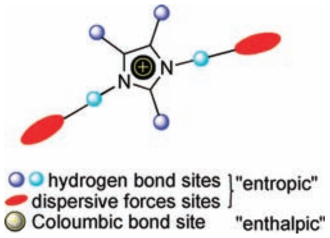
ACCOUNTS
of chemical research

From Molten Salts to Ionic Liquids: A "Nano" Journey

JAIRTON DUPONT*
Laboratory of Molecular Catalysis, Institute of Chemistry, UFRGS, Av. Bento Gonçalves, 9500 Porto Alegre 91501-970 RS, Brazil

RECEIVED ON MARCH 27, 2011

CONSPECTUS



Ionic liquids (ILs), a special group of classical molten salts, are widely used in various fields of science. Historically, researchers have tested ILs out of curiosity or to improve a specific property in a particular system in many areas of chemistry or materials science. However, today, ILs are far from being simple chemical curiosities and sit at the center of various green industrial innovation processes, where they play important roles in materials extraction, reactive catalytic supports, spatial devices, and biotransformations.

In this Account, we describe a journey into a nanostructured universe to better understand the unique properties of ionic liquids and their modern applications. Because molten salts have been known for centuries and have found limited uses, we try to explain why modern nonaqueous ILs deserve increased interest and curiosity. We discuss the characteristics that distinguish modern nonaqueous ILs and compare them with classical molten salts.

One of the main differences between room temperature ILs, especially those based on imidazolium cations, and simple molten salts, is the molecular asymmetry built into at least one of the ions. This asymmetry in modern, nonaqueous ILs opposes the strong charge ordering due to ionic interactions that normally would cause the system to crystallize. In addition, the presence of a cooperative network of hydrogen bonds between the cations and anions induces structural directionality (the entropic effect). Therefore, modern ILs form preorganized structures, mainly through hydrogen bonding, that induce structural directionality. In contrast, classical salts form aggregates only through ionic bonds. In other words, weak interactions order the structures in modern ILs while charges order the structure within classical salts.

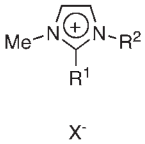
ILs cannot be regarded as merely homogeneous solvents. In fact, ILs form extended hydrogen-bond networks with polar and nonpolar nano domains and therefore are by definition "supramolecular" fluids. Thus, ILs are better described as hydrogen-bonded polymeric supramolecules of the type $[(\mathrm{DAI})_m(\mathrm{X})_{m\_n})]^{n+}[(\mathrm{DAI})_{m\_n}(\mathrm{X})_x)]^{n-}$. This structural pattern is a general trend for both the solid and the liquid phase and is apparently maintained to a large extent even in the gas phase. This structural organization of ILs can be used as entropic drivers (the "IL effect") for the preparation of well-defined nanoscale structures with extended order, either in the bulk phase or at the gas/vacuum interface.

Introduction

Ionic liquids (ILs) are one of the most important components of solution and liquid chemistry, and are widely used in various fields of science. In fact, there is probably not a single subarea of chemistry or materials sciences in which ILs have been not used or tested in order to improve some specific property, or merely because of simple curiosity.[1] However, today, ILs are far from being simple chemical curiosities and are now at the center of various "green" industrial innovation processes, where they play important roles in materials extraction, reactive catalytic supports, spatial devices, and biotransformations.[2−4] Besides forming a special class of classic molten salts,[5] what are the characteristics that make these fluids so special? Why, if molten salts have been known for centuries and have only found limited uses, do modern ILs deserve such increased interest and curiosity? ILs are far from being "a universal fluid" or simply a "solution" of liquid for solution and liquid chemistry, but play a central role in this condensed state of matter.

Our group has been involved in the preparation, characterization, and use of ILs long before their popularization and widespread use in the beginning of the 1990s.[6] The

Published on the Web 07/19/2011 www.pubs.acs.org/accounts
10.1021/ar2000937
© 2011 American Chemical Society



BMI.BF_4, X= BF_4, R^1= H, R^2= Bu^n
BMI.PF_6, X= PF_6, R^1= H, R^2= Bu^n
BMI.FAP, X= $PF_3(CF_2CF_3)_3$, R^1= H, R^2= Bu^n
BMI.NTf_2, X= $N(SO_2CF_3)_2$, R^1= H, R^2= Bu^n
BMI.OTf, X= CF_3SO_3, R^1= H, R^2= Bu^n
BMI.BPh_4, X= BPh_4, R^1= H, R^2= Bu^n
BDMI.PF_6, X= PF_6, R^1= Me, R^2= Bu^n
(BCN)MI.NTf_2, X= $N(SO_2CF_3)_2$, R^1= H, R^2= Bu^n
EMI.$EtSO_4$, X= $EtSO_4$, R^1= H, R^2= Et

FIGURE 1. Examples of imidazolium based ILs.

main goal of this Account is to report and discuss the contributions of our group to the physicochemistry and applications of ILs; in particular, the development of an ionic supramolecular structural model that may help to explain most of the chemistry displayed by these fluids and, more importantly, may enable prediction of their physicochemical behaviors in specific applications. Therefore, this Account is centered on our own results, but, where appropriate, selected results from the immense ocean of data from other groups will be use to clarify, enrich, and expand the discussion.

Classic molten salts, or fused salts, are in general defined as liquid electrolytes composed entirely of ions.[7] The term nonaqueous ionic liquid was traditionally used to described melts of ionic crystals, such as NaCl or $MgCl_2$.[8] These fluids have significant technological importance, because of their high thermal stability, low vapor pressure, good electrical conductivity, low viscosity, extremely broad temperature range, and excellent thermal stability (enabling very high temperatures to be reached). It is not surprising, then, that ILs have been used in metallurgy, electrochemistry, nuclear technology, and, more recently, as electrolytes for alternative energy devices.[5] Although these classical melts have been known for a very long time and have been used mainly in metallurgy, it was not until the advent of so-called nonaqueous room temperature molten salts that these fluids definitely entered the "solution" chemistry scene. Indeed, the advent of organoaluminate molten salts (derived mainly from the association of aluminum trichloride with 1,3-dialkylimidazolium or N-alkylpyridinium halide salts) in the 1950s[9] broadened their use in other areas, such as electrochemistry,[10] and to a lesser extent as fluids for synthesis and catalysis.[11] For example, organoaluminate molten salts have been used for immobilization of nickel complexes in the industrial two-phase catalytic olefin dimerization processes (DIFASOL) introduced at IFP.[12]

However, it was not until the middle of the 1990s, with the advent of more water compatible room temperature ILs[6,13−15] (Figure 1), that these fluids became the main actors in various fields of science, because of their unique modular physicochemical properties (density, viscosity, hydrophobicity, conductivity, thermal and chemical stability, etc.).

Modern noncorrosive fluids that melt below 100 °C are collectively known as ILs[16] and are usually composed of an organic cation (quaternary ammonium or phosphonium, imidazolium, pyridinium, pyrolidinium, etc.) and relatively weak coordinating anions (halides, acetates, tetrafluoroborate, hexafluorophosphate, etc.). Note that modern ILs are neither automatically nonflammable nor noncombustible (some have the capability of fatal combustion),[17] or have very low vapor pressure[18] or are "nonreactive" fluids.[19]

But what characteristics differentiate a classical molten salt from a modern ionic liquid? To answer this question, we have to take a closer look at the structural organization of these two types of salts, both in the bulk phase and at their surfaces (mainly at the vacuum interface).

Solid, Liquid, Solution, and Gas Phase Organization

The degree of order in a classical molten salt, at least at temperatures slightly above the melting point, is similar to that in the solid. Indeed, studies of metal halide melts, using neutron and X-ray diffraction, have demonstrated that melting usually preserves the chemical order found in the crystal.[20,21] Specifically, there is only a 10−15% volume expansion during the transition from the crystalline to the liquid state, and the ion−ion or atom−atom distances are similar in both states. While long-range order is lost on going from a crystal to a liquid, similarities remain, as a consequence of the Coulombic forces between cations and anions of the salts.[22,23]

Coulomb interactions dominate static long-range behavior in classical molten salt systems. These Coulomb interactions give rise to the formation of ion pairs and higher ion clusters, shortening interionic distances and lowering the coordination number of ions, resulting in increased volume upon melting and the formation of "free" volume.[7] Although the same types of Columbic interactions exist in modern ILs, one of the main differences between room temperature ILs and simple molten salts is the molecular asymmetry built into at least one of the ions. This asymmetry opposes the strong charge ordering due to ionic interactions, which normally would cause the system to crystallize in the case of classical molten salts. Another main difference is the presence of a cooperative network of hydrogen bonds between the cations and anions[24−27] that induce structural directionality ("entropic effect").[28] Therefore, modern ILs possess preorganized structures,

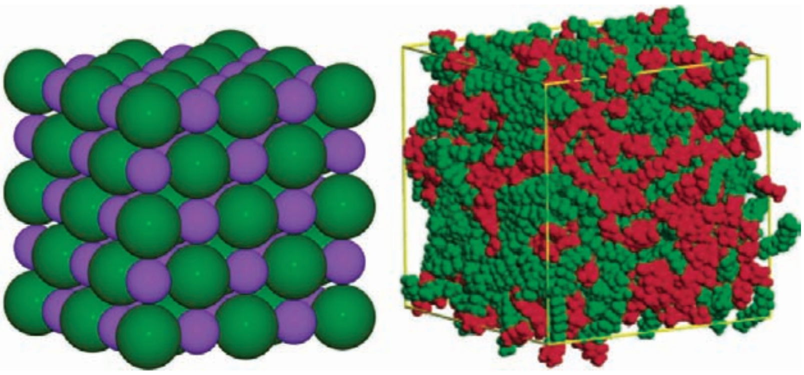


FIGURE 2. Representations of the 3-D structural arrangements of an ionic crystal displaying a classical charge ordering structure (left) and a "modern" 1-alkyl-3-methylimidazolium IL (right), that presents polar (red) and nonpolar (green) nano domains. (Right figure adapted with permission from ref 30. Copyright 2006 American Chemical Society.)

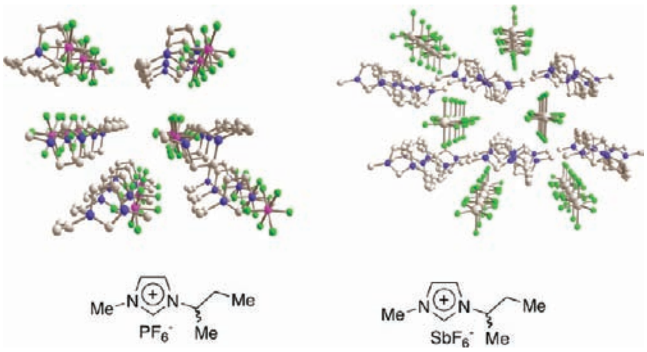


FIGURE 3. Illustration of the two major 3-D arrangements of imidazolium ILs: a cooperative network of hydrogen bonds generates "free" channels in both cases.

mainly through hydrogen bonds that induce structural directionality. In contrast, classical salt aggregates are only formed through ionic bonds (i.e., charge-ordering structures) (Figure 2).[29]

In support of this model, a review of X-ray studies reported in recent years on the structure of 1,3-dialkylimidazoilum salts has revealed a common trend: in the solid state, these salts form an extended cooperative network of cations and anions, connected by hydrogen bonds. The monomeric unit always consists of one imidazolium cation surrounded by at least three anions, and in turn each anion is surrounded by at least three imidazolium cations. Specifically, imidazolium ILs form two major 3-D arrangements: (1) formed through chains of the imidazolium rings (π-stacking, Figure 3 right) with anions accommodated as chains; and (2) formed by columns consisting of alternating cations and anions (Figure 3, left). In both cases, "free" volumes are formed in these structures that also provide polar and nonpolar "nano" regions (i.e., hydrophobic and hydrophilic zones) with a high degree of directionality: akin to that observed in highly concentrated surfactant media. Imidazolium ILs can be better represented as nanostructures of the type $[(\mathrm{DAI})_m(\mathrm{X})_{m\_n})]^{n+}[(\mathrm{DAI})_{m\_n}(\mathrm{X})_x)]^{n-}$, where DAI is the 1,3-dialkylimidazolium cation, X is the anion, and $n \geq 3$.

Importantly, relatively weak bonds (e.g., van der Waals) also start to play an important role in the organization of these salts with increasing alkyl side chain length. In fact, imidazolium ionic liquids with *n*-dodecyl side chains display liquid crystal properties.[31,32] Therefore, most of the IL structural organization pattern is roughly in between classical liquids and liquid crystals.

The presence of hydrogen bonds between imidazolium cations and anions in the condensate have been observed several times using spectroscopic methods:[24,33] for example, in two of the most popular room temperature imidazolium ILs, the hydrophobic BMI.PF_6 and hydrophilic BMI.BF_4.[6,34] In the solid state, the existence of this cooperative network of hydrogen bonds was demonstrated by X-ray diffraction studies on various imidazolium salts[27] that are solid at room temperature. In particular, our group has demonstrated that even very weak $C{-}H\cdots\pi$ bonds induce structural directionality in these salts.[25,26] The presence and relative strength of these hydrogen bonds was corroborated by ESI-MS studies.[35,36] Indeed, using this technique, we were able to identify and detect a series of supramolecular mono and multiply charged cationic and anionic aggregates of the type $[(\mathrm{DAI})_m(\mathrm{X})_{m\_n})]^{n+}[(\mathrm{DAI})_{m\_n}(\mathrm{X})_x)]^{n-}$. A solvent-free relative hydrogen bond scale could then be estimated by ESI-MS/MS experiments, via dissociation of mixed supramolecular clusters. For the five anions studied, the relative order of intrinsic hydrogen-bond strengths to the BMI cation is $CF_3CO_2 > BF_4 > PF_6 > InCl_4 > BPh_4$. Moreover, other evidence that this structural organization is maintained even in solution was furnished by techniques such as NMR and thermochemical studies.[26] This tendency to form aggregates held together by a cooperative network of hydrogen bonds is present even in highly diluted solutions; even only very weak hydrogen bonds are possible, as shown for $BMI.BPh_4$.[25]

Traveling wave ion mobility mass spectrometry was used to determine the intrinsic mobility of a series of these gaseous supraionic aggregates of the type $[(DAI)_{n+1}(X)_n]^+$ versus their respective anions $[(DAI)_n(X)_{n+1}]^-$ for $n = 0-$. Interestingly, a linear dependence of drift time on the mass of the ionic liquid aggregates was found, while the sign of the charge had little effect.[37] These solvent and counterion free intrinsic values contradict surprising mobility values previously measured in the condensed phase, which indicated an anomalous greater mobility for bulkier IL cations.[38,39] This previously reported anomalous behavior seems, therefore, to be related to a structural phenomenon with supramolecular and different polar and nonpolar IL domain interactions likely playing a major role.[40] In support of this, two of the most widely used ILs, $BMI.BF_4$ and $BMI.PF_6$, present large nonlinearities,[41] with a nonlocal character that may be attributable to the presence of polar and nonpolar domains in their structures. More recently, elegant studies based on magnetic field effects for the hydrogen abstraction reaction indicate that these ILs have at least two different viscosity regions.[42]

We were also able to detect the presence of neutral supramolecular IL aggregates, by transferring species from the condensed phase to the gas phase, by means of atmospheric-pressure chemical ionization (APCI) mass spectrometry experiments. This process promotes gentle ambient vaporization at temperatures considerably lower than the boiling point of the ionic liquid, and neutral clusters of the type $[DAI.X]_n$ ($n = 1, 2,$ and 3) have been observed in the gas phase.[43] This result is another indication that the properties of ILs are better correlated with a full range of aggregates rather than isolated ions. The overall physicochemical characteristics of ILs are therefore the result of the average properties of these supramolecular aggregates, rather than those of the individual cations and anions.

Formation of MNPs in ILs

The inherent steric and electronic properties of ILs allows them to be used as solvents and stabilizing agents for the formation and stabilization of various metal nanoparticles (MNPs), by simple reduction of metal salt compounds or decomposition of transition metal organometallic compounds.[44] These methods are so simple that, after we have reported the synthesis of iridium nanoparticles[45] in classical ILs such $BMI.BF_4$ and $BMI.PF_6$, a legion of different size and shape MNPs have been reported.[44] These MNPs can be isolated from the IL and characterized by classical methods, such as transmission electron microscopy (TEM), X-ray diffraction analysis (XRD), or X-ray photoelectron spectroscopy (XPS).

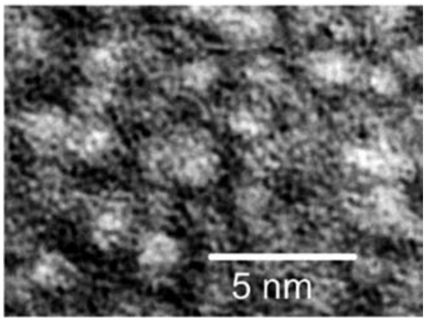
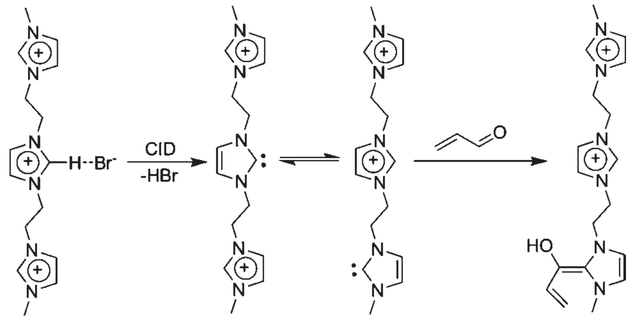


FIGURE 4. TEM micrograph (negative image, underfocus) of Pt(0) in $BMI.PF_6$, showing contrast density fluctuation around the MNPs. (Reprinted with permission from ref 46. Copyright 2003 American Chemical Society.)

Moreover, because of the very low vapor pressure displayed by these ILs, they offer a unique opportunity to investigate the size and shape of NPs by in situ TEM analysis[46] or XPS.[47] The possibility to perform TEM without NP isolation enables investigations into the changes in size and shape of cobalt NPs during thermal treatment.[48] More interestingly, detailed examination of Pt nanoparticles embebed in $BMI.PF_6$ and their surrounding environment revealed a rather strong fluctuation of contrast density (see Figure 4), characteristic of amorphous substrates.

These contrast fluctuations for particles embebed in the ionic liquid and spread over the carbon are quite distinct from those observed for pure carbon films or for pure liquid droplets over a carbon film. The high contrast density fluctuations observed in the image shown in Figure 4 reflect the increased thickness and mass density of an amorphous structure: as if the liquid molecules around the nanoparticles have become immobilized and strongly attached to the nanoparticles, thus demonstrating the interaction between the IL and the metal surface. This direct interaction was also observed by in situ XPS analysis of Ir NPs dispersed in $EMI.EtSO_4$, providing evidence of an effective interaction between the NPs and the surrounding liquid. Monitoring the C 1s signal of the ionic liquid revealed a change in the binding energy of one of its components (C2) in the presence of Ir nanoparticles, suggesting the presence of carbenes at the metal surface. Indeed, the presence of carbenes was also suggested by H/D labeling, mass spectrometry, and NMR experiments during the preparation of NPs in ILs.[49,50] However, transient carbene intermediates were only directly observed very recently, in mass spectrometry experiments

SCHEME 1



(MS-ESI) of multicharged imidazolium salts (Scheme 1).[51] Thus, the formation of carbenes in imidazolium IL solutions (even under relatively "neutral" conditions) is likely to be inevitable, and carbene participation should always be considered in processes performed with imidazolium IL.

While it is clear that ILs provide an adequate media for the generation of MNPs, can we explain or predict the size and shape of these MNPs? This is not a simple task, because soluble MNPs are only kinetically stable. However, based on our nanostructural model, the size of the MNPs was found to be directly related to the length of the N-alkyl imidazolium side chains or anion volume. For example, neutral precursors such as $[Ni(COD)_2]$,[52] ($[Ru(COD)(COT)]$,[53,54] and $[IrCl(COD)_2]$[55,56] (COD = 1,5-cyclooctadiene and COT = 1,3,5-cyclooctatriene) compounds may concentrate preferentially in nonpolar regions of the ILs. In such cases, nanoparticle growth is probably controlled by the local precursor concentration and is consequently limited by the size and shape of IL nonpolar domains, which are imposed by the length of the N-alkyl side chain. Indeed, a linear relationship between NP size and N-alkyl chain length in ILs was observed.[52,53]

In addition, changing the size of the anions may control the volume of the polar domains of the imidazolium ILs. For example, the hydrogen reduction of ionic metal precursors, such as AgX (X = BF_4, PF_6, OTf)[57] or $[Ir(COD)_2]BF_4$,[58] which tends to concentrate in the polar domains of BMI.X (X = BF_4, PF_6, OTf, NTf_2), yields NPs whose diameters (nm) increase linearly with the molecular volume of the ionic liquid anion.[57]

Surface Organization of Imidazolium ILs: Formation of MNPs at the Interface

Although the contribution of our group to the understanding of imidazolium IL surface organization is limited to a few XPS studies,[47,59] we have designed and performed a series of experiments to use this organization as entropic drivers, to generate MNPs at the surface/gas interface. The average surface structure of the ILs can, in principle, be tuned by varying the identity of the anion and cation substituents.[60,61] In fact, IL surface organization involves two interconnected aspects: (1) surface composition and (2) surface ion orientation. Based on these principles, a consensus has been established regarding the surface composition of nonfunctionalized ILs. In this case, both cations and anions are present at the surface in a wide range of pure imidazolium-based ILs, especially ILs containing short alkyl chains, such as 1-ethyl-3-methylimidazolium.[62−65] For ILs with chains longer than ethyl, the imidazolium rings have been shown to be perpendicular to the surface plane, with the alkyl chains projected into the gas phase, independent of anion identity.[66] Anions with long perfluorinated chains tend to populate the vacuum/IL interface, with the long alkyl chains in the firsts few angstroms of the IL surface.[61,63,65] However, for functionalized ILs, the surface composition remains unknown.[67]

During sputter deposition, the bombardment of a metal foil surface with energetic gaseous ions causes physical ejection of surface atoms and/or small metal clusters. Because of the low gas pressure, it is assumed that (depending on the working pressure) there are no considerable gas-phase collisions between the sputtered species in the space between the metal foil and the IL medium. Injection onto the IL surface and/or bulk phase could produce an atom/cluster concentration high enough to self-coalesce, resulting in the formation of nanoparticles.[68,69] Although it is difficult to precisely know where NP nucleation and particle growth occurs, the following three hypotheses are possible: (1) nucleation starts on the IL surface and then diffuses into the liquid phase, where particle growth takes place; (2) both processes occur on the IL surface; or (3) metal atoms and clusters penetrate just below the liquid phase and both processes occur in the bulk IL phase (see Figure 5).

Regardless of the operative process, nanoparticle formation will be strongly dependent on IL surface composition and the structural organization of the bulk phase. Therefore, the formation of MNPs by sputtering deposition on ILs may constitute an interesting chemical probe, to correlate the size and shape of nanoparticles with the structural surface organization of ILs.

Macroscopically, both surface and bulk composition properties depend on IL surface tension and viscosity. Apparently, surface tension influences the initial formation of nanoparticles on the surface of an ionic liquid, while viscosity affects the aggregation process during dispersion of Au particles from the surface into the liquid.[70] Moreover, the

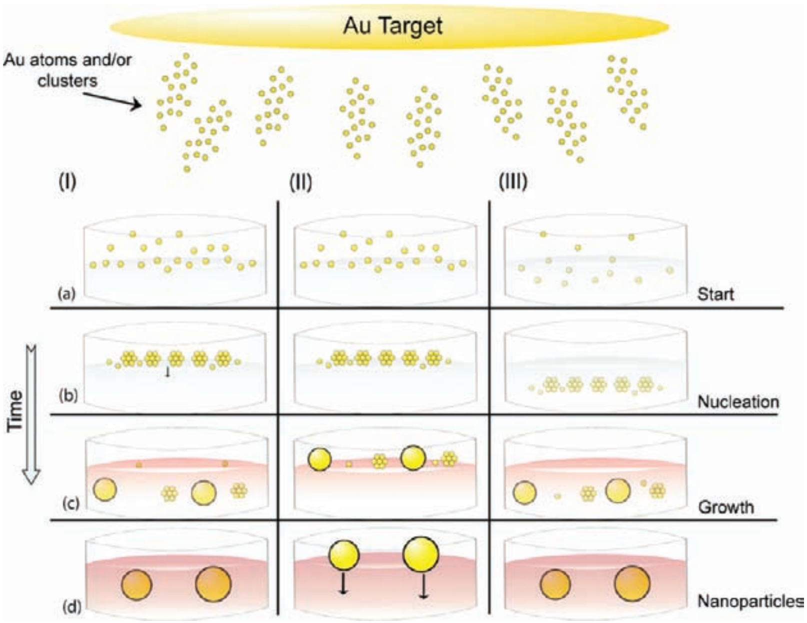


FIGURE 5. Possible mechanisms for the nucleation and growth of sputtered gold nanoparticles in ILs. (Adapted with permission from ref 74. Copyright 2010 American Chemical Society.)

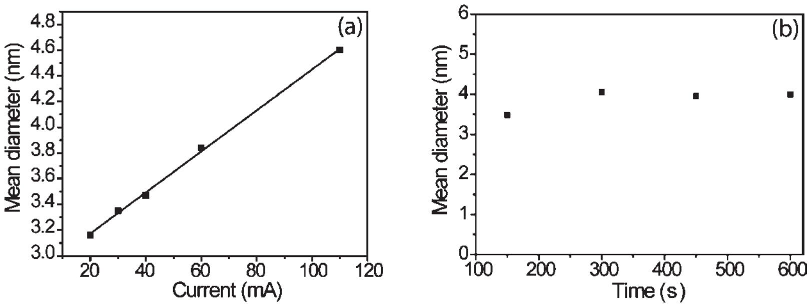


FIGURE 6. (a) Mean diameter of Au NPs obtained in BMI.NTf$_2$ after 150 s of deposition using different discharge currents; (b) diameter versus deposition time for Au NPs obtained in BMI.NTf$_2$ at a fixed sputtering current of 40 mA (325 V). (Adapted with permission from ref 74. Copyright 2010 American Chemical Society.)

energy of the traveling metal atoms/clusters may be also an important parameter, because species with too much energy will penetrate directly into the IL phase, and may increase the IL temperature, consequently decreasing the surface tension and viscosity. Therefore, nanoparticle nucleation may directly depend on the surface structure, while nanoparticle growth may be related to bulk ("inner") IL organization. In support of this, as already discussed above, both experimental and theoretical investigations have recently shown that IL surface composition may be populated with alkyl and/or fluorinated moieties, depending on the type of anion and cation substituents.[62−64,66,71−73]

The sputtering of gold foil onto ILs generates stable and well-dispersed gold NPs of 3−5 nm under conditions of 40 mA, 335 V, and an argon work pressure of 2×10^{-2} mbar. Under these conditions, the sizes and size distributions of gold nanoparticles are independent of sputtering time. However, the size of the resultant nanoparticles depends on the sputtering power, and nanoparticle size increases linearly with increasing sputtering power (Figure 6). When increased sputtering powers are used, more gold atoms with higher energies hit the ionic liquid surface per unit of time, which changes the kinetics of particle growth on the IL surface. Thus, both nucleation and NP growth occur on the IL surface under these experimental conditions. Moreover, changing the IL surface composition by increasing the concentration of fluorinated moieties, and consequently the nonpolar IL surface domains, changes the nanoparticle growth rate and resulting NP sizes considerably. In fact, nanoparticles prepared in BMI.FAP (around 4.9 nm) are significant larger than those prepared in the less "fluorinated" ILs (BMI.BF$_4$, BMI.PF$_6$, or BMI.NTf$_2$, around 3.6 nm).

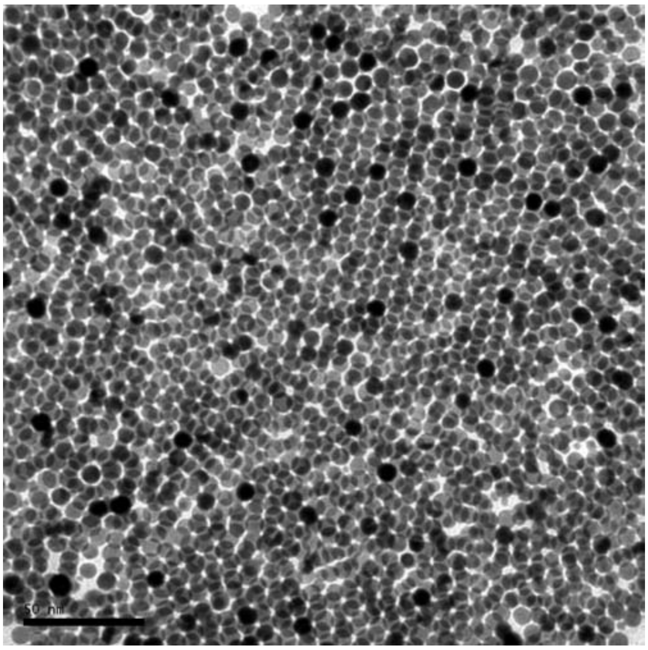


FIGURE 7. TEM image of 3D AuNP superlattices from samples synthesized by sputtering onto (BCN)MI.NTf_2.

We demonstrated that the use of a nitrile functionalized IL changes the interfacial composition of the vacuum/IL, enabling synthesis of "soluble" gold nanospheres (AuNSs) and/or gold nanodisks (AuNDs), self-organized in 2-D and 3-D superlattices. Thus, sputtered "necked" gold atoms/small clusters are capable of forming coordination-like compounds with functionalized ionic liquids, opening up completely new routes for preparing different sized and shaped self-organizing nanoparticles in solution. Sputtering gold onto (BCN)MI.NTf_2 IL under different discharge conditions yields gold nanoparticles of different sizes (3−4 and 7−8 nm) self-organized into 2-D and 3-D superlattices (Figure 7) that are composed of AuNSs and/or AuNDs. The AuND population decreases with increasing discharge voltage, and at voltages greater than 340 V only AuNSs were formed. Interestingly, AuND shape was determined by various techniques, including the first reported tomography of a nanoparticle in solution.[75]

The growth mechanisms of Au in (BCN)MI.NTf_2 likely involve two interconnected parameters: (1) the conformation of the molecular species of the IL surface; and (2) the energy of the sputtered atoms. When Au atoms are sputtered with low average kinetic energy, the atoms tend to bind more with coordinating nitrile groups, forming AuNDs. These disks were formed by preferential 2-D growth, because of a strong interaction between Au atoms and the butyronitrile side chain in the more external regions of the IL surface. In contrast, AuNSs were formed by preferential 3-D growth, due to anion−gold interactions in the more internal region of the IL surface, as observed for nonfunctionalized ILs.[74]

Conclusions

It is evident that ILs can no longer be regarded as merely homogeneous solvents. In fact, because ILs form extended hydrogen-bond networks with polar and nonpolar nanodomains, they are, by definition, "supramolecular" fluids. Therefore, ILs are better described hydrogen-bonded as polymeric supramolecules of the type $[(\mathrm{DAI})_m(\mathrm{X})_{m\_n})]^{n+}$-$[(\mathrm{DAI})_{m\_n}(\mathrm{X})_x)]^{n-}$. This structural pattern is a general trend for both the solid and the liquid phase, and is apparently maintained to a large extent even in the gas phase. This structural organization of ILs can be used as "entropic drivers" (the so-called "IL effect") for spontaneous, well-defined, and extended ordering of nanoscale structures, either in the bulk phase or at the gas/vacuum interface. Although modern nonaqueous ILs still encompass a broad field, they are taking their place as nanostructured liquids, and certainly already play a major role as entropic drivers in "solution" chemistry.

BIOGRAPHICAL INFORMATION

Jairton Dupont received his Ph.D. at the University of Strasbourg (France), and after postdoctoral research at the University of Oxford (U.K.) he became Professor of Chemistry at the Institute of Chemistry, UFRGS (Brazil). He has been an invited Professor at various European Universities (France, Germany, and Spain), is a member of the Brazilian Academy of Sciences, and has received the Humboldt Research Award, the Conrado Wesel Science Award, and the Brazilian Gran Cruz. His research interests are mainly centred on ionic liquids, with special emphasis on catalysis, nanomaterials, and alternative energies.

Thanks are due to all my co-workers, whose names appear in the references since 1992, when we initiated this molten salt journey to nonaqueous ILs. Thanks are also due for financial support from CNPq, CAPES, FAPERGS, INCT-Catal., and PETROBRAS.

FOOTNOTES

*Fax: + 55 51 33087204. E-mail: Jairton.dupont@ufrgs.br.

REFERENCES

1 Weyershausen, B.; Hell, K.; Hesse, U. Industrial application of ionic liquids as process aid. *Green Chem.* **2005**, *7*, 283–287.

2 Plechkova, N.; Seddon, K. Applications of ionic liquids in the chemical industry. *Chem. Soc. Rev.* **2008**, *37*, 123–150.

3 Olivier-Bourbigou, H.; Travers, P.; Chodorge, J. A. Olefin oligomerisation with homogeneous catalysis. *Pet. Technol. Q.* **1999**, *Q4*, 141–149.

4 Lozano, P.; de Diego, T.; Carrie, D.; Vaultier, M.; Iborra, J. L. Lipase catalysis in ionic liquids and supercritical carbon dioxide at 150 degrees C. *Biotechnol. Prog.* **2003**, *19*, 380–382.

5 Osteryoung, R. A. In *Advances in Molten Salt Chemistry*; Mamantov, G. M. D., Ed.; Elsevier: Dordrecht, 1987; Vol. 202.

6 Suarez, P. A. Z.; Dullius, J. E. L.; Einloft, S.; DeSouza, R. F.; Dupont, J. The use of new ionic liquids in two-phase catalytic hydrogenation reaction by rhodium complexes. *Polyhedron* **1996**, *15*, 1217–1219.

7 Sundermeyer, W. Fused Salts And Their Use As Reaction Media. *Angew. Chem., Int. Ed.* **1965**, *4*, 222–238.

8 Barrer, R. M. The viscosity of pure liquids. II. Polymerised ionic melts. *Trans. Faraday Soc.* **1943**, *39*, 59–67.

9 Hurley, F. H.; Wier, T. P. Electrodeposition of metals from fused quaternary ammonium salts. *J. Electrochem. Soc.* **1951**, *98*, 203–206.

10 Chum, H. L.; Koch, V. R.; Miller, L. L.; Osteryoung, R. A. An Electrochemical Scrutiny of Organometallic Iron Complexes and Hexamethylbenzene in a Room Temperature Molten Salt. *J. Am. Chem. Soc.* **1975**, *97*, 3264–3265.

11 Chauvin, Y.; Olivier-Bourbigou, H. Nonaqueous Ionic Liquids As Reaction Solvents. *Chem. Technol.* **1995**, *25*, 26–30.

12 Chauvin, Y.; Gilbert, B.; Guibard, I. Catalytic Dimerization Of Alkenes By Nickel-Complexes In Organochloroaluminate Molten-Salts. *J. Chem. Soc., Chem. Comun.* **1990**, 1715–1716.

13 Wilkes, J. S.; Zaworotko, M. J. Air And Water Stable 1-Ethyl-3-Methylimidazolium Based Ionic Liquids. *J. Chem. Soc., Chem. Comun.* **1992**, 965–967.

14 Chauvin, Y.; Mussmann, L.; Olivier, H. A novel class of versatile solvents for two-phase catalysis: Hydrogenation, isomerization, and hydroformylation of alkenes catalyzed by rhodium complexes in liquid 1,3-dialkylimidazolium salts. *Angew. Chem., Int. Ed.* **1996**, *34*, 2698–2700.

15 Bonhote, P.; Dias, A. P.; Papageorgiou, N.; Kalyanasundaram, K.; Gratzel, M. Hydrophobic, highly conductive ambient-temperature molten salts. *Inorg. Chem.* **1996**, *35*, 1168–1178.

16 Wasserscheid, P.; Keim, W. Ionic liquids - New “solutions” for transition metal catalysis. *Angew. Chem., Int. Ed.* **2000**, *39*, 3773–3789.

17 Chambreau, S. D.; Schneider, S.; Rosander, M.; Hawkins, T.; Gallegos, C. J.; Pastewait, M. F.; Vaghjiani, G. L. Fourier transform infrared studies in hypergolic ignition of ionic liquids. *J. Phys. Chem. A* **2008**, *112*, 7816–7824.

18 Earle, M. J.; Esperanca, J.; Gilea, M. A.; Lopes, J. N. C.; Rebelo, L. P. N.; Magee, J. W.; Seddon, K. R.; Widegren, J. A. The distillation and volatility of ionic liquids. *Nature* **2006**, *439*, 831–834.

19 Dupont, J.; Spencer, J. On the noninnocent nature of 1,3-dialkylimidazolium ionic liquids. *Angew. Chem., Int. Ed.* **2004**, *43*, 5296–5297.

20 Biggin, S.; Enderby, J. E. Comments on the structure of molten-salts. *J. Phys. C: Solid State Phys.* **1982**, *15*, L305–L309.

21 Rovere, M.; Tosi, M. P. Structure and dynamics of molten-salts. *Rep. Prog. Phys.* **1986**, *49*, 1001–1081.

22 Martin, J. D. Structure-property relationships in ionic liquids. *ACS Symp. Ser.* **2002**, *818*, 413–427.

23 Cang, H.; Li, J.; Fayer, M. D. Orientational dynamics of the ionic organic liquid 1-ethyl-3-methylimidazolium nitrate. *J. Chem. Phys.* **2003**, *119*, 13017–13023.

24 Dieter, K. M.; Dymek, C. J.; Heimer, N. E.; Rovang, J. W.; Wilkes, J. S. Ionic structure and interactions in 1-methyl-3-ethylimidazolium chloride-$AlCl_3$ molten-salts. *J. Am. Chem. Soc.* **1988**, *110*, 2722–2726.

25 Dupont, J.; Suarez, P. A. Z.; De Souza, R. F.; Burrow, R. A.; Kintzinger, J. P. C-H-π interactions in 1-n-butyl-3-methylimidazolium tetraphenylborate molten salt: Solid and solution structures. *Chem.—Eur. J.* **2000**, *6*, 2377–2381.

26 Consorti, C. S.; Suarez, P. A. Z.; de Souza, R. F.; Burrow, R. A.; Farrar, D. H.; Lough, A. J.; Loh, W.; da Silva, L. H. M.; Dupont, J. Identification of 1,3-dialkylimidazolium salt supramolecular aggregates in solution. *J. Phys. Chem. B* **2005**, *109*, 4341–4349.

27 Dupont, J. On the solid, liquid and solution structural organization of imidazolium ionic liquids. *J. Braz. Chem. Soc.* **2004**, *15*, 341–350.

28 Antonietti, M.; Kuang, D. B.; Smarsly, B.; Yong, Z. Ionic liquids for the convenient synthesis of functional nanoparticles and other inorganic nanostructures. *Angew. Chem., Int. Ed.* **2004**, *43*, 4988–4992.

29 Hansen, J. P.; McDonald, I. R. *Theory of Simple Liquids*, 2nd ed.; Academic Press: London, 1986.

30 Lopes, J.; Padua, A. A. H. Nanostructural organization in ionic liquids. *J. Phys. Chem. B* **2006**, *110*, 3330–3335.

31 Binnemans, K. Ionic liquid crystals. *Chem. Rev.* **2005**, *105*, 4148–4204.

32 Machado, G.; Scholten, J. D.; de Vargas, T.; Teixeira, S. R.; Ronchi, L. H.; Dupont, J. Structural aspects of transition-metal nanoparticles in imidazolium ionic liquids. *Int. J. Nanotechnol.* **2007**, *4*, 541–563.

33 Wulf, A.; Fumino, K.; Ludwig, R. Spectroscopic Evidence for an Enhanced Anion- “Cation Interaction from Hydrogen Bonding in Pure Imidazolium Ionic Liquids. *Angew. Chem., Int. Ed.* **2010**, *49*, 449–453.

34 Suarez, P. A. Z.; Einloft, S.; Dullius, J. E. L.; de Souza, R. F.; Dupont, J. Synthesis and physical-chemical properties of ionic liquids based on 1-n-butyl-3-methylimidazolium cation. *J. Chim. Phys. Phys.-Chim. Biol.* **1998**, *95*, 1626–1639.

35 Gozzo, F. C.; Santos, L. S.; Augusti, R.; Consorti, C. S.; Dupont, J.; Eberlin, M. N. Gaseous supramolecules of imidazolium ionic liquids: “Magic” numbers and intrinsic strengths of hydrogen bonds. *Chem.—Eur. J.* **2004**, *10*, 6187–6193.

36 Neto, B. A. D.; Ebeling, G.; Goncalves, R. S.; Gozzo, F. C.; Eberlin, M. N.; Dupont, J. Organoindate room temperature ionic liquid: Synthesis, physicochemical properties and application. *Synthesis* **2004**, 1155–1158.

37 Lalli, P. M.; Corilo, Y. E.; de Sa, G. F.; Daroda, R. J.; de Souza, V.; Souza, G. H. M. F.; Campuzano, I.; Ebeling, G.; Dupont, J.; Eberlin, M. N. Intrinsic Mobility of Gaseous Cationic and Anionic Aggregates of Ionic Liquids. *ChemPhysChem* **2011**, *12*, 1444–1447.

38 Every, H.; Bishop, A. G.; Forsyth, M.; MacFarlane, D. R. Ion diffusion in molten salt mixtures. *Electrochim. Acta* **2000**, *45*, 1279.

39 Mamontov, E.; Baker, G. A.; Luo, H.; Dai, S. Microscopic Diffusion Dynamics of Silver Complex-Based Room-Temperature Ionic Liquids Probed by Quasielastic Neutron Scattering. *ChemPhysChem* **2011**, *12*, 944–950.

40 Spohr, H. V.; Patey, G. N. Structural and dynamical properties of ionic liquids: Competing influences of molecular properties. *J. Chem. Phys.* **2010**, *132*, 154504.

41 Souza, R. F.; Alencar, M.; Meneghetti, M. R.; Dupont, J.; Hickmann, J. M. Nonlocal optical nonlinearity of ionic liquids. *J. Phys.: Condens. Matter* **2008**, *20*, 155102.

42 Yago, T.; Wakasa, M. Nanoscale Structure of Ionic Liquid and Diffusion Process as Studied by the MFE Probe. *J. Phys. Chem. C* **2011**, *115*, 2673–2678.

43 Neto, B. A. D.; Santos, L. S.; Nachtigall, F. M.; Eberlin, M. N.; Dupont, J. On the species involved in the vaporization of imidazolium ionic liquids in a steam-distillation-like process. *Angew. Chem., Int. Ed.* **2006**, *45*, 7251–7254.

44 Dupont, J.; Scholten, J. D. On the structural and surface properties of transition-metal nanoparticles in ionic liquids. *Chem. Soc. Rev.* **2010**, *39*, 1780–1804.

45 Dupont, J.; Fonseca, G. S.; Umpierre, A. P.; Fichtner, P. F. P.; Teixeira, S. R. Transition-metal nanoparticles in imidazolium ionic liquids: Recycable catalysts for biphasic hydrogenation reactions. *J. Am. Chem. Soc.* **2002**, *124*, 4228–4229.

46 Scheeren, C. W.; Machado, G.; Dupont, J.; Fichtner, P. F. P.; Texeira, S. R. Nanoscale Pt(0) particles prepared in imidazolium room temperature ionic liquids: Synthesis from an organometallic precursor, characterization, and catalytic properties in hydrogenation reactions. *Inorg. Chem.* **2003**, *42*, 4738–4742.

47 Bernardi, F.; Scholten, J. D.; Fecher, G. H.; Dupont, J.; Morais, J. Probing the chemical interaction between iridium nanoparticles and ionic liquid by XPS analysis. *Chem. Phys. Lett.* **2009**, *479*, 113–116.

48 Scariot, M.; Silva, D. O.; Scholten, J. D.; Machado, G.; Teixeira, S. R.; Novak, M. A.; Ebeling, G.; Dupont, J. Cobalt Nanocubes in Ionic Liquids: Synthesis and Properties. *Angew. Chem., Int. Ed.* **2008**, *47*, 9075–9078.

49 Prechtl, M. H. G.; Campbell, P. S.; Scholten, J. D.; Fraser, G. B.; Machado, G.; Santini, C. C.; Dupont, J.; Chauvin, Y. Imidazolium ionic liquids as promoters and stabilising agents for the preparation of metal(0) nanoparticles by reduction and decomposition of organometallic complexes. *Nanoscale* **2010**, *2*, 2601–2606.

50 Scholten, J. D.; Ebeling, G.; Dupont, J. On the involvement of NHC carbenes in catalytic reactions by iridium complexes, nanoparticle and bulk metal dispersed in imidazolium ionic liquids. *Dalton Trans.* **2007**, 5554–5560.

51 Corilo, Y. E.; Abdelnur, P.; Nachtigall, F. M.; Ebeling, G.; Dupont, J.; Eberlin, M. N.: Charge-Tagged N-Heterocyclic Carbenes. *RSC Advances* 2011, DOI: 10.1039/c1ra00024a.

52 Migowski, P.; Machado, G.; Texeira, S. R.; Alves, M. C. M.; Morais, J.; Traverse, A.; Dupont, J. Synthesis and characterization of nickel nanoparticles dispersed in imidazolium ionic liquids. *Phys. Chem. Chem. Phys.* **2007**, *9*, 4814–4821.

53 Gutel, T.; Santini, C. C.; Philippot, K.; Padua, A.; Pelzer, K.; Chaudret, B.; Chauvin, Y.; Basset, J. M. Organized 3D-alkyl imidazolium ionic liquids could be used to control the size of in situ generated ruthenium nanoparticles? *J. Mater. Chem.* **2009**, *19*, 3624–3631.

54 Gutel, T.; Garcia-Anton, J.; Pelzer, K.; Philippot, K.; Santini, C. C.; Chauvin, Y.; Chaudret, B.; Basset, J. M. Influence of the self-organization of ionic liquids on the size of ruthenium nanoparticles: effect of the temperature and stirring. *J. Mater. Chem.* **2007**, *17*, 3290–3292.

55 Fonseca, G. S.; Machado, G.; Teixeira, S. R.; Fecher, G. H.; Morais, J.; Alves, M. C. M.; Dupont, J. Synthesis and characterization of catalytic iridium nanoparticles in imidazolium ionic liquids. *J. Colloid Interface Sci.* **2006**, *301*, 193–204.

56 Fonseca, G. S.; Umpierre, A. P.; Fichtner, P. F. P.; Teixeira, S. R.; Dupont, J. The use of imidazolium ionic liquids for the formation and stabilization of Ir-0 and Rh-0 nanoparticles: Efficient catalysts for the hydrogenation of arenes. *Chem.—Eur. J.* **2003**, *9*, 3263–3269.

57 Redel, E.; Thomann, R.; Janiak, C. First correlation of nanoparticle size-dependent formation with the ionic liquid anion molecular volume. *Inorg. Chem.* **2008**, *47*, 14–16.

58 Migowski, P.; Zanchet, D.; Machado, G.; Gelesky, M. A.; Teixeira, S. R.; Dupont, J. Nanostructures in ionic liquids: correlation of iridium nanoparticles' size and shape with imidazolium salts' structural organization and catalytic properties. *Phys. Chem. Chem. Phys.* **2010**, 12, 6826–6833.

59 Bernardi, F.; Alves, M. C. M.; Scheeren, C. W.; Dupont, J.; Morais, J. In situ studies of nanoparticles under reaction with sulfur by XAS. *J. Electron Spectrosc. Relat. Phenom.* **2007**, *156*, 186–190.

60 Lovelock, K. R. J.; Villar-Garcia, I. J.; Maier, F.; Steinruck, H. P.; Licence, P. Photoelectron Spectroscopy of Ionic Liquid-Based Interfaces. *Chem. Rev.* **2010**, *110*, 5158–5190.

61 Kolbeck, C.; Cremer, T.; Lovelock, K. R. J.; Paape, N.; Schulz, P. S.; Wasserscheid, P.; Maier, F.; Steinruck, H. P. Influence of Different Anions on the Surface Composition of Ionic Liquids Studied Using ARXPS. *J. Phys. Chem. B* **2009**, *113*, 8682–8688.

62 Krischok, S.; Eremtchenko, M.; Himmerlich, M.; Lorenz, P.; Uhlig, J.; Neumann, A.; Ottking, R.; Beenken, W. J. D.; Hofft, O.; Bahr, S.; Kempter, V.; Schaefer, J. A. Temperature-dependent electronic and vibrational structure of the 1-ethyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)amide room-temperature ionic liquid surface: A study with XPS, UPS, MIES, and HREELS. *J. Phys. Chem. B* **2007**, *111*, 4801–4806.

63 Lovelock, K. R. J.; Kolbeck, C.; Cremer, T.; Paape, N.; Schulz, P. S.; Wasserscheid, P.; Maier, F.; Steinruck, H. P. Influence of Different Substituents on the Surface Composition of Ionic Liquids Studied Using ARXPS. *J. Phys. Chem. B* **2009**, *113*, 2854–2864.

64 Caporali, S.; Bardi, U.; Lavacchi, A. X-ray photoelectron spectroscopy and low energy ion scattering studies on 1-buthyl-3-methyl-imidazolium bis(trifluoromethane) sulfonimide. *J. Electron Spectrosc. Relat. Phenom.* **2006**, *151*, 4–8.

65 Gannon, T. J.; Law, G.; Watson, P. R.; Carmichael, A. J.; Seddon, K. R. First observation of molecular composition and orientation at the surface of a room-temperature ionic liquid. *Langmuir* **1999**, *15*, 8429–8434.

66 Rivera-Rubero, S.; Baldelli, S. Surface characterization of 1-butyl-3-methylimidazollum Br^-, I^-, PF_6^-, BF_4^-, $(CF_3SO_2)_2N^-$, SCN^-, $CH_3SO_3^-$, $CH_3SO_4^-$, and $(CN)_2N^-$ ionic liquids by sum frequency generation. *J. Phys. Chem. B* **2006**, *110*, 4756–4765.

67 Santos, C. S.; Baldelli, S. Gas-liquid interface of room-temperature ionic liquids. *Chem. Soc. Rev.* **2010**, *39*, 2136–2145.

68 Okazaki, K. I.; Kiyama, T.; Hirahara, K.; Tanaka, N.; Kuwabata, S.; Torimoto, T. Single-step synthesis of gold-silver alloy nanoparticles in ionic liquids by a sputter deposition technique. *Chem. Commun.* **2008**, 691–693.

69 Torimoto, T.; Okazaki, K.; Kiyama, T.; Hirahara, K.; Tanaka, N.; Kuwabata, S. Sputter deposition onto ionic liquids: Simple and clean synthesis of highly dispersed ultrafine metal nanoparticles. *Appl. Phys. Lett.* **2006**, *89*, 243117.

70 Hatakeyama, Y.; Okamoto, M.; Torimoto, T.; Kuwabata, S.; Nishikawa, K. Small-Angle X-ray Scattering Study of Au Nanoparticles Dispersed in the Ionic Liquids 1-Alkyl-3-methylimidazolium Tetrafluoroborate. *J. Phys. Chem. C* **2009**, *113*, 3917–3922.

71 Bhargava, B. L.; Balasubramanian, S. Layering at an ionic liquid-vapor interface: A molecular dynamics simulation study of [bmim][PF6]. *J. Am. Chem. Soc.* **2006**, *128*, 10073–10078.

72 Aliaga, C.; Santos, C. S.; Baldelli, S. Surface chemistry of room-temperature ionic liquids. *Phys. Chem. Chem. Phys.* **2007**, *9*, 3683–3700.

73 Hofft, O.; Bahr, S.; Himmerlich, M.; Krischok, S.; Schaefer, J. A.; Kempter, V. Electronic structure of the surface of the ionic liquid [EMIM][Tf2N] studied by metastable impact electron spectroscopy (MIES), UPS, and XPS. *Langmuir* **2006**, *22*, 7120–7123.

74 Wender, H.; de Oliveira, L. F.; Migowski, P.; Feil, A. F.; Lissner, E.; Prechtl, M. H. G.; Teixeira, S. R.; Dupont, J. Ionic Liquid Surface Composition Controls the Size of Gold Nanoparticles Prepared by Sputtering Deposition. *J. Phys. Chem. C* **2010**, *114*, 11764–11768.

75 Wender, H.; Migowski, P.; Feil, A. F.; de Oliveira, L. F.; Prechtl, M. H. G.; Leal, R.;Machado, G.; Teixeira, S. R.; Dupont, J. On the formation of anisotropic gold nanoparticles by sputtering onto a nitrile functionalised ionic liquid. *Phys. Chem. Chem. Phys.* **2011**, DOI: 10.1039/C1CP21406C.