Supplementary Information

Experimental

Synthesis & Characterisation

Synthetic Materials. Triethyl amine (≥ 99% ; Et₃N, Sigma), p-Toluenesulfonyl chloride (puriss., ≥ 99% ; p-OTs-Cl, Sigma), diethylene glycol monomethyl ether (purum, ≥99.0% (GC), Fluka), triethylene glycol monomethyl ether (purum, ≥99.0% (GC), Fluka), tetraethylene glycol monomethyl ether (purum, ≥99.0% (GC), Fluka), Bis(trifluoromethane)sulfonimide lithium salt (99.95%; Li[N(CF₃SO₂)₂] 3M) & sodium dicyanamide (99%, Na[N(CN)₂], Sigma) were used without further purification.

¹H & ¹³C NMR spectra were carried out by the 300 & 400 Mhz Bruker DPX-300 & 400 spectrometers (Provided by Cambridge Isotope Laboratories)

MS – ESI (ES⁺ & ES⁻ analysis) was carried out by the Micromass Platform II API QMS Electrospray Mass Specrometer (cone voltage 20/35 V). Acetonitrile & Methanol were used as the eluents.

For the use of DSC, Density, Viscosity, Conductivity & the measurements of Cyclic Voltammetry, See Experimental 1.2

1.1.1 Synthesis of 2-(2-methoxyethoxy)ethyl 4-methylbenzene sulfonate 1

Sodium hydroxide (8.5g, 0.21 moles) in water (10ml) was added to diethyl glycol monomethyl ether (20g, 0.16 moles) in THF (30 ml) and the solution was cooled
to 0 °C. p-Tosyl chloride (33.64g, 0.17 moles) in THF (40 ml) was added dropwise to the reaction over 30 minutes and reaction mixture was stirred overnight at room temperature under N2. The solution was washed with water (80 ml) and slightly acidified with 6M H2SO4 (pH = 6). The crude product was then extracted with dichloromethane (4 x 50 ml) and concentrated in vacuo. to give a pale yellow oil (42.2 g, yield 88 %) (1H NMR : δ 7.78-7.76 ppm, 1H, d ; δ 7.33-7.31 ppm, 1H, d ; δ 3.67 – 3.65 ppm, 2H, t ; δ 3.50 - 3.56 ppm, 4H, q ; δ 3.58 – 3.56 ppm, 2H, t ; δ 3.50-3.48 ppm, 4H, q ; δ 3.39 ppm, 3H, s ; δ 2.4 ppm, 3H, s ; 13C NMR : δ 145.2 ppm, ; δ 140.1 ppm ; δ130.5 ppm ; δ 126.7 ppm ; δ 72.2 ppm ; δ 66.3 ppm ; δ 64.3 ppm ; δ 62.1 ppm δ 59.9 ppm ; MS [M + Na]+ = 274.33 ; Rf (Ethyl acetate : Hexane 1 :1) = 0.5).

1.1.2 Synthesis of 2-(2-(2-methoxyethoxy)ethoxy)ethyl methylbenzenesulfonate 2

Sodium hydroxide (8.5g, 0.21 moles) in water (10ml) was added to triethyl glycol monomethyl ether (26.2g, 0.16 moles) in THF (30 ml) and the solution was cooled to 0 C. p-Tosyl chloride (33.64g, 0.17 moles) in THF (40 ml) was added dropwise to the reaction over 30 minutes and reaction mixture was stirred overnight at room temperature under N2. The solution was washed with water (80 ml) and slightly acidified with 6M H2SO4 (pH = 6). The crude product was then extracted with dichloromethane (4 x 50 ml) and concentrated in vacuo. to give a pale yellow oil (33.6 g, yield 80 %) (1H NMR : δ 7.78-7.76 ppm, 1H, d ; δ 7.33-7.31 ppm, 1H, d ; δ 3.72 – 3.69 ppm, 2H, t ; δ 3.50 - 3.56 ppm, 2H, t ; δ 3.50-
3.48 ppm, 4H, q; δ 3.46-3.46 ppm, 4H, q; δ 3.39 ppm, 3H, s; δ 2.4 ppm, 3H, s;

$^{13}$C NMR: δ 145.2 ppm; δ 140.1 ppm; δ 130.5 ppm; δ 126.7 ppm; δ 72.2 ppm; δ 71.4 ppm; δ 70.3 ppm; δ 68.8 ppm; δ 64.3 ppm; δ 62.1 ppm δ 59.9 ppm; MS [M + Na]$^+$ = 341.1; Rf (Ethyl acetate : Hexane 1 :1) = 0.6).

### 1.1.3 Synthesis of 2,5,8,11-tetraoxatridecan-13-yl 4-methylbenzene-sulfonate 3

Sodium hydroxide (8.5g, 0.21 moles) in water (10ml) was added to tetraethyl glycol monomethyl ether (15g, 0.16 moles) in THF (30 ml) and the solution was cooled to 0°C. p-tosyl chloride (33.64g, 0.17 moles) in THF (40 ml) was added dropwise to the reaction over 30 minutes and reaction mixture was stirred for 48hrs at room temperature under N$_2$. The solution was washed with water (80 ml) and slightly acidified with 6M H$_2$SO$_4$ (pH = 6). The crude product was then extracted with Dichloromethane (4 x 50 ml) and concentrated in vacuo. to give a pale yellow oil. Further purification of this oil was done by column chromatography [ Eluent – n-Pentane : Ethyl Acetate 1 : 1; Rf = 0.1] (7g, yield 45%)]($^1$H NMR: δ 7.78-7.76 ppm, 1H, d; δ 7.33-7.31 ppm, 1H, d; δ 3.72 – 3.69 ppm, 2H, t; δ 3.58 – 3.56 ppm, 2H, t; δ 3.50-3.48 ppm, 4H, q; δ 3.46-3.46 ppm, 4H, q; δ 3.44-3.41 ppm, 4H, q; δ 3.39 ppm, 3H, s; δ 2.4 ppm, 3H, s; $^{13}$C NMR: δ 145.2 ppm; δ 140.1 ppm; δ130.5 ppm; δ 126.7 ppm; δ 73.2 ppm; δ 72.2 ppm; δ 71.4 ppm; δ 70.3 ppm; δ 68.8 ppm; δ 64.3 ppm; δ 62.1 ppm δ 59.9 ppm; MS (ES) [M + Na]$^+$ : m/z 385.44 (5 : 1 : 0.5); Rf (Ethyl acetate : Hexane 1 :1) = 0.6 ).
Synthesis of Ionic Liquids

**Scheme 3:** Example of the alkoxy based ionic liquid, for N,N,N-triethyl -2-(2-methoxyethoxy)ethanammonium Tosylate \([\text{N}_{222(20201)}]\) \([\text{OTs}]\)

### 1.2.1 Synthesis of N,N,N-triethyl -2-(2-methoxyethoxy) ethanammonium Tosylate \([\text{N}_{222(20201)}]\) \([\text{OTs}]\) 1a

Compound 1 (4.1 g, 0.022 moles) was added dropwise to triethyl amine (2.5 g, 0.025 moles) in acetonitrile (20 ml) under nitrogen. The reaction was refluxed (82 °C) under N₂ for 3 days. The dark yellow solution was concentrated in vacuo to give a dark yellow solid. Recrystalisation (acetonitrile : diethyl ether) afforded white solid (5.78 g, yield 91 %) \((^1\text{H NMR} : \delta 7.78-7.76 \text{ ppm}, 1\text{H}, \text{d} ; \delta 7.33-7.31 \text{ ppm}, 1\text{H}, \text{d} ; \delta 3.75 \text{ ppm}, 2\text{H}, \text{t} ; \delta 3.50 - 3.47 \text{ ppm}, 2\text{H}, \text{t} ; \delta 3.45-3.41 \text{ ppm}, 4\text{H}, \text{q} ; \delta 3.31 \text{ ppm}, 3\text{H}, \text{s} ; \delta 2.4 \text{ ppm}, 3\text{H}, \text{s} ; \delta 3.25 \text{ ppm}, 6\text{H}, \text{q} ; \delta 1.18-1.25 \text{ ppm}, 9\text{H}, \text{t} ; ^{13}\text{C NMR} : \delta 145.2 \text{ ppm} ; \delta 140.1 \text{ ppm} ; \delta 130.5 \text{ ppm} ; \delta 126.7 \text{ ppm} ; \delta 73.2 \text{ ppm} ; \delta 72.2 \text{ ppm} ; \delta 71.4 \text{ ppm} ; \delta 64.3 \text{ ppm} ; \delta 62.1 \text{ ppm} ; \delta 59.9 \text{ ppm} ; \delta 22.9 \text{ ppm} ; \delta 10.6 \text{ ppm} ; \text{MS (ES}^+\text{)} m/z = 204.1, \text{ES}^- \text{m/z} = 171.9 ; \text{m.p} = 67 \pm 0.86 ^\circ \text{C})
1.2.2 Synthesis of N,N,N-triethyl -2-(2-methoxyethoxy) ethanammonium bromide [N$_{222}(20201)$] [Br] 1b

1-bromo -2-(2-(2-methoxyethoxy)ethoxy) (4.3 g, 0.023 moles) was added dropwise to triethyl amine (2.5 g, 0.025 moles) in acetonitrile (20 ml) under nitrogen. The reaction was refluxed (82°C) under N$_2$ for 3 days. The dark yellow solution was concentrated in vacuo to give a dark yellow solid. Recrystallisation (acetonitrile : diethyl ether) afforded off-white solid (6.0 g, yield 91%) ($^1$H NMR : $\delta$ 3.75 ppm, 2H, t; $\delta$ 3.50 – 3.47 ppm, 2H, t; $\delta$ 3.45-3.41 ppm, 4H, q; $\delta$ 3.31 ppm, 3H, s; $\delta$ 2.4 ppm, 3H, s; $\delta$ 3.25 ppm, 6H, q; $\delta$ 1.18-1.25 ppm, 9H, t; $^{13}$C NMR : $\delta$ 73.2 ppm; $\delta$ 72.2 ppm; $\delta$ 71.4 ppm; $\delta$ 64.3 ppm; $\delta$ 62.1 ppm; $\delta$ 59.9 ppm; $\delta$ 22.9 ppm; $\delta$ 10.6 ppm; MS (ES$^+$) m/z = 204.1, (ES$^-$) m/z = 80.1)

1.2.3 Synthesis of N,N,N-triethyl -2-(2-methoxyethoxy) ethanammonium bis[(trifluoromethyl)sulfonyl]imide [N$_{222}(20201)$] [NTf$_2$] 1c

Lithium bis[(trifluoromethyl)sulfonyl]imide (10g, 0.035 moles) was dissolved in dichloromethane (20 ml). Compound 1a (8.0 g, 5.0 x 10$^{-3}$ moles) was added to the mixture and the solution was stirred for 24 hours at room temperature. The crude product was filtered and the filtrate was concentrated in vacuo to give a clear oil (6 g, 80%)

($^1$H NMR : $\delta$ 3.75 ppm, 2H, t; $\delta$ 3.50 – 3.47 ppm, 2H, t; $\delta$ 3.45-3.41 ppm, 4H, q; $\delta$ 3.31 ppm, 3H, s; $\delta$ 2.4 ppm, 3H, s; $\delta$ 3.25 ppm, 6H, q; $\delta$ 1.18-1.25 ppm, 9H, t; $^{13}$C
NMR: $\delta$ 152.1; $\delta$ 73.2 ppm; $\delta$ 72.2 ppm; $\delta$ 71.4 ppm; $\delta$ 64.3 ppm; $\delta$ 62.1 ppm; $\delta$ 59.9 ppm; $\delta$ 22.9 ppm; $\delta$ 10.6 ppm; MS (ES+) m/z = 204.1, (ES-) m/z = 279.9

1.2.4 Synthesis of N,N,N-triethyl -2-(2-methoxyethoxy) ethanammonium dicyanamide [N$_{222}(20201)$] [DCA] 1d

Sodium dicyanamide (5.1 g, 0.058 moles) and silver nitrate (7.8 g, 0.057 moles) were mixed in water (50 ml) for 3 hours at room temperature. The white precipitate was filtered, washed with chilled water (6 x 20 ml) and dried for 30 mins under vaccum. The precipitate was used immediately for the synthesis of 1d.

Silver dicyanamide (10 g, 0.057 moles) and Compound 1b (8.0 g, 0.02 moles) were mixed in water (50 ml) and the reaction mixture was stirred for 24 hours at room temperature. The crude product was filtered and the filtrate was concentrated in vacuo to give a pale yellow oil (5.0 g, 65%).

(1H NMR: $\delta$ 3.75 ppm, 2H, t; $\delta$ 3.50 – 3.47 ppm, 2H, t; $\delta$ 3.45-3.41 ppm, 4H, q; $\delta$ 3.31 ppm, 3H, s; $\delta$ 2.4 ppm, 3H, s; $\delta$ 3.25 ppm, 6H, q; $\delta$ 1.18-1.25 ppm, 9H, t; $^{13}$C NMR: $\delta$ 125.8; $\delta$ 73.2 ppm; $\delta$ 72.2 ppm; $\delta$ 71.4 ppm; $\delta$ 64.3 ppm; $\delta$ 62.1 ppm; $\delta$ 59.9 ppm; $\delta$ 22.9 ppm; $\delta$ 10.6 ppm; MS (ES+) m/z = 204.1, (ES-) m/z = 66.04)

1.2.5 Synthesis of N,N,N-triethyl -2-(2-methoxyethoxy) ethanammonium 4-methylbenzene sulfonate [N$_{222}(20201)$] [OTs] 2a
Compound 2 (7.75 g, 0.028 moles) was added dropwise to triethyl amine (3.0 g, 0.03 moles) in acetonitrile (20 ml) under nitrogen. The reaction was refluxed (82°C) under N\textsubscript{2} for 3 days. The pale yellow solution was concentrated in vacuo to give a off-white solid. Recrystallisation (acetonitrile : diethyl ether) afforded white solid (8.3 g, yield 78 %) (\textsuperscript{1}H NMR : δ 7.78-7.76 ppm, 1H, d ; δ 7.33-7.31 ppm, 1H, d ; δ 3.78 ppm, 2H, t ; δ 3.50 – 3.47 ppm, 2H, t ; δ 3.45-3.41 ppm, 4H, q ; δ 3.43-3.39 ppm, 4H, q ; q ; δ 3.31 ppm, 3H, s ; δ 2.4 ppm, 3H, s ; δ 3.25 ppm, 6H, q ; δ 1.18-1.25 ppm, 9H, t; \textsuperscript{13}C NMR : δ 145.2 ppm, ; δ 140.1 ppm ; δ130.5 ppm ; δ 126.7 ppm ; δ 73.2 ppm ; δ 72.2 ppm ; δ 71.4 ppm ; δ 64.3 ppm ; δ 62.1 ppm ; δ 59.9 ppm ; δ 22.9 ppm ; δ 10.6 ppm ; MS (ES +) m/z = 248.1, (ES-) m/z = 171.9 ; m.p = 37.6 ± 0.12 °C)

1.2.4 Synthesis of N,N,N-triethyl -2-(2-methoxyethoxy) ethanammonium dicyanamide [N\textsubscript{222}(2020201)] [DCA] 2b

Sodium dicyanamide( 5.1 g, 0.058 moles ) and silver nitrate (7.8 g, 0.057 moles) were mixed in water (50ml) for 3 hours at room temperature. The white precipitate was filtered, washed with chilled water (6 x 20ml) and dried for 30 mins under vaccum. The precipitate was used immediately for the synthesis of 1d.

Silver dicyanamide (10g, 0.057 moles) and Compound 1b (8.0 g, 0.02 moles) were mixed in water (50 ml) and the reaction mixture was stirred for 24 hours at
room temperature. The crude product was filtered and the filtrate was concentrated in vacuo to give a pale yellow oil (5.0 g, 65 %).

(1H NMR : \( \delta \) 3.75 ppm, 2H, t ; \( \delta \) 3.50 – 3.47 ppm, 2H, t ; \( \delta \) 3.45-3.41 ppm, 4H, q ; \( \delta \) 3.31 ppm, 3H, s ; \( \delta \) 2.4 ppm, 3H, s ; \( \delta \) 3.25 ppm, 6H, q ; \( \delta \) 1.18-1.25 ppm, 9H, t ; \( ^{13} \)C NMR : \( \delta \) 125.8 ; \( \delta \) 73.2 ppm ; \( \delta \) 72.2 ppm ; \( \delta \) 71.4 ppm ; \( \delta \) 64.3 ppm ; \( \delta \) 62.1 ppm ; \( \delta \) 59.9 ppm ; \( \delta \) 22.9 ppm ; \( \delta \) 10.6 ppm ; MS (ES +) \( m/z = 248.1 \), (ES -) \( m/z = 66.04 \))

1.2.5 Synthesis of 2,5,8,11-tetraoxatridecan-[(trifluoromethyl)sulfonyl]imide [N\(_{222}(202020201)\) [NTf\(_2\)] 3a

Lithium bis [(trifluoromethyl)sulfonyl]imide (10g, 0.035 moles) was dissolved in dichloromethane (20 ml). Compound 1a (8.0 g, 5.0 \( \times \) 10\(^{-3} \) moles) was added to the mixture and the solution was stirred for 24 hours at room temperature. The crude product was filtered and the filtrate was concentrated in vacuo to give a pale-yellow oil (5 g, 73 %)

(1H NMR : \( \delta \) 3.75 ppm, 2H, t ; \( \delta \) 3.50 – 3.47 ppm, 2H, t ; \( \delta \) 3.45-3.41 ppm, 4H, q ; \( \delta \) 3.31 ppm, 3H, s ; \( \delta \) 2.4 ppm, 3H, s ; \( \delta \) 3.25 ppm, 6H, q ; \( \delta \) 1.18-1.25 ppm, 9H, t ; \( ^{13} \)C NMR : \( \delta \) 152.1 ; \( \delta \) 73.2 ppm ; \( \delta \) 72.2 ppm ; \( \delta \) 71.4 ppm ; \( \delta \) 64.3 ppm ; \( \delta \) 62.1 ppm ; \( \delta \) 59.9 ppm ; \( \delta \) 22.9 ppm ; \( \delta \) 10.6 ppm ; MS (ES +) \( m/z = 292.4 \), (ES -) \( m/z = 279.9 \))

1.2.6 Synthesis of 2,5,8,11-tetraoxatridecan-13-yl 4-methylbenzenesulfonate [N\(_{222}(202020201)\) [OTs] 3b
Compound 3 (7.0 g, 0.019 moles) was added dropwise to triethyl amine (5.0 g, 0.05 moles) in acetonitrile (20 ml) under nitrogen. The reaction was refluxed (82 °C) under N₂ for 3 days. The pale yellow solution was concentrated in vacuo to give pale yellow oil (2.00 g, yield 28.5 %) (¹H NMR: δ 7.78-7.76 ppm, 1H, d; δ 7.33-7.31 ppm, 1H, d; δ 3.78 ppm, 2H, t; δ 3.50 – 3.47 ppm, 2H, t; δ 3.45-3.41 ppm, 4H, q; δ 3.43-3.39 ppm, 4H, q; δ 3.38-3.36 ppm, 4H, q; q; δ 3.31 ppm, 3H, s; δ 2.4 ppm, 3H, s; δ 3.25 ppm, 6H, q; δ 1.18-1.25 ppm, 9H, t; ¹³C NMR: δ 143.2 ppm, ; δ 137.1 ppm; δ 130.5 ppm; δ 126.7 ppm; δ 73.2 ppm; δ 72.2 ppm; δ 71.4 ppm; δ 64.3 ppm; δ 62.1 ppm; δ 59.9 ppm; δ 22.9 ppm; δ 10.6 ppm; MS (ES⁺) m/z = 292.4, (ES⁻) m/z = 171.9; m.p = 15 ± 0.24 °C

Density & Viscosity

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Figure 6: Cyclic Voltammetry of 5 mol% ZnCl₂ in [C₅mpyr][NTf₂] at room temperature.