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Bichromophoric Photochromes Based on the Opening and Closing of a Single Oxazine Ring

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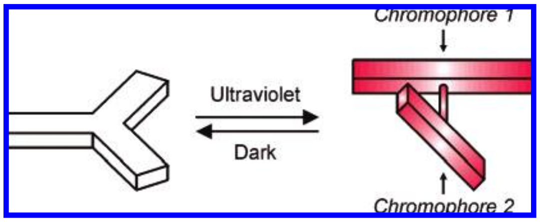

We have designed bichromophoric photochromes based on the photoinduced opening and thermal closing of a [1,3]oxazine ring. In particular, we have synthesized six compounds incorporating fused 3*H*-indole and 4-nitrophenoxy fragments and pendant biphenyl, styryl, biphenylvinyl, or stilbenylvinyl groups. The laser excitation of two of these six molecules cleaves a [C−O] bond and opens their [1,3]oxazine ring in less than 6 ns with quantum yields of 0.08 and 0.28, respectively. This photoinduced process generates simultaneously a 4-nitrophenolate anion and a 3*H*-indolium cation. Both chromophores absorb in the same region of the electromagnetic spectrum. As a result, an intense band appears at ca. 440 nm upon the photoinduced opening of the [1,3]oxazine ring. In both instances, the photogenerated species switches back to the original isomer with first-order kinetics and lifetimes of 38 and 140 ns, respectively. Both compounds have excellent fatigue resistances and retain their photochemical behavior within rigid poly(methyl methacrylate) matrices. However, the thermal reisomerization within the polymer matrix is significantly slower and requires several microseconds to occur. The other four compounds do not undergo ring opening upon excitation under otherwise identical experimental conditions. Indeed, either photoinduced electron transfer or intersystem crossing compete successfully with the ring-opening process.

Introduction

The unique properties of photochromic compounds continue to stimulate the development of a diversity of functional molecules with photoresponsive character.[1−5] Indeed, these molecular switches respond to optical stimulations with significant, but reversible, structural and electronic changes. These modifications at the molecular level can occur in liquid solutions, polymer matrices, or even crystals and translate into drastic alterations of the absorption coefficient and refractive index of the overall material. In fact, photonic materials and devices have already been designed around the absorptive and dispersive effects associated with this particular class of functional compounds.[6−9]

In most instances, photochromic transformations are based on unimolecular photochemical reactions involving ring-closing/opening steps or cis/trans isomerizations.[1−5] Generally, these processes require a single chromophore to absorb a photon and undergo significant stereoelectronic modifications, which even-

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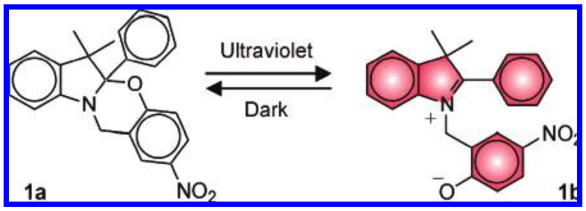

FIGURE 1. Photoinduced and reversible interconversion of the [1,3]-oxazine **1a** and zwitterion **1b**.

tually culminate into a color change. For example, we have demonstrated that the laser excitation of the 4-nitrophenoxy chromophore of **1a** (Figure 1) at 355 nm results in the cleavage of the [C−O] bond in less than 6 ns with a quantum yield of 0.10 in acetonitrile at 20 °C.[10] The photoinduced opening of the [1,3]oxazine ring generates the 4-nitrophenolate chromophore of **1b** (Figure 1) with the concomitant development of an absorption band centered at 440 nm. The photogenerated isomer **1b** reverts thermally to the original species **1a** with a lifetime of 25 ns. This particular photochromic system is remarkably stable and tolerates thousands of switching cycles with no sign of degradation, even in the presence of molecular oxygen. Furthermore, the photoinduced and reversible interconversion of **1a** and **1b** also occurs in rigid poly(methyl methacrylate) matrices with concomitant changes in the absorption coefficient of the doped polymer.

In search of alternative structural designs for photochromic compounds, molecular switches incorporating pairs of identical photoresponsive chromophores have also been developed.[11−17] In these systems, the photoinduced switching of the *two* identical subunits requires the absorption of *two* independent photons in *two* distinct photochemical events. In principle, bichromophoric photochromes can also be designed to operate in response to a *single* photon in a *single* photochemical reaction. Specifically, a photochromic transformation can be engineered to generate a pair of distinct chromophores after the absorption of only one photon. On the basis of these considerations, we have envisaged the possibility of modifying the structural design of our original photochromic oxazine **1a** (Figure 1) to generate a new family of bichromophoric photochromes. In this paper, we report the synthesis of six bichromophoric switches, based on this general design logic, together with their photochemical and photophysical properties.

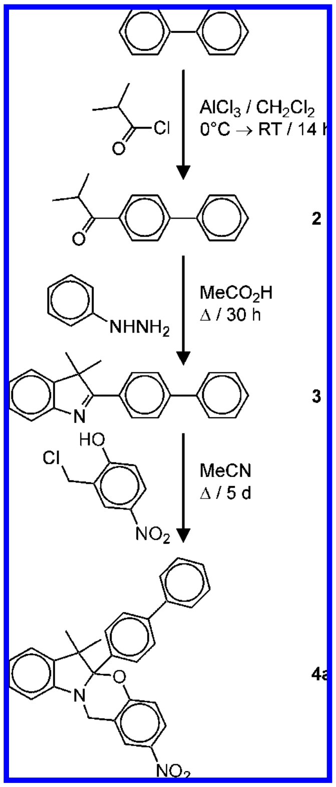

FIGURE 2. Synthesis of the [1,3]oxazine **4a**.

Results and Discussion

Design and Synthesis. The photoinduced opening of the [1,3]-oxazine ring of **1a** (Figure 1) generates a 4-nitrophenolate chromophore able to absorb in the visible region.[10] Additionally, the cleavage of the [C−O] bond at the junction of the two heterocyclic fragments of **1a** brings the adjacent phenyl ring in conjugation with the 3*H*-indolium cation of **1b**. In principle, this transformation can be exploited to generate another chromophore able to absorb in the visible region in addition to the 4-nitrophenolate anion. Indeed, the phenyl substituent of **1a** can be replaced with an extended π-system in order to enhance significantly the conjugation of the 3*H*-indolium cation formed upon photoinduced opening of the [1,3]oxazine ring. Alternatively, conjugated substituents can be introduced in the para position, relative to the nitrogen atom, on the phenylene ring of the 3*H*-indole fragment of **1a**, once again, with the ultimate goal of generating an extended π-system able to absorb in the visible region, after the opening of the [1,3]oxazine ring. On the basis of these considerations, we have designed and synthesized six photochromic oxazines incorporating biphenyl (**4a** in Figure 2), styryl (**6a** in Figure 3), biphenylvinyl (**7a** in Figure 3), or stilbenylvinyl (**8a**, **13a**, and **14a** in Figures 3 and 4) substituents.

We have prepared **4a** (Figure 2) in three steps, with an overall yield of 38%, starting from biphenyl. Specifically, we have acylated biphenyl with isobutyryl chloride in the presence of

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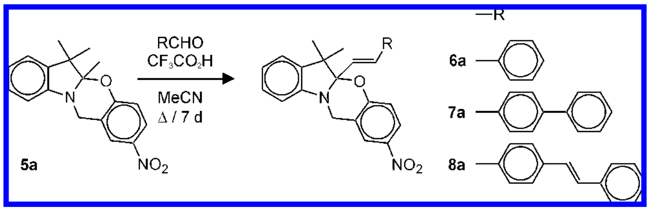

FIGURE 3. Synthesis of the [1,3]oxazines **6a**, **7a**, and **8a**.

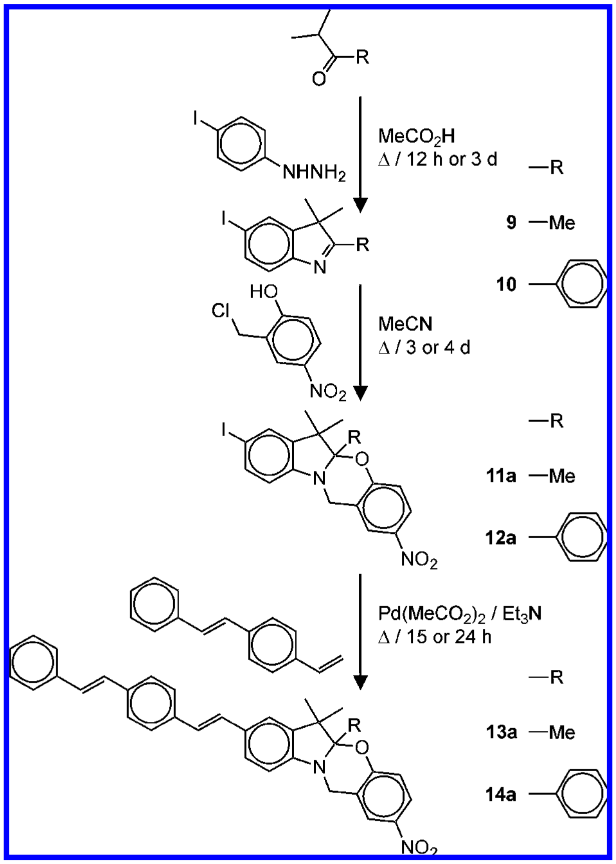

FIGURE 4. Synthesis of the [1,3]oxazines **13a** and **14a**.

aluminum chloride and condensed the resulting ketone **2** with phenyl hydrazine under acidic conditions. We have then reacted the 3*H*-indole **3** with 4-nitro-2-chloromethylphenol to afford the target molecule **4a**. Instead, we have prepared **6a**, **7a**, and **8a** (Figure 3) in a single step, with yields of 76, 40, or 53%, respectively, starting from the known oxazine **5a**.[10b,18] In particular, we have condensed **5a** with benzaldehyde, 4-phenylbenzaldehyde, or *trans*-4-(2-phenylethylene)benzaldehyde under acidic conditions to give **6a**, **7a**, or **8a**, respectively.[19]

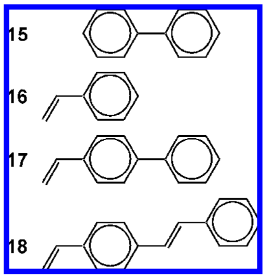

FIGURE 5. Model compounds **15**−**18**.

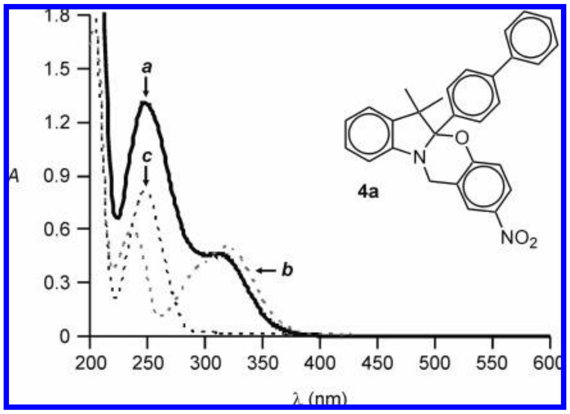

FIGURE 6. Steady-state absorption spectra (0.1 mM, MeCN, 20 °C) of **4a** (a), **5a** (b), and **15** (c).

We have synthesized **13a** and **14a** (Figure 4) in three steps, with overall yields of 21 and 13%, starting from isopropyl methyl ketone and isopropyl phenyl ketone, respectively. Indeed, we have condensed both ketones with 4-iodophenyl hydrazine to generate the 3*H*-indoles **9** and **10**. We have then reacted these compounds with 4-nitro-2-chloromethylphenol to assemble the oxazine skeleton of **11a** and **12a**. Finally, we have coupled these molecules with 1-vinyl-*trans*-stilbene in the presence of triethylamine and palladium(II) bisacetate to afford the target oxazines **13a** and **14a**.

Steady-State Absorption Spectroscopy. The absorption spectra of the oxazines **4a**, **6a**, **7a**, and **8a** are approximately the sum of those of their constituent chromophores (**5a** in Figure 3 and **15**−**18** in Figure 5). For example, the spectrum of **4a** (a in Figure 6) shows one band at 308 nm for the 4-nitrophenoxy chromophore and another at 248 nm for the biphenyl appendage. Both bands closely resemble the absorptions observed in the spectra of the model compounds **5a** and **15** (b and c in Figure 6) respectively. The other three oxazines **6a**, **7a**, and **8a** show essentially the same behavior (Table 1 and Figure S5, Supporting Information). Thus, the 4-nitrophenoxy chromophore and the adjacent π-system have negligible interactions in the ground state of all four compounds.

The [1,3]oxazine ring of **4a**, **6a**, **7a**, and **8a** opens to generate the anionic hemiaminals **4c**, **6c**, **7c**, and **8c** (Figure 7), respectively, in the presence of tetrabutylammonium hydroxide. This transformation causes the appearance of a band in the visible region for the 4-nitrophenolate chromophore of the resulting hemiaminals. For example, the addition of tetrabutylammonium hydroxide to **4a** encourages the evolution of a band at 428 nm (a and b in Figures 8) that resembles the absorption of the tetrabutylammonium salt of 4-nitrophenolate (c in Figure 8). Once again, the other three oxazines **6a**, **7a**, and **8a** show essentially the same behavior upon addition of tetrabutylammonium hydroxide (Figure S16, Supporting Information).

The [1,3]oxazine ring of **4a**, **6a**, **7a**, and **8a** opens to generate the 3*H*-indolium cations **4d**, **6d**, **7d** and **8d** (Figure 7), respectively, in the presence of trifluoracetic acid. This transformation extends the conjugation of the π-system appended

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TABLE 1. Spectroscopic Data[a] for the Oxazines 4a, 6a, 7a, 8a, 13a, and 14a and Their Model Compounds

	λ_A (nm)	ϵ (mM^{-1} cm^{-1})	λ_E (nm)	Φ_F	Φ_P	τ (ns)
1a	316	11.0			0.10	25
4a	248, 308	26.2, 9.3	314	0.02		
5a	318	10.0			0.03	25
6a	244, 315	16.6, 9.7				
7a	248	36.1			0.08	38
8a	330	50.5			0.28	140
13a	368	57.6	424	0.02		
14a	367	58.4	429	0.02		
15	248	16.2	313	0.15		
16	247	14.3	305	0.16		
17	276	31.7	334	0.65		
18	325	30.2	408	0.28		
19	327	14.5				
20	383	28.1				
21	412	35.1				
22	426	33.3				

[a] The absorption wavelength (λ_A), molar extinction coefficient (ϵ) at λ_A, emission wavelength (λ_E), fluorescence quantum yield (Φ_F), and quantum yield (Φ_P) for the photochromic transformation and lifetime (τ) of the photogenerated isomer were measured in MeCN at 20 °C. The λ_A, ϵ, Φ_P, and τ for **1a** and **5a** are from ref 10b. The Φ_F of **15**−**17** are from refs 20 and 21. The error in the determination of Φ_F, Φ_P, and τ is ca. 15%.

to the 3*H*-indolium fragment with a concomitant bathochromic shift in absorption. For example, the band of the biphenyl appendage of **7a** shifts to 421 nm (a and b in Figure 9) upon addition of acid to resemble the absorption of the model compound **21** (c in Figure 9 and Figure 10). A similar effect can be observed in the spectra of **4a**, **6a**, and **8a** (Figure S17, Supporting Information) upon addition of trifluoracetic acid. Indeed, the absorption of the π-system appended to their 3*H*-indolium fragment moves to 308, 388, and 460 nm with the formation of **4d**, **6d**, and **8d**, respectively, to resemble the bands of the model compounds **19**, **20**, and **22** (Figure 10).

The spectra of the oxazines **13a** and **14a** (Figure 4) differ from the sum of those of their constituent components (**1a** or **5a** in Figures 1 or 3 and **18** in Figure 5). Both compounds show a bathochromic shift of 42 nm relative to **18** (Table 1, Figure S18, Supporting Information), indicating that the stilbenylvinyl appendage and the phenylene ring of the 3*H*-indole interact in the ground state. As observed for **4a**, **6a**, **7a**, and **8a**, the addition of either tetrabutylammonium hydroxide or trifluoracetic acid opens the [1,3]oxazine ring of **13a** and **14a**. The formation of **13b** and **14b** (Figure 7) is accompanied, once again, by the appearance of the characteristic absorption for the 4-nitrophenolate chromophore (Figure S19, Supporting Information). Instead, the generation of **13d** and **14d** (Figure 7) has a modest influence on the absorption spectrum. Specifically, the main band of **13a** and **14a** at 367 nm decreases slightly in intensity and broadens with the formation of **13d** and **14d** (Figure S20, Supporting Information), suggesting that the additional double bond on the 3*H*-indolium cation has a modest influence on the absorption characteristics of the adjacent stilbenylvinylphenylene chromophore.

Steady-State Emission Spectroscopy. The model compounds **15**−**18** emit upon ultraviolet excitation with quantum yields ranging from 0.15 to 0.65 (Table 1).[20,21] Instead, the fluorescence of these extended π-systems is effectively quenched in the oxazines **6a**, **7a** and **8a** (Figure S21, Supporting Information). A residual emission can only be observed for the biphenyl appendage of **4a** (a and b in Figure 11). Presumably, the transfer of one electron from the nitrogen atom of the 3*H*-indole fragment of these oxazines to the adjacent fluorophore upon excitation is responsible for quenching. Indeed, the redox potentials[22] of **15**−**18** and **23** (Table 2) suggest that this photoinduced electron-transfer process is exoergonic for the four oxazines with free energy changes more negative than −0.2 eV.[23]

In agreement with a quenching mechanism based on photoinduced electron transfer, the transformation of **4a**, **6a**, **7a**, and **8a** into the hemiaminal anions of **4c**, **6c**, **7c**, and **8c**, after the addition of tetrabutylammonium hydroxide, has negligible influence on their emission spectra. In fact, the 3*H*-indole fragment retains its electron-rich character after ring opening[24] and, thus, can still transfer an electron to the adjacent fluorophores upon excitation. Instead, the treatment of **4a**, **6a**, **7a**, and **8a** with trifluoracetic acid imposes a positive charge on the nitrogen atom of the resulting 3*H*-indolium cations **4d**, **6d**, **7d**, and **8d**. Furthermore, this process brings the 3*H*-indolium cation in conjugation with the adjacent π-system to generate chromophores similar to the model compounds **19**−**22**. Consistently, the conversion of **4a**, **7a**, and **8a** into **4d**, **7d**, and **8d** causes the appearance of broad and weak bands in the emission spectra (Figure S22, Supporting Information), which closely resemble the emissions of **19**, **21**, and **22**.[25]

The two oxazines **13a** and **14a** emit at ca. 425 nm with a quantum yield of 0.02 (Table 1, Figure S23, Supporting Information). Their bands are bathochromically shifted by ca. 20 nm relative to the emission of **18**, as a result of the conjugation of the stilbenylvinyl appendage with the 3*H*-indole fragment. In both instances, the opening of the [1,3]oxazine ring with either tetrabutylammonium hydroxide or trifluoroacetic acid has negligible influence on the emission behavior.

Transient Absorption Spectroscopy. The laser excitation of the 4-nitrophenoxy chromophore of **1a** at 355 nm opens the [1,3]oxazine ring with a quantum yield of 0.10 (Table 1).[10] This process is accompanied by the appearance of a band at 440 nm for the ground-state absorption of the 4-nitrophenolate chromophore (c in Figure 8) of the photogenerated isomer **1b**. This species has a lifetime of 25 ns and reverts thermally to the original isomer with the concomitant monoexponential decay of the 4-nitrophenolate band. In contrast, the transient absorption spectra of **4a** and **6a** do not show any significant signal upon excitation, under otherwise identical experimental conditions. The redox potentials of the model compounds **15**, **16**, and **24** (Table 2) suggest that electron transfer from the biphenyl or styryl appendages of **4a** or **6a**, respectively, to the excited 4-nitrophenoxy fragment is exoergonic with a free energy change more negative than −0.5 eV.[23] Presumably, this photoinduced electron-transfer process competes successfully with the opening of the [1,3]oxazine ring and prevents the formation of the zwitterions **4b** and **6b**.

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(23) The free energy changes for the photoinduced electron transfer processes were estimated with the Rehm−Weller equation (Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259−271) and are listed in Tables S1 and S2, Supporting Information.

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(25) The spectra of **6a** recorded after treatment with trifluoroacetic acid and the one of the model compound **20** do not show any significant emission.

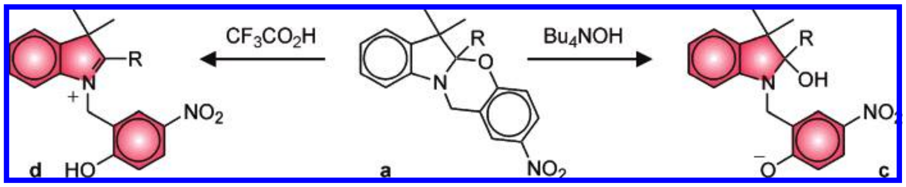

FIGURE 7. Opening of the [1,3]oxazine ring of **a** in the presence of either Bu$_4$NOH or CF$_3$CO$_2$H to form either the anionic hemiaminal **c** or the cationic 3*H*-indolium **d**.

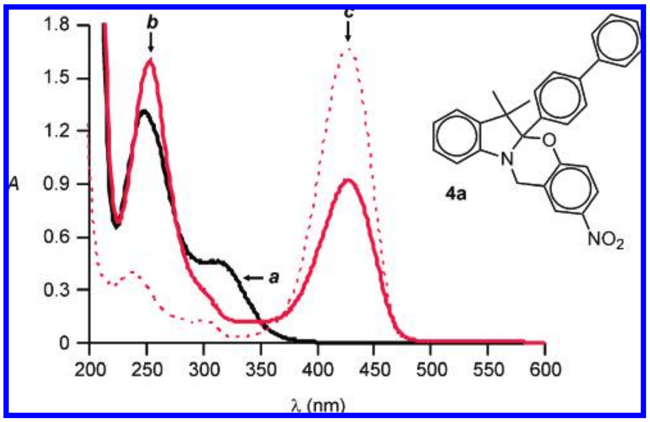

FIGURE 8. Steady-state absorption spectra (0.1 mM, MeCN, 20 °C) of **4a** before (a) and after (b) the addition of Bu$_4$NOH (10 equiv) and of 4-nitrophenol (c) after the addition of Bu$_4$NOH (4 equiv).

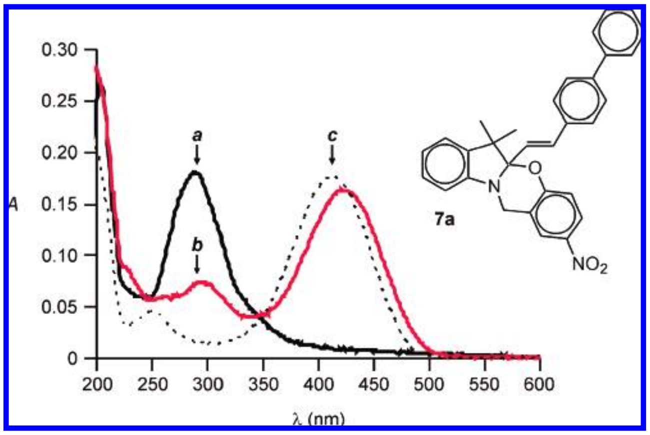

FIGURE 9. Steady-state absorption spectra (0.01 mM, MeCN, 20 °C) of **7a** before (a) and after (b) the addition of CF$_3$CO$_2$H (90 equiv) and of **21** (c).

In analogy to the photochemical behavior of **1a**, the laser excitation of **7a** opens the [1,3]oxazine ring with a quantum yield of 0.08.[26] In both instances, the transient absorption spectrum recorded 30 ns after excitation shows an intense band in the visible region. However, the absorption observed for **7a** (a in Figure 12) is more intense and narrower than that determined for an optically matched solution of **1a** (b in Figure 12) under the same conditions. Indeed, the photoinduced transformation of **1a** into **1b** generates *one* chromophore only, while the conversion of **7a** into **7b** produces *two* chromophoric fragments. In particular, the opening of the [1,3]oxazine ring of **7a** generates a 3*H*-indolium cation with an extended π-system together with the 4-nitrophenolate anion. Both species have ground-state absorptions in the same region of wavelengths[27] (c in Figures 8 and 9), and thus, the photoinduced absorbance change observed for **7a** is approximately twice that for **1a**. Specifically, the transition from the monochromophoric photochrome **1a** to the bichromophoric photochrome **7a** results in an enhancement in coloration efficiency of 1.8 ± 0.3.[28]

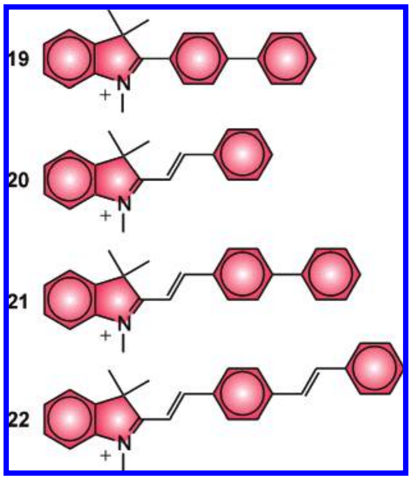

FIGURE 10. Model compounds **19**−**22**.

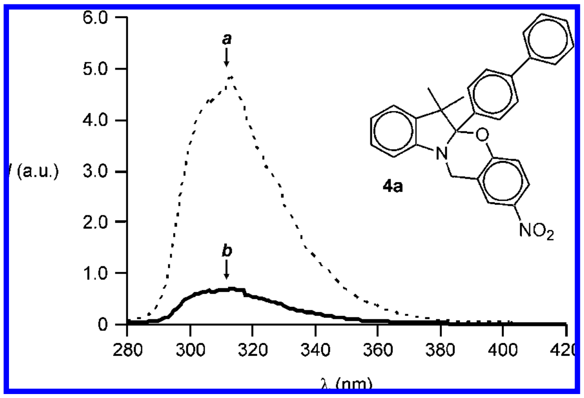

FIGURE 11. Steady-state emission spectra (0.01 mM, MeCN, 20 °C, λ_{Ex} = 249 nm) of **15** (a) and **4a** (b).

The photogenerated isomer **7b** reverts thermally to the original one **7a** on a nanosecond time scale with a concomitant decay in the visible absorbance. The monoexponential fitting of the temporal absorbance evolution (a and b in Figure 13)

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[26] The quantum yield was determined using an optically-matched MeCN solution of **1a** as standard, as described in the supporting information.

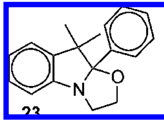
[27] In principle, the two chromophores could be designed to absorb at different wavelengths. Under these conditions, the photoinduced opening of the [1,3]oxazine ring could be exploited to generate two separate bands in the visible region of the absorption spectrum.

[28] The coloration efficiency is the ratio between the number of photons absorbed by the photogenerated isomer at a fixed visible wavelength and the number of photons absorbed by the original isomer at the excitation wavelength.

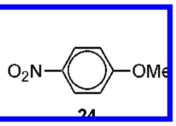
TABLE 2. Electrochemical Data[a] for the Model Compounds 15−18, 23, and 24

	E_{Ox} (V vs Ag/AgCl)	E_{Red} (V vs Ag/AgCl)
15	+1.80	−2.43
16	+1.70	−2.58
17	+1.20	−2.23
18	+1.18	−2.58
23	+0.74	−2.36
24	+2.36	−1.22

[a] The oxidation (E_{Ox}) and reduction (E_{Red}) potentials of **15**−**18** are from ref 22. The E_{Ox} and E_{Red} of **23** and **24** were measured by cyclic voltammetry in a degassed MeCN solution of Bu_4NPF_6 (0.1 M), using a glassy carbon working electrode, a platinum counter electrode, and a Ag/AgCl reference electrode. The structures of the model compounds **23** and **24** are shown in the following diagram:



23



24

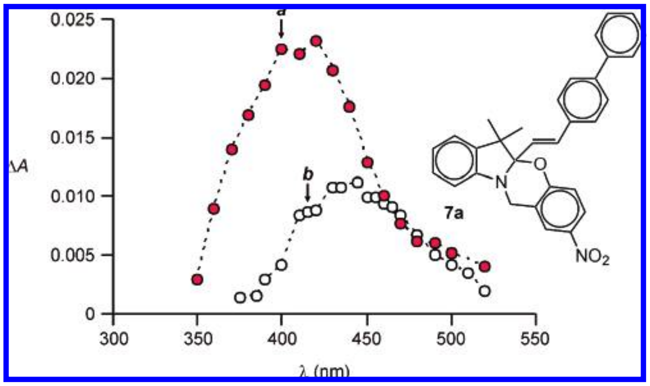


FIGURE 12. Transient absorption spectra of **7a** (0.05 mM, MeCN, 20 °C, a) and of an optically matched solution of **1a** (b) recorded 30 ns after the laser excitation (355 nm, 8 mJ).

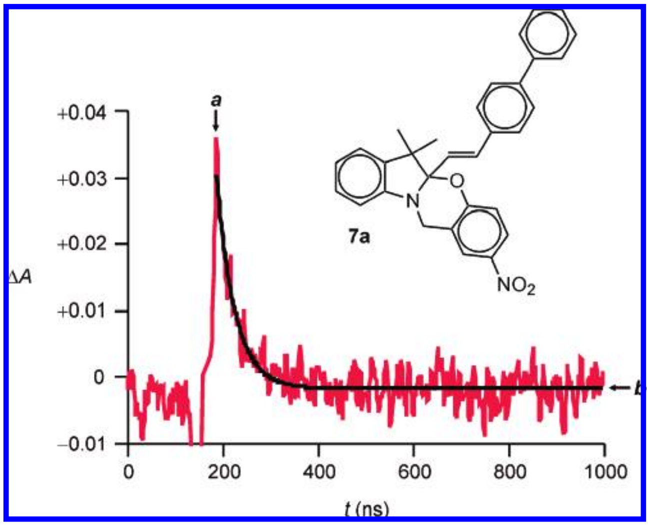


FIGURE 13. Temporal evolution of the absorbance at 430 nm after the excitation (0.05 mM, MeCN, 20 °C, 355 nm, 8 mJ) of **7a** (a) and the corresponding monoexponential fitting (b).

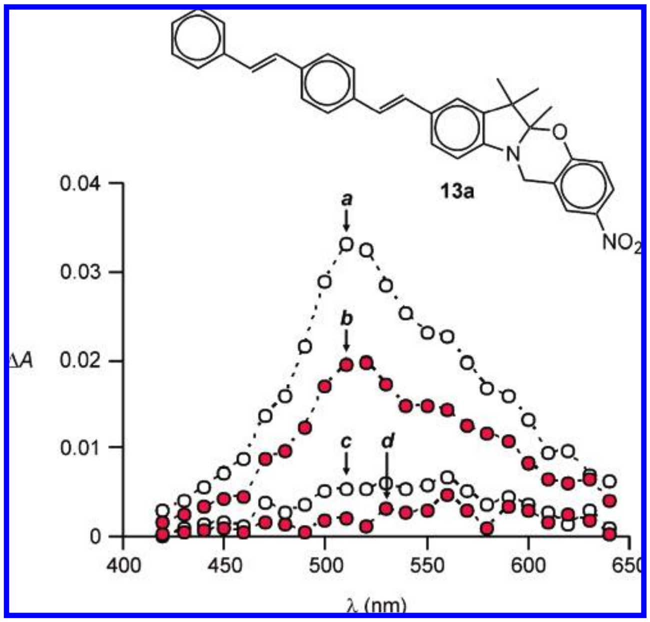


FIGURE 14. Transient absorption spectra (0.01 mM, MeCN, 20 °C) of **13a** recorded 0.08 (a), 2 (b), 5 (c), and 10 μs (d) after the laser excitation (355 nm, 8 mJ).

indicates the lifetime of the photogenerated isomer to be 38 ns. This value is slightly longer than that determined for **1b**, which is only 25 ns.[10] Presumably, the biphenylvinyl appendage conjugated to the 3*H*-indolium cation of **7b** tends to stabilize the photogenerated isomer and delay the reisomerization kinetics relative to **1b**. In addition, the photoinduced and reversible interconversion of **7a** and **7b** tolerates multiple switching cycles with no sign of decomposition. Indeed, the steady-state absorption spectra of **7a** recorded before and after 400 consecutive excitation cycles are essentially identical.

The laser excitation of **8a** results in the opening of the [1,3]-oxazine ring, as observed for **1a** and **7a**, with a quantum yield of 0.28.[26] Once again, the photoinduced process is accompanied by the appearance of a band in the visible region (Figure S25, Supporting Information), which corresponds to ground-state absorptions of the 4-nitrophenolate and 3*H*-indolium chromophores of the photogenerated isomer **8b**. This species reverts thermally to the original one with a concomitant decay in the visible absorbance. In this instance, however, the monoexponential fitting of the temporal evolution of the absorbance indicates the lifetime of the photogenerated isomer to be 140 ns (Figure S26, Supporting Information). This value is considerably longer than those determined for **1b** and **7b** and is, presumably, a result of the extended conjugation of the 3*H*-indolium cation of **8b**, which stabilizes this species relative to **8a** and delays the ring closing step.

The photochemical behavior of **13a** is significantly different from that of **1a**, **5a**, **7a**, and **8a**. Indeed, the laser excitation of **13a** does not result in the opening of the [1,3]oxazine ring, under otherwise identical experimental conditions. A transient absorption at 510 nm (a in Figure 14) is observed instead of the characteristic band at ca. 440 nm for the 4-nitrophenolate chromophore. This band resembles the triplet−triplet absorption of phenylvinylstilbene[29] and decays monoexponentially on a microsecond time scale (a−d in Figure 14). The nonlinear curve fitting of the temporal evolution of this absorption (Figure 15) indicates the lifetime of the transient species to be 2 μs. Thus, the excitation of **13a** encourages intersystem crossing instead of the opening of the [1,3]oxazine ring.

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[29] Hara, M.; Samori, S.; Xichen, C.; Fujitsuka, M.; Majima, T. *J. Org. Chem.* **2005**, *70*, 4370−4374.

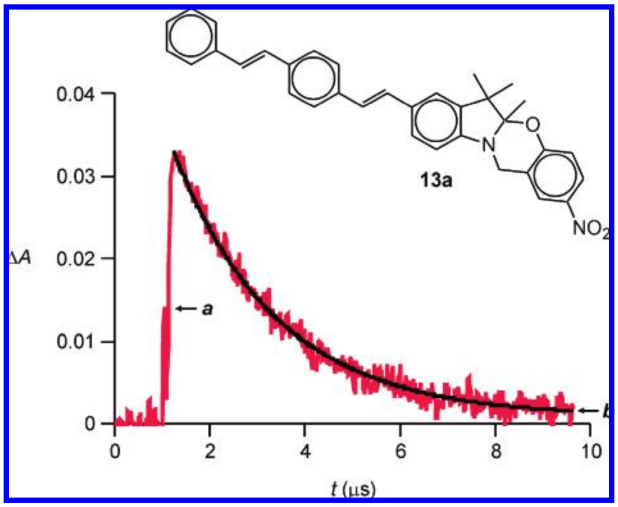

FIGURE 15. Temporal evolution of the absorbance at 510 nm after the excitation (0.01 mM, MeCN, 20 °C, 355 nm, 8 mJ) of **13a** (a) and the corresponding monoexponential fitting (b).

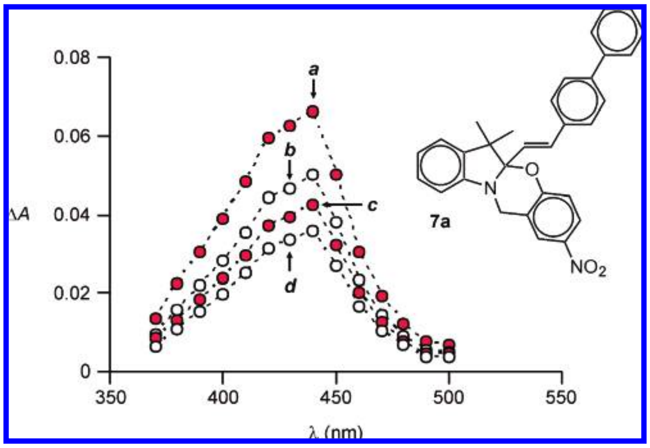

FIGURE 16. Transient absorption spectra of a poly(methyl methacrylate) film doped with **7a** recorded 3 (a), 17 (b), 22 (c), and 33 μs (d) after the laser excitation (355 nm, 8 mJ).

The oxazines **7a** and **8a** can be trapped within rigid poly(methyl methacrylate) matrices and operated under these conditions with a similar response to that observed in acetonitrile solution. Specifically, the laser excitation of poly(methyl methacrylate) films with a thickness of ca. 6 μm and containing either **7a** or **8a** induces the opening of the [1,3]oxazine ring with the appearance of the characteristic transient absorption of the photogenerated isomer **7b** or **8b** (Figure 16, Figure S20, Supporting Information). This band fades with the reisomerization of the zwitterionic isomer back to the original one (a−d in Figure 16 and Figure S27, Supporting Information), as observed in acetonitrile. However, the reisomerization process is significantly slower in the polymer matrix. In particular, the visible absorbance decays biexponentially with lifetimes of 10 and 90 μs for **7a** (Figure 17) and 2 and 25 μs for **8a** (Figure S28, Supporting Information), as observed for **1a** under the same experimental conditions.[10b] 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.[30]

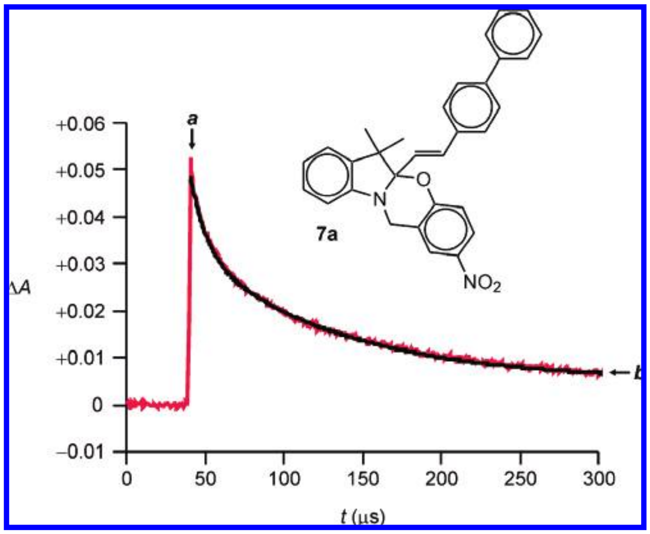

FIGURE 17. Temporal evolution of the absorbance at 430 nm after the excitation a poly(methyl methacrylate) film doped with **7a** (a) and the corresponding biexponential fitting (b).

Conclusions

We have synthesized six compounds incorporating 3*H*-indole and benzooxazine heterocycles fused to each other. In four molecules, a biphenyl, styryl, biphenylvinyl, or stilbenylvinyl appendage is attached to the chiral center at the junction of the two heterocyclic fragments. Their steady-state absorption spectra demonstrate that the aromatic appendages have negligible ground-state interactions with the two heterocyclic fragments. Instead, the emission of the aromatic fluorophores is almost completely suppressed. The redox potentials of model compounds suggest that photoinduced electron transfer from the 3*H*-indole component to the excited fluorophores is responsible for quenching. The selective excitation of the 4-nitrophenoxy chromophore, embedded in the benzooxazine heterocycle of the two compounds incorporating the biphenylvinyl and stilbenylvinyl appendages, cleaves a [C−O] bond to open a [1,3]oxazine ring in less than 6 ns and with quantum yields of 0.08 and 0.28, respectively. In both instances, this photoinduced process generates a 4-nitrophenolate anion and brings the biphenylvinyl and stilbenylvinyl groups in conjugation with a 3*H*-indolium cation. The resulting anionic and cationic chromophores absorb in the same region of wavelengths, and thus, an intense band at ca. 440 nm appears in the absorption spectrum upon excitation. The photogenerated isomers of both compounds revert to the original species after the thermal closing of the [1,3]oxazine ring with lifetimes of 38 and 140 ns, respectively. Thus, a full switching cycle can be completed on a nanosecond time scale with these two photochromic systems. In addition, both molecules can be operated within rigid poly(methyl methacrylate) matrices. Under these conditions, however, the thermal reisomerization process is slower and requires several microseconds to occur. The selective excitation of the 4-nitrophenoxy chromophore, embedded in the benzooxazine heterocycle of the two compounds incorporating the biphenylvinyl and stilbenylvinyl groups, does not lead to ring opening. The redox potentials of model compounds suggest that photoinduced electron transfer

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(30) (a) Krongauz, V. A. In ref 4, pp 793−821, and in ref 6, pp 121−173. (b) Berkovic, G.; Krongauz, V. A.; Weiss, V. In ref 8, pp 1741−1754.

form the biphenyl and styryl groups to the 4-nitrophenoxy fragment competes successfully with the ring opening process. In the other two compounds investigated, a stilbenylvinyl group is connected to the phenylene ring of the 3*H*-indole heterocycle to from an extended π-system. The resulting chromophore absorbs at wavelengths longer than vinylstilbene, preventing the selective excitation of the 4-nitrophenoxy fragment. As a result, the corresponding transient absorption spectrum shows a triplet–triplet absorption for the extended π-system instead of the characteristic ground-state absorption of the ring-opened isomer. In summary, we have designed and synthesized a family of heterocyclic compounds and demonstrated that photochromic transformations with fast switching speeds and excellent fatigue resistances can be implemented in solution and within polymer films with, at least, two of these molecules. Furthermore, the modular design of these compounds offers the opportunity to photoinduce the simultaneous formation of *two* chromophores able to absorb in the visible region in a *single* photochemical event. Thus, photochromic materials with multichromophoric response can, in principle, emerge from our innovative design.

Experimental Section

1-(4-Phenylphenylene)-2-methyl-propan-1-one (2). Sublimed $AlCl_3$ (2.92 g, 22 mmol) was added to a solution of biphenyl (2.35 g, 15 mmol) in CH_2Cl_2 (75 mL) maintained at 0 °C under Ar. Then, a solution of isobutyryl chloride in CH_2Cl_2 (1:10 v/v, 19.5 mL, 18 mmol) was added dropwise over 30 min. The temperature was maintained at 0 °C for a further 2 h and allowed to warm to ambient conditions over the course of 12 h. After the addition of H_2O (10 mL), the mixture was stirred for 10 min and extracted with CH_2Cl_2 (150 mL). The organic phase was washed with H_2O (50 mL), and the solvent was distilled off under reduced pressure to afford **2** (3.42 g, 100%) as a yellowish solid. FABMS: $m/z = 225$ $[M + H]^+$. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.29$ (6H, d, 7 Hz), 3.64 (1H, sep, 7 Hz), 7.41–7.53 (3H, m), 7.64–7.68 (2H, m), 7.70–7.74 (2H, m), 8.06–8.10 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 19.0$, 31.7, 127.3, 128.3, 129.0, 129.1, 132.0, 140.0, 145.5, 204.3.

2-(4-Phenylphenylene)-3,3-dimethyl-3*H*-indole (3). A solution of **2** (2.20 g, 10 mmol) and phenyl hydrazine (1.10 g, 10 mmol) in $MeCO_2H$ (35 mL) was heated under reflux and Ar for 30 h. After the solution was cooled to ambient temperature, aqueous KOH (1M, 50 mL) was added, and the mixture was extracted with CH_2Cl_2 (4 × 25 mL). The solvent of the organic phase was distilled off under reduced pressure, and the residue was purified by column chromatography [SiO_2: hexane → CH_2Cl_2/hexane (3:1, v/v)] to afford **3** (2.30 g, 78%) as a red solid. FABMS: $m/z = 298$ $[M + H]^+$. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.68$ (6H, s), 7.35 (1H, dd, 1 and 7 Hz), 7.42–7.46 (3H, m), 7.50–7.54 (2H, m), 7.71–7.74 (2H, m), 7.78–7.82 (3H, m), 8.31–8.35 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 25.0$, 53.6, 121.0, 126.0, 127.0, 127.2, 127.9, 128.0, 128.9, 129.0, 129.2, 132.5, 140.6, 143.0, 147.8, 153.6, 182.9.

2-Nitro-5a-(4-phenylphenylene)-6,6-dimethyl-5a,6-dihydro-12*H*-indolo[2,1-*b*][1,3]benzooxazine (4a). A solution of 4-nitro-2-chloromethylphenol (0.43 g, 2 mmol) and **3** (0.62 g, 2 mmol) in MeCN (35 mL) was heated under reflux and Ar for 5 d. After the solution was cooled to ambient temperature, the solvent was distilled off under reduced pressure, and the residue was dissolved in CH_2Cl_2 (50 mL). The resulting solution was extracted with NaOH (1M, 5 mL) and H_2O (2 × 15 mL). The solvent of the organic phase was distilled off under reduced pressure, and the residue was purified by column chromatography [SiO_2: CH_2Cl_2/hexane (1:1, v/v) → CH_2Cl_2/hexane (3:1, v/v)] to afford **4a** (0.38 g, 41%) as a white solid. Mp = 170 °C. HPLC [MeCN]: $t_R = 4.7$ min (270 nm), PA = 1.0 (270 nm), APP = 271.6 ± 0.2 nm. FABMS: m/z = 447 $[M + H]^+$. HRMS: m/z calcd for $[M + H]^+$ $C_{29}H_{25}N_2O_3$ 449.1860, found 449.1856. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.91$ (3H, s), 1.63 (3H, s), 4.59 (1H, d, 14 Hz), 4.67 (1H, d, 14 Hz), 6.75 (1H, d, 8 Hz), 6.88–6.95 (2H, m), 7.14–7.21 (2H, m), 7.38 (1H, d, 7 Hz), 7.43–7.48 (2H, m), 7.60–7.72 (6H, m), 7.95–7.98 (2H, m). ^{13}C NMR (100 MHz, CD_3CN): $\delta = 18.6$, 27.9, 41.0, 50.0, 105.5, 109.3, 118.3, 120.3, 121.1, 122.6, 123.4, 124.0, 127.3, 127.4, 127.4, 128.6, 129.1, 135.0, 137.9, 140.5, 141.9, 142.0, 146.9, 159.3.

2-Nitro-5a-(2-phenylethylene)-6,6-dimethyl-5a,6-dihydro-12*H*-indolo[2,1-*b*][1,3]benzooxazine (6a). A solution of **5a** (155 mg, 0.5 mmol), benzaldehyde (150 μL, 1.5 mmol), and CF_3CO_2H (125μL, 0.15 mmol) in MeCN (20 mL) was heated under reflux and Ar for 7 d. After the solution was cooled to ambient temperature, the solvent was distilled off under reduced pressure, and the residue was dissolved in CH_2Cl_2 (25 mL) and washed with H_2O (20 mL). The solvent of the organic phase was distilled off under reduced pressure, and the residue was purified by column chromatography [SiO_2: hexanes/$MeCO_2Et$ (4:1, v/v)] to give **6a** (153 mg, 76%) as a yellowish solid. Mp = 107 °C. HPLC [MeCN]: $t_R = 4.0$ min (254 nm), PA = 1.6 (254 nm), APP = 223.1 ± 0.5 nm. FABMS: $m/z = 399$ $[M + H]^+$. HRMS: m/z calcd for $[M + H]^+$ $C_{25}H_{23}N_2O_3$ 399.1703, found 399.1699. ^1H NMR (300 MHz, CD_3CN): $\delta = 1.33$ (6H, bs), 4.67 (2H, s), 6.48 (1H, d, 16 Hz), 6.73 (1H, d, 8 Hz), 6.81–6.93 (3H, m), 7.04–7.16 (1H, m), 7.18 (1H, dd, 1 and 8 Hz), 7.31–7.34 (3H, m), 7.46–7.50 (2H, m), 7.97 (1H, dd, 3 and 9 Hz), 8.07 (1H, d, 3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 23.1$, 32.0, 41.1, 50.4, 109.2, 118.1, 120.4, 121.1, 122.7, 123.6, 124.3, 124.4, 127.3, 128.1, 128.2, 128.9, 129.1, 136.6, 138.6, 146.8, 156.9.

2-Nitro-5a-(2-(4-phenylphenylene)ethylene)-6,6-dimethyl-5a,6-dihydro-12*H*-indolo[2,1-*b*][1,3]benzooxazine (7a). A solution of **5a** (100 mg, 0.3 mmol), 4-phenylbenzaldehyde (175 mg, 1.0 mmol), and CF_3CO_2H (80 μL, 0.1 mmol) in MeCN (15 mL) was heated under reflux and Ar for 7 d. After the solution was cooled 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 **7a** (60 mg, 40%) as a orange solid. Mp = 194 °C. HPLC (MeCN): $t_R = 4.1$ min (278 nm), PA = 1.4 (278 nm), APP = 236.7 ± 0.3 nm. FABMS: $m/z = 475$ $[M + H]^+$. HRMS: m/z calcd for $[M + H]^+$ $C_{31}H_{27}N_2O_3$ 475.2016, found 475.2024. ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.27$ (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}C NMR (100 MHz, $CDCl_3$): $\delta = 30.1$, 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.

2-Nitro-5a-(2-(4-(2-phenylethylene)phenylene)ethylene)-6,6-dimethyl-5a,6-dihydro-12*H*-indolo[2,1-*b*][1,3]benzooxazine (8a). A solution of **5a** (100 mg, 0.3 mmol), *trans*-4-(2-phenylethylene)-benzaldehyde (200 mg, 1.0 mmol), and CF_3CO_2H (80 μL, 0.01 mmol) in MeCN (15 mL) was heated under reflux and Ar for 7 d. After the solution was cooled to ambient temperature, the solvent was distilled off under reduced pressure. The residue was dissolved in CH_2Cl_2 (25 mL) and washed with H_2O (15 mL). The solvent of the organic phase was distilled off under reduced pressure, and the residue was dissolved in $CHCl_3$ (6 mL). The solution was diluted with hexane (85 mL), and the resulting precipitate was filtered off to yield **8a** (85 mg, 53%). Mp = 188 °C. HPLC (MeCN): t_R = 4.4 min (300 nm), PA = 1.4 (300 nm), APP = 302.2 ± 0.4 nm. FABMS: $m/z = 501$ $[M + H]^+$. HRMS: m/z calcd for $[M + H]^+$ $C_{33}H_{29}N_2O_3$ 501.2173, found 501.2167. ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.27$ (6H, bs), 4.61 (2H, s), 6.39 (1H, d, 16 Hz), 6.65 (1H, d, 8 Hz), 6.82 (1H, d, 16 Hz), 6.88–6.91 (2H, m), 7.11–7.16 (4H, m), 7.36–7.42 (5H, m), 7.49–7.54 (4H, m), 8.00 (1H, dd, 3 and 9 Hz), 8.03 (1H, d, 3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 23.1$, 32.0, 41.1, 50.6, 104.2, 109.2, 118.1, 120.4, 121.1, 122.7, 123.6, 124.1, 124.4, 127.0, 127.2, 127.6, 128.0, 128.1, 128.3, 129.1, 129.7, 135.1, 136.1, 137.5, 138.1, 138.6, 141.1, 159.6.

5-Iodo-2,3,3-trimethyl-3*H*-indole (9). A solution of isopropyl methyl ketone (113 μL, 1.1 mmol) and 4-iodophenyl hydrazine (234 mg, 1.0 mmol) in $MeCO_2H$ (20 mL) was heated under reflux for 12 h. After being cooled to ambient temperature, the reaction mixture was diluted with H_2O (50 mL) and extracted with CH_2Cl_2 (2 × 30 mL). The solvent of the organic phase was distilled off under reduced pressure, and the residue was dissolved in CH_2Cl_2 (8 mL). The addition of hexane (90 mL) caused the formation of a precipitate, which was filtered off to afford **9** (225 mg, 79%) as a purple oil. FABMS: $m/z = 386$ $[M + 1]^+$. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.16$ (6H, s), 2.14 (3H, s), 7.17 (1H, d, 8 Hz), 7.46−7.50 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 15.6$, 23.3, 54.4, 90.5, 122.1, 131.1, 138.3, 148.4, 153.3, 189.0.

5-Iodo-2-phenyl-3,3-dimethyl-3*H*-indole (10). A solution of isopropyl phenyl ketone (193 μL, 1.3 mmol) and 4-iodophenyl hydrazine (275 mg, 1.2 mmol) in $MeCO_2H$ (25 mL) was heated under reflux for 3 d. After being cooled to ambient temperature, the reaction mixture was diluted with H_2O (50 mL) and extracted with CH_2Cl_2 (2 × 30 mL). The solvent of the organic phase was distilled off under reduced pressure, and the residue was dissolved in CH_2Cl_2 (9 mL). The addition of hexane (90 mL) caused the formation of a precipitate, which was filtered off to afford **10** (175 mg, 43%) as a purple oil. FABMS: $m/z = 348$ $[M + 1]^+$. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.59$ (6H, s), 7.46−7.50 (5H, m), 7.68 (1H, s), 8.12−8.15 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 25.0$, 54.3, 91.3, 120.6, 123.1, 128.8, 129.1, 130.5, 131.2, 137.3, 139.7, 150.3, 183.9.

2-Nitro-5a,6,6-trimethyl-5a,6-dihydro-8-iodo-12*H*-indolo[2,1-*b*][1,3]benzooxazine (11a). A solution of **9** (93 mg, 0.3 mmol) and 4-nitro-2-chloromethylphenol (58 mg, 0.3 mmol) in MeCN (25 mL) was heated under reflux and Ar for 3 d. After the solution was cooled to ambient temperature, the solvent was distilled off under reduced pressure. The residue was dissolved in CH_2Cl_2 (30 mL) and washed with H_2O (2 × 10 mL). The solvent of the organic phase was distilled off under reduced pressure, and the residue was purified by column chromatography [SiO_2: CH_2Cl_2/hexane (1:10 → 1:1, v/v)] to afford **11a** (56 mg, 41%) as a pale yellow solid. FABMS: $m/z = 436$ $[M]^+$. ^1H NMR (500 MHz, $CDCl_3$): $\delta =$ 1.19 (3H, s), 1.52 (3H, s), 1.58 (3H, s), 4.56 (1H, d, 18 Hz), 4.62 (1H, d, 18 Hz), 6.38 (1H, d, 9 Hz), 6.75 (1H, d, 9 Hz), 7.36−7.38 (2H, m), 7.98 (1H, dd, 3 and 9 Hz), 8.07 (1H, d, 3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 16.8$, 19.1, 26.3, 40.5, 48.5, 82.6, 102.9, 111.1, 118.6, 118.9, 123.7, 124.6, 131.7, 136.7, 141.3, 147.0, 159.2.

2-Nitro-5a-phenyl-6,6-dimethyl-5a,6-dihydro-8-iodo-12*H*-indolo[2,1-*b*][1,3]benzooxazine (12a). A solution of **10** (85 mg, 0.3 mmol) and 4-nitro-2-chloromethylphenol (41 mg, 0.2 mmol) in MeCN (30 mL) was heated under reflux and Ar for 4 d. After the solution was cooled to ambient temperature, the solvent was distilled off under reduced pressure. The residue was dissolved in CH_2Cl_2 (30 mL) and washed with H_2O (10 mL). The solvent of the organic phase was distilled off under reduced pressure, and the residue was purified by column chromatography [SiO_2: CH_2Cl_2/hexane (1:1, v/v)] to afford **12a** (66 mg, 60%) as a yellowish solid. FABMS: $m/z = 498$ $[M]^+$. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.83$ (3H, s), 1.56 (3H, s), 4.52 (1H, d, 18 Hz), 4.59 (1H, d, 18 Hz), 6.52 (1H, d, 8 Hz), 6.90 (1H, d, 9 Hz), 7.39−7.46 (5H, m), 7.55−7.67 (2H, m), 7.90 (1H, d, 3 Hz), 7.95 (1H, dd, 3 and 9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 18.8$, 27.9, 41.2, 50.1, 105.4, 111.8, 118.5, 120.1, 123.5, 124.3, 128.3, 128.7, 129.1, 129.5, 131.9, 135.7, 136.8, 140.9, 141.3, 147.1, 159.1.

2-Nitro-5a,6,6-trimethyl-5a,6-dihydro-8-(2-(4-(2-phenylethylene)phenylene)ethylene)-12*H*-indolo[2,1-*b*][1,3]benzooxazine (13a). A mixture of **11a** (38 mg, 0.1 mmol), 1-vinyl-*trans*-stilbene (17 mg, 0.1 mmol), and $Pd(MeCO_2)_2$ (20 mg, 0.1 mmol) in degassed Et_3N (20 mL) was heated at 105 °C under Ar for 1 d. After being cooled to ambient temperature, the mixture was diluted with CH_2Cl_2 (30 mL) and washed with H_2O (40 mL). The solvent of the organic phase was distilled off under reduced pressure, and the residue was purified by column chromatography [SiO_2: hexane → CH_2Cl_2/hexane (1:1, v/v)] to afford **13a** (28 mg, 66%) as a yellow solid. HPLC [MeCN]: $t_R = 4.2$ min (350 nm), PA = 1.4 (350 nm), APP = 283.1 ± 0.5 nm. FABMS: $m/z = 515$ $[M+ 1]^+$. HRMS: m/z calcd for $[M + H]^+$ $C_{34}H_{31}N_2O_3$ 515.2329, found 515.2321. ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.25$ (3H, s), 1.57 (3H, s), 1.61 (3H, s), 4.61 (2H, s), 6.58 (1H, d, 9 Hz), 6.75 (1H, d, 9 Hz), 6.97 (1H, d, 16 Hz), 7.07 (1H, d, 16 Hz),7.14−7.15 (2H, m), 7.23−7.26 (1H, m), 7.36−7.40 (4H, m), 7.47−7.54 (6H, m), 7.98 (1H, dd, 3 and 9 Hz), 8.10 (1H, d, 3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 16.9$, 19.3, 26.5, 40.6, 48.4, 103.2, 108.9, 118.6, 119.1, 120.4, 120.9, 122.7, 123.7, 124.5, 125.8, 126.9, 127.2, 127.5, 128.0, 128.6, 128.7, 129.1, 130.7, 136.5, 137.6, 137.8, 139.1, 140.9, 147.0, 159.3.

2-Nitro-5a-phenyl-6,6-dimethyl-5a,6-dihydro-8-(2-(4-(2-phenylethylene)phenylene)ethylene)-12*H*-indolo[2,1-*b*][1,3]benzooxazine (14a). A mixture of **12a** (45 mg, 0.1 mmol), 1-vinyl-*trans*-stilbene (39 mg, 0.2 mmol), and $Pd(MeCO_2)_2$ (13 mg, 0.1 mmol) in degassed Et_3N (20 mL) was heated at 105 °C under Ar for 15 h. After being cooled to ambient temperature, the mixture was diluted with CH_2Cl_2 (30 mL) and washed with H_2O (40 mL). The solvent of the organic phase was distilled off under reduced pressure, and the residue was purified by column chromatography [SiO_2: hexane → CH_2Cl_2/hexane (1:2, v/v)] to afford **14a** (44 mg, 52%) as a yellow solid. HPLC [MeCN]: $t_R = 4.3$ min (360 nm), PA = 1.3 (360 nm), APP = 332.5 ± 0.3 nm. FABMS: $m/z = 577$ $[M]^+$. HRMS: m/z calcd for $[M + H]^+$ $C_{39}H_{33}N_2O_3$ 577.2486, found 577.2484. ^1H NMR (500 MHz, $CDCl_3$): $\delta = 0.89$ (3H, s), 1.65 (3H, s), 4.56 (1H, d, 18 Hz), 4.65 (1H, d, 18 Hz), 6.73 (1H, d, 8 Hz), 6.91 (1H, d, 9 Hz), 7.00 (1H, d, 16 Hz), 7.10−7.13 (3H, m), 7.30−7.32 (2H, m), 7.37−7.44 (6H, m), 7.48−7.55 (6H, m),7.62−7.67 (2H, m), 7.93−7.96 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 18.8$, 28.1, 41.4, 50.1, 105.7, 109.6, 118.5, 120.4, 120.6, 123.5, 124.2, 126.0, 126.8, 126.9, 127.2, 127.5, 128.0, 128.3, 128.7, 128.8, 129.1, 129.4, 131.0, 136.0, 136.6, 137.6, 137.8, 138.8, 141.3, 147.2, 159.3.

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Supporting Information Available: General methods and experimental procedures for the synthesis of **19**−**22**; HPLC traces of **4a**, **6a**, **7a**, **8a**, **13a**, and **14a**; ^1H NMR spectra of **4a**, **6a**, **7a**, **8a**, **13a**, and **14a**; steady-state absorption spectra of **4a**, **6a**, **7a**, **8a**, **13a**, and **14a**; steady-state emission spectra of **4a**, **6a**, **7a**, **8a**, **13a**, and **14a**; determination of the quantum yields for the photochromic transformations; free energy changes for the photoinduced electron-transfer processes; transient absorption spectra of **8a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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