

Supporting Information

SYNTHESIS OF NOVEL FLUOROUS IMIDAZOLIUM IONIC LIQUIDS

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EXPERIMENTAL

General. IR spectra were recorded on Horiba FTIR-720 infrared spectrometer. ^1H and ^{13}C NMR spectra were recorded on JEOL JNM LA-400 or ECA-500 spectrometer. Chemical shifts of ^1H NMR were expressed in parts per million downfield from tetramethylsilane (TMS) with reference to internal residual CHCl_3 ($\delta=7.26$) in CDCl_3 . Chemical shifts of ^{13}C NMR were expressed in parts per million downfield from CDCl_3 ($\delta=77.0$) as an internal standard. Coupling constants (J) were reported in hertz (Hz). Following abbreviations were used to designate the multiplicities: s=singlet; d=doublet; t=triplet; q=quartet; quin=quintet; sext=sextet; br=broad; m=multiplet. Mass spectra were recorded on JEOL JMS-700 mass spectrometer. Melting points were measured on SHIMADZU DSC-60 with TA-60WS thermal analyzer and FC-60A flow controller. Analytical thin layer chromatography (TLC) was performed on precoated glass plates (Merck Kieselgel 60 F₂₅₄, layer thickness 0.25 mm). Visualization was accomplished with UV light (254 nm) and molybdophosphoric acid. Flash column chromatography was carried out using Kanto Chemical silica gel 60 N (40–50 mm) or Fuji Silysia silica gel Chromatorex PSQ 60B. Preparative HPLC was performed on JAI LC-9120NEXT chromatograph equipped with JAIGEL-SIL S-043-15. Unless otherwise noted, commercially available reagents were used without purification. All the solvents were distilled and stored over a drying agent. The sodium hydride (55% dispersion in mineral oil) was washed with pentane to remove the oil and withdrawn the supernatant solvent with a syringe, before it was used.

Typical Procedure for the Preparation of Imidazolium Iodide Having Perfluoroalkyl groups 1a, 2a, 6a, 7a, and 8a. 1,3-Bis(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)imidazolium iodide (**1a**). A solution of imidazole (23 mg, 0.338 mmol) in toluene (3 ml) was added to sodium hydride (13 mg, 0.30 mmol) and stirred for 2 h at room temperature. Then 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl iodide was added to the reaction mixture

and stirred under reflux. After stirring for 20 h, the reaction mixture was cooled to room temperature, and filtered through Celite and concentrated in vacuo. The crude product was then recrystallized in acetone to produce **1a** (64%); a white solid; m.p. 280 °C; IR (neat) 3028, 2962, 1564, 1455, 1332, 1204, 1149, 1024, 972, 735, 656, 558, 530 cm⁻¹; ¹H NMR (acetone-d₆) δ 9.68 (1H, s), 8.00 (2H, d, *J* = 1.7 Hz), 4.66 (4H, t, *J* = 6.9 Hz), 2.48-2.46 (4H, m), 2.40-2.34 (4H, m); ¹³C NMR (acetone-d₆): δ 137.6, 123.9, 49.4, 28.4, 22.0; ¹³C {¹⁹F} NMR (acetone-d₆): δ 119.6, 118.3, 112.3, 112.0, 111.7, 111.5, 111.2, 109.2; HRMS (pos. mode) calcd for C₂₅H₁₅F₃₄N₂ [M-I]⁺ 989.0687, found 989.0678, (neg. mode) calcd for I [M-C₂₅H₁₅F₃₄N₂⁺]⁻ 126.9050, found 126.9044.

1-Methyl-2,3-bis(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptafluoroundecyl)imidazolium iodide (2a): a white solid; m.p. 166 °C; IR (neat) 3074, 2963, 2362, 1537, 1466, 1238, 1206, 1153, 658 cm⁻¹; ¹H NMR (acetone-d₆) δ 7.95 (1H, d, *J* = 1.7 Hz), 7.89 (1H, d, *J* = 1.7 Hz), 4.66 (2H, t, *J* = 7.0 Hz), 4.04 (3H, s), 3.35 (2H, t, *J* = 8.7 Hz), 2.50-2.36 (4H, m), 2.40-2.34 (2H, m), 1.99-1.88 (2H, m); ¹³C NMR (acetone-d₆): δ 145.5, 124.0, 123.7, 49.5, 36.8, 32.1, 29.7, 28.3, 23.5, 22.1; ¹³C {¹⁹F} NMR (acetone-d₆): δ 119.7, 118.4, 118.2, 116.7, 113.2, 112.4, 112.0, 111.7, 111.5, 111.2, 110.9, 110.7, 110.5, 110.1, 109.3, 108.2; HRMS (pos. mode) calcd for C₂₆H₁₇F₃₄N₂ [M-I]⁺ 1003.0843, found 1003.0855, (neg. mode) calcd for I [M-C₂₆H₁₇F₃₄N₂⁺]⁻ 126.9050, found 126.9043.

1,3-Bis[3-tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silylpropyl]imidazolium iodide (6a): The crude product was extracted with FC-72 and THF. The FC-72 layer was concentrated under reduce pressure to give **6a**; a pale yellow oil; IR (neat) 3447, 3079, 2947, 1716, 1560, 1442, 1361, 1242, 1144, 1069, 902, 811, 745, 707, 647, 564, 530 cm⁻¹; ¹H NMR (acetone-d₆) δ 9.71 (1H, s), 7.85 (2H, d, *J* = 1.5 Hz), 4.45 (4H, t, *J* = 7.4 Hz), 2.34-2.32 (12H, m), 2.15-2.12 (4H, m), 1.11-1.06 (12H, m), 1.02-0.99 (4H, m); ¹³C NMR (acetone-d₆): δ 137.5, 123.3, 52.9, 25.9, 25.3, 8.6, 1.5; ¹³C {¹⁹F} NMR (acetone-d₆): δ 119.5, 118.0, 112.2, 112.0, 111.2, 109.4; HRMS (pos. mode) calcd for C₅₇H₃₉F₇₈N₂Si₂ [M-I]⁺ 2289.1401, found 2289.1443, (neg. mode) calcd for I [M-C₅₇H₃₉F₇₈N₂Si₂⁺]⁻ 126.9050, found 126.9057.

1,3-Bis[2-tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silylethyl]imidazolium iodide (7a): The crude product was extracted with FC-72 and ethyl acetate. The FC-72 layer was concentrated under reduce pressure to give **7a**; a pale yellow oil; IR (neat) 3059, 2948, 1716, 1558, 1442, 1361, 1239, 1144, 1069, 898, 745, 707, 649, 565, 539 cm⁻¹; ¹H NMR (acetone-d₆) δ 9.86 (1H, s), 7.85 (2H, s), 4.67 (4H, m), 2.44-2.40 (12H, m), 1.87 (4H, m), 1.22-1.18 (12H, m); ¹³C NMR (acetone-d₆): δ 136.8, 123.0, 47.0, 25.9, 15.0, 1.7; ¹³C {¹⁹F} NMR (acetone-d₆): δ 119.6, 118.0, 112.2, 112.0, 111.2, 109.3; HRMS (pos. mode)

calcd for $C_{55}H_{35}F_{78}N_2Si_2$ $[M-I]^+$ 2261.1088, found 2261.1120, (neg. mode) calcd for I $[M-C_{55}H_{35}F_{78}N_2Si_2]^+$ 126.9050, found 126.9042.

1,3-Bis[4-tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silylbenzyl]imidazolium iodide (8a): The crude product was extracted with FC-72 and ethyl acetate. The FC-72 layer was concentrated under reduce pressure to give **8a**; a pale yellow solid; m.p. 115 °C; IR (neat) 3162, 3120, 3032, 2949, 1575, 1443, 1363, 1239, 1067, 900, 812, 746, 530 cm^{-1} . 1H NMR (acetone- d_6) δ 10.04 (1H, s), 7.88 (2H, s), 7.77 (4H, d, $J = 8.0$ Hz), 7.70 (4H, d, $J = 8.0$ Hz), 5.74 (4H, s), 2.37-2.26 (12H, m), 1.40-1.36 (12H, m); ^{13}C NMR (acetone- d_6): δ 137.8, 137.4, 135.8, 134.6, 129.7, 123.7, 53.2, 26.0, 1.8; ^{13}C $\{^{19}F\}$ NMR (acetone- d_6): δ 119.5, 118.0, 112.2, 112.0, 111.1, 109.4; HRMS (pos. mode) calcd for $C_{65}H_{39}F_{78}N_2Si_2$ $[M-I]^+$ 2385.1401, found 2385.1402, (neg. mode) calcd for I $[M-C_{65}H_{39}F_{78}N_2Si_2]^+$ 126.9050, found 126.9058.

Typical Procedure for the Preparation of Imidazolium Iodide Having Perfluoroalkyl groups 3a, 4a, 5a, 9a, and 10a. 1-Methyl-3-[3-tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silylpropyl]imidazolium iodide (3a). To a solution of 1-methylimidazole (60 mg, 0.73 mmol) in toluene (3 ml) at ambient temperature was added 3-tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silylpropyl iodide (521 mg, 0.42 mmol). After stirring for 24 h under reflux, the reaction mixture was cooled to room temperature and concentrated in vacuo. The crude product was extracted with FC-72 and toluene. The FC-72 layer was concentrated under reduce pressure to give **3a** (96%); a pale yellow oil; IR (neat) 3024, 2864, 1624, 1457, 1368, 1321, 1247, 1211, 1144, 1122, 1070, 986, 811, 746, 698, 652, 523 cm^{-1} ; 1H NMR (acetone- d_6) δ 9.68 (1H, s), 7.90 (1H, d, $J = 1.7$ Hz), 7.80 (1H, d, $J = 1.7$ Hz), 4.50 (2H, t, $J = 7.2$ Hz), 4.09 (3H, s), 2.35-2.34 (6H, m), 2.16-2.15 (2H, m), 1.11-1.08 (6H, m), 1.06-1.02 (2H, m); ^{13}C NMR (acetone- d_6): δ 138.0, 124.7, 123.3, 52.9, 36.9, 26.0, 25.4, 8.63, 1.62; ^{13}C $\{^{19}F\}$ NMR (acetone- d_6): δ 119.5, 118.0, 112.2, 112.0, 111.2, 109.4; HRMS (pos. mode) calcd for $C_{31}H_{24}F_{39}N_2Si$ $[M-I]^+$ 1193.1081, found 1193.1075, (neg. mode) calcd for I $[M-C_{31}H_{24}F_{39}N_2Si]^+$ 126.9050, found 126.9041.

1-Methyl-3-[2-tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silylethyl]imidazolium iodide (4a): a pale yellow oil; IR (neat) 3079, 2949, 1571, 1441, 1362, 1214, 1069, 899, 811, 737, 706, 620, 564, 531 cm^{-1} ; 1H NMR (acetone- d_6) δ 9.54 (1H, s), 7.87 (1H, d, $J = 1.7$ Hz), 7.74 (1H, s), 4.71-4.67 (2H, m), 4.07 (3H, s), 2.43 (6H, t, $J = 9.2$ Hz), 1.88-1.85 (2H, m), 1.24-1.20 (6H, m); ^{13}C NMR (acetone- d_6): δ 137.5, 124.4, 123.0, 46.9, 36.8, 25.9, 15.1, 1.7; ^{13}C $\{^{19}F\}$ NMR (acetone- d_6): δ 119.6, 118.0, 112.1, 112.0, 111.1,

109.3; HRMS (pos. mode) calcd for C₃₀H₂₂F₃₉N₂Si [M-I]⁺ 1179.0924, found 1179.0903, (neg. mode) calcd for I [M-C₃₀H₂₂F₃₉N₂Si⁺]⁻ 126.9050, found 126.9048.

1-Methyl-3-[4-tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silylbenzyl]imidazolium iodide (5a): a brown solid; m.p. 71 °C; IR (neat) 3093, 2949, 1553, 1440, 1361, 1209, 1144, 1068, 900, 814, 735, 642 cm⁻¹; ¹H NMR (acetone-d₆) δ 9.80 (1H, s), 7.89 (2H, dd, *J* = 1.8, 0.9 Hz), 7.77 (2H, dd, *J* = 6.7, 5.0 Hz), 7.72, (1H, s), 7.70 (1H, s), 5.75 (2H, s), 4.10 (3H, s), 2.33-2.30 (6H, m), 1.40-1.36 (6H, m); ¹³C NMR (acetone-d₆): δ 138.1, 137.7, 135.7, 134.4, 129.6, 124.9, 123.3, 52.8, 36.9, 26.0, 1.7; ¹³C {¹⁹F} NMR (acetone-d₆): δ 119.5, 118.0, 112.1, 111.9, 111.1, 109.3; HRMS (pos. mode) calcd for C₃₅H₂₄F₃₉N₂Si [M-I]⁺ 1241.1081, found 1241.1072, (neg. mode) calcd for I [M-C₃₅H₂₄F₃₉N₂Si⁺]⁻ 126.9050, found 126.9043.

1,10-Bis[3-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)imidazolium-1-yl]decane iodide (9a): a white solid; m.p. 161 °C; IR (neat) 3004, 2928, 2847, 1561, 1453, 1350, 1204, 1150, 1025, 730, 631, 559 cm⁻¹; ¹H NMR (acetone-d₆) δ 9.30 (2H, s), 7.87 (2H, d, *J* = 1.7 Hz), 7.86 (2H, d, *J* = 1.7 Hz), 4.33 (4H, t, *J* = 7.2 Hz), 4.18 (4H, t, *J* = 7.2 Hz), 2.28-2.25 (4H, m), 2.12-2.06 (4H, m), 1.81-1.76 (4H, m), 1.22 (12H, s); ¹³C NMR (acetone-d₆): δ 136.2, 122.6, 122.3, 48.9, 47.6, 29.1, 28.6, 28.2, 26.8, 25.4, 20.8; ¹³C {¹⁹F} NMR (acetone-d₆): δ 118.4, 116.5, 110.6, 110.5, 110.3, 110.2, 109.7, 107.8; HRMS (pos. mode) calcd for C₃₈H₃₈F₃₄IN₄ [M-I]⁺ 1323.1593, found 1323.1579, (neg. mode) calcd for I [M-C₃₈H₃₈F₃₄IN₄⁺]⁻ 126.9050, found 126.9059.

1,10-Bis{3-[3-tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silylpropyl]imidazolium-1-yl}decane iodide (10a): a pale yellow oil; IR (neat) 3075, 2931, 2858, 1562, 1442, 1361, 1259, 1069, 901, 811, 737, 649, 531 cm⁻¹; ¹H NMR (acetone-d₆) δ 9.81 (2H, s), 7.90 (2H, s), 7.82 (2H, s), 4.48 (4H, t, *J* = 6.9 Hz), 4.40 (4H, t, *J* = 7.4 Hz), 2.34-2.29 (12H, m), 2.16 (4H, m), 1.96 (4H, m), 1.36 (8H, s), 1.31 (4H, s), 1.10-1.08 (12H, m), 1.00 (4H, t, *J* = 8.3 Hz); ¹³C NMR (acetone-d₆): δ 137.5, 123.6, 123.4, 52.9, 50.4, 30.8, 26.6, 26.1, 25.4, 8.7, 1.7; ¹³C {¹⁹F} NMR (acetone-d₆): δ 119.5, 118.0, 112.1, 112.0, 111.1, 109.3; HRMS (pos. mode) calcd for C₇₀H₆₂F₇₈IN₄Si₂ [M-I]⁺ 2623.2307, found 2623.2323, (neg. mode) calcd for I [M-C₇₀H₆₂F₇₈IN₄Si₂⁺]⁻ 126.9050, found 126.9055.

Typical Procedure for the Anion Exchange of Imidazolium Salts 1a-10a. **1,3-Bis(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)imidazolium bis(trifluoromethanesulfonyl)amide (1b).** To a stirred solution of 1,3-bis(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadeca-

fluoroundecyl)imidazolium iodide **1a** (67 mg, 0.06 mmol) in acetone/water (3:1, 4 mL) at ambient temperature was added sodium tetrafluoroborate (52 mg, 0.47 mmol). After stirring for 5 h, the resulting reaction mixture was concentrated in vacuo. The residue was washed with water for three times by decantation, followed by drying under reduced pressure to afford the corresponding tetrafluoroborate **1b**, which did not require further purification (92%); a white solid; m.p. 89 °C; IR (neat) 3147, 3095, 2962, 1560, 1352, 1203, 1148, 1058, 977, 792, 661, 619, 572, 516 cm⁻¹; ¹H NMR (acetone-d₆) δ 9.25 (1H, s), 7.89 (2H, d, *J* = 1.7), 4.55 (4H, t, *J* = 6.9 Hz), 2.42-2.37 (4H, m), 2.33-2.31 (4H, m); ¹³C NMR (acetone-d₆): δ 137.4, 124.0, 49.5, 28.2, 22.2; ¹³C {¹⁹F} NMR (acetone-d₆): δ 120.9, 119.3, 117.9, 112.0, 111.8, 111.6, 111.5, 111.0, 109.2; HRMS (pos. mode) calcd for C₂₅H₁₅F₃₄N₂ [M-N(CF₃SO₂)₂]⁺ 989.0687, found 989.0669, LRMS (neg. mode) *m/z* 280 [M-C₂₅H₁₅F₃₄N₂]⁻, 100].

1,3-Bis(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)imidazolium tetrafluoroborate (1c): a white solid; m.p. 153 °C; IR (neat) 3160, 3032, 2988, 1567, 1457, 1331, 1198, 1148, 1062, 966, 738, 707, 656, 558, 531 cm⁻¹; ¹H NMR (acetone-d₆) δ 9.31 (1H, s), 7.95 (2H, d, *J* = 1.7 Hz), 4.60 (4H, t, *J* = 7.2 Hz), 2.49-2.42 (4H, m), 2.38-2.34 (4H, m); ¹³C NMR (acetone-d₆): δ 137.4, 124.0, 49.6, 28.5, 21.8; ¹³C {¹⁹F} NMR (acetone-d₆): δ 119.5, 118.3, 112.2, 111.8, 111.6, 111.4, 111.1, 109.3; HRMS (pos. mode) calcd for C₂₅H₁₅F₃₄N₂ [M-BF₄]⁺ 989.0687, found 989.0699, LRMS (neg. mode) *m/z* 87 [M-C₂₅H₁₅F₃₄N₂]⁻, 100].

1,3-Bis(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)imidazolium hexafluorophosphate (1d): a white solid; m.p. 145 °C; IR (neat) 3107, 2967, 1566, 1457, 1332, 1239, 1209, 1149, 1031, 970, 833, 744, 655, 559, 532 cm⁻¹; ¹H NMR (acetone-d₆) δ 9.29 (1H, s), 7.94 (2H, d, *J* = 2.3 Hz), 4.60 (4H, t, *J* = 8.6 Hz), 2.43-2.41 (4H, m), 2.39-2.37 (4H, m); ¹³C NMR (acetone-d₆): δ 137.4, 123.9, 49.5, 28.2, 22.1; ¹³C {¹⁹F} NMR (acetone-d₆): δ 119.5, 118.0, 112.1, 111.9, 111.7, 111.6, 111.1, 109.3; HRMS (pos. mode) calcd for C₂₅H₁₅F₃₄N₂ [M-PF₆]⁺ 989.0687, found 989.0699, LRMS (neg. mode) *m/z* 145 [M-C₂₅H₁₅F₃₄N₂]⁻, 100].

1,3-Bis(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)imidazolium tetrakis[4-dimethyl(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silylphenyl]borate (1e): a pale yellow oil; IR (neat) 3107, 3037, 2962, 1566, 1457, 1332, 1239, 1209, 1149, 1031, 970, 833, 744, 655, 559, 532 cm⁻¹; ¹H NMR (acetone-d₆) δ 8.91 (1H, s), 7.85 (2H, d, *J* = 6.3), 7.43 (8H, s), 7.19 (8H, s), 4.50 (4H, t, *J* = 8.6 Hz), 2.40-2.35 (4H, m), 2.32-2.30 (4H, m), 2.19-2.09 (8H, m), 0.94-0.93 (8H, m), 0.26 (24H, s); ¹³C NMR (acetone-d₆): δ 137.2, 136.8, 131.7, 128.9, 123.9, 49.5, 28.3, 26.8, 26.2, 22.2, 6.0, -3.1; ¹³C {¹⁹F}

NMR (acetone- d_6): δ 137.3, 136.1, 132.2, 131.0, 128.8, 119.7, 119.3, 118.0, 112.2, 112.0, 111.8, 111.6, 111.1, 109.3; HRMS (pos. mode) calcd for $C_{25}H_{15}F_{34}N_2$ [$M-C_{64}H_{56}BF_{52}NSi_4$] $^+$ 989.0687, found 989.0681, LRMS (neg. mode) m/z 1935 [$M-C_{25}H_{15}F_{34}N_2$] $^-$, 100].

1-Methyl-2,3-bis(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)imidazolium

bis(trifluoromethanesulfonyl)amide (2b): a pale yellow oil; IR (neat) 3152, 3082, 2951, 2378, 1539, 1475, 1240, 1207, 1155, 659 cm^{-1} ; 1H NMR (acetone- d_6) δ 7.84 (1H, d, $J = 1.7$ Hz), 7.73 (1H, d, $J = 1.7$ Hz), 4.56 (2H, t, $J = 7.3$ Hz), 4.05 (3H, s), 3.32 (2H, t, $J = 8.4$ Hz), 2.43-2.35 (4H, m), 2.30-2.28 (2H, m), 1.90-1.85 (2H, m); ^{13}C NMR (acetone- d_6): δ 142.3, 123.9, 123.6, 49.3, 36.7, 32.1, 29.8, 28.2, 23.5, 22.2; ^{13}C $\{^{19}F\}$ NMR (acetone- d_6): δ 121.0, 119.8, 118.3, 118.1, 116.7, 113.2, 112.3, 112.0, 111.6, 111.4, 111.2, 110.8, 110.6, 110.4, 110.1, 109.2, 108.2; HRMS (pos. mode) calcd for $C_{26}H_{17}F_{34}N_2$ [$M-N(CF_3SO_2)_2$] $^+$ 1003.0843, found 1003.0833, LRMS (neg. mode) m/z 280 [$M-C_{26}H_{17}F_{34}N_2$] $^-$, 100].

1-Methyl-2,3-bis(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)imidazolium

tetrafluoroborate (2c): a white solid; m.p. 58 $^{\circ}C$; IR (neat) 3162, 3023, 2973, 1547, 1478, 1247, 1203, 1149, 657 cm^{-1} ; 1H NMR (acetone- d_6) δ 7.95 (1H, d, $J = 1.7$ Hz), 7.89 (1H, d, $J = 1.7$ Hz), 4.62 (2H, t, $J = 7.2$ Hz), 4.07 (3H, s), 3.32 (2H, t, $J = 8.5$ Hz), 2.51-2.45 (4H, m), 2.38-2.30 (2H, m), 1.98-1.86 (2H, m); ^{13}C NMR (acetone- d_6): δ 142.3, 123.9, 123.5, 49.3, 36.6, 32.0, 29.9, 28.4, 23.5, 21.9; ^{13}C $\{^{19}F\}$ NMR (acetone- d_6): δ 119.8, 118.4, 118.1, 116.7, 113.2, 112.2, 112.0, 111.7, 111.5, 111.2, 110.9, 110.7, 110.4, 110.1, 109.3, 108.2; HRMS (pos. mode) calcd for $C_{26}H_{17}F_{34}N_2$ [$M-BF_4$] $^+$ 1003.0843, found 1003.0832, LRMS (neg. mode) m/z 87 [$M-C_{26}H_{17}F_{34}N_2$] $^-$, 100].

1-Methyl-2,3-bis(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)imidazolium

hexafluorophosphate (2d): a white solid; m.p. 48 $^{\circ}C$; IR (neat) 3122, 3064, 2963, 1562, 1456, 1238, 1197, 1147, 745, 655 cm^{-1} ; 1H NMR (acetone- d_6) δ 7.93 (1H, d, $J = 1.7$ Hz), 7.87 (1H, d, $J = 1.7$ Hz), 4.60 (2H, t, $J = 7.2$ Hz), 4.05 (3H, s), 3.33 (2H, t, $J = 8.6$ Hz), 2.56-2.51 (4H, m), 2.40-2.36 (2H, m), 1.99-1.86 (2H, m); ^{13}C NMR (acetone- d_6): δ 142.3, 124.0, 123.6, 49.3, 36.6, 32.1, 29.9, 28.3, 23.5, 22.3; ^{13}C $\{^{19}F\}$ NMR (acetone- d_6): δ 119.5, 118.5, 118.1, 116.8, 113.2, 112.3, 112.1, 111.8, 111.6, 111.4, 110.9, 110.6, 110.4, 110.0, 109.2, 108.2; HRMS (pos. mode) calcd for $C_{26}H_{17}F_{34}N_2$ [$M-PF_6$] $^+$ 1003.0843, found 1003.0832, LRMS (neg. mode) m/z 145 [$M-C_{26}H_{17}F_{34}N_2$] $^-$, 100].

1-Methyl-3-[3-tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooethyl)silylpropyl]imidazolium

bis(trifluoromethanesulfonyl)amide (3b): a pale yellow oil; IR (neat) 3154, 3094, 2946, 1716, 1575,

1442, 1353, 1238, 1213, 1144, 1060, 902, 811, 739, 707, 619, 571, 515 cm^{-1} ; ^1H NMR (acetone- d_6) δ 9.10 (1H, s), 7.81 (1H, d, $J = 1.7$ Hz), 7.76 (1H, d, $J = 1.7$ Hz), 4.45 (2H, t, $J = 7.2$ Hz), 4.06 (3H, s), 2.37-2.26 (6H, m), 2.19-2.14 (2H, m), 1.09 (6H, dt, $J = 9.9, 3.9$ Hz), 1.01-0.98 (2H, m); ^{13}C NMR (acetone- d_6): δ 137.6, 125.0, 123.5, 53.1, 36.7, 26.1, 25.2, 8.46, 1.46; ^{13}C $\{^{19}\text{F}\}$ NMR (acetone- d_6): δ 121.0, 119.6, 118.1, 112.3, 112.1, 111.3, 109.4; HRMS (pos. mode) calcd for $\text{C}_{31}\text{H}_{24}\text{F}_{39}\text{N}_2\text{Si}$ $[\text{M}-\text{N}(\text{CF}_3\text{SO}_2)_2]^+$ 1193.1081, found 1193.1067, LRMS (neg. mode) m/z 280 $[\text{M}-\text{C}_{31}\text{H}_{24}\text{F}_{39}\text{N}_2\text{Si}^+]^-$, 100].

1-Methyl-3-[3-tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silylpropyl]imidazolium

tetrafluoroborate (3c): a pale yellow oil; IR (neat) 3081, 2951, 2368, 1572, 1458, 1363, 1240, 1200, 1144, 1071, 901, 811, 737, 708, 645 cm^{-1} ; ^1H NMR (acetone- d_6) δ 9.05 (1H, s), 7.78 (1H, d, $J = 1.7$ Hz), 7.73 (1H, d, $J = 1.7$ Hz), 4.42 (2H, t, $J = 7.2$ Hz), 4.40 (3H, s), 2.36-2.26 (6H, m), 2.16-2.13 (2H, m), 1.11-1.06 (6H, m), 1.00-0.96 (2H, m); ^{13}C NMR (acetone- d_6): δ 137.8, 124.8, 123.4, 53.0, 36.6, 26.1, 25.2, 8.31, 1.43; ^{13}C $\{^{19}\text{F}\}$ NMR (acetone- d_6): δ 119.6, 118.1, 112.2, 112.1, 111.2, 109.4; HRMS (pos. mode) calcd for $\text{C}_{31}\text{H}_{24}\text{F}_{39}\text{N}_2\text{Si}$ $[\text{M}-\text{BF}_4]^+$ 1193.1081, found 1193.1093, LRMS (neg. mode) m/z 87 $[\text{M}-\text{C}_{31}\text{H}_{24}\text{F}_{39}\text{N}_2\text{Si}^+]^-$, 100].

1-Methyl-3-[3-tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silylpropyl]imidazolium

hexafluorophosphate (3d): a pale yellow oil; IR (neat) 3165, 3116, 2941, 1574, 1442, 1353, 1235, 1143, 1070, 1019, 835, 746, 622, 558 cm^{-1} ; ^1H NMR (acetone- d_6) δ 9.05 (1H, s), 7.79 (1H, d, $J = 1.7$ Hz), 7.74 (1H, d, $J = 1.1$ Hz), 4.44 (2H, t, $J = 9.2$ Hz), 4.42 (3H, s), 2.37-2.26 (6H, m), 2.18-2.15 (2H, m), 1.11-1.07 (6H, m), 1.01-0.97 (2H, m); ^{13}C NMR (acetone- d_6): δ 137.5, 124.8, 123.3, 53.1, 36.7, 26.1, 25.2, 8.41, 1.44; ^{13}C $\{^{19}\text{F}\}$ NMR (acetone- d_6): δ 119.6, 118.1, 112.2, 112.0, 111.2, 109.4; HRMS (pos. mode) calcd for $\text{C}_{31}\text{H}_{24}\text{F}_{39}\text{N}_2\text{Si}$ $[\text{M}-\text{PF}_6]^+$ 1193.1081, found 1193.1097, LRMS (neg. mode) m/z 145 $[\text{M}-\text{C}_{31}\text{H}_{24}\text{F}_{39}\text{N}_2\text{Si}^+]^-$, 100].

1-methyl-3-[3-tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silylpropyl]imidazolium

tetrakis[4-dimethyl(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silylphenyl]borate (3e): a pale yellow oil; IR (neat) 3040, 2955, 1578, 1442, 1361, 1238, 1144, 1067, 1020, 949, 896, 838, 737, 706, 651, 530 cm^{-1} ; ^1H NMR (acetone- d_6) δ 8.90 (1H, s), 7.76 (1H, d, $J = 5.3$ Hz), 7.70 (1H, d, $J = 5.3$ Hz), 7.37-7.36 (8H, m), 7.13-7.11 (8H, m), 4.38 (2H, t, $J = 7.2$ Hz), 3.99 (3H, s), 2.27-2.25 (6H, m), 2.12-2.08 (10H, m), 1.07-1.03 (6H, m), 0.97-0.94 (2H, m), 0.91-0.88 (8H, m), 0.22 (24H, s); ^{13}C NMR (acetone- d_6): δ 136.8, 131.6, 128.8, 124.8, 123.4, 53.1, 36.7, 26.8, 25.9, 25.2, 8.6, 6.0, 1.5, -3.1; ^{13}C $\{^{19}\text{F}\}$ NMR (acetone- d_6): δ 137.4, 136.2, 132.2, 131.0, 128.8, 119.8, 119.6, 118.0, 112.2, 112.0, 111.2, 109.4; HRMS (pos. mode)

calcd for C₃₁H₂₄F₃₉N₂Si [M-C₆₄H₅₆BF₅₂NSi₄]⁺ 1193.1081, found 1193.1067, LRMS (neg. mode) *m/z* 1935 [M-C₃₁H₂₄F₃₉N₂Si⁺], 100].

1-Methyl-3-[2-tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silylethyl]imidazolium

bis(trifluoromethanesulfonyl)amide (4b): a pale yellow oil; IR (neat) 3158, 3098, 2955, 1715, 1575, 1442, 1352, 1200, 1144, 1062, 903, 811, 742, 707, 620, 572, 515 cm⁻¹; ¹H NMR (acetone-d₆) δ 9.10 (1H, s), 7.82 (1H, s), 7.74 (1H, s), 4.68 (2H, t, *J* = 9.5 Hz), 4.06 (3H, s), 2.43-2.38 (6H, m), 1.85-1.80 (2H, m), 1.23-1.19 (6H, m); ¹³C NMR (acetone-d₆): δ 136.9, 124.8, 123.0, 47.0, 36.6, 25.7, 14.4, 1.5; ¹³C {¹⁹F} NMR (acetone-d₆): δ 120.9, 119.5, 118.0, 112.2, 112.0, 111.2, 109.3; HRMS (pos. mode) calcd for C₃₀H₂₂F₃₉N₂Si [M-N(CF₃SO₂)₂]⁺ 1179.0924, found 1179.0911, LRMS (neg. mode) *m/z* 280 [M-C₃₀H₂₂F₃₉N₂Si⁺], 100].

1-Methyl-3-[2-tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silylethyl]imidazolium

tetrafluoroborate (4c): a pale yellow oil; IR (neat) 3161, 3122, 3028, 2950, 1575, 1443, 1363, 1239, 1207, 1144, 1067, 900, 811, 745, 707, 650, 565, 532 cm⁻¹; ¹H NMR (acetone-d₆) δ 9.09 (1H, s), 7.81 (1H, s), 7.72 (1H, s), 4.65 (2H, t, *J* = 8.9 Hz), 4.04 (3H, s), 2.42-2.38 (6H, m), 1.82-1.79 (2H, m), 1.22-1.19 (6H, m); ¹³C NMR (acetone-d₆): δ 137.2, 124.7, 122.9, 46.9, 36.5, 25.8, 14.5, 1.6; ¹³C {¹⁹F} NMR (acetone-d₆): δ 119.6, 118.0, 112.2, 112.0, 111.2, 109.4; HRMS (pos. mode) calcd for C₃₀H₂₂F₃₉N₂Si [M-BF₄]⁺ 1179.0924, found 1179.0936, LRMS (neg. mode) *m/z* 87 [M-C₃₀H₂₂F₃₉N₂Si⁺], 100].

1-Methyl-3-[2-tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silylethyl]imidazolium

hexafluorophosphate (4d): a pale yellow oil; IR (neat) 3174, 3126, 3032, 2910, 1575, 1443, 1363, 1239, 1206, 1144, 1069, 845, 745, 707, 625, 557, 532 cm⁻¹; ¹H NMR (acetone-d₆) δ 9.07 (1H, s), 7.81 (1H, s), 7.72 (1H, s), 4.67 (2H, t, *J* = 8.0 Hz), 4.05 (3H, s), 2.42-2.38 (6H, m), 1.84-1.80 (2H, m), 1.23-1.19 (6H, m); ¹³C NMR (acetone-d₆): δ 137.0, 124.7, 122.9, 47.0, 36.6, 25.8, 14.4, 1.5; ¹³C {¹⁹F} NMR (acetone-d₆): δ 119.6, 118.1, 112.2, 112.0, 111.2, 109.4; HRMS (pos. mode) calcd for C₃₀H₂₂F₃₉N₂Si [M-PF₆]⁺ 1179.0924, found 1179.0927, LRMS (neg. mode) *m/z* 145 [M-C₃₀H₂₂F₃₉N₂Si⁺], 100].

1-Methyl-3-[4-tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silylbenzyl]imidazolium

bis(trifluoromethanesulfonyl)amide (5b): a pale yellow oil; IR (neat) 3158, 3104, 3028, 2949, 1715, 1575, 1442, 1352, 1200, 1063, 901, 811, 742, 619, 516 cm⁻¹; ¹H NMR (acetone-d₆) δ 9.23 (1H, s), 7.81 (2H, dd, *J* = 5.7, 2.9 Hz), 7.78 (2H, s), 7.58 (2H, d, *J* = 8.0 Hz), 5.66 (2H, s), 4.10 (3H, s), 2.36-2.29 (6H, m), 1.39-1.36 (6H, m); ¹³C NMR (acetone-d₆): δ 137.8, 137.4, 135.9, 134.7, 129.1, 125.3, 123.6, 53.5,

36.8, 26.0, 1.8; ^{13}C $\{^{19}\text{F}\}$ NMR (acetone- d_6): δ 120.9, 119.4, 118.0, 112.1, 111.9, 111.1, 109.3; HRMS (pos. mode) calcd for $\text{C}_{35}\text{H}_{24}\text{F}_{39}\text{N}_2\text{Si} [\text{M}-\text{N}(\text{CF}_3\text{SO}_2)_2]^-$ 1241.1081, found 1241.1059, LRMS (neg. mode) m/z 280 $[\text{M}-\text{C}_{35}\text{H}_{24}\text{F}_{39}\text{N}_2\text{Si}^+]^-$, 100].

1-Methyl-3-[4-tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silylbenzyl]imidazolium

tetrafluoroborate (5c): a pale yellow oil; IR (neat) 3161, 3029, 2949, 1576, 1442, 1362, 1239, 1068, 901, 811, 733, 624, 530 cm^{-1} ; ^1H NMR (acetone- d_6) δ 9.24 (1H, s), 7.80 (2H, dd, $J = 4.4, 2.7$ Hz), 7.77 (2H, dd, $J = 1.8, 0.9$ Hz), 7.62 (1H, s), 7.60 (1H, s), 5.65 (2H, s), 4.09 (3H, s), 2.33-2.31 (6H, m), 1.41-1.36 (6H, m); ^{13}C NMR (acetone- d_6): δ 138.0, 137.6, 135.8, 134.6, 129.4, 125.2, 123.4, 53.3, 36.8, 26.0, 1.8; ^{13}C $\{^{19}\text{F}\}$ NMR (acetone- d_6): δ 119.5, 118.0, 112.2, 112.0, 111.2, 109.4; HRMS (pos. mode) calcd for $\text{C}_{35}\text{H}_{24}\text{F}_{39}\text{N}_2\text{Si} [\text{M}-\text{BF}_4]^+$ 1241.1081, found 1241.1098, LRMS (neg. mode) m/z 87 $[\text{M}-\text{C}_{35}\text{H}_{24}\text{F}_{39}\text{N}_2\text{Si}^+]^-$, 100].

1-Methyl-3-[4-tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silylbenzyl]imidazolium

hexafluorophosphate (5d): a pale yellow oil; IR (neat) 3170, 3030, 2948, 1559, 1456, 1361, 1196, 1068, 840, 734, 624, 558 cm^{-1} ; ^1H NMR (acetone- d_6) δ 9.20 (1H, s), 7.80 (2H, dd, $J = 6.3, 3.2$ Hz), 7.78 (2H, dd, $J = 2.6, 1.3$ Hz), 7.59 (1H, s), 7.57 (1H, s), 5.66 (2H, s), 4.09 (3H, s), 2.33-2.31 (6H, m), 1.40-1.36 (6H, m); ^{13}C NMR (acetone- d_6): δ 137.9, 137.4, 135.9, 134.7, 129.3, 125.3, 123.5, 53.5, 36.8, 26.1, 1.8; ^{13}C $\{^{19}\text{F}\}$ NMR (acetone- d_6): δ 119.5, 118.0, 112.1, 111.9, 111.1, 109.3; HRMS (pos. mode) calcd for $\text{C}_{35}\text{H}_{24}\text{F}_{39}\text{N}_2\text{Si} [\text{M}-\text{PF}_6]^+$ 1241.1081, found 1241.1077, LRMS (neg. mode) m/z 145 $[\text{M}-\text{C}_{35}\text{H}_{24}\text{F}_{39}\text{N}_2\text{Si}^+]^-$, 100].

1,3-Bis[3-tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silylpropyl]imidazolium

bis(trifluoromethanesulfonyl)amide (6b): a pale yellow oil; IR (neat) 3151, 3081, 2944, 1561, 1441, 1353, 1237, 1198, 1143, 1062, 904, 812, 736, 701, 642, 571, 517 cm^{-1} ; ^1H NMR (acetone- d_6) δ 9.11 (1H, s), 7.82 (2H, s), 4.40 (4H, t, $J = 6.3$ Hz), 2.34-2.30 (12H, m), 2.15-2.13 (4H, m), 1.09-1.07 (12H, m), 0.98 (4H, t, $J = 8.3$ Hz); ^{13}C NMR (acetone- d_6): δ 136.8, 123.6, 53.2, 25.9, 25.2, 8.6, 1.5; ^{13}C $\{^{19}\text{F}\}$ NMR (acetone- d_6): δ 121.0, 119.5, 118.0, 112.2, 112.0, 111.2, 109.4; HRMS (pos. mode) calcd for $\text{C}_{57}\text{H}_{39}\text{F}_{78}\text{N}_2\text{Si}_2 [\text{M}-\text{N}(\text{CF}_3\text{SO}_2)_2]^-$ 2289.1401, found 2289.1432, LRMS (neg. mode) m/z 280 $[\text{M}-\text{C}_{57}\text{H}_{39}\text{F}_{78}\text{N}_2\text{Si}_2^+]^-$, 100].

1,3-Bis[3-tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silylpropyl]imidazolium tetrafluoroborate (6c): a pale yellow oil; IR (neat) 3154, 3094, 2947, 1566, 1442, 1361, 1235, 1144, 1067, 903, 811, 745,

707, 647, 564, 530 cm^{-1} ; ^1H NMR (acetone- d_6) δ 9.14 (1H, s), 7.83 (2H, d, $J = 1.7$ Hz), 4.41 (4H, t, $J = 7.4$ Hz), 2.33-2.30 (12H, m), 2.15-2.13 (4H, m), 1.10-1.06 (12H, m), 0.98-0.97 (4H, m); ^{13}C NMR (acetone- d_6): δ 137.2, 123.4, 53.0, 25.9, 25.2, 8.4, 1.5; ^{13}C $\{^{19}\text{F}\}$ NMR (acetone- d_6): δ 119.6, 118.1, 112.2, 112.1, 111.2, 109.4; HRMS (pos. mode) calcd for $\text{C}_{57}\text{H}_{39}\text{F}_{78}\text{N}_2\text{Si}_2$ $[\text{M}-\text{BF}_4]^+$ 2289.1401, found 2289.1392, LRMS (neg. mode) m/z 87 $[\text{M}-\text{C}_{57}\text{H}_{39}\text{F}_{78}\text{N}_2\text{Si}_2]^+$, 100].

1,3-Bis[3-tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silylpropyl]imidazolium

hexafluorophosphate (6d): a pale yellow oil; IR (neat) 3160, 3103, 3023, 2944, 1568, 1434, 1369, 1246, 1145, 1077, 900, 843, 731, 705, 644, 556, 532 cm^{-1} ; ^1H NMR (acetone- d_6) δ 9.15 (1H, s), 7.85 (2H, s), 4.43 (4H, t, $J = 7.4$ Hz), 2.35-2.28 (12H, m), 2.18-2.16 (4H, m), 1.10-1.07 (12H, m), 1.00-0.97 (4H, m); ^{13}C NMR (acetone- d_6): δ 136.9, 123.5, 53.2, 25.9, 25.2, 8.5, 1.5; ^{13}C $\{^{19}\text{F}\}$ NMR (acetone- d_6): δ 119.5, 118.0, 112.2, 112.0, 111.2, 109.4; HRMS (pos. mode) calcd for $\text{C}_{57}\text{H}_{39}\text{F}_{78}\text{N}_2\text{Si}_2$ $[\text{M}-\text{PF}_6]^+$ 2289.1401, found 2289.1388, LRMS (neg. mode) m/z 145 $[\text{M}-\text{C}_{57}\text{H}_{39}\text{F}_{78}\text{N}_2\text{Si}_2]^+$, 100].

1,3-Bis[2-tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silylethyl]imidazolium

bis(trifluoromethanesulfonyl)amide (7b): a pale yellow oil; IR (neat) 3149, 3085, 2950, 1559, 1442, 1352, 1199, 1141, 1059, 900, 811, 740, 707, 619, 571, 515 cm^{-1} ; ^1H NMR (acetone- d_6) δ 9.23 (1H, s), 7.86 (2H, s), 4.67-4.65 (4H, m), 2.41-2.37 (12H, m), 1.81-1.80 (4H, m), 1.22-1.18 (12H, m); ^{13}C NMR (acetone- d_6): δ 135.7, 123.2, 47.1, 25.8, 14.5, 1.6; ^{13}C $\{^{19}\text{F}\}$ NMR (acetone- d_6): δ 121.0, 119.6, 118.1, 112.2, 112.0, 111.2, 109.4; HRMS (pos. mode) calcd for $\text{C}_{55}\text{H}_{35}\text{F}_{78}\text{N}_2\text{Si}_2$ $[\text{M}-\text{N}(\text{CF}_3\text{SO}_2)_2]^+$ 2261.1088, found 2261.1112, LRMS (neg. mode) m/z 280 $[\text{M}-\text{C}_{55}\text{H}_{35}\text{F}_{78}\text{N}_2\text{Si}_2]^+$, 100].

1,3-Bis[2-tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silylethyl]imidazolium tetrafluoroborate

(7c): a pale yellow oil; IR (neat) 3164, 3033, 2940, 1713, 1557, 1445, 1362, 1239, 1143, 1064, 843, 738, 709, 648, 558, 525 cm^{-1} ; ^1H NMR (acetone- d_6) δ 9.21 (1H, s), 7.83 (2H, s), 4.68-4.60 (4H, m), 2.43-2.35 (12H, m), 1.80-1.77 (4H, m), 1.21-1.18 (12H, m); ^{13}C NMR (acetone- d_6): δ 136.1, 123.1, 47.0, 25.6, 14.5, 1.6; ^{13}C $\{^{19}\text{F}\}$ NMR (acetone- d_6): δ 119.6, 118.1, 112.2, 112.0, 111.2, 109.4; HRMS (pos. mode) calcd for $\text{C}_{55}\text{H}_{35}\text{F}_{78}\text{N}_2\text{Si}_2$ $[\text{M}-\text{BF}_4]^+$ 2261.1088, found 2261.1120, LRMS (neg. mode) m/z 87 $[\text{M}-\text{C}_{55}\text{H}_{35}\text{F}_{78}\text{N}_2\text{Si}_2]^+$, 100].

1,3-Bis[2-tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silylethyl]imidazolium hexafluorophosphate

(7d): a pale yellow oil; IR (neat) 3160, 3125, 3019, 2953, 1561, 1441, 1358, 1200, 1143, 1069, 839, 740, 705, 646, 561, 525 cm^{-1} ; ^1H NMR (acetone- d_6) δ 9.21 (1H, s), 7.84 (2H, s), 4.63-4.60 (4H, m), 2.38-2.34

(12H, m), 1.78-1.74 (4H, m), 1.19-1.15 (12H, m); ^{13}C NMR (acetone- d_6): δ 135.7, 123.1, 47.0, 25.7, 14.4, 1.5; ^{13}C $\{^{19}\text{F}\}$ NMR (acetone- d_6): δ 119.6, 118.1, 112.2, 112.1, 111.2, 109.4; HRMS (pos. mode) calcd for $\text{C}_{55}\text{H}_{35}\text{F}_{78}\text{N}_2\text{Si}_2$ $[\text{M-PF}_6^-]^+$ 2261.1088, found 2261.1072, LRMS (neg. mode) m/z 145 $[\text{M-C}_{55}\text{H}_{35}\text{F}_{78}\text{N}_2\text{Si}_2^+]^-$, 100].

1,3-Bis[4-tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silylbenzyl]imidazolium

bis(trifluoromethanesulfonyl)amide (8b): a pale yellow oil; IR (neat) 3150, 3028, 2942, 1716, 1558, 1443, 1352, 1240, 1063, 901, 811, 737, 619, 515 cm^{-1} ; ^1H NMR (acetone- d_6) δ 9.15 (1H, s), 7.59 (2H, s), 7.53 (4H, d, $J = 8.0$ Hz), 7.35 (4H, d, $J = 7.4$ Hz), 2.07-2.04 (12H, m), 1.14-1.12 (12H, m); ^{13}C NMR (acetone- d_6): δ 137.6, 137.2, 135.9, 134.8, 129.3, 124.3, 53.8, 26.1, 1.8; ^{13}C $\{^{19}\text{F}\}$ NMR (acetone- d_6): δ 121.1, 119.6, 118.1, 112.2, 112.1, 111.2, 109.4; HRMS (pos. mode) calcd for $\text{C}_{65}\text{H}_{39}\text{F}_{78}\text{N}_2\text{Si}_2$ $[\text{M-N}(\text{CF}_3\text{SO}_2)_2]^+$ 2385.1401, found 2385.1389, LRMS (neg. mode) m/z 280 $[\text{M-C}_{65}\text{H}_{39}\text{F}_{78}\text{N}_2\text{Si}_2^+]^-$, 100].

1,3-Bis[4-tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silylbenzyl]imidazolium tetrafluoroborate

(8c): a pale yellow solid; m.p. 92 $^\circ\text{C}$; IR (neat) 3157, 3050, 2951, 1558, 1443, 1361, 1239, 1068, 900, 812, 737, 651, 531 cm^{-1} ; ^1H NMR (acetone- d_6) δ 8.60 (1H, s), 7.00 (2H, s), 6.96 (4H, d, $J = 7.4$ Hz), 6.83 (4H, d, $J = 10.0$ Hz), 4.83 (4H, s), 1.52-1.48 (12H, m), 0.58-0.55 (12H, m); ^{13}C NMR (acetone- d_6): δ 137.7, 137.3, 135.9, 134.8, 129.4, 124.0, 53.6, 26.0, 1.7; ^{13}C $\{^{19}\text{F}\}$ NMR (acetone- d_6): δ 119.5, 118.1, 112.2, 112.0, 111.2, 109.4; HRMS (pos. mode) calcd for $\text{C}_{65}\text{H}_{39}\text{F}_{78}\text{N}_2\text{Si}_2$ $[\text{M-BF}_4^-]^+$ 2385.1401, found 2385.1388, LRMS (neg. mode) m/z 87 $[\text{M-C}_{65}\text{H}_{39}\text{F}_{78}\text{N}_2\text{Si}_2^+]^-$, 100].

1,3-Bis[4-tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silylbenzyl]imidazolium

hexafluorophosphate (8d): a pale yellow solid; m.p. 94 $^\circ\text{C}$; IR (neat) 3174, 3028, 2950, 1559, 1443, 1352, 1211, 1070, 847, 736, 651, 559 cm^{-1} ; ^1H NMR (acetone- d_6) δ 9.44 (1H, s), 7.87 (2H, s), 7.79 (4H, d, $J = 6.9$ Hz), 7.59 (4H, d, $J = 8.0$ Hz), 2.32-2.28 (12H, m), 1.40-1.36 (12H, m); ^{13}C NMR (acetone- d_6): δ 137.6, 137.2, 135.9, 134.9, 129.3, 124.2, 53.7, 26.0, 1.8; ^{13}C $\{^{19}\text{F}\}$ NMR (acetone- d_6): δ 119.5, 118.0, 112.2, 112.0, 111.1, 109.4; HRMS (pos. mode) calcd for $\text{C}_{65}\text{H}_{39}\text{F}_{78}\text{N}_2\text{Si}_2$ $[\text{M-PF}_6^-]^+$ 2385.1401, found 2385.1421, LRMS (neg. mode) m/z 145 $[\text{M-C}_{65}\text{H}_{39}\text{F}_{78}\text{N}_2\text{Si}_2^+]^-$, 100].

1,10-Bis[3-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)imidazolium-1-yl]decane

bis(trifluoromethanesulfonyl)amide (9b): a white waxy solid; IR (neat) 3157, 3098, 2934, 2860, 1569, 1473, 1353, 1203, 1149, 1060, 740, 620, 571, 514 cm^{-1} ; ^1H NMR (acetone- d_6) δ 9.18 (2H, s), 7.83 (2H, s), 7.80 (2H, s), 4.27-4.26 (4H, t, $J = 6.9$ Hz), 4.15-4.14 (4H, t, $J = 6.9$ Hz), 2.35-2.22 (4H, m), 2.14-2.09 (4H,

m), 1.78-1.76 (4H, m), 1.22 (12H, s); ^{13}C NMR (acetone- d_6): δ 136.2, 122.6, 122.4, 48.9, 47.7, 30.7, 29.2, 28.8, 28.4, 25.5, 20.7; ^{13}C $\{^{19}\text{F}\}$ NMR (acetone- d_6): δ 119.5, 118.4, 116.5, 110.7, 110.5, 110.2, 110.2, 109.7, 107.8; HRMS (pos. mode) calcd for $\text{C}_{40}\text{H}_{38}\text{F}_{40}\text{N}_5\text{O}_4\text{S}_2$ $[\text{M}-\text{N}(\text{CF}_3\text{SO}_2)_2]^+$ 1476.1721, found 1476.1742, LRMS (neg. mode) m/z 280 $[\text{M}-\text{C}_{40}\text{H}_{38}\text{F}_{40}\text{N}_5\text{O}_4\text{S}_2]^+$, 100].

1,10-Bis[3-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptafluoroundecyl)imidazolium-1-yl]decane tetrakis[4-dimethyl(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silylphenyl]borate (9e): a colorless oil; IR (neat) 3037, 2957, 1508, 1362, 1241, 1208, 1144, 1066, 897, 838, 793, 707, 527, 419 cm^{-1} ; ^1H NMR (acetone- d_6) δ 8.57 (2H, s), 7.76 (2H, s), 7.67 (2H, s), 7.43 (16H, m), 7.18 (16H, d, $J = 7.4$ Hz), 4.40 (4H, t, $J = 7.4$ Hz), 4.20 (4H, t, $J = 7.4$ Hz), 2.36 (4H, m), 2.26 (4H, s), 2.16-2.13 (16H, m), 1.89-1.87 (4H, m), 1.35-1.33 (8H, m), 1.30-1.28 (4H, m), 0.96-0.92 (16H, m), 0.26 (48H, s); ^{13}C NMR (acetone- d_6): δ 136.8, 131.69, 131.67, 131.65, 128.9, 123.7, 123.6, 50.6, 49.4, 30.8, 27.0, 26.9, 26.7, 26.6, 22.3, 6.0, -3.1; ^{13}C $\{^{19}\text{F}\}$ NMR (acetone- d_6): δ 137.4, 136.1, 132.3, 132.3, 131.1, 131.1, 128.9, 128.9, 119.8, 118.0, 112.3, 112.0, 111.2, 109.4; HRMS (pos. mode) calcd for $\text{C}_{102}\text{H}_{94}\text{BF}_{86}\text{N}_4\text{Si}_4$ $[\text{M}-\text{C}_{64}\text{H}_{56}\text{BF}_{52}\text{NSi}_4]^+$ 3131.5270, found 3131.5311, LRMS (neg. mode) m/z 1935 $[\text{M}-\text{C}_{102}\text{H}_{94}\text{BF}_{86}\text{N}_4\text{Si}_4]^+$, 100].

1,10-Bis{3-[3-tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silylpropyl]imidazolium-1-yl}decane bis(trifluoromethanesulfonyl)amide (10b): a pale yellow oil; IR (neat) 3149, 3087, 2938, 2864, 1561, 1443, 1353, 1241, 1199, 1060, 902, 811, 740, 618, 571, 515 cm^{-1} ; ^1H NMR (acetone- d_6) δ 9.19, (2H, s), 7.83 (4H, m), 4.43 (4H, t, $J = 6.3$ Hz), 4.35 (4H, t, $J = 7.2$ Hz), 2.33-2.29 (12 H, m), 2.16 (4H, m), 1.95 (4H, m), 1.34 (8H, s), 1.29 (4H, s), 1.10-1.06 (12H, m), 1.00-0.95 (4H, m); ^{13}C NMR (acetone- d_6): δ 136.8, 123.7, 123.6, 53.2, 50.6, 30.8, 26.9, 25.7, 25.2, 8.6, 1.5; ^{13}C $\{^{19}\text{F}\}$ NMR (acetone- d_6): δ 121.0, 119.6, 118.1, 112.2, 112.0, 111.2, 109.4; HRMS (pos. mode) calcd for $\text{C}_{72}\text{H}_{62}\text{F}_{84}\text{N}_5\text{O}_4\text{S}_2\text{Si}_2$ $[\text{M}-\text{N}(\text{CF}_3\text{SO}_2)_2]^+$ 2776.2435, found 2776.2421, LRMS (neg. mode) m/z 280 $[\text{M}-\text{C}_{72}\text{H}_{62}\text{F}_{84}\text{N}_5\text{O}_4\text{S}_2\text{Si}_2]^+$, 100].

1,10-Bis{3-[3-tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silylpropyl]imidazolium-1-yl}decane tetrafluoroborate (10c): a pale yellow oil; IR (neat) 3152, 3107, 2933, 2860, 1715, 1566, 1442, 1363, 1240, 1066, 902, 811, 745, 646, 531 cm^{-1} ; ^1H NMR (acetone- d_6) δ 9.18 (2H, s), 7.82 (2H, s), 7.80 (2H, s), 4.42 (4H, t, $J = 7.2$ Hz), 4.35 (4H, t, $J = 7.4$ Hz), 2.34-2.32 (12H, m), 2.15 (4H, m), 1.94 (4H, m), 1.35 (8H, s), 1.29 (4H, s), 1.11-1.07 (12H, m), 0.99-0.96 (4H, m); ^{13}C NMR (acetone- d_6): δ 137.1, 123.6, 123.4, 53.0, 50.4, 30.8, 26.6, 25.9, 25.2, 8.4, 1.5; ^{13}C $\{^{19}\text{F}\}$ NMR (acetone- d_6): δ 119.5, 118.0, 112.1,

111.9, 111.1, 109.3; HRMS (pos. mode) calcd for $C_{70}H_{62}BF_{82}N_4Si_2$ $[M-BF_4]^+$ 2583.3291, found 2583.3270, LRMS (neg. mode) m/z 87 $[M-C_{70}H_{62}BF_{82}N_4Si_2]^+$, 100].

1,10-Bis{3-[3-tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silylpropyl]imidazolium-1-yl}decane hexafluorophosphate (10d): a pale yellow oil; IR (neat) 3162, 3112, 2933, 2861, 1716, 1561, 1457, 1363, 1240, 1068, 845, 745, 645, 557 cm^{-1} ; 1H NMR (acetone- d_6) δ 9.06 (2H, s), 7.79 (4H, brs), 4.40 (4H, s), 4.33 (4H, s), 2.32-2.30 (12H, m), 2.15 (4H, m), 1.93 (4H, m), 1.34 (8H, s), 1.28 (4H, s), 1.09-1.07 (12H, m), 0.97 (4H, t, $J = 8.3$ Hz); ^{13}C NMR (acetone- d_6): δ 136.8, 123.6, 123.5, 53.1, 50.5, 30.7, 26.7, 25.9, 25.1, 8.5, 1.4; ^{13}C $\{^{19}F\}$ NMR (acetone- d_6): δ 119.6, 118.0, 112.2, 112.0, 111.2, 109.4; HRMS (pos. mode) calcd for $C_{70}H_{62}F_{84}N_4PSi_2$ $[M-PF_6]^+$ 2641.2904, found 2641.2923, LRMS (neg. mode) m/z 145 $[M-C_{70}H_{62}F_{84}N_4PSi_2]^+$, 100].

Representative Procedure for Measurement of Partition Coefficients. The organic solvent (Toluene; 1 mL) and the fluoruous solvent (Perfluoro(methylcyclohexane); 1 mL) were added to a vial containing the ionic liquid (0.050 g) and a magnetic stir bar. The samples were stirred at room temperature for 1 h and allowed to stand for 0.5 h for the phases to separate. An aliquot was removed from each phase (0.5 mL). The solvent was removed and the residue dried under vacuum and then weighed.