Surface Structure of Alkyl/Fluoroalkylimidazolium Ionic-Liquid Mixtures

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1. Materials

1.1. Commercial ionic liquid characteristics

While most experiments were performed with ILs prepared in house (see main text), we also performed repeat RAS-LIF measurements at the end of the study on two ILs, [C₈mim][Tf₂N] and [C₁₂mim][Tf₂N], supplied by IoLiTec (Germany) and used as received. Table S1 shows the manufacturer’s characterisation data for these liquids.

| Liquid       | Purity    | [H₂O]  | [Halides] |
|--------------|-----------|--------|-----------|
| [C₈mim][NTf₂] | >99%      | 53 ppm | <100 ppm  |
| [C₁₂mim][NTf₂]| >99.9%    | 57 ppm | <100 ppm  |

**Table S1**: Ionic liquid purity information for commercial samples.
2. Molecular Dynamics Simulations

2.1. Run Parameters and Protocols

A 2 fs time step was used in conjunction with the leap frog integrator. Lengths of all bonds to H atoms were constrained. Shifted potentials with energy and pressure corrections were used with 1.5 nm cut-offs for the van der Waals and Coulomb potentials. The long-range electrostatic potential was calculated using particle-mesh Ewald with an order of 4 and minimum grid spacing of 0.12 nm. The data were saved every 2 ps and 4 ps for the small (800 ion pairs) and large (1600 ion pairs; \( n = 8, x = 0 \) and 0.5 only) simulations respectively.

The composition and dimensions of the systems studied are listed in Table S2. Each liquid was simulated following one of three protocols. The protocols varied slightly in run length for the bulk equilibration phase and in the slab heating and cooling cycles for the slab. Table S3 lists the protocols and the liquids to which they were applied. Tables S4 to S6 show the simulation parameters. The time constants for the barostat and thermostats are represented by \( \tau_p \) and \( \tau_t \) respectively.

| x   | [C\(_n\)mim]\(^+\) | [C\(_8\)mim\(F_{13}\)]\(^+\) | [NTf\(_2\)]\(^+\) | Atoms | Initial box size / nm | Slab size\(^a\) / nm | Liquid ID number |
|-----|-------------------|----------------------|-------------------|-------|----------------------|--------------------|-----------------|
| 0   | 800               | 0                    | 800               | 41600 | \( x = y = 9.0 \)   | \( x = y = 7.934 \) | 1               |
| 0.1 | 720               | 80                   | 800               | 41600 | \( x = y = 8.5 \)   | \( x = y = 7.785 \) | 2               |
| 0.25| 600               | 200                  | 800               | 41600 | \( x = y = 8.5 \)   | \( x = y = 7.831 \) | 3               |
| 0.5 | 400               | 400                  | 800               | 41600 | \( x = y = 9.0 \)   | \( x = y = 7.934 \) | 4               |
| 0.75| 200               | 600                  | 800               | 41600 | \( x = y = 8.5 \)   | \( x = y = 8.031 \) | 5               |
| 1   | 0                 | 800                  | 800               | 41600 | \( x = y = 9.0 \)   | \( x = y = 8.121 \) | 6               |

Large system, \( n = 8 \)

| x   | Atoms | Initial box size / nm | Slab size\(^a\) / nm | Liquid ID number |
|-----|-------|----------------------|--------------------|-----------------|
| 0   | 1600  | 0                    | 1600               | 83200           | \( x = y = 8.5, z = 17.0 \) | \( x = y = 7.746, z = 46.478 \) | 7               |
| 0.5 | 800   | 800                  | 1600               | 83200           | \( x = y = 9.0 \)   | \( x = y = 7.937 \)   | 8               |
### Table S2: System sizes for MD simulations.

*Z* dimension of simulation cell can be obtained by multiplying *x* or *y* by 3.

| Protocol followed | Liquid ID          |
|-------------------|--------------------|
| 1                 | 1, 4, 6            |
| 2                 | 7, 8               |
| 3                 | 2, 3, 5, 9 - 14    |

### Table S3: Protocol followed for each liquid.

| Run | Barostat  | Pressure / bar | τ_p / ps | Thermostat | τ_t / ps | Temp / K | Run length / ns | Total run time / ns |
|-----|-----------|----------------|----------|------------|----------|----------|----------------|---------------------|
|     | Bulk      |                |          | v-rescale  |          | 500      | 0.2            | -                   |

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| Slabs | Run | Barostat                  | Pressure / bar | $\tau_p$ / ps | v-rescale | $\tau_t$ / ps | Temp / K | Run length / ns | Total run time / ns |
|-------|-----|---------------------------|----------------|---------------|-----------|---------------|---------|-----------------|---------------------|
| 1     | Parrinello-Rahman | 1.0 | 2.0 | v-rescale | 0.5 | 320 | 2.0 | - |                      |
| 2     | Parrinello-Rahman | 1.0 | 2.0 | v-rescale | 0.5 | 320 | 2.0 | - |                      |
| 3     | Parrinello-Rahman | 1.0 | 2.0 | v-rescale | 0.5 | 320 | 5 | 5 |                      |
| 4     | Parrinello-Rahman | 1.0 | 2.0 | v-rescale | 0.5 | 320 | 5 | 10 |                      |
| 5     | Parrinello-Rahman | 1.0 | 2.0 | v-rescale | 0.5 | 320 | 5 | 25 |                      |
| 6     | Parrinello-Rahman | 1.0 | 2.0 | v-rescale | 0.5 | 320 | 5 | 30 |                      |
| 7     | Parrinello-Rahman | 1.0 | 2.0 | v-rescale | 0.5 | 320 | 5 | 35 |                      |
| 8     | Parrinello-Rahman | 1.0 | 2.0 | v-rescale | 0.5 | 320 | 5 | 40 |                      |
| 9     | Parrinello-Rahman | 1.0 | 2.0 | v-rescale | 0.5 | 320 | 5 | 45 |                      |
| 10    | Parrinello-Rahman | 1.0 | 2.0 | v-rescale | 0.5 | 320 | 5 | 50 |                      |
| 11    | Parrinello-Rahman | 1.0 | 2.0 | v-rescale | 0.5 | 320 | 5 | 60 |                      |
| 12    | Parrinello-Rahman | 1.0 | 2.0 | v-rescale | 0.5 | 320 | 5 | 65 |                      |
| 13    | Parrinello-Rahman | 1.0 | 2.0 | v-rescale | 0.5 | 320 | 5 | 70 |                      |
| 14    | Parrinello-Rahman | 1.0 | 2.0 | v-rescale | 0.5 | 320 | 5 | 75 |                      |
| 15    | Parrinello-Rahman | 1.0 | 2.0 | v-rescale | 0.5 | 320 | 5 | 80 |                      |
| 16    | Parrinello-Rahman | 1.0 | 2.0 | v-rescale | 0.5 | 320 | 5 | 85 |                      |
| 17    | Parrinello-Rahman | 1.0 | 2.0 | v-rescale | 0.5 | 320 | 5 | 95 |                      |

**Table S4:** Protocol 1.

| Run | Barostat                  | Pressure / bar | $\tau_p$ / ps | v-rescale | $\tau_t$ / ps | Temp / K | Run length / ns | Total run time / ns |
|-----|---------------------------|----------------|---------------|-----------|---------------|---------|-----------------|---------------------|
| 1   | Berendsen | 1.0 | 2.0 | v-rescale | 0.5 | 500 | 0.5 | - |                      |
| 2   | Parrinello-Rahman | 1.0 | 2.0 | v-rescale | 0.5 | 320 | 4.0 | - |                      |
| Slab |  
|------|---|
| 1  | v-rescale 0.5 320 5 5 |
| 2  | v-rescale 0.5 500 5 10 |
| 3  | v-rescale 0.5 320 5 15 |
| 4  | v-rescale 0.5 500 5 20 |
| 5  | v-rescale 0.5 320 5 25 |
| 6  | v-rescale 0.5 500 5 30 |
| 7  | v-rescale 0.5 320 5 35 |
| 8  | v-rescale 0.5 500 5 40 |
| 9  | v-rescale 0.5 320 5 45 |
| 10 | v-rescale 0.5 500 5 50 |
| 11 | v-rescale 0.5 320 10 60 |
| 12 | v-rescale 0.5 500 5 65 |
| 13 | v-rescale 0.5 320 5 70 |
| 14 | v-rescale 0.5 500 5 75 |
| 15 | v-rescale 0.5 320 5 80 |
| 16 | v-rescale 0.5 500 5 85 |
| 17 | v-rescale 0.5 320 10 95 |

Table S5: Protocol 2.

| Run | Barostat | Pressure / bar | \(\tau_p\) / ps | Thermostat | \(\tau_t\) / ps | Temp / K | Run length / ns | Total run time / ns |
|-----|----------|----------------|-----------------|------------|-----------------|---------|-----------------|---------------------|
| **Bulk** | | | | | | | | |
| 1  | Berendsen | 1.0 | 2.0 | v-rescale | 0.5 | 500 | 0.5 |
| 2  | Parrinello-Rahman | 1.0 | 2.0 | v-rescale | 0.5 | 320 | 4.0 |
| **Slab** | | | | | | | | |
| 1  | | v-rescale | 0.5 | 320 | 5 | 5 |
| 2  | | v-rescale | 0.5 | 500 | 5 | 10 |
The experimental bulk densities are shown in table S7.

| Liquid | Exp density / g cm\(^{-3}\) | Simulation / g cm\(^{-3}\) | Error / % |
|--------|-----------------------------|-----------------------------|-----------|
| \(n = 4\) | 1.415 | 1.491 | 5.4 |
| \(n = 6\) | 1.344 | 1.420 | 5.6 |
| \(n = 8\) | 1.292 | 1.361 | 5.3 |
| \(n = 12\) | 1.226 | 1.273 | 3.8 |

**Table S7**: Extrapolated densities from experimental measurements compared against those calculated from MD here.
2.2. ASA Threshold Dependence

The ASA method reports the surface area of each atom in the simulation frame. The algorithm was used with a probe-particle radius of 0.15 nm, corresponding to the van der Waals radius of an oxygen atom, and 10,000 dots for the resolution.

A small number of false atom counts from bulk voids were also detected by the ASA method. For the purposes of carrying out preliminary tests of equilibration and convergence, etc, the false counts were eliminated by applying a surface area threshold, \( T_{\text{area}} \), before a hydrogen atom could be counted as being at the vacuum-liquid interface. An appropriate value was selected by examining the \( x = 0.5 \) to \( x = 1 \) ratio of secondary hydrogen atoms, (where the surface count of secondary hydrogens was averaged over the simulation run starting from 1 ns) as a function of threshold area, for the C8 system. This is shown in figure S1 for different simulation run times. At low \( T_{\text{area}} \), there is a slow decline in the ratio until between 0.15 – 0.20 nm\(^2\), where the ratio does not vary significantly. With larger values of \( T_{\text{area}} \), the ratio can diverge causing an initial increase in the ratio before reaching zero as \( T_{\text{area}} \) exceeds the area that a fully exposed atom presents to the probe particle. This analysis was also applied to the larger 1600 ion pair system, and to the \( x = 0.25 \) C4 mixture, with similar results. Therefore, a threshold value of 0.19 nm\(^2\) was arbitrarily chosen when calculating the surface H-atom count for equilibration tests between runs.

For the subsequent, more-detailed quantitative comparison of the exposures of different atom types, including different positions along alkyl chains, the total exposed area of each type was summed, without applying any threshold. Although, as noted above, this admits a very minor contribution from atoms which are not truly at the surface, it avoids more significant systematic distortions resulting from differential sensitivities of different atom types to the choice of the threshold area.
Figure S1: Ratio of average number of surface secondary hydrogens to that of the neat liquid as the threshold is varied for [C₈mim][C₆mimF₁₃][NTf₂] with x = 0.5. Several runs with the total simulation runtime being are shown. The dashed arrow indicates the chosen threshold value of 0.19 nm².

2.3. Block averaging
A block analysis¹ was used to determine the relaxation times over several 320 K liquid runs. The ASA values (thresholded secondary-H atom count) were calculated from 1 ns after the start of the run to allow the surface to relax from 500 K. The simulation run is divided into blocks of variable length, b, so that the total number of blocks in a simulation run is \( n_b \). Alternatively, \( n_b = T/b \), where \( T \) is the total length of the simulation measured in saved data points. The mean of each block, \( \langle A \rangle_b \), is calculated according to
\[ \langle A \rangle_b = \frac{1}{b} \sum_{i=1}^{b} A_i \quad (Eqn \ S1) \]

where \( A_i \) is the ASA value from a single frame, \( i \), in the simulation and \( \langle A_b \rangle \) is the average for a single block of length, \( b \). The variance of the mean for each block from the overall mean is calculated, and then averaged according to

\[ \sigma^2(\langle A_b \rangle) = \frac{1}{n_b} \sum_{b=1}^{n_b} (\langle A_b \rangle - \langle A \rangle_T)^2 \quad (Eqn \ S2) \]

where \( \sigma^2(\langle A_b \rangle) \) is the averaged variance of the blocks for a given block length, \( b \), \( \langle A \rangle_T \) is the mean ASA value over all of the frames in the simulation (excluding the first 1 ns). The statistical inefficiency was calculated as

\[ s = \lim_{b \to \infty} \frac{b \sigma^2(\langle A_b \rangle)}{\sigma^2(\langle A \rangle_T)} \quad (Eqn \ S3) \]

where \( \sigma^2(\langle A \rangle_T) \) is the variance over all simulation frames. Figures S2 to S4 show representative graphs of \( s \), plotted as a function of step size, for several different systems. Generally, between 0.3-0.6 ns, the graphs show a roll off, indicating the data sampled with this period is becoming uncorrelated. The sampling period of 0.4 ns was chosen as this gave a good compromise between having enough frames to average over from each run and reducing the correlation between frames.
Figure S2: Block analysis applied to run 11 (10 ns length) for [C₈mim][C₈mimF₁₃][1-x][NTf₂] with 800 ion pairs. The arrow shows the selected sampling period of 0.4 ns, occurring near the roll-off for $s$. 
Figure S3: Block analysis applied to run 17 (10 ns length) for the large system, $[\text{C}_8\text{mim}]_x[\text{C}_8\text{mimF}_{13}]_{1-x}[\text{NTf}_2]$, with 1600 ion pairs. The arrow shows the 0.4 ns sampling period.
The convergence of the z-density profiles was monitored for the $x = 0$ and $x = 1$ for the 800 and 1600 ion pair system and it was found from 35 ns, the outer atomic layer did not change significantly. (Further, more extensive tests of convergence, which gave similar results, are given in S2.5 below.) The larger systems reach constant densities at lower values of $z$, corresponding to the middle of the slab, whereas the smaller system still shows some weak undamped density oscillations towards $z = 0$, as shown in Figure S5.
Figure S5: Density profiles for the two different system sizes, 800 ion pairs (top row), 1600 ion pairs (bottom row) for [C₈mim][C₈mimF₁₃]₁₋ₓ[NTf₂] with x = 0 and x = 0.5. The atom types are indicated by lines as shown; they are the same as Figure 13 in the main article. Averages from 35 to 90 ns run time.
Figure S6: Cation density for [C₈mim] and [C₈mimF₁₃] in the [C₈mim]₀.₅[C₈mimF₁₃]₀.₅[NTf₂] mixture. Top frames = top view; bottom frames = side view. The color scheme is as defined in the main text (Figure 8).

The runtime dependence of the exposed secondary-hydrogen exposed atom count, normalised to that for pure [C₈mim] [NTf₂], for the large and small [C₈mim]₀.₅[C₈mimF₁₃]₀.₅[NTf₂] systems is shown in figure S7. We conclude that there are no significant differences between the large and small systems. Also shown in Figure S8 is the runtime dependence for a selection of other liquid mixtures of different composition and chain length, as indicated. In all cases, and as in Fig. S7, results are stable generally, and with
confidence beyond ~45 ns. This is the basis for choosing to analyse surface composition beyond this time to obtain average quantities, as stated in the main text. There are also no significant differences between averaging every frame (‘total mean’), or (much more efficient) sampling every 400 ps, as derived in Section S2.3 and adopted for the analysis of production runs.

**Figure S7:** Relative surface H-density as a function of run time for the large and small system for [C₈mim]₀.₅[C₈mimF₁₃]₀.₅[NTf₂]. Sampling intervals as indicated.
Figure S8: Normalized reactivity (as defined in the main text) as a function of run time for a selection of liquid mixtures, with the compositions indicated. Errors are 1σ SEM.

2.6. MD Areas

ASA-determined areas for different liquids are tabulated below.
|                | ASA Total surface area (all atoms) / nm² | Geometric Slab area (per face) / nm² | Ratio surface/2 slab faces | Ratio Normalised to C8mimF |
|----------------|----------------------------------------|-------------------------------------|-----------------------------|---------------------------|
| C8mim          | 213.1406                                | 59.9234                             | 1.7784                      | 0.9095                    |
| C8mim10        | 218.9873                                | 60.6070                             | 1.8066                      | 0.9239                    |
| C8mim25        | 224.4879                                | 61.3299                             | 1.8301                      | 0.9359                    |
| C8mim50        | 236.6350                                | 62.9541                             | 1.8794                      | 0.9611                    |
| C8mim75        | 250.0592                                | 64.4910                             | 1.9387                      | 0.9914                    |
| C8mimF         | 257.8911                                | 65.9440                             | 1.9553                      | 1.0000                    |

**Table S8:** ASA measured areas and slab areas for C₈mimX liquids. (Mole fraction of fluoro component = x = X / 100 in [C₈mim]₁ₓ[C₈mimF₁₃]ₓ[NTf₂] mixtures.)

|                | ASA Total surface area (all atoms) / nm² | Geometric Slab area (per face) / nm² | Ratio surface/2 slab faces | Ratio Normalised to C12mim |
|----------------|----------------------------------------|-------------------------------------|-----------------------------|---------------------------|
| C4mim          | 160.7555                                | 51.7598                             | 1.5529                      | 0.8436                    |
| C6mim          | 189.3527                                | 55.8547                             | 1.6950                      | 0.9208                    |
| C8mim          | 213.1406                                | 59.9233                             | 1.7784                      | 0.9662                    |
| C12mim         | 248.6578                                | 67.5439                             | 1.8407                      | 1.0000                    |

**Table S9:** ASA measured areas and slab areas for pure Cₙmim (= [Cₙmim] [NTf₂]) liquids.
|          | Surface area / nm² | Ratio          |
|----------|--------------------|----------------|
|          | X                  | Fluoro  | Alkyl  | Anion  | Total  | Fluoro | Alkyl | Anion |
| 0.00     | 0.0000             | 171.8607| 41.2798| 213.1406| 0.000  | 0.806  | 0.194 |
| 0.10     | 47.6554            | 136.6423| 34.6542| 218.9520| 0.218  | 0.624  | 0.158 |
| 0.25     | 87.1703            | 104.9887| 32.2882| 224.4722| 0.388  | 0.468  | 0.144 |
| 0.50     | 151.8677           | 56.3706 | 28.3967| 236.6350| 0.642  | 0.238  | 0.120 |
| 0.75     | 196.0917           | 25.9018 | 28.0129| 250.0064| 0.784  | 0.104  | 0.112 |
| 1.00     | 231.3420           | 0.0000  | 26.4968| 257.8388| 0.897  | 0.000  | 0.103 |

**Table S11:** Total surface areas and fraction of surface occupied by fluoroalkyl cation, alkyl cation and anion for \([\text{C}_8\text{mim}]_{(1-x)}[\text{C}_8\text{mimF}_{13}]_x[\text{NTf}_2]\).
| N  | Fluoro  | Alkyl   | Anion   | Total   | Fluoro | Alkyl   | Anion   |
|----|---------|---------|---------|---------|--------|---------|---------|
| 4  | 122.2086| 39.4535 | 37.7501 | 199.4123| 0.613  | 0.198  | 0.189  |
| 6  | 97.6064 | 75.2617 | 37.0946 | 209.9627| 0.465  | 0.358  | 0.177  |
| 8  | 87.1703 | 104.9887| 32.2882 | 224.4472| 0.388  | 0.468  | 0.144  |
| 12 | 58.6466 | 167.0259| 24.6990 | 250.3715| 0.234  | 0.667  | 0.099  |

**Table S13:** Total surface areas and fraction of surface occupied by fluoroalkyl cation, alkyl cation and anion for [Cₙmim][0.75][C₈mimF₁₃]₀.₂₅[NTf₂].

| x  | C1 H’s | C2 H’s | C3 H’s | C4 H’s | C5 H’s | C6 H’s | C7 H’s | C8 H’s (CH₃) | C1&C2 H’s |
|----|--------|--------|--------|--------|--------|--------|--------|--------------|-----------|
| 0.00| 0.0104 | 0.0265 | 0.0264 | 0.0522 | 0.0589 | 0.0916 | 0.1328 | 0.3374       | 0.0000    |
| 0.10| 0.0082 | 0.0191 | 0.0197 | 0.0380 | 0.0437 | 0.0693 | 0.1035 | 0.2682       | 0.0031    |
| 0.25| 0.0060 | 0.0132 | 0.0142 | 0.0283 | 0.0327 | 0.0501 | 0.0787 | 0.2021       | 0.0046    |
| 0.50| 0.0032 | 0.0075 | 0.0085 | 0.0144 | 0.0165 | 0.0253 | 0.0387 | 0.1010       | 0.0079    |
| 0.75| 0.0017 | 0.0039 | 0.0034 | 0.0066 | 0.0067 | 0.0110 | 0.0159 | 0.0419       | 0.0103    |
| 1.00| -      | -      | -      | -      | -      | -      | -      | -            | 0.0106    |

**Table S14:** Fraction of solvent accessible area of hydrogen atoms by chain position for [C₈mim][1-x][C₈mimF₁₃]ₓ[NTf₂]

| n  | C1 H’s | C2 H’s | C3 H’s | C4 H’s | C5 H’s | C6 H’s | C7 H’s | C8 H’s | C9 H’s | C10 H’s | C11 H’s | C12 H’s |
|----|--------|--------|--------|--------|--------|--------|--------|--------|--------|---------|---------|---------|
| 4  | 0.01   | 0.05   | 0.09   | 0.36   | -      | -      | -      | -      | -      | -       | -       | -       |
|    | 98     | 23     | 92     | 09     | -      | -      | -      | -      | -      | -       | -       | -       |
| 6  | 0.01   | 0.03   | 0.03   | 0.07   | 0.12   | 0.35   | -      | -      | -      | -       | -       | -       |
|    | 44     | 54     | 99     | 87     | 72     | 96     | -      | -      | -      | -       | -       | -       |
| 8  | 0.01   | 0.02   | 0.02   | 0.05   | 0.05   | 0.09   | 0.13   | 0.33   | -      | -       | -       | -       |
|    | 03     | 65     | 65     | 23     | 89     | 16     | 29     | 75     | -      | -       | -       | -       |

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| n  | C1 H's | C2 H's | C3 H's | C4 H's | C5 H's | C6 H's | C7 H's | C8 H's | C9 H's | C10 H's | C11 H's | C12 H's | C1 & C2 H's |
|----|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|-------------|
| 4  | 0.00   | 0.01   | 0.03   | 0.11   | -      | -      | -      | -      | -      | -      | -      | -      | 0.00        |
|    | 71     | 70     | 04     | 26     |        |        |        |        |        |        |        |        | 75          |
| 6  | 0.00   | 0.01   | 0.01   | 0.03   | 0.06   | 0.17   | -      | -      | -      | -      | -      | -      | 0.00        |
|    | 74     | 61     | 94     | 76     | 19     | 40     |        |        |        |        |        |        | 55          |
| 8  | 0.00   | 0.01   | 0.01   | 0.02   | 0.03   | 0.05   | 0.07   | 0.20   | -      | -      | -      | -      | 0.00        |
|    | 59     | 32     | 42     | 83     | 37     | 11     | 78     | 87     | 21     |        |        |        | 46          |
| 12 | 0.00   | 0.01   | 0.01   | 0.02   | 0.02   | 0.03   | 0.04   | 0.04   | 0.06   | 0.09   | 0.22   | 0.00   | 87          |
|    | 47     | 12     | 03     | 11     | 16     | 39     | 52     | 70     | 96     | 65     | 43     | 87     | 27          |

**Table S15:** Fraction of solvent-accessible area of hydrogen atoms by chain position for pure [C₅mim][NTf₂]. Data are used in Figure 13 of main text.

| n  | C1 H's | C2 H's | C3 H's | C4 H's | C5 H's | C6 H's | C7 H's | C8 H's | C9 H's | C10 H's | C11 H's | C12 H's |
|----|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| 4  | 0.35   | 0.32   | 0.30   | 0.31   | -      | -      | -      | -      | -      | -      | -      | -      |
|    | 7       | 5       | 7       | 2       |        |        |        |        |        |        |        |        |
| 6  | 0.51   | 0.45   | 0.48   | 0.47   | 0.48   | 0.48   | -      | -      | -      | -      | -      | -      |
|    | 4       | 6       | 5       | 8       | 4       |        |        |        |        |        |        |        |

**Table S16:** Fraction of solvent accessible area of hydrogen atoms by chain position for [C₅mim]₀.₇₅[C₈mimF₁₃]₀.₂₅[NTf₂]. Data are used in Figure 13 of main text.
Table S17: Ratio of $[\text{C}_{n}\text{mim}](0.75)[\text{C}_{8}\text{mimF}_{13}]0.25[\text{NTf}_2]$ to $[\text{C}_{n}\text{mim}][\text{NTf}_2]$ solvent-accessible area of hydrogen atoms by chain position. Data are used in Figure 13 of main text.

| X  | C1 H’s | C2 H’s | C3 H’s | C4 H’s | C5 H’s | C6 H’s | C7 H’s | C8 H’s |
|----|--------|--------|--------|--------|--------|--------|--------|--------|
| 0.00 | 1.000  | 1.000  | 1.000  | 1.000  | 1.000  | 1.000  | 1.000  | 1.000  |
| 0.10 | 0.792  | 0.722  | 0.745  | 0.726  | 0.742  | 0.756  | 0.779  | 0.794  |
| 0.25 | 0.574  | 0.499  | 0.537  | 0.541  | 0.555  | 0.546  | 0.592  | 0.599  |
| 0.50 | 0.315  | 0.283  | 0.321  | 0.276  | 0.279  | 0.276  | 0.292  | 0.299  |
| 0.75 | 0.165  | 0.147  | 0.129  | 0.126  | 0.114  | 0.120  | 0.119  | 0.124  |
| 1.00 | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  |

Table S18: Ratio of $[\text{C}_{8}\text{mim}](1-x)[\text{C}_{8}\text{mimF}_{13}]x[\text{NTf}_2]$ to $[\text{C}_{8}\text{mim}][\text{NTf}_2]$ solvent-accessible area of hydrogen atoms by chain position.
3. Surface tension measurements

3.1. Surface tension results $[\text{C}_8\text{mim}](1-x)[\text{C}_8\text{mimF}_{13}]_x[\text{NTf}_2]$ 

| $x$  | Surface Tension / mN m$^{-1}$ | 1σ SEM | 95% CL |
|------|-------------------------------|---------|--------|
| 0.00 | 30.42                         | 0.09    | 0.20   |
| 0.05 | 28.65                         | 0.01    | 0.03   |
| 0.2  | 25.59                         | 0.08    | 0.18   |
| 0.35 | 24.30                         | 0.02    | 0.05   |
| 0.5  | 23.52                         | 0.04    | 0.10   |
| 0.65 | 22.96                         | 0.04    | 0.10   |
| 0.8  | 22.52                         | 0.04    | 0.10   |
| 0.95 | 21.96                         | 0.01    | 0.03   |
| 1.00 | 21.90                         | 0.02    | 0.05   |

*Table S19:* Surface tension results from $[\text{C}_8\text{mim}](1-x)[\text{C}_8\text{mimF}_{13}]_x[\text{NTf}_2]$ for varying bulk mole fraction, $x$. 
4. RAS-LIF OH appearance profiles

4.1. Number density profiles for $[C_6\text{mim}](1-x)[C_8\text{mimF}_{13}]_x[\text{NTf}_2]$ and $[C_4\text{mim}](1-x)[C_8\text{mimF}_{13}]_x[\text{NTf}_2]$

Figure S9: RAS-LIF appearance profiles from $[C_6\text{mim}](1-x)[C_8\text{mimF}_{13}]_x[\text{NTf}_2]$ and $[C_4\text{mim}](1-x)[C_8\text{mimF}_{13}]_x[\text{NTf}_2]$ for bulk mole fractions of $x = 0$ and 0.25. Error bars are 95% CL.

Figure S9 shows the OH density profiles for the C4 and C6 chain length mixtures, $[C_n\text{mim}](1-x)[C_8\text{mimF}_{13}]_x[\text{NTf}_2]$, with $x = 0$ and $x = 0.25$ recorded on the Q$_1$(1) line. The profiles have very similar peak arrival times, therefore a density to flux transform was not used in the analysis.
5. **RAS-LIF rotational distributions**

Details of the rotational analysis for the \([\text{C}_8\text{mim}][1-x][\text{C}_8\text{mimF}_{13}]_x[\text{NTf}_2]\) series of mixtures have been given previously.\(^2\) However, it is almost identical to the procedure described here for \([\text{C}_{12}\text{mim}][1-x][\text{C}_8\text{mimF}_{13}]_x[\text{NTf}_2]\).

### 5.1. \([\text{C}_{12}\text{mim}]_{0.5}[\text{C}_8\text{mimF}_{13}]_{0.5}[\text{NTf}_2]\) and \([\text{C}_{12}\text{mim}][\text{NTf}_2]\) rotationally resolved spectra

Rotationally resolved OH (A-X) (1,0) LIF excitation spectra were recorded from \([\text{C}_{12}\text{mim}][1-x][\text{C}_8\text{mimF}_{13}]_x[\text{NTf}_2]\) for \(x = 0\) and \(x = 0.5\). The wavelength step size was 0.0020 nm and data was collected for 40 laser shots at each step. The photolysis-probe delay was fixed at 13 µs corresponding to the peak of the appearance profile. For \(x = 0\), seven wavelength scans were recorded. For \(x = 0.5\), since there was less OH signal from this mixture, twelve scans were recorded. Spectra were recorded on the Q\(_1\) branch only up to \(N = 5\), where \(N\) is the sum of the electron orbital quantum and rotational quantum numbers.

### 5.2. Rotational analysis

LIFBASE\(^3\) was used to fit the spectra for both liquids, the resultant populations were normalized over the five rotational levels recorded and averaged over the number of scans taken for each mixture. Figure S10 shows the normalized Q\(_1\) branch populations of OH reactively scattered from \([\text{C}_{12}\text{mim}][1-x][\text{C}_8\text{mimF}_{13}]_x[\text{NTf}_2]\).
Figure S10: Normalised OH rotational populations from $[\text{C}_{12}\text{mim}][\text{NTf}_2]$ ($x = 1.0$) and with bulk mole fraction, $x = 0.5$, corresponding to $[\text{C}_{12}\text{mim}]_{0.5}[\text{C}_8\text{mimF}_{13}]_{0.5}[\text{NTf}_2]$. Error bars are 95% CL.
6. Integrated RAS-LIF OH number densities to derive reactivity

The OH densities for all liquids were integrated to create a value called reactivity, a single numerical value that represents the exposure of the alkyl chains to incident O(\(^{3}\)P) atoms at the liquid surface. This was done by integrating the OH density as a function of time between 6 \(\mu\)s and 30 \(\mu\)s with a 1 \(\mu\)s step size. The reactivities of each liquid were divided by the reactivity of squalane, to create a dimensionless relative reactivity. This process helped to reduce systematic error due to variations in the experimental conditions.

To help estimate and reduce the experimental uncertainty, the C8 and C12 pure liquids, [C\(_{8,12}\)mim][NTf\(_2\)], were measured at the start and end of the experiment. For the C8 system, after all compositions had been measured, fresh samples of [C\(_{8}\)mim][NTf\(_2\)] (a commercial sample, IoLiTec, and a sample synthesised as part of this work) were loaded into a separate liquid baths, and their reactivities measured. For the C12 system, only a commercial sample (IoLiTec) was measured at the end of the experiments, after mixtures has been measured. The reactivities for [C\(_{8,12}\)mim][NTf\(_2\)] were calculated using a weighted average with instrumental weighting, \(1/\sigma^2\). This averaged value was then taken as the reactivity of the pure component. For the C4 and C6 chain lengths only a single mixture was studied, \(x = 0.25\).

6.1. [C\(_{12}\)mim]\((1-x)[C_{8}\text{mimF}_{13}]x[\text{NTf}_2]\) mixtures

| \(x\)  | Relative Reactivity | 1\(\sigma\) SEM | Normalized reactivity | 1\(\sigma\) SEM | 95% CL |
|-------|---------------------|------------------|-----------------------|----------------|--------|
| 0.000 | 0.625               | 0.002            | 1.000                 | 0.006          | 0.000  |
| 0.020 | 0.557               | 0.003            | 0.891                 | 0.006          | 0.013  |
| 0.050 | 0.438               | 0.003            | 0.701                 | 0.006          | 0.013  |
| 0.100 | 0.334               | 0.002            | 0.534                 | 0.004          | 0.008  |
| 0.250 | 0.211               | 0.001            | 0.338                 | 0.002          | 0.005  |
| 0.370 | 0.161               | 0.001            | 0.258                 | 0.002          | 0.005  |
| 0.500 | 0.122               | 0.001            | 0.195                 | 0.002          | 0.005  |
| 0.750 | 0.074               | 0.001            | 0.118                 | 0.001          | 0.003  |

Table S20: Relative and normalized reactivities for [C\(_{12}\)mim]\((1-x)[C_{8}\text{mimF}_{13}]x[\text{NTf}_2]\) mixtures with varying \(x\).
Table S21: Confirmatory measurements of relative reactivity for custom-synthesized and commercial samples of [C_{12}mim][NTf_2] and resulting weighted average.

|                  | Relative Reactivity | 1σ SEM |
|------------------|---------------------|--------|
| 1                | 0.632               | 0.003  |
| Commercial Sample| 0.611               | 0.004  |
| Weighted Average | 0.625               | 0.002  |

6.2. [C_{8}mim]_{(1-x)}[C_{8}mimF_{13}]_{x}[NTf_2] mixtures

Previously published results\textsuperscript{2} show tabulated values for reactivities relative to squalane with bulk mole fraction \( x \), for \([C_{8}mim]_{(1-x)}[C_{8}mimF_{13}]_{x}[NTf_2]\) mixtures, the data are repeated here for convenience and include the normalized reactivity and associated errors.

| \( x \)  | Relative Reactivity | 1σ SEM | Normalized Reactivity | 1σ SEM | 95% CL |
|----------|---------------------|--------|-----------------------|--------|--------|
| 0.000    | 0.338               | 0.001  | 1.000                 | 0.006  | 0.000  |
| 0.050    | 0.226               | 0.002  | 0.669                 | 0.007  | 0.018  |
| 0.100    | 0.183               | 0.002  | 0.543                 | 0.006  | 0.013  |
| 0.250    | 0.125               | 0.001  | 0.370                 | 0.005  | 0.010  |
| 0.370    | 0.086               | 0.002  | 0.256                 | 0.005  | 0.011  |
| 0.500    | 0.073               | 0.006  | 0.218                 | 0.017  | 0.038  |
| 0.750    | 0.044               | 0.001  | 0.132                 | 0.004  | 0.008  |
| 0.830    | 0.041               | 0.001  | 0.122                 | 0.004  | 0.009  |
| 1.000    | -0.007              | 0.006  | -0.020                | 0.018  | 0.042  |

Table S22: Relative and normalized reactivities for \([C_{12}mim]_{(1-x)}[C_{8}mimF_{13}]_{x}[NTf_2]\) mixtures with varying \( x \).

|                  | OH Density | 1σ SEM |
|------------------|------------|--------|
| 1                | 0.3196     | 0.0065 |
| 2                | 0.3170     | 0.0022 |
| Commercial Sample| 0.3555     | 0.0020 |
| Weighted Average | 0.3376     | 0.0014 |
Table S23: Confirmatory measurements of relative reactivity for custom-synthesized and commercial samples of \([\text{C}_8\text{mim}]\text{[NTf}_2]\) and resulting weighted average.

6.3. \([\text{C}_6\text{mim}]_{1-x} [\text{C}_8\text{mimF}_{13}]_x \text{[NTf}_2]\)

The C6 liquids were studied by having the pure liquid, \([\text{C}_6\text{mim}]\text{[NTf}_2]\) and the \(x = 0.25\) mixture in the carousel at the same time.

![Table S24](image)

Table S24: Relative and normalized reactivities for \([\text{C}_6\text{mim}]_{1-x} [\text{C}_8\text{mimF}_{13}]_x \text{[NTf}_2]\) mixtures with varying \(x\).

6.4. \([\text{C}_4\text{mim}]_{1-x} [\text{C}_8\text{mimF}_{13}]_x \text{[NTf}_2]\)

The C4 liquids were studied by having the pure liquid, \([\text{C}_4\text{mim}]\text{[NTf}_2]\) and the \(x = 0.25\) mixture loaded in the carousel at the same time.

![Table S25](image)

Table S25: Relative and normalized reactivities for \([\text{C}_4\text{mim}]_{1-x} [\text{C}_8\text{mimF}_{13}]_x \text{[NTf}_2]\) mixtures with varying \(x\).
7. Supplementary references

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