PROGRESS REPORT

Photoswitches: From Molecules to Materials

By *Maria-Melanie Russew* and *Stefan Hecht**

Small organic molecules, capable of undergoing efficient and reversible photochemical reactions to switch them between (at least) two (meta)stable isomers associated with markedly different properties, continue to impact the materials world. Such photoswitches are being implemented in a variety of materials for applications ranging from optical devices to "smart" polymers. All approaches exploit the photoswitching molecular entities as gates, which translate an incoming light stimulus to trigger macroscopic property changes of the materials. In this progress report, the most promising recent examples in this field are highlighted and put in perspective. Moving from supramolecular systems in solution to surfaces and finally to bulk materials, important design concepts are discussed, emphasizing both the challenges as well as the great promise of such truly advanced materials.

1. Introduction

The phenomenon of photochromism is well-known, the first examples surfacing in the second half of the 19th century when, in 1867, Fritzsche discovered the bleaching of an orange colored tetracene solution in daylight that then re-colored at night.[1] Since then, compounds changing their color under the influence of daylight have occasionally been reported. However, the general interest was modest until, during the 1950s, comprehensive mechanistic and synthetic studies were carried out, in particular by the research groups of Hirshberg and Fischer.[2] The research field experienced a real boom in the 1980s when the problem of photodegradation was overcome by the development of fatigue-resistant spirooxazines and diarylethenes. Nowadays, scientists have realized that photochromes can do more than color sunglasses, which was one of their earliest applications; they grant access to optical switches and memories and to variable electrical currents, and therefore meet the requirements for today's surge to design an all-optical computer. Furthermore, the incorporation of photoswitches offers the fabrication of photoresponsive polymers and other materials with macroscopic properties that can be externally manipulated by light. Over the past decade the basic palette of available photoswitches has not expanded significantly and some of the most popular classes are shown in **Figure 1**.[3]

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Here, we wish to highlight noticeable achievements over the past three years in the field of exploiting photochromes for the design of advanced materials. This progress report does not claim to be all-encompassing but rather we point to important developments by selecting a few examples from different research areas and putting them into perspective.

2. Switchable Supramolecular Systems in Solution

The relentless miniaturization has potential applications in many different fields such as medicine, energy generation, transportation, and storage, as well as information technology. The rapid development of the latter and the growing demand for high-capacity computers inevitably leads to decreasing sizes of the single components. The existing technologies of "top-down" approaches, using photolithographic and related techniques, have almost reached their inherent limit, as dictated by the operating wavelength.[4] In addition, silicon's band structure will disappear as soon as the silicon layers are reduced to a few atoms thickness. A way out was already foreseen half a century ago by Feynman in his famous lecture "Plenty of room at the bottom",[5] advocating an alternative "bottom-up" approach followed by synthetic chemists working naturally at the bottom. Individual molecules can be used as a model kit for the construction of nanoscopic structures and even machines with the ultimate goal of carrying out complex functions.[6] In this context, Balzani provided a useful definition of a nanomachine as an "assembly of a discrete number of molecular components ... designed to perform specific mechanical movements as the consequence of external stimuli".[7] A great variety of motors, rotors, scissors, elevators, shuttles among others have been synthesized that respond to different external triggers, such as temperature, pH, or electric fields.[8] Arguably, light represents the most advantageous stimulus as it is ubiquitous, does not produce any waste products as compared to chemical "fuels", and offers a very high spatial and temporal resolution, allowing for true remote control. A nanotechnology-based industry powered by light could be independent from conventional energy sources, since future energy supply will be one of the major problems for human civilization. Today's switches exhibit an ultrafast, clean, and highly reversible photochemistry providing sufficient fatigue resistance for technical application but also rendering these systems environmentally friendly.

However, the development of photon-fueled systems is an arduous scientific adventure since even Nature itself knows only

rare examples for the *direct* conversion of light into mechanical motion; one is the rhodopsin retinal protein complex that triggers visual perception via photoisomerization. Nevertheless, Nature accommodates the observing scientist with valuable tricks concerning supramolecular architecture and inspires the design of artificial molecular machines. DNA is undoubtedly the most exciting biomolecule for nanotechnology[9] and it has been utilized for many devices resembling machine-like functions, such as tweezers,[10] walkers,[11] and gears.[12,13] Most of these systems use oligonucleotides as fuel but recently Liang et al. reported fully light-driven molecular tweezers based on photoswitchable DNA hybridization (**Figure 2**).[14]

By covalently attaching azobenzene moieties onto DNA strands it was possible to use photons as a trigger for hybridization. The planar *E*-azobenzene intercalated into the duplex DNA structure favored by stacking interactions with the adjacent base pairs. Upon irradiation the photogenerated nonplanar *Z*-isomer significantly decreased duplex stability due to steric hindrance (ΔT_m = 24 K). The light-driven DNA machine, based on the design of the DNA-fueled tweezers reported by Yurke et al.,[10] was composed of four DNA strands. Strand **A** hybridized with strand **B** and **C** to form two double-stranded arms, which are sufficiently stable. When the overhangs of strands **B** and **C** hybridized with the azobenzene-containing strand **F** the tweezers closed. After irradiations with UV light causing the *E/Z*-photoisomerization of the azobenzene fragments, strand **F** dissociated from the complex and the tweezers opened again. Note that the DNA tweezers have to be operated above the melting temperature of the *Z*-azobenzene containing duplex (T_m = 35 °C). This behavior was monitored using FRET (Förster resonance energy transfer) between the fluorescein donor and the rhodamine acceptor located at the 5' and 3' ends of strand **A**, respectively. The cycling was carried out ten times without decreasing efficiency. This work presents a simple light-driven nanomachine operating continuously by reversible photoswitching of the azobenzene molecules within the DNA strand.
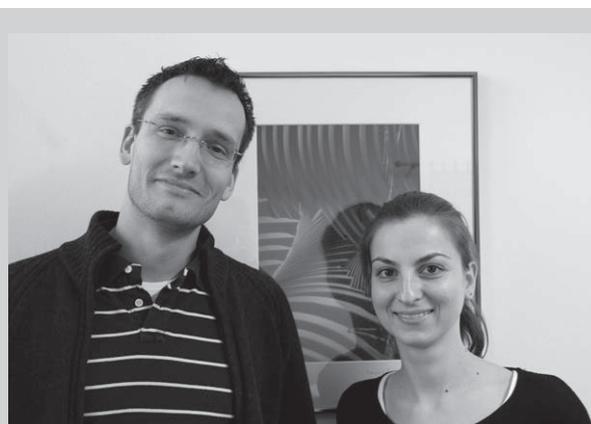
Maria-Melanie Russew (1985) was born and grew up in Berlin (Germany), where she studied chemistry at Humboldt University (2004–2009) to obtain her Diploma working on the synthesis of azobenzene containing click-amers. She is currently carrying out her doctoral studies in the group of Prof. Stefan Hecht at Humboldt University directed towards the design of photoswitchable macromolecules and their assemblies.

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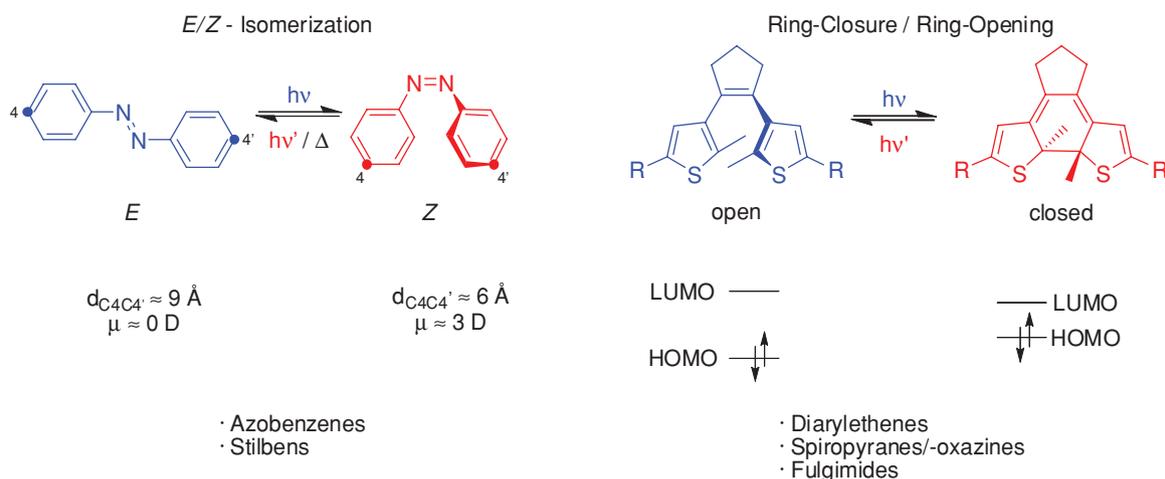
Figure 1. Photochromic molecules: Switching between two independently addressable states leads to reversible structural and electronic changes (e.g., geometry, dipole moments, π-conjugation, HOMO-LUMO gap, redox potential) on the molecular level that affect macroscopic properties (shape, aggregation behavior, conductance etc.) of the resulting materials containing these photoswitches.

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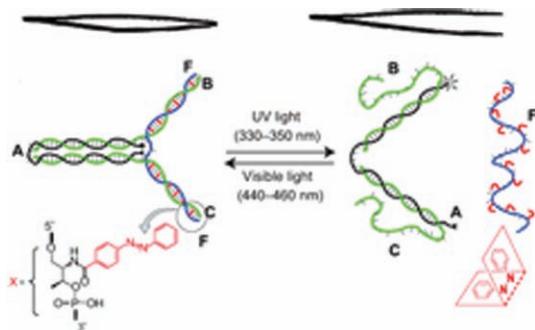
Figure 2. Photoswitchable nano-tweezers: Hybridization of the azobenzene-containing strand **F** with overhanging single stranded termini of strands **B** and **C** leads to the closed state of the tweezers, while opening occurs after irradiation with UV light due to steric hindrance of the non-planar Z-azobenzene and the adjacent base pairs. The switching events are monitored by FRET between fluorescein and rhodamine donor and acceptor dyes at the termini of strand **A**. Reproduced from.[14]
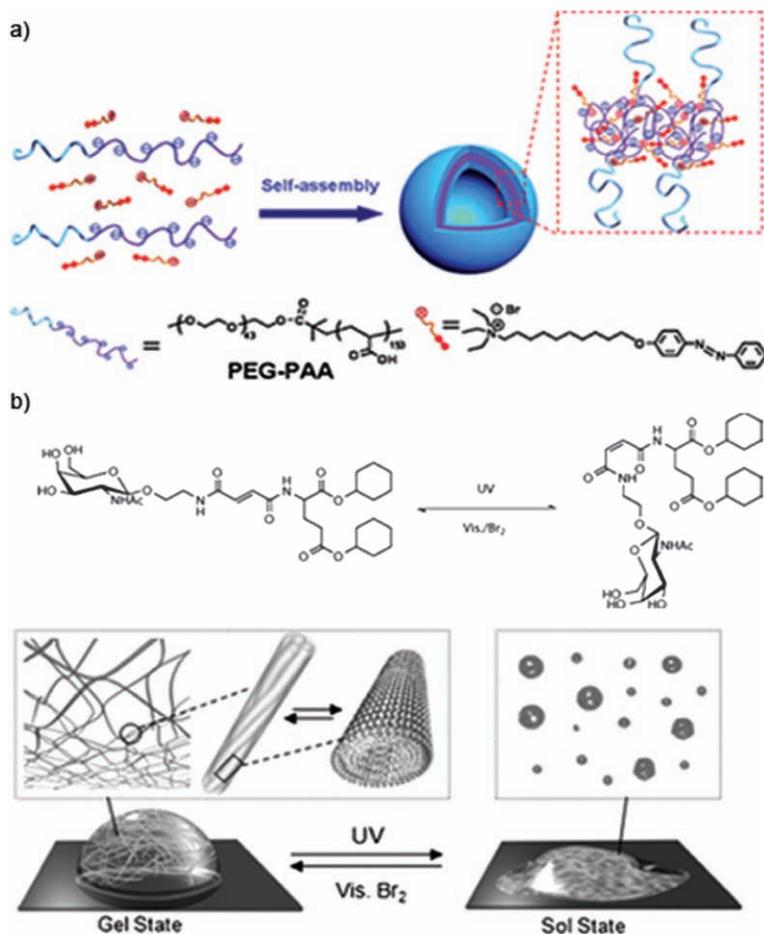
Figure 3. Photocontrolling self-assembly and self-organization: a) Vesicles formed from doubly hydrophilic (non-ionic/anionic) diblock copolymers via complexation of oppositely charged photochromic azobenzene-based surfactants. UV irradiation leads to disassembly of the vesicles presumably due to weakened π,π-stacking interactions.[15] b) Hierarchical self-assembly of small gelator molecules into fibers is suppressed by switching the extended fumaric diamide unit into its corresponding bent maleic diamide, leading to reduced hydrogen bonding and hence to a collapse of the fibrous network of the gel state. Recovery of the gel state was possible by irradiation with visible light in the presence of bromine. Reproduced from.[16] (a) was in part reproduced from ref.[15].

To achieve complex functions, molecular machines themselves are not sufficient; their compartmentalization and transport has to be accomplished as well. In this context, photoresponsive delivery vehicles represent attractive targets. Photocontrolled self-assembly and disassembly of vesicles was achieved with block ionomer complexes.[15] Double-hydrophilic diblock copolymers containing an ionic polyacrylic acid (PAA) block and a charge-neutral poly(ethylene glycol) (PEG) segment could form vesicles in water through complexation with oppositely charged azobenzene-containing surfactants (**Figure 3a**). By adjusting the ratio of azobenzene-containing quaternary ammonium ions to the carboxylate groups of the PAA block ($R_4N^+ : -CO_2^- = 0.5$) and careful choice of the concentration just above the critical micelle concentration, the system could be optimized to exhibit complete disassembly upon UV-irradiation. Generation of the Z-isomer seemed to destabilize the vesicle walls, presumably because of less-efficient packing interactions. This subtle effect was large enough to overcompensate the rather constant electrostatic forces (at the given conditions). The potential use of this system as a light-triggered delivery vehicle was demonstrated by encapsulation of a fluorescent pyrene dye, which could be released after UV-irradiationas shown by a combination of transmission electron microscopy (TEM) as well as confocal fluorescence microscopy.

The examples discussed above illustrate the benefit of incorporated photoswitches to control discrete supramolecular events in solution; however profiting from their capability to generate macroscopic effects, e.g. phase transitions etc., will only be possible if such sophisticated photoresponsive nanosystems can be organized to work in concert. For this purpose the supramolecular bottom-up approach can successfully be utilized not only to create discrete objects on the nanoscale but also to obtain nanofibers forming 3D networks of macroscopic hydrogels. The advantage of such a gel composed of low molecular weight gelators is that the stimulus-responsive unit can easily be incorporated. By varying substitution patterns and molecular geometry, the morphology, chirality, size of the aggregates, and therefore the macroscopic properties can readily be fine-tuned. This approach was successfully followed by Hamachi and coworkers for the photoinduced sol–gel transition of a glycolipid-based supramolecular hydrogel,[16] based on pioneering work by Žinić on fumaric amides as photoresponsive gelators.[17] The individual gelator molecules were composed of hydrophilic sugar head groups and two hydrophobic alkyl tails connected by a photoisomerizable fumaric diamide unit. Hydrogel formation occurred via hierarchical assembly into fibers based on hydrogen-bonding as well as hydrophobic interactions, yet only if the right combination of sugar head group, alkyl tail, and linkage was used. For further studies the GalNAc-cyclohexyl system was used as it forms transparent and rheologically stable hydrogels (Figure 3b). UV-irradiation caused a gel → sol transition if at least 50% of Z-content was generated. Instead of

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extended and entangled fibers, as observed in the gel state, the sol state consists of isolated spherical aggregates, as shown by transmission and scanning electron microscopies. Presumably the fumaric diamide based hydrogen-bonding network present in the gel got lost upon conversion to the maleic diamide. After irradiation of the fluid sol with visible light in the presence of small amounts of bromine the gel state was recovered. The authors showed that particles and molecules entrapped within the meshes of the hydrogel were released in the sol state.

Photoresponsive biocompatible gels could have significant potential in applications in modern medicine but also as sensors and controllable membranes for separations. In contrast to these biomedical functions the beneficial use of state-of-the-art photoswitchable molecules in electronic applications necessitates their connection to flat surfaces and hence careful interfacial engineering.

3. Switch-Assemblies on Surfaces

Surfaces that respond to external stimuli, so-called "smart" surfaces, have considerable potential for controlling phenomena, such as wetting and dewetting, (bio)adhesion, and catalysis, among others. The preparation of such functional surfaces is challenging and requires the delicate interfacing of molecular organic components with the surface layer(s) of inorganic materials. In general, metallic surfaces have received most of the attention, on the one hand because of the well-developed strategies to anchor S-based (thiols, disulfides, etc.) or N-based (amines, pyridines, etc.) moieties to noble metals, in particular gold, and on the other hand because scanning tunneling microscopy (STM), allowing for detailed characterization of the formed self-assembled monolayers (SAMs), necessitates a conducting substrate. After successful – and by no means trivial – immobilization using either physi- or chemisorption approaches, it often proves difficult to retain the molecular properties known from solution.[18] This capricious behavior originates from the close packing of the molecules on the surface, generating steric constraints for chemical reactivity, and/or electronic coupling between the adsorbate molecules and the substrate, leading to quenching of molecular excitations. Both of these factors are decisive for the two complementary approaches followed thus far, involving photoswitch assemblies either physisorbed in a planar adsorption geometry or chemisorbed in a vertical arrangement. While the latter approach clearly benefits from its practicality, the first one provides detailed insight into switching behavior of individual molecules by local probing techniques under controlled conditions (ultrahigh vacuum, low temperatures).

The behavior of azobenzene and its derivatives physisorbed in planar adsorption geometry on noble metal surfaces has been investigated by several groups[19] including our own in collaboration with the Grill and Tegeder groups.[20] Initial work focused on demonstrating the successful switching reaction on a metal surface.[20a] For this purpose 3,3′,5,5′-tetra-tert-butylazobenzene (TBA) was synthesized and its switching behavior was studied on various substrates (**Figure 4**).[20a,e] It turned out that both the high degree of tert-butyl substitution as well as the choice of the underlying substrate play a

crucial role to realize a reversible switching process on the surface. While molecules with fewer tert-butyl groups as compared to TBA could not be switched due to their strong electronic coupling even to a Au(111) surface,[19c] TBA molecules switched on Au(111) only and changing the surface to a more reactive Cu(111) or another gold surface, i.e. Au(100), shuts down isomerization.[20e] The tert-butyl groups furthermore served as labels to facilitate unequivocal assignment of the E- and Z-configurations.

It should be noted that on the surface several reactivity modes exist depending on the stimulus used and the respective operating mechanism. It turned out that reversible E/Z isomerization could be induced directly with the STM tip[20a,e] or by irradiation,[19c,20c,d] however, the latter did not allow shifting of the composition of the photostationary state back to high E-isomer contents. Upon thermal activation only the reverse $Z \rightarrow E$ isomerization took place, as expected but significantly accelerated.[20d] In the case of irradiation, detailed spectroscopic studies suggested charge transfer between the TBA molecules and the gold surface to be responsible for isomerization. In the case of STM-tip induced isomerization, two mechanisms operate depending on the tip-sample distance. While at close distances isomerization proceeded via resonant tunneling into the LUMO,[20e] at medium and even very large tip-sample distances of several nanometers isomerization events could be induced by the electric field in the vicinity of the tip.[20a] The latter mechanism provides the unique opportunity to induce switching over large areas without the need to locally address each individual TBA molecule.

While the switching in an island of TBA occurred randomly (Figure 4b), subtle modification of the molecule by introduction of a single methoxy group led to a markedly different and certainly unique behavior. The 4-methoxy-3,3′,5,5′-tetra-tert-butylazobenzene (MTBA) molecule formed four different morphologies at the surface, from which two exhibited switching characteristics.[20g] While in one of them switching occurred mainly on the ridge of the herringbone reconstruction, presumably for steric reasons, the other one showed a periodic pattern of switching events (Figure 4c). It turned out that every third molecule in every second row switched, thereby defining a "switching lattice". This periodic pattern of successful switching events results from the commensurability of the two overlying lattices, i.e. the lattice of the Au(111) substrate and the lattice of the 2D crystal formed by the MTBA molecules. As the Z-isomers exhibit an increased dipole, they could successfully be removed from the surface, leaving holes at defined positions. In general, the observation and rationalization of this locally defined switching points to a phenomenon, which should enable the precise patterning of surfaces on the scale of few nanometers.

The study of physisorbed molecular switches in planar adsorption geometry provides detailed mechanistic insights into switching processes at surfaces; however, the practical use of such surfaces is rather limited and from an applied standpoint, vertically oriented molecular switches in more robust chemisorbed SAMs promise much more potential for the creation of photoswitchable surfaces. In the context of these photoswitchable surfaces, it is typically observed that densely packed SAMs composed of planar and extended E-azobenzene derivatives
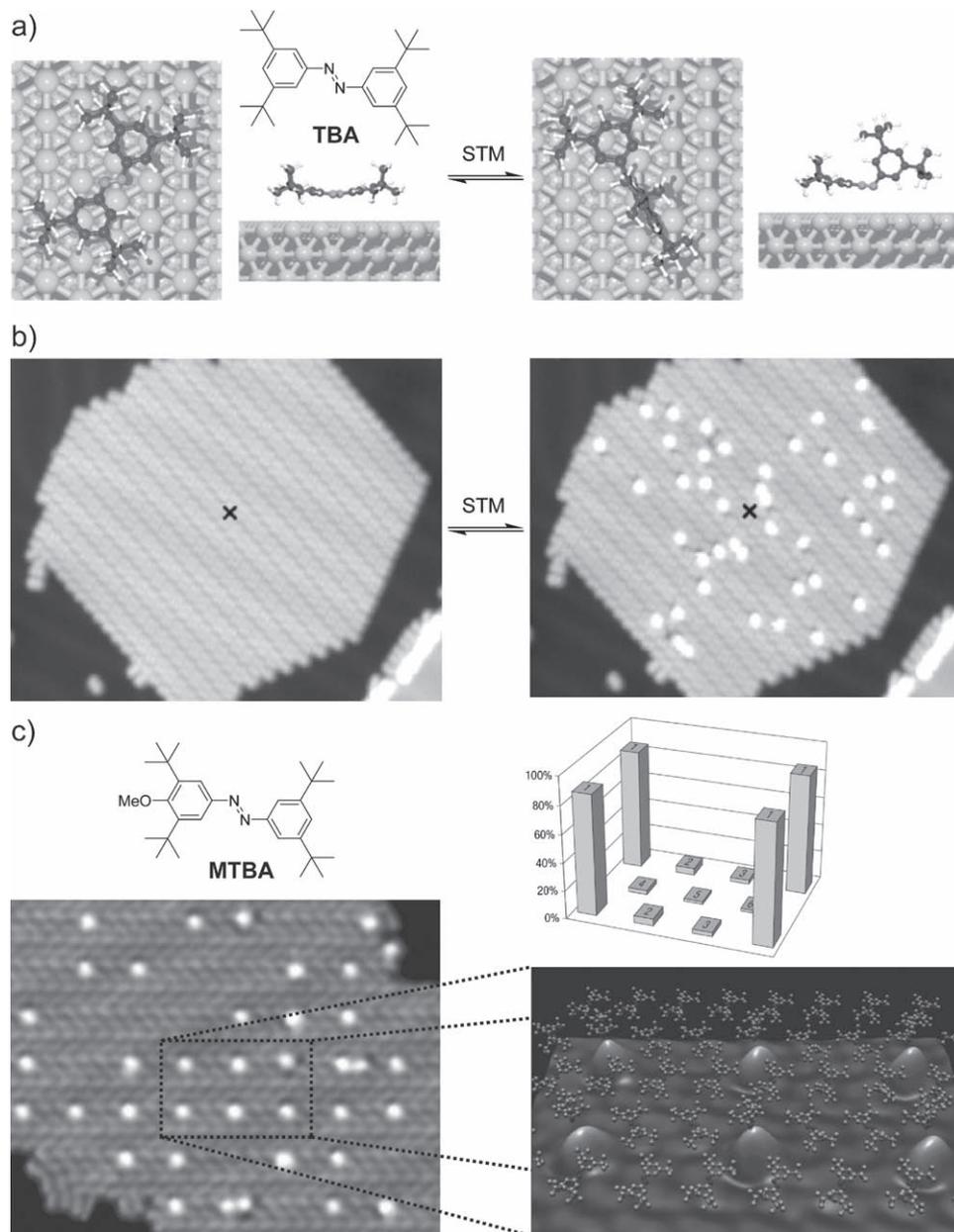
Figure 4. Photoswitching azobenzene derivatives physisorbed in planar adsorption geometries on Au(111): a) TBA and MTBA can reversibly be switched between the flat *E*-isomer (left) and the partially upstanding *Z*-isomer (right), associated with bright protrusions in the STM images (b,c).[20e] While for TBA isomerization occurs randomly in the molecular assembly (b),[20a] in the case of MTBA in one specific arrangement switching occurs at spatially defined locations, defining a "switching lattice" (c).[20g] Figure 4a,b were in part reproduced from ref.[20a] and.[20e]

chemisorbed in vertically adsorption geometry lack the free volume necessary for isomerization to the corresponding non-planar, kinked *Z*-isomer.[18] In addition, direct contact of the photochromic moiety with the metal surface must be avoided because it leads to inhibition of the desired switching function due to electronic coupling.[21] Since SAMs from flexible alkylthiols exposing azobenzene headgroups show only poor photoswitching ability,[22] Mayor, Samori, and coworkers designed a rigid azobenzene exposing a thiol anchoring group for the purpose of chemisorption on a Au(111) surface. SAMs composed of one very particular biphenyl-based azobenzene

derivative (**Figure 5**) underwent a collective isomerization upon light irradiation as observed by STM leading to a unique and practically quantitative switching process at the surface.[23] These SAMs were investigated in a metal-molecule-metal junction to measure local current-voltage characteristics by conducting atomic force microscopy (AFM).[24] Photoswitching led to markedly different *I-V* curves and statistical analysis showed a 30–fold decrease in resistance of the *Z*-azobenzene-SAM as compared to the *E*-azobenzene-SAM. The increased junction conductance of the *Z*-azobenzene-SAM was correlated with the decreased molecular length leading to more efficient tunneling
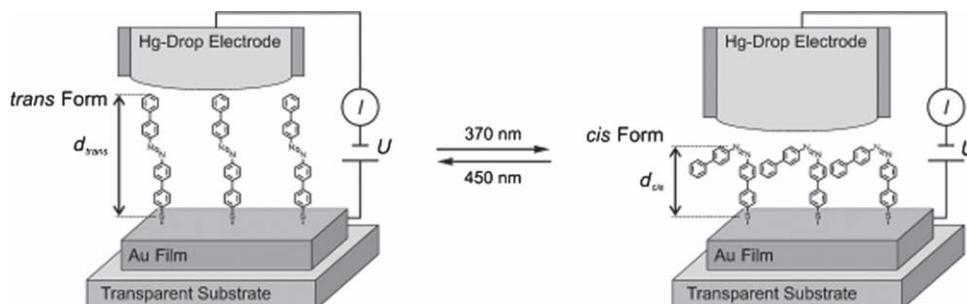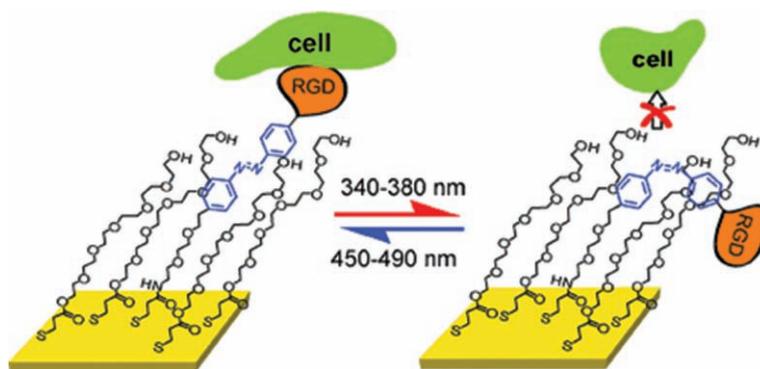
Figure 5. Photoswitching vertically oriented, self-assembled azobenzene monolayers in an electrical metal-molecule-metal junction: Switching the entire monolayer of an extended azobenzene thiol derivative on Au(111) covered by a Hg drop electrode leads to changes in the *I-V* characteristics of the junction due to changing the tunneling distance between the electrodes, which is also associated with mechanical work, i.e. lifting of the Hg drop upon $Z \rightarrow E$ photoisomerization. Reproduced from.[25]

processes. In subsequent work, the authors exploited the significant thickness changes of the SAM, incorporated in a junction between a transparent Au surface and a Hg drop electrode, to convert light energy into mechanical work using their so called "cargo lifter".[25] By following the *I-V* characteristics, it could be shown that photoinduced $Z \rightarrow E$ isomerization indeed led to an expansion of the SAM by approximately 7 Å. This collective motion translates into an individual contribution of 2.6×10^{-14} N for each molecule within the SAM, significantly less than the value measured by Gaub and coworkers using single molecule force experiments.[26]

Despite this remarkably promising example, most of the SAMs incorporating photoswitches suffer from severe steric restriction and hence several alternative strategies to overcome this problem have been followed. A rather simple technique is the dilution of the functionalized thiols with "innocent" alkyl thiols.[27] However, in many cases either phase separation occurs or guest molecules are inserted only at defect sites in the host SAM matrix.[28] Alternatively, introduction of bulky substituents on the azobenzene core seems a more promising route to create the space necessary for the switching process. The Samori and Mayor groups demonstrated this approach by using *ortho*-methylated biphenyl-based azobenzene thiols for the SAMs showing almost no steric hindrance during the *E/Z*-isomerization as suggested by the practically identical *E:Z* ratios in the photostationary state when compared to the values observed in solution.[22] However, SAMs of the substituted molecules suffer from inhomogeneous packing as indicated by the limited resolution of the STM images at the liquid/solid interface and hence no long-range order, as in the case of the nonmethylated form, could be obtained. Complementary to these strategies, a structurally well-defined, functionalized surface can be expected when the functional groups are mounted on a rigid anchoring scaffold, such as a tripod[29] or a flat platform.[30] The latter approach has recently been exploited by Herges and co-workers, who developed the versatile triazatriangulenium (TATA) platform, which enables the positioning of functional entities on a Au(111) surface in well-defined relative distances and orientations.[30] Due to its threefold symmetry, the TATA framework formed hexagonally

ordered adlayers with a planar (flat) orientation relative to the Au(111) substrate. Using a rigid and linear alkyne spacer, functional molecules, such as azobenzene, can readily be attached to the center of the TATA platform leading to a strictly perpendicular alignment of these functionalities relative to the surface normal. Although this approach has great potential, the switching function of the TATA-supported azobenzene assemblies remains to be demonstrated.

While the simple blending of two different thiols suffers from segregation (see above), in some cases it offers arguably the most practical way to tune the properties of the resulting mixed SAMs. Shao, Jiang, and co-workers successfully utilized this strategy to prepare azobenzene functionalized gold surfaces, capable to control mammalian cell adhesion (**Figure 6**).[31] Dynamic control of cell adhesion is crucial for many biological applications, for example cell migration. Although several techniques have already been developed to adhere cells to surfaces and release them as a result of an external signal, most of the systems do not work reversibly. Starting from mixed SAMs of thiol-terminated oligo(ethylene glycol)s containing some azobenzene moieties with appended activated carboxylic acid functionalities, a short peptide containing the necessary tripeptide arginine-glycin-aspartate (RGD) sequence

**Figure 6.** Photocontrolling cell-adhesion: Mixed monolayers obtained by blending oligo(ethylene glycol) thiols with functional derivatives, carrying the arginine-glycine-aspartate (RGD) sequence attached to an azobenzene unit, enable cell adhesion in the *E*-form, which display the RGD sequence, while irradiation with UV light leads to largely reduced cell adhesion as the RGD sequence becomes less accessible. Reproduced from.[31]

was introduced on top of the monolayer. Irradiation led to successful interconversion between the azobenzene's *E*- and *Z*-isomer to either present or mask the peptide and therefore supporting or resisting cell adhesion, respectively. The efficiency of this process was highly dependent on the degree of azobenzene incorporation and it turned out that the best ratio of adhesion/adhesion-resistance was found with an amount of only 0.1% RGD-containing azobenzene. Interestingly, when increasing the amount of azobenzene to 1%, it was not possible to detach the cells after irradiation with UV light, possibly either due to the decreased abilty of the oligo(ethylene glycol) chains to mask the increased amount of RGD or due to an inefficient switching process.

Moving SAMs from flat substrates to the curved surfaces of the 3D world, they constitute an important part of inorganic nanoparticles (NPs), stabilizing them in their metastable high surface energy state by prohibiting agglomeration.

If the protective organic shell of such NPs could be rendered photoswitchable, one should be able to modulate interactions between these particles. Based on this assumption, the group of Grzybowski demonstrated the use of photochromic NPs to create re-writable and self-erasing imaging materials (**Figure 7**).[32] Whereas most of the publications to date dealing with rewritable media describe polymers (or hydrogels) to which the photochromic molecules are attached, the authors used ca. 5 nm Ag or Au NPs covered with mixed SAMs of dodecylamine and azobenzene-terminated thiols. The NPs containing the *E*-isomer show colors originating from surface plasmon resonance bands reminiscent of isolated NPs. Upon UV irradiation intense color changes were observed due to formation of much larger NP aggregates with diameters of ca. 150 nm. The authors proposed that aggregation was triggered by formation of the *Z*-isomer, mediating the NP assembly process through dipole-dipole interactions due to its increased dipole moment. To create rewritable paper these NPs were embedded in a flexible organogel of syndiotactic poly(methyl methacrylate) and injected between two preheated sheets of a flexible polymer. By irradiating through a photomask or by writing with a "light pen" the desired image or message appeared. The colors of the images can be adjusted by the irradiation dose and by the particular NPs used. While Au NPs gave rise to colors from red (non-aggregated) to blue (aggregated), Ag NPs showed yellow to violet coloration. Removal of the light source led to gradual disassembly, which could be accelerated by either visible light or heating, in line with photochemical and thermal $Z \rightarrow E$ isomerization, respectively. The rewriteable organogel could be used over 300 times without degradation of the NPs.
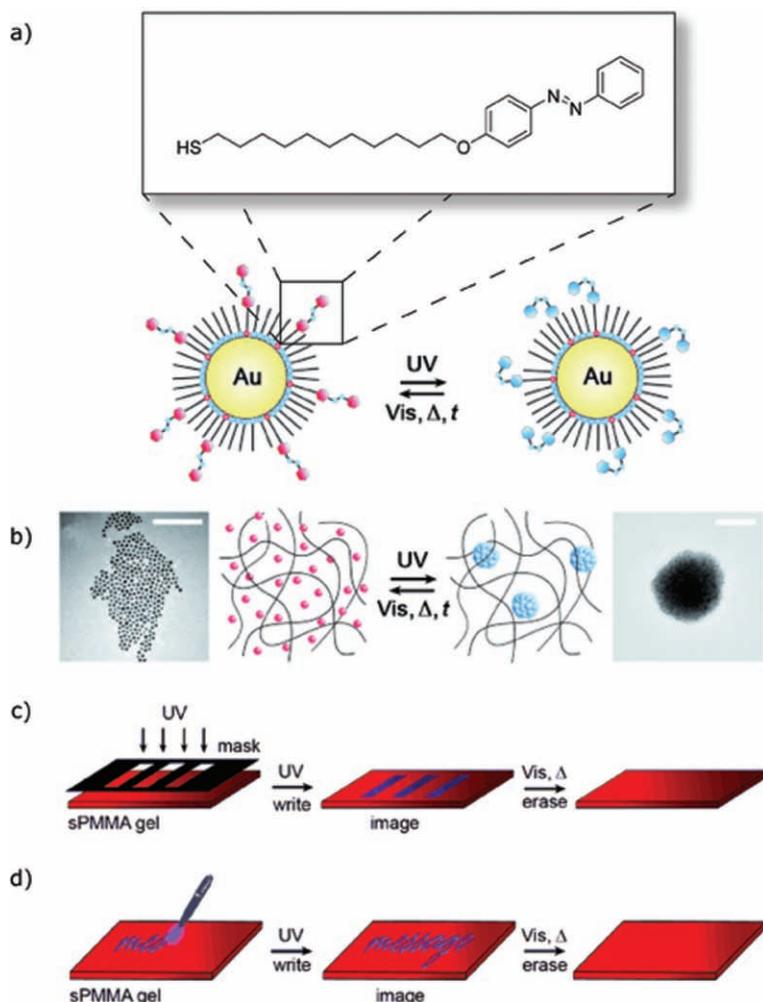
Figure 7. Photoswitching nanoparticle (NP) aggregation: a) Structure of the azobenzene-terminated thiol embedded in a dodecylamine SAM on noble metal NPs. b) UV irradiation triggers the assembly of the NPs to larger aggregates via increased dipole-dipole interactions. These aggregates display different colors as compared to the non-aggregated NPs. Exposure to visible light leads to the disassembly of the NP aggregates. Utilization of the system for temporal information storage using either masks (c) or a light beam (d) for the writing process.[32]

4. Photoresponsive Bulk Materials

Adjusting material properties to the influence and fluctuation of the environment has been and continues to be a demanding challenge. Rendering materials "smart" means they have to be equipped with a built-in ability to respond to subtle changes of the surroundings. The response at the molecular level is manifested in the modulation of macroscopic behavior, e.g. alteration of surface characteristics, objects' shapes, transparency, viscosity etc. A particularly appealing feature of these materials is their reversibility and hence the possibility for repetitive property changes. Potential applications obviously include reversible data storage and the design of sensors and actuators but also lie in the biomedical field. As pointed out above, light represents perhaps the most attractive external control stimulus; however, the field of light-responsive polymeric materials has developed much more slowly than the area of pH and temperature sensitive polymers. Nevertheless, a plethora of articles has been published dealing with the design and processing of light-responsive

polymers and liquid crystals, both being expected to play a pivotal role in future material science. A comprehensive monograph[33] has recently been published and reviews in detail the achievements accomplished until 2008; some of the latest highlights will (also) be presented here.

Naturally, pH and temperature dependence of gelation, especially in hydrogels, has been intensively under investigation since these materials are widely used for clinical purposes, e.g. for surgery and in contact lenses.[34] Due to the significant advantages of light as external stimulus, the interest grows steadily to develop light-responsive gels. In general, chemically cross-linked gels can exist in two distinct states: an expanded and a collapsed microstructure meaning that these materials exhibit a volume phase transition between a swollen and a shrunken form according to their solvent (water) content. These bistable characteristics of gels are attractive features for the design of biomimetic soft actuators or delivery systems.[35,36] But the slow response times of gels, an inherent characteristic of the macroscopic phase-transition phenomenon and (macro)molecular diffusions processes involved during the swelling/deswelling, prevented their technological application. By introduction of porosity into a gel, response times can be improved drastically – a concept that Takeoka and co-workers used to prepare a multicolor photochromic hydrogel with fast response to heat and light (**Figure 8**).[37] The porous structure was attained by free-radical polymerization of N-isopropylacrylamide (NIPAM) in the presence of the photochromic 4-acryloylaminoazobenzene and the cross-linker N,N-methylenebisacrylamide using a close-packed silica colloidal crystal (opal) template. Polymers composed of NIPAM are known to undergo dramatic changes in their hydrophilicity at elevated temperatures, i.e. above their lower critical solution temperature (LCST). The incorporation of azobenzene units into such polymeric network provided additional photosensitivity, thus resulting in two volume states at *one* temperature (below the LCST). Since the diffracted wavelength depends on the diameter of the colloidal particles of the silica template, the maximum of the reflected light shifted towards shorter wavelengths upon rising the temperature towards the LCST due to the decreasing lattice spacing of the shrinking network. The most fascinating property of this porous gel was its ability to adopt two arbitrary colors as a result of the *E/Z*-photoisomerization of the azobenzene moieties at a given temperature. Because the dipole moment of the two isomeric forms of azobenzene differs significantly (Figure 1), formation of Z-azobenzene led to an increased up-take of water and therefore the color of the irradiated parts changed. Hence, the color of the gel could be modulated using both thermal as well as optical stimuli but did not depend on the color of the photochrome.

In principle other photoswitches can be used as well, for example shown by Neckers and co-workers for a p(NIPAM) hydrogel with incorporated spironaphthoxazine switching units, leading to an increased water up-take after UV-irradiation. In this case, the blue coloration of the gel originates from the ring-opened isomer.[38]

Although hydrogels with photoresponsive units exhibit deformation when irradiated, they typically lack the stiffness required for the conversion of photonic energy into mechanical work or motion. This problem can be overcome with liquid crystalline elastomers (LCEs), which were conceptually proposed by de Gennes already in 1975 and first prepared by Finkelmann and co-workers in 1981.[39,40] These materials unite the flexibility, high corrosion resistance, and processability of polymers with several key advantages of liquid crystals (LCs), most notably: (i) the anisotropy of optical and dielectric properties as well as birefringence; (ii) the cooperative effects operating in the alignment process, and (iii) the alignment changes, which can be induced by external fields at surfaces and interfaces. Hence, LCs and LCEs offer superior platforms to amplify a "tiny" light stimulus into a "big" macroscopic event. From the viewpoint of clean photochemistry, ease of synthesis and incorporation, fast response times as well as favorable properties as mesogens, azobenzenes are the preferred photoswitches for integration into LCs and LCEs.

Conventional LCEs exhibit thermoelastic properties: upon transition from the nematic to the isotropic phase they contract along the alignment direction and upon cooling they expand. However, for some applications it is favorable to avoid heating and therefore photo-induced, isothermal phase transitions constitute an attractive alternative. Already a
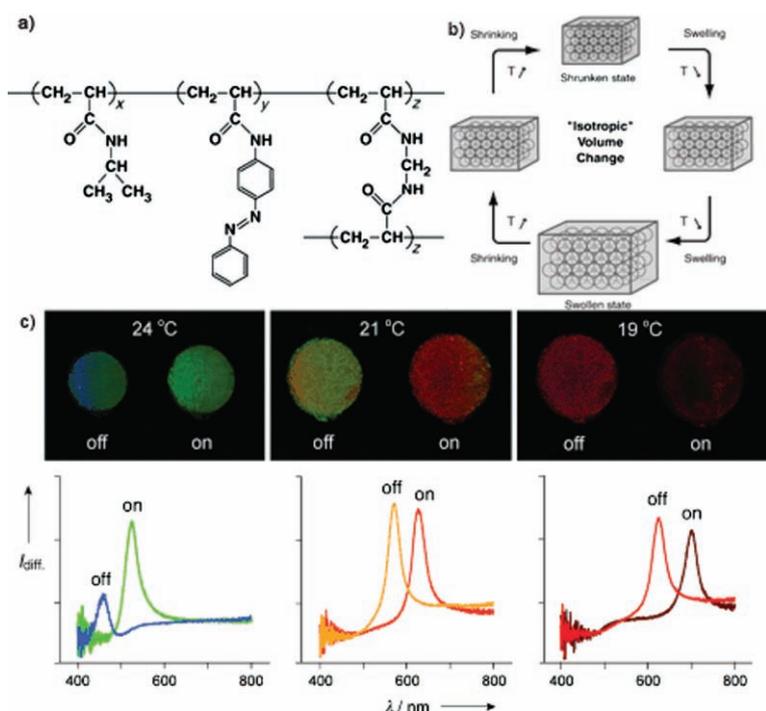
Figure 8. Photoswitchable porous hydrogels: a) Chemical structure of the hydrogel-forming statistical copolymer based on poly(N-isopropyl acrylamide) carrying photochromic azobenzene side chains. b) Swelling/deswelling behavior of the porous hydrogel dictated by temperature and light stimuli. c) The isotropic volume change induced by UV light causes a shift of the maximum reflected wavelengths and therefore, the hydrogel can adopt two arbitrary colors at one given temperature. Reproduced from.[37]
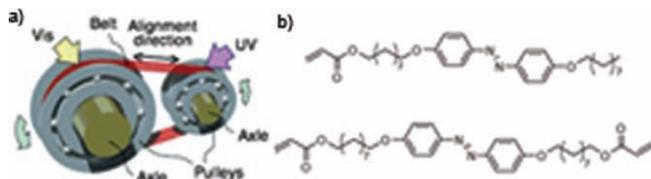
Figure 9. Photodriven rotary motion: a) Simultaneous irradiation of a pulley system, spanned by a laminated plastic belt with UV and visible light leads to overall rotation of the pulleys, as UV light causes contraction of the belt at one location (top right) while visible light induces expansion of the belt at another location (top left). b) Azobenzene-containing monomers used to prepare the photoactive LCE layer. Reproduced from.[42]

slight variation in the nematic order of the LC upon irradiation can cause a significant uniaxial deformation along the alignment direction of the mesogens. The resulting contraction, expansion, and bending motions of the material can be useful for the construction of artificial muscles or even hands.[41] In 2008, Ikeda and co-workers utilized the stretching and contraction of a main chain azobenzene LCE to realize a light-driven motor system.[42] They laminated their LCE layer on a low-density polyethylene film, which provided enough mechanical strength but also flexibility. The ends of this laminated film were connected and the resulting belt was placed over a home-made pulley system. The film was simultaneously irradiated with UV-light in one area and with visible light in another area, resulting in a rotational movement of the whole system (**Figure 9**). The mechanism involves contracting and expanding motions in opposing regions of the film. On the one hand, the E/Z-photoisomerization generated a local contraction force in the UV-irradiated parts of the belt, leading the right pulley to rotate counterclockwise. On the other hand, the parts, exposed to visible light, expanded and the resulting force acted on the left pulley, which started rotating counterclockwise as well. The rotational movement brought new, non-irradiated parts of the belt to be exposed to the UV as well as visible light, leading to continuous rotation. This impressive system converts light directly into mechanical work without the need for an intermediate energy carrier.

Besides rotatory motion, another challenge is photo-induced translational motion, for example for the movement of particles. Recently, Kurihara's group demonstrated the translational motion of polystyrene microspheres on a LC thin film doped with azobenzenes.[43] The particles were placed on the film and upon irradiation with UV-light the microspheres moved consistently towards the light source as monitored by a microscope. On the contrary, the particles moved away when irradiated with visible light. For the development of nanomachines and other devices for the conversion of photonic energy it is crucial that controlled motion can be sustained over a prolonged time.[44] The problem of decelerated movement, appearing when a certain amount of Z-isomer (or E-isomer) is produced, could be overcome by using an Ar$^+$ laser beam ($\lambda = 488$ nm). Both isomers absorb light at this wavelength, so $E \rightarrow Z$ as well as $Z \rightarrow E$ isomerization was simultaneously induced. By this means constant translational movement of the particles was realized without decrease of speed, whereas the

particles' direction could be controlled by simply changing the position of the irradiation source. The driving force of the motion is still uncertain but it was suggested to derive from the reorientation of the LC molecules caused by the isomerization of the azobenzene dopants.

A detailed study on the effects of different amounts of azobenzene incorporation on the LCs' properties was published recently by Tong and Zhao.[45] This study clearly showed a significant difference in the behavior of LCs doped either with high (> 18 %) or low (< 5 %) concentrations of azobenzene mesogen. In the regime of low azobenzene content the usual phase transition behavior for azobenzene doped LCs was observed. The achievable amount of Z-isomer under UV-irradiation was fully miscible with the used LC host and the photochemically induced disordering leads solely to a lower nematic-isotropic phase transition temperature. In strong contrast, high azobenzene contents give LCs, in which the photogenerated Z-isomer could exceed a critical concentration, triggering phase separation. Depending on the rate of Z-isomer formation, the phase separation followed the disordering process or appeared simultaneously. In both cases, the mixture evolved towards two LC phases and these processes could be reversed by simply irradiating the sample with visible light, which caused the reverse $Z \rightarrow E$ isomerization and hence restoration of a single nematic phase. This behavior could be utilized in an optical shutter because the transmittance changed dramatically during the photochemical processes and hence allows switching between reflective or transparent states by illumination.

By carefully tuning the concentration of the incorporated photoswitch, erasable and rewritable imaging is possible with cholesteric LC.[46] The photosensitizing azobenzene effected the selective reflection of the cholesteric LC films. UV-irradiation induced the phase transition to the isotropic state, then image recording was carried out by writing with a green or red laser beam, which restores the reflective, cholesteric state in the irradiated parts due to $E \rightarrow Z$ isomerization. Furthermore, this dynamic material showed wavelength specific interaction, which is important for the next generation all-optical applications.

In the LC field, azobenzenes are by far the most commonly used photochromic dopants. Nevertheless also spiropyrans and fulgides have been incorporated into LCs, yet the observed effects are smaller as compared to azobenzene.[47] As indicated throughout the article, azobenzenes are more applicable in some areas than diarylethenes or spiropyranes, and *vice versa*. On the one hand, whenever a large change in geometry (or dipole moment) is needed, azobenzenes are usually the molecules of choice and the same is true for inserting photoresponsiveness to LCs or LCEs due to the mesogenic features of many azobenzene derivatives. On the other hand, for applications in molecular electronics diarylethenes are undoubtedly the most popular scaffolds, as their open and closed isomers are associated with largely altered electronic properties, i.e. HOMO-LUMO levels and gap and hence absorption, emission as well as redox behavior.

The latter has been exploited recently by Meerholz and co-workers, who prepared a photoprogrammable organic light emitting diode (OLED).[48] For this purpose, they integrated a photochromic layer fabricated from a polymerizable 1,2-dithienylperfluorocyclopentene derivative (XDTE) to control hole transport

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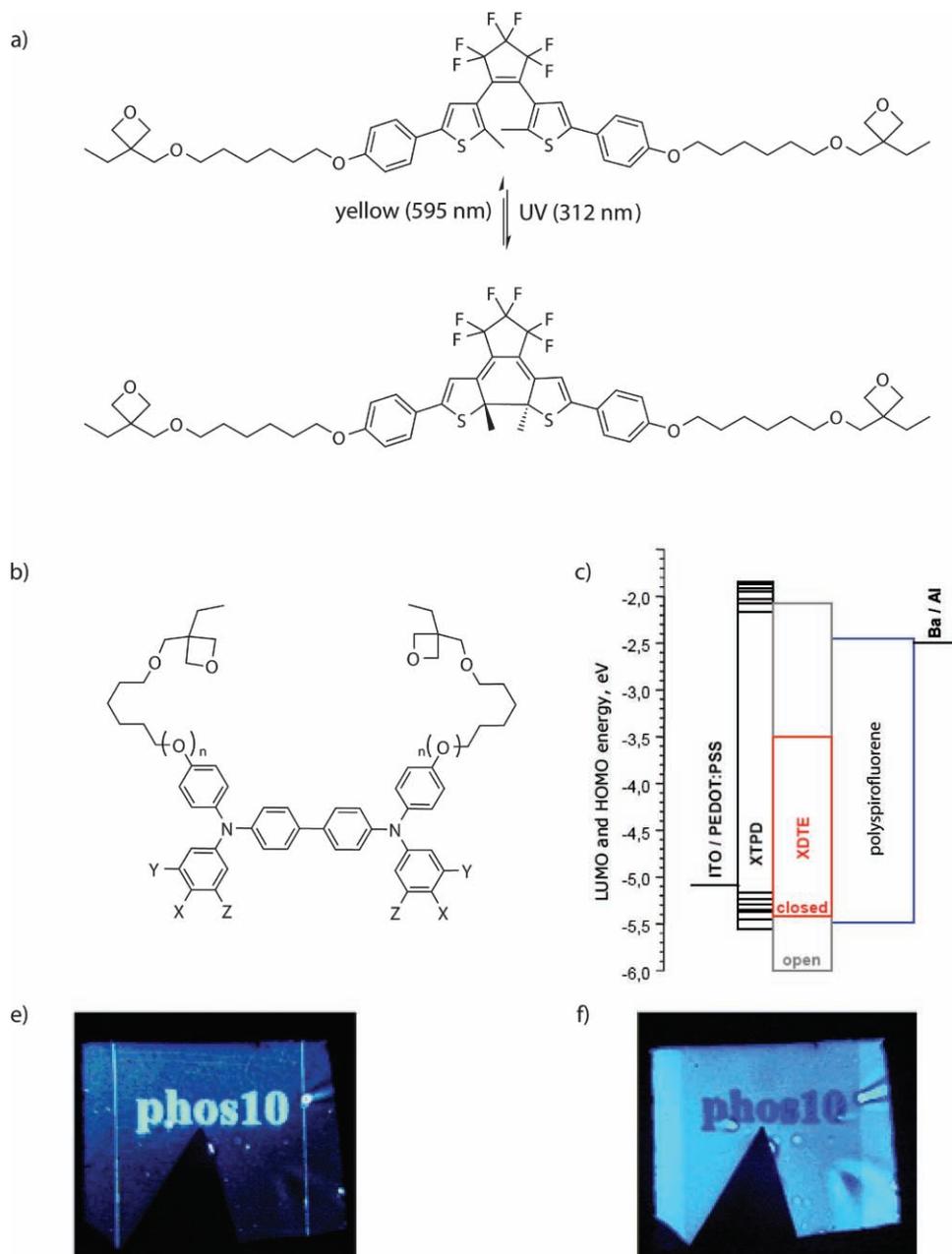
Figure 10. Photoswitchable OLEDs: Incorporation of a photochromic hole transport layer prepared by polymerization of a dithienylethene monomer (XDTE) (a) and fine-tuned hole transport layer from XTPD derivatives (b) into a layered OLED device (c) leads to individually and reversibly addressable emissive areas from the all-ON (d) or all-OFF states (e). Reproduced from.[48]

(**Figure 10**). The concept is based on the significantly decreased oxidation potential of the ring-closed as compared to the ring-opened XDTE isomer, leading to a shift of the HOMO levels by ca. 0.6 V upon photoswitching and hence enable hole transport (and electron blocking) in the ring-closed form. The authors could demonstrate that by careful choosing the other device components this difference can be exploited to create efficient OLEDs with high ON:OFF ratios of up to 3000. The high photoswitching ability characterized by photostationary states composed of more than 90% of the ring-closed isomer could be preserved in the flexible network of the film, prepared by

photoinitiated cationic ring-opening polymerization of the oxetane moieties. Since the electroluminescence efficiency strongly decreased after incorporating the dithienylethenes directly into the polyspirofluorene blue emitting layer and also the photoswitching was inhibited, the authors decided to integrate the photoswitch as an autonomous layer. After performing several optimization cycles for obtaining the best emitting properties and highest ON:OFF ratios, the resulting device was composed of: ITO anode | PEDOT/PSS hole injection layer | crosslinked triphenylamine dimer (XTPD, Figure 10b) hole transport layer | photoswitchable XDTE hole transport layer | (crosslinked XTPD

hole transport/electron blocking layer |) polyspirofluorene emitting layer | Ba electron injection layer | Al cathode. Besides demonstrating device efficiency and significant fatigue resistance ($Z_{80} \approx 190$), the authors could selectively address individual areas by irradiation through masks and hence realize an all optical, reusable storage application (Figure 10e,f).

Although this example implicates that technological application of photoswitches is near, many problems still remain to be overcome. In recent years, one major drawback of commonly used photoswitches, namely the need for UV (or visible) light to induce either E/Z-isomerization or pericyclic ring-closure/ring-opening reactions, has become evident. Especially for biological or medical applications this high energy radiation is detrimental because of its low penetration ability into cellular tissue and the severe cell damage among other unwanted side reactions that might occur. The substitution of one UV photon by two near-IR photons would offer many practical advantages, in addition to the above mentioned deep penetration of IR photons in tissue two-photon laser technology also permits a drastic increase of storage capacity through 3D multilayer design.

A number of candidates for two-photon absorbing photochromes were designed but found to have insufficient two-photon absorption cross sections.[49] An alternative strategy to avoid harmful UV irradiation was described recently by the Branda group[50,51] using up-converting NPs. In this "remote control" process low-energy, near-IR photons were harnessed by the NP, converted to fewer higher energy photons and their energy used to induce photoswitching of a DTE derivative. The chosen up-converting NPs consisted of $NaYF_4$ doped with either Tm^{3+} and Yb^{3+} ($NaYF_4$:TmYb) or Er^{3+} and Yb^{3+} ($NaYF_4$:ErYb) to emit UV and visible light, respectively, upon excitation at 980 nm. Both components, i.e. the NPs and the DTE switch, were incorporated into a flexible poly(ethylene glycol) dimethacrylate film to ensure their close proximity and thereby maximize re-absorption of the up-converted photon. When irradiating in the presence of up-converting $NaYF_4$:TmYb NPs with a 980 nm laser diode, the film changed from colorless to red along the path of the laser beam, indicating formation of the ring-closed DTE isomer. Similarly, a polymer film of the ring-closed form of the DTE with $NaYF_4$:ErYb NPs present decolored after irradiation with the same laser light. The authors could utilize the remote switching of their DTE derivatives to trigger the release of a particular dienophile (diethyl dicyanofumarate) from the ring-opened DTE via a retro-Diels-Alder reaction.[52] Without a doubt this work provides an appealing solution to the quest of how to utilize visible and near-IR light to trigger photoswitching processes. However, before the true potential of this method can be explored, the distinct addressability of each isomer needs to be restored since both up-converting NPs absorb at 980 nm inducing both ring-opening and ring-closing reactions at the same time.

5. Conclusion and Outlook

Without any doubt, photoswitchable molecules are of tremendous potential for several fields, ranging from chemistry, physics, and materials science all the way to biology and medicine. Interestingly, the basic scaffolds of the organic photochromes have not changed significantly and most efforts have been devoted towards tailoring established photochromic systems, in particular azobenzenes, dithienylethenes, and spiropyranes, to a specific application. On the one hand, azobenzenes are superior photochromes when large geometrical changes are desired. The dramatic structural reorganization associated with E/Z- isomerization can be transferred and even amplified in a suitable host material, in particular in LCs and LCEs due to the attractive mesogenic properties of the -isomer. This primarily leads to altered mechanical as well as chemical and optical properties and hence azobenzene-based photoswitchable materials are usually considered for applications in actuation and storage, among others. Complementary to the azobenzenes, diarylethenes display small geometrical but large electronic changes upon photochemical interconversion between their open and closed isomers. This has been utilized to switch the optical and electronic properties of fluorophores and electrophores allowing photocontrol of electronic coupling and energy transfer pathways in multicomponent systems.[53] Another technologically relevant benefit of these photochromes is the thermal stability of both switching states and their high fatigue resistance. Notably, the group of Irie has succeeded in creating photochromic crystals, which show reversible coloration but also contraction/expansion.[54] Spiropyrans offer the unique feature that their dipole moment is largely increased upon photoconversion of the ring-closed to the open merocyanine form, which has been utilized to control the interaction with charged entities and surfaces.[55] Clearly, there are preferred application areas for each class of these photochromes.

While the field is rapidly growing and a lot of exciting progress has been made, several key challenges remain and have thus far not been satisfactorily addressed. One primary aim is to improve the switching efficiency, not only of the photochromic entity itself but of the entire system/material. In cases where the photoswitch is bound to non-innocent substrates, such as metallic surfaces, the system has to be properly designed to retain the photoswitching ability. In many cases, not only efficiency is lost but also reversibility of the photochromic reaction.[18] Thus far, only one example is known, where the switching efficiency in the monolayer was increased as compared to solution.[23] This problem might in part be alleviated when moving to perhaps more technologically relevant substrates, for example silicon or inorganic semiconductors. Ideally, photoinduced changes in a few photochromic molecules serving as the "sergeants" can be amplified in the material using the cooperative interplay with "soldiers". This is demonstrated by the promising examples of switching cholesteric LC phases with azobenzene dopants.[46] Another important aspect concerns the need for photochromic systems that can be triggered by irradiation using visible and near-IR light. Certainly, two-photon technology as well as the use of up-converting NPs[50] promise solutions; however, they are still poorly developed. In general, it would be desirable to enhance the portfolio of photochromic molecules considering this aspect of high switching efficiency, among others such as thermal stability, fatigue resistance, maximized property changes. It will be crucial that property changes, which can be realized by photoswitching, i.e., the ON:OFF ratio, are maximized to meet the stringent requirements of real life applications, for example in organic electronics.

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Considering the dynamics and excitement in this area of research, the significant progress made over the past few years strongly suggests that in the not too distant future photoswitchable molecules will provide an important fundament for novel devices and advanced materials.

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