

Direct Observation of the Labile Imine Formation through Single-crystal-to-single-crystal Reactions in the Pores of a Porous Coordination Network

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Introduction

In-situ preparation of labile species in a single crystalline state is a unique and effective method for the crystallographic observation of unstable molecules that are difficult to isolate as crystals due to their instability. There are, however, several problems in this method: (1) the reactivity of the substrates is considerably reduced in a crystalline state; (2) bulky reagents cannot enter into the crystals; (3) in most cases, crystallinity dramatically decreases as the solid-state reaction proceeds. Therefore, successful examples are extremely limited. Here we utilize the pores of a porous coordination network. Thanks to the pseudo-solution state in the pores, even bulky substrates can easily interpenetrate into the crystals without reducing single crystallinity. We examined the reaction of acetaldehyde with amines to form acetaldehyde imines that are, normally, easily hydrolyzed or isomerized into enamines. The aromatic amines were incorporated in the columnar array of aromatic ligands of an as-synthesized porous network complex. The amino group oriented toward the pore was allowed to react with acetaldehyde that was introduced into the pore of a crystal by diffusion. We found that unstable imines were efficiently formed in the pore in a single-crystal-to-single-crystal fashion.¹ We also found the dynamic rotor-like motion of the amine substrates during the reaction.

Results

A porous coordination network used as a platform for the single-crystal-to-single-crystal reaction was prepared by treating tris(4-pyridyl)triazine (**1**) and 1-aminotriphenylene (**2a**) with ZnI_2 in a nitrobenzene-methanol gradient solution (Figure 1a). Red single crystals with a composition of $[(ZnI_2)_3(1)_2(2a)]_n$ were isolated in a good yield. In this network complex, ligand **1** and amine **2a** were alternatively and infinitely stacked. Along the infinite aromatic stacking, there are two kinds of 1D-pores (**A** and **B**) with different shapes and chemical properties. The amino groups of **2a** are located in pore **A** but not in pore **B** (Figure 1c).

Unstable imine **3a** was produced in a single-crystal-to-single-crystal fashion by the condensation of the amino group of **2a** with acetaldehyde. When needle-shaped single crystals of $[(ZnI_2)_3(1)_2(2a)]_n$ were immersed in a nitrobenzene solution of acetaldehyde (20 wt%) at room temperature, the aldehyde diffused into the pores and the red crystals gradually turned yellow over 4 hours. After isolation of the crystals, the complete conversion to imine

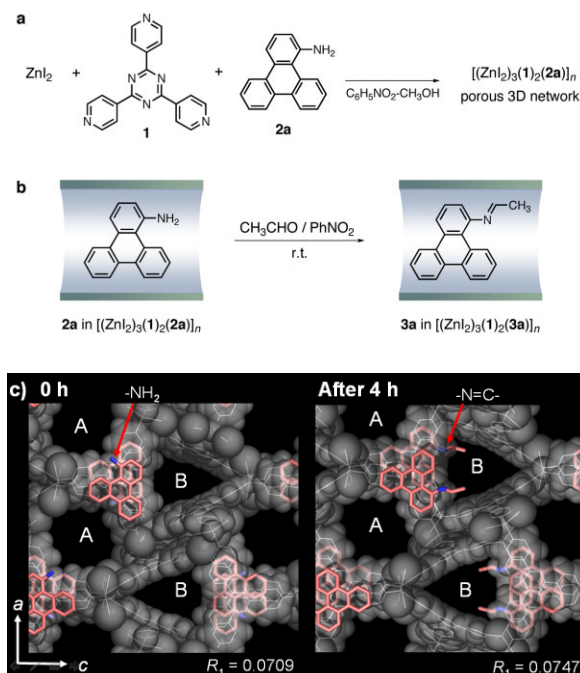


Figure 1. Reaction scheme for the imine formation in a crystal. a) Preparation of porous network complex $[(ZnI_2)_3(1)_2(2a)]_n$. b) Single-crystal-to-single-crystal transformation of **2a** into labile imine **3a** in the pore of the network complex. c) Crystal structures before and after crystalline-state reaction.

3a in the network was confirmed by microscopic IR analysis, elemental analysis and extraction of the product **3a**. The transformed crystals showed no change in size or morphology and were suitable for single crystal X-ray analysis. Crystallographic analysis revealed the formation of unstable imine **3a** in the network (Figure 1c). The amino group of **2a** before the reaction exists only in pore **A**, but, surprisingly, the imino group after the reaction exists both in pore **A** (44%) and in pore **B** (56%). This fact indicates the rotation of imbedded **2a** during the reaction.

References

- [1] T. Haneda, et al *J. Am. Chem. Soc.*, **130**, 1578 -1579 (2008).

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