

Reply to Comment on "An Interesting Case where Water Behaves as a Unique Solvent. 4-Aminophthalimide Emission Profile to Monitor Aqueous Environment"

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Reply to Comments on

**An Interesting Case where Water Behaves as a Unique Solvent. 4-Aminophthalimide
Emission Profile to Monitor Aqueous Environment.**

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† Dedicated to the memory of Prof. Dr. Elsa Abuin who deceased on April 18, 2012

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3 In a recent paper¹ the behavior of 4-aminophthalimide (4-AP), a common molecular
4 probe utilized in solvation dynamics experiments, was revisited in polar aprotic and protic
5 solvents using absorption, steady-state and time-resolved fluorescence (*TRES*) techniques.
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7 Also, the deuterium isotope effect was investigated using D₂O as solvent.
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11 We found that, in accordance with literature, the absorption spectra of 4-AP consist of
12 two absorption bands with maxima around 300 nm (B2 band) and 370 nm (B1 band)
13 depending on the solvents properties, while the emission feature is a single band that also
14 shows solvatochromism. We showed that in all solvents investigated (*excluding water*) the 4-
15 AP photophysics is similar with the emission spectra (*steady-state experiments*) being
16 independent on the excitation wavelength used. However, in water the behavior is unique and
17 the emission spectra maxima are different depending on the excitation wavelength used. The
18 emission maximum wavelength is 561.7 nm upon excitation on the B₂ band ($\lambda_{\text{excB2}} = 303.4$
19 nm). When the excitation wavelength used correspond to B1 band ($\lambda_{\text{excB1}} = 370.0$ nm) the
20 emission maximum wavelength shifts to 545.7 nm.
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23 To obtain insights on those peculiar results we performed time-resolved fluorescence
24 (TRES)² measurements on 4-AP dissolved in different organic solvents and water,
25 monitoring not only at different emission wavelengths but also exciting at different
26 wavelengths. We showed that, while the 4-AP emission decay in water exhibits no emission
27 wavelength dependence at λ_{excB2} , when λ_{excB1} is used it was found time-dependent emission
28 spectra which shift to the blue with time. In order to explain the 4-AP behavior, we proposed
29 a mechanism that tries to account for the steady-state and the time-resolved results in all
30 organic solvents and water. Since our results show that the solvent-mediated proton transfer
31 process display a fundamental role in the 4-AP emission profile and, for the first time the
32 proposed a mechanism explain the 4-AP behavior in every media. The deuterium isotope
33 effect confirms the importance of the proton-transfer process in water, being dramatically
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retarded in deuterated water. No emission maxima dependence neither with the excitation wavelength nor with time was found.

Samanta et al. have written a comment on our work where they have criticized our results and the mechanism used to explain them. In the comment they showed a Figure where the 4-AP emission spectra position (*steady-state experiment*) do not depend on the excitation wavelength used. Unfortunately, the plots in the Figure are normalized and lot of valuable information is lost. We present Figures 1 A-C that show the 4-AP emission maxima dependence with the excitation wavelength that we have obtained for: [4-AP] = 6×10^{-5} M (Sigma or Across Organics 97%) as received, purified by double sublimation and, for [4-AP] = 1×10^{-4} M, respectively. As it can be seen we found again a clear dependence of the 4-AP emission maxima with the excitation wavelength at the red-edge of the B₁ band even at different dye concentration. Samanta et al. suggested that probably we have an instrument problem (bad calibrated or bad fluorescence correction file) that causes artifact in our data. It is known that when instrument has those kinds of problems, all the samples show artifact. Our work¹ clearly shows that in all the organic solvents used (except water), the emission feature is the expected: there is no excitation wavelength dependence on 4-AP emission spectra at both absorption B₁ and B₂ bands. Thus, those results discard the possibility of artifacts from the instruments. Other possibility that has not been taken into account for Samantha et al. and can be the cause of the differences observed between both groups, is the way that 4-AP is introduced in water to prepare the solution. This is not trivial when diluted solutions are prepared using molecular probes with low solubility. The way that our water solution was prepared was described in detail in the work.¹ Also, special care has to be taken when 4-AP is purified crystallizing it from ethanol. It is hard to completely eliminate the solvent since it tends to be occluded in 4-AP structure. To avoid that, we purified 4-AP by double sublimation.

Samanta et al also argued that we have not tried to compare our emission data with those reported in the literature for fixed excitation wavelengths. We want to highlight that in most of the works in the literature it is extremely difficult to find spectroscopic data like excitation wavelengths used or 4-AP emission maxima values. In the majority of the cases they have to be supposed (by reading the work) or estimated from Figures in the paper. Nevertheless, in our work there is a detailed discussion of different works.¹ Samanta et al. pointed out the data obtained from Dobek's group^{3,4} to show that the 4-AP emission band seems to be independent on the excitation wavelength. We present the following data obtained from the literature that were properly referenced in our work. The group of Bhattacharyya et al. showed that for $\lambda_{\text{exc}} = 369 \text{ nm}$ (λ_{excB1}), 4-AP emits at $\lambda_{\text{em}} = 540 \text{ nm}$ ⁵ while, in other work of the same group, when the excitation wavelength used was $\lambda_{\text{exc}} = 300 \text{ nm}$ (λ_{excB2}) the emission maximum value was $\lambda_{\text{em}} \sim 560 \text{ nm}$ ^{6,7}. Even more, Dobek et al. showed that at $\lambda_{\text{exc}} = 369 \text{ nm}$ (λ_{excB1}), 4-AP emits at $\lambda_{\text{em}} = 560 \text{ nm}$ ⁸ while Noukakis et al. showed that at $\lambda_{\text{exc}} = 360 \text{ nm}$ (λ_{excB1}), 4-AP emits at $\lambda_{\text{em}} \sim 545 \text{ nm}$ (obtained through Fig 1b of the reference).⁹ The different data presented in the literature show that the 4-AP emission band is wavelength dependent in concordance with our results. Thus, it seems to us that the 4-AP photophysics is far from being completely understood.

We want to remark that one important point that Samanta et al. have completely omitted in their comment, is the complete and thorough investigation using time-resolved fluorescence (TRES) experiments that we show in the work,¹ data that are obtained in a completely different instrument than the one used to obtain the steady-state emission spectra. Those results were also unusual and showed that, in water, the 4-AP emission band shifts to the blue with time ONLY if the excitation wavelength is the one that correspond to $\lambda_{\text{exc}} = 370 \text{ nm}$ (λ_{excB1}).

With regard to the mechanism proposed to explain our intriguing results that Samantha et al also criticized, we highlight the fact that the mechanism was thought in order to explain the steady-state and the time-resolved results in all solvents used, including water. It is absolutely debatable and probably can be improved if molecular modeling and computer simulation on 4-AP behavior is performed.

In the comments they said that the mechanism is unrealistic and inconsistent with our data but we will show that those statements are not valid. The main objection on the mechanism is that the Scheme 2 shows that 4-AP in the ground state exists in both keto and enol forms in equilibrium, in aqueous solution. If this is the case, then we would make direct excitation of the enol forms and monitor the direct emission from it. Let us say that never in the text of the work¹ we said that there is a keto-enol equilibrium in the 4-AP ground state. On the contrary, we propose that only one 4-AP species exists in the ground state: the keto species. Unfortunately, Scheme 2 C¹ shows a double arrow in the ground state which is a typographical mistake and, we sent the proper correction to the Journal of Physical Chemistry B (See the correct Scheme in the present reply). The key of our explanation summarized in the Scheme, is that the 4-AP excited states are different if the molecule is excited at $\lambda_{\text{exc}} = 300 \text{ nm}$ (B_2), where the locally excited (LE) state is populated, than if the excitation is at $\lambda_{\text{exc}} = 370 \text{ nm}$ (B_1) where the intramolecular charge transfer (ICT) state is populated. In all the solvents, except water, the emission comes always from the same excited state, the keto ICT state, and the emission spectra do not present dependence with the excitation wavelength. In water, the situation seems to be different since when the LE state is populated ($\lambda_{\text{exc}} = B_2$) the fast conversion to the enol LE species makes impossible the formation of the keto ICT state and, the emission comes from the enol LE state. When the ICT state is populated ($\lambda_{\text{exc}} = B_1$) we proposed a keto-enol equilibrium in the 4-AP excited state for the ICT species. The emission goes to different ground states: S_0 for the keto species and S_0' for the enol species,

because the different 4-AP electronic charge distribution of the keto and enol ICT species are not equally solvated by water. Also, we assumed that S_0' is unstable with a short lifetime and rapidly converts to the most stable ground state configuration, S_0 .

Finally, we would like to stimulate the scientific community to investigate more this fascinating molecular probe to put light on its controversial photophysics.

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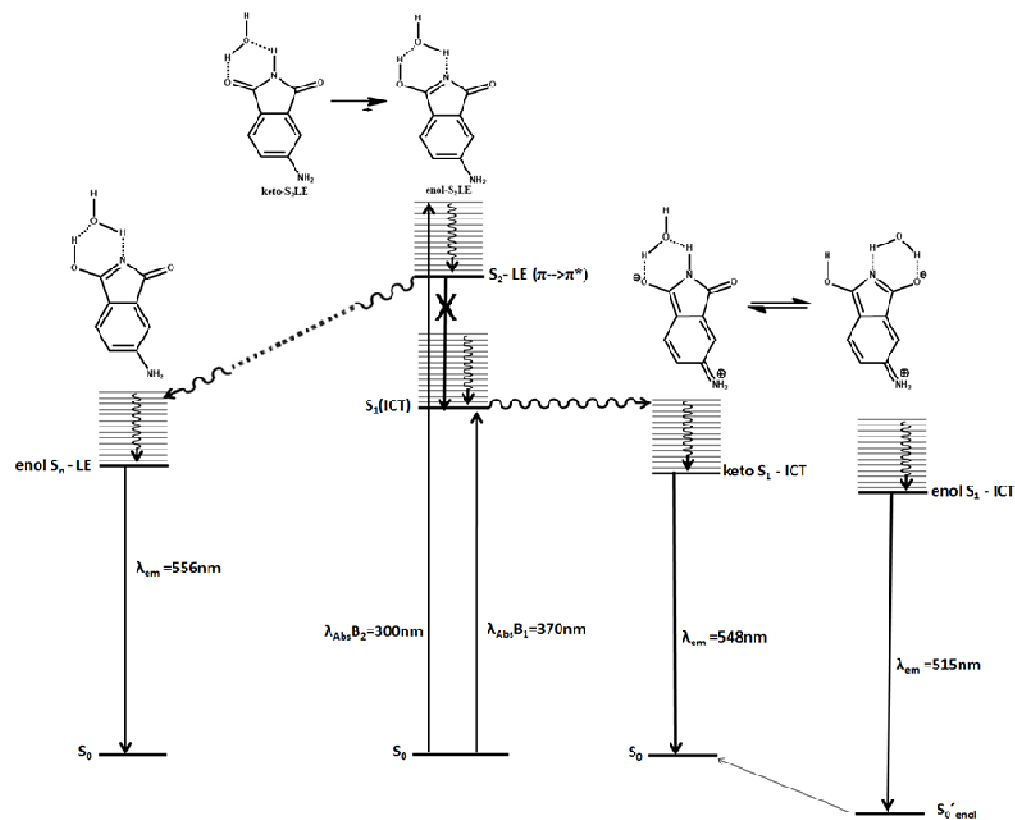
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- 7 4-AP emission band in water is broad and with low intensity thus there is uncertainty in the maxima determination.

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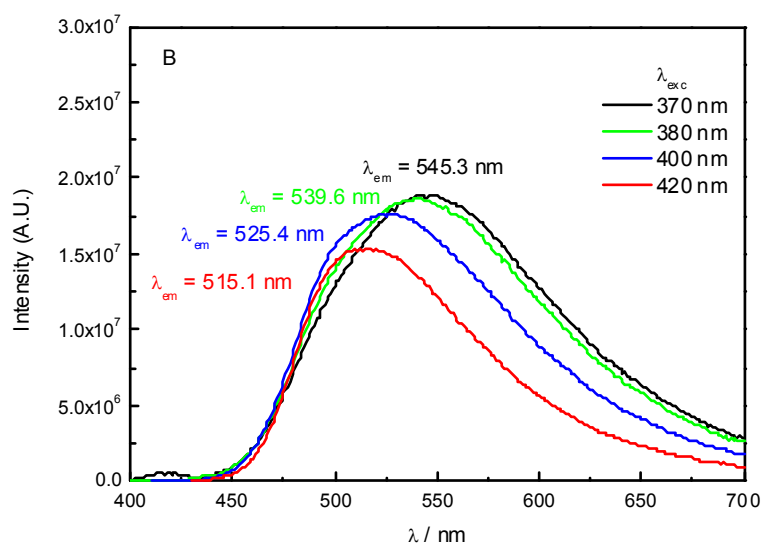
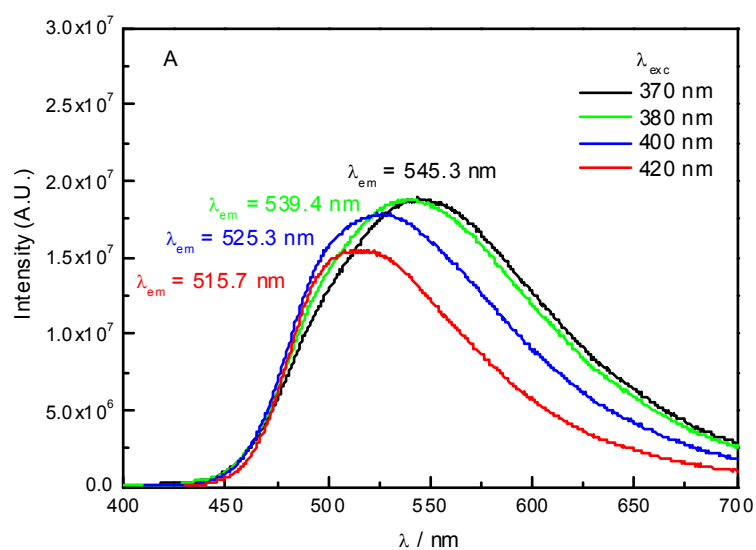
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Scheme. Emission mechanism and the solvent – mediated proton transfer for 4-AP in different media. A) Polar aprotic solvents at any excitation wavelength; B) Protic solvents at any excitation wavelength; C) Water at any excitation wavelength. S₀' represents the unstable with a short lifetime enol-ICT ground state species that rapidly converts to the most stable ground state, S₀.



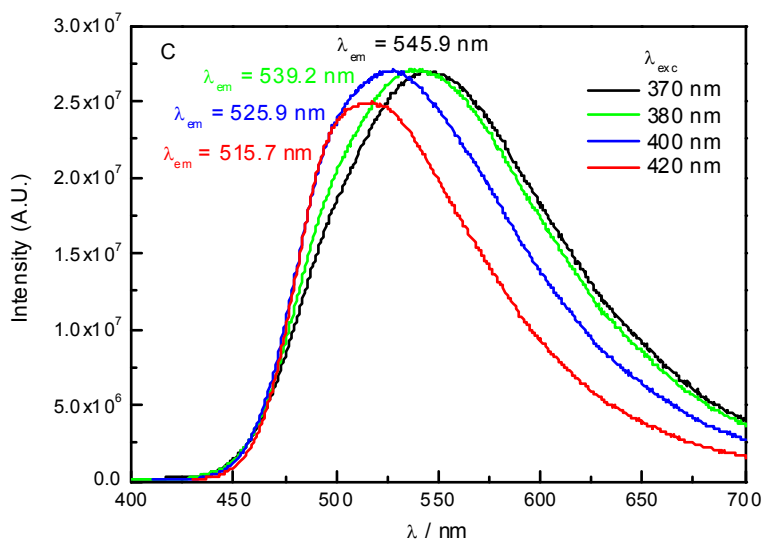


Figure 1. 4-AP Emission spectra in water at different excitation wavelengths. A) [4-AP] = 6×10^{-5} M (Acros Organics or Sigma 97%). B) [4-AP] = 6×10^{-5} M (purified by double sublimation). C) [4-AP] = 1×10^{-4} M (Acros Organics 97%)