Making good on a promise: Ionic liquids with genuinely high degrees of thermal stability

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Brooks D. Rabideau,[a] Kevin N. West,[a] and James H. Davis, Jr.[b]

Dedicated to the memory of a dear friend and colleague, Professor Kenneth Richard Seddon, OBE

Thermally robust materials have been of interest since the middle of the past century for use as high temperature structural materials, lubricants, heat transfer fluids and other uses where thermal stability is necessary or desirable. More recently, ionic liquids have been described as 'thermally robust,' with this moniker often originating from their low volatility rather than their innate stability. As many ionic liquids have vanishingly low vapor pressures, the upper limit of their liquid state is commonly considered to be their degradation temperature, frequently reported from TGA measurements. The short duration ramps often used in TGA experiments can significantly overestimate the temperature at which significant degradation begins to occur when the compounds are held isothermal for even a few hours. Here, we review our recent work, and that of colleagues, in developing thermally robust ionic compounds, primarily perarylphosphonium and perarylsulfonium bistriflimide salts, in some of which cation stability exceeds that of the anion. We have used a combination of molecular design, synthesis, and computational modeling to understand the complex tradeoffs involving thermal stability, low melting point and other desirable physicochemical properties.

Introduction

In the closing months of World War II, an intense competition began between the United States and the Soviet Union to acquire German rocket technologies and to recruit the scientists and engineers who developed them. Those efforts sowed the seeds for what became known as 'the Space Race,' which the Soviets led with the launch of Sputnik in 1957, and which (arguably) ended with the 1969 Moon walk by American astronauts.[1, 2] Although this race fed (and was fed by) by Cold-War tensions between East and West, it had the salutary effect of rapidly driving forward a host of technologies. Among those were new, high-performance materials – not all of which were solids. The very high speeds and low-to-no atmospheric pressure (vacuum) involved with space travel and sometimes with endo-atmospheric aviation led to the need for new lubricants capable of functioning under extreme conditions. The current pinnacle of 'extreme lubricants' development was reached with oligoarylethers, the most widely-used of which is hexa(*m*-phenyl)pentaether, "P6O5" (Figure 1).

It was this novel liquid which made lubrication possible even at the high structural temperatures created by the 3500 km/h airspeed of the legendary SR-71 'Blackbird' reconnaissance aircraft, as well as the low atmospheric pressure (2.80 kPaA) at the 25,000 m altitude at which the aircraft flew. The chemistry and properties of P6O5 and its oligoarylether relatives was reviewed by Joaquim in 1999.[3]

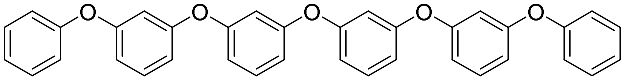

Figure 1: The structure of P6O5

Contemporaneous with the development of thermally stable lubricants for NASA (National Aeronautics and Space Administration) and the USAF (United States Air Force), groups within the latter organization were working to develop electrolytes that would function at temperatures *lower* than those used at the time in the batteries of rockets and missiles. Those researchers turned to what were then more familiarly known as molten salts; yet, the overwhelming majority of salts known at that time were ones which require heating to temperatures of several- to many hundreds of degrees in order to melt. An objective of the latter researchers thus became the formulation of salts which melt at significantly lower temperatures – materials that are now routinely called ionic liquids. An excellent account of those years by John

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[a] Department of Chemical & Biomolecular Engineering, University of South Alabama, Mobile, Alabama 36688 USA.
[b] Department of Chemistry, University of South Alabama, Mobile, Alabama 36688 USA. jdavis@southalabama.edu.

† Footnotes relating to the title and/or authors should appear here.

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Wilkes, a pioneer of modern ionic liquids research, is available.[4]

As time passed, ever more salts with low (sometimes sub-ambient) melting points were prepared, and researchers were increasingly eyeing them as materials of interest for non-battery applications. One of the foremost of those was their use as 'green solvents.' Because ILs are generally devoid of measureable vapour pressures, and one of the main avenues for the introduction of organic pollutants into the environment is evaporation ('fugitive emissions'), the match between need and would-be solution seemed to be a good one. Consequently, in the years since the current era of ionic liquids/molten salt research began, the use of ILs as solvents has been a central rationale for doing research with them.

It was not, however, just a lack of volatility which was put forward as an attribute of IL value. Along with several others, it was frequently asserted that ILs manifest a very high degree of thermal stability. This characteristic thus promised the ability to conduct reactions at high-temperatures without solvent loss or the necessity of using high-pressure vessels. This was especially important for one particular use for which they were envisioned – the 'ionothermal' synthesis of crystalline materials, zeolites and other energy-related substances being especially important among these.[5-8] Conceived of as a counterpart to hydrothermal synthesis – a technique widely used in the fabrication of inorganic solid materials – a huge advantage to the use of ILs was anticipated in that it would be possible to do high-temperature solution phase chemistry at ambient pressures, but still without solvent loss. Interestingly, as ionothermal synthesis has advanced as an IL sub-discipline, it has become apparent that by using currently available ILs, the promise of the technique can only be partially fulfilled. Indeed, at higher temperatures, the ILs employed are often observed to decompose. While this can be advantageous in limited cases (such as in templating the formation of pores in zeolites), the full potential of ionothermal synthesis cannot be achieved without access to ILs that do not decompose at process temperatures. This, then, means that developing ILs more thermally stable than those with which the community currently works will be required for this new approach to materials synthesis to reach its full potential. The same could be said with regard to the development of ionic liquids as lubricants and lubricant additives, as well as heat-transfer and thermal energy storage materials.

Frequent claims to the contrary notwithstanding, there were sober calls relatively early on cautioning against over-generalizations about the thermal stability of ionic liquids.[9-11] However, it was probably not until a 2013 review by Maton, et al.[12] that it became impossible to ignore the fact that ILs are not, as a rule and of necessity, any more thermally stable than many ordinary, neutral organic molecules. Indeed, based upon published data, P6O5 is more thermally stable, for longer periods of time, than a host of familiar ILs containing imidazolium, quaternary ammonium, and tetraalklphosphonium salts.

At the time of the Maton, et al. review, our group had already been involved with ionic liquids research for fifteen years. And, like many others, we were guilty of sometimes uncritically parroting their wondrous attributes – including that of high thermal stability – in the introductory remarks of our papers.[13] Truth be told, to our particular group at the time, any upper limit on IL thermal stability was actually of little concern. Our entire research program to that point had been centred on the design and synthesis of ILs having ions with covalently attached functional groups.[14] Their incorporation imbues ILs with a capacity to act not only as solvents, but as reagents or catalysts as well – and at ambient temperature or lower. We coined the term 'task-specific ionic liquids' or TSILs to describe these types of salts, although we now favour Seddon's proposal of 'functionalized' ionic liquids as a more apt descriptor. Regardless, research involving functionalized ILs has become quite widespread. For example, since their near-simultaneous introduction in 2002, two types pioneered by our group – those having ion-appended sulfonic acid or amine groups – have proven particularly utilitarian; they have been used by numerous investigators as the basis for thousands of subsequent papers.[15, 16]

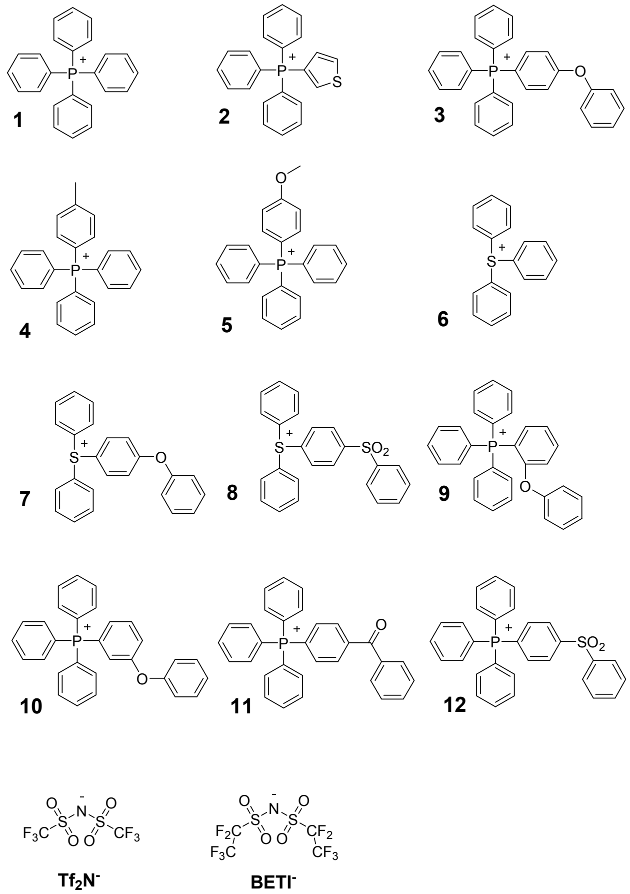


Figure 2: Structures of cations and anions comprising the ILs discussed in this work.

Given our longstanding interest in designing ionic liquids that manifest particular properties or patterns of reactivity, we decided to take up the challenge posed by the often *unremarkable* thermal stability of ionic liquids. In doing so, we have principally worked with the materials shown in Figure 2. These compounds have comprised the workhorses of our research program since 2013, which has been aimed at creating ILs with genuinely high degrees and durations of thermal stability. These efforts have borne considerable fruit, and it is our charge from the editors to describe in this article the genesis of our approach, our discoveries to date, and how we see the chemistry evolving and being used in the future by ourselves and (we hope) others. Please note that it is not our intention to present an exhaustive review of thermal stability studies on ionic liquids. For that, we refer readers to the still-authoritative 2013 review by Maton, DeVos, and Stevens, as well as a more recent one by Xue, et. al. dealing with multiple aspects of IL stability.[17] Readers are also encouraged to consult a recent paper by Hunt, Welton, and co-authors, describing an approach to the creation of thermally stable ILs that differs from that herein described.[18]

Ionic Liquids vs. Molten Salts

We suspect that there are few scientists who are not acutely familiar with the difficulty of securing funds to conduct research; persuasive cases must be made to referees and prospective funders of the value of the proposed work, and the likelihood of it leading to important new discoveries of benefit to humankind. Consequently, it seems quite natural that a group of researchers sharing an interest in a particular area might (consciously or otherwise) frame it as a novel field – to somehow differentiate it by drawing sharp lines between it and foundational work which (arguably) led to it. Indeed, doing so may be vital in order for new research at the edge of an established field to get enough 'breathing room' to develop. Through the lens of our now 20-year experience in ionic liquids research, we see this very natural process as having come into play as those of us interested in 'ionic liquids' sought to distinguish our activities from those of individuals working with 'molten salts.' And, among the sharp lines drawn to do so was one pertaining to temperature – albeit in a different context than that of thermal stability. Rather, in an informal process played out in publications and at various meetings, something approaching a consensus was reached that ionic liquids are salts that melt at less than 100°C, while salts melting above that temperature are molten salts.

The distinction seems to have served us well. Even so, given the level of visibility the field of ionic liquids has now clearly achieved, we propose that the time has come to concede the obvious: 'ionic liquids' and 'molten salts' are simply fuzzy, coincident regions along a thermal continuum. Not to do so seems incongruous. Consider Figure 3. Currently, a salt with a melting temperature below 100°C is an 'ionic liquid.' In turn, liquid NaCl, with its hellishly high melting point of 801°C, is a 'molten salt.' Indeed, the overwhelming majority of wholly inorganic salts likewise melt at many hundreds of degrees centigrade. But, what about the salts that are neither fish nor fowl that inhabit the 'mesothermal' domain between the two? Some (perhaps many) of these are probably salts that were anticipated by their formulators to be ionic liquids, only to disappoint them by melting a few degrees above 100°C! 'Sadly,' our current paradigm would insist, 'those are only molten salts, not ILs." Should this be the case even if the T_m of such salts are closer to those of more ILs than they are to those of most classical inorganic salts? Does that make sense? In addition, such mesothermal ionic liquids share many properties with eutectic mixtures of inorganic salts, which can have melting points near ambient. It also bears noting that it was just such eutectic salts – especially chloroaluminates – that were investigated for their use as room- or sub-room temperature battery electrolytes in the early days of ionic liquid research.[4]

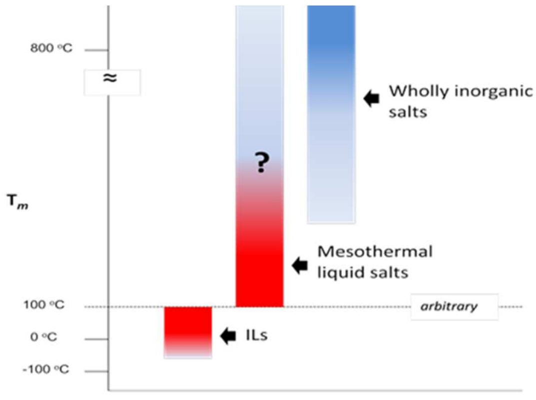


Figure 3: Ionic materials and melting point.

In light of the foregoing, we argue that it is time to stop drawing a line at 100°C to distinguish between 'ionic liquids' and 'molten salts.' There is simply no scientifically phenomenological basis for doing so. We think this is especially important since, from a thermal standpoint, the utility of any liquefied salt in any particular application is simply dependent on it being liquid in the desired application temperature range and remaining stable within that range. In other words, it is the *combined* upper and lower temperature bounds of salt liquidity-stability (liquidus range) versus process temperature that is the real key for assessing the utility of a given salt in a given application. Of course, a corollary to this is that in general, the larger the liquidus range of a salt, the more applications for which it may be suited.

All of the former things being said, why include a discourse on melting points in a review centred on the development of ILs with improved thermal stability? As will become clearer as we proceed, our work has shown that the structural and compositional elements required to increase the thermal stability of ions are likewise elements that tend to produce salts with higher (frequently >100°C) melting points. Hence, this is vital context for the discussion of a large element of our current efforts, which involve not just building ILs with high thermal stabilities, but ones with low melting points as well; in other words, work aimed at globally broadening liquidus ranges.

Stability at High Temperatures

At the risk of stating the obvious, when starting our project it seemed logical to look for insights into how to build thermally stable organic ions by searching the literature dealing with the thermal stability of organic molecules in general. Fortuitously, there were ample, highly relevant publications to be found.[19-28] Moreover, much of the work reported in them was done specifically in the context of identifying structural and compositional elements of organic materials that could be used at the high temperatures demanded of lubricants needed for high speed flight. The development of P6O5 was a direct result of those efforts.[3]

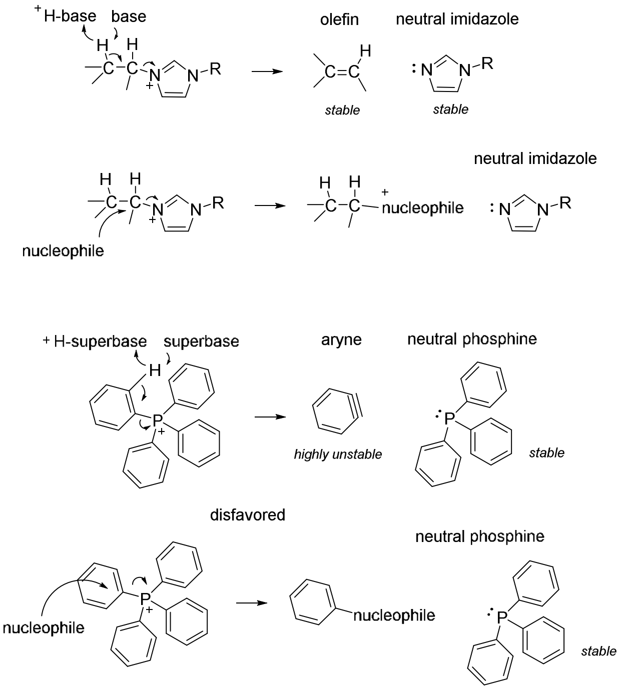


Figure 4. Differential susceptibility of cation types to nucleophile or base-driven de-quaternization.

The upshot of the findings by earlier researchers is simple: aromatic structural elements tend to be thermally stable, aliphatic elements tend not to be. In a similar vein, aromatic carbon-heteroatom (specifically O, N, P, S, Si, and halogen [F, Cl, Br]) bonds can be thermally stable or labile, in a highly structural-context-dependent fashion. What, then, are the implications for ionic liquids? Before addressing this in detail, let us note that in prior studies on the mechanisms of decomposition of ionic liquids, it was the cation which was commonly the less stable of the ions composing an IL. Indeed, it was one anion in particular – Tf_2N^- - that stood head and shoulders above others in terms of its thermal stability.[29]

The comparative instability of IL cations can be readily understood when one considers that almost all commonly used IL cation families –N-functionalized aromatic azaheterocycles, quaternary ammoniums, tetraalkylphosphoniums, trialkylsulfoniums – are susceptible to breakdown by either a retro-Menschutken reaction or Hoffman elimination (Figure 4). Worse still, the higher the temperature, the more facile each of these processes.[29]

What is it about aromatic moieties that suppress the former pathways? Again, consider Figure 4. The elimination of a hydrogen on an aromatic ring in a position β to the expected leaving group (here a would-be neutral triarylphosphine) can create a benzyne intermediate, but extremely strong bases (i.e., sodamide) are typically required for this to occur. At the same time, while the formal aromatic counterpart to retro-Menschutken reactions is known (S_NAr reactions), they are rather uncommon and demand particular reactant attributes. So, in the absence of the former conditions, how might one expect the decomposition of a putative $E(aryl)_x^+$ (E = heteroatom) cation to proceed? Our conjecture was that it would likely occur by, or at least begin with, the same pathway by which ordinary aromatic molecules thermally decompose – the homolytic scission of C-H bonds.

When such scissions occur, the reactive radical fragments thus formed may then: (a) recombine; (b) diffuse then recombine with another radical which may be different from the one with which it was originally paired, (c) scavenge H· from another molecular fragment, or (d) the organic radical may rearrange by hydrogen migration before radical recombination occurs. Obviously, which of these prevails is highly dependent on the lifetimes of the radicals involved, particularly that of the organic partner. As a consequence, the more stable the organic radical, the longer its lifetime and the more likely that outcomes (b), (c), or (d) will prevail. Note that the phenyl radical is comparatively unstable, hence short-lived: outcome (a) predominates, and the molecule (formally) remains intact.

As individuals long involved in designing new salts that met the prevailing rubric of possessing a melting point of <100°C, we were not cheered by the notion of cations rich in aromatic versus aliphatic structural modules. A central paradigm in IL design holds that the 'floppier' and more irregular the structure of an ion, the lower the melting point of its salts will tend to be. Aromatic rings, in contrast, tend to be both regular and rigid – the antithesis of what one would seek to feature in an IL. An immediate objection to this assertion might be that the most common IL cations are built around an aromatic species – the imidazole ring. While true, it must also be borne in mind that the imidazolium ions used to create ILs always have alkyl groups appended to them, and that it is those groups that bring to the cation both a measure of 'floppiness' and asymmetry. It is also those groups which lead to their thermal fragility.

Having trained as an organometallic chemist, one of the authors was familiar with the use of the tetraphenylphosphonium cation to facilitate the crystallization of highly reactive inorganic and organometallic anions. That being the case, we reasoned that since the PPh_4^+ cation was demonstrably inert to many highly reactive species, it might be thermally stable as well. A review of the literature suggested this notion to be well founded. As many others have no doubt observed, when the melting point of a compound is reported in a paper, it may be accompanied by the notation “dec.” – indicating its decomposition upon (or instead of) melting. In surveying the literature of PPh_4^+ salts, we observed this notation to be relatively rare, even though the melting temperatures of most of its salts are high. Hence, it appeared that salts of this cation indeed tend to exhibit a comparatively high degree of thermal stability. Furthermore, salts of PPh_4^+ with any number of anions appeared to be readily accessible by way of simple anion metathesis in water. Consequently, we decided to undertake a proof-of-concept study in which we would make the PPh_4^+ salt of the Tf_2N^- [bis(trifluoromethylsulfonyl)imide] anion, already commonly used to formulate ionic liquids, and already known to be quite stable thermally.

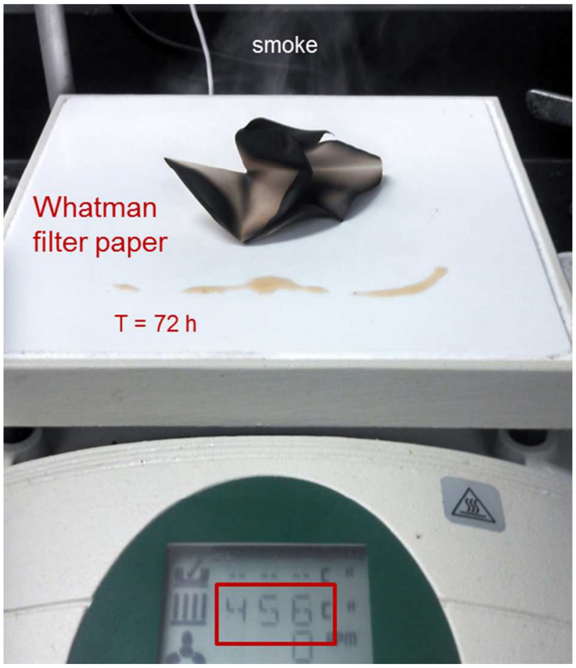


Figure 5: After 72 hrs at ≈450°C, $PPh_4^+Tf_2N^-$ (tan liquid) is unchanged, while paper placed onto the hot surface begins to char immediately.

As it happened, PPh_4Tf_2N, **1**, had been reported some years before (albeit with an incorrect T_m) in one of the early studies investigating the potential for ionic liquids based upon phosphonium ions.[30] That investigation produced a number of salts with low (i.e., sub-100°C) values of T_m. However, those were all salts having tetraalkylphosphonium cations; the structural outlier PPh_4Tf_2N was reported to melt well above that benchmark. We decided to investigate this compound regardless, since the main question to which we sought an answer was that of the temperature at which an arguably representative tetraarylphosphonium salt paired with an ‘IL-friendly’ anion would *decompose*.

With a sample of PPh_4Tf_2N in hand, we began an evaluation of its thermal stability. Further, this was to be no ordinary thermal challenge. Rather, taking a cue from an outstanding 2013 study of IL thermal stability by Fox and co-workers, we placed a sample of the salt directly on the ceramic surface of a thermostatically-controlled hot plate, and heated to a plate temperature of 450°C (see Figure 5).[31] The salt – a cream-coloured crystalline solid of T_m = 135°C – melted into a clear ivory liquid. Yet, after 72 hours at 450°C, in air, the appearance of the melt was unchanged. On cooling, the material re-crystallized, and its NMR spectra (^1H, ^{13}C, ^{19}F, and ^{31}P) were indistinguishable from those of the material prior to heating. Insofar as we can ascertain, this salt is the most thermally stable salt or material heretofore described that is not wholly inorganic in composition.[32] It also merits note that its liquidus range is at least 315°C!

Shortly after demonstrating the remarkably high thermal stability of PPh_4Tf_2N, we reported our data at a conference, along with our observations that when molten, the former salt is miscible with the inorganic salt KTf_2N. During a subsequent conversation, another conference attendee – Professor Peter Wasserscheid – expressed an interest in validating our observations on the thermal stability of PPh_4Tf_2N, as well as its mixtures with inorganic Tf_2N^- salts. Shortly thereafter, he and his collaborators resoundingly confirmed the unusually high thermal stability of PPh_4Tf_2N.[33] Moreover, using sophisticated techniques to which we did not have access, they established that once thermal decomposition *does* occur (at temperatures in excess of around 425°C), the thermal ‘gold-standard’ anion Tf_2N^- decomposes while the PPh_4^+ cation remains intact!

In light of the unusually high thermal stability exhibited by PPh_4Tf_2N, it seemed worthwhile to prepare and study additional Tf_2N^- salts of tetraarylphosphonium cations (Figure 2). Our initial choice of alternate cation structures was guided by a purely pragmatic consideration: the ones chosen were easy to prepare with materials on hand. Two of them proved to have thermal stabilities similar to that of the parent PPh_4Tf_2N: an analogue in which one of the phenyl rings was replaced by a thiophene ring (**2**), and one in which the *para* hydrogen of one of the phenyl rings was replaced with a phenoxyether substituent (**3**). Better still, both had T_m values lower than those of the parent salt – thus demonstrating early on that it is possible to broaden the liquidus range of this class of salts not just by going up in thermal stability, but also down in melting point. At the same time, the thermal stability of two other new salts (**4**, **5**) provided a sobering contrast; they were markedly lower than were those of the former materials.

Before beginning a discussion of the way(s) in which the latter salts had lower thermal stability, it bears elaborating on what is meant by decomposition, how it is or can be assessed, and how it is distinguished from but may still be connected to (in our usage) ‘thermal stability.’ Many discussions of IL thermal stability prior to near-coincident 2013 publications by Fox, et al.[31] and Maton, et al.[29] (respectively) focused on outcomes of thermogravimetric analysis (TGA) experiments. TGA analyses are performed using specialized instruments in which small samples of a material are placed on a balance pan that is suspended inside an oven that is constantly purged with an inert gas. Mass loss is then assessed as a function of temperature, which is either increased at a steady rate (gradient), or which is rapidly ramped to a target value and then held constant (isothermal). Until very recent years most published IL analyses have been those done under gradient conditions, and it is now widely understood that the rate at which the temperature is increased can have a very large impact on the rate of mass loss of compound, and hence the assessment of its thermal stability. Consequently, great care must be exercised when evaluating TGA data to ensure the comparison of apples with apples; making a judgement on the relative thermal stability of two salts evaluated using TGA, one studied at a ramp rate of 10°C per minute and the other at a ramp rate of 5°C per minute, is likely to result in an incorrect conclusion.

It is also important to realize that the TGA experiment, unless the purge gas stream is fed to a mass spectrometer, tells us only how much mass is lost. It does not tell us whether intact material is simply being volatilized, or whether a thermal breakdown event leads to fragments which are then volatilized. Note that it has been known since at least 2006 that certain ILs, under the right conditions, can evaporate.[34] Even so, since the former does not (of necessity) involve compositional or structural rearrangements of the sample molecules, it is a misnomer to describe it as being decomposition, even though non-decomposition mass loss at a given temperature may impact the utility of a given salt in a particular application. In either event, various researchers have quantified thermal stability by measuring the kinetics of mass loss across a series of isothermal TGA experiments.[11] The data produced can be used to fit a decomposition rate expression that allows for calculation of metrics such as $T_{0.01,10h}$, the temperature at which 1 % mass loss is observed after 10 hours; we note that this particular metric, like a number of others, has been proposed as a benchmark against which thermal stability can be assessed. Additional methods that capture both degradation and vaporization have also been demonstrated.[35, 36]

So what about the two salts (**4**, **5**) evaluated in our early work that had what we judged to be lower levels of thermal stability than the parent salt or the thiophene and phenoxyphenyl derivatives? In the case of a p-tolyl derivative (**4**), mass loss was in the low single-digit percentages – even comparable to that of the parent salt. However, its post heating appearance was that of a deep brown-orange, refractory glass. That was markedly different from its pre-heating appearance, which was that of ivory-coloured crystals. Further, while the material was still soluble in chloroform, the ^{1}H, ^{13}C, and ^{31}P NMR spectra were clearly changed – albeit mostly by way of line-broadening. Elemental analysis of the pyrolysate yielded values beyond 0.4% of those calculated for the pure material, but only by a small margin.

Thinking again about the early publications concerning the relationship between the thermal stability of organic molecules and their structures, we realized that the homolytic cleavage of a C-H bond in the tolyl methyl group would create a benzyl radical, and those are very stable. Although it remains speculation on our part at this juncture, we think it likely that radical recombination may occur between cations, leading to the formation of oligomers. This seems consistent with the fact that further heating of the material after the visible changes occur (and those happen within the first few hours of heating) results in little additional mass loss. But, it does lead to the solidification of the material at the elevated temperature over a period of days. If we can achieve a better understanding of this process and how to manipulate it, it might be harnessed as a means to prepare new organic solids with very high thermal stability. We note that Smith et al. have recently been active in the preparation (albeit by very different means) and study of polymers containing perarylphosphonium building blocks.[37-41] In contrast to the tolyl cation, the one with a methoxy substituent (**5**) lost considerable mass (ca. 50%) during the 96 hour heating period of our early studies. Its thermolysis was also accompanied by a change in appearance to that of a deep brown liquid while molten, which likewise solidified into a hard, coffee-coloured glass upon cooling. Also, in contrast to the behaviour of the tolyl compound, the pyrolysate was virtually insoluble in any solvent, precluding further analysis by NMR. Here again, we suspect it too forms radicals upon heating, albeit ones which lead to higher degrees of cross-linking that produce more intractable solids. Parenthetically, we note that a homolytic scission of the O-CH_3 bond in the cation would generate a highly stable phenoxy radical.

Both of the aforementioned solids are highly reminiscent of Bakelite, with which they ostensibly share a compositional and structural similarities in being composed largely of aromatic building blocks. But, regardless of the composition of the post-heating materials, their response to high temperatures made it clear that the introduction of structural elements containing aliphatic C-H bonds was unlikely to produce cations of high thermal stability, and further (unpublished) work on our part with other, longer alkyl substituents attached to the phosphonium aromatic rings bore this out.

With these enlightening preliminary results in hand, it was clearly time to try to systematize the further development of these materials. After considerable thought, we decided to concentrate our efforts along two lines – the tetraarylphosphonium salts with which we had begun, as well as triarylsulfonium salts. The latter, we had learned, shared a number of similarities with the former, especially in the sense that known representatives of the genre had been observed to melt at high(er) temperatures without decomposition, and to be rather chemically inert.[42, 43] Our plan was to prepare derivatives of each of these core cation types in which one or more substituents would be appended to the cation core – per our original study – but limiting those substituents to ones which were aromatic in character. Further, any 'linker' between these would be drawn from those having been established in the 1960s as thermally stable within the context of otherwise wholly aromatic systems: specifically -O-, -C=O-, and –SO_2-. The structures of these materials are shown in Figure 2.

INSERT TABLE 1

Once prepared, samples of each of the new compounds were heated, in air, at 300°C for a period of 90 days (Table 1). During this period, sample mass losses ranging from 0% - 50% occurred. Significantly, however, in all cases, the samples remaining showed *no* evidence of decomposition – whether by NMR (^{1}H, ^{13}C, ^{19}F, and ^{31}P [phosphonium salts]), mass spectroscopy, or elemental analysis. Thinking this strongly suggestive that mass loss with these salts, when observed, was probably from evaporation rather than decomposition, new samples of the compounds were loosely sealed (under air) and again pyrolysed at 300°C for 90 days. As anticipated, there was virtually no mass loss for any of the compounds, and all were unchanged by every analytical metric employed. The obvious conclusion? Not only are Tf_2N^- salts of the parent PPh_4^+ and Ph_3S^+ cations thermally stable, but so too can be many of their derivatives.[44-46] But do (or might) these derivatives also have lower melting points – the whole reason for making them to begin with?[‡]

Towards Rational Design

As mentioned, in designing ionic liquids, there are a number of strategies that are used to achieve a desired set of chemical and physical properties. Chief among these are structural modifications that lower the melting point to make the compounds liquids at or below a desired process temperature. The two most commonly employed concepts are to decrease the surface charge density and decrease the symmetry of the ions. These logically follow from how melting point is affected by enthalpies and entropies of fusion. At the melting point, equilibrium dictates that the Gibbs energy of fusion is zero. This allows for the equation relating Gibbs energy as a function of enthalpy and entropy to be solved for the equilibrium temperature, which, in this case is the melting point.

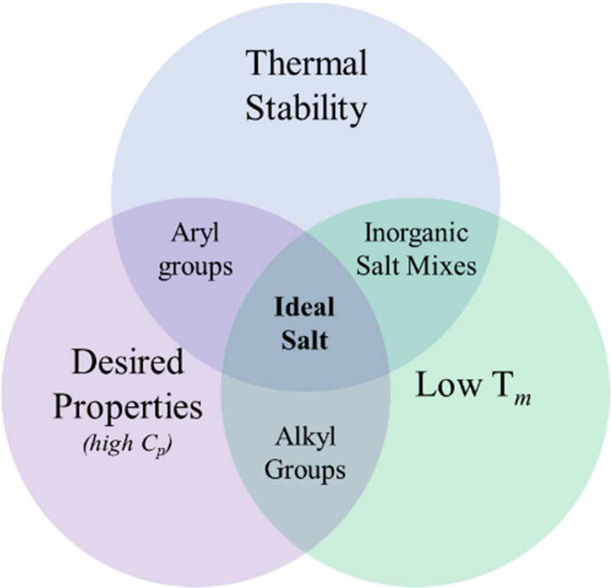
$$\Delta G_{fus} = \Delta H_{fus} - T_m \Delta S_{fus} = 0$$

$$T_m = \frac{\Delta H_{fus}}{\Delta S_{fus}}$$

Decreasing the surface charge density, by using highly inductive groups such as the CF_3 groups on a Tf_2N^- anion or using aromaticity to delocalize charge as on an imidazolium cation, decreases the attractive forces between the ions, thus decreasing the enthalpy of fusion. Likewise, decreasing the symmetry of the ions, often accomplished by adding an alkyl group to a cation such as imidazolium, frustrates solid phase packing and provides increased liquid phase degrees of freedom, increasing the entropy of fusion. Each of these in turn serves to lower the melting point of the salt. However, in this current work, the structural tools to access both of these effects are highly limited as thermal stability is achieved at the expense of structural diversity and low melting point (peraryl cations increase stability but also increase melting point, no alkyl groups, etc). Furthermore, other attractive properties for thermally robust salts, such as high heat capacity, which is also aided by longer alkyl chains, become increasing more difficult to incorporate into ion structures as illustrated in Figure 7. Thus, the design of such ionic liquids is highly constrained.

Because of these constraints, a rational approach to thermally stable ionic liquid design becomes significantly more challenging. So, beyond simply comparing melting points and structures, we endeavor to use thermodynamic analysis to gain insight into how structural variation in the sulfonium and phosphonium cations influenced the molecular level interactions that govern fusion.

Like the melting point, the enthalpy of fusion (*ΔH*$_{fus}$) is obtained from DSC curves; with these values the equation above can be solved to give the entropy of fusion is (*ΔS*$_{fus}$). Additionally, once the *ΔH*$_{fus}$ and *ΔS*$_{fus}$ are known for a homologous series of salts, changes in these quantities can be compared between the compounds to understand how the structural changes affected each property. We anticipated that this analysis, informed by quantum chemical calculations of the surface energies of the ions, would aid in understanding the complex pattern of melting point changes that were observed for substituted perarylsulfonium[45] and perarylphosphonium salts.[44]



To facilitate the comparison, the salt containing the unsubstituted cation was chosen as a reference: triphenylsulfonium (**6**) and tetraphenylphosphonium (**1**). Changes in the *ΔH*$_{fus}$ and *ΔS*$_{fus}$ between the reference compounds and the substituted compounds, and their effect on T_m, inform the influence of the structural changes and enable the determination of whether the change in T_m was enthalpy driven, entropy driven or both. For the sulfonium analysis, two anions, Tf_2N^- and $BETI^-$, were compared and paired with three sulfoniums (**6**-**8**); for the phosphonium analysis, only one anion, Tf_2N, was used and paired with six cations (**1**, **3**, **9**-**12**).

Figure 7: Factors that constrain the search for an ideal salt.

For both series of compounds, a rich and complex behavior was observed. The three sulfonium cations were TPS, DPS-POP and DPS-PSP (**6**-**8**, respectively). For the Tf_2N salts, as the cation is change from TPS to DPS-POP, the melting point decreases 8% and is enthalpically drive, with the ΔH_{fus} and ΔS_{fus} decreasing 47% and 42%, respectively. However, when the cation is changed from TPS to DPS-PSP, the melting point increases 3% and is entropically driven with the ΔH_{fus} and ΔS_{fus} decreasing 10% and 13%, respectively. The difference in these effects was attributed to the difference in polarities of the substituents in DPS-POP and DPS-PSP. We had expected the phenyl ring substitutions to increase the entropy of fusion (by frustrating packing) as commonly observed for imidazolium-based ILs. However, in both cases the ΔS_{fus} decreased. For the DSP-POP salt, this decrease was overcome by the slightly larger decrease in ΔH_{fus}, resulting in a melting point decrease. This is presumably due to weaker overall interactions as the phenoxy ether linker is non-polar in comparison to the SO_2 linker in DPS-PSP. The DSP-PSP salt, however, experienced a slightly smaller decrease in ΔH_{fus} than in ΔS_{fus} (with both changes being only 25% of the change observed for DSP-POP), a result likely due to the higher polarity of the PSP substituent creating stronger interactions than the POP substituent.

For the BETI salt, as the cation is changed from TPS to DPS-PSP, the melting point increases 31% and is enthalpically driven, with the ΔH_{fus} and ΔS_{fus} increasing by factors of 2.7 and 2.1, respectively. This significant increase was attributed to the fact that the reference compound, TPS BETI (**6a**), has a relatively low ΔH_{fus} for these types of salts (likely due to the smaller cation paired with the $BETI^-$ ion which has relatively large fluorous component with weak intermolecular forces). Thus, adding the moderately polar PSP substituent increases the interparticle interactions, increasing ΔH_{fus}, while simultaneously disrupting packing, increasing ΔS_{fus}. The comparison for the cation change from TPS to DPS-POP was not possible as the DPS-POP BETI salt did not form an ordered crystal, but rather it formed an amorphous solid that exhibited only a glass transition temperature (precluding the determination of ΔH_{fus} and ΔS_{fus}).

As there were two anions studied among the three cations, this afforded us the ability to examine the effect of changing the anion in the same manner as above for the TPS and DPS-PSP salts. For the TPS cation, considering the change from Tf_2N^- to $BETI^-$, the melting point decreases 15% with decreases in ΔH_{fus} and ΔS_{fus} of 59% and 51%, respectively. However, with the DPS-PSP salts, the same change in anion results in a 7% increase in melting point with increases in ΔH_{fus} and ΔS_{fus} of 23% and 15%, respectively. Although both sets of changes are enthalpically driven, the TPS has an enthalpy decrease while the DPS-PSP exhibits an enthalpy increase. For the TPS, the melting point decrease is attributed to the increased delocalization of negative charge on the $BETI^-$ anion and larger fluorinated region with weak interactions. For the DPS-PSP BETI salt we postulated that the large cation/large anion combination created enough room in the lattice to maximize possible interactions in the solid phase, increasing both the ΔH_{fus} and ΔS_{fus}, the latter due to the lower entropy of the solid phase fixed to maximize the aforementioned interactions.

As is evident from the above discussion (which is elaborated on in our initial sulfonium publication), for these types of ions, simple structure-property relationships proved elusive. Nevertheless, we again employed this analysis method for the homologous series of perarylphosphonium salts, hoping for a clearer outcome; we were not disappointed. In this instance, we examined not only different substituent groups, but also their location on the ring: examining the thermodynamics of fusion for *ortho* (**9**), *meta* (**10**) and *para* (**3**) versions of phenoxyphenyl-triphenylphosphonium Tf_2N and *para* substituted carbonylphenyl (**11**) and sulfonylphenyl phenyl-triphenylphosphonium (**12**). The structure/property relationships were again rather complex, but a rather complete understanding was possible in conjunction with both quantum chemical and molecular dynamic calculations to aid in understanding the phenomena.

Using the tetraphenylphosphonium cation (TPP) as a reference, the differences in the melting point, ΔH_{fus} and ΔS_{fus} as one of the phenyl rings on the central phosphorous atom was substituted with an *o*- or *p*-phenoxyphenyl were examined; the *meta* substituted salt (**10**) exhibited only a weak glass transition, precluding determination of its melting thermodynamics. Relative to the TPP salt, the *ortho* substituted cation (**9**) exhibited a 7% higher melting point with corresponding ΔH_{fus} and ΔS_{fus} increases of 56% and 46%, while the *p*-substituted cation (**3**) exhibited an 8% decrease in melting point with corresponding ΔH_{fus} and ΔS_{fus} increases of 5% and 14%. In comparing the *p*-substituted carbonylphenyl (**11**) and sulfonylphenyl phenyl-triphenylphosphonium (**12**) salts the *p*-phenoxyphenyl-triphenylphosphonium was used as a reference rather than the TPP to capture the effect of the different linker (CO or SO_2 versus O). Here, the carboxy substituted cation had an 8% lower melting point (ΔH_{fus} and ΔS_{fus} were 42% lower and 37% lower, respectively) and the sulfoxy substituted cation had an 11% higher melting point (ΔH_{fus} and ΔS_{fus} were 35% lower and 41% lower, respectively). Below we summarize the molecular-level understanding of these trends as informed by quantum chemical calculations and molecular dynamic calculations.

Insights from Molecular Simulation

As alluded to above, a direct understanding of how modifications to the chemical structure ultimately influence the melting point, and other properties, is not always a simple task. Structural changes that are intended to lower the melting point, may have unintended consequences that in fact raise it. For example, the addition of a strongly interacting appendage to a base cation, with the intention of lessening its overall free energy in the liquid phase, may induce changes in the crystalline structure that raises the free energy of the crystalline state. Since the melting point of a substance is determined by the temperature at which these two terms are equivalent, these modifications could serve to raise the melting point. In principle, *a priori* prediction of the melting point can be performed with reasonable success using molecular simulation[47-49] however this requires *foreknowing* the crystal structure. Currently, the prediction of crystal structures from chemical structures is a field that has not yet reached maturity.[50] Thus, for true *a priori* predictions, we are limited to studies of the liquid state. Nonetheless, in the course of our present project, we have gained insight into a number of these factors that significantly affect the melting point. Thus, conceptually, the crux of the matter is actually quite simple: molecular interactions are oftentimes classified as originating from either steric or electrostatic effects. And, for ILs especially, these two factors are intimately related.

Consider salts composed of monoatomic ions, such as sodium chloride, are known to have very high melting points. This is a result of both a highly localized charge on each of the ions as well as essentially non-existent sterics that would prevent the ions from coming into close contact. Thus, the ions are able to arrange in a very dense, close packing, having high lattice energy and consequently a very high melting point. By changing one of the monoatomic ions for a larger, molecular ion, as is done in ionic liquids, one is able to delocalize the charge and add steric volume to the ions leading to much more diffuse packing, with the effect of decreasing the melting point considerably. If, however, the molecular size becomes too large, as is seen for alkylimidazolium chlorides at very high chain lengths, the melting point again increases. Thus, there is an optimal size of an ion (on an ion-type dependent basis) for lowering the melting point.

(b)

INSERT FIGURE 8 HERE

Although it is oftentimes useful to think of this increase in the molecular size as preventing the cations and anions from coming into close contact, one must also consider the consequences that it may have on the highly repulsive cation-cation and anion-anion interactions. If one significantly increases the size of the cation, while the anion remains unchanged, this could lead to increased cation-cation interactions for the simple fact that it now comprises a larger percentage of the liquid state. Moreover, large ions generally mean larger lattice spacing, which could push the anions further away from neighboring anions. For example, in our study with the functionalized tetraarylphosphonium cations (see Figure 2), it was shown that the addition of a phenyl ether group to PPh_4^+ at the *ortho*, *meta* or *para* positions led to a significant drop in the strong anion-anion electrostatic repulsions. It was reasoned that the simple fact of increasing the cation size leads to an increase in the overall lattice spacing, which eases these repulsions. Interestingly, cation-anion interactions were least affected by the increased size of the cation. Large changes in the cation-cation electrostatic repulsions were also observed. Significantly, some of these were favorable rather than unfavorable. These were concluded to be the result of directional molecular interactions, a topic that will be addressed later. Nonetheless, slight changes in molecular size can have wide ranging effects that affect lattice spacing, that in turn significantly alters the intermolecular interactions.

As noted earlier, the melting point of a substance is determined by the ratio of ΔH_{fus} and ΔS_{fus}. Thus, the melting point will decrease if there is either a decrease in ΔH_{fus} or an increase in ΔS_{fus}. And, as noted, one way of increasing the latter is by adding a 'floppy' appendage to the base ion. In the solid state this appendage will not add any significant entropy to the system, however in the liquid state its modes should activate, significantly increasing the entropy difference between the two states. However, as noted previously, ΔH_{fus} is not entirely separate from ΔS_{fus}.

The entropy of the liquid states of PPh_4^+, *o*-POP, and *p*-POP were calculated using the two-phase thermodynamic method,[51-53] which allowed us to determine the translational, rotational and vibrational components. There were almost no differences seen between the different ILs. Furthermore, over 65% of the entropy resulted from the vibrational components and were proportional to the number of vibrational degrees of freedom present in each system. Thus, the addition of 'floppy' appendages to the base cation did not have as strong of an effect on the overall entropy as hoped, indicating that just because one adds additional states to a system does not necessarily mean that they will become populated.

(a)

One of the more surprising, and significant, results to come out of our work to date is the observation that cation-cation interactions have a large effect on the enthalpy and melting points of the different ILs. As discussed above, an increase in the cation size through the addition of an additional linked phenyl group to TPP directly increases the lattice spacing. This pushes the anions further away from one another, easing anion-anion repulsion, but it also brings more cation-cation interactions into play. Further, depending upon the location (*ortho*, *meta*, *para*) and the nature of the linking group (O, C=O, SO_2), this either has a beneficial or a detrimental effect on the overall liquid enthalpy.

Shedding an important light on this, data from the construction of radial distribution functions (rdfs) from liquid phase MD simulations showed an increased tendency for the Ph-(R)-Ph group of one cation to be near the phosphorous atom of another cation (see Figure 8(a)).

In these calculations, there was almost no tendency for the cations of *o*-POP to align with neighboring cations while *m*-POP, *p*-POP, *p*-PCOP and *p*-SO_2P all showed a *growing* tendency for cation-cation alignment, in that order. Quantum-based calculations clearly showed that this progression of cations (*o*-POP < *m*-POP < *p*-POP < *p*-PCOP < *p*-SO_2P) was accompanied by an increase in the overall electrostatic range and the overall dipole moment of the cation (Table 2).

INSERT TABLE 2

One important consequence of this for *ortho*, *meta* and *para* POP was increased electrostatic exposure of the electron withdrawing oxygen to the neighboring environment. In other words, when the phenoxy group is linked at the *ortho* position, the oxygen is largely tucked away and obstructed by the linked phenyl group. At the *meta* position, the oxygen is less tucked away and for *para* it is largely exposed to the neighboring environment. This makes for the progressively more facile approach of the phenoxy-O of one cation to the phosphorous centre of another, with significant impacts on the cation-cation interactions. Namely, in unison with the rdf results and the breakdown in ion-ion interactions, it may be concluded that the cations, which face increased contact due to their larger size, are able to orient due to this electrostatic exposure and the overall dipole moment to lessen the cation-cation repulsions (see Figure 8(b)). In combination with the other changes occurring in the liquid states, such as decreased anion-anion interactions and relatively stable cation-anion interactions, this alignment is able to lessen the overall liquid phase enthalpy, in principle lowering the enthalpy differences between the solid and liquid states, which has the overall effect of dropping the melting point.

In fact, this cation-cation alignment, as quantified by the rdfs of the MD simulations as well as the overall dipole moments of the cations, are strongly correlated to the reduction seen in the collected melting points. In fact, the ionic liquid with the lowest melting point, *p*-PCOP, had the second highest dipole moment and the ionic liquid with the highest melting point, *o*-POP, had the lowest dipole moment. The sole exception to this trend is IL **12,** *p*-PSO$_2$P. Note that its sulfonyl linker has a dipole moment that is *substantially* higher than all of the others. MD simulations show that with this strong dipole moment, a tipping point has been passed in which major changes in the liquid structure have occurred that make it considerably different from all of the rest. This fact is clearly seen in Figure 9, which shows the spatial distribution functions produced from the MD simulations for the different cations.

[INSERT FIGURE 9 – DOUBLE COLUMN

The colored volumetric surfaces represent the enhanced density regions that are twice that of the bulk density surrounding an individual cation, with blue representing the nitrogen atom of neighboring anions and orange the phosphorous atom of neighboring cations. The Ph-(R)-Ph group of each cation is oriented towards the top of the page. For all cations aside from p-PSO$_2$P, the tip of this region is populated by neighboring anions. Critically, for p-PSO$_2$P, this region is instead populated by cations (orange), indicating a significant change in the liquid structure relative to the other ILs.

This trend can also be seen in our related study examining the triphenylsulfonium-based cations. When a benzoyl group is added at the *para* position of the base cation, becoming DPS-POP, there is a large drop in the melting point. When the ether linkage is exchanged for a sulfonyl linkage, as in DPS-PSP, the polarity becomes too strong, which likely alters the liquid structure leading to a substantial increase in the melting point.

It seems clear from the foregoing analysis that additional progress in driving downward the melting points of salts containing perarylphosphonium or –sulfonium cations is clearly possible. Furthermore, it seems increasingly clear that we are moving towards achieving at least a limited capacity to predict – through a combination of quantum and molecular dynamics calculations – whether particular structural modifications can be anticipated to lower T$_m$ values of salts of these types.

Future Directions

Despite our progress to date, there remains work to do, both in terms of increasing the upper end of thermal stability with these salts, as well as in decreasing their melting points. Doing so, however, is increasingly likely to require strategies beyond those focused solely on cation structures. As mentioned earlier, in 2016 Wasserscheid, *et al.* established that the Tf$_2$N$^-$ anion – theretofore the pinnacle of IL-ion thermal stability – was less so than the PPh$_4^+$ cation. Around the same time, in two separate presentations, representatives of a leading IL manufacturer spoke of an 'anion crisis' in the field. By this, those individuals were lamenting the relative dearth of activity in developing new anions in contrast to the level of activity in cation development. In this light, we have most recently turned our attention to a search for anions capable of being used in formulating thermally stable ILs.

In 2017, we reported the results of an initial study in which we examined the 96-hour thermal stability of salts of the 'PPN' cation paired with various anions.[54] Among these were anions already known to have very high degrees of thermal stability – i.e., BF$_4^-$, PF$_6^-$, and Tf$_2$N$^-$. Not surprisingly, these salts were highly stable at 300°C for the duration of the experiment. But two others – benzenesulfonate and bis(phenylsulfonyl)imide (Figure 10) – gave particularly encouraging results as well with regard to thermal stability. Better still, those anions are halogen-free and inexpensive, both characteristics regarded as attractive in ions to be used for formulating ILs. Not surprisingly, however, salts of these anions tend to be relatively high-melting, no doubt due to the large, symmetric, and rigid character of the aromatic elements of their structures. However, given our success with modifying perarylated cations in such a way as to decrease the melting points of their salts without sacrificing thermal stability, we posit that this should be possible as well with these anion types by appending to them the same functional groups established in the cation work to be both thermally stable and capable of bringing about lower values of T$_m$.

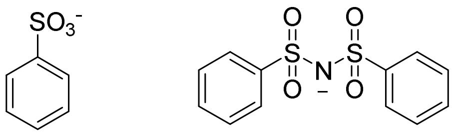


Figure 10: Left: benzenesulfonate. Right: bis(phenylsulfonyl)amidate. Both anions were found to form thermally stable salts and are prospectively modifiable to yield salts with lower melting points that remain thermally stable. Note that the more familiar toluene sulfonate anion does not yield salts of high thermal stability, likely because of the presence in it of aliphatic C-H bonds.

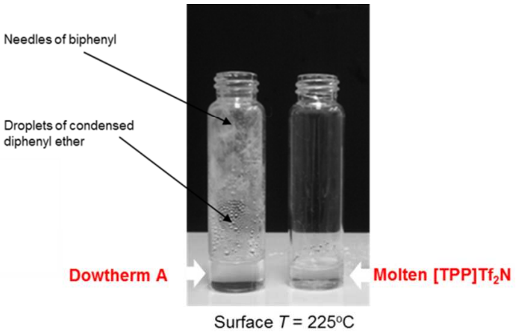


Figure 11. The visually apparent sharp contrast in volatility between Dowtherm A and representative thermally stable IL 1.

Efforts on our part to exploit these new classes of ILs in practical applications are still at an embryonic stage. Even so, we are especially excited about prospects for developing them for heat transfer and lubricant additive applications. In current large-scale applications of non-aqueous heat transfer/cooling fluids, materials such as Dowtherm A (a eutectic mixture of diphenylether and biphenyl) and Dynalene MS-1 (a eutectic mixture of $NaNO_3$ and KNO_3) rule the day. However, the present salts – unlike Dowtherm A – have a sharply diminished capacity for evaporative loss (Figure 11), and also likely lack a flashpoint – unlike Dowtherm A. In turn, the large number of oscillators present in our salts, compared to those making up Dynalene-type molten salt heat transfer fluids – offer the prospect of materials with considerably higher heat capacities than the latter. We are currently in the process of measuring these values.

Finally, we note that there is a vast territory still largely unexplored insofar as the development of these thermally stable salts is concerned – especially with regards to their mixtures with wholly inorganic salts, and with molecular materials of high thermal stability and low vapour pressure – P6O5, for example. Too, there is considerable scope for the development of new systems at the interface between ionic liquids and 'functional molecular materials',[55] as well as the present ILs as a basis for 'solvent-in-salt' systems as recently described by Ananikov and co-workers.[56] We hope others will join us in using the new families of ILs herein described, as well as in developing practical applications built upon them.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

‡ Parenthetically, it bears addressing why neither $(aryl)_4E^+$ salts (E = N, As, Sb) or $(aryl)_3E^+$ (E = O, Se, Te) have not also been developed. In short, salts of three of the heavier Group 15 and 16 elements – As, Sb, and Se – were in fact studied, and found to undergo facile thermolysis at only moderately elevated temperatures; in each case heating resulted in the formation of mirrors of the element on the pyrolysis vessel. In turn, a handful of poorly supported claims aside, the conceptually intriguing $(aryl)_4N^+$ salts are either not synthetically accessible or are unstable, obviating their further development.

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ADDITIONAL GRAPHICAL MATTER

Cation	T_m (°C)	μ (Debye)
PPh_4^+	135.0	0.00
PPh_3-*o*-POP^+	164.7	2.25
PPh_3-*m*-POP^+	-	4.79
PPh_3-*p*-POP^+	102.1	5.09
PPh_3-Ph-*p*-CO-Ph^+	73.6	7.94
PPh_3-Ph-*p*-SO_2-Ph^+	143.0	11.76

Table 2: Melting points, T_m, and calculated dipole moments, μ, of selected tetraarylphosphonium-based ILs.

Table 1. Mass loss during 90 days at 300°C. †Compounds **7a** and **10** were observed to have a glass transition at approximately -20 °C and 13 °C, respectively, with no sharp transition to an isotropic liquid.

Compound	Sulphonium-based Cation	Anion	T_m (°C)	90 day % mass loss @ 300°C Open Container	Close Container
6	TPS^+	NTf_2^-	92.4	0	0
6a	TPS^+	BETI	36.3	0	0
7	DPS-POP^+	NTf_2^-	62.7	0	0
7a	DPS-POP^+	BETI	†	0	0
8	DPS-PSP^+	NTf_2^-	104.6	0	0
8a	DPS-PSP^+	BETI	132.4	0	0
	Phosphonium-based				
1	PPh_4^+	NTf_2^-	135.0	11.2	0
9	PPh_3-*o*-POP^+	NTf_2^-	164.7	25	?2
10	PPh_3-*m*-POP^+	NTf_2^-	†	47.6	?2
3	PPh_3-*p*-POP^+	NTf_2^-	102.1	9.5	0
11	PPh_3-Ph-*p*-CO-Ph^+	NTf_2^-	73.6	10.3	0
12	PPh_3-Ph-*p*-SO_2-Ph^+	NTf_2^-	143.0	0	0

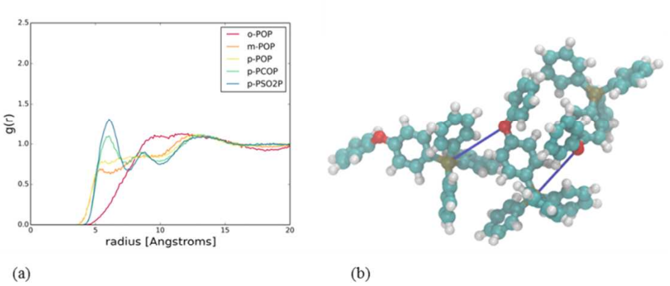
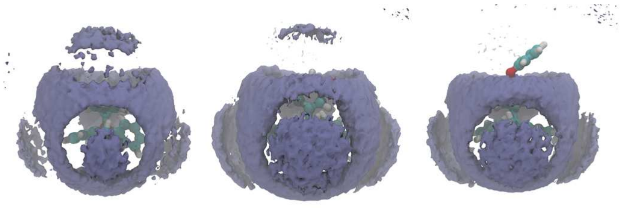
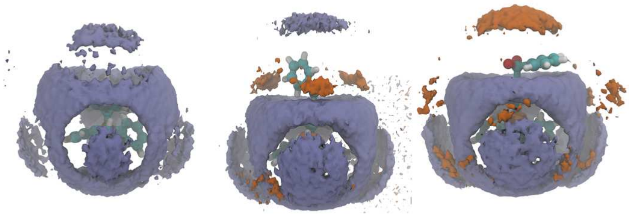


Figure 8: (a) Site -Site radial distribution functions between the phosphorous atom of a cation and the Ph-(R)-Ph group of neighboring cations. (b) A representative arrangement of three p -POP cations in the liquid state showing alignment of their dipole moments, blue lines.



(a) *o*-POP (b) *m*-POP (c) *p*-POP



(d) PPh_4^+ (c) *p*-PCOP (f) *p*-PSO2P

Figure 9: Spatial distribution functions produced from the MD simulations showing enhanced regions of density surrounding the different cations. In each case, the characteristic group is oriented toward the top of the page. Volumetric surfaces represent 2 times the bulk density. Blue represents the nitrogen atom of neighboring anions and orange the phosphorous atom of neighboring cations.