



Experiment title: Structural study of the formation of molecular nano-assemblies at the liquid/air interface by in-situ surface X-ray crystallography

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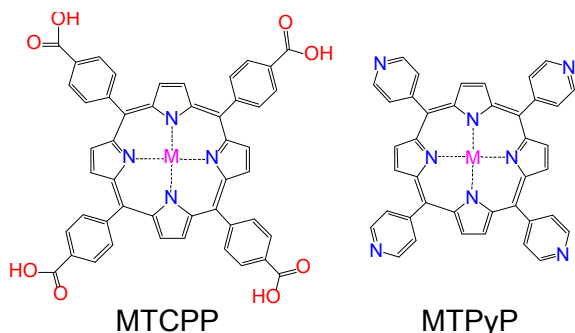
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Abstract. The structure and formation process of highly-ordered molecule-based nano-assemblies at the liquid/air interface were studied by *in-situ* grazing-incidence X-ray diffraction (GIXRD) and X-ray reflectivity (XRR). Observation of a number of Bragg reflections in the GIXRD profiles of porphyrin-based metal-organic framework (MOF) nanosheets unambiguously demonstrated the formation of highly-ordered square lattice assemblies as soon as the porphyrin building units were spread on the subphase which included the metal-ion linkers. Surface compression did not affect the square lattice arrangement but led to an increase in surface roughness and a decrease in sheet domain size. Slow surface reaction protocols using a solution-diffusion technique and a change in the coordinative parts of the molecular building units (from carboxylate to pyridyl groups) led to successful enlargement of the sheet domain size.

Scientific background and aim. The rational design and construction of functional molecular assemblies whose structures are finely controlled at the nanoscale represent key objectives of modern materials science and a key challenge for creating future nanodevices. MOFs, which are highly crystalline porous coordination polymers, have attracted considerable attention because they exhibit various unique properties in the bulk-crystal state such as enhanced gas sorption, molecular separation and catalysis associated with their highly regularized pores. To utilize MOFs or related molecule-based materials in nanotechnological devices such as sensors and catalysts, attempts to grow them in the film state on solid substrates have been actively pursued. We have reported a solution-based film fabrication technique involving the Langmuir Blodgett method, which resulted in a highly-crystalline preferentially oriented MOF nanofilm (NAFS-1) for the first time. However, this was achieved from non-optimal fabrication conditions. Although the new method has emerged as a very promising easy-to-generalise nanofilm growth technique, we lack information about the formation mechanism of the nanostructures in the solution-based processes. Therefore, the aim of the current experiments was to initiate a study of the detailed structure and formation process of molecule-based nanoassemblies, including MOFs by *in-situ* XRD crystallography at the liquid/air interface.

Experimental. An X-ray energy of 8.003 keV was selected. A Vantec detector was used for the XRR measurements and a Gabriel 1D detector with a solar slit collimator was employed for the GIXRD scans. A typical procedure of preparing MOF sheets involved filling the Langmuir trough (W 170 × L 460 × D 5 mm³), set on the goniometer stage with a double antivibration system, with pure water or a copper nitrate aqueous solution. Solutions containing selected molecular building units were spread onto the subphase and the surface pressure was monitored by a filter paper. A barrier was set on the opposite side of the trough to the immersed filter paper and the barrier compression speed was 500 μm/sec. The trough was covered with an acrylicglass–polyimide case and water-vapour-saturated helium gas was introduced into the case. Before each XRR/GIXRD measurement, height alignment was carried out. Collection times for the XRR measurements were 2-10 s/step. GIXRD measurements were performed using 20 steps of 0.01-0.04° and collection time of 10 s/step.

Results and Discussion. An aqueous Cu(NO₃)₂·3H₂O solution was used as the source of metal-ion linkers and introduced into the LB trough as a subphase. Porphyrin derivatives (MTCPP and MTPyP, M = transition metal ion) were chosen as molecular building units and spread onto the subphase. The surface pressure (π) vs molecular area (A)



evident. Further compression resulted in the image occupied by a large sheet which remained stationary during the image collection (Fig. 1(e)). Evolution of the GIXRD profiles with π variation at the liquid/air interface is shown in Fig. 2(f). Bragg reflections indexed as (hk) for a square lattice are observed even at low π conditions, implying that the highly-ordered 2D sheets are formed immediately after spreading the MTCPP solution onto the subphase containing the metal ion linkers without surface pressing. At higher surface pressures, the peaks become broader with increasing surface pressure. This GIXRD profile evolution implies that the surface compression not only gathers the sheet domains pre-formed at the early stage of the experiments to a smaller area, but also forces sheets to come to contact, even resulting in a decreasing domain size at the microscopic level.

In order to achieve enlarged crystalline domain sizes of the MOF sheets, we employed a slow solution-diffusion technique – the MTCPP solution was first spread on a pure water subphase, then a concentrated copper ion solution was injected from the corner of the trough. GIXRD profiles collected for the pure water subphase after spreading MTCPP molecules showed no peaks (Fig. 2, bottom). On the other hand, a number of Bragg reflections appeared in the profile after the metal ion injection (Fig. 2, top) with all their positions identical to those of the MTCPP-Cu sheet fabricated by the conventional method (Fig. 2(f)). Importantly, the FWHM of the peaks observed for the sheets formed by the diffusion technique (0.23° for (110)) is significantly smaller than that of the sheets fabricated with the conventional technique (0.35°), implying successful enlargement of the crystalline domain size of the MOF sheets by a factor of ~ 2 .

In the case of employing MTPyP as a molecular building unit together with Cu^{2+} ion linkers, the measured GIXRD profiles revealed that the MTPyP-Cu sheet formed is also highly ordered with a square lattice, but with peaks significantly sharper than those of the MTCPP-Cu sheets (Fig. 3). The FWHM of the most intense (110) reflection is $\sim 0.08^\circ$, identical to the resolution limit of the experimental setup and implying a sheet domain size of at least 100 nm – this is much larger even than that of MTCPP-Cu fabricated by the diffusion method. Structural studies using the higher resolution setup available on ID10 are needed to allow us to probe further the growth of these 2D nanosheets – this is very important issue as notable emphasis in this field is placed towards achieving enlarged sheet sizes approaching the micrometer scale.

isotherm of a MTCPP-Cu MOF nanosheet is shown in Fig. 1(a). Sheet formation and morphology were followed by Brewster angle microscopy (BAM) installed in the ID10 chemistry laboratory (Fig. 1(b)-(e)). A BAM image collected after spreading the MTCPP solution without compression shows some sheet domains (Fig. 1(c)). Enlarged sheets were observed after surface compression to $\pi = 1$ mN/m (Fig. 1(d)) and continuous movement of the sheets was

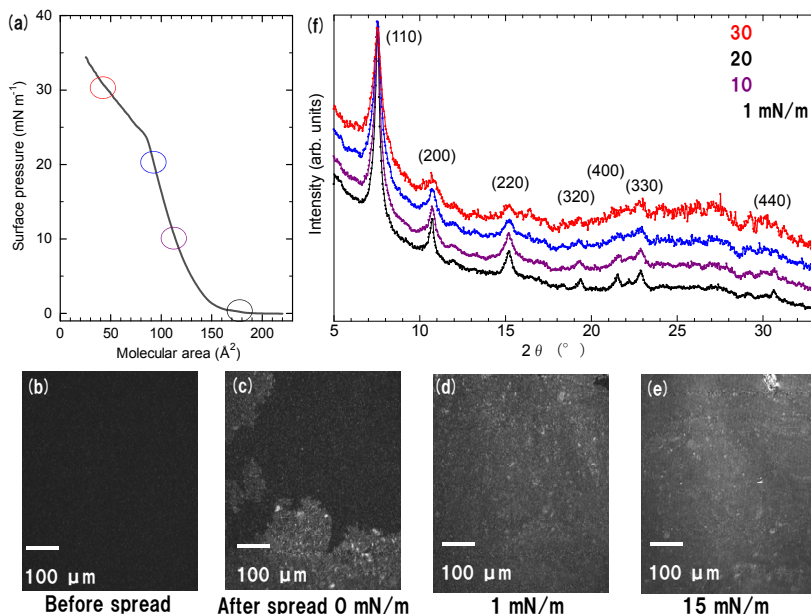


Fig. 1 Structural evolution of the MTCPP-Cu MOF sheets. (a) π -A isotherm. (b)-(e) BAM images. (f) Evolution of the GIXRD ($\lambda=1.549$ Å) profiles with change in surface pressure.

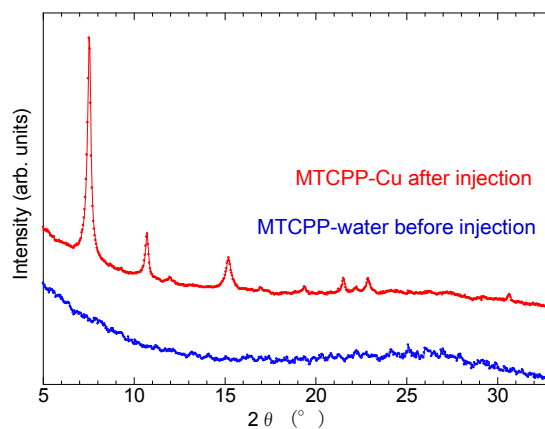


Fig. 2 GIXRD profiles of the MTCPP-Cu sheets formed by the metal ion diffusion method.

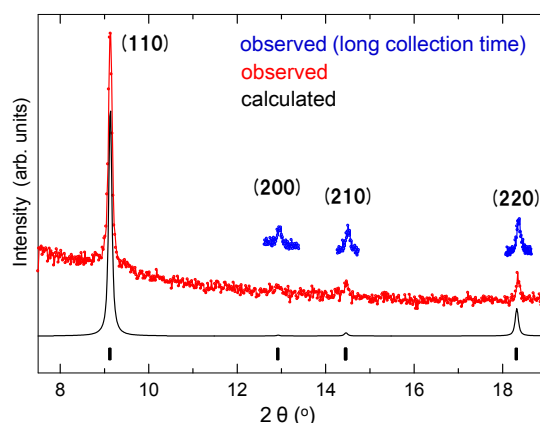


Fig. 3 GIXRD profiles of the MTPyP-Cu nanosheets at the liquid surface.