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Fluorescent Switches Based on Photochromic Compounds

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The photochemical transformations associated with photochromic compounds can be exploited to switch the emission of complementary fluorophores under the influence of optical stimulations. Specifically, fluorescent and photochromic components can be integrated within the same molecular or supramolecular assembly and the significant changes in the stereoelectronic properties associated with the photoinduced interconversion of one component can be designed to modulate the emission intensity and/or wavelength of the other. In particular, the modifications in absorption properties, conjugation, dipole moment, redox potentials and shape of a photochrome can all be transduced effectively into reversible alterations of the emissive behavior of a fluorophore. Furthermore, some of these ingenious mechanisms for fluorescence modulation can be extended from relatively small molecular and supramolecular assemblies to large macromolecular, nanostructured and biomolecular constructs. In fact, a diversity of chemical systems with photoswitchable luminescence have already emerged on the basis of these operating principles and choice of functional components. Ultimately, these fundamental studies on the photochemical and photophysical signature of multicomponent assemblies might well lead to a new generation of photonic materials with unique properties for possible applications in biomedical imaging and sensing as well as in information processing and storage.

1. Photochromism

1.1. History and Definitions

The term "photochromism" was introduced in the early 1950s to indicate the photoinduced and reversible change in color of certain compounds.[1] Since then, the number of publications on photochromism has increased exponentially and, eventually, this area has evolved into a mature and active research field.[2–6] Indeed, numerous families of photochromic compounds have been developed and investigated over the past five decades and their unique properties have led to the realization of a diversity of photochromic materials for various applications.[7–9]

The term photochromism derives from the Greek words "phos" and "chroma", which mean light and color, respectively and indicates literally a photoinduced change in color.[10] When restricted to the molecular world, however, this term implies a *reversible* color change under illumina-

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tion. In most instances, photochromic processes actually involve the photoinduced interconversion of a colorless state into and colored one. The photoinduced transformation of a colored form into a colorless one is also possible, but is definitely less common. In order to distinguish these two classes of photochromic processes, the terms "positive photochromism" and "negative photochromism" are used to indicate photoinduced colorations and decolorations respectively. In both instances, the photogenerated state must be able to revert to the original form. In general, two broad classes of photochromic compounds can be distinguished on the basis of the nature of the reverse process. Thermally reversibly photochromic compounds switch back to the original state when stored in the dark. Thermally irreversible photochromic compounds revert to the original form under irradiation at a different wavelength.

1.2. Photochromic Compounds

Photochromic transformations are generally based on unimolecular or bimolecular reactions.[2–6] The unimolecular processes are definitely more common than their bimolecular counterparts and involve the interconversion of two isomers. For example, the spiropyran **1a** (Figure 1) ring opens to the merocyanine **1b** upon ultraviolet irradiation with a quantum yield of 0.1 in MeCN.[11] The photogenerated and colored isomer **1b** has a lifetime of ca. 400 s and eventually reverts to the colorless state **1a** after thermal ring closing. Similarly, the colorless diarylethene **2a** (Figure 1) ring closes to the colored isomer **2b** upon ultraviolet irradiation with a quantum yield of 0.46 in hexane.[12] In this instance, however, the photogenerated isomer is thermally stable and reverts to the original and colorless state only after visible irradiation with a quantum yield of 0.015. Other common photochromic compounds based on ring opening and closing steps are the dihydroazulenes (e.g., **3a** in Figure 1),[13] the spiroindolizines (e.g., **4a**),[14,15] the dihydropyrans (e.g., **5a**)[16] and the fulgides (e.g., **6a**).[17] In alternative to ring opening and closing reactions, photoinduced *cis*/*trans* isomerizations can also be exploited to implement photochromic transformations. For example, the colorless *trans*-azobenzene **7a** switches to the colored *cis* isomer **7b** upon ultraviolet irradiation with a quantum yield of 0.1 in cyclohexane.[18,19] The photogenerated isomer has a lifetime of ca. 5000 s and reverts to the original species after a thermal *cis* → *trans* isomerization.

1.3. Properties of Photochromic Compounds

The photoinduced interconversion of one state of a photochromic compound into another is generally accompanied by significant structural and electronic transformations.[2–6] For example, the colorless isomer **1a** (Figure 1) combines an indole and benzopyran fragment within its molecular skeleton.[11] The spirocenter joining the two heterocyclic fragments imposes an orthogonal arrangement on them. As a result, there is no electronic communication between them and **1a** absorbs only in the ultraviolet region of the electromagnetic spectrum. The ultraviolet excitation of this compound, however, cleaves the [C–O] bond at the spirocenter and, after the *cis* → *trans* isomerization of the adjacent double bond, generates the colored isomer **1b**. Indeed, the extended π-system of this species absorbs strongly in the visible region of the electromagnetic spectrum. Thus, the profound structural and electronic changes associated with the photoinduced isomerization from **1a** to **1b** alter drastically the spectroscopic response of the photochromic system and ensure coloration. In addition to the absorbance changes in the visible region, the transformation from **1a** to **1b** alters also the dipole moment and molecular polarizability of the photochromic system.[20] For example, AM1 calculations estimate an increase of ca. 4 D in the dipole moment with the formation of **1b**.[21] The photoinduced and reversible changes of these *molecular properties* in turn translate into significant modifications of *macroscopic properties*. In fact, the interconversion of a photochromic system within a liquid solution, a rigid polymer or even in a crystal alters the color and refractive index of the overall material. Hence, photonic materials with unique behavior can be designed around the photoresponsive properties of photochromic compounds.[7–9]

2. Intramolecular Fluorescence Modulation

2.1. Fluorescent and Photochromic Compounds

The structural and electronic modifications that accompany the interconversion of photochromic compounds often translate also into significant changes in fluorescence quantum yield.[8b,21,22] For example, the spiropyran **1a** (Figure 1) and the dihydroazulene **3a** do not emit electromagnetic radiations.[13,23] Instead, their photogenerated isomers **1b** and **3b** fluoresce in the visible region. Similarly, the spiroindolizine **4a** and the dihydropyran **5a** are fluorescent, while their photogenerated isomers **4b** and **5b** are not.[14–16] Thus, the photoinduced and reversible interconversion of these four pairs of isomers results in the modulation of their fluorescence intensity.

An alternative approach to modulate fluorescence with photochromic compounds relies on the integration of fluorescent and photochromic components within the same molecular skeleton. In the resulting systems, the photoinduced isomerization of one component regulates the emissive behavior of the other. Diverse mechanisms can be invoked to implement these operating principles. For example, changes in either the conjugation or the polarity of the photochromic switch can affect the fluorescence quantum yield[24–33] and/or wavelength[34,35] of the fluorescent partner. The two molecular dyads **8a** (Figure 2) and **9a** are representative examples of these mechanisms for fluorescence modulation.[25,29]

The dyad **8a** (Figure 2) combines an emissive tungsten complex with a diarylethene photochrome through a pyridyl ligand.[25] The luminescence quantum yield for this isomer, however, is only 0.03. Upon ultraviolet irradiation, the

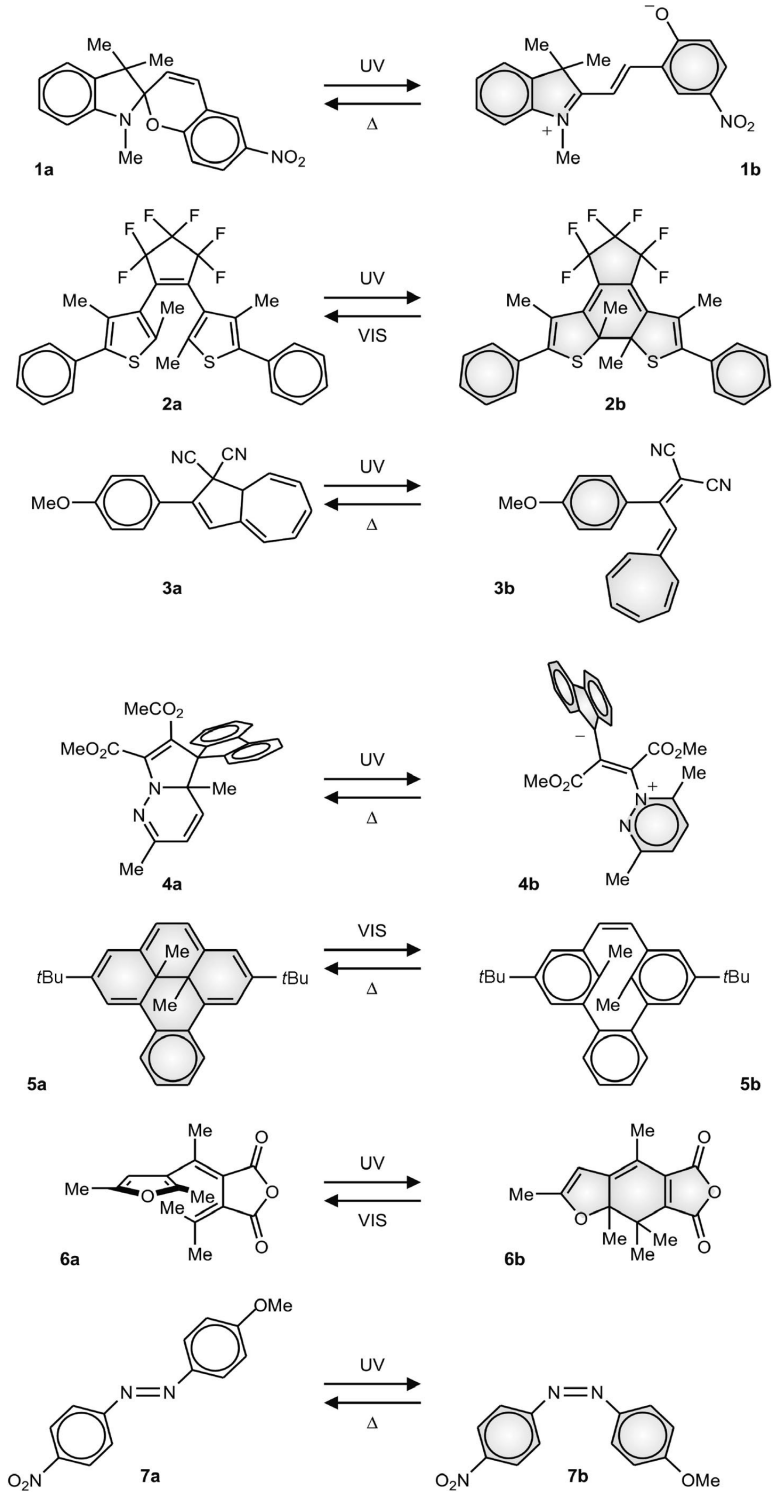

Figure 1. The photoinduced (UV and VIS) and thermal (Δ) transformations of representative photochromic compounds.

diarylethene component undergoes ring closing with a significant change in electronic structure. As a result of the change in conjugation across the photochromic system, the luminescence quantum yield for the tungsten complex increases to 0.15. The process can be reversed by irradiating the dyad with visible light. Indeed, the original diarylethene isomer is regenerated and the luminescence quantum yield returns to the initial low value. Furthermore, similar operating principles can be extended from fluorophore–photochrome dyads to fluorophore–photochrome–fluorophore triads.[26,36–38]

The molecular dyad **9a** (Figure 2) integrates an oxazine fluorophore with a fulgide switch within its molecular skeleton.[29] The photochromic component ring closes upon

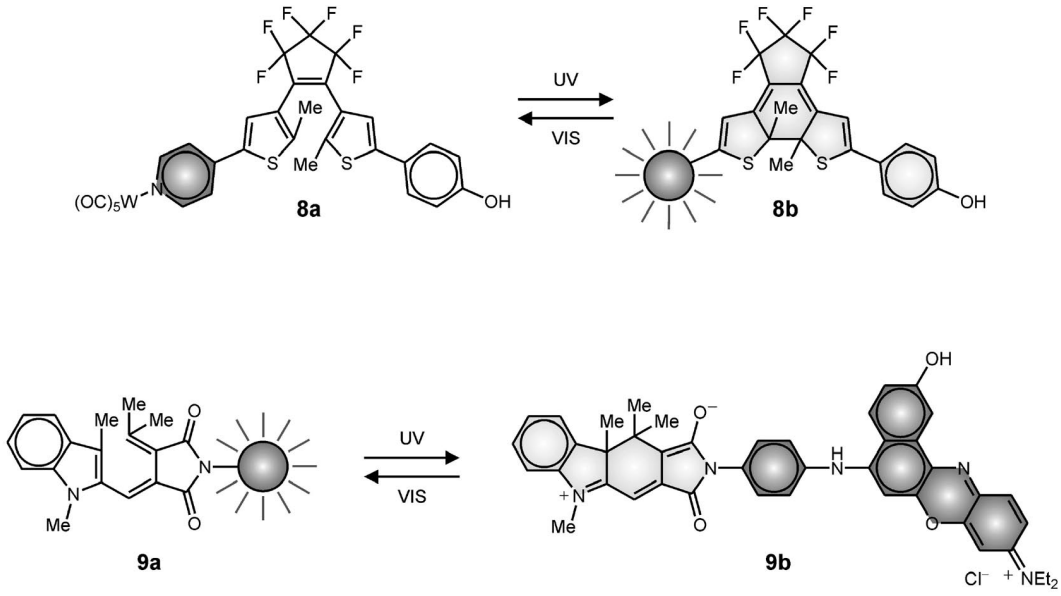

Figure 2. The photoinduced and reversible interconversion between **8a** and **8b** and between **9a** and **9b** results in the modulation of their luminescence quantum yield.

ultraviolet irradiation. The zwitterionic character of the photogenerated isomer translates into a significant enhancement in dipole moment with the isomerization from **9a** to **9b**. The process, however, can be reverted simply by irradiating with visible light. The photoinduced changes in dipole moment alter the local polarity around the adjacent oxazine fluorophore. As a result, the fluorescence quantum yield decreases by 80% with the transformation of **9a** into **9b** and returns to the original value after the photoinduced re-isomerization.

2.2. Electron Transfer

The emissive behavior of a fluorescent component appended to a photochromic switch can also be modulated on the basis of photoinduced electron transfer.[21,39] In fact, the two states of a photochrome often differ in their redox potentials. As a result, the photoinduced and reversible change in either the oxidation or the reduction potential of the photochromic component can be exploited to activate or suppress intramolecular electron transfer pathways in fluorophore–photochrome assemblies.[40–43] For example, the molecular dyad **10a** (Figure 3) incorporates a porphyrin fluorophore and a spiroindolizine photochrome.[41] The local excitation of the porphyrin at 650 nm is followed by intense emission at 720 nm. After ultraviolet irradiation, however, the spiroindolizine photochrome ring opens to the corresponding zwitterionic isomer. This transformation is accompanied by a shift in the reduction potential of the photochromic component by ca. –0.48 V. Under these conditions, the transfer of electrons from the excited porphyrin to the photochrome becomes thermodynamically favorable. Consistently, the porphyrin fluorescence is effectively quenched. After visible irradiation, the zwitterionic state of

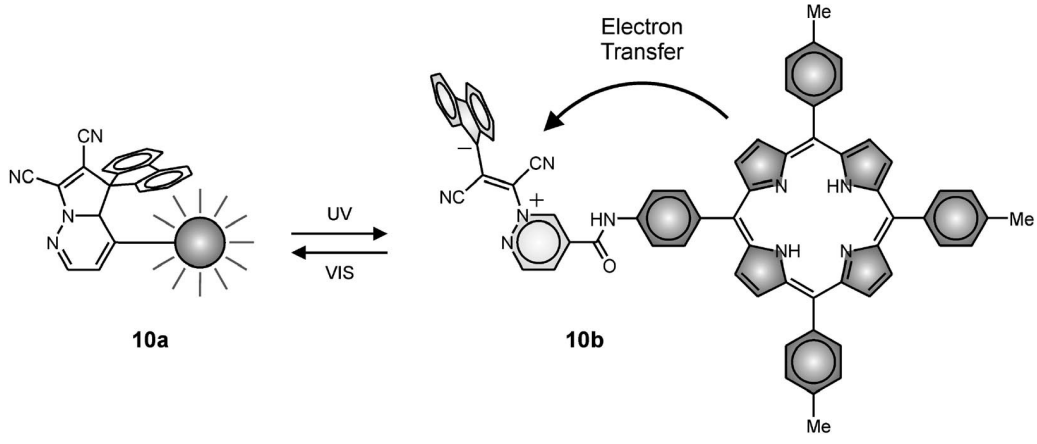

Figure 3. The photoinduced interconversion of **10a** into **10b** activates an electron-transfer pathway quenching the fluorescence of the porphyrin appendage.

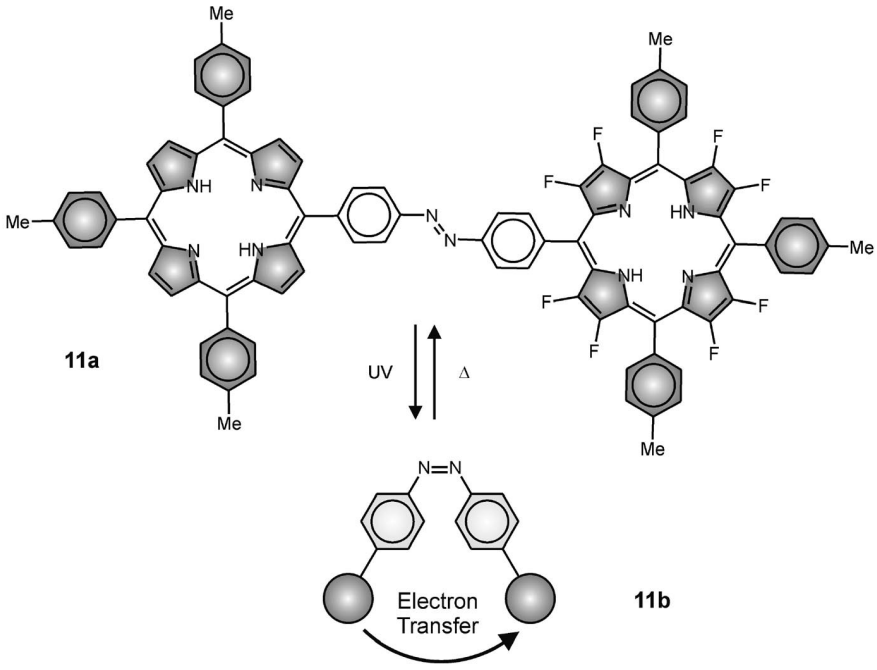

Figure 4. The photoinduced interconversion of **11a** into **11b** activates an electron-transfer pathway quenching the emission of the porphyrin fluorophores.

the photochrome switches back to the original form, suppressing the electron transfer pathway and restoring the initial fluorescence intensity. Thus, the emission of one component can be modulated by operating the other with ultraviolet and visible inputs.

The photoinduced and reversible interconversion of a photochromic compound can also be exploited to regulate the physical separation between an electron donor and a complementary acceptor.[44–49] In the resulting systems, the efficiency of electron transfer varies with the state of the photochrome, even although the interconverting component is not directly involved in the electron transfer process. For example, the triad **11a** (Figure 4) incorporates two porphyrin fluorophores and an azobenzene photochrome.[46] In this molecular assembly, the fluorinated porphyrin can donate electrons to its nonfluorinated counterpart upon excitation. The distance between the two porphyrin units, however, changes with the state of the azobenzene bridge. Specifically, the photoinduced isomerization of the azobenzene from a *trans* to a *cis* configuration shortens significantly the physical separation between the electron donor and the acceptor. As a result, the efficiency of electron transfer increases dramatically and the fluorescence quantum yield drops by ca. 50%. After the thermal re-isomerization of the *cis*-azobenzene to the *trans* state, the original distance between donor and acceptor is restored with the concomitant recovery of the initial emission intensity.

2.3. Energy Transfer

The emissive behavior of fluorophore–photochrome dyads can also be regulated on the basis of energy transfer.[50–57] Indeed, only one of the two interconvertible states of the photochromic component can be designed to absorb in the wavelength range where the fluorescent component emits. Under these conditions, the photoinduced and reversible interconversion of the photochrome controls the intramolecular transfer of the excitation energy of the fluorophore from one component to the other. For example, the dyad **12a** (Figure 5) incorporates an anthracene fluorophore and a diarylethene photochrome.[52d] The ultraviolet irradiation of this molecular assembly induces the ring closing of the diarylethene switch with the formation of the isomer **12b**. The photogenerated state of the photochrome absorbs in a range of wavelengths where the anthracene fluorophore emits. As a result, the transformation of **12a** into **12b** activates an energy transfer pathway from the fluorophore to the photochrome with a concomitant decreases in fluorescence quantum yield from 0.73 to 0.001. After visible irradiation, the photochromic component ring opens to regenerate the original isomer **12a** with the concomitant recovery of the initial fluorescence intensity.

The operating principles regulating the emissive behavior of the fluorophore–photochrome dyad **12a** can be extended to fluorophore–photochrome–fluorophore[58–62] and photochrome–fluorophore–photochrome[63–65] triads. Instead, the molecular triad **13a** (Figure 6) operates according to a different mechanism also based on energy transfer.[66] This molecule incorporates an anthracene donor, a coumarin acceptor and a fulgide photochrome. The local excitation of the anthracene donor is followed by the transfer of excitation energy to the coumarin acceptor, which then emits in the visible region. After ultraviolet irradiation, the fulgide photochrome ring closes to generate the isomer **13b**. The

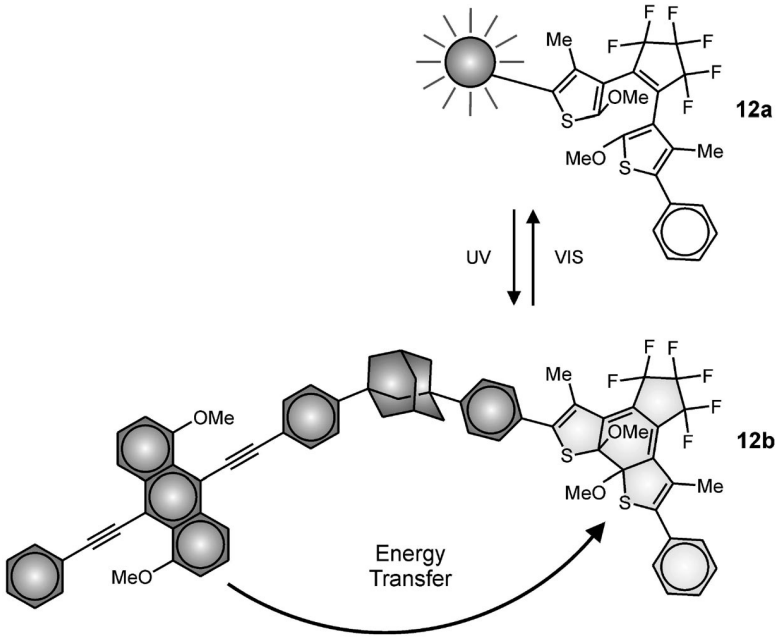

Figure 5. The photoinduced interconversion of **12a** into **12b** activates an energy-transfer pathway quenching the fluorescence of the anthracene appendage.

photochromic component of **13b** can accept the excitation energy of the anthracene donor, preventing the transfer of energy to the coumarin acceptor. As a result, the photoinduced interconversion of **13a** into **13b** results in a significant decrease in the fluorescence intensity of the coumarin appendage. The process can be reversed by irradiating with visible light. Under these conditions, the fulgide photochrome ring opens to regenerate the original state with the concomitant recovery of the initial fluorescence intensity.

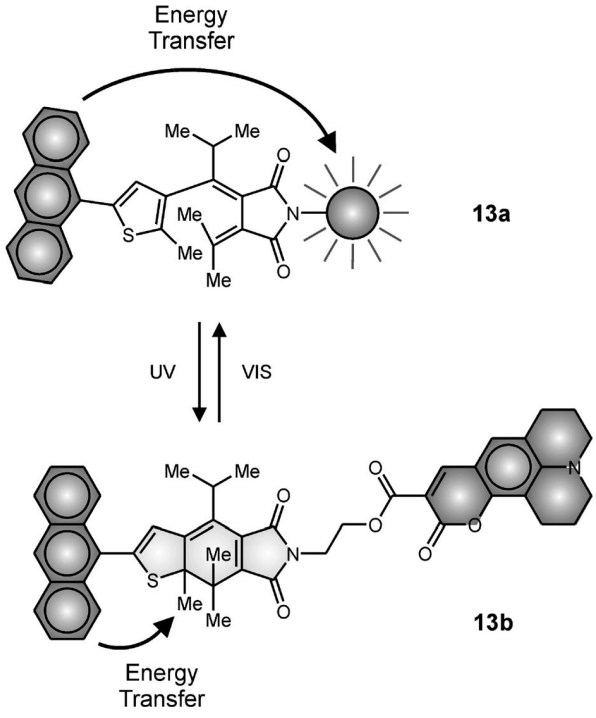

Figure 6. The photoinduced interconversion of **13a** into **13b** turns the photochromic component into an energy acceptor and affects the intramolecular energy-transfer pathway.

3. Intermolecular Fluorescence Modulation

3.1. A Three-State Molecular Switch

We developed a three-state molecular switch on the basis of the spiropyran **14a** (Figure 7).[67] This molecule ring opens upon ultraviolet irradiation to generate the merocyanine **14b**. This transformation is accompanied by the appearance of an intense absorption band in the visible region (***a*** and ***b*** in Figure 8). The merocyanine **14b** reverts thermally to the original spiropyran with a lifetime of 190 s in acetonitrile. In the presence of acid, however, **14b** switches to **14c** with significant changes in the absorption spectrum (***b*** and ***c*** in Figure 8). The protonated merocyanine **14c** can also be generated directly from **14a** after the addition of acid. Furthermore, the protonated species **14c** switches to **14b** upon addition of base and to **14a** upon visible irradiation. Thus, the reversible interconversion of the three states **14a**, **14b** and **14c** can be controlled with ultraviolet and visible inputs, as well as with acid and base, and is accompanied by dramatic absorbance changes in the visible region of the electromagnetic spectrum.

3.2. Modulation in Solution

The absorbance changes associated with the interconversion of **14a** (Figure 7), **14b** and **14c** can be exploited to modulate the emission intensity of a fluorescent partner on the basis of re-absorption effects.[68] For example, the emis-

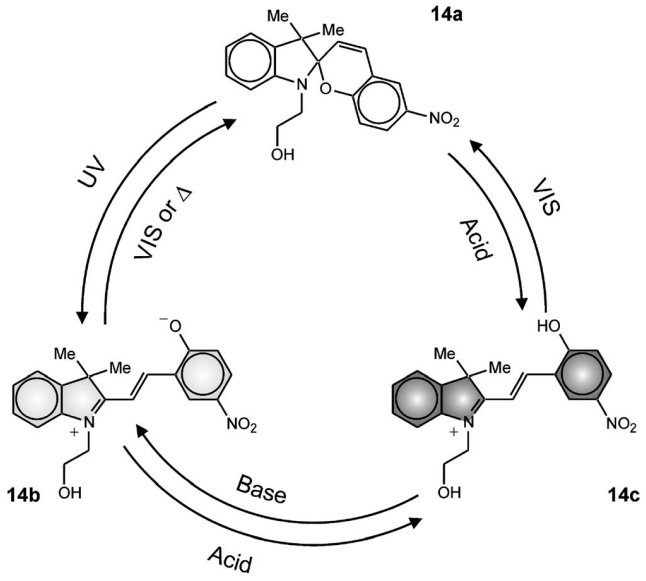

Figure 7. The reversible interconversion of the three states **14a**, **14b** and **14c**.

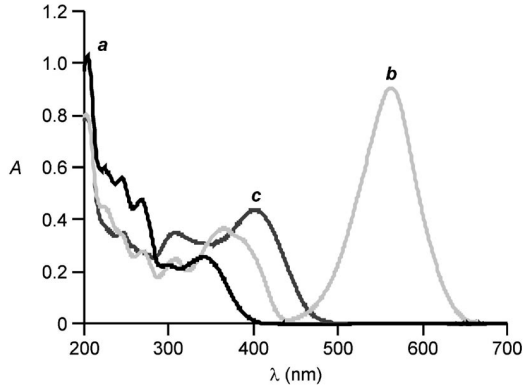

Figure 8. Absorption spectra (0.1 mM, MeCN, 25 °C) of **14a** before (***a***) and after either ultraviolet irradiation (***b***) or the addition of CF_3CO_2H (***c***).

sion of pyrene, co-dissolved with the equimolar amounts of **14a** in acetonitrile, can be modulated operating the photochromic component with ultraviolet, visible and acid inputs.[68a,68c] Indeed, this particular fluorophore has an emission band centered at 374 nm in acetonitrile (***a*** in Figure 9). At this wavelength, the absorbance of **14a** (***a*** in Figure 8) is 0.11 at a concentration of 0.1 mM. Thus, part of the radiations emitted by the pyrene fluorophore are re-absorbed by the spiropyran photochrome and 61% of the fluorescence intensity can be detected (***b*** in Figure 9). After ultraviolet irradiation, **14a** switches to **14b** and the absorbance at 374 nm increases to 0.35. This enhancement translates into an increase in the fraction of radiations re-absorbed by the photochromic component. Consistently, the detected fluorescence intensity drops to 53%. After the addition of acid, **14b** switches to **14c**, but the absorbance at 374 nm does not change significantly. In fact, the detected fluorescence intensity remains approximately the same (***b*** in Figure 9). Only after visible irradiation does the fluorescence intensity return to the original value (***b*** in Figure 9) in agreement with the regeneration of the low absorbing state **14a**. Hence, the interconversion of the photochromic component translates into the modulation of the emission intensity of the fluorescent partner even although the two are not covalently connected to each other. Indeed, similar effects have been also reproduced with diarylethene photochromes and appropriate luminescent partners.[69–72]

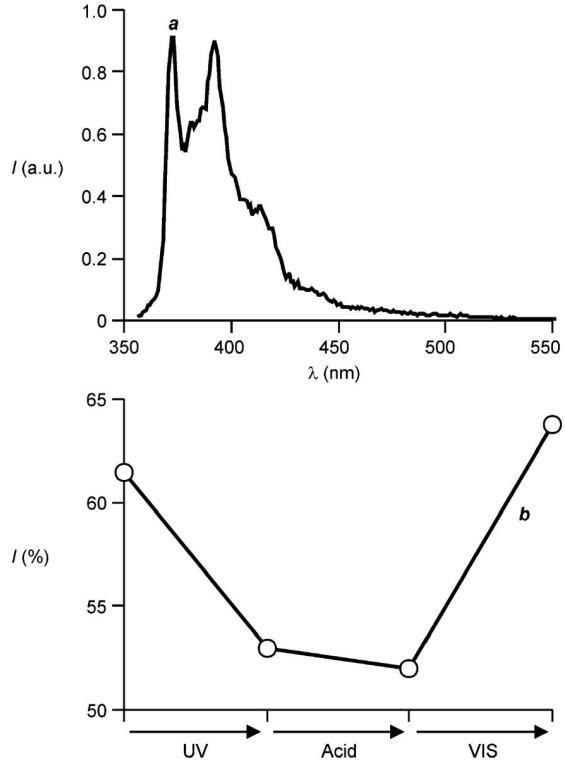

Figure 9. Emission spectrum (0.1 mM, MeCN, 25 °C, λ_{Ex} = 336 nm) of pyrene (***a***) and emission intensity at 374 nm (***b***) of an equimolar solution of pyrene and **14a** (0.1 mM, MeCN, 25 °C, λ_{Ex} = 336 nm).

The modulation of the emission of pyrene (***b*** in Figure 9) by the spiropyran **14a** (Figure 7) was achieved co-dissolving the fluorescent and photochromic compounds in the same solution.[68a,68c] Similar effects can be reproduced by dissolving the two components in independent solutions and by positioning the photochromic solution between the fluorescent solution and the detector.[68b,68c] Furthermore, multiple fluorophores with appropriately spaced emission wavelengths can be used simultaneously. For example, the emission spectra of naphthalene (***a*** in Figure 10), anthracene (***b***) and tetracene (***c***) show that these polycyclic aromatic compounds have emission bands centered at 335, 401 and 544 nm respectively. The colorless state **14a** of the photochromic switch absorbs only at 335 nm (***a*** in Figure 8). Therefore, this species can only absorb and block the emission of naphthalene. The merocyanine **14b** absorbs at all three wavelengths (***b*** in Figure 8). Thus, this state can absorb and block the emission of all three fluorophores. The protonated merocyanine **14c** absorbs at 335 and 401 nm

only (*c* in Figure 8). Hence, it can only absorb and block the emission of naphthalene and anthracene. It follows that the emission of the three fluorophores can be modulated independently, but simultaneously, by operating the photochromic component with ultraviolet, visible and acid stimulations. In fact, the naphthalene emission at 335 nm (*d* in Figure 10) is always low, since all three states of the photochrome can block it. The anthracene emission at 401 nm (*e* in Figure 10) is high only when the photochromic element is in state **14a** and it is low in the other two cases. The tetracene emission at 544 nm (*f* in Figure 10) is low only when the photochromic switch is in state **14b** and it is high in the other two cases.

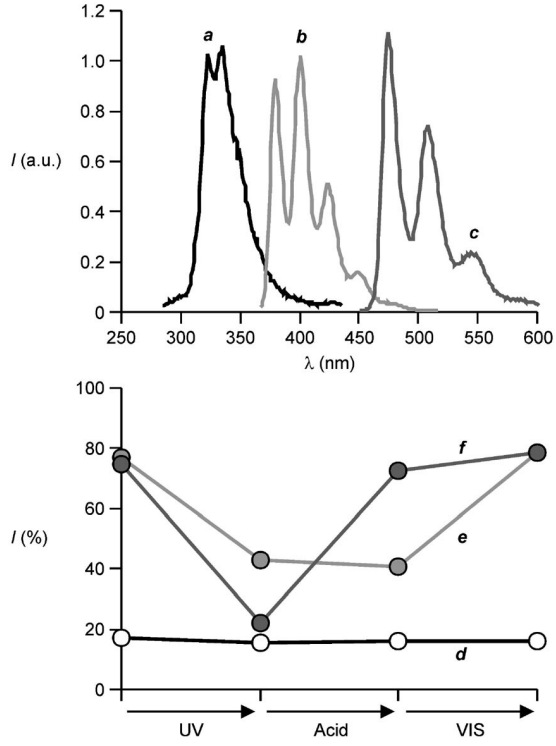

Figure 10. Emission spectra (0.01 mM, MeCN, 25 °C) of naphthalene (*a*, λ_{Ex} = 275 nm), anthracene (*b*, λ_{Ex} = 357 nm) and tetracene (*c*, λ_{Ex} = 441 nm) and emission intensities at 335 (*d*), 401 (*e*) and 544 (*f*) nm of an equimolar solution of naphthalene, anthracene and tetracene (0.01 mM, MeCN, 25 °C) filtered by a solution of **14a** (0.1 mM, MeCN, 25 °C).

3.3. Modulation in Films

The operating principles developed for the intermolecular modulation of the emission intensity of fluorescent compounds with photochromic switches can be reproduced with rigid materials.[72–76] The device configuration in Figure 11, for example, is composed of fluorescent and photochromic layers sandwiched between two quartz slides. Light source A sends a monochromatic radiation through the top quartz slide and the photochromic layer to the fluorescent layer. This component absorbs the incident radiation and emits at a longer wavelength. The emitted radiation travels through the photochromic layer and the top quartz slide to the detector. The absorption properties of the photochromic layer in the same range of wavelengths where the fluorescent layer emits can be regulated by operating light source B. Specifically, the photoinduced interconversion from a low absorbing state to a high absorbing one can be achieved simply by turning on this particular light source. As a result, the radiation emitted by the fluorescent layer is absorbed and blocked by the photogenerated state of the photochromic component. If the original and low absorbing state of the photochromic layer is regenerated either thermally or photochemically, the emitted radiation can travel to the detector restoring the original intensity. Thus, this device configuration offers the opportunity to modulate an optical output, namely the emission of the fluorescent layer, with an optical input, namely the radiation operating the photochromic element.

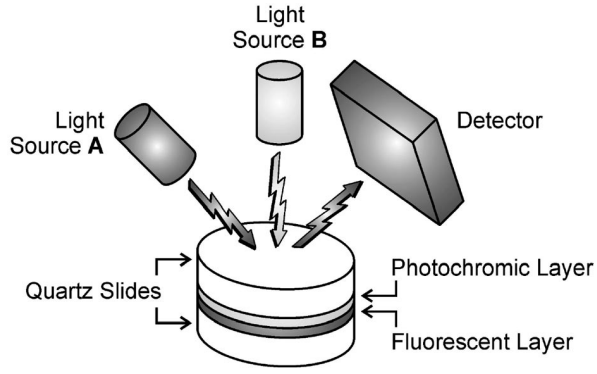

Figure 11. Prototypical device based on the modulation of the emission of a fluorescent layer by a photochromic layer.

The benzofurazan **15** (Figure 12) can be excited at 450 nm, where neither the colorless state **14a** (*a* in Figure 8) nor the colored one **14b** absorb (*b* in Figure 8).[73a] This particular fluorophore emits at 530 nm, where only the colored state **14b** absorbs (*a* in Figure 8). Furthermore, the fluorescent compound **15** and the photochromic switch **14a** can be trapped within rigid poly(methyl methacrylate) films, relying on simple spin-coating procedures. After trapping, both compounds retain their emissive and photochromic behaviors respectively. The resulting films can then be mounted within the device configuration of Figure 11. When the photochromic dopant is in its colorless state **14a**, the emission intensity detected at 530 nm is high (*b* in Figure 12). Indeed, under these conditions the emitted light can travel unaffected through the photochromic layer and reach the detector. After ultraviolet irradiation, however, the colorless dopant **14a** switches to the colored one **14b** with a concomitant increase in absorbance in the very same range of wavelengths where the fluorescent dopant emits. Consistently, the emission intensity detected at 530 nm drops by 14%, since the fluorescence can be absorbed and blocked by the photochromic layer. After visible irradiation, the colored state of the photochromic dopant **14b** switches back to the colorless one **14a** and the emission intensity detected at 530 nm returns to the original value. Thus, the fluorescence

at this particular wavelength can be modulated by switching the photochromic dopant back and forth between its two states.

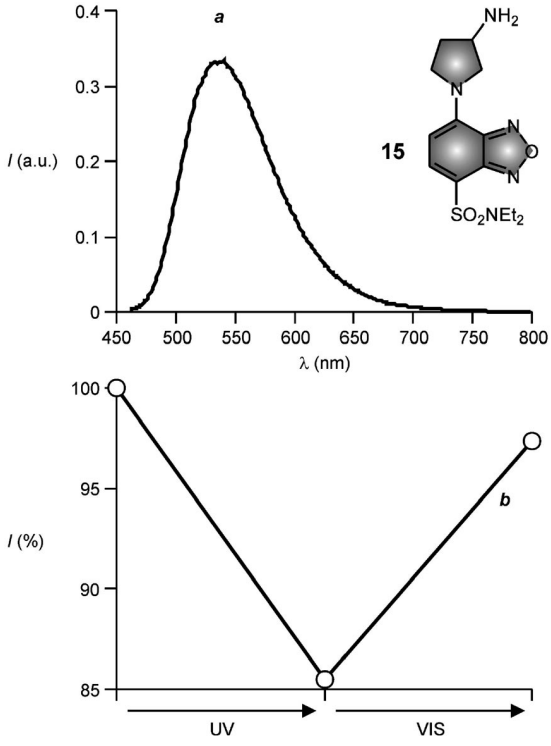

Figure 12. Emission spectrum (λ_{Ex} = 450 nm) of a poly(methyl methacrylate) film doped with **15** (***a***) and emission intensity at 536 nm (***b***) for the device in Figure 11 incorporating poly(methyl methacrylate) films doped with **15** and **14a** as the fluorescent and photochromic layers respectively.

4. Nanostructured Constructs

4.1. Polymers

Photochromic compounds can be incorporated within the main or side chains of macromolecular constructs and switched between their two interconvertible states with optical stimulations under these conditions.[7,8] When one of the two states is fluorescent, the photoinduced transformation of the photochromic components within these polymeric assemblies results in the modulation of the emission intensity.[77,78] Alternatively, independent fluorescent and photochromic components can be integrated within[79–81] or appended to[82] the main chain of a polymer backbone. Similarly, several photochromes can be attached to a single fluorescent polymer[83,84] or a fluorophore can first be connected to a photochrome and then multiple copies of the resulting dyad can be attached to a macromolecular chain.[85] For example, the co-polymer **16a** (Figure 13) bears pendant fluorophore–photochrome dyads along its macromolecular backbone in addition to hydrophilic polyethylene glycol chains.[85] Specifically, this co-polymer has an average of 15 hydrophilic tails per dyad and, as a result, is soluble in aqueous environments. The 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (BODIPY) fluorophores of this macromolecular construct emit at 545 nm (***a*** in Figure 13) after excitation. Upon ultraviolet irradiation, the spiropyran components of **16a** switch to the corresponding merocyanines to generate **16b** with the concomitant appearance of their characteristic absorption at 530 nm. The absorbance at this wavelength indicates that ca. 17% of the photochromic components are in their colored state at the photostationary state. Interestingly, this band overlaps the emission of the

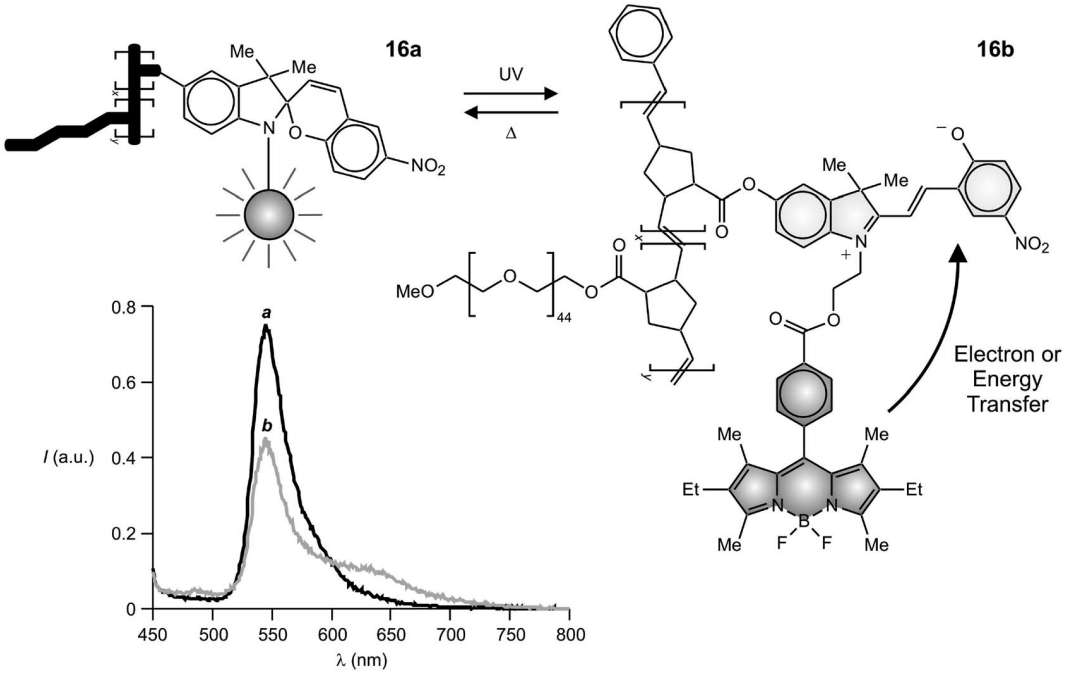

Figure 13. Emission spectra (1.5 mg mL^{-1}, sodium phosphate buffer, pH = 7.0, 25 °C, λ_{Ex} = 440 nm) of the co-polymer **16a** before (***a***) and after (***b***) ultraviolet irradiation.

fluorescent components. Furthermore, the photoinduced coloration of the photochromic components shifts the reduction potential by 0.31 V in the positive direction. The significant changes in the absorption wavelength and reduction potential of the photochromes activate energy and electron transfer pathways respectively. In particular, the excited fluorophore can transfer either energy or an electron to the adjacent photochrome only after the photochemical transformation. Therefore, the photoinduced interconversion of **16a** into **16b** translates into a significant decrease in emission intensity (***b*** in Figure 13). The colored state of the photochromic components, however, has a lifetime of 0.9×10^4 s and, eventually, reverts to the colorless form with first-order kinetics, when the macromolecular construct is stored in the dark. The thermal transformation of **16b** into **16a** prevents the intercomponent electron and energy transfer processes and restores the original emission intensity. Thus, the fluorescence of this particular macromolecular construct can be switched between high and low values simply by turning off and on an ultraviolet source on the basis of a combination of electron and energy transfer processes.

4.2. Nanoparticles

Photochromic compounds can be attached to luminescent inorganic nanoparticles and the emission of the resulting assemblies can be regulated with optical stimulations.[86–91] Alternatively, photochromic ligands, able to emit electromagnetic radiations in one of their two interconvertible states only, or fluorophore–photochrome dyads can be conjugated to nanostructured inorganic scaffolds.[92,93] Once again, the photoinduced interconversion of the photochromic components of the resulting nanostructured materials results in the effective modulation of the emission intensity. The nanoscaled construct **17a** (Figure 14) is a representative example of these functional assemblies.[89a] It incorporates an emissive CdSe core, surrounded by a protective ZnS shell and pendant photochromic ligands. Upon excitation, this luminescent nanostructured emit at 554 nm (***a*** in Figure 14) in dichloroethane, where the colorless state of the photochromic components does not absorb. After ultraviolet irradiation, however, a fraction of the spiropyran ligands switches to the corresponding merocyanines with the concomitant appearance of their characteristic absorption band at 592 nm. This band overlaps the emission of the inorganic components and, as a result, energy can be transferred from the excited CdSe core to the photogenerated state of the photochromes. Consistently, the emission intensity of this nanostructured assembly decreases significantly with the photoinduced transformation of **17a** into **17b** (***b*** in Figure 14). Nonetheless, the colored state of the photochromic ligands has a lifetime of 250 s and, eventually, reverts to the colorless state with first-order kinetics upon storage in the dark. In fact, the original luminescence intensity of the CdSe core is fully restored after the thermal reisomerization of **17b** back to **17a**. Thus, the luminescence of this nanostructured construct can repeatedly be switched between high and low values simply by turning an ultraviolet source on and off.

Fluorescent and photochromic components can also be incorporated within organic nanoparticles to build nanostructured constructs with photoswitchable fluorescence. In fact, some photochromic compounds tend to assemble spontaneously into nanostructured aggregates without

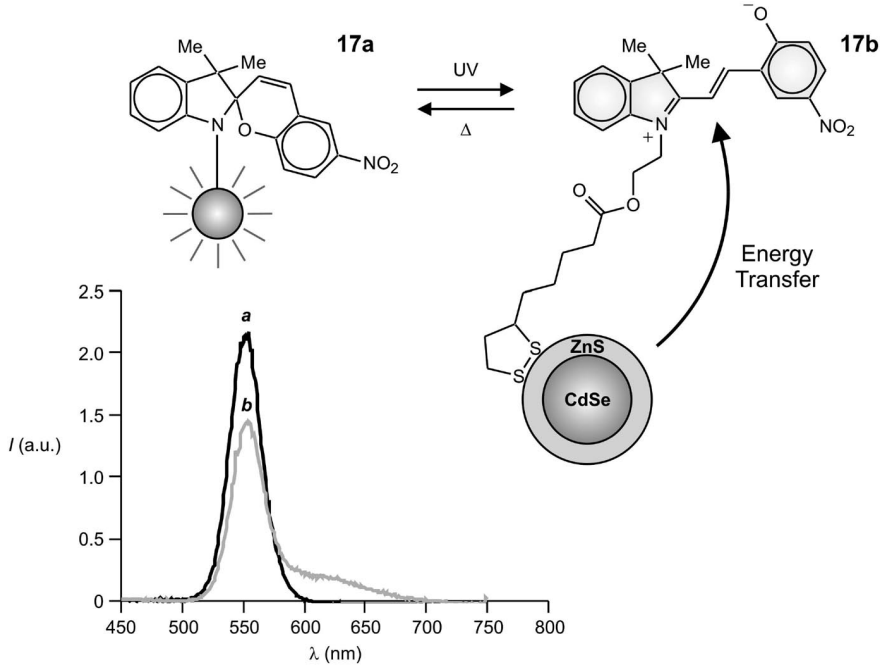

Figure 14. Emission spectra (0.7 μM, dichloroethane, 25 °C, λ_{Ex} = 380 nm) of the nanostructured construct **17a** before (***a***) and after (***b***) ultraviolet irradiation.

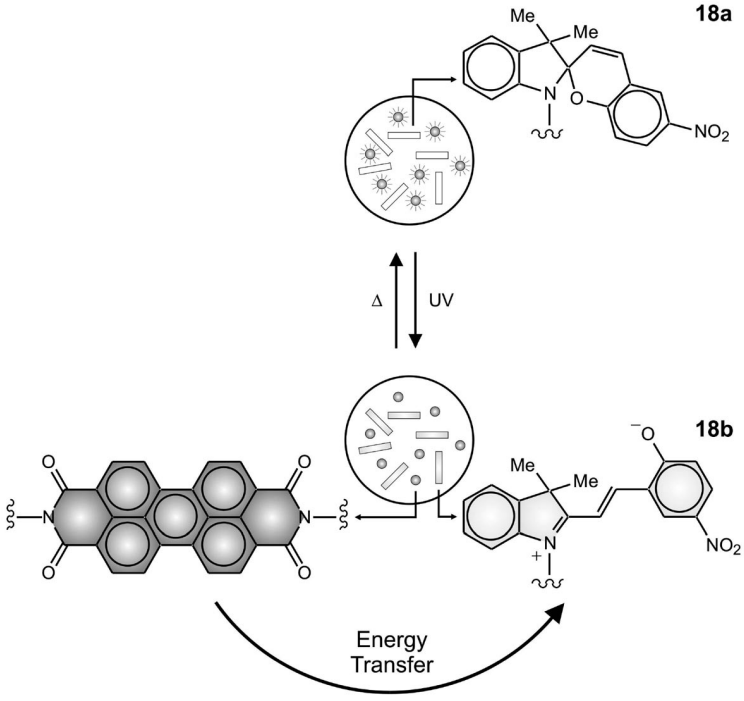

Figure 15. The photoinduced transformation of the spiropyran photochromes, entrapped within the cross-linked polymer nanoparticle **18a**, activates an energy transfer process and quenches the emission of the perylene diimide fluorophores.

loosing their photochemical character.[94–97] When only one of the two states of these photochromic compounds is fluorescent, their photoinduced transformations result in the effective modulation of the emission intensity of the overall assembly. Alternatively, independent fluorescent and photochromic components can be trapped within the hydrophobic interior[98–100] or covalently linked to the macromolecular backbone[101,102] of cross-linked polymer nanoparticles. For example, the nanostructured construct **18a** (Figure 15) can be assembled by co-polymerizing perylene diimide fluorophores and spiropyran photochromes together with *N*-isopracrylamide, divinylbenzene and styrene in aqueous environment.[101b] In the resulting assembly, the fluorescent and photochromic components are integral part of the cross-linked covalent skeleton. Upon excitation, the perylene diimide fluorophores emit at 530 nm, where the spiropyran photochromes do not absorb. After ultraviolet irradiation, the spiropyrans switch to the corresponding merocyanines to form **18b** with the concomitant appearance of their characteristic absorption at 588 nm. The overlap between the emission of the fluorophores and the absorption of the photogenerated state of the photochromes encourages the transfer of energy from one component to the other. Consistently, the perylene diimide emission decreases significantly in intensity. The hydrophobic environment of this nanostructured construct, however, facilitates the radiative deactivation of the excited merocyanines. As a result, the energy transferred form the perylene diimide to the merocyanines components is released in the form of electromagnetic radiations. In fact, the decrease in the perylene diimide fluorescence at 530 nm is paralleled by the growth of an emission band at 670 nm, corresponding to the merocyanine fluorescence. Upon storage in the dark, the photogenerated state of the photochromes reverts to the colorless form, preventing the intercomponent energy transfer process and restoring the original emission spectrum. Hence, the emission intensity can be modulated at two different wavelengths in parallel under the influence of ultraviolet inputs and on the basis of energy transfer with these functional organic nanoparticles.

4.3. Biomolecules

The photoinduced interconversion between the nonemissive and emissive states of certain photochromic compounds can be exploited to probe living cells,[103,104] image biological samples with improved resolution[105] and develop immunoassays.[106] In addition, fluorophore–photochrome dyads can be conjugated to proteins and the emission intensity of the resulting assemblies can be modulated with optical stimulations on the basis of intercomponent energy transfer.[107] Similarly, photochromic components can be appended to fluorescent proteins in order to control the biomolecule emission within living cells under the influence of optical stimulations.[108] For example, the green fluorescent protein (GFP) was labeled with a photochromic spiropyran inside Swiss 3T3 cells to generate the construct **19a** (Figure 16).[108] Under these conditions, the GFP component emits at ca. 510 nm upon excitation, where the colorless state of the photochromes does not absorb. After ultraviolet irradiation, the spiropyran switches to the corre-

sponding merocyanine to generate **19b**. The photogenerated state of the photochromic component absorbs at ca. 540 nm. The pronounced degree of overlap between the GFP emission and the merocyanine absorption results in efficient energy transfer with a concomitant fluorescence quenching. The visible irradiation of **19b**, however, switches the photochromic component back to the original and colorless state, suppressing the energy-transfer pathway and restoring the original fluorescence intensity. Thus, the emission of this particular system can be switched multiple times between high and low values inside living cells simply by illuminating the biological samples with ultraviolet and visible inputs.

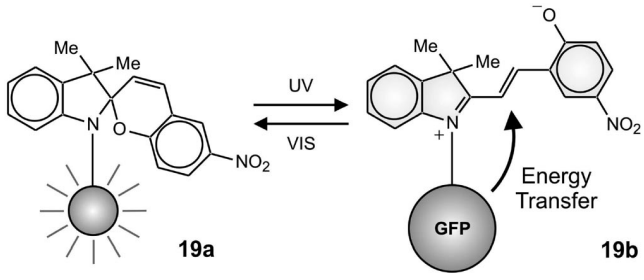

Figure 16. The photoinduced interconversion of the photochromic component of **19a** activates an energy transfer process and quenches the emission of the green fluorescent protein (GFP).

Fluorescent and photochromic components can also be connected through an oligonucleotide strand in order to assemble fluorophore–photochrome dyads with photoswitchable emission.[109] In particular, a fluorescein fluorophore and a merocyanine photochrome were attached to the ends of a cytosine-rich oligonucleotide strand to generate the construct **20a** (Figure 17).[109] At a pH of 5.5, this particular oligonucleotide folds into a compact conformation to bring its two ends in close proximity. Under these conditions, the photochromic component is preferentially in its colored state and, consistently, the absorption spectrum shows a band centered at 520 nm. This band overlaps the emission of the fluorescein component and, as a result, the excitation of the fluorophore is followed by the transfer of the excitation energy to the adjacent merocyanine with a concomitant fluorescence quenching. Upon visible irradiation, the photochromic component switches from its colored state to its colorless form to generate **20b**. This species does not absorb in the range of wavelengths where the fluorophore emits and, hence, it cannot accept its excitation energy. Thus, the visible irradiation of this fluorophore–photochrome dyad causes a significant enhancement in emission intensity. Upon storage in the dark, the colorless state of the photochromic component switches to the colored one over the course of several hours and the emission intensity returns to its original low values. In fact, the alternation of visible irradiation and storage in the dark can be exploited to turn the emission intensity of this particular system from low to high and vice versa.

Conclusions

The photoinduced and reversible interconversion between the two states of a photochromic compound can be exploited to modulate fluorescence. Intrinsically-fluorescent photochromes differ in the luminescence quantum yield of their interconvertible states and, as a result, the transformation of one of their states into the other alters the emission intensity. Alternatively, photochromic switches can be attached covalently to fluorescent partners. In the resulting molecular assemblies, the photoinduced interconversion of one component modulates the emissive behavior of the other on the basis of changes in conjugation, local polarity, electron transfer or energy transfer. The electron transfer mechanisms rely on either a change in the redox potential of the photochromic component or in a change of the separation between an electron donor and an electron acceptor with the interconversion of the photochrome. In both instances, the efficiency of electron transfer and, as a result, the fluorescence quantum yield vary with the state of the photochrome. The energy transfer mechanisms are based on a change in the overlap between the emission band of a

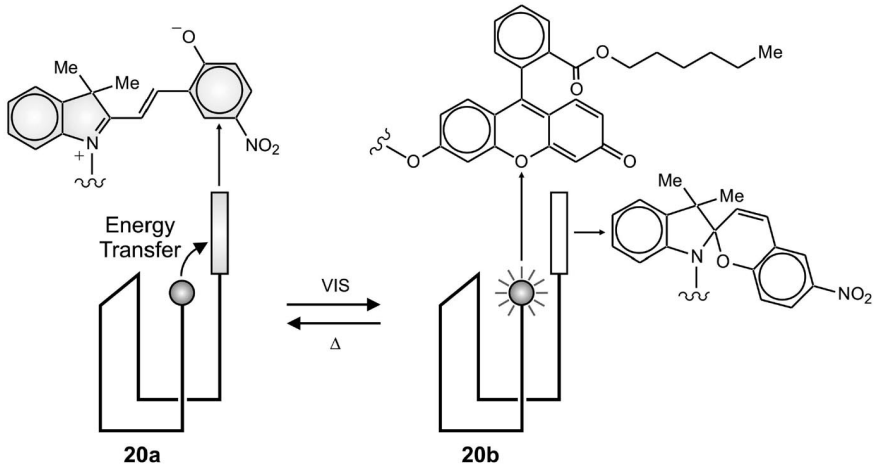

Figure 17. The photoinduced transformation of the photochromic component of **20a** prevents the energy transfer process and restores the emission of the fluorescent component.

fluorescent component and the absorption bands of a photochromic component with the interconversion of the latter. The overall result is a change in energy transfer efficiency and, as a consequence, in emission intensity. Strategies to modulate the fluorescence of an emissive component with a photochromic element can also be extended from the intramolecular to the intermolecular level. Once again the overlap between the emission band of a fluorophore and the absorption bands of a complementary photochrome can be invoked to implement these operating principles. Furthermore, these strategies can be extended to the modulation of multiple fluorophores in parallel within the same or different solution or even within rigid matrices. Similarly, these mechanisms for fluorescence modulation can be adapted to nanostructured constructs. In fact, fluorescent and photochromic components can be incorporated within linear and cross-linked polymers, attached to nanostructured inorganic scaffolds or conjugated to biomolecules. Alternatively, photochromic ligands can be connected to luminescent inorganic nanoparticles. In all these nanostructured constructs, the interconversion of the photochromic components controls the emission of the luminescent components. Thus, the investigation of these fascinating systems can advance our understanding of the subtle factors regulating the photochemical and photophysical properties of inorganic and organic compounds as well as lead to the development of novel materials for the manipulation of optical signals. Indeed, the realization of devices for information storage and of luminescent probes for biomedical application can ultimately be envisaged.

Acknowledgments

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