Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Protic Ammonium Carboxylate Ionic Liquids: Insight into Structure, Dynamics and Thermophysical Properties by Alkyl Group Functionalization

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Supporting information

Table S1: First minima and coordination number from Cation-Cation, Anion-Anion, Cation-Anion centre of mass RDFs

IL	Cation-Cation		Anion-Anion		Cation-Anion	
	First Minima(nm)	Coordination Number	First Minima(nm)	Coordination Number	First Minima(nm)	Coordination Number
MAF	0.65	8.96	0.65	8.97	0.60	7.45
EAF	0.70	9.15	0.69	8.58	0.64	7.34
PAF	0.76	9.91	0.69	7.04	0.68	7.15
EAA	0.70	7.36	0.73	8.80	0.69	7.23
EAP	0.71	6.44	0.79	9.60	0.70	7.09

Table S2: Non-bonding force field parameters for cations

System	Atom	q(e)	σ(Å)	ε(kcal/mol)
MA	C_1	0.0699	3.50	0.0660
	H_1	0.1067	2.50	0.0300
	N	-0.2469	3.25	0.1699
	H_N	0.2589	0.00	0.0000
EA	C_1	0.1015	3.50	0.0660
	H_1	0.0806	2.50	0.0300
	N	-0.3866	3.25	0.1699
	H_N	0.2809	0.00	0.0000
	C_2	-0.2567	3.50	0.0660
	H_2	0.1059	2.50	0.0000
PA	C_1	-0.1056	3.50	0.0660
	H_1	0.1265	2.50	0.0300
	N	-0.3331	3.25	0.1699
	H_N	0.2696	0.00	0.0000
	C_2	-0.0528	3.50	0.0660
	H_2	0.0751	2.50	0.0300
	C_3	-0.0955	3.50	0.0660
	H_3	0.0517	2.50	0.0300

Table S3: Non-bonding force field parameters for anions

System	Atom	q(e)	σ(Å)	ε(kcal/mol)
FRM	C_1	0.6511	3.75	0.1049
	H_1	-0.1593	2.42	0.0150
	O	-0.6359	2.96	0.2100
ACT	C_1	0.7485	3.75	0.1049
	O	-0.6691	2.96	0.2100
	C_2	-0.2191	3.50	0.0660
	H_2	0.0096	2.50	0.0300
PRP	C_1	0.6257	3.75	0.1049
	O	-0.6458	2.96	0.2100
	C_2	0.2128	3.50	0.0660
	H_2	-0.1055	2.50	0.0300
	C_3	-0.0572	3.50	0.0660
	H_3	-0.0196	2.50	0.0300

Table S4 : Self diffusion coefficients ($\times 10^{-7} cm^2/s$) of cation and anion of ILs from MD simulations.

IL	Cation	Anion
MAF	6.30	6.02
EAF	1.33	1.67
PAF	0.40	0.38
EAA	0.51	0.51
EAP	0.35	0.34

Table S5 : OH Coordination numbers.

IL	Coordination number
MAF	1.90
EAF	1.79
PAF	1.77
EAA	1.68
EAP	1.74

Table S6: Fitting parameters of cation-anion NO site-site 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
MAF	0.486	0.267	6.7	86.0	1094.7	0.999
EAF	0.322	0.353	9.4	166.5	1932.2	0.997
PAF	0.256	0.348	3.8	128.0	2159.0	0.993
EAA	0.194	0.361	7.2	327.7	2011.8	0.997
EAP	0.100	0.400	2.0	246.7	2358.3	0.996

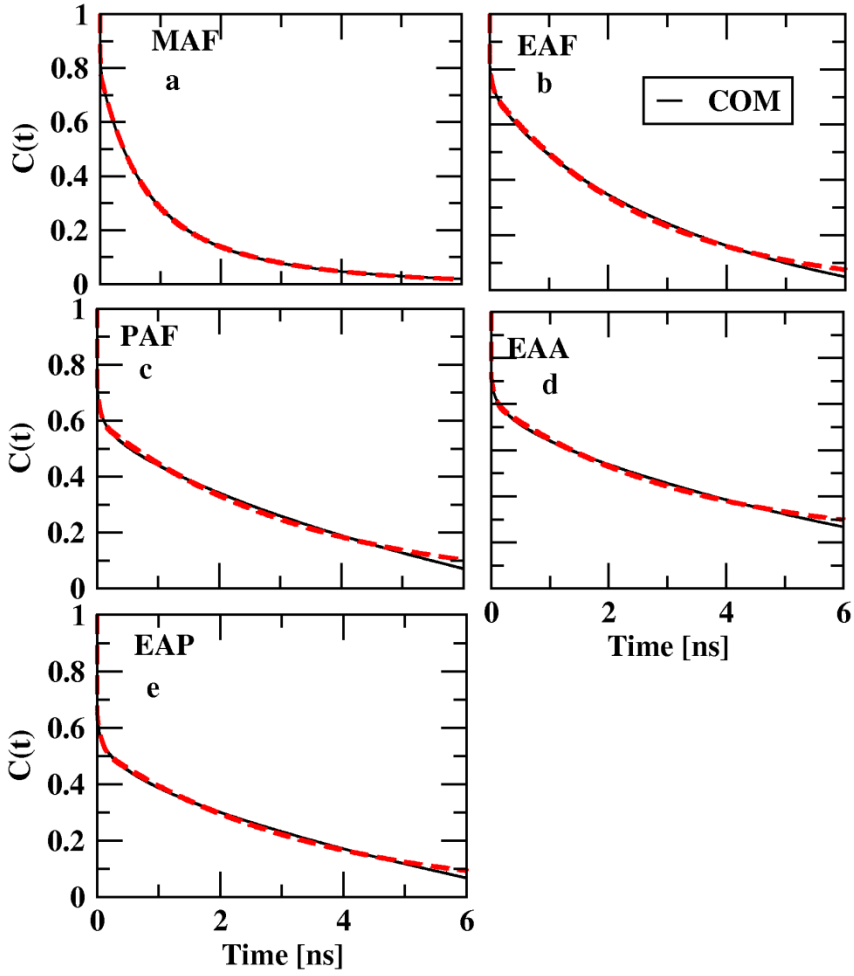
Table S7: Fitting parameters of centre of mass cation-anion residence lifetime autocorrelation functions in eq 8. Correlation coefficient is indicated by c.

IL	a_1	a_2	τ_1(ps)	τ_2(ps)	τ_3(ps)	c
MAF	0.220	0.444	3.0	566.9	2020.4	0.999
EAF	0.177	0.100	0.6	50.0	2641.0	0.994
PAF	0.271	0.129	0.6	51.9	3398.7	0.983
EAA	0.278	0.116	0.6	63.9	3297.7	0.985
EAP	0.350	0.124	0.886	70.3	3478.9	0.981

Table S8: The ionic conductivities from MSD and velocity autocorrelation functions which were calculated from the Nernst-Einstein (σ_{NE}) equation and from the Green-Kubo (σ_{GK}) equation.

IL	σ_{NE}	σ	Ionicity
MAF	39.66	23.80	0.60
EAF	7.75	4.65	0.60
PAF	1.68	0.97	0.58
EAA	2.25	1.08	0.48
EAP	1.36	0.64	0.47

Figure S1. Fitting of centre of mass residence autocorrelation functions with triexponential function. Black curve indicates the original data and red curve indicates the fitting.



xyz files for optimized structures of individual ions.

Methylammonium (MA)

Element	x	y	z
C	0.00000000	-0.80184200	0.00000000
H	0.51600000	-1.14184200	0.89400000
H	0.51600000	-1.14184200	-0.89400000
H	-1.03200000	-1.14184200	0.00000000
N	0.00000000	0.71115800	0.00000000
H	0.95400000	1.08615800	0.00000000
H	-0.47700000	1.08615800	-0.82600000
H	-0.47700000	1.08615800	0.82600000

Ethylammonium (EA)

C	1.31518200	-0.13857000	0.00000000
H	1.43233300	-0.76054200	0.89000000
H	2.12900600	0.58762700	0.00000000
H	1.43233300	-0.76054200	-0.89000000
C	0.00000000	0.61111100	0.00000000
H	-0.12915100	1.23208000	0.88600000
H	-0.12915100	1.23208000	-0.88600000
N	-1.17776400	-0.36417400	0.00000000
H	-1.15261600	-0.97116800	0.82500000
H	-2.07688200	0.12560800	0.00000000
H	-1.15261600	-0.97116800	-0.82500000

Propylammonium (PA)

C	-1.58409100	-0.56095100	0.12917100
H	-1.68709000	-0.60395500	1.21617100

H	-2.58609500	-0.47899200	-0.29182900
H	-1.19005200	-1.52193400	-0.21782900
C	-0.73114000	0.63208400	-0.30882900
H	-0.65014200	0.67508800	-1.39982900
H	-1.21917800	1.56406400	-0.01182900
C	0.65785800	0.67414100	0.31017100
H	1.22882200	1.54716500	-0.00382900
H	0.62685900	0.64114000	1.39917100
N	1.48390800	-0.54082500	-0.11582900
H	1.60790900	-0.56182000	-1.13182900
H	2.41290800	-0.53778700	0.31417100
H	1.01294300	-1.40884400	0.15517100

Formate (FRM)

C	0.00000000	0.00000000	0.31582600
H	0.00000000	0.00000000	1.45182600
O	0.00000000	1.13600000	-0.20917400
O	0.00000000	-1.13600000	-0.20917400

Acetate (ACT)

C	-1.35028000	-0.04725400	-0.00000100
H	-1.73228200	0.47826100	0.88132700
H	-1.73249800	0.48033200	-0.88004900
H	-1.72228300	-1.07459500	-0.00117200
C	0.21008000	0.00119000	-0.00002400
O	0.70371600	1.15539400	0.00000000
O	0.79981700	-1.10634600	0.00000500

Propionate (PRP)

C	-1.90572700	0.08549700	-0.07479800
H	-1.94778700	0.53235400	-1.07207900
H	-1.92769100	0.91190700	0.63792100
H	-2.80846900	-0.52536900	0.06339100
C	-0.63092600	-0.73818500	0.10134400
H	-0.63331500	-1.22867500	1.08279600
H	-0.58365100	-1.54744600	-0.63501600
C	0.70890800	0.06576300	0.00686100
O	1.74019900	-0.64438100	-0.07795400
O	0.61822300	1.31672900	0.04327200