A combined theoretical and experimental study of the ultrafast photophysics of Rhodamine B

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ABSTRACT

The ultrafast dynamics of zwitterionic and cationic Rhodamine B in ethanol have been investigated using TDDFT calculations and ultrafast transient absorption spectroscopy. The calculations show that the zwitterionic form exhibits an electronically excited dark state which could potentially quench the initially photoexcited state, while in the case of cationic form the lowest excited lying dark state is outside the energy region of interest and cannot explain its quenching. Due to similarities in the relaxation dynamics of the two molecules, it is suggested that the electronically excited dark state may not play such an important role in the quenching process of this dye as previously proposed. Experimental evidence presented suggests that a quenching mechanism is active on the picosecond timescale for both forms of Rhodamine B.

1. Introduction

Rhodamine dyes are xanthene derivatives (the structure of Rhodamine B – RhB – is reported in Figure 1) with high absorption cross-sections, high fluorescence quantum efficiencies in the visible range and high photostability. For these reasons they have been used in a wide range of applications such as laser dyes [1] and fluorescence standards [2,3]. Furthermore, these properties have led to RhB being used in the field of biophysics such as in cytometry and fluorescence microscopy [4].

Although the photochemistry of these molecules has been studied for decades, a complete and definitive description of the dynamics of the Rhodamine dyes has not yet been provided. Part of the reason for this lack of clarity is the complexity of the system. For example, in the case of RhB the molecule can exist in three forms; the cationic or protonated form (in acidic solution), the zwitterion (in basic solution) and the lactone (in aprotic solution) and indeed in equilibrium between these structures in many solvents. Furthermore, dimerisation of the RhB takes place in polar solutions of water [5,6]. Clearly each of these forms has distinct photophysical characteristics and a great deal of research has been performed on the temperature, solvent and pH dependence of the photophysics of these molecules.
On the other hand, also a great deal of research has been invested in the dependence of the photophysical properties of the Rhodamines on the substituents of both the amino groups and the carboxyphenyl group [5,7,8]. Through these studies and others, for example, it was observed that if the substituents on the amino groups are either immobilised by a rigid bridge structure (Rhodamine 101 – Rh101 – see Figure 1 for structure) or are H-atoms (Rhodamine 110 – Rh110 – see Figure 1 for structure) then the quantum efficiency for fluorescence is almost unity while the fluorescence of RhB, where the substituent group is flexible, is significantly quenched (fluorescence quantum yield, $\phi_f = 0.7$ for zwitterionic RhB in ethanol [9]). This points to an internal conversion (IC) with both activated and non-activated pathways.

Many models have been proposed in which the activated radiationless decay depends on a variable barrier between the initially photoexcited state and a twisted intramolecular charge transfer (TICT) state, thus explaining the solvent-dependent quantum yield, fluorescence lifetimes and other photophysical properties of many Rhodamines [10–16]. The precise nature of the TICT state involved in this process is somewhat less clear with a large number of models being proposed. In general, the activated channel is assigned to a charge transfer (CT) from one part of a molecule to another following the photoexcitation and a subsequent change in the geometry of the excited state. Initially the most accredited model was the CT from the amino groups to the xanthene ring followed by a twisting of the amino group about the C-N bond [17,18]. The main point being that if the rotation about the amino C-N bond cannot take place the twisted state cannot be formed and thus no quenching occurs.

This model continues to expound support with a very recent comprehensive study which examined the photophysics of phenyl, thienyl and chalcogen substituted Rhodamine dyes also siding with this analysis of the photophysics [19]. Another theory involves the amino groups and their umbrella-like motion. In this case a CT between xanthene and the amino groups followed by an umbrella-like motion of the amino group was proposed [20,21]. Yet another model suggests a process which involves a CT amino $\rightarrow$ xanthene followed by another CT from xanthene $\rightarrow$ phenyl [7]. The involvement of the phenyl group has also been invoked by Savarese et al. [8] who suggest that the CT is due to transfer of electronic density from the xanthene ring to the phenyl moiety. Recently, also the carboxylic group has been called into play in a work suggesting that this group acts as a donor for CT to the xanthylum (at least in the case of RhB) [22]. In this last case the difference in the $\phi_f$ of RhB and Rh101 (constrained amino-alkyl groups) was explained as being due to the presence of a CT state ($S_2$) which crosses the initially locally excited state ($S_1$). The resulting CT state was found to be dark thus leading to quenching channel, while in contrast this CT was not found to exist at low energies in the case of Rh101 thus explaining the lack of quenching in this case without referring (directly) to the inhibition of the rotation of the amino groups.

In light of these various interpretations of the dynamics of the Rhodamine dyes we have decided to perform calculations on the electronically excited states of both the zwitterionic and cationic forms of RhB. Furthermore, we have revisited the short timescale dynamics of both forms of the RhB molecule using transient absorption spectroscopy.
2. Theoretical methods

The description of the geometries and of the electronic structures of the solvated zwitterionic and cationic molecules has been carried out using a density functional theory (DFT) formalism coupled with the polarisable continuum model based on reaction field calculation and the integral equation formalism [23,24]. The excited states have been studied within the time-dependent DFT approach (TDDFT) [25]. The hybrid exchange–correlation functional B3LYP (which stands for Becke, three-parameter, Lee–Yang–Parr) [26–29] has been adopted together with the split-valence double-zeta Pople basis set [30,31] with the addition of extra functions as established by Barone et al. [32] to be used in the framework of effective discrete/continuum solvent models. This basis set consists of the 6-31G plus basis functions described in Table 1 of the above cited paper of Barone and co-workers [32]; this basis set is the parent of the 6-31+G(d,p), and has been specially re-parametrised for use with the B3LYP functional.

In order to check the reliability of the B3LYP functional applied to the calculation of excitations with CT character as is the case for RhB, we have tested the long-range corrected hybrid functional CAM-B3LYP [33] to verify if the non-corrected functional B3LYP is sufficient to correctly reproduce the measured vertical excitation energy of RhB. As a result, we have found that the vertical excitation energy of the zwitterion of RhB is 2.968 eV when calculated using the TD-CAM-B3LYP functional, whereas it is 2.514 eV with TD-B3LYP, which is in better agreement with the experimental value of 2.21 eV. Hence, we conclude that the long-range correction in CAM-B3LYP over corrects the transition energies and therefore all the calculations were carried out with B3LYP functional.

The geometries were fully optimised for the ground and first two excited electronic states. Table 1 reports the geometrical parameters for the zwitterionic and cationic forms of RhB in the minimum energy geometries of the S_0, S_1 and S_2 electronic states. The energy levels of the initially excited and relaxed states of the zwitterionic and cationic forms of RhB are reported in Figure 2. For the S_2 state in zwitterionic Rhodamine B, the minimum energy point corresponds to the crossing between the S_1 and S_2 states (see Section 4). Table 2 reports the excitation energies for the vertical transitions from the S_0 ground state to the S_1 and S_2 excited states in the minimum energy geometry of S_0, i.e. S_1 ← S_0 and S_2 ← S_0, respectively; and the emission energy for the vertical transition from the S_1 (and S_2) excited state to the S_0 ground state in the minimum
Table 1. Geometrical parameters for the zwitterionic and cationic form of Rhodamine B in the minimum energy geometry of the $S_0$, $S_1$ and $S_2$ electronic states. $\tau$ is the dihedral angle for the xanthene-phenyl rotation, and $\gamma$ is the dihedral angle for the carboxyl-phenyl rotation. The $\alpha$ angles refer to the dihedral angles of the amino groups (see Figure 1). The related cartesian coordinates are reported in Tables S1–S6 of the supplementary material.

|        | Zwitterion | Cation |
|--------|------------|--------|
| $S_0$  | $S_1$      | $S_2$  |
| $\tau$ | 96.8       | 98.8   |
| $\gamma$ | 0.8       | 37.2   |
| $\alpha_1$ | 9.4         | 21.5   |
| $\alpha_2$ | 8.7         | 21.4   |
| $\alpha_3$ | 3.8         | 5.2    |
| $\alpha_4$ | 3.2         | 4.6    |
| $S_0$  | $S_1$      | $S_2$  |
| $\tau$ | 91.9       | 120.3  |
| $\gamma$ | 1.1       | 11.2   |
| $\alpha_1$ | 8.3         | 6.6    |
| $\alpha_2$ | 8.0         | 5.9    |
| $\alpha_3$ | 3.0         | 2.9    |
| $\alpha_4$ | 2.7         | 1.8    |
| $S_0$  | $S_1$      | $S_2$  |
| $\tau$ | 123.7      | 123.7  |
| $\gamma$ | 18.5       | 18.5   |
| $\alpha_1$ | 7.9         | 7.9    |
| $\alpha_2$ | 6.9         | 6.9    |
| $\alpha_3$ | 4.9         | 4.9    |
| $\alpha_4$ | 4.0         | 4.0    |

Table 2. Energies ($E$) and oscillator strengths ($f$) for vertical transitions of the zwitterion and cation forms of RhB between the ground states and the two lowest electronic excited states in the minimum energy geometry of the initial state.

|        | Zwitterion | Cation |
|--------|------------|--------|
| $S_0$  | $S_1$      | $S_2$  |
| $E$ (eV) | 2.514      | 1.975  |
| $f$ (a.u.) | 1.197      | 1.093  |
| $S_0$  | $S_1$      | $S_2$  |
| $E$ (eV) | 2.595      | 1.0393 |
| $f$ (a.u.) | 2.595      | 1.0393 |
| $S_0$  | $S_1$      | $S_2$  |
| $E$ (eV) | 2.832      | 0.1950 |
| $f$ (a.u.) | 2.832      | 0.1950 |
| $S_0$  | $S_1$      | $S_2$  |
| $E$ (eV) | 3.118      | 0.0168 |
| $f$ (a.u.) | 3.118      | 0.0168 |

3. Experimental details and data analysis

The dynamics of the RhB molecule were probed in a solution of ethanol ($5 \times 10^{-5}$ M) in order to avoid the effects of dimerisation which complicate the dynamics of the molecule (by providing decay channels not present in the monomer) as it is known that the equilibrium between the monomer and the dimer is heavily favouring the monomer in this solvent [5]. Furthermore, we controlled the cation/zwitterion equilibrium by adding either a drop (0.2 ml) of 0.1 M NaOH or 0.1 M HCl to 2 ml of $5 \times 10^{-5}$ M RhB in ethanol. The addition of the acid drives the equilibrium to the cation side while the addition of the base favours the zwitterion. The pump–probe experiments were performed using a laser system consisting of a 1 kHz, 4 mJ, 35 fs chirped pulse amplifier seeded by a Ti:Sa oscillator. The pump pulse (560 nm) was generated by sum frequency mixing in an optical parametric amplifier while the probe was generated by focusing a small quantity of 800 nm light (3 μJ) into a rotating CaF$_2$ crystal. The optical layout of the commercial transient absorption spectrometer (FemtoFrame II, IB Photonics) consists of a split beam configuration in which 50 % of the white light (350–800 nm) passes through the sample contained in a 1 mm static cell while the remainder is used as a reference to account for pulse to pulse fluctuations in the white light generation. The
Figure 4. (Upper panel) Molecular orbitals of the cationic form of Rhodamine B. (Lower panel) Molecular orbital electron density change on excitation between the orbitals indicated. Green (light gray in grayscale) indicates density depletion while red (dark gray in grayscale) indicated density increase. The data in the three columns refer to the minimum energy geometry of the $S_0$, $S_1$ and $S_2$ electronic states, respectively.

pump pulse is loosely focused (circular spot of diameter = 700 µm) onto the sample with a power density of 150 µJ/cm². The probe pulse is much smaller (approximately 150 µm) and is scanned in time by varying the length of its optical path. All experiments were performed with linear polarisation for both pump and probe pulses and the angle between the electric field vectors of the two was set to the magic angle in order to eliminate effects due to rotational dynamics. The instrument response function was measured to be approximately 80 fs.

The transient absorption spectra produced in this way are reported in Figure 5(a,b) with the wavelength on the x-axis and the time delay between the pump and probe on the y-axis. All spectra have been corrected for the chirp of the probe pulse. In this paper, we have investigated in detail the energy region between 520 and 640 nm where an intense negative signal is centred near 560 nm for both systems studied. Furthermore, Figure 5(c,d) reports the transient absorption spectra for zwitterionic (upper panel) and cationic (lower panel) forms of RhB at specific pump–probe time delays between 1 and 500 ps. We can observe that in the first 50 ps there is a change both in the shape and in the maximum of the signal. In such conditions typical global fitting procedures, which rely on the attempt to fit a number of spectrally constant contributions, each with their own temporal behaviours, are destined to fail, giving fit misleading information. For these reasons, we have fit each transient absorption spectrum with a sum of three Gaussians, i.e. $Z_1$, $Z_2$ and $Z_3$ for the zwitterionic form and $C_1$, $C_2$ and $C_3$ for the cationic form (see Figure 5). For example, the contributions of the three Gaussian peaks to the overall transient absorption of the zwitterion are shown in Figure 5(e) where it can be seen that there are two broad contributions centred at 558.6 nm – $Z_2$ and 618.8 nm – $Z_3$ ($\sigma = 20.0$ and 25.6 nm, respectively) and a narrower contribution centred at 556 nm – $Z_1$ ($\sigma = 8.0$ nm). Attempts to fit the full temporal range of transient spectra with two Gaussian peaks led to a significantly lower quality fit as judged by the residual between the experimental and fit data. The broad spectral features $Z_2/C_2$ and $Z_3/C_3$ correspond to the spectral features of the static fluorescence spectrum and are assigned to the stimulated emission from the $S_1$ state to the ground state and to the hot bands of the ground state, respectively. The $Z_1/C_1$ component, on the other hand, has no correspondence in the static spectrum. Neither does it reflect the absorption spectrum and therefore would not appear to be ground state bleaching. The nature of this component will be discussed in the following section.

The full time dependent transient absorption map is reconstructed from the different contributions obtained from the fit (see Figure S2 in the supplementary material) as shown in the lower panels of Figure S1. The difference map between the original experimental data and the reconstructed data allows the goodness of the fit to be determined (see Figure S3 in the supplementary material). The aim of the procedure was to reproduce the experimental data using as few variables in the fit as possible. The analysis revealed that two of the three contributions used to fit the experimental data ($Z_2/C_2$ and $Z_3/C_3$) present a nanosecond timescale while the third decays on a picosecond timescale ($Z_1/C_1$) – see Figure S2. The contributions with the nanosecond timescale consist of two broad Gaussian-shaped peaks separated by 60 and 50 nm for the zwitterionic and cationic forms of RhB, respectively. We fixed the widths of these contributions thus better controlling the freedom of the fit, accounting for the change both in the shape and in the maximum of the signal to the $Z_1/C_1$ contribution centred around 560 nm. To extract the time constants of these components, the temporal evolution of these contributions has been fit with different exponential functions. In particular, the decay trend of the $Z_1/C_1$ contribution (see Figure 5(e,f)) has been fit using a combination of three exponential decays.
4. Results and discussion

As mentioned in the Introduction the development of advanced theoretical methods such as TDDFT has reopened the discussion on the nature of the excited states in many fluorescent molecules due to new theoretical tools [8,22,35,36] capable of visualising and understanding the excited states of relatively large molecules. The TDDFT calculations on the zwitterionic form of RhB presented in this work confirm the existence of bright and dark (as can be seen from the oscillator strengths in Table 2) electronically excited states with energies in the range of visible excitation/emission of the molecule depending on the geometry, as reported in Figure 2. This is in agreement with Savarese et al. [22] who argued that the initial excitation in RhB occurs to what they called a locally excited state (characterised by a small dipole moment change with respect to the ground state) followed by a geometry change to what they call an ‘asymmetric state’ which changes both τ and γ (see Figure 2). The latter change can be accompanied by electronic coupling and transfer to a dark state thus allowing the quenching of the zwitterionic RhB (φf = 0.7 in ethanol [9]) with respect to the lack of quenching of other Rhodamines such as Rh101 to be explained.

Our results on the zwitterion are largely in agreement with those of Ref. [22] with some minor differences such as the precise geometry of the relaxed ‘asymmetric state’ which, in our case, shows mainly rotation around γ with some rotation around the amino groups (α1 and α2). Also, our calculations show that the lowest energy value of the bright state corresponds with the crossing between S1 and S2 with a geometry change involving τ, γ, α1 and α2 (see Table 1). The geometry change of the bright state mainly involved rotation of the phenyl and carboxylic groups in agreement with Barone et al. [37] who pointed out that the π to π* transition induces repulsion between the xanthene π cloud and the oxygen p orbital of the...
carboxylic group. The results further show that the dark state is due to a CT from the carboxylic group to the xanthene (see lower panel of Figure 3) as also observed by Savarese et al. [22]. While Savarese et al. recognised that the details of the crossing between the S1 and S2 states is impossible to interrogate at the level of theory they used, on the basis of their calculations they made the reasonable hypothesis that dark state plays a role in the quenching of the zwitterionic RhB [22]. However, we have also performed calculations on the cationic state form of RhB which reveals quite a different excited electronic structure with respect to the zwitterion. The main difference is that there is no dark state which crosses the initially excited bright state at energies comparable to those in play in the visible excitation/emission of RhB. While a dark state does exist (S2), its minimum is well above the energetic region of interest (see right panel of Figure 2). Also, it does not have the same CT character as the dark state in the zwitterion (carboxylic group to xanthene). Moreover, the cation geometry change of the bright state S1 mainly involves the τ and γ dihedral angles. It would appear that the energy of this state is strongly changed by the protonation of the carboxylic group in the cation. In any case the lack of a dark state in the correct energy range means that the quenching of the cation (φf = 0.53 in ethanol [9]) which is higher than the zwitterion cannot be explained by the mechanism outlined above. As the behaviour of the photophysical parameters of RhB (φf, fluorescence lifetime, solvachromat shift, absorption cross section, etc.) with variation of the solvent and temperature appears to be quite similar [12–16,38] it is unlikely that the mechanisms of quenching in the two molecules would be of completely different natures. We therefore suggest that the existence of the dark state in the zwitterion should play a minor role in the dynamics possibly due to weak coupling with the bright state. This conclusion has important implications not only for the comparison with Savarese et al. [22] but also for the standard TICT model [10] used to explain the dynamics/quenching of the Rhodamine dyes in general. Indeed, examination of the lower panels of Figure 4 shows that only the locally excited state plays a role in the dynamics of the cationic form and that while some geometry changes occur no CT takes place subsequent to the photoexcitation. This is in contrast to most explanations presented in the literature for the quenching in Rhodamine dyes which are based on large geometry changes (amine rotation [17,18], amine umbrella motion [20,21], phenyl group rotation [8] or carboxy group rotation [22]) accompanied by significant CT leading to a state which is quenched on a long timescale (nanoseconds). While such a CT state exists in the zwitterion our conclusion suggests that it does not take part in the quenching/dynamics.

A large geometry change could in principle be of some relevance in the electronic quenching of the excited Rhodamines due to curve crossings at relatively high energies in a configurational space far from the minimum energy regions investigated by the calculations in this work. We consider this dissipation channel not very probable because the energy potential of the electronic states as a function of dihedral angles of RhB as reported in Figure 2 of Barone et al. [37] indicates that the change of these PES is below 70 kJ/mol (about 0.7 eV) which is well below the 2.0–2.5 eV which separates the minimum energy of the ground state to the vertical excitation in the S1 electronic state. This indicates that if a crossing between the S0 and low energy electronic states occurs, it does not involve the flexible degrees of freedom of the nuclear configurations. The hypothesis that other, more stiff, nuclear degrees of freedom can promote the coupling of the S0 and S1 or S2 states can be neglected: a strong nuclear distortion of the rigid backbone of the RhB in the excited states cannot be easily associated with a shallow change in the excited PES able to cross the S0 electronic state.

Having hypothesised that the dark state and large geometry changes should not play a significant role in the quenching it is necessary to suggest an alternative mechanism which does not contradict the literature to date. We have experimentally investigated the quenching by concentrating on the short timescale dynamics. Unfortunately the short timescale dynamics of large molecules in liquid solutions are extremely complex as testified by several reviews [39,40]. These timescales can contain information on inertial and diffusive solvent rearrangement, intramolecular CT, intramolecular vibrational relaxation, IC and conformational changes of the excited molecule and often it is difficult to associate a single one of the above processes to each timescale observed empirically [39,40]. Nonetheless, we have examined the ultrafast relaxation dynamics of the zwitterion and the cation. In these dynamics three components were observed (see Section 3). Two of these, Z2/C2 and Z3/C3 are related to stimulated emission from the S1 state to the ground state and to the hot bands of the ground state, respectively. These contributions are also observed in fluorescence measurements and simply reflect the standard nanosecond timescale of the fluorescence dynamics of these molecules [10,11,14]. The Z1/C1 spectral features, on the other hand, centred at 556 (zwitterion) and 564 nm (cation) exhibit much faster decay dynamics. Figure 6 reports the exponential trend of the narrower spectral features, together with the resulting fits for both the zwitterionic (blue data) and the cationic (red data) forms. The short timescale of this signal (close to zero after 100 ps) together with the spectral shape which does not reflect
the static absorption suggests that this signal is not due to ground state bleaching. Therefore, we assign it to the stimulated emission of the initially excited short-lived transient absorption species.

Table 3 shows the results of the triple exponential fits of the intensities of the narrow spectral components, Z1 and C1. The shortest timescale for the decay of both Z1 and C1 was the 300 fs timescale which overlaps with the coherent effects due to the presence of both the pump and probe pulses. This aspect has been extensively studied in the literature [41]. This ultrafast timescale may be related to the fast CT or to inertial solvent relaxation or a combination of the two. In the previous works on Rh6G this short timescale has been observed but was assigned exclusively to ultrafast photoinduced electron transfer [42].

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The intermediate timescale observed in both zwitterion (5.3 ps) and cation (7.6 ps) has also been reported in the Rhodamine literature for a range of ultrafast optical experiments from transient gratings to transient absorptions [19,41,43]. A slightly shorter timescale of 1.4 ps was observed in the transient absorption spectra of RhB in MeCN and extracted through a global analysis and assigned to a narrow spectral feature [19]. The longer timescale observed here may be related to the higher polarity of the solvent. Similar timescales were also observed in the transient grating spectra of Rh6G in DMSO (3.3–3.9 ps) [43] and transient absorption in Rh101 in methanol (3.15 and 15.2 ps) [41]. Although various dynamics have been assigned to this timescale we agree with the prevailing assignments to ultrafast solvent rearrangement in response to the new electronic distribution immediately following the photoexcitation of the molecule.

The difference of the longest timescale between the zwitterion (66 ps) and the cation (134 ps) of the narrow spectral component may be explained as being due to the fact that the zwitterion needs to dissipate less energy with respect to the cation (the difference between the initially excited state and the fully relaxed bright state), as predicted by theoretical calculations reported in Figure 2.

Ultrafast timescales are also observed in the rise times of the Z2 component of the zwitterion (115 ± 50 fs) and the C2 component of the cation (4.3 ± 1.5 ps) – see inset of Figure 6. The same trend, not shown here, has been also observed for the Z3/C3 contributions centred at around 620 nm. In the case of an initially excited state which is completely converted to the final fluorescent state a direct inverse relationship must exist between the temporal evolution of their intensity contributions to the spectrum. It is clear from the fits of the rise times that this is not true either in the case of the zwitterion or cation. The fact that the rise time of the broad spectral component is not equal to the decay time of the narrow component suggests the existence of a competing mechanism. A possible explanation for this is the action of the quenching mechanism outlined above.

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A possible competing non-radiative mechanism could be solvent-mediated internal conversion to the ground state. It is possible that such a conversion is speeded up by low frequency vibrations of the Rhodamine molecule [44]. To investigate whether this hypothesis holds up from the point of view of the vibrational frequencies involved, we have performed a vibrational analysis of RhB, Rh101 and Rh110. The details of this analysis are given in the supplementary information. The results of this analysis are summarised in Figure 7 where the cumulative number of vibration states is graphed against energy and shows a significantly higher density of vibrations below 200 cm⁻¹ in RhB with respect to Rh101 and Rh110. Low energy vibrations facilitate interactions with the solvent and thus may promote IC [45] which could explain why Rh101 and Rh110 are characterised by a lower quenching with respect to RhB. For example, the fluorescence quantum yields of the cationic forms of Rh101 and Rh110 in water are 0.98 and 0.88, respectively.
Figure 7. Cumulative number of vibration states (CNVS) below the corresponding energy of cationic (dashed line) and zwitterionic (full line) RhB, Rh101 and Rh110.

[7], which are much higher than the quantum yield of RhB.

5. Conclusions

The ultrafast solvation and conformational dynamics of both the zwitterionic and cationic forms of RhB have been examined from a theoretical and experimental point of view. The TDDFT calculations on the zwitterion confirm previous calculations which demonstrate the presence of both a bright and a dark electronically excited state in the energy range of interest for the optical RhB dynamics. The cationic form, however, was shown to only have a bright state in the energy region of interest. As the quantum efficiency of the fluorescence of both molecules are similar and the solvent and temperature dependence of the photophysical properties of the two are not significantly different, it is suggested that the mechanism of quenching must be similar and hence that the dark state does not play a significant role in the case of the zwitterion. The bright states in the two molecules are similar and essentially consist of a $\pi$ to $\pi^*$ transition within the xanthene ring with a minor contribution of CT from the amino to the xanthene. The geometry changes which occur subsequent to photoexcitation are dominated by rotations of the phenyl and carboxylic groups to different extents in the two cases but no further CT takes place. This is in contrast to most explanations presented in the literature for the quenching in Rhodamine dyes which are based on large geometry changes accompanied by significant CT leading to a state which is quenched on a nanosecond timescale. We in contrast present some empirical evidence for the action of a picosecond quenching mechanism in both forms of RhB.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

DC, PO’K and ST acknowledge funding from the MIUR under PRIN grant number 2015CL3APH.

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