# **Supporting Information**

# Ionic liquid-induced nanoporous structures of a polymer film

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# **EXPERIMENTAL SECTION**

### Materials and chemicals.

Poly(diallyldimethylammonium chloride) (PDADMAC, average Mw < 100 kDa), poly(sodium styrenesulfonate) (PSS, MW = 70 kDa), and 1-Butyl-3-methylimidazolium Chloride (BMIMCl) were obtained from Aldrich and used as received.

#### Substrate preparation

Silicon wafers were firstly cleaned with Piranha solution (70:30 v/v% sulfuric acid/hydrogen peroxide), and then were sonicated in a 1:1 mixture of water and 2-propanol for 15 min. They were further treated in a 5:1:1 mixture of water, hydrogen peroxide (30%) and ammonia solution (29%) at 60 °C for 15 min. After the wafers were rinsed in copious amount of water, they were blown dried with a nitrogen stream.

## Assembly of polyelectrolyte multilayers

The polyelectrolytes were all prepared as 0.5 mg/mL solutions with NaCl or BMIMCl aqueous solutions. Sequential adsorption of the polyelectrolytes on the silicon or glass substrate was then performed by manually dipping. Between alternate exposures to two kinds of polymer solutions for 10 min, there were 3 rinses with water. After the desired layer numbers were deposited, the multilayers were rinsed with water to eliminate the adsorbed salt on the film surface.

## Characterization

AFM measurements were collected using SPI3800N Probe Station and SPA400 SPM Unit (Seiko Instruments Inc.) in a dynamic force mode. The thickness of the multilayers was measured by a variable-angle spectroscopic ellipsometer (model VASE; J. A. Woollam Inc., Lincoln, NE). The contact angles of the multilayers were measured by a DSA 100 water contact measuring system (Krüss, Germany). Spectra were collected on a spectroscopy meter (UV2600, Shimadzu Corp., Tokyo, Japan).

# **RESULTS:**



**Figure S1.** AFM images of the films assembled in (a, b) 0.1 M BMIMCl aqueous solutions and (c, d) 0.3 M BMIMCl aqueous solutions.



**Figure S2.** (a) Water contact angles (WCA) and Hexadecane contact angles (HCA) of PSS/PDADMAC films assembled in BMIMCl and NaCl aqueous solutions. (b) Polar and disperse energies of films.



**Figure S3.** Graphical illustration of the PSS/PDADMAC films assembled in BMIMCl and NaCl aqueous solutions.



**Figure S4.** (a) Typical AFM image of the films assembled in 0.5 M BMIMCl aqueous solutions, (b) Corresponding line profile, and (c) Statistical results of the pore size.



**Figure S5.** Transmission spectra of glass and a PSS/PDADMAC film assembled in 0.5 M BMIMCl aqueous solutions.