

SUPPORTING INFORMATION

Branched isomeric 1,2,3-triazolium-based ionic liquids: New insight into structure-property relationships

M. Lartey,^a J. Meyer-Ilse,^b J. D. Watkins,^a E. A. Roth,^a S. Bowser,^c V. A. Kusuma,^a K. Damodaran,^c X. Zhou,^{a,d} M. Haranczyk,^e E. Albenze,^a D. R. Luebke,^a D. Hopkinson,^a J. B. Kortright,^{b,*} H. B. Nulwala,^{a,f*}

E-mail: J. B. Kortright (JBKortright@lbl.gov); H. B. Nulwala (hnulwala@andrew.cmu.edu)

^a National Energy Technology Laboratory, P.O. Box 10940, Pittsburgh, PA, USA

^b Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

^c Department of Chemistry, University of Pittsburgh, Chevron Science Center, 219 Parkman Ave, Pittsburgh, PA 15260, USA

^d Liquid Ion Solutions, LLC, 1817 Parkway View Drive, Pittsburgh, PA 15205, USA

^e Computational Research Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

^f Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, PA 15213, USA

EXPERIMENTAL

Materials

Sodium azide, sodium ascorbate, copper (II) sulfate pentahydrate, 1-pentyne, 4-methyl-1-butyne, 1-bromopropane, 2-bromopropane, acetonitrile, dimethyl formamide (DMF), dichloromethane, hexane, ethyl acetate were purchased from Fisher Scientific and used as received unless otherwise specified.

Instrumentation and methods: ¹H, ¹³C, ¹⁹F NMR analyses were recorded on Bruker Avance III spectrometers. All chemical shifts were measured in ppm with the solvent peak as the internal reference. All *J*-coupling constants were measured in Hz. FTIR

spectra were collected on Nicolet Spectrum 100 with an ATR apparatus. Viscosity measurements were carried out at 30 °C on a Rheosense Inc. μ Visc equipped with a temperature control unit. Densities of ionic liquids were measured at ambient temperature on a Micromeritic Accupyc II 1340 helium pycnometer. All density measurements were performed in 30 cycles and the average and standard deviation are recorded. TGA was carried out on a TGA Q500 (TA Instruments) in Pt pans with a heating rate of 10 °C/min in N₂. MDSC was carried out on DSC Q2000 (TA Instruments) using aluminum hermetic pans and with an average heating and cooling rate of 1 °C/min, an amplitude of 0.24 °C, and a period of 60 seconds. Two heating cycles were conducted using MDSC and the results reported are from the second heat of the MDSC scan. Additionally, DSC scans using a heating and cooling rate of 5 °C/min and 10 °C/min were also conducted with 4 heating cycles from -100 °C to 150 °C to ensure repeatability of the results. The reported glass transition temperature was calculated using the inflection point, while the melting and cold crystallization temperatures reported were the peak maxima. The Mass of sample for TGA and DSC was 10-20 mg.

LC-MS and MS infusions were performed on a Shimadzu model 2020 mass spectrometer, equipped with a DUIS APCI/ESI probe operating in ESI+/- mode at a scan rate of 2143 m/sec from 30 - 2000 m/z. Flow rates in both cases were 0.4 ml/min. The mobile phase for the infusion experiments was acetonitrile, while the analytical separations were performed on a C8 or C18 column using a linear gradient of acetonitrile/ 40 mM ammonium acetate buffer pH 5.8 over 8 minutes, followed by isocratic flow for 2 minutes and linear return to initial conditions in 2 minutes with

isocratic flow for approximately 4 column volumes. Infusion experiments were performed with a 0.1 μL injection of a 1 mg/ml solution of IL in acetonitrile with a 350 °C interface temperature with 1.5 L/min nebulizer gas flow, 250 °C desolvation temperature (with 15 L/min N_2 drying gas), and 400 °C heat block temperature. All molecular weights were measured in amu.

Self-Diffusion Measurements: NMR spectra were acquired using a Bruker Avance III spectrometer with a Bruker UltraShield magnet operating at a ^1H frequency of 600.71 MHz, equipped with a Bruker BBFO Plus probe. Samples were loaded into 3 mm outer diameter NMR tubes to limit the effect of thermal convection on diffusion measurements. To provide a deuterium signal for the deuterium lock, as well as to provide a reference for accurate chemical shift determination, the 3 mm NMR tubes were inserted coaxially into medium-walled NMR tubes with a sufficient amount of DMSO-d_6 in the outer tube to reach the height of the sample in the inner tube when inserted. Shimming was performed using the TOPSHIM gradient shimming macro incorporated in the Bruker TopSpin software suite, using a ^1H shimming routine with the excitation frequency set to a resonance originating from the IL. The spectrometer was tuned and matched before each experiment, and the 90° pulse widths for the ^1H and ^{19}F spectra were determined using the nutation method via the built-in pulsecal macro.

Temperature was controlled at 30 °C \pm 0.1 *via* the spectrometer variable temperature unit and the probe thermocouple, with a constant gas flow of 670 l/h. Each sample was thermally equilibrated for at least 30 minutes prior to the start of acquisition. The thermocouple was calibrated using the known temperature

dependence of the difference of OH and CH₃ resonances chemical shift of a sample of 80% ethylene glycol in DMSO-d₆.

Pulse field gradient NMR (PFG-NMR) spectra for self-diffusion coefficient determination were recorded using the Bruker pulse sequence `stebpgp1s`, which incorporates a stimulated echo, bipolar gradients pulse, and one spoil gradient. The value of diffusion time, Δ was 1 s and the total gradient pulse width, Δt was 5 ms. Eight spectra, with gradient strength ramped linearly from 2% to 95% of the maximum gradient strength, were acquired with eight transients each, to produce a pseudo-2D spectrum diffusion spectrum. The decays of all observed peaks were fitted to a modified Stejsjal-Tanner equation, incorporating the appropriate correction factors for the bipolar pulses, spoil gradients, and gradient shape, using the built-in relaxation analysis module in the Bruker TopSpin software suite.

Conductivity Measurements: Electrical impedance spectroscopy was performed using a Solartron SI1287 Potentiostat in conjunction with a Solartron 1252A Impedance Analyzer (Solartron Analytical, Hampshire, UK), controlled by Z-Plot (Scribner Associates, Southern Pines, NC, USA). The conductivity cell was InLab 751 (Mettler-Toledo, Columbus, OH, USA). a dip-type conductivity cell model having platinized platinum electrodes and a rated cell constant of 0.97 cm⁻¹. The cell constant was calibrated using a 5000 μ s KCl conductivity standard (Ricca Chemicals, Arlington, TX USA).

Conductivity measurements were carried out inside a home-built dry box. IL samples were loaded into test tubes, which were inserted into a custom-machined aluminum block heater. Temperature was controlled at 30 °C \pm 0.1, the heater unit

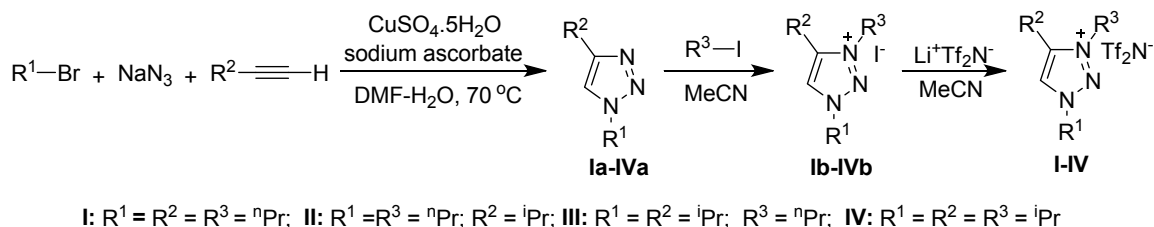
having previously been calibrated using a K-type thermocouple in conjunction with Fluke 9150 Calibration Well. 100 Data points were acquired for each measurement using a logarithmic frequency list between 10 Hz and 300,000 Hz. DC polarization was set to zero vs. the open circuit potential. The AC potential amplitude set to 10, 20, or 30 mV, the larger values being used for the more resistive ILs. Data were plotted as a Nyquist plot using the Z-View software package (Scribner Associates). The DC resistance of the liquid was taken as the first minimum of Z'' . At least three repeat measurements were made for each IL.

NEXAFS (Near Edge X-Ray Absorption Fine Structure) Spectroscopy: The samples were prepared on a gold coated silicon wafer substrates. For this the ILs were dissolved in isopropanol (Sigma-Aldrich: chromasolv, for HPLC, 99.9%); small amounts from each solution were pipetted onto individual substrates making sure that each substrate was wetted. These were then heated on a hotplate to evaporate the solvent leaving a layer of ionic liquid. To make sure that all the solvent was evaporated the samples were then transferred into a vacuum oven, heated to 100 °C for one hour under vacuum, and left in vacuum until shortly before being transferred to the beamline. The soft x-ray absorption measurements were performed at ambient temperature at the ALS beamline 6.3.2. Energy scans across the carbon, nitrogen, oxygen and fluorine K-edges were performed. Direct beam spectra for all energy ranges were recorded before and after the measurements to check for beamline stability and to normalize the NEXAFS spectra. NEXAFS was measured via total electron yield (TEY) with the samples centered on the soft x-ray beam at an incidence angle of 10 degrees. Each sample was measured

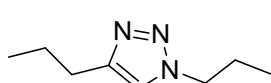
twice at each absorption edge; the two measurements are in good agreement, so for the analysis the two measurements are averaged for an improved signal-to-noise ratio. To remove differences between samples due to thickness and roughness, the measured TEY data were normalized to the jump edge, a standard procedure for NEXAFS.² The soft x-ray absorption data shown here were obtained at ambient temperature (~25 °C) at Advance Light Source ALS beamline 6.3.2. Each sample was seen to be in the undercooled liquid state during measurements. Energy scans across the carbon, nitrogen, oxygen and fluorine K edges were performed. Direct beam spectra for all energy ranges were recorded before and after the measurements to check for beamline stability and to normalize the XAS spectra. NEXAFS spectra were measured via total electron yield (TEY) with the samples centered on the soft x-ray beam at a grazing incidence angle of 10°. Under such conditions the penetration depth of the incident x-rays increases from 50 nm for energies above the C edge to 140 nm above the F edge. These values are at least several times the secondary electron escape depth of approximately 5-10 nm; the escape depth thus sets the TEY sensing depth. Possible saturation effects that result when the x-ray penetration depth approaches the electron escape depth are thus avoided.

Synthesis: All solvents were degassed prior to use. The triazole core was synthesized by the one-pot approach reported in literature.¹ To a 500 mL round-bottom flask containing 50 mL distilled water, was added sodium azide (11.87 g, 183 mmol), sodium ascorbate (2.41 g, 12 mmol) and copper (II) sulfate pentahydrate (0.65 g, 4 mmol). After stirring to dissolve completely, 50 mL dimethyl formamide was added and stirred

followed by the appropriate propyl bromide (5.56 g, 41 mmol) and finally the alkyne (5.00 g, 61 mmol). The mixture was stirred at 70 °C for 12 h. After 12 h, the reaction mixture was cooled to ambient temperature and water was added. The aqueous solution was extracted with dichloromethane and the organic layer was dried over MgSO₄, filtered and concentrated under *in vacuo*. The crude product was further purified by flash column chromatography (hexane:ethyl acetate, 1:1) The triazole core was further quarternized by treatment with alkyl iodide and subjected to ion exchange to obtain the ionic as outlined in scheme 1.



Scheme S1. Generalized synthesis of ionic liquids

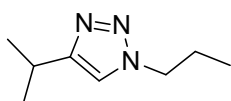


1,4-dipropyl-1H-1,2,3-triazole (Ia)

Yield: 4.4 g, 70 % (pale yellow liquid)

¹H NMR (Chloroform-d, 300 MHz): δ=7.19 (s, 1H), 4.11 (t, *J*=7.2 Hz, 2H), 2.50 (t, *J*=7.5 Hz, 2H), 1.74 (sxt, *J*=7.3 Hz, 2H), 1.51 (sxt, *J*=7.5 Hz, 2H), 0.77 (q, *J*=7.5 Hz, 6H)

¹³C NMR (Chloroform-d, 75 MHz): δ = 147.7, 120.4, 51.3, 27.4, 23.4, 22.4, 13.4, 10.7

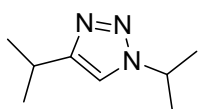


4-isopropyl-1-propyl-1H-1,2,3-triazole (IIa)

Yield: 4.1g, 65 % (pale yellow liquid)

^1H NMR (Chloroform -d, 300 MHz): $\delta=7.17$ (s, 1 H), 4.12 (t, $J=7.2$ Hz, 2 H), 2.90 (d, $J=6.8$ Hz, 1 H), 1.65 - 1.84 (m, 2 H), 1.15 (s, 2 H), 1.13 (s, 3 H), 0.78 (t, $J=7.3$ Hz, 3 H)

^{13}C NMR (Chloroform-d, 75 MHz): $\delta= 154.3, 119.0, 51.6, 25.7, 23.6, 22.4, 10.9$



1,4-di(propan-2-yl)-3-propyl-1,2,3-triazole(IIIb and IVb)

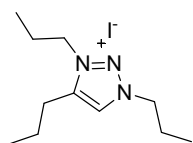
Yield: 4.4 g, 70 % (white solid)

^1H NMR (Chloroform-d, 300 MHz): $\delta=7.29$ (s, 1H), 4.78 (dt, $J=13.3, 6.8$ Hz, 1H), 3.08 (br. s., 1H), 1.55 (d, $J=6.8$ Hz, 6H), 1.29 (d, $J=5.7$ Hz, 6H)

^{13}C NMR (MHz, Chloroform, 101 MHz): $\delta= 153.9, 116.5, 52.4, 25.6, 22.7, 22.3$

General synthesis of 1,3,4-trisubstituted-1H-triazol-1,2,3-ium iodide (Ib-IVb)

Precursor triazoles, **Ia-IVa**, (2.5 g, 16 mmol) were dissolved in 50 mL degassed acetonitrile and the appropriate propyl iodide (7.6 g, 45 mmol) was added and stirred in a sealed tube overnight at 75 °C. At the end of the reaction, acetonitrile was removed under vacuum and hexane was added to the crude product to dissolve unreacted triazole and alkyl halide. (Note: the triazolium halide does not dissolve in hexanes but the precursor triazole and alkyl iodide are soluble in hexanes) The process was repeated 5 times and the product was dried under vacuum.

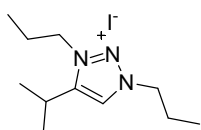


1,3,4-tripropyl-1H-triazol-1,2,3-ium iodide (Ib)

Yield: 4.7 g, 90 % (brown viscous liquid)

^1H NMR (Chloroform- d , 400 MHz): δ =8.87 (s, 1 H), 4.32 (t, J =7.2 Hz, 2 H), 4.19 (t, J =7.2 Hz, 2 H), 2.55 (t, J =7.7 Hz, 2 H), 1.58 - 1.76 (m, 4 H), 1.46 (sxt, J =7.5 Hz, 2 H), 0.54 - 0.72 (m, 9 H)

^{13}C NMR (Chloroform- d , 101 MHz): δ =143.0, 128.3, 54.5, 52.3, 24.5, 22.0, 21.3, 19.8, 12.6, 9.9, 9.7

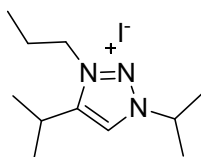


4-(propan-2-yl)-1,3-dipropyl-1H-triazol-1,2,3-ium iodide (IIb)

Yield: 4.7 g, 90% (brown viscous liquid)

^1H NMR (Chloroform- d , 300 MHz): δ =9.04 (s, 1 H), 4.43 (t, J =7.3 Hz, 2 H), 4.31 (t, J =7.3 Hz, 2 H), 3.04 - 3.21 (m, J =13.8, 6.8, 6.8 Hz, 1 H), 1.81 (dq, J =15.3, 7.7 Hz, 4 H), 1.16 (d, J =6.8 Hz, 6 H)

^{13}C NMR (Chloroform- d , 75 MHz): δ =149.0, 127.8, 54.9, 52.6, 23.8, 22.3, 22.0, 21.4, 10.3, 10.1

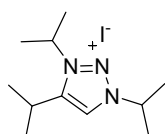


1,4-di(propan-2-yl)-3-propyl-1H-triazol-1,2,3-ium iodide (IIIb)

Yield: 4.4 g, 85 % (brown solid)

^1H NMR (Chloroform- d , 400 MHz): δ =9.50 (s, 1 H), 5.31 (spt, J =6.7 Hz, 1 H), 4.48 (t, J =7.4 Hz, 2 H), 3.16 - 3.36 (m, 1 H), 2.05 (sxt, J =7.4 Hz, 2 H), 1.71 (d, J =6.5 Hz, 6 H), 1.45 (d, J =7.0 Hz, 6 H), 1.03 (t, J =7.4 Hz, 3 H)

^{13}C NMR (Chloroform- d , 101 MHz): δ = 149.6, 127.8, 58.6, 53.1, 24.8, 22.8, 22.5, 22.1



1,3,4-tri(propan-2-yl)-1H-triazol-1,2,3-ium iodide (IVb)

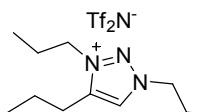
Yield: 3.1 g, 60% (brown solid)

^1H NMR (Chloroform- d , 400 MHz): δ =9.23 (s, 1 H), 5.22 (spt, J =6.7 Hz, 1 H), 5.01 (spt, J =6.7 Hz, 1 H), 3.31 (spt, J =6.9 Hz, 1 H), 1.68 (d, J =6.8 Hz, 6 H), 1.63 (d, J =6.5 Hz, 6 H), 1.42 (d, J =7.0 Hz, 6 H)

^{13}C NMR (Chloroform- d , 75 MHz): δ =148.9, 127.2, 58.6, 55.2, 24.7, 23.1, 22.5, 22.3

General synthesis of 1,3,4-trisubstituted-1H-triazol-1,2,3-ium bis(trifluoromethanesulfonyl)amide

The triazolium iodide, Ib-IVb, (2 g, 6 mmol) and LiTf_2N (2.7 g, 9 mmol) were dissolved in 50 mL degassed acetonitrile and stirred at 75 °C overnight. Acetonitrile was removed *in vacuo* and the crude product was dissolved in water and the product extracted with DCM. The product was further dissolved in methanol and purified to remove UV-active and fluorescent impurities by refluxing over activated charcoal as reported in literature³ to obtain a colorless liquid.



1,3,4-tripropyl-1H-triazol-1,2,3-ium

bis(trifluoromethanesulfonyl)amide (I)

Yield: 2.6 g, 90% (colorless viscous liquid)

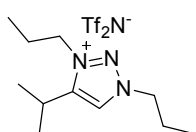
^1H NMR (CHLOROFORM- d , 400 MHz): δ =8.24 (s, 1H), 4.48 (t, J =7.3 Hz, 2H), 4.38 (t, J =7.4 Hz, 2H), 2.76 (t, J =7.9 Hz, 2H), 1.94-2.07 (m, 4H), 1.77 (sxt, J =7.5 Hz, 2H), 0.93-1.08 (m, 9H)

^{13}C NMR (CHLOROFORM-d, 101 MHz): δ =144.5, 128.2, 121.5, 118.3, 55.7, 52.7, 73.5, 25.1, 22.8, 22.4, 20.7, 13.5, 10.8, 10.6

^{19}F NMR (Chloroform-d, 376 MHz): δ =-79.02

LCMS: calculated for $\text{C}_{11}\text{H}_{22}\text{N}_3$: 196 observed: 196 (cation)

calculated for $\text{C}_2\text{F}_6\text{NO}_4\text{S}_2$: 280 observed: 280 (anion)



4-(propan-2-yl)-1,3-dipropyl-1H-triazol-1,2,3-ium

bis(trifluoromethanesulfonyl)amide (II)

Yield: 2.4 g, 85 % (colorless viscous liquid)

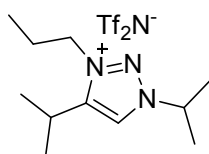
^1H NMR (CHLOROFORM-d, 400MHz): δ =8.25 (s, 1H), 4.48 (t, J =6.8 Hz, 2H), 4.39 (t, J =6.8 Hz, 2H), 3.17 (spt, J =6.9 Hz, 1H), 1.95-2.08 (m, 4H), 1.35 (d, J =6.8 Hz, 6H), 0.98 (d, J =6.8 Hz, 6H)

^{13}C NMR (CHLOROFORM-d, 101 MHz): δ =150.2, 127.1, 121.5, 118.3, 55.7, 52.7, 24.4, 22.8, 22.6, 21.5, 10.8, 10.6

^{19}F NMR (Chloroform-d, 376 MHz): δ =-79.02

LCMS: calculated for $\text{C}_{11}\text{H}_{22}\text{N}_3$: 196 observed: 196 (cation)

calculated for $\text{C}_2\text{F}_6\text{NO}_4\text{S}_2$: 280 observed: 280 (anion)



1,4-di(propan-2-yl)-3-propyl-1H-triazol-1,2,3-ium

bis(trifluoromethanesulfonyl)amide (III)

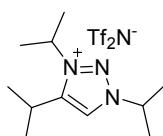
Yield: 2.4 g, 85% (colorless viscous liquid)

^1H NMR (CHLOROFORM-d, 400 MHz): δ =8.15 (s, 1H), 4.89 (spt, J =6.7 Hz, 1H), 4.33 (t, J =7.4 Hz, 2H), 3.11 (spt, J =6.9 Hz, 1H), 1.95 (sxt, J =7.4 Hz, 2H), 1.56 (d, J =6.8 Hz, 6H), 1.27 (d, J =6.8 Hz, 6H), 0.92 (t, J =7.4 Hz, 3H), 0.82-0.99 (m, 3 H)

^{13}C NMR (CHLOROFORM-d, 101 MHz): δ =149.8, 124.9, 124.5, 121.3, 118.1, 114.9, 58.2, 52.5, 24.1, 22.3, 21.6, 21.1, 10.5

^{19}F NMR (Chloroform-d, 376 MHz): δ =-78.98

LCMS: calculated for $\text{C}_{11}\text{H}_{22}\text{N}_3$: 196 observed: 196 (cation)
 calculated for $\text{C}_2\text{F}_6\text{NO}_4\text{S}_2$: 280 observed: 280 (anion)



1,3,4-tri(propan-2-yl)-1H-triazol-1,2,3-ium

bis(trifluoromethanesulfonyl)amide (IV)

Yield: 2.1 g, 75 % (colorless viscous liquid)

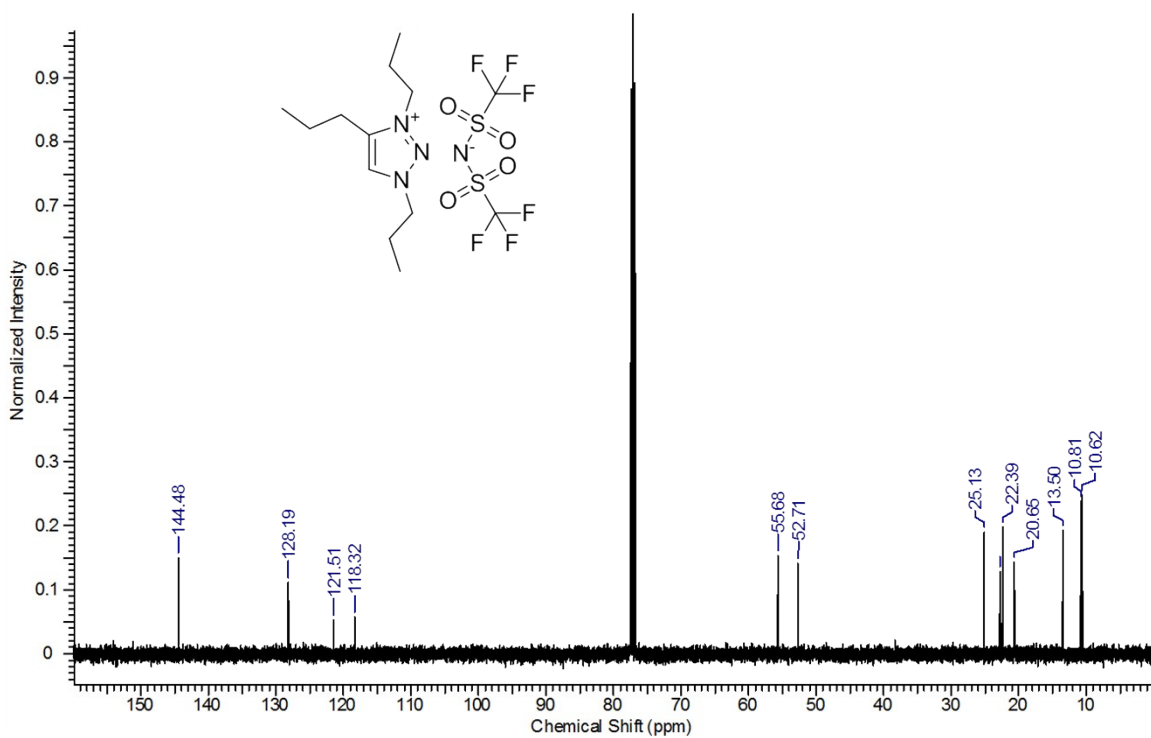
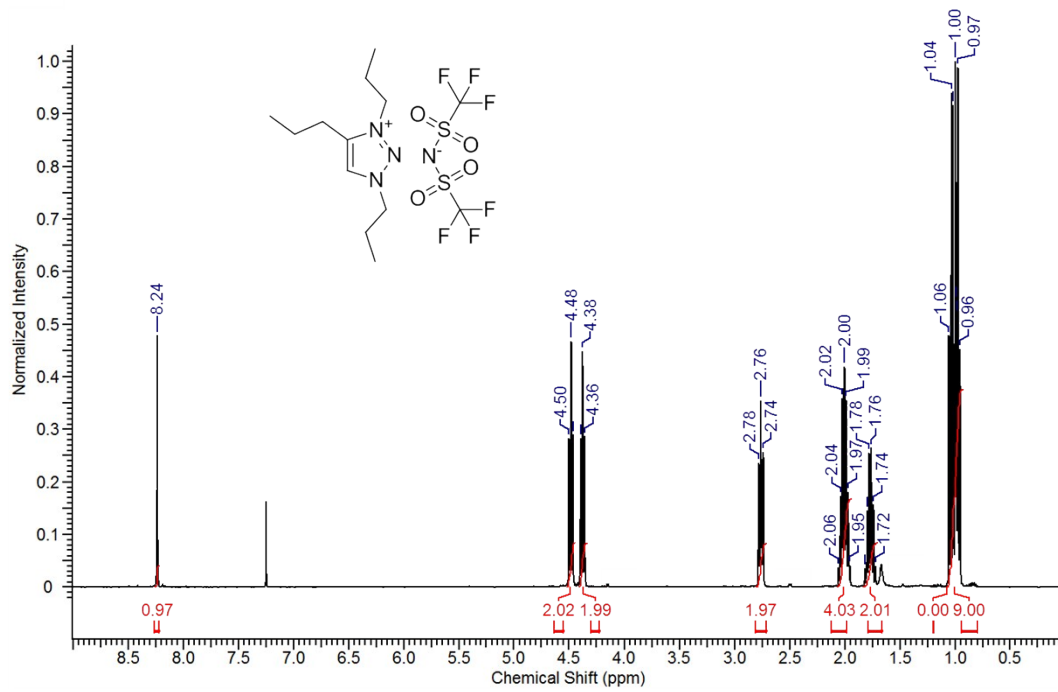
^1H NMR (CHLOROFORM-d, 300 MHz): δ =8.17 (s, 1H), 4.81-5.04 (m, 2H), 3.06-3.28 (m, J =13.8, 6.8, 6.8 Hz, 1H), 1.60 (dd, J =6.8, 4.5 Hz, 12 H), 1.33 (d, J =7.2 Hz, 6 H)

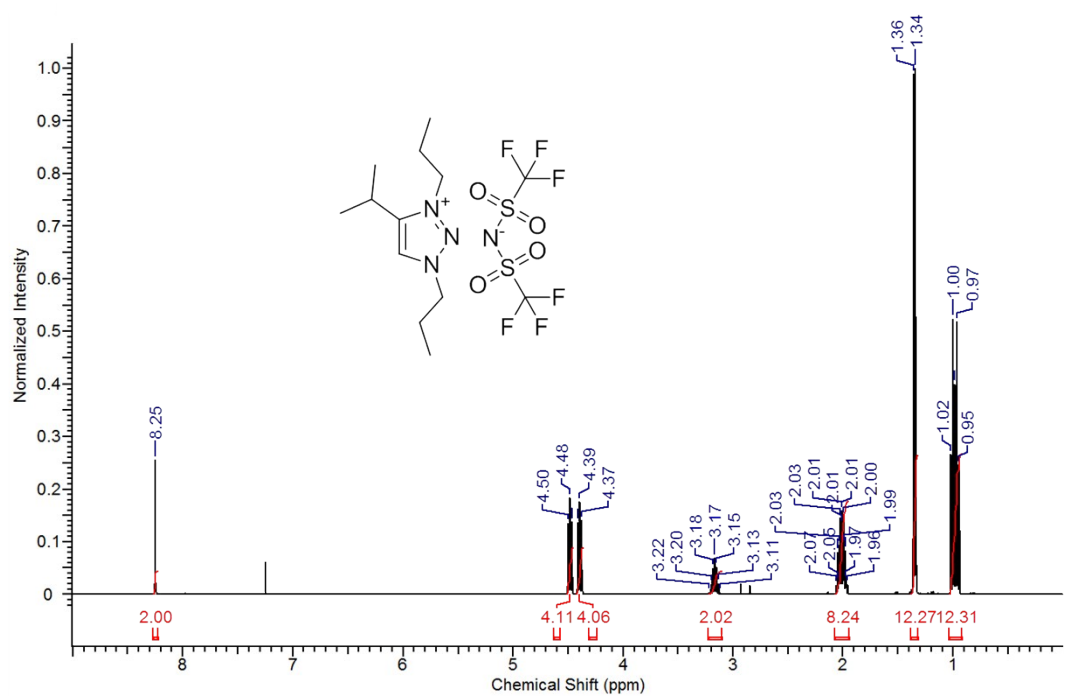
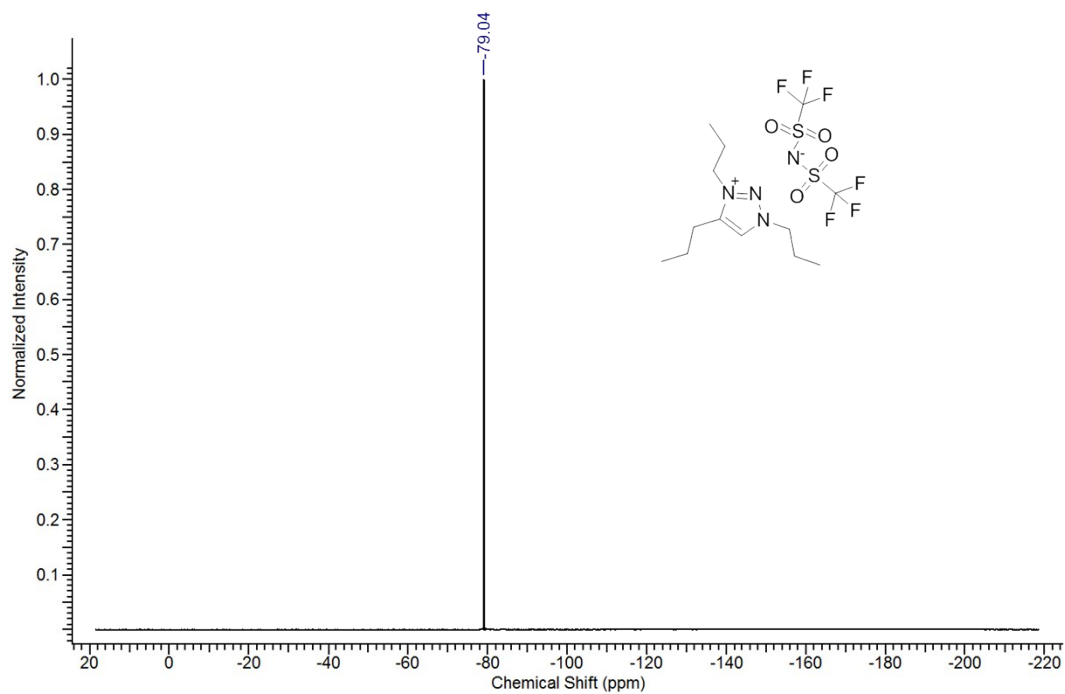
^{13}C NMR (CHLOROFORM-d, 75MHz): δ =149.2, 126.2, 125.0, 122.0, 117.7, 113.4, 58.5, 55.1, 24.2, 22.5, 21.8, 21.4

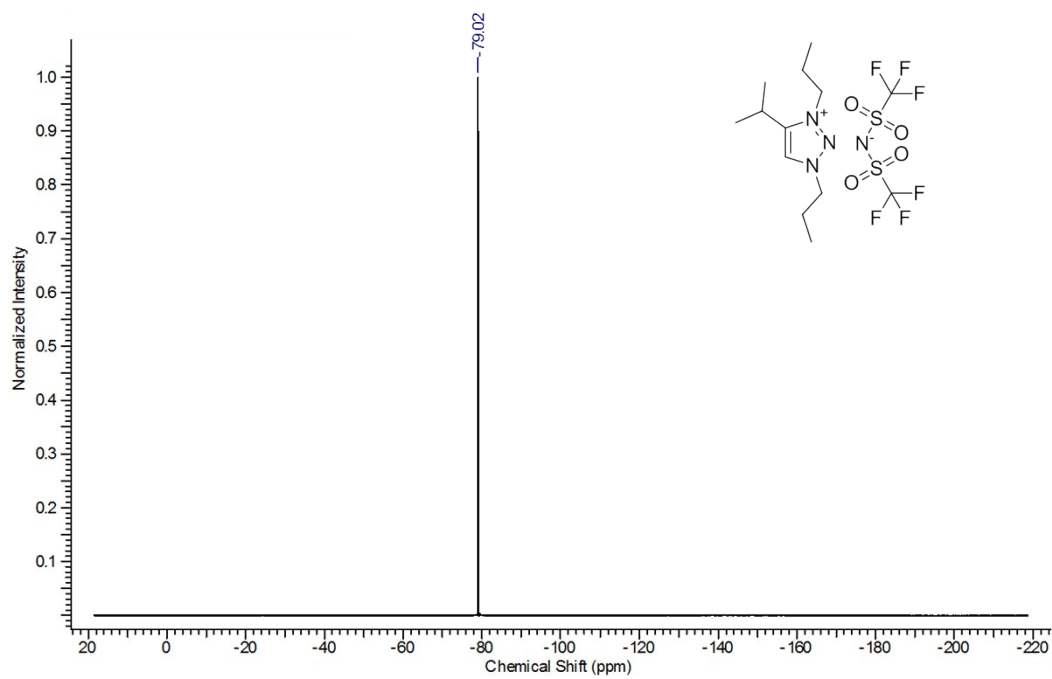
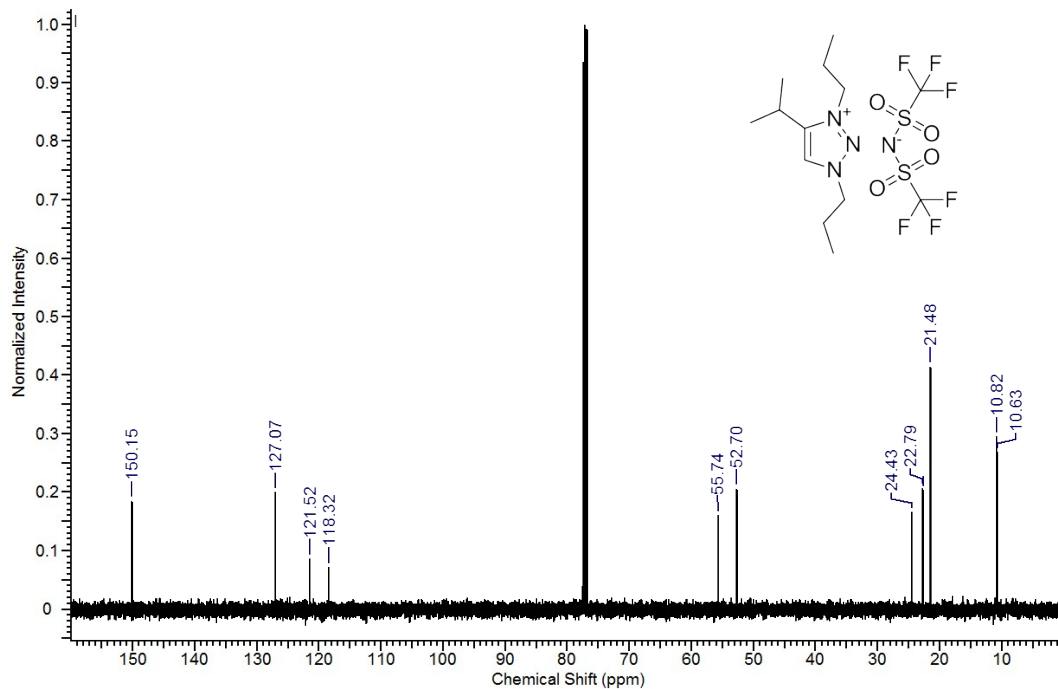
^{19}F NMR (Chloroform-d, 376 MHz): δ =-78.98

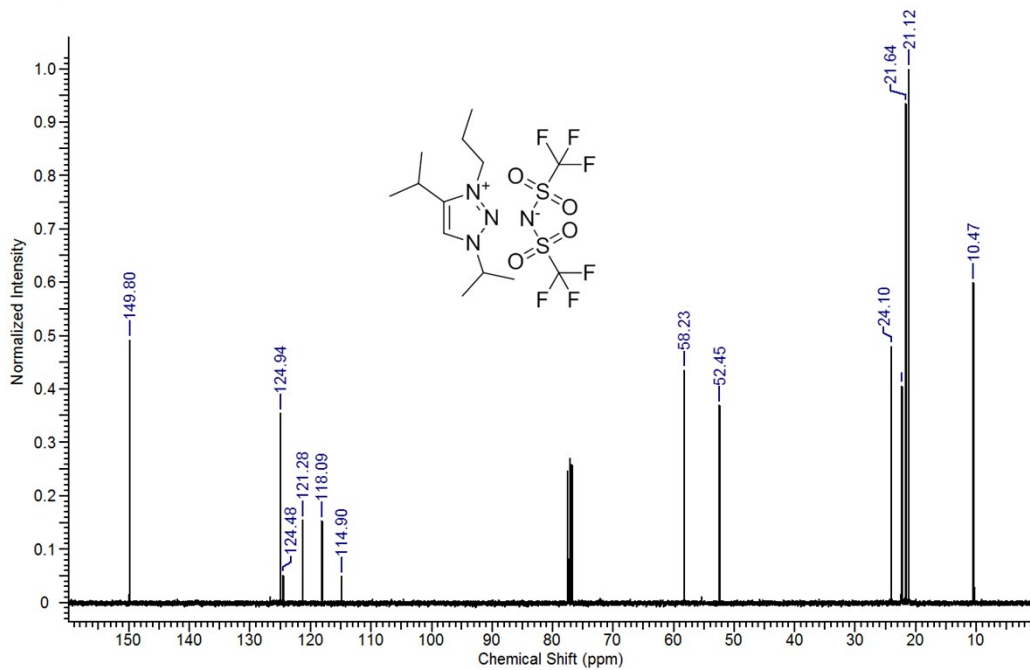
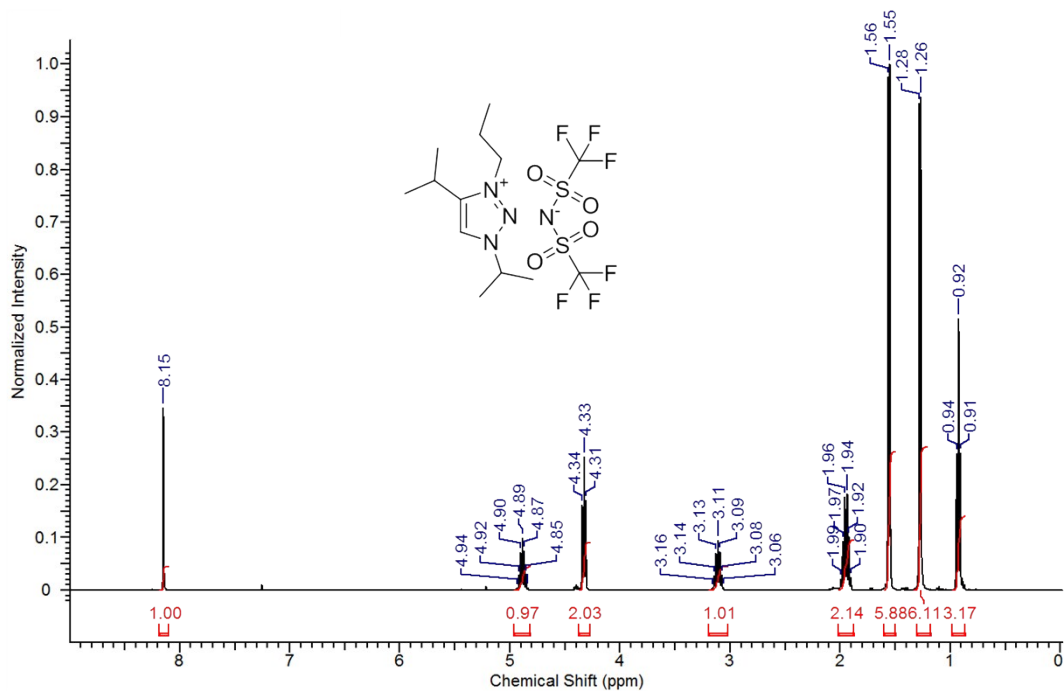
LCMS: calculated for $\text{C}_{11}\text{H}_{22}\text{N}_3$: 196 observed: 196 (cation)
 calculated for $\text{C}_2\text{F}_6\text{NO}_4\text{S}_2$: 280 observed: 280 (anion)

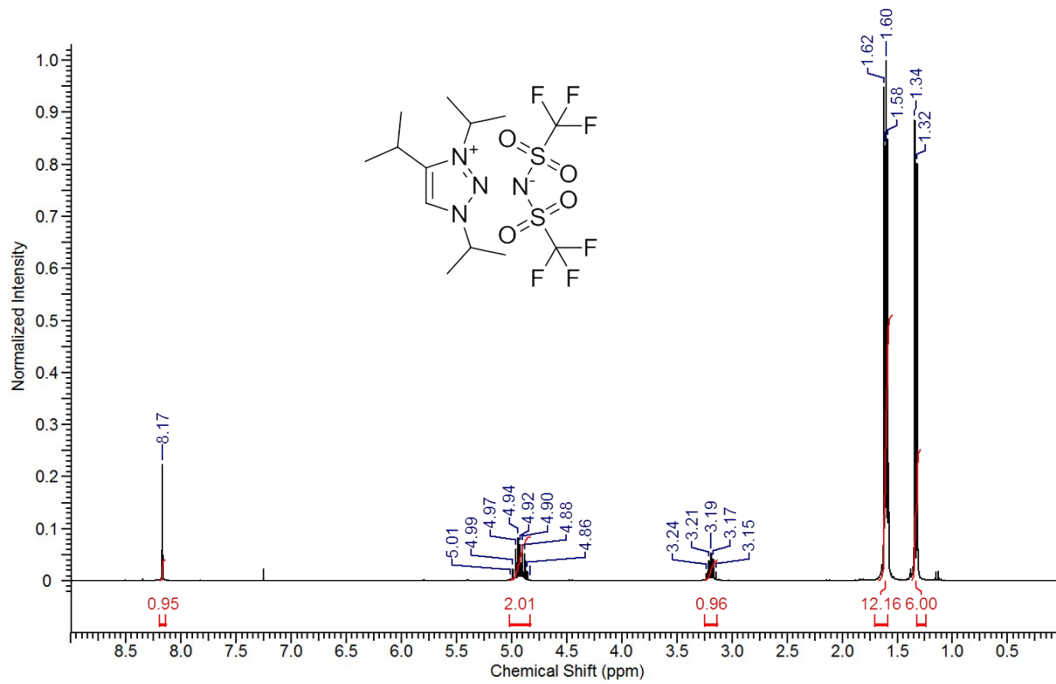
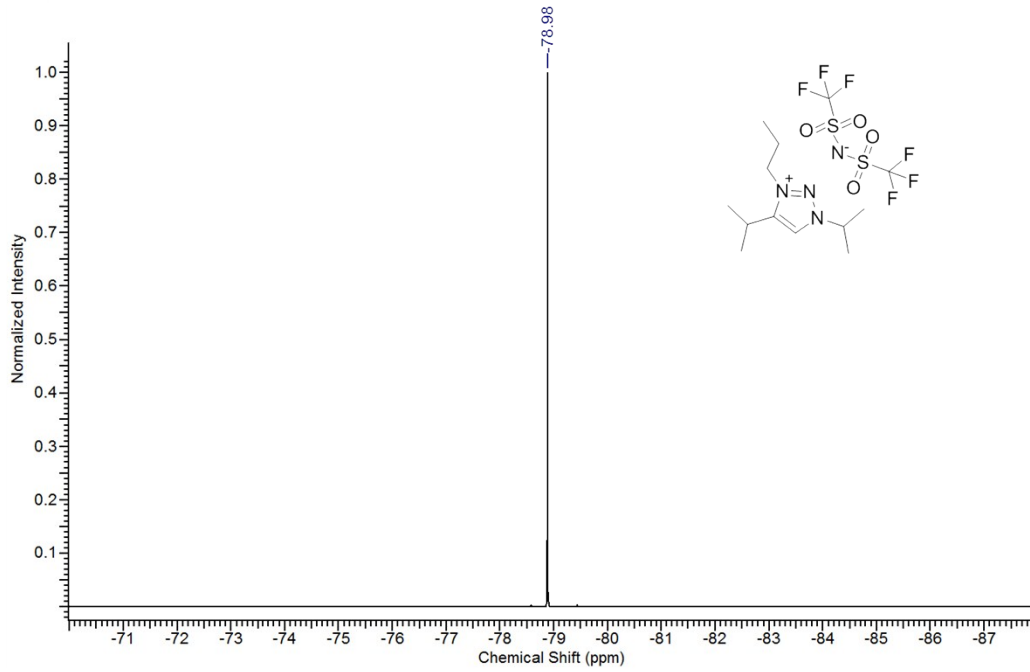
NMR SPECTRA OF ILS

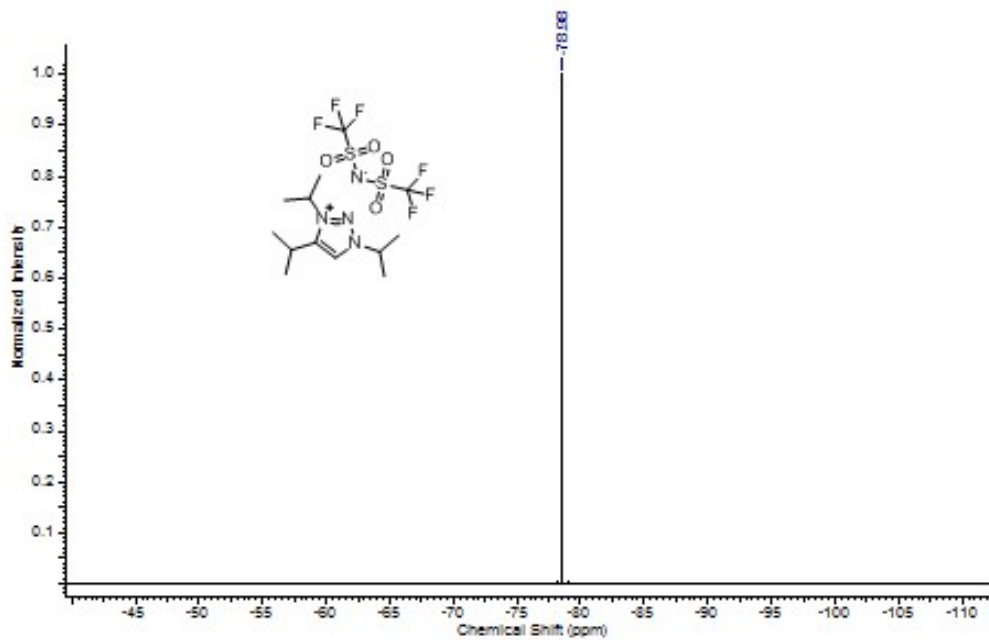
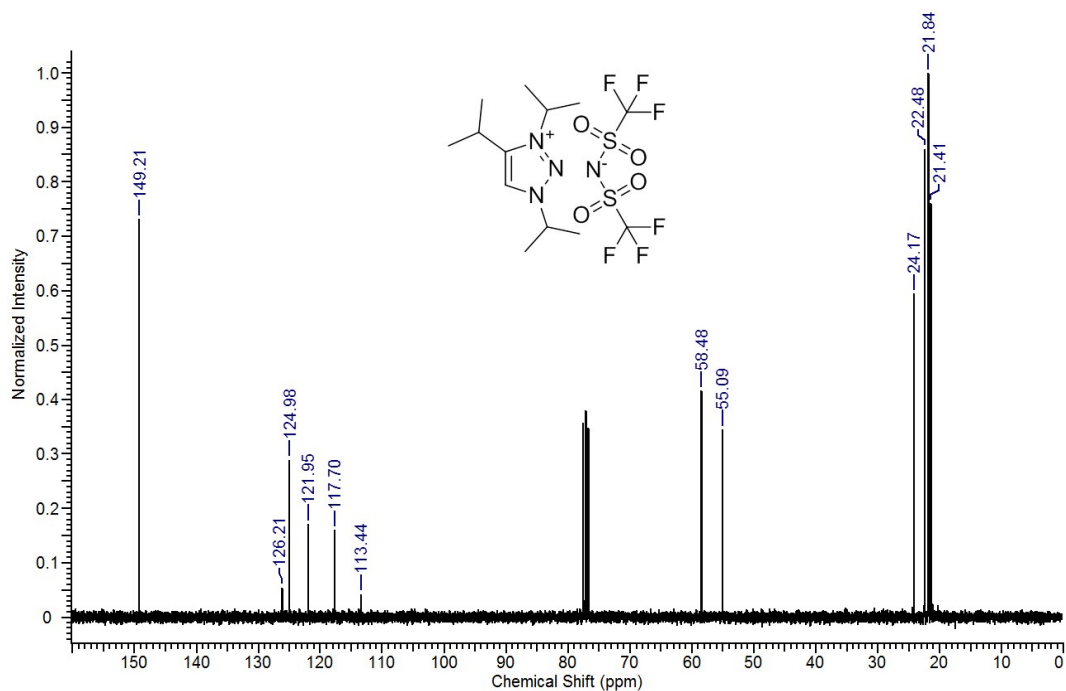












DSC and MDSC Scans

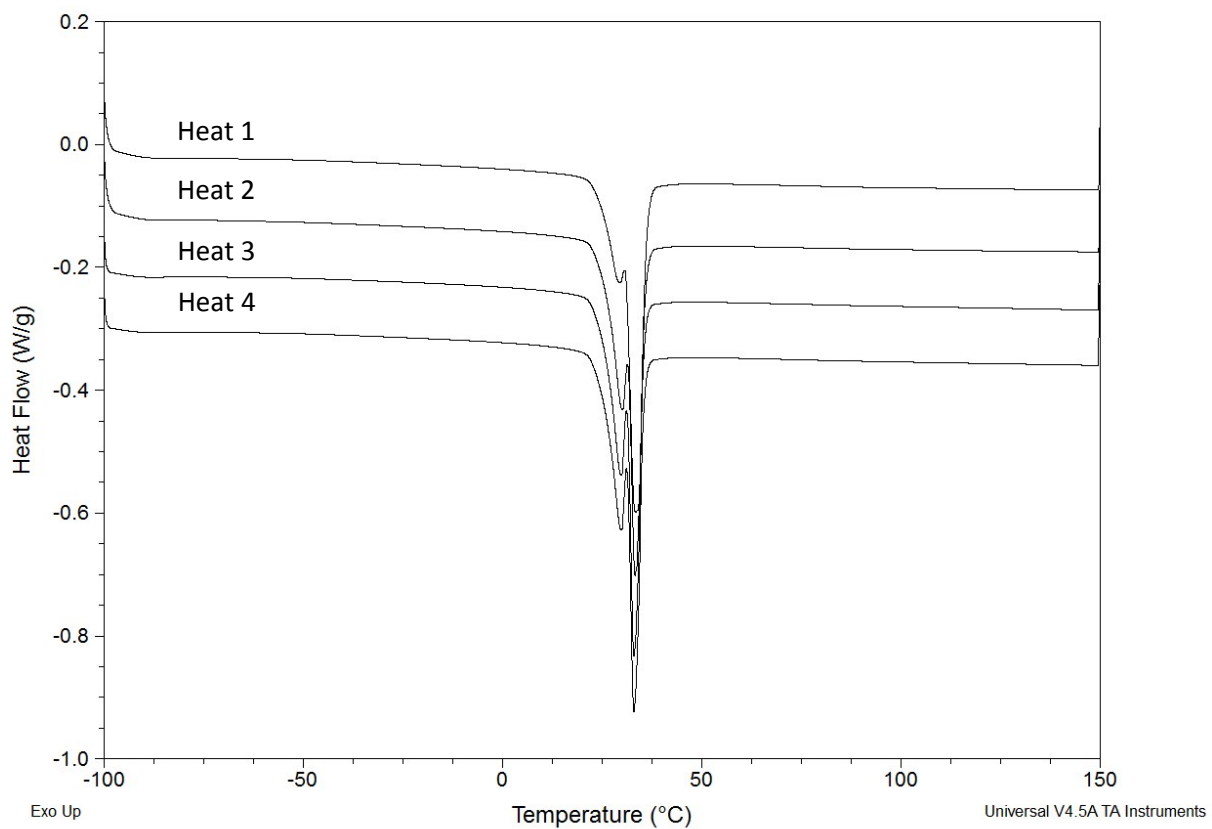


Figure SI.1: DSC heating curves for sample I (5 °C/min heating and cooling rate)

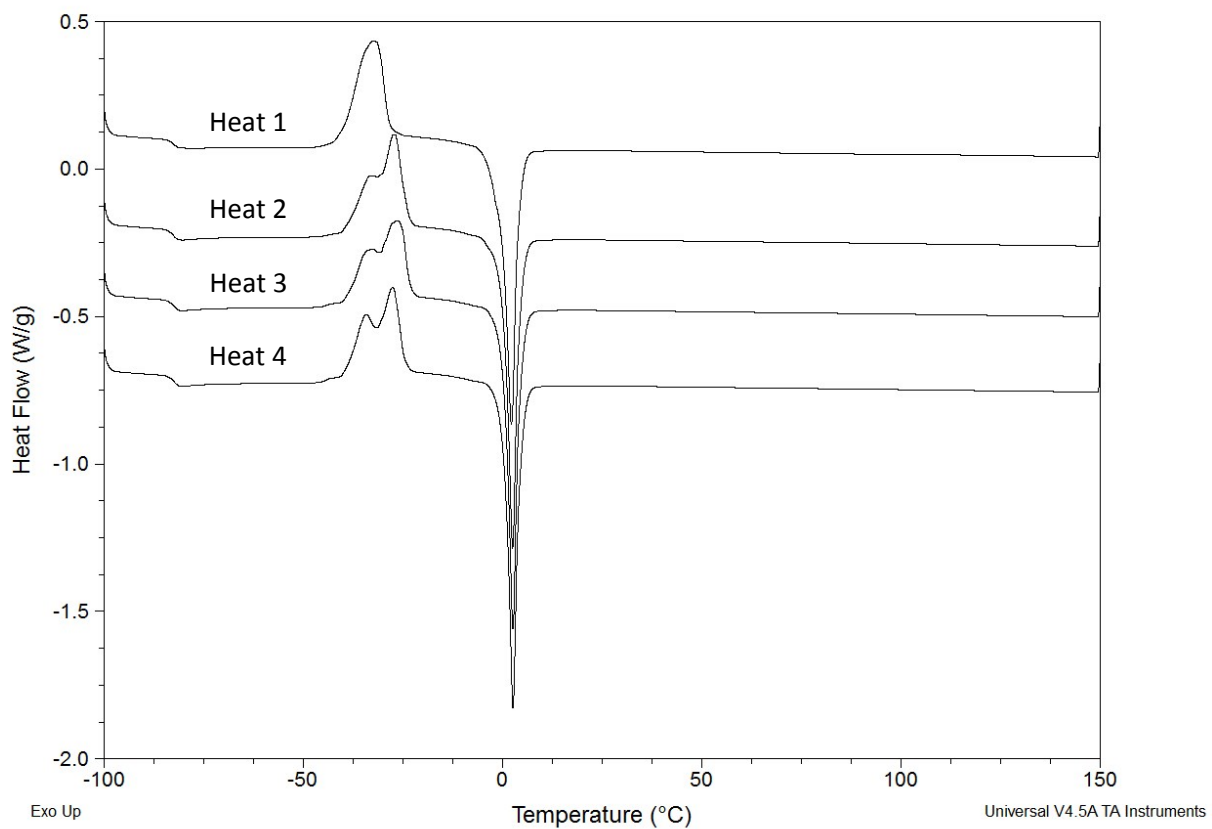


Figure SI.2: DSC heating curves for sample II (5 °C/min heating and cooling rate)

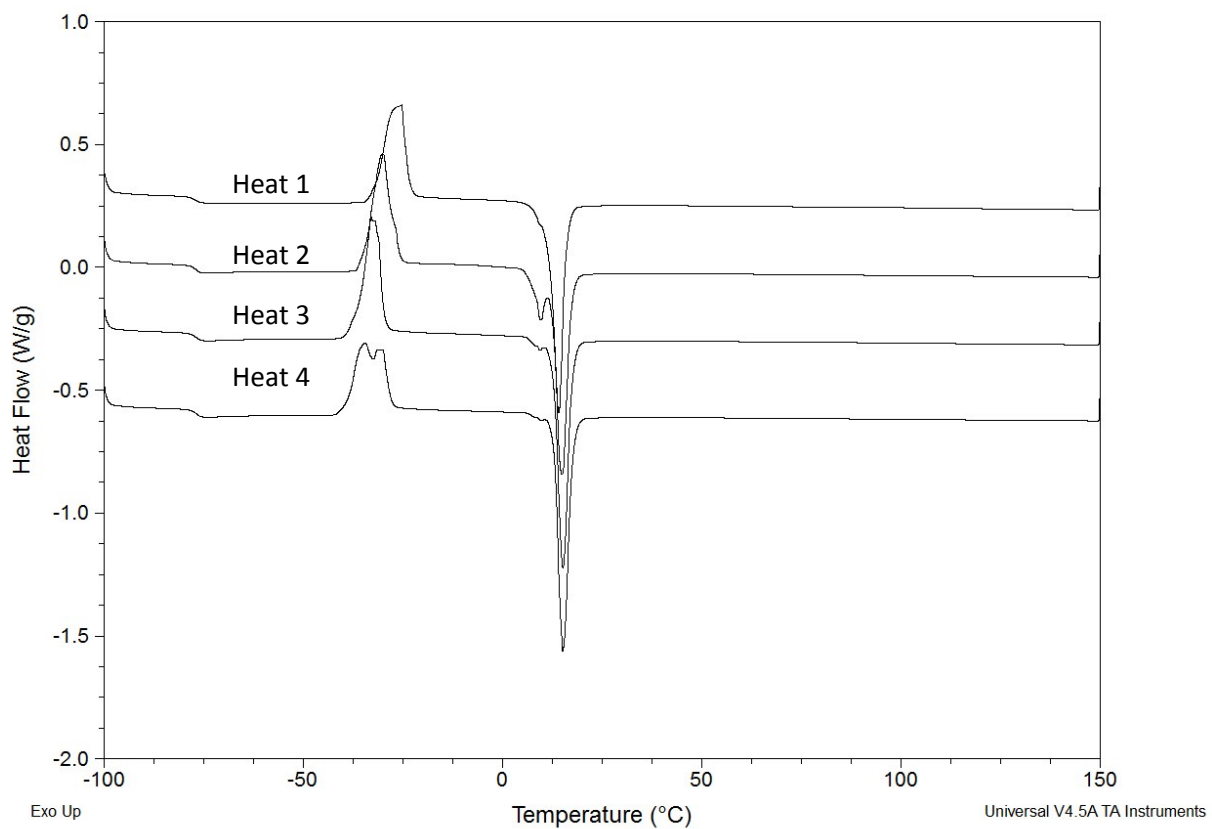


Figure SI.3: DSC heating curves for sample III (5 °C/min heating and cooling rate)

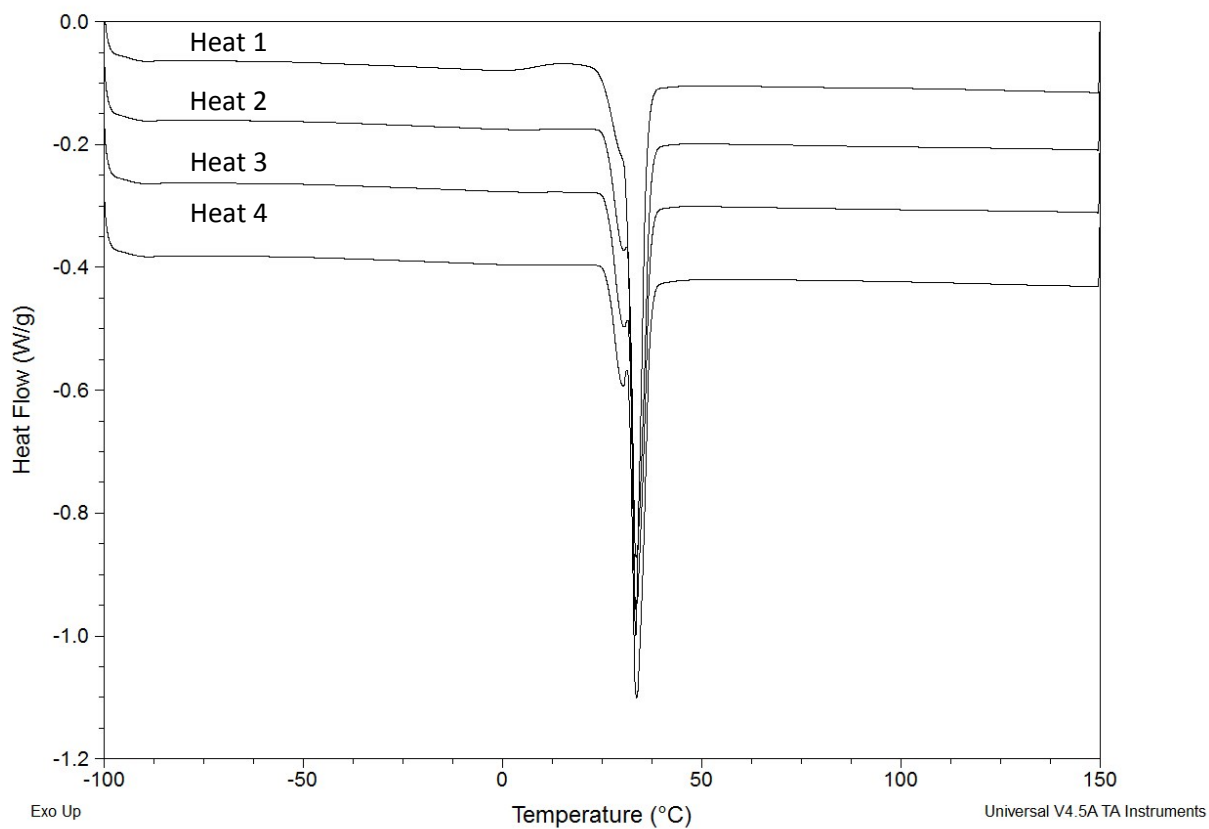


Figure SI.4: DSC heating curves for sample IV (5 °C/min heating and cooling rate)

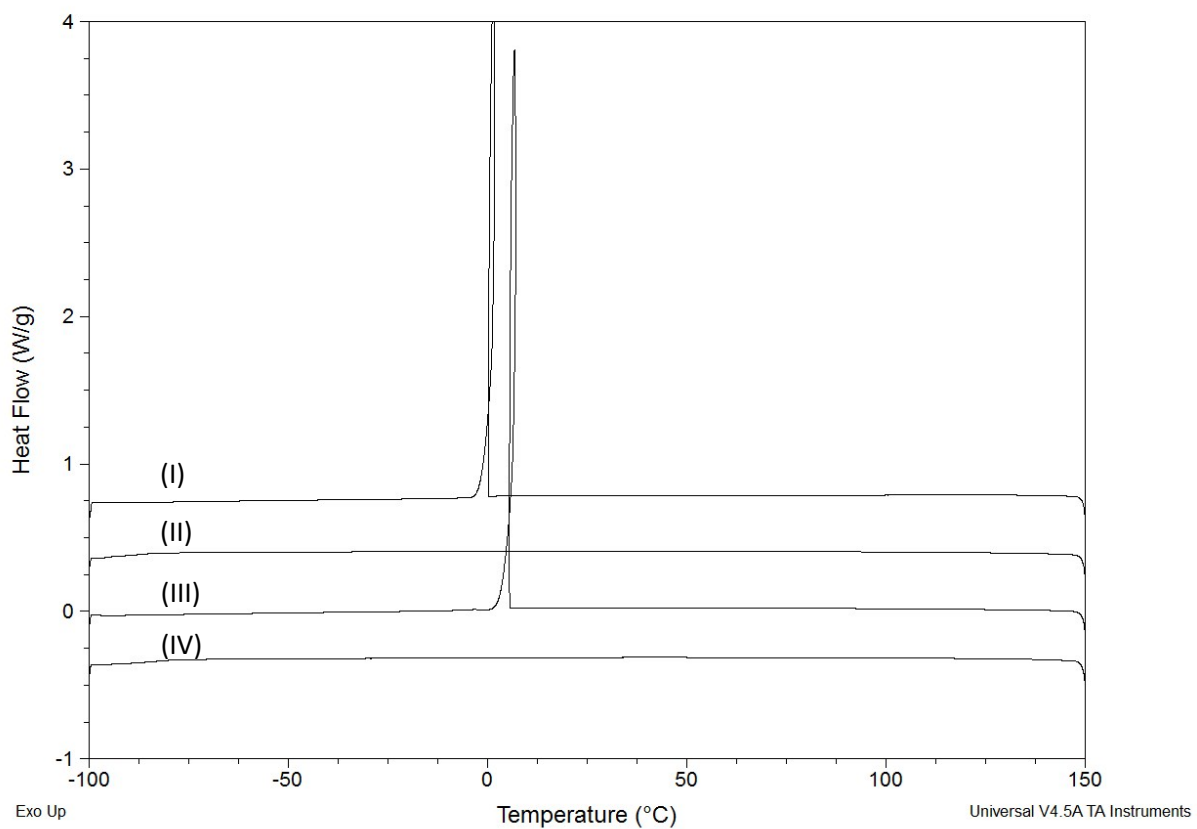


Figure SI.5: DSC Third cooling curve (5 °C/min heating and cooling rate)

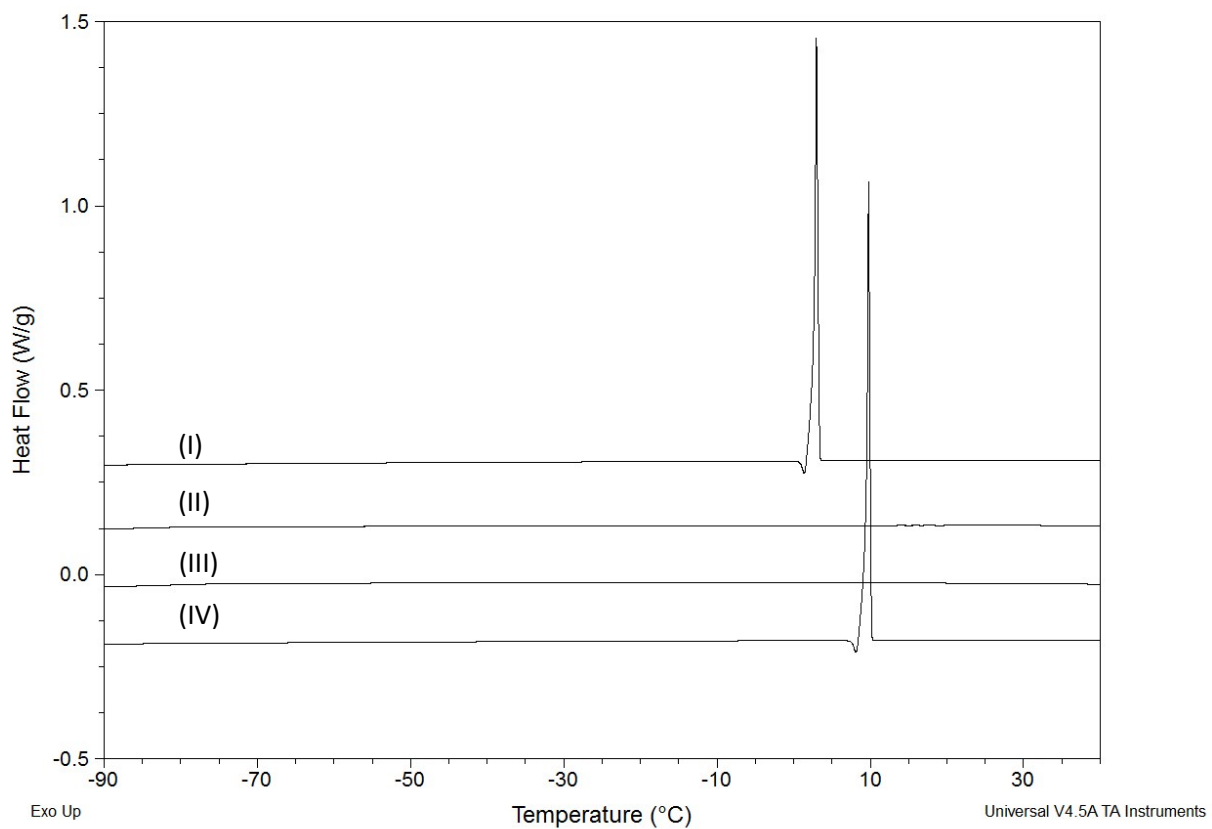


Figure SI.6: MDSC cooling curve (1 °C/min heating and cooling rate)

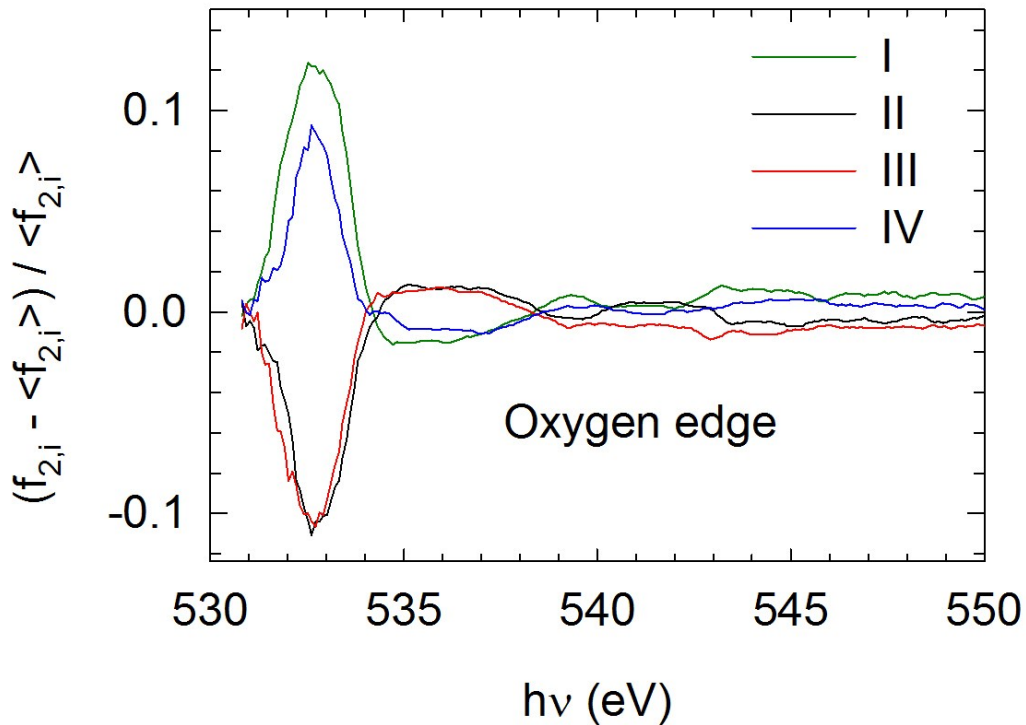


Figure SI.7. The relative size of changes in the O K edge spectra are obtained by normalizing the difference data in Figure 6c by the average, followed by smoothing. The pre-edge shoulder at 533 eV, difficult to see in Figure 6c, shows the largest relative NEXAFS change between samples at all edges studied, while the relative changes at the strong π^* peak at 536 eV are smaller.

REFERENCES

1. R. J. Thibault, K. Takizawa, P. Lowenheim, B. Helms, J. L. Mynar, J. M. J. Fréchet and C. J. Hawker, *J. Am. Chem. Soc.*, 2006, **128**, 12084-12085.
2. J. Stöhr, *NEXAFS Spectroscopy*, Springer Berlin Heidelberg, 1992.
3. A. K. Burrell, R. E. D. Sesto, S. N. Baker, T. M. McCleskey and G. A. Baker, *Green Chem.*, 2007, **9**, 449-454.