

## Tetrakis-imidazolium and benzimidazolium ionic liquids: a new class of biodegradable surfactants

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### Supplementary Information

Structural and characterization data

#### Tetrakis-((2-chloro-acetayloxy)methyl)methane (3)

White colour flakes; yield: 30.8 g (95%); m.p 92–94 °C. Molecular Formula: C<sub>13</sub>H<sub>16</sub>Cl<sub>4</sub>O<sub>8</sub>; mol. wt.: 442.07; FTIR (cm<sup>-1</sup>): 2970, 2875 (C-H)<sub>Aliph</sub>, 1749 (C=O), 1185, 1160 (O-C), 789 (C-Cl); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ: 4.24 (s, 8H, CH<sub>2</sub>-Cl), 4.06 (s, 8H, CH<sub>2</sub>-O); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ ppm: 166.89 (C=O), 63.49 (CH<sub>2</sub>-O), 42.73 (-C-), 40.69 (CH<sub>2</sub>-Cl); EIMS (m/z): 439.9 (8%)(M<sup>+</sup>), 364.9 (22%), 289.0 (30%), 213.0 (57%), 137.0 (73%), 90.9 (87%), 47.0 (100%).

#### Tetrakis-((N-butyl-imidazoliumyl-acetayloxy)methyl)methane chloride (8b)

This compound was prepared analogously to **8a** using tetrakis-((2-chloro-acetayloxy)methyl)methane (compound **3**) (1.9 g, 4.30 mmol) and 1-butyylimidazole (2.14 g, 2.26 mL, 17.2 mmol) to give a white hygroscopic semi-solid in 97% yield (3.91 g). Molecular Formula: C<sub>41</sub>H<sub>64</sub>Cl<sub>4</sub>N<sub>8</sub>O<sub>8</sub>; mol. wt.: 938.81; FTIR (cm<sup>-1</sup>): 3060 (C-H)<sub>Ar</sub>, 2959, 2932, 2865 (C-H)<sub>Aliph</sub>, 1750 (C=O), 1644 (C=N), 1564, 1465 (C=C)<sub>Ar</sub>, 1195, 1160 (C-O); <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ ppm: 9.57 (bt~s, 4H, C-H<sub>Imidazole</sub>, major), 9.52 (bt~s, 4H, C-H<sub>Imidazole</sub>, minor), 9.45 (bt~s, 4H, C-H<sub>Imidazole</sub>, minor), 7.91 (t, *J* = 1.81 Hz, 4H, C-H<sub>Imidazole</sub>, major), 7.86 (t, *J* = 1.81 Hz, 4H, C-H<sub>Imidazole</sub>, major), 7.76 (t, *J* = 1.81 Hz, 4H, C-H<sub>Imidazole</sub>, minor), 7.69 (t, *J* = 1.81 Hz, 4H, C-H<sub>Imidazole</sub>, minor), 5.47 (s, 8H, O-CH<sub>2</sub>, major), 5.44 (s, 8H, O-CH<sub>2</sub>, minor), 5.39 (s, 8H, O-CH<sub>2</sub>, minor), 4.25 (t, *J* = 7.25 Hz, 8H, α-CH<sub>2</sub>, major), 4.20 (s, 8H, N-CH<sub>2</sub>, major), 4.11 (s, 8H, N-CH<sub>2</sub>, minor), 3.98 (t, *J* = 7.25 Hz, 8H, α-CH<sub>2</sub>, minor), 1.81–1.74 (m, 8H, β-CH<sub>2</sub>, major), 1.72–1.64 (m, 8H, β-CH<sub>2</sub>, minor), 1.30–1.18 (m, 8H, (ω-1)-CH<sub>2</sub>), 0.89 (t, *J* = 7.25 Hz, 12H, ω-CH<sub>3</sub>); <sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ ppm: 166.72 (C=O), 137.41 (CH<sub>Imidazole</sub>), 123.96 (CH<sub>Imidazole</sub>), 122.12 (CH<sub>Imidazole</sub>), 63.42 (CH<sub>2</sub>-O), 49.68 (CH<sub>2</sub>-N, minor), 49.58 (CH<sub>2</sub>-N, major), 48.73 (α-CH<sub>2</sub>), 41.38 (-C-), 31.37 (ω-2), 18.78 (ω-1), 13.31 (ω); HRMS: m/z, [M<sup>+</sup>–3H]–4Cl<sup>-</sup> calcd. for C<sub>41</sub>H<sub>61</sub>N<sub>8</sub>O<sub>8</sub><sup>7+</sup>: 793.4612, found: 793.4655.

#### Tetrakis-((N-octyl-imidazoliumyl-acetayloxy)methyl)methane chloride (8d)

This compound was prepared analogously to **8a** using tetrakis-((2-chloro-acetayloxy)methyl)methane (compound **3**) (1.9 g, 4.30 mmol) and 1-octylimidazole (**6d**) (3.10 g, 17.2 mmol) to give a viscous hygroscopic syrup in 98% yield (4.90 g). Molecular Formula: C<sub>57</sub>H<sub>96</sub>Cl<sub>4</sub>N<sub>8</sub>O<sub>8</sub>; mol. wt.: 1163.23; FTIR (cm<sup>-1</sup>): 3063 (C-H)<sub>Ar</sub>, 2955, 2925, 2855 (C-H)<sub>Aliph</sub>, 1750 (C=O), 1619 (C=N), 1563, 1463 (C=C)<sub>Ar</sub>, 1202, 1166 (C-O); <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ ppm: 9.72 (bt~s, 4H, C-H<sub>Imidazole</sub>, major), 9.61 (bt~s, 4H, C-H<sub>Imidazole</sub>, minor), 9.48 (bt~s, 4H, C-H<sub>Imidazole</sub>, minor), 7.99 (t, 4H, *J* = 1.81 Hz, C-H<sub>Imidazole</sub>, major), 7.94 (t, 4H, *J* = 1.81 Hz, C-H<sub>Imidazole</sub>, minor), 7.93 (t, 4H, *J* = 1.81 Hz, C-H<sub>Imidazole</sub>, minor), 7.89 (t, 4H, *J* = 1.81 Hz, C-H<sub>Imidazole</sub>, major), 7.83 (t, 4H, *J* = 1.81 Hz, C-H<sub>Imidazole</sub>, minor), 5.54 (s, 8H, O-CH<sub>2</sub>, major), 5.48 (s,

## Supplementary Information: Tetrakis-imidazolium and benzimidazolium ionic liquids: a new class of biodegradable surfactants

Nassir N. Al-Mohammed, Rusnah Syahila Duali Hussien, Tammar Hussein Ali, Yatimah Alias and Zanariah Abdullah

8H, O-CH<sub>2</sub>, minor), 5.47 (s, 8H, O-CH<sub>2</sub>, minor), 4.27 (t,  $J = 7.70$  Hz, 8H,  $\alpha$ -CH<sub>2</sub>), 4.18 (bs, 6H, N-CH<sub>2</sub>, major), 4.09 (s, 8H, N-CH<sub>2</sub>, minor), 1.82–1.75 (m, 8H,  $\beta$ -CH<sub>2</sub>), 1.23 (bs, 40H, bulk-CH<sub>2</sub>), 0.84 (t,  $J = 6.80$  Hz, 12H,  $\omega$ -CH<sub>3</sub>); <sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  ppm: 168.13 (C=O, minor), 166.72 (C=O, major), 137.45 (CH<sub>Imidazole</sub>, major), 137.22 (CH<sub>Imidazole</sub>, minor), 123.94 (CH<sub>Imidazole</sub>), 122.04 (CH<sub>Imidazole</sub>, major), 121.96 (CH<sub>Imidazole</sub>, minor), 63.86 (CH<sub>2</sub>-O, minor), 63.41 (CH<sub>2</sub>-O, major), 49.78 (CH<sub>2</sub>-N, minor), 49.59 (CH<sub>2</sub>-N, major), 48.96 ( $\alpha$ -CH<sub>2</sub>), 41.52 (-C-), 31.20 ( $\omega$ -2), 29.45, 28.55, 28.37 (bulk-CH<sub>2</sub>), 25.52 ( $\beta$ -CH<sub>2</sub>), 22.10 ( $\omega$ -1), 13.98 ( $\omega$ ); HRMS:  $m/z$ , [M<sup>+4</sup>-3H]-4Cl<sup>-</sup> calcd. for C<sub>57</sub>H<sub>93</sub>N<sub>8</sub>O<sub>8</sub><sup>7+</sup>: 1017.7116, found: 1017.7160.

### Tetrakis-((*N*-decyl-imidazoliumyl-acetayloxy)methyl)methane chloride (8e)

This compound was prepared analogously to **8a** using tetrakis-((2-chloro-acetayloxy)methyl)methane (compound **3**) (1.9 g, 4.30 mmol) and 1-decylimidazole (**6e**) (3.58 g, 17.2 mmol) to give a viscous hygroscopic syrup in 99% yield (5.43 g). Molecular Formula: C<sub>65</sub>H<sub>112</sub>Cl<sub>4</sub>N<sub>8</sub>O<sub>8</sub>; mol. wt.: 1275.45; FTIR (cm<sup>-1</sup>): 3130, 3065 (C-H)<sub>Ar</sub>, 2950, 2925, 2857 (C-H)<sub>Aliph</sub>, 1750 (C=O), 1623 (C=N), 1564, 1482 (C=C)<sub>Ar</sub>, 1202, 1165 (C-O); <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  ppm: 9.73 (bt~s, 4H, C-H<sub>Imidazole</sub>, major), 9.62 (bt~s, 4H, C-H<sub>Imidazole</sub>, minor), 9.48 (bt~s, 4H, C-H<sub>Imidazole</sub>, minor), 7.99 (t,  $J = 1.81$  Hz, 4H, C-H<sub>Imidazole</sub>, major), 7.94 (t,  $J = 1.81$  Hz, 4H, C-H<sub>Imidazole</sub>, minor), 7.93 (t,  $J = 1.81$  Hz, 4H, C-H<sub>Imidazole</sub>, minor), 7.89 (t,  $J = 1.81$  Hz, 4H, C-H<sub>Imidazole</sub>, major), 7.85 (t,  $J = 1.81$  Hz, 4H, C-H<sub>Imidazole</sub>, minor), 7.83 (t,  $J = 1.81$  Hz, 4H, C-H<sub>Imidazole</sub>, minor), 5.54 (s, 8H, O-CH<sub>2</sub>, major), 5.49 (s, 8H, O-CH<sub>2</sub>, minor), 5.47 (s, 8H, O-CH<sub>2</sub>, minor), 4.24 (t,  $J = 7.25$  Hz, 8H,  $\alpha$ -CH<sub>2</sub>), 4.18 (s, 8H, N-CH<sub>2</sub>, major), 4.09 (s, 8H, N-CH<sub>2</sub>, minor), 1.82–1.75 (m, 6H,  $\beta$ -CH<sub>2</sub>), 1.23 (bs, 56H, bulk-CH<sub>2</sub>), 0.84 (t, 12H,  $J = 6.80$  Hz,  $\omega$ -CH<sub>3</sub>); <sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  ppm: 167.10 (C=O, minor), 166.68 (C=O, major), 137.40 (CH<sub>Imidazole</sub>, major), 137.20 (CH<sub>Imidazole</sub>, minor), 123.90 (CH<sub>Imidazole</sub>), 122.01 (CH<sub>Imidazole</sub>), 63.85 (CH<sub>2</sub>-O, minor), 63.31 (CH<sub>2</sub>-O, major), 49.75 (CH<sub>2</sub>-N, minor), 49.55 (CH<sub>2</sub>-N, major), 48.94 ( $\alpha$ -CH<sub>2</sub>), 41.10 (-C-), 31.29 ( $\omega$ -2), 29.42, 28.93, 28.87, 28.69, 28.39 (bulk-CH<sub>2</sub>), 25.50 ( $\beta$ -CH<sub>2</sub>), 22.11 ( $\omega$ -1), 13.96 ( $\omega$ ); HRMS:  $m/z$ , [M<sup>+4</sup>-3H]-4Cl<sup>-</sup> calcd. for C<sub>65</sub>H<sub>109</sub>N<sub>8</sub>O<sub>8</sub><sup>7+</sup>: 1129.8368, found: 1129.8284.

### Tetrakis-((*N*-decyl-benzimidazoliumyl-acetayloxy)methyl)methane chloride (9e)

This compound was prepared analogously to **9b** using tetrakis-((2-chloro-acetayloxy)methyl)methane (compound **3**) (1.9 g, 4.30 mmol) and 1-decyl-benzimidazole (**7e**) (4.44 g, 17.2 mmol) to give a viscous hygroscopic syrup in 97% yield (6.15g). Molecular Formula: C<sub>81</sub>H<sub>120</sub>Cl<sub>4</sub>N<sub>8</sub>O<sub>8</sub>; mol. wt.: 1475.68; FTIR (cm<sup>-1</sup>): 3134 (C-H)<sub>Ar</sub>, 2962, 2923, 2854 (C-H)<sub>Aliph</sub>, 1751 (C=O), 1622 (C=N), 1562 1486, 1463 (C=C)<sub>Ar</sub>, 1203 (C-O); <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  ppm: 10.50 (s, 4H, C-H<sub>BImidazole</sub>, major), 10.38 (s, 4H, C-H<sub>BImidazole</sub>, minor), 10.22 (s, 4H, C-H<sub>BImidazole</sub>, minor), 8.16 (dd,  $J = 8.29$  Hz, 8H, CH<sub>Ar</sub>), 7.63 (dt,  $J = 7.81$  Hz, 8H, CH<sub>Ar</sub>), 5.91 (s, 8H, O-CH<sub>2</sub>, major), 5.85 (s, 8H, O-CH<sub>2</sub>, minor), 5.79 (s, 8H, O-CH<sub>2</sub>, minor), 4.56 (t,  $J = 7.05$  Hz, 8H,  $\alpha$ -CH<sub>2</sub>, major), 4.49 (t,  $J = 7.07$  Hz, 8H,  $\alpha$ -CH<sub>2</sub>, minor), 4.17 (s, 8H, N-CH<sub>2</sub>, major), 4.11 (s, 8H, N-CH<sub>2</sub>, minor), 1.92–1.85 (m, 8H,  $\beta$ -CH<sub>2</sub>), 1.20 (bs, 56H, bulk-CH<sub>2</sub>), 0.83 (t, 12H,  $J = 6.10$  Hz,  $\omega$ -CH<sub>3</sub>); <sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  ppm: 167.07 (C=O, minor), 166.44 (C=O, major), 143.37 (CH<sub>BImidazole</sub>, major), 142.25 (CH<sub>BImidazole</sub>, minor), 131.50 (C<sub>Ar</sub>), 130.61 (C<sub>Ar</sub>), 126.67 (2 × CH<sub>Ar</sub>), 114.19 (CH<sub>Ar</sub>, major), 114.09 (CH<sub>Ar</sub>, minor), 113.74 (CH<sub>Ar</sub>), 63.00 (CH<sub>2</sub>-O), 47.63 (CH<sub>2</sub>-N), 46.79 ( $\alpha$ -CH<sub>2</sub>,

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Nassir N. Al-Mohammed, Rusnah Syahila Duali Hussien, Tammar Hussein Ali, Yatimah Alias and Zanariah Abdullah

major), 46.62 ( $\alpha$ -CH<sub>2</sub>, minor), 41.79 (-C-), 31.28 (( $\omega$ -2), major), 30.69 (( $\omega$ -2), minor), 28.91, 28.86, 28.67, 28.55, 28.45 (bulk-CH<sub>2</sub>), 25.72 ( $\beta$ -CH<sub>2</sub>), 22.08 ( $\omega$ -1), 13.94 ( $\omega$ ).

### Tetrakis-((*N*-dodecyl-benzimidazoliumyl-acetayloxy)methyl)methane chloride (9f)

This compound was prepared analogously to **9b** using tetrakis-((2-chloro-acetayloxy)methyl)methane (compound **3**) (1.9 g, 4.30 mmol) and 1-dodecyl-benzimidazole (**7f**) (4.93 g, 17.2 mmol) to give a viscous hygroscopic syrup in 98% yield (6.69g). Molecular Formula: C<sub>89</sub>H<sub>136</sub>Cl<sub>4</sub>N<sub>8</sub>O<sub>8</sub>; mol. wt.: 1587.89; FTIR (cm<sup>-1</sup>): 3134 (C-H)<sub>Ar</sub>, 2955, 2925, 2855 (C-H)<sub>Aliph</sub>, 1755 (C=O), 1620 (C=N), 1562, 1486, (C=C)<sub>Ar</sub>, 1202 (C-O); <sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>OD)  $\delta$  ppm: 9.84 (s, 4H, C-H<sub>BImidazole</sub>, major), 9.80 (s, 4H, C-H<sub>BImidazole</sub>, minor), 9.75 (s, 4H, C-H<sub>BImidazole</sub>, minor), 8.04–7.96 (m, 8H, CH<sub>Ar</sub>), 7.73–7.54 (m, 8H, CH<sub>Ar</sub>), 5.69 (s, 8H, O-CH<sub>2</sub>, major), 5.67 (s, 8H, O-CH<sub>2</sub>, minor), 5.65 (s, 8H, O-CH<sub>2</sub>, minor), 4.61 (t, *J*=7.32 Hz, 8H,  $\alpha$ -CH<sub>2</sub>, minor), 4.55 (t, *J*=7.32 Hz, 8H,  $\alpha$ -CH<sub>2</sub>, major), 4.37 (s, 8H, N-CH<sub>2</sub>, major), 4.34 (s, 8H, N-CH<sub>2</sub>, minor), 4.25 (s, 8H, N-CH<sub>2</sub>, minor), 2.06–1.98 (m, 8H,  $\beta$ -CH<sub>2</sub>), 1.28 (bs, 72H, bulk-CH<sub>2</sub>), 0.89 (t, *J*=7.07 Hz, 12H,  $\omega$ -CH<sub>3</sub>); <sup>13</sup>C-NMR (100 MHz, CD<sub>3</sub>OD)  $\delta$  ppm: 168.84 (C=O, minor), 167.66 (C=O, major), 166.55 (C=O, minor), 144.15 (CH<sub>BImidazole</sub>), 133.34 (C<sub>Ar</sub>), 132.53 (C<sub>Ar</sub>), 128.59 (CH<sub>Ar</sub>), 128.52 (CH<sub>Ar</sub>), 115.02 (CH<sub>Ar</sub>), 114.76 (CH<sub>Ar</sub>), 64.23 (CH<sub>2</sub>-O, minor), 64.09 (CH<sub>2</sub>-O, major), 63.71 (CH<sub>2</sub>-O, minor), 48.44 (CH<sub>2</sub>-N), 44.32 ( $\alpha$ -CH<sub>2</sub>), 41.78 (-C-), 33.18 ( $\omega$ -2), 30.87 (2), 30.80, 30.70, 30.59, 30.36, 30.32 (bulk-CH<sub>2</sub>), 27.64 ( $\beta$ -CH<sub>2</sub>), 23.86 ( $\omega$ -1), 14.60 ( $\omega$ ).

### Tetrakis-((*N*-benzyl-benzimidazoliumyl-acetayloxy)methyl)methane chloride (9g)

This compound was prepared analogously to **9b** using tetrakis-((2-chloro-acetayloxy)methyl)methane (compound **3**) (1.9 g, 4.30 mmol) and 1-benzyl-benzimidazole (**7g**) (3.58 g, 17.2 mmol) to give a pale yellow hygroscopic solid (m.p 50–52°C) in 99% yield (5.43g). Molecular Formula: C<sub>69</sub>H<sub>64</sub>Cl<sub>4</sub>N<sub>8</sub>O<sub>8</sub>; mol. wt.: 1275.11; FTIR (cm<sup>-1</sup>): 3132, 3032 (C-H)<sub>Ar</sub>, 2935 (C-H)<sub>Aliph</sub>, 1749 (C=O), 1614 (C=N), 1561, 1488, 1455 (C=C)<sub>Ar</sub>, 1183 (C-O); <sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  ppm: 10.19 (s, 4H, C-H<sub>BImidazole</sub>, minor), 10.03 (s, 4H, C-H<sub>BImidazole</sub>, minor), 10.00 (s, 4H, C-H<sub>BImidazole</sub>, major), 8.10–7.99 (m, 8H, C-H<sub>Ar</sub>), 7.70–7.62 (m, 8H, C-H<sub>Ar</sub>), 7.52–7.30 (m, 20H, C-H<sub>Ar</sub>), 5.89 (s, 8H, CH<sub>2</sub>-Ar), 5.88 (s, 8H, CH<sub>2</sub>-Ar), 5.87 (s, 8H, CH<sub>2</sub>-Ar), 5.66 (s, 8H, O-CH<sub>2</sub>, minor), 5.56 (s, 8H, O-CH<sub>2</sub>, minor), 5.53 (s, 8H, O-CH<sub>2</sub>, major), 3.34 (s, 8H, N-CH<sub>2</sub>, major), 3.27 (s, 8H, N-CH<sub>2</sub>, minor); <sup>13</sup>C-NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$  ppm: 168.51 (C=O, minor), 167.84 (C=O, major), 166.58 (C=O, minor), 143.59 (CH<sub>BImidazole</sub>), 133.93 (-C<sub>Ar</sub>-CH<sub>2</sub>-, major), 133.87 (-C<sub>Ar</sub>-CH<sub>2</sub>-, minor), 131.77 (C<sub>BImidazole</sub>), 130.43 (C<sub>BImidazole</sub>), 129.05 (2  $\times$  CH<sub>Ar</sub>), 128.82 (CH<sub>Ar</sub>, major), 128.68 (CH<sub>Ar</sub>, minor), 128.34 (2  $\times$  CH<sub>Ar</sub>), 126.94 (CH<sub>BImidazole</sub>), 126.77 (CH<sub>BImidazole</sub>), 144.29 (CH<sub>BImidazole</sub>, minor), 114.07 (CH<sub>BImidazole</sub>, major), 113.94 (CH<sub>BImidazole</sub>), 60.69 (CH<sub>2</sub>-O), 49.94 (CH<sub>2</sub>-N, major), 49.06 (CH<sub>2</sub>-N, minor), 47.82 (Ar-CH<sub>2</sub>-), 41.58 (-C-); HRMS: *m/z*, [M<sup>+4</sup>-3H]-4Cl<sup>-</sup> calcd. for C<sub>69</sub>H<sub>61</sub>N<sub>8</sub>O<sub>8</sub><sup>7+</sup>: 1129.4612, found: 1129.4690.

### Tetrakis-((*N*-butyl-imidazoliumyl-acetayloxy)methyl)methane bis(trifluoromethylsulfonyl)-amide (10b)

This compound was prepared analogously to **10a** using tetrakis-((*N*-butyl-imidazoliumyl-acetayloxy)methyl)methane chloride **8b** (0.94 g, 1.0 mmole) and Lithium bis-(trifluoromethanesulphonyl)-imide

## Supplementary Information: Tetrakis-imidazolium and benzimidazolium ionic liquids: a new class of biodegradable surfactants

Nassir N. Al-Mohammed, Rusnah Syahila Duali Hussen, Tammar Hussein Ali, Yatimah Alias and Zanariah Abdullah

LiNTf<sub>2</sub> (1.29 g, 4.5 mmol) to give a clear viscous hygroscopic liquid at room temperature in 91% yield (1.75 g). Molecular Formula: C<sub>49</sub>H<sub>64</sub>F<sub>24</sub>N<sub>12</sub>O<sub>24</sub>S<sub>8</sub>; mol. wt.: 1917.58; FTIR (cm<sup>-1</sup>): 3064 (C-H)<sub>Ar</sub>, 2951, 2935, 2855 (C-H)<sub>Aliph</sub>, 1752 (C=O), 1648 (C=N), 1560, 1470 (C=C)<sub>Ar</sub>, 1359, 1218 (C-F), 1357, 1152 (O=S=O), 1203, 1169 (C-O); <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ ppm: 9.55 (bt~s, 4H, C-H<sub>Imidazole</sub>, major), 9.49 (bt~s, 4H, C-H<sub>Imidazole</sub>, minor), 9.42 (bt~s, 4H, C-H<sub>Imidazole</sub>, minor), 7.90 (t, *J*=1.81 Hz, 4H, C-H<sub>Imidazole</sub>, major), 7.85 (t, *J*=1.81 Hz, 4H, C-H<sub>Imidazole</sub>, major), 7.73 (t, *J*=1.81 Hz, 4H, C-H<sub>Imidazole</sub>, minor), 7.67 (t, 4H, *J*=1.81 Hz, C-H<sub>Imidazole</sub>, minor), 5.45 (s, 8H, O-CH<sub>2</sub>, major), 5.40 (s, 8H, O-CH<sub>2</sub>, minor), 4.27 (t, *J*=7.25 Hz, 8H, α-CH<sub>2</sub>), 4.22 (s, 8H, N-CH<sub>2</sub>), 3.99 (t, *J*=7.25 Hz, 8H, α-CH<sub>2</sub>, minor), 1.85–1.79 (m, 8H, β-CH<sub>2</sub>), 1.28–1.19 (m, 8H, (ω-1)-CH<sub>2</sub>), 0.90 (t, *J*=7.25 Hz, 12H, ω-CH<sub>3</sub>); <sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ ppm: 167.25 (C=O, minor), 166.83 (C=O, major), 137.62 (CH<sub>Imidazole</sub>), 124.84 (CH<sub>Imidazole</sub>), 123.75, 120.52, 117.29, 114.06 (q, *J*=321 Hz, CF<sub>3</sub>), 122.70 (CH<sub>Imidazole</sub>), 64.66 (CH<sub>2</sub>-O, minor), 64.17 (CH<sub>2</sub>-O, major), 50.05 (CH<sub>2</sub>-N), 49.01 (α-CH<sub>2</sub>), 40.58 (-C-), 31.09 (ω-2), 19.12 (ω-1), 13.52 (ω). <sup>19</sup>F (336, MHz) δ ppm: -80.22; HRMS: *m/z*, [M<sup>+4</sup>-3H]-4NTF<sub>2</sub><sup>-</sup> calcd. for C<sub>41</sub>H<sub>61</sub>N<sub>8</sub>O<sub>8</sub><sup>7+</sup> 793.4612 found: 793.4644; *m/z*, [NTF<sub>2</sub>]<sup>-</sup> calcd. for C<sub>2</sub>F<sub>6</sub>NO<sub>4</sub>S<sub>2</sub><sup>-</sup>: 279.9173, found: 279.9192.

### Tetrakis-((*N*-dodecyl-imidazoliumyl-acetayloxy)methyl)methane bis(trifluoromethylsulfonyl) amide (10f)

This compound was prepared analogously to **10a** using tetrakis-((*N*-dodecyl-imidazoliumyl-acetayloxy)methyl)methane chloride **8f** (1.39 g, 1.0 mmole) and Lithium bis-(trifluoromethanesulphonyl)-imide LiNTf<sub>2</sub> (1.29 g, 4.5 mmol) to give a clear viscous hygroscopic liquid at room temperature in 93% yield (2.20 g). Molecular Formula: C<sub>81</sub>H<sub>128</sub>F<sub>24</sub>N<sub>12</sub>O<sub>24</sub>S<sub>8</sub>; mol. wt.: 2366.40; FTIR (cm<sup>-1</sup>): 3073 (C-H)<sub>Ar</sub>, 2959, 2928, 2850 (C-H)<sub>Aliph</sub>, 1757 (C=O), 1652 (C=N), 1565, 1460 (C=C)<sub>Ar</sub>, 1359, 1225 (C-F), 1354, 1140 (O=S=O), 1205, 1179 (C-O); <sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>OD) δ ppm: 9.08 (bt~s, 4H, C-H<sub>Imidazole</sub>, minor), 9.03 (bt~s, 4H, C-H<sub>Imidazole</sub>, minor), 8.99 (bt~s, 4H, C-H<sub>Imidazole</sub>, major), 7.80 (t, *J*=1.81 Hz, 4H, C-H<sub>Imidazole</sub>, major), 7.74 (t, *J*=1.81 Hz, 4H, C-H<sub>Imidazole</sub>, minor), 7.63 (t, *J*=1.81, 4H, C-H<sub>Imidazole</sub>, major), 7.60 (t, 4H, *J*=1.81, C-H<sub>Imidazole</sub>, minor), 5.45 (s, 8H, O-CH<sub>2</sub>), 4.33 (t, *J*=7.12 Hz, 8H, α-CH<sub>2</sub>), 4.22 (s, 8H, N-CH<sub>2</sub>), 1.90–1.86 (m, 8H, β-CH<sub>2</sub>), 1.32 (bs, 72H, bulk-CH<sub>2</sub>), 0.90 (t, 12H, *J*=7.07 Hz, ω-CH<sub>3</sub>); <sup>13</sup>C-NMR (100 MHz, CD<sub>3</sub>OD) δ ppm: 168.88 (C=O, minor), 167.83 (C=O, major), 138.77 (CH<sub>Imidazole</sub>), 126.26, 123.04, 119.81, 116.58 (q, *J*=321 Hz, CF<sub>3</sub>), 124.42 (CH<sub>Imidazole</sub>), 121.552 (CH<sub>Imidazole</sub>), 65.03 (CH<sub>2</sub>-O, minor), 64.87 (CH<sub>2</sub>-O, major), 51.74 (CH<sub>2</sub>-N), 50.67 (α-CH<sub>2</sub>), 42.73 (-C-), 33.15 (ω-2), 31.20, 30.82 (2), 30.72, 30.60, 30.26, 30.05 (bulk-CH<sub>2</sub>), 27.38 (β), 23.78 (ω-1), 14.63 (ω, major), 14.58 (ω, minor). <sup>19</sup>F (336, MHz) δ ppm: -80.12; HRMS: *m/z*, [M<sup>+4</sup>-3H]-4NTF<sub>2</sub><sup>-</sup> calcd. for C<sub>73</sub>H<sub>125</sub>N<sub>8</sub>O<sub>8</sub><sup>7+</sup> 1241.9620 found: 1241.9702; *m/z*, [NTF<sub>2</sub>]<sup>-</sup> calcd. for C<sub>2</sub>F<sub>6</sub>NO<sub>4</sub>S<sub>2</sub><sup>-</sup>: 279.9173, found: 279.9157.

### Tetrakis-((*N*-benzyl-imidazoliumyl-acetayloxy)methyl)methane bis(trifluoromethylsulfonyl) amide (10g)

This compound was prepared analogously to **10a** using tetrakis-((*N*-benzyl-imidazoliumyl-acetayloxy)-methyl)methane chloride **8g** (1.08 g, 1.0 mmole) and Lithium bis-(trifluoromethanesulphonyl)-imide LiNTf<sub>2</sub> (1.29 g, 4.5 mmol) to give a clear viscous hygroscopic liquid at room temperature in 96% yield (1.98 g). Molecular Formula: C<sub>61</sub>H<sub>56</sub>F<sub>24</sub>N<sub>12</sub>O<sub>24</sub>S<sub>8</sub>; mol. wt.: 2053.65; FTIR (cm<sup>-1</sup>): 3079 (C-H)<sub>Ar</sub>, 2977 (C-

## Supplementary Information: Tetrakis-imidazolium and benzimidazolium ionic liquids: a new class of biodegradable surfactants

Nassir N. Al-Mohammed, Rusnah Syahila Duali Hussien, Tammar Hussein Ali, Yatimah Alias and Zanariah Abdullah

$^1\text{H-NMR}$  (400 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  ppm: 9.01 (s, 4H, C-H<sub>Imidazole</sub>, minor), 8.99 (s, 4H, C-H<sub>Imidazole</sub>, minor), 8.98 (s, 4H, C-H<sub>Imidazole</sub>, major), 7.67 (bt~s, 8H, C-H<sub>Imidazole</sub>, minor), 7.64 (bt~s, 8H, C-H<sub>Imidazole</sub>, minor), 7.60 (bt~s, 8H, C-H<sub>Imidazole</sub>, major), 7.56 (bt~s, 8H, C-H<sub>Imidazole</sub>, minor), 7.45–7.29 (m, 20H, C-H<sub>Ar</sub>), 5.46 (s, 8H, Ar-CH<sub>2</sub>-, minor), 5.44 (s, 8H, Ar-CH<sub>2</sub>-, minor), 5.42 (s, 8H, Ar-CH<sub>2</sub>-, major), 5.22 (s, 8H, O-CH<sub>2</sub>, minor), 5.20 (s, 8H, O-CH<sub>2</sub>, major), 4.31 (s, 8H, N-CH<sub>2</sub>, major), 4.28 (s, 8H, N-CH<sub>2</sub>, minor), 4.25 (s, 8H, N-CH<sub>2</sub>, minor);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  ppm: 168.87 (C=O, minor), 167.64 (C=O, major), 138.81 (CH<sub>Imidazole</sub>, minor), 138.76 (CH<sub>Imidazole</sub>, major), 135.10 (-C<sub>Ar</sub>-CH<sub>2</sub>-, minor), 134.98 (-C<sub>Ar</sub>-CH<sub>2</sub>-, major), 130.66 (3 × CH<sub>A</sub>), 129.91 (2 × CH<sub>Ar</sub>), 126.10, 122.91, 119.72, 116.54 (q,  $J=320$  Hz, CF<sub>3</sub>), 125.63 (CH<sub>Imidazole</sub>), 123.72 (CH<sub>Imidazole</sub>), 123.71 (CH<sub>Imidazole</sub>, major), 64.48 (CH<sub>2</sub>-O, minor), 64.40 (CH<sub>2</sub>-O, minor), 64.32 (CH<sub>2</sub>-O, major), 54.51 (CH<sub>2</sub>-N), 50.98 (Ar-CH<sub>2</sub>-), 41.71 (-C-).  $^{19}\text{F}$  (336, MHz)  $\delta$  ppm: -80.23; HRMS:  $m/z$ ,  $[\text{M}^{+4}-3\text{H}]-4\text{NTF}_2^-$  calcd. for  $\text{C}_{53}\text{H}_{53}\text{N}_8\text{O}_8^{7+}$ : 929.3986, found: 929.4033;  $m/z$ ,  $[\text{NTF}_2]^-$  calcd. for  $\text{C}_2\text{F}_6\text{NO}_4\text{S}_2^-$ : 279.9173, found: 279.9158.

### Tetrakis-((*N*-hexyl-benzimidazoliumyl-acetayloxy)methyl)methane bis(trifluoromethylsulfonyl)amide (11c)

This compound was prepared analogously to **10a** using tetrakis-((*N*-hexyl-benzimidazoliumyl-acetayloxy)methyl)methane chloride **9c** (1.25 g, 1.0 mmole) and Lithium bis-(trifluoromethanesulphonyl)-imide LiNTf<sub>2</sub> (1.29 g, 4.5 mmol) to give a clear viscous hygroscopic liquid at room temperature in 98% yield (2.18 g). Molecular Formula:  $\text{C}_{73}\text{H}_{88}\text{F}_{24}\text{N}_{12}\text{O}_{24}\text{S}_8$ ; mol. wt.: 2230.03; FTIR ( $\text{cm}^{-1}$ ): 3130 (C-H)<sub>Ar</sub>, 2942, 2923, 2863 (C-H)<sub>Aliph</sub>, 1758 (C=O), 1622 (C=N), 1559, 1487 (C=C)<sub>Ar</sub>, 1355, 1223 (C-F), 1362, 1172 (O=S=O), 1202 (C-O);  $^1\text{H-NMR}$  (400 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  ppm: 9.79 (s, 4H, C-H<sub>BImidazole</sub>, minor), 9.76 (s, 4H, C-H<sub>BImidazole</sub>, minor), 9.71 (s, 4H, C-H<sub>BImidazole</sub>, major), 8.06–7.97 (m, 8H, C-H<sub>BImidazole</sub>), 7.78–7.61 (m, 8H, C-H<sub>Ar</sub>, major), 7.47–7.38 (m, 8H, C-H<sub>Ar</sub>, minor), 5.65 (s, 8H, O-CH<sub>2</sub>, major), 5.62 (s, 8H, O-CH<sub>2</sub>, minor), 4.54 (t,  $J=7.32$  Hz, 6H,  $\alpha$ -CH<sub>2</sub>, major), 4.41 (t,  $J=7.32$  Hz, 8H,  $\alpha$ -CH<sub>2</sub>, minor), 4.22 (s, 8H, N-CH<sub>2</sub>), 1.98–1.92 (m, 8H,  $\beta$ -CH<sub>2</sub>), 1.20 (bs, 24H, bulk-CH<sub>2</sub>), 0.90 (t,  $J=7.07$  Hz, 12H,  $\omega$ -CH<sub>3</sub>);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  ppm: 167.69 (C=O, major), 167.59 (C=O, minor), 144.07 (CH<sub>BImidazole</sub>), 133.33 (C<sub>Ar</sub>), 132.60 (C<sub>Ar</sub>), 128.80 (CH<sub>Ar</sub>), 128.63 (CH<sub>Ar</sub>), 126.20, 122.99, 119.78, 116.57 (q,  $J=319$  Hz, CF<sub>3</sub>), 114.81 (2 × CH<sub>Ar</sub>), 68.09 (CH<sub>2</sub>-O, minor), 67.87 (CH<sub>2</sub>-O, major), 46.72 (CH<sub>2</sub>-N), 41.73 ( $\alpha$ -CH<sub>2</sub>), 40.51 (-C-), 33.19 ( $\omega$ -2), 27.60 (bulk-CH<sub>2</sub>), 23.88 ( $\beta$ ), 20.10 ( $\omega$ -1), 14.60 ( $\omega$ ).  $^{19}\text{F}$  (336, MHz)  $\delta$  ppm: -79.40; HRMS:  $m/z$ ,  $[\text{M}^{+4}-3\text{H}]-4\text{NTF}_2^-$  calcd. for  $\text{C}_{65}\text{H}_{85}\text{N}_8\text{O}_8^{7+}$ : 1105.6490, found: 1105.6445;  $m/z$ ,  $[\text{NTF}_2]^-$  calcd. for  $\text{C}_2\text{F}_6\text{NO}_4\text{S}_2^-$ : 279.9173, found: 279.9162.

### Tetrakis-((*N*-octyl-benzimidazoliumyl-acetayloxy)methyl)methane bis(trifluoromethylsulfonyl)amide (11d)

This compound was prepared analogously to **10a** using tetrakis-((*N*-octyl-benzimidazoliumyl-acetayloxy)methyl)methane chloride **9d** (1.36 g, 1.0 mmole) and Lithium bis-(trifluoromethanesulphonyl)imide LiNTf<sub>2</sub> (1.29 g, 4.5 mmol) to give a clear viscous hygroscopic liquid at room temperature in 98% yield (2.29 g). Molecular Formula:  $\text{C}_{81}\text{H}_{104}\text{F}_{24}\text{N}_{12}\text{O}_{24}\text{S}_8$ ; mol. wt.: 2342.24; FTIR ( $\text{cm}^{-1}$ ): 3132 (C-H)<sub>Ar</sub>, 2932, 2920, 2856 (C-H)<sub>Aliph</sub>, 1748 (C=O), 1618 (C=N), 1563, 1487 1462 (C=C)<sub>Ar</sub>, 1362, 1225 (C-F), 1354, 1170

## Supplementary Information: Tetrakis-imidazolium and benzimidazolium ionic liquids: a new class of biodegradable surfactants

Nassir N. Al-Mohammed, Rusnah Syahila Duali Hussen, Tammar Hussein Ali, Yatimah Alias and Zanariah Abdullah

(O=S=O), 1197(C-O);  $^1\text{H-NMR}$  (400 MHz, DMSO- $d_6$ )  $\delta$  ppm: 10.01 (s, 4H, C-H<sub>BImidazole</sub>, minor), 9.96 (s, 4H, C-H<sub>BImidazole</sub>, major), 8.17-8.04 (m, 8H, CH<sub>Ar</sub>), 7.72-7.65 (m, 8H, CH<sub>Ar</sub>), 5.64 (s, 8H, O-CH<sub>2</sub>, minor), 5.53 (s, 8H, O-CH<sub>2</sub>, major), 4.57 (t,  $J=7.58$ , 8H,  $\alpha$ -CH<sub>2</sub>, major), 4.50 (t,  $J=7.58$ , 8H,  $\alpha$ -CH<sub>2</sub>, minor), 3.33 (s, 8H, N-CH<sub>2</sub>, minor), 3.26 (s, 8H, N-CH<sub>2</sub>, major), 1.93-1.86 (m, 8H,  $\beta$ -CH<sub>2</sub>), 1.22 (bs, 40H, bulk-CH<sub>2</sub>), 0.83 (t, 12H,  $J=6.60$ ,  $\omega$ -CH<sub>3</sub>);  $^{13}\text{C-NMR}$  (100 MHz, DMSO- $d_6$ )  $\delta$  ppm: 168.04 (C=O, major), 166.68 (C=O, minor), 143.32 (CH<sub>BImidazole</sub>), 131.71 (C<sub>Ar</sub>), 130.75 (C<sub>Ar</sub>), 126.98 (CH<sub>Ar</sub>), 126.71 (CH<sub>Ar</sub>), 124.40, 121.21, 118.01, 114.81 (q,  $J=322$ , CF<sub>3</sub>), 113.98 (CH<sub>Ar</sub>), 113.76 (CH<sub>Ar</sub>), 62.12 (CH<sub>2</sub>-O), 47.61 (CH<sub>2</sub>-N), 47.95 ( $\alpha$ -CH<sub>2</sub>), 40.71.43 (-C-), 31.21 ( $\omega$ -2), 28.55 (2), 28.44 (bulk-CH<sub>2</sub>), 25.74 ( $\beta$ ), 22.11 ( $\omega$ -1), 14.07 ( $\omega$ ), minor), 13.90 ( $\omega$ ), major).  $^{19}\text{F}$  (336, MHz)  $\delta$  ppm: -80.20; HRMS:  $m/z$ , [M<sup>+4</sup>-3H]-4NTF<sub>2</sub><sup>-</sup> calcd. for C<sub>73</sub>H<sub>101</sub>N<sub>8</sub>O<sub>8</sub><sup>7+</sup>: 1217.7742, found: 1217.7675;  $m/z$ , [NTF<sub>2</sub>]<sup>-</sup> calcd. for C<sub>2</sub>F<sub>6</sub>NO<sub>4</sub>S<sub>2</sub><sup>-</sup>: 279.9173, found: 279.9212.

### Tetrakis-((*N*-decyl-benzimidazoliumyl-acetayloxy)methyl)methane bis(trifluoromethylsulfonyl)amide (11e)

This compound was prepared analogously to **10a** using tetrakis-((*N*-decyl-benzimidazoliumyl-acetayloxy)methyl)methane chloride **9e** (1.48 g, 1.0 mmole) and Lithium bis-(trifluoromethanesulphonyl)-imide LiNTf<sub>2</sub> (1.29 g, 4.5 mmol) to give a clear viscous hygroscopic liquid at room temperature in 98% yield (2.41 g). Molecular Formula: C<sub>89</sub>H<sub>120</sub>F<sub>24</sub>N<sub>12</sub>O<sub>24</sub>S<sub>8</sub>; mol.wt.: 2454.45; FTIR (cm<sup>-1</sup>): 3130 (C-H)<sub>Ar</sub>, 2950, 2923, 2822 (C-H)<sub>Aliph</sub>, 1749 (C=O), 1625 (C=N), 1566 1485, 1463 (C=C)<sub>Ar</sub>, 1369, 1219 (C-F), 1358, 1165 (O=S=O), 1219,1199 (C-O);  $^1\text{H-NMR}$  (400 MHz, CD<sub>3</sub>OD)  $\delta$  ppm: 9.56 (s, 4H, C-H<sub>BImidazole</sub>, minor), 9.43 (s, 4H, C-H<sub>BImidazole</sub>, major), 9.39 (s, 4H, C-H<sub>BImidazole</sub>, minor), 8.04-7.80 (m, 8H, CH<sub>Ar</sub>), 7.75-7.48 (m, 8H, CH<sub>Ar</sub>), 5.51 (s, 8H, O-CH<sub>2</sub>, minor), 5.50 (s, 8H, O-CH<sub>2</sub>, minor), 5.49 (s, 8H, O-CH<sub>2</sub>, major), 4.58 (t,  $J=7.25$ , 8H,  $\alpha$ -CH<sub>2</sub>), 4.37 (s, 8H, N-CH<sub>2</sub>, minor), 4.32 (s, 8H, N-CH<sub>2</sub>, major), 2.07-1.94 (m, 8H,  $\beta$ -CH<sub>2</sub>), 1.29 (bs, 56H, bulk-CH<sub>2</sub>), 0.88 (t, 12H,  $J=6.80$ ,  $\omega$ -CH<sub>3</sub>);  $^{13}\text{C-NMR}$  (100 MHz, CD<sub>3</sub>OD)  $\delta$  ppm: 167.66 (C=O), 143.99 (CH<sub>BImidazole</sub>, major), 142.84 (CH<sub>BImidazole</sub>, minor), 133.22 (C<sub>Ar</sub>), 132.56 (C<sub>Ar</sub>), 128.59 (2  $\times$  CH<sub>Ar</sub>, major), 128.44 (2  $\times$  CH<sub>Ar</sub>, minor), 126.17, 122.94, 119.72, 116.49 (q,  $J=322$ , CF<sub>3</sub>), 114.78 (2  $\times$  CH<sub>Ar</sub>), 64.84 (CH<sub>2</sub>-O, major), 64.12 (CH<sub>2</sub>-O, minor), 50.93 (CH<sub>2</sub>-N), 45.95 ( $\alpha$ -CH<sub>2</sub>, major), 45.32 ( $\alpha$ -CH<sub>2</sub>, minor), 43.79 (-C-), 33.17 ( $\omega$ -2), 30.83, 30.72, 30.65, 30.53, 30.26 (bulk-CH<sub>2</sub>), 27.58 ( $\beta$ -CH<sub>2</sub>), 24.36 ( $\omega$ -1), minor), 23.85 ( $\omega$ -1), major), 14.57 ( $\omega$ ).  $^{19}\text{F}$  (336, MHz)  $\delta$  ppm: -80.03.