Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting information:

Fluorescence Correlation Spectroscopy Evidence for Structural Heterogeneity in Ionic Liquids

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Experimental section:

The FCS microscope has been described previously.[1] Briefly, the experiment was performed on a Nikon TE2000 inverted microscope operating in epi-illumination mode using the 514.5-nm line from an argon-ion laser as the excitation source. The laser entered the microscope through the back port after spatial filtering and was directed into a high numerical aperture oil immersion objective (Nikon 100×, 1.3 NA) by a dichroic mirror. The objective focused the beam to a diffraction-limited spot. Fluorescence from the sample was collected by the same objective and was directed into either a CCD camera (MicroMax, Roper Scientific) for imaging or a high-efficiency avalanche photodiode (APD) for single photon counting and subsequent calculation of the correlation spectra by a correlator card (ALV-6010, ALV-Laser). Since FCS is based on fluctuations in the total fluorescence intensity, it is essential that background fluorescence be minimized. An interference bandpass filter centered at 580 with a 25 nm bandwidth was used to reduce background fluorescence. A 20× microscope objective (Newport) focused the

fluorescence light into a 62.5-μm diameter multimode optical fiber, which was used in place of a pinhole to effectively reject out-of-focus background fluorescence.

Rhodamine 6G was purchased from Sigma-Aldrich and used as received. To prepare a given sample of Rhodamine 6G in $[C_nMPy][Tf_2N]$ for FCS analysis, a small volume of 5×10^{-6} M ethanolic R6G stock solution was micropipetted into an appropriate volume of $[C_nMPy][Tf_2N]$ to obtain a 10^{-7} M R6G concentration. The resulting solution was pumped under vacuum overnight, and the solution subsequently diluted with the corresponding RTIL to achieve a R6G concentration of $2.5–5 \times 10^{-9}$ M. The solution was then transferred into a sample cuvette constructed by attaching a 0.65 ml thin-walled polypropylene PCR tube with cover (Sorenson Bioscience, Inc.) to a quartz coverslip (Quartz Plus, Inc., 25 × 25 × 0.16 mm) using 5-minute epoxy (Devcon).

Spectroscopy-grade RTILs were synthesized following modifications of a reported procedure.[2] In short, in order to reduce background sufficiently to allow few-molecule spectroscopic studies, it is absolutely essential that all starting heterocycles and alkylhalides be doubly- or triply-distilled. It is also not uncommon for the halide salts to require multiple recrystallizations; FCS-amenable RTILs frequently necessitate repeating this step four or more times. Traces of color and autoluminescence are removed with these steps, however, no discernable differences have been noted in the $^{1}H/^{13}C$ NMR spectra, pointing to the low levels of chromophore/luminophore contamination that obviate FCS studies in conventionally-prepared RTILs. And finally, there are a number of other factors that should be paid close attention, including use of inert atmospheres, careful control of temperature, and protection from light. Even following these stringent preparation routes, one must analyze the RTIL for suitability for FCS on a case-by-case basis.

Full details and procedures will be reported elsewhere (Baker, G. A.; Mahurin, S. M., in preparation.).

References

(1) Mahurin, S. M.; Dai, S.; Barnes, M. D., *J. Phys. Chem. B* **2003,** 107, 13336.
(2) Burrell, A. K.; Del, S. R. E.; Baker, S. N.; McCleskey, T. M.; Baker, G. A., *Green Chem.* **2007,** 9, 449.