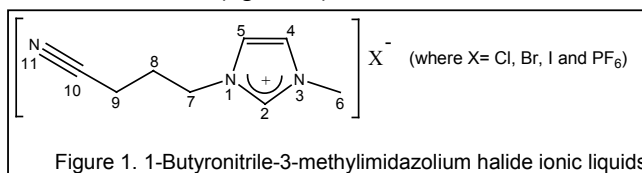


2P014 ELUCIDATION OF STRUCTURE OF FUNCTIONALIZED IONIC LIQUIDS BY RAMAN SPECTROSCOPY AND X-RAY CRYSTALLOGRAPHY

(The University of Tokyo) ○Satyen Saha, S. Hayashi, R. Ozawa, H. Hamaguchi

In recent years, researchers are designing and developing “task specific” or functionalized ionic liquids (ILs). “Task specific” IL is a kind of IL where a functional group is incorporated in cation or anion which exerts a particular reactivity towards a specific solute in solution. For example, sulfonic group appended ILs have been used as solvent-catalyst for the esterification.¹ The ILs with amine, amide, carboxylic functional groups appended cation are also possible. We are interested in ‘nitrile’ functionality based ILs. Presence of ‘nitrile’ or $\text{—C}\equiv\text{N}$ group makes the cation itself spectroscopically active. Also, recently, it is reported that the nitrile incorporated ionic liquids are good solvents for multiphasic catalysis².

We have synthesized a series of new functionalized ILs (figure 1). We are interested in the structural aspects of these ILs in solid and liquid phase and hence have studied, in depth, by Raman spectroscopy and single crystal X-ray



crystallography at different temperatures. Raman spectra were recorded on a laboratory made near-infrared Raman spectroscopic system employing the 1064 nm line of a Nd:YAG laser as the excitation light source and an InP/InGaAsP near-infrared multichannel detector provided by Hamamatsu Photonics. The X-ray diffraction measurements were carried out using a Rigaku/MSM Mercury CCD system with graphite monochromated Mo-K α radiation ($\lambda = 0.71070 \text{ \AA}$) at different temperatures.

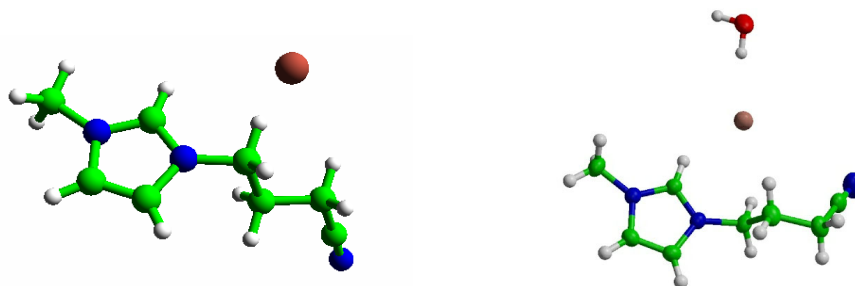


Figure 2. The X-ray crystallographic structures of [nbmim]Cl (where, [nbmim]= 1-butynitrile-3-methylimidazolium). (left): The TT conformation; (right) TG conformation (see text).

The X-ray crystallographic structures of [nbmim]Cl were shown in figure 2. The n-butynitrile group in cation has **TT** conformation (left), where the first **T** indicates the *trans* conformation around the C7-C8 bond and the second **T** indicates the same around the C8-C9 bond. On the other hand, interestingly, when [nbmim]Cl crystallizes with a water molecule, the above configuration is changed to **TG** where the second **G** indicates the *gauche* conformation

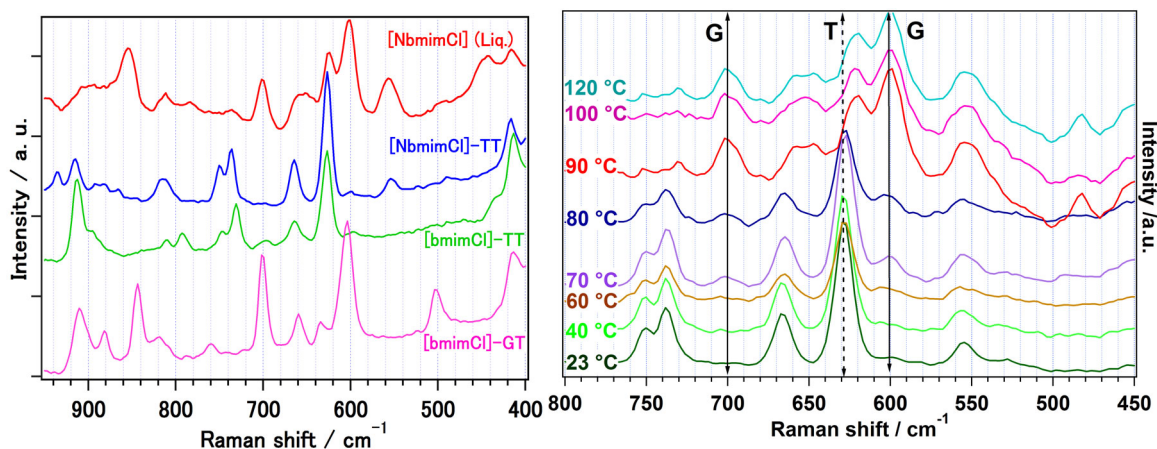


Figure 3. (left) Raman spectra of [nbmim]Cl in crystalline state and super cooled liquid state. The Raman spectra of 1-butyl-3-methylimidazolium chloride, [bmim]Cl³⁻⁵ are also shown for comparison. The Raman spectra of [nbmim]Cl at different temperatures are shown on right.

around the C8-C9 bond. The molecular arrangement in crystal is also quite different in these two cases. It is found that water molecule does not directly interact with butyronitrile or cation but interacts through H-bonding to Cl⁻ thus altering the structure of the cation. This is the first example on the influence of water molecule on the conformation of cation of an IL.

Raman spectra of [nbmim]Cl liquid has more characteristic peaks than that in the crystalline state (figure 3-left). Comparing the spectra of [nbmim]Cl with that of [bmim]Cl³⁻⁵, we can conclude that liquid phase [nbmim]Cl IL, contains more than one conformer. From figure 3-right, we can see the gradual appearance of marker bands for **G** conformation around C7-C8 bond (701, 603 cm⁻¹ and possibly the one at 482 cm⁻¹) on melting. It is interesting to note that before reaching the actual melting point temperature (mp= ~85 °C), these marker bands start to appear (shown by straight arrows)- a indication of premelting phenomenon. On the course of melting, a small shift of **T** marker band (at 628 cm⁻¹, also shown by broken arrows) to lower wavenumber is also interesting.

Acknowledgements:

SS would like to thank Japan Society for the Promotion of Science (JSPS) for the fellowship.

References:

1. A.C. Cole, J.L. Jensen, I. Ntai, K.L.T. Tran, K.J. Weaver, D.C. Forbes, J.H.Jr. Davis, J. Am. Chem. Soc. 124, 5962 (2002).
2. D. Zhao, Z. Fei, R. Scopelliti, P. J. Dyson, Inorg. Chem. 43, 2197 (2004).
3. S. Hayashi, R. Ozawa, H. Hamaguchi, Chem. Lett. 32, 498 (2003).
4. S. Saha, S. Hayashi, A. Kobayashi, H. Hamaguchi, Chem. Lett. 32, 740 (2003).
5. R. Ozawa, S. Hayashi, S. Saha, A. Kobayashi, H. Hamaguchi, 32, 948 (2003)