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Tuneable thermomorphism and applications of ionic liquid analogues of Girard's reagents

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A series of ionic liquids based on Girard's reagents was synthesised. Their tuneable thermomorphic behaviour with water was demonstrated, and slight modifications in the cationic structure led to drastic changes in their water miscibility. Their phase behaviour, involving monophasic-biphasic transitions, drove a number of practical applications, including scavenging water-soluble dyes and the extraction of metals from water.

Introduction

Girard's reagents are water-soluble salts with melting points close to 200 °C. Introduced in the 1930s,[1,2] they were developed for derivatisation of hydrophobic aldehydes or ketones, to facilitate transfer from an organic medium into an aqueous phase. Thus Girard's reagents enable a reversible derivatisation and hence phase-transfer, permitting selective extraction of aldehydes and ketones from complex mixtures of organic compounds, such as enzymatic broths. The systematic names for the salts, more colloquially known as Girard's reagents, are (hydrazinocarbonylmethyl)trimethylammonium chloride (T) and (hydrazinocarbonylmethyl)pyridinium chloride (P), see Figure 1. We refer to the materials described in this paper as Girard's ionic liquids. Other applications include isolation of keto-steroids and volatile carbonyl compounds from foods, rancid oils and marc spirit (brandy).[3] More recently, Girard's reagents also have been used as scavengers for acyl chlorides,[4] as synthetic building blocks for the preparation of combinatorial libraries,[5] as biopolymeric flocculants,[6] as derivatising agents for LC-MS analysis,[7] and as ligands (either as neat reagents, or as structured derivatives) for complexation with metals,[8] leading to (in some cases) potential therapeutic anti-tumour agents.[9]

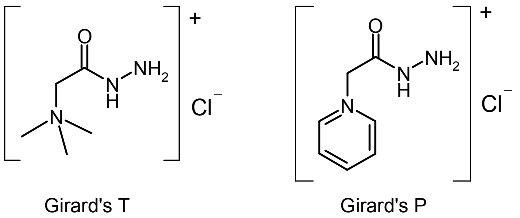


Figure 1: Structures of Girard's reagents, T and P.

The heteroatom-rich polar hydrazide group (-CONHNH$_2$) that exists in Girard's reagents provides an opportunity to create a library of ionic liquids with a range of cationic nitrogenous bases in combination with a variety of anions to impart either hydrophilic or hydrophobic behaviour.[10] The multi-hydrogen bond donor and acceptor ability present in the hydrazide group should show strong affinity towards water or other strongly hydrophilic solvents. In some circumstances, for example, if water-reactive molecules are involved, a desire to avoid the use of an aqueous medium might preclude the use of Girard's reagents. One of the aims of this work was to develop materials that combine the reactive functionality analogous to that of Girard's reagents with properties of an ionic liquid. This has green chemistry principles as a prime driver, since this approach will deliver tuned selectivity, high yields, and recyclable versions Girard's reagents.[11]

Herein, we describe the synthesis of a systematic library of ionic liquids which function as Girard's reagents (see Scheme **1**). In order to achieve a versatile synthetic approach combined with relatively cheap and available reagents, the work described has focussed on replacements for Girard's-T. Of course, it would be possible and straightforward to create a library of Girard's-P analogues (and indeed for potential reagents based on any other N-heterocycles), but here we have confined ourselves to demonstrating proof-of-principle, reagent versatility, and some unpredicted and fascinating properties of this class of reagent. Their phase behaviour with water was examined, their application for scavenging undesirable water-soluble aldehydes was investigated, and a process for removing residual dyes and metal ions from water was also demonstrated.

Experimental

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 (see ESI for details).

General synthesis of chloride ionic liquids

To a solution of the appropriate trialkylamine or *N*-methylimidazole (60 mmol) in methanol (15 cm^3), placed in a round-bottomed flask, methyl chloroethanoate (60 mmol) was slowly added dropwise. The reaction mixture was then stirred at room temperature overnight. After removing the methanol under reduced pressure, precursors (**1**) were isolated in near quantitative yield as pale yellow solids. In the specific case of the reaction with relatively unreactive methyldioctylamine, it was necessary to use methyl bromoethanoate in place of methyl chloroethanoate.

Metathesis with Li[NTf₂]

The methylene ester precursors (**1;** 50 mmol) in dichloromethane (100 cm^3) were shaken with $Li[N(SO_2CF_3)_2]$ (51 mmol) in water (10 cm^3) and the organic layer separated and dried over anhydrous magnesium sulfate. The CH_2Cl_2 layer was decanted passed through a short silica plug, and the solvent the removed *in vacuo* to yield the bistriflamide ionic liquids (**2**). A slightly different procedure was used for methylimidazolium derivative; it was dissolved in methanol with an equimolar quantity of $Li[NTf_2]$, and then the methanol was removed *in vacuo*, and CH_2Cl_2 (50 cm^3) was added followed by stirring. The precipitated solid was collected by filtration through a short silica plug.

Amidation with hydrazine hydrate

Compounds (**2**) were dissolved in methanol (10 cm^3) and treated with $NH_2NH_2.H_2O$ (51 mmol) at room temperature overnight. Methanol, excess hydrazine, and water were removed under reduced pressure to yield viscous liquids (**3**), in near quantitative yields, except $[N_{3\,3\,3\,hcm}][NTf_2]$. These ionic liquids were dried at ~2 mbar at 50 °C, overnight.

As expected, in the NMR spectra of all compounds, rotational isomers were seen owing to restricted rotation about the amide bond. Multiple peaks were observed in both ^1H and ^{13}C NMR spectra, with one rotamer dominating.

Spectroscopic data for bistriflamide ionic liquids (3)

$[N_{1\,1\,2\,hcm}][NTf_2]$

^1H-NMR (CD_3CN, 400 MHz): δ/ppm 4.25, 3.75(s, 2H, $\mathbf{CH_2}$CO), 3.57, 3.49(2q, 2H, $\mathbf{CH_2}CH_3$), 3.14, 3.12(2s, 6H, $N(\mathbf{CH_3})_2$), 1.31, 1.23(2t, 3H, $CH_2\mathbf{CH_3}$).

^{13}C NMR (CD_3CN): δ/ppm 168.2, 163.5. 120.9 (q, NTf_2), 62.6, 62, 61.9, 52.3, 48.

ES-MS(CH_3CN): **cation**; $[M]^+$ calculated: 146.1293, found 146.1293; **anion**; calculated: 279.9173, found: 279.9169.

$[N_{1\,2\,2\,hcm}][NTf_2]$

^1H-NMR (CD_3CN, 400 MHz): δ/ppm 3.79, 3.73 (s, 2H, $\mathbf{CH_2}$CO), 3.6-3.41(m, 4H, $\mathbf{CH_2}CH_3$), 3.08, 3.06 (N-$\mathbf{CH_3}$), 1.29 (t, 3H, $CH_2\mathbf{CH_3}$)

^{13}C: δ/ppm 166.8, 162, 118.6 (q, NTf_2), 58.1, 57.9, 57.6, 56.0, 47.9, 7.0

ESMS: **cation**; $[M]^+$ calculated: 231.11335, found: 231.1132; **anion**; calculated: 279.9173, found. 279.9177

$[N_{2\,2\,2\,hcm}][NTf_2]$

^1H-NMR (CD_3CN, 400 MHz): δ 4.21, 3.72(2s, 2H, $\mathbf{CH_2}$CO), 3.60-3.45(m, 6H, 3 N$\mathbf{CH_2}CH_3$), 1.29(t, 9H, 3 $CH_2\mathbf{CH_3}$)

^{13}C-NMR: 168.1, 163.4, 120.9(q, NTf_2), 56.1, 55.6, 55.1, 8.0

ESMS: **cation**; $[M]^+$ calculated: 174.1606, found: 174.1606; **anion**; calculated: 279.9173, found: 279.9184.

$[N_{1\,1\,4\,hcm}][NTf_2]$

^1H-NMR ($CDCl_3$ + 1 drop CD_3CN, 400 MHz): δ 3.93, 4.10(s, 2H, $\mathbf{CH_2}$CO), 3.53(m, 2H, N$\mathbf{CH_2}CH_2$), 3.25, 3.22(s, 3H, N-$\mathbf{CH_3}$), 1.72(brm, 2H, $NCH_2\mathbf{CH_2}$), 1.39(m, 2H, $CH_2\mathbf{CH_2}CH_3$), 0.99(t, 3H, $CH_2\mathbf{CH_3}$).

^{13}C-NMR: 167, 162.3, 119.6(q, NTf_2), 66, 65.3, 61.4, 60.3, 51.8, 24.3, 19.2, 13.1

ESMS: **cation**; $[M]^+$ calculated: 174.1606, found: 174.1609; **anion**; calculated: 279.9173, found: 279.9181.

$[N_{3\,3\,3\,hcm}][NTf_2]$

^1H-NMR (CD_3CN, 400 MHz): δ 3.82,3.75(s, 2H, $\mathbf{CH_2}$CO), 3.44-3.32(m, 6H, 3x$\mathbf{CH_2}$), 1.73(brm, 6H, 3x$\mathbf{CH_2}CH_2$N), 0.98(t, 9H, 3x$\mathbf{CH_3}$).

^{13}C: 167.2, 162.42, 119.7(q, NTf_2), 62.0, 61.9, 56.5, 15.7, 10.4

ESMS: **cation**; $[M]^+$ calculated: 216.2076, found: 216.2066; **anion**; calculated: 279.9173, found: 279.9185.

$[N_{1\,8\,8\,hcm}][NTf_2]$

^1H-NMR ($CDCl_3$, 400 MHz): δ 3.98(s, 2H, $\mathbf{CH_2}$CO), 3.46(m, 4H, 2x$\mathbf{CH_2}$), 3.18(s, 3H, $\mathbf{CH_3}$-N), 1.70(brm, 4H, 2x$\mathbf{CH_2}CH_2$N), 1.32(brm, 20H, 5x$\mathbf{CH_2}$,), 0.88(t, 6H, 2x$\mathbf{CH_3}$).

^{13}C: 162.2, 119.7(q, NTf_2), 63.3, 59.5, 49.4, 31.5, 28.9, 28.8, 26.1, 22.5, 22.3, 14.0

ESMS: **cation**; $[M]^+$ calculated: 328.3328, found: 328.3332; **anion**; calculated: 279.9173, found: 279.9179.

$[mimhcm][NTf_2]$

^1H-NMR (CD_3CN, 400 MHz): δ 8.52, 8.46(s, 1H, C_2H-Im), 7.39, 7.36(s, 2H, C_4H & C_5H-Im), 5.52, 4.81(s, 2H, $\mathbf{CH_2}$CO), 3.89(s, 3H, N$\mathbf{CH_3}$)

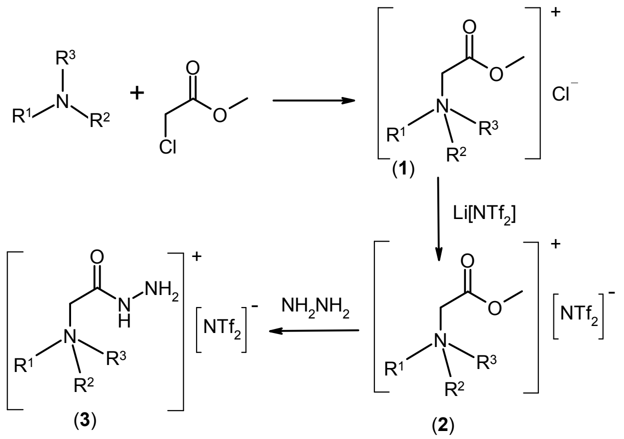
^{13}C: 169.7, 165.3, 138.3, 138.1, 125, 124.6, 124.3, 124, 120.9(q, NTf_2), 50.9, 50.7

ESMS: **cation**; $[M]^+$ calculated: 155.0933, found: 155.0928; **anion**; calculated: 279.9173, found: 279.9186.

Results and discussion

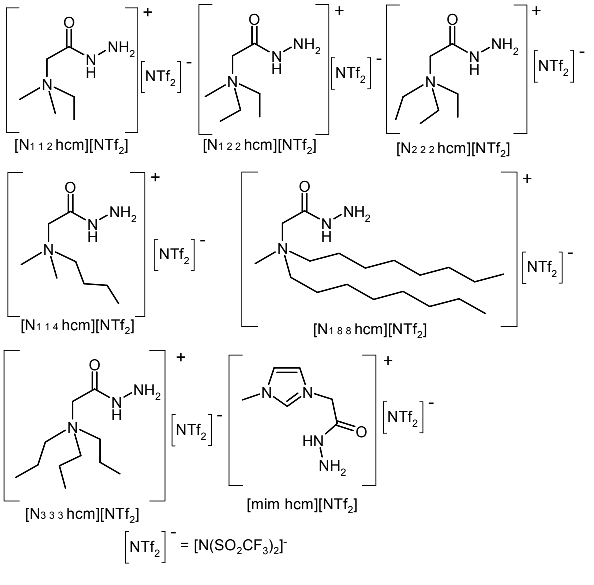
Synthesis of Girard's ionic liquids

The appropriate trialkylamines, $N_{x\,y\,z}$, were treated with methyl chloroethanoate to obtain trialkyl(methylenecarboxymethyl)ammonium chloride (**1**; [N$_{x\,y\,z\,\mathrm{CH2CO2Me}}$]Cl), which were then subjected to metathesis with aqueous lithium bis{(trifluoromethyl)sulfonyl}amide (Li[NTf$_2$]; lithium bistriflamide) to furnish (**2**; [N$_{x\,y\,z\,\mathrm{CH2CO2Me}}$][NTf$_2$]). Compounds (**2**) were treated with hydrazine hydrate to result in the required ionic liquids (**3; **[N$_{x\,y\,z\,\mathrm{hcm}}$][NTf$_2$]). A single example of a Girard's-P analogue was prepared by a parallel route, starting with 1-methylimidazole (mim) and yielding [mimhcm][NTf$_2$]).



Scheme 1: Reaction scheme for the synthesis of ionic liquid analogues of Girard's reagent-T.

A total of seven ionic liquids were prepared as bistriflamide salts (see Scheme 2). Except [N$_{3\,3\,3\,\mathrm{hcm}}$][NTf$_2$], all others were room temperature ionic liquids with melting points in the range, -55 °C to -36 °C.



Scheme 2: A library of ionic liquids presented in this work.

Spectroscopic characterisation of the bistriflamide ionic liquids

In all cases, the ES-MS confirmed the expected identity of the cations and anions in the ionic liquids. In contrast, the proton NMR spectra of these materials contained features worthy of discussion. All the proton NMR spectra showed the presence of two structurally related molecules, with differing relative intensities according to the nature of the cation. This is due to the existence of restricted rotation about the C(O)-N bond, which occurs in every salt (Figure 2). Density functional calculations reveal that the π-electron density from the C=O group has delocalised into the C-N π-system, reducing the Mulliken bond order for the C=O group to 1.8 {r(CO)=1.225 Å} and increasing the Mulliken bond order for the C-N group to 1.12 {r(CN)=1.351Å}. It is this double bond character which gives rise to restricted rotation about the C-N bond, and the observation of two rotamers on the NMR time scale. In every case, there was a major (**1**) and minor (**2**) rotamer which is illustrated in Figure 2 for [N$_{1\,2\,2\,\mathrm{hcm}}$][NTf$_2$]. The major isomer (**1**) is stabilised by the weak interactions between the NH$_2$ protons and the carbonyl oxygen atom.

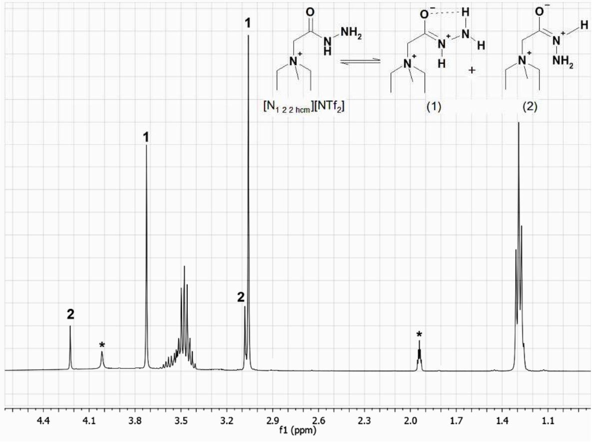


Figure 2: ^{1}H NMR spectrum of [N$_{1\,2\,2\,\mathrm{hcm}}$][NTf$_2$] in CD$_3$CN; major and minor isomers (**1**) and (**2**) are shown on the spectrum and the * denotes solvent residual peaks.

Phase behaviour of [N$_{x\,y\,z\,\mathrm{hcm}}$][NTf$_2$] with water

The application of (ionic liquid-water) systems in separation technology requires knowledge of phase behaviour. This has led to a significant number of articles published on water solubility and phase behaviour.[12-20] Some of the aforementioned publications offer a systematic study on phase behaviour of commercially available hydrophobic bistriflamide ionic liquids with phosphonium,[18] imidazolium,[20] pyridinium,[13b] piperidinium, or pyrrolidinium cations;[13c] however, only a few articles report the phase behaviour of functionalised bistriflamide ionic liquids (with betaine or cholinium cations).[21,22] All report the very common upper critical solution temperature (UCST) behaviour, usually with a high asymmetry centred in the low ionic liquid concentration region. To date, only two (ionic liquid-water) systems are known with the opposite behaviour, showing a lower critical solution temperature (LCST).[23,24]

The phase behaviour of ([N$_{x\,y\,z\,\mathrm{hcm}}$][NTf$_2$]-water) mixtures was studied and temperature-composition (T-χ) phase diagrams were measured through cloud-point temperature determination. As expected, all the systems studied revealed USCT behaviour (Figure 2). But, of more interest, the solubility of these ionic liquids in water can be tuned by varying the length and the structure of the alkyl chains attached to the cation, despite the fact that they are all paired with the same hydrophobic bistriflamide anion. Thus, [N$_{1\,8\,8\,\mathrm{hcm}}$][NTf$_2$] has a significantly lower solubility in water compared to the other members of the family and is almost water immiscible, as it contains the most hydrophobic cation (with two octyl chains). Conversely, no phase splitting could be found in the [mimhcm][NTf$_2$]–water system, even at temperatures close to the freezing point of water. This is one of the rare examples of a bistriflamide ionic liquid that is water miscible at room temperature, at all compositions. In stark contrast, the related [C$_2$mim][NTf$_2$] dissolves water up to χ_{w}= 0.3, whereas it only dissolves in water up to χ_{IL}= 8×10^{-4} at 25 °C.[25] This remarkable behaviour must be attributable to the two hydrogen-bond acceptors and three hydrogen-bond donors in the hydrazide functionality (see Figure 3b). The comparison with the electrostatic potential of the [C$_2$mim]$^+$ cation is shown in Figure 3a). The ability of [mimhmc] cation to form hydrogen-bonds can be clearly visualised by polarisation charge profile and sigma potential as given in Figure 3b. It should be noticed that peaks beyond σ = 0.01/e A^{-2} correspond to hydrogen bond acceptors, while peaks below σ = -0.01/e A^{-2} correspond to hydrogen bond donor. For the other studied ionic liquids, namely [N$_{1\,1\,2\,\mathrm{hcm}}$][NTf$_2$], [N$_{1\,2\,2\,\mathrm{hcm}}$][NTf$_2$], [N$_{2\,2\,2\,\mathrm{hcm}}$][NTf$_2$] and [N$_{1\,1\,4\,\mathrm{hcm}}$][NTf$_2$], the immiscibility envelopes (defined by the binodal curves; see Figure 2) were strongly influenced by the total number of carbon atoms in the alkyl chains, and their distribution. Thus, increasing the number of carbon atoms in the alkyl chains of the cations leads to an increase in critical temperature, and to a decrease in the critical composition. Interestingly, if the two structural isomers [N$_{2\,2\,2\,\mathrm{hcm}}$][NTf$_2$] and [N$_{1\,1\,4\,\mathrm{hcm}}$][NTf$_2$] (both having the same total number of carbon atoms in the alkyl chains) are compared, their UCST behaviour is markedly different. A reasonable explanation for the difference is that closer packing of alkyl chains in [N$_{2\,2\,2\,\mathrm{hcm}}$]$^+$ and formation of van der Waals contacts between the chains, create a smaller cavity in the water, and hence decrease the number of water molecules forced to be in contact with hydrophobic chains. This eventually diminishes hydrophobic effect and gives higher water miscibility compering to the [N$_{1\,1\,4\,\mathrm{hcm}}$]$^+$.[26] It is also plausible that steric factors around the cation or stronger short-range interactions between longer and more flexible butyl chains from two neighbouring cations could also account for the variation in UCST and phase composition observed here.

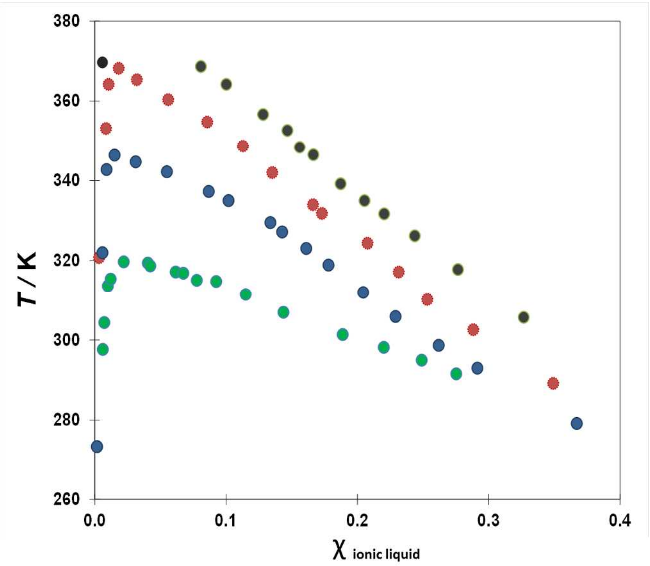


Figure 2: Cloud-point temperature, T, as a function of composition (mole fraction, $\chi_{\text{ionic liquid}}$) of ● [N$_{1\,1\,4\,\mathrm{hcm}}$][NTf$_2$], ● [N$_{2\,2\,2\,\mathrm{hcm}}$][NTf$_2$], ● [N$_{1\,2\,2\,\mathrm{hcm}}$][NTf$_2$], and ● [N$_{1\,1\,2\,\mathrm{hcm}}$][NTf$_2$] ionic liquids in water. Immiscibility regions are located below the curves.

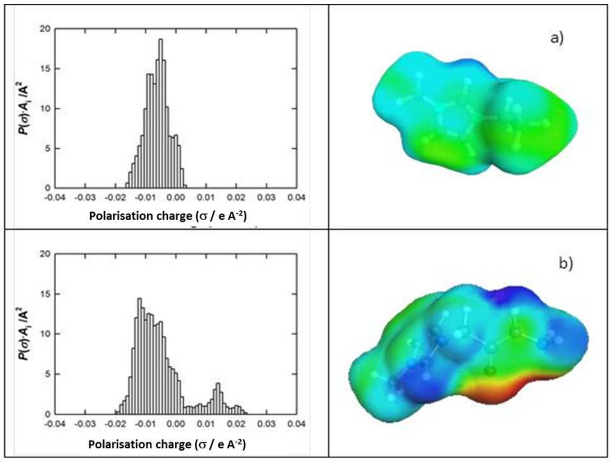


Figure 3: Electrostatic potential surfaces (calculated using DFT (B3LYP; 6-31G*) for (a) [C$_2$mim]$^+$ and (b) [mimhcm]$^+$, (blue is most positive, and red is most negative).

Removal of water soluble dyes with Girard's ionic liquids

The property of these systems to show a UCST and form a single phase at relatively low temperatures, below 50 °C for the system ([N$_{1\,1\,2\,\mathrm{hcm}}$][NTf$_2$] + water), was successfully applied to an extraction process. This was demonstrated by gently heating, to 60 ºC, an aqueous solution of Rhodamine B with [N$_{2\,2\,2\,\mathrm{hcm}}$][NTf$_2$] until the phases merged. Upon cooling, the dye completely transferred to the ionic liquid phase, leaving the aqueous phase nearly colourless. The electronic absorption spectra of the aqueous layers before and after treating with the ionic liquid clearly substantiate the dye transport phenomenon (see Figure 4, inset). Thus, this novel thermomorphic process completely eliminates the requirement for high stirring rate in order to enhance contact between two phases.

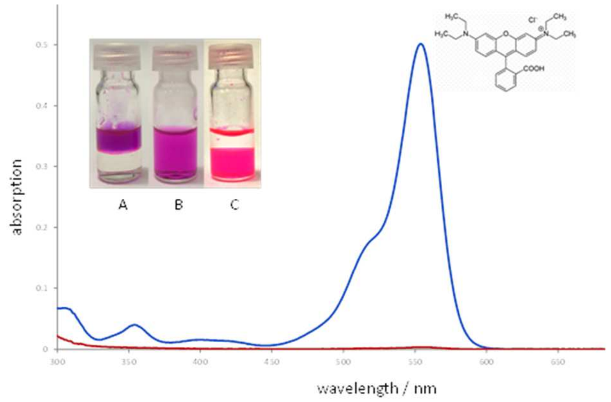


Figure 4: Electronic absorption spectra of an aqueous Rhodamine B solution before (blue) and after (red) treating with $[N_{2\,2\,2\,hcm}][NTf_2]$. The photographs (inset) illustrate **A**: aqueous dye and ionic liquid before mixing/heating; **B**: the homogeneous mixed phase after heating to 60 °C; and **C**: the two-phase separation after cooling, whence the dye has been transported into the ionic liquid. In both A and C, the aqueous phase forms the upper layer.

Presumably, the transport of the dye from water to the ionic liquid occurs *via* the carboxylic acid functionality of Rhodamine B interacting with the hydrazide group of the ionic liquid. Acidification of the ionic liquid with $HN(SO_2CF_3)_2$ repelled the dye back to water. Rogers' group and others reported the transport of triphenylmethane-based dyes from water into different classes of ionic liquids *via* differing mechanisms and in some cases with the aid of a dispersing co-solvent was required.[27] A similar extraction of methyl red or fluorescein dyes from water to most of the ionic liquids included in Scheme 2, except [mimhcm][NTf_2], could be performed efficiently. In a related study, the interaction between fluorescein and $[N_{1\,8\,8\,hcm}][NTf_2]$ is evident in the ^1H NMR spectra of a mixture of the two in dmso-d_6 (see Figure 5). All aromatic signals belonging to fluorescein are shifted up-field, albeit by small but significant shifts, due to weak acid (dye)-weak base (ionic liquid) interactions leading to more ionised carboxylate-like character of the dye.

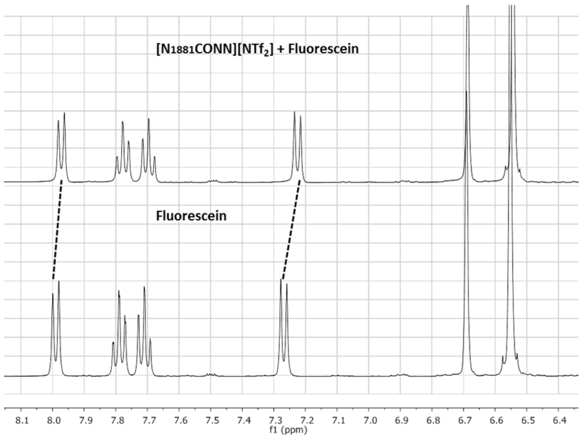


Figure 5: Partial ^1H NMR (400 MHz; dmso-d_6) spectra of: (a) $[N_{1\,8\,8\,hcm}][NTf_2]$ and fluorescein (2:1 molar ratio), and (b) fluorescein.

Scavenging metal ions from water

Since the first report in 1998,[28] ionic liquids have been studied as alternative and potentially environmentally-friendly extractants in hydrometallurgy, and for metal separations. Studies include cobalt/nickel separation,[29] gold/platinum separation,[30] lanthanide extractions,[31] and the use of functionalised ionic liquids for extraction of mercury(II) from aqueous solutions.[32] Many different strategies for metal extraction have already been applied (*e.g.* adding extracting agents to the ionic liquid phase,[33] or anchoring the coordinating moiety to either the anion[34] or cation[35] of the ionic liquid), with mixed success.

To investigate the viability of the Girard's ionic liquids as metal complexing reagents or extractants, four common metal ions, *viz* $[Ni(OH_2)_6]^{2+}$, $[Co(OH_2)_6]^{2+}$, $[Cu(OH_2)_6]^{2+}$ and $[Cr(OH_2)_6]^{3+}$, were studied. In order to determine the distribution coefficients, an aqueous solution of approximately 10 mmol l^{-1} of the metal salt {in this case $Ni(CH_3CO_2)_2{\cdot}6H_2O$, $Co(CH_3CO_2)_2{\cdot}6H_2O$, $Cu(CH_3CO_2)_2{\cdot}4H_2O$ or $Cr(NO_3)_3{\cdot}9H_2O$} was stirred together with the ionic liquid in the homogeneous phase for 20 min at 60 °C. After leaving the mixture to cool and to phase-separate, the metal content of the aqueous phase was analysed by ICP. The distribution coefficients for the metals D_M were calculated using the following equation, Eq. (1):

$$D_\mathrm{M} = \frac{[\mathrm{M}]_0 - [\mathrm{M}]_\mathrm{aq}}{[\mathrm{M}]_\mathrm{aq}} \qquad (1)$$

where $[M]_0$ is the initial concentration of the metal in the aqueous phase and $[M]_{aq}$ the concentration of the metal in the aqueous phase after extraction (see Table 1).

Table 1: Metal concentrations (in ppm) in the aqueous phase before and after extraction with $[N_{2\,2\,2\,hcm}][NTf_2]$ and their distribution coefficients D_M. at 20 °C

Metal ion	Conc. before extraction / ppm	Conc. after extraction / ppm	Distribution coefficient D_M
$[Ni(OH_2)_6]^{2+}$	685.5	0.893	767
$[Cu(OH_2)_6]^{2+}$	657.5	0.023	28586
$[Co(OH_2)_6]^{2+}$	673.0	18.36	36
$[Cr(OH_2)_6]^{3+}$	478.2	75.27	5.4

These data reflect the classical roots of coordination chemistry. The low value of the distribution coefficient of $[Cr(OH_2)_6]^{3+}$ is well understood in terms of the kinetic inertness of the low-spin d^3 electronic configuration in an octahedral ligand field.[36] For the more labile complexes in the 2+ oxidation state, the order of distribution coefficients was Cu(II) >> Ni(II) > Co(II). This is a reflection of the well-known Irving-Williams series.[37] This behaviour, coupled with the electrostatic potential surface for $[N_{2\,2\,2\,hcm}][NTf_2]$, strongly suggests that the functionalised cation behaves as a bidentate chelating ligand to the metal centre (see Figure 7).

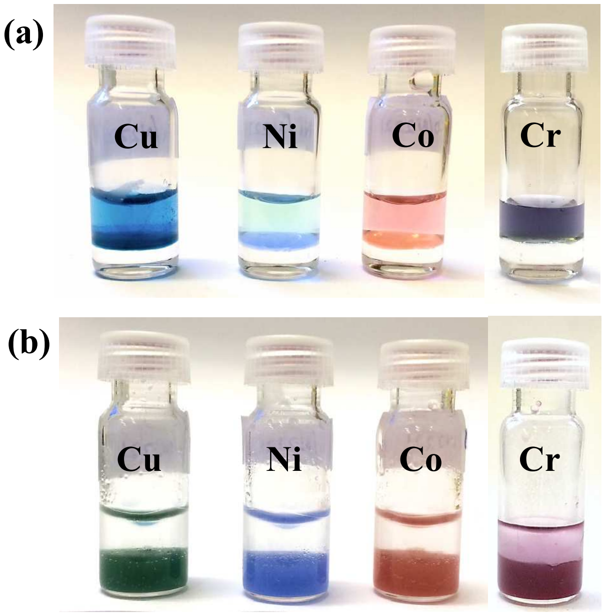


Figure 6: Metal extraction of an aqueous solution of metal salts ($[Ni(OH_2)_6]^{2+}$, $[Co(OH_2)_6]^{2+}$, $[Cu(OH_2)_6]^{2+}$ and $[Cr(OH_2)_6]^{3+}$) into $[N_{2\,2\,2\,hcm}][NTf_2]$; (a) before extraction, and (b) after mixing and extraction. The aqueous phase forms the upper layer, in all cases.

Along with the extracted cation, it is likely that the anions associated with the metal ion are extracted into the ionic liquid. The metals can be transferred back into the aqueous phase by acidification, which was demonstrated for nickel(II), leading to an instant stripping of >95 % of the nickel(II) back into the aqueous phase in one step. The precise stoicheiometries of the formed complexes, the ideal stripping conditions, as well as the pH and concentration dependencies of the distribution coefficients are under current investigation.

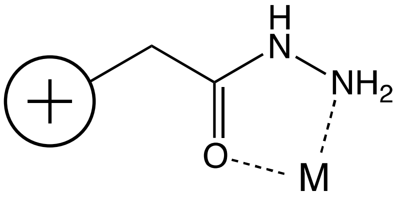


Figure 7: Suggested coordination mode of the functionalised ionic liquid to a metal centre.

It is noteworthy that in these applications, the viscosity and the density of Girard ionic liquids could play a significant role. The viscosities of these ionic liquids are relatively high (> 1000 *cP* at 25 ^{o}C) but manageable for both applications (see ESI for viscosity and density data).

Summary

Custom-designed ionic liquids based on Girard's reagent, containing a hydrazinocarbonyl functionality, $NH_2NHC(O)$-, have been prepared in near quantitative yields, and characterised. They showed temperature dependent (in a convenient temperature range) phase behaviour when contacted with water, and that behaviour could be finely tuned by careful selection of cations. This tuneabilty of their thermomorphic (phase-switching) behaviour with water was shown to be a function of the number of carbon atoms attached to the amine function. We have shown that both anion and cation could have a determining effect on water solubility depending on their mutual hydrophilic/hydrophobic balance. Solubility properties of these new ionic liquids were an important design characteristic of the extraction processes presented in this work. Applications of these reactive ionic liquids as scavengers of water-soluble dyes, and for the selective extraction of metal ions from water, were demonstrated. Research into the reactivity of these materials with 'perfume' aldehydes and ketones is on-going. In conclusion, this versatile and large class of functionalised ionic liquids show great potential as novel media for extracting and isolating both organic and inorganic species from water.

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Notes and references

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† Electronic Supplementary Information (ESI) available: additional DSC, density data, viscosity data, cloud-point measuring protocols and details of DFT calculations are included here. See DOI: 10.1039/b000000x/

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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.

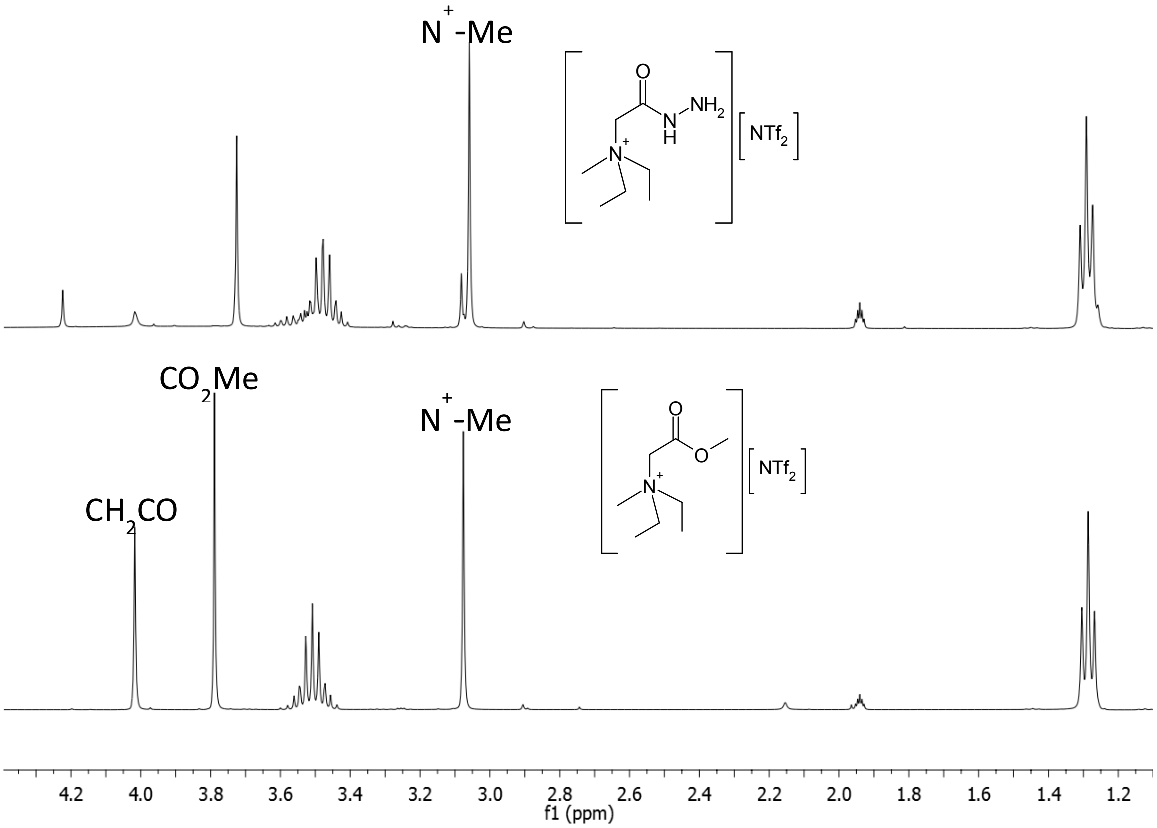
^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 spectrometer (400 MHz). ESMS-mass spectroscopy measurements were carried out on a Waters LCT Premier instrument with an Advion TriVersa NanoMate injection system (cone voltage 50 V, source 120 °C). Both positive and negative ions 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.

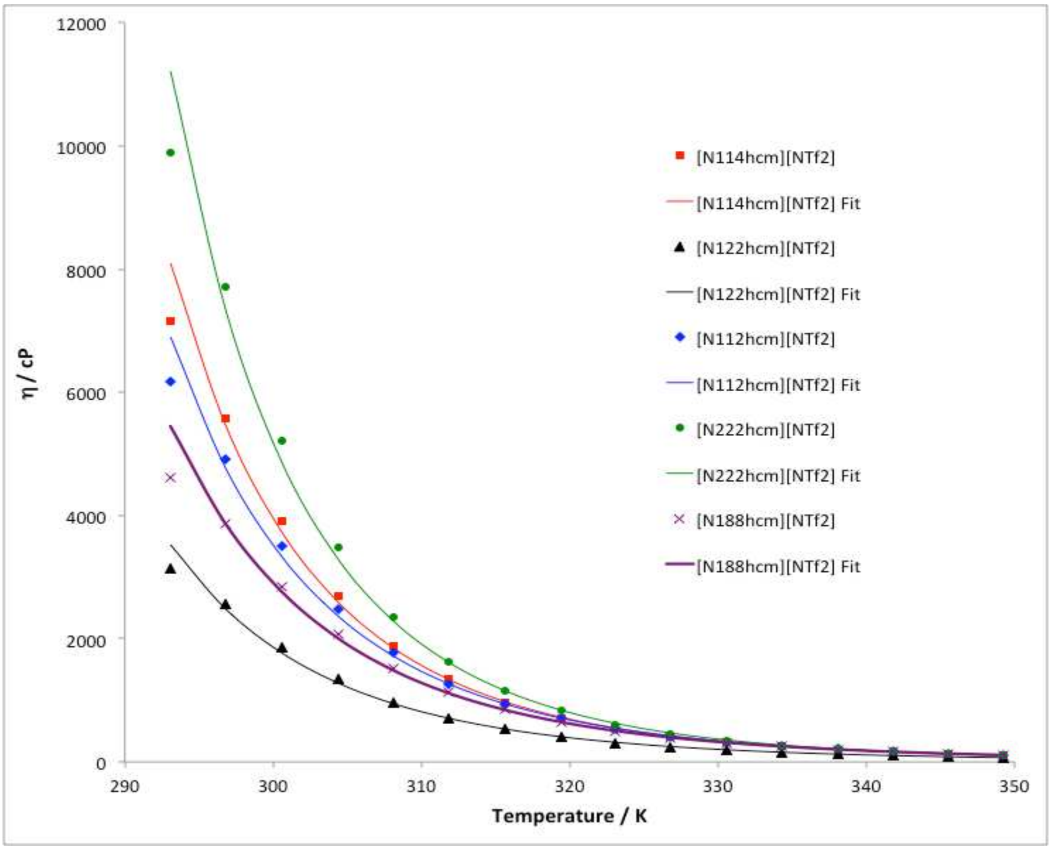


Figure 1: Experimental viscosity data of the studied ionic liquids as a function of the temperature. Fitted VFT lines are shown for each data set.

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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]

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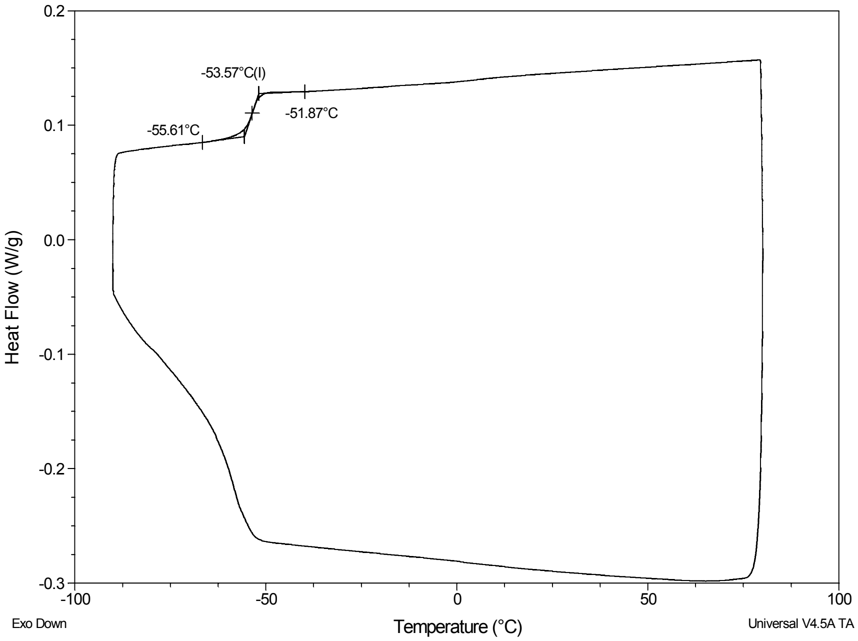
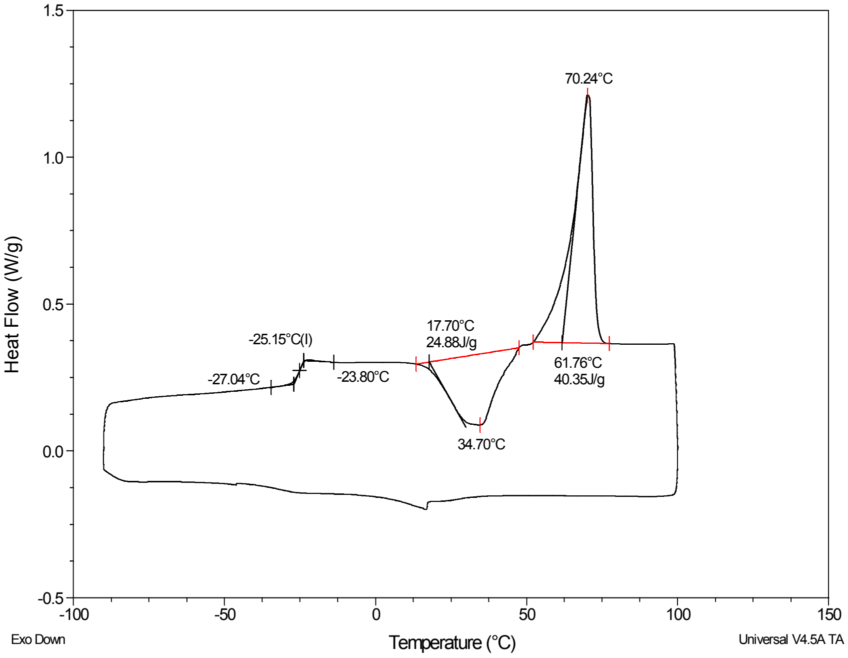
DSCs of Girard's ionic liquids

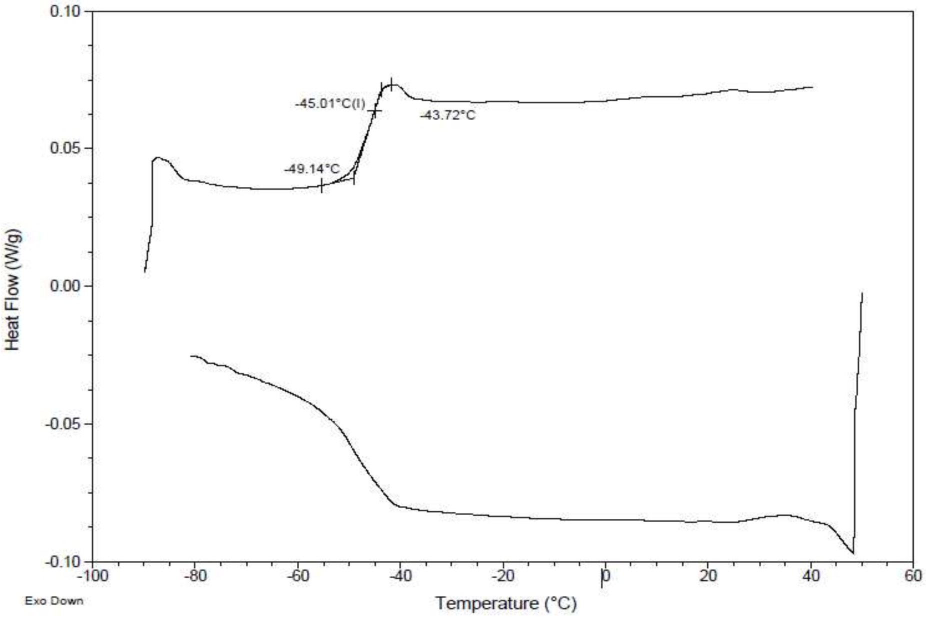
(a) DSC of $[N_{122hcm}][NTf_2]$



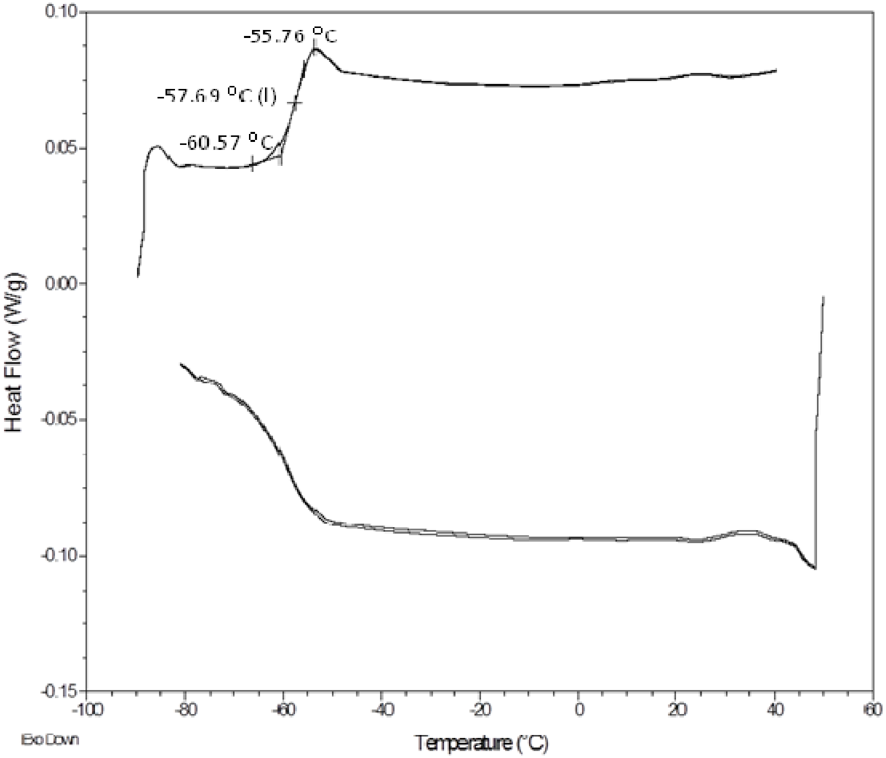
(b) DSC of $[N_{333hcm}][NTf_2]$



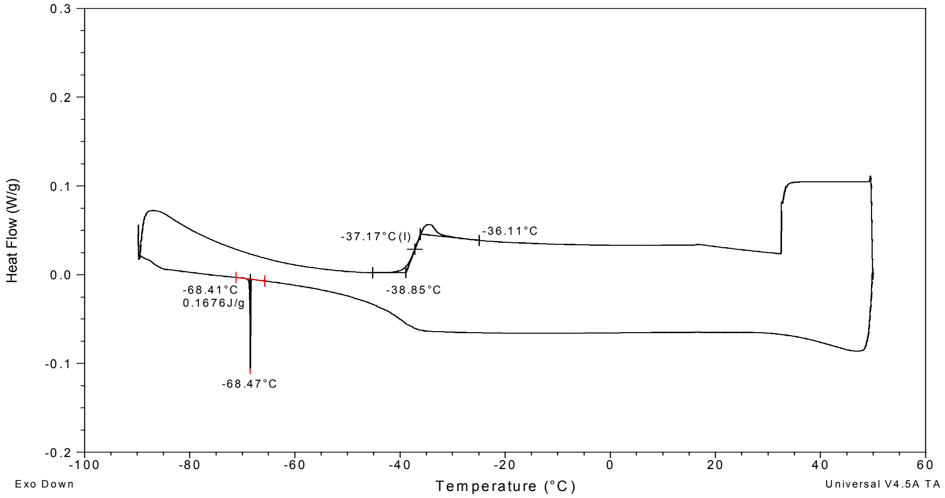
(c) DSC of $[N_{222hcm}][NTf_2]$



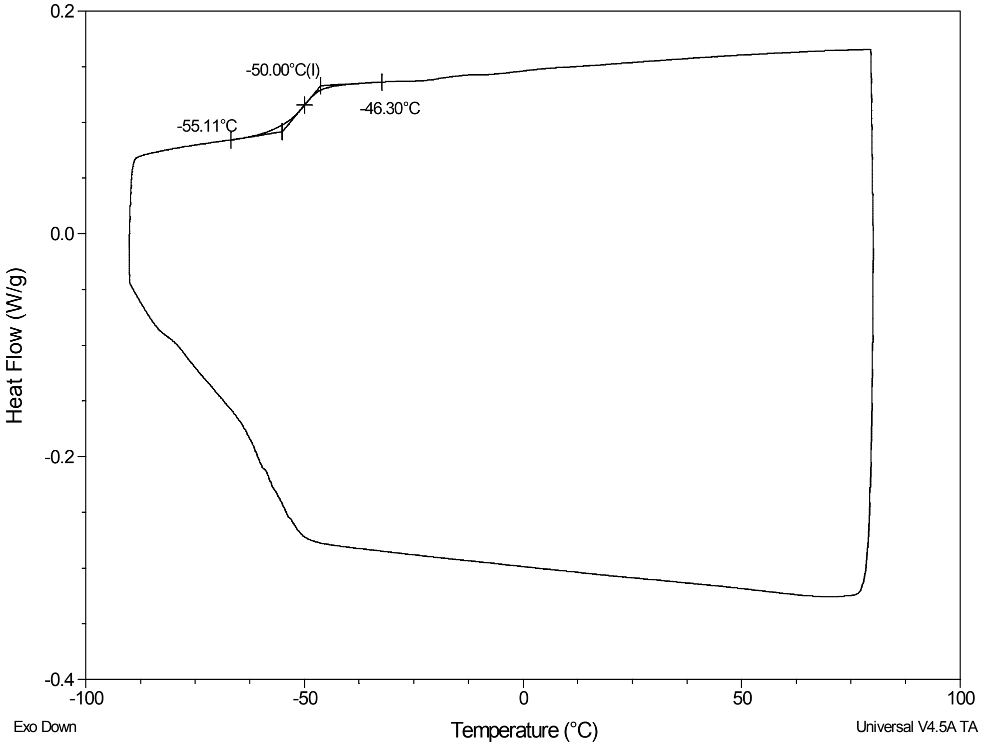
(d) DSC of $[N_{112hcm}][NTf_2]$



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



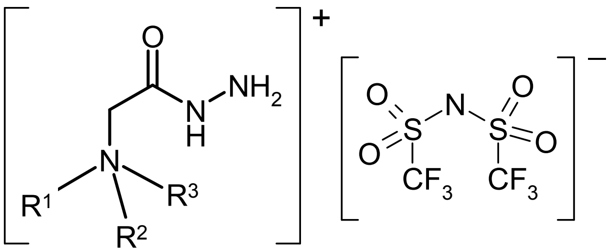
(f) DSC of $[N188hcm][NTf_2]$



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

Graphical Abstract:

Ionic liquid analogues of Girard's reagent exhibit thermomorphism with water that leads to efficient extraction of dyes and metals from water.



Thermomorphic Girard ionic liquids