Supporting Information

Compound 2

Ni(1)-O(1)#1	1.966(7)	Ni(1)-N(1)	2.095(9)
Ni(1)-O(1)#2	1.966(7)	Ni(1)-N(1)#5	2.095(9)
Ni(1)-O(1)#3	1.966(7)	Ni(1)-O(3)#2	2.278(6)
Ni(1)-O(1)#4	1.966(7)	Ni(1)-O(3)#3	2.278(6)
Ni(1)-O(1)#5	1.966(7)	Ni(1)-O(3)#1	2.278(6)
Ni(1)-O(1)	1.966(7)	Ni(1)-O(3)	2.278(6)

O(1)#1-Ni(1)-O(1)#2	60	N(1)-Ni(1)-O(3)#2	90
O(1)#1-Ni(1)-O(1)#3	120	N(1)#5-Ni(1)-O(3)#2	90
O(1)#2-Ni(1)-O(1)#3	180.0(5)	N(1)-Ni(1)-O(3)#3	90
O(1)#1-Ni(1)-O(1)#4	180.0(4)	N(1)#5-Ni(1)-O(3)#3	90
O(1)#2-Ni(1)-O(1)#4	120	O(3)#2-Ni(1)-O(3)#3	180.0(3)
O(1)#3-Ni(1)-O(1)#4	60	N(1)-Ni(1)-O(3)#1	90
O(1)#1-Ni(1)-O(1)#5	120	N(1)#5-Ni(1)-O(3)#1	90
O(1)#2-Ni(1)-O(1)#5	60	O(3)#2-Ni(1)-O(3)#1	60
O(1)#3-Ni(1)-O(1)#5	120	O(3)#3-Ni(1)-O(3)#1	120
O(1)#4-Ni(1)-O(1)#5	60	N(1)-Ni(1)-O(3)	90
O(1)#1-Ni(1)-O(1)	60	N(1)#5-Ni(1)-O(3)	90
O(1)#2-Ni(1)-O(1)	120	O(3)#2-Ni(1)-O(3)	120
O(1)#3-Ni(1)-O(1)	60	O(3)#3-Ni(1)-O(3)	60
O(1)#4-Ni(1)-O(1)	120	O(3)#1-Ni(1)-O(3)	60
O(1)#5-Ni(1)-O(1)	180.0(2)	O(1)#5-Ni(1)-N(1)	90
O(1)#1-Ni(1)-N(1)	90.000(1)	O(1)-Ni(1)-N(1)	90
O(1)#2-Ni(1)-N(1)	90	O(1)#1-Ni(1)-N(1)#5	90.000(1)
O(1)#3-Ni(1)-N(1)	90	O(1)#2-Ni(1)-N(1)#5	90
O(1)#4-Ni(1)-N(1)	90.000(1)	O(1)#3-Ni(1)-N(1)#5	90
O(1)-Ni(1)-N(1)#5	90	O(1)#4-Ni(1)-N(1)#5	90.000(1)
N(1)-Ni(1)-N(1)#5	180	O(1)#5-Ni(1)-N(1)#5	90

Symmetry codes: #1 y+1,-x+y+1,-z, #2 -x+y+2,-x+1,-z, #3 x-y,x-1,z, #4 -y+1,x-y-1,z, #5 -x+2,-y,-z

Compound 3

Ni(1)-O(3)	2.051(4)	Ni(1)-O(4)#1	2.095(4)
Ni(1)-O(1)	2.059(4)	Ni(1)-N(2)#2	2.128(5)
Ni(1)-N(3)	2.091(5)	Ni(1)-N(1)	2.135(5)

O(3)-Ni(1)-O(1)	87.32(17)	N(3)-Ni(1)-N(2)#2	89.6(2)
O(3)-Ni(1)-N(3)	176.50(18)	O(4)#1-Ni(1)-N(2)#2	85.46(18)
O(1)-Ni(1)-N(3)	93.01(19)	O(3)-Ni(1)-N(1)	97.30(18)
O(3)-Ni(1)-O(4)#1	89.66(16)	O(1)-Ni(1)-N(1)	91.56(18)

O(1)-Ni(1)-O(4)#1	172.46(16)	N(3)-Ni(1)-N(1)	86.2(2)
N(3)-Ni(1)-O(4)#1	89.59(19)	O(4)#1-Ni(1)-N(1)	95.68(18)
O(3)-Ni(1)-N(2)#2	86.92(18)	N(2)#2-Ni(1)-N(1)	175.6(2)
O(1)-Ni(1)-N(2)#2	87.48(18)		

Symmetry codes: #1-x+2, -y, -z+1; #2 x+1, y-1, z; #3 x-1, y+1, z; #4 -x+2, -y, -z+2 #5 -x+1, -y, -z+1.

Table S1 Selected Bond Lengths (Å) and angles (°) for compound **2** and **3**.

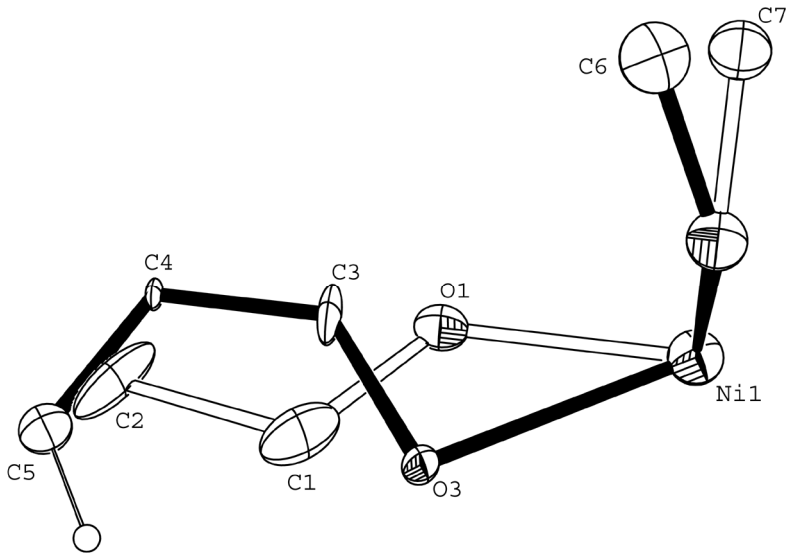

Fig. S1 ORTEP view of the compound **2** with thermal ellipsoids at 30% level. Statistically disordered components of the ligands are shown with two types of bonds (solid and open bonds). The atoms C1 and O2 are in the same position and only C1 is labeled in the figure.

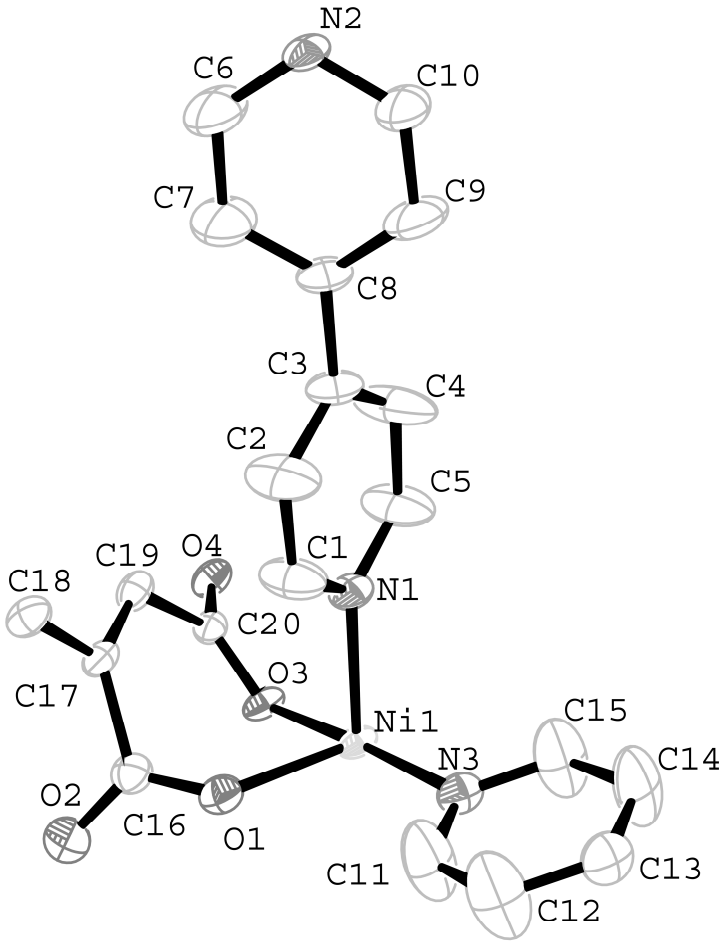

Fig. S2 ORTEP view of the compound **3** with thermal ellipsoids at 50% level. Hydrogen atoms have not been shown for clarity.

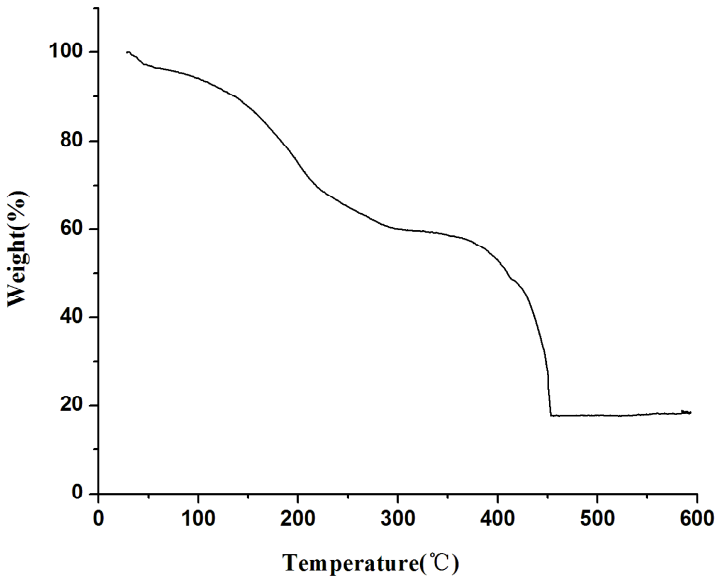

Fig. S3 TG curve of as-synthesized **2**.

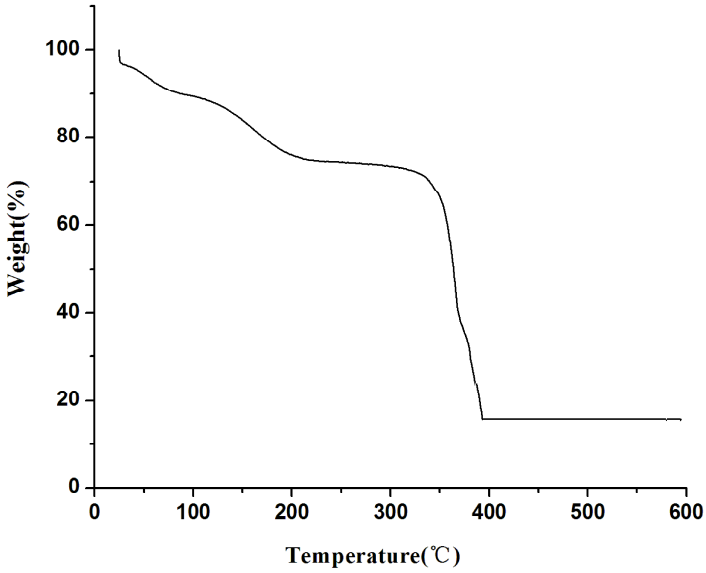

Fig. S4 TG curve of as-synthesized **3**.

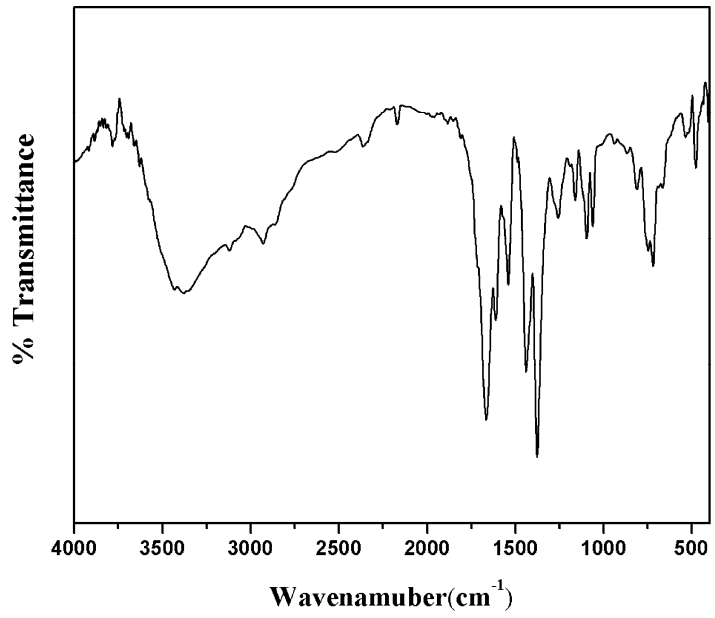

Fig. S5 FT-IR spectrum of as-synthesized sample **2**.

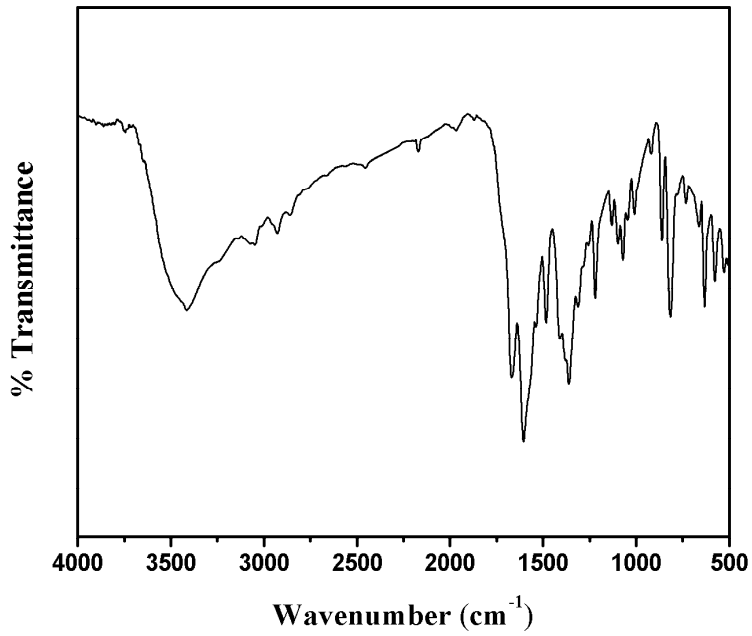

Fig. S6 FT-IR spectrum of as-synthesized sample **3**.

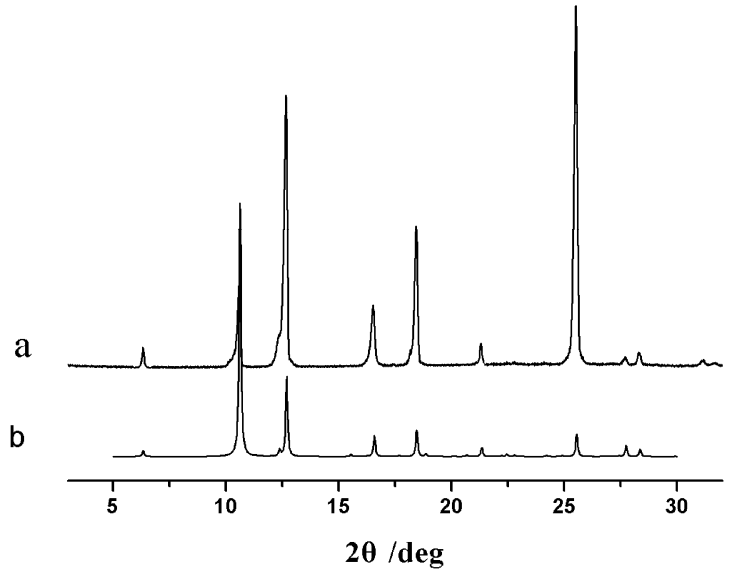

Fig. S7 XRPD patterns of the as-synthesized samples **2** (a) and the simulation based on the single-crystal data of **2** (b).

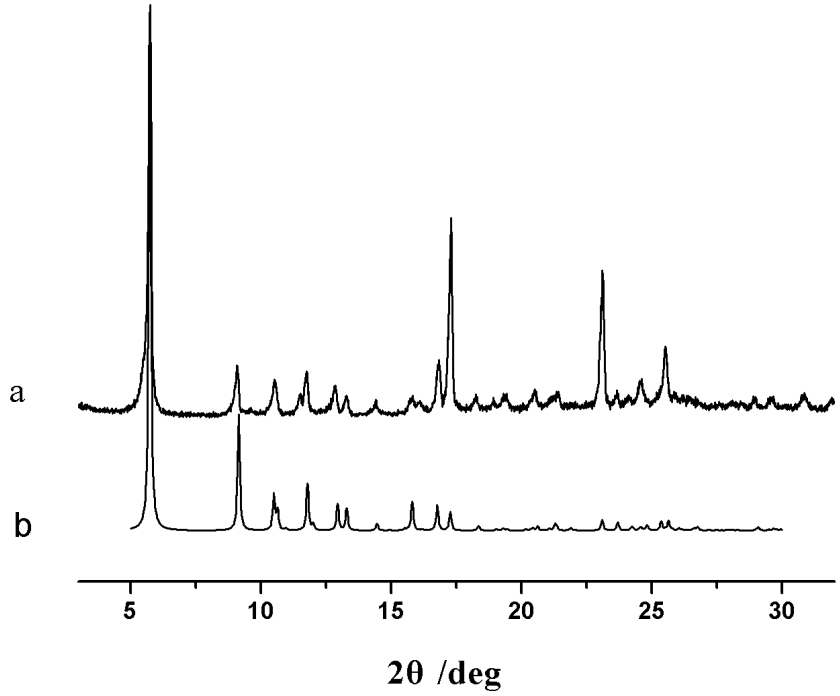

Fig. S8 XRPD patterns of the as-synthesized samples **3** (a) and the simulation based on the single-crystal data of **3** (b).

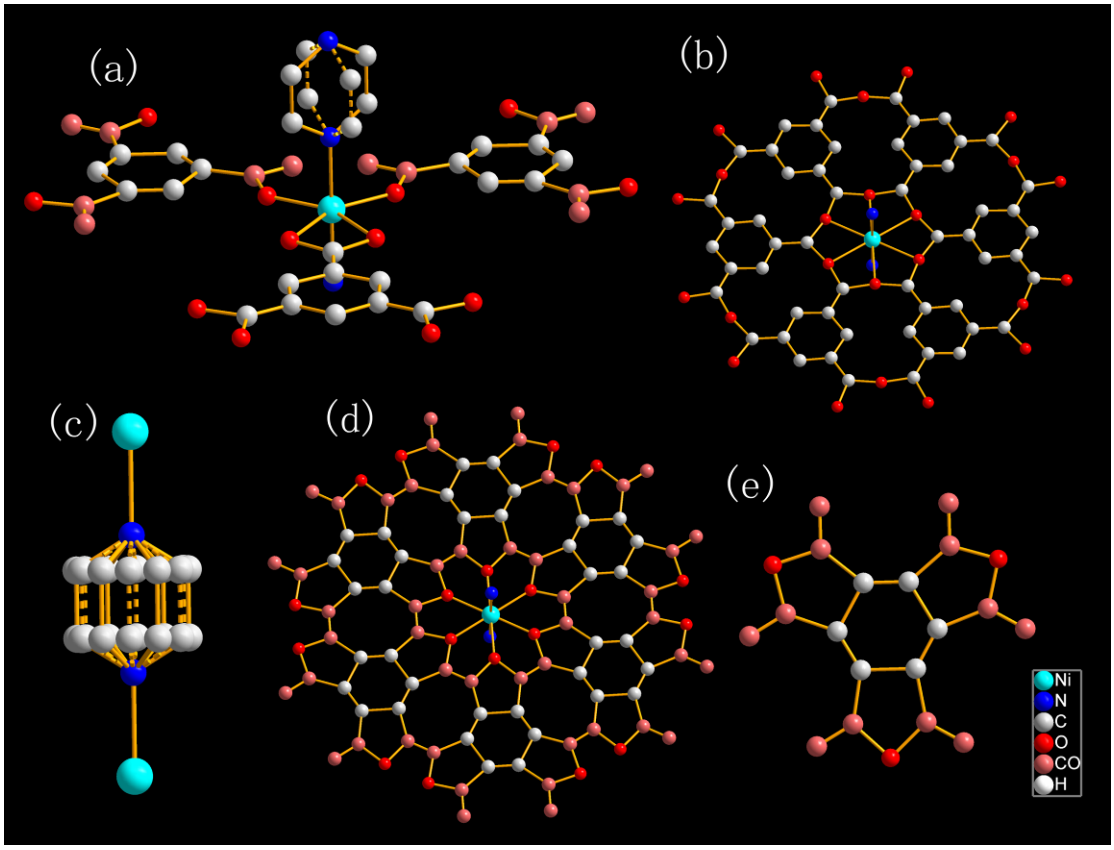

Fig. S9 (a) Coordination mode of the Ni atoms in compound 2 and (b, c, d) the ligands are statistically disordered around the six-fold axis that drill through the N1, Ni1 and N1 atoms. (e) Atoms C1 and O2 which are at the same position are shown in light orange color in the btc associated C1, C2, O1 and O2 atoms.

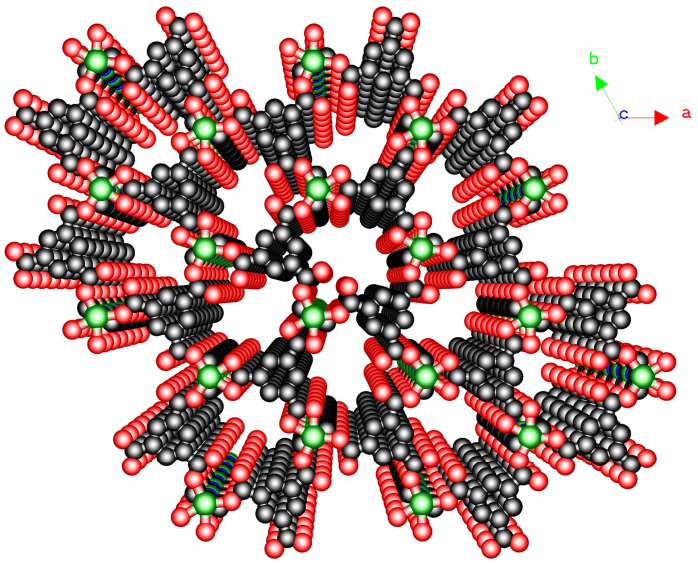

Fig. S10 Perspective view of the framework along the *c*-axis in **2**. For clarity the hydrogen atoms have been omitted. Ni: green; N: blue; O: red; C dark.

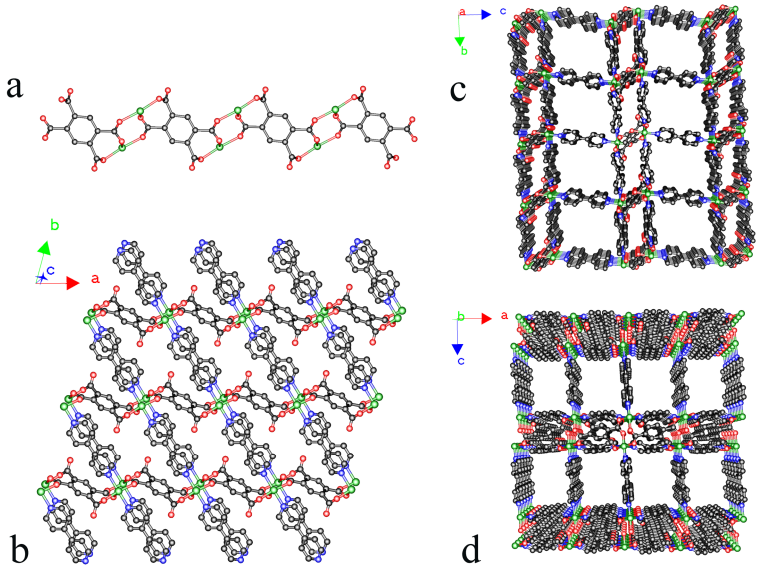

Fig. S11 (a) The infinite ladder chain constructed from Ni^{2+} ions and BTEC ligands in **3**; (b) the 2D layer parallel the *ab* plan; (c) view of the framework of **3** along [100] and (d) [010] directions. For clarity the hydrogen atoms have been omitted. Ni: green; N: blue; O: red; C dark.

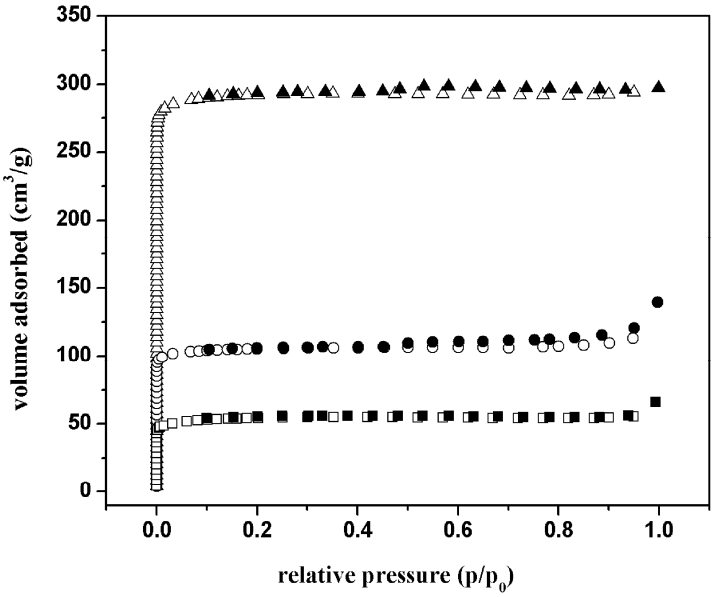

Fig. S12 N_2 gas sorption isotherms (77K) of **1** (triangle), **2** (circles) and **3** (squares) measured measured at 150°C. Open symbols, sorption; filled symbols, desorption; P_o = 1 atm.