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Environmental and complexation effects on the structures and spectroscopic signatures of organic pigments relevant for cultural heritage: the case of Alizarin and Alizarin-Mg(II)/Al(III) complexes

Luciano Carta^a, Malgorzata Biczysko^{*,a}, Julien Bloino^{a,b}, Daniele Licari^a, and Vincenzo Barone^a

^aScuola Normale Superiore, Piazza dei Cavalieri 7, I-56126 Pisa, Italy

^bConsiglio Nazionale delle Ricerche, Istituto di Chimica dei Composti OrganoMetallici (ICCOM-CNR), UOS di Pisa, Area della Ricerca CNR, via G. Moruzzi 1, I-56124 Pisa, Italy

Abstract

An integrated computational approach allowed an unbiased analysis of optical and structural properties of alizarin-based pigments, which can be directly compared with experimental results. Madder lake pigments have been modeled by Mg(II)- and Al(III)-coordinated alizarin taking into account solvation and metal-linkage effects, responsible for colour modifications. Moreover, different environmental conditions have been analyzed for free alizarin, showing in all cases semi-quantitative agreement with experimental spectroscopic data (UV-VIS). Our results point out the ability of *in silico* approaches to unravel the subtle interplay of stereo-electronic, dynamic, and environmental effects in tuning the physico-chemical properties of pigments relevant for cultural heritage.

1 Introduction

Computational modeling recently received significant attention also in the cultural heritage field, in connection with restoration and conservation of art or historical objects^{1,2}. From an experimental point of view, a broad range of methodologies are now employed to investigate artistic materials^{1,3}, such as spectrophotometric and fluorimetric techniques in the ultraviolet-visible (UV-Vis) energy range⁴, infrared (IR)^{5,6} and Raman⁷ spectroscopies, as well as nuclear magnetic resonance (NMR)⁸, with additional important contributions provided by other analytical tools like mass spectrometry (MS)⁹, chromatography and X-Ray diffraction (XRD)¹⁰. Spectroscopic techniques are particularly suited for the characterisation of works of art or other unique objects such as archeological samples, since they provide very detailed information on the system under investigation by means of non-

*malgorzata.biczysko@sns.it.

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invasive studies. However, the analysis of the rich information coming from experimental studies is particularly difficult in the field of cultural heritage, due to the inherent complexity of the materials together with the often unknown composition of the sample. A significant aid in rationalizing experimental data is offered by computational approaches^{2,11-13}, which provide also deeper insights into the nature and composition of the artistic materials and detailed descriptions of the physical and chemical changes that bring to degradation processes responsible for their modifications. It can be foreseen that the availability of reliable and user-friendly computational tools^{14,15} combined with the possibility to describe larger and more complex molecular systems¹⁶⁻²¹ at a reasonable cost will increase the use of computational models in the cultural heritage field. The possibility to simulate and predict the overall spectroscopic properties, has been recently demonstrated for a set of novel chromophores²² or NIR-emitting fluorescence probes²³, for the latter taking into account both the pH-dependence and the possible coexistence of different tautomers in solution. In the present work we will focus on environmental factors responsible for the ageing and colour modification of ancient pigments exploiting recently developed and implemented computational spectroscopy approaches^{15,24} to analyse the optical properties of alizarin-based pigments. It will be shown how the simulation of the electronic band line-shape allows the direct comparison with experimental outcomes and a detailed analysis of experimentally observed vibrational contributions²⁵, taking also into account that the band shape is directly responsible for the colour perceived by the human eye²⁶.

Alizarin is one of the most known and stable organic dyes and is found as the main component, with purpurin and quinizarin, of the *madder lake* pigment, known to painters as *Rose Madder* and *Alizarin Crimson*. Extracted from *Rubia Tinctorum* roots²⁷ since 3.000 BC, it has been widely used in Europe during the XVI century in both artistic painting and textiles. Although alizarin has been nowadays largely replaced by other commercial colorants, its synthetic lake pigment can be still found in contemporary works of art. Due to the availability of an abundant set of experimental data, alizarin-based systems stand as suitable cases to define and validate computational approaches, which can be further applied to the analysis of other ancient pigments, and in general for the application of computational spectroscopy in the field of cultural heritage. Moreover, alizarin as a chromophore received some attention also for technological²⁸⁻³⁰ applications while its capability to form stable complexes with different metal atoms^{31,32}, also shown by its most common derivatives has led to their use in medicine^{33,34} and chemical analysis^{35,36}.

The structure of alizarin is sketched in Figure 1, along with the atom labelling. The chromophoric functional groups (the two carbonyls at positions 9 and 10 and the two hydroxyls bound to carbons 1 and 2) are responsible for alizarin's optical properties in the visible region and, except for the carbonyl in position 10, they can also act as binding groups between the dye and the support base through an intermediate metal atom called *mordant*. Neutral free alizarin can exist in several tautomeric forms in solution while pH increase leads by subsequent deprotonation to mono-anionic and di-anionic forms (see Figure 2). Moreover, for alizarin complexes with metal cations, there are also different possibilities of metal-ligand complexation, namely, 1,2-dihydroxyl alizarin (1,2Aliz) or 1-hydroxy-9-keto alizarin (1,9Aliz) (see Figure 2). It has been postulated^{37,38} that alizarin complexes in

solution are essentially mixtures of these two forms. Absorption and emission processes of free and complexed alizarin in the UV-Vis energy range have been studied both experimentally^{4,39-42} and computationally⁴³⁻⁴⁵, including also environmental effects on the final optical properties. In fact, the strong dependence on environmental conditions (e.g. solvation) was well-known to artists who considered alizarin-based pigments as fugitive colours. This “real life” observation of colour modifications caused by ageing and exposition to pollutants have been confirmed by UV-Vis experimental analysis to be largely related to pH changes^{25,46}. However, the pH and the solvent are not the only possible factors responsible for modifying the chromatic properties of alizarin. Indeed, complexes formed with metals (Al(III), Cr(III), Ni(II), Cu(II), Zn(II), Cd(II), Fe(III))⁴⁷⁻⁴⁹ are reported to red-shift (from 0.34 to 1.55 eV, depending on the metal atom⁴⁷) the visible band with respect to the isolated chromophore, leading eventually to further changes in the madder colour⁵⁰. Both environmental effects are concomitantly present and influence madder lake colour changes, while computational studies allow to dissect the specific role of pH and non-specific environmental effects from the ones related to the metal complexation. In this work we have chosen to consider coordination with magnesium Mg(II) and aluminium Al(III), in order to dissect factors leading to their different effect on alizarin spectra properties, taking also into account that both these metals may act as binding sites in complex molecular systems. Better knowledge about the composition of such ancient pigments (e.g. Maya blue) can also lead to new materials like the stable nano-composites formed by alizarin with palygorskite (component of the Maya blue pigment) which represent innovative solid pH sensors inspired by Mayas “nanotechnologies”⁵¹. In this respect computational modeling of alizarin-metal complexes is a first, necessary, step toward modeling the hybrid nano-pigments⁵². As the complexes with Al(III), the most predominant ingredient of madder lake, have been the focus of several experimental and theoretical investigations⁵³⁻⁵⁵, a more detailed study will be performed on alizarin-Mg complexes, for which only some structural and thermodynamic properties^{47,49,56} are well established, despite the improved environment-friendship of this pigment. Moreover, alizarin complexes with different metal atoms show similar structures, with an almost unaffected anthraquinonic backbone and the metal atom placed very close the molecular plane⁴⁷. This suggests that some conclusions on the spectra line-shape and vibronic contributions can be quite general, and transferable to other alizarin-metal systems.

The paper is organised as follows: details on computational approaches including a discussion on methodological aspects of spectra simulations are gathered in section 2. Environmental, namely: metal complexation and pH effects, modifying electronic spectra line-shape, and in consequence pigment colour are discussed in section 3. General conclusions and perspectives for further developments and applications in cultural heritage and related fields are given in section 4.

2 Computational details

2.1 DFT and TD-DFT computations

All the electronic structure calculations have been performed using methods rooted into the density functional theory (DFT)^{57,58} and its time-dependent extension (TD-DFT)⁵⁹ for the

ground and excited states, respectively. For all systems, full geometry optimisations in the electronic ground state have been performed and followed by harmonic frequency computations. Then, vertical excitation energies (VE) and energy gradients have been computed for the relevant excited electronic states, at the ground-state geometries.

The long-range corrected CAM-B3LYP Coulomb attenuated functional⁶⁰ has been applied to all computations in view of its balanced description of both ground- and excited-state properties, including also vibrational frequencies⁶⁰⁻⁶². This functional has been also shown to perform well over a large spectral range with similar molecular systems, providing, for instance, accurate vertical excitation energies for 9,10-anthraquinone dyes⁶³ and reliable vibrationally-resolved absorption spectra line-shapes for a series of anthraquinoidic dyes⁶⁴. All computations have been performed employing the *aug*-N07D basis set^{65,66}, built from the reliable and effective N07D polarised double-zeta basis set^{67,68} (modified with respect to original formulation to include consistently diffuse *s* functions on all heavy atoms) by adding a set of diffuse *d* functions for heavy atoms.

In order to further check the reliability of adopted computational approach, the relative energies of the two tautomeric forms related to the proton transfer (PT) within the O(11)-H(15)-O(12) frame [PT9: O(11)-H(15)...O(12) and PT1: O(11)...H(15)-O(12)], and corresponding excitation wavelengths computed at DFT/TD-DFT level with CAM-B3LYP/*aug*-N07D have been compared to other theoretical approaches. Table 1 shows clearly that the relative stabilities of the two proton-transfer minima in the ground electronic state are confirmed by all theoretical models, with CAM-B3LYP, ω -B97XD^{69,70} and M06-2X^{71,72} giving PT1 structures slightly more stable than B3LYP⁷³ and PBE0⁷⁴. We note that CAM-B3LYP functional slightly underestimates the proton-transfer barriers, with the Mean Signed Deviations (MSD) lower than 1.5 kJ/mol, but larger deviations, both positive and negative are found for other functionals on their respective optimized geometries⁷⁵. Moreover, for all structures, the CAM-B3LYP/*aug*-N07D excitation energies agree well with the results from M06-2X and ω -B97XD, while standard B3LYP and PBE0 functionals predict the $S_1 \leftarrow S_0$ transition energy to be lower by about 0.4 eV. We note that on the basis of vertical excitation energies only it is difficult to define the best performing functional. The seemingly better agreement between PBE0 and B3LYP vertical excitation energies and experimental λ_{max} in solution may be attributed to the lack of vibronic and solvent dynamic effects as shown by the electronic spectra line-shapes reported in ESI and discussed in Ref.⁷⁶. Taking into account vibronic effects a good agreement with experiment for mono-anionic alizarin and its metal complexes has been obtained by computations with CAM-B3LYP *vide infra*. Moreover, CAM-B3LYP has been already shown to provide improvements over B3LYP for the description of Rydberg and charge transfer states⁷⁷, and recently it has been included (along with M06-2X and ω -B97XD) into the set of the eight best performing density functionals⁷⁸ recommended for excited electronic state studies. On these grounds this functional has been applied in all spectra simulations. We point out that in the present work we will focus on the analysis of electronic spectra line-shapes, which facilitate a qualitative interpretation of environmental effects on dye optical properties. In fact the absolute excitation energy may be often affected by the choice of functional while the band-shape is usually qualitatively well reproduced by several

functionals, at least as far as broad-band in solution are considered⁷⁹. In our opinion simulation of electronic-spectra line-shapes facilitates analysis of experimental results and helps to overcome difficulties related to the accurate estimates of excitation energies. Finally, we note that the *aug*-N07D basis set provides results fully consistent with its larger 6-311+G(d,p) counterpart also for ground- and excited-state energies for systems with Mg(II) and Al(III) ions.

Experimental studies of free and complexed alizarin have been performed in several polar^{25,45,53,80-82} and non-polar⁴⁶ solvents, with all spectra recorded in polar solvents (methanol⁸¹ and mixtures: water-methanol^{53,80}, water-DMSO^{25,45} or water-dioxan⁸²) showing essentially the same spectral features. In the following, the non-specific solvent effects are taken into account by means of C-PCM (*Conductor-Polarizable Continuum Model*)⁸³⁻⁸⁵ using the default parameters for the cavity definition. Moreover solvent effects on the vertical excitation energies are computed with the linear response LR-PCM/TD-DFT approach within the non-equilibrium regime^{59,86-90}. Additionally, specific solute-solvent interactions, namely the metal coordination by explicit water molecules for alizarin-Mg/Al complexes, and solvent effect on the proton transfer in the 1,2NT alizarin, have been taken into account considering up to four explicit H₂O molecules.

2.2 Simulation of electronic spectra line-shape

Computations of vibrationally-resolved electronic spectra have been performed through an integrated procedure (described in detail in references^{15,24}) based on the overlap integrals, also known as Franck-Condon (FC) integrals, between the vibrational wave-functions of the electronic states involved in the transition. It allows to define several computational models and levels of approximations related to the description of normal modes and electronic transition dipole moments. As a general rule, normal modes in the two electronic states are different and the resulting mode-mixing can be taken into account through a linear transformation proposed by Duschinsky⁹¹: $\mathbf{Q} = \mathbf{J}\mathbf{Q}' + \mathbf{K}$; where $\mathbf{Q}$ and $\mathbf{Q}'$ represent the mass-weighted normal coordinates of the initial and final electronic states, respectively; the Duschinsky matrix $\mathbf{J}$ describes the projection of the normal coordinate basis vectors of the initial state on those of the final state and vector $\mathbf{K}$ represents the displacements between the initial and the final state structures. In the present work we have chosen to resort to the vertical gradient model coupled to the Franck-Condon approximation (VG|FC). This is also known in literature as the linear coupling model (LCM)⁹² and relies on the observation that the most intense transitions are vertical. The VG model represents a good compromise between computational cost and accuracy, allowing also an analysis of the main vibronic contributions, whenever Duschinsky effects⁹¹ do not play an important role. The vertical approach is well-suited for the simulation of the broad features of the low-resolution spectrum in solution, and its VG approximation is particularly advocated whenever several electronic states and/or molecular systems need to be considered^{15,92,93}. In order to check the validity of the above mentioned assumptions for alizarin, the adiabatic models, namely Adiabatic Hessian (AH) and its approximated variant Adiabatic Shift (AH, see Ref.⁹³ for a more detailed discussion on the vertical and adiabatic approaches) have been applied to a case study, the lowest electronic transition of the di-deprotonated alizarin (labeled as DA in Figure 3), which shows three distinct features in the 450-650 nm range^{25,45} tentatively

assigned to the vibronic structure²⁵. Spectra simulated with the Adiabatic Shift (AS) and Adiabatic Hessian (AH) models, i.e. with the same normal modes and vibrational frequencies in both electronic states or with frequency differences and normal mode mixing taken into account, respectively, are presented in Figure 5. Both spectra, show very similar line-shapes, but slightly shifted positions in an absolute energy range. These results suggest that Duschinsky effects do not play a significant role and in this case they can be safely neglected (it is also evident from an analysis of overlap matrix $\mathbf{J}$ between the normal modes of the ground and excited electronic states, which is near-diagonal). On the contrary, a shift of the electronic transition origin ($\langle \mathbf{0} | \mathbf{0} \rangle$) should be ascribed to the frequency differences between initial and final states, which in turn affect zero point vibrational energies (ZPVE). It should be noted that the spectrum obtained by the most accurate (and computationally expensive) AH|FC model shows the best match with experiment, so agreement between simulated and experimental spectra discussed in the following sections could be improved by taking into account ZPVE changes. However, results for di-anionic alizarin suggest that since ZPVE corrections are nearly constant (of the order of 0.1 eV), they can be safely neglected in a qualitative analysis of the different effects influencing the overall spectra. Next, comparing the vertical and adiabatic models, we note that the difference between VG|FC and AS|FC is only related to different ways of estimating the shift vector ($\mathbf{K}$) between the equilibrium structures in both electronic states: the elements of the “vertical” $\mathbf{K}$ should be considered “effective” displacements, at variance with the correct displacement used in adiabatic methods. When the harmonic approximation is exact, the vertical and adiabatic approaches are equivalent. In all practical cases, they differ and both have strong and weak points. Generally speaking, adiabatic models are better suited for the analysis of the bands closer to the $\langle \mathbf{0} | \mathbf{0} \rangle$ origin and more generally reproduce better the fine structure of the spectra, while vertical models describe well the region of the spectrum maximum and give a better account of the most intense bands⁹³⁻⁹⁶. In the present case, the good agreement between VG and AS spectra confirms the reliability of the harmonic approximation. Finally, we note that the difference between the AH|FC and VG|FC models is mostly related to frequency changes. The latter lead to the shift of the $\langle \mathbf{0} | \mathbf{0} \rangle$ transition (in the same way the AS model) and to slightly different relative positions of the vibronic absorption maxima. However, both spectra show very similar overall line-shapes, while correction for zero-point vibrational energy (ZPVE) differences, more accurately taken into account in the AH approach leads to a red-shift smaller than 0.1 eV. In order to emphasize the good agreement between the experimental and simulated VG|FC spectra, in particular considering the relative position of the vibronic maxima, the simulated spectra have been red-shifted by 0.22 eV (52 nm, 32 nm would be required in the case of AH|FC). The same red-shift has been applied to the spectra obtained by simple convolution of the vertical excitation energy (with the same HWHM of 500 cm⁻¹ as applied to the VG FC spectra). Such a comparison, presented in Figure 4, clearly shows that inclusion of vibrational contributions is necessary to reproduce correctly the experimental outcomes and can not be obtained by increasing the HWHM used to convolute vertical energy. It is worth noting that agreement on the relative positions between experimental and simulated spectra can be improved also by mean of hybrid QM/QM' models. Such approaches allow to take into account the vibrational structure of electronic bands (computed at the TD-DFT level), and to correct the absolute values of vertical excitation energies by applying more accurate computational approaches⁹⁷

(e.g. larger basis sets, or coupled cluster models⁹⁸). On these grounds, application of VG|FC model to simulate the broad spectral features of free alizarin and its Mg(II) and Al(III) complexes is fully validated. We only note that AH approaches should be always considered for a detailed analysis of well resolved experimental spectra and for a preliminary validation of any approximated model, whenever a new system is to be studied.

Furthermore, in order to simulate the electronic spectra in the full UV-vis energy range, the ground-state equilibrium structure and harmonic frequencies have been computed, along with the energy gradient for each relevant excited electronic state, considering that dark states, which do not contribute to the spectra line-shape can be safely discarded. VE computations have been used to identify dipole-allowed electronic transitions with a medium-to-large oscillator strength (f) value, in order to select the excited states on which to focus our attention. The final FC|VG spectra for each system/conformer have been obtained by summing the single-state transitions of all excited electronic states considered. The stick spectra have been convoluted by means of Gaussian functions with half-width at half-maximum (HWHM) equal to 500 cm^{-1} , this value being chosen according to the broad features of the reference experimental absorption spectra^{25,45,80-82}. Moreover, it has been shown⁴⁴ that, in particular for the mono-anionic form, several, probably co-existing, tautomeric forms need to be taken into account in the spectra simulations. Thus, the final spectra have been obtained by adding the single tautomer contributions, with the weight of the i^{th} tautomer (P_i) computed by Boltzmann averaging at 298 K and 1 atm:

$$P_i = \frac{e^{\frac{-\Delta G_i}{Nk_bT}}}{\sum_{j=1}^n e^{\frac{-\Delta G_j}{Nk_bT}}} \quad (1)$$

where G_i is the relative Gibbs free energy of tautomer i with respect to the most stable one. N and k_b are the Avogadro and Boltzmann constants, respectively. The G_i computed by the standard harmonic-oscillator rigid-rotor (HRR) model have been sufficient for the purpose of the present work, while the computations with anharmonic-oscillator hindered-rotor approach⁹⁹ should be considered for more refined energetic study.

All calculations have been performed with the GAUSSIAN¹⁰⁰ suite of programs.

3 Results and discussion

3.1 Structure of Alizarin and its metal complexes

3.1.1 Free Alizarin—Formation of alizarin metal complexes, is preceded by the formation of ionic forms of alizarin, thus we start from discussion on the most stable tautomeric forms of neutral, mono- and di-anionic alizarin. All structures are shown in Figure 3, while Table 2 reports the most important geometry parameters, Gibbs free energy values (G) and Boltzmann populations. All structures correspond to local minima in the ground electronic state in methanol solution described by continuum (C-PCM⁸³⁻⁸⁵) models. For neutral alizarin, additional effects due to specific solute-solvent interactions have been considered and structures and properties of alizarin complexes with three explicit water molecules are also presented.

Two tautomeric forms of neutral alizarin differ by the the relative positions of their hydroxyl and carbonyl groups in dihydroxyanthraquinone structure, the 1,2NT and the 1,9NT respectively, with the former more stable by 22.7 kJ/mol (ΔG). Such an energy difference suggests that only a minor fraction of alizarin can be related to the 1,9NT tautomer under experimental conditions. Additionally, there are two possible forms of 9,10-dihydroxyanthraquinone, related to the proton position in the O(11)-H(15)-O(12) hydrogen bond, labelled PT1 and PT9, with the 1,2NT-PT1 significantly more stable (by 19.8 kJ/mol with solvent effects described by CPCM and by 34.5 kJ/mol if explicit solvent molecules are included). Thus, taking into account energetic properties the 1,2NT-PT1 form dominates under experimental conditions, and will be considered in the deprotonation reaction. We only note that the 1,2NT-PT9 form has been observed experimentally⁸¹ and discrepancy between computed ΔG and experimental findings has been ascribed to the sensitivity of proton transfer (PT) processes to environmental effects⁸¹, so that explicit solvent models might be required for a well-balanced description of their energetics¹⁰¹. However, our results show an opposite effect of explicit solvent. Thus, taking into account that the global minimum on the lowest excited-state potential energy surface (PES) corresponds to the proton-transfer structure, we suggest a more complex process, starting from the formation of 1,2NT-PT9 through an excited-state PT, followed by its relaxation to the ground state and the subsequent photon absorption of this tautomer⁶⁴.

An increase of pH leads to the deprotonation of alizarin, with two pK_a values, one in the 6.6-7.5 (pK_{a1}) and the other in the 11.8-12.1 (pK_{a2}) range while, at intermediate pH, the molecule is expected to be found in the mono-anionic form^{25,45}. The two different pK_a values suggest that deprotonation goes through two consecutive steps. The geometry parameters listed in Table 2 (e.g. the O(11)-H(15) and O(12)-H(16) distances of 1.66 Å and 2.14 Å, respectively) show that, from the two intermolecular hydrogen bonds of 1,2NT, the O(11)...H(15)-O(12) one, leading to the six-member ring, is significantly stronger than the O(12)...H(16)-O(13) one. This implies that the first deprotonation process is more likely to involve O(13)-H(16) (weaker hydrogen bond) and the removal of H(16). Indeed, the resulting 1,2MA-PT1 structure is the most stable one among all mono-anionic forms, as shown in this work and by the recent study by Prat *et al.*⁴⁴. The second deprotonation step leads to the unique di-deprotonated structure DA, which is characterised by similar distances between O(11)-O(12) and O(12)-O(13), of 2.746 Å and 2.702 Å, respectively, as expected from the lack of any stabilisation by hydrogen-bonding. Additionally, larger negative charges are located on more distant oxygen atoms (Mulliken charges of -0.81 for both O(11) and O(13), -0.75 for O(12)), but this effect is smaller than suggested in previous experimental works²⁵. Moreover, the largest increase of electron density is observed for O(14) (Mulliken charges of -0.86 and -0.62 for di-deprotonated and neutral forms, respectively), so it can be concluded that the negative charge is almost equally distributed over all oxygen atoms.

3.1.2 Mg/Al-Alizarin complexes—The structure of the metal-dye complexes, either 1,2-hydroxyanthraquinone (alizarin) or 1,2,4-hydroxyanthraquinone (1,2,4-HAQ), and the nature of their possible chemical interactions are still under debate¹⁰². However, the formation of di-nuclear chelated complexes shows energetic disadvantages deriving from

two adjacent and negatively charged oxygen atoms⁴⁸, and shall be only considered for other anthraquinoid resonant structures^{48,103,104}. Thus, we have chosen to study only mono-nuclear bidentate forms, which prevail with respect to the monodentate ones for similar systems^{49,105}. Four structures, each one derived from a specific MA conformer, have been considered in the preliminary studies for each metal. It has been shown that both the 1,9MA forms lead to the same 1-hydroxy-9-keto (1,9Mg/Al-Aliz) structure with the H(16) proton bound to the O(13) (as in 1,9MA-PT2), while in case of 1,2MA, two different conformers of 1,2-dihydroxyl (1,2Mg/Al-Aliz) with the H(15) proton bound to O(11) (PT9), or to O(12) (PT1), have been determined. The structures of 1,9- and 1,2-octahedral Mg/Al-Aliz(H₂O)₄ complexes are sketched in figure 6 while table 2 lists the most important geometry parameters and Gibbs free energy values (G). A more detailed study on the effect of Mg coordination by water molecules (see ESI for results on Mg-Aliz(H₂O)₂ complexes) showed that in all cases (tetrahedral and octahedral coordination) the metal-ligand bond is almost symmetric, so the central C(1)=O(12) bond is shortened, and the two lateral ones elongated with respect to the corresponding MA forms. The bond angles near the complexation site are generally less affected by changes in the coordination structure in 1,9Mg-Aliz than in 1,2Mg-Aliz, while bond angles within the aromatic system are not sensitive to complexation and coordination effects. Moreover, metal coordination by solvent molecules has a negligible effect on the spectral properties of the complex (see Table 6 and ESI), so, only hexa-coordinated Mg-Aliz(H₂O)₄ and Al-Aliz(H₂O)₄ will be discussed in the following.

3.2 Metal coordination effects on the spectra of Alizarin

3.2.1 $S_1 \leftarrow S_0$ transition of mono-anionic Alizarin—It has been suggested⁴⁴ that for mono-anionic alizarin, several tautomeric forms can co-exist in an experimental mixture, and contribute to the overall spectrum line-shape. Such effects can be also included in our model, taking into account the relative population of the tautomers. In principle, there are several possibilities to evaluate the composition of a complex molecular mixture. A first option is to simulate fully *ab initio* spectra, with the single contributions estimated from the Boltzmann populations, which in turn are based on more- or less-sophisticated computations of Free Energies (see for example Ref.^{99,106} for definition and application of elaborated theoretical models). Alternatively, the abundances can be estimated from the analysis of some relevant features of the experimental spectra and then used to simulate the overall band shapes¹⁰⁷. It is also possible to estimate relative amounts of sub-components by a procedure involving the fitting of theoretical spectra (varying contributions of single-component ones) to the observed experimental data. In fact, the most reliable conclusions about the molecular system composition can be drawn when both energetic and spectra computations lead to the same results. For mono-anionic alizarin, the fully computational approach, with the G_i in solution computed by standard CPCM model within the harmonic framework, has been applied. Following previous computational studies⁴⁴, all mono-anionic forms where the intramolecular hydrogen bond is preserved have been considered (see Fig. 3 and ESI), while structures with the hydroxyl group shifted in other molecular positions have not been taken into account as significantly less stable (≈ 40 kJ/mol⁴⁴). According to our computations, the most stable structure corresponds to the removal of H(16) (1,2MA-PT1), in line with expectations and previous observations^{44,47}. The second most stable tautomeric form is 1,9MA-PT1, followed by 1,9MA-PT2 and 1,2MA-PT9. The 1,9MA-PT1

form is stabilised through hydrogen-bonding creating a five-member ring, and is less stable than 1,2MA-PT1 (with six-member ring) by about 3.8 kJ/mol, so it accounts for about 16% of the total mono-anionic population. Finally, 1,9MA-PT2 is characterised by the bonding between H(16) and the O(13) carbonyl, a relative energy of about 5.3 kJ/mol, and a population of 9%. These three forms should be considered as participating significantly to the overall spectra, under experimental conditions, while the contribution of 1,2MA-PT9 (less stable by more than 20 kJ/mol) can be safely neglected.

The lowest-energy band of all tautomeric structures of alizarin is related to the HOMO-LUMO transition, and has the same $\pi \rightarrow \pi^*$ character, with essentially similar CT contribution. The $S_1 \leftarrow S_0$ transition leads to some electron density transfer from the catechol part to the leftmost aromatic ring of the molecule and, in particular, the electron density on O(11) increases, while it decreases on O(12) and O(13), as shown in Figure 8 for the 1,2NT(PT1) structure. The simulated VG|FC absorption spectrum related to the lowest electronic transition of mono-anionic alizarinates, obtained as a weighted sum of contributions deriving from the 1,9MA-PT1, 1,9MA-PT2 and 1,2MA-PT1 tautomeric forms is compared to its experimental counterpart measured in the 8–10 pH range^{25,45} in Figure 7. The single tautomer contributions are also reported, showing the absorption maxima near 455, 445 and 515 nm for 1,9MA-PT1, 1,9MA-PT2 and 1,2MA-PT1, respectively. Experimental λ_{max} is located at about 540 nm. MA4 shows the best match to experiment, supporting that this is the predominant mono-anionic tautomer, in line with the relative energetics. Moreover, taking into account all tautomers allows to improve the agreement with experiment, leading to a very good match between the simulated and observed spectra line-shape and the position of absorption maxima.

3.2.2 UV-Vis spectrum of Alizarin-Mg complexes—Simulated UV-Vis spectra of the 1,9Mg-Aliz and 1,2Mg-Aliz complexes are presented in Figure 9 showing in both cases good match with the experimental absorption spectra of Mg-alizarin in dioxane/water solution recorded in the full UV-Vis energy range (200–700 nm)⁸². The overall UV-vis spectrum is composed from the transitions to the first 12 excited electronic states, which are listed in the Table 4 and described through the most relevant molecular orbitals (MOs) (See ESI for MO plots). Except for the highest occupied molecular orbital (HOMO), which is localised mainly in the catechol part of the molecule, all other MOs are delocalised over the whole aromatic system. We also note, that all electronic transitions are localised on the aromatic ring, the molecular orbitals are not extended over the metal ion or solvent molecules (see the ELD plots of the Mg-alizarin complexes displayed in figure 9) and the MO shapes essentially match those of the free alizarin. The situation is similar also in the case of Al(III)-alizarin systems, in agreement with previous B3LYP studies⁵³. So, all electronic transitions have the same character as for the free molecule, mainly $\pi \rightarrow \pi^*$ in line with other theoretical studies performed at the DFT level^{48,53}. Furthermore, only the lowest electronic transition shows a partial charge-transfer (CT) character.

The qualitative interpretation of the UV-Vis spectrum leads in a first approximation to a subdivision into two main bands of increasing intensity located in the wavelength range of about 350–500 nm and 200–300 nm, with the latter showing also a small shoulder on the red-side energy wing. First band is related to the $S_1 \leftarrow S_0$ transition and is less intense, but is

directly responsible for the final colour of the complex. At variance, the most intense band is composed from several electronic transitions, which can be analyzed in detail based on the simulated results (see Figure 10). The possibility to dissect all individual contributions to the overall band-shape allow to identify the most appropriate energy ranges for specific spectrophotometric and fluorimetric measurements^{3,4} (e.g. fluorescence photography under UV light^{108,109}), or laser-assisted removal of overpaints¹¹⁰, as well as to study UV ageing processes^{1,111}. It is interesting to note that a proper account of the vibrational structure of electronic transitions within a static model allows a reliable representation of the overall spectra line-shape including the relative intensities of the observed absorption bands, which is not necessarily the case if simpler models (convolution of vertical excitation energies) are applied. As an example, the $S_1 \leftarrow S_0$ and $S_8 \leftarrow S_0$ contributions to the 1,9Mg-Aliz spectrum show very similar oscillator strengths (see Table 4), hence would result in similar intensity bands for spectrum line-shape obtained from convolution of Vertical Energies. This means, that depending on the choice of the HWHM (large or small), both bands would be broad and not intense, or narrow and intense, respectively. On the contrary, by taking into account the vibronic structure the total intensity corresponds to the area under line-shape, and not band height, as highlighted schematically in Figure 10. Indeed FC|VG computations leads to a broad $S_1 \leftarrow S_0$ band and a narrow $S_8 \leftarrow S_0$ band, in agreement with experimental findings. It has been already demonstrated¹¹² that the account for the band-shape resulting from the vibrational envelope of single electronic transitions can be important even for qualitative interpretation of experimental data. Thus, due to the relatively low computational cost of FC|VG simulations, it might be recommended to go beyond the simplest VE computations whenever feasible.

3.2.3 Electronic spectra of Mg(II)- and Al(III)-Alizarin complexes: visible energy range—

Comparison of the relative free energies between the two possible sets of structures shows a higher stability of the 1,9 complexes for both Mg(II) and Al(III). However, the complexation process of alizarin in alkali solutions obtained by adding Mg(II) or Al(III) salts follows few steps (see Figure 2). The deprotonation of neutral alizarin can be considered as a first step, with the relative stability of mono-anionic forms influencing the complex formation. Thus, taking into account the whole picture, that 1,9Mg/Al-Aliz can be formed from mono-deprotonated MA1 and MA2 whereas 1,2Mg/Al-Aliz originate from MA3 and MA4, and that the MA4 form is predominant (about 75%), it seems plausible to consider significant amount of the 1,2Mg/Al-Aliz in the experimental mixture. Along the same line, the 1,2Mg-Aliz proton transfer conformer (1,2Mg-PT9) can be safely excluded due to its unfavorable energetics (by about 10 kJ/mol with respect to 1,2Mg-PT1) and the fact that its lowest band absorption wavelength is red-shifted by about 100 nm. The situation is very different for 1,2Al-Aliz; in this case the 1,2Al-PT9 proton transfer conformer is more stable by about 20 kJ/mol and its spectra match well the experimental λ_{max} (~470 nm) while the $S_1 \leftarrow S_0$ electronic transition energy of 1,2Al-PT1 is blue-shifted by about 100 nm. It should be noted that, recently, the 1,2Al-PT1 proton-transfer conformer has been postulated as the one observed experimentally⁵³. This contradictory conclusion with respect to our analysis is to be ascribed to the different functional used in the other work to compute vertical excitation energies. In fact, as briefly discussed in section 2, the electronic energies of the $S_1 \leftarrow S_0$ transition (with a partial CT character), computed at the TD-B3LYP level,

are consistently under-estimated with respect to the TD-CAM-B3LYP ones. For this reason, we consider our results to be more reliable since the previous computations did not take into account the relative stabilities of the different tautomers in the ground electronic state.

As already mentioned, direct comparison between the simulated and experimental spectra of Mg-alizarin complex in dioxane/water solution⁸² and in the full UV-vis energy range (200-700 nm) presented in Figure 9, shows a good agreement for both the 1,9Mg(H₂O)₄ and 1,2Mg(H₂O)₄ complexes. Moreover, the much higher intensity of the 1,2Mg spectrum bands at about 270 nm, in line with the red-side shoulder of the experimental band may suggest that, indeed, both complex forms can probably co-exist in solution.

The simulated spectra in the visible energy range for alizarin complexes with Mg(II) and Al(III) are presented in Figure 11. For clarity, the spectra of 1,2Mg/Al-Aliz are shown, as the contributions of the 1,9 ones are not changing the qualitative picture. First, it can be noted that the experimentally observed metal complexation effects, that is to say a large blue-shift of the visible band with respect to the mono-anionic free alizarin for Mg and a small one for Al, along with the colour changes from orange (Mg) to red (Al), are well reproduced by simulation. Moreover, our results suggest that the differences in the alizarin spectral properties caused by Mg(II) or Al(III) complexation can be ascribed to the metal effect on the relative stability of the two proton-transfer tautomers in the O(11)-H(15)-O(12) hydrogen bridge.

Considering the band-shape of the $S_1 \leftarrow S_0$ electronic transition of Mg(II) and Al(III) alizarin complexes, 1,2Mg/Al-Aliz shows a structure-less, broad band, similarly to the neutral alizarin, while some vibronic structure (in the same way as the deprotonated forms) is observed only for 1,9Mg/Al-Aliz. More details are presented in Figure 12 and in Table 5, taking 1,9Mg-Aliz as an example. In line with the electronic transition localised on the aromatic structure, several vibronic transitions corresponding to in-plane vibrations of the aromatic system (19', 20') contribute to the intensity of the electronic band origin. Moreover, additional bands related to the C=O and O-H group vibrations (82') contribute to the spectra line-shape/broadening. Some changes with respect to the free alizarin, caused by metal complexation, involve additional vibronic bands at about 650 cm⁻¹, with respect to the energy of the $\langle 0 | 0 \rangle$ transition, which are related to the O-Mg-O bonding (49'). Considering both free and complexed alizarin, we can conclude that possible hydrogen bondings, in particular the strongest one O(11)-H(15)-O(12), lead to a band broadening and lack of defined vibronic structure, the latter being most pronounced for the fully deprotonated form. In view of alizarine-based pigments it can be suggested that more pronounced vibronic structure can be expected for bi-dentate binding schemes, and structures without intramolecular hydrogen bond. Moreover, results of the Mg(II)- and Al(III)-alizarin complexes in solution suggests that the presence of the metal does not change the nature of the electronic transitions. However, the spectral properties of both complexes are closely related to the relative stability of proton-transfer tautomers, which in turn is influenced by the presence and electronegativity of the metal ion. Thus, for magnesium-based madder lake, only minor colour modifications with respect to the neutral free dye and related to the metal complexation are observed, while the more positively

charged aluminium reverses the stability of the PT tautomers and causes colour change from yellow-orange to red.

3.3 Environmental effects on spectra of Alizarin: pH effects

The most relevant environmental effects on the electronic spectrum of free alizarin are related to the lowest electronic transition, which in fact is responsible for the overall molecular colour. Deprotonation has only a limited effect on the nature of the molecular orbitals (see ESI for the ELD and MO of all forms), but the orbital energies change significantly. Passing from neutral to di-anionic alizarin, the HOMO-LUMO gap and in consequence the vertical excitation energy decreases (see Table 6), and this effect is responsible for the net red-shift of the visible band. However, in addition to the shift in band position, deprotonation can affect also the spectra line-shape and absorption intensities, and such effects can not be easily accounted for by standard electronic structure computations. Experimental⁴⁵ and computed, vibrationally-resolved electronic spectra in the 350-700 nm range are compared in Figure 13. Experimental data refer to spectra measured at different pH conditions, so to neutral, mono-anionic and di-anionic forms, with absorption bands changing from a weak structure-less transition for neutral alizarin to a more intense band with multiple intense absorption maxima for the di-deprotonated species. The normalized experimental spectra have been reported, thus the simulated spectra, for which molar absorption coefficients (in $\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$) are directly computed have been scaled by a uniform factor, so to preserve the relative computed intensities between tautomeric forms.

It is evident that the simulated spectra reproduce qualitatively the bathochromic effect, spectra line-shape modifications and intensity changes observed upon deprotonation. In the case of DA, it has been postulated²⁵, that vibronic progressions are responsible for the band-shape. However, it is often non trivial to judge if the rich line-shape observed experimentally is related to the vibronic structure or shall be rather ascribed to different conformers¹⁴. Vibronic computations lead to a realistic spectra line-shape, thus allowing to compare and verify each hypothesis, and to analyse the band-shape tuning by the environment (pH range).

It can be noted that several vibrations give significant contributions to the band-shape of the $S_1 \leftarrow S_0$ transition (see ESI for single vibronic contributions and the corresponding normal modes of all tautomeric forms of alizarin). These are in-plane, low-frequency vibrations of the overall aromatic system, which are essentially present in the whole pH range, and remain equally important despite environmental changes. Additionally, some higher-frequency vibrations, namely stretchings and bendings of the C-OH and C=O groups contribute to the overall spectra line-shape. For neutral and mono-anionic forms, such vibronic transitions lead to the band broadening, whereas specific vibronic contributions become marked for the di-anionic form. In the latter case, it has been postulated, on the basis of the energy gap between the absorption maxima, that the vibronic structure is mainly due to the C=O stretching vibrations⁴⁴, while the present study suggests a more delocalised character of the most involved vibrational contributions 46DA and 50DA, reported in Figure 4. Finally we note that the simulated spectra reported here and obtained by applying in all

cases the same Gaussian broadening function with a HWHM of 500 cm^{-1} , reproduce qualitatively all experimental observations.

We note that absolute positions of the $S_1 \leftarrow S_0$ transitions for both proton transfer conformers of neutral 1,2NT alizarin are shifted by approximately 50 nm with respect to experiment. This discrepancy can be ascribed to the sensitivity of proton transfer (PT) processes to environmental effects^{81,101}, as well as to the effects of the choice of functional. We have tested both effects; Figure 14 shows that from the the computations performed with B3LYP, CAM-B3LYP and ω B97XD, with or without inclusion of few explicit solvent molecules, neither match the position absorption maxima, but all reproduce correctly the band shape. Moreover, it has been shown recently that the proton-transfer dynamic effects, which are not included in the present static model, are responsible for the band broadening and a larger red-shift⁷⁶.

4 Conclusions

An integrated computational approach has been applied to study structures and electronic properties of free alizarin and its Mg(II) and Al(III) complexes, in solution and under different pH conditions, with an emphasis on the simulation of optical spectra line-shapes directly comparable with their experimental counterparts. The present study demonstrates that environmental and/or complexation effects are qualitatively well reproduced by simulations, underlying the ability to dissect the role of several, concomitant effects in tuning optical properties. It is noteworthy that even structure-less broad electronic bands observed in UV-Vis spectra in solution hide a complex set of vibronic transitions, which are directly responsible for the spectra line-shape. The description of such effects requires a proper account of the vibrational contributions also to describe correctly the ratio in band intensity and respective broadening of the electronic transitions, in particular when they show similar oscillator strengths. The band shapes not only contribute to the correct interpretation of experimental findings, allowing more confident assignments of the electronic transitions, but provide also important improvements with respect to the purely electronic picture, being responsible for the colour perceived by the human eye. The latter aspect is particularly relevant for computational studies of pigments, including the ones used in painting or textile colouration over the years. Realistic computational studies including stereo-electronic, dynamic, and environmental effects already stand as very powerful tools to analyse the composition of original works of arts, and the effects that occurred over the years affecting both the material composition and their chromatic properties. In the next step, a support base linked with the dye through metal ligand shall be considered in a model following lines recently explored by some of us for similar systems⁵².

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1.
Molecular structure and atom labelling of Alizarin

Fig. 2.
Indicative alizarin deprotonation and complexation paths in weakly alkali media.

Fig. 3.
The most relevant tautomeric structures of neutral (NT), mono-anionic (MA) and di-anionic (DA) alizarin.

Fig. 4.

Experimental^{25,45} and theoretical electronic spectra of di-anionic alizarin. The spectra were computed at the VG|FC and VE levels, and red-shifted by 0.22 eV. Both theoretical spectra have been convoluted with a HWHM of 500 cm⁻¹. The VG|FC stick spectrum, which shows the single vibrational contributions to the $S_1 \leftarrow S_0$ electronic transition, is also presented. The most intense transitions for each distinct band are indicated by specifying the normal modes excited in the final state, depicted in the right panel, and the associated number of quanta

Fig. 5. Theoretical electronic spectra of $S_1 \leftarrow S_0$ electronic transition for di-deprotonated alizarin computed within vertical and adiabatic approaches: VG|FC, AS|FC, AH|FC, convoluted by HWHM of 500 cm^{-1} .

Fig. 6.

Possible metal-ligand equilibrium structures of the Mg/Al-Alizarin complexes in dioxane/ water solution (metal replaces one of the hydrogen atoms). The metal binds to the 1-hydroxy and the 9-keto groups and is stabilised in a 6-member ring (1,9Mg/Al-Aliz); the metal binds to the two hydroxyls in positions 1 and 2, leading to a 5-member ring (1,2Mg/Al-Aliz). In all forms, the remaining hydrogen atom creates a bridge with the other chelate ring. Mg-Alizarin complexes were optimized with the solvent described by CPCM model plus 4 water molecules in a solvation sphere. Both parallel and perpendicular (with respect to molecular plane) views are presented.

Fig. 7.

Experimental^{25,45} and theoretical electronic spectra of band I (*vide infra*) for mono-deprotonated alizarin. Simulated total spectrum (TOT) and its components: weighted contributions from three tautomers (1,9MA-PT1, 1,9MA-PT2 and 1,2MA-PT1).

Fig. 8.

Frontier molecular orbitals and changes in electronic density (ELD) during the HOMO→LUMO transition. The regions, which have lost electron density as a result of transition are shown in bright yellow, whereas the darker blue regions gained electron density. ELD densities have been evaluated with an isovalue threshold of 0.0004.

Fig. 9.

Vibrationally resolved electronic spectra of complexed alizarin (1,9Mg (red) and 1,2Mg (blue) forms) in dioxane/water solution, considering 4 explicit H₂O molecules. Experimental spectra were taken from Ref.⁸². For band I which corresponds to the $S_1 \leftarrow S_0$ (HOMO→LUMO) transition, changes in electronic density (ELD) are also reported. The regions, which have lost electron density as a result of the transition, are shown in bright yellow, whereas the darker blue regions gained electron density. ELD densities were evaluated with an isovalue threshold of 0.0004.

Fig. 10.

Total simulated VG|FC spectra for Alizarin Mg-complexes in dioxane-water solution, along with their single-state contributions. 1,9Mg-Aliz (upper panel) and 1,2Mg-Aliz (lower panel).

Fig. 11.

Electronic spectra line-shapes of lowest-energy band for Mg- and Al-alizarin complexes (1,2Mg (orange, dots) and 1,2Al (red, dot-dash)) in dioxane/water solution, simulated by considering 4 explicit H₂O molecules and dioxane modeled with CPCM. Experimental spectra were taken from Ref.⁸²

Fig. 12.
Vibronic contributions to the spectra band shape of the 1,9Mg(H₂O)₄ alizarin complex.

Fig. 13.

Experimental⁴⁵ (blue lines) and theoretical (black lines) electronic spectra of neutral, mono-anionic and di-anionic alizarin. The pH-induced red-shift of the visible band observed experimentally is clearly reproduced by the simulations.

Fig. 14.

Experimental⁸¹ and simulated electronic spectra of the neutral form of free alizarin computed with B3LYP, CAM-B3LYP and ω B97XD functionals and aug-N07D basis set. Simulated VG spectra of 1,2NT(PT1) in methanol solution (CH_3OH) described by CPCM model and by CPCM plus 3 explicit water molecules in the first solvation shell.

Table 1

Relative energies ($E_{PT}=E_{PT1}-E_{PT9}$ [kJ/mol]) of the two proton-transfer (PT1 and PT9) tautomers in the ground state, and absorption wavelengths (λ [nm]) of the $S_1 \leftarrow S_0$ (HOMO-LUMO) electronic transition for free neutral and mono-anionic Alizarin and 1,2Mg/Al-Alizarin complexes in methanol/water solution. DFT/TD-DFT computations with several density functionals and basis sets. Bulk solvent described by the CPCM model, specific solvent effects considered by adding $n=(4)$ water molecules in solvation sphere. All TD-DFT values computed within the non-equilibrium solvation regime.^a

Method	Alizarin				1,2Me-Alizarin complex							
	1,2NT				1,2MA				1,2Mg-Aliz/(H ₂ O) ₄			
	E_{PT}	λ_{PT1}	λ_{PT9}	E_{PT}	λ_{PT1}	λ_{PT9}	E_{PT}	λ_{PT1}	λ_{PT9}	E_{PT}	λ_{PT1}	λ_{PT9}
CAM-B3LYP/aug-N07D	-25.2	369	463	-21.6	506	588	-10.9	423	533	24.3	377	469
B3LYP/aug-N07D	-13.3	434	523	-16.5	619	677	-3.3	511	622	30.8	449	557
PBE0/aug-N07D	-19.9	418	508	-16.9	587	640	-2.6	488	599	30.3	430	535
CAM-B3LYP/6-311+G(d,p)	-30.3	368	462	-23.7	501	587	-13.7	423	532	21.9	376	468
B3LYP/6-311+G(d,p)	-23.3	434	522	-18.0	611	674	-5.9	511	621	28.5	448	556
PBE0/6-311+G(d,p)	-22.0	417	506	-15.8	583	643	-5.1	488	598	27.9	429	534
ω -B97XD/6-311+G(d,p)	-30.8	365	459	-25.3	492	581	-14.4	417	525	23.8	373	463
M06-2X/6-311+G(d,p)	-32.1	370	461	-25.6	496	593	-16.1	415	533	19.4	375	463
Exp.	430 ^b , 429 ^c		550 ^b	540 ^b		427.5 ^d		479.5 ^d , 473 ^c				

^a Geometry structures of alizarin and its complexes are depicted in Figures 3 and 6, respectively.

^b Experimental data from Ref. 81 measured in methanol solution.

^c Experimental data from Ref. 53 measured in methanol-water solution.

^d Experimental data from Ref. 82 measured in dioxan-water solution.

Table 2

Ground-state equilibrium structures and relative free energy values for the alizarin tautomeric forms in methanol solution. All computations were done at the CAM-B3LYP/*aug*-N07D//CPCM level. Bond lengths are in Å, angles in degrees, G in kJ/mol

Bond / Angle	1,2NT			1,9NT			1,9MA			1,2MA			DA
	PT1	PT1(H ₂ O) ₃	PT9	PT9(H ₂ O) ₃	PT1	PT2	PT1	PT2	PT9	PT1	PT9	PT1	
C(9)=O(11)	1.238	1.243	1.295	1.312	1.299	1.227	1.227	1.233	1.313	1.245	1.245	1.248	
C(1)=O(12)	1.342	1.342	1.279	1.287	1.332	1.343	1.343	1.273	1.265	1.340	1.340	1.256	
C(2)=O(13)	1.349	1.340	1.344	1.339	1.270	1.277	1.277	1.345	1.250	1.261	1.261	1.269	
C(10)=O(14)	1.223	1.228	1.223	1.241	1.230	1.236	1.236	1.230	1.247	1.239	1.239	1.254	
O(12)-H(15)	0.997	0.992	1.454	1.410	1.718	-	-	-	1.456	0.992	0.992	-	
O(13)-H(16)	0.969	0.989	0.974	0.991	1.819	1.805	0.991	-	-	-	-	-	
O(11)-H(15)	1.662	1.631	1.046	1.061	0.985	-	-	1.037	1.620	1.620	1.620	-	
O(12)-H(16)	2.138	2.332	2.100	2.417	0.999	0.991	1.810	-	-	-	-	-	
O(11)-O(12)	2.548	2.530	2.439	2.414	2.577	2.716	2.806	2.431	2.523	2.696	2.696	2.702	
O(12)-O(13)	2.665	2.742	2.670	2.822	2.511	2.521	2.513	2.736	2.736	2.696	2.696	2.702	
C(9)-C(17)-C(1)	119.1	119.3	117.7	118.1	120.9	121.5	120.9	117.9	119.2	119.2	119.2	120.5	
O(11)-C(9)-C(17)	120.7	120.4	120.1	119.9	122.1	123.1	124.2	121.3	121.8	121.8	121.8	125.9	
C(17)-C(1)-O(12)	123.7	122.6	123.2	120.8	123.1	125.3	128.8	121.4	122.1	122.1	122.1	125.0	
C(2)-C(1)-O(12)	116.3	117.3	119.2	121.5	113.1	112	114.4	119.4	115.9	115.9	115.9	116.7	
C(1)-C(2)-O(13)	119.5	122.0	116.6	121.3	115.0	116.1	113.1	119.1	120.8	120.8	120.8	119.3	
O(11)-H(15)-O(12)	146.4	147.7	154.2	154.9	143.5	-	-	154.0	149.5	149.5	149.5	-	
O(12)-H(16)-O(13)	112.6	103.8	115.6	103.7	123.3	126.2	125.0	-	-	-	-	-	
G_i (kJ/mol)	0.0	0.0	19.8	34.5	22.7	3.8	5.3 (2.2) ^a	21.6 (18.0) ^a	0.0 (0.0) ^a	-	-	-	

^aData taken from reference⁴⁴

Table 3

Ground-state equilibrium structures and relative free energy values for the complexed alizarin in solution. All computations were done at the CAM-B3LYP/*aug*-N07D//CPCM level. Bond lengths are in Å, angles in degrees, G in kJ/mol

Bond / Angle	Mg-Aliz(H ₂ O) ₄			Al-Aliz(H ₂ O) ₄		
	1,9Mg	1,2Mg-PT1	1,2Mg-PT9	1,9Al	1,2Al-PT1	1,2Al-PT9
C(9)=O(11)	1.255	1.244	1.298	1.259	1.247	1.294
C(1)=O(12)	1.302	1.372	1.298	1.338	1.372	1.323
C(2)=O(13)	1.346	1.308	1.293	1.340	1.331	1.328
C(10)=O(14)	1.220	1.221	1.230	1.223	1.221	1.222
O(12)-H(15)	-	1.013	1.501	-	1.056	1.621
O(12)-Al/Mg	1.957	2.102	2.074	1.833	1.947	1.884
O(13)-H(16)	0.975	-	-	1.012	-	-
O(13)-Al/Mg	-	1.971	2.004	-	1.819	1.828
O(11)-H(15)	-	1.548	1.026	-	1.445	1.001
O(11)-Al/Mg	2.001	-	-	1.873	-	-
O(12)-H(16)	1.965	-	-	1.639	-	-
O(11)-O(12)	2.744	2.479	2.456	2.740	2.422	2.532
O(12)-O(13)	2.578	2.632	2.644	2.427	2.560	2.566
C(9)-C(17)-C(1)	121.1	119.2	118.6	121.4	118.4	120.0
O(11)-C(9)-C(17)	123.1	120.1	120.7	120.6	119.2	120.7
C(17)-C(1)-O(12)	126.9	121.5	122.2	129.0	121.7	123.4
C(2)-C(1)-O(12)	114.9	115.4	117.6	111.4	114.8	115.9
C(1)-C(2)-O(13)	116.2	118.5	116.8	111.7	116.1	115.1
O(11)-H(15)-O(12)	-	150.2	152.3	-	150.8	148.9
O(11)-Al/Mg-O(12)	87.5	-	-	95.3	-	-
O(12)-H(16)-O(13)	118.6	-	-	131.1	-	-
O(12)-Al/Mg-O(13)	-	80.4	80.8	-	85.6	87.5
G_i	0.0	25.2	34.0	0.0	39.1	19.2

Table 4

Excited state properties of 1,9 and 1,2 Mg-Alizarin complexes in dioxane/water solution, with solvent described by the CPCM model and 4 water molecules in solvation sphere, computed at the TD-CAM-B3LYP/aug-N07D//CPCM level within the non-equilibrium solvation regime. Vertical excitation energies (VE) [eV], absorption wavelengths (λ [nm]), oscillator strengths (f) and dipole moment (μ [Debye]) are reported along with the most important molecular orbitals (MOs) involved in the transitions.

1,2Mg-Aliz(PT1)						1,9Mg-Aliz					
MOs	VE [eV]	λ [nm]	State	μ^a [D]	f	MOs	VE [eV]	λ [nm]	State	μ^b [D]	f
H-1 $\rightarrow$ L+1	5.45	227	S ₁₂	16.74	0.39	H-6 $\rightarrow$ L	5.51	225	S ₁₂	20.39	0.00
H-3 $\rightarrow$ L+2	5.39	230	S ₁₁	20.11	0.00	H-1 $\rightarrow$ L+2	5.39	230	S ₁₁	16.41	0.52
H-6 $\rightarrow$ L	5.35	232	S ₁₀	23.43	0.00	H-2 $\rightarrow$ L+1	5.31	233	S ₁₀	16.00	0.00
H $\rightarrow$ L+2	5.31	233	S ₉	18.29	0.05	H-1 $\rightarrow$ L+1	5.23	237	S ₉	19.27	0.35
H-4 $\rightarrow$ L	4.76	260	S ₈	20.52	0.28	H-4 $\rightarrow$ L	4.78	259	S ₈	6.47	0.27
H $\rightarrow$ L+1	4.70	264	S ₇	5.35	0.00	H $\rightarrow$ L+1	4.78	259	S ₇	19.06	0.00
H $\rightarrow$ L+1	4.52	274	S ₆	23.75	0.51	H $\rightarrow$ L+2	4.48	277	S ₆	21.56	0.09
H-2 $\rightarrow$ L	4.19	296	S ₅	16.39	0.01	H-3 $\rightarrow$ L	4.23	293	S ₅	19.37	0.11
H-5 $\rightarrow$ L	4.05	306	S ₄	22.31	0.00	H-5 $\rightarrow$ L	4.09	303	S ₄	21.31	0.00
H-1 $\rightarrow$ L	3.81	325	S ₃	21.16	0.09	H-1 $\rightarrow$ L	3.59	345	S ₃	18.70	0.06
H-3 $\rightarrow$ L	3.39	366	S ₂	17.41	0.00	H-2 $\rightarrow$ L	3.32	374	S ₂	15.84	0.00
H $\rightarrow$ L	3.00	413	S ₁	24.83	0.13	H $\rightarrow$ L	2.90	428	S ₁	19.16	0.23

^a Ground state Dipole moment = 20.12D

^b Ground state Dipole moment = 18.99D

Table 5

Most intense vibrational contributions to the Mg-Alizarin $S_1 \leftarrow S_0$ electronic transition. Energy and intensities of single vibronic contributions for $1,9\text{Mg}(\text{H}_2\text{O})_4$ -Alizarin complexes in dioxane/water solution are reported, with the solvent described by the CPCM model. The absolute energy of the ($S_1 \leftarrow S_0$) transition and the relative energies of the three most intense transition from fundamental state to the single overtones $\langle \mathbf{0} | \mathbf{0} + 1_n \rangle$

Transition	Energy [cm^{-1}]	Intensity
$\langle \mathbf{0} \mathbf{0} \rangle$	21 005	$0.2671 \cdot 10^7$
1_{19}	218	$0.5268 \cdot 10^6$
1_{20}	224	$0.8197 \cdot 10^6$
1_{49}	654	$0.4953 \cdot 10^6$
1_{82}	1518	$0.6316 \cdot 10^6$

Table 6

Properties of the $S_1 \leftarrow S_0$ (HOMO-LUMO) electronic transition of free alizarin (in ethanol/water solution), Mg-Alizarin(H_2O)₄ complexes and Al-Alizarin(H_2O)₄ complexes (in dioxane/water solution). Bulk solvent (ethanol/dioxane) described by the CPCM model, specific solvent effects considered by adding $n=4$ water molecules in a metal coordination sphere. Vertical excitation energies (VE) [eV], absorption wavelengths λ [nm], oscillator strengths (f) and dipole moment (μ [Debye]) are reported. All values are computed at the TD-CAM-B3LYP/*aug*-N07D//CPCM level within the non-equilibrium solvation regime.

Form	VE [eV]	λ [nm]	μ	f
1,2NT(PT1)	3.36	369	5.2	0.20
1,2NT(PT9)	2.67	463	1.1	0.30
1,9MA(PT1)	2.78	446	11.5	0.25
1,9MA(PT2)	2.82	440	9.5	0.27
1,2MA(PT1)	2.45	506	15.0	0.21
1,2MA(PT9)	2.10	588	9.7	0.27
DA	2.37	523	19.2	0.44
1,9Mg	2.90	428	19.2	0.23
1,2Mg(PT1)	3.00	413	24.8	0.13
1,2Mg(PT9)	2.33	533	25.9	0.21
1,9Al	2.79	445	29.4	0.15
1,2Al(PT1)	3.24	383	26.7	0.10
1,2Al(PT9)	2.75	451	30.4	0.15