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Supramolecular Framework with Two Different Kinds of Channels via Self-Assembly of 1D Coordination Polymers in a Prismatic Manner

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Slow diffusion of $Cu(ClO_4)_2$ with p-$C_6H_4(SiMe_2(4\text{-}Py))_2$ yields a supramolecular framework consisting of two kinds of channels via self-assembly of a 1D double-stranded chain in a prismatic fashion. The channel has a 11×11 Å^2 cross section (Cu···C = 11.13 Å) with a 6×6 Å^2 square pore. The channels are infinitely arranged, resulting in another kind of channel with similar pores. Thus, two different kinds of channels with different solvate molecules coexist in a 1:2 ratio. Weak C–H···π interaction may be one of the driving forces in the assembly of the prismatic channel structure.

Delicate construction of a new porous motif from molecular building blocks promises to provide specific functional materials such as photoelectronic devices, ion exchangers, desiccants, molecular sieves, sensors, catalysts, biomimetics.[1−6] The most important advantage of such metal−organic porous materials (MOMs) is their ability to control lining properties such as hydrophilicity, surface area, and chirality.[6] Significant progress has been made in the functional MOMs by self-assembly of metal ions with designed organic tectonics including flexibility, length, and angle,[7−10] even though serendipitous motifs have been frequently constructed owing to the presence of unpredictable weak interactions such as hydrogen bondings, van der Waals forces, metal−metal interactions, and $\pi-\pi$ interactions.[11] Among various building blocks, a series of silicon-containing pyridines have been used as useful tectonics for rational molecular materials[8,12−14] because bis(4-pyridyl)dimethylsilane has been exploited as a spacer for palladium(II) and platinum(II) rhomboids by Stang's group.[15] Such silicon-containing tectonics possess a potential multidentate, a tetrahedral angle around silicon, a controllable bipyridyl length, conformational nonrigidity, and manageable properties in addition to inductive and steric effects of the silicon atom. We report a new conceptual channel framework formed via the reaction of $Cu(ClO_4)_2$ with 1,4-bis(dimethyl-4-pyridylsilyl)benzene (L) as a key tectonic. The channel framework consists of two kinds of channels via self-assembly of a 1D double-stranded chain in a prismatic fashion.

The new L was prepared according to the literature method.[15] Slow diffusion of $Cu(ClO_4)_2$ with L in methanol/dichloromethane produced purple crystals.[16] Formation of the product was not significantly affected by the change of the reactant mole ratio and the concentrations, indicating that the structure of the product is a stable species. X-ray characterization[17] on a single crystal has provided a double-stranded (30-membered-ring) chain of the building block, $[CuL_2](ClO_4)_2$ (**1**; Chart 1). Each copper(II) ion is a pseu-

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(16) **1**: A dichloromethane solution (2 mL) of L (17 mg, 0.05 mmol) was slowly diffused into a methanol solution (6 mL) of $Cu(ClO_4)_2$ (9 mg, 0.025 mmol). Blue crystals formed at the interface and were obtained in 12 days in 70% yield. Chemical analysis results are not satisfactory owing to the evaporation of solvate molecules, but the analysis value of a completely desolvated compound is consistent with the calculated values. IR (KBr, cm^{-1}): $\nu(ClO_4)$ 1121 (s).

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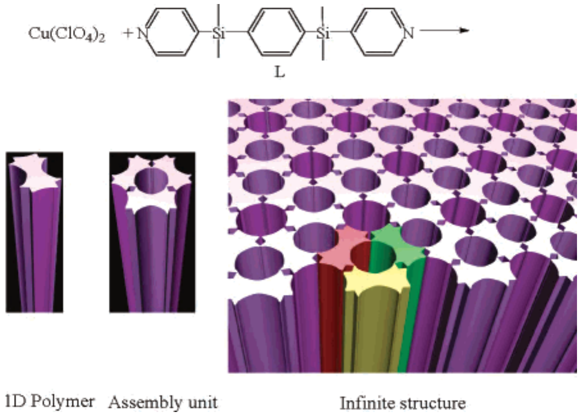
Chart 1



dooctahedral coordination sphere with two ClO_4^- anions in a trans position [O−Cu−O = 177.9(2)°] and four pyridine units in a propeller fashion [Cu−N = 2.003(4) and 2.036(4) Å]. The ClO_4^- acts as a counteranion rather than a ligand (Cu···O = 2.53 Å). The dihedral angle between two adjacent CuN_4 planes (54.9°) induces the double-stranded chain to look like a monorail. The closest intrachain Cu···Cu distance is 14.36 Å. The most fascinating feature is that an unprecedented supramolecular channel motif is formed via self-assembly of three 1D double-stranded chains in a prismatic manner (Chart 1 and Figure 1). The channel has a 6×6 Å^2 square pore. The pore size is carried out by a combination of the space-filling structure with the radii of the carbon atoms. The channels (A channel: light-purple color in Chart 1) are infinitely arranged, resulting in another kind of channel with a similar pore (Si···Si =11.50 Å; B channel: dark-purple color). Thus, two different kinds of A and B channels coexist in a ratio of 2:1. Thus, three A and three B channels lie around an A channel, whereas six A channels exist around a B channel. The channels are aligned with the long *c* axis of the parallelpiped-shaped crystals. It is noteworthy that solvate dichloromethane molecules are nestled in A channels whereas solvate methanol molecules are incorporated in B channels. The total solvent occupied volume is approximately 14%. The disordered dichloromethane molecules were refined by the X-ray analysis, but the severely disordered methanol molecules within the dark-purple channel were confirmed by ^1H NMR in Me_2SO-d_6 (see the Supporting Information). The NMR data show that the ratio of CH_3OH/CH_2Cl_2 is about 3. The ratio is a reasonable value because the A channel has ClO_4^- counteranions along with their different sizes. This two-component channel skeleton aggregates spontaneously if $\Delta G < 0$ (free energy of crystal formation), with the guest molecules acting as templates.[18] However, the included guest molecules within a rigid, well-defined host have a certain degree of intrachannel translational as well as rotational freedom. Thus, such freedoms of guest molecules may be indebted to the significant positional disorders.

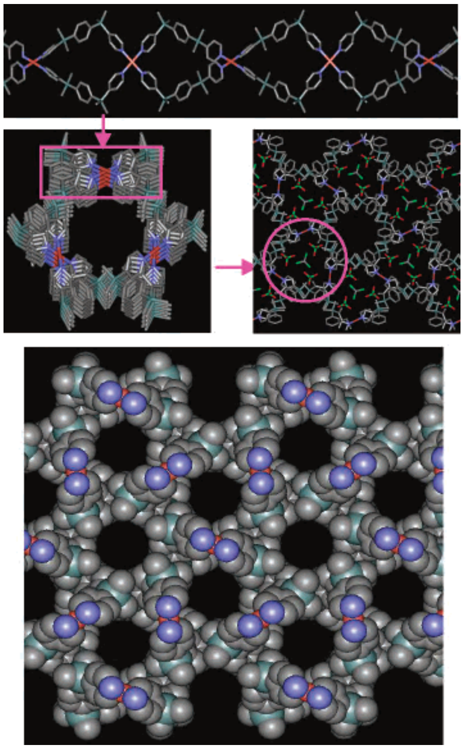


Figure 1. Double-stranded chain (top), an assembled-channel unit (middle-left and middle-right), and a space-filling infinite X-ray structure (bottom) of **1**. Anions, hydrogen, and solvent molecules were omitted for clarity except in the middle-right structure.

The construction of such a channel motif seems to come from the C−H···π interaction (perpendicular distances = 2.02−3.00 Å), presumably owing to the inductive effect of the silicon atom. The Si−CH_3 group interacts with the phenylene ring rather than the pyridyl moiety of the adjacent 1D chain. This fact may be ascribed to the decrease of the π-electron density of the pyridyl group via the coordination of a Lewis basic nitrogen heteroatom. The C−H···π interaction is one of the driving forces in the assembly of the prismatic channel structure. Even though each C−H···π interaction is very weak, the overall interactions are more stable when they are involved in an infinite structure. Of course, a subtle combination of the geometry of the copper(II) ion with the appropriate length, conformation, and steric effects of L is, needless to say, another important factor for the formation of the supramolecular channel. The ClO_4^-···H−C (the shortest distance = 2.22 Å) interaction may contribute to the formation of the channel structure.

The thermogravimetric analysis (TGA) shows that the skeleton has a thermal stability up to 289 °C and a capacity for the channel linings (Figure 2). An exothermic peak of the differential scanning calorimetry (DSC) curve was observed around 241 °C, indicating a slight structural change

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(17) Crystal data for **1**, $C_{40}H_{48}N_4O_8Cl_2Si_4Cu{\cdot}(CH_2Cl_2)_{0.67}$: hexagonal, *P*6*cc*, $a = 19.6312(3)$ Å, $b = 19.6312(3)$ Å, $c = 28.715(1)$ Å, $V = 9583.5(4)$ Å^3, $F(000) = 3162$, $\lambda = 0.710\,73$ Å, $\mu = 0.596$ mm^{-1}, crystal size $0.45 \times 0.40 \times 0.40$ mm^3, $Z = 6$, R1 (wR2) = 0.0704 (0.1644) on 7691 reflections with $I > 2\sigma(I)$, GOF = 0.970, 279 parameters refined. The CH_2Cl_2 solvate molecule is positioned in a 3-fold symmetry, and, thus, its occupancy is 0.1667. Other solvate methanol molecules were squeezed owing to the severe disorder. A Bruker SMART automatic diffractometer with a CCD detector at 173(2) K was used. Sheldrick, G. M. *SHELXS-97 and SHELXL-97: Programs for Structure Determination and Refinement*; University of Göttingen: Göttingen, Germany, 1997.

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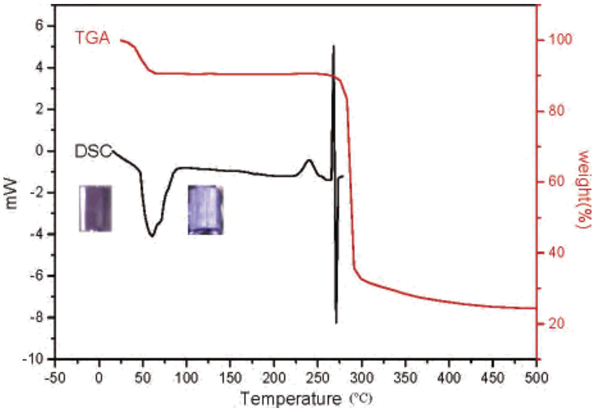

Figure 2. Overlay of TGA and DSC of **1** along with the pictures of the crystal.

without any weight loss. The exothermic peak may result from slight distortion of the ordered weak interactions. Actually, IR spectra before and after 241 °C do not give a fine distinction even though the crystal color is slightly different. The first TGA and DSC changes are apparently associated with the removal of disordered solvent molecules at the wide temperature range of 25−75 °C (calcd for 1.98MeOH + $0.66CH_2Cl_2$/**1**: 11.87%). Evaporation of the solvate molecules turned the crystal brittle and pale purple. The purple crystal bleached after the evaporation of solvate molecules, but resaturation of the solvate molecules under a mixture of CH_3OH and CH_2Cl_2 (CH_3OH/CH_2Cl_2 = 3) reduced the crystal to its original color. Unfortunately, the X-ray powder diffraction (see the Supporting Information) does not clearly indicate that the deadsorbed material regains its original skeletal structure after readsorption of the mixture solvent.

In conclusion, the present compound is a conceptually advanced 3D supramolecular framework with two different kinds of prismatic channels with two different guest molecules. Further experiments will provide more detailed information on the enormous potentials such as catalytic properties, adsorption−desorption, hydrophilicity, stable storage, and intrachannel reactivity.

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Supporting Information Available: ^{1}H and ^{13}C NMR data of L, X-ray data (CCDC 284901), and IR spectra, X-ray diffraction powder pattern, and ^{1}H NMR spectra of $[Cu(L)_2](ClO_4)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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