

## Supporting information

### *Technical details*

To describe molecular interactions the widely used all-atom model developed by Canongia-Lopes and Pádua was applied.<sup>1,2</sup> 512 ion pairs were simulated on the NVT ensemble in a rectangular simulation box of dimensions 5 nm × 5 nm × 13 nm using the Gromacs simulation package.<sup>3</sup> The thickness of the fluid was around 7 nm. The temperature was kept constant at 298.15 K with the velocity rescaling method.<sup>4</sup> Electrostatic interactions were truncated in real space beyond a cut-off radius of 1.5 nm. To account for the long range part of the electrostatic interaction the PME method was used.<sup>5</sup> Dispersion interactions were truncated by smoothly decreasing to zero between 1.1 and 1.2 nm, with long range corrections applied beyond this region. After a 12 ns long equilibration run, several independent calculations were performed with a total simulation length of 80 ns. The time step of the simulation was 2 fs. Configurations were stored at every 2 ps during the production giving in total a sample of 40000 configurations. According to the original parameterization of the potential, all C–H bonds were kept fixed as well as the geometry of the rigid anion using the SHAKE algorithm.<sup>6</sup>

For the basis of the applied ITIM method for detecting the true set of interfacial molecules the reader is referred to the paper of Pártay et al.<sup>7</sup> Test lines were arranged in a 100 × 100 grid along the XY face of the simulation cell. This test line density gives an optimal grid spacing of 0.05 nm.<sup>8</sup> The radius of the probe spheres was set to 0.2 nm, since this value was successfully applied to several different organic phases.<sup>8,9</sup> Note, however, that this parameter should be, in principle, optimized for each phase, but this was left for future work. One can, however, reasonably argue that the precise value of this parameter should have only a small influence on the results, as demonstrated previously.<sup>7-9</sup> Intrinsic properties were calculated by constructing a surface passing through all the surface atoms, based on an efficient triangular interpolation.<sup>10</sup> We obtained symmetric profiles,

hence all density profiles shown here are averaged over the two sides of the liquid phase. For the orientation analysis we adopted the bivariate distribution method of Jedlovsky et al. with the coordinate frame described in Figure 1.<sup>11</sup>

### Additional Figures

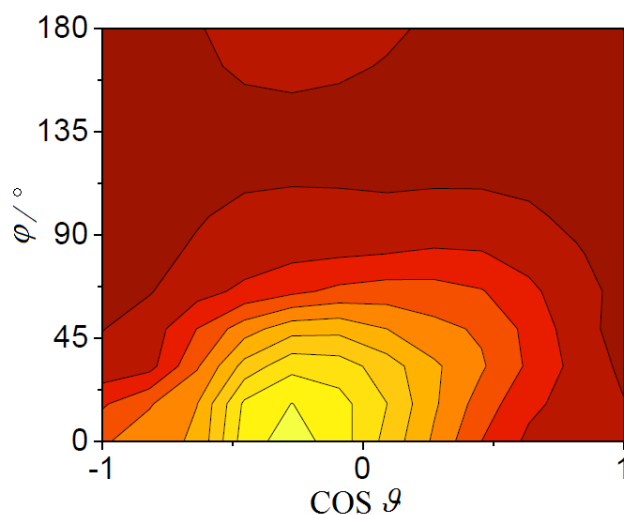
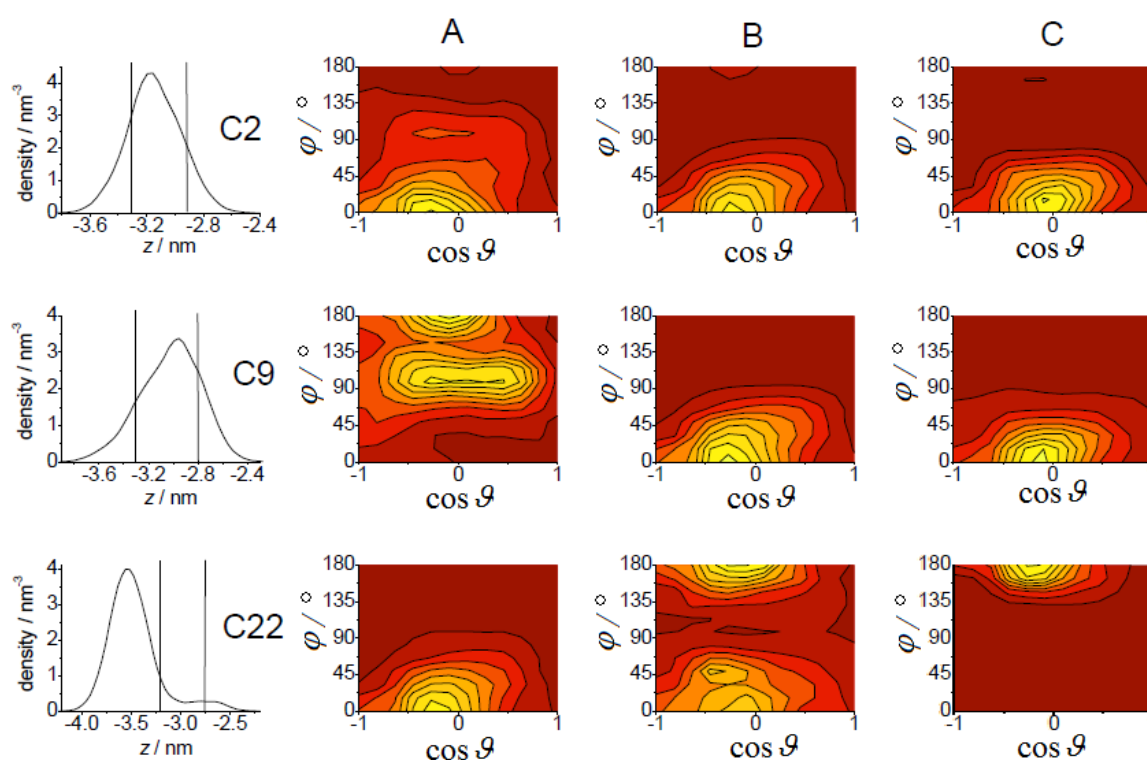


Figure S1. Orientation distribution of cation rings in the whole interfacial layer. The map is dominated by the most prevalent orientation (orientation I).



*Figure S2.* Orientation maps corresponding to different regions of the global density profiles. Brighter tones represent higher probabilities. Three atoms having the most structured profiles were chosen for this analysis: C2 (i.e. the carbon atom that is located symmetrically between the two nitrogen atoms), C9 (i.e. the center of the methyl group), and C22 (i.e. the terminal carbon of the butyl chain). The global distance range was divided as illustrated in the first column to highlight the most interesting orientations. Regions toward the vapor and the bulk were denoted by A and C, respectively, while B refers to an intermediate region.

#### References:

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