Editor's Choice

Modeling of charge transfer processes to understand photophysical signatures: The case of Rhodamine 110

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A B S T R A C T

Photophysical signatures, namely absorption and emission energies, lifetime and quantum yields, have been computed through TD-DFT approaches and compared with experimental counterparts for the Rhodamine 110 dye in aqueous solution. Thanks to a new protocol of analysis, based on the use of very promising electronic based indices, it has been possible to investigate the interplay between Rhodamine 110 dye's structure, degree of charge transfer upon excitation, and fluorescence signatures. This combined analysis is very promising to support the understanding of charge transfer based mechanisms affecting dyes photophysics.

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1. Introduction

In recent years, the interest for chromophores suitable for fluorescence signaling and encoding [1,2], such as fluorescence encoding multiplex system [3–5], has drammmatically grown.

Among the great amount of fluorophores nowadays available on the market, rhodamine dyes family has distinguished for its photo physical properties [6], well suited for a variety of applications [7–9].

Many of rhodamine derivatives present a very high quantum yield, ϕ, in both aqueous and organic solvents [10,11], Rhodamine 101, for example, is used as quantum yield standard due to the near unity ϕ in a variety of solvents [12–14]. Nonetheless, the modeling of rhodamines photophysical signatures still remains a challenging purpose considering that, for example, in spite of a great number of works [11,15–18], a full photophysical characterization of rhodamine dyes is far to be completely set up. Recently, from a theoretical point of view, particular care has been paid to reproduce the different quantum yields of the various rhodamine dyes [19] and

to give a mechanistic insight for their radiative and non-radiative decay pathways [20].

Indeed among possible non radiative decays, several authors recently proposed that both intra- and inter-molecular photoinduced electron transfers (PETs) for Rhodamine B and Rhodamine 101 [12,21] constitute suitable pathways.

In this context, theoretical approaches can be of great support to provide a more detailed description of the phenomena occurring at the excited state. A first challenge, when treating photophysical processes, regards the accurate description of both the ground and the excited potential energy surfaces (PES) associated to a given phenomenon, allowing one to provide a deep understanding and control over excited state events.

It was observed that the presence of an excited state with a significant degree of charge transfer from the xanthene toward the phenyl moiety is a peculiar feature of lower quantum yields rhodamines [19].

In order to investigate further these charge transfer (CT) events and to finely understand the related processes, an interpretation of the CT phenomenon is necessary and can be provided by the theoretical simulations. In this respect, density based tools, such electronic density based indices [22], namely parameters ad hoc designed to search and analyze the excited state evolution [23], could provide substantial insight on possible excited state signatures [23–27] and minimum energy reaction pathways [23].

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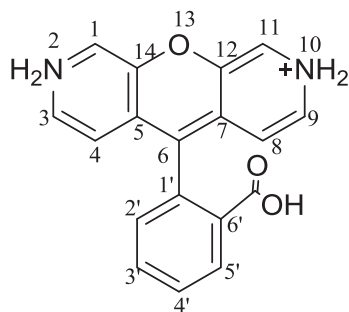
Scheme 1. Rhod110 structure and labels.

In this work a combined protocol making use of TD-DFT approaches and densities based indices is applied to disclose the photophysical signatures of the two states involved in Rhodamine 110 (Rhod 110, Scheme 1 for structure and labels) excited state behavior.

To illustrate this approach all photophysical signatures (lifetime, quantum yield, absorption and emission maxima and charge transfer character) will be considered and computed in the case of Rhodamine 110 (Rhod 110, Scheme 1) in aqueous solution.

The letter is organized as follows: after a description of the adopted computational protocol and of electronic density indices here applied (Section 2), the calculated photophysical properties are presented in Section 3.1 and interpreted in Section 3.2. Finally some general conclusions are given in Section 4.

2. Computational details

DFT and TD-DFT [28–30] were employed to obtain both ground and excited state minimum energy structures for Rhod110.

The solvent, water in all cases, was described by the conductor-like continuum model, CPCM, including also the non-electrostatic terms for cavitation, dispersion, and repulsion [31].

Structure optimizations were performed at the B3LYP-D/6-31+G(d,p)/CPCM and TD-B3LYP-D/6-31+G(d,p)/CPCM levels of theory for the ground and excited states, respectively.

Grimme correction was also included in the B3LYP [32] functional, to account for dispersion forces [33].

The same level of theory was exploited to obtain emission signatures. Radiative decay constant, K_r, calculated radiative lifetime, τ_r, and quantum yield ϕ, were obtained according to a protocol previously formulated by some of us [19] which will be summarized in the following.

By considering the S_1 minimum energy structure as the one from which the fluorescence event takes place, it is possible to calculate the radiative decay constant, K_r, according to:

$$K_r = \frac{4}{3} \frac{\Delta E^3}{c^3} \mu_{10}^2 \tag{1}$$

where ΔE is the emission energy at the S_1 minimum, c is the light speed and μ_{10}^2 is the transition dipole strength. It follows that, the fluorescence lifetime, τ_r, is simply the inverse of K_r:

$$\tau_r = \frac{1}{K_r} \tag{2}$$

Finally, it is possible to obtain the quantum yield, ϕ, by combining the computed K_r with the experimental lifetime, τ_{exp} as follows:

$$\Phi = \frac{\tau_{exp}}{\tau_r} \tag{3}$$

For the analysis of the charge transfer character along a path connecting the Franck–Condon structure (min_{S0}) and the S_1 minimum energy structure (min_{S1}) a linear synchronous path (LSP)

Table 1
Main structural parameters for ground (S_0) and excited (S_1) minimal energy structures of Rhod110 (distances in Å and dihedral angles in degree).

	S_0	S_1
C_{14}-O_{13}	1.36	1.37
C_{12}-O_{13}	1.36	1.37
C_1-N_2	1.35	1.42
C_{11}-N_{10}	1.35	1.35
C_6-$C_{1'}$	1.49	1.47
C_{14}-C_5	1.43	1.43
C_{12}-C_7	1.43	1.42
$|\chi_1|$	113.00	128.29
$|\chi_2|$	12.41	10.17

along 9 intermediate structures linking them was set up. Hence, the S_0 defined linear synchronous coordinate, C_{LSP}, represents the structural evolution from the min_{S0}, ($C_{LSP} = 0$) to the min_{S1} ($C_{LSP} = 1$). Energy profiles for both the ground and S_1 excited states were calculated at (TD)-B3LYP-D/6-31+G(d,p)/CPCM level. To obtain a description of the degree of the CT character along the LSP a D_{CT} analysis was performed. For a detailed description of the D_{CT} index please see Ref. [22]. Shortly, D_{CT} index is the distance between barycenters of two collection of spatial points, ρ_+ and ρ_-, which represent, respectively, the grid points in which an increment or a depletion of the electron density results upon the absorption event, giving a measure of the electronical reorganization upon the vertical excitation.

Moreover, a new index, $D_{CT,react}$ [23] has been applied to follow the evolution of Rhod110 along the LSP. This index describes the reorganization due to both electronic and structural changes going from the minimum on the S_0 potential energy surface to a given point on the S_1 PES. It follows that for S_0 minimum energy structure, the D_{CT} and $D_{CT,react}$ values coincide.

All calculations were performed with the GAUSSIAN09 suite of programs [34]. D_{CT} and $D_{CT,react}$ indices were evaluated using a in house developed software, as previously described in Ref. [22].

3. Results and discussion

3.1. Photophysical signatures

In analogy with previous studies on Rhodamine19 [19], Rhodamine 110 (Scheme 1) has been considered in its cationic form. Before describing in more details the photophysical signatures of Rhod110, ground and excited state structures will be briefly illustrated.

Rhodamine 110 consists of two molecular moieties: (i) the xanthene ring and (ii) a phenyl group with a carboxylic substituent at the C_6 (Scheme 1). Overall, the main structural features can be monitored considering two dihedral angles: χ_1 which regulates the relative orientation of the phenyl substituent and the xanthene molecular portion, and χ_2 which describes the torsion of the carboxyl substituent with respect to the phenyl one. In Table 1, the main structural parameters computed for Rhod110 are reported for both the ground and the excited state minimum energy structures.

On inspection of Scheme 1 it can be observed that structures with high symmetry are those dihedral angles $|\chi_1|$ and $|\chi_2|$ close to these values 90° and 0°, respectively. Any variation from these values reveals a distortion from the overall ideal C_s symmetry. As observed in a previous work [19], the subtle balance between non classical (i.e. dispersion forces) and coulombic interactions along with solvation effects modulate the χ_1/χ_2 values. While coulombic interactions and steric hindrance between carboxyl and xanthene groups stabilize a symmetrical structure, dispersive forces involving the two molecular moieties can favor a more distorted orientation. Moreover favorable interactions of the