# Supporting Information

## Phase-out-compliant fluorosurfactants: Unique methimazolium derivatives including room temperature ionic liquids

Michael Hummel[a,b], Marta Markiewicz[c], Stefan Stolte[c], Michael Noisternig[b], Doris E. Braun[b], Thomas Gelbrich[b], Ulrich J. Griesser[b], Gabriel Partl[d], Benjamin Naier[d], Klaus Wurst[d], Biljana Krüger[e], Holger Kopacka[d], Gerhard Laus[d], Hubert Huppertz[d], and Herwig Schottenberger[d]*

[a]*Department of Forest Products Technology, Aalto University, P.O.Box 16300, 00076 Aalto, Finland*

[b]*Institute of Pharmacy, Department of Pharmaceutical Technology, Leopold-Franzens University Innsbruck, Innrain 52, Innsbruck, Austria*

[c]*UFT - Center for Environmental Research and Sustainable Technology, University of Bremen, Leobener Strasse, 28359 Bremen, Germany.*

[d]*Institute of General, Inorganic and Theoretical Chemistry, Leopold-Franzens University Innsbruck, Innrain 80-82, Innsbruck. Austria*

[e]*Institute of Mineralogy and Petrography, Leopold-Franzens University Innsbruck, Innrain 52, Innsbruck. Austria*

# 1. Crystal structures

## 1. 1. Molecular geometry

Table S1. Crystallographic data and structure refinement details.

| Compound | **II**-a1 | **II**-a3 | **II**-b3 |
|---|---|---|---|
| Empirical formula | $C_{12}H_{10}F_{13}N_2SCl$ | $C_{12}H_{10}F_{13}IN_2S$ | $C_{24}H_{20}F_{32}N_4S_2Si$ |
| Moiety formula | $(C_{12}H_{10}F_{13}N_2S)^+$ $Cl^-$ | $(C_{12}H_{10}F_{13}N_2S)^+$ $I^-$ | $2(C_{12}H_{10}F_{13}N_2S)^+$ $(SiF_6)^{2-}$ |
| Formula weight | 496.73 | 588.18 | 1064.65 |
| Crystal system | Triclinic | Triclinic | Monoclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ | $P2_1/c$ |
| *a*, / Å | 6.3654(4) | 6.4269(3) | 18.463(5) |
| *b* / Å | 9.2363(5) | 8.9443(5) | 8.901(3) |
| *c* / Å | 16.0361(12) | 16.368(1) | 11.595(3) |
| α / ° | 75.231(5) | 85.570(5) | 90 |
| β / ° | 83.709(5) | 81.795(4) | 102.185(9) |
| γ / ° | 76.855(5) | 86.766(5) | 90 |
| Unit cell volume /Å$^3$ | 886.44(10) | 927.5(1) | 1862.6(9) |
| *Z* | 2 | 2 | 2 |
| $D_{calcd}$ / g cm$^{-3}$ | 1.861 | 2.11 | 1.898 |
| Absorption coefficient / mm$^{-1}$ | 0.465 | 1.97 | 0.364 |
| *F*(000) / e | 492 | 564 | 1052 |
| Crystal size / mm$^3$ | 0.40 × 0.10 × 0.06 | 0.20 × 0.12 × 0.11 | 0.13 × 0.04 × 0.04 |
| $\theta_{max(full)}$ / ° | 25.2 | 25.4 | 25.2 |
| *hkl* range | $-7 \le h \le 7$ | $-6 \le h \le 7$ | $-21 \le h \le 21$ |
| | $-11 \le k \le 11$ | $-10 \le k \le 9$ | $-10 \le k \le 10$ |
| | $-19 \le l \le 19$ | $-19 \le l \le 19$ | $-13 \le l \le 13$ |
| *T* / K | 173(2) | 173 | 173(2) |
| Reflections collected | 13865 | 5693 | 14436 |
| Independent reflections ($R_{int}$) | 3236 (0.046) | 3363 (0.027) | 3229 (0.0880) |
| Reflections [$I < 2\,\sigma(I)$] | 2536 | 2961 | 1900 |
| Restraints / parameters | 1 / 276 | 1 / 266 | 1 / 290 |
| Goodness-of-fit on $F^2$ | 1.03 | 1.02 | 1.05 |
| $R_1$ / w$R_2$ indices [$I < 2\,\sigma(I)$] | 0.044 / 0.103 | 0.029 / 0.052 | 0.090 / 0.155 |
| $R_1$ / w$R_2$ indices (all data) | 0.0620 / 0.114 | 0.036 / 0.056 | 0.156 / 0.213 |
| $\Delta\rho_{max,\ min}$ / e Å$^{-3}$ | 0.43, −0.30 | 0.40, −0.47 | 0.93 / −0.43 |

| Compound | **II**-k2 | **V**-a3 | **IX** |
|---|---|---|---|
| Empirical formula | $C_{20}H_{10}F_{30}I_2N_2S$ | $C_{20}H_{13}F_{26}IN_2S$ | $C_{15}H_{15}F_{13}N_2O_3S_2$ |
| Moiety formula | $(C_{12}H_{10}F_{13}N_2S)^+I^- \cdot C_8F_{17}I$ | $(C_{20}H_{13}F_{26}N_2S)^+$ $I^-$ | $C_{15}H_{15}F_{13}N_2O_3S_2$ |
| Formula weight | 1134.16 | 934.28 | 582.40 |
| Crystal system | Triclinic | Triclinic | Orthorhombic |
| Space group | $P\bar{1}$ | $P\bar{1}$ | *Pbca* |
| *a*, / Å | 6.4954(5) | 5.8881(3) | 8.6657(2) |
| *b* / Å | 9.2039(8) | 10.274(1) | 10.1187(4) |
| *c* / Å | 27.9195(19) | 25.481(1) | 48.601(2) |
| α / ° | 94.848(6) | 89.763(4) | 90 |
| β / ° | 91.767(6) | 87.419(4) | 90 |
| γ / ° | 95.367(7) | 77.726(3) | 90 |
| Unit cell volume /Å$^3$ | 1654.6(2) | 1504.7(2) | 4261.6(3) |
| *Z* | 2 | 2 | 8 |
| $D_{calcd}$ / g cm$^{-3}$ | 2.276 | 2.06 | 1.82 |
| Absorption coefficient / mm$^{-1}$ | 2.153 | 1.31 | 0.39 |
| *F*(000) / e | 1072 | 900 | 2336 |
| Crystal size / mm$^3$ | 0.20 × 0.19 × 0.08 | 0.39 × 0.08 × 0.03 | 0.11 × 0.08 × 0.05 |
| $\theta_{max(full)}$ / ° | 25.4 | 25.0 | 25.2 |
| *hkl* range | $-7 \le h \le 7$ | $-6 \le h \le 6$ | $-9 \le h \le 10$ |
| | $-11 \le k \le 7$ | $-12 \le k \le 10$ | $-12 \le k \le 12$ |
| | $-33 \le l \le 33$ | $-28 \le l \le 30$ | $-57 \le l \le 57$ |
| *T* / K | 173(2) | 233 | 233 |
| Reflections collected | 9260 | 7370 | 16437 |
| Independent reflections ($R_{int}$) | 5964 (0.038) | 4840 (0.038) | 3820 (0.074) |
| Reflections [$I < 2\,\sigma(I)$] | 4502 | 3459 | 2650 |
| Restraints / parameters | 448 / 592 | 0 / 452 | 1139 / 455 |
| Goodness-of-fit on $F^2$ | 1.06 | 1.07 | 1.03 |
| $R_1$ / w$R_2$ indices [$I < 2\,\sigma(I)$] | 0.0462 / 0.0977 | 0.059 / 0.152 | 0.056 / 0.128 |
| $R_1$ / w$R_2$ indices (all data) | 0.0686 / 0.1120 | 0.092 / 0.168 | 0.094 / 0.145 |
| $\Delta\rho_{max,\ min}$ / e Å$^{-3}$ | 0.12, −1.24 | 1.37, −0.70 | 0.45, −0.36 |

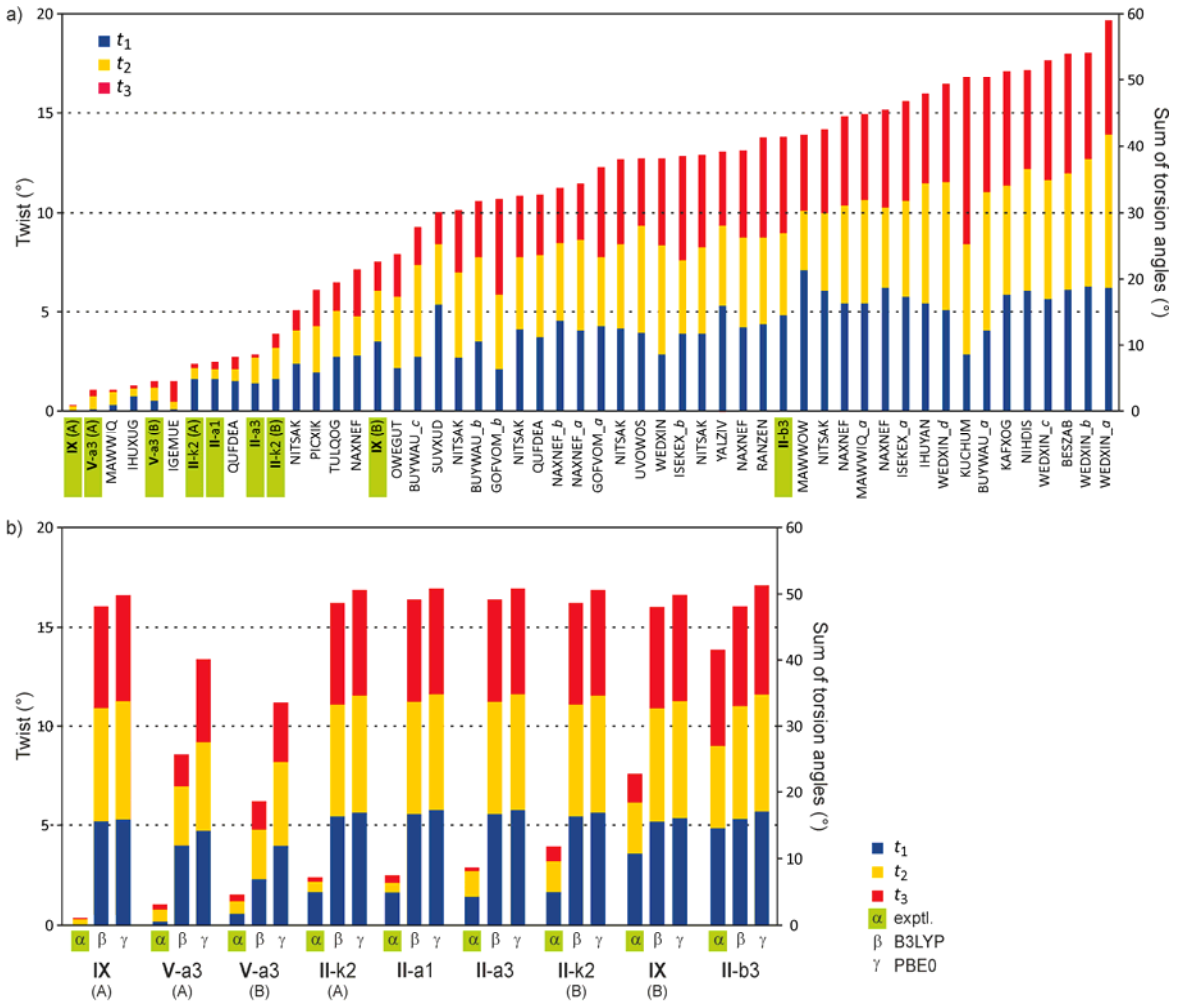


Figure S1. Torsions angles $t_1$, $t_2$ and $t_3$ (see article **Figure 2**) characterizing the twist of the fluoroalkyl tails of $CH_2C_6F_{13}$ chains a) for crystal structures contained in the CSD (CCDC refcodes) and for the crystal structures investigated in this study (green labels); b) for the six experimental crystal structures and the corresponding parameters for optimized geometries starting from the experimental conformations (B3LYP and PBE0, using the 6-31G(d,p) basis set).

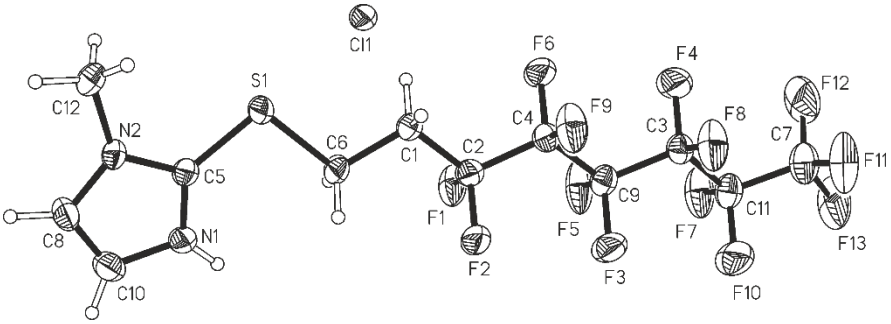


Figure S2. Asymmetric unit of **II**-a1 with thermal ellipsoids drawn at the 50% level. H atoms are drawn as spheres of arbitrary size.

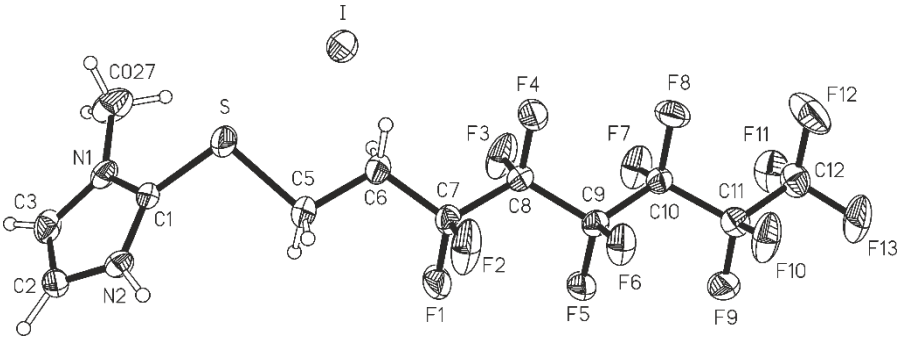


Figure S3. Asymmetric unit of **II**-a3 with thermal ellipsoids drawn at the 50% level. H atoms are drawn as spheres of arbitrary size.

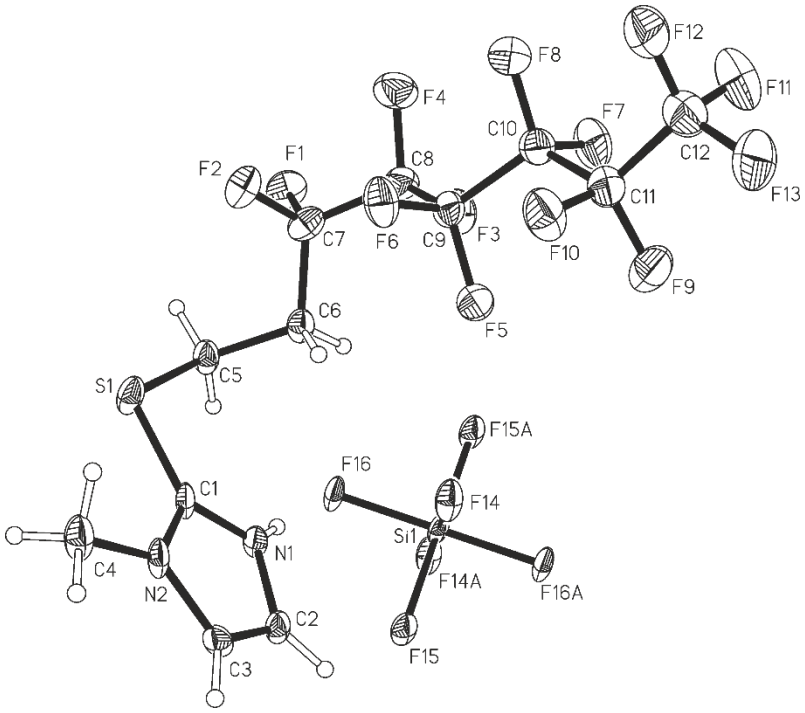


Figure S4. Molecular structure of **II**-b3 with thermal ellipsoids drawn at the 30% level. H atoms are drawn as spheres of arbitrary size (symmetry operation A: $1 - x$. $1 - y$. $1 - z$)

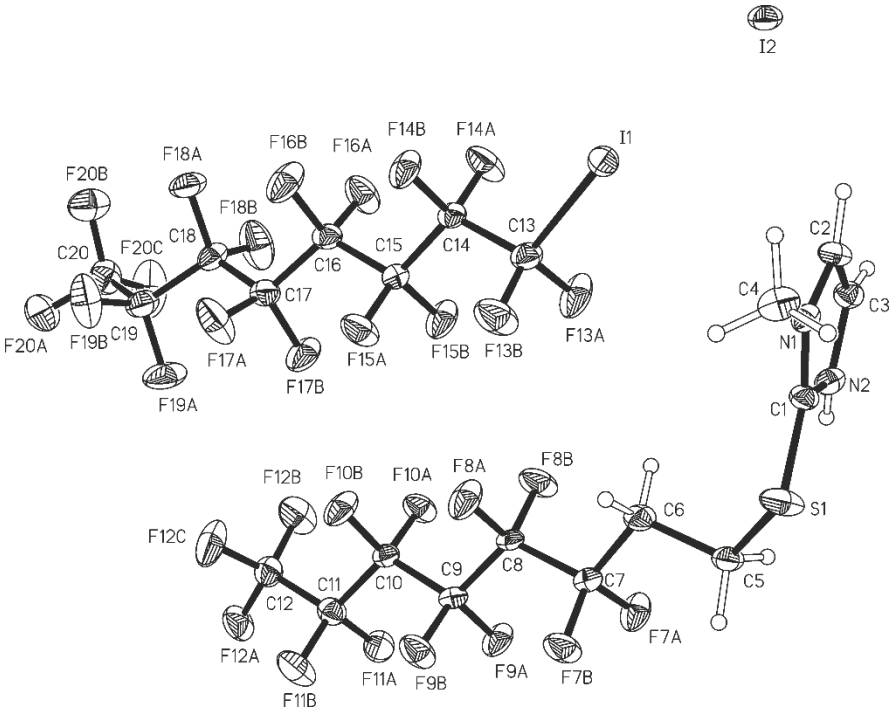


Figure S5. Asymmetric unit of **II**-k2 (main component of disorder only) with thermal ellipsoids drawn at the 30% level. H atoms are drawn as spheres of arbitrary size.

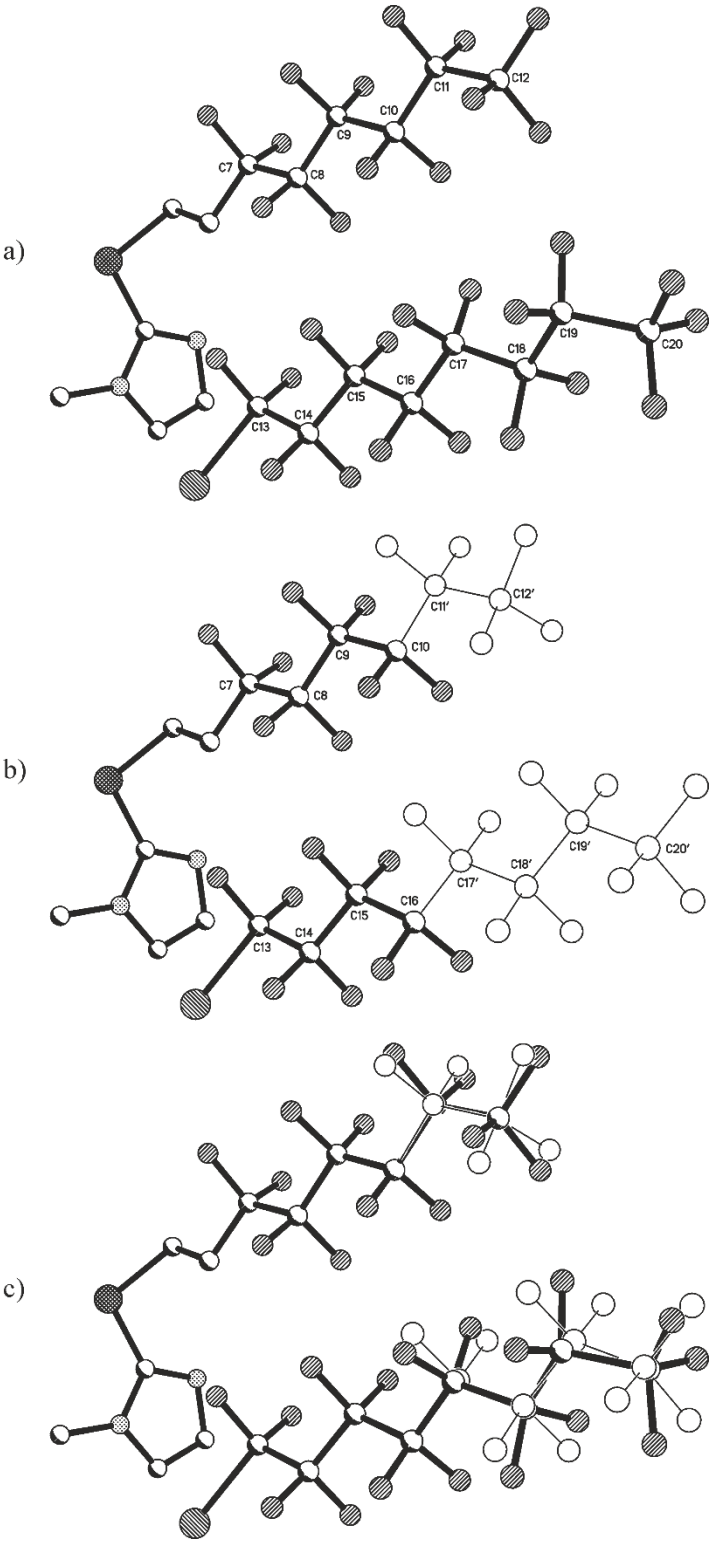


Figure S6. Disorder model for fluoroalkyl chains in **II**-k2: a) main and b) minor disorder component and c) both together. H atoms and the iodide ion are omitted for clarity.

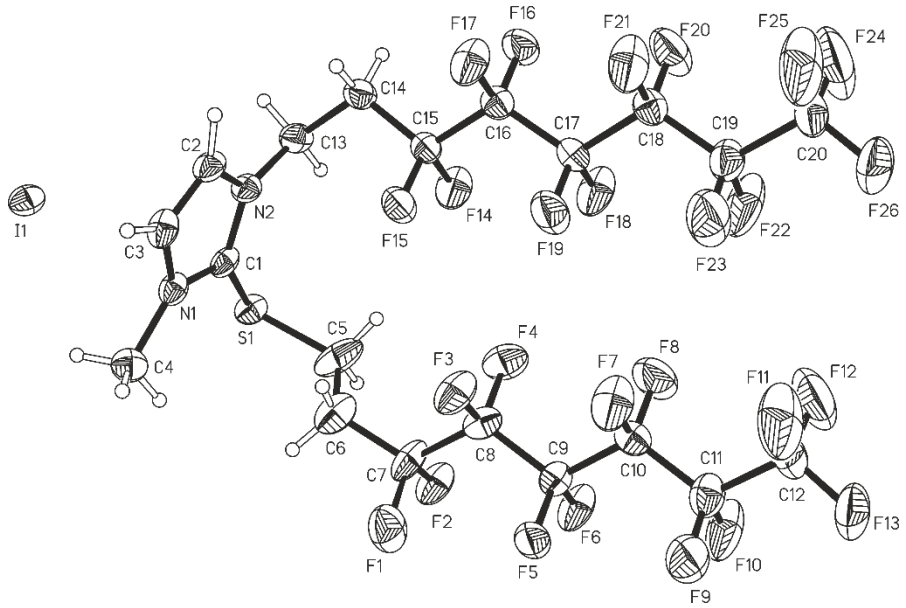


Figure S7. Asymmetric unit of **V**-a3 with thermal ellipsoids drawn at the 30% level. H atoms are drawn as spheres of arbitrary size.

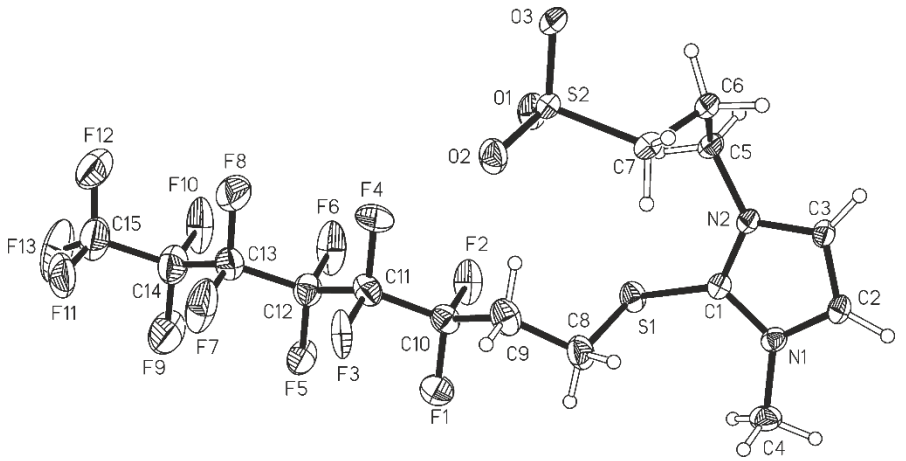


Figure S8. Asymmetric unit of **IX** (main component of disorder only) with thermal ellipsoids drawn at the 30% level. H atoms are drawn as spheres of arbitrary size.

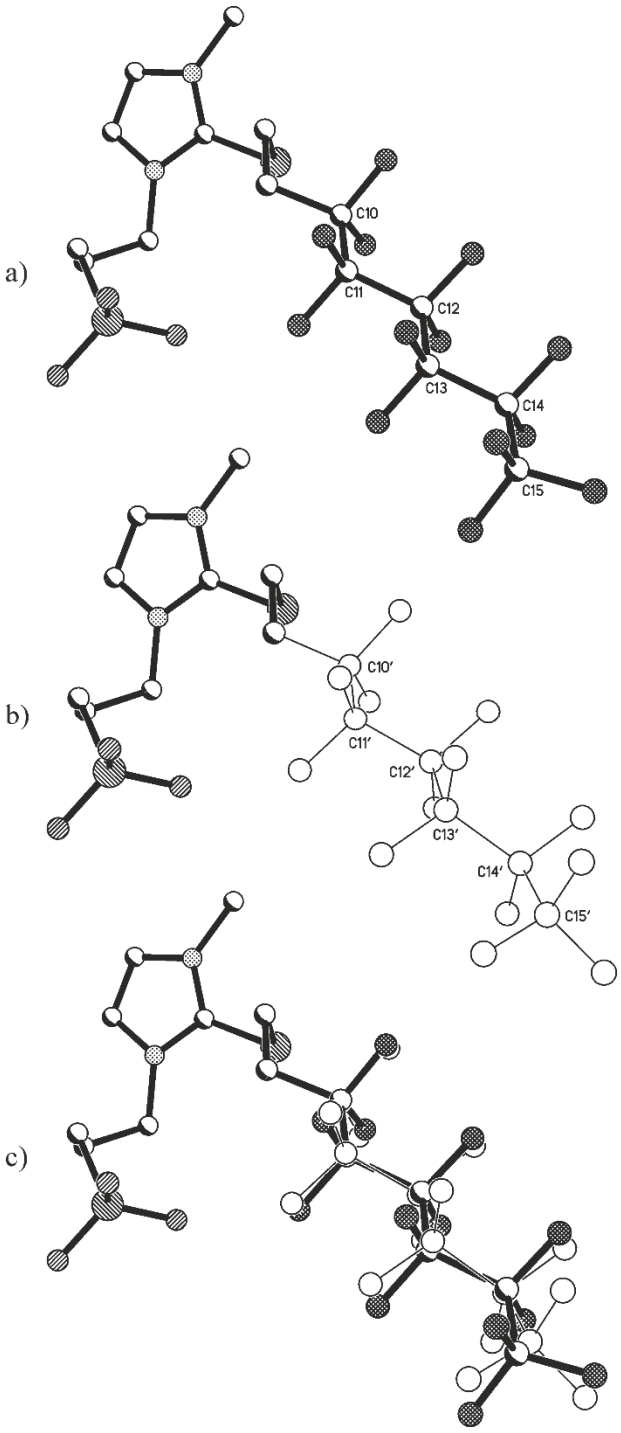


Figure S9. Disorder model for fluoroalkyl chains in **IX**: a) main and b) minor disorder component and c) both together. H atoms are omitted for clarity.

Table S2. Experimental torsion angles $t_A - t_D$ and $t_1 - t_3$ (in °) and characterizing the conformation of the cations **II** and **V** and the conformation of the zwitter ion **IX** and the twist angles (in °) of the respective $C_6F_13$ chain fragments.

| Structure | $t_A$ | $t_A$ | $t_B$ | $t_C$ | $t_D$ | $t_1$ | $t_2$ | $t_3$ | *Twist* |
|---|---|---|---|---|---|---|---|---|---|
| **II**-a1 | 172.4 | -172.3 | -177.2 | 179.6 | 175.1 | -175.1 | -178.6 | -178.8 | 2 |
| **II**-a3 [a] | 132.5 | -146.3 | -176.1 | -174.1 | -179.9 | -175.7 | -176.1 | -179.4 | 1 |
| **II**-b3 | 171.9 | -71.1 | -97.0 | -178.8 | -61.3 | -165.5 | -167.5 | -165.5 | 14 |
| **II**-k2 (A) | 148.5 | -65.8 | -159.8 | -171.9 | -173.6 | -175.0 | -178.4 | 179.3 | 2 |
| **II**-k2 (B) | 148.5 | -65.8 | -159.8 | -171.9 | -173.6 | -175.0 | -175.4 | -177.8 | 4 |
| **V**-a3 (A) [a] | 93.4 | -59.6 | -173.0 | -77.3 | -171.1 | -179.6 | -178.2 | -179.0 | 1 |
| **V**-a3 (B) [a] | 93.4 | -59.6 | -173.0 | -77.3 | -171.1 | -178.3 | -178.1 | -179.0 | 2 |
| **IX** (A) | 75.4 | 122.6 | 71.8 | 173.2 | 177.2 | 177.1 | -179.2 | -179.8 | 0 |
| **IX** (B) | 75.4 | 122.6 | 71.8 | 173.2 | 177.2 | 169.3 | 172.3 | 175.6 | 8 |

[a] Structure model inverted.

## 1. 2. Intermolecular interactions

Table S3. Geometric parameters for hydrogen bonds.

| *D*–H···*A* | *d*(*D*–H) / Å | *d*(H···*A*) / Å | *d*(*D*···*A*) / Å | ∠(*D*H*A*) / ° |
|---|---|---|---|---|
| **II**-a1 | | | | |
| N1–H1···Cl1[i] | 0.859(10) | 2.171(12) | 3.019(2) | 169(3) |
| **II**-a3 | | | | |
| N2–H2···I[ii] | 0.877(18) | 2.582(19) | 3.443(3) | 167(3) |
| **II**-b3 | | | | |
| N1–H1···F16 | 0.858(10) | 1.905(16) | 2.759(7) | 173(8) |
| **II**-k2 | | | | |
| N2–H2···I2[iii] | 0.90(2) | 2.59(3) | 3.462(5) | 165(5) |

Symmetry transformations: (i) *x*+1. *y*. *z*; (ii) *x*–1. *y*. *z*; (iii) *x*. *y*+1. *z*;

Table S4. Number of intermolecular F···F contact distances $d$ (in Å) per molecule which are associated with short C–F···F–C interactions for which the expression ($d < S + \Delta$) is true (with $S = 2.94$ Å, which is twice the van der Waals radius[1] of fluorine).

| Structure | $\Delta = -0.1$ Å | $\Delta = 0.0$ Å | $\Delta = 0.1$ Å | $\Delta = 0.2$ Å | $\Delta = 0.3$ Å |
|---|---|---|---|---|---|
| **II**-a1 | 0.5 | 0.5 | 2.5 | 5.0 | 6.0 |
| **II**-a3 | 1.0 | 2.0 | 7.0 | 11.0 | 15.0 |
| **II**-b3 | 1.0 | 4.0 | 4.0 | 8.0 | 8.0 |
| **II**-k2 [a] | 0.5 | 2.5 | 4.5 | 9.0 | 14.0 |
| **II**-k2 [b] | 0.5 | 4.5 | 8.5 | 12.0 | 16.0 |
| **V**-a3 [a] | 0.0 | 0.5 | 2.0 | 5.0 | 11.0 |
| **V**-a3 [c] | 0.0 | 0.5 | 2.0 | 5.0 | 9.0 |
| **IX** (A) | 2.5 | 2.5 | 3.0 | 3.0 | 4.0 |

[a] $SCH_2C_6F_6$ chain at ring atom C2

[b] $IC_8F_{17}$

[c] $CH_2C_6F_6$ chain at ring atom C3

## 2. Optimization of molecular structures

Geometry optimizations of the molecular conformations of **II**-a1, **II**-a3, **II**-b3, **II**-k2, **V**-a3, and **IX** were performed at the B3LYP/6-31G(d,p) and PBE0/6-31G(d,p) levels using GAUSSIAN09.[2] The optimizations started from the experimental conformations, either without any restraints (*opt*) or fixing selected torsion angles to the experimentally observed values (*conopt* and *exptl*). For more details, see Table S5.

In order to establish the geometric and energy differences between planar and helical fluoroalkyl chain fragments, geometry optimization calculations have been performed at the B3LYP/6-31G(d,p) and PBE0/6-31G(d,p) levels of theory. The torsion angles resulting from these optimizations have been compared with their counterparts in the six investigated structures (Figure S1b). Each of the experimental fluoroalkyl chain fragments minimizes to a helical conformation. At the B3LYP/6-31G(d,p) and PBE0/6-31G(d,p) levels of theory, the average twist angle for all structures except **V**-a3 is 16° and 17°, respectively.

By contrast, the two $C_6F_{13}$ chain fragments of the cation of **V**-a3 minimize to significantly smaller twist angles of 6° and 9° (B3LYP) and 11° and 13° (PBE0). This is probably due to the presence of two $C_6F_{13}$ chains in close proximity in cation **V** which enables short intramolecular C–F···F–C contacts[3] (Figure S12 of the Supporting Information).

The optimized geometries differ considerably from the experimental fluoroalkyl chain conformations ($t_1$, $t_2$, and $t_3$) (Figure S1b). The energy penalty due to the distortion of the molecular geometry has to be compensated by improved intermolecular energy contributions from crystal packing.

Table S5. Computed conformational energy differences between optimized *(opt*), constrained optimized (*conopt*) and experimental (*exptl*) $C_6F_{13}$ chain fragments.

| **Compound** | **Torsion angles fixed at experimental values (Fig. 2)** | | | **$\Delta E_{intra}$ calculation** | **$\Delta E_{intra}$ / kJ mol$^{-1}$** | | **Average twist angles / °** |
|---|---|---|---|---|---|---|---|
| | opt | conopt | exptl | | B3LYP/6-31G(d,p) | PBE0/6-31G(d,p) | exptl |
| **II**-a1 | – | $t_A$, $t_B$, $t_C$ | $t_A$, $t_B$, $t_C$, $t_D$, $t_E$, $t_1$, $t_2$, $t_3$ | exptl – opt | 4.54 | 5.16 | |
| **II**-a1 | – | $t_A$, $t_B$, $t_C$ | $t_A$, $t_B$, $t_C$, $t_D$, $t_E$, $t_1$, $t_2$, $t_3$ | exptl – conopt | 4.38 | 4.97 | 2 |
| **II**-a3 | – | $t_A$, $t_B$, $t_C$ | $t_A$, $t_B$, $t_C$, $t_D$, $t_E$, $t_1$, $t_2$, $t_3$ | exptl – opt | 8.00 | 9.08 | |
| **II**-a3 | – | $t_A$, $t_B$, $t_C$ | $t_A$, $t_B$, $t_C$, $t_D$, $t_E$, $t_1$, $t_2$, $t_3$ | exptl – conopt | 4.42 | 4.99 | 3 |
| **II**-b3 | – | $t_A$, $t_B$, $t_C$ | $t_A$, $t_B$, $t_C$, $t_D$, $t_E$, $t_1$, $t_2$, $t_3$ | exptl – opt | 12.21 | 11.78 | |
| **II**-b3 | – | $t_A$, $t_B$, $t_C$ | $t_A$, $t_B$, $t_C$, $t_D$, $t_E$, $t_1$, $t_2$, $t_3$ | exptl – conopt | 1.37 | 1.83 | 14 |
| **II**-k2 | | $t_A$, $t_B$, $t_C$ | $t_A$, $t_B$, $t_C$, $t_D$, $t_E$, $t_1$, $t_2$, $t_3$ | exptl – opt | 10.40 (A)<br>9.61 (B) | 10.43 (A)<br>9.66 (B) | |
| **II**-k2 | | $t_A$, $t_B$, $t_C$ | $t_A$, $t_B$, $t_C$, $t_D$, $t_E$, $t_1$, $t_2$, $t_3$ | exptl – conopt | 5.92 (A)<br>5.14 (B) | 6.26 (A)<br>5.48 (B) | 2 (A)<br>4 (B) |
| **V**-a3 | – | $t_A$, $t_B$, $t_C$ | $t_A$, $t_B$, $t_C$, $t_D$, $t_E$, $t_1$, $t_2$, $t_3$ | exptl – conopt | 3.99 | 0.86 | 1 |
| **IX** | – | $t_A$, $t_B$, $t_C$, sidechain | $t_A$, $t_B$, $t_C$, $t_D$, $t_E$, $t_1$, $t_2$, $t_3$, sidechain | exptl – conopt | 9.66 (A)<br>7.68 (B) | 10.03 (A)<br>7.78 (B) | 0 (A)<br>8 (B) |

Geometry optimizations of the experimental structures have been performed to quantify the intramolecular energy penalties ($\Delta E_{intra}$) that are associated with experimental fluoroalkyl chain fragments (Table S5). These optimizations have been carried out either with no restraints at all (*opt*) or with key torsion angles fixed (*conopt*) at experimental (*exptl*) values. This procedure enabled the quantification of energy differences associated with four distinct experimental conformations (article Figure 2) of cation **II**. These differ substantially from one another in the torsion angles describing the orientation of the fluoroalkyl chain with respect to the imidazole ring. The fluoroalkyl chain of **II**-a1 represents the best match ($\Delta E_{intra}$ < 5.2 kJ mol$^{-1}$) with the global conformational energy minimum conformation in terms of geometry and energy (Fig. S10 of the Supporting Information), while the $\Delta E_{intra}$ values for the chain conformations of **II**-a3, **II**-k2 (two orientations) and **II**-b3 differ from the optimized cation structure by < 9.1 kJ mol$^{-1}$, < 10.4 kJ mol$^{-1}$, and < 12.2 kJ mol$^{-1}$, respectively. The fraction of $\Delta E_{intra}$ penalties attributable solely to the $C_6F_{13}$ chain ($t_D$, $t_E$, $t_1$, $t_2$, $t_3$) is estimated to be < 6.2 kJ mol$^{-1}$ for the planar conformations **II**-a1, **II**-a3, and **II**-b3. In contrast, $\Delta E_{intra}$ for the helical **II**-k2 fluoroalkyl chain is calculated as < 1.8 kJ mol$^{-1}$. Overall, energy penalties arising from planar (rather than helical) zig-zag chains are well within the conformational energy range observed for flexible molecules. Molecules of this kind are known to frequently adopt geometries that deviate from those of the lowest energy (global minimum) conformer. Instead, a higher energy

conformer is present which enables an optimum balance between the effects of inter- and intramolecular interactions in the crystal. The energy penalties ($\Delta E_{intra}$) reported for such examples are as high as 25 kJ mol$^{-1}$.[4] With this in mind, it is not surprising that planar fluoroalkyl chains can exist in solid structures.

The imidazole rings of **V** and **IX** differ from those of **II** in that both positions 2 and 3 are substituted with a flexible side chain, which coincides with the smallest average experimental twist angles of all the investigated compounds (Figure S1b). The overall intramolecular energy penalty ($\Delta E_{intra}$) associated with the two experimental fluoroalkyl chains of **V**-a3 with respect to the optimized geometry (local energy minimum) was calculated to be less than 4 kJ mol$^{-1}$ (Table S5 & Figure S12). A $\Delta E_{intra}$ value was estimated for each of the two disordered fluoroalkyl chains of **IX** (Table S5).

Even though the twist angles of the two disordered components differ significantly (0° and 8°, see Figure 3a), their $\Delta E_{intra}$ values deviate by less than 2.3 kJ mol$^{-1}$. This suggests that a rearrangement of the fluoroalkyl chain from planar to zig-zag and *vice versa* is facile and crystal packing, i.e. the formation of close intermolecular contacts, can critically affect the (fluoroalkyl) chain geometry.

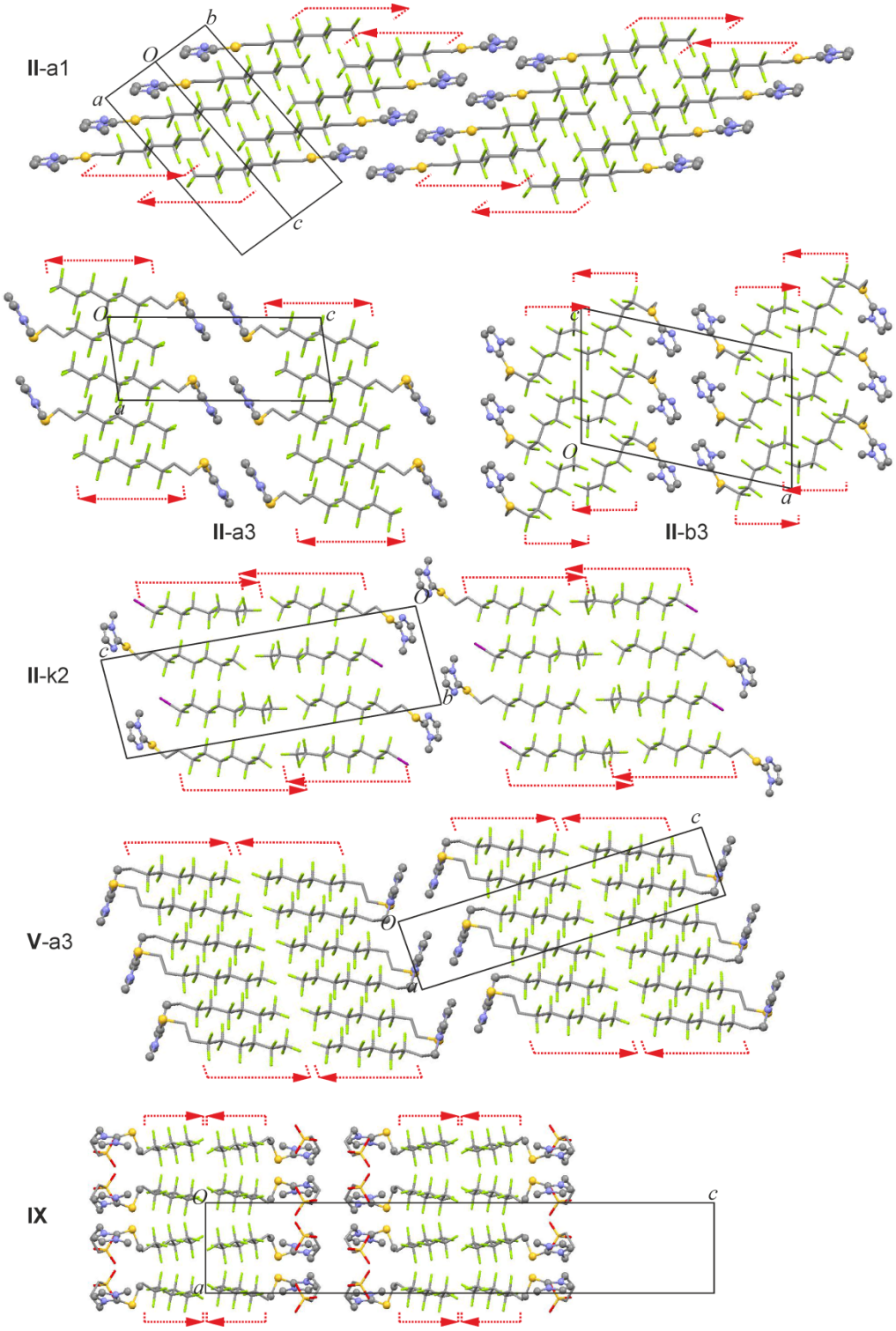


Figure S10. Crystal packing diagrams showing the stacking of fluoroalkyl chains in **II**-a1, **II**-a3, **II**-b3, **II**-k2, **V**-a3, and **IX**. Red brackets indicate 2D regions in stacks of molecules which are dominated by intermolecular F···F contacts. Arrows highlight the orientation of the individual fluoroalkyl chains in each stack. H atoms, anion moieties, and secondary disorder components (**II**-k2, **IX**) are omitted for clarity. Atoms of the imidazole fragment are drawn as balls.

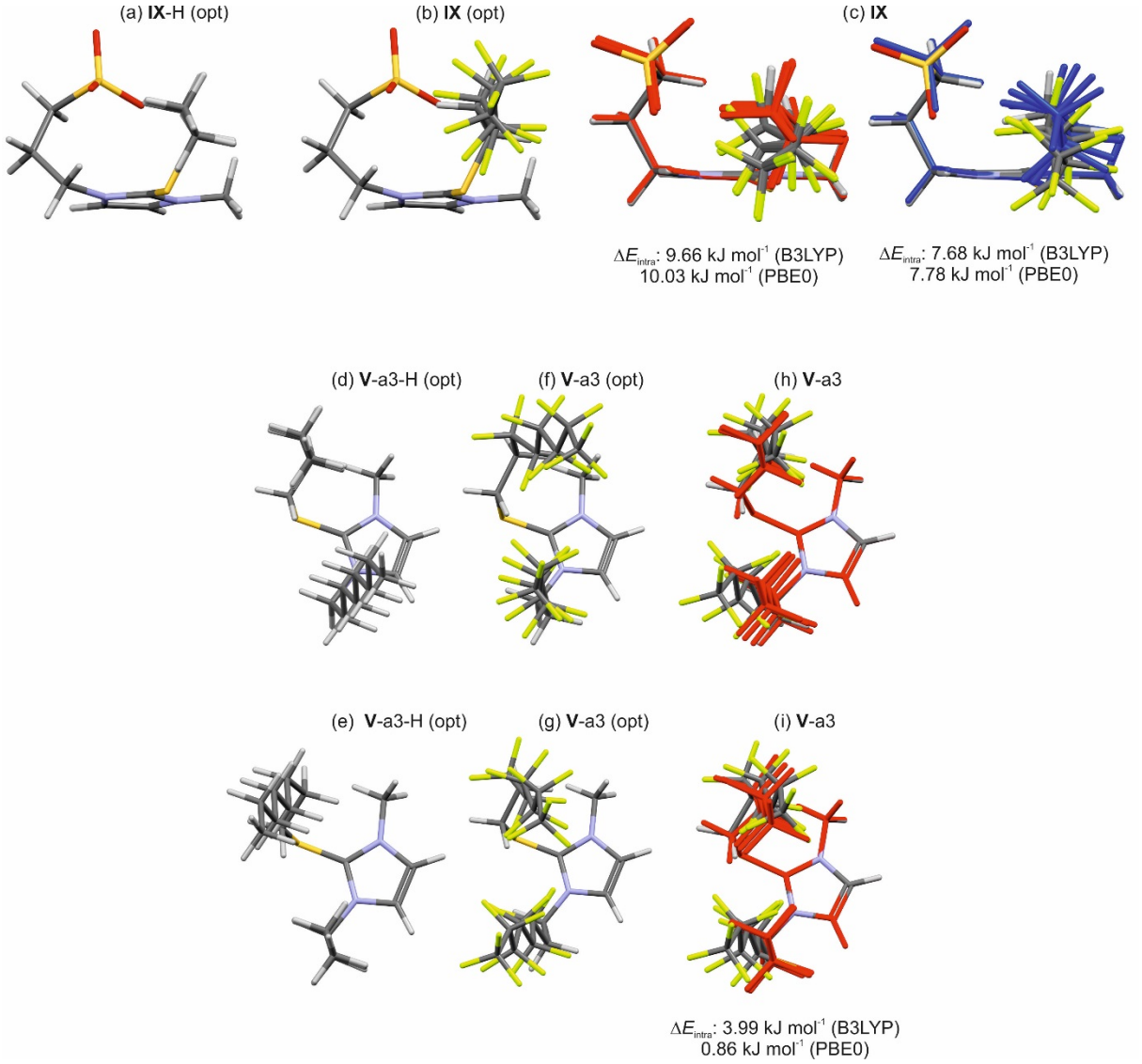


Figure S11. (a,b,d-g) **IX**-H (opt), **V**-a3-H (opt), **IX** (opt) and **V**-a3 (opt) optimized at B3LYP and PBE0 level of theory with the 6-31G(d.p) basis set. F-atoms were replaced with hydrogen atoms in (a,d,e). (c,h,i) Overlay of the *conopt* (colored by element. Table S5) and *experimental* (red and blue) molecular geometries. Intramolecular energy differences ($\Delta E_{intra}$) between *conopt* and *experimental* fluorocarbon chains are given for two levels of theory.

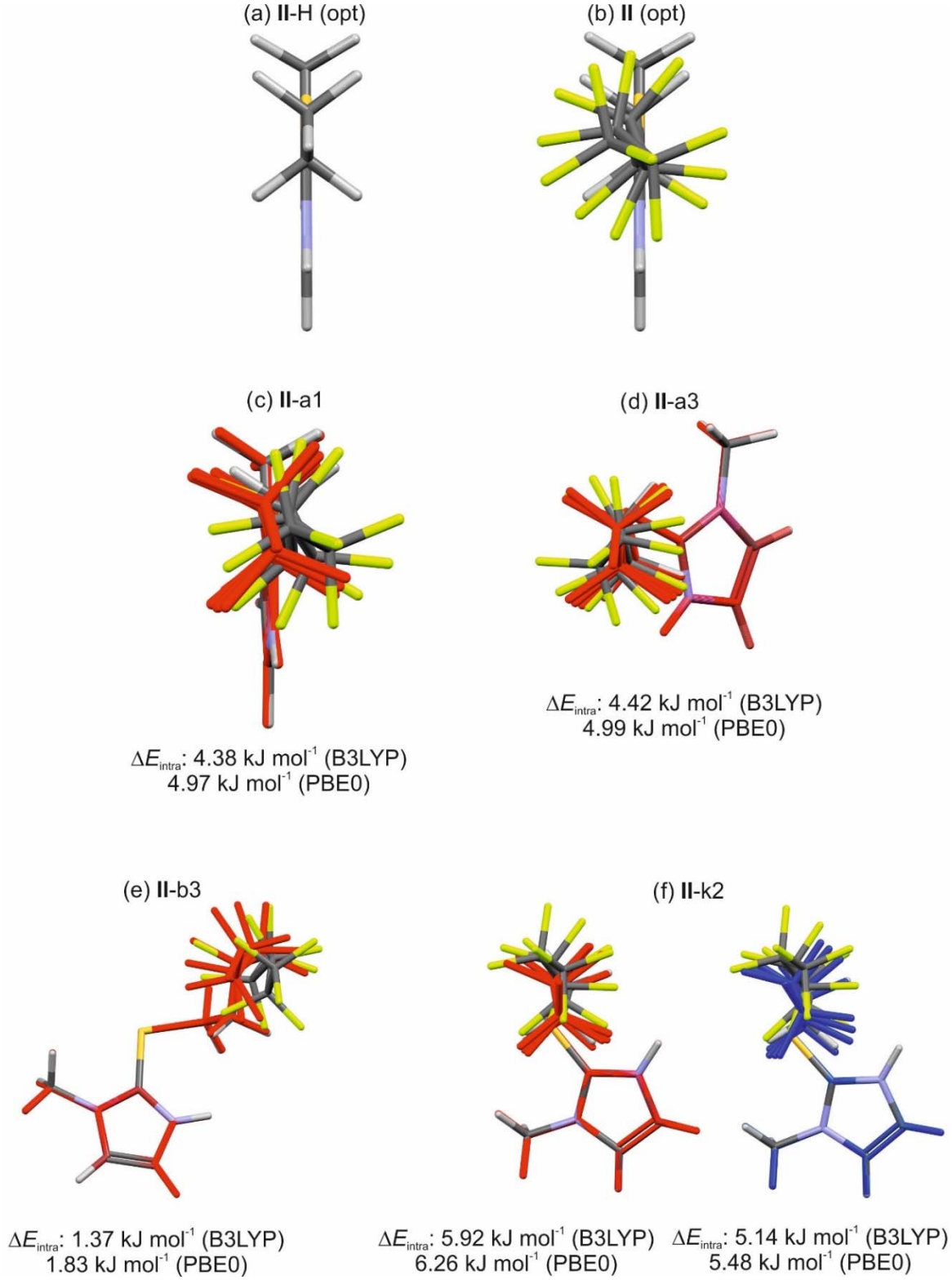


Figure S12. (a) **II**-H (opt) and (b) **II** (opt) cations optimized at B3LYP and PBE0 level of theory with the 6-31G(d.p) basis set. F-atoms were replaced with hydrogen atoms in (a). (c–f) Overlay of the *conopt* (colored by element. Table S5) and *experimental* (red and blue) molecular geometries. Intramolecular energy differences ($\Delta E_{intra}$) between *conopt* and *experimental* fluorocarbon chains are given for two levels of theory.

## 3. Surfactant properties

Table S6. Surface tension and critical micelle concentration of aqueous solutions of selected compounds.

| | Surface tension (mN/m) | | | |
|---|---|---|---|---|
| compound | 0.5 wt% | 0.1 wt% | 0.01 wt% | cmc (g/L) |
| **II**-h3 | 16.6 | 20.15 | 28.7 | n.d. |
| **II**-j2 | 16.1 | 18.5 | 27.7 | n.d. |
| **V**-a1 | 14.5 | 15 | 16.3 | 0.25 |
| **VI**-a1 | 34.2 | 54.5 | 68.7 | n.d. |
| **IX** | 24.0 | 18.1 | 41.8 | 1 |
| PFOS | 21.9 | 25.6 | 51.4 | 2.5 |

*Modified Bikerman's test*

The foaming properties of aqueous solutions of the compounds were determined using a modified Bikerman's test as described before.[5] A column of 3.4 cm internal diameter was charged with 150 mL of each solution. $N_2$ was purged through the solution via a 0.4 cm diameter pipe at a flow rate of 104 mL/min. The foam formation was followed over time and the $N_2$ flow rate was stopped once the foam had attained its dynamic equilibrium, *i.e.* once the height remained constant. The foam stability was then assessed by plotting the evolution of the foam height with time.

Table S7. Molar mass and concentration of surfactants.

| | Molar mass [g/mol] | Concentration g / 150 ml (mol/L ) |
|---|---|---|
| 1-methyl-2-((1H,1H,2H,2H-perfluorooctyl)thio)-1H-imidazolium chloride (**II**a1) | 496.72 | 1.70 (0.023) |
| Sodium dodecyl sulfate (SDS) | 288.4 | 1.74 (0.040) |

The effect of the surfactants on the foam properties of respective aqueous solutions was also studied for **II**-a1. The foam generated with **II**-a1 was denser and the maximum foam height was bigger than in the case of sodium dodecyl sulfate (SDS). Also the foam was generated faster as comped to SDS (see Figure S13).

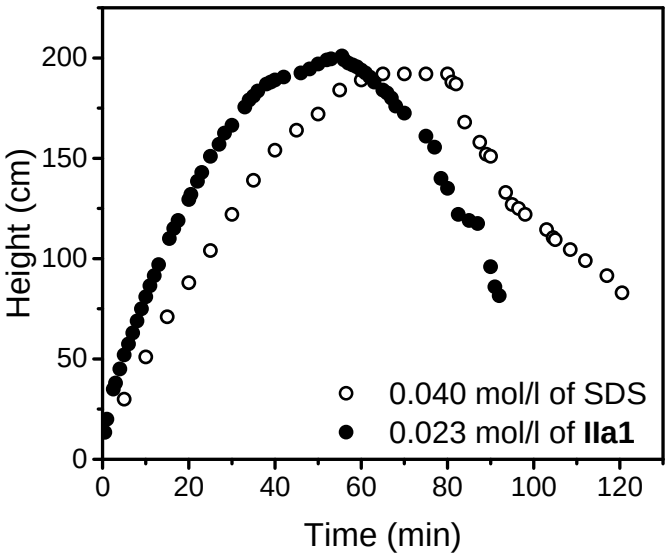


Figure S13. Foam evolution with time of an aqueous sodium dodecyl sulfate (SDS) solution and a solution of **II**-a1. The collapse of the foam was observed instantly after cessation of the gas flow.

## 4. Synthesis

Table S8. Summary of all compounds. The sample code corresponds to the Tables 1 and 2 in the main manuscript.

| | | | | | | |
|---|---|---|---|---|---|---|
| **I**-a3 | **II**-c2 | **II**-g1 | **II**-i1 | **II**-m | **VI**-a1 | **IX** |
| **I**-l1 | **II**-c3 | **II**-g2 | **II**-i2 | **II**-n | **VI**-a3 | **X**-g1 |
| **II**-a1 | **II**-d1 | **II**-g3 | **II**-j1 | **II**-o | **VI**-e3 | **X**-l1 |
| **II**-a2 | **II**-d2 | **II**-g4 | **II**-j2 | **II**-q | **VI**-f1 | **XI**-a2 |
| **II**-a3 | **II**-e1 | **II**-h1 | **II**-j3 | **III**-a3 | **VI**-p | dep-**I** |
| **II**-b1 | **II**-e2 | **II**-h2 | **II**-k1 | **IV**-a3 | **VII**-a2 | dep-**II** |
| **II**-b2 | **II**-e3 | **II**-h3 | **II**-k2 | **V**-a1 | **VII**-b1 | dep-**III** |
| **II**-b3 | **II**-f1 | **II**-h4 | **II**-l1 | **V**-a3 | **VIII**-a3 | dep-**II**-Ti |
| **II**-c1 | **II**-f2 | **II**-h5 | **II**-l2 | **V**-k2 | **VIII**-l1 | |

2-(3,3,4,4,4-pentafluorobutylthio)-1-methylimidazolium iodide **I**-a3

10.10 g (36.9 mmol) of 3,3,4,4,4-pentafluorobutyl iodide, 6.31 g (55.3 mmol, 1.5 eq) 2-mercapto-1-methylimidazole, and ca. 80 ml of ethanol were placed in a 250ml round-bottom flask and refluxed for 15 h. Ethanol was stripped off *via* use of a rotary evaporator and the obtained crude product was re-crystallised in 25 ml of $CH_2Cl_2$. The purified product was filtered off, washed 2 times with cold $CH_2Cl_2$ and finally dried in a vacuum desiccator. Yield: 8.23 g (58%).

IR (ATR, neat) 3085, 2947, 1573, 1484, 1338, 1295, 1181, 1114, 1089, 1063, 988, 955, 770, 677, 639, 526 $cm^{-1}$.$^1$H NMR (300 MHz, $CDCl_3$) δ 7.51 (1H, d), 7.46 (1H, d), 3.93 (3H, s), 3.77 (2H, t), 2.58 (2H, tt) ppm; mp: 154 ºC.

2-(3,3,4,4,4-pentafluorobutylthio)-1-methylimidazolium bis(trifluoromethanesulfonyl)imide **I**-l1

$LiN(Tf)_2$ (1.30 g; 4.53 mmol; 1.58 eq) was dissolved in 5 ml of water and filtered directly via syringe filter into a 50ml round-bottom flask containing **I**-a3 (1.11g, 2.86 mmol) suspended in 5 ml $H_2O$. The mixture was stirred for 2 h at room temperature before 10 ml of $CH_2Cl_2$ were added. Phases were separated by means of a separatory funnel and the organic phase was washed with $H_2O$ and dried over $Na_2SO_4$. $CH_2Cl_2$ was removed by means of rotary evaporator and the product was finally dried in high vacuum of a rotary vane pump. Yield: 1.40 g (90%).

IR (ATR, neat) 3157, 1581, 1489, 1346, 1177, 1131, 1092, 1051, 991, 958, 925, 791, 740, 654, 612, 670, 510 $cm^{-1}$. $^1$H NMR (300 MHz, $CD_3CN$) δ 10.03 (1H, s(br)), 7.49 (1H, d), 7.46 (1H, d), 3.84 (3H, s), 3.29 (2H, t), 2.54 (2H, tt) ppm.

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylimidazolium chloride **II**-a1

To 4.6 g (10.0 mmol) of dep-**II** in 50 ml of diethyl ether, 10 ml of an ethereal hydrogen chloride solution (1M, 10.0 mmol) were added dropwise under vigorous stirring; the product precipitated immediately. After complete addition of the hydrogen chloride solution, the product was filtered off and washed with 50 ml of diethyl ether, then dried *in vacuo*. This affords 4.84 g (9.74 mmol, 97% of theoretical yield) of pure-white **II**-a1. Single crystals of **II**-a1 were obtained by slow evaporation of a solution of **II**-a1 in dichloromethane.

IR (ATR, neat) 3093, 2941, 2543, 1577, 1498, 1366, 1308, 1228, 1188, 1141, 1121, 1089, 1073, 1017, 959, 916, 900, 861, 773, 745, 729, 708, 689, 647, 631, 566, 531, 443, 412 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CD_3OD$) δ 7.75 (1H, d), 7.69 (1H, d), 3.96 (3H, s), 3.44 (2H, t), 2.68 (2H, tt) ppm. $^{13}C$ NMR (75 MHz, $CD_3OD$) δ 140.81 (s), 127.26 (s), 122.47 (s), 124-100 (6C, m), 36.21 (s), 32.58 (t), 27.77 (t) ppm; mp: 119 °C (under immediate dec., hb).

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylimidazolium bromide **II**-a2

To a solution of 9.21 g (20.00 mmol) of dep-**II** in 50 ml of diethyl ether, 3,8 ml of a 33 wt.% solution of HBr in glacial acetic acid (22.00 mmol), additionally diluted with 50 ml of diethyl ether, were added dropwise under strong stirring; the product precipitates immediately. After complete addition of the HBr, the product was filtered off and washed with 100 ml of diethyl ether, then dried *in vacuo*. This affords 10.58 g (19.55 mmol, 98% of theoretical yield) of pure-white **II**-a2.

IR (ATR, neat) 3110, 3082, 2963, 2791, 2717, 1577, 1490, 1442, 1363, 1316, 1294, 1215, 1183, 1139, 1102, 1075, 964, 921, 787, 768, 723, 705, 638, 567, 528, 434, 406 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CD_3OD$) δ 7.92 (1H, d), 7.82 (1H, d), 4.10 (3H, s), 3.60 (2H, t), 2.81 (2H, tt) ppm. $^{13}C$ NMR (75 MHz, $CD_3OD$) δ 140.77 (s), 127.35 (s), 122.47 (s), 124-100 (6C, m), 36.57 (s), 32.64 (t), 28.06 (t) ppm; mp: 149 °C (under dec., hb).

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylimidazolium tetrafluoroborate **II**-b1

1.76 g of a 50 wt% solution of $HBF_4$ in water (10.00 mmol) was added dropwise to 2.30 g (5.00 mmol) of dep-**II** under vigorous stirring; the product precipitates immediately. Subsequently, the product was filtered off and washed with 50 ml of water, then dried *in vacuo*. This affords 2.21 g (4.03 mmol, 80% of theoretical yield) of pure-white **II**-b1.

IR (ATR, neat) 3152, 2947, 2793, 1581, 1493, 1444, 1363, 1315, 1232, 1186, 1142, 1122, 1054, 959, 915, 847, 813, 768, 745, 723, 706, 643, 605, 564, 526, 408 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CD_3OD$) δ 7.64 (1H, d), 7.57 (1H, d), 3.92 (3H, s), 3.38 (2H, t), 2.65 (2H, tt) ppm. $^{13}C$ NMR (75 MHz, $CD_3OD$) δ 140.62 (s), 126.97 (s), 123.47 (s), 124-100 (6C, m), 35.47 (s), 32.53 (t), 27.45 (t) ppm; mp: 84 °C (hb).

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylimidazolium hexafluorophosphate **II**-b2

1.26 g (7.73 mmol) of ammonium hexafluorophosphate and 3.07 g (5.22 mmol) of **II**-a3 were stirred overnight at room temperature in a mixture of each 10 ml of water and diethyl ether. The biphasic mixture was transferred to a separatory funnel. The aqueous phase was extracted with another 10 ml of diethyl ether once, and the combined organic phases were extracted with 10 ml of water, followed by desiccation with sodium sulphate and evaporation of diethyl ether *via* a rotary evaporator. Finally, the product, a pure-white crystalline powder, was dried in high vacuum overnight. This affords 2.18 g (4.73 mmol, 91% of theoretical yield) of **II**-b2.

IR (ATR, neat) 3078, 1581, 1562, 1490, 1452, 1361, 1317, 1233, 1196, 1138, 1120, 1072, 961, 830, 776, 735, 704, 695, 647, 637, 600, 557, 527, 494 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CD_3OD$) δ 7.64 (1H, d), 7.59 (1H, d), 3.93 (3H, s), 3.38 (2H, t), 2.65 (2H, tt) ppm. $^{13}C$ NMR (75 MHz, $CD_3OD$) δ 140.58 (s), 127.11 (s), 122.80 (s), 124-100 (6C, m), 35.87 (s), 32.47 (t), 27.51 (t) ppm; mp: 130 °C (hb).

Bis(2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylimidazolium) hexafluorosilicate **II**-b3

0.81 ml of a 34 wt.% solution of $H_2SiF_6$ in water (1.06 g, 2.50 mmol) were added dropwise under stirring to a solution of 2.30 g (5.00 mmol) of dep-**II** in 5 ml of methanol. This solution was kept at 4°C overnight, during which time crystallisation of the product took place. The next day, the obtained crystals were filtered, washed with 50 ml of diethyl ether and dried *in vacuo*. 2.10 g (1.97 mmol, 79% of theoretical yield) of colourless crystals were isolated. Single crystals suitable for structure determination were obtained serendipitously by reacting dep-**II** with a 4-fold excess of Olah's reagent [62778-11-4] and transferring this solution into a borosilicate NMR tube. However, **II**-b3 appears to exhibit polymorphism, since crystals prepared this way show a different crystal structure than crystals prepared from a methanolic solution like above.

IR (ATR, neat) 3186, 3129, 3006, 2831, 1583, 1499, 1442, 1423, 1365, 1316, 1297, 1234, 1197, 1143, 1095, 1071, 890, 837, 800, 780, 727, 703, 669, 644, 566, 528, 475, 447 $cm^{-1}$. $^{1}H$ NMR (300 MHz, 3:1 $CD_3OD$/DMSO-d6) δ 7.71 (2H, d), 7.63 (2H, d), 3.92 (6H, s), 3.47 (4H, t), 2.69 (4H, tt) ppm. $^{13}C$ NMR (75 MHz, 3:1 $CD_3OD$/DMSO-d6) δ 140.62 (2C, s), 126.70 (2C, s), 123.79 (2C, s), 124-100 (12C, m), 35.73 (2C, s), 32.35 (2C, t), 27.33 (2C, t) ppm; mp: 171 °C (dec. starting at 117 °C, hb).

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylimidazolium nitrate **II**-c1

3.0 ml of a 65 wt% solution of $HNO_3$ in water (43.10 mmol) were added to 2.30 g (5.00 mmol) of dep-**II**; the resulting solution was left standing until all of the solvent and surplus acid evaporated. This affords 2.61 g (5.0 mmol, 100% of theoretical yield) of a white, polycrystalline material.

IR (ATR, neat) 3137, 1918, 1743, 1586, 1489, 1445, 1399, 1364, 1301, 1185, 1141, 1093, 1073, 1030, 961, 913, 899, 849, 813, 790, 757, 736, 723, 707, 684, 642, 606, 565, 529, 459, 413 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CD_3OD$) δ 7.74 (1H, d), 7.67 (1H, d), 3.96 (3H, s), 3.44 (2H, t), 2.69 (2H, tt) ppm. $^{13}C$ NMR (75 MHz, $CD_3OD$) δ 140.73 (s), 127.15 (s), 122.61 (s), 124-100 (6C, m), 36.00 (s), 32.53 (t), 27.60 (t) ppm; mp: 128 °C (discoloration, effervescence and dec., hb).

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylimidazolium dihydrogen phosphate **II**-c2

1.00 g (2.01 mmol) of **II**-a1 was added to a suspension of 313 mg (2.01 mmol) of sodium dihydrogen phosphate dihydrate in 30 ml of acetone, and the resulting reaction mixture was stirred at room temperature overnight. The next day, precipitated NaCl was filtered off, followed by evaporation of the solvent and drying of the product in high vacuum. 1.10 g (1.97 mmol, 98% of theoretical yield) of white powder were obtained.

IR (ATR, neat) 3147, 3091, 2945, 2545, 1578, 1497, 1365, 1229, 1186, 1140, 1120, 1088, 1069, 1017, 973, 959, 913, 897, 770, 745, 728, 707, 696, 669, 647, 524, 486, 442 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CD_3OD$) δ 7.60 (1H, d), 7.50 (1H, d), 3.89 (3H, s), 3.38 (2H, t), 2.64 (2H, tt) ppm. N-H and O-H signals not visible due to H-D exchange. $^{13}C$ NMR (75 MHz, $CD_3OD$) δ 140.77 (s), 126.51 (s), 124.74 (s), 124-100 (6C, m), 35.47 (s), 32.61 (t), 27.35 (t) ppm; mp: 122 °C (hb).

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylimidazolium perchlorate **II**-c3

840 mg (5.00 mmol) of a 60 wt.% solution of perchloric acid in water were added dropwise under vigorous stirring to a solution of 2.30 g (5.00 mmol) of dep-**II** in 50 ml of diethyl ether; the product precipitated immediately. After complete addition of the perchloric acid, the product was filtered off and washed with 50 ml of diethyl ether, then dried *in vacuo*. This affords 2.66 g (4.75 mmol, 95% of theoretical yield) of pure-white **II**-c3.

IR (ATR, neat) 3147, 3005, 1580, 1492, 1444, 1363, 1311, 1219, 1188, 1139, 1092, 1071, 1052, 960, 921, 848, 813, 749, 723, 706, 685, 643, 621, 565, 530, 467, 410 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CD_3OD$) δ 7.69 (1H, d), 7.63 (1H, d), 3.97 (3H, s), 3.41 (2H, t), 2.67 (2H, tt) ppm. $^{13}C$ NMR (75 MHz, $CD_3OD$) δ 140.53 (s), 127.26 (s), 122.38 (s), 124-100 (6C, m), 36.13 (s), 32.43 (t), 27.59 (t) ppm; mp: 151 °C (discoloration of liquid, hb).

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylimidazolium [tris(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)manganate(II)] **II**-d1

(This synthesis was performed following a procedure described by Zhang et al.[6]) First, 1.72 g (8.25 mmol) of hexafluoroacetylacetone were dissolved in 10 ml of acetonitrile, followed by dropwise addition of 0.63 ml (8.25 mmol) of 25 wt% $NH_3$-solution. The resulting reaction mixture was stirred at room temperature for 24 h. Next, evaporation of the solvent was accomplished *via* a rotary evaporator. The crude product was washed with 40 ml of n-hexane, and then dried in high vacuum overnight. This afforded 1.83 g of ammonium hexafluoroacetylacetonate ($NH_4$-hfac, 98% of theoretical yield).

0.900 g (4.00 mmol) of freshly produced $NH_4$-hfac were dissolved in 10 ml of acetonitrile, followed by addition of 0.264 g (1.33 mmol) of $MnCl_2 \cdot 4\ H_2O$ to the solution. This reaction mixture was stirred for 18 h at room temperature, after which precipitated $NH_4Cl$ was filtered off. To the now clear solution, 0.660 g (1.33 mmol) of **II**-a1 was added, followed by stirring at room temperature for another 20 h. Precipitated $NH_4Cl$ was filtered off again, the solvent was evaporated. The residue was dissolved in 20 ml of diethyl ether. This solution was extracted with 10 ml of $H_2O$ thrice, the ethereal solution then dried with $Na_2SO_4$

followed by evaporation of the solvent and drying of the product in high vacuum. This affords 1.00 (0.88 mmol, 66% of theoretical yield) g of **II**-d1, an intensely orange, highly viscous fluid.

IR (ATR, neat) 3151, 1645, 1556, 1529, 1503, 1251, 1192, 1134, 1092, 961, 948, 796, 741, 723, 707, 664, 582, 527 $cm^{-1}$. (Due to the paramagnetism of Mn(II), characterisation of **II**-d1 *via* NMR spectroscopy was not feasible.)

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylimidazolium [tetrachloridoferrate(III)] **II**-d2

2.17 ml of etheric hydrogen chloride solution (1M, 2.17 mmol) were added to a solution of 352 mg (2.17 mmol) of anhydrous iron(III) chloride in 10 ml of diethyl ether. Subsequently, 1.00 g (2.17 mmol) of dep-**II** were added dropwise to the mixture. After stirring for a few minutes, diethyl ether was evaporated *via* use of a rotary evaporator. The yellow-brownish product is liquid at first, but solidifies after drying *in vacuo*. 1.36 g (2.06 mmol, 95% of theoretical yield) of **II**-d2 were isolated.

IR (ATR, neat) 3322, 3268, 3169, 3140, 1575, 1486, 1431, 1367, 1319, 1297, 1236, 1184, 1139, 1093, 1069, 1026, 891, 807, 768, 729, 701, 649, 608, 567, 523, 415 $cm^{-1}$. (Due to the paramagnetism of Fe(III), characterisation of **II**-d2 *via* NMR spectroscopy was not feasible); mp: 63 °C (hb).

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylimidazolium trifluoroacetate **II**-e1

570 mg (383 µl, 5.00 mmol) of trifluoroacetic acid were added dropwise under stirring to a solution of 2.30 g (5.00 mmol) of dep-**II** in 30 ml of diethyl ether. Following complete addition, the mixture was stirred for a few minutes, after which the solvent was evaporated. The product appeared to be a liquid at first, but crystallised slowly at room temperature after drying *in vacuo*. 2.85 g (4.96 mmol, 99% of theoretical yield) of **II**-e1 were obtained.

IR (ATR, neat) 3108, 2953, 1659, 1588, 1496, 1449, 1417, 1364, 1317, 1232, 1177, 1139, 1120, 1093, 1073, 1019, 964, 895, 814, 797, 737, 719, 706, 684, 644, 628, 565´, 530, 441, 411 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CD_3OD$) δ 7.68 (1H, d), 7.60 (1H, d), 3.93 (3H, s), 3.42 (2H, t), 2.66 (2H, tt) ppm. $^{13}C$ NMR (75 MHz, $CD_3OD$) δ 163.03 (q), 140.85 (s), 126.90 (s), 123.39 (s), 124-100 (7C, m), 35.77 (s), 32.66 (t), 27.47 (t) ppm; mp: 55 °C.

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylimidazolium perfluorobutanoate **II**-e2

0.739 g (3.45 mmol) of perfluorobutyric acid were dissolved in 5 ml of $H_2O$, 1.59 g (3.45 mmol) of **dep-II** were added, and the mixture was stirred at room temperature. After a few hours, 10 ml of $CH_2Cl_2$ were added and the biphasic mixture was transferred to a separatory funnel. After phase separation, the organic phase was extracted with 10 ml of water, followed by desiccation with sodium sulphate and evaporation of $CH_2Cl_2$ *via* a rotary evaporator. This afforded 2.09 g (3.10 mmol, 90% of theoretical yield) of **II**-e2.

IR (ATR, neat) 1680, 1586, 1495, 1331, 1201, 1142, 1115, 1074, 962, 926, 845, 801, 738, 707, 646, 565, 529, 456 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$) δ 15.63 (1H, s) 7.37 (1H, d), 7.24 (1H, d), 3.77 (3H, s), 3.45 (2H, t), 2.48 (2H, tt) ppm. $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 161.96 (q), 140.125 (s), 123.92 (s), 123.10 (s), 120-105 (9C, m), 34.70 (s), 31.32 (t), 25.84 (t) ppm.

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylimidazolium perfluorooctanoate **II**-e3

2.14 g (3.64 mmol) of **II**-a3 were dissolved in 20 ml of $H_2O$. 1.60 g (3.71 mmol) of ammonium perfluorooctanoate was added to the solution and the mixture was ultrasonicated. A sticky solid formed on the bottom which was dissolved in diethyl ether. The biphasic mixture was transferred to a separatory funnel. After phase separation, the organic phase was extracted with 10 ml of water, followed by desiccation with sodium sulphate and evaporation of diethyl ether *via* a rotary evaporator. This afforded 2.99 g (3.42 mmol, 94% of theoretical yield) of **II**-e3.

IR (ATR, neat) 3110, 1667, 1584, 1495, 1444, 1386, 1357, 1318, 1282, 1232, 1194, 1142, 1124, 1100, 1073, 1013, 912, 885, 838, 804, 737, 722, 707, 661, 630, 603, 560, 527, 418 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$) δ 14.25 (1H, s(br)) 7.44 (1H, d), 7.17 (1H, d), 3.78 (3H, s), 3.57 (2H, t), 2.53 (2H, tt) ppm. $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 162.12 (q), 140.52 (s), 123.492 (s), 123.10 (s), 120-105 (14C, m), 34.82 (s), 31.28 (t), 25.91 (t) ppm.

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylimidazolium 4,8-dioxa-3H-perfluorononanoate **II**-f1

2.01 g (3.42 mmol) of **II**-a3 was added to 4.5 ml of a 30wt% solution of ammonium 4,8-dioxa-3H-perfluorononanoate (3.42 mmol). A sticky solid formed on the bottom which was dissolved in diethyl ether. The biphasic mixture was transferred to a separatory funnel. After phase separation, the organic phase was extracted with 10 ml of water, followed by desiccation with sodium sulphate and evaporation of diethyl ether *via* a rotary evaporator. This afforded 2.41 g (2.87 mmol, 84% of theoretical yield) of **II**-f1.

IR (ATR, neat) 3116, 1657, 1587, 1495, 1454, 1397, 1363, 1283, 1232, 1183, 1141, 1121, 1049, 961, 892, 828, 800, 762, 725, 708, 691, 645, 564, 532 $cm^{-1}$. $^1H$ NMR (300 MHz, $CD_3CN$) δ 7.40 (1H, d), 7.38 (1H, d), 6.55 (1H, dxt), 3.77 (3H, s), 3.36 (2H, t), 2.60 (2H, tt) ppm. $^{13}C$ NMR (75 MHz, $CD_3CN$) δ 164.76 (q), 140.61 (s), 126.32 (s), 124.33 (s), 122-100 (12C, m), 36.03 (s), 33.90 (t), 27.27 (t) ppm.

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylimidazolium 3,6,9-trioxa-perfluorotridecanoate **II**-f2

2.50 g (4.35 mmol) of perfluoro-3,6,9-trioxatridecanoic acid were added dropwise under stirring to a solution of 2.00 g (4.35 mmol) of dep-**II** in 30 ml of diethyl ether. Following complete addition, the mixture was stirred for a few minutes, after which the solvent was evaporated. Upon drying *in vacuo*, the oily liquid product appeared to solidify partially, but reverted to the liquid state immediately after returning to standard conditions. 4.10 g (4.01 mmol, 92% of theoretical yield) of **II**-f2 were isolated.

IR (ATR, neat) 1685, 1587, 1496, 1365, 1307, 1186, 1139, 1103, 1058, 953, 896, 805, 746, 735, 706, 681, 646, 565, 533 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CD_3OD$) δ 7.70 (1H, d), 7.63 (1H, d), 3.94 (3H, s), 3.43 (2H, t), 2.65 (2H, tt) ppm. $^{13}C$ NMR (75 MHz, $CD_3OD$) δ 162.50 (t), 140.97 (s), 127.01 (s), 122.94 (s), 124-100 (15C, m), 35.90 (s), 32.68 (t), 27.54 (t) ppm.

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylimidazolium trifluoromethanesulfonate **II**-g1

652 mg (381 µl, 4.35 mmol) of trifluoromethanesulfonic acid were added dropwise under stirring to a solution of 2.00 g (4.35 mmol) of dep-**II** in 30 ml of diethyl ether. Following complete addition, the mixture was stirred for a few minutes, after which the solvent was evaporated. Finally, the resulting white powder was dried *in vacuo*. This yielded 2.50 g (4.10 mmol, 94% of theoretical yield) of **II**-g1.

IR (ATR, neat) 3189, 3126, 2964, 2847, 1584, 1492, 1445, 1364, 1292, 1234, 1223, 1174, 1140, 1121, 1096, 1073, 1022, 961, 918, 848, 813, 762, 736, 722, 706, 684, 632, 576, 524, 518, 431, 410 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CD_3OD$) δ 7.61 (1H, d), 7.55 (1H, d), 3.85 (3H, s), 3.31 (2H, t), 2.56 (2H, tt) ppm. $^{13}C$ NMR (75 MHz, $CD_3OD$) δ 140.88 (s), 127.39 (s), 122.59 (s), 121.93 (q), 124-100 (6C, m), 36.21 (s), 32.68 (t), 27.76 (t) ppm; mp: 77 °C (hb).

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylimidazolium perfluorobutanesulfonate **II**-g2

A mixture of 3.44 g (5.85 mmol) of **II**-a3, 2.02 g (5.85 mmol) of potassium perfluorobutanesulfonate, and 20 ml of $H_2O$ was stirred at room temperature for 24 h. Diethyl ether was added and the biphasic mixture was transferred to a separatory funnel. After phase separation, the organic phase was extracted with 10 ml of water, followed by desiccation with sodium sulphate and evaporation of diethyl ether *via* a rotary evaporator. This afforded 3.89 g (5.12 mmol, 87% of theoretical yield) of **II**-g2.

IR (neat) 3142, 2838, 1582, 1489, 1452, 1354, 1295, 1230, 1211, 1180, 1132, 1088, 1074, 1057, 1046, 1017, 958, 918, 846, 804, 771, 736, 724, 708, 695, 642, 615, 595, 566, 523, 414 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CD_3OD$) δ 7.45 (1H, s(br)), 7.33 (1H, s(br)), 3.86 (3H, s), 3.52 (2H, t), 2.54 (2H, tt) ppm. $^{13}C$ NMR (75 MHz, $CD_3OD$) δ 140.94 (s), 124.89 (s), 122.10 (s), 35.75 (s), 31.26 (t), 26.50 (t) ppm; mp: 55-60 °C

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylimidazolium perfluorohexanesulfonate **II**-g3

A mixture of 2.79 g (4.74 mmol) of **II**-a3, 2.12 g (4.74 mmol) of potassium perfluorohexanesulfonate, and 20 ml of $H_2O$ was stirred at room temperature for 24 h. Diethyl ether was added and the biphasic mixture was transferred to a separatory funnel. After phase separation, the organic phase was extracted with 10 ml of water, followed by desiccation with sodium sulphate and evaporation of diethyl ether *via* a rotary evaporator. This afforded 3.24 g (3.77 mmol, 79% of theoretical yield) of **II**-g3.

IR (neat) 3144, 1581, 1491, 1362, 1228, 1194, 1144, 1122, 1071, 1028, 986, 964, 919, 889, 805, 778, 737, 707, 681, 638, 622, 564, 525, 456 $cm^{-1}$. $^1H$ NMR (300 MHz, $CD_3OD$) δ 7.49 (1H, d), 7.31 (1H, d), 3.87 (3H, s), 3.56 (2H, t), 2.57 (2H, tt) ppm. $^{13}C$ NMR (75 MHz, $CD_3OD$) δ 141.12 (s), 124.64 (s), 122.20 (s), 35.70 (s), 31.21 (t), 26.43 (t) ppm; mp: 67-69 °C.

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylimidazolium perfluorooctanesulfonate **II**-g4

1.03 g (2.06 mmol) of potassium perfluorooctanesulfonate were dissolved in 20 ml of $H_2O$ and 1.21 g (2.06 mmol) of **II**-a3 were added. The mixture was ultrasonicated for 1 h and the formed white precipitate isolated via filtration, washed with water and finally dried in a vacuum desiccator. This afforded 1.36 g (1.41 mmol, 69% of theoretical yield) of **II**-g3.

IR (neat) 1463, 1362, 1230, 1196, 1143, 1090, 985, 947, 845, 947, 854, 809, 746, 708, 649, 628, 561, 525 $cm^{-1}$. $^1H$ NMR (300 MHz, $CD_3OD$) δ 7.70 (1H, d), 7.63 (1H, d), 3.96 (3H, s), 3.41 (2H, t), 2.65 (2H, tt) ppm. $^{13}C$ NMR (75 MHz, $CD_3OD$) δ 140.79 (s), 127.26 (s), 122.57 (s), 124-100 (14C, m), 36.10 (s), 32.55 (t), 27.64 (t) ppm; mp: 104 °C (hb).

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylimidazolium methanesulfonate **II**-h1

920 mg (2.00 mmol) of dep-**II** were added to a solution of 192 mg (2.00 mmol) of methanesulfonic acid in 10 ml of methanol and the resulting mixture was stirred for 15 min at room temperature. After that, the solvent was evaporated and the resulting product dried *in vacuo* overnight.1.03 g (1.85 mmol, 93% of theoretical yield) of **II**-h1 were obtained.

IR (ATR, neat) 3121, 2524, 1587, 1500, 1444, 1365, 1325, 1231, 1182, 1158, 1138, 1119, 1109, 1073, 1027, 960, 905, 848, 812, 765, 739, 722, 707, 682, 642, 607, 564, 542, 524, 434, 412 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.48 (1H, d), 7.41 (1H, d), 3.83 (3H, s), 3.58 (2H, t), 2.76 (3H, s), 2.61 (2H, tt) ppm. $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 140.47 (s), 124.59 (s), 122.60 (s), 124-100 (6C, m), 39.53 (s), 35.49 (s), 31.33 (t), 26.28 (t) ppm; mp: 117 °C (hb).

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylimidazolium sulfamate **II**-h2

2.30 g (5.00 mmol) of dep-**II** were added to a dispersion of 486 mg (5.00 mmol) of amidosulfonic acid in 30 ml of methanol, and the resulting mixture was stirred for 15 min at room temperature. After that, the solvent was evaporated and the resulting, still liquid product dried *in vacuo* overnight, during which time it solidified. 2.78 g (4.99 mmol, 100% of theoretical yield) of powdery, white **II**-h2 were isolated.

IR (ATR, neat) 3339, 3244, 3146, 3111, 2555, 1583, 1494, 1440, 1365, 1321, 1273, 1229, 1210, 1160, 1139, 1092, 1029, 957, 914, 895, 789, 770, 745, 722, 706, 695, 645, 579, 566, 555, 488 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CD_3OD$) δ 7.69 (1H, d), 7.59 (1H, d), 3.93 (3H, s), 3.42 (2H, t), 2.66 (2H, tt) ppm. $^{13}C$ NMR (75 MHz, $CD_3OD$) δ 140.61 (s), 126.88 (s), 124.10 (s), 124-100 (6C, m), 35.75 (s), 32.47 (t), 27.43 (t) ppm; mp: 106 °C (under dec., hb).

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylimidazolium camphor-10-sulfonate **II**-h3

2.00 g (4.35 mmol) of dep-**II** were added to a dispersion of 1.03 g (4.35 mmol) of racemic camphor-10-sulfonic acid (beta) in 5 ml of methanol and the resulting mixture was stirred for 15 min at room temperature, during which time a solution formed. After that, the solvent was evaporated and the resulting white solid dried *in vacuo* overnight. 3.00 g (4.34 mmol, 100% of theoretical yield) of **II**-h3 were obtained.

IR (ATR, neat) 3148, 2958, 2740, 2558, 1741, 1586, 1494, 1471, 1457, 1438, 1407, 1394, 1364, 1351, 1318, 1229, 1199, 1177, 1163, 1143, 1125, 1095, 1070, 1035, 965, 941, 905, 894, 828, 769, 744, 719, 705, 687, 640, 598, 584, 531, 506, 497, 467, 424, 411 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CD_3OD$) δ 7.80 (1H, d), 7.73 (1H, d), 3.99 (3H, s), 3.49 (2H, t), 3.29 (1H, d), 2.77 (1H, d), 2.71 (2H, tt), 2.66 (1H, m), 2.32 (1H, dt), 2.02 (2H, m), 1.87 (1H, d), 1.63 (1H, ddd), 1.41 (1H, m), 1.12 (3H, s), 0.85 (3H, s) ppm. $^{13}C$ NMR (75 MHz, $CD_3OD$) δ 217.89 (s), 140.68 (s), 127.20 (s), 122.64 (s), 124-100 (6C, m), 59.49 (s), 48.78 (s), 48.26 (s), 43.97 (s), 43.60 (s), 36.14 (s), 32.43 (t), 27.76 (s), 27.64 (t), 25.74 (s), 20.36 (s), 20.09 (s) ppm; mp: 112 °C (hb).

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylimidazolium naphthalene-1,5-disulfonate **II**-h4

2.00 g (4.35 mmol) of dep-**II** were added to a solution of 810 mg (2.17 mmol) of naphthalene-1,5-disulfonic acid tetrahydrate (Armstrong's acid, 97%) in 5 ml of methanol and the resulting mixture was stirred for 15 min at room temperature. After that, the solvent was evaporated and the resulting white solid dried *in vacuo* overnight. 2.60 g (2.15 mmol, 99% of theoretical yield) of **II**-h4 were obtained.

IR (ATR, neat) 3135, 2956, 2527, 1582, 1495, 1448, 1365, 1317, 1249, 1228, 1187, 1174, 1142, 1122, 1092, 1073, 1016, 965, 912, 846, 833, 798, 789, 765, 722, 706, 642, 611, 563, 522, 467, 415 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CD_3OD$) δ 8.99 (2H, d), 8.19 (2H, d), 7.56 (2H, t), 7.50 (2H, d), 7.45 (2H, d), 3.79 (6H, s), 3.33 (4H, t), 2.61 (4H, tt) ppm. $^{13}C$ NMR (75 MHz, $CD_3OD$) δ 142.73 (2C, s(br)), 140.55 (2C, s), 131.08 (2C, s), 130.97 (2C, s), 126.95 (2C, s), 126.89 (2C, s), 126.00 (2C, s), 122.23 (2C, s), 124-100 (12C, m), 35.96 (2C, s), 32.35 (2C, t), 27.49 (2C, t) ppm; mp: 179 °C (hb).

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylimidazolium 1-diazo-2-naphthol-4-sulfonate **II**-h5

2.30 g (5.00 mmol) of dep-**II** were added to a solution of 1.34 g (5.00 mmol) of 1-diazo-2-naphthol-4-sulfonic acid (93%, contains 7% water) in 10 ml of methanol and the resulting mixture was stirred for 15 min at room temperature. After that, the solvent was evaporated and the resulting yellow-orange solid dried *in vacuo* overnight. 3.54 g (4.98 mmol, 99% of theoretical yield) of **II**-h5 were isolated.

IR (ATR, neat) 3136, 2959, 2101, 1610, 1567, 1489, 1479, 1452, 1363, 1338, 1298, 1228, 1184, 1141, 1120, 1089, 1040, 960, 909, 885, 836, 763, 746, 698, 644, 577, 526, 492, 447, 413 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CD_3OD$) δ 8.62 (1H, d), 7.68 (1H, d), 7.62 (1H, d), 7.57-7.25 (4H, m), 3.91 (3H, s), 3.39 (2H, t), 2.65 (2H, tt). $^{13}C$ NMR (75 MHz, $CD_3OD$) δ 181.07 (s), 154.17 (s), 140.71 (s), 131.15 (s), 130.74 (s), 128.98 (s), 127.11 (s), 125.55 (s), 124.54 (s), 122.67 (s), 122.63 (s), 121.41 (s), 124-100 (6C, m), 36.01 (s), 32.42 (t), 27.55 (t) ppm. Note: one quaternary carbon atom was not detected. mp: 80 °C (under dec. and discoloration; dec. starts at 74 °C; also photosensitive; hb).

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylimidazolium 3-hydroxy-4-[2-(2-hydroxy-5-methylphenyl)diazenyl]-naphthalene-1-sulfonate, **II**-i1

2.00 g (4.35 mmol) of dep-**II** were added to a solution of 1.56 g (4.35 mmol) of Calmagite [3147-14-6] in 100 ml of ethanol and the resulting mixture was ultrasonicated for 30 min at room temperature, then stirred overnight. After that, the solvent was evaporated and the resulting deep red solid dried *in vacuo* overnight. 3.52 g (4.30 mmol, 99% of theoretical value) of **II**-i1 could be isolated.

IR (ATR, neat) 3137, 2947, 1615, 1593, 1556, 1494, 1448, 1362, 1186, 1142, 1121, 1090, 1043, 994, 957, 913, 885, 844, 809, 746, 707, 647, 617, 598, 565, 528, 448 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CD_3OD$) δ 8.73 (2H, m), 7.93-6.83 (8H, m), 3.74 (3H, s), 3.18 (2H, t), 2.53 (2H, tt), 2.34 (2H, s). N-H and O-H signals not visible due to H-D exchange. $^{13}C$ NMR (75 MHz, $CD_3OD$) δ 169.72 (s), 151.16 (s), 148.95 (s), 140.76 (s), 135.16 (s), 132.93 (s), 131.50 (s), 131.44 (s), 131.23 (s), 129.58 (s), 128.98 (s), 128.71 (s), 126.18 (s), 124.85 (s), 124.71 (s), 122.46 (s), 120.41 (s), 118.83 (s), 117.31 (s), 124-100 (6C, m), 34.29 (s), 32.75 (t), 26.58 (t), 20.80 (s) ppm. mp: N/A, dec. and discoloration starting at 116 °C (hb).

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylimidazolium 1-amino-4-[[3-(ethenylsulfonyl)phenyl]amino]-9,10-dihydro-9,10-dioxo-2-anthracenesulfonate, **II**-i2

343 mg (0.691 mmol) of **II**-a1 were added to a solution of 500 mg (0.691 mmol) of acid blue 215 (70%, [14541-90-3]) in 20 ml of acetone and the resulting reaction mixture was stirred at room temperature overnight. The next day, precipitated NaCl was filtered off, followed by evaporation of the solvent and drying of the product in high vacuum. 650 mg (0.688 mmol, 99% of theoretical yield) of a dark blue lacquer-like powder were obtained.

IR (ATR, neat) 3403, 3269, 3128, 1588, 1569, 1533, 1488, 1406, 1365, 1303, 1231, 1185, 1140, 1091, 1037, 1019, 932, 892, 793, 746, 727, 697, 680, 663, 632, 546, 504, 480, 448, 405 $cm^{-1}$. $^{1}H$ NMR (300 MHz, acetone-d6) δ 11.90 (1H, s), 8.29 (1H, s), 8.21 (2H, dd), 7.90-7.55 (8H, m), 7.01 (1H, dd), 6.42 (1H, d), 6.20 (1H, d), 4.00 (3H, s), 3.55 (2H, t), 2.74 (2H, tt) ppm. N-H signals other than imine signal not visible due to H-D exchange. $^{13}C$ NMR (75 MHz, acetone-d6) δ 184.92 (s), 183.62 (s), 145.80 (s), 142.64 (s),

142.35 (s), 142.13 (s), 140.35 (s), 139.69 (s), 139.47 (s), 135.37 (s), 134.54 (s), 134.05 (s), 133.48 (s), 131.71 (s), 129.16 (s), 127.43 (s), 127.00 (s), 126.92 (s), 126.56 (s), 124.14 (s), 122.62 (s), 121.05 (s), 115.10 (s), 111.49 (s), 124-100 (6C, m), 36.03 (s), 32.08 (t), 27.27 (t) ppm; mp: 150 °C (also, starts reacting at 120 °C, possibly polymerisation; hb).

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylimidazolium 2-acrylamido-2-methylpropanesulfonate, **II**-j1

1.84 g (4.00 mmol) of dep-**II** were added to a solution of 826 mg (4.00 mmol) of 2-acrylamido-2-methylpropanesulfonic acid in 30 ml of methanol and the resulting mixture was stirred for 15 min at room temperature. After that, the solvent was evaporated, the residue washed twice with 5 ml of hexane, and the product dried *in vacuo*. 2.24 g (3.36 mmol, 84% of theoretical yield) of **II**-j1 were obtained.

IR (ATR, neat) 3263, 3164, 3110, 2982, 2663, 1654, 1612, 1569, 1495, 1440, 1406, 1363, 1340, 1322, 1295, 1281, 1239, 1219, 1105, 1159, 114, 1118, 1068, 1035, 987, 961, 922, 869, 805, 785, 759, 733, 722, 706, 678, 629, 621, 602, 550, 521, 508, 475, 413 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CD_3OD$) δ 7.75 (1H, d), 7.70 (1H, d), 6.25-6.07 (2H, m), 5.57 (1H, dd), 3.96 (3H, s), 3.44 (2H, t), 3.24 (2H, s), 2.69 (2H, tt), 1.57 (6H, s) ppm. $^{13}C$ NMR (75 MHz, $CD_3OD$) δ 167.56 (s), 140.93 (s), 133.69 (s), 127.35 (s), 125.73 (s), 122.68 (s), 124-100 (6C, m), 60.28 (s), 53.60 (s), 36.21 (s), 32.63 (t), 27.78 (t), 27.19 (2C, s) ppm. mp: 97 °C (hb).

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylimidazolium 2-(acryloyloxy)ethane-1-sulfonate, **II**-j2

4.60 g (10.00 mmol) of dep-**II** were added to a solution of 1.80 g (10.00 mmol) of 2-(acryloyloxy)ethane-1-sulfonic acid in 10 ml of methanol and the resulting mixture was stirred for 15 min at room temperature. After that, the solvent was evaporated and the residue was dried *in vacuo*. 6.15 g (9.40 mmol, 94% of theoretical yield) of **II**-j2 were obtained.

IR (ATR, neat) 3135, 1710, 1641, 1583, 1455, 1364, 1318, 1297, 1245, 1217, 1164, 1141, 1122, 1091, 1073, 1032, 1013, 945, 913, 814, 786, 725, 708, 686, 670, 644, 611, 565, 525, 445, 407 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CD_3OD$) 7.73 (1H, d), 7.69 (1H, d), 6.12 (1H, m), 5.61 (1H, m), 4.49 (2H, t), 3.96 (3H, s), 3.43 (2H, t), 3.17 (2H, t), 2.68 (2H, tt), 1.92 (3H, s) ppm. $^{13}C$ NMR (75 MHz, $CD_3OD$) 168.71 (s), 140.94 (s), 137.71 (s), 127.35 (s), 126.57 (s), 122.70 (s), 124-100 (6C, m), 61.73 (s), 51.33 (s), 36.18 (s), 32.65 (t), 27.76 (t), 18.51 (s) ppm. mp: 89 °C (hb).

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylimidazolium vinylphosphonate, **II**-j3

0.38 g (3.52 mmol) of vinylphosphonic acid were added to 1.62 g (3.52 mmol) of dep-**II** at 40 °C. The reaction mixture was stirred at 40°C for 30 minutes, then stored at 4 °C for 5 hours. 2.00 g (3.52 mmol, 100% of theoretical yield) of highly viscous, liquid **II**-j3 were obtained.

IR (ATR, neat) 3126, 2949, 2333, 1583, 1495, 1462, 1444, 1401, 1363, 1317, 1232, 1187, 1142, 1121, 1089, 1069, 989, 956, 842, 808, 770, 724, 706, 645, 605, 565, 525, 443 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CD_3OD$) δ 7.54 (1H, d), 7.43 (1H, d), 6.32-5.73 (3H, m), 3.86 (3H,s), 3.38 (2H, t), 3.35 (1H, s), 2.62 (2H, tt) ppm. $^{13}C$ NMR (75 MHz, $CD_3OD$) δ 140.67 (s), 133.29 (d), 129.86 (d), 126.21 (s), 125.44 (s), 124-100 (6C, m), 35.26 (s), 32.61 (t), 27.24 (t) ppm.

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylimidazolium iodide • perfluorohexyl iodide, **II**-k1

1.35 g (3.00 mmol) of perfluorohexyl iodide (98%) was added to a dispersion of 1.76 g (3.00 mmol) of **II**-a3 in 8 ml of acetone, upon which a yellowish solution formed. This solution was kept unsealed overnight in order to allow for evaporation of the solvent. 3.04 g (2.94 mmol, 98% of theoretical yield) of yellowish **II**-k1 were isolated.

IR (ATR, neat) 3086, 2966, 2832, 1575, 1483, 1361, 1317, 1288, 1191, 1140, 1124, 1088, 1074, 1024, 960, 917, 838, 806, 777, 734, 723, 706, 685, 643, 606, 566, 528, 435 $cm^{-1}$. $^{1}H$ NMR (300 MHz, acetone-d6) δ 10.93 (1H, s(br)), 7.96 (1H, d), 7.81 (1H, d), 4.11 (3H, s), 3.69 (2H, t), 2.84 (2H, tt) ppm. $^{13}C$ NMR (75 MHz, acetone-d6) δ 140.18 (s), 126.71 (s), 121.79 (s), 124-97 (12C, m), 36.65 (s), 32.33 (t), 28.21 (t) ppm; mp: N/A; fast evaporation of perfluorohexyl iodide at 120 °C, fast dec. at 150 °C (hb).

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylimidazolium iodide • perfluorooctyl iodide, **II**-k2

1.67 g (3.00 mmol) of perfluorooctyl iodide (98%) was added to a dispersion of 1.76 g (3.00 mmol) of **II**-a3 in 7 ml of acetone, upon which a yellowish solution formed. This solution was kept unsealed overnight in order to allow for evaporation of the solvent. 3.28 g (2.89 mmol, 96% of theoretical yield) of yellow **II**-k2 were isolated. Single crystals of **II**-k2 suitable for structure determination were obtained through slow diffusion of chloroformic solutions of **II**-a3 and perfluorooctyl iodide.

IR (ATR, neat) 3112, 3032, 2990, 1575, 1483, 1365, 1324, 1195, 1141, 1086, 1038, 962, 917, 769, 734, 722, 706, 638, 566, 555, 527, 431 $cm^{-1}$. $^{1}H$ NMR (300 MHz, acetone-d6) δ 9.82 (1H, s(br)), 7.94 (1H, d), 7.81 (1H, d), 4.11 (3H, s), 3.68 (2H, t), 2.83 (2H, tt) ppm. $^{13}C$ NMR (75 MHz, acetone-d6) δ 140.25 (s), 126.75 (s), 122.08 (s), 124-96 (14C, m), 36.55 (s), 32.36 (t), 28.08 (t) ppm; mp: 94 °C (hb).

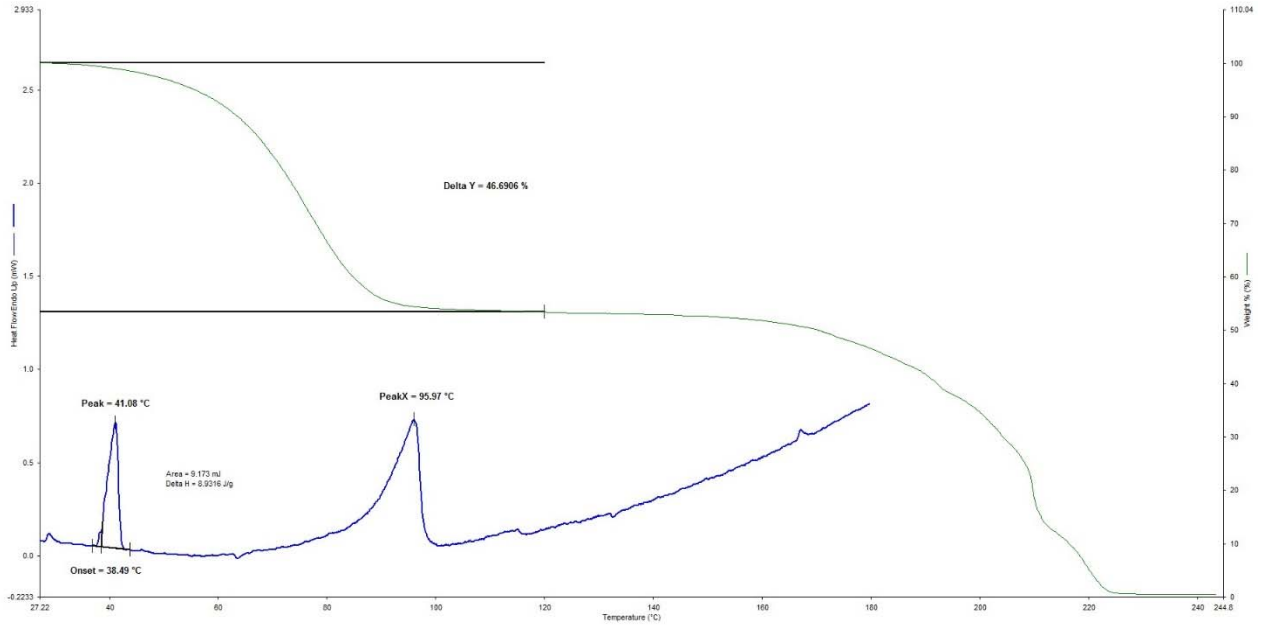


Figure S14. TGA/DSC: observed weight loss until 120 °C: 46.7 %; theoret. weight loss for one $C_8F_{17}I$ unit: 48.1 %.

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylimidazolium bis(trifluoromethanesulfonyl)imide, **II**-l1

**II**-l1 was prepared following the procedure described for **I**-l1: (39.3 g; 137 mmol; 1.61 eq) of lithium bis(trifluoromethanesulfonyl)imide and (50.0g; 85.0 mmol) of **II**-a3 yielded 59.8 g (95% of theory).

IR (neat) 3167, 1562, 1490, 1348, 1234, 1184, 1140, 1092, 1056, 961, 830, 744, 707, 651, 615, 601, 570, 511 $cm^{-1}$; $^1H$ NMR (300 MHz, DMSO-d6) δ 13.22 (1H, s(br)), 7.83 (1H, d), 7.79 (1H, d), 3.83 (3H, s), 3.37 (2H, t), 2.66 (2H, tt) ppm.

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylimidazolium bis(pentafluoroethylsulfonyl)imide, **II**-l2

1.35 g (3.50 mmol) of lithium bis(pentafluoroethylsulfonyl)imide were dissolved in 30 ml of water, followed by addition of 30 ml of diethyl ether. 2.00 g (3.40 mmol) of **II**-a3 were added to the mixture, which was then stirred at room temperature overnight. Following this step, the now clear, biphasic solution was transferred to a separatory funnel. The aqueous phase was extracted with another 50 ml of diethyl ether once, and the combined organic phases were extracted with 50 ml of water, followed by desiccation with sodium sulphate and evaporation of diethyl ether *via* a rotary evaporator. Finally, the product, a colourless, viscous oil, was dried in high vacuum overnight. This affords 2.10 g (2.50 mmol, 74% of theoretical yield) of **II**-l2.

IR (ATR, neat) 3155, 1581, 1489, 1445, 1350, 1328, 1209, 1164, 1141, 1089, 977, 843, 809, 772, 743, 707, 642, 613, 522 $cm^{-1}$. $^1H$ NMR (300 MHz, DMSO-d6) δ 13.50 (1H, s(br)), 7.83 (1H, d), 7.79 (1H, d), 3.84 (3H, s), 3.37 (2H, t), 2.66 (2H, tt) ppm. $^{13}C$ NMR (75 MHz, DMSO-d6) δ 138.83 (s), 125.80 (s), 121.61 (s), 124-100 (10C, m), 35.15 (s), 31.01 (t), 26.15 (t) ppm.

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylimidazolium picrate, **II**-m

2.30 g (5.00 mmol) of dep-**II** were added to a solution of 1.15 g (5.00 mmol) of picric acid in 10 ml of methanol and the resulting mixture was stirred for 30 min at room temperature. After that, the solvent was evaporated and the yellow product dried *in vacuo* overnight. 3.34 g (4.85 mmol, 97% of theoretical yield) of **II**-m were obtained.

IR (ATR, neat) 3133, 2954, 2646, 1629, 1614, 1567, 1550, 1522, 1487, 1429, 1363, 1337, 1312, 1263, 1232, 1186, 1163, 1141, 1120, 1068, 964, 940, 911, 837, 803, 786, 769, 745, 723, 700, 644, 605, 565, 525, 429 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CD_3CN$) δ 12.70 (1H, s(br)), 8.71 (2H, s), 7.47 (1H, d), 7.43 (1H, d), 3.80 (3H, s), 3.39 (2H, t), 2.58 (2H, tt) ppm. $^{13}C$ NMR (75 MHz, $CD_3CN$) δ 162.89 (s), 143.37 (s), 140.68 (s), 128.91 (s), 126.96 (s), 126.54 (s), 123.93 (s), 36.38 (s), 32.72 (t), 27.59 (t) ppm; mp: 66 °C (hb).

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylimidazolium docusate, **II**-n

2.48 g (5.00 mmol) of **II**-a1 were added to a solution of 2.22 g (5.00 mmol) of sodium docusate [577-11-7] in 20 ml of acetone and the resulting reaction mixture was stirred at room temperature overnight. The precipitated NaCl was filtered off, followed by evaporation of the solvent and drying of the product in high vacuum. 4.37 g (4.95 mmol, 99% of theoretical yield) of a highly viscous colourless oil were isolated.

IR (ATR, neat) 3127, 2961, 2933, 2862, 1732, 1583, 1492, 1463, 1416, 1381, 1362, 1317, 1235, 1192, 1143, 1121, 1091, 1033, 1071, 961, 908, 846, 808, 771, 745, 707, 736, 646. 566, 527 $cm^{-1}$. $^{1}H$ NMR (300 MHz, acetone-d6) δ 7.81 (1H, d), 7.63 (1H, d), 3.99 (8H, m), 3.63 (2H, t), 3.10 (2H, m), 2.81 (2H, tt), 1.57 (2H, m), 1.33 (16H, m), 0.89 (12H, m) ppm. $^{13}C$ NMR (75 MHz, acetone-d6) δ 171.64 (s), 169.20 (s), 140.14 (s), 126.64 (s), 122.70 (s), 124-100 (6C, m), 67.51 (s), 67.12 (s), 62.72 (s), 39.51 (s), 39.47 (s), 36.11 (s), 34.65 (s), 31.98 (t), 30.90 (s), 30.81 (s), 30.76 (s), 29.51 (s), 27.14 (t), 24.21 (s), 24.10 (s), 23.48 (s), 23.46 (s), 14.19 (s), 14.16 (s), 11.13 (s), 11.07 (s) ppm.

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylimidazolium 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate, **II**-o

2.30 g (5.00 mmol) of dep-**II** were added to a solution of 1.06 g (5.00 mmol) of hexafluoroacetylacetone (98%) in 10 ml of acetone and the resulting mixture was stirred for 15 min at room temperature. After that, the solvent was evaporated and the resulting colourless liquid dried *in vacuo* overnight. 3.34 g (5.00 mmol, 100% of theoretical yield) of **II**-o were obtained.

IR (ATR, neat) 3128, 2960, 1714, 1669, 1581, 1531, 1364, 1239, 1183, 1132, 1019, 960, 898, 788, 745, 737, 707, 659, 646, 574, 529, 446 $cm^{-1}$. $^{1}H$ NMR (300 MHz, acetone-d6) δ 15.83 (1H, s(br)), 7.63 (1H, d), 7.40 (1H, d), 5.85 (1H, s), 3.87 (3H, s), 3.55 (2H, t), 2.59 (2H, tt) ppm. $^{13}C$ NMR (75 MHz, acetone-d6) δ 175.05 (2C, q), 139.96 (s), 125.06 (s(br)), 123.64 (s(br)), 119.01 (2C, q), 124-100 (6C, m), 86.36 (s(br)), 34.99 (s), 31.95 (t), 27.05 (t) ppm.

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylimidazolium O,S-dimethyl phosphorothioate, **II**-q

2.50 g (5.00 mmol) of **II**-a1 were added to a dispersion of 821 mg (5.00 mmol) of sodium O,S-dimethyl phosphorothioate in 30 ml of acetone and the resulting reaction mixture was stirred at room temperature overnight. The next day, precipitated NaCl was filtered off, followed by evaporation of the solvent and drying of the product in high vacuum. 2.90 g (4.81 mmol, 96% of theoretical yield) of a highly viscous colourless oil were isolated.

IR (ATR, neat) 3127, 2946, 2842, 1713, 1582, 1495, 1442, 1364, 1317, 1230, 1187, 1142, 1045, 1121, 1090, 959, 888, 845, 808, 766, 746, 706, 646, 567, 529, 439 $cm^{-1}$. $^{1}H$ NMR (300 MHz, acetone-d6) δ 9.39 (1H, s(br)), 7.62 (1H, d), 7.42 (1H, d), 3.89 (3H, s), 3.59 (3H, d), 3.53 (2H, t), 2.78 (2H, tt), 2.16 (3H, d) ppm. $^{13}C$ NMR (75 MHz, acetone-d6) δ 140.26 (s), 125.99 (s), 125.11 (s), 124-100 (6C, m), 52.83 (d), 34.99 (s), 32.36 (t), 26.47 (t), 12.64 (d) ppm.

2-(1H,1H,2H,2H-perfluorodecylthio)-1-methylimidazolium iodide **III**-a3

9.31 g (16.2 mmol) of 1H,1H,2H,2H-perfluorodecyl iodide, 3.00 g (98%, 26.3 mmol, 1,62 eq) 2-mercapto-1-methylimidazole, and 30 ml of ethanol were placed in a 100 ml-round bottom flask and refluxed for 20 h. Ethanol was stripped off by means of a rotary evaporator and the crude product was recrystallised in 45 ml of $CH_2Cl_2$. The obtained product was filtered off, washed 2 times with cold $CH_2Cl_2$ and finally dried in a vacuum desiccator. Yield: 9.63 g (94%).

IR (ATR, neat) 3084, 2948, 2831, 1574, 1784, 1439, 1368, 1328, 1196, 1143, 1114, 1094, 1037, 956, 773, 704, 635, 600, 559, 527 $cm^{-1}$; $^{1}H$ NMR (300 MHz, $CDCl_3$) δ 7.50 (1H, d), 7.42 (1H, d), 3.91 (3H, s), 3.74 (2H, t), 2.61 (2H, tt) ppm; mp: 155 ºC (hb).

3-(3,3,4,4,4-pentafluorobutyl)-2-((3,3,4,4,4-pentafluorobutyl)thio)-1-methylimidazolium iodide **IV**-a3

2.41 g (9.26 mmol) of **dep-I** and 4.95 g (18.07 mmol) of 3,3,4,4,4-pentafluorobutyl iodide were refluxed in acetonitrile for 24 h. After cooling, a white precipitate formed which was isolated via a glass frit (pore 3) and washed with small amounts of cold $CH_2Cl_2$. The product was dried under vacuum to yield 1.24 g (25 % of theory).

IR (ATR, neat) 3488, 3077, 1562, 1491, 1452, 1432, 1358, 1339, 1317, 1300, 1285, 1234, 1197, 1181, 1137, 1117, 1072, 1057, 1006, 985, 961, 922, 892, 777, 734, 695, 674, 648, 635, 599, 564, 547, 526, 494, 418 $cm^{-1}$; $^{1}H$ NMR (300 MHz, $CD_3OD$) δ 8.07 (1H, d), 7.93 (1H, d), 4.77 (2H, t), 4.08 (3H, s), 3.41 (2H, t), 2.99 (2H, tt), 2.69 (2H, tt) ppm. $^{13}C$ NMR (75 MHz, $CD_3OD$) δ 141.19 (s), 127.50 (s), 125.60 (s), 124-110 (4C, m), 43.43 (t), 37.93 (s), 31.89 (t), 31.78 (t), 28.57 (t) ppm; mp: 88 °C (hb).

3-(1H,1H,2H,2H-perfluorooctyl)-2-((1H,1H,2H,2H-perfluorooctyl)thio)-1-methylimidazolium chloride **V**-a1

0.60 g (4.20 mmol) of silver chloride were added to 3.76 g (4.02 mmol) of **V**-a3 in 50 ml of methanol. The resulting mixture was stirred at room temperature overnight, after which precipitated silver iodide was filtered off and the now clear solution was evaporated. After drying in high vacuum, 3.20 g (3.80 mmol, 95% of theoretical yield) of off-white **V**-a1 were obtained.

IR (ATR, neat) 3069, 2958, 1564, 1494, 1457, 1438, 1364, 1319, 1227, 1197, 1179, 1137, 1093, 1076, 960, 801, 736, 726, 705, 694, 636, 566, 527, 497, 477, 429 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CD_3OD$) δ 8.04 (1H, d), 7.91 (1H, d), 4.78 (2H, t), 4.07 (3H, s), 3.39 (2H, t), 3.00 (2H, tt), 2.79 (2H, tt) ppm. $^{13}C$ NMR (75 MHz, $CD_3OD$) δ 141.26 (s), 127.61 (s), 125.63 (s), 124-100 (12C, m), 43.23 (t), 37.37 (s), 32.09 (t), 31.92 (t), 27.95 (d) ppm; mp: 94 °C (hb).

3-(1H,1H,2H,2H-perfluorooctyl)-2-((1H,1H,2H,2H-perfluorooctyl)thio)-1-methylimidazolium iodide **V**-a3

9.48 g (20.0 mmol) of 1H,1H,2H,2H-perfluorooctyl iodide was added to 4.60 g (10.0 mmol) of dep-**II**. The resulting mixture was stirred at 100 °C for 24 h. After the reaction mixture was cooled to room temperature, 100 ml of diethyl ether were added which induced precipitation of the product. The heterogeneous mixture was then ultrasonicated for an hour. Following this step, the product was filtered off, washed with 100 ml of diethyl ether and dried in high vacuum overnight. This afforded 8.46 g (9.05 mmol, 91% of theoretical yield) of off-white **V**-a3. Single crystals of **V**-a3 suitable for structure determination were obtained from acetonitrile solution.

IR (ATR, neat) 3484, 3414, 3145, 3079, 2926, 1562, 1491, 1452, 1432, 1359, 1340, 1318, 1301, 1285, 1237, 1198, 1182, 1138, 1118, 1073, 1006, 985, 962, 923, 892, 776, 735, 696, 675, 649, 636, 600, 565, 527, 494, 418 $cm^{-1}$ (The low solubility of the product in any solvent did not allow for comparative NMR spectra). mp: 115 °C (under dec., hb).

3-(1H,1H,2H,2H-perfluorooctyl)-2-((1H,1H,2H,2H-perfluorooctyl)thio)-1-methylimidazolium iodide • perfluorooctyl iodide **V**-k2

1.20 g (2.14 mmol) of perfluorooctyl iodide (98%) were added to a dispersion of 2.00 g (2.14 mmol) of **V**-a3 in 30 ml of acetone upon which a yellowish solution formed. This solution was kept at open atmosphere and over the course of 3 days the solvent evaporated entirely. 3.28 g (2.89 mmol, 96% of theoretical yield) of yellow, macrocrystalline **II**-k2 were isolated.

IR (ATR, neat) 3082, 1562, 1491, 1450, 1412, 1367, 1321, 1196, 1139, 1119, 1088, 1038, 959, 918, 896, 843, 831, 774, 746, 735, 723, 707, 696, 676, 641, 555, 527, 418 $cm^{-1}$. $^{1}H$ NMR (300 MHz, acetone-d6) δ 8.29 (1H, d), 8.12 (1H, d), 5.00 (2H, t), 4.22 (3H, s), 3.60 (2H, t), 3.20 (2H, tt), 2.88 (2H, tt) ppm. $^{13}C$ NMR (75 MHz, acetone-d6) δ 140.97 (s), 127.33 (s), 125.53 (s), 124-96 (20C, m), 43.08 (t), 37.82 (s), 32.05 (t), 31.92 (t), 28.13 (t) ppm; mp: 70 °C (hb).

2-(1H,1H,2H,2H-perfluorooctylthio)-1,3-dimethylimidazolium chloride **VI**-a1

1.43 g (10.00 mmol) of silver chloride were added to 5.00 g (8.30 mmol) of **VI**-a3, dissolved in 20 ml of methanol. The resulting mixture was stirred at room temperature overnight, after which precipitated silver iodide was filtered off and the now clear solution was evaporated. After drying in high vacuum, 4.06 g (7.95 mmol, 96% of theoretical yield) of pure-white **VI**-a1 were obtained.

IR (ATR, neat) 3048, 2994, 2939, 1628, 1570, 1511, 1449, 1436, 1413, 1364, 1317, 1298, 1252, 1197, 1179, 1136, 1118, 1093, 1074, 1029, 964, 915, 813, 707, 690, 640, 608, 564, 528, 479cm$^{-1}$. $^{1}$H NMR (300 MHz, $CD_3OD$) δ 7.86 (2H, s), 4.05 (6H, s), 3.37 (2H, t), 2.72 (2H, tt) ppm. $^{13}$C NMR (75 MHz, $CD_3OD$) δ 140.86 (s), 126.78 (2C, s), 124-100 (6C, m), 37.25 (2C, s), 32.28 (t), 27.61 (t) ppm; mp: 231 °C (under immediate dec., hb).

2-(1H,1H,2H,2H-perfluorooctylthio)-1,3-dimethylimidazolium iodide **VI**-a3

5.60 g (2.50 ml, 40.2 mmol) of methyl iodide were added to 9.77 g (21.2 mmol) of dep-**II** dissolved in 20 ml of acetonitrile. The mixture was refluxed for 24 h, during which time some precipitate formed. After the reaction mixture had cooled to room temperature, 100 ml of diethyl ether were added to assure complete product precipitation. The product was filtered off, washed with 100 ml of diethyl ether and dried in high vacuum overnight. This afforded 12.15 g (20.17 mmol, 95% of theoretical yield) of high-purity **VI**-a3.

IR (ATR, neat) 3069, 3050, 1664, 1570, 1504, 1436, 1424, 1360, 1312, 1232, 1186, 1140, 1120, 1093, 1072, 1031, 962, 904, 848, 814, 793, 782, 736, 705, 662, 643, 628, 565, 531, 481, 407 cm$^{-1}$. $^{1}$H NMR (300 MHz, $CD_3OD$) δ 7.88 (2H, s), 4.09 (6H, s), 3.42 (2H, t), 2.77 (2H, tt) ppm. $^{13}$C NMR (75 MHz, $CD_3OD$) δ 140.94 (s), 126.71 (2C, s), 124-100 (6C, m), 37.41 (2C, s), 32.32 (t), 27.85 (t) ppm; mp: 218 °C (under immediate dec.).

2-(1H,1H,2H,2H-perfluorooctylthio)-1,3-dimethylimidazolium perfluorooctanoate **VI**-e3

3.01 g (5.00 mmol) of **VI**-a3 were added to 2.60 g (5.00 mmol) of silver perfluorooctanoate dissolved in 10 ml of acetone. The mixture was stirred at room temperature overnight, after which precipitated silver iodide was filtered off. The solvent was removed carefully *via* a rotary evaporator, the resulting white solid product then dried in high vacuum overnight. 4.00 g (4.50 mmol, 90% of theoretical yield) of **VI**-e3 were isolated.

IR (ATR, neat) 3077, 3059, 1683, 1572, 1510, 1434, 1354, 1319, 1233, 1196, 1142, 1100, 1087, 1068, 1011, 886, 837, 802, 779, 746, 729, 721, 698, 698, 645, 604, 560, 529, 409 cm$^{-1}$. $^{1}$H NMR (300 MHz, DMSO-d6) δ 7.97 (2H, s), 6.58 (1H, ddd), 3.91 (6H, s), 3.27 (2H, t), 2.67 (2H, tt) ppm. $^{13}$C NMR (75 MHz, DMSO-d6) δ 157.45 (t), 138.68 (s), 125.32 (2C, s), 124-100 (13C, m), 36.17 (2C, s), 30.56 (t), 26.01 (t) ppm; mp: 130 °C (hb).

2-(1H,1H,2H,2H-perfluorooctylthio)-1,3-dimethylimidazolium 4,8-dioxa-3H-perfluorononanoate **VI**-f1

3.01 g (5.00 mmol) of **VI**-a3 were added to 2.43 g (5.00 mmol) of silver 4,8-dioxa-3H-perfluorononanoate dissolved in 20 ml of acetone. The mixture was stirred at room temperature overnight, after which precipitated silver iodide was filtered off. The solvent was removed carefully *via* a rotary evaporator, the oily product finally dried in high vacuum overnight, whereupon it solidified. 4.07 g (4.78 mmol, 96% of theoretical yield) of **VI**-f1 were isolated.

IR (ATR, neat) 3101, 1663, 1570, 1506, 1342, 1342, 1230, 1193, 1140, 1122, 1053, 983, 892, 862, 827, 808, 745, 725, 707, 645, 565, 529 $cm^{-1}$. $^{1}H$ NMR (300 MHz, DMSO-d6) δ 7.98 (2H, s), 6.58 (1H, ddd), 3.92 (6H, s), 3.28 (2H, t), 2.67 (2H, tt) ppm. $^{13}C$ NMR (75 MHz, DMSO-d6) δ 160.78 (t), 138.71 (s), 125.39 (2C, s), 124-100 (12C, m), 36.18 (2C, s), 30.61 (t), 26.05 (t) ppm.

2-(1H,1H,2H,2H-perfluorooctylthio)-1,3-dimethylimidazolium methyl sulfate **VI**-p

0.64 g (5.00 mmol) of dimethyl sulfate were added to 2.30 g (5.00 mmol) of dep-**II** dissolved in 5 ml of acetonitrile. The resulting mixture was then refluxed for 3 hours before the solvent was evaporated and the oily product was dried *in vacuo* overnight, whereupon it solidified. 2.89 g (4.93 mmol, 99% of theoretical yield) of **VI**-p were isolated.

IR (ATR, neat) 3146, 3105, 2952, 1569, 1507, 1433, 1365, 1318, 1188, 1141, 1087, 1059, 1006, 922, 838, 808, 779, 731, 700, 647, 609, 577, 555, 531, 433 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CD_3OD$) δ 7.81 (2H, s), 4.04 (6H, s), 3.65 (3H, s), 3.35 (2H, t), 2.71 (2H, tt) ppm. $^{13}C$ NMR (75 MHz, $CD_3OD$) δ 140.71 (s), 126.76 (2C, s), 124-100 (6C, m), 55.00 (s), 37.15 (2C, s), 32.19 (t), 27.49 (t) ppm.

2-(1H,1H,2H,2H-perfluorooctylthio)-1-ethyl-3-methylimidazolium bromide **VII**-a2

0.77 g (7.00 mmol) of ethyl bromide were added to 2.30 g (5.00 mmol) of dep-**II** dissolved in 5 ml of acetonitrile. The resulting mixture was then refluxed overnight. After cooling to room temperature, 50 ml of diethyl ether were added to the mixture, resulting in precipitation of the product. The product was filtered off, washed with 50 ml of diethyl ether and dried in high vacuum overnight. 1.10 g (1.77 mmol, 35% of theoretical yield) of virtually pure **VII**-a2 were obtained.

IR (ATR, neat) 3460, 3127, 3053, 2968, 2934, 1563, 1497, 1466, 1424, 1362, 1317, 1231, 1199, 1173, 1142, 1086, 1067, 1034, 1004, 884, 836, 804, 778, 746, 728, 709, 697, 676, 647, 639, 565, 531, 501 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CD_3OD$) δ 8.01 (1H, d), 7.94 (1H, d), 4.49 (2H, q), 4.09 (3H, s), 3.41 (2H, t), 2.75 (2H, tt), 1.57 (3H, t) ppm. $^{13}C$ NMR (75 MHz, $CD_3OD$) δ 140.08 (s), 127.30 (s), 125.04 (s), 124-100 (6C, m), 46.46 (s), 37.43 (s), 32.26 (t), 28.19 (t), 15.90 (s) ppm; mp: 119 °C (hb).

2-(1H,1H,2H,2H-perfluorooctylthio)-1-ethyl-3-methylimidazolium tetrafluoroborate **VII**-b1

0.64 g (3.37 mmol) of triethyl oxonium tetrafluoroborate were added to 1.38 g (3.00 mmol) of dep-**II** dissolved in 5 ml of dry $CH_2Cl_2$ while cooled by means of an ice bath. The resulting mixture was then stirred at room temperature overnight. The solvent was removed via vacuum pump and the residual dissolved in a mixture of $CH_2Cl_2$ and $H_2O$. The biphasic solution was transferred to a separatory funnel, the organic phases washed with water, followed by desiccation with sodium sulphate and evaporation of $CH_2Cl_2$ *via* a rotary evaporator to yield 1.53 g (2.66 mmol, 89% of theoretical yield) of **VII**-b1.

IR (ATR, neat) 3170, 3141, 1571, 1503, 1466, 1363, 1316, 1232, 1188, 1143, 1122, 1028, 964, 915, 848, 810, 774, 738, 706, 644, 565, 528 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CD_3OD$) δ 7.83 (1H, d), 7.77 (1H, d), 4.43 (2H, q), 4.02 (3H, s), 3.33 (2H, t), 2.68 (2H, tt), 1.52 (3H, t) ppm. $^{13}C$ NMR (75 MHz, $CD_3OD$) δ 139.83 (s), 127.20 (s), 124.86 (s), 124-100 (6C, m), 46.25 (s), 36.92 (s), 32.05 (t), 27.77 (t), 15.60 (s) ppm; mp: 105 °C (hb).

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methyl-3-octylimidazolium iodide **VIII**-a3

8.64 g (36.0 mmol) of octyl iodide were added to 13.81 g (30.00 mmol) of dep-**II**. The resulting mixture was stirred at 100 °C for 48 h. After letting the reaction mixture cool to room temperature, 300 ml of diethyl ether were added, which first led to the formation of a separate liquid phase. However, upon manual stirring, this phase solidified and turned into a white powder with time. The product was filtered off, washed with 100 ml of diethyl ether twice and dried in high vacuum overnight. This afforded 14.00 g (20.00 mmol, 67% of theoretical yield) of **VIII**-a3.

IR (ATR, neat) 3076, 3042, 2963, 2932, 2860, 1564, 1496, 1459, 1417, 1360, 1318, 1296, 1232, 1188, 1143, 1120, 1091, 1069, 1032, 960, 893, 845, 804, 771, 745, 722, 705, 677, 641, 605, 565, 527, 431 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CD_3OD$) δ 8.05 (1H, d), 7.98 (1H, d), 4.51 (2H, t), 4.18 (3H, s), 3.50 (2H, t), 2.84 (2H, tt), 2.04 (2H, quin), 1.48 (10H, m), 1.01 (3H, s) ppm. $^{13}C$ NMR (75 MHz, $CD_3OD$) δ 140.24 (s), 127.20 (s), 125.40 (s), 124-100 (6C, m), 51.23 (s), 37.57 (s), 32.88 (s), 32.20 (t), 31.32 (s), 30.18 (s), 30.13 (s), 28.43 (t), 27.40 (s), 23.62 (s), 14.36 (s) ppm; mp: 90 °C (under dec., hb).

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methyl-3-octylimidazolium bis(trifluoromethanesulfonyl)imide **VIII**-l1

50 ml of diethyl ether and 5.00 g (7.14 mmol) of **VIII**-a3 were added to 2.10 g (7.14 mmol) of lithium bis(trifluoromethanesulfonyl)imide dissolved in 10 ml of water. The heterogeneous mixture was vigorously stirred for 1 h and then the phases separated using a separatory funnel. The aqueous phase was extracted with another 50 ml of diethyl ether once, and the combined organic phases were extracted with 50 ml of water, followed by desiccation with sodium sulphate and evaporation of diethyl ether via a rotary evaporator. Finally, the resulting highly viscous, colourless oil was dried in high vacuum overnight. This afforded 5.21 g of **VIII**-l1 (6.10 mmol, 86% of theoretical yield).

IR (ATR, neat) 3141, 2933, 2861, 1567, 1496, 1459, 1348, 1229, 1180, 1135, 1092, 1055, 960, 895, 789, 739, 707, 651, 615, 600, 570, 511, 407 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CDCl_3$) δ 7.50 (1H, d), 7.48 (1H, d), 4.23 (2H, t), 3.94 (3H, s), 3.21 (2H, t), 2.48 (2H, tt), 1.78 (2H, quin), 1.25 (10H, m), 0.82 (3H, t) ppm. $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 138.27 (s), 126.13 (s), 124.11 (s), 119.80 (2C, q), 124-100 (6C, m), 50.25 (s), 36.54 (s), 31.60 (s), 31.01 (t), 30.18 (s), 28.88 (s), 28.81 (s), 27.16 (t), 26.17 (s), 22.45 (s), 13.69 (s) ppm.

3-(2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylímidazolium-3-yl)-propane-1-sulfonate **IX**

3.00 g (6.52 mmol) of dep-**II**, 0.92 g (7.50 mmol) of 1,3-propanesultone, and 5 ml of acetonitrile were mixed and the resulting solution was refluxed for 18 h, during which time some precipitate formed. After the reaction mixture was allowed to cool to room temperature, 50 ml of diethyl ether were added to induce complete precipitation. The white, powdery product was then filtered off, washed with 50 ml of diethyl ether once and dried in high vacuum overnight. 3.56 g of pure **IX** were isolated (6.11 mmol, 94% of theoretical yield). Single crystals of **IX** suitable for structure determination were obtained via reaction of dep-**II** with 1,3-propanesultone in dichloromethane.

IR (ATR, neat) 3152, 3104, 3088, 3064, 2952, 1575, 1507, 1454, 1421, 1367, 1352, 1319, 1298, 1244, 1209, 1179, 1140, 1093, 1067, 1029, 931, 888, 844, 807, 768, 742, 729, 705, 639, 570, 518, 489 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CD_3OD$) δ 7.99 (1H, d), 7.88 (1H, d), 4.64 (2H, t), 4.08 (3H, s), 3.40 (2H, t), 2.92 (2H, t), 2.78 (2H, tt), 2.38 (2H, quin) ppm. $^{13}C$ NMR (75 MHz, $CD_3OD$) δ 140.66 (s), 127.14 (s), 125.63 (s), 124-100 (6C, m), 49.70 (s), 48.66 (s), 37.06 (s), 32.04 (t), 27.96 (t), 27.13 (s) ppm; mp: 190 °C.

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methyl-3-(3-sulfopropyl)imidazolium trifluoromethanesulfonate **X**-g1

255 mg (1.70 mmol) of trifluoromethanesulfonic acid were added to 1.00 g (1.70 mmol) of **IX** dissolved in 10 ml of methanol and the resulting reaction mixture stirred for 10 min at room temperature. Subsequently, the solvent was evaporated using a rotary evaporator. Finally, the obtained oily liquid was dried at 50 °C *in vacuo* for 24 h, whereupon the product solidified. 1.19 g (1.62 mmol, 95% of theoretical yield) of pure-white, powdery **X**-g1 was isolated.

IR (ATR, neat) 3170, 3148, 1567, 1494, 1446, 1417, 1363, 1286, 1219, 1192, 1159, 1140, 1120, 1095, 1069, 1026, 961, 885, 842, 807, 772, 743, 723, 708, 632, 599, 582, 565, 515, 481, 431 $cm^{-1}$. $^{1}H$ NMR (300 MHz, acetone-d6) δ 8.00 (1H, d), 7.94 (1H, d), 4.69 (2H, t), 4.13 (3H, s), 3.48 (2H, t), 3.17 (2H, t), 2.83 (2H, tt), 2.42 (2H, quin) ppm. $^{13}C$ NMR (75 MHz, acetone-d6) δ 140.08 (s), 127.11 (s), 125.30 (s), 121.88 (q), 124-100 (6C, m), 48.95 (s), 48.78 (s), 37.18 (s), 31.87 (t), 27.66 (t), 26.02 (s) ppm; mp: 66 °C (hb).

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methyl-3-(3-sulfopropyl)imidazolium bis(trifluoromethanesulfonyl)imide **X**-l1

480 mg (1.70 mmol) of bis(trifluoromethanesulfonyl)amine were added to 1.00 g (1.70 mmol) of **IX** dissolved in 10 ml of methanol and the resulting reaction mixture stirred for 10 min at room temperature. Subsequently, the solvent was evaporated using a rotary evaporator. Finally, the obtained oily liquid was dried at 50 °C *in vacuo* for 24 h, whereupon the product solidified. 1.43 g (1.66 mmol, 98% of theoretical yield) of pure-white, powdery **X**-l1 were isolated.

IR (ATR, neat) 3181, 3157, 3006, 2953, 1570, 1498, 1465, 1445, 1420, 1363, 1325, 1181, 1139, 1127, 1090, 1050, 1034, 964, 915, 814, 791, 764, 745, 723, 710, 665, 645, 601, 571, 528, 502, 473, 436, 407 $cm^{-1}$. $^{1}H$ NMR (300 MHz, acetone-d6) δ 8.00 (1H, d), 7.94 (1H, d), 4.72 (2H, t), 4.15 (3H, s), 3.49 (2H, t), 3.20 (2H, t), 2.84 (2H, tt), 2,45 (2H, quin) ppm. $^{13}C$ NMR (75 MHz, acetone-d6) δ 140.25 (s), 127.11 (s), 125.25 (s), 120.94 (2C, q), 124-100 (6C, m), 48.98 (s), 48.83 (s), 37.22 (s), 31.92 (t), 27.72 (t), 25.92 (s) ppm; mp: 55 °C (hb).

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methyl-3-(2-propinyl)imidazolium bromide **XI**-a2

0.75 g (5.00 mmol) of an 80 wt%-solution of propargyl bromide in toluene was added to 2.30 g (5.00 mmol) of dep-**II** dissolved in 5 ml of acetonitrile. The resulting mixture was then refluxed overnight. After cooling to room temperature, 50 ml of diethyl ether were added to the already heterogeneous mixture, resulting in complete precipitation of the product. The product was filtered off, washed with 50 ml of diethyl ether and dried in high vacuum overnight. 2.10 g (3.63 mmol, 73% of theoretical yield) of relatively pure **XI**-a2 were obtained.

IR (ATR, neat) 3318, 3187, 3042, 2915, 1566, 1495, 1435, 1363, 1318, 1296, 1233, 1184, 1143, 1122, 1094, 1073, 1029, 959, 913, 831, 803, 772, 746, 736, 719, 705, 687, 639, 566, 529, 419 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CDCl_3$) δ 8.28 (1H, d), 8.14 (1H, d), 5.44 (2H, d), 4.15 (3H, s), 3.50 (2H, t), 2.69 (1H, t), 2.57 (2H, tt) ppm. $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 139.28 (s), 126.62 (s), 124.77 (s), 124-100 (6C, m), 77.21 (s), 75.09 (s), 40.42 (s), 37.58 (s), 31.59 (t), 27.78 (t) ppm; mp: 174 °C (under dec., hb).

General deprotonation procedure:

The respective imidazolium iodide was placed in a round-bottom flask, then equal volumes of diethyl ether and 2 eq $NaHCO_3$ (0.5 M solution) slowly added. $CO_2$ formation was observed immediately and the solution was stirred at room temperature for 5 h. Phases were separated by means of a separatory funnel and the etheric phase washed with $H_2O$ and dried over $Na_2SO_4$. $Et_2O$ was removed by means of a rotary evaporator and the product finally dried in high vacuum of a rotary vane pump.

2-(3,3,4,4,4-pentafluorobutylthio)-1-methylimidazole **dep-I**

**I**-a3 (2.41 g, 6.21 mmol). Yield: 1.42 g (88%).

IR (ATR, neat) 2974, 2933, 1735, 1652, 1543, 1457, 1384, 1198, 1146, 1100, 1037, 966, 920, 853, 726, 527 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.02 (1H, d), 6.91 (1H, d), 3.57 (3H, s), 3.18 (2H, t), 2.48 (2H, tt) ppm.

2-(1H,1H,2H,2H-perfluorooctylthio)-1-methylimidazole **dep-II**

**II**-a3 (150.0 g, 0.250 mol). Yield: 105.0 g (90 %). Single crystals of dep-**II** were obtained *via* a two-step procedure: first, a seed crystal was fashioned by slowly cooling a bit of dep-**II** to around 4 °C. Second, this seed crystal was added to 20 g of dep-**II** at room temperature, which caused dep-**II** to completely crystallise over the course of approximately three days.

IR (neat) 3107, 2952, 1510, 1464, 1414, 1361, 1279, 1232, 1186, 1142, 1120, 1089, 1072, 1019, 957, 914, 845, 809, 745, 736, 725, 707, 687, 646, 565, 531, 444 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.00 (1H, d), 6.89 (1H, d), 3.56 (3H, s), 3.18 (2H, t), 2.52 (2H, tt) ppm.$^{13}C$ NMR (75 MHz, $CDCl_3$) δ 140.06 (s), 129.65 (s), 122.65 (s), 124-100 (6C, m), 33.07 (s), 32.12 (t), 24.82 (t) ppm.

2-(1H,1H,2H,2H-perfluorodecylthio)-1-methylimidazole **dep-III**

**III**-a3 (5.00 g, 7.27 mmol). Yield: 3.21 g (79 %).

IR (neat) 3139, 3111, 1570, 1504, 1460, 1416, 1363, 1330, 1314, 1275, 1245, 1194, 1143, 1114, 1091, 1035, 951, 914, 744, 721, 705, 681, 643, 618, 605, 574, 559, 528, 481, 445 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$) δ 6.98 (1H, d), 6.86 (1H, d), 3.53 (3H, s), 3.16 (2H, t), 2.51 (2H, tt) ppm. $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 140.10 (s), 129.65 (s), 122.61 (s), 124-100 (8C, m), 32.98 (s), 32.15 (t), 24.81 (t) ppm; mp: 55,5 °C.

[Tetrachlorido-bis(1-methyl-2-(1H,1H,2H,2H-perfluorooctylthio)imidazole)titanium(IV)], dep-**II**-Ti

0.28 ml (2.50 mmol) of $TiCl_4$ were added dropwise under Argon counter flow to 2.30 g (5.00 mmol) of dep-**II**, dissolved in 10 ml of absolute, amylene-stabilised $CH_2Cl_2$ under Argon atmosphere. Upon addition, the formerly colourless solution immediately turned intensely red. After 10 min of stirring at room temperature, the solvent was removed *in vacuo*. This afforded a quantitative amount of dep-**II**-Ti, a red (orange when ground) solid susceptible to hydrolysis.

IR (ATR, neat) 3217, 3131, 1576, 1539, 1486, 1443, 1363, 1318, 1297, 1231, 1185, 1142, 1122, 1089, 1068, 1019, 950, 892, 838, 806, 745, 707, 696, 646, 565, 528 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.61 (2H, s(br)), 7.28 (2H, s), 3.93 (6H, s), 3.28 (4H, s(br), 2.55 (4H, t(br)) ppm. Note: real multiplicities are probably the same as in dep-**II**, broadening of the signals is due to complexation. $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 139.46 (2C, s(br)), 130.54 (2C, s(br)), 123.88 (2C, s(br)), 124-100 (12C, m), 35.08 (2C, s), 30.44 (2C, t), 26.81 (2C, t) ppm.

## References

(1) Bondi, A., van der Waals Volumes and Radii. *J. Phys. Chem.* **1964,** *68* (3), 441-451.
(2) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Gaussian Inc.: Wallingford CT, 2009.
(3) Omorodion, H.; Twamley, B.; Platts, J. A.; Baker, R. J., Further Evidence on the Importance of Fluorous–Fluorous Interactions in Supramolecular Chemistry: A Combined Structural and Computational Study. *Crystal Growth & Design* **2015,** *15* (6), 2835-2841.
(4) Thompson, H. P. G.; Day, G. M., Which conformations make stable crystal structures? Mapping crystalline molecular geometries to the conformational energy landscape. *Chem. Sci.* **2014,** *5* (8), 3173-3182.
(5) Lavergne, A.; Zhu, Y.; Pizzino, A.; Molinier, V.; Aubry, J.-M., Synthesis and foaming properties of new anionic surfactants based on a renewable building block: Sodium dodecyl isosorbide sulfates. *J. Colloid Interface Sci.* **2011,** *360* (2), 645-653.
(6) Zhang, P.; Gong, Y.; Lv, Y.; Guo, Y.; Wang, Y.; Wang, C.; Li, H., Ionic liquids with metal chelate anions. *Chem. Commun.* **2012,** *48* (17), 2334-2336.