Isomerism Effect on Flexibility of Layered Frameworks in Organic Salts of 4,4′-Biphenyldisulfonic Acid with Primary Amines

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Organic salt of 4,4′-biphenyldisulfonic acid with isopropylamine yields a flexible layered framework with guest-responsive channels, while the salt with *n*-propylamine does a rigid one with fixed channels. The flexibilities of the framework are modulated by an isomerism effect of alkyl groups on the basis of different directions of methyl groups.

Host frameworks to include guest molecules have recently met with increasing interests as organic zeolites which have sophisticated abilities such as molecular separation, sorption, and storage.[1] So far, the frameworks have been formed mainly by using rigid compounds such as TPP,[2] disubstituted anthracene,[3] bicyclic diols,[4] and guanidinium organosulfonates.[5] In these cases, the organic frameworks are basically connected three-dimensionally via robust hydrogen bonds, and therefore the resulting molecular channels involve invariable spaces. In contrast, we have designed the frameworks composed of both rigid and flexible compounds for tuning sizes and shapes of the channels.[6] Focusing on salts of organic sulfonic acids with various amines, we have found that the salt of 4,4′-biphenyldisulfonic acid (BPDS) with isopropylamine (*i*-PrA) provides a drastically variable layered framework in response to guests. Interestingly, the flexibility of the framework comes from isomerism of the amines (Chart 1).

BPDS and various primary amines were mixed in methanol with a 1:2 molar ratio. Evaporating the solutions yielded their powdered salts, which were recrystallized from a mixture of methanol and corresponding solvents to obtain inclusion crystals.[7] The resulting crystals were subjected to single-crystal X-ray structural analyses.

It was confirmed that BPDS•*n*-PrA and BPDS•*i*-PrA specifically yield inclusion crystals with benzene and 1,4-dioxane. Figures 1a to 1d show their crystal structures.[8] It can be seen that the salts form common layered host frameworks with molecular channels. The remarkable difference is that benzene molecules are included into the channels with different modes. Namely, a molar ratio of BPDS to benzene is 1:1 for BPDS•*n*-PrA (Figure 1a), while 1:3 for BPDS•*i*-PrA (Figure 1b). In contrast, 1,4-dioxane molecules are incorporated by the salts in the same 1:1 molar ratios, as shown in Figures 1c and 1d.

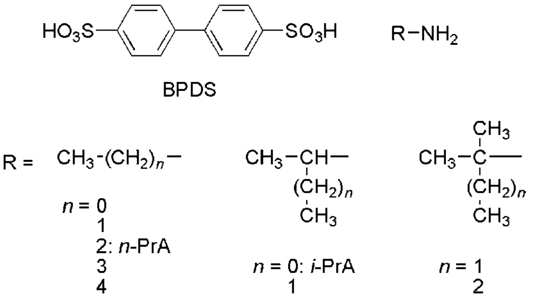

Chart 1.

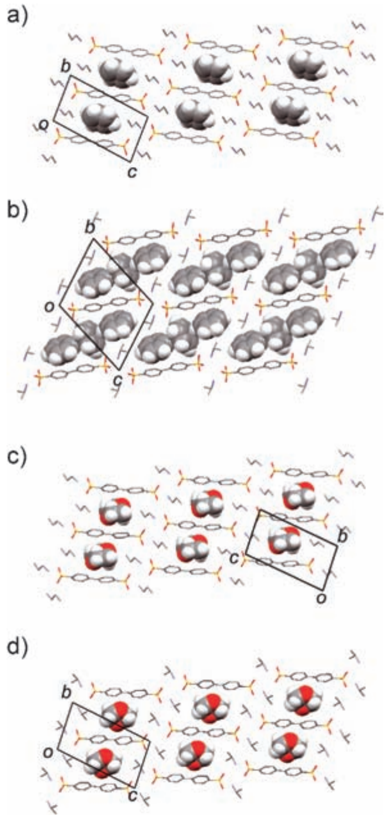

Figure 1. Molecular packing diagrams of inclusion crystals of the BPDS salts. (a) BPDS•*n*-PrA with benzene, (b) BPDS•*i*-PrA with benzene, (c) BPDS•*n*-PrA with 1,4-dioxane, and (d) BPDS•*i*-PrA with 1,4-dioxane.

These observations indicate that BPDS•*n*-PrA provides the similar channels for both of the guests due to a rigid framework, whereas BPDS•*i*-PrA does different-sized channels in response to the guests due to a flexible framework. This may be of interest, because isomerism of the amines modulates the guest-dependent layered structures followed by the changes of channel sizes and incorporation quantity.

In order to elucidate the isomerism effect, we examined construction manners of the layered structures through non-covalent interactions step by step.[9] The resolution basically comes from design of organic clay mimic structures in primary ammonium carboxylate salts by our research group.[10] Figure 2 schematically exhibits the interpretation of the layered structures of the BPDS salts. First, the components of the salts form a one-dimensional

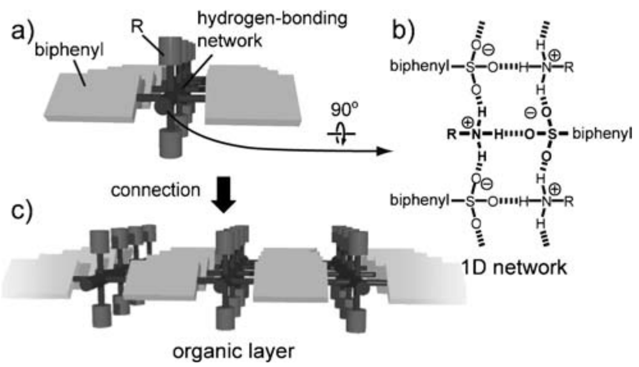

Figure 2. Hierarchical interpretation of the crystal structures of BPDS salts. (a) 1D assembly involving substituents of the amines with opposite direction, (b) 1D hydrogen-bonding network, (c) the organic layer by connection.

(1D) arrangement (Figure 2a) with 1D hydrogen-bonding networks (Figure 2b). In this case, the substituents of amines are oppositely directed against the network (Figure 2a). The networks are connected through the intermediates of biphenyl backbones to produce two-dimensional (2D) organic layer (Figure 2c). The layers are stacked along the crystallographic *b*-axis to yield the framework with molecular channels. It is considered that the stacking manners affect the sizes of the channels and the corresponding incorporation quantity of the guests.

The stacking manners are exactly dependent on the isomerism of the amines, as shown in Figure 3. Linear-shaped *n*-propyl group of BPDS•*n*-PrA lean on the biphenyl moieties (Figure 3a), allowing the 1D hydrogen-bonding networks to be located close to the other networks between the layers through electrostatic interactions. Actually, the distance between cations and anions (N···O) of the neighbored layers are 3.28 Å for BPDS•*n*-PrA with benzene and 3.38 Å for 1,4-dioxane. Such a short interlayer interaction brings about the rigid framework of BPDS•*n*-PrA for both of the guests (Figure 3a). In contrast, one branched methyl group of *i*-PrA is located perpendicular to the biphenyl moieties (Figure 3b), leading to the sterically hindered contact between the networks. In fact, the distance between the ions is 4.47 Å for BPDS•*i*-PrA with 1,4-dioxane. Therefore, the layers can slide in response to the guest molecules (Figure 3c), with the above distance of 9.76 Å for BPDS•*i*-PrA with benzene. This reasonably explains the formation of the framework with variable channels. In addition, intermolecular CH/π interactions of benzene molecules may compensate the lost interaction among the ions, leading to the novel structure with three molar amounts of incorporation.

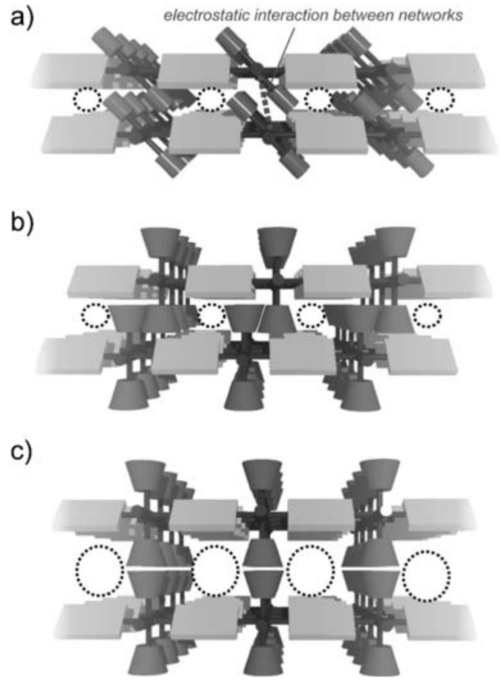

Figure 3. Three kinds of stacking manners of the layers of the BPDS salts. (a) BPDS•*n*-PrA with benzene or 1,4-dioxane, (b) BPDS•*i*-PrA with 1,4-dioxane, (c) BPDS•*i*-PrA with benzene. Dashed circles represent the molecular channels.

In summary, we have demonstrated that the flexibility of the layered framework can be modulated only by isomerism of the amines. The isomerism effect is attributed to steric control of the interlayer interactions on the basis of the directions of the methyl groups. In addition, the flexible framework may lead to the creation of crystalline materials with dynamic behavior such as an intercalation, and polymerization.

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7 Example for, BPDS•*i*-PrA was dissolved in methanol, and the same volume of the solvent benzene was added on heating. Cooling of the solution yielded the inclusion crystal.

8 These crystallographic data have been deposited with CCDC as nos. CCDC 627554–627557. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html. These crystal parameters are available as supporting information on the CSJ Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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