

Enlightening Materials with Photoswitches

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Incorporating molecular photoswitches into various materials provides unique opportunities for controlling their properties and functions with high spatiotemporal resolution using remote optical stimuli. The great and largely still untapped potential of these photoresponsive systems has not yet been fully exploited due to the fundamental challenges in harnessing geometrical and electronic changes on the molecular level to modulate macroscopic and bulk material properties. Herein, progress made during the past decade in the field of photoswitchable materials is highlighted. After pointing to some general design principles, materials with an increasing order of the integrated photoswitchable units are discussed, spanning the range from amorphous settings over surfaces/interfaces and supramolecular ensembles, to liquid crystalline and crystalline phases. Finally, some potential future directions are pointed out in the conclusion. In view of the exciting recent achievements in the field, the future emergence and further development of light-driven and optically programmable (inter)active materials and systems are eagerly anticipated.

reversible conversion between their stable and (meta)stable isomers triggered by light. The return to their native, thermodynamically most stable isomer is generally induced by using another wavelength of light or simply by heat, depending on the thermal stability of the (meta)stable isomer. Retinal—the prototypical photoswitch in biology—showcases impressively how structural changes occurring during a light-induced double-bond isomerization can lead to vision or allow microorganisms to convert photons into metabolic energy. In analogy, over the years, scientists have learned that the light-driven isomerization of small molecules can be collected, possibly amplified, and transformed into macroscopic property changes, such as mechanical motion,^[1] charge carrying ability,^[2] assembly and disassembly of macroscopic aggregates,^[3] as well as switching of surfaces and their properties.^[4]

1. Introduction

The incorporation of photoswitchable molecules into materials has been proven to be a blueprint to collectively, and thus effectively, capitalize on their individual light-induced (re)actions. Photoswitches are photochromic molecules, which undergo a


Materials, which for the purpose of this review are considered to be solid objects or organized assemblies in solution, provide unique advantages to enhance the function of photoswitches and even create new functions when compared to their stand-alone molecular selves (for the primarily discussed photochromic molecules herein, see **Figure 1**). One must, however, consider the inherent challenges that may present themselves when working with photoswitches in close proximity to one another. Intermolecular interactions, such as aggregation, excitation quenching, low free-volume, as well as the potentially much higher optical density of materials can drastically lower the overall photoresponse. Yet with proper macromolecular and supramolecular design, functions can be achieved through the incorporation of photoswitches in a material that simply cannot be obtained by an isolated molecule on its own. Here, we highlight recent examples from the literature that have appeared during the past decade since our previous review in this journal,^[5] with particular focus on the order of the photoswitches in relation to their environment and its impact on material properties and device performance.

Conceptually, one can think about maximizing a photoswitching unit's effect by giving it “order” with relation to its surrounding, in particular to other switching units (**Figure 2**). The lowest possible order is undoubtedly demonstrated by dispersing photochromic molecules in a bulk amorphous material. If aggregation of the photoswitches can be overcome, switching units are placed in random orientation to each other giving rise to a more or less isotropic material. Starting from this scenario of randomly distributed photochromic entities, one can think about providing order in two dimensions by placing

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photoswitches on a surface, where their position is fixed with relation to the underlying substrate but not necessarily with respect to each other. Whether being a flat, patterned, or nanoparticulate surface a conformal coating with light-responsive moieties at an interface can be achieved. Introducing order on a 2D surface by noncovalent or covalent anchoring provides physi- and chemisorbed (mono)layers, respectively. Expanding into three dimensions long-range order can be provided by organizing the switching entities in supramolecular systems, where noncovalent interactions and packing effects confine them either in aggregates in solution, in liquid crystalline phases, or in the bulk. Finally, the highest degree of order is reached in crystalline materials, where a precise and long-range orientation of the photoswitches is present in all three dimensions. This can be achieved by either crystallizing the photoswitchable molecule itself or in the presence of a nonswitchable matrix, which results either in porous or nonporous bulk (co) crystals. In the following, we will structure the discussion along this theme of increasing order of the photoswitchable units within the materials.

2. Photoswitches in an Amorphous Setting

Although the dispersion of photochromic molecules into an amorphous environment is seemingly the most straightforward method to create photoresponsive materials, it requires a profound knowledge of the physical and/or chemical interplay between the photoswitching entity and its surroundings to obtain the desired effect upon illumination with light. Crucial hurdles such as phase segregation, self-aggregation, or high optical density must be overcome to guarantee an efficient photochemical performance. Once these requirements are fulfilled, photoswitchable molecules can be utilized for a variety of applications, which range from electronic and memory devices to healable plastics.

2.1. Modulating Charge Transport

One of the bulk properties that can readily be controlled with molecular photoswitches is conductivity based on the material's charge carrying capacity.^[2] Small molecule dopants have extensively been used for years to affect the electronic structure of a given semiconductor by acting as traps for charges, thereby modulating the conductance of the material (Figure 3). Blending a photoswitchable molecule, such as a diarylethene (DAE) derivative with largely different HOMO and LUMO levels in its ring-open and ring-closed isomers, respectively, into a film composed of either p-type or n-type organic semiconductors permits gating of charge transport with light. This was initially demonstrated in a p-type poly(3-hexylthiophene) (P3HT) matrix using DAE switches to trap holes at their closed isomers (Figure 3a, top), which led to a decreasing conductance.^[6] It could be shown that UV-light-induced ring-closure switches the current "OFF," whereas visible light-induced ring-opening turns it back "ON." Later on this concept was expanded to trap electrons localized at the closed isomers of strongly electron-deficient DAEs with LUMO levels below that of an n-type fullerene (Figure 3a, bottom), again resulting in a photomodulation of charge transport.^[7]



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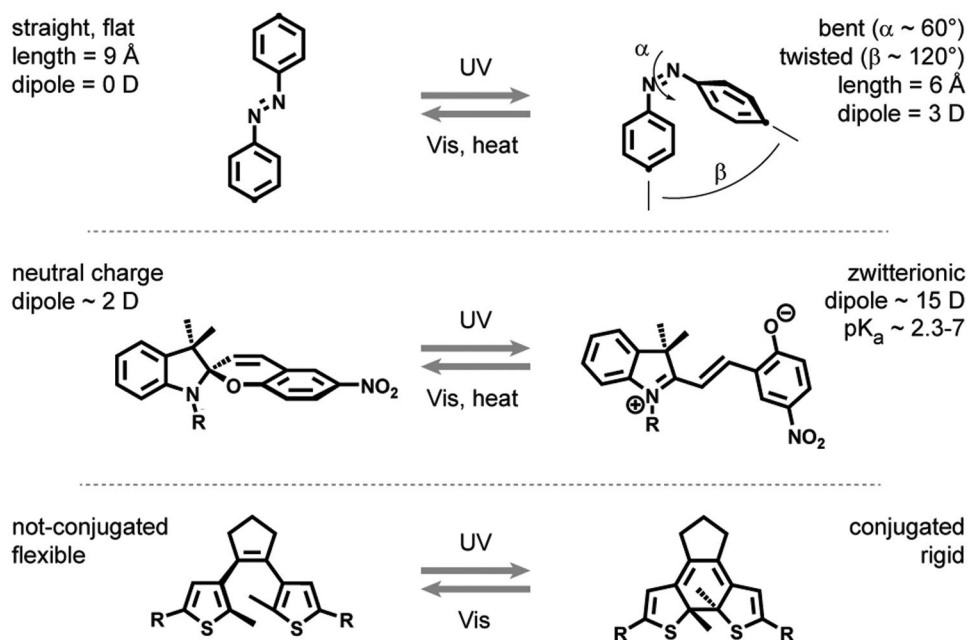


Figure 1. Structure of the photoswitches most prominently discussed here. Azobenzene (top) undergoes a UV-light-induced double-bond isomerization to a metastable Z isomer, which is shorter, bent, twisted, and more polar than the E isomer. Upon UV light irradiation, spiropyran (middle left) undergoes a ring-opening reaction to the zwitterionic metastable merocyanine (middle right) isomer, which is more polar and functions as a base to yield a phenol. Diarylethene (bottom) undergoes a 6π electrocycloaddition with UV light to a thermally stable, conjugated, rigid, ring-closed isomer, which opens again with visible light.

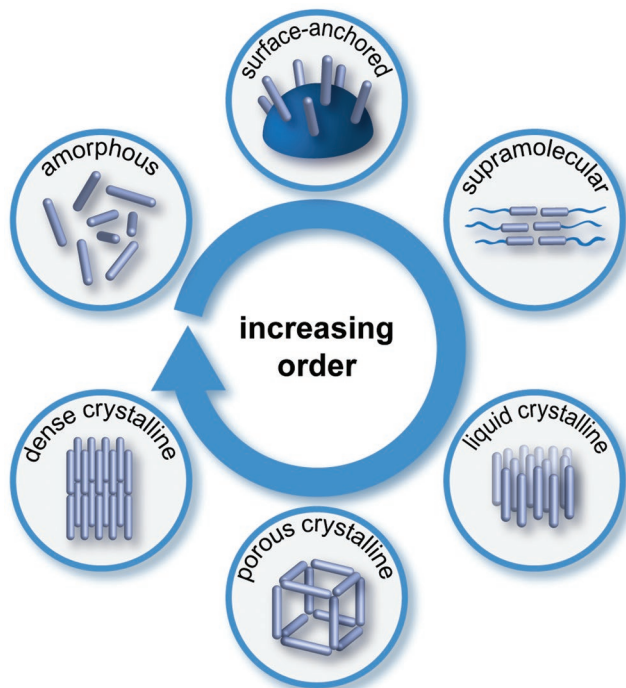


Figure 2. Controlling materials properties by integrating photoswitchable molecular building blocks with an increasing degree of order: from isotropically distributed molecules blended into an amorphous solid matrix over two-dimensionally organized switches on flat/curved surfaces, 3D supramolecular aggregates, as well as liquid crystalline systems, to porous and nonporous crystalline systems.

Considering the morphology of the blends, polymers such as P3HT with an intrinsic dispersity provide on the one hand highly crystalline domains for high charge carrier mobilities. On the other hand, they also consist of amorphous regions, in which the photoswitches reside without significantly decreasing the inherent mobility of the matrix as confirmed by X-ray scattering.^[6] Importantly, the blending approach is not only limited to polymeric semiconducting matrices (such as P3HT), also air-stable, solution-processable, small molecules, for example, 2,7-dialkyl-benzothieno(3,2-b)benzothiophenes (BTBTs), can be used.^[9] In this case, the DAE switches have to be tailored not only with regard to their electronic structure (HOMO/LUMO levels) but also with respect to their supramolecular interactions with the BTBT matrix to allow for control over the bulk morphology of the blend. Substitution of the DAE core with bulky *tert*-butyl groups prevents phase segregation and hence provides a better overall film morphology and device performance. In contrast, another DAE derivative carrying small methyl groups provides poorer device morphology, but allows for larger current modulation by light due to the stronger interactions between switch and matrix in the highly crystalline regions.^[9] This highlights the importance of not only considering the relevant energy levels of the molecular components in the blend but also tailoring the interactions of the photochromic molecules with the host matrix. By taking these interactions into account, the same methyl-functionalized DAE was used to fabricate a memory device upon blending with P3HT. By tuning the duration of light irradiation, up to 400 distinct, thermally stable current-intensity levels can be written using 3 ns pulses of light forming an 8-bit flexible optically

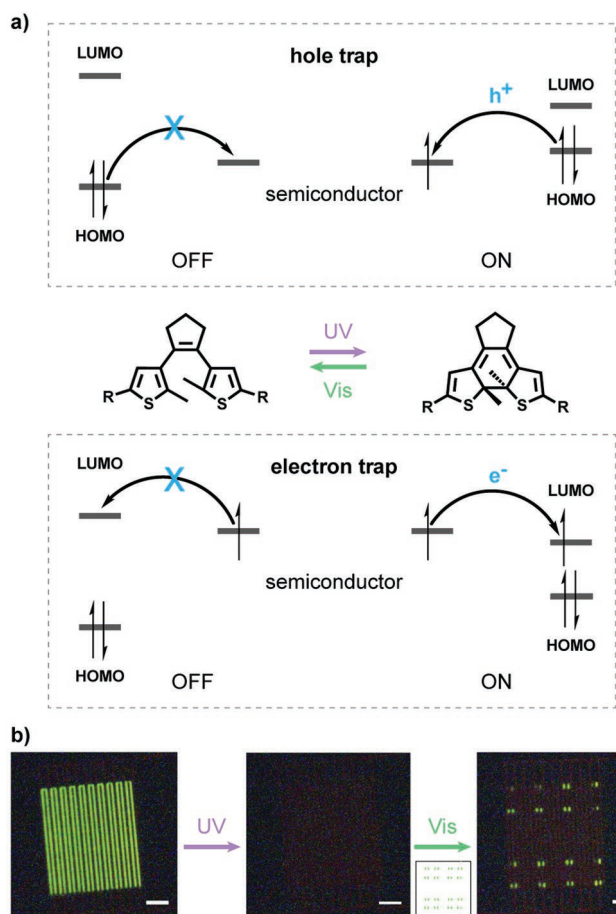


Figure 3. Photomodulating charge transport by switching trapping levels ON and OFF. a) Tailoring DAEs such that the HOMO or LUMO levels of their open and closed isomers are above or below a p-type or n-type semiconducting matrix leads to trapping of holes (top) but not at the open isomer (left). b) Optical images of an organic light-emitting transistor consisting of DAE charge traps in combination with emissive polymers enabling to write and erase pixels in all three primary colors (shown here for green, the white scale bar is 100 μm). a,b) Adapted with permission.^[8] Copyright 2019, Springer Nature.

written memory device.^[10] Moreover, blending suitable DAEs with various π -conjugated luminescent polymers encoding the three primary colors has recently enabled the realization of light-emitting transistors, which is of particular interest for high-resolution full-color display applications (Figure 3b).^[8]

DAEs have furthermore successfully been employed in creating a stimuli-responsive microsupercapacitor, which in general is a promising technology for on-chip energy storage due to its high-power density and quick charge–discharge rates. In order to fabricate the device, a simple DAE derivative was spin-coated on top of two graphene layers followed by the deposition of a gold microelectrode. As ring-closed DAEs possess an energetically reduced LUMO level, UV-light-induced ring-closure decreases the injection barrier of electrons from the graphene electrode into the LUMO of the DAE molecular layer and thus the total capacitance of the device was increased by 20%.^[11]

Aside from making use of the altered HOMO and LUMO levels, which encode for largely modulated ionization energies and electron affinities, respectively, one can also make use of changes in the charge or the dipole moment of a photo-switchable unit. This was exploited in a poly(methyl methacrylate) copolymer bearing spiropyran (SP) units in the side chain, onto which a pentacene conducting layer was deposited to yield an organic field effect transistor (a basic building block for numerous circuits and displays).^[12]

Switching the SP to its zwitterionic merocyanine (MC) valence tautomer led to an increase of the capacitance of the photo-responsive polymer layer and a higher number of charge carriers in the semiconducting layer. The latter was accompanied by a pronounced conductivity boost, giving rise to highly sensitive photodetectors. In related work, a spirooxazine layer was shown to affect the conductivity of an n-type semiconducting fullerene layer when irradiated with light.^[13] In this case, the effect of light alone was found to be only modest in terms of increasing the conductivity of the semiconducting layer. However, when the light was applied in combination with a small current, photo-switching of the conductivity was significant, reflected in ON/OFF ratios of the drain current between 10^3 and 10^4 , and could be repeated over extended periods of operation (up to 1 year).

2.2. Storing Ions and Energy

The zwitterionic MC form can also aid the shuttling of protons across a polymeric membrane.^[14] Irradiating the charge neutral SP with UV light on one side of the membrane locally generates the MC form, which abstracts a proton due to its revealed basic phenoxide functionality (Figure 4). The net transport of a proton was accomplished with the aid of a bulky borate counteranion, which can cross the membrane, and irradiation with visible light on the other side of the membrane that triggered the back isomerization to the SP form accompanied by the release of the proton. Simultaneous UV and visible light irradiation on opposite sides of the membrane led to a pumping action, effectively cycling the generated storage potential of the device. The obtained proton flux was shown to have an electrical efficiency of 0.12%, which is limited in part by the reported quantum yield of the applied photoswitch of 0.1. Yet an open-circuit voltage of 210 mV and a potential to create a gradient of 3.6 pH units between the two sides of the membrane could be generated.

The photogenerated charged MC form has also been explored in porous polyaromatic frameworks, in which the nanopores are decorated with the photoswitchable unit.^[15] As the pores provide a satisfying degree of conformational freedom, the photochromic molecules switch readily even in the solid state. This approach gives rise to modulate the optical properties of the frameworks since only the MC exhibits fluorescence, while the SP isomer is nonfluorescent. Due to the vast differences in polarity between both isomers, copper ions can reversibly be captured and released from solution, thereby possibly allowing to regulate metal-catalyzed reactions with light. The photostability of the SPs in these materials was furthermore found to be far better than in solution due to the distant spacing of the photoswitches, preventing irreversible intermolecular reactions, which are one of the most common pathways for SP photodegradation.

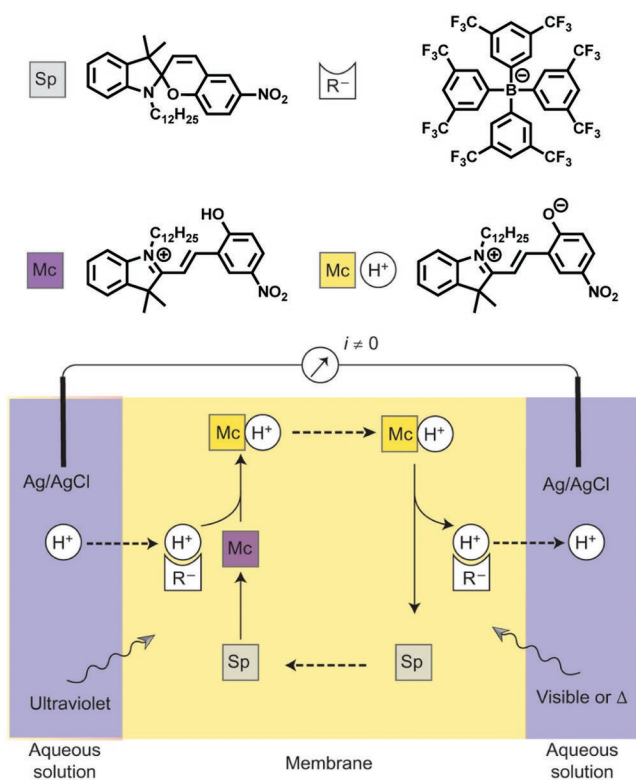


Figure 4. Light-driven proton pumping across a polymer membrane. UV light irradiation of charge-neutral SP on one side of the membrane (left) leads to formation of a zwitterionic MC isomer, which abstracts a proton and releases it upon visible-light-induced back switching on the other side of the membrane (right). Adapted with permission.^[14] Copyright 2014, Springer Nature.

Storing energy from (sun) light is a research direction for molecular switches that has been pursued for some time as they are perfect transducers of light into other forms of energy.^[16] In the context of soft materials, direct conversion of light into mechanical work is appealing and one inspiring example has been reported by Giuseppone and co-workers (Figure 5).^[17] They took advantage of the unidirectional rotation of the light-driven motor, developed by the Feringa group,^[18] and incorporated it as a cross-linking node into a polymeric gel. Upon irradiation with UV light, the motors rotate constantly in one direction and thereby lead to a supercoiling of the polymer chains and overall contraction of the macroscopic structure. Thus, this material is able to store light energy due to a loss of conformational entropy. This light-driven contraction process, however, cannot be reversed and therefore is limited to a single event. This issue could be addressed by also integrating a DAE into the gel, which acts as stress reliever upon orthogonal irradiation with visible light. After building up the contracted polymeric structure with constant UV light irradiation, the supercoiled and shrunk gel could almost completely be transformed back to its initial volume with visible light as the incorporated ring-closed DAE switches back to its open isomer. The open DAE provides sufficient flexibility, which leads to an unbraiding of the polymer chains.^[19]

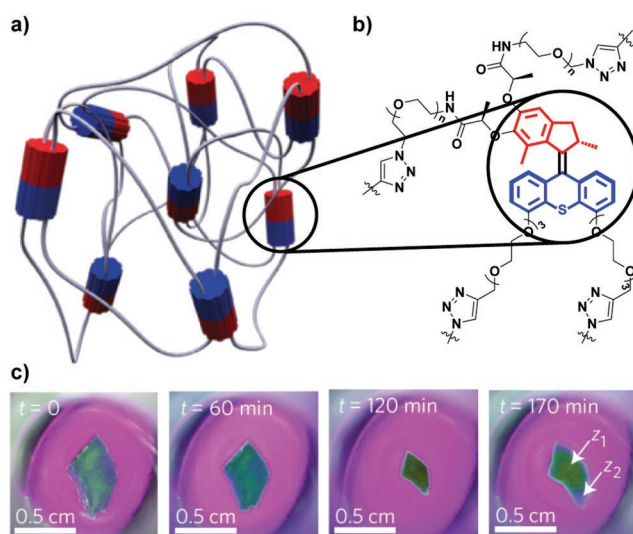


Figure 5. Storing light energy through shape changes of soft materials. a) Schematic representation of the network with the molecular motors acting as crosslinking points; note the red and blue portions, which rotate in relation to each other. b) Chemical structure of the motor with the appended polymeric arms, upon irradiation the arms on the top and bottom of the motor are wound irreversibly around each other. c) Images of the gel undergoing compression upon UV light irradiation from 0 to 120 min, at 170 min the collapse of the gel becomes apparent. a–c) Adapted with permission.^[17] Copyright 2015, Springer Nature.

The latent energy that is stored in the Z isomer of azobenzenes (ABs) is another promising tool to harvest solar energy and release it as heat on-demand by converting it back to the E isomer.^[20] Many photoactive materials have been designed ranging from composites of fabric and AB molecules^[21] over AB-grafted graphene nanosheets^[22] to polymer-based films.^[23] Although a lot of research efforts have been dedicated toward the development of efficient AB-based storage materials, crucial limitations are still to overcome. For instance, E→Z isomerization is typically not quantitative under full-spectrum solar irradiation, the thermal half-life of the Z isomer is short, and the amount of energy stored in the Z isomer is rather small.

2.3. Healing Damage with Light

The development of self-healable materials that are able to recover from damage and thus prolong the lifetime of polymer products is an important challenge in material sciences. Employing photochromic molecules, which can regulate or even enable the repair process, is a clever strategy as light can be applied precisely and locally to heal a defect. One approach comprises the use of photoswitches as externally addressable crosslinking units to manipulate the connection of linear polymer chains and thereby to alter material properties, such as (self)healing ability, elasticity, and texture. The functionalization of photoswitches with chemical groups able to undergo reversible bond formation through dynamic covalent chemistry^[24] opens the door to control the connection and disconnection of molecular building blocks in materials with light.

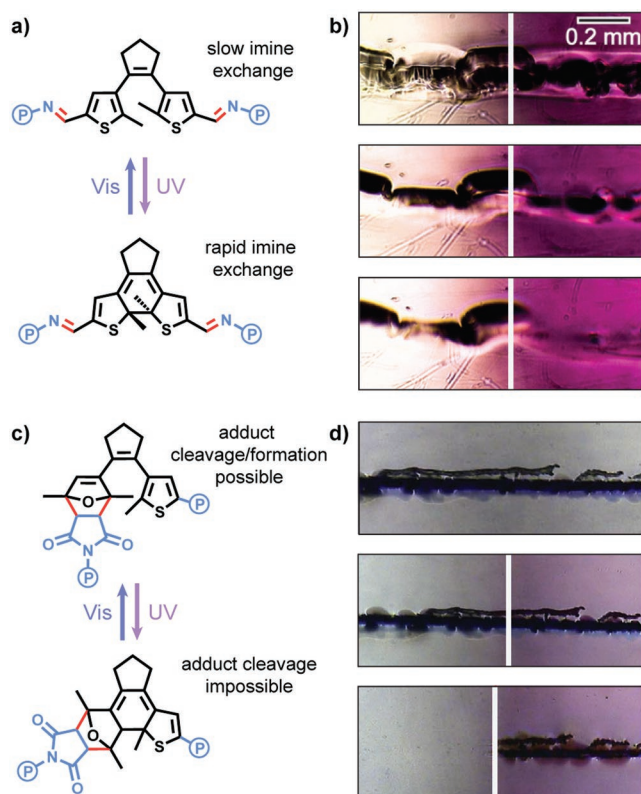


Figure 6. Diarylethenes able to modulate the rate and control the formation of dynamic covalent bonds within polymer networks. a,b) The top example shows: a) UV-light-accelerated imine exchange due to the higher reactivity of the ring-closed isomer, evidenced by b) optical microscopy images of scratches that self-heal faster in UV-light-exposed areas (right) as compared to non-exposed areas (left). a,b) Adapted with permission.^[26] Copyright 2016, Wiley-VCH. c,d) The bottom example depicts: c) a Diels–Alder adduct, which in the open isomer allows for thermal reversibility and thus dynamic (un)crosslinking. Meanwhile, in the closed isomer, the retro-Diels–Alder reaction is suppressed, leading to control over defect healing as evidenced by d) microscopy images of scratches, which thermally heal in non-exposed areas (left), whereas they remain in UV-light-exposed areas (right). c,d) Adapted under the terms of the CC-BY Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>).^[27] Copyright 2016, The Authors, published by Springer Nature.

In principle, there are two strategies that can be followed. The first one is based on phototuning the reactivity of an attached functional group, such as a carbonyl electrophile.^[25] For example, a DAE bearing two formyl groups exhibits different reaction rates with amines depending on the irradiation conditions (Figure 6a).^[26] The ring-open isomer resembling a rather electron-rich and thus less reactive aldehyde, reacts much slower than the corresponding ring-closed isomer, in which π -conjugation enables cooperative activation due to the electron-withdrawing nature of the terminal formyl/imine substituents. Blending this bifunctional DAE as a crosslinker into an amine functionalized polymer furnishes a material that can heal damage much faster when the DAE is in the ring-closed isomer (Figure 6b). This allows one to gate the recycling and remodeling of the material with light.

The second strategy is to use light-driven valence bond tautomerization to rearrange bonds in a fashion that reactivity is made to appear or disappear. For example, a DAE bearing an electron-rich furan as the diene component is able to undergo a thermally reversible Diels–Alder reaction (Figure 6c).^[28] The ring-closed DAE destroys the (cisoid) diene motif necessary for this reaction and as such it is nonreactive. More importantly, the Diels–Alder adduct itself can undergo UV-light-induced ring-closure to a structure that cannot undergo thermal retro-Diels–Alder reaction and thus effectively locks the adduct. The latter static connection can be rendered dynamic again by visible light-induced ring-opening. Blending a maleimide-bearing polymer with such furan-functionalized DAE crosslinker allows one to control the mechanical properties as well as the ability of the material to thermally heal damage with light (Figure 6d).^[27,29]

Photochromic crosslinkers offer the great advantage of low optical density and thus efficient photochemical operation since only a few weight percentage are required. One can also integrate photoswitches into the monomer, for example, in the main chain or the side chain. This was demonstrated by Wu and co-workers, who prepared AB-appended polyacrylates with the aim to reduce the glass transition temperature (T_g) upon $E \rightarrow Z$ photoisomerization (Figure 7a). Indeed, the polymer with all AB moieties in the E configuration has a higher transition temperature ($T_g = 48\text{ }^\circ\text{C}$, solid) as compared with the irradiated polyacrylate with 95% of the AB units switched to the Z isomer ($T_g = -10\text{ }^\circ\text{C}$, liquid). This light-triggered and reversible solid-to-liquid transition could be utilized to heal cracks in the

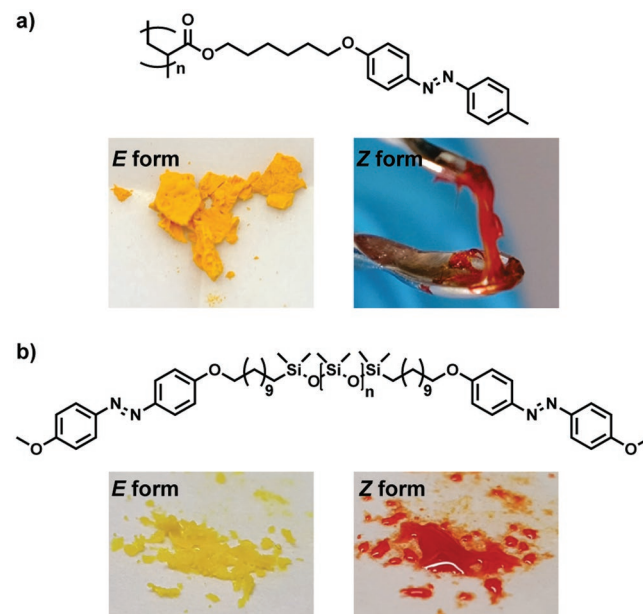


Figure 7. Modulating thermal polymer properties by azobenzene side chains or terminal substitution. a) Chemical structure of a polyacrylate with azobenzene pendants and optical images of a nonirradiated (solid) and UV-light-exposed (liquid) polymer sample. Adapted with permission.^[30] Copyright 2016, Springer Nature. b) Chemical structure of a discrete polysiloxane functionalized with terminal azobenzene units and optical images of a polymer sample before and after UV light irradiation. Adapted with permission.^[31] Copyright 2017, Wiley-VCH.

polymeric material repeatedly and is envisioned to facilitate the processing of hard coatings under ambient conditions without the use of plasticizing solvents.^[30] The Meijer group followed a similar approach by incorporating AB units as the end groups of discrete and well-defined siloxane oligomers, which form highly ordered, self-assembled nanostructures with a melting transition of 46 °C (Figure 7b). Upon exposure to UV light, the precise arrangement of the oligomeric chains is disturbed and thus the material exhibits properties that are typical for regular linear polysiloxanes (oily texture, melting transition below −60 °C).^[31]

3. Photoswitches on Surfaces

Anchoring switches to a surface (or more generally at an interface^[32]) is arguably the easiest method to manipulate the characteristics of the underlying material and its interaction with the environment, for example, by modifying the surface energy. When attaching photoswitches, care must be taken to provide the molecules with sufficient space to actually switch, in particular when densely packed in a layer,^[33] or place them far enough from the substrate to prevent surface quenching.^[34] Several strategies have been developed to overcome this detrimental quenching, which include spacing photoswitches by mounting them vertically on molecular platforms that are attached to the surface^[35] or leaving space between photoswitches by either mixing the self-assembled monolayer (SAM) with non-photoresponsive units or increasing surface curvature to give the molecules more space to actuate.^[36]

3.1. Controlling Surface Charges and Electronic Properties

Photoswitches have successfully been used to modulate the work function of various underlying substrates. For example, thin films of DAEs have been investigated using photoelectron spectroscopy and significant shifts on the order of ≈ 1 eV between the ionization potentials of the open and closed isomers have been revealed. Both the ability to chemically tune the energy levels through chemical substitution^[37] as well as the orientation of the DAE molecules with regard to the surface were found to have a large effect on the work function of the surface.^[38] In addition to thin films,^[38,39] also SAMs have been used to modulate charge injection barriers. Incorporating thiol anchoring groups into the structure of DAEs was used to prepare SAMs on a gold electrode, which allowed for switching of device characteristics by light when applied in an organic thin-film transistor (OTFT).^[40] This research endeavor is an important step toward multifunctional optoelectronic devices, in which several interfaces are brought together that can be addressed individually by external stimuli to gain control over the electrical output of an electric device. Photoswitchable SAMs have moreover been used to tune the energy levels of various (semi)conducting oxides, such as ZnO and indium tin oxide.^[41–43] The observed effect was attributed to the fact that the frontier molecular orbitals are energetically perfectly suited to allow for resonant tunneling through the closed but not the open isomer. The latter has also been observed for various DAEs at the single molecule level.^[44–47]

In addition to DAEs, which are particularly well suited for dramatic light-induced electronic changes of their structure, ABs can also be used in this context. For instance, when ABs are set up on a dielectric layer acting as an effective trapping site, either as a base layer for a pentacene conducting top coat or as an interstitial pillar in between a layer of pentacene molecules. Both strategies gate the conductivity of the pentacene layer with light by having the AB in the system act as a trap for either electrons or holes.^[48] Also SAMs of ABs composed of a biphenyl moiety bearing a thiol anchor and an electron-poor pentafluorophenyl moiety have been used to modulate the work function of a gold electrode.^[49] Although the extent of photo-tuning was only 220 meV, the robustness and ready availability of ABs makes them particularly applicable to gold surfaces and generally important for controlling metallic electrode surfaces.

All of the above examples rely on the light-induced modulation of the electronic levels of photoswitchable molecules that affect the charge-carrying ability of the underlying substrate. There is, however, another option that relies on the introduction of a charge or dipole moment itself by isomerizing a noncharged SP to its zwitterionic MC form. SAMs of SP molecules on a hafnium oxide surface allowed to gate the superconductivity of a tetrathiafulvalene (TTF)–copper crystal placed on top of the monolayer (Figure 8).^[50,51] The resistance at 5 K could be tuned by light from a Mott insulating phase all the way to a partially superconducting phase. The system was found to be thermally bistable and reversible by light. It was furthermore shown that the effect of the naked charge on the open MC form propagates several layers into the TTF crystal, indicating that the switching is not a pure surface phenomenon and illustrating that amplification is needed to achieve superconductivity.^[50]

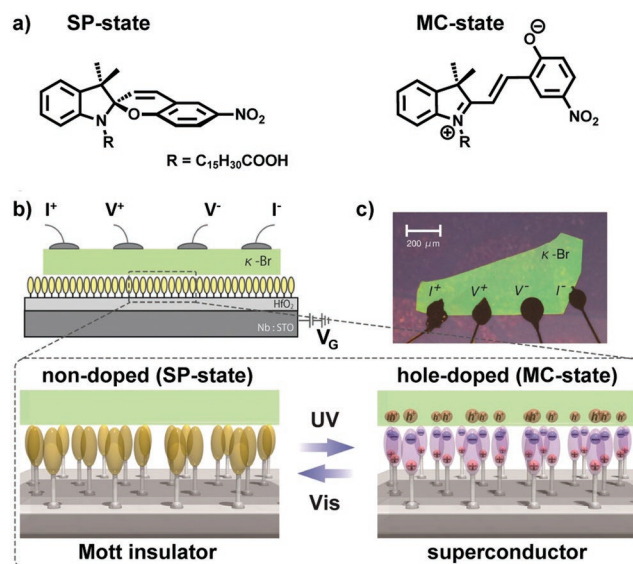


Figure 8. Photoswitchable (low temperature) superconductivity. a) Chemical structure of the spiro[pyran] and merocyanine form. b) Schematic of the superconductor structure, where a light-responsive spiro[pyran] layer gates the conductivity of a layered tetrathiafulvalene–copper crystal since the open merocyanine form generates a Mott superconducting phase. c) Picture of the crystal with the leads attached. a–c) Adapted with permission.^[50] Copyright 2015, American Association for the Advancement of Science.

Rather recently, there has been a surge into the area of 2D materials due to their outstanding physical properties for optoelectronics. Among them, transition metal dichalcogenides (TMDCs) have been found particularly attractive as they provide efficient charge transport combined with finite bandgaps. Therefore, it is not surprising that these have been functionalized with SP-MC^[52] as well as DAE photoswitches.^[53] In both cases, large photomodulation of their conductivity could be achieved without sacrificing their intrinsic performance and as a result such optically controlled TMDCs offer great promise for future multifunctional and high-performance devices.

3.2. Modulation of Surface Energy and Supramolecular Interactions

There are many examples of light-responsive surfaces where photoswitches are used to tune surface energy. A particularly nice demonstration from the Feringa group shows that their light-driven molecular motor can also be used for this purpose, however, only when properly oriented in an altitudinal fashion with relation to the surface. The rotation upon irradiation with UV light makes each motor pass through its four stable isomers, alternating between revealing and hiding a perfluorinated chain, which results in a large change of the water contact angle (Figure 9).^[54] The effect could only be achieved by anchoring the motors to a gold surface by using a rigid and wide tripod to ensure that they were mounted perpendicular to it and leaving enough space for each motor to rotate. In addition, the motor molecules needed to be placed far enough away from the gold surface to prevent quenching of the excited state, which would otherwise prohibit the rotation.

Pillar[5]arene type molecules bearing four pendant ABs branching from the arene core show excellent film forming properties on surfaces and give rise to the formation of supramolecular assemblies on a surface.^[55] By isomerization of the AB moieties with light, it was possible to control various surface properties such as wettability, photoalignment, and surface energy. Although this is not the first time that ABs have been used for this purpose, the value of the work arises from the fact that the tubular framework provides sufficient free volume for each AB unit and therefore enables a very efficient switching process.

In a more versatile approach developed by the Scherman group, ternary cucurbit[8]uril complexes with AB and methyl viologen have been used to switch surface properties.^[56] In this case, thiol-terminated ABs were anchored on a gold substrate and only in their *E* configuration complex formation together with dye-labeled methyl viologens within the cucurbit[8]uril macrocycles took place. Either light irradiation or reduction led to dissociation of the complex that could be reverted by using the appropriate wavelength or reoxidation. This approach allowed for an orthogonal and reversible alteration of properties from wettability to fluorescence, thus representing a useful tool for data storage in memory devices due to the underlying writing-erasing principle.

Another method to modulate any given surface is to release a specific chemical agent at command. For example, hydroxyl radicals generated from ambient water and sunlight at titanium dioxide surfaces help to kill bacteria. A more selective oxidizing

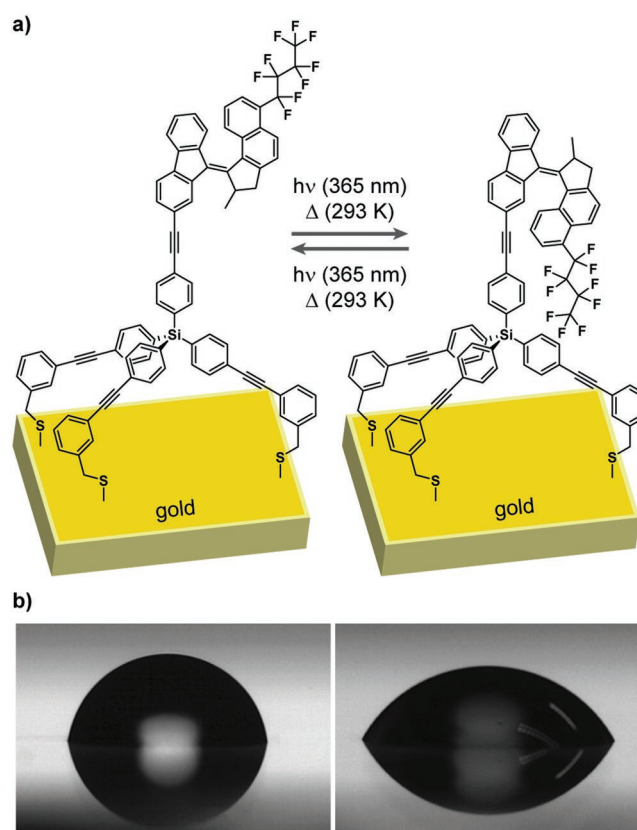


Figure 9. Light-driven motors to control surface polarity. a) Chemical structures of a molecular motor bearing a tripodal stator, which is anchored to a gold surface, and a hydrophobic perfluorobutyl group. The latter is either exposed to the interface in the *E* isomer of the motor (left) or hidden from the interface in the *Z* isomer (right). b) Optical images of a water droplet placed on the gold surface showing different contact angles depending on the conformation of the motor unit (contact angles: *E* = $82 \pm 1^\circ$ (left), *Z* = $60 \pm 1^\circ$ (right)). a,b Adapted with permission.^[54] Copyright 2014, American Chemical Society.

agent is singlet oxygen, which can be released from surfaces bearing dihydropyrene photoswitches.^[57] First, irradiation of the surface with red light led to the ring-opening of the photochromic molecules and the trapping of molecular dioxygen as an endo peroxide. Subsequent exposure to UV light caused the ring-closure of the photoswitches and triggered the release of singlet oxygen to the environment.

3.3. Light-Responsive Nanoparticle Surfaces

Light can be used to steer the aggregation of nanoparticles through modulating their surface energy, which is dependent on the interaction of the photoswitchable shell with the solvent^[58] and ideally very different in both isomers due to changes in dipole moment or formation of charged species. To this end, the Klajn group could achieve orthogonal aggregation of differently sized gold nanoparticles in a nonpolar solvent by a clever design involving two AB units that differ in their absorption profile (Figure 10).^[59] On the one hand, smaller nanoparticles that are decorated with an amino-AB can

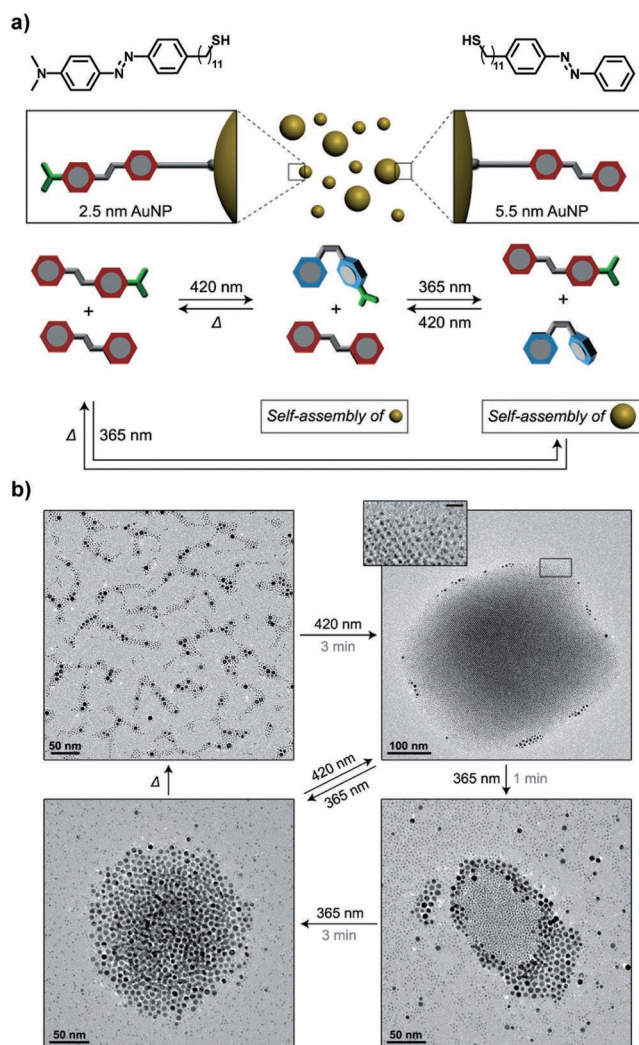


Figure 10. Orthogonal light-induced aggregation of differently sized nanoparticles. a) Light of different wavelengths can be utilized to selectively induce the self-assembly of gold nanoparticles with different sizes from a mixture of smaller nanoparticles (2.5 nm) decorated with electron-donor substituted azobenzenes and larger nanoparticles (5.5 nm) functionalized with the parent azobenzene. Due to the different absorption profiles of the applied azobenzenes blue light (420 nm) solely triggers the self-assembly of the smaller nanoparticles, while subsequent illumination with UV light (365 nm) leads to their disassembly and the simultaneous assembly of the larger nanoparticles. b) TEM images showing the light-induced orthogonal self-assembly of the gold nanoparticles. Adapted with permission.^[59] Copyright 2015, Wiley-VCH.

selectively be addressed with light of 420 nm, leading to solvophobic driven aggregation due to the $E \rightarrow Z$ isomerization. On the other hand, light of 365 nm triggers the back isomerization of the electron-rich AB units, which results in the redispersion of the smaller nanoparticles into the solution. At the same time, larger nanoparticles that are present in the same solution and functionalized with the parent AB also absorb the UV light that causes the formation of aggregates consisting only of larger nanoparticles instead.

The effect of this aggregation could be exploited to create confined spaces, so called “nanoflasks,” in which chemical

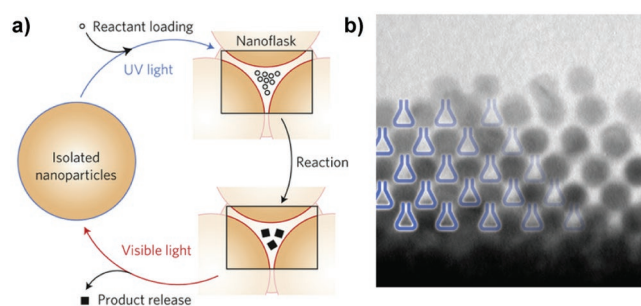


Figure 11. Light-driven assembly of azobenzene functionalized nanoparticles into “nanoflasks”: a) UV light induces aggregation and thus reactant loading into a confined space between the nanoparticles, where a reaction takes place, after which visible light breaks the aggregates and the products are released into solution. Reproduced with permission.^[62] Copyright 2015, Springer Nature. b) Electron microscopy image showing the assembled nanoparticles after exposure to UV light. Reproduced with permission.^[60] Copyright 2015, Springer Nature.

reactions could be accelerated and their selectivity enhanced.^[60] This effect used similar AB photoswitches tethered to gold nanoparticles, whose aggregation was similarly controlled with light. UV light caused the expected $E \rightarrow Z$ isomerization to assemble the nanoparticles (Figure 11) and visible light could disperse them again. When conducting these assembly–disassembly cycles in a nonpolar solvents such as toluene with a minimal amount of polar cosolvent such as methanol or water, the polar solvent was found to become trapped in the interstitial space between the nanoparticles. The increased local concentration within the nanoflasks led to accelerated reactions and the specific preorganization of the reactants gave rise to enhanced diastereoselectivity as demonstrated in the case of photochemical anthracene dimerization. When the nanoparticles as well as the photoresponsive AB were additionally functionalized with a chiral group, enantiomeric enrichment of a racemic mixture could be achieved. The utility of these nanoflasks arises from their dynamic nature based on their light-driven reversible assembly and disassembly. Moreover, the authors’ approach seems generally applicable as the aggregation of nanoparticles could also be controlled by the polarity changes upon SP-MC switching, demonstrating that AB is not the only molecule suited to this task.^[61]

In addition to modulating the assembly of nanoparticles, one can also control their emission properties as in the case of CdSe/CdS/ZnS core–shell–shell quantum dots covered in a DAE bearing polymer (Figure 12).^[63] Quantum dots are widely used as highly stable and bright fluorescent probes for biological analysis, which makes it particularly interesting to tune their light emission externally and on-demand. In this work, the DAE’s closed isomer acts as a Förster resonance energy transfer (FRET) acceptor and quenches the fluorescence of the quantum dot, whereas in the open isomer due to its much larger HOMO–LUMO gap does not interfere with luminescence. This approach makes deliberate use of the advantages of quantum dots, in particular their high emission quantum yields and long excited-state lifetimes. By decreasing the distance between the quantum dot surface and the photoswitch through modulation of the tether length from 16.2 Å all the way down to 3.7 Å, the quenching efficiency increased. A critical finding of this work is

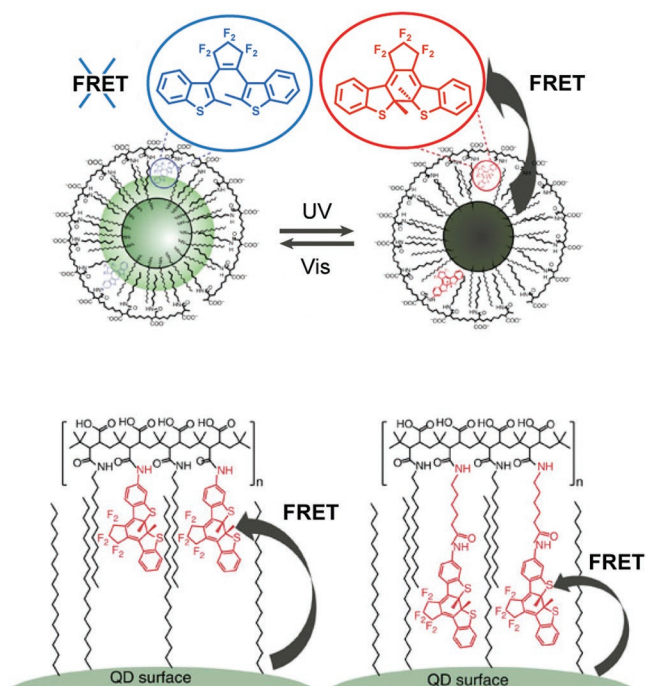


Figure 12. Photoswitchable quantum dot emitter. DAE-functionalized polymers are coated onto CdSe/CdS/ZnS core-shell-shell quantum dots. The open isomer (blue structure, top left) does not interfere with quantum dot fluorescence, while the closed isomer (red structure, top right) quenches it via FRET, which critically depends on the distance between the photoswitch and the quantum dot (bottom). Note that the quenching mechanism regenerates the open isomer and thus enables self-regulation of the quantum dot emission. Adapted with permission.^[63] Copyright 2015, Springer Nature.

that the FRET-based quenching mechanism leads to excitation and thus subsequent opening of the closed isomer, giving rise to a feedback loop. Upon decreasing absorbance of the DAEs in the UV region, which indicates the formation of a significant amount of closed isomer, excitation of the quantum dots increases to the point where FRET leads to the opening of the generated closed isomers. This provides a means to self-regulate the quantum dot emission. The reverse switching process, induced by exposure of the closed isomers to visible light, was not affected by this problem and afforded the fully open DAEs without any interfering FRET. These findings highlight some of the fundamental challenges of working with photoswitches in electronically coupled environments.

4. Photoswitches in Supramolecular and Liquid Crystalline Environments

Supramolecular interactions, such as hydrogen-bonding, metal coordination, electrostatic effects, hydrophobic forces, and π - π interactions, can be used to organize photochromic molecules and thereby enable the preparation of materials with tunable macroscopic properties. In particular, liquid crystalline systems give rise to well-ordered assemblies over a long range and thus small light-induced changes within a photoswitchable unit can have a large impact. By exploiting the anisotropy of

the organizing medium advanced materials can be created that perform sophisticated tasks, for instance grabbing an object,^[64] autonomously and solely fueled by light.

4.1. Light-Induced Assembly and Disassembly

Supramolecular and liquid crystalline light-responsive materials provide numerous possibilities for giving order to the incorporated photochromic molecules in relation to their surroundings.^[65] A simple example involves blending commercially available SP switches into reverse micelles composed of cholesterol bile salts and phospholipids in cyclohexane solution.^[66] UV-light-induced formation of the MC form leads to a 10-fold decrease in viscosity of the initially viscoelastic fluid that is fully recovered after thermal back reaction to the charge-neutral SP form. The observed light-controlled change in viscosity was attributed to the strong coulombic interactions of the zwitterionic MC and the charged head groups of lecithin and sodium cholate that modulates the length of the worm-like reverse micelles and constitutes the first example of a reversible photorheological fluid. In addition to coulombic forces, the Harada group has made extensive use of the cyclodextrin-AB host-guest interaction and introduced photoswitchability.^[67] Supramolecular crosslinking of two types of polymer chains, one appended with AB and another one with cyclodextrin moieties, leads to gelation in water. The formed hydrogels can reversibly be liquified with UV light due to isomerization of the pendant ABs to their Z configuration, which no longer bind to the cyclodextrin-bearing polymer chain, effectively uncrosslinking the gel.^[68] In a more recent work, the same group took advantage of mechanically interlocked systems, so called daisy chains, to realize light-driven contraction-extension cycles in hydrogels (Figure 13).^[69]

Another strength of photoswitchable molecules is their ability to act as an orthogonal handle in combination with another (e.g., chemical) stimulus. For example, sulfonated AB dimers could coassemble with oppositely charged poly(amidoamine) (PAMAM) dendrimers into nanoparticles, which upon UV light irradiation grow further to give opalescent samples.^[70] In addition to photoresponsivity due to $E \rightarrow Z$ isomerization, the electrostatic self-assembly could be independently controlled by adjusting pH from aggregation-promoting acidic (pH 3.5) to disassembling basic (pH 10.5). Taking inspiration from biology, Aida and co-workers attached SP photoswitches to the surface of GroEL barrel proteins, enabling them to recognize each other in the presence of bridging magnesium ions, but only if the MC form is present (Figure 14).^[71] In this case, the addition of the photoswitch provides an additional orthogonal handle to control tubular assembly and disassembly not only by ions but light as well. Under magnesium-rich assembly conditions, irradiation with visible light converts the MC back to the SP form, removing the coordinating phenoxide residues, and thereby breaks the salt-bridges and the tubular assembly. This represents the first example of a photoreconfigurable bionanotube, which has the potential to be utilized for time and space resolved guest delivery in biological media.

The self-assembly of amphiphilic DAEs in water has intensely been investigated by the Matsuda group for some

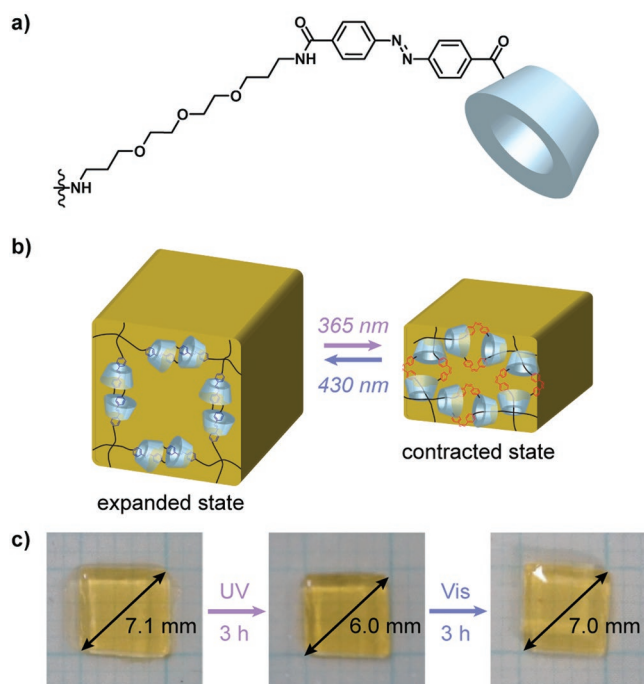


Figure 13. Photoresponsive gels built from [c2]daisy chains, which are based on a four-armed poly(ethylene glycol) compound bearing azobenzene (guest component)-functionalized side arms that are linked to a cyclodextrin moiety (host component). a) Chemical structure of the azobenzene side arm with cyclodextrin depicted as the blue cone-like object. b) Scheme showing the light-induced contraction/expansion of the gel, and c) optical images of the hydrogels displaying the reversible shrinkage upon light irradiation. a–c) Adapted with permission.^[69] Copyright 2016, Springer Nature.

time. Using either temperature or different wavelengths, which dictate the ratio of open and closed isomers in the photostationary state, the authors could switch the morphology of the assemblies.^[72] Specifically, when exposing colorless microspheres with UV light, colored fibers grew out of the sphere. Illumination with green light led to the collapse of the fibers and the sphere was restored at its original position. Similar light-controlled shape changes of aggregates were achieved with a water-soluble version of the Feringa motor, which assembled into large nanotubes in its thermally stable *E* isomer.^[73] Upon UV light irradiation the tubes dynamically reorganized into vesicles, which subsequently converted into more stable vesicles before reforming the original nanotubes. This work shows reversible switching and motor operation in water, and in addition it illustrates the importance of understanding systems with coupled processes leading to more than two switching states.

The dynamic nature of aggregates could also be used to transmit and amplify chiral information in a system. The same authors could assemble fibers from a mixture of amphiphilic DAE derivatives composed of enantiomerically pure, closed “sergeant” DAEs and open “soldier” DAEs, with the latter being able to rapidly interchange between their *M* and *P* helical forms.^[74] Upon irradiating the aggregates with UV light the chirality transfer from few “sergeants” was transferred to many “soldiers,” which were subsequently locked in the closed form and thereby promoted into “sergeants” themselves. After

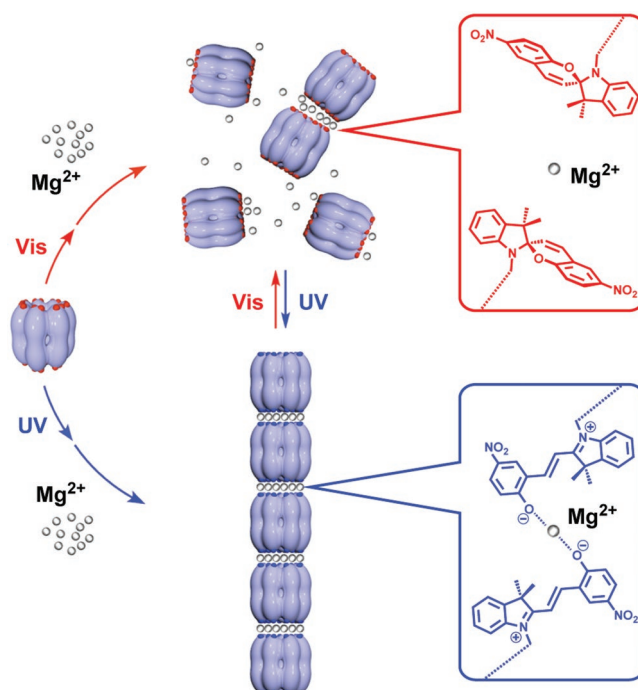


Figure 14. Photoreconfigurable bionanotubes. GroEL barrel proteins decorated with multiple spiropyran units can reversibly form nanotubular assemblies based on the UV-light-induced conversion to the zwitterionic merocyanine form, which is able to coordinate to bridging magnesium ions. Adapted with permission.^[71] Copyright 2013, American Chemical Society.

dissociation and new assembly, the overall process resulted in an amplification of chirality. In a related molecular design that involves the introduction of larger groups and another chiral H-bonding motif at the termini of a DAE, the formation of well-ordered superhelices in the rigid closed isomer could be realized, whereas helical assembly was completely suppressed in the more flexible open isomer.^[75] This work shows how chiral communication between molecular and supramolecular levels (similar to natural systems, such as proteins and DNA) can be regulated with light.

Another popular columnar self-assembly motif that is based on 1,3,5-trisubstituted benzene molecules, in particular trisamides, has also been modified with AB moieties as photoswitchable residues. In specific mixtures of organic solvents and water, these star-shaped AB trimers assembled into various self-assembly structures, including vesicles and fibers, the latter of which could be disassembled and reassembled by light.^[76] While the UV-light-induced conversion of some flat *E* isomeric units effectively disrupted the columnar stacking and broke the fibers, visible light regenerated the all-*E* configured monomer and the fibers were recovered. By breaking the symmetry and introducing amphiphilicity the Aida group was able to assemble hexabenzocoronenes (HBC) appended with DAE units into extended nanotubes that are able to generate photocurrent.^[77] Interestingly, in addition to driving photocurrent generation light could also be used to modulate it depending on whether the DAE was in its open or closed isomer. Nanotubes composed of the latter favor electron transfer from the

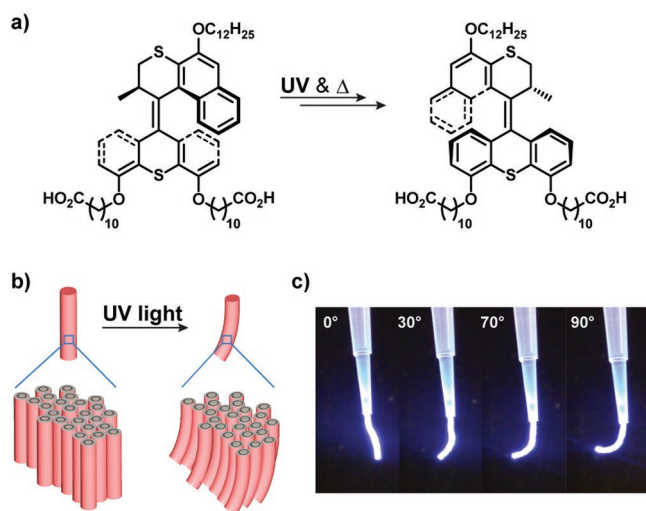


Figure 15. Light-driven artificial molecular muscles. a,b) Chemical structure of an amphiphilic molecular motor (a), that self-assembles into nanofibers (b), whose hierarchical order can be influenced by light. c) Optical images showing the muscle-like bending movement of a string toward the UV light source upon illumination. a–c) Adapted with permission.^[78] Copyright 2017, Springer Nature.

excited HBC and thus exhibited a five times higher photoconductivity as compared to the ones carrying the open DAE.

The vast potential of supramolecular systems for soft robotics has impressively been demonstrated by the Feringa group, who fabricated hierarchical fibers that bend toward a UV light source (Figure 15).^[78] In their work, amphiphilic molecular motors were employed that self-assemble into nanofibers in water and upon exposure of the dissolved aggregates to a CaCl₂ solution centimeter-long strings can be drawn, in which the nanofibers are unidirectionally aligned in bundles. The photochemically and thermally induced unidirectional rotation of the implemented motor unit propagates and accumulates through the supramolecular material, which is mostly composed of water. This results in the muscle-like contractile movement that can be translated into mechanical work by lifting objects in water as well as in air.

4.2. Changing Liquid Crystalline Properties

Liquid crystalline (LC) systems are an excellent way of introducing order to liquid and soft environments. For example, the Kato group could show that an imidazolium unit functionalized with three AB arms forms a smectic (homeotropic) phase at room temperature, which could be disordered to an isotropic phase before being aligned with linearly polarized light to a smectic (homogeneous) phase (Figure 16).^[79] In both LC phases, the imidazolium moieties are aligned either parallel or perpendicular to the plane of the film and the adjacent substrate and provide preferred orthogonal ion conduction pathways. Thus, light enables alignment to ionic LC materials with high conductivity perpendicular to the electrode surface and has potential for rewritable ionic circuitry.

As discussed above the helical chirality of the photochromic molecules plays an important role in their self-assembly that

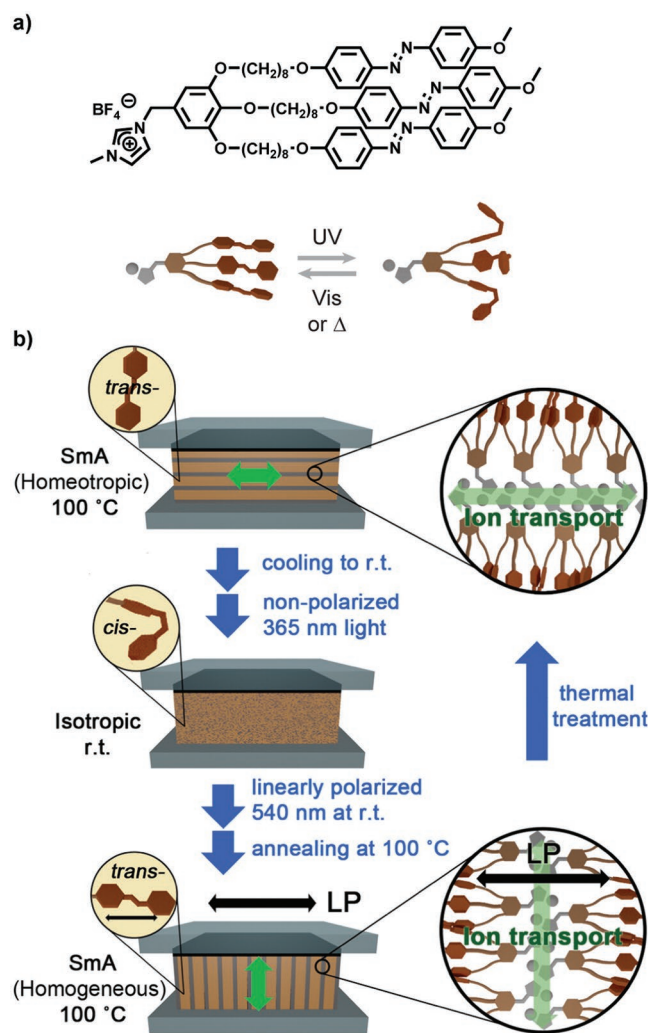


Figure 16. Photoaligning LC phases to provide orthogonal ion conduction pathways. a) Imidazolium salt bearing three photoswitchable azobenzene pendants. b) Cycle of photoisomerization and annealing steps to interconvert LC phases and orient ionic conduction pathways either parallel or perpendicular to the substrate. a,b) Adapted with permission.^[79] Copyright 2014, American Chemical Society.

consequently influences the overall switching behavior. A successful molecular design involves a DAE core appended on each side by chiral units, either having point chirality (see above) or axial chirality, for example, binaphthyls. The latter molecules have very successfully been used as chiral dopants to bias the twist sense in chiral nematic LC phases. For example, the structural changes upon light-induced ring-closure of a DAE core can be transmitted to the binaphthol termini, effectively changing their dihedral angle and thereby switching the phase behavior of the surrounding LC matrix. This effect has been maximized such that the helical pitch of a chiral nematic phase could successfully be inverted using light.^[80] In recent years, this molecular design has extensively been used by the Li group to design light-responsive soft materials. By using capillary-assisted microfluidic extrusion they prepared monodisperse droplets containing axially chiral DAE derivatives and demonstrated the droplets' remarkable light-responsive properties (Figure 17).^[81]

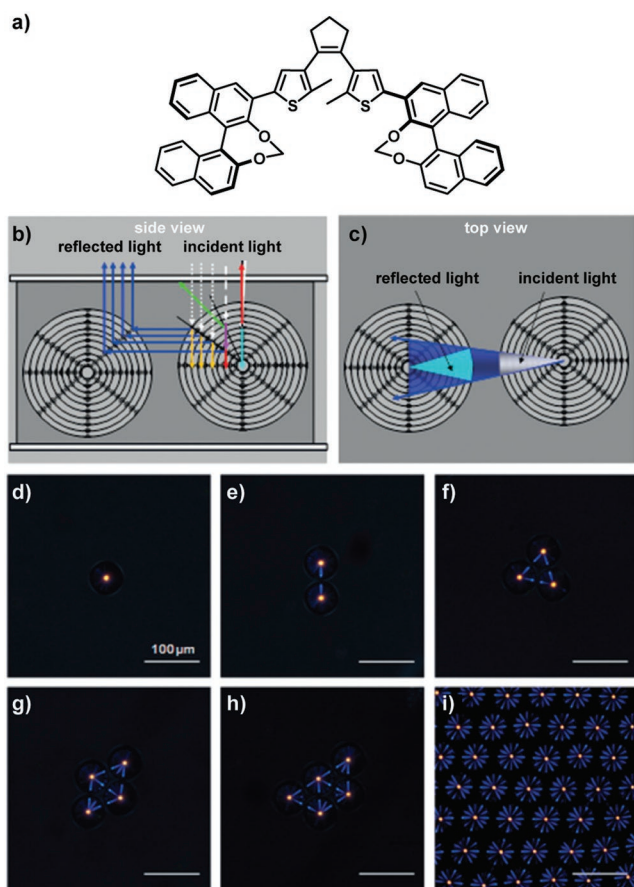


Figure 17. Monodisperse microdroplets provide tunable structural color. a) Chemical structure of the DAE employed as photoswitchable chiral dopant. b) Schematic of light irradiation viewed from the side of the droplets. White light from above results in a blue reflection at 45° and red reflection from 0° ; other wavelengths travel through the droplet. c) From the top, blue light is reflected onto nearby droplets. d) View of a single droplet under irradiation, e) two droplets, and their cross-talk, f) three droplets forming a triangle of communication, g) four nearby droplets, note the difference in angles at each “corner” of the arrangement, h) five droplets cross-talking, and i) a long-range hexagonal close-packed array. Note that the intensity of the cross-talk is weaker when the partner droplet is further away. a–i) Adapted with permission.^[81] Copyright 2014, Wiley-VCH.

UV-light-induced ring-closing of the DAE led to a reversible increase in the helical twisting power, which in the spherical droplets manifests itself in a phototunable Bragg diffraction pattern. As a result, the apparent color of the droplets can remotely be controlled under full-spectrum irradiation to appear anywhere from white to red when viewed from above. Moreover, the authors found that “communication” between individual droplets in close proximity has a large effect on their optical appearance, demonstrating a rather sophisticated version of “structural color.” Due to the ease of their fabrication and tunability, such microdroplets offer an attractive platform for soft photonic materials. To highlight the subtle effects of molecular structure on the overall material properties, please note that a tiny chemical modification of the DAE derivative, i.e., changing the linker between the binaphthol oxygens atoms from a one carbon to a four carbon chain, furnishes a photoswitch that is

able to change the helical axis of a chiral nematic liquid crystal even in three dimensions exclusively with light.^[82]

Axially chiral binaphthyl systems could also be rendered photoswitchable using two AB pendant groups.^[83] In solution and in a nematic liquid crystal the *E,E* isomer gave rise to the formation of long-range right-handed helices, while upon UV light irradiation the (partially) *Z* configured molecule organized into a left-handed helix. Variations of the molecular design were shown to be able to switch various liquid crystals with different efficiencies. The switch does not necessarily have to be a dopant within an established liquid crystal but could also be a mimic of a mesogen itself. Based on this strategy, a synthetic mimic of a known cyanobiphenyl dimer, in which one unit was replaced by an AB, was used to trigger a twist-bend nematic to nematic phase transition by UV-light-induced *E*→*Z* isomerization.^[84] Nowadays, there are several examples of LC transitions being manipulated by light, essentially controlling the phase of a LC material. Equally interesting is the idea of creating a LC phase from an isotropic mixture, i.e., the on-demand ordering of molecules in a liquid. This was achieved by conjugating a terphenyl moiety to a SP switch, which upon UV light irradiation generates the corresponding MC form that due to its large dipole moment facilitates molecular ordering. This effect can be used either for formation of nematic phases from isotropic phases or, depending on the temperature of the system, switching of a nematic phase to a smectic one, resulting in light-driven dichroism.^[85] Instead of creating light-responsive LC soft matter, it is furthermore possible to fabricate micro-particles that exhibit interesting morphologies and tunable LC properties. Here, an azopyridine-functionalized polymer as a hydrogen-bond acceptor and a variety of dicarboxylic acids as hydrogen-bond donors were used to generate microparticles by a simple phase-reversion method.^[86] The surface of these particles could be adjusted from wrinkled to smooth depending on the choice of carboxylic acid. Light illumination caused a LC-to-isotropic phase transition accompanied with a breakdown of the particles.

4.3. Motion with Liquid Crystals

Using light as the energy supply to power motion is highly attractive since there is no need for converting solar into electrical and subsequently into mechanical energy. In addition, no direct contact between the actuating device and the energy source and controller is necessary. Motion in typically AB-containing LC films has been known for about two decades and termed the optomechanical or photomechanical effect. Alternatively to using polarized light, the direction of motion can also be biased by supramolecular organization of the material as shown by the Aida group.^[87] In particular, anisotropic stress is built into the material by hot-pressing the liquid crystal between two uniaxially stretched Teflon sheets giving rise to a homeotropic arrangement of the polymer backbone with the AB side chains being aligned horizontally. These films bend rapidly upon irradiation with UV and visible light and maintain their programmed direction of motion. Note that the alignment only works with polymers that bear multiple really densely packed ABs in their side chains.

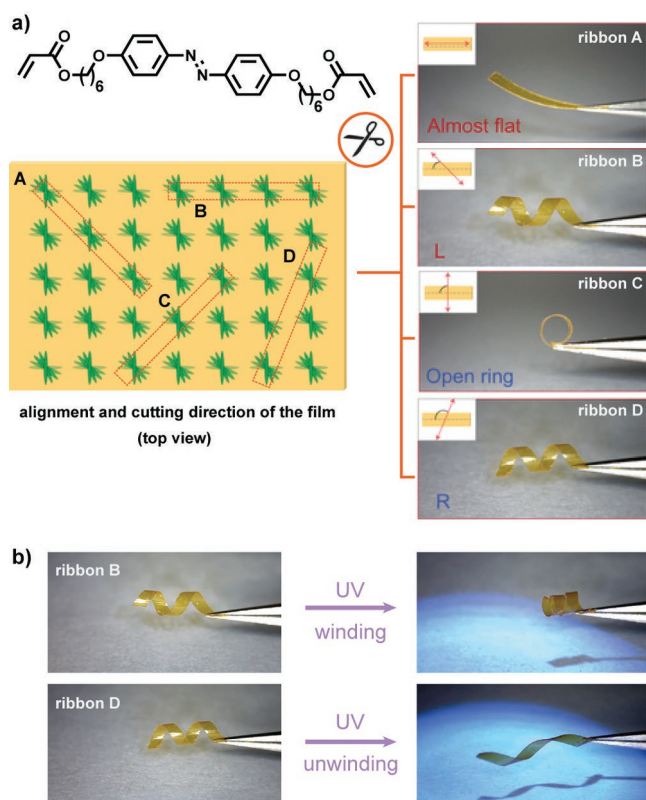


Figure 18. Ribbons with various shapes depending on cutting direction of LC film. a) Chemical structure of the azobenzene crosslinker (top left), which is blended in a commercial LC mixture to induce a chiral pitch. The orientation of the azobenzene alignment in the LC film (green) and various possible cutting patterns (orange) provide ribbons, which undergo predictable motions ranging from bending to curling in either direction. b) Spiral ribbons exhibit winding and unwinding motions, respectively, upon UV light irradiation dictated by their initial shape. a,b) Adapted with permission.^[89] Copyright 2014, Springer Nature.

More often stress is introduced into the material during synthesis via covalent crosslinking into LC elastomer networks. However, by incorporating reversible phenolic ester crosslinks, which can undergo transesterification at elevated temperature, the resulting films can be reshaped at will and different motions can be observed after the physical programming.^[88] Motion beyond simple bending was achieved by polymerizing AB-containing monomers in the presence of a nematic twist and removing the resulting film. Sections of the free-standing polymer film could then be cut with different orientations with respect to the original LC-templated pitch, which aligned the photochromic molecules with relation to the material dimensions (Figure 18).^[89] As a result, complex motions from bending to winding, unwinding and helix inversion could be achieved, all combined into a single material simply by controlling the sections that were cut from the cast film. In this manner, the action of the light-induced stresses could be focused in a given direction, leading to bio-inspired wrapping motions reminiscent of plant tendrils guiding plant growth toward light. Incorporating *ortho*-fluorinated ABs^[90,91] endowed visible light response to the films as well as making their shape changes persistent on a scale of many days given the long thermal half-life of

the ABs.^[92] By designing a photopatterned LC polymer network with regions of low and high degrees of order and subsequent isomerization of the incorporated ABs, the light-induced stress, manifested in elastic energy, was built up slowly in the soft material until it was released in a rapid actuation, thereby mimicking the explosive opening of seedpods in nature.^[93] Other bioinspired motions that were realized with photoresponsive LC films are the helical motion of pythons,^[94] circadian rhythms of leaves,^[95] and the motion of dolphins,^[96] among others.

The motions described in most of the cases deal with a starting point, corresponding to one isomer of the photoswitch within the material, and a final point, which is enriched in the second isomer. A clever dispersion of AB with stearic acid afforded LC films that could go through a flapping motion under constant irradiation with blue light, which triggered both the $E \rightarrow Z$ and $Z \rightarrow E$ isomerization simultaneously. Irradiation at this wavelength stimulated constant motion initiated by a bending that was followed by a light-independent phase transition. Subsequently, light of the same wavelength triggered bending in the opposite direction followed by a second phase transition, allowing the cycle to start anew ad infinitum.^[97]

The use of *ortho*-fluorinated ABs allows both switching directions to be triggered by visible light.^[90,91] Consequently, LC films with incorporated tetra(*ortho*-fluoro)azobenzenes show a never-ending chaotic motion when irradiated with green and blue light simultaneously or simply exposed to sunlight.^[98] Subsequent work by the same authors has focused on using the same system to prepare photoprogrammable surfaces with control over their topography. The latter can be used to optically control and manipulate local cell adhesion.^[99]

The motions that are demonstrated in some of the simplest life forms, such as the motion of cilia and flagella, are of ever-present interest to replicate since they would permit micro- and nanoscale movement of matter.^[100] Free-standing arrays of small fibers made from AB-functionalized LC networks were shown to bend toward a light source in a concerted fashion.^[101] This light-controlled cooperative motion creates a flow that is able to actively transport objects over a surface. The optomechanical response depends on light wavelength and intensity as well as temperature and could be tuned by blending with crosslinkers of different lengths. The Fischer group used more sophisticated light patterns in the shape of waves to deform LC films and thereby to move macroscopic objects, such as tubes and discs, through liquids.^[102] This work impressively demonstrates that the optical control over local actuation dynamics dictates the micro-objects' macroscopic locomotion, providing ample opportunities in microscale robotics.

Taking actuation even a step further, AB-doped LC elastomers were recently designed by the Priimagi group to respond to light in a self-regulating fashion, meaning that sensing of an external light stimulus and performing a specific action accordingly are comprised within one material. They created a light-driven artificial flytrap, which is able to differentiate between various objects depending on their optical features (Figure 19).^[64] Only under proper conditions, the polymeric film eventually bends and grips the object automatically. As soon as the light source is turned off, the object gets released again. Following the same concept, the first self-regulating

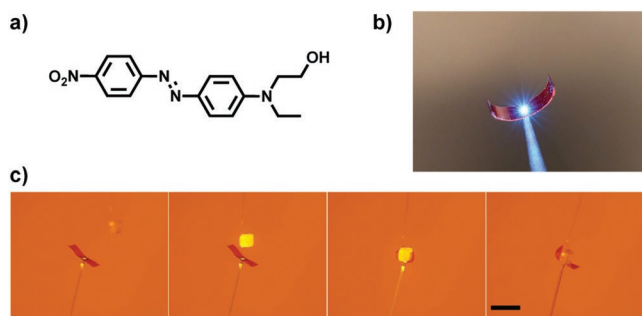


Figure 19. Light-driven artificial flytrap able to optically detect and grab a micro-sized object. a) Chemical structure of the azobenzene dopant in the LC elastomer. b) Photograph of a polymeric stripe attached to the tip of an optical fiber. c) Optical images showing the working principle of the artificial flytrap: a small object enters the field of view of the flytrap and due to the reflection of UV light the polymeric stripe bends and captures the object, which can be released again by turning the light off. a–c) Adapted under the terms of the CC-BY Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>).^[64] Copyright 2017, The Authors, published by Springer Nature.

artificial iris was manufactured, which closes its segments once blue light hits the polymeric film.^[103] The light transmission through the “pupil” could thereby reversibly be reduced by a factor of seven (from 70% transmission in the open state to 10% in the closed form). These examples represent early stages of the potential evolution of microrobots that operate in an intelligent and fully autonomous way. Naturally, adaptive soft robots are not restricted to light as an exclusive external trigger, a recently developed artificial nocturnal flower demonstrates that the smart design of a LC network also enables the response to ambient moisture in combination with light, leading to a humidity-gated photoactuation.^[104]

Light waves, consisting of local light intensity variations, can also be used to induce asymmetric deformation of microtubules to enable the active transport of liquids, thereby mimicking the pumping action of an artery (Figure 20).^[105] A high molecular weight polymer bearing AB side chains was uniformly coated on the inside of glass capillaries by simple solvent evaporation and subsequently removing the surrounding glass by chemical etching. The resulting free-standing tubes are highly robust and can move various solvents unidirectionally along a gradient of light while even having them pick up cargo such as chemicals or nanoparticles. The device also sets the record for the fastest light-controlled movement of a liquid by moving hexane at 5.9 mm/s through the 8 μm diameter tube.

5. Light-Responsive Porous Crystalline Materials

A porous crystalline setting, such as a metal–organic framework (MOF), provides the advantage of isolating and placing discrete photochromic entities in a well-defined environment with a fixed distance and orientation to one another. To introduce additional properties and functions to MOFs, typically new functionalities are integrated onto the organic linkers, which are held together in a long-range 3D arrangement by metal corners or nodes. The first light-responsive MOF was reported by the Herges group, who demonstrated that the

AB photoswitches need to be attached perpendicular to the strut linker and not in the linker itself to retain its switching ability.^[106] Clearly, the large geometrical change induced by $E \rightarrow Z$ photoisomerization, effectively shortening and bending the linker, cannot be accommodated within the rigid MOF scaffold. However, this general rule seems to be contradicted by two intriguing examples, in which either 4,4'-azobenzene dicarboxylic acid or 3,3',5,5'-azobenzene tetracarboxylic acid linkers were used as the strut of zinc-based MOFs.^[107,108] In both cases, UV light irradiation leads to reversible uptake and release of CO₂ that has been attributed to localized bending due to the highly unfavored AB photoisomerization followed by the rapid thermal back isomerization. The resulting dynamic short-range motion seems to be responsible for the observed effect on gas uptake as well as release and highlights the importance of metal and resulting MOF architecture selection as this directly influences the photoswitch performance.

5.1. Control Over Guest Uptake and Release

The immediate application of photoswitchable porous materials is the gating of molecular adsorption and desorption behavior by modulating the void space reversibly and noninvasively with light. As MOFs and their covalent organic framework (COF) analogues follow in the footsteps of zeolites as materials with ultrahigh surface areas, their pore properties can be affected by the geometrical changes of ligands bearing photoswitchable units, which alter their shape in response to light. In particular, ABs converting from an extended, rod-like, nonpolar *E* isomer to a contracted, bent, polar *Z* isomer are particularly suited to control the characteristics of porous crystals, i.e., size, geometry, and polarity of the pores.^[109]

Azobenzene in MOFs has been shown to provide photocontrolled uptake and release of CO₂ gas based on a difference in the pore size of a zinc-based MOF.^[110] In a different study, it could be demonstrated that the photoinduced polarity change between the two AB isomers in a zirconium-based MOF is the reason why the diffusion kinetics of CO₂ gas could be altered with light. On the contrary, argon gas, which has an almost identical kinetic diameter but is less polarizable, was not affected by the switching process.^[111] Another strategy to change the properties of a crystalline porous framework involves the incorporation of the photoswitch in the pores of a flexible MOF. By inserting AB molecules in the pores of a zinc-based MOF, the pore size could be increased upon $E \rightarrow Z$ photoisomerization resulting in a more than eightfold higher uptake of N₂ gas. The pores could be returned to their native shape by heating via thermal relaxation of the AB molecules to the favored *E* isomer.^[112] Going one step further, also the permeation of different gas mixtures (e.g., H₂/CO₂ or H₂/C₂H₄) could selectively and repeatedly be tuned by creating a smart membrane material based on a MOF, in which AB molecules decorate the pores.^[113,114]

Control over guest uptake and release is not limited to small gas molecules. The groups of Yaghi, Stoddart, and Zink used a magnesium-based MOF, which provides long hexagonal channels to accommodate an AB switch pendant to a terphenyl strut. From calculations, a pore-size of 8.3 Å was predicted for

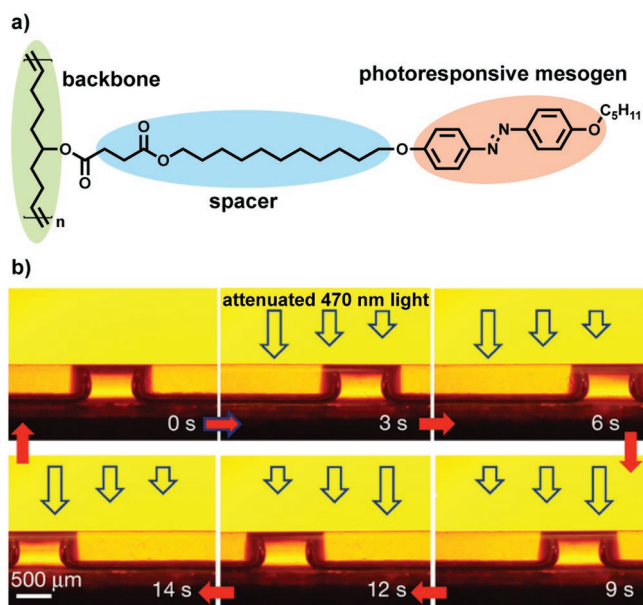


Figure 20. Light-driven pumping based on gradual propagation of photoactuation along a tube. a) Chemical structure of the azobenzene functionalized polymer. b) Photoresponsive polymeric capillary encloses a liquid (silicon oil) and upon irradiation with attenuated light (longer arrows represent more intense illumination) the liquid can be moved at will through the capillary. a,b) Adapted with permission.^[105] Copyright 2016, Springer Nature.

the “closed” *E* configured pore and a larger size of 10.3 Å for the “open” *Z* configured pore (Figure 21).^[115] This effect was studied by the uptake and release of a dye, which could be inserted into the pores while they were in the “open” configuration. Interestingly, optimal release was not achieved simply by opening the pores as initially postulated, but by irradiating the MOF at the isosbestic point of the *E* and *Z* AB absorption such that the dynamic *E*↔*Z* forward and backward isomerization cycle essentially pushes the dye out of the channels through constant molecular motion.

Generally, the switching behavior of ABs in MOFs is not guaranteed since the choice of metal ion (node) drastically affects the flexibility and the conformation of the ABs. For example, MIL MOFs (MIL = Matériaux Institut Lavoisier) made of gallium ions can act as hosts for AB guests that are able to reversibly isomerize with light and thereby tune the shape of the MOF. However, identical MOFs consisting of aluminum ions lead to such tight packing of the AB guests that isomerization is completely inhibited.^[116] In the context of integrating photoswitches in these materials, fundamental questions about how intrinsically isomerizable molecules are able to switch in a constrained environment were only recently answered by careful measurements in surface-mounted metal-organic frameworks (SURMOFs). As sufficient free volume for switching is of paramount importance, the choice of the linker was critical to achieve good switching performance. Thereby, the 3D environment including all other linkers in the system has to be taken into account, as has been done both experimentally and theoretically.^[117] In addition, potential quenching of the necessary photoexcitation by the surrounding metal complexes has

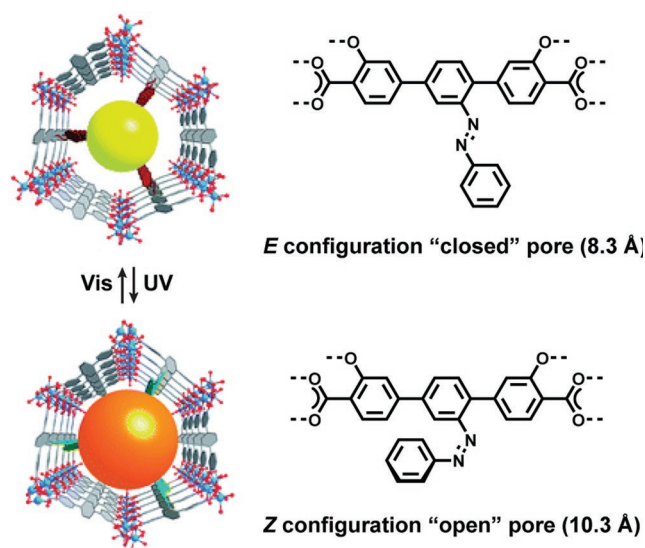


Figure 21. Photoswitching pore size in MOFs: Illustration of the pore architecture (left) made from terphenyl linkers (right) with integrated azobenzene moieties, which point into the hexagonal pore channels, leading to a change in the pore diameter between “closed” *E* and “open” *Z* configurations. Adapted with permission.^[115] Copyright 2013, Royal Society of Chemistry.

to be avoided. Once again *ortho*-fluoroazobenzenes, which allow operation with visible light only, play a vital role as their absorption is red-shifted as compared to many MOFs, for example frameworks based on zirconium or zinc, thus precluding energy transfer as a competing deactivation pathway.^[118]

Along with the 3D control over placement and orientation of the photoswitch with relation to its neighboring moieties, layer by layer growth can be used to control the overall structure even more specifically. In pioneering work, the Wöll group employed sequential growth of a SURMOF to cover container-type host layers by a photoswitchable layer and could demonstrate light-modulated release of small molecules (1,4-butanediol) as monitored by a quartz-crystal microbalance.^[119] This strategy provides a clever solution for the inherent problem of light penetration into solid materials as the photoswitchable units are located only on the surface of the material and thus are easily accessible to light. In a somewhat related approach, the surface of MOF crystals can be functionalized with photoresponsive moieties by a process called solvent assisted ligand exchange, in which nonfunctionalized ligand molecules of the outer shell are slowly replaced by AB-bearing linkers in solution. Thereby, well-defined zirconium MOFs with perfect octahedral shape were formed with a thin layer consisting of linkers carrying two *tetra-ortho*-fluorinated AB units (Figure 22).^[120] This design provides remarkable photochemical performance since the ABs, implemented in the MOF structure, can be operated with visible light in both switching directions without fatigue over several switching cycles and with high photoconversions that do not deviate from the free AB units studied in dilute solution. Uptake and release experiments with 1-pyrenecarboxylic acid, methylene blue, and 8-hydroxypyrene-1,3,6-trisulfonic acid trisodium salt as the guests successfully demonstrated that the photoresponsive outer shell of the MOFs acts as a gate, which

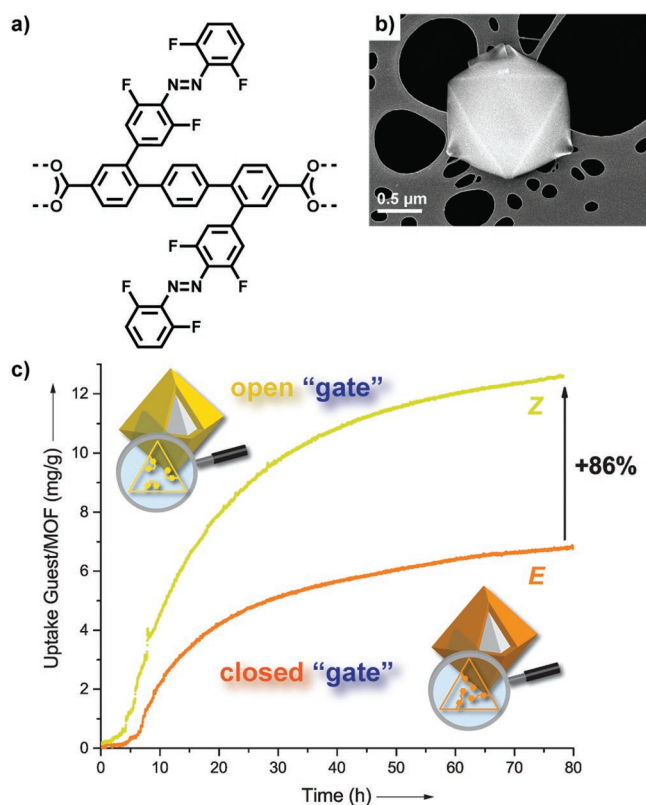


Figure 22. Light-controlled porous nanocontainers. a) Chemical structure of terphenyl linker carrying two decoupled tetra-*ortho*-fluorinated azobenzene moieties. b) SEM image of a perfect octahedral MOF crystal. c) Uptake experiment of 1-pyrenecarboxylic acid followed by UV-vis spectroscopy, showing an enhanced uptake capability for the open shell layer with azobenzene moieties in the Z configuration. a–c) Adapted with permission.^[120] Copyright 2019, Wiley-VCH.

can be closed on-demand when the ABs were switched to their all-*E* state and opened when converted back.

Another approach of gating MOF accessibility via modulation of the shell layer is based on cyclodextrin binding to ABs that are accessible only on the surface. Complexation of the outer *E* AB units by cyclodextrin trapped a large dye molecule (rhodamine B) in the framework. Release was triggered by light-induced isomerization to the *Z* isomer, which leads to decomplexation of the cyclodextrin and thus the dye was able to diffuse out of the framework due to the absence of this mechanical “plug.”^[121]

Unlike AB, DAEs do not undergo large changes in free volume or polarity. However, the increase in flexibility from the closed to the open isomer allows for increased free rotation of chemical bonds within the photoswitch scaffold. The associated more subtle structural change can be exploited to regulate the pore volume of a MOF reversibly by transferring this enhanced flexibility to the framework, which allows for a 75% increase in CO₂ uptake.^[122] In addition to this change in flexibility, DAEs offer electronic control over the linker and resulting MOF. Incorporation of a DAE bearing pyridine groups attached to the end of each thiophene ring allowed for the synthesis of a two-component zinc-paddlewheel MOF with a carboxylic acid functionalized porphyrin oriented toward the other axis.^[123] The

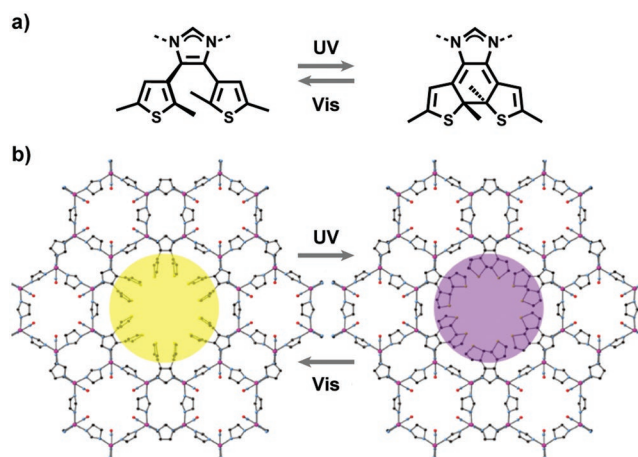


Figure 23. MOF with photoswitchable pores based on linkers integrated in the DAE core. a) Chemical structure of an imidazole-functionalized DAE in its open and closed isomer. b) Illustration of reversible light-driven pore modulation within the MOF framework. a,b) Adapted with permission.^[125] Copyright 2017, American Chemical Society.

reversible switching of the DAE from the open (high LUMO) to the closed (low LUMO) isomer gated the energy transfer of the porphyrin to the DAE linker in the framework, which resulted in the quenching of the porphyrin's fluorescence. A similar technique was used in a two-component MOF employing DAEs in combination with porphyrins.^[124] While the open DAE allows the porphyrin to generate singlet oxygen upon irradiation with visible light, an alternative energy transfer path leads to quenching of the porphyrin excitation in the presence of the closed DAE and consequently halts the production of singlet oxygen. This regulation of singlet oxygen generation could be used to control the oxidation of small molecules within the framework with light. Instead of integrating DAEs via the terminal aryl moieties, the DAE core can be replaced by an imidazole ligand, which serves as a ditopic linker (Figure 23).^[125] This approach provides more versatility concerning the structural design of the DAE units since the aryl termini are appended and not interconnected to the MOF. Thus, the switching event is localized in the pores and not in the framework itself, avoiding potential light-induced defects in the MOF due to the mechanical stress upon photoisomerization. Light-driven modulation of pore size and local environment could be used to control the uptake of analyte/guest molecules.

6. Crystalline Photoswitchable Materials

Typically, and as discussed above, photoswitchable molecules are incorporated into a given material with other components. The reason for this obvious ignorance of neat crystals is presumably that for a long time, tight packing of photochromic molecules appeared detrimental and was believed to inhibit their photoswitching behavior. Truly pioneering work to disprove this myth and realize photoswitching even in the crystalline state^[126] has been carried out by the Irie group over the past two decades. In addition to demonstrate light-induced shape changes in crystals, the researchers also made rod-like

crystals perform mechanical work, as visualized in the reversible movement of a 3 mm steel ball.^[127] Moreover, by taking advantage of the growing expertise in the field of crystal engineering^[128,129] one can in principle orient and organize photochromic molecules along defined axes in their crystalline state and thereby gain precise control over their photophysics (excitation) and photochemistry (switching).

Due to the changes in the structure of a DAE between the open and closed isomer, different motions can be achieved based on their packing within the crystal beyond simple elongation along one axis. By breaking the molecular symmetry of DAEs, the symmetry of the crystal is altered in a way that light irradiation no longer produces extension/contraction in one direction but can cause reversible twisting motion in either a left- or right-handed direction based on the crystal face that is exposed to light.^[130] Long-range curling can also be achieved with a nonclassical dimethyl-2(3-(anthracen-9-yl)allylidene)malonate (DMAAM) photoswitch, in which a double bond adjacent to the anthracene moiety undergoes reversible *E*↔*Z* isomerization upon illumination with visible light (Figure 24).^[131] This constant motion results in a remarkable shrinkage, as demonstrated by ≈50 μm long crystal needles that curl into small bundles of less than a tenth of their original dimension. Red-shifting the crystals' absorption could be achieved by substituting the two ester with two cyano groups affording selective curling with green light and uncurling with UV light.^[132]

Beyond single crystals of one and the same DAE photoswitch, cocrystallization of two different DAE derivatives can be used as an advantageous approach to engineer different motions in crystals. By cocrystallizing DAEs bearing thiazole rings with DAEs carrying thiophene rings, three types of motion could be achieved (Figure 25).^[133] First a bending motion was realized through ring-closing the bulk photoswitch population since there was no separation of absorption bands

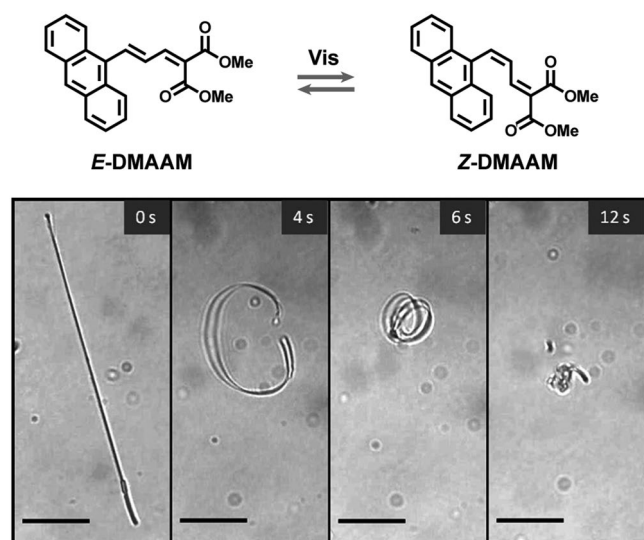


Figure 24. Light-driven reversible contraction of crystalline rods. Rods of crystalline *E*-DMAAM undergo rapid contraction upon irradiation with visible light due to the cycling of the molecules back and forth from *E* to *Z* (the black scale bar is 10 μm). A similar effect can also be attained through crystallization of pure *Z*-DMAAM. Adapted with permission.^[131] Copyright 2013, Wiley-VCH.

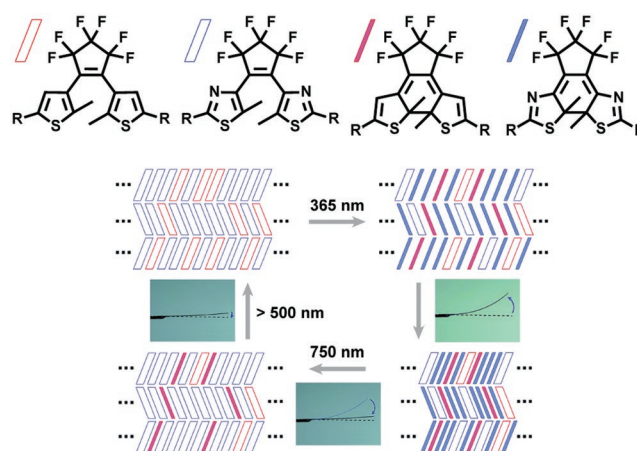


Figure 25. Light-controlled macroscopic motion of two co-crystallized DAEs. A cycle begins with the ring-closure of all open isomers with UV light, after which the thiophene DAEs are selectively ring-opened with 750 nm light followed by the ring-opening of the thiazole DAEs with 500 nm light. Adapted with permission.^[133] Copyright 2015, Royal Society of Chemistry.

and hence no selective excitation of only one of the two photochromic molecules. Subsequently, the two closed isomers could, however, selectively be opened due to their different absorption spectra, which led to the stepwise recovery of the original shape. Locking the crystal through the introduction of supramolecular hydrogen-bonding urethane motifs causes mechanical stress to build-up upon UV light irradiation that results in the crystals “exploding” after accumulating enough stress.^[134] This rare phenomenon, termed the “photosalient effect,”^[135] could also be shown in the case of remarkable hollow-shaped crystals of a DAE with the classical perfluorocyclohexene bridge, while single-wall crystals of the same molecule experienced photoinduced bending.^[136,137] The intensity^[138] as well as the direction of incident light affect the resulting motion, for example, stepwise irradiation triggered delayed motion in certain DAE crystals,^[139] whereas irradiating a crystal with two different wavelengths of UV light triggered the crystal to move in two different directions. This surprising observation was rationalized by a difference in the depth of light penetration, which resulted in isomerization at different depths of the crystal and diverse manifestation of the thus generated local stress.^[140]

The free-volume change between the two isomers of a DAE is not very pronounced, which was an initial rationalization for photomotion being possible in these crystals. As a consequence of this assumption, the large free-volume change required in crystalline AB was thought to preclude motion, however, the first motion of dimethylamino-AB thin plate-like crystals was indeed only observed one decade ago.^[141] Since then, many examples have been discovered of either *E* or *Z* AB crystals or cocrystals exhibiting motion. The motion was shown to be relatively general among many different ABs, with push-pull derivatives having a faster shape recovery due to the low thermal half-life of these dyes.^[142] The use of *ortho*-fluorinated ABs with long thermal half-lives^[90,91] allowed for obtaining crystals of the pure *Z* isomer, which upon irradiation could move (while retaining crystallinity)^[126] irreversibly away from the

visible light source.^[143] Appending chiral groups on the AB photoswitches affect the behavior of their crystals upon light irradiation. A curling motion with a longer thermal half-life was observed for crystals composed of the pure enantiomer as opposed to crystals of the racemate.^[144]

Halogen-substituted *Z* configured ABs, cocrystallized with pyridyl spacers, formed crystals that could bend dramatically when exposed to light. These were irradiated while acquiring a single-crystal X-ray diffraction pattern to show that the single-crystal to single-crystal transformation of *Z*→*E* cocrystals is mediated by an amorphous phase and hence requires sufficiently elevated temperatures to prevent the formation of an all-*E* amorphous material.^[145] The underlying principle, with which these crystals bend, has historically been explained by a bilayer model, where competing tensile and compressive forces on opposite sides of a crystal push into or out of the light. Naumov and co-workers have provided a new explanation for this phenomenon by studying the time-dependence of the motion of crystals from an AB dye (Disperse Red 1) in response to light. This model gives insight into the gradual evolution of the photoisomerization product in the crystal and the time-dependent changes within the material.^[146]

Moreover, the very assembly of crystals can be light-controlled based on changes in the crystal phase, such as melting of AB crystals. This crystal melting was observed by X-ray crystallography and is explained by the ordered π - π interactions that are present in the *E* configuration but not retained in the *Z* isomer.^[147] A similar phenomenon could be induced in ionic crystals of AB, where the *E* isomer remained crystalline and the *Z* isomer melted. This light-induced melting caused an increase of the ionic conductivity by two orders of magnitude in the liquid state.^[148] Upon thermally induced crystallization to the *E* isomer energy in form of heat (97.1 kJ mol⁻¹) is released, which is almost twice the conformational energy difference between the *E* and *Z* isomers (50 kJ mol⁻¹) and provides a possible path to thermal energy storage. By setting the ambient temperature below, above, or near the melting temperature of the *Z* isomer of an AB crystal, multidirectional deformations could be achieved as the light-induced change in volume within the crystal significantly depends on the aggregation state of both isomers.^[149] Besides, photochromic molecules theoretically have more than one crystallization pattern based on the isomer of the photoswitchable moieties. The Credi group synthesized a star-shaped AB tetramer, which shows a highly symmetric arrangement in the crystal structure of the all-*E* isomer. Interestingly, due to the molecular order and rigidity of the all-*E* isomer a microporous crystalline material is obtained that provides on the one hand sufficient space for a high photoisomerization efficiency in the solid state and on the other hand can be utilized for the capture of CO₂ from the gas phase.^[150] Crystallinity, porosity, as well as gas uptake can reversibly be tuned by the *E*→*Z* photoisomerization, which in combination with its synthetic accessibility make this material potentially interesting for technological applications.

Moreover, light-induced crystalline motion can be employed to control charge transport, thereby transforming an optical signal into an electronic signal via mechanical transduction. Specifically, the coating of 14 μ m thin DAE crystals with a layer of gold allowed for the retention of the crystals' bending

ability and gave rise to highly reversible ON/OFF switching of an electric circuit by making and breaking contact between the two ends of a circuit.^[151] Beyond mechanical switching of electronic circuitry, light-triggered motion can also be used to construct mechanical microtools. For example, AB trimers could be grown into crystalline nanopillars, which display light-driven reversible motion.^[152] Key structural element was the C₃-symmetric structure of the AB and the 1.7 μ m displacement omnidirectional based on the direction of incoming light. Since these microdevices can be simply printed, micro-tweezers could be constructed that are capable of handling 4 μ m small polystyrene microspheres.

Finally, single crystals can truly translocate, i.e., move, by light. The Norikane group demonstrated that single crystals of 3,3'-dimethylazobenzene (DMAB) can crawl toward visible light (inducing *Z*→*E* isomerization) and away from UV light (inducing reverse isomerization) due to the lengthening of the crystal in the direction of the visible light and a shrinking of the crystal by UV light (Figure 26).^[153] Over the course of 20 min, crystals hundreds of microns in size could be moved laterally with directionality on a scale of their own size while retaining the direction of crystal orientation. The shape of the crystals does collapse, however, through the light-driven reorganization of the structure. A similarly simple 4-methoxyazobenzene could be moved as it floated on water based on the orientation of blue light.^[154] The irradiated face of the crystal isomerized to the *Z* configuration, which was then able to dissolve in the water owing to its generally higher dipole moment. The subsequent movement of the crystal with a velocity of 1 cm s⁻¹ is presumably caused by propulsion based on the generated concentration gradient as the local concentration of the dissolved *Z* AB is high where the light is applied.

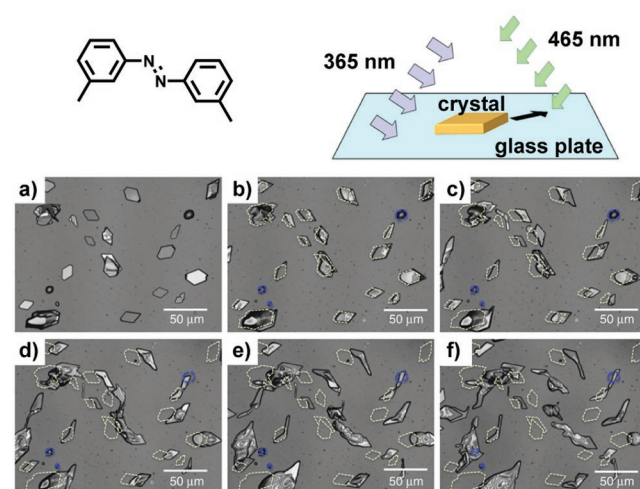


Figure 26. Phototaxis of single azobenzene crystals. The structure of *E* DMAB is shown in the top left, while the horizontal motion of a crystal on a surface in response to the two different light sources is illustrated in the top right. a–f) The optical microscopy images show the crystals of DMAB moving in a vertical direction following irradiation for 0, 3, 6, 10, 15, and 20 min. The dashed lines represent the initial positions and shapes of the crystals. a–f) Adapted under the terms of the CC-BY Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>).^[153] Copyright 2015, Springer Nature.

7. Conclusion and Outlook

The incorporation of photochromic molecules in materials can result in large-scale effects that are more than just simple color changes. The combination of judiciously chosen photo-switchable molecules and their integration into hierarchically structured materials can lead to remarkable and reversible control of their properties and functions. Herein, we have highlighted how properly designed photoswitches can modulate assembly, motion, charge transport, as well as the capture and release of guest molecules and analytes, to name only a few of the functions realized thus far. Due to the multidisciplinary approach that has proven successful in tackling these problems, tremendous advancement has been made in the past decade in understanding how one can design and exploit photoswitchable molecules and systems in the context of materials science. When trying to transduce molecular level switching events to macroscopic property changes, it is clear that considering the photoswitchable molecule alone is not sufficient, but the interactions between the switch and its environment are of utmost importance. These can effectively be tuned through chemical functionalization as illustrated by the influence of film morphology when incorporating DAEs in semiconductors and electronic devices thereof.^[9]

During the last decade the realm of possible tasks enabled by synthetically evolved photoswitches has significantly been expanded, opening the door to molecular motors now being able to operate in bulk polymers^[17] or on surfaces efficiently.^[54] Phenomena, which could have been considered detrimental to achieving good switching behavior, such as high optical density, can be overcome to provide unique motion in well-designed crystalline systems.^[133,143] Theoretical understanding, supported by recent experimental observations, helps explaining motion in crystals,^[146] progress which may lead to future applications for these intriguing materials. Likewise, knowledge about the relaxation pathways of photoexcited molecules has been critical in designing materials, where these molecules reside much closer to each other,^[35] as well as various surfaces and interfaces.^[34] This has been exploited to induce wonderful effects, such as optical modulation of photoemission^[63,123] or singlet-oxygen generation.^[57,124] Last but not least, on the road to mimicking biology, amplifying the motion and work done by a single photoswitchable entity has remained a central topic.^[50,74] While nonlinear responses are common in the natural world, they are far from general in synthetic materials but have great potential to maximize the efficiency of light-driven molecular systems in optomechanics and beyond. In this context, the design of materials being able to amplify optical switching events has continued to evolve and contribute to boosting the sensitivity of analytical detection systems.

The field of molecular photochromism has matured tremendously over the past decades and nowadays there is a solid basis of fundamental understanding with regard to the design on the molecular level. While this knowledge is often scattered and some of it has been forgotten, the switching behavior of new derivatives in established families of photoswitches has become predictable and can in part be rationally designed, also in the context of material science applications.^[155] There is still plenty

of room and need for improvement. Important performance parameter of molecular photoswitches to be optimized include photoefficiency (quantum yields and composition of photostationary states) upon irradiation with convenient and benign light sources (visible and NIR excitation) as well as (photo)chemical and thermal stability. However, ample progress has been made along this line in recent years—also in our group—and thus we foresee future challenges primarily in the integration of such optimized photoswitches in sophisticated materials that have unique properties and allow for new functions.

Throughout this review it has become apparent that increasing system complexity leads to challenging analytical problems yet offers the prospect of discovering new phenomena. Systems containing multiple switches are of increasing interest,^[156] as they provide access to complex scenarios and materials with more than two (meta)stable states and allow one to “dose” a desired element independently.^[133] Coupling multiple switches and controlling their communication as well as providing chemical and optical feedback loops will impart self-regulation and external light-guided programming. This could lead to highly complex systems, which will start to mimic neural networks and functions. Based on these features, it should be possible to condition and train materials, provide means to read out their history, and optimize their performance in operandi. Moreover, diabatic photochemical processes at the heart of photochromism are perfectly suited to drive chemical systems out of equilibrium^[157] and realize dissipative systems and structures.^[158] From a practical perspective, more sophisticated photoswitches have provided new functions and handles to modify materials with light, yet present themselves as double-edged swords since the significant synthetic efforts involved may hamper translation from the lab to production and real-life applications. Thus, simplified motifs for switches^[159] or motors^[160] should be investigated as potentially more practical analogues of current complex synthetic molecules. But also “low-tech” applications in the context of enabling the developing world, for example, cheap diagnostics, should be explored.^[161,162] With this in mind, we should critically remind the field that at this point in time, the only massively commercially successful application of photoswitchable materials has been photochromic lenses for adaptive sunglasses. We are, however, absolutely convinced that with continued crossdisciplinary efforts and creativity molecular photoswitches will advance to become a key ingredient of interactive materials and enable functions unimaginable today, yet crucial to our future.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

material science, photochemistry, photoswitches, responsive materials, smart devices

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