SUPPLEMENTARY INFORMATION
Toxicity of Ionic Liquids towards *Escherichia coli*

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Materials

$[C_{3O1}mpip][NTf_2]$ and $[C_2mim][C_1(OC_2)_3OSO_3]$ were gifts from Merck. The phosphonium halides were a gift from CYTEC. $[N_{1\,8\,8\,8}]Cl$ and $[N_{1\,8\,8\,8}]Br$ were purchased from Aldrich. All trialkylamines, dimethyl and diethyl sulfates, and haloalkanes were purchased from Aldrich.

Preparation of Ionic Liquids

The following salts were known and they were synthesised using known procedures:[1-13] $[C_2mim]Cl$, $[C_2mim][lactate]$, $[C_2mim]Br$, $[C_2mim][C_1OSO_3]$, $[C_2mim][C_8OSO_3]$, $[C_2mim][C_2OSO_3]$, $[C_4mim][C_1OSO_3]$, $[C_4mim][lactate]$, $[C_4mim]I$, $[C_8mim]I$, $[C_4mim]Br$, $[C_8mim]Br$, $[C_4mim][C_1COO]$, $[C_4mim]Cl$, $[C_6mim]Cl$, $[C_8mim]Cl$, $[C_{10}mim]Cl$, $[C_4mim][C_2OSO_3]$, $[C_4mim][^1C_3OSO_3]$, $[C_4mim][C_3OSO_3]$, $[C_4mim][C_2OC_2OSO_3]$, $[C_4mim][^1C_4OSO_3]$, $[C_4mim][C_1OC_2OSO_3]$, $[C_6mim]Br$, $[C_6mim]I$, $[C_6mim][sacch]$, $[C_8mim][sacch]$, $[C_4eim][C_2OSO_3]$, $[C_4mpyrr][lactate]$, $[C_4mpyrr][C_1OSO_3]$, $[C_4mpyrr]Cl$, $[N_{1\,1\,2\,4}]Br$, $[N_{1\,1\,2\,4}][C_1OSO_3]$, $[N_{2\,4\,(2OH)2}]Br$, $[N_{1\,1\,2\,3OH}]Br$, and $[N_{1\,1\,4\,3OH}]Cl$.

The silver-free synthesis of $[C_4mim][lactate]$ will be published elsewhere.

General preparation for 1-alkyl-3-methylimidazolium halides

All 1-alkyl-3-methylimidazolium halides were synthesised by treating 1-methylimidazole with the appropriate haloalkane using known methodology.[2, 4]

Saccharin-based salts

Saccharin based ionic liquids were synthesised according to a procedure developed by Davis *et al.*[8]

$[N_{1\,8\,8\,8}][sacch]$: ^{1}**H δ** ($CDCl_3$) / p.p.m.: 7.82-7.55 (4H, m, ArH), 3.33-3.30 (4H, m, $2xNCH_2$), 3.24 (3H, s, NCH_3), 1.65 (4H, m, $2xNCH_2\mathbf{CH_2}$), 1.28-1.21 (30H, m, $15xCH_2$), 0.83 (9H, t, $3xCH_3$)
ESIMS: M^+(cation; calc. 368.4256, obs. 368.4163,); M^-(anion; calc 181.9912, obs. 181.9809)

$[N_{1\,1\,4\,8}][sacch]$: ^{1}**H δ** ($CDCl_3$) / p.p.m.: 7.77-7.50 (4H, m, ArH), 3.35-3.30 (4H, m, $2xNCH_2$), 3.24 (6H, s, $2xNCH_3$), 1.63 (4H, m, $2xNCH_2\mathbf{CH_2}$), 1.32-1.17 (12H, m, $6xCH_2$), 0.88 (3H, t, CH_3), 0.83 (3H, t, CH_3)
ESIMS: M^+(cation; calc 214.2535, obs. 214.2541); M^-(anion; calc 181.9912, obs. 181.9829)

$[C_4m_\beta py][sacch]$: ^{1}**H δ** ($CDCl_3$) / p.p.m.: 8.26-7.57 (8H, m, ArH), 4.84 (2H, t, Py^+CH_2), 2.59 (3H, s, CH_3), 1.97 (2H, m, CH_2), 1.35 (2H, m, CH_2), 0.89 (3H, m, CH_3)
ESIMS: M^+(cation; calc 150.1283, obs. 150.1293); M^-(anion; calc 181.9912, obs. 181.9889)

General preparation of alkylsulfate salts

Dialkyl sulfate (0.2 mol) was added dropwise to the appropriate trialkylamine (0.2 mol) and stirred at room temperature overnight. No solvent was used in this reaction. The resulting viscous ionic liquid was shown to have undergone a complete and clean reaction by ^{1}H NMR spectroscopy.

Alkyl substitution at the methyl or ethyl sulfate anion was carried out by a transesterification procedure, with the appropriate alcohol, developed by Wasserscheid.[5, 14, 15]

Analytical data for alkylsulfate ionic liquids are given below:

$[N_{2\,4\,(2OH)2}][C_2OSO_3]$: ^{1}**H δ** ($D_2O$) / p.p.m.: 4.07 (6H, m, $2xCH_2OH\&OCH_2$), 3.59 (6H, m, $3xCH_2N^+$), 3.44 (2H, m, CH_2), 1.77 (2H, m, CH_2), 1.45 (2H, m, CH_2), 1.38 (2H, m, CH_2), 1.28 (3H, s, $OCH_2\mathbf{CH_3}$), 1.02 (3H, s, CH_3)
ESIMS: M^+(cation; calc. 190.1807, obs. 190.1789); M^-(anion; calc 124.9909, obs. 124.9901)

$[N_{1\,1\,2\,8}][C_2OSO_3]$: ^{1}**H δ** ($D_2O$) / p.p.m.: 4.08 (2H, q, CH_2-O), 2.33 (2H, q, CH_2N^+), 2.23 (2H, m, CH_2N^+), 2.99 (6H, s, N^+Me_2), 1.70 (2H, m, CH_2), 1.4-1.25 (10H, m, $5xCH_2$), 1.28 (3H, s, $OCH_2\mathbf{CH_3}$), 0.92 (3H, t, CH_3)
ESIMS: M^+(cation; calc. 186.2222, obs. 186.2212); M^-(anion; calc 124.9909, obs. 124.9896)

$[N_{1\,1\,2\,4}][C_2OSO_3]$: ^{1}**H δ** ($D_2O$) / p.p.m.: 4.07 (2H, q, CH_2-OS), 2.32 (2H, q, CH_2N^+), 2.22 (2H, m, CH_2N^+), 3.00 (6H, s, N^+Me_2), 1.70 (2DiH, m, CH_2), 1.28 (3H, s, $OCH_2\mathbf{CH_3}$), 1.23 (2H, m, CH_2), 0.92 (3H, t, CH_3)
ESIMS: M^+(cation; calc. 130.1596, obs. 130.1568); M^-(anion; calc 124.9909, obs. 124.9896)

$[N_{1\,1\,2\,2OH}][C_2OSO_3]$: ^{1}**H δ** ($D_2O$) / p.p.m.: 4.02 (2H, q, CH_2-OS), 3.71 (2H, t, CH_2OH), 3.36 (4H, m, $2xCH_2$), 3.03 (6H, s, Me_2N^+), 1.35 (3H, t, CH_3), 1.26 (3H, t, $OCH_2\mathbf{CH_3}$)
ESIMS: M^+(cation; calc. 118.1232, obs. 118.1204); M^-(anion; calc 124.9909, obs. 124.9891)

$[N_{1\,1\,2\,3OH}][C_2OSO_3]$: ^{1}**H δ** ($D_2O$) / p.p.m.: 4.03 (2H, q, CH_2-OS), 3.70 (2H, t, CH_2OH), 3.39 (4H, m, $2xCH_2$), 3.06 (6H, s, Me_2N^+), 1.99 (2H, m, CH_2), 1.35 (3H, t, CH_3), 1.26 (3H, t, $OCH_2\mathbf{CH_3}$)
ESIMS: M^+(cation; calc. 132.1388, obs. 132.1336); M^-(anion; calc 124.9909, obs. 124.9886)

$[N_{1\,2\,8\,8}][C_2OSO_3]$: ^{1}**H δ** ($CDCl_3$) / p.p.m.: 4.03 (2H, q, CH_2O), 3.46 (2H, q, CH_2N^+), 3.27 (4H, m, $2xCH_2N^+$), 3.10 (3H, s, CH_3N^+), 1.66 (4H, brm, $2xCH_2$), 1.34-1.24 (23H, brm, $10xCH_2$ & CH_3), 0.86 (6H, t, $2xCH_3$)
ESIMS: M^+(cation; calc. 284.3317, obs. 284.3328); M^-(anion; calc 124.9909, obs. 124. 9898)

$[N_{1\,1\,2\,8}][C_2OSO_3]$: ^{1}**H δ** ($CDCl_3$) / p.p.m.: 4.04 (2H, q, CH_2O), 3.52 (2H, q, CH_2N^+), 3.35 (2H, m, CH_2N^+), 3.18 (6H, s, Me_2N^+), 1.70 (2H, brm, CH_2), 1.39-1.24 (13H, brm, $5xCH_2$ & CH_3), 0.87 (3H, t, CH_3)
ESIMS: M^+(cation; calc. 186.2222, obs. 186.2213); M^-(anion; calc 124.9909, obs. 124.9888)

$[N_{1\,2\,8\,8}][C_6OSO_3]$: ^{1}**H δ** ($CDCl_3$) / p.p.m.: 4.01 (2H, q, CH_2O), 3.46 (2H, q, CH_2N^+), 3.25 (4H, m, $2xCH_2N^+$), 3.12 (3H, s, CH_3N^+), 1.65 (6H, brm, $3xCH_2$), 1.40-1.20 (29H, brm, $13xCH_2\&CH_3$), 0.87 (9H, t, $3xCH_3$)
ESIMS: M^+(cation; calc. 284.3317, obs. 284.3332); M^-(anion; calc 181.0535, obs. 181.0526)

$[N_{2\,(2O2O1)3}][C_2OSO_3]$: ^{1}**H δ** ($CDCl_3$) / p.p.m.: 4.07 (2H, q, CH_2-OS), 3.92 (6H, brm, $6xOCH_2$), 3.77 (6H, brm, $6xOCH_2$), 3.5 (8H, m, $6xOCH_2\&CH_2N^+$), 3.34 (9H, s, $3xOCH_3$), 1.83 (3H, t, CH_3), 1.27 (3H, t, CH_3)
ESIMS: M^+(cation; calc. 352.2691, obs. 352.2699); M^-(anion, calc. 124.9909, obs.125.1101)

$[N_{1\,(2OH)3}][C_1OSO_3]$: ^{1}**H δ** ($D_2O$, 300 MHz) / p.p.m.: 4.05 (6H, m, O-CH_2), 3.73 (3H, s, OCH_3), 3.66 (6H, t, N-CH_2), 3.24 (3H, s, N-CH_3)
ESIMS: M^+(cation; calc. 164.1287, obs 164.1239); M^-(anion, calc. 110.9752 obs 111.0111)

$[N_{1\,1\,2\,4}][C_4OSO_3]$: ^{1}**H δ** ($D_2O$, 300 MHz) / p.p.m.: 4.05 (2H, t, O-CH_2), 3.34 (2H, q, N^+CH_2), 3.26 (2H, m, N^+CH_2), 3.01 (6H, s, N^+CH_3), 1.67 (4H, m, 2xCH_2), 1.36 (7H, m, 2xCH_2&CH_3), 0.93 (6H, m, 2x-CH_3)
ESIMS: M^+(cation; calc. 130.1596, obs. 164.1576); M^-(anion, calc. 153.0222, obs 153.0191)

$[N_{1\,1\,8\,8}][C_1OSO_3]$: ^{1}**H δ** ($CDCl_3$) / p.p.m.: 3.67 (3H, s, CH_3O), 3.32 (4H, m, 2xCH_2N^+), 3.18 (3H, s, N^+CH_3), 1.65 (4H, brm, 2xCH2), 1.3-1.2 (20H, m, 10xCH_2), 0.85 (6H, t, 2xCH_3)
ESIMS: M^+(cation; calc. 270.3161, obs. 270.3141,); M^-(anion, calc. 110.9752, obs 111.0011)

$[C_4mpyrr][C_1OSO_3]$: ^{1}**H δ** (D_2O) / p.p.m.: 3.72 (3H, s, MeN), 3.31-3.26 (6H, m, 3xCH_2N^+), 2.99 (3H, s, CH_3O), 1.83 (4H, m, 2xCH_2), 1.70 (2H, m, CH_2), 1.63 (2H, m, CH_2), 1.36 (2H, m, CH_2), 0.93 (3H, t, CH_3)
ESIMS: M^+(cation; calc. 142.1596, obs. 142.1558); M^-(anion, calc. 110.9752, obs. 110.9735)

$[C_6mpip][C_1OSO_3]$: ^{1}**H δ** ($CDCl_3$) / p.p.m.: 3.69 (3H, s, OCH_3), 3.62-3.43 (6H, m, 3xCH_2-pip & C_6 chain), 3.18 (3H, CH_3N^+), 1.90-173 (8H, brm, 4xCH_2-pip & C_6-chain), 1.35 (4H, brm, 2xCH_2), 0.89 (3H, t, CH_3)
ESIMS: M^+(cation; calc. 184.2065, obs. 184.2045); M^-(anion, calc. 110.9752, obs. 110.9705)

$[P_{1\,8\,8\,8}][C_1OSO_3]$: ^{1}**H δ** ($CDCl_3$) / p.p.m.: 3.71 (3H, s,$OCH_3$), 2.26 (6H, brm, 3x$CH_2P^+$), 1.93 (3H, d, CH_3P^+), 1.48 (6H, brm, 3xCH_2), 1.27 (30H, brm, 15xCH_2), 0.88 (9H, brt, 3xCH_3)
ESIMS: M^+(cation; calc. 385.3963, obs. 385.3931); M^-(anion, calc. 110.9752, obs. 110.9705,)

General preparation for 4-toluenesulfonate (tosylate) salts:
Trialkylamine or 1-alkylimidazole (0.2 mol) were heated with ethyl-4-toluenesulfonate ester (0.2 mol) at 70-80 ºC overnight. No solvent was used in this reaction. The resulting viscous ionic liquid was kept under high vacuum (~0.1-0.5 bar) at 80 ºC overnight to remove any volatile compounds.

$[C_2mim][tosylate]$: ^{1}**H δ** ($CDCl_3$) / p.p.m.: 9.5 (1H, s,Im-H), 7.71 (2H, d, ArH), 7.41 (1H, s, im-H), 7.42 (1H, s, im-H), 7.1 (2H, d, ArH), 4.14 (2H, q, CH_2Im^+), 3.84 (3H, s, CH_3im^+), 2.29 (3H, s, $ArCH_3$)
ESIMS: M^+(cation; calc. 111.0922, obs. 111.0913); M^-(anion, calc. 171.0116, obs. 171.0075)

$[N_{1\,2\,8\,8}][Tosylate]$: ^{1}**H δ** ($CDCl_3$) / p.p.m.: 7.76 (2H, d, ArH), 7.12 (2H, d, ArH), 3.49 (2H, q, CH_2N^+), 3.25 (4H, m, 2xCH_2N^+), 3.16 (3H, s, CH_3N^+), 2.33 (3H, s,$ArCH_3$), 1.60 (4H, brm, 2xCH_2), 1.25 (23H, brm, 10xCH_2 & CH_3), 0.88 (6H, t, 2xCH_3)
ESIMS: M^+(cation; calc. 284.3317, obs. 284.3319); M^-(anion, calc. 171.0116, obs. 171.0106)

Dimethyl phosphate ionic liquids
Dimethylphosphate salts were synthesised by reacting equimolar quantities of the appropriate amine and trimethylphosphate at 60-70 ºC, according to a known procedure.[18]

$[N_{1\,1\,1\,4}][(C_1O)_2PO_2]$: ^{1}**H δ** ($CDCl_3$) / p.p.m.: 3.54 (6H, 2xs, OCH_3), 3.48 (2H, m, CH_2N^+), 3.34 (9H, s, 3xCH_3), 1.73 (2H, m, CH_2), 1.42 (2H, m, CH_2), 0.99 (3H, s, CH_3)
ESIMS: M^+(cation; calc 116.1439, obs. 116.1387); M^-(anion; calc. 125.0004, obs. 124.9988)

$[C_4mpyrr][(C_1O)_2PO_2]$: ^{1}**H δ** ($CDCl_3$) / p.p.m.: 3.78 (4H, m, 2xCH_2), 3.56-3.53 (8H, 2xs & m, CH_2 & 2xCH_3), 2.27 (4H, m, 2xCH_2), 1.75 (2H, m, CH_2), 1.44 (2H, m, CH_2), 0.99 (3H, t, CH_3)
ESIMS: M^+(cation; calc. 142.1596, obs. 142.1516); M^-(anion; calc. 125.0004, obs. 124.9993)

Preparation of $[N_{1\,1\,4\,8}]$Br and $[N_{1\,1\,4\,8}]$I
Both compounds were prepared by heating N,N-dimethyl octylamine (50 mM) with either 1-bromobutane (50 mM) or 1-iodobutane (50 mM) in ethanenitrile (20 cm^3), in a sealed tube, at 80 ºC for 18 h. After removing the solvent, the residues were treated with diethyl ether (50 cm^3), resulting solids were filtered and dried.

$[N_{1\,1\,4\,8}]$Br: ^{1}**H δ** ($CDCl_3$) / p.p.m.: 3.57 (4H, m, 2xCH_2N^+), 3.41 (6H, s, 2xCH_3N^+), 1.71 (4H, 2xCH_2), 1.49-1.46 (12H, brm, 6xCH_2), 1.00 (3H, t, CH_3), 0.88 (3H, t, CH_3)
ESIMS: M^+(cation; calc 214.2535, obs. 214.2521); M^+(anion; calc 78.9138, obs. 78.9200)

$[N_{1\,1\,4\,8}]$I: ^{1}**H δ** ($CDCl_3$) / p.p.m.: 3.56 (4H, m, 2xCH_2N^+), 3.38 (6H, s, 2xCH_3N^+), 1.73 (4H, 2xCH_2), 1.50-1.40 (12H, brm, 6xCH_2), 1.01 (3H, t, CH_3), 0.88 (3H, t, CH_3)
ESIMS: M^+(cation; calc. 214.2535, obs. 214.2522); M^-(anion; calc. 126.9045, obs. 126.9067)

Synthesis of 1-alkyl-1-methylpyrrolidinium and 1-alkyl-1-methylpiperidinium salts

$[C_6mpyrr]$Br
1-Bromohexane (0.250 mol) was added to 1-methylpyrrolidine (0.225 mol) in ethanenitrile and stirred vigorously at ambient conditions (4 d). Solvent was removed *in vacuo* (rotary evaporator), and the residue was dried under high vacuum (~0.1-0.5 bar, 80 °C, 3 d), leaving a brown crystalline solid (35.64 g, 63 % yield). Elemental analysis % calc. (% found): C 52.80 (51.07), H 9.67 (9.45), N 5.60 (4.94), Br 31.93 (32.06); 0.18 wt.% H_2O.
^{1}**H δ** (D_2O, 300 MHz) / p.p.m.: 3.46 (m, 4H, $H_2^{2,5}$), 3.30 (m, 2H, $H_2^{3,4}$), 3.00 (s, 3H, NCH_3), 2.17 (m, 4H, NCH_2), 1.77 (m, 2H, NCH_2CH_2), 1.2-1.4 (m, 6H, $N(CH_2)_2(CH_2)_3CH_3$), 0.85 (m, 3H, $N(CH_2)_5CH_3$)
ESIMS: M^+(cation; calc. 170.1909, obs. 170.1911); M^-(anion; calc. 78.9183, 80.9163, obs. 78.9187, 80.9166)

$[C_4mpip]$Br
1-Methylpiperidine (0.425 mol) and 1-bromobutane (0.445 mol) were combined and stirred under dry reflux (19 h). The reaction mixture was dissolved in hot propan-2-ol, allowed to cool to room temperature, and the product was precipitated by dropwise addition of dry diethyl ether and allowing the mixture to settle (room temperature, 3 d; 4 °C, 5 h). The cream-coloured precipitate was isolated *via* vacuum filtration under flowing dry dinitrogen, washed with dry diethyl ether, and dried under high vacuum (~0.1-0.5 bar, 80 °C, 15 h), giving a yield of 88.06 g (88 %). Elemental analysis % calc. (% found): C 50.85 (50.91), H 9.39 (9.59), N 5.93 (5.63), Br 33.83 (33.46); 0.31 wt.% H_2O.
^{1}**H δ** (D_2O, 300 MHz) / p.p.m.: 3.60-3.90 (m, 6H, $H_2^{2,6}$, NCH_2), 3.34 (s, 3H, NCH_3), 1.62-2.05 (m, 8H, $H_2^{3,4,5}$, NCH_2CH_2), 1.46 (m, 2H, $N(CH_2)_2CH_2CH_3$), 0.88-1.14 (m, 3H, $N(CH_2)_3CH_3$)
ESIMS: M^+(cation; calc. 156.1742, obs. 156.1743); M^-(anion; calc. 78.9167, 80.9163, obs. 78.9188, 80.9166)

$[C_6mpip]$Br
1-Bromohexane (0.228 mol) and 1-methylpiperidine (0.189 mol) were stir-heated in ethanenitrile (68 ºC, 5 d). Solvent was removed *in vacuo*, and a white solid was recrystallised from propan-2-ol / ethyl ethanoate. The precipitate was isolated *via* vacuum filtration under flowing dry dinitrogen atmosphere, washed with ethyl ethanoate and dried under high vacuum (~0.1-0.5 bar, 80 ºC, 15 h), yielding a powdery white solid product (21.98 g, 44 % yield). M.p. 193-200 ºC.

^{1}**H δ** (D_2O, 300 MHz) / p.p.m.: 3.30 (m, 6H, $H_2^{2,6}$, NCH_2), 2.98 (s, 3H, NCH_3), 1.5-1.9 (m, 8H, $H_2^{3,4,5}$, NCH_2CH_2), 1.31 (m, 6H, $N(CH_2)_2(CH_2)_3CH_3$), 0.84 (t, 3H, $N(CH_2)_5CH_3$)
LSIMS: $M^+([C_1C_6pip]^+$ calc. 184, obs. 184); $M^-(\{(C_1C_6pip)_2Br\}^+$ calc. 447, obs. 447)

[C_8mpip]Br
1-Bromooctane (0.206 mol) and 1-methylpiperidine (0.171 mol) were combined in ethanenitrile and stirred vigorously at ambient conditions (24 h), then stir-heated under a condenser and drying tube (60 ºC, 5 d). Dry diethyl ether was added to the mixture and stirred vigorously at room temperature (3 h), then decanted, leaving behind a beige solid. The solid was recrystallised from dichloromethane / ethyl ethanoate, and the precipitate was isolated *via* vacuum filtration under flowing dry dinitrogen, then dried under high vacuum (~0.1-0.5 bar, 90 ºC, 24 h), to yield white crystals (18.34 g, 37 % yield).
^{1}**H δ** (D_2O, 300 MHz) / p.p.m.: 3.10-3.46 (m, 6H, $H_2^{2,6}$, NCH_2), 2.98 (s, 3H, NCH_3), 1.84 (m, 4H, $H_2^{3,5}$), 1.52-1.77 (m, 4H, H_2^4, NCH_2CH_2), 1.00-1.45 (m, 10H, $N(CH_2)_2(CH_2)_5CH_3$), 0.84 (t, 3H, $N(CH_2)_7CH_3$)

[C_4mpip][C_1COO]
Freshly prepared silver(I) ethanoate (0.0578 mol) was added to aqueous $[C_1C_8pip]Br$ (0.05755 mol in 110 cm^3 distilled water) in a round-bottomed flask. The flask was sealed under aluminium foil and stirred at room temperature (3 d), forming a grey-green precipitate. The precipitate was removed *via* vacuum filtration, and water was removed from the filtrate *in vacuo* (rotary evaporator 65 °C). Dichloromethane and activated charcoal (~3 g) were added to the dark coloured viscous residue, and the mixture was sealed and stirred under ambient conditions (1 h). It was then removed from stirring and cooled (4 °C, 15 h). The charcoal was removed *via* vacuum filtration, and dichloromethane was removed from the filtrate *in vacuo* (rotary evaporator, high vacuum (~0.1-0.5 bar, 68 °C, 15 h). A yield of 11.25 g (72 %) was obtained.
^{1}**H δ** (D_2O, 300 MHz) / p.p.m.: 3.23-3.40 (m, 6H, $H_2^{2,6}$, NCH_2), 3.01 (s, 3H, NCH_3), 1.81-1.96 (m, 4H, $H_2^{3,5}$), 1.56-1.81 (m, 4H, H_2^4, NCH_2CH_2), 1.20-1.44 (m, 10H, $N(CH_2)_2(CH_2)_5CH_3$), 0.86 (t, 3H, $N(CH_2)_7CH_3$)
ESIMS: M^+(cation; calc. 212.2378, obs. 212.2317); M^-(anion too small for the detection method)

Cholinium ionic liquids
Cholinium alkanoates were all prepared by neutralisation of cholinium hydrogencarbonate, $[N_{1\,1\,1\,2OH}][HCO_3]$, with a molar equivalent of Brønsted acid (HA) to produce the desired salt, $[N_{1\,1\,1\,2OH}][A]$ along with water and carbon dioxide. Reactions were performed in aqueous or water/ethanol solution under ambient conditions, stirring until gas ceased to evolve. The solvent was evaporated *in vacuo*, using a rotary evaporator followed by high vacuum (~0.1-0.5 bar) to yield the desired product.

Cholinium ethanoate [$N_{1\,1\,1\,2OH}$][C_1COO]: ^{1}**H δ** (D_2O, 300 MHz) / p.p.m.: 1.864 (s, 3H, CH_3COO); 3.146 (s, 9H, $N(CH_3)_3$); 3.463 (t, 2H, CH_2OH); 4.006 (m, 2H, NCH_2). MS ES+ m/z (% rel. Intensity): $104M^+$ (100). Calc. 104.1075, obs. 104.1078. For the ethanoate anion, the molecular weight was too low to be detected using the standard method.

Cholinium propanoate [$N_{1\,1\,1\,2OH}$][C_2COO]: ^{1}**H δ** (D_2O, 300 MHz) / p.p.m.: 1.12 (t, 3H, CH_3CH_2); 2.24 (m, 2H, CH_2COO); 3.31 (s, 9H, $N(CH_3)_3$); 3.59 (t, 2H, CH_2OH); 4.12 (m, 2H, NCH_2). MS ES+ m/z (% rel. Intensity): 104M+ (100). Calcd. for $C_5H_{14}NO$ 104.1075, found 104.1079. MS ES- m/z (% rel. Intensity): $73M^-$ (100). Calcd. for $C_3H_5O_2$ 73.0710, found 73.0290.

Cholinium hexanoate [$N_{1,1,1,2OH}$][C_5COO]: ^{1}**H δ** (D_2O, 300 MHz) / p.p.m.: 0.75 (t, 3H, CH_3CH_2); 1.17 (m, 4H, $CH_3(CH_2)_2$); 1.42 (m, 2H, CH_2CH_2COO); 2.03 (t, 2H, CH_2COO); 3.07 (s, 9H, $N(CH_3)_3$); 3.39 (t, 2H, CH_2OH); 3.93 (m, 2H, NCH_2). MS ES+ m/z (% rel. Intensity): $104M^+$ (100). Calcd. for $C_5H_{14}NO$ 104.1075, found 104.1077. MS ES- m/z (% rel. Intensity): $115M^-$ (100). Calcd. for $C_6H_{11}O_2$ 115.0759, found 115.0758.

General procedure for synthesis of bistriflamide ionic liquids
$[C_2mim][NTf_2]$,[1] $[C_4mim][NTf_2]$,[2] $[C_6mim][NTf_2]$,[1] $[C_8mim][NTf_2]$,[3] $[C_4mpyrr][NTf_2]$,[4] $[N_{1\,8\,8\,8}][NTf_2]$[5] are all known.[6,19-22]
$[N_{1\,1\,4\,8}][NTf_2]$ and $[N_{1\,1\,4\,10}][NTf_2]$: These two ionic liquids were synthesised by treating *N,N*-dimethylbutylamine with 1-bromooctane or 1-bromodecane, repectively, to obtain the corresponding bromide salts. These salts were dissolved in dichloromethne and shaken with a 1.1 equivalent of lithium bistriflamide in water. The organic layers were washed four times with water, filtered, and the solvent was removed under vacuum (~0.1-0.5 bar) to give final products.

$[N_{1\,1\,4\,8}][NTf_2]$: ^{1}**H δ (**$CDCl_3$**)** / p.p.m.: 3.25-3.20 (4H, m, $2xCH_2N^+$), 3.05 (6H, s, Me_2N^+), 1.69-1.60 (4H, brm, $2xCH_2$), 1.41 (2H, m, CH_2), 1.30-1.25 (10H, brm, $5xCH_2$), 0.99 (3H, t, CH_3), 0.88 (3H, t, CH_3)
ESIMS: M^+(cation; calc. 214.2535, obs. 214.2521); M^-(anion; calc. 279.9173, obs. 279.9096)

$[N_{1\,1\,4\,10}][NTf_2]$: ^{1}**H δ (**$CDCl_3$**)** / p.p.m.: 3.58-3.51 (4H, m, $2xCH_2N^+$), 3.42 (6H, s,Me_2N^+), 1.71 (4H, brm, $2xCH_2$), 1.45 (2H, m, CH_2), 1.36-1.25 (14H, brm, $7xCH_2$), 1.01 (3H, t, CH_3), 0.88 (3H, t, CH_3)
ESIMS: M^+(cation; calc. 242.2848, obs. 242.2797); M^-(anion; calc. 279.9173, obs. 279.9091)

$[N_{1\,12\,(2OH)2}][NTf_2]$: As mentioned above, $[N_{1,12,(2OH)2}]Cl$ was treated with Li-bistriflamide to obtain the final product.
^{1}**H δ (**$CDCl_3$**)** / p.p.m.: 4.04 (4H, brt, $2xCH_2OH$), 3.53 (4H, brt, $2xCH_2N^+$), 3.38 ((2H, brt, CH_2N^+), 3.13 (3H, s, CH_3N^+), 1.70 (2H, brm, CH_2), 1.32-1.26 (18H, brm, $9xCH_2$), 0.88 (3H, t, CH_3)
ESIMS: M^+(cation; calc. 288.2903, obs. 288.2900); M^-(anion; calc. 279.9173, obs. 279.9193)

General procedure for synthesis of docusate ionic liquids
$[C_2mim][AOT]$, $[C_4mim][AOT]$, $[C_6mim][AOT]$, $[C_4mpyrr][AOT]$, $[N_{1\,1\,2\,4}][AOT]$, $[N_{4\,4\,4\,4}][AOT]$ are all known.[23,24] The rest of the docusate ionic liquids were synthesised according to a procedure developed by Davis *et al*[25]. An equimolar mixture of Na[AOT] and 1-alkyl-3-methylpyridinium halides or phosphonium halides were dissolved in dichloromethane/diethyl ether and stirred for 24 h at room temperature. A high speed (8000 rpm) centrifuge was employed to facilitate the removal of precipitated sodium halides form dichloromethane/ diethyl ether solutions of ionic liquids before filtering them through a short silica plug. Solvents were removed on a Rotovaporator to produce docusate ionic liquids. The solvent residues from all docusate ionic liquids were removed under vacuum (~0.1-0.5 bar) at 70-80 °C.

[$C_4m_\beta py$][AOT]
^{1}**H δ (**$CDCl_3$**)** / p.p.m.: 9.14 (1H, s, ArH), 9.07 (1H, d, ArH), 8.20 (1H, d, ArH), 8.00 (1H, t, ArH), 4.80 (2H, t, N-CH_2), 4.17 (1H, dd, SCH), 4.1-3.9 (4H, m, OCH), 3.2-3.1 (2H, m, CH_2), 2.62 (3H, s, Ar-CH_3), 1.98 (2H, pt, CH_2), 1.62-1.2 (18H, m, $9CH_2$), 1.1 (3H, t, CH_3), 0.87 (12H, t, $4xCH_3$)
LSIMS: ($C_4m_\beta py$+H; Calc. 150.1283, obs. 150.1270), (AOT anion; Calc. 421.2260, obs. 421.2275)

[$C_6m_\beta py$][AOT]: ^{1}**H δ (**$CDCl_3$**)** / p.p.m.: 9.10 (1H, s, ArH), 9.01 (1H, d, ArH), 8.21 (1H, d, ArH), 8.00 (1H, t, ArH), 4.76 (2H, t, N-CH_2), 4.13 (1H, dd, SCH), 4.1-3.94 (4H, m, OCH), 3.22-3.11 (2H, m, CH_2), 2.60 (3H, s, Ar-CH_3), 1.98 (2H, pt, CH_2), 1.61-1.26 (22H, m, 11xCH_2), 0.85 (15H, m, 5xCH_3)

ESIMS: ($C_6m_\beta py$+H; Calc. 178.1576, obs.178.1542), (AOT anion; Calc. 421.2260, obs. 421.2271)

[$P_{6\,6\,6\,14}$][AOT]: ^{1}**H δ (**$CDCl_3$**)** / p.p.m.: 4.13-3.89 (5H, m, 2xOCH_2 & CH), 3.32 (1H, dd, CH), 3.13 (1H, dd, CH), 2.27 (8H, brm, 4xCH_2-P^+), 1.50 (14H, brm, 7xCH_2), 1.31-1.26 (46H, brm, 23xCH_2), 0.91-0.88 (24H, brm, 8xCH_3)

ESIMS: M^+(cation; calc. 483.5059, obs. 483.4982,); M^-(anion, calc. 421.2260, obs. 421.2182,)

[$P_{8\,8\,8\,14}$][AOT]: ^{1}**H δ (**$CDCl_3$**)** / p.p.m.: 4.08-3.87 (5H, m, 2xOCH_2 & CH), 3.23 (1H, dd, CH), 3.10 (1H, dd, CH), 2.32 (8H, brm, 4xCH_2-P^+), 1.50 (20H, brm, 10xCH_2), 1.24 (28H, brm, 14xCH_2), 0.96 (12H, t, 4xCH3), 0.86 (12H, t, 4xCH3)

ESIMS: M^+(cation; calc. 567.5998, obs. 567.5967); M^-(anion, calc. 421.2260, obs. 421.2161)

General procedure for synthesis of diisooctylphosphinate ionic liquids

Diisooctylphosphinate ionic liquids were synthesised by treating equimolar quantities of sodium diisooctylphosphinate (50 mM) with the corresponding [cation]Cl (50 mM) in dry propanone (400 cm^3) and then heating under reflux overnight. The cooled reaction mixture was filtered to remove NaCl, and propanone from the resulting filtrate was removed on a rotary evaporator and final traces of the solvent were removed under vacuum (~0.1-0.5 bar) at 60 ^oC.

[$C_4m_\beta py$][(^{i}C_8O)$_2$$PO_2$]: ^{1}**H δ (**$CDCl_3$**)** / p.p.m.: 8.69 (1H, s, py-H), 8.63 (1H, d, py-H), 8.33 (1H, d, py-H), 7.91 (1H, d, py-H), 4.78 (2H, t, CH_2N^+), 2.63 (3H, s, CH_3-Py), 2.00-1.96 (4H, m, 2xPCH & CH_2)), 1.61-1.51 (2H, brm, 2xPCH), 1.42 (2H, brq, C**H**-CH_3), 1.34-1.23 (6H, brm, 3xCH_2), 1.08 (6H, d, 2xCH_3), 0.90 (21H, overlapping m, 7xCH_3)

ESIMS: M^+(cation; calc.150.1283, obs.150.1281); M^-(anion, calc. 289.2296, obs. 289.2283)

[$N_{1\,1\,4\,8}$][(^{i}C_8O)$_2$$PO_2$]: ^{1}**H δ (**$CDCl_3$**)** / p.p.m.: 3.48-3.40 (4H, m, 2xCH_2N^+), 3.33 (6H, s, 2xCH_3N^+), 1.88 (2H, brH, 2xPCH), 1.66 (4H, m, 2xCH2), 1.50 (2H, brm, 2xPCH), 1.41 (2H, brq, C**H**-CH_3), 1.31-1.23 (16H, brm, 8xCH_2), 1.07 (6H, d, 2xCH_3) , 0.96 (3H, t, CH_3), 0.89 (21H, overlapping m, 7xCH_3)

ESIMS: M^+(cation; calc. 214.2435, obs. 214.2426); M^-(anion, calc. 289.2296, obs. 289.2289)

[$N_{1\,8\,8\,8}$][(^{i}C_8O)$_2$$PO_2$]: ^{1}**H δ (**$CDCl_3$**)** / p.p.m.: 3.43-3.40 (6H, m, 3xCH_2N^+), 3.33 (3H, s, CH_3N^+), 1.98 (2H, brH, 2xPCH), 1.66 (4H, m, 2xCH2), 1.50 (2H, brm, 2xPCH), 1.41 (2H, brq, C**H**-CH_3), 1.37-1.23 (16H, brm, 8xCH_2), 1.12 (8H,overlapping m, 2xCH_3 & CH_2), 0.91 (18H, overlapping s, 6xCH_3), 0.87 (9H, overlapping m, 3xCH_3)

ESIMS: M^+(cation; calc. 368.4256, obs. 368.4238,); M^-(anion, calc. 289.2296, obs. 289.2286)

[$N_{1\,4\,8\,8}$][linoleate]:

Equimolar quantities of [$N_{1\,4\,8\,8}$]Cl and sodium linoleate were suspended in dry propanone and heated under reflux overnight. The cooled solution was filtered to remove NaCl and the solvent evaporated from the filtrate to furnish the required product.

[$N_{1,4,8,8}$][linoleate]: ^{1}**H δ (**$CDCl_3$**)** / p.p.m.: 4.74 (4H, brm, alkene-H), 3.47 (6H, brm, 3xN^+CH_2), 3.30 (3H.s, CH_3N^+), 2.33 (2H,brt, CH_2), 1.69 (8H, brm, 4xCH_2), 1.47-1.23 (40H, brm, 20xCH_2), 1.03 (3H, t, CH_3) 0.89 (9H, brt, 3xCH_3)

ESIMS: M^+(cation; calc. 312.3630, obs. 312.3613); M^-(anion, calc. 279.2324, obs. 279.2323)

[$N_{H\,(2O2O1)3}$][linoleate]:

Equimolar quantities of tris[2-(2-methoxyethoxy)ethyl]amine and linoleic acid were mixed together without a solvent. The required protic ionic liquid was obtained in quantitave yield.

^{1}**H δ (**$CDCl_3$**)** / p.p.m.: 5.34 (4H, brm, alkene-H), 3.59 (12H, m, 6xOCH_2), 3.55 (6H, m, 3xOCH_2), 3.39 (9H, s, 3xOMe), 2.79 (6H, t, 3xNCH_2), 2.77 (2H, t, CH_2), 2.34 (2H, t, CH_2), 2.05 (4H, m, 2xCH_2), 1.63 (2H, m, CH_2), 1.32 (14H, brm, 7xCH_2), 0.89 (3H, t, CH_3)

ESIMS: M^+(cation; calc. 324.2386, obs. 324.2379,); M^-(anion, calc. 279.2324, obs. 279.2327).

Purity of ionic liquids

All ionic liquids contained <0.05 wt.% halide (the detection limit of the analytical method). All ionic liquids were purified and purity confirmed by CHN elemental analysis.

1. P. Nockemann, B. Thijs, K. Driesen, C. R. Janssen, K. Van Hecke, L. Van Meervelt, S. Kossmann, B. Kirchner and K. Binnemans, *J. Phys. Chem. B*, 2007, **111**, 5254-5263.
2. W. Kubo, T. Kitamura, K. Hanabusa, Y. Wada and S. Yanagida, *Chem. Commun.*, 2002, 374-375.
3. J. D. Holbrey, W. M. Reichert, R. P. Swatloski, G. A. Broker, W. R. Pitner, K. R. Seddon and R. D. Rogers, *Green Chem.*, 2002, **4**, 407-413.
4. P. Nockemann, K. Binnemans and K. Driesen, *Chem. Phys. Lett.*, 2005, **415**, 131-136.
5. S. Himmler, S. Hormann, R. van Hal, P. S. Schulz and P. Wasserscheid, *Green Chem.*, 2006, **8**, 887-894.
6. P. Bonhote, A. P. Dias, N. Papageorgiou, K. Kalyanasundaram and M. Gratzel, *Inorg. Chem.*, 1996, **35**, 1168-1178.
7. G. H. Tao, L. He, W. S. Liu, L. Xu, W. Xiong, T. Wang and Y. Kou, *Green Chem.*, 2006, **8**, 639-646.
8. E. B. Carter, S. L. Culver, P. A. Fox, R. D. Goode, I. Ntai, M. D. Tickell, R. K. Traylor, N. W. Hoffman and J. H. Davis, *Chem. Commun.*, 2004, 630-631.
9. J. H. Davis, *World patent*, WO2005/072376 (2005).
10. J. Pernak, M. Smiglak, S. T. Griffin, W. L. Hough, T. B. Wilson, A. Pernak, J. Zabielska-Matejuk, A. Fojutowski, K. Kita and R. D. Rogers, *Green Chem.*, 2006, **8**, 798-806.
11. W. Xu, L. M. Wang, R. A. Nieman and C. A. Angell, *J. Phys. Chem. B*, 2003, **107**, 11749-11756.
12. E. Dinda, S. Si, A. Kotal and T. K. Mandal, *Chem. Eur. J.*, 2008, **14**, 5528-5537.
13. A. E. Bradley, C. Hardacre, M. Nieuwenhuyzen, W. R. Pitner, D. Sanders, K. R. Seddon and R. C. Thied, *Inorg. Chem.*, 2004, **43**, 2503-2514.
14. A. G. Bowing, A. Jess and P. Wasserscheid, *Chem. Ing. Tech.*, 2005, **77**, 1430-1439.
15. C. Hilgers, R. van Hal, and P. Wasserscheid, *US Patent*, US2006/0063945 A1 (2006)
16. D. R. MacFarlane, S. A. Forsyth, J. Golding and G. B. Deacon, *Green Chem.*, 2002, **4**, 444-448.
17. D. R. MacFarlane, J. Golding, S. Forsyth, M. Forsyth and G. B. Deacon, *Chem. Commun.*, 2001, 1430-1431.
18. J. H. Werntz, *US Patent*, US2563506 (1953).
19. H. Chen, Y. He, J. Zhu, H. Alias, Y. Ding, P. Nancarrow, C. Hardacre, D. Rooney and C. Tan, *Int. J. Heat Fluid Flow*, 2008, **29**, 149-155.
20. L. Alonso, A. Arce, M. Francisco and A. Soto, *J. Chem. Eng. Data*, 2008, **53**, 1750-1755.
21. R. Vijayaraghavan and D. R. MacFarlane, *Macromolecules*, 2007, **40**, 6515-6520.

22. J. M. Fraile, J. I. Garcia, C. I. Herrerias, J. A. Mayoral, D. Carrie and M. Vaultier, *Tetrahedron: Asymmetry*, 2001, **12**, 2223-2223.
23. J. H. Davis and R. Moulton, US patent US 2005/0131118 A1 (2005).
24. J. H. Davis and R. Moulton, US patent US 2009/0200513 A1 (2009).
25. J. R. Harjani, R. D. Singer, M. T. Garciac and P. J. Scammells, *Green Chem.*, 2009, **11**, 83-90.