

Supporting Information

Supramolecular assembly-mediated lithium ion transport in nanostructured solid electrolytes

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Experimental Section

Materials

A cytosine-terminated polypropylene glycol (Cy-PPG) was prepared by Michael addition of poly(propylene glycol) diacrylate 800 (PPG diacrylate, ca. 14 repeat units) to cytosine. UrCy-PPG was prepared by isocyanate chemistry of Cy-PPG in the presence of *n*-butylisocyanate using sodium tert-butoxide as the base. Detailed synthetic procedures for Cy-PPG and UrCy-PPG have been described in previous reports.³⁸ LiAsF₄ (purity, 99%) was purchased from Alfa Aesar (Ward Hill, MA, USA). All chemicals were of analytical reagent grade (at least), and were purchased from Sigma-Aldrich (Louis, MO, USA) and used as received without further purification.

Characterizations

Solid state ⁷Li magic angle spinning (MAS) NMR. ⁷Li NMR spectra were obtained on a Bruker

DSX-400 NMR spectrometer at 298 K using a 7 mm double-resonance probe. The static magnetic field was 9.4 T, and the central frequency was set at 155.27 MHz for the ^7Li nucleus. Operating conditions involved a $\pi/2$ pulse length of 10 μs , delay τ of 2 μs , recycle delay of 8 s, decoupling field strength of 65 kHz, spinning speed of 2 kHz and 0.1 M aqueous solution of LiCl (0 ppm, taken as reference)

Synchrotron wide-angle X-ray scattering (WAXD). XRD measurements were performed using a BL17A1 wiggler beamline at the National Synchrotron Radiation Research Center (NSRRC), Taiwan. Radiation with a wavelength of 0.1341891 nm was used. The beam was pinhole collimated with an incident beam diameter of 20.0 mm. The measured q -value range was approximately 0.8 to 25 nm^{-1} , providing structural information at length scales ($2\pi/q$) between 0.25 and 7.85 nm.

Differential scanning calorimetry (DSC). A TA Instruments (New Castle, DE, USA) Q-20 DSC was used to perform thermal measurements at a heating and cooling rate of 10 $^{\circ}\text{C}/\text{min}$. Approximately 5 mg of each sample was placed in an aluminum pan and analyzed over the temperature range of -70 $^{\circ}\text{C}$ to 120 $^{\circ}\text{C}$. Typically, the second heating scan for each sample is shown in **Fig. 2a**.

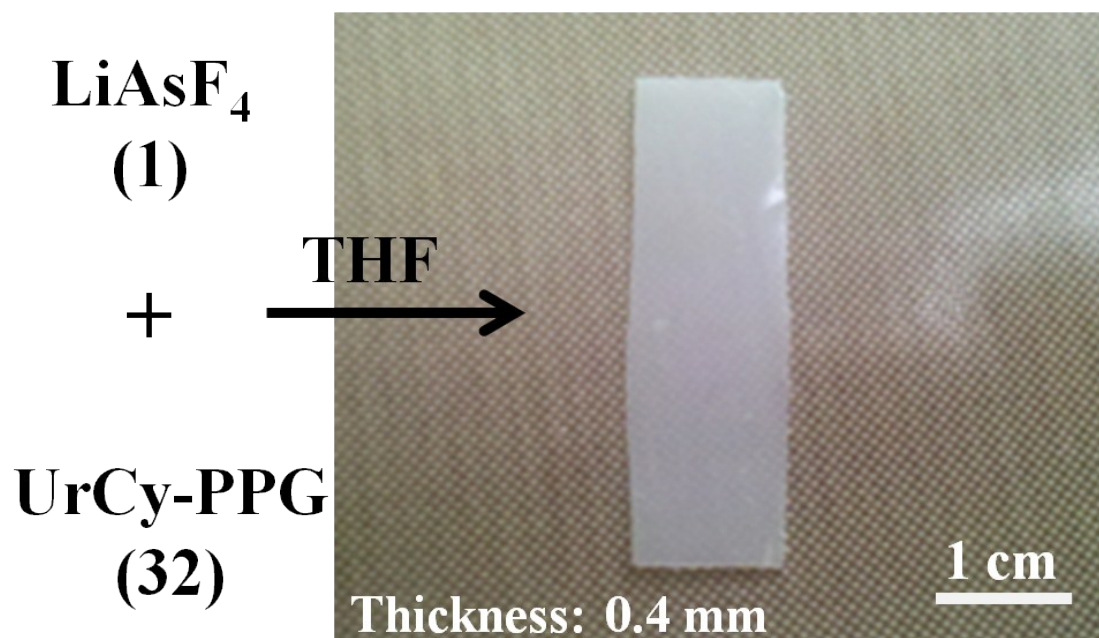
Tensile tests. Tensile tests were conducted at a constant cross-head speed of 0.5 mm/min using a universal tensile tester (EZ-L; Shimadzu Corp, Kyoto, Japan). All tests were performed at 25 $^{\circ}\text{C}$ and 40% relative humidity.

Ionic conductivity measurements. The frequency-dependent impedance properties (from 10 kHz to 10 Hz) of the SPEs were measured using an Autolab instrument (Eco Chemie, Utrecht, Netherlands). The samples were pressed into disks typically 10 mm in diameter and 0.3 mm in thickness. For conductivity measurements, the disk was placed in a conductivity cell between stainless steel blocking electrodes and measured over a temperature range of 30 $^{\circ}\text{C}$ to 80 $^{\circ}\text{C}$ at relative humidity levels below approximately 25 to 30%. Conductivity was calculated according to the equation:

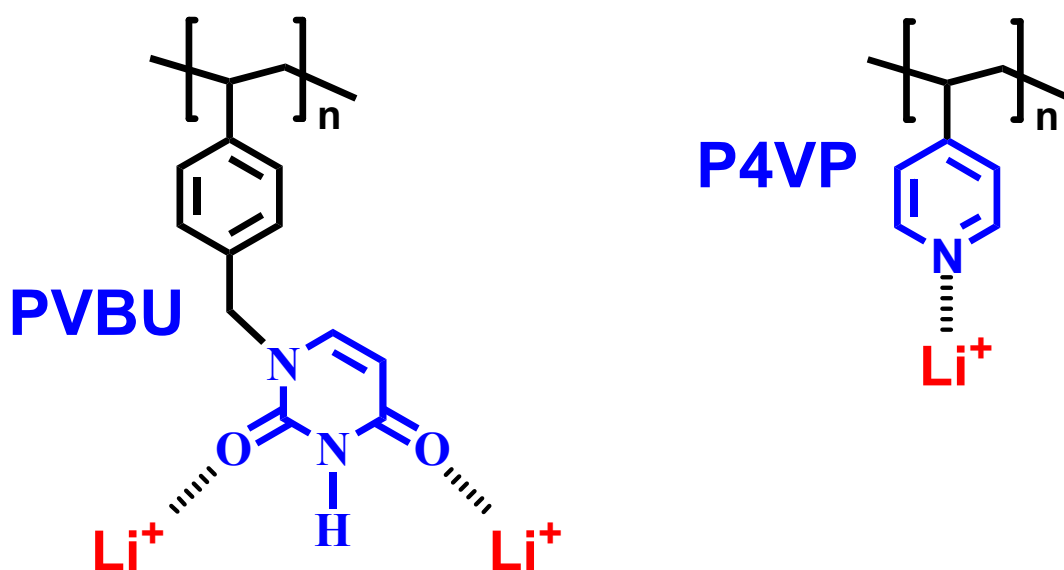
$$\sigma = \frac{L}{AR_b}$$

where σ is conductivity, L is the thickness of the SPE film, A is the section area of the stainless steel

electrode, and R_b is bulk resistance.



Scheme S1. Appearance of 32/1 UrCy-PPG/LiAsF₄ film prepared by solvent blending from THF and subsequently thermally annealed at 100 °C.



Scheme S2. Structural representation of the ionic interactions between the PVBU/Li⁺ and P4VP/Li⁺ systems.

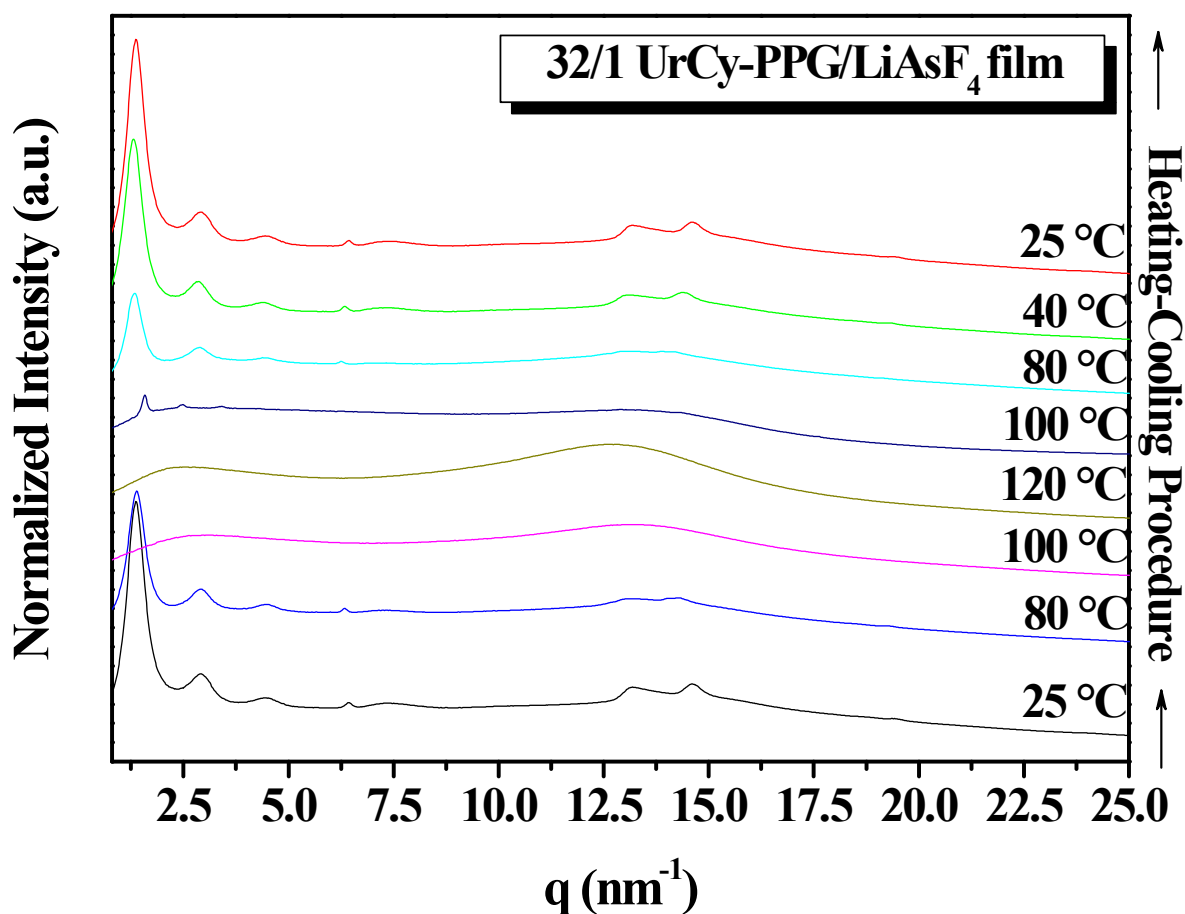


Fig. S1: Variable-temperature WAXS data of the 32/1 UrCy-PPG/LiAsF₄ film presented in the ranges 0.8–25 nm⁻¹.

To further understand the impacts of temperature perturbation on hydrogen bonding, variable temperature WAXS experiment was carried out and the results were shown in Fig. S1. As the temperature was increased gradually from 25 °C to 120 °C, a periodic WAXS peak was not observed, indicating a long-range ordered structure did not form due to melting of the lamellar phase. Surprisingly, as soon as the sample was slowly cooled to 25 °C, the scattering pattern spontaneously returned to its original lamellar structure, indicating that the strong hydrogen bonding interactions between the UrCy groups exhibited distinct temperature sensitivity and excellent thermoreversible interactions