

## Supporting Information for

# Ion Transport in Polycarbonate Based Solid Polymer Electrolytes: Experimental and Computational Investigations

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Table S1. Apparent activation energies ( $E_a$ ) obtained from the temperature-dependence of the longitudinal relaxation times ( $T_1$ ) in the range of 295 to 333 K.

	PTMC <sub>8</sub> LiTFSI			P(TMC/CL) <sub>4,6</sub> LiTFSI		
	<sup>7</sup> Li	<sup>1</sup> H	<sup>19</sup> F	<sup>7</sup> Li	<sup>1</sup> H	<sup>19</sup> F
$E_a$ [kJ/mol]	13.5	14.9	4.7/2.9	7.2	8.1/4.3	5.3/4.1

Table S2. Self-diffusion coefficients and transference numbers of PTMC<sub>8</sub>LiTFSI and P(TMC/CL)<sub>4,6</sub>LiTFSI obtained from MD simulations ranging from 303 to 423 K.

	T(K)	Self-diffusion coefficients (m <sup>2</sup> /s × 10 <sup>-13</sup> )		Transference numbers	
		Li <sup>+</sup>	TFSI <sup>-</sup>	Li <sup>+</sup>	TFSI <sup>-</sup>
		PTMC <sub>8</sub> LiTFSI	303	3.0	6.0
	348	9.0	14.0	0.39	0.61
	423	139.0	158.0	0.47	0.53
P(TMC/CL) <sub>4,6</sub> LiTFSI	303	0.1	0.3	0.25	0.75
	348	1.3	0.8	0.62	0.38
	423	15.8	19.9	0.44	0.56

Table S3. Apparent activation energies for the translational self-diffusion of the cation and the anion..

PTMC <sub>8</sub> LiTFSI		P(TMC/CL) <sub>4,6</sub> LiTFSI	
[kJ/mol]		[kJ/mol]	
TFSI <sup>-</sup>	Li <sup>+</sup>	TFSI <sup>-</sup>	Li <sup>+</sup>
52.4	65.6*	61.3	44.9

\*A high temperature measurement was performed on <sup>7</sup>Li for PTMC<sub>8</sub>LiTFSI in the range of 363 to 423 K. All other samples/nuclei were measured in the range of 323 to 333 K.

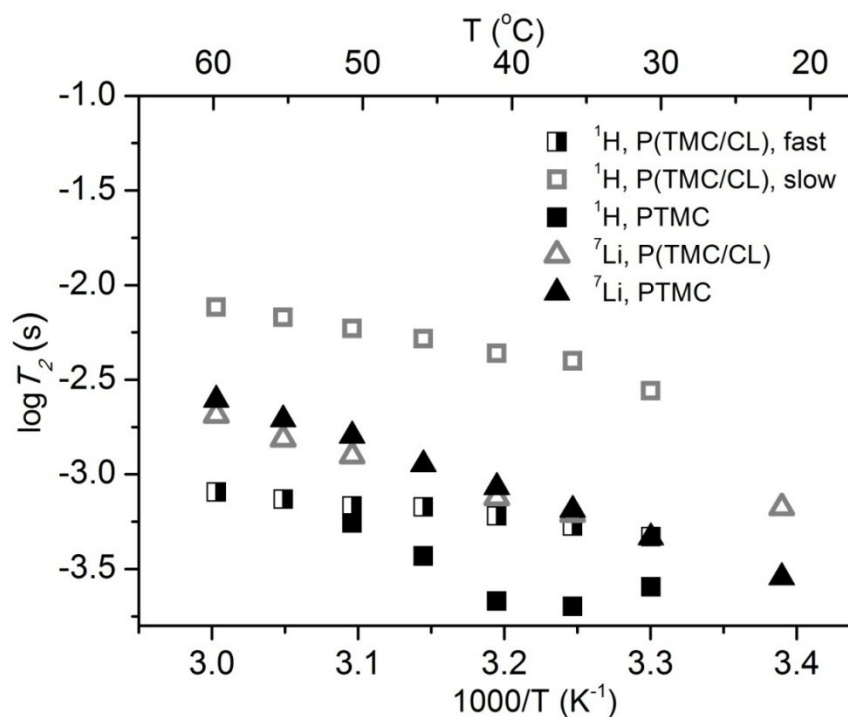


Figure S1. Temperature dependence of the transverse relaxation ( $T_2$ ) of  $^7\text{Li}$  (triangles) and  $^1\text{H}$  (squares) for both PTMC<sub>8</sub>LiTFSI (solid symbols), and P(TMC<sub>20</sub>CL<sub>80</sub>)<sub>4.6</sub>LiTFSI (half-filled and non-filled symbols).

The  $^1\text{H}$  transverse relaxation of the polymer showed a dominating fast relaxation (at least 98% in amplitude). A slower component with *ca.* 1-2 % in amplitude (shown here but not in Fig. 3) was also observed, very close to noise level, and possibly an artifact or impurity. The influence of particular experimental conditions to the relaxation behaviour of quadrupolar nuclei for  $^7\text{Li}$  could be more complicated. Previous studies have suggested that the  $^1\text{H}$  relaxation times could be governed by proton–proton and proton–Li magnetic dipole interactions.<sup>1</sup> Other explanations to the observed variations might be fast processes of a rotational character for the salt complexes and slow processes with a translational character for the polymer matrix simultaneously present.

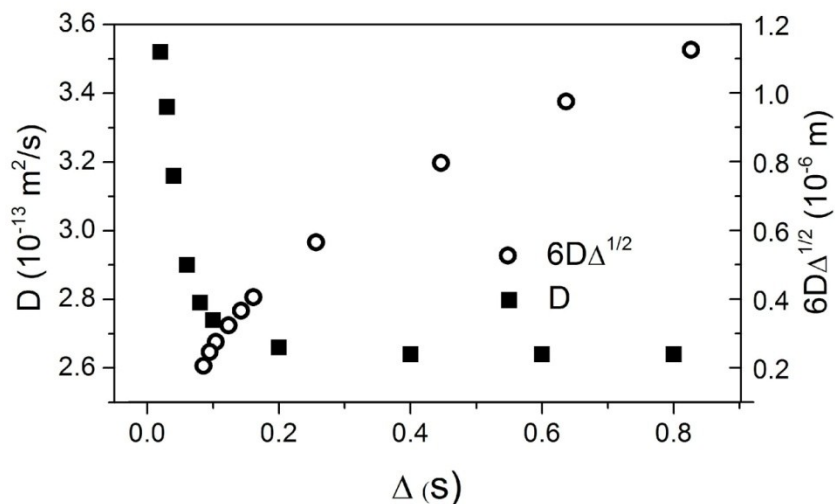


Figure S2. The dependence of the TFSI<sup>-</sup> apparent diffusion coefficient (filled squares) and the mean-square displacement (empty circles) on the diffusion time  $\Delta$  for P(TMC<sub>20</sub>CL<sub>80</sub>)<sub>4.6</sub>LiTFSI at 60 °C.

The variation of obtained diffusion coefficient  $D$  with increasing diffusion time  $\Delta$  could have been recorded for the anion, but not for the cation since the <sup>19</sup>F relaxation parameters permit more freedom for the NMR diffusion experiment than do the <sup>7</sup>Li relaxation parameters.

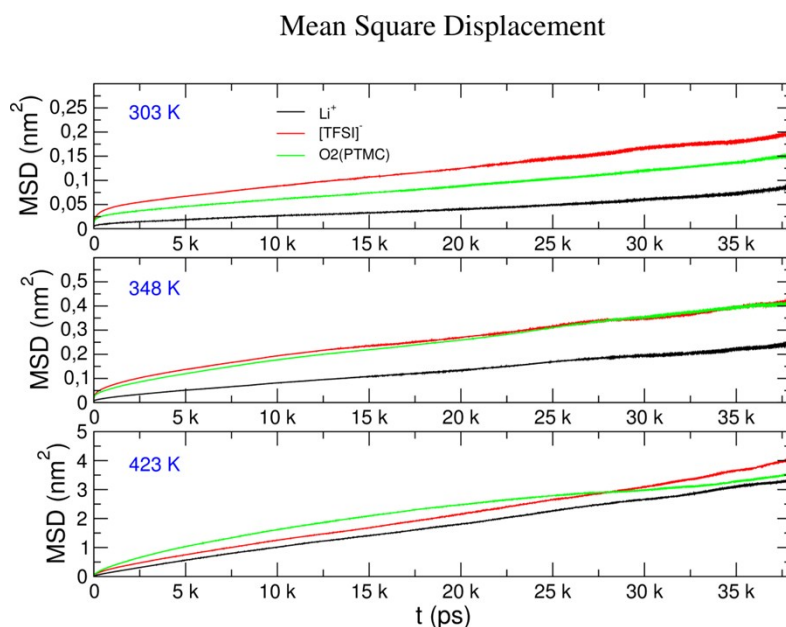


Figure S3. Mean square displacements (MSD) of ions in PTMC<sub>8</sub>LiTFSI at 303, 348 and 423 K.

From the MD studies the self-diffusion coefficients for  $\text{Li}^+$ , TFSI, and carbonyl oxygen atoms from the PTMC chains can be derived from the linear regime of the mean-square displacement (MSD) by applying the Einstein equation:

$$D_i = \lim_{t \rightarrow \infty} \frac{\langle [R_i(t) - R_i(0)]^2 \rangle}{6t}$$

in which  $\mathbf{R}_i(t)$  is the vector position of species  $i$  at time  $t$ , the brackets refer to the ensemble average, and the MSD is the quantity in the brackets as a function of time simulated at specific temperatures. The self-diffusion coefficient of any ionic species at each temperature can be extracted straight-forwardly for simulation times longer than a nanosecond, when the ionic motion generally becomes diffusive.

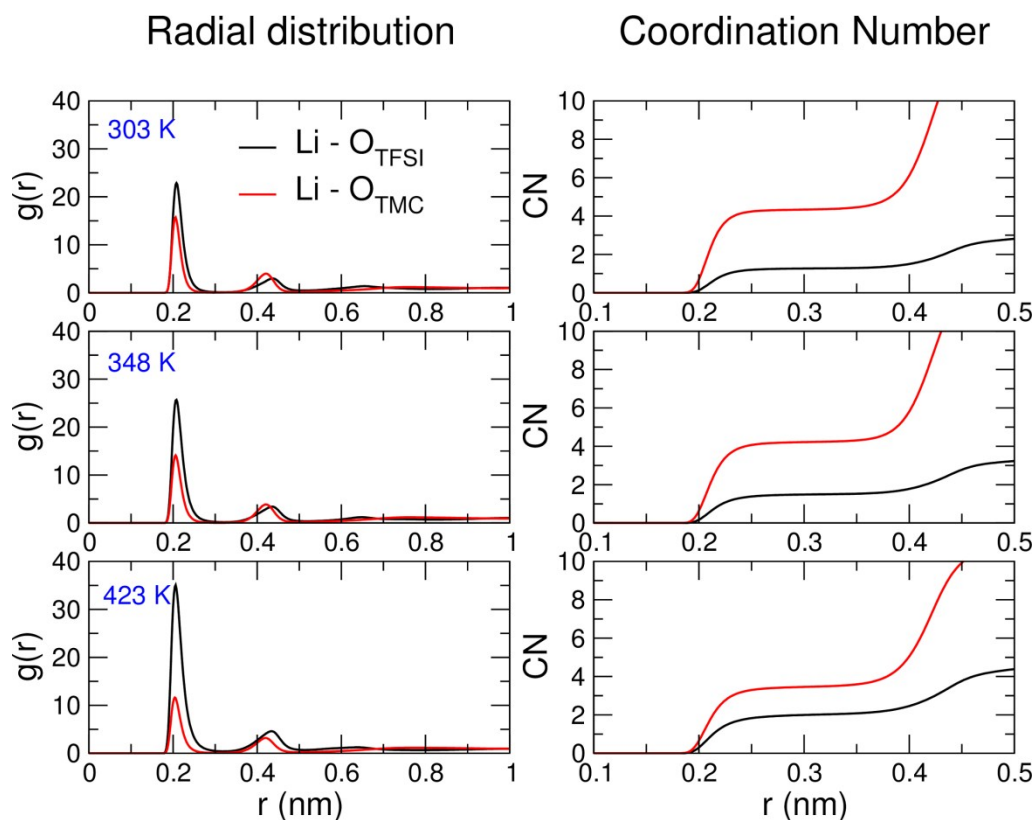


Figure S4. Radial distribution functions,  $g(r)$ , and coordination number (CN) functions of  $\text{Li}^+$ – $\text{O}_{\text{TFSI}}$  and  $\text{Li}^+$ – $\text{O}_{\text{PTMC}}$  in  $\text{PTMC}_3\text{LiTFSI}$  simulated at 303, 348 and 423 K, respectively.

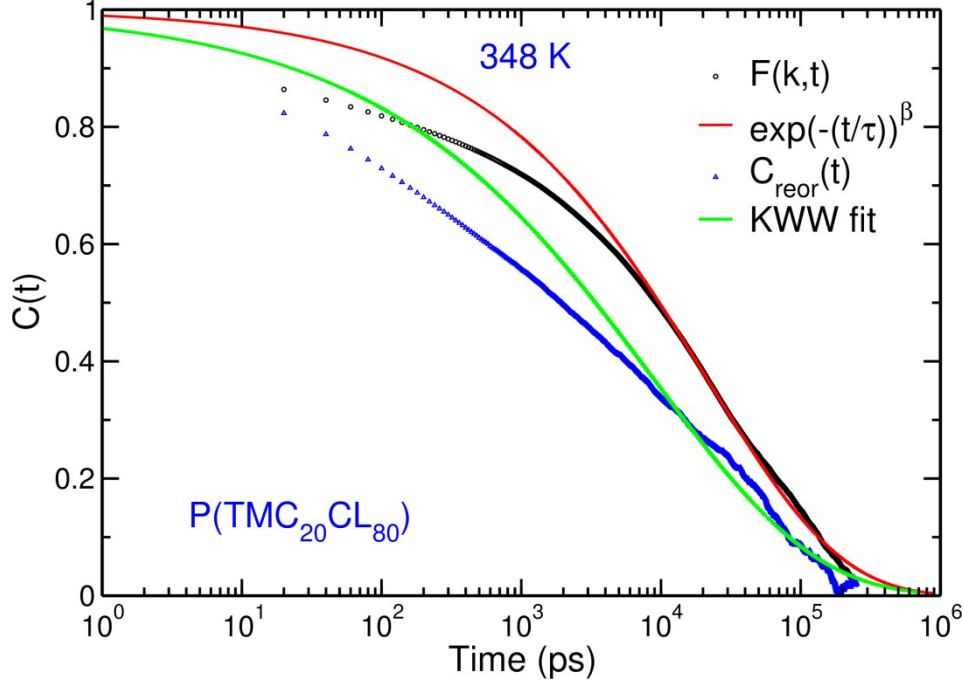


Figure S5. Simulated time-scales of the intermediate scattering function  $F(\mathbf{k},t)$ , the stretched exponential function  $\Phi(t)$ , the re-orientational correlation time  $C_{\text{reor}}(t)$  and the Kohlrausch-Williams-Watts (KWW) fit from  $\text{P}(\text{TMC}_{20}\text{CL}_{80})_{4.6}\text{LiTFSI}$  at 348 K.

Analysis of the intermediate scattering function,  $F(\mathbf{k},t)$ , for the  $\text{P}(\text{TMC}_{20}\text{CL}_{80})$  system was performed using 250 ns of trajectories for configurations saved each 20 ps. The long time relaxation ( $\alpha$  relaxation) could be fitted with a stretched exponential function based on the equation below:

$$\phi(t) = f \exp\left[-\left(\frac{t}{\tau}\right)^\beta\right]$$

where the relaxation time of  $\alpha$ ,  $\tau_\alpha$  can be obtained from the best fit parameters of  $\tau$ ,  $f$  and  $\beta$  to the Gamma function:

$$\langle \tau_\alpha \rangle = \frac{\tau}{\beta} \Gamma\left(\frac{1}{\beta}\right)$$

The intermediate scattering function,  $F(\mathbf{k},t)$  can be determined and provides information on the density fluctuations of the different spatial scales on a given wave vector modulus  $\mathbf{k}$ :

$$F(\mathbf{k}, t) = \left\langle \sum_i \sum_j e^{i\mathbf{k} \cdot [\mathbf{r}_i(t) - \mathbf{r}_j(0)]} \right\rangle$$

The correlated relaxation time,  $\tau$ , for the intermediate scattering function,  $F(\mathbf{k}, t)$  and re-orientation,  $C_{\text{reor}}$ , could be determined as *ca.* 20 ns and 9 ns, respectively. Moreover, the function decay demonstrated stretched exponential behavior since the parameter  $\beta$  displays a value of 0.51, in good agreement with previous calculations for PEO based SPEs.<sup>2-4</sup>

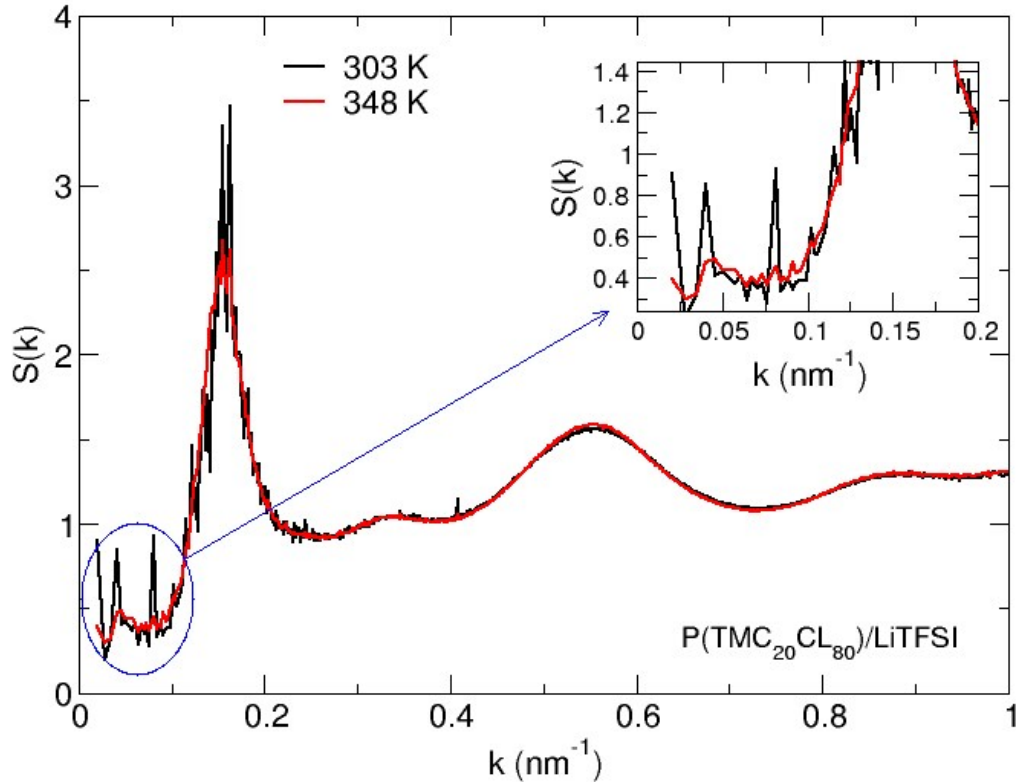


Figure S6. The structure factor of  $\text{P}(\text{TMC}_{20}\text{CL}_{80})_{4.6}\text{LiTFSI}$  at 303 and 348 K.

The structural relaxation of the system can be calculated from the intermediate structure factor,  $F(\mathbf{k}, t)$ . This was carried out using the main peak of  $S(k)$  at  $0.175 \text{ nm}^{-1}$ , related to the whole system. In Fig. S5 two pronounced pre-peaks around  $0.05$  and  $0.1 \text{ nm}^{-1}$  appear at lower temperature, typical for systems with an intermediate range order (IRO). At 348 K there is only a slight pre-peak at  $0.05 \text{ nm}^{-1}$  - a typical pattern for a polymeric system. From  $F(\mathbf{k}, t)$  it is possible to obtain the structural relaxation time using a KWW fitting procedure, for the system  $\sim 20$  ns. In order to get the re-orientational relaxation time and compare with the NMR value, we calculated the ACF for a rotational vector defined at the N-S bond in the TFSI

anion. This function is plotted together with  $F(\mathbf{k}, t)$  in order to show the relative behavior of the two relaxation times. With a relaxation time  $\sim 9$  ns for the  $C_{\text{reor}}$ , the re-orientation of the TFSI anion is twice as fast as the structural relaxation, indirectly related to the sluggish translational dynamics of the system.

## References

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