.9	41.8	41.1	45.9

1 T. Panda, P. Pachfule and R. Banerjee, *Chem. Commun.*, 2011, **47**, 7674.

2 J. F. Eubank, L. Wojtas, M. R. Hight, T. Bousquet, V. Ch. Kravtsov and M. Eddaoudi, *J. Am. Chem. Soc.*, 2011, **133**, 17532.

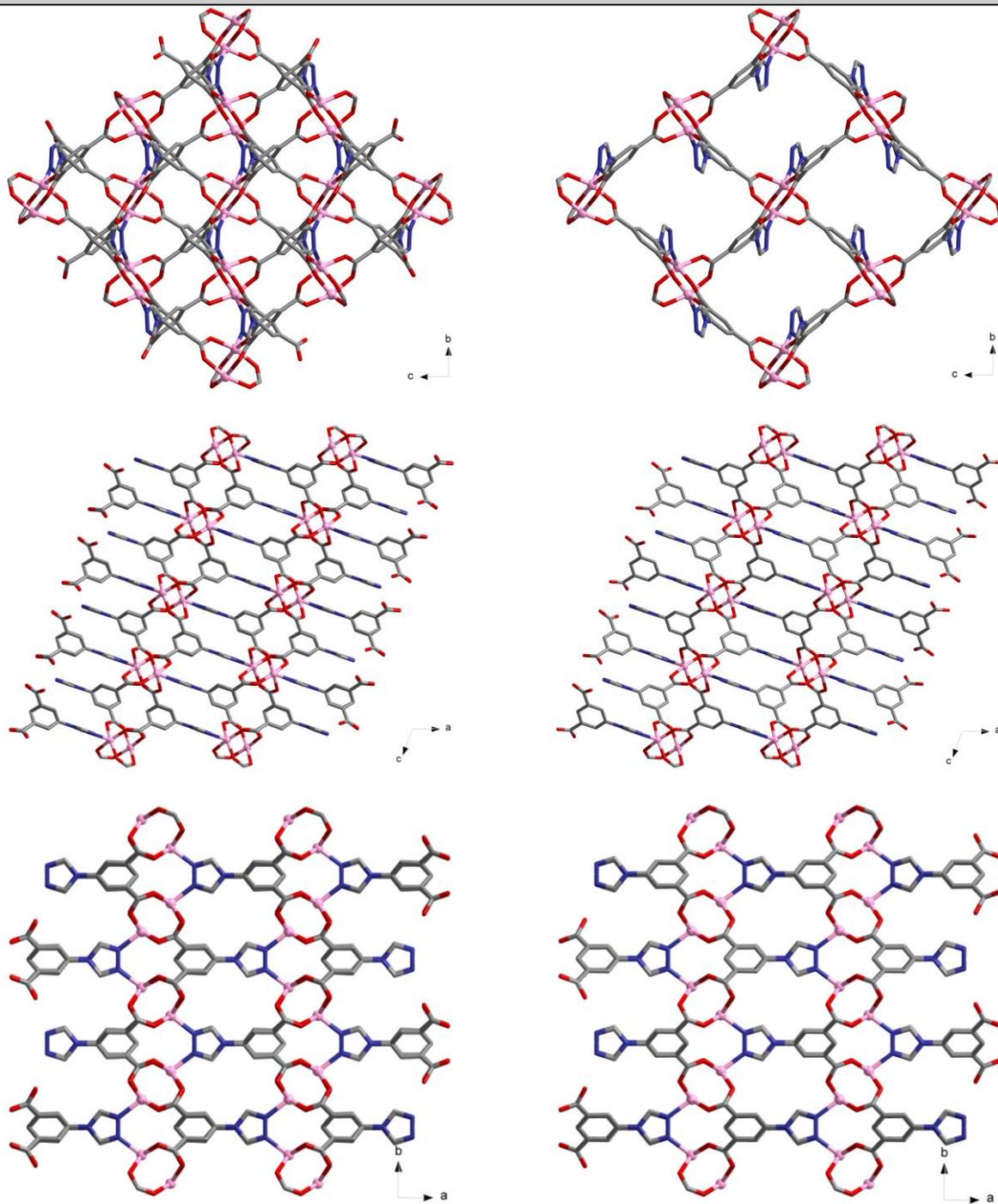
3 Z. Yao, Z. Zhang, L. Liu, Z. Li, W. Zhou, Y. Zhao, Y. Han, B. Chen, R. Krishna and S. Xiang, *Chem.–Eur. J.*, 2016, **22**, 5676.

4 M. Kobalz, J. Lincke, K. Kobalz, O. Erhart, J. Bergmann, D. Lässig, M. Lange, J. Möllmer, R. Gläser, R. Staudt and H. Krautscheid, *Inorg. Chem.*, 2016, **55**, 3030.

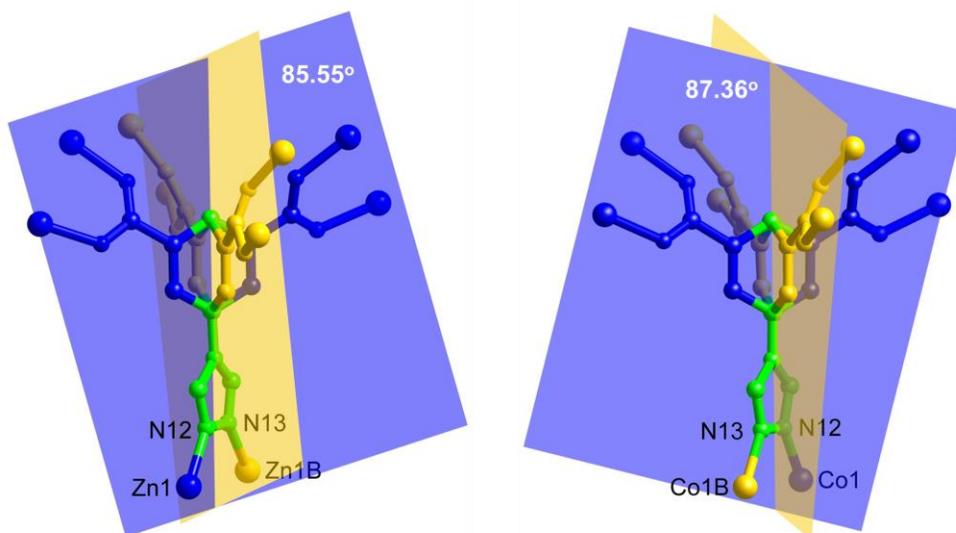
5 D.-M. Chen, X.-Z. Ma, W. Shi and P. Cheng, *Cryst. Growth Des.*, 2015, **15**, 3999.

**The disordered framework**

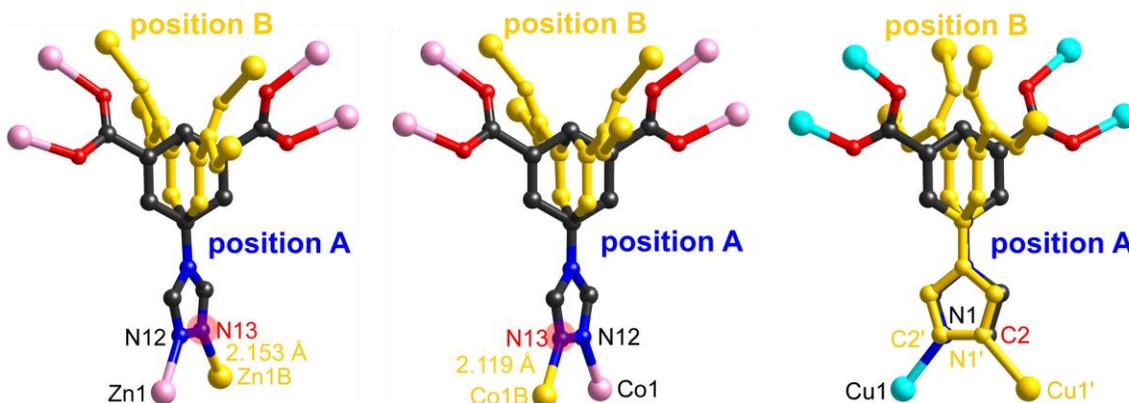
**The ordered framework**



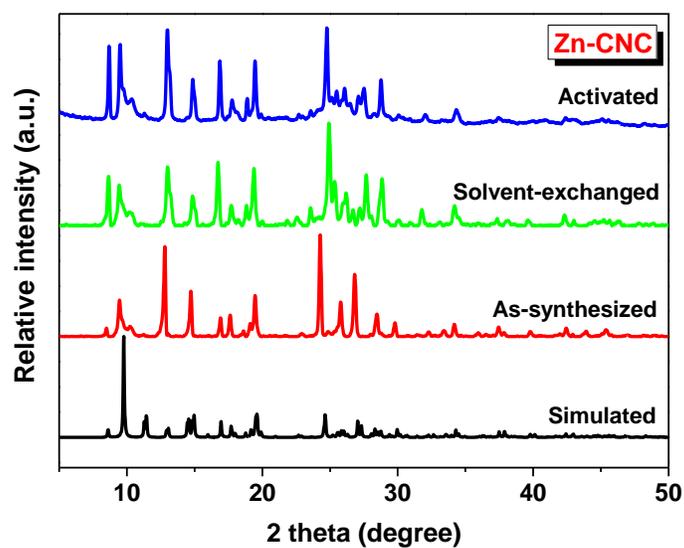
**Figure S1** Comparison of the disordered and ordered frameworks based on  $H_2L_{\text{triaz}}$  viewed along *a*- (top), *b*- (middle), and *c*- (bottom) axis directions. Solvated molecules and H atoms are omitted for clarity.



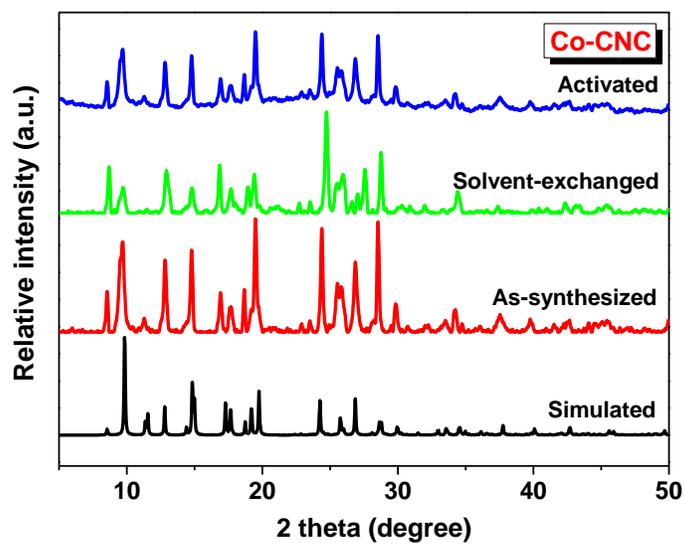
**Figure S2** View of the dihedral angle between benzene rings of positions A and B in Zn-CNC (left) and Co-CNC (right).



**Figure S3** The distances between the metal ion of position B and nitrogen atom of position A in Zn-CNC (left) and Co-CNC (middle). View of the location of two disordered parts (position A and position B) in  $T_{\text{imi}}$ -Cu (right).

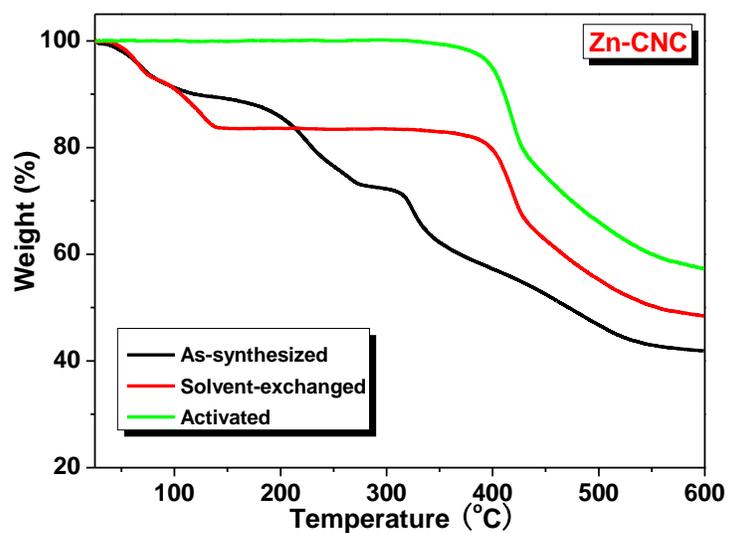


(a)

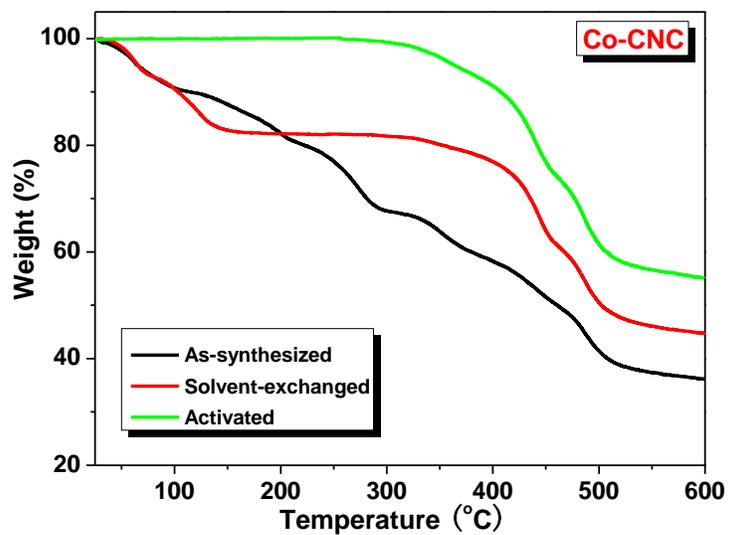


(b)

**Figure S4** Powder X-ray diffraction patterns of samples for Zn-CNC (a) and Co-CNC (b).



(a)



(b)

Figure S5 TGA curves of samples for Zn-CNC (a) and Co-CNC (b).