Nanoconfined Ionic Liquids: Optically Active Ionogels

Tyler Haddock Literature Seminar December 14, 2017

The first major research center devoted to the study of ionic liquids—the Queen's University Ionic Liquids Laboratories—opened in Belfast in 1999. A year later, NATO invited researchers in the field to the first international meeting devoted to ionic liquids. There were 65 members were in attendance.[1,2] What was then a niche field has now been explored in every division of chemistry for many applications—as recoverable solvents, liquid and solid electrolytes, lubricants, and even optical materials—yielding 1000s of journal articles and patents per year.[3]

Ionic liquids are salts containing bulky organic cations and inorganic or organic anions. The steric hindrance from aromatic rings and long side chains on the cation prevent the ion pair from easily crystallizing, giving them a melting point less than 100 °C.[4] Bulk scale ionic liquids have become popular amongst chemists due to their unique physical and chemical properties, making them candidates for improved solvents, electrolytes, and even catalysts. Ionic liquids can exhibit relatively high conductivity, thermal stability over 400 °C,[5] vapor pressure 13 orders of magnitude less than water in ambient conditions,[6] and the ability to dissolve a wide range of complex substances such as wood chips.[4] The most exciting features of ionic liquids are their mix of complex intermolecular interactions and high tunability (Figure 2). [4,7] Ionic liquid ions can often be exchanged to produce a solvent or electrolyte with the desired properties.

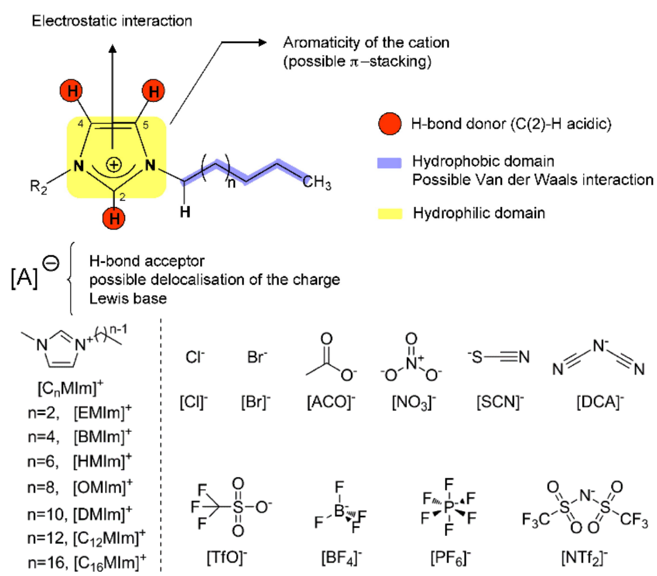

Figure 1. Top: Ionic liquids have complex structures. The cation is often capable of many different intermolecular interactions such as H-bonding, van der Waals, and electrostatic interaction. Bottom: Various ionic liquid cations and anions. Ionic liquid ions can often be exchanged to tune its physical and chemical properties.

The major shortcomings of ionic liquids are their high cost and difficulty in storage and handling. Much attention has thus been given to immobilizing ionic liquids by either covalently grafting monolayers to a substrate or by physically confining them within a porous material.[4] Besides the chemical difficulty in linking the cations to a surface, physically confining ionic liquids has been shown to better preserve—or even enhance—the ionic liquids' properties.

Just about every nanoporous material—notably, carbon nanotubes, metal organic frameworks, zeolites, and aerogels have been explored for nanoconfining ionic liquids.[4] The synthesis and/or confinement of ionic liquids in soft gels such as aerogels, termed *ionogels*, has been used both as an immobilizing method and as an alternative aerogel synthesis. The use of water in standard aerogel synthesis limits the ionic liquids that can be implemented. Ionic liquids are highly sensitive to impurities such as water, which greatly diminish many of their properties.[3] The first non-hydrolytic synthesis of ionogels was performed by Dai et al. to aide in the synthesis of aerogels without requiring the complicated supercritical drying step.[8] They used formic acid, tetramethoxysilane, and ionic liquids as the sol-gel precursors. This opened the door to many candidate ionic liquids in ionogels.

The transparency of many ionic liquids in the visible and IR region has led to interest in producing optically active ionogels. The non-volatile, highly conductive, and possibly shape tuning ionogels could find applications as flexible LEDs or other optical devices. Lanthanide containing ionic liquids such as those based europium(III) β-diketonates have shown strong luminescence from the $^5D_0 \rightarrow {}^7F_2$ at 612 nm in the red.[9] However, the sensitivity of the Eu(III)-based ionic liquid anion to formic acid required a alteration in the non-hydrolytic ionogel procedure. Lunstroot et al. developed a procedure which first involved synthesizing ionogels using typical ionic liquids (non-Eu containing) $[C_6mim][Tf_2N]$, tetramethoxysilane, and formic acid.[10] The ionic liquid was then Soxhlet extracted using acetonitrile. Finally, the gels were then simply dipped in europium(III) complex/$[C_6mim][Tf_2N]$ mixture and the remaining organic solvents were evaporated off.

The resulting ionogels showed high photoluminescence in the $^5D_0 \rightarrow {}^7F_2$ under UV irradiation giving them a bright red glow (Figure 2). The emission spectrum under 360 nm excitation was highly monochromatic, with an exceptional intensity ratio between $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ of 21.6.[11]

The physical properties of the ionogel were largely the same as the pre-Eu-doped gel. The gel was fully transparent and colorless with no cracks.

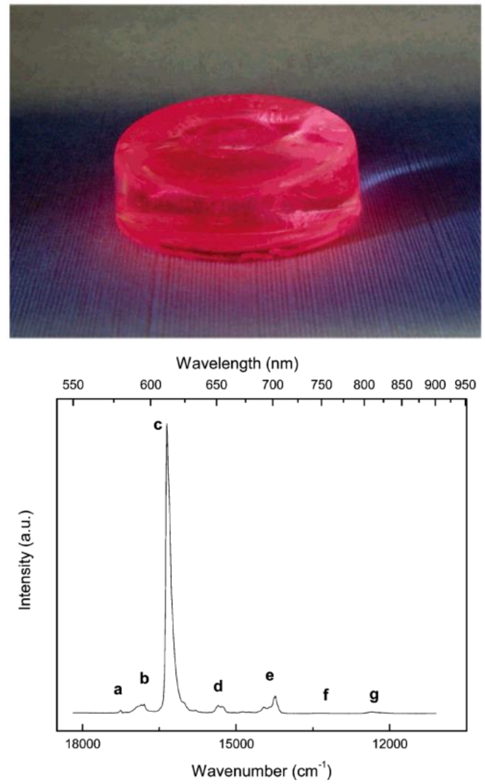

Figure 2. Top: Eu based ionogel under UV irradiation showing bright red photluminscence. Bottom: The strongest peak (c) is due to the $^5D_0 \rightarrow {}^7F_2$ transition in Eu at 612 nm.

Another form of ionogels are those made from doping ionic liquids into polymers. One effect of doping polymers such as poly(methylmethacrylate) PMMA with ionic liquids is added flexibility, as the ionic liquids act as plasticizers.[12]

Wang et al. showed that Ln^{3+} based ionic liquids could be doped into PMMA to produce flexible ionogels.[12] Depending on the lanthanide, these ionogels could be made to photoluminescence in the red and green (Figure 3).

In this method, ionogels were synthesized using no organic solvents, and with the recoverability of the ionic liquids, the ionogel synthesis is relatively environmentally friendly.

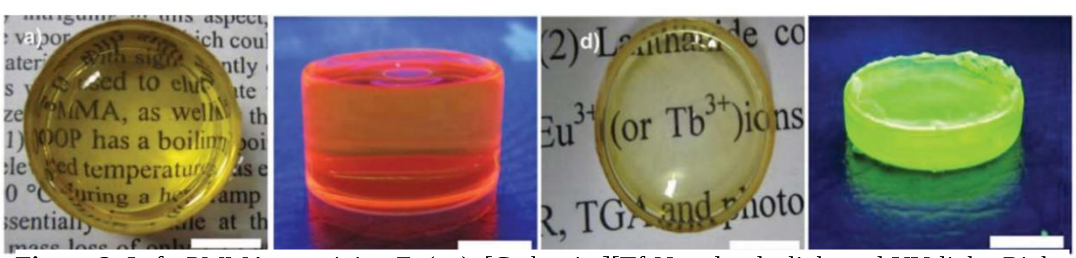

Figure 3. Left: PMMA containing Eu(tta)–[Carb-mim][Tf_2N under daylight and UV-light. Right: PMMA containing Tb(Sal)–[Carb-mim] [Tf_2N]- PMMA under daylight and UV-light.

In summary, the nanoencapsulation of ionic liquids in porous materials allows the remarkable properties of ionic liquids to be used in safe, cost efficient materials. Immobilizing ionic liquids in ionogels has been used successfully as an ionic liquid confining material and as an alternative in aerogel synthesis. The transparency of ionogels has led to studies into their optical properties. Ionogels could find use as flexible LEDs with high shape tuning. The degree of utility with respect to the high electrical conductivity of ionogels should be explored for photoluminescent ionogels.

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