Supplementary Information

Dried foam films with a triple bilayer structure induced by ionic liquids

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1. Preparation of dried foam films

Dodecylphosphocholine (DPC) and 3-(dodecyldimethylammonio)propanesulfonate (DPS) were purchased from *C/D/N Isotopes* and *Sigma*, respectively. 1-Ethyl-3-methylimidazolium chloride (EMICl), 1-ethyl-3-methylimidazolium bromide (EMIBr), 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIBF_4$), and 1-ethyl-3-methylimidazolium hexafluorophosphate ($EMIPF_6$) were purchased from *Kanto Chemical* and used without further purification.

2000-mesh copper microgrid, 1000-mesh copper microgrid, and TEM microgrid with a perforated polymer membrane (150-mesh type) were products of *Okenshoji*. Porous alumina membrane (Anodisc-25) with pores of 0.2 μm was purchased from *Whatman* and used as the substrate for FTIR measurements. These grids and substrate have pores suitable for capturing small droplets of aqueous DPC (or DPS) solutions containing ionic liquids. In general, a porous substrate was immersed into the solution for a few seconds and pulled up perpendicularly. The substrate was then allowed to stand for one hour in air at a humidity of 40 - 50 %. Then, the small droplets captured by the substrate spontaneously transformed to the corresponding dried foam films. Throughout experiments, the concentration of DPC (or DPS) was 5.6 mM.

2. Experimental details

Transmission electron microscope (TEM) observations were made by using a JEM-1010 (JEOL) instrument at an acceleration voltage of 100 kV. Scanning electron microscope (SEM) images were obtained by using a Hitachi S-4800. The cross-sectional specimen was prepared by carefully ripping off a 2000-mesh copper microgrid covered with dried foam films. The specimen was set on a vertical sample holder. Scanning transmission electron microscope (STEM) measurements and energy dispersive X-rays (EDX) analyses were carried out on a JEM-2100F at an acceleration voltage of 200 kV.

TEM and SEM observations were conducted after depositing a 2-nm thick platinum layer by using a Hitachi E-1030 ion sputter in order to prevent electric charging of the specimens. The deposition was conducted at room temperature under an argon atmosphere of 10 Pa or lower. The current density for the deposition was 10 mA. The thickness of the platinum layer was calibrated by using a quartz crystal microbalance technique. In our experimental conditions, platinum nanoparticles of about 0.8 nm uniformly deposited on the surfaces of any kind of dried foam films. Therefore, the deposition did not have any effect on the film morphology. However, the deposition of more than 10 nm was prone to disrupt the films probably due to the high surface tension of the platinum layer. STEM and EDX measurements were conducted without platinum deposition.

Fourier transform infrared (FTIR) spectra were obtained by using a Bio-Rad Win-IR spectrometer.

The measurement was conducted in a chamber filled with dried nitrogen gas.

3. Thermal properties

The dried foam films formed in a perforated polymer membrane on a TEM microgrid are shown in Figure S1. The pores of a few micrometers in diameter (shown in **A**) could be uniformly covered with the DPC films containing EMICl. At the bottom of image **B**, there was an uncovered pore, which showed a little light color. The larger pore of more than 5 μm was also covered by the film. The coverage (the percentage of covered pores) was larger than 98 %, as examined for more than 600 pores. The films were extremely smooth and uniform. There was no defect or pinhole in the films, as confirmed by high-magnification TEM observation (**C** and **D**).

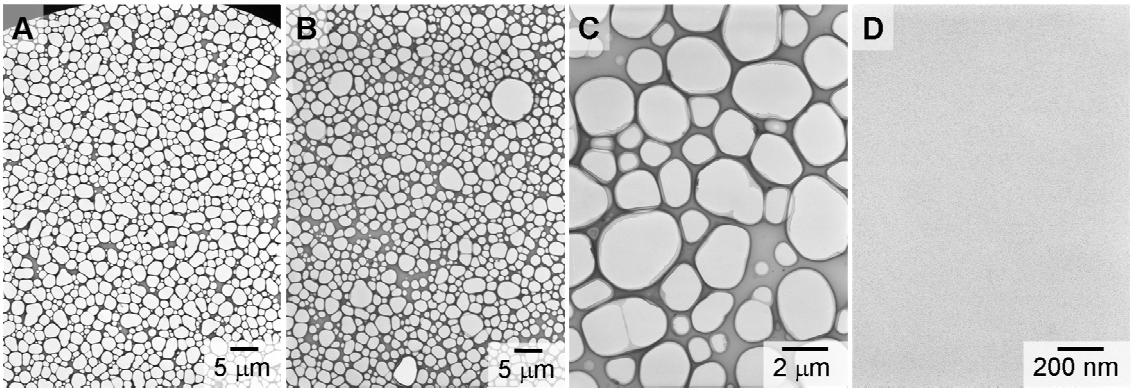

Fig. S1 TEM images of a perforated polymer membrane on a TEM microgrid (**A**) and dried foam films in the pores of the polymer membrane (**B**)-(**D**). The films were prepared from the aqueous solution of DPC containing equimolar of EMICl. Magnification increases from (**B**) to (**D**).

Figure S2 shows TEM images of the dried foam films after heating at a given temperature. These films were prepared from the aqueous solution of DPC containing equimolar of EMICl (same as in Figure S1). After heating at 120 °C for 15 min, the films gave coverage of 98-94 % (**A**). The coverage dropped to 20 % when the films were heated at 130 °C (**B**), and almost all the films were disappeared by heating at 140 °C (**C**). Therefore, we concluded that the thermal stability of the films prepared from the 1/1 mixture of DPC and EMICl was 120 °C.

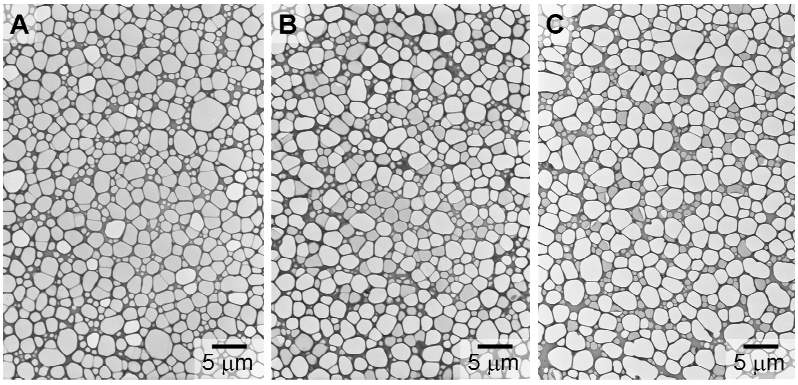

Fig. S2 TEM images of dried foam films after heating at 120 °C (**A**), 130 °C (**B**), and 140 °C (**C**). The films were prepared from the 1/1 mixture of DPC and EMICl.

Similarly, we examined the thermal stability of the films prepared at different conditions. The results are summarized in Table 1 of our manuscript and Figure S3. When the molar ratio of EMICl/DPC was 0.5, the films were stable up to 140 °C. The thermal stability decreased to 120 °C, 110 °C, and 100 °C, when the molar ratio of EMICl against DPC was 1, 2, and 3, respectively. When the ratio was 4 and 5, the films were stable up to 80 °C. The coverage shown in Figure S3 was determined by examining more than 600 pores at each temperature and molar ratio.

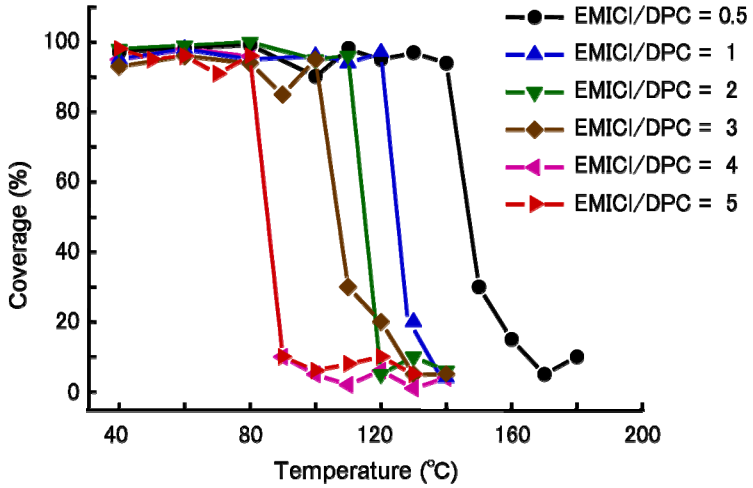

Fig. S3 Temperature dependence of the coverage of DPC/EMICl films prepared at different molar ratios.

4. EDX measurements at the edge of DPC/EMICl film

We explained in our manuscript that 89 % of ionic liquid drained to the edge of DPC/EMICl film during the thinning process. In order to verify this hypothesis, we measured EDX spectra at the edge of the film. The typical spectrum is shown in Figure S4. The sharp peaks at 2.03 keV and 2.62 keV were attributed to phosphorus and chlorine, respectively. Their atomic ratio (P/Cl) was estimated to be 1.02, which was very close to the atomic ratio of 1.00 in DPC/EMICl (1/1 mol/mol) solution.

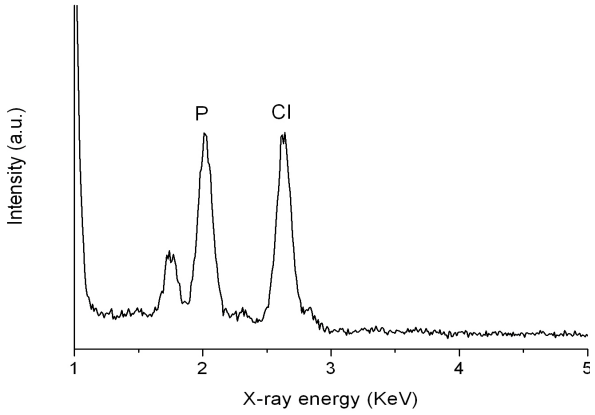

Fig. S4 EDX spectrum obtained at the edge of DPC/EMICl film. The film was prepared from DPC/EMICl (1/1 mol/mol) solution.