JOC Article

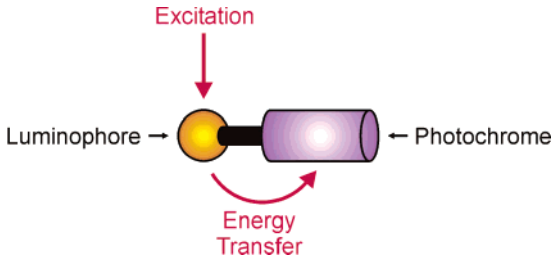
Synthesis and Properties of Benzophenone−Spiropyran and Naphthalene−Spiropyran Conjugates

Massimiliano Tomasulo,[†] Sireesha L. Kaanumal,[†] Salvatore Sortino,*[,‡] and Françisco M. Raymo*[,†]

Center for Supramolecular Science, Department of Chemistry, University of Miami, 1301 Memorial Drive, Florida, 33146-0431, and Dipartimento di Scienze Chimiche, Universitá di Catania, viale Andrea Doria 8, Catania, I-95125, Italy

ssortino@unict.it; fraymo@miami.edu

Received September 28, 2006



We have designed and synthesized four compounds integrating luminescent and photochromic components in their molecular skeletons. Two of them combine a nitrospiropyran photochrome with either one or two naphthalene fluorophores and can be prepared in three synthetic steps. The other two consist of a nitrospiropyran photochrome and a benzophenone phosphore connected by either ether or ester linkages and can be prepared in six or five, respectively, synthetic steps. The luminescent components of these assemblies are expected to transfer energy intramolecularly to the photochromic species upon excitation and encourage their photoisomerization. Consistently, the phosphorescence of the benzophenone units and the fluorescence of the naphthalene components are effectively quenched when these species are connected covalently to a nitrospiropyran. Nonetheless, the photoisomerization of the photochrome becomes significantly less efficient after the covalent attachment to the luminescent partner. The fraction of incident radiations absorbed by either the benzophenone or the naphthalene fragment does not promote the isomerization of the photochromic appendage. Instead, irreversible transformations occur upon irradiation of the luminophore−photochrome assemblies. Thus, the covalent attachment of a benzophenone or a naphthalene to a nitrospiropyran is not a viable strategy to improve the photocoloration efficiency of the photochromic component. Even although the very same luminophores are known to sensitize intermolecularly the isomerization of nitrospiropyrans, the transition to covalent luminophore−photochrome assemblies tends to promote degradation, rather than sensitization, upon irradiation.

Introduction

Photochromic compounds alter reversibly their ability to absorb electromagnetic radiations in response to optical stimulations.[1−5] The photoisomerization of spiropyrans, for example, is a typical photochromic transformation.[6−10] This process occurs in liquid solutions or within rigid polymer matrices upon ultraviolet irradiation and results in the conversion of a colorless isomer into a colored one (e.g., **SP1** and **ME1** in

[†] University of Miami.
[‡] Universitá di Catania.

(1) Dorion, G. H.; Wiebe, A. F. *Photochromism*; Focal Press: New York, 1970.
(2) Brown, G. H., Ed. *Photochromism*; Wiley: New York, 1971.
(3) El'tsov, A. V., Ed. *Organic Photochromes*; Consultants Bureau: New York, 1990.
(4) Bouas-Laurent, H., Dürr, H., Eds. *Photochromism: Molecules and Systems*; Elsevier: Amsterdam, 1990.
(5) Crano, J. C., Guglielmetti R., Eds. *Organic Photochromic and Thermochromic Compounds*; Plenum Press: New York, 1999.
(6) (a) Bertelson, R. C. In ref 1, pp 45−431. (b) Bertelson, R. C. In ref 5, Vol. 1, pp 11−83.
(7) Kholmanskii, A. S.; Dyumanev, K. M. *Russ. Chem. Rev.* **1987**, *56*, 136−151.
(8) Guglielmetti, R. In ref 4, pp 314−466 and 855−878.
(9) Tamai, N.; Miyasaka, H. *Chem. Rev.* **2000**, *100*, 1875−1890.

10.1021/jo062004d CCC: $37.00
Published on Web 12/21/2006

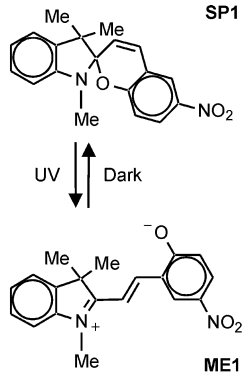


FIGURE 1. Reversible interconversion of the spiropyran **SP1** and the merocyanine **ME1** upon ultraviolet (UV) irradiation and storage in the dark.

Figure 1). The photogenerated species reverts back to the original state upon storage in the dark. The reversible interconversion of the two isomers imposes significant changes on the absorption coefficient and refractive index of their host material. In fact, diverse applications in the realm of photonics have been envisaged on the basis of the photoinduced absorptive and dispersive effects associated with this class of functional organic molecules.[6b,11−17]

The mechanism responsible for the photoinduced isomerization of spiropyrans has been the subject of detailed investigations for decades.[6−10] These studies have demonstrated that the incorporation of a nitro group in the para position, relative to the oxygen atom, of the benzopyran fragment facilitates the photocoloration. Recent laser flash photolysis analyses suggest that the ultraviolet excitation of a nitrospiropyran (e.g., **SP1** in Figure 1) induces efficient intersystem crossing.[18] The population of the first triplet excited state (T_1) is then followed by the cleavage of the [C−O] bond at the spirocenter with the opening of the pyran ring. The resulting ring-opened intermediate is typically formed within subnanosecond timescales.[19−23] This species undergoes a *cis* → *trans* isomerization, about the double bond joining the indolium cation to the phenolate anion, along the potential energy surface of T_1 and then decays to the ground electronic state (S_0). Alternatively, the ring-opened intermediate can first decay to S_0 and then undergo a *cis* → *trans* isomerization along the potential energy surface of S_0. In both instances, the final product of these transformations is a colored merocyanine (e.g., **SP1** in Figure 1) and is formed on a microsecond time scale.[24]

The participation of T_1 in the photoisomerization of nitrospiropyrans was confirmed with quenching and sensitization experiments.[18,24d,25−30] In particular, the transfer of energy from the T_1 of an appropriate sensitizer to the T_1 of a complementary nitrospiropyran was found to encourage the isomerization of the latter upon excitation of the former. In fact, the quantum yield for the photoisomerization of **SP1** increased from 0.12 to 0.31 in the presence of 40 equiv of benzophenone.[28] Similarly, an enhancement of approximately 1 order of magnitude in the photoisomerization quantum yield of spiropyrans was also observed in the presence of naphthalene.[18b,e] In principle, these sensitization processes can be facilitated by integrating sensitizer and photochrome within the same molecular skeleton. The covalent connection would constrain the two components in close proximity and promote the transfer of energy from one to the other upon excitation. Nonetheless, the analysis of the photochemical behavior of three sensitizer−nitrospiropyran dyads did not reveal any significant sensitization.[31] Actually, the presumed sensitizers were found to have a depressive effect on the isomerization of their photochromic partners as well as on their fatigue resistance. Puzzled by these apparent contradictions, we have designed four luminophore−photochrome assemblies with the ultimate goal of developing nitrospiropyrans with improved quantum yields. Here we report the synthesis of these multicomponent assemblies as well as their photochemical and photophysical properties.

Results and Discussion

Synthesis. The compounds **SP2** and **SP3** (Figure 2) combine a nitrospiropyran photochrome with one or two naphthalene sensitizers within their molecular skeletons. These molecules can be prepared in three synthetic steps starting from 2,3,3-trimethyl-3*H*-indole. Specifically, the *N*-alkylation of this precursor with the bromide **1** and **4** yields the indolium cations

(10) Minkin, V. I. *Chem. Rev.* **2004**, *104*, 2751−2776.
(11) (a) Ichimura, K. In ref 4, pp 903−918. (b) Ichimura, K.; Seki, T.; Kawamishi, Y.; Suzuki, Y.; Sakuragi, M.; Tamaki, T. In *Photo-Refractive Materials for Ultrathin Density Optical Memory*; Irie, M., Ed.; Elsevier: Amsterdam, 1994; pp 55−83. (c) Ichimura, K. In *Photochromic Polymers*; Crano, J. C., Guglielmetti, R., Eds.; Plenum Press: New York, 1999; Vol. 2, pp 9−63. (d) Ichimura, K. *Chem. Rev.* **2000**, *100*, 1847−1873.
(12) Crano, J. C.; Kwak, W. S.; Welch, C. N. In *Applied Photochromic Polymer Systems*; McArdle, C. B., Ed.; Blackie: Glasgow, 1992; pp 31−79.
(13) (a) Krongauz, V. In ref 12, pp 121−173. (b) Berkovic, G.; Krongauz, V.; Weiss, V. *Chem. Rev.* **2000**, *100*, 1741−1754.
(14) Irie, M. In *Applied Photochromic Polymer Systems*; McArdle, C. B., Ed.; Blackie: Glasgow, 1992; pp 174−206.
(15) Hibino, J.; Hashida, T.; Suzuki, M. In ref 11b, pp 25−53.
(16) Kawata, S.; Kawata, Y. *Chem. Rev.* **2000**, *100*, 1777−1788.
(17) Delaire, J. A.; Nakatani, K. *Chem. Rev.* **2000**, *100*, 1817−1845.
(18) (a) Atabekyan, L. S.; Chibisov, A. K. *Zh. Prikl. Spektrosk.* **1987**, *46*, 651−654. (b) Görner, H.; Atabekyan, L. S.; Chibisov, A. K. *Chem. Phys. Lett.* **1996**, *260*, 59−64. (c) Görner, H. *Chem. Phys.* **1997**, *222*, 315−329. (d) Chibisov, A. K.; Görner, H. *J. Photochem. Photobiol. A* **1997**, *105*, 261−267. (e) Chibisov, A. K.; Görner, H. *J. Phys. Chem. A* **1997**, *101*, 4305−4312. (f) Görner, H. *Chem. Phys. Lett.* **1998**, *282*, 381−390. (g) Görner, H. *Phys. Chem. Chem. Phys.* **2001**, *3*, 416−423.
(19) (a) Krysanov, S. A.; Alfimov, M. V. *Chem. Phys. Lett.* **1982**, *91*, 77−80. (b) Krysanov, S. A.; Alfimov, M. V. *Laser Chem.* **1984**, *4*, 129−138.
(20) Kalisky, Y.; Orlowski, T. E.; Williams, D. J. *J. Phys. Chem.* **1983**, *87*, 5333−5338.
(21) (a) Ito, T.; Hiramatsu, M.; Hirano, I.; Ohtani, H. *Macromolecules* **1990**, *23*, 4528−4532. (b) Ito, T.; Hiramatsu, M.; Hosoda, M.; Tsuchiya, Y. *Rev. Sci. Instrum.* **1991**, *62*, 1415−1419.
(22) Ernsting, N. P.; Arthen-Engeland, T. *J. Phys. Chem.* **1991**, *95*, 5502−5509.
(23) Poisson, L.; Raffael, K. D.; Soep, B.; Mestdagh, J.-M.; Buntinx, G. *J. Am. Chem. Soc.* **2006**, *128*, 3169−3178.
(24) Early reports suggest alternative mechanisms for the photoinduced isomerization of nitrospiropyrans. See refs 19−21 and: (a) Irie, M.; Menju, A.; Hayashi, K. *Macromolecules* **1979**, *12*, 1176−1180. (b) Krongauz, V.; Kiwi, J.; Grätzel, M. *J. Photochem.* **1980**, *13*, 89−97. (c) Kalisky, Y.; Williams, D. J. *Macromolecules* **1984**, *17*, 292−296. (d) Lenoble, C.; Becker, R. S. *J. Phys. Chem.* **1986**, *90*, 62−65. (e) Tamaki, T.; Sakuragi, M.; Ichimura, K.; Aoki, K. *Chem. Phys. Lett.* **1989**, *161*, 23−26.
(25) Bercovici, T.; Fisher, E. *J. Am. Chem. Soc.* **1964**, *86*, 5687−5688.
(26) Becker, R. S.; Roy, J. K. *J. Phys. Chem.* **1965**, *69*, 1435−1436.
(27) Lashkov, G. I.; Ermolaev, V. L.; Shablya, A. V. *Optika Spectr.* **1965**, *19*, 305−307.
(28) Bach, H.; Calvert, J. C. *J. Am. Chem. Soc.* **1970**, *92*, 2608−2614.
(29) Reeves, D. A.; Wilkinson, F. *J. Chem. Soc., Faraday Trans. 2* **1973**, *9*, 1381−1390.
(30) Eloy, D.; Escaffre, P.; Gautron, R.; Jardon, P. *Bull. Soc. Chim. Belg.* **1992**, *101*, 779−790.
(31) (a) Tamaki, T.; Sakuragi, M.; Ichimura, K. Aoki, K. *Chem. Phys. Lett.* **1989**, *161*, 23−26. (b) Sakuragi, M.; Aoki, K.; Tamaki, T.; Ichimura, K. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 74−79.

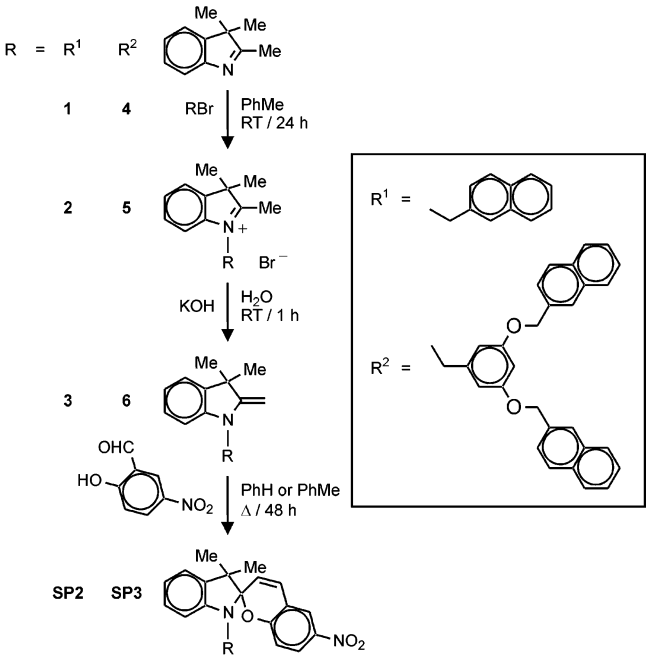


FIGURE 2. Synthesis of the nitrospiropyrans **SP2** and **SP3**.

2 and **5** respectively. The treatment of **2** and **5** with aqueous KOH gives the corresponding indoles **3** and **6**. Their condensation with 2-hydroxyl-5-nitrobenzaldehyde affords the target nitrospiropyrans **SP2** and **SP3**.

The compound **SP5** (Figure 3) is composed of a benzophenone sensitizer and a nitrospiropyran photochrome. This molecule and its model **SP4** can be prepared in five synthetic steps starting from 4-hydrazinobenzoic acid. In particular, the condensation of this precursor with isopropylmethylketone under acidic conditions yields the indole **7**. The *N*-alkylation of this compound with MeI gives the indolium **8**, which can be treated with aqueous KOH to generate the indole **9**. The condensation of **9** with 2-hydroxyl-5-nitro-benzaldehyde affords the nitrospiropyran **10**. The treatment of this molecule with $SOCl_2$ in the presence of Et_3N, followed by esterification with either MeOH or 4-hydroxybenzophenone, affords the target nitrospiropyrans **SP4** and **SP5**.

The compound **SP7** (Figure 4) combines a benzophenone sensitizer and a nitrospiropyran within its molecular skeleton. This molecules and its model **SP6** can be prepared in six and four synthetic steps, respectively, starting from 4-methoxyphenylhydrazine hydrochloride. The condensation of this precursor with isopropylmethylketone gives the indole **12**. The *N*-alkylation of **12** with MeI affords the indolium **13**, which can be converted into the indole **14** with aqueous KOH. The condensation of **14** with 2-hydroxyl-5-nitrobenzaldehyde affords the nitrospiropyran **SP6**. Alternatively, **12** can be reacted with BBr_3 to generate the indole **15**, which can be *N*-alkylated with MeI to afford the indolium **16**. The condensation of **16** with 2-hydroxyl-5-nitrobenzaldehyde in the presence of piperidine yields the nitrospiropyran **17**. The *O*-alkylation of **17** with 1,4-diiodobutane in the presence of K_2CO_3 gives the nitrospiropyran **18**. This molecule can be reacted with 4-hydroxybenzophenone again in the presence of K_2CO_3 to afford the target nitrospiropyran **SP7**.

Spectroscopy. The absorption spectra of the naphthalene **19** (***a*** in Figure 5 and Figure 6) and of the nitrospiropyran **SP1**

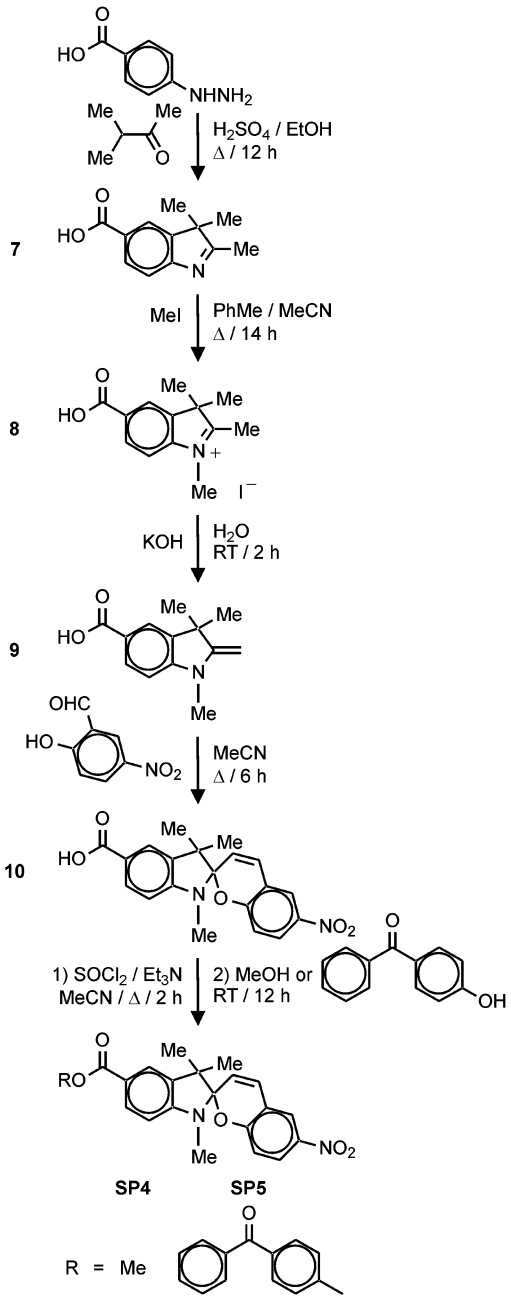


FIGURE 3. Synthesis of the nitrospiropyrans **SP4** and **SP5**.

(***b*** in Figure 5) show bands in the ultraviolet region only. Their sum (***c*** in Figure 5) closely resembles the spectrum of the naphthalene−nitrospiropyran dyad **SP2** (***d*** in Figure 5), suggesting that the two main chromophoric fragments of the dyad do not interact significantly in the ground state. The emission spectrum of **19** (***e*** in Figure 5) reveals the characteristic bands associated with the fluorescence of naphthalene derivatives with a lifetime (τ) of 10.1 ns (Table 1). These emission bands extend from 310 to 390 nm and overlap one of the main absorptions of the nitrospiropyran **SP1** (***b*** in Figure 5). Thus, the first singlet excited state (S_1) of the naphthalene fragment of **SP2** can in principle transfer energy to the S_1 of the appended nitrospiropyran. Consistently, the emission spectrum of **SP2** (***f*** in Figure 5) shows that the naphthalene fluorescence is effectively quenched with a τ of 6.2 ns and a relative luminescent quantum

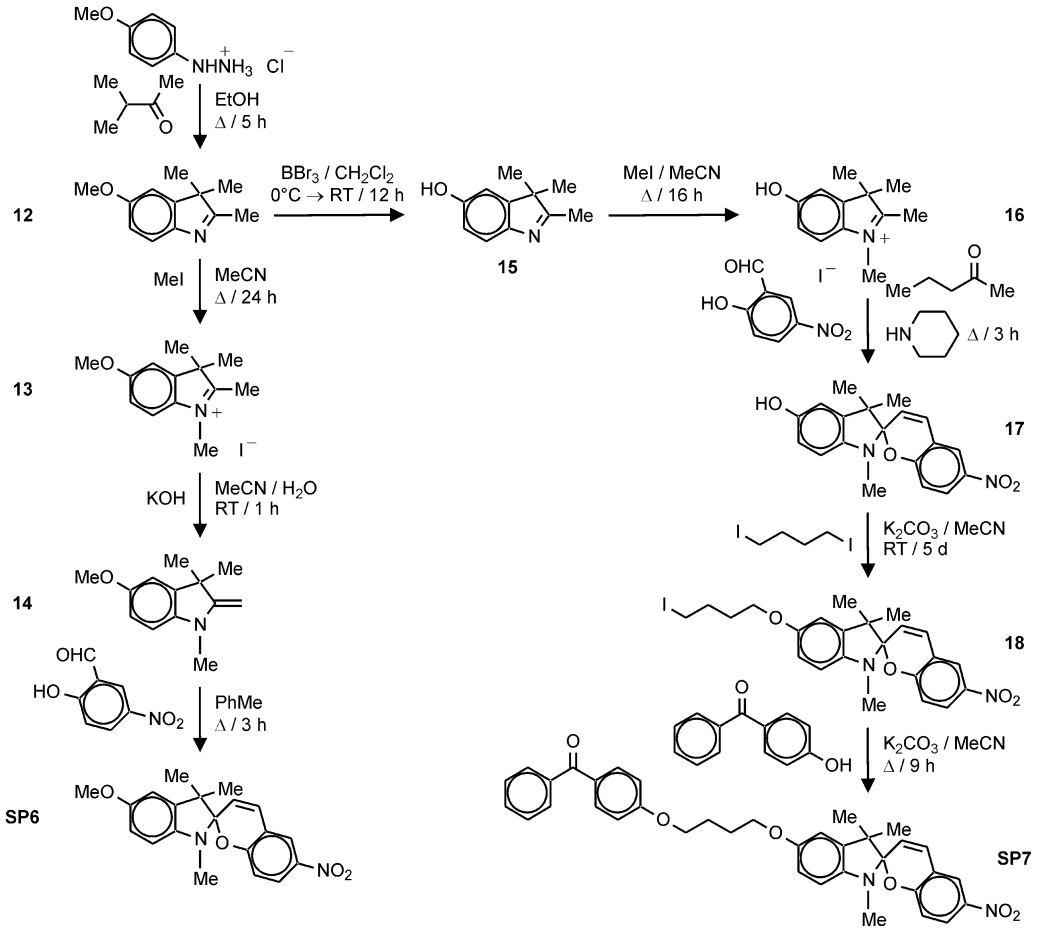


FIGURE 4. Synthesis of the nitrospiropyrans **SP6** and **SP7**.

yield (Φ_L) of 0.005.[32] This particular value of Φ_L indicates that the covalent attachment of the naphthalene fluorophore to the nitrospiropyran photochrome imposes a 200-fold decrease on the emission intensity. Similarly, intermolecular sensitization experiments suggest that the T_1 of the very same naphthalene fragment can also transfer energy to the T_1 of adjacent nitrospiropyran.[18b,e] Thus, the fraction of light absorbed by the naphthalene component of the dyad should facilitate the photoisomerization of the adjacent nitrospiropyran on the basis of either $S_1 \rightarrow S_1$ and/or $T_1 \rightarrow T_1$ energy transfer.

Despite the expected sensitization, the absorption spectra of the model **SP1** (***g*** in Figure 5) and of the dyad **SP2** (***h*** in Figure 5), recorded after ultraviolet irradiation, show that the photoisomerization is significantly less efficient for the dyad. Indeed, the characteristic band for the merocyanine isomer of **SP1** in the visible region is markedly more intense than that for the merocyanine isomer of **SP2**. The relative photoisomerization quantum yield (Φ_P) is 0.18 (Table 1).[33] This value corresponds to a 6-fold decrease in the photocoloration efficiency with the covalent attachment of the naphthalene luminophore to the nitrospiropyran photochrome. Furthermore, the photoisomerization of **SP1** is fully reversible and the original absorption spectrum is restored after storing the irradiated solution in the dark.[34] Instead, a residual absorbance in the region between 400 and 500 nm (***i*** in Figure 5) can still be observed after storing an irradiated solution of **SP2** in the dark. Thus, the photoisomerization of **SP2** is accompanied by irreversible transformations.

The absorption spectra of the model compounds **20** (Figure 6 and ***a*** in Figure 7) and **SP1** (***b*** in Figure 7) show significant absorptions only at wavelengths shorter than 400 nm. Their sum

(32) The relative luminescence quantum yield (F_L) is the ratio between the luminescence quantum yield of the luminophore−nitrospiropyran assembly and that of the corresponding model luminophore. The value of F_L was determined with eq 1. The parameters I_L and I_{LSP} are the emission intensities of the model luminophore and the luminophore−nitrospiropyran assembly respectively. The parameters A_L and A_{LSP} are the absorbances of the model luminophore and the luminophore−nitrospiropyran assembly, respectively, at the excitation wavelength.

$$\Phi_L = \frac{I_{LSP}(1 - 10^{-A_L})A_{LSP}}{I_L(1 - 10^{-A_{LSP}})A_L} \quad (1)$$

(33) The relative photoisomerization quantum yield (F_P) is the ratio between the photoisomerization quantum yield of the luminophore−nitrospiropyran assembly and that of the corresponding model nitrospiropyran. The value of F_P was determined with eq 2, assuming that the molar extinction coefficients for the photogenerated isomers of the luminophores−nitrospiropyran assembly and the corresponding model nitrospiropyran are equal. The parameters A_{SP} and A_{LSP} are the absorbances of the model nitrospiropyran and the luminophore−nitrospiropyran assembly respectively at the excitation wavelength. The parameters A_{ME} and A_{LME} are the absorbances for the photogenerated isomers of the model nitrospiropyran and the luminophore−nitrospiropyran assembly, respectively, in the visible region.

$$\Phi_P = \frac{A_{LME}(1 - 10^{-A_{SP}})}{A_{ME}(1 - 10^{-A_{LSP}})} \quad (2)$$

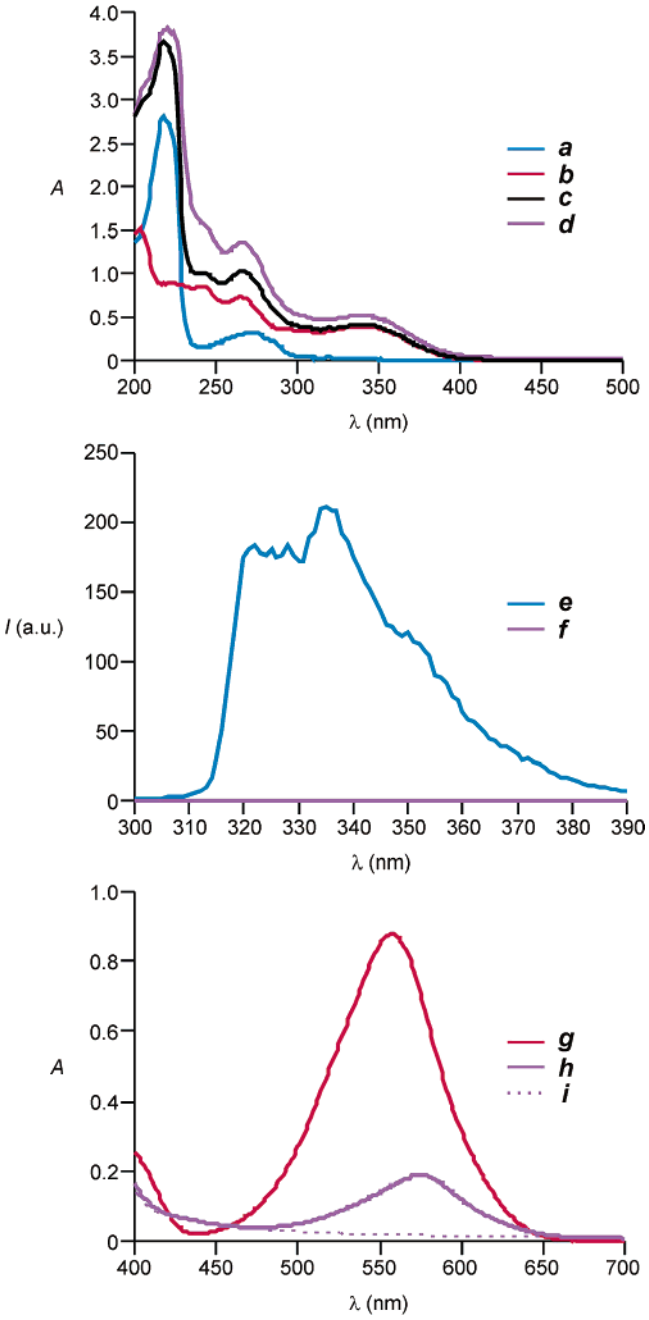


FIGURE 5. Steady-state absorption spectra (0.1 mM, MeCN, 20 °C) of **19** (***a***), **SP1** (***b***), **SP2** (***d***), and the sum of the absorption spectra of **19** and **SP1** (***c***). Steady-state emission spectra (0.1 mM, MeCN, 20 °C, $\lambda_{ex} = 272$ nm) of **19** (***e***) and **SP2** (***f***). Steady-state absorption spectra (0.1 mM, MeCN, 20 °C) of **SP1** (***g***) and **SP2** (***h***) after irradiation (254 nm, 0.4 mW cm^{-2}, 10 min) and of **SP2** (***i***) after storage of the irradiated solution in the dark.

(***c*** in Figure 7) is similar to the spectrum of the (naphthalene)$_2$−nitrospiropyran triad **SP3** (***d*** in Figure 7), indicating that the three chromophoric units of this compound do not interact significantly in the ground state. The emission spectrum of **20** (***e*** in Figure 7) shows the characteristic fluorescence of its two naphthalene chromophores with a τ of 2.3 ns (Table 1). Once again, the naphthalene emission overlaps the nitrospiropyran

(34) The lifetime of the photogenerated isomer of **SP1** is 400 s in MeCN at 25 °C (see ref 18g).

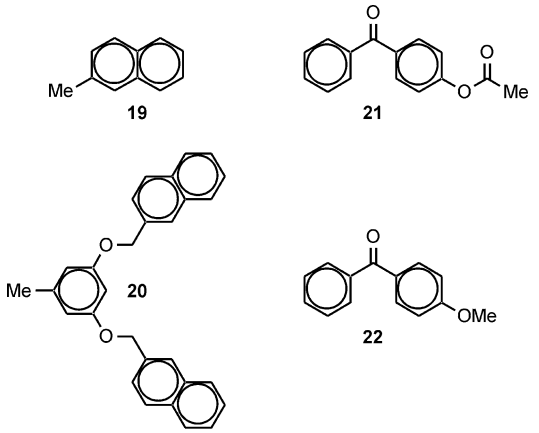


FIGURE 6. Model compounds **19**−**22**.

TABLE 1. Relative Luminescence Quantum Yields, Luminescence Lifetimes, and Relative Photoisomerization Quantum Yields

compd	Φ_L[a]	τ[b]	Φ_P[c]
19		10.1 ns	
SP2	0.005	6.2 ns	0.18
20		2.3 ns	
SP3	0.56	1.8 ns	0.03
21		10.2 μs	
SP5	0.04	9.1 μs	0.60
22		5.1 μs	
SP7	0.05	4.9 μs	0.01

[a] The relative luminescence quantum yield (Φ_L) was determined in degassed MeCN at 20 °C and is defined in ref 32. [b] The luminescence lifetime (τ) was determined in degassed MeCN at 20 °C from the monoexponential fitting of the temporal evolution of the emission intensity. The coefficient of determination (COD) of the fitting was greater than 0.98 in all instances. [c] The relative photoisomerization quantum yield (Φ_P) was determined in degassed MeCN at 20 °C, irradiating at 254 nm (0.4 mW cm^{-2}) for 10 min, and is defined in ref 33.

absorptions and, in fact, the fluorescence of the triad **SP3** (***f*** in Figure 7) is effectively quenched with a τ of 1.8 ns and a Φ_L of 0.56 (Table 1). This particular value of Φ_L corresponds to a 2-fold decrease in emission intensity with the covalent connection of the naphthalene fluorophores and the nitrospiropyran photochrome.

The ultraviolet irradiation of the model nitrospiropyran **SP1** causes the appearance of an intense band in the visible region (***g*** in Figure 7), as a result of the formation of the merocyanine isomer. This band can barely be observed in the absorption spectrum of **SP3** recorded after irradiation (***h*** in Figure 7). In fact, the corresponding Φ_P of only 0.03 indicates a 30-fold decrease in the photoisomerization efficiency with the transition from **SP1** to **SP3**. In addition, an absorption between 400 and 450 nm appears in the absorption spectrum of **SP3** (***i*** in Figure 7) upon irradiation and persists after storage in the dark. Thus, irreversible photoinduced processes seem to be in competition with the isomerization of the nitrospiropyran component of the triad **SP3**.

The quenching of the naphthalene fluorescence in the luminophore−photochrome assemblies **SP2** and **SP3** is indicative of interactions between the S_1 of the luminophore and the S_0 of the photochrome. The very same interactions are, presumably, responsible for the irreversible transformations that accompany the irradiation of **SP2** and **SP3** and are in competition with the photosensitization of the isomerization process. Indeed, literature data suggest that $T_1 \rightarrow T_1$ energy transfer is responsible for the intermolecular photosensitization of nitro-

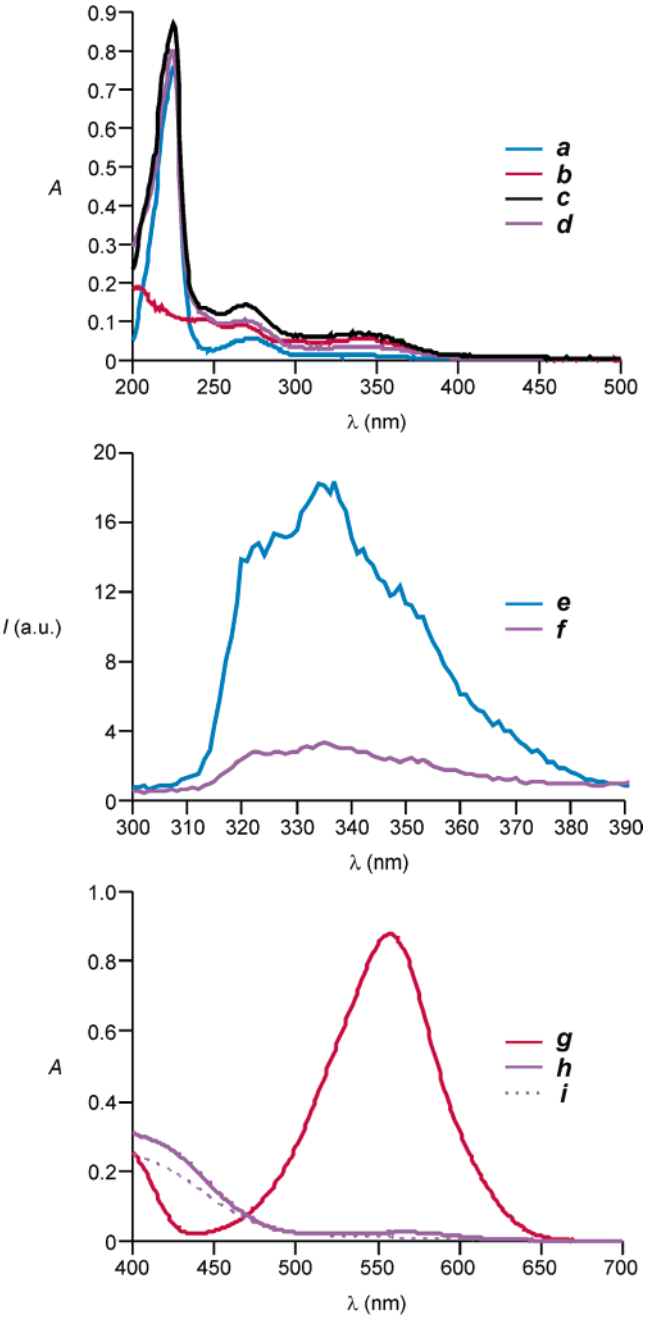


FIGURE 7. Steady-state absorption spectra (0.01 mM, MeCN, 20 °C) of **19** (***a***), **SP1** (***b***), **SP3** (***d***), and the sum of the absorption spectra of **20** and **SP1** (***c***). Steady-state emission spectra (0.1 mM, MeCN, 20 °C, $\lambda_{ex} = 272$ nm) of **20** (***e***) and **SP3** (***f***). Steady-state absorption spectra (0.1 mM, MeCN, 20 °C) of **SP1** (***g***) and **SP3** (***h***) after irradiation (254 nm, 0.4 mW cm^{-2}, 10 min) and of **SP3** (***i***) after storage of the irradiated solution in the dark.

spiropyrans in the presence of naphthalene.[18b,e] However, the quenching of the naphthalene S_1 in **SP2** and **SP3** prevents intersystem crossing and the effective population of T_1. In fact, the absorption spectrum of the model compound **20** (***a*** in Figure 8), recorded 0.2 μs after laser excitation (266 nm), shows the characteristic absorption for the naphthalene T_1 at ca. 400 nm. This band cannot be observed in the spectrum of **SP3** (***c*** in Figure 8), recorded under identical experimental conditions, which instead closely resembles that of the model spiropyran **SP1** (***c*** in Figure 8). Thus, the T_1 of the naphthalene component

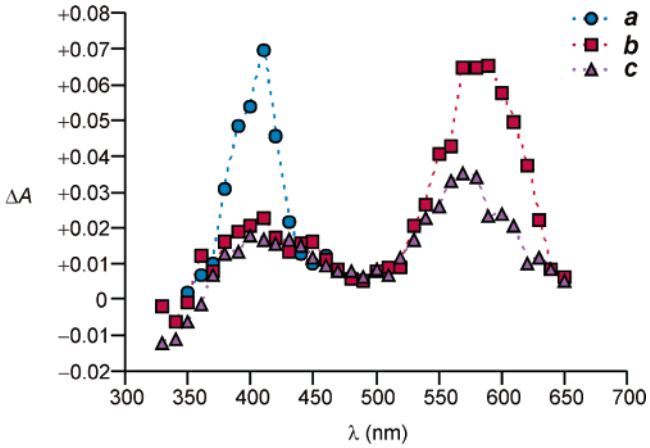


FIGURE 8. Absorption spectra recorded 0.2 μs after laser excitation (266 nm, ~8 mJ) of a degassed solution (0.03 mM, MeCN, 20 °C) of **20** (***a***) and optically matched solutions of **SP1** (***b***) and **SP3** (***c***).

is not effectively populated in these luminophore−photochrome assemblies. As a result, the expected sensitization of the photochromic transformation via $T_1 \rightarrow T_1$ energy transfer is not observed.

The absorption spectra of the benzophenone **21** (Figure 6 and ***a*** in Figure 9) and of the nitrospiropyran **SP4** (***b*** in Figure 9) show bands in the ultraviolet region only. Their sum (***c*** in Figure 9) differs from the spectrum of the benzophenone−nitrospiropyran dyad **SP5** (***c*** in Figure 9). Thus, the ester linkage between the two main chromophoric fragments of this dyad does not isolate electronically the two components. The emission spectrum of **21** (***e*** in Figure 9) reveals the characteristic benzophenone phosphorescence with a τ of 10.2 μs (Table 1). In agreement with the expected $T_1 \rightarrow T_1$ energy transfer from the benzophenone phosphore to the nitrospiropyran photochrome, the phosphorescence of **SP5** (***f*** in Figure 9) is effectively quenched with a τ of 9.1 μs and a Φ_L of 0.004 (Table 1). This particular value of Φ_L corresponds to a 25-fold decrease in emission intensity with the transition from **SP4** to **SP5**.

The absorption spectrum of the model nitrospiropyran **SP4** (***g*** in Figure 9), recorded after ultraviolet irradiation, show the characteristic band for the merocyanine isomer in the visible region.[35] A similar absorption can also be observed in the spectrum of **SP5** (***h*** in Figure 9) upon irradiation. However, the band observed for the photogenerated isomer of the dyad is significantly less intense than that for the merocyanine state of **SP4**. The corresponding Φ_P is 0.60, indicating a 2-fold decrease in the photoisomerization efficiency with the integration of the benzophenone phosphore within the same molecular skeleton of the nitrospiropyran photochrome. Furthermore, the spectrum recorded after storage of the irradiated solution of **SP5** in the dark shows a residual absorbance in the region between 400 and 450 nm (***i*** in Figure 9). Thus, the photoisomerization of the dyad is, once again, accompanied by irreversible transformations.

The absorption spectra of the benzophenone **22** (Figure 6 and ***a*** in Figure 10) and of the nitrospiropyran **SP6** (***b*** in Figure 10) reveal bands at wavelength shorter than 400 nm only. Their sum (***c*** in Figure 10) resembles the spectrum of the corresponding benzophenone−spiropyran dyad **SP7** (***d*** in Figure 10),

(35) The lifetime of the photogenerated isomer of **SP4** is 15 s in MeCN at 20 °C.

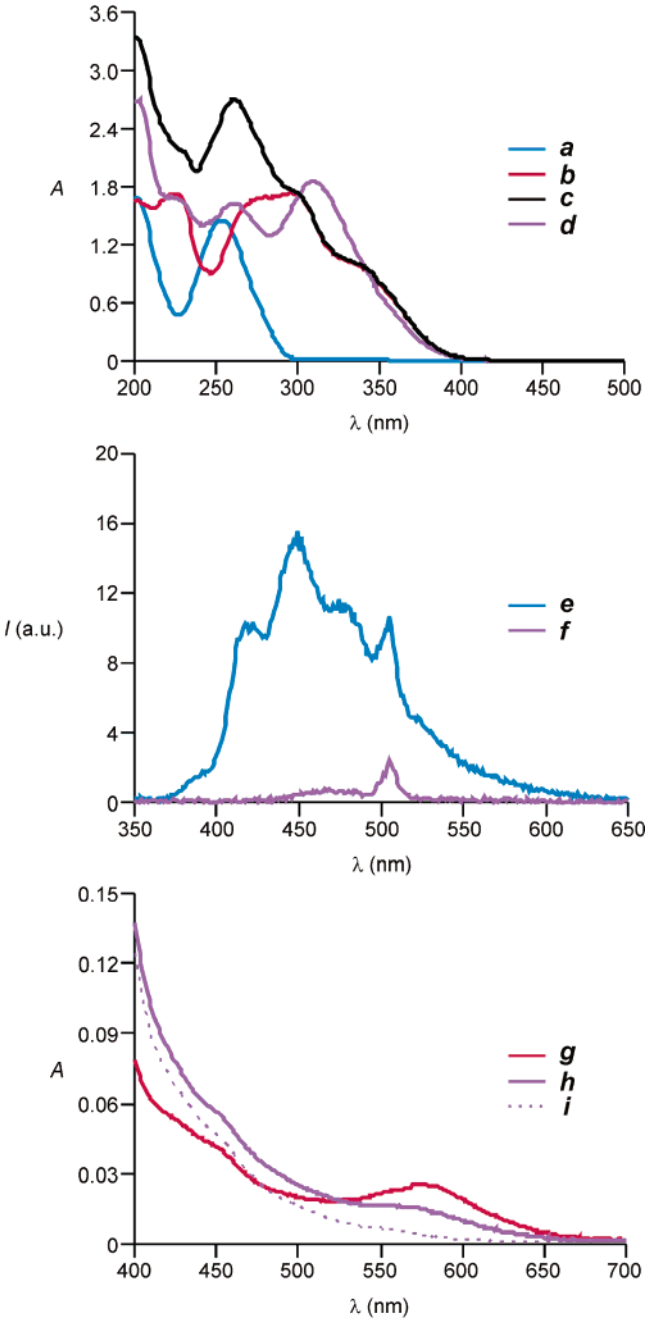


FIGURE 9. Steady-state absorption spectra (0.1 mM, MeCN, 20 °C) of **21** (***a***), **SP4** (***b***), **SP5** (***d***), and the sum of the absorption spectra of **21** and **SP4** (***c***). Steady-state emission spectra (0.1 mM, MeCN, 20 °C, λ_{ex} = 252 nm) of **21** (***e***) and **SP5** (***f***) (the peak at 504 nm is an excitation artifact). Steady-state absorption spectra (0.1 mM, MeCN, 20 °C) of **SP4** (***g***) and **SP5** (***h***) after irradiation (254 nm, 0.4 mW cm^{-2}, 10 min) and of **SP5** (***i***) after storage of the irradiated solution in the dark.

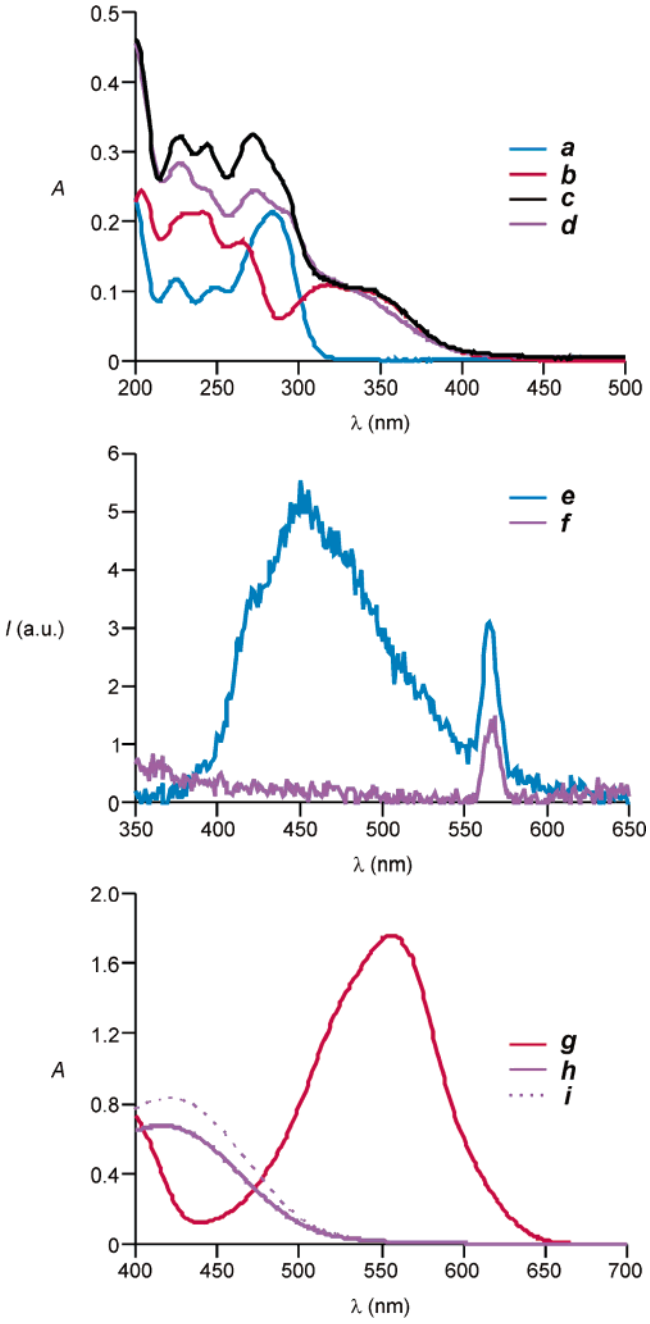


FIGURE 10. Steady-state absorption spectra (0.01 mM, MeCN, 20 °C) of **22** (***a***), **SP6** (***b***), **SP7** (***d***), and the sum of the absorption spectra of **22** and **SP6** (***c***). Steady-state emission spectra (0.1 mM, MeCN, 20 °C, λ_{ex} = 282 nm) of **22** (***e***) and **SP6** (***f***) (the peak at 564 nm is an excitation artifact). Steady-state absorption spectra (0.1 mM, MeCN, 20 °C) of **SP6** (***g***) and **SP7** (***h***) after irradiation (254 nm, 0.4 mW cm^{-2}, 10 min) and of **SP7** (***i***) after storage of the irradiated solution in the dark.

indicating a lack of significant ground state interactions between the two main components of the dyad. The emission spectrum of **22** (***e*** in Figure 10) shows the characteristic benzophenone phosphorescence with a τ of 5.1 μs (Table 1). Consistent with the anticipated $T_1 \rightarrow T_1$ energy transfer from the benzophenone phosphore to the nitrospiropyran photochrome, the phosphorescence of **SP7** (***f*** in Figure 10) is effectively quenched with a τ of 4.9 μs and a Φ_L of 0.05 (Table 1). This particular value of Φ_L corresponds to a 20-fold decrease in emission intensity with the transition from the isolated luminophore to the luminophore−photochrome assembly.

The band of the merocyanine isomer of **SP6** can clearly be observed in the absorption spectrum of model recorded after irradiation (***g*** in Figure 10).[36] Despite the expected sensitization, the spectrum of the dyad **SP7** (***h*** in Figure 10), measured under

(36) The lifetime of the photogenerated isomer of **SP6** is 3600 s in MeCN at 20 °C.

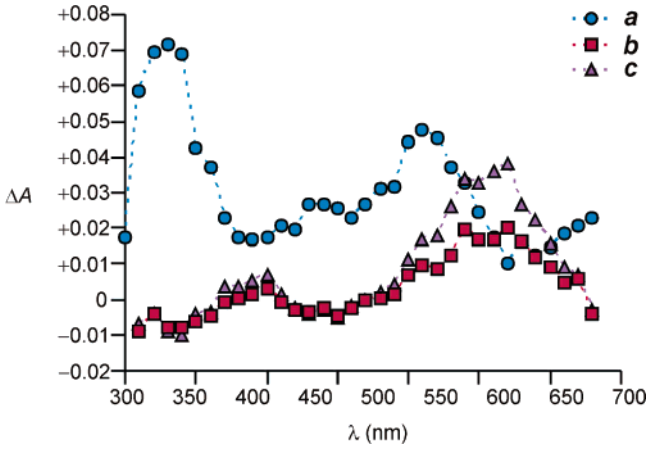


FIGURE 11. Absorption spectra recorded 0.2 μs after laser excitation (266 nm, ~8 mJ) of a degassed solution (0.03 mM, MeCN, 20 °C) of **22** (***a***) and optically matched solutions of **SP6** (***b***) and **SP7** (***c***).

the same conditions, shows only a modest absorbance increase in the same range of wavelengths. In fact, the Φ_P of only 0.01 corresponds to a 100-fold decrease in photoisomerization efficiency with the transition from **SP6** to **SP7**. In addition, the ultraviolet irradiation of **SP7** causes the appearance a band centered at 417 nm (***h*** in Figure 10), which persists even after the prolonged storage of the solution in the dark (***i*** in Figure 10). Thus, the irradiation of the benzophenone−nitrospiropyran dyad **SP7** induces preferentially irreversible transformations, rather than the isomerization of the photochromic component.

The low Φ_L of the dyads **SP5** and **SP7** indicates that the phosphorescence of their benzophenone components is effectively suppressed by the adjacent nitrospiropyrans. The difference in τ between the dyads **SP5** and **SP7** and the model compounds **21** and **22**, however, is negligible. This apparent contradiction between the values of Φ_L and τ suggests that the presence of the nitrospiropyran components prevents the effective population of the benzophenone T_1, rather quenching this particular state. Consistently, the characteristic absorptions (***a*** in Figure 11) for the T_1 of the model benzophenone **22** cannot be observed in the absorption spectrum of the dyad **SP7** (***c*** in Figure 11) recorded 0.2 μs after laser excitation (266 nm). Instead, the spectrum of this species closely resembles that of the model nitrospiropyran **SP6** (***b*** in Figure 11). Presumably, intramolecular interactions between the S_1 of the benzophenone and the S_0 of the adjacent nitrospiropyran prevent intersystem crossing and, as a result, the expected sensitization. Instead, these interactions seem to encourage irreversible transformations of the benzophenone−nitrospiropyran assembly.

Conclusions

Benzophenone and naphthalene are known to sensitize the photoisomerization of nitrospiropyrans on the basis of intermolecular $T_1 \rightarrow T_1$ energy transfer.[18b,e,24d−30] The covalent connection of either one of these two luminophores to a nitrospiropyran, however, does not result in the expected facilitation of the sensitization process. In fact, the photoisomerization of all four luminophore−photochrome assemblies studied is from 2 up to 100 times less efficient than that of model nitrospiropyrans. In addition, the photoisomerization of the nitrospiropyran component of these molecules is accompanied by irreversible transformations, which are not observed for the corresponding model photochromes under identical experimental conditions. Interestingly, the luminescence of the emissive component is effectively suppressed after the covalent attachment to the photochromic system. It appears, however, that the photochromic component prevents the effective population of the luminophore T_1 and, as a result, the expected intramolecular $T_1 \rightarrow T_1$ energy transfer. Instead, the intramolecular interactions responsible for the efficient luminescence quenching tend to encourage the photodegradation of these systems. Perhaps, the intramolecular transfer of electrons form one component of the luminophore−photochrome assemblies to the other might well be responsible for these irreversible photoinduced processes. In summary, our studies demonstrate that the integration of either benzophenone or naphthalene sensitizers and nitrospiropyrans within the same covalent backbone is not a viable strategy to improve the photocoloration efficiency of these systems.

Experimental Procedures

2,3,3-Trimethyl-1-naphth-2′-ylmethyl-3*H*-indolium Bromide (2). A solution of 2,3,3-trimethyl-3*H*-indole (200 mg, 1.3 mmol) and **1** (347 mg, 1.6 mmol) in PhMe (25 mL) was stirred at ambient temperature for 24 h under reflux and N_2. After the mixture was cooled to ambient temperature, the solvent was distilled off under reduced pressure. The residue was suspended in hexane (30 mL), sonicated for 30 min, and filtered to afford **2** (333 mg, 55%) as a pink solid: mp = 180 °C; FABMS m/z = 300 $[M - Br]^+$; ^{1}H NMR (400 MHz, CD_3CN) δ = 1.64 (6H, s), 2.89 (3H, s), 5.83 (2H, s), 7.44 (1H, dd, 2 and 9 Hz), 7.50−7.63 (4H, m), 7.69 (1H, d, 8 Hz), 7.74−7.76 (1H, m), 7.80 (1H, bs), 7.86−7.93 (2H, m), 7.96 (1H, d, 9 Hz); ^{13}C NMR (100 MHz, CD_3CN) δ = 15.9, 23.3, 36.4, 52.6, 55.7, 117.3, 125.0, 125.9, 128.0, 128.5, 128.6, 129.2, 129.3, 130.1, 130.7, 130.8, 131.4, 131.6, 134.6, 142.7, 143.4.

3,3-Dimethyl-2-methylene-1-naphth-2′-ylmethyl-3*H*-indole (3). A solution of **2** (217 mg, 0.6 mmol) and KOH (64 mg, 1.1 mmol) in H_2O (10 mL) was stirred at ambient temperature for 1 h. The mixture was washed with CH_2Cl_2 (3 × 20 mL), and the organic phase was dried over $MgSO_4$. The solvent was distilled off under reduced pressure to afford **3** (113 mg, 66%) as yellowish oil: FABMS m/z = 299 $[M]^+$; ^{1}H NMR (400 MHz,$CDCl_3$) δ = 1.33 (6H, s), 3.79 (1H, d, 2 Hz), 3.84 (1H, d, 2 Hz), 4.79 (2H, s), 6.45 (1H, d, 8 Hz), 6.70 (1H, dt, 1 and 8 Hz), 6.98 (1H, dt, 1 and 8 Hz), 7.07 (1H, dd, 1 and 8 Hz), 7.26 (1H, dd, 2 and 9 Hz), 7.31−7.34 (2H, m), 7.55 (1H, bs), 7.63−7.70 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 30.4, 44.5, 46.6, 74.7, 105.7, 119.0, 122.2, 125.0, 125.3, 126.2, 126.3, 127.9, 128.7, 132.9, 133.7, 135.0, 137.7, 146.3, 162.0.

1′-(Naphth-2′′-ylmethyl)-3′,3′-dimethyl-6-nitrospiro[2*H*-1-benzopyran-2′,2′-3H-indole] (SP2). A solution of **3** (75 mg, 0.3 mmol) and 2-hydroxyl-5-nitrobenzaldehyde (68 mg, 0.4 mmol) in PhH (20 mL) was heated under reflux and N_2 for 48 h. After the mixture was cooled to ambient temperature, the solvent was distilled off under reduced pressure. The residue was purified by column chromatography [SiO_2: CH_2Cl_2/hexanes (1:1, v/v)] to afford **SP2** (73 mg, 65%) as a purple-red solid: HPLC (analytical) t_R = 3.6 min, PA = 1.6, APP = 256.6 ± 0.4 nm; mp = 80 °C; FABMS m/z = 448 $[M]^+$; ^{1}H NMR (400 MHz,$CDCl_3$) δ = 1.36 (3H, s), 1.37 (3H, s), 4.38 (1H, d, 17 Hz), 4.69 (1H, d, 17 Hz), 5.97 (1H, d, 10 Hz), 6.43 (1H, d, 8 Hz), 6.75−6.77 (1H, m), 6.86−6.92 (2H, m), 7.07 (1H, dt, 1 and 8 Hz), 7.16 (1H, dd, 1 and 8 Hz), 7.41−7.47 (3H, m), 7.69−7.83 (4H, m), 7.97−8.00 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.3, 20.1, 26.2, 31.8, 48.0, 52.9, 106.9,

108.1, 115.7, 118.7, 120.2, 121.9, 122.8, 123.0, 125.2, 125.4, 125.9, 126.0, 126.4, 127.8, 128.0, 128.6, 128.7, 132.9, 133.6, 136.3, 141.3, 147.4, 159.7.

1-[3′,5′-Bis(naphtha-2″-ylmethoxy)benzyl]-2,3,3-trimethyl-3*H*-indolium Bromide (5). A solution of 2,3,3-trimethyl-3*H*-indole (187 mg, 1.2 mmol) and **4** (472 mg, 1.0 mmol) in PhMe (25 mL) was heated under reflux and N_2 for 3 d. After the mixture was cooled to ambient temperature, the solvent was distilled off under reduced pressure. The residue was suspended in hexane (30 mL), sonicated for 30 min, and filtered to afford **5** (586 mg, 93%) as a pink solid: FABMS $m/z = 562$ $[M - Br]^+$; ^{1}H NMR (400 MHz, CD_3CN) $\delta = 1.34$ (6H, s), 2.36 (3H, s), 4.45 (2H, s), 5.21 (4H, s), 6.67 (1H, t, 2 Hz), 6.72 (2H, d, 2 Hz), 7.25−7.35 (4H, m), 7.49−7.55 (6H, m), 7.84−7.91 (8H, m); ^{13}C NMR (100 MHz, CD_3CN) $\delta = 14.3$, 22.9, 31.8, 33.8, 70.5, 102.5, 108.5, 125.3, 126.2, 126.5, 126.6, 127.9, 128.1, 128.6, 128.8, 132.2, 132.3, 133.3, 133.5, 134.2, 140.0, 160.3.

1-[3′,5′-Bis(naphth-2″-ylmethoxy)benzyl]-3,3-dimethyl-2-methylene-3*H*-indole (6). A solution of **5** (146 mg, 0.3 mmol) and KOH (29 mg, 0.5 mmol) in H_2O (10 mL) and MeCN (3 mL) was stirred at ambient temperature for 1 h. The mixture was washed with CH_2Cl_2 (3 × 20 mL), and the organic phase was dried over $MgSO_4$. The solvent was distilled off under reduced pressure to afford **6** (90 mg, 62%) as a greenish oil: FABMS $m/z = 562$ $[M + H]^+$; ^{1}H NMR (300 MHz,$CDCl_3$) $\delta = 1.42$ (6H, s), 3.92 (2H, d, 2 Hz), 3.95 (2H, d, 2 Hz), 4.69 (2H, s), 5.20 (4H, s), 6.70 (1H, t, 2 Hz), 6.75 (2H, d, 2 Hz), 7.28−7.40 (4H, m), 7.50−7.60 (6H, m), 7.87−7.92 (8H, m); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 23.1$, 33.7, 53.5, 70.2, 102.3, 108.4, 125.3, 125.4, 126.1, 126.2, 126.3, 126.4, 126.5, 127.6, 127.7, 127.8, 128.0, 128.5, 133.1, 133.3, 134.1, 139.9, 160.2.

1′-(3″,5″-Bis(naphtha-2‴-ylmethyloxy)benzyl)-3′,3′-dimethyl-6-nitrospiro[2*H*-1-benzopyran-2′,2′-3*H*-indole] (SP3). A solution of **6** (97 mg, 0.2 mmol) and 2-hydroxyl-5-nitrobenzaldehyde (43 mg, 0.3 mmol) in PhMe (30 mL) was heated under reflux and N_2 for 30 h. After being cooled to ambient temperature, the solvent was distilled off under reduced pressure. The residue was purified by column chromatography [SiO_2: CH_2Cl_2/hexanes (1:1, v/v)] to afford **SP3** (65 mg, 53%) as a yellowish solid. HPLC (analytical): $t_R = 4.7$ min, PA = 1.4, APP = 256.4 ± 0.6 nm; mp = 60 °C; FABMS $m/z = 712$ $[M]^+$; ^{1}H NMR (500 MHz,$CDCl_3$) $\delta = 1.18$ (3H, s), 1.30 (3H, s), 4.10 (1H, d, 17 Hz), 4.38 (1H, d, 17 Hz), 5.18 (4H, s), 5.71 (1H, d, 10 Hz), 6.37 (1H, d, 13 Hz), 6.56 (2H, d, 2 Hz), 6.61 (1H, m), 6.67 (1H, d, 15 Hz), 6.72 (1H, d, 9 Hz), 6.88 (1H, t, 7 Hz), 7.04 (1H, t, 7 Hz), 7.10 (1H, d, 12 Hz), 7.45−7.52 (6H, m), 7.80−7.87 (8H, m), 7.92 (1H, d, 3 Hz), 8.00 (1H, dd, 3 and 21 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 20.0$, 26.3, 33.7, 48.0, 52.8, 70.8, 102.6, 106.3, 106.8, 108.1, 108.5, 115.7, 118.7, 120.2, 121.7, 121.8, 122.8, 125.4, 125.5, 126.4, 126.5, 126.6, 127.9, 128.1, 128.4, 128.6, 133.4, 133.5, 134.3, 134.5, 138.9, 147.2, 159.7, 160.6.

2,3,3-Trimethyl-5-carboxy-3*H*-indole (7). A solution of isopropylmethylketone (3.9 mL, 36 mmol) and 4-hydrazinobenzoic acid (5.0 g, 33 mmol) in EtOH (120 mL) and concd H_2SO_4 (1.0 mL) was heated under reflux for 12 h. After being cooled to ambient temperature, the mixture was filtered. A saturated aqueous solution of $NaHCO_3$ (50 mL) was added to the filtrate, and the resulting solution was washed with CH_2Cl_2 (3 × 20 mL). The pH of the aqueous phase was adjusted to ca. 4 with aqueous HCl (1 M), and then the solution was washed with CH_2Cl_2 (2 × 10 mL). The solvent of the combined organic phases was distilled off under reduced pressure to yield **7** (6.7 g, 92%) as a brownish solid: mp = 192 °C; FABMS $m/z = 204$ $[M + H]^+$; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.35$ (6H, s), 2.40 (3H, s), 7.69 (1H, d, 8 Hz), 8.07 (1H, d, 1 Hz), 8.15 (1H, dd, 1 and 8 Hz), 10.64 (1H, bs); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 15.6$, 23.0, 54.1, 119.7, 123.4, 128.4, 130.9, 145.5, 156.7, 171.0, 192.9.

1,2,3,3-Tetramethyl-5-carboxy-3*H*-indolium iodide (8). A solution of **7** (1.80 g, 9 mmol) and MeI (0.55 mL, 2 mmol) in PhMe/MeCN (2:1, v/v) was heated under reflux and Ar for 14 h. The mixture was cooled to 0 °C, and the resulting precipitate was filtered off. The residue was washed with EtOH (5 mL) and hexane (40 mL) to afford **8** (1.6 g, 52%) as a white solid: FABMS $m/z = 219$ $[M + H]^+$; ^{1}HNMR [400 MHz, CD_3CN/CD_3OD (5:1, v/v)] $\delta = 2.93$ (6H, s), 4.07 (3H, s), 5.32 (3H, s), 9.18 (1H, d, 8 Hz), 9.63 (1H, dd, 1 and 8 Hz), 9.68 (1H, d, 1 Hz); ^{13}C NMR [75 MHz, CD_3CN/CD_3OD (5:1, v/v)] $\delta = 22.4$, 36.0, 56.0, 116.4, 125.5, 132.2, 133.5, 143.2, 167.5.

1,3,3-Trimethyl-2-methylene-5-carboxy-3*H*-indole (9). A solution of **8** (1.15 g, 3 mmol) in aqueous KOH (0.32 M, 21 mL) was stirred at ambient temperature for 2 h. The pH was adjusted to ca. 7 with aqueous HCl (1 M), and the solution was washed with *i*-PrOH/CH_2Cl_2 (1:1, v/v, 6 × 15 mL). The organic phase was dried over $MgSO_4$, and the solvent was distilled off under reduced pressure to yield **9** (0.72 g, 99%) as a white solid: FABMS $m/z = 218$ $[M + H]^+$; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.37$ (6H, s), 3.11 (3H, s), 4.00−4.02 (2H, m), 6.56 (1H, d, 8 Hz), 7.79 (1H, d, 2 Hz), 7.98 (1H, dd, 2 and 8 Hz); ^{13}C−NMR (100 MHz, $CDCl_3$) $\delta = 29.1$, 30.0, 43.8, 104.5, 119.1, 123.9, 132.2, 137.9, 151.2, 162.3, 171.6.

1′,3′,3′-Trimethyl-5′-carboxy-6-nitrospiro[2*H*-benzopyran-2,2′-3*H*-indole] (10). A solution of **9** (115 mg, 0.5 mmol) and 2-hydroxyl-5-nitrobenzaldehyde (97 mg, 0.6 mmol) in MeCN (25 mL) was heated under reflux and Ar for 6 h. The mixture was cooled to 0 °C, and the resulting precipitate was filtered off. The residue was washed with hexane (50 mL) to yield **10** (121 mg, 63%): FABMS $m/z = 367$ $[M + H]^+$; ^{1}H NMR [400 MHz, $(CD_3)_2$-SO] $\delta = 1.13$ (3H, s), 1.24 (3H, s), 2.76 (3H, s), 6.02 (1H, d, 10 Hz), 6.70 (1H, d, 8 Hz), 6.92 (1H, d, 9 Hz), 7.26 (1H, d, 10 Hz), 7.69 (1H, d, 8 Hz), 7.81 (1H, dd, 2 and 8 Hz), 8.02 (1H, dd, 3 and 9 Hz), 8.24 (1H, d, 3 Hz), 12.39 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 19.5$, 25.5, 28.4, 51.5, 105.9, 106.2, 115.4, 118.8, 120.9, 121.6, 122.8, 122.9, 125.8, 128.5, 130.8, 135.9, 140.7, 151.2, 158.9, 167.3.

1′,3′,3′-Trimethyl-5′-methoxycarbonyl-6-nitrospiro[2*H*-1-benzopyran-2′,2′-3*H*-indole] (SP4). A solution of **10** (259 mg, 0.7 mmol), $SOCl_2$ (114 μL, 2 mmol), and Et_3N (200 μL, 2 mmol) in MeCN (20 mL) was heated under reflux and Ar for 2 h. MeOH (4 mL) was added, and the solution was allowed to cool to ambient temperature over 12 h. The solvent was distilled off under reduced pressure, and the residue was suspended in CH_2Cl_2 (10 mL) and filtered through a Florisil plug. The solvent was distilled off under reduced pressure to give **SP4** (231 mg, 85%) as a red solid: HPLC (analytical) $t_R = 4.7$ min, PA = 1.4, APP = 256.4 ± 0.6 nm; mp = 178 °C; FABMS $m/z = 381$ $[M + H]^+$; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.24$ (3H, s), 1.33 (3H, s), 2.82 (3H, s), 3.89 (3H, s), 5.85 (1H, d, 10 Hz), 6.55 (1H, d, 8 Hz), 6.77 (1H, d, 8 Hz), 6.96 (1H, d, 10 Hz), 7.76 (1H, d, 2 Hz), 7.97 (1H, dd, 2 and 8 Hz), 8.02−8.08 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 20.1$, 26.0, 29.0, 51.9, 52.2, 106.4, 115.7, 118.7, 121.1, 121.7, 123.0, 123.5, 126.2, 128.8, 131.5, 136.3, 141.5, 151.8, 159.5, 167.5.

1′,3′,3′-Trimethyl-5′-(4″-benzoylbenzoyl)-6-nitrospiro[2*H*-1-benzopyran-2′,2′-3*H*-indole] (SP5). A solution of **10** (77 mg, 0.2 mmol), $SOCl_2$ (50 μL, 0.6 mmol), and Et_3N (200 μL, 2 mol) in MeCN (20 mL) was heated under reflux and Ar for 6 h. 4-Hydroxybenzophenone (55 mg, 0.3 mmol) was added, and the mixture was allowed to cool to ambient temperature under Ar over the course of 12 h. The solvent was distilled off under reduced pressure, and the residue was purified by column chromatography [SiO_2, $EtCO_2Me/CH_2Cl_2$ (1:10, v/v)] to afford **SP5** (54 mg, 47%) as a red solid: HPLC (analytical) $t_R = 3.7$ min, PA = 1.2, APP = 276.1 ± 0.6 nm; mp = 100 °C; FABMS $m/z = 547$ $[M + H]^+$; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.25$ (3H, s), 1.37 (3H, s), 2.87 (3H, s), 5.88 (1H, d, 10 Hz), 6.64 (1H, d, 8 Hz), 6.80 (1H, d, 8 Hz), 7.06 (1H, d, 10 Hz), 7.35 (2H, d, 9 Hz), 7.49−7.52 (2H, m), 7.61 (1H, tt, 1 and 7 Hz), 7.84 (2H, m), 7.92 (3H, m), 8.04−8.07 (2H, m), 8.16 (1H, dd, 2 and 8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta =$

21.3, 26.0, 29.0, 52.2, 106.2, 106.5, 115.7, 118.6, 120.2, 120.9, 122.1, 123.1, 124.1, 126.3, 128.6, 129.0, 130.2, 132.0, 132.6, 132.7, 135.0, 136.7, 137.8, 141.5, 152.7, 154.9, 159.4, 165.0, 195.9.

2,3,3-Trimethyl-5-methoxy-3*H*-indole (12). A solution of isopropylmethylketone (1.5 mL, 14 mmol) and 4-methoxyphenylhydrazine hydrochloride (2.5 g, 14 mmol) in EtOH (60 mL) was heated under reflux for 5 h. After the mixture 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 (2 × 20 mL). The organic phase was dried over $MgSO_4$, and the solvent was distilled off under reduced pressure to yield **12** (2.3 g, 84%) as a red solid: FABMS $m/z = 190$ $[M]^+$; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.77$ (6H, s), 1.81 (3H, s), 3.33 (3H, s), 6.39 (1H, d, 8 Hz), 6.51 (1H, s), 7.03 (1H, d, 8.0); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 14.2$, 22.2, 52.7, 54.5, 107.3, 111.3, 119.1, 146.1, 146.4, 157.2, 184.7.

***1,2,3,3-Tetramethyl-5-methoxy-3H-indolinium Iodide* (13).** A solution of **12** (279 mg, 1.5 mmol) and MeI (100 μL, 1.6 mmol) in MeCN (30 mL) was heated under reflux and Ar for 24 h. After cooling the mixture down to ambient temperature, the solvent was distilled off under reduced pressure. The residue was dissolved in $CHCl_3$ (5 mL). The resulting solution was diluted with hexane (40 mL), sonicated for 30 min and filtered to afford **13** (240 mg, 49%) as a dark red solid: FABMS $m/z = 204$ $[M - I]^+$; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.63$ (6H, s), 3.01 (3H, s), 3.92 (3H, s), 4.21 (3H, s), 7.02−7.04 (2H, m), 7.60 (1H, d, 9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 14.3$, 23.5, 37.5, 54.5, 56.5, 109.5, 114.7, 116.5, 135.3, 143.5, 161.8, 192.8.

1,3,3-Trimethyl-2-methylene-5-methoxy-3*H*-indole (14). A solution of **13** (239 mg, 0.7 mmol) in MeCN (5 mL), H_2O (10 mL) and aqueous KOH (0.3 M, 2.5 mL) was stirred at ambient temperature for 1 h. The mixture was washed with CH_2Cl_2 (3 × 20 mL), and the organic layer was dried over $MgSO_4$. The solvent was distilled off under reduced pressure to yield **14** (102 mg, 70%) as a yellow solid: FABMS $m/z = 203$ $[M]^+$; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.39$ (6H, s), 3.04 (3H, s), 3.76−3.83 (5H, m), 6.44 (1H, d, 2 Hz), 6.69 (1H, dd, 1 and 2 Hz), 6.76 (1H, d, 1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 29.1$, 30.1, 44.6, 56.2, 72.3, 104.7, 110.2, 112.2, 139.2, 140.9, 153.5, 163.4.

1′,3′,3′-Trimethyl-5′-methoxy-6-nitrospiro[2*H*-1-benzopyran-2′,2′-3*H*-indole] (SP6). A solution of **14** (76 mg, 0.4 mmol) and 2-hydroxyl-5-nitrobenzaldehyde (62 mg, 0.4 mmol) in PhMe (45 mL) was heated under reflux and Ar for 3 h. After the mixture was cooled to ambient temperature, the solvent was distilled off under reduced pressure. The residue was purified by column chromatography [SiO_2, hexane/CH_2Cl_2 (1:2, v/v)] to afford **SP6** (70 mg, 54%) as a red solid: mp = 120 °C; FABMS $m/z = 352$ $[M]^+$; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.20$ (3H, s), 1.29 (3H, s), 2.70 (3H, s), 3.81 (3H, s), 5.86 (1H, d, 10 Hz), 6.47 (1H, d, 9 Hz), 6.73−6.75 (2H, m), 6.78 (1H, d, 9 Hz), 6.92 (1H, d, 10 Hz), 8.01−8.04 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 20.1$, 26.0, 29.4, 52.6, 56.1, 107.1, 107.4, 109.8, 111.6, 115.6, 118.9, 121.5, 122.6, 126.1, 128.4, 130.0, 131.9, 137.9, 141.1, 142.1.

2,3,3-Trimethyl-5-hydroxy-3*H*-indole (15). A solution of BBr_3 in CH_2Cl_2 (1.0 M, 11.4 mL) was added dropwise to a solution of **12** (1.10 g, 6 mmol) in CH_2Cl_2 (40 mL) maintained at 0 °C under Ar. After 1 h, the mixture was allowed to warm to ambient temperature over the course of 12 h. A saturated aqueous solution of $NaHCO_3$ (30 mL) was washed with CH_2Cl_2 (3 × 20 mL). The organic phase was dried over $MgSO_4$, and the solvent was distilled off under reduced pressure to afford **15** (0.75 g, 75%) as a greenish solid: FABMS $m/z = 176$ $[M]^+$; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.26$ (6H, s), 2.26 (3H, s), 6.81 (1H, dd, 2 and 8 Hz), 6.88 (1H, d, 2 Hz), 7.32 (1H, d, 8 Hz), 8.93 (1H, bs); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 13.7$, 21.9, 34.6, 53.2, 79.3, 110.3, 115.0, 116.0, 143.7, 159.0.

1,2,3,3-Tetramethyl-5-hydroxy-3*H*-indolinium Iodide (16). A solution of **13** (0.89 g, 5 mmol) and MeI (0.35 mL, 6 mmol) in MeCN (20 mL) was heated under reflux and Ar for 16 h. After the solution was cooled to ambient temperature, the solvent was distilled off under reduced pressure and the residue was dissolved in $CHCl_3$ (5 mL). The resulting solution was diluted with hexane (40 mL), sonicated for 20 min, and filtered. The residue washed hexane (50 mL) to afford **16** (1.35 g, 83%) as a red solid: FABMS $m/z = 190$ $[M - I]^+$; ^{1}H NMR [300 MHz, $(CD_3)_2SO$] $\delta = 1.46$ (6H, s), 2.70 (3H, s), 3.91 (3H, s), 6.95 (1H, dd, 1 and 3 Hz), 7.13 (1H, d, 1 Hz), 7.69 (1H, d, 3 Hz), 8.35 (1H, s); ^{13}C NMR [75 MHz, $(CD_3)_2$-SO] $\delta = 14.3$, 23.1, 34.6, 53.7, 110.0, 114.5, 119.8, 144.1, 147.1, 156.2, 186.4.

1′,3′,3′-Trimethyl-5′-hydroxy-6-nitro-spiro[2*H*-1-benzopyran-2′,2′-3*H*-indole] (17). A solution of **16** (183 mg, 0.6 mmol), 2-hydroxyl-5-nitrobenzaldehyde (96 mg, 0.6 mmol), and piperidine (57 μL, 0.6 mmol) in 2-butanone (30 mL) was heated under reflux and Ar for 3 h. After the mixture was cooled to ambient temperature, the solvent was distilled off under reduced pressure and the residue was dissolved in $CHCl_3$ (5 mL). The resulting solution was diluted with hexane (40 mL), sonicated for 30 min, and filtered. The residue was washed with hexane (20 mL) to yield **17** (153 mg, 78%) as a red solid: mp = 71 °C; FABMS $m/z = 338$ $[M]^+$; ^{1}H NMR (400 MHz, CD_3CN) $\delta = 1.14$ (3H, s), 1.22 (3H, s), 2.64 (3H, s), 5.92 (1H, d, 10 Hz), 6.41 (1H, d, 8 Hz), 6.52−6.64 (2H, m,), 6.73 (1H, d, 9 Hz), 7.03 (1H, d, 10 Hz), 8.00 (1H, dd, 3 and 9 Hz), 8.07 (1H, d, 3 Hz); ^{13}C NMR (75 MHz, CD_3CN) $\delta = 20.1$, 24.9, 29.6, 53.2, 108.0, 108.3, 111.0, 114.3, 116.2, 120.1, 122.6, 123.8, 126.6, 129.1, 129.4, 129.7, 138.9, 151.9, 160.8.

1′,3′,3′-Trimethyl-5′-(4″-iodobutyloxy)-6-nitrospiro[2*H*-1-benzopyran-2′,2′-3*H*-indole] (18). A suspension of **17** (0.44 g, 1 mmol), 1,4-diiodobutane (2.8 mL, 21 mmol), and K_2CO_3 (2.8 g 22 mmol) in MeCN (80 mL) was stirred at ambient temperature under Ar for 5 d. The solvent was distilled off under reduced pressure, and the residue was suspended in CH_2Cl_2 (20 mL) and washed with H_2O (4 × 15 mL). The organic phase was dried over $MgSO_4$, and the solvent was distilled off under reduced pressure. The residue was purified by column chromatography [SiO_2: hexane → hexane/CH_2Cl_2 (1:1, v/v)] to yield **18** (0.17 g, 25%) as a yellowish solid: FABMS $m/z = 520$ $[M]^+$; ^{1}H NMR (500 MHz, CD_3CN) $\delta = 1.15$ (3H, s), 1.24 (3H, s), 1.81−1.83 (2H, m), 1.95−1.97 (2H, m), 2.66 (3H, s), 3.31 (2H, t, 5 Hz), 3.95 (2H, t, 6 Hz), 5.92 (1H, d, 10 Hz), 6.48 (1H, d, 8 Hz), 6.69−6.72 (2H, m,), 6.77 (1H, d, 3 Hz), 7.04 (1H, d, 10 Hz), 7.99 (1H, dd, 3 and 9 Hz), 8.07 (1H, d, 3 Hz); ^{13}C NMR (125 MHz, CD_3CN) $\delta = 8.7$, 20.4, 26.5, 29.9, 31.5, 31.6, 53.6, 68.9, 108.7, 111.5, 114.0, 116.6, 120.5, 123.0, 124.1, 127.0, 129.5, 139.2, 143.4, 154.9, 161.2.

1′,3′,3′-Trimethyl-5′-(4″-(4‴-benzoylbenzoyl)butoxy)-6-nitrospiro[2*H*-1-benzopyran-2′,2′-3*H*-indole] (SP7). A suspension of **18** (35 mg, 0.1 mmol), 4-hydroxybenzophenone (133 mg, 0.7 mmol), and K_2CO_3 (0.93 g, 7 mmol) in MeCN (25 mL) was heated under reflux and Ar for 9 h. After the mixture 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 (4 × 10 mL). The organic phase was dried over $MgSO_4$, the solvent was distilled off under reduced pressure, and the residue was purified by HPLC (semipreparative) to afford **SP7** (10 mg, 25%) as a red solid: HPLC (analytical) $t_R = 3.7$ min, PA = 2.0, APP = 263.1 ± 0.3 nm; $m/z = 592$ $[M + H]^+$; ^{1}H NMR (400 MHz, CD_3CN) $\delta = 1.15$ (3H, s), 1.23 (3H, s), 1.90−1.99 (4H, m), 2.66 (3H, s), 4.01 (2H, t, 6 Hz), 4.17 (2H, t, 6 Hz), 5.93 (1H, d, 10 Hz), 6.49 (1H, d, 8 Hz), 6.72 (1H, dd, 3 and 8 Hz), 6.77 (2H, d, 3 Hz), 7.02−7.06 (3H, m), 7.49−7.53 (2H, m), 7.60−7.62 (1H, m), 7.70−7.72 (2H, m), 7.77−7.79 (2H, m), 7.99 (1H, dd, 3 and 9

Hz), 8.07 (1H, d, 3 Hz); ^{13}C NMR (125 MHz, CD_3CN) δ = 20.1, 26.0, 26.2, 26.4, 29.4, 52.6, 68.1, 68.4, 107.0, 107.4, 110.4, 112.5, 114.2, 115.7, 118.9, 121.8, 122.9, 126.1, 128.4, 129.9, 132.1, 132.8, 138.0, 138.6, 141.1, 142.2, 153.7, 160.1, 162.8, 195.8.

Acknowledgment. We thank the National Science Foundation (CAREER Award CHE-0237578) and the University of Miami for financial support. We are grateful to Professor V. Ramamurthy for sharing his time-resolved emission spectrometer with us.

Supporting Information Available: General methods and experimental procedures for the synthesis of **4**, **20**, **21**, and **22**; HPLC traces of **SP2**, **SP3**, **SP5**, and **SP7**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO062004D