Supporting Information

Electron solvation dynamics and reactivity in ionic liquids observed by picosecond radiolysis techniques

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Synthesis and characterization of the ionic liquids

$N$-methylpyrrolidine (97%), 1-bromobutane (99%), and lithium bis(trifluoromethylsulfonfonyl)-imide (99.95%) were purchased from Aldrich and used as received. MP Alumina N – Super I was purchased from MP Biomedicals Germany GmbH. All solvents were of AR grade or higher.

The bromide salts of the ionic liquids were synthesized employing two different approaches – the “classical” wet chemistry method and a novel microwave reactor synthesis. $^1$H and $^{13}$C n.m.r. spectra of the products from both the microwave and classical synthesis were consistent with those reported in literature.¹

The classical synthesis of the pyrrolidinium bromide salts was adapted from published procedures.¹,² Briefly, $N$-methylpyrrolidine was reacted with a slight excess of bromobutane in acetonitrile for 24 hours at 50 °C under an inert atmosphere. Following removal of the solvent and excess volatile starting material, the ionic liquid was redissolved in a small amount of acetonitrile then washed with ethyl acetate, stirred with activated charcoal overnight and passed through an activated alumina column.

$I$-methyl-$1$-butyl-pyrrolidinium bromide ($P_{14}Br$), microwave synthesis

$N$-methylpyrrolidine (15.8 g, 0.180 mol) and 1-bromobutane (25.4 g, 0.184 mol) were dissolved in acetonitrile (15 mL). The solution was placed in the microwave reactor and the synthesis was performed at 45 °C for 6 minutes following a ramping time of 2 minutes. The total power was limited to 40 W. The reaction mixture was cooled to 5 °C and left in a refrigerator overnight during which time white crystals of the product formed. Cold ethyl acetate (~10 mL) was added and the product was separated by filtration and washed several times with ethyl acetate. The crystals were dried in a vacuum desiccator and recrystallized from acetonitrile. The product was dried in a vacuum oven at 40 °C for least 3 days to yield 38.4 g (96 %) of white crystals.

Conversion of the pyrrolidinium halides to bis(trifluoromethylsulfonfonyl)imide salts were performed using equimolar quantities of the halide salt and LiNTf$_2$ in aqueous solution according to published procedures.¹,² The aqueous layer was removed and the liquid was washed with aliquots of water until no halide was detectable in the washings (silver acetate test). The pyrrolidinium NTf$_2$ ionic liquids were further purified by stirring with activated charcoal overnight then passing through an activated alumina column. Ionic liquids containing the bis(trifluoromethylsulfonfonyl)imide anion are known to be hydrophobic. However, trace impurities of water in the liquids can dramatically lower the viscosity of the liquids. All ionic liquids used were dried at reduced pressure at 45 °C for at least 24 hours prior to characterization. The typical water content for 1-methyl-1-butyl-pyrrolidinium bis(trifluoromethylsulfonfonyl)imide was below 20 ppm.
Figure 1S. Time-resolved pulse-probe pulse radiolysis transient absorption traces at 800 and 900 nm for neat [C₄mim][NTf₂] showing the mutual fidelity of the pulse-probe and OFSS detection methods. The pulse-probe data at 800 nm and 900 nm are the average of three and two runs, respectively, totaling 143 and 107 shots/point, respectively. The OFSS data at 800 nm and 900 nm are the average of 36 and 32 shots, respectively. The OFSS data were arbitrarily scaled to overlap the pulse-probe data, however the original OFSS absorbance signal levels are within 5% of the pulse-probe ones. (This is a coincidence - the optical configurations and accelerator performance parameters on the days in question are different.)
Figure 2S. Time-resolved pulse-probe pulse radiolysis transient absorption traces for neat [C₄mim][NTf₂] under argon atmosphere over the full time scale recorded.

Figure 3S. Original pulse-probe absorbance vs. time traces and traces reconstructed from the SVD analysis using only the two largest singular values. The reconstructed traces are the smoother ones. There is good agreement except for 700 and 800 nm at early times.
Figure 4S. Spectral correlation function for the solvation of excess electrons in [C₄mpyr][NTf₂] constructed in the same manner as typically used for fluorescence Stokes shifts. a) Fitting spectra to time slices constructed from the kinetics data. b) Peak energies of the fitted spectra as a function of time and a biexponential fit to the correlation function. c) Same as b) but plotted against log time.
Figure 5S. Comparison of the kinetics of the electron solvation process (black line), electron quenching at 800 nm by 162 mM DQ and 281 mM (supersaturated) DQ (red line), and the raw pulse-probe absorbance data taken at 1600 nm in neat [C₄mpyr][NTf₂] showing that the scavenging decay process coincides with the solvation process.

References