

Electronic Supplementary Information

**'Click' conjugated microporous polymer nanofilm with a large domain size  
created by a liquid/liquid interfacial protocol**

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## General experimental

All starting material and solvents were purchased from Tokyo Chemical Industry (TCI) Co., Ltd. Dichloromethane was purified with a Glass Coutour Solvent Dispensing System (Nikko Hansen & Co., Ltd.). Water was purified using the Milli-Q purification system (Merck KGaA). 1,3,5-tris(4-azidophenyl)benzene **3**,<sup>S1</sup> a complex between CuCl<sub>2</sub> and tris[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]amine (CuCl<sub>2</sub>-TBTA),<sup>S2</sup> and 4,4'-diazido-2,2'-biphenyl disodium disulfonate **5**<sup>S3</sup> were synthesized according to previous literatures. Silicon wafers (P-doped, purchased from Yamanaka Semiconductor, cut into squares (12 × 12 mm). HMDS-modified SiO<sub>2</sub>/Si substrates were prepared by depositing HMDS ((CH<sub>3</sub>)<sub>3</sub>Si)<sub>2</sub>NH) on SiO<sub>2</sub>/Si substrates. Subsequently vacuuming for 10 min was performed, and then a flow of Ar was used to complete the treatment. The HMDS-modified SiO<sub>2</sub>/Si substrate was kept in anhydrous ethanol. FE-SEM images were collected using JEOL JSM-7400 FNT equipped with an EDS analyzer (JEOL EX-2300). Fluorescence microscope observation was conducted using reflected fluorescence system BX51 and mercury lamp USH-103OL (Olympus). XPS data were acquired using an ULVAC-PHI PHI 5000 VersaProbe spectrometer. Al K<sub>α</sub> (15 kV, 25 W) was used as the X-ray source, and the beam was focused on a 100 μm<sup>2</sup> area. The spectra were analyzed using MultiPak Software and standardized using the C 1s peak at 284.6 eV. AFM measurements were carried out using an Agilent Technologies 5500 scanning probe microscope under ambient conditions in tapping mode with a silicon cantilever Nano World PPP-NCL probe. Thermogravimetric analysis was performed under N<sub>2</sub> atmosphere with Rigaku Thermoplus2 TG8120. Al<sub>2</sub>O<sub>3</sub> was used as a reference compound, and both nanofilm and Al<sub>2</sub>O<sub>3</sub> were mounted on an Al pan. The temperature was controlled from r.t. to 500°C with a scan rate of 10 °C s<sup>-1</sup>. IR spectra were recorded using a JASCO FT/IR 620v spectrometer. All samples were pelletized with KBr (Wako Pure Chemical Industries, Ltd.). Raman spectra were collected using a HORIBA LabRAM HR Evolution (laser wavelength is 633 nm). Optical microscopic images were taken using an optical microscope (LV100, Nikon) equipped with a camera (DP71, Olympus). Gas adsorption/desorption measurements were performed using a BELSORP-Max II (BEL-Japan, Inc.). Samples were activated at 200°C for 3 h before the measurement. Proton conductivity measurements were conducted with a Solartron SI 1287 and 1255B frequency response analyzer in the frequency range 100 Hz to 1MHz. The electrodes were prepared by sputtering gold on porous glasses with the pore size of 4 nm (Akagawa Glass). Temperature and humidity were controlled by using an Espec Corp. SH-222 incubator.

## Liquid/liquid interfacial synthesis of NF1

Azide **3** (7 μmol) in 5 mL of dichloromethane was added to a solution of terminal alkyne **2** (7 μmol) in 5 mL of dichloromethane in a glass vial with a diameter of 40 mm. Subsequently, an aqueous solution of sodium ascorbate ascorbic acid (5 mL, 28 μmol) was then put gently on the dichloromethane solution in order to form a calm liquid/liquid interface. Then, a 5 mL solution of CuCl<sub>2</sub>-TBTA (14 μmol) in 10% a mixture of H<sub>2</sub>O/DMSO (9:1 v/v) was added slowly to the aqueous phase. After the final addition the color of the aqueous phase changed to white, indicative of "in-situ" reduction of Cu(II) to Cu(I). The biphasic reaction system was left standing calm in the closed glass vial at room temperature for 48 h, during which **NF1** emerged gradually at the interface as a yellowish film. Afterwards, resultant **NF1** was picked up from the interface, which was the soaked in dichloromethane, 5% HClaq, water, and acetone (for 24 h in total) to remove residual monomers, oligomers, and the catalyst. Note that

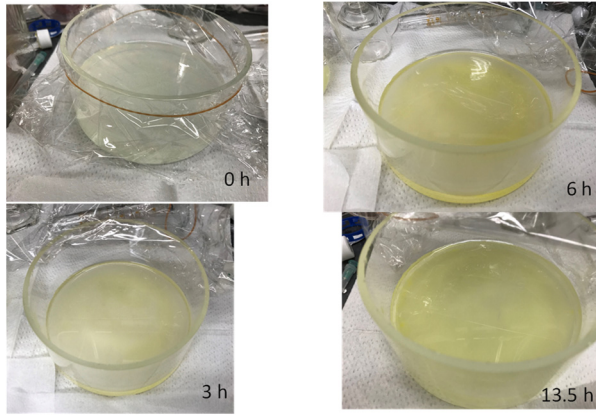
the lateral dimension of **NF1** could be tuned at will by changing the diameter of the glass vial: for example, a 12-cm domain could be realized (Figure 2a). With 10.6 and 31.7 mg of terminal alkyne **2** and azide **3** resulted in the formation of 10.9 mg of **NF1**. This result corresponds to a yield of 27%. Herein, we employed a 12-cm-diameter glass cylinder, 50 mL of the aqueous and organic phases, and 277 and 173 mg of  $\text{CuCl}_2\cdot\text{TBTA}$  and sodium ascorbate, and these conditions should also affect the yield.

### **Liquid/liquid interfacial synthesis of NF4**

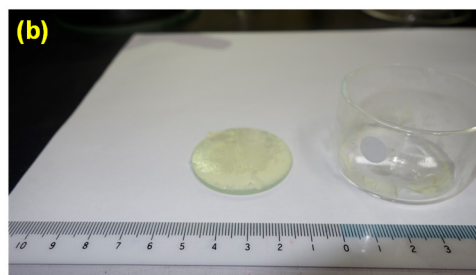
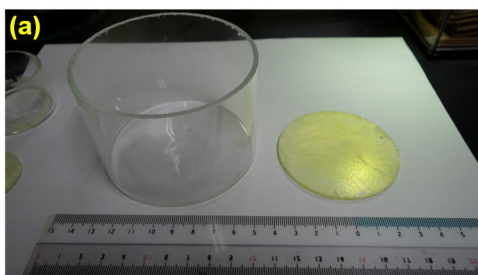
Azide **5** (17  $\mu\text{mol}$ ) in 10 mL of distilled water was added in a glass vial with a diameter of 4 cm. Subsequently, the solution of terminal alkyne **2** (10  $\mu\text{mol}$ ) in 4 mL of ethyl acetate was added, and a 4 mL ethyl acetate solution of TBTA (10  $\mu\text{mol}$ ) was then added gently to form a calm liquid/liquid interface. Finally, a 2 mL solution of  $\text{CuI}$  (10  $\mu\text{mol}$ ) in acetonitrile was added slowly to the organic phase. The liquid/liquid interfacial system was left standing in a closed glass vial, at room temperature for 48 h, while **NF4** emerged gradually at the interface. Afterwards, **NF4** was picked up from the interface, and then dipped in acetone, 20% aqueous hydrochloric acid, pure water, and acetonitrile (for 24 h in total) to remove residual monomers, oligomers, and the catalyst. The area of **NF4** could be tuned by changing the diameter of the glass vial.

### **Preparation of Pt@NF1**

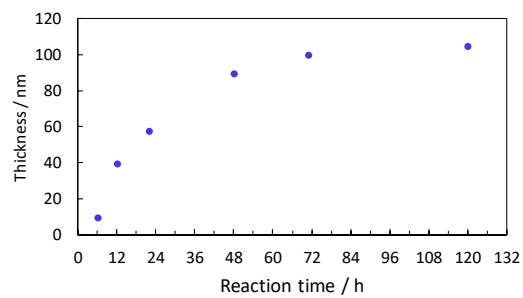
**NF1** was immersed in an aqueous solution of  $\text{K}_2\text{PtCl}_4$  solution (0.1 M) for 1 d. After washing the modified **NF1** with water, it was subjected to immersion into  $\text{NaBH}_4$  aq (0.125 M) for 15 min. Resultant **Pt@NF1** was washed with water and methanol, and dried under vacuo.



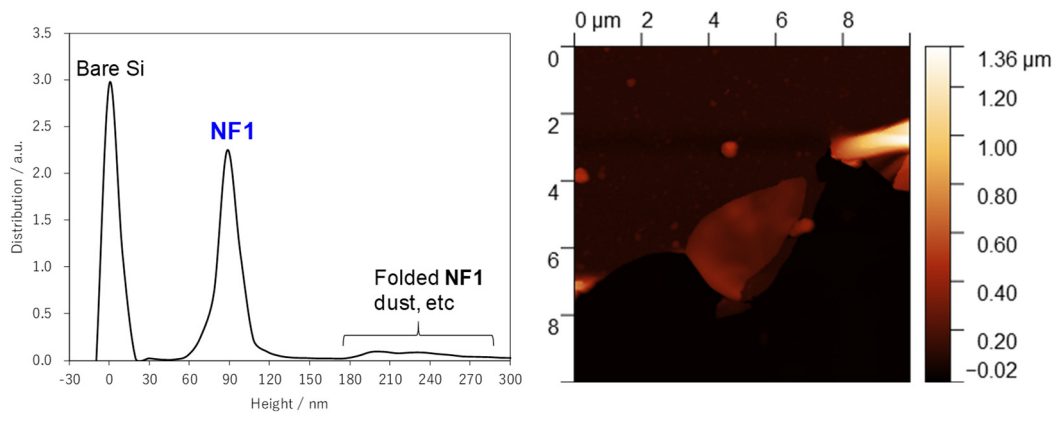
**Fig. S1.** Time-course **NF1** growth.



**Fig. S2.** Dependence of the diameter of **NF1** on the size of the reaction container. (a) 9-cm-diameter container and **NF1** on a 7-cm-glass plate. (b) 5-cm-diameter container and **NF1** on a 4-cm-glass plate.

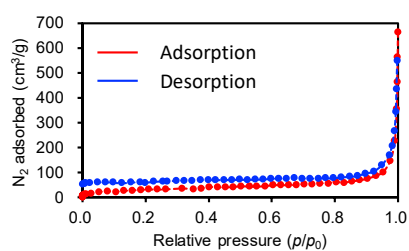


**Fig. S3.** Relationship between the thickness of **NF1** and reaction time.

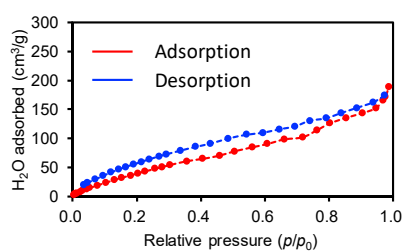


**Fig. S4.** Height histogram (-30 ~ 300 nm range) for **NF1** on a SiO<sub>2</sub>/Si(111) substrate.

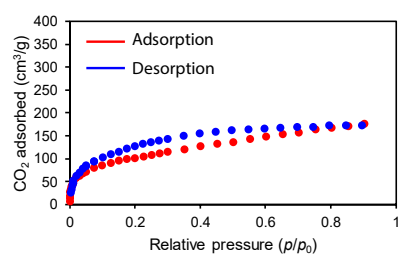
(a)



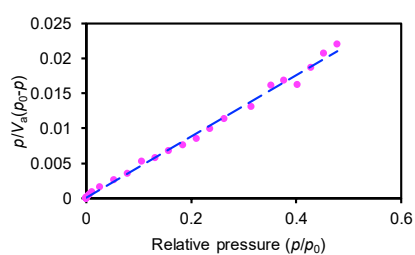
(b)



(c)

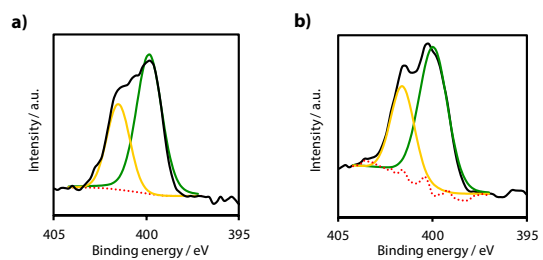


(d)

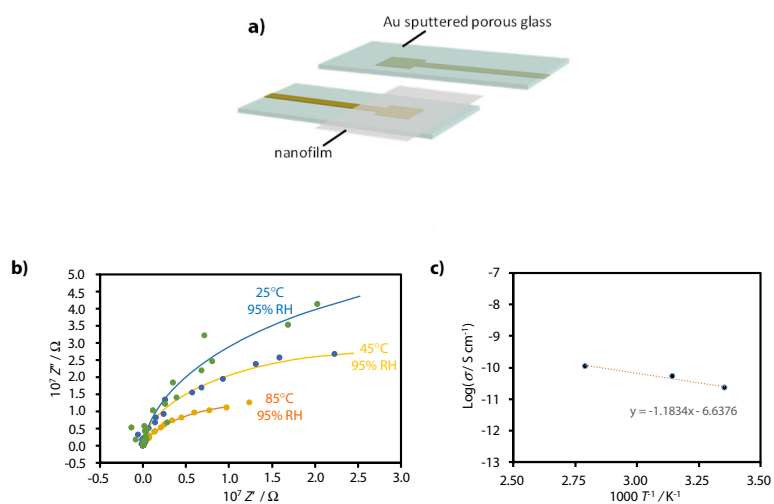


**Fig. S5.** (a) N<sub>2</sub> adsorption (red symbols) and desorption (blue symbols) isotherms at 77 K for **NF1**. (b) H<sub>2</sub>O adsorption (red symbols) and desorption (blue symbols) isotherms at 298 K for **NF1**. (c) CO<sub>2</sub> adsorption (red symbols) and desorption (blue symbols) isotherms at 195 K for **NF1**. (d) BET analysis for the N<sub>2</sub> isotherm.

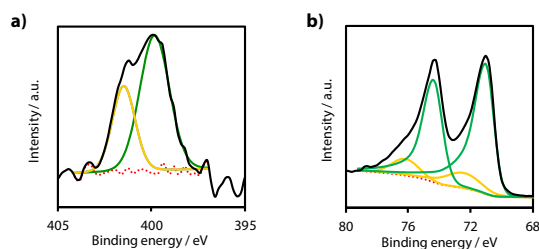




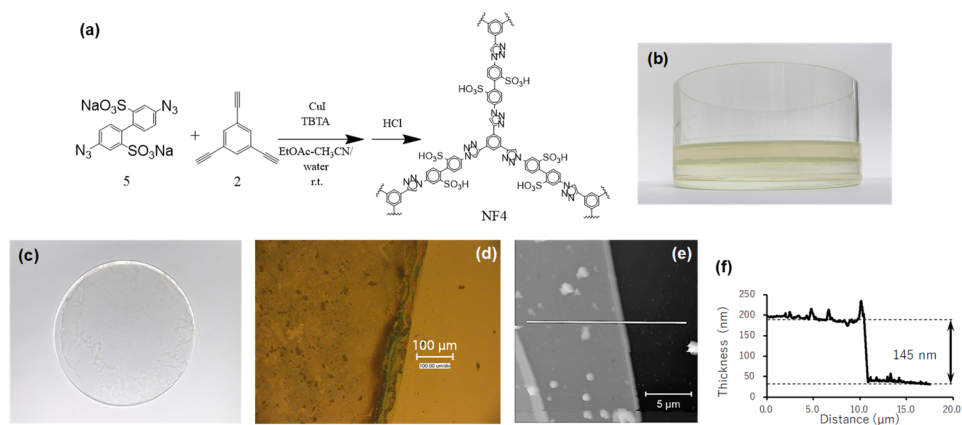
**Fig. S6.** (a,b) XPS for **NF1** on a SiO<sub>2</sub>/Si(111) substrate after immersing an aqueous solution of (a) 10 M HCl or (b) 10 M NaOH for 10 d at room temperature. Black solid: experimental; yellow and green: fitting Gaussian functions; red dotted: residual error.



**Fig. S7.** (a) Schematic illustration of a set-up for the proton conductivity measurement of **NF1**. (b) Nyquist plots at various temperatures. (c)  $\text{Log } \sigma - 1000 T^{-1}$  plot.



**Fig. S8.** (a,b) XPS for **Pt@NF1** on a SiO<sub>2</sub>/Si substrate: (a) narrow scan focusing on the N 1s region. Black solid: experimental; yellow and green: fitting Gaussian functions; red dotted: residual error. (b) narrow scan focusing on the Pt 4f region. Black solid: experimental; green and yellow: fitting Gaussian functions; red dotted: residual error. The main contribution in (b) is provided by Pt(0) for 4f<sub>7/2</sub> and Pt 4f<sub>5/2</sub>, while the minor one presumably by Pt(δ+), a positive Pt species that surrounds the Pt(0) matter. The binding energies for nitrogen in **Pt@NF1** underwent slight positive shifts against those in metal-free **NF1** (400.8→401.4 for -N-N=N- species; 399.4→399.8 for -N-N=N- species, Fig. 3b). This should stem from electron donation from nitrogen to platinum upon coordination.



**Fig. S9.** Preliminary result for another click nanofilm **NF4**. (a) Synthetic scheme. (b) Liquid/liquid interfacial synthesis using a 12-cm-diameter glassware. (c) **NF4** on a 7-cm-diameter glass plate. (d) Optical micrograph for **NF4** on a glass plate. (e) AFM height image for **NF4** on SiO<sub>2</sub>/Si(111). (f) Cross-section along the white line in (e).

## References for SI

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