Physicochemical Properties of 1,2,3-Triazolium Ionic Liquids

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Supporting Information

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1. Experimental Details

Materials. All the commercially available reagents were purchased from Alfa –Aesar or Sigma Aldrich and were used as received.

Characterization. ^{1}H-NMR and ^{13}C-NMR spectra were obtained on a Bruker DPX-300 or Bruker Avance-400 NMR spectrometer. Electrospray ionization mass spectra were acquired using an Esquire-LC ion trap instrument (Bruker Daltonics, Billerica MA) equipped with a standard ESI source. Spectra were obtained in positive ion modes from samples dissolved in methanol (10^{-5} M), infused into the spectrometer using a syringe pump at a constant flow rate of 2 uL/min. Typical operating conditions employed were: needle voltage 3.5 kV, N_2 nebulizer gas, desolvation temperature 150 °C, capillary exit voltage 110 V, scan range 50 - 1200 m/z. Thermo gravimetric analysis (TGA) was performed using a TA instruments TGA 2950 thermogravimetric analyzer at a heating rate of 10 °C/min under nitrogen flow of 20 mL/min. Glass transition temperatures were obtained using TA instrument DSC Q200 differential scanning calorimeter by heating and cooling the samples at a rate of 10 °C/min under helium flow (25 mL/min).

Conductivity versus temperature data were obtained via impedance spectroscopy measurements using a Solartron 1260 Impedance/Gain Phase Analyzer by applying an excitation voltage of 30 mV with a logarithmic frequency sweep from 1 MHz to 0.1 Hz under vacuum to ensure an anhydrous environment. Samples were placed in home-built cells composed of ~4 mm section of polytetrafluoroethylene (PTFE) tubing sealed between two tight-fitting brass electrodes and clamped into custom holders of identical construction. Using customized in house developed software and hardware, the samples were kept at 180 °C under vacuum for ~10 hours and then the system was allowed to cool slowly under vacuum to near ambient temperature, while impedance spectra were continually sampled; this method ensures that samples are brought to a thermally stable condition before temperature dependence data is recorded on the cooling phase, mitigating artifacts due to thermal history and solvent or humidity effects. For each spectrum, the plateau of the impedance magnitude Bode plot occurring in the intermediate frequency range was fit to a constant value function; this plateau also corresponds to a region of minimal phase angle and likewise minimal imaginary component magnitude (reactance) response. Thus, the value of impedance magnitude in this regime was taken to be the resistance of ionic transport in the bulk of the sample. Conductivity σ was computed from the fitted resistance R as $\sigma = t/(R*A)$ where t and A are thickness and area of known sample geometry respectively.

Cyclic Voltammetry was conducted on Basi Epsilon MF 9092. The salts were dried under vacuum overnight and 0.1 M solution in anhydrous acetonitrile was prepared, and then the solution was purged with nitrogen for at least 10 minutes to minimize the effect of water and oxygen on cyclic voltammograms. In order to avoid the effect of degradation products deposited on the electrode from scanning to one potential limit on reversing the potential, potential was swept either between 0 to +3.2 V or between 0 to -3.2 V with clean electrodes and fresh electrolyte. The positive and the negative scans were then combined and plotted for each of the salts. The values for the cathodic and anodic limit are reported from the second scan which was reproducible upon further scans.

General procedure for Tz1 and Tz2 salts: In a 100 mL round bottom flask equipped with a magnetic stir-bar, 1-hexyne (0.68 g, 8.3 mmol), $CuSO_4$ $5H_2O$ (0.19 g, 0.75 mmol), sodium ascorbate (0.3 g, 1.5 mmol) and 30 mL of t-butanol/H_2O (2:1) were combined. Then the corresponding azide (7.52 mmol) was added to the reaction mixture and the solution was allowed to stir at room temperature for 2 days. The reaction was stopped by adding H_2O (50 mL) and the product was extracted using ethyl acetate (4 × 50 mL). The organic fraction was washed with 5% NH_4OH (4 × 50 mL) and then with brine. Further, the organic fractions were dried over $MgSO_4$ and then the solution was concentrated by rotary evaporation. The crude product was purified by flash chromatography using ethyl acetate : hexane (1:1) to yield (80 - 90%) of triazole as a white solid which was used for further alkylation with methyl tosylate or methyl triflate to yield 1,2,3-triazolium salts.

General Procedure for Tz3 salts Synthesis modified from a literature procedure.[1] 1-hexyne (86 mg, 1.05 mmol), sodium azide (68 mg, 1.05 mmol), methyl iodide (0.06 mL, 1 mmol), $CuSO_4 \cdot 5H_2O$ (49 mg, 0.2

mmol), sodium ascorbate (49 mg, 0.25 mmol) and 3 mL of t-butanol/H_2O (1:1) were combined in a microwave vial equipped with a stir bar and then the vial was sealed with an aluminium crimp top. The mixture was irradiated at 100 °C for 15 minutes. The microwave power fluctuated between 20 W – 25 W to maintain a constant temperature of 100 °C. The mixture was then diluted with water and the product was extracted with dichloromethane (3 × 10 mL). The product was further purified by passing through neutral alumina giving 1-methyl-4-butyl-1,2,3-triazole as a white solid (27 mg, 18%) and was used for further alkylation.

General procedure for Tz4 salts Synthesis modified from a literature procedure.[2] 1*H*-1,2,3-triazole (0.39 g, 5.6 mmol, 1eq.), sodium hydroxide (0.23 g, 1.05 eq.) and water (0.5 mL) were combined in a round bottom flask equipped with a stir bar and heated at 100 °C for 15 minutes. The solution was further dried under vacuum over night to remove water and then the resulting sodium salt of 1,2,3-triazole was used for further alkylation.

Quaternization of 1,2,3-triazoles and 1-methylimidazole was performed using methyl tosylate or methyl triflate following a procedure described by Begtrup.[3] **Caution** must be taken in the synthesis of triazoles as azides are explosive in nature.

1-benzyl-3-methyl-4-butyltriazolium tosylate (Tz1Tos): Yield: 87%, yellow viscous liquid; ^{1}H-NMR (300 MHz, D_2O): δ = 0.76 (t, 3H), 1.22 (m, 2H), 1.49 (m, 2H), 2.21 (s, 3H), 2.64 (t, 2H), 3.99 (s, 3H), 5.56 (s, 2H), 7.19 (m, 2H), 7.34(m, 5H), 7.52 (m, 2H), 8.14 (s, 1H); ^{13}C-NMR (75 MHz, D_2O): δ = 12.67, 20.38, 21.22, 22.2, 28.04, 36.79, 56.69, 125.24, 127.27, 129.00, 129.35, 129.64, 131.93, 139.35, 142.38, 145.07; FAB-HRMS calcd: *m/z*: 230.16 $[C_{14}H_{20}N_3]^+$; found: *m/z*: 230.2.

1-benzyl-3-methyl-4-butyltriazolium triflate (Tz1OTf): Yield: 87%, brown viscous liquid; ^{1}H-NMR (400 MHz, CD_3OD): δ = 0.96 (t, 3H), 1.45 (m, 2H), 1.71 (m, 2H), 2.81 (t, 2H), 4.21 (s, 3H), 5.72 (s, 2H), 7.45 (m, 5H), 8.44 (s,1H); ^{13}C-NMR (100 MHz, CD_3OD): δ = 13.48, 22.33, 23.15, 28.94, 37.54, 57.64, 120.64 ($^1J_{CF}$ = 317 Hz), 128.09, 129.61, 130.03, 131.36, 145.11; EI-HRMS calcd: *m/z*: 230.16 $[C_{14}H_{20}N_3]^+$; found: *m/z*: 230.12.

1-phenyl-3-methyl-4-butyltriazolium tosylate (Tz2Tos): Yield: 82%, white powder; ^{1}H-NMR (300 MHz, D_2O): δ = 0.85 (t, 3H), 1.35 (m, 2H), 1.65 (m, 2H), 2.24 (s, 3H), 2.81 (t, 2H), 4.18 (s, 3H), 7.19 (d, 2H), 7.5 (m, 5H), 7.74 (m, 2H), 8.72 (s, 1H); ^{13}C-NMR (75 MHz, D_2O): δ 13.55, 21.23, 22.19, 23.18, 29.10, 38.05, 121.27, 125.83, 127.23, 128.46, 130.24, 131.41, 134.91, 138.96, 143.99, 146.11; FAB-HRMS calcd: *m/z* : 216.15 $[C_{13}H_{18}N_3]^+$; found: *m/z*: 216.2.

1-phenyl-3-methyl-4-butyltriazolium triflate (Tz2OTf): Yield: 82%, white powder; ^{1}H-NMR (400 MHz, CD_3OD): δ = 0.98 (t, 3H), 1.49 (m, 2H), 1.82 (m, 2H), 2.98 (t, 2H), 4.3 (s, 3H), 7.63 (m, 3H), 7.93 (m, 2H), 8.94 (s, 1H); ^{13}C-NMR (100 MHz, CD_3OD): δ = 13.49, 22.31, 23.35, 29.06, 38.05, 120.82 ($^1J_{CF}$ = 329 Hz), 121.59, 126.61, 130.59, 131.97, 134.91, 146.15; EI-MS calcd: *m/z*: 216.15 $[C_{13}H_{18}N_3]^+$; found: *m/z*: 216.08.

1,3-dimethyl-4-butyltriazolium tosylate (Tz3Tos): Yield 18%; yellow solid; ^{1}H-NMR (300 MHz, CD_3OD): δ = 1.03 (t, 3H), 1.52 (m, 2H), 1.75 (m, 2H), 2.4 (s, 3H), 2.87 (t, 2H), 4.26 (s, 3H), 4.3 (s, 3H), 7.26 (d, 2H), 7.73 (d, 2H), 8.51 (s, 1H); ^{13}C-NMR (75 MHz, CD_3OD): δ = 12.64, 20.35, 21.25, 22.15, 28.11, 36.66, 39.25, 125.35, 128.33, 129.42, 139.45, 142.43, 144.78; ESI-MS calcd: *m/z*: 154.23 $[C_8H_{16}N_3]^+$; found: *m/z*: 154.6.

1,3-dimethyl-4-butyltriazolium triflate (Tz3OTf): Yield 18%; brown liquid; ^{1}H-NMR (300 MHz, CD_3OD): δ = 0.99 (t, 3H), 1.46 (m, 2H), 1.73 (m, 2H), 2.85 (t, 2H), 4.19 (s, 3H), 4.26 (s, 3H), 8.45 (s, 1H); ^{13}C-NMR (75 MHz, CD_3OD): δ = 13.84, 22.98, 23.09, 29.88, 37.67, 40.23, 121.76 ($^1J_{CF}$ = 324 Hz), 130, 146.20; ESI-MS calcd: *m/z*: 154.23 $[C_8H_{16}N_3]^+$; found: *m/z*: 154.6.

1,3-dimethyltriazolium tosylate (Tz4Tos): Yield 25%; white powder; ^{1}H-NMR (300 MHz, D_2O): δ = 2.26 (s, 3H), 4.16 (s, 6H), 7.24 (d, 2H), 7.54 (d, 2H), 8.33 (s, 1H); ^{13}C-NMR (75 MHz, D_2O): δ = 20.37, 39.39, 125.33, 129.6, 131.15, 139.3, 142.6; ESI-MS calcd: *m/z*: 98.13 $[C_4H_8N_3]^+$; found: *m/z*: 98.8.

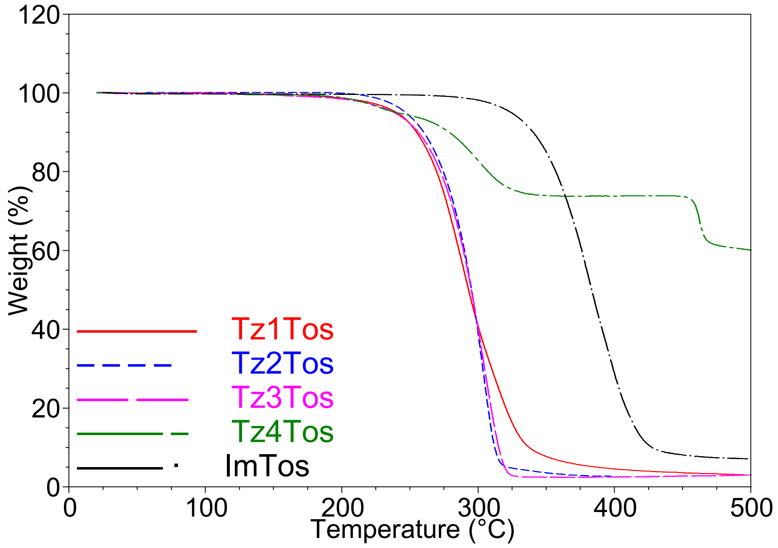
1,3-dimethyltriazolium triflate (Tz4OTf): Yield 25%; brown viscous liquid; ^{1}H-NMR (400 MHz, D_2O): δ = 4.17 (s, 6H), 8.33 (s, 2H); ^{13}C-NMR (100 MHz, D_2O): δ = 39.64, 119.67 ($^1J_{CF}$ = 315 Hz), 131.17; ESI-MS calcd: *m/z*: 98.13 $[C_4H_8N_3]^+$; found: *m/z*: 98.8.

1,3-dimethylimidazolium tosylate (ImTos): Yield: 99%, white solid; ^{1}H-NMR (300 MHz, D_2O): $\delta = 2.23$ (s, 3H), 3.68 (s, 6H), 7.2 (m, 4H), 7.52 (d, 2H), 8.41 (s, 1H); ^{13}C-NMR (75 MHz, D_2O): $\delta = 0.38$, 35.44, 123.23, 125.21, 129.31, 136.25, 139.42, 142.29; ESI-MS calcd: *m/z*: 97.14 $[C_5H_9N_2]^+$; found: *m/z*: 97.8.

1,3-dimethylimidazolium triflate (ImOTf): Yield: 99%, light yellow solid; ^{1}H-NMR (300 MHz, D_2O): $\delta = 3.79$ (s, 6H), 7.31(s, 2H), 8.53 (s, 1H); ^{13}C-NMR (75 MHz, D_2O): $\delta = 35.51$, 119.63 ($^1J_{CF} = 315$ Hz), 123.33, 136.44; ESI-MS calcd: *m/z*: 97.14 $[C_5H_9N_2]^+$; found: *m/z*: 97.8.

2. Thermal Stability

a)



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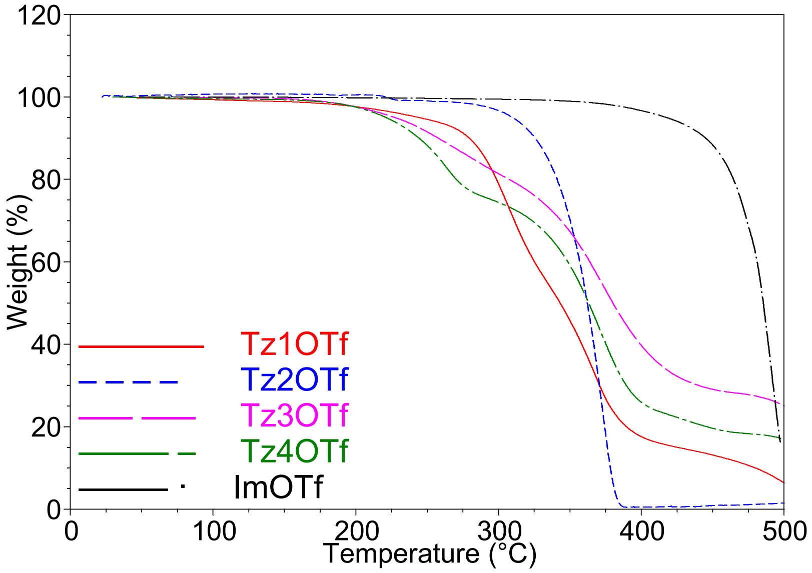

Figure S1. TGA traces a) tosylate series b) triflate series

3. Ionic Conductivity

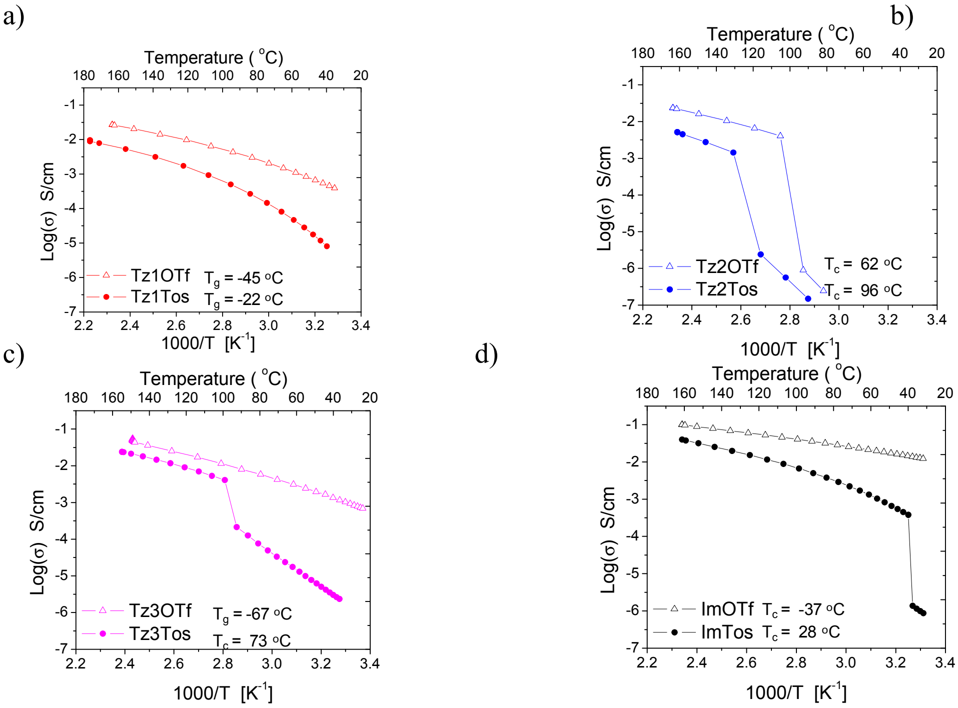

Figure S2. Comparison of ionic conductivity between two salts with same cation and different anion a) Tz1Tos vs. Tz1OTf b) Tz2Tos vs. Tz2OTf c) Tz3Tos vs. Tz3OTf d) ImTos vs. ImOTf

4. Cyclic Voltammetry

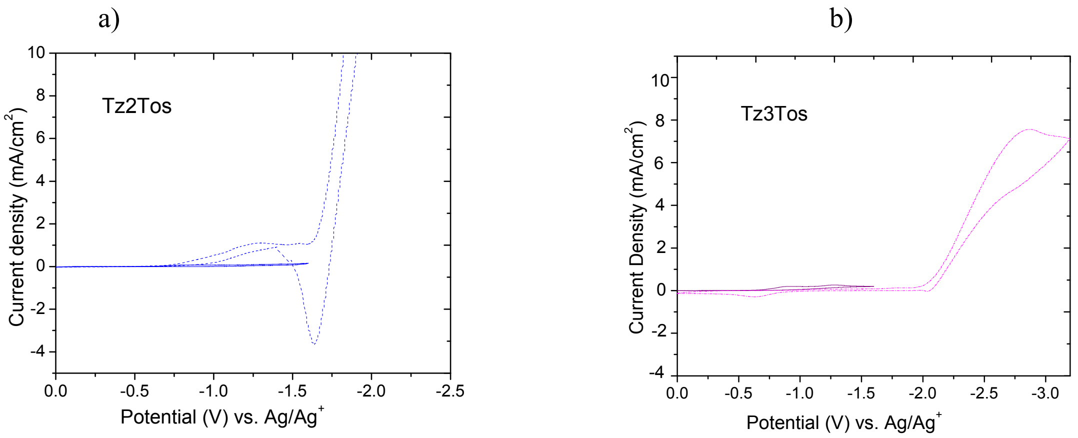

Figure S3. Discharge effect a) Tz2 cation is stable up to -1.6 V (bold line) and shows an oxidation current around -1.6 V (dotted line) only when scanned to a potential more negative than its $E_{cathodic}$ limit. b) Similarly Tz3 cation is stable up to -2.1 V and shows an oxidation current around -0.5 V (dotted line) when scanned above its $E_{cathodic}$ limit.

References

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3. M. Begtrup, *Acta Chem. Scand.*, 1971, **25**, 249-259.