

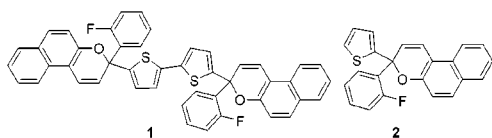
A Smart Photochromophore through Synergistic Coupling of Photochromic Subunits

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The design and synthesis of photochromic molecules is an intense research area because of their potential applications for information storage, imaging devices, smart windows, ophthalmic lenses, protective lenses, and filters.^{1,2} A current goal in this area is the development of smart photochromophores displaying greater optical density, fatigue resistance, and tunability. In the search for novel structures, the majority of investigations have produced molecules incorporating single photochromophores which in turn display only simple photochromism marked by binary on/off behavior.^{3,4} We have been interested in the design of molecules including two photochromophores with the objective of identifying fully functional, smart systems displaying optical properties not observed with the corresponding monomer such as differential coloration response as a function of the intensity and duration of incident radiation. The synergistic optical coupling between two chromophore units required for such properties is a feature that has not been observed in the known systems that follow the structural-design strategies described to date. Herein, we document a novel bis-naphthopyran **1** with unprecedented photochromism, wherein the linking site and



a bis-thiophene connector synergistically conspire to furnish optical properties that are unique, differing substantively from a simple first-order superimposition of the monomeric constituents. Such a photochromophore not only has great promise in the development of smart optical devices, but also simulates the response in living systems to light, as it is sensitive to the energy of incident light, as well as to the duration and intensity of the stimuli.

In contrast to the numerous studies of monomeric photochromophores, the study of bis-photochromophores is considerably limited. Importantly, in none of the reported systems has irradiation-controlled synergism between the two constituent photochromic units been documented that would offer significantly different behavior from that observed with monomer mixtures.^{3,4} In general, for the limited number of reported bis-naphthopyrans, when photochromism has been observed, either light-induced ring opening occurred at only a single photochromophore with the second remaining inactive, or only small changes in the photochromic properties relative to the monomer were documented.

In our approach to the design of electronically coupled bis-photochromophores, we sought to examine bis-naphthopyrans linked at C(3) through a bis-thiophene. This plan was predicated on the hypothesis that such tethering would provide a unique linking strategy for the electronic coupling of two photochromophores. In this scenario, the tether not only functions as a substituent but also

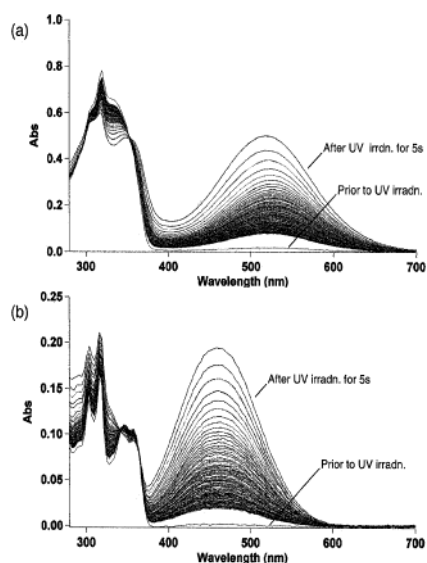


Figure 1. Absorption spectra of dimer **1** (a) and **2** (b) in CHCl_3 (2.5×10^{-5} mol/L) before and after UV irradiation at 366 nm for 5 s. Photo bleaching is monitored over 8.5 min with scan/6.32 s.

undergoes time-dependent change in its electronic behavior during irradiation and coloration. Thus, the linking bis-thiophene operates as an electron-rich substituent on the unopened units, but importantly, following irradiation and opening of the first naphthopyran, its electron-donating ability is significantly reduced, thereby exerting a markedly different influence on the subsequent opening of the second unit. Implementation of the hypothesis was effected through the synthesis of **1**, which, as detailed below, furnishes the first example of a system wherein covalently coupled photochromophores work synergistically.

The coloration and bleaching of dimeric **1** and monomer **2** following irradiation are shown in Figure 1. The absorption spectrum of **1** is characterized by three maxima: 307 nm ($\epsilon = 25000$), 319 nm ($\epsilon = 31200$), and 334 nm ($\epsilon = 26100$), whose intensities are more than four times that of monomer **2**: 304 nm ($\epsilon = 5520$), 316 nm ($\epsilon = 6400$), 346 nm ($\epsilon = 4360$), and as 358 nm ($\epsilon = 4200$).⁵ The fact that as a substituent the bithiophene produces an increase in the ϵ in the closed form without an accompanying marked shift in the maxima suggests the two photochromophores are relatively insulated from each other. This is consistent with the fact that covalent linking of the two photochromophores occurs through two sp^3 -hybridized carbons in the closed form. Following irradiation for 5 s, the opened-colored form of **1** ($\lambda_{\text{max}} = 517$ nm) displays a bathochromic shift of 60 nm relative to monomeric **2** ($\lambda_{\text{max}} = 457$ nm).

Exposure of **1** and **2** for extended periods of time produced remarkable results (Figure 2). Irradiation for 150 s leads to further

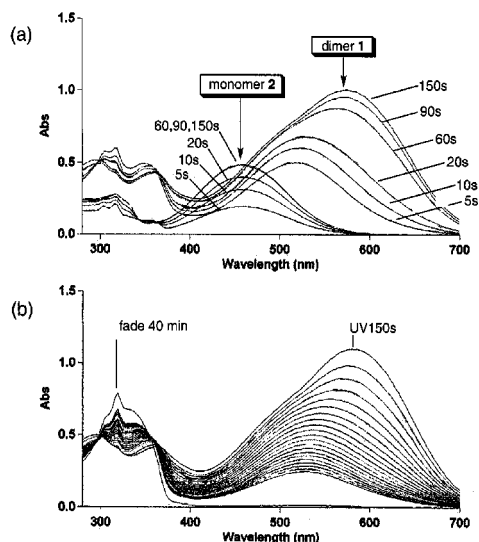


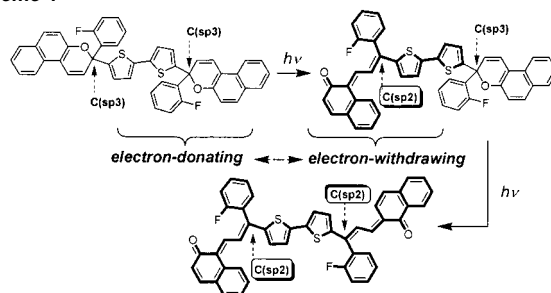
Figure 2. (a) Time-dependent absorption spectra of **1** and **2** in CHCl_3 (2.5×10^{-5} mol/L). (b) Fading of **1** after irradiation at 366 nm for 150 s with scan/24.9 s for 21 scans, as well as fade over 40 min.

increase in the absorption intensities. However, while the coloration of monomeric **2** reaches saturation within 60 s, **1** reaches saturation only after 150 s. Moreover, the new band produced after 150 s has an absorption maximum at 580 nm, a shift of 63 nm from the initially observed colored species and 103 nm longer than that of the colored form of **2**. Such large bathochromic shifts are unusual for photochromic naphthopyrans, suggesting that a second process has taken place, namely ring-opening and coloration of the second naphthopyran. It is also noteworthy that dimeric **1** has better colorability. Thus, after 5 s irradiation, **1** displays $A = 0.499$ (λ_{max} 517 nm), which is substantively greater than that of **2** $A = 0.194$ (λ_{max} 457 nm). Moreover, it is even larger than $A = 0.485$ ($\lambda_{\text{max}} = 457$) of **2** at saturation after 90 s irradiation.

It is useful to compare dimeric **1** and monomeric **2** under conditions in which the concentration of photochromophore is the same, $[\mathbf{2}]/[\mathbf{1}] = 2$. After irradiation for 5 and 150 s, a 50 μM solution of **2** gives $A = 0.326$ and $A = 0.988$ (λ_{max} 457 nm), respectively. In stark contrast, under the same conditions 25 μM solution of **1** gives $A = 0.499$ (λ_{max} 517 nm) after 5 s, and $A = 0.807$ (λ_{max} 520 nm) as well as $A = 0.996$ (λ_{max} 580 nm) after 150 s irradiation. Thus, relative to monomer, dimeric **1** displays broader absorption, better colorability and bathochromism. Examination of the data in Figure 2 indicates that the opening of the second unit in **1** is slower than that of the first and reaches maximum after 150 s. We then examined the fading behavior of **1** and **2** following 150 s irradiation. The hypsochromic shift of λ_{max} 580 nm \rightarrow 520 nm observed during bleaching suggests that the fully opened form of **1** passes through the mono-opened state.

The study delineated above highlights that the linking of the photochromophores in **1** leads to a unique system with unusual synergistic coupling between each of the units (Scheme 1). In dimer **1**, the bis-thiophene links two insulated photochromic units through two $\text{C}(\text{sp}^3)$ -hybridized spirocyclic carbons. Following irradiation, one naphthopyran unit exhibits rapid response and coloration because of the electron-rich bis-thiophene substituent. However, it is important to note that opening of the first naphthopyran is accompanied by a hybridization change at the spirocyclic $\text{C}(3)$ carbon from $\text{C}(\text{sp}^3)$ to $\text{C}(\text{sp}^2)$, resulting in conjugation of the electron-deficient photomerocyanine to the bis-thiophene. Consequently, once the first unit is opened, the initial role of the bis-thiophene as an electron-donating substituent is considerably

Scheme 1



reduced. This change dramatically impacts the properties of the second photochromophore. Opening of the second unit leads to full conjugation of the two photochromophores through two $\text{C}(\text{sp}^2)$ -hybridized carbons, affording a new bis-merocyanine displaying considerable bathochromism relative to the monomers. During fading, the effects are reversed such that bleaching of the mono-opened form is slower.

We have developed a new bis-naphthopyran in which the individual photochromophores are electronically coupled to afford a dimeric system generating one or two colored forms. Such systems should have important applications in the generation of smart optic devices that respond to the nature and intensity of incident radiation; such properties have only been possible to date through the use of mixtures of multiple photochromophores of different structural types. Importantly, in a broader sense, the strategic construct we have described in the design of the first smart bis-photochromophore, wherein linkage of the two chromophores is effected through the carbon-center whose hybridization changes in the course of irradiation and bleaching, may find use in the design of other smart photosystems involving electro- and thermochromophores. Additional studies are underway and will be reported as they become available.

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Supporting Information Available: Characterization data for **1** and tabulation of absorption and fade of naphthopyrans and the fade of the colored form under various irradiation times (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Crano, J. C.; Guglielmetti, R. *Organic Photochromic and Thermochromic Compounds*; Plenum Press: New York, 1999.
- (2) (a) Irie, M.; Kobatake, S.; Horichim M. *Science* **2001**, *291*, 1769. (b) Koumura, N.; Zijistra, R. W. L.; van Delden, R. A.; Harada, N.; Feringa, B. L. *Nature* **1999**, *401* (6749), 152. (c) Huck, N. P. M.; Jager, W. F.; Lange, B.; Feringa, B. L. *Science* **1996**, *273*, 1086. (d) Berkovic, G.; Krongauz, V.; Weiss V. *Chem. Rev.* **2000**, *100*, 1741. (e) Willner, I. *Acc. Chem. Res.* **1997**, *30*, 347.
- (3) (a) Ortica, F.; Levi, D.; Brun, P.; Guglielmetti, R.; Mazzucato, U.; Facaro, G. *J. Photochem. Photobiol., A* **2001**, *139* (2–3), 133. (b) Ortica, F.; Levi, D.; Brun, P.; Guglielmetti, R.; Mazzucato, U.; Favaro, G. *J. Photochem. Photobiol., A* **2001**, *138* (2), 123. (c) Frigoli, M.; Moustrou, C.; Samat, A.; Guglielmetti, R. *Helv. Chim. Acta* **2000**, *83*, 3043. (d) Flerova, A. N.; Prokhoda, N. P.; Yudina, N. P.; Zaitseva, E. L.; Krongauz, V. A. *Khim. Geterotsikl. Soedin.* **1973**, 1631. (e) Gitina, R. M.; Prokhoda, N. P.; Yudina, N. P.; Zaitseva, E. L.; Krongauz, V. A. *Khim. Geterotsikl. Soedin.* **1973**, 1639. (f) Ribes, F.; Guglielmetti, R.; Metzger, J. *Bull. Soc. Chim. Fr.* **1972**, 143. (g) Keum, S. R.; Lee, S. S.; Min, B. H.; Kazmaier, P. M.; Buncel, E. *Dyes Pigm.* **1994**, *30*, 225. (h) Keum, S. R.; Lee, J. H.; Seok, M. K. *Dyes Pigm.* **1994**, *25*, 21. (i) Strokach Y.; Alfimov, M.; Barachevsky, V.; Arsenov, V.; Gorelik, A. *Mol. Cryst. Liq. Cryst.* **1997**, *298*, 97.
- (4) A limited number of other bis-spiropyran have also been reported; however, their photochromic properties were not addressed in detail. See, for example: (a) Bertelson, R. C. In *Photochromism*; Brown, G. H., Ed.; Wiley-Interscience: New York, 1971; pp 733–840. (b) Guglielmetti, R. In *Photochromism: Molecules and Systems*; Durr, H., Bouas-laurent, H., Eds.; Elsevier: Amsterdam, 1990; pp 314–466.
- (5) Noustrou, C.; Rebiere, N.; Samat, A.; Guglielmetti, R.; Yassar, A. E.; Dubest, R.; Aubard, J. *Helv. Chim. Acta* **1998**, *81*, 1293.

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