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A Porous Coordination Network Catalyzes an Olefin Isomerization Reaction in the Pore

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Catalysis is an important and highly desirable application of porous coordination networks[1] and is a major focal point of the network field. The few reports on catalysis by porous coordination networks have assumed that the reactions occurred within the pores.[2] In this report, we describe a catalytic olefin isomerization within a porous network. The olefin substrate we examined here is retinal, whose *cis*−*trans* isomerization has been exhaustively studied.[3,4] We found that this standard reaction is catalyzed by only a trace amount of crystals of a porous network in cyclohexane. By demonstrating (i) that the retinal in solution (*out*-retinal) rapidly diffused into the pore, (ii) that only retinal within the pore (*in*-retinal) isomerized,[5] (iii) that the *in*- and *out*-retinal are in rapid equilibrium, and finally (iv) that a similar complex with no absorption property for retinal did not show the catalysis, we conclude that the reaction took place inside the pores of the coordination network.

The coordination network $[(ZnI_2)_3(TPT)_2 \cdot x(\mathbf{G})]_n$ (**1**) [TPT = 2,4,6-tris(4-pyridyl)triazine; **G** = guest] crystallized upon coordination of the TPT ligand with ZnI_2 in a 4:1 nitrobenzene/methanol solvent mixture (Figure 1a).[6,7] The large pores of network **1** are bounded by electron-deficient coordinated TPT ligands (Figure 1b). The pores initially contained excess nitrobenzene, which was first exchanged with cyclohexane by immersing the crystalline **1** in cyclohexane. The tiny block-shaped crystals of **1** were subsequently immersed in an orange cyclohexane solution of all-*trans* retinal [360 fold-excess per $(ZnI_2)_3(TPT)_2$ unit]. The pale-yellow crystals immediately (<1 s) turned orange, indicating the very rapid diffusion of retinal into the crystal pores. The crystals remained suspended in the cyclohexane solution for 1 week under an Ar atmosphere in the dark. An aliquot of the supernatant solution was directly analyzed by ^{1}H NMR spectroscopy and found to contain 75% all-*trans* retinal and 25% 13-*cis* isomer (Figure 2). In the absence of crystalline network **1**, the isomerization did not occur. The porous crystals act as a heterogeneous catalyst for the *trans*−*cis* isomerization of retinal. Only a tiny crystal sufficed to convert the entire solution, and the turnover number was estimated to be ∼90 per $(ZnI_2)_3(TPT)_2$ unit.[8]

We confirmed that the reaction occurs within the network pores by the following several experiments. (1) The isomerized retinal was directly extracted from the crystals. After treatment with retinal, the suspended crystals were collected, dried, and subjected to elemental analysis. A composition of $\{[(ZnI_2)_3(TPT)_2] \cdot (\text{retinal})_{1.1} \cdot (\text{cyclohexane})\}_n$ was revealed, confirming that the crystals included retinal. From these crystals, the *in*-retinal was directly extracted with $CDCl_3$. After extraction, the crystals returned to their original pale-yellow color. The ^{1}H NMR analysis revealed that the extracted *in*-retinal was a 75:25 mixture of the all-*trans* and 13-*cis* isomers. (2) The reaction was catalytically promoted by the rapid exchange of *in*-retinal with the supernatant *out*-retinal. The *in*-retinal, equilibrated at all-*trans*/13-*cis* = 75:25, easily diffused out into the supernatant (Figure 2 and Figure S4 in the Supporting Information). (3) Surface reaction was ruled out because suppression of the *in*−*out* exchange resulted in isomerization only in the crystal. Changing the solvent to *t*-BuOH reduced the guest exchange rate, as the retinal prefers the more hydrophobic domain within the pores. Upon treatment of crystals of network **1** with a *t*-BuOH solution of all *trans*-retinal for 1 week, anaerobic conditions again resulted in a 75:25 all-*trans*/13-*cis* ratio for the enclathrated *in*-retinal, as determined by NMR analysis. In the supernatant *t*-BuOH solution, however, only a trace amount of isomerized 13-*cis*-retinal was detected, indicating that guest exchange was prohibited and thus that the reaction occurred only within in the network pores (Figure S1). (4) A related ZnI_2−TPT complex with smaller pores, $[(ZnI_2)_3(TPT)_2 \cdot x(\mathbf{G})]_n$,[9] did not absorb retinal and showed no catalytic activity for the retinal isomerization. (5) A leaching test indicated the heterogeneous catalysis of the crystals: the all-*trans* to 13-*cis* isomerization was obviously

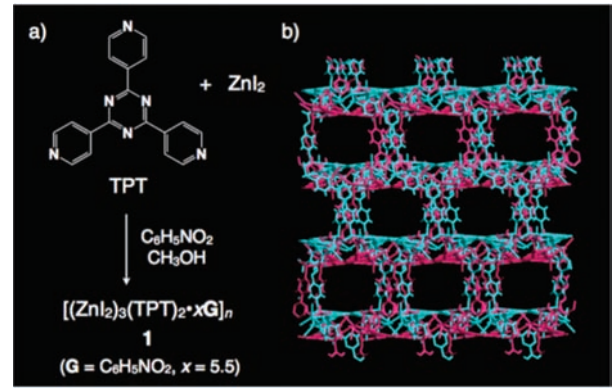

Figure 1. Preparation and structure of the porous network $[ZnI_2(TPT)_3 \cdot x\mathbf{G}]_n$ (**1**). (a) Reaction scheme. (b) Crystal structure of **1**. Guest molecules (**G**) in the pores have been omitted for clarity.

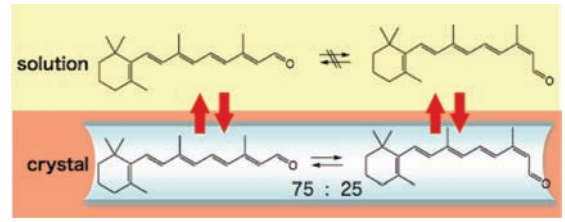

Figure 2. Isomerization of retinal catalyzed by the pores of **1**.

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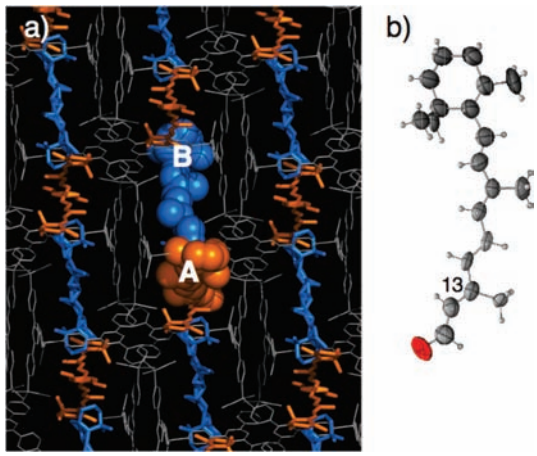

Figure 3. (a) Crystal structure of $\{[(ZnI_2)_3(TPT)_2]\cdot(retinal)_{1.1}\cdot(cyclohexane)\}_n$. Retinal **A** (orange, ~90% occupancy) is observed as the all-*trans* isomer, while retinal **B** (blue, ~20% occupancy) is considerably disordered. The disordered structures have been overlaid except for those drawn in the space-filling presentation. Cyclohexane has been omitted for clarity. (b) ORTEP drawing of retinal **A**. Ellipsoids are set at the 30% probability level.

hampered when the catalyst crystals were removed by filtration during the isomerization (Figure S6).[10,11]

X-ray crystallographic analysis of the retinal-treated crystals unequivocally revealed the presence of retinal in the network pores. Two crystallographically independent retinal molecules (**A** and **B**) were observed in single crystals of **1** (Figure 3). Retinal **A** exists as the all-*trans* form. The molecular structure of retinal falls within normal parameters (Figure 3b), and no specific van der Waals contacts with surrounding TPT ligands or Zn(II) ions are observed. No disorder indicating the presence of the 13-*cis* isomer was observed. In contrast, the other retinal, retinal **B**, is considerably disordered. The refinement of retinal **B** into a reasonable structure was unsuccessful because of many possible conformations, and no appropriate frameworks without severe distortions were obtained. Nevertheless, the obtained X-ray crystal structure clearly shows that retinal molecules do exist in the pores of **1**, suggesting that these pores serve as favorable sites into which retinal molecules can penetrate.

In summary, we have found that catalytic thermal isomerization of an olefin proceeded within an artificial porous coordination network. We note that the present results clearly demonstrate that the catalysis proceeded inside the pore, in contrast to previous reports in which it could not be clearly determined whether the reaction proceeds on the surface or within the network pores.[2,13] Given the nature of the pores and increased host−guest electronic interaction, we expect that more organic transformations can potentially be catalyzed and controlled with high regio- and stereoselectivity within porous networks.

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Supporting Information Available: Experimental procedures, NMR and ESR spectra, and X-ray structural data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) ESR analysis showed the presence of radical species in the retinal-containing crystals, whereas the empty crystals (containing only nitrobenzene) were ESR-silent (Figure S2). Since we have previously observed charge/electron transfer from electron-rich guests to electron-deficient Pd(II)−TPT cagelike coordination hosts,[12] isomerization via radical species could also account for the isomerization. For *cis*−*trans* isomerization of polyenes via electron transfer, see: (a) Polyakov, N.; Leshina, T.; Kispert, L. *RIKEN Rev.* **2002**, *44*, 140. (b) Yamabe, T.; Akagi, K.; Ohzeki, K.; Fukui, K.; Shirakawa, H. *J. Phys. Chem. Solids* **1982**, *43*, 577.

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