

## Supplementary Information

### Experimental

#### *Synthesis & Characterisation*

**Synthetic Materials.** Triethyl amine ( $\geq 99\%$  ; Et<sub>3</sub>N, Sigma), *p*-Toluenesulfonyl chloride (puriss.,  $\geq 99\%$  ; *p*-OTs-Cl, Sigma), diethylene glycol monomethyl ether (purum,  $\geq 99.0\%$  (GC), Fluka), triethylene glycol monomethyl ether (purum,  $\geq 99.0\%$  (GC), Fluka), tetraethylene glycol monomethyl ether (purum,  $\geq 99.0\%$  (GC), Fluka), Bis(trifluoromethane)sulfonimide lithium salt (99.95% ; Li[N(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>], 3M) & sodium dicyanamide (99%, Na[N(CN)<sub>2</sub>], Sigma) were used without further purification.

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

MS – ESI (ES<sup>+</sup> & ES<sup>-</sup> 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 N<sub>2</sub>. The solution was washed with water (80 ml) and slightly acidified with 6M H<sub>2</sub>SO<sub>4</sub> (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 %) (<sup>1</sup>H 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 3.58 – 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 ; <sup>13</sup>C NMR : δ 145.2 ppm ; δ 140.1 ppm ; δ 130.5 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]<sup>+</sup> = 274.33 ; R<sub>f</sub> (Ethyl acetate : Hexane 1 :1) = 0.5 ).

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

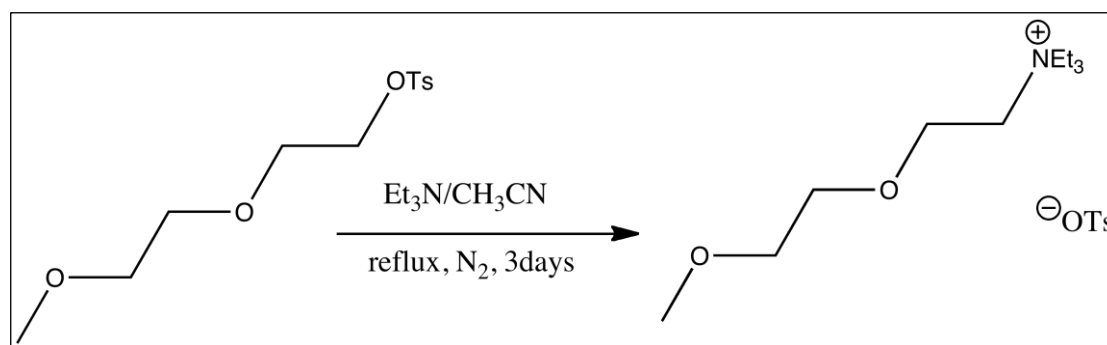
Sodium hydroxide (8.5g, 0.21 moles) in water (10ml) was added to triethyl glycol monomethyl ether (26.2g, 0.16 moles) in THF (30 ml) and the solution was cooled to 0 C. *p*-Tosyl chloride (33.64g, 0.17 moles) in THF (40 ml) was added dropwise to the reaction over 30 minutes and reaction mixture was stirred overnight at room temperature under N<sub>2</sub>. The solution was washed with water (80 ml) and slightly acidified with 6M H<sub>2</sub>SO<sub>4</sub> (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 %) (<sup>1</sup>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 ;  $\delta$  3.46-3.46 ppm, 4H, q ;  $\delta$  3.39 ppm, 3H, s ;  $\delta$  2.4 ppm, 3H, s ;  
 $^{13}\text{C}$  NMR :  $\delta$  145.2 ppm ;  $\delta$  140.1 ppm ;  $\delta$  130.5 ppm ;  $\delta$  126.7 ppm ;  $\delta$  72.2 ppm ;  $\delta$   
71.4 ppm ;  $\delta$  70.3 ppm ;  $\delta$  68.8 ppm ;  $\delta$  64.3 ppm ;  $\delta$  62.1 ppm  $\delta$  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<sub>2</sub>. The solution was washed with water (80 ml) and slightly acidified with 6M H<sub>2</sub>SO<sub>4</sub> (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 %) ( $^1\text{H}$  NMR :  $\delta$  7.78-7.76 ppm, 1H, d ;  $\delta$  7.33-7.31 ppm, 1H, d ;  $\delta$  3.72 – 3.69 ppm, 2H, t ;  $\delta$  3.58 – 3.56 ppm, 2H, t ;  $\delta$  3.50-3.48 ppm, 4H, q ;  $\delta$  3.46-3.46 ppm, 4H, q ;  $\delta$  3.44-3.41 ppm, 4H, q ;  $\delta$  3.39 ppm, 3H, s ;  $\delta$  2.4 ppm, 3H, s ;  $^{13}\text{C}$  NMR :  $\delta$  145.2 ppm ;  $\delta$  140.1 ppm ;  $\delta$  130.5 ppm ;  $\delta$  126.7 ppm ;  $\delta$  73.2 ppm ;  $\delta$  72.2 ppm ;  $\delta$  71.4 ppm ;  $\delta$  70.3 ppm ;  $\delta$  68.8 ppm ;  $\delta$  64.3 ppm ;  $\delta$  62.1 ppm  $\delta$  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)ethan ammonium Tosylate [N<sub>222(20201)</sub>] [OTs]

### 1.2.1 Synthesis of N,N,N-triethyl -2-(2-methoxyethoxy) ethan ammonium Tosylate [N<sub>222(20201)</sub>] [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 N<sub>2</sub> for 3 days. The dark yellow solution was concentrated in vacuo to give a dark yellow solid. Recrystallisation (acetonitrile : diethyl ether) afforded white solid (5.78 g, yield 91 %) (<sup>1</sup>H NMR : δ 7.78-7.76 ppm, 1H, d ; δ 7.33-7.31 ppm, 1H, d ; δ 3.75 ppm, 2H, t ; δ 3.50 – 3.47 ppm, 2H, t ; δ 3.45-3.41 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 ; <sup>13</sup>C NMR : δ 145.2 ppm, ; δ 140.1 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<sup>+</sup>) m/z = 204.1, (ES<sup>-</sup>) m/z = 171.9 ; m.p = 67 ± 0.86 °C)

### 1.2.2 Synthesis of N,N,N-triethyl -2-(2-methoxyethoxy) ethan ammonium bromide [N<sub>222(20201)</sub>] [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<sub>2</sub> 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 %) (<sup>1</sup>H NMR : δ 3.75 ppm, 2H, t ; δ 3.50 – 3.47 ppm, 2H, t ; δ 3.45-3.41 ppm, 4H, 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 ; <sup>13</sup>C NMR : 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<sup>+</sup>) m/z = 204.1, (ES<sup>-</sup>) m/z = 80.1)

### 1.2.3 Synthesis of N,N,N-triethyl -2-(2-methoxyethoxy) ethan ammonium bis [(trifluoromethyl)sulfonyl]imide [N<sub>222(20201)</sub>] [NTf<sub>2</sub>] **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<sup>-3</sup> 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%)

(<sup>1</sup>H NMR : δ 3.75 ppm, 2H, t ; δ 3.50 – 3.47 ppm, 2H, t ; δ 3.45-3.41 ppm, 4H, 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 ; <sup>13</sup>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<sup>+</sup>) m/z = 204.1, (ES<sup>-</sup>) m/z = 279.9)

#### **1.2.4 Synthesis of N,N,N-triethyl -2-(2-methoxyethoxy) ethan ammonium dicyanamide [N<sub>222(20201)</sub>] [DCA] 1d**

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 vacuum. 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 %).

(<sup>1</sup>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 ; <sup>13</sup>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) ethan ammonium 4-methylbenzene sulfonate [N<sub>222(2020201)</sub>] [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<sub>2</sub> 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 %) (<sup>1</sup>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 ; <sup>13</sup>C NMR : δ 145.2 ppm, ; δ 140.1 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 = 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) ethan ammonium dicyanamide [N<sub>222</sub>(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 vacuum. 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 %).

(<sup>1</sup>H NMR : δ 3.75 ppm, 2H, t ; δ 3.50 – 3.47 ppm, 2H, t ; δ 3.45-3.41 ppm, 4H, 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 ; <sup>13</sup>C NMR : δ 125.8 ; 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 = 66.04)

### **1.2.5 Synthesis of 2,5,8,11-tetraoxatridecan-[(trifluoromethyl)sulfonyl]imide** **[N<sub>222</sub>(202020201)] [NTf<sub>2</sub>] **3a****

Lithium *bis* [(trifluoromethyl)sulfonyl]imide (10g, 0.035 moles) was dissolved in dichloromethane (20 ml). Compound **1a** (8.0 g, 5.0 x 10<sup>-3</sup> 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%)

(<sup>1</sup>H NMR : δ 3.75 ppm, 2H, t ; δ 3.50 – 3.47 ppm, 2H, t ; δ 3.45-3.41 ppm, 4H, 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 ; <sup>13</sup>C NMR : δ 152.1 ; 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<sup>+</sup>) m/z = 292.4 (ES<sup>-</sup>) m/z = 279.9)

### **1.2.6 Synthesis of 2,5,8,11-tetraoxatridecan-13-yl 4-methylbenzenesulfonate** **[N<sub>222</sub>(202020201)] [OTs] **3b****



Compound **3** (7.0g, 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 N<sub>2</sub> for 3 days. The pale yellow solution was concentrated in vacuo to give pale-yellow oil (2.00 g, yield 28.5 %) (<sup>1</sup>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 ; 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 ; <sup>13</sup>C 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<sup>+</sup>) m/z = 292.4, (ES<sup>-</sup>) m/z = 171.9 ; m.p = 15 ± 0.24 °C)

#### *Density & Viscosity*

	$\eta$ (mPa.s)		$\rho$ (g/ml)	
	30 °C	70 °C	30 °C	70 °C
[N <sub>222(20201)</sub> ] [OTs]	-	56 ± 3.0	-	-
[N <sub>222(2020201)</sub> ] [OTs]	173 ± 3.0	23 ± 3.0	1.15 ± 0.1	1.13 ± 0.1
[N <sub>222(202020201)</sub> ] [OTs]	65 ± 3.0	14 ± 3.0	1.14 ± 0.1	1.12 ± 0.1
[N <sub>222(20201)</sub> ] [NTf <sub>2</sub> ]	49 ± 2.0	13 ± 2.0	1.35 ± 0.1	1.32 ± 0.1
[N <sub>222(20201)</sub> ] [DCA]	56 ± 3.0	15 ± 3.0	1.35 ± 0.1	1.36 ± 0.1
[N <sub>222(2020201)</sub> ] [DCA]	20 ± 3.0	11 ± 3.0	1.12 ± 0.1	1.08 ± 0.1
[N <sub>222(202020201)</sub> ] [NTf <sub>2</sub> ]	30 ± 3.0	9.0 ± 2.0	1.30 ± 0.2	1.26 ± 0.1

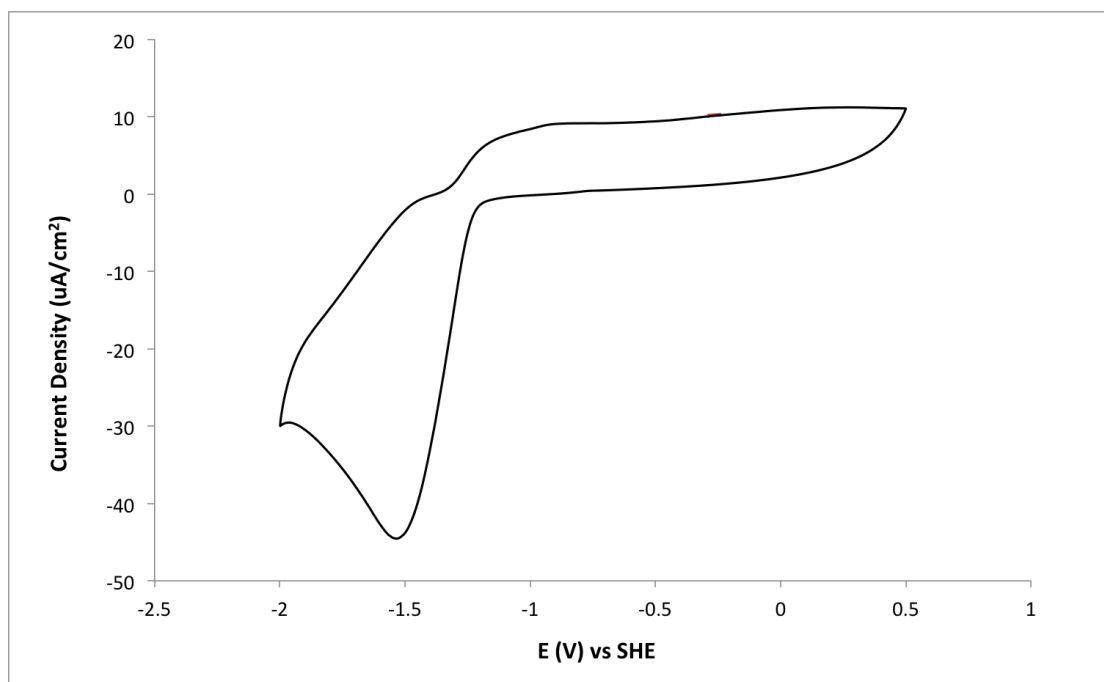


Figure 6 : Cyclic Voltammetry of 5 mol% ZnCl<sub>2</sub> in [C<sub>2</sub>mpyr][NTf<sub>2</sub>] at room temperature.