Reply to Comment on "On the Evidence Obtained by Exciting 7-Azaindole at 320 nm in 10^{-2} M Solutions"

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I believe the Comment by Chou et al.[1] originated from the misuse of additional evidence found in our work[2] (viz. that provided by the fluorescence excitation spectra) to support the presence of more than one type of 7AI aggregate in solutions as highly concentrated as 2×10^{-2} M in hydrocarbon solvents. They ended their comment by saying that "We thus conclude that the existence of various 7AI aggregates in hydrocarbon solvents, at least, could not be inferred from the excitation spectra shown in" the original paper. This reply is intended to show that this conclusion is unwarranted and that the presence of various aggregates can indeed also be inferred from the excitation spectra reported in ref 2.

In our paper,[2] we supported the presence of more than one type of aggregate contributing to the emission centered at 480 nm in the spectra for 7AI in 2×10^{-2} M solutions in hydrocarbon solvents on the basis of the following facts:

(a) The room-temperature (rt) absorption spectra for 2×10^{-2} M solutions of 7AI in hydrocarbon solvents have their onset at ca. 335 nm (see Figures 2 and 3 in ref 2). On the other hand, the 0−0 component of the $S_0 \rightarrow S_1$ transition in the C_{2h} dimer of 7AI lies at 315 nm, with its onset at 320 nm.

(b) As the operating temperature is lowered, the absorption spectrum for the previous solution reveals that the optically active aggregate above 320 nm is reconverted into the more stable C_{2h} dimer (Figure 4 in ref 2).

(c) If excitation is done in the 330 nm region, then the room temperature spectrum for the solution continues to have its emission centered at 480 nm (Figure 5 in ref 2).

(d) The excitation spectra obtained along the emission region centered at 480 nm do not allow one to discriminate between the two species involved (Figure 6 in ref 2). More important, the onset of these excitations lies in the 330−340 nm region, which is consistent with (a) above (see Figure 6 in ref 2).

In addition, our fluorescence excitation spectra were obtained primarily with a view to identifying their onset and, secondarily, to attempt the discrimination of various species. This is clearly asserted in the Abstract, which states: "The corresponding fluorescence excitation spectra confirm that the onset of the excitation lies between 335 and 340 nm". Also, under the heading "On the emission of a 2×10^{-2} M solution of 7AI excited at its red edge", we stated that "Figure 6 shows the fluorescence excitation spectra normalized at the maximum by recording light along the emission band peaking at 480 nm (specifically, it shows the spectra obtained by monitoring light at 440, 480, 520, and 540 nm). Note that these spectra are virtually superimposable and that their onsets lie between 335 and 340 nm". Clearly, the arguments of Chou et al. revolving around the overall shape of the excitation spectrum are misfocused.

In contrast to the conventional situation,[1] the arrangement used in our work to obtain the excitation spectra for this type of solution involved a 90° angle, i.e., the same experimental arrangement and sample were used for excitation and emission,[3] as stated in a previous paper[4] where the corresponding spectra were for the first time used to characterize a 10^{-4} M solution of 7AI in 2-methylbutane. It is widely accepted[5] that the intensity absorbed (I_a) at the point where the sample emission is detected and the excitation intensity (I_0) are only linearly related if the absorbance of the sample (A) is kept below 0.05 (where the relation, $I_a = 2.303 I_0 A$, is quite acceptable). For these reasons, we assumed that, for 7AI solutions at concentrations above 10^{-4} M[2,4] and despite the optical arrangements and sample used in these experiments, the distortion in the excitation spectrum also increases with increasing absorbance. In fact, we should note that even the excitation spectrum obtained by Chou et al. using a 0.01 path length and denoted by circles in their figure fails to accurately reproduce the absorption maximum (see the absorption spectrum of Figure 1a in ref 2).

However, for a given concentration and arrangement of these samples, the distortion in the excitation spectrum will not depend on the specific emission wavelength that is monitored; it is thus acceptable to normalize the excitation spectra recorded along the first absorption band in order to identify the contribution of different aggregates, for example. Likewise, the normalization would make no sense if the concentrated samples differed in their concentration or if a different path length were used with each (see figure in the comment by Chou et al.[6]).

The previous reasoning does not preclude the use of excitation spectra if the aim is to identify the onsets of the excitation spectra, which, by definition, will correspond to the absorbances where the absorbed intensity and the sample absorbance are linearly related, with no distortions. Therefore, if the onset for a 2×10^{-4} M 7AI solution in 3-methylpentane lies at 335−340 nm (see Figure 6 in ref 2) and that for a 10^{-4} M solution is at 320 nm (see Figure 8 in ref 2), then a clustered species other than the normal species (C_{2h}) must be present in the 2×10^{-2} M solution.

Based on the foregoing, the reasoning of Chou et al. revolving around the overall envelope of the excitation spectra warrants no alteration of the conclusions drawn in our paper.[2]

References and Notes

(1) Chou, P. T.; Cheng, Y. M.; Yu, W. S.; Pu, S. C. *J. Phys. Chem. A* **2003**, *107*, 5640.

(2) Catalán, J. *J. Phys. Chem. A* **2002**, *106*, 6738.

(3) This approach avoids potential optical artifacts resulting from changes in the assembly of such thin samples (1−0.01 mm) as those used by Chou et al.[2]

(4) Catalán, J.; Kasha, M. *J. Phys. Chem. A* **2000**, *104*, 10821.

(5) Skoog, D. A.; Hollar, F. J.; Nieman, T. A. In *Principles of Instrumental Analysis*, 5th ed.; Saunders Publishing Co.: London, 1992; Chapter 5.

(6) If, as stated by these authors, one can assume these solutions to cause no distortion, in the excitation spectra, at wavelengths in the region of 320 nm, then one might think that, to compare the spectra obtained at 1 mm [curve a, squares] and 0.01 mm [curve c, circles], one would need to use the same number of excited molecules (i.e., by multiplying curve c by a factor of nearly 100). If one makes such calculations, curve c initially follows curve a but eventually surpasses it in the region of 320 nm.

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