10.1071/CH19047_AC

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Supplementary Material

Solubility of Cellulose in Binary Mixtures of 1-Alkyl-3-methylimidazolium Acetate and Dimethyl Sulfoxide: Influence of Alkyl Chain Length in the Cation

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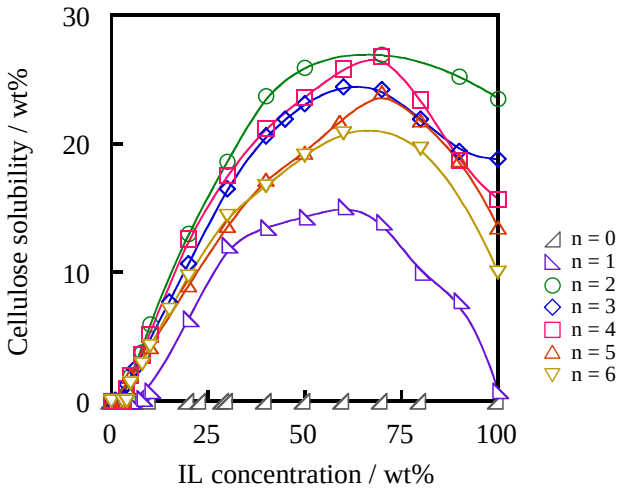


Fig. S1. Dependence of cellulose solubility (wt%) on IL concentration (wt%) in a [C_nMIM][OAc]-DMSO binary system with various alkyl chain lengths at 25 °C.

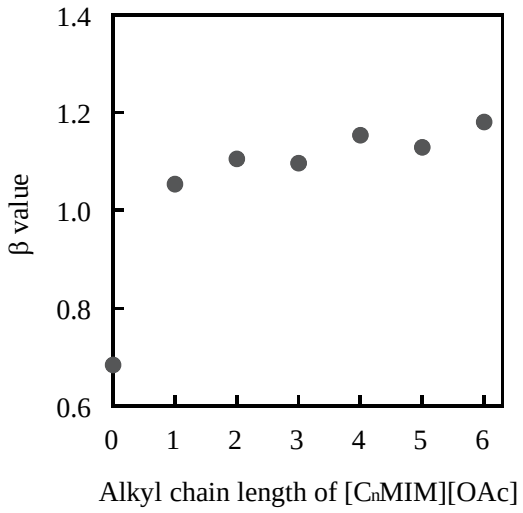
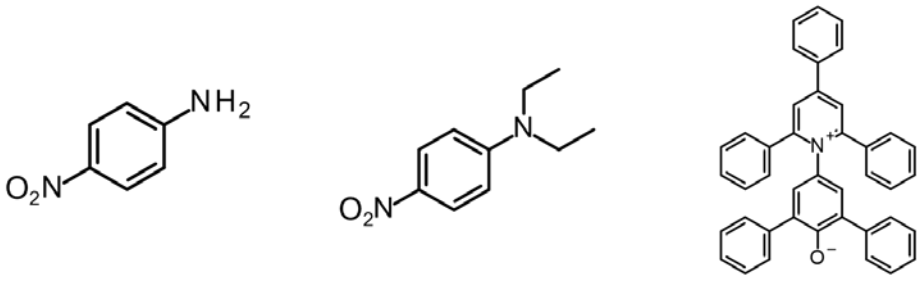


Fig. S2. Dependence of the β value (hydrogen bond basicity) of neat [C_nMIM][OAc] on cation alkyl chain length (n=0–6).



4-nitroaniline (4NA) | N,N-diethyl-4-nitroaniline (DENA) | Reichardt's dye (RD)

Fig. S3. Structures of solvatochromic dyes.

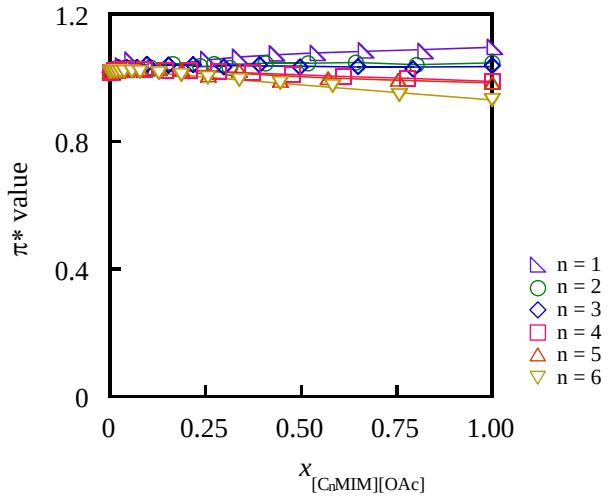


Fig. S4. Dependence of the π* value (dipolarity-polarizability) of [C_nMIM][OAc]-DMSO binary systems on IL mole fraction (x_{IL}) at 25 °C.

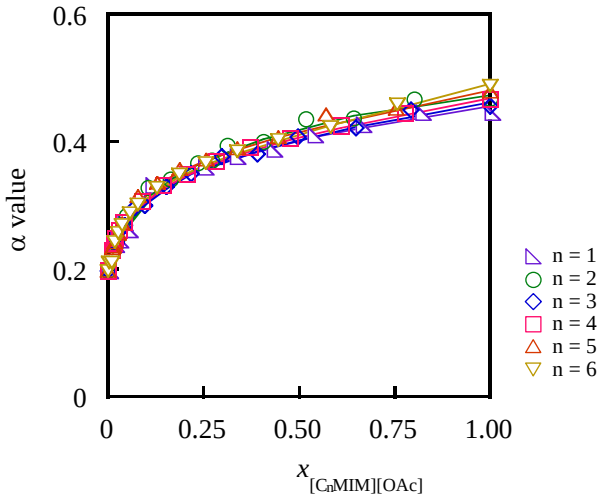


Fig. S5. Dependence of the α value (hydrogen bond acidity) of [C_nMIM][OAc]-DMSO binary systems on IL mole fraction (x_{IL}) at 25 °C.

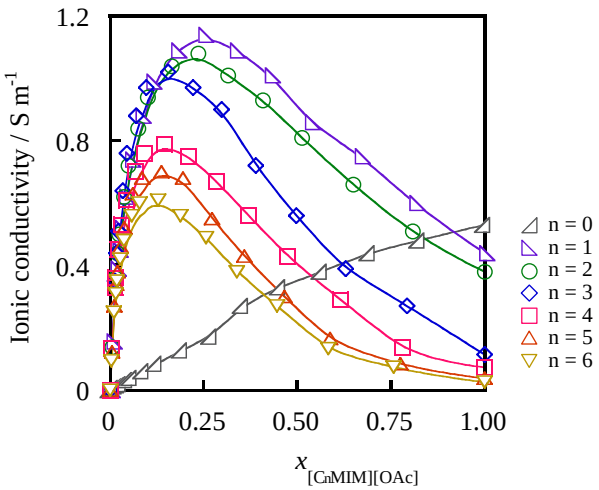


Fig. S6. Dependence of ionic conductivity (S/m) on IL mole fraction (x_{IL}) in a [C_nMIM][OAc]-DMSO binary system with various alkyl chain lengths at 25 °C.

Table S1. Cellulose solubility (g/mol-IL) in neat ionic liquids

Ionic liquids	Measured data		Literature data		
	Solubility / g mol^{-1}(IL)	Cellulose type	Solubility / g mol^{-1}(IL)	Cellulose type	Ref.
[C_2MIM][OAc]	40 (25°C)	Avicel	48 (110℃)	Avicel (225)	[33]
[C_3MIM][OAc]	35 (25°C)	Avicel	22 (80℃)	MCC	[22]
[C_4MIM][OAc]	31 (25°C)	Avicel	31 (70℃)	MCC	[14]
[C_6MIM][OAc]	23 (25°C)	Avicel	15 (80℃)	MCC	[22]

Table S2. β value of neat ionic liquids.

Ionic liquids	Measured data	Literature data	Ref.
[C_2MIM][OAc]	1.11 (25℃)	1.09 (25℃)	[28]
[C_4MIM][OAc]	1.15 (25℃)	1.19 (100℃)	[35]

Synthesis of ionic liquids

A. Synthesis of 1-alkyl-3-methylimidazolium halide

Ionic liquids, 1-alkyl-3-methylimidazolium halide, were synthesized as described previously. [39] Synthesis scheme was shown in **Fig. S7-A**. An equimolar amount of 1-halidealkane and 1-methylimidazol was mixed in a beaker. The mixture was heated at 30-60 ^{o}C and stirred for 24 h. Subsequently, the viscous solution was distilled under reduced pressure with a rotary evaporator at 60^{o}C, for 72 h to remove unreacted solvents. Obtained ionic liquids were characterized using ^{1}H-NMR at 25^{o}C. The ^{1}H-NMR spectra were shown in **Fig. S8**.

B. Synthesis of 1-alkyl-3-methylimidazolium acetate

Ionic liquids, 1-alkyl-3-methylimidazolium acetate, were synthesized following the previously reported protocol with some modifications. [40] Synthesis scheme was shown in **Fig. S7-B**. 1-Alkyl-3-methylimidazolium halide (0.4 mol) and lead (II) acetate trihydrate (0.2 mol) were dissolved in 60 mL and 140 mL of ultrapure water, respectively. The 1-alkyl-3-methylimidazolium halide solution was poured into lead (II) acetate trihydrate solution under vigorous stirring. Immediately after mixing, white solid (lead (II) bromide: $PbBr_2$) or yellow solid (lead (II) iodine: PbI_2) was precipitated out. The mixture was stirred at room temperature for 24 h. Subsequently, the mixture was cooled at 4^{o}C for 24 h, and the precipitates were filtered off. The filtrates were distilled under reduced pressure to remove the water. The obtained ionic liquids 1-alkyl-3-methylimidazolium acetate were subject to silver nitrate solution test. A green solid precipitation upon to the addition of a few drops of silver nitrate implied the existence of halide impurity such as unreacted halide ionic liquids.

Therefore, the unreacted halide ionic liquids were reacted with silver acetate in the same protocol, so that halide impurity was no longer confirmed by silver nitrate solution test. Finally, the obtained ionic liquids were characterized with ^{1}H-NMR, and the spectra were shown in **Fig. S8**.

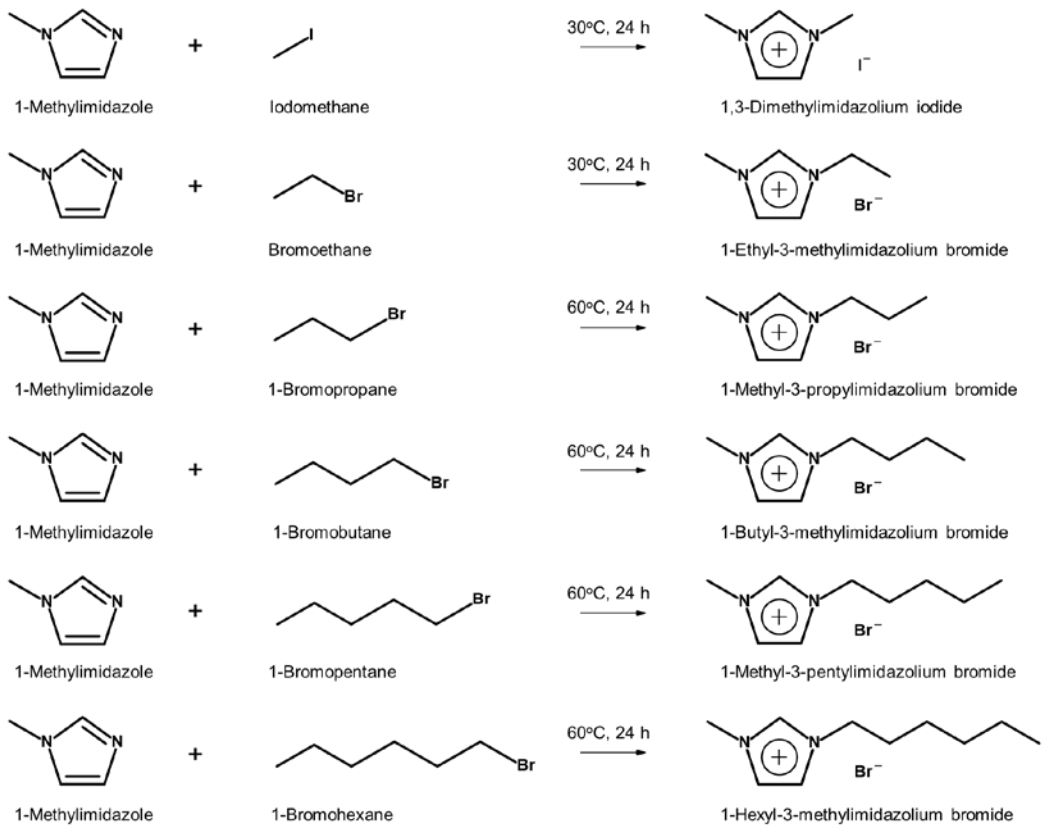


Fig. S7-A. Synthesis scheme of 1-alkyl-3-methylimidazolium halide

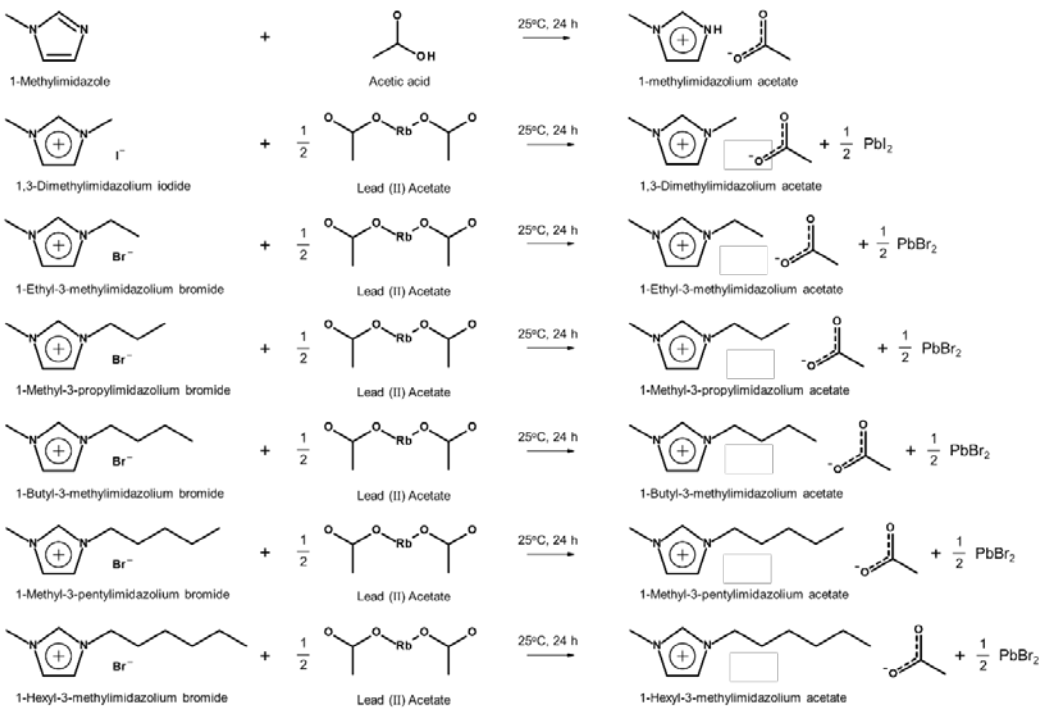
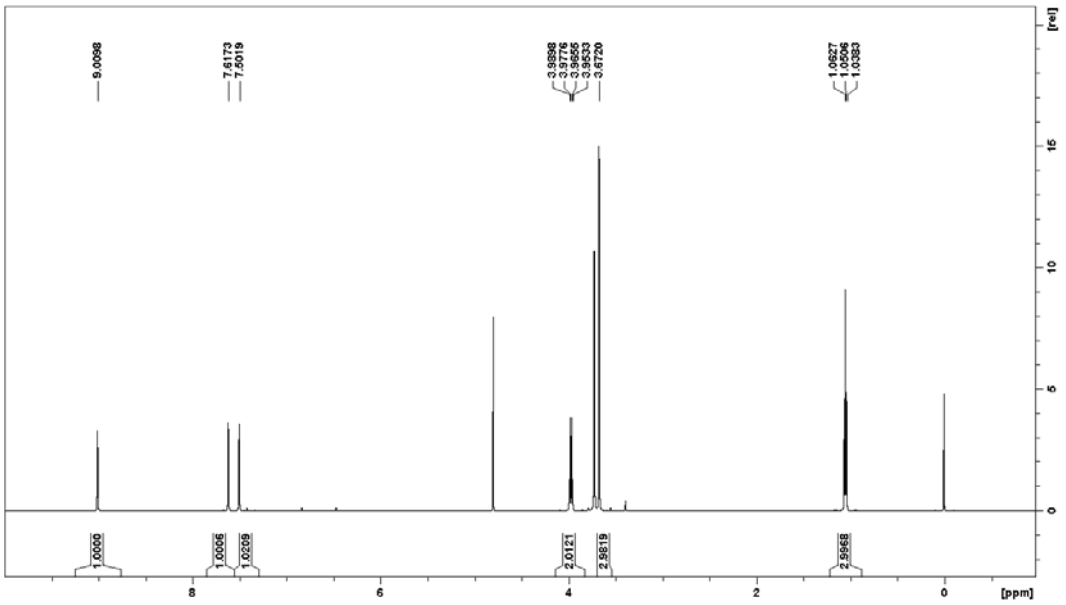


Fig. S7-B Synthesis scheme of 1-alkyl-3-methylimidazolium acetate

1-Ethyl-3-methyimidazolium bromide

$[C_2MIM][Br] + H_2O$



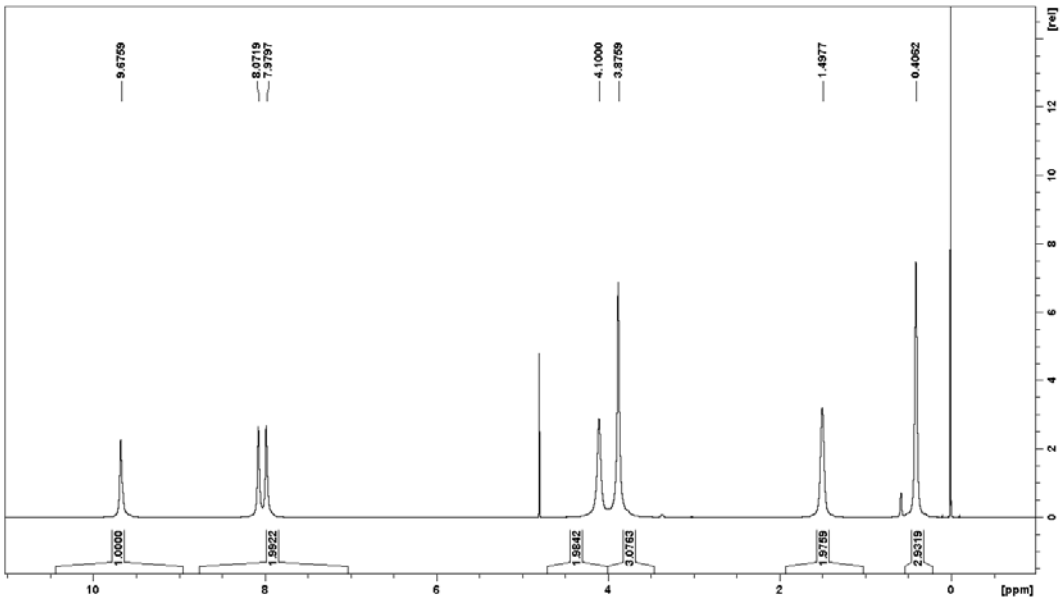
^{1}H-NMR (600 MHz, D_2O) δ=9.0098 (1H, s), δ=7.6173 (1H, s), δ=7.5019 (1H, s), δ=3.9716 (2H, q, 22.02 Hz), δ=3.6720 (3H, s), δ=1.0505 (3H, t, 14.52 Hz).

※ The solid ionic liquid was dissolved in water for ^{1}H-NMR measurement.

(IL concentration 80.5 wt%)

1-Methyl-3-propylimidazolium bromide

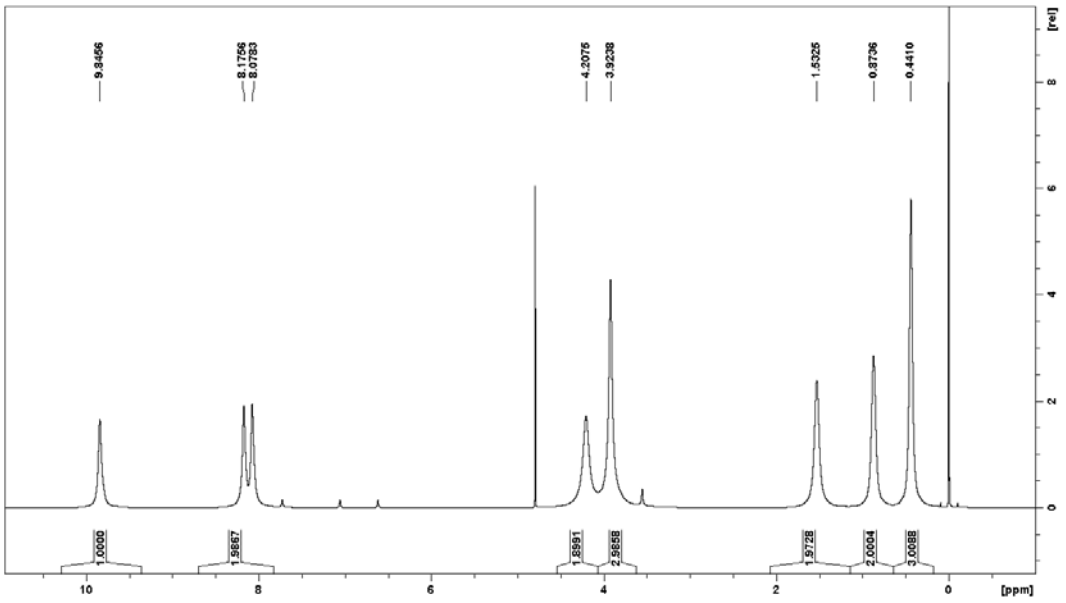
$[C_3MIM][Br]$



^{1}H-NMR (600 MHz, D_2O) δ=9.6759 (1H, s), δ=8.0719 (1H, s), δ=7.9797 (1H, s), δ=4.1000 (2H, s), δ=3.8759 (3H, s), δ=1.4977 (2H, s), δ=0.4062 (3H, s).

1-Butyl-3-methylimidazolium bromide

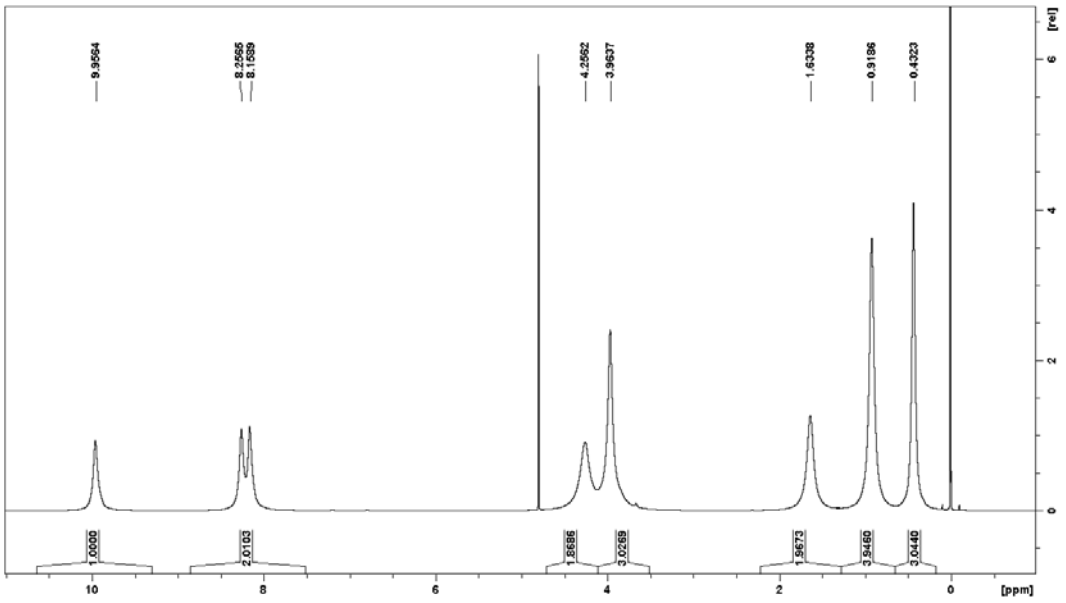
$[C_4MIM][Br]$



^{1}H-NMR (600 MHz, D_2O) δ=9.8456 (1H, s), δ=8.1756 (1H, s), δ=8.0783 (1H, s), δ=4.2075 (2H, s), δ=3.9238 (3H, s), δ=1.5325 (2H, s), δ=0.8736 (2H, s), δ=0.4410 (3H, s).

1-Methyl-3-pentylimidazolium bromide

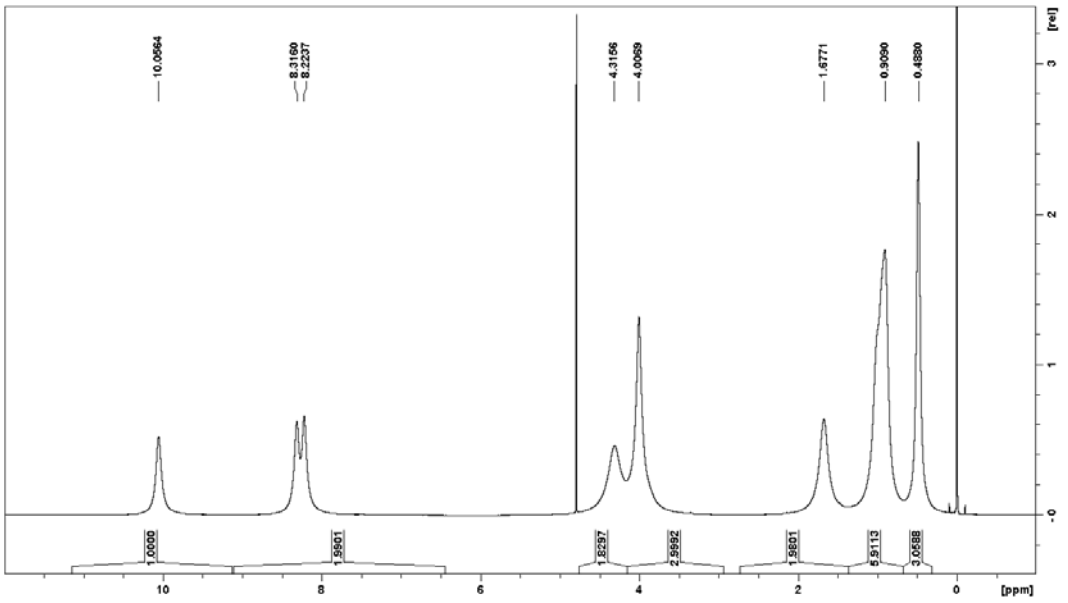
$[C_5MIM][Br]$



^{1}H-NMR (600 MHz, D_2O) δ=9.9564 (1H, s), δ=8.2565 (1H, s), δ=8.1589 (1H, s), δ=4.2562 (2H, s), δ=3.9637 (3H, s), δ=1.6338 (2H, s), δ=0.9186 (4H, s), δ=0.4323 (3H, s).

1-Hexyl-3-methyimidazolium bromide

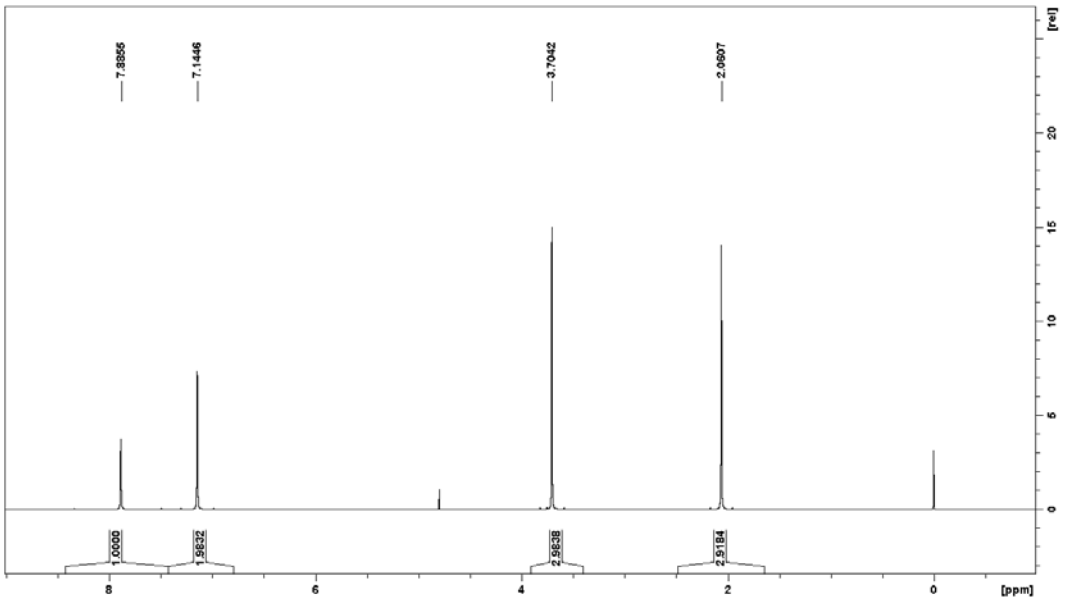
$[C_6MIM][Br]$



^{1}H-NMR (600 MHz, D_2O) δ=10.0564 (1H, s), δ=8.3160 (1H, s), δ=8.2237 (1H, s), δ=4.3156 (2H, s), δ=4.0069 (3H, s), δ=1.6771 (2H, s), δ=0.9090 (6H, s), δ=0.4880 (3H, s).

1-Methylimidazolium acetate

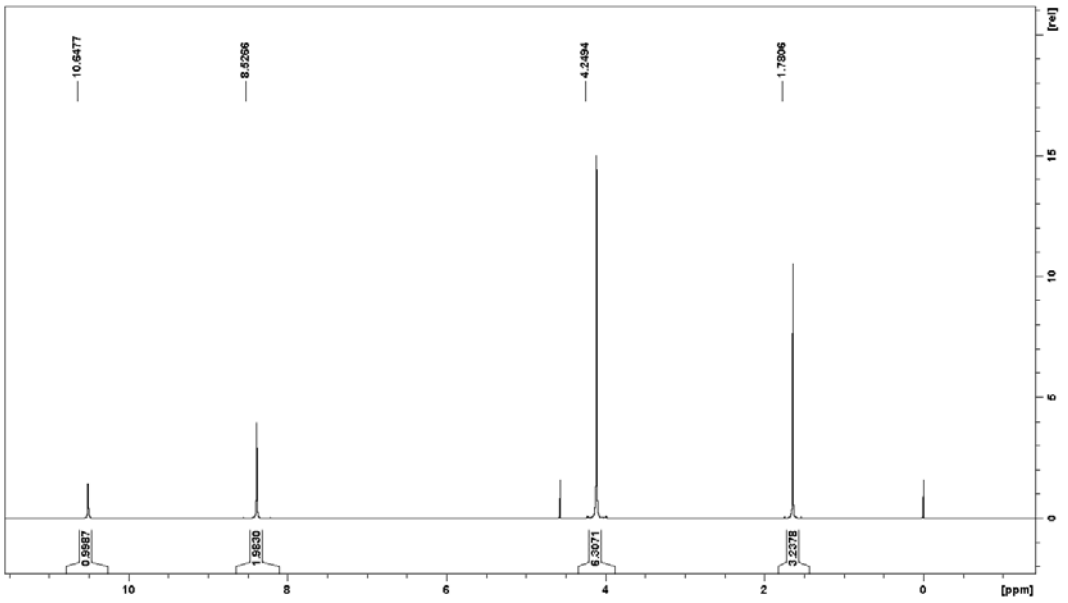
[C_0MIM][OAc]



^{1}H-NMR (600 MHz, D_2O) δ=7.8855 (1H, s), δ=7.1446 (2H, s), δ=3.7042 (3H, s), δ=2.0607 (3H, s).

1,3-Dimethylimidazolium acetate

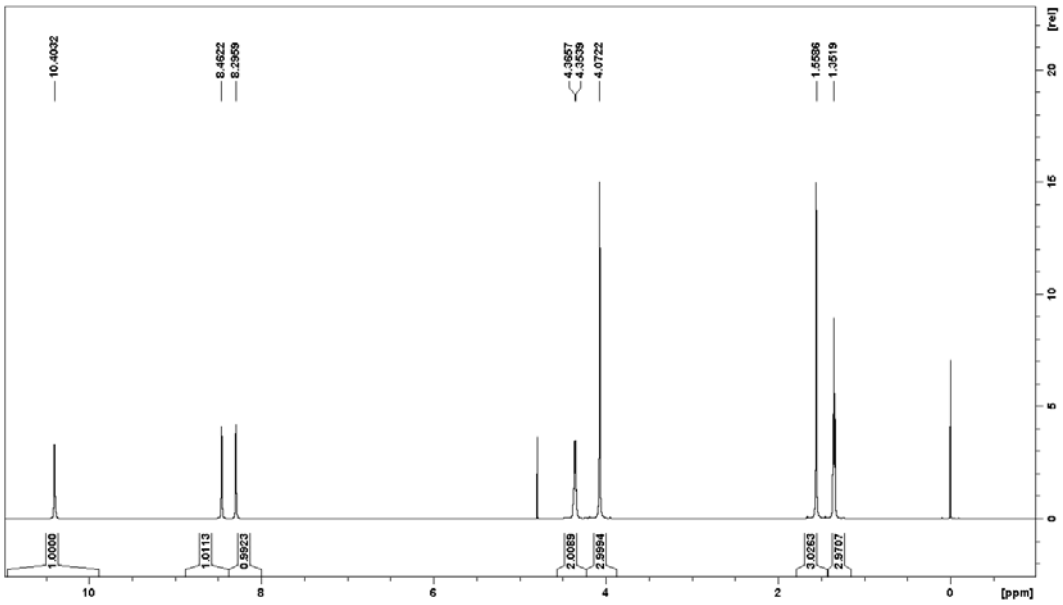
[C_1MIM][OAc]



^{1}H-NMR (600 MHz, D_2O) δ=10.6477 (1H, s), δ=8.5266 (2H, s), δ=4.2494 (6H, s), δ=1.7806 (3H, s).

1-Ethyl-3-methylimidazolium acetate

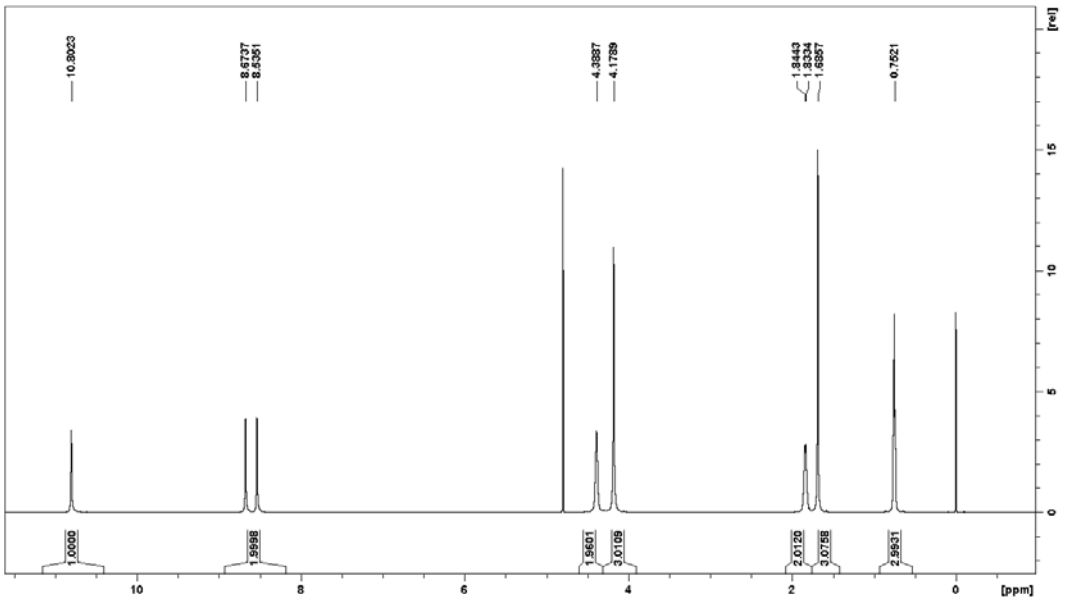
[C_2MIM][OAc]



^{1}H-NMR (600 MHz, D_2O) δ=10.4032 (1H, s), δ=8.4622 (1H, s), δ=8.2959 (1H, s), δ=4.3598 (2H, q, 22.18 Hz), δ=4.0722 (3H, s), δ=1.5586 (3H, s), δ=1.3519 (3H, t, 14.52 Hz).

1-Methyl-3-propylimidazolium acetate

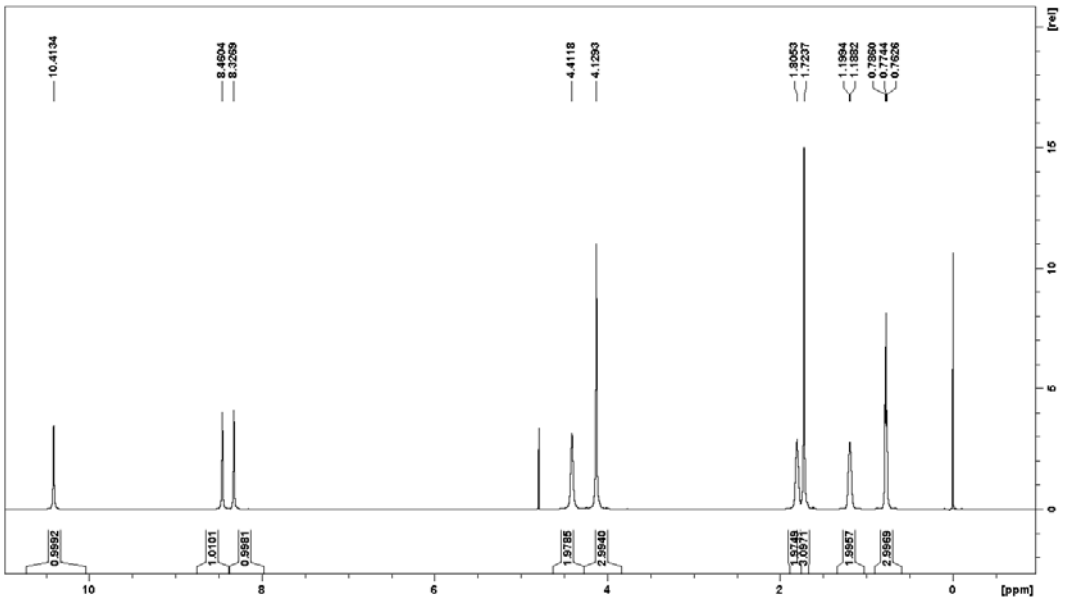
[C_3MIM][OAc]



^{1}H-NMR (600 MHz, D_2O) δ=10.8023 (1H, s), δ=8.6737 (1H, s), δ=8.5351 (1H, s), δ=4.3887 (2H, s), δ=4.1789 (3H, s), δ=1.8389 (2H, q, 20.46 Hz), δ=1.6857 (3H, s), δ=0.7521 (3H, t, 14.54 Hz).

1-Butyl-3-methylimidazolium acetate

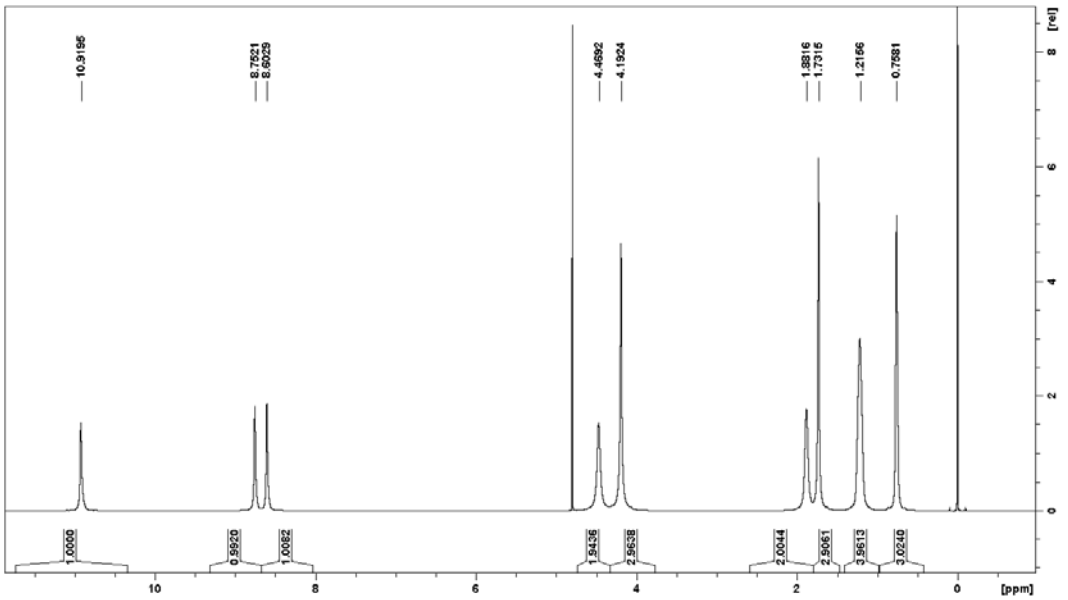
[C_4MIM][OAc]



^{1}H-NMR (600 MHz, D_2O) δ=10.4134 (1H, s), δ=8.4604 (1H, s), δ=8.3269 (1H, s), δ=4.118 (2H, s), δ=4.1293 (3H, s), δ=1.8053 (2H, s), δ=1.7237 (3H, s), δ=1.1938 (2H, t, 21.40 Hz), δ=0.7743 (3H, t, 14.17 Hz).

1-Methyl-3-pentylimidazolium acetate

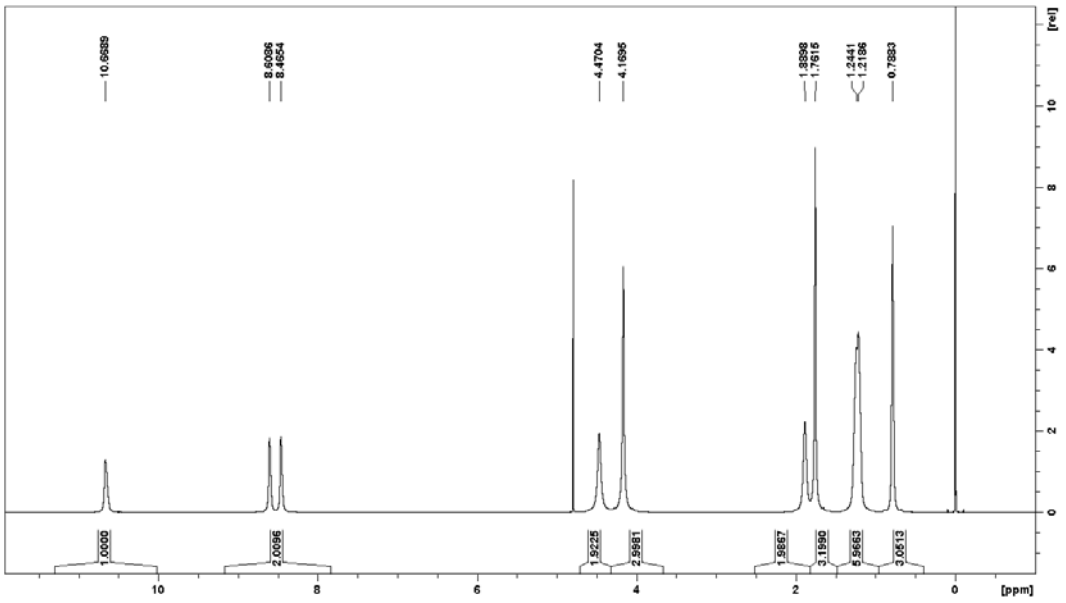
$[C_5MIM][OAc]$



^{1}H-NMR (600 MHz, D_2O) δ=10.9195 (1H, s), δ=8.7521 (1H, s), δ=8.6029 (1H, s), δ=4.4692 (2H, s), δ=4.924 (3H, s), δ=1.8816 (2H, s), δ=1.7315 (3H, s), δ=1.2156 (4H, s), δ=0.7581 (3H, s).

1-Hexyl-3-methylimidazolium acetate

$[C_6MIM][OAc]$



^{1}H-NMR (600 MHz, D_2O) δ=10.6689 (1H, s), δ=8.6086 (1H, s), δ=8.4654 (1H, s), δ=4.4704 (2H, s), δ=4.1695 (3H, s), δ=1.8898 (2H, s), δ=1.7615 (3H, s), δ=1.2313 (6H, t, 18.11 Hz), δ=0.7883 (3H, s).

Fig. S8. ^{1}H-NMR spectra of synthesized ionic liquids