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Supporting Information

Probing the Structure-Property Relationship of Regioisomeric Ionic Liquids by Click Chemistry

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Section S1

Experimental Section

Materials and Methods. All chemicals were purchased with the highest purity from commercial sources and used as received. ^{1}H (300 to 700 MHz), ^{13}C (75 to 176 MHz) and ^{19}F (471 to 565 MHz) NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on a Bruker Avance III 500 or 700 spectrometer. Fourier transform infrared (FT-IR) spectra were measured using a Nicolet IR100 FT-IR spectrometer, equipped with an attenuated total reflectance (ATR) accessory with a diamond crystal. A Mettler Toledo TGA/DSC 1 was used to measure the decomposition temperature, which was determined as 5% mass loss, at a heating rate of 10 ^{o}C/min under nitrogen. All samples were dried at 100 °C under vacuum overnight. TGA (Figure S11) shows less than 2% weight loss for all the samples indicating small amount of water. A TA Instruments Q200 differential scanning calorimeter equipped with the Refrigerated Cooling System 40 accessory was used to determine glass transition temperatures, which are taken as the mean of the second and third heating scans. The experiments were conducted under nitrogen at a heating rate of 10 ^{o}C/min. Density of the ionic liquids was determined using automatic density meter (Model DDM 2911 from Rudolph Research Analytical) or gas pycometer (AccuPyc II 1390 from Micromeritics) at 25 and 37 ^{o}C.

Mass spectroscopy was performed using an Agilent 6520 Accurate mass Q-TOF LC/MS (Agilent Technologies, Santa Clara, CA). Agilent Mass Hunter software (Version B.02.01) was used for data acquisition and processing. The samples were eluted at 0.4 mL/min using 70:30 (v/v) acetonitrile/water or 90:10 MeCN:$(CH_3)_2CO$,. For MS, the flow rate of the drying gas (N_2) was 11 L/min, and the gas temperature was 350 °C. The fragmentor voltage and capillary voltage were fixed at 100 V and 3000 V respectively.

The purity of the ionic liquid was determined by the combination of NMR and LCMS. No other materials were detectable either with NMR or mass spec. Representative spectra's are included in S2.

Ab initio quantum calculations have been performed at the B3LYP/6-311++g(d,p) level for geometry optimization, vibrational frequencies and atomistic charges using the CHELPG protocol.[1] All calculations have been performed using GAUSSIAN 03 program.[2] Vibrational frequency analysis confirms that all reported structures are energy minimum. For each cation, two sets of calculations were performed using different initial configurations, which lead to different optimized structures. Only the structure corresponding to a lower energy minimum is reported. Election density of the phenyl ring is the sum of electron for C_5H_6. The angle between the triazoyl ring and phenyl ring is defined as the N_{Tr}-N_{Tr}-C_{Ph}-C_{Ph} bonding or N_{Tr}-C_{Tr}-C_{Ph}-C_{Ph} bonding.

To characterize CO_2 solubility, the gas sorption properties of ionic liquids as a function of time was carried out using a pressure decay sorption system (Setarm PCTPro – 2000, Setaram Inc., Newark, Ca.). All of the ionic liquids were dried in vacuo at room temperature to remove dissolved gases before they were loaded into the pressure decay sorption system. The amount of ionic liquid was between 0.2 and 0.3 g. CO_2 solubility for these ionic liquids was recorded at 37 ^oC from 1 to 5 bar. The data were extracted for solubility calculations when the CO_2–ionic liquid equilibrium reached a plateau (no change in the slope) in the CO_2 absorption versus time curve. After 6 hour, this plateau is both visually and mathematically determined to confirm the equilibrium. The general features such as kinetic and equilibrium values in the sorption graph for these ionic liquid are similar. A linear line was fitted for the plot of CO_2 molar fraction versus pressure. In Figure 4 of the paper, the CO_2 solubility of triazolium-based ionic liquids was calculated from the resulting equation when the pressure is 3 bar.

General Procedure for the Preparation of Azide

In a typical example, sodium azide (0.30 mol) was added to a solution of alkyl bromide (0.10 mol) and *N*,*N*-dimethylformamide (100 mL). The mixture was stirred for 24 h at room temperature. Afterward, water (300 mL) was added to dissolve the excess sodium azide and *N*,*N*-dimethylformamide. Hexane was used to extract product. The organic layer was washed thrice with water. The resulting organic mixture was concentrated or used as is in the click reaction. The product was characterized either by FT-IR or ^{1}H NMR spectroscopy.

The preparation of 1-azidopropane from 1-bromopropane (8.2 mmol) and sodium azide (23 mmol) was the same as above, but the product was immediately used without characterization. 4-azidopyridine and azidobenzene were synthesized according to references [3] and [4], respectively.

1-azido-2-(2-(2-methoxyethoxy)ethoxy)ethane. The product was prepared from 2-(2-(2-methoxyethoxy)ethoxy)ethyl methanesulfonate (0.083 mol) and sodium azide (0.083 mol) at 60 ^{o}C using a similar procedure as above. Yield: 97%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.30 – 3.45 (m, 5H), 3.50 – 3.59 (m, 2H) and 3.60 – 3.76 (m, 8H).

1-azidohexane. Yield: 90%. ATR-IR (ν, cm^{-1}): 2085 (C-N_3).

(azidomethyl)benzene. Yield: 67%. ATR-IR (ν, cm^{-1}): 2094 (C-N_3).

(azidomethyl)trimethylsilane. Yield: 98%. ATR-IR (ν, cm^{-1}): 2088 (C-N_3).

General Procedure for the Preparation of 1,2,3-Triazoles

In a typical example, alkyne (1.0 mol), azide (1.0 mol), $CuSO_4$ (0.01 mol) and sodium ascorbate (0.03 mol) were added to a 2:1 (v/v) solution of butanol and water. The reaction was stirred at room temperature for 24 h. The product was extracted with ethyl acetate or dichloromethane. The organic layer was washed thrice with water, dried with $MgSO_4$ (or $NaSO_4$), filtered and concentrated. The product was purified by either flash column chromatography or recrystallization and characterized with different spectroscopic methods.

Cu-catalyzed click chemistry was also performed using Cu/C according to references [5] and [6].

1-benzyl-4-phenyl-1*H*-1,2,3-triazole. Yield: 60%. ^{1}H NMR (700 MHz, $CDCl_3$): δ 5.56 (s, 2H), 7.32 (d, J = 7.0 Hz, 3H), 7.35 – 7.47 (m, 5H), 7.71 (s, 1H) and 7.83 (d, J = 7.9 Hz, 2H) ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ 54.2, 119.7, 125.7, 128.1, 128.2, 128.8, 128.9, 129.2, 130.6, 134.8 and 148.2 ppm.

1-benzyl-4-propyl-1*H*-1,2,3-triazole. Yield: 92%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.91 (t, J = 7.4 Hz, 3H), 1.63 (sxt, J = 7.5 Hz, 2H), 2.63 (t, J = 7.7 Hz, 2H), 5.45 (s, 2H), 7.17 - 7.23 (m, 3H) and 7.27 - 7.34 (m, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 13.77, 22.64, 27.69, 53.86, 120.7, 127.9, 128.5, 129.0 and 135.1 ppm.

1-hexyl-4-phenyl-1*H*-1,2,3-triazole. Yield: 46%. ^{1}H NMR (700 MHz, $CDCl_3$): δ 0.89 (t, J = 6.4 Hz, 3H), 1.12 - 1.60 (m, 6H), 1.93 (quin, J = 6.6 Hz, 2 H), 4.39 (t, J =6.5 Hz, 1H), 7.33 (t, J = 6.6 Hz, 1H), 7.42 (t, J = 7.0 Hz, 2H), 7.75 (s, 1H) and 7.84 (d, J = 8.4 Hz, 2H) ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ 14.0, 22.5, 26.2, 30.4, 31.2, 50.5, 119.5, 125.7, 128.1, 128.9, 130.8 and 147.7 ppm.

4-hexyl-1-phenyl-1*H*-1,2,3-triazole. Yield: 43%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.86 (t, J = 7.0 Hz, 3H), 1.23 - 1.32 (m, 4H), 1.33 - 1.41 (m, 2H), 1.70 (quin, J = 7.7 Hz, 2H), 2.75 (t, *J* = 7.9 Hz, 2H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.45 (t, *J* = 7.9 Hz, 2H), 7.69 (d, *J* = 7.9 Hz, 2H) and 7.73 (s, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 14.09, 22.59, 25.68, 28.96, 29.40, 31.60, 118.9, 120.3, 128.4, 129.6, 137.2 and 149.2 ppm.

1-hexyl-4-propyl-1*H*-1,2,3-triazole. Yield: 30%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7.0 Hz, 3H), 0.97 (t, *J* = 7.3 Hz, 3H), 1.24 - 1.38 (m, 6H), 1.69 (sxt, *J* = 7.5 Hz, 2H), 1.88 (quin, *J* = 7.3 Hz, 2H), 2.69 (t, *J* = 7.6 Hz, 2H), 4.30 (t, *J* = 7.3 Hz, 2H) and 7.26 (s, 1H) ppm.

4-hexyl-1-propyl-1*H*-1,2,3-triazole. Yield: 15%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.85 (t, *J* = 6.7 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H), 1.20 - 1.39 (m, 6H), 1.63 (quin, *J* = 7.5 Hz, 2H), 1.89 (sxt, *J* = 7.3 Hz, 2H), 2.68 (t, *J* = 7.8 Hz, 2H), 4.25 (t, *J* = 7.2 Hz, 2H) and 7.25 (s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 11.18, 14.17, 22.67, 23.87, 25.81, 29.05, 29.59, 31.70, 51.87, 120.6, and 148.5 ppm.

1-{2-[2-(2-methoxyethoxy)ethoxy]ethyl}-4-phenyl-1*H*-1,2,3-triazole. Yield: 96%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.29 (s, 3H), 3.38 – 3.69 (m, 8H), 3.85 (t, *J* = 4.9 Hz, 2H), 4.54 (t, *J* = 4.9 Hz, 2H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.80 (d, J = 6.8 Hz, 1H) and 7.95 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 50.4, 59.0, 69.5, 70.5, 70.6, 71.9, 121.0, 125.7, 128.0, 128.8, 130.9 and 147.7 ppm.

1-{2-[2-(2-methoxyethoxy)ethoxy]ethyl}-4-propyl-1*H*-1,2,3-triazole. Yield: 50%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.83 (t, *J* = 7.4 Hz, 3H), 1.55 (sxt, *J* = 7.3 Hz, 2H), 2.54 (t, *J* = 7.5 Hz, 2H), 3.23 (s, 3H), 3.36 - 3.43 (m, 2H), 3.44 - 3.52 (m, 6H), 3.72 (t, *J* = 5.0 Hz, 2H), 4.37 (t, *J* = 5.0 Hz, 2H) and 7.38 (s, 1H) ppm.

4-(4-phenyl-1H-1,2,3-triazol-1-yl)pyridine. Yield: 92%. ^{1}H NMR (700 MHz, $CDCl_3$): δ 7.41 (t, *J* = 7.3 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.80 (d, *J* = 5.7 Hz, 2H), 7.92 (d, *J* = 7.5 Hz, 2H), 8.32 (s, 1H) and 8.82 (br. s., 2H) ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ 113.9, 116.8, 126.2, 129.1, 129.2, 129.7, 143.2, 149.3, and 151.9 ppm.

4-(4-propyl-1H-1,2,3-triazol-1-yl)pyridine. Yield: 56%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93 (t, J = 7.4 Hz, 3H), 1.69 (sxt, J = 7.4 Hz, 2H), 2.70 (t, J = 7.7 Hz, 2H), 7.66 (d, J = 6.3 Hz, 2H), 7.87 (s, 1H) and 8.67 (d, J = 6.3 Hz, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 13.77, 22.51, 27.57, 113.5, 118.3, 143.2, 149.7 and 151.6 ppm.

1-phenyl-4-((trimethylsilyl)methyl)-1*H*-1,2,3-triazole. Yield: 13%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.08 (s, 9H), 2.19 (s, 2 H), 7.38 (t, J = 7.3 Hz, 1H), 7.50 (t, J = 7.7 Hz, 2H), 7.60 (s, 1H) and 7.71 (d, J = 7.5 Hz, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ -1.57, 15.40, 115.9, 117.8, 120.3, 128.4, 129.8, 137.4 and 146.7.

4-phenyl-1-((trimethylsilyl)methyl)-1*H*-1,2,3-triazole. Yield: 70%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.18 (s, 9H), 3.95 (s, 2H), 7.32 (t, J = 7.5 Hz, 1H), 7.42 (t, J = 7.7 Hz, 2H), 7.64 (s, 1H) and 7.83 (d, J = 7.7 Hz, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ -2.26, 42.27, 120.4, 125.8, 128.1, 129.0 and 131.0 ppm.

1-propyl-4-((trimethylsilyl)methyl)-1*H*-1,2,3-triazole. Yield: 5%. Mass Spec: calculated for $C_9H_{19}N_3Si$, 197.13; found 198 $[M+H]^+$.

4-propyl-1-((trimethylsilyl)methyl)-1*H*-1,2,3-triazole. Yield: 80%. ^{1}H NMR (700 MHz, $CDCl_3$): δ 0.12 (s, 9H), 0.95 (t, J = 7.5 Hz, 3H), 1.68 (sxt, J = 7.5 Hz, 2H), 2.66 (t, J = 7.5 Hz, 2H), 3.87 (s, 2H) and 7.13 (s, 1H) ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ -2.30, 14.38, 22.93, 27.87, 41.95, 121.4 and 148.1 ppm.

General Procedure for the Preparation of Triazolium Iodide

In a typical example, triazole was refluxed with excess iodomethane in acetonitrile for >12h. The solution was concentrated after cooling to room temperature. The product was rinsed with organic solvents, recrystallized with ethyl acetate, and dried in vacuo.

1-benzyl-3-methyl-4-phenyl-1*H*-1,2,3-triazol-3-ium iodide 4-I. Yield: quantitative. ^{1}H NMR (700 MHz, $CDCl_3$): δ 4.23 (s, 3H), 5.92 (s, 2H), 7.28 (s, 3H), 7.35 - 7.47 (m, 3H), 7.61 (s, 4H) and 9.29 (s, 1H) ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ 39.5, 57.0, 121.2, 128.7, 129.0, 129.3, 129.3, 129.6, 130.9, 131.6 and 142.6 ppm. Mass Spec: calculated for $C_{16}H_{16}IN_3$, 377.04; found 376.75.

1-benzyl-3-methyl-4-propyl-1*H*-1,2,3-triazol-3-ium iodide 4p-I. Yield: quantitative. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.93 (t, *J* = 7.3 Hz, 3H), 1.69 (sxt, *J* = 7.6 Hz, 2H), 2.80 (t, *J* = 7.6 Hz, 2H), 4.21 (s, 3H), 5.84 (s, 2H), 7.27 - 7.29 (m, 3H), 7.50 - 7.54 (m, 2H) and 9.08 (s, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 13.43, 20.26, 25.47, 38.92, 56.83, 128.6, 129.1, 129.3, 129.6, 131.2 and 144.2 ppm. Mass Spec: calculated for $C_{13}H_{18}IN_3$, 343.05; found 342.99.

1-hexyl-3-methyl-4-phenyl-1*H*-1,2,3-triazol-3-ium iodide 1-I. Yield: quantitative. ^{1}H NMR (700 MHz, $CDCl_3$): δ 0.83 (t, 3H), 1.18 – 1.35 (m, 4H), 1.35 – 1.45 (m, 2H), 2.05 (quin, *J* = 7.3 Hz, 2H), 4.31 (s, 3H), 4.75 (t, *J* = 6.6 Hz, 2H), 7.50 – 7.66 (m, 3H), 7.75 (d, *J* = 7.5 Hz, 2H) and 9.48 (s, 1H) ppm. ^{13}C NMR (176 MHz, $CDCl_3$,): δ 14.0, 22.4, 25.9, 29.5, 31.0, 39.6, 54.6, 121.8, 129.6, 129.8, 132.0 and 142.9 ppm. Mass Spec: calculated for $C_{15}H_{22}IN_3$, 371.09; found 370.95.

4-hexyl-3-methyl-1-phenyl-1H-1,2,3-triazol-3-ium iodide 1A-I. Yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.77 (t, *J* = 7.0 Hz, 3H), 1.09 - 1.45 (m, 6H), 1.80 (quin, *J* = 7.7 Hz, 2H), 2.98 (t, *J* = 7.8 Hz, 2H), 4.38 (s, 3H), 7.41 - 7.57 (m, 3H), 7.89 - 8.05 (m, 2H) and 9.47 (s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 13.86, 22.29, 24.05, 27.10, 28.62, 31.03, 39.52, 121.4, 127.2, 130.2, 131.7, 134.5 and 145.9 ppm. Mass Spec: calculated for $C_{15}H_{22}IN_3$, 371.09; found 370.80.

1-hexyl-3-methyl-4-propyl-1*H*-1,2,3-triazol-3-ium iodide 1p-I. Yield: 95%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.83 (t, J = 7.0 Hz, 3H), 1.04 (t, J = 7.4 Hz, 3H), 1.12 - 1.44 (m, 6H), 1.81 (sxt, J = 7.5 Hz, 2H), 1.99 (quin, J = 7.5 Hz, 2H), 2.91 (t, J = 7.8 Hz, 2H), 4.29 (s, 3H), 4.66 (t, J = 7.4 Hz, 2H) and 9.15 (s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 13.77, 13.98, 20.74, 22.36, 25.82, 29.51, 30.99, 38.94, 54.30, 129.4 and 144.5 ppm. Mass Spec: calculated for $C_{12}H_{24}IN_3$, 337.10; found 337.15.

4-hexyl-3-methyl-1-propyl-1*H*-1,2,3-triazol-3-ium iodide 1pA-I. Yield: quantitative. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, J = 7.2 Hz, 2H), 1.03 (t, J = 7.4 Hz, 3H), 1.27 - 1.35 (m, 4H). 1.39 - 1.49 (m, 2H), 1.79 (quin, J = 7.6 Hz, 2H), 2.09 (sxt, J = 7.3 Hz, 2H), 2.93 (t, J = 7.5 Hz, 2H), 4.29 (s, 3H), 4.70 (t, J = 7.3 Hz, 2H) and 9.22 (s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 11.00, 14.16, 22.62, 23.28, 24.21, 27.37, 28.94, 31.38, 38.69, 55.89, 129.7 and 144.8 ppm. Mass Spec: calculated for $C_{12}H_{24}IN_3$, 337.10; found 336.80.

1-{2-[2-(2-methoxyethoxy)ethoxy]ethyl}-3-methyl-4-phenyl-1*H*-1,2,3-triazol-3-ium iodide 3-I. Yield: 58%. ^{1}H NMR (400 MHz, $CDCl_3$): 3.21 (s, 3H), 3.37 – 3.45 (m, 2H), 3.50 – 3.66 (m, 4H), 3.70 – 3.78 (m, 2H), 4.13 (t, = 4.9 Hz, 2H), 4.31 (s, 3H), 4.97 (t, J = 4.8 Hz, 2H), 7.50 – 7.64 (m, 3H), 7.74 (dd, J_1 = 7.7 Hz, J_2 = 1.9 Hz, 2H) and 9.12 (s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 39.3, 54.4, 58.9, 67.7, 70.2, 70.3, 70.4, 71.7, 122.0, 129.7, 129.9, 130.0, 131.9 and 143.1 ppm. Mass Spec: calculated for $C_{16}H_{24}IN_3O_3$, 433.09; found 432.70.

1-{2-[2-(2-methoxyethoxy)ethoxy]ethyl}-3-methyl-4-propyl-1*H*-1,2,3-triazol-3-ium iodide 3p-I. Yield: quantitative. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.07 (t, J = 7.4 Hz, 3H), 1.82 (sxt, J = 7.5 Hz, 2H), 3.34 (s, 3H), 3.48 - 3.53 (m, 2H), 3.59 (m, 4H), 3.67 - 3.72 (m, 2H), 4.04

(t, *J* = 5.00 Hz, 2H), 4.30 (s, 3H), 4.86 (t, *J* = 4.8 Hz, 2H) and 8.86 (s, 1H) ppm. Mass Spec: calculated for $C_{13}H_{26}IN_3O_3$, 399.10; found 398.80.

3-methyl-4-phenyl-1-(pyridin-4-yl)-1H-1,2,3-triazol-3-ium iodide 5-I. Yield: quantitative. ^{1}H NMR (700 MHz, DMSO-*d*$_6$): δ 4.38 (s, 3H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 2H), 7.96 (d, *J* = 7.0 Hz, 2H), 8.70 (d, *J* = 7.5 Hz, 2H), 9.23 (d, *J* = 7.5 Hz, 2H) and 9.77 (s, 1H) ppm. ^{13}C NMR (176 MHz, DMSO-*d*$_6$): δ 47.55, 116.3, 120.6, 125.6, 128.9, 129.1, 129.3, 146.9, 148.0 and 148.5 ppm. Mass Spec: calculated for $C_{14}H_{13}IN_4$, 364.02; found 363.80.

3-methyl-4-propyl-1-(pyridin-4-yl)-1H-1,2,3-triazol-3-ium iodide 5p-I. Yield: 67%. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 0.96 (t, *J* = 7.4 Hz, 3H), 1.70 (sxt, *J* = 7.4 Hz, 2H), 2.73 (t, *J* = 7.4 Hz, 2H), 4.37 (s, 3H), 8.65 (d, *J* = 7.5 Hz, 2H), 9.06 (s, 1H) and 9.19 (d, *J* = 7.0 Hz, 2H) ppm. ^{13}C NMR (101 MHz, DMSO-*d*$_6$): δ 13.50, 21.65, 26.77, 47.47, 116.0, 121.3, 146.87, 147.8 and 149.6 ppm. Mass Spec: calculated for $C_{11}H_{15}IN_4$, 330.03; found 330.05.

3-methyl-4-phenyl-1-((trimethylsilyl)methyl)-1*H*-1,2,3-triazol-3-ium iodide 2-I. Yield: quantitative. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.17 (s, 9H), 4.29 (s, 3H), 4.45 (s, 2H), 7.37 - 7.57 (m, 3H), 7.71 (d, *J* = 7.5 Hz, 2H) and 9.32 (s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ -2.40, 39.55, 46.31, 121.7, 129.6, 129.7, 131.8 and 142.7 ppm. Mass Spec: calculated for $C_{13}H_{20}IN_3Si$, 373.05; found 373.03.

3-methyl-1-phenyl-4-((trimethylsilyl)methyl)-1*H*-1,2,3-triazol-3-ium iodide 2B-I. Yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.15 (m, 9H), 2.66 (s, 2H), 4.32 (s, 3H), 7.44 - 7.62 (m, 3H), 7.90 - 8.08 (m, 2H) and 9.52 (s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ -1.16, 14.90, 39.19, 121.3, 125.4, 130.3, 131.7, 134.5 and 145.3 ppm. Mass Spec: calculated for $C_{13}H_{20}IN_3Si$, 373.05; found 372.85.

3-methyl-4-propyl-1-((trimethylsilyl)methyl)-1*H*-1,2,3-triazol-3-ium iodide 2p-I. Yield: quantitative. ^{1}H NMR (700 MHz, $CDCl_3$): δ 0.19 (s, 9H), 1.05 (t, *J* = 7.5 Hz, 3H), 1.82 (sxt, *J* = 7.6 Hz, 2H), 2.92 (t, *J* = 7.5 Hz, 2H), 4.28 (s, 3H), 4.39 (s, 2H) and 9.07 (s, 1H) ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ -2.38, 13.79, 20.87, 25.85, 38.75, 46.24, 129.8 and 144.3 ppm. Mass Spec: calculated for $C_{22}H_{10}IN_3Si$, 339.06; found 339.50.

3-methyl-1-propyl-4-((trimethylsilyl)methyl)-1*H*-1,2,3-triazol-3-ium iodide 2pB-I. Yield: quantitative. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.21 (s, 9H), 1.04 (t, *J* = 7.4 Hz, 3H), 2.12 (sxt, *J* = 7.4 Hz, 2H), 2.47 (s, 2H), 4.18 (s, 3H), 4.73 (t, *J* = 7.4 Hz, 2H) and 9.23 (s, 1H) ppm. Mass Spec: calculated for $C_{22}H_{10}IN_3Si$, 339.06; found 339.05.

General Procedure for the Preparation of Triazolium Tf_2N

In a typical ion-exchange reaction, triazolium iodide (1 mol) and lithium bis[(trifluoromethyl)sulfonyl]amide (1.2 mol) were refluxed for >12h in acetonitrile. The solution was concentrated and dissolved in a mixture of ethyl acetate and water. The organic layer was collected, washed thrice with water, dried with $MgSO_4$, filtered, concentrated and dried in vacuo.

In an another method, the titled compound was synthesized by reacting triazolium iodide (1 mol) and lithium bis[(trifluoromethyl)sulfonyl]amide (1.2 mol) in water or methanol. The reaction was stirred at room temperature for 24 h, in which the product precipitated from the solution. The workup procedure was the same as above.

1-benzyl-3-methyl-4-phenyl-1H-1,2,3-triazol-3-ium bis[(trifluoromethyl)sulfonyl]-amide 4-Tf$_2$N. Yield: 84%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.25 (s, 3H), 5.77 (s, 2H), 7.37 – 7.71 (m, 10H) and 8.26 (s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 38.6, 57.9, 115.0 (CF_3), 118.2 (CF_3), 121.4 (CF_3), 121.6, 124.6 (CF_3), 127.7, 129.3, 129.7, 129.7, 130.3, 130.7, 132.1

and 143.8. ^{19}F NMR (471 MHz, $CDCl_3$): δ -81.62 ppm. Mass Spec: calculated for $C_{18}H_{16}F_6N_4O_4S_2$, 530.05; found 529.99.

1-benzyl-3-methyl-4-propyl-1H-1,2,3-triazol-3-ium bis[(trifluoromethyl)sulfonyl]-amide 4p-Tf$_2$N. Yield: quantitative. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.00 (t, *J* = 7.4 Hz, 3H), 1.71 (sxt, *J* = 7.6 Hz, 2H), 2.73 (t, *J* = 7.5 Hz, 2H), 4.14 (s, 3H), 5.62 (s, 2H), 7.42 (s, 5H), and 8.04 (s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 13.36, 20.26, 25.10, 37.57, 57.58, 115.0 (CF_3), 118.2 (CF_3), 121.4 (CF_3), 124.5 (CF_3), 127.5, 129.4, 129.7, 130.2, 131.0 and 145.1 ppm. ^{19}F NMR (471 MHz, $CDCl_3$): δ -81.67 ppm. Mass Spec: calculated for $C_{15}H_{18}F_6N_4O_4S_2$, 496.07; found 495.97.

1-hexyl-3-methyl-4-phenyl-1*H*-1,2,3-triazol-3-ium bis[(trifluoromethyl)sulfonyl]-amide 1-Tf$_2$N. Yield: 92%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.89 (t, *J* = 7.3 Hz, 3H), 1.28 - 1.37 (m, 4H), 1.37 - 1.45 (m, 2H), 2.04 (quin, *J* = 7.7 Hz, 2H), 4.23 (s, 3H), 4.57 (t, *J* = 7.9 Hz, 2H), 7.51 - 7.63 (m, 5H) and 8.40 (s, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 13.94, 22.36, 25.87, 29.11, 30.98, 38.64, 54.46, 116.0 (CF_3), 118.6 (CF_3), 121.2 (CF_3), 121.8, 123.7 (CF_3), 128.1, 129.4, 129.8, 132.1 and 143.6 ppm. ^{19}F NMR (471 MHz, $CDCl_3$): δ -81.60 ppm. Mass Spec: calculated for $C_{17}H_{22}F_6N_4O_4S_2$, 524.10; found 524.07.

4-hexyl-3-methyl-1-phenyl-1H-1,2,3-triazol-3-ium bis[(trifluoromethyl)sulfonyl]-amide 1A-Tf$_2$N. Yield: 95%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (s, 3H), 1.24 - 1.37 (m, 4H), 1.37 - 1.49 (m, 2H), 1.77 (q, *J* = 7.7 Hz, 2H), 2.86 (t, *J* = 7.5 Hz, 2H), 4.26 (s, 3H), 7.54 - 7.62 (m, 3H), 7.75 - 7.85 (m, 2H) and 8.49 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 14.01, 22.49, 23.46, 26.84, 28.78, 31.20, 37.96, 115.1 (CF_3), 118.3 (CF_3), 121.5 (CF_3), 121.6, 124.7 (CF_3), 125.9, 130.5, 132.1, 134.9 and 146.1. ^{19}F NMR (471 MHz, $CDCl_3$): δ -81.63 ppm. Mass Spec: calculated for $C_{17}H_{22}F_6N_4O_4S_2$, 524.10; found, 524.25.

1-hexyl-3-methyl-4-propyl-1*H*-1,2,3-triazol-3-ium bis[(trifluoromethyl)sulfonyl]-amide 1p-Tf_2N. Yield: 59%. ^1H NMR (500 MHz, $CDCl_3$): δ 0.87 (t, *J* = 7.5 Hz, 3H), 1.03 (t, *J* = 7.4 Hz, 3H), 1.26 - 1.38 (m, 6H), 1.75 (sxt, *J* = 7.6 Hz, 2H), 1.95 (quin, *J* = 7.6 Hz, 2H), 2.76 (t, *J* = 8.2 Hz, 2H), 4.15 (s, 3H), 4.47 (t, *J* = 7.6 Hz, 2H) and 8.15 (s, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 13.42, 13.93, 20.34, 22.36, 25.09, 25.82, 29.19, 30.98, 37.51, 54.18, 116.1 (CF_3), 118.6 (CF_3), 121.2 (CF_3), 123.7 (CF_3), 127.9 and 144.9 ppm. ^{19}F NMR (471 MHz, $CDCl_3$): δ -81.66 ppm. Mass Spec: calculated for $C_{14}H_{24}F_6N_4O_4S_2$, 490.11; found 490.06.

4-hexyl-3-methyl-1-propyl-1*H*-1,2,3-triazol-3-ium bis[(trifluoromethyl)sulfonyl]-amide 1pA-Tf_2N. Yield: 67%. ^1H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, *J* = 5.3 Hz, 3H), 0.98 (t, *J* = 7.4 Hz, 3H), 1.21 - 1.35 (m, 4H), 1.35 - 1.48 (m, 2H), 1.70 (quin, *J* = 7.4 Hz, 2H), 2.00 (sxt, *J* = 7.2 Hz, 2H), 2.77 (t, *J* = 7.5 Hz, 2H), 4.15 (s, 3H), 4.44 (t, *J* = 7.3 Hz, 2H) and 8.13 (s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 10.59, 13.96, 22.44, 22.76, 23.34, 26.82, 28.70, 31.19, 37.50, 55.62, 115.1 (CF_3), 118.3 (CF_3), 121.5 (CF_3), 124.7 (CF_3), 127.9 and 145.1 ppm. ^{19}F NMR (471 MHz, $CDCl_3$): δ -81.65 ppm. Mass Spec: calculated for $C_{14}H_{24}F_6N_4O_4S_2$, 490.11; found 489.95.

1-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-3-methyl-4-phenyl-1*H*-1,2,3-triazol-3-ium bis[(trifluoromethyl)sulfonyl]amide 3-Tf_2N. Yield: quantitative. ^1H NMR (400 MHz, $CDCl_3$): δ 3.18 (s, 3H), 3.37 – 3.45 (m, 2H), 3.54 – 3.67 (m, 4H), 3.67 – 3.74 (m, 2H), 3.98 – 4.07 (m, 2H), 4.23 (s, 3H), 4.79 (t, *J* = 4.8 Hz, 2H), 7.56 – 7.66 (m, 5H) and 8.60 (s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 38.4, 54.0, 58.6, 67.4, 70.1, 70.2, 71.6, 116.0 (CF_3), 118.5 (CF_3), 121.1 (CF_3), 121.9, 123.6 (CF_3), 129.0, 129.4, 129.7, 132.0 and 143.4 ppm. ^{19}F NMR (471 MHz, $CDCl_3$): δ -81.54 ppm. Mass Spec: calculated for $C_{18}H_{24}F_6N_4O_7S_2$, 586.10; found 586.04.

1-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-3-methyl-4-propyl-1*H*-1,2,3-triazol-3-ium bis[(trifluoromethyl)sulfonyl]amide 3p-Tf$_2$N. Yield: quantitative. ^{1}H NMR (500 MHz, CDCl$_3$): δ 1.02 (t, *J* = 7.3 Hz, 3H), 1.73 (sxt, *J* = 7.6 Hz, 2H), 2.75 (t, *J* = 7.9 Hz, 2H), 3.32 (s, 3H), 3.48 - 3.53 (m, 2H), 3.55 - 3.60 (m, 4H), 3.61 - 3.67 (m, 2H), 3.93 (t, *J* = 5.0 Hz, 2H), 4.14 (s, 3H), 4.65 (t, *J* = 4.7 Hz, 2H) and 8.23 (s, 1H) ppm. ^{13}C NMR (126 MHz, CDCl$_3$): δ 13.38, 20.31, 25.01, 37.43, 53.70, 58.89, 67.63, 70.22, 70.32, 71.69, 116.0 (*C*F$_3$), 118.5 (*C*F$_3$), 121.1 (*C*F$_3$), 123.6 (*C*F$_3$), 128.6 and 144.6 ppm. ^{19}F NMR (471 MHz, CDCl$_3$): δ -81.61 ppm. Mass Spec: calculated for $C_{15}H_{26}F_6N_4O_7S_2$, 552.11; found 552.06.

3-methyl-4-phenyl-1-(pyridin-4-yl)-1H-1,2,3-triazol-3-ium bis[(trifluoromethyl)-sulfonyl]amide 5-Tf$_2$N. Yield: quantitative. ^{19}F NMR (565 MHz, CDCl$_3$): δ -78.71 ppm. Mass Spec: calculated for $C_{16}H_{13}F_6N_5O_4S_2$, 517.03; found 516.93.

3-methyl-4-propyl-1-(pyridin-4-yl)-1H-1,2,3-triazol-3-ium bis[(trifluoromethyl)-sulfonyl]amide 5p-Tf$_2$N. Yield: 30%. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 0.97 (t, *J* = 7.3 Hz, 3H), 1.71 (sxt, *J* = 7.4 Hz, 2H), 2.75 (t, *J* = 7.4 Hz, 2H), 4.35 (s, 3H), 8.64 (d, *J* = 7.0 Hz, 2H), 9.01 (s, 1H) and 9.16 (d, *J* = 6.9 Hz, 2H) ppm. ^{13}C NMR (101 MHz, DMSO-*d*$_6$): δ 13.45, 21.71, 26.81, 47.39, 114.7 (*C*F$_3$), 116.1, 117.9 (*C*F$_3$), 121.1 (*C*F$_3$), 121.2, 124.3 (*C*F$_3$), 147.0, 147.9 and 149.7 ppm. ^{19}F NMR (565 MHz, CDCl$_3$): δ -78.80 ppm. Mass Spec: calculated for $C_{13}H_{15}F_6N_5O_4S_2$, 483.05; found 482.99.

3-methyl-1-phenyl-4-((trimethylsilyl)methyl)-1*H*-1,2,3-triazol-3-ium bis[(trifluoro-methyl)sulfonyl]amide 2B-Tf$_2$N. Yield: 77%. ^{1}H NMR (400 MHz, CDCl$_3$-*d*): δ 0.16 (s, 9H), 2.44 (s, 2H), 4.22 (s, 3H), 7.61 (m, 3H), 7.84 (m, 2H) and 8.46 (s, 1H). ^{13}C NMR (101 MHz, CDCl$_3$-*d*): δ -1.73, 14.09, 37.82, 115.0 (*C*F$_3$), 118.2 (*C*F$_3$), 121.4 (*C*F$_3$), 121.6, 124.2, 124.6

(CF_3), 126.7, 130.6, 132.2, 134.8 and 145.5. ^{19}F NMR (565 MHz, $CDCl_3$): δ -81.65 ppm. Mass Spec: calculated for $C_{15}H_{20}F_6N_4O_4S_2Si$, 526.06; found, 526.14.

3-methyl-4-phenyl-1-((trimethylsilyl)methyl)-1*H*-1,2,3-triazol-3-ium bis[(trifluoromethyl)sulfonyl]amide 2-Tf$_2$N. Yield: quantitative. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.20 (s, 9H), 4.22 (s, 5H), 7.38 - 7.71 (m, 5H) and 8.32 (s, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ -2.84, 38.60, 46.19, 115.2 (CF_3), 118.4 (CF_3), 121.6 (CF_3), 121.8, 124.7 (CF_3), 128.2, 129.4, 129.9, 132.1 and 143.6 ppm. ^{19}F NMR (471 MHz, $CDCl_3$): δ -81.61 ppm. Mass Spec: calculated for $C_{15}H_{20}F_6N_4O_4S_2Si$, 526.06; found 525.96.

3-methyl-1-propyl-4-((trimethylsilyl)methyl)-1*H*-1,2,3-triazol-3-ium bis[(trifluoromethyl)sulfonyl]amide 2pB-Tf$_2$N. Yield: 45%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.15 (s, 9H) 1.00 (t, J = 7.4 Hz, 3H), 2.03 (sxt, J = 7.4 Hz, 2H), 2.35 (s, 2H), 4.13 (s, 3H), 4.49 (t, J = 7.3 Hz, 2H) and 8.14 (s, 1H) ppm. ^{19}F NMR (565 MHz, $CDCl_3$): δ -81.69 ppm. Mass Spec: calculated for $C_{12}H_{22}F_6N_4O_4S_2Si$ 492.08; found 492.07.

3-methyl-4-propyl-1-((trimethylsilyl)methyl)-1*H*-1,2,3-triazol-3-ium bis[(trifluoromethyl)sulfonyl]amide 2p-Tf$_2$N. Yield: quantitative. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.14 (s, 9H), 1.01 (t, J = 7.4 Hz, 3H), 1.74 (sxt, J = 7.6 Hz, 2H), 2.75 (t, J = 7.7 Hz, 2H), 4.11 (s, 2H), 4.13 (s, 3H) and 8.05 (s, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ -2.99, 13.36, 20.35, 24.99, 37.35, 45.87, 76.98, 77.49, 116.1 (CF_3), 118.6 (CF_3), 121.2 (CF_3), 123.7 (CF_3), 128.5 and 144.7 ppm. ^{19}F NMR (471 MHz, $CDCl_3$): δ -81.68 ppm. Mass Spec: calculated for $C_{12}H_{22}F_6N_4O_4S_2Si$, 492.08; found 492.01.

Section S2

Supporting Figures

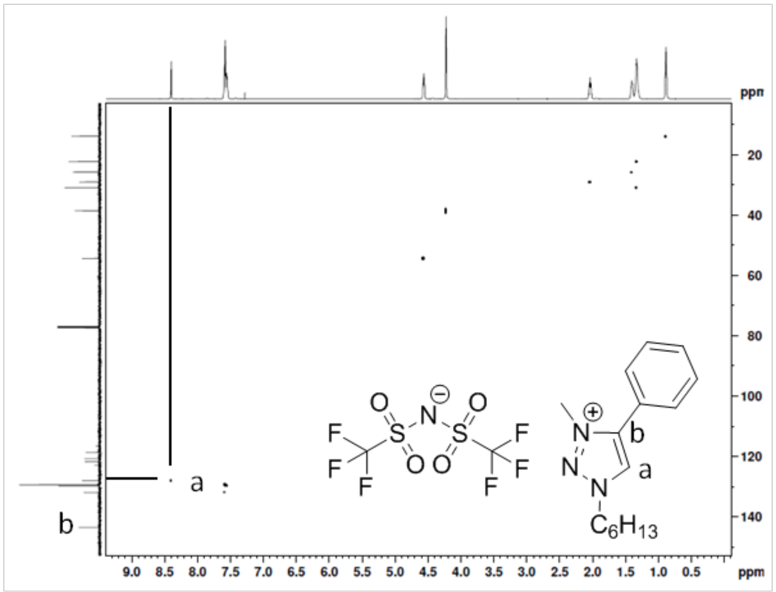


Figure S1: ^{1}H-^{13}C HETCOR NMR spectrum of 1-hexyl-3-methyl-4-phenyl-1*H*-1,2,3-triazol-3-ium bis[(trifluoromethyl)sulfonyl]amide.

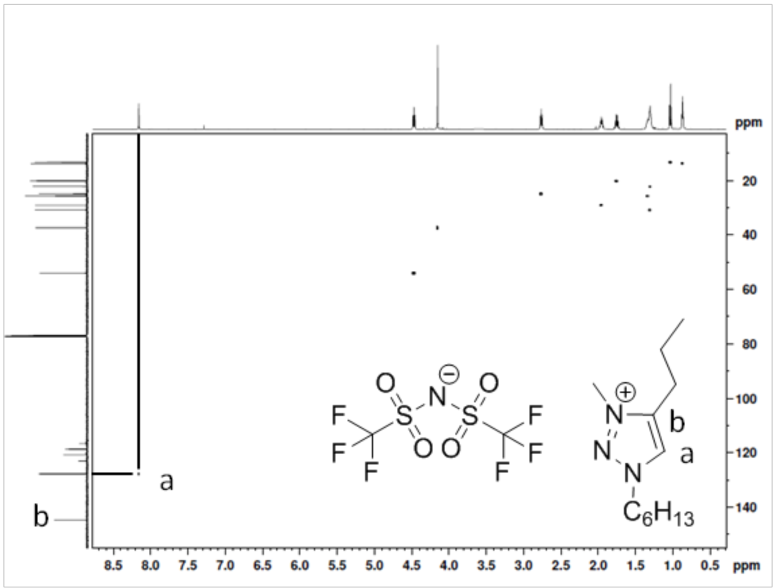
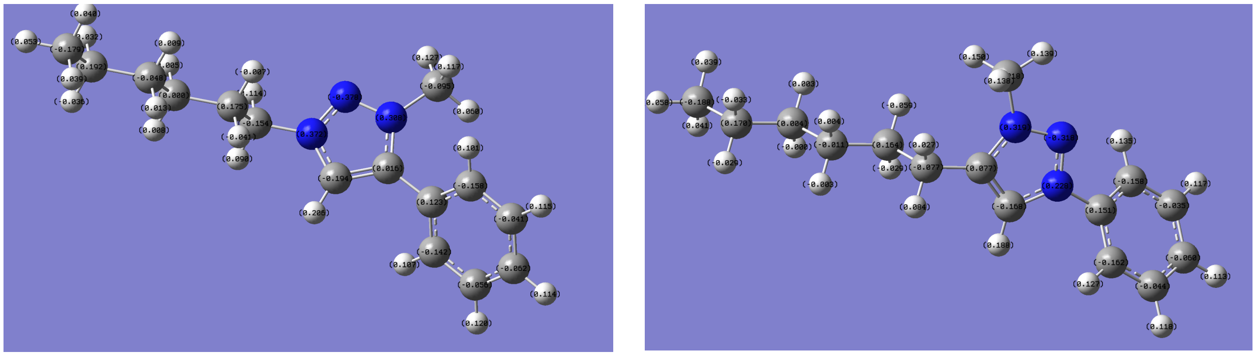
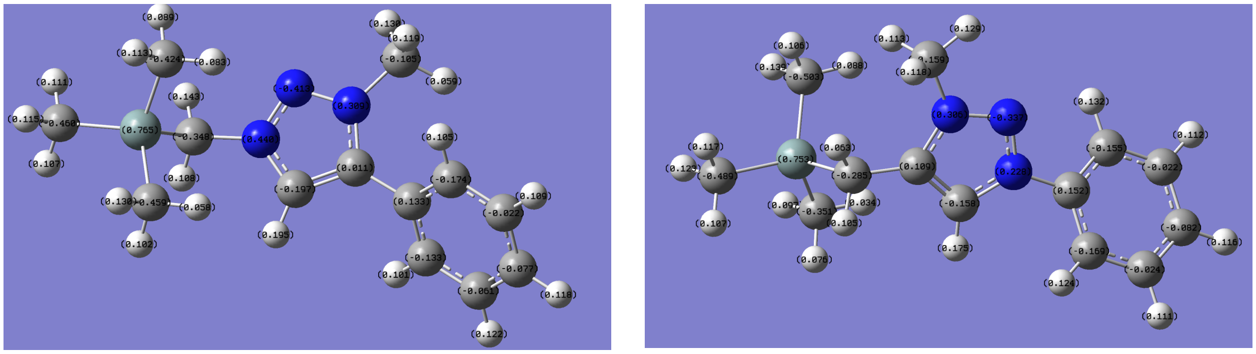


Figure S2: ^{1}H-^{13}C HETCOR NMR spectrum of 1-hexyl-3-methyl-4-propyl-1*H*-1,2,3-triazol-3-ium bis[(trifluoromethyl)sulfonyl]amide.



IL 1
q_{Ph} = 0.221
$\theta_{Ph\text{-}Tr}$ = 51.2°

IL 1A
q_{Ph} = 0.302
$\theta_{Ph\text{-}Tr}$ = 40.3°



IL 2
q_{Ph} = 0.221
$\theta_{Ph\text{-}Tr}$ = 49.5°

IL 2B
q_{Ph} = 0.295
$\theta_{Ph\text{-}Tr}$ = 38.9°

Figure S3: Election density of the phenyl ring (q_{Ph}) and angle between the triazoyl ring and phenyl ring ($\theta_{Ph\text{-}Tr}$) for isomeric triazolium-based ionic liquids with phenyl/hexyl and phenyl/TMS substituents.

Figure S4: ^{19}F NMR spectra of triazolium-based ILs 1p-Tf_2N (top), 1-Tf_2N (middle), and 1A-Tf_2N (bottom); * = trifluoroacetic acid.

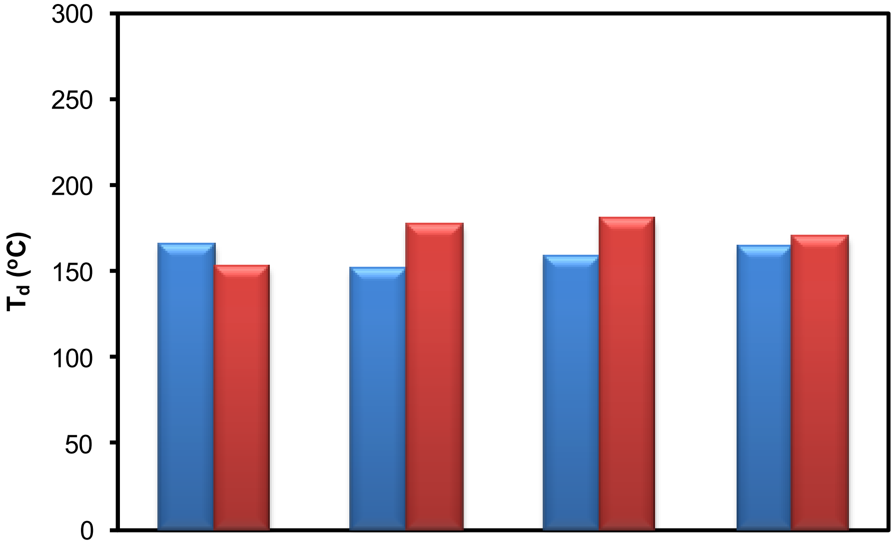


Figure S5: Thermal decomposition temperature (T_d) of 4-phenyl (blue) and 4-propyl (red) substituted triazolium-based ILs with iodide as an anion.

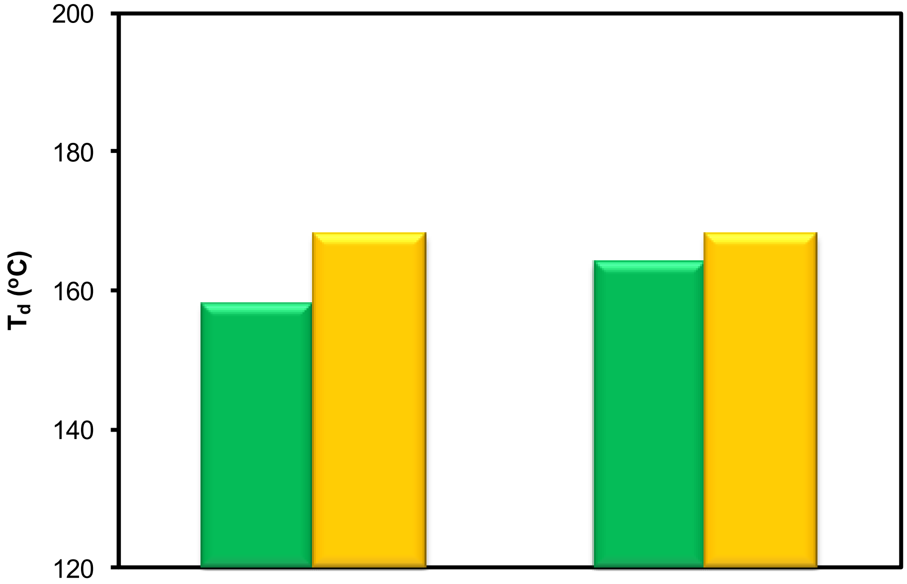


Figure S6: Thermal decomposition temperature (T_d) of regioisomeric triazolium-based ionic liquids with phenyl/hexyl and phenyl/(trimethylsilyl)methyl substitutents on the cation and iodide as an anion.

Figure S7: ^{13}C NMR spectra of 1pA-Tf_2N (top) and 1A-Tf_2N (bottom).

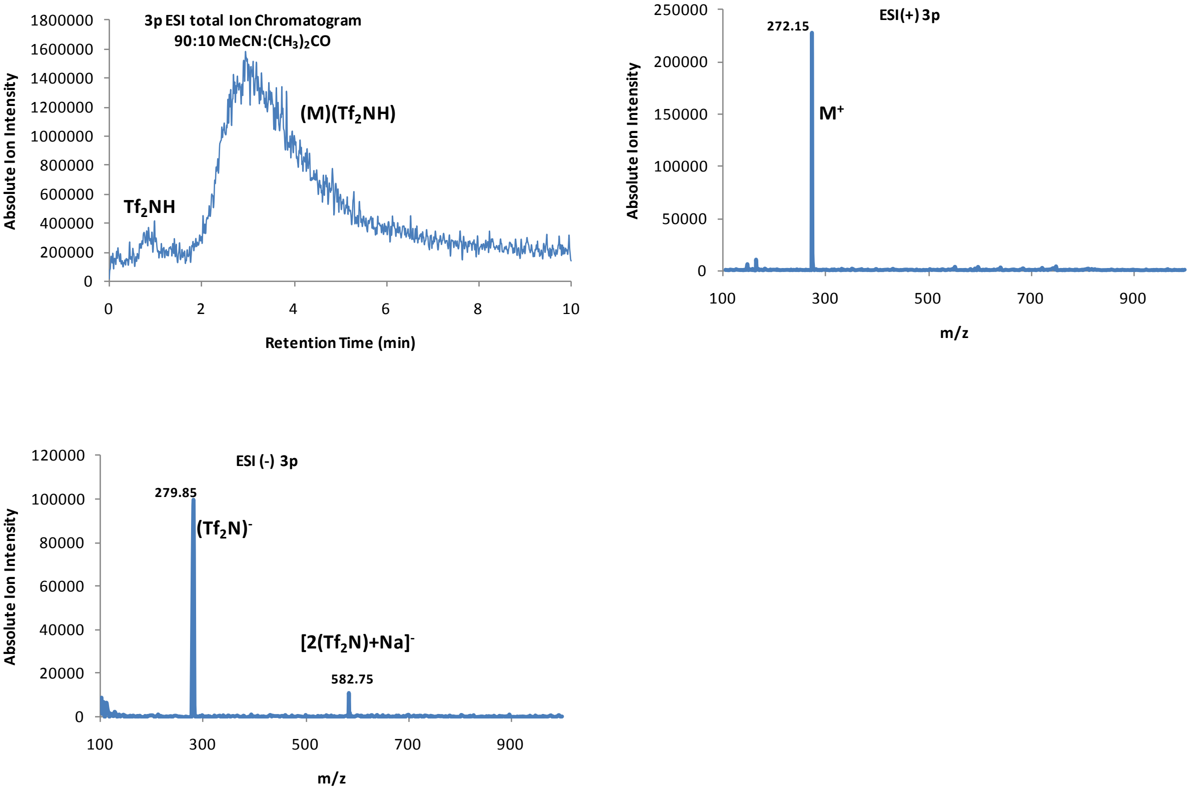


Figure S8: LCMS data for 1-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-3-methyl-4-propyl-1*H*-1,2,3-triazol-3-ium bis[(trifluoromethyl)sulfonyl]amide 3p-Tf_2N

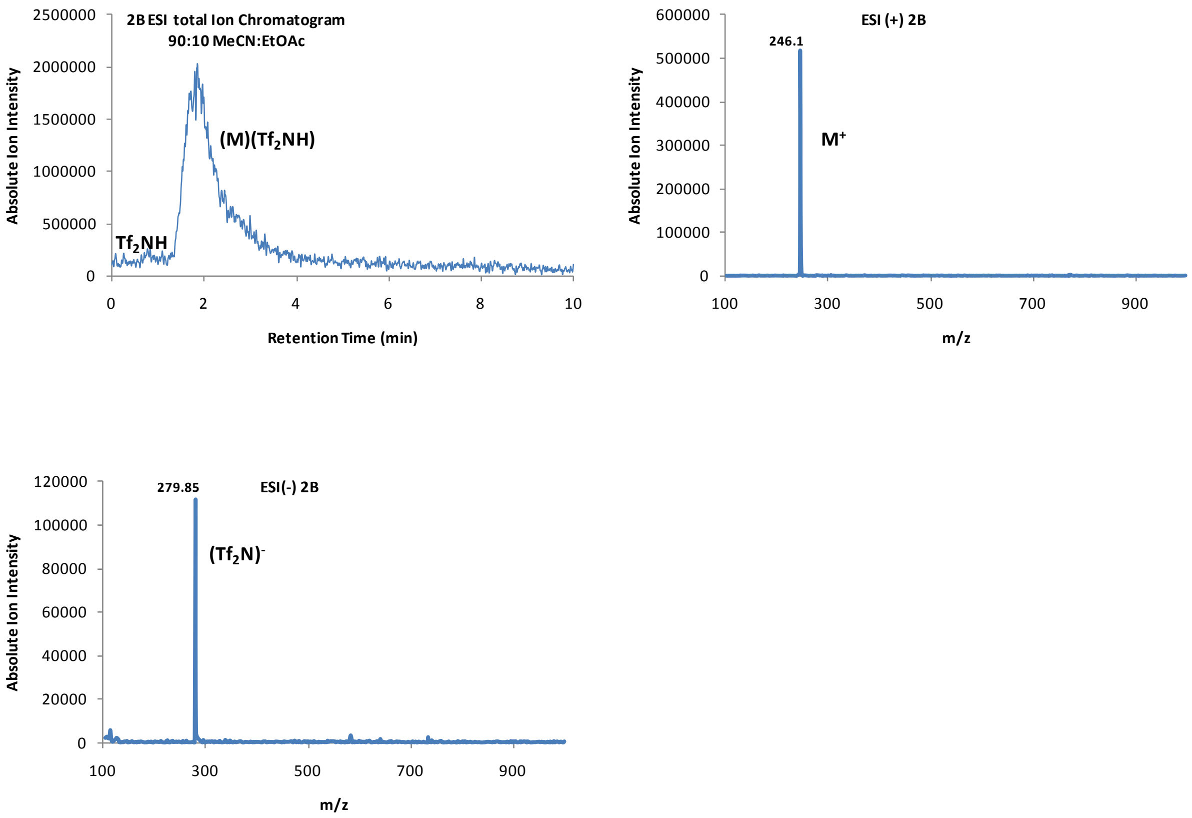


Figure S9: LCMS data for 3-methyl-1-phenyl-4-((trimethylsilyl)methyl)-1*H*-1,2,3-triazol-3-ium bis[(trifluoro- methyl)sulfonyl]amide 2B-Tf_2N

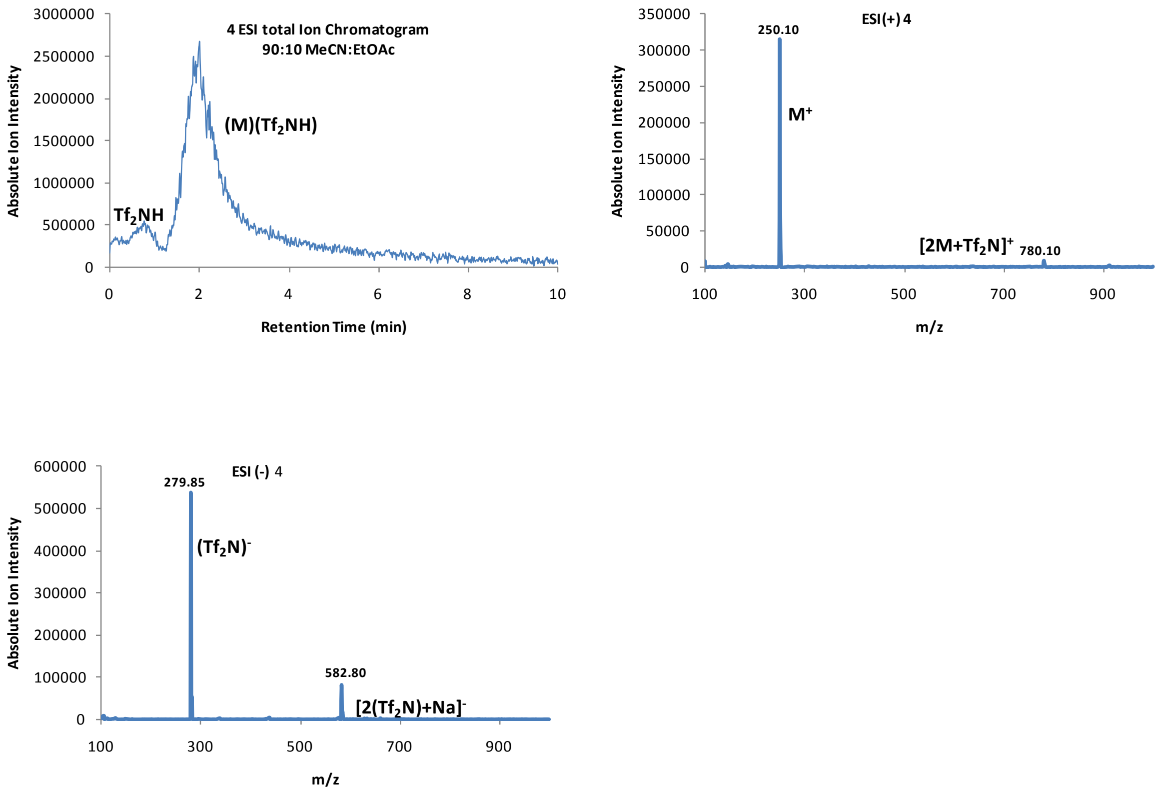


Figure S10: 3-methyl-1-phenyl-4-((trimethylsilyl)methyl)-1H-1,2,3-triazol-3-ium bis[(trifluoromethyl)sulfonyl]amide 2B-Tf2N

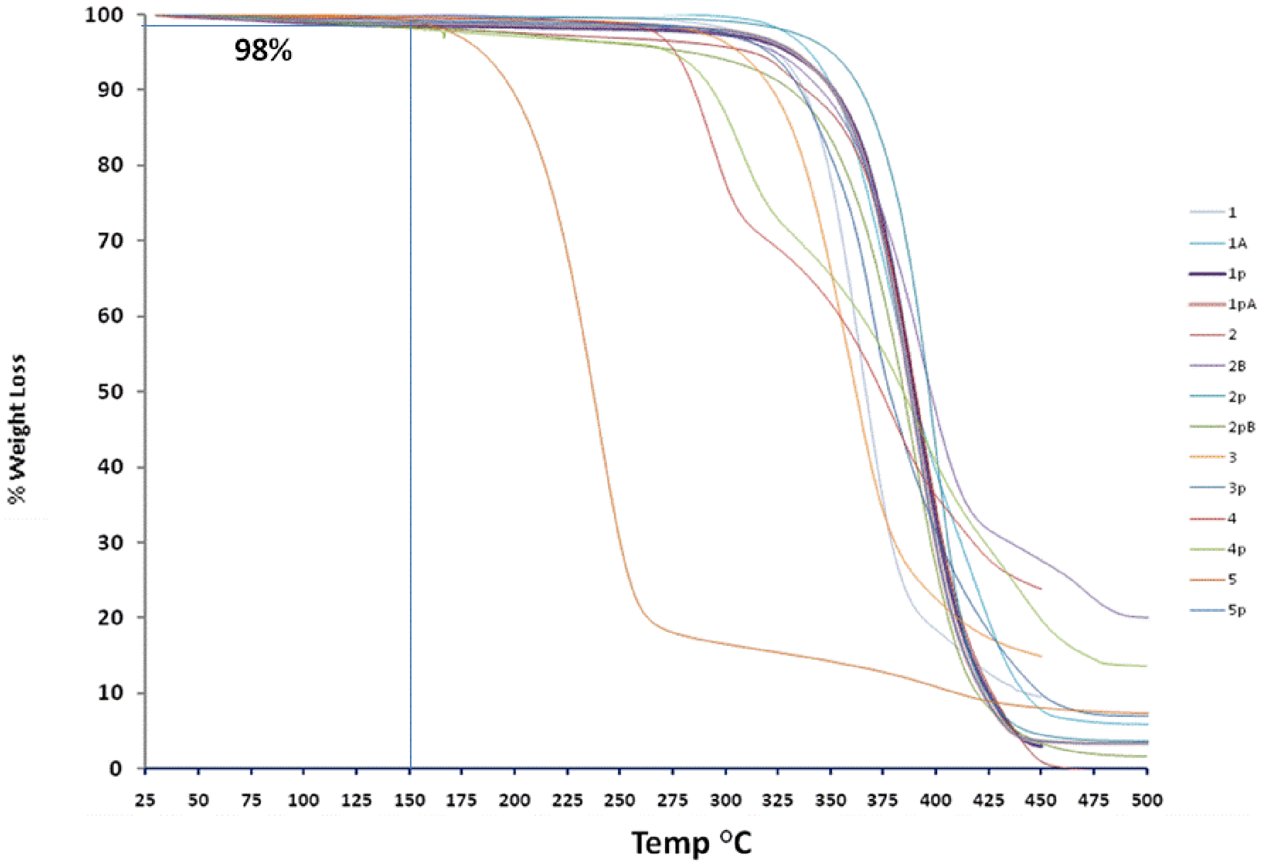


Figure S11: Thermal Gravimetric Analysis (TGA). In all samples weight loss was less than 2% till 150°C.

Section S3

References

[1] C. M. Breneman, K. B. Wiberg, *J. Comput. Chem.* **1990**, *11*, 361.

[2] R. C. Gaussian 03, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.;

Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.

[3] Z. Jia, Q. Zhu, *Bioorg. Med. Chem. Lett.* **2010**, *20*, 6222.

[4] W. Zhu, D. Ma, *Chem. Commun.* **2004**, 888.

[5] H. Nulwala, K. Takizawa, A. Odukale, A. Khan, R. J. Thibault, B. R. Taft, B. H. Lipshutz, C. J. Hawker, *Macromolecules* **2009**, *42*, 6068.

[6] B. H. Lipshutz, B. R. Taft, *Angew. Chem.* **2006**, *118*, 8415.