Surface molecular architecture : Highly crystalline metal-organic framework nanofilms assembled by Langmuir-Blodgett and layer-by-layer methods

The recent remarkable research activities and interest in new metal-organic frameworks (MOFs), porous coordination polymers (PCPs) or related porous hybrid solids arising from the virtually unlimited structural possibilities involving combinations of inorganic and organic building components have implications for general fundamental crystal growth techniques and for a number of potential applications in a wide range of fields from materials science to life science. In many cases of the targeted synthesis of polycrystalline or single-crystalline bulk MOFs using solvothermal reactions, the desired structures with well-defined pores were generated following rational molecular design routes, strategic choice of the combination of molecular components based on coordination chemistry knowledge and exploration of reaction conditions. On the other hand, controlling the size of porous objects at the nanoscale and aligning such objects on/with various substances in certain desired ways (e.g., sequentially layered on top of each other, patterned on surfaces) has remained a challenge that needs to be addressed, especially when we consider that such thin-film architectures are necessary for applications of these porous materials in nanotechnological devices. In addition, understanding the roles played by the nanoscale size and by the interfacial conditions in integrated systems in defining the properties of such porous solids can lead to the optimization of their potential functionalities.

Here, we introduce our recent study on the facile bottom-up fabrication at ambient temperature of a perfect preferentially oriented MOF nanofilm on a solid surface (NAFS-1), consisting of metalloporphyrin building units [1,2]. The construction of NAFS-1 was achieved by an unconventional integration in a modular manner of a layer-by-layer growth technique coupled with the Langmuir-Blodgett (LB) method. NAFS-1 is endowed with highly crystalline order in both the out-of-plane and in-plane orientations relative to the substrate, as demonstrated by synchrotron X-ray surface crystallography.

The fabrication strategy we developed is based on the principle of attempting first to prepare well-ordered 2D arrays of the desired building blocks on liquid surfaces by the LB method. In this way, we were able to remove any influence of the solid substrate on the in-plane molecular arrangement – such an influence can be of paramount (and often detrimental) importance when conventional epitaxial growth techniques on solid surfaces are undertaken. Having fabricated ordered monolayers at the air-water interface, these can then be deposited on appropriate substrates and sequentially stacked by following an LbL growth protocol (Fig. 1). We selected as the molecular component in our attempted formation of 2D arrays the CoTCPP metalloporphyrin (5,10,15,20-tetrakis(4-carboxyphenyl) porphyrinato-cobalt(II)) together with a source of copper(II) ions to serve as secondary building units and pyridine (py) as a coordination-saturating ligand (CoTCPP-py-Cu). The fabrication protocol was initiated by spreading a solution of CoTCPP and py onto an aqueous solution of $CuCl_2 \cdot 2H_2O$ at room temperature. The 2D array of CoTCPP-py-Cu formed on the liquid surface was transferred to the solid substrate at room temperature. The substrate with the CoTCPP-py-Cu sheet was then rinsed with flowing distilled water, immersed in distilled water for 3 min, and finally dried by blowing nitrogen. To stack additional layers, CoTCPP-py-Cu monolayers

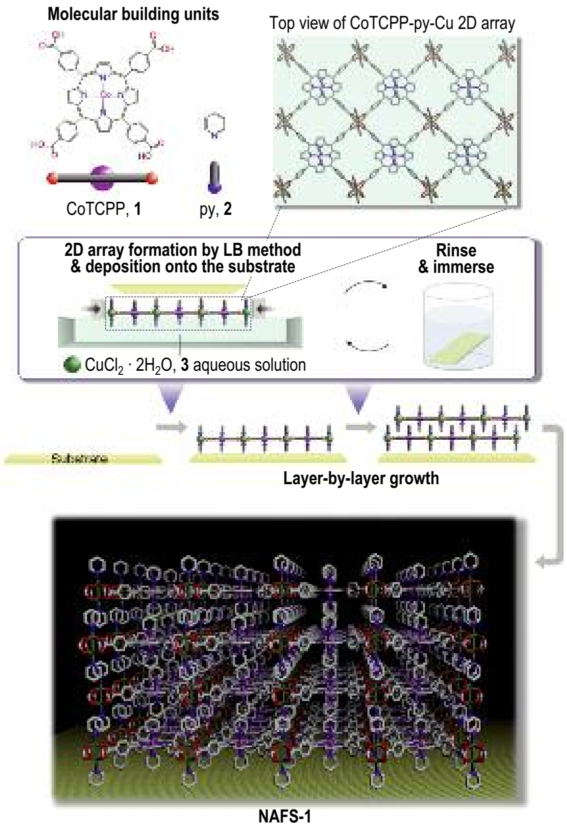

Fig. 1. Schematic illustration of the fabrication method of NAFS-1. The solution mixture of 5,10,15,20-tetrakis(4-carboxyphenyl) porphyrinato-cobalt(II) (CoTCPP), **1** and pyridine (py), **2** molecular building units is spread onto $CuCl_2 \cdot 2H_2O$ **3** aqueous solution in a Langmuir trough. Pressing the surface with barrier walls leads to the formation of a copper-mediated CoTCPP 2D array (CoTCPP-py-Cu) (LB method). The 2D arrays are deposited onto the substrate by the horizontal dipping method at room temperature. The substrate is then immersed in the pure solvent to remove excess starting materials or physisorbed components and dried. The repetitive process of successive sheet deposition and rinsing/solvent immersion leads to the sequential layer-by-layer growth of NAFS-1 with any desired thickness.

on the subphase were repeatedly transferred onto the substrate. The number of layers deposited is controlled by the number of cycles of sheet deposition and rinsing/solvent immersion/drying. The successive LbL growth procedure of NAFS-1 was monitored by UV-vis spectroscopy [1,2]. The linear increase in the absorbance of the CoTCPP Soret band indicates that roughly the same amount of CoTCPP is deposited in each step of the layer stacking protocol.

Detailed insight into the crystallinity, preferred orientation and homogeneity of the fabricated NAFS-1 films was obtained by synchrotron X-ray (λ = 1.554 Å) diffraction, carried out in two different scattering geometries – out-of-plane mode, which is sensitive to the lattice parameter in the growth direction, and in-plane (grazing incidence) mode, which is sensitive to the in-plane lattice dimensions. Figure 2 shows the XRD pattern recorded in the out-of-plane geometry for NAFS-1 with 20 stacking cycles fabricated on a Si(100) substrate. Three diffraction peaks are observed, revealing the highly oriented nature of the material. They can be indexed as (001), (002), and (003), leading to a 0.9380(3) nm interlayer spacing. Figure 3(a) shows the in-plane XRD pattern for the NAFS-1 sample measured at an incident angle α = 0.1°. Seven diffraction peaks are observed up to a scattering angle 2θ of 45° and index as (110), (200), (320), (400), (330), (440), and (550)/(710) on a metrically tetragonal unit cell with basal plane dimensions, $a = b = 1.6460(3)$ nm. An important point to note here is that none of the Bragg reflections observed in grazing incidence geometry coincides with any of the peaks measured in the out-of-plane XRD pattern and that all the in-plane XRD peaks indexed as (hk0) – no (hkl) ($l \neq 0$) reflections are present. This signifies not only that NAFS-1 is characterized by highly crystalline order in the in-plane orientation but also that it grows in a perfect preferentially oriented directionally controlled manner. Our structural model for NAFS-1 consists of a 2D "checkerboard" motif of CoTCPP units linked by binuclear $Cu_2(COO)_4$ paddle-wheels for each stacked sheet (Fig. 3(b)). In the NAFS-1 structural model, two monodentate pyridine molecules axially coordinate to both the copper dinuclear block and CoTCPP to complete the coordination sphere and retain two-dimensionality (Fig. 3(c)). As shown in Fig. 3(a), the simulation of the in-plane XRD pattern (including only (hk0) peaks) is in excellent agreement with experiments for this structural model. We expect that the versatility of the solution-based growth strategy presented here will enable the fabrication of various well-ordered MOF nanofilms, the way for their use in a range of important applications.

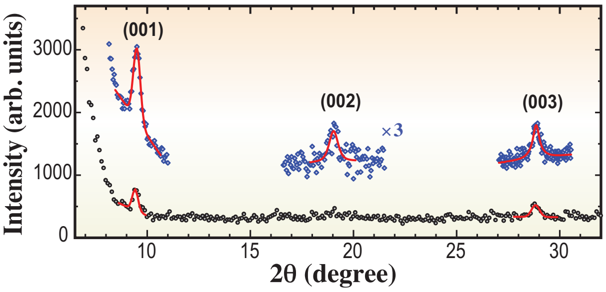

Fig. 2. Out-of-plane synchrotron XRD patterns of NAFS-1. Observed (solid circles) and fitted (red solid line) out-of-plane synchrotron X-ray diffraction profiles (λ = 1.554 Å) for an NAFS-1 thin film (20 deposition cycles) on a Si(100) substrate. The inset shows additional higher statistics fine scans collected in the vicinity of the three diffraction peaks.

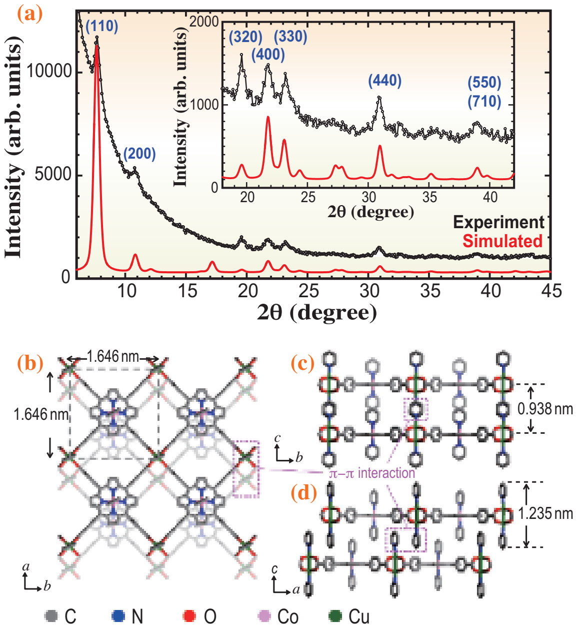

Fig. 3. In-plane synchrotron XRD patterns and the derived structural model for NAFS-1. **(a)** Observed (solid circles) and calculated (red line) in-plane synchrotron X-ray diffraction profiles (λ = 1.554 Å) for a NAFS-1 thin film (20 deposition cycles) on a Si(100) substrate. **(b)** Basal plane projection of the proposed crystalline structure for NAFS-1. **(c, d)** Schematic diagrams of the proposed crystalline structure for NAFS-1 viewed along the *a*- and *b*-axes, respectively. The interdigitated layer stacking can be driven by attractive π–π interactions between adjacent Cu^{2+}-coordinated pyridine molecules that protrude from the 2D sheets.

Rie Makiura[a,b,*] and Hiroshi Kitagawa[b,c]

[a] Nanoscience and Nanotechnology Research Center,
Osaka Prefecture University
[b] JST-CREST
[c] Division of Chemistry, Kyoto University

*E-mail: r-makiura@21c.osakafu-u.ac.jp

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