Solvothermal Synthesis of van der Waals Molecular Sieves Based on Cylindrical-Porphyrinwires

Lu-Lin Li and Kuan-Jiuh Lin

Department of Chemistry
National Chung-Hsing University
Taichung, Taiwan 402, R.O.C.
E-mail: kjlin@dragon.nchu.edu.tw

Abstract

Highly stable organic solids, based on van der Waals interactions between cylindrical porphyrinwires, exhibit unique square iodine-channels (10 × 10 Å) and exceptionally hollow porphyrinwires. The functionalized iodine-cavities could be capable of conferring specific adsorption behavior for mercury and lead ions, whereas hollow porphyrinwires might serve as a model for the development of hybrid electronic and ionic transfer materials.

Key Words: Microporosity, Porphyrinoids, Solid State Array, Supramolecular Chemistry, Zeolite Analogues

1. Introduction

Supermolecules or coordination polymers have attracted great interest from diverse areas of material science and technology [1–3]. For fragile and entropic reasons, thermally stable and highly porous networks sustained by directional π-stacking interactions are still rare or lacking. Moreover, supramolecular architectures with π-electron backbones have potential fundamental and practical implications in areas such as chemical sensors, biomimetic chemistry, molecular conductors, and solar energy devices. Among them, solid state porphyrin-based arrays may be particularly promising in such efforts because porphyrin materials are capable of mediating electron and energy transfer [4,5]. Important models for the design of artificial systems exhibiting such structural morphologies may be borrowed from naturally occurring uroporphyrins within a discotic phase. To day, however, the synthesis of freebase-porphyrin discotic phases is difficult to perform in a controlled manner. It would be very useful if the tools of molecular synthesis could be brought to bear on this problem. Many attempts, in our laboratory, have been made to prepare solid state porphyrin arrays formed by self-assembly of cylindrical rods. The resulting products are of poor crystalline or do not maintain their rigid structure due to the relatively weak intermolecular forces of the molecular tectons. In exploring new classes of coordination zeolites under hydrothermal techniques [6], de novo one-step C-N(\(sp^2\)) bond formation was found serendipitously, thereby opening the way to the rational design and synthesis of novel nanoporous solids within polycationic porphyrinwires (Figure 1).

2. Experimental

We synthesized two freebase porphyrinwires formed by columnar self-assembly of peripherally substituted H₂tpyp (5,10,15,20-tetrakis(4-pyridyl)porphyrin), which we collectively named SMTP-2, by employing solvent-thermal conditions [7]. Needle-like crystals of both products were grown in a static autoclave at 180 °C under autogenous pressure for 72 hours. Most reactions yielded bunched aggregates of individual crystals, but single crystals large enough for X-ray diffraction studies were also obtained. Although crystalline SMTP-2 is stable in air and is insoluble in most organic solvent, it is slightly soluble in hot water probably due to quaternary ammonium motifs. The secondary building units (SBU) of SMTP-2
were identified with the general formula \( \{(\text{H}_2\text{tpyp-R}_4) \ (\text{CdI}_4)_2\}_4 \cdot \text{G} \) (1: R = CH\textsubscript{3}CH\textsubscript{3}, 2: R = CH\textsubscript{3}CH\textsubscript{2}OH; \ G = 8\text{H}_2\text{O} \cdot 4\text{CH}_3\text{COOH} \) by single-crystal analysis, elemental analysis, thermogravimetric analysis, NMR and FTIR spectroscopy [8].

3. Results and Discussion

The structure of SMTP-2 exhibits an open-framework containing two independent sets of one-dimensional functionalized channels, namely, polycationic porphyrinwires and square iodine-channels (Figure 2). The porphyrin cores self-assemble into columnar aggregates sustained by noncovalent \( \pi \cdot \pi \) interactions, a separation of 4.0 Å between adjacent porphyrins. As polycationic \( \pi \)-conjugated backbones are created, the charge-compensating tetrahedral \( \text{CdI}_4^2- \) ions are self-included to benefit the stability of well-order porphyrinwires from CH…I hydrogen bonds and aromatic \( \pi \cdots \pi \) interactions. The cylindrical porphyrinwires are further glued together by a combination of efficient van der Waals and electrostatic interactions, unprecedentedly yielding two-dimensional tetragonal packing rather than hexagonal topologies. Therefore, square iodine-channels of 10 × 10 Å are generated parallel to the crystallographic c axis.

Figure 1. Scheme showing the fabrications of the productions of SMTP-2, (a) the formation of \([\text{R}_4\cdot\text{H}_2\text{tpyp}]^{1+}\); (b) stacks of freebase porphyrins into a polycationic porphyrinwire (stick-and-ball representation from the crystal structure of SMTP-2: N blue; C black; H green); (c) a porphyrin square, as SBU for SMTP-2, held together by non-covalent interactions

Figure 2. Perspective view of the open-framework structure of SMTP-2 along the crystallography c-axis, (a) skeletal representation; (b) space-filling representations. The square iodine-channels have the dimension of 10 × 10 Å. Hydrogen and solvent molecules are omitted for clarity. (C white; N red; Cd green; I yellow)
The most intriguing feature of the SMTP-2 structure is the presence of the highly disorder guest molecules trapped in the square pores or channels. Thermogravimetric analysis reveals that the guest molecules are liberated below 100 °C, a weight loss of 4.3% consistent with the loss of all guest molecules in the channels; however, the crystal lattice is thermally stable up to 350 °C. Moreover, powder X-ray diffraction patterns showed that the porous framework was retained after the loss of solvent molecules on heating the materials at 250 °C for 8 hours. Owing to the protrusion of the “soft” iodine atoms of CdI4 groups into the square channels, the functionalized voids have a high affinity for binding mercury, lead, and other heavy metals (Figure 3, route I). Adsorption behaviors of heavy metal ions were verified by electron energy-dispersive X-ray (EDS) spectroscopy. Mercury can be detected in the EDS spectrum after immersion of the crystals in a solution containing mercury ions for 3 hours (Figure 3a). Removal of the mercury ions is also accomplished by treatment of the crystals with 1 N HCl for 3 hours at room temperature. This result shows that our SMTP-2 molecular sieve may function as environmentally benign solids and heavy metal sensors [9]. Further studies of the ability of SMTP-2 materials to remove mercury and other heavy metals from contaminated solutions are in progress.

![Figure 3](image)

Figure 3 Scheme shows two routes for the metal absorption and intercalation study in two independent sets of functionalized channels of SMTP-2. Route I, upon heating crystals at 100 °C for 3 h, iodine-cavities can be used to bind heavy metals after the loss of partial guest solvents. (a) Mercury can be observed in the EDS spectrum. Route II, hollow porphyrinwires formed by immersion of the crystals in a KOH solution provide further metalations by using electrochemical techniques. (b) Magnesium was observed in the EDS spectrum. Inset shows electronic adsorption spectrum of solids, showing the visible Q-bands that are more intense than the near-ultra-violet Soret-bands for magnesium intercalation.

Another equally unusual feature in SMTP-2 is the polycationic porphyrinwires in which may function as potent light-harvesting antenna systems [10]. Using electrochemical technique, hollow porphyrinwires provide new possibilities for partial metalation in solid state (Figure 3, route II). We have made measurements of the EDS spectrum for magnesium intercalation [11], and find that electronic adsorption spectrum of crystals of Mg/SMTP-2 exhibits split Soret-bands (354 and 446 nm) as well as much higher molar absorptivity throughout the visible Q-bands (Figure 3b). Recently, Rogers and coworkers have found a hybrid of freebase-porphyrin and metallo-porphyrin system, in which revealed an
enhanced intensity around the Q-bands at higher metallated-porphyrin [12]. As anticipated, the intriguing possibility exists that may be possible to achieve both electronic and ionic conduction when metal ions were partially occupied in the porphyrin columns. Also, these preliminary results may reveal interesting optoelectric, magnetic, catalytic, and photosensitizing properties.

Acknowledgment

This work was supported by the National Science Council of the Republic of China and the Chinese Petroleum Corporation.

References

[7] Synthesis of SMTP-2(1): A mixture of H2tpyp (0.0732 g), CdI2 (0.0619 g), I2 (0.3 g), CH3COOH (4 mL) and ethanol (4 mL) was sealed in a 23-mL Teflon-lined stainless autoclave, heating to 180 °C for 48 h, and cooled to 70 °C at 6 Kh-1. Needle-shaped purple crystals were filtered of and wash with ethanol. The yield of crystalline material was 87 % (0.1847 g) based on H2tpyp, and the synthesis was highly reproducible. Elemental analysis (%): calcad: C 29.00, N 5.41, O 3.09, H 2.63; found: C 28.21, N 5.42, O 3.40, H 2.92.
[8] X-ray data for SMTP-2(1): tetragonal, space group P42/n, a = b = 29.078(3) Å, c = 8.134(1) Å, V = 6872(1) Å3, R1 = 0.065, wR2(F2) = 0.173, GOF = 0.943. The pore solvent molecules could not be completely located in the structure analysis. However, element analysis and results of the thermogravimetric analysis are in agreement in indicating four acetic acid molecules and eight water molecules per unit cell in these channels. For SMTP-2(2), most needle-shaped crystals adhere small individual crystals and thus their diffraction qualities are poor. However, its tetragonal unit cell parameters, a = 28.598(2), b = 28.598(2), and c = 8.152(1) Å, was determined by a least-square fit of selected 344 reflections with 6 < 2θ < 40° on a BRUKER smart-CCD diffractometer. Furthermore, the homogeneity of two bulk products (SMTP-2(1) and SMTP-2(2)) was confirmed by comparison of the observed and calculated powder patterns derived from single crystal structure analysis as well as by comparison of the IR and NMR-spectra.
[9] After immersion of 5 mg of SMTP-2 in a solution containing 10 ppm lead ions for 3 h, only 10.27 % lead was sorbed by employing anodic stripping voltammetry methods.
[11] Crystals of SMTP-2 bonded into an electrode form is immersed in a polar solvent in which magnesium sulfate is dissolved. A sheet of magnesium metal serves as the anode. On shorting the two electrodes, magnesium ions intercalate SMTP-2, the charge-compensating electrons passing through the external circuit (50 V, 0.1 mA).