Electronic Supplementary Material (ESI) for Green Chemistry.

Girard's reagent-based ionic liquids: Synthesis, tuneable thermomorphism and their interaction with metal ions, dyes and carbonyl compounds

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Electronic supplementary information

Unless otherwise stated, all chemicals were purchased from Sigma-Aldrich and used without further purification.

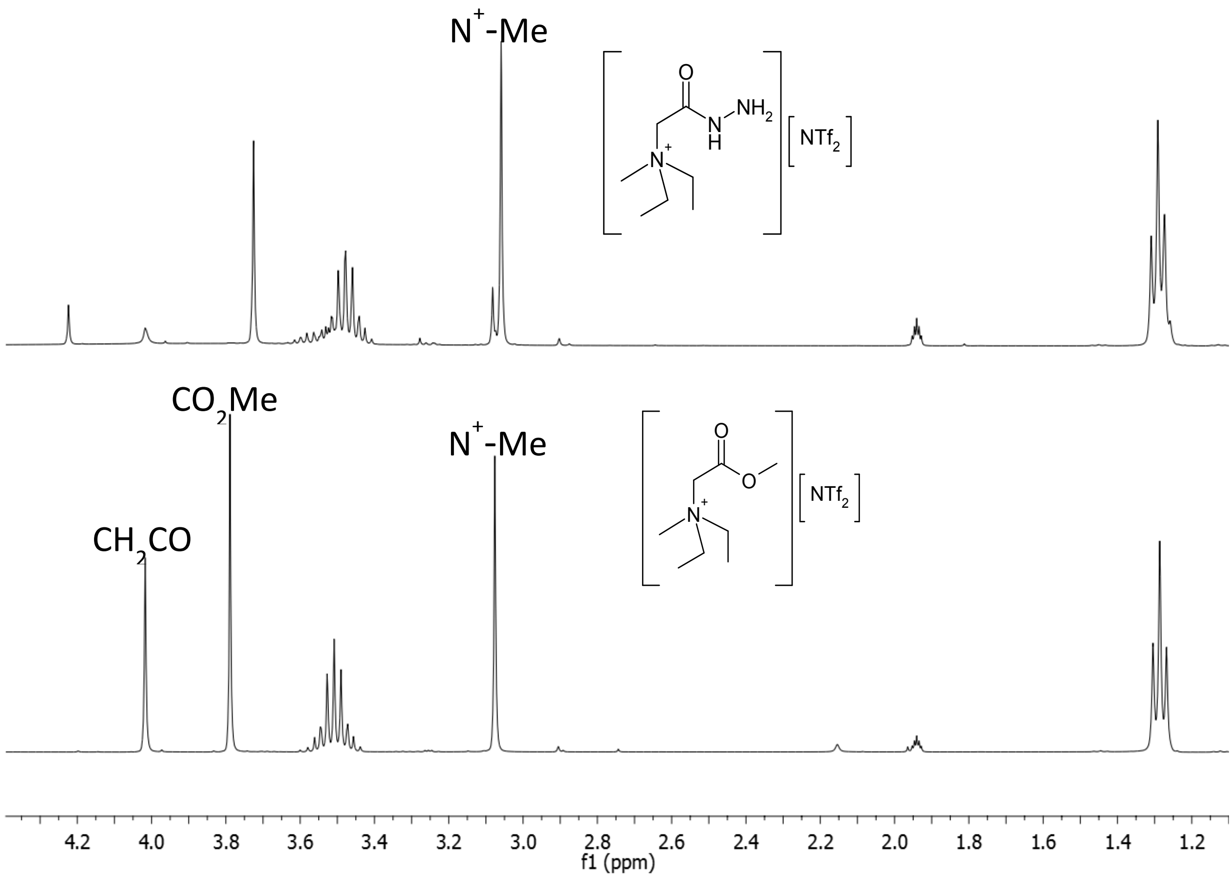
^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 spectrometer (400 MHz). ESMS-mass spectroscopy measurements were carried out on a Waters LCT Premier instrument with an Advion TriVersa NanoMate injection system (cone voltage 50 V, source 120 °C). Both positive and negative ions were detected, with an m/z range of 50 to 1500. Samples were injected as dilute solutions in acetonitrile. All DSC scans were obtained using a TA DSC Q2000 model with a TA Refrigerated Cooling System 90 (RCS) and an autosampler. To obtain DSC traces three cycles were carried out for each sample at a scan rate of 5 ^{o}C per minute. Viscosities were measured using Bohlin Gemini GEM150 Rheometer cone/plate CP 4^{o}/40 mm system with a Peltier heating system. Electronic absorption spectra were obtained using a Perkin Elmer Lamda 950 spectrophotometer using a cuvette with 1 cm path length. Metal analysis was performed using ICP on a Thermo Elemental IRIS Intrepid ICP-OES. The Limits of detection for Ni^{2+}, Cu^{2+}, Co^{2+} and Cr^{3+} on ICP-EOS are 0.001, 0.006, 0.001 and 0.004 ppm, respectively.

Liquid - Liquid equilibrium (LLE)

All cloud-point determinations on the temperature-composition liquid-liquid phase diagrams at a nominal pressure of 0.1 MPa were performed using a dynamic method with visual detection of the solution turbidity. For this purpose, Pyrex glass view cells with magnetic stirring were used. Samples were gravimetrically prepared directly inside the cells using an analytical high precision balance (±0.1 mg). The cells, containing ionic liquids and deionised water, were then immersed in a thermostatic bath. Under continuous stirring, we cooled off or heated the solutions usually in two or three runs with the two last runs being carried out very slowly (the rate of temperature change near the cloud point was no more than 10 $K.h^{-1}$). Beginning in the homogeneous region, upon cooling, the temperature at which the first sign of turbidity appeared was taken as the temperature of the liquid-liquid phase transition.

The overall uncertainty of the transition temperature measurements, resulting from the visual observation of the turbidity (LLE) is estimated to be ± 1 K.

Comparison of ^{1}H NMR (400 MHz) spectra of [$N_{1\,2\,2}CH_2CO_2Me$][NTf_2] and [$N_{1\,2\,2}$hcz][NTf_2] in CD_3CN.



Viscosity data on room temperature Girard's ionic liquids

Viscosity measurements for the room temperature ionic liquids studied were performed between 20 and 76 °C. The temperature dependence of the viscosity for all the studied Girard's ionic liquids is graphically depicted in Fig. 1.

A decrease in viscosity with increasing temperature is observed (see Fig. 1). Such a decrease is more dramatic for ionic liquids of higher viscosity. As usual for other ionic liquids,[1] a viscosity-temperature correlation based on the Vogel-Fülcher-Tammann[2] (VFT) equation is

$$\ln(\eta) = \ln(\eta_o) + {}^{B}/(T - T_o)$$

proposed, where η is the experimental viscosity in cP, T is given in Kelvin, and η_o, B and T_o represent the correlation parameters. The reduction in viscosity with increasing temperature is dramatic, as can be seen in Figure 1.

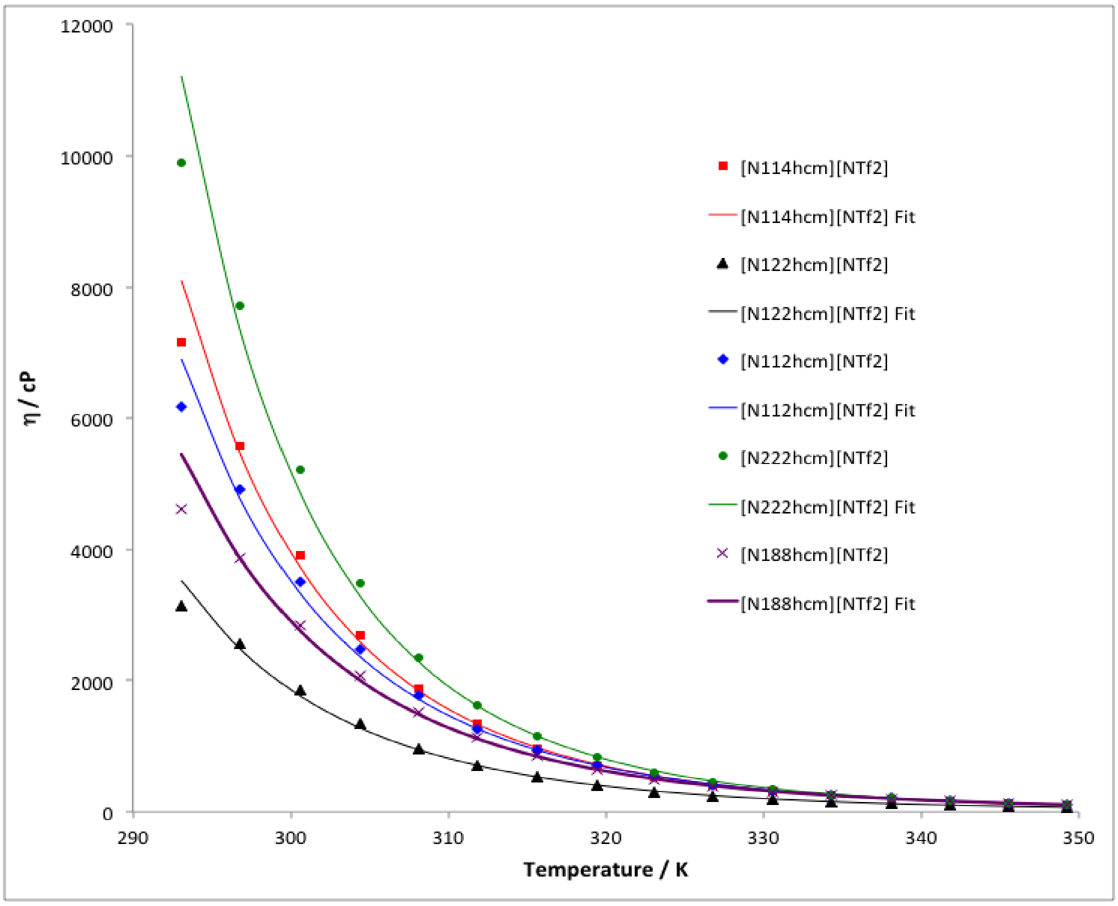


Figure 1: Experimental viscosity data of the studied ionic liquids as a function of the temperature. Fitted VFT lines are shown for each data set.

1 A. A. Fannin, D. A. Floreani, L.A. King, J. S. Landers, B. J. Piersma, D. J. Stech, R. L. Vaughn, J. S. Wilkes and J. L. Williams, *J. Phys. Chem.*, 1984, 88, 2614–2621.

2 G. Tamman and W. Z. Hesse, *Z. Anorg. Allg. Chem.*, 1926, 156, 245–257.

Densities of some Girard ionic liquids (Measured using Mettler Toledo DM40 density meter**)**

Ionic liquid	Density at 25 °C (g cm^{-3})
[$N_{1\,12}$hcm][NTf_2]	1.549
[$N_{1\,2\,2}$hcm][NTf_2]	1.506
[$N_{2\,2\,2}$hcm][NTf_2]	1.488
[$N_{1\,1\,4}$hcm][NTf_2]	1.469

Determination of the electrostatic potential surfaces:

To highlight differences on the structure and charge distribution between the two cations: i.e. the $[C_2mim]^+$ and $[mimhcm]^+$ selected for this study, the same methodology as already presented previously, [i-iii] was used to optimize each structure using firstly the HF/6-311G++(d,p) ab-initio method and then DFT calculations based on the B3LYP method and the DBTZVP basic set within Gaussian version 3.0-D1.[iv] The resultant optimized structure of each cation was then used to generate the COSMO file within the Turbomole program,[v] in this case, using the BP-DFT method and the Ahlrichs-TZVP basic set for all species.[vi]

The sigma profile of each cation reported in Figure 3 (in the main article) was then generated using COSMOthermX software (version 2.1, release 01.08).[vii]

(i) Ab Manan, N.; Hardacre, C.; Jacquemin, J.; Rooney, D.W.; Youngs, *J. Chem. Eng. Data* 2009, **54**, 2005-2022.

(ii) Jacquemin, J.; Bendová, M.; Sedláková, Z.; Blesic, M.; Holbrey, J. D.; Mullan, C.L.; Youngs, T.G.A.; Pison, L.; Wagner, Z.; Aim, K.; *ChemPhysChem*, 2012, **13**, 1825-1835.

(iii) Dougassa, Y.R.; Tessier, C.; El Ouatani, L.; Anouti, M.; Jacquemin, J., *J. Chem. Thermodyn.*, 2013, **61**, 32-44.

(iv) *GaussView, Version 3.0*; Dennington, R.; Keith, T.; Millam, J.; Semichem Inc.: Shawnee Mission, KS, 2000-2003.

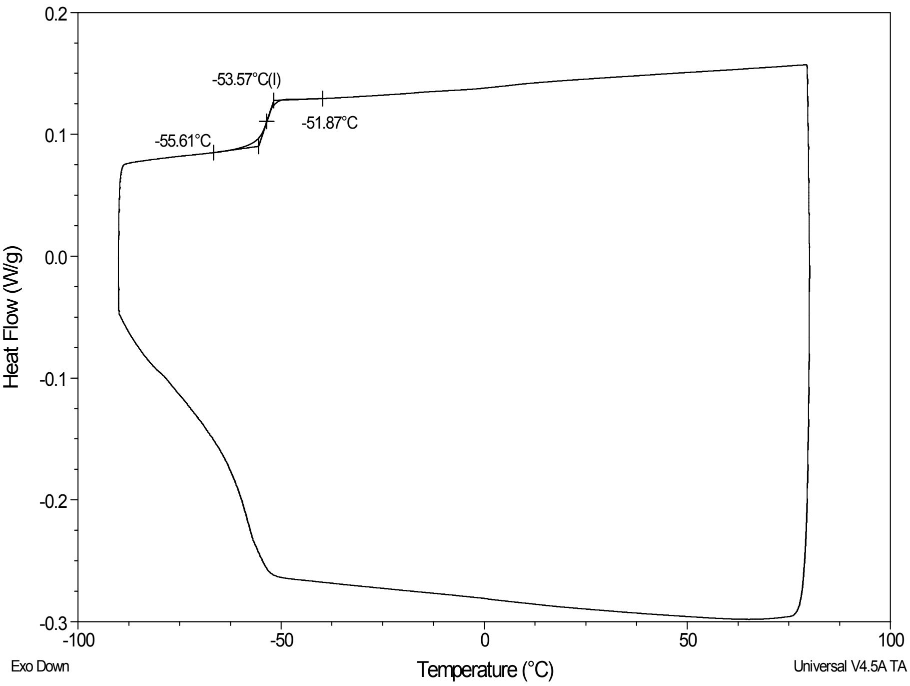
(v) Ahlrichs, R., *TURBOMOLE User's Manual, Version 5.7*; COSMOlogic GmbH & Co. KG: Leverkusen, Germany, 2004.

(vi) Schafer, A.; Huber, C.; Ahlrichs, R., *J. Chem. Phys*. 1994, **100**, 5829-5835.

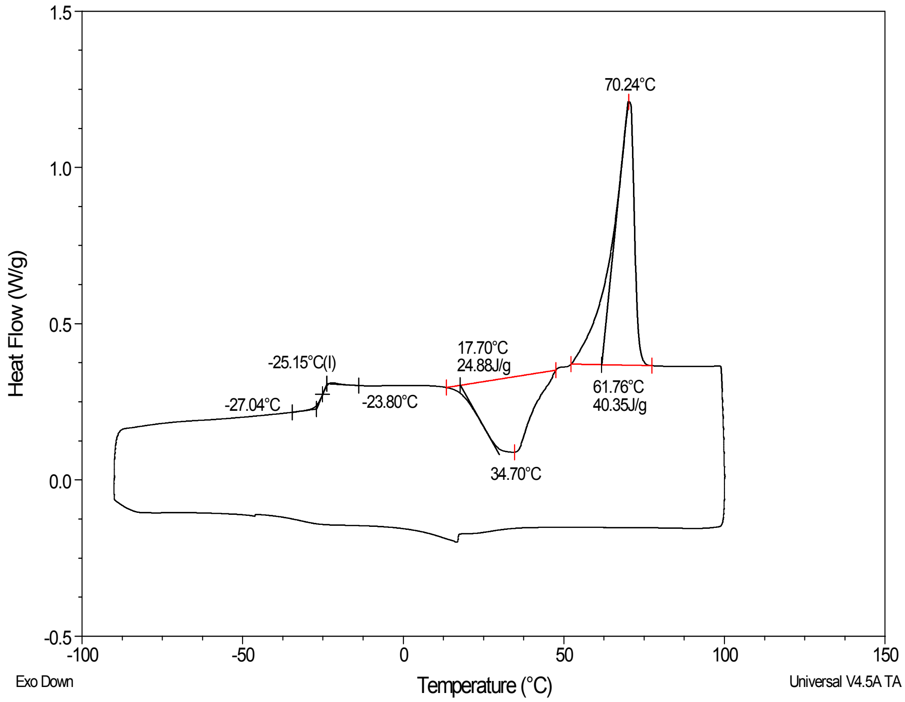
(vii) Eckert, F.; Klamt, A. *COSMOtherm User's Manual, Version C2.1*, Release 01.08; COSMOlogic GmbH & Co. KG: Leverkusen, Germany, 2008.

DSCs of Girard's ionic liquids

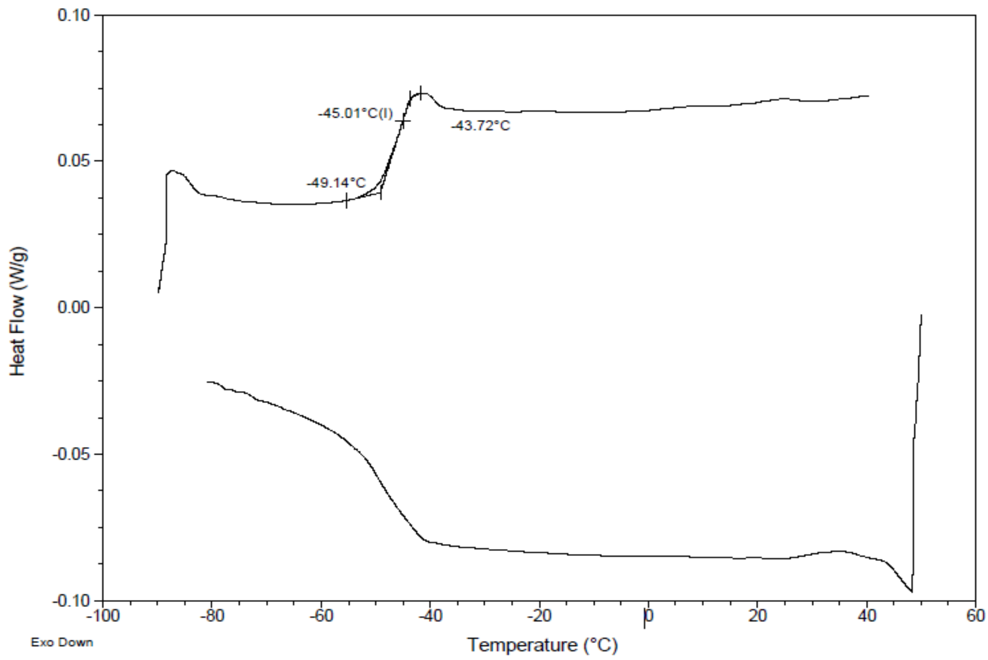
(a) DSC of $[N_{122hcm}][NTf_2]$



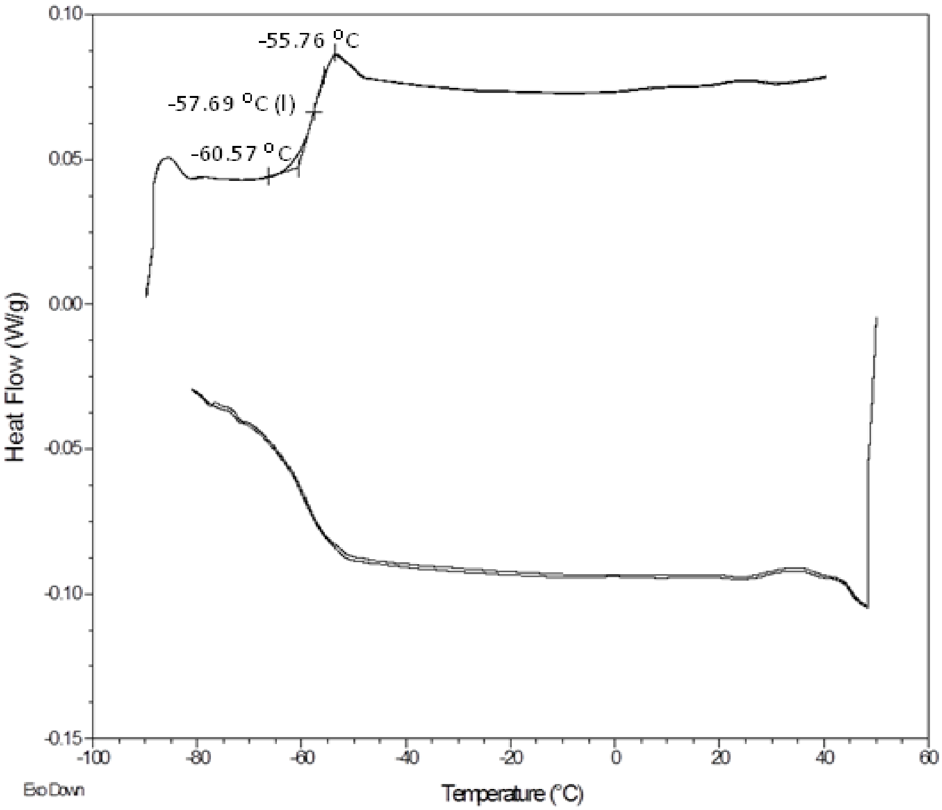
(b) DSC of $[N_{333hcm}][NTf_2]$



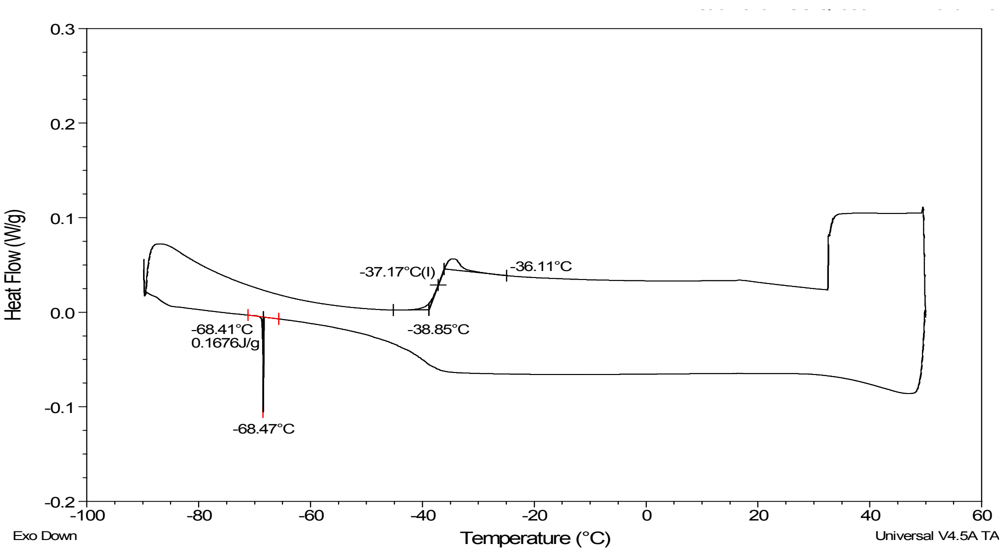
(c) DSC of $[N_{222hcm}][NTf_2]$



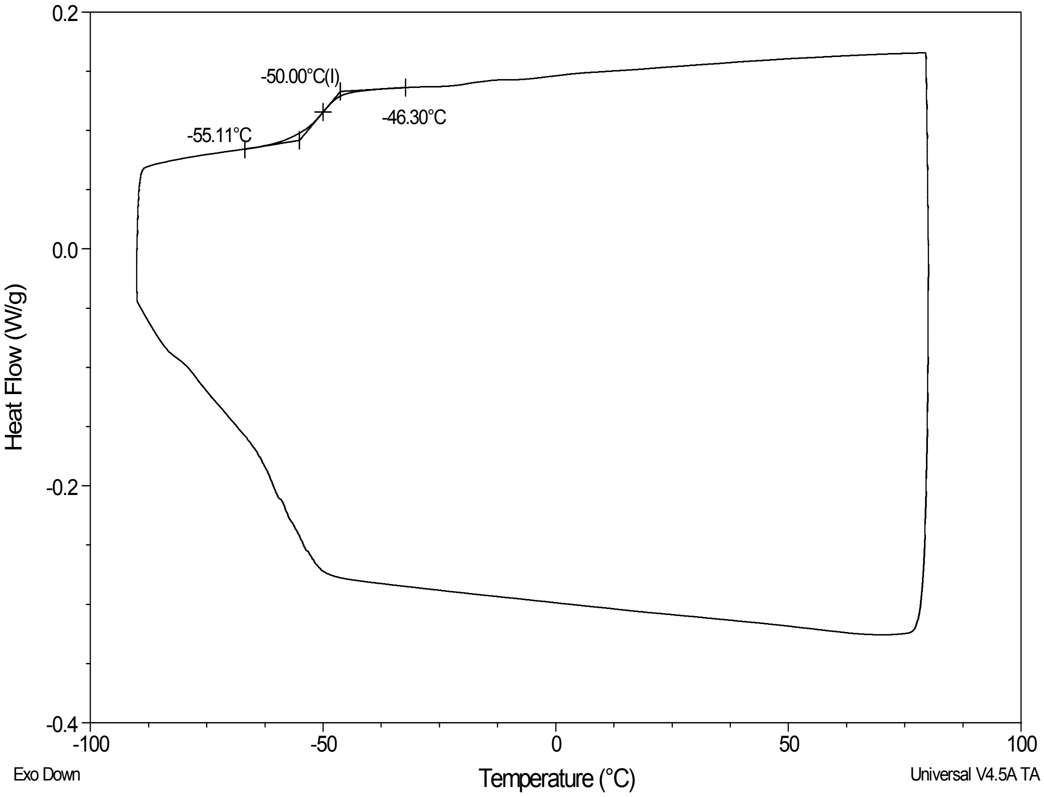
(d) DSC of $[N_{112hcm}][NTf_2]$



(e) DSC of $[mimhcm][NTf_2]$



(f) DSC of $[N188hcm][NTf_2]$


0.2
0.0
-0.2
-0.4
Heat Flow (W/g)
-50.00°C(I)
-55.11°C
-46.30°C
-100
-50
0
50
100
Temperature (°C)
Exo Down
Universal V4.5A TA