Effect of Organic Polymer Additive on Crystallization of Porous Coordination Polymer

Takashi Uemura,[†] Yousuke Hoshino,[†] Susumu Kitagawa,*,[†] Kaname Yoshida,[‡] and Seiji Isoda[‡]

Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Kyoto 615-8510, Japan, and Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

Poly(vinylsulfonic acid, sodium salt) (PVSA) is a polymer capable of complexing and stabilizing Cu^{2+} by electrostatic interaction, which affects crystallization of a porous coordination polymer [{Cu_2pzdc$_2$-(pyz)}$_n$] (pzdc = pyrazine-2,3-dicarboxylate, pyz = pyrazine; **1**) in the self-assembly process. It is shown that the addition of PVSA to the reaction mixtures significantly affects the nucleation process of **1**, which determines the crystal size of **1** in the range of 1−100 μm. Scanning electron microscopy, X-ray powder diffraction, and electron diffraction measurements show that PVSA controls not only the crystal size and shape but also the preferential orientation of the plate crystals, which results in alignment of the channel direction of **1** in the bulk powdery state. The N_2 adsorption measurement of each sample showed characteristic typical micropore adsorption isotherms independent of the crystal size of **1**; however, the adsorption speed for the samples showed a novel size-dependent feature because of changes in the diffusion length of N_2 in the one-dimensional channels of **1**.

Introduction

The study of coordination polymers (CPs) prepared by assembling metal complexes has been the focus of much attention because of their unique structural and physical properties.[1] In particular, precise control of crystal growth of CPs is currently a key challenge in developing them as intelligent building blocks in optical, electronic, and catalytic applications.[2] There have been several advanced studies in which template molecules such as surfactants, organic polymers, vesicles, Langmuir−Blodgett films, and self-assembled organic monolayers (SAMs) serve as fields for nucleation and/or growth of the crystallization of CPs, while controlling size, morphology, and orientation of the resulting crystals.[2] In this regard, there is a tendency to augment those studies by the use of simple inorganic CPs such as Prussian blue analogues, which is driven by their novel properties and their potentials as new magnetic, optical, and electronic materials.[3] Besides materials based on the Prussian blue family, we should note that there are many other CPs composed of organic ligands. With diverse structures and designable functionalities, these organic ligands play impor-

tant roles in the properties of CPs. However, little attention has been paid to the crystal growth control of CPs with organic ligands to date.

For CP chemistry, CPs with regular microporous channels in their metal−organic frameworks are of great interest because of their applications to ion exchange, reaction fields, gas adsorption, guest molecular alignment, and so on.[4] Construction of porous CPs with the desired crystal sizes and geometries promises not only to improve the zeolitic functions but also to open doors for new applications such as microelectronic devices. The important issues in the potentials of such materials should be unprecedented adsorption, precise guest inclusion, channel orientation, and fundamental understanding of the adsorption mechanism. For example, control of the crystal size of porous CPs enables fine-tuning of the guest diffusion process, which is very important for their adsorption, separation, and catalytic selectivity. For CP materials with one-dimensional channels, this size change is particularly useful in a number of practical applications such as modulated channel-based nanoreactors

* To whom corresponding should be addressed. E-mail: kitagawa@sbchem.kyoto-u.ac.jp.
† Department of Synthetic Chemistry and Biological Chemistry, Kyoto University.
‡ Institute for Chemical Research, Kyoto University.

(1) (a) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *202*, 1629. (b) Janiak, C. *Dalton Trans*. **2003**, 2781.
(2) (a) Uemura, T.; Kitagawa, S. *Chem. Lett.* **2005**, *34*, 132. (b) Talham, D. R. *Chem. Rev.* **2004**, *104*, 5479. (b) Vaucher, S.; Fielden, J.; Li, M.; Dujardin, E.; Mann, S. *Nano Lett.* **2002**, *2*, 225. (c) Su, C.-Y.; Goforth, A. M.; Smith, M. D.; Pellechia, P. J.; zur Loye, H.-C. *J. Am. Chem. Soc.* **2004**, *126*, 3567. (d) Hermes, S.; Schröder, F.; Chelmowski, R.; Wöll, C.; Fisher, R. A. *J. Am. Chem. Soc.* **2005**, *127*, 13744.

(3) (a) Uemura, T.; Kitagawa, S. *J. Am. Chem. Soc.* **2003**, *125*, 7814. (b) Uemura, T.; Ohba, M.; Kitagawa, S. *Inorg. Chem.* **2004**, *43*, 7339. (c) Catala, L.; Cacoin, T.; Boilot, J.-P.; Riviere, E.; Paulsen, C.; Lhotel, E.; Mallah, T. *Adv. Mater*. **2003**, *15*, 826. (d) Culp, J. T.; Park, J.-H.; Strakis, D.; Meisei, M. W.; Talham, D. R. *J. Am. Chem. Soc.* **2002**, *124*, 10083. (e) Mingotaud, C.; Lafuente, C.; Amiell, J.; Delhaes, P. *Langmuir* **1999**, *15*, 956. (f) Einaga, Y.; Sato, O.; Iyoda, T.; Fujishima, A.; Hashimoto, K. *J. Am. Chem. Soc.* **1999**, *121*, 3754.
(4) (a) Kitagawa, S.; Kitaura, R.; Noro, S.-i. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334. (b) Bradshaw, D.; Claridge, J. B.; Cussen, E. J.; Prior, T. J.; Rosseinsky, M. J. *Acc. Chem. Res*. **2005**, *38*, 273. (c) Langley, P. J.; Hulliger, J. *Chem. Soc. Rev.* **1999**, *28*, 279. (d) Rowsell, J. L. C.; Millward, A. R.; Park, K. S.; Yaghi, O. M. *J. Am. Chem. Soc.* **2004**, *126*, 5666. (e) Manspoch, D.; Molina, D. R.; Wurst, K.; Domingo, N.; Cavallini, M.; Biscarini, F.; Tejada, J.; Rovira, C.; Veciana, J. *Nat. Mater*. **2003**, *2*, 190.
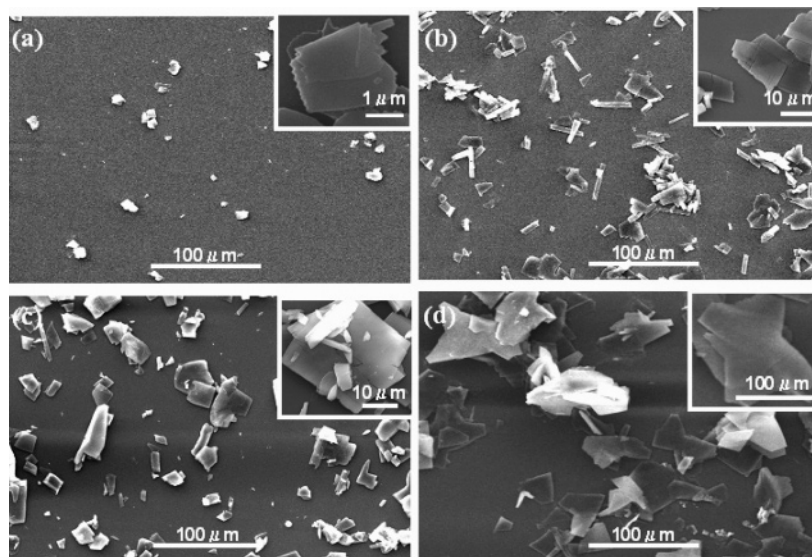
Figure 1. SEM images of **1** prepared at the condition of PVSA/Cu^{2+} = 0 (a), 1 (b), 5 (c), and 15 (d). The average sizes of the resultant crystals are 2, 14, 26, and 70 μm, respectively.

and molecular extrusion, where the channel length affects the yield, conversion, and structure of the products. In addition, depending on the crystal morphology, the porous CP crystals can act as intelligent building blocks to control the alignment of the encapsulated guest molecules in the programmed nanochannel networks, which will give novel anisotropic properties from the guest molecular assembly. Very recently, a unique nanopatterning method for porous CP crystals on SAMs, in combination with soft lithographic techniques, has been investigated;[2d] however, there have been few studies on the significance of the crystal size and the structural order of the porous CPs on the adsorption properties and their contributions.

In this paper, successful tuning of crystal growth of a porous CP and a novel size effect on the adsorption property of the resulting crystals are demonstrated. The material employed here is [{Cu$_2$pzdc$_2$(pyz)}$_n$] (pzdc = pyrazine-2,3-dicarboxylate, pyz = pyrazine; **1**) having 0.4 × 0.6 nm^2 microporous one-dimensional channels in the framework, which have been utilized for gas adsorption and molecular alignment.[5] This complex consists of a two-dimensional sheet of [{Cu(pzdc)}$_n$] and pillar pyz ligands that bridge each sheet.

Results and Discussion

Control of the crystallization of **1** is achieved by using poly(vinylsulfonic acid, sodium salt) (PVSA) as an additive reagent. PVSA should have an effective influence on the crystallization of **1** through electrostatic interaction between Cu^{2+} and the polymeric sulfonate moiety. In the usual experiment without the PVSA additive, mixing of aqueous solutions of Cu(NO$_3$)$_2$, Na$_2$pzdc, and pyz at room temperature rapidly forms powdery crystalline **1** within 30 min. In

contrast, reaction of the same mixture in the presence of PVSA (repeating unit of PVSA/Cu^{2+} = 1−15) proceeded very slowly because of the electrostatic and steric stabilization by PVSA. After leaving the mixture for 24 h and subsequent washing with water, pure crystalline **1** was obtained as a sky-blue powder and characterized by X-ray powder diffraction (XRPD) and elemental analysis.[6] X-ray photoelectron spectroscopy (XPS) analysis of the product shows no sulfur content, indicating that PVSA is not adsorbed on the surface of the powder.

Figure 1 shows scanning electron microscopy (SEM) images of the powder products. It was found that the morphology of the crystals is a two-dimensional sheet (plate crystal), and the mean size of the plates becomes larger as the amount of PVSA added increases. When **1** is prepared without PVSA, the average size of the plate crystals is 2 μm (Figure 1a). In contrast, the largest crystals with an average size of 70 μm are obtained with PVSA/Cu^{2+} = 15 (Figure 1d), indicating the remarkable effect of PVSA on the crystallization of **1**. This phenomenon is rather interesting, because the conventional route for size tuning of crystals usually exhibits the opposite behavior: higher concentrations of additives yield smaller crystals such as nanoparticles because of effective suppression of crystal growth.[3a,b,7] In this regard, the synthesis of colloidal crystals from homogeneous solutions involves two consecutive stages: formation of nuclei (nucleation stage) and growth of these nuclei (growth stage). In a supramolecular crystal growth system, crystals can grow until the reversible reaction between monomeric precursor and solid crystal reaches equilibrium. Thus, control over the nucleation process in the preparation of CPs should strongly affect the size of the final crystals.[8]

(5) (a) Kondo, M.; Okubo, T.; Asami, A.; Noro, S.; Yoshitomi, T.; Kitagawa, S.; Ishii, T.; Matsuzaka, H.; Seki, K. *Angew. Chem., Int. Ed.* **1999**, *38*, 140. (b) Kitaura, R.; Kitagawa, S.; Kubota, Y.; Kobayashi, T. C.; Kindo, K.; Mita, Y.; Matsuo, A.; Kobayashi, M.; Chang, H. C.; Ozawa, T. C.; Suzuki, M.; Sakata M.; Takata, M. *Science* **2002**, *298*, 2358. (c) Matsuda, R.; Kitaura, R.; Kitagawa, S.; Kubota, Y.; Belosludov, R. V.; Kobayashi, T. C.; Sakamoto, H.; Chiba, T.; Takata, M.; Kawazoe, Y.; Mita, Y. *Nature* **2005**, *436*, 238.

(6) Addition of PVSA over the ratio of PVSA/Cu^{2+} = 20 showed extremely slow reaction and gave an amorphous compound only after 24 h. It takes about a few weeks for this reaction mixture to give crystalline precipitates of **1**.

(7) Leff, D. V.; Ohara, P. C.; Heath, J. R.; Gelbart, W. M. *J. Phys. Chem.* **1995**, *99*, 7036.

(8) Shevchenko, E. V.; Talapin, D. M.; Schnablegger, H.; Komowski, A.; Festin, Ö.; Svedlindh, P.; Haase, M.; Weller, H. *J. Am. Chem. Soc.* **2003**, *125*, 9090.

Scheme 1. Schematic Representation for Crystal-Size-Controlled Preparation of 1
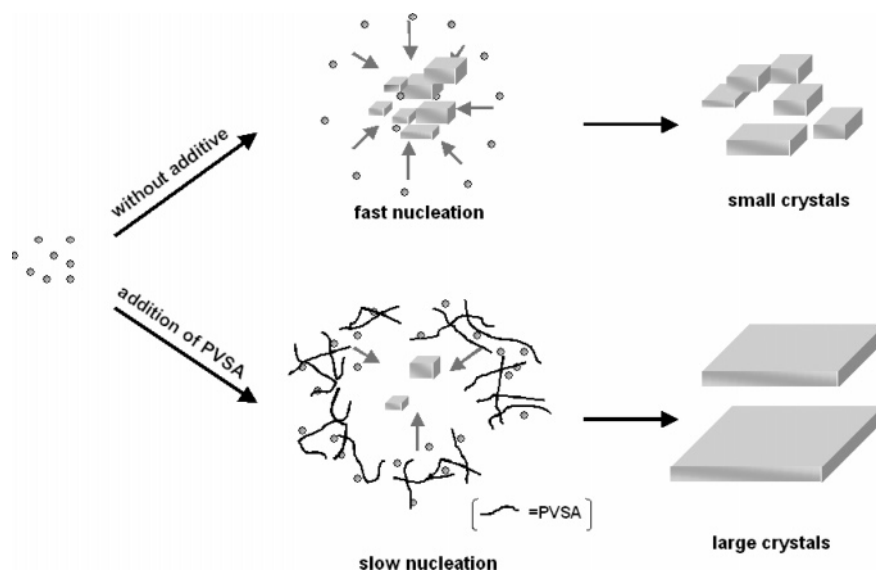
The following expression shows the crystal nucleation rate per unit volume (J_N), given by classical nucleation theory:[8,9]

$$J_N = B_N \exp\left(-\frac{\Delta G^N}{RT}\right)$$

$$\Delta G^N = \frac{16\pi\gamma^3 V_m{}^2}{3|\Delta\mu|^2}$$

where ΔG^N is the activation energy for homogeneous nucleation; γ indicates the surface tension; V_m is the molar volume of the solid; $\Delta\mu$ is the difference in chemical potential between solid and monomers; and B_N means the preexponential factor. In the preparation of **1**, PVSA forms stable polymer complexes with Cu^{2+}, which precedes the nucleation stage. This polymer complex distinctly decreases the oversaturation of the precursor monomers, resulting in a decrease in the parameter $\Delta\mu$. Hence, addition of PVSA to the reaction mixture leads to a slow rate of nucleation (fewer nuclei) and consequently provides larger crystals, as illustrated in Scheme 1.

The XRPD measurement of the plate crystals gives the typical pattern of crystalline structure **1** and shows interesting pattern changes dependent on the crystal size (Figure 2). It is observed that the diffractions corresponding to (0k0) become intense with increased crystal size, clearly representing preferential orientation of the large plate crystals. We measured the electron diffraction pattern of the crystals with an electron beam perpendicular to the plate crystal, which reveals its single crystalline nature and indicates that the direction of crystal growth is parallel to the *ac* plane (Figure 3). Because the channel direction of **1** is parallel to the *a* axis,[5] addition of PVSA in the preparation of **1** leads not only to precise change of the crystal size but also to facile alignment of channel direction even in the bulk powdery state.
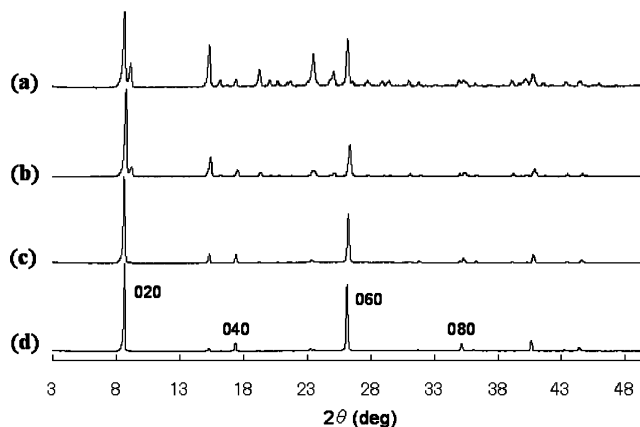
(9) (a) Sugimoto, T. *Monodisperse Particles*; Elsevier: New York, 2001. (b) Auer, S.; Frenkel, D. *Nature* **2001**, *409*, 1020.

Figure 2. XRPD patterns of plate crystals **1** with average sizes of (a) 2, (b) 14, (c) 26, and (d) 70 μm.
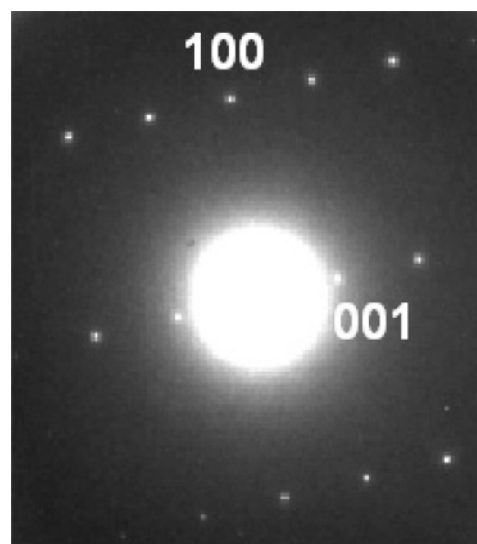

Figure 3. Electron diffraction pattern of **1** with the electron beam perpendicular to the plate crystal.

The adsorption isotherms of nitrogen on samples with various mean crystal sizes (2, 26, and 70 μm) were measured at 77 K (Figure 4b). The isotherms were characteristic of typical type I adsorption isotherms (micropore adsorption), as defined by the IUPAC classification scheme,[10] and showed
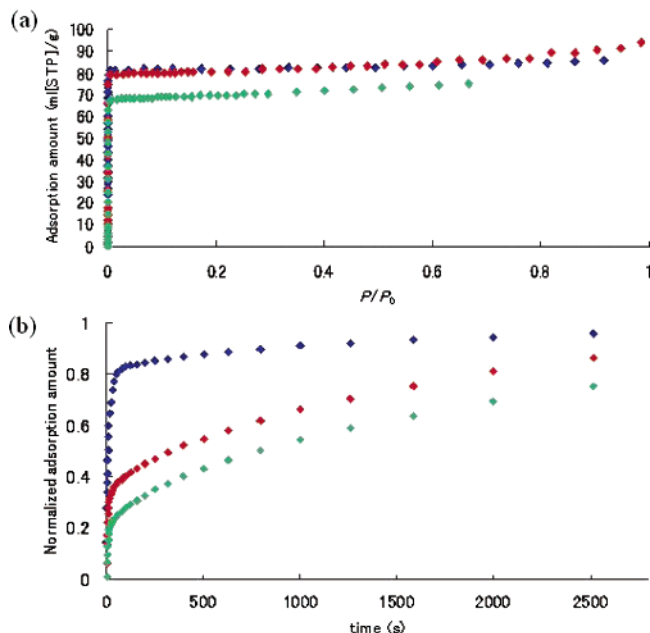
Figure 4. (a) N_2 adsorption isotherms of **1** with average sizes of 2 (blue), 26 (red), and 70 μm (green) at 77 K. (b) N_2 adsorption amount for the same samples as a function of time. In this profile, the adsorption amounts have been normalized to the saturated adsorption value. The introduction pressure of N_2 was 684 mmHg.

that the adsorption amount is independent of the crystal size of **1**.[11] However, profiles of adsorption speed for the samples showed distinct size dependence (Figure 4b). It was observed that the larger crystals of **1** showed much slower adsorption of nitrogen in the nanochannels. This result also shows that the plate crystals have fewer defect structures as single crystalline materials, and elongation of the narrow one-dimensional channels of **1** consequently leads to high resistance to gas diffusion.[12] To our knowledge, such a crystal size-dependent property of CPs composed of organic ligands has not been previously reported.

Conclusion

High-quality plate crystals of **1** with mean sizes between 2 and 70 μm were prepared in a predictable manner via addition of PVSA to the reaction mixture of metal ion and ligands sources. The resulting plate morphology allowed anisotropic depositions onto substrates to align the channel

(10) Rouquerol, F.; Rouquerol, J.; Sing, K. *Adsorption by Powders and Porous Solids*; Academic Press: London, 1999.
(11) The adsorption amount for the sample with mean crystal size of 70 μm was slightly less compared to those for the other samples, probably as a result of the long diffusion process of the large crystals.
(12) Karger, A.; Ruthven, D. M. *Diffusion in Zeolites and Other Microporous Solids*; J. Wiley & Sons, Inc.: New York, 1992.

direction of **1**. It is also noteworthy that the porous crystals of **1** showed interesting size-dependent adsorption properties, which will give useful information for practical application of the porous CPs as catalysts, membrane, and sorbents. Our strategy described here should be generally applicable to other CP systems, given the availability of a number of different ionic polymers and metal ions.

Experimental Section

Materials. All reagents and chemicals were obtained from commercial sources and used without further purification. PVSA was purchased from Aldrich as 25 wt % solution in water.

Preparation of Na$_2$pzdc. An aqueous solution (25 mL) of pyrazine-2,3-dicarboxylic acid (5.0 g, 30 mmol) and NaOH (2.4 g, 60 mmol) was stirred for 3 h, and then the solution was poured into MeOH (25 mL). The resulting white precipitate was filtrated and dried in a vacuum (3.3 g, 77%).

Growing the Crystals of 1. To the aqueous mixture (15 mL) of $Cu(NO_3)_2 \cdot 2H_2O$ (58 mg, 0.25 mmol) and PVSA (addition ratio of PVSA to Cu^{2+} = 0, 1, 5, or 15) was added an aqueous solution (15 mL) of pyz (500 mg, 6.25 mmol) and Na$_2$pzdc (54 mg, 0.25 mmol) slowly. After the mixture was left for 24 h without stirring at room temperature, the resulting precipitate was collected, washed repeatedly with water, and dried in a vacuum. Yield: PVSA 0 equiv, 43 mg (60%); 1 equiv, 32 mg (44%); 5 equiv, 30 mg (42%); 15 equiv, 23 mg (36%).

Measurement. XRPD data were collected on a Rigaku RINT 2000 Ultima diffractometer with Cu Kα radiation. XPS spectra were recorded on an ULVAC-PHI PHI 5600. SEM was performed by the use of a JEOL JSM-5600 at an accelerating voltage of 20 kV. For the SEM measurements, a sample dispersion in EtOH was dropped onto a silicon wafer and the grid was dried in air for 10 min. The mean sizes of the crystals were calculated by counting 30 crystals from the SEM images. The electron diffraction pattern was obtained by use of a JEOL JEM200FX-II at the accelerating voltage of 200 kV as a Nanotechnology Support Project of the Ministry of Education, Culture, Sports, Science and Technology. The adsorption isotherms of nitrogen at 77 K and the adsorption speed profiles were measured with BELSORP 18 volumetric adsorption equipment from Bel Japan, Inc. Dried host crystals were obtained by treatment under reduced pressure ($<10^{-2}$ Pa) at 110 °C for more than 5 h. Neither serious damage nor cracking of the crystals was observed after this treatment.