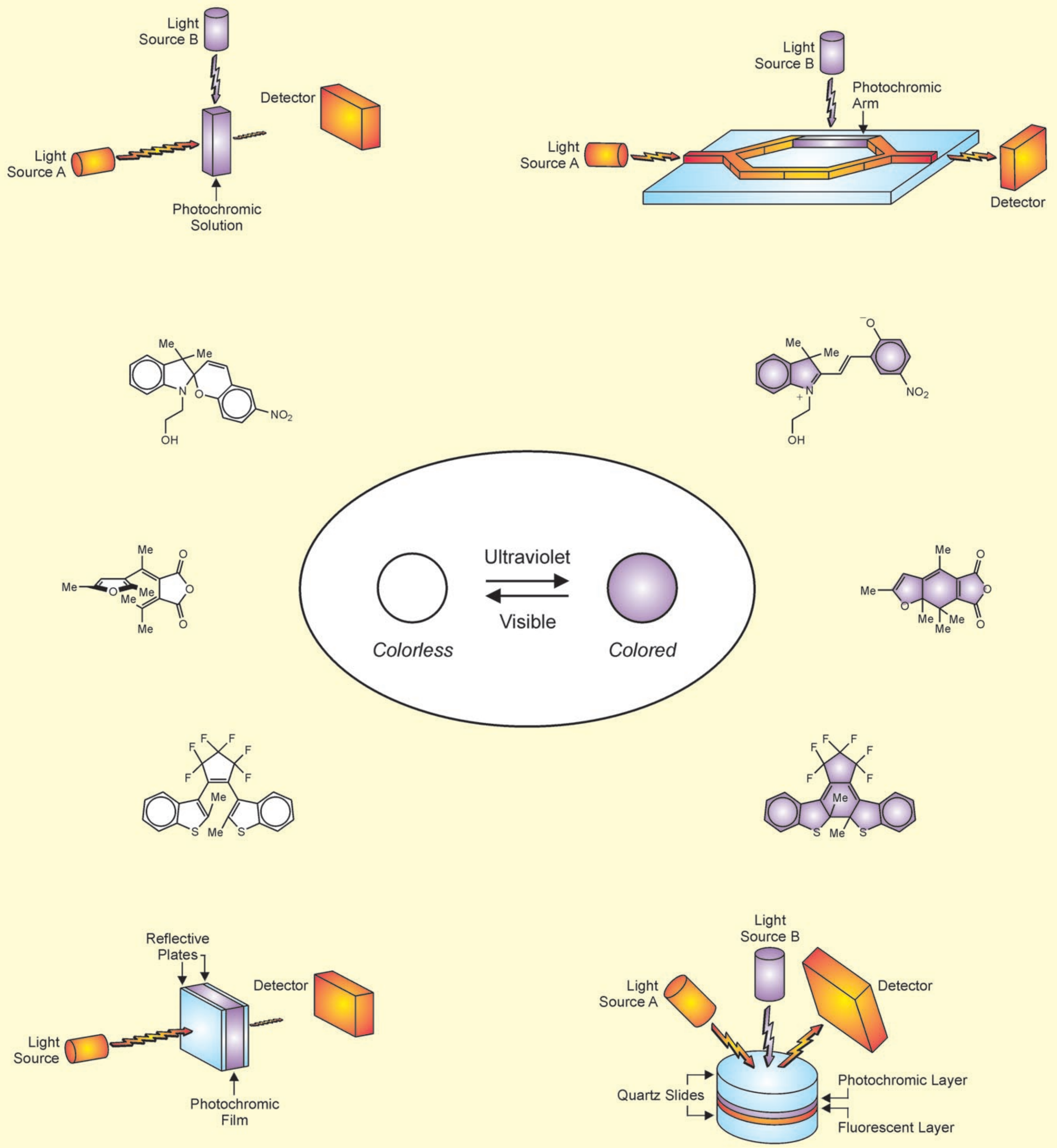
# Photochromic Switches



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# Optical Processing with Photochromic Switches

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**Abstract:** The absorbance, fluorescence, and refractive index of a photochromic material can be modulated under the influence of optical stimulations. The reversible modification of these macroscopic properties is a result of photoinduced transformations at the molecular level. These processes can be exploited to mediate the interplay of optical signals and offer the opportunity to design and implement photonic devices for optical processing based on molecular components.

**Keywords:** fluorescence • isomerization • molecular devices • photochemistry • photochromism

## Photochromic Compounds

Photochromic compounds change color in response to optical stimulations.[1–5] In most instances, they switch from a colorless to a colored state. Though less common, the opposite transformation is also possible. In fact, the terms "positive" and "negative" photochromism are generally used to indicate photoinduced coloration and decoloration processes, respectively. Both transformations, however, must be reversible by definition. Indeed, the photogenerated state of a photochromic compound must be able to switch back to the original one either thermally, once irradiation is terminated, or photochemically, upon illumination at a different wavelength.

The photoinduced and reversible coloration or decoloration of a photochromic compound is generally a result of unimolecular reactions. In particular, ring-closing and -opening steps, *cis*→*trans* and *trans*→*cis* isomerizations, and intramolecular proton-transfer processes have all been invoked to operate photochromic molecules. Alternatively, photochromic transformations can be designed around certain bimolecular reactions. For example, photoinduced cycloadditions and intermolecular electron-transfer processes have both been used successfully in this context.

Photochromic compounds can be operated in liquid solutions, within rigid polymer matrices, and, often, even in the absence of a solvent in amorphous form or crystalline state. In all instances, the associated transformations impose significant electronic changes at the molecular level. In turn, these modifications alter the ability of the photoresponsive species to absorb visible radiation and even their emissive behavior and redox response. Furthermore, these processes can also modify the structure and shape of photochromic compounds and, therefore, alter their dipole moments and polarizabilities. The photoregulation of this broad collection of *molecular* properties translates into profound modifications of *macroscopic* properties. Most noticeably, the color and refractive index of either liquid or solid materials incorporating photochromic compounds can both be modulated effectively under the influence of optical stimulations. As a result, photochromic materials can mediate the interplay of optical signals on the basis of absorptive and dispersive effects, offering the opportunity to control light with light.[6] Indeed, a diversity of operating principles for optical processing have been designed around the unique properties of photochromic materials over the past four decades.[7–9] In this article, we provide a general overview of these mechanisms for the manipulation of optical signals by illustrating representative protocols and configurations to photoregulate the intensities of radiation transmitted through or emitted by photochromic materials.

## Transmittance Modulation

The pronounced absorbance changes associated with the reversible interconversion of photochromic compounds can be exploited to modulate the transmittance of liquid or solid materials.[7–9] For example, the absorption spectrum (**a** in Figure 1) of a solution of the colorless spiropyran **1** in aceto-

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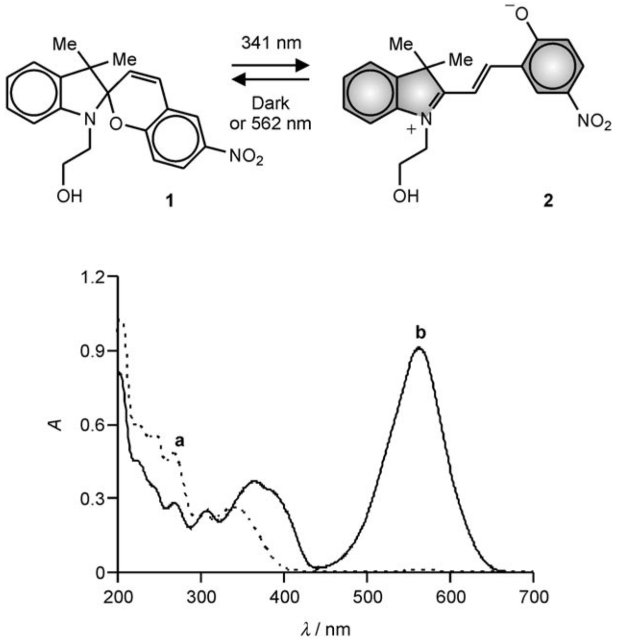


Figure 1. Absorption spectra of a solution of **1** in acetonitrile recorded before (**a**) and after (**b**) irradiation at 341 nm.

nitrile shows bands in the ultraviolet region only.[10] However, a strong absorption band appears at approximately 560 nm (**b** in Figure 1) after continuous irradiation at 341 nm. The photoinduced formation of the colored merocyanine **2** is responsible for the significant absorbance changes in the visible region. The colored isomer **2** reverts to the colorless form **1** in the dark or even after irradiation at 562 nm. In both instances, the original absorption spectrum is fully restored. As a result, the transmittance of the photochromic solution at 560 nm can be modulated simply by turning an ultraviolet source on and off. It follows that a monochromatic beam with a wavelength of 560 nm traveling from a visible source (light source A in Figure 2) through the photochromic solution to a detector can be switched under the influence of an ultraviolet input (light source B).[11] When the input is off, the monochromatic beam propagates through the colorless state of the photochromic solution and the intensity transmitted to the detector is high. When the input is on, the photogenerated colored state of the solution absorbs the incident light at 560 nm and the transmitted output is low. Thus, the photochromic element imposes an inverse relation between the incident input and the transmitted output: when the former is off the latter is high and vice versa. Of course, the very same input–output correlation can be replicated essentially with any photochromic compound operating in solution and even with films of photochromic proteins.[12] Furthermore, this particular input–output correlation is equivalent to the logic operation executed by a NOT gate.[13] Indeed, the binary output of a NOT gate is 1 only when its input is 0 and vice versa. In fact, collections of independent photochromic solutions can be operated either in parallel or in series with discrete ultraviolet inputs to implement a variety of all-optical logic functions relying on the general mechanism for transmittance modulation illustrated in Figure 2.[11,14,15]

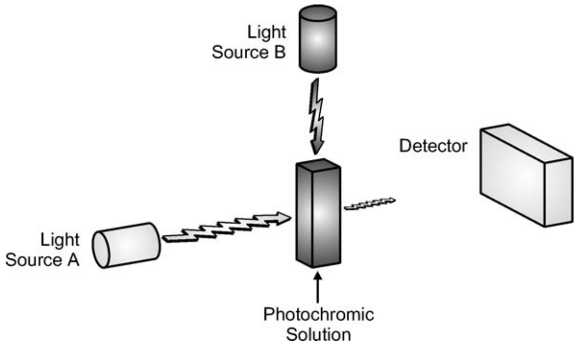


Figure 2. Light source A sends a monochromatic beam through the photochromic solution to the detector. Light source B induces the photochromic transformation and, as a result, controls the intensity of the radiation transmitted to the detector.

Photochromic transformations often cause significant refractive-index modifications in parallel to the characteristic absorbance changes.[7–9] The reversible alteration of both parameters can be exploited to modulate the transmittance of a Fabry–Perot interferometer (Figure 3).[16] This particular device is composed of two partially transmitting and reflecting plates parallel to each other and separated by a fixed distance ($l$). An incident radiation can partially be transmitted through the two plates only when its wavelength ($\lambda$) satisfies Equation (1), in which $m$ is an integer number.

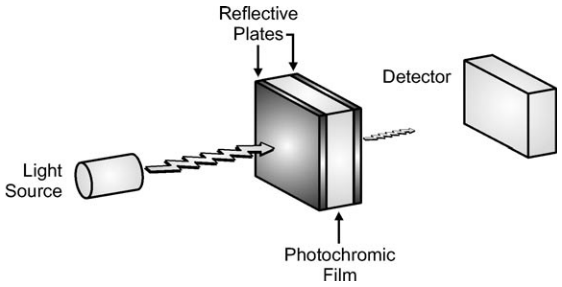


Figure 3. The light source sends a monochromatic beam through a photochromic film, sandwiched between the two reflective plates of a Fabry–Perot interferometer, to the detector.

$$m\lambda = 2l \tag{1}$$

Under these conditions, multiple reflections on the opposing faces of the two plates lead to constructive interference and ensure the partial transmission of radiation out of the interferometer cavity. When Equation (1) is not satisfied, destructive interference prevents the transmission of radiation through the interferometer cavity. Thus, a Fabry–Perot interferometer is essentially a filter that allows the passage of radiations at discrete wavelengths only.

The transmitted intensity of a Fabry–Perot interferometer increases linearly with the incident intensity, when the medium between the two plates cannot absorb the propagating radiation and its refractive index does not vary with the incident intensity.[16,17] Instead, the correlation between incident and transmitted intensities deviates from linearity when a photochromic material fills the interferometer cavity.[18–20] The photoinduced absorbance and refractive-index changes associated with the photochromic transformation are responsible for the nonlinear response. For example, the irradiation of a polymethylmethacrylate film doped with the fulgide **3** at 366 nm causes the appearance of a band in the visible region of the absorption spectrum (**a** and **b** in Figure 4) and a concomitant increases in refractive index (**c**).[19] The photoinduced formation of the colored isomer **4** is responsible for these changes. The photogenerated species **4** is thermally stable, but reverts to the colorless form **3** upon irradiation at 515 nm. In fact, the simultaneous irradiation at both wavelengths ensures the continuous interconversion of **3** and **4**. The process can be reproduced in the cavity of a Fabry–Perot interferometer tuned to transmit radiation at 515 nm and irradiated simultaneously with a 366 nm source of constant intensity and a 515 nm source of variable intensity. Under these conditions, the absorbitive and dispersive effects associated with the photochromic transformation impose a hysteresis loop (**d** in Figure 4) on a plot of the interferometer transmittance at 515 nm against the incident intensity at the same wavelength. The differential gain in the forward scan of the loop can be exploited to implement logic operations and to interconnect cascades of identical interferometers.[21,22] Furthermore, the forward and backward scans show that two distinct transmittance values are possible at the very same incident intensity in the loop region. This noticeable bistability could, in principle, form the basis for the implementation of memory devices.

The reversible changes in absorbance and refractive index associated with a photochromic transformation can also be exploited to regulate the output intensities of a variety of photonic devices with diverse configurations.[23–28] For example, a Mach–Zender interferometer[16] (Figure 5) can be operated on the basis of these mechanisms.[23,26b,c,27] In this particular device, a monochromatic radiation splits into two equivalent beams, which recombine after passing through two separate arms. When the two arms have the same refractive index, the two propagating beams meet in phase and interfere constructively. A modification of the refractive index in one arm relative to the other can de-phase the two propagating beams and ensure their destructive interference. Thus, the modulation of the refractive index in one arm translates into the regulation of the intensity transmitted out of the interferometer. In fact, the photoinduced interconversion of a photochromic compound in one of the two arms can be exploited to control the refractive index and, as a result, the transmitted intensity.

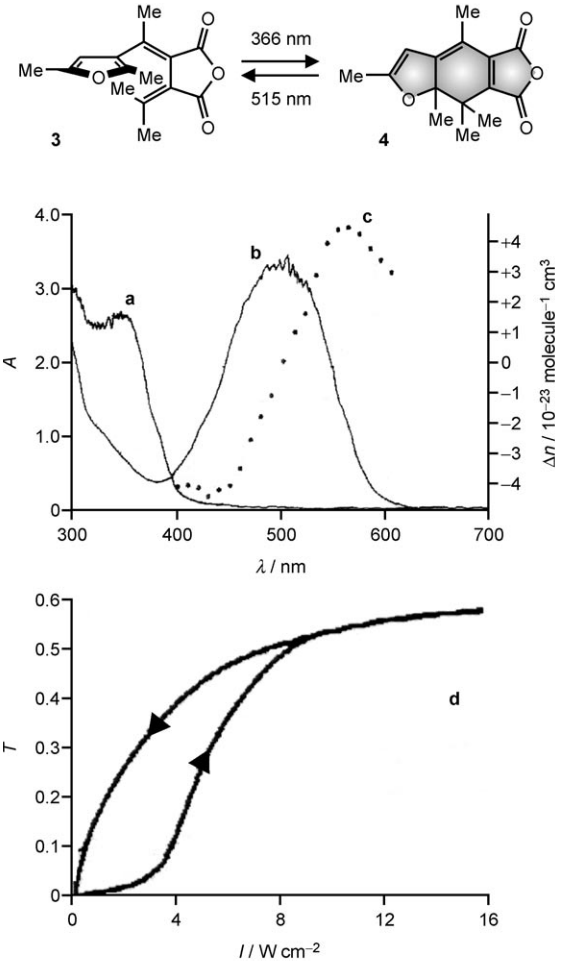


Figure 4. Absorption spectra of a polymethylmethacrylate film doped with **3** recorded before (**a**) and after (**b**) irradiation at 366 nm and the associated change in refractive index (**c**). Correlation between the transmittance at 515 nm of a Fabry–Perot interferometer, incorporating a polymethylmethacrylate film doped with **3** between its reflective plates, and the incident intensity at the same wavelength (partially reproduced with permission from reference [19a]).

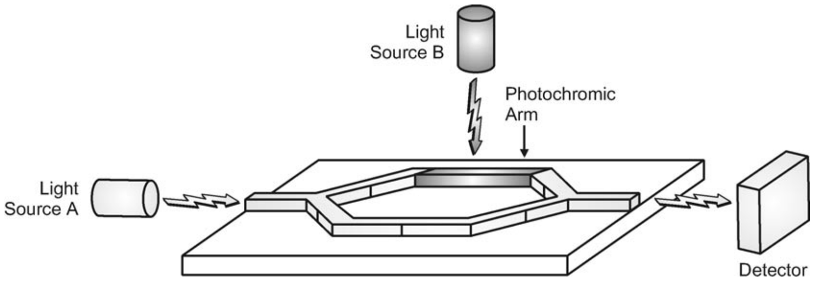


Figure 5. Light source A sends monochromatic radiation through a Mach–Zender interferometer to a detector. The radiation splits into two equal beams, which propagate through two waveguide arms and recombine before leaving the device. Light source B regulates the refractive index of the photochromic arm and the interference of the two beams.

The photochromic diarylethene **5** can be switched to the colored isomer **6** within a rigid polycarbonate matrix by irradiating the material at 365 nm.[26b,c] The photoinduced isomerization alters significantly the absorption spectrum (**a** and **b** in Figure 6) and the refractive index (**c** and **d**) of the polymer film. The original state is, however, restored upon illumination at 515 nm. Thus, the refractive index of this photochromic material can easily be modulated by alternating ultraviolet and visible irradiation. Relying on conventional photolithographic, dry-etching, and spin-coating techniques, the waveguides of a Mach–Zender interferometer can be patterned in a film of this dye–polymer composite deposited on a silicon wafer. The resulting assembly, with the exception of one of the two interferometer arms, can then be covered with a thick gold layer. Under these conditions, the reversible isomerization of the photochromic dopant occurs only within the exposed arm under consecutive ultraviolet and visible irradiation steps. It follows that the intensity of a beam with a wavelength of 1.55 μm propagating from light source A (Figure 5) through the device to the detector is modulated by the refractive-index changes associated with the photochromic transformation and induced by light source B.

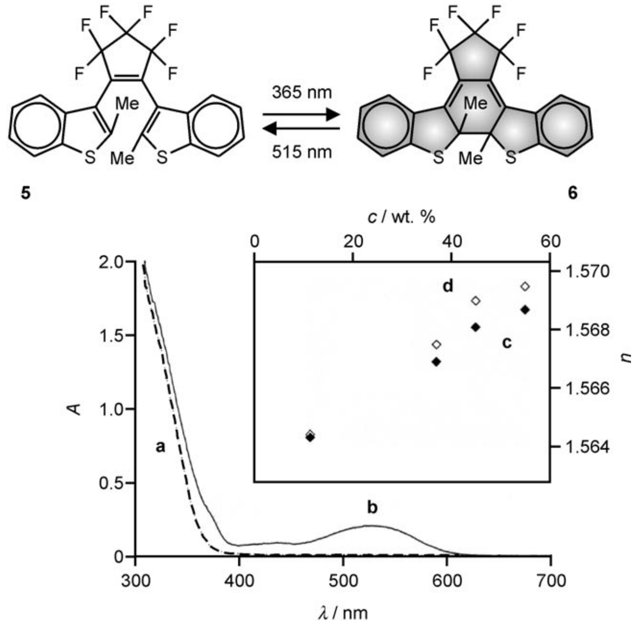


Figure 6. Absorption spectra and refractive index of a polycarbonate film doped with **5** before (**a** and **c**) and after (**b** and **d**) irradiation at 365 nm (partially reproduced with permission from reference [26c]).

## Fluorescence Modulation

The stereoelectronic transformations associated with photochromic processes often alter the ability of the interconverting species to emit light.[9,29,30] Under these conditions, the photoinduced and reversible isomerization from one form to the other results in the efficient modulation of the fluorescence intensity. Furthermore, the photochromic transformation and the excitation of the fluorescent isomer can both occur as a result of two-photon absorption.[31] For example, the simultaneous absorption of two photons of appropriate wavelengths can excite the non-emissive isomer of a photochromic system, encouraging its transformation into the emissive one. At this point, a second two-photon absorption process can excite the fluorescent species and encourage its emission. It follows that two consecutive two-photon excitation processes can be exploited to define (write) and identify (read) the state of a photochromic compound. Indeed, the combination of the unique properties of photochromic compounds and the spatial resolution of two-photon processes offers the opportunity to develop three-dimensional optical memories.

Compound **7** (Figure 7) is a promising candidate for the development of optical storage media based on these operating principles.[32] This molecule combines a photochromic fulgide and a fluorescent oxazine within its skeleton. In 1-propanol, the local excitation of the oxazine component at 650 nm results in emission at 695 nm (**a** in Figure 7). The irradiation of this compound at 400 nm, however, induces the isomerization of the fulgide appendage with the formation

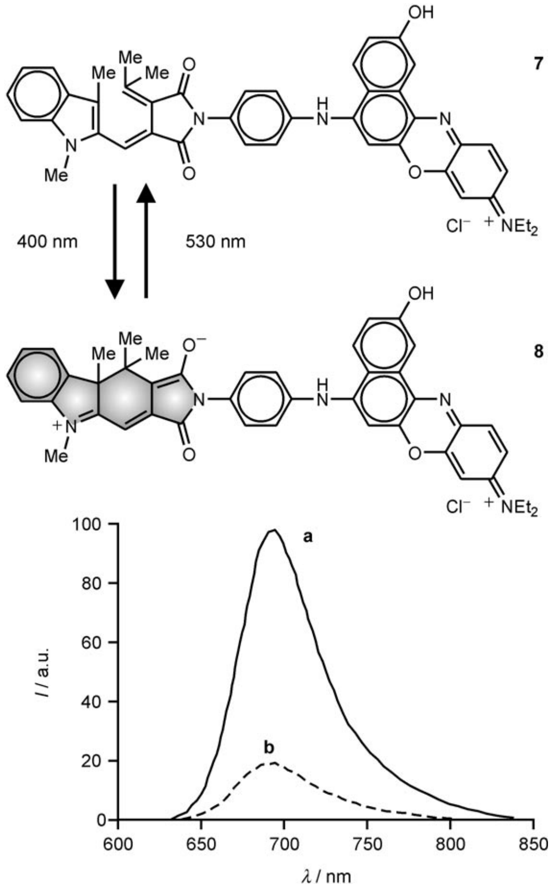


Figure 7. Emission spectra ($\lambda_{ex} = 650$ nm) of a solution of **7** in 1-propanol before (**a**) and after (**b**) irradiation at 400 nm (partially reproduced with permission from reference [32c]).

of **8**. The partial zwitterionic character of the photogenerated fragment alters the local polarity in close proximity to the fluorescent oxazine. As a result of this microenvironmental change, the fluorescence intensity decreases significantly (**b** in Figure 7). The original isomer **7** and its intense emission band can be restored by irradiating the compound at 530 nm. Thus, the state of the photochromic system can be "written" and "erased" by irradiating at 400 and 530 nm, respectively. Furthermore, the written state can be "read" by measuring the fluorescence intensity at 695 nm. Essentially the same processes can be reproduced with polymethylmethacrylate films doped with **7**.[32c] In fact, two orthogonal lasers of appropriate wavelengths can both be focused at any point within the bulk of a doped polymer. The photochromic molecules located at the intersection of the two beams can absorb two photons simultaneously and switch from the fluorescent state **7** to the nonfluorescent form **8** or vice versa. The two lasers can then be refocused on a different spot to write point by point bits of data within the volume of the photochromic material. Alternatively, an entire plane of bits can be written in one step by projecting a predefined pattern through a spatial light modulator with one of the two lasers. Relying on this protocol, hundreds of data layers, each containing submicron-sized bits, can be recorded within millimeter-thick disks of this photochromic material. The written data can then be read nondestructively by illuminating the recorded material at 650 nm, while reading the fluorescence at 695 nm.

The emission intensity of molecular dyads incorporating fluorescent and photochromic components can also be modulated by relying on intramolecular energy transfer.[30] For example, compound **9** (Figure 8) combines an anthracene fluorophore and a diarylethene photochrome within its molecular skeleton.[33] In toluene, the local excitation of the anthracene component at 488 nm is followed by intense emission at 503 nm. Instead, the irradiation of **9** at 325 nm encourages its transformation into **10**. The photogenerated state of the photochromic appendage absorbs in the wavelength range in which the anthracene fluorophore emits. As a result, intramolecular energy transfer from the excited fluorophore to the photochrome occurs in **10**, quenching the anthracene fluorescence. The original and emissive state, however, is fully regenerated after illumination at 488 nm. The reversible interconversion between the fluorescent state **9** and the non-emissive form **10** can be reproduced in Zeonex films. Furthermore, individual molecules can be imaged by confocal microscopy under these conditions. Indeed, the fluorescence image **a** in Figure 8 shows the emission of four distinct molecules of **9**. After 3 s of continuous irradiation at 325 nm (0.27 mW cm$^{-2}$), the fluorescence response is lost (**b** in Figure 9) as a result of the isomerization from **9** to **10**. The original image is restored after continuous irradiation of the sample at 488 nm (200 W cm$^{-2}$) for 10 s. Thus, this protocol can be employed, in principle at least, to write optically bits of information in individual molecules and to read optically the stored information.

The fluorescent and photochromic components of **10** are covalently connected and the intramolecular transfer of energy from one to the other is responsible for fluorescence quenching. Similar operating principles can be reproduced intermolecularly in solution,[34] as well as in polymer matrices,[35] on the basis of re-absorption effects. Specifically, the photoinduced coloration of a photochromic compound can be exploited to re-absorb the fluorescence of an independent fluorophore, if the photogenerated absorption band of the former overlaps significantly the emission band of the latter. For example, the benzofurazan **11** (Figure 9) in polymethylmethacrylate films emits at 536 nm, after excitation at 450 nm.[35a] The colorless spiropyran **1** in poly-*n*-butylmethacrylate films does not absorb at wavelengths longer than 400 nm. After irradiation at 341 nm, **1** switches to the colored isomer **2**. This species does not absorb at wavelengths at which **11** is excited, but absorbs in the wavelength range at which **11** emits. Thus, the photoinduced formation of **2** can be exploited to re-absorb and, therefore, attenuate the fluorescence of **11** within the device configuration of Figure 9. In this multilayer assembly, two micrometer-thick polymer films doped with the fluorophore **11** and the photochrome **1**, respectively, are sandwiched between two quartz plates. An excitation source (light source A) sends a monochromatic beam at 450 nm through the top quartz plate

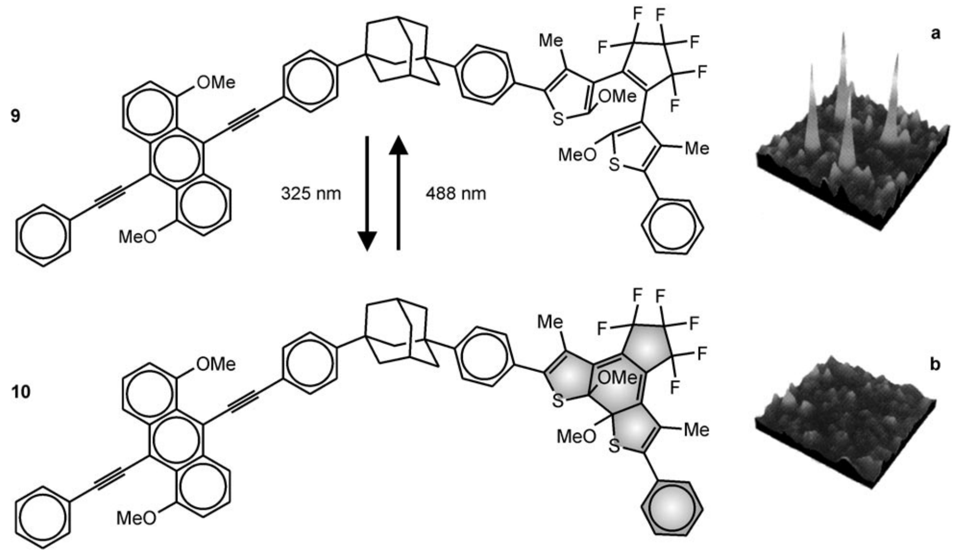
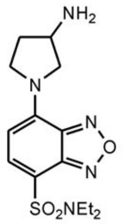


Figure 8. Fluorescence images of **9** in Zeonex films before (**a**) and after (**b**) irradiation at 325 nm (partially reproduced with permission from reference [33a]).



**11**

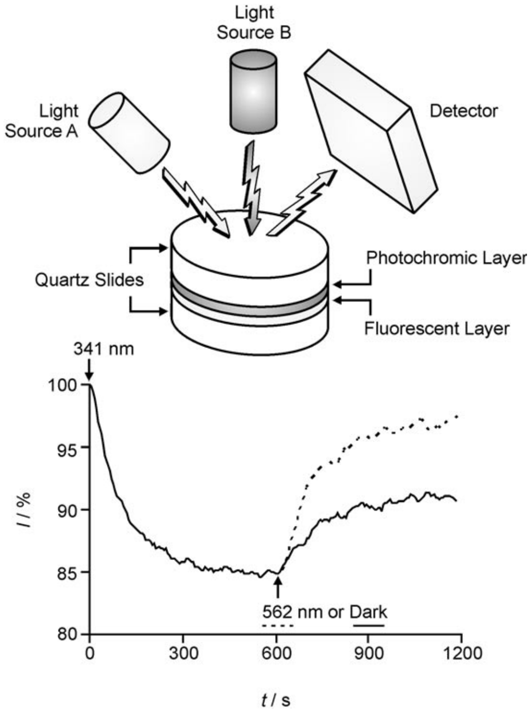


Figure 9. Light source A excites the fluorescent layer, consisting of a polymethylmethacrylate film doped with **11**. The emitted light travels back to the detector after passing through the photochromic layer, which is a poly-*n*-butylmethacrylate film doped with **1**. Light source B controls the state of the photochromic component and, as a result, the detected fluorescence intensity.

and photochromic film to the fluorescence layer. The fluorophore **11** absorbs the incident radiation and emits at 536 nm. The fluorescence travels back through the photochromic layer containing **1** and the top quartz plate to the detector. When the multilayer assembly, however, is illuminated at 341 nm with a second source (light source B), the photochromic dopant switches from **1** to **2**. The photogenerated isomer absorbs the fluorescence and causes a decrease of the detected emission intensity. If light source B is turned off or if its wavelength is changed to 562 nm, the colored isomer **2** switches back to the colorless species **1**. Under these conditions, the fluorescence of **11** cannot be absorbed by the photochromic layer and the detected intensity returns to a high value. The plot in Figure 9 shows the evolution of the detected intensity during a complete switching cycle achieved by turning light source B on and then either switching it off or changing its wavelength from 341 to 562 nm. Thus, this device configuration and choice of materials offer the opportunity to write and read information optically, since light source B defines (writes) the state of the photochromic component and light source A identifies (reads) it through the emission of the fluorescent component.

## Conclusion

The photoinduced and reversible changes in absorbance characteristic of any photochromic transformation can also be accompanied by significant modifications in refractive index. The photoregulation of both parameters can be exploited to control the transmission of electromagnetic radiations through photochromic materials on the basis of absorptive and dispersive effects. The photoinduced coloration of any photochromic solution, for example, can be exploited to absorb and attenuate a visible beam propagating through it, offering the opportunity to control light with light. When operated in the cavity of Fabry–Perot interferometers, photochromic materials impose differential gain and bistability on the transmittance profile. These nonlinear effects permit the implementation of all-optical logic operations, the interconnection of cascades of independent logic elements, and the design of protocols for optical data storage. Furthermore, photochromic transformations can be employed to photoregulate the refractive index in one of the two arms of a Mach–Zender interferometer. The overall result is the optical control of the output intensity with potential implications in the development of all-optical modulators and routers. In addition to radiations transmitted through photochromic materials, the light emitted by photochromic ensembles can also be modulated under influence of optical stimulations. Photoinduced changes in local polarity, intramolecular energy transfer, and re-absorption effects can all be used to regulate the emission intensity of a fluorescent component relying on the interconversion of a photochromic partner. The unique properties of the resulting assemblies have led to the development of three-dimensional optical storage media, as well as to impressive demonstrations of digital switching at the unimolecular level. Although the unique properties of photochromic compounds have indicated viable operating principles for optical processing, it is important to stress that most of the device configurations developed so far using these materials remain at a prototypical stage. Their potential evolution into practical photonic devices continues to demand fundamental investigations on the photochemical and photophysical properties of their molecular components. It is essential to advance our basic understanding on the stereoelectronic factors regulating the fatigue resistances, quantum yields, and switching speeds of these photoresponsive molecules. Only then, will it be possible to adjust these parameters and, eventually, improve the performance of photochromic compounds to generate a set of valuable molecular building blocks for the construction of innovative all-optical devices.

## Acknowledgements

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