

Highly-fluorinated Triaminocyclopropenium Ionic Liquids

Owen J. Curnow* and Rathiga Senthooan^[a]

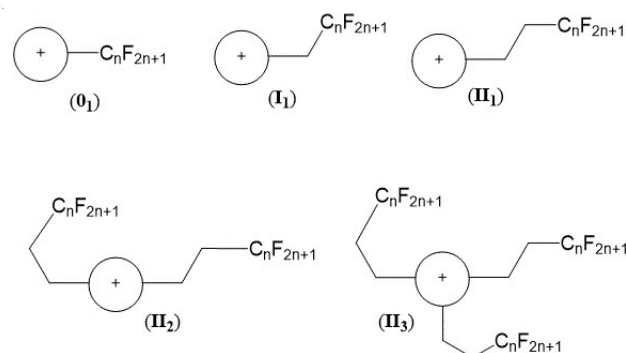
Abstract: A series of highly-fluorinated triaminocyclopropenium salts, with up to six fluororous groups, were prepared and their properties as ionic liquids investigated. Reaction of pentachlorocyclopropane or tetrachlorocyclopropene with bis(2,2,2-trifluoroethyl)amine, $\text{HN}(\text{CH}_2\text{CF}_3)_2$, occurs in the presence of a trialkylamine, NR_3 , to give cations with two fluorinated amino groups, $[\text{C}_3(\text{N}(\text{CH}_2\text{CF}_3)_2)_2(\text{NR}_2)]^+$ ($\text{R} = \text{Et}, \text{Pr}, \text{Bu}, \text{Hex}$), with traces of $[\text{C}_3(\text{N}(\text{CH}_2\text{CF}_3)_2)_3]^+$. Use of appropriate reagent ratios and reaction times and subsequent addition of a dialkylamine, $\text{HNR}'\text{R}''$, gives cations with one fluorinated amino group, $[\text{C}_3(\text{N}(\text{CH}_2\text{CF}_3)_2)(\text{NR}_2)(\text{NR}'\text{R}'')]^+$ ($(\text{NR}_2)(\text{NR}'\text{R}'') =$

$(\text{NBu}_2)_2, (\text{NEt}_2)(\text{NPr}_2), (\text{NBu}_2)(\text{NBuMe})$). These cations were isolated as chloride salts and some of these were converted to bistriflamide, dicyanamide and triflate salts to provide ionic liquids. These salts were characterised by thermal (DSC and TGA) measurements and miscibility/solubility properties (determined in a range of solvents). Ionic liquids (ILs) were also characterised by density, viscosity and conductivity measurements where possible. X-ray diffraction studies of chloride salts showed the formation of fluororous regions and more hydrophilic ionic regions in the solid state.

Introduction

Research on ionic liquids (ILs) and their applications is now an intense area of activity. The reasons are well-known: in particular, their effectively zero vapor pressure, low flammability, easy tunability and potential for recycling.^[1] Inclusion of fluorine atoms in an ionic liquid can cause a significant change to their properties. A wide range of IL properties such as melting point, viscosity, density, conductivity, solubility, liquid range, thermal stability and electrochemical stability can be altered by modifying non-fluorinated ILs into fluorinated ILs.

The fluorinated ionic liquids (FILs) reported so far most commonly contain fluorinated anions (FA-ILs), for which there is a large variety; such as BF_4^- , PF_6^- , triflate (OTf^-), bistriflamide (NTf_2^-), $\text{CF}_3(\text{CF}_2)_n\text{CO}_2^-$, $\text{CF}_3(\text{CF}_2)_n\text{SO}_3^-$ and $[\text{PF}_3(\text{C}_2\text{F}_5)_3]^-$.^[2,3] In contrast, there is a much smaller number of ILs with fluorinated cations (FC-ILs).^[3–8] Many of the FC-ILs in fact have both ions fluorinated (FAC-ILs). The first FC-ILs, with 3-methyl-1-(2,2,2-trifluoroethyl)imidazolium, were reported by Bonhôte and co-workers in 1996 and were characterized as hydrophobic, highly conductive, ambient-temperature molten materials.^[6] However, the vast majority of fluorinated cations contain a single fluorinated alkyl chain with an ethylene spacer, $-\text{CH}_2\text{CH}_2(\text{CF}_2)_n\text{F}$ to the cationic moiety (Scheme 1, class II₁). The value of n varies greatly, but six is most common. Although the cationic moiety



Scheme 1. Classes of known FC-ILs based on the number of fluorinated groups and the spacing to the cationic moiety.

is typically imidazolium,^[3,5,7,9–13] examples with a cation such as pyridinium,^[11,14,15] ammonium,^[15,16] phosphonium^[14,16] or triazolium are also known.^[11,17] There is also a number of examples with longer spacer groups.^[6,11,13,18–20] Related to this class is the benzyl-functionalised imidazolium (IM) IL $[\text{BuIMCH}_2\text{C}_6\text{F}_5]\text{NTf}_2$ which contains a perfluorophenyl group.^[21] Methylene spacers are much less common (class I₁), and are mostly associated with a single 2,2,2-trifluoroethyl group on imidazolium or pyridinium.^[7,8,22] These FC-ILs are fundamentally different from other FC-ILs due to the close proximity of both the cationic charge and the electronegative F atoms to the methylene protons, which can therefore make them significant hydrogen-bond donor groups. FC-ILs with no spacer (class 0_I) are also very rare. These have been attached to imidazolium and triazolium cations.^[23,24]

FC-ILs with more than one fluorinated alkyl group are only known for classes II₂^[10,16,25,26] (imidazolium, triazolium, pyridinium, ammonium and phosphonium) and II₃ (phosphonium).^[27] Alpers *et al.* also reported some dicationic diammonium and diphosphonium ILs with two fluorinated alkyl groups.^[16]

[a] Dr. O. J. Curnow, Dr. R. Senthooan
School of Physical and Chemical Sciences
University of Canterbury
Private Bag 4800, Christchurch 8140
(New Zealand)
E-mail: owen.curnow@canterbury.ac.nz

Supporting information for this article is available on the WWW under <https://doi.org/10.1002/asia.202200139>

© 2022 The Authors. Chemistry - An Asian Journal published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.

Fluorine-containing ILs are interesting materials as they can be used in applications such as gas absorption and for the formation of hydrophobic materials. Vanhoutte *et al.* have studied the solubility of oxygen in piperidinium and pyrrolidinium FAC-ILs and concluded that the concentration of dissolved oxygen in fluorinated ILs is higher than that of commercial ILs without a fluorinated alkyl chain.^[18] Tindale and Ragogna have synthesized a series of highly-fluorinated phosphonium-based ILs and investigated them as media for the generation of superhydrophobic coatings.^[27]

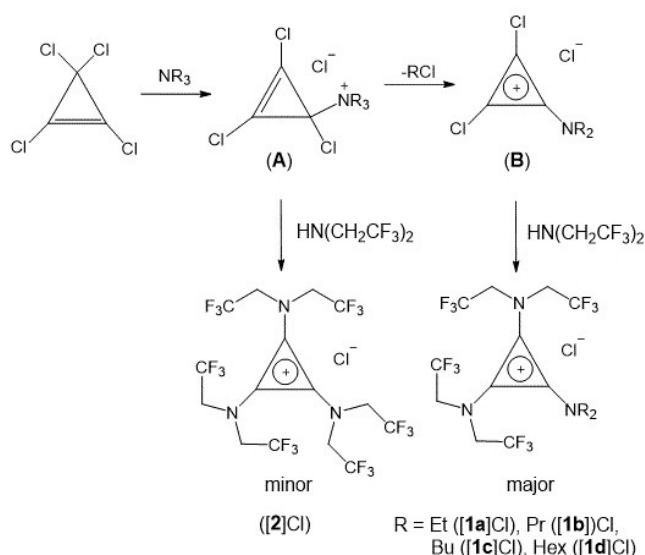
As noted by Pereira and coworkers, the physical characterisations of most of the FC-ILs reported to date has been very limited and would typically only include the synthesis and thermal (DSC and TGA) properties.^[3] Coupled with the limited number of FC-ILs, it is therefore often difficult to distinguish clear trends in their properties. However, the viscosity of fluorinated ILs is generally quite high, and conductivity is rather low.^[19]

In the work reported here we will describe the synthesis and properties of FC-ILs based on triaminocyclopropenium (TAC) cations which allow us to introduce up to six fluorinated alkyl groups. TAC salts have been investigated for almost 50 years,^[28] but interest in applications of TAC salts has significantly increased lately due to the favourable properties that these cations exhibit. They have a high-lying HOMO, which results in particularly weak interactions with anions,^[29–32] and a reversible oxidation to the radical dication, which makes them useful for electrochemical processes.^[33] TAC salts also have excellent thermal stability, despite the ring strain, due to their aromaticity, charge delocalization, and high-energy HOMO. Other areas of interest include anion switches,^[34] polyurethanes,^[35] ionic liquid crystals,^[36] polyelectrolytes,^[37] phase-transfer catalysis,^[38,39] organocatalysis,^[40] hypergolic fluids,^[41] and lipase activation.^[42] We initially reported the IL properties of TAC-based salts in 2011,^[43] and this was followed by studies on tris(dialkylamino)cyclopropenium (TDAC) NTf₂[−] ILs^[44] and dicyanamide (DCA) ILs,^[45] as well as protic and amino acid-functionalised TAC ILs.^[46,47] We now report our use of trifluoroethyl groups to produce fluorinated TAC cations of the new classes I₂, I₄ and I₆ (cations with 2, 4 and 6 CH₂CF₃ groups, respectively) along with an investigation of their properties.

Results and Discussion

Synthesis

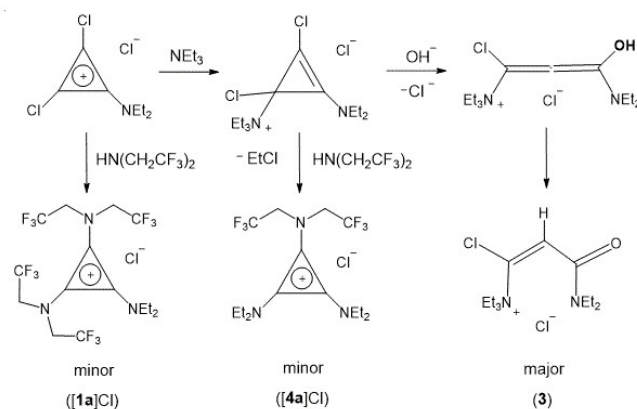
Addition of secondary amines to either pentachlorocyclopropane or tetrachlorocyclopropene is well known for the synthesis of triaminocyclopropenium (TAC) salts.^[28c,d] However, this does not work well with weakly-nucleophilic amines such as bis(2,2,2-trifluoroethyl)amine, NH(CH₂CF₃)₂. We found however, that the addition of a trialkylamine NR₃ (R = Et, Pr, Bu, Hex) to a solution with C₃Cl₄ and NH(CH₂CF₃)₂ would readily give a TAC salt with two fluorinated amino groups and one dialkylamino group derived from the trialkylamine, [C₃(N(CH₂CF₃)₂)₂(NR₂)]Cl. A proposed mechanism is shown in Scheme 2 in which C₃Cl₄



Scheme 2. Synthesis of TAC salts with two or three fluorinated amino groups.

initially undergoes nucleophilic substitution by an amine, with loss of Cl[−], to give intermediate A which can then lose a chloroalkane to form the dichloroaminocyclopropenium intermediate B (we isolated PrCl from a reaction using NPr₃). This cationic salt is now more readily attacked by NH(CH₂CF₃)₂ to form the resultant TAC chloride salt ([1a–d]Cl). Interestingly, a small amount (ca. 8%) of [C₃(N(CH₂CF₃)₂)₃]Cl ([2]Cl) is also formed; this does not form in the absence of NR₃. We believe that this is due to a slow reaction of NH(CH₂CF₃)₂ with the cationic intermediate A (which would be faster than a reaction with neutral C₃Cl₄).

Optimization of reagent ratios is critical to maximizing the yield of the desired product. With an excess of NEt₃, for example, the major product is instead [Et₃NCCICHCONEt₂]Cl (3) with [1a]Cl and [C₃(N(CH₂CF₃)₂)₂(NEt₂)₂]Cl ([4a]Cl) as minor products (Scheme 3). It's not clear where the O atom in 3 came

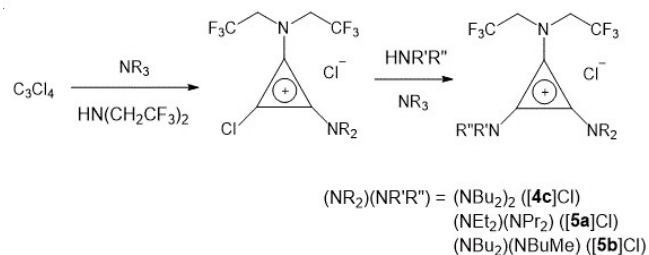


Scheme 3. Reaction of C₃Cl₄ with NH(CH₂CF₃)₂ and an excess of NEt₃ (starting from intermediate B).

from, but we presume it came from traces of water in the undried amine. ES-MS of the crude product mixtures was found to be useful by giving near quantitative information on the product ratios (see Supporting Information). It was found that C_3Cl_5H could also be used instead of C_3Cl_4 , but the reactions were not as clean. For the synthesis of [1 a]Cl, a $C_3Cl_5H/NH(CH_2CF_3)_2/NEt_3$ ratio of 1:5:2 was found to be best.

Salt 3 was also characterized crystallographically as the monohydrate and found to contain a rare discrete 1D linear $\{Cl(H_2O)^-\}_\infty$ chain.^[32] Details are provided in the Supporting Information.

TAC cations with one fluorinated amino group could be prepared in two steps by the later addition of a secondary dialkylamine NHRR' which reacts faster than the remaining $NH(CH_2CF_3)_2$. Thus, if addition of $NH(CH_2CF_3)_2/NBu_3$ is followed by addition of $HNBu_2$ (with further tertiary amine) then the C_{2v} -symmetric cation [4 c]Cl is formed (Scheme 4). In this manner, it is also possible to form C_5 -symmetric cations with three different amino groups, and we isolated $[C_3(N(CH_2CF_3)_2)(NEt_2)(NPr_2)]Cl$ ([5 a]Cl) and $[C_3(N(CH_2CF_3)_2)(NBu_2)(NBuMe)]Cl$ ([5 b]Cl) via this route.



Scheme 4. Synthesis of TAC salts with one fluorinated amino group.

Interestingly, we were able to prepare a C_5 -symmetric cation with two fluorinated amino groups by using a shorter time for stirring with more $NH(CH_2CF_3)_2$ and NBu_3 followed by addition of $HNBuMe$ to give $[C_3(N(CH_2CF_3)_2)_2(NBuMe)]Cl$ ([1 e]Cl). This suggests the presence of fluorinated analogues of intermediate A in Scheme 2 and that the route taken and the products formed depends on a number of factors such as the concentration, relative proportions of the reagents, time allowed between steps, and the nature of the tertiary amine.

Attempts to prepare [2]Cl in greater yield were unsuccessful. We also found that it was always isolated with a significant impurity in which one F atom has been replaced by an H atom to give $[C_3(N(CH_2CF_3)_2)_2(N(CH_2CF_3)(CH_2CHF_2))]Cl$ ([6]Cl), as confirmed by 1H -NMR and ES-MS (Supporting Information). However, the mechanism for the formation of this compound is unclear.

In order to investigate the potential usefulness of these cations in forming ionic liquids, a selection of the chloride salts was converted to salts with bistriflamide, dicyanamide and triflate anions, as listed in Table 1, using conventional metathesis routes. We then investigated their physical properties (DSC, TGA, viscosity, density and conductivity) where possible. Unfortunately, we were unable to prepare ionic liquids with 2^+ due to the low yields and very low solubility of the chloride salt in organic solvents.

DSC and TGA data

DSC data was collected at $10^\circ C min^{-1}$ and the results are summarized in Table 1. For the chloride salts (Figure 1), melting point is primarily dependent on the number of fluorinated amino groups with [2]Cl (F_{18}) having the highest m.p. ($236^\circ C$)

Table 1. DSC and TGA data for fluorinated TAC salts.

Salt	Yield/%	$T_g/^\circ C$	$T_m/^\circ C$	T_d at $1^\circ C min^{-1}/^\circ C$	T_d at $10^\circ C min^{-1}/^\circ C$
$[C_3(N(CH_2CF_3)_2)_2(NEt_2)]Cl$ ([1 a]Cl)	41	–	206	243	273
$[C_3(N(CH_2CF_3)_2)_2(NPr_2)]Cl$ ([1 b]Cl)	39	–	191	238	271
$[C_3(N(CH_2CF_3)_2)_2(NBu_2)]Cl$ ([1 c]Cl)	41	–	174	238	273
$[C_3(N(CH_2CF_3)_2)_2(NHex_2)]Cl$ ([1 d]Cl)	10	–	120	238	268
$[C_3(N(CH_2CF_3)_2)_2(NBuMe)]Cl$ ([1 e]Cl)	15	–	191	236	267
$[C_3(N(CH_2CF_3)_2)_3]Cl$ ([2]Cl)	6	–	236	231	260
$[C_3(N(CH_2CF_3)_2)(NBu_2)_2]Cl$ ([4 c]Cl)	35	–	81.3	246	280
$[C_3(N(CH_2CF_3)_2)(NEt_2)(NPr_2)]Cl$ ([5 a]Cl)	16	–	63.7	250	281
$[C_3(N(CH_2CF_3)_2)(NBu_2)(NBuMe)]Cl$ ([5 b]Cl)	43	–39.4	RTIL	242	275
$[C_3(N(CH_2CF_3)_2)_2(NEt_2)]NTf_2$ ([1 a]NTf ₂)	71	–	88.1	273	328
$[C_3(N(CH_2CF_3)_2)_2(NBu_2)]NTf_2$ ([1 c]NTf ₂)	90	–37.0	56.6	277	331
$[C_3(N(CH_2CF_3)_2)_2(NHex_2)]NTf_2$ ([1 d]NTf ₂)	89	–38.2	36.4	283	330
$[C_3(N(CH_2CF_3)_2)_2(NBuMe)]NTf_2$ ([1 e]NTf ₂)	90	–	88.8	278	336
$[C_3(N(CH_2CF_3)_2)(NBu_2)_2]NTf_2$ ([4 c]NTf ₂)	88	–59.1	RTIL	305	388
$[C_3(N(CH_2CF_3)_2)(NBu_2)(NBuMe)]NTf_2$ ([5 b]NTf ₂)	73	–55.3	RTIL	311	368
$[C_3(N(CH_2CF_3)_2)_2(NBu_2)]DCA$ ([1 c]DCA) ^[a]	64	–21.4	68.7	199	235
$[C_3(N(CH_2CF_3)_2)_2(NHex_2)]DCA$ ([1 d]DCA) ^[a]	80	–29.8	RTIL	186	232
$[C_3(N(CH_2CF_3)_2)(NBu_2)_2]DCA$ ([4 c]DCA) ^[a]	80	–47.1	RTIL	206	252
$[C_3(N(CH_2CF_3)_2)(NBu_2)(NBuMe)]DCA$ ([5 b]DCA) ^[a]	64	–45.4	RTIL	218	254
$[C_3(N(CH_2CF_3)_2)_2(NBu_2)]OTf$ ([1 c]OTf)	76	–28.2	RTIL	253	342
$[C_3(N(CH_2CF_3)_2)_2(NHex_2)]OTf$ ([1 d]OTf)	91	–28.8	RTIL	275	343
$[C_3(N(CH_2CF_3)_2)(NBu_2)_2]OTf$ ([4 c]OTf)	91	–45.1	RTIL	306	357
$[C_3(N(CH_2CF_3)_2)(NBu_2)(NBuMe)]OTf$ ([5 b]OTf)	74	–43.5	RTIL	294	366

[a] DCA = dicyanamide $[N(CN)_2]^-$.

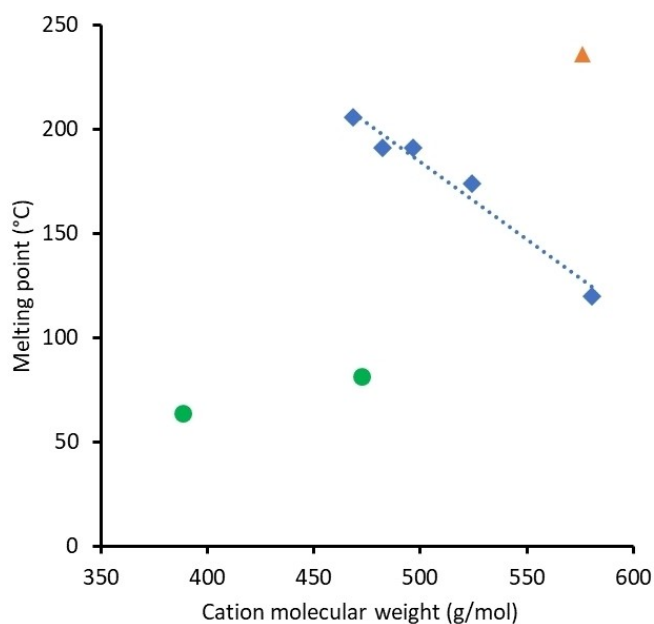


Figure 1. Melting points of fluorinated TAC chloride salts. Green circles (F₆ salts), blue diamonds (F₁₂ salts), orange triangle (F₁₈ salt [2]Cl).

and only the mono-fluorinated amino-group (F₆) salts being ILs; secondarily on symmetry, with the m.p. decreasing from [4c]Cl to [5a]Cl to [5b]Cl (81.3 °C, 63.7 °C and RTIL, respectively); and finally on alkyl chain length with decreasing m.p. for the difluorinated amino-group (F₁₂) salts [1a–d]Cl (206 °C, 191 °C, 174 °C and 120 °C, respectively). Similar trends are found for the NTf₂⁻ and DCA salts, however, all of these classify as ILs, with the F₆ salts being RTILs. In the case of the triflate salts, all of these are RTILs.

Thermal decomposition temperatures (*T_d*) were determined at both 1 °C min⁻¹ and 10 °C min⁻¹ and are given in Table 1. The main factor that determines *T_d* in these salts is the anion, with *T_d* decreasing NTf₂⁻ > OTf⁻ > Cl⁻ > DCA. For comparison, TDAC NTf₂⁻ salts (without any Me groups) have *T_d* values around 400 °C, which is about 70 °C higher than the F₁₂ NTf₂⁻ salts.^[44] The lower stability of the DCA salts compared to the Cl⁻ salts is interesting, especially in light of their much lower m.p.s.^[48] F₁₂ DCA salts have *T_d* values about 100 °C lower than TDAC DCA

salts.^[45] On the other hand, F₁₂ Cl⁻ salts have *T_d* values about only 30 °C higher than TDAC Cl⁻ salts.^[43,44] The nature of the alkyl group has very little effect on *T_d* whereas an additional fluorinated amino group decreases *T_d* by 10–20 °C for the Cl⁻, OTf⁻ and DCA salts and 30–50 °C for the NTf₂⁻ salts.

Density

Density data were determined from 20–90 °C for the relatively low viscosity IL [4c]NTf₂ (Tables 1S and 2S). At 20 °C, the density is 1.298202 g/cm³ with a molar volume of 579.82 cm³/mol. Parameters *a* and *b*, for the linear fit of the data using the equation $\rho = a - bT$, were found to be 1.317240 g/cm³ and 0.000955 g cm⁻³ K⁻¹, respectively.

The densities of the other, more viscous, ILs at 20 °C was estimated using the group additivity method for determining molecular volume (Tables 2 and 3S). The molecular volume of [4c]NTf₂ is 962.5 Å³. We used the following volumes for the individual groups as determined by various authors: 280 Å³ for the [C₃(NMe₂)₃]⁺ core, 27.7 Å³ (CH₂), 5 Å³ (H), 80 Å³ (DCA), 248 Å³ (NTf₂⁻), 125 Å³ (OTf⁻) and 27 Å³ (Cl⁻).^[44,45,49] The volume for a CF₃ group was thus found to be 56.2 Å³.

Viscosity

Viscosity data were collected from 20–90 °C where possible; the results for the 20 °C and 50 °C data are given in Table 2 and the complete set of data is provided in the Supporting Information (Table 4S). The discussion here will refer to the 50 °C data, which is more comprehensive. Firstly, additional fluorinated amino groups increase the viscosities significantly, for example, 480 cP for [4c]OTf versus 5425 cP for [1c]OTf. Similarly, the F₆ ILs [4c]NTf₂ and [5b]NTf₂ (979 and 492 cP, respectively) have much higher viscosities than TDAC NTf₂⁻ ILs of similar MW, which have viscosities of about 200 cP.^[44] Likewise, TDAC DCA ILs have viscosities of about 250 cP versus 3906 and 6770 cP for [4c]DCA and [5b]DCA, respectively.^[45] A similar trend was reported for fluorinated versus non-fluorinated imidazolium ILs.^[12,19,50] In terms of anion effects, the ability to hydrogen bond and a small size appear to be key factors, with Cl⁻ ≫ OTf⁻ > DCA ≫ NTf₂⁻.

Table 2. MW and selected density, viscosity, and conductivity data for fluorinated ILs.

Ionic liquid	MW [g/mol]	Density [g cm ⁻³]		Viscosity [cP]		Conductivity [mS cm ⁻¹]		Δ <i>W</i> at 20 °C
		20 °C	50 °C	20 °C	50 °C	20 °C	50 °C	
[C ₃ (N(CH ₂ CF ₃) ₂)(NBu ₂)(NBuMe)]Cl ([5b]Cl)	465.95	1.175 ^[a]	–	–	2510	0.0033	0.0481	
[C ₃ (N(CH ₂ CF ₃) ₂)(NBu ₂) ₂]NTf ₂ ([4c]NTf ₂)	752.72	1.298202	1.269463	979	142	0.0858	0.389	0.31
[C ₃ (N(CH ₂ CF ₃) ₂)(NBu ₂)(NBuMe)]NTf ₂ ([5b]NTf ₂)	710.64	1.342 ^[a]	–	492	83	0.1082	0.500	0.56 ^[b]
[C ₃ (N(CH ₂ CF ₃) ₂)(NHEx ₂)]DCA ([1d]DCA)	646.56	1.276 ^[a]	–	–	2818	0.0021	0.0396	
[C ₃ (N(CH ₂ CF ₃) ₂)(NBu ₂) ₂]DCA ([4c]DCA)	538.62	1.125 ^[a]	–	3906	321	0.0371	0.320	0.16 ^[b]
[C ₃ (N(CH ₂ CF ₃) ₂)(NBu ₂)(NBuMe)]DCA ([5b]DCA)	496.54	1.159 ^[a]	–	6770	411	0.0452	0.352	1.02 ^[b]
[C ₃ (N(CH ₂ CF ₃) ₂)(NBu ₂) ₂]OTf ([1c]OTf)	673.48	1.442 ^[a]	–	–	5425	0.0007	0.0215	
[C ₃ (N(CH ₂ CF ₃) ₂)(NHEx ₂)]OTf ([1d]OTf)	729.59	1.367 ^[a]	–	–	2878	0.0003	0.0083	
[C ₃ (N(CH ₂ CF ₃) ₂)(NBu ₂) ₂]OTf ([4c]OTf)	621.64	1.229 ^[a]	–	6919	480	0.0710	0.325	–0.40 ^[b]
[C ₃ (N(CH ₂ CF ₃) ₂)(NBu ₂)(NBuMe)]OTf ([5b]OTf)	579.56	1.272 ^[a]	–	9766	555	0.0158	0.1465	0.15 ^[b]

[a] Calculated density; [b] Estimated using the calculated density at 20 °C.

The much lower viscosities of the NTf_2^- ILs compared to the DCA ILs is in complete contrast to the TDAC ILs in which the NTf_2^- ILs have slightly higher viscosities.^[44,45] Presumably, steric effects hinder the NTf_2^- ions from hydrogen bonding with the CH_2CF_3 groups.

The viscosity data was fit to both the Arrhenius and Vogel-Fulcher-Tammann equations; these parameters are given in the Supporting Information (Table 5S). The values of D , a measure of the deviation from Arrhenius behavior, lie in the range 5–10 which is typical for “fragile” liquids.^[51] A “fragility plot” of $\log(\text{viscosity})$ versus T_g/T (Figure 1S) also confirms that these are fragile ILs.

Conductivity

Conductivity data was collected from 20–90 °C where possible. Results at 20 °C and 50 °C are given in Table 2 and the complete set of data, along with the fitting data (to both the Arrhenius and Vogel-Fulcher-Tammann equations), is provided in the Supporting Information (Tables 6S and 7S). Conductivity generally decreases with an increase in the viscosity of the IL, but ion-pairing or clustering will also have a significant impact on the conductivity. Thus, conductivity is found to be lowest for the F_{12} ILs as well as the chloride IL [5b]Cl, as these all have high viscosities. Of these, [1d]OTf has an especially low conductivity relative to its viscosity. On the other hand, of the F_6 ILs, [4c]OTf has a relatively high conductivity for its viscosity.

Ionicity

A Walden plot, $\log(\Lambda)$ versus $\log(1/\eta)$, is frequently used to investigate the ionicity of an IL (Figure 2). The deviation from

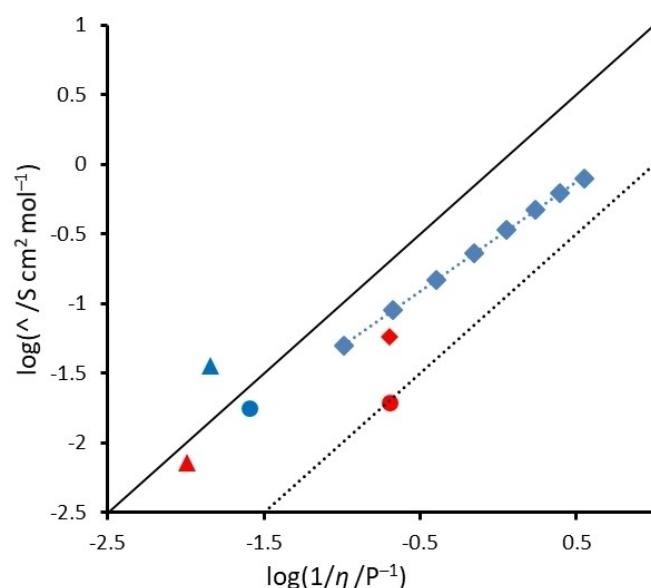


Figure 2. Walden plot for fluorinated TAC ILs. The solid diagonal line represents 1 M KCl(aq). Blue 4c^+ ; red 5b^+ ; diamonds NTf_2^- ; circles DCA; triangles OTf^- .

the diagonal line on the Walden plot (ΔW) is given in Table 2. Low ionicity is generally attributed to the formation of ion-pairs, ion-triplets or cluster aggregates, however, correlated and anti-correlated motions of ions, for example, provide alternative explanations for decreased conductivity.^[52] Methods to determine ionicity have been discussed recently by Nordness and Brennecke.^[53]

A Walden plot requires knowledge of the fluid’s density to determine the molar conductivity. Unfortunately, we were only able to measure one set of density data, so the density for the other five ILs that are liquid at 20 °C was estimated as described above. Thus, ΔW for these ILs are estimates. From Figure 2 we can see that the NTf_2^- salts are “good” ILs, the triflate salts are “very good” to “superionic” ILs and the DCA salts are highly variable.

Miscibility and solubility

The miscibility and solubility properties were investigated at 25 °C (Table 3). As would be expected, the chloride salts are soluble or miscible in the amphiprotic solvents water and ethanol and insoluble/immiscible in toluene and hexane, although the low-symmetry and conformationally-flexible salt [5b]Cl is miscible with toluene (and diethylether) and has some miscibility in hexane. Proton acceptor ability seems to be quite important as these salts are soluble/miscible in ethylacetate (and acetonitrile) and most have some solubility in diethylether. Conversely, a number of them have low solubility in the polar solvent CH_2Cl_2 , contrary to typical ILs. This is likely because CH_2Cl_2 is a very weak proton-acceptor solvent.

The NTf_2^- , DCA and OTf^- salts tend to have similar solubility properties: they are all insoluble/immiscible in water but soluble/miscible in EtOH, CH_2Cl_2 and EtOAc. Differences appear when using non-polar solvents. Notably, the NTf_2^- salts tend to be less miscible/soluble in these solvents, which is not the case for TDAC salts.^[44,45] They are also more soluble/miscible in diethyl ether than toluene or hexane, presumably due to hydrogen bonding between the cation CH_2 groups and the ether O atom. Interestingly, the DCA salts have very similar miscibilities in toluene, diethylether and hexane, being mostly partially miscible. In this case, the methylene groups are presumably hydrogen bonding with DCA rather than ether. The triflate salts, however, are mostly fully miscible in diethylether, suggesting weaker hydrogen bonding between the cation and anion.

Solid state structures

We have previously reported the solid-state structures and infrared spectra of some of the chloride salts as discrete chloride hydrates. In particular, [1c]Cl.H₂O forms a dichloride dihydrate square $[\text{Cl}_2(\text{H}_2\text{O})_2]^{2-}$,^[30] [1d]Cl.0.5H₂O forms a dichloride hydrate $[\text{Cl}_2(\text{H}_2\text{O})]^{2-}$,^[31] [1e]Cl.H₂O forms a 1D chain $[\text{Cl}(\text{H}_2\text{O})]_{\infty}$,^[32] [4c]Cl.H₂O forms a dichloride dihydrate square $[\text{Cl}_2(\text{H}_2\text{O})_2]^{2-}$,^[30] and [5a]Cl.H₂O forms a tetrachloride tetrahy-

Table 3. Miscibility and solubility properties of fluorinated TAC salts at 25 °C.^[a]

Compound	Water	EtOH	CH ₂ Cl ₂	EtOAc	Toluene	Et ₂ O	Hexane
[C ₃ (N(CH ₂ CF ₃) ₂) ₂ (NEt ₂)]Cl (1 a)	S	S	I	S	I	I	I
[C ₃ (N(CH ₂ CF ₃) ₂) ₂ (NPr ₂)]Cl (1 b)	S	S	P	S	I	P	I
[C ₃ (N(CH ₂ CF ₃) ₂) ₂ (NBu ₂)]Cl (1 c)	S	S	S	S	I	P	I
[C ₃ (N(CH ₂ CF ₃) ₂) ₂ (NHex ₂)]Cl (1 d)	S	S	S	S	I	P	I
[C ₃ (N(CH ₂ CF ₃) ₂) ₂ (NBuMe)]Cl (1 e)	S	S	P	S	I	I	I
[C ₃ (N(CH ₂ CF ₃) ₂) ₃]Cl (2)	S	S	I	S	I	I	I
[C ₃ (N(CH ₂ CF ₃) ₂)(NBu ₂) ₂]Cl (4 c)	S	S	S	S	I	P	I
[C ₃ (N(CH ₂ CF ₃) ₂)(NBu ₂)(NBuMe)]Cl (5 b)	M	M	M	M	M	M	≥ 53% IL
[C ₃ (N(CH ₂ CF ₃) ₂) ₂ (NEt ₂)]NTf ₂ (1 a)	I	S	P	S	I	P	I
[C ₃ (N(CH ₂ CF ₃) ₂) ₂ (NBu ₂)]NTf ₂ (1 c)	I	S	S	S	I	P	I
[C ₃ (N(CH ₂ CF ₃) ₂) ₂ (NHex ₂)]NTf ₂ (1 d)	I	S	S	S	N	S	I
[C ₃ (N(CH ₂ CF ₃) ₂) ₂ (NBuMe)]NTf ₂ (1 e)	I	S	P	S	I	P	I
[C ₃ (N(CH ₂ CF ₃) ₂)(NBu ₂) ₂]NTf ₂ (4 c)	N	M	M	M	≥ 50% IL	M	≥ 56% IL
[C ₃ (N(CH ₂ CF ₃) ₂)(NBu ₂)(NBuMe)]NTf ₂ (5 b)	N	M	M	M	≥ 53% IL	M	≥ 53% IL
[C ₃ (N(CH ₂ CF ₃) ₂) ₂ (NBu ₂)]DCA (1 c)	I	S	S	S	I	P	I
[C ₃ (N(CH ₂ CF ₃) ₂) ₂ (NHex ₂)]DCA (1 d)	N	M	M	M	≥ 67% IL	≥ 53% IL	≥ 53% IL
[C ₃ (N(CH ₂ CF ₃) ₂)(NBu ₂) ₂]DCA (4 c)	N	M	M	M	≥ 53% IL	≥ 53% IL	≥ 59% IL
[C ₃ (N(CH ₂ CF ₃) ₂)(NBu ₂)(NBuMe)]DCA (5 b)	N	M	M	M	≥ 50% IL	≥ 53% IL	≥ 53% IL
[C ₃ (N(CH ₂ CF ₃) ₂) ₂ (NBu ₂)]OTf (1 c)	N	M	M	M	≥ 59% IL	≥ 53% IL	≥ 53% IL
[C ₃ (N(CH ₂ CF ₃) ₂)(NHex ₂)]OTf (1 d)	N	M	M	M	≥ 59% IL	M	≥ 67% IL
[C ₃ (N(CH ₂ CF ₃) ₂)(NBu ₂) ₂]OTf (4 c)	N	M	M	M	M	M	≥ 71% IL
[C ₃ (N(CH ₂ CF ₃) ₂)(NBu ₂)(NBuMe)]OTf (5 b)	N	M	M	M	M	M	≥ 53% IL

[a] S = soluble; I = insoluble; M = miscible; N = immiscible liquid; P = partial solubility/miscibility.

drate [Cl₄(H₂O)₄]⁴⁻.^[32] We now report the solid-state structures of three additional chloride salts, the anhydrous salt **[2]Cl**, the monohydrate **[1 b]Cl·H₂O** which contains a [Cl₂(H₂O)₂]²⁻ square, and the hydrate **[1 a]Cl·2.17H₂O** which contains a discrete 1D ribbon of the chloride hydrate {[Cl₆(H₂O)₁₃]⁶⁻}_∞. We also report the structure of the bistriflamide salt **[1 a]NTf₂**.

[C₃(N(CH₂CF₃)₂)₃]Cl (**[2]Cl**) crystals were obtained by slow evaporation of an acetonitrile/DCM solution at room temperature. It crystallizes in the triclinic space group *P*-1 and the asymmetric unit has one cation and chloride anion (Table 8S). Each chloride ion is surrounded by three cations and has six CH–Cl hydrogen-bond interactions, with the closest α -hydrogen atoms as shown in Figure 3. The cation adopts a conformation in which fluoroalkyl chains in two of the amino groups are alternating either side of the C₃ plane and in the other amino group they are on the same side of the C₃ plane. Every chloride

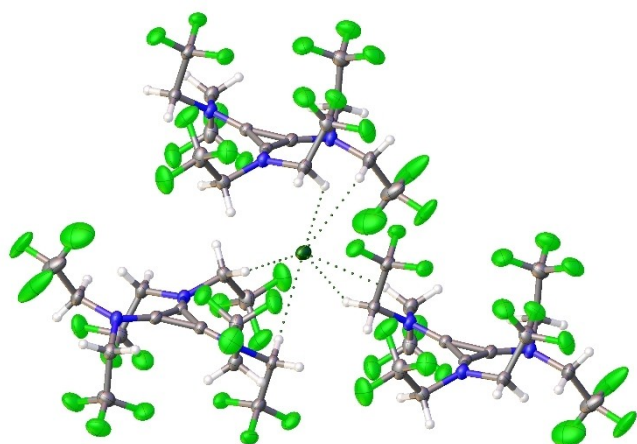


Figure 3. Plot of **[2]Cl** illustrating the environment around the chloride ion.

is “chelated” by three cations and every cation chelates three chlorides to form a 3D network of CH–Cl⁻ hydrogen bonds (Table 14S). This extensive network accounts for its high melting point of 236 °C.

Despite the electronegativity of the trifluoromethyl groups, the ring C–C and exocyclic C–N bond distances (average 1.381 Å and 1.335 Å, respectively) are typical for peralkylated TAC salts.^[54] Two of the amino groups are relatively planar and in the plane of the C₃ ring, however, one is a distorted trigonal plane (sum of angles = 355.3°) with one substituent rotated out of the C₃ plane (C3-C2-N2-C23 = –46.4(4)°). However, these distortions are not especially unusual.^[54]

Suitable crystals of **[1 b]Cl** for X-ray diffraction were grown by slow evaporation of an undried CH₂Cl₂/MeOH solution. The salt crystallizes in the monoclinic space group *C2/c* (Table 9S) in which the asymmetric unit consists of one cation, a chloride ion and two half-water solvates (Figure 4a). The chloride hydrate then forms a [Cl₂(H₂O)₂]²⁻ square with crystallographic C_{2v} symmetry (Figure 4b). The cation adopts a conformation in which three trifluoroethyl groups and one propyl group are in one side of the C₃N₃ plane while one trifluoroethyl group and one propyl group are in the opposite side of the plane. The dichloride dihydrate cluster is sandwiched between two cations with four additional cations which also have hydrogen-bonding interactions with the cluster (Figure 6S and Table 17S).

Due to the different π -donor abilities of the amino groups, the exocyclic C–N bond to the NEt₂ group is shorter than to the N(CH₂CF₃)₂ groups (1.3101(15) Å versus 1.3388 Å average, respectively) and the cyclic C–C bond opposite the NEt₂ group is also shorter (1.3690(14) Å versus 1.3884 Å average, respectively). However, the average C–C and C–N distances are essentially the same as **[2]Cl** (1.382 Å and 1.329 Å versus 1.381 Å and 1.335 Å, respectively). Also like **2⁺**, two of the amino groups are relatively planar and in the plane of the C₃ ring, while one is

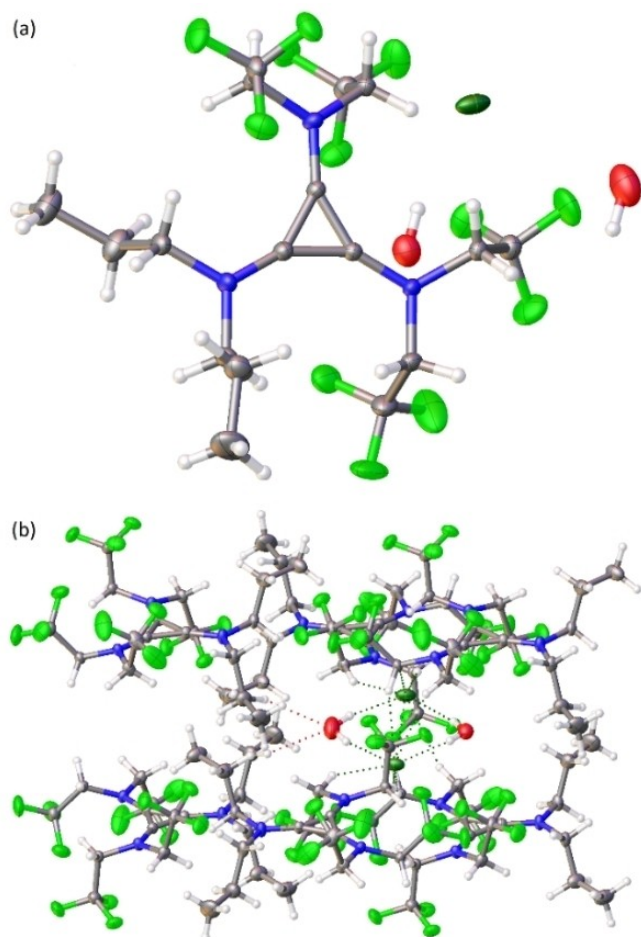


Figure 4. (a) Asymmetric unit of [1 b]Cl.H₂O; (b) The [Cl₂(H₂O)₂]²⁻ cluster and its environment within [1 b]Cl.H₂O.

a distorted trigonal plane (sum of angles = 355.9°) with one substituent rotated out of the C₃ plane (C1-C2-N2-C21 = 20.5(3)°). Regarding the chloride hydrate cluster, there is only one other reported C_{2v}-symmetric [Cl₂(H₂O)₂]²⁻ cluster, in the closely-related [1 c]Cl.H₂O salt.^[30] The cluster in [1 b]Cl.H₂O has longer Cl–O distances (3.262(5) and 3.31(5) Å versus 3.2051(15) and 3.2975(15) Å) and, consequently, the infrared stretching bands (Figure 7S) are at higher energy and the bending bands are at lower energy (Table 18S). Curnow and Crittenden have recently reviewed the structures and infrared spectra of halide hydrates in the solid state.^[55]

Crystals of [C₃(N(CH₂CF₃)₂)₂(NEt₂)]Cl·2.17H₂O ([1 a]Cl·2.17H₂O) were obtained by slow evaporation of a CH₂Cl₂/EtOH solution at room temperature. It crystallizes in the triclinic space group *P*-1 (Table 9S). The asymmetric unit contains six cations and anions along with 12 fully-occupied water molecules and two half-occupied water molecules, thus the stoichiometry is 13 waters per six cations and anions (Figure 5). Two of the cations have disordered CH₂CF₃ groups. In all of the cations, the CH₃ groups are alternating either side of the C₃N₃ plane. On the other hand, a variety of conformations relative to the C₃N₃ plane are observed for the CH₂CF₃ groups: in four of the cations, the CF₃

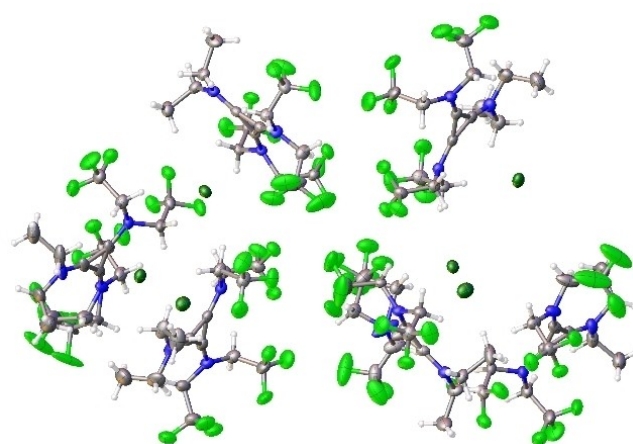


Figure 5. Asymmetric unit of [1 a]Cl·2.17H₂O (the waters are not shown for clarity).

groups are on the same side of the plane; while in the other two cations, two CF₃ groups are on same side of the plane and the other two are alternating either side of the plane (Figure 20S).

The chloride hydrate forms a 1D ribbon of {[Cl₆(H₂O)₁₃]⁶⁻}_∞ within relatively hydrophilic (CH₂) channels (Figure 6) to form ionic regions within the crystal. The chloride anions have a number of weak hydrogen-bonding interactions with the cation; there are 20 CH–Cl hydrogen bonding interactions with

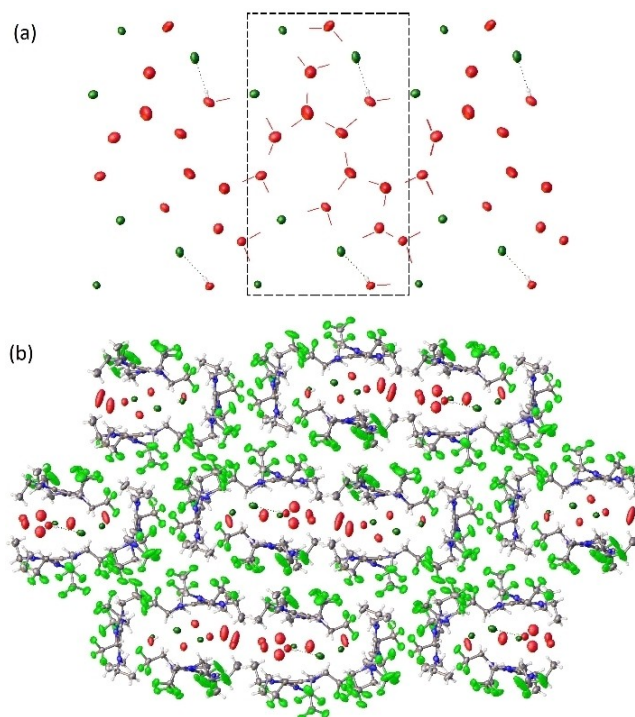


Figure 6. (a) The {[Cl₆(H₂O)₁₃]⁶⁻}_∞ ribbon in [1 a]Cl·2.17H₂O (the likely hydrogen-bonding arrangement is indicated; the two half-occupied waters are in essentially the same position-on top of each other in this view); (b) chloride hydrate ribbons within ionic channels surrounded by fluororous regions.

H–Cl distances within 2.61–3.00 Å (Figure 19S and Table 21S). Of those 20 hydrogen bonds, only one is associated with an ethyl group; this illustrates the better hydrogen-bond donor ability of trifluorinated ethyl groups. Figure 6b clearly illustrates the formation of ionic regions surrounded by fluororous regions.

The structure of the bistriflamide salt of [1a]⁺ was also determined; crystals of [1a]NTf₂ were obtained by slow evaporation of a methanol solution at room temperature. It crystallizes in the monoclinic space group C2/c (Table 9S) and the asymmetric unit contains one and a half independent cations and one and a half anions (Figure 7). In both cations, the CF₃ and CH₃ groups are alternating either side of the C₃N₃ plane. All of the nitrogen atoms are trigonal planer with the sum of the C–N–C angle around each of the nitrogen atom close to 360° (N1 = 359.9°; N2 = 358.8°; N3 = 358.7°). One of the anions is disordered. The anions are each surrounded by seven cations via weak CH–F, CH–O and CH–N hydrogen bonds as detailed in the Supporting Information.

Conclusion

We have prepared a series of highly-fluorinated TAC salts. Trialkylamines NR₃ were found to facilitate the reaction of the amine HN(CH₂CF₃)₂ with C₃Cl₄ or C₃Cl₃H. This allows the preparation of TAC cations with one, two or three fluorinated amino groups, including cations with three different amino groups. The use of trialkylamines to promote the addition of a weakly-nucleophilic amine suggests that a general route for the addition of similar weakly-nucleophilic amines is now available. Curiously, the cation with three fluorinated amino groups, 2⁺, was found to readily form a cation with just one F atom replaced by an H atom. Unfortunately, these salts were not available in high yields.

Melting points were found to increase significantly with fluorinated amino groups, decrease with alkyl chain length and lower symmetry, and decrease with the anion in the order Cl[−] > NTF₂[−] > DCA ~ OTf[−]. *T_d* values were found to significantly

decrease with the addition of fluorinated amino groups, especially for the DCA anion, but not so much for chloride.

Viscosities for the ILs are generally much higher (and conductivities lower) than TDAC salts, and this can be attributed to hydrogen bonding with the methylenes on the fluorinated groups. Interestingly, the NTF₂[−] salts have lower viscosities than the DCA salts, which is probably also related to the hydrogen bonding ability.

Miscibilities and solubilities appear to be highly dependent on the hydrogen-bonding ability of the solvent. Thus, CH₂Cl₂ is sometimes a poor solvent and diethylether is generally a better solvent than both toluene and hexane.

The solid state structure of [1a]Cl·2.17H₂O displays the clear formation of ion-rich regions (including the CH₂ groups of the cations) surrounded by fluororous regions.

The synthesis of novel highly-fluorinated cations by use of TAC cations, with up to six fluororous groups, is a significant step towards our goal to synthesize cations that are either completely fluorinated or are fully encased within a sphere fluororous groups. These species promise to provide significant differences in their physical properties compared to the partially-fluorinated cations known to date.

Supporting Information Summary

Synthesis and characterization details; density data (with fit parameters) for [4c]NTf₂, calculated molar volumes and densities at 20 °C; viscosity, viscosity fit parameters, a fragility plot, conductivity, conductivity fit parameters; IR spectrum and assignments for [1b]Cl·H₂O; and crystallographic data, bond lengths and angles for 3, [2]Cl, [1b]Cl·H₂O, [1a]Cl·2.17H₂O and [1a]NTf₂; ES-MS spectra of crude product mixtures. Crystallographic data (CDCC 2141678-2141682) is also available free of charge from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; E-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

Dr. Matthew Polson (University of Canterbury) for X-ray data collection and refinement. RS thanks UGC/Sri Lanka for partial funding of her PhD studies (grant UGC/VC/DRIC/PG2016(ii)/UJA/01). Open access publishing facilitated by University of Canterbury, as part of the Wiley - University of Canterbury agreement via the Council of Australian University Librarians.

Conflict of Interest

The authors declare no conflict of interest.

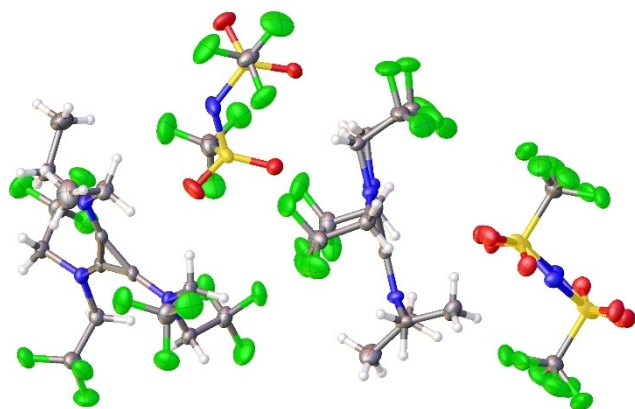


Figure 7. Thermal ellipsoid plot of the independent cations and anions in [C₃(N(CH₂CF₃)₂)(NET₂)]NTf₂ ([1a]NTf₂).

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: amines · aromaticity · ionic liquids · small ring systems · X-ray diffraction

- [1] For example: a) *Ionic Liquids in Synthesis*, 2nd Ed. (Eds.: P. Wasserscheid, T. Welton), Wiley-VCH, **2008**; b) *Ionic Liquids as Green Solvents: Progress and Prospects* (Ed.: R. D. Rogers, K. R. Seddon), *ACS Symp. Ser.*, vol. 856, American Chemical Society, Washington D. C., **2003**; c) *Green Solvents II: Properties and Applications of Ionic Liquids* (Eds.: A. Mohammad, Dr. Inamuddin), Springer Netherlands, **2012**; d) N. V. Plechkova, K. R. Seddon, *Chem. Soc. Rev.* **2008**, *37*, 123; e) T. L. Greaves, C. J. Drummond, *Chem. Rev.* **2008**, *108*, 206.
- [2] a) Z. B. Zhou, H. Matsumoto, K. Tatsumi, *Chem. Eur. J.* **2005**, *11*, 752–766; b) C. S. M. Kang, X. Zhang, D. R. Macfarlane, *J. Phys. Chem. C* **2018**, *122*, 24550–24558; c) M. L. Ferreira, J. M. M. Araújo, L. F. Vega, F. Llovel, A. B. Pereiro, *J. Mol. Liq.* **2020**, *302*, 112489; d) J. E. Sosa, R. P. P. L. Ribeiro, P. J. Castro, J. P. B. Mota, J. M. M. Araújo, A. B. Pereiro, *Ind. Eng. Chem. Res.* **2019**, *58*, 20769–20778.
- [3] A. B. Pereiro, J. M. M. Araújo, S. Martinho, F. Alves, S. Nunes, A. Matias, C. M. M. Duarte, L. P. N. Rebelo, I. M. Marrucho, *ACS Sustainable Chem. Eng.* **2013**, *1*, 427–439.
- [4] H. Xue, J. M. Shreeve, *Eur. J. Inorg. Chem.* **2005**, 2573–2580.
- [5] T. L. Merrigan, E. D. Bates, S. C. Dorman, J. H. Davis Jr., *Chem. Commun.* **2000**, *20*, 2051–2052.
- [6] H. Shao, L. Jiang, W. D. Meng, F. L. Qing, *J. Fluorine Chem.* **2003**, *124*, 89–91.
- [7] C. Lu, D. Vanderveer, D. D. Desmarteau, *Org. Lett.* **2008**, *10*, 5565–5568.
- [8] P. Bonhte, A. P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, *Inorg. Chem.* **1996**, *35*, 1168–1178.
- [9] a) D. Almantariotis, A. S. Pensado, H. Q. N. Gunaratne, C. Hardacre, A. A. H. Padua, J.-Y. Coxam, M. F. Costa Gomes, *J. Phys. Chem. B* **2017**, *121*, 426–436; b) I. Zama, G. Gorni, V. Borzatta, M. C. Cassani, C. Crupi, G. Di Marco, *J. Mol. Liq.* **2016**, *223*, 749–753; c) D. Rauber, F. Heib, M. Schmitt, R. Hempelmann, *J. Mol. Liq.* **2016**, *216*, 246–258; d) J. M. Breen, S. Olejarz, K. R. Seddon, *ACS Sustainable Chem. Eng.* **2016**, *4*, 387–391; e) J. H. Davis, Jr., K. J. Forrester, T. Merrigan, *Tetrahedron Lett.* **1998**, *39*, 8955–8958; f) G. D. Smith, O. Borodin, J. J. Magda, R. H. Boyd, Y. Wang, J. E. Bara, S. Miller, D. L. Gin, R. D. Noble, *Phys. Chem. Chem. Phys.* **2010**, *12*, 7064–7076.
- [10] a) R. P. Singh, S. Manandhar, J. M. Shreeve, *Tetrahedron Lett.* **2002**, *43*, 9497–9499; b) R. P. Singh, S. Manandhar, J. M. Shreeve, *Synthesis* **2003**, *10*, 1579–1585.
- [11] R. P. Singh, R. W. Winter, G. L. Gard, Y. Gao, J. M. Shreeve, *Inorg. Chem.* **2003**, *42*, 6142–6146.
- [12] D. Almantariotis, T. Gefflaut, Padua, A. A. H. Coxam, J. Y. Gomes, M. F. C. *J. Phys. Chem. B* **2010**, *114*, 3608–3617.
- [13] J. E. Bara, C. J. Gabriel, T. K. Carlisle, D. E. Camper, A. Finotello, D. L. Gin, R. D. Noble, *Chem. Eng. J.* **2009**, *147*, 43–50.
- [14] a) R. P. Singh, J. M. Shreeve, *Chem. Commun.* **2003**, 1366–1367; b) R. P. Singh, J. M. Shreeve, *Inorg. Chem.* **2003**, *42*, 7416–7421; c) J. J. Tindale, C. Na, M. C. Jennings, P. J. Ragogna, *Can. J. Chem.* **2007**, *85*, 660–667; d) D. Rauber, F. Heib, M. Schmitt, R. Hempelmann, *Colloids Surf. A* **2018**, *537*, 116–125; e) D. Rauber, P. Zhang, V. Huch, T. Kraus, R. Hempelmann, *Phys. Chem. Chem. Phys.* **2017**, *19*, 27251–27258.
- [15] O. D. Gupta, P. D. Armstrong, J. M. Shreeve, *Tetrahedron Lett.* **2003**, *44*, 9367–9370.
- [16] T. Alpers, T. W. T. Muesmann, O. Temme, J. Christoffers, *Synthesis* **2018**, *50*, 3531–3539.
- [17] V. Adamer, G. Laus, U. J. Griesser, H. Schottenberger, *Zeit. Naturforsch. B* **2013**, *68*, 1154–1162.
- [18] G. Vanhoutte, S. D. Hojniak, F. Bardé, K. Binnemans, J. Fransaera, *RSC Adv.* **2018**, *8*, 4525–4530.
- [19] L. V. N. R. Ganapatibhotla, L. Wu, J. Zheng, X. Jia, D. Roy, J. B. McLaughlin, S. Krishnan, *J. Mater. Chem.* **2011**, *21*, 19275–19285.
- [20] a) M. Hummel, M. Markiewicz, S. Stolte, M. Noisternig, D. E. Braun, T. Gelbrich, U. J. Griesser, G. Partl, B. Naier, K. Wurst, et al, *Green Chem.* **2017**, *19*, 3225–3237; b) T. Merrigan, E. D. Bates, S. C. Dorman, J. H. Davis, Jr., *Chem. Commun.* **2000**, 2051–2052; c) J. Kim, R. P. Singh, J. M. Shreeve, *Inorg. Chem.* **2004**, *43*, 2960–2966; d) F. Lo Celso, I. Pibiri, A. Triolo, R. Triolo, A. Pace, S. Buscemi, N. Vivona, *J. Mater. Chem.* **2007**, *17*, 1201–1208.
- [21] F. D'Anna, S. Marullo, P. Vitale, R. Noto, *ChemPhysChem* **2012**, *13*, 1877–1884.
- [22] J. Zhang, G. R. Martin, D. D. Desmarteau, *Chem. Commun.* **2003**, 2334–2335.
- [23] H. Xue, B. Twamley, J. M. Shreeve, *J. Org. Chem.* **2004**, *69*, 1397–1400.
- [24] J. E. Knoop, J. R. Alston, *MRS Advances* **2020**, *5*, 1449–1456.
- [25] T. Alpers, T. W. T. Muesmann, O. Temme, J. Christoffers, *Eur. J. Org. Chem.* **2018**, 4331–4337.
- [26] T. Alpers, M. Schmidtman, T. W. T. Muesmann, O. Temme, J. Christoffers, *Eur. J. Org. Chem.* **2017**, 4283–4290.
- [27] J. J. Tindale, P. J. Ragogna, *Chem. Commun.* **2009**, *14*, 1831–1833.
- [28] a) Z. Yoshida, Y. Tawara, *J. Am. Chem. Soc.* **1971**, *93*, 2573; b) Z. Yoshida, *Top. Curr. Chem.* **1973**, *40*, 47; c) K. Komatsu, T. Kitagawa, *Chem. Rev.* **2003**, *103*, 1371; d) J. S. Bandar, T. H. Lambert, *Synthesis* **2013**, *45*, 2485.
- [29] a) R. Weiss, T. Brenner, F. Hampel, A. Wolski, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 439; b) R. Weiss, M. Reching, F. Hampel, A. Wolski, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 441; c) R. Weiss, O. Schwab, F. Hampel, *Chem. Eur. J.* **1999**, *5*, 968; d) R. Weiss, K. Schloter, *Tetrahedron Lett.* **1975**, 3491; e) J. R. Butchard, O. J. Curnow, D. J. Garrett, R. G. A. R. MacLagan, *Angew. Chem. Int. Ed.* **2006**, *45*, 7550; f) J. R. Butchard, O. J. Curnow, D. J. Garrett, R. G. A. R. MacLagan, E. Libowitzky, P. M. B. Piccoli, A. J. Schultz, *Dalton Trans.* **2012**, *41*, 11765; g) M. S. Abdelbassit, O. J. Curnow, M. Ferreras, D. L. Crittenden, *ChemPlusChem* **2020**, *85*, 927–932; h) M. S. Abdelbassit, O. J. Curnow, E. Libowitzky, R. O. Piltz, M. I. J. Polson, *J. Phys. Chem. A* **2020**, *124*, 9244–9251.
- [30] R. Senthoooran, O. J. Curnow, T. Brenner, R. Weiss, M. Ferreras, D. L. Crittenden, *ChemPlusChem* **2020**, *85*, 2272–2280.
- [31] O. J. Curnow, R. Senthoooran, *Dalton Trans.* **2020**, *49*, 9579–9582.
- [32] R. Senthoooran, O. J. Curnow, D. L. Crittenden, *ChemPlusChem* **2021**, *86*, 1297–1306.
- [33] a) C. S. Sevov, S. K. Samaroo, M. S. Sanford, *Adv. Energy Mater.* **2017**, *7*, 1602027; b) K. H. Hendriks, S. G. Robinson, M. N. Braten, C. S. Sevov, B. A. Helms, M. S. Sigman, S. D. Minter, M. S. Sanford, *ACS Cent. Sci.* **2018**, *4*, 189; c) H. Huang, Z. M. Strater, M. Rauch, J. Shee, T. J. Sisto, C. Nuckolls, T. H. Lambert, *Angew. Chem. Int. Ed.* **2019**, *58*, 13318; d) E. C. Montoto, Y. Cao, K. Hernandez-Burgos, C. S. Sevov, M. N. Braten, B. A. Helms, J. S. Moore, J. Rodriguez-Lopez, *Macromolecules* **2018**, *51*, 3539.
- [34] R. Le Sueur, M. G. Guest, L. Belding, M. Pilkington, T. Dudding, *Tetrahedron Lett.* **2019**, *60*, 150928.
- [35] R. H. Lambeth, M. H. Baranoski, A. M. Savage, B. F. Morgan, F. L. Beyer, B. A. Mantooth, N. E. Zander, *ACS Macro Lett.* **2018**, *7*, 846.
- [36] J. Litterscheidt, P. Judge, A. Buehlmeier, K. Bader, J. S. Bandar, T. Lambert, S. Laschat, *Liq. Cryst.* **2018**, *45*, 1250.
- [37] a) Y. Jiang, J. L. Freyer, P. Cotanda, S. D. Brucks, K. L. Killops, J. S. Bandar, C. Torsitano, N. P. Balsara, T. H. Lambert, L. M. Campos, *Nat. Commun.* **2015**, *6*, 5950; b) J. L. Freyer, S. D. Brucks, G. S. Gobieski, S. T. Russell, C. E. Yozwiak, M. Sun, Z. Chen, Y. Jiang, J. S. Bandar, B. R. Stockwell, T. H. Lambert, L. M. Campos, *Angew. Chem. Int. Ed.* **2016**, *55*, 12382.
- [38] J. S. Bandar, A. Tanaset, T. H. Lambert, *Chem. Eur. J.* **2015**, *21*, 7365.
- [39] L. Belding, P. Stoyanov, T. Dudding, *J. Org. Chem.* **2016**, *81*, 553.
- [40] J. Xu, J. Liu, Z. Li, S. Xu, H. Wang, T. Guo, Y. Gao, L. Zhang, C. Zhang, K. Guo, *Polym. Chem.* **2018**, *9*, 2183.
- [41] Y. Jin, B. Wang, W. Zhang, S. Huang, K. Wang, X. Qi, Q. Zhang, *Chem. Eur. J.* **2018**, *24*, 4620.
- [42] S. Kadotani, R. Inagaki, T. Nishihara, T. Nokami, T. Itoh, *ACS Sustainable Chem. Eng.* **2017**, *5*, 8541.
- [43] O. J. Curnow, D. R. MacFarlane, K. J. Walst, *Chem. Commun.* **2011**, *47*, 10248.
- [44] K. J. Walst, R. Yunis, P. M. Bayley, D. R. MacFarlane, C. J. Ward, R. Wang, O. J. Curnow, *RSC Adv.* **2015**, *5*, 39565.
- [45] O. J. Curnow, M. I. J. Polson, K. J. Walst, R. Yunis, *RSC Adv.* **2018**, *8*, 28313.
- [46] O. J. Curnow, R. Yunis, *RSC Adv.* **2016**, *6*, 70152.
- [47] O. J. Curnow, K. J. Walst, R. Yunis, *ChemistrySelect* **2020**, *5*, 6978.
- [48] a) C. Maton, N. De Vos, C. V. Stevens, *Chem. Soc. Rev.* **2013**, *42*, 5963; b) A. F. Ferreira, P. N. Simões, A. G. M. Ferreira, *J. Chem. Thermodyn.* **2012**, *45*, 16–27; c) N. Papaiconomou, J. Estager, Y. Traore, P. Bauduin, C. Bas, S. Legeai, S. Viboud, M. Draye, *J. Chem. Eng. Data* **2010**, *55*, 1971–1979; d) K. C. Lethesh, S. N. Shah, M. I. A. Mutalib, *J. Chem. Eng. Data* **2014**, *59*, 1788–1795; e) P. Navarro, M. Larriba, E. Rojo, J. García, F. Rodríguez, *J. Chem. Eng. Data* **2013**, *58*, 2187–2193; f) W.-C. Lin, W.-L.

- Yu, S.-H. Liu, S.-Y. Huang, H.-Y. Hou, C.-M. Shu, *J. Therm. Anal. Calorim.* **2018**, *133*, 683–693.
- [49] a) C. Ye, J. M. Shreeve, *J. Phys. Chem. A* **2007**, *111*, 1456; b) Y. Marcus, *J. Mol. Liq.* **2015**, *209*, 289; c) H. D. B. Jenkins, H. K. Roobottom, *Inorg. Chem.* **1999**, *38*, 3609–3620; d) S. Akhil, O. J. Curnow, K. J. Walst, R. Wang, R. Yunis, manuscript in preparation.
- [50] A. N. Tran, T. N. Van Do, L. P. M. Le, T. N. Le, *J. Fluorine Chem.* **2014**, *164*, 38–43.
- [51] C. M. S. S. Neves, K. A. Kurnia, J. A. P. Coutinho, I. M. Marrucho, J. N. Canongia Lopes, M. G. Freire, L. P. N. Rebelo, *J. Phys. Chem. B* **2013**, *117*, 10271–10283.
- [52] a) K. R. Harris, *J. Phys. Chem. B* **2016**, *120*, 12135–12147; b) J. G. McDaniel, C. Y. Son, *J. Phys. Chem. B* **2018**, *122*, 7154–7169; c) H. K. Kashyap, H. V. R. Annapureddy, F. O. Raineri, C. J. Margulis, *J. Phys. Chem. B* **2011**, *115*, 13212–13221; d) K. R. Harris, *J. Phys. Chem. B* **2010**, *114*, 9572–9577; e) F. Philippi, D. Rauber, M. Springborg, R. Hempelmann, *J. Phys. Chem. A* **2019**, *123*, 851–861; f) F. Philippi, A. Quinten, D. Rauber, M. Springborg, R. Hempelmann, *J. Phys. Chem. A* **2019**, *123*, 4188–4200.
- [53] a) O. Nordness, J. F. Brennecke, *Chem. Rev.* **2020**, *120*, 12873–12902; b) O. Nordness, L. D. Simoni, M. A. Stadtherr, J. F. Brennecke, *J. Phys. Chem. B* **2019**, *123*, 1348–1358.
- [54] J. R. Butchard, O. J. Curnow, R. J. Pipal, W. T. Robinson, R. Shang, *J. Phys. Org. Chem.* **2008**, *21*, 127.
- [55] O. J. Curnow, D. L. Crittenden, *ChemPlusChem* **2022**, *87*, e202100535.

Manuscript received: February 14, 2022
Revised manuscript received: March 2, 2022
Accepted manuscript online: March 3, 2022
Version of record online: March 16, 2022