Electronic Supporting Information (ESI)

Construction of polyhedron decorated MOF with unique network through the combination of two classic secondary building units

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S1. Materials and general methods

All the chemicals used for synthesis are of analytical grade and commercially available. IR spectrum was measured on a Tensor 27 OPUS (Bruker) FT-IR spectrometer with KBr pellets. Powder X-ray diffraction (PXRD) spectra were recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA for a Cu-target tube and a graphite monochromator. Thermogravimetric analyses (TGA) were carried out on a Rigaku standard TG-DTA analyzer with a heating rate of 10 °C min⁻¹, with an empty Al₂O₃ crucible used as reference. Simulation of the PXRD pattern was carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program version 3.0. X-ray photoelectron spectroscopy (XPS) studies were carried out using PHI5000VersaProbe. Magnetic measurements were carried out using a Magnetic Property Measurement System (MPMS3).

S2. Adsorption measurements

Prior to treatment, the DMF solvated MOF samples were soaked in anhydrous DMF for 48 h, and then the samples were immersed in anhydrous CH_2Cl_2 to exchange the occluded solvent for 48 h. Then the processed samples were loaded in sample tubes and activated under high vacuum (less than 10⁻⁵ Torr) at 100 °C. Degassed samples were used for gas sorption measurements. Gas adsorption measurements were performed using an ASAP 2020 M gas adsorption analyzer. The H₂ sorption isotherms were collected at 77 K in a liquid nitrogen bath, and 87 K in the liquid helium bath. The CO₂ sorption isotherms were collected at 273 K in an ice water mixture bath, as the center-controlled air conditioner was set up at 25 °C, a water bath was used for adsorption isotherms at 298 K.

The Virial equation was used to fit the H_2 and CO_2 isotherm data for **1** for the evaluation of isosteric heat of adsorption.^{1,2} The H_2 and CO_2 isotherm data at two temperatures can be fitted to the Virial expression:

$$\ln(p) = \ln(n) + (1/T) \sum_{i=0}^{m} a_{i}n^{i} + \sum_{j=0}^{n} b_{j}n^{j}$$

In the equation, p is pressure, n is amount adsorbed, T is temperature, and a_i and b_j are temperature independent empirical parameters. Based on the parameters

obtained from the fitted isotherms, the isosteric heat of adsorption (Q_{st}) as a function of gas uptake can be obtained over a wide loading range with the following equation:

$$Q_{st} = -R\sum_{i=0}^{m} a_i n^i$$

S3. Crystal structure determination

Single crystal X-ray diffraction measurement was carried out on Agilent SuperNova at 100 K for **1** with Cu-K α radiation ($\lambda = 1.5418$ Å). The structure was solved by direct methods using the SHELXS program of the SHELXTL package and refined with SHELXL.³ It should be noted that the guest molecules in **1** are highly disordered and could not be modeled properly, so the diffused electron densities resulting from them were removed by the SQUEEZE routine in PLATON⁴ and the results were appended in the CIF files. 'sadi', 'simu', 'flat' and 'delu' restraint instructions were applied to the NA⁻ ligand for its geometry and atomic displacement parameters, and 'isor' restrain was applied to the big and non-spherical atoms.

Crystal data for 1: C₈₄H₄₈N₆Ni₉O₄₁, M_r =2325.49, Cubic, Fm-3m, a = b = c =41.4694(4) Å, $\alpha = \beta = \gamma = 90$ (4)°, V = 71315(2) Å³, Z = 16, $\rho_{calcd} = 0.886$ g cm⁻³, T =100 K, $R_{int} = 0.0801$, $R_I = 0.1638$ ($I > 2\sigma$ (I)), $wR_2 = 0.3793$ (all data), GOF = 1.218.

S4. Synthesis of compound 1

A mixture of Ni(NO₃)₂·6H₂O (0.5 mmol), H₂BDC (0.5 mmol), HNA (0.5 mmol) and LiNO₃ (0.5 mmol) in 12 mL DMF was sealed in a 20 ml Teflon-lined autoclave and heated at 150 °C for 48 hours. After that, the reaction vessel was cooled to room temperature in 24 h. Green crystals were collected by filtration, washed with DMF and dried in air (yield: 20-25% based on Ni(NO₃)₂·6H₂O). Element analysis after activation (%): Calcd. for C₈₄H₄₈N₆Ni₉O₄₁ (2325.49): C 43.38, H 2.08 N 3.61; found: C 43.22, H 3.78, N 5.58. The difference between the calculated and experiment value should be attributed to locked guest molecules in this MOF.

S5. Bond valence sum (BVS)

The valence of a bond between two atoms, i and j is given by S_{ij} . The sum of S_{ij} is the valence of the i atom. The calculated results are shown in the following tables, which are closed to that reported in the literatures.^{5,6}

		13 50		
Ni ²⁺	r ₀	r _{ij}	В	$S_{ij}=exp[(r_0-r_{ij})/B]$
Ni(1)-O(3)	1.670	1.994	0.37	0.4168
Ni(1)-O(7)	1.670	2.033	0.37	0.3749
Ni(1)-O(7)	1.670	2.033	0.37	0.3749
Ni(1)-O(4)	1.670	2.039	0.37	0.3689
Ni(1)-O(4)	1.670	2.039	0.37	0.3689
Ni(1)-N(1)	1.647	2.097	0.37	0.2963

Table S1. BVS for Ni²⁺ and μ_3 -oxygen atom in the trimetallic SBU.

 $VNi1=\Sigma S_{ij}=2.200$ $VO3=3\times S_{Ni1-O3}=1.250$

Table S2. BVS for Ni³⁺ and μ_3 -oxygen atom in the trimetallic SBU.

Ni ³⁺	r ₀	r _{ij}	В	$S_{ij}=exp[(r_0-r_{ij})/B]$
Ni(1)-O(3)	1.750	1.994	0.37	0.5174
Ni(1)-O(7)	1.750	2.033	0.37	0.4654
Ni(1)-O(7)	1.750	2.033	0.37	0.4654
Ni(1)-O(4)	1.750	2.039	0.37	0.4579
Ni(1)-O(4)	1.750	2.039	0.37	0.4579
Ni(1)-N(1)	1.731	2.097	0.37	0.3719

 $VNi1=\Sigma S_{ij}=2.7360$ $VO3=3\times S_{Ni1-O3}=1.552$

S6. XPS measurement, magnetic measurement, theoretical calculations

The main peak at 855.9 and 873.7 eV should be assigned to the Ni²⁺, while the relatively weak binding energy values at 857.8 and 875.3 eV could be attributed to the existence of valence state with slight higher than Ni²⁺,⁷ which should be attributed to the presence of delocalized positive charge in the trinuclear Ni cluster.



Fig. S1 XPS spectrum of compound 1.

Magnetic measurement

Magnetic measurements are performed in order to determine the oxidation states of the metal ions. The data is corrected for the diamagnetism, and then fitted to the Curie-Weiss law in the temperature range 2-300 K. The fitted Curie constant *C* of 9.95 cm³ K mol⁻¹ is higher than the theoretical value of 9.00 cm³ K mol⁻¹ for 9 Ni²⁺ (*S* = 1 for Ni²⁺, g = 2.0), but smaller than the theoretical value of 10.75 cm³ K mol⁻¹ for 7 Ni²⁺ and 2 Ni³⁺ per formula unit (*S* = 3/2 for Ni³⁺, g = 2.0) which may be attributed to the antiferromagnetic exchange interactions among the Ni ions. The apparent value of *C*, which seems to be an average of Ni²⁺ and Ni³⁺, should be due to the presence of delocalized positive charge in the trinuclear Ni cluster. The χ_M T value of 9.92 cm³ K mol⁻¹ at room temperature is consistent with the Curie constant. The magnetic data meet the agreement of the reported MOFs with similar SBU.^{5,6}



Fig. S2 Plots of $\chi_M T$ versus *T* (square), $1/\chi_M$ versus *T* (triangle) and linear fitting to the Curie-Weiss law (red) for sample of **1**.

Theoretical calculations

To verify whether three Ni ions would have the same charge, we have performed the first-principles calculations via VASP⁸ package. As the unit cell of the MOF structure has too many atoms, we used a cluster containing three Ni ions and their ligands in the calculation (Fig. S3). This cluster is placed in $30 \times 30 \times 30$ Å³ supercell to avoid the interactions between periodic images. The PAW⁹ method with PBE¹⁰ exchange-correlation functional is used in the calculations. The cut off energy of the plane wave basis set is 400 eV, and only Gamma point is considered in K-sampling. The cluster is fully relaxed until the force acting on each atom is less than 0.05 eV/Å. Based on Bader analysis¹¹, we find that the Bader Charge on three Ni ions are 8.76, 8.74, 8.75, respectively (10 for Ni atom in the pseudo potential). Considering the numeric error, the charge on the three Ni ions should be equal. For Ni in NiO bulk, which has formal charge of +2, the Bader Charge is 8.87 from our calculation. And this indicates that the Ni ions in the cluster (or MOF) should have a little higher formal charge (or valence) than +2.



Fig. S3 The molecular model for first-principles calculations (brown: C, red: O, blue: N, white: H, light blue: Ni).

S7. Structural figure, supplementary characterizations



Fig. S4 The formation of open metal sites in the paddle wheel SBU2.



Fig. S5 The topology of compound **1**.



Fig. S6 Comparison of intersection angles and corresponding MOPs in MCF-19,⁶ MIL-101¹² and compound **1** (MCF-19: trigonal pyramid and tetrahedron, MIL-101: tetrahedron, compound **1**: tetrahedron and hexahedron).



Fig. S8 TGA curves of compound 1.



Fig. S9 IR spectrum of compound 1.



Fig. S10 N_2 adsorption isotherm of compound 1.



Fig. S11 H_2 adsorption isotherms for 1, and the respective Virial fits (red lines). Fit parameters

a0	al	a2	a3
-814.59643	95984.9511	-1.56648E7	2.83492E9
a4	b0	b1	b2
-2.1673E11	24.98440	-565.19685	29229.75696

Adj. R-Square = 0.99998



Fig. S12 CO₂ adsorption isotherms for 1, and the respective Virial fits (red lines).

a0	al	a2	a3
-2854.11809	364212.41309	-2.01844E8	5.58764E10
a4	b0	b1	b2
-1.13967E13	27.08064	-781.0527	340659.9

Adj. R-Square = 0.99998



Fig. S13 Color changes of crystalline sample: before the degassing treatment (a), after activation (b) and re-exposed to air after adsorption measurement (c).

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