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Construction of a Three-Dimensional Polynuclear Zinc Compound Based on Unique Metallophthalocyanine-like Subunits

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A polynuclear zinc compound, $[Zn_7(BTA)_7(OABDC)(\mu_3\text{-}OH)_2(\mu_2\text{-}OH)_2 \cdot H_2O]$ (**1**), has been prepared by using benzotriazole (HBTA) and 5-oxyacetatoisophthalic acid (H_3OABDC) as ligands under hydrothermal conditions. For compound **1**, an unprecedented metallophthalocyanine-like "$Zn_2(\mu_3\text{-}OH)_2 \subset [Zn_4BTA_4]$" subunit is constructed from η^3-BTA ligands and Zn atoms and further linked via μ_2-OH, outer four-connected Zn atoms, and 5-oxyacetateisophthalic acid to form a novel three-dimensional framework.

Nowadays, there is an increasing interest in the design and preparation of inorganic−organic hybrid compounds, owing to their intriguing structures and potential applications as functional solid materials.[1] On the basis of the knowledge of both metal coordination preferences and ligand geometries, extensive research in polynuclear metal clusters, including metallocrowns,[2] metalloporphyrin-like subunits, and so on[3,4] has been carried out. On the other hand, as a rich family of multifunctional materials, metallophthalocyanines (MPCs) have been studied widely in the fields of catalysis, optics, electronics, and magnetics for many years.[5,6] Up to now, various phthalocyanines and phthalocyanine derivatives have been successfully synthesized, which led to a wide range of applications in molecular electronics and photonics;[7,8] nevertheless, high-dimensional MPC compounds have been rarely reported because of the phthalocyanines often existing as stacked lattices in the solid state.[9] It is well-known that the properties of compounds are inherently associated with their structures, so the construction of polynuclear cluster polymers, especially for subunits with phthalocyanine-like structure, may facilitate the development of new functional materials. However, to date, the mechanism of the formation of high-nuclearity clusters is still obscure. Hence, it is a big challenge for chemists to construct high-nuclearity-cluster polymers in pursuit of multifunctional materials.

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In the present work, a new polynuclear zinc coordination polymer with benzotriazole (HBTA) and 5-oxyacetatoisophthalic acid (H_3OABDC) as ligands has been prepared hydrothermally. The resultant compound, $[Zn_7(BTA)_7(OABDC)(\mu_3\text{-}OH)_2(\mu_2\text{-}OH)_2 \cdot H_2O]$ (**1**), exhibits a charming three-dimensional framework built from unprecedented MPC-like "$Zn_2(\mu_3\text{-}OH)_2 \subset [Zn_4BTA_4]$" subunits, which are sustained via μ_2-OH, outer four-connected Zn atoms, and 5-oxyacetatoisophthalic acid. The framework is very stable in air, and it begins to decompose when it is heated up to 422 °C (Figure S1 in the Supporting Information). Also, it is worth noting that compound **1** shows interesting photoelectronic properties because of its unique MPC-like subunits; thus, it may be used as a candidate of semiconductor materials in the future.

Single-crystal structural analysis[10] reveals that compound **1** crystallizes in the monoclinic space group $P2_1/m$ and has a three-dimensional coordination framework. The molecular structure exhibits an unusual assembly of Zn atoms and organic ligands. For the sake of understanding, the structure was explained from two aspects, namely, the MPC-like hexanuclear subunit and the assembly of these subunits with outer four-connected Zn5 atoms and OABDC ligands. As shown in Figure S2 in the Supporting Information, **1** includes five crystallographically independent Zn^{II} atoms, four BTA ligands, and one OABDC ligand (the coordination environments of Zn atoms are described in the Supporting Information). It can be observed that the linkage of four equatorial η^3-BTA ligands and four Zn^{II} atoms results in a nearly planar tetrametallamacrocyclic motif that is an analogue of 12-metallacrown-4 reported by Pecoraro et al.[2c,11] In contrast to a recently reported metalloporphyrin-like subunit, in which four Cu^{II} ions and four triazole rings form an unusual cyclic moiety, the tetrametallamacrocyclic motif described herein resembles phthalocyanine in that both contain coplanar five- and six-membered rings, except that metal atoms occupy the corresponding positions of bridging N atoms and benzotriazoles replace isoindolyls (Figure 1). Compared to phthalocyanine, the macrocyclic moiety in compound **1** has four N atoms pointing toward the center, with the adjacent N−N distances of 5.5 and 3.1Å, which are significantly larger than those in phthalocyanine, because of the longer Zn−N distances compared with C−N distances. Additionally, the distorted square-pyramidal environment of the Zn4 atom is completed by two μ_3-OH groups, one μ_2-OH group, and two 2-position N atoms of the BTA ligands. Two Zn4 atoms are filled in the cavity via coordination of the 2-position N atoms of equatorial η^3-BTA ligands and the bridging of two μ_3-O groups, thereby forming an unprecedented MPC-like subunit, denoted as $Zn_2(\mu_3\text{-}OH)_2 \subset [Zn_4BTA_4]$.

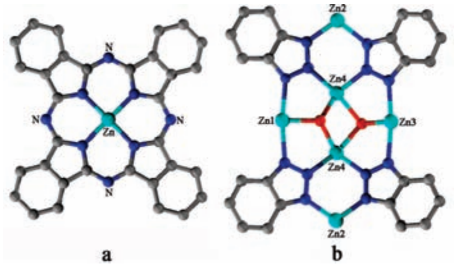

Figure 1. (a) View of MPC-like zinc. (b) View of MPC-like subunit $Zn_2(\mu_3\text{-}OH)_2 \subset [Zn_4BTA_4]$ of **1**.

Notably, in the MPC-like subunit, the different coordination environments of Zn atoms result in a $Zn_2(\mu_3\text{-}OH)_2 \subset [Zn_4BTA_4]$ subunit with profuse coordination preferences. The bridging μ_2-OH groups link with Zn2 and Zn4 of adjacent subunits from the convex side, forming 1D chains along the *b* axis direction (Figure S3 in the Supporting Information). As shown in Figure S4 in the Supporting Information, on the concave side of MPC-like subunits, the four-connected Zn5 atom links with Zn1 and Zn3 atoms of the same $Zn_2(\mu_3\text{-}OH)_2 \subset [Zn_4BTA_4]$ subunit via one 1,3-μ BTA ligand and one flexible carboxyl group of the OABDC ligand, respectively. Meanwhile, the Zn5 atom is also connected with two different Zn2 atoms of the alternate $Zn_2(\mu_3\text{-}OH)_2 \subset [\ Zn_4BTA_4]$ subunits through the linking of two 1,3-μ BTA ligands. Thus, the four-connected Zn5 atom joins three $Zn_2(\mu_3\text{-}OH)_2 \subset [Zn_4BTA_4]$ subunits affiliated to two adjacent 1D chains, forming a 2D plane along the *c* axis direction (Figure S5 in the Supporting Information).

Furthermore, the OABDC ligand including one flexible and two rigid carboxyl groups offers an appropriate coordination geometry in the assembly process of compound **1**.[12] As displayed in Figure S6 in the Supporting Information, each OABDC ligand links with three $Zn_2(\mu_3\text{-}OH)_2 \subset [Zn_4BTA_4]$ subunits through three carboxyl groups: one rigid carboxyl group and a flexible carboxyl group link with two subunits of adjacent 1D chains, consequently stabilizing the 2D layer; the other rigid carboxyl group links with one subunit of an adjacent 2D layer. Such connectivity between OABDC ligands and layers forms a complex 3D framework (Figures 2 and S7 in the Supporting Information).

As reported in the literature,[13] the deprotonated parent heterocycle can coordinate up to three metal atoms. In compound **1**, the coordination of the η^3-BTA ligand is similar to that but acts as a segmental ligand in the process of the selective formation of MPC-like subunits. Different from the

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(10) *Crystallographic data for* **1**: $C_{52}H_{38}N_{21}O_{12}Zn_7$, $M = 1606.62$, monoclinic, space group $P2_1/m$, $a = 12.5552(8)$ Å, $b = 18.0199(12)$ Å, $c = 13.8109(10)$ Å, $\beta = 105.3590(10)°$, $V = 3013.0(4)$ Å^3, $Z = 2$, $\mu = 2.817$ mm^{-1}, $D_c = 1.772$ Mg m^{-3}, $F(000) = 1608$, 4516 unique ($R_{int} = 0.0621$), R1 = 0.0487, wR2 = 0.1151 [$I > 2\sigma(I)$], GOF = 1.009. The intensity data were collected on a Smart Apex II CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å) at room temperature. All absorption corrections were performed by using the SADABS program. The structure was solved by direct methods, and all non-H atoms were subjected to anisotropic refinement by full-matrix least squares on F^2 using the *SHELXTL* program. CCDC 689993.

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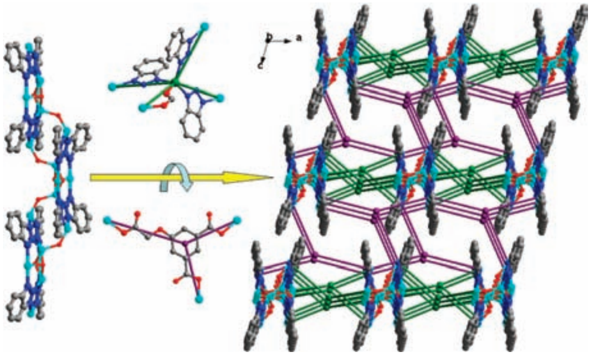

Figure 2. Schematic view of a 3D framework about compound **1** along the *b* axis. For clarity, Zn5 atoms are treated as green four-connected nodes and OABDC ligands are treated as purple three-connected nodes.

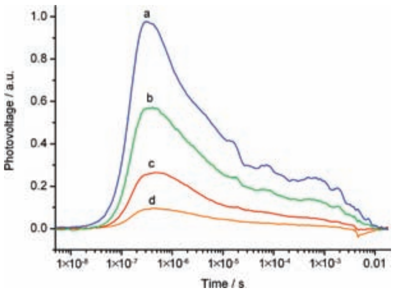

Figure 3. Transient PV response of the ITO/**1**/ITO sandwich cell under illumination of a 355 nm pulse laser at various intensities. From curves a−d, the corresponding light intensities are 0.05, 0.10, 0.20, and 0.30 mJ.

highly symmetrical Zn atom located at the center of a polymetallic cluster,[13a,d,e] here the $Zn_2(\mu_3\text{-}OH)_2$ unit fills in the center of $Zn_2(\mu_3\text{-}OH)_2 \subset [Zn_4BTA_4]$, for which the special size and coordination environment of $Zn_2(\mu_3\text{-}OH)_2$ play important roles in its construction and stabilization. Simultaneously, the outer four-connected Zn atoms and half-rigid OABDC ligands provide an appropriate coordination environment, which not only stabilizes $Zn_2(\mu_3\text{-}OH)_2 \subset [Zn_4]$ through coordination with Zn atoms but also further forms a novel 3D framework.

Encouraged by the single-crystal X-ray diffraction results that reveal the presence of hexanuclear zinc $Zn_2(\mu_3\text{-}OH)_2 \subset [Zn_4BTA_4]$ subunits in the framework, photovoltage (PV) transients for **1** were recorded under atmospheric pressure and at room temperature.[14] Figure 3 shows PV transients of **1** at various intensities of exciting laser pulses (355 nm). Although the intensities of the exciting laser pulses are different (0.05, 0.10, 0.20, and 0.30 mJ), the times of their PV maxima are similar (approximately 3×10^{-7} s). The maxima are related to the separation of charge at the **1**/ITO interface, and the gradient of excess electron and hole concentrations is caused by the nonhomogeneous absorption of light with $h\nu$ larger than the optical band gap (E_g). Additionally, the PV transient signals are positive, which means that the photoexcited electrons move faster than the holes toward the **1**/ITO interface. The transient photovoltaic response of the MPCs has been studied based on an Al/MPc/ITO sandwich cell.[15] The results show that the PV transient signals are positive through the ITO electrode when the MPC film was illuminated under a 355 nm pulse laser, which corresponds to the B absorption band of the MPC absorption spectrum. It is known that a PV signal will arise whenever light-induced excess charge carriers are separated in space and that PV transients can be used in the characterization of semiconductor materials.[16] Thus, compound **1** may be a potential candidate for semiconductor materials because of its unique MPC-like subunits.

In summary, a novel 3D polynuclear framework, compound **1**, which contains unprecedented MPC-like subunits, has been synthesized by using HBTA and H_3OABDC as ligands under hydrothermal conditions. For compound **1**, η^2-BTA ligands and 5-oxyacetateisophthalic acid link with MPC-like subunits and outer four-connected Zn atoms to form a novel 3D framework. To the best of our knowledge, compound **1** represents the first example of a 3D metal−organic framework based on MPC-like hexanuclear cluster subunits. Furthermore, it is worth noting that compound **1** exhibits interesting photoelectronic properties because of the MPC-like subunits, which suggests that compound **1** may be a promising candidate for semiconductor materials. Undoubtedly, all of these interesting results will stimulate future studies of this new type of multifunctional materials with special subunits.

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Supporting Information Available: Crystallographic data in CIF format, synthetic procedures, thermogravimetric analysis curve, luminescent spectra, frontier molecular orbital calculation by the density functional theory method, and complementary drawings for crystal structure. This material is available free of charge via the Internet at http://pubs.acs.org.

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