

General procedure for synthesis of imidazolium-based compounds (1a and 2a)

To a vigorously stirred solution of 1-methylimidazole or 1-vinylimidazole (30 mmol) in toluene (20 mL) at 0 °C was added 3-chloro-1-propene (2.85 mL, 35 mmol). The solution was heated to reflux at 110 °C for 24 hours, after which the toluene was decanted and the remaining viscous liquid washed with n-hexane and dried under vacuum to give a yellow or red viscous liquid (1a or 2a) in approximately 90% yield.

1-Allyl-3-methylimidazolium chloride (1a)

¹H-NMR (300 MHz, D₂O) δ (ppm): 8.65 (s, 1H), 7.43 (dd, 1H), 7.36 (dd, 1H), 6.11 (m, 1H), 5.35 (dd, 1H), 5.19 (dd, 1H), 4.69 (d, 2H), 3.61 (s, 3H). ¹³C NMR (75 MHz, D₂O) δ (ppm): 135.1, 133.2, 123.0, 122.8, 117.6, 52.3, 44.6. IR (KBr, v/cm⁻¹): 3426, 3145, 3032, 1668, 1573, 1268, 1112, 949. Anal. Calcd. For C₇H₁₁N₂Cl (158.5): C, 52.99; H, 6.94; N, 17.66%; found: C, 52.90; H, 6.87; N, 17.57%.

1-Allyl-3-vinylimidazolium chloride (2a)

¹H-NMR (300 MHz, D₂O) δ (ppm): 9.05 (s, 1H), 7.78 (d, 1H), 7.56 (d, 1H), 7.11 (m, 1H), 6.01 (m, 1H), 5.77 (dd, 1H), 5.43 (dd, 1H), 5.41 (t, 2H), 4.84 (dd, 2H). ¹³C NMR (75 MHz, D₂O) δ (ppm): 208.11, 135.48, 130.52, 127.93, 123.24, 121.32, 109.15, 52.61. IR (KBr, v/cm⁻¹): 3057, 2856, 1649, 1545, 1423, 1369, 13069, 1168, 950, 835. Anal. Calcd. For C₈H₁₁N₂Cl (170.5): C, 56.30; H, 6.45; N, 16.42%; found: C, 56.22; H, 6.37; N, 16.34%.

General procedure for synthesis of ammonium-based compounds (4a-7a)

2-Azido-N, N-dimethylethyl amine (DMAZ) was prepared according to a literature method in which 2-chloro-N, N-dimethyl ethanol amine hydrochloride was reacted with sodium azide in water, followed by ether extraction to get a good yield [10].

Ammonium-based salts (4a-7a) were prepared by alkylation of DMAZ (3) with alkyl or allyl halides such as methyl, ethyl, butyl iodide and 3-chloro-1-propene according to the following method.

To a vigorously stirred solution of DMAZ (3.42 g, 30 mmol) in acetonitrile (20 mL) at 0 °C was added alkyl or allyl halide (35 mmol). The solution was heated to reflux at 60 °C for 24 hours, after which the precipitate was filtered, washed with n-hexane and dried under vacuum to give a white or cream oil/semi-crystalline product (93% yield).

N-(2-azidoethyl)-N, N, N-trimethyl ammonium iodide (4a)

¹H NMR (300 MHz, D₂O) δ (ppm): 3.83 (t, 2H), 3.46 (t, 2H), 3.10 (s, 9H). ¹³C NMR (75 MHz, D₂O) δ (ppm): 64.03, 53.29, 44.44. IR (KBr, v/cm⁻¹): 3019, 2986, 2130, 2007, 1488. Anal. Calcd. For C₅H₁₃N₄I (256): C, 23.43; H, 5.07; N, 21.87%; found: C, 23.38; H, 4.96; N, 21.77.

N-(2-azidoethyl)-N, N-dimethyl- N-ethyl ammonium iodide (5a)

¹H NMR (300 MHz, D₂O) δ (ppm): 4.00(t, 2H), 3.55 (m, 2H), 3.50 (t, 2H), 3.19 (s, 6H), 1.44(t, 3H). ¹³C NMR (75 MHz, D₂O) δ (ppm): 61.21, 60.74, 50.20, 44.31, 7.30. IR (KBr, v/cm⁻¹): 3034, 2972, 2141, 2010, 1645, 1481, 1293, 12.44. Anal. Calcd. For C₆H₁₅N₄I (270): C, 26.66; H, 5.55; N, 20.74%; found: C, 26.59; H, 5.47; N, 20.66.

N-(2-azidoethyl)-N, N-dimethyl- N-butyl ammonium iodide (6a)

¹H NMR (300 MHz, D₂O) δ (ppm): 3.88(t, 2H), 3.49 (t, 2H), 3.31 (t, 2H), 3.09 (s, 6H), 1.71(m, 3H), 1.33(m, 2H), 0.92(t, 3H). ¹³C NMR (75 MHz, D₂O) δ (ppm): 64.93, 61.63, 50.77, 44.32, 23.74, 18.97, 12.72. IR (KBr, v/cm⁻¹): 3035, 2965, 2874, 2140, 2009, 1481. Anal. Calcd. For C₈H₁₉N₄I (298): C, 32.21; H, 6.37; N, 18.79%; found: C, 32.13; H, 6.30; N, 18.68.

N-(2-azidoethyl)-N, N-dimethyl-prop-2-en-1-ammonium chloride (7a)

¹H NMR (300 MHz, D₂O) δ (ppm): 6.07(m, 1H), 6.01(m, 1H), 5.55(dd, 1H), 4.07(d, 2H), 3.56(t, 2H), 3.43 (t, 2H), 3.14 (s, 6H). ¹³C NMR (75 MHz, D₂O) δ (ppm): 128.93, 121.89, 68.05, 63.96, 56.11, 50.87. IR (KBr, v/cm⁻¹): 3005, 2862, 2100, 1650, 1551, 1468, 1421, 1253, 1173. Anal. Calcd. For C₇H₁₅N₄Cl (190.5): C, 44.10; H, 7.87; N, 29.39%; found: C, 43.95; H, 7.80; N, 29.29%

General procedure for synthesis of halide-functionalized ammonium-based salts (8b and 9b)

To a stirred solution of 2-(dimethylamino) ethanol (3.00 mL, 30 mmol) in acetonitrile (20 mL) at 0 °C was added methyl iodide (1.86 mL, 35 mmol) or 3-chloro-1-propene (2.85 mL, 35 mmol). The solution was heated to reflux at 60 °C for 12 hours, after which the precipitate was filtered, washed with n-hexane and dried under vacuum to give a white or cream solid product (8a and 9a, 93% yield).

Compounds 8b and 9b were prepared by reaction of 8a and 9a with thionyl chloride. A solution of the ammonium-based salt (8a or 9a) (30 mmol) in chloroform (20 mL) was cooled in an ice-water bath and a solution of thionyl chloride (4.41 mL, 37.5 mmol) in chloroform (20 mL) was added dropwise with stirring. After the mixture was left at reflux for 3-4 hours, the precipitate was filtered. The crude product was purified by dissolving it in boiling ethanol and then the impurities were separated by filtration. The product was dried under vacuum to give a yellow (8b, 86% yield) or light brown (9b, yield: 81%) solid.

N-(2-hydroxyethyl)-N, N, N-trimethyl ammonium iodide (8a)

^1H NMR (300 MHz, D_2O) δ (ppm): 3.67 (t, 2H), 3.37 (t, 2H), 3.10 (s, 9H). ^{13}C NMR (75 MHz, D_2O) δ (ppm): 56.51, 42.11, 40.32. IR (KBr, v/cm^{-1}): 3396, 2957, 1488, 1385, 1048, 752. Anal. Calcd. For $\text{C}_5\text{H}_{14}\text{INO}$ (231): C, 25.97; H, 6.06; N, 6.06%; found: C, 25.91; H, 5.93; N, 5.96%.

N-(2-chloroethyl)-N, N, N-trimethyl ammonium iodide (8b)

^1H NMR (300 MHz, DMSO) δ (ppm): 4.08 (t, 2H), 3.79 (t, 2H), 3.18 (s, 9H). ^{13}C NMR (75 MHz, D_2O) δ (ppm): 64.77, 52.58, 40.33. IR (KBr, v/cm^{-1}): 3382, 2972, 1486, 1302, 1245, 731. Anal. Calcd. For $\text{C}_5\text{H}_{13}\text{IClN}$ (249.5): C, 24.04.98; H, 5.21; N, 5.84%; found: C, 23.96; H, 5.13; N, 5.76%.

N-(2-hydroxyethyl)-N, N-dimethyl-prop-2-en-1-ammonium chloride (9a)

^1H NMR (300 MHz, D_2O) δ (ppm): 5.76 (m, 1H), 5.64 (dd, 1H), 5.46 (dd, 1H), 3.91 (m, 2H), 3.72 (t, 2H), 3.30 (t, 2H), 3.00 (s, 6H). ^{13}C NMR (75 MHz, D_2O) δ (ppm): 129.12, 124.19, 67.18, 64.49, 55.08, 50.62. IR (KBr, v/cm^{-1}): 3404.6, 3067.4, 2848.6, 1636.1, 1488.2, 1334.5, 1188.6, 1050.6, 877.1, and 752.9. Anal. Calcd. For $\text{C}_7\text{H}_{16}\text{ClNO}$ (165.5): C, 50.75; H, 9.66; N, 8.45%; found: C, 50.63; H, 9.57; N, 8.36%.

N-(2-chloroethyl)-N, N-dimethyl-prop-2-en-1-ammonium chloride (9b)

^1H NMR (300 MHz, DMSO- d_6) δ (ppm): 6.00 (m, 1H), 5.68 (dd, 1H), 5.57 (dd, 1H), 4.13 (m, 2H), 4.11 (t, 2H), 3.77 (t, 2H), 3.13 (s, 6H). ^{13}C NMR (75 MHz, DMSO- d_6) δ (ppm): 127.95, 125.84, 65.64, 62.68, 49.90, 38.65. IR (KBr, v/cm^{-1}): 3010.3, 2933.4, 1636.1, 1472.5, 1336.4, 1275.3, 1149.1, 1001.3, 758.8, and 701.6. Anal. Calcd. For $\text{C}_7\text{H}_{15}\text{Cl}_2\text{N}$ (184): C, 45.65; H, 8.15; N, 7.60%; found: C, 45.33; H, 8.06; N, 7.51%.

General procedure for synthesis of ammonium-imidazolium based compounds (10a-13a)

1-methylimidazole or 1-vinylimidazole (30 mmol) was slowly added into a stirred solution of halide-functionalized ammonium salt (8b or 9b) (35 mmol) in acetonitrile (30 mL). The reaction mixture was heated to reflux at 110 °C for 24 hours to give a semi-crystalline liquid. The product was washed with a mixture of acetonitrile and ethyl acetate (50:50) and dried under vacuum at 80 °C to give a yellow viscous (10a and 11a) or dark red (12a and 13a), semi-crystalline liquid in approximately 90% yield.

3-(N, N, N-trimethylammonio) ethyl-1-methyl-1-H-imidazol-3-ium chloride iodide (10a)

^1H NMR (300 MHz, D_2O) δ (ppm): 8.68 (s, 1H), 7.44 (d, 1H), 7.38 (d, 1H), 3.97 (t, 2H), 3.85(s, 3H), 3.71 (t, 2H), 3.15 (s, 9H). ^{13}C NMR (75 MHz, D_2O) δ (ppm): 123.59, 122.34, 122.28, 66.08, 53.48, 43.57, 33.18. IR (KBr, v/cm^{-1}): 3424, 3014, 2970, 1561, 1484, 1304, 733. Anal. Calcd. For $\text{C}_9\text{H}_{19}\text{ClIN}_3$ (204.5): C, 52.81; H, 9.29; N, 20.53%; found: C, 52.74; H, 9.20; N, 20.44%.

3-(N, N, N-trimethylammonio) ethyl-1-vinyl-1-H-imidazol-3-ium chloride iodide (11a)

^1H NMR (300 MHz, D_2O) δ (ppm): 8.93 (s, 1H), 7.66 (d, 1H), 7.41 (d, 1H), 6.96 (m, 1H), 5.61 (dd, 1H), 5.26 (dd, 1H), 3.84 (t, 2H), 3.66 (t, 2H), 3.01 (s, 9H). ^{13}C NMR (75 MHz, D_2O) δ (ppm): 126.78, 121.77, 119.27, 117.9, 109.52, 66.05, 35.46, 42.97. IR (KBr, v/cm^{-1}): 3384, 3010, 2972, 1628, 1488, 1302, 731. Anal. Calcd. For $\text{C}_{10}\text{H}_{19}\text{ClIN}_3$ (343): C, 34.98; H, 5.54; N, 12.24%; found: C, 30.87; H, 5.53; N, 12.16%.

3-(2-Allyldimethylammonio) ethyl-1-methyl-1-H-imidazol-3-ium dichloride (12a)

^1H NMR (300 MHz, D_2O) δ (ppm): 8.33 (s, 1H), 7.27 (d, 1H), 7.24 (d, 1H), 5.88 (m, 1H), 5.63 (dd, 1H), 5.57 (dd, 1H), 3.90 (m, 2H), 3.77 (s, 3H), 3.63 (t, 2H), 3.37 (t, 2H), 3.02 (s, 6H). ^{13}C NMR (75 MHz, D_2O) δ (ppm): 135.95, 129.16, 123.37, 122.41, 121.77, 66.97, 56.92, 49.96, 41.72, 35.54. IR (KBr, v/cm^{-1}): 3097.8, 2933.4, 16035.9, 1580.1, 1523.7, 1470.9, 1336.4, 1284.9, 1234.0, 1011.0, 832.1, and 799.2. Anal. Calcd. For $\text{C}_{11}\text{H}_{21}\text{Cl}_2\text{N}_3$ (266): C, 49.62; H, 7.89; N, 15.78%; found: C, 49.54; H, 7.81; N, 15.68%.

3-(2-Allyldimethylammonio) ethyl-1-vinyl-1-H-imidazol-3-ium dichloride (13a)

^1H NMR (300 MHz, D_2O) δ (ppm): 8.38 (s, 1H), 7.84 (d, 1H), 7.80 (d, 1H), 7.02 (m, 1H), 5.92 (m, 1H), 5.64 (dd, 1H), 5.62 (dd, 1H), 5.55 (dd, 1H), 5.21 (dd, 1H), 3.92 (m, 2H), 3.85 (m, 2H), 3.64 (t, 2H), 3.38 (t, 2H), 3.04 (s, 6H). ^{13}C NMR (75 MHz, D_2O) δ (ppm): 132.29, 129.66, 128.76, 122.99, 122.25, 119.41, 109.89, 67.41, 60.06, 49.96, 43.38. IR (KBr, v/cm^{-1}): 3087.7, 3005.4, 1649.4, 1555.8, 1480.3, 1369.0, 1232.1, 1176.9, 1006.5, and 753.9. Anal. Calcd. For $\text{C}_{12}\text{H}_{21}\text{Cl}_2\text{N}_3$ (278): C, 51.79; H, 7.55; N, 15.10%; found: C, 51.68; H, 7.47; N, 15.02%.

General procedure for synthesis of dicyanamide-based ILs

Silver dicyanamide was prepared by mixing equal molar amounts of silver nitrate and sodium dicyanamide in aqueous solutions followed by filtration. The dicyanamide-based ILs were prepared by metathesis of corresponding salts with silver dicyanamide according to a literature method [31].

1-Allyl-3-methylimidazolium dicyanamide (1b)

^1H -NMR (300 MHz, D_2O) δ (ppm): 8.63 (s, 1H), 7.45 (dd, 1H), 7.36 (dd, 1H), 6.10-5.77 (m, 1H), 5.37 (dd, 1H), 5.16 (dd, 1H), 4.68 (d, 2H), 3.60 (s, 3H). ^{13}C NMR (75 MHz, D_2O) δ (ppm): 137.3, 124.2, 123.8, 118.5, 55.4, 46.7. IR (KBr, v/cm^{-1}):

3431, 3144, 3084, 2233, 2194, 2135, 1625, 1573, 1312, 1167, 947. Anal. Calcd. For C₉H₁₁N₅(189): C, 57.14; H, 5.82; N, 37.03%; found: C, 57.03; H, 5.76; N, 36.95%.

1-Allyl-3-vinylimidazolium dicyanamide (2b)

¹H-NMR (300 MHz, D₂O) δ (ppm): 9.07 (s, 1H), 7.83 (d, 1H), 7.60 (d, 1H), 7.15 (m, 1H), 6.06 (m, 1H), 5.82 (dd, 1H), 5.50 (dd, 1H), 5.45 (t, 2H), 4.87 (dd, 2H). ¹³C NMR (75 MHz, D₂O) δ (ppm): 206.21, 136.35, 131.56, 129.71, 124.24, 122.24, 120.59, 109.86, 52.78. IR (KBr, v/cm⁻¹): 3551, 3423, 3087, 2856, 2233, 2194, 2127, 1653, 1423, 1312, 1172, 952, 829, 756. Anal. Calcd. For C₁₀H₁₁N₅ (201): C, 59.70; H, 5.47; N, 34.82%; found: C, 59.61; H, 5.39; N, 34.76%.

N-(2-azidoethyl)-N, N, N-trimethyl ammonium dicyanamide (4b)

¹H NMR (300 MHz, DMSO) δ (ppm): 3.97 (t, 2H), 3.51 (t, 2H), 3.27 (s, 9H). ¹³C NMR (75 MHz, D₂O) δ (ppm): 118.23, 68.13, 55.32, 46.53. IR (KBr, v/cm⁻¹): 3042, 2992, 2252, 2192, 2130, 2100, 1478, 1308, 1252, 934. Anal. Calcd. For C₇H₁₃N₇(195): C, 43.07; H, 6.66; N, 50.25%; found: C, 42.95; H, 6.58; N, 50.18.

N-(2-azidoethyl)-N, N-dimethyl-N-ethyl ammonium dicyanamide (5b)

¹H NMR (300 MHz, DMSO) δ (ppm): 3.90 (t, 2H), 3.49 (m, 2H), 3.41 (t, 2H), 3.10(6H, s), 1.34 (t, 3H). ¹³C NMR (75 MHz, D₂O) δ (ppm): 118.98, 64.36, 46.81, 63.21, 51.63, 10.45. IR (KBr, v/cm⁻¹): 2931, 2859, 2240, 2193, 2138, 1636, 1480, 1305, 1016. Anal. Calcd. For C₈H₁₅N₇(209): C, 45.93; H, 7.17; N, 46.89%; found: C, 45.86; H, 7.09; N, 46.81.

N-(2-azidoethyl)-N, N-dimethyl, N-butyl ammonium dicyanamide (6b)

¹H NMR (300 MHz, D₂O) δ (ppm): 3.81(t, 2H), 3.42 (t, 2H), 3.23 (t, 2H), 3.02 (s, 6H), 1.60(m, 3H), 1.23(m, 2H), 0.84(t, 3H). ¹³C NMR (75 MHz, D₂O) δ (ppm): 119.1, 68.61, 63.76, 51.22, 46.03, 25.87, 20.16, 14.21. IR (KBr, v/cm⁻¹): 3029, 2962, 2875, 2238, 2168, 2099, 1478, 1298, 1252. Anal. Calcd. For C₁₀H₁₉N₇(237): C, 50.63; H, 8.01; N, 41.35%; found: C, 50.55; H, 7.92; N, 41.23%

N-(2-azidoethyl)- N, N-dimethyl-prop-2-en-1-ammonium dicyanamide (7b)

¹H NMR (300 MHz, D₂O) δ (ppm): 5.99(m, 1H), 5.92(m, 1H), 5.47(dd, 1H), 4.00(d, 2H), 3.79(t, 2H), 3.35 (t, 2H), 3.05 (s, 6H) ¹³C NMR (75 MHz, D₂O) δ (ppm): 129.31, 123.14, 68.79, 64.47, 56.83, 51.55. IR (KBr, v/cm⁻¹): 3031, 2245, 2183, 2131, 2832, 2110, 1642, 1581, 1476, 1452, 1281, 1150. Anal. Calcd. For C₉H₁₅N₇(221): C, 48.86; H, 6.78; N, 44.34%; found: C, 48.78; H, 6.69; N, 44.25%

3-(N, N, N- trimethylammonio) ethyl-1-methyl-1-H-imidazol-3-ium di-dicyanamide (10b)

¹H NMR (300 MHz, D₂O) δ (ppm): 8.22 (s, 1H), 7.65 (d, 1H), 7.55 (d, 1H), 3.91 (t, 2H), 3.87(s, 3H), 3.76 (t, 2H), 3.30 (s, 9H). ¹³C NMR (75 MHz, D₂O) δ (ppm): 125.59, 124.25, 122.20, 119.69, 62.73, 53.58, 42.46, 35.58. IR (KBr, v/cm⁻¹): 3410, 3146, 3026, 2235, 2131, 1636, 1578, 1482, 1328, 1172. Anal. Calcd. For C₁₃H₁₉N₉ (301): C, 51.82; H, 6.31; N, 41.86%; found: C, 51.73; H, 6.25; N, 41.79%.

3-(N, N, N- trimethylammonio) ethyl-1-vinyl-1-H-imidazol-3-ium di-dicyanamide (11b)

¹H NMR (300 MHz, D₂O) δ (ppm): 8.28 (s, 1H), 7.84 (d, 1H), 7.69 (d, 1H), 7.10 (m, 1H), 5.84 (dd, 1H), 5.79 (dd, 1H), 3.95 (t, 2H), 3.71 (t, 2H), 3.17 (s, 9H). ¹³C NMR (75 MHz, D₂O) δ (ppm): 127.78, 127.79, 120.12, 120.01, 119.79, 110.25, 66.13, 35.49, 42.96. IR (KBr, v/cm⁻¹): 3495, 3012, 2233, 2190, 2134, 16.53, 1555, 1482, 1314, 1176. Anal. Calcd. For C₁₄H₁₉N₉ (313): C, 53.62; H, 6.07; N, 40.25%; found: C, 53.56; H, 5.92; N, 40.11%.

3-(2-allyldimethylammonio) ethyl-1-methyl-1-H-imidazol-3-ium di-dicyanamide (12b)

¹H NMR (300 MHz, D₂O) δ (ppm): 8.10 (s, 1H), 7.13 (d, 1H), 7.08 (d, 1H), 5.75 (m, 1H), 5.56 (dd, 1H), 5.53 (dd, 1H), 3.80 (m, 2H), 3.64 (s, 3H), 3.27 (t, 2H), 2.93 (t, 2H), 2.72 (s, 6H). ¹³C NMR (75 MHz, D₂O) δ (ppm): 136.42, 129.75, 123.99, 123.35, 122.43, 122.09, 67.33, 60.40, 50.22, 43.06, 35.46. IR (KBr, v/cm⁻¹): 3088.3, 3013.7, 2850.6, 2233.1, 2194.7, 2138.2, 1632.3, 1578.5, 1473.0, 1423.8, 1365.7, 1234.0, 1085.3, 963.7, 834.1, and 721.9. Anal. Calcd. For C₁₅H₂₁N₉ (327): C, 55.04; H, 6.42; N, 38.53%; found: C, 54.95; H, 6.37; N, 38.44%.

3-(2-allyldimethylammonio) ethyl-1-vinyl-1-H-imidazol-3-ium di-dicyanamide (13b)

¹H NMR (300 MHz, D₂O) δ (ppm): 7.95 (s, 1H), 7.37 (d, 1H), 7.28 (d, 1H), 6.92 (m, 1H), 5.87 (m, 1H), 5.59 (dd, 1H), 5.53 (dd, 1H), 5.36 (dd, 1H), 4.68 (dd, 1H), 3.85 (m, 2H), 3.33 (t, 2H), 2.95 (t, 2H), 2.77 (s, 6H). ¹³C NMR (75 MHz, D₂O) δ (ppm): 134.49, 129.72, 128.23, 127.72, 123.17, 122.56, 119.78, 109.91, 67.38, 60.13, 50.13, 42.93. IR (KBr, v/cm⁻¹): 3081.6, 2957.0, 2233.6, 2194.9, 2135.0, 1650.1, 1555.0, 1479.5, 1384.5, 1336.4, 1178.1, 961.0, 760.3, and 723.0. Anal. Calcd. For C₁₆H₂₁N₉ (339): C, 56.63; H, 6.19; N, 37.16%; found: C, 53.53; H, 6.11; N, 37.08%.