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Single Crystalline Molecular Flasks: Chemical Transformation with Bulky Reagents in the Pores of Porous Coordination Networks

Takehide Kawamichi, Tomoki Kodama, Masaki Kawano, †,* and Makoto Fujita*
Department of Applied Chemistry, School of Engineering, The University of Tokyo, and JST, CREST, 7-3-1 Hongo, Bunkyo-ku, Tokyo, 113-8656, Japan

Introduction

In situ observation of solid-state reactions by X-rays provides direct information on reaction processes and final structures. Crystallographic analysis of reactions involving bulky reagents within crystals are also limited due to restricted diffusion in close-packed crystals and the often concurrent crystal degradation. Recently, we reported a robust coordination network complex possessing pores.[1] The pore channels facilitate increased mobility and rapid diffusion of included guest molecules. Large organic molecules can readily enter into the pores via guest exchange. In this sense, the pore interior is a pseudo-solution state where chemical reactions may proceed as in a solution, yet can be directly analyzed by crystallography. Here, we show that single-crystal-to-single-crystal chemical reactions with large, common reagents proceed quite smoothly inside the pores of the network. Taking advantage of the network's robust crystallinity, we succeeded in the acylation and ureidation of aromatic amines and imine formation from aromatic aldehydes within a single crystal. The pores of the network complexes thus serve as "single crystalline molecular flasks".[2] In related studies, we have reported the preliminary results of the diffusion of aldehydes into the pores of porous networks to form imine.[3]

Results

The porous complex **3a** was obtained as single crystals by the reaction of triazine ligand **1** and ZnI_2 in the presence of 2-aminotriphenylene (**2a**).[1b] The network structure of **3a** features the presence of two distinct, large pores (A and B) delineated by pillars consisting of alternatively stacked ligand **1** and triphenylene. The amino groups on the embedded triphenylene molecules are pointed into pore A and ready to react with various reagents.

When crystals of **3a** were dipped into an acetic anhydride/cyclohexane solution, the crystal turned from red to yellow within 1 d. Diffraction study revealed that crystallinity was maintained even after 100% conversion and crystallographic analysis revealed newly formed amide **4a** (Figure 1). Single crystal microscopic FT-IR spectra of complex **3a** and $\{[(ZnI_2)_3(\mathbf{1})_2(\mathbf{4a})]\bullet(C_4H_6O_3)_x\}_n$ (**5a**) also indicated the quantitative conversion from **3a** to **5a**.

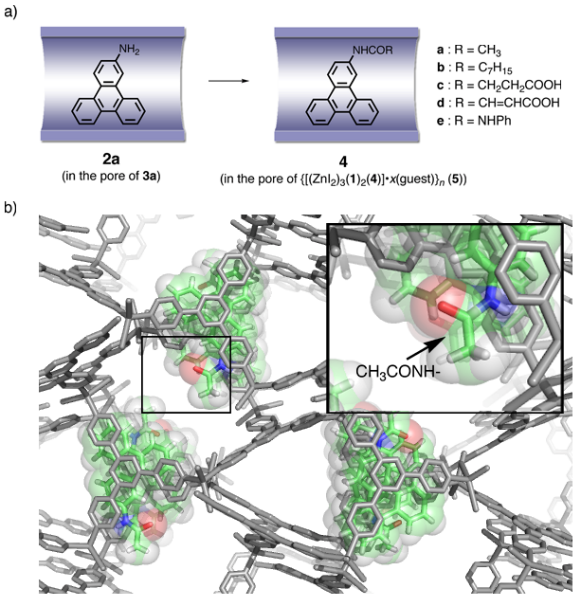

Figure 1 a) Acylation reactions of **2a** in the pore of crystalline **3a**. b) $[(ZnI_2)_3(\mathbf{1})_2(\mathbf{3a})]$ (**5a**).

The reactions within the pores provide a facile method for post-modifications of the pore interior. Carboxylic acid groups (COOH) can strongly bind metal ions and are very difficult to be insert unprotected within porous network complexes. When 2-triphenylenecarboxylic acid (**2c**) was employed instead of **2a**, no porous networks were obtained because the carboxylic groups sequester the Zn(II) ions and prevent network formation. Exposing complex **3a** to succinic anhydride, however, converts the amines to amides and deftly lines the pore interior with free carboxylic acids. Similarly, treatment with maleic anhydride places –CH=CHCOOH groups in the pores.

In situ preparation and in situ observation of reaction intermediates or labile molecules will be achieved by utilizing the "single crystalline molecular flasks".

References

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*mkawano@postech.ac.kr
† Present address: POSTECH, Pohang, Korea