

Supplementary Information

Quantifying the ion coordination strength in polymer electrolytes

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Figures

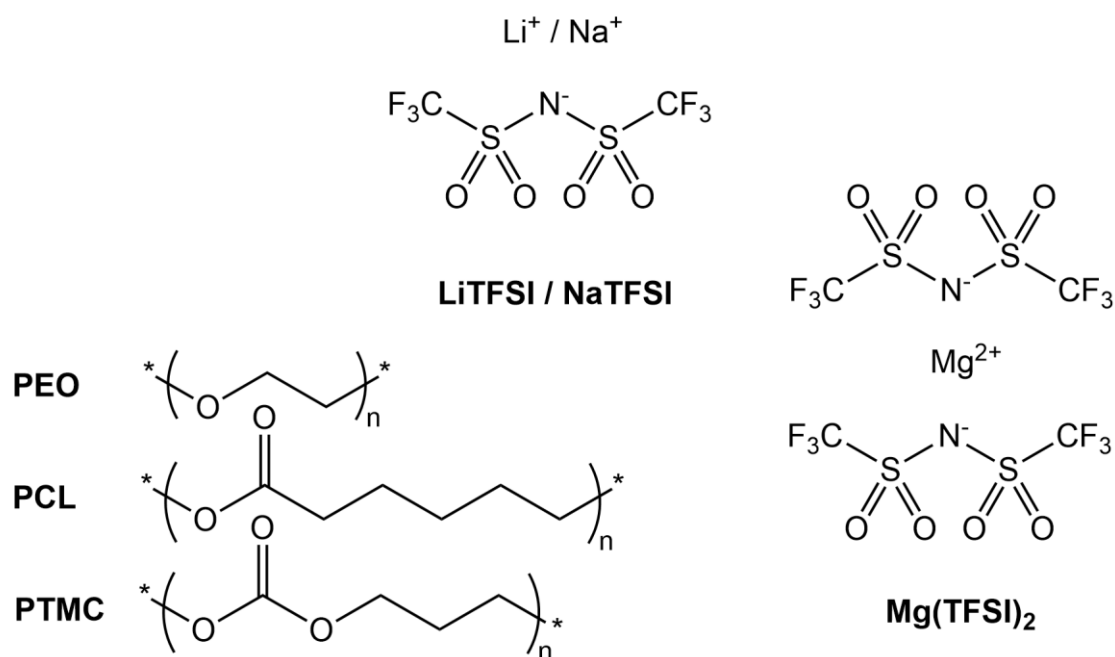


Figure S1: Molecular structures of the polymers PEO, PCL and PTMC, and the salts LiTFSI, NaTFSI and Mg(TFSI)₂.

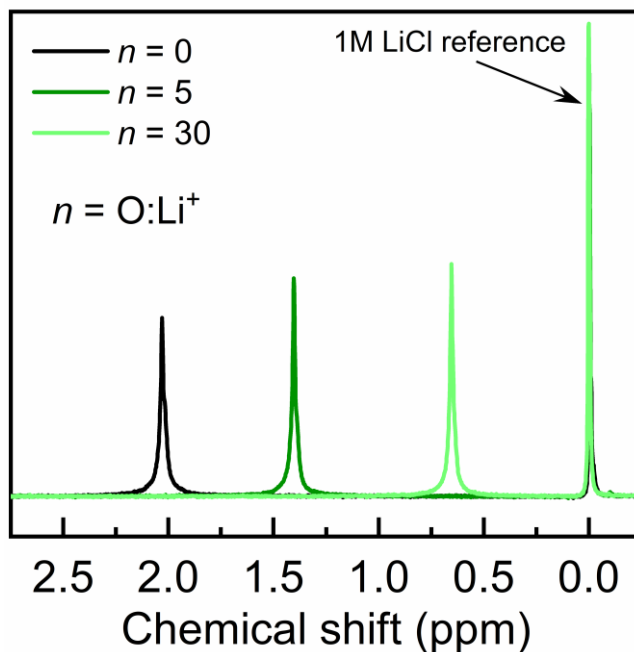


Figure S2: ${}^7\text{Li}$ NMR spectra of LiTFSI in ACN ($n = 0$) and with PEO added to the solution ($n = 5$ and 30). The chemical shift was referenced to a 1 M LiCl solution in D_2O placed in a sealed capillary added into the NMR tube during the measurements.

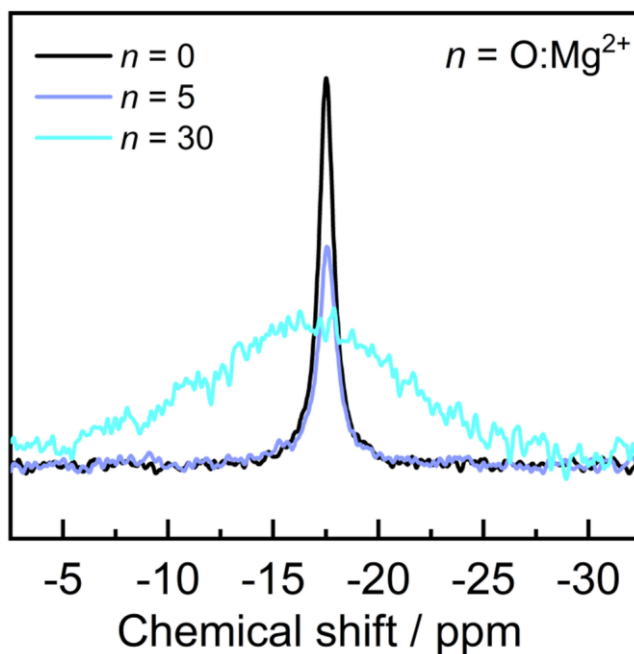


Figure S3: ${}^{25}\text{Mg}$ chemical shift of $\text{Mg}(\text{TFSI})_2$ dissolved in ACN and PEO at three different polymer concentrations and a constant concentration of the salt, revealing the excessive peak broadening and small chemical shift change upon addition of polymer to the solution. The measurements were conducted at 30.616 MHz with a Bruker Avance III 500 MHz spectrometer equipped with a 10 mm liquids broadband observe probe.

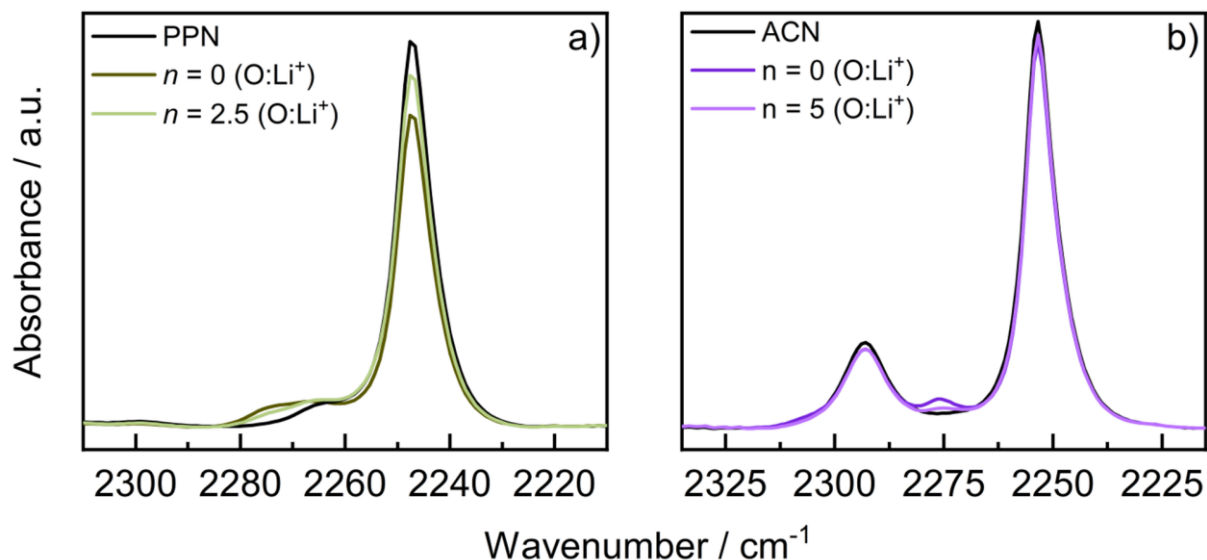


Figure S4: Absorption spectra of Li^+ in a) ACN and b) PPN at different concentrations of PEO. Addition of salt decreases the large absorption band corresponding to non-coordinating solvent molecules and a new absorption band appears corresponding to the coordinating solvent–cation coordination. The latter band decreases with the addition of polymer as the solvent competes with the polymer for coordination of the cations.

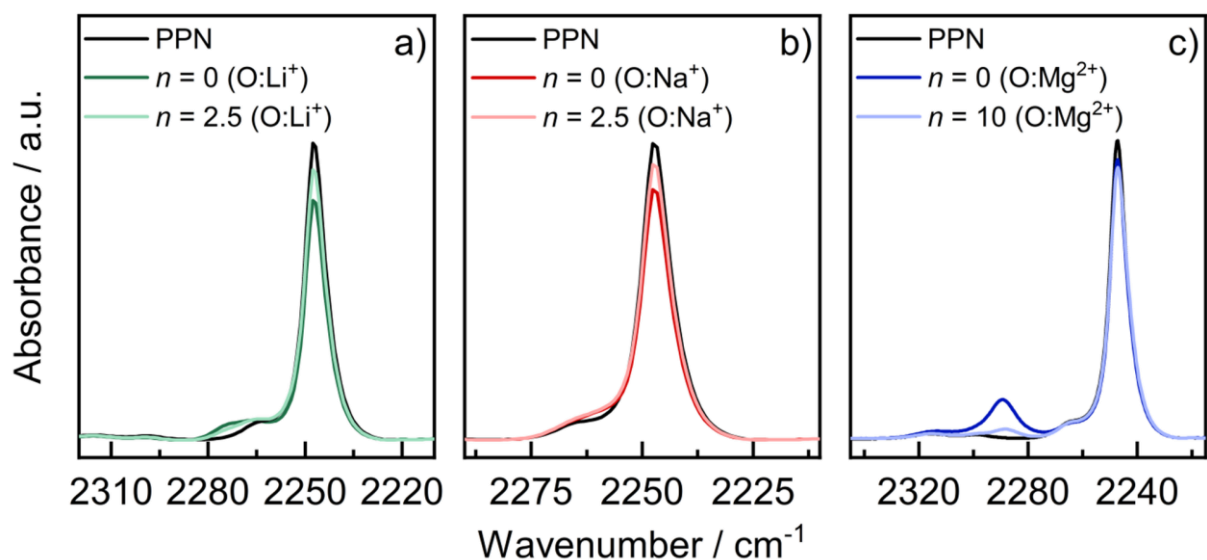


Figure S5: Absorption spectra of a) Li^+ , b) Na^+ and c) Mg^{2+} in PPN at different concentrations of PEO. Addition of salt decreases the large absorption band corresponding to non-coordinating solvent molecules and a new absorption band appears corresponding to the coordinating solvent–cation coordination. The latter band decreases with the addition of polymer as the solvent competes with the polymer for coordination of the cations.

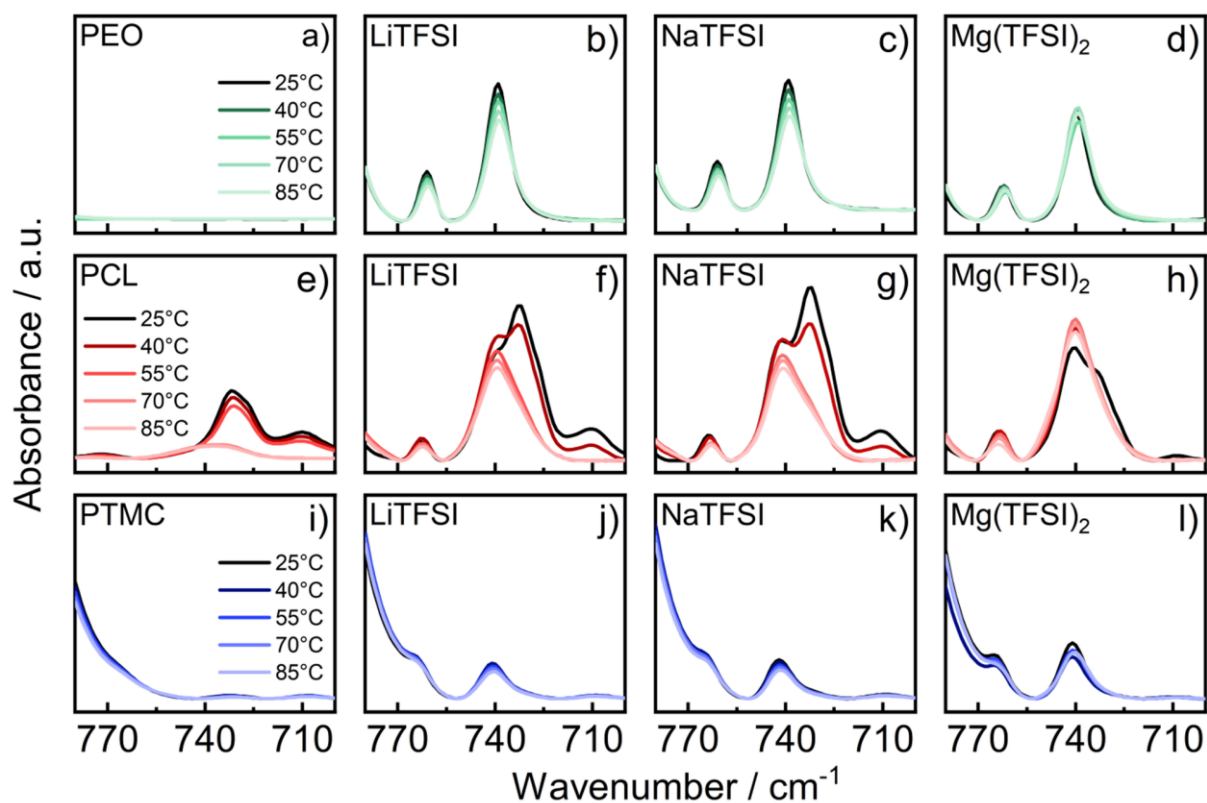


Figure S6: FTIR temperature sweep results of LiTFSI, NaTFSI and Mg(TFSI)₂ dissolved in a–d) PEO, e–h) PCL and i–l) PTMC. The results of the pure polymers are displayed in a) PEO, e) PCL and i) PTMC. The absorption band at 740 cm⁻¹ was utilized for determination of the extent of ion-ion association.

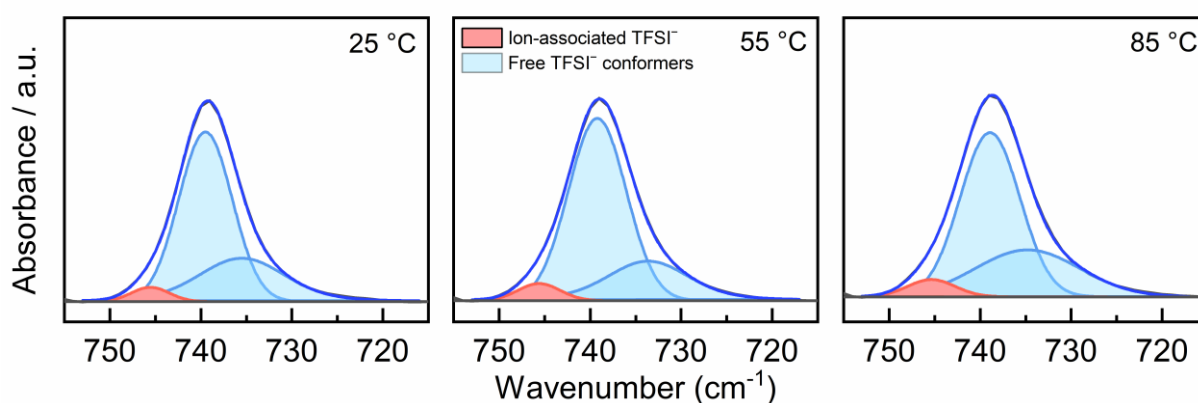


Figure S7: An example of the deconvolution of the S–N absorption band at 740 cm⁻¹ of the TFSI anion at 25, 55 and 85 °C of LiTFSI dissolved in PEO. In the spectra, a small relative increase of the ion-associated TFSI peak compared to the sum of the free TFSI peaks can be observed at higher temperatures. The dark blue line corresponds to the experimental data.

Tables

Table S1: Densities of the studied polymer electrolytes.

Salt	Polymer	$\rho / \text{g mol}^{-1}$
LiTFSI	PEO	1.32
	PCL	1.13
	PTMC	1.14
NaTFSI	PEO	1.22
	PCL	1.12
	PTMC	1.18
Mg(TFSI)₂	PEO	1.25
	PCL	1.20
	PTMC	1.31

Equations

Empirical fit to measured NMR and FTIR data:

$$y = \frac{a}{1 + e^{bx}} + c \quad (\text{S1})$$

Empirical fit to measured NMR and FTIR data including the additional parameter ϕ :

$$y = \frac{a}{1 + e^{bx+\phi}} + c \quad (\text{S2})$$