Experimental

N-methylpyrrolidine (97%) and *N*-methylimidazole (99%) were purchased from Sigma-Aldrich. The amines were dried by distillation over KOH, and stored over 4A molecular sieves. Glacial acetic acid and formic acid 98% were purchased from BDH. Trifluoroacetic acid was purchased from Pierce. The acetic acid was dried using calcium hydride as the dehydrating agent followed by distillation. The formic acid and the trifluoroacetic acid were used without further purification. The acid was added dropwise to the base and stirred for one hour under nitrogen. The ionic liquids were then distilled at reduced pressure and collected in a liquid N_2-trap. The products were identified before and after distillation using ^1H NMR and MS.

[Hmpy][trifluoroacetate] δ_H (400MHz, D_2O): 1.96 (m, 4H, $CH_2\text{-}\underline{CH_2}\text{-}\underline{CH_2}\text{-}CH_2$), 1.79 (s, 3H, $N\text{-}\underline{CH_3}$), 4.63 (m, 4H, $\underline{CH_2}\text{-}N\text{-}\underline{CH_2}$). δ_F (300MHz, D_2O): Before; –74.7 (3F, s, CF_3COOH). After; –74.7 (3F, s, CF_3COOH), -175.7 (0.7F, s). *m/z* (EI^+) 86 (100%, $Hmpy^+$). *m/z* (EI^-) 113 (100, CF_3COO^-), 69 (50, CF_3^-).
[Hmim][trifluoroacetate] δ_H (400MHz, D_2O): 3.80 (s, 3H, $N\text{-}C\underline{H_3}$), 7.31 (s, 2H, $N\text{-}C\underline{H}{=}C\underline{H}\text{-}N$), 8.46 (s, 1H, $N{=}C\underline{H}\text{-}N$). δ_F (300MHz, D_2O): Before; –74.7 (3F, s, CF_3COOH) After; -74.7 (3F, s, CF_3COOH), -175. 7 (0.3F, s). *m/z* (EI^+) 83 (100%, $Hmim^+$), *m/z* (EI^-) 113 (100, CF_3COO^-), 69 (50, CF_3^-).
[Hmpy][acetate]: δ_H (400MHz, D_2O): 1.80 (m, 4H, $CH_2\text{-}\underline{CH_2}\text{-}\underline{CH_2}\text{-}CH_2$), 1.96 (s, Before; 3H, After; 3.5H, $\underline{CH_3}\text{-}COOH$), 2.78 (s, 3H, $N\text{-}\underline{CH_3}$), 3.21 (m, 4H, $\underline{CH_2}\text{-}N\text{-}\underline{CH_2}$). *m/z* ($EI^+$) 86 (100%, $Hmpy^+$), *m/z* (EI^-) 59 (100, CH_3COO^-).
[Hmpy][formate]: δ_H (400MHz, D_2O): 1.92 (m, 2H, $CH_2\text{-}CH_2\text{-}\underline{CH_2}\text{-}CH_2$), 2.06 (m, 2H, $CH_2\text{-}\underline{CH_2}\text{-}CH_2\text{-}CH_2$), 2.82 (s, 3H, $N\text{-}\underline{CH_3}$), 2.96 (m, 2H, $CH_2\text{-}N\text{-}\underline{CH_2}$), 3.54 (m, 2H, $\underline{CH_2}\text{-}N\text{-}CH_2$), 8.33 (s, Before; 1H, After; 1.1H, $\underline{H}\text{-}COOH$). *m/z* ($EI^+$) 86 (100%, $Hmpy^+$), *m/z* (EI^-) 45 (100, $HCOO^-$). Any excess base in [Hmpy][formate] will form a separate layer from the salt mixture.
[Hmim][acetate]: δ_H (400MHz, D_2O): 1.80 (s, Before; 3H, After; 2.9H, $\underline{CH_3}\text{-}COOH$), 3.79 (s, 3H, $N\text{-}\underline{CH_3}$), 7.29 (s, 2H, $N\text{-}C\underline{H}{=}C\underline{H}\text{-}N$), 8.45 (s, 1H, $N{=}C\underline{H}\text{-}N$). *m/z* ($EI^+$) 83 (100%, $Hmim^+$), *m/z* (EI^-) 59 (100, CH_3COO^-).
[Hmim][formate]: δ_H (400MHz, D_2O): 3.76 (s, 3H, $N\text{-}C\underline{H_3}$), 7.26 (s, 2H, $N\text{-}C\underline{H}{=}C\underline{H}\text{-}N$), 8.33 (s, Before; 1H, After; 1H, $\underline{H}\text{-}COOH$), 8.45 (s, 1H, $N{=}C\underline{H}\text{-}N$). *m/z* ($EI^+$) 83 (100%, $Hmim^+$), *m/z* (EI^-) 45 (100, $HCOO^-$).

As a result of the differences in the volatilities of the respective acids and amines distillation can result in a slight inequivalency of the acid and base in the distilled ILs. The MS showed the same ions before and after the distillation. The ILs were stored over 4A molecular sieves before further characterisation. The water content was measured with Karl Fisher using Hydranal Coulomat AG as titration solution. Conductivity was obtained in a locally designed cell, made from two platinum vires, by measuring the complex impedance between 0.1Hz and 1 MHz using a Solartron 1260. The cell constant was determined by calibration after each sample measurement with 0.01 M KCl solution at 25°C. Thermal behaviour was studied from –150 °C to 25 °C at a heating/cooling rate of 10°C/min using a Perking Elmer TA Q100. The thermal stability was measured from 25 °C to 300 °C at a heating rate of 10°C/min on a Perking Elmer Pyris 1. The viscosity was measured on an Anton Paar AMVn viscometer using a rolling ball / falling ball principle.