ESI: Superbase ionic liquids for effective cellulose processing from dissolution to carbonisation.

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I Synthesis of ILs

1. Carboxylate imidazolium ionic liquids

1-ethyl-3-methylimidazolium acetate, [C_2C_1im][OAc], was synthesised following established procedure.[1]

^{1}H NMR (400 MHz, DMSO-d6): δ 9.98 (1H, s), 7.86 (1H, t), 7.77 (1H, t), 4.21 (2H, quartet), 3.87 (3H, s), 1.55 (3H, s), 1.40 (3H, t).

1-ethyl-3-methylimidazolium hexanoate, [C_2C_1im][Hex], was synthesised according to the following procedure: a Paar apparatus was charged with freshly distilled ethyl imidazole (50g, 0.52 mol), anhydrous dimethyl carbonate (108g, 1.20 mol) and anhydrous MeOH (416 mL) and stirred at 140°C overnight (max pressure observed, 10bar). After cooling and pressure release ^{1}H NMR indicated incomplete reaction. Vessel was charged with additional dimethyl carbonate (2 mL) and heated to 140°C overnight. The content was transferred to a round bottomed flask, cooled in an ice-bath and the basic solution treated dropwise with hexanoic acid (63g, 0.55 mol) with stirring overnight. The solvent was removed by rotary evaporation and water (200 mL) and charcoal (3.5 g) were added to the brown oil. After stirring vigorously at 40°C overnight the mixture was filtered through Celite and a PTFE microfilter. The water was removed under rotary evaporation. Drying under high vacuum afforded a light yellow viscous oil (104.54g, 89%).

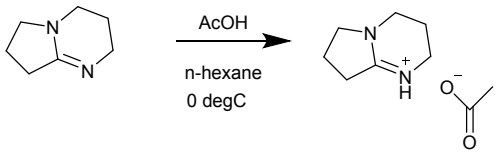
^{1}H NMR (400 MHz, DMSO-d6): δ 10.13 (1H, s), 7.92 (1H, t), 7.82 (1H, t), 4.23 (2H, quartet), 3.88 (3H, s), 1.84 (2H, t), 1.41-1.37 (5H, m), 1.26-1.12 (4H, m), 0.80 (3H, t). ^{13}CNMR (101 MHz, DMSO-d6) δ 176.10, 137.68, 123.54, 122.00, 43.91, 38.81, 35.45, 31.83, 26.33, 22.23, 15.26, 14.00.

m/z 111 ([C_2C_1im]$^+$, 100%), 267 ({[C_1im][im][$C_5H_{11}COO$]}$^+$, 45%), 201 ([im][$C_5H_{11}COO$][H_2O]$^-$, 50%), 357 ({[C_2C_1Im][$C_5H_{11}COO$]$_2$[H_2O]}$^-$, 100%).

2. Carboxylate superbase ionic liquids

The superacid derived ionic liquids were prepared by neutralization of the distilled base with the appropriate carboxylic acids in dry n-hexane with cooling in an ice bath. After addition of the required amount of acid, the solution was left to stir for 24 h at room temperature under an inert atmosphere.

The obtained SILs were repeatedly washed with dry n-hexane. Scheme 1 represents a reaction for synthesis of [DBNH][OAc].



Scheme 1. Reaction synthesis of [DBNH][OAc].

1,5-diazabicyclo[4.3.0]non-5-enium acetate, [DBNH][OAc]: ^{1}HNMR (400 MHz, DMSO-d6) δH 3.51 (2H, t), 3.32 (2H, t), 3.25 (2H, t), 2.74 (2H, t), 1.98 (2H, quintet), 1.85 (2H, quintet), 1.65 (3H, s).

1,5-diazabicyclo[4.3.0]non-5-enium butanoate, [DBNH][But]: ^{1}HNMR (400 MHz, DMSO-d6) δH 10.57 (1H, bs), 3.49 (2H,t), 3.32 (2H, t), 3.25 (2H, t), 2.72 (2H, t), 1.97 (2H, quintet), 1.92-1.81 (4H, m), 1.43 (2H, sextet), 0.83 (3H, t). ^{13}CNMR (101 MHz, DMSO-$_{d6}$), δC 176.60, 163.61, 52.78, 42.41, 38.35, 29.91, 19.76, 19.11, 19.04, 14.72.

m/z 125 ([DBNH]$^{+}$, 100%), 87 ([C_3H_7COO]$^{+}$ 67%).

1,5-diazabicyclo[4.3.0]non-5-enium hexanoate, [DBNH][Hex]: ^{1}HNMR (400 MHz, DMSO-d6) δH 13.30 (bs, 1H), 3.54 (t, 2H), 3.34 (t, 2H), 3.26 (t, 2H), 2.78 (t, 2H), 2.03-1.83 (m, 6H), 1.43 (quintet, 2H), 1.30-1.16 (m, 4H), 0.85 (t, 3H). ^{13}CNMR 101 MHz, (DMSO-d6), δ 176.74, 163.61, 52.78, 42.42, 38037, 37.86, 32.02, 29.91, 26.23, 22.59, 19.11, 19.04, 14.44.

m/z 125 ([DBNH]$^{+}$, 100%), 239 ({[DBN][$C_5H_{11}COO$]}$^{-}$ 100%).

1,8-diazabicyclo[5.4.0]undec-7-enium acetate, [DBUH][OAc]: ^{1}HNMR (400 MHz, DMSO-d6) δH 3.50 (2H, m), 3.42 (2H, t), 3.22 (2H, t), 2.72 (2H, m), 1.87 (2H, m), 1.66-1.58 (9H, m); ^{13}CNMR (101 MHz, DMSO-d_6) δC 174.15, 165.35, 53.37, 48.21, 38.16, 31.46, 28.93, 26.80, 25.44, 24.33;

m/z 153 ([DBUH]$^{+}$, 100%), 59 ([CH_3COO]$^{-}$, 100%), 119 ([$(CH_3COO)_2H$]$^{-}$, 35%).

1,8-diazabicyclo[5.4.0]undec-7-enium propanoate, [DBUH][Prop]: ^{1}HNMR (400 MHz, DMSO-$_{d6}$), δH 3.48 (t, 2H), 3.42 (t, 2H), 3.22 (t, 2H), 2.75 (t, 2H), 1.91-1.82 (m, 4H), 1.67-1.55 (m, 6H), 0.90 (t, 2H). ^{13}CNMR (101 MHz, DMSO-d6), δC 177.56, 165.41, 53.35, 48.21, 38.14, 31.34, 31.10, 28.91, 26.83, 24.35, 19.82, 11.48.

m/z 153 ([DBUH]$^{+}$, 100%), 225 ([DBU][C_2H_5COO]$^{-}$, 100%), 73 ([C_2H_5COO]$^{-}$, 45%).

1,8-diazabicyclo[5.4.0]undec-7-enium hexanoate, [DBUH][Hex]: ^{1}HNMR (400 MHz, DMSO-d6) δH 3.49 (t, 2H), 3.43 (t, 2H), 3.22 (t, 2H), 2.74 (t, 2H), 1.91-1.83 (m, 4H), 1.67-1.56 (m, 6H), 1.42 (quintet, 2H), 1.29-1.16 (m, 4H), 0.85 (t, 3H). ^{13}CNMR (101 MHz, DMSO-d6), δC 176.61, 165.36, 53.40, 48.23, 38.19, 32.07, 31.52, 28.92, 26.81, 26.36, 24.33, 22.61, 19.81, 14.48.

m/z 153 ([DBUH]$^{+}$, 100%), 268 ([DBU][$C_5H_{11}COO$]$^{-}$ 100%).

1,1,3,3-Tetramethylguanidinium acetate, [TMGH][OAc]: ^{1}HNMR (400 MHz, DMSO-d6) δH 2.86 (11H, s), 1.66 (3H, s); ^{13}CNMR (101 MHz, DMSO-d6) δC 173.82, 162.38, 25.39;

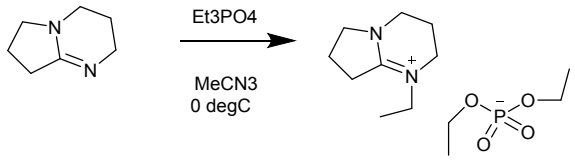
m/z 116 ([TMGH]$^{+}$, 100%), 96 (61), 59 ([CH_3COO]$^{-}$. 100%).

1, 5, 7-Triazabicyclo [4.4. 0] dec-5-enium acetate, [TBDH][OAc]: ^{1}HNMR (400 MHz, DMSO-d_6) δH 10.94 (2H, s), 3.24 (4H, t), 3.11 (4H, t), 1.86 (4H, quintet), 1.64 (3H, s); ^{13}CNMR (101 MHz, DMSO-d_6) δC 176.59, 151.63, 46.52, 37.47, 25.53, 21.00;

m/z 140 ($[TBDH]^+$, 100%), 59 ($[CH_3COO]^-$, 100%), 119 ($[(CH_3COO)_2H]^-$);

3. Phosphate ionic liquids

3-Methylimidazole, 1,5-diazabicyclo[4.3.0]non-5-ene or 1,8-diazabicyclo[5.4.0]undec-7-ene was neutralised in acetonitrile with triethyl phosphate or trimethyl phosphate, as per the example synthesis of [DBNEt][DEP] (Scheme 2). All structures were confirmed with ^{1}H NMR.



Scheme 2. Synthesis of [DBNEt][DEP].

1-ethyl-3-methylimidazolium diethyl phosphate, [C_2C_1im][DEP] ^{1}H NMR (400 MHz, DMSO-d6) δH 9.38 (1H, s), 7.81 (1H, s), 7.73 (1H, s), 4.22 (2H, quartet), 3.86 (3H, s), 3.60 (4H, quintet), 1.42 (3H, t), 1.06 (6H, t). ^{13}C NMR (101 MHz, DMSO-d_6) δC 164.86, 54.23, 51.62, 46.58, 42.01, 30.44, 19.07, 18.18.

m/z 111 ($[C_2C_1im]^+$, 45%), 153 ($[DEP]^-$, 100%), 375 ($\{[C_2C_1im]_2[DEP]\}^-$, 63%),

1-methyl-1,5-diazabicyclo[4.3.0]non-5-enium dimethylphsophate, [DBNMe][DMP]: ^{1}H NMR (400 MHz, DMSO-d6) δH 3.65 (2H, t), 3.36 (2H, t), 3.33 (2H, t), 3.25 (3H, s), 3.23 (3H, s), 3.11 (3H, s), 2.98 (2H, t), 2.03 (2H, quintet), 1.98 (2H, quintet), ^{13}C NMR (101 MHz, DMSO-d_6) δC 164.86, 54.23, 51.62, 46.58, 42.01, 30.44, 19.07, 18.18.

m/z 139 ($[DBNMe]^+$, 100%), 125 ($[DMP]^-$, 100%),

1-ethyl-1,5-diazabicyclo[4.3.0]non-5-enium diethylphsophate, [DBNEt][DEP]: ^{1}H NMR (400 MHz, DMSO-d6) δH 3.65 (2H, quartet), 3.58 (4H, quartet), 3.44 (2H, t), 3.40 (2H, t), 3.35 (2H, t), 3.02 (2H, t), 2.04 (2H, quintet), 1.98 (2H, quintet), 1.17(3H, t), 1.06 (6H, t), ^{13}C NMR (101 MHz, DMSO-d_6) δC 164.17, 59.35, 54.14, 47.77, 43.83, 42.26, 29.94, 19.09, 18.26, 17.28, 12.98.

m/z 153 ($[DBNEt]^+$, 100%), 153 ($[DEP]^-$, 100%).

1-ethyl-1,8-diazabicyclo[5.4.0]undec-7-enium diethylphosphate, [DBUEt][DEP]: ^{1}H NMR (400 MHz, DMSO-d6) δH 3.64 (2H, m), 3.58 (6H, quartet), 3.46 (4H, m), 2.87 (2H, m), 1.97 (2H,t), 1.69(2H, m), 1.64 (4H, m), 1.16 (3H, t), 1.06 (6H, t); ^{13}C NMR (101 MHz, DMSO-d_6) δC 166.18, 59.41, 54.31, 48.87, 48.52, 46.33, 28.24, 27.40, 25.96, 23.15, 10.07, 17.19, 14.04;

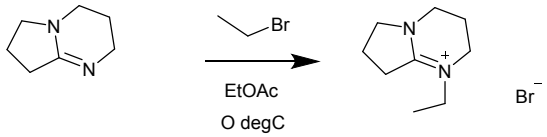
m/z 181 ($[DBUEt]^+$, 100%), 153 ($[DEP]^-$, 100%).

1-ethyl-1,5-diazabicyclo[4.3.0]non-5-enium acetate, [DBNEt][OAc]: ^{1}H NMR (400 MHz, DMSO-d6) δH 3.65 (2H, t), 3.44 (2H, t), 3.40 (2H, quartet), 3.33 (3H, s), 3.21 (2H, t), 3.02 (2H, t), 2.04 (2H, quintet), 1.98 (2H, quintet), 1.15 (3H, t); ^{13}C NMR (101 MHz, DMSO-d_6) δC 174.70, 124.08, 122.73, 46.66, 43.71, 30.93, 27.30, 19.25, 17.97, 15.22.

m/z 153 ($[DBNEt]^+$, 100%), 59 ($[CH_3COO]^-$, 100%).

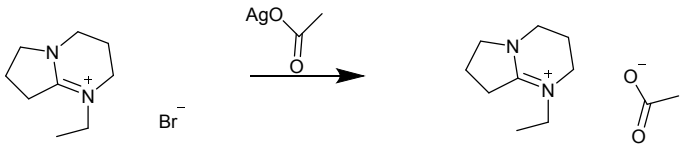
Synthesis of **1-ethyl-1,5-diazabicyclo[4.3.0]non-5-enium acetate [DBNEt][OAc]** was performed in two stages.

1) Ethyl bromide was added to 1-ethyl-1,5-diazabicyclo[4.3.0]non-5-ene in ethyl acetate under cooling to produce [DBNEt]Br (Scheme 3a).



Scheme 3a. Alkylation of 1-ethyl-1,5-diazabicyclo[4.3.0]non-5-en.

2) Anion exchange between [DBNEt]Br and silver acetate in ethyl acetate (Scheme 3b) with subsequent filtering of AgBr and repeated washing of residual bromide until clear on halogen $AgNO_3$ test.



Scheme 3b. Anion exchange to produce [DBNEt][OAc].

II Thermal stability

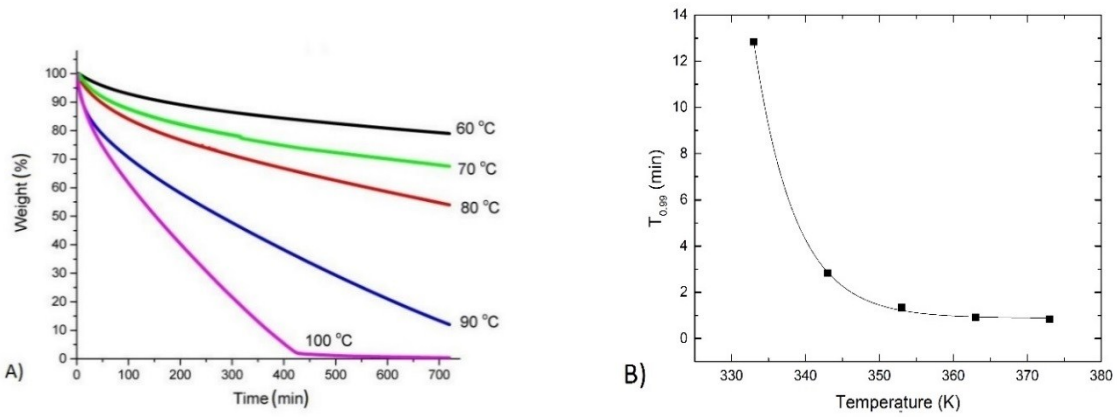


Fig. S1. a) Isothermal TGA analysis of [DBNH][OAc] b) The $t_{0.99}$ (time taken for 1% decomposition to occur) values plotted against temperature (T) in Kelvin. The solid line is an exponential fit to the data. The fitted curve was extrapolated backwards to find $T_{0.01}/10$ corresponding.

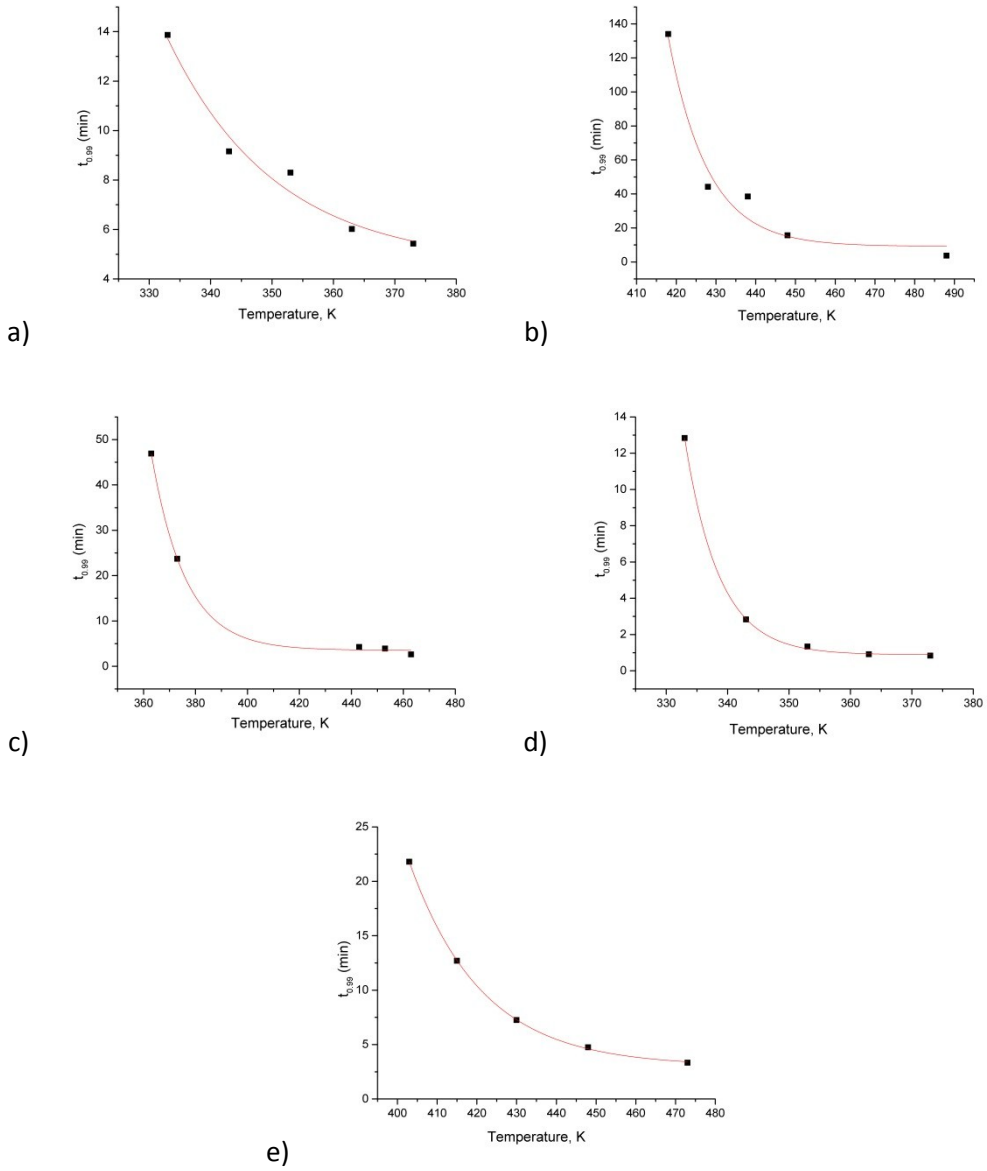


Fig. S2. The $t_{0.99}$ (time taken for 1% decomposition to occur) values plotted against temperature (T) in Kelvin, giving an exponential fit. The fitted curve was extrapolated backwards to find $T_{0.01/10}$ corresponding to $t_{0.99}$ = 600 min/10 hours: a) [C_2C_1im][DEP], b) [DBNH][OAc], c) [DBUH][OAc], d)[DBNEt][DEP], e)[DBUEt][DEP].

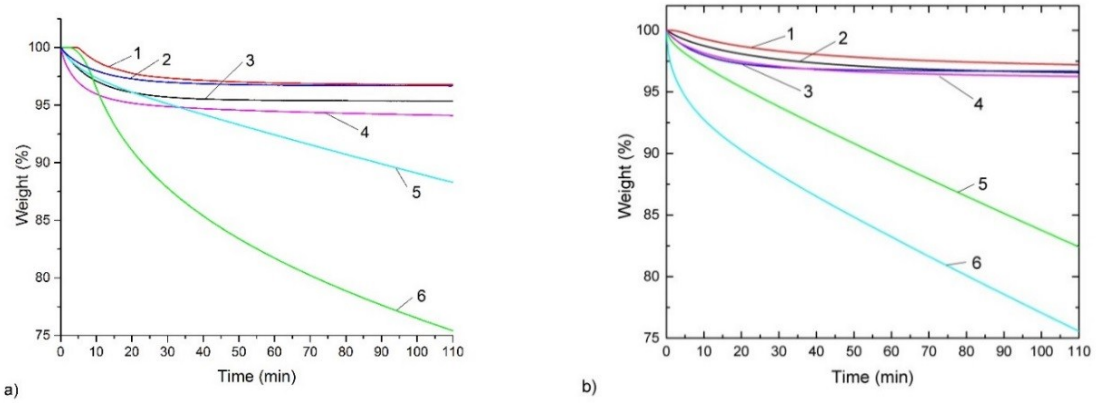
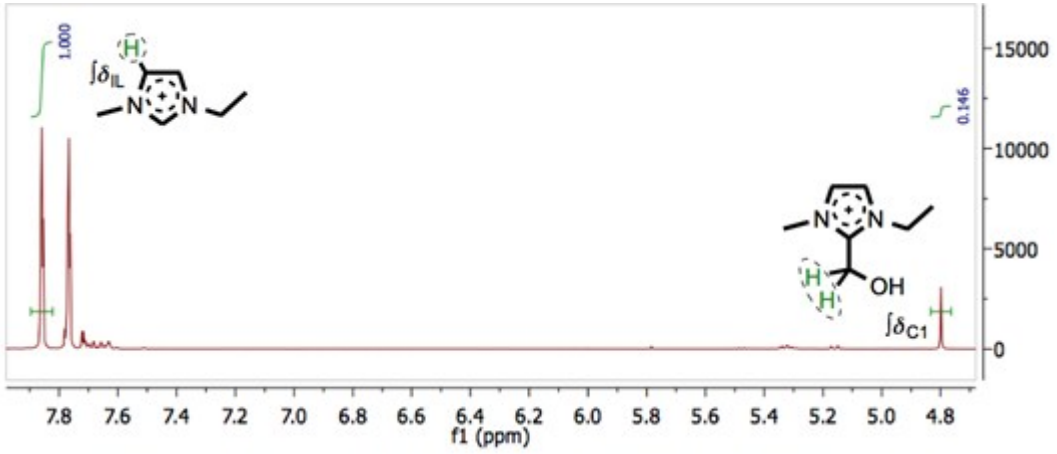
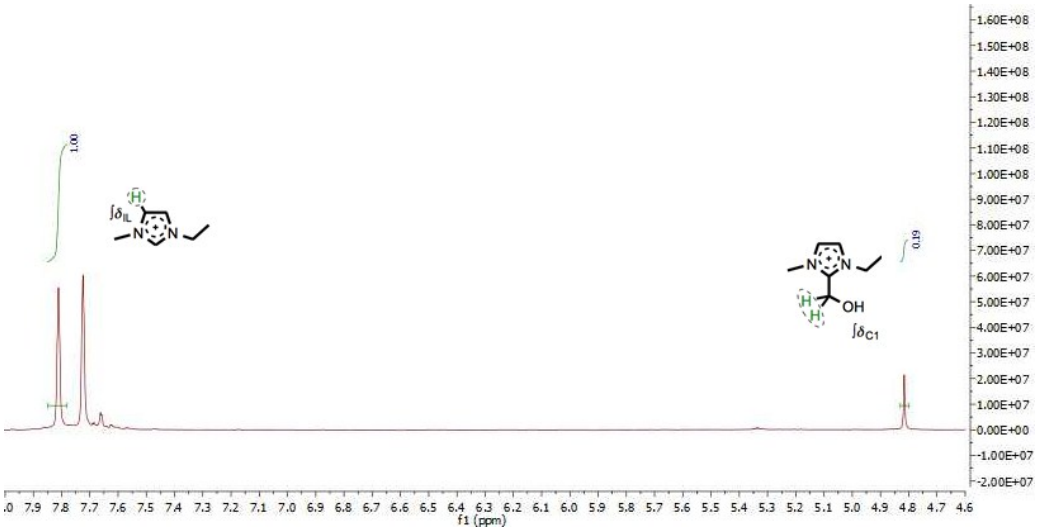


Fig. S3. Isothermal TGA analysis of selected ILs (a), of 15 wt% cellulose solutions in selected ILs (b):1) $[C_2C_1im][DEP]$, 2) [DBNEt][DEP], 3) $[C_2C_1im][OAc]$, 4)[DBUEt][DEP], 5) [DBUH][OAc], 6)[DBNH][OAc].

III Reactivity of imidazolium ILs toward cellulose



a)



b)

c)

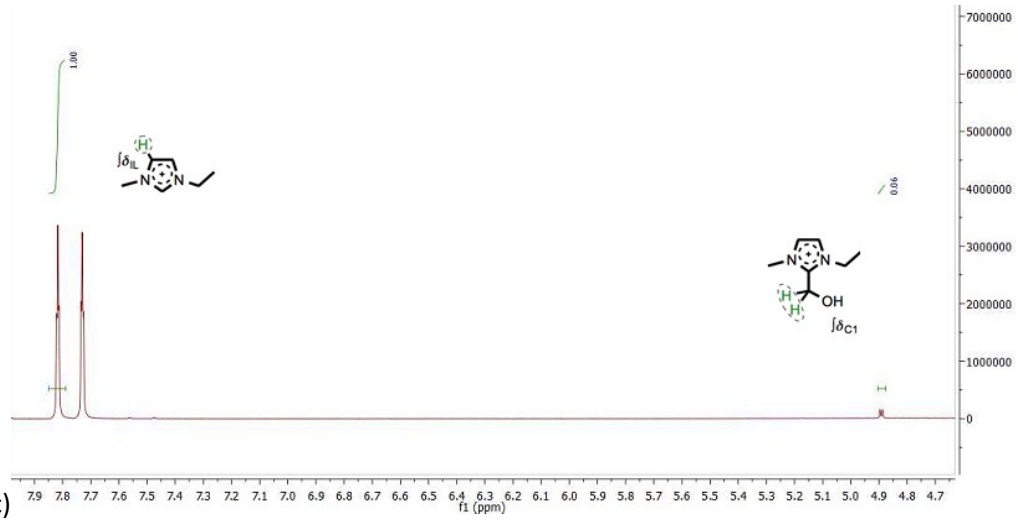


Fig. S4. Example annotated ^{1}H NMR spectra demonstrating the relative concentrations of the C1 adduct cation, $[C_2C_1(HO)C_1{}^2im]^+$, against the parent IL cation, $[C_2C_1im]^+$ for: a) $[C_2C_1im][OAc]$,[2] b) $[C_2C_1im][Hex]$, c) $[C_2C_1im][DEP]$.

References:

1 M. T. Clough, K. Geyer, P. A. Hunt, J. Mertes and T. Welton, *Phys. Chem. Chem. Phys.*, 2013, **15**, 20480–20495.

2 M. T. Clough, J. A. Griffith, O. Kuzmina and T. Welton, *Green Chem.*, 2016, **18**, 3758–3766.