Enabling high proton conductivity in a fluorine-free protic ionic liquid through rational design of its constituents

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In the field of energy-related applications, protic ionic liquids (PILs) have attracted growing interest for their electrochemical properties and their viable preparation procedures.[1] In particular, high proton conductivity is crucial for applications such as proton exchange membranes in fuel cells. With the aim of achieving fast proton transfer through an intrinsic mechanism, we designed a novel PIL, namely *N*,*N*-diethyl-3-sulfopropan-1-ammonium hydrogen methanedisulfonate [DESPA][HMDS] (Figure 1), which is characterized by the presence of sulfonic acid moieties, of almost equivalent proton affinity, both in the anion and cation structure.[2] The electrochemical properties of [DESPA]HMDS] revealed a superionic behaviour at high temperature, as indicated by a positive deviation in the Walden plot, and by a inverse Haven ratio up to 1.55. Diffusional NMR studies revealed an unprecedented two- to three-fold increase in the mobility of the exchangeable proton, compared to that of the molecular species, again at high temperature (> 373 K). These results point towards the presence of a non-vehicular proton transport mechanism. Notably, while the best performing PILs present in the literature are often based on fluorinated or perfluorinated compounds,[3,4] [DESPA][HMDS] was designed to be fluorine-free, since perfluoroalkyl substances (PFASs) constitute a recognized concern for health and the environment, and might be subject to a ban in the European Union over the coming years.[5]

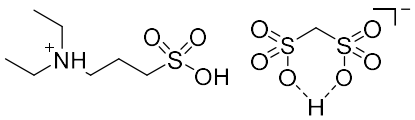

Figure 1: Molecular structure of [DESPA][HMDS].

Keywords: *protic ionic liquid, superionicity, diffusional NMR, fluorine-free*

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