A photoswitchable bichromophoric oxazine with fast switching speeds and excellent fatigue resistance

Erhan Deniz, Stefania Impellizzeri, Salvatore Sortino, and Françisco M. Raymo

Abstract: In search of strategies to regulate the photochemical and photophysical properties of photochromic oxazines, we designed a multichromophoric compound incorporating 3*H*-indole, benzooxazine, and 2-(4-dimethylaminophenyl)ethynyl fragments. We synthesized this molecule in two steps in an overall yield of 51%, starting from commercial precursors. The ultraviolet irradiation of this photochrome opens a [1,3]oxazine ring in less than 6 ns to generate a zwitterionic isomer with a quantum yield of 0.10. In particular, the photoinduced ring opening generates a 4-nitrophenolate anion and a 3*H*-indolium cation. Additionally, this process brings the 2-(4-dimethylaminophenyl)ethynyl appendage into conjugation with the 3*H*-indolium cation. As a result, two distinct bands for the anionic and cationic fragments of the photogenerated zwitterion appear in the visible region of the absorption spectrum. The photogenerated isomer has a lifetime of 2 µs and switches back to the original form with first-order kinetics. Furthermore, this bichromophoric photochrome tolerates hundreds of switching cycles with no sign of degradation and can be operated within rigid polymer matrices. Thus, this particular structural design can lead to the development of a new family of bichromophoric photochromes and photoresponsive materials with microsecond switching times and excellent fatigue resistances.

Key words: heterocycles, molecular switches, oxazines, photochromism, photoisomerization.

Résumé : Dans le cadre d’une recherche sur des stratégies qui pourraient permettre de régulariser les propriétés photochimiques et photophysiques d’oxazines photochromiques, on a développé un composé multichromophorique comportant des fragments 3*H*-indole, benzooxazine et 2-(4-diméthylaminophényl)éthynyle. Cette molécule a été synthétisée en deux étapes, avec un rendement de 51 %, à partir de précurseurs commerciaux. L’irradiation ultraviolette de ce photochrome provoque l’ouverture d’un noyau [1,3]diazine en moins de 6 ns pour conduire à la formation d’un isomère zwitterionique avec un rendement quantique de 0,10. En particulier, l’ouverture de cycle photoinduite génère un anion 4-nitrophénolate et un cation 3*H*-indolium. De plus, ce processus conduit le groupe 2-(4-diméthylaminophényl)éthynyle à se placer en conjugaison avec le cation 3*H*-indolium. Il en résulte que la région visible du spectre d’absorption comporte deux bandes distinctes, l’une pour le fragment anionique et l’autre pour le fragment cationique du zwitterion photogénéré. Le temps de vie de l’isomère photogénéré est de 2 µs et il retourne à la forme originale avec une cinétique du premier ordre. De plus, ce photochrome bichromophorique tolère des centaines de cycles sans signe apparent de dégradation et il peut être utilisé dans des matrices de polymères rigides. Cette structure particulière pourrait donc conduire au développement d’une nouvelle famille de photochromes bichromophoriques et de matériaux photosensibles ayant des temps de commutation de l’ordre de la microseconde et une excellente capacité à résister à la fatigue.

Mots-clés : hétérocycles, commutateurs moléculaires, oxazines, photochromie, photoisomérisation.

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Introduction

The term photochromism refers to the photoinduced and reversible change in color of a collection of molecules.[1–5] The process can be a consequence of photoinduced ring opening–closing steps, cis–trans isomerizations, intramolecular proton transfers, intermolecular electron transfers, cycloadditions, or the reorganization of ligands around a metal center. All these transformations alter the electronic structure of the photoresponsive compound and result in significant changes in the absorption spectrum. In addition, these structural alterations at the molecular level can translate into noticeable changes in refractive index. As a result, photochromic transformations can be exploited to modulate the absorption coefficient and refractive index of a substrate under the influence of optical stimulations. Indeed, a diver-

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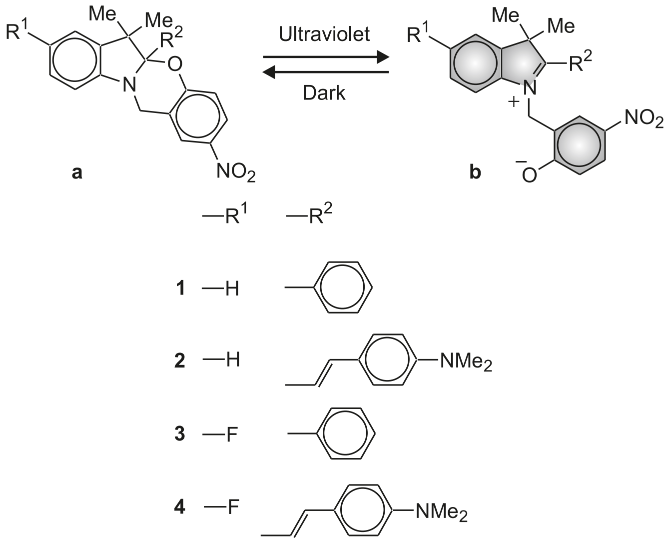
sity of photoresponsive materials and devices have already been designed around the absorptive and dispersive effects associated with photochromic compounds.[6–8] In fact, promising examples of all-optical logic gates,[9–13] optical limiters,[14–18] photoresponsive filters,[19] and photoswitchable probes[20–26] have all been implemented on the basis of the photochromism associated with certain organic compounds.

Nitrospiropyrans switch from a colorless to a colored state under ultraviolet irradiation and revert thermally to the original form.[27–31] Because of their photochemical behavior and their synthetic accessibility, they have become one of the most popular classes of photochromic compounds. However, their switching speeds are relatively slow and a full switching cycle can only be completed on a timescale of minutes. Furthermore, the involvement of the triplet state in the photoisomerization mechanism tends to encourage degradation and these compounds can only tolerate a few tens of switching cycles. In search of strategies to improve their switching speeds and fatigue resistances, we developed a new family of photochromic compounds based on the photoinduced opening and thermal closing of [1,3]oxazine rings.[32] Our molecules switch from a colorless to a colored state in less than 6 ns upon ultraviolet excitation and revert to the original form on a nanosecond timescale. In addition, they survive thousands of switching cycles unaffected, even in the presence of molecular oxygen, and can be operated in solution as well as within rigid polymer matrices. The integration of these compounds into photonic materials and devices, however, requires a basic understanding of the stereoelectronic factors regulating their spectroscopic signature and photochromism. In particular, we need to learn how their molecular skeleton should be modified to tune the color of the photogenerated state, the timescales of the isomerization processes, and the quantum efficiency of their coloration without compromising their excellent fatigue resistance.

Laser excitation of **1a** (Fig. 1) at 355 nm opens its [1,3]oxazine ring in less than 6 ns to generate the zwitterionic isomer **1b** with a quantum yield of 0.10 in acetonitrile at 20 °C.[32a,32b] The original state **1a** does not absorb in the visible region, while the 4-nitrophenolate chromophore of the photogenerated species **1b** absorbs at 440 nm. Therefore, the photoinduced transformation of **1a** into **1b** is accompanied by the appearance of a transient band in the visible region of the absorption spectrum. This band decays monoexponentially on a nanosecond timescale with the thermal reisomerization of **1b** back to **1a**.

The introduction of a 2-(4-dimethylaminophenyl)ethynyl group in place of the phenyl ring of **1a** generates a bichromophoric switch in the shape of **2a**.[32g] Specifically, the photoinduced opening of the [1,3]oxazine ring of this compound brings the 2-(4-dimethylaminophenyl)ethynyl appendage into conjugation with the 3*H*-indolium cation. The resulting chromophore absorbs at 540 nm and, hence, the formation of **2b** is accompanied by the appearance of a transient band centered at this wavelength together with one at 440 nm for the 4-nitrophenolate anion. Both bands decay monoexponentially on a microsecond timescale and with identical kinetics, as **2b** reisomerizes thermally to **2a**. Thus, structural modifications of the group (R^2 in Fig. 1) attached to the chiral center at the junction of the two heterocyclic fragments of our oxazines can be exploited to regulate the absorption properties of their photogenerated states in the visible region and impose bichromophoric character on them. However, the transition from **1a** to **2a** has a depressive effect on the photoisomerization efficiency and the quantum yield decreases from 0.10 to 0.07.

Fig. 1. Photoinduced transformation of the [1,3]oxazines **1a**–**4a** into the zwitterions **1b**–**4b**.



The introduction of a fluorine substituent in the para position (R^1 in Fig. 1) relative to the nitrogen atom of the 3*H*-indole fragment of **1a** facilitates the photoinduced opening of the [1,3]oxazine ring. Specifically, the quantum yield increases from 0.10 to 0.29 with the transition from **1a** to **3a**.[32g] On the basis of these considerations, we envisaged the possibility of introducing a fluorine substituent also on the 3*H*-indole fragment of the bichromophoric switch **2a** to improve the quantum yield for its photoisomerization. In particular, we designed compound **4a** and here we report its synthesis, spectroscopic characterization, and photochemical properties in solution and within a rigid polymer matrix.

Results and discussion

Synthesis

We synthesized **4a** in two steps (Fig. 2), starting from commercial precursors, with an overall yield of 51%. Specifically, the condensation of 2,3,3′-trimethyl-5-fluoro-3*H*-indole with *N*,*N*-dimethyl-4-aminobenzaldehyde under acidic conditions gave the extended 3*H*-indole **5**, which was reacted with 2-chloromethyl-4-nitrophenol to afford the target oxazine **4a**. Similarly, the reaction of **5** with methyl iodide produced the iodide salt of the model 3*H*-indolium cation **6**.

Steady-state absorption spectroscopy

The spectrum of **4a** reveals a band centered at 306 nm (*a* and *d* in Fig. 3) for the overlapping absorptions of the 2-(4-dimethylaminophenyl)ethynyl and 4-nitrophenoxy chromophores. Upon addition of acid, the [1,3]oxazine ring of **4a** opens to generate the cationic species **4c** (Fig. 4). This transformation extends the conjugation of the 2-(4-dimethylaminophenyl)ethynyl appendage and shifts its absorption to

Fig. 2. Synthesis of the [1,3]oxazine **4a** and model compound **6**.

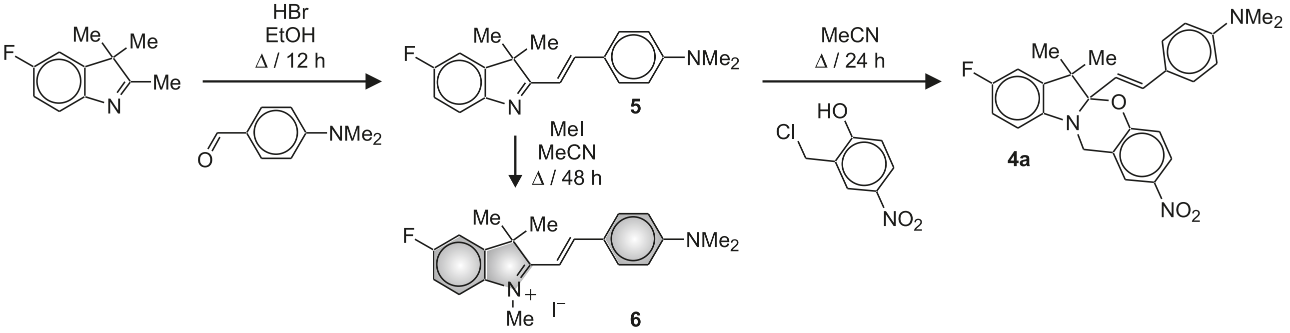
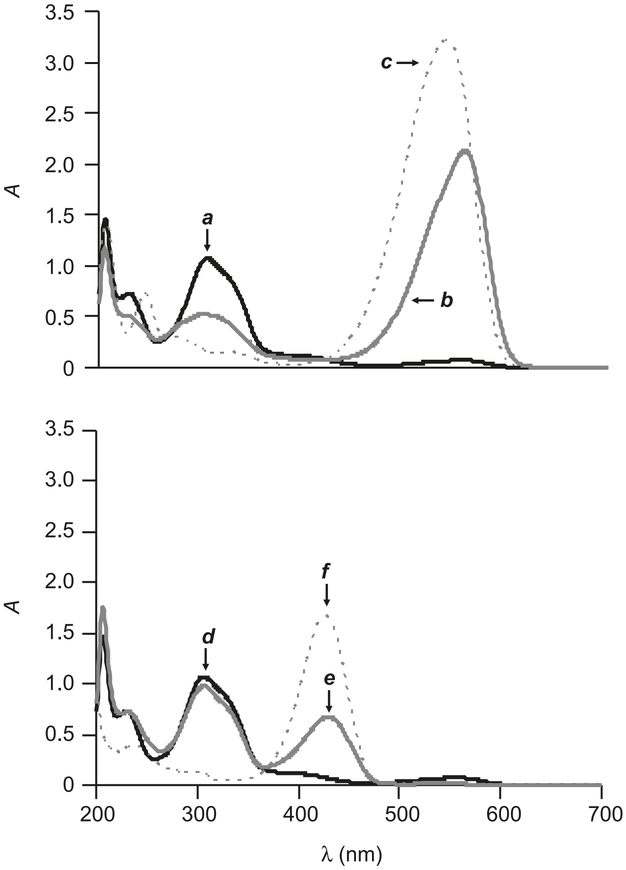


Fig. 3. Steady-state absorption spectra of solutions (0.1 mmol/L, MeCN, 20 °C) of **4a** before (*a* and *d*) and after the addition of either CF_3CO_2H (1 equiv., *b*) or Bu_4NOH (5 equiv., *e*), **6** (*c*), and 4-nitrophenol after the addition of Bu_4NOH (4 equiv., *f*).



559 nm (*b* in Fig. 3). Indeed, this band resembles that of the model 3*H*-indolium cation **6** (*c* in Fig. 3).

The addition of base also opens the [1,3]oxazine ring of **4a** to generate the anionic species **4d**. This process causes the appearance of a band at 427 nm (*e* in Fig. 3), corresponding to the 4-nitrophenolate chromophore of **4d**. In fact, this absorption is reminiscent of that associated with the tetrabutylammonium salt of 4-nitrophenolate (*f* in Fig. 3).

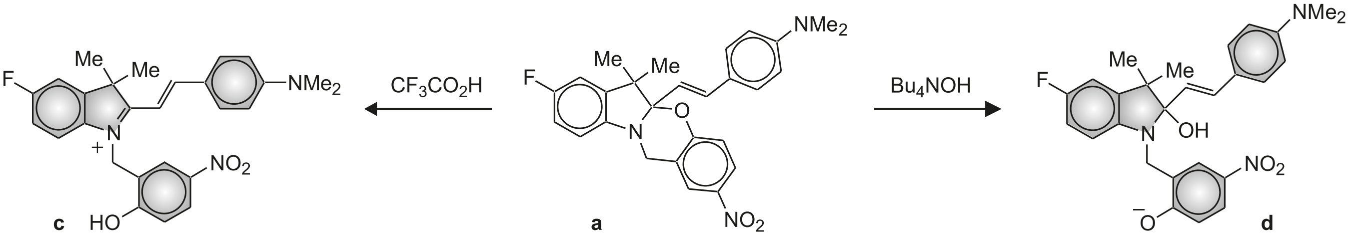
Transient absorption spectroscopy

In acetonitrile at 20 °C, the laser excitation of **4a** at 355 nm is accompanied by the appearance within 6 ns of two transient bands at 420 and 540 nm (*a* in Fig. 5) in the absorption spectrum. They resemble those observed in the steady-state spectra of **4d** and **4c**, respectively (*e* and *b* in Fig. 3) and correspond to ground-state absorptions of the 4-nitrophenolate anion and 3*H*-indolium cation, respectively, of **4b**. Thus, the [1,3]oxazine ring of **4a** opens upon excitation to generate the bichromophoric isomer **4b**, in analogy to the behavior of **2a** and **2b**. However, the transition from **2a** to **4a** results in an increase in quantum yield from 0.07 to 0.10.[33] Indeed, plots (*b* and *c* in Fig. 5) of the absorbance change measured at 540 nm upon laser excitation against the pulse energy show a noticeable increase in slope on going from **2a** to **4a**, consistent with an enhancement in quantum efficiency. Thus, the presence of a fluorine substituent on the 3*H*-indolium fragment of **4a** facilitates the photochromic transformation. Presumably, this effect is a consequence of the reduced electron density on the nitrogen atom of the 3*H*-indole fragment of **4a**, relative to that of **2a**, with the suppression of competitive photoinduced electron transfer to the adjacent nitro group. Indeed, the cyclic voltammograms of the model compounds **7** and **8** (Fig. 6) demonstrate that the oxidation potential of the 3*H*-indole fragment shifts by 70 mV in the positive direction with the introduction of an electron-withdrawing fluorine substituent.[34]

The photogenerated isomer **4b** reverts spontaneously to **4a** on a microsecond timescale. As a result, the two bands of **4b** decay with identical first-order kinetics. Curve fitting of both temporal profiles (*d* and *e* in Fig. 5) reveals the lifetime of **4b** to be 2 µs in acetonitrile at 20 °C. This value is identical to that of **2b**, demonstrating that the fluorine substituent has no influence on the reisomerization kinetics. Thus, a full switching cycle can be completed in a few microseconds with both photochromic systems. In addition, they tolerate hundreds of switching cycles with no sign of degradation. Specifically, the steady-state absorption spectra recorded before and after 300 excitation cycles are virtually identical, indicating the lack of any significant degradation under these experimental conditions.

The bichromophoric photochrome **4a** can be incorporated within a rigid poly(methyl methacrylate) (PMMA) matrix on the basis of a spin-coating procedure. The laser excitation of the resulting film at 355 nm is also accompanied by the appearance within 6 ns of two transient bands (*a* in Fig. 7). Once again, these bands resemble those observed in the steady-state spectra of **4d** and **4c** in solution and correspond to ground-state absorptions of the 4-nitrophenolate anion and

Fig. 4. Transformation of the [1,3]oxazine **4a** into the cation **4c** or anion **4d** under the influence of acid or base, respectively.



3*H*-indolium cation of **4b**. As observed in solution, the photogenerated isomer **4b** reverts spontaneously back to **4a** also within the PMMA matrix. Concomitantly, both absorption bands decay with the reisomerization process, though with biexponential kinetics in this instance. Curve fitting of the corresponding temporal profiles (*b* in Fig. 7) indicates lifetimes of 4 and 130 µs. The biexponential decay is consistent with that observed for **2b** in PMMA and suggests the coexistence of two main environments for the photochromic dopants within the polymer matrix.

Conclusions

Bichromophoric photochromes can be synthesized in two steps, starting from commercial precursors, by fusing 3*H*-indole and benzooxazine fragments and appending a 2-(4-dimethylaminophenyl)ethynyl group to the chiral center at the junction of the two heterocycles. The ultraviolet excitation of these compounds opens their [1,3]oxazine ring in less than 6 ns to produce a zwitterionic isomer, incorporating a 4-nitrophenolate anion and a 3*H*-indolium cation. These two chromophoric fragments absorb at 440 and 540 nm, respectively, and, therefore, the photoinduced transformation is accompanied by the appearance of two bands in the visible region of the absorption spectrum. The introduction of a fluorine substituent in the para position, relative to the nitrogen atom, of the 3*H*-indole heterocycle increases the photoisomerization quantum yield. Indeed, the electron-withdrawing character of the substituent reduces the electron density on the nitrogen atom of the 3*H*-indole heterocycle and facilitates the photoinduced ring-opening process. Instead, this particular substituent has essentially no influence on the lifetime of the photogenerated isomer, which reverts to the original form with first-order kinetics on a microsecond timescale. In fact, these bichromophoric photochromes can be switched back and forth between their two states in a few microseconds and tolerate hundreds of switching cycles with no sign of degradation. In addition, they can be operated within rigid PMMA matrices, though with slower reisomerization kinetics than in acetonitrile solution. Thus, our structural design for the realization of bichromophoric photochromes can lead to the development of novel photoresponsive materials with fast switching speeds and excellent fatigue resistances.

Experimental procedures

Materials and methods

Chemicals were purchased from commercial sources and used as received with the exception of MeCN, which was distilled over CaH_2. Compounds **7** and **8** were prepared according to literature procedures.[32a,32g] All reactions were monitored by thin-layer chromatography, using aluminum sheets coated with silica (60, F_{254}). Fast atom bombardment mass spectra (FABMS) were recorded with a VG Mass Lab Trio-2 spectrometer in a 3-nitrobenzyl alcohol matrix. Nuclear magnetic resonance (NMR) spectra were recorded with Bruker Avance 400 or 500 spectrometers. Steady-state absorption spectra were recorded with a Varian Cary 100 Bio spectrometer, using quartz cells with a path length of 0.5 cm. Time-resolved absorption spectra were recorded with a Luzchem Research mLFP–111 spectrometer, after excitation with a Continuum Surelite II–10 Nd–YAG laser (pulse width = 6 ns (FWHM), wavelength = 355 nm). The photochromic films were prepared by spin-coating a CH_2Cl_2 solution of **4a** (1.0 mg/mL) and PMMA (52 mg/mL) on a glass plate at 420 rpm for 9 s. The thickness (6 µm) of the resulting films was measured with a Tencor Instruments 10-00090 surface profilometer. Cyclic voltammograms were recorded with a CH Instruments 660 workstation in degassed MeCN solutions of Bu_4NPF_6 (0.1 mol/L) under an atmosphere of Ar, using a glassy-carbon working electrode, a platinum counter electrode, and a Ag/AgCl reference electrode.

Synthesis of 5

A solution of 2,3,3′-trimethyl-5-fluoro-3*H*-indole (1.09 g, 6.15 mmol), *N,N*-dimethyl-4-aminobenzaldehyde (0.92 g, 6.15 mmol), and HBr (0.5 mL, 33% in AcOH) in EtOH (10 mL) was heated under reflux for 12 h. After cooling to ambient temperature, the solvent was distilled off under reduced pressure. The residue was dissolved in CH_2Cl_2 (30 mL) and washed with a saturated aqueous solution of $NaHCO_3$ (2 × 20 mL). The organic phase was dried over Na_2SO_4 and the solvent was distilled off under reduced pressure to give **5** (1.6 g, 85%) as an orange solid. ^1H NMR ($CDCl_3$) δ : 1.44 (6H, s), 2.98 (6H, s), 6.69 (2H, d, J = 8 Hz), 6.85 (1H, d, J = 16 Hz), 7.00 (2H, t, J = 7 Hz), 7.49–7.51 (3H, m), 7.66 (1H, d, J = 16 Hz). ^{13}C NMR ($CDCl_3$) δ: 24.4, 40.6, 53.4, 109.3, 112.5, 115.0, 121.0, 124.3, 129.4, 139.0, 148.9, 150.7, 151.6, 160.3, 162.7, 184.3. FABMS *m/z*: 310 $[M + H]^+$.

Synthesis of 4a

A solution of **5** (278 mg, 0.9 mmol) and 2-chloromethyl-4-nitrophenol (169 mg, 0.9 mmol) in MeCN (20 mL) was heated under reflux for 24 h. After cooling to ambient temperature, the solvent was distilled off under reduced pressure and the residue was dissolved in CH_2Cl_2 (3 mL). The addition of Et_2O (20 mL) caused the precipitation of a purple solid. The solid was dissolved in CH_2Cl_2 (30 mL) and washed with H_2O (20 mL). The organic phase was dried over Na_2SO_4 and the solvent was distilled off under reduced

Fig. 5. Transient absorption spectrum (0.04 mmol/L, MeCN, 20 °C) of **4a** (*a*) recorded 0.1 µs after laser excitation (355 nm, 6 ns, 12 mJ). Absorbance change (0.04 mmol/L, MeCN, 20 °C) at 540 nm recorded 0.1 µs after laser excitation (355 nm, 6 ns) of **2a** (*b*) and **4a** (*c*) against the pulse energy. Temporal evolution of the absorbance (0.04 mmol/L, MeCN, 20 °C) at 440 (*d*) and 540 nm (*e*) after excitation (355 nm, 6 ns, 12 mJ) of **4a** and the corresponding monoexponential fittings.

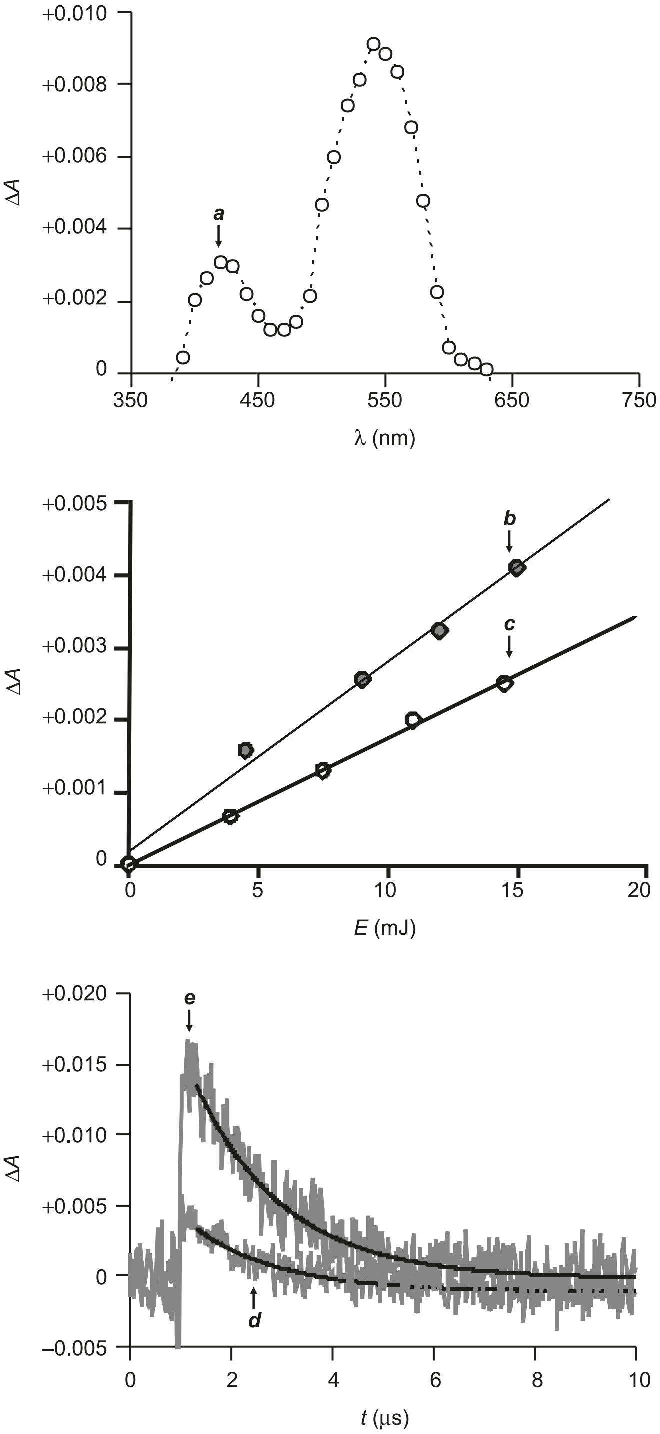
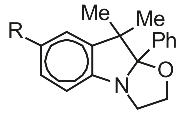


Fig. 6. Model compounds **7** and **8**.

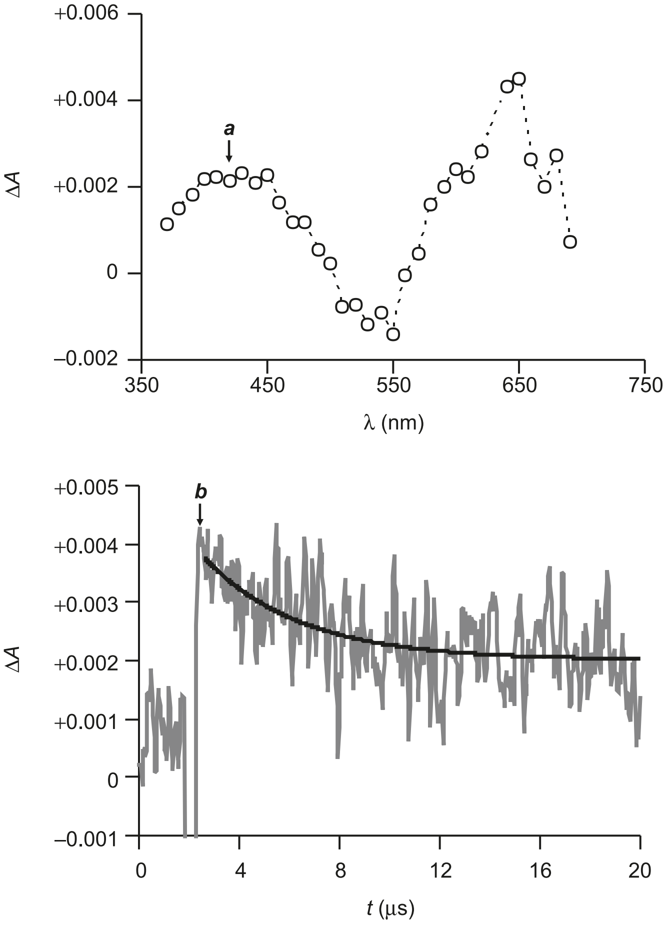


—R

7 —H

8 —F

Fig. 7. Transient absorption spectrum (2% *w*/*w*, PMMA, 20 °C) of **4a** (*a*) recorded 0.1 µs after laser excitation (355 nm, 6 ns, 12 mJ). Temporal evolution of the absorbance at 640 nm (*b*) after excitation and the corresponding biexponential fitting.



pressure to give **4a** (248 mg, 60%) as a purple solid. ^{1}H NMR (DMSO) δ: 1.34 (6H, s), 2.93 (6H, s), 4.85 (2H, s), 6.42 (1H, d, J = 16 Hz), 6.67 (2H, d, J = 9 Hz), 6.88–6.95 (4H, m), 7.20 (1H, d, J = 8 Hz), 7.44 (2H, d, J = 8 Hz), 7.95 (1H, d, J = 9 Hz), 8.10 (1H, s). ^{13}C NMR (DMSO) δ: 23.9, 24.8, 26.2, 45.0, 45.4, 50.8, 111.1, 111.3, 111.9, 112.8, 114.7, 118.3, 121.6, 123.8, 125.4, 130.2, 139.6, 141.9, 142.6, 152.2, 155.0, 157.9, 160.2, 190.7. FABMS *m/z*: 461 [M + H]$^+$

Synthesis of 6

A solution of **5** (120 mg, 0.39 mmol) and MeI (113 mg, 0.8 mmol) in MeCN (10 mL) was heated under reflux for 48 h. After cooling to ambient temperature, the solvent was distilled off under reduced pressure and the residue was dissolved in CH_2Cl_2 (3 mL). The addition of Et_2O (20 mL) caused the precipitation of a purple solid, which was filtered off to give **6** (141 mg, 80%). ^{1}H NMR ($CDCl_3$) δ: 1.79 (6H, s), 3.19 (6H, s), 4.18 (3H, s), 6.79 (2H, d, J = 8 Hz), 7.18 (2H, d, J = 8 Hz), 7.26 (1H, d, J = 20 Hz), 7.44-–7.47 (1H, m), 8.04–8.08 (3H, m). ^{13}C NMR ($CDCl_3$) δ: 28.0, 36.2, 40.9, 51.4, 105.5, 110.8, 113.1, 114.9, 116.5, 122.9, 135.8, 138.3, 144.4, 155.1, 155.8, 163.9, 179.4. FABMS: m/z = 323 $[M - I]^+$.

Acknowledgments

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(34) The oxidation potentials of **7** and **8** are +1.16 and +1.23 V vs. Ag/AgCl, respectively.