

Watching Chemical Reactions in Crystalline Molecular Flasks

High-flux monochromatized synchrotron X-rays from beamline AR-NW2A have been successfully used to visualize chemical reactions inside a particular pore of a coordination network - inside a *crystalline molecular flask*. The solution-like pore enables bulky reagents to approach reaction sites and perform condensation reactions without deterioration of crystallinity, allowing in situ chemical crystallography. The reactions within the pores provide a facile method for post-modifications of the pore interior.

In situ crystallographic observation of solid-state reactions provides direct information on reaction processes and structures [1]. Recently, we reported the observation of a robust coordination network complex possessing large pores [2, 3]. The pore channels facilitate the increased mobility and rapid diffusion of guest molecules while retaining crystallinity. 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 smoothly inside the pores of the network [4]. Taking advantage of the network's robust crystallinity, we succeeded in observing several condensation reactions for an amine group within a single crystal. The pores of the network complexes thus serve as "single crystalline molecular flasks". Synchrotron X-rays from beamline AR-NW2A played a crucial role in determining the crystal structures, because small crystals are essential for successful observations of in situ reactions with no deterioration of crystallinity.

The porous complex **3a** (see Fig. 1) was obtained as single crystals by the reaction of triazine ligand **1** and Zn₂ in the presence of 2-aminotriphenylene (**2a**) [2b].

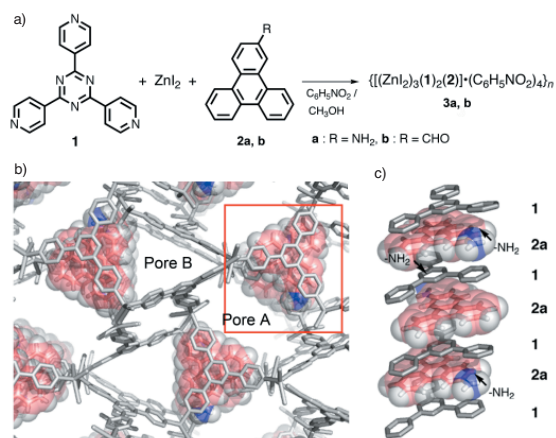


Figure 1 a) Preparation of 3D porous networks **3a**, **b**. c) Crystal structure of porous network **3a** (b: View along direction of pores. c: perpendicular view to direction of pores, showing the columnar stacking of **1** and **2a** in the network **3a**).

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 are ready to react with various reagents (Fig. 1).

When crystals of **3a** were dipped into an acetic anhydride/ cyclohexane solution, the crystal turned from red to yellow within 3 hours. The X-ray diffraction study revealed that crystallinity was maintained even after 100% conversion, and crystallographic analysis revealed newly formed amide **4a** (Fig. 2). The robust nature of the crystal network tolerates the rapid diffusion of acetic anhydride into the pore, and the complete conversion of **2a** to amide **4a**. The pores also accommodate the larger octanoic anhydride and, after diffusion into the pore, octanoic amide is obtained. Octanoic acid is formed as a by-product, and exits the crystals. Surprisingly, the pores also allow diffusion of the bulky phenyl isocyanate and maleic anhydride, which quantitatively converted the included **2a** into phenyl urea **5a** and **6a**, respectively (see Fig. 2). These results indicate that even large molecules have considerable mobility in the pore.

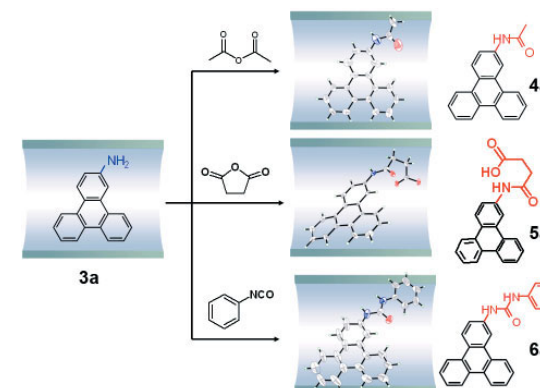


Figure 2 In situ reactions in the molecular flask.

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 insert into 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 lines the pore interior with free carboxylic acids. Similarly, treatment with maleic anhydride places $-\text{CH}=\text{CHCOOH}$ groups in the pores.

After establishing that relatively mild reagents (anhydrides and an isocyanate) easily diffuse into the pores without loss of crystallinity, we also examined whether the network can withstand treatment with free amines. The aldehyde functionalized network **3b** was prepared from 2-formyltriphenylene (**2b**). After dipping crystals of **3b** into an aniline/ethyl acetate solution, crystallinity was maintained and 100% conversion to imine was observed. Likewise 3-aminobenzoic acid also reacted to

give imine. The crystal networks of **3a** and **3b** are quite robust and tolerate post-modification with both basic NH₂ and acidic COOH groups.

REFERENCES

- [1] M. Kawano, Y. Kobayashi, T. Ozeki and M. Fujita, *J. Am. Chem. Soc.*, **128** (2006) 6558.
- [2] a) O. Ohmori, M. Kawano and M. Fujita, *Angew. Chem.*, **117** (2005) 1998; *Angew. Chem. Int. Ed.*, **44** (2005) 1962; b) M. Kawano, T. Kawamichi, T. Haneda, T. Kojima and M. Fujita, *J. Am. Chem. Soc.*, **129** (2007) 15418.
- [3] a) S. Batten, and R. Robson, *Angew. Chem.*, **110** (1998) 1558; *Angew. Chem. Int. Ed.*, **37** (1998) 1460; b) S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem.*, **116** (2004) 2388; *Angew. Chem. Int. Ed.* **43** (2004) 2334; c) M. Kawano and M. Fujita, *Coord. Chem. Rev.*, **251** (2007) 2592.
- [4] T. Haneda, M. Kawano, T. Kawamichi and M. Fujita, *J. Am. Chem. Soc.*, **130** (2008) 1578.

BEAMLINE

AR-NW2A

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