

## Supplementary Material

### 1. Synthesis of protic ionic liquids

#### *3-(Propoxymethyl)-1H-imidazol-3-ium salicylate ([H-Im-C<sub>1</sub>OC<sub>3</sub>][Sal])*

Yield: 90%; colorless thick liquid;

Elem. Anal. Calc. (%) for C<sub>14</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>: C, 60.41; H, 6.53; N, 10.07. Found: C, 60.52; H, 6.47; N, 10.12.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C): δ 0.87 (t, *J* = 7.4 Hz, 3H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.55 (sext, *J* = 7.4 Hz, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.36 (t, *J* = 6.6 Hz, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 5.34 (s, 2H, N-CH<sub>2</sub>-O), 6.86 (m, 1H, ar), 6.95 (dd, *J* = 1.1 Hz, *J* = 8.3 Hz, 1H, ar), 7.13 (m, 1H, im), 7.30 (m, 1H, im), 7.40 (m, 1H, ar), 7.94 (dd, *J* = 1.8 Hz, *J* = 7.9 Hz, 1H, ar), 8.26 (m, 1H, im), 14.08 (br); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 10.4, 22.5 (2xC), 71.3, 114.8, 117.1, 118.7, 119.3, 126.1, 130.7, 134.7, 136.5, 161.9, 174.3.

#### *3-(Butoxymethyl)-1H-imidazol-3-ium salicylate ([H-Im-C<sub>1</sub>OC<sub>4</sub>][Sal])*

Yield: 96%; colorless thick liquid;

Elem. Anal. Calc. (%) for C<sub>15</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub>: C, 61.62; H, 6.91; N, 9.58. Found: C, 61.79; H, 6.99; N, 9.42.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C): δ 0.88 (t, *J* = 7.3 Hz, 3H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.32 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.53 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.41 (t, *J* = 6.5 Hz, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 5.34 (s, 2H, N-CH<sub>2</sub>-O), 6.87 (m, 1H, ar), 6.95 (m, 1H, ar), 7.13 (m, 1H, im), 7.29 (m, 1H, im), 7.41 (m, 1H, ar), 7.94 (dd, *J* = 1.8 Hz, *J* = 7.9 Hz, 1H, ar), 8.16 (m, 1H, im), 13.12 (br); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 13.7, 19.1 (2xC), 31.2, 69.4, 114.9, 117.1, 118.7, 119.2, 126.3, 130.7, 134.7, 136.5, 161.9, 174.3.

*3-(Pentyloxymethyl)-1H-imidazol-3-ium salicylate ([H-Im-C<sub>1</sub>OC<sub>5</sub>][Sal])*

Yield: 98%; colorless thick liquid;

Elem. Anal. Calc. (%) for C<sub>16</sub>H<sub>22</sub>N<sub>2</sub>O<sub>4</sub>: C, 62.71; H, 7.25; N, 9.14. Found: C, 62.59; H, 7.29; N, 9.21.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C): δ 0.87 (m, 3H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.27 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.54 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.41 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 5.36 (s, 2H, N-CH<sub>2</sub>-O), 6.86 (m, 1H, ar), 6.95 (dd, *J* = 0.8 Hz, *J* = 8.3 Hz, 1H, ar), 7.15 (m, 1H, im), 7.32 (m, 1H, im), 7.41 (m, 1H, ar), 7.94 (dd, *J* = 1.6 Hz, *J* = 7.9 Hz, 1H, ar), 8.30 (m, 1H, im), 12.25 (br); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 14.0, 22.4 (2xC), 28.0, 28.9, 69.8, 114.7, 117.1, 118.8, 119.3, 125.7, 130.7, 134.8, 136.5, 161.9, 174.3.

*3-(Hexyloxymethyl)-1H-imidazol-3-ium salicylate ([H-Im-C<sub>1</sub>OC<sub>6</sub>][Sal])*

Yield: 98%; colorless thick liquid;

Elem. Anal. Calc. (%) for C<sub>16</sub>H<sub>22</sub>N<sub>2</sub>O<sub>4</sub>: C, 62.71; H, 7.25; N, 9.14. Found: C, 62.59; H, 7.29; N, 9.21.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C): δ 0.87 (t, *J* = 6.7 Hz, 3H, ali), 1.28 (m, 6H, ali), 1.55 (m, 2H, ali), 3.41 (t, *J* = 6.5 Hz, 2H, ali), 5.35 (s, 2H, N-CH<sub>2</sub>-O), 6.87 (m, 1H, ar), 6.95 (m, 1H, ar), 7.14 (m, 1H, im), 7.30 (m, 1H, im), 7.41 (m, 1H, ar), 7.94 (m, 1H, ar), 8.22 (m, 1H, im), 12.19 (br); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 14.0, 22.5 (2xC), 25.6, 29.1, 31.4, 69.8, 114.7, 117.1, 118.7, 119.3, 126.1, 130.7, 134.8, 136.5, 161.9, 174.3.

*3-(Heptyloxymethyl)-1H-imidazol-3-ium salicylate ([H-Im-C<sub>1</sub>OC<sub>7</sub>][Sal])*

Yield: 97%; colorless thick liquid;

Elem. Anal. Calc. (%) for  $C_{18}H_{26}N_2O_4$ : C, 64.63; H, 7.85; N, 8.38. Found: C, 64.69; H, 7.75; N, 8.32.

$^1H$  NMR ( $CDCl_3$ , 25 °C):  $\delta$  0.87 (t,  $J = 6.6$  Hz, 3H, ali), 1.27 (m, 8H, ali), 1.55 (m, 2H, ali), 3.41 (t,  $J = 6.5$  Hz, 2H, ali), 5.36 (s, 2H, N- $CH_2$ -O), 6.87 (m, 1H, ar), 6.95 (dd,  $J = 0.8$  Hz,  $J = 8.3$  Hz, 1H, ar), 7.14 (m, 1H, im), 7.31 (m, 1H, im), 7.41 (m, 1H, ar), 7.94 (dd,  $J = 1.7$  Hz,  $J = 7.9$  Hz, 1H, ar), 8.28 (m, 1H, im), 12.20 (br);  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  14.1, 22.6 (2xC), 25.8, 28.9, 29.1, 31.7, 69.8, 114.7, 117.1, 118.8, 119.3, 125.9, 130.7, 134.8, 136.5, 161.9, 174.3.

*3-(Octyloxymethyl)-1H-imidazol-3-ium salicylate ([H-Im- $C_1OC_8$ ][Sal])*

Surfactant content: 99.7%; Yield: 94%; colorless thick liquid;

Elem. Anal. Calc. (%) for  $C_{19}H_{28}N_2O_4$ : C, 65.48; H, 8.12; N, 8.04. Found: C, 65.30; H, 8.29; N, 8.14.

$^1H$  NMR ( $CDCl_3$ , 25 °C):  $\delta$  0.87 (t,  $J = 6.5$  Hz, 3H, ali), 1.27 (m, 10H, ali), 1.55 (m, 2H, ali), 3.41 (t,  $J = 6.5$  Hz, 2H, ali), 5.36 (s, 2H, N- $CH_2$ -O), 6.88 (m, 1H, ar), 6.96 (m, 1H, ar), 7.14 (m, 1H, im), 7.31 (m, 1H, im), 7.42 (m, 1H, ar), 7.94 (m, 1H, ar), 8.24 (m, 1H, im), 11.16 (br);  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  14.1, 22.6 (2xC), 25.9, 29.2 (2xC), 29.25, 31.8, 69.8, 114.7, 117.2, 118.8, 119.2, 126.1, 130.7, 134.9, 136.5, 161.9, 174.3.

*3-(Nonyloxymethyl)-1H-imidazol-3-ium salicylate ([H-Im- $C_1OC_9$ ][Sal])*

Surfactant content: 99.9%; Yield: 97%; colorless thick liquid;

Elem. Anal. Calc. (%) for  $C_{20}H_{30}N_2O_4$ : C, 66.26; H, 8.36; N, 7.73. Found: C, 66.13; H, 8.49; N, 7.82.

$^1H$  NMR ( $CDCl_3$ , 25 °C):  $\delta$  0.87 (t,  $J = 6.5$  Hz, 3H, ali), 1.27 (m, 12H, ali), 1.55 (m, 2H, ali), 3.41 (t,  $J = 6.5$  Hz, 2H, ali), 5.36 (s, 2H, N- $CH_2$ -O), 6.88 (m, 1H, ar), 6.96 (m, 1H, ar),

7.14 (m, 1H, im), 7.31 (m, 1H, im), 7.41 (m, 1H, ar), 7.94 (m, 1H, ar), 8.26 (m, 1H, im),  
11.16 (br);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  14.1, 22.6 (2xC), 25.8, 29.3 (2xC), 29.4 (2xC), 31.7, 69.8,  
114.7, 117.2, 118.8, 119.2, 126.1, 130.7, 134.9, 136.5, 161.9, 174.3.

*3-(Decyloxymethyl)-1H-imidazol-3-ium salicylate ([H-Im- $\text{C}_1\text{OC}_{10}$ ][Sal])*

Surfactant content: 99.6%; Yield: 95%; colorless thick liquid;

Elem. Anal. Calc. (%) for  $\text{C}_{21}\text{H}_{32}\text{N}_2\text{O}_4$ : C, 66.98; H, 8.58; N, 7.44. Found: C, 66.80; H,  
8.72; N, 7.49.

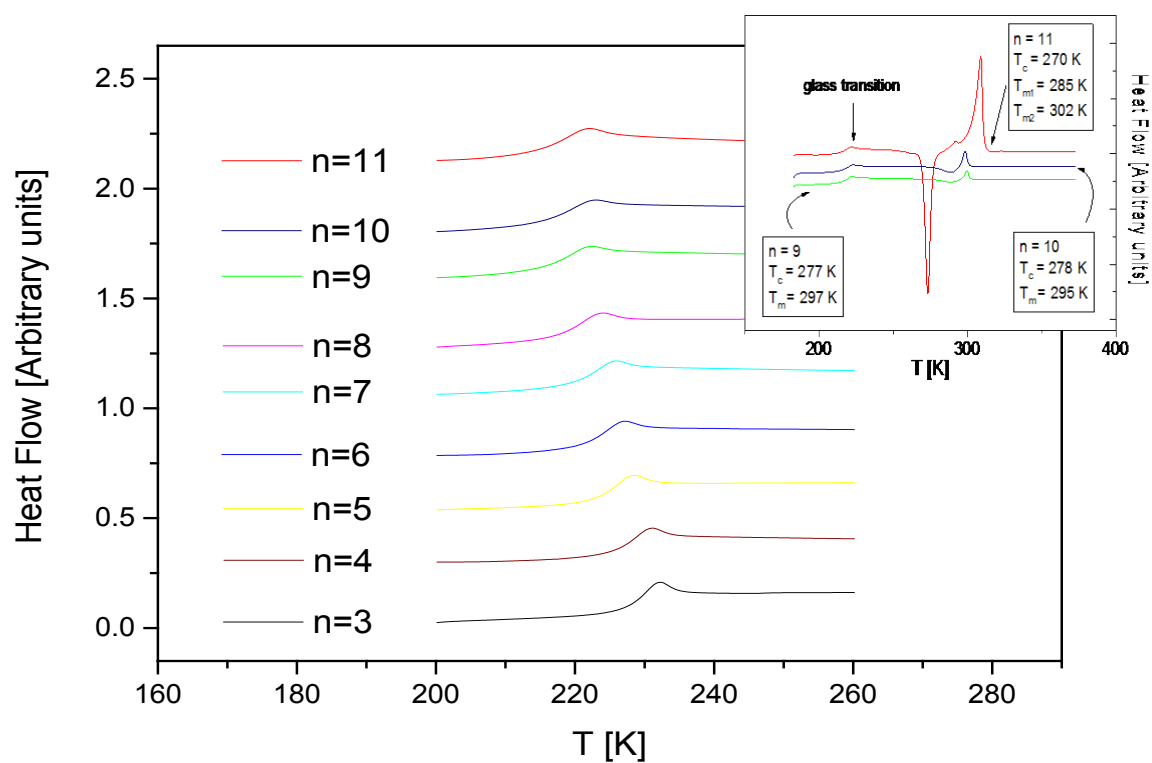
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 25 °C):  $\delta$  0.88 (t,  $J = 6.5$  Hz, 3H, ali), 1.27 (m, 14H, ali), 1.55 (m, 2H,  
ali), 3.41 (t,  $J = 6.5$  Hz, 2H, ali), 5.35 (s, 2H, N- $\text{CH}_2$ -O), 6.88 (m, 1H, ar), 6.96 (m, 1H, ar),  
7.14 (m, 1H, im), 7.31 (m, 1H, im), 7.42 (m, 1H, ar), 7.95 (m, 1H, ar), 8.23 (m, 1H, im),  
12.08 (br);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  14.1, 22.6 (2xC), 25.8, 29.2 (2xC), 29.6 (2xC), 31.1, 31.7,  
69.8, 114.7, 117.2, 118.8, 119.2, 126.1, 130.7, 134.9, 136.5, 161.9, 174.3.

*3-(Undecyloxymethyl)-1H-imidazol-3-ium salicylate ([H-Im- $\text{C}_1\text{OC}_{11}$ ][Sal])*

Surfactant content: 99.7%; Yield: 98%; colorless thick liquid;

Elem. Anal. Calc. (%) for  $\text{C}_{22}\text{H}_{34}\text{N}_2\text{O}_4$ : C, 67.65; H, 8.79; N, 7.17. Found: C, 67.79; H,  
8.54; N, 7.02.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 25 °C):  $\delta$  0.88 (t,  $J = 6.5$  Hz, 3H, ali), 1.27 (m, 16H, ali), 1.55 (m, 2H,  
ali), 3.42 (t,  $J = 6.5$  Hz, 2H, ali), 5.36 (s, 2H, N- $\text{CH}_2$ -O), 6.88 (m, 1H, ar), 6.96 (m, 1H, ar),  
7.14 (m, 1H, im), 7.31 (m, 1H, im), 7.42 (m, 1H, ar), 7.95 (m, 1H, ar), 8.24 (m, 1H, im),  
11.34 (br);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  14.1, 22.7 (2xC), 25.9, 29.2, 29.3, 29.35, 29.5, 29.6,  
29.65, 31.9, 69.8, 114.6, 117.2, 118.8, 119.3, 126.0, 130.7, 134.9, 136.5, 161.9, 174.2.



**Fig. S1** DSC thermograms of salicylates obtained during heating at a rate of 10 K/min. In the inset panel data for three compounds with longest alkyl substituents are presented with indicated temperatures of crystallization and melting