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Supplementary information

Enhanced antimicrobial activities of 1-alkyl-3-methyl imidazolium ionic liquids based on silver or copper containing anions

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1-alkyl-3-methylimidazolium chloride. A mixture of distilled (vacuum distilled from CaH2 suspension) 1-methylimidazole (82.1 g, 1.00 mol) and 1-chloroalkane (1.05 mol, 1-chlorohexane = 126.7 g, 1-chlorooctane = 156.1 g, 1-chlorodecane = 185.6 g, 1-chlorododecane = 215.0 g, 1-chlorotetradecane = 273.9 g, 1-chlorohexadecane = 162.4 g, 1-chlorooctadecane = 303.3 g) (uses as supplied from Aldrich) was heated with an oil bath at 100 °C in a one neck round bottom flask (500 cm^3) equipped with a stirrer bar and reflux condenser, under an inert dinitrogen atmosphere. The end of the reaction was confirmed by testing for the presence of unreacted 1-methylimidazole, by adding a few drops of the reaction mixture to a solution of copper(II) sulfate in water. The development of a blue coloration indicates the reaction is not complete and should be heated for longer. After 3 days and a negative 1-methylimidazole test, the reaction mixture was connected to a high vacuum pump (at 1 mBar) and heated for 4 hours at 100 °C (for [$C_{6\text{-}10}$mim]Cl) to distil out unreacted 1-chloralkane, or recrystalised from boiling ethyl ethanoate (for [$C_{12\text{-}18}$mim]Cl).

1-alkyl-3-methylimidazolium bromide. A mixture of distilled (vacuum distilled from CaH_2 suspension) 1-methylimidazole (41.1 g, 0.50 mol) and 1-bromooalkane (0.52 mol, 1-bromohexane = 85.8 g, 1-bromooctane = 100.4 g, 1-bromodecane = 115.0 g, 1-bromododecane = 129.6 g, 1-bromotetradecane = 144.2 g, 1-bromohexadecane = 158.8 g, 1-bromooctadecane = 173.4 g) (uses as supplied from Aldrich) was heated with an oil bath at 100 °C in a one neck round bottom flask (500 cm^3) equipped with a stirrer bar and reflux condenser, under an inert dinitrogen atmosphere. After 24 hours the reaction mixture was connected to a high vacuum pump (at 1 mBar) and heated for 4 hours at 100

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°C (for [C_{6-10}mim]Br) to distil out unreacted 1-bromoalkane, or recrystalised from boiling ethyl ethanoate (for [C_{12-18}mim]Br).

1-alkyl-3-methylimidazolium dibromoarginate(I)

In a 25 cm^3 round bottom flask, a solution of 1-alkyl-3-methylimidazolium bromide (5 mmol) was heated (fused) silver(I) bromide (0.93 g, 5.0 mmol), at 120 °C (for [C_{14-18}mim]Br toluene (20 cm^3) was added as a solvent), to give a straw coloured oil. This was concentrated on a rotary evaporator to remove toluene if used, and heated at 80 °C, under vacuum, to give [1-alkyl-3-methylimidazolium]$_2$[$AgBr_2$] which formed a glass standing.

1-alkyl-3-methylimidazolium tetrachlorocuprate

In a 100 cm^3 round bottom flask, a solution of 1-alkyl-3-methylimidazolium chloride (20 mmol) dissolved in methanol (30 cm^3) was mixed with a methanol (20 cm^3) solution of copper(II) chloride dihydrate (1.70 g, 10 mmol), to give a yellow/brown solution. This was concentrated on a rotary evaporator, and heated at 80 °C, under vacuum, to give yellow brown crystals of [1-alkyl-3-methylimidazolium]$_2$[$CuCl_4$].

Melting Point Determination. Differential scanning calorimetry (DSC 4000, Perkin Elmer) was used to examine the thermal properties of all ionic liquids. The instrument was calibrated for temperature drift using indium prior to the tests. 3-5 mg of sample was accurately weighed, placed in an open aluminum pan and subjected to a heating rate of 20ºC/min under nitrogen flow (20cm^3/min). For samples that were solid under ambient conditions, the DSC ramping range was set as -10ºC ~ 180oC; whereas for liquid samples the tests were performed from -70oC ~ 120ºC. All DSC data were analysed using Pyris™ software supplied by Perkin Elmer. Melting points for each compound are given below in Table 1.

C_n	[$CuCl_4$] / (ºC)	[$AgBr_2$] / (ºC)
8	†	†
10	†	†
12	55.0	44.67
14	54.0	58.21
16	68.0	66.94
18	71.24	72.74

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† No clear melting point observed

Strains and growth media. The following strains were used in this study Gram positives; Staphylococcus aureus NCTC 10788, Staphylococcus epidermidis (methicillin resistant/MRSE) ATCC 35984 and Staphylococcus epidermidis ATCC 12228, Staphylococcus aureus (methicillin resistant/MRSA) ATCC 43300, Gram negatives; Escherichia coli NCTC 8196, Pseudomonas aeruginosa PA01, Klebsiella aerogenes NCTC 7427, Bacillus cereus NCTC 9945, Proteus mirabilis NCTC 12442 and fungi; Candida tropicalis NCTC 7393. All microbial strains used in this study were stored at -70°C in Microbank vials (Pro-Lab Diagnostics, Cheshire, UK) according to manufacturer's directions. All strains were subcultured to Müeller Hinton Agar (MHA; Oxoid, Basingstoke, UK) before testing.