# Thickness-dependent molecular arrangement and topography of ultrathin ionic liquid films on a silica surface

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SUPPORTING INFORMATION

## 1. Dip coating process

RTIL is applied on the silicon wafers by dip-coating based on a previously established "dip-withdraw" procedure in our lab. The silicon wafers (with 2 nm native oxides, P/B <100> 1-10 OHM-CM; 279 ± 25μm, Silicon Quest International, Inc.) were UV-ozone cleaned right before the dip-coating. DMPIIm was applied on the UV-Ozone cleaned silicon wafers, with Vetrel (2,3-dihydrodecafluoropentane, Miller Stephenson Chemical Co., HPLC grade) as solvent, by dip-coating using a KSV-DCX2 dip-coater equipped with a Kinetic Systems vibration free platform at a withdraw rate of 1 mm/second. The thicknesses of the film, ranging from 0.4 nm to 1.0 nm, were controlled by adjusting the solution concentration.

## 2. Ellipsometry measurement of the film thickness

The bare silicon substrate was first measured to determine the thickness of native oxides.[18] To avoid thickness and index correlation between the very thin polymer films, we fixed their optical constants using a Cauchy dispersion equation:

$$n(\lambda) = 1.45 + \frac{0.00250}{\lambda^2}$$

Here n is the refractive index and λ is the wavelength in microns. Fig. S1 shows a typical fitting result of RTIL ultrathin film on the silicon substrate. As shown in Table S1, MSE values of the films with different thickness calculated by ellipsometer are low, indicating good fitting results.

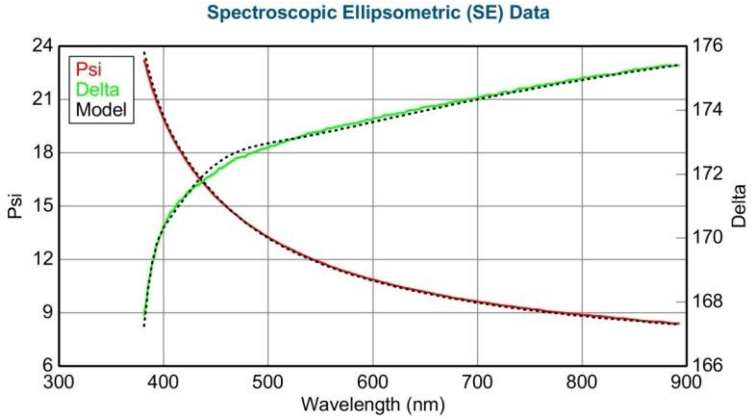



**Fig. S1** Typical fitting result of RTIL ultrathin film on the silicon substrate.

**Table S1**. MSE of the ultrathin films with different thicknesses.

| Thickness (nm) | 0.41 | 0.50 | 0.62 | 0.70 | 0.86 | 1.02 |
|---|---|---|---|---|---|---|
| MSE | 1.881 | 1.844 | 1.956 | 1.971 | 2.188 | 2.388 |

## 3. Thickness-concentration relationship

As shown in Fig. S2, six different thicknesses, ranging from 0.4 nm to 1.0 nm, were obtained according to dip-coating concentration from 0.06 g/L to 0.5 g/L, respectively.

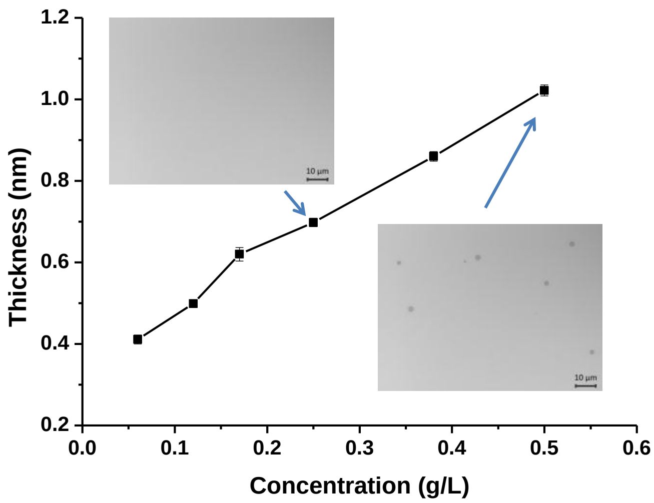
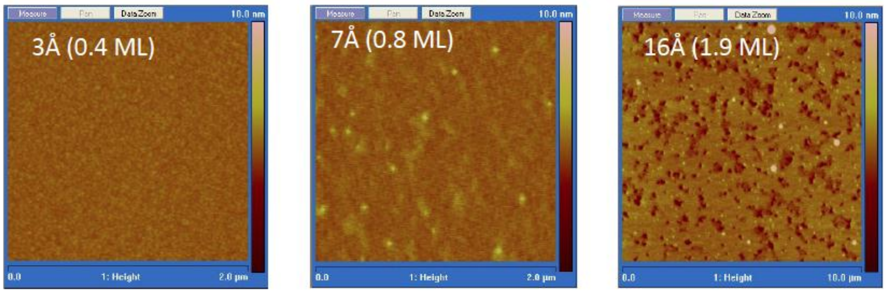
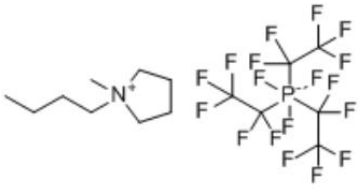



**Fig. S2** RTIL film thickness as a function of dip-coating concentration.

## 4. AFM of BMFAP/Silica samples



1-butyl-1-methylpyrrolidinium tris (pentafluoroethyl)trifluorophosphate (BMFAP)

Fig. S3 AFM topography images of BMFAP IL thin films on the silicon wafer

Compared to DMPIIm, the BMFAP has more $CF_3$ segments in its anion and thus has lower surface tension. Interestingly, at higher thickness, the “sponge” structure, which is more “continuous” than the big droplets (higher total surface area), is more prominent than in DMPIIm nanofilms. This can be explained by the fact that lower surface tension will result in higher total surface area.

## 5. <u>Water contact angle (WCA) experiments</u>

The static water contact angle (θ) measurement was measured using a VCA optima XE video contact angle goniometer at 24 °C and 48% relative humidity. A 2 μL water droplet was formed at the end of the needle and then lowered carefully until it touched the sample (DMPIIm/Silica) surface. Right after this step, the needle was withdrawn so that the water droplet was left on the sample surface. The image of the droplet was taken with a CCD camera immediately and the value of the static contact angle was determined by the VCA software. It took about 45 seconds to finish the measurement and the reported values were based on at least three repeats.