Photochemical pK_a-Modulation and Gated Photochromic Properties of a Novel Diarylethene Switch

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The unsymmetrical dithienylethene photochrome **1a** exhibits proton-gated photochromic properties as well as novel chemical reactivity. The dimethoxylated derivative **9a** represents a light-triggered proton switch whose dissociation constant is increased by a factor of 16 upon photochemical cyclization to **9b**. Such compounds are of potential interest for multiplexing photochemical systems.

The development of bistable molecular systems for which a given physical property may be controlled by external stimulation is of central importance to the creation of electronic devices which function at the molecular and supramolecular levels[1]. We have described[2–4] a number of photocontrolled diarylethene-based "molecular switches"[5] for which electron conduction and nonlinear-optical, redox (electrochromic) and fluorescent properties may be reversibly activated or deactivated by irradiation at well-separated frequencies. The remarkable light-triggered behavior of these devices relies on a photochromic dithienylethene[6] "switching unit" which may be photochemically interconverted between stable states through which electronic communication is either facilitated or completely blocked. In principle, any property dependent on the conjugation between two functional domains within a molecule may be brought under photochemical control by introduction of the photochrome switch between them. The different degree of rigidity between the open and cyclized photoisomers has also been exploited to modulate molecular recognition properties in a light-controlled manner[7].

In the present work, we apply this concept (Figure 1) to the stabilization of the negative charge of a dissociated acid by an electron-withdrawing group to which it is conjugated. Photo-controlled establishment or disruption of this stabilization through the switching unit may be used to modulate the acid strength. Molecules **1** (Schemes 1 and 2) thus represent a prototype proton-generation switch for which pK_a-modulation by light is possible. It is also noteworthy that compound **1** and the derivatives **9** possess proton-gated photochromic properties – the coloration process being very sensitive to the protonation state. Finally, the study of this system has yielded some insight into the novel chemical reactivity of this fluorinated class of diarylethene photochromes with implications for their practical application.

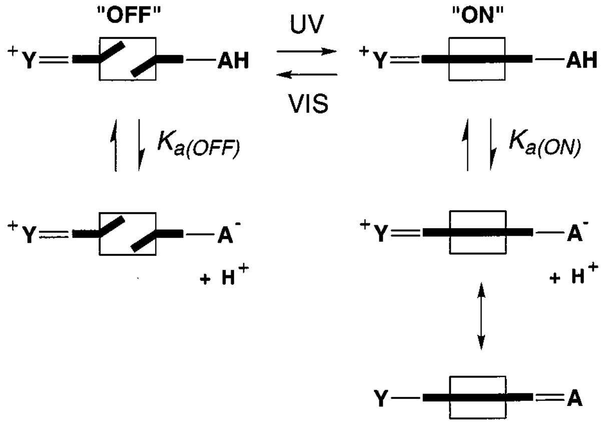

Figure 1. The concept of photocontrolled pK_a-modulation; upon cyclization to the "ON" state of the photochrome, the dissociation constant of –AH is increased due to the conjugative stabilization of A^- by Y^+ which is not possible in the "OFF" state

Synthesis of the Photochromic Molecules 1 and 8

The target photochrome in its open state **1a** was prepared according to Scheme 1. The arylthiophenes **2** and **3** were prepared by the Suzuki coupling[8] of 3-bromo-2-methylthiophene-5-boronic acid with 4-bromopyridine or 4-bromoanisole as described previously.[3][4] The fluorinated cyclopentenes **4** and **5** were obtained as minor products in the preparation of their corresponding symmetrical dithienylcyclopentene photochromes,[3][4] by lithiation of the corresponding arylthiophenes followed by the addition of 0.5 equivalents of perfluorocyclopentene. Compounds **4** and **5** were obtained in yields of 36 and 27%, respectively, when a full equivalent of the fluorinated cycle was employed.

The reaction of the monoadduct **4** with the lithiated derivative of anisidylthiophene **3** gave the photochrome **6** as a yellow-green syrup in 71% yield. The analogous condensation of molecule **5** and pyridylthiophene **2** afforded a

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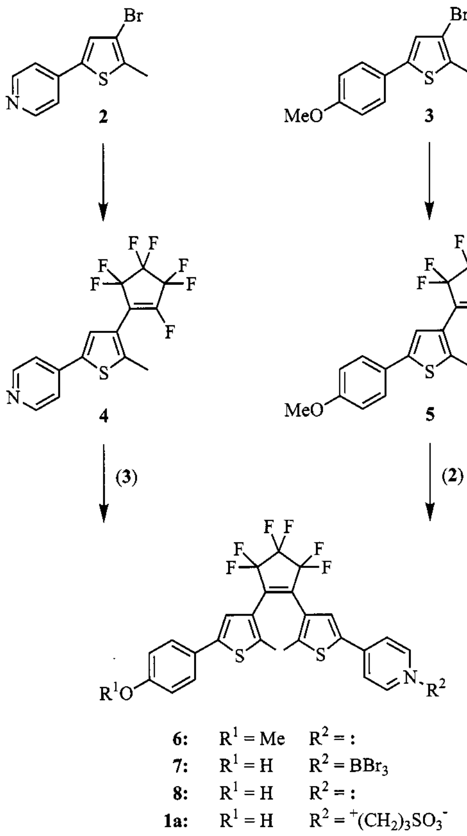


Scheme 1. Synthesis of photochrome **1a**

compound which was identical in all respects to the product obtained above, in 65% yield. The deprotection of the methyl group using a large excess of boron tribromide[9] gave the essentially pure pyridine-boron[10] complex **7**, which was found to be very stable to both concentrated acid and various nucleophiles. Strongly basic conditions (1:2:3, sodium hydroxide/water/methanol, by weight) were required to hydrolyze the complex, giving the pyridyl-phenol compound **8** in 76% yield from **6**. Finally, selective *N*-alkylation[11] with 1,3-propane sultone in refluxing acetonitrile gave the target photochrome **1a** as a yellow powder in 92% yield.

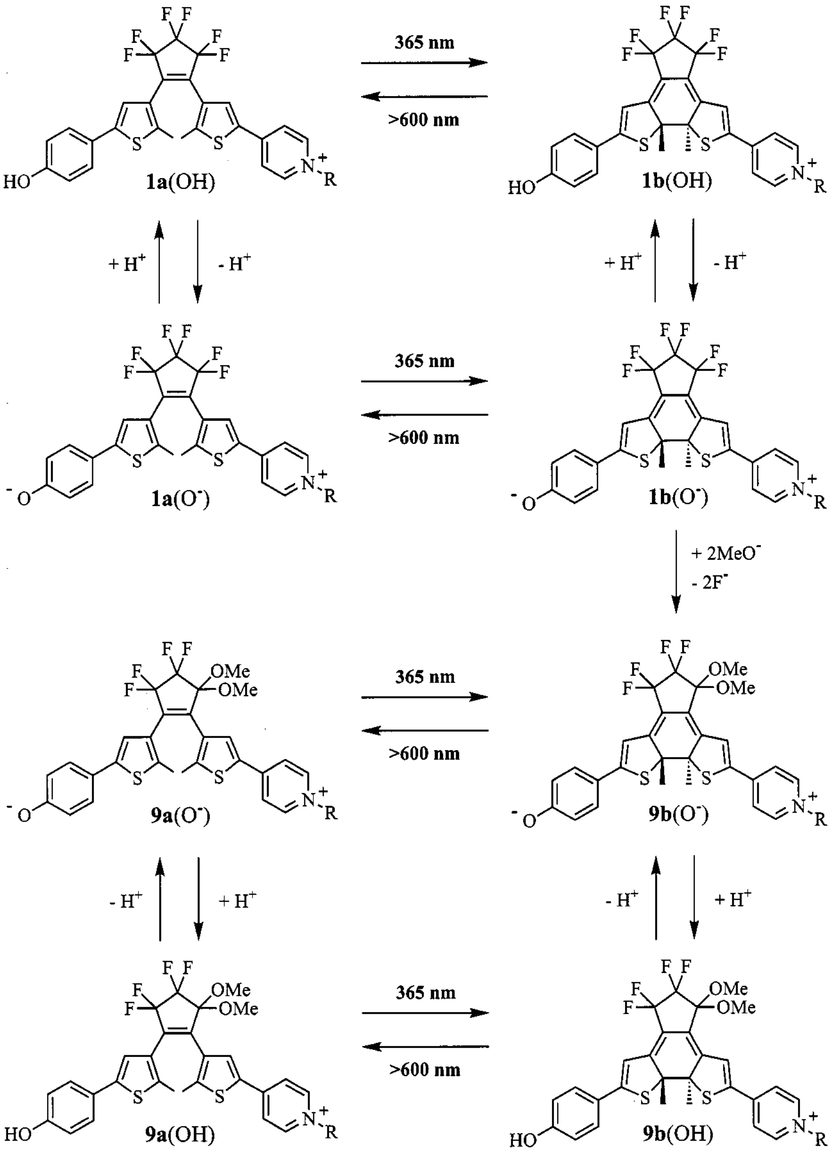
Photochromic Properties of 1 and 8

The photochromic properties of both **1** and its precursor **8** were studied with the combined proton NMR-UV protocol described in earlier work.[3] Irradiation of a solution of pyridylphenol **8** in benzene with light of 365 nm resulted in the decrease and eventual disappearance of the signals in the NMR spectrum (Table 1) of the open isomer and the appearance of a new series of peaks corresponding to the cyclized form. At the photostationary state, no trace of the open compound could be detected, corresponding to a conversion of greater than 98%. By UV-Vis spectroscopy, the photocyclization was observed as a decrease in the band at 296 nm (**8** open) and the appearance of a broad absorption centered at 602 nm, responsible for the deep blue color of the closed photoisomer. Subsequent irradiation of the sample with visible (red) light of wavelength >600 nm resulted in a clean reconversion into the colorless open state. The spectral data for compounds **1**, **8** and **9** are given in Table 2.

Despite the presence of the charged groups in **1a**, the molecule was found to have limited solubility in water, and initial studies were carried out in methanol. Irradiation of a solution of the open isomer **1a** (presumably in its protonated form **1a**(OH), see Scheme 2) with UV light (365 nm) resulted, once again, in essentially complete conversion (>98%) into the intensely blue, cyclized form **1b**, as determined by proton NMR spectroscopy. The process was observed by UV-Vis spectroscopy as a decrease in the absorptions centered at 293 and 350 nm, and the appearance of a broad band at 671 nm. However, this colored isomer was not stable, the UV spectrum evolving in a complex manner in the dark. Surprisingly, this apparent decomposition could be completely inhibited by acidification of the solution. After passing a small volume of HCl gas through a methanolic solution of open photochrome [i.e. **1a**(OH)], the closed form **1b**(OH) could be easily generated photochemically and was found to be stable in the dark for several days. The open photochrome **1a**(OH) could then be fully regenerated by irradiation with visible (red) light. These transformations could also be carried out in a water-methanol mixture as shown in Figure 2. As a preliminary experiment, base was added to a solution of closed form **1b**(OH), resulting in an immediate color change from blue to green and a shift in the absorption maximum from 671 to 761 nm. Reacidification with HCl gas resulted in regeneration of the blue color.

Methoxide Substitution of Photochrome 1

The observations described above for compounds **1** were initially interpreted as simply being the deprotonation and reprotonation of the cyclized molecule [i.e. **1b**(OH) (**1b**(O$^-$) (**1b**(OH)]. However, closer examination of the UV-Vis spectra (see Figure 3) revealed that the final blue species obtained above was not **1b**(OH), the spectrum differing slightly with an absorption maximum at 666 nm. Moreover, this new species (whose structure determination is described below) was easily decolorized by irradiation with red light to give a presumably open photochrome whose UV-Vis spectrum was similar, but not identical, to that of **1a** in its protonated (OH) form. To determine the structure of this new compound, a small sample of **1a** in acidified methanol was photocyclized, treated with base, the solution acidified and evaporated, and the proton NMR spectrum (Table 1) of the resulting blue solid then recorded. Apart from noticeable changes in the chemical shifts of the thiophene protons, the spectrum appeared similar to that of **1b**(OH). However, two new signals, each integrating to three protons, were observed at 3.34 and 3.52 ppm (in [D$_4$]methanol). The same experiment was repeated with the additional step of irradiating the final deep blue solution with red light. A



Scheme 2. Interconversions between the various forms of photochromes **1** and **9** [R = -$(CH_2)_3SO_3^-$]; the species **1b**(O^-) is never observed due to its rapid conversion into **9b**(O^-) under basic conditions in methanol-containing solvent systems

yellow solid was thus obtained after removal of the solvent whose proton NMR spectrum was, in this case, roughly similar to that of **1a**(OH) except for a broad singlet integrating to six protons at 3.41 ppm.

These observations suggested that two of the fluorine atoms had been replaced by methoxy groups in the new species, which was corroborated by ^{19}F NMR spectroscopic studies (Table 3). The ^{19}F NMR spectrum of **1a**(OH) presented three very finely split singlets, each assignable to a CF_2 group of the central cycle, whereas the new photochrome, like its open isomer, presented only two. Marked changes in the spectra of both **1b**(OH) and the new molecule occurred upon photocyclization. In the case of the former, three AB quadruplets, each exhibiting couplings in the 260 Hz range, were observed as expected for a rigid cyclized structure in which the geminal fluorine atom pairs are no longer equivalent. In contrast, only two AB quadruplets were observed for the new compound in the closed state, again indicating a structure with two fewer fluorine atoms and, more specifically, consistent with the presence of only two difluoromethylene groups. Based on these observations, it appears that under basic conditions the methoxide ions present in the solution displace the fluorine atoms of one of the allylic CF_2 groups of **1b**(O^-) to yield **9b**(O^-), and that the two products isolated in the above experiments are **9b**(OH) and **9a**(OH). The structures are also supported by the negative-ion electrospray mass spectrum of **9b**(OH) which shows an $[M - H]^-$ ion, as well as a fragment corrsponding to the loss of dimethyl ether.

A surprising aspect of the allylic substitution reaction is that it only takes place for the cyclized form of the photochrome. The reaction from **1b**(O^-) to **9b**(O^-) is extremely rapid; the former species is never observed. In marked contrast, the open isomer **1a**(OH) is stable in methoxide solu-

Table 1. ^{1}H NMR spectroscopic data for compounds **1**, **8** and **9**[a]

δ/ppm (*J*/Hz)	$(CH_2)_3SO_3$	thio-Me	thio-H	C_6H_4–OH[b]	C_5H_4NR[b]
1a(OH)	2.42	2.00	7.14	6.79 (8.6)	8.25 (7.0)
	2.86	2.15	8.15	7.38 (8.6)	8.85 (7.0)
	4.73				
1b(OH)	2.44	2.21	6.77	6.87 (8.8)	8.20 (7.0)
	2.86	2.23	7.45	7.59 (8.8)	8.92 (7.0)
	4.78				
9a(OH)[c]	2.42	1.96	7.29	6.79 (8.6)	8.18 (6.9)
	2.86	2.10	7.95	7.37 (8.6)	8.81 (6.9)
	4.71				
9b(OH)[d]	2.44	2.14	6.83	6.84 (8.7)	8.17 (6.9)
	2.87	2.20	7.43	7.50 (8.7)	8.90 (6.9)
	4.77				
8(open)[e]		1.64	–[f]	6.43 (8.6)	6.80 (6.1)
		1.65	7.30	7.19 (8.6)	8.40 (6.1)
8(closed)[e]		2.04	6.56	6.29 (8.7)	6.63 (6.1)
		2.08	6.59	7.05 (8.7)	8.40 (6.1)

[a] 200 MHz, in $[D_4]$methanol unless otherwise indicated. – [b] AA′BB′ systems, apparent coupling constants given in parentheses. – [c] Methoxy singlet at 3.41 ppm. – [d] Methoxy signals at 3.38 (s) and 3.52 (d, *J* = 1.2 Hz) ppm. – [e] In C_6D_6. – [f] Hidden beneath the solvent peak.

Table 2. Spectral data for compounds **1**, **8** and **9**[a]

	λ_{max} ($\varepsilon \times 10^{-3}$)			
1a(OH)	292 (28)	350 (27)		
1b(OH)	287 (23)	407 (17)		671 (20)
1a(O^-)	344 (36)			
9a(OH)	292 (26)	356 (24)		
9b(OH)	285 (25)	361 (14)	404 (14)	666 (19)
9a(O^-)	346 (31)			
9b(O^-)	290 (22)	423 (16)		745 (25)
9b(O^-)[b]	292 (22)	424 (16)		761 (25)
8(open)[c]	296 (30)			
8(closed)[c]		348 (14)		602 (13)

[a] In 5:2 methanol/water. – [b] In methanol. – [c] In benzene.

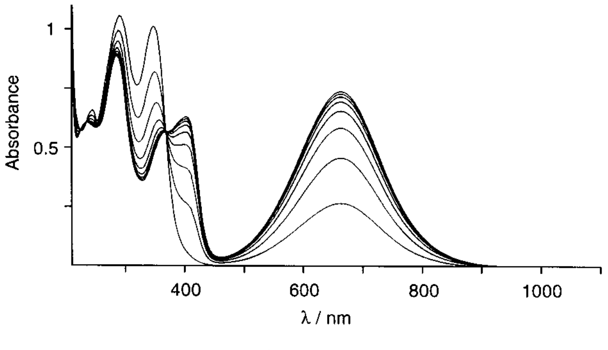


Figure 2. Photocyclization of **1a**(OH) to **1b**(OH); changes in absorption spectra upon nine successive 1 min irradiations of **1a** (3.7×10^{-5} M in 5:2 methanol/water, pH′ 3.0) with light of 365 nm

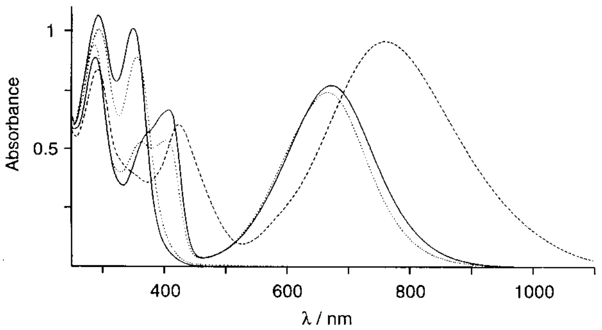


Figure 3. Absorption spectra of **1a**(OH) and **1b**(OH): [––––], **9a**(OH) and **9b**(OH): [·······], **9b**(O^-): [– – – –] in 5:2 methanol/water (3.0×10^{-5} M); see Table 2 for absorption maxima and extinction coefficients

Table 3. ^{19}F NMR spectoscopic data for compounds **1** and **9**[a]

	δ/ppm ($^2J_{F\text{-}F}$/Hz)		
1a(OH)	−3.87	+17.71	+18.12
1b(OH)	−5.94/−4.96	+12.86/+15.94	+15.61/+16.57
	(249)	(259)	(260)
9a(OH)	−0.17	+16.93[b]	
9b(OH)	−4.22/−2.03	+9.19/+21.78	
	(234)	(259)	

[a] In $[D_4]$methanol at 188 MHz. Chemical shifts with respect to $C_6H_5CF_3$ assigned a value of +63 ppm. All signals showed fine structure due to $^3J_{F\text{-}F}$ and $^4J_{F\text{-}F}$ < 2 Hz. – [b] Broad signal.

tions [as **1a**(O^-)] for prolonged periods of time (no detectable change after over 12 hours of standing at ambient temperature). It is noteworthy that such a transformation does not occur during the conversion of **7** to **8** (open forms), which requires very strongly basic conditions. The examination of models shows that for the open isomers of these photochromes, in which the thiophene rings are rotated far out of the plane of the central fluorinated cycle, attack by a nucleophile on the allylic carbons of the central fluorinated ring is strongly hindered. On the other hand, these centers are accessible once the system is closed and essentially planar. The flatness of the cyclized form also allows the electron-withdrawing pyridinium group to activate the allylic center towards attack by the alkoxide nucleophile.

We have also observed the analogous substitution reactions when the closed photochrome **1b** is treated with ethoxide, ammonia or methylamine. It is important to note that this type of transformation may be of great practical significance in that it provides a ready means of covalently attaching fluorinated diarylethenes of this type to polymers[12] or other materials which bear have pendant nucleophilic groups. Photochromic materials based on dithienylethenes have great potential as media for photon-mode optical data storage.[13] The substitution of the alkoxy groups hardly alters the photochromic or spectral properties of the diarylethenes. Therefore, the fully fluorinated compounds may be simply prepared by straightforward means prior to attachment, thus circumventing the need to prepare modified compounds bearing functionalities requisite for polymer incorporation.

Photochromism of 9

Unlike photochromes **1**, the dimethoxy compounds **9** are very stable under either acidic, neutral or basic conditions in methanol or methanol/water mixtures. Furthermore, they possess very good photochromic properties, being readily

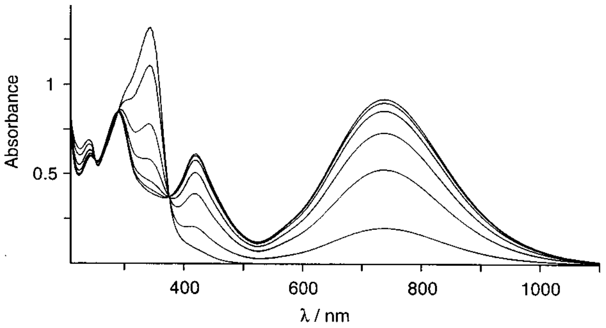


Figure 4. Photocyclization of **1a**(O$^-$) to **9b**(O$^-$); changes in absorption spectra upon irradiation of **1a** (3.7 × 10^{-5} M in 5:2 methanol/water, pH′ 11.0) with light of 365 nm after total irradiation times of 0, 2, 6, 10, 15, 20, 30 and 40 min

interconverted between open and closed states when in their protonated forms. The species **9b** may be generated in methanol by either of two routes: the cyclization of **1a**(OH) to **1b**(OH) followed by the addition of base, or by simply irradiating **1a** under basic conditions. In the latter case, the closed isomer **1b**(O$^-$), initially generated from **1a**(O$^-$), does not accumulate due to its immediate conversion into **9b**(O$^-$) upon cyclization, as evidenced by the superimposed UV-Vis spectra of the sample (Figure 4), which exhibits a clean isosbestic point at 378 nm. In a variety of experiments, the phenolate **9b**(O$^-$) was interconverted either by means of light or a pH change between all of its photochromic and acid-base forms, for example, along the sequence **1a**(OH) → **1b**(OH) → **9b**(O$^-$) → **9b**(OH) → **9a**(OH) → **9a**(O$^-$) → **9a**(OH) → **9b**(OH) → **9a**(OH), throughout which the three spectra of **9a**(OH) remained unchanged (data not shown).

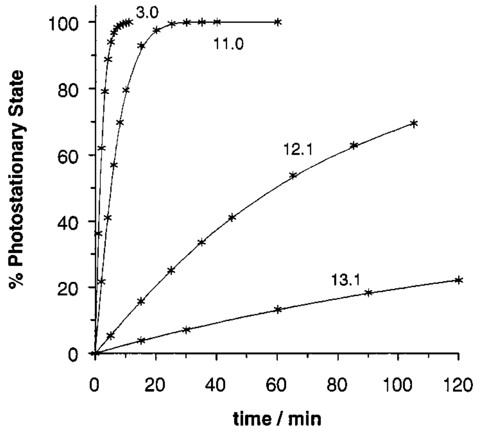


Figure 5. pH-Dependence of the rate of photocyclization of **1a**; progress curves for the photocyclization of **1a**(OH) to **1b**(OH) at pH′ 3.0, and those for the coloration of **1a**(O$^-$) to **9b**(O$^-$) at pH′ 11.0, 12.1 and 13.1 (2.5 × 10^{-5} M, 5:2 methanol/water, irradiation wavelength of 365 nm, photostationary state of >98% conversion into the closed isomer)

Proton-Gated Properties

In the course of these studies, it became apparent that the rate of photocyclization of open **1a** was highly dependent on the apparent pH (pH′) of the solution, being rapid under acidic conditions while sluggish at high pH′. In the latter case, the dimethoxyphenolate **9b**(O$^-$) is formed. The pH dependence was studied by carrying out a series of colorations under identical conditions (Figure 5) in methanol/water. [About 5% more light is absorbed by the basic sample because, at 365 nm, **1a**(O$^-$) has an extinction coefficient slightly higher than that of **1b**(OH)]. Under acidic conditions (pH′ 1 to 5), the observed rate of cyclization was pH-independent. Conversely, at pH′ values greater than the pK_a of the phenolic proton of **1a**(OH) (10.5 in 5:2 methanol/water), increasing the base concentration by a factor of 10 resulted in a decrease in the relative rate of cyclization by roughly an order of magnitude (Figure 5). At pH′ values of 3.0, 11.0, 12.1 and 13.1, the relative rates for coloration were found to be 1, 0.3, 0.02, and 0.003, respectively. In all cases, clean open to closed [i.e. **1a** (**1b**(OH) or **9b**(O$^-$)] conversion was observed. At pH′ 14, irradiation with UV light for one hour resulted in only 8% coloration (compared to complete cyclization within 10 minutes at low pH). When the same sample was subsequently acidified, however, the rapid photochemical conversion from **1a**(OH) to **1b**(OH) took place. The same pH-dependency was observed for the photocyclization of **9a**. In marked contrast, the photochemical opening of **9b**(O$^-$) was found to be only slightly slower than that of its protonated form **9b**(OH). Control reactions were also carried out to ensure that the observed changes in relative cyclization rate were not, at least in part, due to variations in the ionic strength of the media. Colorations carried out in the standard water/alcohol system containing varying concentrations of potassium chloride clearly showed that the rate of photocyclization was independent of the presence of salt.

Compounds **1** and **9**, therefore, present proton-gated photochemical reactivity dependent on the Brönsted acid-base equilibrium of the phenolic proton. Few photochromic systems possessing gated behavior have been developed. Models for optical memory based on protonation-dependent photochromism have been described.[14] Solvent-regulated and chemically gated diarylethene systems have also been reported.[15]

Two possible explanations exist for the pH-dependent behavior of photochromes **1** (and **9)** or, in more precise terms, for why the quantum yield for the photocyclization of **1a**(O$^-$) is much lower than that for **1a**(OH): i) once deprotonated, an ionic interaction between the phenolate and pyridinium groups locks the molecule in a parallel conformation which may not undergo photocyclization[16], or ii) changes in the molecule's electronic distribution upon deprotonation result in a much less efficient cyclization. To distinguish between these, controlled UV-colorations of the pyridyl-phenol compound **8**, for which the latter explanation cannot apply, were carried out. While the results obtained were not as clear as those obtained for compounds **1** and **9**, the relative rates of photocyclization carried out at high pH were clearly much lower than those under either neutral or acidic conditions. It therefore appears that the marked pH-dependence of the photocyclization rate of these photochromes is due to electronic factors which lower the quantum yield for photocyclization of the phenolate species, perhaps owing to the great disymmetry of the ionized forms **1a**(O$^-$) and **9a**(O$^-$).

Photochemical Switching of pK_a

In its cyclized, deprotonated form **9b**(O$^-$), the molecule may be regarded as a merocyanine dye for which two canonical forms may be considered, a zwitterionic form (as depicted) or a neutral quinonoid-type structure in which the negative charge on the phenolate is cancelled. For our purposes, the extent to which the latter form contributes to the resonance hybrid is of central importance in that it should translate itself into enhanced acidity of the phenolic proton for the closed form of the switch.

N-Methylpyrid-4-one, whose conjugate acid has a very low pK_a of 3.33, may be taken as an extreme example of a pyridinio-phenolate for which the ″quinonoid structure″ is completely favored over a zwitterionic form.[17] Brönsted acidities have also been measured for stilbazolium vinylogues of the above molecule in which pyridinium and phenol rings are separated by a double bond. The acidity of these compounds was found to be greater than that of the corresponding 4-unsubstituted phenols.[18] In light of our earlier work involving diarylethenes related to **1**, which indicated excellent conjugation across the rigid polyolefinic bridge joining aryl end-groups in the cyclized forms of the photochromes, we hoped that a substantial decrease in pK_a would be observed in transforming **9a** into **9b**. Moreover, the ready formation of extended quinones[4] (either chemically or electrochemically) derived from colored diphenolic analogues of **1** indicated the lack of any obvious impediment to a quinonoid-type resonance form.

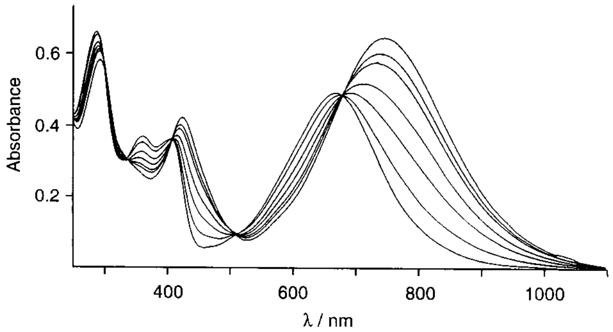


Figure 6. Absorption spectra of **9b** (2.5×10^{-5} M, 5:2 methanol/water) at pH′ values of 12.15, 10.22, 9.97, 9.56, 9.19, 8.66 and 7.99 used to determine the pK_a′ of **9b**(OH)

Thus, the apparent pK_a values of **9a**(OH) and its closed counterpart **9b**(OH) were determined spectroscopically in 5:2 methanol/water, yielding values of 10.5 and 9.3 (see Figure 6 for the UV-titration spectra of **9b**). While the switching effect is clearly evident, we were somewhat surprised that the increase in dissociation constant upon photocyclization was not more than the observed factor of 16 in the K_a. We interpret this as being due to a poor resonance contribution by the quinonoid form for **9b**(O$^-$). This, in turn, may be rationalized in terms of the cost of disrupting two aromatic rings. The question of the relative importance of the zwitterionic and quinonoid structures in simple biaryl and stilbazolium merocyanines has long been a subject of investigation and intense debate.[19] It is clear, however, that internal charge-cancellation is increasingly disfavored with increasing polarity of the medium, which is the case in the present study. Both the proton NMR spectrum of **9b**(O$^-$) and the hypsochromic shift in going from methanol to methanol/water, are, for the most part, consistent with a charge-separated electronic distribution for the molecule. This suggests that the decrease in pK_a upon the light-induced establishment of conjugation between the acidic group and the pyridinium moiety is largely due to inductive effects. Larger light-induced pK_a changes may be achievable by increasing the acidity of the closed system by the introduction of a stabilizing group of greater acceptor strength.

Finally, the connection between photochemical and chemical ionization properties in the present compounds makes them potentially interesting as components of multiplexing systems based on multiple states generated by the combination of several different functional (photoactive, redoxactive, chemoactive, etc.) features.

Experimental Section

General: Starting materials were commercially available (Aldrich) and were used without further purification. Perfluorocyclopentene (1,2,3,3,4,4,5,5-octafluorocyclopentene) was purchased from Heraceus (Karlsruhe). Tetrahydrofuran, dichloromethane and acetonitrile were distilled from lithium aluminium hydride, phosphorus pentoxide and calcium hydride, respectively. All manipulations involving dithienylethenes (eg. flash chromatography − Kieselgel 60, Merck 230−400 mesh) were carried out so as not to expose the samples to ambient light. − Melting points: Electrothermal 1A9100 digital apparatus (uncorrected). − NMR: Bruker AM 200 SY spectrometer (200.13 MHz, 50.33 MHz and 188 MHz for ^{1}H, ^{13}C and ^{19}F, respectively). For ^{1}H NMR, TMS used as internal standard for CDCl$_3$, δ_C = 77.00; [D$_4$]methanol δ_H = 3.30, [D$_6$]DMSO δ_H = 2.49, [D$_6$]benzene δ_H = 7.26, [D$_6$]acetone δ_H = 2.05, [D$_8$]THF δ_C = 67.57/25.37. ^{19}F NMR chemical shifts and coupling constant data are provided in Table 3. External C$_6$H$_5$CF$_3$ in CDCl$_3$, assigned a value of δ_F = + 63.00, was used as the reference. − UV: Perkin−Elmer 554 and Beckman DU 640 spectrophotometers (spectrograde solvents). Ultraviolet absorption data are provided in Table 2. − MS: Chemical ionization (CI) mass spectrometry was carried out by the Laboratoire de Chimie Structural 1, ERS 73 (Paris) using a NERMAG R30−10 triple quadrapole spectrometer. Negative-ion electrospray (ES) mass spectra were obtained on a Fisons Model VG Platform II instrument by ISSI Laboratories, Inc. (Piscataway, NJ, USA). Elemental analyses were determined by the Service Régional de Microanalyse, Université M. & P. Curie (Paris).

1-[2′-Methyl-5′-(4′′-pyridyl)thien-3′-yl]perfluorocyclopentene (4): To a stirred solution of bromothiophene **2** (4.18 g, 16.4×10^{-3} mol) in 240 mL of freshly distilled tetrahydrofuran was added a solution of *n*-butyllithium (12.4 mL, 1.4 M in hexane, 17.3×10^{-3} mol) at −78 °C under a nitrogen atmosphere. After 10 min, perfluorocyclopentene (2.1 mL, 16×10^{-3} mol) was added with a cooled syringe. (Note: Due to the low boiling point of the fluorinated cycle, the reagent was previously transferred with a double-tipped needle to a small, dried bottle which was sealed with a septum. Prior to the addition, the bottle was cooled to −78°C under nitrogen. A gas-tight syringe was then placed in a stoppered test-tube and cooled in a freezer. The addition was carried out as quickly as possible to ensure that condensed water was not introduced into the reaction.) After an additional hour of stirring, the reaction was allowed to warm to ambient temperature and then quenched with 30 mL of hydrochloric acid (1.2 N). The solvents were removed *in vacuo* and the resulting tar was extracted twice with 200 mL of dichloromethane and washed twice with 200 mL of saturated aqueous sodium hydrogencarbonate. The combined organic phases were then dried over magnesium sulfate, filtered and evaporated to a brown tar. Flash chromatography over silica gel with dichloromethane/ethyl ether (1:1) as the eluent afforded 2.04 g of the monoadduct **4** (36%) as a pale yellow syrup. − ^{1}H NMR ($CDCl_3$): δ = 2.50 (d, $J_{H2',F2}$ = 3.0 Hz, 3 H, 2′-Me), 7.40 (A of AA′BB′, J_{app} = 6.2 Hz, 2 H, H-3″,5″), 7.43 (s, 1 H, H-4′), 8.60 (B of AA′BB′, J_{app} = 6.2 Hz, 2 H, H-2″,6″). − ^{13}C NMR ($CDCl_3$): δ = 14.62 (d, *J* = 5.0 Hz, 2′-CH_3), 119.49 (C-3″,5″), 120.85 (C-3′), 124.53 (C-4′), 139.30 (C-2′), 140.00 (C-5′), 145.08 (C-4″), 150.43 (C-2″,6″). − MS (CI, NH_3); *m/z* (%): 367 (M^+, 80), 348 (8) [M^+ − F], 317 (22) [M^+ − CF_3], 296 (71), 286 (16) [M^+ − C_2F_3], 258 (24), 244 (68), 186 (41), 174 (12) [M^+ − C_5F_7], 91 (100); exact mass $C_{15}H_8F_7NS$: calcd. 367.0266, found 367.0265.

1-[5′-(4″-Methoxyphenyl)-2′-methylthien-3′-yl]perfluorocyclopentene (5): The bromothiophene **3** (1.80 g, 6.36 × 10^{-3} mol) was lithated and treated with perfluorocyclopentene (850 μL, 6.4 × 10^{-3} mol) in anhydrous tetrahydrofuran as described above for the preparation of compound **4**. The usual workup and chromatography over silica gel with hexane/dichloromethane (5:1) as the eluent provided 671 mg of the monoadduct **5** (36%), colorless crystals, m.p. 65.5−66°C. − ^{1}H NMR ($CDCl_3$): δ = 2.46 (d, $J_{H3',F2}$ = 3.2 Hz, 3 H, 2′-Me), 3.84 (s, 3 H, OMe), 6.92 (A of AA′BB′, J_{app} = 8.8 Hz, 2 H, H-2″,6″), 7.13 (broad s, 1 H, H-4′), 7.47 (B of AA′BB′, J_{app} = 8.8 Hz, 2 H, H-3″,H-5″). − ^{13}C NMR ($CDCl_3$): δ = 14.48 (d, *J* = 5.0 Hz, 2′-Me), 55.30 (OMe), 114.40 (C-3″,5″), 120.20 (C-3′), 121.16 (C-4′), 125.94 (C-1″), 127.01 (C-2″,6″), 141.91 (C-2′), 142.48 (C-5′), 159.63 (C-4″). − MS (CI, NH_3); *m/z* (%): 397 (100) [MH^+], 381 (18) [MH^+ − CH_4], 353 (8). − $C_{17}H_{11}F_7OS$ (396.33): calcd. C 51.52, H 2.80; found C 51.75, H, 2.80.

1-[5′-(4″-Methoxyphenyl)-2′-methylthien-3′-yl]-2-[2′′′-methyl-5′′′-(4′′′′-pyridyl)thien-3′′′-yl]perfluorocyclopentene (6). − From 4: To a stirred solution of anisidylthiophene 3 (1.34 g, 4.73 × 10^{-3} mol) of in 50 mL of freshly distilled tetrahydrofuran was added *n*-butyllithium (1.5 M in hexane, 3.2 mL, 4.8 × 10^{-3} mol) at −78°C under a nitrogen atmosphere. After 10 min, a solution of cyclopentene 4 (1.50 g, 4.08 × 10^{-3} mol) in 15 mL of anhydrous tetrahydrofuran was added (by double-tipped needle) to the reaction, which was then stirred in the dark. After 1 h, the solution was allowed to warm to ambient temperature (over 30 min) and 5 mL of 1.2 N hydrochloric acid was added. The solvents were then removed *in vacuo* and the residue extracted twice with 200 mL of dichloromethane and washed twice with 200 mL of saturated aqueous sodium hydrogencarbonate. The combined organic phases were dried over magnesium sulfate, filtered and evaporated to yield a brown syrup which was chromatographed over silica gel with dichloromethane/ethyl acetate (8:1 to 4:1) as the eluent to give 1.60 g of the unsymmetrical photochrome 6 (71%) as a pale green syrup. − **From Cyclopentene 5:** The bromothiophene **2** (402 mg, 1.58 × 10^{-3} mol) was lithiated and coupled to cyclopentene **5** (570 mg, 1.44 × 10^{-3} mol) in a manner identical to that described above to give 515 mg of photochrome **6** (65%) as a pale green syrup. − ^{1}H NMR ($CDCl_3$): δ = 1.94 (s, 3 H, 2′-Me), 2.00 (s, 3 H, 2′′′-Me), 3.84 (s, 3 H, OMe), 6.92 (A of AA′BB′, J_{app} = 8.8 Hz, 2 H, H-2″,6″), 7.15 (s, 1H, H-4′), 7.41 (A of AA′BB′, J_{app} = 6.2 Hz, 2 H, H-3′′′′,5′′′′), 7.46 (B of AA′BB′, J_{app} = 8.8 Hz, 2 H, H-3″,5″), 7.48 (s, 1 H, H-4′′′), 8.60 (B of AA′BB′, J_{app} = 6.2 Hz, 2 H, H-2′′′′,H-6′′′′). − MS (CI, NH_3); *m/z* (%): 551 (4) [M^+], 421 (44), 365 (96) and 43 (100); exact mass $C_{27}H_{19}F_6NOS_2$: calcd. 551.0812; found 551.0811.

1-[5′-(4″-Hydroxyphenyl)-2′-methylthien-3′-yl]-2-[2′′′-methyl-5′′′-(4′′′′-pyridyl)thien-3′′′-yl]perfluorocyclopentene (8): Boron tribromide (0.50 mL, 5.3 × 10^{-3} mol) was added to a solution of methyl ether **6** (970 mg, 1.76 × 10^{-3} mol) in 45 mL of dry dichloromethane and the reaction was heated to reflux under a nitrogen atmosphere in the dark. After 4 h, the reaction was cooled and extracted twice with 100 mL of dichloromethane and washed twice with 200 mL of water. The combined organic phases were then dried over magnesium sulfate, filtered and evaporated *in vacuo* to yield 1.30 g of the deprotected boron tribromide complex **7** as a pale orange solid, which was used without further purification. − ^{1}H NMR ($CDCl_3$): δ = 1.95 (s, 3 H, 2′-Me), 2.11 (s, 3 H, 2′′′-Me), 6.87 (A of AA′BB′, J_{app} = 8.6 Hz, 2 H, H-2″,6″), 7.12 (s, 1 H, H-4′), 7.41 (B of AA′BB′, J_{app} = 8.6 Hz, 2 H, H-3′′,5′′), 7.76−7.81 (m, 3 H, H-3′′′′,5′′′′ and 4′′′), 9.45 (broad s, 2 H, H-2′′′′,6′′′′).

The crude product **7** obtained above was dissolved in 30 mL of methanol, and 30 mL of aqueous sodium hydroxide (33% w/w) was then slowly added. After vigorous stirring in the dark for 24 h at ambient temperature, the mixture was diluted with 100 mL of water and neutralized with concentrated hydrochloric acid. The resulting suspension was extracted twice with 100 mL of ethyl acetate and washed twice with 300 mL of water. The combined organic phases were dried over magnesium sulfate, filtered and the solvent removed *in vacuo* to yield a yellow glass. Chromatography over silica gel, with dichloromethane-ethyl acetate (3.5:1 to 2:1) as the eluent, afforded 772 mg of phenol **8** (82% from **6**) as a pale yellow glass. Crystalline material was obtained by recrystallization from acetone, m.p. 221°C (dec.) − ^{1}H NMR ([D_6]acetone): δ = 2.02 (s, 3 H, 2′-Me), 2.10 (s, 3 H, 2′′′-Me), 6.88 (A of AA′BB′, J_{app} = 8.7 Hz, 2 H, H-2″,6″), 7.29 (s, 1 H, H-4′), 7.47 (B of AA′BB′, J_{app} = 8.7 Hz, 2 H, H-3′′,5′′), 7.60 (A of AA′BB′, J_{app} = 6.2 Hz, 2 H, H-3′′′′,5′′′′), 7.78 (s, 1sH, H-4′′′), 8.58 (B of AA′BB′, J_{app} = 8.7 Hz, 2 H, H-2′′′′,H-6′′′′), 8.64 (s, exchangeable, 1 H, -OH). − ^{13}C NMR ([D_8]THF): δ = 15.78 and 15.98 (2′-CH_3 and 2′′′-CH_3), 117.93 (C-3′′,5′′), 121.47 (C-3′′′′,5′′′′), 122.84 (C-4′), 126.94 (C-1′′), 127.36 (C-4′′′), 127.61 (C-3′′′), 128.60 (C-3′), 129.06 (C-2′′,6′′), 141.76 (2C) and 142.14 (C-2′, 2′′′ and 5′′′), 145.64 and 145.90 (C-5′ and 4′′′′), 152.76 (C-2′′′′,6′′′′), 160.28 (C-4″). − MS (CI, NH_3); *m/z* (%): 537 (42) [M^+], 43 (100). − $C_{26}H_{17}F_6NOS_2$ (537.55): calcd. C 58.10, H 3.19, N 2.60; found C 58.37, H, 3.45, N 2.47.

1-[5′-(4″-Hydroxyphenyl)-2′-methylthien-3′-yl]-2-{2′′′-methyl-5′′′-[*N*-(3′′′′′-oxysulfonyl propyl)-pyrid-4′′′′-yl]thien-3′′′-yl}-per-fluorocyclopentene (1a): A mixture of pyridine 8 (120 mg, 0.223 × 10^{-3} mol) and 1,3-propane sultone (40 μL, 0.46 × 10^{-3} mol) of in 2.5 mL of anhydrous acetonitrile was heated to reflux under a nitrogen atmosphere in the dark, resulting in the dissolution of the starting materials and the rapid appearance of a precipitate. After 20 h, the reaction was cooled and the resulting fine solid was filtered and washed repeatedly with acetone and dichloromethane to give 136 mg of the alkylated product 1a(OH) after drying *in vacuo* (92%) as a pale yellow powder, m.p. >300°C (dec.), darkens at 220°C. − ^{1}H NMR (CD_3OD): δ = 2.00 (s, 3 H, 2′-Me), 2.15 (s, 3 H, 2′′′-Me), 2.42 (quint., J_{app} = 6.9 Hz, 2 H, H-2′′′′′), 2.86 (t, *J* = 6.7 Hz, 2 H, H-3′′′′′), 4.73 (t, *J* = 7.1, 2 H, H-1′′′′′), 6.79 (A of

AA′BB′, J_{app} = 8.6 Hz, 2 H, H-2″,H-6″), 7.14 (s, 1 H, H-4′), 7.38 (B of AA′BB′, J_{app} = 8.6 Hz, 2 H, H-3′′,H-5′′), 8.15 (s, 1 H, H-4′′′), 8.25 (A of AA′BB′, J_{app} = 7.0 Hz, 2 H, H-3′′′′,H-5′′′′), 8.85 (B of AA′BB′, J_{app} = 7.0 Hz, 2 H, H-2′′′′,H-6′′′′. − ^{1}H NMR ([D$_6$]DMSO): δ = 9.74 (1H, broad s, exchangeable, -OH). − MS (ES, neg. ion); *m/z* (%): 658 (100) [M − H]$^-$, 536 (35) [(M − H)$^-$ − (CH$_2$)$_3$SO$_3$]. − C$_{29}$H$_{23}$F$_6$NO$_4$S$_3$·H$_2$O (677.71): calcd. C 51.40, H 3.72, N 2.07; found C 51.30, H, 3.71, N 2.01.

Photochemical Preparation of 1-[5′-(4″-Hydroxyphenyl)-2′-methylthien-3′-yl]-2-{2′′′-methyl-5′′′-[*N*-(3′′′′′-oxysulfonylpropyl)pyrid-4′′′′-yl]thien-3′′′-yl}-3,3-dimethoxy-perfluorocyclopentene (9a) and Its Closed Isomer (9b): A solution of photochrome 1a (2.4 mg) in 2 mL of methanol was placed in a 5 mm quartz NMR tube and irradiated with UV light of 365 nm for 1.5 h, resulting in complete cyclization. The sample was then transferred to a round-bottom flask and excess base (saturated methanolic potassium hydroxide) was then added. After brief stirring, the solution was acidified with a stream of hydrogen chloride gas and then evaporated *in vacuo* to give a dark blue-green solid. After each manipulation, an aliquot was diluted and the UV spectrum recorded. The product was then taken up in [D$_4$]methanol, the potassium chloride filtered off and the NMR spectrum of the closed form 9b(OH) recorded. − ^{1}H NMR ([D$_4$]methanol): δ = 2.14 and 2.20 (two s, 6 H, 2′-Me and 2′′′-Me), 2.44 (quint, J_{app} = 7 Hz, 2 H, H-2′′′′′), 2.87 (t, J = 7 Hz, H-3′′′′′), 3.38 (s, 3 H, OMe), 3.52 (fine d, J = 1.2 Hz, 3 H, OMe), 4.77 (t, J = 7 Hz, 2 H, H-1′′′′′), 6.83 (s, 1 H, s, H-4′), 6.84 (A of AA′BB′, J_{app} = 8.7, 2 H, H-2″,6″), 7.43 (s, 1 H, H-4′′′), 7.50 (B of AA′BB′, J_{app} = 8.7, 2 H, H-3′′,5′′), 8.17 (A of AA′BB′, J_{app} = 6.9, 2 H, H-3′′′′,5′′′′), 8.90 (B of AA′BB′, J_{app} = 6.9, 2 H, H-2′′′′,6′′′′). − MS (ES, neg. ion); *m/z* (%): 682 (100) [M − H]$^-$, 636 (44) [(M − H)$^-$ − (CH$_3$)$_2$O], 560 (32) [(M − H)$^-$ − (CH$_2$)$_3$SO$_3$]. − A solution of closed photochrome was prepared as described above and was then irradiated in a 10 mm cuvette with visible (red) light of wavelength >600 nm for 2 h. Removal of the solvent *in vacuo* afforded the open photochrome **9a**(OH) as a pale yellow solid. ^{1}H NMR ([D$_4$]methanol): δ = 1.96 (s, 3 H, 2′-Me), 2.10 (s, 3 H, 2′′′-Me), 2.42 (quint, J_{app} = 6.9 Hz, 2 H, H-2′′′′′), 2.86 (t, 2 H, J_{app} = 6.9 Hz, H-3′′′′′), 3.41 (s, 6 H, 2 × OMe), 4.71 (t, 2 H, J = 7 Hz, H-1′′′′′), 6.79 (A of AA′BB′, J_{app} = 8.6 Hz, 2 H, H-2″,6″), 7.29 (s, 1 H, H-4′), 7.37 (B of AA′BB′, J_{app} = 8.6 Hz, 2 H, H-3′′,5′′), 7.95 (s, 1 H, H-4′′′), 8.18 (A of AA′BB′, J_{app} = 6.9 Hz, 2 H, H-3′′′′,5′′′′), 8.81 (B of AA′BB′, J_{app} = 6.9 Hz, 2 H, H-2′′′′,6′′′′).

Determinations of pK_a: pH measurements were carried out using a Tacussel Electronic pH meter equipped with an Ingold electrode without correction for the difference in electrode solvent and the measured solutions.

A solution of **1a**(OH) in 5:2 methanol/water (2.5 × 10^{-5} M, 2 mL) at pH′ 3.0 (HCl) was irradiated in a 10 mm cuvette with light of 365 nm. After complete coloration of the sample, aqueous potassium hydroxide (35 μL, 2.0 N solution) was then added to convert **1b**(OH) into **9b**(O$^-$), the final pH′ value being *ca.* 13. Small volumes of HCl gas were then passed through the solution and the pH′ values and UV spectra recorded. For the open form, a solution of **9b**(O$^-$) in 5:2 methanol/water was prepared in the same manner and the pH′ of the sample raised to *ca.* 14, followed by irradiation of the sample with visible (red) light of wavelength >600 nm. The resulting solution of **9a**(O$^-$) was then titrated as described above. The apparent pK_a values were calculated by the relationship: pK_a = pH − log([A$^-$]/[HA]) by using the values of [A$^-$] and [HA] derived from the spectral data.

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