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Hui Jin, Xiang Li, and Mark Maroncelli*: Heterogeneous Solute Dynamics in Room-Temperature Ionic Liquids

Pages 13473–13478. In ref 1, we reported marked changes to the steady-state emission spectrum of crystal violet lactone (CVL) in the ionic liquid *N*-propyl-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [Pr₃₁][Tf₂N], as a function of excitation wavelength. These results were offered as an example of the effect of dynamic heterogeneity on photophysical processes in ionic liquids. We have recently measured the spectra of CVL in a number of ionic liquids including two new samples of [Pr₃₁][Tf₂N], and we do not find changes of the magnitude reported in Figure 4 of ref 1 in any of these samples. Santhosh and Samanta² also just reported observing no excitation dependence of CVL emission in the ionic liquid 1-butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide. From these observations, we conclude that the spectra in ref 1 were the erroneous, probably as the result of impurity fluorescence which was not adequately subtracted from the relatively weak fluorescence of CVL. In [Pr₃₁][Tf₂N] and the other ionic liquids that we have studied, the ratio of the LE/CT band intensities does sometimes appear to vary systematically with excitation wavelength, but these variations are only at the level of 10–20% and are comparable to the estimated uncertainties in the area ratios. Thus, despite the fact that simulations³ predict that the rate of the LE → CT reaction of CVL in [Pr₃₁][Tf₂N] should indeed be sensitive to excitation wavelength, steady-state spectra provide only marginal evidence for this sensitivity. Better evidence for this type of effect on dual fluorescent molecules has very recently been reported for the charge transfer reaction of *p*-dimethylaminobenzonitrile⁴ and the tautomerization of diethylaminoxyflavone⁵ in ionic liquids.

References and Notes

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