Synthesis and Properties of a Double-sided and Multi-layered Metal Organic Framework

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Abstract. Two new double-sided and multi-layered network porous compound named 1 $[Ni_2(BTC)_2(DABCO)(DEA)_2]$ have been synthesized by solvent thermal synthesis method. Which, for the first time, exhibit an unusual double-sided and multi-layered MOF. The double-sided MOF structure extended to regular hexagon morphology in accordance with schematic representation of the 2D topological net of 1 and also confirmed by the SEM images. The N₂ and H₂ sorption certified it can be used as gas absorption.

Introduction

Porous metal–organic frameworks (MOFs) also known as porous coordination polymers, are crystalline coordination networks consisting of metal ions/clusters and organic linkers, are currently under intensive investigation because of their rich structural chemistry and outstanding properties, regarding not only the specific surface area and storage capacities, but also the flexibility of the framework.^[1-3] The systematic design and construction of coordination polymers by using organic molecular building blocks and metal ions appeared in the early half of the 1990s, More than 20000 MOF structures have been reported and studied since then. In 1999, two archetypical MOFs, MOF-5(Zn₄O(bdc)₃, bdc=terephthalate) and HKUST-1(Cu₃(btc)₂, btc=1,3,5-benzenetricarboxylate)^[4,5] were synthesized and characterized, symbolizing a benchmark in MOF chemistry with their high porosity indicated by crystal structures and confirmed by low pressure gas sorption studies.

A key structure feature of MOFs is the ultrahigh porosity (up to 90% free volume) and incredibly high internal surface areas, extending beyond a Langmuir surface area of 10000 m² g⁻¹, which play a crucial role in functional applications, typically in storage and separation,^[6] sensing,^[7] proton conduction^[8] and drug delivery.^[9] One of the most interesting features of MOFs is that frequently their structure can be deduced from the directionality of organic linkers and the coordination geometry of metal building blocks. In this way, MOFs can be engineered to a large extent and can be synthesized by design with the desired structure and dimension. In this regard, we have constructed a **Two-Dimensional** new multi-layered Network porous compound named 1 $[Ni_2(BTC)_2(DABCO)(DEA)_2]$, (Nickel nitrate hexahydrate H₃btc=1,3,5-benzenetricarboxylate acid(Bridge ligand), DABCO=1,4-diazabicyclo[2.2.2]octane (Auxiliary ligand), DEA =Diethylamine) by using rigidly designed carboxylate ligands in solvent thermal synthesis method, which, for the first time, exhibit an unusual double-sided and multi-layered MOF. The N₂ sorption isotherms show that it has a large Brunauer-Emmett-Teller (BET) surface area and pore volume. In its structure, Ni atoms to adopt irregular quadrilateral double-heap coordination model. Every Ni atoms coordinated with four O atoms(two come from one bivalent carboxylic group of one btc, (two O atoms are in mono dentate coordination come from two monobasic carboxylate O ions of two btc ligand in a planar separately), the two pairs of O atoms form a square-planar coordination around the Ni atom (Figure 1. a)). DABCO as bridging ligands, which act as pillars to extend the double-sided 2D layers (Figure 1. b)). The DABCO pillar molecules, which occupy the axial positions of the [Ni₂(BTC)₂(DABCO)(DEA)₂] paddle-wheels, the double-sided 2D layers structure further interconnect and extend into a multi-layered architecture by Van der Waals force and H-bond interaction(Figure 1. e)). Two N atoms axially coordinated to one Ni come from DABCO and DEA. The four O atoms form a planar coordinated around the central Ni atom, Axis of N-Ni-Ni-N perpendicular to the planar, the six Ni atoms build up a isosceles triangular prism constructure. The bonds length of Ni-O are 2.1873 Å and 2.0594 Å, The bonds length Ni-N are 2.0913 Å and 2.1811 Å separately. The Ni...Ni distance connected by a ligand DABCO are of 6.9590 Å.



Figure 1. a) the coordination modes of six-connected $Ni_2(BTC)_2(DABCO)(DEA)_2$ SBUs; b) a isosceles triangular prism in 1; c) View of the porous framework of 1 viewed close to [100] direction; d) schematic representation of the 2D topological net of 1 (viewed close to the [100] direction; green connection point representing the dummy node of triangle plane(three Ni) of a isosceles triangular prism; e) View of the multi-layered porous framework of 1 viewed close to [010] direction; f) Schematic representation of Ni₂(BTC)₂(DABCO)(DEA)₂.

Experimental Section.

Chemicals were purchased from commercial sources and used without further purification. Powder X-ray diffraction (PXRD) was carried out with an X-ray diffractometer of Rigaku, Rint 2000. C, H, and N elemental analyses were conducted on a Perkin–Elmer 240C elemental analyzer. Thermo gravimetric analyses (TGA) were carried out on a Perkin–Elmer TG-7 analyzer heated from room temperature to 873 K at a ramp rate of 5 K/min⁻¹ under nitrogen. The N₂ and H₂ sorption measurements were performed on automatic volumetric adsorption equipment (Belsorp mini II). Before gas adsorption measurements, the sample was treated with ethanol and dichloromethane. Before the measurement, the sample was dried again by using the "outgas" function of the surface area analyzer for 12 h at 393 K.

The data were collected by using graphite-monochromatized enhanced ultra Cu radiation at 293 K. The data sets were corrected for empirical absorption correction by using spherical harmonics, as implemented in the SCALE3 ABSPACK scaling algorithm. The structures of the compound **1** were solved by direct methods^[10] and refined by full-matrix,^[11] least-square methods with the SHELX-97 program package. Determinations of the unit cells and data collection for crystal of **1** were performed on an Oxford Xcalibur Gemini Ultra diffractometer with an Atlas detector^[12]. The solvent molecules in the compound are highly disordered, and the SQUEEZE^[13] subroutine of the PLATON^[14] software suite was used to remove the scattering from the highly disordered guest

molecules. The resulting new files were used to further refine the structures. The H atoms on C atoms were generated geometrically.^{15]}

Crystal data for Ni₂(BTC)₂(DABCO)(DEA)₂: T=293 K, empirical formula=Ni₂C₃₂H₃₄O₁₂N₄, cryst syst=trigonal, M_r=785.42, a =17.00 (3) Å, b=17.00(3) Å, c =30.00(3) Å, $\alpha = 90^{\circ}$, $\beta = 90^{\circ}$, $\gamma = 120^{\circ}$, V = 7508Å³, Z=1, D_{calc} =0.793 g/cm³, final R1 = 0.0854,

Synthesis of the metal-organic framework Ni2(BTC)2(DABCO)(DEA)2.

A typical preparation, a solid mixture of H₃BTC (H₃BTC =1,3,5-benzenetricarboxylate acid(0.420 g, 2 mmol), DABCO (DABCO =1,4- diazabicyclo [2.2.2] octane (0.112 g, 1 mmol), DEA (DEA= Diethylamine, 0.128 g, 2 mmol and Ni(NO₃)₂·6H₂O (0.580 g, 2 mmol) was dissolved in DEF (DEF= N,N-Diethylformamide; 15 ml). The resulting solution would turn to limpid from cloudy suspension after drop concentrated nitric acid (at an approximate ratio of one drip every 10 ml), distributed among two 20 ml vials. The vials were then heated at 100 °C in an isothermal oven for 72 h. After cooling the vials to room temperature, the green crystals product was isolated by decanting with the mother liquor and washed in DEF (3 × 3 ml) for 2 days. Solvent exchange was carried out with ethanol (3 × 10 ml) at room temperature for 2 days. The material was then evacuated under vacuum at 60 °C for 6 h, yielding 0.495 g of Ni₂(BTC)₂(DABCO)(DEA)₂ in the form of solid (63% yield).

Elemental analysis: calcd(%) for [Ni₂(BTC)₂(DABCO)(DEA)₂: Ni, 14.9; O, 24.4; C, 48.9; H, 4.32; N, 7.1; found (%):Ni, 14.8; O, 24.5; C, 49.2; H, 4.12; N, 7.2.



Figure 2. (a) The TGA curves of the compound 1; (b) XRD patterns of compound 1; (c)N2 sorption isotherms for compound 1 at 77 K;(d) H2 sorption isotherms for 1 at 77 K.



Figure 3. SEM images of the prepared Ni2(BTC)2(DABCO)(DEA)2: a) The regular hexagon picture of compound 1; b) The multi-layered picture of compound 1.

Conclusions

The present work shows a further example $Ni_2(BTC)_2(DABCO)(DEA)_2$. Which exhibit an unusual double-sided and multi-layered MOF. The DABCO pillar molecules, which occupy the axial

positions of the $[Ni_2(BTC)_2(DABCO)(DEA)_2]$ paddle-wheels, the double-sided 2D layers structure further interconnect and extend into a multi-layered architecture by Van der Waals force and H-bond interaction. The double-sided MOF structure extended to regular hexagon morphology in accordance with schematic representation of the 2D topological net of **1** (Figure 1. (d)). That also confirmed by the SEM images of the prepared Ni₂(BTC)₂(DABCO)(DEA)₂ (Figure 3.). The N₂ sorption isotherm for **1** shows a typical external adsorption behavior at 77 K. Giving maximum uptakes of 77.2 cm³/g , he highest H₂ uptake of 72.6 cm³/g. The Langmuir surface areas are 2986 m²/g , which smaller than and surface area (3214 m²/g) calculated by Materials Studio 6.0, the theoretical pore volume (0.81 cm³/g) respectively and the density is 0.793 g/cm³.

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