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ARTICLE

Redefining the established understanding of excitation dynamics of photochromic oxazines

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Since the introduction of the photochromic indolo-benzoxazines, difference absorption of these photoexcited compounds has been assigned to the ground state of the ring-opened isomer. This assignment relies on the alleged resemblance of the spectra of photo- and chemically-induced forms. In this paper, we expose the issue of discrepancy between the absorption spectra of photoproducts and the corresponding chemically opened forms. As a result, a substantial change of the current explanation of photodynamics of photochromic oxazines is proposed. The spectral features earlier ascribed to the photoproduct are suggested to arise from the absorption of triplet state. This hypothesis was tested and confirmed in acetonitrile by measuring the effect of oxygen quenching of the photoproduct states. In view of this interpretation, light-induced ring opening does not occur in indolo-benzoxazines dissolved in acetonitrile, and, consequently these molecules should no longer be regarded as molecular switches. On the other hand, we show that methanol solutions UV light does produce small amounts of the ring-opened form of the molecule.

Introduction

One of the most recent introductions in the field of photochromic materials are indolo-benzoxazines (referred to as photochromic oxazines), a family of photochromic compounds based on photoinduced opening of the [1,3]oxazine ring.^{1, 2} The core of these compounds combines two fused heterocyclic rings, 3*H*-indole and benzo[1,3]oxazine (Figure 1). The absorption of UV photon induces C–O bond cleavage at the junction of the heterocycles, generating a zwitterionic photoproduct, with cationic 3*H*-indolium and anionic 4-nitrophenolate parts.^{1, 2} The appearance of induced absorption bands in the visible region of the transient spectra of photochromic oxazines is attributed to 4-nitrophenolate chromophore, with characteristic band around 430 nm.^{1–3} Photochromic oxazines are distinguished for their very fast switching speeds: ring-opened species are formed within the ns laser excitation and they thermally revert to original form within tens of nanoseconds.

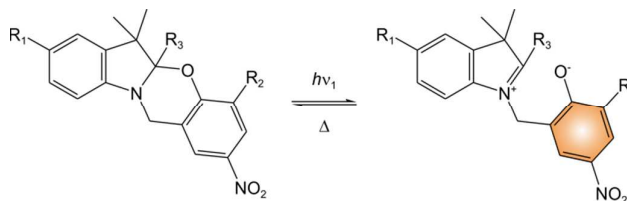


Figure 1. The accepted photochromic conversion of photochromic oxazines: UV excitation promotes the opening of the ring-closed isomer.

Photochemical properties of photochromic oxazines can be tuned by structural modifications (positions R_1 – R_3 in Figure 1) of the parent indolo[2,1-*b*][1,3]benzoxazine molecule. Numerous compounds were synthesized and their properties reported.^{3–9} Recently, we introduced a series of new compounds of photochromic oxazines.^{10, 11} Compounds with phenylic substituents in the indole ring exhibited peculiar induced absorption spectra: two well-resolved bands in the blue and nIR regions.¹⁰ The observed spectral structure contrasts sharply with the spectra of chemically opened species (see Figure 2), characterized by a typical single absorption band of 4-nitrophenolate. Chemical opening of photochromic oxazines under basic or acidic conditions yields ionized ring-opened forms with anionic or cationic fragments, corresponding to those of the zwitterionic photoproduct shown in Figure 1. The addition of base (usually, TBAH) promotes ring opening and the formation of 4-nitrophenolate anion, while indole part of the compound is in neutral hemiaminal form. Thus, base-opened form features a chromophoric fragment, which is identical

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to that of the photoinduced compound. Under acidic conditions, an opposite effect is observed, as 3H-indolium chromophoric fragment is formed, while nitrophenolium part remains neutral due to protonation.⁹ Acid treated solutions of photochromic oxazines remain colourless, unless there are aromatic substituents R_3 (in conjugation with 3H-indolium fragment), because both nitrophenolium and 3H-indolium have absorption in the UV region. Therefore, the bands in the transient absorption spectra of photoinduced compounds should correspond to the bands of their respective chromophoric fragments in the steady state absorption of chemically opened species*. Indeed, the resemblance was deemed to be close enough in the earlier works and was not addressed further. Nevertheless, a more thorough comparison of spectra indicates that such attribution is dubious. In fact, even in the case of simplest unmodified photochromic oxazine, the maximum of the transient spectrum band (440 nm) does not coincide with absorption maximum of chemically induced form (430 nm); furthermore, there is a broad induced absorption plateau extending to the red from the main induced absorption band, which is absent in the absorption spectra of chemically opened compound.^{1, 4} Therefore, the very assignment of transient absorption bands of photochromic oxazines to ring-opened forms is

excited state dynamics and suggested a branched model of photoproduct formation. However, the only evidence of photoinduced formation of the ring-opened form was assumed from the resemblance of transient spectra to those of chemically opened compounds and was not questioned further. Therefore, the mentioned studies do not address the question of the electronic nature of the photoinduced form of the indolo-benzoxazine compounds.

This unaddressed discrepancy between the spectra of photoinduced and chemically opened forms suggests an alternative explanation of photodynamics of photochromic oxazines, which is the subject of this study. Naturally, it is impossible to cover the entire family of indolo-benzoxazine photochromic compounds with one study. Most of the investigated photochromic oxazines revert to the original ground state with lifetimes of < 50 ns, which makes them very fast molecular switches. These "classical", fast photochromic oxazines, such as the unmodified parent molecule^{1, 2} and compounds with phenylic substituents in R_1 and R_2 positions¹⁰ are the subject of this work. We hypothesize that (constrained to ns timescale) photoexcitation of photochromic oxazines in acetonitrile does not result in ring opening and the observed induced absorption is instead assigned to absorption from triplet state. In

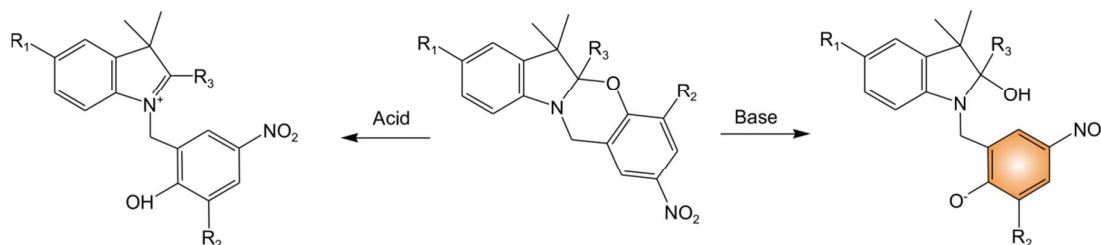


Figure 2. Chemical opening of [1,3]oxazine ring in photochromic oxazines under acidic or basic conditions, respectively. TBAH induced form on the right is referred to as *chemically opened form* throughout the text.

in question.

In contrast to the oldest and well-studied photochromic families, such as spiropyrans and diarylethenes,¹²⁻¹⁴ very little is known about excitation dynamics of photochromic oxazines. The photoinduced opening of photochromic oxazine ring was suggested to occur in the triplet state potential energy surface due to experimentally observed triplet-triplet energy transfer in BODIPY-oxazine dyads.¹⁵ A computational study provided a mechanistic model of excitation dynamics, in which ring-opened photoisomer is formed in the triplet state, followed by intersystem crossing to the singlet ground state of ring-opened species.¹⁶ Femtosecond time resolution studies^{11, 17, 18} revealed the complexity of the early

this work, we report a standard test for our hypothesis of the triplet state involvement in ns excited state dynamics of (fast) photochromic oxazines in acetonitrile. Two compounds were selected for investigation to represent typical fast photochromic oxazines (chemical formulas given in Figure 3): first, the unmodified parent compound **IB**; second, **I-A**, a compound from the group with phenylic substituents in indole ring (R_1 position) with untypical two-banded induced absorption spectra. The well-known effect of triplet state quenching with oxygen was exploited and yielded results, which allowed us to redefine the current view of photochromic oxazines as photoswitchable compounds in acetonitrile. In addition, in order to test the influence of the solvent on the photoinduced dynamics of the chosen representative compounds, we performed measurements in alcohol solutions. It was found that in alcohols, photoinduced ring opening most likely does occur. The ring-opened form manifests as a long-lived component in the transient absorption signal with a ca. 200 ns lifetime. Finally, we show that even though the decay of induced absorption of **IB** and **I-A** in acetonitrile is not monoexponential with

*One may notice that 4-nitrophenolate is connected to 3H-indolium cation in zwitterionic photoinduced forms, while in the case of TBAH base-induced species it is connected to neutral hemiaminal. However, such a slight structural difference has a negligible influence on the absorption spectra of nitrophenolate part of the molecule. In both cases the effect of indole part on the electronic structure, hence on absorption spectrum of nitrophenolate part is minor, conjugation is impossible, because the parts are separated with methylene bridge.

a long-lived component also present, the spectral features observed on the longer time scales cannot be clearly attributed to the ring-opened form of the molecule.

Materials and methods

Sample preparation

Polycrystalline samples (synthesis described in¹⁰) were dissolved in acetonitrile or methanol (both from Sigma Aldrich, LiChrosolv, gradient grade) and diluted to an optical density of 1 at the excitation wavelength (355 nm) in a 4 mm quartz cell. For chemical opening of the [1,3]benzoxazine ring tetrabutylammonium hydroxide (TBAH) 1M solution in methanol (Alfa Aesar) and trifluoroacetic acid (TFA, Sigma Aldrich) were added to the solution, until clear spectral changes emerged. For deoxygenation experiments, samples were purged with Ar gas by immersing a plastic pipette tip directly in quartz cells and adjusting gas flow rate to obtain steady bubbling in the solution. To restore equilibrium oxygen concentration, samples were likewise purged with filtered laboratory air employing homemade peristaltic pump. After purging procedures, cells were thoroughly capped and were directly proceeded to spectroscopic measurements.

Spectroscopy

Steady state absorption spectra of the solutions were measured using a scanning spectrophotometer Shimadzu UV-3101PC. Flash photolysis setup was described in detail earlier.¹⁰ In short, samples were excited with 355 nm, 5 ns, 4 mJ Nd:YAG laser pulses, and probed with Xe lamp flashes, recording the probe intensity with a high-speed photodiode on a high-bandwidth oscilloscope. All nanosecond kinetic traces presented here were obtained by averaging at least 30 experimental measurements. The time resolution of the experiments was about 6 ns.

Data analysis

Nanosecond resolution flash-photolysis experimental data was analysed using global analysis techniques described elsewhere.¹⁹

Results and discussion

Revisiting the resemblance of photo- and chemically induced spectra

Difference absorption spectra of **IB** and **I-A** in acetonitrile, recorded immediately after the excitation with 5 ns laser pulse are shown in Figure 3. In order to define the shape of the transient spectra more accurately, they were measured with the spectral resolution of 5 nm. The steady state absorption of chemically opened forms is given in the same plot for comparison. Only spectra of TBAH induced forms are shown, because the addition of acid to the

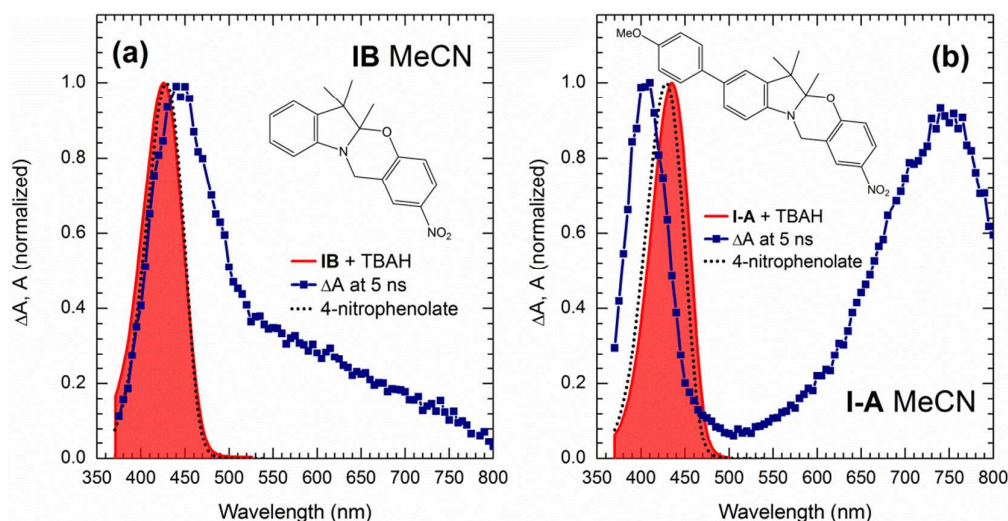


Figure 3. Spectra of photo- and chemically induced forms of investigated photochromic oxazines: difference absorption spectra of **IB** (a) and **I-A** (b) in acetonitrile after the excitation with 5 ns laser pulse compared to the steady-state absorption spectra of the ring-opened forms, measured after addition of TBAH (all spectra are normalized). Chemical formulae of the compounds and steady state absorption spectrum of 4-nitrophenolate chromophore in acetonitrile (obtained by adding TBAH to 4-nitrophenol solution) are also given.

photochromic solutions did not produce any absorption changes in the visible spectral range. Cationic (3*H*-indolium) parts of the ring-opened forms of both compounds absorb further in the UV region (>380 nm), therefore, just anionic part (4-nitrophenolate

chromophore) determines the visible absorption. Absorption of 4-nitrophenolate (prepared by adding TBAH to 4-nitrophenol solution in acetonitrile) is also plotted in Figure 3: a band at 430 nm is nearly identical to that of the chemically-opened **IB**, while corresponding spectrum of **I-A** is slightly shifted to the red, peaking at 434 nm. Such spectral shift illustrates the influence of substituents (i.e., indole part in hemiaminal form, leftmost in Figure 2) on the 4-nitrophenolate chromophore. The results of our previous work on a series of photochromic oxazines¹⁰ reveal that in compounds with phenylic substituents R_1 in the indole part (like **I-A**) characteristic 430 nm 4-nitrophenolate absorption band of TBAH-induced forms is slightly (at most by 4–5 nm) shifted to the red, while a substantially larger 10–20 nm bathochromic shift is typically observed when phenylic substituents are introduced to the nitrophenol part (R_2 in Figure 2).

In the earlier works, that introduced photochromic oxazines for the first time,^{1, 2} the difference absorption of **IB** was registered with lower signal-to-noise, and the spectral resolution was worse. As a result, the resemblance of the photo- and TBAH-induced spectra was assumed to be good enough and transient absorption band of **IB** at 440 nm was assigned to the ground state absorption of 4-nitrophenolate chromophore. In contrast, the spectra in Figure 3(a) show that such attribution is unjustified. First, the positions of maxima differ by almost 15 nm (426 nm vs. 440 nm). Second, a featureless absorption plateau, spanning from 500 nm to the red throughout the entire spectral window constitutes a significant part of the induced absorption signal, while TBAH induced form has no absorption beyond ca. 480 nm. In the case of **I-A** (Figure 3(b)), the difference between the spectra of photoinduced and chemically opened forms is dramatic. Transient absorption spectrum of **I-A** features two bands of similar intensity located at 410 nm and 750 nm, without any discernible contribution from 4-nitrophenolate band, while chemically opened form features typical single absorption band at 434 nm.

A similar trend is observed for most of the other reported photochromic compounds of indolo-benzoxazine family:^{3–10} usually, there is a difference in position and overall spectral shape of corresponding photo- and chemically induced spectra. The compounds with phenylic substituents in the indole ring (such as **I-A**) serve as an example of the most extreme difference between spectra of photoexcited and chemically opened photochromic

oxazines: the light-induced form exhibits two strong bands in the blue and nIR regions, whereas the chemically open form has just one in the VIS range, and its wavelength does not coincide with any of the light-induced bands.^{10, 11} On the other hand, some reported oxazines exhibit strong resemblance between photo- and chemically induced forms. This is characteristic to bichromophoric oxazines, which, in addition to anionic nitrophenolate chromophore absorption, also feature a second, cationic absorption band in the visible region.^{4, 20, 21} Recently bichromophoric oxazines have been a subject of considerable scientific interest and were employed in developing photoswitchable fluorescent systems.^{22–24} The relaxation of the excited state of these compounds occurs on the μ s timescale, and their photoinduced absorption bands match those of the chemically ring-open forms rather well, which puts these compounds outside the scope of this work.

Aside from several exceptions, the discussed discrepancy between the spectra has largely been ignored in earlier studies. It is not clear why photoinduced and chemical ring opening pathways should result in ring-opened isomers with such dramatically different absorption spectra. The difference absorption of the excited compounds was by default assigned to ring-opened form, supported by no evidence other than claimed resemblance of the spectra. To address this problem with the accepted interpretation of the data, the observed induced absorption must be assigned to an excited species other than ring-opened isomer. Despite rather short lifetimes (a few tens of ns), the involvement of triplet state seems a plausible candidate, because it has been demonstrated that the excited photochromic oxazines participate in triplet-triplet energy transfer.¹⁵ Accordingly, the transient absorption, recorded after excitation with a ns pulse, could be attributed to species in *triplet state*, instead of ring-opened form.

Triplet state involvement was tested in the earliest works on photochromic oxazine, very similar to **IB**.^{1, 2} Singlet oxygen emission measurements in the course of photoexcitation of the investigated compound resulted in quantum yield value of 0.02 and triplet state involvement was excluded. However, in the case of short-lived triplet states, such approach may be very inaccurate and result in significantly reduced quantum yield values. To our knowledge, oxygen quenching experiments on fast photochromic oxazines have not been reported earlier.

Testing the triplet state

The triplet character of a state is commonly tested by removing dissolved oxygen from the solution. Upon removal of oxygen, which effectively quenches excited triplet states, an increase of triplet state lifetime is observed. Transient absorption of **IB** (**I-A**) at 440 (400) nm was monitored before and after the oxygen removal by purging the acetonitrile solution with argon for 15 min. The results shown in Figure 4 reveal a slight prolongation of the relaxation time after oxygen removal in the case of **IB**, and a more pronounced change is observed with **I-A**. The initial decay rate of both compounds, as estimated by monoexponential fitting of the kinetic traces, is equal to 21 ns. For **IB**, a 2 ns increase was observed; in the case of **I-A** it was 4 ns. We note that the observed change in lifetime is very small, albeit discernible. To rule out the possibility of this observation being due to some modification of the sample during the Ar purging procedure (i.e. contamination), after the measurement on the de-oxygenated sample, the solution was

purged with air to restore the equilibrium oxygen concentration. The control measurement on re-oxygenated sample revealed the recovery of the original kinetic traces (compare the black and red traces in Figure 4).

From the first glance, the effect of oxygen removal does not seem substantial enough to enable far-reaching conclusions. In order to estimate whether the observed increase of relaxation time is significant, it must be compared to a calculated value, obtained from Stern-Volmer relationship:

$$\frac{\tau_0}{\tau_q} = 1 + k_q \tau_0 [Q] \quad (1),$$

where τ_0 and τ_q are the lifetimes of the excited state without and with the quencher, respectively; k_q is quencher rate coefficient, and $[Q]$ is the concentration of the quencher. Rate constants k_q for

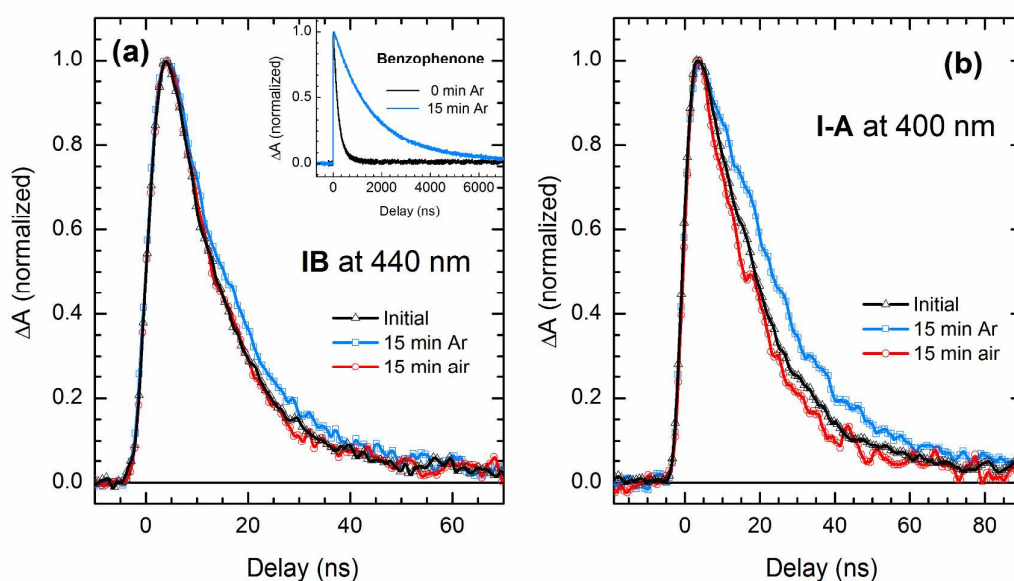


Figure 4. Kinetic traces of **IB** (a) and **I-A** (b) in acetonitrile, measured at the maximum of the induced absorption (440 and 400 nm, respectively) before and after purging the solution with Ar for 15 min. The effect of oxygen removal is demonstrated in the inset of panel (a): under the same experimental conditions, the lifetime of transient absorption of benzophenone increased ca. 7-fold (measured at 520 nm). Red traces correspond to recovered original traces obtained after Ar purged solutions were flushed with ambient air. All traces are normalized to allow direct comparison.

oxygen quenching depend on the energy of triplet state, therefore k_q must be measured for each compound individually.²⁵⁻³⁰ Diffusion-controlled rate constant for oxygen quenching in acetonitrile has been reported to be ca. $4 \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$,³¹ while k_q values are usually smaller by the order of magnitude.²⁵

As we were not able to measure the oxygen concentration in acetonitrile solutions directly, we have estimated it indirectly from Stern-Volmer relationship by deoxygenating benzophenone solution under the same experimental conditions (see inset in panel (a) in Figure 4). A 7-fold increase of initial benzophenone lifetime $\tau_q = 220 \text{ ns}$ was achieved by Ar purging. Rate constant for oxygen quenching of the benzophenone triplet state is $2.3 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$.³² Various maximum values of benzophenone lifetime were reported; one can safely assume that τ_0 is longer than $10 \mu\text{s}$.^{33, 34} Thus, we can calculate the oxygen concentration from rearranged Equation 1, which can be simplified for benzophenone, as its lifetimes fulfill the condition $\tau_0 \gg \tau_q$:

$$[Q] = \left(\frac{1}{\tau_q} - \frac{1}{\tau_0} \right) \approx \frac{1}{\tau_q k_q} \quad (2).$$

A value of 1.98 mM, calculated for the initial oxygen concentration, is in very good agreement with literature data. In fact, oxygen concentration in air-saturated acetonitrile solutions at room temperature is reported to be ca. 1.9 mM.^{35, 36} Accordingly, the oxygen concentration after Ar purging is 0.36 mM. Now we can use the calculated oxygen concentrations to determine the unknown values of k_q and τ_0 of the studied photochromic compounds by solving a system of two Equations 1 (corresponding to acetonitrile solutions before and after Ar purging). For **IB**, this yields $\tau_0 = 23.5 \text{ ns}$ and $k_q = 2.5 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$, and for **I-A** $\tau_0 = 25.5 \text{ ns}$ and $k_q = 4.4 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The values of rate constants for oxygen quenching for photochromic oxazines are not known; reported values for various other compounds all are on the order of $10^9 \text{ M}^{-1} \text{ s}^{-1}$ in acetonitrile as well as in other solvents.^{25, 29} Therefore, our calculated values for quenching constants are very realistic. Very importantly, the corresponding τ_0 values appear to be very short, just a few ns longer than those in the presence of the quencher. According to Stern-Volmer relationship, the shorter the lifetime of the unquenched excited state, the smaller effect of the quenching. For lifetimes as short ca. 20 ns, a complete removal of the quencher would result in 10–20% increase of the lifetime. This means that the quantitative effect of oxygen removal, observed in our experiments, is perfectly consistent with the calculations, assuming the triplet character of the excited state.

To summarize, a new interpretation of indolo-benzoxazine dynamics is needed to account for the following experimental facts: a) the discrepancy between the absorption spectra of light-induced and chemically opened molecular forms; b) the dependence of the lifetime of light-induced form on oxygen concentration in the solution; c) the reported triplet energy transfer in BODIPY-oxazine diads.¹⁵ We propose that the induced absorption of **IB** and **I-A**, until

recently assigned to the ring-opened photoproduct, is in fact a triplet state absorption. Assuming similar underlying photophysics, it is reasonable to expect that the same applies to other photochromic oxazines with similar features, namely, with fast relaxation and mismatching spectra of photo- and chemically induced forms. Intersystem crossing was proposed to compete with ring-opening in several earlier works,^{4, 6, 8} however, transient absorption was assigned to triplet state for several long-lived compounds with μs relaxation times. In addition, the formation of ring-opened isomer on the potential surface of triplet state, followed by intersystem crossing to the ground state of the open form has been suggested earlier.^{15, 16} However, deoxygenation experiments imply that the final species in photodynamic evolution of the typical, fast oxazine compounds **IB** and **I-A** are in triplet state, and they return directly to the original state without spectrally detectable intermediate forms. Therefore, the interpretation for the discrepancy between the spectra of the photoinduced and chemically ring-opened species becomes obvious, as UV-excitation does not result in formation of ring-opened photoproduct. Naturally, this finding conflicts with the current picture of photochromic oxazines as molecular switches. To answer the question if photoswitching ever takes place in these compounds, further investigations are needed.

Acetonitrile vs. alcohols: ring opening

Our deoxygenation experiments, described in the previous section, were performed in acetonitrile. To date, the absolute majority of the published works on photochromic oxazines report the experimental results obtained in this aprotic solvent. However, a more effective solvation and stabilization of the zwitterionic ring-opened forms could be expected in protic solvents. To our knowledge, a single exception is a work by Prostota et. al,¹⁸ which presented a set of photochromic oxazines and reported results, obtained in ethanol and DMSO solutions. A significant increase of the lifetime of optically generated forms was demonstrated in ethanol and DMSO, however, the solvent effect was not addressed further. To test the solvent influence on the excited state dynamics of **IB** and **I-A**, we performed flash-photolysis measurements in methanol and ethanol solutions.

In both compounds, transient absorption is virtually identical in both tested alcohols, therefore, only results in methanol are discussed further (Figures 5 and 6). Immediately after the nanosecond excitation, the emergent transient spectra are very similar to those observed in acetonitrile. The induced absorption either spans the entire spectral region with a maximum located at ca. 440 nm for **IB** (Figure 5(b)), or features two bands, located at ca. 410 and 760 nm, in the case of **I-A** (Figure 6(b)). However, the maximum amplitude of the induced absorption of **IB** in alcohols is roughly 2.5-fold smaller compared to that observed in acetonitrile (under the same experimental conditions). It is most likely due to very fast relaxation, which is faster than the IRF of the setup (6 ns).

Within the next 5 ns, a significant rearrangement of the initial transient spectra occurs: the initially dominant bands rapidly decay, the spectral maximum shifts blueward, exposing a long-lived band centered at ca. 400 nm, which is more pronounced in the case of **IB**. In **I-A** it constitutes a smaller part of the initial signal amplitude and becomes visible only at later probe times (>50 ns), by the time the low-energy band decays completely. Final spectral shape is fully settled after 20 ns, when a long-lived band with a well-defined Gaussian-like shape, a peak at 400 nm and no induced absorption

beyond 470 nm is formed. This band persists in the transient spectra for longer than a hundred nanoseconds.

The presence of two transient species is also clearly discernible in the kinetic traces (panels (a) in Figures 5 and 6). Firstly, the initial signal decays very rapidly at all wavelengths, with lifetimes shorter than our IRF; subsequently, in the second stage of the spectral evolution kinetic traces in the 380–460 nm region, instead of decaying to zero, reveal the emergent contribution of the long-lived

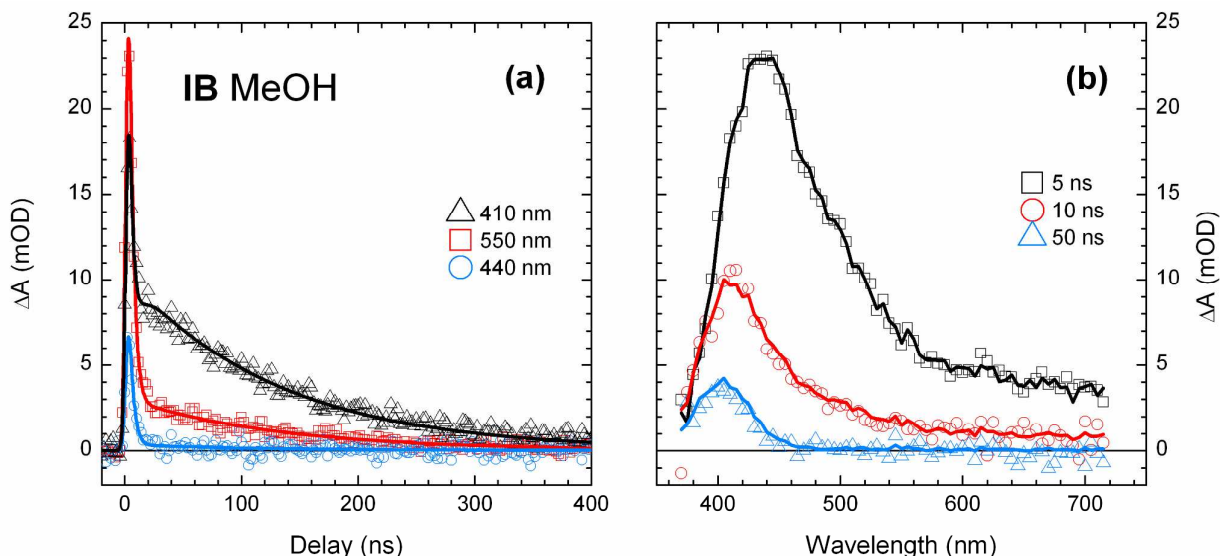


Figure 5. Flash photolysis results of **IB** in methanol solution: (a) difference absorption kinetic traces at selected wavelengths; (b) difference absorption spectra at selected delay times. Experimental points are given in symbols; lines correspond to results of global fitting (see Figure 7 for model).

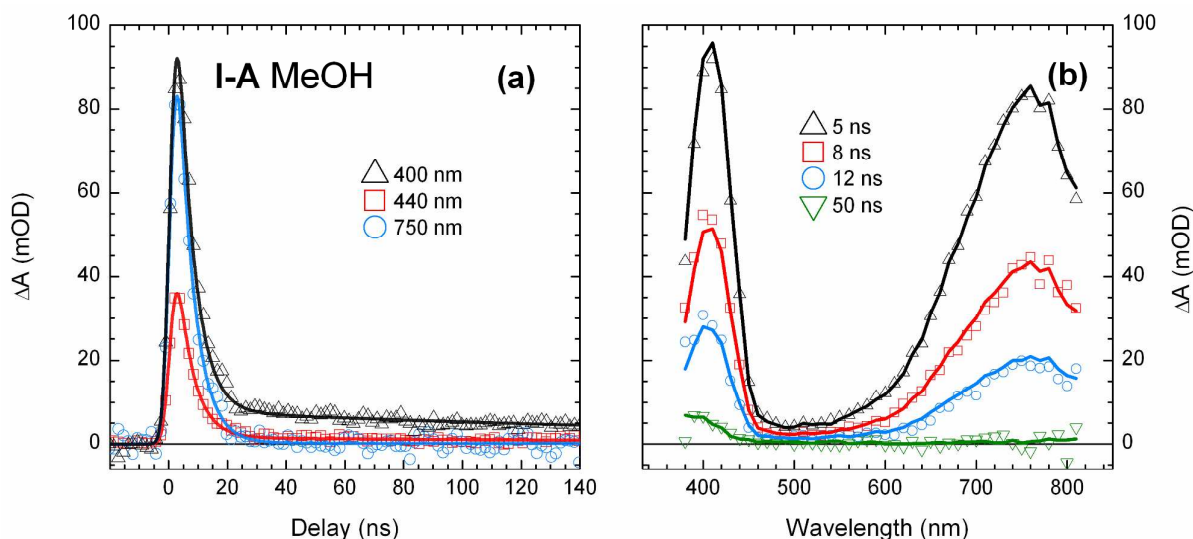


Figure 6. Flash photolysis results of **I-A** in methanol solution: (a) difference absorption kinetic traces at selected wavelengths; (b) difference absorption spectra at selected delay times. Experimental points are given in symbols; lines correspond to results of global fitting (see Figure 7 for model).

component with an absorption band, centered at 400 nm. In **IB**, the formation of the long-lived species is not instantaneous: after the rapid decay of the initial signal, the induced absorption amplitude continues to grow until reaching the maximum after ca. 15 ns (see the accumulation of the signal at 410 nm in Figure 5(b)). This effect is not noticeable in kinetic traces of **I-A**, where the long-lived component manifests only as an offset, which comprises about 10% of the initial signal amplitude.

Apparently, excited state dynamics of **IB** and **I-A** in alcohols is very different and more complex than that observed in acetonitrile, where the evolution of the induced absorption is fairly satisfactorily described by monoexponential decay function, and the signal decays in unison at all wavelengths.^{1, 2} (As we will see further, a closer analysis of flash-photolysis data in acetonitrile reveals more complexity present, thus also rendering the simple (monoexponential decay) model insufficient.)

In order to quantitatively describe the entire experimental dataset, we applied global analysis. The observed trends in transient absorption dynamics were captured in a simple connectivity scheme, shown in Figure 7(a). First, short-lived **1** species are formed right after the ns excitation. These initial species decay within few ns, transferring the excited population to state **2** (corresponding to

long-lived species) or, alternatively, via direct relaxation to the ground state, signified as $1 \rightarrow S_0$. In **IB**, the former pathway dominates, which is indicated by a large signal gain of the long-lived component. A direct relaxation to the ground state $1 \rightarrow S_0$ may be also taken into account, although this transition must be considerably slower than $1 \rightarrow 2$, therefore, it has a negligible effect on the fitting results. On the other hand, in **I-A** the major depopulation channel of excited species **1** is $1 \rightarrow S_0$, while $1 \rightarrow 2$ transition is several times slower. Relaxation time, corresponding to the decay of **2** to the ground state $2 \rightarrow S_0$ is supposed to be on the timescale of ca. 200 ns for both compounds.

Fitting experimental data to given model in **IB** yielded satisfactory results when time of $1 \rightarrow 2$ transition equals to 4.7–5 ns and the decay time $2 \rightarrow S_0$ varies within 180–190 ns. In the case of **I-A**, fitting estimated the decay time of ca. 6 ns for $2 \rightarrow S_0$, 30 ns for $1 \rightarrow 2$, and ca. 200 ns for $2 \rightarrow S_0$ transition. The achieved adequacy of fitting is illustrated in Figures 5 and 6, where experimental points and fitting results are plotted as symbols and lines, correspondingly. The spectra of excited species were resolved; the resulting species associated difference spectra (SADS) are shown in panels (b) and (c) of Figure 7. Obviously, in both compounds, the shape of SADS of **1** closely resembles the earliest transient spectra, while SADS of **2** is similar to transient spectra, observed at later (tens of ns) probe

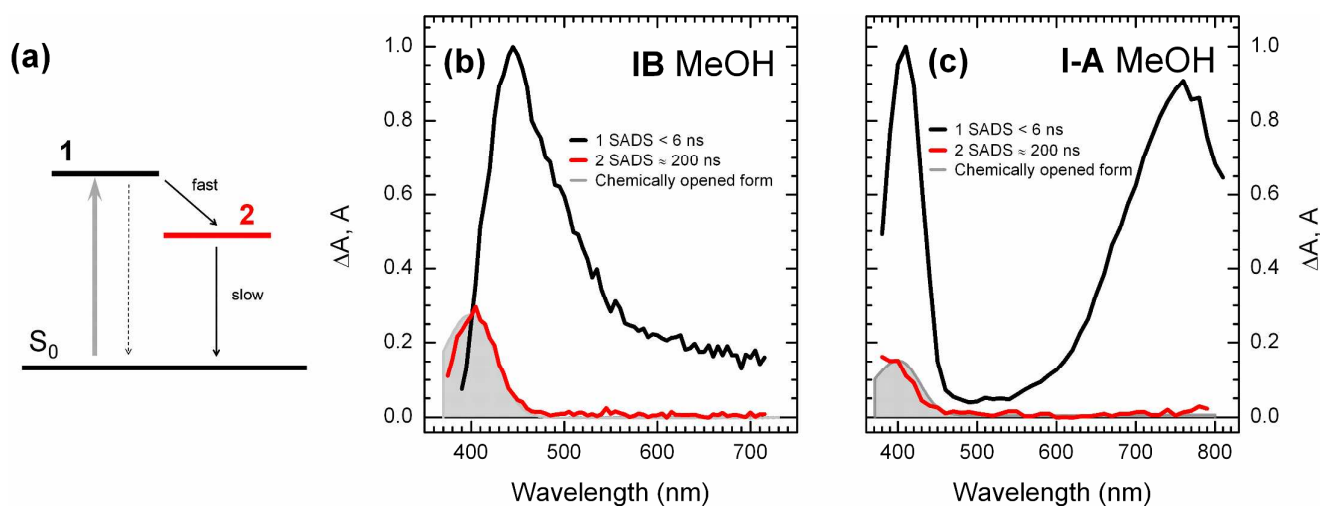


Figure 7. Global analysis of the nanosecond flash photolysis data of **IB** and **I-A** in methanol: (a) connectivity scheme employed in fitting; species associated difference spectra (SADS) of (b) **IB** and (c) **I-A**; grey plots depict the steady state absorption spectra of chemically opened forms in methanol.

times.

At this point, let us discuss the nature of the excited species. Presumably, short-lived species **1**, observed in methanol, could correspond to the triplet state, analogously to the results in acetonitrile solution. SADS of **1** bear a close resemblance to transient spectra of corresponding compounds in acetonitrile. However, in this case, we cannot test this assumption by removing the oxygen, because for lifetimes so short (~ 5 ns) the expected effect of quenching will be far too small to be detected with temporal resolution of our setup (see the discussion in previous section).

The shape of SADS of **2**, makes it very tempting to ascribe this spectrum to the absorption of ring-opened form. The steady state absorption spectrum of TBAH opened forms in methanol is plotted in the same graph (grey area plots in panels (b) and (c) of Figure 7). In this case, a resemblance to the transient spectrum of long-lived species is obvious. The peak position and shape of both spectra match very well, and, most importantly, the induced absorption of long-lived species is zero above 500 nm, where the largest discrepancies were observed directly comparing light-induced and TBAH-induced spectra in acetonitrile. The only discrepancy between the red and grey curves in Figure 6 is observed in the UV region below 380 nm, where the data is less reliable. In this spectral range, the signal-to-noise ratio is worse due to significant attenuation of the probing light by sample absorption. Therefore, we safely conclude that the long-lived spectral features correspond well to the absorption spectra of ring-open forms.

Provided the long-lived species are indeed the ring-opened isomers, photochromic oxazines do not have the advantage of being fast molecular switches in alcohol solutions, as the relaxation of the

excited species takes hundreds of ns. However, one must have in mind that the argument of resemblance is not sufficient to claim the ring-opening, as the similarity may be accidental; to confirm it, further investigations may be needed.

In principle, the process of photoinduced ring opening may also take place in acetonitrile, albeit very inefficiently. As was shown earlier, in methanol both studied compounds have different dominant relaxation pathways, hence different efficiency of the formation of the long-lived species. The induced absorption decay (after ns laser excitation) of photochromic oxazines in acetonitrile was assumed to be monoexponential in the earlier works.¹⁻⁹ However, tiny long-lived components were observed in most of the reported cases: instead of decaying to zero, kinetic traces retain a slight offset, extending beyond the timescale of hundreds of nanoseconds.¹⁻⁹ In addition, the contribution of the long-lived component increases in the kinetic signals in the blue part of the spectrum. Figure 8 illustrates the deviation from the monoexponential decay kinetics of the difference absorption of **IB** and **I-A** in acetonitrile. Normalized kinetic traces at different wavelengths evidence increasing decay times and larger long-lived offset values at shorter detection wavelengths. In order to extract the spectra of the long-lived component from the weak and noisy data, we applied global analysis together with the same relaxation model, used for fitting of the data, recorded in methanol (see Figure 7 (a)).

In our previous work on photochromic oxazines with phenylic substituents, global analysis of the flash photolysis data also revealed the presence of a long-lived component, and a second compartment was necessary to satisfactory fit the experimental data.¹⁰ A simple sequential model was used for fitting, the resulting SADS of the long-lived species was a broad plateau with minuscule

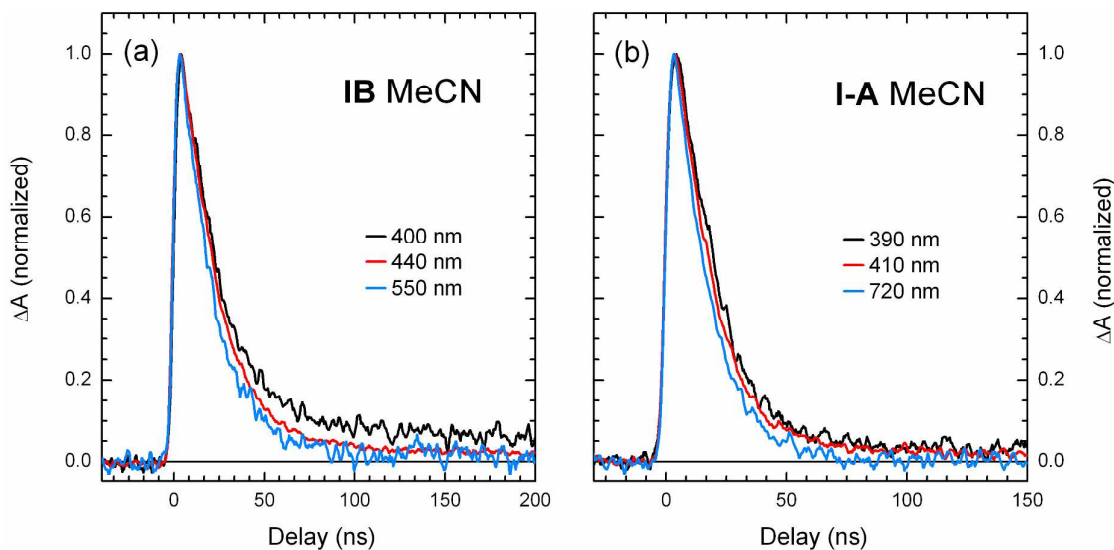


Figure 8. Normalized kinetic traces of **IB** (a) and **I-A** (b) in acetonitrile at selected wavelengths.

amplitude. Here, the sequential connectivity scheme features an additional transfer route for the first component directly to the ground state. The most of the difference absorption signal of **IB** and **I-A** in acetonitrile decays with a lifetime of 21 ns. Therefore, direct relaxation to the ground state $1 \rightarrow S_0$ is a fast process, while $1 \rightarrow 2$ transition is inefficient, so it must be at least several times slower than the dominant relaxation to the ground state.

Fitting results turned out to be rather insensitive to the value of the decay time of 2, which may vary in the range of 300–800 ns. Due to very small amplitude of the long-lived signals, changing the value of this parameter is merely reflected in the ratio of the amplitudes of the two SADS. The same applies to the time parameter corresponding to $1 \rightarrow 2$ transition, with values in the range of 160–200 ns yielding virtually identical fits, while only affecting the relative amplitude of SADS of 2.

assigned to the open form isomers of the investigated compounds; in fact, the nature of this species remains to be determined. One candidate for these spectral features would be the radical of the molecule formed by direct, multi-step or multi-photon ionization. If one of the latter mechanisms is responsible, excitation energy dependence would allow to unravel the nature of these long-lived spectral forms.

In the end we would like to remark that the findings of this study require reassessing the earlier works on the subject and redefining the interpretation of the past experiments. A very interesting and important inquiry is the redefining of the femtosecond excited state dynamics of photochromic oxazines,¹¹ as well as the results of optical switching experiments,¹⁸ in the new light, involving the triplet states instead of ring-opened photoproduct. On the other hand, further experiments are needed to clarify the unknown issues, such as the solvent influence on the photodynamics of

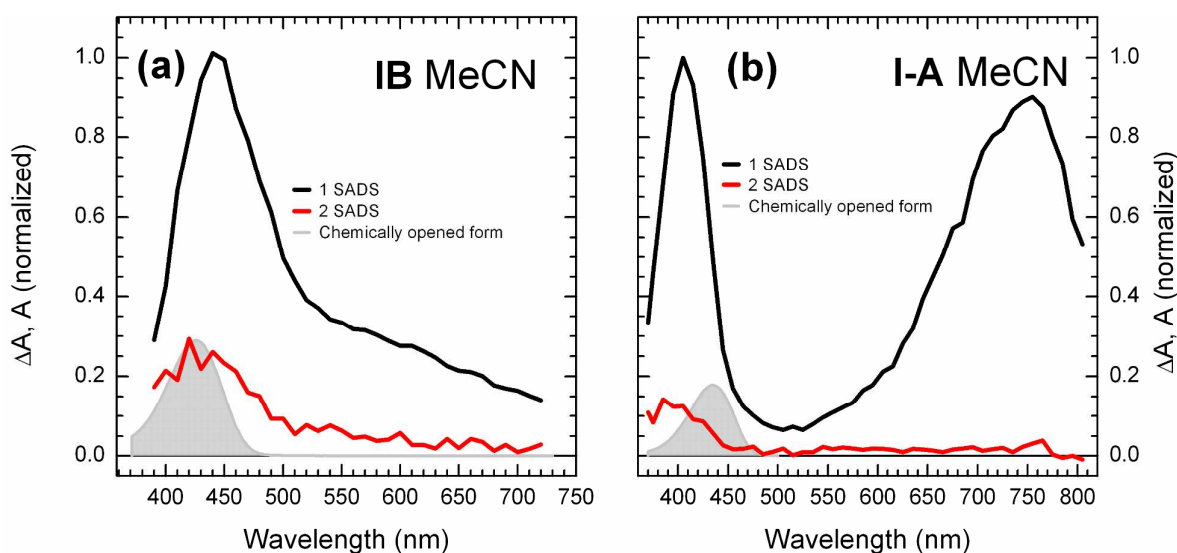


Figure 9. Global analysis of the nanosecond flash photolysis data of **IB** (a) and **I-A** (b) in acetonitrile: species associated difference spectra (SADS); grey plots depict the steady state absorption spectra of chemically opened forms in acetonitrile.

Figure 9(a) shows SADS of **IB**, obtained from fitting with values equal to 640 ns and 200 ns for transitions $2 \rightarrow S_0$ and $1 \rightarrow 2$, respectively. Results for **I-A**, shown in panel (b) of Figure 9, correspond to values of 400 ns and 200 ns for the respective transitions. In acetonitrile, SADS of the long-lived species is much noisier and worse resolved compared to those in methanol. Even though the maximum of SADS of 2 is at 430 nm (SADS of 1 peaks at 440 nm), is close to that of the chemically opened form, the resemblance between the spectra (compare the red and grey lines in Figure 9(b)) is poor. The overall spectral shapes differ considerably: the absorption band of SADS 2 is much broader and red-shifted compared to that of the chemically opened form, and, importantly, the former features a broad absorption plateau. Variation of the parameters did not influence the spectral shape of SADS. Consequently, the long-lived species cannot be clearly

photochromic oxazines, the nature of the observed short-lived species in methanol and the formation of the untypically short-lived triplet state in the excited state.

Conclusions

Photochromic oxazines are established as very fast molecular switches, based on light-induced bond breakage and formation of the ring-opened isomer. The current interpretation of the experimental results and the assignment of transient absorption to the ring-opened forms of photochromic oxazines are based on alleged resemblance between the absorption spectra of photoinduced compounds and chemically opened

forms. However, more accurate spectral measurements have shown that the extent of this resemblance does not justify the attribution of photoinduced species. We suggest that the photoinduced absorption of photochromic oxazines is due to the excited triplet state. In the two compounds chosen to represent the “typical” photochromic oxazines: **IB**, the unmodified parent molecule and **I-A**, a compound with phenylic substituent in indole ring, we observed the effect of oxygen quenching, which quantitatively confirmed the presence of triplet state. This result was obtained in acetonitrile, which is the solvent used in most prior studies on photochromic oxazines. The experiments in alcohol solutions revealed spectral signatures similar to those observed in acetonitrile with an important addition of a long-lived (ca. 200 ns) species, exhibiting excellent spectral resemblance to chemically opened forms. The similarity of the initial transient spectra to those recorded in acetonitrile allows tentative attribution of these spectra to the triplet states. The long-lived spectral features we fairly confidently assign to the ring-opened isomers. Finally, the connectivity scheme, used in global analysis of the experimental data in alcohols, was tested on data obtained in acetonitrile to re-examine tiny small long-lived components observed (but largely ignored) in previous studies. However, the global analysis revealed the spectra of the long-lived species bearing little resemblance to that of the chemically opened forms, and the origin of the long-lived spectral features observed in acetonitrile remains to be determined.

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References

- M. Tomasulo, S. Sortino and F. M. Raymo, *Org. Lett.*, 2005, 7, 1109-1112.
- M. Tomasulo, S. Sortino, A. J. White and F. M. Raymo, *J. Org. Chem.*, 2005, 70, 8180-8189.
- M. Tomasulo, S. Sortino and F. M. Raymo, *J. Photochem. Photobiol., A*, 2008, 200, 44-49.
- E. Deniz, M. Tomasulo, S. Sortino and F. M. Raymo, *J. Phys. Chem. C*, 2009, 113, 8491-8497.
- M. Tomasulo, E. Deniz, T. Benelli, S. Sortino and F. M. Raymo, *Adv. Funct. Mater.*, 2009, 19, 3956-3961.
- M. Tomasulo, S. Sortino and F. M. Raymo, *J. Org. Chem.*, 2008, 73, 118-126.
- M. Tomasulo, S. Sortino, A. J. White and F. M. Raymo, *J. Org. Chem.*, 2006, 71, 744-753.
- M. A. Petersen, E. Deniz, M. B. Nielsen, S. Sortino and F. M. Raymo, *Eur. J. Org. Chem.*, 2009, DOI: 10.1002/ejoc.200900604, 4333-4339.
- Y. Prostota and P. J. Coelho, *Dyes Pigm.*, 2013, 98, 93-99.
- V. Voiciuk, K. Redeckas, V. Martynaitis, R. Steponavičiūtė, A. Šačkus and M. Vengris, *J. Photochem. Photobiol., A*, 2014, 278, 60-68.
- K. Redeckas, V. Voiciuk, R. Steponavičiūtė, V. Martynaitis, A. Šačkus and M. Vengris, *J. Photochem. Photobiol., A*, 2014, 285, 7-15.
- T. L. Dawson, *Color. Technol.*, 2010, 126, 177-188.
- H. Dürr and H. Bouas-Laurent, *Photochromism: Molecules and systems*, Elsevier, Amsterdam, 2003.
- N. Tamai and H. Miyasaka, *Chem. Rev.*, 2000, 100, 1875-1890.
- E. Deniz, M. Battal, J. Cusido, S. Sortino and F. M. Raymo, *Phys. Chem. Chem. Phys.*, 2012, 14, 10300-10307.
- F. M. Raymo, *The journal of physical chemistry. A*, 2012, 116, 11888-11895.
- M. Barkauskas, V. Martynaitis, A. Sackus, R. Rotomskis, V. Sirutkaitis and M. Vengris, *Lith. J. Phys.*, 2008, 48, 231-242.
- K. Redeckas, V. Voiciuk, R. Steponavičiūtė, V. Martynaitis, A. Sackus and M. Vengris, *The journal of physical chemistry. A*, 2014, 118, 5642-5651.
- I. H. M. van Stokkum, D. S. Larsen and R. van Grondelle, *Biochim. Biophys. Acta-Bioenerg.*, 2004, 1658, 262-262.
- E. Deniz, S. Impellizzeri, S. Sortino and F. M. Raymo, *Canadian Journal of Chemistry*, 2010, 89, 110-116.
- Y. Prostota, J. Berthet, S. Delbaere and P. J. Coelho, *Dyes Pigm.*, 2013, 96, 569-573.
- E. Deniz, S. Sortino and F. M. Raymo, *The Journal of Physical Chemistry Letters*, 2010, 1, 3506-3509.
- E. Deniz, M. Tomasulo, J. Cusido, I. Yildiz, M. Petriella, M. L. Bossi, S. Sortino and F. M. Raymo, *The Journal of Physical Chemistry C*, 2012, 116, 6058-6068.
- J. Garcia-Amoros, S. Swaminathan, S. Sortino and F. M. Raymo, *Chemistry (Weinheim an der Bergstrasse, Germany)*, 2014, 20, 10276-10284.
- F. Wilkinson and A. A. Abdel-Shafi, *J. Phys. Chem. A*, 1997, 101, 5509-5516.
- D. J. McGarvey, P. G. Szekeres and F. Wilkinson, *Chem. Phys. Lett.*, 1992, 199, 314-319.
- F. Wilkinson, D. J. McGarvey and A. F. Olea, *The Journal of Physical Chemistry*, 1994, 98, 3762-3769.
- W. M. Nau, W. Adam and J. C. Scaiano, *J. Am. Chem. Soc.*, 1996, 118, 2742-2743.
- F. Wilkinson and A. A. Abdel-Shafi, *J. Phys. Chem. A*, 1999, 103, 5425-5435.
- A. Garner and F. Wilkinson, *Chem. Phys. Lett.*, 1977, 45, 432-435.
- A. P. Darmanyan and C. S. Foote, *The Journal of Physical Chemistry*, 1993, 97, 4573-4576.
- S. K. Chattopadhyay, C. V. Kumar and P. K. Das, *Journal of Photochemistry*, 1985, 30, 81-91.
- R. V. Bensasson and J.-C. Gramain, *J. Chem. Soc., Faraday Trans.*, 1980, 76, 1801-1810.

ARTICLE

Journal Name

34. J. A. Bell and H. Linschitz, *J. Am. Chem. Soc.*, 1963, 85, 528-533.
35. C. Franco and J. Olmsted, 3rd, *Talanta*, 1990, 37, 905-909.
36. S. L. Murov, I. Carmichael and G. L. Hug, *Handbook of Photochemistry, Second Edition*, Taylor & Francis, 1993.