Photoswitches

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Visible-Light-Activated Molecular Switches

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The ability to influence key properties of molecular systems by using light holds much promise for the fields of materials science and life sciences. The cornerstone of such systems is molecules that are able to reversibly photoisomerize between two states, commonly referred to as photoswitches. One serious restriction to the development of functional photodynamic systems is the necessity to trigger switching in at least one direction by UV light, which is often damaging and penetrates only partially through most media. This review provides a summary of the different conceptual strategies for addressing molecular switches in the visible and near-infrared regions of the optical spectrum. Such visible-light-activated molecular switches tremendously extend the scope of photoswitchable systems for future applications and technologies.

1. Introduction

Living organisms respond to their environment via the activation of specialized receptors in response to chemical and physical stimuli. Light in particular triggers several processes in bacteria (light-energy conversion through ion pumps), plants (photosynthesis, phototaxis, phototropism), and animals (vision, circadian timing). While the initial steps in photosynthesis rely on energy transfer and charge separation, vision and photoinduced movements are typically activated through the conformational isomerization of a chromophore confined in an exquisitely optimized protein, for example retinals in rhodopsins, *para*-hydroxycinnamic acid in photoactive yellow proteins, or bilins in phytochromes.[1] With the exception of the photochemistry taking place in the skin, for example, the UV-light-induced synthesis of vitamin D,[2] most of these processes are regulated by the visible region of the solar spectrum. The benefits of visible light comprise its predominance in the portion of the solar spectrum reaching the surface of the earth, a large window of available wavelengths, and its harmless character. By contrast, UV light typically damages cells, is nonselectively absorbed by any chromophores, and is quickly attenuated in tissues.[3]

For the same reasons, research in several different areas is dedicated to developing synthetic photosensitive systems that respond primarily to visible and near-infrared (NIR) light, for example, photocatalysts based on transition-metal complexes for H_2 evolution[4] or photochemical synthesis,[5] alternating donor–acceptor low-bandgap polymers for photovoltaic cells,[6] sensitizers for photodynamic therapy,[7] or engineered rhodopsins for optogenetics,[8] to name a few.

Molecular switches such as spiropyrans,[9] stilbenes,[10] azobenzenes,[11] and diarylethenes,[12] among others,[13] are of particular interest for constructing reversible photosensitive systems. Remarkable examples in the context of materials applications[14] include photoactuators[15–17] and optically switchable electronic devices[18,19] as well as photoregulated catalysts.[20,21] Recent promising advances related to chemical biology[22,23] should be emphasized as well, in particular, the optical control of neuronal activity,[24] and in the field of photopharmacology,[25] the development of drugs that can be activated by light and possibly auto-deactivate over time.[26]

For most of these applications, the visible and NIR regions are undeniably more suitable than UV light (see above), however, photoswitches are traditionally rather small molecules, which necessitate high-energy photons for isomerization in at least one direction. Accordingly, the development of photoswitchable systems that do not require UV light for activation has recently blossomed, with the first all-visible-light switches reported about two decades ago for diarylethenes,[27] and in 2009 for azobenzenes.[28] In addition to the traditional performance criteria for photochromic compounds, such as photoconversions, that is, the composition of the photostationary state (PSS) mixture, quantum yields for switching in both directions, the thermal half-life of the thermodynamically less stable isomers, and fatigue resistance,

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the ability to isomerize without UV light can be considered a key feature.

The aim of this Minireview is to provide an update on the recent developments of visible-light switches and discuss these examples in the conceptual framework of general strategies to activate photochromic compounds without UV light. Based on mechanistic considerations, the different strategies followed thus far can be divided into three distinct groups (Figure 1). The first general strategy and the most direct (yet not straightforward) tackles the intrinsic molecular design of photoswitches, which upon adequate HOMO–LUMO gap engineering can be directly activated by visible light (Figure 1 a). The second strategy makes use of sensitizers, such as triplet photosensitizers (Figure 1 b, left), upconverting nanoparticles, or multiphoton antennae (Figure 1 b, right), which are able to absorb one or multiple quanta of long-wavelength light and drive the isomerization through (non)trivial energy transfer to the switch. Finally, the third strategy relies on the design of photochromic switches, for which replacement of UV-light activation is achieved by inducing switching in one direction through oxidation/reduction, which can be triggered either electrochemically or through visible-light irradiation by exploiting photoinduced electron transfer to/from a sensitizer (Figure 1 c). An interesting aspect of this approach is the possible generation of (photo)redox catalytic cycles, in which a few electrons (or photons) can trigger many isomerization events. It should be noted that some of the conceptual approaches—although theoretically feasible—have yet to be demonstrated in the context of creating an all-visible-light switch. The details of all these three different strategies, related examples, and operating mechanisms are discussed in the following sections. Since most examples involve azobenzenes (ABs)[11,29] or diarylethenes (DAEs),[12,30] the Minireview will primarily focus on these two well-known classes of photoswitches (Figure 2).

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Stefan Hecht (right) studied chemistry at Humboldt-Universität zu Berlin and obtained his PhD from the University of California at Berkeley in 2001, working under the guidance of Prof. Jean M. J. Fréchet. After establishing his own research group at the Freie Universität Berlin and a subsequent position as a group leader at the Max-Planck-Institut für Kohlenforschung in Mülheim an der Ruhr, he returned to his alma mater in 2006. His research interests range from synthetic macromolecular and supramolecular chemistry to surface science, with a particular focus on utilizing photochromic molecules for the remote control of materials, devices, and processes.

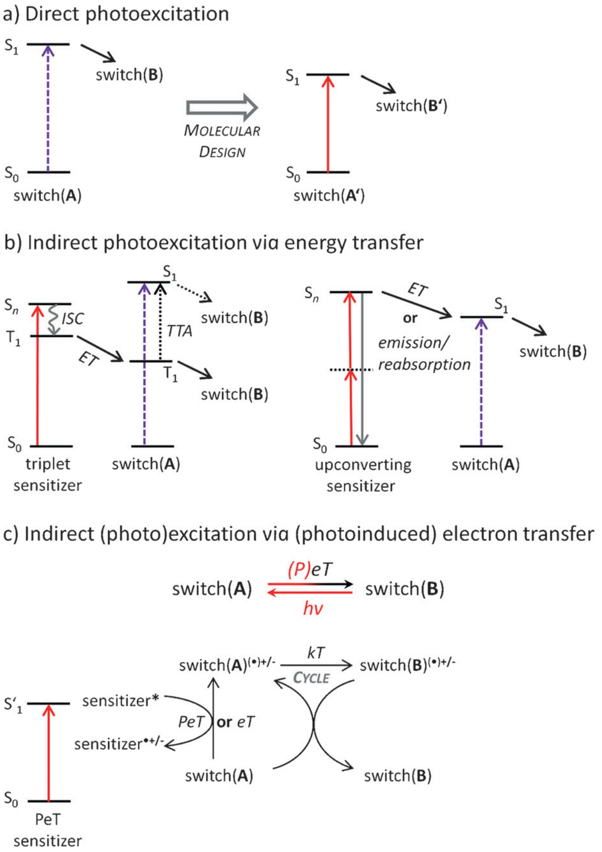


Figure 1. General strategies for replacing UV light (violet dashed arrows) with visible light (red solid arrows) to trigger interconversion between two switching forms A and B. a) Direct photoexcitation as conferred by molecular design. b) Energy transfer from a triplet (left) or an upconverting (right) sensitizer to the switch (left: note that the TTA pathway shown in dotted arrows has not been demonstrated yet; right: photon upconversion can occur via virtual states in the case of multiphoton antennae or intermediate long-lived excited states in the case of lanthanide-doped nanoparticles). c) Switching involving redox reactions in one direction (as shown in the upper equilibrium) that can be coupled to a sensitizer, which has been excited by visible light and initiates the catalytic chain through photoinduced electron transfer (S_0: ground state, S_1: first singlet excited state, T_1: first triplet state, ISC: intersystem crossing, TTA: triplet–triplet annihilation, ET: energy transfer, (P)eT: (photoinduced) electron transfer).

2. Direct Photoexcitation

In this section, we summarize the existing approaches towards the design of photochromic compounds that can be directly addressed with visible light in both directions

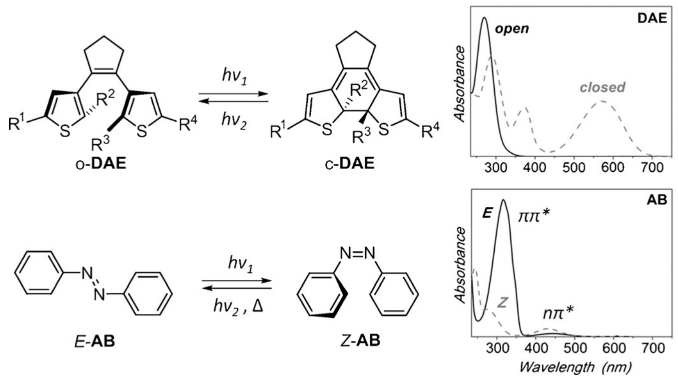


Figure 2. Molecular structures and UV/Vis absorbance spectra of the open- and closed-ring isomers of diarylethenes (o-DAE and c-DAE) and the *E*- and *Z*-isomers of azobenzene (*E*-AB and *Z*-AB).

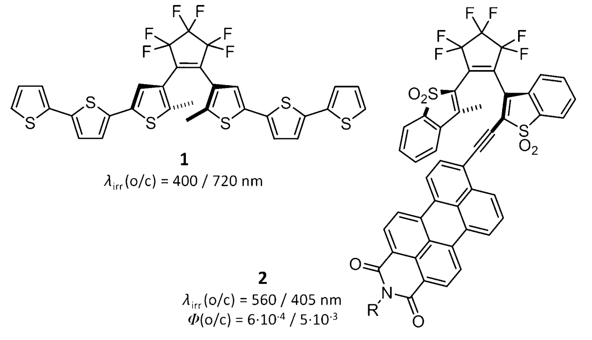


Figure 3. Example of bistable all-visible-light diarylethenes with extended π systems at the terminal 5,5′-positions (compound **1**)[27] or internal 2-position of the heterocycles (compound **2**).[33] (Φ(o/c) and λ_{irr}(o/c): quantum yields and wavelengths used for the o→c/c→o isomerizations).

(general strategy depicted in Figure 1 a). Two distinct types of photoswitches will be distinguished, depending on the relative thermal stabilities of the two isomers.[31] The first type, referred to as T-type photochromism, comprises compounds for which one isomer is thermally unstable and typically reverts to the thermodynamically stable form within milliseconds to a few minutes. Although this type of compound is usually not addressable in both directions with visible light, the high rate of thermal back-isomerization allows reversion of the switch by simply stopping the irradiation. The second type, referred to as P-type photochromism, involves switches for which both isomers are thermally stable. The typical criterion used to differentiate between the two classes is the thermal half-life ($\tau_{1/2}$) of the thermodynamically less stable isomer. Whenever available, the $\tau_{1/2}$ values (which are sometimes highly dependent on the polarity of the solvent) will be indicated.

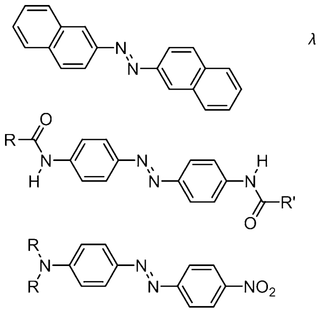
2.1. Extended π conjugation and push–pull systems

The most obvious approach for designing visible-light switches is to extend the π system of a known compound in order to lower the HOMO–LUMO gap and hence red-shift its absorption. A drawback of this strategy, however, is that by extending π conjugation, the photoswitching ability can be lost and hence successful results are not easily obtained.

The first successful attempt at red-shifting the absorption of DAEs without compromising their photoswitching abilities was reported by Lehn and coworkers (compound **1**, Figure 3).[27] For this molecule, π conjugation was extended at the most obvious positions of the thiophene rings by introducing two additional thiophene units in the 5- and 5′-positions of the dithienylethene. This led to a red-shift of both characteristic bands of the open- and closed-ring isomers, which could be used to induce the cyclization and cycloreversion of **1** at 400 and 720 nm, respectively, although no quantum yields were reported for these processes. Other DAEs coupled at the side positions with longer π systems, such as carotenoids, were described shortly thereafter,[32] but in these cases, extremely low cycloreversion quantum yields were reported, thus preventing the exploitation of these compounds as actual switches.

The 2,2′-positions of the DAE unit, which are involved in bond formation upon ring closure and are typically substituted with "dummy" methyl groups, are alternative connecting points for implementing extended π systems. In contrast to the previous approach, where ring closure of **1** leads to a red-shift of the absorption maximum, introducing a chromophore in the 2-position may produce DAE derivatives for which the ring-closed isomer is blue-shifted compared to the ring-open one. Such a molecule (compound **2**, Figure 3) was reported by Irie and co-workers,[33] who introduced a perylene monoimide (PMI) dye at one active carbon atom of the DAE unit. Compound **2** could be successfully switched between open and closed forms by alternating irradiation at 560 and 405 nm, with high photoconversions (> 90 % in both directions) yet very low quantum yields of less than 1 % (see Figure 3). However, when a perylene diimide (PDI) dye was used instead of the PMI, or when the same PMI dye was introduced at the opposite 5-position of the heterocycle, or even when the sulfur atoms of the benzothienyl groups were not oxidized, the corresponding DAEs lost their photoswitching ability. These results illustrate the risks of this design approach.

Extending the π system of azobenzenes may also lead to all-visible-light switches, although as in the case of DAEs, this approach has some drawbacks. ABs exhibit two main electronic transitions (see Figure 2). The π→π* band located in the UV region (typically between 310 and 360 nm) is used to induce the *E*→*Z* isomerization, and the n→π* band in the visible region (usually centered around 450 nm) typically serves to activate the *Z*→*E* isomerization. Extending the π system in ABs can significantly red-shift the π→π* band, whereas the n→π* transition is only slightly affected. As a result, the two bands tend to overlap and the two isomers cannot be addressed selectively anymore. One strategy therefore consists of extending the π system at the limit of a total overlap between the π→π* and *n*→π* bands. In this case, blue and green light can be used to induce the *E*→*Z* and *Z*→*E* isomerizations, respectively, as exemplified by 2,2′-azonaphthalene (compound **3**, Figure 4).[34] This strategy was used by Ikeda and co-workers, for example, for the con-



3
$\lambda_{irr}(E/Z)$ = 410 / > 500 nm
$\tau_{1/2}$ = 15 h (MeCN)

4
$\lambda_{irr}(E)$ = 400 nm
$\tau_{1/2}$ = 8 min (H_2O)

5
$\lambda_{irr}(E)$ = 500 nm
$\tau_{1/2}$ = 1 s (THF)

Figure 4. Examples of red-shifted azobenzenes with increasing T-type character obtained through extension of the π system (compound **3**),[34] push–push substitution (compound **4**),[37,38] and push–pull substitution (compound **5**)[39,40] ($\lambda_{irr}(E/Z)$: wavelengths used for the $E\rightarrow Z/Z\rightarrow E$ isomerizations).

struction of visible-light actuators based on azotolane derivatives (azobenzenes *para*-substituted with phenylacetylene derivatives).[35] Nevertheless, the effective red-shifting obtained by extending the π system in ABs is generally accompanied by a substantial decrease in $\tau_{1/2}$ (from several days to several hours or less), and hence in the practically attainable *Z*-isomer content in the PSS.

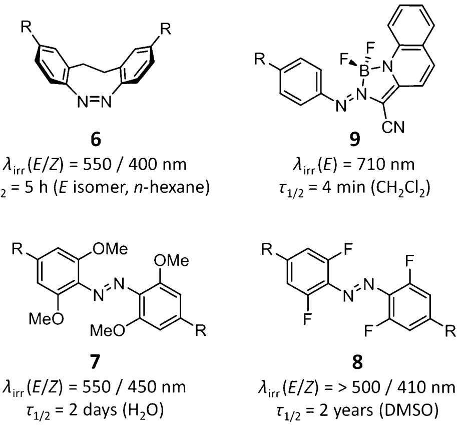
A classical way to lower the gap and therefore red-shift the absorption of ABs is to introduce electron-donating groups (EDGs) and/or electron-withdrawing groups (EWGs) *ortho* or *para* to the N=N to give so-called "amino" azobenzenes, for which one or both rings are functionalized with EDGs, or "push–pull" azobenzenes, in which one ring is functionalized with an EWG while the other one bears an EDG (see compounds **4** and **5**). As a result, the π→π* bands are red-shifted in the 400–600 nm region and concomitantly the thermal stability of the *Z* isomers decreases, and these two effects become more pronounced with the strength of the donor/acceptor substituents. Typically, amino azobenzenes such as **4** can still be switched with light in both directions via their π→π* and n→π* excitations, and are stable for minutes to hours, whereas in the push-pull class, the π→π* and n→π* bands totally overlap and $\tau_{1/2}$ typically ranges from nanoseconds[36] to seconds. Bis(amido) azobenzenes **4** have recently been used in the context of light-gated ion channels[37] or introduced into rigid aromatic backbones for the construction of optomechanical gels that are able to reversibly bend upon alternating irradiation with blue (442 nm) and green (> 490 nm) light,[38] while derivatives of so-called "disperse-red" (compound **5**; R = $(CH_2)_2OH$) have been extensively used in recent decades for photo-inducing motion in polymer materials.[39] In the past century, a multitude of ABs with different push–pull patterns and extended π systems have been industrially synthesized to give several dyes that are still in commercial use, including artificial food colorants. In the more modern context of photoswitching (with the exception of data storage), compounds of this class are increasingly in demand because they can be actively converted to one isomer with visible light and this isomer then thermally reverts in the dark, in other words, they undergo spontaneous deactivation.

Therefore, in the case of ABs, both strategies (π extension and push–pull substitution) typically produce photoswitches that can be activated with visible light and convert back in the dark. Note that several other fast-relaxing switches driven by visible light have been reported that belong to the class of negative photochromic compounds, that is, photoswitches for which the stable form is red-shifted relative to the less stable one. These include some specific spiropyranes,[41] spiropyranes in certain environments,[42] thioindingos,[43] dihydropyrenes,[44] binaphthyl-bridged imidazole dimers,[45] and so-called donor–acceptor Stenhouse adducts "DASAs".[46,47]

2.2. Azobenzenes completely addressable in the visible region

In the preceding part, we have discussed strategies to red-shift the absorption of photoswitches, which often leads to compounds that have either lost their photoswitching ability or undergo rapid relaxation such that they cannot be considered bistable molecules (with the noticeable exception of DAEs **1** and **2**). In the case of ABs, other means exist for obtaining photoswitches for which the two isomers exhibit well separated bands and are therefore selectively addressable in the visible region.

In 2009, inspired by an old report[48] describing an AB bridged in the *ortho* positions with an ethylene linker (compound **6**, R = H, Figure 5), Herges and co-workers realized that the large separation of the n→π* transitions of the *E* and *Z* isomers in cyclic azobenzene derivatives **6** could be used to create a photoswitch that is addressable with visible light only.[28] Such a large splitting of the n→π* bands, which in that case originates from geometrical constraints, is quite remarkable and its potential had not been recognized prior to the report by Herges. Thanks to this large separation of the bands, **6** could be switched quantitatively in both directions by using alternating irradiation with blue and green light.[28,49] Another consequence of the ring strain is the inverse thermal stability of the two isomers: in contrast to



6
$\lambda_{irr}(E/Z)$ = 550 / 400 nm
$\tau_{1/2}$ = 5 h (*E* isomer, *n*-hexane)

9
$\lambda_{irr}(E)$ = 710 nm
$\tau_{1/2}$ = 4 min (CH_2Cl_2)

7
$\lambda_{irr}(E/Z)$ = 550 / 450 nm
$\tau_{1/2}$ = 2 days (H_2O)

8
$\lambda_{irr}(E/Z)$ = > 500 / 410 nm
$\tau_{1/2}$ = 2 years (DMSO)

Figure 5. *Ortho*-functionalized (**6**,[28,49] **7**,[50] and **8**[51,53]) and BF_2-coordinated (**9**)[55,56] azobenzenes addressable with visible light only.

most ABs the *E* isomer of **6** is thermally less stable than the *Z* isomer ($\tau_{1/2}$ of ca. 5 h in *n*-hexane).

In 2011, the group of Woolley, and shortly thereafter we ourselves, followed a related strategy with ABs functionalized in the *ortho* positions with either methoxy π-EDGs (compound **7**, Figure 5)[50] or fluorine σ-EWGs (compound **8**, Figure 5).[51] Similar to the bridged azobenzenes **6**, both compound types exhibit a splitting of the n→π* absorption bands in the visible region. In those two cases however the origin of the separation is mainly due to electronic effects originating from the *ortho* substituents, and a rigorous explanation can only be given by taking into account the modulation of the energetic levels of the n and π* orbitals of *E* and *Z* isomers. The origin of the splitting in the case of the *ortho*-methoxy compound was rationalized by the authors as follows: in the *E* form, the proximity of O and N lone pairs creates unfavorable interactions, which are released in the *Z* isomer. Therefore, compared to *Z*-**7**, the n orbital of *E*-**7** is raised in energy and the main contribution to the splitting is a red-shift of the *E* isomer without any significant blue-shift of the *Z*-isomer. On the other hand, the *ortho*-fluorinated ABs **8** were specifically designed with the expectation that *ortho*-EWGs would stabilize the n orbital of the *Z* form by reducing the electronic repulsion centered on the N=N unit, and thereby increase the energy of the n→π* transition. In fact, the π* orbitals of the fluorinated *E* and *Z* isomers are also stabilized, thus leading to an overall blue-shift of the n→π* band of the *Z* isomer and a red-shift of the n→π* transition of the *E* isomer. In these *ortho*-fluorinated AB derivatives, a maximum separation of the n→π* transitions (by 50 nm) is reached when additional EWGs, such as carboxylic acid derivatives (esters and amides), are introduced *para* to the azo N=N unit. As a consequence, similarly to the bridged compound (**6**), *ortho*-methoxy ABs and *ortho*-fluoro ABs can be addressed with visible light via n→π* transitions and with high photoconversions. Later, it was reported that replacing F by Br or Cl atoms in the *ortho* position leads to ABs with similar electronic transitions features.[52] Notably, in addition to offering visible-light addressability, isomerizing ABs via n→π* transitions is also quite efficient (typical quantum yields of $\Phi = 0.3$–0.5 via n→π* transitions vs. $\Phi = 0.1$–0.2 via π→π* transitions).[53]

A second remarkable consequence of introducing *ortho*-F atoms into ABs is the very high thermal stability of the *Z* isomers: $\tau_{1/2} = 2$ years (!) for **8** (R = H) vs. a few days for unsubstituted ABs. This effect can be partly attributed to pronounced stabilization of the n orbital of the *Z* isomer (while the n orbital of the transition state is less stabilized),[53] which eventually leads to a larger barrier for the thermal *Z*→*E* reaction and places *ortho*-fluoro ABs among the most stable azobenzenes ever reported. Such high thermal stability opens up promising possibilities and has already been used, for example, to create single crystals of *Z*-ABs that exhibit permanent photomechanical shape modification upon irradiation with blue light.[54]

Another possibility for visible-light addressability through well separated bands was discovered by the group of Aprahamian in BF_2-coordinated azo compounds (**9**, Figure 5).[55,56] This new class of photoswitches exhibits well separated π→π* transitions, which in contrast to conventional ABs, are lower in energy than the n→π* transitions and shifted to the red part of the visible spectrum. This last feature is particularly interesting in term of molecular design, since the π→π* band can now be red-shifted without overlapping with the n→π* band. When EDGs were introduced in *para* positions, the π→π* bands of the *E* and *Z* isomers were both red-shifted from 530 and 480 nm (**9**, R = H), to approximately 600 and 520 nm (R = OMe), and even 680 and 620 nm (R = NMe_2). This design provides addressability in the red region of the spectrum, however, as with regular ABs (see section 2.1), such a large red-shift led to a significant decrease of the thermal stability of the *Z* isomers. Indeed, unsubstituted (**9**, R = H) and *para*-methoxy (R = OMe) BF_2-coordinated azo compounds are relatively stable ($\tau_{1/2}$ of ca. 10 h in deoxygenated CH_2Cl_2 and 20 min in regular CH_2Cl_2), but the N-alkyl derivatives relax rather quickly ($\tau_{1/2}$ of several minutes). Moreover, while the photoconversion values are more than 90 % for the methoxy substitution, for the N-alkyl derivative it drops to approximately 60 %. Although these compounds present some drawbacks, they nevertheless belong to the very exclusive group of photoswitches that can be directly activated with light at a wavelength of less than 700 nm.

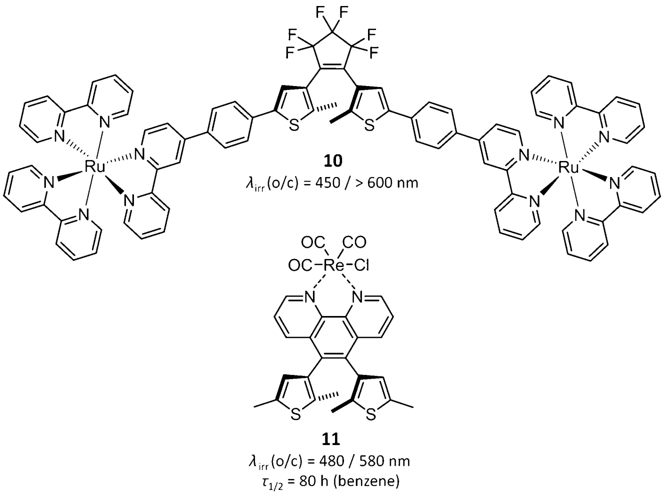
3. Energy Transfer

Besides the design of photochromic compounds that can be directly addressed in the visible region, strategies exist based on inter- or intramolecular energy transfer from a sensitizer to the switch (general strategy depicted in Figure 1 b). The photosensitizer can be either a triplet sensitizer, a two-photon absorber/emitter, or an upconverting nanoparticle (UCNP), all of which are able to absorb radiation in the visible or even NIR region and transfer the collected higher excitation energy to the molecular switches, thereby driving their isomerization. Depending on the chosen chromophore system, energy transfer can occur either in a non-trivial fashion via exchange Dexter-type energy transfer or dipole–dipole Förster-type resonance energy transfer (FRET) or in a trivial fashion simply involving UV emission and subsequent reabsorption by the switch.

3.1. Triplet sensitization

Since triplet states are lower in energy than their corresponding singlet states, they potentially enable photoisomerization with light of higher wavelength. However, in many cases, triplet states can only inefficiently be populated directly owing to limited intrinsic intersystem crossing (ISC) efficiencies of the switch itself, and therefore triplet sensitizers are needed. Two different pathways based on triplet sensitization can be envisioned, whether the isomerization occurs from the triplet (T_1) or from a (higher) singlet (S_1) excited state of the switch (see energy diagram, Figure 1 b, left). For both scenarios, the S_1–S_0 energy gap of the sensitizer must be smaller than that of the switch in order to use light of longer wavelength, and the triplet state of the sensitizer should be higher in energy than T_1 of the switch for the energy transfer to take place.

In the first scenario, the isomerization of the switch proceeds from its triplet state (T_1). The first examples describing this strategy with DAEs were reported in 2004 by the groups of De Cola[57] and Yam[58] (compounds **10** and **11**, Figure 6). These two examples exploit metal-to-ligand charge-transfer (MLCT) bands arising from the connection between the photoswitch and a metal–ligand complex.[59] In compound **10**, the termini of the DAE core were functionalized with Ru–bipyridine (bpy) complexes. As a consequence, the MLCT bands at around 450 nm could be used to induce photocyclization via the triplet state of the switch. Interestingly, ring closure from the triplet state ($\lambda_{irr} = 450$ nm) and from the singlet state ($\lambda_{irr} = 345$ nm) occurred with very similar quantum yields. In compound **11**, a Re^{I}–phenantroline complex was directly integrated into the DAE framework, thereby resulting in a MLCT band centered around 400 nm. Irradiation at 480 nm into the tail of this band produced the ring-closed isomer with relatively high quantum yields ($\Phi = 0.65$ at $\lambda = 440$ nm vs. $\Phi = 0.52$ at $\lambda = 313$ nm). Although the latter design is quite elegant since it involves a rather compact structure compared to compound **10**, the closed isomer was found to be thermally rather unstable for a DAE derivative ($\tau_{1/2}$ of ca. 80 h in benzene). Triplet sensitization was later also carried out with classical organic sensitizers such as xanthone[60] and biacetyl.[61]



10
λ_{irr}(o/c) = 450 / > 600 nm

11
λ_{irr}(o/c) = 480 / 580 nm
$\tau_{1/2}$ = 80 h (benzene)

Figure 6. Triplet-sensitized diarylethenes obtained by combining the photochromic moiety with metal–ligand complexes.[57,58] Photocyclization to the closed isomers can be induced by irradiating the metal-to-ligand charge-transfer (MLCT) bands.

Isomerization from the triplet state can also occur in Z-stilbene derivatives.[62] This knowledge was exploited by Feringa and co-workers for the design of a visible-light-driven rotary motor.[63] An overcrowded alkene was coupled to a Pd–porphyrin derivative serving as a triplet sensitizer (compound **12**, Figure 7) to give a system requiring no UV light to operate. Similarly to the two cases described above (compounds **10** and **11**), the isomerization occurred via the T_1 state of the overcrowded alkene upon irradiation at 530 nm, with similar efficiency to direct excitation of the motor with UV light (quantum yields $\Phi \approx 0.1$), as well as with comparable photoconversion (67 %). Similarly to the process induced by direct excitation of the switch, the triplet-sensitized cycle could be made unidirectional by combining reversible visible-light isomerization with unidirectional thermal relaxation. The system was shown to operate in an intermolecular fashion as well, that is, with the two components simply mixed rather than linked together. Note that in a related earlier example,[64] an azobenzene derivative connected to a porphyrin moiety could surprisingly undergo $E \rightarrow Z$ isomerization upon irradiation at 500 nm as well. However, in that case the mechanism is most likely different. Importantly, in ABs, triplet sensitization can supposedly induce only $Z \rightarrow E$ isomerization because the triplet state is calculated to have an energy minimum at a C-N=N-C torsion angle of approximately 110° and therefore decay from the triplet to the ground state should exclusively lead to the E isomer,[65] in a similar manner to what is known for stilbene derivatives.[62]

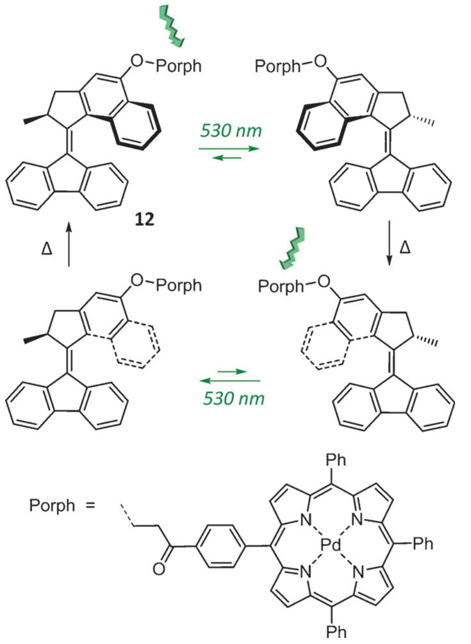


Figure 7. A triplet-sensitized unidirectional rotary motor obtained by combining a porphyrin triplet sensitizer with an overcrowded alkene switch.[63] The motor is driven by alternating green light ($\lambda = 530$ nm) irradiation and thermal helix inversion.

In the second scenario, when the molecule cannot isomerize from T_1, the only option to obtain a visible-light switch is to populate the above singlet excited state (S_1) via a triplet–triplet annihilation (TTA) mechanism,[66] in which two switch molecules both in the T_1 state interact to produce one switch in the S_1 state while the other one relaxes to the ground state (S_0). Although theoretically feasible, this approach has to the best of our knowledge not been reported. There have been examples that connect TTA upconversion with molecular photoswitches, however, the TTA process itself typically involves anthracene[67] or perylene[68] triplet acceptors, which after annihilation transfer their singlet excitation energy in a classical “downhill” fashion to the AB[67] or DAE[68] switches. While in the first case, this phenomenon was used to operate AB-based liquid-crystalline soft actuators with low-power red light, in the latter case, the DAE was used as a photoswitchable quencher to turn the TTA process on or off.

The lack of reports describing photoisomerization by direct TTA upconversion leaves us to speculate that the requirement of a long-lived triplet state in the switch is rather difficult to achieve, most likely because direct isomerization from the triplet state is usually quite fast.

3.2. Upconverting nanoparticles

Upconversion processes are characterized by the successive absorption of multiple photons and the subsequent emission of shorter-wavelength radiation.[69] Systems exploiting this phenomenon can therefore be used to first absorb several quanta of NIR light and subsequently transfer their upconverted excitation energy to the switch either via trivial UV emission and reabsorption by the switch or non-trivial FRET. In 2009, the group of Branda demonstrated that lanthanide-doped upconverting nanoparticles (UCNPs) can photoisomerize DAE derivatives with NIR light.[70] This pioneering work describes the preparation of polymer composite materials comprising a DAE derivative blended with either $NaYF_4$:TmYb nanoparticles that emit UV photons able to induce the electrocyclic ring closure, or $NaYF_4$:ErYb nanoparticles that emit green light appropriate to induce the cycloreversion of the switch. However, since the same wavelength (980 nm) had to be used to excite either type of nanoparticle, this particular system was not reversible, and two different films containing either the open or the closed DAE had to be prepared for the proof of principle.

In order to produce a reversible system, the same group described in 2010 the use of only one type of UCNP (core–shell–shell $NaYF_4$ nanocrystals containing Er^{3+}/Yb^{3+} and Tm^{3+}/Yb^{3+} ions doped into separate successive layers; see Figure 8c), for which the emission wavelength could be modulated by the intensity of the 980 nm excitation light.[71] At high intensity, the emission is predominantly in the UV region, whereas at low intensity, the UCNPs emit mainly visible light (Figure 8d). Therefore, one type of nanoparticle could be used to reversibly toggle between the two isomers of **13** (Figure 8a,b), simply by modulating the intensity of the laser beam. These processes are quite efficient since solutions of **13** containing 1.5 wt% UCNPs irradiated at 980 nm were shown to perform very similarly in terms of PSS, compared to direct excitation of the open and closed isomers with UV and visible light, respectively. The same type of UCNPs has also been used to drive the isomerization of ABs doped into a liquid-crystalline matrix.[72]

From this work, it becomes apparent that nanoparticles doped with lanthanide ions can be used to drive the isomerization of photochromic compounds in one direction, whereas complex core–shell–shell structures are necessary to photoisomerize in both directions. Although the later approach arguably offers more possibilities, the former has nevertheless successfully been used to activate caged (irreversible) systems[73,74] and rapidly relaxing photoresponsive (reversible) materials such as photo-actuators.[75]

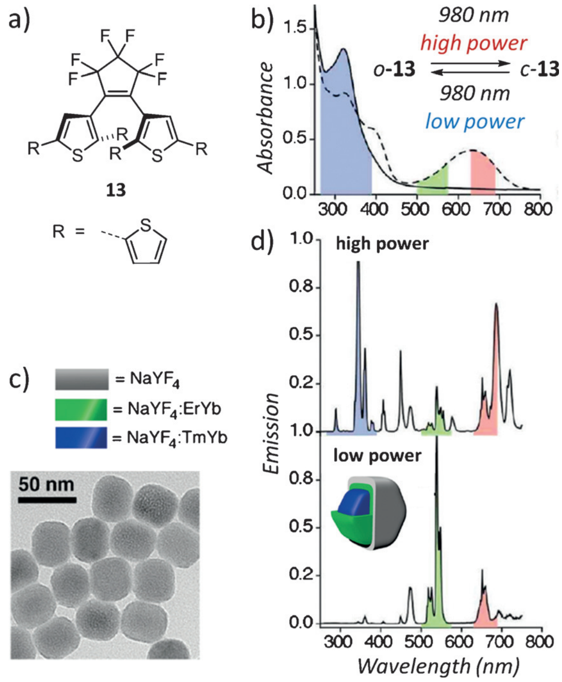


Figure 8. Photoswitching diarylethenes with 980 nm light by using lanthanide-doped upconverting nanoparticles. a) Molecular structure and b) UV/Vis spectrum of DAE derivative **13**. c) Composition and TEM images of the core–shell–shell Tm:Er nanoparticles. d) The nanoparticles exhibit different emission spectra at high- (top) and low- (bottom) intensity irradiation at 980 nm. Adapted with permission from Ref. [71].

3.3. Multiphoton absorption

Two- and more generally multi-photon absorption processes are a way of accessing excited states with photons of half (or less) of the energy of the corresponding one-photon transition,[76] and as such they constitute a good option for activating photochromic compounds with visible/NIR light. Owing to their nonlinear intensity dependence, that is, the two-photon absorption (TPA) increases with the square of the light intensity, these processes provide supreme 3D spatial resolution. This feature is of particular interest in the context of photoswitching, for example, in materials science for 3D optical storage devices,[77] but also in chemical biology and the life sciences with the possibility to localize irradiation in a particular volume of a targeted tissue or cell. One severe limitation, however, is the typically small TPA cross-section of molecular dyes and hence the necessity to use intense laser beams. A few photoswitchable compounds exhibit a non-negligible intrinsic TPA cross-section and can therefore be excited directly by two-photon stimulation. Those include some push–pull ABs (typically 300–800 GM at 730 nm),[78] spiropyrans,[77] and DAE derivatives.[79] In general, indirect two-photon excitation of photoswitches via energy transfer from a TPA antenna is more efficient and versatile than direct two-photon excitation.

The most straightforward approach consists in either blending or covalently connecting the switchable compound and a two-photon fluorophore, the emission of which should overlap with the absorption band of the switch in order for FRET to take place. This strategy was used by Zink and coworkers[80] (Figure 9 a) to build mesoporous silica nanoparticles containing both an azobenzene derivative (**14**) and a two-photon-absorbing fluorophore (TPA-F), which could release an encapsulated bioactive compound upon irradiation at 760 nm thanks to the $E \rightarrow Z$ isomerization induced by FRET. The fluorophore was selected for its fluorescence emission ($\lambda = 420$ nm), which overlaps with the azobenzene $\pi \rightarrow \pi^*$ absorption band. Effective energy transfer was deduced from the fluorescence quenching of the fluorophore and successful isomerization of the azobenzene as demonstrated by cancer cell death, that is, the loaded drug was indeed released upon two-photon excitation.

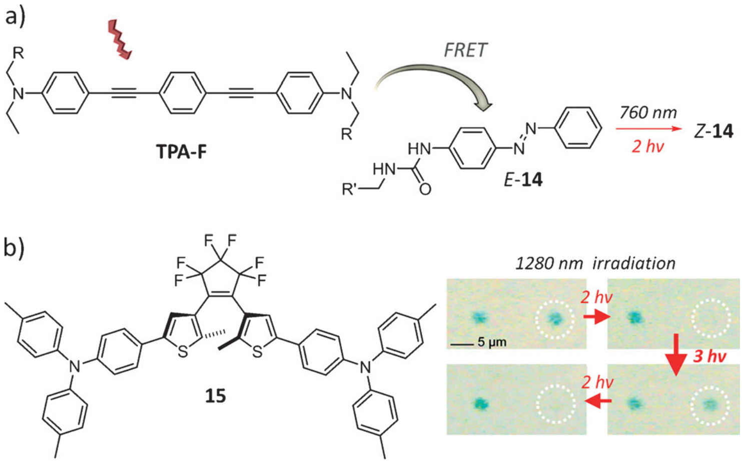


Figure 9. Photoswitching via multiphoton absorption processes. a) Azobenzene **14** isomerizes with 760 nm light via Förster resonance energy transfer (FRET) from a two-photon absorber fluorophore (TPA-F). The system was embedded in mesoporous silica nanoparticles together with a bioactive compound for delivery to cancer cells.[80] b) Connecting a diarylethene moiety to a triphenylamine multiphoton absorption promoter gives **15**, which could ring-open via two-photon excitation and ring-close via three-photon excitation by varying the intensity of a 1280 nm laser beam.[82] The disappearance/regeneration of c-**15** (green spot) under the laser beam was directly visualized on an amorphous film of o-**15**. Adapted with permission from Ref. [82].

An intramolecular version of this approach was also developed for the photo-activation of neurons, with a push–pull azobenzene covalently linked to a naphthalene two-photon antenna.[81] Although two-photon energy transfer at 880 nm was demonstrated, the naphthalene–photoswitch dyad did not exhibit any improvement compared to the parent push–pull azobenzene without the antenna, that is, the intrinsic TPA cross-section of the AB derivative was high enough to induce significant neuronal activity via two-photon excitation.

While processes involving the simultaneous absorption of two photons are usually investigated, three-photon absorption processes also offer some interesting possibilities, as demonstrated by Uchida, Irie, Miyasaka, and co-workers (Figure 9 b).[82] By attaching a triphenylamine derivative that promotes multiphoton absorption in direct conjugation to a DAE moiety (compound **15**), the authors could use a single NIR wavelength ($\lambda = 1.28$ μm) to ring-close and ring-open **15** by varying the intensity of femtosecond Cr:F laser pulses. At higher intensity, the three-photon process dominates and the open form of **15**, which absorbs in the UV region, could be closed, while at lower intensity, the two-photon process takes place thus re-opening c-**15**, which absorbs light around 650 nm. The three-photon cyclization and two-photon cycloreversion could be followed by absorption spectroscopy and was directly observed through the coloration/decoloration of an amorphous film of **15** under the laser beam (Figure 9 b). This example can be compared to the example of Figure 8, in which modulating the intensity of the laser beam could trigger either the ring opening or ring closure of the DAE **13** via the emission of different colors of light by the UCNPs.

4. Electron Transfer

In addition to the energy transfer and upconversion processes outlined in the previous section, the energy stored in an excited (sensitizer) molecule can also be used to drive electron transfer to or from the switch, thereby leading to the formation of a more reactive (radical) charged species. In this last section, we briefly show how such electron-transfer processes can be used to replace UV-light-induced isomerization events by redox catalysis, which can furthermore be coupled to visible-light excitation by using photoinduced electron transfer (general strategy depicted in Figure 1 c). Switching via oxidation/reduction of the switch provides an orthogonal stimulus (electrons instead of photons) and furthermore offers the great advantage of a tremendously increased efficiency and hence sensitivity owing to the potential involvement of a catalytic chain reaction. Such an amplification mechanism, in which few electrons trigger many switching events, has been demonstrated for the ring opening of some DAE derivatives, for which Kawai and coworkers could determine net current efficiencies of up to 900 %,[83] as well as for reductively induced $Z \rightarrow E$ isomerization of AB derivatives.[84] Importantly, such redox-initiated switching processes are not limited by overlapping spectra of the two switching forms, which typically yield PSS mixtures, but instead they are purely thermodynamically driven and therefore lead to quantitative isomerization. This feature is accompanied by the drawback that such oxidatively/reductively initiated switching processes only proceed in one direction, that is, from the thermodynamically less stable to the more stable (radical) cation/anion species.

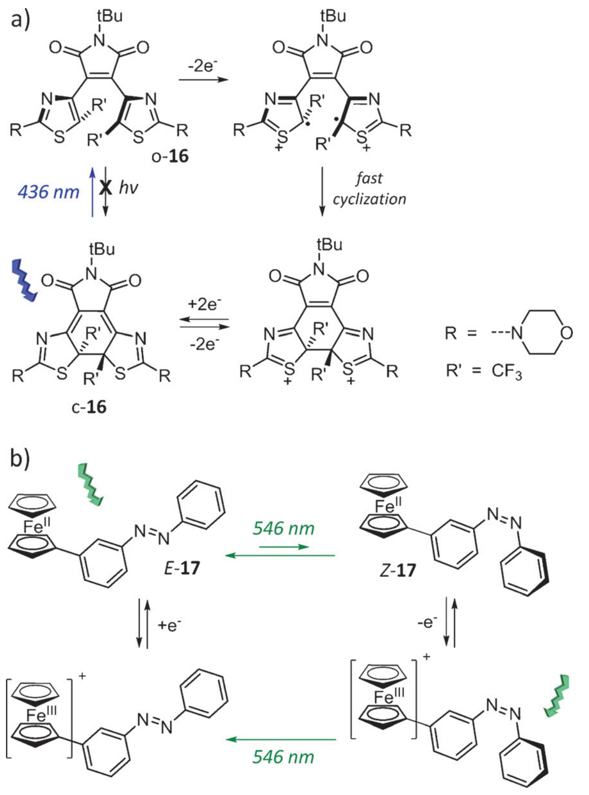


Figure 10. Switching with light and electrons. a) Orthogonal diarylethene **16** can interconvert between ring-open and ring-closed isomers upon alternating between electrochemically induced oxidation and reduction steps and blue light ($\lambda = 436$ nm) irradiation.[87] b) The ferrocene–azobenzene dyad **17** equilibrates between *E* and *Z* isomers upon green light ($\lambda = 546$ nm) irradiation (top), while the same green light quantitatively induces the *Z*→*E* isomerization in the oxidized ferrocenium dyad (bottom).[88]

Nowadays, simple dual photochromism, in which (visible) light is used to isomerize the molecule in one direction, while the reverse reaction is induced by an (electrochemically induced) oxidation or reduction step, is quite well established and has been reported for several photoswitch families, such as DAEs,[85] dihydropyrenes,[86] and ABs.[84] A special case is orthogonal switches, that is, compounds in which one isomerization can only be induced by light, while the reverse reaction can only be triggered electrochemically. Such an orthogonal switch has been realized by the design of DAE derivative **16** (Figure 10a), which undergoes electrocyclization upon oxidation (thereby avoiding the use of UV light) and the reverse cycloreversion upon blue light ($\lambda = 436$ nm) irradiation.[87] The combination of an electron-poor maleimide bridge and electron-rich morpholino termini was crucial for the successful design, since this donor–acceptor structure prevents ring closure upon UV-light irradiation (presumably through the formation of a twisted intramolecular charge-transfer state), while electrochemical oxidation could effectively induce the desired ring-closure (Figure 10a). The introduction of trifluoromethyl groups at the reactive central carbon atoms was crucial, on the one hand to avoid the formation of an irreversible side product during oxidation, and on the other hand to increase the cycloreversion quantum yields ($\Phi_{c\rightarrow o} = 0.13$ for R′ = Me vs. $\Phi_{c\rightarrow o} = 0.37$ for R′ = CF_3). The clear advantage of such a system is that quantitative conversion can be achieved in both switching directions because ring closure proceeds through (thermally driven) cyclization of the oxidized species (thus avoiding overlapping absorption bands of the ring-open and ring-closed forms in the UV region), and ring opening can be induced selectively by exciting only the ring-closed isomer in the visible range of the spectrum.

In an alternative approach, the photoswitching behavior of two isomers of a photochromic molecule can be modulated by changing the redox state of an attached metal center and using a single color of light to toggle between the two isomers. Such a redox-conjugated reversible photoisomerization cycle was described by Nishihara and co-workers for the ferrocene–azobenzene dyad **17** (Figure 10b).[88] The cycle works as follows: the visible band of Fc^{II}–*E*-**17** centered around 450 nm, most likely a mix of the $n\rightarrow\pi^*$ and MLCT transitions, is irradiated with green light ($\lambda = 546$ nm) to create a PSS enriched in *Z* isomers. The ferrocene Fc^{II} is then oxidized to ferrocenium Fc^{III}, either chemically or electrochemically. Consequently the spectral features of the switch are modified (notably with the appearance of a LMCT band at 730 nm), and the same 546 nm green light can now induce the complete conversion to Fc^{III}–*E*-**17**. Finally, the initial solution of Fc^{II}–*E*-**17** can be recovered by electrochemical reduction. Although the quantum yield for the *E*→*Z* isomerization is quite good ($\Phi = 0.5$), only a relatively low amount of the *Z* isomer (35 %) can be accumulated in the PSS when irradiating the neutral photoswitch. Connecting the Fc and AB units through a *meta* linkage was found to be essential since in the related *para*-connected compound, the Fc^{III}–*Z*-AB isomer was not thermally stable and only 6 % of *Z* isomer could be generated in the PSS of the neutral state.

In order to harness the efficiency of the oxidatively/reductively induced switching process and couple it to (visible-) light illumination, one has to implement a photoredox catalyst, which upon excitation initiates the catalytic chain with a photoinduced electron-transfer step (Figure 1c). This strategy based on photoinduced electron transfer combines the advantages of catalysis with a light stimulus and does not require activation by externally applied electrodes or added chemical reducing/oxidizing agents. The group of Nam optimized such a system for the ring opening of electron-poor DAE derivatives (Figure 11),[89] which upon "normal" visible-light activation, is known to be quite inefficient. A series of Ir^{III} complexes were employed as photoredox catalysts since they exhibit long-lived triplet excited states which facilitates photoinduced electron transfer in solution at moderate concentration (10^{-3} M) of both the catalyst and the DAE photoswitch. The best combination was obtained with 4-pyridyl-terminated DAE **18** and an Ir^{III} complex bearing two methoxy groups. In this particular system, the overall cycloreversion efficiency was increased by one order of magnitude, from $\Phi \approx 0.01$ for the direct approach (without catalyst) to $\Phi = 0.38$ for the photoredox approach. In principle, quantum yields exceeding unity should be achievable if side reactions during the initiation could be minimized and the catalytic turnover be maximized.

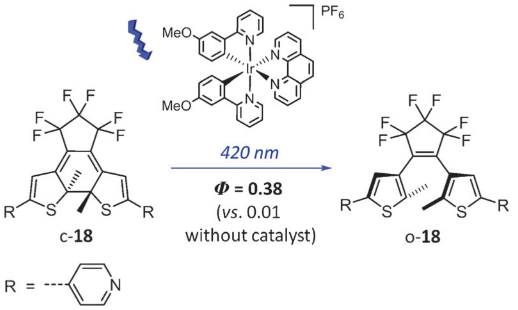


Figure 11. Photoredox catalysis with Ir^{III} complexes for the ring opening of diarylethenes.[89] Following blue light ($\lambda = 420$ nm) irradiation, photoinduced electron transfer from the complex to the switch occurs, thereby initiating a catalytic cycle (as depicted in Figure 1 c). In the presence of the photoredox catalyst, the overall photoefficiency is greatly enhanced compared to direct excitation ($\Phi = 0.38$ with 20%mol of catalyst vs. $\Phi = 0.01$ without catalyst).

5. Conclusion and Outlook

In recent years, several conceptual strategies have been developed to address photoswitchable molecules in the visible region of the optical spectrum, thereby avoiding the need for high-energy photons to trigger photoisomerization processes. In this Minireview, we have classified these strategies based on mechanistic considerations and divided them into few main approaches (see Figure 1): a) direct visible-light excitation of a cleverly designed photoswitch and b) indirect visible-light excitation of a suitable sensitizer, which subsequently either transfers its excitation energy to the photoswitch or donates/accepts an electron to/from the photoswitch, thereby initiating redox catalytic isomerization. While most of the operating mechanisms have recently been demonstrated, we hope that our conceptual comparison of the different available options to address photoswitches with visible light will facilitate the development of this young and burgeoning field of research.

Although tremendous progress has been made, several challenges remain. Most importantly, no bistable photoswitch has yet been realized that is fully addressable in both directions by long-wavelength light (red or NIR photons), which does not cause radiation damage yet is able to penetrate into (bio)materials. In particular, NIR light would be highly desirable for biomedical applications, for which the ideal optical window, in which both absorption and scattering by tissues are minimized and hence light has its maximum penetration depth, is around 650–900 nm (for $\lambda > 900$ nm, absorption by water and lipids increases). When considering such biological applications, the desired photochromic system—regardless of whether direct excitation or indirect excitation in a dyad is being used—should ideally be a rather compact single-molecular entity and needs to operate at low concentrations in physiological media. By contrast, in bulk materials such as polymer films, these stringent criteria do not necessarily apply and multicomponent systems with non-aqueous environments and processing conditions can also be explored. In addition to the energetic resolution that enables photoswitches to be addressed in the red or even NIR part of the visible spectrum, the corresponding low-energy photons can provide enhanced spatial resolution, in particular when two- or multi-photon processes are involved. Hence, another related challenge is to integrate such additional nonlinear optical features into the photoswitches, thereby enabling 3D localized switching in one or even both directions. Last but not least, the use of photons in the visible region relates very much to harvesting the solar spectrum and converting sun light into electrical energy, chemical fuels, and mechanical work. Naturally, these important areas will greatly benefit from photochromic systems that can be operated with visible-light photons.

Apart from the potential of using low-energy photons to trigger and drive reversible isomerization processes, the photoswitches should also be optimized with regard to their sensitivity towards such irradiation, that is, their overall photoisomerization efficiency. In this context, catalytic processes that lead to the amplification of a few optical excitation events by a chain reaction should be heavily exploited and integrated into the design since they offer a powerful means to realize quantum yields exceeding unity. However, increasingly complex systems involving ever more components call for extremely high selectivity in the elementary steps in order to maintain a critical robustness of the system. This aspect of achieving high photostability over many switching cycles is perhaps the most crucial for any future application and needs to be seriously addressed by the community.

The development of clever new solutions to the above-mentioned (and other) challenges through the creation and optimization of photochromic systems that can be selectively and efficiently addressed in the visible-light region will have an impact on many fields, from materials science to life sciences, and without doubt such designed photoswitches will be key components in future technologies. Fiat lux!

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