



Three supramolecular compounds of 1,4-benzeneditetrazole (H₂BDT): Syntheses, crystal structures, and crystal to crystal transformation



Ji-Hua Deng ^{a,1}, Ya-Qiong Wen ^{a,1}, Jie Luo ^a, Zhi-Qiang Huang ^{b,**}, Di-Chang Zhong ^{a,*}

^a College of Chemistry & Chemical Engineering, Gannan Normal University, Ganzhou, 341000 China

^b College of Engineering, Jiangxi University of Science and Technology, Ganzhou, 341000 China

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ABSTRACT

Three supramolecular compounds based on 1,4-benzeneditetrazole (H₂BDT), (NH₄)₂(BDT) (**1**), [Mg(H₂O)₆](HBDT)₂·2H₂O (**2**), and [Mg(CH₃OH)₄(H₂O)₂](HBDT)₂·2CH₃OH (**3**) have been solvothermally synthesized and structurally characterized by single-crystal/powder X-ray diffraction. Structural analyses indicated that these compounds are 3D supramolecular structures stabilized by electrostatic interactions and intermolecular hydrogen bonds. The crystal to crystal transformation between **2** and **3** were investigated. The result showed that **2** is readily transform to **3** after immersed in methanol solution, while **3** can not be converted to **2** after immersed in distilled water solution.

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1. Introduction

With potential functions in molecular recognition, molecular catalysis, molecular transport and so on, the self-assembly of supramolecular architectures have received considerable attentions during the past several decades [1,2]. Supramolecular architectures are usually stabilized by intermolecular noncovalent interactions including hydrogen bond, $\pi \cdots \pi$ stacking interaction, hydrophobic interaction and so on [3,4]. It is well-known that the characteristic and structure of the building block are key factors for constructions of functional supramolecular materials. An ideal building block generally possesses multi-interaction sites to bind with other molecules, and directs the crystal growth to get desired supramolecular networks.

1,4-benzeneditetrazole (H₂BDT) is a multi-topic ligand that has been extensively used to build coordination polymers [5–10]. We and others have found that H₂BDT usually acts as bridge to link metal centers together, affording a number of porous polymer frameworks with diverse functions [11–13]. Very recently, we have constructed an *in situ* synthesis system for H₂BDT, from which the formation of beneditetrazole through cycloaddition reaction has been observed step by

step, and the metal catalysis in *in situ* cycloaddition reaction of nitrile with azide has been proved to be the activation to –CN group in nitrile by coordination interaction [12]. Additionally, we have also found that H₂BDT is good building block for weaving supramolecular networks. In this article, we report three supramolecular compounds of H₂BDT, (NH₄)₂(BDT) (**1**), [Mg(H₂O)₆](HBDT)₂·2H₂O (**2**), and [Mg(CH₃OH)₄(H₂O)₂](HBDT)₂·2CH₃OH (**3**). Their syntheses, crystal structures, and crystal to crystal transformation have been detailedly investigated and discussed.

2. Experimental

2.1. Materials and physical measurements

All of the chemicals were commercially available and used without further purification. Elemental analyses were determined using Elementar Vario EL elemental analyser.

2.2. Syntheses

2.2.1. Synthesis for **1**

A mixture of Zn(NO₃)₂·6H₂O (0.5 mmol, 0.149 g), H₂BDT (0.5 mmol, 0.107 g), aqueous ammonia (0.2 mL), and H₂O (8 mL) was heated at 110 °C for 48 h in a 20 mL sealed Teflon-lined stainless steel vessel. After the autoclave was cooled over a period of 16 h at a rate of 5 °C·h⁻¹, light yellow block-shaped crystals of **1**

* Corresponding author.

** Corresponding author.

E-mail address: zhong_dichang@hotmail.com (D.-C. Zhong).

¹ These authors contribute equally to this work.

were isolated by filtration. Yield: 0.028 g, 23% based on H₂BDT. Anal. Calcd for C₁₆H₂₄N₂₀ (**1**): C, 38.71; H, 4.87; N, 56.42%. Found: C, 38.62; H, 4.95; N, 56.35%.

2.2.2. Synthesis for **2**

A mixture of MgCl₂·6H₂O (1.0 mmol, 0.203 g), H₂BDT (0.5 mmol, 0.107 g), and H₂O (10 mL) was heated in an oven at 130 °C for 72 h. After the oven was cooled to room temperature, brown block-shaped crystals of **2** were isolated by filtration. Yield: 0.051 g, 34% based on H₂BDT. Anal. Calcd for C₁₆H₂₆N₁₆O₈Mg (**2**): C, 32.31; H, 4.41; N, 37.68%. Found: C, 32.42; H, 4.39; N, 37.61%.

2.2.3. Synthesis for **3**

A mixture of MgCl₂·6H₂O (1.0 mmol, 0.203 g), H₂BDT (1.0 mmol, 0.214 g), and 8 mL solvent of methanol and distilled water (*v/v* = 1/1) was heated in an oven at 80 °C for 72 h. After the oven was cooled to room temperature, the mixture was filtrated. The resulted clear colorless solution was allowed to slowly evaporate at room temperature. One month later, brown block crystals of **3** were isolated, collected by hand and dried in air. Yield: 0.092 g, 27% based on H₂BDT. Anal. Calcd for C₂₂H₃₈N₁₆O₈Mg (**3**): C, 38.92; H, 5.64; N, 33.01%. Found: C, 38.81; H, 5.66; N, 33.09%.

2.3. Studies of the transformation between **2** and **3**

2 to **3**: Crystalline sample of **2** (*ca.* 0.2 g) was immersed in an absolute methanol solution (20 mL) for one day. Then the solution was poured out, and 20 mL fresh absolute methanol solution was added. After treated for three times, the solid sample was isolated by centrifugation.

3 to **2**: The procedure is similar to that for **2** to **3** except using distilled H₂O instead of absolute methanol.

2.4. X-ray diffraction

Single-crystal data for **1–3** were collected on a Bruker Smart 1000 CCD diffractometer with graphite-monochromated Mo K α radiation (λ = 0.71073 Å) at 173(2) K, and Powder X-ray diffraction patterns for **1–3** were recorded on D8 ADVANCE X-Ray Diffractometer at room temperature. All empirical absorption corrections were applied using the SADABS program [14]. The structure was solved using direct methods, which yielded the positions of all non-hydrogen atoms of the whole framework. These were refined first isotropically and then anisotropically. Positions of the hydrogen atoms attached to the carbon atoms were geometrically placed, and were isotropically refined as a riding mode using the default SHELXTL parameters. The hydrogen atoms attached to the lattice H₂O and methanol molecules were located by difference Fourier maps and refined in isotropic approximation. All calculations were

performed using the SHELXTL system of computer programs [15].

3. Results and discussion

3.1. Crystal structures

3.1.1. Crystal structure of **1**

The single crystal X-ray diffraction analysis revealed that in the asymmetric unit of **1**, there is one BDT²⁻ anion and two NH₄⁺ ion (Fig. 1a). Each NH₄⁺ ion donates four H atoms to four N atoms from four individual BDT²⁻ anions to form four N–H···N hydrogen bonds, and each BDT²⁻ anion accepts eight H atoms from eight individual NH₄⁺ ions to generate eight N–H···N hydrogen bonds (Fig. 1b; Table 2). Rely on these strong hydrogen bonds and electrostatic interactions between BDT²⁻ anions and NH₄⁺ ions, a 3D supramolecular structure with (4,8)-connected topology network has been weaved (Fig. 1b).

3.1.2. Crystal structure of **2**

2 crystallizes in monoclinic crystal system, *P*2₁/*c* space group (Table 1). The asymmetric unit of **2** is composed of one [Mg(H₂O)₆]²⁺ complex unit, two HPIDC⁻ anions, and two lattice H₂O molecules (Fig. 2a). [Mg(H₂O)₆]²⁺ complex unit connects with HPIDC⁻ anions by hydrogen bonds between coordinated H₂O molecules of [Mg(H₂O)₆]²⁺ and tetrazolyl N atoms of HPIDC⁻, to form a 2D supramolecular layer along the *bc* plane (Fig. 2b, Table 2). The adjacent 2D supramolecular layers are further linked together along the *a* axis through the inter-layer hydrogen bond interactions among [Mg(H₂O)₆]²⁺ unit, HPIDC⁻ anion, and lattice H₂O molecules, to generate a 3D supramolecular structure, in which lattice H₂O molecules serve as hydrogen bond bridges for the connection of [Mg(H₂O)₆]²⁺ unit and HPIDC⁻ anion. (Fig. 2c, Table 2).

3.1.3. Crystal structure of **3**

The result of single crystal X-ray diffraction analysis revealed that **3** crystallizes in triclinic crystal system, with *P*-1 space group (Table 1). In the asymmetric unit of **3**, there is one [Mg(CH₃OH)₄(H₂O)₂]²⁺ complex unit, two HBBDT⁻ anions, and two lattice CH₃OH molecules (Fig. 3a). It is interesting to find that **2** and **3** show similar compositions. The difference is that the coordinated solvent molecules around Mg(II) in **2** are six H₂O molecules, while these in **3** are four CH₃OH molecules and two H₂O molecules, as well as the lattice guests in **2** are H₂O molecules, while these in **3** are CH₃OH molecules. There are strong hydrogen bond interactions among [Mg(CH₃OH)₄(H₂O)₂]²⁺, HBBDT⁻, and lattice CH₃OH molecules. The coordinated H₂O molecule (O3) in [Mg(CH₃OH)₄(H₂O)₂]²⁺ donate H atoms to N5 and N6 of HBBDT⁻ anions, to form strong O–H···N hydrogen bond (Table 2). The coordinated CH₃OH molecules (O1 and O2) also donate H atoms to N1 of HBBDT⁻ anion and

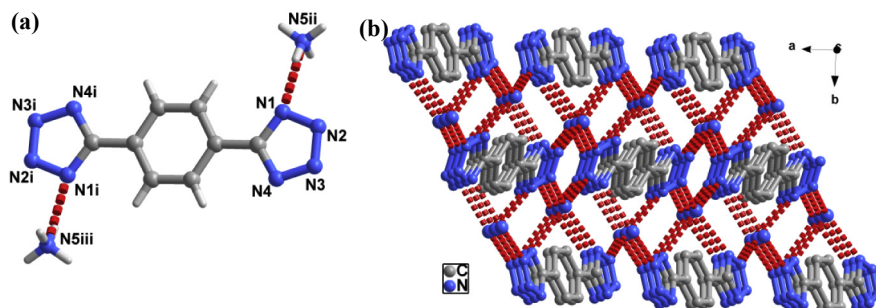


Fig. 1. (a) Molecular structure of **1** (Symmetric code: *i* = 1-*x*, 1-*y*, 1-*z*; *ii* = -0.5 + *x*, 0.5-*y*, 0.5 + *z*; *iii* = 1.5-*x*, 0.5 + *y*, 0.5-*z*); (b) 3D supramolecular structure of **1**.

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