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FEATURE ARTICLE

Fluorescence Modulation with Photochromic Switches

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Photochromic compounds change their color under illumination. In most instances, a colorless state switches to a colored one upon ultraviolet irradiation. The photogenerated species reverts to the original one either by thermal means or upon visible irradiation. These reversible transformations are accompanied by pronounced structural and electronic modifications, which often alter the ability of the photochromic compound to emit light. Under these conditions, the photoinduced and reversible interconversion of the colorless and colored states results in the modulation of the fluorescence intensity. Alternatively, fluorescence modulation can be implemented by attaching covalently a fluorescent group to a photochromic compound. Photoinduced changes in the dipole moment or conjugation of the photochromic component can then be designed to alter the emissive behavior of the fluorescent appendage. Similarly, photoinduced shifts in the redox potential or absorption wavelength of the photochromic fragment can be engineered to activate electron or energy, respectively, transfer pathways. Both processes can efficiently quench the fluorescence of the emissive component. Furthermore, the reversible absorption changes of a photochromic compound can effectively filter the emission of a compatible, but separate, fluorophore as long as the emission bands of the latter overlap the absorption bands of one of the two states of the former. When this design requirement is satisfied, fluorescence modulation can be achieved even if the two functional components are operated in distinct environments. Thus, either one of these ingenious mechanisms can be exploited to regulate the emissive behavior of collections of molecules in solution or even in rigid matrixes. In fact, the investigation of these fascinating systems can eventually lead to novel photoresponsive materials for photonic applications, while contributing to advance our basic understanding of the photochemical and photophysical properties of organic compounds.

1. Photochromic Switches

1.1. History. The photoinduced and reversible change in color of certain organic compounds was observed to occur in solution, and even in the solid state, more than a century ago.[1] These fascinating observations date back to the late 1800s, but a term to describe this phenomenon was only coined much later. In the early 1950s, Hirshberg introduced the word "photochromism" to indicate a reversible change in color under illumination.[2] His seminal work and the advent of modern spectroscopic techniques have eventually contributed to evolve these studies from the realm of chemical curiosities into a mature field of research.[3−7] Indeed, the number of publications on photochromism has grown exponentially since then, and photochromic compounds have become convenient building blocks for the construction of a diversity of photoresponsive materials.[8−10]

1.2. Definitions. The term photochromism indicates literally a photoinduced change in color.[11] Rather than the interconversion between two colored forms, however, these transformations generally involve a transition from a colorless to a colored state. Though less common, photoinduced transitions from colored to colorless forms are also possible. Indeed, the definitions "positive photochromism" and "negative photochromism" are often employed to distinguish coloration and decoloration processes, respectively.[1] In any case, a photochromic transformation is always accompanied by profound absorbance changes in the visible region.[12] In fact, visible absorption spectroscopy is the most convenient analytical method to study these processes.

Reversibility is an essential requirement for photochromic transformations.[1] The photoinduced absorbance changes must be reversible by definition. In fact, photochromic compounds can be classified into two broad categories depending on the nature of the reverse process. Both classes share in common the ability to switch from one state to another when irradiated at a fixed wavelength. Thermally stable photochromic compounds retain the photogenerated state even after turning off the illumination source but return to the original form after irradiation at a different wavelength. Thermally reversible photochromic compounds, instead, return to the original state spontaneously when the irradiation is terminated.

Photochromic transformations are generally based on either unimolecular or bimolecular reactions.[1] In most instances, unimolecular photochromic processes involve the interconversion of two isomers. They can be based on photoinduced ring opening/closing, cis/trans isomerizations or intramolecular proton transfer. Bimolecular photochromic processes are less

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common. They rely on either the photoinduced cycloaddition of two identical reactants into a single product or on the photoinduced transfer of an electron from a donor to a complementary acceptor.

1.3. Compounds. Several families of photochromic compounds have been developed since the inception of the field.[3−7] Representative examples are illustrated in Tables 1 and 2.[13−19] Compounds **1**−**4** (Table 1) switch from colorless (isomer **A**) to colored (isomer **B**) states upon ultraviolet irradiation with quantum yields (Φ_1) ranging from 0.1 to 0.4. The photogenerated isomers revert to the original forms once the ultraviolet source is turned off. Their lifetimes (τ) span from only 140 s for **4B** to 14300 s for **3B**. Thus, all four compounds undergo photoinduced coloration and thermal decoloration. The opposite behavior applies to **5**. This species switches from the colored form **5A** to the colorless state **5B**, albeit with a Φ_1 of only 0.04, and returns to the original form thermally with a lifetime greater than 5760 s. The coloration and decoloration of **1** and **3**−**5** are based on ring-opening and -closing reactions, respectively. Instead, **2** relies on trans → cis and cis → trans isomerizations of the central [N═N] bond. All transformation involve substantial structural and electronic changes, which translate into profound modifications of the dipole moment (μ) and molecular polarizability.[20] In particular, μ tends to increase with coloration (Table 1), according to AM1 calculations.[21] This enhancement is especially evident with the transformation of **1A** into **1B** and of **4A** and **4B**. In both instances, the photogenerated isomer has zwitterionic character and μ increase by ca. 4 D.

The colorless compounds **6A** and **7A** (Table 2) switch to their colored isomers **6B** and **7B** after ring-closing reactions. In contrast to **1B**−**5B**, however, the photogenerated states **6B** and **7B** are thermally stable. They revert to the original forms **6A** and **7A** only after visible irradiation. Once again, these reversible transformations are accompanied by profound structural modifications but cause only modest changes in μ (Table 2).

1.4. Photokinetics. The photoinduced coloration of **1**−**4** and decoloration of **5** can be monitored by absorption spectroscopy using pump/probe configurations.[22] Indeed, the two isomers of each photochromic system absorb at distinct wavelengths (λ_1 and λ_2 in Table 1). Hence, these transformations cause an absorbance decrease at λ_1 and increase at λ_2. When the rate constant for the thermal transformation of isomer **A** into **B** and the molar extinction coefficients of isomer **A** at λ_2 and **B** at λ_1 are all negligible, the differential equations (1) and (2) control the evolution of the absorbance at λ_1 (A_1) and λ_2 (A_2) over time (t). According to this kinetic model,[23] the quantum yield (Φ) of the photoisomerization, the intensity (I_0) of the pump beam, the molar extinction coefficients of isomer **A** at λ_1 (ϵ_1) and **B** at λ_2 (ϵ_2), the path length (l) of the probe and pump beams, the rate constant (k) for the thermal re-isomerization and the total concentration (c) of the two isomers regulate the temporal profiles of A_1 and A_2.

$$\frac{\mathrm{d}A_1}{\mathrm{d}t} = \Phi I_0 \epsilon_1 l(10^{-A_1} - 1) + k(\epsilon_1 lc - A_1) \tag{1}$$

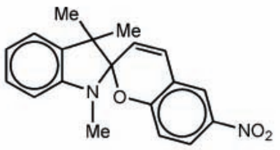
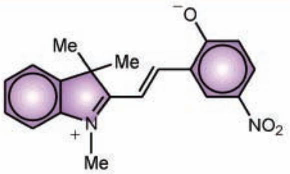
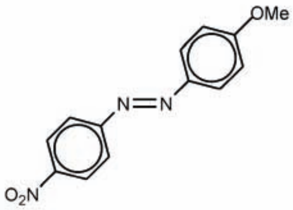
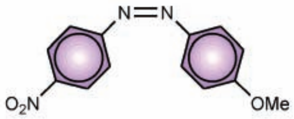
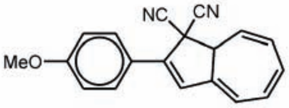
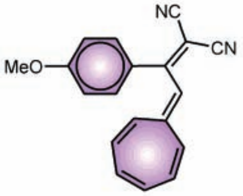
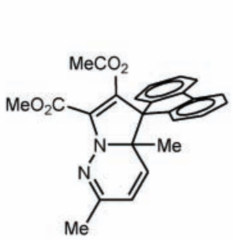
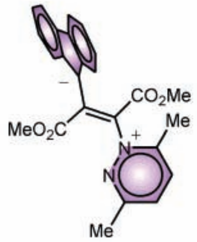
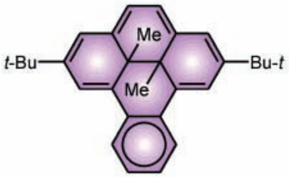
$$\frac{\mathrm{d}A_2}{\mathrm{d}t} = \Phi I_0 \epsilon_2 l[1 - 10^{((A_1\epsilon_1/\epsilon_2) - \epsilon_1 lc)}] - kA_2 \tag{2}$$

The simulated evolutions of A_1 and A_2 for a generic photochromic system are illustrated in Figure 1.[24] The pairs of plots in chart a show that the time required to reach photostationary values of A_1 and A_2 shortens with an increase in Φ. Essentially the same result is obtained with an enhancement in either I_0 or ϵ_1. The actual value of A_1 at the photostationary state is instead controlled by k. Specifically, an increase in k translates into an enhancement of the photostationary value of A_1 (Figure 1b).[25] The opposite trend applies to the photostationary value of A_2, which is also related to c and ϵ_2 and increases with both parameters. Thus, a fine balance of interrelated terms regulates the isomerization kinetics of photochromic compounds. In fact, their switching speeds and degree of coloration/decoloration can be manipulated with the careful adjustment of molecular (Φ, ϵ_1, ϵ_2, and k) and instrumental (I_0 and l) parameters.

2. Fluorescence Modulation

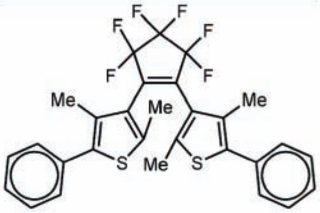
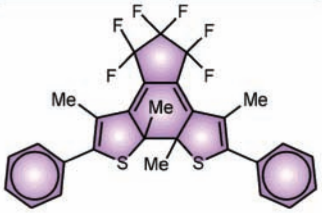
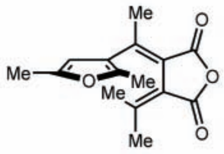
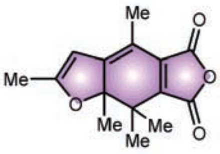
2.1. Fluorescent and Photochromic Compounds. The structural modifications associated with the photoinduced transformation of a photochromic compound can alter the molecule ability to emit light in addition to its absorption behavior.[10,26] In most instances, only one of the interconverting states has a significant fluorescence quantum yield. Under these

TABLE 1: Spectroscopic (λ_1, λ_2, Φ_1, τ)[a] and Structural (μ)[b] Parameters Associated with Representative Examples of Thermally Reversible Photochromic Compounds

	Isomer **A**	Parameters		Isomer **B**	Parameters		Ref.
1		λ_1 (nm)	341		λ_2 (nm)	558	13
		Φ_1	0.1		τ (10^2 s)	4	
		μ (D)	5.4		μ (D)	9.1	
2		λ_1 (nm)	369		λ_2 (nm)	450	14
		Φ_1	0.1		τ (10^3 s)	5	
		μ (D)	7.1		μ (D)	6.5	
3		λ_1 (nm)	360		λ_2 (nm)	465	15
		Φ_1	0.4		τ (10^2 s)	143	
		μ (D)	4.4		μ (D)	6.4	
4		λ_1 (nm)	388		λ_2 (nm)	508	16
		Φ_1	0.4		τ (10 s)	14	
		μ (D)	3.0		μ (D)	6.9	
5		λ_1 (nm)	503		λ_2 (nm)	245	17
		Φ_1	0.04		τ (10 s)	>576	
		μ (D)	0.3		μ (D)	0.1	

[a] Absorption wavelengths of **A** (λ_1) and **B** (λ_2). Quantum yield (Φ_1) for the photoinduced isomerization from **A** to **B**. Lifetime (τ) for the thermal isomerization from **B** to **A**. The spectroscopic data were determined at 25 °C in MeCN for **1** and **3**, in cyclohexane (λ_1, λ_2, τ) for **2**, in EtOH (λ_1, λ_2, τ) or CH_2Cl_2 (Φ_1) for **4** and in cyclohexane for **5**. The Φ_1 of **2** was measured at −30 °C in a mixture of methylcyclohexane and *i*-hexane (2:1, v/v). [b] The dipole moment (μ) was calculated with Gaussian 98 (ref 21) for the optimized geometries (AM1) of the colorless and colored isomers.

TABLE 2: Spectroscopic (λ_1, λ_2, Φ_1, Φ_2)[a] and Structural (μ)[b] Parameters Associated with Representative Examples of Thermally stable Photochromic Compounds

	Isomer **A**	Parameters		Isomer **B**	Parameters		Ref.
6		λ_1 (nm)	234		λ_2 (nm)	534	18
		Φ_1	0.46		Φ_2	0.015	
		μ (D)	3.9		μ (D)	4.0	
7		λ_1 (nm)	350		λ_2 (nm)	487	19
		Φ_1	0.12		Φ_2	0.20	
		μ (D)	7.1		μ (D)	6.6	

[a] Absorption wavelengths of **A** (λ_1) and **B** (λ_2). Quantum yields for the photoinduced isomerization from **A** to **B** (Φ_1) and from **B** to **A** (Φ_2). The spectroscopic data were determined in hexane at 22 °C for **4** and in C_2Cl_4 at 22 °C for **6**. [b] The dipole moment (μ) was calculated with Gaussian 98 (ref 21) for the optimized geometries (AM1) of the colorless and colored isomers.

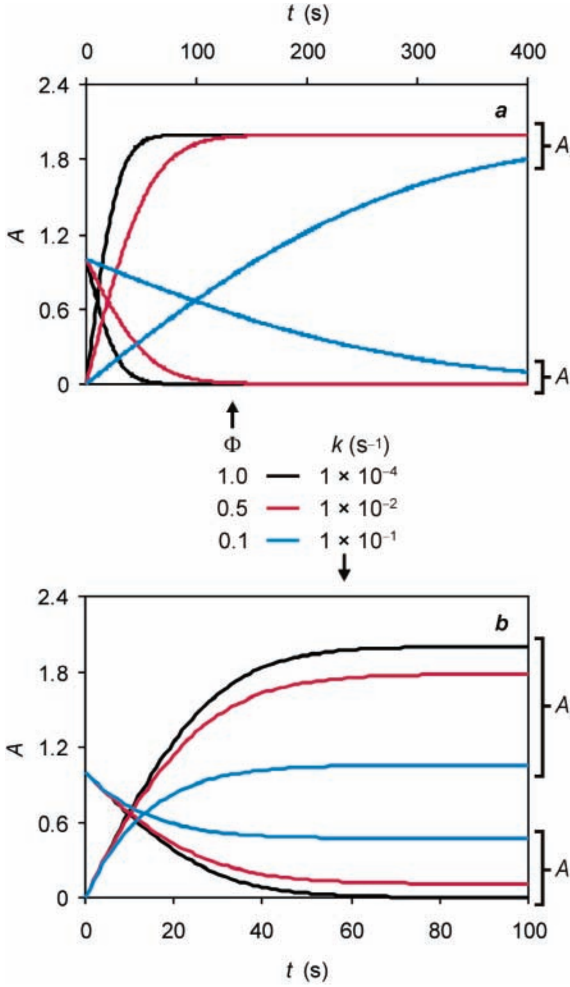


Figure 1. Influence of the photoisomerization quantum yield (Φ) (a) and re-isomerization rate constant (k) (b) on the simulated (ref 24) time (t) dependence of the absorbance (A_1 and A_2) of the two interconverting isomers of a generic photochromic system under continuous irradiation.

TABLE 3: Spectroscopic Parameters (λ_{Ex}, λ_{Em}, Φ_F, τ_F)[a] Associated with Representative Examples of Photochromic Compounds

	λ_{Ex} (nm)	λ_{Em} (nm)	Φ_F	τ_F (ns)	ref
1B	545	642	0.012	0.2	27
3B	376	497	0.4	2.4	15
4A	340	493	0.0038	0.23	16
5A	414	620	0.0009	2.4	17

[a] Excitation (λ_{Ex}) and emission (λ_{Em}) wavelengths. Fluorescence quantum yield (Φ_F) and lifetime (τ_F). The spectroscopic data were determined in EtOH at 24 °C for **1B**, in 2-methyltetrahydrofuran at −190 °C for **3B**, in CH_2Cl_2 at 25 °C for **4A** and in cyclohexane at 20 °C for **5B**.

conditions, the emission intensity of a photochromic compound can be modulated by switching back and forth between its emissive and nonemissive forms. For example, the thermally stable isomers **1A** and **3A** do not emit light, whereas the photogenerated species **1B** and **3B** fluoresce in the visible region (Table 3).[15,27] Similarly, the thermally stable isomers **4A** and **5A** are fluorescent, whereas the photogenerated species **4B** and **5B** are not.[16,17] Thus, the photoinduced transformation of isomer **A** into **B** and the thermal re-isomerization from **B** to **A** can be employed to switch reversibly the fluorescence of all four compounds. In this context, 2-indolylfulgides are particularly attractive.[28] These photochromic compounds are closely related to **7** but incorporate an indolyl group in place of the furyl ring. A representative example is shown in Figure 2. The absorption spectrum of the isomer **8A** shows a band centered at 462 nm in hexane.[28f] Upon irradiation at 470 nm, **8A** switches to **8B** with a quantum yield of 0.047. The photogenerated isomer absorbs at 548 nm and reverts to **8A** with a quantum yield 0.013, when irradiated at 610 nm. The species **8A** is not fluorescent (Figure 2a), whereas **8B** emits at 622 nm (Figure 2b) with a quantum yield of 0.18. Thus, the reversible interconversion between **8A** and **8B** modulates the intensity of the emitted light at this particular wavelength.

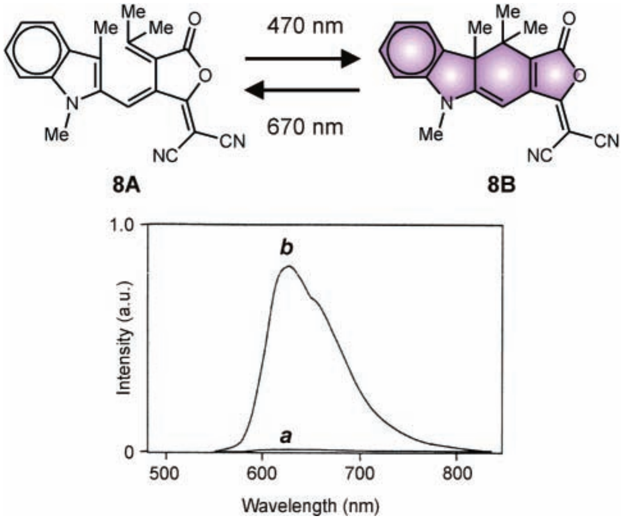


Figure 2. Emission spectra (λ_{Ex} = 580 nm, hexane) of **8A** (a) and **8B** (b) and photoinduced interconversion of the two isomers (partially reproduced from ref 28f with permission).

2.2. Photoinduced Conjugation Changes. In analogy to intrinsically fluorescent photochromic compounds, the emissive behavior of molecular dyads combining a fluorescent and a photochromic component within the same skeleton can be modulated with optical stimulations. Specifically, the electronic structure of the fluorophore changes with the state of the photochromic component when delocalization is possible across their covalent connector. Under these conditions, the reversible transformation of the photochromic switch results in the modulation of the emission intensity[29−33] and/or wavelength[34,35] of the fluorescent component. Furthermore, the photoinduced changes in conjugation operating these fluorophore−photochrome dyads can easily be adapted to fluorophore−photochrome-fluorophore triads.[31,36−38] The behavior of the dyad **9** (Figure 3) is a representative example of this mechanism in action.[29] In this compound, a pyridyl ligand connects a tungsten fluorophore to a diarylethene switch. The fluorescence quantum yield is only 0.03 for isomer **9A**. Upon irradiation at 240 nm, **9A** switches to **9B** and the fluorescence quantum yield increases to 0.15. Indeed, the photoinduced ring closing of the diarylethene switch extends considerably the conjugation across the molecular assembly enhancing the fluorescence intensity. The process, however, is fully reversible. The original and weakly fluorescent state is regenerated after irradiation at wavelengths longer than 600 nm.

2.3. Photoinduced Polarity Changes. The emissive behavior of fluorophore-photochrome dyads can vary with the state of the photochromic fragment even when their covalent connector prevents delocalization. In fact, the structural and electronic modifications associated with the reversible transformation of the photochromic switch are often sufficient to alter the emission quantum yield[39] and/or wavelength[40] of the proximal fluorophore. Specifically, the changing dipole moment of the photo-

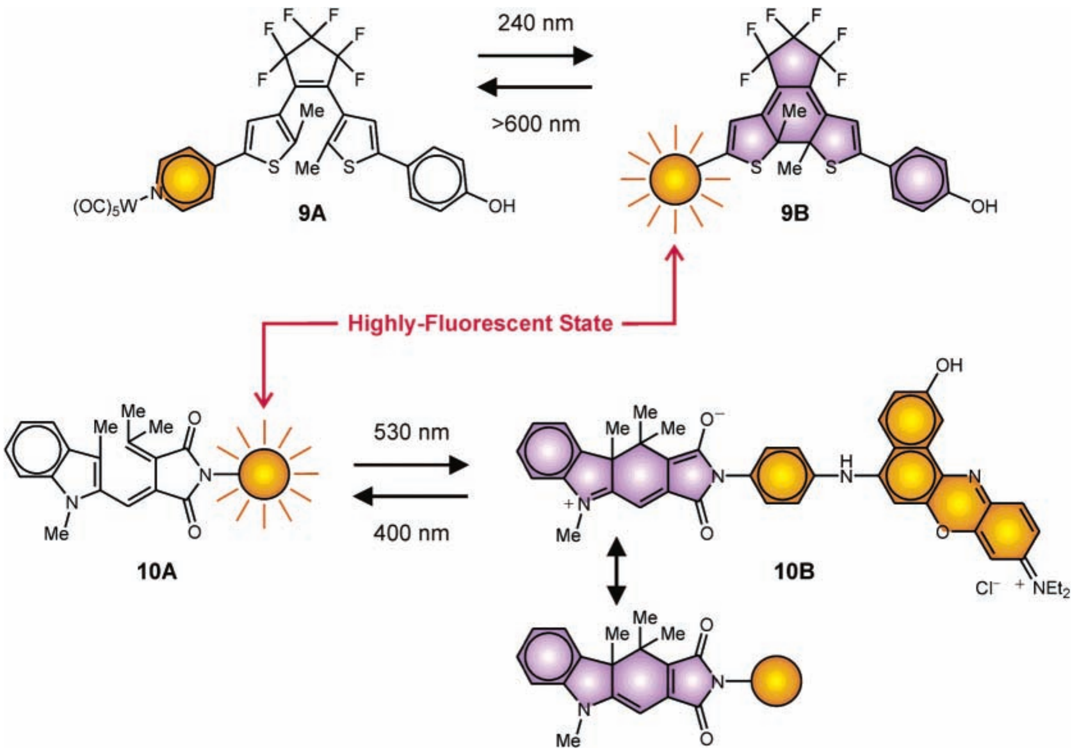


Figure 3. Photoinduced interconversion of **9A** and **9B** and of **10A** and **10B**.

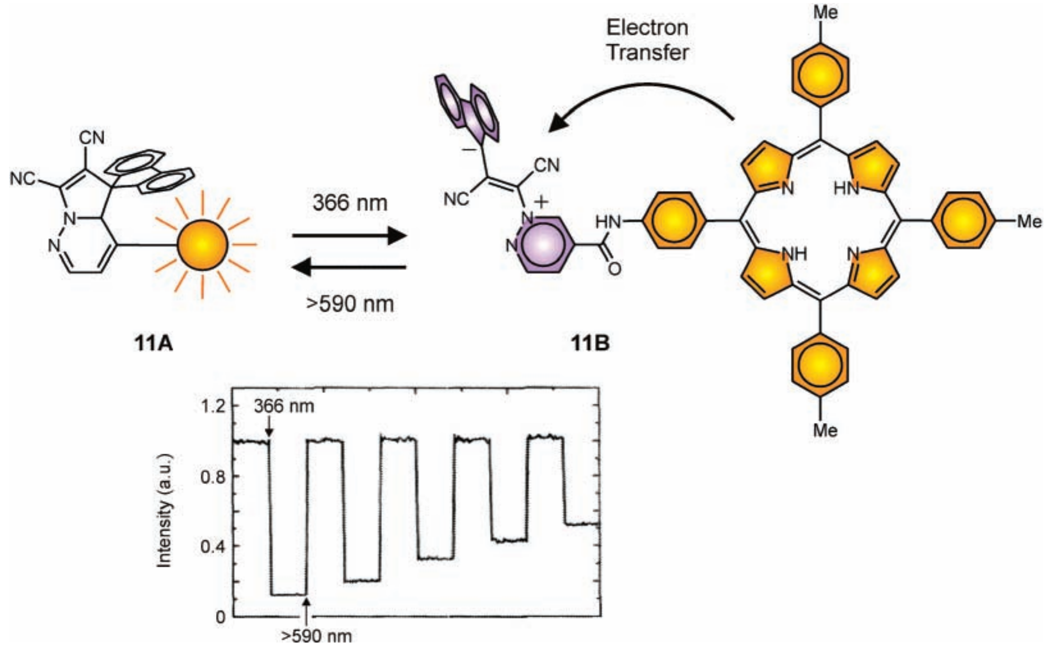


Figure 4. Changes in fluorescence intensity ($\lambda_{Ex} = 650$ nm, $\lambda_{Em} = 720$ nm, 2-methyltetrahydrofuran) with the photoinduced interconversion of **11A** and **11B** (partially reproduced from ref 42b with permission).

chromic component can be exploited to affect the local polarity around the fluorophore and, as a result, its spectroscopic signature. The dyad **10** (Figure 3) operates on the basis of this mechanism.[39] The skeleton of this molecule pairs a fulgide switch to an oxazine fluorophore. Upon irradiation at 400 nm, the isomer **10A** switches to **10B**. The process is fully reversed after illumination at 530 nm and is accompanied by a drastic change in dipole moment. Indeed, the zwitterionic character of **10B** imposes a relatively large dipole moment on this particular state of the photochromic system. In turn, the oxazine fluorophore is particularly sensitive to polarity changes and its fluorescence quantum yield in 2-propanol drops by ca. 80% with the transformation of **10A** into **10B**. Thus, the photoinduced interconversion of these two isomers translates into the reversible modulation of the emission intensity of the overall assembly.

2.4. Photoinduced Electron Transfer. In addition to the dipole moment, the photoinduced interconversion between the two states of a photochromic compound can also alter the oxidation and/or reduction potential. Changes in either one of these two parameters offer the opportunity to activate or suppress intramolecular electron transfer pathways.[41,42] The dyad **11** (Figure 4) was designed according to these operating principles.[42] This molecule incorporates a spiroindolizine switch and a porphyrin fluorophore. The fluorescent component can be

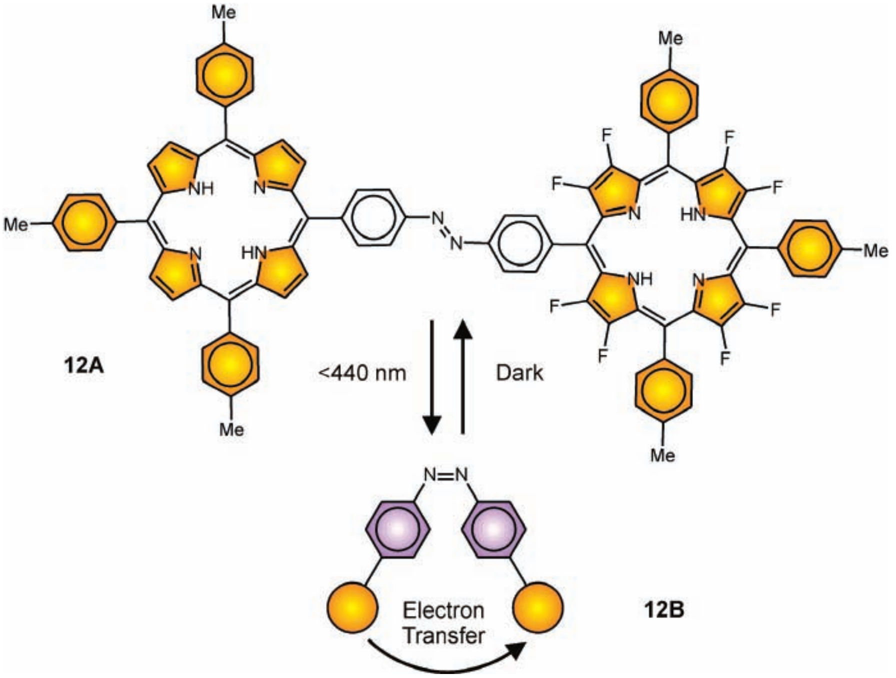


Figure 5. Photoinduced interconversion of **12A** and **12B**.

excited selectively by irradiating the dyad at 650 nm. In the isomer **11A**, the local excitation of the porphyrin is followed by the radiative deactivation of its first singlet excited state with the appearance of an intense band centered at 720 nm in the emission spectrum. Upon irradiation at 366 nm, ring opening of the photochromic fragment occurs with the formation of the isomer **11B**. This photoinduced transformation shifts the reduction potential of the photochromic compound by ca. -0.48 V. As a consequence, electron transfer from the excited porphyrin to the photochromic fragment becomes thermodynamically favorable and results in a significant quenching of the porphyrin fluorescence. Specifically, the free energy difference for the electron transfer process can be estimated to vary from $+0.26$ eV in **11A** to -0.22 eV in **11B** from the cyclic voltammograms of model compounds. The original state, however, is restored upon illumination of the dyad at wavelengths longer than 590 nm. Thus, the efficiency of the intramolecular electron transfer pathway and, therefore, the fluorescence quantum yield can be modulated by switching back and forth between **11A** and **11B**. The chart in Figure 4 illustrates the obvious changes in fluorescence intensity for nine consecutive switching steps.

Alternatively to the reduction potential of the electron acceptor, the photoinduced interconversion of a photochromic component can also be exploited to regulate the physical donor−acceptor separation and, as a result, the electron transfer efficiency. The structural changes associated with certain photochromic compounds can, in fact, cause drastic changes in distance between chromophoric appendages[43−46] or encourage supramolecular contacts in host−guest assemblies.[47] For example, the separation between the two porphyrin ends of the triad **12** (Figure 5) varies with the isomerization of the central azobenzene.[44] In both isomers, the excitation of the porphyrin chromophores at 430 nm is followed by electron transfer from the nonfluorinated to the fluorinated end. Indeed, the cyclic voltammograms of model compounds suggest that the reduction potential of the fluorinated porphyrin is ca. 0.71 V more positive than that of the nonfluorinated counterpart. The photoinduced transfer of an electron form one porphyrin to the other competes with the radiative deactivation. Consistently, the fluorescence quantum yields of both isomers are significantly smaller than those of the isolated porphyrins. Nonetheless, the fluorescence quantum yield of the isomer **12A** is more than twice that of **12B**. This difference is a result of the longer separation between the two porphyrins in **12A**, which limits the electron transfer efficiency. Thus, the irradiation of the triad at wavelengths shorter than 440 nm induces the isomerization from **12A** to **12B** and causes a decrease in fluorescence, which is restored after the thermal re-isomerization from **12B** to **12A**.

2.5. Fluorescence Resonance Energy Transfer. Alternatively to the transfer of electrons, the intramolecular transfer of energy can also be exploited to regulate the emissive behavior of fluorophore-photochrome dyads.[48−52] Specifically, the emission and absorption bands of the two components can be designed to overlap significantly in one of the two states of the photochromic fragment only. Under these conditions, the photoinduced transformations of the photochromic component can activate or suppress the intramolecular transfer of the excitation energy from the fluorescent to the photochromic fragment. The dyad **13** (Figure 6) is a representative example of this mechanism for fluorescence modulation.[50d] In the isomer **13A**, the local excitation of the anthracene fluorophore at 488 nm is followed by intense emission at 530 nm. The fluorescence quantum yield and lifetime are 0.73 and 4.9 ns, respectively. Upon irradiation at 313 nm, **13A** switches to **13B** with a quantum yield of 0.12 and the concomitant appearance of a broad absorption centered at 630 nm. This band overlaps considerably the emission band of the anthracene fluorophore. As a consequence, energy transfer from the excited fluorophore to the photochromic component can now compete efficiently with the radiative deactivation of the anthracene first singlet excited state. Indeed, the fluorescence quantum yield lowers below 0.001 and the lifetime decreases to 4.5 ps. Continuous irradiation of the dyad at wavelengths longer than 450 nm, however, restores the original and highly emissive state. The chart in Figure 6 shows the evolution of the fluorescence intensity for a switching cycle. This mechanism for the intramolecular transfer of energy can also be extended to the intermolecular level. For example, the luminescence intensity and lifetime of a ruthenium(II) complex vary with the state of a diarylethene switch operated in the same solution, once again,

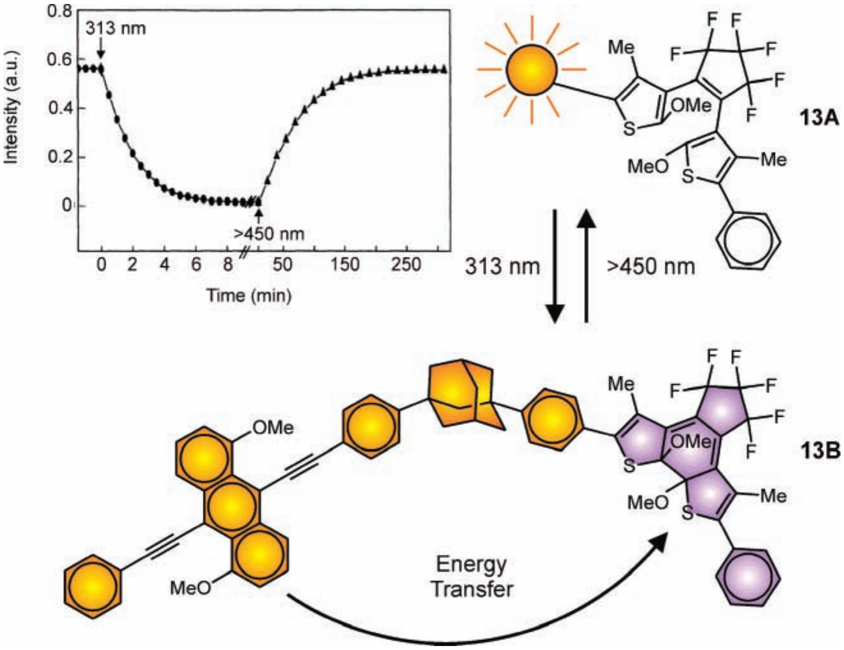


Figure 6. Changes in fluorescence intensity ($\lambda_{\mathrm{Ex}} = 488$ nm, $\lambda_{\mathrm{Em}} = 503$ nm, toluene) with the photoinduced interconversion of **13A** and **13B** (partially reproduced from ref 50d with permission).

as a result of photoinduced energy transfer from the emitting to the photochromic component.[53]

The intramolecular transfer of excitation energy can also be exploited to regulate the emissive behavior of fluorophore−photochrome−fluorophore[54−56] and photochrome−fluorophore−photochrome[57,58] triads with mechanisms essentially identical to that regulating the dyad **13**. A modification of these operating principles for fluorescence modulation was, instead, implemented in the form of the triad **14** (Figure 7).[59] In this molecule, a fulgide switch bridges an anthracene to a coumarin fluorophore. In the isomer **14A**, the local excitation of the anthracene end at 400 nm is followed by energy transfer to the coumarin end, which then emits at 475 nm. Upon irradiation at 320 nm, **14A** switches to **14B** after the ring closing of the fulgide component. In the isomer **14B**, the excitation energy of the anthracene donor is transferred preferentially to the photochromic component rather than to the coumarin fluorophore. As a result, the coumarin fluorescence decreases in intensity with the interconversion of **14A** into **14B**. The original and highly emissive state is, however, restored upon irradiation at 520 nm, after the photoinduced ring opening of the photochromic component. The chart in Figure 7 illustrates the evolution of the coumarin fluorescence during one switching cycle.

2.6. Photoinduced Filter Effects. The characteristic changes in absorption that accompany any photochromic transformation can be designed to filter the fluorescence of a compatible emitter. The main requirement that has to be satisfied to implement these operating principles is the need of a significant degree of overlap between the emission bands of the fluorophore and the absorption bands of one of the states of the photochromic component. Under these conditions, the photochromic compound can reabsorb the light emitted by the fluorophore when the two components are co-dissolved in the same solution. However, the detected emission intensity varies with the state of the photochromic compound, because only one of them can actually absorb light in the wavelength range where the fluorophore emits. Indeed, we have demonstrated the viability of this simple approach to fluorescence modulation by operating a photochromic spiropyran in the presence of pyrene.[60] The emission intensity at 374 nm associated with an acetonitrile solution of pyrene decreases when the co-dissolved and colorless spiropyran is photoswitched to a colored merocyanine. Furthermore, the

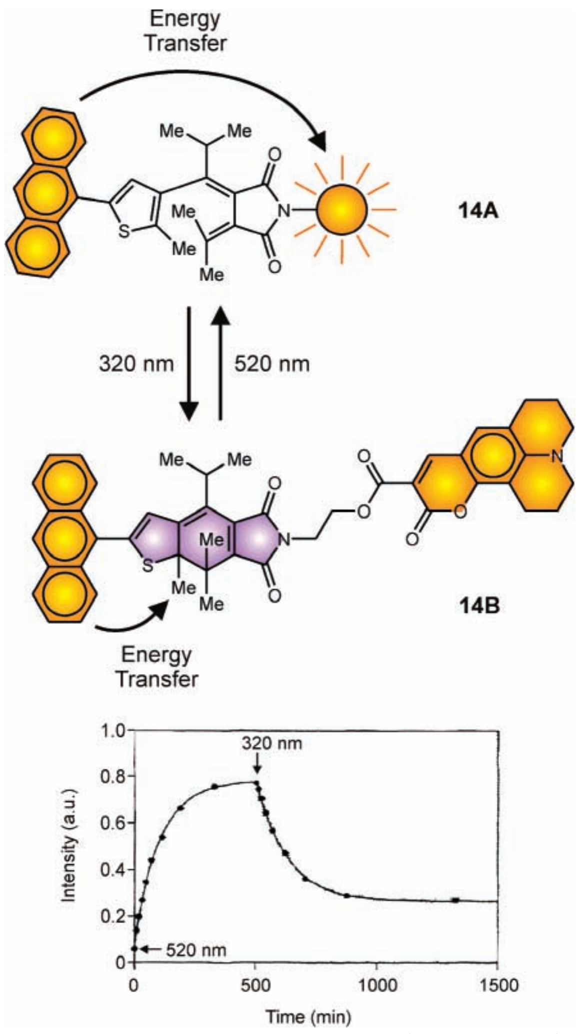


Figure 7. Changes in fluorescence intensity ($\lambda_{\mathrm{Ex}} = 400$ nm, $\lambda_{\mathrm{Em}} = 475$ nm, CH_2Cl_2) with the photoinduced interconversion of **14A** and **14B** (partially reproduced from ref 59a with permission).

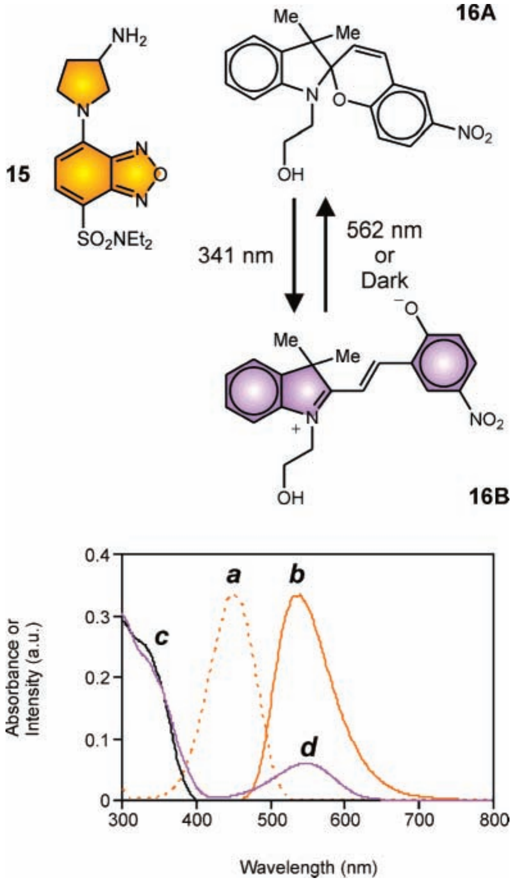


Figure 8. Excitation (a) ($\lambda_{\mathrm{Em}} = 536$ nm) and emission (b) ($\lambda_{\mathrm{Ex}} = 450$ nm) spectra of **15** in poly(methyl methacrylate) and absorption spectra of **16** in poly(*n*-butyl methacrylate) before (c) and after (d) irradiation at 341 nm.

lack of covalent bonds between the fluorescent and photochromic components offers the opportunity to separate the two species in different environments without loosing the ability to modulate fluorescence.[61] For example, the benzofurazan **15** (Figure 8) can be trapped in a rigid poly(methyl methacrylate) matrix following a spin-coating procedure.[61b] The excitation (Figure 8a) and emission (Figure 8b) spectra of the resulting film show bands centered at 450 and 536 nm, respectively. Relying on similar experimental protocols, the spiropyran **16A** can also be trapped in a poly(*n*-butyl methacrylate) film. This particular polymer has a relatively low glass transition temperature (15 °C), which ensures fast isomerization kinetics for the photochromic dopant. The absorption spectrum **16A** in this matrix (Figure 8c) does not show any absorption in the visible region. This dopant cannot absorb light in the wavelength range where **15** is excited and where it emits. Upon ultraviolet irradiation, however, **16A** switches to **16B** and a band at 560 nm appears in the absorption spectrum (Figure 8d). This particular absorption overlaps the emission band of **15**, but not its excitation. Thus, **15** can be excited without affecting **16B**, but its emission can be re-absorbed and filtered by **16B**. On the basis of the absorption and emission properties of these materials, we have designed and assembled the device in Figure 9. It consists of two quartz slides sandwiching overlaid films of **15** and **16A**. An excitation source (light source A in Figure 9) positioned above the assembly can illuminate the fluorescent layer of **15** through the top quartz slide and the film of **16A**, because both layers are transparent at 450 nm. The light reaching **15** is absorbed and re-emitted at 536 nm in the form of fluorescence. The emitted light travels through the film of **16A** and top quartz slide to reach the detector. Upon ultraviolet irradiation (light source B in Figure 9), however, **16A** switches to **16B**. This isomer absorbs and blocks the fluorescence coming from the bottom layer. Consistently, the detected intensity decreases during ultraviolet irradiation (chart in Figure 9). Once the ultraviolet source is turned off, **16B** reverts thermally and partially to **16A** and the detected fluorescence increases. Alternatively, the assembly can be irradiated with visible light to switch **16B** almost completely back to **16A** and restore most of the original emission intensity.

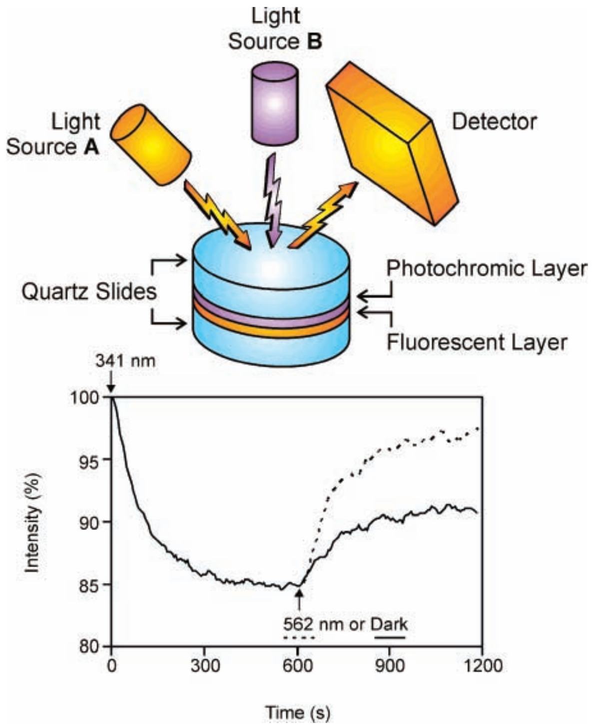


Figure 9. Changes in emission intensity ($\lambda_{\mathrm{Ex}} = 450$ nm, $\lambda_{\mathrm{Em}} = 536$ nm) of the fluorescent layer (**15** in poly(methyl methacrylate)) with the state of the photochromic layer (**16** in poly(*n*-butyl methacrylate)).

3. Conclusions

The structural and electronic changes accompanying the photoinduced transformations of photochromic compounds have suggested a wealth of applications over the past four decades. In recent years, these compounds have emerged as convenient building blocks for the construction of photoswitchable luminescent assemblies. In these systems, the interconversion between the various states of a photochromic compound modulates the fluorescence intensity of the overall assembly. Besides photochromic compounds with intrinsic emissive behavior, at least six different mechanisms have been identified to operate these fluorescent switches. Most of them require the integration of photochromic and fluorescent components within the same molecular skeleton and exploit the changing dipole moment, conjugation, redox potential, absorption wavelength or dimensions of one component to alter the emissive behavior of the other. Alternatively, simple filter effects can be exploited to regulate the emission of a fluorophore with an independent photochromic component on the basis of fluorescence reabsorption. The motivation behind these studies lies in the need to (1) advance our basic understanding of the photochemical and photophysical properties of organic molecules, (2) learn how to engineer their photoresponsive character through careful molecular design, and (3) explore the fundamental factors regulating electron and energy transfer processes. Furthermore, the promising prospects offered by photonic technology have also contributed to stimulate these investigations with the ultimate goal of developing innovative photoresponsive materials for information processing, storage, and visualization.

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(11) The term photochromism derives from the Greek words "phos" and "chroma", which mean light and color respectively (ref 1).

(12) The term photochromism is sometimes extended to processes that involve absorbance changes in the ultraviolet, rather than visible, region (ref 1).

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(23) The kinetic model leading to the differential equations (1) and (2) assumes that the photoisomerization is performed in liquid solution at a fixed temperature under constant stirring, the pump and probe beams have identical path lengths, the quantum yields of photochemical processes other than the transformation of isomer **A** into **B** are all negligible.

(24) The Euler method built in the ordinary differential equation (ODE) solver of PSI−Plot 7.5 (Poly Software International, Inc.: Pearl River, NY) was employed to simulate the temporal profiles of A_1 and A_2 with equations (1) and (2). All plots (Figure 1) were determined with a step size of 1 s, a I_0 of 4×10^{-6} M s^{-1}, ϵ_1 and ϵ_2 of 1×10^4 and 2×10^4 M^{-1} cm^{-1}, respectively, a c of 1×10^{-4} M, and a l of 1 cm. The three pairs of plots in chart a were modeled with a k of 1×10^{-4} s^{-1} and a Φ of 0.1, 0.5 or 1.0. Those in chart b were calculated with a Φ of 1.0 and a k of 1×10^{-4}, 1×10^{-2} or 5×10^{-2} s^{-1}.

(25) The k values of thermally stable photochromes (e.g., **6** and **7**) are negligible and their absorbance profiles are regulated solely by the first terms of the differential equations (1) and (2).

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