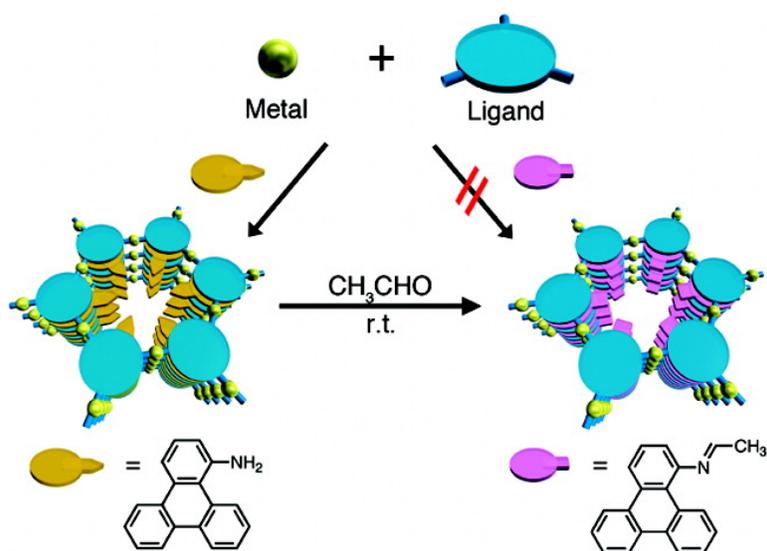## Communication

# 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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# 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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In situ preparation of labile compounds 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.[1] 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.[2,3] Thanks to the pseudo-solution state in the pores, even bulky substrates can easily interpenetrate into the crystals without reducing single crystallinity.[4] We examined the reaction of acetaldehyde with amines to form acetaldehyde imines that are, normally, easily hydrolyzed or isomerized into enamines (Scheme 1).[5] The aromatic amines were incorporated in the columnar array of aromatic ligands of an as-synthesized porous network complex.[6] 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.[7,8] From the in situ crystallography, we show not only the labile imine structures but also the dynamic rotor-like motion[9] of the amine substrates during the reaction.

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. Red single crystals with a composition of $[(ZnI_2)_3(\mathbf{1})_2(\mathbf{2a})(C_6H_5NO_2)_x]_n$ were isolated in a good yield.[6] In this network complex, ligand **1** and amine **2a** were alternatively and infinitively stacked (Figure 1a,b). Along the infinite aromatic stacking, there are two kinds of 1-D 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). The pores contain disordered solvents.

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 $[(ZnI_2)_3(\mathbf{1})_2(\mathbf{2a})(C_6H_5NO_2)_x]_n$ 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 h. The change of crystal color arises from the decrease in the donor ability of aromatic amine **2a** by the imine formation. It is important to note that the color change starts from the ends and progresses along the long axis of the crystal (Figure 2). After isolation of the crystals, the complete conversion to imine **3a** in the network was confirmed by microscopic IR analysis, elemental analysis, and

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**Scheme 1.** Formation of Labile Imines by Single-Crystal-to-Single-Crystal Reactions in the Pores of a Porous Coordination Network
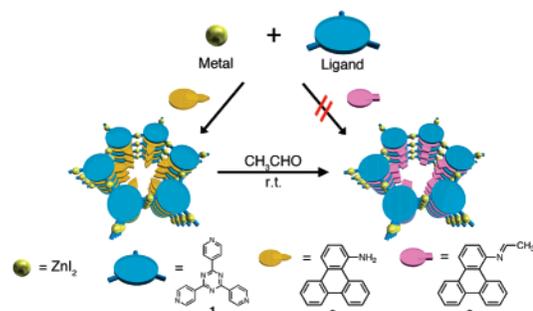


extraction of the product **3a** (see also Supporting Information). The transformed crystals showed no change in size or morphology and were suitable for single-crystal X-ray analysis.

Crystallographic analysis revealed the formation of unstable imine **3a** in the network (Figure 1d). The conversion of **2a** to **3a** in the crystalline state was quantitative, in agreement with microscopic IR analysis. 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%). The imbedded **2a** must rotate during the reaction.

The single-crystal-to-single-crystal formation of a more labile imine in the pore was also examined with 2-aminotriphenylene (**2b**). The single-crystalline network complex $[(ZnI_2)_3(\mathbf{1})_2(\mathbf{2b})(C_6H_5NO_2)_x]_n$ was prepared and subjected to the condensation with acetaldehyde by immersing the crystals in a dioxane solution of acetaldehyde (see Supporting Information). The expected imine **3b** itself is too unstable to be isolated. However, we successfully observed the formation of **3b** in the network complex in a single-crystal-to-single-crystal fashion. The conversion was approximately 60%. In contrast to the case of imine **3a** formation, no rotation of the triphenylene core was observed during the reaction of amine **2b** with acetaldehyde.

To obtain insight into the rotation of the imbedded aromatic amines during the reaction, we examined the reaction of **2a** with two additional aldehydes. By the reaction of $[(ZnI_2)_3(\mathbf{1})_2(\mathbf{2a})(C_6H_5NO_2)_x]_n$ with hexanal and *p*-anisaldehyde, the corresponding imines (**4a**, and **5a**, respectively) were also formed in a single-crystal fashion. In situ crystallography showed that the imino groups from hexanal exist in pore **A**, whereas those from *p*-anisaldehyde are only in pore **B** (Figure 3). Although the aldehydes can diffuse into both pores, the reaction selectively proceeds in one specific pore where the imine is more stabilized. In the case of *p*-anisaldehyde,
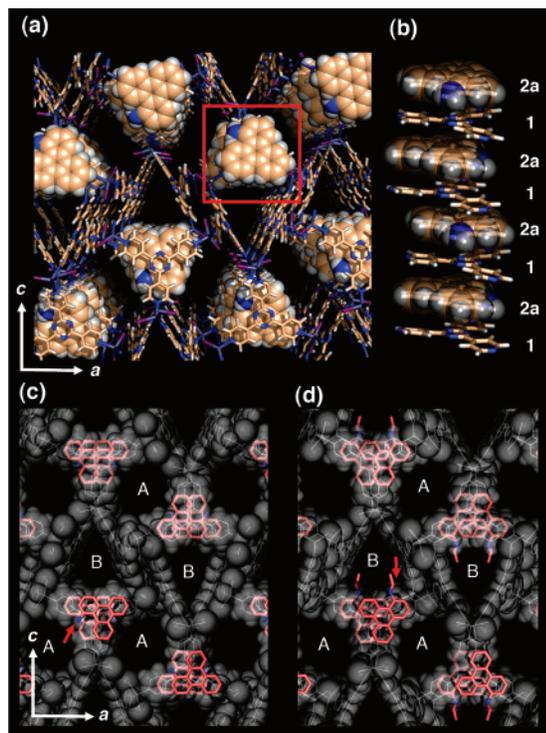
**Figure 1.** Crystal structures of the porous networks before and after the crystal-to-crystal imine formation. (a) The porous network of $[(ZnI_2)_3(1)_2$-$(2a)(C_6H_5NO_2)_x]_n$ viewed along the $b$-axis. Shapes and dimensions of pores: **A**, rectangular (10 × 15 Å); **B**, equilateral triangle with a side 12 Å long. Nitrobenzene molecules in the pore are omitted for clarity. (b) The infinite aromatic stacking of ligand **1** and amine **2a** at the highlighted square region in Figure 1a. (c) Crystal structure of the porous network of $[(ZnI_2)_3$-$(1)_2(2a)(C_6H_5NO_2)_x]_n$ viewed along the $b$-axis. The arrow indicates an $NH_2$ group of **2a**. (d) Crystal structure of the porous network of $[(ZnI_2)_3(1)_2$-$(3a)(C_6H_5NO_2)_x(CH_3CHO)_y]_n$. The arrow indicates the newly formed imine moiety of **3a** (56%) protruding into pore **B**. The imines (44%) protruding into pore **A** were omitted for clarity.
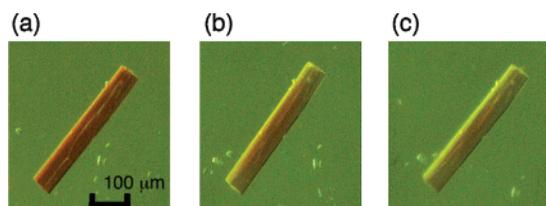


**Figure 2.** Photographs of a single crystal of the clathrate $[(ZnI_2)_3(1)_2(2a)$-$(C_6H_5NO_2)_x]_n$: (a) before reaction; (b) 15 min after immersing into acetaldehyde/nitrobenzene (1:4) solution at room temperature (the color change progressed along the pore direction of the crystal); (c) after 30 min.

the amine must first rotate before the condensation can occur. Once the reaction takes place, the new bulky imino substituents inhibit the rotation.

In summary, we have succeeded in the crystallographic analysis of labile molecules via in situ preparation in the fluid state of voids of a crystalline porous coordination network. This method allowed us to observe not only the structure of the labile molecules but also macroscopic dynamics in their formation. Our approach overcomes many problems of in situ crystallography: the coordination network preserves crystallinity and even a long alkyl chain such as hexanal can freely diffuse into the pores, where subsequent chemical reactions involving large conformational changes can occur. We believe that our results will enable the exploration of the new aspects and applications of single-crystal-to-single-crystal transformations.
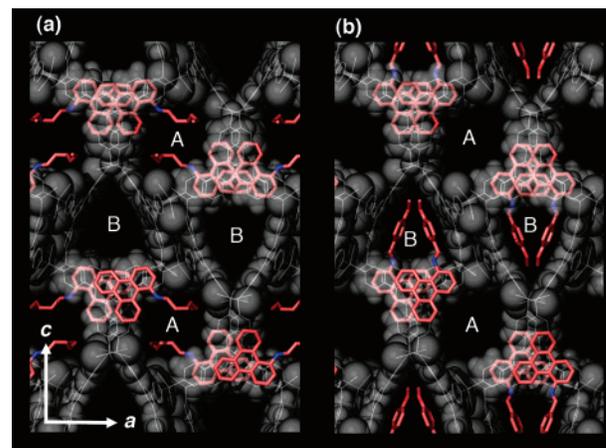


**Figure 3.** Crystal structures of clathrate complexes $[(ZnI_2)_3(1)_2(imine)_x$-$(amine)_y]_n$ prepared by the crystalline state reaction of **2a** with aldehydes via diffusion of aldehydes. (a) Formation of hexanal imine **4a** in a crystal ($x = 1$, $y = 0$). Substituted triphenylene molecules are shown as sticks (C, pink; N, blue). Unreacted hexanal molecules in both pores are omitted for clarity. (b) Formation of $p$-anisaldehyde imine **5a** in a crystal ($x = 0.5$, $y = 0.5$). Substituted triphenylene molecules are shown as sticks (C, pink; N, blue; O, red). Unreacted amine **2a** (50% in pore **A**) and $p$-anisaldehyde (in pores **A** and **B**) are omitted for clarity.

**Supporting Information Available:** Experimental details, FT-IR spectra, and UV−vis spectra. The crystallographic details are described in the cif files deposited in CCSD (Nos. 661044−661047). This material is available free of charge via the Internet at http://pubs.acs.org.

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JA7111564