# DFT/TDDFT investigation on UV-vis fluorescence properties of alizarin dye

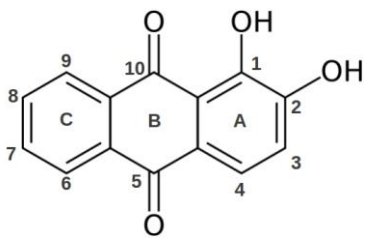
**Anna Amat,*[a] Costanza Miliani,[b] Aldo Romani[c] and Simona Fantacci*[a]**

***Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X***
***First published on the web Xth XXXXXXXXX 200X***
**DOI: 10.1039/b00000000x**

The photophysical and photochemical properties of alizarin, a fluorescent organic red dye of the family of the anthraquinones, have been theoretically investigated, focusing our attention on the emission properties in relation to an excited state internal proton transfer from the phenolic hydroxyl group to the carbonylic oxygen. The potential energy curve of the proton transfer in the first excited state has been computed in solvents of different polarity and the emission spectra of both tautomers simulated including the vibronic effects by means of the FC approximation. Calculations performed equilibrating the solvent with the excited state geometry and electron density by means of a self-consistent procedure have lead to interesting differences with respect to their linear response counterpart. The results obtained point out that while the emission energy of alizarin is sensitive to the solvent polarity, that of the proton-transfer tautomer is computed at similar wavelengths independently on the medium. The comparison between the computed and the experimental data has allowed us to rationalize the alizarin double emission measured in non-polar solvents.

## Introduction

Anthraquinones are a family of organic compounds widely used for their pharmaceutical properties.[1-4] Among them, the hydroxyanthraquinones (HAQ), extracted from the roots of plants belonging to the Rubiaceae family, are brightly coloured derivatives that have been used as dyes since antiquity due to their strong absorption in the visible and their availability.[5-10] Alizarin (1,2-HAQ), see Scheme 1, is a natural occurring hydroxyanthraquinone that, together with purpurin (1,2,4-HAQ), constitutes the main colouring matters of madder. Extracted from Rubia tinctoria L., madder was one of the most popular dyestuffs and was used to dye textiles and as a red lake in paintings by precipitation of the water extract with metal salts. Nowadays, alizarin is currently prepared synthetically, and in the last years it has also been used as a sensitizer for dye-sensitized solar cells (DSC).[11-20]




**Scheme 1** Alizarin

Due to the great interest in the chromatic properties of alizarin, for different application fields, its photophysics and photochemistry have been widely experimentally investigated. Previous computational studies exploiting DFT and TDDFT methodologies have been reported on the structural and electronic properties of the ground state and on the electronic absorption spectra of alizarin[21-25] and alizarin metal complexes[25--28] and, recently, some interesting theoretical studies have been published on the interaction of alizarin with $TiO_2$ surfaces in the framework of DSC.[11-20] While these studies have evidenced the accuracy of theoretical methods in the simulation of the absorption spectra of alizarin, to the best of our knowledge, no theoretical investigations have been reported on its emission properties.

We propose here to characterize the excited states and emission properties of alizarin, taking into account the occurrence of an internal proton transfer. Since many natural organic dyes show peculiar fluorescence properties, i.e. excited state internal proton transfer and wavelengths dependent emissions, the comprehension of alizarin double emission can be relevant both in cultural heritage field, for identification purposes, and in DSC field to design new dyes with optimized target functionalities.

Computational simulations can play an important role in describing the relationships between structural and optical properties at the ground and excited states.[29-33] Recent advances in this field, as the possibility to compute TDDFT analytical gradients in solvent[34,35] and the inclusion of vibronic contributions to the computed spectra,[36-40] according to the Frank-Condon theory, lead

the excited state calculations to accuracies similar to those of the ground state. Moreover, vibrationally-resolved computed emission spectra allow for a more meaningful comparison between the simulated and the experimental data as has been demonstrated in a recent study on the absorption spectra of alizarin by Carta et al.[25]

Alizarin has been used in this investigation to setup a methodology for the calculation of the emission properties that can be then generally extended to the study of different organic dyes. Experimentally, alizarin presents a broad absorption band at ca. 430 nm[41-44] and a weak emission at ca. 640 nm[44,45] that gives rise to a large Stokes shift suggesting a marked change in the molecular geometry of the excited state that was ascribed to an excited state internal proton transfer (ESIPT).[44] A slightly different emission behaviour in different solvents was also reported in Ref. [44] with a wavelength dependent double emission measured in benzene and a single broad band in polar solvents. In particular, in benzene exciting at 465 nm a double emission with peaks at 565 and 610 nm and a low intensity shoulder at ca. 660 nm were measured. Exciting at higher energies the high energy band lowered in intensity while the low energy band became less sharp and was red-shifted. On the other hand, in acetonitrile and ethanol solvents a broad band with a plateau-like maximum between 610 and 660 nm was measured thus hypothesizing the emission originating only from the proton transfer tautomer.[44]

In the present paper, the structural and electronic properties of alizarin in the first excited ($S_1$) state have been studied in different media. Either alizarin (ALZ), see Scheme 1, and its proton transfer tautomer (ALZ_PT) have been found stable in the first excited state. To get insight into the proton transfer process, the potential energy curve as a function of the proton-transfer $O_{10}H$ coordinate has been computed and the excited-state barrier energy of the tautomerization analysed. The optical properties of both tautomers have been also investigated, focusing our attention on the photophysics of the excited state. The emission spectra including the vibronic effects have been computed and compared to the available experimental data to rationalize the double emission measured in benzene and the changes observed with the increase of the solvent polarity.

Two different procedures for the inclusion of solvation effects with a polarizable continuum model (PCM) in the excited states have been evaluated: the linear response (LR-PCM) and the state specific[46-48] one (SS-PCM) where the solvent is equilibrated with the excited state geometry and electron density by means of a self-consistent procedure. The obtained results point out that both procedures lead to significantly different results, not only on the computed stabilities but they also have a noticeable impact on the structural properties of the excited states.

## Computational Details

All the calculations have been performed with DFT[49] and its Time-Dependent extension TDDFT[50-52] as implemented in Gaussian09 (G09) program package,[53] using B3LYP[54-56] as exchange-correlation functional and 6–31g** basis set.[57,58] Solvation effects have been included by means of PCM,[46] as implemented in G09. Optimizations of the excited states have been performed using a linear response (LR-PCM) approach. To get a more accurate description of the solvent effects in the excited state, the solvent reaction field has been equilibrated to the excited state electron density using a state specific self-consistent procedure (SS-PCM)[47,48] on the optimized LR-PCM structures. This procedure should provide in principle to a better description of the solute-solvent interactions in the excited state.[47,48]

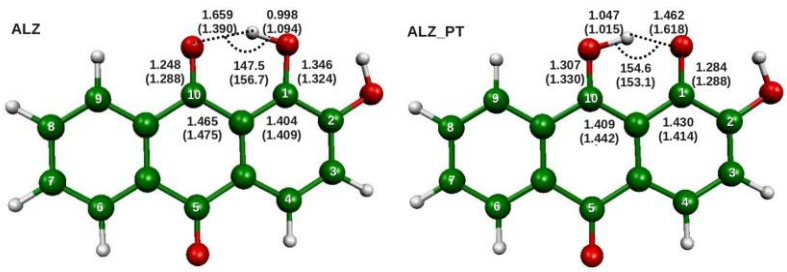



**Figure 1.** Optimized molecular structures of ALZ (left) and ALZ_PT (right). The main geometrical parameters (bond lengths in Å and angles in degrees) computed in benzene in the ground (first excited) state are shown, see Scheme 1 for atom numbering.

The potential energy curves related to the proton transfer in the excited state have been computed by freezing the $O_{10}H$ coordinate from 0.850 Å to 1.850 Å in steps of 0.050 Å and freely optimizing the rest of the coordinates. SS-PCM calculations have been performed on the obtained optimized structures to equilibrate the solvent with the solute geometry, thus computing different potential energy curves.

The vibrationally resolved emission spectra have been computed using the Franck-Condon approximation within the adiabatic Hessian approach by means of the FC Classes code as implemented in G09.[37-40] This approach is quite time-demanding as both states are treated at the same level of calculation and optimization and frequency calculations have to be performed for both the ground- and excited-state. Analytical frequency calculations are used in the ground state while for the excited state first and second derivatives are computed analytically and numerically, respectively. The numerical second derivatives are performed by applying finite differences to the three cartesian coordinates of each atom on the excited state geometry thus resulting in a total

number of 6N+1 analytical first derivative calculations, being N the number of atoms in the molecule.
All the computed emission spectra have been convoluted with a Lorentzian function using a full width at half maximum (FWHM) of 600 $cm^{-1}$ to fit the experimental shape.

## Molecular structure

The molecular structure of alizarin and its possible photo-tautomer have been optimized at ground ($S_0$) and first excited states ($S_1$), see Figure 1. Geometry optimizations performed in vacuo, ethanol and benzene provide stable tautomers in both states. Contradictory computational information is found in literature regarding the stability of the proton-transfer tautomer in the ground state and stable[25,59]/not stable[22] structures are reported. We performed frequency calculations on the optimized structures, finding all positive frequencies in all the different media, confirming therefore the structures for both tautomers are real minima, consistently with experimental stability data.[59]

Calculations performed in the different media do not show relevant differences in the optimized structural parameters. Figure 1 reports the main distances and angles optimized in benzene, while the results in vacuo and in ethanol are collected in the Supporting Information (SI).

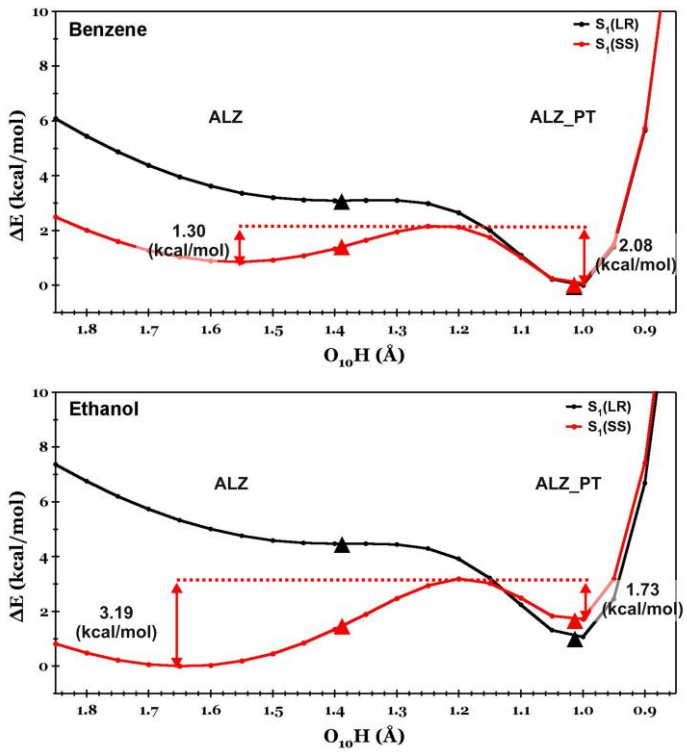



**Fig 2.** Potential $S_1$ energy curves as a function of the $O_{10}H$ distance computed in benzene (top) and ethanol (bottom). The red and black lines are obtained using the LR and SS approaches, respectively. ▲ and ▲markers indicate the LR and the SS stabilities computed on the freely optimized LR geometries.

In the ground state the only noticeable differences between ALZ and ALZ_PT optimized geometrical parameters are retrieved in the distances and angles between the atoms involved in the proton transfer. $CO_{10}$ distance increases as expected when passing from the carbonyl (ALZ) to the alcoholic configuration (ALZ_PT) while the contrary is true for the $C\text{-}O_1$ distance. When the proton is bound to $O_1$ (ALZ) the OH bond length is shorter than when bound to $O_{10}$ (ALZ_PT) reflecting the major acidity of $O_{10}$ with respect to $O_1$. On the other hand, the $O_1HO_{10}$ angle increases of ca. 10° in the proton transfer tautomer.

For ALZ the main differences going from the ground to the $S_1$ excited state are retrieved on the distance $O_1(O_{10})H$ that decreases(increases) of ca. 0.1(0.3) Å while the $O_1HO_{10}$ angle opens by ca. 10°. For ALZ_PT we observe an opposite trend, a lengthening of the $O_1H$ bond by ca. 0.2 Å and the shortening of the distance between the proton and the carbonyl oxygen $O_{10}H$, while the $O_1HO_{10}$ angle is almost unchanged with respect to the ground state geometry.

The relative stabilities of both tautomers computed in the ground state show that the ALZ tautomer is 4.83/4.81/4.78 kcal/mol more stable than ALZ_PT in vacuo/benzene/ethanol. To compute the $S_1$ relative stabilities in solution, the solvent has been equilibrated to the excited state electronic distribution on the LR-PCM optimized $S_1$ geometries. ALZ_PT is computed 2.89/1.40 kcal/mol more stable than ALZ in vacuo/benzene while in ethanol the two tautomers are almost isonergetic, with ALZ found more

stable by only 0.20 kcal/mol. Attempts to locate the transition states structures between the two tautomers using the LR-PCM optimization failed. Therefore, the potential energy curves in the excited state along the proton transfer coordinate have been computed for both tautomers.

The molecular structures were optimized in the first excited state at different fixed $O_{10}H$ distances. On each constrained optimized molecular structure a SS-PCM calculation was performed to equilibrate the solvent with the excited state electronic density, the obtained results are reported in Figure 2. Interestingly, we notice that the LR-PCM calculations do not report any consistent barrier in the proton transfer pathway which explains the failure to locate the transition state. Only the ALZ_PT are real minima in the $S_1$ and the optimized ALZ structures correspond to a flat region of the energy curve around between $O_{10}H$ = 1.5 and 1.3 Å. The optimized LR-PCM ALZ structures have been reported with triangle markers on Figure 2. On the contrary, the energy curves computed using the SS-PCM method show two clear minima corresponding to the ALZ and the ALZ_PT tautomers and a non-negligible barrier height. The ALZ minima are found at $O_{10}H$ = 1.550 and 1.650 Å in benzene and ethanol, respectively, different from the 1.390 Å value computed with the LR-PCM optimization in both solvents.

In benzene the ALZ_PT minimum is located 0.80 kcal/mol below that of ALZ and barrier heights of 1.30 and 2.08 kcal/mol are computed for the proton and the back-proton transfer, respectively. Surprisingly, in ethanol the ALZ is computed 1.46 kcal/mol more stable than ALZ_PT and the barrier height is computed 3.19 kcal/mol and 1.73 kcal/mol with respect to the ALZ and the ALZ_PT tautomers. It has to be pointed out, considering the protic nature of the solvent, that specific solute-solvent interactions might be present and influence the ESIPT process. These interactions are neglected in our approach even though they might similarly count for both tautomers. To check this effect and to disentangle the H-bondig effects from the polarity of the solvent, we repeated the same calculations on ALZ and ALZ_PT using acetonitrile as solvent. Moreover, the choice to perform calculations in acetonitrile is justified by the fact that experimentally the emission spectra of alizarin measured in ethanol and acetonitrile show the same main features. It is worth noting that both the LR-PCM and SS-PCM energy potential curves of the ESIPT process in acetonitrile are very similar to those computed in ethanol (see SI for further details). In acetonitrile, the ALZ is computed 1.83 kcal/mol more stable than ALZ_PT and the barrier height is computed 3.24 kcal/mol and 1.41 kcal/mol with respect to the ALZ and the ALZ_PT tautomers. We therefore find that the most stable species in the lowest excited state in polar solvent is the ALZ and that its relative stability increases by increasing the polarity of the solvent.

As a general conclusion, the comparison between the LR-PCM and the SS-PCM results points out the importance of the solvent equilibration in the excited state. Not only different potential energy curves are computed but also the geometrical structures of the minima are different, with the $O_{10}H$ distance in the ALZ minima of the SS-PCM and LR-PCM potential energy curves varying by as much as 0.2 Å.

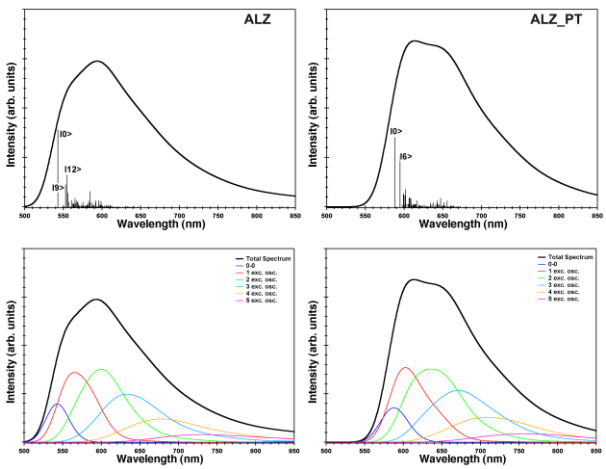



**Fig 3.** Emission spectra computed in benzene of ALZ (left) and ALZ_PT (right) with the main vibronic transitions involved (top) and decomposition of the spectra in contributions from the 0-0 transition and the n (n=1,5) simultaneously excited oscillators (bottom).

## Vibrationally resolved emission spectra

To fully characterize the emission process of alizarin and the involvement of both the tautomers, we computed the emission energies of ALZ and ALZ_PT. The vertical transition energies and the emission energies from the $S_1$ state of both tautomers in vacuo, benzene and ethanol using the state specific approach for the calculation of the solvent reaction field have been computed. Both the optimized LR-PCM geometries (Figure 1) and the minima molecular structures obtained from the $S_1$ SS curves (Figure 2) have been used to compute the emission transitions. In table 2, the results using the minima molecular structures taken by the

$S_1$ SS curves are reported together with the obtained results in vacuo, while the emission computed wavelengths and energies using the standard LR approach and SS on the LR optimized structures are reported in SI.

**Table 2** Alizarin and alizarin proton transfer tautomer computed emission wavelengths and (energies) in the ground and first excited state in vacuo and in different solvents.

| | **ALZ** | **ALZ_PT** |
|---|---|---|
| | **Trans. nm (eV)** | **Trans. nm (eV)** |
| **Vacuo** | 576 (2.15) | 659 (1.88) |
| **Benzene** | 585 (2.12) | 657 (1.89) |
| **Ethanol** | 611 (2.03) | 653 (1.90) |

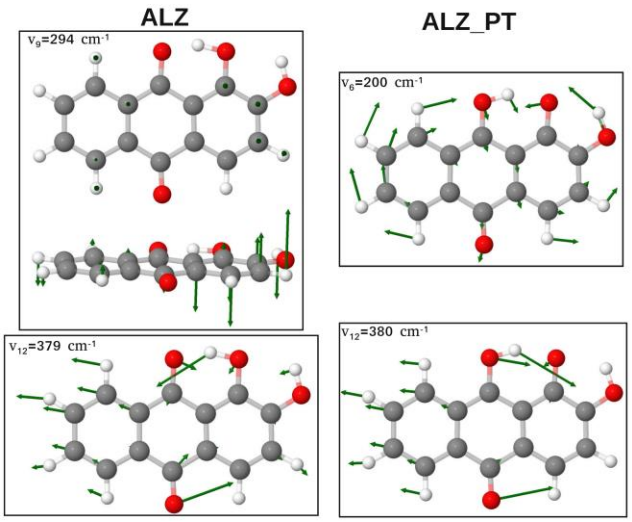



**Fig 4.** Vibrations modes $\nu_9$ (top) and $\nu_{12}$ (bottom) for ALZ (left) and vibration modes $\nu_6$ (top) and $\nu_{12}$ (bottom) for ALZ_PT computed in benzene.

The ALZ emission spectrum computed in benzene, see Figure 3 (left, top), shows a maximum at 595 nm, a shoulder blue-shifted with respect to the emission maximum at ca. 560 nm and a long tail at low energies. The emission peak is mainly due to transitions of double simultaneously excited oscillators with minor contributions of single and triple excited oscillators, see Figure 3 (left, bottom). The shoulder at 560 nm is due to the 0-0 transition and to transitions of single excited oscillators, being the most intense the <0|9> and <0|12> transitions. The tail at low energies is instead due to the triple transitions with a minor contribution from 2 and 4 simultaneously excited oscillators transitions. Mode $\nu_9$ at 294 cm$^{-1}$ corresponds to an out-of-plane boat-like vibration of the external rings, manly C-ring, see Figure 4, while mode $\nu_{12}$ at 379 cm$^{-1}$ corresponds to the two carbonyl bending and to $C_1OH$ bending in phase with the C=O bending plus a breathing of the A-Ring. This latest vibrational mode drives the alizarin tautomerization by assisting the inter-molecular proton transfer decreasing the $O_{10}H$ distance.

The shape of the emission spectrum computed for ALZ_PT in benzene is quite similar to that of ALZ though red-shifted and slightly more intense. We computed two bands at 610 and 645 nm and a long tail at low energies, see Figure 3 (right, top). The band at higher energies is slightly more intense than the band at 645 nm, contrarily to what computed for ALZ. The band at 610 nm is formed by the 0-0 transition and single quanta transitions, in particular <0|6> and <0|12>. On the other hand, the band at 645 is mainly due to double and triple excited oscillator transitions and the low energy tail is essentially due to triple and quadruple excited oscillator transitions, see Figure 3 (right, bottom). Vibrational normal mode $\nu_6$ is computed at 200 cm$^{-1}$ and manly accounts for the rigid bending of A and C-rings towards the axis formed by the two carbonyls of ring B, the $\nu_{12}$ computed at 380 cm$^{-1}$ is equivalent to the $\nu_{12}$ mode computed for ALZ and assists the back-proton transfer, see Figure 4.

Experimentally in benzene a double emission has been

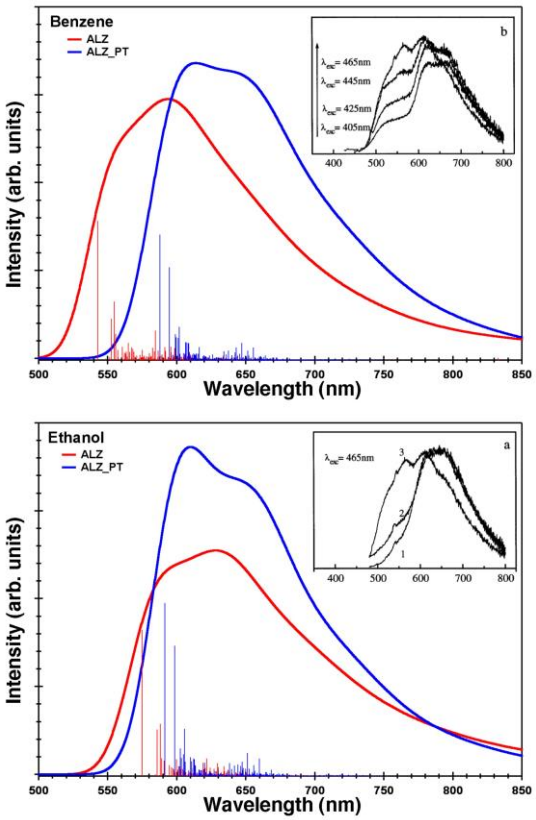



**Fig 5.** Computed emission spectra in benzene (top) and ethanol (bottom) of ALZ (red) and ALZ_PT (blue). Experimental spectra in benzene/ ethanol at different excitation wavelengths from ref. [44].

measured for alizarin and has been ascribed to the deactivation of both tautomers. As already discussed in previous sections, the computed similar stability for ALZ and ALZ_PT along with the small barrier associated to the proton transfer would suggest that both the lowest excited states of ALZ and ALZ_PT should be populated. Therefore, it is reasonable to hypothesize that the emission spectrum might be the result of the fluorescence spectra of both tautomers whose contribution depends on their relative distribution given by their relative stabilities that determine the number of molecules that have been allowed to overcome the barrier at a given excitation wavelength. Figure 5 (top) reports the vibrationally resolved emission spectra in benzene of ALZ and ALZ_PT with the corresponding transitions compared to the available experimental data.

The results computed in benzene are compatible with the experimental picture from ref. [44] and the simulated spectrum that would come from a combination of the ALZ and the ALZ_PT is in good agreement in terms of energy with the experimental data. When exciting at high energy, 405 nm (3.06 eV), a larger ratio of the molecules overcomes the barrier and emit from the ALZ_PT tautomer increasing the relative intensity of the emission band between 620-690 nm (2.03-1.80 eV). This band is in excellent agreement, within 0.05 eV, with the theoretical emission of ALZ_PT that is computed between 600-660 nm (2.00-1.85 eV). On the other hand, exciting at lower energy 465 nm (2.66 eV) the emission from the ALZ tautomer increases and two distinguishable bands are measured; the band at high energy is reproduced by the signal computed for ALZ (0-0 and singles) while the experimental emission maximum at 610 nm is described by contributions from both the low energy band of ALZ (doubles) and the high energy band of ALZ_PT (0-0 and singles).

For alizarin, in polar solvents as ethanol and acetonitrile, a single broad emission band at ca. 640 nm was measured in contrast with the double band retrieved in benzene, thus hypothesising a higher barrier height and an emission coming only from the proton transfer tautomer for polar solvents.[41] Our computed relative stabilities estimated from the SS approach suggest that the ALZ is more stable than the ALZ_PT species in polar solvents, and that a quite high energy barrier is associated to the proton transfer process (3.19 kcal/mol). However, results in ethanol might be affected by an incomplete treatment of the solvent effects with the continuum polarizable model used in this investigation. Bearing this in mind, we can not exclude from our calculations the presence of none of the tautomers; Figure 5 (bottom) reports the computed emission in ethanol for both tautomers. The composition of the computed emission spectra in ethanol in terms of classes and transitions contributions is essentially the same as in benzene and is therefore reported only in SI.

Comparing the emission spectra of Figure 5 it can be observed that while that of ALZ_PT is essentially unchanged with the increase of the solvent polarity, the ALZ spectrum is red-shifted with respect to its benzene counterpart. The emission spectrum of ALZ_PT is more intense than that of ALZ, as already observed in benzene, even though the ratio between the intensity is higher in ethanol. We notice from the bottom panel of Figure 5 that the computed emission spectra of ALZ and ALZ_PT tautomers lay in

the same spectral region and are both compatible with the experimental emission, both in terms of energy and spectral shape, presenting a plateau-like maximum between 590 and 670 nm. Therefore, no definitive conclusions regarding the species present in polar solvents can be inferred from calculations. Experimental spectra would be compatible with an emission coming from ALZ only, ALZ_PT only or from a combination of both species though according to the relative stabilities computed and the estimated barrier associated to the proton transfer only ALZ should be in principle responsible for the emission spectrum. From our calculations we can exclude the double emission in polar solvents, independently by the relative tautomer stabilities.

## Solvatochromism: the electronic factors

To explain the solvatochromism shown in emission by alizarin with respect to solvents of different polarity, we analyzed the electronic charge distribution of ALZ and ALZ_PT at the $S_0$ and $S_1$ geometries as a function of the media. Solvatochromism is a very complex phenomenon which gives a measure of a different response to the solvation effects of the dye charge distribution at the ground and first excited state.[60,61] These effects can be specific or not-specific depending on the nature of the solvent (protic/non protic solvents) and on its dielectric constant (polar/non polar solvents). The change of charge distribution between ground and excited states can be roughly monitored by analyzing the dipole moment of the ground and lowest excited states, $\mu(S_0)$ and $\mu(S_1)$, even though dynamical effects should be properly taken into account.[61] For alizarin the presence of the proton transfer tautomer (ALZ_PT) at the lowest excited state makes the interpretation picture even more complex.

To find a rationale for the alizarin solvatochromism, we therefore computed the $\mu(S_0)$ and $\mu(S_1)$ of both ALZ and ALZ_PT species; for the ground state we refer to the optimized structure, while for the excited state structure we refer to the minima of the SS-PCM curve reported in Figure 2. The computed dipole moments in the different considered media along with the differences between the lowest excited state dipole moment and the ground state dipole moment ($\Delta\mu$ $S_1$-$S_0$) are reported in Table 3. For ALZ, $\mu(S_0)$ in vacuo is ca. 2.0 D while in the excited state increases up to ca. 2.8 D. While the $\mu(S_0)$ weakly changes with respect to the different media (0.61 D from vacuo to ethanol), a more polar $S_1$ structure is stabilized in ethanol, the $\mu(S_1)$ passing from 2.77 D (vacuo) to 5.06 D (ethanol).

The ALZ_PT $\mu(S_0)$ varies similarly to that of ALZ increasing by 0.97 D passing from vacuo to ethanol, while $\mu(S_1)$ has a different behaviour markedly decreasing with respect to that of the ground state by a factor 3, and being slightly affected by the medium, passing from 0.66 D (vacuo) to 0.98 D (ethanol). From the analysis of the $\Delta\mu(S_1\text{-}S_0)$, which can be roughly related to the sovatochromism, we found that ALZ shows a marked increase of the difference between the dipole moment of $S_0$ and $S_1$ by increasing the solvent polarity. On the other hand, for the ALZ_PT species we computed a similar $\Delta\mu(S_1\text{-}S_0)$ independently on the solvent polarity, and with an opposite sign with respect to ALZ. On overall, our results highlight the two tautomers intrinsically respond to solvents of different polarity in a completely different way: (i) in ALZ the more polar excited state is more stabilized by polar solvent than the ground state showing a positive solvachromism; (ii) in ALZ_PT the ground state is more polar than $S_1$ state and is stabilized in polar solvent thus showing a weak negative solvatochromism.

The different charge distribution of ground and excited states of ALZ and ALZ_PT implies different stabilization of the two $S_0$ and $S_1$ states in different solvents further explaining the computed emission behaviour. In fact the two tautomers oppositely behave in different solvents showing for ALZ a red shift in ethanol with respect to vacuo and benzene, while ALZ_PT does not change the emission wavelength from vacuo to ethanol.

**Table 3.** Dipole moments of the ground and first excites states for the both tautomers.

| | **ALZ** | | **ALZ_PT** | |
|---|---|---|---|---|
| | **$\mu$ $S_0$ ($S_1$)** Debye | **$\Delta\mu$ $_{S1\text{-}S0}$** Debye | **$\mu$ $S_0$ ($S_1$)** Debye | **$\Delta\mu$ $_{S1\text{-}S0}$** Debye |
| **Vacuo** | 2.03 (2.77) | 0.74 | 2.85 (0.66) | -2.19 |
| **Benzene** | 2.31 (3.94) | 1.63 | 3.29 (0.76) | -2.53 |
| **Ethanol** | 2.64 (5.06) | 2.42 | 3.82 (0.98) | -2.84 |

## Summary and Conclusions.

DFT and TDDFT have been employed to study the photophysical and photochemical properties of alizarin, a widely investigated fluorescent organic dye, focusing our attention on its optical properties in relation to internal proton transfer. The two tautomers associated with a proton transfer from the phenolic hydroxyl group to the carbonylic oxygen have been computed in the ground state. Both tautomers are true minima, as confirmed by frequency calculations, even though the ALZ species are more stable by ca. 5 kcal/mol in the different media.

We have focused our attention on the photophysics of the excited state of interest ($S_1$) to rationalize the emission process in solvents of different polarity. Geometry optimizations and frequency calculations using LR-PCM confirm that both ALZ and ALZ_PT are stable in $S_1$. ALZ_PT tautomer is more stable by 1.40 kcal/mol than ALZ in benzene while in ethanol ALZ is more stable by only 0.20 kcal/mol. The potential energy curve of the proton transfer has been then computed by fixing the $O_{10}H$

distance and allowing the rest of the atoms to freely optimize. The potential energy curves obtained equilibrating the solvent on the LR-optimized geometries substantially differs from their LR counterparts. LR potential energy curves show no clear barrier height and a flat zone around 1.3 Å $O_{10}H$ distance, the curves computed being very similar in benzene and in ethanol. Interestingly, equilibration of the solvent leads in benzene to a real minimum for each tautomer and a barrier height of ca. 2 kcal/mol while in ethanol, ALZ is computed ca. 1.9 kcal/mol more stable than ALZ_PT.

The small computed energy differences suggest an equilibria of both forms in the two different solvents. The vertical emission excitations have been computed and compared to the experiment by equilibrating the solvent reaction field to $S_1$. On overall, the ALZ_PT emission is red-shifted between 0.27 and 0.13 eV with respect to that of ALZ. The ALZ_PT emission energies are almost insensitive to the solvent polarity, while the ALZ ones are red-shifted when passing from benzene to ethanol.

The emission spectra of ALZ and ALZ_PT have been simulated including the vibronic effects by means of the FC approximation. Both spectra have similar shapes with two distinguishable bands that are of similar intensity for ALZ while for ALZ_PT the signal at higher energies is more intense. On overall, the ALZ_PT spectrum is more intense and red-shifted with respect to that of ALZ. The band at higher energy of both tautomers shows essentially contributions from the 0-0 and the overtones with a smaller contribution from 2-simultaneously excited state transitions. The band at lower energy has contributions from the 2,3-simultaneously excited state transitions. The vibrationally resolved emission spectra computed in the two investigated solvents are very similar, a part from a red-shift of the ALZ spectrum in ethanol compared to benzene.

In benzene both ALZ and ALZ_PT species contribute to the emission, the result is an emission spectrum which accounts for the spectral features of both tautomers emission spectra. The wavelength dependent double emission measured[44] is compatible with the presence of two stable tautomers in the excited state and the computed spectra of both tautomers are in good agreement with the retrieved experimental bands. When exciting at high energy a larger ratio of the molecules overcomes the barrier and emit from the ALZ_PT tautomer, whose emission is computed between 620 and 670 nm, increasing the relative intensity of the experimental emission band retrieved between 610 and 690 nm. On the other hand, the experimental band between 525 and 575 nm is compatible with the computed spectra of the ALZ tautomer. This signal would increase when exciting at lower energies resulting in a double band emission spectra with peaks centered at 610 and 540 nm that would correspond to emission coming from both ALZ_PT and ALZ and from only ALZ, respectively.

A more complex picture is found for ethanol, since the computed emission spectra of both tautomers are consistent with the experimental emission, therefore from the comparison of computed and experimental spectra is not possible to chose for the presence of one or the other tautomer. The ground state and excited state dipole moments strongly vary for ALZ going from benzene to ethanol, showing a marked sovatochromism of the emission, while the two dipole moments undergo more slight changes for ALZ_PT, which emits at similar energies in benzene and ethanol. Including energy considerations, from our calculations only the ALZ species is responsible of the emission spectrum and this species by its own is able to explain the measured emission spectrum. The analysis of the variation of the dipole moment of $S_0$ and $S_1$ in solvents of different polarity allows us to relate the different solvatochromic behaviour of the two tautomers to a larger increase of charge polarization in the ALZ $S_1$, which therefore results more stabilized in polar solvents than ground state.

Results obtained for alizarin show that the recent advances in computational chemistry have allowed to achieve a such accuracy in the excited state computed properties almost comparable to that obtained for the ground state. Our calculations on the emission spectra of alizarin are in good agreement with the experimental data reproducing the trend of the experimental fluorescence with the increase of the excitation energy and with the changes on the solvent polarity.

**Aknowledgments:** AA and SF thank MIUR-PRIN 2010-2011 Project No. 20104XET32 "DSSCX"

## Notes and references

[a]*Computational Laboratory for Hybrid/Organic Photovoltaics (CLHYO), CNR-ISTM, Via Elce di Sotto 8, I-06123, Perugia, Italy, Fax: +39 075 585 5606; Tel: +39 075 585 5618/+39 075 585 5522; E-mail: anna@thch.unipg.it, simona@thch.unipg.it*
[b]*CNR-ISTM, Via Elce di Sotto 8, I-06123, Perugia, Italy, Fax: +39 075 585 5606; Tel: +39 075 585 5639; E-mail: miliani@thch.unipg.it*

† Electronic Supplementary Information (ESI) available: [$S_0$ and $S_1$ main structural parameters for ALZ, ALZ_PT in vacuo/benzene/Ethanol; Computed emission for ALZ and ALZ_PT in vacuo/benzene/Ethanol using SS and LR approaches on the LR fully optimized geometries; Decomposition in terms of classes of the vibrationally resolved emission spectra ethanol for ALZ and ALZ_PT; Vibrationally resolved emission spectra in benzene and ethanol using the SS emission energies computed on the fully optimized LR structures.]. See DOI: 10.1039/b000000x/

1 M. Hovaneissian, P. Archier, and C. Vieillescazes, *Dyes and Pigments*, 2007, **74**, 706.
2 D.S. Alves, L. Perez-Fons, A. Estepa, and V. Micol, *Biochemical Pharmacology*, 2004, **68**, 549.
3 S.A. Norton, *J. of the Am. Academy of Dermatology*, 1998, **39**, 484.
4 A.D. Dixon, and D.A.N. Hoyte, *The Anatomical Rec.*, 1963, **145**, 101.
5 R. de la Rie, *Stud. Conserv*. 1982, **27**, 1; R. de la Rie, *Stud. Conserv*. 1982, **27**, 65, R. de la Rie, *Stud. Conserv*. 1982, **27**, 102.
6 M. Matteini and A. Moles, La Chimica nel Restauro. Nardini: Florence, 1986.
7 P. Novotna, V. Pacakova, Z. Bosakova, and K. Stulik, *J. of Chromat. A*, 1999, **863**, 235.
8 J. Orska-Gawrys, I. Surowiec, J. Kehl, H. Rejniak, K. Urbaniak-Walczak, and M. Trojanowicz, *J. of Chromat. A*, 2003, **989**, 239.
9 B. Szostek, J. Orska-Gawrys, I. Surowiec, and M. Trojanowicz, *J. of Chromat. A*, 2003, **1012,** 179.
10 J. Wouters and N. Rosario-Chirinos, *J. of the Am. Inst. for Cons.*, 1992, **31**, 237.

11 W. R Duncan, O. V. Prezhdo, *Annu. Rev. Phys. Chem.*, 2007, **58**, 143
12 W. R Duncan, W. M.; Stier, and O. V. Prezhdo, *J. Am. Chem. Soc*., 2005, **127**, 7941
13 A. Nawrocka and S. Krawczyk, *J. Phys. Chem. C*, 2008, **112**, 10233.
14 W. R Duncan and O. V. Prezhdo, *J. Phys. Chem. B*, 2005, **109**, 365.
15 W. R Duncan, C. F. Craig and O. V. Prezhdo, *J. Am. Chem. Soc.*, 2007, **12**, 8528
16 W. R Duncan and O. V. Prezhdo, *J. Am. Chem. Soc.*, 2008, **130**, 9756
17 S. Kaniyankandy, S. Verma, J. A. Mondal, D. K. Palit and H. N. Ghosh, *J. Phys. Chem. C*, 2009, **113**, 3593.
18 R. Sánchez-de-Armas, M. A. San-Miguel, J. Oviedo and J. Fdez. Sanz, *J. Chem. Theory, Comput.*, 2010, **6**, 2856.
19 J. Li, I. Kondov, H. Wang and M. Thoss, *J. Phys. Chem C*, 2010, **114**, 18481.
20 Y Di Iorio, M. A. Brusa, A. Feldhoff, and M. A. Grela, *ChemPhysChem*, 2009, **10**, 1077.
22 J. Preat, A. D. Laurent, C. Michaux, E. A. Perpète and D. Jacquemin, *J. Mol. Struc. (THEOCHEM)*, 2009, **901**, 24.
23 M. Savko, S. Kascakova, Peter Gbur, P. Miskovsky and J. Ulicny, *THEOCHEM*, 2007, **823** 78-86 .
24 P. Cysewski, T. Jelinski, M. Przybyeka and A. Shyichukb , *New J. Chem.*, 2012, **36**, 1836-1843.
25 L. Carta, M. Biczysko, J. Bloino, D. Licari and V. Barone Phys. Chem. Chem. Phys., 2014, **16**, 2897.
26 I. Kondov, H. Wang and M. Thoss, *Int. J. of Quant. Chem.*, 2006, **106**, 1291.
27 N. Komiha, O. K. Kabbaj and M. Chraibi, *J. Mol. Struc. (THEOCHEM)*, 2002, **594**, 135.
28 S. Say-Liang-Fat and J. P. Cornard, *Polyhedron*, 2011, **30**, 2326.
29 A. Amat, F. Rosi, C. Miliani, A. Sgamelloti and S. Fantacci, *J. Mol. Struct*. **2011**, 993 43.
30 A. Amat, C. Clementi, C. Miliani, A. Romani, A. Sgamellotti and S. Fantacci, *Phys. Chem. Chem. Phys*. **2010**, 12, 6672.
31 A. Amat, C. Clementi, F. De Angelis, A. Sgamellotti, S. Fantacci, J. *Phys. Chem. A* **2009**, 113, 15118.
32 F. De Angelis, S. Fantacci, E. Mosconi, M. K. Nazeeruddin and M. Grätzel, *J. Phys. Chem. C* **2011**, 115, 8825.
33 F. De Angelis, S. Fantacci, R. Gebauer, R., *J. Phys. Chem. Lett*. **2011**, 2, 813.
34 G. Scalmani, M. J. Frisch, B. Mennucci, J. Tomasi, R. Cammi and V. Barone, *J. Chem. Phys.*, 2006, **124**, 094107.
35 R. Improta, V. Barone, and F. Santoro, *J. Phys. Chem. B*, 2007, **111**, 14080.
36 R. Improta, F. Santoro, and V. Barone, *Angew. Chem. Int. Ed.* 2007, **46**, 405.
37 F. Santoro, R. Improta, A. Lami, J. Bloino, and V. Barone, *J. Chem. Phys.*, 2007, **126**, 084509.
38 F. Santoro, A. Lami, R. Improta, and V. Barone, *J. Chem. Phys.*, 2007, **126**, 184102.
39 F. Santoro, A. Lami, R. Improta, J. Bloino, and V. Barone, *J. Chem. Phys.*, 2008, **128**, 224311.
40 V. Barone, J. Bloino, M. Biczysko, and F. Santoro, J. *Chem. Theory and Comput.*, 2009, **5**, 540.
41 C. Miliani, A. Romani and G. Favaro, *J. Phys. Org. Chem*, 2000, **13**, 141.
42 R.C. Weast, Handbook if Chemistry and Physics, 51st Ed, The Chemical Rubber Company, Ohio, 1970.
43 R.H. Thomson, Naturally occurring Quinones, 2nd Ed., Academic Press, London, 1971.
44 C. Miliani, A. Romani and G. Favaro, *Spectrochimica Acta Part A*, 1998, **54**, 581.
45 C. Grazia, C. Clementi, C. Miliani and A. Romani, *Photochem. & Photobiol. Sci.*, 2011, **10**, 1249-1254.
46 J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.*, 2005, **105**, 2999.
47 R. Improta, G. Scalmani, M. J. Frisch and V. Barone, *J. Chem. Phys.*, 2007, **127**, 074504.
48 R. Improta, V. Barone, G. Scalamani and M. J. Frisch, *J. Chem Phys*, 2006, **125**, 054103.
49 P. Hohenberg and W. Kohn, *Phys. Rev.*, 1964, **136**, B864.
50 R. E. Stratmann, G. E. Scuseria and M. J. Frisch, *J. Chem. Phys.*, 1998, **109**, 8218.
51 R. Bauernschmitt and R. Ahlrichs, *Chem. Phys. Lett.*, 1996, **256**, 454.
52 M. E. Casida, C. Jamorski, K. C. Casida and D. R. Salahub, *J. Chem. Phys.*, 1998, **108**, 4439.
53 Gaussian 09, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
54 A. D. Becke, J. Chem. Phys., 1993, **98**, 5648.
55 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter*, 1988, **37**, 785.
56 B. Miehlich, A. Savin, H. Stoll and H. Preuss, *Chem. Phys. Lett.*, 1989, **157**, 200.
57 V. A. Rassolov, M. A. Ratner, J. A. Pople, P. C. Redfern and L. A. Curtiss, *J. Comput. Chem.*, 2001, **22**, 976.
58 V. A. Rassolov, J. A. Pople, M. A. Ratner and T. L. Windus, *J. Chem. Phys.*, 1998, **109**, 1223.
59 A. Le Person, J. P. Cornard, S. Say-Liang-Fat, Chem. Phys. Lett. 2011, **517**, 41-45.
60 M. Homocianu, Anton Airinei, D. Ortansa Dorohoi, *J. of Adv. Res. in Phys.*, 2011, **2**, 011105.
61 A. Marini, A. Munoz-Losa, A. Biancardi, B. Mennucci, *J. Phys. Chem. B*, 2010, **114**, 17128–17135