Kinetic Assembly of a Thermally Stable Porous Coordination Network Based on Labile CuI Units and the Visualization of I₂ Sorption
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Introduction
The advantage of porous coordination network synthesis is designability by changing metal sources and ligands. So far, to the best of our knowledge, there is no report focusing on usage of labile metal sources for selective network formation. One of the promising methods to produce unique networks with such labile metal sources is kinetic control because labile metal sources produce various species in solution. Here we first report selective syntheses of thermally stable porous coordination networks using a labile Cu₄I₄ cubane cluster and a rigid Tₐ-symmetry ligand by kinetic and thermodynamic control. We succeeded in kinetically and selectively preparing porous network crystals composed of novel CuI helical chains which can keep the crystallinity up to 673 K. It also shows chemisorption of I₂ by making a covalent bond with an iodide of part of the framework to form an I₃⁻ group. On the other hand, as a thermodynamic product, we obtained Cu₂I₂ dimer network which shows remarkably efficient physisorption of I₂.[1]

Scheme 1. Selective preparation of kinetic and thermodynamic networks 3a and 3b.

Results
On heating of the mixture of cubane cluster [Cu₄I₄(PPh₃)₄] (1) and Tₐ ligand (tetra-4-(4-pyridyl)phenyl-methane (2) in DMSO in air at 453 K, a homogenous colorless solution was obtained. By cooling of the resultant solution, two kinds of network crystals were first obtained. Because, depending on the cooling rate, the ratio of the two crystals changed, we assumed that this result is attributed to kinetic/thermodynamic effects. As we expected, rapid cooling (~20 K min⁻¹) exclusively produced yellow needle crystals, {[(CuI)₂(2)]•solvent}ₙ (3a), in 99% yield. On the other hand, slow cooling (~3 K min⁻¹) produced orange block crystals, {[(Cu₂I₂)(2)]•solvent}ₙ (3b), in 95% yield.

The crystal structure of 3a determined by synchrotron radiation at AR-NW2A revealed that along the c axis CuI helical chains bridged by ligand 2 form a non-interpenetrated porous network (Figure 1a,c). The network 3a has one-dimensional channels with the pore window of 5.8 × 5.5 Å in diameter and 35% void space against the unit cell volume. On the other hand, the crystal structure of 3b determined by synchrotron radiation at AR-NW2A revealed that 3b is a quadruply interpenetrated network consisting of Cu₂I₂ dimer units and ligand 2 (Figure 1b,d). The network 3b has one-dimensional channels with the pore window of 4.0 × 3.9 Å in diameter and 22% void space.

Surprisingly, these networks show unique sorption behavior of I₂. The crystal structure analysis revealed that a pore of 3a encapsulates I₂ by chemisorption, on the other hand, a pore of 3b encapsulate I₂ by physisorption. Interestingly, the physisorbed I₂ retained by 440 K due to exact fit of I₂ to the channel.

In summary, we successfully demonstrated kinetic control of network formation using even labile metal sources that show unique I₂ encapsulation. We believe that kinetic control can be one of useful synthetic strategies to create a new class of porous materials.

Reference
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