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Photochromic Oxazines with Extended Conjugation

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We synthesized four compounds with indole and benzooxazine fragments fused in their molecular skeleton and differing in the substituent in the *para* position, relative to the oxygen atom, of their phenoxy chromophore. This particular substituent extends the conjugation of the phenoxy chromophore and shifts its absorption bathochromically by up to 60 nm, relative to a parent compound with a 4-nitrophenoxy group. The 1,3-oxazine ring of all compounds opens upon addition of base to generate a hemiaminal incorporating a phenolate chromophore. Once again, the substituents on this fragment shift its absorption bathochromically by up to 60 nm, relative to the parent compound. Upon laser excitation at a wavelength within the absorption range of the phenoxy chromophore, the 1,3-oxazine ring of the compound incorporating a 4-nitrophenyl substituent opens in less than 6 ns to generate a zwitterionic isomer with a quantum yield of 0.11 in acetonitrile. Under these conditions, the photogenerated isomer has a lifetime of 29 ns and reverts spontaneously to the original species with first-order kinetics. Furthermore, this photochromic system tolerates hundreds of switching cycles with no sign of degradation even in the presence of molecular oxygen. However, the excitation dynamics of the other three compounds, incorporating a 4-nitrobiphenyl, 4-nitrostyryl or 4-nitrophenylethynyl substituent, are dominated by intersystem crossing. Consistently, the corresponding transient spectra reveal predominantly triplet–triplet absorptions. Thus, our studies demonstrate that the excitation wavelength and color of this class of photochromic compounds can be regulated by extending the conjugation of their phenoxy fragment with negligible influence on the photochromic performance only if the structural modification does not encourage intersystem crossing.

Introduction

Photochromic compounds alter reversibly their ability to absorb visible radiations in response to optical stimulations.[1–5] These spectral changes in the visible region are a result of significant modifications in stereoelectronic properties and can be a consequence of photoinduced *cis*/*trans* isomerizations, ring-opening/closing steps, intramolecular proton transfer, intermolecular electron transfer or cycloadditions. In each case, the photogenerated species must be able to revert back to the original form either thermally or photochemically. As a result, the color of a liquid solution containing photochromic compounds or of a rigid polymer matrix doped with photochromic molecules can be controlled reversibly under the influence of optical inputs. In addition to the absorbance of the overall material, these photoinduced transformations at the molecular level can also control its refractive index. Indeed, diverse devices have already been designed around the photoinduced absorptive and dispersive effects associated with photochromic materials.[6–8]

Nitrospiropyrans are members of one of the most common families of photochromic compounds.[9–13] They switch from a colorless to a colored state under ultraviolet irradiation and revert back to the original species in the dark. Their photochemical behavior and synthetic accessibility have already encouraged the integration of these compounds in a diversity of photoresponsive materials. However, the relatively slow switching speeds and poor fatigue resistances of nitrospiropyrans have prevented so far the evolution of these systems from clever laboratory demonstrations to practical technological applications. Indeed, nitrospiropyrans switch from colorless to colored states in few microseconds, but revert back to the colorless forms only after hundreds of seconds. In addition, the participation of a relatively long-lived triplet state in their photoisomerization translates in their ability to tolerate only few tenths of switching cycles before decomposing.

In search of strategies to improve the photochromic performance of nitrospiropyrans, we developed close relatives of these compounds with fast switching speeds and excellent fatigue resistances.[14] For example, the ultraviolet excitation of **1a** (Figure 1) opens its 1,3-oxazine ring in less than

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6 ns to generate **1b** with a quantum yield of 0.10 in acetonitrile at 20 °C. Under these conditions, the photogenerated isomer has a lifetime of 25 ns and, eventually, reverts to the original species with first-order kinetics. Furthermore, this system survives thousands of switching cycles unaffected, even in the presence of molecular oxygen. Thus, our innovative structural design offers access to nanosecond switching speeds and outstanding fatigue resistances and, in principle, can lead to the development of photochromic materials for the implementation of logic gates,[15–19] optical limiters,[20–24] photoresponsive filters[25] and photoswitchable probes.[26–29] Each one of these applications, however, imposes stringent requirements on the excitation wavelength, quantum efficiency, color and isomerization kinetics. As a result, it is essential to learn how to control and, eventually tune, the photochemical and photophysical properties of our photochromic compounds in view of possible technological applications. In this context, we envisaged the possibility of introducing structural modifications on the main skeleton of our 1,3-oxazines and investigate their influence on the photochromic performance. In this article, we report the synthesis of four new members of this novel class of photochromic compounds and the spectroscopic characterization of the photochemical and photophysical properties.

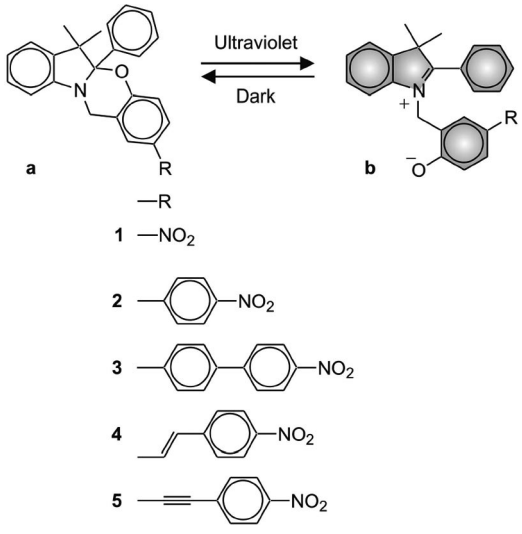

Figure 1. Photoinduced transformation of the 1,3-oxazines **1a**–**5a** into the zwitterions **1b**–**5b**.

Results and Discussion

Design and Synthesis

The ground-state absorption of the 4-nitrophenoxy fragment of **1a** is centered at 316 nm (Table 1) in acetonitrile. Laser excitation in the tail of this band opens the 1,3-oxazine ring and generates the 4-nitrophenolate anion of **1b** with the concomitant appearance of the ground-state absorption of this chromophore at 440 nm. In principle, the position of both bands and, hence, the excitation wavelength and color of the photochromic system can be regulated by replacing the nitro group with other substituents. Specifically, the introduction of groups capable of extending the conjugation of the phenoxy fragment should translate into the possibility of elongating the excitation wavelength and tuning the color across the entire visible region. On the basis of these considerations, we designed the 1,3-oxazines **2a**–**5a** (Figure 1), which incorporate a 4-nitrophenyl, 4-nitrobiphenyl, 4-nitrostyryl and 4-nitrophenylethynyl substituent in place of the nitro group of **1a**.

Table 1. Spectroscopic data[a] for the 1,3-oxazines **1a**–**5a** and their model compounds **11**–**14** and **19**–**22**.

	λ [nm]	ε [mM^{-1} cm^{-1}]
1a	316	11.0
2a	338	15.1
3a	337	19.9
4a	377	23.9
5a	354	23.3
11	336	16.7
12	340	21.1
13	376	25.7
14	352	20.0
19	450	15.2
20	443	8.8
21	521	13.2
22	469	19.4

[a] The absorption wavelength (λ) and molar extinction coefficient (ε) at λ were measured in MeCN at 20 °C. The data for **1a** are from ref.[14a] The data for **19**–**22** were recorded after adding Bu_4NOH (> 100 equiv.) to solutions of **15**–**18**.

We synthesized the 1,3-oxazines **2a** and **3a** in one step starting from the corresponding diols **7** and **8** (Figure 2). In particular, we treated **7** and **8** with phosphorus tribromide and then with **6** in situ to generate **2a** and **3a** with yields of 36 and 21%, respectively. According to a similar protocol and starting from the diol **9** (Figure 2), we prepared also the 1,3-oxazine **10a**. Then, we treated this compound with either 4-nitrostyrene or 4-nitrophenylacetylene (Figure 3) to generate the 1,3-oxazines **4a** and **5a** with yields of 81 and 16%, respectively.

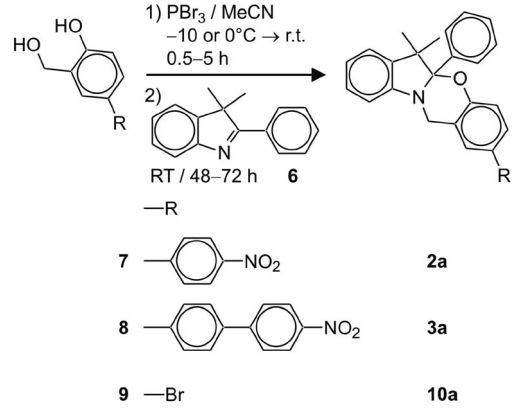

Figure 2. Synthesis of the 1,3-oxazines **2a**, **3a** and **10a**.

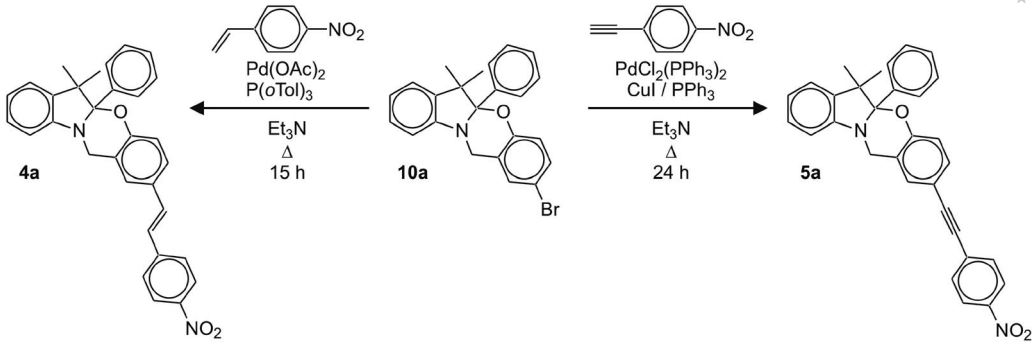

Figure 3. Synthesis of the 1,3-oxazines **4a** and **5a**.

Steady-State Absorption Spectroscopy

The steady-state absorption spectra (***a*** and ***e*** in Figures 4 and 5) of **2a**–**5a** show bands centered at 338, 337, 377 and 354 nm (Table 1), respectively, for the ground-state absorptions of the corresponding phenoxy chromophores. Indeed, these bands closely resemble the ones observed in the spectra (***b*** and ***f*** in Figures 4 and 5) of the model compounds **11**–**14** (Figure 6). Upon addition of base, the 1,3-oxazine ring of **2a**–**5a** opens to generate the hemiaminals **2c**–**5c** (Figure 7). These transformations are accompanied by the appearance of bands at 469, 412, 511 and 443 nm in the corresponding spectra (***c*** and ***g*** in Figures 4 and 5) for the ground-state absorptions of the phenolate chromophores of

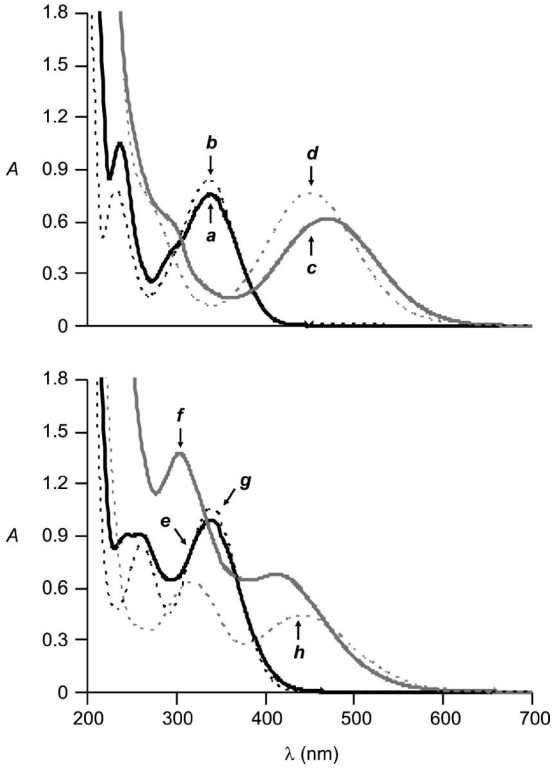

Figure 4. Steady-state absorption spectra (0.1 mM, MeCN, 20 °C) of **2a** before (***a***) and after (***c***) the addition of Bu_4NOH (496 equiv.), **11** (***b***), **15** (***d***) after the addition of Bu_4NOH (496 equiv.), **3a** before (***e***) and after (***g***) the addition of Bu_4NOH (993 equiv.), **12** (***f***), **16** (***h***) after the addition of Bu_4NOH (993 equiv.).

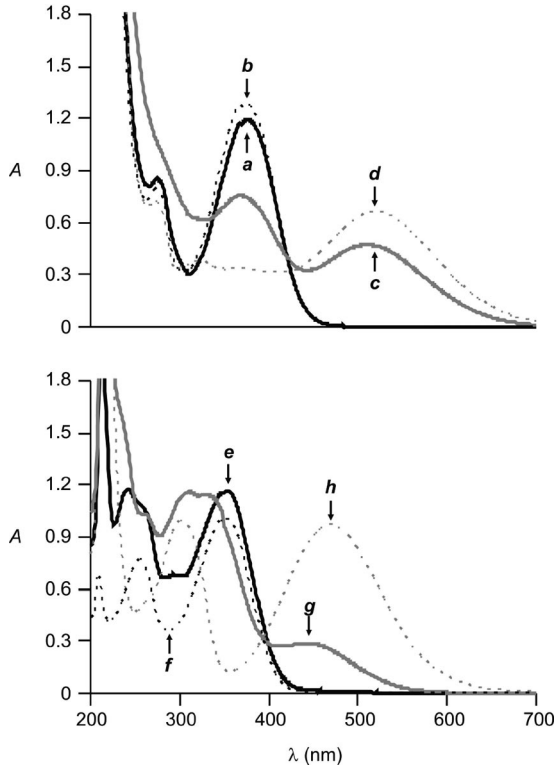

Figure 5. Steady-state absorption spectra (0.1 mM, MeCN, 20 °C) of **4a** before (***a***) and after (***c***) the addition of Bu_4NOH (101 equiv.), **13** (***b***), **17** (***d***) after the addition of Bu_4NOH (101 equiv.), **5a** before (***e***) and after (***g***) the addition of Bu_4NOH (100 equiv.), **14** (***f***), **18** (***h***) after the addition of Bu_4NOH (100 equiv.).

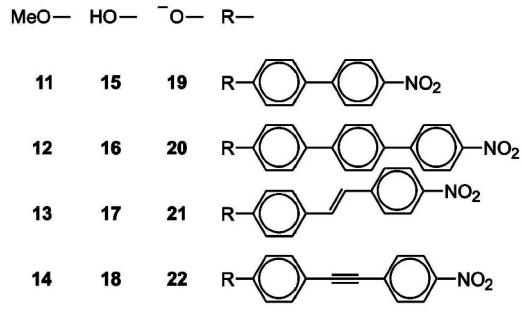

Figure 6. Model compounds **11**–**22**.

2c–**5c**. Consistently, these bands are reminiscent of those observed in the spectra (***d*** and ***h*** in Figures 4 and 5) of the model compounds **19**–**22** (Figure 6).

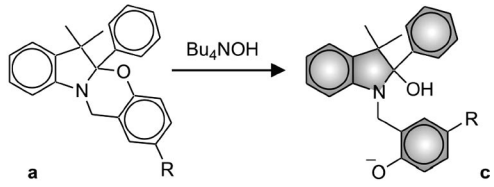

Figure 7. Transformation of the 1,3-oxazines **2a**–**5a** into the hemiaminals **2c**–**5c** under the influence of base.

Transient Absorption Spectroscopy

The laser excitation of **2a** at 355 nm opens its 1,3-oxazine ring to generate the zwitterionic isomer **2b** in less than 6 ns and with a quantum yield of 0.11. Consistently, the absorption spectrum (***a*** in Figure 8), recorded 50 ns after excitation, shows a band at 510 nm for the ground-state absorption of the phenolate chromophore of **2b**. Indeed, this band resembles that observed in the steady-state spectrum (***d*** in Figure 4) of the model phenolate **19**. In agreement with this assignment, the transient spectrum (***b*** in Figure 8) of the model **11**, recorded under otherwise identical conditions, shows that the triplet state associated with the 4-nitrobiphenoxy chromophore absorbs instead at 650 nm. Furthermore, the transient absorption of **2b** decays in nanoseconds (***c*** in Figure 8), whereas that of **11** fades in microseconds (***e*** in Figure 8). Nonlinear curve fittings of both absorbance profiles (***d*** and ***f*** in Figure 8) indicate the lifetime of **2b** and the triplet state of **11** to be 29 ns and 2 μs, respectively. Thus, a full switching cycle, from **2a** to **2b** and back, can be completed in few tens of nanoseconds. In addition, the steady-state absorption spectra of **2a**, recorded before and after 300 excitation pulses, are essentially identical, indicating that this photochromic compound can withstand multiple switching cycles with no sign of degradation.

The spectroscopic analysis of **2a** indicates that the introduction of a 4-nitrophenyl substituent in place of the nitro group of **1a** has negligible influence on the quantum yield for the photoinduced ring opening and the lifetime of the photogenerated isomer. Indeed, the quantum yield is ca. 0.1 and the lifetime is close to 30 ns for both systems. However, the extended conjugation of the 4-nitrobiphenolate chromophore of **2b**, relative to the 4-nitrophenolate anion of **1b**, shifts bathochromically the absorption wavelength of the photogenerated isomer. According to steady-state absorption spectra of the model phenolates **20**–**22** (***d*** and ***h*** in Figures 4 and 5), the introduction of 4-nitrobiphenyl, 4-nitrostyryl and 4-nitrophenylethynyl substituents, in place of the nitro group of **1b**, is also expected to elongate the absorption wavelength of the ring-opened isomers **3b**–**5b**. Nonetheless, the absorption spectra (***a*** and ***c*** in Figure 9) of **3a** and **4a**, recorded 50 ns after excitation, show instead bands resembling those of the model phenoxy chromophores **12** and **13** (***b*** and ***d*** in Figure 9). These bands correspond to triplet–triplet absorptions of these particular chromophoric fragments and decay on a microsecond timescale. In agreement with this assignment, the transient species responsible for these bands are all quenched by molecular oxygen. In contrast to the behavior of **3a** and **4a**, the spectrum of **5a** (***e*** in Figure 9), recorded 50 ns after excitation, does not show the broad and intense transient absorption of the corresponding phenoxy chromophore **14** (***f*** in Figure 9) at wavelengths higher than 550 nm. Instead, it resembles that of the model phenolate **22** (***g*** in Figure 9) and, presumably, corresponds to a triplet–triplet absorption of the ring-opened isomer **5b**. These observations suggest that intersystem crossing dominates the excitation dynamics of **3a**–**5a** and competes with the ring-opening process of **3a** and **4a**.

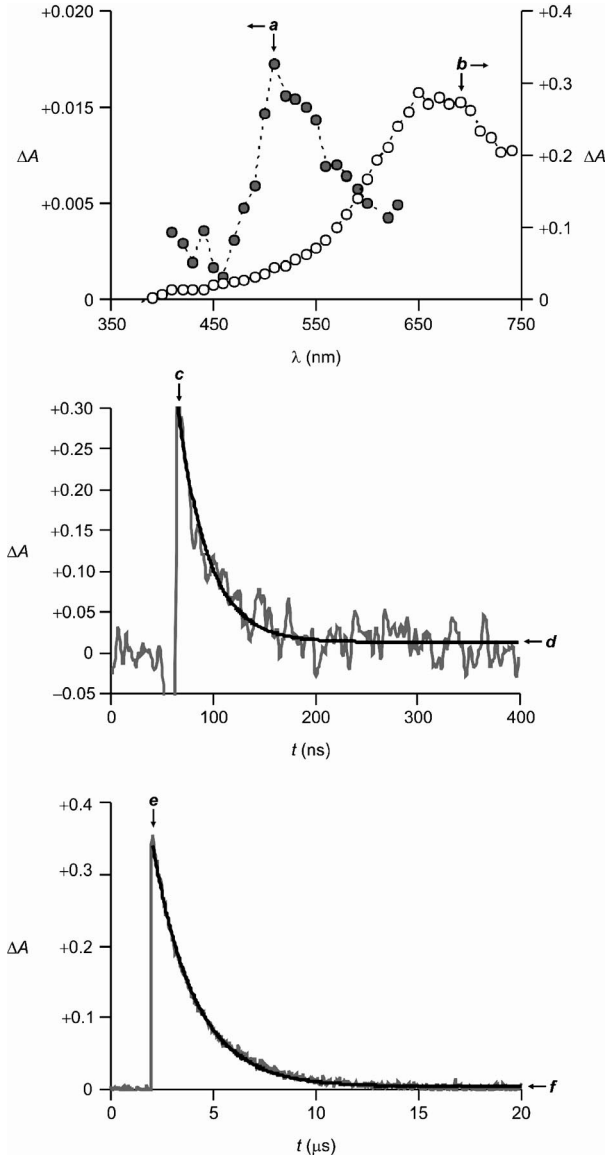

Figure 8. Transient absorption spectra (0.05 mM, MeCN, 20 °C) of **2a** (***a***) and **11** (***b***) recorded 50 ns after laser excitation (355 nm, 12 mJ). Temporal evolution of the absorbance at 500 nm for **2a** (***c***) and 650 nm for **11** (***e***) after excitation and the corresponding monoexponential fittings (***d*** and ***f***).

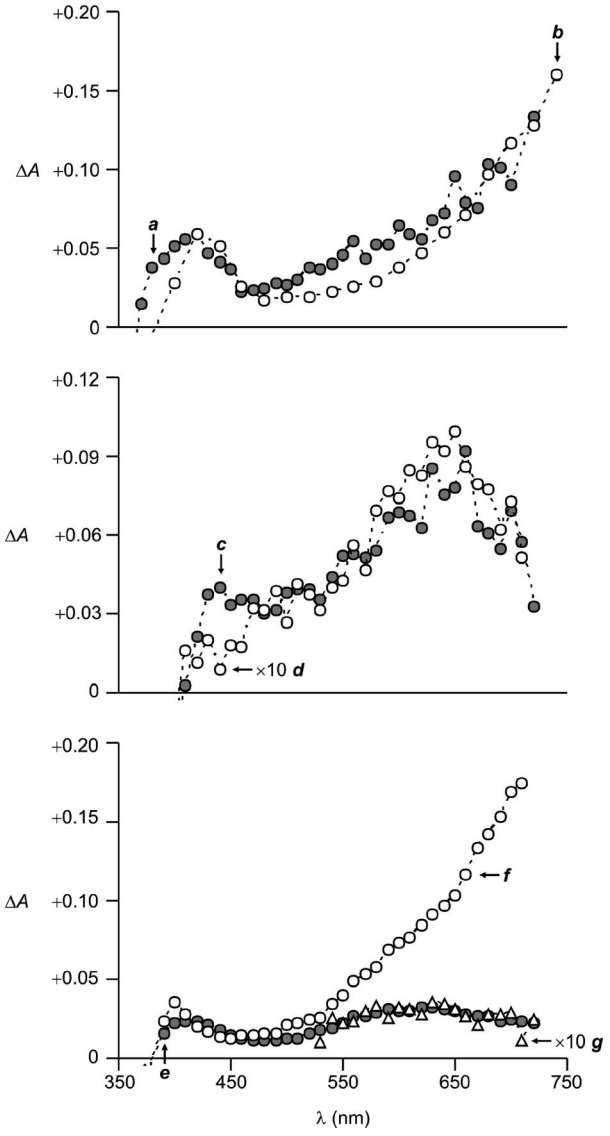

Figure 9. Transient absorption spectra (MeCN, 20 °C) of **3a** (*a*, 0.03 mM), **12** (*b*, 0.03 mM), **4a** (*c*, 0.03 mM), **13** (*d*, 0.12 mM), **5a** (*e*, 0.03 mM), **14** (*f*, 0.03 mM) and **18** (*g*, 0.15 mM) after the addition of Bu_4NOH (100 equiv.) recorded 50 ns after laser excitation (355 nm, 12 mJ) respectively.

Conclusions

The conjugation of the phenoxy chromophore of photochromic benzooxazines can be extended by introducing 4-nitrophenyl, 4-nitrobiphenyl, 4-nitrostyryl and 4-nitrophenylethynyl substituents in the *para* position, relative to the oxygen atom. These compounds can be prepared in one or two steps from readily available precursors and isolated in yields ranging from 16 to 81%. Their steady-state spectra show a main absorption centered within 337 and 377 nm for the phenoxy chromophores. After the addition of base, the 1,3-oxazine ring of all compounds opens, converting the phenoxy chromophore into phenolate anions and shifting their absorption to 412–511 nm. The laser excitation of the compounds with a 4-nitrophenyl substituent opens the 1,3-oxazine ring in less than 6 ns with a quantum yield of 0.11. The resulting photogenerated isomer has a lifetime of 29 ns and eventually reverts to the original form with first-order kinetics. Furthermore, this compound tolerates hundreds of switching cycles with no sign of degradation even in the presence of molecular oxygen. This behavior is equivalent to that of a parent compound incorporating a nitro group in place of the 4-nitrophenyl substituent. Thus, the extension in conjugation with the transition from a nitro group to a 4-nitrophenyl substituent can be exploited to elongate the absorption wavelength of the photogenerated isomer without compromising the fast switching speeds and excellent fatigue resistances of these photochromic oxazines. Instead, intersystem crossing dominates the excitation dynamics of the other three compounds, and triplet–triplet absorptions are predominantly observed in the corresponding transient spectra. Hence, these photochromic compounds tolerate structural modifications with negligible influence on their photochemical character only if these changes do not encourage intersystem crossing.

Experimental Section

Materials and Methods: Chemicals were purchased from commercial sources and used as received with the exception of MeCN and CH_2Cl_2, which were distilled from CaH_2, and THF, which was distilled from Na and Ph_2CO. Compounds **6**, **11**–**17** and **23** were synthesized according to literature procedures.[14a,30–36] Compounds **7**, **8** and **18** were prepared as reported in the Supporting Information. All reactions were monitored by thin-layer chromatography, using aluminum sheets coated with silica (60, F_{254}). Melting points are uncorrected. Fast atom bombardment mass spectra (FABMS) were recorded with a VG Mass Lab Trio-2 in a 3-nitrobenzyl alcohol matrix. High-resolution electrospray ionization mass spectra (HRESIMS) were recorded with an Agilent LCTOF spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded with Bruker Avance 400 and 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].

6,6-Dimethyl-2-(4′-nitrophenyl)-5a-phenyl-5a,6-dihydro-12*H*-indolo-[2,1-*b*][1,3]benzooxazine (2a): PBr_3 (0.04 mL, 0.4 mmol) was added dropwise to a solution of **7** (56 mg, 0.2 mmol) in MeCN (3 mL) maintained under Ar at 0 °C. After stirring for 2 h, **6** (53 mg, 0.2 mmol) was added, and the reaction mixture was warmed to ambient temperature and stirred for 48 h. After the addition of sodium phosphate buffer (25 mL, pH = 7.0), the mixture was extracted with CH_2Cl_2 (3 × 25 mL). The organic phase was washed with sodium phosphate buffer (25 mL, pH = 7.0), brine (25 mL), dried (Na_2SO_4), and the solvent was distilled off under reduced pressure. The residue was purified by column chromatography [SiO_2, CH_2Cl_2/hexane (2:3, v/v)] to give **2a** (37 mg, 36%) as a bright yellow powder. M.p. 218–220 °C. FABMS: *m*/*z* = 449 $[M + H]^+$. HRMS: calcd. for $C_{29}H_{24}N_2O_3Na$ $[M + Na]^+$ 471.1685; found 471.1710. ^1H NMR ($CDCl_3$): δ = 8.21 (dd, *J* = 2, 7 Hz, 2 H, ar), 7.69 (d, *J* = 7 Hz, 2 H, ar), 7.57 (dd, *J* = 2, 7 Hz, 2 H, ar), 7.40–7.28 (m, 4 H, ar), 7.21 (d, *J* = 2 Hz, 1 H, ar), 7.15 (t, *J* = 8 Hz, 2 H, ar), 6.93–6.88 (m, 2 H, ar), 6.73 (d, *J* = 8 Hz, 1 H, ar), 4.64 (d,

J = 17 Hz, 1 H, CH_aH_b), 4.55 (d, J = 17 Hz, 1 H, CH_bH_a), 1.61 (s, 3 H, CH_3), 0.83 (s, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 154.4, 147.4, 147.1, 146.5, 137.9, 136.7, 130.7, 128.5, 128.4, 128.1, 127.5, 126.9, 126.6, 125.6, 124.0, 122.3, 120.4, 120.2, 118.4, 108.8, 103.7, 49.5, 41.0, 27.6, 18.5 ppm.

6,6-Dimethyl-2-(4′-nitrobiphenyl)-5a-phenyl-5a,6-dihydro-12*H*-indolo-[2,1-*b*][1,3]benzooxazine (3a): PBr_3 (0.03 mL, 0.3 mmol) was added dropwise to a solution of **8** (40 mg, 0.1 mmol) in MeCN (10 mL) maintained under Ar at –10 °C. The mixture was warmed to ambient temperature and stirred for 5 h. Then, **6** (30 mg, 0.1 mmol) and Et_3N (0.03 mL, 0.2 mmol) were added, and the mixture was stirred for 48 h. After the addition of sodium phosphate buffer (25 mL, pH = 7.0), the mixture was extracted with CH_2Cl_2 (3 × 25 mL). The organic phase was washed with sodium phosphate buffer (25 mL, pH = 7.0), brine (25 mL), dried (Na_2SO_4), and the solvent was distilled off under reduced pressure. The residue was purified by column chromatography [SiO_2, CH_2Cl_2/hexane (2:3, v/v)] to give **3a** (13 mg, 21%) as a bright yellow powder. M.p. 194–196 °C. FABMS: m/z = 525 $[M + H]^+$. HRMS: calcd. for $C_{35}H_{29}N_2O_3$ $[M + H]^+$ 525.2178; found 525.2161. ^{1}H NMR ($CDCl_3$): δ = 8.29 (d, 2 H, ar), 7.74 (d, J = 9 Hz, 2 H, ar), 7.70 (d, J = 7 Hz, 2 H, ar), 7.63 (d, J = 9 Hz, 2 H, ar), 7.57 (d, J = 9 Hz, 2 H, ar), 7.40–7.14 (m, 7 H, ar), 6.91 (d, J = 9 Hz, 1 H, ar), 6.87 (t, J = 8 Hz, 1 H, ar), 6.74 (d, J = 8 Hz, 2 H, ar), 4.64 (d, J = 17 Hz, 1 H, CH_aH_b), 4.55 (d, J = 17 Hz, 1 H, CH_bH_a), 1.59 (s, 3 H, CH_3), 0.82 (s, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 25 °C, 77.0): δ = 153.5, 147.6, 147.2, 147.0, 141.4, 138.0, 136.9, 136.8, 132.2, 128.5, 128.3, 128.2, 127.6, 127.5, 127.2, 126.2, 125.2, 124.1, 122.3, 120.1, 118.2, 108.8, 103.5, 49.5, 41.1, 27.7, 18.5 ppm.

2-Bromo-6,6-dimethyl-5a-phenyl-5a,6-dihydro-12*H*-indolo[2,1-*b*][1,3]-benzooxazine (10a): PBr_3 (0.1 mL, 1.0 mmL) was added dropwise to a solution of **9** (103 mg, 0.5 mmol) in MeCN (5 mL) maintained under Ar at 0 °C. After stirring for 30 min, **6** (110 mg, 0.5 mmol) was added, and the reaction mixture was warmed to ambient temperature and stirred for 72 h. After the addition of sodium phosphate buffer (25 mL, pH = 7.0), the mixture was extracted with CH_2Cl_2 (2 × 50 mL). The organic phase was washed with sodium phosphate buffer (25 mL, pH = 7.0), brine (25 mL), dried (Na_2SO_4), and the solvent was distilled off under reduced pressure. The residue was purified by column chromatography [SiO_2, CH_2Cl_2/hexane (1:9, v/v)] to give **10a** (70 mg, 37%) as a colorless oil. FABMS: m/z = 406 $[M + H]^+$. HRMS: calcd. for $C_{23}H_{21}BrNO$ $[M]^+$ 406.0807; found 406.0815. ^{1}H NMR ($CDCl_3$): δ = 7.63 (d, J = 6 Hz, 2 H, ar), 7.39–7.31 (m, 3 H, ar), 7.21–7.10 (m, 3 H, ar), 7.07 (s, 1 H, ar), 6.87 (t, J = 7 Hz, 1 H, ar), 6.70 (d, J = 8 Hz, 2 H, ar), 4.53 (d, J = 17 Hz, 1 H, CH_aH_b), 4.44 (d, J = 17 Hz, 1 H, CH_bH_a), 1.55 (s, 3 H, CH_3), 0.80 (s, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 152.5, 147.4, 137.9, 136.5, 130.4, 129.2, 128.5, 128.3, 128.1, 127.5, 122.3, 121.8, 120.2, 119.5, 112.2, 108.8, 103.5, 49.4, 40.7, 27.6, 18.4 ppm.

6,6-Dimethyl-2-(4′-nitrostyryl)-5a-phenyl-5a,6-dihydro-12*H*-indolo-[2,1-*b*][1,3]benzooxazine (4a): A mixture of **10a** (78 mg, 0.2 mmol), 4-nitrostyrene (50 mg, 0.3 mmol), $Pd(OAc)_2$ (6 mg, 14%), P(*o*-Tol)$_3$ (6 mg, 10%) in degassed Et_3N (2 mL) was heated under reflux and Ar for 15 h. After cooling to ambient temperature and the addition of sodium phosphate buffer (25 mL, pH = 7.0), the mixture was extracted with CH_2Cl_2 (3 × 25 mL). The organic phase was washed with brine (25 mL), dried (Na_2SO_4), and the solvent was distilled off under reduced pressure. The residue was purified by column chromatography [SiO_2, CH_2Cl_2/hexane (2:3, v/v)] to give **4a** (73 mg, 81%) as a yellow powder. M.p. 210–212 °C. FABMS: m/z = 475 $[M + H]^+$. HRMS: calcd. for $C_{31}H_{27}N_2O_3$ $[M + H]^+$ 475.2022; found 475.2047. ^{1}H NMR ($CDCl_3$): δ = 8.17 (d, J = 9 Hz, 2 H, ar), 7.66 (d, J = 7 Hz, 2 H, ar), 7.52 (d, J = 9 Hz, 2 H, ar), 7.40–7.33 (m, 3 H, ar), 7.22 (dd, J = 2, 9 Hz, 1 H, ar), 7.17–7.12 (m, 3 H, ar), 7.07 (d, J = 16 Hz, 1 H, CH=), 6.91–6.82 (m, 3 H, ar + CH=), 6.72 (d, J = 8 Hz, 1 H, ar), 4.59 (d, J = 17 Hz, 2 H, CH_aH_b), 4.50 (d, J = 17 Hz, 1 H, CH_bH_a), 1.56 (s, 3 H, CH_3), 0.82 (s, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 154.3, 147.5, 146.4, 144.2, 137.9, 136.7, 132.9, 128.6, 128.5, 128.3, 128.1, 127.5, 126.4, 125.5, 124.1, 124.0, 122.3, 120.2, 120.1, 118.2, 108.8, 103.7, 49.5, 40.9, 27.6, 18.5 ppm.

6,6-Dimethyl-2-[(4′-nitrophenyl)ethynyl]-5a-phenyl-5a,6-dihydro-12*H*-indolo[2,1-*b*][1,3]benzooxazine (5a): A suspension of **10a** (80 mg, 0.2 mmol), (4-nitrophenyl)acetylene (34 mg, 0.2 mmol), $PdCl_2$-$(PPh_3)_2$ (14 mg, 0.02 mmol), CuI (7.6 mg, 0.04 mmol) and PPh_3 (10.5 mg, 0.04 mmol) in Et_3N (5 mL) was heated under reflux and Ar for 24 h. After cooling to ambient temperature, the solvent was distilled off under reduced pressure, and the residue was purified by column chromatography [SiO_2, hexanes/CH_2Cl_2 (1:1, v/v)] to afford **5a** (15 mg, 16%) as a yellow solid. M.p. 202–204 °C. FABMS: m/z = 473 $[M]^+$. HRMS: calcd. for $C_{31}H_{24}N_2O_3$ $[M + H]^+$ 473.1865; found 473.1870. ^{1}H NMR ($CDCl_3$): δ = 8.19 (d, J = 9 Hz, 2 H, ar), 7.66 (d, J = 7 Hz, 2 H, ar), 7.57 (d, J = 9 Hz, 2 H, ar), 7.35–7.41 (m, 3 H, ar), 7.22 (d, J = 8 Hz, 1 H, ar), 7.14–7.18 (m, 3 H, ar), 6.89 (t, J = 7 Hz, 1 H, ar), 6.83 (d, J = 8 Hz, 1 H, ar), 6.72 (d, J = 8 Hz, 1 H, ar), 4.57 (d, J = 17 Hz, 1 H, CH_bH_a), 4.48 (d, J = 17 Hz, 1 H, CH_aH_b), 1.58 (s, 3 H, CH_3), 0.82 (s, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 18.8, 28.0, 41.1, 49.9, 86.8, 95.5, 104.4, 109.2, 114.1, 118.5, 120.6, 120.7, 122.7, 124.0, 127.9, 128.5, 128.8, 129.0, 130.9, 131.0, 131.8, 132.3, 136.9, 138.2, 147.1, 147.7, 155.0 ppm.

Supporting Information (see footnote on the first page of this article): Experimental procedures for the preparation of **7**, **8** and **18**; determination of the quantum yield for the photochromic transformation of **2a**.

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[1] G. H. Dorion, A. F. Wiebe, *Photochromism*, Focal Press, New York, **1970**.
[2] G. H. Brown (Ed.), *Photochromism*, Wiley, New York, **1971**.
[3] A. V. El'tsov (Ed.), *Organic Photochromes*, Consultants Bureau, New York, **1990**.
[4] H. Bouas-Laurent, H. Dürr (Ed.), *Photochromism: Molecules and Systems*, Elsevier, Amsterdam, **1990**.
[5] J. C. Crano, R. Guglielmetti (Eds.), *Organic Photochromic and Thermochromic Compounds*, Plenum Press, New York, **1999**.
[6] C. B. McArdle (Ed.), *Applied Photochromic Polymer Systems*, Blackie, Glasgow, **1992**.
[7] a) M. Irie (Ed.), *Photo-Reactive Materials for Ultrahigh Density Optical Memory*, Elsevier, Amsterdam, **1994**; b) M. Irie, *Chem. Rev.* **2000**, *100*, 1683–1890.
[8] a) F. M. Raymo, *Angew. Chem. Int. Ed.* **2006**, *45*, 5249–5251; b) F. M. Raymo, M. Tomasulo, *Chem. Eur. J.* **2006**, *12*, 3186–3193.
[9] a) R. C. Bertelson, in ref.[1], p. 45–431; b) R. C. Bertelson, in ref.[5], vol. 1, p. 11–83.
[10] A. S. Kholmanskii, K. M. Dyumanev, *Russ. Chem. Rev.* **1987**, *56*, 136–151.
[11] R. Guglielmetti, in ref.[4], p. 314–466 and 855–878.
[12] N. Tamai, H. Miyasaka, in ref.[7b], p. 1875–1890.
[13] V. I. Minkin, *Chem. Rev.* **2004**, *104*, 2751–2776.
[14] a) M. Tomasulo, S. Sortino, A. J. P. White, F. M. Raymo, *J. Org. Chem.* **2005**, *70*, 8180–8189; b) M. Tomasulo, S. Sortino, F. M.

Raymo, *Org. Lett.* **2005**, *7*, 1109–1112; c) M. Tomasulo, S. Sortino, F. M. Raymo, *Asian Chem. Lett.* **2007**, *11*, 219–222; d) M. Tomasulo, S. Sortino, F. M. Raymo, *Adv. Mater.* **2008**, *20*, 832–835; e) M. Tomasulo, S. Sortino, F. M. Raymo, *J. Org. Chem.* **2008**, *73*, 118–126; f) M. Tomasulo, S. Sortino, F. M. Raymo, *J. Photochem. Photobiol. A: Chem.* **2008**, *200*, 44–49; g) E. Deniz, M. Tomasulo, S. Sortino, F. M. Raymo, *J. Phys. Chem. C* **2009**, *113*, 8491–8497.

[15] a) A. P. de Silva, G. D. McClean, N. D. McClenaghan, T. S. Moody, S. M. Weir, *Nachr. Chem.* **2001**, *49*, 602–606; b) G. J. Brown, A. P. de Silva, S. Pagliari, *Chem. Commun.* **2002**, 2461–2463; c) A. P. de Silva, N. D. McClenaghan, *Chem. Eur. J.* **2004**, *10*, 574–586; d) A. P. de Silva, S. Uchiyama, *Nat. Nanotechnol.* **2007**, *2*, 399–410.

[16] M. D. Ward, *J. Chem. Educ.* **2001**, *78*, 321–328.

[17] F. M. Raymo, *Adv. Mater.* **2002**, *14*, 401–414.

[18] D. Steinitz, F. Remacle, R. D. Levine, *ChemPhysChem* **2002**, *3*, 43–51.

[19] a) V. Balzani, A. Credi, M. Venturi, *ChemPhysChem* **2003**, *4*, 49–59; b) A. Credi, *Angew. Chem. Int. Ed.* **2007**, *46*, 5472–5475.

[20] L. W. Tutt, T. F. Boggess, *Prog. Quantum Electron.* **1993**, *17*, 299–338.

[21] J. W. Perry in *Nonlinear Optics of Organic Molecules and Polymer* (Eds.: H. S. Nalwa, S. Miyata), CRC Press, Boca Raton, **1997**, p. 813–840.

[22] E. W. Van Stryland, D. J. Hagan, T. Xia, A. A. Said, in *Nonlinear Optics of Organic Molecules and Polymers* (Eds.: H. S. Nalwa, S. Miyata), CRC Press, Boca Raton, **1997**, p. 841–860.

[23] Y.-P. Sun, J. E. Riggs, *Int. Rev. Phys. Chem.* **1999**, *18*, 43–90.

[24] R. A. Ganeev, *J. Opt. A: Pure Appl. Opt.* **2005**, *7*, 717–733.

[25] J. C. Crano, W. S. Kwak, C. N. Welch in ref.[6], p. 31–79.

[26] a) S. W. Hell in *Topics in Fluorescence Spectroscopy* (Ed.: J. R. Lakowicz), Plenum Press, New York, **1997**, p. 361–422; b) S. W. Hell, *Nat. Biotechnol.* **2003**, *21*, 1347–1355; c) S. W. Hell, M. Dyba, S. Jakobs, *Curr. Opin. Neurobiol.* **2004**, *14*, 599–609; d) S. W. Hell, *Phys. Lett. A* **2004**, *326*, 140–145; e) S. W. Hell, K. I. Willig, M. Dyba, S. Jakobs, L. Kastrup, V. Westphal in *Handbook of Biological Confocal Microscopy* (Ed.: J. B. Pawley), Springer, New York, **2006**, p. 571–579; f) S. W. Hell, L. Kastrup, *Nachr. Chem.* **2007**, *55*, 47–50; g) S. W. Hell, *Science* **2007**, *316*, 1153–1158; h) S. W. Hell, A. Schönle in *Science of Microscopy* (Eds.: P. W. Hawkes, J. C. H. Spence), Springer, New York, **2007**, vol. 2, p. 790–834; i) S. W. Hell, *Nat. Methods* **2009**, *6*, 24–32.

[27] M. Bates, B. Huang, X. Zhuang, *Curr. Opin. Chem. Biol.* **2008**, *12*, 505–514.

[28] M. Fernández-Suárez, A. Y. Ting, *Nat. Rev. Mol. Cell Biol.* **2008**, *9*, 929–943.

[29] J. Lippincott-Schwartz, S. Manley, *Nat. Methods* **2009**, *6*, 21–23.

[30] W. Su, S. Urgaonkar, P. A. McLaughlin, J. G. Verkade, *J. Am. Chem. Soc.* **2004**, *126*, 16433–16439.

[31] P. Culling, G. W. Gray, D. Lewis, *J. Chem. Soc.* **1960**, 2699–2704.

[32] J. Wu, D. Li, D. Zhang, *Synth. Commun.* **2005**, *35*, 2543–2551.

[33] J.-H. Li, J.-L. Li, D.-P. Wang, S.-F. Pi, Y.-X. Xie, M.-B. Zhang, X.-C. Hu, *J. Org. Chem.* **2007**, *72*, 2053–2057.

[34] N. Gisch, J. Balzarini, C. Meier, *Med. J. Chem.* **2007**, *50*, 1658–1667.

[35] Y. Kitamura, A. Sakurai, T. Udzu, T. Maegawa, Y. Monguchi, H. Sajiki, *Tetrahedron* **2007**, *63*, 10596–10602.

[36] V. Diemer, H. Chaumeil, A. Defoin, C. Carre, *Synthesis* **2007**, 3333–3338.

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