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Template Synthesis of Porous Polypyrrole in 3D Coordination Nanochannels

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Porous coordination polymers (PCPs), built up by self-assembly of metal ions with organic ligands, are of tremendous interest because of their diverse structures and significant functions.[1] In this area, an increasing number of papers on controlled reactions within the regular channels of PCPs have appeared recently reporting their applications in heterogeneous catalysis and ship-in-bottle synthesis.[2] Our strategy for a successful application of PCPs is polymerization of monomers within the confined PCP matrices to force polymers into unusual structures and topologies.[3] If the host PCP templates can then be carefully removed from the composites, the isolated polymers would show unique properties based on their specific nanostructures and molecular packing that are different from those of the conventional bulk polymer systems.[3b]

Templating techniques for generating porous solids have been extensively studied in materials science.[4] In particular, template synthesis of porous organic polymers has emerged as a promising subject because of the great potential of porous polymers in chromatography, sensing, and membranes.[5] Several hard matrices such as silica particles, zeolite, and mesoporous silica have been used as templates. However, in these systems, most of the polymers that are obtained after template removal are meso- or macroporous materials. Moreover, restructuring of the polymer products often results in the collapse of the porous structures during the isolation process.[5c,6] Thus, development of new templating systems for obtaining porous polymers is desired.

$[Cu_3(BTC)_2]_n$ (**1**; BTC = benzene-1,3,5-tricarboxylate) has three-dimensional (3-D) interconnected channels with the pore size of 9×9 Å^2, and can be used for reaction catalysts because of the accessible Cu(II) sites on the pore surface.[7] In this paper, we report a feasible method for providing a porous structure of polypyrrole (PPy) by oxidative polymerization of pyrrole (Py) in the 3D channels of **1** and the subsequent isolation of the resulting PPy. To date, such an approach to the synthesis of porous organic polymers using PCPs as templates has not been explored.

The oxidative polymerization of Py in **1** was performed as follows. The Py monomer was adsorbed in the channel by immersion of **1** in Py, followed by removal of excess Py external to the host crystals under reduced pressure. The inclusion compound (**1**$\supset$Py; number of Py/unit cell of **1** = 4.3) was then heated at 100 °C for 24 h under an oxygen atmosphere. In these conditions, oxidative polymerization of Py proceeded, with some cross-linkages occurring, in the framework of **1**,[8] and finally provided a black powder composite (**1**$\supset$PPy). The solid-state reflection spectrum of **1**$\supset$PPy revealed additional absorptions from 350 to 1400 nm, which are attributable to the formation of PPy in the sample (Figure 1a).[3b,9] We measured X-ray powder diffractions (XRPD) of **1** and **1**$\supset$PPy, and found that the host framework of **1** was maintained during the reaction (Figure 1b). The relative peak intensity of **1** was drastically changed before and

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(1) (a) Kitagawa, S.; Kitaura, R.; Noro, S.-i. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334–2375. (b) Ockwig, N. W.; Delgado-Friedrichs, O.; O'Keefe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2005**, *38*, 176–182. (c) Férey, G. *Chem. Soc. Rev.* **2008**, *37*, 191–214.

(2) (a) Cho, S.-H.; Ma, B.; Nguyen, S. B. T.; Hupp, J. T.; Albrecht-Schmitt, T. E. *Chem. Commun* **2006**, 2563–2565. (b) Horike, S.; Dinc, M.; Tamaki, K.; Long, J. R. *J. Am. Chem. Soc.* **2008**, *130*, 5854–5855. (c) Pan, L.; Liu, H.; Lei, X.; Huang, X.; Olson, D. V.; Turro, N. J.; Li, J. *Angew. Chem., Int. Ed.* **2003**, *42*, 542–546. (d) Wu, C.-D.; Lin, W. *Angew. Chem., Int. Ed.* **2007**, *46*, 1075–1078. (e) Alkordi, M. H.; Liu, Y.; Larsen, R. W.; Eubank, J. F.; Eddaoudi, M. *J. Am. Chem. Soc.* **2008**, *130*, 12639–12641.

(3) (a) Uemura, T.; Horike, S.; Kitagawa, S. *Chem. Asian J.* **2006**, *1*, 36–44. (b) Yanai, N.; Uemura, T.; Ohba, M.; Kadowaki, Y.; Maesato, M.; Takenaka, M.; Nishitsuji, S.; Hasegawa, H.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 9883–9886. (c) Uemura, T.; Yanai, N.; Kitagawa, S. *Chem. Soc. Rev.* **2009**, *38*, 1228–1236.

(4) (a) Schüth, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 3604–3622. (b) Boettcher, S. W.; Fan, J.; Tsung, C.-K.; Shi, Q.; Stucky, G. D. *Acc. Chem. Res.* **2007**, *40*, 784–792. (c) Liu, B.; Shioyama, H.; Akita, T.; Xu, Q. *J. Am. Chem. Soc.* **2008**, *130*, 5390–5391. (d) Yu, J.-S.; Kang, S.; Yoon, S. B.; Chai, G. *J. Am. Chem. Soc.* **2002**, *124*, 9382–9383.

(5) (a) Sozzani, P.; Bracco, S.; Comotti, A.; Simonutti, R.; Valsesia, P.; Sakamoto, Y.; Terasaki, O. *Nat. Mater.* **2006**, *5*, 545–551. (b) Wang, Y.; Caruso, F. *Chem. Mater.* **2006**, *18*, 4089–4100. (c) Thomas, A.; Goettmann, F.; Antonietti, M. *Chem. Mater.* **2008**, *20*, 738–755. (d) Johnson, S. A.; Ollivier, P. J.; Mallouk, T. E. *Science* **1999**, *283*, 963–965.

(6) Wang, Y.; Liu, Z.; Han, B.; Li, J.; Gao, H.; Wang, J.; Zhang, J. *J. Phys. Chem. B* **2005**, *109*, 2605–2609.

(7) (a) Chui, S. S.-Y.; Lo, S. M.-F.; Charmant, J. P. H.; Orpen, A. G.; Williams, I. D. *Science* **1999**, *283*, 1148–1150. (b) Schlichte, K.; Kratzke, T.; Kaskel, S. *Microporous Mesoporous Mater.* **2004**, *73*, 81–88. (c) Alaerts, L.; Séguin, E.; Poelman, H.; Thibault-Starzyk, F.; Jacobs, P. A.; De Vos, D. E. *Chem.—Eur. J.* **2006**, *12*, 7353–7363. (d) Biemmi, E.; Scherb, C.; Bein, T. *J. Am. Chem. Soc.* **2007**, *129*, 8054–8055.

(8) (a) Street, G. B. In *Handbook of Conducting Polymers*; Skotheim T., Ed.; Dekker: New York, 1986; Vol. *1*, pp. 265−291. (b) Castillo-Ortega, M. M.; Inoue, M. B.; Inoue, M. *Synth. Met.* **1989**, *28*, 65–70. (c) Saunders, B. R.; Fleming, R. J.; Murray, K. S. *Chem. Mater.* **1995**, *7*, 1082–1094.

(9) Uehara, H.; Miyake, M.; Matsuda, M.; Sato, M. *J. Mater. Chem.* **1998**, *8*, 2133–2136.

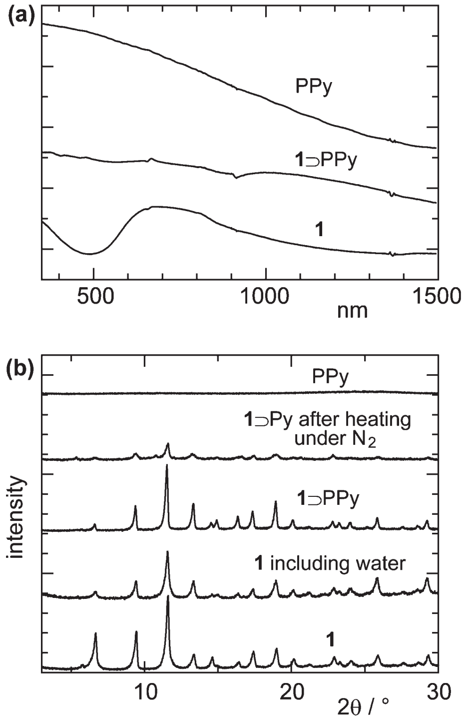

Figure 1. (a) UV−vis−NIR spectra of **1**, **1**⊃PPy, and PPy isolated from **1**⊃PPy. (b) XRPD patterns of **1**, **1** including water, **1**⊃PPy, **1**⊃Py after heating under N_2, and PPy isolated from **1**⊃PPy.

after the guest inclusions, and the peak pattern of **1**⊃PPy seems very similar to that of **1** including water in the channels.[7b] This result clearly suggests that PPy is embedded in the nanochannels of **1**, which is ascribable to the change of electron density in the pores.[10] Scanning electron microscopy (SEM) (Figure 2) and analysis of particle size distribution showed that the particle size, shape, and surface of **1** were not changed during the polymerization, showing that the oxidative polymerization of Py proceeded only inside the channels of **1**. The formation of PPy inside the channels of **1** was also confirmed by adsorption measurement, where no adsorption property of **1**⊃PPy was observed.[11] When **1**⊃Py was heated under a nitrogen atmosphere, the XRPD profile of the final product showed very weak peaks for **1** (Figure 1b) because the formation of Cu(I) induced the collapse of the host framework, as revealed by X-ray photoelectron spectroscopy (XPS). In addition, the reaction of Py under oxygen without **1** gave no product, thus the Cu(II) sites on the pore surfaces of **1** indeed worked as catalytic sites for the oxidative polymerization of Py.[8b]

Isolation of the accommodated polymer from **1**⊃PPy was performed by complete dissolution of the host framework in various basic solutions, such as ammonia (pK_b = 5.1), tetramethylethylenediamine (TMEDA; pK_b = 4.6), tetrasodium ethylenediaminetetraacetate (Na-EDTA; pK_b = 3.8), or NaOH (pK_b = 0.2),[12] which successfully gave polymeric product as a black precipitate. The XRPD measurement of the material gave only amorphous profile and did not show the contamination of **1** in the sample. IR spectrum of the product isolated from **1**⊃PPy showed characteristic peaks for the formation of neutral PPy.[8,13] To understand whether the polymer organization was retained during the isolation process, we performed SEM on the resulting PPy (Figure 2). The SEM image of the PPy isolated in ammonia solution showed that the morphology of the PPy objects is similar to those of the original host **1** and **1**⊃PPy. However, the sizes of the PPy objects became smaller as **1**⊃PPy was treated with stronger bases, which is consistent with the results of the particle size distribution measurements. It has been reported that PPy is insoluble in organic solvents, but shows a slight dispersibility in strongly basic solutions.[14] Because of this affinity, treatment of **1**⊃PPy with stronger bases tore the PPy assembly into small particles. In contrast, the organization of PPy seems to be maintained during the isolation process when using ammonia.

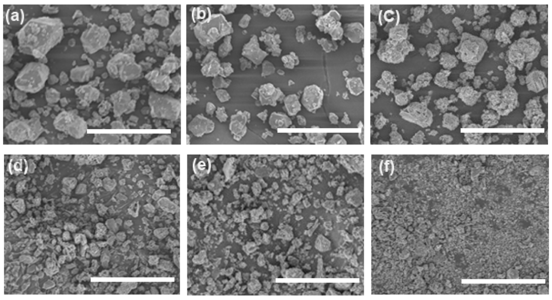

Figure 2. SEM images of (a) **1**, (b) **1**⊃PPy, and PPy isolated from **1**⊃PPy by treating with solutions of (c) ammonia (2.3 M), (d) TMEDA (1.7 M), (e) Na-EDTA (1.0 M), and (f) NaOH (1.0 M). Scale bars = 50 μm.

In this polymerization, network structure of PPy was prepared in 3D channels of **1**, and then could be isolated by removal of the host matrix. To examine the porosity of the isolated PPy material, we carried out nitrogen adsorption measurements at 77 K. A reference sample of PPy prepared in the bulk condition did not adsorb the gas because of the nonporous arrangement of PPy (Figure 3a). In contrast, the PPy materials prepared in this work clearly showed an adsorption property, and the amount of adsorption gradually increased as the weaker bases were employed for the isolation of PPy (Figure 3a). This is probably because the PPy chains were restructured to pack the space efficiently during the treatment with strongly basic solutions. In this work, the PPy isolated by ammonia exhibited the maximum adsorption ability, and the amount of adsorption was almost independent of the ammonia concentration in the isolation process. Note

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(10) (a) Uemura, T.; Kitagawa, K.; Horike, S.; Kawamura, T.; Kitagawa, S.; Mizuno, M.; Endo, K. *Chem. Commun.* **2005**, 5968–5970. (b) Marler, B.; Oberhagemann, U.; Vortmann, S.; Gies, H. *Microporous Mater.* **1996**, *6*, 375–383.

(11) (a) Moller, K.; Bein, T.; Fischer, R. X. *Chem. Mater.* **1998**, *10*, 1841–1852. (b) Uemura, T.; Kitaura, R.; Ohta, Y.; Nagaoka, M.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 4112–4116.

(12) Values of pK_b were calculated by using Marvin Sketch pK_a Plugin.

(13) Treatment of PPy with basic solutions results in dedoping of PPy. See: (a) Inganas, O.; Erlandsson, R.; Nylander, C.; Lundstrom, I. *J. Phys. Chem. Solids* **1984**, *45*, 427–432. (b) Zotti, G.; Schiavon, G.; Comisso, N. *Synth. Met.* **1991**, *40*, 309–316. (c) Gustafsson, G.; Lundstrom, I.; Liedberg, B.; Wu, C. R.; Inganas, O. *Synth. Met.* **1989**, *31*, 163–179.

(14) Gardini, G. P. *Adv. Heterocycl. Chem.* **1973**, *15*, 67–98.

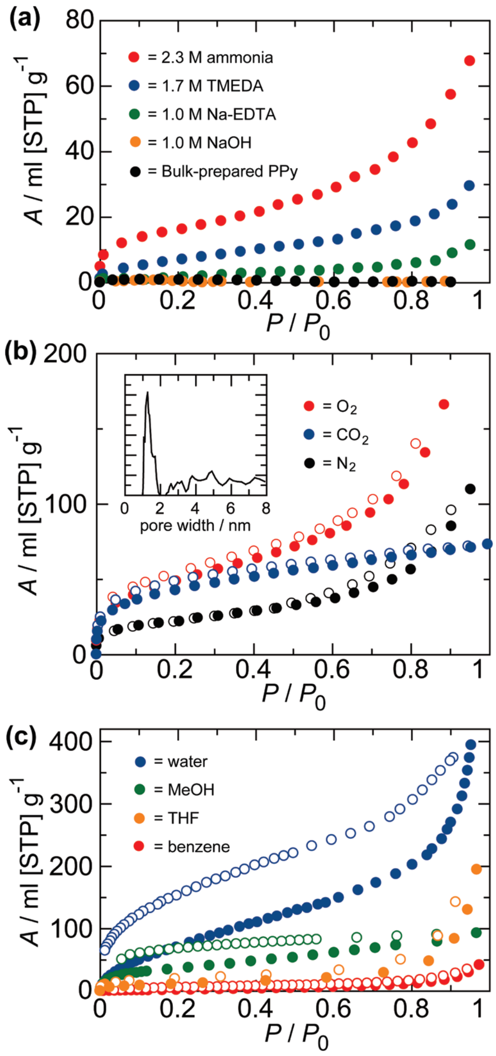

Figure 3. (a) Nitrogen adsorption isotherms at 77 K on bulk-prepared PPy and PPy isolated from **1**⊃PPy in various basic solutions. (b) Adsorption isotherms for oxygen and nitrogen at 77 K and carbon dioxide at 195 K on PPy isolated from **1**⊃PPy in 23 M ammonia. The inset shows pore-size distribution of PPy prepared in **1** using nonlocalized density functional theory, determined from N2 adsorption profile. (c) Isotherms for vapor adsorptions at 298 K on PPy isolated from **1**⊃PPy in 23 M ammonia. Filled circles = adsorption, open circles = desorption.

that treatment of the bulk-prepared PPy with ammonia solution did not improve the adsorption property, clearly supporting the template effect of **1**. The porosity of the PPy materials were not so large (BET surface area = 90 m^2/g), however, the pore-size distribution for the PPy isolated by ammonia showed a peak at 1.3 nm (Figure 3b), where this pore size might reflect the thickness of pore walls in **1** (ca. 1.2 nm). Interestingly, the porous structure of PPy obtained in our system is stable, and not affected by treatments with heating at 120 °C or some common solvents.

Detailed adsorption properties of the PPy material were examined by using the different adsorbates. In the adsorption measurement of oxygen at 77 K, the adsorption amount was much higher than that for nitrogen (Figure 3b) probably because of the specific interaction between the electron-sufficient π-conjugated system of PPy and the electron-deficient oxygen molecules.[15] The adsorption measurement of carbon dioxide at 195 K (Figure 3b) showed an increase of the adsorption amount in the low pressure range compared to that observed in the nitrogen adsorption measurement at 77 K, which would result from efficient diffusion of CO_2 molecules at higher temperature. From this adsorption profile, the BET surface area of the PPy material could be determined to be 154 m^2/g, which is larger than that obtained from the nitrogen adsorption measurement. In addition, solvent vapor adsorption measurements of the PPy material (Figure 3c) showed no adsorption of benzene; however, it showed a high affinity for hydrophilic molecules. In the isotherms of hydrophilic molecules such as water and MeOH, clear hystereses between the adsorption and desorption curves were observed, which is ascribable to the effect of the polar amine groups in the PPy structure.[16]

In conclusion, we have demonstrated a template synthesis of PPy in 3D coordination channels to give a polymer material with a certain porosity. This work has also unveiled pore functions characteristic of PPy. Recently, porous organic polymers have been the focus of much research for applications in storage and separations.[17] Our methodology has potential advantages not only for tailored design of porous structures by tuning the host matrix or preparation conditions but also for developing new porous properties based on attractive functions of polymers.

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Supporting Information Available: Detailed experimental procedures, channel structure of **1**, XPS, IR, SEM, EDX, particle size distributions, and adsorption isotherms (PDF). This materials is available free of charge via the Internet at http://pubs.acs.org.

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(15) (a) Adachi, A.; Yamauchi, J. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 811–814. (b) Pfluger, P.; Krounbi, M.; Street, G. B.; Weiser, G. *J. Chem. Phys.* **1983**, *78*, 3212–3218.

(16) Bailey, R. A.; Persaud, K. C. *Anal. Chim. Acta* **1998**, *363*, 147–156.

(17) (a) El-Kaderi, H. M.; Hunt, J. R.; Mendoza-Cortés, J. L.; Côte, A. P.; Taylor, R. E.; O'Keeffe, M.; Yaghi, O. M. *Science* **2007**, *316*, 268–272. (b) McKeown, N. B.; Budd, P. M. *Chem. Soc. Rev.* **2006**, *35*, 675–683. (c) Germain, J.; Fréchet, J. M. J.; Svec, F. *Chem. Commun.* **2009**, 1526–1528. (d) Jiang, J.-X.; Su, F.; Trewin, A.; Wood, C. D.; Niu, H.; Jones, J. T. A.; Khimyak, Y. Z.; Cooper, A. I. *J. Am. Chem. Soc.* **2008**, *130*, 7710–7720.