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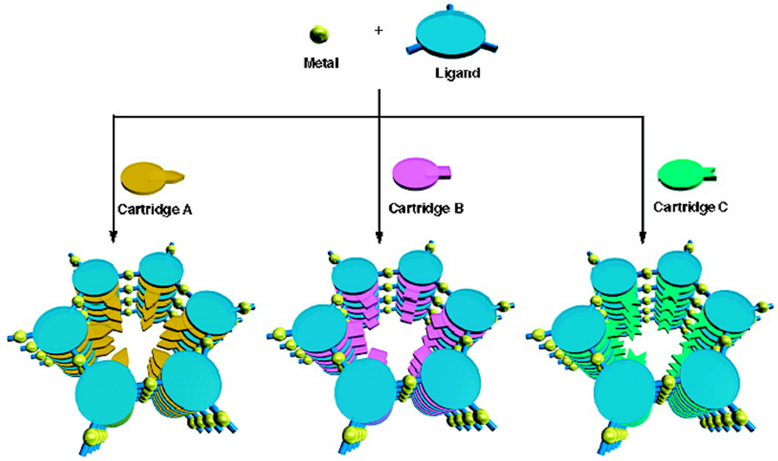

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The Modular Synthesis of Functional Porous Coordination Networks

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Although numerous porous coordination networks have been synthesized to date,[1] the functionalization of the pores at will without changing the network frameworks is still a difficult task despite the high designability of organic ligand components.[2] This is because the porous network formation is very sensitive to the ligand structure. Namely, the introduction of even a small functional group to the ligand often brings about the formation of completely different, unpredictable network structures. We have previously synthesized a unique porous coordination network composed of two interpenetrating networks in which the pores are surrounded by aromatic bricks.[3] The bricks consist of alternatively layered 2,4,6-tris(4-pyridyl)-1,3,5-triazine (**1**) and triphenylene (**2a**); the former, **1**, forms infinite 3D network via coordination to $\mathrm{ZnI_2}$, whereas the latter, **2a**, is involved in the 3D framework without forming any covalent or coordination bonds with other components. Here, we report that the noncovalently intercalated **2a** in this porous complex can be replaced with functionalized triphenylenes **2b**−**f** without causing any change in the porous network structure (Figure 1). In these porous complexes, intercalated triphenylenes **2a**−**f** are regarded as the cartridges of functional groups. We emphasize that the facile control of the pore nature by simply replacing the cartridge provides a family of porous networks.

The porous complex was prepared by treating triazine ligand **1** and triphenylene **2** with $\mathrm{ZnI_2}$ in a nitrobenzene-methanol gradient solution and isolated as single crystals with the formula of $\{[(\mathrm{ZnI_2})_3(\mathbf{1})_2(\mathbf{2})]\cdot x(\mathrm{C_6H_5NO_2})\cdot y(\mathrm{CH_3OH})\}_n$ (**3**), wherein the $[(\mathrm{ZnI_2})_3(\mathbf{1})_2(\mathbf{2})]$ composite constitutes the porous framework whose pore is filled with nitrobenzene and methanol. For a typical procedure, the single crystals of $\{[(\mathrm{ZnI_2})_3(\mathbf{1})_2(\mathbf{2b})]\cdot 4(\mathrm{C_6H_5NO_2})\}_n$ (**3b**), having acidic phenolic pore, were grown from a triple-layered solution consisting of a methanol solution (0.5 mL) of $\mathrm{ZnI_2}$ (0.03 mmol) as the top layer, methanol (0.5 mL) as the middle layer, and a nitrobenzene/methanol solution (4:1, 5 mL) of **1** (0.02 mmol) and the cartridge molecule **2b** (0.1 mmol) as the bottom layer. After 2 days, the crystals were grown and isolated by filtration in 47% yield (Scheme 1). In a similar way, the use of cartridge **2c** afforded another porous complex **3c** with the acidic phenolic hydroxyl group arrayed at different positions in the pore (27% yield). From cartridges **2d**,**e** with a 2- or 1-$\mathrm{NH_2}$ group on the triphenylene core, complexes **3d**,**e** with a basic pore were formed (32% and 30% yields, respectively). Similarly, cartridge **2f** with a polar $\mathrm{NO_2}$ group gave a polar pore in **3f** (18% yield).

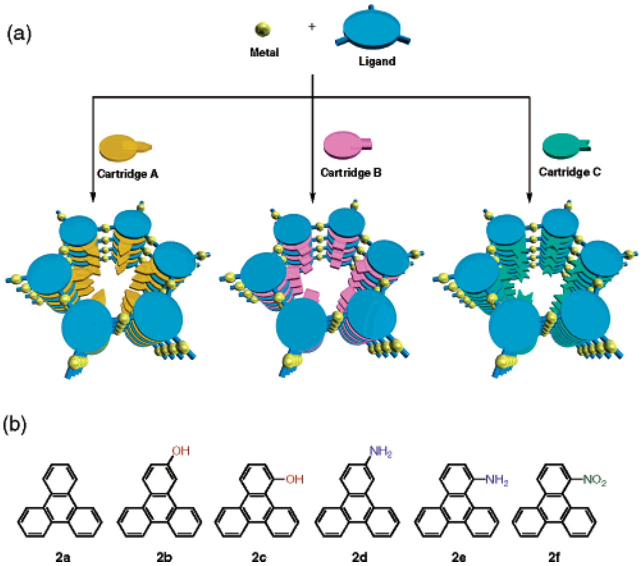
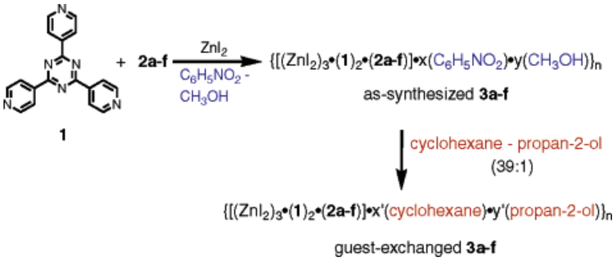


Figure 1. (a) Cartoon representation of the modular synthesis. (b) The library of the cartridges.

Scheme 1. Preparation and Guest-Exchange of 3D Porous Networks **3a**-**f**.



All the complexes **3a**−**f** were characterized by X-ray crystallographic analysis and shown to have the identical porous network frameworks of $[(\mathrm{ZnI_2})_3(\mathbf{1})_2(\mathbf{2})]$, whose pores were filled with nitrobenzene and, in the case of **2c**, methanol (Supporting Information). All the porous complexes **3a**−**f** have in fact two distinct pores, A (cylindrical) and B (trigonal prismatic) (Figure 2a). The acidic OH groups of **3b** are mainly directed to the pore A (68% occupancy), while the remaining 32% is located in the boundary between pores A and B. In most of the cases each substituent of **3a**−**f** is mainly directed to specific pore either A or B (Supporting Information).

Owing to the acidic nature of the pore A, the guest-exchange property of **3b** strikingly differs from that of **3a** having less polar pores. The crystals of as-synthesized **3b** were immersed in a mixed solvent of propan-2-ol and cyclohexane (1:39). Interestingly, despite its very low concentration, propan-2-ol was selectively taken up to the pore A, replacing nitrobenzene molecules filled in the pore A of the as-synthesized **3b** (Figure 2d). The selective uptake of propan-2-ol is driven by hydrogen-bond formation of propan-2-ol with the acidic phenolic hydroxyl group of cartridge **2b** via a water molecule, as discussed later. Such a selective uptake of propan-2-ol by pore A was not observed for **3a** because its pore A is hydrophobic;

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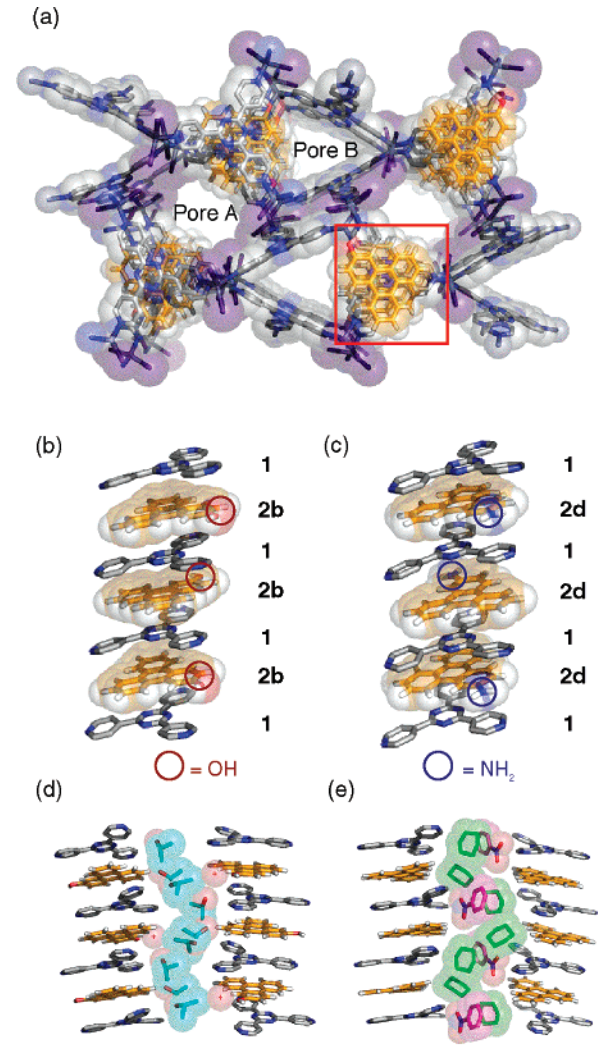

Figure 2. (a) Porous structure of **3b**. Guests in the pores are omitted for clarity. (b) The view of the aromatic layers of **3b** (square region in panel a) from pore A. Acidic OH groups are pointed toward the pore A. (c) The same view of **3d**. Basic NH_2 groups are pointed toward the pore A. (d) Channel of the guest (propan-2-ol) formed in the pore A of **3b** via hydrogen bonding with phenolic OH groups. (e) Channel of the guest (cyclohexane) formed in the neutral pore A of **3a**.

instead, cyclohexane was taken up by the pore A of **3a** (Figure 2e). The pore B of **3a** and **3b** are both hydrophobic. Thus, nitrobenzene in the pore B of as-synthesized **3a**,**b** was fully exchanged with cyclohexane.

Crystallinity remained intact during the guest exchange allowing the detailed crystallographic analysis after the guest exchange. In the pore A of **3b**, propan-2-ol is hydrogen bonded via one water molecule with the OH group of the cartridge **2b**. The interatomic distances of $O_{OH}\cdots O_{water}$ and $O_{water}\cdots O_{propan-2-ol}$ are 2.53 Å and 3.33 Å, respectively (Figure 2d). Another disordered OH group (32%) also forms hydrogen bonds with two propan-2-ol ($O_{OH}\cdots O_{propan-2-ol}$, 2.67 Å and 2.86 Å).

With another acidic cartridge **2c**, the OH group was directed to the pore A of **3c** with 100% occupancy. Thus, the pore A of the as-synthesized **3c** contained hydrogen-bonded methanol ($O_{OH}\cdots O_{methanol}$ is 2.76 Å) together with nitrobenzene solvent. When **3c** was immersed in the 1:39 mixed solvent of propan-2-ol and cyclohexane, again the pore A took up propan-2-ol only via hydrogen bonds with the OH group ($O_{OH}\cdots O_{propan-2-ol}$, 2.74 Å and 2.76 Å), while neutral pore B did cyclohexane only. In contrast with **3b**, no water molecule in **3c** was involved for propan-2-ol recognition.

In summary, we succeeded in the preparation of various biporous networks via modular synthesis and the fine-tuning of the channel atmosphere by simple modification of the cartridge molecules. Noteworthy is that alcohol molecules are selectively recognized by the biporous networks. We expect that a porous coordination network with properly modified pores will be a promising candidate for membrane materials because alcohol separation is an urgent issue for biofuel production in industry.

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Supporting Information Available: Experimental details; TG analysis; crystallographic details (.cif; see also CCDC (No.647842−647849)). This material is available free of charge via the Internet at http://pubs.acs.org.

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