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Porous Networks

A Selective Instant Synthesis of a Coordination Network and Its Ab Initio Powder Structure Determination**

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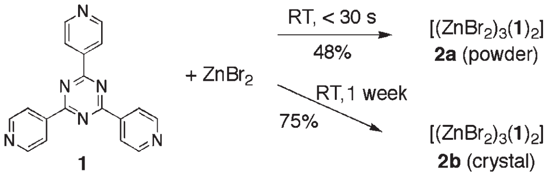
Porous coordination networks have attracted considerable attention as a new class of materials because of the unique physical properties associated with their flexible frameworks, which allow them to be used in the fields of separation, catalysis, magnetism, gas uptake, etc.[1] These coordination networks are formed under either thermodynamic or kinetic control, depending on the complexation rate constant. In general, a thermodynamically controlled product formed by slow complexation can be well characterized by single-crystal X-ray diffraction analysis, whereas the structure of a kinetic product formed instantly as microcrystals can seldom be solved by this method. Herein we report the preparation of the kinetically controlled porous flexible network $[(\mathrm{ZnBr}_2)_3(\mathbf{1})_2]\cdot 5\,\mathrm{C_6H_5NO_2}\cdot\mathrm{H_2O}$ (**2a**) by instant complexation of ZnBr_2 with 2,4,6-tris(4-pyridyl)triazine (**1**; Scheme 1) and the determination of its ab initio structure by synchrotron powder X-ray diffraction (PXRD).[2,3] To the best of our knowledge, there is no report of the ab initio PXRD structural determination of a flexible porous coordination network having a large channel. Interestingly, slow complexation by a layer-diffusion method produces a totally different thermodynamic network in high yield (Scheme 1). We also demonstrate that the instant synthesis method employed here[4] exclusively produces a fine powder of the kinetically controlled porous network suitable for ab initio powder structural determination.[5]



Scheme 1. Selective syntheses of porous coordination networks.

Addition of a methanol solution (8 mL) of ZnBr_2 (0.24 mmol) to a vigorously stirred nitrobenzene/methanol solution (32/4 mL) of **1** (0.16 mmol) in two portions immediately produced a uniform microcrystalline powder of **2a** (48% yield). The SEM images (Figure 1a) of this powder show that the microcrystals of **2a** have a relatively uniform size ($< 10\ \mu\mathrm{m}$) and identical morphology. The powder sample was dried overnight under vacuum and then sealed in a capillary. Powder X-ray diffraction data were collected at 300 K on a diffractometer equipped with a blue IP detector at SPring-8 (BL19B2 beam line). The structure determination of **2a** was carried out directly with the PXRD data using the simulated annealing method in the program DASH, followed by Rietveld refinement using the program RIETAN-FP to refine the position of each atom with bond-length restraints. The good agreement between the calculated and experimental PXRD patterns in the final Rietveld refinement (Figure 1b) clearly indicates that the framework structure of **2a** is exclusively determined and only a single phase is present in the powder sample. The crystal structure of **2a** (Figure 2) is isostructural with that of $[(\mathrm{ZnI}_2)_3(\mathbf{1})_2]\cdot 5.5\,\mathrm{C_6H_5NO_2}$,[6,7] which has a large flexible channel capable of reversible guest exchange in the crystalline state.[8]

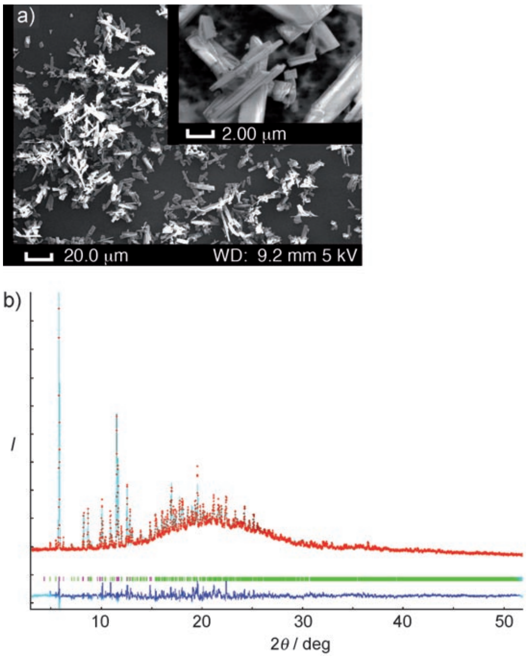


Figure 1. a) SEM images of the network complex **2a**. b) Experimental (red), calculated (pale blue), and difference (dark blue) powder X-ray diffraction profiles for the final Rietveld refinement of **2a**.

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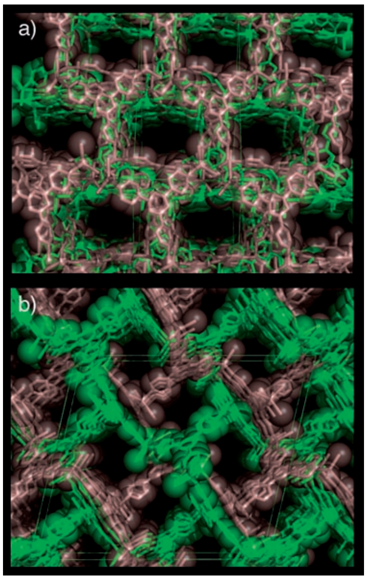

Figure 2. Crystal structures of network complex **2a**. a) View along the [101] direction. b) View along the [010] direction. The solvent molecules in the pores have been omitted.

We attempted to obtain a single crystal of **2a** suitable for single-crystal X-ray analysis by a slow layer-to-layer diffusion method with the same stoichiometries of starting reagents. Interestingly, however, after a week we obtained single crystals of the 3D network structure $[(\mathrm{ZnBr_2})_3(\mathbf{1})_2]\cdot 6\,\mathrm{C_6H_5NO_2}$ (**2b**), which has 1D channels formed by the π–π stacking of **1** (Figure 3), in 75% yield. The channels in **2b** (diameter: 25 Å) are larger than in **2a** and its simulated powder pattern is completely different from that of **2a**.[9]

The difference between the structures of **2a** and **2b** can be readily explained by considering kinetic versus thermodynamic formation of these complexes. In other words, the crystal nucleation is kinetically controlled in the instant synthesis and gives the kinetic product **2a**, whereas slow crystallization allows equilibration of the nucleated crystals and forms the thermodynamic product **2b**. This proposal is supported by the PXRD and DSC analyses of **2a** and **2b** (see the Supporting Information). The PXRD measurements show that heating **2a** and **2b** to 280 °C causes them to have identical powder diffraction patterns. The DSC curves of **2a** and **2b** show that the exothermic energy of powder **2a** (40.10 $\mathrm{kJ\,mol^{-1}}$) centered at 280 °C is about three times larger than that of **2b** (13.09 $\mathrm{kJ\,mol^{-1}}$). These facts clearly indicate that **2a** is a metastable kinetic product whereas **2b** is a thermodynamic product.

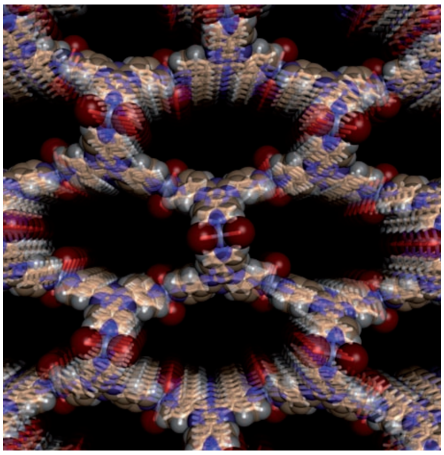

Figure 3. Crystal structure of complex **2b** in the [001] direction. The solvent molecules in the pores have been omitted.

We also investigated the effect of the solvent on the product of the instant synthesis. Ligand **1** is insoluble in methanol, and when a suspension of $\mathrm{ZnBr_2}$ and **1** was vigorously stirred in methanol instead of methanol/nitrobenzene the nonporous network complex $[(\mathrm{ZnBr_2})(\mathbf{1})]$ (**3**) was obtained. The crystal structure of **3** was successfully solved by ab initio PXRD (Figure 4), which showed it to have a 1D network structure due to π-π stacking of **1** and to contain no solvate.[10] These facts indicate that the solvent plays a crucial role in this instant synthesis as a template for the network formation.

We have also found another example of selective instant synthesis. Thus, the instant complexation of $\mathrm{ZnBr_2}$ with triphenylene and ligand **1** selectively produces a biporous network complex[11] as the kinetic product, whereas slow bilayer crystallization generates a porous 1D chain network with triphenylene stacked between molecules of ligand **1** as the thermodynamically controlled product.

In conclusion, the instant synthesis method employed here is a significant advance in the preparation and character-

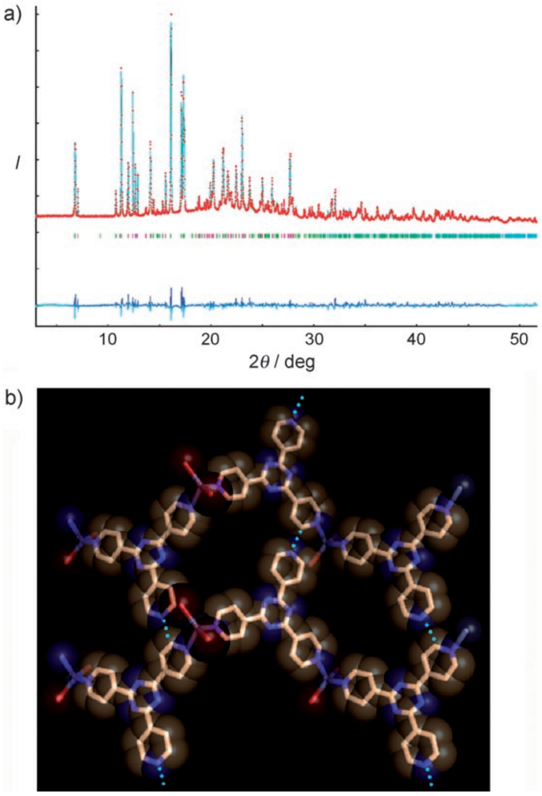

Figure 4. a) Experimental (red), calculated (pale blue), and difference (dark blue) powder X-ray diffraction profiles for the final Rietveld refinement of complex **3**. b) Crystal structure of complex **3** in the [100] direction. The dashed lines represent the hydrogen bonds.

ization of coordination networks as a large quantity of complex can be easily prepared in quite a short time (<30 s). Similarly, the product is obtained as uniform microcrystals, which means that it can easily be characterized by ab initio PXRD structural determination. Finally, the structure is kinetically controlled and is likely to be totally different to that of the thermodynamic product produced by conventional slow crystallization methods. We thus believe that this combination of instant synthesis and ab initio PXRD will lead to significant progress in coordination network chemistry.

Experimental Section

C,H,N analyses (%): **2a**: $[(ZnBr_2)_3(\mathbf{1})_2]\cdot 5\,C_6H_5NO_2\cdot H_2O$: calcd: C 40.99, H 2.66, N 12.31; found: C 40.96, H 2.83, N 12.08. **2b**: $[(ZnBr_2)_3(\mathbf{1})_2]\cdot 6\,C_6H_5NO_2$: calcd: C 42.41, H 2.67, N 12.37; found: C 42.27, H 2.75, N 12.25.

A high quality PXRD pattern of **2a** was recorded at 300 K in transmission mode [0.3 mm capillary; synchrotron radiation $\lambda = 1.29918$ Å; Blue-IP detector; 2θ range: 2–70°; step size: 0.02°; data collection time: 20 min].

The PXRD pattern of **2a** was indexed with the program DICVOL91[12] to give a monoclinic unit cell ($a = 35.2329$, $b = 14.6917$, $c = 30.9462$ Å, $\beta = 103.113°$) with excellent figures of merit ($M(18) = 11.0$ and $F(18) = 43.2$). The unit cell volume is 15601 Å^3, which is slightly smaller than that of the ZnI_2 complex $[(ZnI_2)_3(\mathbf{1})_2]\cdot 5.5\,C_6H_5NO_2$ (**4**) also prepared by instant synthesis. The space group was assigned as *C*2/*c* from the systematic absences. Unit cell and profile refinement were carried out using the Pawley method, which resulted in an excellent fit ($R_{wp} = 13.31\,\%$, Pawley $\chi^2 = 2.864$) for this unit cell and space group.

Structure determination was performed by the simulated annealing method with the program DASH.[13] The three rigid groups of $ZnBr_2$ and the two rigid groups of **1** in the asymmetric unit and $Z = 8$ for space group *C*2/*c* were input by using a constrained Z-matrix description and their molecular geometries were taken from the known crystal structure.[6] Fifty runs of 5×10^6 Monte Carlo moves each were conducted and the same excellent fits to the data for 42 out of the 50 attempts were obtained with a Profile χ^2 value of 138.13. Three nitrobenzene positions were then determined from the fixed positions of the host framework (Profile $\chi^2 = 23.28$). The best structure solution was taken as the starting structural model for Rietveld refinement.

The final Rietveld refinement of the crystal structure was performed with the program RIETAN-FP.[14] Restraints but no constraints for all bond lengths were employed to maintain the molecular geometry. Thermal temperature factors were refined isotropically and uniform values were applied to the framework and solvent atoms. $a = 35.218(2)$, $b = 14.6836(7)$, $c = 30.951(2)$ Å, $\beta = 103.036(3)°$, $R_{wp} = 4.17\,\%$ ($R_e = 1.99\,\%$), $R_p = 3.15\,\%$, $R_B = 9.08\,\%$, $R_F = 4.33\,\%$; 4900 profile points; 281 refined variables.

The diffraction data for **2b** were recorded with a Bruker APEX-II/CCD diffractometer equipped with a focusing mirror ($Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å) with a cryostat system equipped with an N_2 generator (Japan Thermal Eng. Co., Ltd.). $C_{36}H_{27}Br_3N_9O_6Zn_{1.5}$, $M_r = 1019.45$, crystal dimensions $0.3 \times 0.02 \times 0.01$ mm^3, orthorhombic, space group, *Fdd*2, $a = 49.574(6)$, $b = 50.307(6)$, $c = 6.1937(8)$ Å, $V = 15446(3)$ Å^3, $T = 80$ K, $Z = 16$, $\rho_{calcd} = 1.754$ g cm^{-3}, 8662 unique reflections out of 9564 with $I > 2\sigma(I)$, 501 parameters, $1.62 < \theta < 28.98°$, final R factors $R_1 = 0.0249$ and $wR_2 = 0.0679$.

CCDC 645603 (**2a**), 645604 (**2b**), 645605 (**3**), and 645606 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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