The Second Evolution of Ionic Liquids: From Solvents and Separations to Advanced Materials—Energetic Examples from the Ionic Liquid Cookbook

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ABSTRACT

In this Account of the small portion of the recent research in ionic liquids (ILs) by the Rogers Group, we fast forward through the first evolution of IL research, where ILs were studied for their unique set of physical properties and the resulting potential for tunable "green solvents", to the second evolution of ILs, where the tunability of the cation and anion independently offers almost unlimited access to targeted combinations of physical and chemical properties. This approach is demonstrated here with the field of energetic ionic liquids (EILs), which utilizes this design flexibility to find safe synthetic routes to ILs with high energy content and targeted physical properties.

A Chance Encounter

The interests of the Rogers Group in the field of ionic liquids (ILs) can be traced to a meeting in 1996 with Ken Seddon (The Queen's University in Belfast) at a NATO Advanced Study Institute on crystal engineering in Digby, Canada.[1] Interestingly, while the conference had virtually nothing to do with ILs, it was co-organized by Mike

MSc Marcin Smiglak was born the 15th of November 1979 in Poznań, Poland. He obtained his MSc, Eng. at the Poznań University of Technology in Prof. Pernak's group and is currently a graduate student in Prof. Rogers' group in Tuscaloosa. His primary interests are energetic ionic liquids, as well as development of novel halide-free synthetic protocols for the formation of ILs.

Dr. Andreas Metlen was born in Eupen, Belgium, the 22nd of March 1976. After receiving his Diploma in Chemistry at the RWTH Aachen in Germany, he joined Prof. Peter Wasserscheid's group and worked in the field of aromatic substitution reactions in ionic liquids. After obtaining his Ph.D., he joined Prof. Rogers' team as a postdoctoral researcher. He now is focused in the synthesis of ionic liquids and new applications thereof.

Prof. Robin D. Rogers was born in Fort Lauderdale, Florida, on March 4, 1957. After obtaining both B.S. and Ph.D. from The University of Alabama, he joined the faculty at Northern Illinois University, DeKalb, IL. In 1996, he returned to his Alma Mater where he currently holds the titles of Robert Ramsay Chair of Chemistry, Distinguished Research Professor, and Director of the Center for Green Manufacturing. He is the Founding Editor-in-Chief of the American Chemical Society journal *Crystal Growth & Design* and is a member of the Editorial Board for *Separation Science & Technology* and *Solvent Extraction and Ion Exchange*. He also serves on the International Advisory boards for *Green Chemistry* and *Chemical Communications*. This year he will join the faculty of The Queen's University of Belfast as Chair in Green Chemistry and Co-Director of The Queen's University Ionic Liquid Laboratory (QUILL), while retaining an appointment at The University of Alabama as Director of the Center for Green Manufacturing.

Zaworotko (credited with John Wilkes in preparing some of the first viable water-stable IL solvents[2]) and Ken Seddon (credited with the boom in academic and industrial interest in using ILs as solvents in organic chemistry[3]). It was Zaworotko (a graduate school colleague of Prof. Rogers at The University of Alabama) who issued the invitation to speak at the summer school but Seddon who suggested the use of 1-butyl-3-methylimidazolium hexafluorophosphate (here abbreviated as [1-Bu-3-Me-im][PF$_6$] but commonly described in the literature as [bmim][PF$_6$] or [C$_4$mim][PF$_6$]), one of Wilkes' and Zaworotko's water-stable salts in our work!

Until that point, we had been working under the banner of "Green Chemistry" to obviate the need for the use of volatile organic compounds (VOCs) in liquid/liquid extraction with rather complicated, wholly aqueous systems, known as aqueous biphasic systems (ABS) (based on the salting out of poly(ethylene glycol)s with kosmotropic salts).[4] However, the ABS systems have several drawbacks, such as elongated separation times or mutual miscibility of the phases. Hoping to overcome these disadvantages the concept of a hydrophobic liquid salt with no vapor pressure fit well with our search for green extraction processes. Our first "IL" paper was published in 1998,[5] where we described the use of [1-Bu-3-Me-im][PF$_6$] for extractions from aqueous solution. Encouraged by these results, we soon started to investigate ILs for metal ion extraction and quickly learned that using ILs did not necessarily simplify separations, but actually could make them much more complicated,[6–9] and possibly even much less green,[10,11] than traditional solvent-based approaches.

These latter lessons are still being learned by many researchers today. Although there are now in excess of 8000 papers on ILs, too many of these make sweeping overgeneralizations about the "green" nature of ILs, or any of a variety of desirable physical properties, which all salts meeting the IL definition simply cannot possess. Nonetheless, in this first evolution of IL research, the focus on the physical property set available from ILs and how to obtain them has driven the field.[12–18] Researchers from around the world have raced to prepare and characterize new combinations of ions that could meet the definition of an "ionic liquid", to try to predict physical properties from structure,[19,20] and to use the more attractive accessible physical properties (e.g., nonvolatility or low volatility; large liquidus ranges; etc.) in new applications.

Much of our early research as well was focused on making use of the unique, tunable physical property set offered by ILs and their use as solvents. We have studied, and continue to study, ILs as solvents for separations,[21] polymerizations,[22,23] and crystallization.[24,25] We have even made use of the unique solvating power of some ILs to dissolve such intractable biopolymers as cellulose[26] and extract biopolymers directly from biomass such as wood.[27]

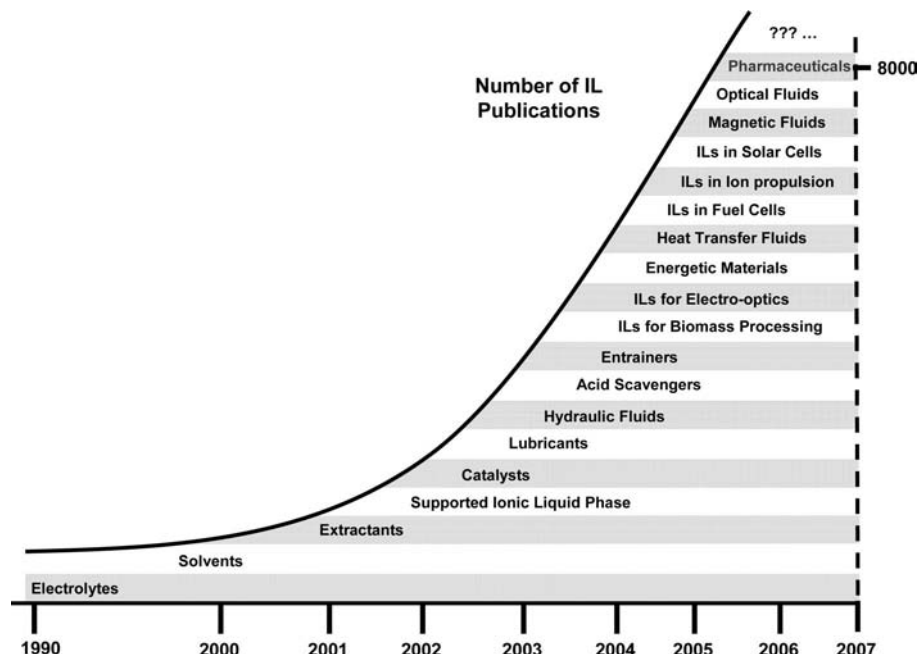* E-mail: RDRogers@bama.ua.edu.

FIGURE 1. Growth in the number of IL publications and representative areas of interest. Data obtained from SciFinder Scholar 2006 using the search terms "ionic liquid" OR "ionic liquids" and then refined by publication year. The data for total publications includes the number of patents, and the area of the particular field does not represent the number of publications in the subfield.[77]

Nonetheless, here we wish to highlight the materials applications of ILs.

The Second Evolution of Ionic Liquids: Targeted Physical and Chemical Properties

As the number of researchers in a variety of disciplines joined the ranks of the IL community, it was inevitable that new directions would emerge and new applications would be found (Figure 1). In the past few years ILs have found useful application in sensors,[28,29] solar cells, solid-state photocells,[30] and batteries[31] and as thermal fluids,[32] lubricants,[33,34] hydraulic fluids,[35] and ionogels,[36] to name only a few. Despite the fact that ILs today are defined by one physical property (melting point), many of the potential applications make use of a particular chemical property set combined with IL physical properties.

We have actually started to view ILs as tunable, multipurpose materials for a variety of applications rather than as just solvents. From this vantage, we believe that it is possible to form any specific IL composition depending on the user's needs and that the desired chemical and physical properties can be realized in a single salt by proper selection of the component ions or in mixtures of component ions. Thus, essentially an IL cookbook arises from the inherent modularity of ILs, where a suitable combination of ions, or mixture of ions, can be developed to solve each given problem by providing the exact combination of physical and chemical properties needed.

Energetic Ionic Liquids

In 2002, another chance encounter motivated us to explore this concept in the field of energetic ionic liquids (EILs). In discussions with Dr. Greg Drake, then of

Edwards Air Force Base, it became apparent that the IL cookbook holds excellent recipes for unique liquid energetic materials. The problems facing modern energetic materials would seem to be an ideal platform with which to test the generality of the IL concept.

Many modern energetic materials, even though highly advanced and understood in terms of their performance and behavior, suffer from safety issues and environmental concerns, which call for novel approaches.[37,38] New materials are needed that exclude the use of hazardous and potentially toxic compounds such as hydrazine, metals, halides, and perchlorate. Problematic issues limiting safe storage and handling must be addressed, such as those related to the solid state of most energetic materials, for example, polymorphism (a possible factor in the sensitivity of the material), high melting points, and the need to use plasticizers for processing the materials.[39] Nonetheless, new energetic materials that exhibit liquid-state rheological properties (thus being easier to handle) must not exhibit common disadvantages of the liquid state such as high vapor pressures, which may result in loss of material, composition changes, and increased hazards through formation of explosive fumes. A seemingly perfect challenge for ILs!

The concept of using salts in general as energetic materials is, of course, not new (Table 1). Additionally, many currently used molecular energetic materials can often be derivatized into ionic compounds, thus opening new possibilities for modification and further IL formation.[40–42] There are commonly used materials on the market today, such as trimethylammonium nitrate (a component in fusible explosives), that in fact already fit the definition of an EIL.[43] Even salts reported in the 19th century such as hydroxyethylammonium nitrate (mp 52–55 °C)[44] and

Table 1. Examples of Known Energetic Salts

ammonium azide	ammonium nitrate
triazoethanol nitrate	ammonium chlorate
diisopropylamine trinitrate	ammonium perchlorate
ethylenediamine dinitrate	hydrazinium nitroformate
ammonium dinitramide	hydrazinium nitrate
diammonium 5,5′-bi-1H-tetrazolate	guanidinium perchlorate
ammonium picrate	guanidinium picrate
ammonium 2-amino-4,6-dinitrophenolate	triaminoguanidine nitrate
ammonium 2-amino-4,6-dinitropicrate	1,2,3-propanetriol trinitrate

Table 2. Performance Requirements for EILs[76]

Physical Properties	
melting point	less than −40 °C
surface tension	<100 dyne cm^{-1}
density	>1.4 g cm^{-3}
viscosity	as low as possible
Hazard Sensitivity	
impact	>50 kg cm
friction	>120 N
electrostatic discharge sensitivity	>5000 V at 0.25 J
Thermal Stability	
TGA (75 °C, isothermal)	<1% loss of material over 24 h
TGA (rate 10 °C/min)	>120 °C for T_{decomp}
Thermodynamic Properties	
heat of formation	as positive as possible
heat of combustion	>6 kcal g^{-1}
Toxicology	
LD_{50}	>0.5 g kg^{-1}
AMES	negative

ethylammonium nitrate (mp 34 °C,[45] often referred to as the first "IL"), can be considered EILs.

In the mid-1980s, the need for insensitive energetic compounds led to the development of the first nitro- or amine-functionalized (or both) triazoles (e.g., 5-amino-3-nitro-1,2,4-triazole (ANTA)[46] and 3,5-dinitro-1,2,4-triazole (DNT)[47,48]). These first results showed that substituting the aromatic core with electron-withdrawing groups leads to products with high energy content, favorable density, comparably low sensitivity, and good heat resistance. These and other literature reports on the topic of energetic materials,[49–51] along with the growing knowledge of ILs, suggested that the ILs as additives to or replacements of currently used energetic materials could greatly advance this field.

Klapötke et al.[52] published one of the first papers on energetic ionic liquids in which he reported explosive N-containing salts like hydrazinium azides, which were obtained as viscous room temperature ionic liquids or as low melting solid salts, depending on the substitution pattern of the hydrazinium cation. Shortly after that, Drake et al. described in more detail the approach of combining the IL platform with energetic materials, where 1,2,4-triazolium, 4-amino-1,2,4-triazolium, and 1,2,3-triazolium cations were paired with small inorganic energetic anions ($[NO_3]^-$, $[ClO_4]^-$, and $[N(NO_2)_2]^-$) and the resulting salts were characterized.[53]

Considering all of the above, ILs appear to be a very reasonable platform on which novel energetic materials can be designed, and it appears that basic "rules-of-thumb" for the design of EILs are already available.[54–57] Combining nonvolatility, high thermal stability, and low melting points with properly designed energetic functionalities can lead to a variety of new liquid energetic materials,[53] while at the same time improving safety issues related to transportation, handling, and processing from production to end-use.

Recently, a working group funded by the Air Force Office of Scientific Research helped to establish target physical and chemical properties accessible by IL materials and needed for ideal energetic materials (Table 2). These general property goals for ideal, safe, high performance advanced energetic materials have allowed researchers, including us, to focus attention on the interplay of individual physical and chemical properties on the bulk properties of the fluid.

Since 2003, in collaboration with Professor Alan Katritzky (University of Florida), we have directed our approach

toward fostering development of new EILs from our modular design perspective to select and synthesize target compounds that separately implement each specific property needed for an ideal composition of ions. In our research, we do not direct our efforts toward the manufacture of new energetic fluids, but rather toward an understanding that will enable the links between the desired chemical functionality and the physical and thermodynamic properties required for EILs. This approach will ultimately allow the prediction of ion combinations with the desired property sets in a modular "ionic liquid" platform for the custom design of energetic materials.

Thus, we are trying to take advantage of the dual-functional nature of ILs, which in concept and in practice, allows for the modular, interchangeable use of ions to achieve desired chemical and physical properties. Additionally, we have envisioned that due to the ionic composition of those salts, each ion component of the product can be tuned separately and brought to the final product in the last step of synthesis. Each component, anion and cation, may be independently modified toward the desired final material through incorporation and modification of functional groups (Figure 2). We should note, however, that anyone using these design criteria to make energetic materials should exercise extreme care. Transferring our results to highly energetic ions may lead to extremely unstable materials, and appropriate safety procedures must be followed.

We have directed our approach toward understanding how EILs might be designed from a modular design perspective. That is, each targeted property (melting point, density, viscosity, long-term thermal stability, etc.) is investigated separately to allow for a better understanding of how structural modification in *either ion* affects the IL properties as a whole. This knowledge allows us to develop an "IL toolbar", from which a variety of IL design options can be brought to bear on any synthetic scheme based on the desired set of final IL properties. Figure 3 illustrates this modular approach. Each target property is considered
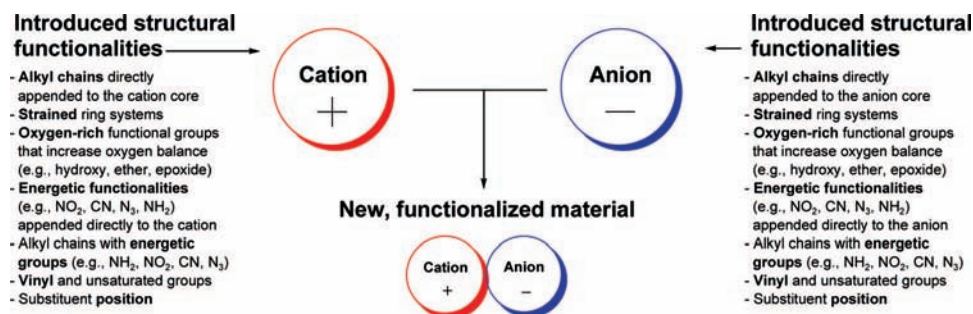
FIGURE 2. Independent design of components in multifunctional EILs.

separately as the primary property, and all other target properties are designated as secondary during any given iteration. In the example provided in Figure 3, the primary property was set to be the thermal stability.

First Design Cycle: Protonated EILs

For our first research goal, we selected the most straightforward, fast, and simple synthetic approach for the formation of ILs via acid–base neutralization reaction to form protonated azolium-based salts. The hypothesis behind this choice was that the more easily the product can be synthesized (manufactured), the more likely it could find an application as an energetic material. Seddon and McFarlane have suggested that to meet the IL definition, the products must be >99% ionized, and thus careful selection of acids and bases based on their pK_a values is required.[58] Although knowledge and control of the speciation within such ILs is required, it is possible that such a strict criterion is not needed for a given EIL.

Utilizing the cation module, we initially selected a variety of imidazole-based compounds (Figure 4) based on their substitution patterns and homological differences in the imidazole ring structure. Working with the strong heterocyclic chemistry group of Prof. A. R. Katritzky, systematic changes were implemented in the substitution patterns of *N*-alkyl imidazole cores, ranging from C-alkyl-substituted to energetically substituted cations (NO_2 and CN groups directly appended to the imidazolium core). This approach allowed us to screen a large range of products and to evaluate their properties in terms of usefulness to EILs.

At first, the obtained salts looked promising. The initial melting point analysis revealed that generally, due to the size and shape of the anion, the nitrate salts exhibit significantly lower melting points than their picrate equivalents (Table 3). Thermogravimetric analyses (TGA) of nitro-substituted and nonsubstituted protonated imidazolium salts revealed that thermal stabilities range from ~70 to 200 °C, with picrate salts exhibiting higher stabilities (by ~40 °C) than nitrate salts.[59] Disappointingly, however, the thermal stabilities of these protonated salts were significantly lower than those of alkylated derivatives (Figure 5).

In collaboration with Dr. John Wilkes from the U.S. Air Force Academy, we tested these salts for their ability to ignite[10] and found ready combustion (thus destroying

another myth regarding the overgeneralized safety of ILs). Our preliminary results suggest that the ILs tested are themselves not flammable (i.e., having a flash point below 37.8 °C[60]) but their gaseous decomposition products are.

To better understand this decomposition and the energetic character of the ILs, we studied these salts using TGA and accelerating rate calorimetry (ARC) in collaboration with Dr. Joseph S. Thrasher (The University of Alabama). The results suggest that vigorous exothermic decomposition reactions occur in protonated EILs, which results in large amounts of thermal energy and highly flammable (combustible) gases, which can easily ignite upon contact with a flame source.[10,59] Additionally, it was observed that in comparison with Cl^- salts of the same cations, nitrate and picrate anions have a significant influence on the rapid exothermic decomposition processes, thereby making these anions suitable candidates for future design of other EILs.

Overall, the melting points of the protonated ILs we studied were in acceptable ranges, and the overall structure/property trends were satisfactory, but the relatively narrow liquidus ranges and especially the low temperatures of decomposition are problematic. In order for this class of compounds to be considered further, new design options are needed to overcome these limitations.

Second Design Cycle: Alkylated EILs

Analysis of the results of the first design cycle led back to the design scheme and consideration of the use of permanent cations (e.g., *N,N*-dialkyl imdazolium), and addition of energetic $-NO_2$ or $-CN$ modifications to the cation. To simplify the systems, we initially focused on using commonly known IL-forming anions such as methylsulfate, triflate, and bistriflimide (Figure 6).[61]

In general, the methylsulfate and triflate salts exhibited melting points in the range of 70 to 140 °C. We thus paired the cations with the bistriflimide (NTf_2^-) anion, known to result in lower melting, less viscous ILs.[62] Salts of 1,3-dimethyl-4-nitroimidazolium and 1-ethyl-3-methyl-4-nitroimidazolium with this anion were indeed found to be low melting, with melting points close to room temperature (18–35 °C). Comparing our results with those reported by Shreeve and co-workers,[63] for iodide, perchlorate, and nitrate salts, further indicates how anions can affect melting points. Additionally, by comparison of the data for 1,2,3-trimethyl-
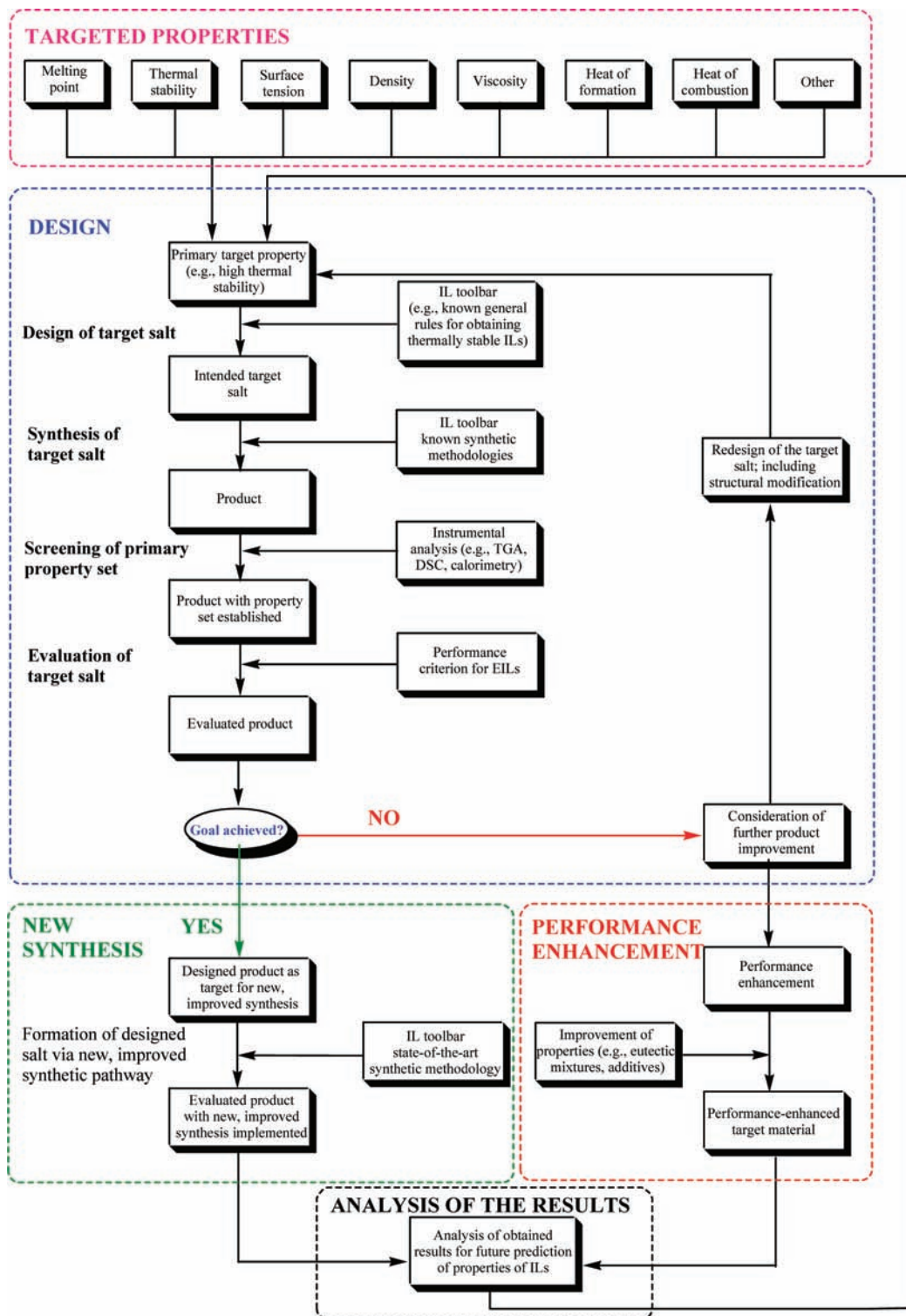
FIGURE 3. Modular design approach for the development of EILs.

4-nitroimidazolium salts, the effect of a methyl group attached to the C2 position of the imidazolium ring can be clearly seen in this set (Table 4).

Using crystalline analogs, we have also analyzed the effect of nitro substitution on crystal packing of five nitro-appended imidazolium salts.[61] No major hydrogen-bonding or directional close contacts were observed, suggesting that in the solid state, the nitro group has a very limited effect, beyond its steric contribution, in the crystal pack-

ing. This indeed suggests that the nitro substituents can be added without major increases of the melting points.

Also importantly, TGA analyses of these alkylated imidazolium-based salts revealed substantial improvement of the thermal stability compared with the protonated cation homologues. In most of the analyzed salts, the decomposition temperatures exceeded 220 °C, allowing consideration of this class of cations in the future design of EILs.
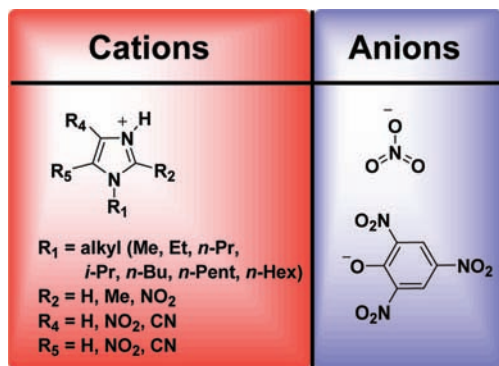
FIGURE 4. Investigated protonated imidazolium cores with functional groups appended to the heterocyclic core.

Table 3. Influence of Substitution Patterns on the Melting Point of Protonated EILs (Representative Data)[59]

cation	picrate mp (°C)	nitrate mp (°C)
1-methyl-3-*H*-imidazolium	159	59
1-hexyl-3-*H*-imidazolium	40	1
1,2-dimethyl-3-*H*-imidazolium	181	79

Third Design Cycle: Azolate-Based EILs—When Failure Directs Success

The second design cycle included several attempts to synthesize dinitro- and dicyano-substituted, alkylated, and protonated alkylimidazolium salts, with only limited success (dicyano derivatives were possible). The functionalization of these heterocycles with electron-withdrawing substituents such as NO$_2$ or CN results in a reduction in nucleophilicity of the heterocycle and thus a reduced ability to form quaternary salts by S$_N$2 alkylation, even with strong alkylating agents (e.g., methyltriflate or fluorosulfonate) or acids (e.g., nitric acid, picric acid). Indeed, the isolation of a cocrystal of 1-methyl-2,4-dinitroimidazole and picric acid (Figure 7) revealed rather dramatically that due to the high electron density of the nitro groups attached to the imidazole core, the imidazole ring was not protonated. Imidazolium salts with two nitrile substituents could be obtained only via the reaction of 1-methyl-4,5-dicyano-imidazole with the strong alkylating agents MeOSO$_2$F and (MeO)$_2$SO$_2$.[61]

In an effort to fully explore the synthetic limitations suggested by these results, we began a study in collaboration with Dr. David Dixon (The University of Alabama) on a computational investigation of proton and methylene group affinities and cation stabilities relative to the parent azoles.[64] This study concluded that when electron-withdrawing groups are added to the heterocyclic ring system, the application of stronger alkylating/protonating agents becomes necessary, and in the case of dinitroimidazolium salts, when calculated under ideal conditions, only the triflates were reactive enough to alkylate the dinitro-imidazole precursor. However, the dicyano-substituted imidazoles were predicted to be more reactive and their salts to be accessible through the reaction with methyl triflate, confirmed experimentally as mentioned above. The theoretical results also suggested that the alkylation of tricyano alkylimidazoles should be possible
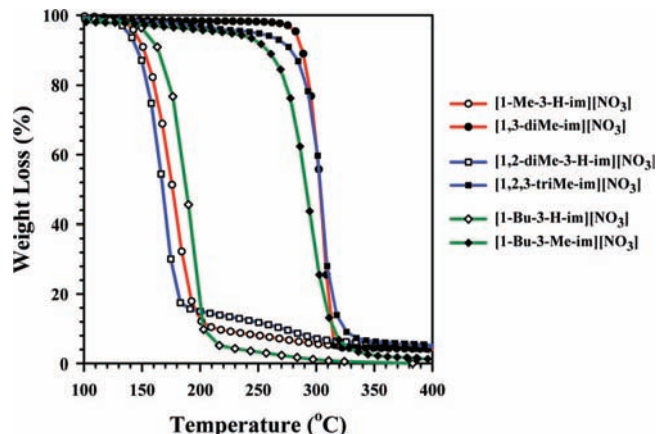

FIGURE 5. Thermal stabilities of protonated vs. alkylated imidazolium nitrate salts.
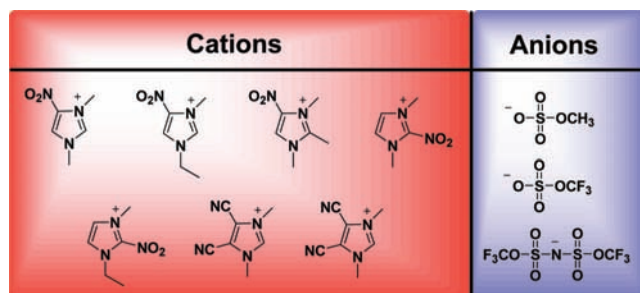

FIGURE 6. Investigated energetically substituted imidazolium-based salts.

Table 4. Influence of Anion Type and C2 Methyl Group Substitution on the Melting Points[61]

cation/anion	anion				
	I$^-$	ClO$_4^-$	NO$_3^-$	CH$_3$SO$_4^-$	NTf$_2^-$
1,3-dimethyl-4-nitroimidazolium	180	172	163	104	34
1,2,3-trimethyl-4-nitroimidazolium	191	182	161	150	110

under ideal conditions with methyl triflate; however, we have not pursued this line of investigation. Finally, as supported by experimental data, it was found that weakly electron-donating groups, such as a methyl group, have the opposite effect by slightly enhancing the basicity of the ring, facilitating quaternization reactions.

Unfortunately, even though the designed property (thermal stability) was greatly improved by changing from protonated cations to their alkylated analogs, the synthetic limitations for introducing energetic groups directly to the heterocyclic ring narrowed the range of available reactive precursors suitable for cation formation. Nonetheless, these results led us to speculate that the addition of enough electron-withdrawing groups to the neutral imidazole would eventually lead to ready azolate formation, where the tunability inherent in azolium cations could also be implemented in azolate anions (Figure 8).

In collaboration with the Katritzky group, we thus synthesized a variety of energetically substituted azolate anions that were later paired with common IL-forming cations (Figure 9). The resulting products were analyzed for their thermal behavior and initially assessed to be a
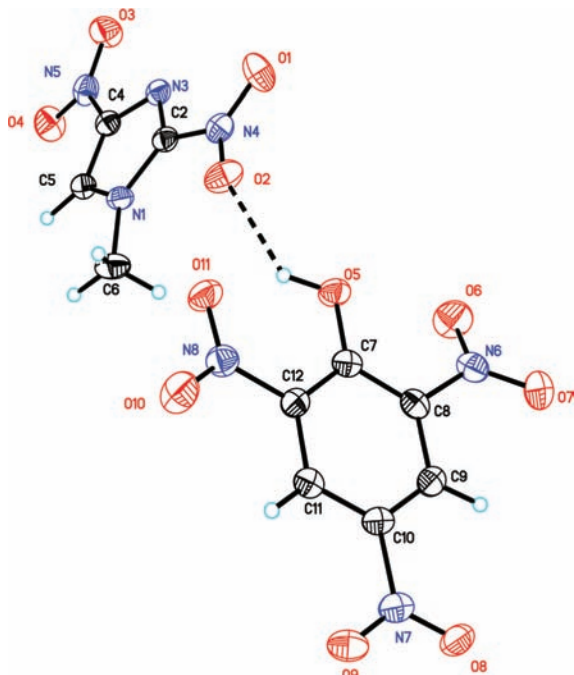
FIGURE 7. Cocrystal of unreacted 1-methyl-2,4-dinitroimidazole and picric acid; Yellow needles; $C_{10}H_7N_7O_{11}$; MW 401.23; Monoclinic; P2$_1$; a = 6.287(1)Å; b = 11.646(2)Å; c = 10.307(2)Å; β = 93.367(3)°; V = 753.3(2)Å^3; D_{calc} = 1.769 g cm^{-3}; R_1, wR_2 [I > 2σ(I)] = 0.0235, 0.0551; R_1, wR_2 (all data) = 0.0254, 0.0560.
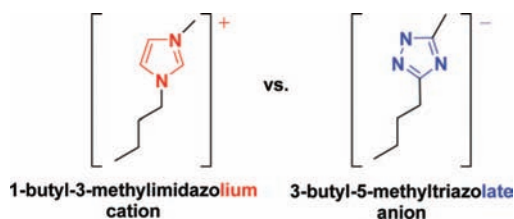

FIGURE 8. Similarity in the structural platforms for cation and anion tunability.

very promising group of compounds that should be further studied.[65,66]

It is important to note that up until this point, ILs were typically thought of as salts composed of organic cations and inorganic anions, with perhaps a few exceptions in the literature. In our studies, although we were looking at azolate anions as designed strictly for energetic materials, we were trying to introduce the concept of new, flexible, and designable anions that could be used for the formation of a variety of ILs. This was also the topic of concurrent work by Ohno et al., who published the synthesis of triazolate-based ILs.[67]

Our first studies concentrated on pairing the azolates with common quaternary ammonium cations to allow us to screen the influence of the anion structure on the resulting salt's physical properties. TGA analysis revealed that the azolate anions allow for the formation of highly stable salts with decomposition temperatures ranging from 165 °C (for tetramethylammonium 4-nitroimidazolate) to 235 °C (for tetramethylammonium 3,5-dinitro-1,2,4-triazolate). Additionally, the general trend in thermal stability among azolate anions was determined to be

nitroimidazolate ≤ tetrazolate ≤ 4-nitro-1,2,3-triazolate < dinitroimidazolate < dinitro-1,2,4-triazolate. These results suggested that the more substituted the azolate anion is with electron-withdrawing groups and the more nitrogen atoms are present in the heterocycle, the better is its anion charge delocalization and consequently its thermal stability.[66]

As expected, the melting points of the symmetric quaternary ammonium salts were insufficiently low, and only in a few cases (e.g., tetraethylammonium and tetrabutylammonium azolates) were melting points recorded below 100 °C. We thus shifted our focus to the modification/tuning of the melting point and began introducing common IL-forming cations such as [1-Bu-3-Me-im]$^+$.[67] As expected, pairing the dialkylimidazolium cations with energetically substituted azolate anions, often resulted in the formation of salts with very low melting points, reaching −82 °C in the case of [1-Bu-3-Me-im][tetrazolate]. In fact, all combinations of the [1-Bu-3-Me-im]$^+$ cation with the nine azolate anions our group has studied resulted in the formation of room temperature ionic liquids. Additionally, the thermal stabilities of the formed salts remained in similar ranges as previously determined for the analogous tetraalkylammonium salts providing wide liquidus ranges. In parallel studies, Shreeve et al.[68,69] and Klapötke et al.,[70] have also reported a wide range of energetic azolium azolate salts with melting points below or approaching the definition of ILs.

Referring back to our design scheme and analyzing all of the thermal behavior for the azolium azolate salts we studied, we concluded that this platform is valuable for the development of novel energetic materials. Additionally, analysis of current research progress in this field suggests a range of possible target ions (Figure 10) that could be considered, after slight structural modifications if necessary, as valuable precursors for the formation of other energetic azolium azolate salts.

The IL Platform Is More than Component Ion Design: New Synthetic Methodology for the Formation and Delivery of ILs

Our early EIL research has primarily focused on the investigation of the influence of cation and anion structures on the resulting physical and chemical properties of novel EILs. However, realizing the growing need for improved synthetic methodologies for the formation of new ILs, we have initiated a research program aimed at synthetic and delivery systems based on the IL platform. For example, by considering the dual-component nature of ILs and the ability to independently design and introduce desired physical and chemical properties to both cationic and anionic components of the salts, formation of the desired products can be achieved via separate synthesis of innocuous components of the final product (neutral or charged species) that can be later combined on-site and on-demand, resulting in the formation of targeted material and easy to remove byproducts.
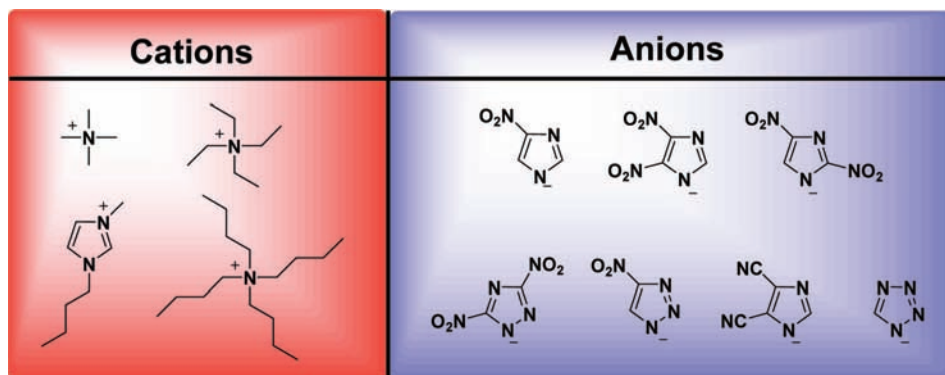
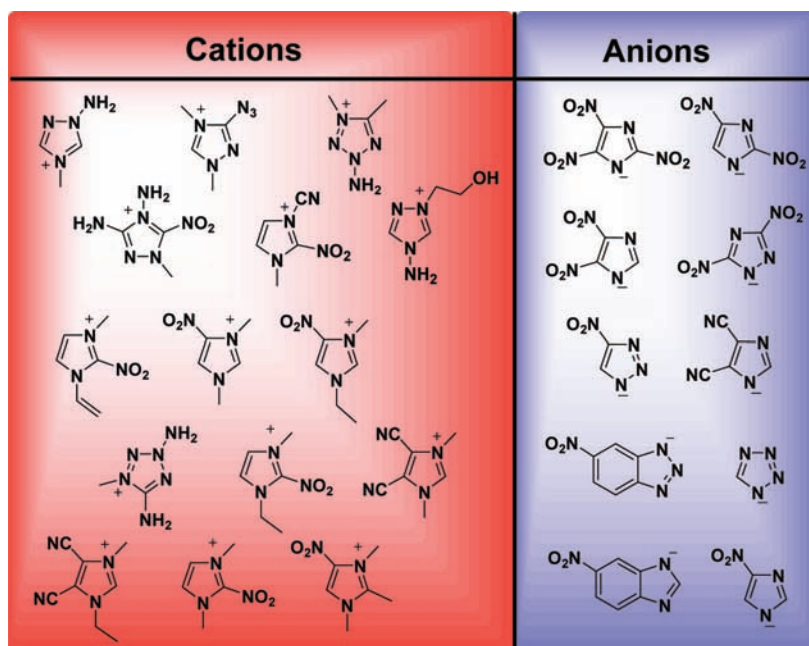**FIGURE 9.** Investigated energetically substituted azolate-based salts.

FIGURE 10. Examples of possible ions for use in formation of azolium azolate EILs.

Utilizing some of our previous work,[71] we developed synthetic methodology for halide- and metal-free, time- and cost-efficient, environmentally-sound synthesis of azolium salts, including azolium azolates, via reaction of azolium-2-carboxylate zwitterions with virtually any acid.[72] This protocol allows for the formation of pure ILs without the need for elaborate purification, since the only byproduct present after complete reaction is CO_2, which can be removed under vacuum with moderate heating.

We have proven this concept with the reaction of 1,3-dimethylimidazolium-2-carboxylate with both inorganic and organic acids and found that this protocol generally works for all strong acids ($pK_a < 1$) without the need of a catalyst and for weaker acids ($pK_a \approx 1-10$) with the addition of the Krapcho reaction catalyst DMSO (Figure 11). Moreover, this protocol can also be easily adapted to the synthesis of energetic azolium azolate salts.[73] In addition, our recent work on the synthesis of the first imidazolium hydrogencarbonate salt, using carbonic acid in the decarboxylation reaction of zwitterionic dialkylimidazolium-2-carboxylates, opens additional avenues for the halide-free formation of imidazolium salts.
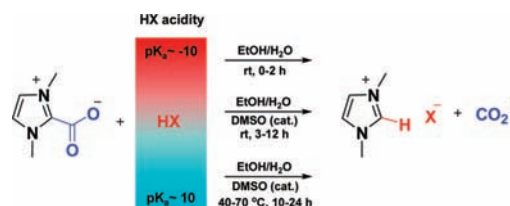

FIGURE 11. New byproduct-free synthetic methodology toward formation of ionic liquids.[72]

Performance Enhancements Using the IL Platform

We have considered that at times, it may be difficult to implement all targeted physical and chemical properties in one single salt. If the EILs fall short of one or more of the target criteria (melting point, thermal stability, density, heat of formation), while at the same time offering superior performance in several others, two alternative approaches may be implemented. First, the original design can be reconsidered for further synthetic modification with specific interest in the structure–property relationships that did not meet expectations. Alternatively, rather than modifying the structure of the designed target, a
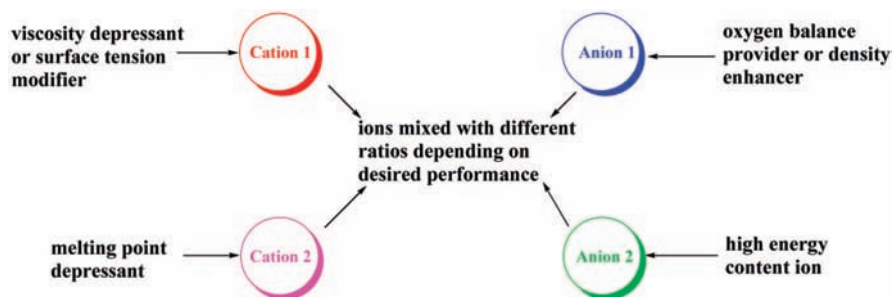
FIGURE 12. Concept of multicomponent EIL mixtures for enhancement of material properties.

Table 5. Eutectic Composition Melting Point Depression for the [1,3-diMe-im][4,5-diNO$_2$-im]/ [1,3-diMe-im][4-NO$_2$-tri] Salt System[74]

analyzed salt	mp (°C)
[1,3-diMe-im][4,5-diNO$_2$-im]	99
[1,3-diMe-im][4-NO$_2$-tri]	87
eutectic mixture (at 62.9 mol% [1,3-diMe-im] [4-NO$_2$-tri]/37.1 mol% [1,3-diMe-im][4,5-diNO$_2$-im])	70

multicomponent approach to enhance the IL performance can be envisioned by utilizing the known solvent properties of the IL, for example, by formation of eutectic mixtures with other ionic components or addition of other (perhaps molecular) property modifiers.

A simplified example of this concept is presented in the Figure 12. In our opinion, this approach, utilizing the unique solvent properties of ILs, can be especially attractive for tuning properties of energetic materials, since from the application perspective it is not crucial that these products be composed of a single salt. The eutectic approach appears to be particularly attractive since it does not involve any chemical reactions. In many cases, it can consist of simply introducing structural isomers or similar cations or anions to the salt to suppress its melting point, as illustrated in Table 5 with the mixed EIL system [1,3-diMe-im][4,5-diNO$_2$-im]/[1,3-diMe-im][4-NO$_2$-tri].[74] Moreover, formation of eutectic compositions can potentially allow for the introduction of another degree of multifunctionality to the final product by means of combination of properties brought together by different ion components in the mixture.

Progress and Prospects

Salts are in! The number of possible combinations of ions that can form unique ILs, the rapidly expanding fundamental knowledge base about ILs, the growing number of applications where flexibility of the IL concepts leads to process optimization, and the growing number of new IL patents, all indicate tremendous interest in the fundamental and applied chemistry of ILs. Understanding ILs and the impact that modifications of the ions and ion combinations have on IL properties is vital to the continued growth of this field. The evolution of ILs will continue as the field changes to a materials approach where target criteria (whether physical properties, chemical properties, or even biological[75] properties) are considered first, and then the IL is designed by appropriate choice of ions to deliver these exact properties. Progress

will also be realized by taking advantage of the unique properties of ILs, in our view, primarily the inherent modular nature of ILs, which gives greater level of control over the physical, chemical, and biological properties of salts than possible for molecular compounds. We anticipate that a natural outgrowth of the intense scrutiny of ILs by many different disciplines will ultimately lead to a much greater fundamental understanding of the interplay of strong and weak interactions in heterogeneous media. Let the fun continue!

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