

## Supplementary Information

### Bottom-up assembly of ultrathin sub-micron size metal-organic framework sheets

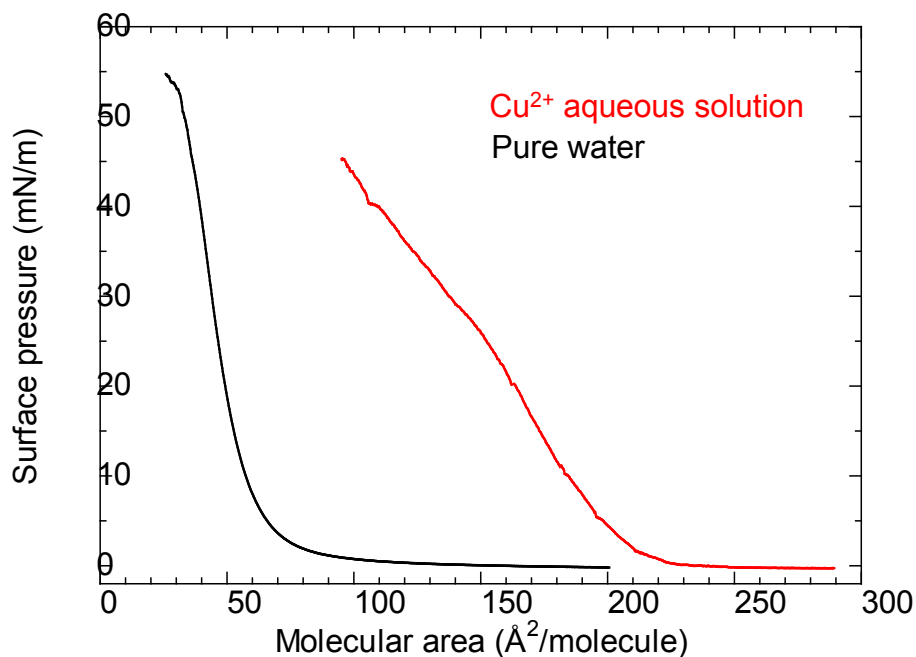
**Rie Makiura<sup>a, b, c \*</sup>, Oleg Konovalov<sup>d</sup>**

<sup>a</sup> *Nanoscience and Nanotechnology Research Center, Research Organization for the 21st Century, Osaka Prefecture University, Sakai, Osaka 599-8570, Japan, Fax& Tel: +81 72 254 985; E-mail: r-makiura@21c.osakafu-u.ac.jp*

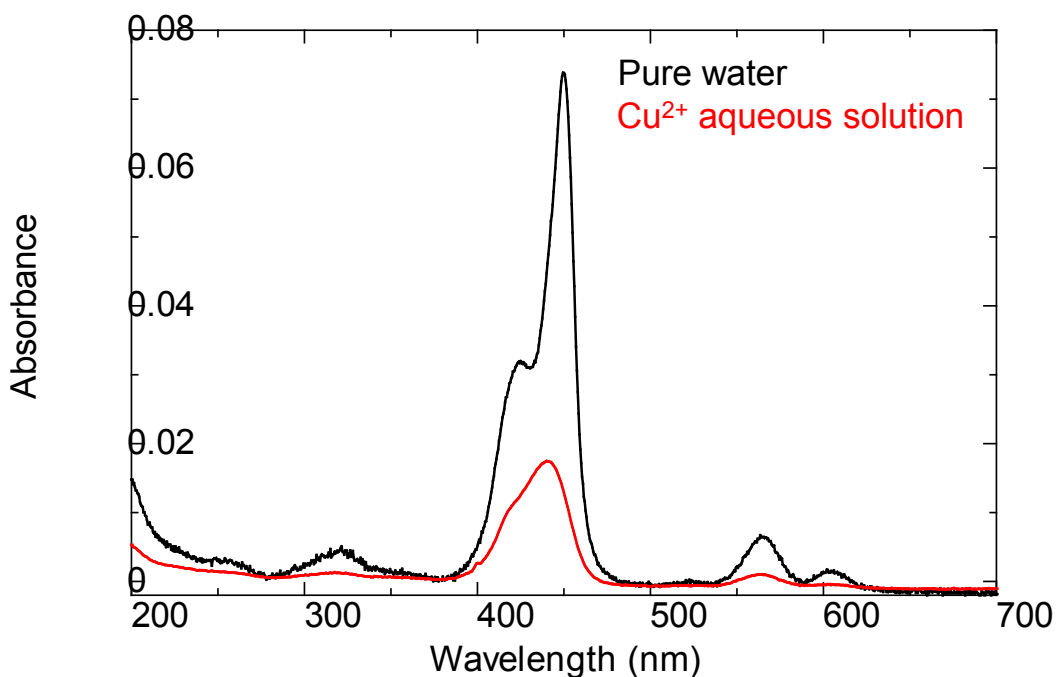
<sup>b</sup> *PRESTO, Japan Science and Technology Agency, Saitama, Japan*

<sup>c</sup> *CREST, Japan Science and Technology Agency, Saitama, Japan*

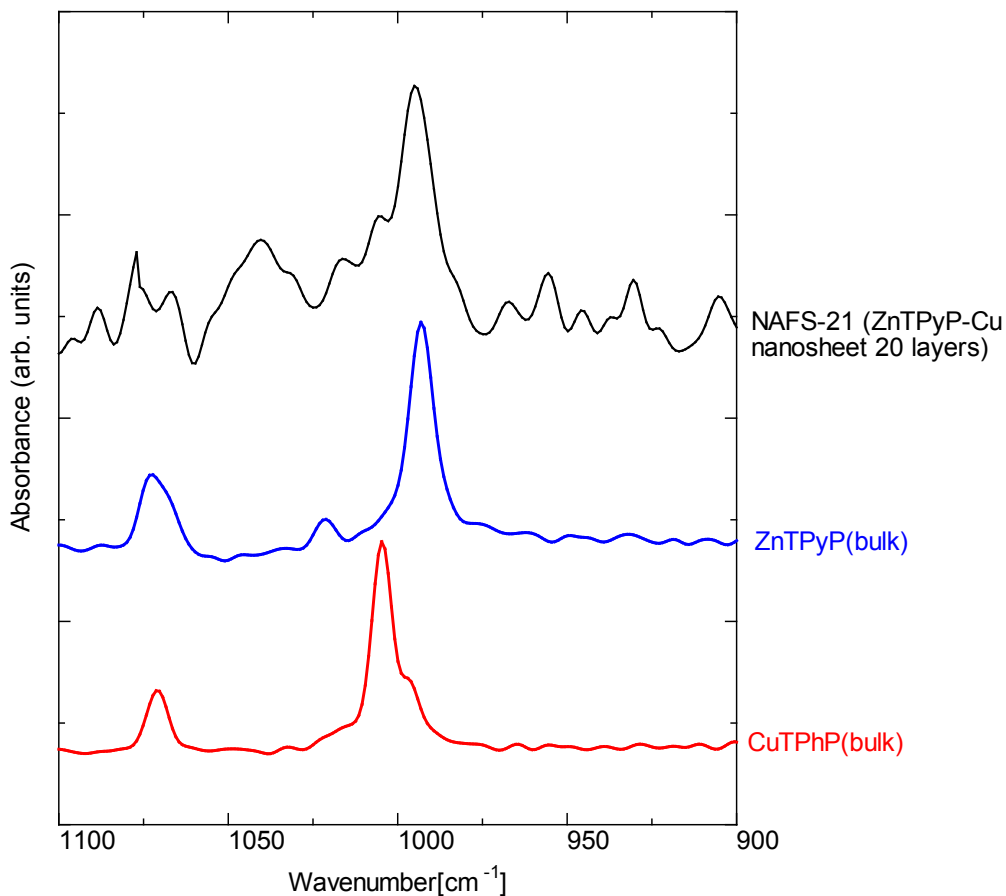
<sup>d</sup> *European Synchrotron Radiation Facility, Grenoble Cedex 38043, France*



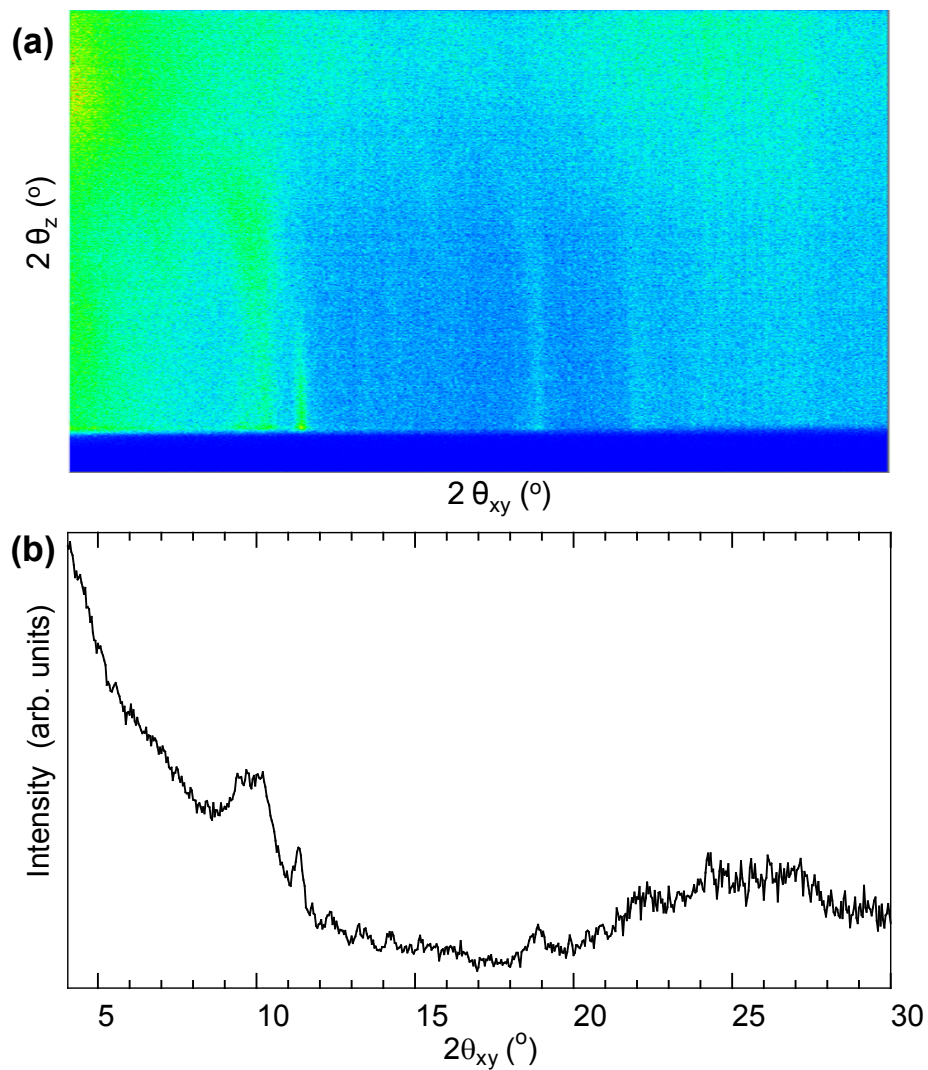
**Figure S1** Surface pressure-molecular area ( $\pi$ - $A$ ) isotherms for the NAFS-21 nanosheet. A solution of the molecular building units comprising of ZnTPyP, **1** was spread onto 10 mM  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , **2** aqueous solution (red solid line) or pure water (black solid line) as a subphase. In the case of the copper ion solution subphase, the larger molecular area observed for the NAFS21 sheet is consistent with copper linking of the tetratopic ZnTPyP molecules and indicates that they lie flat onto the solution surface (the porphyrin 2D plane is parallel to the surface). For the pure water subphase, the smaller molecular area implies that the ZnTPyP molecules either pack more closely remaining in the horizontal orientation or stand vertically at some angle to the solution surface.



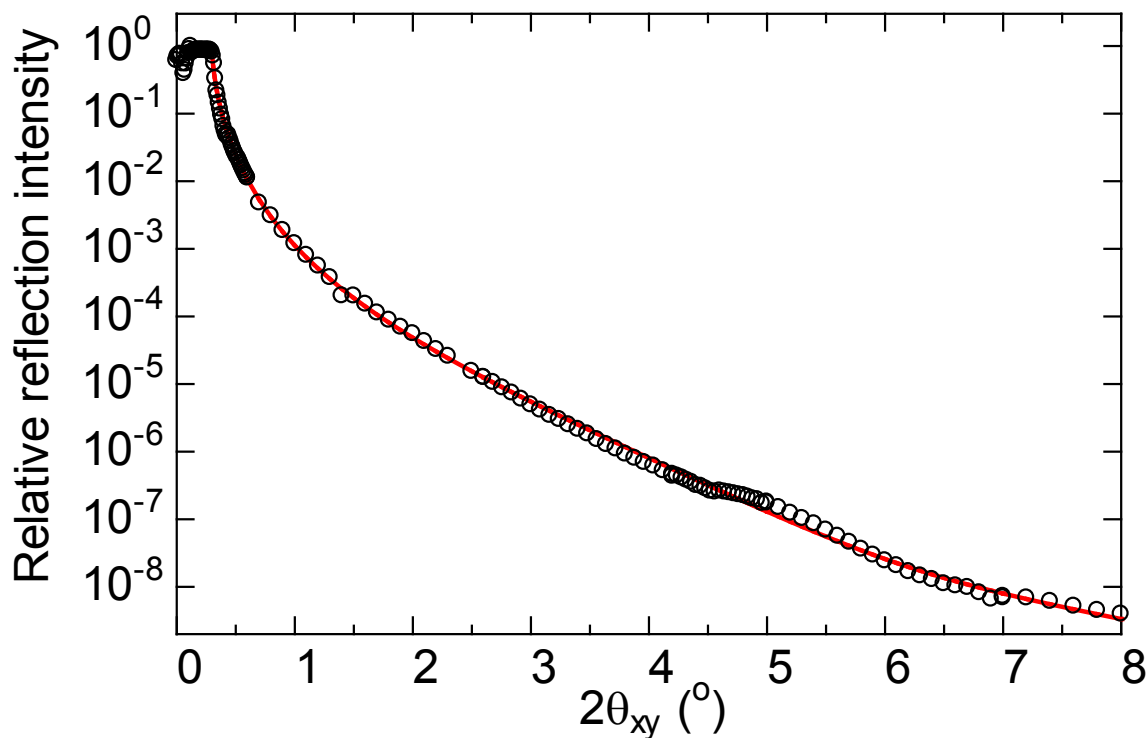
**Figure S2** UV-vis absorption spectra for ZnTPyP nanosheets fabricated on 10 mM  $\text{Cu}(\text{NO}_3)_2$  aqueous solution (NAFS-21, red solid line) or pure water (black solid line) subphase. The films formed at a surface pressure of 5 mN/m were deposited onto quartz substrates and the spectra were measured after a rinsing/solvent immersion/drying process. The increased absorbance in the LB film fabricated on pure water is consistent with a larger number of ZnTPyP units packing in the same area of the monolayer than for the NAFS-21 film fabricated on  $\text{Cu}(\text{NO}_3)_2$  aqueous solution. This result is consistent with the ZnTPyP molecular packing motif derived from the  $\pi$ - $A$  isotherm measurements shown in Fig. S1.



**Figure S3** Infrared absorption spectra of NAFS-21 nanosheets (20 layer-by-layer deposition cycles). NAFS-21 nanosheets formed at a surface pressure of 5 mN/m were deposited onto a Si substrate. After each deposition, the nanosheets were subjected to a rinsing/solvent immersion/drying process. The spectrum shown is recorded for a sample with 20 deposited layers of NAFS-21 nanosheets (black line). For comparison, the IR spectra of the starting material ZnTPyP (blue line) and of 5,10,15,20-tetraphenyl-porphine copper (II) (CuTPhP) (red line) are also shown. The observed absorption band for the NAFS-21 nanofilm at  $994\text{ cm}^{-1}$  is at an identical position as that of the starting material, ZnTPyP ( $993\text{ cm}^{-1}$ ), while the absorption band of the reference compound, CuTPhP occurs at  $1005\text{ cm}^{-1}$ . This is consistent with the absence of any metal exchange reaction occurring in the course of the formation process of the NAFS-21 nanofilms.



**Figure S4** (a) *In-situ* grazing incidence X-ray diffraction reciprocal space map (diffracted intensity along  $2\theta_{xy}$  (horizontal) and  $2\theta_z$  (vertical) diffraction angles,  $\lambda = 1.549 \text{ \AA}$ , incidence angle,  $\alpha = 0.12^\circ$ ) of the ZnTPyP array formed on the pure water subphase at a surface pressure,  $\pi = 10 \text{ mN/m}$ . (b) Integrated in-plane XRD profile (summed over the vertical diffraction angle,  $2\theta_z$  range of  $0\text{-}10.5^\circ$ ). The appearance of a broad diffuse scattering hump peaking at around  $2\theta_{xy} = 25^\circ$  ( $d$  spacing  $\approx 3.6 \text{ \AA}$ ) implies that the ZnTPyP molecules stand on the water surface at some angle.



**Figure S5** Observed (black circles) and fitted (two-layer model, red solid line) *in-situ* X-ray reflectivity (XRR) curves collected at the air/liquid interface for the ZnTPyP array on the pure water subphase at a surface pressure,  $\pi = 10$  mN/m. The density of the water substrate was fixed to  $1.0 \text{ g/cm}^3$ . The thickness, density and surface roughness of the ZnTPyP array were evaluated as  $0.91(3) \text{ nm}$ ,  $1.041(7) \text{ g/cm}^3$  and  $0.419(7) \text{ nm}$ , respectively.