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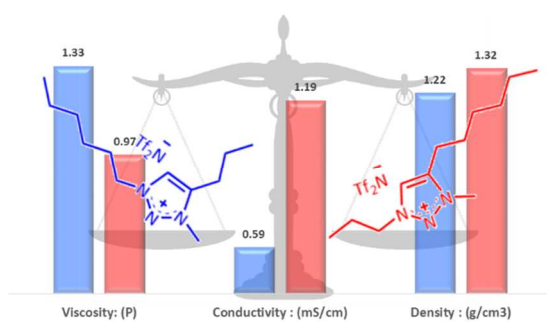
Effects of side group placement was studied on triazolium ionic liquids and how minor change in alkyl group placement results in very different properties.

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Ionic liquid regioisomers: Structure effect on the thermal and physical properties

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A systematic study was performed on two triazolium ionic liquid isomers which included examination of thermal, physical, and electrochemical properties. It was found that a minor change in structure significantly influences physical and thermal properties of ionic liquids.

Room temperature ionic liquids exist entirely as ions and ion pairs but with melting points below 100°C, giving them high chemical and electrochemical stability, low vapor pressure, and inherently high conductivity. This combination of properties has drawn interest for many applications especially in the electrochemical field where high electrochemical stability and conductivity are key parameters.[1]

It is known that the identities of the cation, anion, and various substituents are key parameters affecting physical and chemical properties of ionic liquids. The effect of the anion,[2] and cation[3] on the physical properties of ionic liquids has been evaluated by many groups. The impact of the length of alkyl substituents on properties including molar free volume, viscosity, gas solubility, conductivity, solute diffusion and water solubility has also been examined.[4]

The concept of ionicity in ionic liquids was first introduced by MacFarlane *et al.* who suggested that many property trends in ionic liquids may be explained by the degree to which the ions are free as opposed to electrostatically paired.[5] Previous studies of structural effects on ionicity have been reported by Watanabe *et al.* for a wide range of ionic liquids.[6] It is difficult to separate the roles of cations and anions in various ionic liquids in order to predict the effect on physical and electrochemical properties. In reality, the ionic liquid properties result from a synergistic effect of a combination of both the cation and anion. The effect of substitutions on various triazolium physical properties has already been reported in an attempt to tune CO_2 solubility.[7] However, it is also known that ionic liquid properties depend heavily on their molar free volume,[8] but as yet a systematic study of this parameter in 1,2,3-triazolium ionic liquids has not been attempted. One previous study has shown the effect of triazolium structure on the electrochemical properties.[9] The triazolium ionic liquids are an excellent probe system to understand and carry out systematic studies of physical properties due to their

ease of synthesis and functionalization.[10] This simplicity of synthesis also facilitates the study of poly-ionic liquids.[11]
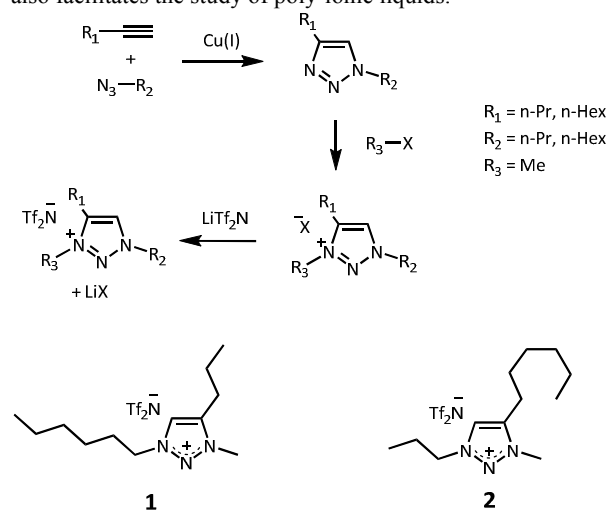

Figure 1. The structures of two 1,2,3-triazolium regioisomers with interchanged hexyl and propyl chains.

Our search for better materials for a variety of applications has led us to probe isomeric ionic liquids (Figure 1) for changes in molar free volume, ionicity, thermal, and electrochemical properties.

It is known that the water content of ionic liquids can have a large effect on their physical properties. Even though Tf_2N based ionic liquids are generally considered hydrophobic, the imidazolium ionic liquids are known to contain a significant amount of water.[12] For the purposes of this study viscosity, conductivity and density measurements were taken under dry conditions. Samples were dried by use of a Karl Fisher apparatus while measuring the water content of the samples. The water content of **1** was found to be 2790 ppm whereas the content of sample **2** was found to be 3030 ppm, as compared to a commercial sample of HMIM Tf_2N which was found to contain 4680 ppm water.

Thermal characterization was carried out using modulated differential scanning calorimetry (MDSC). The samples were run with a 10 °C/min heating and cooling rate for three cycles before the MDSC scan was run to ensure the exact same thermal history for each sample. The heat capacities were calculated using a quasi-isothermal method. The reported heat capacity values were calculated by averaging the last 5 minutes of the reversing heat capacity signal at each temperature.

Table 1. Heat capacity results for samples **1** and **2**

	Heat Capacity / ($J\ g^{-1}\ ^{\circ}C^{-1}$) ±2%			
	25 °C	**50 °C**	**75 °C**	**100 °C**
1	1.62	1.64	1.65	1.66
2	1.61	1.62	1.64	1.65

MDSC results for the triazolium ionic liquids **1** and **2** are shown in Figure 2 with a summary of the thermal data in Table 2.
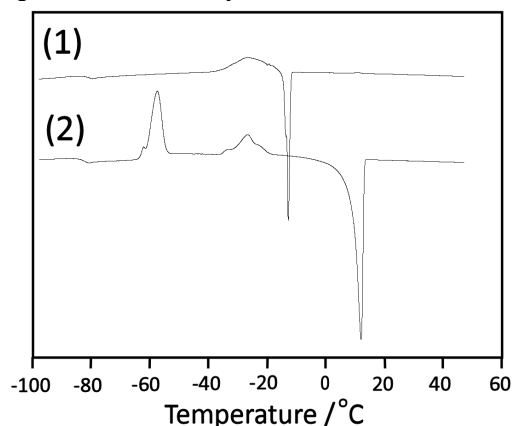

Figure 2. MDSC of total heat flow for triazolium regioisomers **1** and **2** with an average heating rate of 0.5 °C/min, amplitude of ±0.12 °C and a period of 60 seconds.

Table 2. MDSC heating curve results for **1** and **2**

	T_g (°C)	Cold Crystallization (°C)	Crystal Perfection (°C)	Melting Point (°C)
1	-78.5	N/A	-26.8	-12.6
2	-79.8	-57.5	-26.7	11.7

From the thermal data in Table 1, Figure 2 and Table 2, it is clear that the triazolium isomers possess many similarities in their thermal characteristics. Firstly, they have very similar heat capacities, as expected from their structure having the same carbon chain numbers and lengths.[13] Similarly their glass transition temperatures (T_g) are also very close. Both isomers also show an exothermic crystallization peak with a peak maximum of approximately -27 °C seen in the non-reversing signal prior to the endothermic melting peak. Additionally, both samples show an enthalpic recovery peak in the non-reversing signal. It is interesting that there are two distinct and clear exothermic crystallization peaks for sample **2**, while sample **1** only shows a small crystal perfection peak before a sharp melting peak.

Another significant difference between the regioisomers is the difference in the melting peaks. Sample **2** shows a relatively large and broad melting peak at a much higher temperature of 11.7°C with a peak area of 39 J/g. Sample **1** has a very sharp melting peak at   -

12.6 °C and a peak area of approximately 6.8 J/g. This is most likely due to the hexyl-hexyl peak stacking. In the case of **2** the hexyl chain is connected to a relatively non-polar carbon on the triazolium ring. Whereas in isomer **1** hexyl is connected to a charged nitrogen on the triazolium ring resulting in lower melting point. Other physical properties measured were viscosity, density, and conductivity. The results are summarized in Table 3.

Considering the similarities of the regioisomers with identical functional groups and molecular masses, the results are clear evidence that regioisomerism is playing a crucial role on how these molecules pack. This effect is illustrated by the difference in the density, viscosity, and conductivity (Table 3).

Table 3 Effect of regioisomerism on physical properties.

T / °C	η / (cP) ±2%		σ / (mS/cm)		ρ / (g/cm^3) ±5%	
	1	**2**	**1**	**2**	**1**	**2**
20	133.8	97.6	0.59 ± 0.01	1.19 ± 0.03	1.22	1.32
25	103.2	77.0	0.78 ± 0.00	1.48 ± 0.04	1.22	1.32
30	80.3	61.5	0.96 ± 0.03	1.95 ± 0.01	1.22	1.32
35	65.5	50.5	1.16 ± 0.03	2.34 ± 0.10		
40	53.9	40.9	1.39 ± 0.03	2.90 ± 0.03		
45	44.4	33.8	1.66 ± 0.04	3.39 ± 0.19		
50	36.8	28.3	1.99 ± 0.05	4.06 ± 0.06		

η - viscosity; σ - ionic conductivity; ρ – density

Generally, it would be expected that the free volume, and thus density, would remain fairly constant for ionic liquid isomers.[14] However, in the case of these regioisomers, an 8% difference in density equates to a roughly 30 $cm^3 mol^{-1}$ difference in molar free volume. This large change in density is surprising. One potential explanation of large different in density is how the ionic liquid molecule orients itself. The experimental results reveal important insight on the interaction between anion and cation and how the placement of the alkyl groups can influence molecular arrangements. Certainly, further studies are needed to gain deeper understanding. Usually the heat capacity of ionic liquids is seen to increase with increasing chain length,[15] due to an increased number of translational, rotational, and vibrational modes of freedom within the alkyl chain. In the case of the regioisomers stated here, the heat capacity is identical within the experimental error due to the roughly equal chain mobility of alkyl chains attached to either the nitrogen or triazolium backbone.

Further results in Table 3 show that the triazolium regioisomers **1** and **2** have remarkably different viscosities and conductivities despite their identical molecular mass and substitutions. This result suggests a difference in ionicity between the triazolium regioisomers. As expected, the lower viscosity ionic liquid shows better ion mobility and thus a higher ionic conductivity.

The ionicity may be analysed in a Walden plot (Figure 3) by graphing the logarithm of the molar conductivity against the inverse of the viscosity, to qualitatively assess the relative ionicity of each of the ionic liquids. As can be seen, the plotted points for the triazolium regioisomer **2** lie closer to the 'ideal' KCl line suggesting more ion dissociation. Interestingly, the results for ionic liquids **1** and **2**, which differ only in the relative positioning of the hexyl and propyl chain, suggest that the ionicity is greatly affected by this isomerism. A greater dissociation is seen with a shorter (propyl) chain attached to a nitrogen atom than that seen for a hexyl nitrogen substitution. This effect is likely due to the steric hindrance of the charged nitrogen atom when substituted with a hexyl rather than propyl chain

allowing less access of the anion. A similar trend is seen with increasing chain lengths in imidazolium based ionic liquids.[6b] This result again indicates that not just substitution or chain length, but the position of the alkyl chain is also important in ionic liquid design in targeting the right properties of ILs.
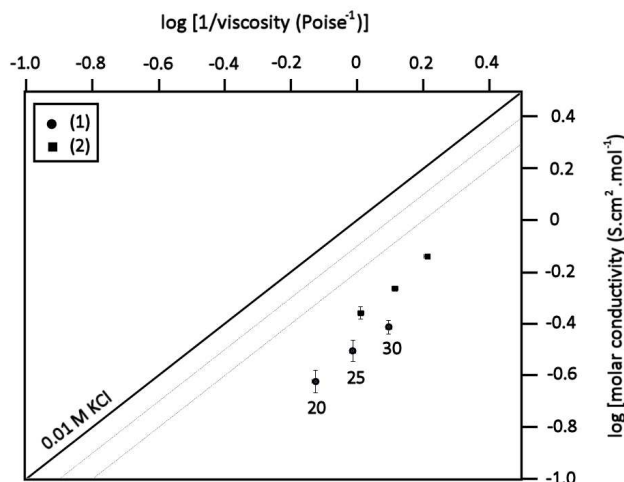

Figure 3. A Walden plot showing the relative ionicity of triazolium ionic liquids **1** and **2**. Where not visible, error bars were too small to be included. The numbers represent the temperature in °C.

The 'ideal' KCl line is used as the dissociation standard for ionic conductivity due to the assumed full dissociation of the salt as well as the equal relative diffusion speeds of K^+ and Cl^- in aqueous solutions. However, it is a matter of debate how 'ideal' this standard really is.[16] Despite the controversy, the Walden plot is a well-established method, and the assumption of ideality was deemed suitable for the qualitative description of the relative ionicity of ionic liquids in this temperature range.

To determine the electrochemical windows for the triazolium regioisomers, cyclic voltammograms were determined. It was found that the comparative electrochemical windows are very similar despite their large differences in physical and thermal properties(See supplemental information). The electrochemical stability is similar to that seen for imidazolium ionic liquids.[17] Their stability, combined with their decreased viscosity and ease of functionalization, could allow triazolium-based ILs to find use in a wide variety of electrochemical applications.

Conclusions

Triazolium ionic liquids have been easily and cleanly synthesized to show, for the first time, a trend in ionic liquid properties not only with alkyl chain identity but also with regioisomerism. An equivalent study using the imidazolium core would be far more synthetically challenging.

It has been shown that the regioisomerism of alkyl groups can play a huge role in dictating physical and thermal properties. Understanding the underlying effects of structure will allow us to develop materials targeted specifically for various applications. This study highlights how small variations in structure result in vastly different properties. The ability to fine tune the properties of such materials is an important analytical and materials development tool.

Notes and references

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