Supplementary information for

# New ionic liquid crystal based on imidazolium salts.

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## Experimental Section

### Measurements:

The NMR spectroscopy experiments were performed with a Brucker AVANCE 300 spectrometer at the resonating frequencies 300.13 MHz for $^1$H NMR spectra and at 75.48 MHz for $^{13}$C NMR spectra. $CDCl_3$ was used as solvent for the NMR experiments. For internal calibration the solvent peak of $CDCl_3$ was used: $\delta$ ($^1$H) = 7.27 ppm; $\delta$ ( $^{13}$C )= 77 ppm.
Elemental analyses were performed by the analytical service at the Institut Charles Sadron and by the analytical service at the Université Louis Pasteur (Strasbourg, France).

### 1-(4-dodecyloxybenzyl)-3-methyl-1*H*-imidazol-3-ium thiocyanate: 1c

Same experimental procedure as for 1b (3-(4-dodecyloxybenzyl)-1-methyl-1*H*-imidazolium bromide (250 mg, 0.57mmol) potassium thiocyanate (55mg, 0.57 mmol)). Yield white solid 226 mg, 95 % (Found C, 66.3; H, 9.0; N, 9.6. $C_{24}H_{37}N_3O_1S.H_2O$ requires C, 66.5; H, 9.1; N, 9.7). $\nu_{max}$/cm$^{-1}$ 3147 (C-H aromatic); 2916 and 2849 (C-H aliphatic); 2064 ($SCN^{(-)}$), 1514 (C=C aromatic); 1249 (aromatic ether). $\delta_H$ ( 300 MHz; $CDCl_3$): 0.82 (3 H, t, J 6.8, C$\underline{H_3}$ aliphatic chain) ; 1.20 (16 H, br s, C$\underline{H_2}$ aliphatic chain) ; 1.33-1.38 (2 H, m, C$\underline{H_2}$ aliphatic chain) ; 1.71 (2 H, q, J= 6.8 Hz, O-CH$_2$-C$\underline{H_2}$) ; 3.88 (2 H, t, J 6.5, OC$\underline{H_2}$) ; 4.02 (3 H, s, C$\underline{H_3}$-N); 5.36 (2 H, s, N-C$\underline{H_2}$-Ph) ; 6.86 (2 H, d, J 8.6, C$\underline{H}$ phenyl) ; 7.08 (1 H, m, C$\underline{H}$ imidazolium) ; 7.13 (1 H, m, C$\underline{H}$ imidazolium) ; 7.31 (2 H, d, J 8.6, C$\underline{H}$ phenyl) ; 9.63 (1 H, s, N-C$\underline{H}$-N). $\delta_c$ (75 MHz; $CDCl_3$): 14.05 ($\underline{C}H_3$ aliphatic chain) ; 22.60 ; 25.94 ; 29.10 ; 29.26 ; 29.33 ; 29.50 ; 29.52 ; 29.55 ; 29.58 ; 31.83 ($\underline{C}H_2$ aliphatic chain) ; 36.72 (N-$\underline{C}H_3$) ; 52.26 (N-$\underline{C}H_2$-Ph) ; 68.12 (O-$\underline{C}H_2$) ; 115.27 ($\underline{C}$H phenyl) ; 121.80 ; 123.54 ($\underline{C}$H imidazolium) ; 124.22 ($\underline{C}$ phenyl) ; 130.66 ($\underline{C}$H phenyl) ; 131.66 (S$\underline{C}$N) ; 136.64(N-$\underline{C}$H-N) ; 160.01 ($\underline{C}$ phenyl).

### 1-(4-dodecyloxybenzyl)-3-methyl-1*H*-imidazol-3-ium hexafluorophosphate: 1d

Same experimental procedure as for 1b (3-(4-dodecyloxybenzyl)-1-methyl-1*H*-imidazolium bromide (250 mg, 0.57mmol) and potassium hexafluorophosphate (105mg, 0.57 mmol)). Yield: white solid 285 mg, 99 % (Found C, 54,8; H, 7,0; N, 5,6 $C_{23}H_{37}F_6N_2OP$ requires C, 55,0; H, 7.4; N, 5.6). $\nu_{max}$/cm$^{-1}$ 3178 (C-H aromatic), 2916 and 2850 (C-H aliphatic), 1251 (aromatic ether), 823 ($PF_6^{(-)}$). $\delta_H$ ( 300 MHz; $CDCl_3$): 0.87 (3 H, t, J 6.8, C$\underline{H_3}$ aliphatic chain) ; 1.27 (16 H, br s, C$\underline{H_2}$ aliphatic chain) ; 1.39-1.46 (2 H, m, C$\underline{H_2}$ aliphatic chain) ; 1.78 (2 H, q, J 6.8, O-CH$_2$-C$\underline{H_2}$) ; 3.93 (3 H, s, C$\underline{H_3}$-N) ; 3.94 (2 H, t, J 6.6, OC$\underline{H_2}$) ; 5,24 (2 H, s , N-C$\underline{H_2}$-Ph) ; 6.93 (2 H, d, J 9.0, C$\underline{H}$ phenyl) ; 7.10 (1 H, m, C$\underline{H}$ imidazolium) ; 7.17 (1 H, m, C$\underline{H}$ imidazolium) ; 7.31 (2 H, d, J 8.7, C$\underline{H}$ phenyl) ; 8.69 (1 H, s, N-C$\underline{H}$-N). $\delta_c$ (75 MHz; $CDCl_3$): 14.09 ($\underline{C}H_3$ aliphatic chain) ; 22.66 ; 26.00 ; 29.17 ; 29.33 ; 29.40 ; 29.56 ;

29.59 ; 29.61 ; 29.65 ; 31.90 (C$H_2$ aliphatic chain) ; 36.21 (N-C$H_3$) ; 53.09 (N-C$H_2$-Ph) ; 68.17 (O-C$H_2$) ; 115.35 (CH phenyl) ; 121.65 ; 123.95 (CH imidazolium) ; 123.95 (C phenyl) ; 130.57 (CH phenyl) ; 135.82 (N-CH-N) ; 160.13 (C phenyl).

### 1-(4-dodecyloxybenzyl)-3-methyl-1*H*-imidazol-3-ium bis[(trifluoromethyl)sulfonyl]azanide: 1f

Same experimental procedure as for 1b (3-(4-dodecyloxybenzyl)-1-methyl-1*H*-imidazolium bromide (250 mg, 0.57mmol) and lithium bis[(trifluoromethyl)sulfonyl]azanide (164mg, 0.57 mmol)). Yield: crystalline white solid 363 mg, 93 % (Found C, 47.15; H, 5.9; N, 6.6 $C_{25}H_{37}F_6N_3O_5S_2$ requires C, 47.1; H, 5.85; N, 6.6). $\nu_{max}$/cm$^{-1}$ 3156 (C-H aromatic), 2918 and 2848 (C-H aliphatic), 1517 (C=C aromatic), 1353 and 1180 ($[CF_3SO_2]_2N^-$). $\delta_H$ ( 300 MHz; CDCl$_3$): 0.89 (3 H, t, J 6.8, C$H_3$ aliphatic chain) ; 1.27 (16 H, br s, C$H_2$ aliphatic chain) ; 1.40-1.47 (2 H, m, C$H_2$ aliphatic chain) ; 1.79 (2 H, m, O-C$H_2$-C$H_2$) ; 3.96 (2 H, t, J 6.5, OC$H_2$) ; 3.99 (3 H, s, C$H_3$-N) ; 6.94 (2 H, d, J 8.6, CH phenyl) ; 7.12 (1 H, m, CH imidazolium) ; 7.16 (1 H, m, CH imidazolium) ; 7.31 (2 H, d, J 8.6, CH phenyl) ; 8.93 (1 H, s, N-CH-N). $\delta_c$ (75 MHz; CDCl$_3$): 14.04 (C$H_3$ aliphatic chain) ; 22.62 ; 25.95 ; 29.12 ; 29.29 ; 29.34 ; 29.52 ; 29.55 ; 29.58 ; 29.60 ; 31.86 (C$H_2$ aliphatic chain) ; 36.27 (N-C$H_3$) ; 53.15 (N-C$H_2$-Ph) ; 68.15 (O-C$H_2$) ; 115.36 (CH phenyl) ; 119.76 (quadruplet, J= 321.2 Hz, C$F_3$) 121.89 ; 123.70 (CH imidazolium) ; 123.79 (C phenyl) ; 130.48 (CH phenyl) ; 135.63 (N-CH-N) ; 160.20 (C phenyl).

## DOSY NMR $^{1}$H experimental Section

**NMR:** Spectra were recorded on a Bruker Avance500 spectrometer, at 11.7 Tesla, at the resonating frequencies of 500.13 MHz for $^{1}$H. The diffusion NMR experiments were performed with a Pulsed Field Gradient Stimulated Echo sequence, using bipolar gradients.(REF) The bipolar gradient duration and the diffusion time were optimized (respectively 1 ms and 200 ms). The incremented pulsed field gradient was applied linearly between 1 and 50 G/cm. DOSY spectra were generated by the program GIFA 5.2 – DOSY module, developed by the NMRTec company, using adapted algorithms like invert Laplace transform and maximum entropy to build the diffusion dimension.

**Figure S1:** $^{1}$H NMR DOSY spectrum of **1a** at low concentration. All diffusion peaks are centred to 700 $\mu m^{2}.s^{-1}$, implying that the solution contains one type of molecular object. Here, **1a** is free in solution.

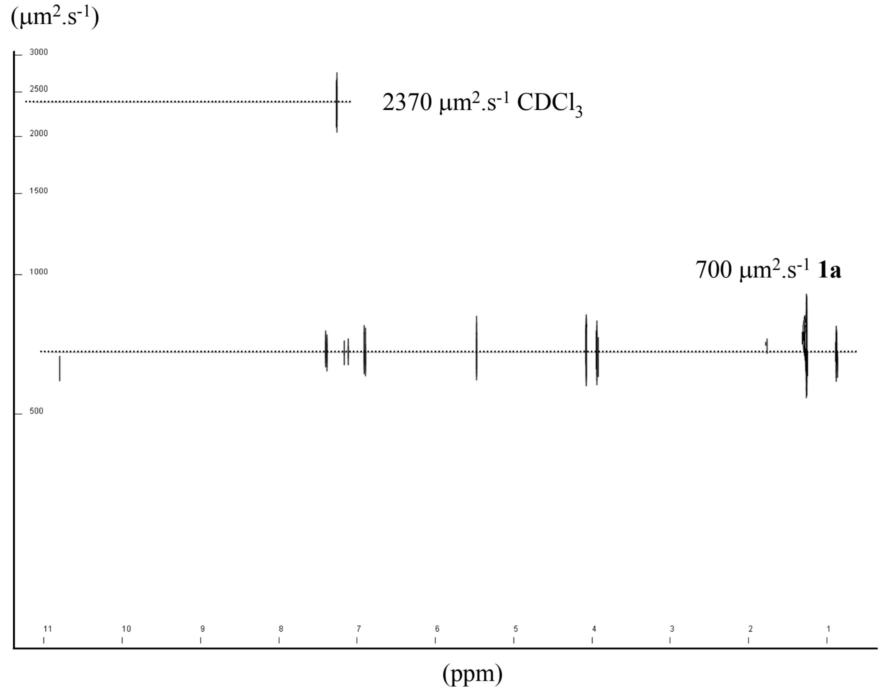
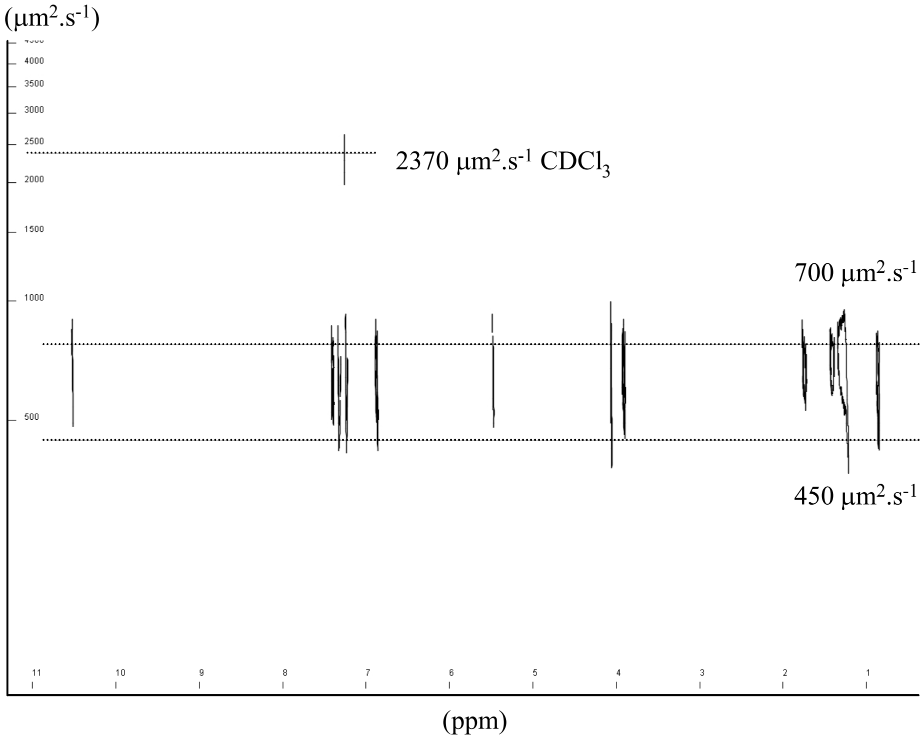


**Figure S2:** $^1$H NMR DOSY spectrum of **1a** at high concentration. Diffusion peaks are spread out from 450 to 700 µm$^2$.s$^{-1}$, implying that the solution contains several types of molecular object, bigger in size than **1a**. The solution is a polydisperse mixture, composed by molecular aggregates.



# Supplementary Material (ESI) for New Journal of Chemistry
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**Mesomorphic Section**

The optical textures of the mesophases were studied with a Leitz polarizing microscope equipped with a Mettler FP80 hot -stage and an FP80 central processor. The transition temperatures and enthalpies were measured by differential scanning calorimetry with a Perkin-Elmer DSC-7 instrument operated at a scanning rate of 5 °C.min$^{-1}$ on heating. The apparatus was calibrated with indium (156.6 °C, 28.4 J.g$^{-1}$) and gallium (29.8 °C) as the standards. The TGA measurements were carried out on a SDTQ 600 apparatus at scanning rate of 10 °C.min$^{-1}$. The transmission Guinier geometry was used for obtain the XRD patterns. In this case, a linear monochromatic Cu-K$\alpha_1$ beam ($\lambda$ = 1.5405 Å) was obtained using a sealed-tube generator (900 W) equipped with a bent quartz monochromator. For all compounds, the crude powder was filled in Lindemann capillaries of 1 mm diameter and the result was recorded on an image plate. In each case, exposure times were varied from 12 to 24 h.

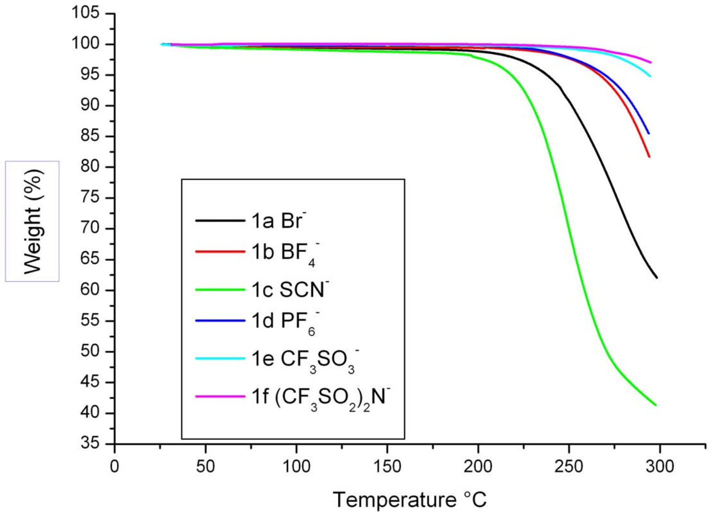
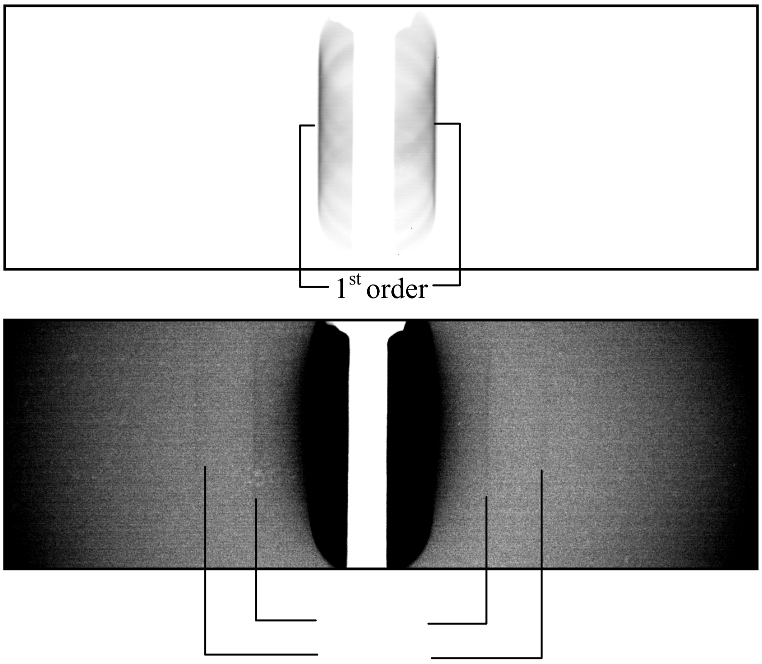


**Figure S3:** TGA measurements of all compounds **1a-f**.



2nd order
3rd order

**Figures S4** top**:** XRD plate image of **1b** ($BF_4^-$); bottom: a more contrasted view of the plate.

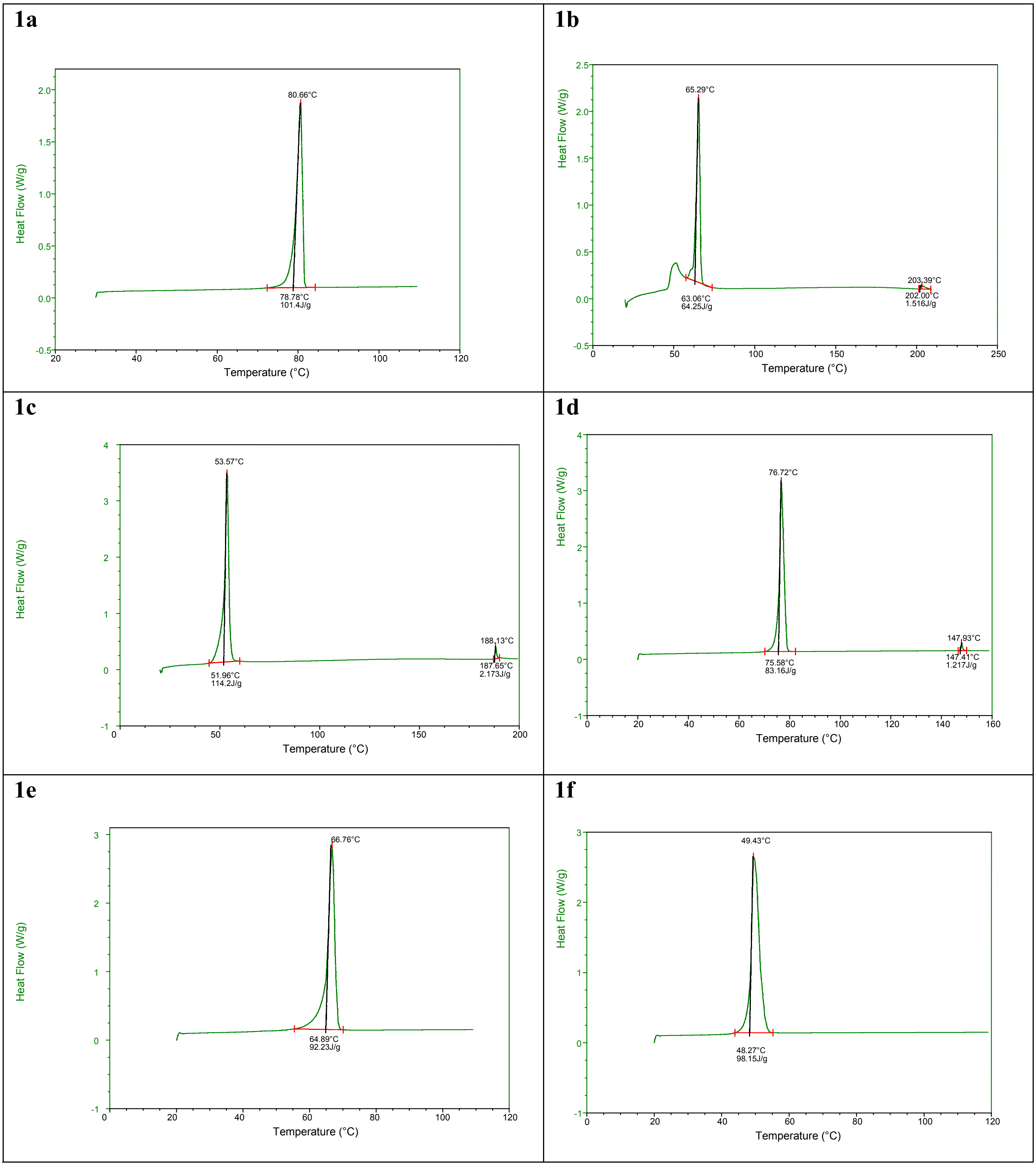


**Figure S5:** DSC thermograms of **1a-1f**. Phase transition temperatures (°C) and corresponding enthalpy (J/g) were measured from the 1st heating cycle, except for the Liquid Crystal-Isotrope transition of **1a**, which has been determined during the TGA experiment.

**Electrochemical Section**

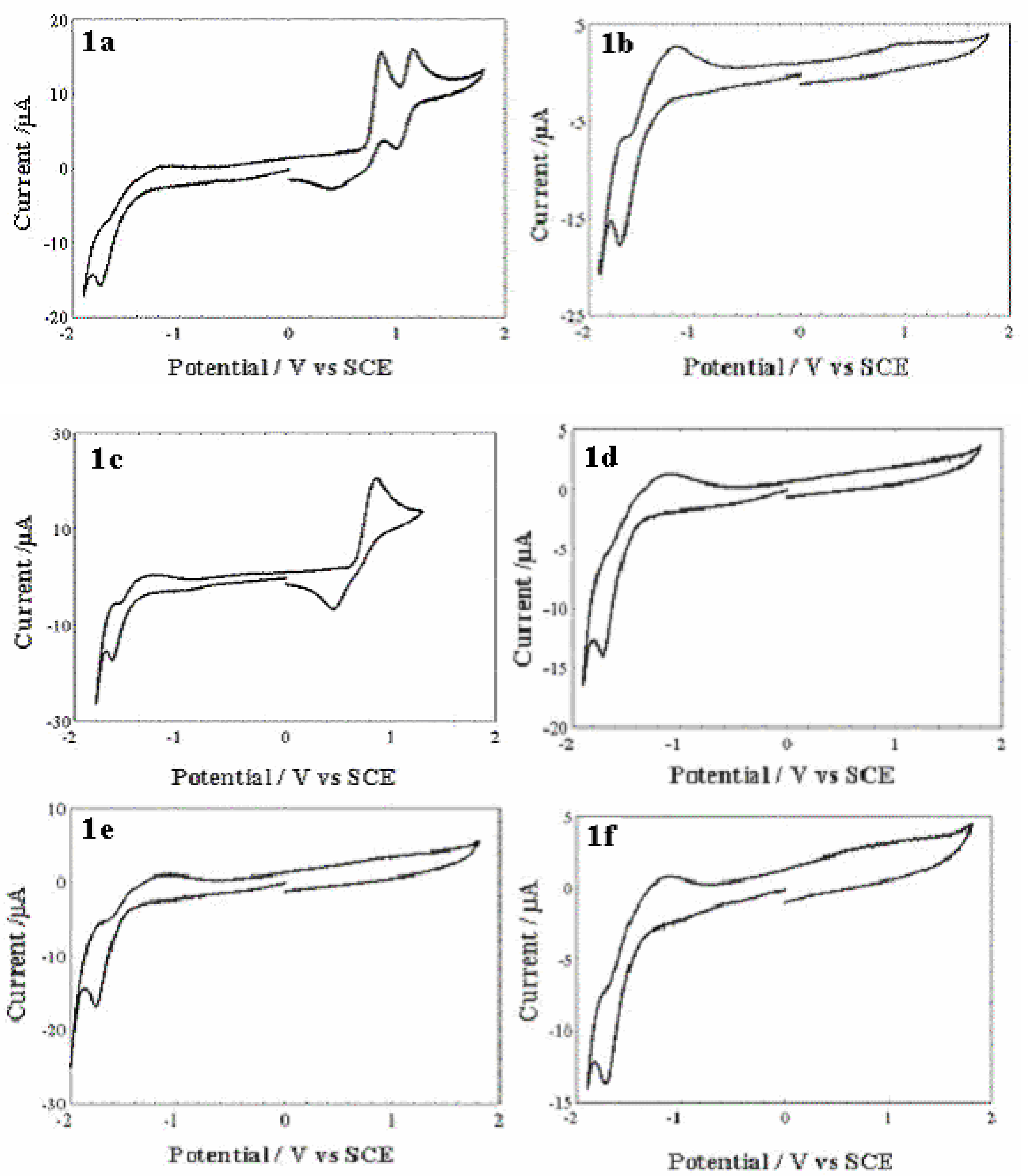


**Figure S6** Cyclic voltammograms of ionic liquids **1a-1f** in $CH_3CN$ (0.1 M $NBu_4PF_6$). Scan rate 100 mV $s^{-1}$.