

# Supporting Information

## Influence of Nanosegregation on the Surface Tension of Fluorinated Ionic Liquids

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## **Synthesis and Characterization of 1-butyl-3-methylimidazolium perfluorobutanesulfonate ([C<sub>4</sub>C<sub>1</sub>im][C<sub>4</sub>F<sub>9</sub>SO<sub>3</sub>]) and 1-decyl-3-methylimidazolium perfluorobutanesulfonate ([C<sub>10</sub>C<sub>1</sub>im][C<sub>4</sub>F<sub>9</sub>SO<sub>3</sub>])**

For the synthesis of 1-butyl-3-methylimidazolium perfluorobutanesulfonate ([C<sub>4</sub>C<sub>1</sub>im][C<sub>4</sub>F<sub>9</sub>SO<sub>3</sub>]) and 1-decyl-3-methylimidazolium perfluorobutanesulfonate ([C<sub>10</sub>C<sub>1</sub>im][C<sub>4</sub>F<sub>9</sub>SO<sub>3</sub>]) we have used ion exchange resin methods, as developed by Ohno et al.<sup>S1</sup> They have also successfully been used as alternative anion exchange processes in our laboratory.<sup>S2-S4</sup> In the synthetic procedure, 1-butyl-3-methylimidazolium bromide ([C<sub>4</sub>C<sub>1</sub>im]Br, ≥97%; Fluka, Buchs, Switzerland) and 1-decyl-3-methylimidazolium chloride ([C<sub>10</sub>C<sub>1</sub>im]Cl, ≥98%; IoLiTec, Heilbronn, Germany) were first transformed into hydroxides by the use of an ionic exchange column (SUPELCO AMBERLITE IRN78) in water. The prepared hydroxides were then neutralized with nonafluoro-1-butanesulfonic acid (≥98%; TCI, Tokyo, Japan).

Neat FILs were obtained after eliminating the excess of both water and acid by evaporation and washing, respectively. All isolated products were completely characterized by <sup>1</sup>H and <sup>19</sup>F NMR, and CHN elemental analysis in order to check their expected structures and final purities. Additionally, the quantitative integration of their characteristic <sup>1</sup>H and <sup>19</sup>F NMR resonance peaks unfold the expected cation/anion correlations, using 1,4-difluorobenzene (99%; Alfa Aesar, Karlsruhe, Germany) as internal standard. Also, there were no peaks assigned to impurities in either the <sup>1</sup>H or <sup>19</sup>F NMR spectra. The structures of the two synthesized FILs are depicted in Table 1 of the manuscript.

The <sup>1</sup>H and <sup>19</sup>F NMR spectra were carried out on a Bruker AVANCE 400 spectrometer operated at room temperature with 16 and 32 scans, respectively. All spectra were acquired using DMSO

for field-frequency lock and NMR internal standard. Elemental analysis was done on an element analyser (Vario EL Elemental Analyser).

**1-Butyl-3-methylimidazolium perfluorobutanesulfonate ([C<sub>4</sub>C<sub>1</sub>im][C<sub>4</sub>F<sub>9</sub>SO<sub>3</sub>])**

$\delta_H$  (400 MHz; DMSO) 9.11 (1H, s, N=CH-N), 7.77 (1H, t, J = 1.7 Hz, N-CH=CH-NCH<sub>3</sub>), 7.70 (1H, t, J = 1.7 Hz, N-CH=CH-NCH<sub>3</sub>), 4.16 (2H, t, J = 7.2 Hz, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C<sub>1</sub>im), 3.85 (3H, s, CH<sub>3</sub>N), 1.82 – 1.70 (2H, m, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C<sub>1</sub>im), 1.32 – 1.20 (2H, m, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C<sub>1</sub>im), 0.91 (3H, t, J = 7.4, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C<sub>1</sub>im);  $\delta_F$  (377 MHz; DMSO) -80.18 – -80.59 (m, CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>S), -114.82 (t, J = 13.5 Hz, CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>S), -121.08 – -121.52 (m, CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>S), -125.48 – -125.77 (m, CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>S); Elemental analysis for C<sub>12</sub>F<sub>9</sub>H<sub>15</sub>N<sub>2</sub>O<sub>3</sub>S<sub>1</sub>: calculated C, 32.9, H, 3.4, N, 6.4; found C, 32.6, H, 3.7, N, 6.4%.

**1-Decyl-3-methylimidazolium perfluorobutanesulfonate ([C<sub>10</sub>C<sub>1</sub>im][C<sub>4</sub>F<sub>9</sub>SO<sub>3</sub>])**

$\delta_H$  (400 MHz; DMSO) 9.10 (1H, s, N=CH-N), 7.77 (1H, t, J = 1.7 Hz, N-CH=CH-NCH<sub>3</sub>), 7.70 (1H, t, J = 1.7 Hz, N-CH=CH-NCH<sub>3</sub>), 4.15 (2H, t, J = 7.2 Hz, CH<sub>3</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>7</sub>CH<sub>2</sub>C<sub>1</sub>im), 3.85 (3H, s, CH<sub>3</sub>N), 1.85 – 1.70 (2H, m, CH<sub>3</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>7</sub>CH<sub>2</sub>C<sub>1</sub>im), 1.25 (14H, s, CH<sub>3</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>7</sub>CH<sub>2</sub>C<sub>1</sub>im), 0.86 (3H, t, J = 6.8, CH<sub>3</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>7</sub>CH<sub>2</sub>C<sub>1</sub>im);  $\delta_F$  (377 MHz; DMSO) -80.42 (t, J = 9.6 Hz, CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>S), -114.84 (t, J = 13.5 Hz, CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>S), -121.16 – -121.60 (m, CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>S), -125.46 – -125.93 (m, CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>S); Elemental analysis for C<sub>18</sub>F<sub>9</sub>H<sub>27</sub>N<sub>2</sub>O<sub>3</sub>S<sub>1</sub>: calculated C, 41.4, H, 5.2, N, 5.4; found C, 41.3, H, 5.3, N, 5.6%.

**Table S1. Density,  $\rho$ ,<sup>a</sup> of the Pure Fluorinated Ionic Liquids Synthetized in our Laboratory as a Function of Temperature. Experiments Performed under a Typical Average Laboratory Atmospheric Pressure of 1.015 bar<sup>b</sup>.**

<i>T</i> /K	$\rho$ /g·cm <sup>-3</sup>	<i>T</i> /K	$\rho$ /g·cm <sup>-3</sup>
	[C <sub>4</sub> C <sub>1</sub> im][C <sub>4</sub> F <sub>9</sub> SO <sub>3</sub> ]		[C <sub>10</sub> C <sub>1</sub> im][C <sub>4</sub> F <sub>9</sub> SO <sub>3</sub> ]
293.15	1.4646	293.15	-
298.15	1.4591	298.15	-
303.15	1.4537	303.15 <sup>a</sup>	1.3028 <sup>c</sup>
308.15	1.4484	308.15	1.2982
313.15	1.4432	313.15	1.2936
318.15	1.4380	318.15	1.2891
323.15	1.4329	323.15	1.2847
328.15	1.4279	328.15	1.2803
333.15	1.4229	333.15	1.2759
338.15	1.4179	338.15	1.2716
343.15	1.413	343.15	1.2672
348.15	1.4080	348.15	1.2628
353.15	1.4032	353.15	1.2584
358.15	-	358.15	1.2540
363.15	-	363.15	1.2498

<sup>a</sup> The expanded uncertainty with a 0.95 level of confidence is estimated as  $\pm 0.1$  % for the density with a standard uncertainty of the temperature of  $\pm 0.02$  K.

<sup>b</sup> Standard uncertainty of  $\pm 0.01$  bar.

<sup>c</sup> Density value for the supercooled ionic liquid.

**Table S2. Melting Temperature,  $T_m$ ,<sup>a</sup> of Fluorinated Ionic Liquids. Experiments Performed under a Typical Average Laboratory Atmospheric Pressure of 1.015 bar<sup>b</sup>.**

FIL	$T_m$ / K
[C <sub>4</sub> C <sub>1</sub> im][C <sub>4</sub> F <sub>9</sub> SO <sub>3</sub> ]	288
[C <sub>10</sub> C <sub>1</sub> im][C <sub>4</sub> F <sub>9</sub> SO <sub>3</sub> ]	307

<sup>a</sup> Standard uncertainty is estimated as  $\pm 2$  K.

<sup>c</sup> Standard uncertainty of  $\pm 0.01$  bar.

**Table S3. Simulation Conditions and Size of the Equilibrated Boxes.**

System	$N$ ion pairs	$Dimensions_{box}$ (nm <sup>3</sup> )
[C <sub>2</sub> C <sub>1</sub> im][C <sub>4</sub> F <sub>9</sub> SO <sub>3</sub> ]	350	4.0 x 4.0 x 10.5
[C <sub>4</sub> C <sub>1</sub> im][C <sub>4</sub> F <sub>9</sub> SO <sub>3</sub> ]	250	4.0 x 4.0 x 8.5
[C <sub>6</sub> C <sub>1</sub> im][C <sub>4</sub> F <sub>9</sub> SO <sub>3</sub> ]	250	4.0 x 4.0 x 10.1
[C <sub>8</sub> C <sub>1</sub> im][C <sub>4</sub> F <sub>9</sub> SO <sub>3</sub> ]	250	4.0 x 4.0 x 10.9
[C <sub>10</sub> C <sub>1</sub> im][C <sub>4</sub> F <sub>9</sub> SO <sub>3</sub> ]	250	4.0 x 4.0 x 12.3
[C <sub>12</sub> C <sub>1</sub> im][C <sub>4</sub> F <sub>9</sub> SO <sub>3</sub> ]	250	4.0 x 4.0 x 12.9

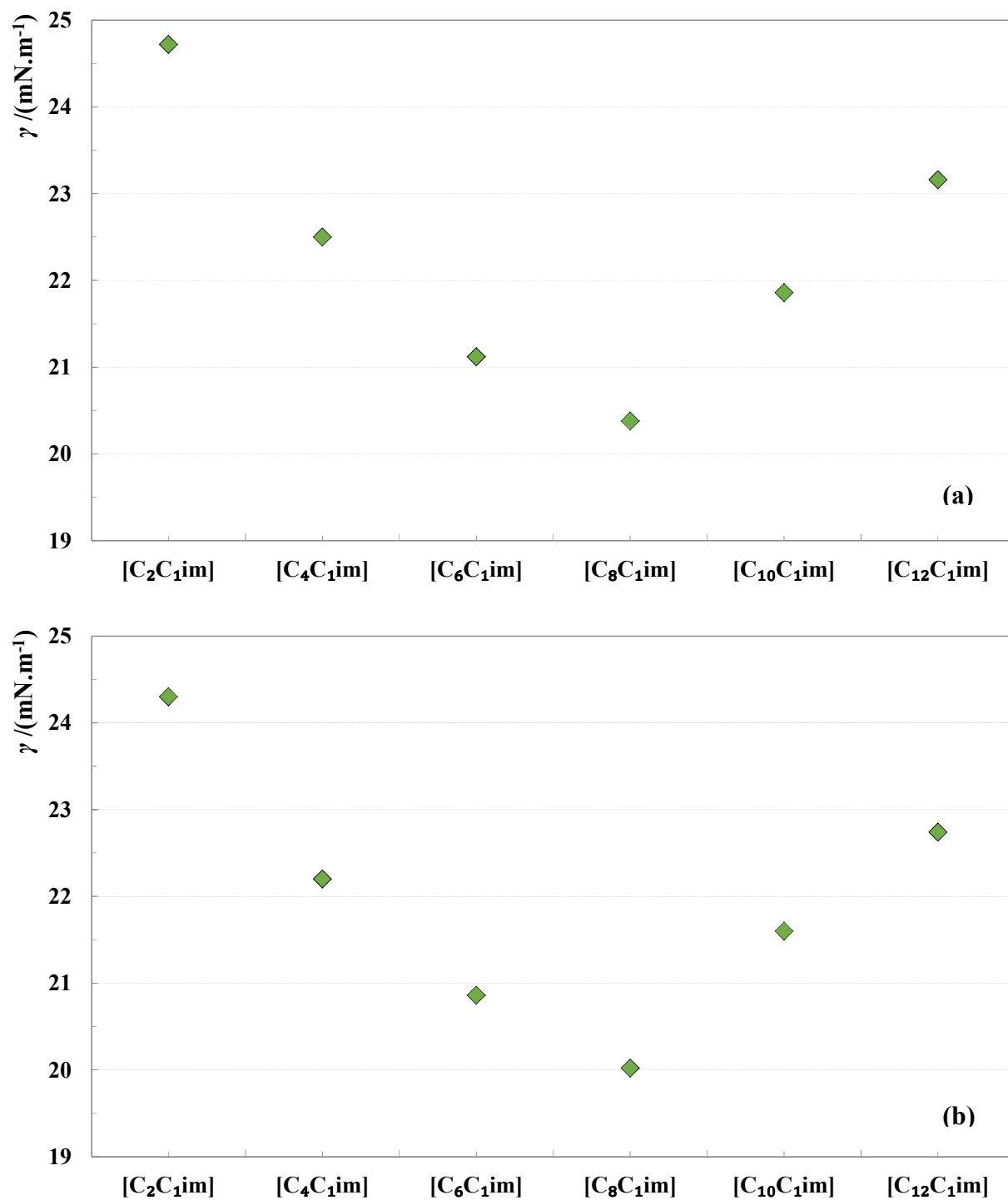
**Table S4. Experimental Surface Tension of the FILs. Experiments Performed under a Typical Average Laboratory Atmospheric Pressure of 1.015 bar<sup>a</sup>.**

$T$ (K) <sup>b</sup>	$\gamma^c$ (mNm <sup>-1</sup> )	$T$ (K) <sup>b</sup>	$\gamma^c$ (mNm <sup>-1</sup> )	$T$ (K) <sup>b</sup>	$\gamma^c$ (mNm <sup>-1</sup> )
[C <sub>2</sub> C <sub>1</sub> im][C <sub>4</sub> F <sub>9</sub> SO <sub>3</sub> ]		[C <sub>4</sub> C <sub>1</sub> im][C <sub>4</sub> F <sub>9</sub> SO <sub>3</sub> ]		[C <sub>6</sub> C <sub>1</sub> im][C <sub>4</sub> F <sub>9</sub> SO <sub>3</sub> ]	
298.2	25.96	298.3	23.43		
303.2	25.70	303.2	23.13	303.2	21.58
313.2	25.14	318.0	22.83	313.6	21.36
323.2	24.72	328.0	22.50	323.7	21.12
333.1	24.30	338.1	22.20	333.6	20.86
342.9	23.82	347.7	21.98	343.0	20.58
[C <sub>8</sub> C <sub>1</sub> im][C <sub>4</sub> F <sub>9</sub> SO <sub>3</sub> ]		[C <sub>10</sub> C <sub>1</sub> im][C <sub>4</sub> F <sub>9</sub> SO <sub>3</sub> ]		[C <sub>12</sub> C <sub>1</sub> im][C <sub>4</sub> F <sub>9</sub> SO <sub>3</sub> ]	
313.3	20.57	313.2	22.05	313.2	23.42
323.5	20.38	323.2	21.86	323.5	23.16
333.4	20.02	334.0	21.60	333.2	22.74
342.9	19.81	343.2	21.39	342.9	22.27
353.2	19.50	353.3	21.04	353.4	21.78

<sup>a</sup> Standard uncertainty of  $\pm 0.01$  bar.

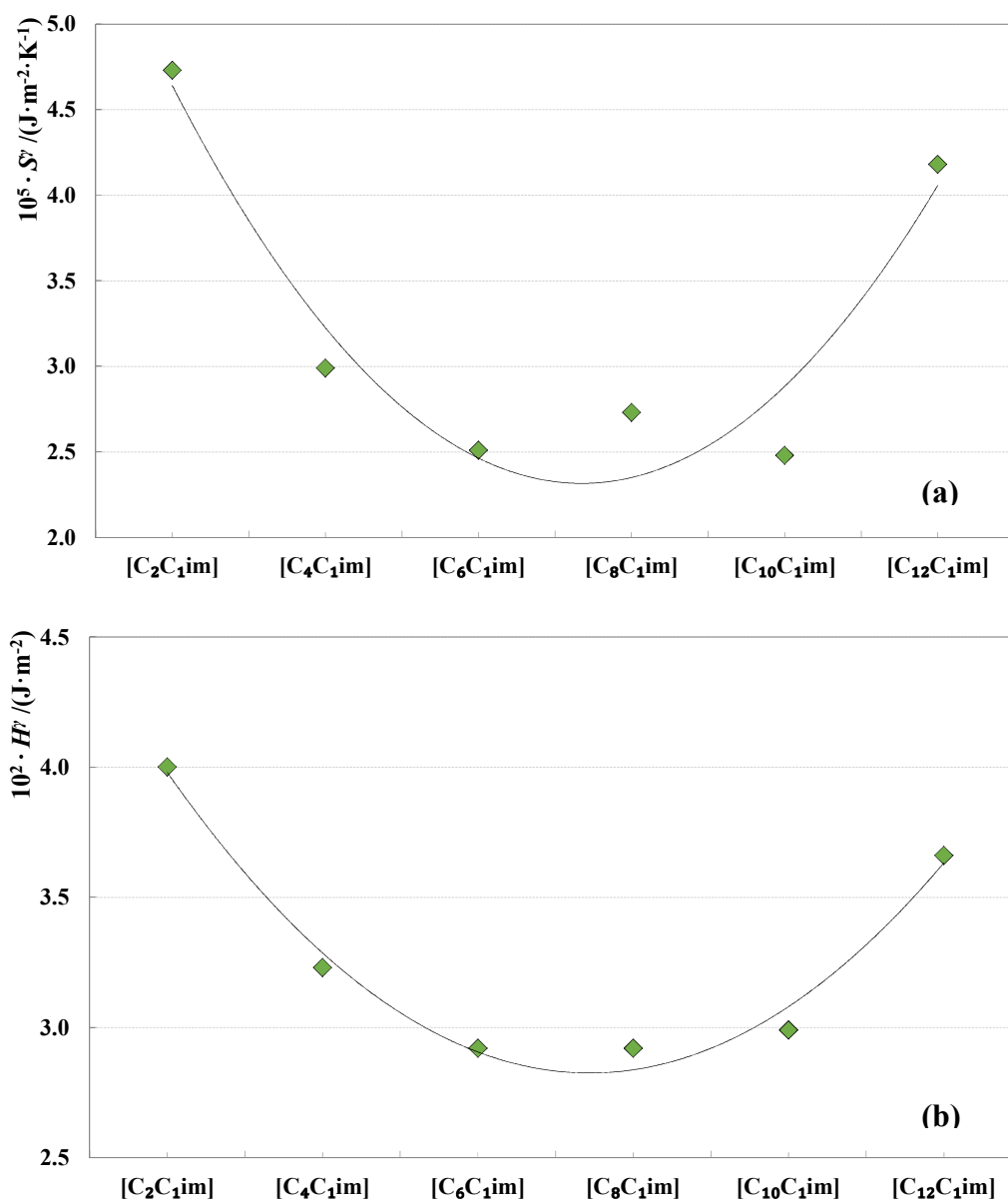
<sup>b</sup> Standard uncertainty of  $\pm 0.1$  K.

<sup>c</sup> Expanded uncertainty is  $\pm 0.13$  with a 0.95 level of confidence.



**Figure S1.** Surface tension as a function of the imidazolium alkyl chain size for the  $[\text{C}_n\text{C}_1\text{im}][\text{C}_4\text{F}_9\text{SO}_3]$  series ( $n = 2, 4, 6, 8, 10$  and  $12$ ) at: (a) 323.15 K, and (b) 333.15 K.





**Figure S2.** Surface thermodynamic properties as a function of the imidazolium alkyl chain size for the  $[C_nC_1im][C_4F_9SO_3]$  series ( $n = 2, 4, 6, 8, 10$  and  $12$ ) where: (a) surface entropy, and (b) surface enthalpy. The line is an eye-guide.

## REFERENCES

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