Protic Ionic Liquids with Fluorous anions: Physicochemical Properties and Self-Assembly Nanostructure

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Experimental Methods

All materials were used as supplied for the synthesis of the FPILs. The amine bases used were ethylamine (70% in water, Fluka Chemika), ethanolamine (99.5%, Sigma-Aldrich), diethylamine (99.5%, Aldrich), triethylamine (99.5%, Fluka), butylamine (99%, BDH), pyrrolidine (99%, MERCK), 2-pyrrolidinone (99.5%, Sigma-Aldrich), 1-methylimidazole (99%, Sigma). The fluorinated acids used were heptafluorobutyric acid (HPLC Grade, PIERCE) and pentadecafluorooctanoic acid (COCC). The acid used was octanoic acid (99.5%, Sigma-Aldrich).

There are many cations and anions available for incorporation into ionic liquids, which means that there a large number of potential FPILs. In this investigation, eight conventional hydrocarbon cations, Figure 1, and two fluorinated anions, Figure 2, were explored from an ionic liquids perspective to build an understanding of structure-property relationships using a methodology similar to previous research undertaken into the properties of non-fluorous PILs.[31, 43, 44]

The cations included were primary, secondary and tertiary ammonium cations, both with and without hydroxyl groups. The presence of a hydroxyl group on the alkyl chain has previously led to beneficial properties, particularly in producing PILs which are good amphiphile self-assembly media.[13, 38] In addition the cyclic and heterocyclic cations 1-methylimidazolium, 2-pyrrolidinonium and pyrrolidinium were chosen. Fluorinated anions were used in this investigation of trifluoroacetate, pentafluoropropionate, heptafluorobutyrate and pentadecafluorooctanoate. Unfortunately, incomplete proton transfer was observed in all reactions conducted with trifluoroacetic and pentafluoropropionic acid with butylamine due to the highly hydrophobic nature of the anion. This generated mixtures of salt and molecular acid and base which were not further studied. Through combinations of the other cations and anions, 11 new fluorous protic ionic liquids (FPILs) were synthesized and characterised. In addition, the equivalent non-fluorous PILs using the octanoate anion (EAO, EOAO and BAO) were prepared to enable direct comparison between the properties of the non-fluorous and fluorous ionic liquids. Please note that whilst they may have also enabled a better general comparison, due to the highly lachrymatory nature of butyric acid these ionic liquids were unable to be simply prepared.

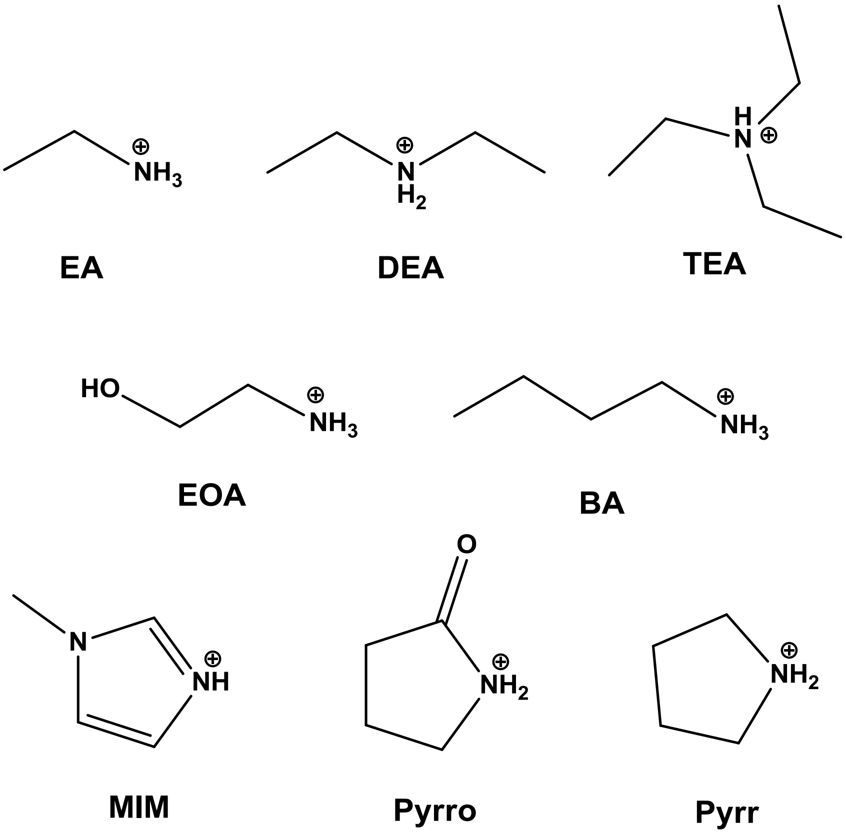


Figure S1. Structures and abbreviations of cations used: ethylammonium (EA), diethylammonium (DEA), triethylammonium (TEA), ethanolammonium (EOA), butylammonium (BA), 1-methylimidazolium (MIM), 2-pyrrolidonium (Pyrro), pyrrolidinium (Pyrr).

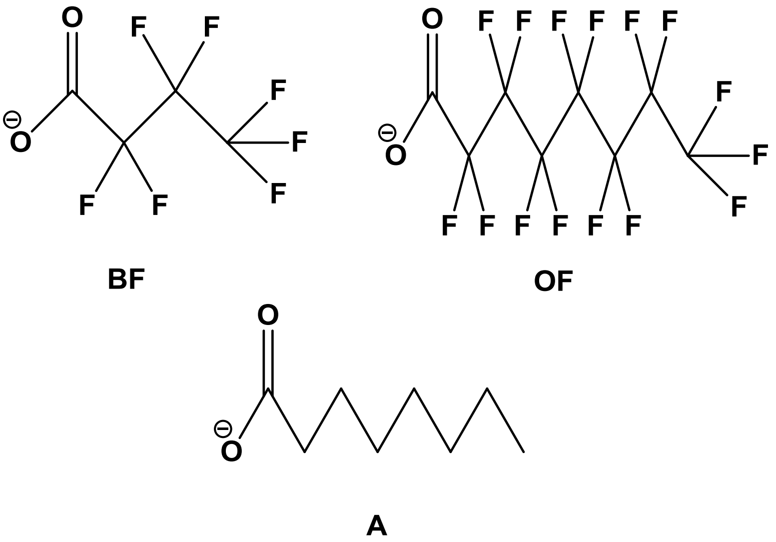
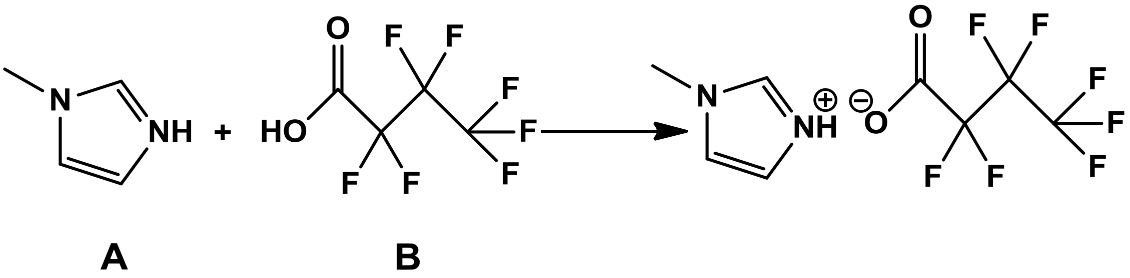


Figure S2. Chemical structures and abbreviations of the anions incorporated in the FPILs and PILs: heptafluorobutyrate (BF), pentadecafluorooctanoate (OF), octanoate (A).

General method for the synthesis of the FPILs



SCHEME S1: Synthesis of the FPIL 1-methylimidazolium heptafluorobutyrate (MIMBF)

A= ethylamine (EA), diethylamine (DEA), trimethylamine (TEA), ethanolamine (EOA), butylamine (BA), methylimidazole (MIM), 2-pyrrolidinone (Pyrro), pyrrolidine (Pyrr)
B= heptafluorobutyric acid (BF), pentadecafluorooctanoic acid (OF), octanoic acid (A).

The FPILs were synthesised using a similar approach to previously reported methods for the preparation of PILs, as shown representatively in Scheme 1.[31, 44] They were prepared by the slow addition of equimolar quantities of the appropriate acid using a dropping funnel to the appropriate amine contained in a round-bottom flask with stirring

<u>Preparation of 1-methylimidazolium heptafluorobutyrate (MIMBF)</u>

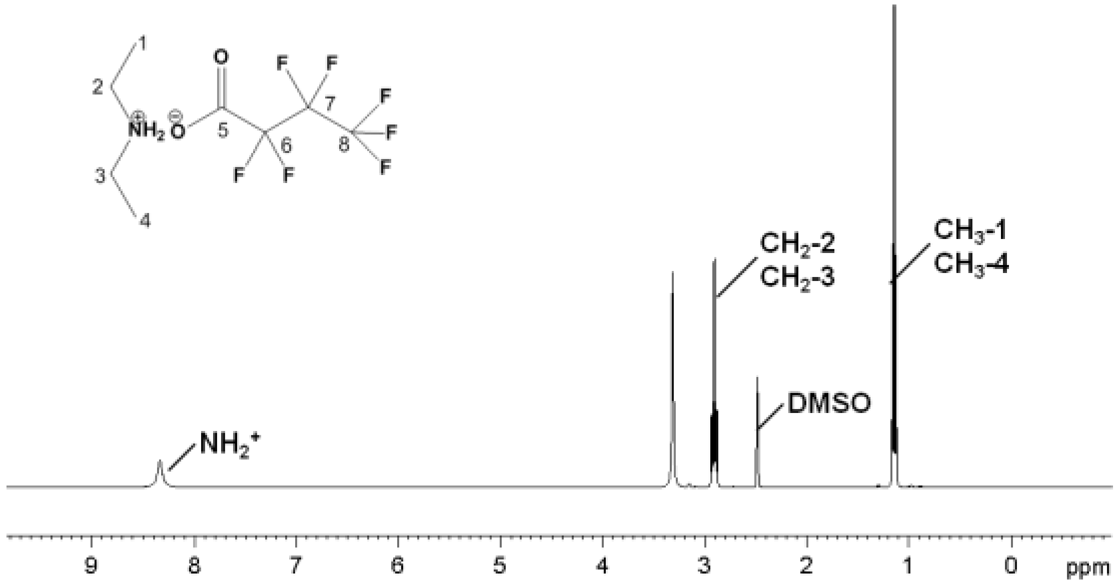
A solution of 1-methylimidazole (1.6422 g, 20mmol) in 20 ml of methanol was stirred in a 100 ml round-bottom flask. The temperature of the flask was maintained below -40 °C during reaction using a dry ice and ethanol bath. Then pentadecafluofooctanoic acid (8.2814 g, 20 mmol) was dissolved in 20 ml of methanol and added dropwise into the stirred reaction mixture using a dropping funnel over 5 hours. The reaction mixture was allowed to warm to room temperature and was stirred for a further 5 hours. Excess solvent was removed on a rotary evaporator and the final traces of water were removed by freeze-drying. Fresh samples were used for all experiments in order to minimize possible complications caused by potential amide formation and moisture uptake.

Characterization of PILs

Karl Fischer titration was used to determine the water content of the dried salts with a Metler Toledo DL39 Karl Fisher titrator. ^{1}H NMR (200.13 MHz) and ^{19}F NMR (188.31 MHz) spectroscopy were performed in deuterated DMSO at 298K using a Bruker BioSpin Av200 NMR spectrometer. ^{1}H- and ^{19}F-decoupled ^{13}C NMR (125.76 MHz) spectroscopy were performed on a Bruker BioSpin Av500 NMR spectrometer utilising a 4 mm X/H-F MAS probe. The samples were either static or spun at up to 5 kHz, the temperature was unregulated, high-powered decoupling was employed and chemical shifts were referenced to those of adamantane acquired in a separate experiment. Differential scanning calorimetry (DSC) was performed with a Mettler 3000 system under a nitrogen atmosphere. The samples were run in an aluminium pan in a sealed furnace, from -150 ^{o}C to 200 ^{o}C at a rate of 5 ^{o}C/min. The melting point were accurately determined at 2.5 ^{o}C/min. Thermal gravimetric analysis (TGA) was conducted with a Mettler Toledo 851 system, under a static nitrogen atmosphere, from 20 ^{o}C to 300 ^{o}C at a rate of 5 ^{o}C/min.

The density of the FPILs was measured using a Mettler Toledo Densito 30PX system. The refractive indices were measured with a RFM 81 refractometer maintained at 25 ^{o}C using an external water bath. Viscosity was measured with a SV-Series Vibro Viscometer using the AX-SV-37, a water jacket assembly was used to maintain a constant temperature of 25 ^{o}C. The surface tensions of the PILs were measured using the pendant drop method with a KSV CAM 200 instrument. The specific conductivity was measured using an in-house rig designed to determine the conductivity of small quantities of ILs under an inert atmosphere. This rig consisted of a conductivity meter (Agilent precision LCR meter 4284A) coupled with a PC controlled temperature controller (Eurotherm) in a custom-made air-tight stainless steel cell. The conductivity cell–electrode combination was calibrated with 0.01M KCl solutions from which a cell constant [L/A] of ~0.2 cm^{-1} was calculated, with L= the distance between the current carrying electrodes and A= the area of the electrodes.

(a) ^{1}H NMR spectrum



(b) ^{19}F NMR spectrum

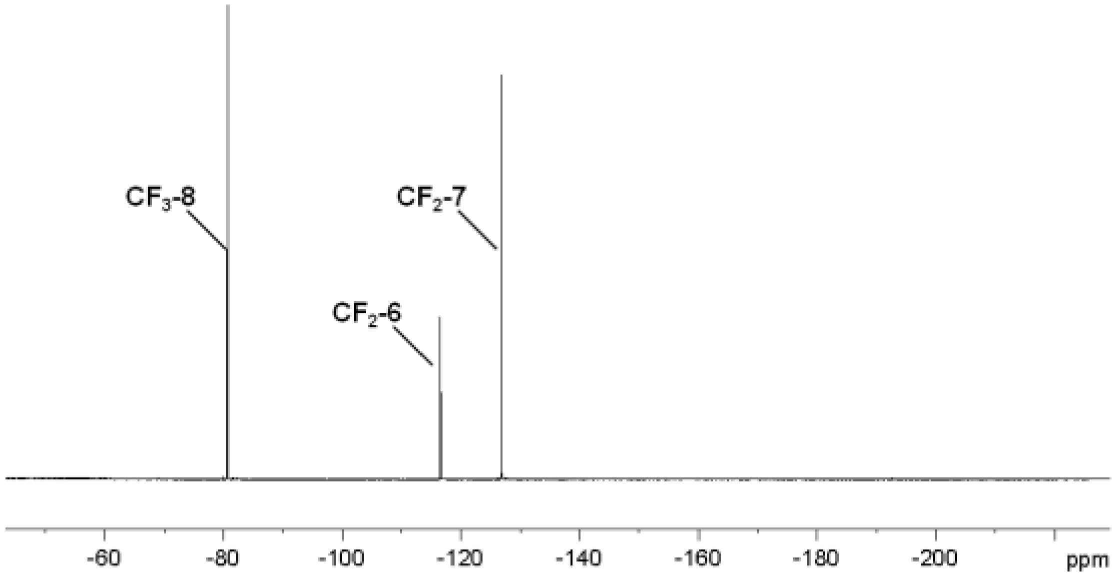
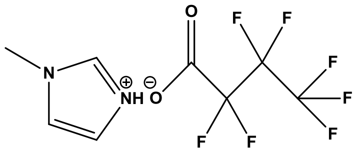


Figure S3. Representative NMR spectra for pure Diethylammonium heptafluorobutyrate (a) ^{1}H NMR spectrum (DMSO-d_6); (b) ^{19}F NMR spectrum (DMSO-d_6).

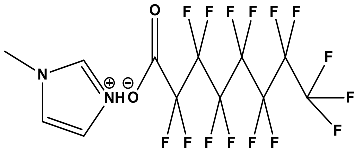
1-methylimidazolium heptafluorobutyrate (MIMBF)



White solid, yield 94.0%

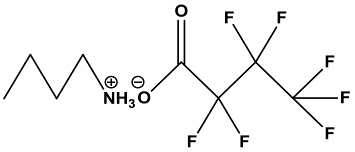
^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.92(s, 1H), δ 7.65 (s, 1H), δ 7.61 (s, 1H), δ 3.84(s, 3H) ppm; ^{19}F NMR (DMSO-d_6, 200 MHz): δ -80.54~-80.63(t, 3F), δ -116.22~-116.35(m, 2F), δ -126.64(s, 2F) ppm; ^{13}C NMR(^{19}F-HPDEC, 5kHz): δ 162.07, 136.86, 123.70, 118.43, 109.80, 35.29 ppm.

1-methylimidazolium pentadecafluorooctanoate (MIMOF)



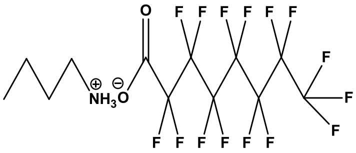
White solid, yield 97.4%
^{1}H NMR (DMSO-d_6, 200 MHz): δ 8.93(s, 1H), δ 7.63 (s, 1H), δ 7.58 (s, 1H), δ 3.83(s, 3H) ppm; ^{13}C NMR(^{19}F-HPDEC,5kHz): δ 161.70, 136.59, 121.79~111.57, 34.42 ppm.

Butylammonium heptafluorobutyrate (BABF)



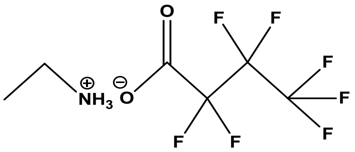
White solid, yield 97.7%
^{1}H NMR (DMSO-d_6, 200 MHz): δ 7.66(s, broad, 3H), δ 2.72 ~2.79 (t, J=7.34Hz, 2H), δ 1.24~1.53 (m, 4H), δ0.83~0.90(t, J=7.34Hz, 3H) ppm; ^{19}F NMR (DMSO-d_6, 200 MHz): δ -80.70~-80.79(t, 3F), δ -116.53~-116.67(m, 2F), δ -126.81(s, 2F) ppm; ^{13}C NMR(19F-HPDEC, 5kHz): δ 163.00, 118.53, 109.49, 40.29, 29.82, 19.90, 13.40 ppm.

Butylammonium pentadecafluorooctanoate (BAOF)



Yellow solid, yield 95.9%
^{1}H NMR (DMSO-d_6, 200 MHz): δ 7.77(s, broad, 3H), δ 2.74 ~2.82 (t, J=7.42Hz, 2H), δ 1.27~1.59 (m, 4H), δ 0.89~0.92(t, J=7.18Hz, 3H) ppm; ^{13}C NMR(19F-HPDEC, 5kHz): δ 163.12, 118.63, 114.14~109.17, 40.23, 29.78, 19.83, 13.12 ppm.

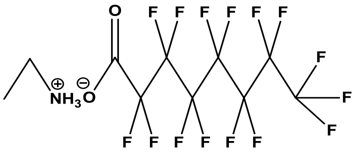
Ethylammonium heptafluorobutyrate (EABF)



White solid, yield 98.0%

^{1}H NMR (DMSO-d_6, 200 MHz): δ 7.71(s, 3H), δ 2.76~2.86 (m, 2H), δ 1.08~1.15(t, J=7.27Hz, 3H) ppm; ^{19}F NMR (DMSO-d_6, 200 MHz): δ -80.55~-80.64(t, 3F), δ -116.22~-116.35(m, 2F), δ -126.66(s, 2F) ppm; ^{13}C NMR (^{19}F-HPDEC, 5kHz): δ 162.70, 118.34, 109.34, 35.54, 12.28 ppm.

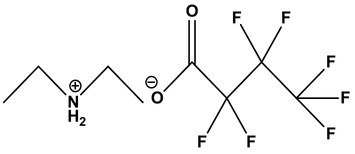
Ethylammonium pentadecafluorooctanoate(EAOF)



White solid, yield 97.0%

^{1}H NMR (DMSO-d6, 200 MHz): δ 7.63(s, broad, 3H), δ 2.75 ~2.86 (m, 2H), δ 1.08~1.11 (t, J =7.27Hz, 3H) ppm; ^{13}C NMR(^{19}F-HPDEC, 5kHz): δ 163.05, 118.56~110.07, 34.86, 11.74 ppm.

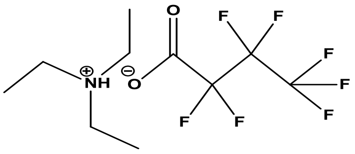
Diethylammonium heptafluorobutyrate (DEABF)



White solid, yield 91.1%

^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.34(s, broad, 2H), δ 2.88 ~2.94 (m, 4H), δ 1.12~1.16 (t, *J* =7.28Hz, 6H) ppm; ^{19}F NMR (DMSO-d_6, 200 MHz): δ -80.62~-80.71(t, 3F), δ -116.41~-116.54(m, 2F), δ -126.75(s, 2F) ppm; ^{13}C NMR(^{19}F-HPDEC, 5kHz): δ 162.07, 118.88, 109.56, 42.65, 10.30 ppm.

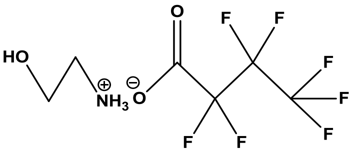
Triethylammonium heptafluorobutyrate (TEABF)



White solid, yield 93.6%

^{1}H NMR (DMSO-d_6, 200 MHz): δ 9.31(s, broad, 1H), δ 3.01~3.15 (m, 6H), δ 1.12~1.19 (t, J=7.28Hz, 9H) ppm; ^{19}F NMR (DMSO-d_6, 200 MHz): δ -80.58~-80.67(t, 3F), δ -116.34~-116.39(m, 2F), δ -126.70(s, 2F) ppm; ^{13}C NMR (^{19}F-HPDEC, 5kHz): δ 161.38, 118.79, 109.75, 46.91, 8.32 ppm.

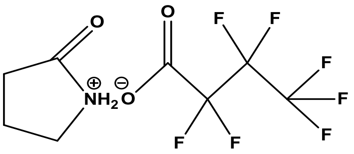
Ethanolammonium heptafluorobutyrate (EOABF)



White solid, yield 98.2%

^{1}H NMR (DMSO-d_6, 200 MHz): δ 7.71(s, 3H), δ 5.13(s, H) δ 3.53~3.59 (m, 2H), δ 2.81~2.86 (t, J=5.36Hz, 2H) ppm; ^{19}F NMR (DMSO-d_6, 200 MHz): δ -80.63~-80.72(t, 3F), δ -116.40~-116.53(m, 2F), δ -126.74(s, 2F) ppm; ^{13}C NMR (^{19}F-HPDEC, 5kHz): δ 163.39, 118.20, 109.33, 58.20, 42.31 ppm.

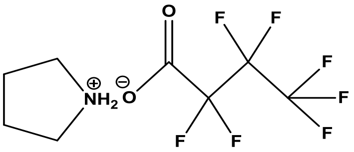
2-pyrrolidinonium heptafluorobutyrate (PyrroBF)



Yellow liquid, yield 64.0%

^{1}H NMR (DMSO-d_6, 200 MHz): δ 7.36 (s, broad, 2H), δ 3.15~3.22 (t, J=6.96Hz ,2H), δ 1.88~2.10 (m, 4H) ppm; ^{19}F NMR (DMSO-d_6, 200 MHz): δ -80.83~-80.92(t, 3F), δ -119.24~-119.37(m, 2F), δ -127.39(s, 2F) ppm; ^{13}C NMR(^{19}F-HPDEC, 5kHz): δ 181.58, 160.99, 118.36, 109.10, 108.66, 43.42, 30.25, 20.57 ppm.

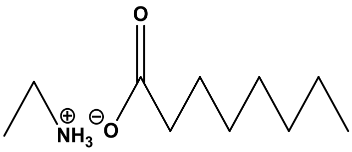
Pyrrolidinium heptafluorobutyrate (PyrrBF)



Yellow liquid, yield 94.3%

^{1}H NMR (DMSO-d_6, 200 MHz): δ 3.05~3.12 (m, 4H), δ 1.78~1.85 (m, 4H) ppm; ^{19}F NMR (DMSO-d_6, 200 MHz): δ -80.65~-80.74(t, 3F), δ -116.44~-116.57(m, 2F), δ -126.77(s, 2F) ppm; ^{13}C NMR (^{19}F-HPDEC, 5kHz): δ 162.25, 118.56, 109.57, 45.04, 24.08 ppm.

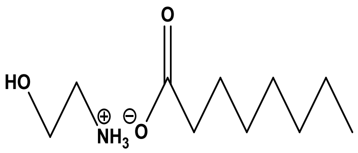
Ethylammonium octanoate (EAOA)



Yellow liquid, yield 98.0%

^{1}H NMR (DMSO-d_6, 200 MHz): δ 6.56 (s, broad, 3H), δ 2.63~2.74 (m, 2H), δ 1.95 ~2.03 (t, J=7.24Hz, 2H), δ 1.39~1.46 (t, J=7.07Hz, 2H),δ 1.21 (s, 8H), δ 1.03~1.10 (t, J=,7.21Hz, 3H), δ 0.80 ~0.87 (t, J=6.52Hz, 3H) ppm; ^{13}C NMR (DMSO-d_6, 200 MHz): δ 177.18, 48.96, 37.2, 34.35, 31.73, 29.51, 29.09, 26.23, 22.52, 14.32, 13.90 ppm.

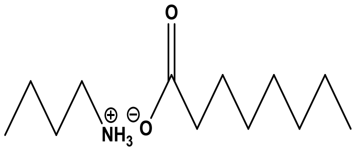
Ethanolammonium octanoate (EOAOA)



Yellow solid, yield 99.0%

^{1}H NMR (DMSO-d$_{6}$, 200 MHz): δ 4.33 (s, broad, 3H), δ 3.38~3.43 (t, J=,5.54Hz, 2H), δ 2.60~2.66 (t, J =5.54Hz, 2H), δ 2.00 ~2.08 (t, J=,7.27Hz, 2H), δ 1.40~1.47 (t, J=,7.09Hz, 2H),δ 1.21 (s, 8H), δ 0.80 ~0.87 (t, J=,6.50Hz, 3H) ppm; ^{13}C NMR (DMSO-*d*$_{6}$, 200 MHz): δ 177.53, 59.81, 42.56, 37.15, 31.72, 29.49, 29.09, 26.12, 22.52, 14.35 ppm.

Butylammonium octanoate (BAOA)



Yellow liquid, yield 98.5%

^{1}H NMR (DMSO-*d*$_{6}$, 200 MHz): δ 5.74 (s, broad, 3H), δ 2.57 ~2.64 (t, J=,6.93Hz, 2H), δ 1.95 ~2.02 (t, J=,7.26Hz, 2H), δ 1.29~1.49 (m, 6H),δ 1.21 (s, 8H), δ 0.80 ~0.88 (m,6H) ppm; ^{13}C NMR (DMSO-*d*$_{6}$, 200 MHz): δ177.37, 48.94, 37.47, 31.75, 30.77, 29.55, 29.14, 26.32, 22.53, 19.77, 14.29, 13.94 ppm.

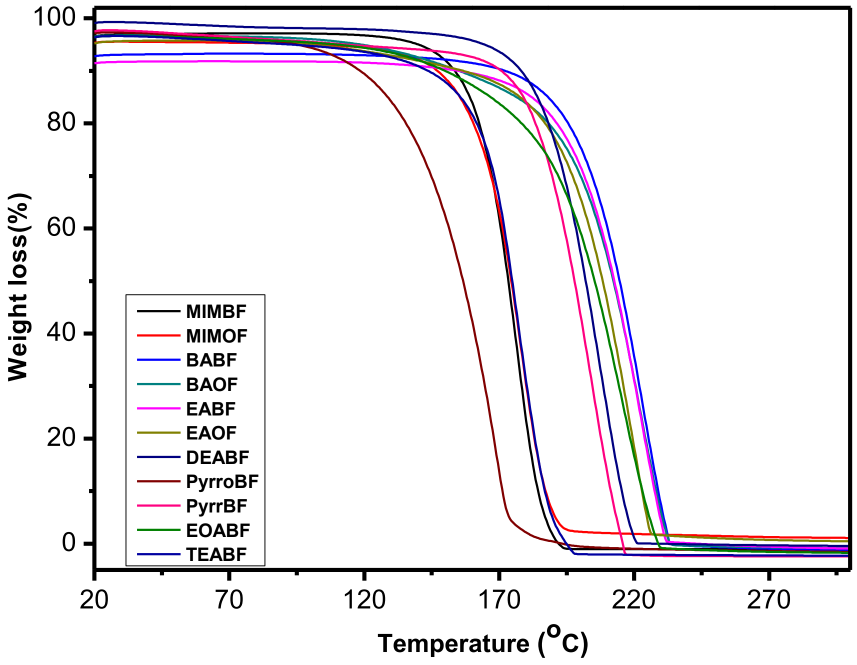


Figure S1. TGA traces at 5 deg C/min of FPILs