Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting information

The influence of interfacial interactions on the conductivity and phase behaviour of organic ionic plastic crystal/polymer nanoparticle composite electrolytes

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Scanning electron microscopy images

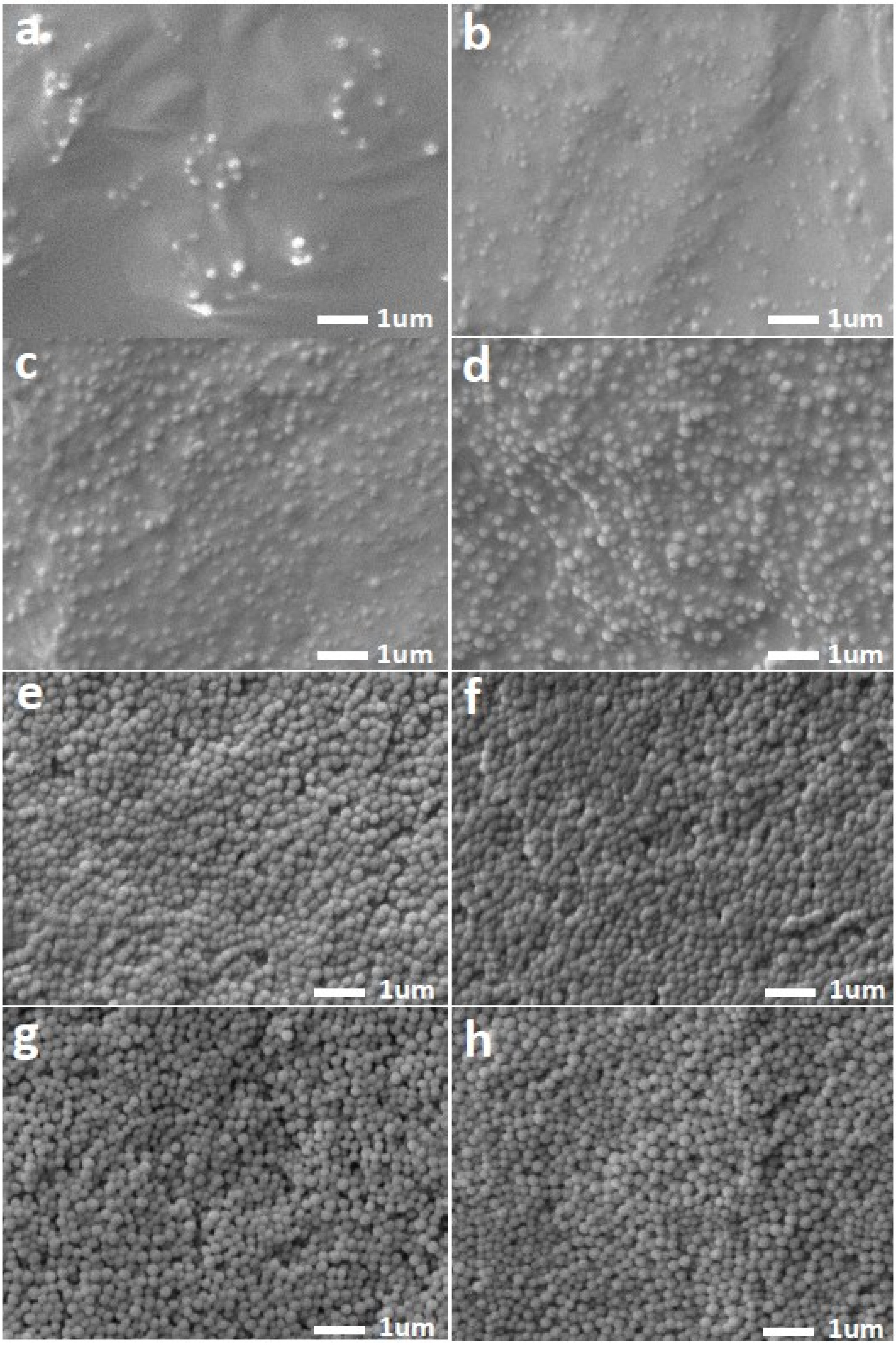


Figure S1: SEM micrographs of; a. 90/10 [C_2mpry][FSI]/PVDF b. 80/20 [C_2mpry][FSI]/PVDF c. 70/30 [C_2mpry][FSI]/PVDF d. 60/40 [C_2mpry][FSI]/PVDF e. 50/50 [C_2mpry][FSI]/PVDF f. 40/60 [C_2mpry][FSI]/PVDF g. 30/70 [C_2mpry][FSI]/PVDF and h. PVDF

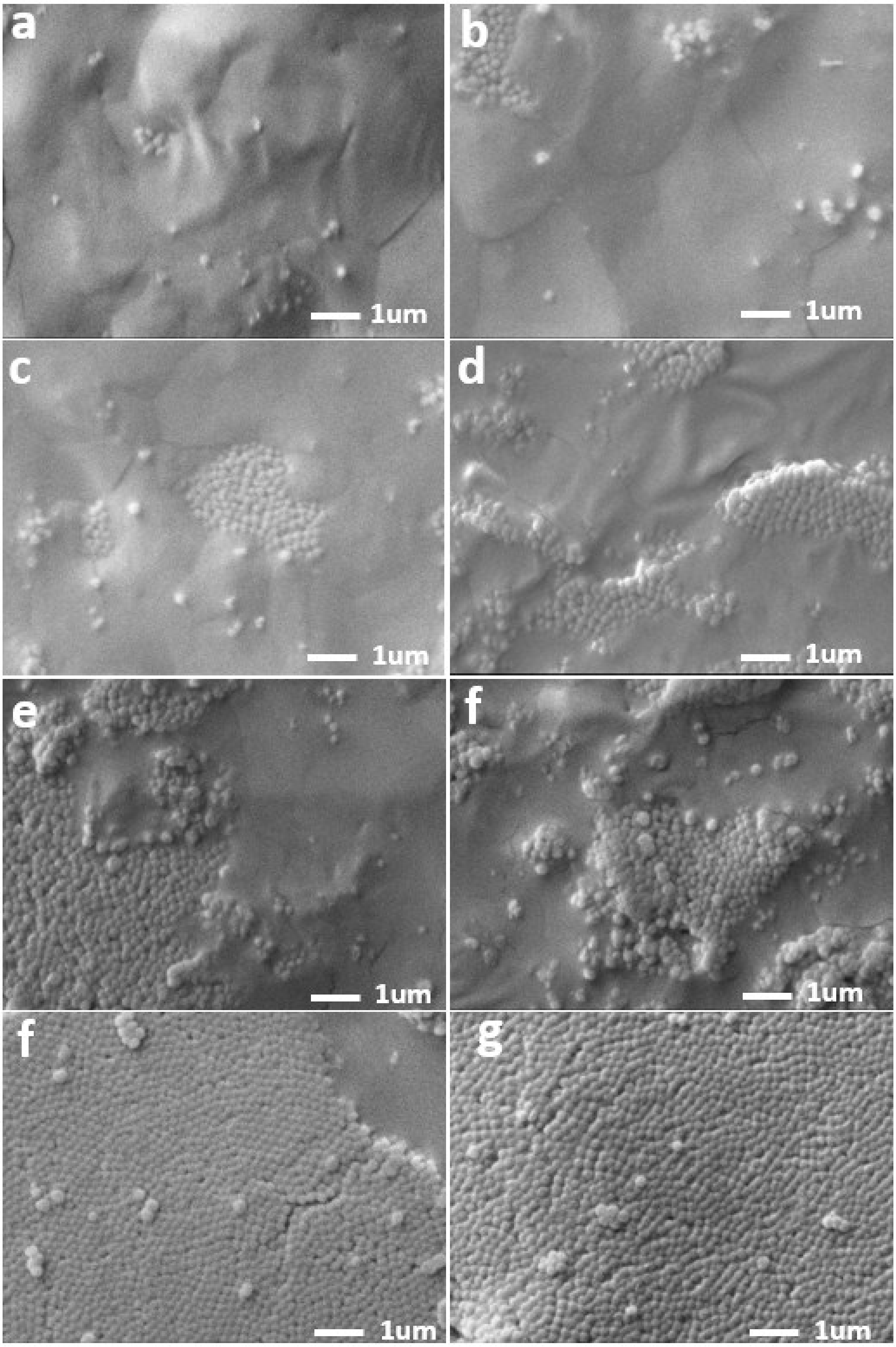


Figure S2: SEM micrographs of; a. 90/10 [C_2mpry][FSI]/PS b. 80/20 [C_2mpry][FSI]/PS c. 70/30 [C_2mpry][FSI]/PS d. 60/40 [C_2mpry][FSI]/PS e. 50/50 [C_2mpry][FSI]/PS f. 40/60 [C_2mpry][FSI]/PS g. 30/70 [C_2mpry][FSI]/PS and h. PS

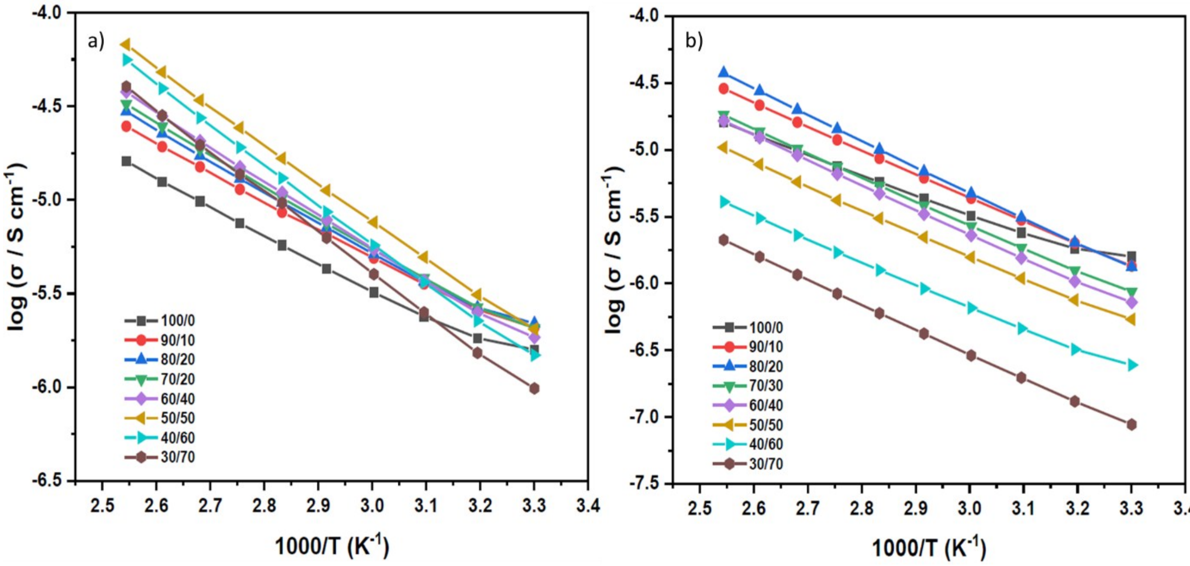


Figure S3: a. The temperature dependence of ionic conductivities for neat [C_2mpyr][FSI] and [C_2mpyr][FSI]/PVDF composites and b. Conductivity measurements of [C_2mpyr][FSI] and [C_2mpyr][FSI]/PS composites with increasing volume fraction of particle (vol%).

Table S1. Table of activation energies for [C_2mpyr][FSI]/PVDF and [C_2mpyr][FSI]/PS composites

Composition of particles (vol%)	Activation energy (Ea) ±0.05 (KJ/mol)	
	PVDF particles	PS particles
0	10.8	10.8
10	12.0	14.6
20	12.9	15.9
30	13.4	14.6
40	14.6	15.0
50	16.7	14.2
60	17.4	13.6
70	17.8	15.2

Ageing and Thermal effects

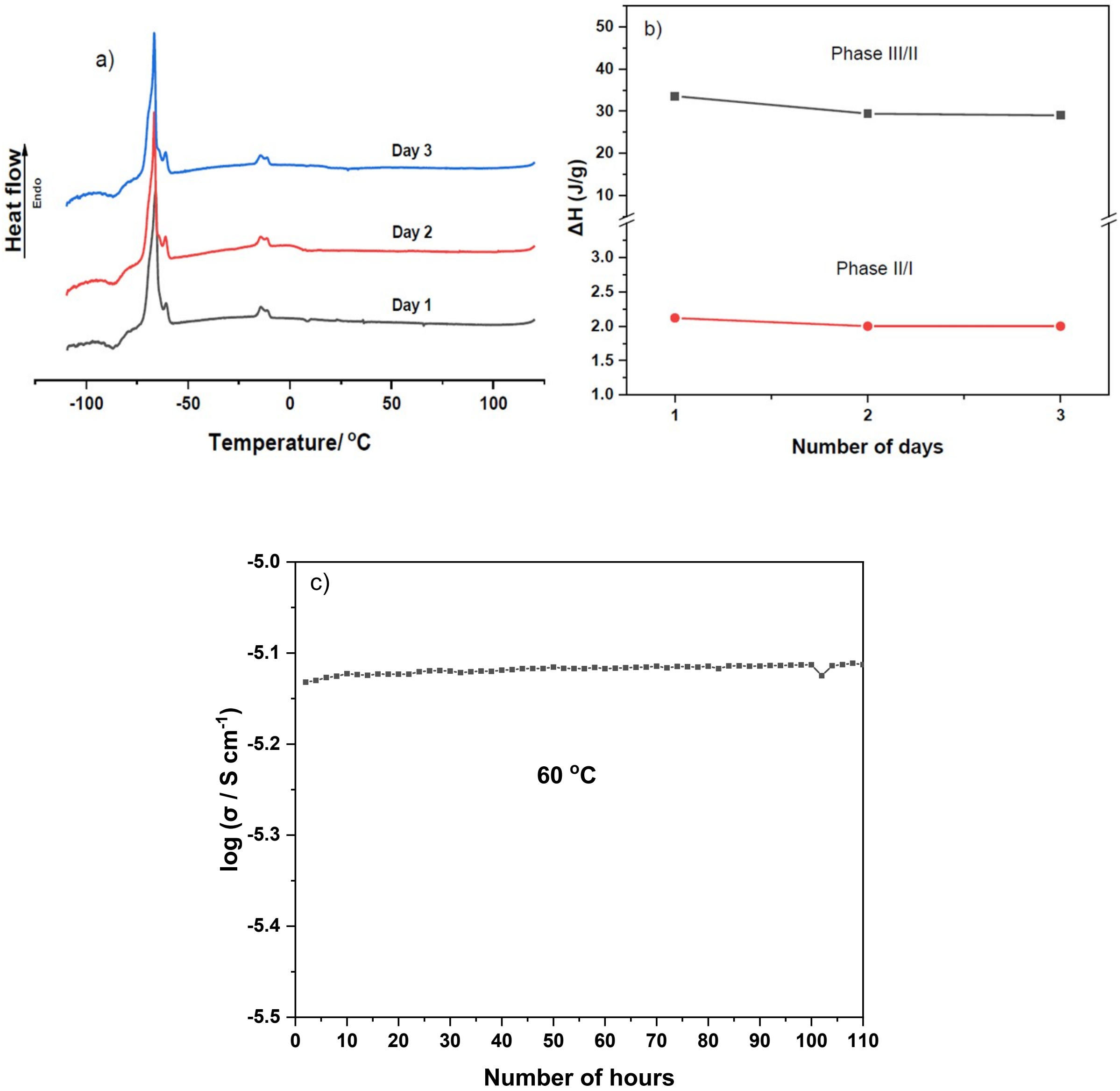


Figure S4:

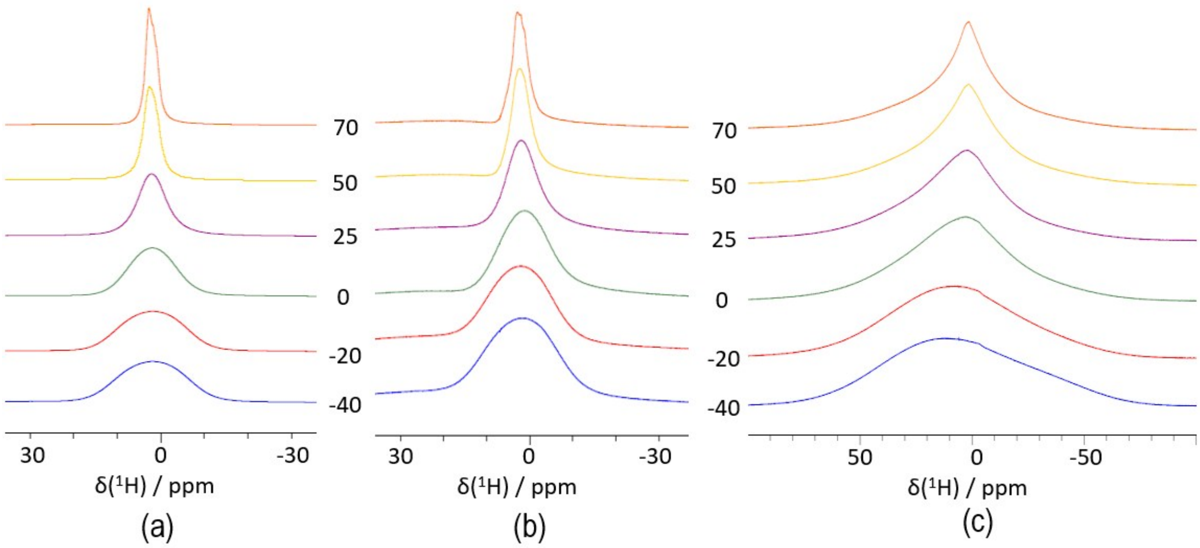
a) DSC heating traces of 50/50 vol% [C_2mpyr][FSI]/PVDF measured on three different days

b) Comparison of the enthalpy changes of the first and second solid-solid transitions of 50/50 vol% [C_2mpyr][FSI]/PVDF sample taken on different days.

c) Ion conductivities of 50/50 vol% [C_2mpyr][FSI]/PVDF taken at two-hour intervals at 60 °C

NMR

^{1}H Static PVDF



^{1}H Static PS

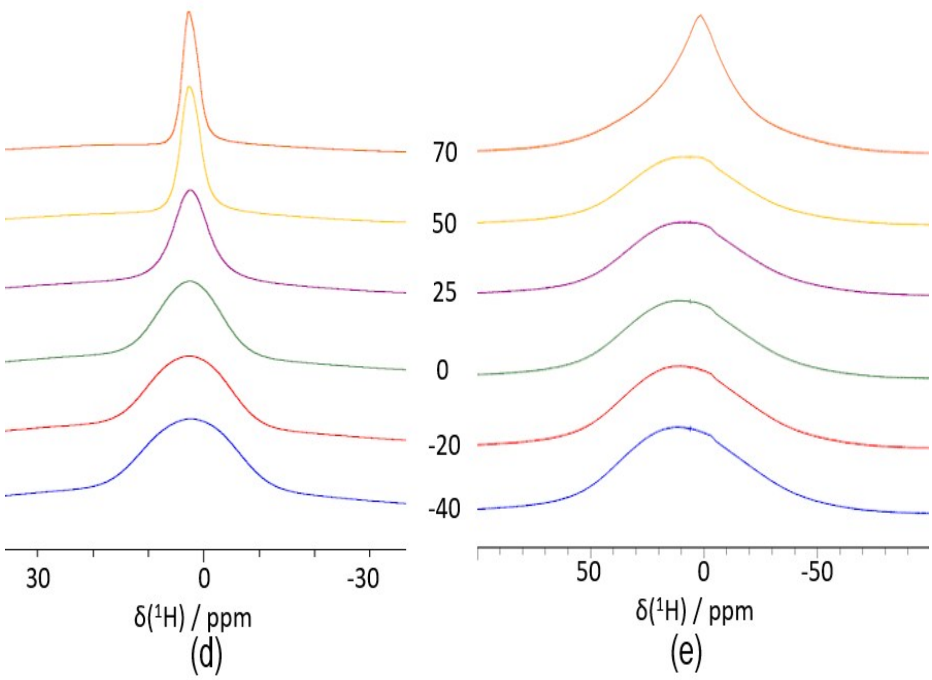
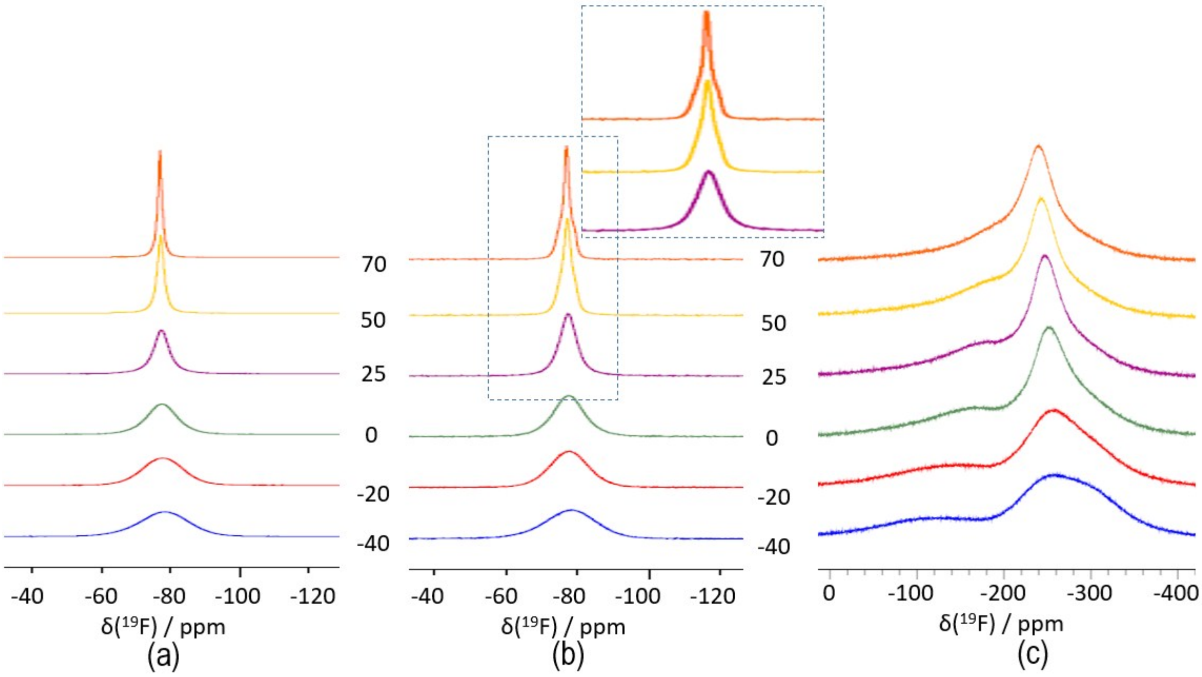


Figure S5: ^{1}H NMR spectra at different temperature for: (a) [C_2mpyr][FSI]; (b) [C_2mpyr][FSI]/PVDF; (c) PVDF; (d) [C_2mpyr][FSI]/PS; and (e) PS

^{19}F Static PVDF



^{19}F Static PS

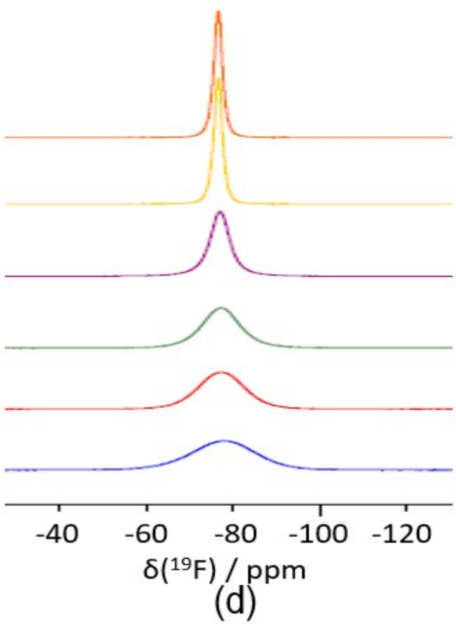


Figure S6: ^{19}F NMR spectra at different temperature for: (a) [C_2mpyr][FSI]; (b) [C_2mpyr][FSI]/PS; (c) PVDF; and (d) [C_2mpyr][FSI]/PS

FTIR

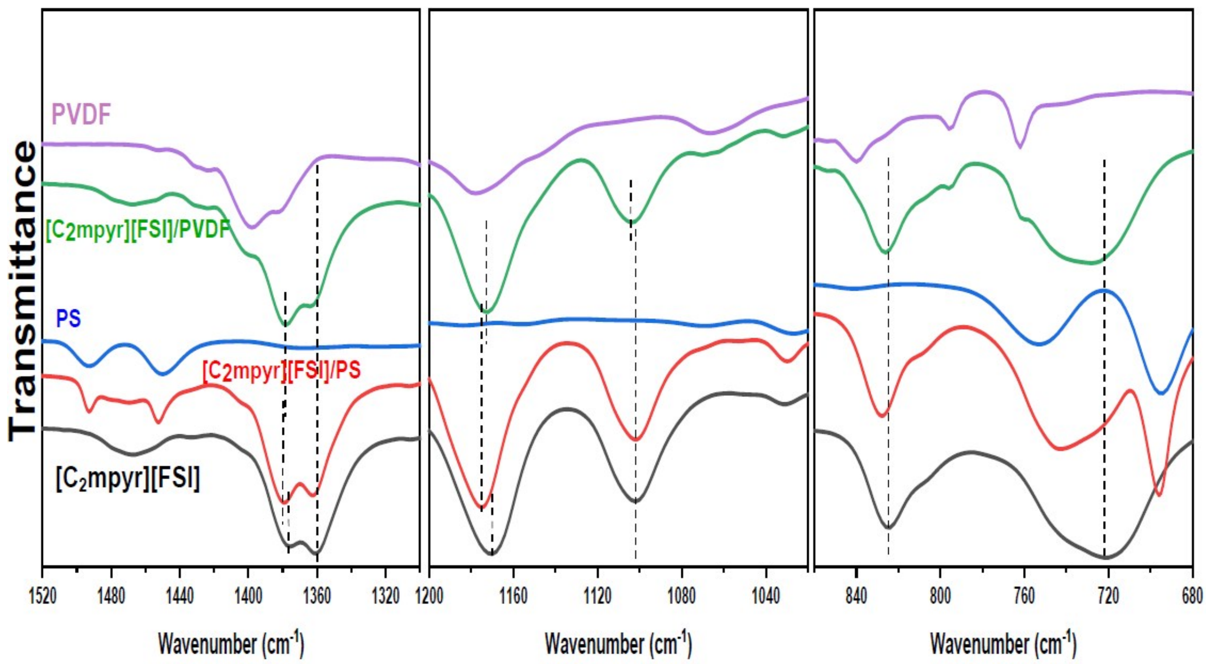
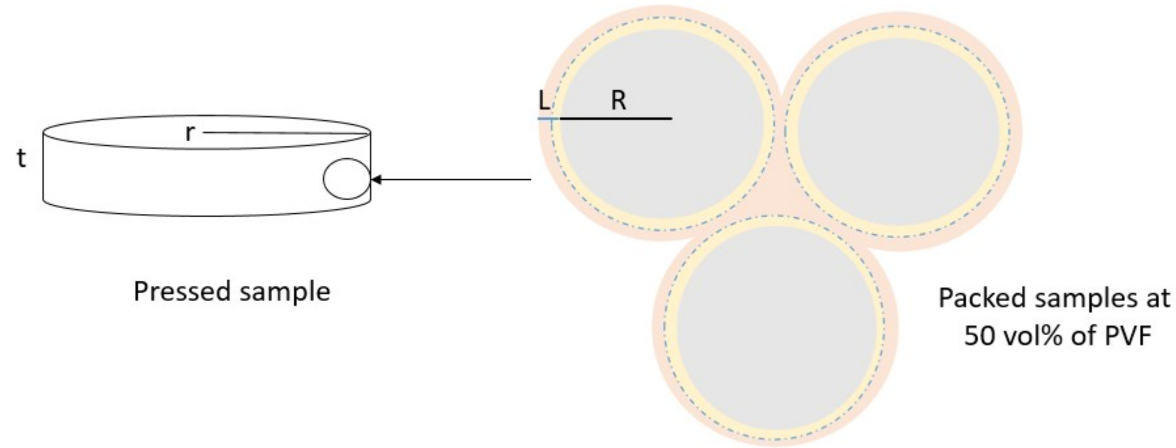


Figure S7: Comparison of the FTIR spectra of [C_2mpyr][FSI], 50/50 vol% [C_2mpyr][FSI]/PS and 50/50 vol% [C_2mpyr][FSI]/PVDF composites

Estimation of the thickness of the disordered interphase

According to the theory of random close packing (RCP) of spherical particles, randomly packed particles occupy 64% of the total volume of the sample.[1,2] The percolation threshold of the PVDF particles is found to occur well below the volume fraction of nanoparticles associated with a random close-packed network suggesting the presence of the disordered interphase. This suggests that the particles assume a new radius (radius of the particles, together with the disordered interphase covering the particles). Therefore, the difference between the new radius and the actual radius of the particles accounts for the thickness of the disordered interphase.



Based on these assumptions, the thickness of the interfacial layer is calculated as follows:

The volume of the pressed sample = $\pi r^2 \times t$

Where r is the radius of the pressed sample and t is the thickness of the pressed sample, R is the radius of the PVDF particles and L is the thickness of the disordered interphase

Volume of particles in the 50 vol% sample is equivalent 64 vol%, at close packing.

Volume of particles at 50 vol% = Volume of particles at 64 vol%

$$\frac{0.50 \times \pi r^2 \times t \times r^3}{4/3\, \pi r^2 \times (R + L)^3} = \frac{0.64 \times \pi r^2 \times t \times r^3}{4/3\, \pi r^2 \times R^3}$$

$$L = 1.086 \times R - R$$

Where PVDF particle size is 360 nm, L= 15.5

Reference

1. Wang, X. *et al.* Organic Ionic Plastic Crystal-Based Composite Electrolyte with Surface Enhanced Ion Transport and Its Use in All-Solid-State Lithium Batteries. *Adv. Mater. Technol.* **2**, 1700046 (2017).

2. *General Chemistry: Principles & Modern Applications R. H. Petrucci, W. S. Harwood, F. G. Herring, and Jeffry D. Madura. New Jersey: Pearson Education, Inc., 2007. 501-508. , ninth Edition.* (2007).