



## Abstract Listing

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### **415052: Imidazolium melts with carborane anions. Why are ionic liquids liquid?**

#### **IEC 0 [415052]: Imidazolium melts with carborane anions. Why are ionic liquids liquid?**

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#### **ACCEPTED**

**Topic Selection:** *Green (or Greener) Industrial Applications of Neoteric Solvents: Ionic and Supercritical Fluids: Structure and Photochemistry*

**Invited:** *Y*

**Comments to Organizer:** *In scheduling my presentation, please try avoid conflict with the I&EC Symposium "New Chemistry of Fullerenes and Nanotubes. Also, I must depart San Diego on the Wednesday. Thank you.*

**Preferred Presentation Format:** *OralOnly*

**Consider for Sci-Mix:** *N*

**Conforms to Bylaw 6:** *Y*

**Last Modified:** *2000-11-19*

#### **Abstract**

A new class of low melting N,N'-dialkylimidazolium salts has been prepared with carborane counterions, some of the most inert and least nucleophilic anions presently known. The cations and anions have been systematically varied with combinations of 1-ethyl-3-methyl- (EMIM<sup>+</sup>), 1-octyl-3-methyl- (OMIM<sup>+</sup>), 1-ethyl-2,3-dimethyl- (EDMIM<sup>+</sup>) and 1-butyl-2,3-dimethyl- (BDMIM<sup>+</sup>) imidazolium cations and CB<sub>11</sub>H<sub>12</sub><sup>-</sup>, CB<sub>11</sub>H<sub>6</sub>Cl<sub>6</sub><sup>-</sup> and CB<sub>11</sub>H<sub>6</sub>Br<sub>6</sub><sup>-</sup> carborane anions in order to elucidate the factors which affect their melting points. From trends in melting points, which range from 156 down to 45 ° C, it is clear that the alkylation pattern on the imidazolium cation is the main determinant of melting point and that packing inefficiency of the cation is the intrinsic cause of low melting points. C-alkylation of the anion can also contribute to low melting points by the introduction of a further packing inefficiency. Nine of the thirteen salts have been the subject of X-ray crystal structural determination. Notably, crystallographic disorder of the cation is observed in all but one of these salts. It is the most direct evidence to date that packing inefficiency is the major reason why unsymmetrical N,N' -dialkylimidazolium salts can be liquids at room temperature.

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### **418666: 1-Alkyl-3-methylimidazolium tetrachloropalladate(II) and platinate(II) salts, the structure of ionic liquid catalysts**

**IEC 0 [418666]: 1-Alkyl-3-methylimidazolium tetrachloropalladate(II) and platinate (II) salts, the structure of ionic liquid catalysts**

**John D. Holbrey**, Susanne Johnston, Mark Nieuwenhuyzen, and Kenneth R. Seddon, The QUILL Centre, Queen's University of Belfast, The David Kier Building, Stranmillis Road, Belfast BT9 5AG, United Kingdom, Fax: int+4428-90661462, j.holbrey@qub.ac.uk

**ACCEPTED**

**Topic Selection:** *Green (or Greener) Industrial Applications of Neoteric Solvents: Ionic and Supercritical Fluids: Structure and Photochemistry*

**Invited:** N

**Preferred Presentation Format:** *Oral*

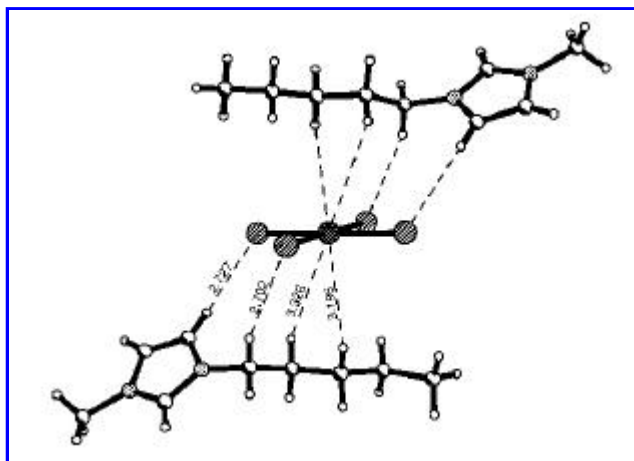
**Consider for Sci-Mix:** *Y*

**Conforms to Bylaw 6:** *Y*

**Last Modified:** 2000-11-19

**Abstract**

Palladium-containing 1-alkyl-3-methylimidazolium tetrachlorometallate salts are active catalysts for Heck coupling reactions and the hydrodimerisation of butadiene in ionic liquid systems. Series of 1-alkyl-3-methylimidazolium and 1-alkyl-2,3-dimethylimidazolium tetrachloropalladate(II) and tetrachloroplatinate(II) salts with linear alkyl-chains containing between one and eighteen carbons have been systematically prepared and the solid-state structures characterised by single-crystal X-ray diffraction. Unusual, and unexpected hydrogen-bonding motif has been observed which controls the crystal structures of these salts, and may have implications in their utilisation as catalysts.

**419237: Photochemical and photophysical investigations in ionic liquids****IEC 0 [419237]: Photochemical and photophysical investigations in ionic liquids**

**Charles M. Gordon**<sup>1</sup>, Mark J. Muldoon<sup>1</sup>, Ian R. Dunkin<sup>1</sup>, and Andrew J. McLean<sup>2</sup>. (1) Department of Pure & Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow G1 1XL, United Kingdom, Fax: 44 141 548 4822, c.m.gordon@strath.ac.uk, (2) Department of Chemistry and Chemical Engineering, University of Paisley

**ACCEPTED**

**Topic Selection:** *Green (or Greener) Industrial Applications of Neoteric Solvents: Ionic and Supercritical Fluids: Structure and Photochemistry*

**Invited:** *Y*

**Preferred Presentation Format:** *Oral*

**Consider for Sci-Mix:** *N*

**Conforms to Bylaw 6:** *Y*

**Last Modified:** *2000-11-19*

**Abstract**

Relatively little information exists about the nature of ionic liquids as solvents. We have investigated the effect of ionic liquids on a range of photophysical and photochemical processes to address this gap in understanding. We will report the manner in which ionic liquids interact with different solute molecules, using a range of photophysical probes. Such probe systems are very sensitive to the interactions between solute and solvent. Our investigations will show that it is difficult to categorise ionic liquids on any one existing solvent polarity scale. The second part of the paper will report our investigations into photochemical reactions in ionic liquids. We have studied the electron transfer reaction between photoexcited [Ru(bpy)<sub>3</sub>]<sup>2+</sup> and methylviologen dication. Initial investigations suggest that, while the encounter reaction is largely diffusion controlled, there is a much larger degree of cage escape than might be expected by comparison with conventional solvent systems. Other systems to be reported include energy transfer and hydrogen abstraction reactions of benzophenone, and the reactions of photogenerated singlet oxygen.

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**420353: Fluorescence quenching of polycyclic aromatic hydrocarbons within room-temperature ionic liquids****IEC 0 [420353]: Fluorescence quenching of polycyclic aromatic hydrocarbons within room-temperature ionic liquids**

**Siddharth Pandey**, Kristin A. Fletcher, and Ashley E. Hendricks, Department of Chemistry, New Mexico Institute of Mining and Technology, Socorro, NM 87801, Fax: 505-835-5364, pandey@nmt.edu

**ACCEPTED**

**Topic Selection:** *Green (or Greener) Industrial Applications of Neoteric Solvents: Ionic and Supercritical Fluids: Structure and Photochemistry*

**Invited:** *Y*

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**Consider for Sci-Mix:** *N*

**Conforms to Bylaw 6:** *Y*

**Last Modified:** *2000-11-19*

**Abstract**

A major concern among chemical industries as well as research academia is to replace volatile, toxic, and environmentally-damaging organic solvents that are used on a large scale. Recently designed room-temperature ionic liquids, such as 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM] PF<sub>6</sub>) among others, have shown potential as unique solvents with wide range of solubility, miscibility,

and other physicochemical properties accompanied by an extremely promising nonvolatile behavior. To date, these novel ionic liquids have shown important applications in synthesis, catalysis, polymerization, separation, and extraction processes. We explore the potential of [BMIM]PF<sub>6</sub> as the solvent media for spectroscopic investigation and applications. We investigate photophysics and fluorescence quenching behavior of polycyclic aromatic hydrocarbons (PAH) dissolved in [BMIM]PF<sub>6</sub> in the presence of external quenching agents operating with variety of quenching mechanisms. These various carefully designed fluorescence quenching experiments provide us key information about the accessibility and diffusion behavior of PAHs toward these quenching agents within [BMIM]PF<sub>6</sub>.

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### **422374: Designing structure in ionic liquids: A consideration of shape, charge density and composition**

#### **IEC 0 [422374]: Designing structure in ionic liquids: A consideration of shape, charge density and composition**

**James D. Martin**, Department of Chemistry, North Carolina State University, Box 8204, Raleigh, NC 27695-8204, Fax: 919-515-8909, [jdmartin@ncsu.edu](mailto:jdmartin@ncsu.edu)

#### **ACCEPTED**

**Topic Selection:** *Green (or Greener) Industrial Applications of Neoteric Solvents: Ionic and Supercritical Fluids: Structure and Photochemistry*

**Invited:** *Y*

**Preferred Presentation Format:** *OralOnly*

**Consider for Sci-Mix:** *N*

**Conforms to Bylaw 6:** *Y*

**Last Modified:** *2000-11-19*

#### **Abstract**

Properties of "ionic liquids" such as solubility and reactivity are heavily influenced by the structure of that liquid, and thus, the ability to design and control liquid structure provides solvent tunability. In metal-halide based liquids including AlCl<sub>3</sub>, ZnCl<sub>2</sub> and CuCl, for example, a significant network structure persists to temperatures well above their melting point. The addition of a second component, such as an alkylammonium halide, generally reduces the melting point, and also causes the depolymerization of the metal-halide network. The shape of the templating cation can further direct the structural organization of the remaining network. As the extent of the metal-halide oligomerization decreases, the charge density of the resultant anion increases. Nevertheless the low charge density of the oligomeric anions, as well as the low charge density of the alkylammonium cations, results in the limited ionic character of "ionic liquids." Neutron and X-ray scattering data demonstrating the structural organization in "ionic liquids" ranging from isotropic liquids to liquid crystals will be discussed to demonstrate the principles of structural design in metal-halide liquids.

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### **438417: Structural studies of imidazolium based ionic liquids**

#### **IEC 0 [438417]: Structural studies of imidazolium based ionic liquids**

**C Hardacre**<sup>1</sup>, **JD Holbrey**<sup>1</sup>, **SEJ McMath**<sup>1</sup>, **M Nieuwenhuyzen**<sup>1</sup>, and **C Hanke**<sup>2</sup>. (1) School of

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**ACCEPTED**

**Topic Selection:** *Green (or Greener) Industrial Applications of Neoteric Solvents: Ionic and Supercritical Fluids: Structure and Photochemistry*

**Invited:** *N*

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**Consider for Sci-Mix:** *N*

**Conforms to Bylaw 6:** *Y*

**Last Modified:** *2000-11-19*

**Abstract**

The solvent and reactive properties of ionic liquid systems are likely to be linked to structure of the ionic liquid. This paper describes results from x-ray and neutron diffraction, x-ray reflectivity and exafs measurements on short- and long-chain imidazolium based ionic liquid systems. The study provides information on the short and long range order in the ionic liquid as well as changes in the structure of the solvent and solute on dissolving both metal complexes and small molecules. The structural data obtained is correlated with the physical and chemical properties of the systems investigated.

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**445129: Intermission**

**0 [445129]: Intermission**

**ACCEPTED**

**Topic Selection:** *Green (or Greener) Industrial Applications of Neoteric Solvents: Ionic and Supercritical Fluids: Structure and Photochemistry* **Preferred Presentation Format:** *Break*

**Consider for Sci-Mix:**

**Last Modified:** *2000-11-24*

**Abstract:** Abstract text not available.

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**445130: Discussion**

**0 [445130]: Discussion**

**ACCEPTED**

**Topic Selection:** *Green (or Greener) Industrial Applications of Neoteric Solvents: Ionic and Supercritical Fluids: Structure and Photochemistry* **Preferred Presentation Format:** *Break*

**Consider for Sci-Mix:**

**Last Modified:** *2000-11-24*

**Abstract:** Abstract text not available.

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