Electron and energy transfer modulation with photochromic switches

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This *tutorial review* illustrates how work on the reversible interconversion between the colorless and colored forms of photochromic compounds can be exploited to modulate electron and energy transfer processes. Indeed, a photochrome can be designed to accept electrons or energy from a complementary donor in one of its two states only. Alternatively, the photoinduced transformations associated with a photochromic switch can be engineered to control the relative orientation and distance of donor–acceptor pairs. If either the donor or the acceptor is fluorescent, the photoregulated transfer of energy or electrons results in the modulation of the emission intensity. Thus, these fascinating molecular and supramolecular systems can advance the basic understanding of electron and energy transfer processes, while leading to viable operating principles to control light with light.

1 Photochromism

The term photochromism, derived from the Greek words *phos* (light) and *chroma* (color), means the generation of color under the influence of light. When restricted to the molecular world, this term implies the *reversible* photoinduced coloration of an ensemble of molecules in an amorphous, crystalline or solution state.[1] The photogenerated and colored form must be able to revert back to the original and colorless state. The decoloration process can occur thermally and/or photochemically. A photoinduced decoloration, however, requires the irradiation wavelength to be sufficiently different from that causing coloration. Generally, visible light is employed to encourage decoloration, while ultraviolet radiation is used to promote coloration.

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Early observations of the reversible photocoloration of organic compounds have been reported in the literature more than a century ago.[1] Only much later with the advent of modern spectroscopic techniques, however, have studies on photochromic compounds evolved into a mature field of research.[2–5] Over the course of the past four decades, numerous families of organic molecules with photochromic properties have been identified and studied in detail. Most of them rely on unimolecular reactions for their coloration and decoloration, which generally involve ring closing and opening steps or *trans* → *cis* and *cis* → *trans* isomerizations. Bimolecular processes, based on photoinduced cycloadditions or electron transfer, have also been employed to design and implement photochromic systems, although they are certainly less common than their unimolecular counterparts.

The photoresponsive character associated with this fascinating class of organic molecules has suggested a wealth of

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potential applications in a wide diversity of areas, ranging from biomedical research to information technology.[6–8] Indeed, some of these compounds have evolved into convenient building blocks for the fabrication of commercial ophthalmic lenses. Furthermore, their potential implications in the alignment of liquid crystals, the realization of diffraction gratings and holograms, the development of switches and memories is stimulating intense and highly promising interdisciplinary research efforts.

2 Fluorescence modulation

The stereoelectronic properties of the two interconverting states of a photochromic compound are designed to be significantly different. This distinction is necessary to ensure drastic changes in the visible region of the absorption spectrum with the photochemical transformation. Only under these conditions can color be generated and bleached. A significant modification of the structural and electronic character of an organic molecule, however, can also be accompanied by noticeable changes in emission properties. Thus, the two states of a photochromic switch differ in their ability to absorb and, in some instances, even to emit light.[8,9] For example, the fluorescence intensity of diarylethenes and fulgides incorporating indole groups changes significantly upon coloration. The photoinduced ring-closure of the colorless and fluorescent form of indolyl diarylethenes produces a colored and non-emissive isomer.[10] By contrast, the photoinduced coloration of indolyl fulgides is accompanied by an increase in emission intensity.[11]

The reversible isomerizations of fluorescent and photochromic switches can be monitored by either absorption or emission spectroscopy. Both methods, however, demand the colored and/or fluorescent form of the photochromic switch to absorb light and, therefore, can encourage its photoisomerization. In order to avoid the destructive reading of the switch state, it is possible to monitor the emission of a fluorophore appended to the photochromic compound, rather than measuring the fluorescence of the switch itself. Indeed, the interconversion between the two forms of the photochromic component can alter the intensity, or even the wavelength,[12–14] of the fluorescent appendage relying on diverse mechanisms. For example, the conjugation of the open form of a diarylethene switch with a pyridine ligand enhances the luminescence of appended transition metal complexes.[15,16] Similarly, changes in local polarity associated with the reversible interconversion of the open and closed forms of a fulgide modulate the emission intensity of an oxazine appendage.[17–19] When the fluorescent and photochromic components of these molecular assemblies are electronically isolated, the local excitation of the emissive component does not trigger the photoisomerization of the photochrome. Under these conditions, the state of a photochromic switch can be probed nondestructively with relatively simple fluorescent measurements.

The emissive behavior of certain fluorophores can also be controlled relying on the transfer of electrons or energy. Both processes can be modulated either intramolecularly or intermolecularly by operating a photochromic switch. In the first case, the fluorescent and photochromic components are integrated within the same molecular skeleton. In the other, they can be paired within a supramolecular assembly or even be in separate environments. The local excitation of the fluorophore is then followed by efficient electron or energy transfer to one of the states of the photochrome or, in some instances, to a third accepting component. The quenching of the singlet excited state of the fluorophore results in the efficient suppression of the emission. Occasionally, the fluorophore itself acts as electron or energy acceptor in the presence of a quenching or sensitizing, respectively, donor. Thus, these clever operating principles can be exploited to manipulate the flow of electrons and energy in multicomponent ensembles in order to control a fluorescence output as well as, in certain systems, a voltammetric response.[20–22]

3 Intramolecular energy transfer

The first example of intramolecular energy transfer modulation with a photochromic switch was reported in 1993.[23] It is based on a molecular assembly (**1** in Fig. 1) incorporating an anthracene donor, a fulgide switch and a coumarin acceptor. This compound can be operated in liquid solutions[23] as well as in rigid polymer matrices.[24–27] Excitation of the anthracene appendage at 258 or 400 nm encourages local $S_0 \rightarrow S_3$ or $S_0 \rightarrow S_1$ transitions, respectively, but leads to coumarin emission

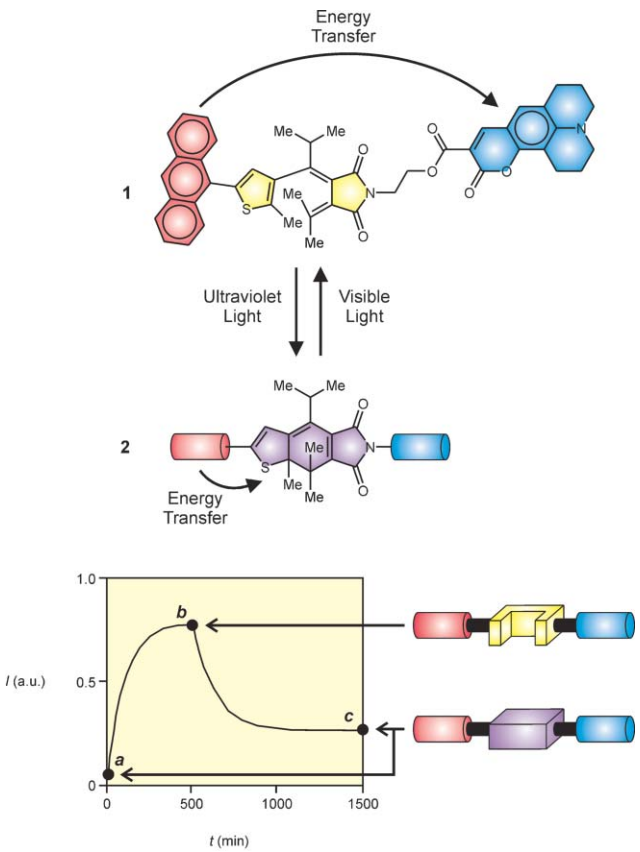

Fig. 1 Recovery (from ***a*** to ***b***) of the coumarin fluorescence (excitation at 400 nm) during irradiation at 520 nm and its subsequent decay (from ***b*** to ***c***) with illumination at 320 nm. Reproduced in part from ref. 23 with permission from Elsevier.

between 450 and 550 nm.[23] Indeed, the excited anthracene donor transfers energy to the emitting coumarin acceptor with a quantum yield of 0.90 and a time constant of 1.7 ps.[25]

Upon irradiation at 320 nm, the photochromic fulgide embedded in **1** switches to the corresponding closed form, producing the isomer **2** (Fig. 1) with a quantum yield of 0.15.[23] At this stage, the excitation of the anthracene chromophore does not lead to a significant coumarin fluorescence. The excited anthracene donor transfers energy to the closed form of the fulgide switch, rather than to the coumarin fluorophore. The quantum yield of this intramolecular energy transfer process is 0.88.[25]

The closed fulgide switch in **2** reverts to the open form in **1** with a quantum yield of 0.12, after irradiation at 520 nm. This transformation activates the original energy transfer pathway from the anthracene donor to the coumarin acceptor. Consistently, the coumarin fluorescence, probed by exciting the anthracene donor at 400 nm, increases back to the original value (from ***a*** to ***b*** in Fig. 1) during the isomerization from **2** to **1**. It decreases again (from ***b*** to ***c*** in Fig. 1) after photoisomerization from **1** to **2**. Thus, the fluorescence intensity of the coumarin appendage can be modulated by routing the excitation energy within the multicomponent assembly with the aid of appropriate optical stimulation. Presumably, the overlap between the anthracene emission and the coumarin absorption in isomer **1** and between the same emission and the fulgide absorption in isomer **2** dictates the preferred energy transfer pathway.[25]

The coumarin emission in **1** and **2** is regulated by controlling the amount of excitation energy that is transferred from the anthracene donor to the fluorescent acceptor. Alternatively, the fluorescence of a multicomponent assembly can be quenched by transferring the excitation energy away from the emissive component. These operating principles can be implemented with diarylethene–anthracene–diarylethene,[28] spiropyran–fluorescein–spiropyran[29] and spiropyran–perylenediimide–spiropyran[30] triads, in which a single fluorophore bridges two identical photochromes. For example, the anthracene fluorophore in **3** (Fig. 2) is flanked by two diarylethene switches. In tetrahydrofuran, the anthracene bridge emits at *ca.* 500 nm (***a*** in Fig. 2) with a quantum yield of 0.83, upon excitation at 450 nm.[28] The open states of the two photochromic fragments do not absorb in the range of wavelengths where the fluorophore emits and, therefore, have a negligible influence on its fluorescence. Irradiation at 313 nm closes one of the two photochromic switches in **3**, forming the isomer **4** (Fig. 2). Interestingly, the other diarylethene fragment remains in the open form. Presumably, energy transfer from its excited state to the closed form of the other switch prevents isomerization. After chromatographic separation from the original isomer **3**, the emission spectrum of the photoproduct **4** does not reveal the characteristic fluorescence of the anthracene bridge (***b*** in Fig. 2). Indeed, the closed diarylethene switch in **4** can absorb the light emitted between 500 and 600 nm. The result is a dramatic decrease in fluorescence quantum yield to 0.001. Consistently, the fluorescence at the photostationary state, reached after irradiation of **3** at 313 nm, is significantly less intense than the original value, which is restored in full upon illumination at wavelengths longer than

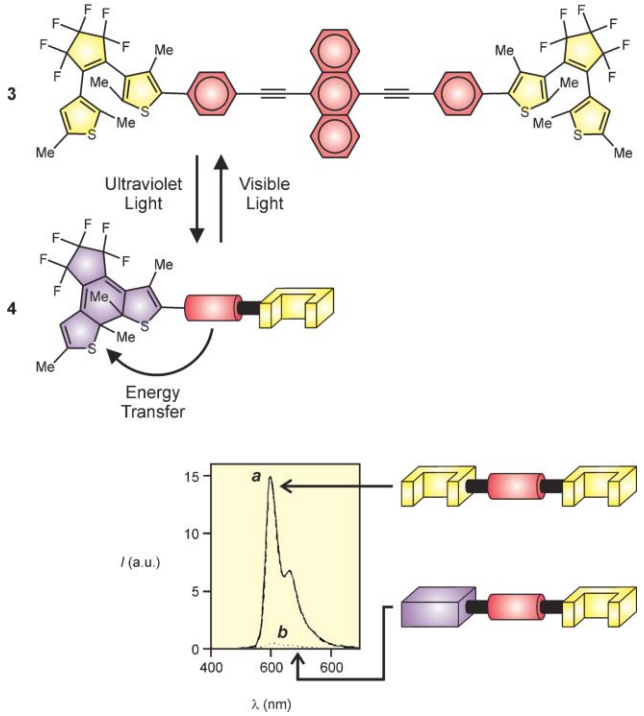

Fig. 2 Emission spectra of **3** (***a***) and **4** (***b***) recorded after excitation at 450 nm. Reproduced in part from ref. 28 with permission from the Royal Society of Chemistry.

500 nm. Under visible irradiation, the closed diarylethene switch in **4** reverts to the open form and regenerates the original isomer **3**.

The photoinduced interconversion of one of the two photochromic fragments in **3** is sufficient to regulate the emissive behavior of the anthracene fluorophore. The other switch does not contribute to the energy transfer process responsible for fluorescence quenching and, therefore, can be omitted without compromising the emissive and photochromic properties of the molecular assembly. In fact, essentially the same operating principles can be implemented with dihydroazulene–anthracene,[31,32] fulgide–binaphthol,[33] spiropyran–porphyrin,[34] diarylethene–anthracene[35,36] and pyrazoline–azobenzene[37] dyads, in which a single photochrome is paired to a single fluorophore. For example, the anthracene fluorescence of a compound similar to **3**, but lacking one of the two switches, is maintained when the single diarylethene fragment is in the open form.[35] Ultraviolet irradiation closes the photochromic switch with a quantum yield of 0.12. After photoisomerization, the fluorescence quantum yield drops from 0.73 to less than 0.001 and the fluorescence lifetime decreases from 4.9 ns to only 4.5 ps. These remarkable changes are, once again, a consequence of energy transfer from the anthracene excited state to the closed form of the diarylethene switch with unitary quantum yield. Under visible irradiation, the closed diarylethene reverts to the open form, although the quantum yield for this process is only 8×10^{-5}. The photogenerated open state of the photochromic fragment lacks absorption bands in the wavelength range where the anthracene fluorophore emits. As a result, the excitation energy of the anthracene fluorophore cannot be

transferred efficiently to the photochrome and the original emission intensity is restored.

The operating principles regulating the emissive behavior of triads incorporating *one* fluorophore between *two* photochromes (*e.g.*, **3** in Fig. 2) can be replicated successfully by inserting *one* photochrome between *two* fluorophores. In particular, oligothiophene–diarylethene–oligothiophene[38,39] and porphyrin–diarylethene–porphyrin[40–43] assemblies display fluorescence modulation when operated with alternating ultraviolet and visible irradiation. Compound **5** (Fig. 3), for example, has two porphyrin fluorophores and a central diarylethene photochrome.[40,42] The open form of the switch does not absorb in the wavelength range where the two fluorophores emit. Thus, the local excitation of the porphyrin appendages at 430 nm results in intense emission at 655 nm. The irradiation of **5** at 313 nm closes the photochromic fragment to produce the isomer **6** (Fig. 3). At the photostationary state, the ratio between **5** and **6** is *ca.* 31 : 69 in favor of the photogenerated species. The closed form of the photochromic fragment absorbs light between 500 and 600 nm. Consistently, the excitation of the porphyrin appendages at 430 nm is followed by intramolecular energy transfer to the photochromic switch. As a result, the fluorescence intensity detected at the photostationary state is significantly less intense than the original value. The photochromic switch reverts to the open form, after irradiation at wavelengths longer than 480 nm. The re-isomerization from **6** to **5** suppresses the ability of the central photochrome to accept the excitation energy of the appended fluorophores and the original fluorescence is restored. It follows that the porphyrin fluorescence can be modulated efficiently by switching back and forth between the two isomers. The plot in Fig. 3 illustrates the fluorescence change for six consecutive switching cycles achieved by alternating ultraviolet and visible irradiation.

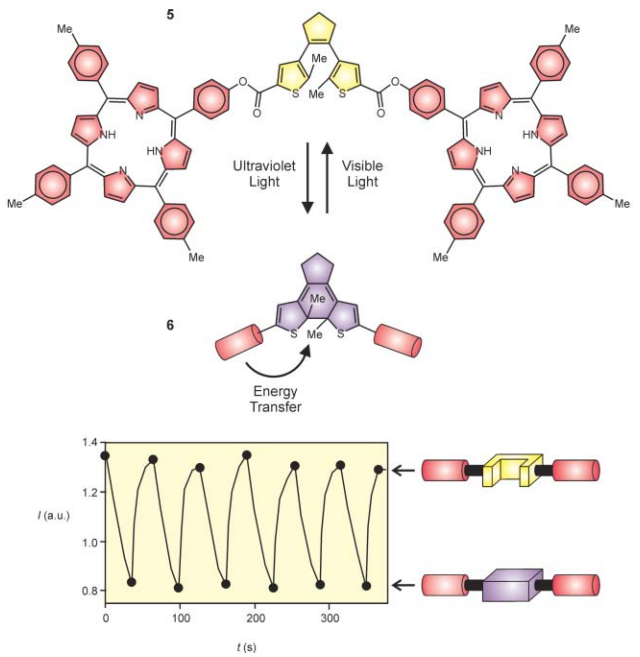

Fig. 3 Modulation of the porphyrin fluorescence (excitation at 430 nm) with the interconversion of **5** and **6** induced by alternating irradiation at 313 and >480 nm. Reproduced in part from ref. 40 with permission from the American Chemical Society.

Only one of two isomers in Fig. 3, however, retains its state after prolonged irradiation at the porphyrin excitation wavelength. Indeed, the transfer of energy from the excited porphyrins to the closed form of the switch encourages the ring opening of the diarylethene fragment, transforming **6** into **5**. This limitation can be circumvented with a modification of the molecular design. The free-base porphyrins covalently attached to the diarylethene switch can be replaced with ruthenium(II) porphyrins coordinated to pyridine ligands at the termini of the photochromic fragment.[41,42] The resulting molecular assembly can be irradiated at 365 nm to close the diarylethene switch and at 470–685 nm to encourage the re-isomerization. The metal-containing porphyrins can be excited at 455 nm, where neither one of the two switch states absorbs. The local excitation of these two chromophores is followed by phosphorescence at 730 nm, only when the photochromic switch is in the open form. The closed state of the photochromic bridge suppresses the luminescence the two porphyrin termini. Interestingly, this particular state of the photochromic switch does not absorb at the luminescence wavelength. Furthermore, control experiments with a model compound lacking one of the two porphyrins revealed essentially the same behavior. Thus, neither radiative energy transfer nor intramolecular porphyrin–porphyrin interactions can be responsible for the luminescence quenching in this particular system. Perhaps the changes in π-conjugation associated with the interconversion of the two forms of the switch are responsible for the phosphorescence modulation, as observed for the luminescence of transition metal complexes appended to related diarylethene switches.[15,16]

4 Intramolecular electron transfer

The interconversion between the two states of most photochromes involves major geometrical changes at the molecular level. In particular, *trans* → *cis* and *cis* → *trans* isomerizations

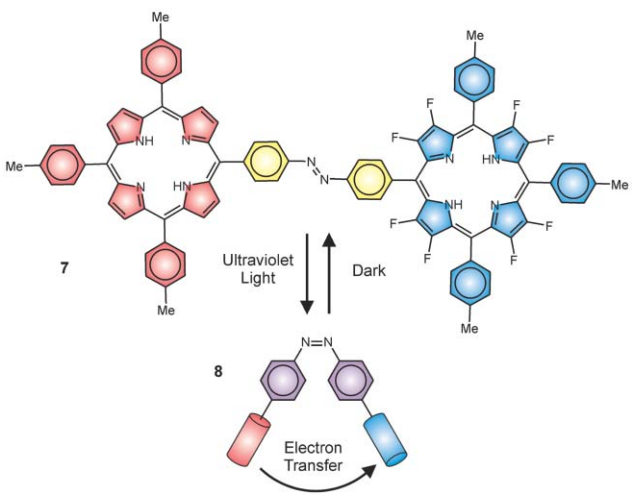

Fig. 4 Photoinduced interconversion of **7** and **8** with the associated intramolecular electron transfer.

shorten and elongate, respectively, azobenzene and stilbene switches. These modifications can be exploited to alter reversibly the distance between electron donors and acceptors appended to the *para*-positions of the phenylene rings of these particular photochromes. In turn, the distance modulation results in the reversible regulation of the electron transfer efficiency. This intriguing mechanism can be implemented with porphyrin–azobenzene–porphyrin[44] and porphyrin–stilbene–pyromellitic diimide[45] triads, in which a central photochrome bridges an electron donor to an appropriate acceptor. Alternatively, the distance dependence of electron transfer can be also exploited in azobenzene–porphyrin–azobenzene assemblies,[46] in which one of the photochromic switches donates an electron to the porphyrin core upon excitation.

An example of this class of multicomponent molecular assemblies is illustrated in Fig. 4. The azobenzene in **7** switches from a *trans* to a *cis* configuration upon irradiation at wavelengths shorter than 440 nm.[44] The photoinduced interconversion from **7** to **8** is confirmed by a pronounced decrease of the absorption band corresponding to the $\pi \rightarrow \pi^*$ transition of the *trans*-azobenzene fragment, which is centered at 408 nm. This band, however, is recovered in *ca.* 1 h upon storage in the dark. Under these conditions, the *cis* isomer **8** reverts thermally to the more stable *trans* form **7**.

Control experiments with model compounds suggest that the reduction potential of a porphyrin core shifts in the positive direction, if electron withdrawing fluorine substituents are introduced on the four pyrrole rings.[44] Thus, the fluorinated porphyrin at one end of **7** and **8** (Fig. 4) has a pronounced electron accepting character relative to the non-fluorinated porphyrin at the other end. Consistently, excitation of either **7** or **8** at 430 nm is followed by electron transfer from the non-fluorinated to the fluorinated porphyrin. This process competes with the radiative deactivation of the porphyrin singlet excited states and, in fact, the fluorescence quantum yields of **7** and **8** are one order of magnitude lower than those of the isolated porphyrin fluorophores. However, the distance between donor and acceptor in the *cis* isomer **8** is shorter than that in the *trans* from **7**. As a result, the electron transfer process in **8** is more efficient than in **7**. Indeed, the quantum yield for the porphyrin fluorescence drops from 0.024 to 0.011 with the isomerization from **7** to **8** and returns to the original value, after the thermal re-isomerization.

In alternative to the photoregulation of the donor–acceptor separation, intramolecular electron transfer can be modulated by activating competitive energy transfer pathways. Specifically, the photochromic element can be operated to switch reversibly between electron and energy transfer. Compound **9** (Fig. 5) is a remarkable example of this clever mechanism for fluorescence modulation.[26,47] This molecule incorporates an anthracene donor, a diarylethene switch and a pyridinium acceptor. It can be synthesized in six steps, starting from thiophene, with an overall yield of 4%. In acetonitrile, photoinduced electron transfer from the donor to the acceptor occurs upon excitation at 387 nm. This process involves the local excitation of the anthracene chromophore and the subsequent transfer of an electron from the excited donor to the acceptor with a time constant of *ca.* 1.7 ps.[48] Consistently, the transient absorption spectrum (***a*** in Fig. 5), recorded after

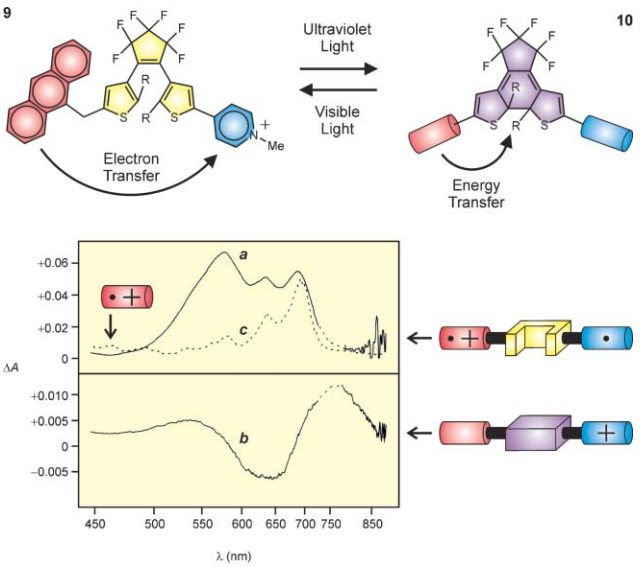

Fig. 5 Transient absorption spectra of **9** (***a***) and **10** (***b***) recorded 7 ps after excitation at 387 nm (R = *n*-hexyl) and absorption spectrum of the 9-methylanthracene radical cation (***c***). Reproduced in part from ref. 47 with permission from the American Chemical Society.

7 ps, shows the characteristic bands of the anthracene radical cation (***c***). Despite the photoinduced electron transfer process, however, the fluorescence spectrum of **9** maintains the characteristic bands of the anthracene S_1 emission.

The irradiation of **9** at 350 nm closes the six-membered ring of the diarylethene switch producing the isomer **10** (Fig. 5). At the photostationary state, the ratio between the two isomers is *ca.* 9 : 1 in favor of **10**. At this point, the excitation of the anthracene chromophore at 387 nm is not followed by electron transfer to the pyridinium acceptor. The transient absorption spectrum (***b*** in Fig. 5), recorded after 7 ps, does not show the characteristic bands of the anthracene radical cation (***c***). Under these conditions, *energy* transfer from the anthracene donor to the closed diarylethene switch competes successfully with *electron* transfer to the pyridinium acceptor. Indeed, the free energy change associated with the energy transfer process is *ca.* −1.67 eV, while that corresponding to electron transfer is only *ca.* −1.37 eV. Furthermore, the energy transfer process quenches efficiently the fluorescence of the anthracene donor and the emission spectrum of **10** does not show bands between 400 and 900 nm. After irradiation at 528 nm, however, the diarylethene switch reverts to the original form and the anthracene fluorescence is restored.

The photoinduced and reversible switching between electron and energy transfer can also be achieved with triads in which the donor, rather that the photochrome, is positioned between the other two functional components. In compound **11** (Fig. 6), a porphyrin donor bridges a diarylethene switch and a fullerene acceptor.[49] This molecule can be synthesized in six steps, starting from 3-bromo-2-methylthiophene-5-boronic acid, with an overall yield of 8%. In 2-methyltetrahydrofuran, photoinduced electron transfer from the donor to the acceptor occurs with a quantum yield of unity, upon excitation at 550 nm. Indeed, the local excitation of the porphyrin chromophore is followed by the transfer of an electron from

the S_1 state of the donor to the acceptor with a time constant of 25 ps. The photogenerated fullerene radical anion absorbs at 1000 nm (***a*** in Fig. 6) and decays with a time constant of 3 ns, after back electron transfer.

The irradiation of **11** at 360 nm closes the diarylethene switch forming the isomer **12** (Fig. 6). In this compound, energy transfer from the excited porphyrin to the diarylethene switch competes successfully with electron transfer to the fullerene acceptor. In fact, the energy transfer process occurs within 2.3 ps of excitation and depresses the quantum yield of electron transfer to only 0.09. Consistently, the transient absorption spectrum of **12** (***b*** in Fig. 6), recorded 100 ps after excitation of the porphyrin chromophore, does not show the characteristic absorption of the fullerene radical anion. After irradiation at 600 nm, however, this band can be observed again. Under these irradiation conditions, the diarylethene switch of **12** reverts to the open form and reactivates the electron transfer pathway associated with the original isomer **11**.

Similar results can be achieved by replacing the diarylethene fragment of **11** with a dihydropyrene switch.[50] The oxidation potential of this particular unit is *ca.* 0.62 V lower than that of the porphyrin donor. In fact, the photoinduced electron transfer from the excited porphyrin to the fullerene acceptor is followed by a shift of the positive charge from the porphyrin radical cation to the dihydropyrene fragment within 150 ps. The result is the formation of a charge-separated state with a remarkably long lifetime of 2 μs in a quantum yield of 0.94. By contrast, the photoinduced interconversion of the dihydropyrene switch to the cyclophanediene form inhibits the charge shift. The oxidation potential of the cyclophanediene fragment is too close to that of the porphyrin chromophore for the charge shift to compete successfully with back electron transfer from the porphyrin chromophore to the fullerene acceptor.

The photoinduced electron and energy transfer processes operating in **7/8**, **9/10** and **11/12** compete with the radiative deactivation of the singlet excited states of the corresponding anthracene and porphyrin fluorophores. As a result, the fluorescence of these chromophores is partially quenched in both states of each switch. The changes in emission intensity associated with the isomerizations of these systems are a consequence of the different quenching efficiencies in the two isomeric states. In the context of fluorescence modulation, however, it would be advantageous to have a quenching pathway in place for only one of the two interconverting isomers. The difference in the reduction potentials of the closed and open forms of a dihydroindolizine switch (Fig. 7), for example, can be exploited to turn on and off intramolecular electron transfer from an appended porphyrin donor.[51] In compound **13**, the porphyrin chromophore and the closed form of the photochromic switch do not interact. Consistently, the excitation of the porphyrin at 550 nm results in significant fluorescence (***a*** in Fig. 7). Irradiation of **13** at 366 nm opens the dihydroindolizine fragment to the corresponding betaine to produce the isomer **14** (Fig. 7). This photoinduced transformation shifts the reduction potential of the photochromic component by *ca.* +0.48 V. Under these conditions, electron transfer from the excited porphyrin to the photochrome becomes thermodynamically allowed with a free energy change of *ca.* −0.22 eV. Indeed, the local excitation of the porphyrin chromophore is, now, followed by electron transfer from the excited donor to the betaine acceptor with a time constant of 50 ps and a quantum yield of unity. The efficient quenching of the porphyrin singlet excited state results in the suppression of the fluorescence bands (***b*** in Fig. 7). Irradiation at 590 nm reverts the photochromic switch to its original state with a quantum yield of 0.02 and restores the initial fluorescence.

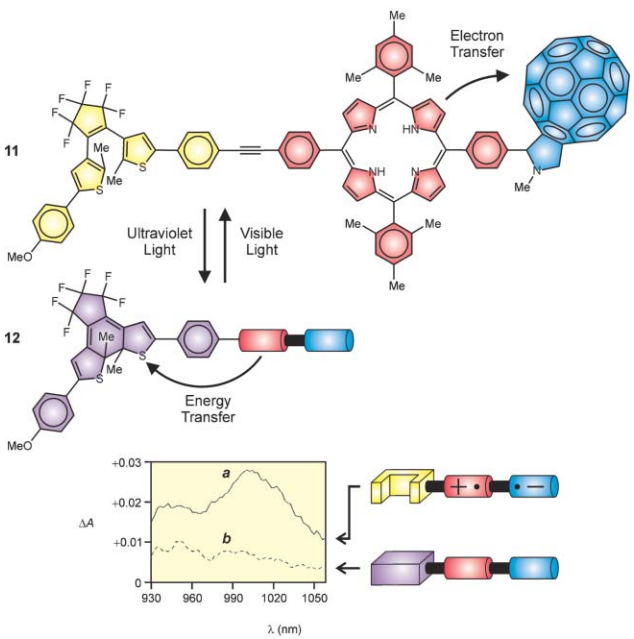

Fig. 6 Transient absorption spectra of **11** (***a***) and **12** (***b***) recorded 100 ps after excitation at 550 nm. Reproduced in part from ref. 49 with permission from the American Chemical Society.

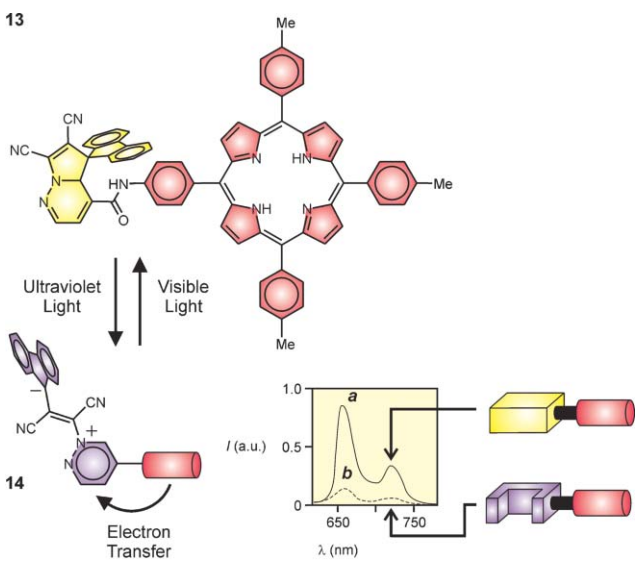

Fig. 7 Fluorescence spectra of **13** (***a***) and **14** (***b***) recorded after excitation at 550 nm. Reproduced in part from ref. 51 with permission from the American Chemical Society.

5 Intermolecular electron transfer

The mechanisms devised to regulate the transfer of electrons within multicomponent molecular assemblies under the control of photochromic fragments can be reproduced at the intermolecular level. One of the main requirements for electron transfer to occur, however, is a close proximity of the donor and acceptor components. In molecular assemblies, intramolecular electron transfer involves subunits integrated within a single covalent skeleton. In the intermolecular case, inclusion phenomena,[52] supramolecular forces[53] or even diffusional contacts[54] can be invoked to enforce short separations between independent donors and acceptors.

Dendrimer **15** (Fig. 8) has 32 azobenzenes at its periphery and 30 tertiary amine groups along its branches.[52] Irradiation at 365 nm induces the *trans* → *cis* isomerization of the azobenzene fragments. This transformation causes a marked increases in absorbance at 450 nm, where a band for the n → π* transition of the *cis*-azobenzenes is centered. At the photostationary state, the ratio between the original isomer **15** and the photogenerated one **16** can be estimated to be 5 : 95. In the presence of eosin Y (**17** in Fig. 8), essentially the same behavior is observed for the azobenzene-containing dendrimer. Similarly, the absorption spectrum of eosin Y is not altered by the isomerization of the azobenzene switches at the periphery of the dendrimer. By contrast, the emission intensity of the eosin fluorophore (***a*** in Fig. 8) drops to 67% (***b***) in the presence of **15**. It decreases even more to 50% (***c*** in Fig. 8), after the photoinduced *trans* → *cis* isomerization of the azobenzene appendages. Nonetheless, the decrease in fluorescence intensity is not accompanied by a significant change in fluorescence lifetime, which remains *ca.* 3.8 ns. The negligible influence of the isomerization on this particular parameter, coupled to the low concentrations of the species, suggests that a static, rather than a dynamic, quenching mechanism is responsible for the suppression of the emission intensity. Indeed, the dendrimer is sufficiently porous for the eosin fluorophore to approach closely the tertiary amines in its interior. There, the local excitation of eosin Y is followed by electron transfer from the amine donors to the eosin acceptor. The result is the partial quenching of the eosin fluorescence. However, this effect is more pronounced when the azobenzene switches are in a *cis* configuration. It is believed that this particular arrangement increases the ability of the dendrimer to host eosin guests.

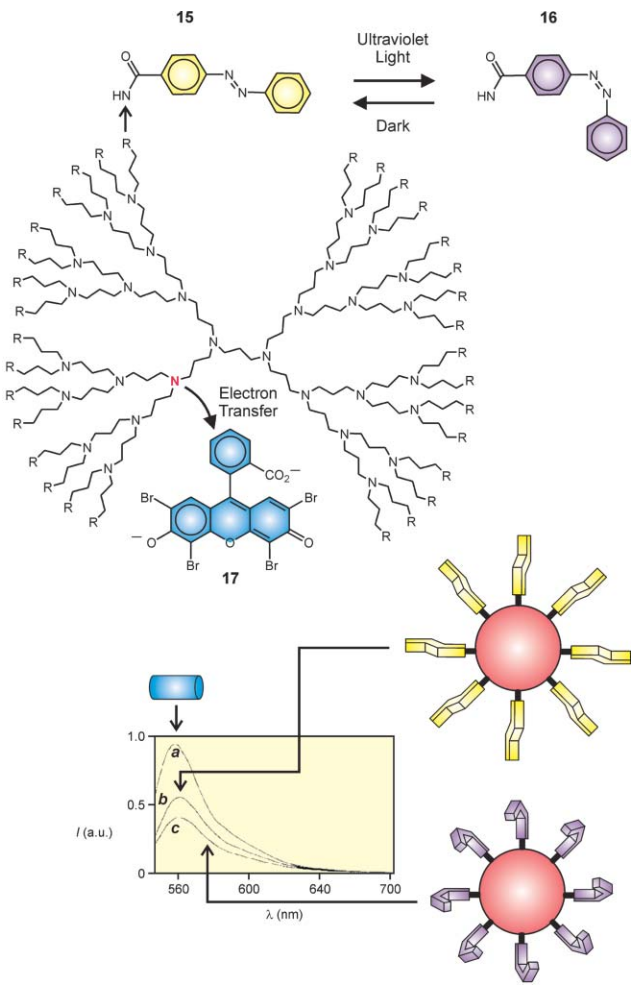

Fig. 8 Fluorescence spectra of **17** (excitation at 535 nm) in the absence (***a***) and presence of either **15** (***b***) or **16** (***c***). Reproduced in part from ref. 52 with permission from the American Chemical Society.

Short donor–acceptor separations can be also enforced with the aid of hydrogen bonding interactions. For example, two hydrogen bonds hold together the urea and carboxylate groups of the porphyrin fluorophore **18** (Fig. 9) and the quinone switch **19**.[53] In dichloromethane, this particular porphyrin emits at 652 nm, after excitation at 560 nm. A fluorescence enhancement (***a*** in Fig. 9) is observed in the presence of increasing amounts of tetrabutylammonium benzoate. This effect is, presumably, a consequence of hydrogen bonding between the urea of the fluorophore and the carboxylate of the benzoate. The *trans*-quinone **19** has a similar effect on the emission intensity of the porphyrin **18**. In this instance, however, the fluorescence increase with the carboxylate concentration is less pronounced (***b*** in Fig. 9). Presumably, the fluorescence enhancement associated with the supramolecular interaction is compensated for by a partial quenching of the porphyrin singlet excited state. Indeed, intermolecular electron transfer from the porphyrin donor to the quinone acceptor is exergonic with a free energy change of 0.04 eV.

The *trans*-quinone **19** switches to the *ana*-isomer **20** (Fig. 9), upon irradiation at 365 nm.[53] At the photostationary state, the ratio between the two isomers is 5 : 1 in favor of **20**. A ^{1}H-NMR spectroscopic analysis reveals that both isomers bind the porphyrin **18**, causing pronounced chemical shift changes for the resonances associated with the urea protons. The corresponding free energies of complexation are -6.15 kcal mol^{-1} for **19** and -5.15 kcal mol^{-1} for **20**. Interestingly, the fluorescence intensity of the porphyrin decreases with the concentration of the *ana*-isomer **20** (***c*** in Fig. 9). This trend is in marked contrast with that observed for the *trans*-isomer **19** (***c*** in Fig. 9). Indeed, the cyclic voltammograms of both isomers indicate that the isomerization from the *trans* to the *ana* form is accompanied by a shift of +0.4 V in the reduction potential. Thus, the intermolecular electron transfer from the excited porphyrin to the *ana*-isomer **20** is significantly more exergonic than that to the *trans*-isomer **19**.

The photochromic quinone reverts from the *ana* to the *trans* form upon irradiation at wavelengths longer than 434 nm. As a result, the original fluorescence intensity is fully restored. It follows that the emission of the porphyrin component can be regulated by switching back and forth between the two states of the quinone. Interestingly, however, the fluorescence modulation possible with this supramolecular complex cannot be achieved with an equivalent molecular assembly.[55] When the fluorescent donor and photochromic acceptor are covalently linked with amide and/or ether bonds, the quinone loses its photochromic character and the porphyrin emission cannot be regulated. Instead, essentially the same operating principles of the supramolecular complex in Fig. 9 can be reproduced effectively, if the two functional components are covalently appended to a polymer backbone *via* ring opening metathesis.[56]

6 Intermolecular energy transfer

The transfer of an electron from a donor to an acceptor can only occur when the two components are sufficiently close to each other. This stringent distance requirement applies to intramolecular as well as intermolecular processes and demands the careful design of covalent skeletons or non-covalent interactions to regulate the relative orientation of donor and acceptor. Instead, the ability of electromagnetic radiation to propagate through space can be exploited to transfer energy radiatively from a donor to a remote acceptor. It is necessary, however, to engineer appropriately the emission properties of the donor and the absorption character of the acceptor. Only if the donor emits in a range of wavelengths where the remote acceptor absorbs significantly can energy be transferred from one to the other.

Similar design criteria can be extended to pairs of fluorescent and photochromic compounds to modulate the emission intensity of the fluorescent component. The interconversion of the switch states must be accompanied by an appreciable change in the degree of overlap between the emission bands of the fluorophore and the absorption bands of the photochrome. Under these conditions, the amount of re-absorbed emission is expected to vary with the state of the photochromic switch. Furthermore, the energy absorbed by the photochrome must be dissipated either non-radiatively or in the form of emission at wavelengths differing from those of the original fluorescence. If all these requirements are met, the interconversion of the photochromic switch alters the detectable intensity of the emission originated from the fluorescent component.

We have implemented experimentally these operating principles with the spiropyran **21** (Fig. 10).[57,58] In acetonitrile, this compound does not absorb radiation with wavelengths longer than 400 nm (***a*** in Fig. 11).[59,60] Upon irradiation at 341 nm, the pyran ring of **21** opens and, then, the adjacent double bonds switches from a *cis* to a *trans* configuration, producing the isomer **22** (Fig. 10). This compound has an intense absorption band in the visible region (***b*** in Fig. 11) and reverts to **21** either thermally or after irradiation at 560 nm. Furthermore, acidification of **22** results in the protonation of the phenolate appendage with the formation of **23** (Fig. 10). The protonation induces significant changes in the absorption

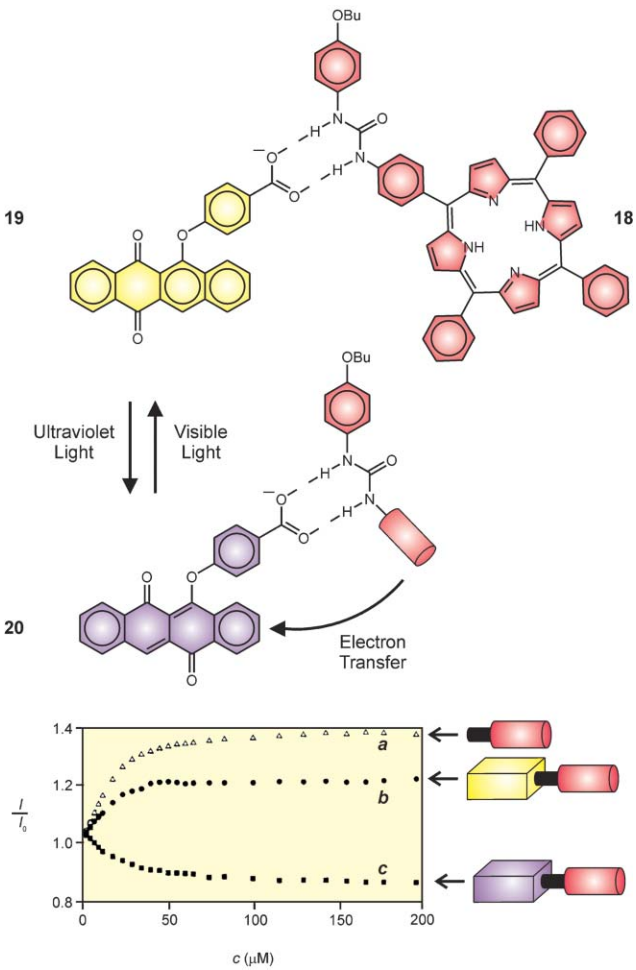

Fig. 9 Fluorescence intensity of **18** (excitation at 560 nm) in the presence of increasing amounts of tetrabutylammonium benzoate (***a***), **19** (***b***) or **20** (***c***). Reproduced in part from ref. 53 with permission from the American Chemical Society.

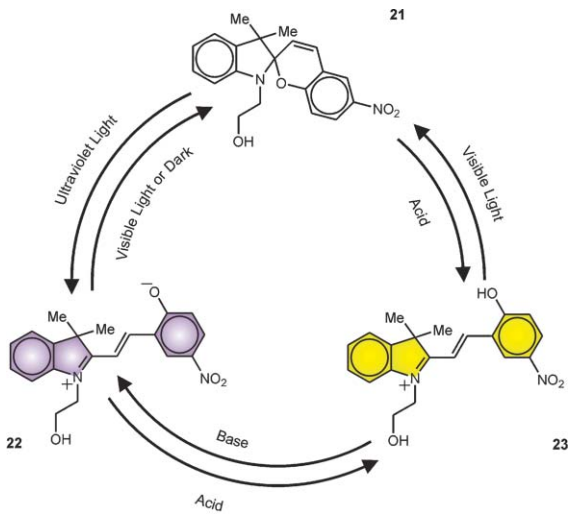

Fig. 10 Interconversion of **21**, **22** and **23** under the influence of optical and chemical stimulation.

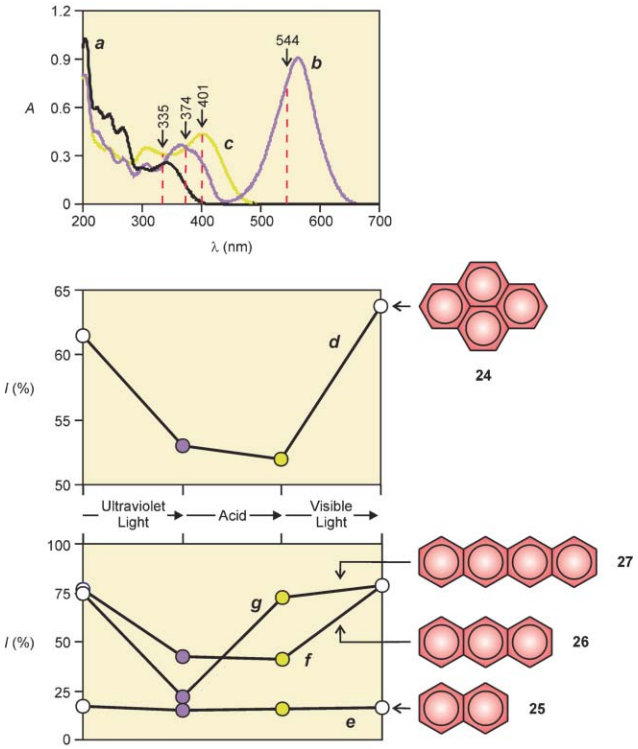

Fig. 11 Absorption spectra of **21** (***a***), **22** (***b***) and **23** (***c***) in acetonitrile. Influence of **21**, **22** and **23** on the emission at 374 nm (***d***, excitation at 336 nm) of an acetonitrile solution prepared co-dissolving equimolar amounts of **21** and **24**. Influence of **21**, **22** and **23** on the emission of a distinct solution containing equimolar amounts of **25**, **26** and **27** at 335 (***e***, excitation at 275 nm), 401 (***f***, excitation at 357 nm) and 544 nm (***g***, excitation at 441 nm).

spectrum (***c*** in Fig. 11). The addition of a base to **23** restores **22**, while the illumination of **23** at 410 nm produces the original state **21**. Finally, the acidification of **21** results in the thermal formation of the protonated form **23**.

The marked and reversible absorption changes associated with the interconversion of the three states **21**, **22** and **23** can be exploited to modulate the fluorescence of pyrene (**24** in Fig. 11).[57,58] In acetonitrile, pyrene emits at 374 nm when excited at 336 nm. At this particular emission wavelength, the absorbances of **22** and **23** (***b*** and ***c*** in Fig. 11) are identical and significantly greater than that of **21** (***a***). When pyrene is co-dissolved with the spiropyran **21**, approximately 60% of its fluorescence is detected at 374 nm (***d*** in Fig. 11). Upon ultraviolet irradiation of the solution, **21** isomerizes to **22** and the absorbance of the photochromic component at 374 nm increases dramatically (***a*** and ***b*** in Fig. 11). As a result, a larger fraction of the light emitted by **24** is now absorbed by the photochromic switch and the detected fluorescence decreases below 55% (***d*** in Fig. 11). At this point, the acidification of the solution has a negligible influence on the detected intensity (***d*** in Fig. 11). Indeed, the transformation of **22** into **23** does not alter the absorbance of the photochrome at the fluorescence wavelength (***b*** and ***c*** in Fig. 11). However, the original value is fully restored upon visible irradiation (***d*** in Fig. 11). Under these conditions, **23** switches back to **21** lowering the absorbance at 374 nm (***c*** and ***a*** in Fig. 11).

The lack of covalent bonding between fluorophore and photochrome, as well as of stringent distance requirements, implies that the two components can be in distinct environments. For example, a solution of the photochrome in an appropriate container can be interposed between the detector, designed to measure the intensity of the emitted light, and another solution containing the fluorophore. Furthermore, the fluorescence of multiple emissive components can be modulated simultaneously with this configuration. In acetonitrile, naphthalene (**25** in Fig. 11), anthracene (**26**) and tetracene (**27**) emit at 335, 401 and 544 nm, when excited at 275, 357 and 441 nm respectively.[58,61] At the emission wavelength of naphthalene, all three states of the photochromic system **21**, **22** and **23** absorb (***a***, ***b*** and ***c*** in Fig. 11). Consistently, the detected fluorescence intensity at this particular wavelength (***e*** in Fig. 11) is always low, if a solution of the photochromic component is operated between the detector and the fluorescent solution. Under the same conditions, the fluorescence of anthracene (***f*** in Fig. 11) and tetracene (***g***) are instead modulated by the photochromic switch. Indeed, only the state **21** of the photochromic switch *cannot* absorb the fluorescence of anthracene at 401 nm (***a*** in Fig. 11) and only the state **22** *can* absorb the emission of tetracene at 544 nm (***b***). Thus, the detected intensities at these two wavelengths vary with the interconversion of **21**, **22** and **23**.

7 Conclusions

The two interconvertible states of a photochromic switch differ in structural and electronic properties. Their distinct stereoelectronic character can be exploited to modulate electron and energy transfer processes, when the photochrome is operated in conjunction with complementary donors and acceptors. In particular, chemical synthesis can be invoked to integrate energy donors and photochromic fragments in a single molecular skeleton. In the resulting systems, one of the two states of the photochrome is designed to accept energy from the excited donor. Under these conditions, an intramolecular energy transfer process can be activated or suppressed by operating the photochromic component with optical stimulation. Alternatively, an additional energy acceptor can be incorporated within the covalent backbone of a donor–photochrome assembly. The photoinduced interconversion of the switching component then directs the flow of energy from the excited donor to either one of the two competing acceptors. Similar design logics can be extended to the regulation of intramolecular electron transfer. The photochromic fragment of a multicomponent assembly can be engineered to accept an electron, rather than energy, from an excited donor in one its two states only. Alternatively, it can activate a competing energy transfer pathway designed to suppress the intramolecular transfer of an electron from an excited donor to a complementary acceptor.

The mechanisms devised to photoregulate the intramolecular transfer of electrons with photochromic switches can be applied to supramolecular assemblies. Under the influence of noncovalent interactions and inclusion phenomena, distinct donors and acceptors can be enforced in close proximity. If one of the two components is also photochromic, the

intermolecular transfer of electrons from one to the other varies significantly in efficiency with the state of the interconverting species. In the case of intermolecular energy transfer, the proximity of donor and acceptor is not a strict requirement. In fact, fluorescent donors and photochromic acceptors can even be operated in separate environments, while maintaining their ability to exchange energy radiatively.

The identification and implementation of operating principles to control electron and energy transfer with photochromic compounds is contributing to the fundamental understanding of the basic factors regulating these processes. Furthermore, these studies can ultimately lead to the development of a new generation of photoresponsive materials with unique properties. Their ability to modulate a fluorescence output under the influence of optical stimulation, for example, is particularly attractive in the context of data storage, signal processing and sensing applications. Perhaps, possible implications in information technology and biomedical research will eventually emerge, as this fascinating area of research continues to evolve.

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