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Amplification of the Coloration Efficiency of Photochromic Oxazines**

By Massimiliano Tomasulo, Salvatore Sortino,* and Francisco M. Raymo*

Photochromic compounds alter reversibly their ability to absorb visible radiations under the influence of optical stimulations.^[1–5] In fact, their photoinduced transformations can be exploited to switch the color of liquid solutions, rigid polymer matrices or even crystals with optical inputs. Furthermore, these photoinduced processes are generally accompanied by significant structural modifications at the molecular level, which can translate into pronounced changes in the refractive index of the host matrix. Indeed, a diversity of photonic materials and devices have already been designed around the unique absorptive and dispersive effects associated with photochromic compounds.^[6–9]

Photochromic transformations are commonly based on unimolecular reactions.^[1–5] They generally involve ring closing/opening steps, *cis/trans* isomerizations or intramolecular proton transfer. These processes alter the structure of a single chromophoric unit and induce a change in color as a result. In some instances, pairs of photoresponsive chromophores have also been integrated within the same covalent backbone to generate bichromophoric photochromes.^[10–27] In the resulting molecular assemblies, the photoisomerizations of the *two* photochromic units require the absorption of *two* independent photons. Furthermore, the photoinduced transformation of one component can affect the spectroscopic response of the other and *vice versa*. In principle, similar processes can be designed to occur on the basis of a single photochemical event. Specifically, the absorption of *one* photon can be engineered to generate simultaneously *two* chromophoric units able to absorb in the same region of the visible spectrum. Hence, the coloration efficiency^[28] of the resulting bichromophoric photochromes can be significantly greater than that of their monochromophoric counterparts. On the basis of these considerations, we have designed a bichromophoric compound based on the photoinduced opening and thermal closing of a

[1,3]oxazine ring. In this article, we illustrate our design logic and report the synthesis and photochemical properties of a representative example of this novel class of bichromophoric photochromes.

We have recently discovered that the ultraviolet irradiation of either **1a** or **2a** (Fig. 1) cleaves the C–O bond at the junction of the indole and benzooxazine heterocycles with the opening of the [1,3]oxazine ring.^[29–31] In MeCN, this process

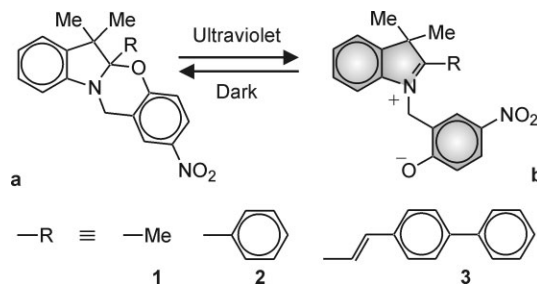


Figure 1. The reversible interconversion of the [1,3]oxazines **1a**, **2a**, and **3a** and the corresponding zwitterions **1b**, **2b**, and **3b**.

occurs in less than 6 ns to generate the colored isomers **1b** and **2b** with quantum yields of 0.03 and 0.1, respectively. These species revert thermally to the original [1,3]oxazines with a lifetime of 25 ns in both instances. The photoinduced opening of the [1,3]oxazine ring converts the 4-nitrophenoxyl fragment of **1a** and **2a** into the 4-nitrophenolate anion of **1b** and **2b** with the concomitant shift of an absorption band from ca. 315 to 440 nm. Thus, a *single* chromophore able to absorb in the visible region is produced after the photoinduced reaction. The cleavage of the C–O bond, however, generates an indolium cation in addition to the 4-nitrophenolate anion. This transformation brings the group (R in Fig. 1) on the chiral center of **1a** and **2a** in conjugation with the indolium cation of **1b** and **2b**. In principle, this photoinduced change in conjugation can be exploited to shift another absorption band from the ultraviolet to the visible region, if the nature of R is adjusted accordingly. In fact, the ultraviolet excitation of the resulting system would generate simultaneously *two* independent chromophores both able to absorb in the visible region, leading to an amplification of the coloration efficiency. On the basis of these considerations, we have designed the [1,3]oxazine **3a** (Fig. 1), which incorporates a 2-(4-phenylphenylene)ethylene group on its chiral center. We have synthesized this compound in one step starting from **1a** (Fig. 2). Spe-

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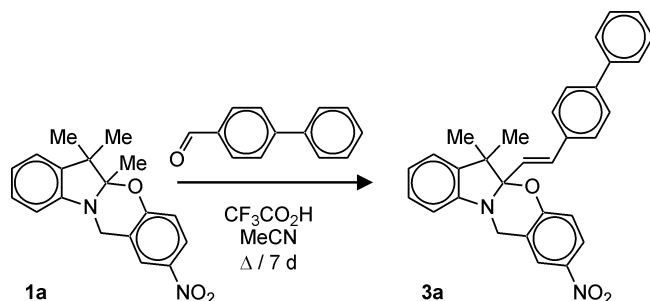


Figure 2. Synthesis of the photochromic [1,3]oxazine **3a**.

cifically, we have condensed **1a** and 4-biphenylcarboxaldehyde in the presence of $\text{CF}_3\text{CO}_2\text{H}$ to afford **3a** in a yield of 52 %.

The steady-state absorption spectrum (Fig. 3a) of **3a** shows a band at 288 nm for the 4-nitrophenoxy and biphenyl chromophores. In the presence of Bu_4NOH , the [1,3]oxazine ring of **3a** opens to generate the hemiaminal **3c** (Fig. 4). This process converts the 4-nitrophenoxy fragment of **3a** into the 4-nitrophenolate chromophore of **3c**. Consistently, an absorption at 431 nm appears in the spectrum (Fig. 3b) after the addition of increasing amounts of Bu_4NOH . This new band resembles the absorption of the model anion **4** (Figs. 3c and 4), confirm-

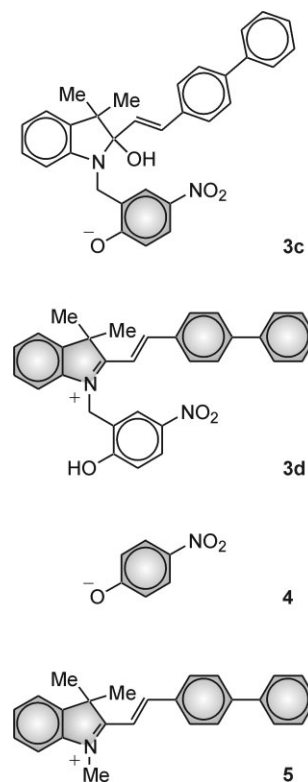


Figure 4. The hemiaminal **3c**, indolium **3d** and the model compounds **4** and **5**.

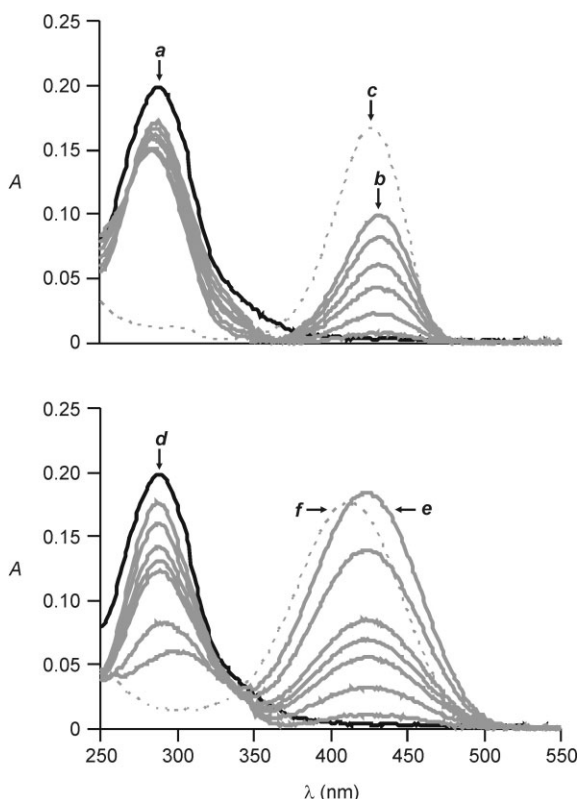


Figure 3. Steady-state absorption spectra (0.01 mM, MeCN, 20 °C) of **3a** before (a and d) and after the addition of increasing amounts of either Bu_4NOH (40–240 equiv., b) or $\text{CF}_3\text{CO}_2\text{H}$ (0.2–10 equiv., e), the tetrabutylammonium salt of **4** (c) and the hexafluorophosphate salt of **5** (d).

ing that it is associated with the 4-nitrophenolate chromophore of **3c**.

The treatment of **3a** with $\text{CF}_3\text{CO}_2\text{H}$ opens the [1,3]oxazine ring to form the indolium **3d** (Fig. 4). As a result, the absorbance at 288 nm decreases significantly and a new band at 421 nm appears in the steady-state absorption spectrum (Fig. 3d and e). This additional band closely resembles the one of the model cation **5** (Figs. 3f and 4).

The steady-state absorption spectra of **3c** and **3d** (Fig. 3b and e) demonstrate that the 4-nitrophenolate anion of the former and the indolium cation of the latter absorb in the visible region. Both chromophores are integrated within the molecular skeleton of **3b** (Fig. 1). Therefore, they can be generated simultaneously by photoinducing the opening of the [1,3]oxazine ring of **3a**. Indeed, the transient absorption spectrum of **3a** (Fig. 5a), recorded 30 ns after laser excitation, shows an intense absorption at 430 nm. This band corresponds to ground-state absorptions of the 4-nitrophenolate and indolium chromophores of the photogenerated isomer **3b**.^[32] In fact, its absorbance is approximately twice that of the transient band observed for an optically-matched solution of **2a** (Fig. 5b), which can only generate the 4-nitrophenolate chromophore upon ring opening. Thus, the transition from the monochromophoric [1,3]oxazine **2a** to the bichromophoric counterpart **3a** enhances the coloration efficiency by a factor of 1.8 ± 0.3 .

The quantum yield^[33] for the photoinduced ring opening of **3a** is 0.1. This value is essentially identical to the one deter-

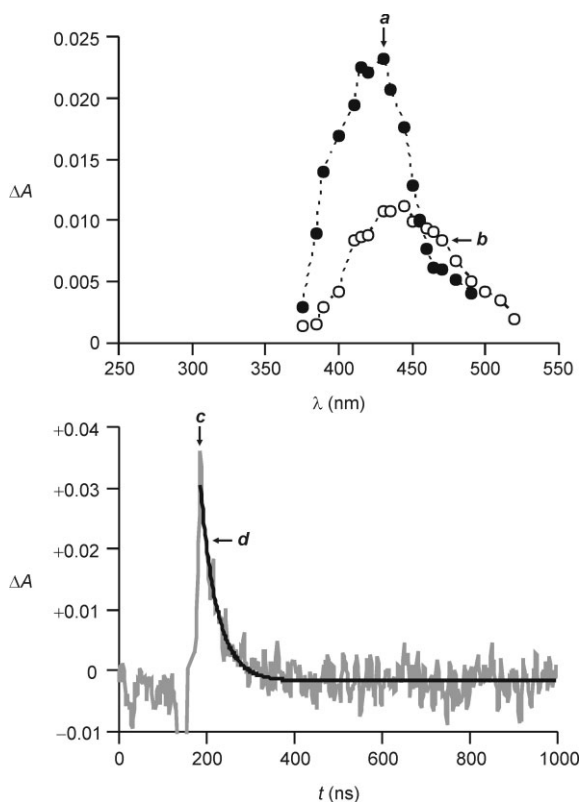


Figure 5. Transient absorption spectra of **3a** (0.05 mM, MeCN, 20 °C, a) and of an optically-matched solution of **2a** (b) recorded 30 ns after the laser excitation (355 nm, 8 mJ). Temporal evolution of the absorbance at 430 nm after the excitation of **3a** (c) and the corresponding monoexponential fitting (d).

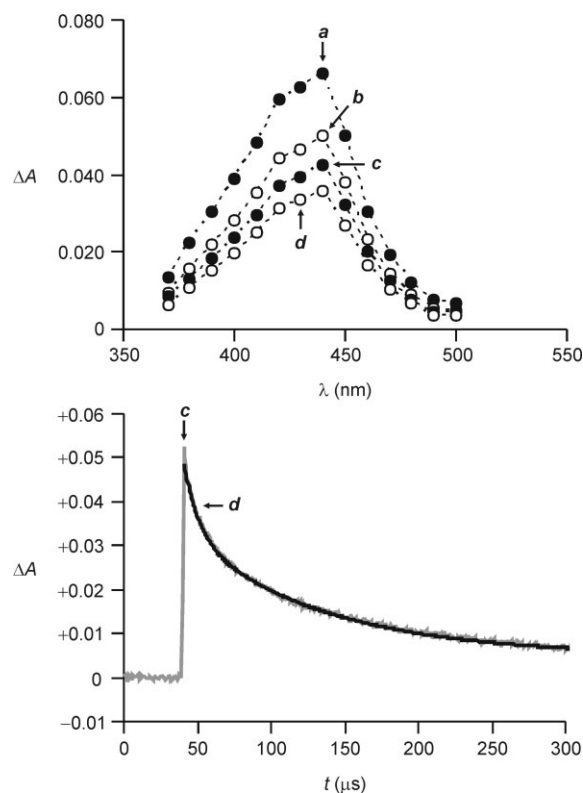


Figure 6. Transient absorption spectra of a PMMA film doped with **3a** recorded 3 (a), 17 (b), 22 (c), and 33 μ s (d) after the laser excitation (355 nm, 8 mJ). Temporal evolution of the absorbance at 430 nm after the excitation of the film (c) and the corresponding biexponential fitting (d).

mined for **2a**.^[29,30] The photogenerated isomer **3b** ring closes thermally and, consistently, the absorbance at 430 nm decays on a nanosecond timescale (Fig. 5c). The monoexponential fitting (Fig. 5d) of the absorbance profile indicates the lifetime of **3b** to be 38 ns. This value is slightly longer than the one determined for **2b**, which is 25 ns.^[29,30] Presumably, the extended conjugation of the indolium cation of **3b** tends to stabilize this photogenerated isomer and delay the ring closing step relative to **2b**. Furthermore, this particular photochromic system has an excellent fatigue resistance. Indeed, the steady-state absorption spectra of **3a** recorded before and after 400 consecutive excitation cycles are essentially identical and, thus, do not reveal any sign of degradation.

The photochromic oxazine **3a** can also be trapped and operated within rigid polymer matrices. Specifically, the spin coating of a CH_2Cl_2 solution of polymethylmethacrylate (PMMA) and **3a** on a glass slide produces a photochromic film with a thickness of ca. 6 μm . The laser excitation of the resulting material opens the [1,3]oxazine ring of **3a** with the concomitant appearance of a transient absorption centered at ca. 430 nm (Fig. 6a) for the photogenerated isomer **3b**. As observed in MeCN solution, this band fades with the thermal reisomerization of **3b** back to **3a** (Fig. 6a–d). The temporal evolution of this absorption, however, shows that the ring closing process

within the PMMA matrix is slower than in MeCN solution. In particular, the absorbance at 430 nm decays biexponentially with lifetimes of 10 and 90 μs , as observed for **2a** under the same experimental conditions.^[30] This behavior parallels the biexponential kinetics for the thermal decoloration of nitrospiropyrans in polymer matrices and is, presumably, a result of the aggregation of the photogenerated isomers into relatively long-lived supramolecular assemblies.^[34–36]

In summary, we have designed a bichromophoric photochrome around the photoinduced opening and thermal closing of a [1,3]oxazine ring. The cleavage of a C–O bond responsible for ring opening generates simultaneously two chromophores able to absorb in the same region of the visible spectrum. One of them is a 4-nitrophenolate anion and the other is an indolium cation conjugated to a 2-(4-phenylphenylene)ethylene group. Both species absorb at ca. 430 nm with molar extinction coefficients of ca. 22 and 35 $\text{mM}^{-1}\text{cm}^{-1}$, respectively. As a result, the laser excitation of this photochromic compound generates a band in the visible region with an absorbance that is approximately twice that of an analogous compound incorporating the 4-nitrophenolate chromophore only. Consistently, the coloration efficiency of this bichromophoric photochrome is approximately twice that of its monochromophoric counterpart. Thus, this molecular design can

lead to a valuable strategy for the amplification of the coloration efficiency of photochromic oxazines and, eventually, to a new family of multichromophoric photochromes with tunable spectroscopic response.

Experimental

Materials and Methods: Chemicals were purchased from commercial sources and used as received with the exception of MeCN, which was distilled over CaH_2 . The [1,3]oxazines **1a** and **2a** were prepared according to literature procedures [29–31]. The synthesis of the model compound **5** is reported in the supporting information. The reaction was monitored by thin-layer chromatography, using aluminum sheets coated with silica (60, F_{254}). The melting point (mp) was determined with an Electrothermal Mel-Temp apparatus. High performance liquid chromatography (HPLC) was performed with a BDS column (dimensions = 4.6×250 mm, flow rate = 1.0 mL min^{-1} , injection volume = $20 \mu\text{L}$, sample concentration = 0.1 mM , solvent = MeCN) using a Varian Prostar HPLC system. The retention time (RT) and the peak asymmetry (PA) were determined at a wavelength of 278 nm. The average purity parameter (APP) was calculated for the peak heart in the wavelength range 200–800 nm. The fast atom bombardment mass spectra (FABMS) were recorded with a VG Mass Lab Trio-2 spectrometer, using 3-nitrobenzyl alcohol as matrix. The nuclear magnetic resonance (NMR) spectra were recorded with Bruker Avance 300, 400, or 500 spectrometers. The steady-state absorption spectra were recorded with a Varian Cary 100 Bio spectrometer, using quartz cells with a path length of 0.5 cm. The transient absorption spectra were recorded in degassed solutions with a Luzchem Research mLFP-111 apparatus coupled to a Nd-YAG Continuum Surelite II-10 laser, using quartz cells with a path length of 1.0 cm. The photochromic films were prepared by spin-coating a CH_2Cl_2 solution of **3a** (1.3 mg mL^{-1}) and PMMA (130 mg mL^{-1}) on a glass plate at 420 rpm for 9 s, using a Chemat Technologies KW-4A spin coater. The thicknesses ($6 \mu\text{m}$) of the resulting film was measured with a Tencor Instruments 10-00090 surface profilometer.

2-Nitro-5a-2-(4-phenylphenylene)ethylene-6,6-dimethyl-5a,6-dihydro-12H-indolo[2,1-b][1,3]benzooxazine (3a): A solution of **1a** (100 mg, 0.3 mmol), 4-biphenylcarboxaldehyde (175 mg, 1.0 mmol), and $\text{CF}_3\text{CO}_2\text{H}$ (80 μL , 0.1 mmol) in MeCN (15 mL) was heated under reflux and Ar for 7 d. After cooling down to ambient temperature, the solvent was distilled off under reduced pressure. The solid residue was dissolved in CH_2Cl_2 (5 mL) and the solution was diluted with hexane (50 mL). The resulting precipitate was filtered off and crystallized from PhMe (10 mL) to give **3a** (60 mg, 40%) as a orange solid. m.p. = 194°C ; HPLC: RT = 4.1 min, PA = 1.4, APP = $(236.7 \pm 0.3) \text{ nm}$; FABMS: $m/z = 475$ $[M+H]^+$; $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ = 1.27 (6H, s), 4.61 (2H, s), 6.42 (1H, d, 16 Hz), 6.62 (1H, d, 7 Hz), 6.85–6.91 (3H, m), 7.11–7.16 (2H, m), 7.36 (1H, t, 7 Hz), 7.35–7.38 (4H, m), 7.58–7.60 (4H, m), 7.99 (1H, dd, 3 and 9 Hz), 8.02 (1H, d, 3 Hz); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 30.1, 41.1, 50.5, 104.1, 109.2, 118.1, 120.4, 121.1, 122.7, 123.6, 124.3, 124.4, 127.4, 127.7, 127.8, 128.0, 128.1, 129.2, 134.9, 136.1, 138.6, 140.8, 141.1, 141.9, 146.8, 159.6.

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