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# Electronic Supplementary Information

# A 9-connected metal–organic framework with gas adsorption properties

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**Table S1.**

Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters ($Å^2$ x $10^3$) for **1**

| | x | y | z | *U*(eq) |
|---|---|---|---|---|
| C(1) | 7031(1) | 7031(1) | 9143(2) | 35(1) |
| C(2) | 6714(1) | 7480(1) | 9463(1) | 48(1) |
| C(3) | 5453(1) | 7529(2) | 5453(1) | 56(2) |
| C(4) | 6869(1) | 7597(2) | 10062(1) | 45(1) |
| C(5) | 5615(2) | 7566(2) | 4840(2) | 102(2) |
| C(6) | 6919(1) | 6919(1) | 8461(2) | 27(1) |
| C(7) | 5948(1) | 7453(2) | 5948(1) | 44(1) |
| N(1) | 7323(1) | 7323(1) | 10358(1) | 29(1) |
| Ni(1) | 6188(1) | 7320(1) | 7320(1) | 19(1) |
| O(1) | 6525(1) | 7257(1) | 8212(1) | 43(1) |
| O(3) | 5766(1) | 7411(1) | 6482(1) | 66(1) |
| O(2) | 6993(1) | 6993(1) | 6993(1) | 26(1) |

**Table S2.**

Selected bond lengths and angles

| Bond | Distance(Å) | Bond | Distance(Å) |
|---|---|---|---|
| N(1)-Ni(1)#4 | 2.105(3) | Ni(1)-N(1)#6 | 2.105(3) |
| Ni(1)-O(2) | 2.0104(6) | Ni(1)-Ni(1)#7 | 3.4666(8) |
| Ni(1)-O(3) | 2.0419(18) | Ni(1)-Ni(1)#1 | 3.4666(8) |
| Ni(1)-O(3)#5 | 2.0419(18) | O(2)-Ni(1)#7 | 2.0104(6) |
| Ni(1)-O(1)#5 | 2.0712(17) | O(2)-Ni(1)#1 | 2.0104(6) |
| Ni(1)-O(1) | 2.0712(17) | | |

| Angle | Degree | Angle | Degree |
|---|---|---|---|
| O(3)#5-Ni(1)-O(1) | 90.50(9) | O(2)-Ni(1)-O(1)#5 | 89.98(10) |
| O(1)#5-Ni(1)-O(1) | 89.91(12) | O(3)-Ni(1)-O(1)#5 | 90.50(9) |
| O(2)-Ni(1)-N(1)#6 | 178.48(15) | O(3)#5-Ni(1)-O(1)#5 | 173.73(8) |
| O(3)-Ni(1)-N(1)#6 | 84.81(9) | O(2)-Ni(1)-O(1) | 89.98(10) |
| O(3)#5-Ni(1)-N(1)#6 | 84.81(9) | O(3)-Ni(1)-O(1) | 173.73(8) |
| O(1)#5-Ni(1)-N(1)#6 | 88.95(7) | O(1)#5-Ni(1)-Ni(1)#1 | 114.25(5) |
| O(1)-Ni(1)-N(1)#6 | 88.95(7) | O(1)-Ni(1)-Ni(1)#1 | 72.79(5) |
| O(2)-Ni(1)-Ni(1)#7 | 30.44(2) | N(1)#6-Ni(1)-Ni(1)#1 | 149.772(9) |
| O(3)-Ni(1)-Ni(1)#7 | 71.81(6) | Ni(1)#7-Ni(1)-Ni(1)#1 | 60.0 |
| O(3)#5-Ni(1)-Ni(1)#7 | 112.65(7) | C(6)-O(1)-Ni(1) | 133.1(2) |
| O(1)#5-Ni(1)-Ni(1)#7 | 72.79(5) | C(7)-O(3)-Ni(1) | 134.6(2) |
| O(1)-Ni(1)-Ni(1)#7 | 114.25(5) | Ni(1)#7-O(2)-Ni(1) | 119.12(4) |
| N(1)#6-Ni(1)-Ni(1)#7 | 149.772(9) | Ni(1)#7-O(2)-Ni(1)#1 | 119.12(4) |
| O(2)-Ni(1)-Ni(1)#1 | 30.44(2) | Ni(1)-O(2)-Ni(1)#1 | 119.12(4) |
| O(3)-Ni(1)-Ni(1)#1 | 112.65(7) | O(2)-Ni(1)-O(3) | 96.28(10) |
| O(3)#5-Ni(1)-Ni(1)#1 | 71.81(6) | O(2)-Ni(1)-O(3)#5 | 96.28(10) |

| | | | |
|---|---|---|---|
| C(4)#1-N(1)-Ni(1)#4 | 121.71(16) | O(3)-Ni(1)-O(3)#5 | 88.42(15) |
| C(4)-N(1)-Ni(1)#4 | 121.71(16) | | |

Symmetry transformations used to generate equivalent atoms: #1 y,x,z; #2 z,y,x; #3 -z+1,y,-x+1; #4 -z+3/2,-y+3/2,x+1/2; #5 x,z,y; #6 z-1/2,-x+3/2,-y+3/2; #7 y,z,x

**Table S3.**

Bond valence sum

| Ni2+ | $r_0$ | $r_{ij}$ | B | $S_{ij}=\exp[(r_0-r_{ij})/B]$ |
|---|---|---|---|---|
| Ni1-O2 | 2.010 | 1.670 | 0.370 | 0.399 |
| Ni1-O1 | 2.071 | 1.670 | 0.370 | 0.338 |
| Ni1-O1 | 2.071 | 1.670 | 0.370 | 0.338 |
| Ni1-O3 | 2.042 | 1.670 | 0.370 | 0.366 |
| Ni1-O3 | 2.042 | 1.670 | 0.370 | 0.366 |
| Ni1-N1 | 2.105 | 1.647 | 0.370 | 0.290 |

$V_{Ni1}=\sum S_{ij}=2.097$ $V_{O2}=3\times S_{Ni1\text{-}O2}=1.197$

| N3+ | $r_0$ | $r_{ij}$ | B | $S_{ij}=\exp[(r_0-r_{ij})/B]$ |
|---|---|---|---|---|
| Ni1-O2 | 2.010 | 1.750 | 0.370 | 0.495 |
| Ni1-O1 | 2.071 | 1.750 | 0.370 | 0.420 |
| Ni1-O1 | 2.071 | 1.750 | 0.370 | 0.420 |
| Ni1-O3 | 2.042 | 1.750 | 0.370 | 0.454 |
| Ni1-O3 | 2.042 | 1.750 | 0.370 | 0.454 |
| Ni1-N1 | 2.105 | 1.731 | 0.370 | 0.364 |

$V_{Ni1}=\sum S_{ij}=2.607$ $V_{O2}=3\times S_{Ni1\text{-}O2}=1.485$

The bond valence sum results are closed to the literature results (*Chem. Commun.* 2007, 840-842 and *Angew. Chem., Int. Ed.* 2009, **48**, 5287 –5290). And the valence of the trinuclear cluster has been proved through magnetic measurements.

Magnetic susceptibility data were collected over the temperature range 300-2 K at a magnetic field of 1000 Oe for **1** on a Quantum Design MPMS-5 SQUID magnetometer. The data were not corrected for the diamagnetism, and then fitted to the Curie-Weiss law in the temperature range 180 K < T < 300 K. The experimental value $C_{exp}$ of 3.86 $cm^3$ K $mol^{-1}$ matches to a Curie constant of 3.88. It has been revealed that per formula unit is constituted with 2 $Ni^{2+}$ (S=1) and 1 high spin $Ni^{3+}$ (S=3/2).

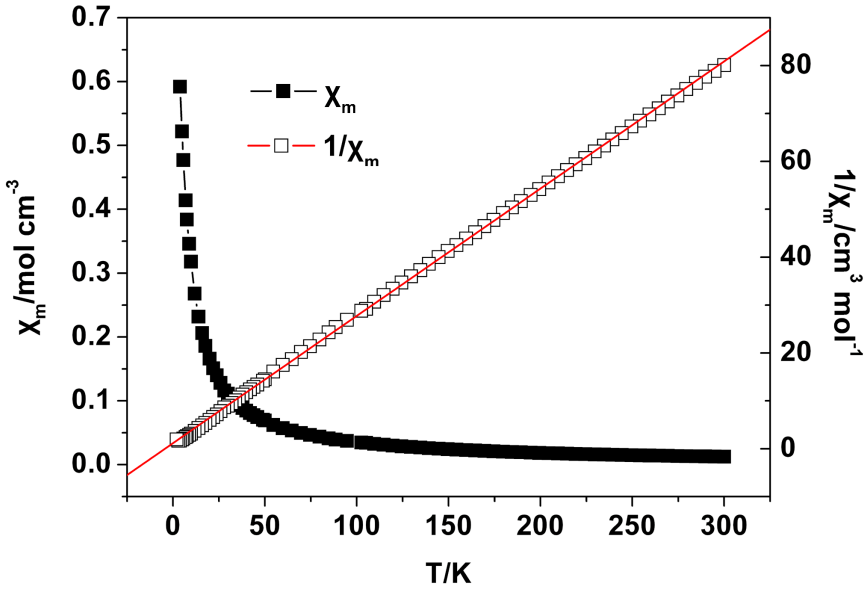


**Figure S1.** Plots of $\chi_m$ versus T (square solid), $1/\chi_m$ versus T (open) and linear fitting to the Curie-Weiss law (red) for as-synthesized sample of **1**.

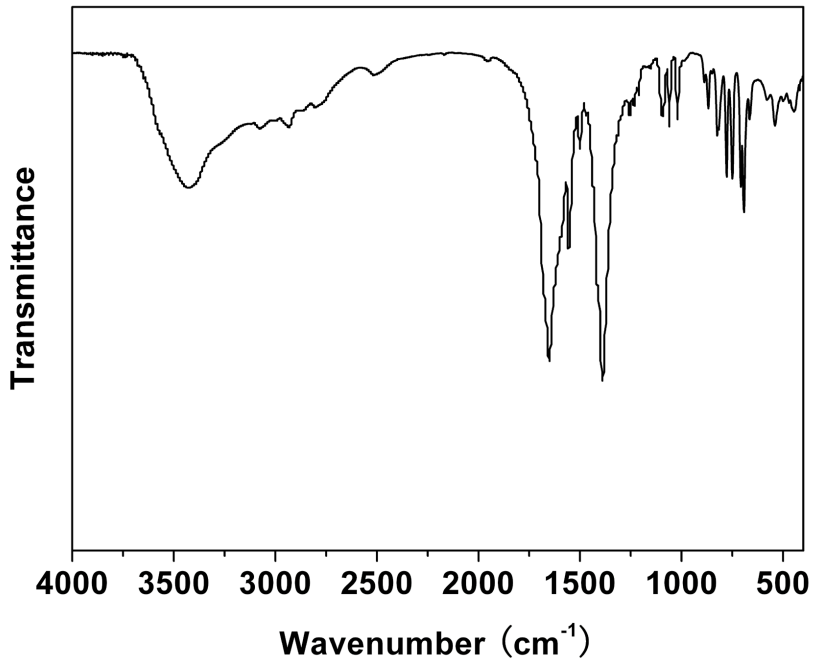


**Figure S2.** IR spectrum of the as-synthesized sample of **1**.

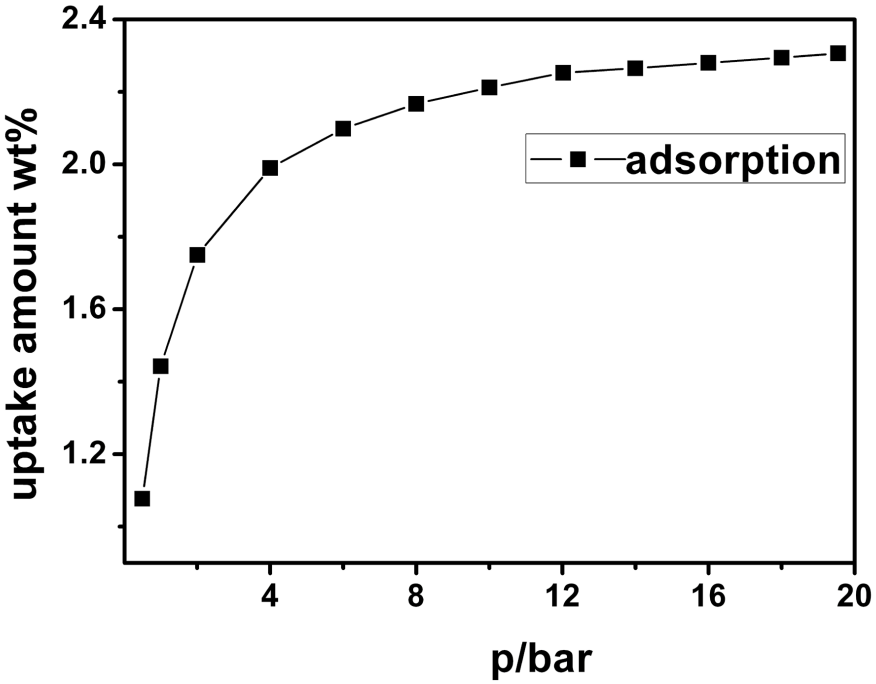


**Figure S3**. Gravimetric hydrogen adsorption isotherm of **1** at 20 bars.

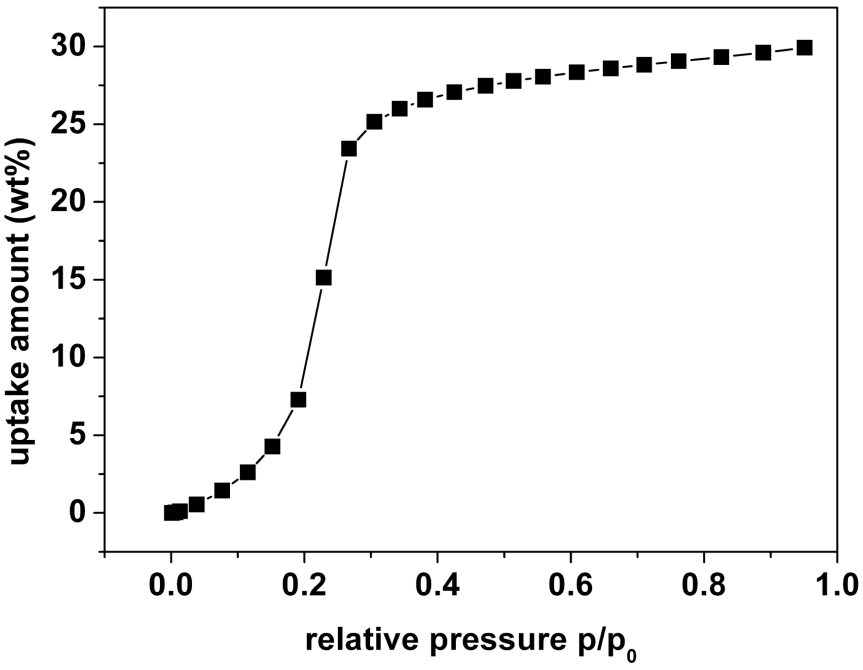


**Figure S4**. Ethanol adsorption isotherm of **1** at 298K.

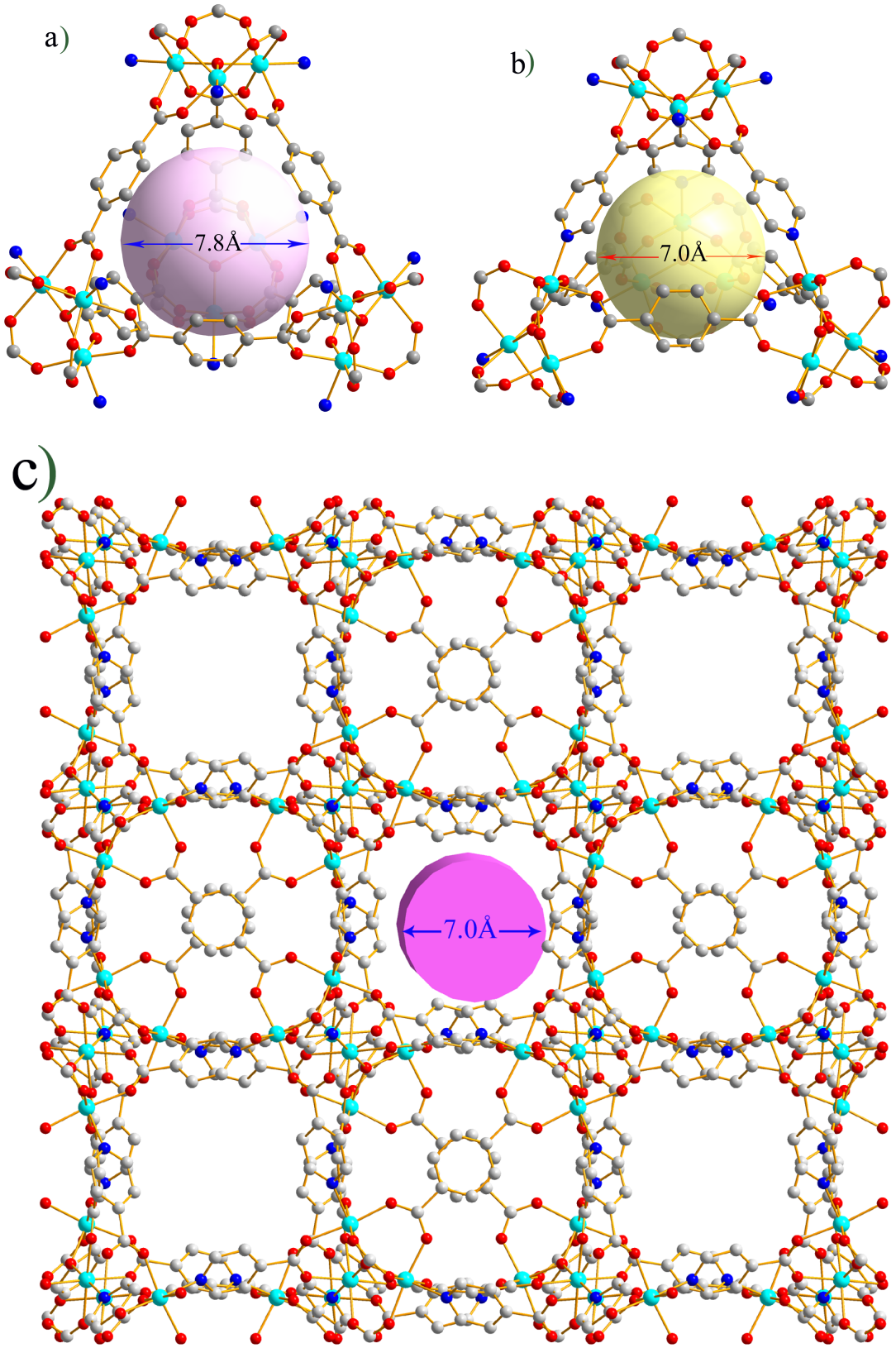


**Figure S5**. a) Tetrahedron cage constructed from 4 trinuclear clusters and 6 BDC ligands (diameter about 7.8Å), b) triangular pyramid cage constructed from 4 trinuclear clusters, 3 BDC and 3 Ina ligands (diameter about 7.0Å), c) 3D pore size (about 7.0 Å).