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

Supporting Information to

Targeted Modifications in Ionic Liquids – from Understanding to Design

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Contents

1. Abbreviations

Abbreviations for ions in this perspective are given in Figure S1.

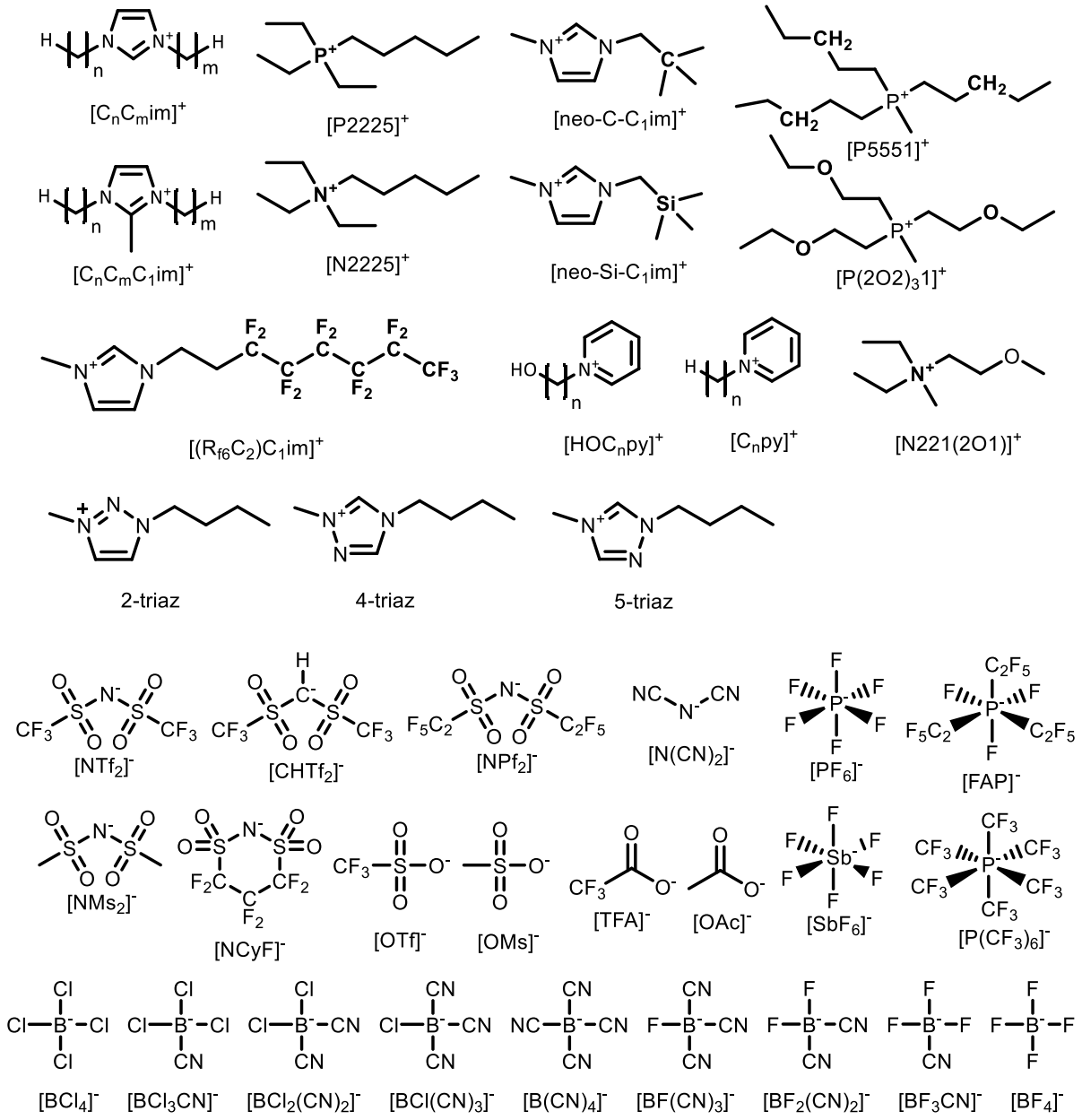

Figure S1: Abbreviations for cations (top) and anions (bottom).

2. Potential energy calculations

We followed the approach described in Ref. [S1] to obtain the potential energy as a function of the dihedral angle in 5° steps at the full MP2/cc-pVTZ//B3LYP-GD3BJ/6-311+G(d,p) level of theory using the Gaussian software package, revision D.01.[S2]

Table S1: Energy as a function of dihedral angles for rotation around the given bonds. Energies are given in kJ/mol.

	[neo-C-C_1im]$^+$		[neo-Si-C_1im]$^+$			[neo-C-C_1im]$^+$		[neo-Si-C_1im]$^+$	
Angle / degrees	C–C bond	N–C bond	C–Si bond	N–C bond	Angle / degrees	C–C bond	N–C bond	C–Si bond	N–C bond
0	21.8	20.6	8.5	8.5	185	0.2	23.6	0.0	10.3
5	21.4	20.6	8.2	8.5	190	1.1	23.2	0.3	10.1
10	19.9	20.5	8.0	8.5	195	2.5	22.5	0.7	9.7
15	17.8	20.2	7.3	8.4	200	4.4	21.5	1.4	9.2
20	15.2	19.9	6.5	8.2	205	6.7	20.4	3.5	8.6
25	12.4	19.3	5.5	7.9	210	9.3	19.1	4.5	7.9
30	9.6	18.6	4.4	7.6	215	12.2	17.5	5.6	7.2
35	7.0	17.6	3.4	7.3	220	15.1	15.7	6.6	6.4
40	4.7	16.4	1.4	6.9	225	17.8	13.5	6.6	5.6
45	2.8	14.7	0.7	6.4	230	20.0	11.3	7.5	4.7
50	1.3	12.5	0.2	5.7	235	21.4	9.0	8.2	3.8
55	0.4	10.2	0.0	4.9	240	21.8	6.8	8.5	3.0
60	0.0	7.7	0.0	4.0	245	21.2	4.9	8.5	2.2
65	0.1	5.5	0.0	3.1	250	19.5	3.2	8.1	1.4
70	0.8	3.6	0.4	2.1	255	17.1	1.8	7.5	0.8
75	2.1	2.0	0.9	1.3	260	14.3	0.8	6.7	0.3
80	3.8	0.9	2.6	0.7	265	11.4	0.2	5.7	0.1
85	6.0	0.2	3.7	0.2	270	8.6	0.0	4.7	0.0
90	8.6	0.0	4.7	0.0	275	6.0	0.2	2.5	0.2
95	11.4	0.2	5.7	0.1	280	3.8	0.9	1.6	0.7
100	14.3	0.8	6.7	0.3	285	2.1	2.0	0.9	1.3
105	17.1	1.8	6.8	0.8	290	0.8	3.6	0.3	2.1
110	19.5	3.2	7.6	1.4	295	0.1	5.5	0.0	3.1
115	21.1	4.9	8.2	2.2	300	0.0	7.7	0.0	4.0
120	21.8	6.8	8.5	3.0	305	0.4	10.2	0.0	4.9
125	21.5	9.0	8.4	3.8	310	1.3	12.5	0.2	5.7
130	20.0	11.3	8.0	4.7	315	2.8	14.7	0.7	6.4
135	17.8	13.5	7.4	5.6	320	4.7	16.4	1.4	6.9
140	15.1	15.7	6.5	6.4	325	7.0	17.6	2.2	7.3
145	12.2	17.5	5.6	7.2	330	9.6	18.6	4.4	7.6
150	9.3	19.1	4.5	7.9	335	12.4	19.3	5.4	7.9
155	6.7	20.4	3.5	8.6	340	15.2	19.9	6.5	8.2
160	4.4	21.5	2.5	9.2	345	17.8	20.2	7.3	8.4
165	2.5	22.5	0.7	9.7	350	19.9	20.5	8.0	8.5
170	1.1	23.2	0.3	10.1	355	21.3	20.6	8.4	8.5
175	0.2	23.6	0.0	10.3	360	21.8	20.6	8.5	8.5
180	0.0	23.7	0.0	10.3					

3. Volume and charge arm calculations

Ab initio calculations to obtain ion volumes were performed following the approach in Ref. [S1] at the full MP2/cc-pVTZ//B3LYP-GD3BJ/6-311+G(d,p) level of theory using the Gaussian software package, revision D.01.[S2] Then, the Multiwfn[S3,4] software package was used to integrate the MP2 density as described in Ref. [S5]. For completeness, volumes and relative charge arm lengths for the B3LYP-GD3BJ/6-311+G(d,p) level of theory are given in Table S2.

Table S2: Volumes and charge arm lengths at the DFT level of theory.

Anion (cation is always $[C_2C_1im]^+$)	Volume	Relative charge arm
$[B(CN)_4]^-$	156	0
$[BF(CN)_3]^-$	136	0.09
$[BF_2(CN)_2]^-$	115	0.12
$[BF_3(CN)]^-$	94	0.12
$[BF_4]^-$	73	0
$[B(CN)_4]^-$	156	0
$[BCl(CN)_3]^-$	154	0.01
$[BCl_2(CN)_2]^-$	152	0.01
$[BCl_3(CN)]^-$	150	0.02
$[BCl_4]^-$	147	0

4. Melting points of imidazolium $[NTf_2]^-$ salts

20 different methylation patterns of the imidazolium cation are possible. Melting points of the corresponding $[NTf_2]^-$ salts, where available to a structure search on SciFinder, are given in Figure S2.

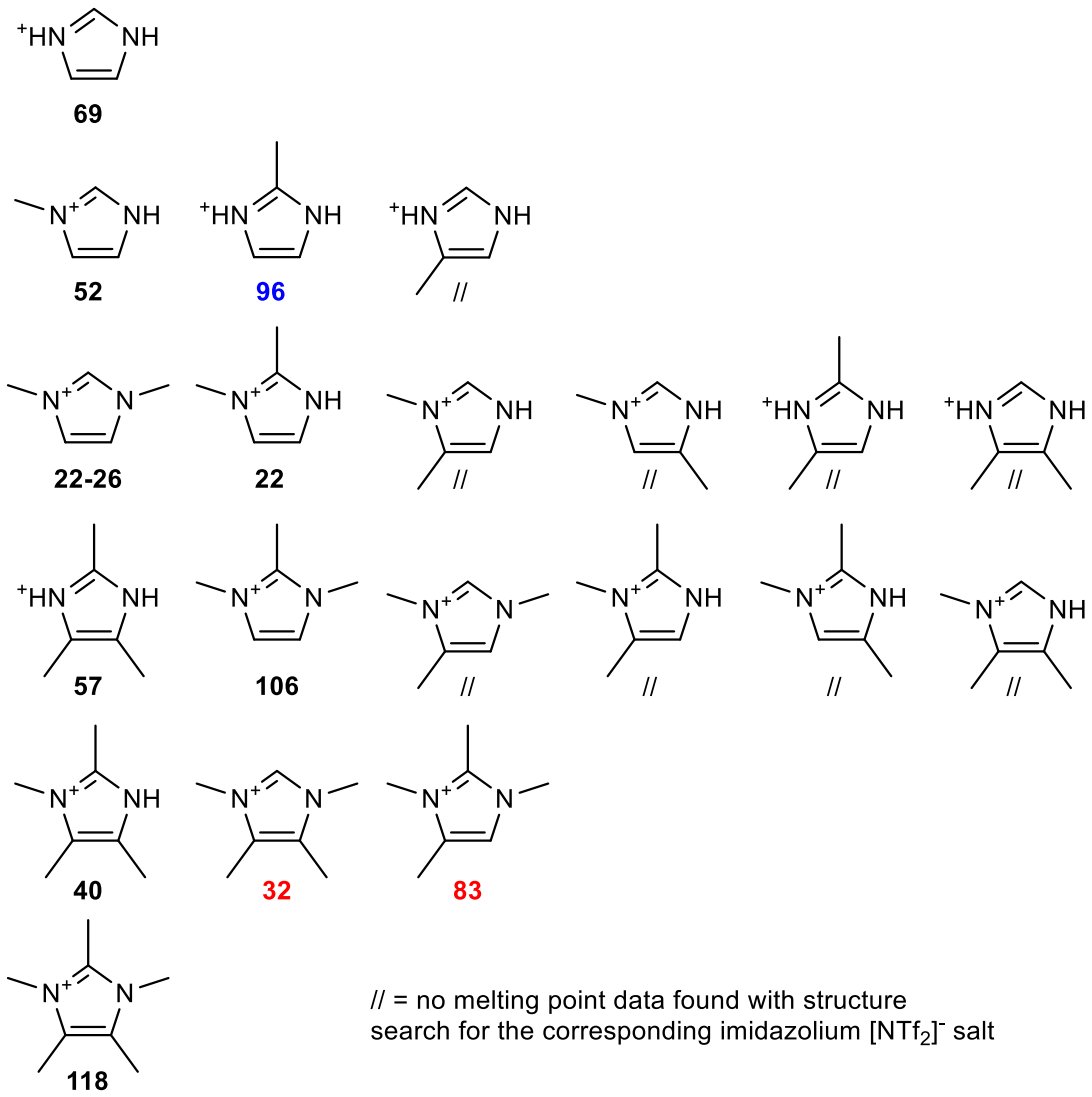

Figure S2: Possible imidazolium methylation patterns. The numbers are the melting points of the corresponding $[NTf_2]^-$ salts. Data from [S6], [S7] and [S8].

5. Isodensity conditions for $[C_4C_1im][NTf_2]$

Pressure dependent data for $[C_4C_1im][NTf_2]$[S9] allow us to estimate the viscosity at isodensity conditions, Figure S3. The viscosity at isodensity conditions is 73.1 mPa s as obtained from the fit. The pressure at isodensity conditions was interpolated, Figure S4, to yield a required pressure of 30.0 MPa.

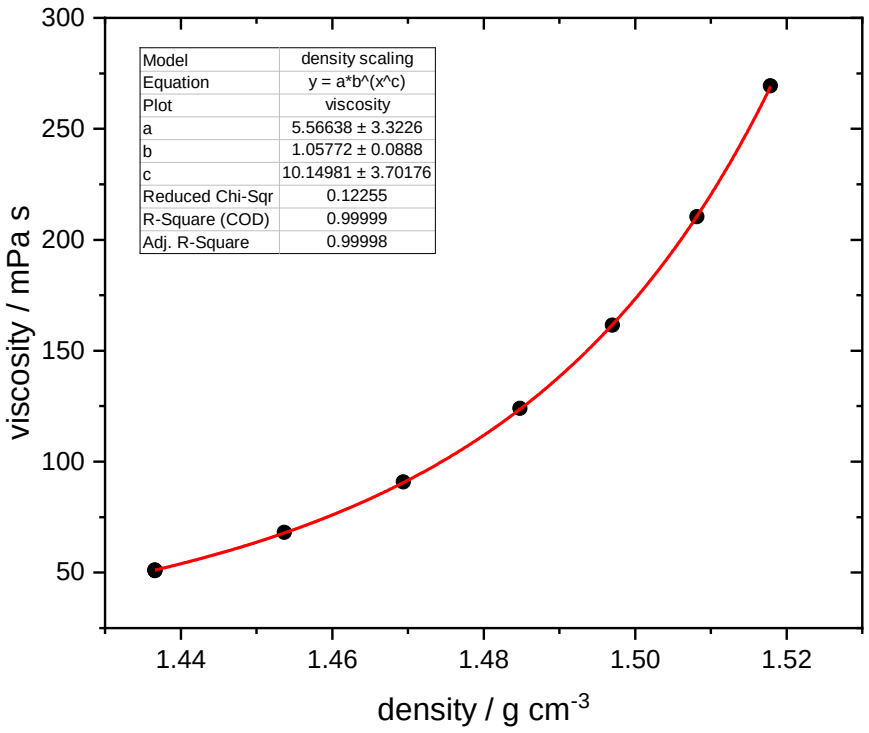

Figure S3: Viscosity as a function of density for $[C_4C_1im][NTf_2]$[S9]. The red line is a fit using a density scaling model.

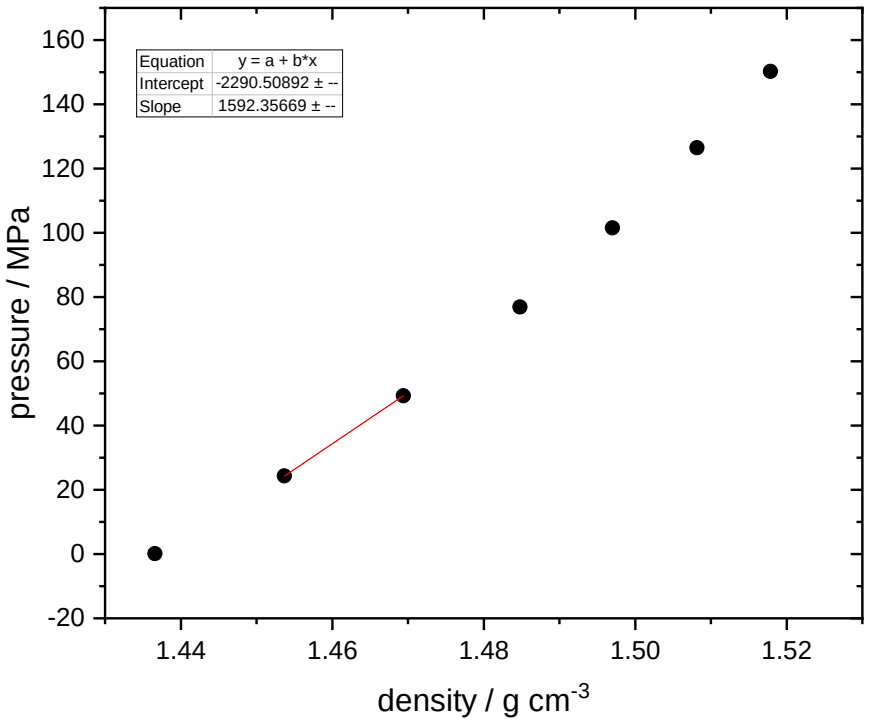

Figure S4: Pressure as a function of density for $[C_4C_1im][NTf_2]$[S9]. The required pressure was estimated by linear interpolation in the relevant region.

6. References

[S1] F. Philippi, D. Rauber, B. Kuttich, T. Kraus, C. W. M. Kay, R. Hempelmann, P. A. Hunt, T. Welton, *Phys. Chem. Chem. Phys.* **2020**, *22*, 23038–23056.

[S2] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2013**.

[S3] T. Lu, F. Chen, *J. Comput. Chem.* **2012**, *33*, 580–592.

[S4] T. Lu, F. Chen, *J. Mol. Graph. Model.* **2012**, *38*, 314–323.

[S5] F. Philippi, A. Quinten, D. Rauber, M. Springborg, R. Hempelmann, *J. Phys. Chem. A* **2019**, *123*, 4188–4200.

[S6] T. Peppel, C. Roth, K. Fumino, D. Paschek, M. Köckerling, R. Ludwig, *Angew. Chemie Int. Ed.* **2011**, *50*, 6661–6665.

[S7] D. Shang, S. Zeng, X. Zhang, X. Zhang, L. Bai, H. Dong, *J. Mol. Liq.* **2020**, *312*, 113411.

[S8] K. Fumino, T. Peppel, M. Geppert-Rybczyńska, D. H. Zaitsau, J. K. Lehmann, S. P. Verevkin, M. Köckerling, R. Ludwig, *Phys. Chem. Chem. Phys.* **2011**, *13*, 14064.

[S9] K. R. Harris, M. Kanakubo, L. A. Woolf, *J. Chem. Eng. Data* **2007**, *52*, 1080–1085.