Heterogeneity in Microstructure and Dynamics of Tetraalkylammonium Hydroxide Ionic Liquids: Insight from Classical Molecular Dynamics Simulations and Voronoi Tessellation Analysis

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Supporting Information

Equations used for the calculation of structure factor.

$$I(q) = \frac{\sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j f_i(q) f_j(q) H_{ij}(q)}{\left[\sum_{i=1}^{N} x_i f_i(q)\right]\left[\sum_{i=1}^{N} x_j f_j(q)\right]} \qquad (S1)$$

In equation 2, x_i, and x_j are the number concentrations of atomic species of type i and j in the stoichiometric unit, respectively; f_i and f_j are the atomic structure factors. Partial structure factors are denoted by $H_{ij}(q)$. $H_{ij}(q)$ are calculated from Fourier transform of the pair correlation function, and q is the scattering variable,

$$H_{ij}(q) = 4\pi\rho_0 \int_0^{r_{max}} r^2 [\, g_{ij}(r) - 1] \frac{\sin\,(qr)}{qr} \omega(r) dr \qquad (S2)$$

$$\omega(r) = \frac{\sin\,(2\pi/L)}{2\pi/\mathrm{L}}$$

$\omega(r)$ is the Lorch window function and is used to limit the finite truncation effects of r.[95,96] Half of the box length is denoted by r_{max}. $g_{ij}(r)$ are the pair correlation functions, and ρ_0 (electrons^2/nm^3) is the bulk number density.

Table S1: Non-bonding force field parameters for ions used in this study.

System	Atom	q(e)	σ(Å)	ε(kcal/mol)
TEA	C_1	0.0797	3.475	0.1094
	H_1	0.0715	1.960	0.1570
	N	-0.1884	3.296	0.1500
	C_2	-0.2454	3.475	0.1094
	H_2	0.1066	2.650	0.1570
TPA	C_1	0.0054	3.475	0.1094
	H_1	0.0800	1.960	0.1570
	N	-0.3465	3.296	0.1500
	C_2	0.0644	3.475	0.1094
	H_2	0.0584	1.960	0.1570
	C_3	-0.3395	3.475	0.1094
	H_3	0.1100	2.650	0.1570
TBA	C_1	-0.0454	3.475	0.1094
	H_1	0.0499	1.960	0.1570
	N	0.2226	3.296	0.1500
	C_2	-0.1145	3.475	0.1094
	H_2	0.0735	1.960	0.1570
	C_3	0.0440	3.475	0.1094
	H_3	0.0387	1.960	0.1570
	C_4	-0.2540	3.475	0.1094
	H_4	0.0800	2.650	0.1570
OH	O	-1.2558	3.166	0.1554
	H	0.2558	0.000	0.0000

Table S2: First minima and coordination number from Cation-Cation, Anion-Anion, Cation-Anion centre of mass RDFs.

IL	Cation-Anion		Cation-Cation		Anion-Anion	
	First Minimum [nm]	Coordination Number	First Minima[nm]	Coordination Number	First Minima[nm]	Coordination Number
TEAH	0.53	3.36	0.94	13.40	0.90	12.13
TPAH	0.57	3.02	0.93	8.92	0.89	8.00
TBAH	0.61	2.84	0.90	5.72	0.90	6.05

Table S3. Domain analysis of cation and anion subunits. D-Vol indicates domain volume and D-Surf indicates domain surface.

Subunit	IL	Domain count	D-Vol($Å^3$)	D-Surf($Å^2$)	Q^{peri}
Cation					
	TEAH	1.0	112872	22654	0.35
	TPAH	1.0	163822	22603	0.51
	TBAH	1.0	211735	22711	0.66
Anion					

	TEAH	497	24	45	0.83
	TPAH	500	24	45	0.82
	TBAH	500	24	45	0.76

Table S4. Surface Coverage of different domains from Voronoi tesselation

IL				
	Cation	Anion	Cation	Anion
	Cation coverage		Anion coverage	
TEAH	80.5	19.5	100.0	0.0
TPAH	86.4	13.6	100.0	0.0
TBAH	89.3	10.7	100.0	0.0

Table S5: Fitting parameters of centre of mass cation-anion residence lifetime autocorrelation functions in eq 8. Correlation coefficient is indicated by c.

IL	a_1	a_2	τ_1(ps)	τ_2(ps)	τ_3(ps)	c
TEAH	0.42	0.08	0.56	224.8	12292	0.985
TPAH	0.62	0.11	0.53	290.2	13486	0.973
TBAH	0.51	0.11	0.53	133.1	13789	0.971

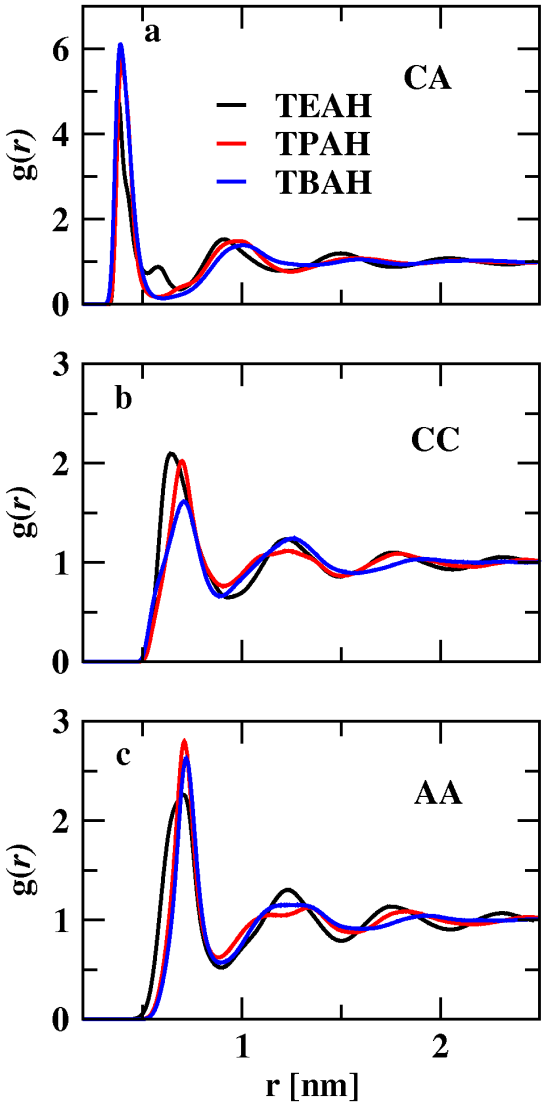


Figure S1: Comparing the COM RDFs of different ILs. a. Cation-anion (CA) b. Cation-cation (CC) c. Anion – anion (AA).

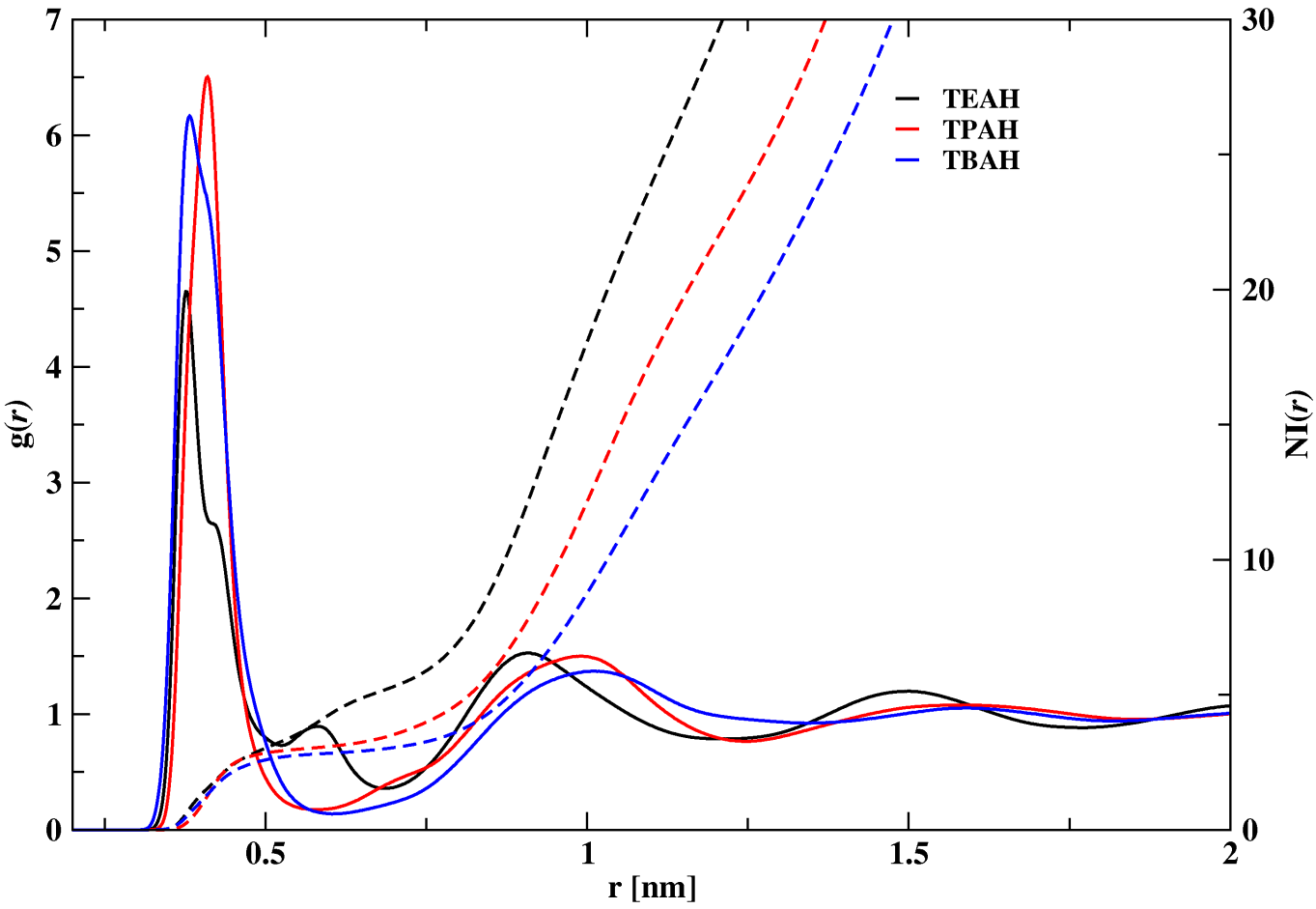


Figure S2: Radial distribution functions between nitrogen atom of cation and oxygen atom of anion. Solid and dashed lines indicate the RDFs and number integrals respectively.

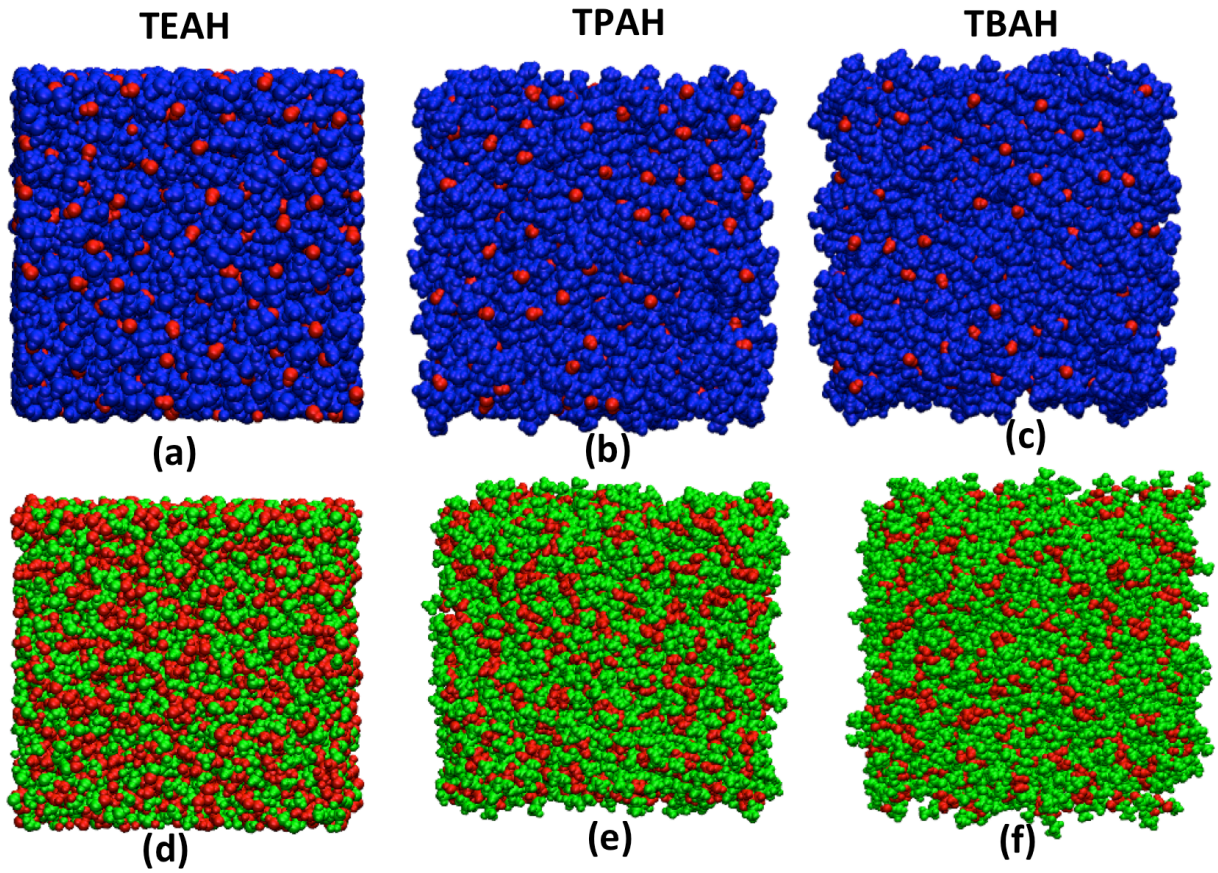


Figure S3: (a-c). Cations are shown with blue and anions are shown with red colours. (d-f) Polar part is shown with red colour and non-polar part is shown with green colour. Polar part includes anion and nitrogen atoms of cation and the methylene groups attached to the nitrogen of cation. non-polar parts include the ethyl, propyl and butyl groups of cation. TEAH, TPAH and TBAH are shown in left, middle and right columns, respectively.

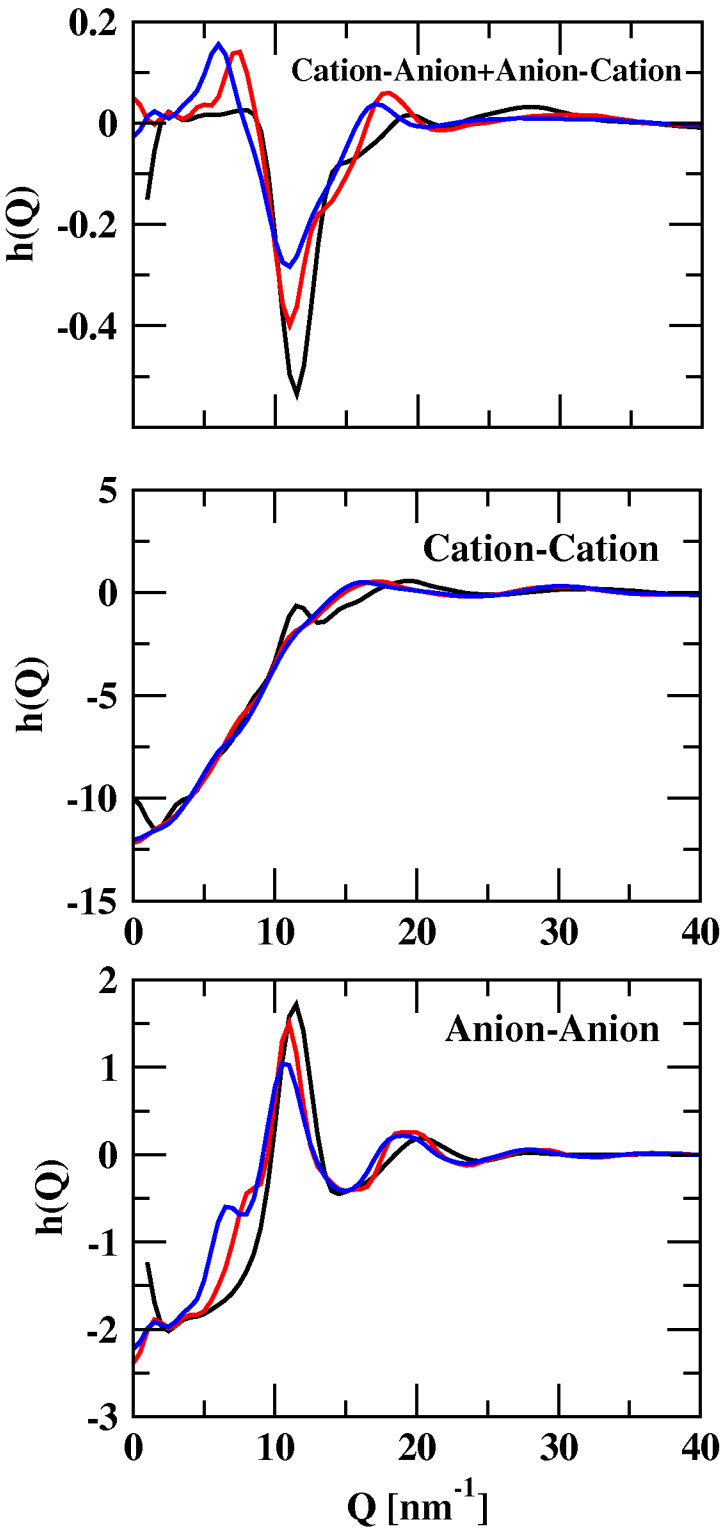
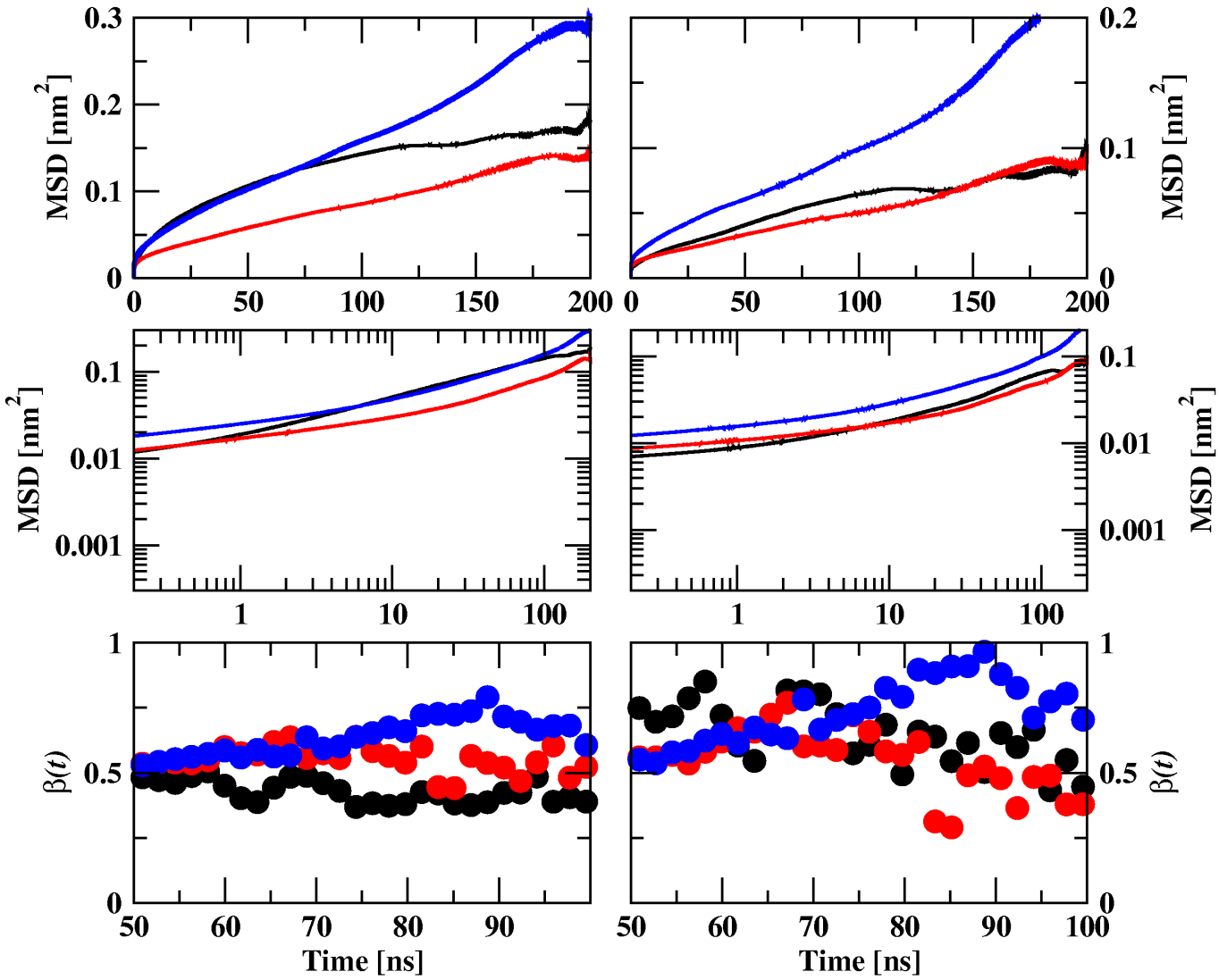


Figure S4: Cation-anion+anion-cation, cation-cation and anion-anion structure functions.



$$\beta(t) = \frac{\mathrm{d}\,\ln\langle \Delta r^2(t)\rangle}{\mathrm{d}\,\ln(t)}$$

Figure S5: Mean square displacements (top) of cation and anion in ILs. Log-log plots (middle) and β values (bottom) of ions are shown in figure. Black, red, blue colors indicate TEAH, TPAH and TBAH respectively. Left column indicates cation and right column represents anions.

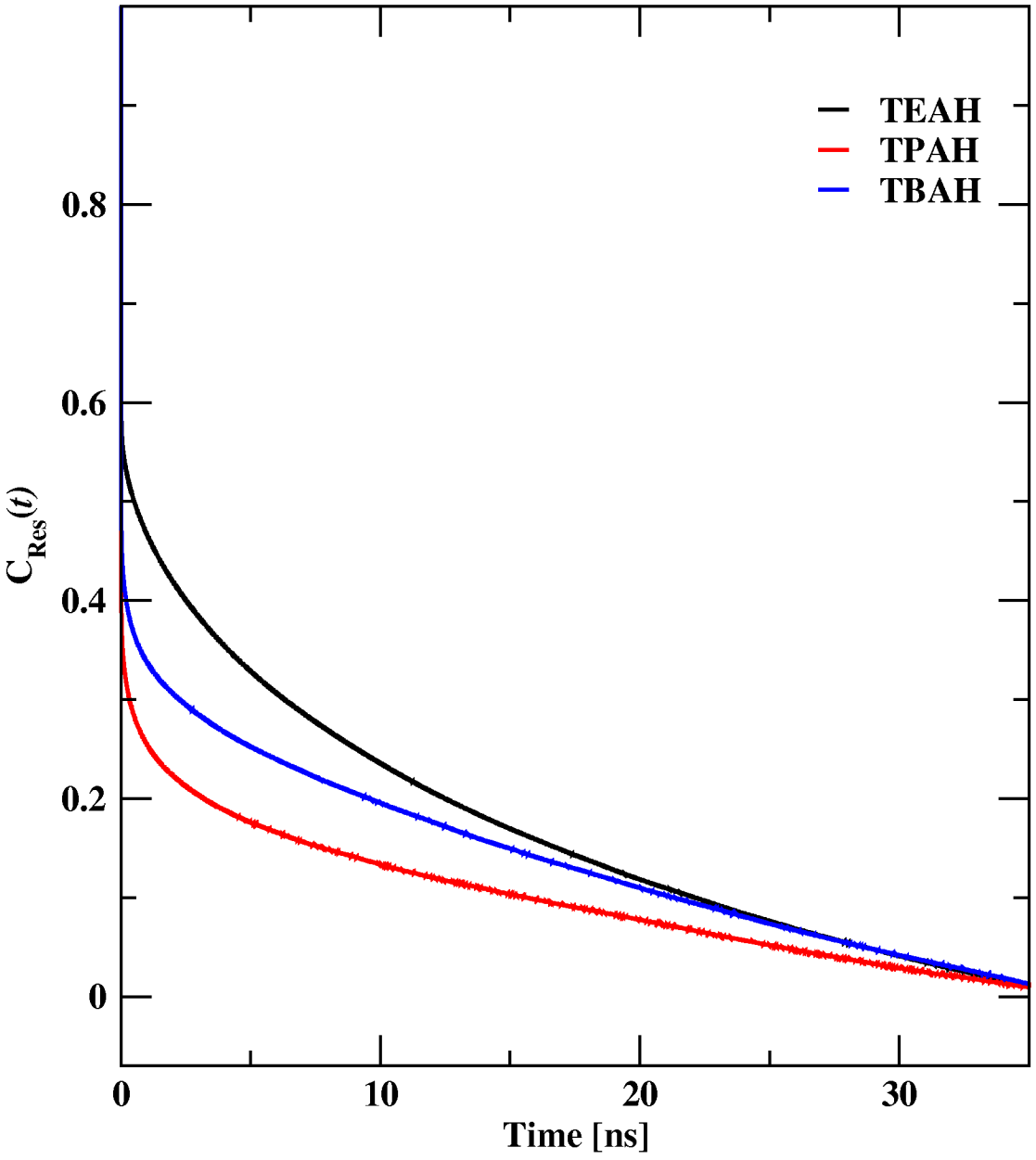

TEAH
TPAH
TBAH
0.8
0.6
0.4
0.2
0
$C_{Res}(t)$
0
10
20
30
Time [ns]

Figure S6: Centre of mass residence auto correlation functions between cation and anion.

Optimized structures of ions in XYZ format

TEA

N	0.000	0.000	0.000
C	0.000	1.225	0.915
H	-0.875	1.118	1.553
H	0.875	1.118	1.553
C	0.000	2.579	0.226
H	-0.887	2.748	-0.384
H	0.000	3.341	1.008
H	0.887	2.748	-0.384
C	-0.000	-1.225	0.915
H	-0.875	-1.118	1.553
H	0.875	-1.118	1.553
C	-0.000	-2.579	0.226
H	0.887	-2.748	-0.384
H	-0.000	-3.341	1.008
H	-0.887	-2.748	-0.384
C	-1.225	0.000	-0.915
H	-1.118	-0.875	-1.553
H	-1.118	0.875	-1.553
C	-2.579	0.000	-0.226
H	-3.341	0.000	-1.008
H	-2.748	-0.887	0.384
H	-2.748	0.887	0.384
C	1.225	-0.000	-0.915
H	1.118	-0.875	-1.553
C	2.579	-0.000	-0.226
H	2.748	-0.887	0.384
H	3.341	-0.000	-1.008
H	2.748	0.887	0.384
H	1.118	0.875	-1.553

TPA

N	0.000	0.000	0.000
C	0.000	1.263	0.864
H	0.977	1.299	1.345
H	-0.055	2.097	0.168
C	-1.106	1.387	1.907
H	-1.072	0.554	2.613
H	-2.091	1.370	1.436
C	-0.945	2.704	2.677
H	-1.014	3.567	2.012
H	-1.729	2.801	3.428
H	0.017	2.751	3.194
C	1.263	-0.000	-0.864
H	2.097	0.055	-0.168
H	1.299	-0.977	-1.345
C	1.387	1.106	-1.907
H	1.370	2.091	-1.436
H	0.554	1.072	-2.613
C	2.704	0.945	-2.677
H	2.801	1.729	-3.428
H	3.567	1.014	-2.012
H	2.751	-0.017	-3.194
C	-1.263	0.000	-0.864
H	-2.097	-0.055	-0.168
C	-0.000	-1.263	0.864
H	0.055	-2.097	0.168
H	-0.977	-1.299	1.345
C	1.106	-1.387	1.907
H	1.072	-0.554	2.613
H	2.091	-1.370	1.436
C	0.945	-2.704	2.677
H	1.729	-2.801	3.428
H	-0.017	-2.751	3.194
H	1.014	-3.567	2.012
C	-1.387	-1.106	-1.907
H	-1.370	-2.091	-1.436
H	-0.554	-1.072	-2.613
C	-2.704	-0.945	-2.677
H	-2.751	0.017	-3.194
H	-2.801	-1.729	-3.428
H	-3.567	-1.014	-2.012
H	-1.299	0.977	-1.345

TBA

N	-0.111	-0.064	-0.055
C	-0.854	1.242	-0.341

H	-1.448	1.449	0.549
H	-0.084	2.006	-0.410
C	-1.742	1.271	-1.582
H	-2.502	0.490	-1.525
H	-1.155	1.087	-2.486
C	-2.449	2.633	-1.726
H	-3.185	2.533	-2.527
H	-3.023	2.842	-0.817
C	0.595	0.060	1.296
H	-0.190	0.281	2.018
H	0.983	-0.931	1.525
C	1.705	1.100	1.406
H	1.323	2.104	1.202
H	2.499	0.905	0.681
C	2.309	1.080	2.819
H	1.520	1.271	3.554
H	2.694	0.078	3.035
C	0.894	-0.313	-1.182
H	0.299	-0.440	-2.084
C	-1.077	-1.250	0.008
H	-0.469	-2.110	0.278
H	-1.430	-1.404	-1.011
C	-2.261	-1.134	0.963
H	-2.889	-0.278	0.705
H	-1.924	-0.987	1.991
C	-3.114	-2.411	0.900
H	-3.448	-2.574	-0.130
H	-2.493	-3.275	1.163
C	1.839	-1.499	-1.016
H	1.281	-2.434	-0.924
H	2.443	-1.394	-0.112
C	2.777	-1.602	-2.229
H	3.344	-0.671	-2.330
H	2.180	-1.699	-3.142
H	1.460	0.611	-1.288
C	-1.523	3.809	-2.042
H	-2.104	4.717	-2.209
H	-0.824	4.026	-1.230
H	-0.940	3.621	-2.947
C	-4.326	-2.349	1.829
H	-4.912	-3.267	1.764
H	-4.023	-2.223	2.871
H	-4.984	-1.517	1.568
C	3.742	-2.782	-2.121
H	3.204	-3.731	-2.058
H	4.395	-2.830	-2.994
H	4.378	-2.698	-1.236
C	3.428	2.107	2.990
H	3.065	3.123	2.818
H	3.838	2.068	4.000
H	4.249	1.921	2.292

OH

O	0.000	0.000	0.107
H	0.000	0.000	-0.859