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

Supporting Information

Exploring the influence of the cation type and polymer support in bis(fluorosulfonyl)imide-based plastic crystal composite membranes for CO_2/N_2 separation

Fernando Ramos,[a] Yady Garcia,[a] Colin Kang,[a] Luke O'Dell,[a] Maria Forsyth,[a] and Jennifer M. Pringle*[a]

Thermal analysis

Table S1. Thermal data of the neat polymers (PVDF and PEO) and the neat OIPCs ([C_2mpyr][FSI], [P_{1222}][FSI], [HMG][FSI], [N_{1111}][FSI], [N_{111CN}][FSI]), plus their co-cast composites at different ratios of study (80:20 and 50:50).

	phase III-II		phase II-I		Polymer or combined OIPC/polymer melting		OIPC melting	
	T [°C] ±1°C	ΔH [J g^{-1}] ±10%	T [°C] ±1°C	ΔH [J g^{-1}] ±10%	T [°C] ±1°C	ΔH [J g^{-1}] ±10%	T [°C] ±1°C	ΔH [J g^{-1}] ±10%
PVDF	-	-	-	-	160	33.9	-	-
PEO	-	-	-	-	70	126.6	-	-
[C_2mpyr][FSI]	-66	33.0	-15	3.7	-	-	203	25.3
80[C_2mpyr][FSI]-20PVDF	-66	25.1	-16	1.9	140	10.1	198	7.1
50[C_2mpyr][FSI]-50PVDF	-66	14.3	-15	0.9	143	26.2	-	-
80[C_2mpyr][FSI]-20PEO	-61	24.0	-14	1.8	62	24.6	203	8.4
50[C_2mpyr][FSI]-50PEO	-64	6.0	-14	0.6	62	72.6	-	-
[P_{1222}][FSI]	-	-	-52	29.4	-	-	47	23.4
80[P_{1222}][FSI]-20PVDF	-	-	-55	6.6	122	12.0	47	12.0
50[P_{1222}][FSI]-50PVDF	-	-	-53	1.2	142	28.8	48	1.8
80[P_{1222}][FSI]-20PEO	-	-	-51	20.4	53	42.0	-	-
50[P_{1222}][FSI]-50PEO	-	-	-52	1.2	61	67.2	-	-
[HMG][FSI]	10	31.2	67	37.8	-	-	88	6.6
80[HMG][FSI]-20PVDF	10	0.6	68	22.2	115	9.0	85	2.4
50[HMG][FSI]-50PVDF	11	1.2	68	9	132	25.2	86	0.6
80[HMG][FSI]-20PEO	-	-	-	-	62	62.4	-	-
50[HMG][FSI]-50PEO	-	-	-	-	70	101.4	-	-
[N_{1111}][FSI]	-	-	76	51.6	-	-	311	39.0
80[N_{1111}][FSI]-20PVDF	-	-	77	43.2	158	13.8	n/a	n/a
50[N_{1111}][FSI]-50PVDF	-	-	77	21.0	160	36.6	n/a	n/a
80[N_{1111}][FSI]-20PEO	-	-	78	43.2	61	32.4	n/a	n/a
50[N_{1111}][FSI]-50PEO	-	-	77	19.2	64	71.4	n/a	n/a
[N_{111CN}][FSI]	-	-	-66	4.2	-	-	100	74.4
80[N_{111CN}][FSI]-20PVDF	-	-	-65	3.0	165	12.0	103	49.8
50[N_{111CN}][FSI]-50PVDF	-	-	-	-	167	40.8	96	24.6
80[N_{111CN}][FSI]-20PEO	-	-	-65	3.0	53	26.6	101	43.2
50[N_{111CN}][FSI]-50PEO	-	-	-66	1.8	51	66.6	82.4	9.0

Polarised optical microscopy

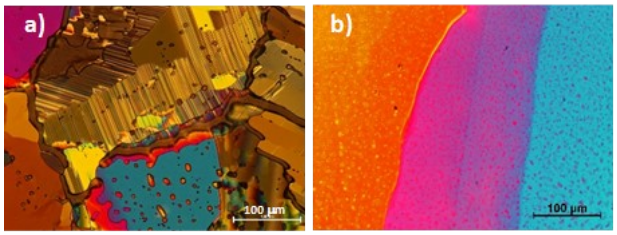


Figure S1: Polarized optical micrographs taken at 200x magnification at room temperature after melt and recrystallization on a microscope slide in a hot stage (cooling rate 10 °C min^{-1}) of a) neat [HMG][FSI], and b) neat [P_{1222}][FSI].

Gas permeability-selectivity

Table S2. CO_2 and N_2 permeability and selectivity of the neat polymers and the OIPC/polymer composites at 35 and 75 °C.

OIPC	Polymer (wt%)	*T* (K)	P_{CO2}	P_{N2}	$\alpha_{CO2/N2}$
-	100 PVDF	308	0.7 ± 0.3	0.02 ± 0.003	31 ± 15.8
		348	3 ± 0.1	0.4 ± 0.08	7 ± 0.7
-	100 PEO	308	118 ± 0.5	4.6 ± 1.36	26 ± 8.8
[C_2mpyr][FSI]	20 PVDF	308	57 ± 5.8	1.3 ± 0.13	43± 1.3
		348	95 ± 9.2	5.5 ± 0.50	17 ± 2.7
	50 PVDF	308	63 ± 14.1	4.4 ± 1.95	14 ± 7.0
		348	75 ± 2.2	6.4 ± 0.37	12 ± 1.2
	20 PEO	308	47 ± 1.6	1.4 ± 0.01	33 ± 7.6
	50 PEO	308	54 ± 7.5	2.3 ± 0.01	23 ± 3.3
[P_{1222}][FSI]	20 PVDF	308	100 ± 8.3	3.6 ± 0.08	28 ± 2.3
		348	351 ± 51.1	21.8 ± 1.89	16 ± 1.0
	50 PVDF	308	361 ± 5.0	12.4 ± 0.55	29 ± 1.2
		348	479 ± 6.8	36.9 ± 0.51	13 ± 0.0
	80 PEO	308	N/A	N/A	N/A
	50 PEO	308	38 ± 3.2	2.1 ± 0.77	17 ± 6.0
[HMG][FSI]	20 PVDF	308	12 ± 1.7	0.4 ± 0.14	29 ± 5.6
		348	504 ± 59.0	40.6 ± 4.74	12 ± 2.7
	50 PVDF	308	16 ± 7.7	0.6 ± 0.03	26 ± 11.1
		348	279 ± 22.9	21.3 ± 1.07	13 ± 1.8
	20 PEO	308	3 ± 0.4	0.5 ± 0.66	5 ± 7.6
	50 PEO	308	14 ± 0.7	6.8 ± 2.80	2 ± 1.3
[N_{1111}][FSI]	20 PVDF	308	1.6 ± 0.0	0.4 ± 0.02	4 ± 0.2
		348	57 ± 0.9	4.9 ± 0.08	11 ± 0.5
	50 PVDF	308	2 ± 1.7	0.9 ± 0.23	3 ± 1.6
		348	29 ± 1.3	4.5 ± 0.21	6 ± 0.5
	20 PEO	308	N/A	N/A	N/A
	50 PEO	308	6 ± 2.4	0.5 ± 0.21	13 ± 2.8
[N_{111CN}][FSI]	20 PVDF	308	N/A	N/A	N/A
		348	N/A	N/A	N/A
	50 PVDF	308	5 ± 1.5	0.9 ± 0.11	6 ± 1.8
		348	2 ± 0.2	1.9 ± 0.36	1 ± 1.0
	20 PEO	308	2 ± 0.6	0.7 ± 0.09	2 ± 0.5
	50 PEO	308	N/A	N/A	N/A

Synchrotron powder X-ray diffraction

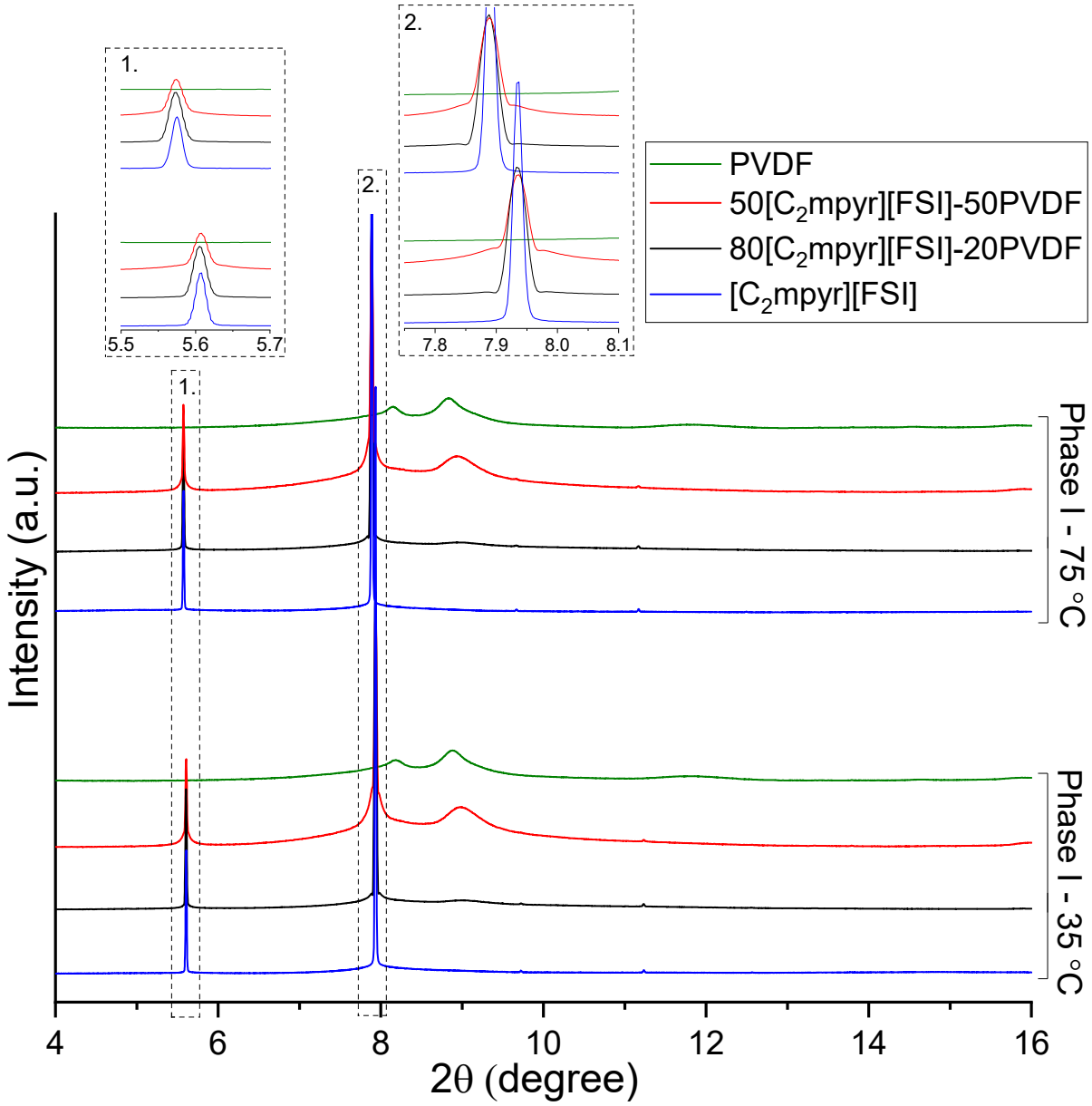


Figure S2: Synchrotron powder XRD patterns collected at 35 and 75 °C (λ = 0.6882361(4) Å) for neat [C_2mpyr][FSI] (blue), neat PVDF (green) and the composites 80[C_2mpyr][FSI]:20PVDF (black), and 50[C_2mpyr][FSI]:50PVDF (red). Details of the peaks are magnified and numbered.

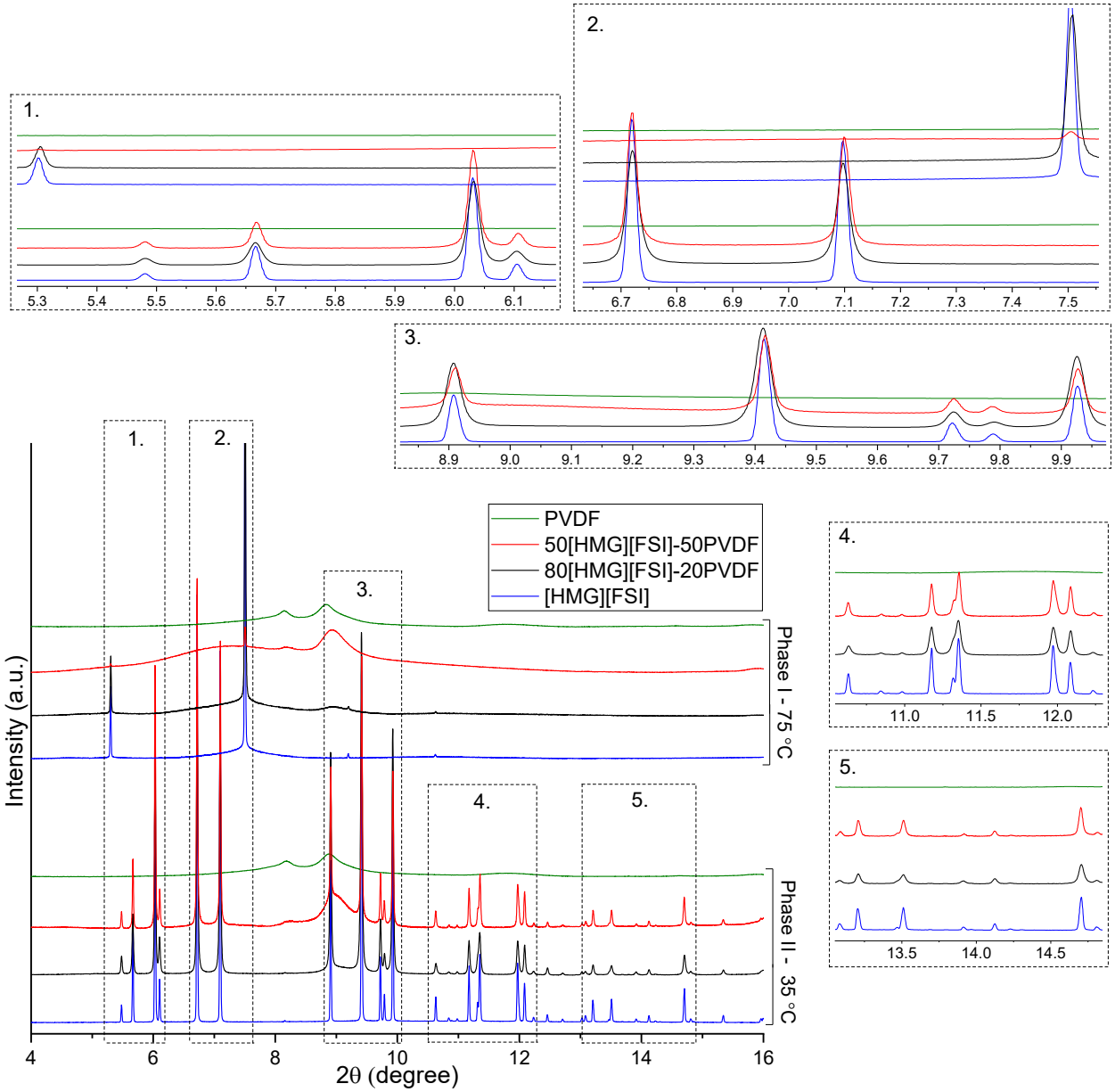


Figure S3: Synchrotron powder XRD patterns collected at 35 and 75 °C (λ = 0.6882361(4) Å) for neat [HMG][FSI] (blue), neat PVDF (green) and the composites 80[HMG][FSI]:20PVDF (black), and 50[HMG][FSI]:50PVDF (red). Details of the peaks are magnified and numbered.

Line width (FWHMs) and Area fraction of narrow peak

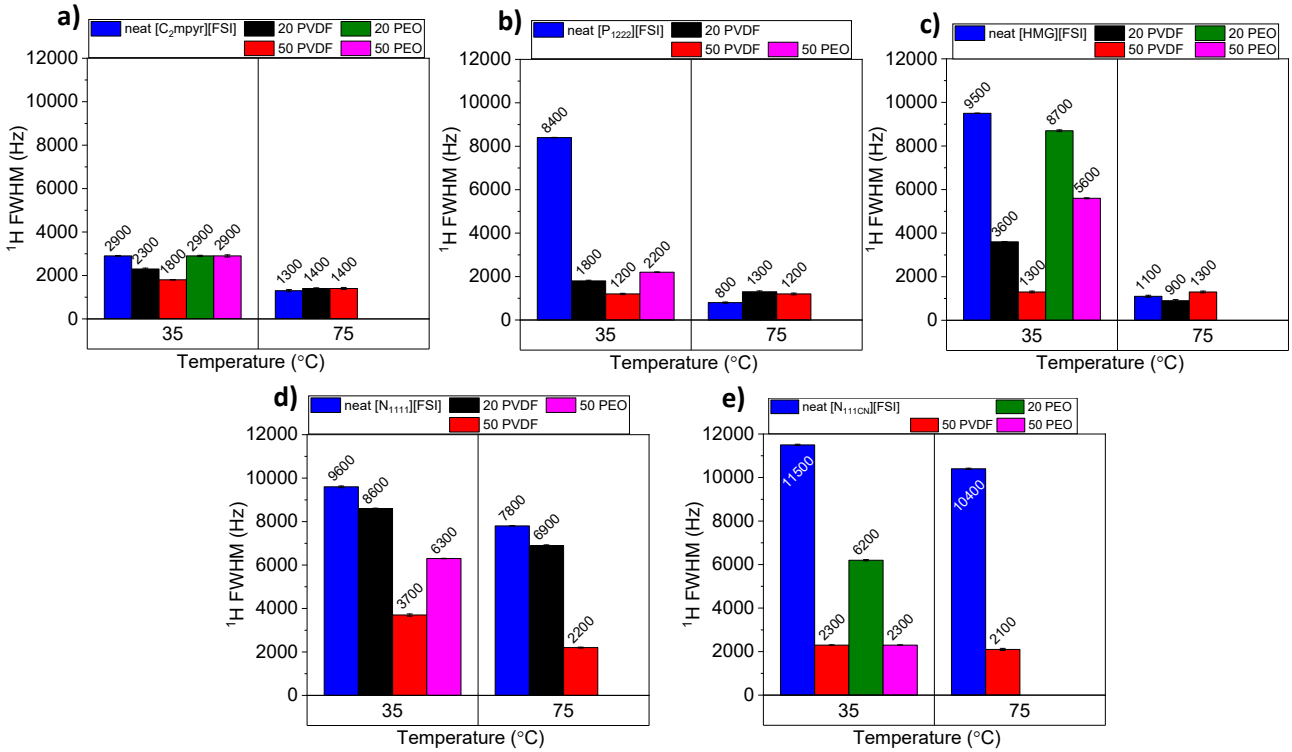


Figure S4. ^{1}H Line full width at half-maximum (FWHMs) b) neat [P_{1222}][FSI], c) neat [HMG][FSI], d) neat [N_{1111}][FSI], e) neat [N_{111CN}][FSI], and their corresponding PVDF and PEO composites.

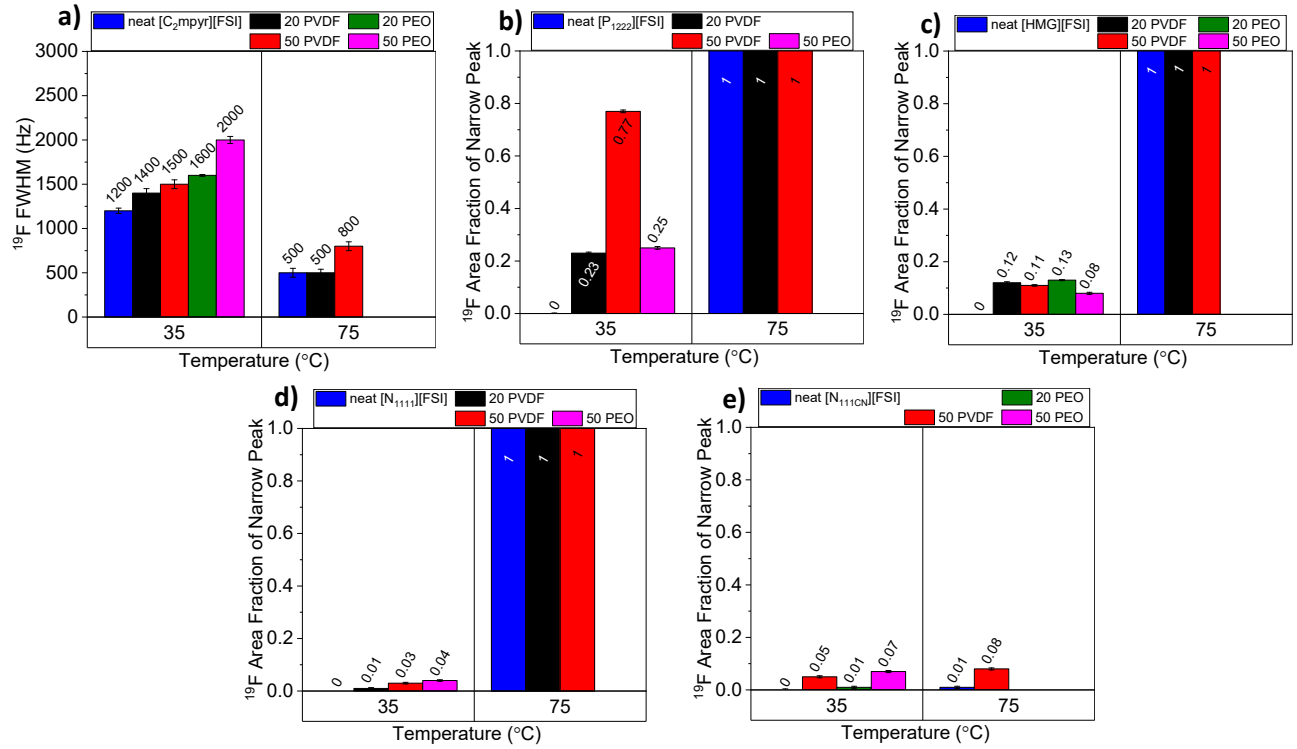
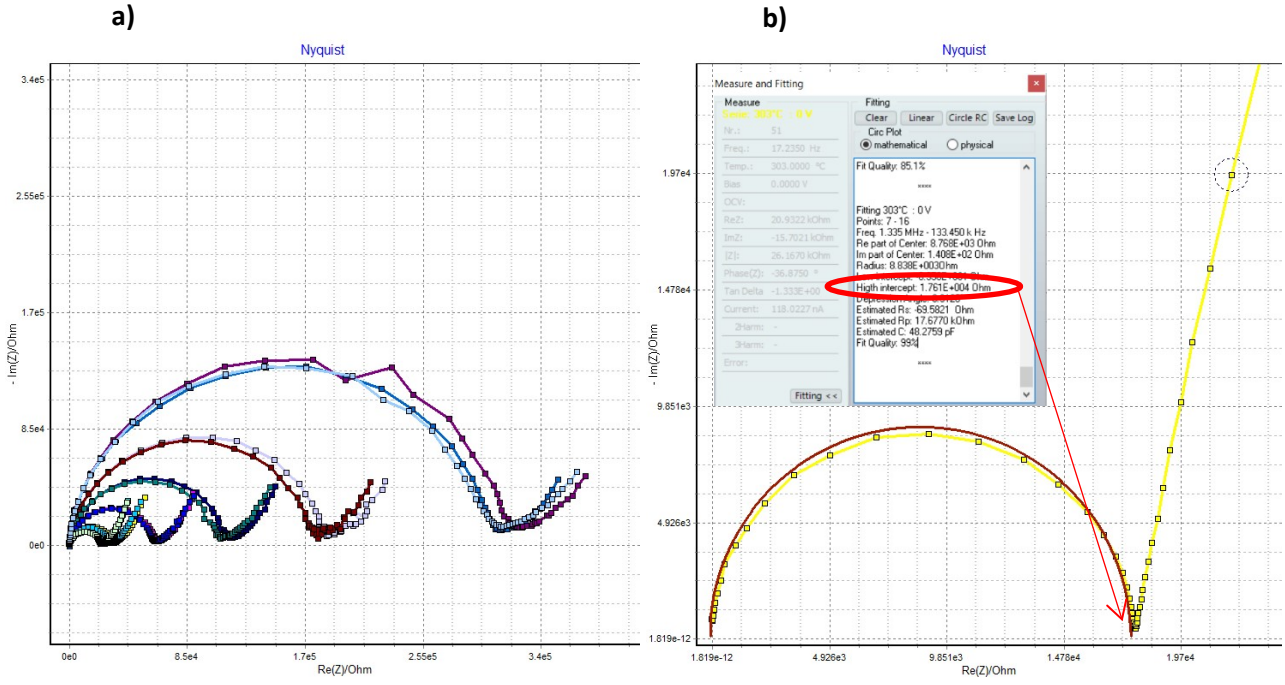


Figure S5. a) ^{19}F Line full width at half-maximum (FWHMs) of neat [C_2mpyr][FSI] and its PVDF and PEO composites. ^{19}F Area Fraction of Narrow Peak of: b) neat [P_{1222}][FSI], c) neat [HMG][FSI], d) neat [N_{1111}][FSI], e) neat [N_{111CN}][FSI], and their corresponding PVDF and PEO composites.

Table S3. Fitting parameters of the fluorine nuclei in the OIPCs. The parameters of the FSI anion were extracted from ^{19}F NMR spectra of the pure OIPCs at 35°C by iterative fitting to a simulated CSA pattern and gauss/Lorentzian line shape function using the DMfit software.

OIPC	Model	Chemical shift (ppm)	Relative Intensity	δ(CSA)	η(CSA)
$[C_2mpyr][FSI]$	gauss/Lorentzian	95.6	1	-	-
[HMG][FSI]	CSA	95.8	1	-73.51	0.99
$[P_{1222}][FSI]$	gauss/Lorentzian	95.6	0.01	-	-
	CSA	94.2	0.99	49.5	0.14
$[N_{1111}][FSI]$	CSA	91.5	1	-129	0.46
$[N_{111CN}][FSI]$	gauss/Lorentzian	93.9	0.00	-	-
	CSA	94.3	0.1	78.85	0.26

Surprisingly, the $[FSI]^-$ anions exhibit very different CSA pattern shapes depending on the OIPC cation. The CSA line shapes are quantified by parameters including the asymmetry parameter (η) which indicates how much the environment around the fluorine nucleus deviates from axial symmetry and takes values between 0 and 1.[1] The shape of the $[P_{1222}][FSI]$ CSA pattern presents a CSA asymmetry parameter (η) near zero (~0.14) and suggests that fluorine atoms have an axially symmetry in the [FSI] anion. The value of η increases, $[N_{111CN}][FSI]$< $[N_{1111}][FSI]$< [HMG][FSI], and indicates a deviation of the axially symmetry of the fluorine in these OIPCs (Figure 9)(Table S3). These differences are a result of the symmetry, size and packing of cations that surround them.



Electrochemical impedance spectroscopy (EIS)

Figure S6. a) Example of Nyquist plot acquisition over a temperature range in neat [HMG][FSI] pellet. b) Example of Nyquist plot fitting to obtain resistance value of 50$[C_2mpyr][FSI]$:50PVDF.

References SI

[1] H. W. Spiess, in *Dynamic NMR Spectroscopy* (Eds.: A. Steigel, H. W. Spiess), Springer Berlin Heidelberg, Berlin, Heidelberg, **1978**, pp. 55-214.