

Synthesis, crystal structure and gas uptake properties of a urea-functionalized rht-type metal–organic framework



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ABSTRACT

A hexatopic C₃-symmetrical 5,5',5''-(((benzene-1,3,5-triyltris(azanediyl))tris(carbonyl))tris-(azanediyl))-triisophthalic acid (**H₆-1**) linker containing tri-urea groups has been designed and synthesized through the reaction between 1,3,5-benzenetriisocyanate and aniline, which was employed to construct a new copper(II) metal–organic framework (MOF **Cu-TUH**) under the solvothermal reaction with Cu(NO₃)₂ in *N,N*-dimethylformamide. As expected, single crystal X-ray diffraction study reveals that the MOF **Cu-TUH** is composed of 3D packing of nanosized cuboctahedral, truncated tetrahedral, and truncated octahedral cages with a (3,24)-connected rht-topology. Furthermore, the preliminary gas uptake investigations of the activated MOF were conducted to evaluate its application in the area of gas storage and purifications.

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1. Introduction

Metal–organic frameworks (MOFs), also known as porous coordination polymers (PCPs), are constructed by the self-assembly of metal or metal-oxo nodes and multitopic bridging organic linkers via coordination bonds of moderate strength typically under solvothermal conditions [1–2]. Due to their chemical diversity, permanent porosity, high surface area as well as adjustable pore size and shape [1–5], MOFs have received extensive research and industrial interest over the past decades and shown their great promise in a wide variety of applications [6–11], including gas storage and separation, heterogeneous catalysis, conductivity, sensing, light harvesting, and biomedical area. A large number of MOF materials with tremendous structures and specific applications have been constructed through the judicious combination of metal centers and organic linkers. Moreover, various functional groups can be readily incorporated into MOFs via either ligand design or post-synthetic modifications [12–14], which affords a unique advantage over other traditional porous materials, such as zeolites.

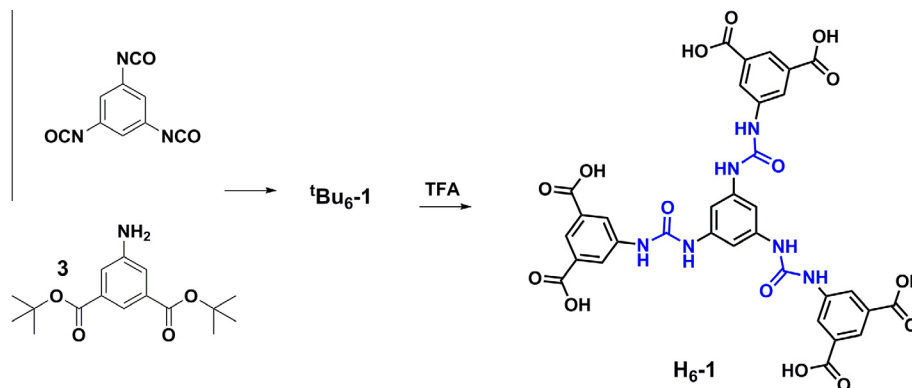
Because of the inherent modularity of MOFs, the rational design and preparation of these materials with predetermined ordered structures and topologies can be realized by the strategy of reticular chemistry [15]. Among the topologies, a fascinating rht-type of

isorecticular MOFs has recently emerged and gained extensive attentions [16–30], where the cuboctahedral metal–organic polyhedra (MOP) with a chemical formula [M(II)₂(BDC)₂(H₂O)₂]₁₂ (M typically is Cu²⁺, BDC = 1,3-benzenedicarboxylate) is cross-linked by a rigid triangular central core through the 24 vertices from 5-position of each BDC, resulting in a (3,24)-connected framework. Moreover, such topology serves as an ideal platform for constructions of novel MOFs, through combining such well-defined 24-connected MOP with a suitable ligand that consists of three coplanar BDC moieties having overall C₃-symmetry [16–30]. In the context, a series of dendritic hexacarboxylate organic linkers composed of three coplanar isophthalates have been synthesized and employed to construct such versatile rht-MOFs.

To enhance the performance and/or endow more delicate properties of rht-MOFs, some polar groups such as acylamide and triazole have been used to cross-link the BDC units except for alkyl [26–29]. Urea also is a very common polar group encountered in organic chemistry, which recently has been incorporated into MOFs as hydrogen-bond-donating (HBD) catalytic sites [31–33]. However, to our knowledge, the urea has not been used to synthesize the hexacarboxylate organic ligand. In this work, we utilized the urea group to cross-link three BDC units generating a new hexacarboxylate linker, i.e., 5,5',5''-(((benzene-1,3,5-triyltris(azanediyl))tris(carbonyl))tris(azanediyl))triisophthalic acid (**H₆-1**, Scheme 1). Subsequently, a urea-functionalized rht-MOF (**Cu-TUH**) was successfully prepared. Subsequently, the gas sorption of the resulting MOF was preliminarily investigated.

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Scheme 1. Synthetic route for linker **H₆-1**.

2. Experimental

2.1. Materials and methods

Unless specifically mentioned, all chemicals were purchased from commercial source and used as received. Toluene and triethylamine (TEA) were distilled over sodium/benzophenone ketyl and CaH₂ under a nitrogen atmosphere prior to use, respectively. Di-*tert*-butyl 5-aminoisophthalate [31] and 1,3,5-triisocyanatobenzene [34] were prepared according to the literature procedures. IR-spectra were recorded as KBr-pellet on a Perkin-Elmer 1760X FT-IR spectrometer. NMR spectra were taken on Bruker AV400 at room temperature. High-resolution mass spectral measurements were carried out on a Waters Q-tof Premier MS. EI mass spectra were obtained in a positive ion mode on a Waters GCT Premier. Elemental analyses (C, H, and N) were obtained from EuroVector Euro EA Elemental Analyzer. Thermogravimetric analysis (TGA) was carried out on a TGA-Q500 thermoanalyzer with a heating rate of 10 °C/min under nitrogen atmosphere. The powder X-ray diffraction (PXRD) measurements were taken on a Bruker D8 diffractometer using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) at room temperature.

2.2. Preparations

2.2.1. Synthesis of compound **^tBu₆-1**

To an aqueous solution (10 ml) of NaN₃ (1.22 g, 19 mmol) was added dropwise a tetrahydrofuran (THF, 5 ml) solution of 1,3,5-benzenetricarbonyl trichloride (0.50 g, 1.9 mmol) while cooling with an ice bath. The reaction suspension was stirred for another 2 h and then poured into water (50 ml), extracted with toluene (50 ml \times 2). The combined organic layer was washed by saturated NaHCO₃ solution and brine, dried over anhydrous Na₂SO₄ and concentrated by evaporating until a volume of around 40 ml was reached. The obtained toluene solution of 1,3,5-benzenetricarbonyl triazide was gradually heated to 120 °C and stirred for 2 h. The 1,3,5-triisocyanatobenzene was formed in the solution, which was then cooled to 80 °C and used as such without characterizations.

To the above obtained toluene solution of 1,3,4-triisocyanatobenzene was added a dry THF (20 ml) solution of di-*tert*-butyl 5-aminoisophthalate (1.67 g, 5.7 mmol) at 80 °C. The reaction mixture was stirred overnight and then evaporated in vacuo to dryness. The crude product was purified by silica gel flash column chromatography (CH₂Cl₂/CH₃OH, 100/2) to give **^tBu₆-1** as a white solid (1.77 g, 1.6 mmol, yield: 84%). ¹H NMR (400 MHz, DMSO) δ 9.02 (s, 3H), 8.86 (s, 3H), 8.24 (d, $J = 1.5 \text{ Hz}$, 6H), 8.01 (t, $J = 1.5 \text{ Hz}$, 3H), 7.37 (s, 3H), 1.57 (s, 54H). ¹³C NMR (101 MHz, DMSO) δ 164.12, 152.31, 140.45, 140.07, 132.17, 122.64, 122.26, 102.38, 81.30, 27.70. ESI-TOF-HRMS: m/z calcd for C₅₇H₇₃N₆O₁₅: 1081.5115. Found: 1081.5134 [M+H]⁺.

2.2.2. Synthesis of linker **H₆-1**

To a solution of the ester **^tBu₆-1** (1.77 g, 1.6 mmol) in CH₂Cl₂ was added trifluoroacetic acid (TFA, 15 mL). The mixture was stirred at room temperature over 5 h, obtaining a precipitate. The suspension was filtered, washed with CH₂Cl₂ to remove excess TFA, and then dried under vacuum giving **H₆-1** (0.97 g, 1.3 mmol, yield: 81%) as light gray solid. ¹H NMR (400 MHz, DMSO) δ 13.23 (br, 6H), 8.98 (s, 3H), 8.90 (s, 3H), 8.31 (d, $J = 1.2 \text{ Hz}$, 6H), 8.09 (s, 3H), 7.42 (s, 3H). ¹³C NMR (75 MHz, DMSO) δ 166.71, 152.49, 140.55, 140.19, 131.83, 123.33, 122.81, 102.71. ESI-TOF-HRMS: m/z calcd for C₃₃H₂₅N₆O₁₅: 745.1365. Found: 745.1378 [M+H]⁺.

2.2.3. Synthesis of MOF **Cu-TUH**

Compound **H₆-1** (20 mg, 0.027 mmol) and Cu(NO₃)₂·3H₂O (19 mg, 0.075 mmol) were dissolved in *N,N*-dimethylformamide (DMF, 15 mL). Then, several drops of HNO₃ were added into the mixture. The solution was placed in a tightly capped 20 mL vial and heated in an oven at 75 °C for 3 days. The green block crystals were collected after cooling to room temperature. Then, these crystals were washed by fresh DMF for several times (5 mg, yield: 20%). Elemental analysis Calc. for Cu₃(**1**)(H₂O)₃·5DMF·10H₂O: C, 37.71; H, 5.21; N, 10.08. Found: C, 38.12; H, 5.41; N, 10.56 (%). Selected

Table 1

Crystal data and structure refinement for **Cu-TUH**.

Empirical formula	C ₃₃ H ₂₄ Cu ₃ N ₆ O ₁₈
Formula weight	983.21
Wavelength (Å)	1.54184
Crystal system	tetragonal
Space group	<i>I4/m</i>
Unit cell dimensions	
<i>a</i> (Å)	31.0865(6)
<i>b</i> (Å)	31.0865(6)
<i>c</i> (Å)	44.596(3)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å ³)	43 096(3)
<i>Z</i>	16
<i>D</i> _{calc} (mg m ⁻³)	0.604
Absorption coefficient (mm ⁻¹)	0.962
<i>F</i> (000)	7872
Crystal size (mm)	0.13 \times 0.16 \times 0.18
Index ranges	$-34 \leq h \leq 12$, $-34 \leq k \leq 33$, $-42 \leq l \leq 48$
Reflections collected	35442
Independent reflections (<i>R</i> _{int})	14267 (0.136)
Absorption correction	multi-scan
Maximum and minimum transmission	0.882 and 0.841
Refinement method	full-matrix least-squares on <i>F</i> ²
Goodness-of-fit (GOF) on <i>F</i> ²	0.879
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0860, <i>wR</i> ₂ = 0.2139

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