

Tunable properties make ionic liquids an attractive reaction medium, but how 'green' are these solvents? Learn more in the Review by Scammells, Scott, and Singer (p. 155).

# AUSTRALIAN JOURNAL OF CHEMISTRY

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### Editorial

### **Introducing Research Fronts**

Alison J. Green

Aust. J. Chem. 2005, 58, 153-154.

A Research Front is a cluster of papers in a new or rapidly developing area. The first Research Front, on the neglected issues of ionic liquids, heads up this issue and includes the Review and the first two Rapid Communications. The concept and the topic are introduced in this Editorial.

### **RESEARCH FRONT: Ionic Liquids—The Neglected Issues**

### Review

#### Ionic Liquids: The Neglected Issues

Peter J. Scammells, Janet L. Scott, Robert D. Singer

Aust. J. Chem. 2005, 58, 155-169.

$$H_3C$$

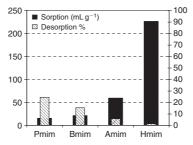
Low-temperature molten organic salts (such as the example shown, referred to as ionic liquids) have provided synthetic chemists with a range of new reaction media of great diversity. Although there are numerous reviews on the topic of ionic liquids, very little literature is available on their purity, stability, biodegradability, toxicity, and recyclability.

### Rapid Communications

Preliminary Assessment of the Sorption of some Alkyl Imidazolium Cations as used in Ionic Liquids to Soils and Sediments

Piotr Stepnowski

Aust. J. Chem. 2005, 58, 170-173.

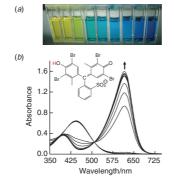


The use of ionic liquids is increasing with their growing popularity as 'green' solvents. However, few environmental impact studies have been conducted. Here, the sorption of a series of imidazolium ionic liquids on a selection of soils and sediments increased with increasing alkyl side-chain length, and was governed by the extent of both hydrophobic and hydrophillic interactions.

### A Simple Colorimetric Assay of Ionic Liquid Hydrolytic Stability

Gary A. Baker, Sheila N. Baker

Aust. J. Chem. 2005, 58, 174-177.



A colorimetric method has been developed to assess the hydrolytic stabilities of air- and water-stable ionic liquids. Ionic liquids containing fluorinated anions were subjected to temperatures between 25 and 50°C and for extended periods. Hydrolysis was monitored by observing the color change of a pH-sensitive dye.

### Rapid Communication

### General Solution to the Band-Broadening Problem in Polymer Molecular Weight Distributions

Jeffrey V. Castro, Kim Y. van Berkel, Gregory T. Russell, Robert G. Gilbert

Aust. J. Chem. 2005, 58, 178-181.

$$S(t) = \left(\frac{2\pi}{z^{-2} + \sigma^{-2}}\right)^{1/2} \exp\left(\frac{-t^2}{2(z^2 + \sigma^2)}\right)$$

The molecular weight distribution (MWD) of a polymer records its synthesis history. In principle an MWD reveals the mechanisms of formation of a polymer; in practice this is hard as band broadening distorts the measured MWD. Reported herein is a method that shows, under particular circumstances, band broadening effects exactly cancel, and thereby allow the use of MWDs to study polymerization mechanisms.

### **Full Papers**

### Naked-Eye Bead Property Estimation Using a Red Safety-Catch Linker

Philipp Heidler, Andreas Link

Aust. J. Chem. 2005, 58, 182-187.

Colorimetric techniques used in the visual monitoring of solid-phase syntheses are often faster and cheaper than the more traditional destructive methods. Through insertion of a phenylazo moiety into a modified Kenner linker, the authors developed the polymer-bound 4-(4-sulfamoylphenylazo)benzoic acid, which gives rise to a deep red bead colour, the depth of which allows the direct estimation of the loading level by naked-eye inspection.

### The Synthesis of Various 1,6-Disulfide-Bridged D-Hexopyranoses

Ethan D. Goddard-Borger, Robert V. Stick

Aust. J. Chem. 2005, 58, 188-198.

The disulfide shown here contains an interesting and novel ring system that encourages an exploration of its reactivity and conformation. This D-gluco disulfide, 'angyalosan', named in honour of Stephen Angyal, who turned 90 last year, was synthesized and successfully oxidized to a single thiosulfinate.

### The Conformation of Some 1,6-Disulfide-Bridged D-Hexopyranoses

Ethan D. Goddard-Borger, Brian W. Skelton, Robert V. Stick, Allan H. White

Aust. J. Chem. 2005, 58, 199-205.

The conformations of five 1,6-disulfide-bridged D-hexopyranoses were investigated by using a combination of  $^{1}$ H NMR spectroscopy and, where possible, single-crystal X-ray crystallography. The D-*galacto* triacetate pictured was unusual in that it was present in solution as two slowly interconverting conformers in approximately equal proportions, with the dithiane ring of each conformer existing as a boat ( $B_{S,O}$ ).

# Dipyridophenazine Complexes of Cobalt(III): DNA Photocleavage and Photobiology

Alison M. Funston, Carleen Cullinane, Kenneth P. Ghiggino, W. David McFadyen, Stanley S. Stylli, Peter A. Tregloan

Aust. J. Chem. 2005, 58, 206-212.

The intercalation and photochemistry of  $[Co(en)_2(DPPZ)]^{3+}$  was investigated using calf thymus DNA, plasmid DNA, and 2'-deoxyguanosine. The compound displayed efficient light-activated nuclease activity. While the cytotoxicity of  $[Co(en)_2(DPPZ)]^{3+}$  and analogues was high, these compounds may provide a platform for potential phototherapy applications.

### Potentiometric Investigation of the Weak Association of Sodium and Oxalate Ions in Aqueous Solutions at 25°C

Andrew Tromans, Glenn Hefter, Peter M. May

Aust. J. Chem. 2005, 58, 213-217.

Sodium ion-selective electrode potentiometry was used to determine the formation constant of  $\mathrm{Na}^+$ –oxalate ion pairs in CsCl and tetramethylammonium chloride solutions, as shown. Solutions contained ions in high concentrations, to model conditions present in Bayer process solutions. Na contamination is discussed as a limitation of the technique.

Reference half cell Salt bridge Test solution 
$$\text{Ag } \left| \begin{array}{c|c} \text{AgCl} & \textit{I} & \textit{I$$

# The S<sub>2</sub> Oxygen Atoms Are Essential for the Pronounced Fungitoxicity of the Sulfur-Rich Natural Product, Dysoxysulfone

Sharon A. Bewick, Stephen Duffy, Stephen P. Fletcher, Richard F. Langler, Heather G. Morrison, Erin M. O'Brien, Charles Ross, Vanessa C. Stephenson

Aust. J. Chem. 2005, 58, 218-223.

 $\label{eq:ch3SO2CH2SCH2SCH2SO2CH3} \mathbf{CH_3SO_2CH_2SCH_2SO_2CH_3}$ 

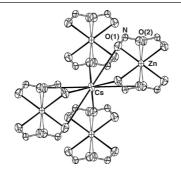
CH<sub>3</sub>SO<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>SSCH<sub>2</sub>SCH<sub>3</sub>

Dysoxysulfone 1 has, among others, antifungal properties; structure–activity results suggest the  $\alpha$ -sulfone disulfide structure is the key. Synthesis and testing of the analogue 2, reported here, has established that the absence of oxygen atoms at S2 leads to a sharply diminished antifungal activity. The synthesis of 2 also revealed a novel oxidative conversion of unsymmetrical  $\gamma$ -sulfonyl disulfides into the corresponding symmetrical  $\gamma$ -sulfonyl disulfides.

### Crystal Structure of Cs<sub>2</sub>Zn(NO<sub>2</sub>)<sub>4</sub>: Influence of Steric Crowding on Nitrite Coordination

Susan G. Oates, Michael A. Hitchman, Brian W. Skelton, Robert Stranger, Horst Stratemeier, Allan H. White

Aust. J. Chem. 2005, 58, 224-227.



The chelation of the nitrite ion in  $Cs_2[Zn(NO_2)_4]$  was determined by X-ray crystal structure analysis (see Fig.). The presence of one short and one long Zn–O bond for each nitrite ion in the complex indicated an intermediate chelation between symmetrical and *syn*-unidentate. The geometry is discussed in terms of steric crowding.

### **Short Communications**

Solvent Free Rapid Synthesis of 3-Alkoxycyclohex-2-en-1-one from 1,3-Cyclohexanedione Promoted by Indium(III) Chloride/Silica Gel

R. Murugan, R. Kamakshi, Boreddy S. R. Reddy

Aust. J. Chem. 2005, 58, 228-230.



3-Alkoxycyclohex-2-en-1-ones act as dienophiles in Diels—Alder reactions and are synthetic precursors to optically active cyclohexenones, which serve as starting materials for many terpenoids. An efficient and rapid synthesis from 1,3-diketones catalyzed by indium(III) chloride on silica gel under solvent-free conditions and microwave irradiation is described.

# Synthesis of Arylmethylenemalononitriles Catalyzed by $KF-Al_2O_3$ under Ultrasound

Ji-Tai Li, Guo-Feng Chen, Shu-Xiang Wang, Lin He, Tong-Shuang Li

Aust. J. Chem. 2005, 58, 231-233.



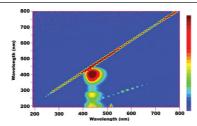
Arylmethylenemalononitriles are traditionally synthesized through a Knoevenagel condensation of malononitrile with aromatic aldehydes using organic bases as catalysts. The process described here employs KF–Al<sub>2</sub>O<sub>3</sub> as a catalyst and ultrasound irradiation to gain the desired products in higher yields and shorter reaction times.

### Focus

Monitoring Colour and Fading: Fluorescent Pigments in Works of Art

Maria Kubik

Aust. J. Chem. 2005, 58, 234.



A three-dimensional fluorescence spectrum (as shown here for 'Kremer Daylight Blue') offers a standardless method to quantitatively measure colours for paints and dyes, which is otherwise difficult for unstable fluorescent pigments.