

Synthesis and properties of dicationic ionic liquids with pentasiloxane linker

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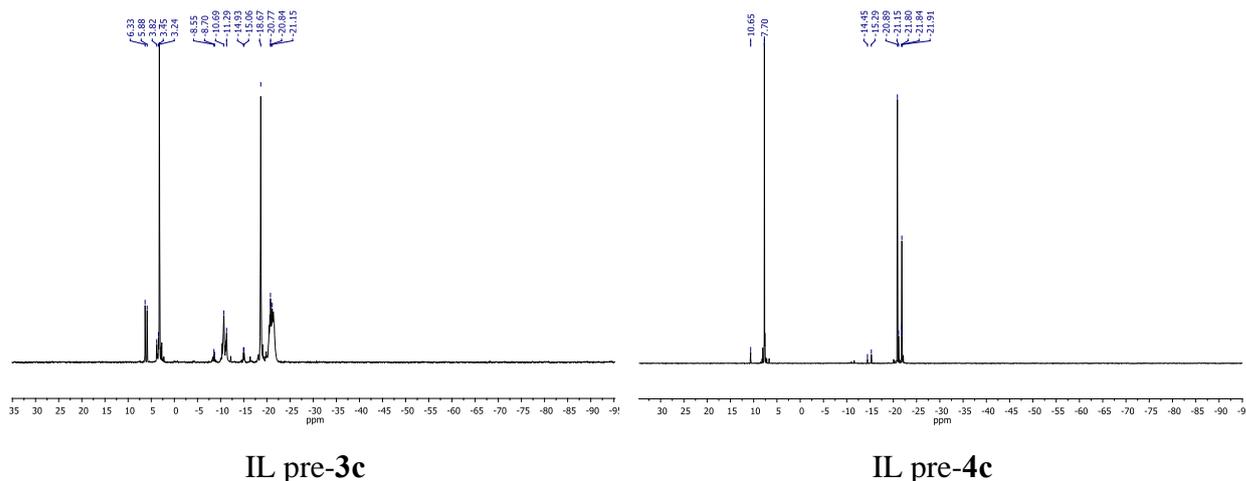
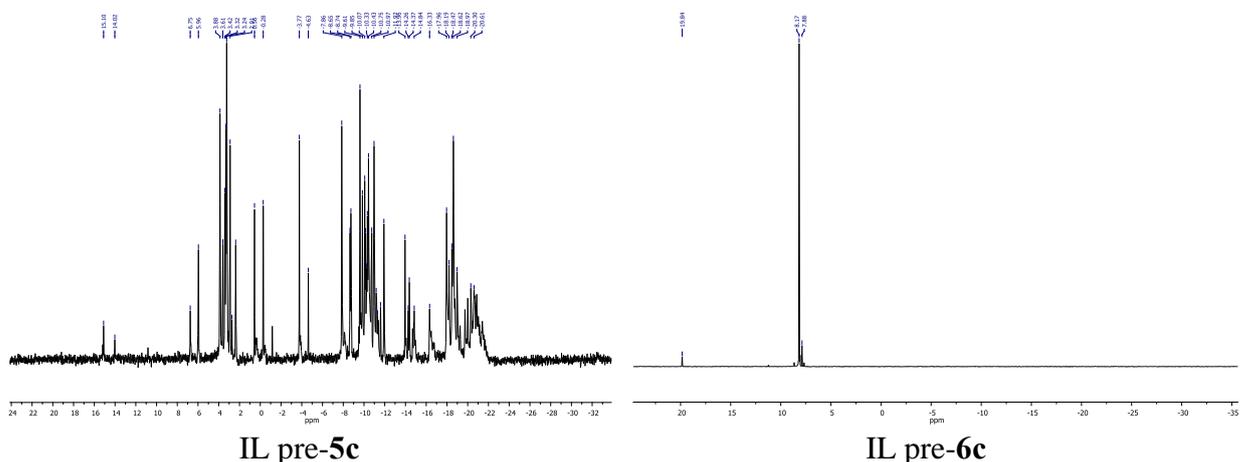


Figure S1 ^{29}Si NMR spectra of chloride pentasiloxane dicationic ILs with methylene (IL pre-3c) or propylene (IL pre-4c) spacers in the linker structure.



reaction mixture is cooled with stirring to room temperature, and toluene (300 ml) is added. Methanol and the toluene-water azeotrope are distilled off with a Dean-Stark trap until the vapor temperature reached the boiling point of toluene. The mixture is cooled to room temperature, the target product is collected by filtration and washed with absolute toluene on a Schott filter in an argon flow. Traces of toluene are removed *in vacuo*.

1.2. Synthesis of pentasiloxane linkers **1** and **2** (α,ω -bis(chloroalkyl)decamethylpentasiloxanes)

Sodium 1,1,3,3,5,5-hexamethyltrisiloxane-1,5-diolate (21.2 g, 0.07 mol) and absolute toluene (250 ml) are placed into a 1 L four-necked flask equipped with a mechanical stirrer, reflux condenser, dropping funnel and inert gas (argon) inlet. The reaction mixture is cooled to -20 °C, and chloro(chloroalkyl)dimethylsilane (0.16 mol) is added dropwise. After the addition is complete, the mixture is stirred under cooling for 30 minutes, the cooling is then removed, and the mixture is stirred until it reaches room temperature. Pyridine (10 ml) and water (100 ml) are added, and the mixture is washed with water until neutral in a separating funnel. The organic layer is dried over Na₂SO₄. Toluene is removed at atmospheric pressure, and the target product, α,ω -(dichloroalkyl)decamethylpentasiloxane, is isolated by vacuum distillation.

2. Experimental data of linkers **1** and **2**.

2.1. Sodium 1,1,3,3,5,5-hexamethyltrisiloxane-1,5-diolate



The yield was 79%. White crystals. Molecular formula C₆H₁₈O₄Si₃Na₂, FW 284.45. Calculated, %: C 25.34, H 6.38, Si 29.62, Na 16.16; found, %: C 25.13, H 6.77, Si 29.31, Na 16.02. NMR and IR spectra of sodium 1,1,3,3,5,5-hexamethyltrisiloxane-1,5-diolate are reported previously (Ref. 31 of the main text).

2.2. 1,9-Bis(chloromethyl)-1,1,3,3,5,5,7,7,9,9-decamethylpentasiloxane (1)



The yield was 73%, bp 113-114°C (1 Torr), GC purity 95%. Colourless liquid. ^1H NMR (CDCl_3 , 300.13 MHz) δ ppm 0.10 (s, 18H), 0.24 (s, 12H), 2.76 (s, 4H). ^{13}C NMR $\{^1\text{H}\}$ (CDCl_3 , 75.47 MHz) δ ppm -1.43, 0.99, 30.75. ^{29}Si NMR $\{^1\text{H}\}$ (DCCl_3 , 59.60 MHz) δ ppm -21.49, -20.00, 2.02. IRS (ATR) cm^{-1} 2962, 1397, 1278, 1180, 1076, 1024, 842, 791, 750, 697, 619, 497. Molecular formula: $\text{C}_{12}\text{H}_{34}\text{O}_4\text{Cl}_2\text{Si}_5$, FW 453.74. Calculated, %: C 31.77, H 7.55, Cl 15.63, Si 30.95. Found, %: C 31.51, H 7.93, Cl 15.59, Si 30.84.

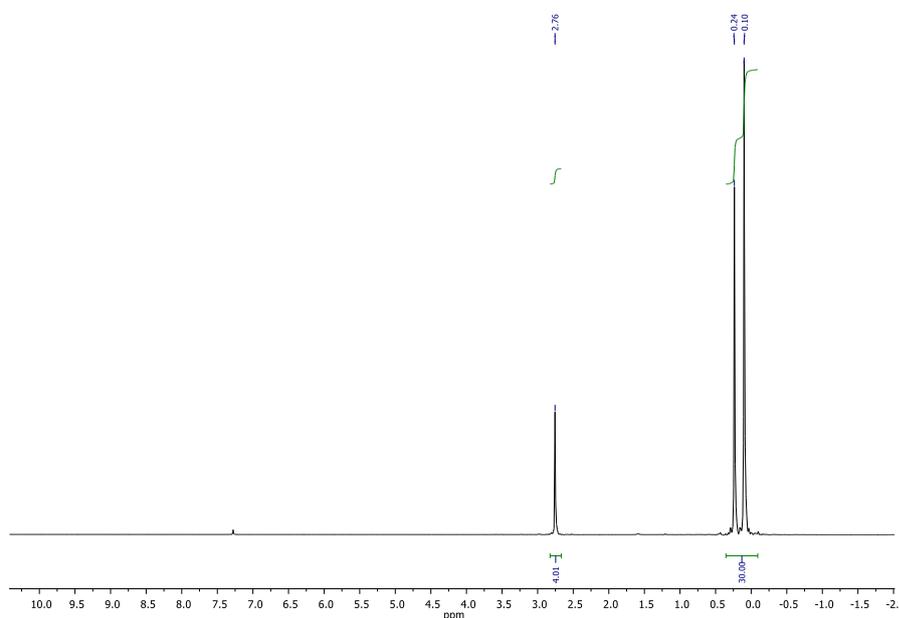


Figure S3. ^1H NMR spectrum of linker 1.

2.3. 1,9-Bis(3-chloropropyl)-1,1,3,3,5,5,7,7,9,9-decamethylpentasiloxane (2)



The yield was 67%, bp 151-152°C (1 Torr), GC purity 93%. Colourless liquid. ^1H NMR (CDCl_3 , 300.13 MHz) δ ppm 0.08, 0.09, 0.12 (3s, 30H), 0.67 (m, 4H), 1.82 (m, 4H), 3.53 (m, 4H). ^{13}C NMR $\{^1\text{H}\}$ (CDCl_3 , 75.47 MHz) δ ppm 0.09, 1.05, 1.13, 15.83, 27.03, 47.78. ^{29}Si NMR $\{^1\text{H}\}$ (CDCl_3 , 59.60 MHz) δ ppm -21.84, -20.95, 7.33. IRS (ATR) cm^{-1} 2958, 2901, 1437, 1412, 1257,

1159, 1073, 1024, 833, 789, 703, 505. Molecular formula: C₁₆H₄₂O₄Cl₂Si₅, FW weight 509.85. Calculated, %: C 37.69, H 8.30, Cl 13.91, Si 27.55. Found, %: C 31.46, H 8.47, Cl 13.83, Si 27.29.

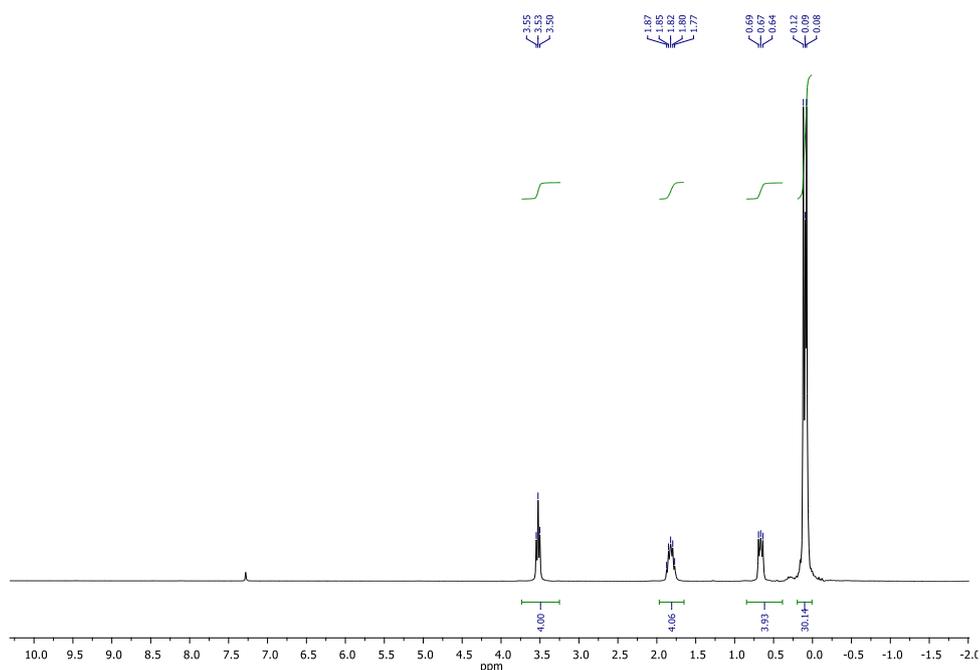


Figure S4. ¹H NMR spectrum of linker **2**.

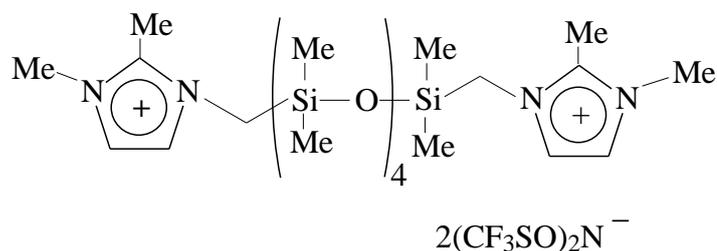
3. General method for the synthesis of pentasiloxane dicationic ILs **3a-c** and **4a-c**

3.1. Synthesis of chloride ILs pre-3a-c and pre-4a-c. The corresponding substituted imidazole was quaternized with a pentasiloxane linker **1** or **2** in acetonitrile (50% solution) with an equimolar amount of the initial reagents under reflux for 72 hours. The liquid phase was decanted, and the precipitate was dried *in vacuo*.

3.2. Synthesis of bis(trifluoromethylsulfonyl)imide ILs 3a,b and 4a-c. A mixture of chloride IL from the previous stage and 30% solution of lithium bis(trifluoromethylsulfonyl)imide (10% excess) in acetonitrile was stirred at room temperature for 90 minutes. Acetonitrile was removed *in vacuo*, the resulting bis(trifluoromethylsulfonyl)imide IL was dissolved in dichloromethane (30% solution), and excess Tf₂NLi and LiCl were removed by washing with water until the negative AgNO₃ test of the washing water toward chloride anion. The ionic liquid was dried by azeotropic distillation with absolute CH₂Cl₂ (100 ml CH₂Cl₂ per 1 g of IL).

4. Experimental data of ILs

4.1. 1',1',3,3',5',5',7',7',9',9'-Decamethyl-1',9'-bis[(2,3-dimethylimidazolium-1-yl)methyl]pentasiloxane bis(trifluoromethylsulfonyle)imide (**3a**)



The yield was 91%. White solid. ^1H NMR (DMSO- d_6 , 300.13 MHz) δ ppm: 0.05, 0.05, 0.19 (3 s, 30H), 2.54 (s, 6H), 3.76 (s, 6H), 3.83 (s, 4H), 7.43 (m, 2H), 7.63 (m, 2H). ^{13}C NMR $\{^1\text{H}\}$ (DMSO- d_6 , 75.47 MHz) δ ppm: -0.53, 1.34, 9.68, 35.22, 40.36, 113.53* (q*, $J_{\text{F}} = 321.7$ Hz), 117.79*, 121.80, 122.06*, 122.73, 126.33*, 143.94. IR (ATR) cm^{-1} : 3192, 3147, 2966, 1591, 1524, 1447, 1412, 1347, 1331, 1259, 1185, 1173, 1051, 1026, 841, 823, 795, 740, 713, 665, 569, 514. Molecular formula: $\text{C}_{26}\text{H}_{50}\text{N}_6\text{O}_{12}\text{F}_{12}\text{S}_4\text{Si}_5$, FW 1135.39. Calculated, %: C 27.50, H 4.44, N 7.40, F 20.08, S 11.30, Si 12.37. Found, %: C 27.23, H 4.61, N 7.22, F 20.04, S 10.98, Si 12.21.

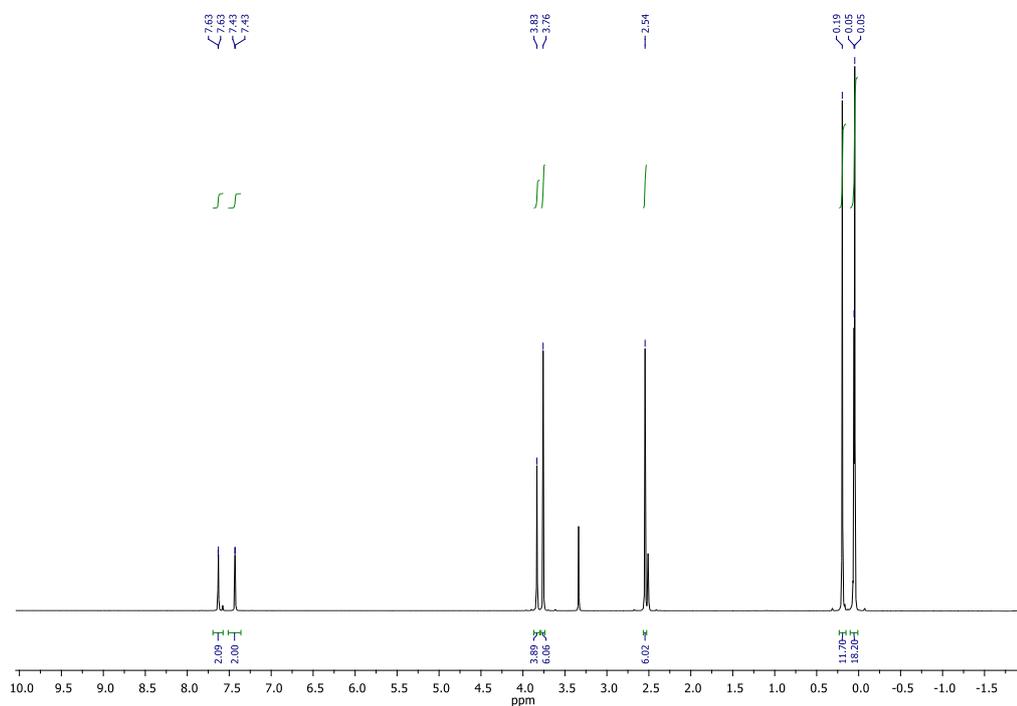
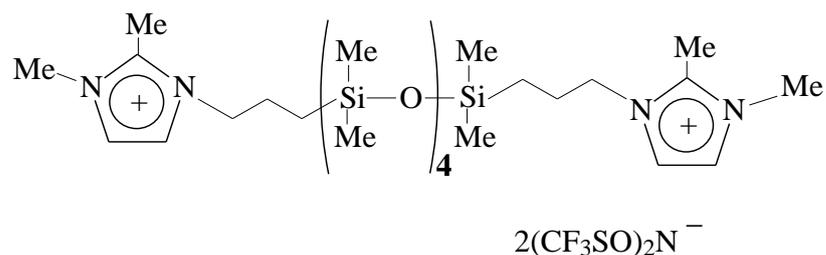


Figure S5. ^1H NMR spectrum of IL **3a**.

4.2. *1',1',3',3',5',5',7',7',9',9'-Decamethyl-1',9'-bis[3-(2,3-dimethylimidazolium-1-yl)propyl]-pentasiloxane bis(trifluoromethylsulfonyl)imide (4a)*



The yield was 96%. Colorless liquid. ^1H NMR (DMSO- d_6 , 300.13 MHz) δ ppm: 0.04, 0.09 (2 s, 30H), 0.48 (m, 4H), 1.71 (m, 4H), 2.57 (s, 6H), 3.75 (s, 6H), 4.08 (s, 4H), 7.62 (m, 4H). ^{13}C NMR $\{^1\text{H}\}$ (DMSO- d_6 , 75.47 MHz) δ ppm: 0.40, 1.55, 9.57, 14.47, 23.93, 35.10, 50.48, 115.91*(q*, $J_{\text{F}} = 321.5$ Hz), 118.67*, 121.27+*, 122.78, 124.03*, 144.63. IR (ATR) cm^{-1} : 3150, 2961, 2898, 1591, 1540, 1462, 1417, 1353, 1261, 1197, 1139, 1059, 1041, 840, 803, 740, 667, 618, 571. Molecular formula: $\text{C}_{30}\text{H}_{58}\text{N}_6\text{O}_{12}\text{F}_{12}\text{S}_4\text{Si}_5$, FW weight 1191.50. Calculated, %: C 30.24, H 4.91, N 7.05, F 19.13, S 10.76, Si 11.79. Found, %: C 30.07, H 5.12, N 6.89, F 19.12, S 10.41, Si 11.50.

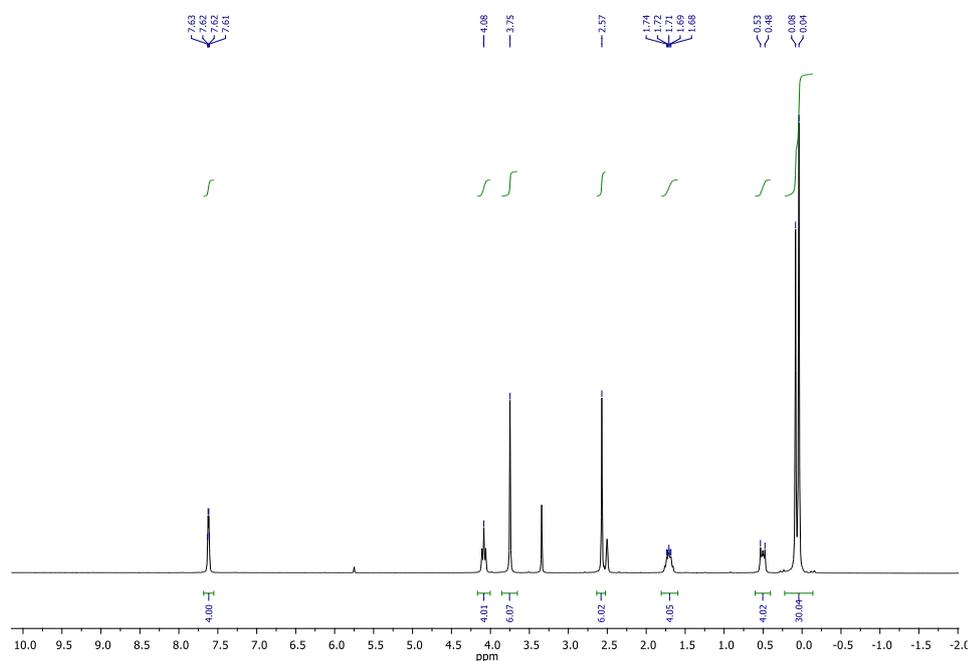
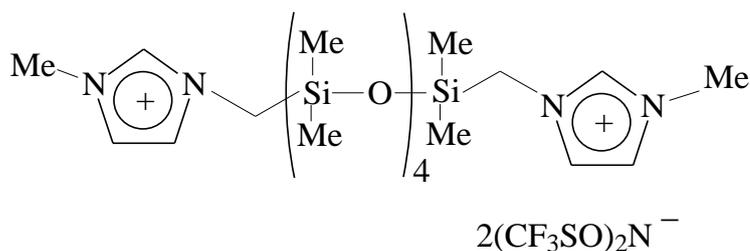


Figure S6. ^1H NMR spectrum of IL **4a**.

4.3. *1',1',3',3',5',5',7',7',9',9'*-Decamethyl-1',9'-bis[(3-methylimidazolium-1-yl)methyl]penta-siloxane bis(trifluoromethylsulfonyl)imide (**3b**)



The yield was 94%. Colorless liquid. ^1H NMR (DMSO- d_6 , 300.13 MHz) δ ppm: 0.04, 0.05, 0.20 (3 s, 30H), 3.86 (s, 6H), 3.89 (s, 4H), 7.53 (m, 2H), 7.70 (m, 2H), 8.93 (s, 2H). ^{13}C NMR { ^1H } (DMSO- d_6 , 75.47 MHz) δ ppm: -0.84, 1.24, 36.14, 41.43, 113.58* (q*, $J_{\text{F}} = 321.6$ Hz), 117.81*, 122.08*, 123.51, 124.09, 126.43*, 136.32. IRS (ATR) cm^{-1} : 3153, 3104, 2963, 1569, 1405, 1349, 1331, 1262, 1226, 1181, 1135, 1102, 1052, 1018, 836, 795, 762, 739, 648, 613, 600, 569, 510. Molecular formula: $\text{C}_{24}\text{H}_{46}\text{N}_6\text{O}_{12}\text{F}_{12}\text{S}_4\text{Si}_5$, FW 1107.33. Calculated, %: C 26.03, H 4.19, N 7.59, F 20.59, S 11.58, Si 12.68. Found, %: C 25.88, H 4.42, N 7.21, F 20.54, S 11.23, Si 12.49.

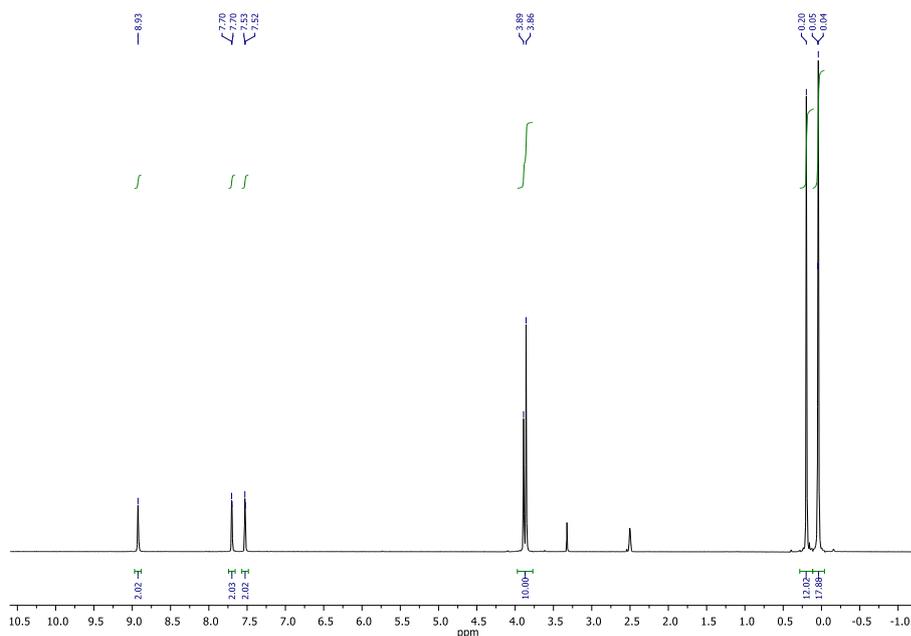
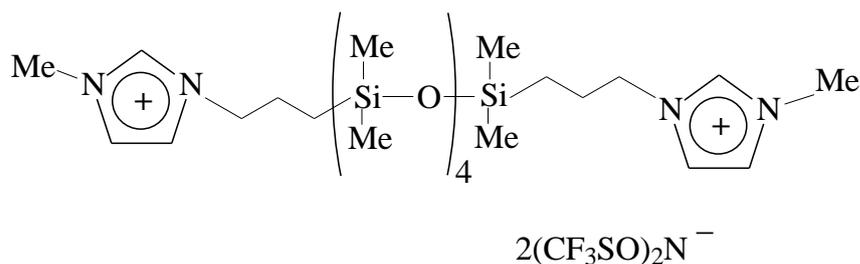


Figure S7. ^1H NMR spectrum of IL **3b**.

4.4. *1',1',3',3',5',5',7',7',9',9'-Decamethyl-1',9'-bis[(3-(3-methylimidazolium-1-yl)propyl)]-pentasiloxane bis(trifluoromethylsulfonyl)imide (4b)*



The yield was 92%. Colorless liquid. ^1H NMR (DMSO- d_6 , 300.13 MHz) δ ppm: 0.04, 0.09 (2s, 30H), 0.49 (m, 4H), 1.77 (m, 4H), 3.85 (s, 6H), 4.13 (m, 4H), 7.70 (m, 2H), 7.74 (m, 2H), 9.10 (s, 2H). ^{13}C NMR $\{^1\text{H}\}$ (DMSO- d_6 , 75.47 MHz) δ ppm: 0.36, 1.50, 14.45, 24.25, 36.15, 51.86, 112.72* (q^* , $J_F = 321.4$ Hz), 117.81*, 122.07*, 122.63, 124.07, 127.17*, 136.95. IR (ATR) cm^{-1} : 3155, 3120, 2962, 2904, 1573, 1466, 1414, 1353, 1261, 1197, 1138, 1059, 840, 802, 740, 708, 654, 618, 571. Molecular formula: $\text{C}_{28}\text{H}_{54}\text{N}_6\text{O}_{12}\text{F}_{12}\text{S}_4\text{Si}_5$, FW 1163.44. Calculated, %: C 28.91, H 4.68, N 7.22, F 19.60, S 11.02, Si 12.07. Found, %: C 28.62, H 4.90, N 7.04, F 19.62, S 10.83, Si 11.87.

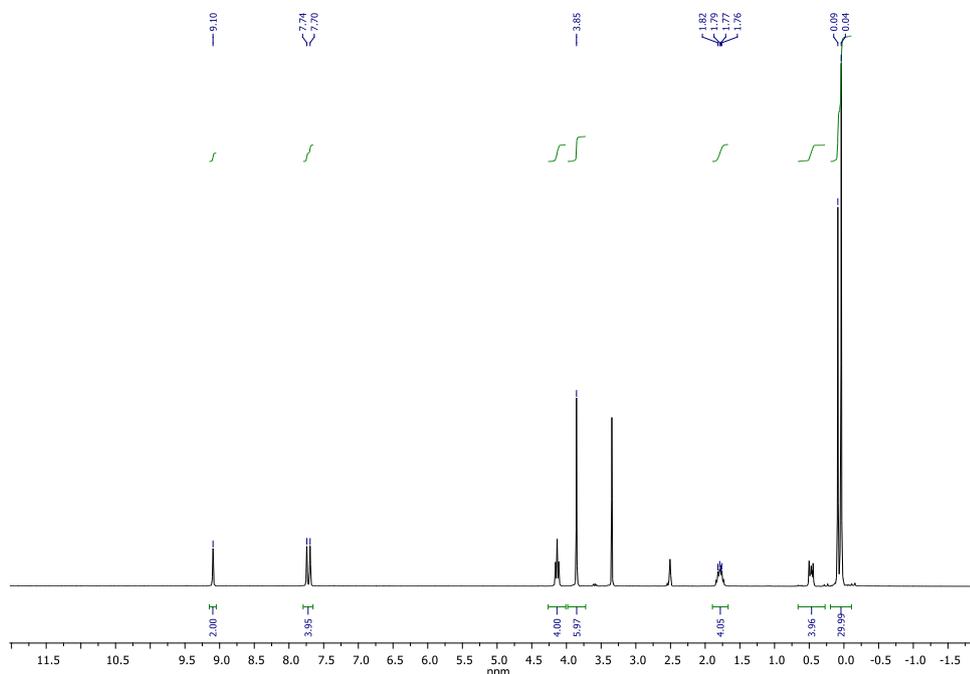
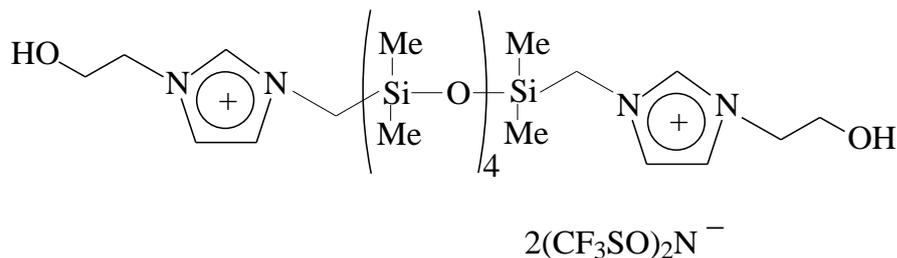


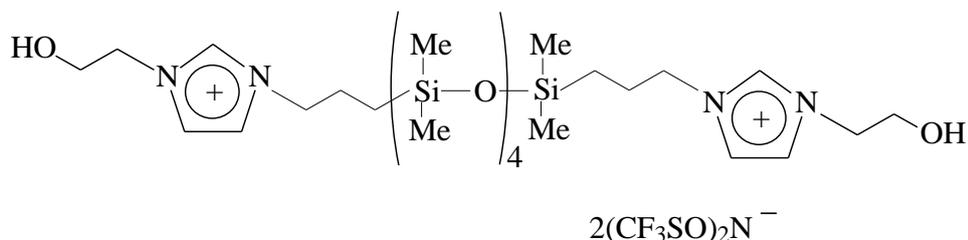
Figure S8. ^1H NMR spectrum of IL **4b**.

4.5. *1',1',3',3',5',5',7',7',9',9'-Decamethyl-1',9'-bis[(3-(2-hydroxyethyl)imidazolium-1-yl)-methyl]pentasiloxane bis(trifluoromethylsulfonyl)imide 3c (attempted synthesis)*



Upon quaternization of 1-(2-hydroxyethyl)imidazole with linker **1**, the target chloride IL pre-**3c** is destroyed (see Figure S1).

4.6. *1',1',3',3',5',5',7',7',9',9'-Decamethyl-1',9'-bis[3-(3-(2-hydroxyethyl)imidazolium-1-yl)-propyl]pentasiloxane bis(trifluoromethylsulfonyl)imide (4c)*



The yield was 87%. Colorless liquid. ^1H NMR (DMSO- d_6 , 300.13 MHz) δ ppm: 0.04, 0.09 (2s, 30H), 0.45 (m, 4H), 1.77 (m, 4H), 3.74 (m, 4H), 4.18 (m, 8H), 5.17 (s, 2H), 7.74 (m, 4H), 9.13 (s, 2H). ^{13}C NMR $\{^1\text{H}\}$ (DMSO- d_6 , 75.47 MHz) δ ppm: 0.35, 1.50, 14.45, 24.28, 51.84, 52.14, 59.71, 113.54* (q*, $J_{\text{F}}=321.8$ Hz), 117.81*, 122.07*, 122.52, 123.73, 126.34*, 136.74. IR (ATR) cm^{-1} : 3542, 3151, 3104, 2961, 2900, 1565, 1448, 1413, 1353, 1261, 1198, 1137, 1058, 822, 801, 741, 654, 618, 571. Molecular formula: $\text{C}_{30}\text{H}_{58}\text{N}_6\text{O}_{14}\text{F}_{12}\text{S}_4\text{Si}_5$, FW 1223.50. Calculated, %: C 29.45, H 4.78, N 6.87, F 18.63, S 10.48, Si 11.48. Found, %: C 29.23, H 5.02, N 6.59, F 18.66, S 10.17, Si 11.29.

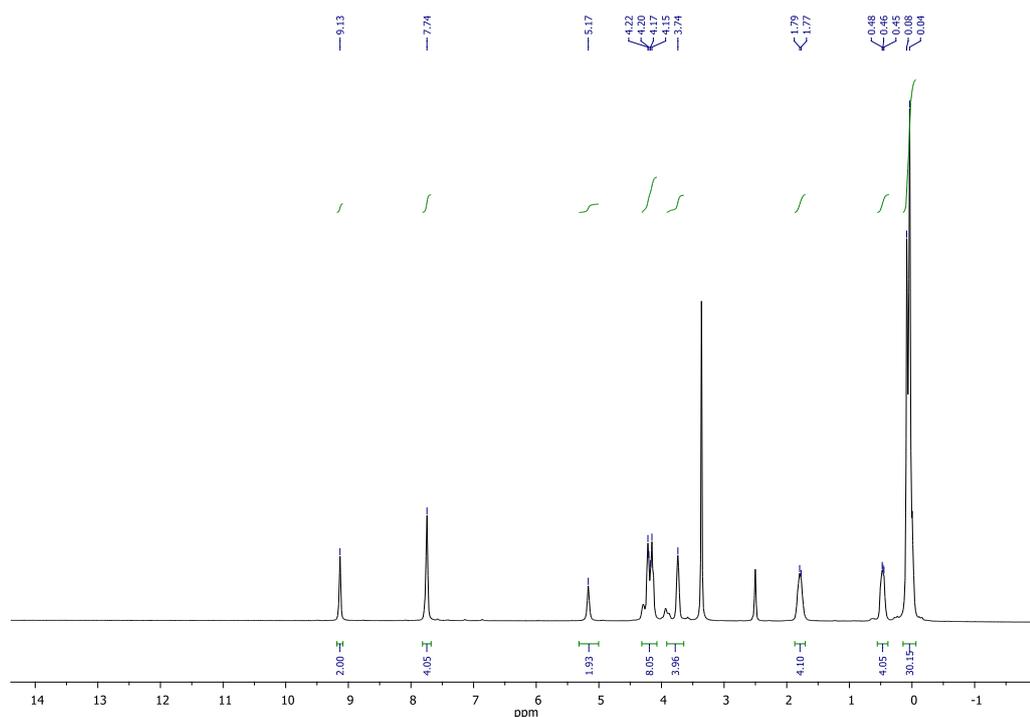


Figure S9. ^1H NMR spectrum of IL **4c**.

5. Methods and Materials

^1H , ^{13}C and ^{29}Si NMR spectra were recorded on a Bruker AM300 spectrometer. ATR IR spectra were measured on a Nicolet iS50 IR spectrometer (built-in attachment with diamond crystal), resolution 4 cm^{-1} and number of scans 32. Thermogravimetric analysis was performed on a Derivatograph-C instrument (MOM, Hungary) in an argon atmosphere at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ (sample mass, $\sim 20\text{ mg}$). The glass transition temperatures were determined via differential scanning calorimetry (DSC) using a DSC-822e instrument (Mettler-Toledo, Switzerland) in the temperature range of -100 to 100°C at a sample heating rate of $10^\circ\text{C min}^{-1}$ in an argon atmosphere. Kinematic viscosity was measured using an Ostwald viscometer with capillary diameter of 0.8 mm . The viscometer was calibrated at $25\text{ }^\circ\text{C}$ using ethylene glycol (Aldrich, 99.8%, water content $< 0.01\%$) as the reference liquid. Elemental analysis was carried out using CHNS analyzer Vario Micro cube (Germany) (C, H, N, S), UV-Visible spectrophotometer Cary-100 (USA) (F, Si) and flame photometer BWB-XP (England) (Na).

Chloro(chloromethyl)dimethylsilane (98%), chloro(3-chloropropyl)dimethylsilane (97%), octamethylcyclotetrasiloxane (98%), 1-methylimidazole (99%), 1,2-dimethylimidazole (98%), 1-(2-hydroxyethyl)imidazole (97%), lithium bis(trifluoromethylsulfonyl)imide (99%) were purchased from Acros and Sigma-Aldrich. Imidazole derivatives were dried by azeotropic distillation with absolute acetonitrile. All organic solvents used in the synthesis were previously dried with CaH_2 and distilled.