SUPPLEMENTARY INFORMATION

Structural and Dynamical Heterogeneities at the Nanoscale in Alkali/Earth Alkaline Ionic Liquid Electrolytes: Experiment and Molecular Simulation

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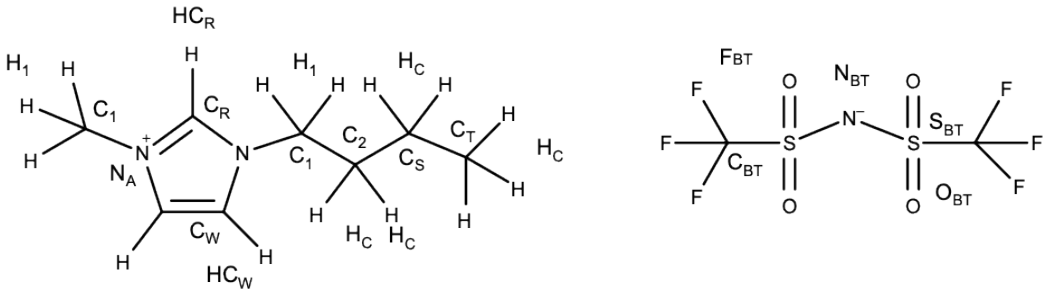


Figure S1 : Nomenclature used for identification of BMIm and TFSI ions.

Table S1: partial charges and Lennard Jones of each atoms force field parameters

Atoms	q (e)	σ (Å)	ε (kcal.mol^{-1})
Li	1.00	2.8700	0.000146
Na	1.00	3.8100	0.000146
K	1.00	4.5300	0.000146
Cs	1.00	5.1700	0.000146
Mg	2.00	1.6300	0.141010
N_A	0.15	3.2500	0.170
C_1	-0.17	3.5000	0.066
C_2	0.01	3.5000	0.066
C_s	-0.12	3.5000	0.066
C_T	-0.18	3.5000	0.066
C_R	-0.11	2.1300	0.105
C_w	-0.13	3.0175	0.049
H_1	0.13	2.5000	0.030
H_c	0.06	2.5000	0.030
HC_R	0.21	1.4520	0.045
HC_W	0.21	2.0570	0.021
C_{BT}	0.35	3.1500	0.019794
N_{BT}	-0.66	3.250000	0.050987
S_{BT}	1.02	4.082500	0.074981
O_{BT}	-0.53	3.463200	0.062985
F_{BT}	-0.16	2.655000	0.015896

Table S2 : composition of simulation boxes used for molecular dynamics studies of BMImTFSI/XTFSI electrolytes. Larger boxes used for determination of S(Q) are 27 (3×3×3) times bigger.

	f=0	f=0.1	f=0.2	f=0.4
X = Li^+, Na^+ or Cs^+ (alkali)				
Li/Na/Cs	0	12	20	35
BMIm	124	112	104	89
TFSI	124	124	124	124
X = Mg^{2+} (earth alkali)				
Mg	0	10	18	N/A
BMIm	124	104	88	N/A
TFSI	124	124	124	N/A

Table S3 : densities of [X][BMImTFSI] electrolytes / MD / 300K

	f=0	f=0.1	f=0.2	f=0.4
BMImTFSI pure	1.43			
Li		1.41	1.40	1.34
Na			1.42	
K			1.43	
Cs		1.41	1.44	1.45
Mg		1.39	1.27	

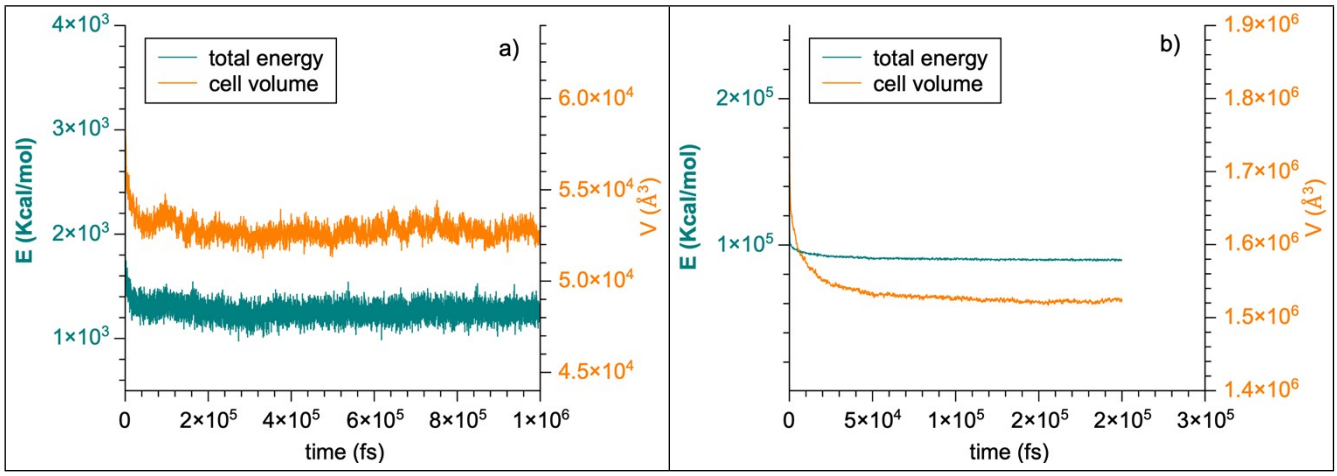


Figure S2 : MD equilibration run of samples. Evolution of the total energy and the cell volume along a trajectories after a quench from 500K to 300K for a) a standard box of [Li][BMIm]*0.4* b) larger box (3x3x3) of [Li][BMIm]*0.2*

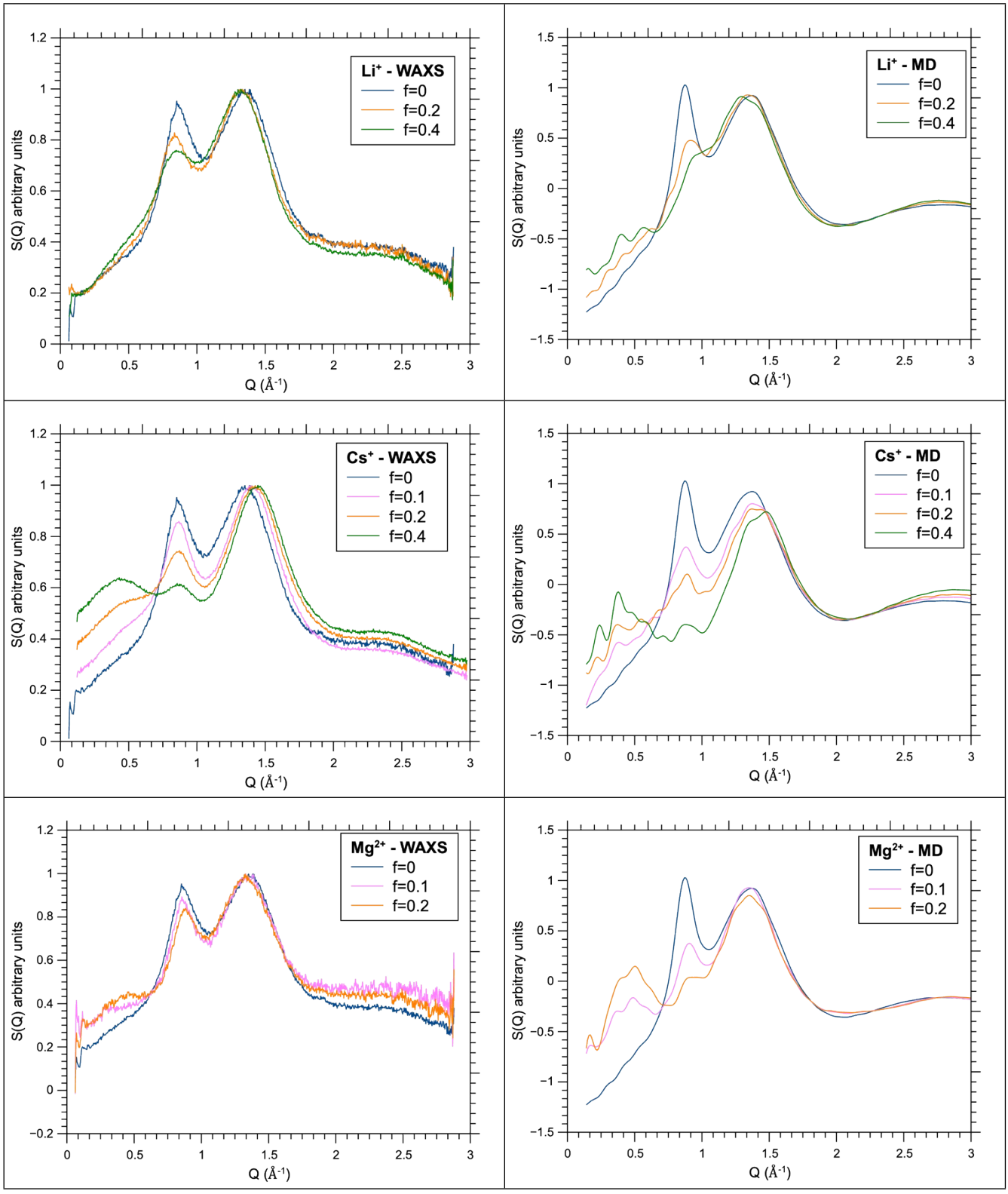


Figure S3 : WAXS diffraction pattern of pure BMImTFSI and BMImTFSI/XTFSI electrolytes (X=Li^+ (top), Cs^+ (middle) Mg^{2+} (bottom)) (a) experiments at room temperature (b) molecular dynamics at 300K.

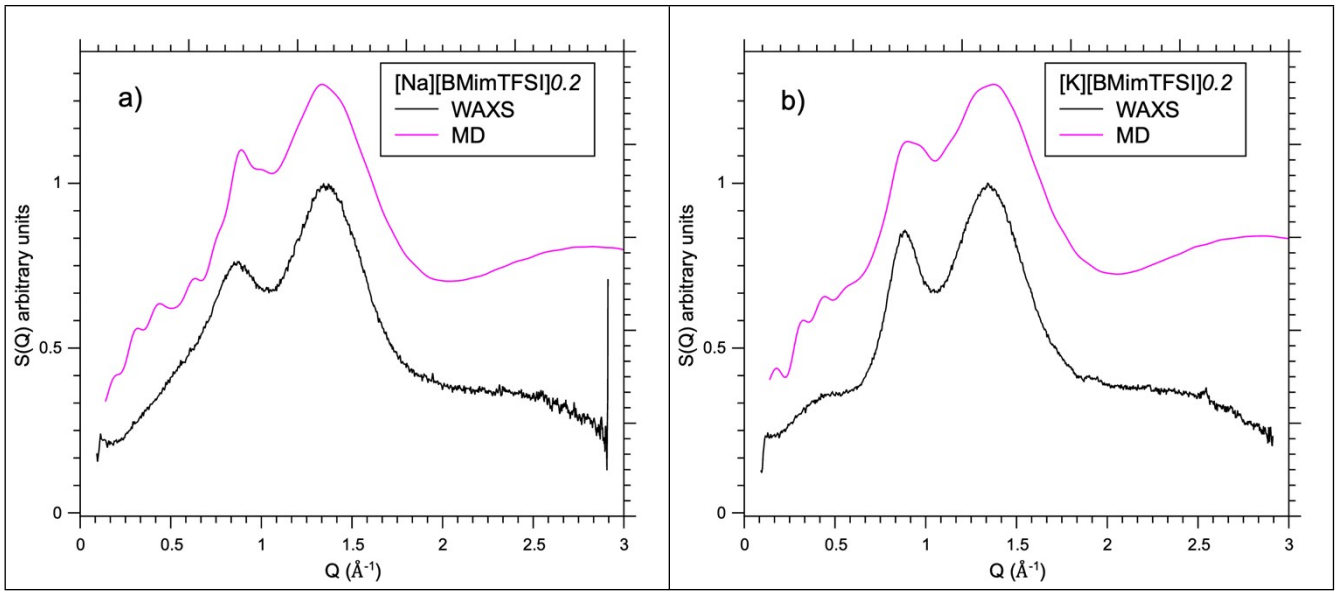


Figure S4: WAXS diffraction pattern - comparison of experiments (RT) and molecular dynamics (300K) for (a) [Na][BMImTFSI]*0.2* and b) [K][BMImTFSI]*0.2*

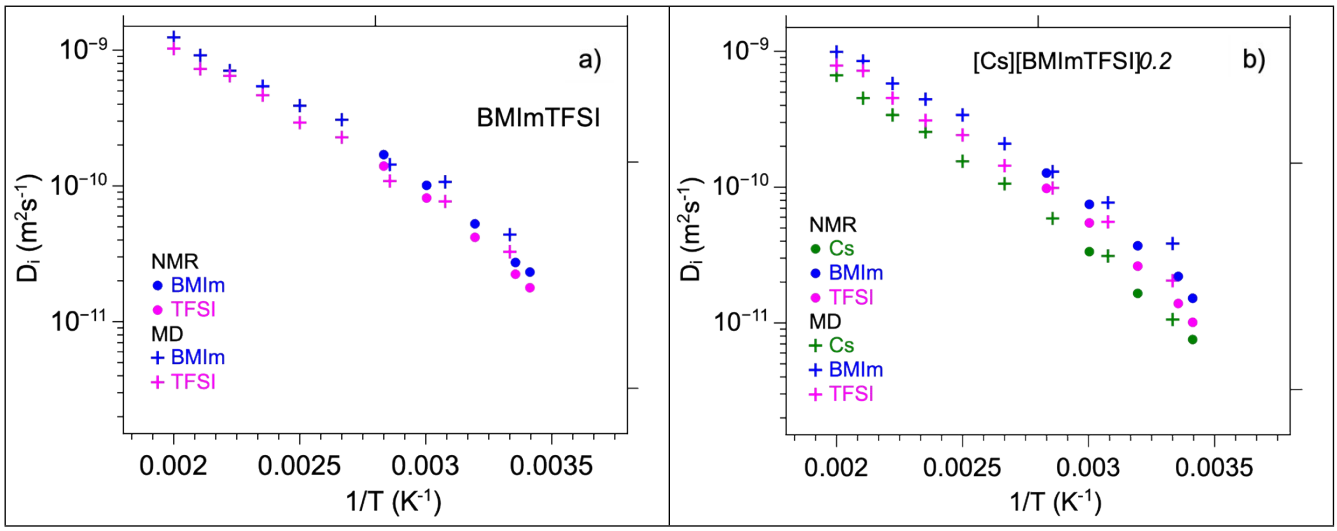


Figure S5: Evolution of individual self-diffusion coefficients with temperature. Comparison of NMR experimental values with MD for a) BMImTFSI, b) [Cs][BMImTFSI]*0.2*

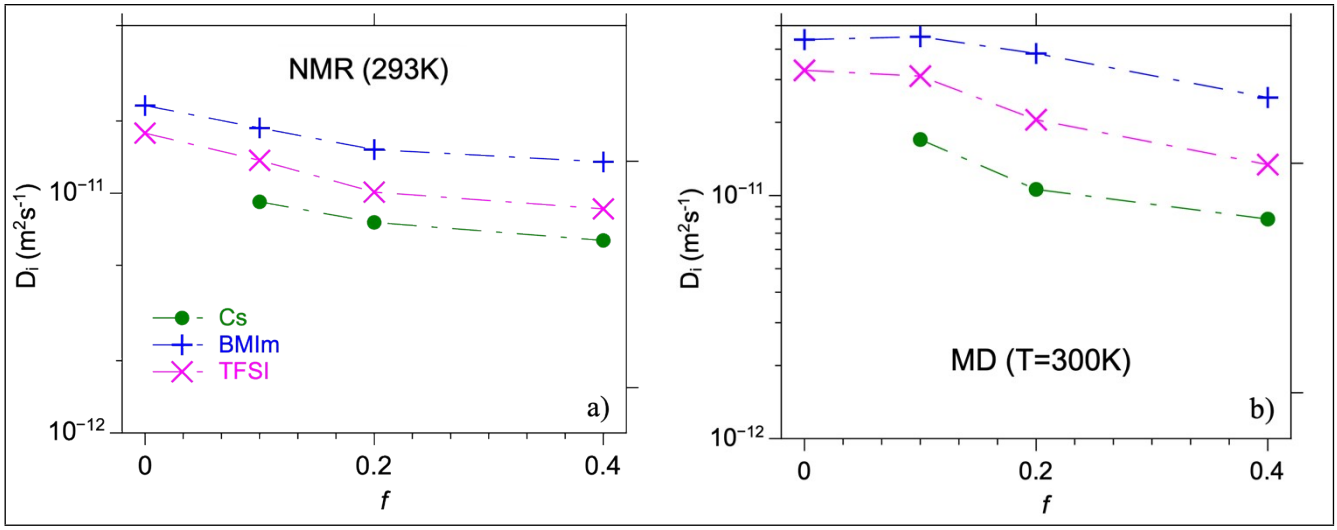


Figure S6: Individual self-diffusion coefficients in [Cs][BMImTFSI]*f* as function of the electrolyte composition (*f*) measured by NMR experiment (left side, T=293K) and determined from MD trajectories (right side T=300K).

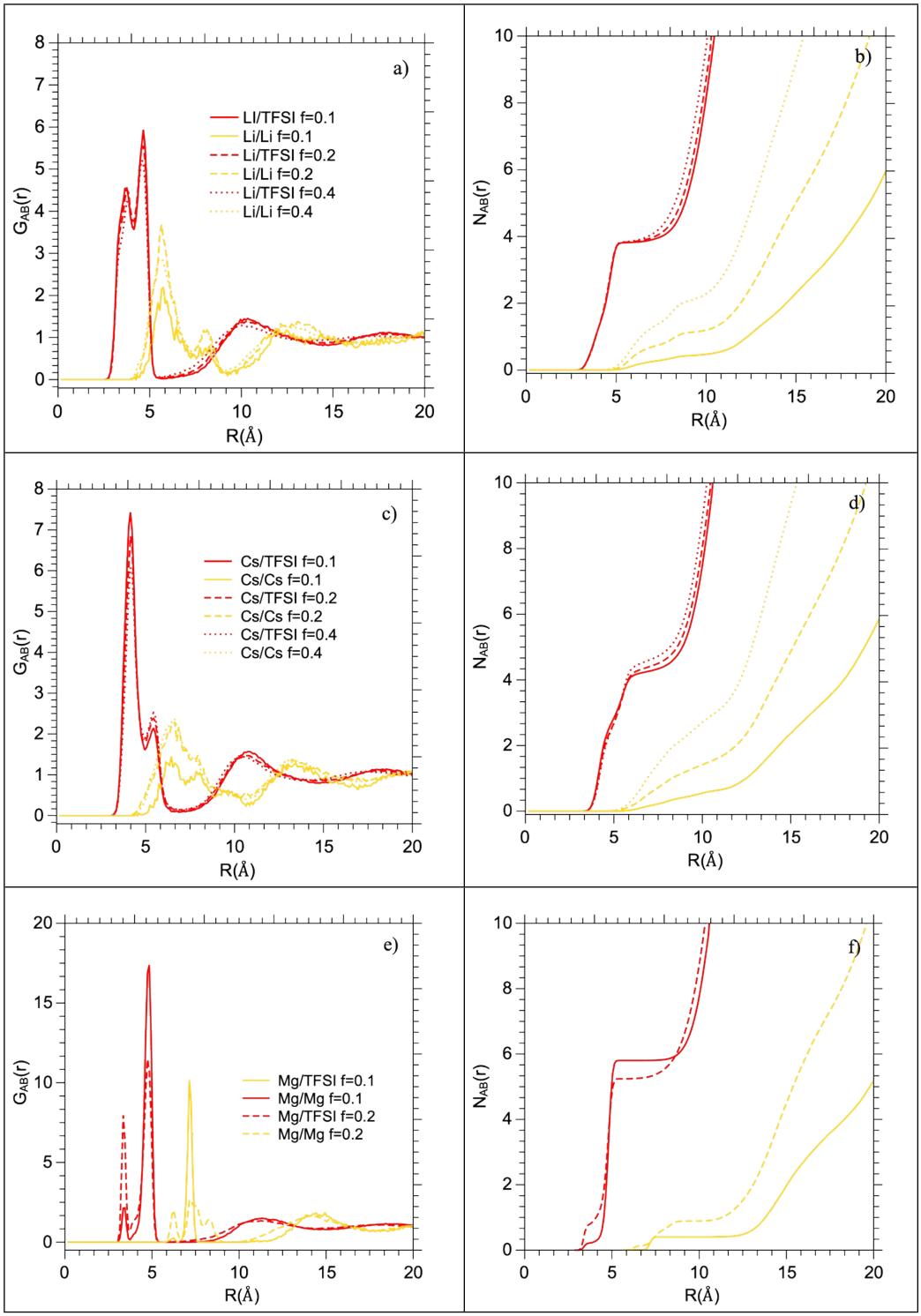


Figure S7: left side : COM $G_{AB}(R)$ for different representative ion couples (X-TFSI, X-X) and right side : number of neighbors for these ion couples as obtained from $G_{AB}(R)$ for a) and b) [Li][BMImTFSI] (*f*=0.1, 0.2, 0.4), c) and d) [Cs][BMImTFSI] (*f*=0.1, 0.2, 0.4), e) and f) [Mg][BMImTFSI] (*f*=0.1, 0.2) electrolytes integration :

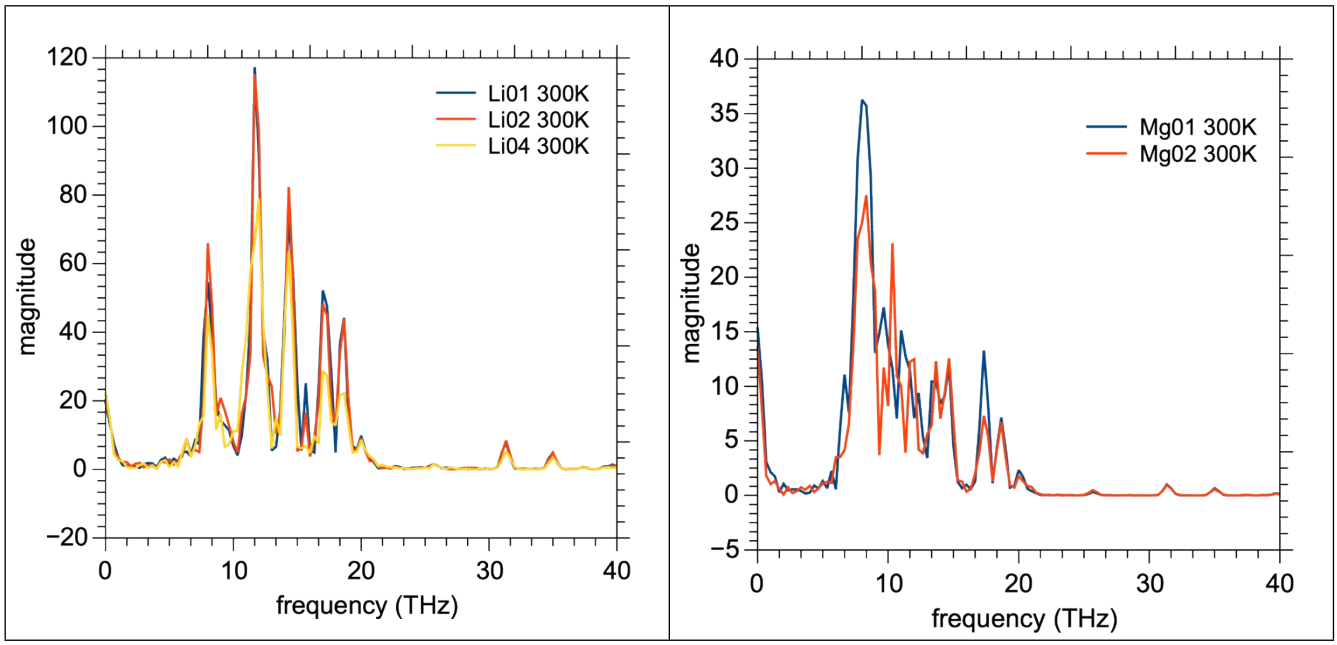


Figure S8: effect of alkali concentration on vacf to evidence the rattling frequencies.

Table S4: comparaison of structural characterization data (number of X-TFSI and X-X number, ratio of free X cations) between standard box and larger boxes (3×3×3) at 300K.

T(K)	X cation	Li^+			Na^+	K^+	Cs^+			Mg^{2+}	
	f	0.1	0.2	0.4	0.2	0.2	0.1	0.2	0.4	0.1	0.2
	X-TFSI cutoff distance	6.1 Å	6.1 Å	6.1 Å	6.5 Å	6.5 Å	7.0 Å	7.0 Å	7.0 Å	6.0 Å	6.0 Å
	X-X cutoff distance	9.5 Å	9.5 Å	9.5 Å	10.0Å	10.5Å	11.5 Å	11.5Å	11.5Å	11.0 Å	11.0 Å
standard box	number of $TFSI^-$ in X coordination shell	4.2	4.1	3.9	4.2	4.2	4.2	4.4	4.5	5.6	5.3
	number of X^+ in X coordination shell	0.2	1.1	2.7	0.7	1.2	0.5	1.4	3.2	0.6	0.9
	% free Li^+	91	62	36	70	56	65	56	27	70	70
large box	number of $TFSI^-$ in X coordination shell	3.8	3.9	3.8	4.1	4.2	4.2	4.3	4.6	5.8	5.2
	number of X^+ in X coordination shell	0.5	1.2	2.5	1.2	1.4	0.7	1.8	3.2	0.4	0.9
	% free Li^+	81	59	40	58	56	71	46	28	80	70

T(K)	X cation	Li^+			Na^+	K^+	Cs^+			Mg^{2+}	
	f	0.1	0.2	0.4	0.2	0.2	0.1	0.2	0.4	0.1	0.2
300K	number of $TFSI^-$ around X^+				(2.1) 4.1	(2.3) 4.2	(2.5) 4.2	(2.4) 4.3	(2.3) 4.6	(0.3) 5.8	(0.8) 5.2
	number of X^+ in first coordination shell				1.2	1.4	0.7	1.8	3.2	0.4	0.9
	mean X-X statistical distance				14.1	14.2	17.0	14.2	11.5	17.7	14.2
	% free X^+				58	56	71	46	28	80	70
500K	number of $TFSI^-$ around X^+				(2.1) 3.9	3.9	4.0	(2.3) 4.2	4.2	5.8	5.2
	number of X^+ in first coordination shell				1.2	1.3	0.7	1.6	2.9	0.5	0.8
	mean Li-Li statistical distance				14.9	15.0	17.9	15.0	12.1	18.5	14.9
	% free X^+				59	58	74	50	31	80	71

Table S5: transport properties of [X][BMImTFSI]*f* electrolytes ([X]=Li, Cs, Mg; $0 \leq f \leq 0.4$: comparison of self-diffusion coefficients of the different species D_s and alkali transport number t_{alk} as measured from PFG NMR experiments and obtained from the molecular dynamics MSD. Comparison of ionic conductivity measured by electrochemical impedance[1] (σ^{exp}) and values obtained from MD by Nernst-Einstein relationship (σ^{NE}).

Property	*f*=0		Li ; *f*=0.1			Li ; *f*=0.2			Li ; *f*=0.4		
	BMIm	TFSI	Li	BMIm	TFSI	Li	BMIm	TFSI	Li	BMIm	TFSI
D_s^{NMR} (293K) ($\times 10^{11}$ m^2s^{-1})	2.32	1.78	0.68	1.72	1.40	0.45	1.25	0.73	0.21	0.68	0.31
D_s^{MSD} (300K) ($\times 10^{11}$ m^2s^{-1})	4.38	3.27	0.84	3.4	2.0	0.44	1.90	1.01	0.21	1.4	0.64
D_s^{NMR} (353K) ($\times 10^{11}$ m^2s^{-1})	17.0	14.0				5.66	12.2	7.82			
D_s^{MSD} (350K) ($\times 10^{11}$ m^2s^{-1})	14.5	10.9				1.71	8.06	4.00			
t_{Li}^{NMR} (298K)			0.023			0.049			0.105		
t_{Li}^{MSD} (300K)			0.016			0.034			0.054		
t_{Li}^{NMR} (350K)						0.060					
t_{Li}^{MSD} (350K)						0.032					
σ^{exp} (298K) (mS/cm)	4.0		3.1			2.3			1.2		
σ^{NE} (300K) (mS/cm)	10.4		7.4			4.0			2.7		

Property	f=0		Cs ; *f*=0.1			Cs ; *f*=0.2			Cs ; *f*=0.4		
	BMIm	TFSI	Cs	BMIm	TFSI	Cs	BMIm	TFSI	Cs	BMIm	TFSI
D_s^{NMR} (293K) ($\times 10^{11}$ m^2s^{-1})	2.32	1.78	0.92	1.87	1.37	0.76	1.52	1.01	0.63	1.35	0.86
D_s^{MSD} (300K) ($\times 10^{11}$ m^2s^{-1})	4.38	3.27	1.7	4.5	3.1	1.06	3.84	2.05	0.80	2.53	1.34
t_{Cs}^{NMR} (298K)			0.029			0.064			0.131		
t_{Cs}^{MSD} (300K)			0.023			0.040			0.101		
σ^{exp} (298K) (mS/cm)	4.0		3.2			3.0			1.8		
σ^{NE} (300K) (mS/cm)	10.4		9.8			7.9			5.2		

Property	Mg ; *f*=0.1			Mg ; *f*=0.2		
	Mg	BMIm	TFSI	Mg	BMIm	TFSI
D_s^{MSD} (300K) ($\times 10^{11}$ m^2s^{-1})	0.32	2.16	1.22	n/a	1.70	0.68
D_s^{MSD} (500K) ($\times 10^{11}$ m^2s^{-1})	15.9	79.7	49.1	6.6	61.4	19.6
t_{Mg}^{MSD} (300K)	0.02					
t_{Mg}^{MSD} (500K)	0.02				0.02	
σ^{exp} (298K) (mS/cm)	2.5			1.2		
σ^{NE} (300K) (mS/cm)	4.5			n/a		

(1) H. P. K. Ngo, E. Planes, C. Iojoiu, P. Soudant, A.-L. Rollet and P. Judeinstein, Transport properties of alkali/alkaline earth cations in ionic-liquid based electrolytes, Journal of Ionic Liquids, 2022, **2**, 100044.

Table S6: correlation distances (in Å) between the different ion pairs corresponding to the first minimum of $G_{AB}(R)$

COM distance correlation (Å)	X-TFSI	X-X	X-BMIm	BMIm-TFSI
BMImTFSI	n/a	n/a	n/a	9.5
[Li][BMImTFSI]*f*	6	9.5	12.5	9.5
[Na][BMImTFSI]*f*	6.7	10.0		
[K][BMImTFSI]*f*	6.7	10.5		
[Cs][BMImTFSI]*f*	7	10.5	12.5	9.3
[Mg][BMImTFSI]*f*	6	10	12.0	9.2

Table S7: correlation times τ_c *(ps)* computed from the time correlation function $P(t) = P_0 exp(-t/\tau_c)$.

COM	X-TFSI	X-X	X-BMIm	BMIm-TFSI
BMImTFSI (500K)	n/a	n/a	n/a	135
BMImTFSI (300K)	n/a	n/a	n/a	1462
[Li][BMImTFSI]*0.1* (500K)	1095	1384		168
[Li][BMImTFSI]*0.2* (300K)	134000	120000		10620
[Li][BMImTFSI]*0.2* (500K)	1290	1129		205
[Li][BMImTFSI]*0.4* (500K)	1586	1628		423
[Na][BMImTFSI]*0.2* (500K)	660	730		140
[K][BMImTFSI]*0.2* (500K)	349	350		140
[Cs][BMImTFSI]*0.2* (300K)	10700	13900		5500
[Cs][BMImTFSI]*0.1* (500K)	263	300		128
[Cs][BMImTFSI]*0.2* (500K)	283	291		156
[Cs][BMImTFSI]*0.4* (500K)	268	303		175
[Mg][BMImTFSI]*0.1* (500K)	> 200000	> 200000		190

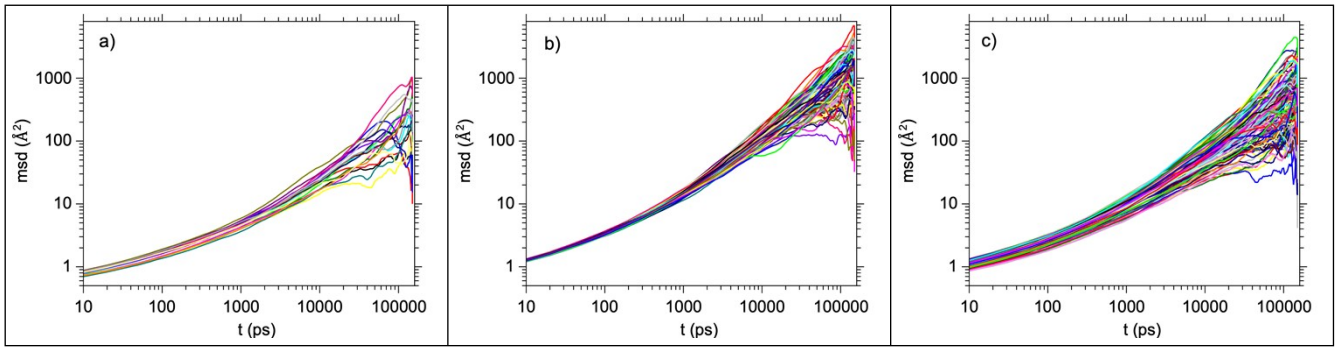


Figure S9 : Individual COM msd for all ions inside [Li][BMImTFSI]*0.2* at 300K along a 150ns trajectory: a) the 20 Li^+ ions, b) the 104 $BMIm^+$ cations and c) the 124 $TFSI^-$ anions. Even if trajectories have been performed up to 150ns, the curves are presented only up to 40ns as the statistic on an unique individual ion is very low

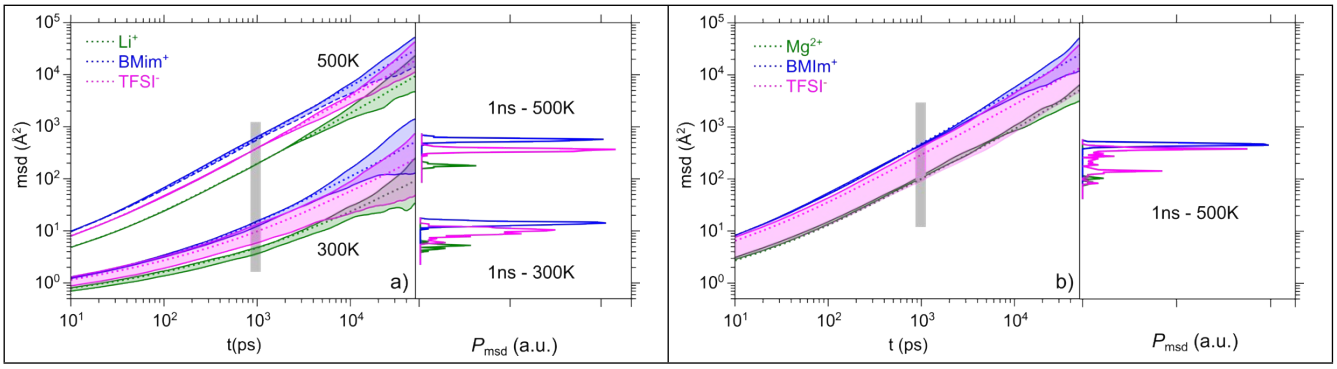
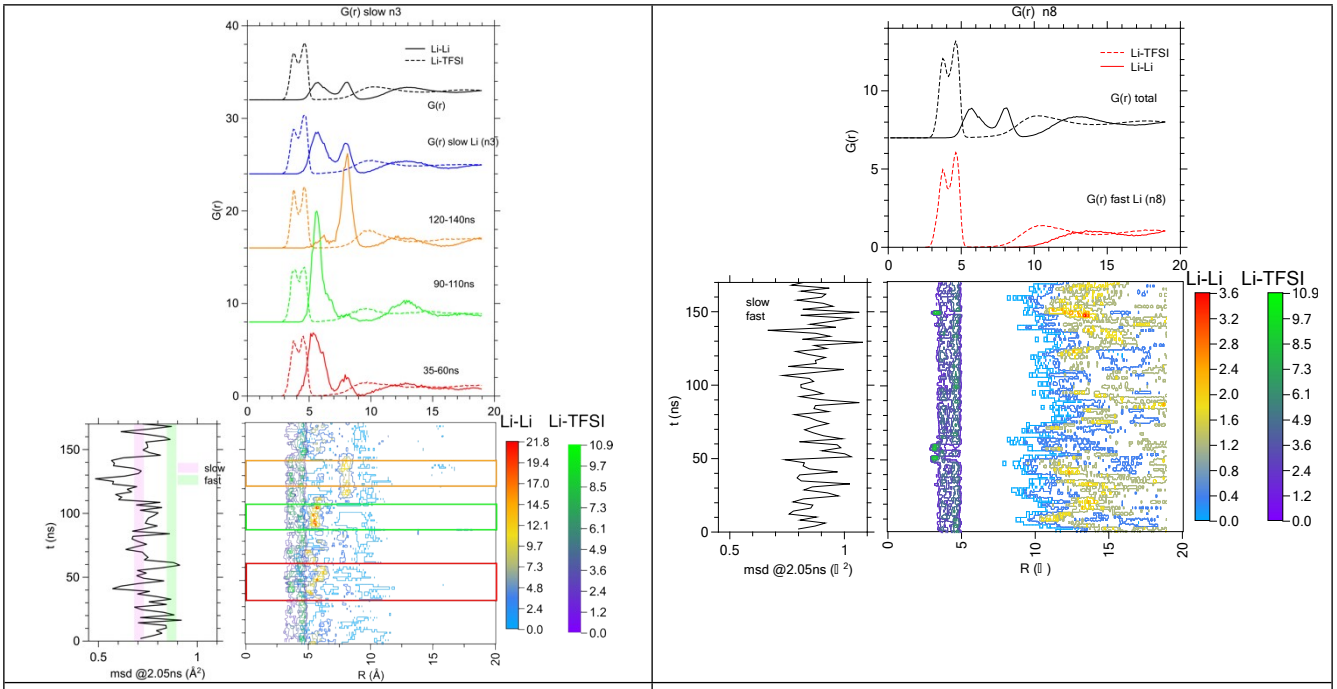


Figure S10: Individual dynamic properties of [X][BMImTFSI]*f* electrolytes. msd for a) X=Li, *f*=0.2, T=300K and 500K b) X=Mg, *f*=0.1, T=500K. Green, pink and blue correspond respectively to Li^+, $TFSI^-$ and $BMIm^+$ species. Left part of the figures correspond to the evolution of msd with trajectory duration. The broad light colored zone corresponds to the spannig of the individual msds, the thin dashed lines to the average value for each species, while the solid lines spanning around the light colored zones corresponds to the msd curves for the slowest and fastest ions of each families. The right side of these graphs corresponds to the distribution of msd (P_{msd}) measured for a trajectory of 1ns for the three species. They are presented and discussed in the main text and Figure 7.



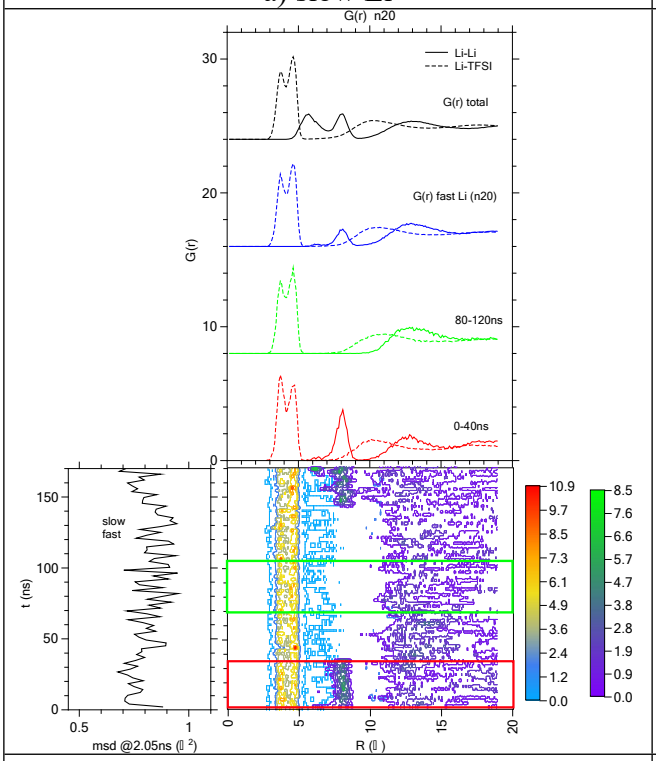


Figure S11: Time dependance of the radial distribution function along a 170ns trajectory for [Li][BMIm][TFSI]*0.2* at 300K around selected individual Li^+ ions : a) 'slow', b) 'fast' and c) 'mean'A sampling of 2ns was selected to obtain clear-cut dynamical, structural and cross coupled informations. Central : 2D level map for $G_{Li\text{-}TFSI}(r)$, $G_{Li\text{-}Li}(r)$. top : projections of $G_{AB}(r)$ for selected trajectory sections. Left : msd calculated for 2ns range (msd_{2ns}) along the trajectory. The msd_{2ns} correspondinng to "slow" and "fast" regime also presented as pale colored broad vertical lines.

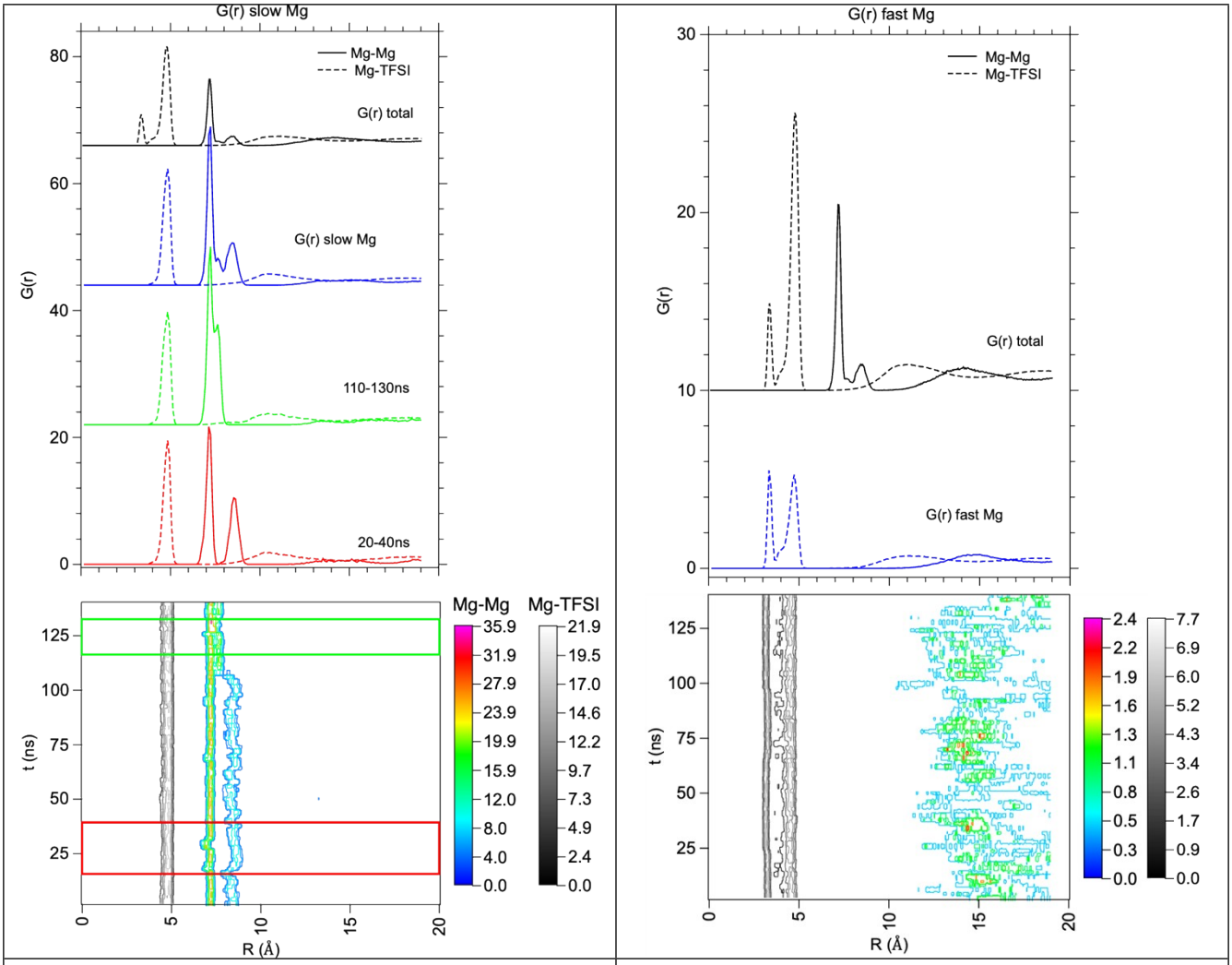


Figure S12: Time dependance of the radial distribution function along a 170ns trajectory for [Li][BMIm][TFSI]*0.1* at 300K around selected individual Mg^{2+} ions : a) 'slow', b) 'fast' and c) 'mean'A sampling of 2ns was selected to obtain clear-cut dynamical, structural and cross coupled informations. Central : 2D level map for $G_{Mg\text{-}TFSI}(r)$, $G_{Mg\text{-}Mg}(r)$. top : projections of $G_{AB}(r)$ for selected trajectory sections.