Molecular Flasks

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

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Monitoring of solid-state reactions in situ by X-ray crystallography provides direct information on reaction processes and final structures.[1] However, to preserve crystallinity, this powerful analytical method is limited to reactions in which the structural changes during the reaction are very small.[2] Crystallographic analysis of reactions involving bulky reagents within crystals are also limited owing to restricted diffusion in close-packed crystals and the often concurrent crystal degradation.

Recently, we reported a robust coordination network complex with large pores.[3,4] The pore channels facilitate increased mobility and rapid diffusion of included guest molecules. Large organic molecules can easily enter into the pores by guest exchange. In this sense, the pore interior is a pseudo-solution state in which chemical reactions may proceed as in a solution, yet can be directly analyzed by crystallography. Herein, we show that single-crystal-to-single-crystal chemical reactions with large, common reagents proceed quite smoothly inside the pores of the network.[5,6] 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. In related studies, we have reported the preliminary results of the diffusion of aldehydes into the pores of porous networks to form Schiff bases.[6b] Postsynthetic modification of a network complex with acylation agents has been recently reported.[5e,f]

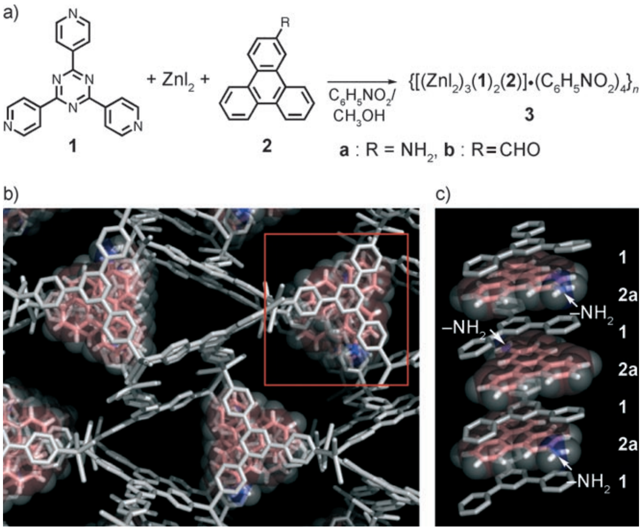

Figure 1. a) Depiction of the preparation of 3D porous networks **3a**,**b**. b,c) Crystal structure of porous network **3a**. b) View along direction of pores. c) Perpendicular view to direction of pores, showing the columnar stacking of **1** and **2a** in the network **3a**.

The 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** (Figure 1a).[4b] The network structure of **3a** features 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, oriented to react with various guest molecules (Figure 1b).

When crystals of **3a** were dipped into a cyclohexane solution of acetic anhydride, the crystal turned from red to yellow within 3 h. Diffraction studies revealed that crystallinity was maintained, even after quantitative conversion and crystallographic analysis revealed that amide **4a** had formed (Figure 2). Single-crystal microscopic FT-IR spectra of complex **3a** and {[(ZnI$_2$)$_3$(**1**)$_2$(**4a**)]·(C$_4$H$_6$O$_3$)$_x$}$_n$ (**5a**) also indicated the quantitative conversion from **3a** into **5a** (see Supporting Information, Figure S18).

The robust nature of the crystal network tolerates the rapid diffusion of acetic anhydride into the pores and the complete conversion of **2a** into amide **4a**. The pores also accommodate the larger octanoic anhydride and, after diffusion into the pores, octanoic amide **4b** is obtained. Octanoic acid forms as a by-product, but leaves the crystals and is not detected in the crystallographic analysis. Surprisingly, the pores also allow diffusion of the bulky phenyl isocyanate, and the bound **2a** is quantitatively converted into the phenyl urea **4e**. These results indicate that even large molecules have considerable mobility in the pores.

The reactions within the pores provide a facile method for postsynthetic modifications of the pore interior. Carboxylic acid groups (COOH) can strongly bind metal ions and are very difficult insert unprotected into porous network com-

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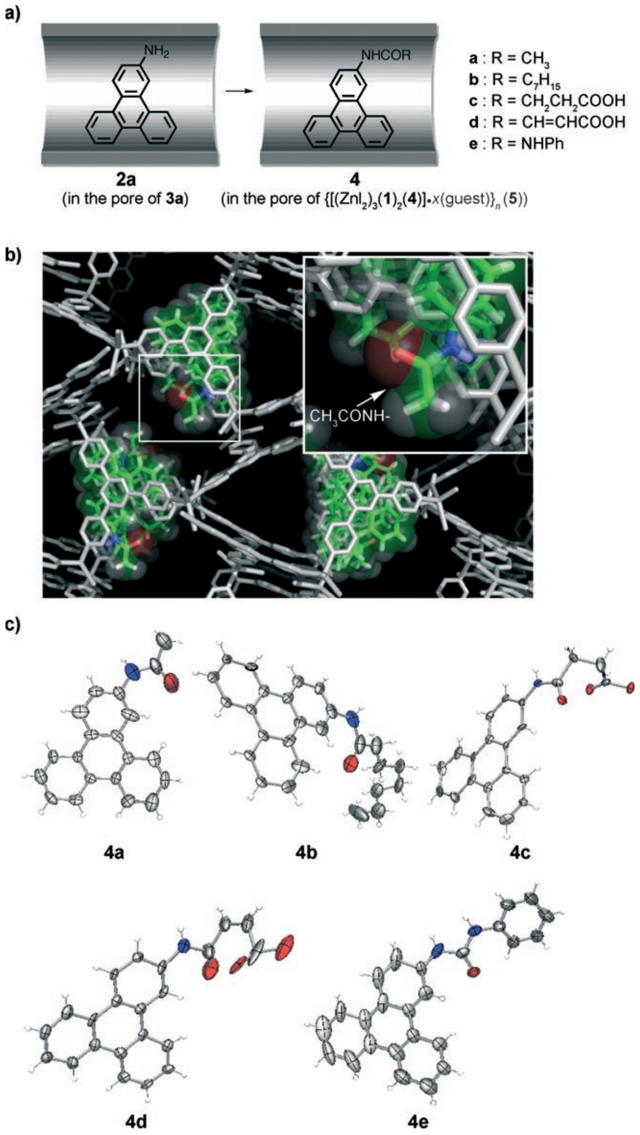

Figure 2. a) Depiction of the acylation reactions of **2a** in the pore of crystalline **3a**. b) Crystal structure of porous network **5a**. c) Molecular structures of **4a–e**, directly formed from **2a** in the pore. Ellipsoids set at 30% probability.

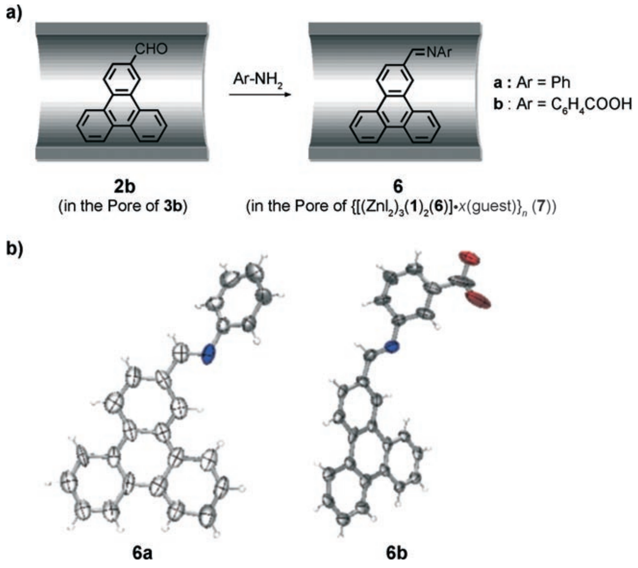

Figure 3. a) Depiction of the acylation reactions of **2b** in the pore of crystalline **3b**. b) Molecular structures of **6a**, **6b**, directly formed from **2b** in the pore. Ellipsoids set at 30% probability.

plexes.[7] 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 into amides and deftly lines the pore interior with free carboxylic acids. Similarly, treatment with maleic anhydride places −CH=CHCOOH groups in the pores.

After establishing that relatively mild reagents (anhydrides and an isocyanate) easily diffuse into the pores without damaging the crystals, 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 ethyl acetate solution of aniline, crystallinity was maintained and clean conversion into imine **6a** was detected (Figure 3). 3-aminobenzoic acid also reacted similarly to give imine **6b**. The crystal networks of **3a** and **3b** are quite robust and tolerate postsynthetic modification with both basic NH_2 and acidic COOH groups.

In summary, we have demonstrated that common organic transformations with bulky reagents can proceed smoothly within the pores of coordination networks. The bulky reagents diffuse readily through the network pores and show reactivity similar to that in solution. However, unlike solution-state reactions and many solid-state reactions, the reactions within the pores can be easily analyzed by crystallography. Our results overcome a fatal problem in solid-state reactions, namely the preservation of crystallinity, and provide a new application of porous coordination complexes. In situ preparation and determination of reaction intermediates or labile molecules can be achieved by utilizing these "single-crystalline molecular flasks".

Experimental Section

Typical procedure of single-crystal-to-single-crystal reactions: Reagents and solvents were obtained from commercial suppliers and used without further purification. Crystals of **3a** (2.5 mg) were immersed in a cyclohexane solution (2 mL) of acetic anhydride (v/v = 29:1), octanoic anhydride (v/v = 1:1), and phenyl isocyanate (v/v = 9:1), or a 100 mM ethyl acetate solution (2 mL) of succinic anhydride or maleic anhydride at room temperature. After the color of the crystals had completely changed from red to yellow (**5a**: 1 d, **5b**: 10 d, **5c–e**: 3 d), a crystal was removed from the solution and characterized by X-ray crystallographic analysis. Crystals of **3b** (20 mg) were immersed in an cyclohexane solution of aniline (16 mL, v/v = 100:1) or the 110 mM ethyl acetate solution of 3-aminobenzoic acid (16 mL) at 60 °C. After a complete color change, a crystal was removed from the solution (**7a**: 1 d, **7b**: 2 d) and was characterized by X-ray analysis. The crystallographic details were described in the cif files.

Elemental analyses (%):

3b: calcd for $\{[(ZnI_2)_3(\mathbf{1})_2(\mathbf{2b})]\cdot(C_6H_5NO_2)_{4.5}\}_n$: C 41.17, H 2.46, N 9.66; found: C 41.22, H 2.42, N 9.61. **5a**: calcd for $\{[(ZnI_2)_3(\mathbf{1})_2$-

$(\mathbf{4a})]\cdot(C_4H_6O_3)_4\}_n$: C 38.00, H 2.79, N 8.00; found: C 38.01, H 3.03, N 8.15. **5b**: calcd for $\{[(ZnI_2)_3(\mathbf{1})_2(\mathbf{4b})]\cdot(C_6H_{12})_{2.8}\}_n$: C 43.27, H 3.90, N 8.32; found: C 43.03, H 4.02, N 8.03. **5c**: calcd for $\{[(ZnI_2)_3(\mathbf{1})_2(\mathbf{4c})]\cdot(H_2O)\cdot(C_4H_8O_2)_{3.5}\}_n$: C 38.40, H 3.18, N 8.09; found: C 38.30, H 3.36, N 8.02. **5d**: calcd for $\{[(ZnI_2)_3(\mathbf{1})_2(\mathbf{4d})]\cdot(H_2O)\cdot(C_4H_8O_2)_{3.5}\}_n$: C 38.43, H 3.09, N 8.09; found: C 38.62, H 3.18, N 7.97. **5e**: calcd for $\{[(ZnI_2)_3(\mathbf{1})_2(\mathbf{4e})]\cdot(C_6H_{12})\cdot(C_7H_5NO)_3\}_n$: C 44.29, H 2.91, N 9.98; found: C 44.59, H 2.97, N 10.27. **7a**: calcd for $\{[(ZnI_2)_3(\mathbf{1})_2(\mathbf{6a})]\cdot(H_2O)_{1.5}\cdot(C_6H_{12})_3\}_n$: C 43.26, H 3.68, N 8.30; found: C 43.37, H 3.49, N 8.03. **7b**: calcd for $\{[(ZnI_2)_3(\mathbf{1})_2(\mathbf{6b})]\cdot(H_2O)_4\cdot(C_4H_8O_2)_{2.5}\}_n$: C 38.43, H 3.09, N 8.09; found: C 38.23, H 2.79, N 7.87.

Crystallographic data: The diffraction data of **5a**, **5b** and **5e** were measured on a Bruker APEX-II/CCD diffractometer equipped with a focusing mirror (MoKα radiation: $\lambda = 0.71073$ Å) and the diffraction data of **3b**, **5c**, **5d**, **7a** and **7b** were measured on a RIGAKU/MSC Mercury CCD X-ray diffractometer by using synchrotron radiation ($\lambda = 0.6890$ Å) at PF-AR (NW2 beamline) of the High Energy Accelerator Research Organization (KEK). The structures were solved by direct methods (SHELXS 97) and refined by full-matrix least-squares calculations on F^2 (SHELXL-97) using the SHELX-TL program package. Hydrogen atoms were fixed at calculated positions and refined using a riding model.

3b: $C_{65.53}H_{45.07}I_6N_{14}O_{4.92}Zn_3$, $M_r = 2064.84$, space group *Pbca*, $a = 28.1745(4)$ Å, $b = 13.8238(2)$ Å, $c = 45.1995(8)$ Å, $V = 17604.2(5)$ Å^3, $T = 90$ K, $Z = 8$, $\rho_{calcd} = 1.558\ g\,cm^{-3}$, 7830 unique reflections out of 16270 with $I > 2\sigma(I)$, 1334 parameters, $1.12 > \theta > 24.95°$, final R factors $R_1 = 0.0986$ and $wR_2 = 0.3113$ for all data.

5a: $C_{68.64}H_{57.97}I_6N_{13}O_{10.48}Zn_3$, $M_r = 2190.24$, *Pbca*, $a = 27.749(6)$ Å, $b = 13.817(3)$ Å, $c = 44.362(10)$ Å, $V = 17009(7)$ Å^3, $T = 80$ K, $Z = 8$, $\rho_{calcd} = 1.711\ g\,cm^{-3}$, 13773 unique reflections out of 20942 with $I > 2\sigma(I)$, 1031 parameters, $1.71 > \theta > 28.29°$, final R factors $R_1 = 0.0560$ and $wR_2 = 0.1643$ for all data.

5b: $C_{74.77}H_{73.04}I_6N_{13}OZn_3$, $M_r = 2127.20$, *Pbca*, $a = 28.012(4)$ Å, $b = 13.7873(19)$ Å, $c = 45.388(6)$ Å, $V = 17529(4)$ Å^3, $T = 80$ K, $Z = 8$, $\rho_{calcd} = 1.612\ g\,cm^{-3}$, 11656 unique reflections out of 17873 with $I > 2\sigma(I)$, 1159 parameters, $1.71 > \theta > 26.37°$, final R factors $R_1 = 0.0609$ and $wR_2 = 0.1725$ for all data.

5c: $C_{124}H_{96}I_{12}N_{26}O_{12}Zn_6$, $M_r = 4057.29$, $P2_12_12_1$, $a = 13.82960(10)$ Å, $b = 28.1807(3)$ Å, $c = 44.3094(5)$ Å, $V = 17268.6(3)$ Å^3, $T = 90$ K, $Z = 4$, ρ_{calcd} $1.561\ g\,cm^{-3}$, 22667 unique reflections out of 32480 with $I > 2\sigma(I)$, 1621 parameters, $1.40 > \theta > 24.84°$, final R factors $R_1 = 0.0723$ and $wR_2 = 0.2031$ for all data.

5d: $C_{62}H_{46}I_6N_{13}O_6Zn_3$, $M_r = 2026.63$, *Pbca*, $a = 27.9987(2)$ Å, $b = 13.8164(3)$ Å, $c = 44.1589(5)$ Å, $V = 17082.5(4)$ Å^3, $T = 90$ K, $Z = 8$, $\rho_{calcd} = 1.576\ g\,cm^{-3}$, 17133 unique reflections out of 22034 with $I > 2\sigma(I)$, 1054 parameters, $1.41 > \theta > 27.72°$, final R factors $R_1 = 0.0614$ and $wR_2 = 0.2072$ for all data.

5e: $C_{84.72}H_{71.78}I_6N_{15.91}O_{2.91}Zn_3$, $M_r = 2316.96$, *Pbca*, $a = 28.857(3)$ Å, $b = 13.7063(16)$ Å, $c = 45.188(5)$ Å, $V = 17873(4)$ Å^3, $T = 86$ K, $Z = 8$, ρ_{calcd} $1.722\ g\,cm^{-3}$, 14485 unique reflections out of 21981 with $I > 2\sigma(I)$, 1119 parameters, $1.67 > \theta > 28.27°$, final R factors $R_1 = 0.0623$ and $wR_2 = 0.1886$ for all data.

7a: $C_{85}H_{89}I_6N_{13}Zn_3$, $M_r = 2250.20$, *Pbca*, $a = 13.6728(3)$ Å, $b = 45.5987(7)$ Å, $c = 28.4576(3)$ Å, $V = 17742.2(5)$ Å^3, $T = 90$ K, $Z = 8$, ρ_{calcd} $1.685\ g\,cm^{-3}$, 10945 unique reflections out of 24652 with $I > 2\sigma(I)$, 964 parameters, $1.39 > \theta > 28.92°$, final R factors $R_1 = 0.0761$ and $wR_2 = 0.2128$ for all data.

7b: $C_{70.27}H_{56.54}I_6N_{13}O_{7.14}Zn_3$, $M_r = 2154.74$, *Pbca*, $a = 27.8060(3)$ Å, $b = 13.80910(10)$ Å, $c = 45.1378(6)$ Å, $V = 17331.8(3)$ Å^3, $T = 90$ K, $Z = 8$, ρ_{calcd} $1.652\ g\,cm^{-3}$, 11038 unique reflections out of 16305 with $I > 2\sigma(I)$, 1057 parameters, $1.13 > \theta > 24.79°$, final R factors $R_1 = 0.0636$ and $wR_2 = 0.2054$ for all data.

CCDC 689677 (**3b**), 689678 (**5a**), 689679 (**5b**), 689680 (**5c**), 689681 (**5d**), 689682 (**5e**), 689683 (**7a**), and 689684 (**7b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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