Supplementary Material (ESI) for Green Chemistry

Dicationic Molten Salts (Ionic Liquids) as Re-usable Media for the Controlled Pyrolysis of Cellulose to Anhydrosugars.

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Electronic Supplementary Information

This document contains:

1. A general preparative method for the dicationic salts **6a-e** and **7.**

2. NMR spectroscopic data for the dicationic salts.

3. NMR spectroscopic data for the three principle cellulose pyrolysis products **1, 3** and **4.**

General Procedure for the Preparation of the Dicationic Salts, 6a-6d

All dicationic dihalide salts described in this manuscript were prepared using the same general procedure based on that published by Armstrong *et al.*[1] exemplified below.

$[C_4(mim)_2]Cl_2$ (6a)

A 3-neck, 250ml round-bottomed flask under argon was fitted with a condenser, a thermometer and an addition funnel, and charged with 1-methylimidazole (79.0 g, 962 mmol). The temperature was brought to 80-90 °C and 1,4-dichlorobutane (60.8 g, 479 mmol, 0.498 equiv.) was added dropwise over one hour. On completion of the addition, the temperature was raised to 120 °C for 2 hours. The reaction mixture was then cooled to room temperature, dissolved in distilled water (200 ml) and washed with ethyl acetate (100 ml). The aqueous layer was evaporated under reduced pressure and the small amount of residual 1-methylimidazole was removed by repeated pulverization of the solid and heating of the powder under high vacuum at 90 °C for 2 hour periods. $[C_4(mim)_2]Cl_2$ was collected as a white powder (138 g, 99%).

^{1}H NMR (300 MHz, CD_3OD) δ 1.90 (4H, quint., J = 3.6 Hz), 3.90 (6H, s), 4.26 (4H, t, J = 6.6 Hz), 7.55 (2H, t, J = 1.8 Hz), 7.65 (2H, t, J = 1.8 Hz), 9.01 (2H, s).

^{13}C NMR (75 MHz, CD_3OD) δ 27.9, 36.6, 50.0, 123.7, 125.1, 138.1.

$[C_6(mim)_2]Cl_2$ (6b)

^{1}H NMR (300 MHz, CD_3OD) δ 1.40 (4H, quint., J = 3.6 Hz), 1.89 (4H, quint., J = 7.2 Hz), 3.94 (6H, s), 4.24 (4H, t, J = 7.5 Hz), 7.60 (2H, t, J = 1.8 Hz), 7.69 (2H, t, J = 1.8 Hz), 9.06 (2H, s).

^{13}C NMR (75 MHz, CD_3OD) δ 26.2, 30.5, 36.3, 50.3, 123.4, 124.7, 137.6.

$[C_6(mim)_2]Br_2$ (6c)

^{1}H NMR (300 MHz, CD_3OD) δ 1.35 (4H, quint., J = 3.6 Hz), 1.83 (4H, quint., J = 6.9 Hz), 3.87 (6H, s), 4.17 (4H, t, J = 7.2 Hz), 7.50 (2H, d, J = 1.8 Hz), 7.60 (2H, d, J = 1.8 Hz), 8.96 (2H, s).

^{13}C NMR (75 MHz, CD_3OD) δ 26.5, 30.8, 36.6, 50.6, 123.7, 125.0, 137.8.

$[C_9(mim)_2]Br_2$ (6d)

^{1}H NMR (300 MHz, D_2O) δ 1.05 (10H, br. s), 1.63 (4H, m), 3.65 (6H, s), 3.94 (4H, t, J = 7.0 Hz), 7.21 (4H, dt, J = 1.5, 14.0 Hz), 8.47 (2H, s).

$[C_6(mim)_2][NTf_2]_2$ (6e)

To a solution of $[C_6(mim)_2]Br_2$ (**6c**) (3.44 g, 8.43 mmol) in H_2O (7 ml) in a 25 ml round-bottomed flask was added, with stirring, a solution of $LiNTf_2$ (5.0 g, 17.4 mmol, 2.06 equiv.) in H_2O (7ml) and the reaction mixture was stirred overnight at room temperature. The resulting biphasic mixture was extracted with EtOAc (3 x 10 ml), the organic layers were combined, dried over anhydr. $MgSO_4$ and filtered. Evaporation under reduced pressure afforded the pure $[C_4(mim)_2][NTf_2]_2$ as a clear, colourless liquid in 100% yield.

^{1}H NMR (300 MHz, d^6-DMSO) δ 1.26 (4H, quint., J = 3.6 Hz), 1.76 (4H, quint., J = 7.2Hz), 3.84 (6H, s), 4.14 (4H, t, J = 7.5 Hz), 7.70 (2H, t, J = 1.8 Hz), 7.75 (2H, t, J = 1.8 Hz), 9.08 (2H, s).

$[C_4(py)_2]Cl_2$ (7)

The same general procedure was used as described for **6a**, substituting an equivalent molar quantity of pyridine for 1-methylimidazole.

^{1}H NMR (300 MHz, CD_3OD) δ2.18 (4H, quint., J = 3.6 Hz), 4.80 (4H, t, J = 6.0 Hz), 8.16 (4H, t, J = 7.2 Hz), 8.64 (2H, m), 9.13 (4H, d, J = 5.7 Hz).

^{13}C NMR (75 MHz, CD_3OD) δ 28.7, 61.7, 129.3, 145.9, 146.8.

Anhydrosugar Products from Cellulose Pyrolysis

1,6-Anhydro-3,4-dideoxy-β-D-glycero-hex-3-enopyranos-2-ulose (levoglucosenone, 1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.80 (1H, d, J = 6.9 Hz), 3.93 (1H, dd, J = 4.8, 6.9 Hz), 5.04 (1H, t, J = 4.8 Hz), 5.38 (1H, d, J = 1.5 Hz), 6.15 (1H, dd, J = 1.5, 9.9 Hz), 7.28 (1H, dd, J = 4.5, 9.9 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 66.6, 71.8, 101.7, 127.0, 148.1, 188.9.

These data are in accordance with those published in the literature.[2]

1-(2-Furanyl)-2-hydroxyethanone (3).

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.35 (1H, t, J = 4.8Hz), 4.73 (1H, d, J = 4.8Hz), 6.59 (1H, dd, J = 1.8, 3.6 Hz), 7.29 (1H, dd, J = 0.6, 3.6 Hz), 7.62 (1H, dd, J = 0.6, 1.8 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 65.0, 112.5, 117.8, 147.0, 150.0, 187.6.

These data are in accordance with those published in the literature.[3]

5-(Hydroxymethyl)furfural (4).

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.68 (1H, br s), 4.71 (2H, d, *J* = 3.3 Hz), 6.51 (1H, d, *J* = 3.6 Hz), 7.22 (1H, d, *J* = 3.6 Hz), 9.58 (1H, s).

^{13}C NMR (75 MHz, $CDCl_3$) δ 57.7, 110.9, 124.8, 153.9, 163.2, 179.5.

These data are in accordance with those published in the literature.[4]

References

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