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The Cartridge Synthesis of Functional Porous Coordination Networks

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Introduction

Although numerous porous coordination networks have been synthesized to date, the functionalization of the pores at will without changing the network frameworks is still a difficult task in spite of the high designability of organic ligand components. This is because the porous network formation is very sensitive to the ligand structure. We have previously synthesized a unique porous coordination network in which the pores are surrounded by aromatic bricks. 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 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 non-covalently intercalated **2a** in this porous complex can be replaced with functionalized triphenylenes **2b-f** without causing any change in the porous network structure, which we would like to term "*cartridge synthesis*". (Figure 1).[1]

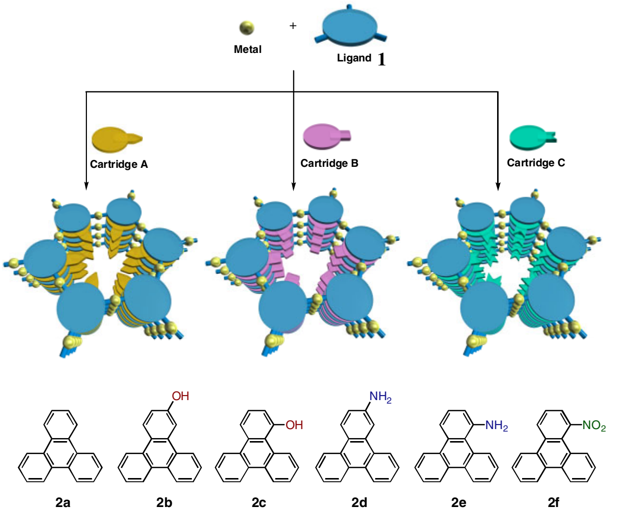

Figure 1. (a) Cartoon representation of the cartridge synthesis. (b) The library of the cartridges.

Results

The porous complex was prepared by treating triazine ligand **1** and triphenylene **2** with ZnI_2 in a nitrobenzene-methanol gradient solution and isolated as single crystals with the formula of $\{[(ZnI_2)_3(\mathbf{1})_2(\mathbf{2})]\cdot x(C_6H_5NO_2)\cdot y(CH_3OH)\}_n$ (**3**). The use of cartridge **2c** afforded another porous complex **3c** with the acidic phenolic hydroxyl group arrayed at different positions in the pore. From cartridges **2d**,**e** with 2- or 1-NH_2 group and **2f** with polar NO_2 group, complexes **3d**,**e** with a basic pore and **3f** with a p0085olar pore were formed, respectively.

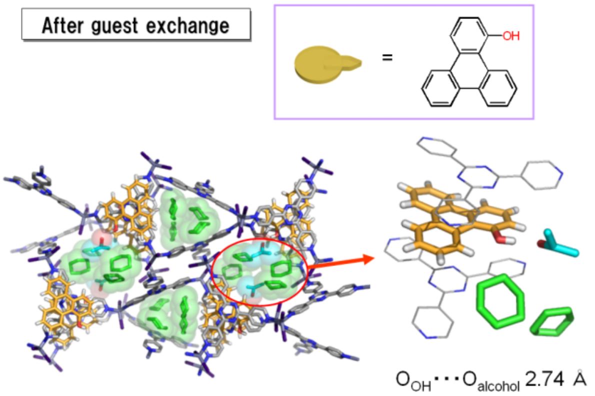

Figure 2. Crystal structure of porous coordination network, $[(ZnI_2)_3(\mathbf{1})_2(\mathbf{2c})]$ (**3c**), after guest exchange with propan-2-ol in cyclohexane.

All the complexes **3a-f** characterized by X-ray analysis have the identical porous network frameworks of $[(ZnI_2)_3(\mathbf{1})_2(\mathbf{2})]$, whose pores were filled with nitrobenzene and, in the case of **2c**, methanol. All the porous complexes **3a-f** have two distinct pores A (cylindrical) and B (trigonal prismatic). The acidic OH groups of **3c** are directed to the pore A.

Due to the acidic nature of the pore A, the guest-exchange property of **3c** strikingly differs from that of **3a** having less polar pores. The crystals of as-synthesized **3c** 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 **3c**. 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 **2c**. Such a selective uptake of propan-2-ol by pore A was not observed for **3a** because its pore A is hydrophobic; instead, cyclohexane was taken up by the pore A of **3a**. 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.

Reference

[1] M. Kawano, et al *J. Am. Chem. Soc.*, **129**, 15418-15419 (2007).

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