

Supporting Information

Glycine-betaine-derived ionic liquids: synthesis, characterization and ecotoxicological evaluation

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Section S1: Elemental analysis

Tri(n-butyl)(2-ethoxy-2-oxoethyl)ammonium saccharinate ([Bu₃NC₂][Sac], 0.7 water). Colorless viscous oil. Yield 11.5 g, 24.6 mmol, 82%). Elemental analysis: Found: C, 59.28; H, 8.09; N, 6.35; S, 6.62%. Calculated for C₂₃H₃₈N₂O₅S·0.5 H₂O (M = 467.23): C, 59.13; H, 8.50; N, 6.00; S, 6.86%. ¹H NMR δ/ppm (250 MHz, CDCl₃): 0.91 (9H, t, H_a); 1.25 (3H, t, H_f); 1.34 (6H, m, H_b); 1.70 (6H, m, H_c); 3.53 (6H, m, H_d); 4.24 (2H, q, H_e); 4.50 (2H, s, H₂); 7.50 (2H, m, H_{Ph}); 7.71 (1H, m, H_{Ph}); 7.75 ppm (1H, m, H_{Ph}). ¹³C NMR δ/ppm (62.5 MHz, CDCl₃): 13.5 (C_a); 13.9 (C_g); 19.6 (C_b); 24.3 (C_c); 57.1 (C_d); 60.2 (C₂); 62.8 (C_e); 119.5, 123.1, 131.0, 131.6, 135.1, 145.0 (C_{Ph}), 164.8 (C₁), 169.8 (C=O). IR (ν/cm⁻¹): 34650 (OH); 2962, 2923, 2875 (CH); 1741, 1633 (C=O); 1246 (C-N), 1580, 1455, 756 (C=C).

Tri(n-butyl)(4-ethoxy-4-oxobutyl)ammonium saccharinate ([Bu₃NC₄][Sac]). White powder, melting point, 95 °C. Yield (11.7 g, 24.3 mmol, 81%). Elemental analysis: Found: C, 62.23; H, 9.05; N, 6.06; S, 6.57%. Calculated for C₂₅H₄₂N₂O₅S (M = 482.68): C, 62.21; H, 8.77; N, 5.80; S, 6.64%. ¹H NMR δ/ppm (250 MHz, CDCl₃): 0.99 (9H, t, H_a); 1.27 (3H, t, H_f); 1.43 (6H, m, H_b); 1.73 (6H, m, H_c); 2.05 (2H, m, H₃); 2.62 (2H, m, H₂); 3.33 (6H, m, H_d); 3.60 (2H, m, H₄); 4.14 (2H, t, H_e); 7.54 (2H, m, H_{Ph}); 7.79 (2H, m, H_{Ph}). ¹³C NMR δ/ppm (62.5 MHz, CDCl₃): 13.4 (C_a); 14.5 (C_f); 16.7 (C₃); 19.1 (C_b); 22.9 (C_c); 29.8 (C₂); 56.6, 57.5, 60.2 (C_e); 119.0, 122.4, 130.9, 131.4, 135.6, 145.1 (C_{Ph}), 169.4 (C₁); 171.9 (C=O). IR (ν/cm⁻¹): 3000, 2940 (CH); 1682, 1664 (C=O); 1255 (C-N), 1594, 1455, 752 (C=C).

Tri(n-butyl)(2-ethoxy-2-oxoethyl)phosphonium saccharinate ([Bu₃PC₂][Sac], 0.9 water). Colorless viscous oil. Yield (12.9 g, 26.2 mmol, 87%). Elemental analysis: Found: C, 56.37; H, 7.92; N, 3.19; S, 6.77%. Calculated for C₂₃H₃₈NO₅PS (M = 487.80): C, 56.63; H, 8.22; N, 2.87; S, 6.57%. ¹H NMR

δ /ppm (250 MHz, CDCl₃): 0.91 (9H, t, H_a, J = 7.5 Hz); 1.25 (3H, t, H_f); 1.34 (6H, m, H_b); 1.70 (6H, m, H_c); 3.53 (6H, m, H_d); 4.24 (2H, q, H_e); 4.50 (2H, s, H₂); 7.50 (2H, m, H_{Ph}); 7.71 (1H, m, H_{Ph}); 7.75 (1H, m, H_{Ph}). ¹³C NMR δ /ppm (62.5 MHz, CDCl₃): 13.4 (C_a); 13.9 (C_f); 19.3 (C_d); 23.6 (C_b); 23.8 (C_c); 26.7 (C₂), 62.9 (C_e); 119.7, 123.2, 131.2, 131.8, 134.6, 144.5 (C_{Ph}); 165.7 (C₁); 169.6 (C=O). IR (ν /cm⁻¹): 3465 (OH); 2959, 2933, 2872 (CH); 1726, 1632 (C=O); 1246 (C-N), 1582, 1455, 753 (C=C).

Tri(*n*-butyl)(4-ethoxy-4-oxobutyl)phosphonium saccharinate ([Bu₃PC₄][Sac], 0.8 water). White powder, melting point, 58 °C. Yield (12.3g, 24 mmol, 82%). Elemental analysis: Found: C, 58.46; H, 8.25; N, 3.01; S, 6.41%. Calculated for C₂₅H₄₂NO₅PS·0.8 H₂O (M = 514.05): C, 58.41; H, 8.55; N, 2.72; S, 6.24%. Melting point, 58 °C. ¹H NMR δ /ppm (250 MHz, CDCl₃): 0.77 (9H, t, H_a); 1.13 (3H, t, H_f); 1.42 (12H, m, H_b + H_c); 1.76 (2H, m, H₃); 2.13 (6H, m, H_d); 2.33 (2H, m, H₄); 2.44 (2H, m, H₂); 4.02 (2H, t, H_e); 7.45 (2H, m, H_{Ph}); 7.61 (1H, m, H_{Ph}); 7.69 (1H, m, H_{Ph}). ¹³C NMR δ /ppm (62.5 MHz, CDCl₃): 13.3 (C_a); 14.1 (C_f); 16.9 (C₃); 18.0 (C_d); 18.4 (C_e); 23.4, 23.7, 33.6, 60.6 (C_h); 119.5, 123.2, 131.2, 131.7, 134.5, 144.6 (C_{Ph}); 169.1 (C₁); 172.4 (C=O). IR (ν /cm⁻¹): 3460 (OH); 2956, 2931, 2871 (CH); 1721, 1650 (C=O); 1243 (C-N), 1584, 1467, 753 (C=C).

Dodecylbetainium docusate [Me₃NC₂OC₁₂][Doc], 1.5 water. Yield (20.3 g, 27.6 mmol, 92%). Elemental analysis: Found: C, 60.64; H, 10.42; N, 2.02; S, 4.458%. Calculated for C₃₇H₇₃NO₉S·1.5 H₂O (M = 735.06): C, 60.46; H, 10.42; N, 1.91; S, 4.36%. ¹H NMR δ /ppm (250 MHz, DMSO-*d*₆): 0.85 (15H, m, CH₃); 1.25 (38H, m, CH₂); 1.50 (1H, m, CH₂CH₂O); 1.65 (2H, m, CH₂C=O_{Doc}); 2.85 (2H, m, CHCH₂O); 3.25 (9H, s, (CH₃)₃N); 3.65 (1H, dd, CHSO₃⁻); 3.90 (4H, t, CH₂CHCH₂); 4.20 (t, 2H, CH₂OC=O); 4.40 (s, 2H, CH₂COO). ¹³C NMR δ /ppm (62.5 MHz; DMSO-*d*₆): 10.69, 13.62 (CH₃); 22.06, 22.36, 22.39, 25.19, 27.79, 28.32, 28.60, 28.70, 28.69, 29.02, 31.28, 34.05 (CH₂); 38.13 (CH₂Et); 53.13 ((CH₃)₃N); 61.42 (CHSO₃⁻); 62.43 (OCH₂), 65.64, 66.02 (CH₂CO); 164.88, 168.29, 170.96 (C=O). IR: (ν /cm⁻¹): 3420 (OH); 2957, 2924, 2855 (CH); 1734 (C=O); 1036 (SO₃⁻).

Tetradecylbetainium docusate [Me₃NC₂OC₁₄][Doc], water. Yield (21.1 g, 28 mmol, 94%). Elemental analysis: Found: C, 62.06; H, 10.70; N, 1.84; S, 4.23%. Calculated for C₃₉H₇₇NO₉S·H₂O (M = 754.11): C, 62.12; H, 10.56; N, 1.86; S, 4.25%. ¹H NMR δ /ppm (250 MHz, DMSO-*d*₆): 0.85 (15H, m, CH₃); 1.25 (38H, m, CH₂); 1.50 (1H, m, CH₂CH₂O); 1.62 (2H, m, CH₂C=O_{Doc}); 2.90 (2H, m, CHCH₂O); 3.22 (9H, s, (CH₃)₃N); 3.64 (1H, dd, CHSO₃⁻); 3.90 (4H, t, CH₂CHCH₂); 4.18 (t, 2H, CH₂OC=O); 4.45 (s, 2H, CH₂COO). ¹³C NMR δ /ppm (62.5 MHz; DMSO-*d*₆): 10.69, 13.67 (CH₃); 22.06, 22.36, 22.39, 25.19, 27.80, 28.33, 28.60, 28.70, 28.93, 29.02, 29.73, 31.28, 34.05 (CH₂); 38.20 (CH₂Et); 53.13 ((CH₃)₃N); 61.42 (CHSO₃⁻);

62.43 (OCH₂), 65.64, 66.02 (CH₂CO); 164.88, 168.29, 170.96 (C=O). IR (ν/cm⁻¹): 3420 (OH); 2956, 2923, 2854 (CH); 1735 C=O; 1036 (SO₃⁻).

Dodecylbetainium thiocyanate ([Me₃NC₂OC₁₂][SCN]). (Yield (8.8 g, 25.5 mmol, 85%). Melting point, 96 °C. Elemental analysis: Found: C, 63.10; H, 10.87; N, 8.30; S, 8.90%. Calculated for C₁₈H₃₆N₂O₂S (M = 344.25): C, 62.75; H, 10.53; N, 8.13; S, 9.30%. ¹H NMR δ/ppm (250 MHz; DMSO-d₆): 0.87 (3H, t, CH₃); 1.27 (18H, m, CH₂); 1.61 (2H, m, CH₂CH₂O); 3.22 (9H, s, (CH₃)₃N); 4.19 (2H, t, CH₂O); 4.44 (2H, s, CH₂COO). ¹³C NMR δ/ppm (62.5 MHz; DMSO-d₆): 14.94 (CH₃); 23.10, 26.22, 28.81, 29.60, 29.71, 29.94, 29.97, 30.01, 30.05, 32.30 (CH₂); 54.18 ((CH₃)₃); 63.55 (CH₂O); 66.77 (CH₂CO); 165.85 (C=O). IR (ν/cm⁻¹): 2918, 2849 (CH); 2050 (SCN); 1744 C=O).

Tetradecylbetainium thiocyanate ([Me₃NC₂OC₁₄][SCN], 0.2 water). (Yield (9.8 g, 26.1 mmol, 87%). Melting point, 98 °C. Elemental analysis: Found: C, 63.86; H, 10.81; N, 7.65; S, 8.80%. Calculated for C₂₀H₄₀N₂O₂S · 0.2 H₂O (M = 376.21): C, 63.85; H, 10.82; N, 7.45; S, 8.52%. ¹H NMR δ/ppm (250 MHz; DMSO-d₆): 0.90 (3H, t, CH₃); 1.30 (22H, m, CH₂); 1.60 (2H, q, CH₂CH₂O); 3.25 (9H, s, (CH₃)₃N); 4.20 (2H, t, CH₂O); 4.45 (2H, s, CH₂COO). ¹³C NMR δ/ppm (62.5 MHz; DMSO-d₆): 14.38 (CH₃), 22.53, 25.66, 28.25, 29.04, 29.15, 29.40, 29.48, 31.73, (CH₂); 53.60 ((CH₃)₃); 62.97 (CH₂O); 66.19 (CH₂CO); 165.30 (C=O). IR (ν/cm⁻¹): 3460 (OH); 2918, 2849(CH); 2050 (SCN); 1744 C=O).