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Publication Date

2019-12-01

DOI

10.1016/j.molliq.2019.111677

Peer reviewed

Fluoroalkyl-functional imidazoles and imidazolium–based ionic liquids prepared via thiol-ene/yne click chemistry

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ABSTRACT

A fluorinated thiol was systematically investigated against a diverse set of –ene- and –yne-bearing imidazole and imidazolium substrates in the pursuit of new cation-fluorinated, omniphobic (hydrophobic and oleophobic) ionic liquids for aerospace applications. Compounds were prepared using UV-initiated click chemistry at quantitative conversion and purified with relative ease. Seven ionic liquids were synthesized and have isolated yields ranging

from 74% to greater than 99%. Five of the new cation-fluorinated ionic liquids are hydrophobic and two of which are liquids at room temperature. In addition to hydrophobicity, the seven ionic liquids' solubilities were qualitatively examined across a wide spectrum of conventional organic solvents. Of note, the majority of the prepared ionic liquids are insoluble in water and hexanes yet soluble in methanol, acetone, acetonitrile, and dichloromethane. In addition to intriguing solubility properties, the ionic liquids in this study have high densities without the incorporation of heavy atoms, ranging from 1.596 to 1.924 g cm^{-3}. The fluorinated salts also show good short-term thermal stability in air, ranging from 215 °C to 320 °C. Other relevant characterization methods include spectroscopy, thermal analysis, and physical property measurements where appropriate. The X-ray crystal structure of a divalent, cation-fluorinated ionic liquid from this study was also obtained and shows unique fluorous domains in the extended structure, providing valuable insight into the materials' physical properties. This work highlights a family of compounds moving towards omniphobic ionic liquids yielding potential possibilities for future applications.

1. INTRODUCTION

Ionic liquids are a ubiquitous class of compounds due to their attractive and tunable physiochemical properties and plethora of potential applications.[1] The conventional definition of an ionic liquid is a salt that melts

at a temperature lower than 100 °C. Room temperature ionic liquids are especially attractive because of their liquid nature under most standard laboratory conditions. Notable applications include reaction solvent media,[2] impurity extraction agents,[3] and crystal engineering additives in the pharmaceutical industry.[4] There are a number of significant potential applications for ionic liquids within the aerospace industry including repellent coatings, anti-icing agents, and lubricants. In general, the materials need to survive in harsh operational conditions such as high temperatures, corrosive environments, or oxidative atmospheres. Therefore, some of the desirable properties would include omniphobicity (both hydrophobicity and oleophobicity), low vapor pressure, high thermal and chemical stability, as well as good processability (e.g. low viscosity). While there are a number of existing hydrophobic ionic liquids, additional work is needed in order to capture the required physical and chemical properties needed for a given application.

A promising avenue for exploration in this area is thiol-ene and thiol-yne “click” reactions—well-studied pathways that have produced new classes of compounds of significant importance.[5] This type of organic transformation is useful to the synthetic chemist owing to the generally high rates of reactions, yields, and stereoselectivity (anti-Markovnikov). Click chemistry has been utilized in a diverse set of applications, such as surface modification (e.g. films, coatings, lithography),[6] polymer functionalization,[7] and bioconjugation.[8] Although there are practical limitations on the types of

alkenes, alkynes, and thiols that can be utilized, the theoretical range of compounds that can be prepared via this chemistry is virtually limitless.

A relatively new area of exploration is the synthesis of novel ionic liquids via thiol-ene and thiol-yne click chemistry. Several bio-inspired works have been reported in recent years owing to the lipid-like properties of these compounds.[9,10] An area that is largely unexplored is the preparation of omniphobic ionic liquids using thiol-ene/yne click chemistry.[11,12] While there are already several commercially-available hydrophobic ionic liquids, they typically suffer from poor solubility in organic solvents. A synthetic strategy for obtaining hydrophobic ionic liquids is to incorporate fluorinated anions,[13] commonly bis(trifluoromethylsulfonyl)imide (Tf_2N^-) and hexafluorophosphate (PF_6^-), or cations with fluorinated arms or "ponytails."[14-17] It should be noted that cation-fluorinated moiety development has received considerably less attention, probably due to high materials cost and synthetic challenges.[14,18-19] Fluorinated ionic liquids should have lower surface energies relative to their hydrocarbon analogues, offering an intriguing new array of potential omniphobic applications.

The work presented here is a step towards omniphobic ionic liquids prepared using thiol-ene and thiol-yne click chemistry. A fluorinated thiol was systematically investigated against a diverse set of –ene- and –yne-bearing substrates based on imidazole and imidazolium salts and were extensively characterized using chemical, physical, and thermal methods. Seven new ionic liquids with a fluorinated cation component are reported and two are

liquids at room temperature. In addition to their hydrophobicity, the seven ionic liquids' solubility properties were qualitatively examined across a wide spectrum of conventional organic solvents. Of note, the majority of the prepared ionic liquids are insoluble in water, toluene, and hexanes yet soluble in methanol, acetonitrile, tetrahydrofuran, and dichloromethane. Although not omniphobic in the purest sense, the materials' solubility in some organic solvents with varying, moderate polarity enhances their processability potential for future applications such as spin-coating or the manufacturing of thin-films. Furthermore, the high short-term thermal stability of these materials makes them especially interesting to the aerospace industry where materials frequently need to survive harsh operating conditions such as extreme temperatures or corrosive environments. This work highlights a family of compounds moving towards omniphobic ionic liquids yielding intriguing possibilities for future applications.

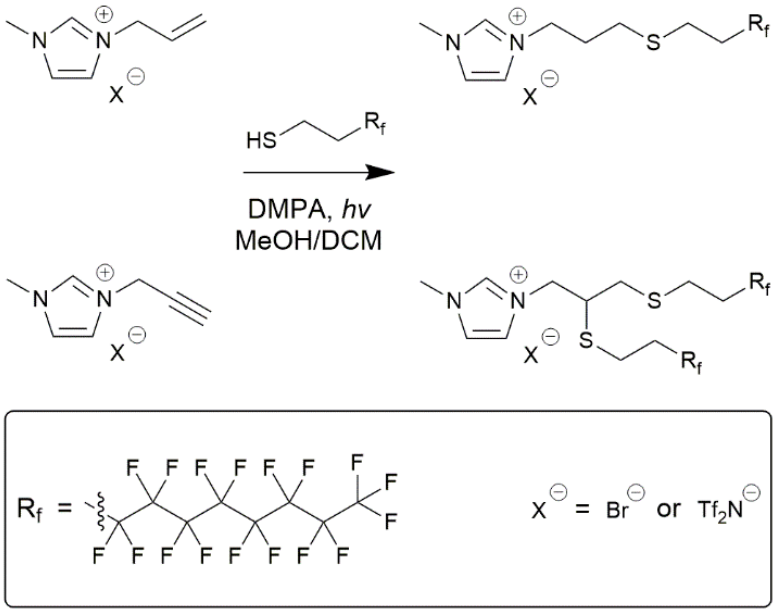
2. RESULTS AND DISCUSSION

2.1 Synthesis and Purification

Representative UV-initiated thiol-ene and thiol-yne reaction schemes are presented in Scheme 1, showing the facile method in which a fluorous functional group can be attached to an ene- or yne-functional imidazolium species. This route avoids the use of a fluoroalkyl iodide as the source of the

fluorinated moiety, as has been reported previously as a preferred route.[20] The iodide route involves a light-sensitive reaction and leads to a product that is susceptible to degradation upon storage. A series of ene- and yne-functional imidazole-based compounds were selected to explore the structure-property relationships between the differing architectures that govern their physiochemical properties.

Scheme 1. Representative formation of fluorinated imidazolium compounds through thiol-ene (top) and thiol-yne (bottom) click chemistry, with 1*H*,1*H*,2*H*,2*H*-pefluorodecanethiol as the fluorinated thiol. DMPA = 2,2-dimethoxy-2-phenylacetophenone.



The precursors selected are presented in Figure 1, and were synthesized from previous literature if not commercially available. The

imidazoles have widely varying functionalities, exhibiting neutral compounds (**1**, **2**, and **4**[21]), their methyl salts (**3a**,[22] **3b**,[23] **5a**,[24] and **5b**[25]), and difunctional species (**6a**,[22] **6b**,[26] **7a**,[27] **7b**, **8a**, and **8b**). Precursor compounds **7b**, **8a**, and **8b** are first reported here. All precursors were prepared in moderate to good yields, and detailed characterization data of new materials are presented in the Experimental section and Supporting Information.

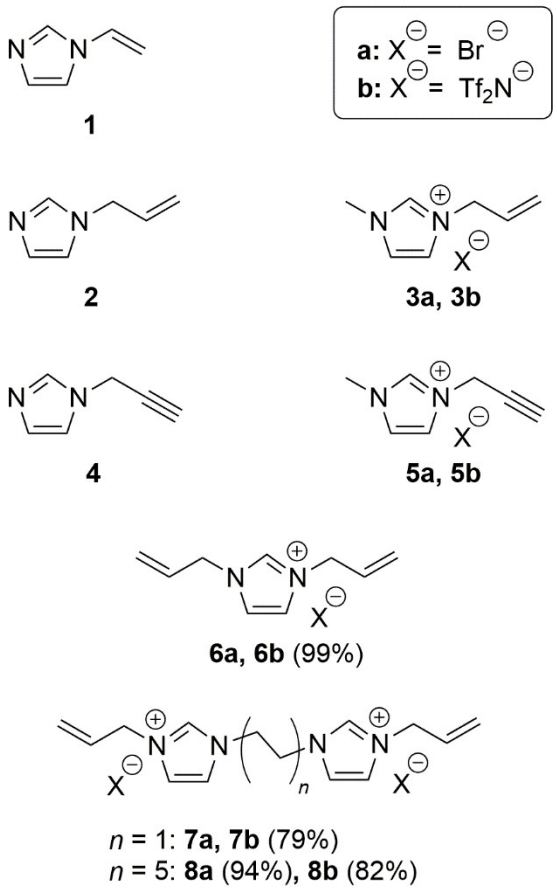


Figure 1. Substrate scope for photoinitiated thiol-ene/yne click preparation of fluorinated imidazole and imidazolium compounds. Isolated yields are given in parentheses for previously unreported compounds.

The architecture and synthesis of this class of compounds—modular ionic liquids via click chemistry—was established by Mirjafari *et al*.,[10] and initially, the reaction conditions from their study were utilized in the synthesis of our compounds presented in Figure 2. Namely, 50 mol% initiator with respect to ene was originally utilized, with a 5-fold excess of thiol to ene, and a reaction time of 16 hours. These conditions were unsuitable for the reactions presented here, due to the nature of the fluorinated thiol utilized. Initial experiments utilizing this procedure resulted in a reaction mixture with many byproducts, the most problematic being the fluorinated disulfide, $R_fCH_2CH_2S–SCH_2CH_2R_f$, which often precipitated out of solution in the reaction mixture as colorless needles. Its solubility was mirrored by that of the target compounds, so different reaction conditions were developed to reduce the formation of this byproduct, as additional purification steps led to significantly diminished yields. While disulfide formation may have been present in previous reports for the hydrogenated analogs, it is not explicitly mentioned and its complications or significance is not discussed.[10] We speculate that this is due to favorable solubility and ease of purification afforded by the hydrogenated disulfide compared to the fluorinated disulfide, leading to the possibility that it may not have been detected if it was formed.

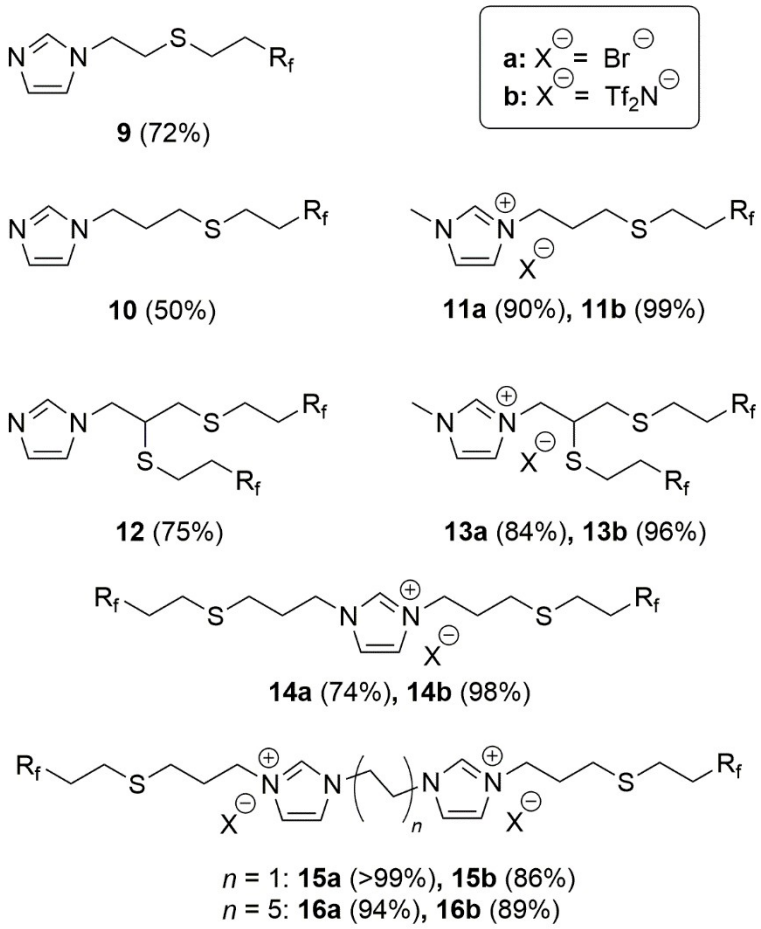


Figure 2. Product scope and isolated yields of fluorinated imidazoles prepared via UV-initiated thiol-ene click chemistry.

To reduce the number of radicals present at any given time, which we hypothesize led to the formation of the disulfide impurity, the initiator loading was reduced to 5 mol% with respect to the ene, the thiol:ene ratio was reduced to 2:1, and the irradiation time was reduced from 16 hr to 1 hr. Lower ratios of thiol:ene were attempted, but 2:1 gave the best performance. The small loss of thiol due to disulfide formation, as well as the difficulty in removing unreacted ene-functional starting material,

necessitated the excess of thiol. These reaction conditions gave quantitative conversion of ene (observed via NMR) while drastically reducing the formation of the undesired disulfide and easing purification of the target compounds. The only exception was the click reaction from 3,3'-(1,10-decadiyl)bis-1,1'-allylimidazolium bis(trifluoromethylsulfonyl)imide (to produce compound **16b**), where incomplete conversion of the ene to thioether was observed via NMR after the initial hour of reaction time. Another 5 mol% of DMPA was added to the reaction mixture and irradiated for another hour. The ene was fully converted after the additional reaction time. It is interesting to note that the anion exchange (Br^- to Tf_2N^-) must be done prior to the click reaction to obtain the products in this study. We originally attempted the reverse order, but observed that the anion exchange reactions were prohibitively complicated by solubility of the prepared clicked bromide compounds, especially their poor solubility in water.

The compounds synthesized via this modified route were able to be purified by following a simple protocol of solvent washes with hexanes and/or ether, with slight variations as noted in the Experimental section. In general, the salt compounds gave higher yields/recoveries compared to their neutral counterparts due to their comparatively lower solubilities in the nonpolar solvents. Since NMR spectra of the crude reaction mixtures showed complete conversion of the ene in all cases, the changes in yield were attributed to losses in purification, exemplified by the neutral allylimidazole click product

10, which has a much lower recovery than its methylated counterparts, **11a** and **11b**.

NMR analysis revealed that there was a small but consistent amount of Markovnikov addition that took place across the allyl bonds (see Supporting Information for NMR spectra). There is no evidence of this occurring with the vinyl species. Previous studies report that the addition selectivity of the thiol across the double bond, i.e., Markovnikov v. anti-Markovnikov, can be changed with solvent polarity.[10] This was not observed here, as no change in the amount of Markovnikov addition was observed when changing the solvent polarity from 1:1 DCM:MeOH to solely MeOH.

Preparation of the corresponding vinyl analogues was attempted, though NMR revealed that oligomerization occurred, despite the preponderance of thiol present. The clicked products obtained from 1-methyl-3-vinylimidazolium bromide, 3,3'-(1,2-ethanediyl)bis-1,1'-vinylimidazolium bromide, and 3,3'-(1,10-decadily)bis-1,1'-vinylimidazolium bromide (analogues of **11a**, **15a**, and **16a**, respectively) showed evidence of oligomerization, exhibiting peaks corresponding to polymeric backbone peaks via NMR.[28] There was no report of incomplete functionalization when the 1-methyl-3-vinylimidazolium salt was used as a substrate for a click reaction with a hydrogenated aliphatic thiol, however.[12,29] Interestingly, the neutral vinylimidazole click product **9** was able to be synthesized and characterized with no evidence of oligomerization. This change in reactivity is hypothesized to result from the electrostatics of the species participating

in the reactions, due to the salts' greater partial positive charge on the vinyl functionality, as well as on the thiyl radical due to the electron withdrawing nature of the fluorine atoms.[30] The positive-positive interactions of the vinyl group of the salts and the thiyl radical may be slow enough, compared to the neutral vinyl compound, to permit radical reactions other than thiol additions, including oligomerization.

2.2 Physical Properties

Solubility is an important property with regard to applications, especially where hydrophobicity or omniphobicity is desired. In general, the seven ionic liquids (**11a**, **11b**, **13a**, **13-16b**) prepared in this study are insoluble in water, toluene, hexanes, representing the two extremes of solvent polarity as shown in Table 1. A very small quantity of the clicked products (**11a** and **16a**) derived from 1-allyl-3-methylimidazolium bromide and 3,3'-(1,10-decadiyl)bis-1,1'-allylimidazolium bromide are at least partially soluble in water, however, leading to surfactant-like suspensions with most of the remaining compounds suspended as a white solids. The seven ionic liquids are soluble in methanol, acetone, acetonitrile, and dichloromethane. In addition, all of the Tf_2N^- salt click products (**11b**, **13-16b**) are soluble in tetrahydrofuran while the Br^- analogs are insoluble. The entire Tf_2N^- series is particularly interesting due to their solubility in dichloromethane yet insolubility in chloroform. It is noteworthy that the salts are stable in solution over the course of months, as well as stored neat in a

desiccator. There was no observed degradation as with previously reported iodide-containing salts.

Table 1. Solubility profile for the click products produced in this study. Compound numbers refer to Figure 2.

Br^- anions	**Hexanes**	**Toluene**	**$CHCl_3$**	**CH_2Cl_2**	**THF**	**Ether**	**Acetone**	**CH_3CN**	**MeOH**	**H_2O**
11a*	N	N	Y	Y	N	N	Y	Y	Y	S
13a*	N	N	Y	Y	N	Y	Y	Y	Y	N
14a	N	N	Y	Y	N	Y	Y	Y	Y	N
15a	N	N	N	N	N	N	N	N	Y	N
16a	N	N	Y	Y	N	N	Y	Y	Y	S
Tf2N– anions										
11b*	N	N	N	Y	Y	N	Y	Y	Y	N
13b*	N	N	N	Y	Y	Y	Y	Y	Y	N
14b*	N	N	N	Y	Y	Y	Y	Y	Y	N
15b*	N	N	N	Y	Y	N	Y	Y	Y	N
16b*	N	N	N	Y	Y	N	Y	Y	Y	N

* = ionic liquid; Y = soluble; N = insoluble; S = surfactant-like suspension

The density values of the materials are listed in Table 2 along with other relevant physical and chemical data. Upon inspection, the Br^- anion analogs are higher in density compared to their Tf_2N^- counterparts. This can be attributed to the smaller size of Br^- which allows for more efficient packing in the solid state. Of note, the bis-clicked salt (**13a**) obtained from 1-

methyl-3-propargylimidazolium bromide has the highest density due to the possession of the highest amount of fluorine in the series. The same is true for the analogous compound **13b** in the Tf_2N^- series. The 1,10-decadiyl salts **16a** and **16b** have the lowest density values for their respective series. This may be due to the high amount of hydrogen-saturated carbons, leading to separated fluorinated and hydrogenated domains (*vide infra*). The remaining compounds share comparable density values with no significant observable trend.

Viscosity and surface tension data were obtained for the two room temperature ionic liquids in this study, **11b** and **16b**. Upon raising the temperature to 50 °C, both room temperature ionic liquids show a significant drop in viscosity. The viscosity of the clicked salt prepared from (1-allyl-3-methylimidazolium) bis(trifluoromethylsulfonyl)imide, **11b**, decreases by a factor of five (1,500 cP to 300 cP) while the viscosity of the product produced from 3,3'-(1,10-decadiyl)bis-1,1'-allylimidazolium bis(trifluoromethylsulfonyl)imide, **16b**, decreases by a factor of eight (18,000 cP to 2,200 cP) when the temperature is raised from 25 °C to 50 °C. The lower viscosity at modestly raised temperatures greatly enhances the processability and handling of these materials. Although ionic liquid **16b** has a significant hydrogenated component, it is curious that both have very similar surface tension values of approximately 19 mN m^{-1}. For reference, this is comparable to the surface tension of hexanes with a value of 20 mN m^{-1}.

Table 2. Physical and thermal properties of the clicked salt products in this study.

Br^- anions	**Density ($g\ cm^{-3}$)[a]**	**Viscosity (cP)[c]**	**Surface Tension ($mN\ m^{-1}$)[d]**	**T_g (°C)[e]**	**$T_{m'}$ (°C)[f]**	**T_m (°C)[g]**	**$T_{d,\ 5\%}$ (°C)[h]**
11a*	1.812(2)	–	–	–	–	80	221
13a*	1.924(2)	–	–	4	70	80	215
14a	1.833(1)	–	–	–	–	111	225
15a	1.856(4)	–	–	–	–	210 (dec.)	238
16a	1.693(3)	–	–	–	80	105	237
Tf_2N^- anions							
11b*	1.672(2)	1,500; 300	19.2(2)	–60	–	8	278
13b*	1.837(3)	–	–	–	–	47	228
14b*	1.787(1)	–	–	–19	23	80	279
15b*	1.805(1); 1.876[b]	–	–	–14	22	65	295
16b*	1.596(2)	18,000; 2200	18.7(2)	–34	–	17	320

* = ionic liquid
a) Solid densities were measured via pycnometry at 25 °C. Liquid densities (**11b** and **16b**) were measured by U-tube mechanical oscillation at 25 °C.
b) Density calculated from X-ray diffraction experiment at –173 °C.
c) Dynamic viscosity measured at 25; 50 °C.
d) Surface tension determined from pendant drop method at 25 °C.
e) Glass transition temperature determined via DSC. In several cases, denoted by "–", glass transition temperatures were not observed even at the instrument's lowest accessible temperature (–80 °C).
f) First endotherm observed via DSC. Visually, this is the point where the compound wets.
g) Melting point determined via DSC if under 175 °C and visually otherwise.

h) TGA temperature (air, 5 °C/min) at which 5 wt% loss of compound is observed.

2.3 Thermal Properties

Target fluorinated products were examined using differential scanning calorimetry (DSC). Second-heat traces of the fluorinated, ionic products **11a**, **11b**, **13-16a**, and **13-16b** are shown in Figure 3, and melting points determined from DSC endotherm data are tabulated in Table 2. Notably, **11b** and **16b** are room-temperature ionic liquids, and all target ionic click products are ionic liquids with the exception of **14a**, **15a**, and **16a**, which have melting points above 100 °C, similar to a previously reported fluoro-functional quaternary ammonium bromide prepared via click chemistry.[31]

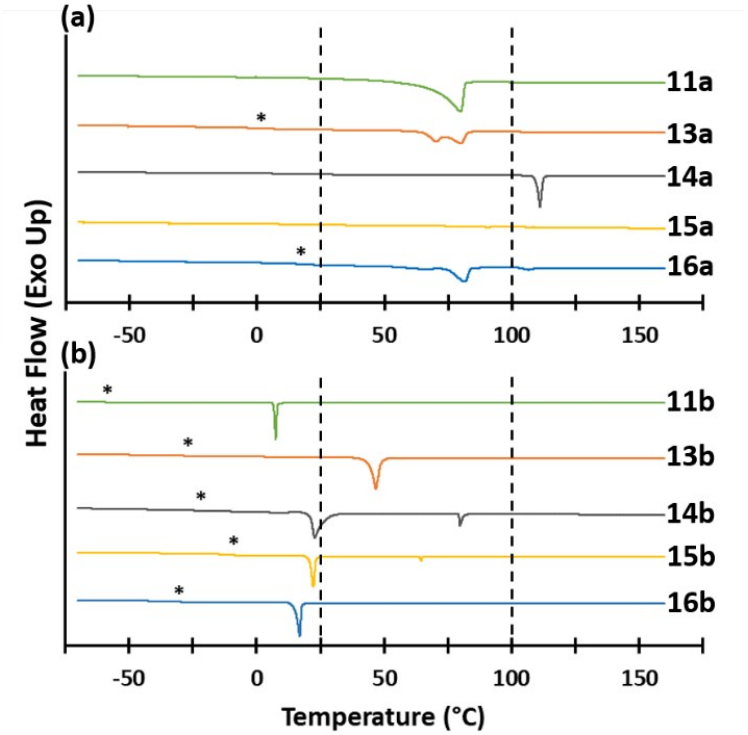


Figure 3. Compiled second-heat DSC thermograms of the (a) bromide and (b) bis(trifluoromethylsulfonyl)imide click products. The *y* axes have been

offset for clarity. Asterisks indicate glass transitions. Dashed lines are at 25 °C and 100 °C.

Many of the fluorinated click products exhibit two distinct endotherms, evident in Figure 3. Thermal transitions are given in Table 2 for the examined salts (neutral fluorinated click products **9**, **10**, and **12** are in Table S1 within Supporting Information), and in the cases where two endotherms are noted, the higher temperature is the one above which the compound melts completely into a liquid. Prior works have offered explanations for this behavior when found in similar compounds featuring fluoroalkyl chains attached to non-fluorinated alkane structures. In one report, the semi-fluorinated molecules aggregate themselves into fluorinated and non-fluorinated supramolecular domains, which then can each melt at different temperatures, resulting in a lower-temperature alkane-melt endotherm and a higher-temperature, fluoroalkane-melt endotherm.[32] Other partially-fluorinated systems reported endothermic changes in crystalline packing when heated followed by melting at a higher temperatures, resulting in two endothermic transitions.[33,34] In this case, the endotherm around 80 °C is hypothesized to belong to the melting transition of a fluorous phase, due to its consistency through the different compounds. Additionally, the size of the endotherm decreases with the decreasing fraction of fluorinated alkane in the bulk material in the series **14b**, **15b**, and **16b**.

The addition of fluoroalkyl arms with the click reaction detailed in Scheme 1 increases the melting temperatures of both the ionic and neutral compounds as expected, with the exception of the 3,3’-(1,10-decadiyl)bis-1,1’-allylimidazolium bromide **8a** and its corresponding click product **16a**.

Here, the click reaction decreases the melt temperature by approximately 50 °C. This is possibly due to the fluoroalkane arms disrupting the crystalline packing of the bromide salt, which outweighs the effect of intramolecular attraction between the fluoroalkyl arms and neighboring molecules. A similar decrease in melt temperature does not occur between the Tf_2N^- analogues **8b** and **16b** because the large Tf_2N^- anion already sufficiently disrupts crystalline packing in both the precursor and the click product. The propargyl click products **12** and **13a** have melting points equal to or lower than the corresponding allyl click products **10** and **11a**, contrary to expectations, while the Tf_2N^- analogues **11b** and **13b** behave as expected. Addition of an extra ten carbons, eight of them perfluorinated, would lead to an expected increase in the melting point as compared to the allyl click products. The expected change is consistent with previous studies, where comparable hydrogenated compounds were examined. An analogue to product **11a** had a melting point of 12 °C,[10] and an analogue to product **13a** had a melting point of 41 °C.[9] We hypothesize that, in the case of the neutral compounds and bromide salts, the enantiomeric center of the propargyl click product produces enough disorder in the system to disrupt the packing brought on by the additional perfluoroalkyl chain and depresses the melting point to below that of the allyl click products. However, with the Tf_2N^- compounds, the bulkier anion already sufficiently disrupts packing such that the additional disorder caused by the enantiomeric center in the propargyl species does not contribute as significantly to melting point depression.

The fluorinated click salts were also examined via thermal gravimetric analysis (TGA) in order to gain insight into the materials' thermal stability. Figures 4 shows the thermal plots measured in air for the Br^- and Tf_2N^- salt series, respectively. All of the Tf_2N^- salts have higher short-term stability compared to their Br^- analogs, as determined by the temperature at which 5% weight loss occurs, tabulated in Table 2. Interestingly, the thiol-yne click products (**13a** and **13b**) have the lowest 5% weight loss temperature for both series at 215 °C and 228 °C, respectively. The highest 5% weight loss temperature is observed in the 1,10-decadiyl bridged bis(trifluoromethanesulfonyl)imide salt **16b** at 320 °C. The 1,2-ethanediyl and 1,10-decadiyl salts for both the Br^- and Tf_2N^- series show the highest 5% weight loss temperatures, presumably due to the increasing number of hydrogen-saturated carbons.

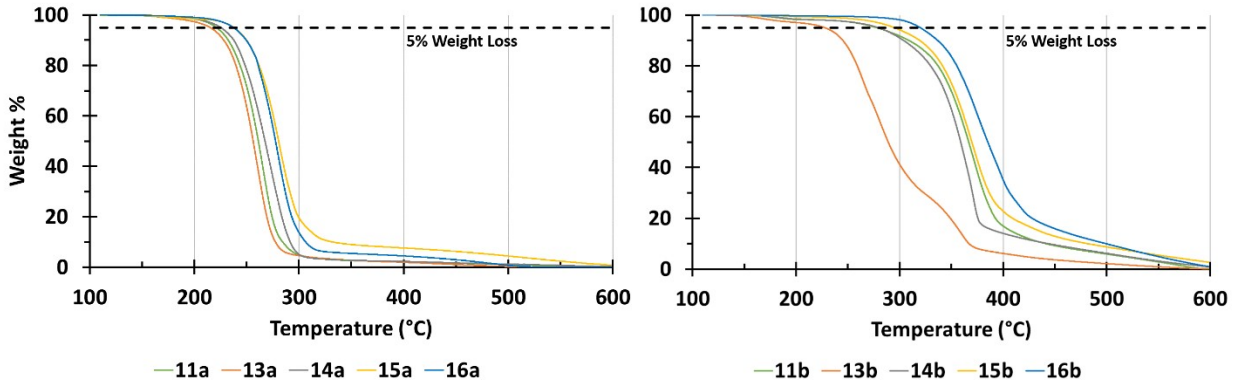


Figure 4. TGA plots for the bromide salt series (left) and bis(trifluoromethanesulfonyl)imide salt series (right) in air. A dashed line is

shown to represent 5%wt loss. Heating ramp rate was performed at 5 °C/min after an isothermal temperature hold at 110 °C for 1 h.

2.4 Single-crystal X-ray Diffraction

Compound **15b** was crystallized from methanol, and the crystal structure is illustrated in Figure 5 (crystallographic details available in Supporting Information). The crystal structure shows a wealth of intermolecular contacts, namely hydrogen bonding (Figure 6a) and F---F halogen-halogen interactions (Figure 6b). It is clear that there is aggregation of fluorinated groups, and perhaps domain separation. However, we are still unsure of the exact cause of the multiple endotherms.

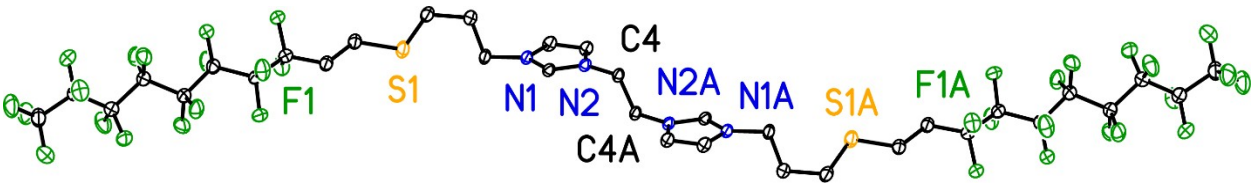


Figure 5. Molecular components of the **15b** cation drawn with 50% thermal contours. Hydrogen and anion positions are omitted for clarity.

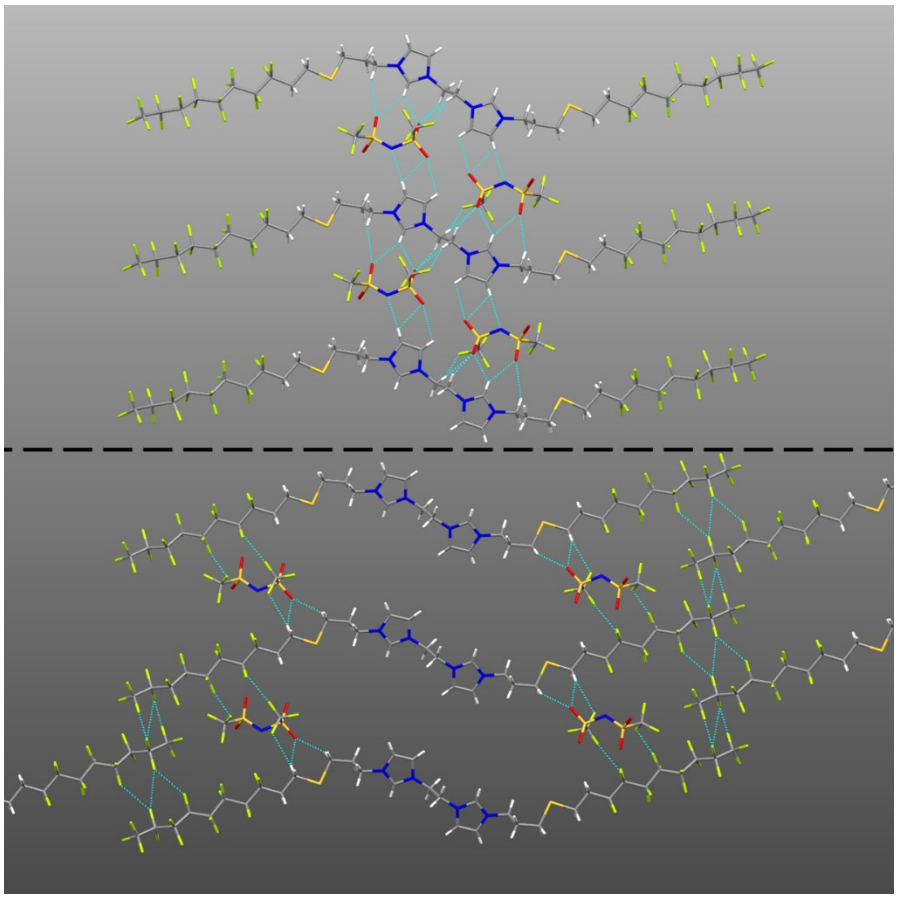


Figure 6. (a) Packing slice of **15b** showing the interactions between cationic heads and anions. (b) Packing slice of **15b** showing the F---F interactions between fluorous tails including those belonging to the anion.

3. CONCLUSION

In summary, this is the first report of the synthesis of cation-fluorinated imidazole and imidazolium-based ionic liquids through the use of thiol-ene and thiol-yne click chemistry. This scheme allows for the facile addition of a fluorous group to an imidazole or imidazolium cation at high conversion, with easy purification steps, and fair to excellent yields. Vinyl-functional starting

materials did not lend themselves to clean reactions, forming oligomers in the reaction mixture despite the preponderance of thiol present. Allyl-functional starting materials gave predominantly the anti-Markovnikov addition product. Some compounds exhibit interesting thermal behavior, with two endothermic transitions as seen by DSC, attributed to phase separation into fluorous and ionic domains. The facile nature of this transformation establishes a path towards the development of new fluorinated, hydrophobic ionic liquids paving the way towards omniphobic applications.

4. EXPERIMENTAL

4.1. Materials

Imidazole was purchased from Alfa Aesar and used as received. 1-Methylimidazole, allyl bromide, propargyl bromide (80 wt% toluene solution), 1,2-dibromoethane, 1,10-dibromodecane, and 2,2-dimethoxy-2-phenylacetophenone (DMPA) were purchased from Sigma and used without further purification. 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol was purchased from SynQuest Labs and used as received. 1-vinylimidazole and 1-allylimidazole were purchased from Sigma and Alfa Aesar, respectively, and were distilled and refrigerated prior to use. All other solvents and reagents were obtained commercially and used as received.

4.2. Spectroscopic measurements

NMR data were obtained on a Bruker AVANCE III HD 400 MHz spectrometer using CD_3OD as solvent. Chemical shifts for ^{1}H and ^{13}C spectra were referenced with respect to the solvent. ^{19}F spectra were referenced externally against $CFCl_3$. All spectra were acquired at or near the solubility limit in CD_3OD. Peaks from the minor Markovnikov product as well as the fluorinated carbons (many small peaks from ~125 to 105 ppm) are not reported in the ^{13}C peak listing for simplicity, but are evident in the recorded spectra. FTIR data were acquired on a Nicolet iS50 spectrometer equipped with an attenuated total reflectance (ATR) accessory with an acquisition window ranging from 525-4000 cm^{-1} at 4 cm^{-1} resolution. Samples were dried in a vacuum oven prior to measurement.

4.3. Physical and thermal properties measurements

Visual melting points were obtained on a Stanford Research Systems MPA100 automated melting point system at a heating rate of 2 °C/min. DSC data were recorded on a TA Instruments Discovery differential scanning calorimeter using a heat/cool/heat cycle with temperature limits of −80 and 175 °C, a heating rate of 10 °C/min, and a cooling rate of 5 °C/min. Melting points below 175 °C were determined via DSC, while those above were determined visually unless specified otherwise. TGA data were recorded in air on a TA Instruments TGA5500 from 110 to 600 °C with a heating rate of 5 °C/min following an isothermal hold at 110 °C for 1 h. Solid density was

measured using a Micrometrics AccuPyc II 1340 pycnometer at 25 °C. Liquid density was measured using a Rudolph Research Analytical DDM 2911 density meter at 25 °C. Surface tension was measured via acquisition of a silhouette of an axisymmetric pendant fluid droplet at 25 °C.[35,36] Iterative fitting of the Young-Laplace equation was utilized to balance the gravitational deformation of the drop with the restorative interfacial tension. A Future Digital Scientific Corporation, Optical Contact Angle System (OCA-20) was employed to capture the silhouette images of the ionic liquids in air, within a temperature-controlled chamber at 25 °C. For each ionic liquid, three separate images were analyzed using the open source software package Open Drop v1.1. Dynamic viscosity was measured at 25 and 50 °C using a Brookfield RVDV-II + Pro CP viscometer.

4.4. High-resolution mass spectrometry (HRMS)

HRMS was performed using ESI-Q-TOF-MS. Data were acquired using a Waters Synapt High Definition Mass Spectrometer equipped with a non-ESI source in positive mode employing acetonitrile or methanol as solvent. MS conditions are as follows: capillary voltage (3.0 kV), sample cone voltage (33.0 V), extraction cone voltage (4.0 V), flow rate (1.000 nL/min), acquisition range (*m*/*z* 390-1500), source temperature (80 °C). HRMS was not performed on anion-exchanged species because the cation is unchanged.

4.5. Crystal growth and X-ray structure determination

Colorless crystals of **15b** were grown via slow evaporation from a saturated solution in methanol. A suitable crystal (colorless lath) was mounted in the 100 K nitrogen cold stream provided by an Oxford Cryostream low-temperature apparatus on the goniometer head of a Bruker D8 diffractometer equipped with a PHOTONII CMOS detector operating in shutterless mode. Data were collected employing synchrotron radiation (λ = 0.7288 Å) at Beamline 12.2.1 at the Advanced Light Source, Lawrence Berkeley National Laboratory. The dataset was reduced utilizing Bruker SAINT,[37] and a multiscan absorption correction was applied using SADABS.[37] Structure solution and refinement were executed utilizing SHELXT-2018[38] and SHELXL-2018,[39] respectively. Crystallographic data are tabulated in Supporting Information. CCDC deposition number: 1909302.

4.6. Synthesis and purification

Ene- or yne-functional starting materials were synthesized according to established literature procedures if not commercially available as cited in the main text.

4.6.1. 3,3'-(1,10-Decadiyl)bis-1,1'-allylimidazolium bromide (8a)

1-Allylimidazole (2.27 g, 21.0 mmol) and 1,10-dibromodecane (3.00 g, 10.0 mmol) were weighed into a round bottom flask and heated under an inert atmosphere at 70 °C overnight, resulting in a white solid. The solid was broken up, ground with a mortar and pestle, and washed with ethyl acetate,

affording the product as a white solid. Yield: white powder, 4.83 g, 94%. Melting point (DSC) = 150 °C. ^{1}H NMR (400 MHz, CD_3OD) δ_H 9.17 (s, 2H) 7.76-7.66 (m, 4H), 6.17-6.07 (m, 2H), 5.47-5.42 (m, 4H), 4.92 (d, J = 6.2 Hz), 4.29 (t, J = 7.4 Hz, 4H), 1.93 (br, 4H), 1.37 (br, 12H). ^{13}C NMR (101 MHz, CD_3OD) δ_C 137.0, 132.1, 123.9, 123.7, 121.9, 52.8, 51.0, 31.1, 30.3, 30.0, 27.2. HRMS (ESI/Q-TOF) m/z: [**8a** – Br]$^{+}$ calculated for $C_{22}H_{36}BrN_4$: 435.2123, found: 435.2130. FTIR-ATR (cm^{-1}): 3129, 3059, 2926, 2855, 2162, 1980, 1646, 1561, 1464, 1442, 1419, 1367, 1353, 1329, 1311, 1227, 1167, 1134, 1110, 1034, 995, 934, 833, 770, 730, 630, 580.

4.7. Anion metathesis general procedure

The starting ene- or yne-functional bromide (5 mmol) was dissolved in water (5 mL), a stoichiometric amount of $LiTf_2N$ was added to the solution, and some of the product immediately phase separated. The mixture was allowed to stir overnight, the monobromide species at room temperature, and the dibromide bridged species at 60 °C. Dichloromethane was added to the reaction mixture, the organic layer was washed three times with deionized water, and the solvent removed via rotary evaporation. The resulting material was then dried overnight under vacuum at 80 °C.

4.7.1. 1,3-Bis(allyl)imidazolium bis(trifluoromethanesulfonyl)imide (6b)

Yield: yellow oil, 2.147 g, 79 %. Melting point (DSC) = –35 °C. ^{1}H NMR (400MHz, CD_3OD) δ_H 8.93 (s, 1H), 7.60 (m, 2H), 6.13-6.03 (m, 2H), 5.46-5.40 (m, 4H), 4.86-4.84 (m, 4H). ^{13}C NMR (101 MHz, CD_3OD) δ_C 137.3, 131.8, 123.9, 122.0, 121.2 (q, J_{CF} = 322 Hz), 52.92. ^{19}F NMR (376 MHz, CD_3OD) δ_F -80.6. FTIR-ATR (cm^{-1}): 3151, 3118, 3094, 2940, 1589, 1564, 1443, 1408, 1351, 1332, 1293, 1239, 1195, 1145, 1134, 1116, 1090, 1057, 1037, 999, 955, 870, 834, 790, 778, 763, 739, 726, 705, 683, 654, 615, 570, 559, 550.

4.7.2. 3,3'-(1,2-Ethanediyl)bis-1,1'-allylimidazolium bis(trifluoromethanesulfonyl)imide (7b)

Yield: light yellow oil, 4.023 g, 93%. Melting point (DSC) = –51 °C. ^{1}H NMR (400 MHz, CD_3OD) δ_H 8.88 (s, 2H), 7.66-7.56 (m, 4H), 6.11-6.01 (m, 2H), 5.48-5.42 (m, 4H), 4.85-4.84 (m, 4H), 4.76 (s, 4H). ^{13}C NMR (101 MHz, CD_3OD) δ_C 137.8, 131.4, 124.7, 123.9 122.7, 121.1 (q, J_{CF} = 322 Hz), 53.2, 50.0. ^{19}F NMR (376 MHz, CD_3OD) δ_F -80.6. FTIR-ATR (cm^{-1}): 3148, 3119, 3097, 2971, 2950, 2923, 2859, 1632, 1570, 1561, 1458, 1444, 1439, 1405, 1364, 1341, 1329, 1309, 1284, 1198, 1183, 1145, 1132, 1116, 1107, 1084, 1059, 997, 958, 863, 852, 790, 775, 763, 740, 711, 703, 685, 651, 640, 625, 599, 583, 571, 558.

4.7.3. 3,3'-(1,10-Decadiyl)bis-1,1'-allylimidazolium bis(trifluoromethanesulfonyl)imide (8b)

Yield: light yellow oil, 4.584 g, 92%. Melting point (DSC) = –66 °C. ^{1}H NMR (400 MHz, CD_3OD) δ_H 8.93 (s, 2H), 7.65-7.57 (m, 4H), 6.12-6.03 (m, 2H), 5.46-5.38 (m, 4H), 4.84 (m, 4H), 4.29 (t, J = 7.4 Hz, 4H), 1.89 (m, 4H), 1.35 (m, 12H). ^{13}C NMR (101 MHz, CD_3OD) δ_C 137.1, 131.9, 123.9, 123.8, 121.9, 121.2 (q, J_{CF} = 322 Hz), 52.8, 51.0, 31.0, 30.3, 29.9, 27.2. ^{19}F NMR (376 MHz, CD_3OD) δ_F -80.6. FTIR-ATR (cm^{-1}): 3149, 3115, 3092, 2934, 2861, 1564, 1445, 1409, 1349, 1330, 1185, 1143, 1133, 1115, 1091, 1055, 1000, 969, 954, 928, 869, 867, 829, 788, 763, 738, 726, 704, 726, 685, 653, 616, 600, 570, 559, 550.

4.8. Click Reaction General Procedure

All click products were synthesized and purified with the same procedure, unless specified otherwise. To a 20 mL scintillation vial equipped with a magnetic stir bar was added 2.6 mmol of ene (1.3 mmol compound for difunctional materials, propargyl species included), 5.2 mmol (2.5 g) 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol, and 0.07 mmol (33 mg) DMPA. Ten mL of a 1:1 v/v mixture of DCM:MeOH was added, the mixture capped, and then stirred until complete dissolution of the solids. The mixture was subject to broadband UV irradiation (centered at 365 nm) for 1 hr with stirring. After irradiation, the reaction mixture was transferred to a round bottom flask and solvent was removed via rotary evaporation. For the bromide click products, 50 mL hexanes were added to the solids and heated with stirring for 1 hr. The mixture was allowed to come to room temperature, the hexanes

decanted, and 50 mL diethyl ether added. This was stirred for an additional hour, and the solids were collected via vacuum filtration, and washed with another 50 mL portion of diethyl ether. For the bis(trifluoromethanesulfonyl)imide click products, two hexanes washes were utilized, as the products were partly soluble in ether. The product was subject to a vacuum line (10^{-2} torr) to remove residual solvent.

4.8.1. 1-[2-(1H,1H,2H,2H-Perfluorodecylthio)ethyl]imidazole (9)

Solvent was removed from crude reaction mixture via rotary evaporation, and the resulting solids were washed twice with heptane. Yield: white powder, 1.080 g, 72%. Melting point (DSC) = 89 °C. ^{1}H NMR (400 MHz, CD_3OD) δ_H 7.73 (s, 1H), 7.20 (s, 1H), 6.98 (s, 1H), 4.25 (t, J = 6.5 Hz, 2H), 2.98 (t, J = 6.6 Hz, 2H), 2.66-2.62 (m, 2H), 2.47-2.33 (m, 2H). ^{13}C NMR (101 MHz, CD_3OD) δ_C 137.3, 127.6, 119.3, 108.3, 46.7, 32.7, 31.5 (t, J_{CF} = 22 Hz), 22.2. ^{19}F NMR (376 MHz, CD_3OD) δ_F -82.4, -115.3, -122.7, -122.9, -123.7, -124.3, -127.7. HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calculated for $C_{15}H_{12}F_{17}N_2S$: 575.0450, found: 575.0457. FTIR-ATR (cm^{-1}): 3110, 2936, 1681, 1507, 1444, 1368, 1331, 1199, 1146, 1136, 1115, 1080, 1033, 1000, 955, 929, 907, 871, 821, 778, 737, 726, 685, 659, 650, 621, 604, 572.

4.8.2. 1-[3-(1H,1H,2H,2H-Perfluorodecylthio)propyl]imidazole (10)

Product was soluble in ether, so it was subjected to two hexane washes instead. Yield: yellow solid, 0.771 g, 50 %. Melting point (DSC) = 83 °C. ^{1}H NMR (400 MHz, CD_3OD) δ_H 7.67 (s, 1H), 7.13 (s, 1H), 6.98 (s, 1H), 4.14 (t, J = 6.8 Hz, 2H), 2.77-2.73 (m, 2H), 2.54-2.37 (m, 4H), 2.07 (quint., J = 7.0 Hz, 2H). ^{13}C NMR (101 MHz, CD_3OD) δ_C 137.2, 127.7, 119.2, 45.1, 31.5 (t, J_{CF} = 22 Hz), 30.1, 28.0, 21.9 (t). ^{19}F NMR (376 MHz, CD_3OD) δ_F -82.5 (t), -115.4 (p), -122.8 (t), -123.0, -123.8, -124.4, -127.4 (p). HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calculated for $C_{16}H_{14}F_{17}N_2S$: 589.0606, found: 589.0600. FTIR-ATR (cm^{-1}): 3107, 2937, 1677, 1508, 1443, 1367, 1331, 1281, 1199, 1146, 1136, 1115, 1079, 1031, 1000, 955, 908, 871, 820, 778, 737, 726, 704, 684, 650, 625, 619, 606, 283, 572, 558, 546.

4.8.3. 1-Methyl-3-[3-(1H,1H,2H,2H-perfluorodecylthio)propyl]imidazolium bromide (11a)

Yield: white powder, 1.601 g, 90 %. Melting point (DSC) = 80 °C. ^{1}H NMR (400MHz, CD_3OD) δ_H 9.00 (s, 1H), 7.67 (s, 1H), 7.62 (s, 1H), 4.36 (t, J = 7.1 Hz, 2H), 3.94 (s, 3H), 2.83-2.79 (m, 2H), 2.67 (t, J = 7.1 Hz, 2H), 2.56-2.43 (m, 2H), 2.21 (quint., J = 7.1 Hz, 2H). ^{13}C NMR (101 MHz, CD_3OD) δ_C 123.7, 122.3, 53.9, 48.6, 35.1 (t, J_{CF} = 22 Hz), 27.8, 21.9. ^{19}F NMR (376 MHz, CD_3OD) δ_F -82.4, -115.3, -122.7, -122.9, -123.7, -124.3, -127.3. HRMS (ESI/Q-TOF) m/z: [**11a** – Br]$^+$ calculated for $C_{17}H_{16}F_{17}N_2S$: 603.0763, found: 603.0754. FTIR-ATR (cm^{-1}): 3392, 3142, 3052, 2961, 2867, 2050, 1980, 1171, 1635, 1578, 1561, 1444, 1370, 1332, 1198, 1145, 1115, 1092, 1077, 1031, 999, 956,

889, 871, 836, 781, 762, 754, 738, 726, 706, 683, 646, 620, 606, 590, 579, 559.

4.8.4. 1-Methyl-3-[3-(1H,1H,2H,2H-perfluorodecylthio)propyl]imidazolium bis(trifluoromethanesulfonyl)imide (11b)

Yield: yellow oil, 2.285 g, 99 %. Melting point (DSC) = 8 °C. ^{1}H NMR (400MHz, CD_3OD) δ_H 8.88 (s, 1H), 7.62 (s, 1H), 7.55 (s, 1H), 4.33 (t, J = 7.1 Hz, 2H), 3.92 (s, 3H), 2.82-2.78 (m, 2H), 2.65 (t, J = 7.1 Hz, 2H), 2.54-2.41 (m, 2H), 2.19 (m, 2H). ^{13}C NMR (101 MHz, CD_3OD) δ_C 138.0, 125.1, 123.7 (q, J_{CF} = 323 Hz), 49.5, 36.5, 32.8 (t, J_{CF} = 22 Hz), 30.4, 29.1, 23.2. ^{19}F NMR (376 MHz, CD_3OD) δ_F -80.7, -82.4, -115.3, -122.7, -122.9, -123.8, -124.4, -127.3. FTIR-ATR (cm^{-1}): 3157, 3121, 3103, 1733, 1575, 1567, 1465, 1458, 1452, 1444, 1431, 1388, 1348, 1330, 1239, 1182, 1143, 1133, 1115, 1091, 1055, 1000, 970, 954, 928, 866, 829, 789, 763, 739, 726, 704, 686, 653, 617, 601, 579, 570, 562, 560, 559, 550.

4.8.5. 1-[2,3-Bis(1H,1H,2H,2H-perfluorodecylthio)propyl]imidazole (12)

Yield: dark yellow solid, 1.044 g, 75 %. Melting point (DSC) = 57 °C. ^{1}H NMR (400 MHz, CD_3OD) δ_H 7.76 (s, 1H), 7.23 (s, 1H), 7.00 (s, 1H), 4.42 (dd, $^{2}J_{H\text{-}H}$ = 14.3 Hz, $^{3}J_{H\text{-}H}$ = 5.2 Hz, 1H), 4.23 (dd, $^{2}J_{H\text{-}H}$ = 14.3 Hz, $^{3}J_{H\text{-}H}$ = 8.0 Hz, 1H), 3.25 (m, 1H), 2.44-2.90 (br, 10H). ^{13}C NMR (101 MHz, CD_3OD) δ_C 139.3, 129.1,

121.3, 51.3, 49.1, 36.3, 33.1 (m), 24.4, 23.4. ^{19}F NMR (376 MHz, CD_3OD) δ_F -82.4, -115.2, -122.7, -122.9, -123.8, -124.3, -127.3. HRMS (ESI/Q-TOF) *m*/*z*: $[M + H]^+$ calculated for $C_{26}H_{17}F_{34}N_2S_2$: 1067.0290, found: 1067.0261. FTIR-ATR (cm^{-1}): 3109, 2935, 1683, 1505, 1442, 1367, 1332, 1199, 1145, 1135, 1115, 1083, 1030, 1001, 955, 906, 871, 822, 778, 737, 726, 705, 684, 659, 651, 621, 604, 571, 558.

4.8.6. 1-Methyl-3-[2,3-bis(1H,1H,2H,2H-perfluorodecylthio)propyl]imidazolium bromide (13a)

Yield: white powder, 1.510 g, 84 %. Melting point (DSC) = 80 °C. ^{1}H NMR (400 MHz, CD_3OD) δ_H 9.19 (s, 1H), 7.81 (s, 1H), 7.65 (s, 1H), 4.69 (dd, $^2J_{H-H}$ = 14.4 Hz, $^3J_{H-H}$ = 8.3 Hz, 1H), 4.48 (dd, $^2J_{H-H}$ = 14.4 Hz, $^3J_{H-H}$ = 8.3 Hz) 1H, 4.00 (s, 3H), 3.40 (m, 1H), 2.97-2.86 (br, 6H), 2.58-2.47 (br, 4H). ^{13}C NMR (101 MHz, CD_3OD) δ_C 138.9, 124.9, 124.5, 53.26, 48.1, 36.8, 36.2, 32.9 (m), 24.4, 23.4. ^{19}F NMR (376 MHz, CD_3OD) δ_F -82.4, -115.2, -122.7, -122.9, -123.8, -124.3, -127.3. HRMS (ESI/Q-TOF) *m*/*z*: [**13a** – Br]$^+$ calculated for $C_{27}H_{19}F_{34}N_2S_2$: 1081.0447, found: 1081.0414. FTIR-ATR (cm^{-1}): 3050, 2961, 1574, 1560, 1443, 1369, 1332, 1200, 1169, 1147, 1115, 1086, 1028, 999, 954, 926, 871, 835, 747, 735, 726, 705, 650, 621, 579, 559.

4.8.7. 1-Methyl-3-[2,3-bis(1H,1H,2H,2H-perfluorodecylthio)propyl]imidazolium bis(trifluoromethanesulfonyl)imide (13b)

Yield: dark yellow solid, 1.693 g, 96 %. Melting point (DSC) = 47 °C. ^{1}H NMR (400 MHz, CD_3OD) δ_H 8.99 (s, 1H), 7.70 (t, 1H), 7.60 (t, 1H), 4.63-3.36 (m, 2H), 3.96 (s, 3H), 3.39 (m, 1H), 2.98-2.79 (br, 6H), 2.59-2.48 (br, 4H). ^{13}C NMR (101 MHz, CD_3OD) δ_C 138.8, 125.0, 124.5, 123.7, (q, J_{CF} = 323 Hz), 53.1, 47.9, 36.6, 36.1, 32.9 (m), 24.4, 23.2. ^{19}F NMR (376 MHz, CD_3OD) δ_F -80.7, -82.5, -115.2, -122.7, -123.0, -123.8, -124.4, -127.4. FTIR-ATR (cm^{-1}): 3152, 3120, 1576, 1563, 1547, 1443, 1431, 1348, 1330, 1295, 1196, 1144, 1136, 1115, 1088, 1056, 1038, 1001, 970, 956, 897, 878, 871, 828, 790, 778, 763, 739, 725, 705, 684, 653, 613, 570, 559, 550.

4.8.8. 1,3-Bis[3-(1H,1H,2H,2H-perfluorodecylthio)propyl]imidazolium bromide (14a)

Yield: off-white powder, 1.451 g, 94 %. Melting point (DSC) = 111 °C. ^{1}H NMR (400 MHz, CD_3OD) δ_H 9.20 (s, 1H), 7.74 (s, 1H), 7.73 (s, 1H), 4.40 (t, J = 6.9 Hz, 4H), 2.82-2.66 (m, 8H), 2.50-2.41 (m, 4H), 2.27-2.20 (quint., J = 7.0 Hz, 4H). ^{13}C NMR (101 MHz, CD_3OD) δ_C 137.77, 124.04, 49.7, 32.8 (t, J_{CF} = 22 Hz), 30.3, 29.3, 23.3. ^{19}F NMR (376 MHz, CD_3OD) δ_F -82.4, -115.3, -122.7, -122.9, -123.8, -124.3, -127.3. HRMS (ESI/Q-TOF) m/z: [**14a** – Br]$^{+}$ calculated for $C_{29}H_{23}F_{34}N_2S_2$: 1109.0760, found: 1109.0757. FTIR-ATR (cm^{-1}): 3136, 3043, 2988. 2954. 2937. 2859, 1566, 1442, 1369, 1332, 1199, 1146, 1115, 1083, 1030, 1000, 955, 872, 738, 726, 705, 683, 651, 621, 605, 572, 559.

4.8.9. 1,3-Bis[3-(1H,1H,2H,2H-perfluorodecylthio)propyl]imidazolium bis(trifluoromethanesulfonyl)imide (14b)

Yield: yellow solid, 1.766 g, 98 %. Melting point (DSC) = 80 °C. ^{1}H NMR (400 MHz, CD_3OD) δ_H 9.20 (m, 1H), 7.74 (m, 2H), 4.40 (t, J = 7.0 Hz, 4H), 2.82-2.66 (m, 8H), 2.54-2.41 (m, 4H), 2.27-2.20 (m, 4H). ^{13}C NMR (101 MHz, CD_3OD) δ_C 137.6, 124.0, 121.2 (q, J_{CF} = 322 Hz), 49.7, 32.8 (t, J_{CF} = 22 Hz), 30.3, 29.3, 23.3 (m). ^{19}F NMR (376 MHz, CD_3OD) δ_F -80.6, -82.5, -115.4, -122.8, -123.0, -123.8, -124.4, -127.4. FTIR-ATR (cm^{-1}): 3151, 3118, 3094, 2940, 1589, 1564, 1443, 1409, 1351, 1332, 1293, 1239, 1194, 1145, 1134, 1116, 1090, 1057, 1037, 999, 955, 870, 834, 790, 778, 763, 739, 726, 705, 654, 683, 615, 570, 559, 550.

4.8.10. 3,3'-(1,2-Ethanediyl)bis-1,1'-[3-(1H,1H,2H,2H-perfluorodecylthio)propyl]imidazolium bromide (15a)

Yield: white powder, 1.774 g, >99 %. Melting point (visual) = 210 °C (decomp.). ^{1}H NMR (400 MHz, CD_3OD) δ_H 7.72 (m, 4H), 4.41-4.37 (m, 4H), 2.85-2.65 (m, 12H), 2.57-2.44 (m, 4H), 2.23 (quint., J = 7.1 Hz, 4H). ^{13}C NMR (101 MHz, CD_3OD) δ_C 138.3, 124.6, 124.1, 50.0, 32.8 (t, J_{CF} = 22 Hz), 30.3, 29.2, 23.2. ^{19}F NMR (376 MHz, CD_3OD) δ_F -82.4, -115.2, -122.7, -122.9, -123.8, -124.3, -127.3. HRMS (ESI/Q-TOF) m/z: [**15a** – Br]$^{+}$ calculated for $C_{34}H_{30}BrF_{34}N_4S_2$: 1283.0552, found: 1283.0486. FTIR-ATR (cm^{-1}): 3409, 3136, 3050, 2958, 2866, 2467, 1654, 1563, 1443, 1369, 1332, 1294, 1199, 1174,

1146, 1135, 1115, 1083, 1028, 1000, 955, 854, 792, 778, 738, 740, 726, 683, 651, 634, 620, 587, 573.

4.8.11. 3,3'-(1,2-Ethanediyl)bis-1,1'-[3-(1H,1H,2H,2H-perfluorodecylthio)propyl]imidazolium bis(trifluoromethanesulfonyl)imide (15b)

Yield: white powder, 1.774 g, 86 %. Melting point (DSC) = 65 °C. ^{1}H NMR (400 MHz, CD_3OD) δ_H 7.7 (m, 4H), 4.77 (s, 4H), 4.38-4.35 (m, 4H), 2.83-2.43 (m, 12H), 2.24-2.17 (m, 4H). ^{13}C NMR (101 MHz, CD_3OD) δ_C 138.0, 124.8, 124.0, 121.2 (q, J_{CF} = 321 Hz), 50.0, 49.9, 32.8 (m), 30.2, 29.1, 23.2. ^{19}F NMR (376 MHz, CD_3OD) δ_F -80.63, -82.4, -115.2, -122.7, -122.9, -123.7, -124.3, -127.3. FTIR-ATR (cm^{-1}): 3148, 1339, 3097, 2971, 2950, 2923, 2859, 1632, 1570, 1561, 1458, 1444, 1439, 1405, 1364, 1341, 1329, 1309, 1284, 1198, 1183, 1145, 1132, 1116, 1107, 1084, 1059, 997, 958, 863, 842, 790, 775, 763, 740, 711, 703, 685, 651, 640, 625, 599, 583, 571, 558.

4.8.12. 3,3'-(1,10-Decadiyl)bis-1,1'-[3-(1H,1H,2H,2H-perfluorodecylthio)propyl]imidazolium bromide (16a)

Yield: white powder, 1.920 g, 94 %. Melting point (DSC) = 105 °C. ^{1}H NMR (400 MHz, CD_3OD) δ_H 9.19 (s, 2H), 7.72 (m, 4H), 4.42-4.24 (m, 8H), 2.83-2.20 (m, 16H), 1.95-1.90 (m, 4H), 1.35 (br, 12H). ^{13}C NMR (101 MHz, CD_3OD) δ_C 138.0, 124.0, 123.9, 51.0, 32.8 (t, J_{CF} = 22 Hz), 31.1, 30.5, 30.3, 30.0, 29.3, 27.2 23.3. ^{19}F NMR (376 MHz, CD_3OD) δ_F -82.4, -115.2, -122.7, -122.9, -123.8,

-124.3, -127.3. HRMS (ESI/Q-TOF) *m/z*: [**16a** – 2Br]$^{2+}$ calculated for $C_{21}H_{23}F_{17}N_2S$: 658.1310, found: 658.1293. FTIR-ATR (cm^{-1}): 3054, 2983, 2923, 2854, 2162, 1980, 1565, 1444, 1370, 1333, 1198, 1146, 1135, 1115, 1085, 1028, 1000, 955, 871, 835, 778, 739, 726, 705, 684, 637, 621, 606, 588, 575.

4.8.13. 3,3'-(1,10-Decadiyl)bis-1,1'-[3-(1H,1H,2H,2H-perfluorodecylthio)propyl]imidazolium bis(trifluoromethanesulfonyl)imide (16b)

Yield: light yellow oil, 2.174 g, 89 %. Melting point (DSC) = 17 °C. ^{1}H NMR (400 MHz, CD_3OD) δ_H 8.97 (s, 2H), 7.66-7.64 (m, 4H), 4.36-4.19 (m, 8H), 2.81-2.17 (m, 16H), 1.93-1.88 (m, 4H), 1.35 (br, 12H). ^{13}C NMR (101 MHz, CD_3OD) δ_C 137.2, 123.9, 123.8, 121.2 (q, J_{CF} = 322 Hz), 51.0, 49.6, 32.8 (t, J_{CF} = 22 Hz), 31.0, 30.4, 30.2, 29.9, 29.2, 27.2 23.3. ^{19}F NMR (376 MHz, CD_3OD) δ_F -80.6, -82.4, -115.3, -122.7, -122.9, -123.7, -124.3, -127.3. FTIR-ATR (cm^{-1}): 3149, 3115, 3092, 2934, 2861, 1564, 1445, 1410, 1349, 1330, 1185, 1143, 1133, 1115, 1091, 1055, 1000, 969, 954, 928, 869, 867, 829, 788, 763, 738, 725, 704, 685, 653, 616, 600, 570, 559, 550.

ACKNOWLEDGEMENTS

The support of the Air Force Office of Scientific Research (19RQCOR098) and the Air Force Research Laboratory, Aerospace Systems Directorate is gratefully acknowledged. This research used resources of the Advanced Light

Source, which is a DOE Office of Science User Facility under contract no. DE-AC02-05CH11231.

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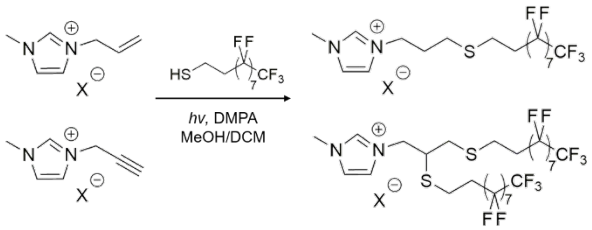

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