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**Independent tuning of acidity and ionicity in protic ionic liquids and their polymers. Comparing Li<sup>+</sup> to H<sup>+</sup> transport**

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Protic ionic liquids (PILs) form an interesting and versatile subclass of the low temperature ionic liquid field, the exponential expansion of which, in recent times, is well known. PILs are formed by transfer of protons from a Brønsted acid to a Brønsted base, and their properties depend strongly on the free energy change accompanying the transfer (the proton “energy gap”).<sup>1</sup> An energy level diagram from which this gap can be predicted for different acid base combinations has been derived from aqueous pKa data,<sup>2</sup> and recently shown to be almost quantitative, by direct electrochemical interrogation of a range of PILs.<sup>3</sup> Because of the wide variations in possible proton gaps, the “ionicity” of the PIL subclass is highly variable. Furthermore, (a) although a “pH” cannot be defined in the absence of H<sub>2</sub>O solvent, the equivalent “activity” of the proton can be assessed approximately from the above energy diagram, as the mean of acid and base levels, and can be quantified by such metrics as the N-<sup>1</sup>H chemical shift<sup>4</sup> for the transferred proton, or the corresponding N-H infrared vibration frequency<sup>5</sup>: and (b) the PILs can be obtained in polymeric form by having either the base or the acid pendant from a polymer backbone and then protonating or deprotonating the polymer with an appropriate acid or base moiety. We show how, by tuning the proton gap, we can induce different degrees of decoupling of the proton mobility from the backbone (or the neutralizing moiety) to obtain “dry” proton conductors. We contrast the mobility of protons obtained in this way with the mobility of Li<sup>+</sup> ions in fast-ion conducting polymers and glasses.

<sup>1</sup>Belieres, J.-P.; Angell, C. A., . *J. Phys. Chem. B* **2007**, 111, 4926 -4937.

<sup>2</sup>Ibid.

<sup>3</sup>Bautista-Martinez, J. A.; Tangi, L.; Belieres, J.-P.; Zeller, R.; Angell, C. A., *J. Phys. Chem. B* **2009**, 113, 12586-12593.

<sup>4</sup>Shuppert, J. W.; Angell, C. A., C. A. Angell and J. W. Shuppert, *J. Phys. Chem.*, 84, 538 (1980). *J. Phys. Chem.* **1980**, 84, 538.

<sup>5</sup>Stoyanov, E. S.; Kim, K.-C.; Reed, C. A., *J. Amer. Chem. Soc.* **2006**, 128, 8500