Supporting Information

Design and synthesis of hydrophobic and chiral anions from amino acids as precursor for functional ionic liquids

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Characterization and physico-chemical properties of trifluoromethanesulfonyl amino acid methyl ester

[I-Ala]: N-Trifluoromethanesulfonylalanine methyl ester
From 3.2g (36 mmol) of l-alanine and equi-molar of trifluoromethanesulfonic anhydride, 5.2g of I-Ala was obtained (Yield: 63%).

$^1$H NMR (500MHz, CDCl$_3$, $\delta$/ppm relative to TMS): 1.54 (d, $J$=3.8 Hz, 3H), 3.83 (s, 3H), 4.32 (q, $J$=10.8Hz, 1H), 5.68 (s, 1H). ESI–TOF–MS: Calcd. for C$_5$H$_8$NO$_4$SF$_3$ [M-1+2Na]$^+$: m/z = 280.15; Found: 280.06, [M-1$^{-}$]: m/z = 234.17; Found: 233.82.

$[\alpha]_{D}^{25}$ = -26.3 ($c$ = 1.0 g/ 100 ml MeOH), $T_{m}$ = 68.0 °C, $T_{decomp}$ = 119.6 °C.

[I-Val]: N-Trifluoromethanesulfonylvaline methyl ester
From 4.2g (36 mmol) of l-valine and equi-molar of trifluoromethanesulfonic anhydride, 4.9g of I-Val was obtained (Yield: 53%).

$^1$H NMR (500MHz, CDCl$_3$, $\delta$/ppm relative to TMS): 0.93 (d, $J$=3.5 Hz, 3H), 1.05(d, $J$=3.3 Hz, 3H), 2.22(m, $J$=16 Hz, 1H), 3.81 (s, 3H), 4.08 (q, $J$=6.5 Hz, 1H), 5.68 (d, $J$=4Hz, 1H). ESI–TOF–MS: Calcd. for C$_7$H$_{12}$NO$_4$SF$_3$ [M-1+2Na]$^+$: m/z = 308.21; Found: 308.09, [M-1$^{-}$]: m/z = 262.23; Found: 261.83.

$[\alpha]_{D}^{25}$ = -9.1 ($c$ = 1.0 g/ 100 ml MeOH), $T_{m}$ = 44.6 °C, $T_{decomp}$ = 137.0 °C.

[I-Leu]: N-Trifluoromethanesulfonylleucine methyl ester
From 4.5g (34 mmol) of l-leucine and equi-molar of trifluoromethanesulfonic anhydride, 6.3 g of I-Leu was obtained (Yield: 66%).

$^1$H NMR (500MHz, CDCl$_3$, $\delta$/ppm relative to TMS): 0.97 (d, $J$=5.8 Hz, 6H), 1.64 (m, $J$=28 Hz, 2H), 1.80 (m, $J$=16.8 Hz, 1H), 3.80 (s, 3H), 4.23 (q, $J$=7.3, 1H), 5.74 (s, 1H). ESI–TOF–MS: Calcd. for C$_8$H$_{14}$NO$_4$SF$_3$ [M-1+2Na]$^+$: m/z = 322.23; Found: 322.12, [M-1$^{-}$]: m/z = 276.25; Found: 275.83.

$[\alpha]_{D}^{25}$ = -28.2 ($c$ = 1.0 g/ 100 ml MeOH), $T_{m}$ = 14.0 °C, $T_{decomp}$ = 132.9 °C.
Characterization of ionic liquids

[bmim][I-Ala]: *1-butyl-3-methylimidazolium trifluoromethanesulfonylalanine methyl ester salt*

\(^1\)H NMR (500MHz, CDCl\(_3\), \(\delta/\)ppm relative to TMS): 0.95 (t, \(J=7.5\) Hz, 3H), 1.36 (m, \(J=16.5\)Hz, 5H), 1.86 (m, \(J=15\)Hz, 2H), 3.67 (s, 3H), 4.01 (s, 3H), 4.20 (q, \(J=10\)Hz, 1H), 4.27 (m, \(J=11.5\)Hz, 2H), 7.29 (d, \(J=1\)Hz, 1H), 7.36 (d, \(J=1\)Hz, 1H), 7.39 (s, 1H). ESI–TOF–MS: Calcd. for [C\(_8\)H\(_{15}\)N\(_2\)][C\(_5\)H\(_7\)NO\(_4\)SF\(_3\)]: [bmim]^+ \(m/z = 139.22\); Found: 139.13, [I-Ala]^−: \(m/z = 234.17\); Found: 233.82.

[bmim][I-Val]: *1-butyl-3-methylimidazolium trifluoromethanesulfonylvaline methyl ester salt*

\(^1\)H NMR (500MHz, CDCl\(_3\), \(\delta/\)ppm relative to TMS): 0.94 (m, \(J=13.75\) Hz, 9H), 1.37 (m, \(J=18.8\)Hz, 2H), 1.85 (m, \(J=15.3\)Hz, 2H), 1.94 (m, \(J=16.8\)Hz, 1H), 3.65 (s, 3H), 3.82 (d, \(J=3\)Hz, 1H), 4.04 (s, 3H), 4.28 (m, \(J=31.7\)Hz, 2H), 7.30 (d, \(J=0.75\)Hz, 1H), 7.37 (d, \(J=1\)Hz, 1H), 10.3 (s, 1H). ESI–TOF–MS: Calcd. for [C\(_8\)H\(_{15}\)N\(_2\)][C\(_7\)H\(_{11}\)NO\(_4\)SF\(_3\)]: [bmim]^+ \(m/z = 139.22\); Found: 139.13, [I-Val]^−: \(m/z = 262.23\); Found: 261.81.

[bmim][I-Leu]: *1-butyl-3-methylimidazolium trifluoromethanesulfonylleucine methyl ester salt*

\(^1\)H NMR (500MHz, CDCl\(_3\), \(\delta/\)ppm relative to TMS): 0.91 (q, \(J=5\)Hz, 6H), 0.96 (t, \(J=18.8\)Hz, 6H), 1.37 (m, \(J=18.5\)Hz, 2H), 1.52 (t, \(J=7\)Hz, 2H), 1.82 (m, \(J=32.7\)Hz, 3H), 3.66 (s, 3H), 4.02 (s, 3H), 4.11 (t, \(J=7\)Hz, 1H), 4.28 (m, \(J=29\)Hz, 2H), 7.27 (t, \(J=2.3\)Hz, 1H), 7.33 (t, \(J=1.8\)Hz, 1H), 10.28 (s, 1H). ESI–TOF–MS: Calcd. for [C\(_8\)H\(_{15}\)N\(_2\)][C\(_8\)H\(_{13}\)NO\(_4\)SF\(_3\)]: [bmim]^+ \(m/z = 139.22\); Found: 139.13, [I-Leu]^−: \(m/z = 275.83\); Found: 275.83.

[TBP][I-Ala]: *n-tetrabutylphosphonium trifluoromethanesulfonylalanine methyl ester salt*

\(^1\)H NMR (500MHz, CDCl\(_3\), \(\delta/\)ppm relative to TMS): 0.94 (m, \(J=7\) Hz, 12H), 1.32 (d, \(J=3.5\)Hz, 3H), 1.52 (m, \(J=11.4\)Hz, 16H), 2.28 (m, \(J=14.5\)Hz, 8H), 3.74 (s, 3H), 4.12 (q, \(J=10.5\)Hz, 1H). ESI–TOF–MS: Calcd. for [C\(_{16}\)H\(_{36}\)P][C\(_5\)H\(_7\)NO\(_4\)SF\(_3\)]: [TBP]^+ \(m/z = 259.43\); Found: 259.33, [I-Ala]^−: \(m/z = 234.17\); Found: 233.82.

[TBP][I-Val]: *n-tetrabutylphosphonium trifluoromethanesulfonylvaline methyl ester salt*

\(^1\)H NMR (500MHz, CDCl\(_3\), \(\delta/\)ppm relative to TMS): 0.89 (d, \(J=3.5\)Hz, 3H), 0.97 (t, \(J=7\)Hz, 15H), 1.52 (t, \(J=3.5\)Hz, 16H), 1.91 (m, \(J=17\)Hz, 1H), 2.27 (m, \(J=13.8\)Hz, 8H), 3.63 (s, 3H), 3.67 (d, \(J=3.5\)Hz, 1H). ESI–TOF–MS: Calcd. for [C\(_{16}\)H\(_{36}\)P][C\(_7\)H\(_{11}\)NO\(_4\)SF\(_3\)]: [TBP]^+ \(m/z = 259.43\); Found: 259.33, [I-Val]^−: \(m/z = 262.23\); Found: 261.83.

[TBP][I-Leu]: *n-tetrabutylphosphonium trifluoromethanesulfonylleucine methyl ester salt*

\(^1\)H NMR (500MHz, CDCl\(_3\), \(\delta/\)ppm relative to TMS): 0.90 (q, \(J=5.8\)Hz, 6H), 0.97 (t, \(J=7\) Hz, 12H),
1.51 (m, $J=6.5$ Hz, 18H), 1.79 (m, $J=20$ Hz, 1H), 2.28 (m, $J=14.5$ Hz, 8H), 3.63 (s, 3H), 4.03 (t, $J=7.3$ Hz, 1H). ESI–TOF–MS: Calcd. for $[C_{16}H_{36}P][C_{8}H_{13}NO_{4}SF_{3}]$: $[TBP]^+$: $m/z = 259.43$; Found: 259.33, $[I$-Leu$]$: $m/z = 276.25$; Found: 275.83.