ARTICLE TYPE

Supplementary Information for

"Enhancement of 'dry' proton conductivity by self-assembled nanochannels in all-solid polyelectrolytes"

Azhar Hussain Shah,[b,c] Jiaye Li,[c] Hengrui Yang,[d] Usman Ali Rana,[e] Vijayaraghavan Ranganathan,[c] Humaira M. Siddigi,[b] Douglas R. MacFarlane,[b] Maria Forsyth,[a] and Haijin Zhu*[a]

[a] *Institute for Frontier Materials and ARC Centre of Excellence for Electromaterials Science, Deakin University, Waurn Ponds, VIC 3216, Australia. Tel: +61 3 5227 3696; E-mail: h.zhu@deakin.edu.au*
[b] *Department of Chemistry, Quaid-I-Azam University Islamabad, 45320, Pakistan.*
[c] *School of Chemistry, Monash University, Clayton VIC 3800, Australia.*
[d] *Institute for Frontier Materials, Deakin University, Waurn Ponds, VIC 3216, Australia.*
[e] *Sustainable Energy Technologies (SET) center, College of Engineering, PO Box 800, King Saud University, Riyadh 11421, Saudi Arabia.*

Received Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
First published on the web Xth XXXXXXXXXX 200X
DOI: 10.1039/b000000x

* Corresponding author: H. Zhu. Tel: +61 3 5227 3696; E-mail: h.zhu@deakin.edu.au

Proton conductivity of the poly([NH122][STFSI]

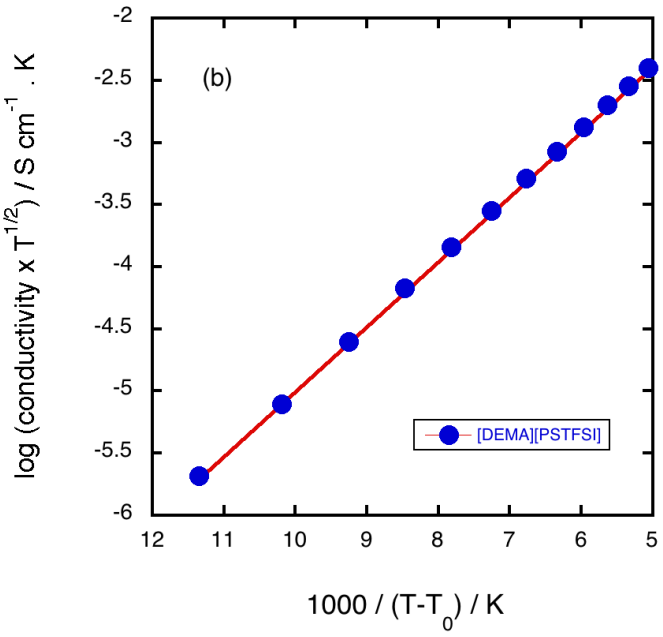

Fig. S1 Arrhenius plot of ionic conductivity using VTF equation for the polymeric PIL poly([NH122][STFSI]. The solid red line represents the best fit to the experimental data (blue dots), and the fitting parameters are listed in table 1.

FTIR spectroscopy analysis

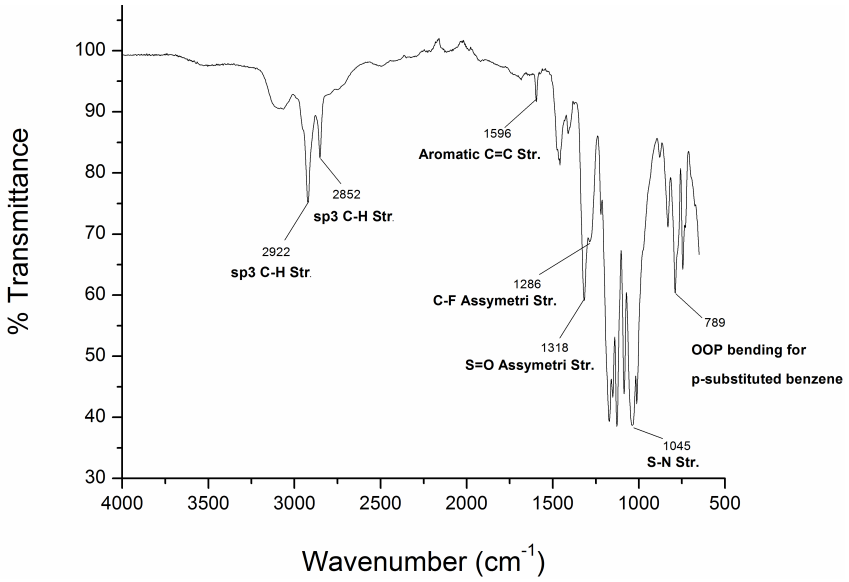

Fig. S2 ATR-FTIR spectrum of poly([NH122][STFSI]).

ATR-FTIR spectroscopic studies were carried out to investigate the interactions between the cation and polyanion. In the FTIR spectrum (Fig S2 in the supplementary information), the band appearing at ca. 1318 cm^{-1} is attributed to the asymmetric stretching vibrations of the S=O in trifluoromethylsulfonimide (SO_2-N-SO_2F_3)[1] and the one appearing at 1286 cm^{-1} is due to CF_3[2]. The position of these absorption bands are quite comparable to the Poly(Li[STFSI])[2] and Poly(Na[STFSI])[3] forms of the polymers. The sharp absorption band for S=O stretching vibrations indicates the strengthening of the S=O bond, which is most likely due to the S=O groups not participating in the cation-anion interaction[3,4]. In both the aforementioned Li and Na systems, the absorption band appeared at around 1250 cm^{-1} was observed, which was attributed to the S=O that were interacting with the cations. Thus the FTIR result suggests that the $[NH122]^+$ cation is free and is not coordinating with the anionic moieties.

Elemental analysis of poly([NH122][STFSI])

Table S1 Elemental analysis of the poly([NH122][STFSI]).

	% of Carbon	% of Hydrogen	% of Nitrogen
Thoretical	47.78	5.26	6.96
Experimental	41.1	5.26	6.68

Elemental analysis was performed to confirm the composition and purity of the synthesized polymer, as tabulated in the Table S1. The theoretical percentages of these elements were calculated on the basis of polymer. The experimentally determined values are in good agreement with the calculated percentages of the elements, thus confirmed the purity and composition of the synthesized polymer.

Solution NMR of the monomer and polymer

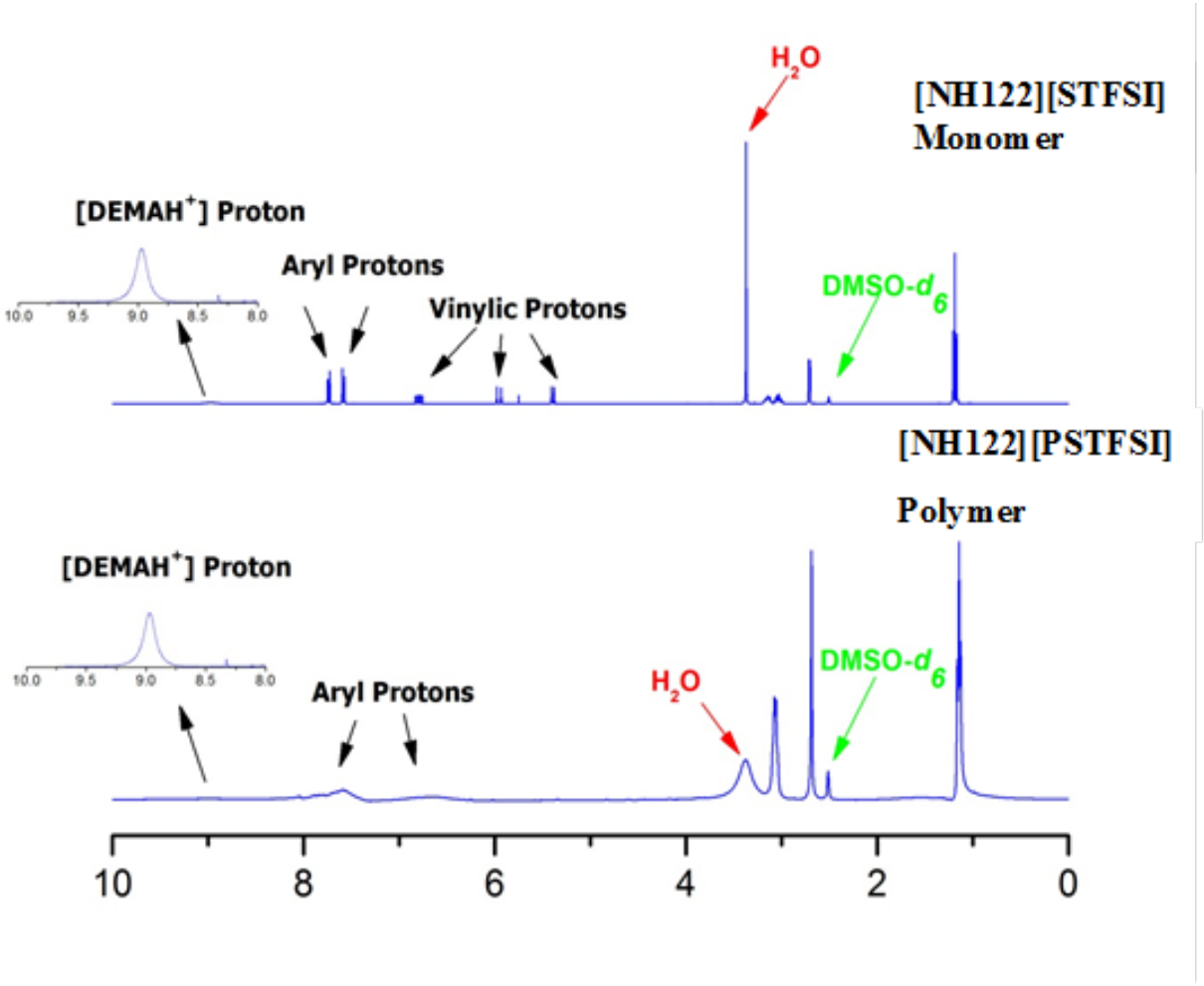

Fig. S3 Comparison of the solution NMR of the monomer [NH122][STFSI] and poly[NH122][STFSI].

The solution NMR of the monomer and polymer are compared in the Figure S3. The disappearance of vinyl protons and appearance of broad peak at about 5.96 ppm and 6.83 ppm are indicative of the successful polymerization of the monomer.

XRD of poly([NH122][STFSI])

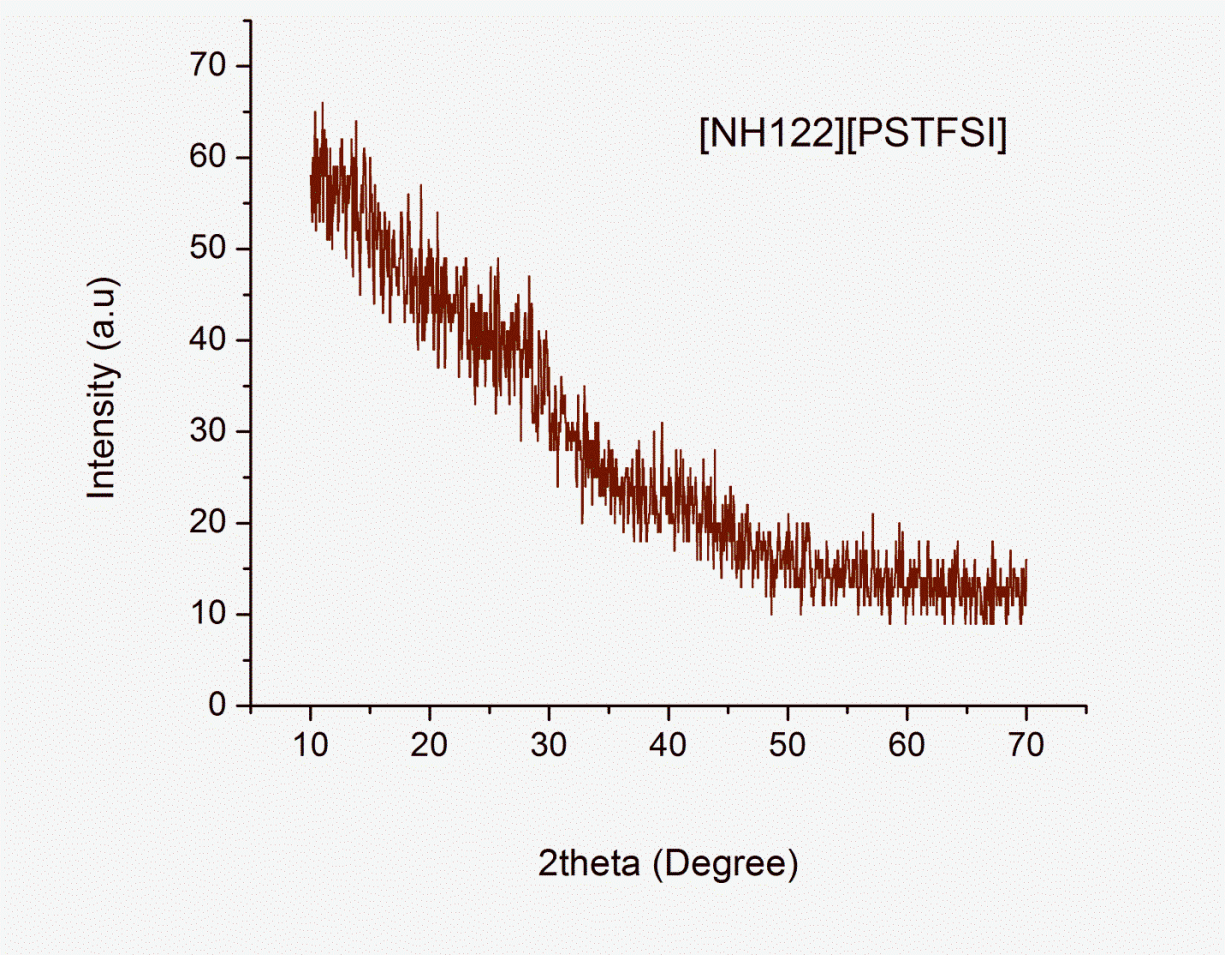

Fig. S4 XRD pattern of poly[NH122][STFSI].

XRD measurement was performed on the poly([NH122][STFSI]) sample at room temperature, and the result is shown in Figure S4. The XRD pattern of the polymer clearly shows that no crystalline peaks was observed and the polymer is purely amorphous. This result is in a good agreement with DSC data.

References

1 Z.-H. Ma, H.-B. Han, Z.-B. Zhou and J. Nie, *Journal of Molecular Catalysis A: Chemical*, 2009, **311**, 46–53.
2 R. Meziane, J.-P. Bonnet, M. Courty, K. Djellab and M. Armand, *Electrochimica Acta*, 2011, **57**, 14–19.
3 J. Li, H. Zhu, X. Wang, M. Armand, D. R. MacFarlane and M. Forsyth, *Electrochimica Acta*, 2015, **175**, 232–239.
4 N. R. Dhumal and S. P. Gejji, *The Journal of Physical Chemistry A*, 2006, **110**, 219–227.