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# System-pH-dependent supramolecular isomers of puckered three-dimensional layered hydrogen-bonded networks: Syntheses, characterization and fluorescent properties

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**Abstract**

Two true supramolecular isomers (**1** and **2**) formulated as $[Zn(bipy)(H_2btc)_2]_n$ (bipy = 2,2′-bipyridine, $H_3btc$ = benzene-1,3,5-tricarboxylic acid) have been hydrothermally prepared through systematically changing the pH value of reaction mixture, and characterized by single-crystal X-ray diffraction, element analysis, infrared spectra (IR), and differential scanning calorimetry (DSC). Isomer **1** crystallizes in triclinic space group *P*-1, tetrahedral Zn(II) ions possess four-coordinated environment, while isomer **2** crystallizes in monoclinic space group *C*2/*c* and the distorted octahedral Zn(II) ions adopt six-coordinated fashion. **1** and **2** can be regarded as supramolecular structural isomers, the formation of which should be undoubtedly attributed to the preference for pH-dependent crystallization leading to multiple connectivity (monodentate and chelating bidentate) of organic ligand despite the same stoichiometry employed. The supramolecular chemistry, which organizes the coordination complexes into three-dimensional (3D) layered open structure, is driven by a combination of hydrogen-bond and $\pi$–$\pi$ interactions. Moreover, **1** emits fluorescence at 350.1 nm ($\lambda_{ex} = 310.0$ nm) and **2** exhibits fluorescent property at about 351.4 nm ($\lambda_{ex} = 302.0$ nm).

*Keywords:* pH-dependent; Supramolecular isomers; Fluorescence; Hydrothermal synthesis; Characterization

## 1. Introduction

Long time ago, isomer was extensively investigated in the field of organic chemistry. Importantly,when the difference between coordination polymers [1] and supramolecular architectures [2] became unconspicuous, the concept of supramolecular isomerism [3] was introduced into crystal engineering by Zaworotko and coworkers to interpret their synthetic and structural relationship. For given metal centers and multifunctional bridging ligands, various connectivity manners can result in a series of supramolecular isomers which were defined as the occurrence of more than one superstructure arising from the same reagent. The final arrangements of supramolecule are significantly influenced by comprehensive factors such as reaction time, temperature, pH value, medium and the metal-to-ligand ratio. Therefore, it is still a formidable challenge to predict the precise superstructure of those high-dimensional polymers with complicated ligands.

Much attentions [4–14] have been recently paid to the deliberate design and controlled synthesis of supramolecular isomerism owing to their potential applications as well as abundant structural information. Taking into account the different structure characteric, several cases of structural isomerism [5,7] conformational isomerism [10,13] and optical isomerism [14] have been reported previously. Based on the cause to isomerism, some examples tuned via template molecules (solvent guest) [6–8], conformational conversion of ligand [10,13], *ring-opening polymerization* [6b,9,10a,14] and reaction-temperature-induced isomerism [12b,12c], have been published in the literature. Because different solvent molecules were involved in the corresponding coordination networks, most of those mentioned above should be classified as pseudo-polymorphism [5,6]. Strictly speaking, only several cases of

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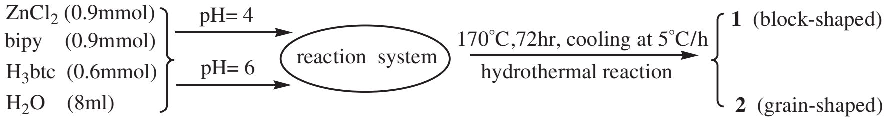

Scheme 1. The synthetic procedure of isomers **1** and **2**.

true supramolecular isomerism with a fixed stoichiometry for all components were documented [10c,11,12a,12b] so far, which can be further categorized into two types, namely the building blocks intrinsic-nature-induced (conformational ligand) and extrinsic-stimulation-induced (temperature and acidity/basicity) isomers.

Aromatic polycarboxylic acids are widely used as space ligands because of their sterical rigidity and chemical robustness, in which multiple coordination fashions of carboxyl such as monodentate, bidentate (bridging) and chelating, can likely yield structural isomers. As illustrated in the two compounds $\alpha$-[Co(dcbp)(H$_2$O)$_2$] and $\beta$-[Co(dcbp)(H$_2$O)$_2$] (dcbp = 4,4′-dicarboxy-2,2′-bipyridine) [12a], they display different 3D architectures as a result of various coordination modes of carboxyl in dcbp ligand: the former is bis-monodentate while the latter have both bridging bidentate and noncoordinated carboxylate groups. Although three cases of pH-induced pseudo-polymorphs Co$_3$(TMA)$_2$ (TMA = benzene-1,3,5-tricarboxylate) with solvent molecules were ever described [15], we select polycarboxylic H$_3$btc to synthesize true supramolecular isomer through changing the pH value of reaction system.

On the other hand, $d^{10}$ electron configuration transition metal complexes possibly possess luminescent properties. The aforementioned ideas prompt us to employ multidentate H$_3$btc as organic linkers and chelated bipy as an auxiliary ligand. In this contribution, we present two true supramolecular isomers without guest molecules, the formation of which were found to be extremely sensitive to the pH values of the reaction mixture (see Scheme 1). Of particular interest is that they both possess extended open structures, which evidently differ from the interconversion between polymeric chain and closed ring. Another feature is that the 3D frameworks are mainly sustained by hydrogen-bond interactions.

## 2. Experimental

### 2.1. Materials and general procedures

All chemicals were of reagent grade and were used as purchased from the Rgent company of chemical reagent in Tianjin without further purification. The IR spectra were recorded as KBr pellets on a FT-IR 170SX (Nicolet) spectrometer in the 4000–400 cm$^{-1}$ region. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240 analyzer. Fluorescent analyses were carried out on an Edinburgh Instruments analyzer model FL920. The DSC measurements were performed on a NETZSCH DSC 204 with a heating rate of 10 °C/min in the temperature range of 25–590 °C.

### 2.2. Syntheses

Two same mixtures of ZnCl$_2$ (0.123 g, 0.9 mmol), bipy (0.140 g, 0.9 mmol), and H$_3$btc (0.126 g, 0.6 mmol) in the molar ratio of 3:3:2 were both dissolved in 8 ml distilled water. The pH values were adjusted to 4(**1**) and 6(**2**) with 2 M KOH, respectively. Then, the resulting solution were transferred and sealed in two 25 mL Teflon-lined stainless-steel vessels, which were heated at 170 °C for 3 days. After the reactors were slowly cooled to room temperature at a rate of 5 °C/h, colorless block-shaped (**1**) and grain-shaped (**2**) crystals were filtered off, washed with distilled water and dried in air (yield: 52% and 56% based on ZnCl$_2$, respectively). Anal. Calcd. (%) for [Zn(bipy)(H$_2$btc)$_2$] (Mr = 639.81): C, 52.56; H, 2.84; N, 4.38. Found (**1**): C, 52.11; H, 2.93; N, 4.42. Found (**2**): C,52.20; H, 2.97; N, 4.34. Selected IR spectra for **1**: $\nu$ (cm$^{-1}$) = 1715, 1698 s, 1614, 1558, 1541, 1442 m, 1252 s, 700 m; and for **2**: $\nu$ (cm$^{-1}$) = 1717 s, 1698, 1613, 1444 m, 1221 s, 764, 753 m.

### 2.3. Crystal structure determinations

Crystal data and experimental details are summarized in Table 1. Single crystal analyses were performed at 293(2) K with a Bruker SMART 1000 CCD diffractometer with Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) by the $\omega - 2\theta$ scan technique. All data were collected for absorption by semi-empirical method using SADABS program. The program SAIN [16] was applied for integration of the diffraction profiles. Data analysis was carried out with program XPREP. The structure was solved with direct method using SHELXS-97 followed by structure refinement on $F^2$ with program SHELXL-97 [17]. All nonhydrogen atoms were refined anisotropically. Aromatic hydrogen atoms were assigned to calculated positions with isotropic thermal parameters. Carboxylic acid hydrogen atoms were placed from different maps and refined subject to O–H distance restraints. The CCDC reference numbers are 281580 (**1**) and 281579 (**2**). Selected bond lengths and angles are listed in Table 2.

## 3. Results and discussion

### 3.1. Description of crystal structures

Single-crystal X-ray diffraction analysis reveals that **1** and **2** are structural isomers without any guest molecules in