Reply to Comment on "Magnetic Field Effects on Exciplex Luminescence in Water−Tetrahydrofuran and Water−Dioxane Mixtures"

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We thank Dr. Petrov[1] for pointing out an error in our MFE^{max} data[2] in benzene/dimethyl sulfoxide (DMSO) solvent mixtures. We have repeated some of our experiments and been able to trace the source of discrepancy in data, which, we believe, arose from incomplete drying of solvents. In our earlier publications[3] we reported the MFE^{max} for the pyrene−DMA system in THF/DMF solvent mixtures as 9%. This was also confirmed by Petrov et al.[4] We have now dried THF by keeping it on solid KOH overnight, refluxing, and distilling it with sodium and benzophenone, and dimethylformamide (DMF) by distilling it with CaH_2 under reduced pressure. The MFE^{max} in THF/DMF solvent mixture has now shot up to 13.5%. Similarly, if we dry DMSO and benzene by distillation with CaH_2 (the former under reduced pressure), we get the MFE^{max}, measured by direct method as well as by our phase-sensitive detection technique, as 17%, a value close to that obtained by Petrov.[4] The net consequence of this upward correction of data in both solvents is that the ratio of MFE^{max} in dry benzene/DMSO and dry THF/DMF is only 1.3 as against 2.0 claimed by Petrov.[4]

We would like to reiterate that the main focus of our paper[2] was not the correction of *data* of Petrov et al., but that the (MFE)^{max} in water/THF or water/dioxane mixtures does not follow the microdomain model proposed by them. In this Comment[1] Petrov ascribes this to strong hydrophobicity of pyrene and consequent insolubility in water. To answer this point, we have replaced pyrene by pyrenebutyric acid as well as by anthracene-9-carboxylic acid. In both cases we found the (MFE)^{max} to be distinctly lower in THF/water mixture compared to that in the benzene/DMSO mixture, in spite of the polarity difference being larger in the former case. Also, the absolute value of (MFE)$^{max}_{water/THF}$ is lower for pyrenebutyric acid−DMA compared to that for pyrene−DMA, in spite of the fact that the former has more solubility in water. This is not consistent with the explanation offered by Petrov for our results in THF/water medium. The explanation needs to be searched elsewhere.

We feel that it is not fair to compare MFE of mixed solvents with that of neat solvents, for MFE is a strong function of the dielectric constant which cannot be varied in the latter case. What is pertinent, therefore, is a comparison of various mixed solvents as a function of polarity difference between the two components. In this regard, the cause of reversal of expected (from the Petrov model) relative values of (MFE)$^{max}_{Py-DMA}$ for following pairs of solvent mixtures—benzene/DMSO[4] and toluene/DMSO;[1] dioxane/water[2] and THF/water;[2] acetone (neat)[2] and butanol/water[2] or chloroform/DMSO[2]—needs to be investigated.

References and Notes

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(4) (a) Petrov, N. Kh.; Borisenko, V. N.; Starostin, A. V.; Alfimov, M. V. *J. Phys. Chem.* **1992**, *96*, 2901. (b) Petrov, N. Kh.; Borisenko, V. N.; Alfimov, M. V. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 109.

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