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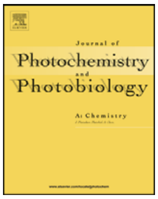

A new family of photochromic compounds based on the photoinduced opening and thermal closing of [1,3]oxazine rings

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ABSTRACT

We have developed a new family of photochromic compounds with fast switching speeds and outstanding fatigue resistances. Their molecular skeleton combines a 3*H*-indole heterocycle and a phenoxy fragment to form a [1,3]oxazine core, which can be assembled in two synthetic steps starting from commercial reagents. Following this general synthetic strategy, we have prepared ten compounds differing in the substituent (R^1) on the chiral center of their [1,3]oxazine ring, the group (R^2) in the *para* position, relative to the oxygen atom, of their phenoxy fragment and/or the substituent (R^3) in the *para* position, relative to the nitrogen atom, on the 3*H*-indole heterocycle. The [1,3]oxazine ring of four of these compounds opens in less than 6 ns, upon laser excitation, with quantum yields ranging from 0.08 to 0.28. The photoinduced ring-opening process generates zwitterionic isomers, incorporating a 3*H*-indolium cation and a phenolate anion. These two fragments can be designed independently to absorb in the visible region by regulating the nature of the substituents R^1 and R^2. The photogenerated isomers revert thermally to the original species with first-order kinetics and lifetimes ranging from 25 to 140 ns. In fact, a complete switching cycle can be completed on a nanosecond timescale with these photochromic compounds. Furthermore, their photoinduced isomerization is not accompanied by degradation and they tolerate thousand of switching cycles in air even in the presence of molecular oxygen. Thus, our novel photochromic compounds can, in principle, evolve into innovative photonic materials with unprecedented performance.

1. Introduction

Nitrospiropyrans are members of one of the most popular families of photochromic compounds [1–4]. Their molecular skeleton combines a 3*H*-indole and a nitrobenzopyran through a spirocenter. The two fragments are orthogonal to each other and, hence, do not communicate electronically in the ground state (S_0). As a result, these compounds are generally colorless. Upon ultraviolet irradiation, however, they switch to a colored form. For example, the nitrospiropyran **1a** (Fig. 1) switches to the merocyanine **1b** upon irradiation with a quantum yield (ϕ in Table 1) of 0.10 in acetonitrile at 25 °C [5]. The photogenerated isomer has an extended π-system and, hence, absorbs in the visible region. In fact, the photoinduced transformation of **1a** into **1b** is accompanied by the appearance of color. The colored species, however, is thermally unstable and reverts to the original isomer with first-order kinetics and a lifetime (τ in Table 1) of 400 s in acetonitrile at 25 °C upon storage in the dark. As a result, the colorless and colored isomers can repeatedly be interconverted simply by turning on and off an ultraviolet source. Furthermore, these compounds can be operated in solution as well as within rigid materials and their transformations can be exploited to photoregulate the absorption coefficient and refractive index of the overall material. Indeed, the photoinduced absorptive and dispersive effects associated with the transformation of these compounds have already been employed to develop a diversity of photoresponsive materials and devices [1b,6–12].

The ultraviolet excitation of **1a** results in the efficient population of its first triplet state (T_1) [5,13]. After intersystem crossing, the [C—O] bond at the spirocenter cleaves to form a ring-opened intermediate on a picosecond timescale [14–18]. Once formed, this species can undergo a *cis* → *trans* isomerization about the [C═C] bond adjacent to the spirocenter and then decay to S_0. Alternatively, it can decay to S_0 first and then undergo the *cis* → *trans* isomerization. In both instances, the final product is the colored isomer **1b**, which is formed on a microsecond timescale [5,13]. This species reverts to the original form **1a** on a minute timescale [5,13], after a slow *trans* → *cis* isomerization followed by the fast reformation of the [C—O] bond at the spirocenter [19]. The relatively long time required for the thermal decoloration imposes a stringent limi-

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Table 1
Quantum yield (ϕ) for the photoinduced isomerization of the spiropyran **1a** and of the [1,3]oxazines **2a**, **3a**, **8a** and **9a** and lifetime (τ) of the photogenerated isomers[a]

	ϕ	τ (ns)	Ref.
1a	0.10	4×10^{11}	[5]
2a	0.03	25	[37b,h]
3a	0.10	25	[37a,b,h]
8a	0.08	38	[37f,g]
9a	0.28	140	[37f]

[a] ϕ and τ were determined by laser flash photolysis in acetonitrile at 20–25 °C.

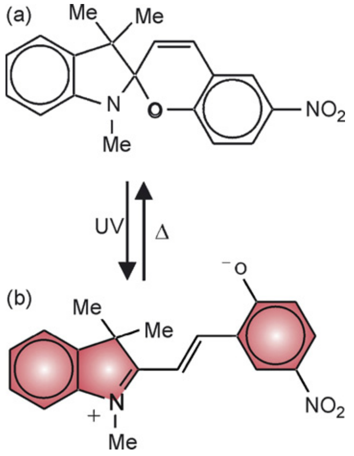


Fig. 1. The ultraviolet (UV) irradiation of the colorless spiropyran **1a** generates the colored merocyanine **1b**, which reverts to the original species upon storage in the dark [5,13].

tation on the switching rate of these systems, which can only be in the Hertz regime. In fact, several minutes are required to complete a single switching cycle. In addition, the involvement of a relatively long-lived T_1 in the photoisomerization process causes the formation of singlet oxygen ($^1\Delta_g$) with a quantum yield of 0.10 [5,13f]. This species promotes the oxidative degradation of the photochromic switch. Consistently, the fatigue resistances of nitrospiropyrans increase considerably in the presence of singlet-oxygen scavengers [20,21].

In principle, all-optical logic gates [22–26], optical limiters [27–31] photoresponsive filters [7] and switchable probes [32] can all be designed around the unique properties of thermally reversible photochromic compounds. The poor fatigue resistances of nitrospiropyrans together with their slow switching speeds, however, have limited considerably their practical applications and restricted their use to the implementation of only few prototypical devices [33–36]. In search of viable strategies to overcome these limitations, we have designed a new family of photochromic compounds [37]. In this account, we illustrate the logic behind our design and provide an overview on the photochemical properties of this novel class of photochromic switches.

2. Design and synthesis

The analysis of the mechanism responsible for the reversible interconversion of **1a** and **1b** shows that two main chemical steps are responsible for both the coloration and decoloration processes [5,13]. In one instance, the [C—O] bond at the spirocenter of **1a** cleaves first and then the adjacent [C═C] bond undergoes a *cis* → *trans* isomerization to form **1b**. In the other instance, the [C═C] bond of **1b** undergoes a *trans* → *cis* isomerization first and then the [C—O] bond is reformed to regenerate the spirocenter of **1a**. The changes in the configuration of the [C═C] bond, however, are significantly slower than the cleavage/formation of the [C—O] bond. Thus, the need for *cis* → *trans* and *trans* → *cis* isomerizations is mainly responsible for the relatively slow switching speeds of this class of photochromic compounds. On the basis of these considerations, we have envisaged the possibility of designing photochromic switches based exclusively on the photoinduced cleavage and thermal formation of a [C—O] bond. Specifically, we have synthesized the [1,3]oxazines **2a**–**11a** (Fig. 2) [37,38]. In analogy to **1a**, these compounds incorporate a carbon atom between a nitrogen atom and oxygen atom, but lack the adjacent [C═C] bond. Upon ultraviolet irradiation, their [C—O] bond is expected to cleave and open the [1,3]oxazine ring. The resulting isomers **2b**–**11b** incorporate a phenolate chromophore, which can be engineered to absorb in the visible region by regulating the substituent (R^2) in the *para* position relative to the oxygen atom. Upon storage in the dark, the photogenerated isomers **2b**–**11b** are expected to switch back to the original forms **2a**–**11a** after the reformation of the [C—O] bond. Thus, the photoinduced coloration and thermal decoloration of these molecular switches does not require slow *cis*/*trans* isomerizations and can be significantly faster than those associate with the interconversion of **1a** and **1b**.

The [1,3]oxazines **2a**–**6a** can be prepared in two steps starting from phenyl hydrazine (Fig. 3) [37a,b,d–f]. In particular, this reagent can be condensed with an appropriate ketone, under acidic conditions, to generate the corresponding 3*H*-indoles. The resulting compounds can be *N*-alkylated with either a chloromethylphenol or a bromomethylphenol to assemble the target molecules, after the spontaneous cyclization of their [1,3]oxazine ring. Instead, the compounds **7a**–**9a** can be synthesized in one step starting from the [1,3]oxazine **3a** [37f,g]. Specifically, they can be prepared by condensing **3a** with benzaldehyde, 4-phenylbenzaldehyde or *trans*-4-(2-phenylethylene)-benzaldehyde, respectively, under acid conditions. Finally, the [1,3]oxazines **10a** and **11a** can be synthesized by coupling *trans*-1-vinylstilbene and preformed [1,3]oxazines with an iodide atom in the *para* position, relative to the nitrogen atom, of the 3*H*-indole (R^3 = I), under the assistance of triethylamine amine and palladium(II) bisacetate [37f].

3. Spectroscopy

The [1,3]oxazines **2a** and **3a** are the first two members of this novel class of photochromic compounds that we have synthesized and investigated [37a,b,h]. They both incorporate a nitro group in the *para* position, relative to the oxygen atom, of the phenoxy fragment ($R^2 = NO_2$) and a hydrogen atom in the *para* position, relative to the nitrogen atom, of their 3*H*-indole component (R^3 = H). However, they differ in the nature of the group attached to the chiral center of their [1,3]oxazine ring, which is a methyl group for **2a** (R^1 = Me) and a phenyl ring for **3a** (R^1 = Ph). Their steady-state absorption spectra (a in Fig. 4), recorded in acetonitrile at 25 °C, show a band at 308 nm, corresponding to the $S_0 \rightarrow S_1$ transition of the 4-nitrophenoxy fragment. In fact, this band resembles the ground-state absorption (b in Fig. 4) of 4-nitroanisole. The laser excitation of **2a** and **3a** at a wavelength (355 nm) within the tail of this band results in the cleavage of the [C—O] bond and the opening of the [1,3]oxazine ring with quantum yields (ϕ in Table 1) of 0.03 and 0.10, respectively. The photogenerated isomers **2b** and **3b** incorporate a 4-nitrophenolate chromophore, which absorbs in the visible region. Consistently, the absorption spectra (c in Fig. 4), recorded 30 ns after the excitation of **2a** and **3a**, show a band centered at 440 nm, corresponding to the $S_0 \rightarrow S_1$ transition of the 4-nitrophenolate fragment of **2b** and **3b**. In fact, this band resembles the ground-state absorption of tetrabutylammonium 4-nitrophenolate (d in Fig. 4). In agreement with this

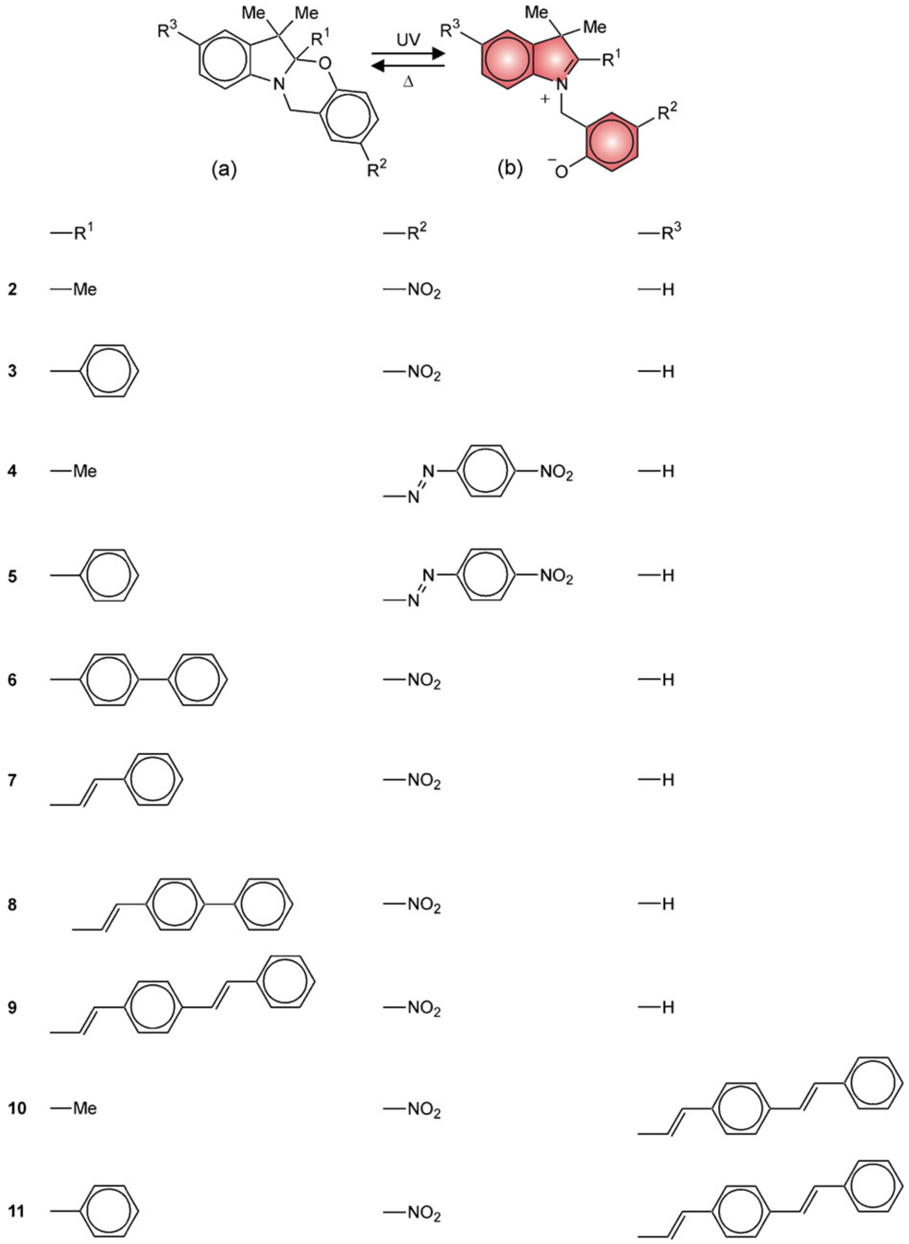
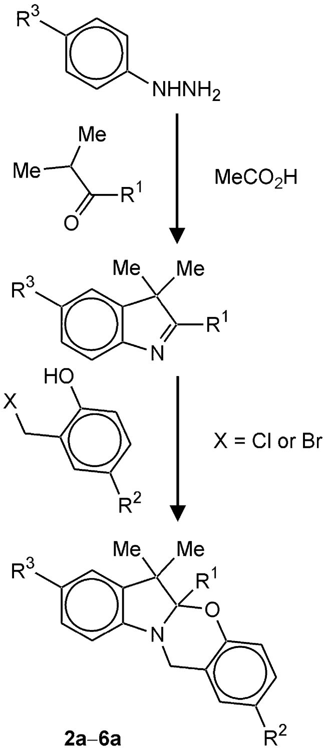


Fig. 2. The ultraviolet (UV) irradiation of the colorless [1,3]oxazines **2a**–**11a** is expected to generate the colored zwitterions **2b**–**11b**, which can revert to the original species upon storage in the dark [37,38].

assignment, the transient absorption spectrum of 4-nitroanisole, recorded under otherwise identical conditions, does not show any significant absorption in the same temporal regime [39]. Furthermore, the laser excitation of **2a** and **3a** is not accompanied by the generation of singlet oxygen, excluding the participation of long-lived triplet states in the photoisomerization.

The photogenerated isomers **2b** and **3b** revert thermally to the original species **2a** and **3a** with first-order kinetics and a lifetime (τ in Table 1) of 25 ns in both instances. Consistently, the absorbance at 440 nm (Fig. 5) decays monoexponentially with these transformations. Thus, a full switching cycle can be completed on a nanosecond timescale with these photochromic compounds. Furthermore, the lack of singlet oxygen translates into outstanding fatigue resistances. For example, the steady-state absorption spectra of **3a**, recorded before and after 3000 switching cycles performed in the presence of molecular oxygen, are virtually identical, showing that the reversible interconversion of **3a** and **3b** is not accompanied by any degradation.

The group (R^2) in the *para* position, relative to the oxygen atom, on the phenolate chromophore dictates the absorption wavelength of the photogenerated state of our photochromic compounds. In principle, the introduction of a 4-nitrophenylazo appendage in place of the nitro group of **2b** and **3b** can be exploited to shift bathochromically their absorption bands. On the basis of these considerations, we have synthesized and investigated the [1,3]oxazines **4a** and **5b** [37d,e]. Their steady-state absorption spectra (a in Fig. 6), recorded in acetonitrile at 22 °C, show an intense band at 377 nm, corresponding to a $S_0 \rightarrow S_1$ transition of their *trans*-4-nitrophenylazophenoxy chromophore. Consistently, this band resembles the ground-state absorption of *trans*-4-nitrophenylazoanisole (b in Fig. 6). However, the [1,3]oxazine ring of these compounds does not open upon laser excitation. The absorp-



2a–6a

Fig. 3. The [1,3]oxazines **2a**–**6a** can be prepared in two steps starting form phenyl hydrazine [37,38].

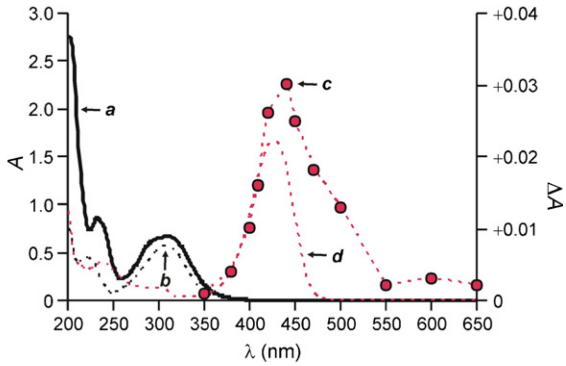


Fig. 4. Steady-state absorption spectra (0.1 mM, MeCN, 22 °C) of **3a** (a), 4-nitroanisole (b) and tetrabutylammonium 4-nitrophenolate (d). Transient absorption spectrum (0.1 mM, MeCN, 22 °C) of **3a** (c) recorded 30 ns after laser excitation (355 nm, 6 ns, 8 mJ) [37a,b,h].

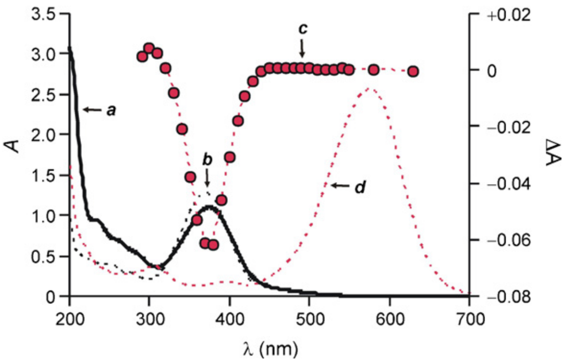


Fig. 6. Steady-state absorption spectra (0.1 mM, MeCN, 22 °C) of **5a** (a), *trans*-4-nitrophenylazoanisole (b) and tetrabutylammonium *trans*-4-nitrophenylazophenolate (d). Transient absorption spectrum (0.1 mM, MeCN, 22 °C) of **5a** (c) recorded 4 μs after laser excitation (355 nm, 6 ns, 8 mJ) [37d,e].

tion spectra (c in Fig. 6), recorded 4 μs after excitation, do not reveal the absorption of the *trans*-4-nitrophenylazophenolate chromophore of **4b** and **5b**, which is supposed to be centered at 576 nm (d in Fig. 6). Instead, the spectra show the bleaching of the band associated with the *trans*-4-nitrophenylazophenoxy chromophore. This change is persistent on a microsecond timescale (Fig. 7), but eventually the original steady-state absorption spectra are fully restored, after several milliseconds. This behavior is indicative of the *trans* → *cis* isomerization of the 4-nitrophenylazophenoxy chromophore followed by its thermal *cis* → *trans* reisomerization. Thus, this particular photoinduced transformation competes successfully with the opening of the [1,3]oxazine ring and prevents the formation of the ring-opened isomers **4b** and **5b**.

The photoinduced opening of the [1,3]oxazine ring of **2a** and **3a** brings the group (R^1) on their chiral center in conjugation with the 3*H*-indolium cation of the resulting isomers **2b** and **3b**. In principle, the introduction of an extended π-system in place of the methyl group of **2a** or phenyl ring of **3a** can be exploited to generate another chromophore able to absorb in the visible region, after the photoinduced transformation. Indeed, the corresponding photogenerated isomers would incorporate an 3*H*-indolium cation with extended conjugation in addition to the 4-nitrophenolate anion. On the basis of this design logic, we have synthesized and investigated the [1,3]oxazines **6a**–**9a** [37f,g]. Their steady-state absorption spectra (a in Fig. 8), recorded in acetonitrile at 20 °C, are approximately the sum of those (b and c in Fig. 8) of their constituent chromophores. Upon laser excitation, however, only **8a** and **9a** ring open to generate the corresponding isomers **8b** and **9b** with quan-

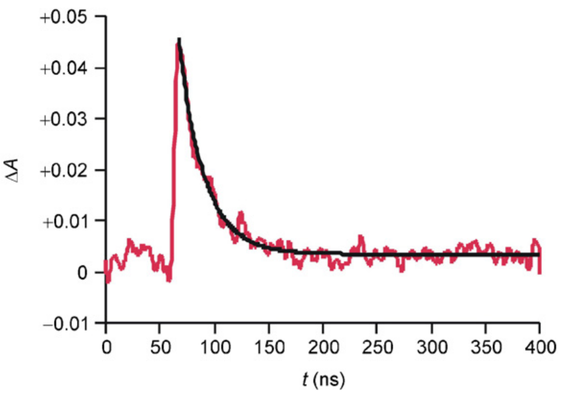


Fig. 5. Temporal evolution of the absorbance at 440 nm of a solution of **3a** (0.1 mM, MeCN, 22 °C) after laser excitation (355 nm, 6 ns, 8 mJ) [37a,b,h].

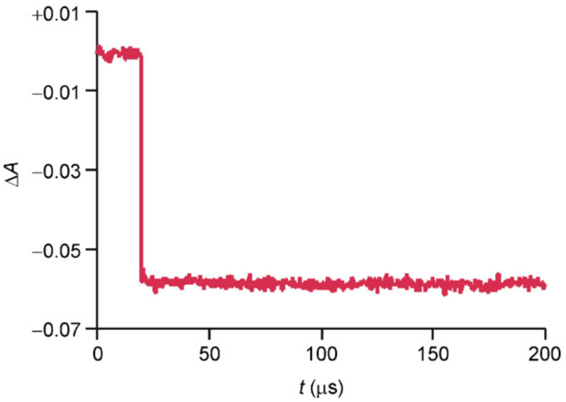


Fig. 7. Temporal evolution of the absorbance at 380 nm of a solution of **5a** (0.1 mM, MeCN, 22 °C) after laser excitation (355 nm, 6 ns, 8 mJ) [37d,e].

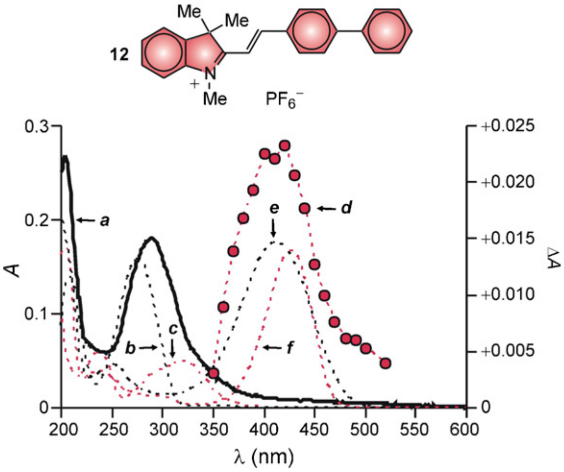


Fig. 8. Steady-state absorption spectra (0.01 mM, MeCN, 20 °C) of **8a** (a), 4-vinylbiphenyl (b), 4-nitroanisole (c), **12** (e) and tetrabutylammonium 4-nitrophenolate (f). Transient absorption spectrum (0.05 mM, MeCN, 20 °C) of **8a** (d) recorded 30 ns after laser excitation (355 nm, 6 ns, 8 mJ) [37f,g].

tum yields (ϕ in Table 1) of 0.08 and 0.28, respectively. The redox potentials of model compounds suggest that the transfer of one electron from R^1 to the excited 4-nitrophenoxy fragment of **6a** and **7a** is exoergonic with a free energy change of −0.5 and −0.6 eV, respectively. Presumably, the photoinduced electron transfer process competes successfully with the ring-opening step and prevents the formation of **6b** and **7b**.

In the case of **8a**, the absorption spectrum (d in Fig. 8), recorded 30 ns after excitation, shows an intense band at 430 nm. This band is the sum of the ground-state absorptions of its 3*H*-indolium cation and phenolate anion and, in fact, resembles the steady-state bands of the model 3*H*-indolium cation **12** (e in Fig. 8) and tetrabutylammonium 4-nitrophenolate (f in Fig. 9). As a result of the bichromophoric character of the photogenerated isomer **8b**, the photoinduced change in absorbance associated with this particular photochromic system is approximately twice that observed for an optically matched solution of the parent photochrome **3a**. Indeed, the transition from the monochromophoric photochrome **3a** to the bichromophoric photochrome **8a** translates into an increase in coloration efficiency of 1.8 ± 0.3 [40].

In the case of **9a**, the absorption spectrum, recorded after laser excitation, shows a band at 420 nm. As observed for **8b**, this band is the sum of the ground-state absorptions of the 3*H*-indolium cation and 4-nitrophenolate anion of **9b**. Both photogenerated isomers revert to the original species with first-order kinetics. Consistently, their absorbance in the visible region decays monoexponentially. However, their lifetimes (τ in Table 1) are longer than those of **2b** and **3b**. Specifically, the lifetime of **8b** is 38 ns, while that of **9b** is 140 ns. The increase in lifetime is, presumably, as a result of the extended conjugation of the 3*H*-indolium cation of the photogenerated isomers, which can stabilize these species and delay the ring-closing process.

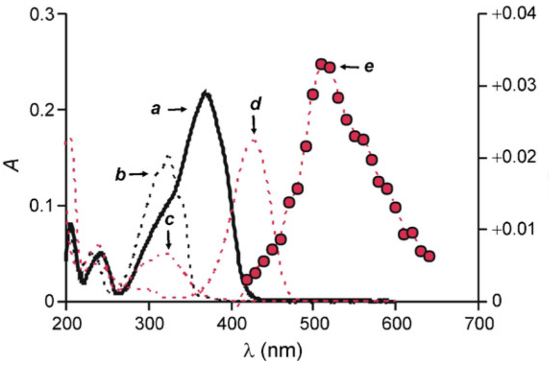


Fig. 9. Steady-state absorption spectra (0.02 mM, MeCN, 20 °C) of **10a** (a), *trans*-4-vinylstilbene (b), 4-nitroanisole (c), and tetrabutylammonium 4-nitrophenolate (d). Transient absorption spectrum (0.01 mM, MeCN, 20 °C) of **10a** (e) recorded 80 ns after the laser excitation (355 nm, 8 mJ) [37f].

The introduction of an extended π-system in the *para* position (R^3), relative to the nitrogen atom, on the 3*H*-indole fragment can also be exploited to generate bichromophoric photochromes. The photoinduced opening of the [1,3]oxazine ring of the resulting compounds should extend the conjugation of the corresponding 3*H*-indolium cation, forming a chromophore able to absorb in the visible region together with the 4-nitrophenolate anion. On the basis of these considerations, we have synthesized and investigated the [1,3]oxazines **10a** and **11a** [37f]. Both incorporate a *trans*-stilbenylvinyl appendage on their 3*H*-indole fragment (R^3), but differ in the nature of the substituent attached to their chiral center, which is a methyl group for **10a** (R^1 = Me) and a phenyl ring for **11a** (R^1 = Ph). Their steady-state absorption spectra (a in Fig. 9), recorded in acetonitrile at 20 °C, reveal an intense band at 368 nm. This band is bathochromically shifted by 42 nm relative to that of *trans*-4-vinylstilbene (b in Fig. 9), suggesting that the *trans*-stilbenylvinyl appendage and 3*H*-indole fragment interact in the ground state. In addition, this band has a tail at shorter wavelengths corresponding to the $S_0 \rightarrow S_1$ transition of the 4-nitrophenoxy chromophore (c in Fig. 9). Upon laser excitation, however, the characteristic absorption of the 4-nitrophenolate chromophore (d in Fig. 9) of the ring-opened isomers cannot be detected. Indeed, most of the exciting photons at 355 nm are absorbed by the extended π-system associated with the 3*H*-indole fragment, rather than the 4-nitrophenoxy chromophore. As a result, the absorption spectrum (e in Fig. 9), recorded 80 ns after excitation, shows a band at 510 nm corresponding to a transition in the triplet manifold of the *trans*-stilbenylvinyl-3*H*-indole assembly. Consistently, this band resembles the $T_0 \rightarrow T_1$ absorption of *trans*-4-phenylvinylstilbene [41] and decays monoexponentially with a lifetime of 2 μs. Thus, intersystem crossing competes successfully with the ring opening of **10a** and **11a**, preventing the formation of **10b** and **11b**.

4. Conclusions

Photochromic compounds with fast switching speeds and outstanding fatigue resistances can be designed around the photoinduced opening and thermal closing of a [1,3]oxazine ring. The core of these compounds can be assembled in two synthetic steps, which culminate with the fusion of 3*H*-indole and benzo[1,3]oxazine heterocycles within the same molecular skeleton. The substituent (R^1) on the chiral center of their [1,3]oxazine ring, that (R^2) in the *para* position, relative to the nitrogen atom, on the 3*H*-indole heterocycle and/or the one (R^3) in the *para* position, relative to the oxygen atom, on the phenoxy fragment can easily be varied either during or after the assembly of the [1,3]oxazine core. Four of the ten compounds constructed according to this synthetic strategy ring open upon laser excitation. In particular, the [C—O] bond at the junction of the two heterocyclic fragments cleaves with quantum yields ranging from 0.08 to 0.28 to generate a zwitterionic product, incorporating a 3*H*-indolium cation and a phenolate anion. The absorption properties of the cationic and anionic components of the photogenerated species can independently be regulated by varying R^1 and R^2. In fact, either one or both chromophores can be designed to absorb in the visible region. The photogenerated isomers have lifetimes ranging from 25 to 140 ns and revert to the original species after the thermal reformation of the [1,3]oxazine ring. Thus, these compounds can be switched back and forth between two states on a nanosecond timescale, under the influence of ultraviolet excitation. Furthermore, they tolerate thousands of switching cycles with no sign of degradation, even in the presence of molecular oxygen. Hence, our innovative structural design for the realization of fast and stable photochromic compounds can lead to the development of valuable photoresponsive materials for photonic applications.

Acknowledgments

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