Nontrivial network driven modifications of ion transport in ionic liquid confined inside polymer system

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Materials and methods:

1. *Chemical details:*

The 1-butyl-1-methyl-pyrrolidinium bis (trifluoromethane sulfonyl) imide ($PY_{14}TFSI$) ionic liquid, lithium-bis(trifluoromethane sulfonyl) imide (LiTFSI) salt, acrylonitrile (AN), 3-(trimethoxy silyl) propyl methacrylate (MSMA) monomers, azo-bis isobutyro nitrile (AIBN) initiator are brought from Sigma Aldrich with 99.9 % purity.

2. *Synthesis of polymer network based gel electrolytes:*

Prior to use, double distillation is carried out for monomers to improve purity of sample. The monomers are purged with Ar gas immediately after distillation to avoid oxygen contamination. Further evacuation of monomers is carried out while transferring in glove box. The gel electrolytes are prepared via in situ polymerisation of acrylonitrile (AN) and 3-(trimethoxy silyl) propyl methacrylate (MSMA) simultaneously in 1-butyl-1-methyl-pyrrolidinium bis (trifluoromethane sulfonyl) imide ($PY_{14}TFSI$) ionic liquid. The requisite amount of LiTFSI salt is dissolved in ionic liquid to maintain salt concentration of 0.5M. The MSMA monomer are dissolved in IL-LiTFSI electrolyte with different weight percentages

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ranging from 0%, 10 %, 13%, 16% (with respect to AN+MSMA) maintaining $W_{(AN+MSMA)}/W_{IL}$ as 0.2 for all the samples. The monomer solutions are polymerised via free radical polymerisation using AIBN as initiator at 65 ^{o}C for 4-5 hours to complete polymerisation. The AIBN initiator is added as 1 weight percentage of total monomer weight added in IL-LiTFSI. The synthesis procedure is carried out in in 5-10 mm vial inside Ar filled glove box. The PN-10 and PN-13 gels appeared as the self-stranding film with thickness of 1-1.2 mm, and diameter of 10 mm. The detail of compositions is presented in table ST1.

Experimental details:

1. *Structural characterization:*

(a) Thermal analysis

The glass transition, melting, crystallisation transitions in ionic liquid and PN gels are studied via differential scanning caloriemetry (DSC) with Mettler Toledo DSC 823^{e} instrument, within temperature ranges from -140 ^{o}C to 70 ^{o}C, at heating rate of 10 ^{o}C min^{-1}, under N_2 atmosphere. Thermo gravimetric analysis (TGA/SDTA851, Mettler Toledo) are carried out within the temperature range 25 ^{o}C to 700 ^{o}C, at heating rate of 10 ^{o}C/min, under N_2 atmosphere.

(b) Dynamics Rheology

The frequency dependent elastic modulus (G') and viscous modulus (G'') are measured (0.1 to 600 s^{-1}) using stress controlled Rheometer, MCR 300, Anton Paar, with parallel-plate geometry with 25 mm plate diameter and 0.8 mm gap, at constant strain of 0.5%. The shear stress as a function of shear strain and regime of elastic response are evaluated from amplitude sweep (G', G'' vs stain) ranging from 0.1 to 100 % strain. The strain at elastic regime of 0.5% was fixed to perform frequency sweep.

(c) FTIR and FT-Raman spectroscopy:

Fourier transform Raman (FT-Raman) spectra of IL-*X* M LiTFSI, at various LiTFSI salt concentrations (*X* ranging from 0 to 0.5M) and PN gels are recorded on a Bruker RFS 100/S FT-Raman Spectrometer, with 1064 nm laser, 300 mW laser power, at a spectral resolution of 4 cm^{-1} in the transmission mode, within 250-300 cm^{-1} Raman shift.

(d) Brillouin scattering:

Brillouin spectra of the samples were carried out with a 532 nm Nd-YAG laser with a power of ~ 5 mW, in back scattering geometry. A 10X objective lens is used for focusing the light on the sample. A free spectral range of 25 GHz is used for the measurements. The scattered light from the sample is analysed using a 3+3 tandem Fabry-Perot interferometer (JRS scientific instruments, Switzerland) equipped with an avalanche diode (Perkin Elmer, Canada) detector. The detected signal was processed by a multi-channel analyser with 1024 channels. All samples are inserted inside capillary tube with their ends sealed with heat transmitting grease (H-grease or N-grease, Apiezon). The sample capillary preparation is carried out inside the argon filled glove box (MBraun, MB 20G LMF, pressure: 3 mbar, H_2O < 0.5 ppm, O_2< 0.5 ppm).

(e) Pulsed field gradient NMR:

NMR measurements were carried out on 9.4 T Bruker Advance 400 NMR spectrometer equipped with a Bruker diffusion probe diff30 and a temperature controller (stability and accuracy of ± 0.2 °C). NMR resonance frequencies are 400.13 MHz, 376.50 MHz, and 155.51 MHz for ^{1}H, ^{19}F, and ^{7}Li nuclei, respectively.

NMR tubes of 3 mm were used to avoid convection phenomena; they were filled in a glove box and sealed in order to avoid any water uptake.

The self-diffusion measurements were performed with the pulsed field gradient stimulated echo (PFG NMR). The gradient pulse duration, δ, was set between 0.6 ms and 1.5 ms and

diffusion times, Δ (delay between the gradient pulses) between 30 ms, and 100 ms were performed depending on the diffusion coefficient of mobile species, D. This enables the attenuation of spin echo amplitude over a range of at least 2 decades leading to a good accuracy (< 5%) of the self-diffusion coefficient values. They were determined from the classic relationship: $\ln I/I_0 = -D^{NMR}\gamma^2(\Delta-\delta/3)\delta^2 g^2$

wherein g is the magnitude of the two gradient pulses, γ is the gyromagnetic ratio of the nucleus under study, and I and $I0$ are, respectively, the area of the signal obtained with or without gradient pulses.

2. Electrochemical measurements

The electrochemical window of electrolytes are measured by cyclic voltammetry technique by using CH Instruments (CH608C) in the voltage range -0.5–5 V at a scan rate of 0.25 mVs^{-1}. Galvanostatic cycling is performed using an Arbin Instruments (BT 2000 Corp., USA) at C/10 C-rate in the voltage range of (0- 2.5) V (versus Li^+/Li). The lithium interface stability of PN gels are evaluated by the electrochemical impedance measurements, carried out with impedance analyser (Novocontrol Alpha-A; frequency range: 1 to 1×10^6 Hz). The cells are assembled with PN gels as electrolyte without separator in lithium symmetrical cell configuration.

3. *Sample preparation for ionic conductivity measurements:*

The ionic conductivity is measured by ac-impedance spectroscopy (Novocontrol Alpha-A; frequency range: 1 to 1×10^6 Hz). The gel as well as ionic liquid electrolytes is sandwiched between two stainless steel electrodes in home-built glass cells for conductivity measurements. The circular gel films with thickness of 1.2 mm and diameter of 9 mm are used for conductivity measurements. Cell constants measured as 0.2 cm^{-1} for all of the measurements. In order to carryout temperature dependent measurements, the conductivity

cells are inserted in home-built glass jackets, which is emerged into thermostat (FP50MC) containing ethylene glycol-water mixture (40 : 60 v/v). All measurements are performed within the temperature ranges (0-60) ^{o}C at a temperature interval of 5 ^{o}C for both heating and cooling cycles. All of the sample preparations and cell assemblies are carried out in argon filled glove box (MBraun, MB 20G LMF, pressure: 3 mbar, H_2O < 0.5 ppm, O_2< 0.5 ppm).

4. Electrode preparation:

The lithium iron phosphate (LFP) is synthesised via sol-gel method proposed in our earlier publication[1]. In brief, the aqueous solution of 0.03 mole ferric citrate is prepared and stirred at 60 ^{o}C for one hour. In another beaker, 0.02 mole Phosphoric acid and 0.01 mole lithium phosphate is dissolved in water and stirred at 60 ^{o}C for one hour. Two aqueous solutions are mixed thoroughly at 60 ^{o}C for one hour to obtain clear solution. 0.5 wt% MWCNT (with respect to LFP) is added to the clear solution and stirred at same temperature until homogeneous mixtures are formed. The homogeneous mixture is heated to evaporate solvent in petry plate at 60 ^{o}C for 24 hours to form greenish xero-gel. The xero-gel was heated at 700 ^{o}C for 10 hours at heating rate 3^{o}C/min to obtain 0.95 wt% LFP/0.5 wt % MWCNT composite.

5. Cell assemblies for electro chemical measurements:

The electrochemical cell for cyclic voltammetry measurement is assembled with stainless steel as working electrode and lithium as reference as well as counter electrode in Li/GPE/SS configuration. The electrochemical window of electrolytes is measured by cyclic voltammetry technique by using CH Instruments (CH608C) in the voltage range -0.5–5 V at a scan rate of 0.25 mVs^{-1}. The lithium interface studies are performed with lithium symmetrical cells with configuration Li/GPE/Li.

The galvanostatic charge discharge is carried out using Swagelok^{TM} cells with lithium foil (Aldrich) as the counter and reference electrodes, LFP/MWCNT as the working electrode. The gel electrolytes act as both electrolyte as well as separator. The active electrode material, LFP/MWCNT is homogeneously mixed with PVDF and carbon black in a weight ratio of 8:1:1 (LFP: PVDF: C). Slurry was made with the mixture and N-methyl-2-pyrrolidone (NMP) solvent and drop cast on circular Al foil (thickness = 20 µm, Ranga Techno Impex). The cast electrodes are dried at 110 ^{o}C overnight under vacuum. Galvanostatic cycling is performed using an Arbin Instruments (BT 2000 Corp., USA) at C/10 C-rate in the voltage range of (0- 2.5) V (versus Li^{+}/Li).

Table ST1: Composition of PN gels

All of the weight percentages presented here is calculated with respect to (W_{AN}+W_{MSMA}+W_{IL}).

Abbreviation	Weight % of AN	Weight % of MSMA	Weight % of IL
PN-0	21	0	79
PN-10	20	2.3	77.7
PN-13	18	2.4	79.6
PN-16	16	2.5	81.5

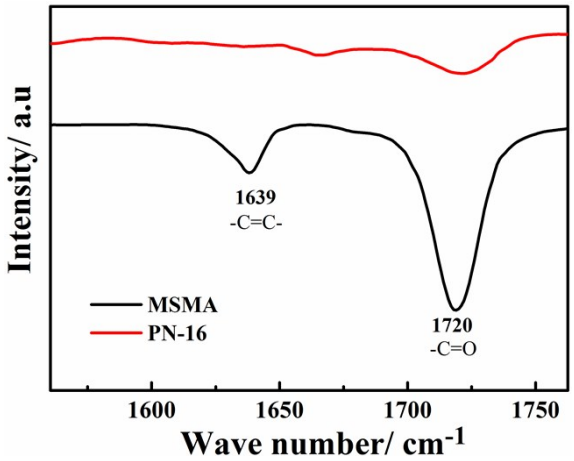

Fig. S1 FTIR spectra of PN-16 gel and MSMA monomer within 1560-1672 cm^{-1}.

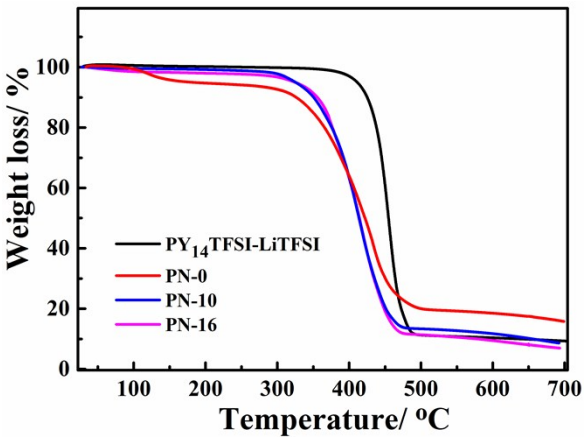

Fig. S2 TGA of PN-*x* gels with *x* ranging from 0 to 16.

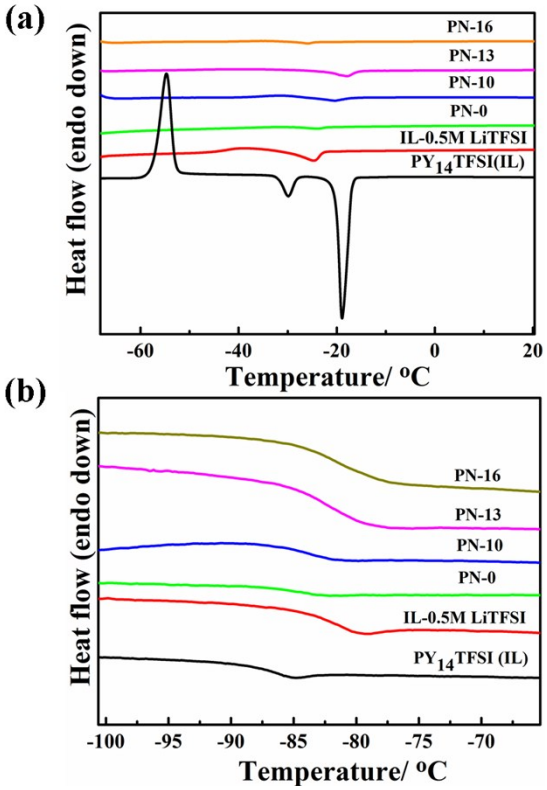

Fig. S3 DSC isotherm of ionic liquid integrated PN-GPE within the temperature ranges from (a) -68 °C to 65 °C, characterising melting isotherm and (b) -100 °C to -65 °C, characterising glass transition temperature.

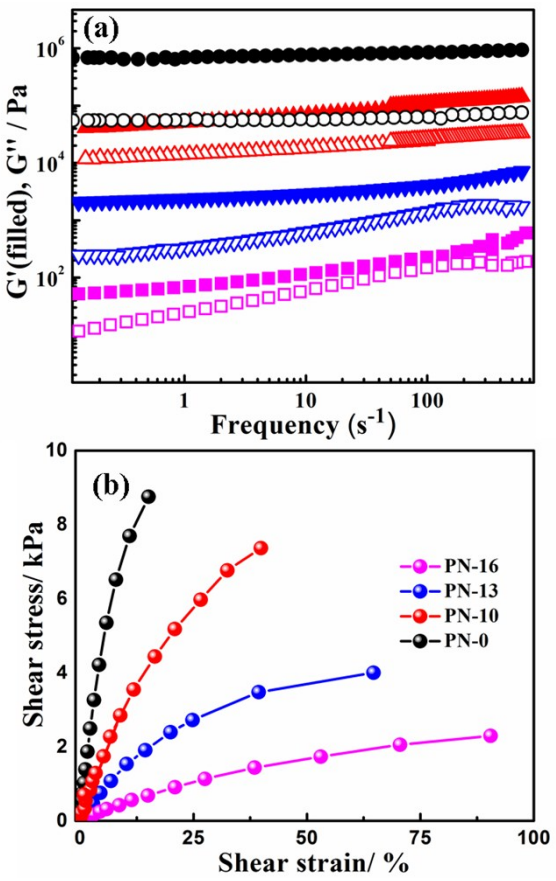

Fig. S4 (a) G' (filled symbols) and G" (open symbols) versus frequency of PN-0 (black), PN-10 (red), PN-13 (blue), PN-16 (magenta) gels. (b) Shear stress versus shear strain of PN-0 (black), PN-10 (red), PN-13 (blue), PN-16 (magenta).

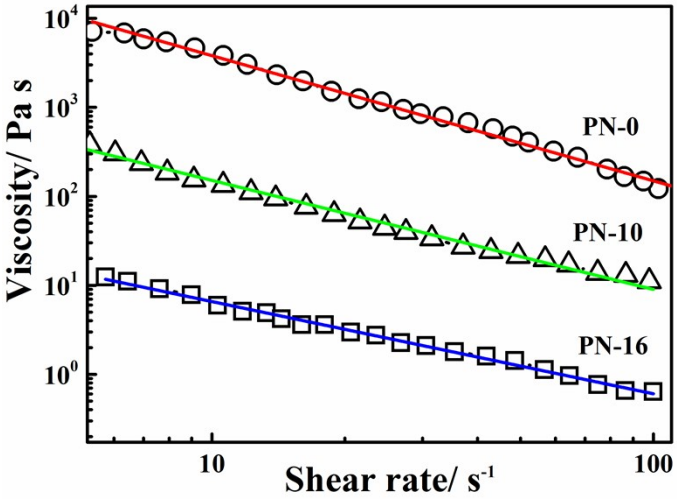

Fig. S5 Steady-shear viscosity versus shear rate of PN gels.

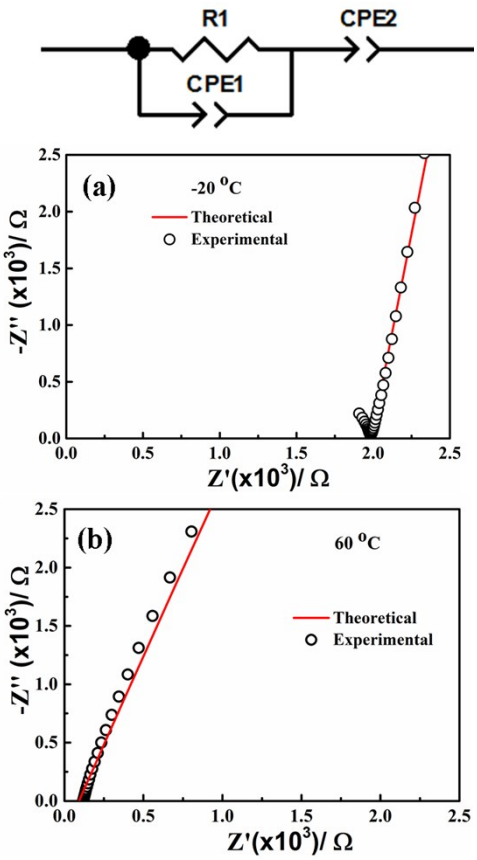

Fig. S6 Equivalent circuit fitting of Cole-Cole plot of ionic conductivity of PN-13 gel at -20 °C and 60 °C.

Table ST2 : VTF fitting parameters for PN gels:

Compositions	σ_0/ $\Omega^{-1}cm^{-1}$	T_0	**B/K**	**B/K with T0 fixed = 207**	T_g from DSC
IL-0.5M LiTFSI	0.15	136.6	931.7	-	191.4
PN-0	0.28	135.6	1042	-	187.7
PN-10	0.08	207	345.6	345.6	188.8
PN-13	0.11	211	363.6	373	191.5
PN-16	0.26	193	715.9	300	192.7

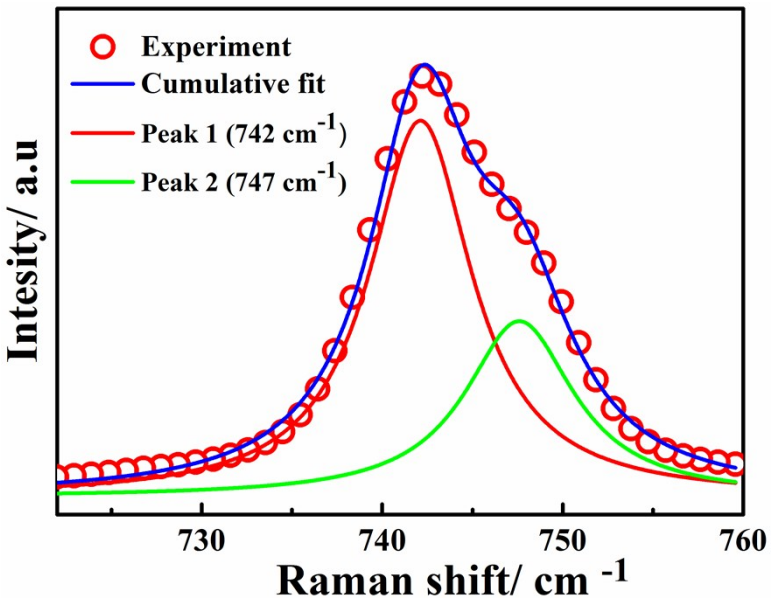

Fig. S7 Lorentz fit of spectra within 720-760 cm^{-1} region for IL-0.3M LiTFSI.

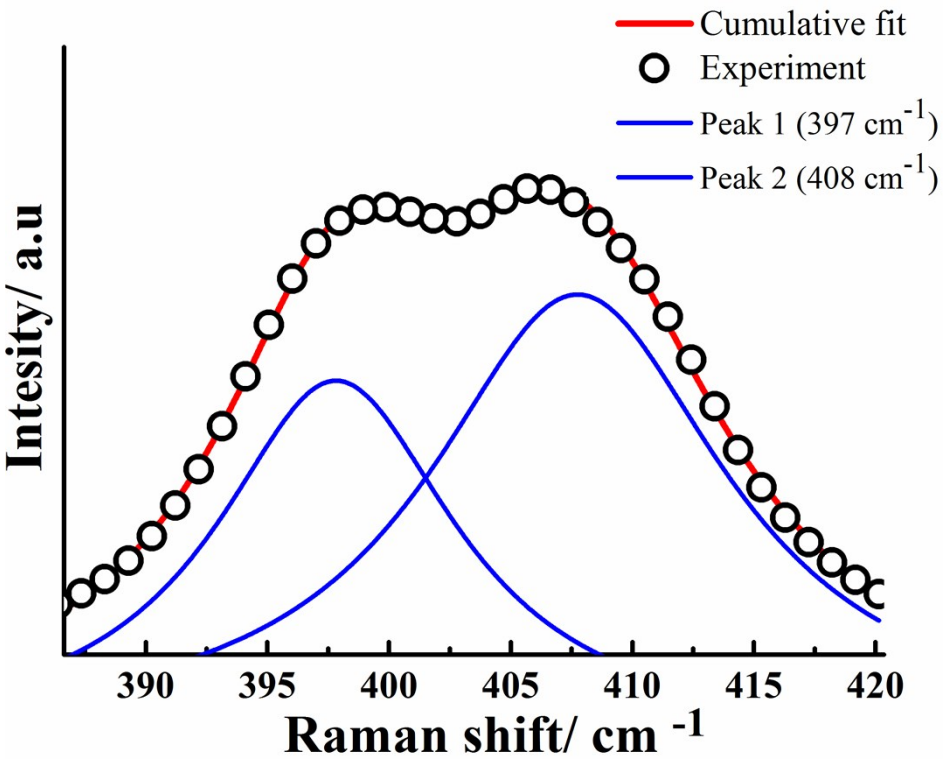

Fig. S8 Characteristic Lorentz fit of a spectrum within 387-420 cm^{-1} region for PN-16 gel.

Pure $PY_{14}TFSI$ ionic liquid (figure 3c) exhibits nine Raman bands in the range of 250-500 cm^{-1} characteristics of both cis (C_1) (279 cm^{-1}, 287 cm^{-1}, 312 cm^{-1}, 327 cm^{-1}, 353 cm^{-1}, 407 cm^{-1}) and trans (C_2) conformers (298 cm^{-1}, 340 cm^{-1}, 397 cm^{-1}).

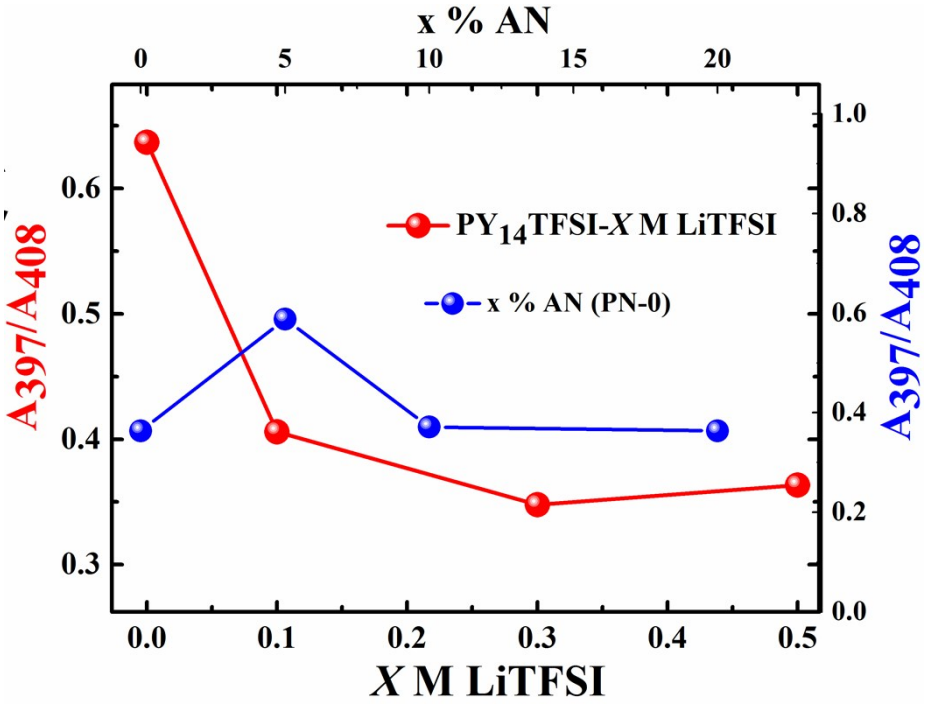

Fig. S9 Area intensity of peak at 397 cm^{-1} (for C_1 conformer of TFSI) with respect to that of 408 cm^{-1} (C_2 conformer), within 383-430 cm^{-1} for IL-*X* M LiTFSI (*X* ranging from 0 to 0.5; plotted along bottom x axis) and PN-0 (at various AN concentrations; denoted by x % , plotted along top x axis).

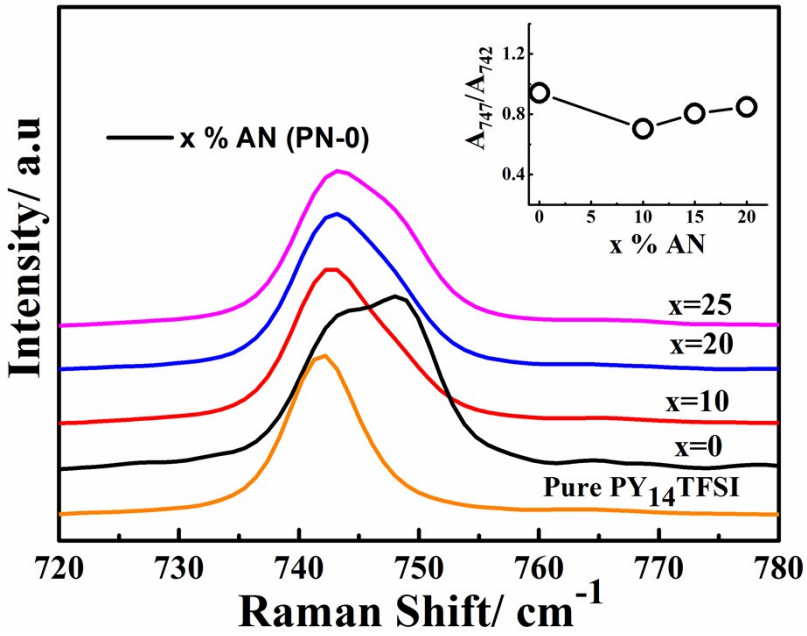

Fig. S10 Raman spectroscopic analysis of ion pair formation in PN-0 gels with varying AN concentrations (x wt % in PN-0).

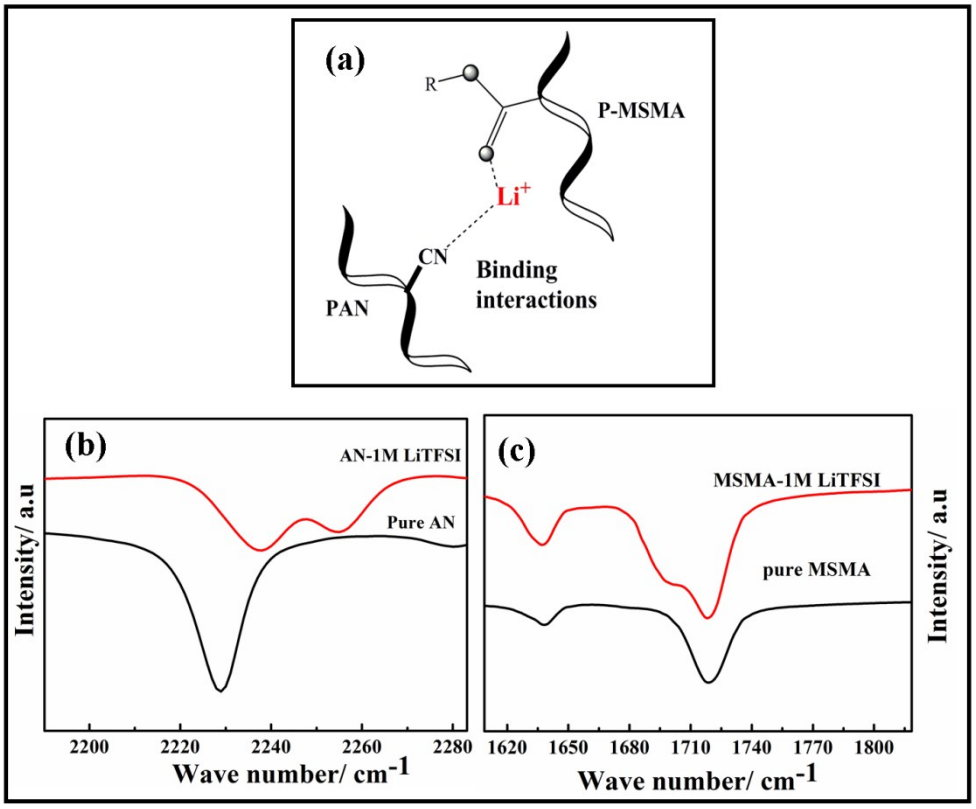

Fig. S11 (a) Schematic representation of lithium binding interactions to polymers. FTIR spectra of lithium binding interaction in AN-LiTFSI (b) and MSMA-LiTFSI (c).

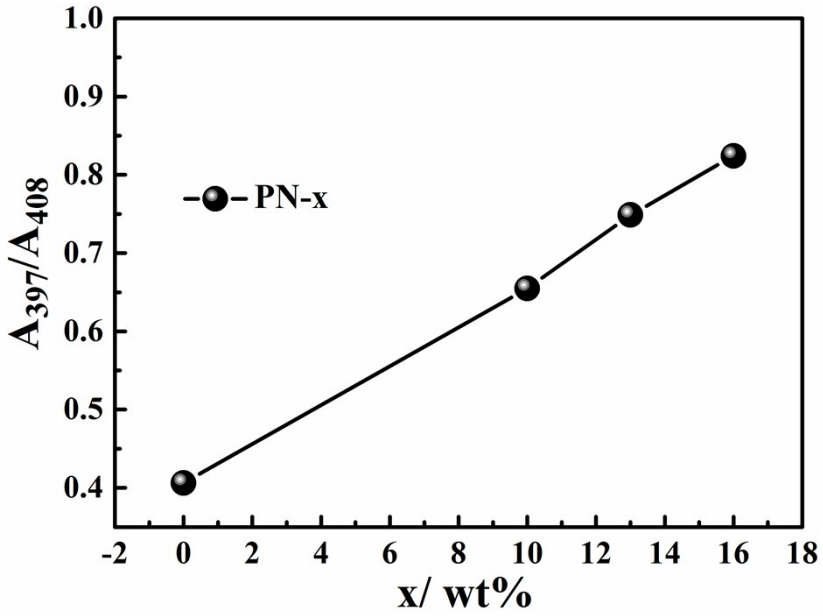

Fig. S12 Area intensity of peak at 397 cm^{-1} (for C_1 conformer of TFSI) with respect to that of 408 cm^{-1} (C_2 conformer), evaluated from multiple peak lorentzian fitting of spectra within 383-430 cm^{-1} for PN-*x* gel at various MSMA concentrations.

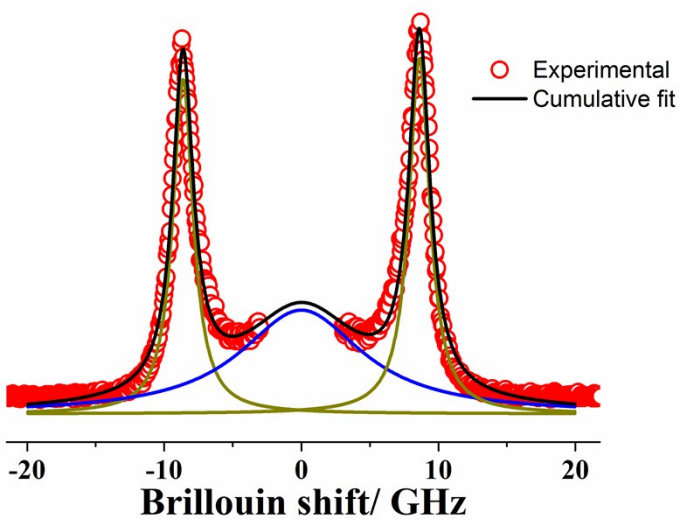

Fig. S13 Lorentz fit of brillouin scattering spectra of PN-13.

Table ST3: Activation energies from Arrhenius fitting of ^{1}H, ^{19}F and ^{7}Li diffusion for $PY_{14}TFSI$-0.5M LiTFSI and PN-13 gel and compared with the one obtained using conductivity values:

Sample	$E_{a\ Li^+}$ (D)/ kJmol^{-1}	$E_{a\ TFSI^-}$ (D)/ kJmol^{-1}	$E_{a\ PY14^+}$(D)/ kJmol^{-1}	E_a/ (Cond) kJmol^{-1}
Il-0.5M LiTFSI	38	33	32	28
PN-13	30.6	31	24.5	30

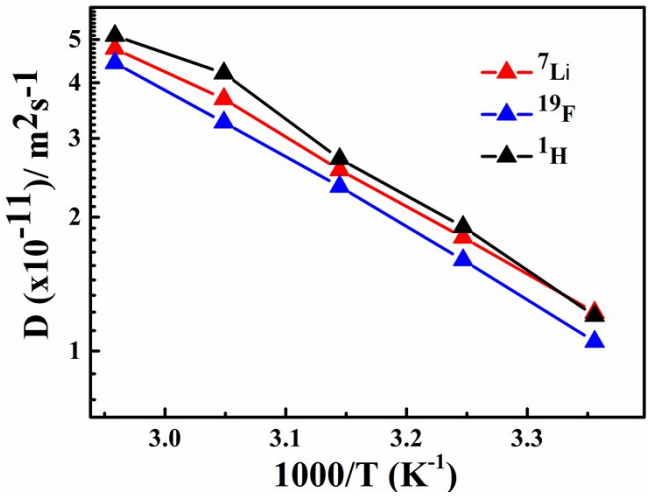

Fig. S14 D vs 1000/T for ^{7}Li (Red), ^{19}F (blue), ^{1}H (black) nuclei in PN-0 gel.

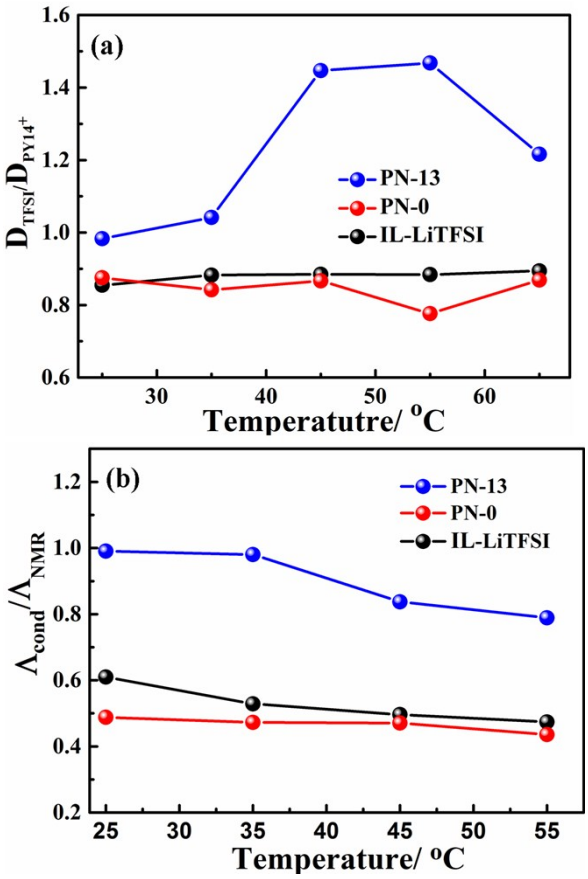

Fig. S15 (a) D_{TFSI^-}/D_{PY14^+} vs temperature for PN gel. (b) Ionicity, representing degree of salt dissociation ($\Lambda_{cond}/\Lambda_{NMR}$) at various temperatures.

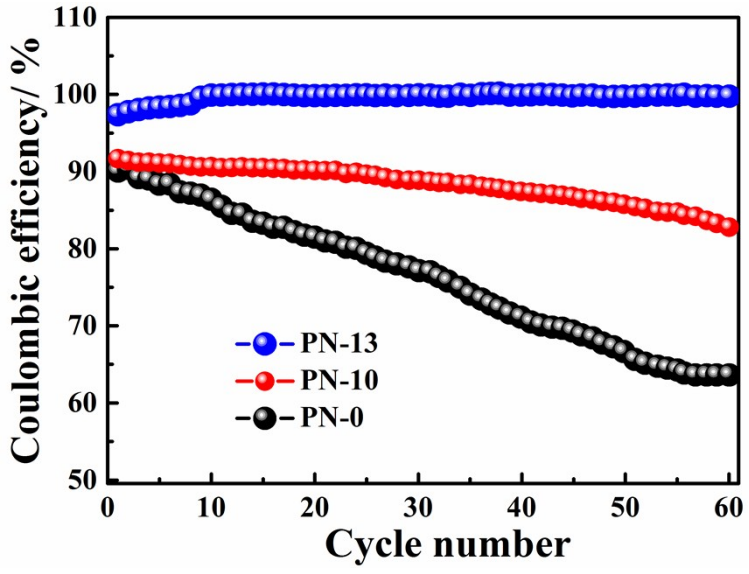

Fig. S16 Columbic efficiency vs cycle number for PN gels.