

# Unique I<sub>2</sub> Sorption to a Kinetic Assembling Porous Coordination Network

Hakuba Kitagawa, Hiroyoshi Ohtsu, and Masaki Kawano\*

The Division of Advanced Materials Science

Pohang University of Science and Technology (POSTECH)

77 Cheongam-Ro, Nam-Gu, Pohang, Gyeongbuk, 790-784, Korea

## 1 Introduction

Kinetic assembly produces a new class of porous coordination networks because it can generate interactive pores. We investigated kinetic/thermodynamic assembly of porous coordination networks using labile CuI units; by changing cooling ratio of a hot DMSO solution of Cu<sub>4</sub>L<sub>4</sub>(PPh<sub>3</sub>)<sub>4</sub> and TPPM, we selectively prepared two porous coordination networks. The kinetic network **1** from rapid cooling of the solution consists of CuI helical chain structure with interactive iodide on the pore surface. On the other hand, the thermodynamic network **2** from slow cooling of the solution consists of CuI dimer structure with a small pore. Herein, we report unique I<sub>2</sub> encapsulation into the pores of these networks to demonstrate unique properties of the kinetic network. Nowadays, I<sub>2</sub> sorption to porous compounds has significant meaning, for example, as nuclear fission product absorber.

## 2 Experiment

I<sub>2</sub> encapsulation to **1**, desolvated **1** (**1'**), **2** and desolvated **2** (**2'**) was performed by vapor I<sub>2</sub> diffusion; A vial (5 mL) containing the crystals of the network (ca. 5 mg) and a vial (5 mL) containing the solid iodine (ca. 15 mg) were put in a bigger vial (50 mL). After the vial was closed and kept for 1 d. The black crystals that suggest iodine encapsulation were collected. The inclusion of iodine was confirmed by elemental analysis, X-ray analysis, weight increase and TG.

## 3 Results and Discussion

The crystal structure analysis of the desolvated crystal of **1'** exposed on I<sub>2</sub> vapor for 1 d resulted in (**1'**·0.96I<sub>2</sub>)<sub>n</sub>. The diffraction became better (the maximum resolution of X-ray diffraction changed from 0.91 Å to 0.75 Å) than before I<sub>2</sub> encapsulation. The crystal structure analysis revealed that a pore of solvated isomer **1** and desolvated isomer **1'** encapsulated I<sub>2</sub> by chemisorption through the formation of I<sub>3</sub><sup>-</sup> group on the bridging iodides with reasonable geometry of I<sub>3</sub><sup>-</sup> anion (Fig. 1a).

On the other hand, desolvated network **2'** shows physisorption of I<sub>2</sub>: the desolvated crystals of isomer **2'** turned black within 5 min, resulting in (**2'**·2.125I<sub>2</sub>)<sub>n</sub>. The crystal structure analysis revealed that I<sub>2</sub> molecules are arranged linearly along 1D channel and highly disordered (Figure 1c, d). Moreover, compared with (**1'**·0.96I<sub>2</sub>)<sub>n</sub>, (**2'**·2.125I<sub>2</sub>)<sub>n</sub> shows remarkable affinity of I<sub>2</sub>: I<sub>2</sub> desorption temperature in TG measurement, 380 K for

(**1'**·0.96I<sub>2</sub>)<sub>n</sub>; 450 K for (**2'**·2.125I<sub>2</sub>)<sub>n</sub>. The large desorption temperature difference can be explained by steric repulsion between adsorbed I<sub>2</sub> molecules and the framework. Because the crystal structures of desolvated isomer **1'** and **2'** at 80 K show severe disorder of phenyl and pyridyl rings, at high temperature these rings can rotate freely. Network (**2'**·2.125I<sub>2</sub>)<sub>n</sub> has no steric hindrance with encapsulated I<sub>2</sub> molecules. However, in the case of (**1'**·0.96I<sub>2</sub>)<sub>n</sub> severe collision can occur between adsorbed I<sub>2</sub> molecules and the pyridine rings (Fig. 1b). Therefore, (**1'**·0.96I<sub>2</sub>)<sub>n</sub> shows smooth desorption of I<sub>2</sub> over 380 K even chemisorption. Furthermore, because the pore window of the isomer **2'** is exactly fit for iodine, the physisorbed I<sub>2</sub> can be retained in the pore up to 450 K.

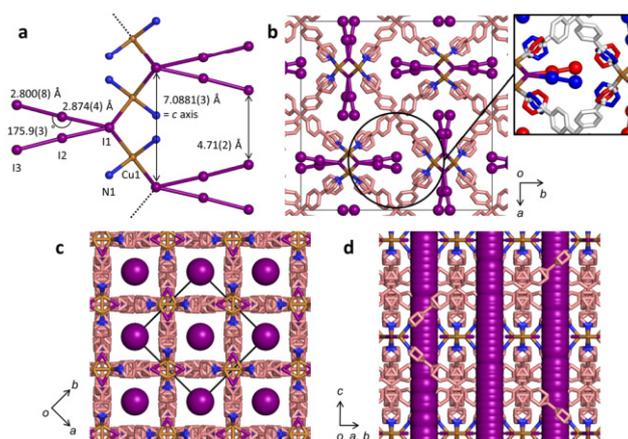


Fig. 1: Structures of (a), (b) (**1'**·0.96I<sub>2</sub>)<sub>n</sub> and (c), (d) (**2'**·2.125I<sub>2</sub>)<sub>n</sub>.

I<sub>2</sub> adsorption was further tested using I<sub>2</sub> solution. When the crystals of **1'** or **2'** were immersed, the I<sub>2</sub> solution color was gradually faded because of encapsulation. In fact, the kinetic analyses of UV-Vis spectroscopy indicate the chemisorption of **1'** and physisorption of **2'**.

In summary, the kinetic network **1** shows unique I<sub>2</sub> adsorption based on the interactive pore: I<sub>2</sub> is trapped by chemisorption through I<sub>3</sub><sup>-</sup> formation. However, the chemisorbed I<sub>2</sub> readily desorbed over 380 K due to dynamic motion of the framework. On the other hand, thermodynamic network **2** shows physisorption of I<sub>2</sub>. The physisorbed I<sub>2</sub> retained by 450 K due to exact fit of I<sub>2</sub>.

## References

[1] H. Kitagawa *et al.*, *Angew. Chem. Int. Ed.* **52**, 12395 (2013).

\*mkawano@postech.ac.kr