AR-NW2A/2010G039

Crystal surface mediated structure transformation of a kinetic framework composed of multi-interactive ligand TPHAP and Co(II)

Yumi Yakiyama, Akira Ueda, Yasushi Morita, and Masaki Kawano*
Division of Advanced Materials Science, Pohang University of Science and Technology (POSTECH), San-31, Hyoja-dong, Nam-gu, Pohang, Gyeongbuk 790-784, South Korea

Introduction

In the biological systems, multi-point weak intermolecular interactions play a crucial role in maintaining life activity by stabilizing key metastable intermediates. If we can control intermediate phases, a variety of active networks can be created. Such study focusing kinetic system is not trivial at all because obtaining structural information of kinetic species is still very difficult. One of approaches to preparing a metastable dynamic network is to use a ligand having multi-recognition sites. However, there are a few ligands having multi-recognition sites. Here we designed and synthesized a multi-interactive ligand, 2,5,8-tri(4´-pyridyl)-1,3,4,6,7,9-hexaazaphenalene (TPHAP, Fig. 1), on gram scale by a simple one-pot reaction. Using exactly same starting materials, we succeeded in preparing several networks by changing temperatures or complexation speed. Interestingly, the kinetic network crystal showed a structure transformation on the crystal surface. X-ray analysis unambiguously revealed the transformation mechanism.

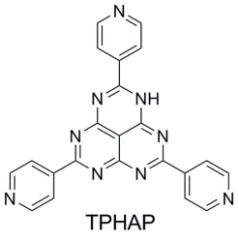

Figure 1. The molecular structure of TPHAP.

Results

The new ligand TPHAP can be obtained as a potassium salt ($K^+ \cdot TPHAP^-$) from commercially available reagents in a moderate yield. Using $K^+ \cdot TPHAP^-$ and Co(II) ions, we succeeded in trapping a crystal of a kinetic network, $[Co(TPHAP^-)_2(CH_3OH)_2(H_2O)] \cdot 3C_6H_5NO_2 \cdot HNO_3 \cdot 5H_2O$ (**TPHAP-Co$_{Kin}$**) and clarifying a crystal structure by synchrotron X-ray diffraction (Fig. 2). Within a few days after the formation of **TPHAP-Co$_{Kin}$**, **TPHAP-Co$_{Kin}$** crystal transformed to more thermally stable network of $[Co(NO_3^-)(TPHAP^-)(CH_3OH)_2] \cdot CH_3OH \cdot C_6H_5NO_2 \cdot 2HNO_3 \cdot H_2O$ (**TPHAP-Co$_{Therm}$-1**) with keeping of the same structural feature observed in **TPHAP-Co$_{Kin}$** (Fig. 2).

In order to clarify the mechanism of the transformation, we investigated the crystal face of **TPHAP-Co$_{Kin}$**. As the result, it is indicated that the structure transformation is initiated by the attack of NO_3^- anion to the Co(II) center from less-bulky position in the kinetic network. It is noteworthy that during the network reorganization, weak intermolecular interactions associated with $TPHAP^-$ play a crucial role in stabilization of the systems. Such a structure transformation of open-frame network on the crystal surface triggered by the ligand exchange has been reported rarely.

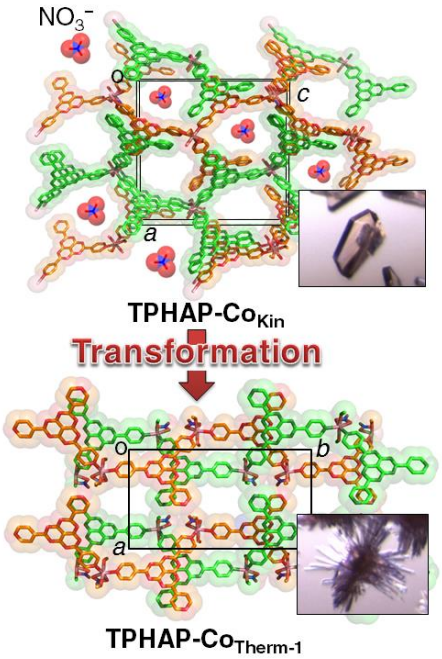

Figure 2. The surface mediated structure transformation from **TPHAP-Co$_{Kin}$** to **TPHAP-Co$_{Therm}$-1**.

Furthermore, we found another network, $[Co(NO_3^-)(TPHAP^-)(CH_3OH)_2] \cdot CH_3OH \cdot 2.5(C_6H_5NO_2) \cdot H_2O$ (**TPHAP-Co$_{Therm}$-2**) by higher temperature crystallization. It was revealed from *in-situ* PXRD analysis that **TPHAP-Co$_{Therm}$-1** crystals were generated only through the kinetic network of **TPHAP-Co$_{Kin}$** and **TPHAP-Co$_{Therm}$-2** was not generated through **TPHAP-Co$_{Kin}$** nor **TPHAP-Co$_{Therm}$-1**.

In conclusion, we developed the gram-scale one-pot synthesis of multi-interactive anionic ligand, $TPHAP^-$, which can afford a variety of network structures via effective interaction sites. The kinetic network is converted to a more stable network by the unique crystal surface mediated transformation.

Reference

[1] Y. Yakiyama *et al.*, *Chem. Commun.* **48**, 10651 (2012).
*mkawano@postech.ac.kr