Poly(ionic liquid) Electrolytes for Solid-State Batteries

Dr. Fangfang Chen, Dr Shinji Kondou, Dr Xiaoen Wang, Prof Maria Forsyth

Institute for Frontier Materials

Deakin University

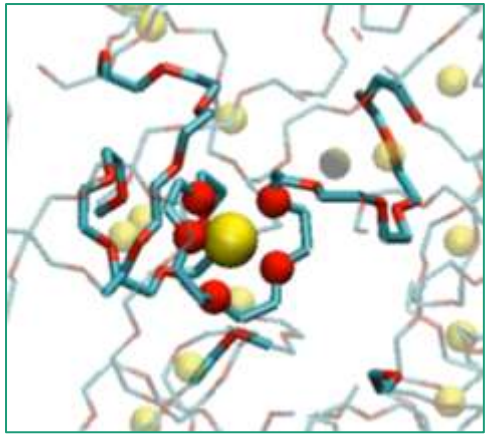
chenf@deakin.edu.au

Solid Polymer electrolytes for batteries

A Polymer electrolyte use a polymer as a solid matrix to conduct charged ions, such as Li^+ for lithium batteries.

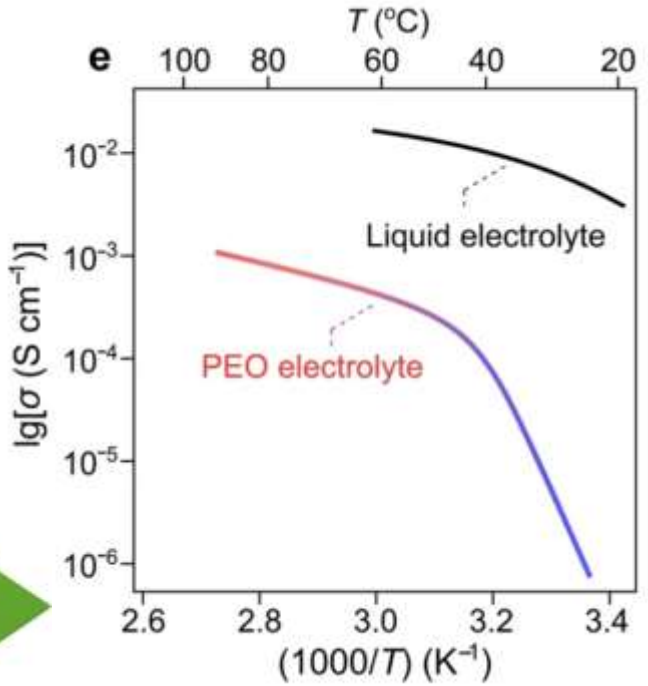
Prof Peter Wright

Prof Michel Armand



First Polymer electrolyte in 1978 Polyethylene oxide (PEO)

Advantages
- good mechanic strength
- good thermal and electrochemical stability
- high flexibility
- Lightweight
- Wide operating temperature range
- Reduced dendrite formation and improved safety

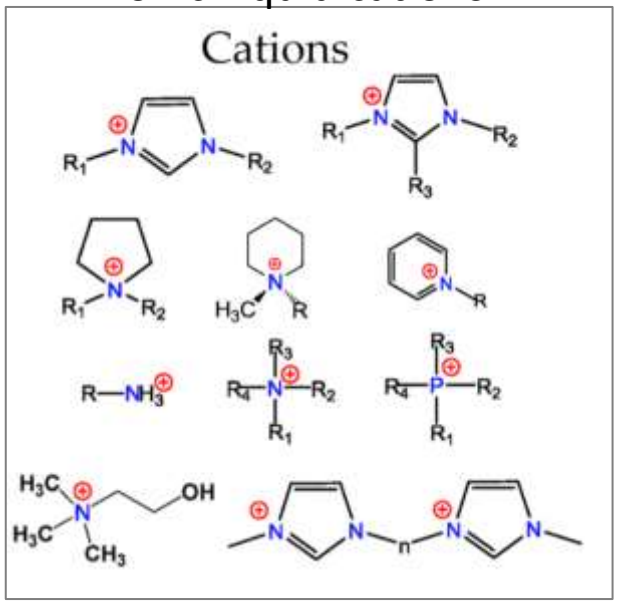


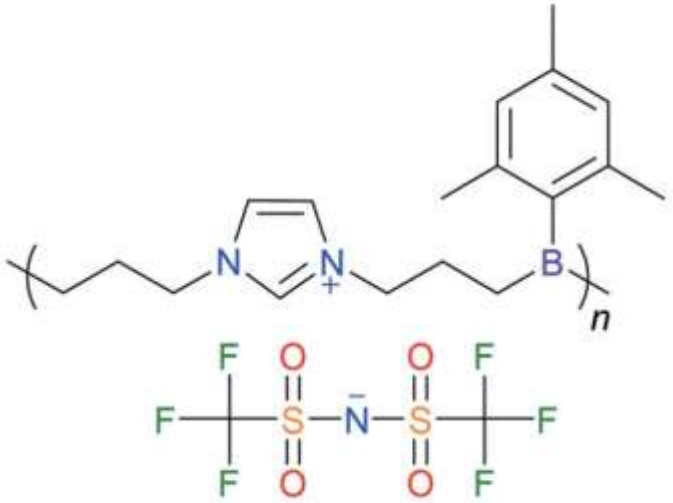
Low ionic conductivity, Low T_{li}= $\frac{\sigma_{Li}}{\sigma}$

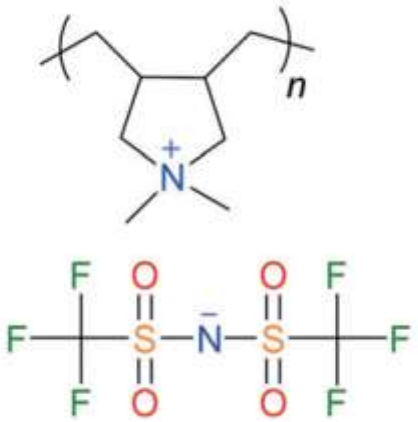
Cationic Polymeric ionic liquids (PolyILs)

In PolyIL, ionic liquid cations are polymerised to form a cationic backbone. PolyILs have both function of polymers and ionic liquids.

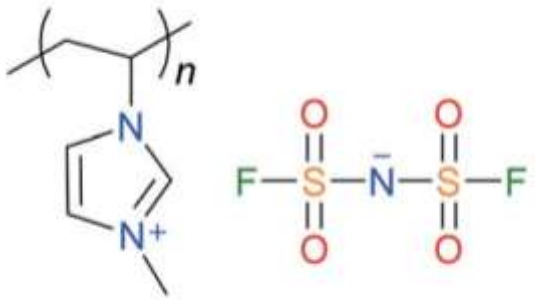
Ionic Liquid cations

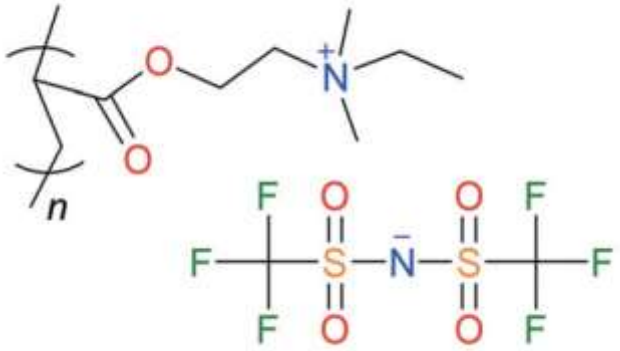






Cationic unit on polymer backbone

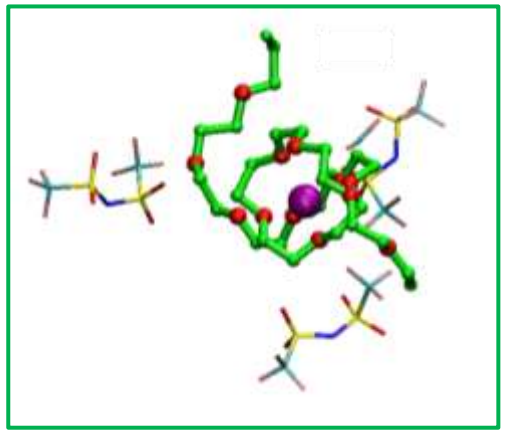




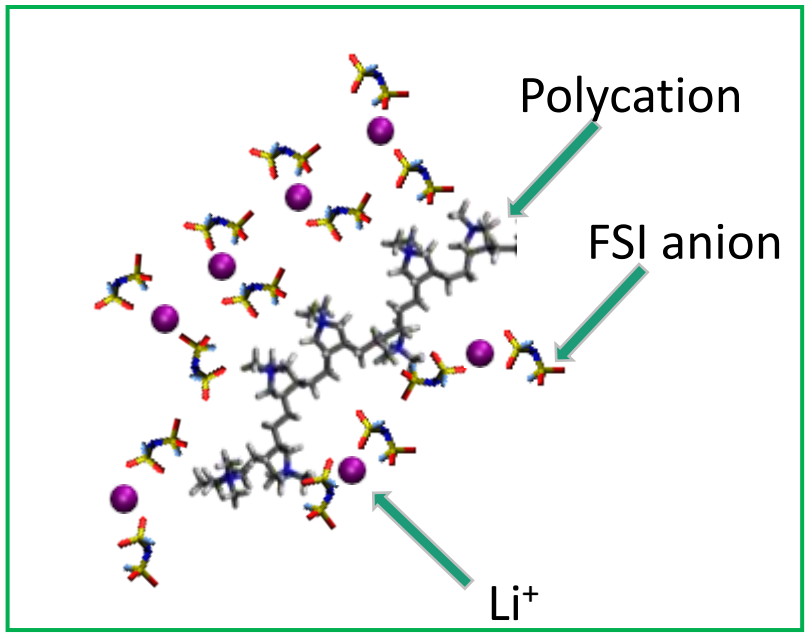
Cationic unit in polymer side chain

Ion Co-coordination structure

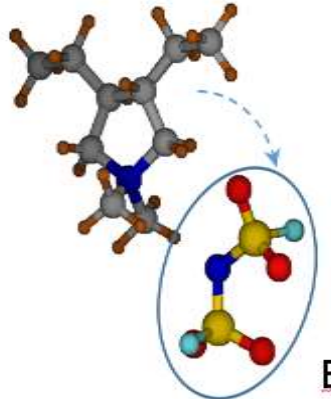
Li is solvated by PEO polymer backbone



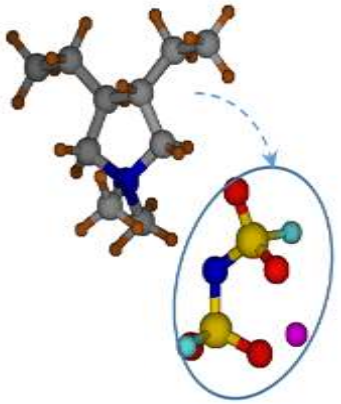
Polycation-anion-Li co-coordination in polyIL



Binding energy between polycation and FSI anion



E_b= -293.47 kJ mol^{-1}



E_b= -50.5 kJ mol^{-1} with Li^+
-62.6 kJ mol^{-1} with Na^+

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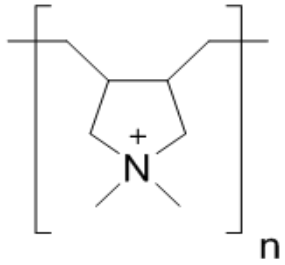
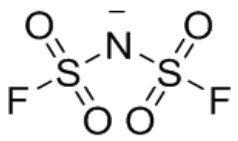
Salt effect & PolyIL-in-salt



Poly(DADMA)$^+$



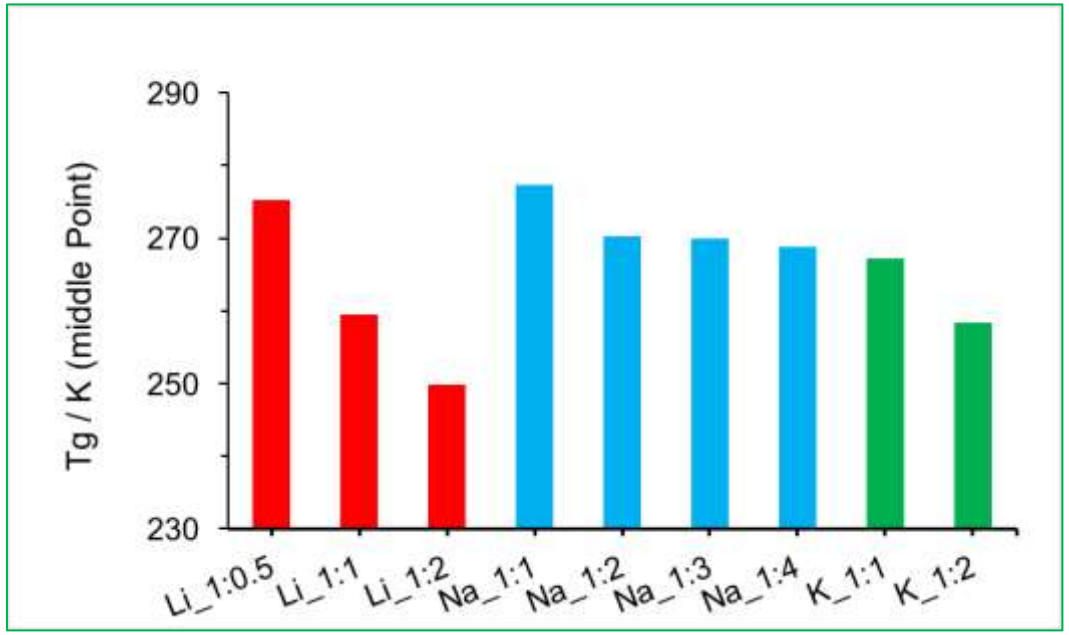
FSI^-

+ LiFSI (NaFSI or KFSI)

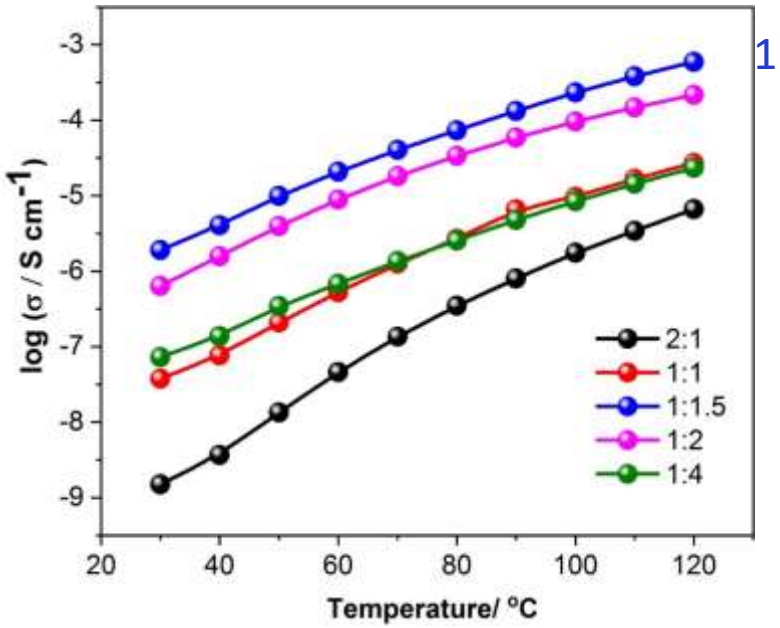
Li_1 : 1.5

Dr. Xiaoen Wang

Tg of Poly(DADMA)FSI with LiFSI, NaFSI and KFSI



Conductivity of PDADMA FSI with LiFSI



1:1.5

X Wang and F Chen et al, Joule, 2019, 3 (11), 2687-2702

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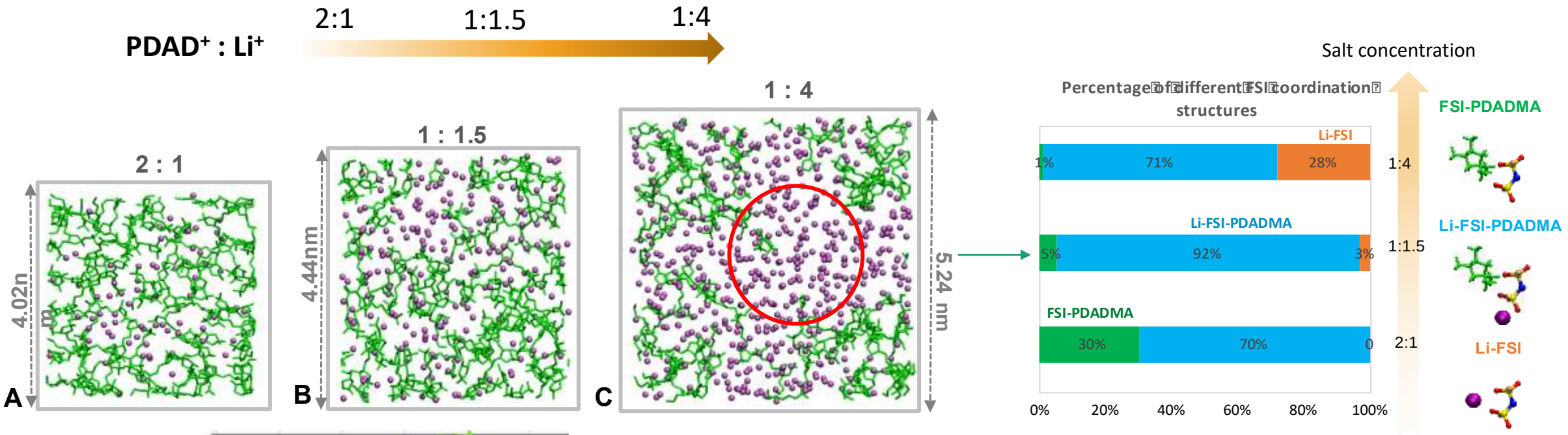
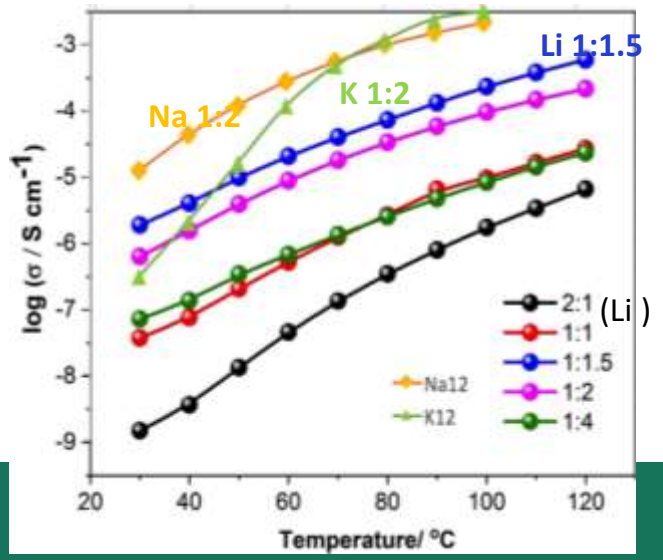
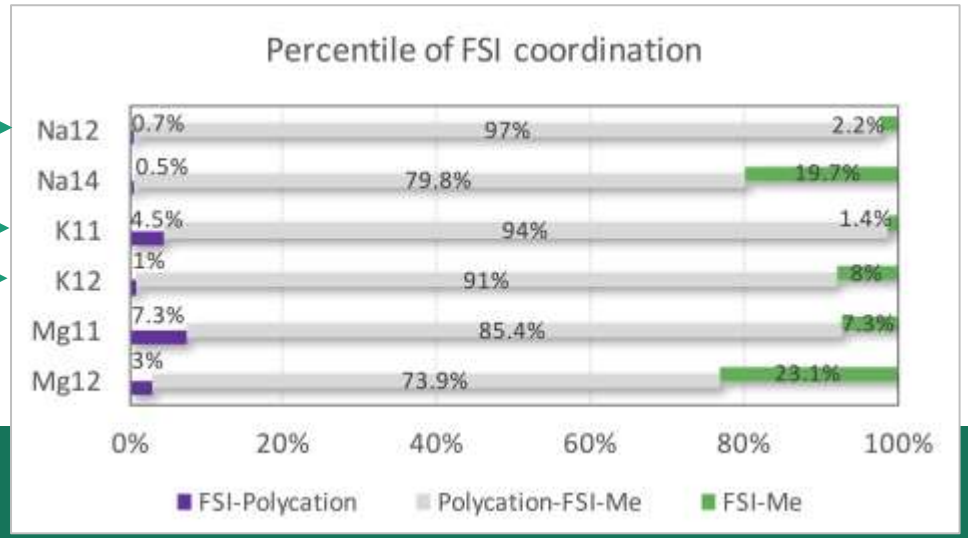
Co-coordination structure

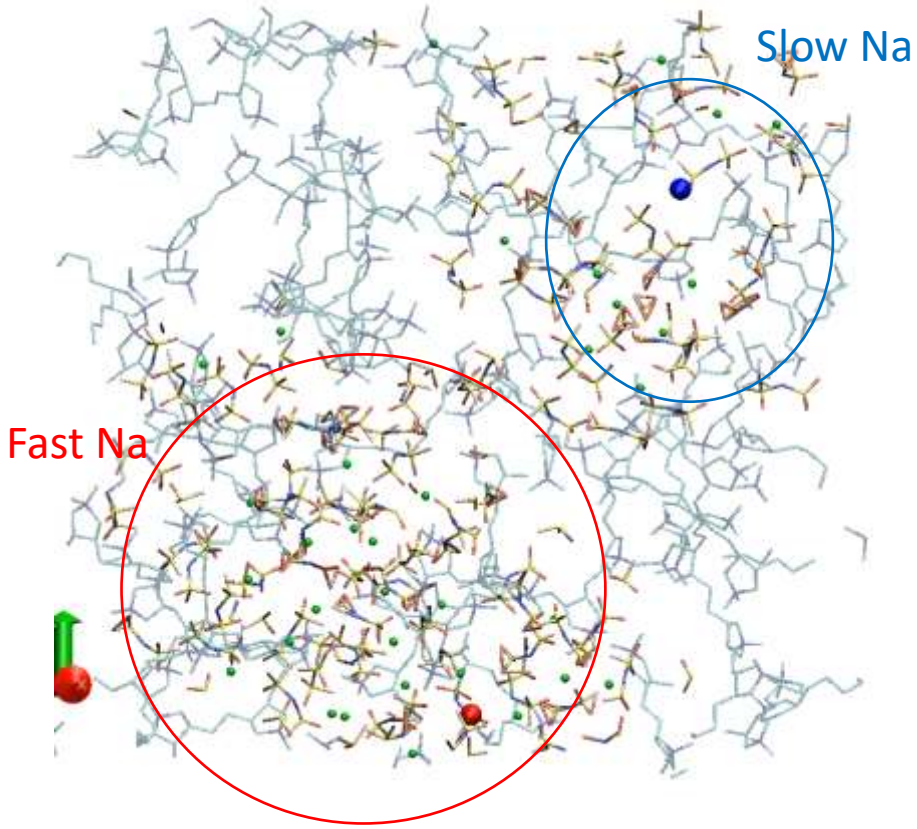
X Wang and F Chen et al, Joule, 2019, 3 (11), 2687-2702
F Chen et al, *Nat Mater,* 2022, 21, 1175-1182

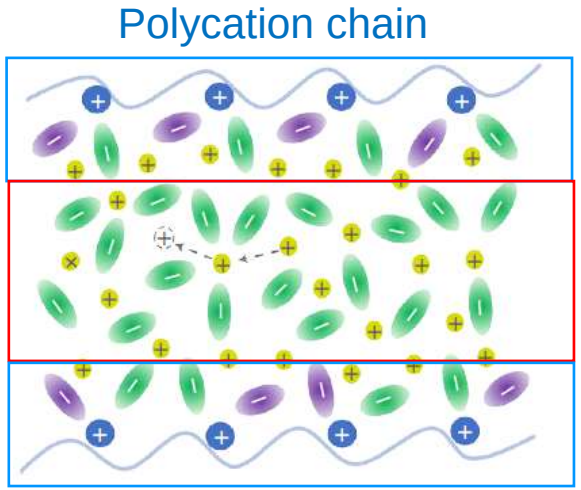


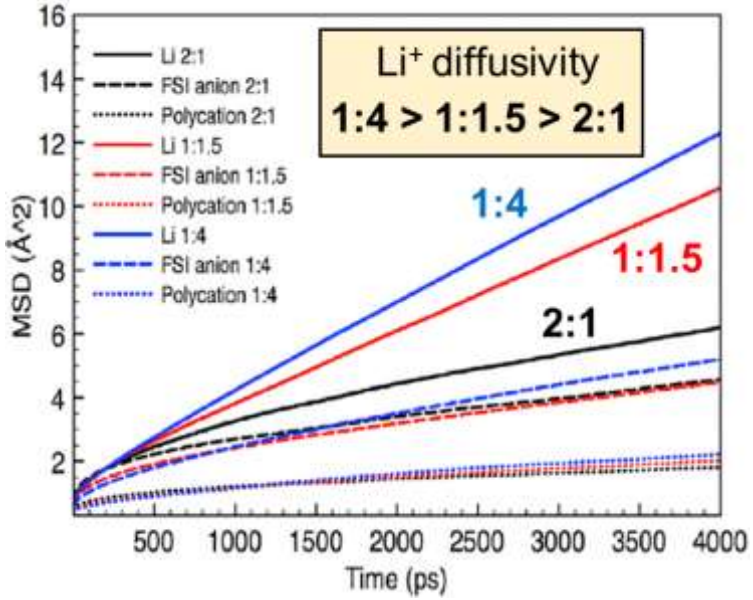




Analysis of fast Na ion chemical environment







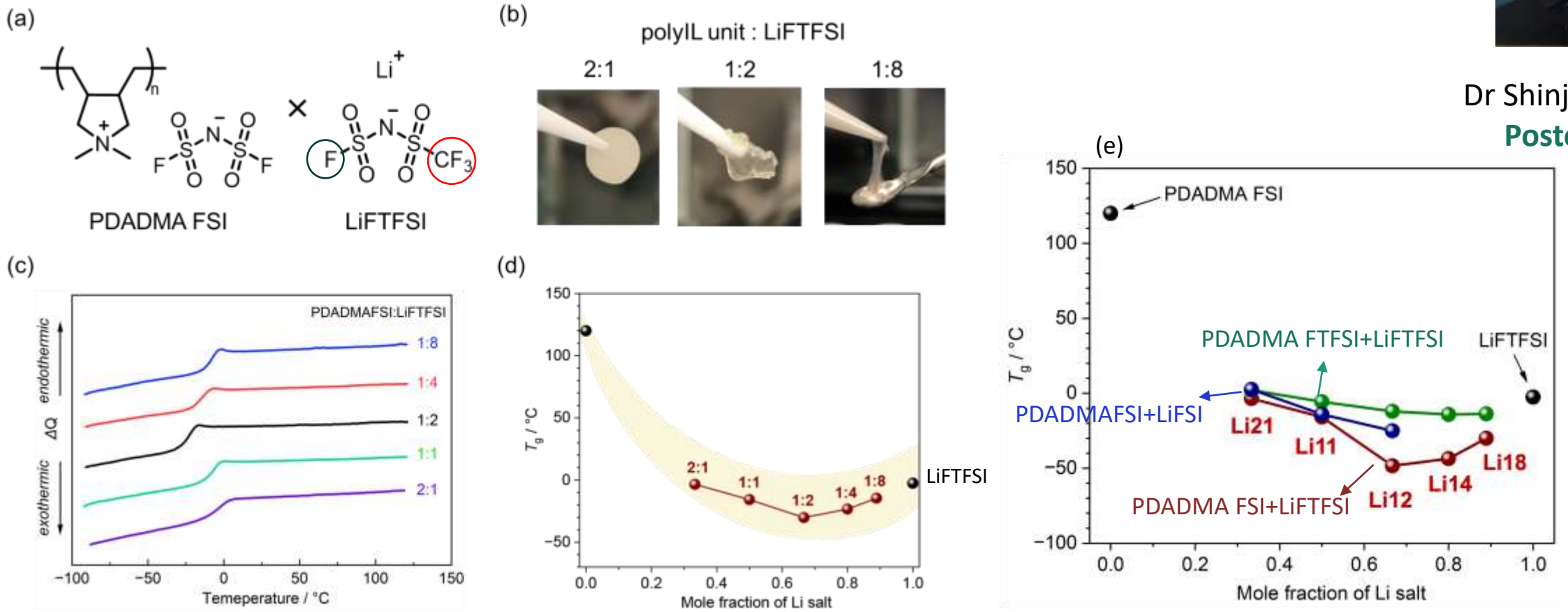
Theoretical prediction:
If ion aggregates remain in a molten salt state, it facilitates Na diffusion.

Real-life Challenge:
Crystallization occurs at high salt concentrations

Pushing up salt limit by mixing a second asymmetric anion

Dr Shinji Kondo

Poster 25



The use of mixed anions lowers the Tg of electrolyte compared to the single anions system. But the increased salt later starts to increase the Tg in the mixed anion system .

Ion Transport Properties

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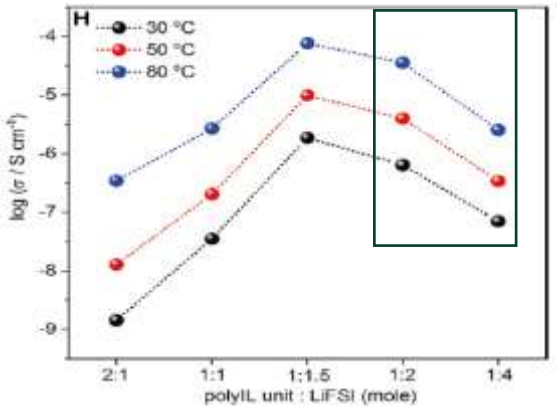
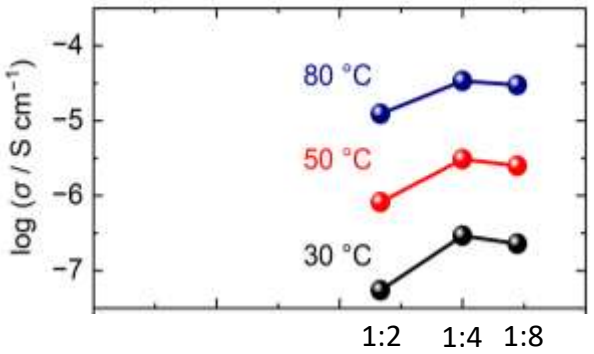
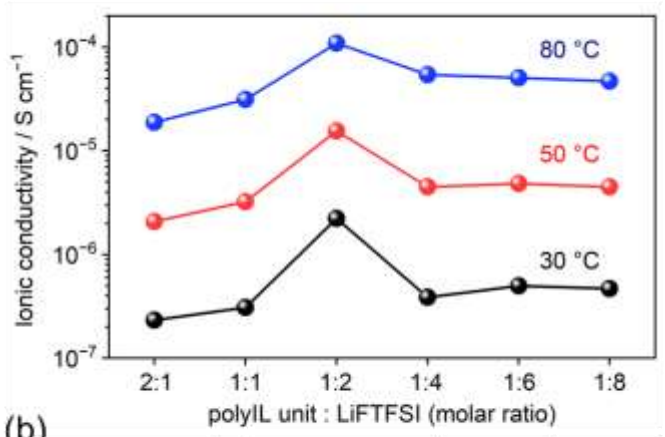
PDADMA FSI+LiFSI



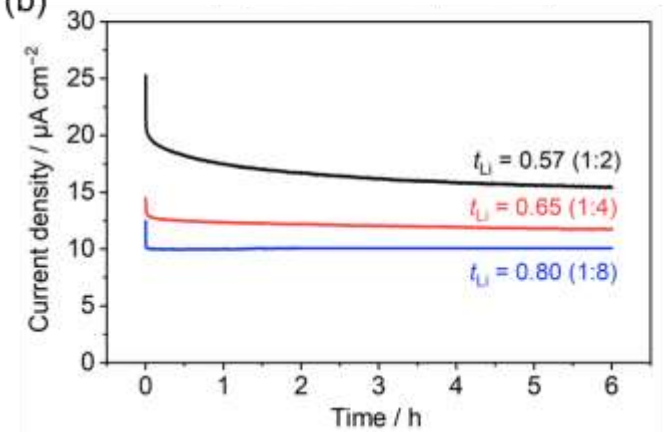
PDADMA FTFSI+LiFTFSI



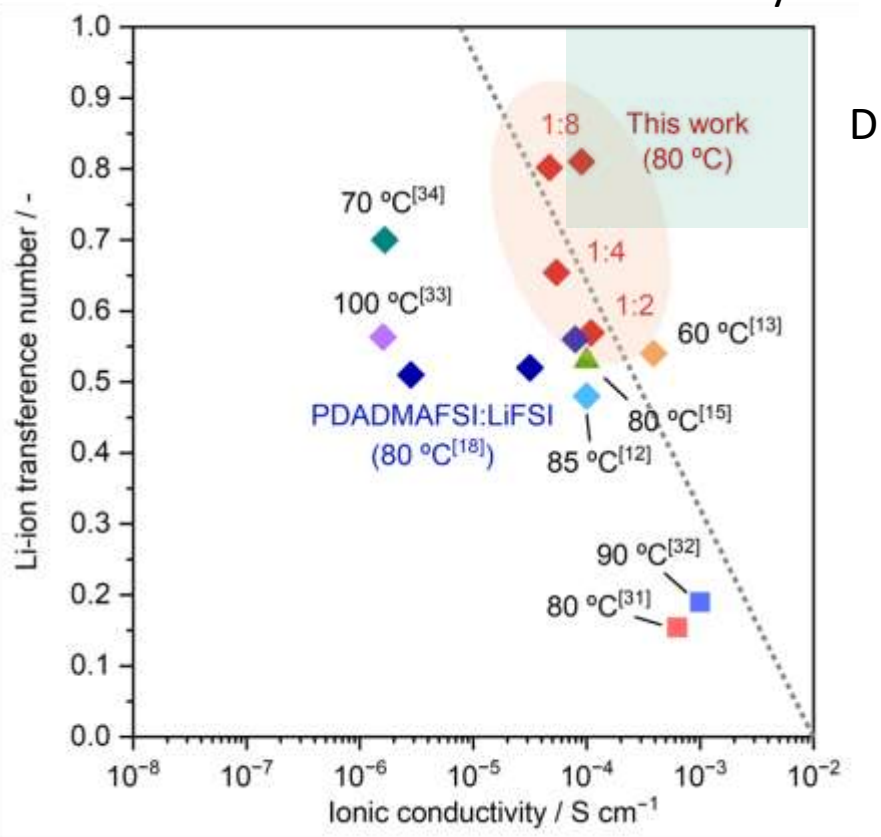
(a) PDADMA FSI+LiFTFSI



(b)



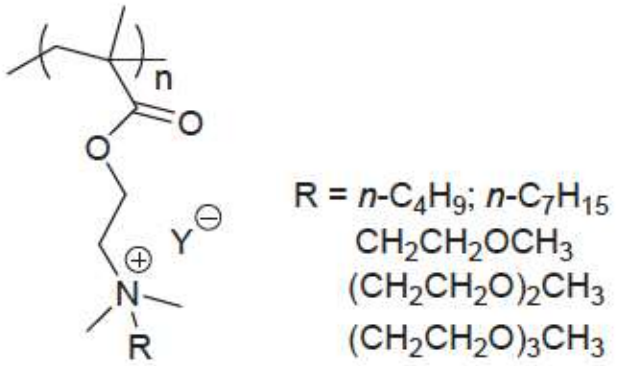
(c) Idea electrolyte



- ✓ Using the asymmetric anion and mixed anions, the conductivity changes within the same order of magnitude in different salt concentrations. A high Li transference number of 0.8 is obtained.

Alkyl and Alkoxy Side Chain effect

Polymer 55 (2014) 3339-3348



R = *n*-C_4H_9; *n*-C_7H_{15}
$CH_2CH_2OCH_3$
$(CH_2CH_2O)_2CH_3$
$(CH_2CH_2O)_3CH_3$

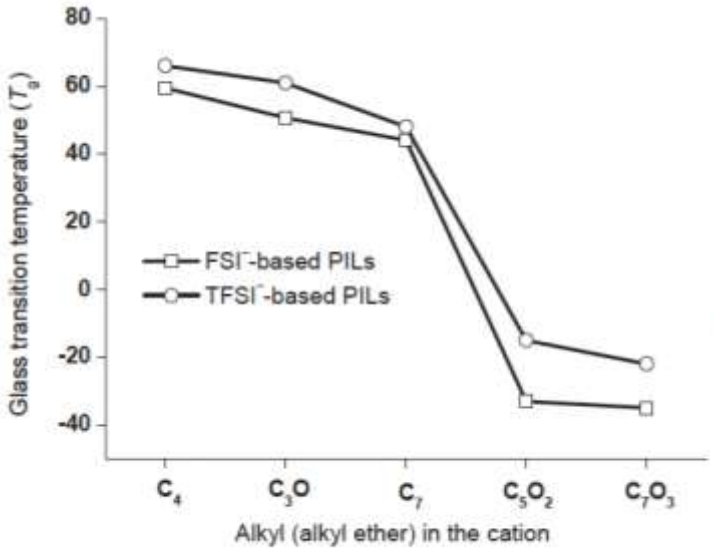
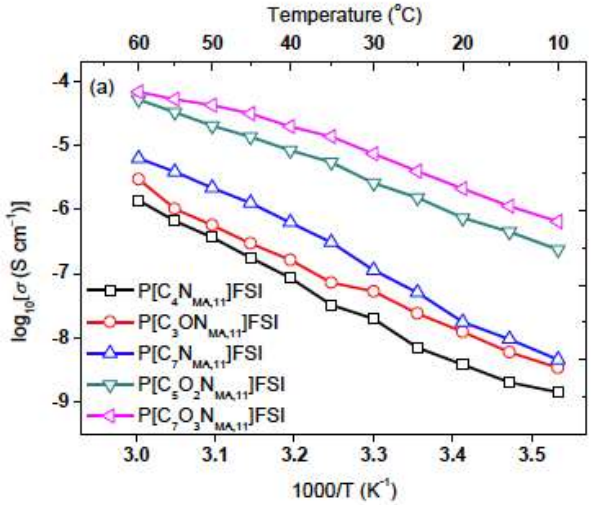
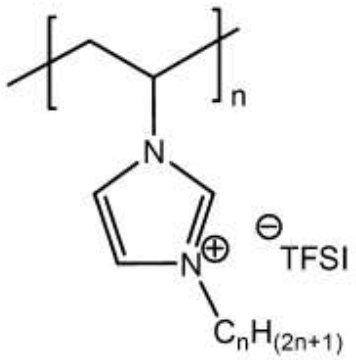


Fig. 8. Glass transition temperature of various polymeric ionic liquids (PILs).



Macromolecules 2017, 50, 4309−4321



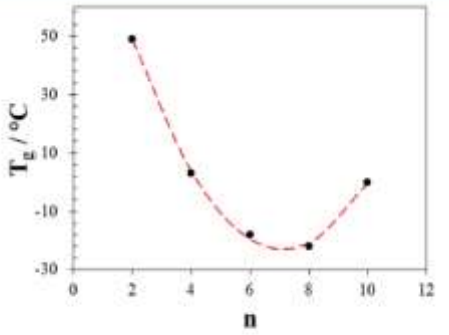
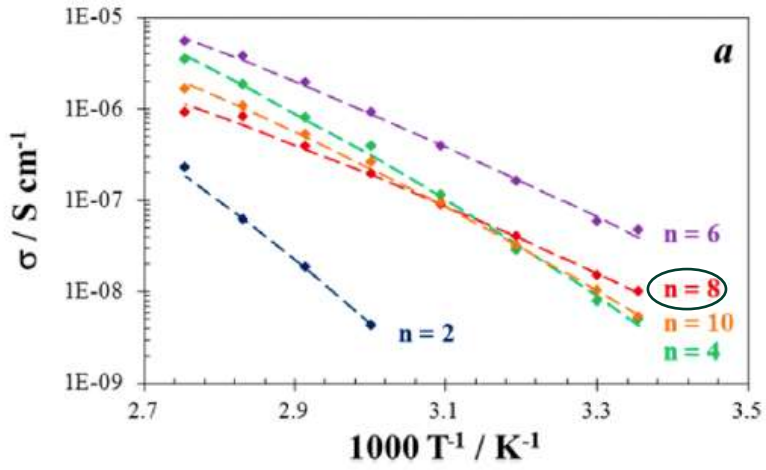
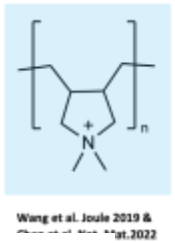


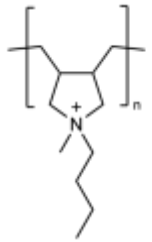
Figure 2. Glass transition temperature T_g as a function of the alkyl chain length for the different p(C_nVIm-TFSI) poly(IL) homopolymers.



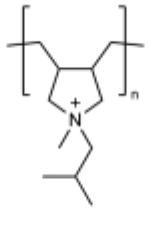
How does the side chain affect PolyIL with polycations on backbone?



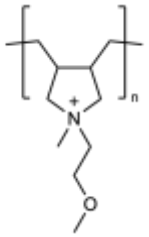
poly(diallyl dimethyl ammonium) (PDADMA, Poly(N1111))



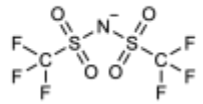
poly(diallyl methylbutyl ammonium) (PDAMBA, Poly(N1114))



poly(diallyl methylpropyl ammonium) (PDAMPA, Poly(N11i4))



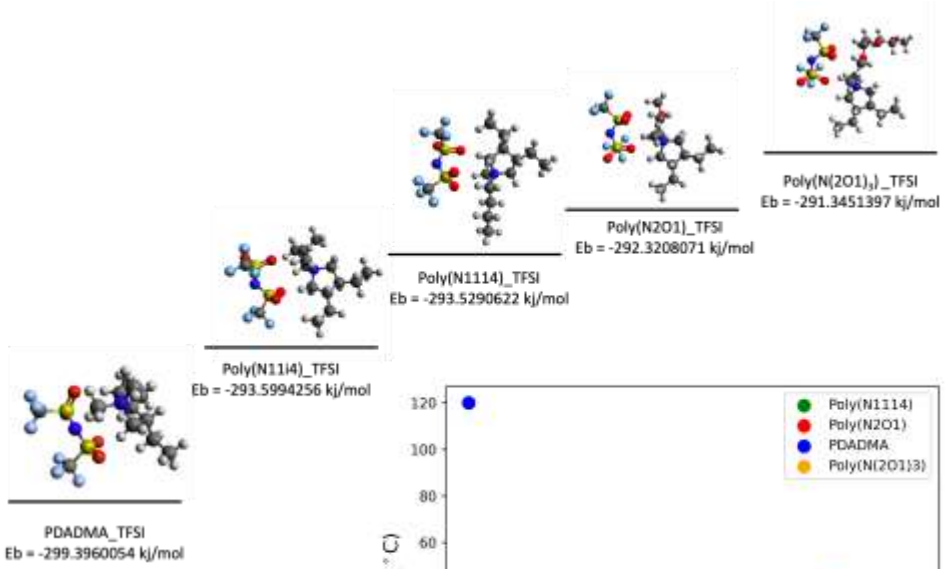
poly(diallyl methoxyethyl ammonium) (PDAMOA, Poly(N2O1))

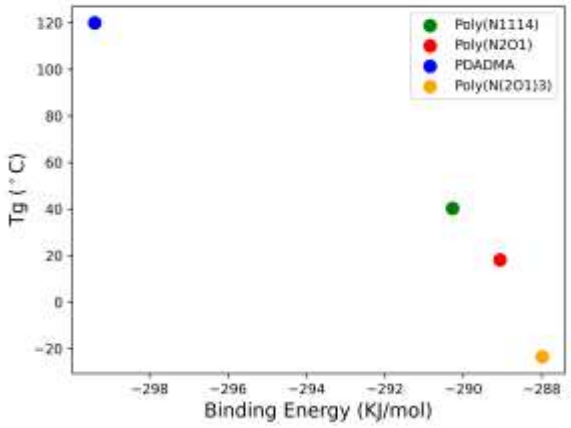


bis(trifluoromethanesulfonyl)imide (Bistrifimide,TFSI or NTf_2)

Kewei Cai
Poster 4

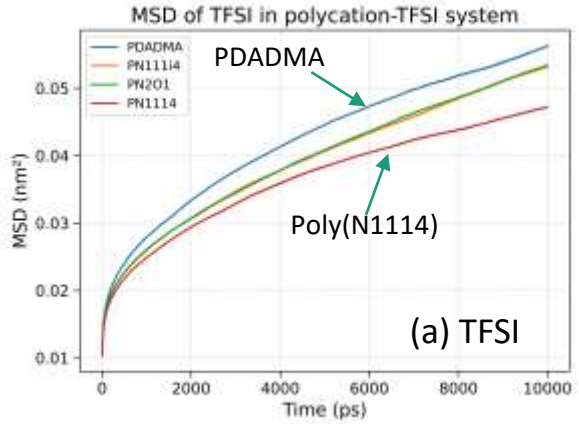
Polycation-anion binding energy





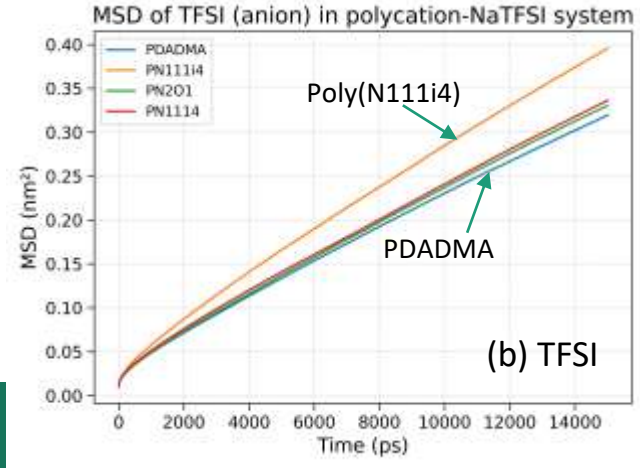
Polycation with a shorter side chain gives higher binding energy and is associated with a larger Tg

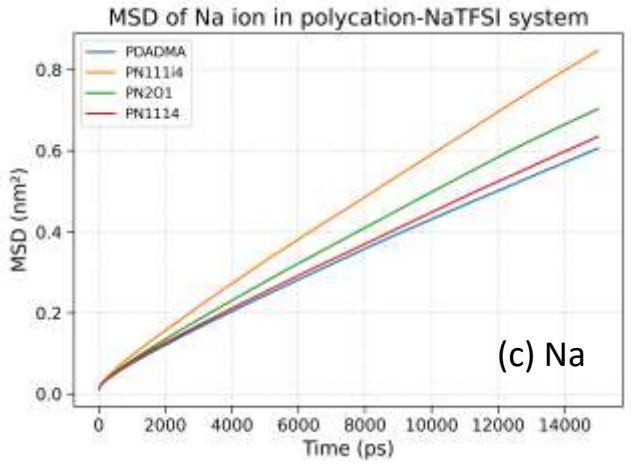
(a) PolyIL



- The ion diffusion in the neat PolyIL and the salt system do not follow the same trend.
- It can't be judged only through Tg.

(b)& (c) 1:2 PolyIL :NaTFSI





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Dr Xiaoen Wang
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Prof Maria Forsyth

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Thank you for your attention!