

Hydrophobic Brønsted Acid–Base Ionic Liquids Based on PAMAM Dendrimers with High Proton Conductivity and Blue Photoluminescence

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Room-temperature ionic liquids (ILs) are defined as salts that melt at or below room temperature.^{1–5} There has been a recent resurgence of interest in these novel solvents for various applications in catalysis, analysis, separation, and electrochemistry based on their unique physicochemical properties, such as thermal stabilities, negligible vapor pressures, and relatively high ionic conductivities.^{1,2} ILs can be either aprotic or protic in nature, formed either by transfer of an alkyl (or equivalent) group, usually through S_N2 reaction, or by proton transfer between Brønsted acids and bases. Aprotic ILs have been most widely studied as highly conductive media with wide electrochemical potential windows (~ 3.5 – 5.5 V) for a range of electrochemical applications and as solvents for catalysis. More recently, interest in the development of protic ILs has considerably increased because of the great potential offered by ILs for proton-transfer applications in advanced fuel-cell technologies.^{6–8} In particular, many systems showing low melting points (T_m) well below 100 °C and high ionic conductivities of over 10^{-2} S cm^{-1} at 130 °C have been developed based on proton-transfer reactions between a wide variety of tertiary amines and acids. Herein, we describe a simple strategy toward a novel class of macromolecular ILs whose Brønsted base component consists of a dendrimeric (polycation) unit. This new strategy for the synthesis of protonic ILs has resulted in a new series of highly promising low-temperature molten ILs that are air stable, hydrophobic, and highly proton conductive.

The dendrimer system used here to demonstrate the basic principle is based on the polyamidoamine (PAMAM) dendrimer, which is miscible with water. PAMAM dendrimers have drawn considerable interest in recent years due to their potential applications in medicine, nanotechnology, and catalysis, among other areas.^{9–13} These macromolecules can, for example, incorporate transition-metal ions via complexation reactions. The transformation of such dendrimer-immobilized ions to the corresponding metal nanoparticles has been demonstrated.¹¹ The resulting nanoparticle-decorated dendrimer system exhibits a variety of novel properties when employed in homogeneous catalysis.^{12,13} Functionalized or modified PAMAMs can also be immobilized on solid supports and employed as “heterogenized” homogeneous catalysts.^{14,15} In this communication, we chose a PAMAM dendrimer as the source of proton-affinity bases for the formation of Brønsted acid–base ILs. It is well-known that PAMAM dendrimers are monodisperse, hyperbranched polymers possessing a very high concentration of primary and tertiary amine groups, which can be readily protonated to form cationic centers. Additionally, because of the high surface charge density in higher generation PAMAM dendrimers,¹⁶ we expected that favorable electrostatics would also contribute to higher proton conductivities.

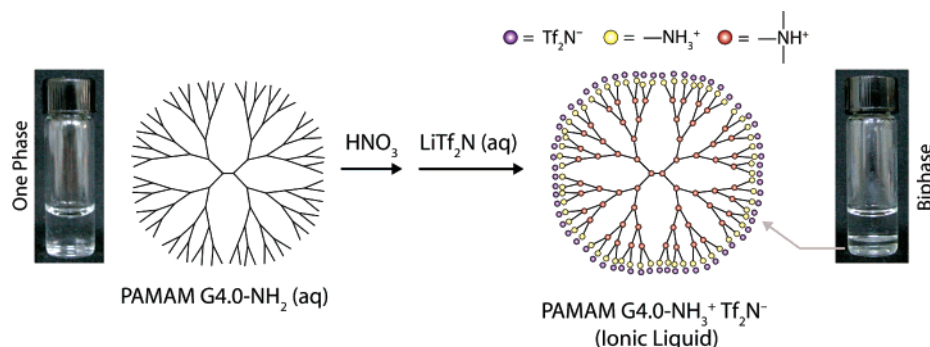
The essence of our methodology for the formation of the dendrimer cations of ILs is through simple acid–base chemistry of the neutral amine (free and tertiary) groups on a dendrimer with a Brønsted acid, followed by a metathesis reaction of the resulting aqueous electrolyte solution with an anion donor. We chose lithium bis(trifluoromethane sulfonyl)imide ($LiTf_2N$) as a candidate for anion exchange because Tf_2N^- anions have high thermal stabilities and weakly coordinating properties, which are crucial to the generation of hydrophobic ILs with low viscosity. The synthetic protocol is summarized in Scheme 1. The specific dendrimer used here for demonstration of our basic approach is an amine-terminated fourth-generation (G) PAMAM dendrimer (PAMAM G4.0-NH₂, 10%, Aldrich). Protonated PAMAM G4.0-NH₃⁺ NO₃[−] was obtained via a neutralization reaction with nitric acid (15.8 M, Aldrich) in aqueous solution. The corresponding IL was synthesized by the metathesis reaction of PAMAM G4.0-NH₃⁺ NO₃[−] and $LiTf_2N$ (99.99%, Aldrich) in aqueous solution. A milky white suspension was initially produced. The resulting cloudy solution subsequently became clear after stirring for 30 min. When the molar ratio of H⁺ to PAMAM G4.0-NH₂ was higher than ~ 190 , a biphasic solution system was obtained, indicating the formation of a hydrophobic IL. The dense (lower) phase contained the hydrophobic IL PAMAM G4.0-NH₃⁺ Tf_2N^- . The IL layer was washed exhaustively with distilled–deionized water to remove $LiNO_3$ residues. The subsequent removal of water and methanol residues by rotary evaporation produced the desired ionic liquid as a colorless liquid with a very low liquidus temperature ($T_m \approx -2.5$ °C). We tentatively attribute this to the flexible nature of the dendritic backbone.

The conductivity of PAMAM G4.0-NH₃⁺ Tf_2N^- was determined to be 2.21 mS cm^{-1} at 24 °C. The high conductivity of the as-produced liquid confirms the formation of the IL. The structure of the IL was also confirmed using ¹H and ¹³C NMR and IR spectroscopy (see Supporting Information). Both the FT-IR and NMR spectra of this IL are consistent with the structure composed of PAMAM G4.0-NH₃⁺ and Tf_2N^- .^{17,18} The hydrophobicity of this IL can be understood from its molecular structure (Scheme 1). The hydrophilicity of PAMAM G4.0-NH₃⁺ is significantly reduced by the spontaneous electrostatic assembly of Tf_2N^- onto the surface ammonium groups and protonated tertiary amine groups within its interior via Coulombic interactions. The periphery is essentially “coated” with Tf_2N^- moieties, resulting in a surface hydrophobic IL dendrimer.

Thermal gravimetric analysis (TGA) results under nitrogen showed an unexpected increase in the thermal stability of PAMAM G4.0-NH₃⁺ incorporated into an IL (see Supporting Information). It is known that weight loss for PAMAM G4.0-NH₂ resulting from thermal degradation starts around 120 °C.¹⁹ However, the decomposition temperature of PAMAM G4.0-NH₃⁺ under nitrogen increased to as high as 250 °C. The onset for Tf_2N^- decomposition begins near 350 °C. Apparently, the formation of surface ammonium

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Scheme 1. One-Pot Formation of PAMAM G4.0-NH₃⁺ Tf₂N⁻ Ionic Liquid

and protonated tertiary amines offers some measure of protection for the PAMAM dendrimer against thermal oxidation.¹⁹ In fact, the PAMAM G4.0-NH₃⁺ to Tf₂N⁻ mole ratio of 127 estimated from the TGA results for the IL accords remarkably well with the fact that there are 126 total nitrogen ligands in PAMAM G4.0-NH₂ available for protonation. That is, for PAMAM dendrimers, there are 2^{G+2} primary amino groups and 2^{G+2}-2 tertiary amines (i.e., 64 and 62, respectively, for G = 4.0). Clearly, this observation suggests quantitative anion exchange. Further, Angell and co-workers have recently observed a simple relation between the limit set by the boiling point for ILs of this type and the aqueous pK_a of the acid and base constituents.⁶ Given that ΔpK_a ≈ 20 here, the boiling point elevation is likely so high that mass loss by Tf₂NH vaporization will likely be preempted by decomposition.

Wang et al. have reported that the protonated PAMAM G4.0-NH₂ has a high quantum yield of blue photoluminescence.²⁰ Therefore, similarly strong blue photoemission is not unexpected for the PAMAM G4.0-NH₃⁺ Tf₂N⁻. Figure 1a shows both excitation and emission spectra of the PAMAM G4.0-NH₃⁺ Tf₂N⁻ IL. The strong blue photoluminescence near 436 nm is consistent with the above conjecture. A methanolic solution of PAMAM G4.0-NH₂ (Figure 1b) and PAMAM G4.0-NH₃⁺ NO₃⁻ (not shown) both exhibit, however, relatively weak fluorescent signals. In fact, the phase separation between the aqueous and IL phases can be readily visualized through the photoluminescence of PAMAM G4.0-NH₃⁺ Tf₂N⁻, as shown in Figure 1 (inset a).

In summary, we have described a simple and general strategy for preparing a range of novel hydrophobic Brønsted acidic ILs based on PAMAM-type dendrimers and, in principle, other

polyamines, as well. The resulting ILs exhibit strong photoluminescence and proton conductivity with several potential applications in sensor design and nonaqueous proton-conducting electrolytes. Such ILs may be especially well suited for the encapsulation of nanoparticle precursors in catalysis or use as task-specific ILs in metal ion or gas separations.

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Note Added after ASAP Publication. There was an error in the name of the funding organization for this work in the version published on the Internet August 27, 2005. The version published August 30, 2005, is correct.

Supporting Information Available: FT-IR spectra, ¹H and ¹³C NMR spectra, and TGA curves. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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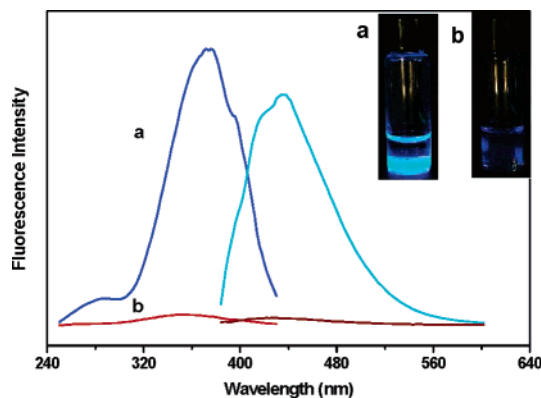


Figure 1. Excitation and emission photoluminescence spectra of (a) PAMAM G4.0-NH₃⁺ Tf₂N⁻ ionic liquid compared with (b) 10 vol % PAMAM G4.0-NH₂ in methanol. Inset: The corresponding samples under UV illumination.