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Kinetic Assembly of a Thermally Stable Porous Coordination Network Based on Labile CuI Units and the Visualization of I_2 Sorption

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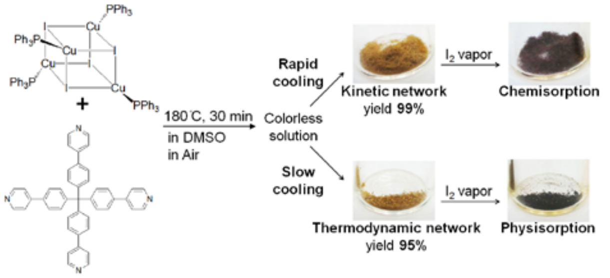
Introduction

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 Cu_4I_4 cubane cluster and a rigid T_d-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 I_2 by making a covalent bond with an iodide of part of the framework to form an I_3^- group. On the other hand, as a thermodynamic product, we obtained Cu_2I_2 dimer network which shows remarkably efficient physisorption of I_2.[1]



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

Results

On heating of the mixture of cubane cluster $[Cu_4I_4(PPh_3)_4]$ (**1**) and T_d 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 $\mathrm{Kmin^{-1}}$) exclusively produced yellow needle crystals, $\{[(CuI)_2(\mathbf{2})]\bullet solvent\}_n$ (**3a**), in 99% yield. On the other hand, slow cooling (~3 $\mathrm{Kmin^{-1}}$) produced orange block crystals, $\{[(Cu_2I_2)(\mathbf{2})]\bullet solvent\}_n$ (**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 Cu_2I_2 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 I_2. The crystal structure analysis revealed that a pore of **3a** encapsulated I_2 by chemisorption, on the other hand, a pore of **3b** encapsulate I_2 by physisorption. Interestingly, the physisorbed I_2 retained by 440 K due to exact fit of I_2 to the channel.

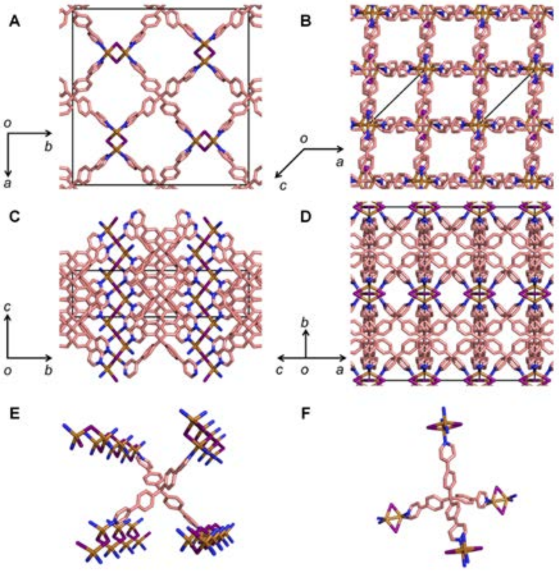


Figure 1. The X-ray crystal structure of **3a** and **3b**.

In summary, we successfully demonstrated kinetic control of network formation using even labile metal sources that show unique I_2 encapsulation. We believe that kinetic control can be one of useful synthetic strategies to create a new class of porous materials.

Reference

[1] H. Kitagawa *et al.*, *submitted.*

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