Decoupling Mechanics from Ion Transport in Polymers

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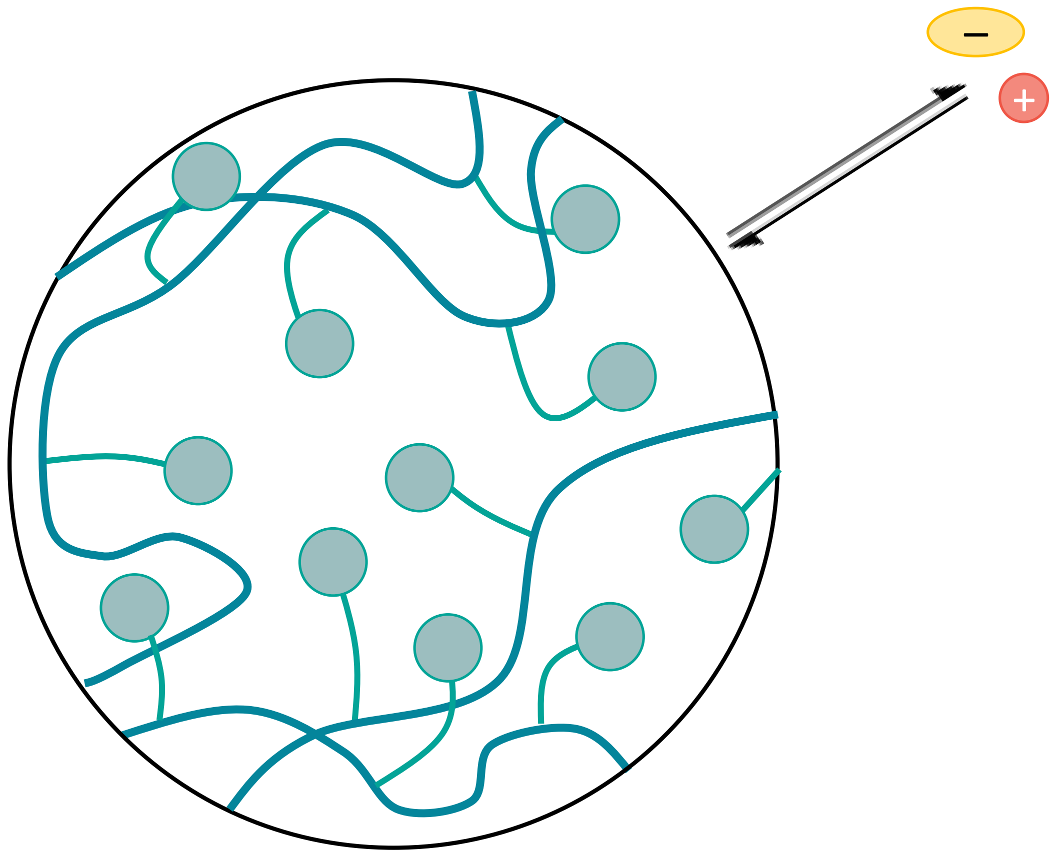
APS March Meeting 2020
Padden Award Symposium

Segalman and Seshadri groups
University of California, Santa Barbara

March 4, 2020

Ionic conductivity enabled through salt dissolution and ion motion



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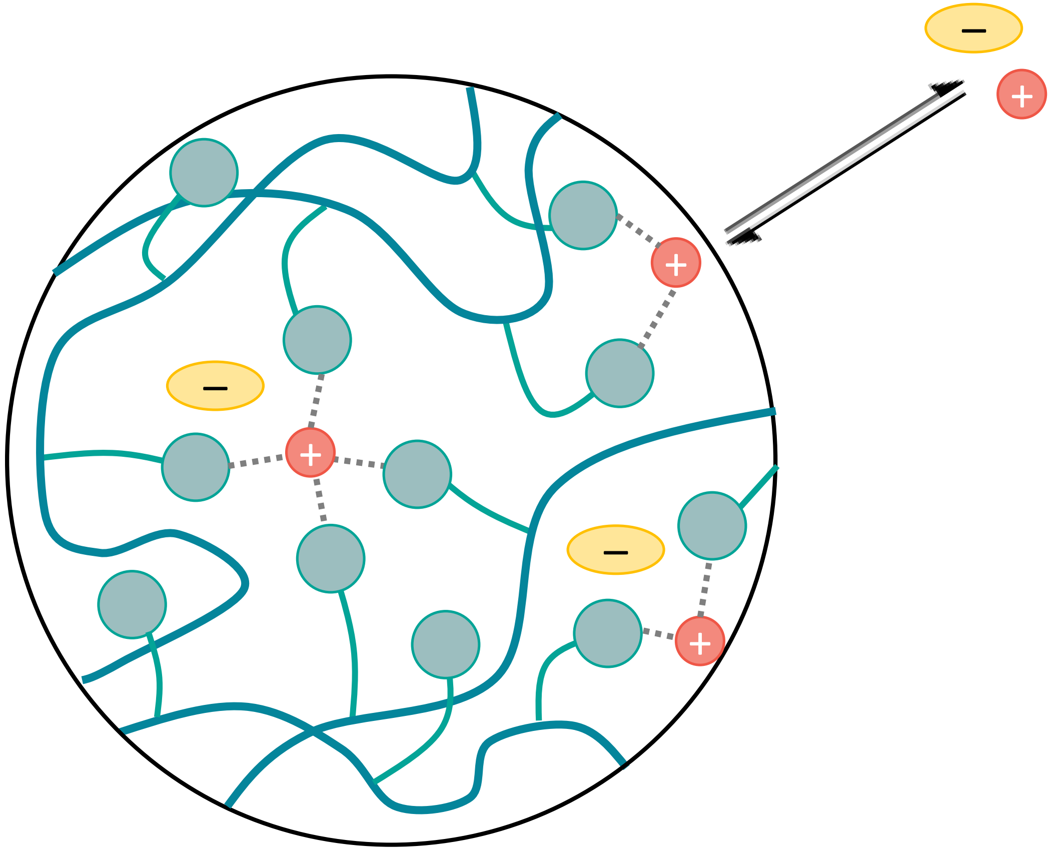
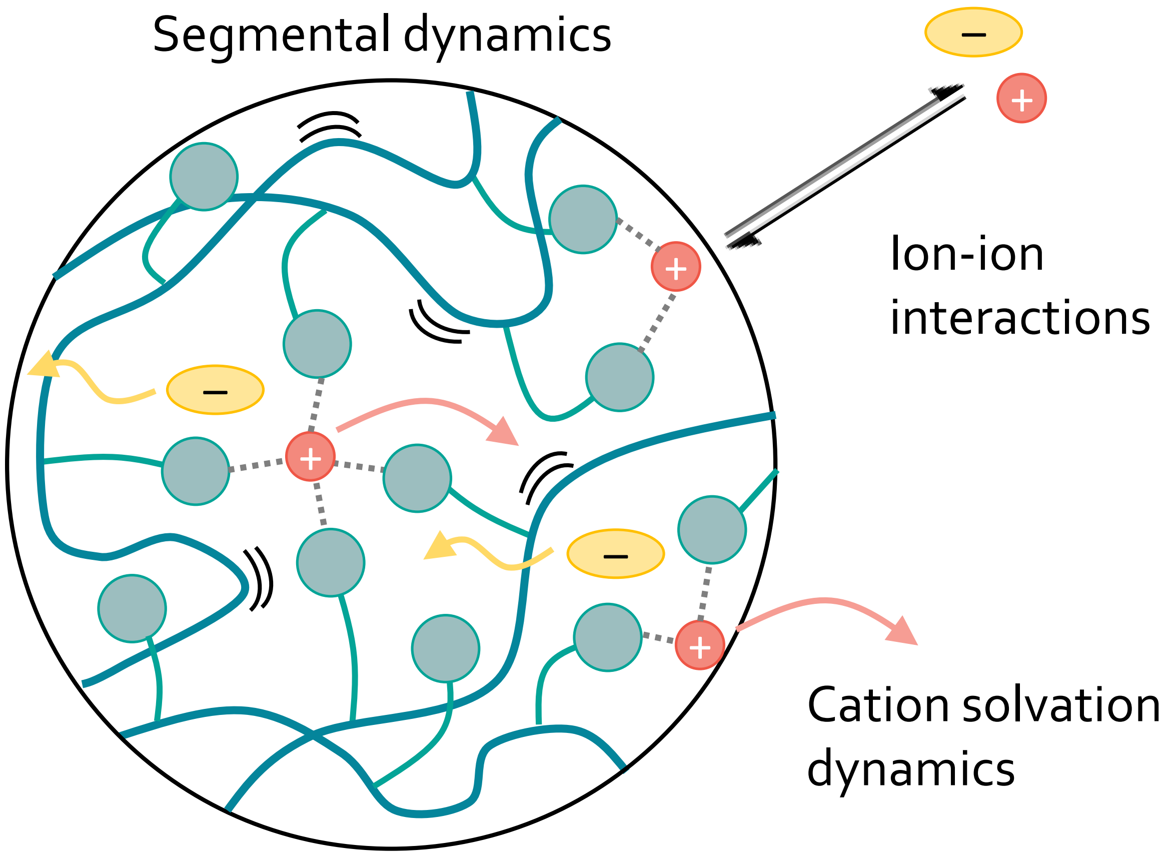


Ion conductivity depends on ion-polymer interactions and polymer architecture



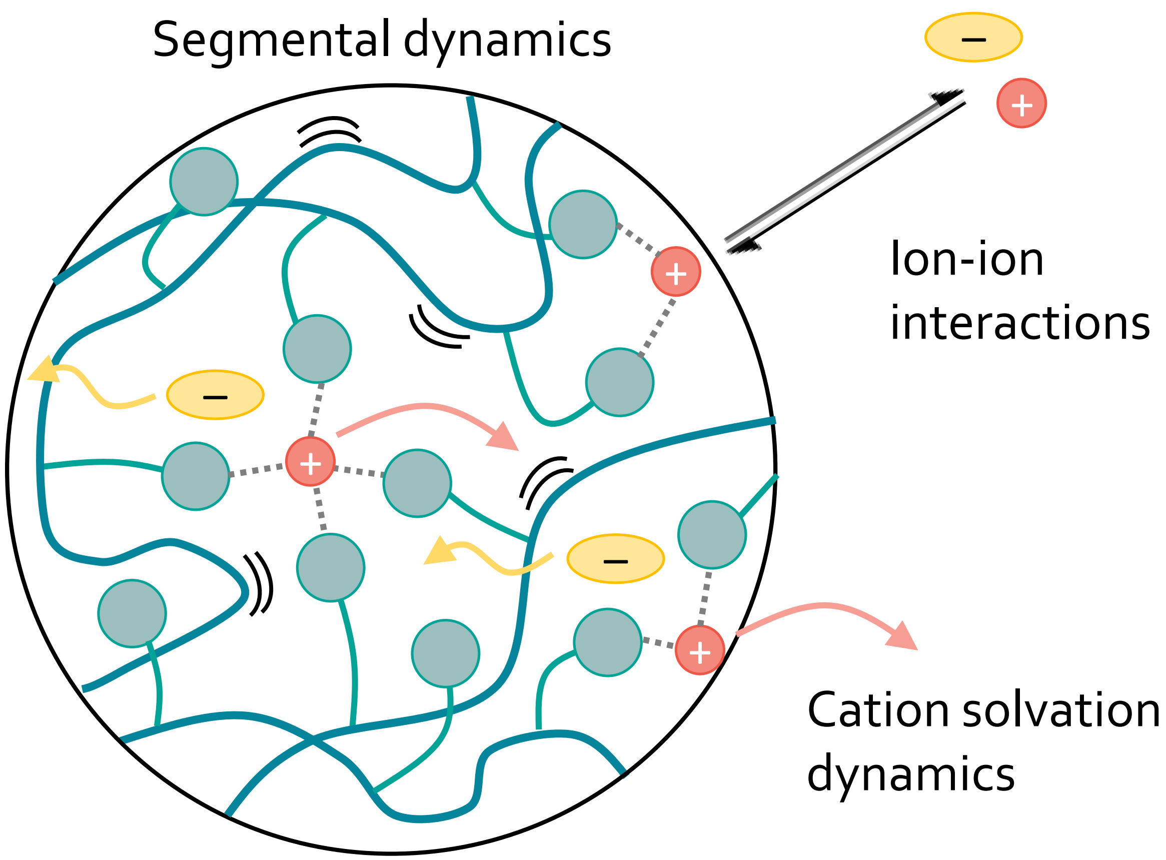
Ion conductivity depends on ion-polymer interactions and polymer architecture

Total ionic conductivity depends on ion concentration and mobility

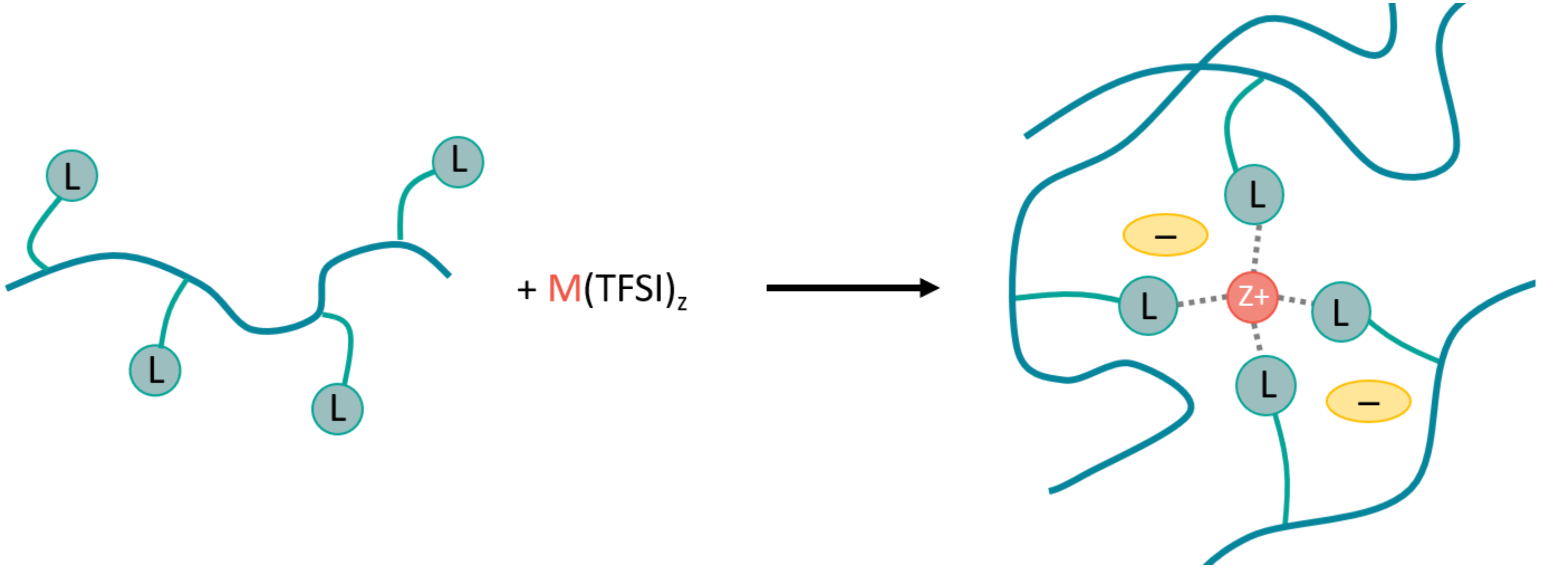
$$\sigma = \frac{F^2}{RT}\left(z_+^2 c_+ D_+ + z_-^2 c_- D_-\right)$$

Cation contribution given by transference number

$$t_+ = \frac{\sigma_+}{\sigma_{total}} = \frac{z_+ D_+}{z_+ D_+ + z_- D_-}$$

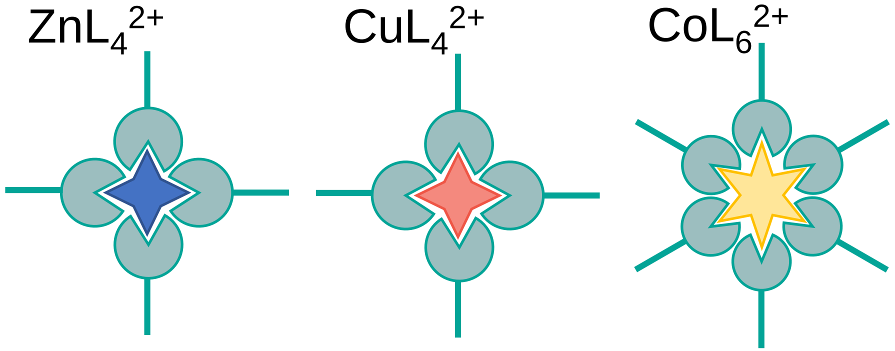


Labile metal-ligand coordination provides inspiration



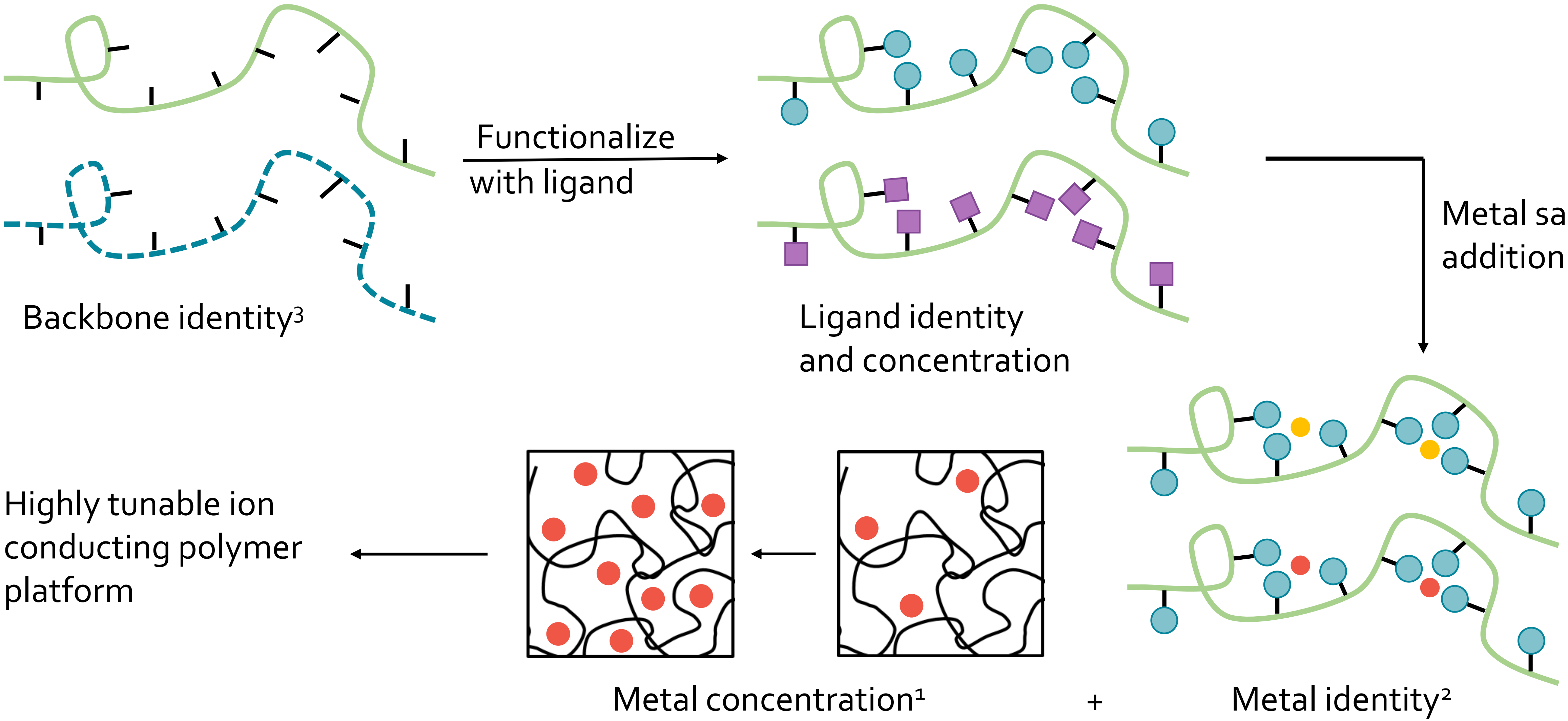
Metal–ligand interactions are

- well-defined
- highly tunable
- dynamic



Self-healing: Mozhdehi, Neal, Grindy, Cordeau, Ayala, Holten-Andersen, Guan. *Macromolecules* **2016,** *49*, 6310-6321.

Synthetic platform for systematic tunability



1. Sanoja, Schauser, Bartels, Evans, Helgeson, Seshadri, Segalman. *Macromolecules* **2018,** *51*, 2017-2026.
2. Schauser, Sanoja, Bartels, Jain, Hu, Han, Walker, Helgeson, Seshadri, Segalman. *Chem. Mater.* **2018,** *30*, 5759-5769.
3. Schauser, Grzetic, Tabassum, Kliegle, Le, Susca, Antoine, Keller, Delaney, Han, Seshadri, Fredrickson, Segalman, *J. Am. Chem. Soc. Under revision.*

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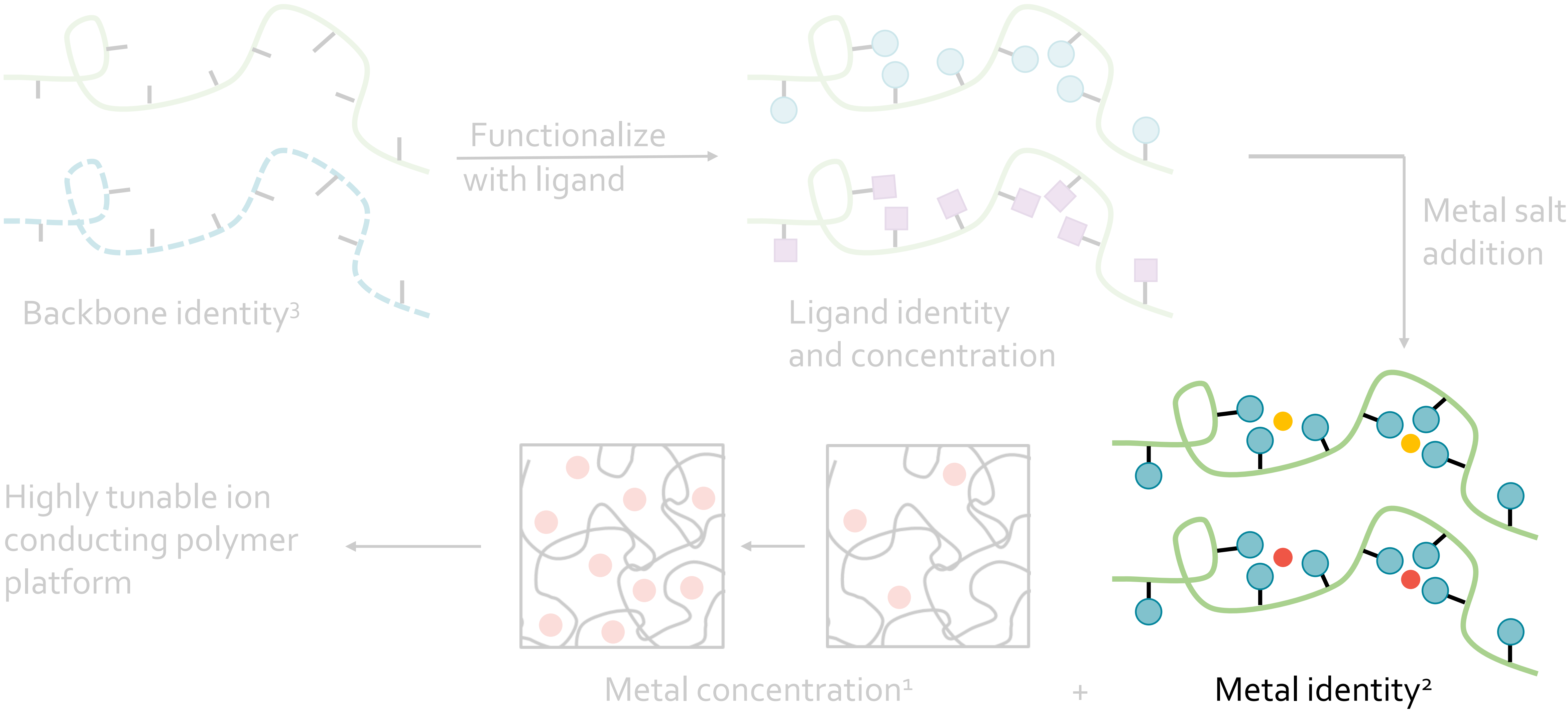

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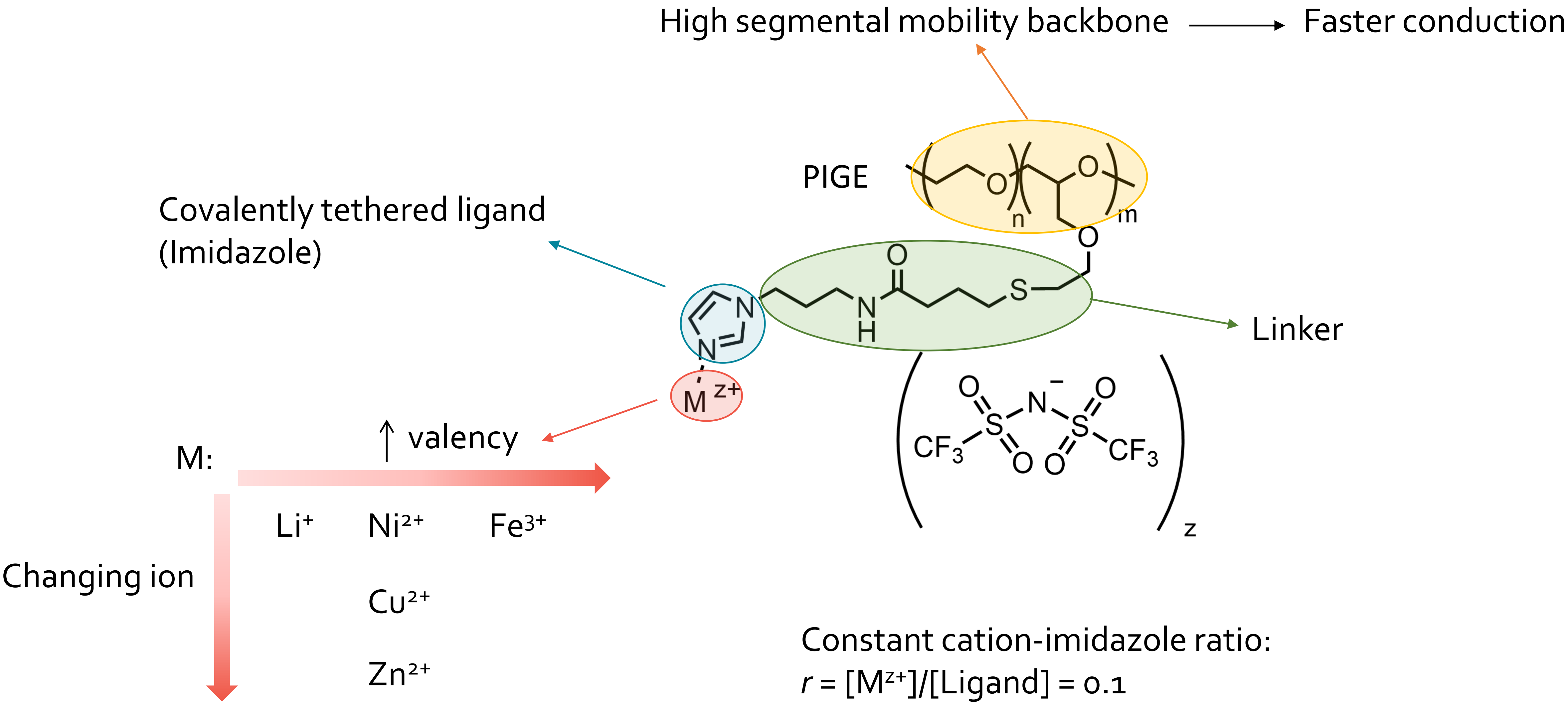
Critical questions about multivalent polymer electrolytes

1. Can we achieve appealing mechanical properties without a detrimental effect on conductivity?

2. Do multivalent ions conduct?

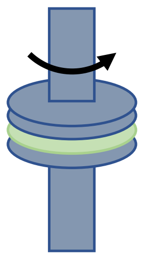
3. Can we develop design rules for improved conductivity performance?

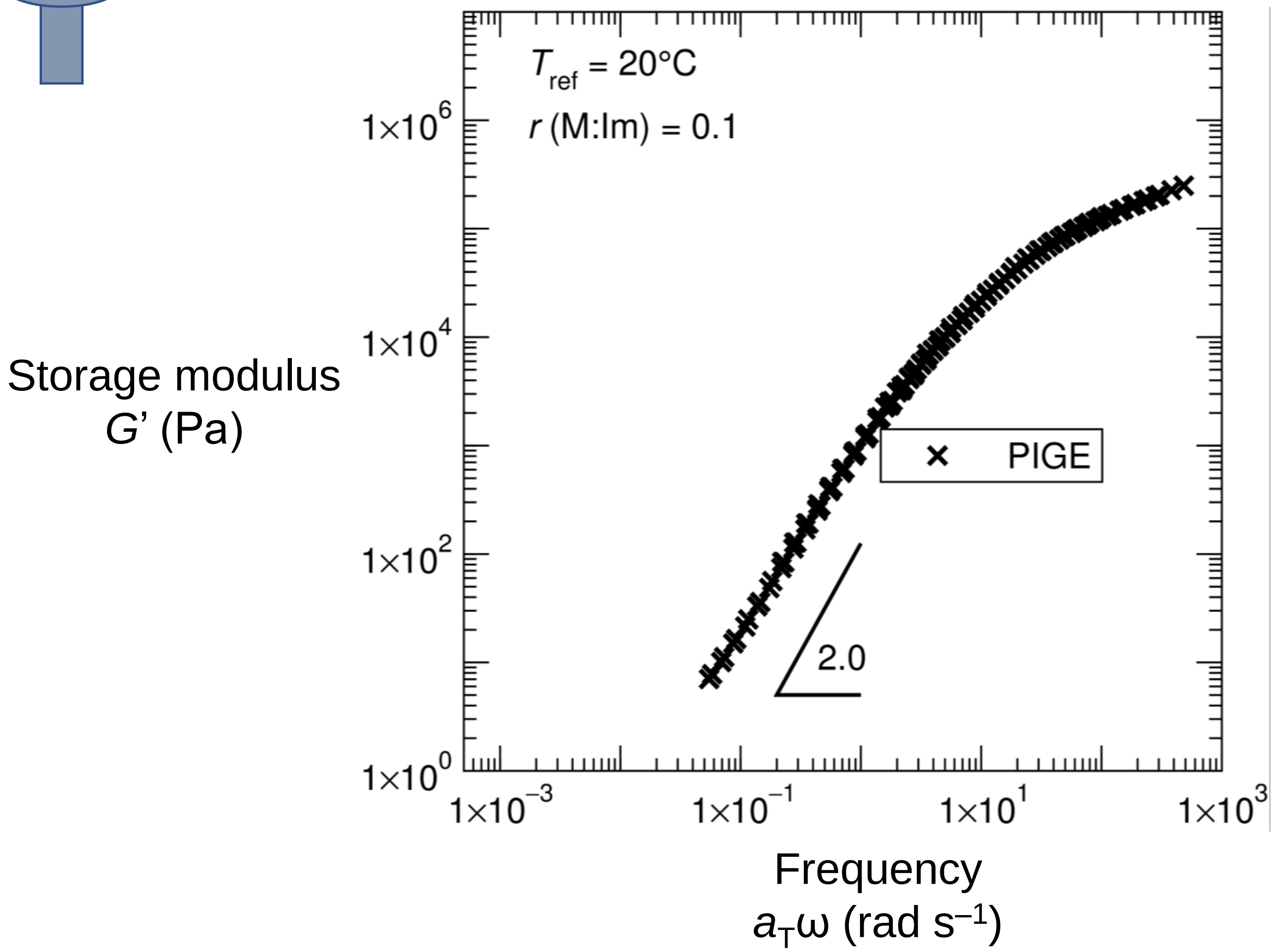
PEO derivative enables understanding effect of metal identity

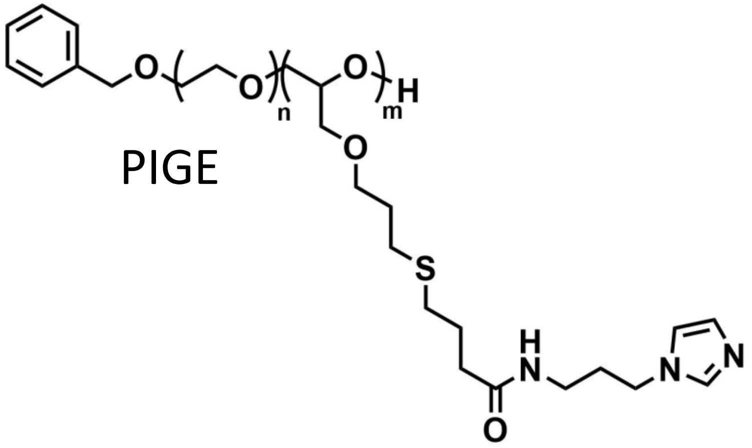


Constant cation-imidazole ratio:
$r = [M^{z+}]/[\text{Ligand}] = 0.1$

Dramatic tunability in polymer mechanics with metal identity







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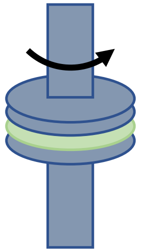
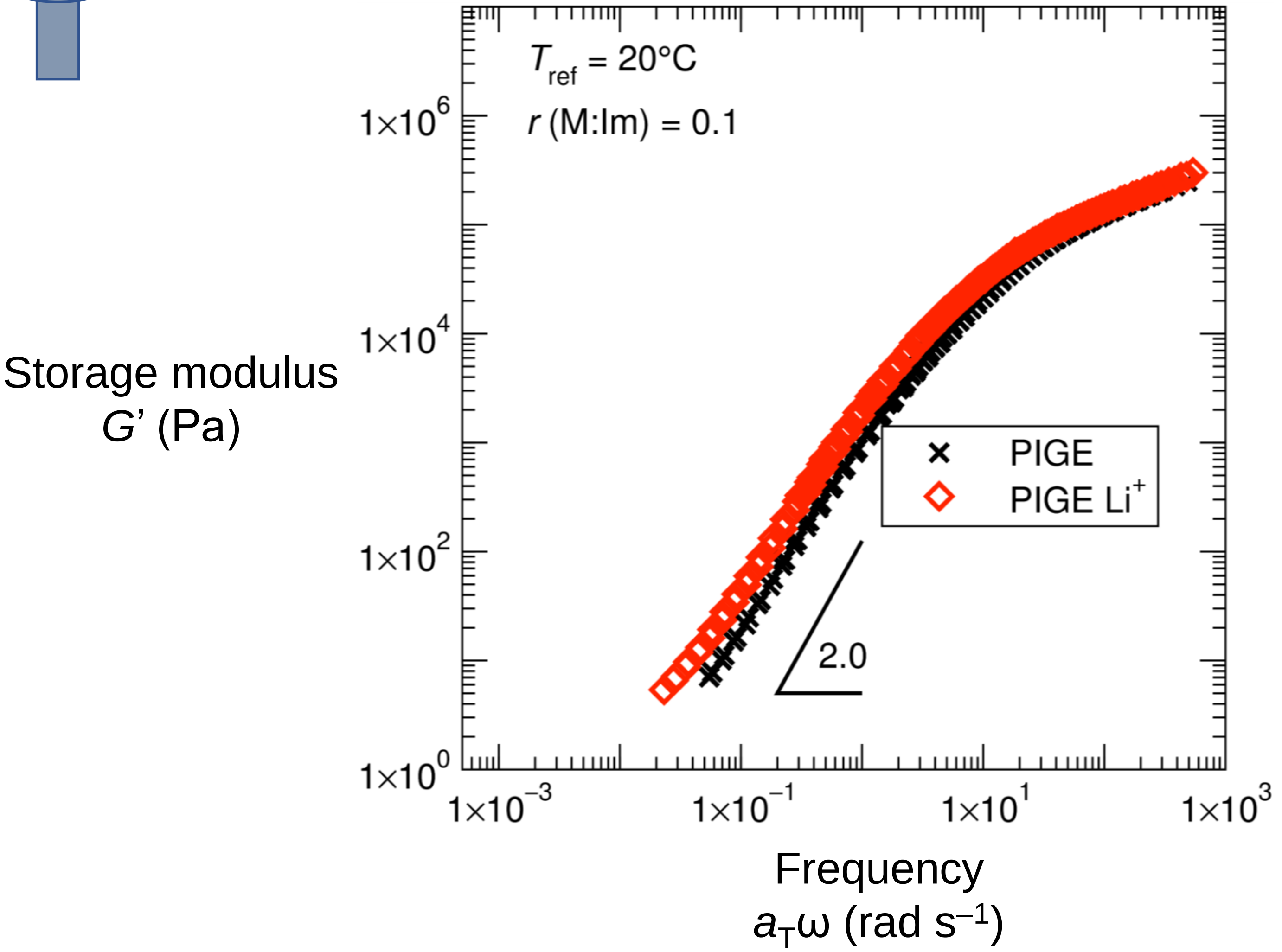
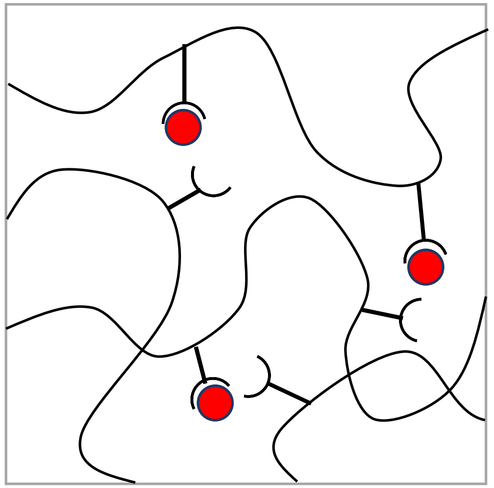
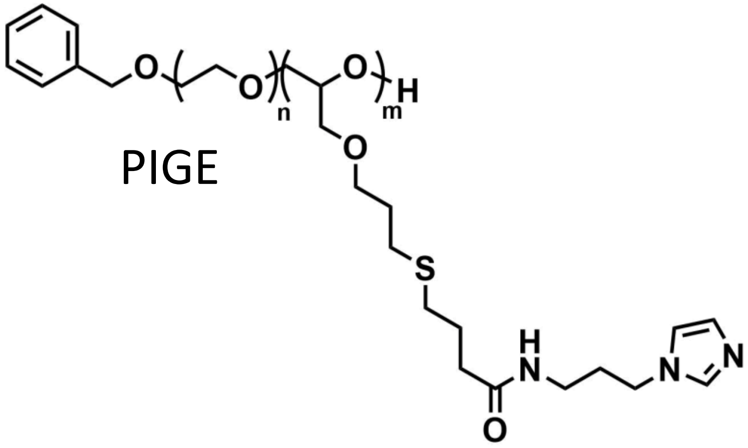


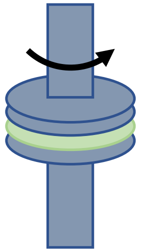


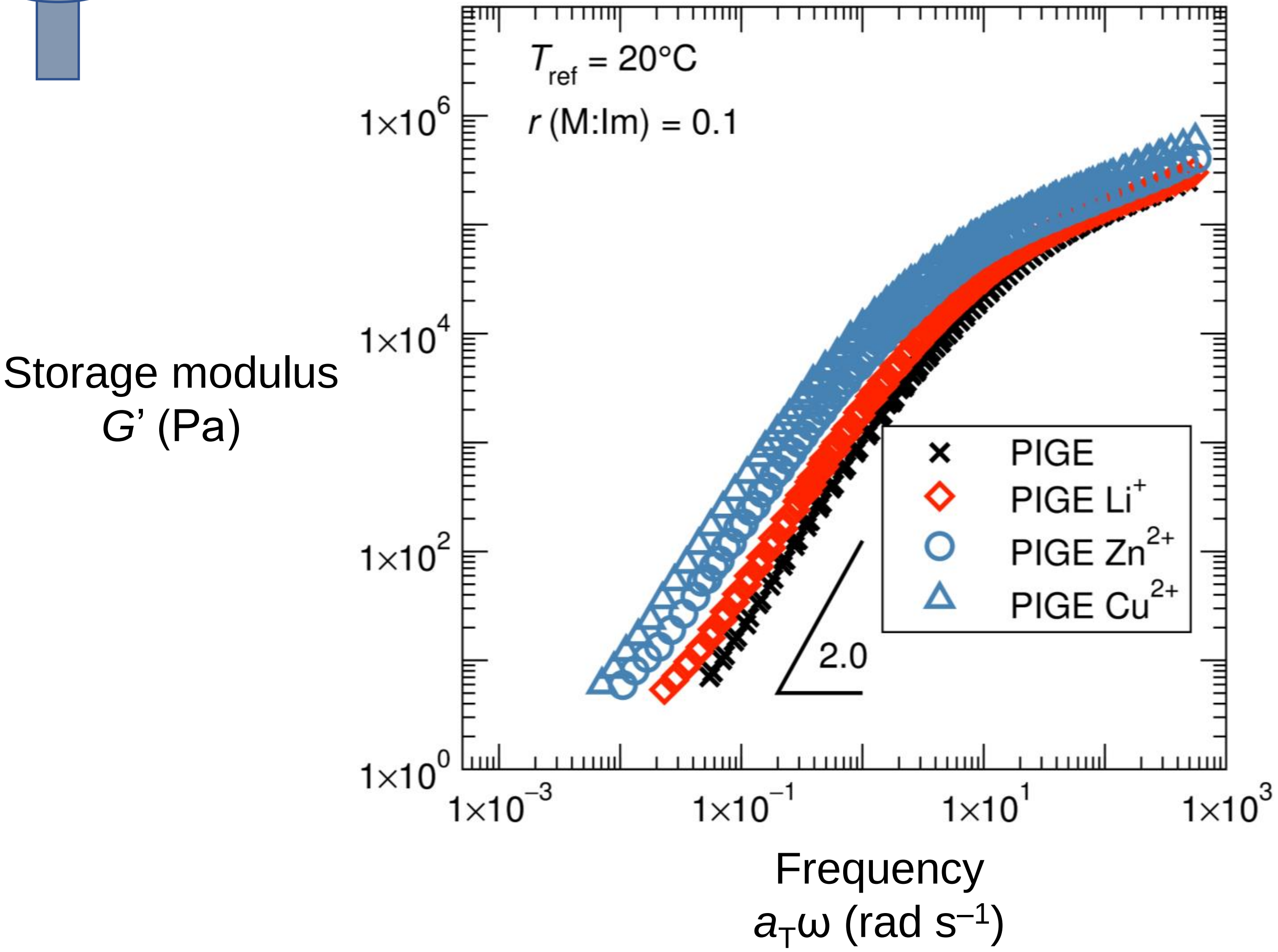


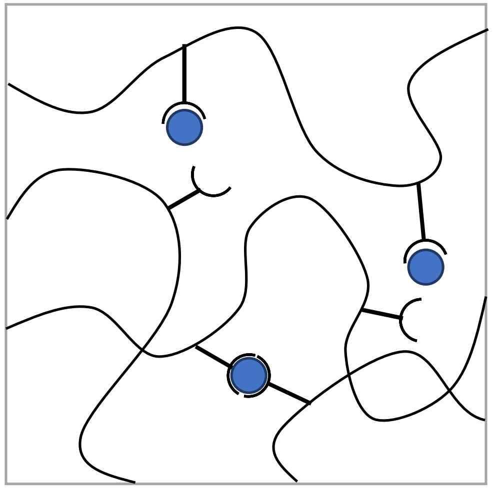


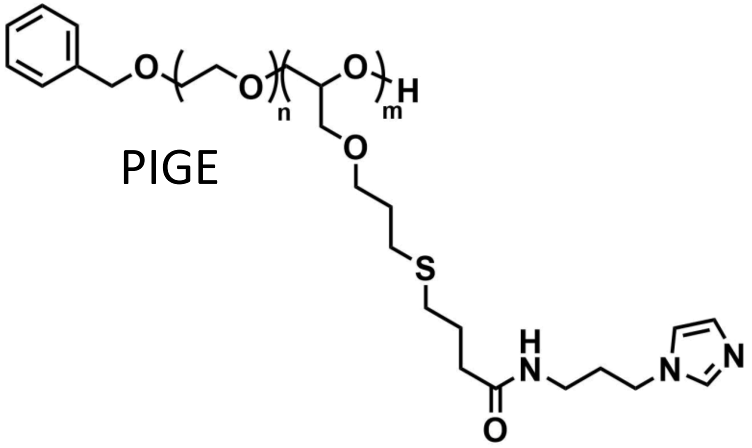
PIGE

Dramatic tunability in polymer mechanics with metal identity









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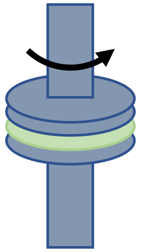
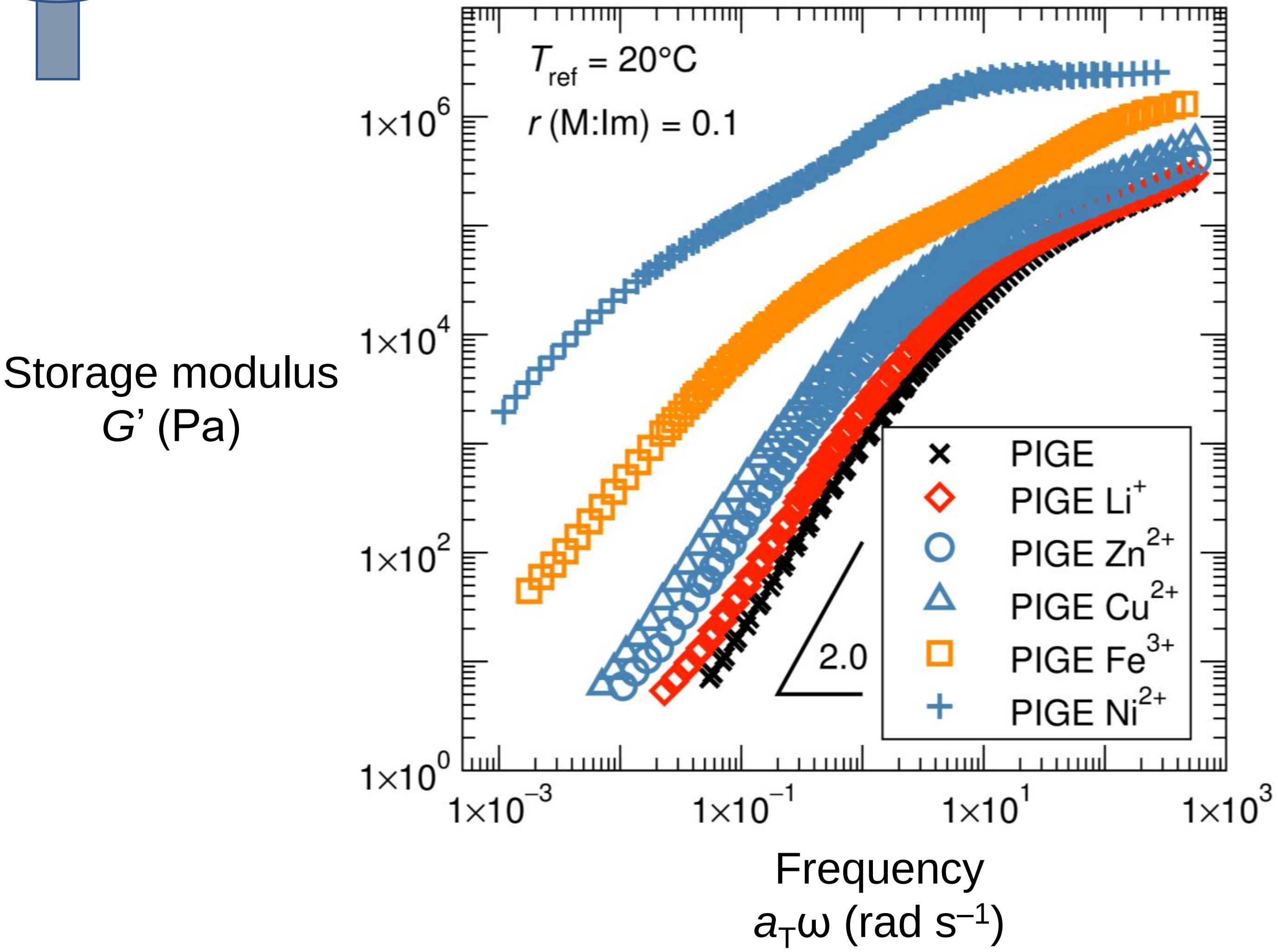
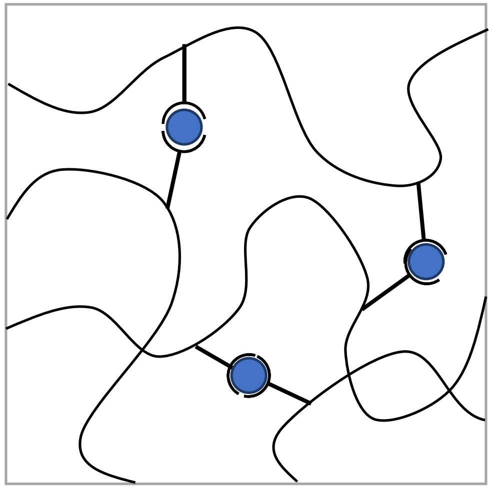
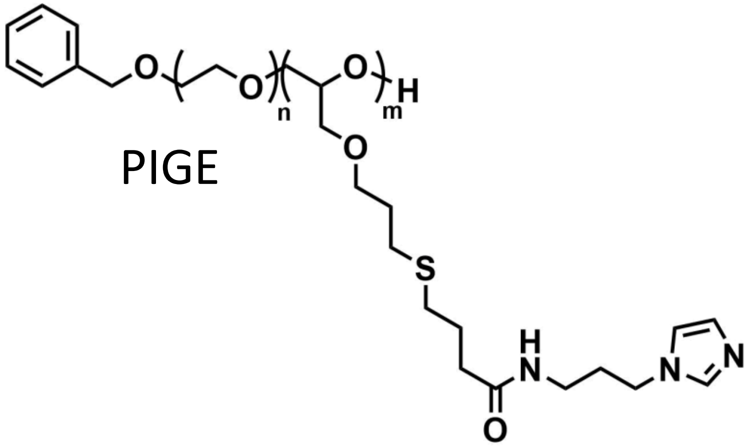


Metal-ligand coordination interaction results in slower network dynamics
Valency not a good indicator of binding strength

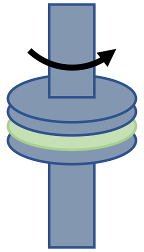






PIGE

Dramatic tunability in complex viscosity with metal identity



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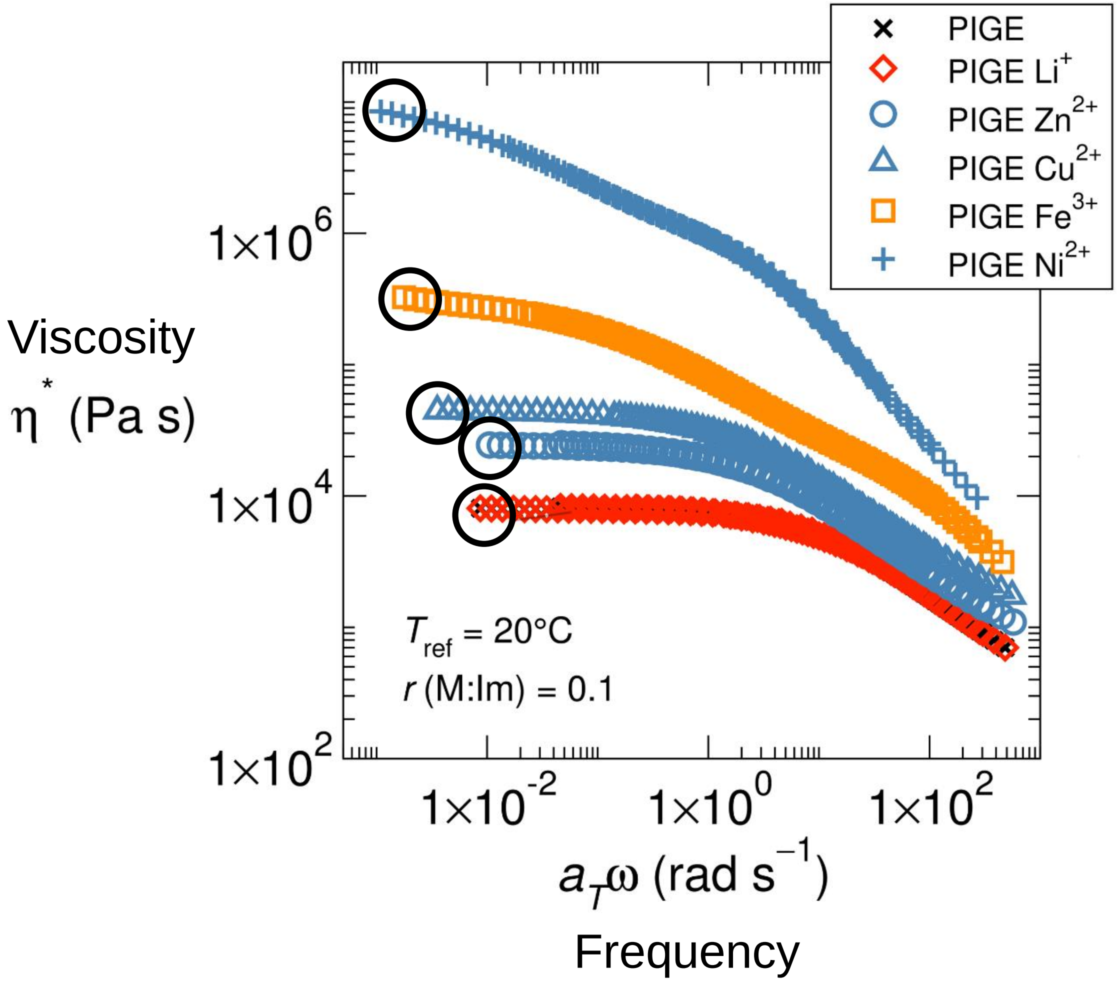
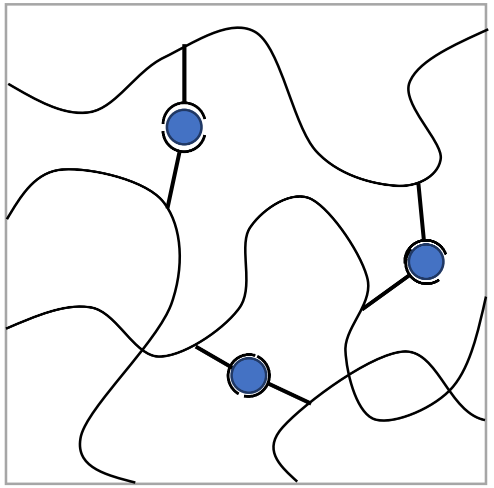
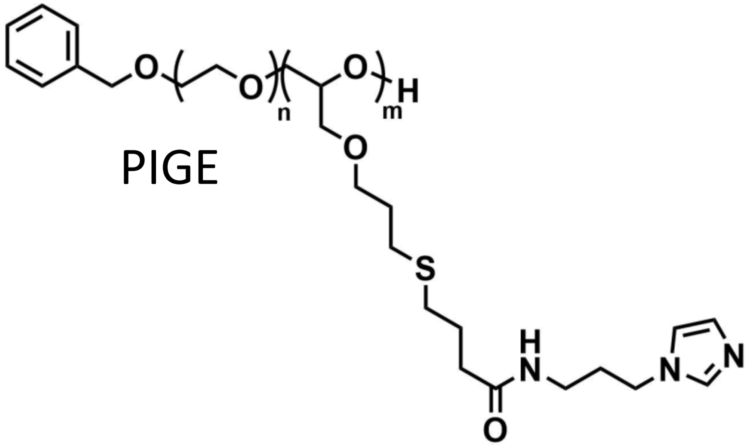
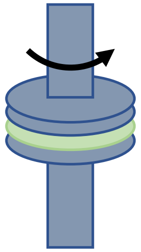
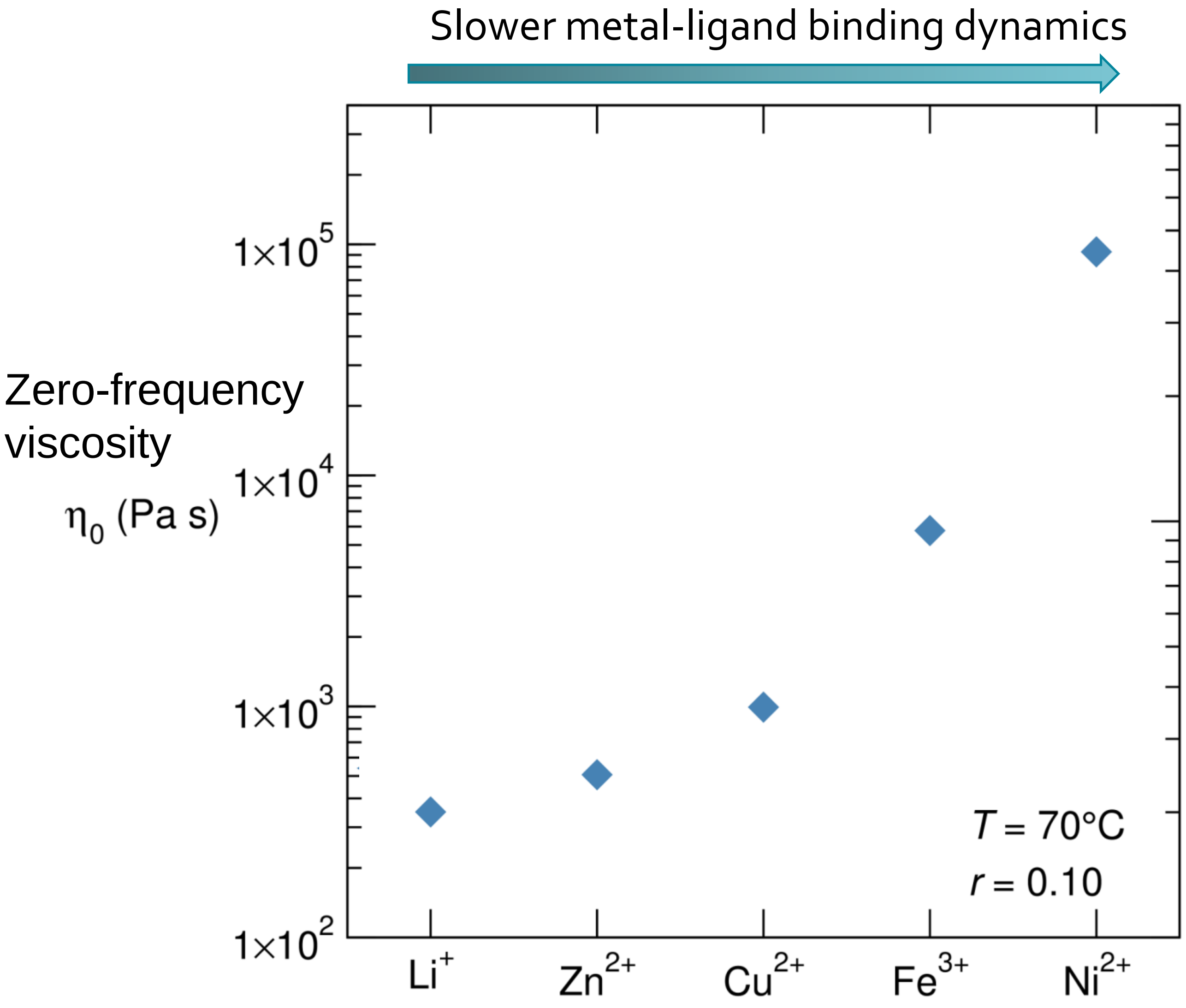






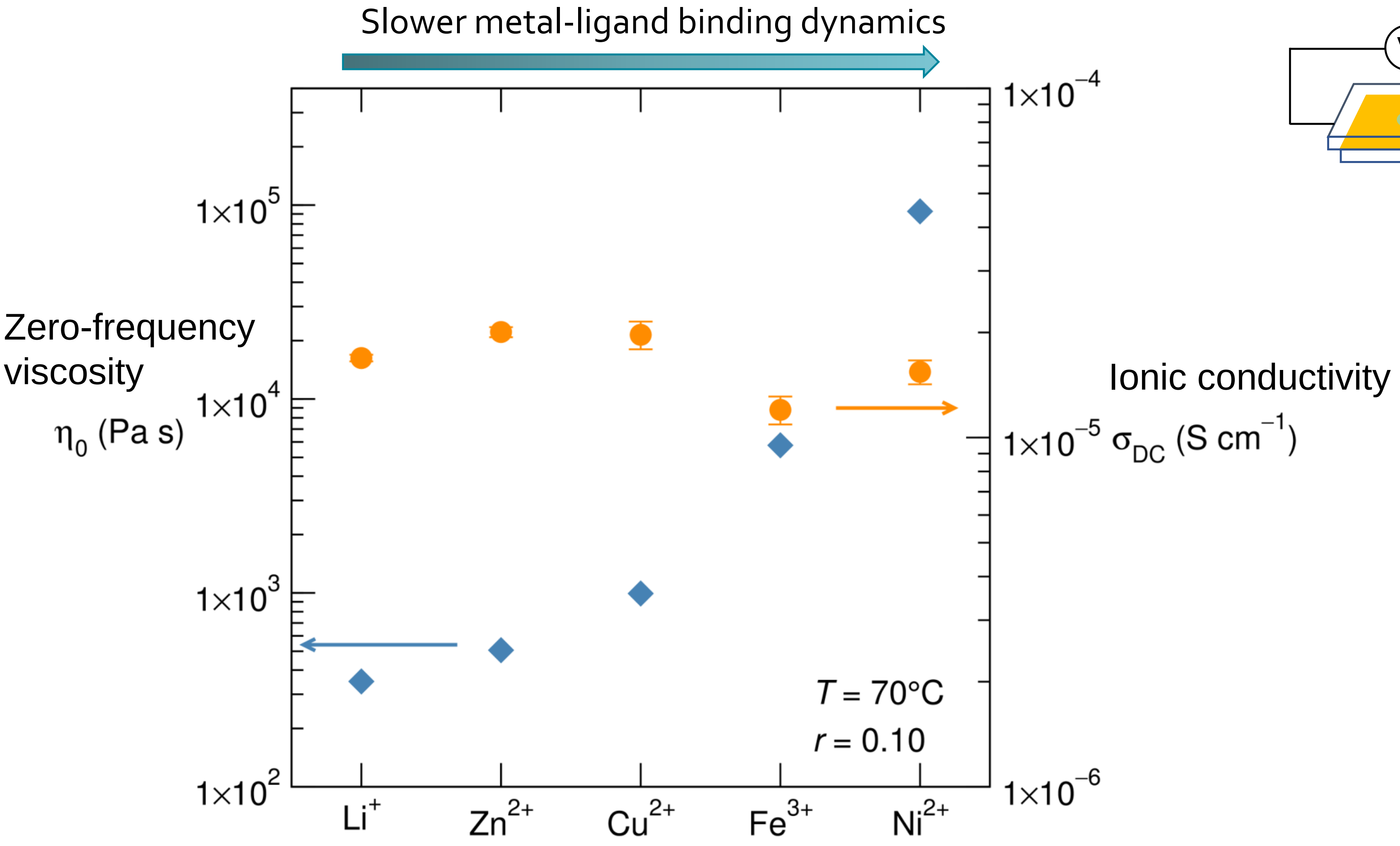
Increase in viscosity without decrease in conductivity

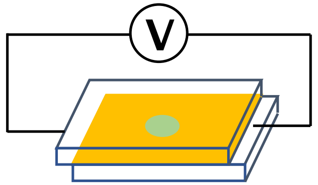




Zero frequency viscosity increases by ~10^3

Increase in viscosity without decrease in conductivity





Zero frequency viscosity increases by ~10^3

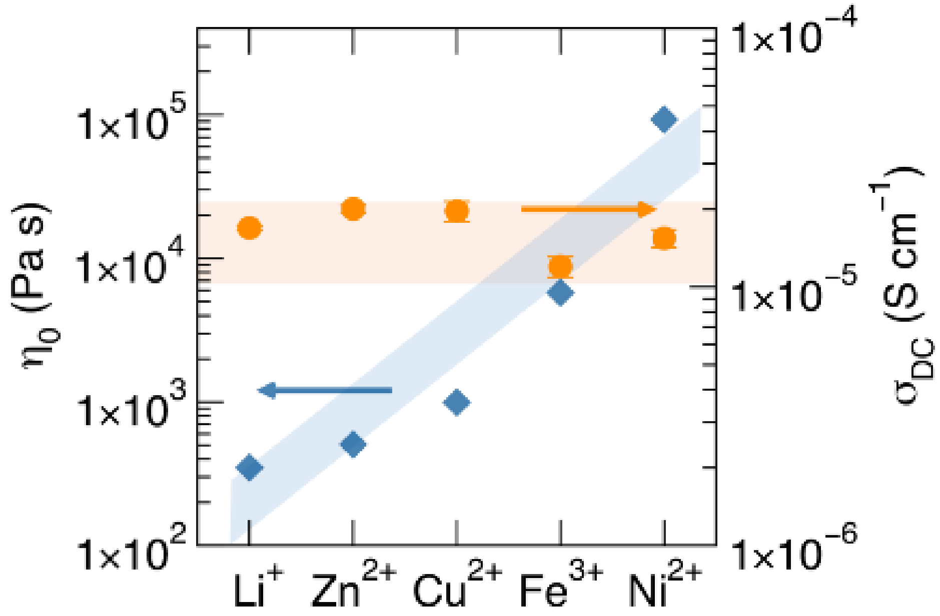
Ionic conductivity remains flat

Critical questions about multivalent polymer electrolytes

1. Can we achieve appealing mechanical properties without a detrimental effect on conductivity?
→ *Bulk mechanical properties are decoupled from total ionic conductivity*

2. Do multivalent ions conduct?

3. Can we develop design rules for improved conductivity performance?



Which ions are contributing to the total measured ionic conductivity?

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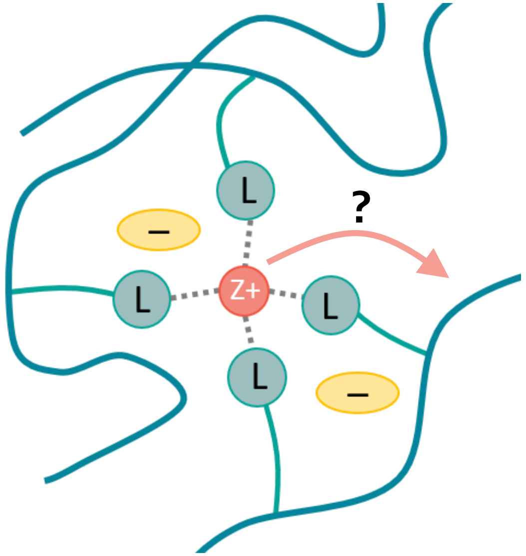
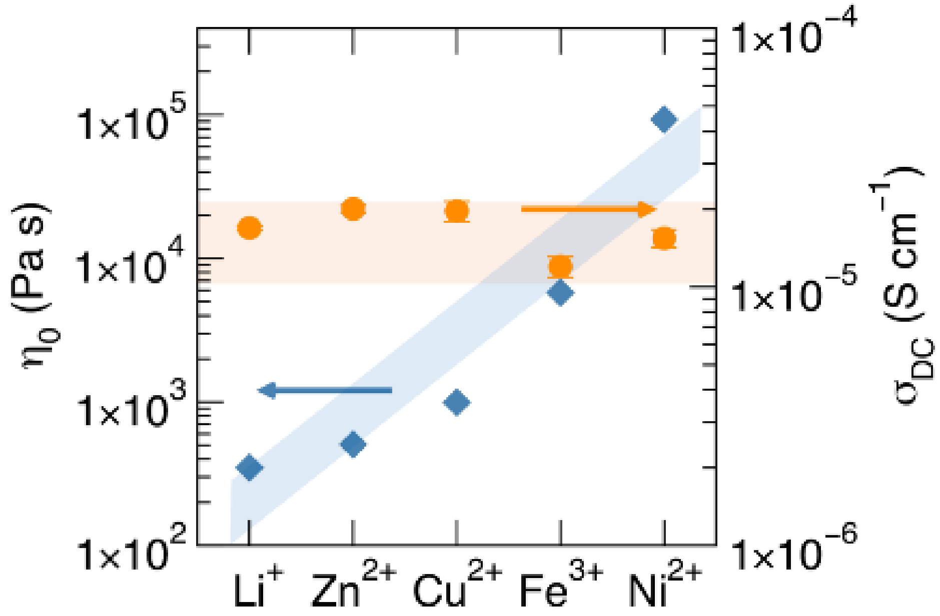
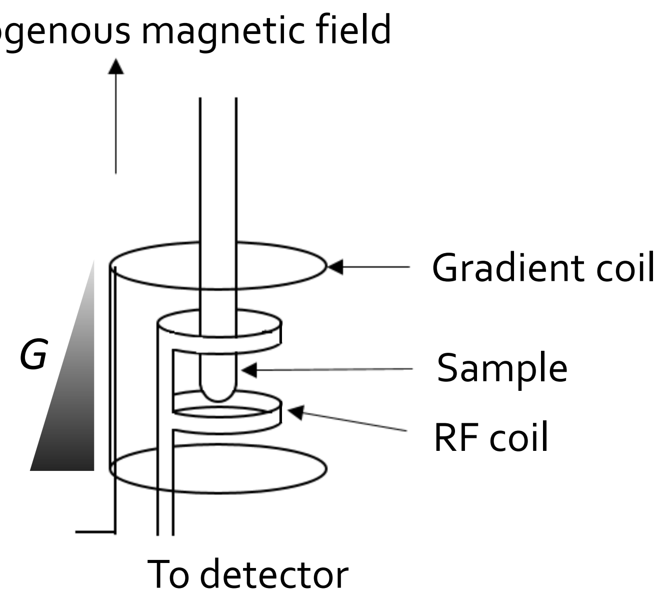


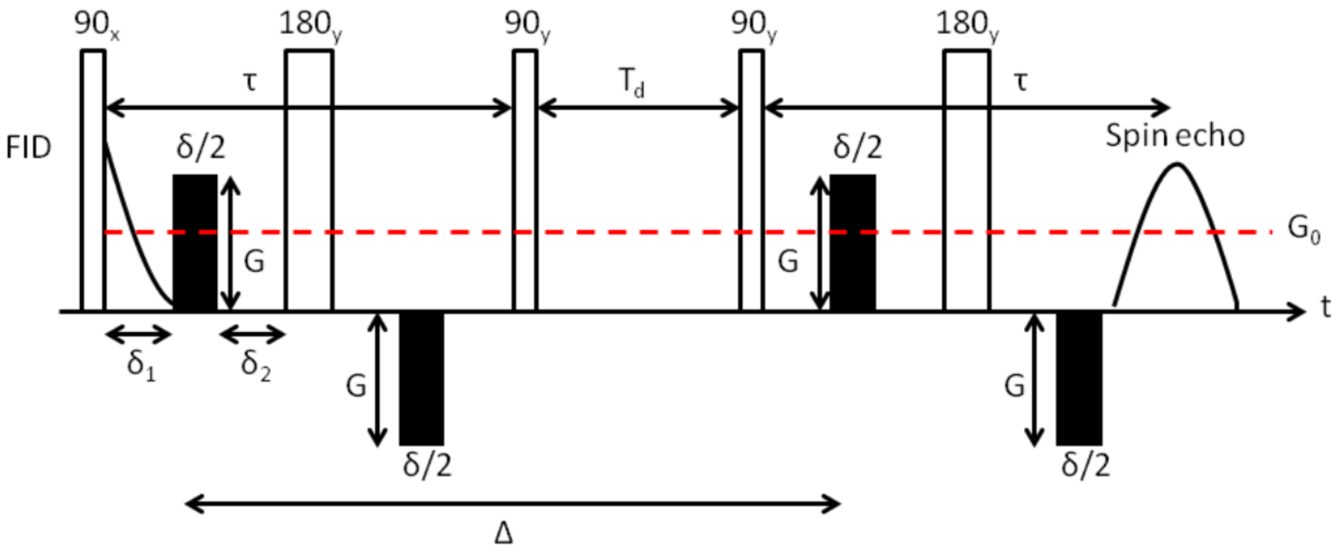
Mechanical properties dominated by cation identity

Does the cation also contribute to the ionic conductivity?



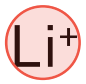
Pulsed-field-gradient NMR measures ion diffusion

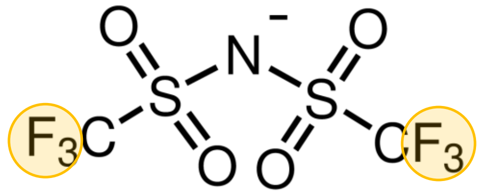




Measure diffusion coefficients *via* pulsed-field-gradient NMR

$$I = I_0 e^{-\gamma^2 G^2 D \delta^2 (\Delta - \frac{\delta}{3})}$$

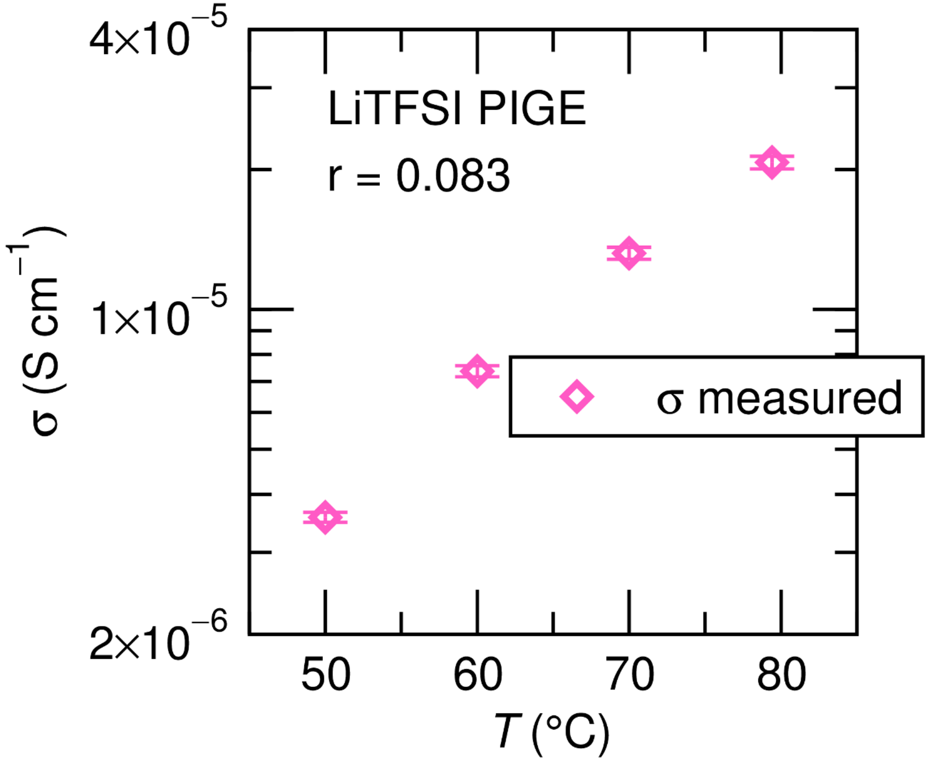




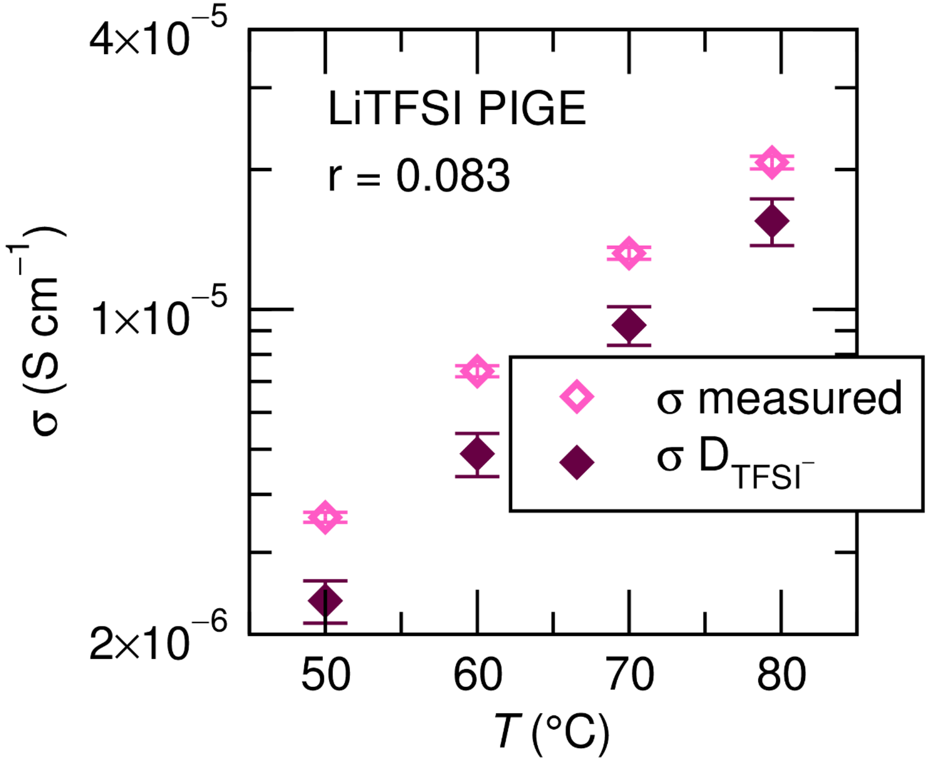
$$\sigma = \frac{F^2}{RT}(z_+{}^2 c_+ D_+ + c_- D_-)$$

Sorland. *Dynamic Pulsed-Field-Gradient NMR, Ch 1.* Berlin, Heidelberg: Springer (2014)
Wu, Chen, Johnson. *J. Magn. Reson., Ser. A.* **1995**, *115*, 260–264.

Cations contribute to the ionic conductivity

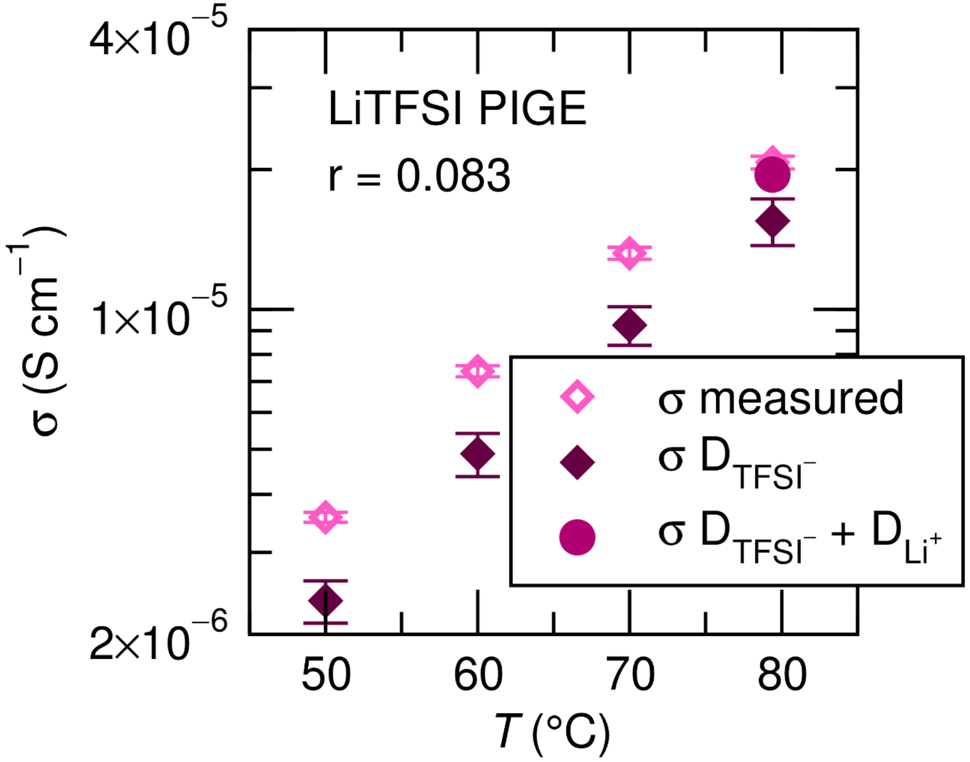


Cations contribute to the ionic conductivity



$$\sigma = \frac{F^2 c_+}{RT}(z_+ D_{\mathrm{TFSI}})$$

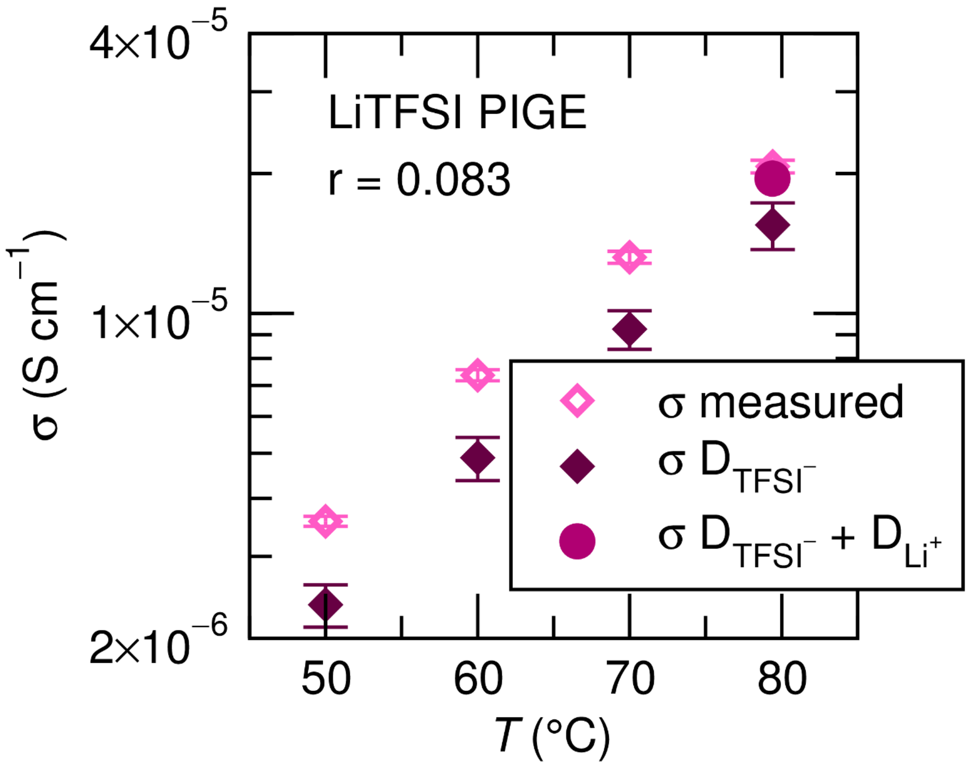
Cations contribute to the ionic conductivity

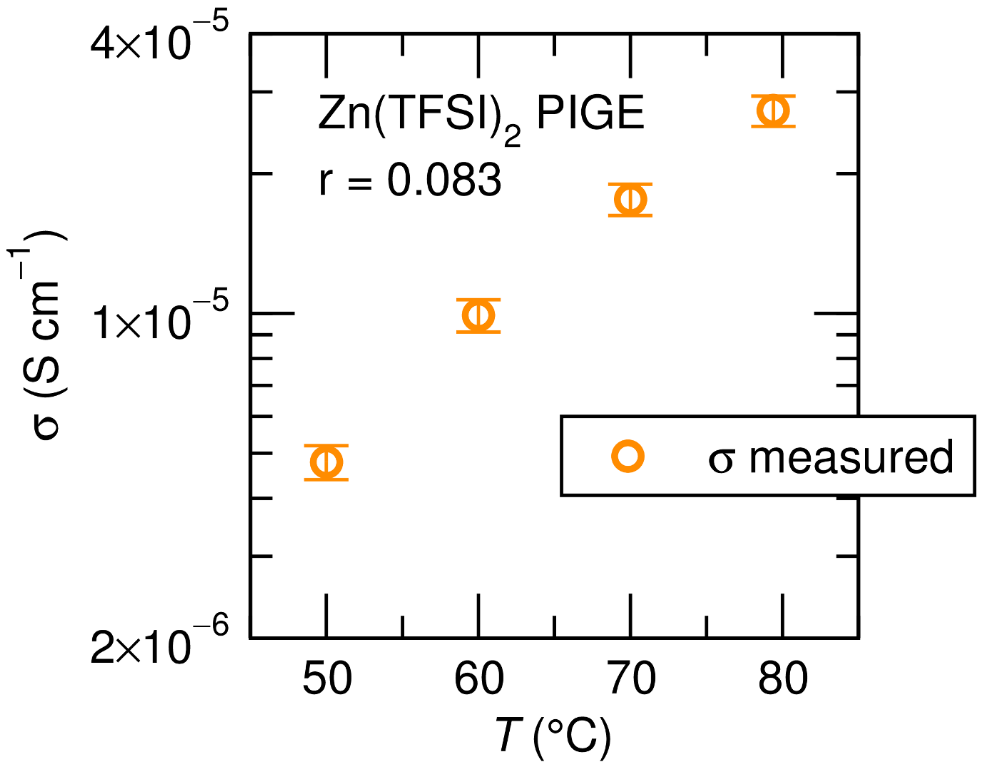


$$\sigma = \frac{F^2 c_+}{RT}\left(z_+^2 D_{\mathrm{Li}} + z_+ D_{TFSI}\right)$$

Both Li^+ and $TFSI^-$ contribute to conductivity

Cations contribute to the ionic conductivity





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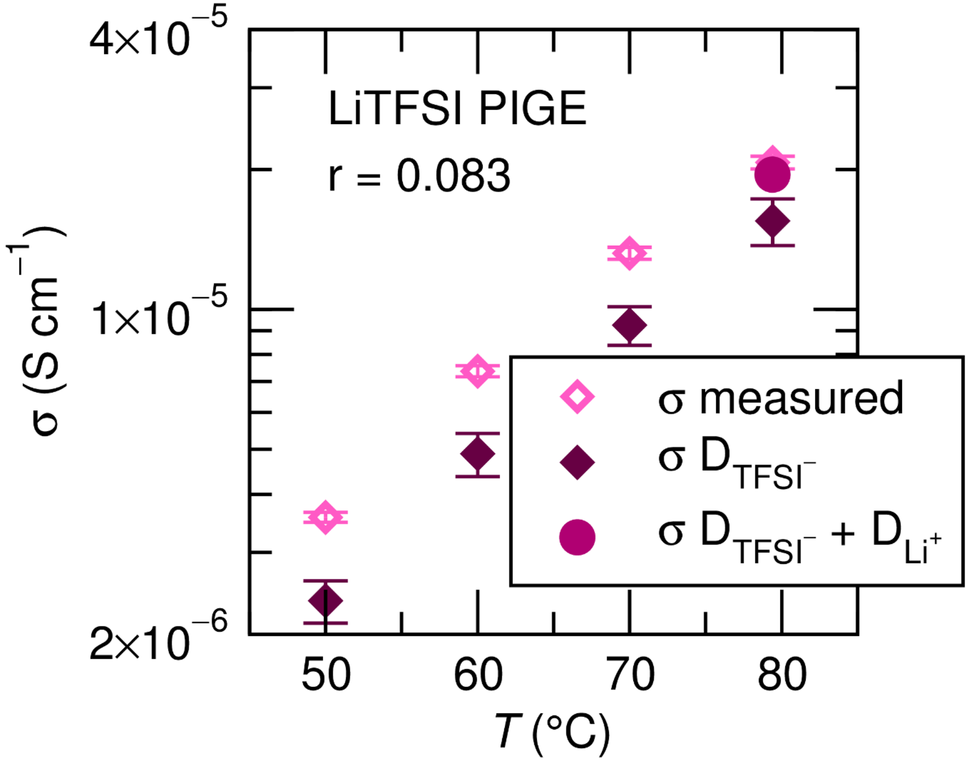

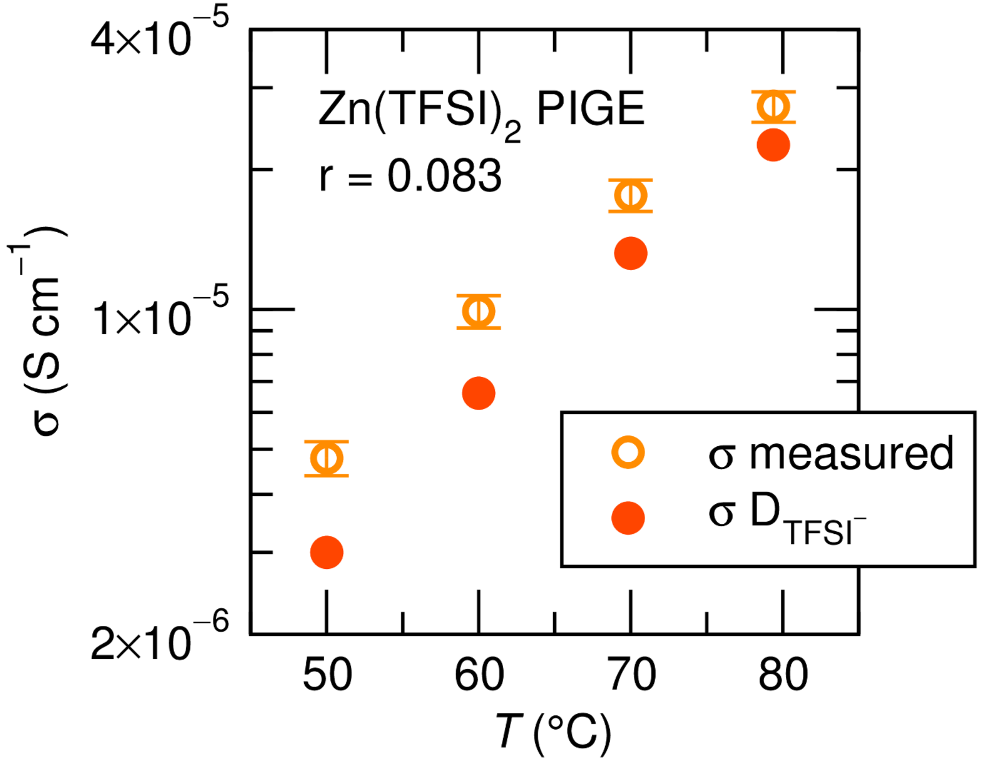

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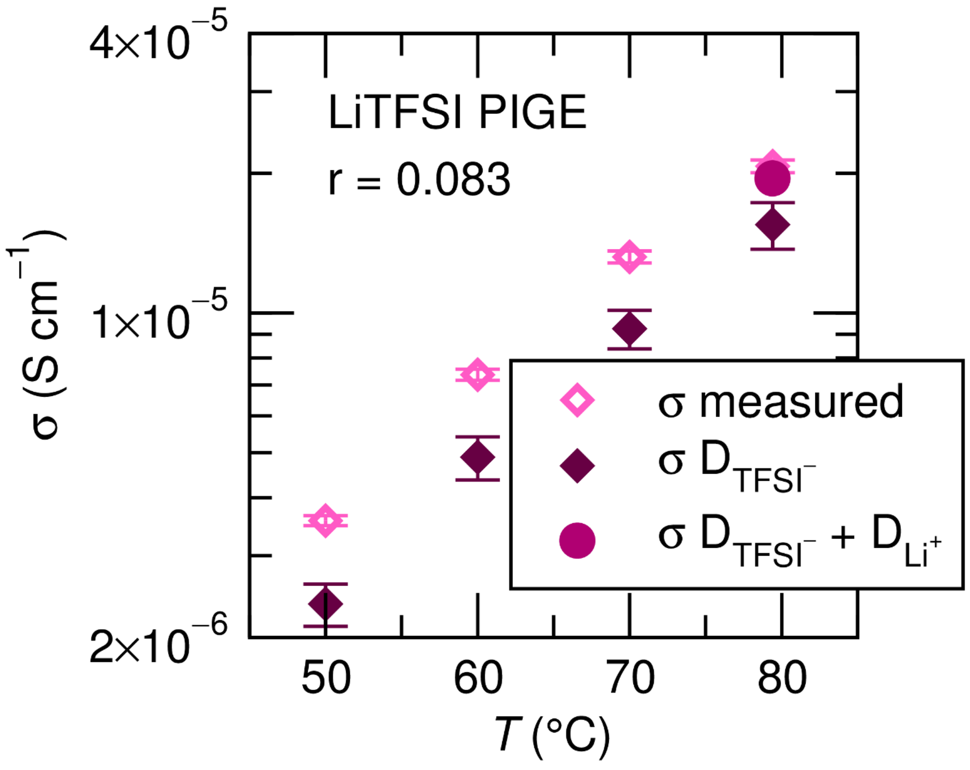
Cations contribute to the ionic conductivity



$$\sigma = \frac{F^2 c_+}{RT}(z_+^2 D_{\mathrm{Li}} + z_+ D_{TFSI})$$

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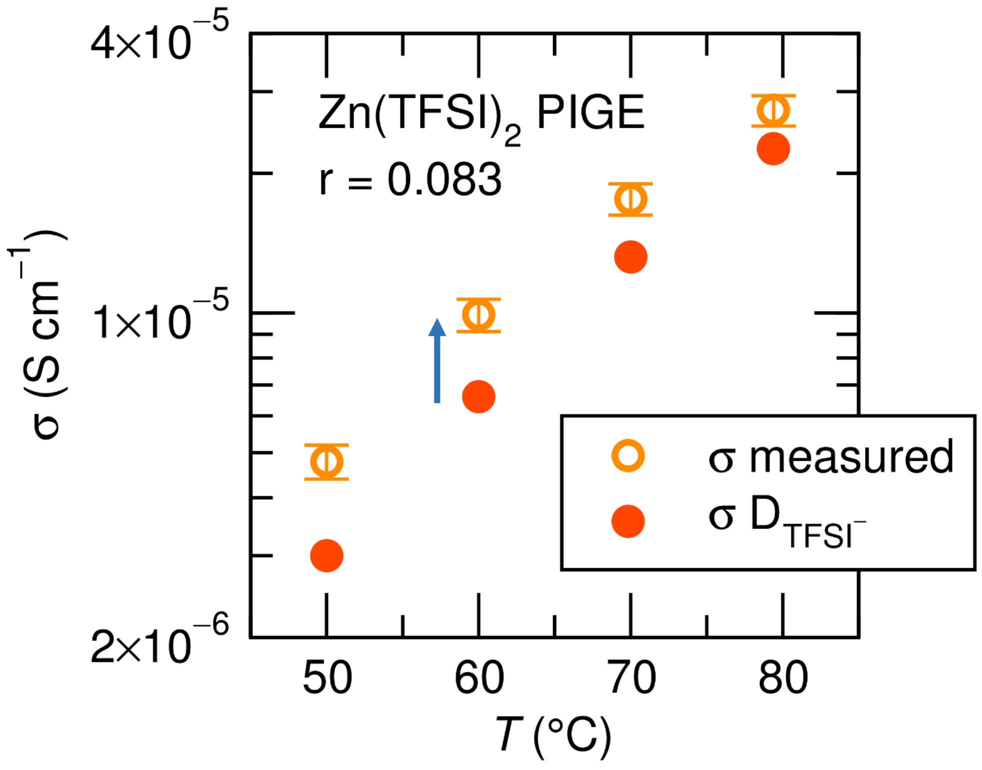


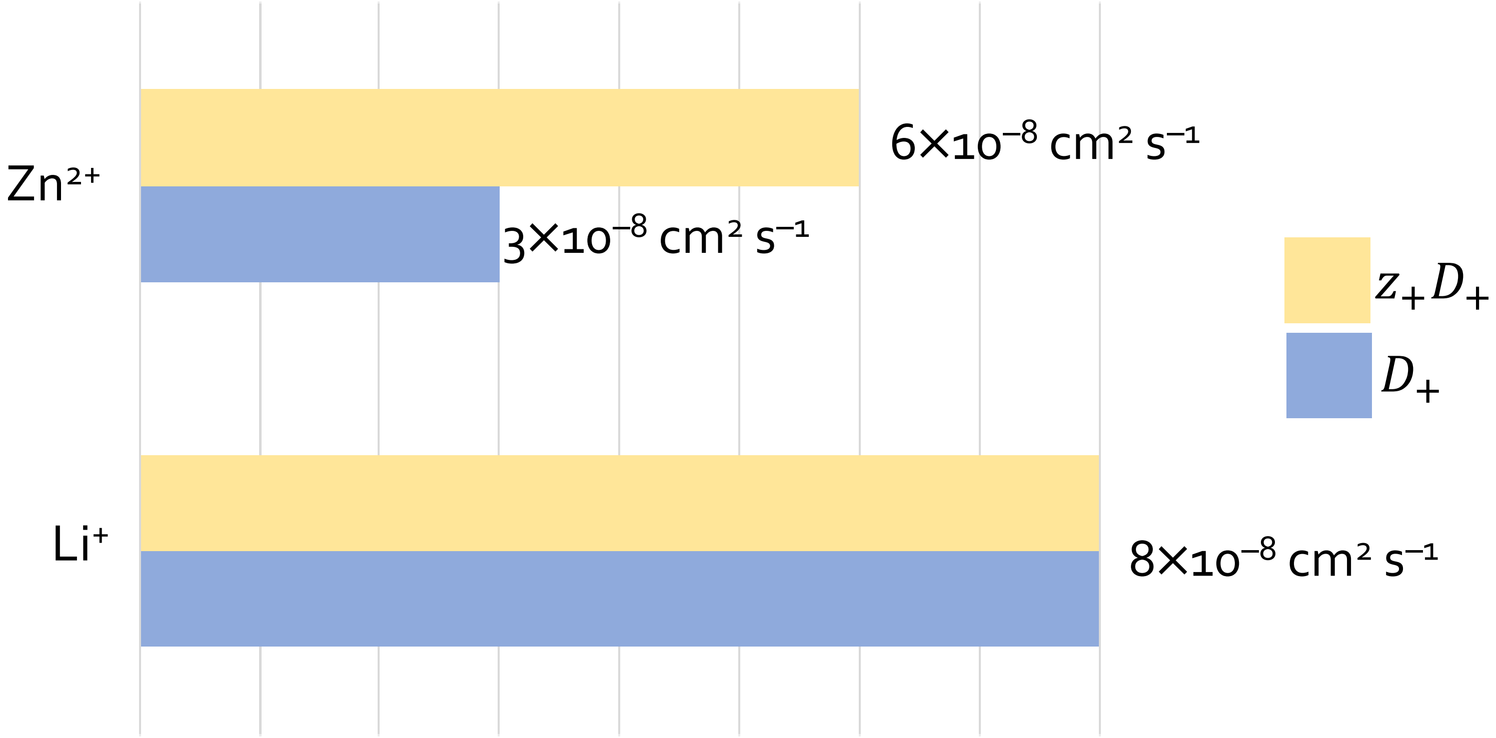
$$\sigma = \frac{F^2 c_+}{RT}(z_+^2 \boxed{D_{Zn}} + z_+ D_{TFSI})$$

?

Likely Zn^{2+} and $TFSI^-$ contribute to conductivity

Divalent species contribute similarly to monovalent ones

T = 80 °C



$$t_+ = \frac{z_+D_+}{z_+D_+ + z_-D_-}$$

Zn^{2+}: $t_+ = 0.13$

Li^+: $t_+ = 0.18$

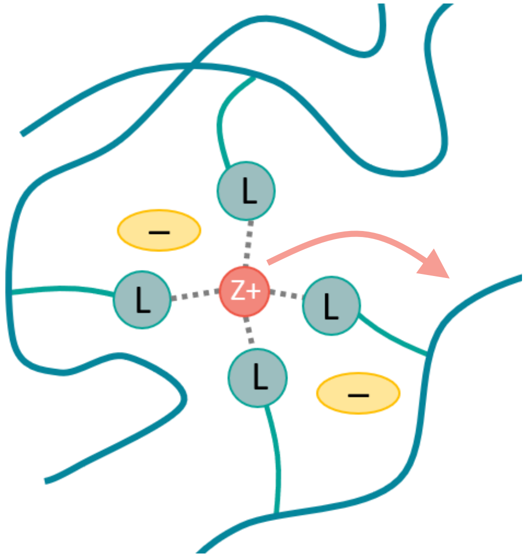
Divalent species move slower, but carry twice the charge

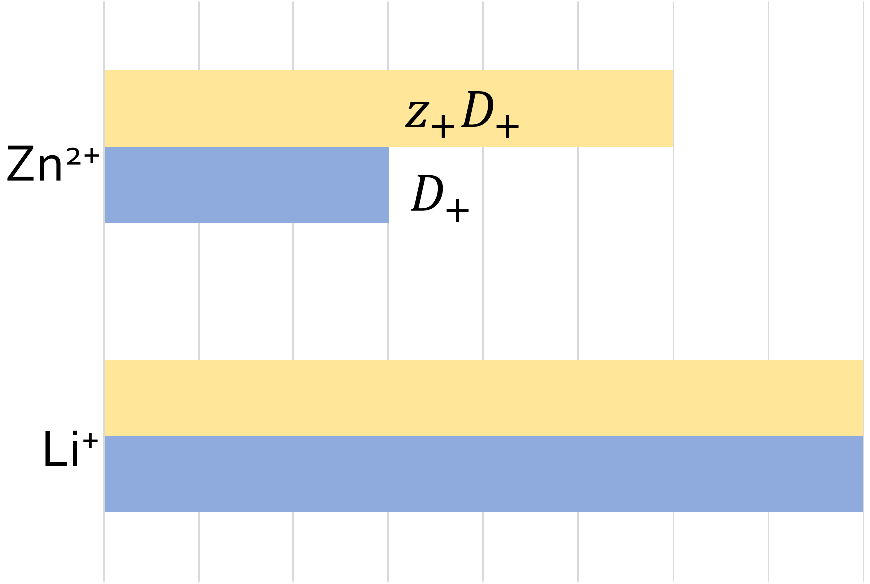
Critical questions about multivalent polymer electrolytes

1. Can we achieve appealing mechanical properties without a detrimental effect on conductivity?
   → *Bulk mechanical properties are decoupled from total ionic conductivity*

2. Do multivalent ions conduct?
   → *Transference numbers measured by PFG NMR suggest divalent cation contribution to conductivity*

3. Can we develop design rules for improved conductivity performance?





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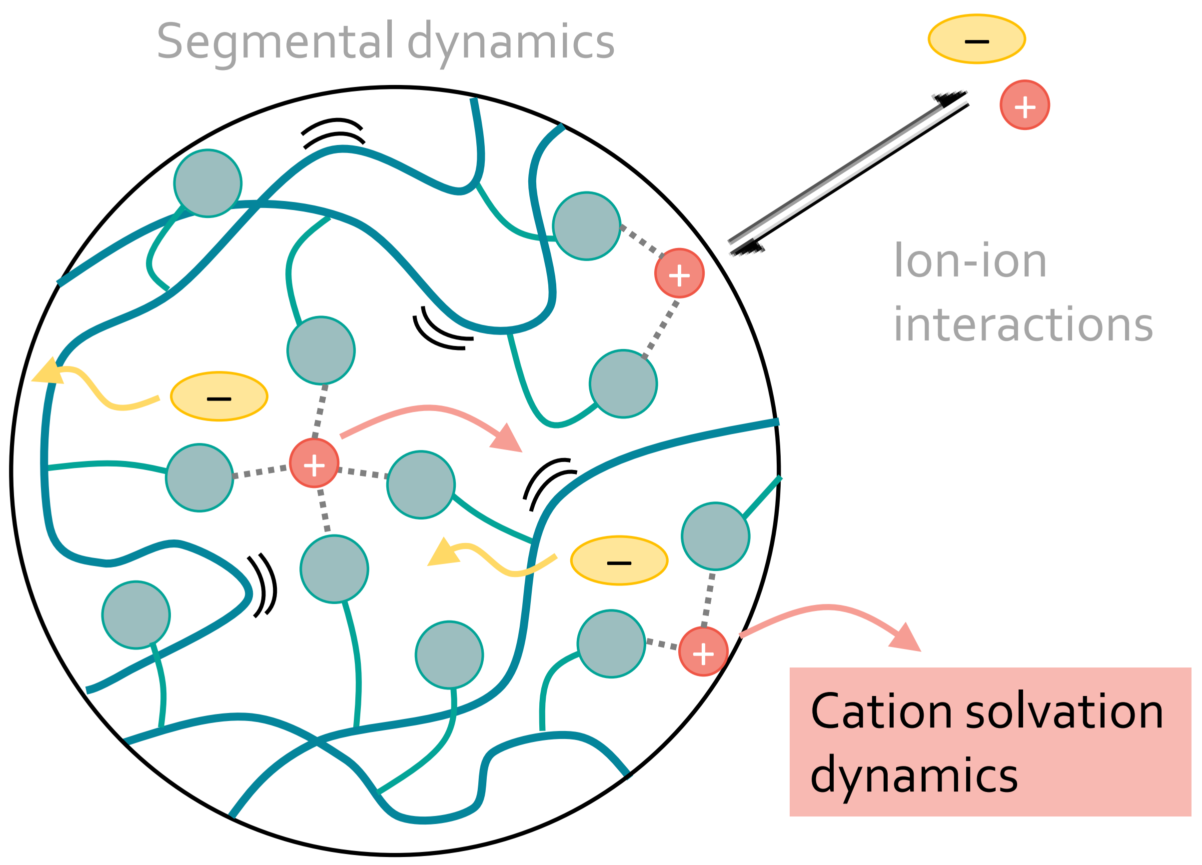
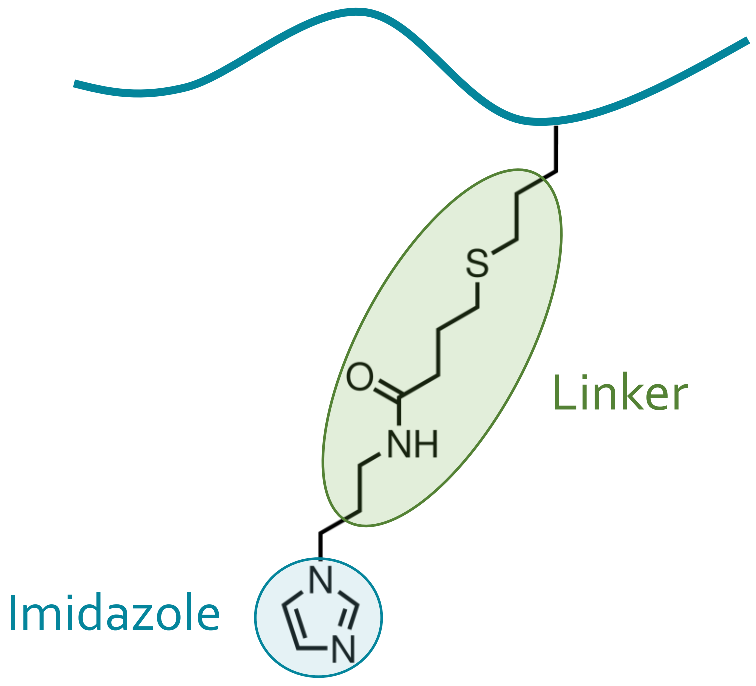
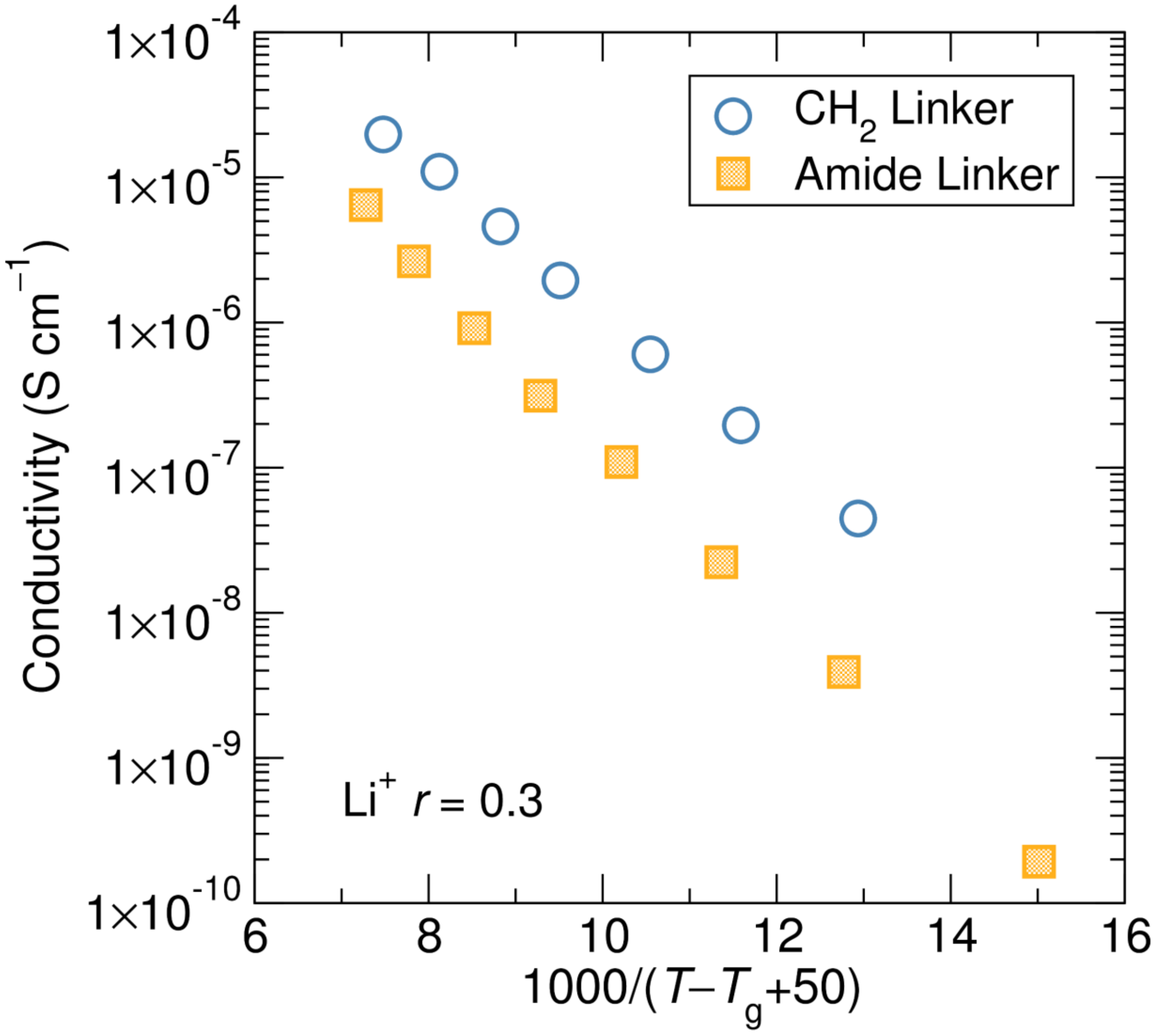
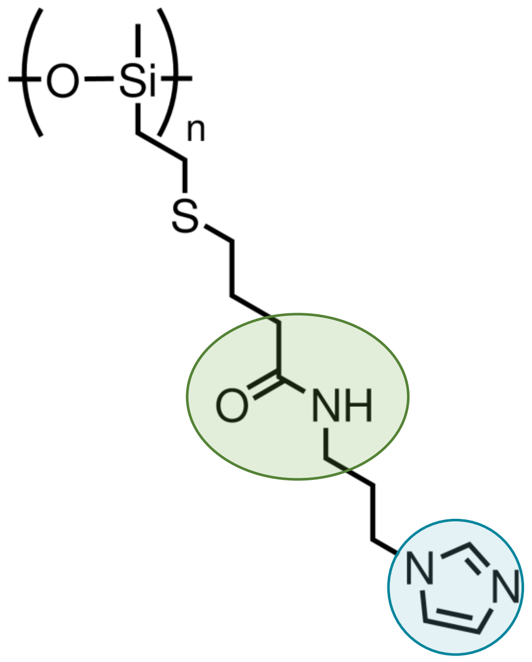
Ionic conductivity can be improved by tuning linker chemistry

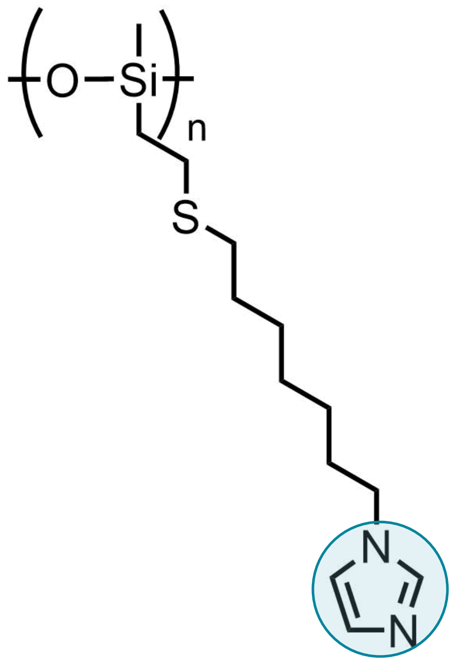




Removal of amide group enables 10x improvement in conductivity with larger transference number







$t_{+,Amide} = 0.18$

$t_{+,CH_2} = 0.46$

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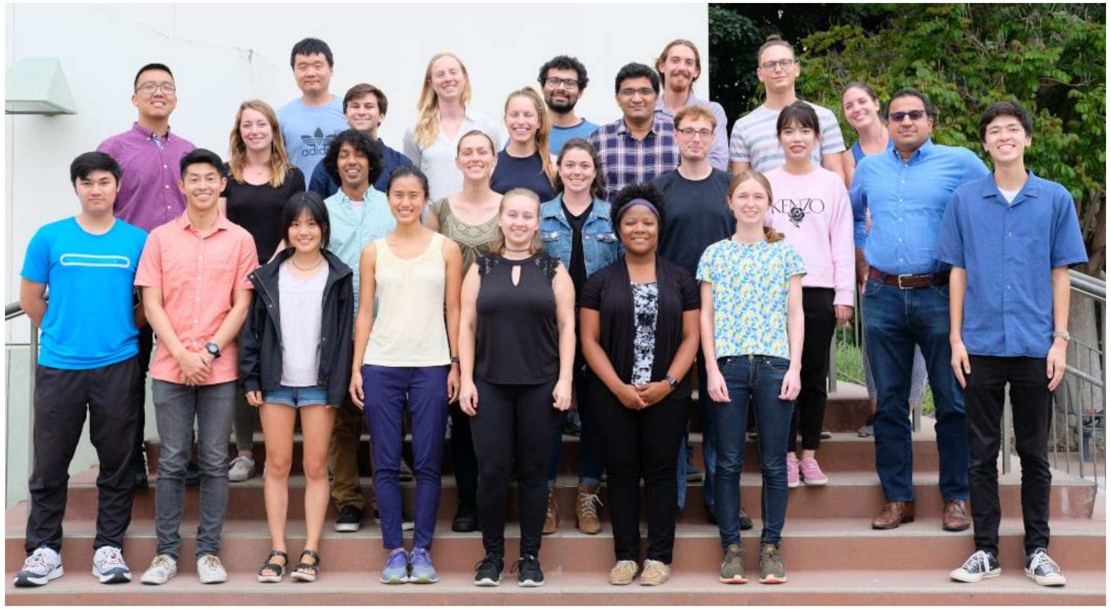
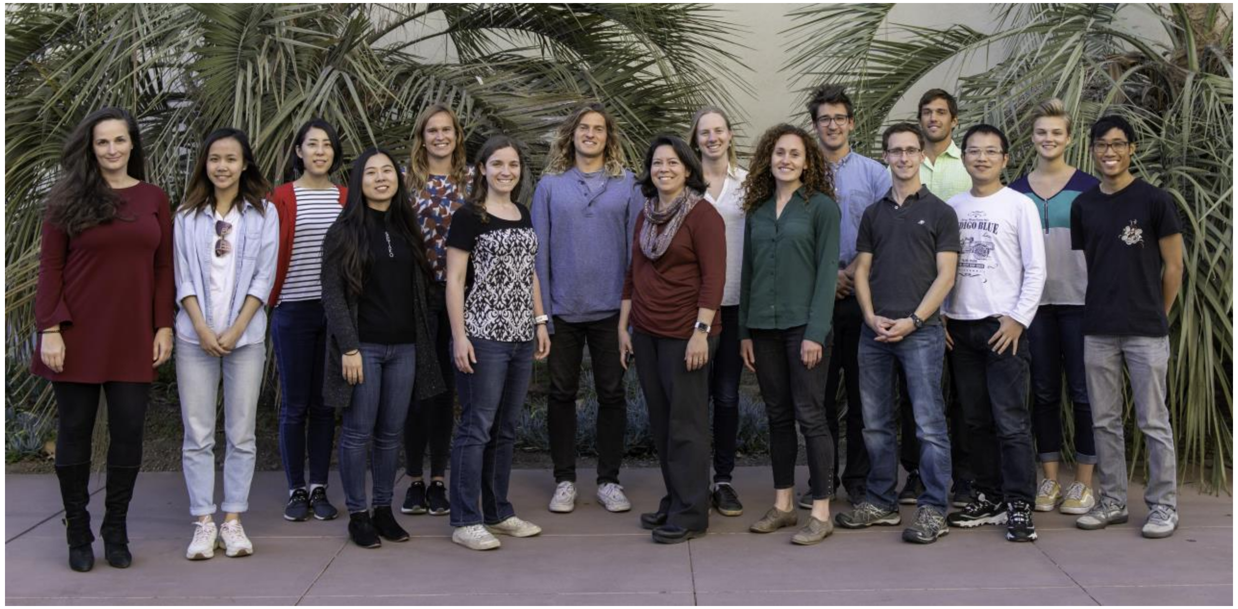
3. Can we develop design rules for improved conductivity performance?
   → *Eliminate deleterious interactions between ions and polar groups*

Acknowledgements





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