Synthesis and physico-chemical properties of new hydrophobic ionic liquids containing dimethylpyridinium and trimethylpyridinium cations

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Supporting information:

Synthesis and characterizations of ionic liquids.

1-Butyl-3-methyl-5-methylpyridinium bromide [B3M5MPYR][Br]
10 g (0.093 mol) of 3,5-lutidine was mixed with 21 g (0.154 mol) of bromobutane in 50 mL of ethyl acetate. Solution was stirred for 24 hours at 75 °C. The resulting white solid precipitate at the bottom of the flask was filtered, washed with ethyl acetate (3 x 50 mL) and ether (3 x 50 mL) and dried under high vacuum (0.05 mbar) for 12 hours. 20.1 g of a white powder was obtained. Yield: 88 %.

1H NMR (400 MHz, CDCl₃, δ): 9.201 (2H, s, PyrR-CH₂o), 7.969 (1H, s, PyrR-CH₃), 4.891-4.854 (2H, t, CH₂), 2.563 (6H, s, 2CH₃-Pyr), 2.026-1.950 (2H, m, CH₂), 0.944-0.907 (3H, t, CH₃).
IR (cm⁻¹): 2993 (νC-H aromatic), 2954, 2927, 2871 (νC-H aliphatic), 1629 (νC=N), 1503, 1455 (νC=C).

1-Butyl-2-methyl-3-methylpyridinium bromide [B2M3MPYR][Br]
10 g (0.103 mol) of 2,3-lutidine was mixed with 21 g (0.154 mol) of bromobutane in 100 mL of acetonitrile. Solution was stirred for 72 hours at 75 °C. Solvent was removed by rotary evaporation, and resulting white powder was washed with ethyl acetate (3 x 50 mL), ether (3 x 50 mL) and dried under high vacuum (0.05 mbar) for 12 hours. 13.6 g of a white powder was obtained. Yield: 60 %.

1H NMR (400 MHz, CDCl₃, δ): 9.457-9.442 (1H, d, CH₃-Pyr), 8.206-8.186 (1H, d, CH-Pyr), 7.793-7.774 (1H, t, CH-Pyr), 4.892-4.853 (2H, t, CH₂), 2.814 (3H, s, CH₃-Pyr), 1.882-1.805 (2H, m, CH₂), 1.490-1.396 (2H, m, CH₂), 0.927-0.890 (3H, t, CH₃).
IR (cm⁻¹): 2997 (νC-H aromatic), 2956, 2872 (νC-H aliphatic), 1618 (νC=N), 1512, 1467 (νC=C).

1-Butyl-2-methyl-5-ethylpyridinium bromide [B2M5EPYR][Br]
11.9 g (0.100 mol) of 2-methyl-5-ethylpyridine was mixed with 21 g (0.154 mol) of bromobutane in 100 mL of acetonitrile. Solution was stirred for 72 hours at 75 °C. Solvent was then removed by rotary evaporation, and resulting light yellow solid was washed with ethyl acetate (3 x 50 mL), ether (3 x 50 mL) and dried under high vacuum (0.05 mbar) for 12 hours. 21.8 g of a dark white powder was obtained. Yield: 84 %.

1H NMR (400 MHz, CDCl₃, δ): 9.516-9.512 (1H, d, PyrR-CH₂o), 8.141-8.116 (1H, quad, Pyr-Pyr), 7.870-7.849 (1H, d, Pyr-Pyr), 4.858-4.819 (2H, t, CH₂), 1.918-1.840 (2H, m, CH₂), 1.528-1.434 (2H, m, CH₂), 0.970-0.933 (3H, t, CH₃).

1-Butyl-2,3,5-trimethylpyridinium bromide [B2M3M5MPYR][Br]
11.9 g (0.098 mol) of 2,3,5-collidine was mixed with 21 g (0.154 mol) of bromobutane in 100 mL of acetonitrile. Solution was stirred for 24 hours at 75 °C. After removing the solvent by rotary evaporation, the resulting light yellow viscous liquid was washed with ethyl acetate (3 x 50 mL) and ether (3 x 50 mL) and dried under high vacuum (0.05 mbar) for 12 hours. 21.8 g of a dark white powder was obtained. Yield: 84 %.

1H NMR (400 MHz, CDCl₃, δ): 9.516-9.512 (1H, d, Pyr-Pyr), 8.141-8.116 (1H, quad, Pyr-Pyr), 7.870-7.849 (1H, d, Pyr-Pyr), 4.858-4.819 (2H, t, CH₂), 2.909-2.842 (5H, m, CH₃-Pyr, CH₂-Pyr), 1.918-1.840 (2H, m, CH₂), 1.528-1.434 (2H, m, CH₂), 0.970-0.933 (3H, t, CH₃).
mL), ether (3 x 50 mL) and dried under vacuum (0.05 mbar) for 12 hours. 18.5 g of a yellow viscous liquid was obtained. Yield: 72 %.

1H NMR (400 MHz, CDCl₃, δ): 9.398 (1H, s, Pyr-CH₀), 7.928 (1H, s, Pyr-CH₃), 4.850-4.811 (2H, t, CH₂), 2.743 (3H, s, CH₃-Pyr), 2.484 – 2.469 (6H, d, 2CH₃-Pyr), 1.892-1.814 (2H, m, CH₂), 1.510-1.416 (2H,m,CH₂), 0.946-0.910 (3H, t, CH₃).

IR (cm⁻¹): 3045 (νC=H aromatic), 2954, 2914, 2869 (νC=H aliphatic), 1626 (νC=C).

1-Octyl-3-methyl-5-methylpyridinium bromide [O3M5MPYR][Br]
7.5 g (0.070 mol) of 3,5-lutidine was mixed with 30 g (0.155 mol) of bromooctane in 100 mL of ethyl acetate. Solution was stirred for 24 hours at 75 °C. The resulting white solid precipitate at the bottom of the flask was filtered, washed with ethyl acetate (3 x 50 mL) and ether (3 x 50 mL) and dried under high vacuum (0.05 mbar) for 12 hours. 19.9 g of a white powder was obtained. Yield: 89 %.

1H NMR (400 MHz, CDCl₃, δ): 9.181 (2H, s, Pyr-CH₀), 7.971 (1H, s, Pyr-CH₃), 4.864-4.827 (2H, t, CH₂), 2.553 (6H, s, 2CH₃-Pyr), 2.019 - 1.945 (2H, m, CH₂), 1.323-1.179 (10H, m, C₅H₁₀), 0.821R0.787 (3H, t, CH₃).

IR (cm⁻¹): 2997 (νC=H aromatic), 2920, 2853 (νC=H aliphatic), 1629, 1604 (νC=N), 1500, 1467 (νC=C).

1-Octyl-2-methyl-3-methylpyridinium bromide [O2M3MPYR][Br]
8 g (0.075 mol) of 2,3-lutidine was mixed with 30 g (0.155 mol) of bromooctane in 100 mL of acetonitrile. Solution was stirred for 72 hours at 75 °C. After removing the solvent by rotary evaporation, the resulting white powder was washed with ethyl acetate (3 x 50 mL), ether (3 x 50 mL) and dried under high vacuum (0.05 mbar) for 12 hours. 17.2 g of a white powder was obtained. Yield: 76 %.

1H NMR (400 MHz, CDCl₃, δ): 9.482-9.467 (1H, d, CH-Pyr), 8.191R8.175 (1H, d, CH-Pyr), 7.839-7.804 (1H, t, CH-Pyr), 4.916-4.877 (2H, t, CH₂), 2.823 (3H, s, CH₃-Pyr), 2.527 (3H, s, CH₃-Pyr), 1.914- 1.836 (2H, m, CH₂), 1.460-1.385 (2H, m, CH₂), 1.325-1.171 (8H, m, C₄H₈), 0.834-0.800 (3H, t, CH₃).

IR (cm⁻¹): 3014,3000 (νC=H aromatic), 2954, 2920, 2853 (νC=H aliphatic), 1613 (νC=N), 1509, 1467 (νC=C).

1-Octyl-2,3,5-trimethylpyridinium bromide [O2M3M5MPYR][Br]
10 g (0.083 mol) of 2,3,5-collidine was mixed with 30 g (0.155 mol) of bromooctane in 100 mL of acetonitrile. Solution was stirred for 48 hours at 75 °C. After removing the solvent by rotary evaporation, the resulting light light brown viscous liquid was washed with methylene chloride/water mixtures and dried under vacuum (0.05 mbar) for 12 hours. 23.7 g of a yellow viscous liquid was obtained. Yield: 90 %.

1-Octyl-2-methyl-5-ethylpyridinium bromide [B2M5EPYR][Br]
11.9 g (0.100 mol) of 2-methyl-5-ethylpyridine was mixed with 30 g (0.155 mol) of bromooctane in 100 mL of acetonitrile. Solution was stirred for 72 hours at 75 °C. Solvent was then removed by rotary evaporation, and resulting light yellow solid was washed with ethyl acetate (3 x 50 mL), ether (3 x 50 mL) and dried under high vacuum (0.05 mbar) for 12 hours. 22.3 g of a white powder was obtained. Yield: 85 %.
1-Octyl-3-methyl-5-methylpyridinium iodide  \[O3M5MPYR\][I]
9.7 g (0.090 mol) of 3,5-lutidine was mixed with 30 g (0.125 mol) of iodoctane in 100 mL of ethyl acetate. Solution was stirred for 24 hours at 75 °C. The resulting white solid precipitate at the bottom of the flask was filtered, washed with ethyl acetate (3 x 50 mL) and ether (3 x 50 mL) and dried under high vacuum (0.05 mbar) for 12 hours. 25.5 g of a white powder was obtained. Yield: 91 %.

\[^1H\ NMR (400 MHz, CDCl_3, \delta): 8.847 (2H, s, PyrRCH\_o), 8.314 (1H, s, Pyr-CH\_p), 4.515-4.466 (2H, t, CH\_2), 2.467 (6H, s, 2CH\_3-Pyr), 1.969-1.835 (2H, m, CH\_2), 1.284R1.257 (10H, m, C\_5H\_10), 0.888R0.851 (3H, t, CH\_3).\]

IR (cm\(^{-1}\)): 3003, 2924, 2848 (vCRC\_aliphatic), 1627 (vC=C), 1347, 1226, 1464, 1303, 1191, 899, 694 (vCRC).

1-Octyl-2-methyl-5-ethylpyridinium iodide  \[O2M5EPYR\][I]
9.9 g (0.082 mol) of 2-methyl-5-ethylpyridine was mixed with 30 g (0.125 mol) of iodoctane in 100 mL of ethyl acetate. Solution was stirred for 24 hours at 75 °C. The resulting light yellow solid precipitate at the bottom of the flask was filtered, washed with ethyl acetate (3 x 50 mL) and ether (3 x 50 mL) and dried under high vacuum (0.05 mbar) for 12 hours. 27.1 g of a white powder was obtained. Yield: 91 %.

\[^1H\ NMR (400 MHz, DMSO, \delta): 8.903 (2H, s, PyrRCH\_o), 8.399R8.364 (1H, d, Pyr-CH\_m), 7.970-7.950 (1H, d, Pyr-CH\_p), 4.510-4.470 (2H, t, CH\_2), 2.796-2.746 (5H, m, CH\_3-Pyr + CH\_2-Pyr), 1.880-1.805 (2H, m, CH\_2), 1.322-1.224 (13H, m, C\_5H\_10 + CH\_3-RCH\_2-Pyr), 0.876-0.842 (3H, t, CH\_3).\]

IR (cm\(^{-1}\)): 2921, 2855 (vCRC\_aliphatic), 1628 (vC=C), 1507, 1457, 1379, 1272, 1023, 884, 711 (vCRC).

1-Octyl-2,3,5-trimethylpyridinium iodide  \[O2M3M5MPYR\][I]
10 g (0.083 mol) of 2,3,5-collidine was mixed with 30 g (0.125 mol) of iodoctane in 100 mL of acetonitrile. Solution was stirred for 48 hours at 75 °C. After removing the solvent by rotary evaporation, the resulting light yellow viscous liquid was washed with methylene chloride/water mixtures and dried under vacuum (0.05 mbar) for 12 hours. 26.4 g of a yellow viscous liquid was obtained. Yield: 88 %.

\[^1H\ NMR (400 MHz, DMSO, \delta): 8.781 (1H, s, PyrRCH\_o), 8.236 (1H, d, Pyr-CH\_m), 7.970-7.950 (1H, d, Pyr-CH\_p), 4.553-4.514 (2H, t, CH\_2), 2.684 (3H, s, CH\_3-Pyr), 2.442 (3H, s, CH\_3-Pyr), 2.397 (3H, s, CH\_3-Pyr), 1.847-1.772 (2H, m, CH\_2), 1.356-1.254 (10H, m, C\_5H\_10), 0.874-0.840 (3H, t, CH\_3).\]

IR (cm\(^{-1}\)): 3004, 2926, 2854 (vCRC\_aliphatic), 1633 (vC=C), 1517, 1456, 1224, 1173, 874, 710 (vCRC).

\[B3M5MPYR\]^+\[NTf\_2\^-\]. 2.50 g (10.2·10\(^{-3}\) mol) of \[B3M5MPYR\]^+\[Br\]^- and 3.70 g (11.5·10\(^{-3}\) mol) of potassium bis(trifluoromethylsulfonyl)imide, used as received from Wako chemicals (98 % purity), were mixed in a flask containing 40 mL of water for 12 h. After extraction of a clear liquid with methylene chloride, solvent was removed by rotary evaporation. The resulting light yellow liquid was then washed with methylene chloride and water (3 x 25 mL of each solvent). After 24 h under vacuum, 4.08 g (yield: 90 %) was obtained as a clear liquid.
\(^{1}\)H NMR (400 MHz, DMSO, \(\delta\)):  8.806 (2H, s, Pyr\(\text{RCH}_{\text{o}}\)), 8.280 (1H, s, Pyr\(\text{RCH}_{\text{p}}\)), 4.485-4.459 (2H, t, CH\(_2\)), 2.459 (6H, s, 6 CH\(_3\)-Pyr\(_{\text{m}}\)), 1.943-1.868 (2H, m, CH\(_2\)), 1.350-1.257 (2H, m, CH\(_2\)), 0.939-0.902 (3H, t, CH\(_3\)).

IR (cm\(^{-1}\)): 3098 (v CRH aromatic), 2965, 2941, 2880 (v CRH aliphatic), 1620 (v C=C), 1486, 1346, 1178, 1133, 1053 (v CRF).

\([\text{B}_{2}\text{M}_{3}\text{MPYR}]^{+}[\text{NTf}_{2}]^{-}\). 2.50 g (10.2\(\times\)10\(^{-3}\) mol) of \([\text{B}_{2}\text{M}_{3}\text{MPYR}]^{+}[\text{Br}]^{-}\) and 3.70 g (11.5\(\times\)10\(^{-3}\) mol) of potassium bis(trifluoromethylsulfonylimide, used as received from Wako chemicals (98 % purity), were mixed in a flask containing 40 mL of water for 12 h. After extraction of a yellow liquid with methylene chloride, solvent was removed by rotary evaporation. The resulting light yellow liquid was then washed with methylene chloride and water (3\(\times\)25 mL of each solvent). After 24 h under vacuum, 4.01 g (yield: 88 %) was obtained as a clear liquid.

\(^{1}\)H NMR (400 MHz, DMSO, \(\delta\)):  8.832 (1H, d, Pyr\(\text{RCH}_{\text{o}}\)), 8.347 (1H, d, Pyr\(\text{RCH}_{\text{m}}\)), 7.856 (1H, d, Pyr\(\text{RCH}_{\text{p}}\)), 4.602 (2H, t, CH\(_2\)), 2.737 (3H, s, CH\(_3\)-Pyr\(_{\text{o}}\)), 2.484 (3H, s, CH\(_3\)-Pyr\(_{\text{m}}\)), 1.833 (2H, m, CH\(_2\)), 1.431 (2H, m, CH\(_2\)), 0.956 (3H, t, CH\(_3\)).

IR (cm\(^{-1}\)): 3078 (v CRH aromatic), 2966, 2939, 2882 (v CRH aliphatic), 1635, 1610 (v C=C), 1499, 1347, 1177, 1133, 1052 (v CRF).

\([\text{B}_{2}\text{M}_{3}\text{M}_{5}\text{MPYR}]^{+}[\text{NTf}_{2}]^{-}\). 2.50 g (9.7\(\times\)10\(^{-3}\) mol) of \([\text{B}_{2}\text{M}_{3}\text{M}_{5}\text{MPYR}]^{+}[\text{Br}]^{-}\) and 3.70 g (11.5\(\times\)10\(^{-3}\) mol) of potassium bis(trifluoromethylsulfonylimide, used as received from Wako chemicals (98 % purity), were mixed in a flask containing 40 mL of water for 12 h. After extraction of a clear liquid with methylene chloride, solvent was removed by rotary evaporation. The resulting liquid was then washed with methylene chloride and water (3\(\times\)25 mL of each solvent). After 24 h under vacuum, 4.08 g (yield: 90 %) was obtained as a clear liquid.

\(^{1}\)H NMR (400 MHz, DMSO, \(\delta\)):  8.724 (1H, s, Pyr\(\text{RCH}_{\text{o}}\)), 8.211 (1H, s, Pyr\(\text{RCH}_{\text{p}}\)), 4.557 (2H, t, CH\(_2\)), 2.687 (3H, s, CH\(_3\)-Pyr\(_{\text{m}}\)), 2.446 (3H, s, CH\(_3\)-Pyr\(_{\text{m}}\)), 2.402 (3H, s, CH\(_3\)-Pyr\(_{\text{m}}\)), 1.849 (2H, m, CH\(_2\)), 1.437 (2H, m, CH\(_2\)), 0.943 (3H, t, CH\(_3\)).

IR (cm\(^{-1}\)): 3082 (v CRH aromatic), 2970, 2941, 2879 (v CRH aliphatic), 1631 (v C=N), 1509, 1347, 1178, 1134, 1053 (v CRF).

\([\text{O}_{2}\text{M}_{5}\text{EPYR}]^{+}[\text{NTf}_{2}]^{-}\). 2.81 g (10.7\(\times\)10\(^{-3}\) mol) of \([\text{O}_{2}\text{M}_{5}\text{EPYR}]^{+}[\text{Br}]^{-}\) and 3.75 g (11.7\(\times\)10\(^{-3}\) mol) of potassium bis(trifluoromethylsulfonylimide, used as received from Wako chemicals (98 % purity), were mixed in a flask containing 40 mL of water for 12 h. After extraction of a light yellow liquid with methylene chloride, solvent was removed by rotary evaporation. The resulting light yellow liquid was then washed with methylene chloride and water (3\(\times\)25 mL of each solvent). After 24 h under vacuum, 4.80 g (yield: 92 %) was obtained as a light yellow liquid.

\(^{1}\)H NMR (400 MHz, DMSO, \(\delta\)):  8.885 (1H, s, Pyr\(\text{RCH}_{\text{o}}\)), 8.379 (1H, s, Pyr\(\text{RCH}_{\text{p}}\)), 4.507-4.467 (2H, t, CH\(_2\)), 2.793-2.763 (5H, m, CH\(_3\)-Pyr\(_{\text{m}}\) + CH\(_2\)-Pyr\(_{\text{m}}\)), 1.868-1.790 (2H, m, CH\(_2\)), 1.437-1.344 (2H, m, CH\(_2\)), 1.263-1.226 (3H, t, CH\(_3\)-CH\(_2\)-Pyr\(_{\text{m}}\)), 0.963-0.926 (3H, t, CH\(_3\)).

IR (cm\(^{-1}\)): 3079 (v CRH aromatic), 2970, 2940, 2879 (v CRH aliphatic), 1631 (v C=N), 1509, 1347, 1178, 1134, 1053 (v CRF), 1053 (v S=O).

\([\text{O}_{2}\text{M}_{5}\text{EPYR}]^{+}[\text{NTf}_{2}]^{-}\). 2.00 g (6.4\(\times\)10\(^{-3}\) mol) of \([\text{O}_{2}\text{M}_{5}\text{EPYR}]^{+}[\text{Br}]^{-}\) and 2.2 g (6.9\(\times\)10\(^{-3}\) mol) of potassium bis(trifluoromethylsulfonylimide, used as received from Wako chemicals (98 % purity), were mixed in a flask containing 40 mL of water for 12 h. After extraction of a light yellow liquid with methylene chloride, solvent was removed by rotary evaporation. The resulting light yellow liquid was then washed with methylene chloride and water (3\(\times\)25 mL of each solvent). After 24 h under vacuum, 4.00 g (yield: 88 %) was obtained as a clear liquid.
purity), were mixed in a flask containing 40 mL of water for 12 h. After extraction of a light yellow liquid with methylene chloride, solvent was removed by rotary evaporation. The resulting light yellow liquid was then washed with methylene chloride and water (3 × 25 mL of each solvent). After 24 h under vacuum, 2.94 g (yield: 88 %) was obtained as a yellow liquid.

\[ \text{H NMR (400 MHz, DMSO, } \delta \text{): 8.890 (2H, s, PyrRCHO)} \]

\[ \text{8.376-8.351 (1H, d, PyrRCH}_p \text{)}, 7.957-7.937 (1H, d, Pyr-CH}_p \text{), 4.497-4.458 (2H, t, CH}_2 \text{)}, 2.800-2.744 (5H, m, CH}_3 \text{Pyr}_o + CH}_2 \text{Pyr}_m \text{), 1.843-1.804 (2H, m, CH}_2 \text{), 1.332-1.225 (13H, m, 5CH}_2 + CH}_3 \text{).} \]

\[ \text{13C NMR (400 MHz, DMSO, d): 152.695, 144.980, 144.419, 142.002, 129.836, 121.443, 118.243, 57.614, 31.510, 29.807, 28.842, 28.747, 24.990, 22.386, 19.319, 14.702, 14.258.} \]

IR (cm\(^{-1}\)): 3090 (v CR=H aromatic), 2976, 2931, 2860 (v CR=H aliphatic), 1636 (v C=NH), 1528 (v C=C), 1347, 1222, 1180, 1134 (v=SO).

\[ [\text{O2M3MPYR}]^+ [\text{NTf}_2^-]. 3.10 g (10.3 \times 10^{-3} \text{ mol}) of [O2M3MPYR]+[Br] and 3.80 g (11.9 \times 10^{-3} \text{ mol}) of potassium bis(trifluoromethylsulfonyl)imide, used as received from Wako chemicals (98 % purity), were mixed in a flask containing 40 mL of water for 12 h. After extraction of a light yellow liquid with methylene chloride, solvent was removed by rotary evaporation. The resulting clear liquid was then washed with methylene chloride and water (3 × 25 mL of each solvent). After 24 h under vacuum, 4.50 g (yield: 90 %) was obtained as a clear liquid.

\[ \text{H NMR (400 MHz, DMSO, } \delta \text{): 8.830-8.816 (2H, d, PyrRCHO)} \]

\[ \text{8.353-8.334 (1H, d, PyrRCH}_p \text{)}, 7.865-7.830 (1H, d, Pyr-CH}_p \text{), 4.604-4.565 (2H, t, CH}_2 \text{)}, 2.726 (3H, s, CH}_3 \text{Pyr}_o \text{), 2.509-2.479 (3H, m, CH}_3 \text{Pyr}_m \text{), 1.812-1.774 (2H, m, CH}_2 \text{), 1.322-1.257 (10H, m, 5CH}_2 + CH}_3 \text{).} \]


IR (cm\(^{-1}\)): 3090 (v CR=H aromatic), 2976, 2930, 2860 (v CR=H aliphatic), 1621 (v=NH), 1500 (v=CH), 1347, 1222, 1180, 1134 (v=CH=), 1054 (v=SO).

\[ [\text{O2M3M5MPYR}]^+ [\text{NTf}_2^-]. 3.00 g (10.0 \times 10^{-3} \text{ mol}) of [O2M3M5MPYR]+[Br] and 3.80 g (11.9 \times 10^{-3} \text{ mol}) of potassium bis(trifluoromethylsulfonyl)imide, used as received from Wako chemicals (98 % purity), were mixed in a flask containing 40 mL of water for 12 h. After extraction of a light yellow liquid with methylene chloride, solvent was removed by rotary evaporation. The resulting clear liquid was then washed with methylene chloride and water (3 × 25 mL of each solvent). After 24 h under vacuum, 4.58 g (yield: 92 %) was obtained as a clear liquid.

\[ \text{H NMR (400 MHz, DMSO, } \delta \text{): 8.807 (2H, s, PyrRCHO)} \]

\[ \text{8.287 (1H, d, PyrRCH}_p \text{), 4.485-4.448 (2H, t, CH}_2 \text{), 2.504-2.461 (6H, m, 2 CH}_3 \text{Pyr}_m \text{), 1.922-1.889 (2H, m, CH}_2 \text{), 1.275-1.248 (10H, m, 5CH}_2 + CH}_3 \text{).} \]


IR (cm\(^{-1}\)): 3090 (v CR=H aromatic), 2976, 2930, 2860 (v CR=H aliphatic), 1621 (v=NH), 1500 (v=CH), 1347, 1222, 1180, 1134 (v=CH=), 1054 (v=SO).

\[ [\text{O2M3M5MPYR}]^+ [\text{NTf}_2^-]. 1.45 g (4.61 \times 10^{-3} \text{ mol}) of [O2M3M5MPYR]+[Br] and 1.80 g (5.63 \times 10^{-3} \text{ mol}) of potassium bis(trifluoromethylsulfonyl)imide, used as received from Wako chemicals (98 % purity), were mixed in a flask containing 40 mL of water for 12 h. After extraction of a light yellow liquid with methylene chloride, solvent was removed by rotary evaporation. The resulting clear liquid was then washed with methylene chloride and water (3 × 25 mL of each solvent). After 24 h under vacuum, 1.81 g (yield: 80 %) was obtained as a clear liquid.
$\text{H NMR (400 MHz, DMSO, } \delta: 8.725 (1H, s, Pyr-CH$_2$), 8.210 (1H, s, Pyr-CH$_2$), 4.540-4.501 (2H, t, CH$_2$), 2.678 (3H, s, 2 CH$_3$-Pyrm), 2.671-2.385 (6H, m, 2 CH$_3$-Pyrm), 1.816-1.777 (2H, m, CH$_2$), 1.332-1.261 (10H, m, 5CH$_2$), 0.863-0.846 (3H, t, CH$_3$).

IR (cm$^{-1}$): 3089 (v CR aromatic), 2930, 2860 (v CR aliphatic), 1630 (v C=C), 1507, 1348, 1179, 1134, 1053, (v CRF).

$\text{[B2M3MPYR]}^+ [\text{TfO}^-]$. 2.50 g (10.2·10$^{-3}$ mol) of $\text{[B2M3MPYR]}^+ [\text{Br}]$ and 2.60 g (13.2·10$^{-3}$ mol) of potassium trifluoromethanesulfonate, used as received from Sigma (98 % purity), were mixed in a flask containing 40 mL of acetonitrile for 12 h. After filtering, removal of acetonitrile by rotary-evaporation, washing with methylene chloride (3× 25 mL), and drying under vacuum for 24 h, 2.80 g (yield: 88 %) of a clear yellow liquid was obtained.

$\text{H NMR (400 MHz, DMSO, } \delta: 8.831-8.816 (1H, d, Pyr-CH$_2$), 8.359-8.339 (1H, d, Pyr-CH$_2$), 7.868-7.832 (1H, t, Pyr-CH$_2$), 4.619-4.580 (2H, t, CH$_2$), 2.736 (3H, s, CH$_3$-Pyrm), 2.483 (3H, s, CH$_3$-Pyrm), 1.824-1.766 (2H, m, CH$_2$), 1.421-1.328 (2H, m, CH$_2$), 0.953-0.916 (3H, t, CH$_3$).

IR (cm$^{-1}$): 3090 (v CR aromatic), 2965, 2939, 2878 (v CR aliphatic), 1620 (v C=N), 1485 (v C=C), 1256, 1223, 1149 (v CRF), 1029 (v S=O).

$\text{[B3M5MPYR]}^+ [\text{TfO}^-]$. 2.50 g (10.2·10$^{-3}$ mol) of $\text{[B3M5MPYR]}^+ [\text{Br}]$ and 2.78 g (14.8·10$^{-3}$ mol) of potassium trifluoromethanesulfonate, used as received from Sigma (98 % purity), were mixed in a flask containing 40 mL of acetonitrile for 12 h. After filtering, removal of acetonitrile by rotary-evaporation, washing with methylene chloride (3× 25 mL), and drying under vacuum for 24 h, 2.96 g (yield: 93 %) of a white solid was obtained.

$\text{H NMR (400 MHz, DMSO, } \delta: 8.809 (2H, s, Pyr-CH$_2$), 8.293 (1H, s, Pyr-CH$_2$), 4.502-4.465 (2H, t, CH$_2$), 2.453 (6H, s, 6 CH$_3$-Pyrm), 1.933-1.858 (2H, m, CH$_2$), 1.336-1.243 (2H, m, CH$_2$), 0.933-0.896 (3H, t, CH$_3$).

$\text{13C NMR (400 MHz, DMSO, d): 146.029, 141.422, 137.872, 122.521, 118.976, 60.225, 32.389, 18.688, 17.578, 13.182.}

IR (cm$^{-1}$): 3059 (v CR aromatic), 2978, 2943 2870 (v CR aliphatic), 1628, 1607 (v C=N), 1503 (v C=C), 1256, 1223, 1149 (v CRF), 1029 (v S=O).

$\text{[O3M5MPYR]}^+ [\text{TfO}^-]$. 2.00 g (6.6·10$^{-3}$ mol) of $\text{[O3M5MPYR]}^+ [\text{Br}]$ and 1.70 g (9.0·10$^{-3}$ mol) of potassium trifluoromethanesulfonate, used as received from Sigma (98 % purity), were mixed in a flask containing 25 mL of water for 12 h. After filtering, removal of acetonitrile by rotary-evaporation, washing with methylene chloride (3× 25 mL), and drying under vacuum for 24 h, 2.16 g (yield: 78 %) of a white solid was obtained.

$\text{H NMR (400 MHz, DMSO, } \delta: 8.809 (2H, s, Pyr-CH$_2$), 8.295 (1H, s, Pyr-CH$_2$), 4.502-4.465 (2H, t, CH$_2$), 2.455 (6H, s, 6 CH$_3$-Pyrm), 1.933-1.858 (2H, m, CH$_2$), 1.336-1.243 (2H, m, CH$_2$), 0.933-0.896 (3H, t, CH$_3$).

$\text{13C NMR (400 MHz, DMSO, d): 146.029, 141.422, 137.872, 122.521, 118.976, 60.225, 32.389, 18.688, 17.578, 13.182.}

IR (cm$^{-1}$): 3066 (v CR aromatic), 2978, 2943 2870 (v CR aliphatic), 1628, 1607 (v C=N), 1503 (v C=C), 1258, 1223, 1153 (v CRF), 1026 (v S=O).

$\text{[O2M3MPYR]}^+ [\text{TfO}^-]$. 3.00 g (10.0·10$^{-3}$ mol) of $\text{[O2M3MPYR]}^+ [\text{Br}]$ and 2.10 g (11.1·10$^{-3}$ mol) of potassium trifluoromethanesulfonate, used as received from Sigma (98 % purity), were mixed in a flask containing 25 mL of water for 12 h. After filtering, removal of acetonitrile by rotary-
evaporation, washing with methylene chloride and water (3 × 25 mL for each solvent), and drying under vacuum for 24 h, 3.36 g (yield: 91 %) of a white solid was obtained.

$^1$H NMR (400 MHz, DMSO, $\delta$): 8.830-8.815 (2H, d, PyrR$\text{CH}_o$), 8.357-8.337 (1H, d, Pyr-CH$_m$), 7.868-7.833 (1H, d, Pyr-CH$_p$), 4.604-4.565 (2H, t, CH$_2$), 2.727 (3H, s, CH$_3$-Pyr$_m$), 2.480 (3H, s, CH$_3$-Pyr$_m$), 1.847-1.773 (2H, m, CH$_2$), 1.338-1.256 (10H, m, 5CH$_2$), 0.877-0.843 (3H, t, CH$_3$).


IR (cm$^{-1}$): 3091 (vCH aromatic), 2928, 2858 (vCH aliphatic), 1620 (vC=N), 1485 (vC=C), 1255, 1224, 1151 (vCF), 1029 (vS=O).

[O$_2$M$_3$M$_5$MPYR]$^+$$[\text{TFO}^-]$. 1.14 g (3.6·10$^{-3}$ mol) of [O$_2$M$_3$M$_5$MPYR]$^+$$[\text{Br}]^-$ and 0.93 g (4.8·10$^{-3}$ mol) of potassium trifluoromethanesulfonate, used as received from Sigma (98 % purity), were mixed in a flask containing 25 mL of acetone for 12 h. After filtering, removal of acetone by rotary evaporation, washing with methylene chloride (3 × 25 mL), and drying under vacuum for 24 h, 1.42 g (yield: 84 %) of a white solid was obtained.

$^1$H NMR (400 MHz, DMSO, $\delta$): 8.726 (1H, s, PyrR$\text{CH}_o$), 8.218 (1H, s, PyrR$\text{CH}_p$), 4.537-4.498 (2H, t, CH$_2$), 2.676 (3H, s, 2 CH$_3$-Pyr$_m$), 2.439 (3H, s, CH$_3$-Pyr$_m$), 2.439 (3H, s, CH$_3$-Pyr$_m$), 1.825-1.791 (2H, m, CH$_2$), 1.326-1.283 (10H, m, 5CH$_2$), 0.879-0.846 (3H, t, CH$_3$).

IR (cm$^{-1}$): 3069 (vCH aromatic), 2929, 2858 (vCH aliphatic), 1630 (vC=N), 1509 (vC=C), 1255, 1223, 1151 (vCF), 1029 (vS=O).

[B$_3$M$_5$MPYR]$^+$$[\text{SCN}^-]$. 2.50 g (10.2·10$^{-3}$ mol) of [B$_3$M$_5$MPYR]$^+$$[\text{Br}]^-$ and 1.9 g (19.6·10$^{-3}$ mol) of potassium thiocyanate, used as received from Sigma (98 % purity), were mixed in a flask containing 40 mL of acetone for 12 h. After filtration, acetone was removed by rotary evaporation, and the resulting light orange liquid was washed with methylene chloride (3 × 25 mL) at -18 °C. After 24 h under vacuum, 1.97 g (yield: 87 %) was obtained as a clear liquid.

$^1$H NMR (400 MHz, DMSO, $\delta$): 8.842 (2H, s, Pyr-CH$_o$), 8.306 (1H, s, Pyr-CH$_p$), 4.537-4.498 (2H, t, CH$_2$), 2.676 (3H, s, 2 CH$_3$-Pyr$_m$), 2.439 (3H, s, CH$_3$-Pyr$_m$), 2.394 (3H, s, CH$_3$-Pyr$_m$), 1.825-1.791 (2H, m, CH$_2$), 1.326-1.283 (10H, m, 5CH$_2$), 0.879-0.846 (3H, t, CH$_3$).

IR (cm$^{-1}$): 3032 (vCH aromatic), 2960, 2932, 2874 (vCH aliphatic), 2048 (vC=N).

[O$_2$M$_3$M$_5$MPYR]$^+$$[\text{SCN}^-]$. 4.89 g (15.8·10$^{-3}$ mol) of [O$_2$M$_3$M$_5$MPYR]$^+$$[\text{Br}]^-$ and 2.30 g (23.7·10$^{-3}$ mol) of potassium thiocyanate, used as received from Sigma (98 % purity), were mixed in a flask containing 20 mL of water for 12 h. After filtering, removal of water by rotary evaporation, washing with methylene chloride (3 × 25 mL), and drying under vacuum for 24 h, 4.12 g (yield: 89 %) of dark yellow viscous liquid was obtained.

$^1$H NMR (400 MHz, DMSO, $\delta$): 8.738 (1H, s, Pyr-CH$_o$), 8.224 (1H, s, Pyr-CH$_p$), 4.545-4.505 (2H, t, CH$_2$), 2.682 (3H, s, 2 CH$_3$-Pyr$_m$), 2.443 (3H, s, CH$_3$-Pyr$_m$), 2.398 (3H, s, CH$_3$-Pyr$_m$), 1.848-1.773 (2H, m, CH$_2$), 1.325-1.257 (10H, m, 5CH$_2$), 0.877-0.843 (3H, t, CH$_3$).

IR (cm$^{-1}$): 3034 (vCH aromatic), 2923, 2856 (vCH aliphatic), 2048 (vC=N).

[O$_2$M$_3$MPYR]$^+$$[\text{SCN}^-]$. 3.00 g (10.0·10$^{-3}$ mol) of [O$_2$M$_3$MPYR]$^+$$[\text{Br}]^-$ and 1.20 g (12.3·10$^{-3}$ mol) of potassium thiocyanate, used as received from Sigma (98 % purity), were mixed in a flask containing 20 mL of water for 12 h. After filtering, removal of water by rotary evaporation,
washing with methylene chloride and water (3× 25 mL for each solvent), and drying under vacuum for 24 h. 2.46 g (yield: 89 %) of a light orange liquid was obtained.

\[ \text{[B3M5MPYR]}\text{[N(CN)]}_2\text{J}\]. 2.24 g (9.17×10⁻³ mol) of [B3M5MPYR]\text{[Br]} and 1.83 g (10.4×10⁻³ mol) of silver dicyanamide were mixed in a flask containing 30 mL of ethanol for 12 h. After filtering, removal of ethanol by rotary-evaporation, washing with methylene chloride (3× 25 mL), and drying under vacuum for 24 h, 1.78 g (yield: 85 %) of a clear liquid was obtained.

\[ \text{[B2M3MPYR]}\text{[N(CN)]}_2\text{J}\]. 2.00 g (7.0×10⁻³ mol) of [O2M3MPYR]\text{[I]} and 1.43 g (8.2×10⁻³ mol) of silver dicyanamide were mixed in a flask containing 30 mL of ethanol for 12 h. After filtering, removal of ethanol by rotary-evaporation, washing with methylene chloride (3× 25 mL), and drying under vacuum for 24 h, 1.21 g (yield: 75 %) of a clear liquid was obtained.

\[ \text{[O3M5MPYR]}\text{[N(CN)]}_2\text{J}\]. 1.71 g (5.75×10⁻³ mol) of [O3M5MPYR]\text{[I]} and 0.60 g (6.9×10⁻³ mol) of sodium dicyanamide, used as received from Sigma (98 % purity), were mixed in a flask containing 15 mL of water for 12 h. After filtering, removal of water by rotary-evaporation, washing with methylene chloride (3× 25 mL), and drying under vacuum for 24 h, 1.46 g (yield: 85 %) of a light yellow liquid was obtained.

\[ \text{[O2M5EPYR]}\text{[N(CN)]}_2\text{J}\]. 3.00 g (8.3×10⁻³ mol) of [O2M5EPYR]\text{[I]} and 1.05 g (11.8×10⁻³ mol) of sodium dicyanamide, used as received from Sigma (98 % purity), were mixed in a flask containing 15 mL of water for 12 h. After filtering, removal of water by rotary-evaporation, washing with diethyl ether (2× 15 mL) methylene chloride and water (3× 25 mL of each solvent), and drying under vacuum for 24 h, 2.17 g (yield: 84 %) of a clear yellow liquid was obtained.
**Figure S1.** DSC curves for selected ionic liquids. a): DSC curve for [O2M3MPYR][NTf₂]. b): DSC curve for [O2M3M5MPYR][SCN]. c): DSC curve for [B3M5MPYR][SCN]. d): DSC curve for [O3M5MPYR][BF₄]

**Figure S2.** TGA curves for ionic liquids containing 1-octyl-3,5-dimethylpyridinium cations. △, [O3M5MPYR][I]; ×, [O3M5MPYR][SCN]; ■, [O3M5MPYR][N(CN)₂]; ◊, [O3M5MPYR][TfO]; ○, [O3M5MPYR][BF₄]; —, [O3M5MPYR][NTf₂]
Figure S3. Plot of $t_{5\%}$ as a function of $t_{1\%}$ for ionic liquids studied here. ●, Ionic liquid containing iodide anion; ■, Ionic liquids containing SCN anion; △, Ionic liquids containing N(CN)$_2$ anion; ▼, Ionic liquids containing TfO anion; ○, Ionic liquids containing NTf$_2$ anion; □, Ionic liquid containing BF$_4$ anion.

Figure S4. UV-Vis spectra for selected ionic liquids. —, UV-Vis spectra for [O2M3MPYR][TfO] ($\lambda_{max} = 271$ nm); ---, UV-Vis spectra for [O3M5MPYR][NTf$_2$] ($\lambda_{max} = 271$ nm); ×, UV-Vis spectra for [O2M5EPYR][NTf$_2$] ($\lambda_{max} = 273$ nm); ○, UV-Vis spectra for [O2M3M5MPYR][NTf$_2$] ($\lambda_{max} = 277$ nm).
Figure S5 – Electrochemical window for [O2M3MPYR][NTf₂].

Figure S6 – Electrochemical window for [O2M5EPYR][NTf₂]. Cyclic voltametry started at 0 V towards negative potentials. The oxidation peak centered around -500 mV is due to the oxidation of reduced compounds obtained below -1.2 V.
Figure S7 – Electrochemical window for [O3M5MPYR][NTf₂]

Figure S8 – Electrochemical window of [O2M3M5MPYR][NTf₂]