Supplementary Material for Chemical Communications

Experimental details

General Methods:

All reagents and solvents were pure analytical grade materials purchased from commercial sources and were used without further purification, if not stated otherwise. Methanol and ethyl ether were purified by standard procedures. The NMR spectra were recorded in d_6-DMSO on a Varian 300 MHz instrument with TMS as internal standard. The ionic liquids with the same cation have approximate spectra. All IR samples were taken as KBr plates. The spectra were recorded on a Bruker Tensor 27 Fourier transform infrared spectrophotometer with a resolution of 1 cm^{-1}. Secondary ion mass spectrometry (SIMS) was performed on an APEXII FT-ICR mass spectrograph. Glass transition temperatures (T_g) and melting points (T_m) from the onset position were determined from the first heating cycle, after initially cooling samples to -70~ -100 °C. T_g and T_m were recorded on a Thermal Analysis DSC2010 differential scanning calorimeter with heating at 2 °C min^{-1} under nitrogen. Decomposition temperatures (T_{dec}) were determined with a Thermal Analysis SDT2960 simultaneous differential technique analyzer with heating rate of 5 °C min^{-1} under nitrogen. Elemental analyses were performed on a Vario EL elemental analysis instrument. Special rotation values of the ILs in solution in CH_3OH (c = 2) were obtained with a Model 341LC polarimeter.

Typical procedure for preparation of [AA]X:

L-alanine nitrate (L-AlaNO_3)

8.91 g (0.10 mol) of L-alanine was dissolved in 20 mL water. One mole equivalent of (3 mol/L) nitric acid was added dropwise. The reaction mixture then was heated at 60 °C for 24 h. Thereafter the solid was collected and recrystallized from methanol/ether. After drying in vacuo at 60 °C, 15.2 g of white solid L-alanine nitrate was obtained. $[\alpha]_D^{20}$=+15.9° (c = 2 in CH_3OH). ^{1}H-NMR: δ=8.23 (s, 3H, NH_3), 3.99 (q, ^3J(H,H)=7.2 Hz, 1H, CH), 1.38 (d, ^3J(H,H)=7.2 Hz, 3H, CH_3)ppm. ^{13}C-NMR: δ=171.62, 47.87, 15.77ppm. IR: $\tilde{\upsilon}$ =3215, 3009, 1729, 1631, 1514, 1328, 1224, 1145, 1113, 1041, 1010, 872, 731, 640cm^{-1}. Anal. Found: C, 23.71; H, 5.47; N, 18.54; O, 52.28%. Calc. for $C_3H_8N_2O_5$ (MW 152.04): C, 23.69; H, 5.30; N, 18.42; O, 52.59%. m/z (SIMS, positive ion) 90.0549 [$C_3H_8NO_2^+$]. m/z (SIMS, negative ion) 61.9884 [NO_3^-].

Typical procedure for preparation of [AAE]Y:

L-alanine methyl ester nitrate (L-AlaC_1NO_3)

8.91 g (0.10 mol) of L-alanine was dispersed in 33 mL methol. Under the protection of N_2, 8.0 mL (0.11 mol) of thionyl chloride was added dropwise at 0 °C, the reaction mixture then was warmed up to 40 °C and stirred for 2 h. Thereafter the solution was concentrated and added to 80 mL ethyl ether. The precipitate was collected and recrystallized from methanol/ether. After drying in vacuo at 60 °C, 17.8 g L-alanine methyl ester hydrochloride (L-AlaC_1Cl), was gotten. Then 2.79 g (0.020 mol) of L-AlaC_1Cl and 3.40 g (0.020 mol) of $AgNO_3$ were separately dissolved in methanol. After mixing two solutions and filtering the precipitate, the resulting liquid was evaporated in vacuo at 60 °C. The product was purified from methanol/ether untill no Ag^+ salt remained. The product L-AlaC_1NO_3 is colourless transparent liquid which crystallized to white solid after one week. Yield: 90%. $[\alpha]_D^{20}$=+6.2° (c = 2 in CH_3OH). ^{1}H-NMR: δ=8.32 (s, 3H, NH_3), 4.13 (q, ^3J(H,H)=7.2 Hz, 1H, CH), 3.76 (s, 3H, CH_3), 1.39 (d, ^3J(H,H)=7.2 Hz, 3H, CH_3)ppm. ^{13}C-NMR: δ=170.57, 53.02, 48.13, 15.85ppm. IR (KBr plate): $\tilde{\upsilon}$ =3422, 2957, 1750, 1597, 1504, 1391, 1249, 1208, 1117, 976, 904, 841, 826, 754 cm^{-1}. Anal. Found: C, 28.63; H, 6.11; N, 16.93; O, 48.33%. Calc. for $C_4H_{10}N_2O_5$ (MW 166.13): C, 28.92; H, 6.07; N, 16.86; O, 48.15%. m/z (SIMS, positive ion) 104.0706 [$C_4H_{10}NO_2^+$]. m/z (SIMS, negative ion) 61.9884 [NO_3^-].

NMR spectra of [AA]X:

Glycine nitrate (GlyNO_3)

^{1}H-NMR: δ=8.13 (s, 3H, NH_3), 3.67 (s, 2H, CH_2)ppm. ^{13}C-NMR: δ=169.05, 39.87ppm.

L-valine nitrate (L-ValNO_3)

^{1}H-NMR: δ=8.28 (s, 3H, NH_3), 3.81 (d, ^{3}J(H,H)=4.5 Hz, 1H, CH), 2.17 (m, 1H, CH), 1.00 (d, ^{3}J(H,H)=6.9 Hz, 3H, CH_3), 0.97 (d, ^{3}J(H,H)=6.9 Hz, 3H, CH_3)ppm. ^{13}C-NMR: δ=170.33, 57.24, 29.07, 18.06, 17.78ppm.

L-isoleucine nitrate (L-IleNO_3)
^{1}H-NMR: δ=8.35 (s, 3H, NH_3), 3.86 (d, ^{3}J(H,H)=3.3 Hz, 1H, CH), 1.89(m, 1H, CH), 1.21-1.51 (m, 2H, CH_2), 0.93 (d, ^{3}J(H,H)=7.2 Hz, 3H, CH_3), 0.90 (t, ^{3}J(H,H)=7.2 Hz, 3H, CH_3)ppm. ^{13}C-NMR: δ=170.21, 56.04, 35.76, 25.26, 14.49, 11.70ppm.

L-threonine nitrate (L-ThrNO_3)
^{1}H-NMR: δ=4.12 (m, 1H, CH), 3.71 (d, ^{3}J(H,H)=3.9 Hz, 1H, CH), 1.21 (d, ^{3}J(H,H)=7.2 Hz, 3H, CH_3)ppm. ^{13}C-NMR: δ=169.74, 64.84, 57.98, 20.41ppm.

L-proline nitrate (L-ProNO_3)
^{1}H-NMR: δ=9.53 (s, 1H, NH_2), 8.83 (s, 1H, NH_2), 4.34 (m, 1H, CH), 3.26 (m, 2H, CH_2), 2.24-2.34 (m, 1H, CH_2), 1.87-2.05 (m, 3H, CH_2, CH_2)ppm. ^{13}C-NMR: δ=170.51, 58.97, 45.58, 27.96, 23.27ppm.

NMR spectra of [AAE]Y:

Glycine methyl ester nitrate (GlyC_1NO_3)
^{1}H-NMR: δ=8.51 (s, 3H, NH_3), 4.08 (s, 2H, CH_2), 3.82 (s, 3H, CH_3)ppm. ^{13}C-NMR: δ=166.82, 51.23, 39.25ppm.

L-alanine ethyl ester nitrate (L-AlaC_2NO_3)
^{1}H-NMR: δ=8.46 (s, 3H, NH_3), 4.21 (q, ^{3}J(H,H)=7.2 Hz, 2H, CH_2), 4.10 (q, ^{3}J(H,H)=7.2 Hz, 1H, CH), 1.40 (d, ^{3}J(H,H)=7.2 Hz, 3H, CH_3), 1.24 (t, ^{3}J(H,H)=7.2 Hz, 3H, CH_3)ppm. ^{13}C-NMR: δ=170.08, 62.00, 48.04, 15.80, 14.07ppm.

L-valine methyl ester nitrate (L-ValC_1NO_3)
^{1}H-NMR: δ=8.57 (s, 3H, NH_3), 3.88 (d, ^{3}J(H,H)=2.7 Hz, 1H, CH), 3.76 (s, 3H, CH_3), 2.17 (m, 1H, CH), 0.99 (d, ^{3}J(H,H)=6.9 Hz, 3H, CH_3), 0.94 (d, ^{3}J(H,H)=6.9 Hz, 3H, CH_3)ppm. ^{13}C-NMR: δ=169.33, 57.38, 52.65, 29.40, 18.39, 17.60ppm.

L-leucine methyl ester nitrate (L-LeuC_1NO_3)
^{1}H-NMR: δ=8.48 (s, 3H, NH_3), 4.02 (t, ^{3}J(H,H)=6.9 Hz, 1H, CH), 3.76 (s, 3H, CH_3), 1.60-1.75 (m, 3H, CH_2, CH), 0.90 (d, ^{3}J(H,H)=6.3 Hz, 6H, CH_3, CH_3)ppm. ^{13}C-NMR: δ=170.40, 52.94, 50.58, 23.83, 22.13, 22.08ppm.

L-isoleucine methyl ester nitrate (L-IleC_1NO_3)
^{1}H-NMR: δ=8.34 (s, 3H, NH_3), 3.99 (d, ^{3}J(H,H)=3.9 Hz, 1H, CH), 3.76 (s, 3H, CH_3), 1.89(m, 1H, CH), 1.22-1.52 (m, 2H, CH_2), 0.93 (d, ^{3}J(H,H)=6.9 Hz, 3H, CH_3), 0.89 (t, ^{3}J(H,H)=7.2 Hz, 3H, CH_3)ppm. ^{13}C-NMR: δ=170.28, 56.19, 52.78, 36.05, 25.34, 14.37, 11.59ppm.

L-phenylalanine methyl ester nitrate (L-PheC_1NO_3)
^{1}H-NMR: δ=8.45 (s, 3H, NH_3),7.21~7.35 (m, 5H, Ph), 4.33 (q, ^{3}J(H,H)=6.9Hz, 1H, CH), 3.67 (s, 3H, CH_3), 3.08 (d, ^{3}J(H,H)=6.9 Hz, 2H, CH_2)ppm. ^{13}C-NMR: δ=169.47, 134.53, 129.39, 128.70, 127.39, 53.29, 52.68, 36.07ppm.

L-threonine methyl ester nitrate (L-ThrC_1NO_3)
^{1}H-NMR: δ=8.29 (s, 3H, NH_3), 4.15 (m, 1H, CH), 3.99 (d, ^{3}J(H,H)=3.9Hz, 1H, CH), 3.76 (s, 3H, CH_3), 1.20 (d, ^{3}J(H,H)=6.6 Hz, 3H, CH_3)ppm. ^{13}C-NMR: δ=169.73, 64.90, 57.82, 52.97, 20.38ppm.

L-serine methyl ester nitrate (L-SerC_1NO_3)

^{1}H-NMR: δ=8.45 (s, 3H, NH_3), 4.17 (t, ^{3}J(H,H)=6.6 Hz, 1H, CH), 3.83 (d, ^{3}J(H,H)=6.6 Hz, 2H, CH_2), 3.76(s, 3H, CH_3)ppm. ^{13}C-NMR: δ=168.59, 59.52, 54.33, 52.90ppm.

L-proline methyl ester nitrate (L-ProC_1NO_3)
^{1}H-NMR: δ=9.73 (s, 1H, NH_2), 9.10 (s, 1H, NH_2), 4.46 (m, 1H, CH), 3.77 (s, 3H, CH_3), 3.28 (m, 2H, CH_2), 2.25-2.34 (m, 1H, CH_2), 1.89-2.05 (m, 3H, CH_2, CH_2)ppm. ^{13}C-NMR: δ=169.44, 58.96, 53.27, 45.78, 27.86, 23.30ppm.

L-proline ethyl ester nitrate (L-ProC_2NO_3)
^{1}H-NMR: δ=9.79 (s, 1H, NH_2), 9.08 (s, 1H, NH_2), 4.42 (m, 1H, CH), 4.23 (q, ^{3}J(H,H)=7.2 Hz, 2H, CH_2), 3.23 (m, 2H, CH_2), 2.23-2.35 (m, 1H, CH_2), 1.88-2.06 (m, 3H, CH_2, CH_2), 1.25 (d, ^{3}J(H,H)=7.2 Hz, 3H, CH_3)ppm. ^{13}C-NMR: δ=168.91, 62.26, 58.84, 45.61, 27.86, 23.18, 14.00ppm.