Table S1 Crystallographic data

Compound	**1**	**2**	**3**
Empirical formula	$C_{66}H_{46}Co_3N_8O_{13}$	$C_{80}H_{62}Co_5N_8O_{22}$	$C_{27}H_{20}Co_2N_4O_8$
Formula weight	1335.90	1782.02	646.34
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	P2(1)/c
a(Å)	10.750(2)	11.560(3)	15.831(1)
b(Å)	16.747(4)	13.891(3)	11.1386(8)
c(Å)	17.011(4)	14.765(4)	27.232(3)
α(º)	95.475(2)	93.156(2)	90
β(º)	100.277(3)	107.051(3)	99.996(5)
γ(º)	101.979(2)	96.782(4)	90
V(Å^3)	2919.7(11)	2240.8(9)	4729.1(7)
Z	2	1	4
D_{calcd}(g·cm^{-3})	1.520	1.321	0.908
μ(mm^{-1})	0.918	0.976	0.734
R_{int}	0.0951	0.0512	0.0655
Final R indicaes	R_1=0.0500	R_1 = 0.0409 wR_2 =	R_1 = 0.0500
[I>2σ(I)]	wR_2=0.0881	0.1029	wR_2= 0.1238
R indices(all data)	R_1=0.0722	R_1 = 0.0555	R_1 = 0.0645
	wR_2=0.0934	wR_2 = 0.1068	wR_2 = 0.1302
Goof	0.910	1.012	1.032

[a] $R_1 = \sum \| F_o | - | F_c \| / \sum | F_o |$, $wR = \{\sum[w(F_o^2 - F_c^2)^2] / [\sum w(F_o^2)^2]\}^{1/2}$

Table S2 Selected bond lengths(Å)and bond angles(º)of compound 1

Co(1)-O(8)	2.034(2)	Co(1)-O(4)	2.080(2)	Co(1)-N(1)	2.087(2)
Co(1)-O(6A)	2.13(2)	Co(1)-O(5A)	2.182(2)	Co(1)-O(10)	2.185(2)
Co(2)-O(3)	1.966(2)	Co(2)-O(7)	1.984(2)	Co(2)-N(3)	2.020(2)
Co(2)-O(10)	2.022(2)	Co(3)-O(11)	1.973(2)	Co(3)-O(1B)	1.988(2)
Co(3)-N(7)	2.030(2)	Co(3)-N(5)	2.033(2)		

O(8)-Co(1)-O(4)	88.08(9)	O(8)-Co(1)-N(1)	176.4(1)
O(4)-Co(1)-N(1)	89.54(8)	O(8)-Co(1)-O(6A)	87.91(8)
O(4)-Co(1)-O(6A)	170.29(8)	N(1)-Co(1)-O(6A)	94.01(8)
O(8)-Co(1)-O(5A)	89.31(8)	O(4)-Co(1)-O(5A)	110.02(8)
N(1)-Co(1)-O(5A)	88.90(8)	O(6A)-Co(1)-O(5A)	61.09(7)
O(8)-Co(1)-O(10)	92.64(8)	O(4)-Co(1)-O(10)	94.03(8)
N(1)-Co(1)-O(10)	90.28(8)	O(6A)-Co(1)-O(10)	94.99(7)
O(5A)-Co(1)-O(10)	155.93(7)	O(3)-Co(2)-O(7)	101.77(9)
O(3)-Co(2)-N(3)	116.56(9)	O(7)-Co(2)-N(3)	97.07(9)
O(3)-Co(2)-O(10)	120.52(9)	O(7)-Co(2)-O(10)	101.96(8)
N(3)-Co(2)-O(10)	113.45(8)	O(11)-Co(3)-O(1B)	122.20(9)
O(11)-Co(3)-N(7)	93.99(9)	O(1B)-Co(3)-N(7)	114.24(9)

O(11)-Co(3)-N(5)	91.04(9)	O(1B)-Co(3)-N(5)	110.48(9)
N(7)-Co(3)-N(5)	122.6(1)		

Symmetry Code:A,x+1,y,z; B,x,y,z-1

Table S3 Selected bond lengths(Å)and bond angles(º)of compound 2

Co(1)-O(5A)	2.011(2)	Co(1)-O(5)	2.011(2)	Co(1)-O(10)	2.043(2)
Co(1)-O(10A)	2.043(2)	Co(1)-O(9A)	2.217(2)	Co(1)-O(9)	2.217(2)
Co(2)-O(10)	2.060(2)	Co(2)-N(1)	2.066(2)	Co(2)-O(7B)	2.085(2)
Co(2)-O(6A)	2.093(2)	Co(2)-N(4)	2.140(2)	Co(2)-O(9)	2.340(2)
Co(3)-O(8B)	1.952(2)	Co(3)-O(3)	1.954(2)	Co(3)-O(10)	1.959(2)
Co(3)-O(1C)	1.994(2)				

O(5A)-Co(1)-O(5)	180.0	O(5A)-Co(1)-O(10)	94.33(7)
O(5)-Co(1)-O(10)	85.67(7)	O(5A)-Co(1)-O(10A)	85.67(7)
O(5)-Co(1)-O(10A)	94.33(7)	O(10)-Co(1)-O(10A)	180.0
O(5A)-Co(1)-O(9A)	88.51(7)	O(5)-Co(1)-O(9A)	91.49(7)
O(10)-Co(1)-O(9A)	96.57(7)	O(10A)-Co(1)-O(9A)	83.43(7)
O(5A)-Co(1)-O(9)	91.49(7)	O(5)-Co(1)-O(9)	88.51(7)
O(10)-Co(1)-O(9)	83.43(7)	O(10A)-Co(1)-O(9)	96.57(7)
O(9A)-Co(1)-O(9)	180.0	O(10)-Co(2)-N(1)	173.52(7)
O(10)-Co(2)-O(7B)	94.47(7)	N(1)-Co(2)-O(7B)	91.96(8)
O(10)-Co(2)-O(6A)	91.09(7)	N(1)-Co(2)-O(6A)	87.75(8)
O(7B)-Co(2)-O(6A)	92.96(7)	O(10)-Co(2)-N(4)	86.19(8)
N(1)-Co(2)-N(4)	94.19(9)	O(7B)-Co(2)-N(4)	94.10(8)
O(6A)-Co(2)-N(4)	172.61(7)	O(10)-Co(2)-O(9)	80.05(6)
N(1)-Co(2)-O(9)	93.49(7)	O(7B)-Co(2)-O(9)	173.90(7)
O(6A)-Co(2)-O(9)	84.51(6)	N(4)-Co(2)-O(9)	88.25(7)
O(8B)-Co(3)-O(3)	97.90(8)	O(8B)-Co(3)-O(10)	105.90(8)
O(3)-Co(3)-O(10)	125.71(8)	O(8B)-Co(3)-O(1C)	131.29(9)
O(3)-Co(3)-O(1C)	101.57(9)	O(10)-Co(3)-O(1C)	97.97(8)

Symmetry Code: A,-x+1,-y,-z;B,x,y+1,z;C, -x+2,-y,-z

Table S4 Selected bond lengths(Å)and bond angles(º)of compound 3

Co(1)-O(4A)	2.082(2)	Co(1)-O(7B)	2.095(2)	Co(1)-O(1)	2.102(2)
Co(1)-N(4C)	2.116(2)	Co(1)-O(7)	2.121(2)	Co(1)-O(6D)	2.125(2)
Co(2)-O(7)	1.982(2)	Co(2)-O(5D)	1.984(2)	Co(2)-O(3E)	2.003(2)
Co(2)-N(1)	2.070(2)	Co(2)-O(1)	2.277(2)		

O(4A)-Co(1)-O(7B)	96.47(6)	O(4A)-Co(1)-O(1)	169.29(7)
O(7B)-Co(1)-O(1)	92.56(6)	O(4A)-Co(1)-N(4C)	88.83(9)
O(7B)-Co(1)-N(4C)	93.38(8)	O(1)-Co(1)-N(4C)	96.40(8)
O(4A)-Co(1)-O(7)	94.08(7)	O(7B)-Co(1)-O(7)	80.13(7)
O(1)-Co(1)-O(7)	81.78(6)	N(4C)-Co(1)-O(7)	173.14(8)

O(4A)-Co(1)-O(6D)	85.13(7)	O(7B)-Co(1)-O(6D)	172.47(7)
O(1)-Co(1)-O(6D)	85.19(6)	N(4C)-Co(1)-O(6D)	94.01(8)
O(7)-Co(1)-O(6D)	92.43(7)	O(7)-Co(2)-O(5D)	103.33(8)
O(7)-Co(2)-O(3E)	111.68(7)	O(5D)-Co(2)-O(3E)	142.58(8)
O(7)-Co(2)-N(1)	104.41(9)	O(5D)-Co(2)-N(1)	93.91(9)
O(3E)-Co(2)-N(1)	89.95(8)	O(7)-Co(2)-O(1)	80.64(6)
O(5D)-Co(2)-O(1)	85.76(8)	O(3E)-Co(2)-O(1)	87.22(7)

Symmetry Code: A, x,y+1,z; B, -x,-y,-z; C, x+1,y,z; D, -x,y+1/2,-z+1/2; E,-x,-y-1,-z

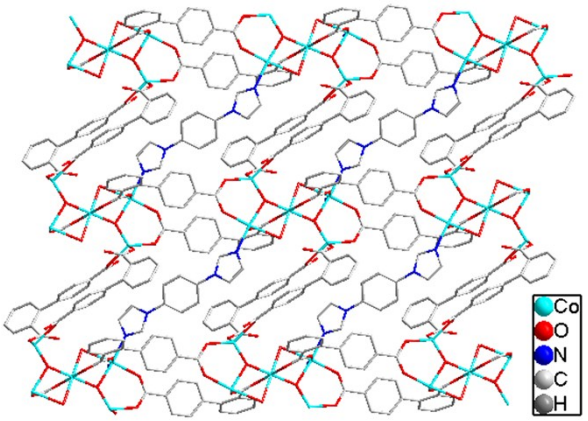

Fig. S1 View of the $[Co_5(OH)_2(H_2O)_2(bpda)_4\,(bib)]$ layer in compound **2**

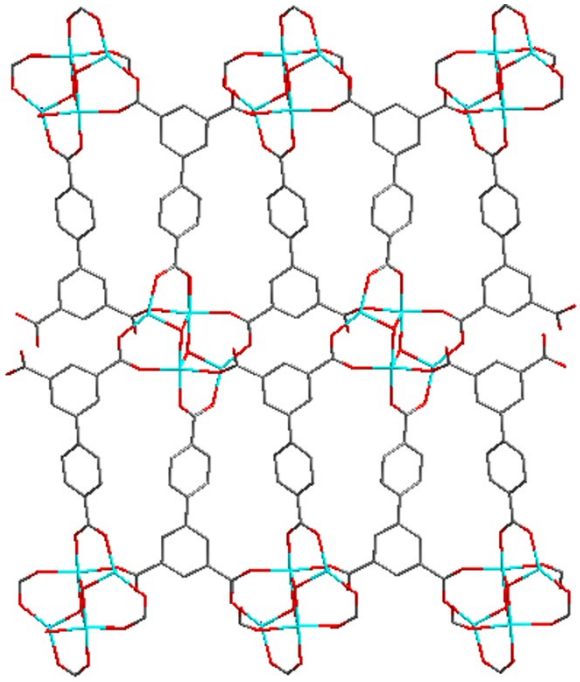

Fig. S2 View of the $[Co_2(\mu_3\text{-}OH)(bpt)_3]_n$ layer in compound **3**

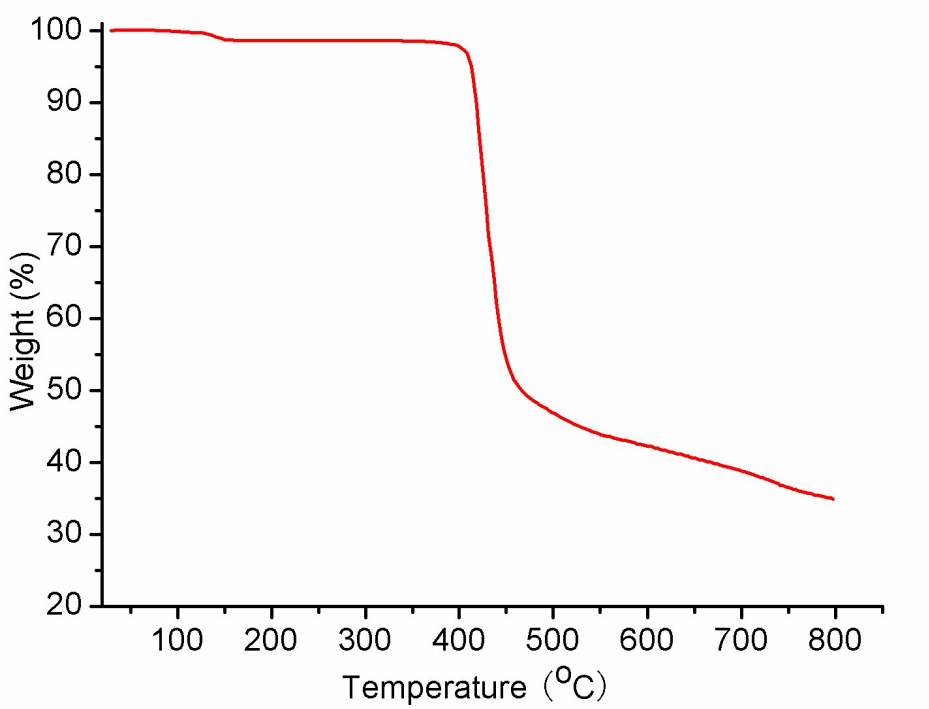

Fig. S3 The TG curve of compound **1**

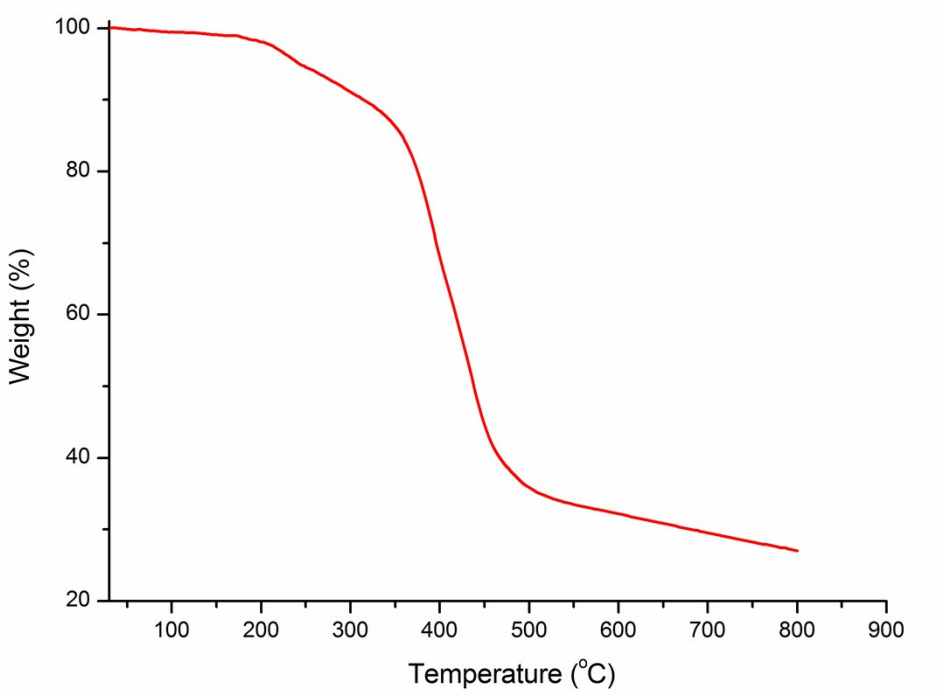

Fig. S4 The TG curve of compound **2**.

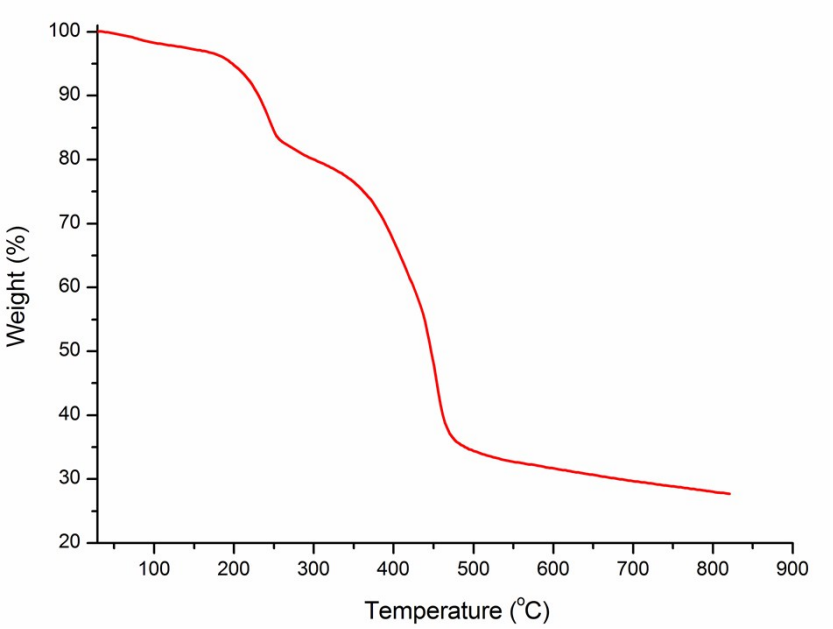

Fig. S5 The TG curve of compound **3**.

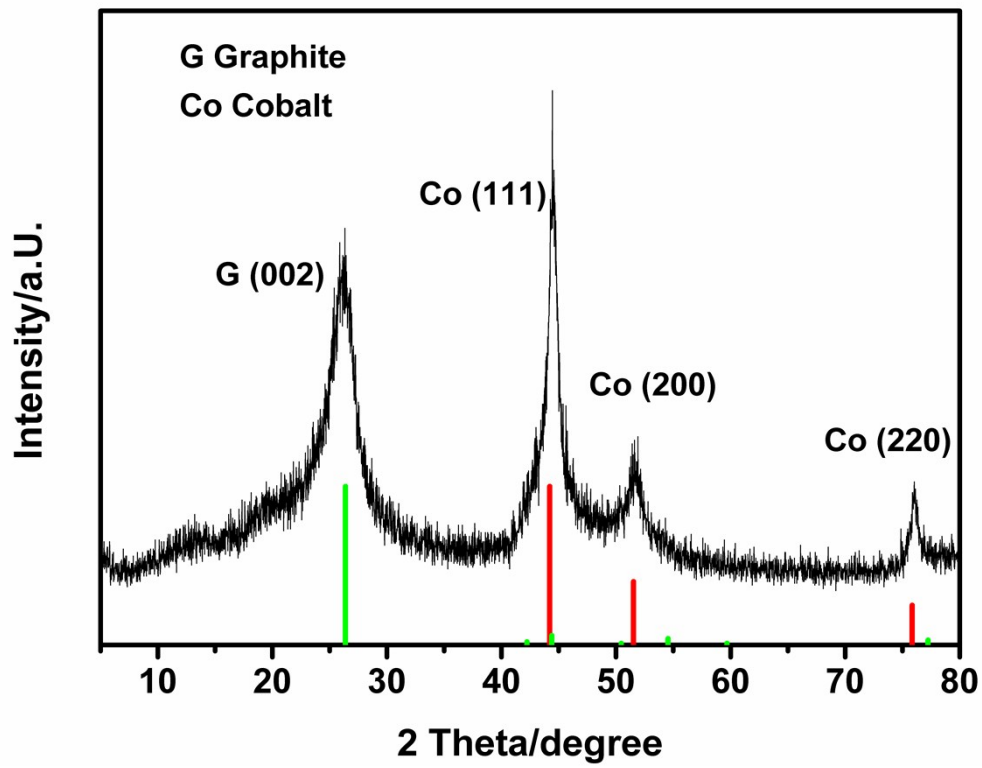

Fig. S6. Powder XRD patterns of **CoNC-3**

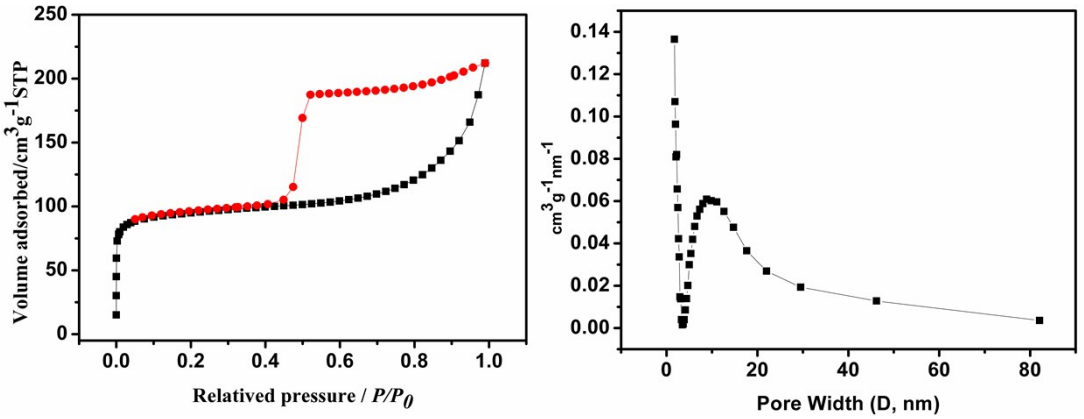

Fig. S7 N_2 adsorption and desorption isotherms for **CoNC-3** materials

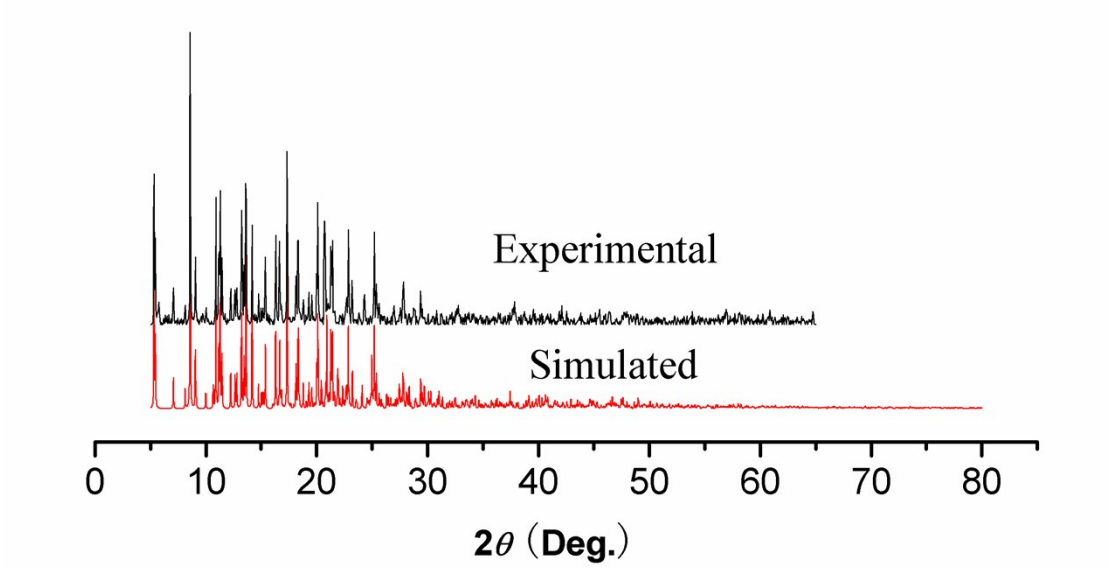

Fig. S8 Experimental X-ray powder pattern and simulated powder pattern based on the results from single-crystal X-ray diffraction for **1**

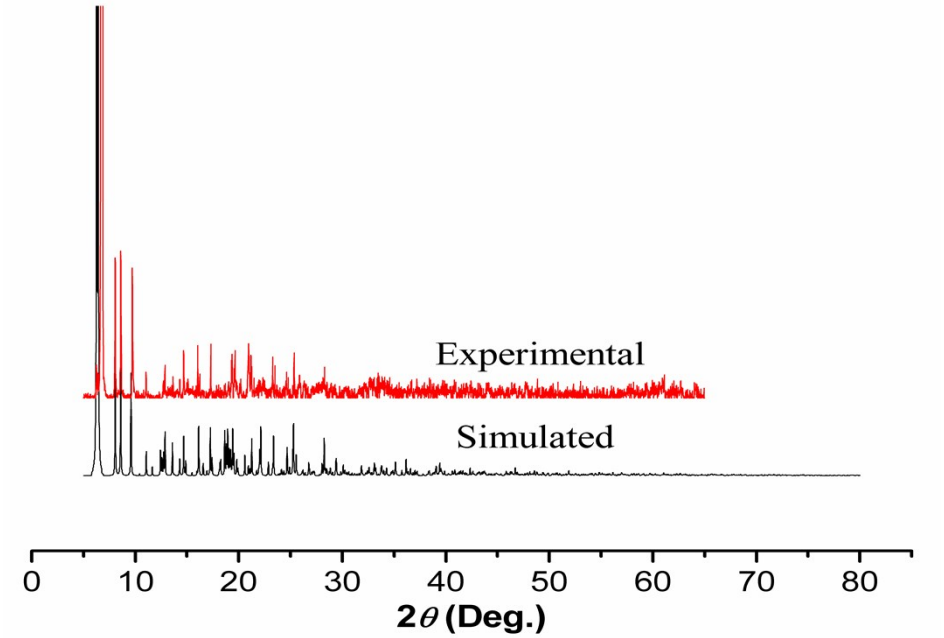

Fig. S9 Experimental X-ray powder pattern and simulated powder pattern based on

the results from single-crystal X-ray diffraction for **2**

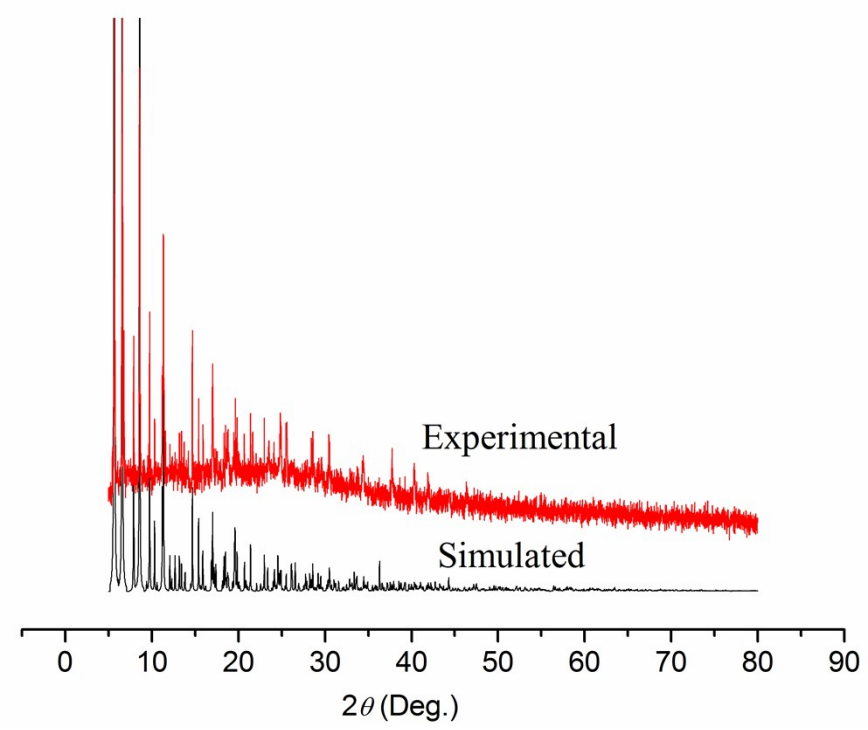

Fig. S10 Experimental X-ray powder pattern and simulated powder pattern based on the results from single-crystal X-ray diffraction for **3**

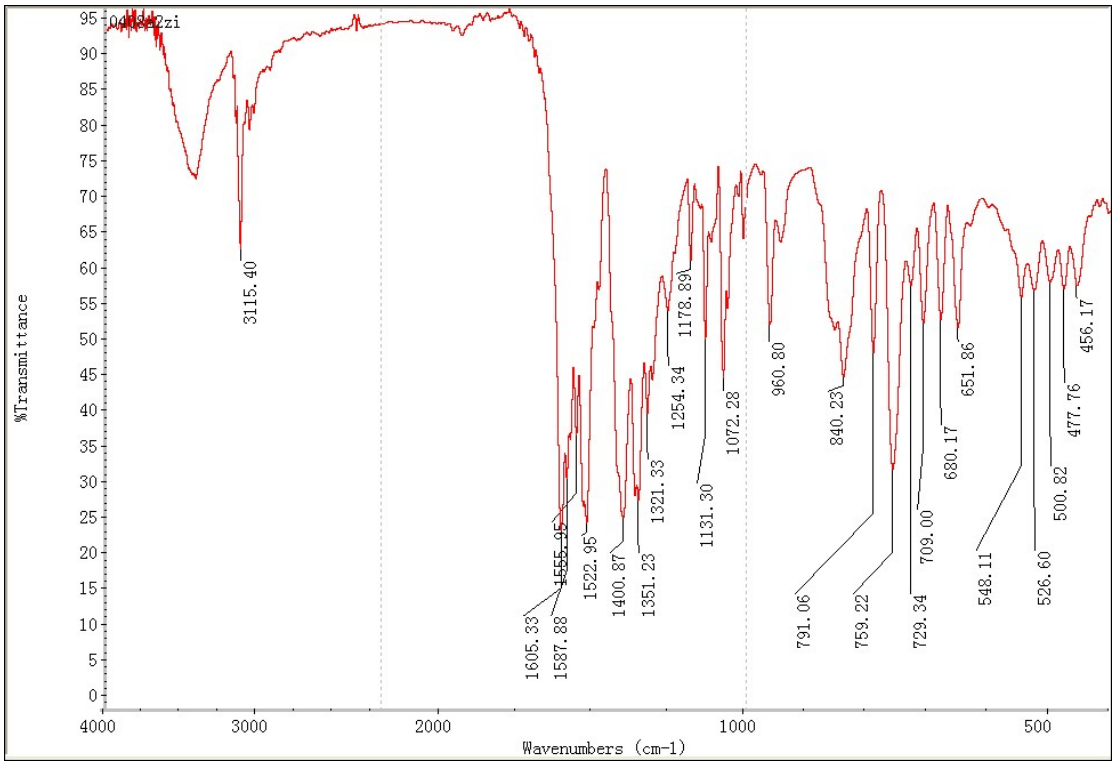

Fig. S11 IR of the compound 1

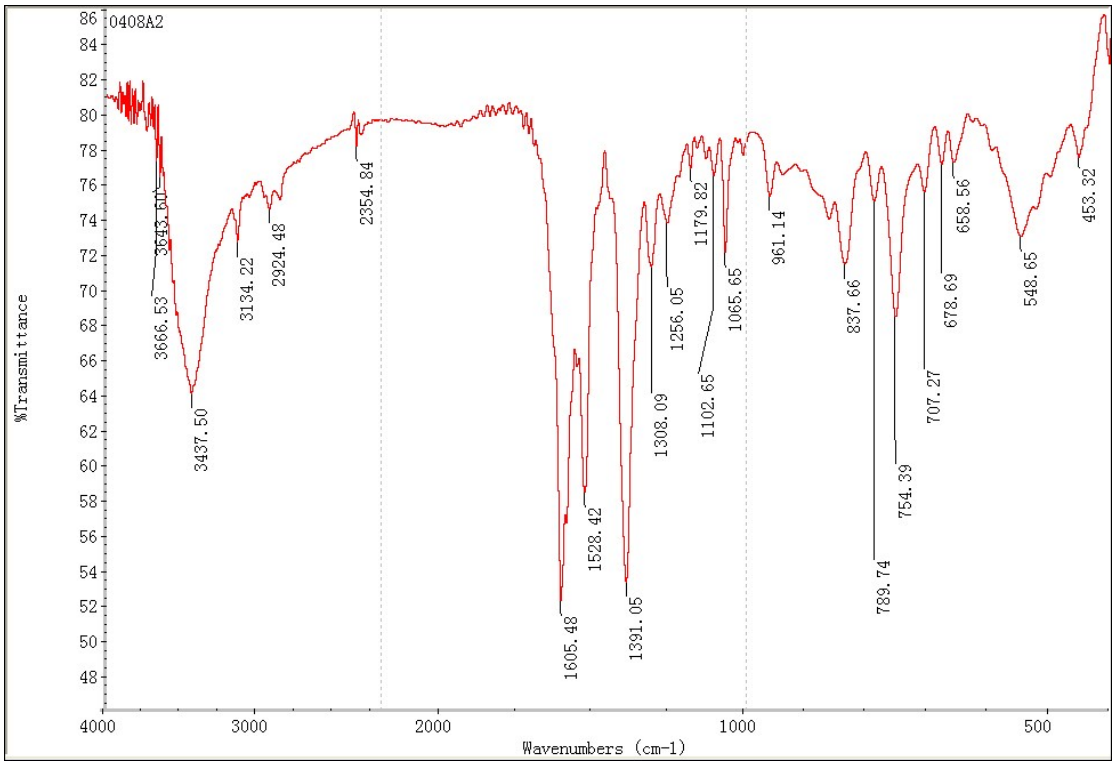

Fig. S12 IR of the compound **2**

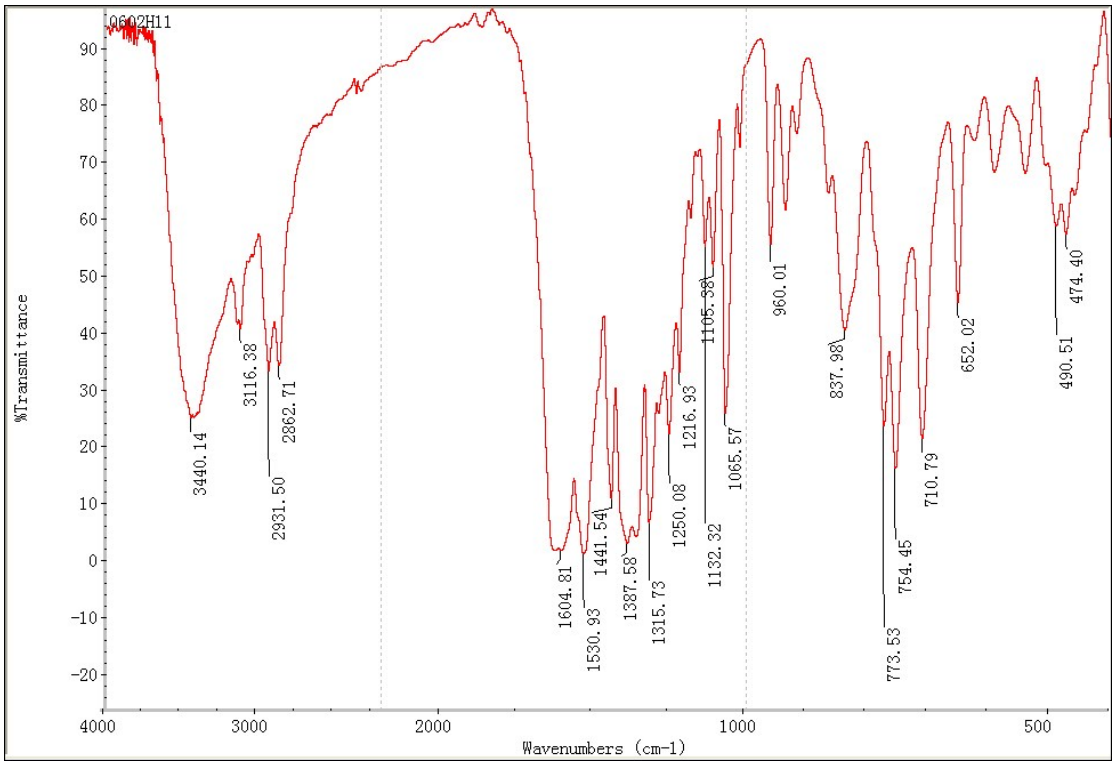

Fig. S13. IR of the compound **3**