Coordinatively Immobilized Monolayers on Porous Coordination Polymer Crystals**

Mio Kondo, Shuhei Furukawa,* Kenji Hirai, and Susumu Kitagawa*

The formation of self-assembled monolayers (SAMs), whereby chemisorbed organic molecules spontaneously organize on metal or metal oxide substrates,[1] is the most developed method used to modify the interfacial properties of surfaces, such as work function and wettability, and to impart new functions, such as switching properties and catalytic reactivity. Porous coordination polymers (PCPs) or metal–organic frameworks (MOFs),[2] comprising an alternate arrangement of metal ions and bridging ligands, can be utilized as molecular-based crystalline substrates for the assembly of functional molecules on their surfaces. That use allows better tuning of their porous properties, which is advantageous for applications such as selective sorption,[3] heterogeneous catalysis,[4] and chemical sensing,[5] as the incorporation of guest molecules is influenced by the interfacial structures of PCP crystals. Herein we focus on the development of the methodology to form SAM-like monolayers on PCP surfaces and show the fabrication of a fluorescent organic monolayer on targeted surfaces of PCP crystals by taking advantage of the equilibrium state of coordination bonds.

The relatively weak interactions of coordination bonds that dominate the construction of PCPs are also useful to hybridize PCPs with other materials. There have been reports that demonstrate the direct formation of PCPs on the SAM-modified substrates.[6] In this system, the coordination moiety introduced into the SAM molecules plays a key role in determining the orientation of the crystal growth. Moreover, the coordination equilibrium between the metal precursor and the SAM has a significant impact on the initiation of

nucleation of PCP crystals on the surface.[7] The lability of coordination bonds is such that within a PCP material, in which the ligands participate in the construction of the crystalline framework, bond cleavage or ligand exchange reactions triggered by chemical or physical stimuli can occur and have been characterized, despite the diffusion and confinement restrictions of the porous structure.[8] The surfaces of such materials once in solution will be extremely sensitive to the coordination equilibrium, whereby the organic ligand and solvent molecules compete to terminate the surfaces by coordination bonds.[9] When appropriate postsynthesis reaction media have been found, that is, the crystals do not degrade and the reactivity of the crystal surfaces is preserved, the use of the coordination equilibrium then allows specific and selective functionalization of the surfaces by desirable organic molecules provided that the latter have the same coordination ability (Figure 1a).
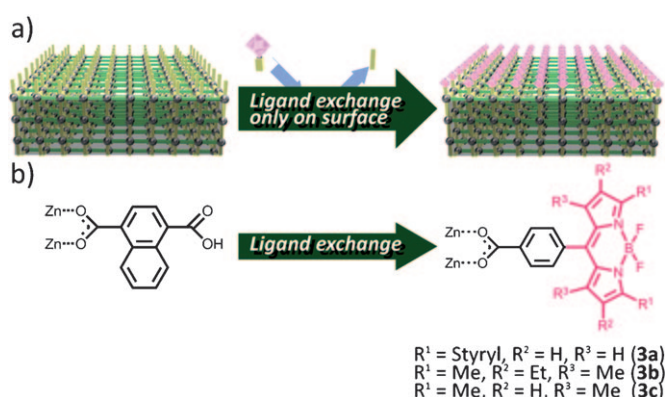

Figure 1. a) Surface modification process, and b) ligand-exchange reaction with BODIPY dyes (**SL1–3**).

Unlike the "PCP-on-PCP" (or "MOF-on-MOF") concept that we recently demonstrated, in which the epitaxial growth of the shell crystal requires the careful choice of bridging ligands to laterally match the lattice distances at the interfaces between two crystals,[10] the formation of an organic monolayer allows the free choice of functional molecules by a simple ligand-exchange reaction involving coordination bonds on the crystal surface alone. Our strategy to decorate the crystal surface differs from a few pioneering studies on surface modifications of zeolites[11] and PCPs,[12] as we take advantage of the formation of coordinatively immobilized monolayers (CIMs) instead of the immobilization of functional molecules through covalent bonds. Unlike SAMs on metal substrates, the assembled structure of CIMs is most

[*] Dr. M. Kondo, Dr. S. Furukawa, Prof. S. Kitagawa
Institute for Integrated Cell-Material Sciences (iCeMS)
Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501 (Japan)

Dr. S. Furukawa, Prof. S. Kitagawa
ERATO Kitagawa Integrated Pores Project
Japan Science and Technology Agency (JST)
Kyoto Research Park Bldg #3, Shimogyo-ku, Kyoto 600-8815 (Japan)
E-mail: shuhei.furukawa@kip.jst.go.jp

K. Hirai, Prof. S. Kitagawa
Department of Synthetic Chemistry & Biological Chemistry
Graduate School of Engineering, Kyoto University
Katsura, Nishikyo-ku, Kyoto 615-8510 (Japan)
E-mail: kitagawa@sbchem.kyoto-u.ac.jp

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likely determined by the lattice structure of PCPs, directly assisted by coordination bonds with metal ions at the lattice points.

A series of tetragonal frameworks, $[\{Zn_2(bdc)_2(dabco)\}_n]$ (**F1**) and $[\{Zn_2(ndc)_2(dabco)\}_n]$ (**F2**), (bdc = 1,4-benzenedicarboxylate, ndc = 1,4-naphthalenedicarboxylate, dabco = 1,4-diazabicyclo[2.2.2]octane), in which two different coordination bonds—namely zinc–carboxylate and zinc–amine—participate to construct the framework, was selected as substrate PCP crystals.[13] Both **F1** and **F2** exhibit rectangular prism morphology. Four surfaces are terminated by zinc–carboxylate bonds, denoted as the {100} surfaces, and the other two surfaces are terminated by zinc–amine bonds, denoted as the {001} surfaces. Because the metal–carboxylate coordination bonds participate in constructing most PCPs, the {100} surfaces were targeted to emphasize the applicability of our concept. The well-known fluorescent dye, boron dipyrromethene (BODIPY),[14] as shown in Figure 1b, was chosen as the functional organic moiety for detecting the formation of CIMs on PCP crystals by using confocal laser scanning microscopy (CLSM).

The reaction conditions (temperature, concentration of BODIPY dyes, and soaking time) to modify the crystal surfaces were optimized to avoid the degradation of the crystals. More moderate conditions than that for the synthesis of **F2** (120°C, 48 h) were therefore applied, and it is known that the ligand-exchange reaction of the zinc paddlewheel units could proceed even in such moderate conditions, as previously described in the synthesis of PCPs composed of the zinc paddlewheel units by liquid-phase epitaxy[6f].

On the basis of this strategy, the ligand-exchange reactions with the BODIPY dyes with carboxylic acid moieties (denoted surface ligands **SL1–3**; Figure 1b) on the surfaces of **F1** and **F2** were performed according to the following procedure. Single crystals of **F1** or **F2** were immersed in 0.05 mM solutions of BODIPY dyes (**SL1–3**) in dehydrated DMF for 3 h at 45°C, and then washed with dehydrated DMF 10 times. The PCP crystals were also treated with BODIPY dyes without a coordination moiety as references (denoted reference ligands **RL1–3** as shown in Schemes S1 and S2 in the Supporting Information).

The results of the CLSM studies shown in Figure 2 demonstrate that the surface-modified PCP crystals (denoted surface ligand/framework **SL1/F2**) exhibited emission only at the crystal surfaces by excitation at 635 nm, whereas the crystals treated with **RL1** exhibited no fluorescence (Figure S1 in the Supporting Information). The fluorescence spectra of **SL1/F2** under the CLSM conditions (obtained at the red area in Figure 2) correspond to that of **SL1** in DMF as shown in Figure 3a, which indicates that the fluorescence obtained under the microscope originated from the BODIPY dye **SL1**.

Note that two different crystal orientations of **SL1/F2** were observed under CLSM conditions (Figure 2). Horizontally sliced CLSM images of one of the crystal orientations at two different focal points are shown in Figure 2a. Whereas no fluorescence was detected in the sliced image at the focal point $z = A$ (the bottom of the crystal), slicing at the focal point $z = B$ (the middle of the crystal) gave an image with
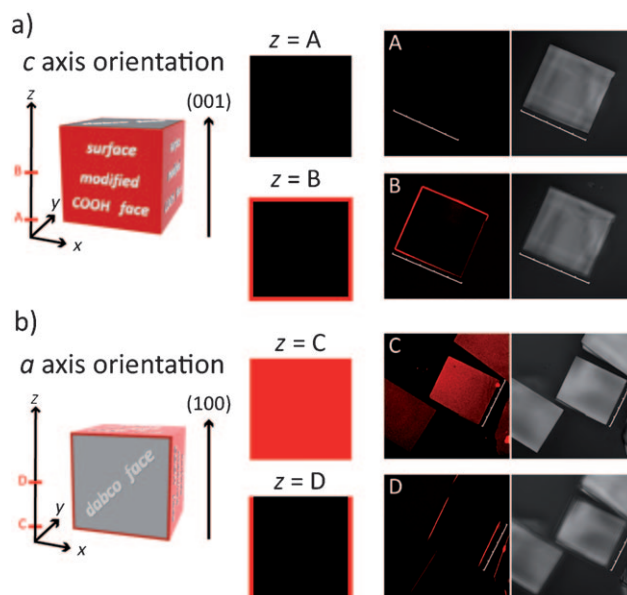

Figure 2. Representations of surface-modified crystals (left), CLSM images (middle) and transmission images (right) of **SL1/F2** at $z = A$ and $z = B$ in a) the *c* axis orientation and b) the *a* axis orientation. Scale bars: A, 180 μm; B, 190 μm; C, 130 μm; D, 130 μm.
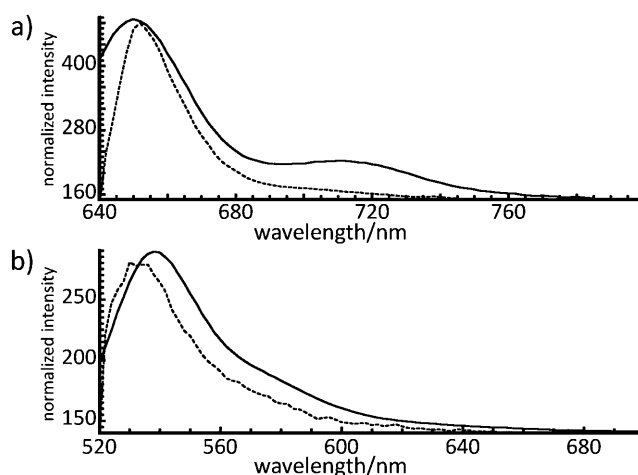

Figure 3. Fluorescence spectra of a) **SL1** in DMF (solid line) and **SL1/F2** under the CLSM conditions (dashed line) and b) **SL2** in DMF (solid line) and **SL2/F3** under the CLSM conditions (dashed line).

fluorescence at four sides of the crystal. The other orientation shown in Figure 2b exhibited a different trend—fluorescence at the whole face of the crystal at the focal point $z = A$, and fluorescence at only two sides at the focal point $z = B$. In both orientations, four surfaces of the crystals had intense fluorescence due to the BODIPY dye (**SL1**).

Because of the tetragonal crystal system, only four {100} surfaces of the crystal have zinc–carboxylate coordination bonds in the [100] direction, in which the ligand-exchange reaction with **SL1** can take place. To elucidate the modified surfaces of **SL1/F2**, face index analysis as the same crystal investigated by CLSM was carried out by using a single-crystal X-ray diffractometer. Indeed, the four surfaces

modified with BODIPY dyes were identified as the {100} surfaces and the remaining two surfaces without modification as the {001} surfaces. Hence, the BODIPY dye with a monocarboxylic acid moiety (**SL1**) recognizes the {100} surfaces of the tetragonal PCP crystal (**F2**) and is immobilized by a ligand-exchange reaction only on these surfaces. A similar tendency, namely that the BODIPY dyes (**SL1–3**) recognize the {100} surfaces of **F1**, leading to the formation of the surface modified PCP crystals (**SL1–3/F1**), was observed (Figures S3–11 in the Supporting Information).

The change of surface morphology upon surface modification was investigated by atomic force microscopy (AFM) as shown in Figure 4. Figure 4a shows a topographic image of
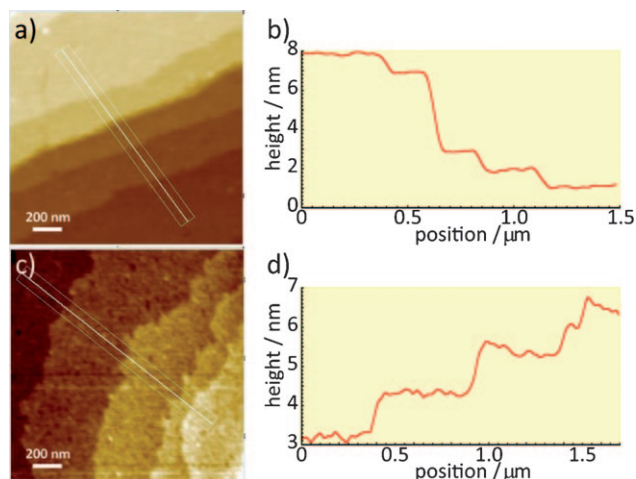

Figure 4. AFM images of the (100) surfaces of a) **F2** and c) **SL1/F2**. Averaged topographic profiles of the selected parts (indicated as white boxes) of the (100) surfaces of b) **F2** and d) **SL1/F2**.

the (100) surface of the bare crystal (**F2**). The step-edge structure with the height (about 1 nm) corresponding to the length (1.09 nm) of the *a* axis[13] clearly reveals the atomically flat nature of the (100) surface. Surprisingly, the surface of the modified crystal **SL1/F2** still maintained a similar step-edge structure with the corresponding step height, even though the morphology of the step-edge structure changed into an obscure feature, and the terraces became rather rough. The step structure observed in the modified crystal indicates the formation of a highly uniform monolayer of **SL1** without aggregation because the chemical structure of **SL1** does not induce the stable formation of uniform multilayers. Therefore, it is suggested that the monolayer of BODIPY dyes is most likely fabricated on the {100} surface of the PCP crystal.

To confirm the general applicability of our method, crystal surface modification of [{Cu₃(btc)₂}ₙ],[15] (HKUST-1, **F3**), (btc=1,3,5-benzenetricarboxylate) was also performed. The framework **F3** has a cubic crystal system $Fm\bar{3}m$, in which the paddlewheel-type Cu₂ dimer units are connected by btc ligands. The crystal structure of **F3** exhibits regular octahedral morphology, and all the surfaces are denoted as the {111} faces terminated by btc ligands,[6e] which should have a similar surface structure to the {100} surfaces of **F1** and **F2**. The

surface modification of **F3** was performed according to the following procedure. Single crystals of **F3** were immersed in 0.5 mm solutions of BODIPY dyes (**SL2**) in methanol for 20 h at 60 °C, and then washed with dehydrated DMF 10 times. A higher concentration of BODIPY dye, higher reaction temperature, and longer reaction time than were used for the Zn-based tetragonal frameworks were required to promote the ligand-exchange reaction. These harsher reaction conditions are required because copper–carboxylate coordination bonds are stronger than zinc–carboxylate bonds. The CLSM sliced images (Figure 5) at different heights, and the fluorescence spectrum of **SL2/F3** under the microscope
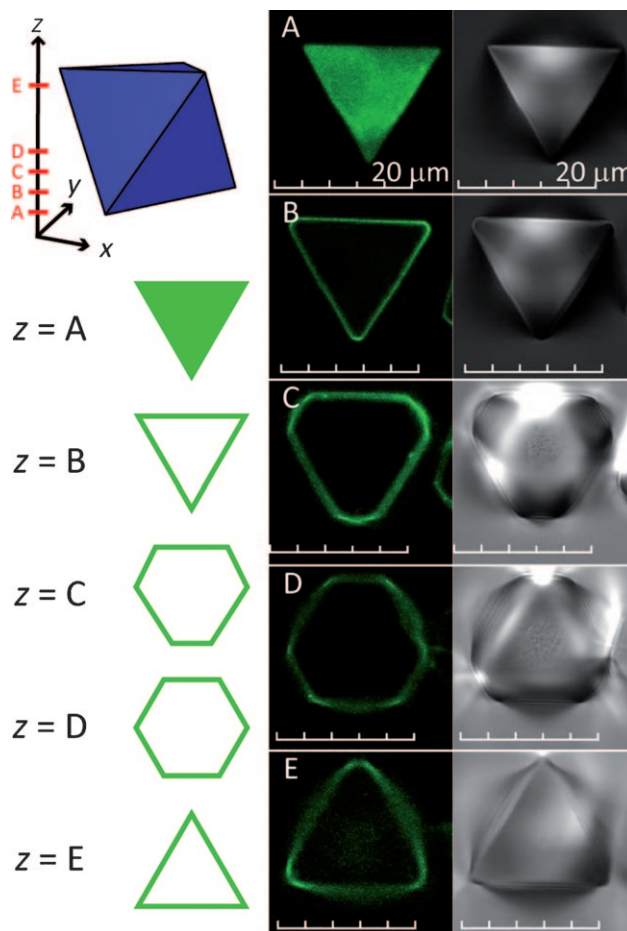

Figure 5. Representations of surface-modified crystals (left), CLSM images (middle), and transmission images (right) of **SL2/F3** at *z*=A–E. The sequential slicing images from the bottom of crystal (at *z*=A) to the top of crystal (at *z*=E) reveal the octahedral crystal morphology of **F3**.

(Figure 3b and Figure S12 in the Supporting Information) indicated that all the crystal surfaces of **F3** were eventually covered and that the dye molecules were not incorporated into the pores. These results clearly reveal that the coordinatively immobilized monolayer can be constructed on the various surfaces of PCP crystals terminated by reactive carboxylate ligands.

In conclusion, we provided the first clear evidence for the formation of monolayers assisted by coordination bonds with the immobilization of dyes on PCP single-crystal surfaces. The key to ensuring that the reaction only takes place on crystal surfaces is the dynamic nature of PCP crystal surfaces, namely, coordination equilibria. The versatility of this method was confirmed by using three different functional ligands with two crystal systems. Moreover, the reaction conditions can be modified depending on the strength of the coordination bonds between the metal ions and the carboxylates. This versatility enables this methodology to be expanded to a variety of PCP crystals constructed on the basis of metal–carboxylate coordination interactions. The present study will open the way to fabricating the functional PCP crystal surfaces on which precisely controlled gating or sensing properties with fluorescence (fluorescence sensing) can be integrated.

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