Molecular Dynamics Simulations of Ammonium/Phosphonium-based Protic Ionic Liquids: Influence of Alkyl to Aryl group†

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Supporting Information:

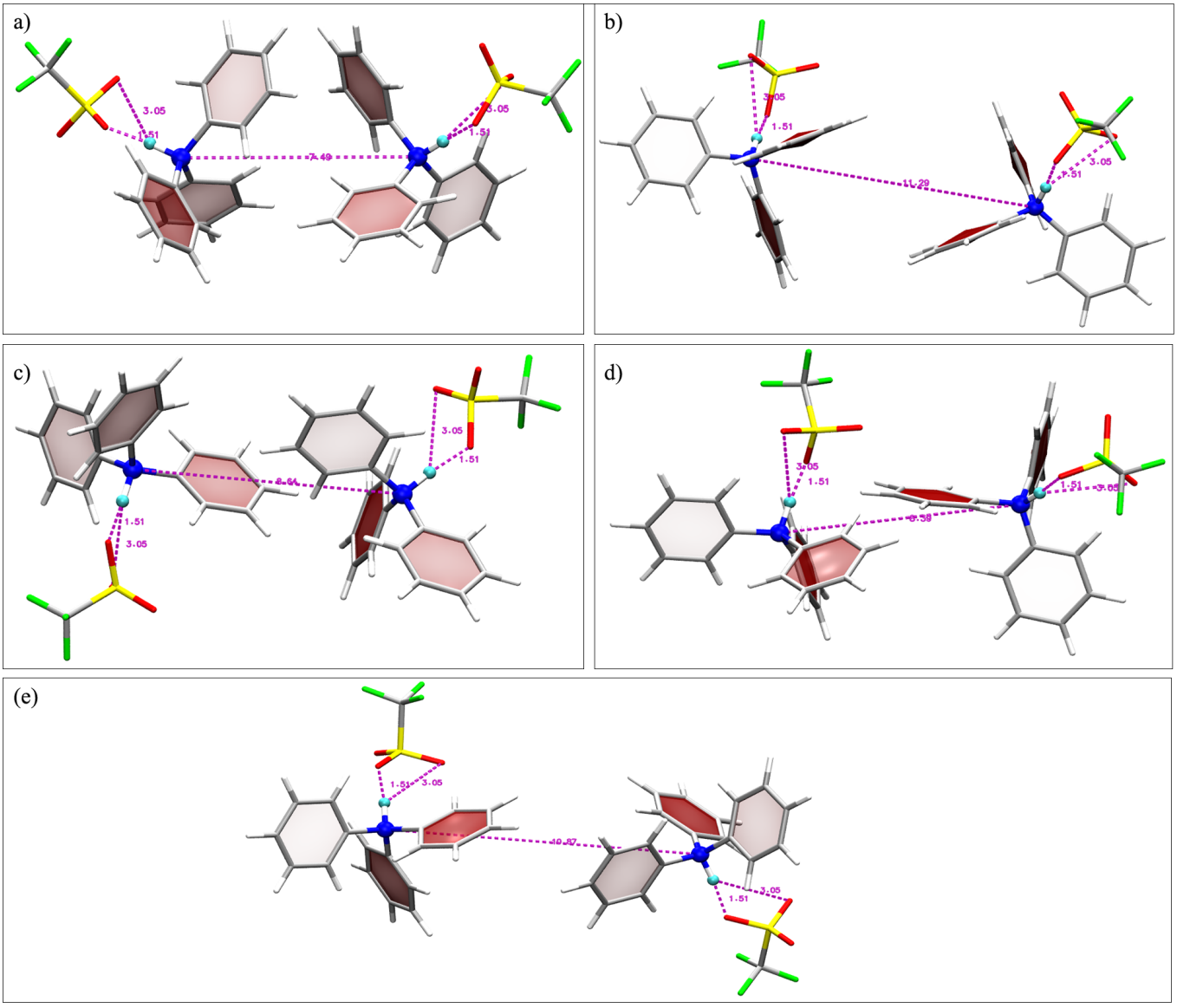


Figure S1: (a-e) Initial five configuration of $[HN(Ph)_3][TFO]$ dimer chosen from molecular dynamics simulations trajectory for geometry optimization. Similarly, Initial five configuration were chosen for all geometry optimization calculations.

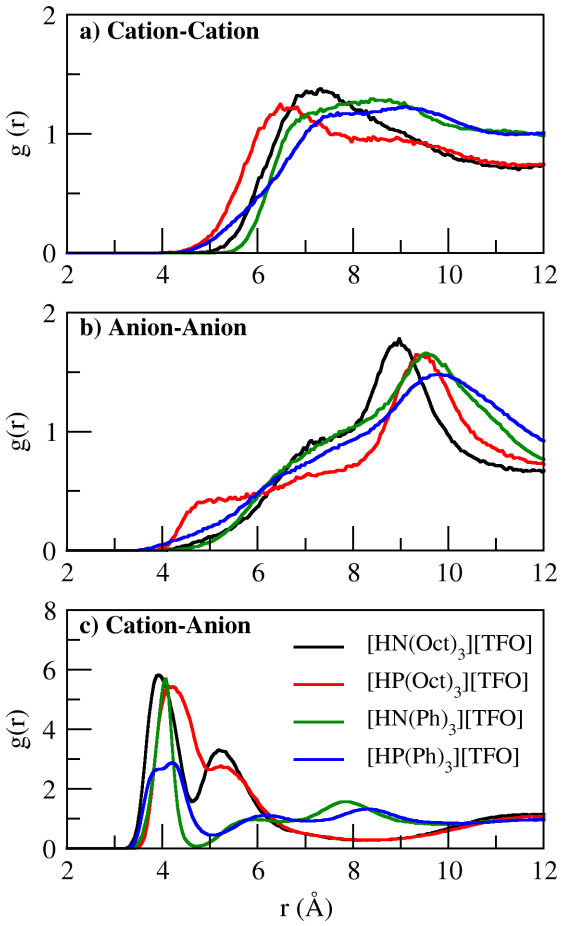


Figure S2: Center of mass radial distribution functions (RDF) of PILs calculated from MD simulations for a) cation-cation, b) anion-anion, and c) cation-anion.

Table S1: Partial charges on cations and anions except alkyl H-atoms of $[HN(Oct)_3][TFO]$ and $[HP(Oct)_3][TFO]$ PILs.

$[HN(Oct)_3][TFO]$				$[HP(Oct)_3][TFO]$			
Atom	**q**	**Atom**	**q**	**Atom**	**q**	**Atom**	**q**
N1	0.066465	C18	-0.335340	P1	0.766050	C18	-0.329009
H2	0.242201	C19	-0.073979	H2	0.013265	C19	-0.420372
C3	-0.098059	C20	-0.190648	C3	-0.444449	C20	-0.090018
C4	-0.180680	C21	-0.111450	C4	-0.080590	C21	-0.125451
C5	-0.116401	C22	-0.136636	C5	-0.132874	C22	-0.136031
C6	-0.133621	C23	-0.127941	C6	-0.134696	C23	-0.127197
C7	-0.127661	C24	-0.144015	C7	-0.129010	C24	-0.142829
C8	-0.144207	C25	-0.064543	C8	-0.139568	C25	-0.059798
C9	-0.061334	C26	-0.327284	C9	-0.065352	C26	-0.330815
C10	-0.333611	C78	0.457767	C10	-0.331992	C78	0.456468
C11	-0.108311	S79	1.118753	C11	-0.446683	S79	1.110954
C12	-0.170702	O80	-0.597085	C12	-0.070656	O80	-0.616202
C13	-0.115060	O81	-0.639948	C13	-0.130923	O81	-0.592324
C14	-0.133530	O82	-0.557984	C14	-0.134149	O82	-0.557875
C15	-0.129696	F83	-0.203052	C15	-0.127443	F83	-0.206201
C16	-0.145518	F84	-0.175192	C16	-0.145022	F84	-0.175825
C17	-0.056925	F85	-0.180487	C17	-0.059266	F85	-0.184408
Note: For anion atoms - refer to serial number 78 to 85.							

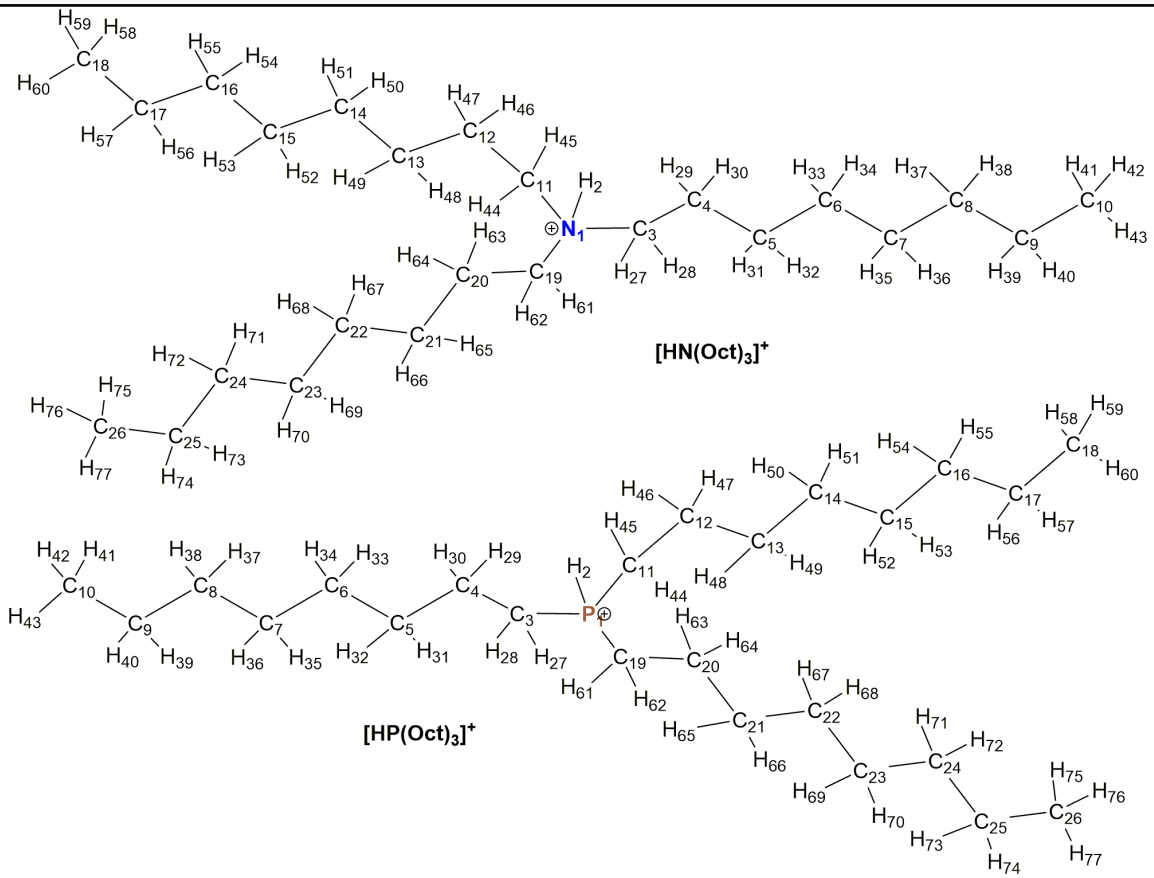
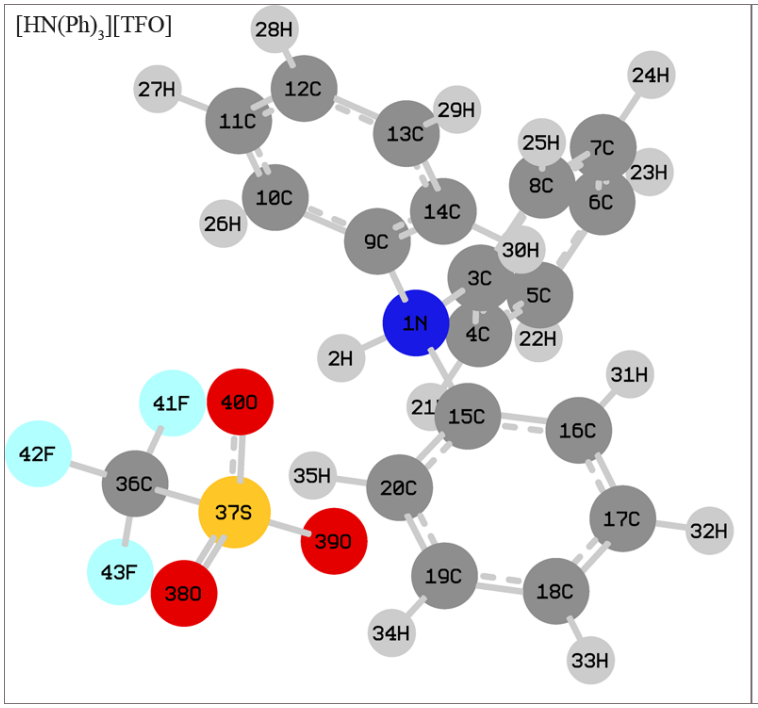


Table S2: Partial charges on H-atoms bonded with carbon atoms of alkyl chain of $[HN(Oct)_3][TFO]$ and $[HP(Oct)_3][TFO]$ PILs.

$[HN(Oct)_3][TFO]$				**$[HP(Oct)_3][TFO]$**			
Atom	**q**	**Atom**	**q**	**Atom**	**q**	**Atom**	**q**
H27	0.107480	H53	0.059071	H27	0.161239	H53	0.059318
H28	0.084152	H54	0.070904	H28	0.145889	H54	0.072305
H29	0.119723	H55	0.064146	H29	0.108768	H55	0.064739
H30	0.083028	H56	0.059281	H30	0.073274	H56	0.058616
H31	0.075741	H57	0.056588	H31	0.075443	H57	0.056608
H32	0.064973	H58	0.099057	H32	0.067507	H58	0.099284
H33	0.078852	H59	0.099700	H33	0.079066	H59	0.099214
H34	0.067407	H60	0.097653	H34	0.067857	H60	0.093072
H35	0.065963	H61	0.086800	H35	0.066357	H61	0.145101
H36	0.063988	H62	0.080503	H36	0.063686	H62	0.141250
H37	0.069002	H63	0.114011	H37	0.069803	H63	0.105605
H38	0.065207	H64	0.090036	H38	0.065274	H64	0.077065
H39	0.060362	H65	0.069438	H39	0.059013	H65	0.068784
H40	0.058224	H66	0.060561	H40	0.058478	H66	0.061756
H41	0.100796	H67	0.086875	H41	0.098810	H67	0.086712
H42	0.098520	H68	0.070848	H42	0.100452	H68	0.070766
H43	0.098854	H69	0.064789	H43	0.097411	H69	0.064010
H44	0.104338	H70	0.060726	H44	0.162459	H70	0.059792
H45	0.085459	H71	0.070277	H45	0.146475	H71	0.071277
H46	0.110317	H72	0.066003	H46	0.103478	H72	0.067998
H47	0.079412	H73	0.059231	H47	0.067976	H73	0.055852
H48	0.075180	H74	0.058594	H48	0.075665	H74	0.053594
H49	0.059824	H75	0.100182	H49	0.061313	H75	0.100219
H50	0.086724	H76	0.096412	H50	0.085277	H76	0.097626
H51	0.065160	H77	0.096460	H51	0.066538	H77	0.096444
H52	0.068882			H52	0.065776		

Table S3: Partial charges on cations and anions of $[HN(Ph)_3][TFO]$ and $[HP(Ph)_3][TFO]$PILs.

$[HN(Ph)_3][TFO]$				$[HP(Ph)_3][TFO]$			
Atom	**q**	**Atom**	**q**	**Atom**	**q**	**Atom**	**q**
N1	0.013919	H23	0.123230	P1	0.639512	H23	0.120490
H2	0.249935	H24	0.118675	H2	0.052585	H24	0.124493
C3	0.116049	H25	0.135651	C3	-0.190612	H25	0.111467
C4	-0.173763	H26	0.165503	C4	-0.067713	H26	0.140571
C5	-0.062867	H27	0.122672	C5	-0.107540	H27	0.129785
C6	-0.127347	H28	0.124492	C6	-0.081950	H28	0.117435
C7	-0.074024	H29	0.120834	C7	-0.114604	H29	0.122787
C8	-0.203854	H30	0.137245	C8	-0.066752	H30	0.108096
C9	0.128400	H31	0.135578	C9	-0.199174	H31	0.121397
C10	-0.184159	H32	0.118802	C10	-0.051020	H32	0.128645
C11	-0.064441	H33	0.125268	C11	-0.109035	H33	0.119439
C12	-0.125715	H34	0.127855	C12	-0.080513	H34	0.122532
C13	-0.071231	H35	0.156055	C13	-0.119653	H35	0.113307
C14	-0.198277	C36	0.484406	C14	-0.069980	C36	0.477587
C15	0.121896	S37	1.068187	C15	-0.186086	S37	1.055113
C16	-0.196100	O38	-0.540139	C16	-0.048576	O38	-0.526015
C17	-0.072219	O39	-0.553733	C17	-0.103979	O39	-0.579793
C18	-0.126890	O40	-0.613413	C18	-0.082548	O40	-0.542373
C19	-0.053206	F41	-0.187322	C19	-0.113469	F41	-0.201456
C20	-0.185813	F42	-0.181703	C20	-0.071286	F42	-0.178952
H21	0.154159	F43	-0.178713	H21	0.140781	F43	-0.180907
H22	0.126118			H22	0.127964		



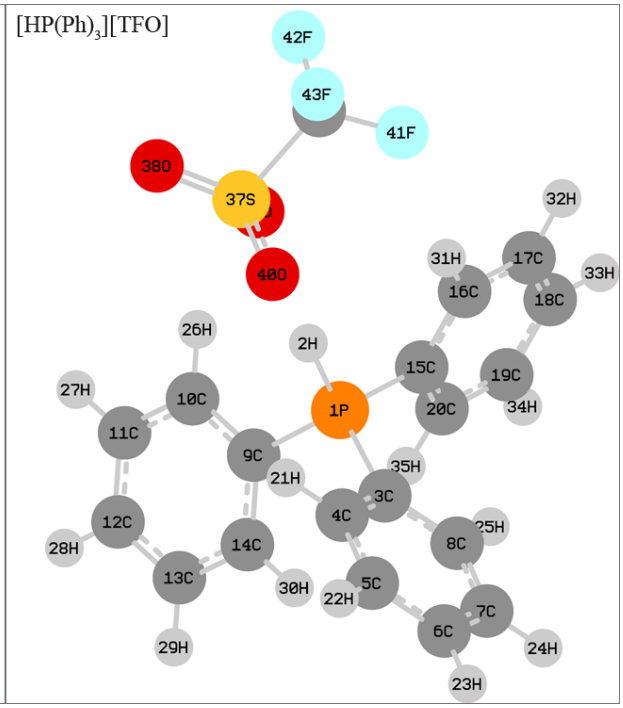


Table S4: Non-bonding (except partial charges) and bonding force field parameters for $[HN(Ph)_3][TFO]$ and $[HP(Ph)_3][TFO]$.

Atom	ε (kcal/mol)	σ (Å)		
N	0.1500	3.2960		
P	0.8368	3.7420		
H_X	0.1570	1.1050		
CA	0.0700	3.5500		
HA	0.0300	2.4200		
C	0.0359	3.5000		
F	0.1800	3.5500		
S	0.1000	2.8000		
O	0.0429	2.9500		
bond	k (kcal/(mol Å^2)	bond length (Å)		
X - H_X	434.000	1.090 (for N) & 1.437 (for P)		
X - CA	481.000	1.340 (for N) & 1.840 (for P)		
CA - CA	469.000	1.400		
CA - HA	367.000	1.080		
C - S	235.421	1.818		
F - C	441.802	1.323		
S - O	637.069	1.442		
Angle	k_θ (kcal/(mol rad^2))	bond angle (θ°)		
X - CA - CA	70.00	120.1		
H_X - X - CA	35.00	111.0		
CA - X - CA	50.00	109.5		
CA - CA - CA	63.000	120.0		
CA - CA - HA	35.000	120.0		
C - S - O	207.935	102.6		
S - C - F	165.869	111.8		
O - S - O	231.596	115.3		
F - C - F	186.663	107.1		
Dihedral	C_1	C_2	C_3	C_4
X - CA - CA - CA	0.000	7.250	0.000	0.00
X - CA - CA - HA	0.000	7.250	0.000	0.00
H_X - X - CA - CA	0.000	2.030	0.000	0.00
CA - CA - X - CA	-7.582	3.431	3.198	0.00
CA - CA - CA - CA	0.000	7.250	0.000	0.00
CA - CA - CA - HA	0.000	7.250	0.000	0.00
HA - CA - CA - HA	0.000	7.250	0.000	0.00
F - C - S - O	0.000	0.000	0.347	0.00

X: N- or P- atom; H_X: Hydrogen atom attached to Nitrogen or Phosphorus; CA: aromatic carbon atom; HA: aromatic hydrogen atom, and dihedral coefficients are in kcal/mol.

Table S5: Non-bonding (except partial charges) and bonding force field parameters for $[HN(Oct)_3][TFO]$ and $[HP(Oct)_3][TFO]$.

Atom	ε (kcal/mol)	σ (Å)		
N	0.1500	3.296		
P	0.8368	3.742		
CM	0.1094	3.475		
CE	0.1094	3.475		
CT	0.0894	3.564		
H_X	0.0157	1.105		
HM	0.0157	1.960		
HE	0.0157	2.650		
C	0.0359	3.500		
F	0.0450	3.350		
S	0.3400	3.831		
O	0.0960	3.314		
bond	k (kcal/(mol Å^2))	bond length (Å)		
X - H	434.000	1.010 (for N) & 1.437 (for P)		
X - CM	382.000	1.448		
C - HM	340.000	1.090		
CM - CE	268.000	1.529		
C - HE	340.000	1.090		
F - C	441.802	1.323		
S - C	235.421	1.818		
S - O	637.069	1.442		
Angle	k_θ (kcal/(mol rad^2))	bond angle (θ°)		
C - X - C	51.800	107.20		
C - X - H	35.000	109.50		
X - C - H	35.000	109.50		
X - C - C	56.200	109.47		
C - C - H	37.500	110.70		
C - C - H	37.500	110.70		
H - C - H	33.000	107.80		
H - C - H	33.000	107.80		
F - C - F	186.663	107.10		
S - C - F	165.869	111.80		
O - S - C	207.935	102.60		
O - S - O	231.596	115.30		
C - C - C	116.700	112.70		
Dihedral	C_1	C_2	C_3	C_4
C - X - C - H	0.000	0.000	0.560	0.000
C - C - X - H	0.416	-0.128	0.695	0.000
C - X - C - C	-0.190	-0.417	0.418	0.000
H - X - C - H	0.000	0.000	0.400	0.000
X - C - C - H	-1.013	-0.709	0.473	0.000
H - C - C - H	0.000	0.000	0.318	0.000
F - C - S - O	0.000	0.000	0.347	0.000

X: N- or P- atom; H_X: Hydrogen atom attached to N or P atom; CM: Carbon attached to N or P atom; CE: CH_2 carbon; CT: terminal alkyl chain carbon, and dihedral coefficients are in kcal/mol.

Table S6: The distance and respective angle calculated from optimized structure of $[HN(Ph)_3][TFO]$ and $[HP(Ph)_3][TFO]$ for Hydrogen-bonding and C-H/π (Phenyl ring) interactions.

$[HN(Ph)_3][TFO]$	**monomer**	**dimer**	**trimer**	**tetramer**
N–H$\cdots$O	1.43 Å (173°)	1.43 Å (173°)	1.41 Å (175°)	1.43 Å (174°)
		1.44 Å (171°)	1.41 Å (178°)	1.43 Å (173°)
			1.50 Å (172°)	1.44 Å (164°)
				1.47 Å (174°)
C–H$\cdots\pi$	-	2.8 Å (147°)	2.65 Å (153°)	3.43 Å (150°)
			2.98 Å (158°)	2.90 Å (158°)
$[HP(Ph)_3][TFO]$	**monomer**	**dimer**	**trimer**	**tetramer**
P–H$\cdots$O	1.50 Å (175°)	1.60 Å (170°)	1.81 Å (168°)	1.75 Å (178°)
			1.81 Å (169°)	1.76 Å (173°)
			1.83 Å (166°)	1.75 Å (165°)
				1.76 Å (175°)
C–H$\cdots\pi$	-	2.74 Å (147°)	2.50 Å (153°)	2.57 Å (145°)
			2.50 Å (153°)	2.60 Å (158°)
				2.57 Å (145°)
				2.60 Å (158°)
Note: For $[HP(Ph)_3][TFO]$ dimer, only one hydrogen bond is observed which fulfil hydrogen bond distance and angle criteria.				

Table S7: Diffusion coefficients ($\times 10^{-6}$ cm^2 s^{-1}) calculated from MD simulations of tri-octyl/tri-phenyl ammonium triflate and tri-octyl/tri-phenyl phosphonium triflate PILs.

	Cation				**Anion**			
PIL	**393 K**	**417 K**	**441 K**	**465 K**	**393 K**	**417 K**	**441 K**	**465 K**
$[HN(Oct)_3][TFO]$	0.83	1.79	4.68	7.40	0.91	2.22	5.16	8.98
$[HP(Oct)_3][TFO]$	1.20	2.99	6.23	11.38	1.41	3.86	7.60	14.12
$[HN(Ph)_3][TFO]$	0.55	1.96	5.43	11.46	0.59	2.44	6.42	13.50
$[HP(Ph)_3][TFO]$	5.27	11.67	20.43	32.74	6.77	14.87	26.80	41.89

The ionic conductivity within the approximation of independent ion motion can be calculated using the Nernst-Einstein relation $\sigma_{NE} = \frac{N_i q^2}{V k_B T}(D^+ + D^-)$

where V is the volume, temperature is T, the number of ion-pairs is N_i, q is the effective net charge of the ions and k_B is the Boltzmann constant.

Table S8: N-E Conductivity (σ_{NE} in S m^{-1}) calculated from diffusion coefficient of tri-octyl/tri-phenyl ammonium triflate and tri-octyl/tri-phenyl phosphonium triflate PILs.

PIL	**393 K**	**417 K**	**441 K**	**465 K**
$[HN(Oct)_3][TFO]$	0.05	0.11	0.26	0.41
$[HP(Oct)_3][TFO]$	0.08	0.19	0.35	0.60
$[HN(Ph)_3][TFO]$	0.05	0.18	0.46	0.88
$[HP(Ph)_3][TFO]$	0.47	0.95	1.57	2.31