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Formation of a Thermally Stable, Porous Coordination Network via a Crystalline-to-Amorphous-to-Crystalline Phase Transition

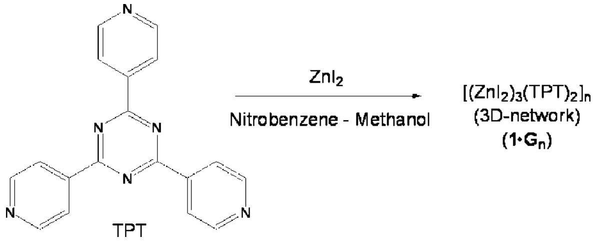
Kazuaki Ohara,[†] Javier Martí-Rujas,[†] Tsuyoshi Haneda,[†] Masaki Kawano,[*,†] Daisuke Hashizume,[‡]
Fujio Izumi,[§] and Makoto Fujita[*,†]

Department of Applied Chemistry, School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku,
Tokyo 113-8656, Japan, Advanced Technology Support Division, RIKEN, Hirosawa, Wako, Saitama 351-0198, Japan,
and Quantum Beam Center, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

Received January 22, 2009; E-mail: mkawano@appchem.t.u-tokyo.ac.jp; mfujita@appchem.t.u-tokyo.ac.jp

The chemistry of porous coordination networks has undergone explosive growth in the past decade,[1] mainly because its advantage over zeolites and related materials that detailed structure analysis can be done by the most reliable structure determination method, single-crystal X-ray diffraction.[2,3] This powerful method is, however, limited to single crystals of network complexes prepared by slow crystallization methods, typically on a small scale at room temperature in excess solvent. As a result, the crystals often include large quantities of solvent and do not have thermal stabilities comparable to those of zeolites.[4] Stable structures often appear via thermal phase transitions, and the new structures can be analyzed by powder X-ray diffraction (PXRD) analysis;[5,6] however, detailed structural information is usually difficult to obtain. In this paper, we report that a thermally stable coordination network is obtained after a crystalline-to-amorphous-to-crystalline phase transition. After the solid-state phase transition, the resultant structure is remarkably uniform and was successfully solved by ab initio PXRD. The new crystalline phase is porous and capable of reabsorbing large guest molecules. The new porous network is remarkably robust and thermally stable (no decomposition up to 673 K).[7]

The porous network **1** was prepared by the "instant synthesis" method[8] from tris(4-pyridyl)triazine (TPT) and ZnI_2. A fine, microcrystalline powder of the network $[(\mathrm{ZnI_2})_3(\mathrm{TPT})_2\cdot 5.5(\mathbf{G})]_n$ ($\mathbf{1}\cdot\mathbf{G}_{5.5}$, where **G** = nitrobenzene)[2f] was immediately and selectively obtained by rapid mixing of ZnI_2 (0.24 mmol) with TPT (0.16 mmol) in an 8:1 nitrobenzene/methanol solution (36 mL) solution. PXRD analysis agreed well with the simulated pattern generated from the X-ray crystal structure of the same complex, which had been previously prepared by slow diffusion of a layered solution.[9]



Upon heating network **1** from room temperature to 673 K, we observed a crystalline-to-amorphous-to-crystalline phase transition of **1** by PXRD. The initial crystalline phase (phase I) is stable from 300 to 473 K but changes to an amorphous phase (phase II) at 473 K. Further heating caused a new crystalline phase (phase III) to appear at 573 K (Figure 1). The colorless crystals of phases I and II turned light-yellow in phase III. Thermogravimetric analysis−differential scanning calorimetry (TG−DSC) experiments showed that the enclathrated nitrobenzenes are gradually lost (300 to 473 K) and that the framework is stable up to ~673 K.[9] At 723 K, crystallinity was lost, and new, sharp diffraction peaks corresponding to the formation of ZnO appeared.[10]

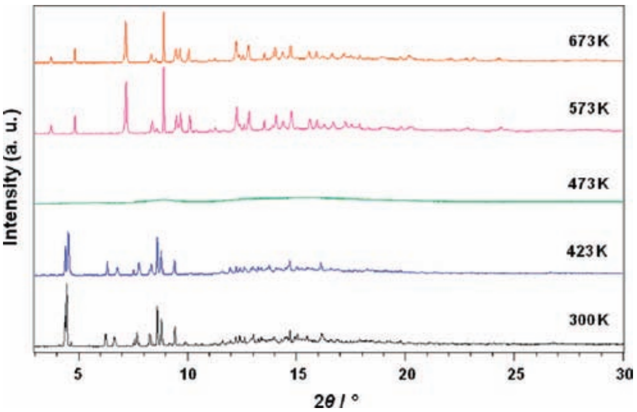


Figure 1. PXRD patterns of **1** recorded at various temperatures.

Crystalline phase III is highly uniform, and the structure of phase III was determined directly from PXRD data.[11,12] In phase III, two molecules of TPT are connected together through two ZnI_2, forming a series of "saddle-type" structures running along the *b* axis, yielding a one-dimensional chain (Figure 2b,c). Figure 3 shows the PXRD pattern from the final Rietveld refinement of phase III. Adjacent chains are held together by intermolecular $\pi-\pi$ interactions between stacked pyridyl and triazine rings (3.608 Å). Such interactions are responsible for the color change from colorless (phases I and II) to light-yellow (phase III). The stacking of individual chains along the crystallographic *c* axis gives rise to the formation of noninterpenetrated one-dimensional channels (Figure 2b,d) with pore windows of ~6.2 × 8.5 Å and pore dimensions of ~8.3 × 10.5 Å.

Phase I contains two interpenetrated networks (Figure 2a), whereas there is only one network in phase III. Thus, the formation of the phase III structure necessitated a major transformation in molecular connectivity. Such a drastic reorganization (from an interpenetrated to a noninterpenetrated structure) may be the cause of the amorphous phase (phase II) at very high temperatures (423−523 K).

Although phase II is an amorphous state, some structural memory of crystalline phase I remains. In a control experiment, an amorphous solid was prepared by grinding a mixture of TPT and

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[†] The University of Tokyo.
[‡] RIKEN.
[§] National Institute for Material Science.

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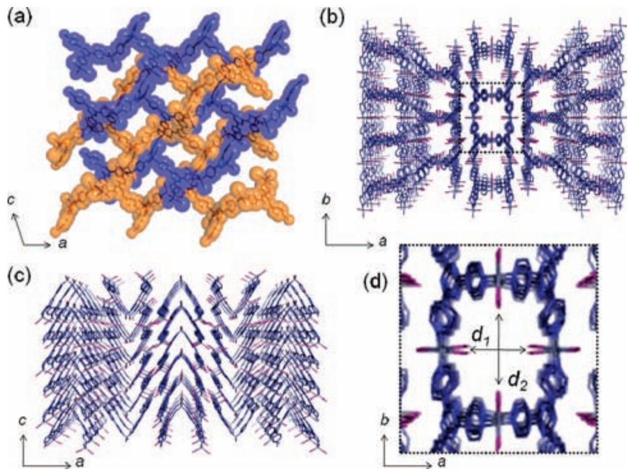

Figure 2. (a) Crystal structure of **1** (phase I) showing the interpenetration of two networks[2f] (blue and orange). (b) Noninterpenetrated structure of phase III viewed along the pore direction (crystallographic *c* axis). (c) View of phase III along the *b* axis, showing the "saddle-type" structure. (d) Dimensions of the pore windows (d_1 = 6.2 Å and d_2 = 8.5 Å).

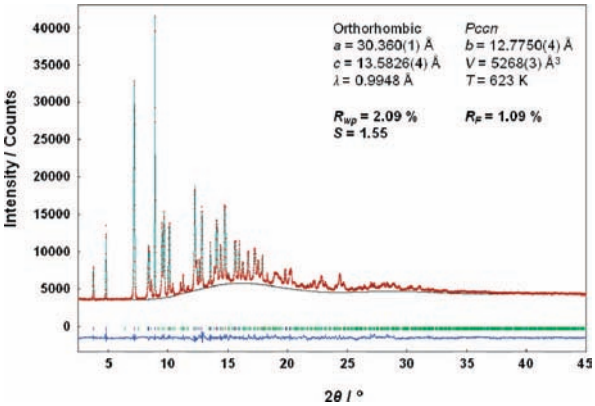

Figure 3. Experimental (red), calculated (pale-blue), and difference (dark-blue) PXRD profiles from the final Rietveld refinement of phase III.

ZnI_2. However, the ground solid mixture did not generate phase III at 573 K. It is likely that the structural preorganization of crystalline phase I is essential for the formation of the phase III structure and that the structural memory of phase I persists in amorphous phase II.

Phase III contains no guest molecules but maintains porosity and can reabsorb new guest molecules. When phase III was immersed in nitrobenzene for 30 min at room temperature, bubbles escaping from the solid (most likely containing entrapped air) were observed. The sample was removed from nitrobenzene, filtered, and dried. The synchrotron PXRD clearly indicated guest inclusion (Figure S10), and elemental analysis and TG−DSC data confirmed that one nitrobenzene was included to give a new coordination network $[(ZnI_2)_3(TPT)_2 \cdot x(\mathbf{G})]_n$ with $x = 1$ ($\mathbf{1 \cdot G}$). A complete structure determination carried out using PXRD[9] showed that the included nitrobenzene molecule does not cause any significant structural change in the framework and that the initial network topology remains unaltered. When $\mathbf{1 \cdot G}$ was heated to 573 K, the nitrobenzene molecule was released and phase III returns.[9] The porous phase III can accommodate other guest molecules, such as I_2.[13]

In summary, a coordination network prepared by simple "instant synthesis"[8] was transformed into a thermally stable, robust porous network after a crystalline-to-amorphous-to-crystalline phase transition. We believe that this method can be applied to other coordination networks and can give rise to new molecular solids with interesting physicochemical properties that otherwise cannot be obtained directly using traditional synthetic methods.

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Supporting Information Available: Experimental details, elemental analysis and TG−DSC results, and crystallographic details (CIF; also see CCDC entries 717391 and 717392). This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) For the ab initio PXRD structure solution for **1**, see: Kawano, M.; Haneda, T.; Hashizume, D.; Izumi, F.; Fujita, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 1269–1271. Single-crystal X-ray diffraction data for **1** is given in ref 2f.

(9) See the Supporting Information.

(10) Liu, B.; Shioyama, H.; Akita, T.; Xu, Q. *J. Am. Chem. Soc.* **2008**, *130*, 5390–5391. Also see Figure S5 in the Supporting Information, which shows PXRD data for phase III measured at 723 K that indicates the presence of ZnO.

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(12) A high-quality PXRD pattern of phase III was recorded at 623 K in transmission mode (0.3 mm capillary; synchrotron radiation, $\lambda = 0.9948$ Å; 2θ range, 2−70°; step size, 0.01°; data collection time, 20 min) on a diffractometer equipped with a blue-IP detector at the SPring-8 BL19B2 beam line.

(13) The crystal structure of phase III containing I_2 as an included guest was successfully determined by PXRD and will be reported elsewhere.

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