Supplementary Information

Polycationic scaffolds for Li ion exchange transport mechanism in gel polymer electrolytes

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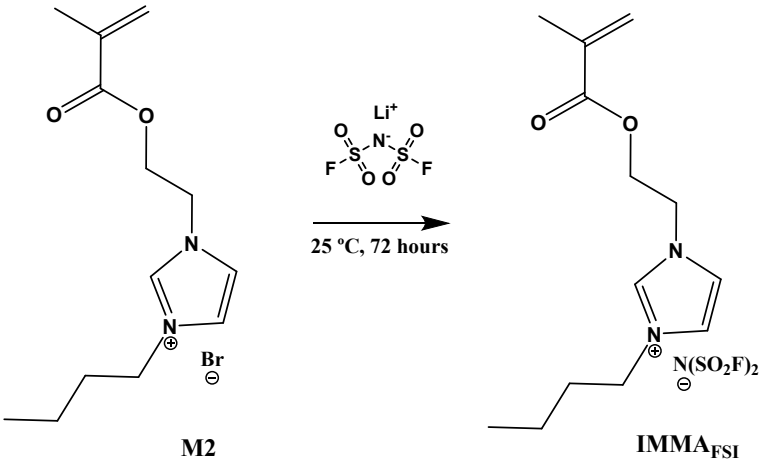
Synthesis of intermediates 2-bromoethyl methacrylate (**M**1), 1-(2-Methacryloyloxy)ethyl-3-butylimidazolium Bromide (**M2**) and -(2-Methacryloyloxy)ethyl-3-butylimidazolium Bis(trifluoromethane sulfonyl)imide) (**IMMATFSI**) are described in previous work.[1]

Synthesis of 1-(2-Methacryloyloxy)ethyl-3-butylimidazolium Bisfluorosulfonylimide (IMMAFSI)



Scheme S1. Synthesis of monomer IMMAFSI

In an ace round-bottom pressure flask, a mixture of **M2** (1 g., 0.00315 mol) and bis(fluorosulfonylimide) lithium salt (LiFSI, 0.589 g., 0.00315 mol) were diluted in 80 ml of milliQ H_2O, and was stirred at 25ºC for 4 days to induce a liquid-liquid phase separation. The organic layer was isolated and diluted with dichloromethane (15 mL). This solution was washed with water (3 × 30 mL). The product was concentrated under

[1] J. L. Pablos, N. García, L. Garrido, J. Guzmán, F. Catalina, T. Corrales, P. Tiemblo; Highly efficient mixed Li^+ transport in ion gel polycationic electrolytes, *J Membrane Sci 545* (2018) 133–139.

reduced pressure to obtain a viscous ligth brown oil. Yield: 0.8 g. (60.7 %). ^{1}H-NMR (400 MHz, DMSO-d_6): δ (ppm) 9.24 (s, 1H), 7.78 (d, J = 11.4 Hz, 2H), 6.03 (s, 1H), 5.69 (s, 1H), 4.60 – 4.39 (m, 4H), 4.19 (s, 2H), 1.84 (s, 3H), 1.82 – 1.71 (m, 2H), 1.24 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H).^{13}C NMR (400 MHz, DMSO-d_6) δ (ppm) δ 166.00, 136.51, 135.25, 126.49, 122.80, 122.49, 62.42, 48.78, 48.15, 31.35, 18.73, 17.79, 13.13 FTIR (wavenumbers, cm^{-1}): $\upsilon_{C=O}$ 1726; st(C=C) 1640; st (C-O) 1153; st (C=C) 1559; st (C=N) 1460; st (C-N) 1295; st (C-H) 2970; st(=-C-H) 3150-3000. 1350-1050 and 900-650 FSI bands.

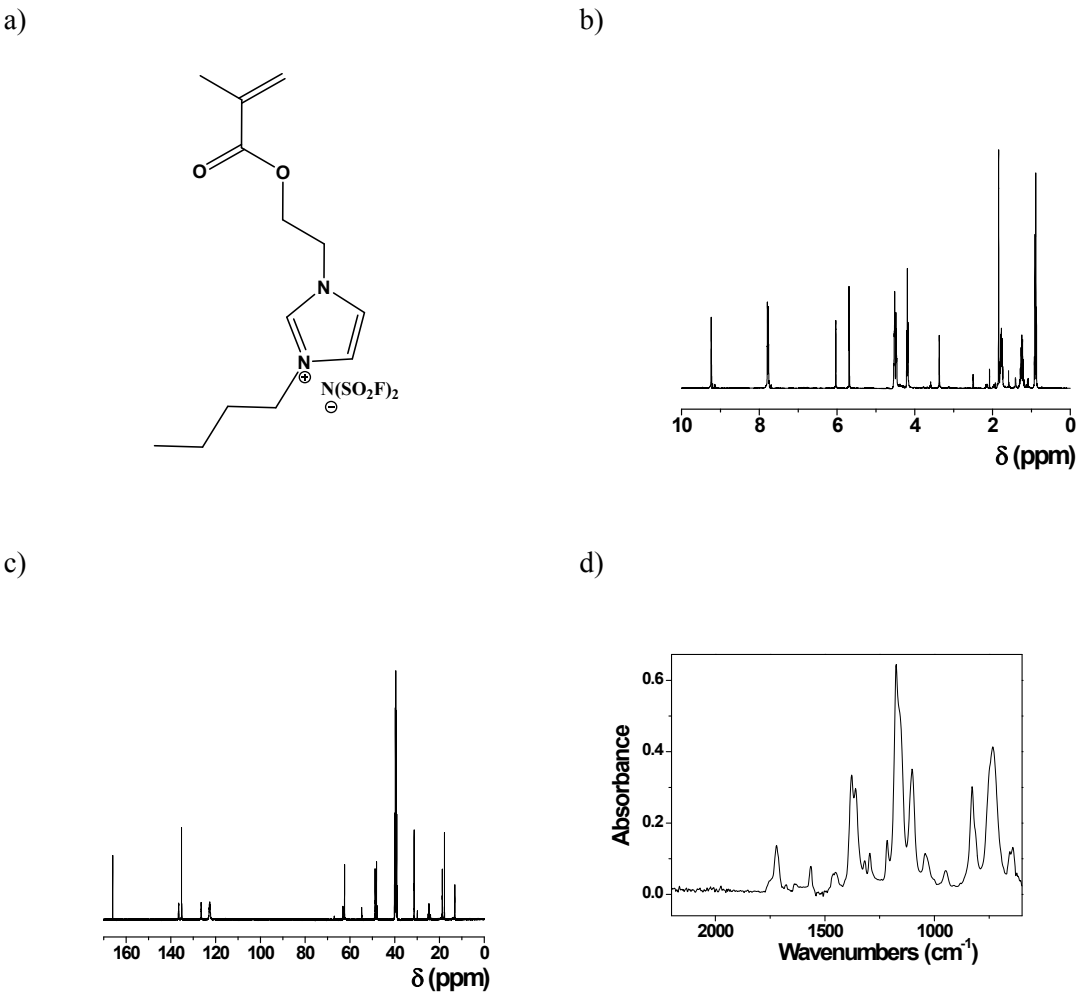
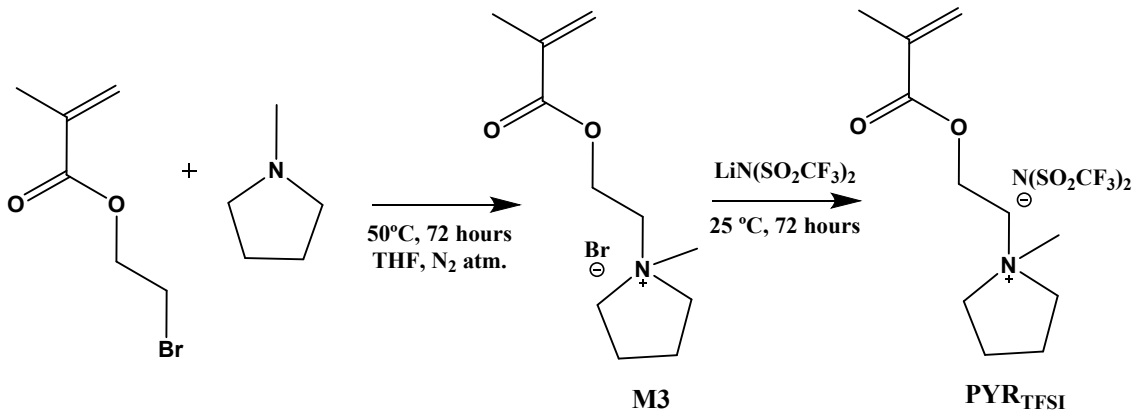


Figure S1. Characterization of **IMMAFSI**: a) Chemical structure; b) ^{1}H NMR; c) ^{13}C NMR (NMR solvent: DMSO-d_6); d) FT-IR

B- Synthesis of pyrrolidonium based ionic liquids



Scheme S2. Synthesis of monomer PYRTFSI

Synthesis of 1-(2-Methacryloyloxy)ethyl-1-methylpyrrolidinium Bromide (M3).

In an ace round-bottom pressure flask, a mixture of *N-methylpyrrolidine* (1.22 mL., 11.7 mmol) and 2-bromoethyl methacrylate (**M1**) (2.25 g., 11.7 mmol) in 15 ml of THF with a small amount of hydroquinone to inhibit the thermal polymerization of the resulting monomer, was stirred at 50 ºC for 72 hours to induce a liquid-liquid phase separation. The organic layer was isolated, washed with fresh THF, isolated again and diluted with dichloromethane (15 mL). The product was filtered and concentrated under reduced pressure to obtain a viscous ligth brown oil. The product was collected and dried in vacuo. ^{1}H-NMR (400 MHz, DMSO-d_6): δ (ppm) δ 6.07 (s, 1H), 5.73 (s, 1H), 4.52 (m, 2H), 3.85 (m, 2H), 3.60 (m, 4H), 3.11 (s, 3H), 2.10 (m, 4H), 1.88 (t, J = 1.3 Hz, 3H). ^{13}C NMR (400 MHz, DMSO-d_6) δ (ppm) δ 165.88, 135.32, 126.66, 64.06, 61.28, 58.91, 47.81, 20.86, 17.92. FTIR (wavenumbers, cm^{-1}): $\upsilon_{C=O}$ 1726; st(C=C) 1640; st (C-O) 1153; st (C=C) 1559; st (C-N) 1295; st (C-H) 2970; st(=-C-H) 3150-3000.

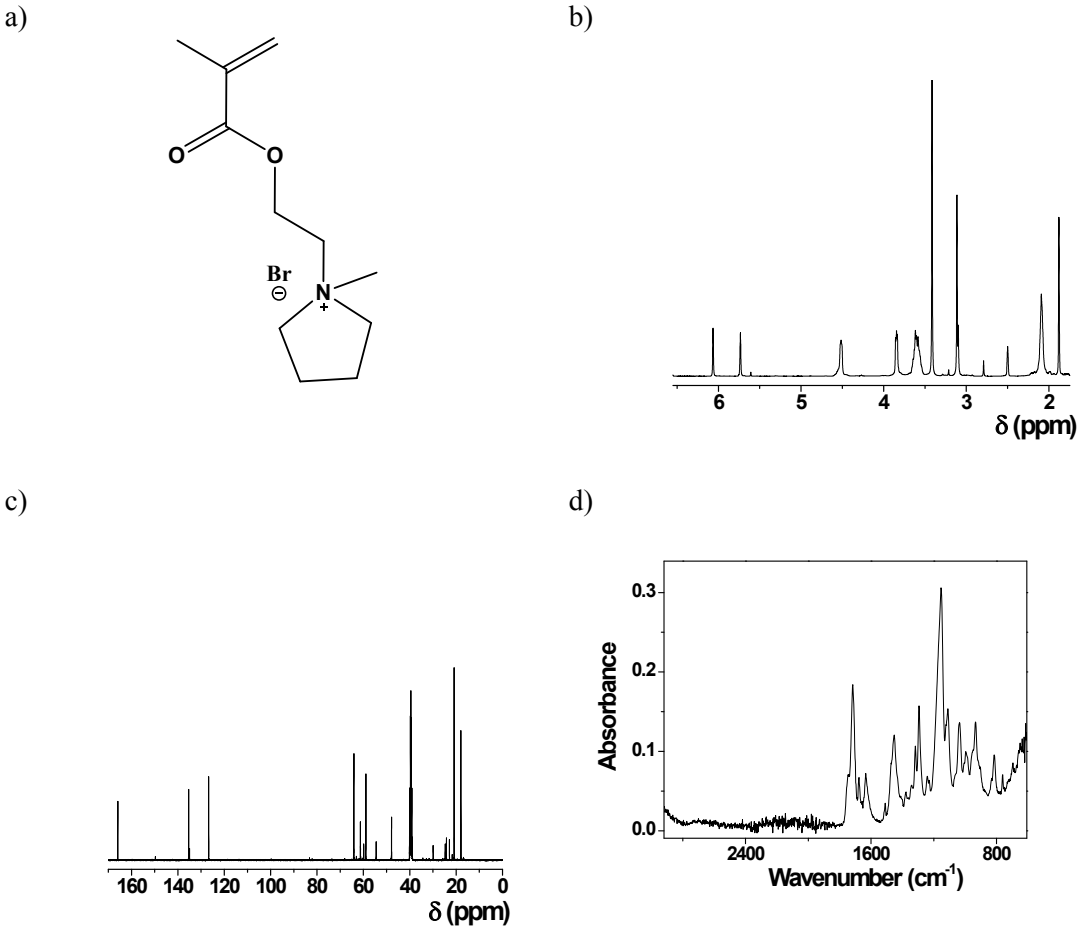


Figure S2. Characterization of **M3**: a) Chemical structure; b) ^{1}H NMR; c) ^{13}C NMR (NMR solvent: DMSO-d_6); d) FT-IR

Synthesis of 1-(2-Methacryloyloxy)ethyl-1-methylpyrrolidinium Bis(trifluoromethane sulfonyl)imide (PYRTFSI).

In an ace round-bottom pressure flask, a mixture of **M3** (1 g., 35.9 mmol) and bis(trifluoromethane) sulfonimide lithium salt (0.95 g., 33.1 mmol) were diluted in 80 ml of milliQ water, and was stirred at 25ºC for 3 days to induce a liquid-liquid phase separation. The organic layer was isolated and diluted with dichloromethane (15 mL). This solution was washed with water (3 x 30 mL). The product was concentrated under reduced pressure to obtain a viscous ligth brown oil. Yield: 1.3 g. (76 %). ^{1}H-NMR (400 MHz, DMSO-d_6): δ (ppm) 6.10 (s, 1H), 5.72 (s, 1H), 4.54 (m, 2H), 3.78 (m, 2H), 3.57 (m, 4H), 3.09 (s, 3H), 2.15 (m, 4H), 1.91 (s, 3H). ^{13}C NMR (400 MHz, DMSO-d_6) δ

(ppm) δ 166.00, 135.48, 126.47, 124.44, 121.24, 118.04, 114.84, 64.41, 61.76, 58.81, 47.92, 20.92, 17.74. Quartet arising from CF_3 in the TFSI anion 124.44, 121.24, 118.04, 114.84.[2] FTIR (wavenumbers, cm^{-1}): $\upsilon_{C=O}$ 1726; st(C=C) 1640; st (C-O) 1153; st (C=C) 1559; st (C-N) 1295; st (C-H) 2970; st(=-C-H) 3150-3000. 1350-1050 and 900-650 TFSI bands.

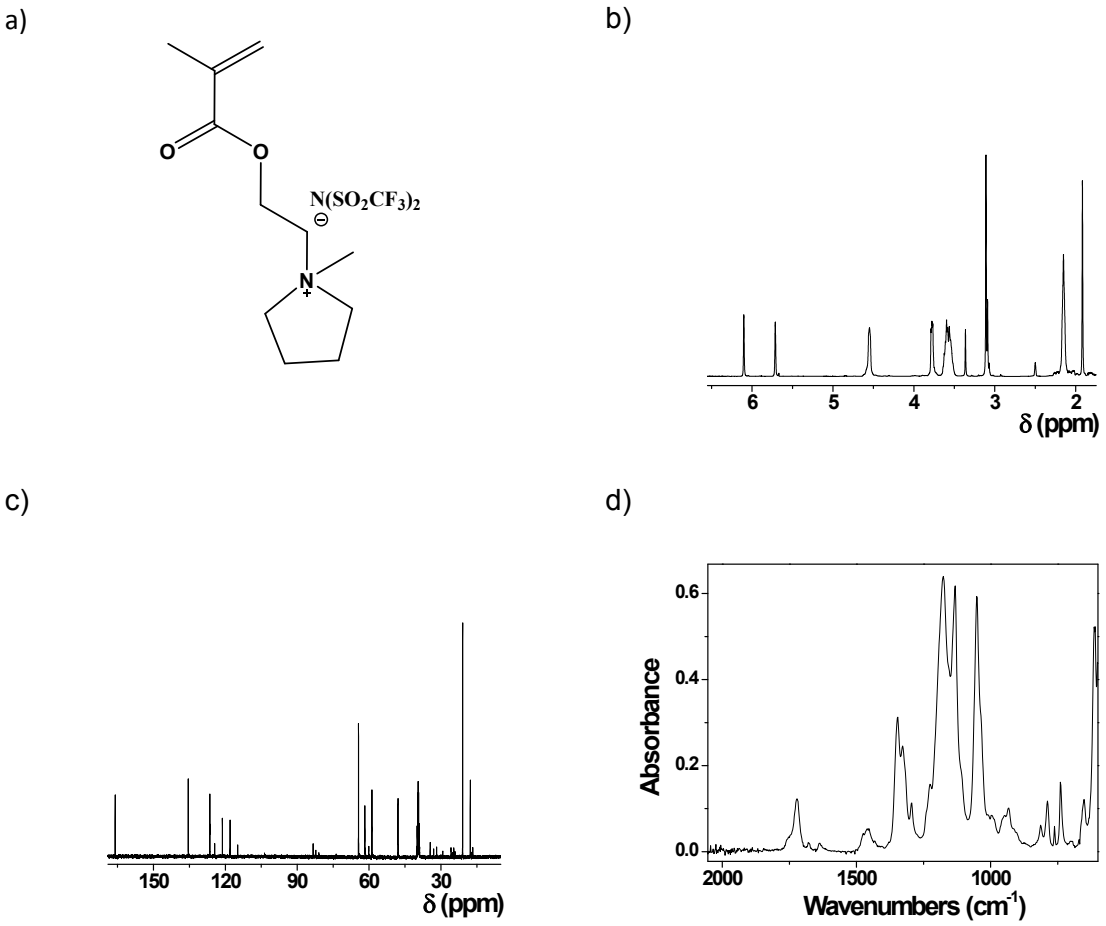
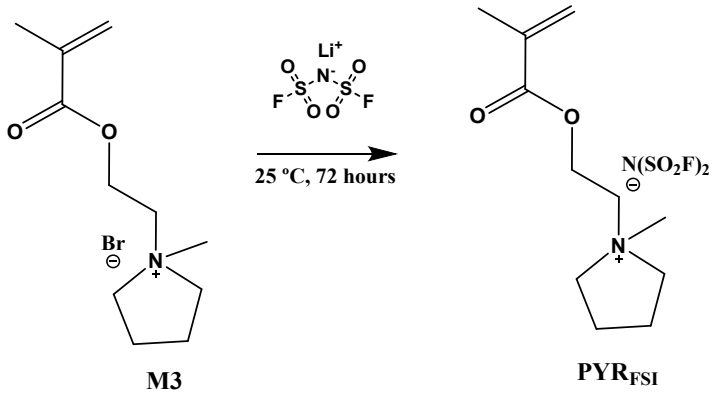


Figure S3. Characterization of **PYRTFSI**: a) Chemical structure; b) ^{1}H NMR; c) ^{13}C NMR (NMR solvent: DMSO-d_6); d) FT-IR

Synthesis of 1-(2-Methacryloyloxy)ethyl-1-methylpyrrolidinium Bisfluorosulfonylimide (PYRFSI)

[2] Patent Application Publication, United States, Pub. No.: US 2012/0326073 A1, Dec, 27, 2012.



Scheme S3. Synthesis of monomer PYRFSI

In an ace round-bottom pressure flask, a mixture of **M3** (1 g., 0.00315 mol) and bis(fluorosulfonylimide) lithium salt (LiFSI, 0.67 g., 0.00315 mol) were diluted in 80 ml of milliQ H_2O, and was stirred at 25ºC for 4 days to induce a liquid-liquid phase separation. The organic layer was isolated and diluted with dichloromethane (15 mL). This solution was washed with water (3 × 30 mL). The product was concentrated under reduced pressure to obtain a viscous ligth brown oil, **PYRFSI**. Yield: 0.75 g. (55 %). ^{1}H-NMR (400 MHz, DMSO-d_6): δ (ppm) 6.09 (s, 1H), 5.74 (s, 1H), 4.53 (m, 2H), 3.80 – 3.69 (m, 2H), 3.56 (dd, J = 13.4, 7.0 Hz, 4H), 3.07 (d, J = 8.9 Hz, 2H), 2.12 (m, 4H), 1.91 (s, 3H).^{13}C NMR (400 MHz, DMSO-d_6) δ (ppm) -165.94, 135.40, 126.57, 64.33, 61.65, 59.76, 58.79, 47.85, 20.92, 17.84.FTIR (wavenumbers, cm^{-1}): $\upsilon_{C=O}$ 1726; st(C=C) 1640; st (C-O) 1153; st (C=C) 1559; st (C-N) 1295; st (C-H) 2970; st(=-C-H) 3150-3000. 1350-1050 and 900-650 FSI bands.

a) b)

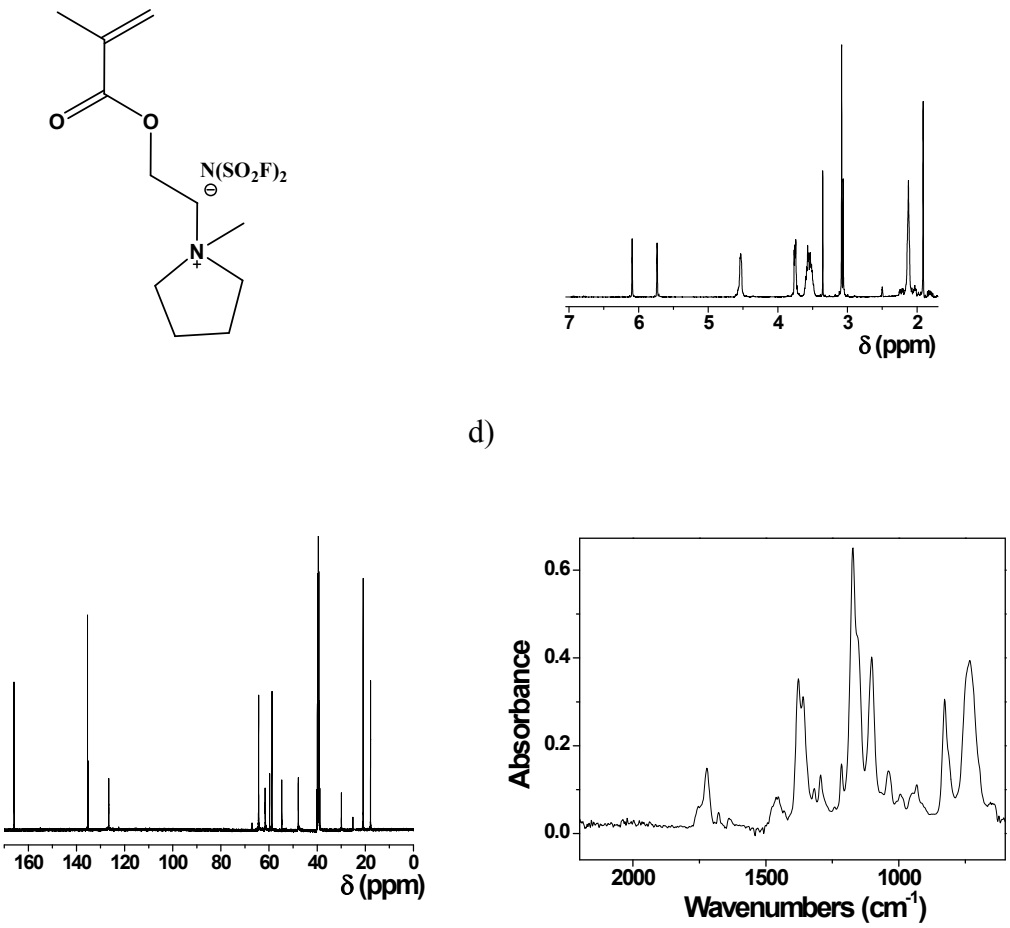


Figure S4. Characterization of **PYRFSI**: a) Chemical structure; b) ^{1}H NMR; c) ^{13}C NMR (NMR solvent: DMSO-d_6); d) FT-IR

C- FTIR analysis of TFSI/FSI bands of polymerizable ionic liquids.

The anion exchange in monomers IMMA TFSI/FSI and PYRTFSI/FSI was confirmed by FTIR. The spectra of the monomers allow to characterize the presence of bands of the anions TFSI and FSI. To help to shed light on the FTIR interpretation, spectra of lithium salt (LiFSI and LiTFSI) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide/bisfluorosulfonylimide (EMIMTFSI/FSI) were also recorded and included in the Figure S5. The TFSI spectrum (as counter-anion of Li or of polycation) shows characteristic bands in the region of 1120-1200 cm^{-1} assigned to

asymmetric and symmetric vibration, $\upsilon(CF_3)$ (Figure S5-a).[3] Similarly, FSI spectrum shows the bands assigned to $\upsilon_s(SO_2)$ vibrations around 1170 cm^{-1} presents in FSI anion of FSI-lithium salt (Figure S5-b).[4] These clearly confirm the presence of TFSI and FSI anions in polymerizable ionic liquid monomer synthetized.

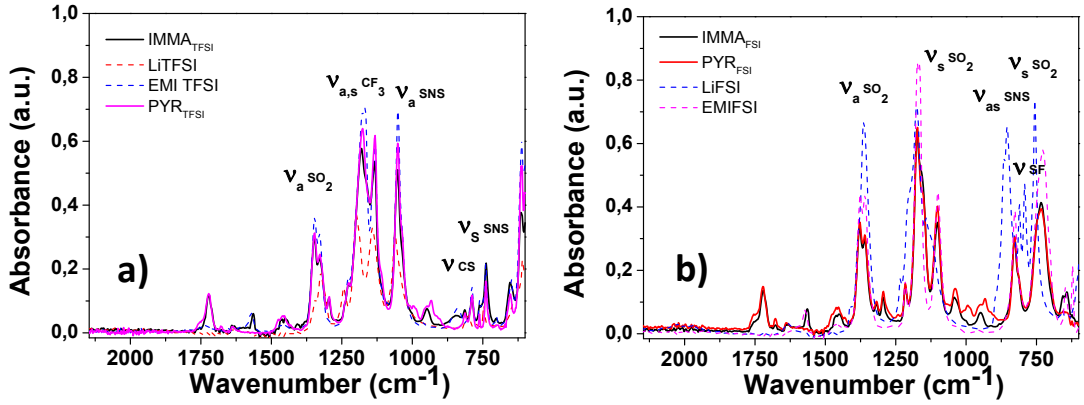


Figure S5. FTIR spectra of ionic liquid monomers, lithium salt (LiFSI and LiTFSI) and EMITFSI/FSI.

S.2. Characterization

S.2.1 Rheological measurements.

Rheological measurements were performed using an Advance rheometer AR2000 with a 20 mm steel crosshatched plate under nitrogen flow to avoid oxidative degradation. 1250 µm thick electrolyte gels were prepared by photopolimerization and stabilized at 25 ºC. Oscillatory frequency sweeps were performed in the frequency range of 10^{-2}–10^{2} Hz at 0.1% strain and in the % strain range of 10^{-2}–10^{2} at 1 Hz. (Table S1).

S.2.2. NMR.

[3]I. Rey, P. Johansson, J. Lindgren, J. C. Lasse`gues, J. Grondin, L. Servant; Spectroscopic and Theoretical Study of $(CF_3SO_2)_2N^-$ ($TFSI^-$) and $(CF_3SO_2)_2NH$ (HTFSI), *J. Phys. Chem. A. 102 (*1998) 3249-3258.
[4]J. Huang, A. F. Hollenkamp, Thermal Behavior of Ionic Liquids Containing the FSI Anion and the Li^+ Cation, *J. Phys. Chem. C 114 (*2010) 21840–21847.

Intermediates and monomers were characterized by ^{1}H-NMR and ^{13}C-NMR spectra recorded on a *Varian-Mercury* 400 MHz using DMSO-d_6 as the solvent. The chemical shifts (δ) are given in section S1.

S.2.3. Thermogravimetric analysis (TGA)

Measurements were carried out in a TA Q-500 under air atmosphere, from 25ºC to 800ºC at a heating rate of 10 ºC min^{-1}. The samples for TGA were films of about 30 mg. The decomposition temperatures that resulted in 5% weight loss (T_5) appear listed in Table S1.

Table S1: Thermal stability described as T_5 of ion gel polyelectrolytes.

Electrolyte	**TGA** T_5 (ºC)
PMMA/Li/EMI*FSI*	222
PIM*TFSI*-MMA$_{0.61}$/Li/EMI*FSI*	218
PIM*TFSI*-MMA$_{0.34}$/Li/EMI*FSI*	230
PIM*TFSI*/Li$_{0.86}$/EMI*FSI*	254
PIM*TFSI*/Li/EMI*FSI*	235
PYR*TFSI*/Li/PMP*FSI*	210
PYR*TFSI*-MMA/Li/PMP*FSI*	226
PIMT*FSI*/Li/PMP*FSI*	208
PYR*TFSI*/Li/EMI*FSI*	229
PIM*TFSI*/Li/EMI*TFSI*	342
PYR*TFSI*/Li/EMI*TFSI*	336
PYR*FSI*/Li/EMI*FSI*	175
PIM*FSI*/Li$_{0.6}$/EMI*FSI*	247
PIM*FSI*/Li$_{0.8}$/EMI*FSI*	247
PIM*FSI*/Li$_{1.0}$/EMI*FSI*	169
PIM*FSI*/Li$_{1.2}$/EMI*FSI*	173
PIM*FSI*/Li$_{1.2}$/EMI*TFSI*	251

S.3. Rheology characterization and conductivity measurements

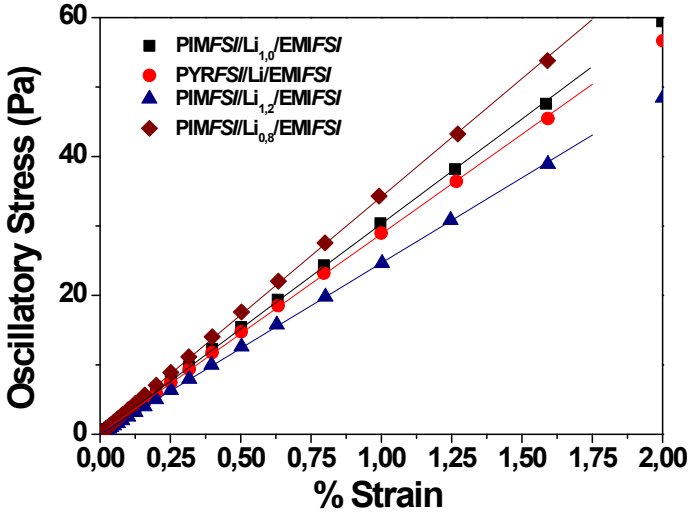


Figure S6. Rheology characterization of the gel electrolytes at 25 ºC: Oscillatory stress at 1 Hz as a function of strain

Table S2. G´and G´´ values for IGP: Frequency (1 Hz) and Strain (0.1 %)

Electrolyte	Frequency (1Hz)		Strain (0.1 %)	
	G´ (Pa)	G´´ (Pa)	G´ (Pa)	G´´ (Pa)
PIM*FSI*/$Li_{1.0}$/EMI*FSI*	2722	197	2692	304
PYR*FSI*/Li/EMI*FSI*	2600	214	2782	420
PIM*FSI*/$Li_{1.2}$/EMI*FSI*	2100	242	2636	392
PIM*FSI*/$Li_{0.8}$/EMI*FSI*	2911	323	3564	563

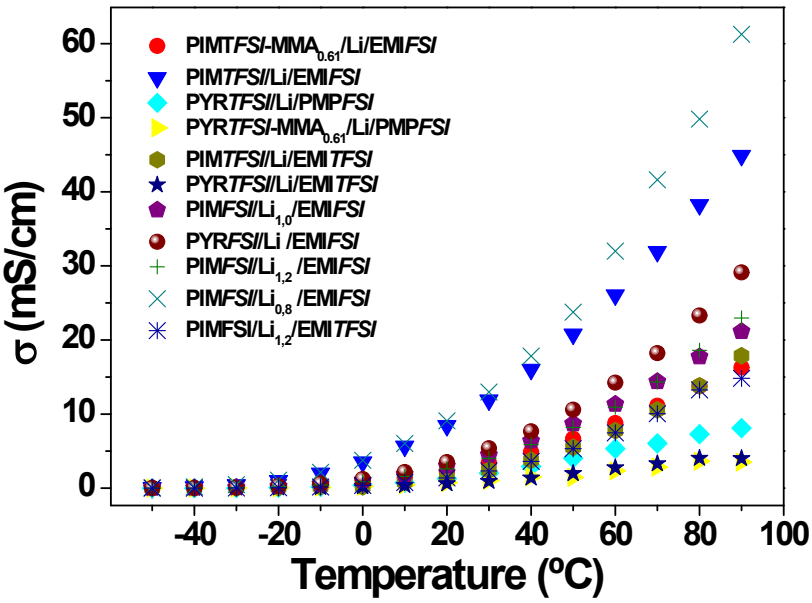


Figure S7. Conductivity (σ) as a function of temperature for some of the electrolytes.

S.4. X Ray Diffraction

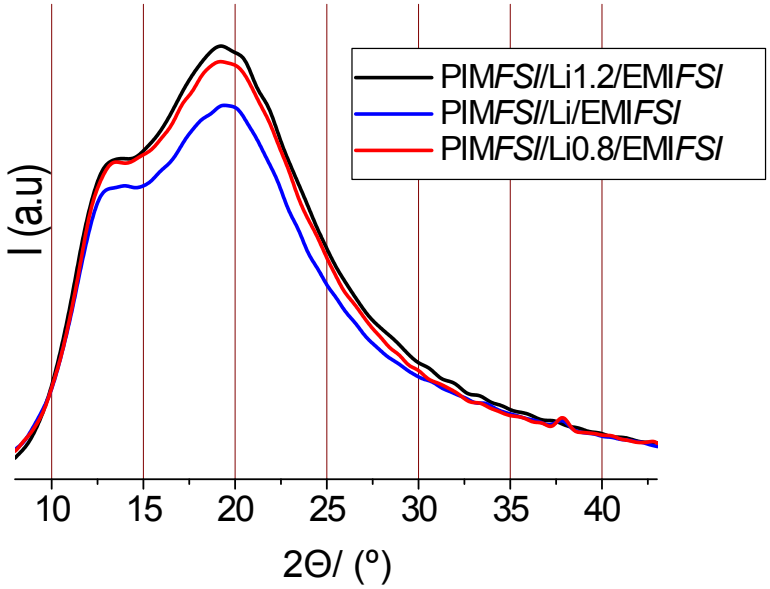


Figure S8. XRD of polyimidazolium IGP prepared with different [Li], PIMFSI/$Li_{1.2}$/EMIFSI, PIMFSI/Li/EMIFSI and PIMFSI/$Li_{0.8}$/EMIFSI, displaying a diffraction close to 13º.

S5. Confocal Raman Microscopy

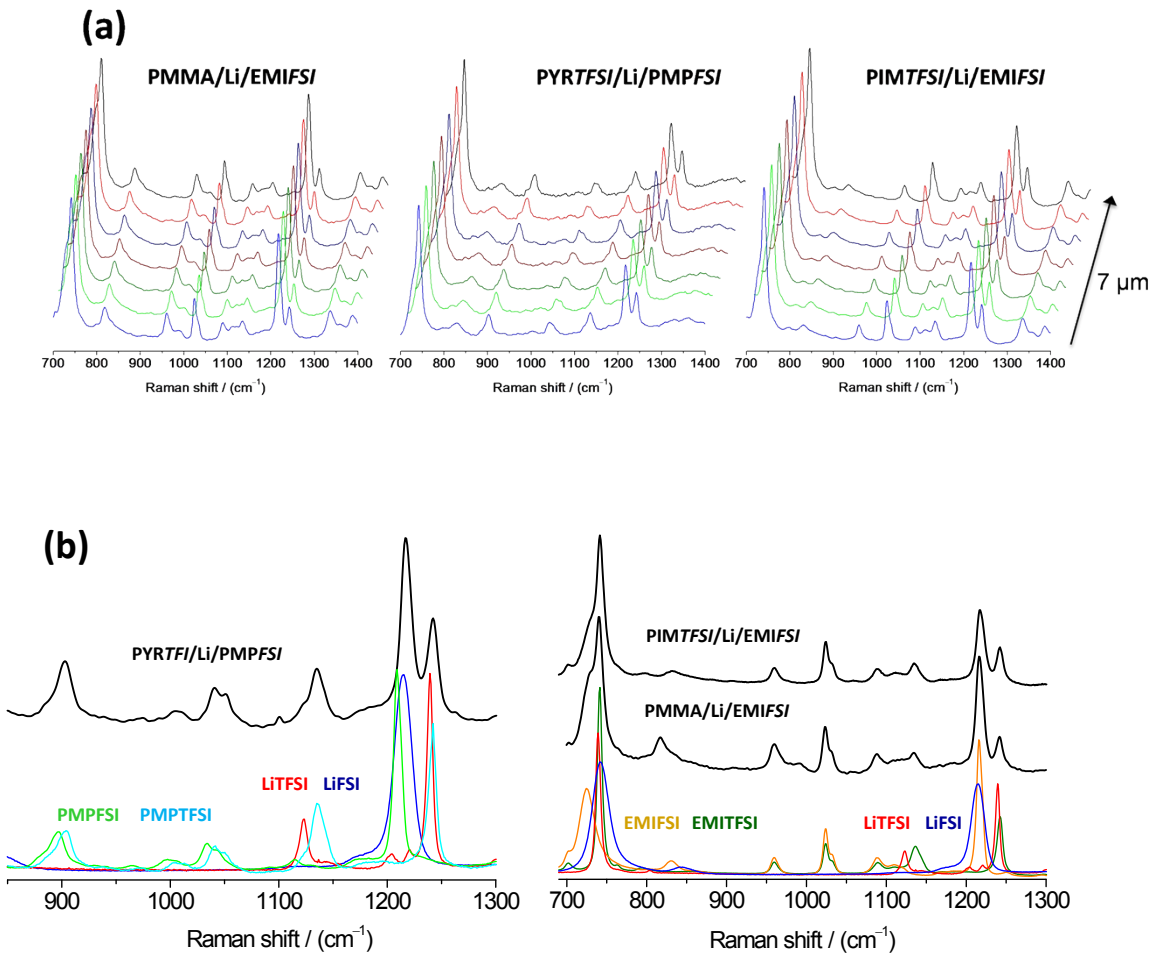


Figure S9. (a) Confocal raman microscopy spectra collected every micron along 7 µm of PMMA/Li/EMIFSI (left), PYRTFSI/Li/PMPFSI (center) and PIMTFSI/Li/EMIFSI (right), and (b) Raman spectra of PYRTFSI/Li/PMPFSI (left) and PMMA/Li/EMIFSI and PIMTFSI/Li/EMIFSI (right), together with the pure ionic liquids and Li salts in their formulation.