Light Switching of Molecules on Surfaces

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self-assembled monolayer, polymer immobilization, bilayers, photochemistry, photoswitching

Abstract

Smart surfaces, surfaces that respond to an external stimulus in a defined manner, hold considerable potential as components in molecular-based devices, not least as discrete switching elements. Many stimuli can be used to switch surfaces between different states, including redox, light, pH, and ion triggers. The present review focuses on molecular switching through the electronic excitation of molecules on surfaces with light. In developing light-responsive surfaces, investigators face several challenges, not only in achieving high photostationary states and fully reversible switching, but also in dealing with fatigue resistance and the effect of immobilization itself on molecular properties. The immobilization of light-responsive molecules requires the design and synthesis of functional molecular components both to achieve light switching and to anchor the molecular entity onto a surface. This review discusses several demonstrative examples of photoswitchable molecular systems in which the photochemistry has been explored in the immobilized state under ambient conditions and especially on electroactive surfaces, including self-assembled monolayers, bilayers, and polymer films.

1. INTRODUCTION

Smart surfaces, surfaces that can respond to a specific external stimulus in a specific manner, are of increasing interest in areas as diverse as cell culture (1, 2), microfluidics (3, 4), organic electronics (5), and coatings (6, 7). When combined with the flexibility provided through molecular synthesis, supramolecular chemistry, and surface science, exciting opportunities emerge toward the development of smart molecular materials and devices. Designing and preparing such surfaces are major challenges and require the interfacing of functional molecular components (e.g., photo- and electrochromic molecular switches) with nonmolecular materials. Once the molecule is immobilized, an appropriate stimulus is required to change the molecular structure and hence switch molecular properties (e.g., the conductivity of the molecule being turned on and off, the electronic absorption spectrum altered). It is in the area of molecular switching that the optical switching of properties stands out. However, whereas the (often reversible) photochemistry in solution for a wide range of photoactive organic and inorganic compounds has been explored extensively, key challenges remain in surface and polymer immobilized photoswitchable systems (8). This review discusses several approaches taken to immobilizing photoswitchable compounds, focusing on examples of how immobilization affects photochemistry (e.g., through changes in photochemical quantum yields and the opportunities presented by immobilization in terms of addressability). The scope of this review is concerned primarily with photoswitchable molecular systems that have been investigated in the immobilized state under ambient conditions and especially on electroactive surfaces.

In the present context, a photoswitchable molecule can be converted from one form to another with light of one wavelength and can either revert thermally to the original state or can be reverted by irradiation with light of a different wavelength (**Figure 1**). Here we focus primarily on unimolecular switching and do not consider further those systems based on rotaxanes and catananes (10). Examples of some of the most-studied classes of photoswitchable organic systems are shown in **Figures 2** and **3**.

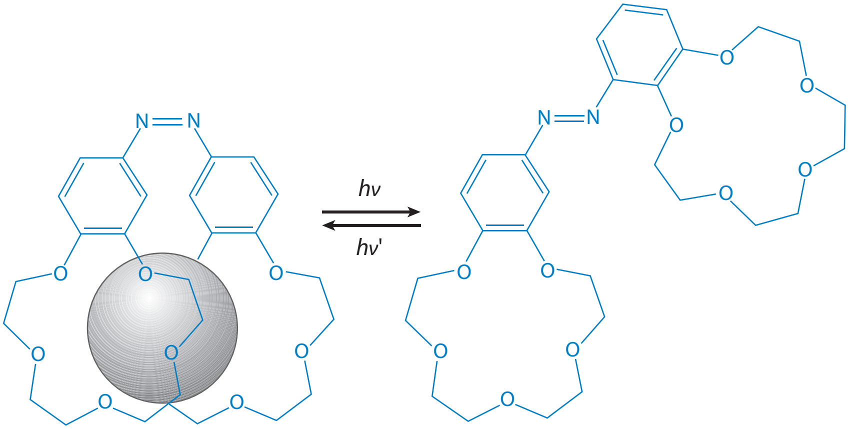

Figure 1

A simple photoswitchable molecule. The *cis-trans* isomerization of an azobenzene unit can control the interaction of two functional groups (i.e., two crown ether units). These units can be brought together or separated by the isomerization of the azobenzene unit, allowing for reversible ion binding and release (9).

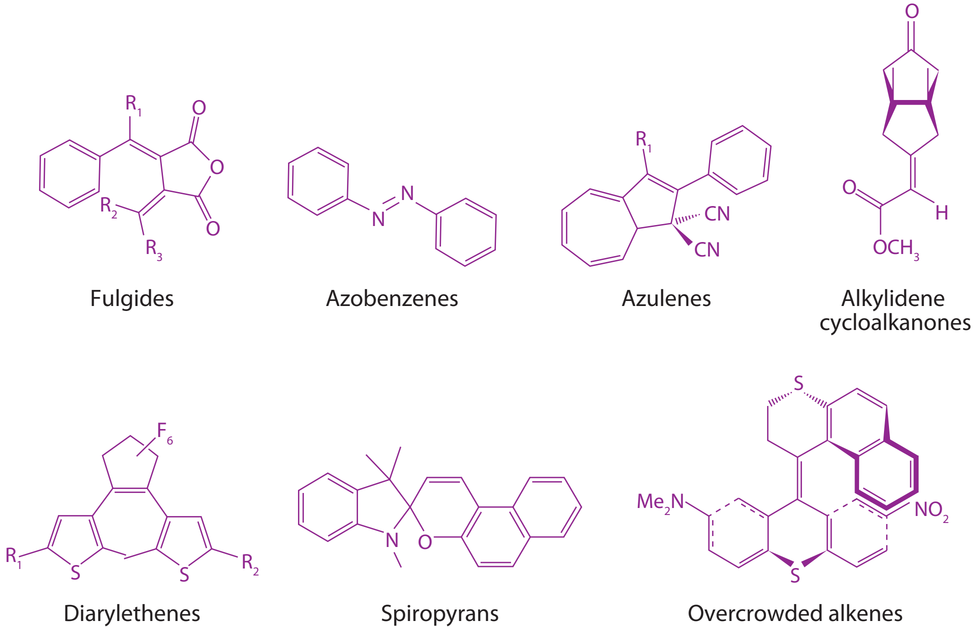

Figure 2

Examples of the more commonly employed classes of photoswitchable molecular systems.

2. PHOTOACTIVE SELF-ASSEMBLED MONOLAYERS

The immobilization of photoswitchable molecules onto surfaces has been, and continues to be, an active area of photochromic research. In general, conducting, metallic, surfaces have received the most attention partly because of the affinity of pyridyl and sulfur moieties for the noble metals,

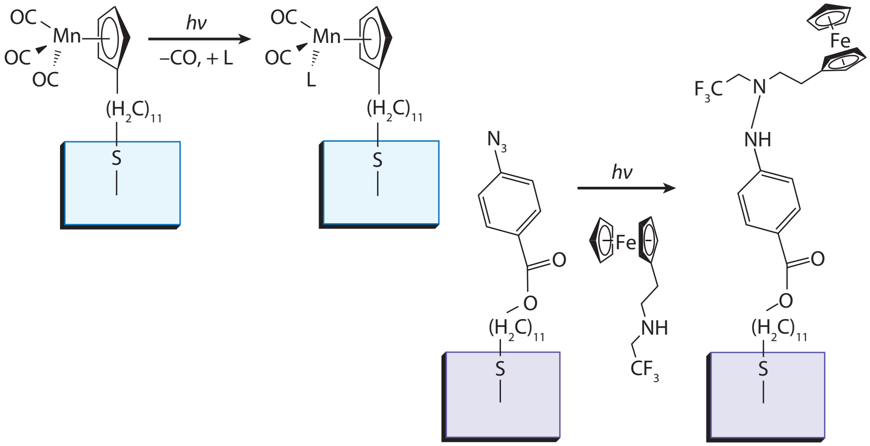

Figure 3

Irreversibly switchable self-assembled monolayers. A photoswitchable molecule is attached to the surface followed by the formation of a nitrene or photolabilization of a ligand (e.g., CO), which is then followed by the reaction of the photoswitched surface with a second unit to introduce new functionality to the surface (16).

with platinum and gold as the electrode materials of choice (11). Nevertheless, there has been increasing interest in the use of silicon (12) and semiconductor materials (13) as substrates for the formation of switchable self-assembled monolayers (SAMs). In the case of silicon, its ubiquitous usage in electronics and photovoltaics presents the prospect of introducing a photoswitching element into field-effect transistors. Furthermore, because the physical characteristics (e.g., conductivity, polarity) of both pure silicon and metastable photochromic switches such as spiropyrans (14) are dependent on light intensity and temperature, fascinating opportunities in device construction are opened up when these molecular and nonmolecular components are combined in one device. In the case of metal-oxide semiconductors, although they are not atomically flat [and hence inaccessible to scanning tunneling microscopy (STM)], they are transparent to visible light, allowing for facile optical reading of the state of the photoswitchable unit.

STM: scanning tunneling microscopy

A distinct drawback of immobilizing molecular photoswitches on surfaces as SAMs is the limited amount of material available in the SAM (typically 10^{-11} to 10^{-9} mol cm^{-2}). Nevertheless, sensitivity to these amounts is a significant advantage when employing electrochemical methods; hence many studies of the photochemistry of SAMs have focused on electrochemical detection (15, and references therein). Indeed distinct advantages can be found in electrochemical detection of switchable molecular systems on surfaces, including the ability to address the entire sample rapidly by an electrochemical perturbation and moreover the ability to control precisely the doping of a monolayer with molecules in a higher or lower oxidation state by controlling the potential applied. In contrast, the limited amount of material requires highly sensitive spectroscopic detection, which has become generally available only in recent years.

2.1. Photochemically Reactive Self-Assembled Monolayers: Irreversible Photoswitching

The irreversible photoswitching of surfaces has proven particularly useful in photolithography, in which the patterned modification of a surface can be achieved, typically using photolysis, through a mask of radical initiators mixed with polymerizable monomers. An alternative to surface modification is seen in the SAMs of photoswitchable molecules based on cyclopentadienyl manganese tricarbonyls [$HS\text{-}C_{11}H_{22}\text{-}CpMn(CO)_3$] and azides employed by Wrighton and coworkers (16, 17). These systems can be employed to prepare photoactive surfaces that, via photosubstitution reactions, can be used for high-resolution lateral image patterning. In this example, the photoactivation of an azide, which reacts subsequently with secondary amines (e.g., a redox-active substituted ferrocene unit), is complemented by a second system in which the photolysis of the Mn-CO bond of the manganese tricarbonyl complex, which releases carbon monoxide, makes a coordination site for the ligation of a phosphine ligand available (**Figure 3**). These irreversibly switchable surfaces offer access to a wide range of molecularly modified surfaces with functionalities that are incompatible with the synthetic procedures required to produce, for example, a thiol anchor unit. Furthermore, the modification of the surface can proceed with diffraction-limited spatial control.

The photochemical exchange of ligands with solvent is particularly interesting in the development of inorganic photoswitchable surfaces. Recently Forster et al. (18) reported the photosubstitution of chlorido for aqua ligands in an Ru(II) polypyridyl complex, $[Ru(bpy)_2(bpe)Cl]^+$ [where bpe is *trans*-1,2-bis(4-pyridyl)ethylene]. The complex forms well-defined SAMs and undergoes loss of either the bpe anchoring ligand or the chlorido ligand, depending on the solvent employed, with aqueous solvents favoring the substitution of the latter ligand. This allows for the exchange of a single ligand of the complex or the complete dissociation of the metal, leaving behind a monolayer of bpe.

2.2. Photochemically Reactive Self-Assembled Monolayers: Reversible Photoswitching

Although the irreversible switching of a SAM can be useful in photopatterning and activation toward further modification of surfaces, reversible switching between stable states (bistability) is of practical interest for application in molecular and organic electronic devices. This section discusses a few examples of how the reversible photo-induced switching of SAMs is both achieved and detected and how SAMs are incorporated as functional elements in devices.

Willner and coworkers (19) have demonstrated a surprisingly simple, yet remarkably effective, approach to using SAMs of photoswitchable molecules as components in functional devices (**Figure 4**). In this system, changes in the polarity of the switchable molecule, a spiropyran, under irradiation with ultraviolet (UV) or visible light result in concomitant changes in the polarity of the monolayer and hence the surface as a whole. This simple molecular change can achieve, among other applications, the inhibition or enhancement of the rate of electron transfer between the surface and solution. In this example, a redox-active cytochrome enzyme is controlled by the molecular state of the surface. The state of the surface is determined readily by the ability of the SAM to facilitate electron transfer through the reduction of the enzyme (**Figure 4**). More recently these systems have formed the basis of a read/write and erase magnetic-patterning system (20).

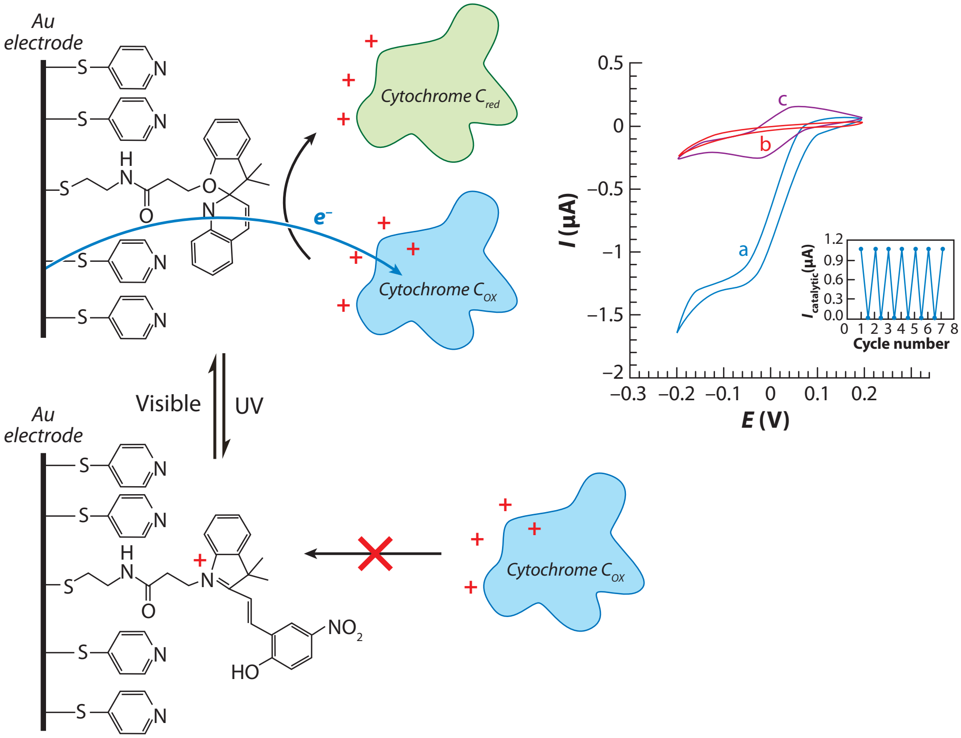

Figure 4

An enzyme-based redox system comprising a self-assembled monolayer (spiropyran) modified gold electrode and a cytochrome *c* enzyme with a positively charged surface. The polarity of the surface is switched and increases and decreases with light. In the polar state, the enzyme cannot approach the electrode and engage in electron transfer, whereas it can in the apolar state. The insert shows the changes in current upon alternating irradiation with UV and visible light. Figure reproduced from Reference 19. Copyright 1997.

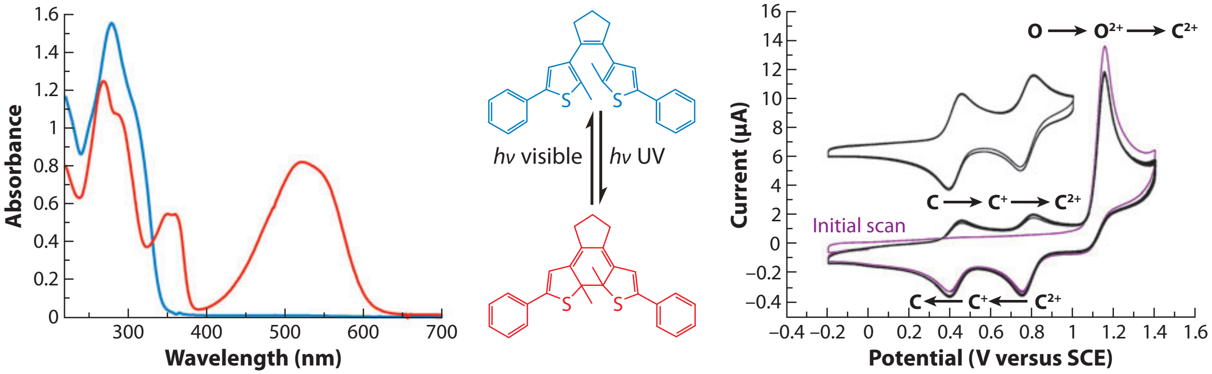

Figure 5

Ultraviolet/visible absorption spectra and cyclic voltammetry of a dithienylcyclopentene in its open (o) and closed (c) form in $CH_2Cl_2/TBAPF_6$ (0.1 M), 0.1 V s^{-1}; potentials are relative to the saturated calomel electrode (SCE). Figure taken from Reference 25. Copyright Wiley 2005.

The diarylethene class of photochromic switches, in contrast to spiropyrans, exists in two thermally stable forms: the so-called open, colorless form and the closed, colored form (**Figure 5**). Despite extensive studies on the photochemistry of the dithienylcyclopentene class of photoswitchable compounds (21), only relatively recently has the electrochromic and general electrochemical behavior of this important class of molecular switches received a similar level of attention (22–27).

Several studies have focused on the intrinsic molecular properties of dithienylethenes in solution (21); however, interfacing these photo/electrochromic switchable systems with nonmolecular systems (i.e., the macroscopic world) requires their immobilization on surfaces. The covalent self-assembly of diarylethenes on indium titanium oxide (ITO) (28) and gold (29–31) surfaces has been reported. A typical example is the photo-/redox-active system o/c, which can be switched between the open and closed state by UV and visible irradiation, respectively (**Figure 5**). This system can be closed, partially, using electrochemistry in solution as well. However, the electrochemical switching of diarylethenes is essentially unidirectional and incomplete in solution, and the direction of the switching is controlled only through the synthetic tuning of the molecular structure (26). In contrast, when immobilized on a surface, electrochemical switching can be achieved in both directions in a fully reversible and rapid manner (**Figure 6**) (28). The change in the behavior of the dithienylethene when immobilized does not result from a change in its molecular properties but instead results from the effect of immobilization in the SAM on the rates of electron transfer reactions, such as disproportionation. Furthermore, on a surface such as ITO or gold, as a SAM, the entire sample can be addressed electrochemically in a rapid and complete manner, yielding considerable added value in the case of the photochromic dithienylethenes.

The effect of surfaces, specifically gold, on the photoactivity of dithienylethenes is particularly important because of the use of these molecular switches in molecular electronic devices. Recently, the influence of the anchor unit on the quenching of the photochemistry of dithienylethenes immobilized as SAMs on gold was reported (**Figure 7**) (30). Three systems, which varied in either the anchor unit or the electronic nature of the photochromic unit itself, were examined by electrochemistry. Surprisingly, although both anchors maintained an essentially identical separation between the dithienylethene and the gold surface, the electronic properties of the dithienylethene appeared to be more important in determining the effect of incorporation into a SAM on the photochemical switching. That is, changes in photochemical activity on gold cannot be ascribed easily to a simple quenching model (*vide infra*).

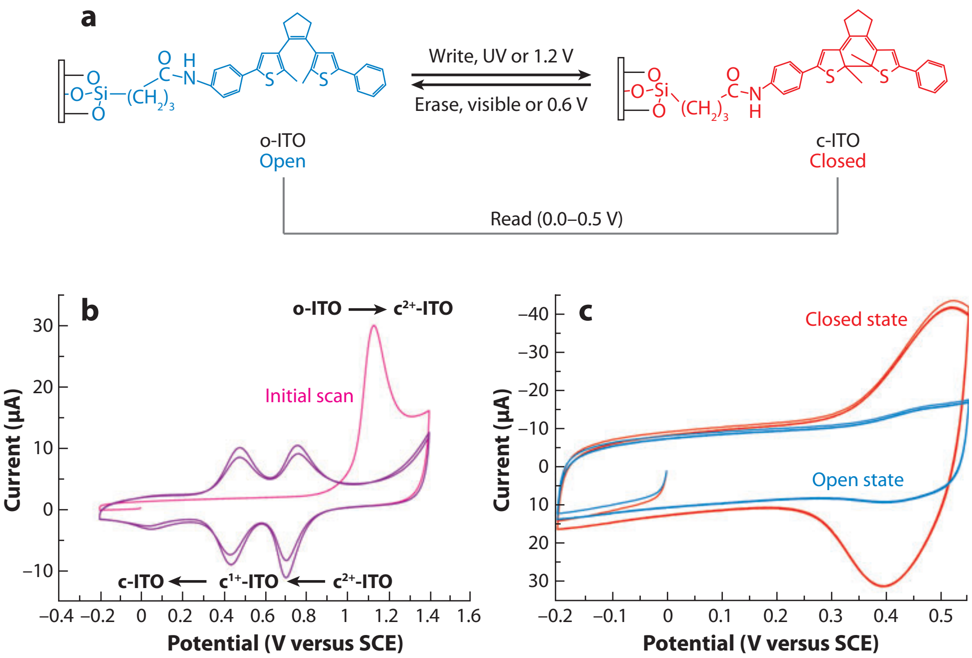

Figure 6

(*a*) A dithienylethene molecular switch open (o) immobilized on ITO via triethoxysilyl anchors. (*b*) Electrochemical ring closing of o-ITO to closed (c-)ITO by cyclic voltammetry. (*c*) Electro- and photochemical write and erase functions with readout achieved nondestructively through cyclic voltammetry. SCE, saturated calomel electrode. Figure adapted from Reference 28. Copyright The Royal Society of Chemistry, 2006.

3. LIGHT SWITCHING OF CONDUCTANCE OF INDIVIDUAL MOLECULES AND MONOLAYERS

In developing optoelectronic molecular devices, the observation of the photo-induced switching of conductance under ambient conditions presents a key challenge, in particular when studying photoswitching in molecular devices under conditions similar to those that would be confronted by

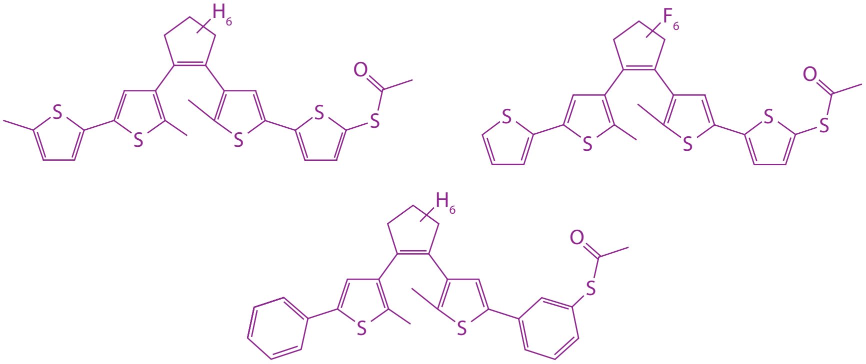

Figure 7

Structure of dithienylcyclopentenes immobilized on gold electrodes and nanoparticles.

molecules in real devices (i.e., molecules assembled on nanoscopic metallic electrodes under ambient conditions). Forming well-defined (i.e., single-molecule) bridges between nano-electrodes is not a trivial task. Issues arise, such as charge transport in molecules, the stability of the molecule-electrode contact versus potential, stochastic conformational changes versus conductance changes, and stochastic switching versus controlled switching. The most difficult challenge in molecular-based electronics is without doubt the necessity of demonstrating that the data obtained in using molecular bridges between electrodes do not result from artifacts (32). The techniques available for measuring individual molecules [e.g., STM (33–36), mechanically controlled break junction (MCBJ) (37–39), and more recently the nanosquid (40)] require the design of suitable molecular candidates for switch devices to help resolve these fundamental issues.

MCBT: mechanically controlled break junction

3.1. Photoswitchable Molecularly Modified Surfaces

One of the earliest reported studies correlating photochromic switching to changes in the conductance of individual molecules employed azobenzene derivatives embedded in *n*-dodecanethiol SAMs assembled on Au(111) (41). Azobenzenes undergo a *cis-trans* isomerization that alters the physical height of the molecules (**Figure 8**), albeit without significant change to molecular conductance. In the mixed SAMs, an STM tip provides a nanoscale probe of charge transport through the switch. The comparison of unequal apparent STM heights for the *trans* and *cis* isomers provides direct evidence of light-induced switching for individual azobenzene molecules. The apparent changes in conductivity observed by STM were attributed to the switching of the molecules' height and not to a change in molecular resistivity due to internal rearrangements. Importantly, even in the absence of light, conductance switching was observed. This phenomenon was attributed to reversible *trans-cis* isomerization driven by an external electric field and current flow. This voltage-induced switching could be suppressed by controlling the applied potentials.

In the azobenzene system, the photoactive unit was isolated from the Au(111) surface by an insulating propyl group. An alternative approach can be found in the light-induced switching of individual azobenzenes physisorbed on Au(111) under ultrahigh vacuum conditions (42). *tert*-Butyl groups were used to lift the switching unit off the substrate, the goal being to increase molecular photomechanical activity by decreasing molecule-surface interactions. In cases in which the azobenzene contained zero or two *t*-butyl legs, isomerization was not observed, a phenomenon ascribed to the stronger electronic coupling of the switching unit with the substrate.

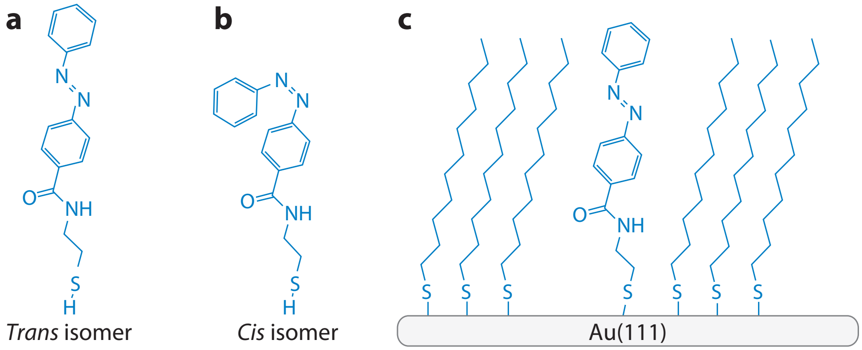

Figure 8

An azobenzene-derivative (*a*) *trans* isomer and (*b*) *cis* isomer used to form self-assembled monolayers (SAMs) on gold through an S-Au bond. (*c*) The *trans* isomer was embedded in a SAM of *n*-dodecanethiol.

The transition from quenched to active photomechanical behavior highlights the role played by electromechanical coupling between a molecule and substrate in controlling single-molecule photoswitching.

In both the studies discussed above, the conductance switching of azobenzene derivatives relies on the switching of height rather then a direct switching of intrinsic molecular resistivity, thus requiring the use of a technique sensitive to height switching (as is STM) in any device that employs the azobenzene as a photoswitchable component. In contrast, in diarylethene photochromic switches, the rearrangement of double and single bonds through photoswitching (**Figure 5**) is expected to be accompanied by significant modification in molecular conductance, as indeed is observed by electrochemistry (*vide supra*), whereas their physical height is not altered significantly. The potential of dithienylethenes in molecular electronics was first demonstrated in studies of the conductivity of a dithienylethene switch with thiophene groups as spacers and functionalized by two thiol groups chemisorbed on each of two MCBJ electrodes (43). These experiments demonstrated that the switching of a molecule from the closed to the open form results in a significant resistance increase of three orders of magnitude. This is another indication that closed and open forms exhibit intrinsically different charge-transport properties. However, once the switch is connected to gold via the Au-S bond, it can only be switched from the closed to the open form. These results were corroborated subsequently in studies of the monothiol analog of the switch by STM (44). In addition to one-way photoswitching (as for azobenzenes), random (stochastic) switching with a strong applied voltage dependence was observed. The importance of these control studies cannot be underestimated as both effects (light-induced and stochastic switching) are of the same order of magnitude. The lack of reversibility in these systems was investigated theoretically and attributed to the quenching of the excited state of the open form by gold (45, 46). More specifically, density functional theory calculations suggested that the quenching observed may result from the alignment of the Fermi level of gold with the molecular orbitals of the open isomers. The deep-lying highest occupied molecular orbital level lies at a high metal density of states, thus facilitating electron transfer events, and thereby reducing the lifetime of the hole created after excitation. In contrast, the highest occupied molecular orbital of the closed isomer is higher in energy and lies in a region of low density of states of gold; hence ring opening can take place.

Recently the direct observation of the reversible photoswitching of individual photochromic molecules on gold was reported (47). In contrast to the previous example (in which homogeneous SAMs were formed), in this case switching molecules were embedded in *n*-dodecanethiol SAMs formed on Au(111) as for the azobenzene system described above. The use of a mixed SAM facilitated the imaging of individual molecules and the characterization of the state of the molecules (i.e., open and closed) and their surroundings. Reversible light-induced switching was accompanied by large changes in conductance. Furthermore, this approach allows for the statistical analysis of single-molecule switching events at a level not available with the MCBJ techniques.

A diarylethene derivative with one CH_2 group separating the aromatic unit of the switch from the gold surface was investigated using a repetitive break junction method based on STM (48). Statistical analysis of the single-molecule conductance properties is possible as a gold probe is pushed repeatedly into a gold surface and withdrawn again to form a thin gold filament in a solution containing the switchable molecules. Resistances of 526 MΩ in the open form and 4 MΩ in the closed form were determined. The isolation of the switching unit using a partly conjugated linker allowed for the retention of reversible photochromism. In a more recent example of this approach, the group of Guo and Nuckolls used carbon nanotubes in place of gold (49). This study is a major advance as it allows for the use of electrodes that circumvent issues faced by metallic electrodes such as atom migration on the electrode surface.

3.2. Photoswitchable Molecularly Modified Nanoparticles

Generating functional surfaces through the immobilization of photoactive molecules in which the molecular species is interfaced with nonmolecular bulk materials is essential to their incorporation into electronic devices. This approach, however, presents considerable challenges as well as opportunities. Indeed, forming stable bonds between the surface and the molecule of interest and controlling molecular orientation with respect to the surface are challenging aspects: However, even with high surface densities, the total amount of the molecular material available for analysis is at the nanomol per squared centimeter level or lower. Therefore, metallic surfaces, in particular gold, have received the most attention in part because of their conductivity and hence suitability for surface analysis by methods such as X-ray photoelectron spectroscopy (50–52), STM, surface-enhanced Raman spectroscopy (53), and electrochemistry (15) and because of the ease with which relatively simple ligands can be employed as anchors (i.e., pyridine and thiolates). Metal nanoparticles, however, present a compromise between solution and surface. The size of the nanoparticles means that the molecule sees, to some extent, a bulk surface, but the total amount of material available in a sample space allows for characterization by electronic spectroscopy in a manner comparable with that achieved in solution. Furthermore, metal nanoparticles offer excellent opportunities for furthering our understanding of molecule-surface interactions owing to the range of nanoparticle sizes that can be accessed uniformly (e.g., 54–56). As such, they offer a convenient model system for mimicking properties of bulk solids, with the additional benefit of being able to tune size-dependent properties, in particular surface plasmon energies (57). The self-assembly of photoswitches on the surface of metal nanoparticles provides two primary contributions to the chemistry of molecular switches. First, direct electronic coupling of a nanoparticle core with a chromophore due to proximity (55) might result in the complete quenching of the photoreaction, and second, steric constraints, which limit the conformational freedom of the molecular entities immobilized, affect photochemistry to varying degrees depending on the system. For example, the *trans-cis* isomerization of azobenzenes and stilbenes, chemisorbed on gold nanoparticles via a range of alkylthiol linker chain lengths, has been described (58, 59). In these studies a clear dependence of photochemical quantum yield on chain length was observed, which was assigned to a distance-dependent quenching of the excited state through electronic coupling with the metal nanoparticle. Similarly, the *trans*-to-*cis* isomerization of an analogous stilbene monolayer was not observed on planar gold owing to the dense packing of the formed SAM (60). This demonstrates the importance of conformational restrictions on the photoreactivity of photochromic molecules in addition to electron coupling quenching mechanisms. Asymmetric azobenzene disulfides have been employed in an attempt to realize efficient isomerization on colloidal gold surfaces (61). In the SAMs formed, the free volume for the photoreaction of azobenzenes was provided by the 50% dilution due to the second alkyl leg of the disulfide. As a result, both the *trans*-to-*cis* and *cis*-to-*trans* isomerization processes proceeded, unimpeded by steric constraints (62).

Light-driven molecular motors based on overcrowded alkenes compose a special class of switchable molecule in that the switching function is used as part of a multistep mechanical cycle involving both photochemical and thermal switching events (63). Immobilization is a crucial step to overcome Brownian motion, observed in solution, and ultimately to build nanodevices that employ molecular motors. The anchoring of molecular motors to surfaces to interface them with the macroscopic world requires that their mechanical function is not compromised. A so-called second-generation (64) molecular rotary motor was immobilized successfully on gold nanoparticles, as well as on flat surfaces, to facilitate spectroscopic analysis and importantly to confirm that the unidirectionally light-driven rotation observed in solution was retained on the surface (**Figure 9**) (65). In this system, the rotor axis is normal to the surface, and the stator unit is

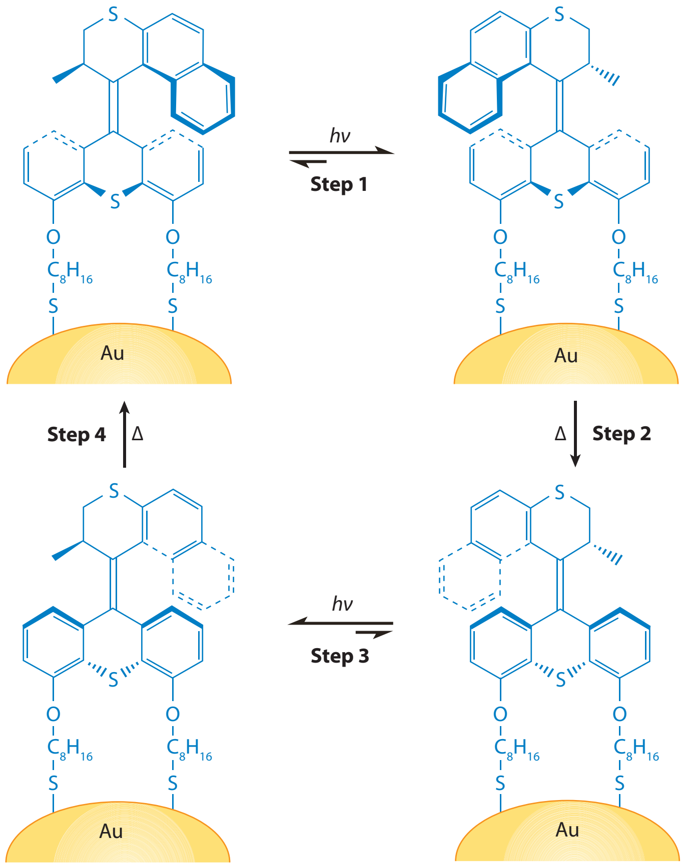

Figure 9

The (four-step) rotary cycle of an overcrowded alkene-based molecular motor anchored to gold nanoparticles via two alkylthiol legs. Two of the steps require a photochemical *cis-trans* isomerization, whereas the other two steps proceed via thermally activated conformational changes. Figure reproduced from Reference 65. Copyright Nature 2005.

attached to the surface by two legs terminated with thiol anchor groups. The connection through two attachment points at the stator precludes the uncontrolled thermal rotation of the entire motor with respect to the surface while retaining the propeller function.

Continuous unidirectional rotation with respect to the surface was characterized by circular dichroism spectroscopy and was characterized indirectly by nuclear magnetic resonance spectroscopy in which the two anchors could be discriminated by ^{13}C-isotope labeling (65). The separation of the motor molecules from the gold surface by two eight-methylene-unit linkers ensured that the photochemical and thermal reactivity of the molecular motor observed in solution was retained upon immobilization onto the gold surface. The barrier for the thermal isomerization of molecules grafted on gold nanoparticles was slightly higher than for the molecules in solution, a change attributed to the decrease in the molecules' conformational freedom.

In contrast to the previous examples, in which isomerization was accompanied by large changes in molecular structure, for diarylethenes, steric effects arising from close packing in SAMs should not significantly influence the molecular photochemistry. This is because the geometric changes

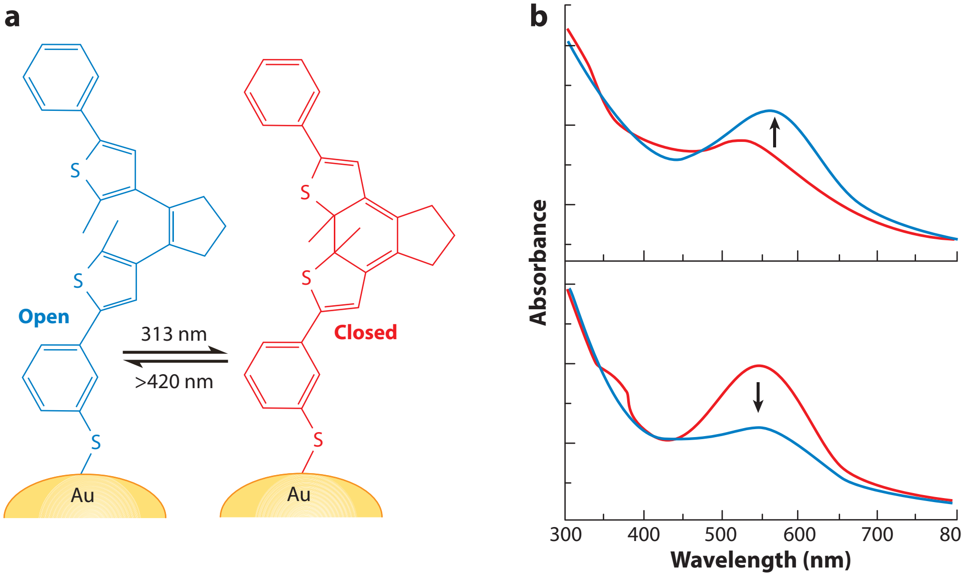

Figure 10

(*a*) The photoisomerization from open to closed switch states of a dithienylethene while anchored to gold nanoparticles. (*b*) UV/visible spectra of the open form measured in dry toluene before (*red line*) and after (*blue line*) irradiation at 313 nm (*top panel*), and UV/visible spectra of the closed form measured in dry toluene before (*red line*) and after (*blue line*) irradiation at >420 nm (*bottom panel*).

required to change from one state to the other are minimal. Indeed photochemistry is preserved even in crystalline states (66–68). Initial attempts to study the photoswitching of diarylethenes self-assembled on a surface of gold nanoparticles showed that when the switching unit is isolated from the surface by a linker based on a pentamethylene alkyl chain, the photochromism of the compound is retained (69), with both ring closure and ring opening on gold nanoparticles proceeding in a manner similar to that observed in solution.

Although this approach is effective in retaining photochemical properties in the SAM, the inclusion of alkyl spacers can have negative consequences on charge-transport properties in molecular devices. This results from the requirement of a degree of electronic communication (overlap) between the switching unit and the metal to make molecular-based electronic devices feasible. As a result, it is necessary to link photochromic molecules directly to the surface using conjugated anchor units. Kudernac et al. (70) have examined the influence of various aromatic spacer units on the photochemistry of diarylethenes on gold nanoparticles. Whereas the ring-opening process was unaffected by anchoring on gold (**Figure 10**), the corresponding ring-closing reaction was affected to a greater or lesser extent, depending on the linker unit employed: The *meta*- and *para*-substituted phenyl units allowed for ring closing, whereas thienyl anchor units showed no evidence of ring closing. Because the distance of the photoswitching unit from the surface for all spacers is essentially the same, the origin of the difference in switching behavior is not trivial and may lie either in a different proximity of states, and consequently different mixing of energy levels of the gold nanoparticles and photoswitches, or in a specific orientation of the molecules in the SAM with respect to the surface. Similar results were obtained on flat gold electrodes (*vide supra*), which implies that surface plasmon resonance/molecule interactions may not be the primary reason for the loss in reactivity observed (30).

4. PHOTOSWITCHABLE SYSTEMS IN LIPID BILAYERS

Although a bilayer is not normally considered a surface, bilayers nevertheless form interfaces in devices (e.g., in patch clamps); hence we briefly mention the recent use of photoswitchable molecules in these functional biomolecular devices. Light-driven changes in molecular polarity can be used to power the opening and closing of a nanovalve (71). **Figure 11** illustrates the use of the spiropyran-mercyanine system for this purpose.

The mechanosensitive channel protein of large conductance (MsCL) acts as a type of safety pressure-release valve for certain cells. A buildup of osmotic pressure or membrane tension forces the tightly closed membrane-embedded protein complex to open a 3-nm pore to allow material to flow out of the cell. Incorporating cysteins into each protein unit in the pentamer complex allows for light-switchable molecular units to be attached at predetermined sites. The photochemical ring opening of a spiropyran to a merocyanine induces sufficient changes in the protein conformation and hydrophilic nature of the constriction zone to open the channel. The light-triggered reversible opening and closing were demonstrated by patch-clamp techniques. Including the hybrid photoactive protein channel in the bilayer of a giant vesicle allowed the contents of the vesicle to be released upon irradiation. This system holds potential for controlled drug delivery through the use of such switchable nanovalves.

An alternative biohybrid approach to photochemical valve control involves controlling a channel by changing the lateral membrane pressure either through photoresponsive azobenzene-based lipid bilayers (72) or through an allosteric approach (73). A semisynthetic ligand–gated ion channel that is switchable (on and off by UV and visible light irradiation, respectively) uses the well-known azobenzene optical switch (**Figure 1**). The azobenzene switch is attached to the protein and a glutamate residue, which is specific for the allosteric site (a signal binding site on the protein that regulates the operation of a separate remote functional component) responsible for closing the protein channel. The point of attachment is critical to its operation, and the switching unit attaches to the outside of the channel rather than the inside, in contrast with the previous example. The large change in molecular geometry due to a *trans*-to-*cis* photo-isomerization of the azobenzene unit allows the glutamate residue to bind to the receptor and open the channel. In this

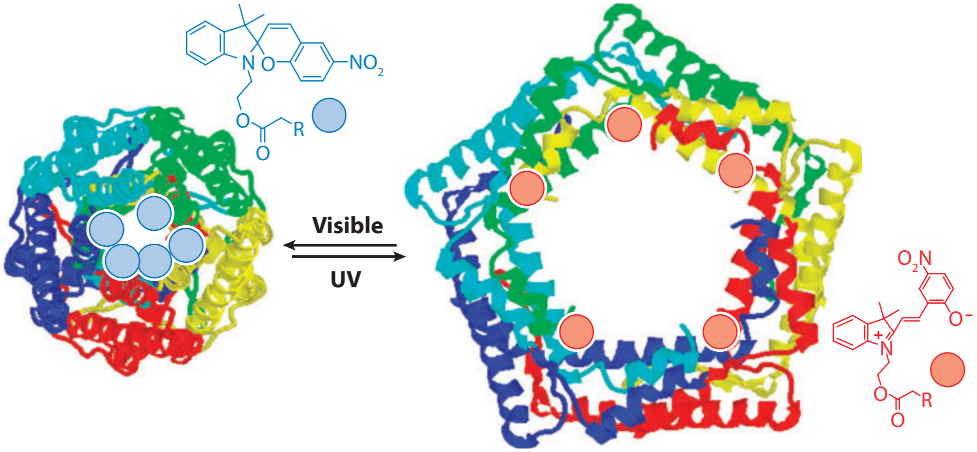

Figure 11

The light-driven opening and closing of a biohybrid nanovalve based on the MsCL protein. Figure reproduced from Reference 71. Copyright AAAS 2005.

nanomechanical valve, light-controlled reversible channel gating is achieved by several structural units and functions operating in concert.

5. PHOTOSWITCHING IN POLYMERS

Whereas the immobilization of photoswitchable molecules in SAMs offers advantages with regard to self-organization, the limited amounts of switchable material present can limit applications. An alternative approach to generating photoswitchable surfaces is the use of polymer immobilization. The nature of the polymer backbone used to immobilize the photoactive unit, however, is nontrivial. The monomer used to synthesis the polymer and the polymerization process itself must be compatible. This is especially important with regard to photo/electroactive switching units because of their often limited stability under standard polymerization conditions (e.g., anionic polymerization, oxidative and reductive electropolymerization, UV light–initiated radical polymerization). Furthermore, for less robust photoswitchable systems, the effect of the polymer matrix on the properties of the photoactive unit itself and importantly on the stability during operation must be considered as well.

For example, a photo/electrochromic dithienylcyclopentene (similar to those described above) can be immobilized on a surface as a thin film through the electropolymerization of a methoxystyryl unit attached to the photoactive unit (**Figure 12**) (74). The oxidative electropolymerization of the methoxystyryl unit produces only thin films (<10 nm) because of the limited conductivity of the polymer backbone. The polymer films formed can undergo complete switching between the open form and the closed form electrochemically and by irradiation with UV and visible light (*vide supra*). However, although the photoswitchable unit, the dithienylcyclopentene, is functional in the polymer matrix as in the SAMs described above, the stability is much lower. Oxidation of the closed form at low scan rates or extended irradiation with UV light leads to the rapid destruction of the photochromic functional unit. In this case, it is the reactivity of the polymer backbone itself that is responsible for the instability.

As discussed above, the *cis-trans* isomerization of azobenzenes is accompanied by a change in molecular shape and size (the distance between the *para* positions of the arene termini changes by 0.35 nm). When incorporated into the backbone of a polymer chain, this change in length can be used to modify the polymer's modulus of elasticity, as demonstrated in the work of Gaub and coworkers (75). Alternating UV and visible irradiation generates the forces associated with the contraction and expansion of the polymer chain, respectively. The light-induced work against an atomic force microscope tip was measurable by scanning probe techniques (**Figure 13**).

Whereas organic photoswitchable polymer systems have received widespread attention (76), reversibly photoswitchable inorganic systems have featured much less in the literature. This may be because inorganic photochemistry is dominated largely by either energy and electron transfer (77, 78) or by ligand dissociation through the population of ligand-field-centered excited states. Indeed inorganic photochemistry typically requires the recoordination of solvent or electrolytes, for example, to reverse the process, and the reversal is favored thermodynamically (*vide supra*). Nevertheless, the photo- and redox-triggered linkage isomerization of nitrosyl (79) and sulfoxyl (80) inorganic complexes demonstrates the potential versatility of inorganic photochemistry. In systems in which a ligand can engage in two alternate coordination modes, such as in the sulfoxide ligand of the complex $[\mathrm{Ru^{II}(tpy)(pic)(DMSO)}]^+$ (where tpy stands for terpyridine acid and pic for picolinic acid) (**Figure 14**), the rate of the photo-induced switching is less sensitive to the immediate environment, and the complex can be employed in a similar manner to organic photoswitches. This offers a considerable advantage when these complexes are immobilized in polymer films as then the rate of solvent diffusion is a minor (or nonexistent) issue (80).

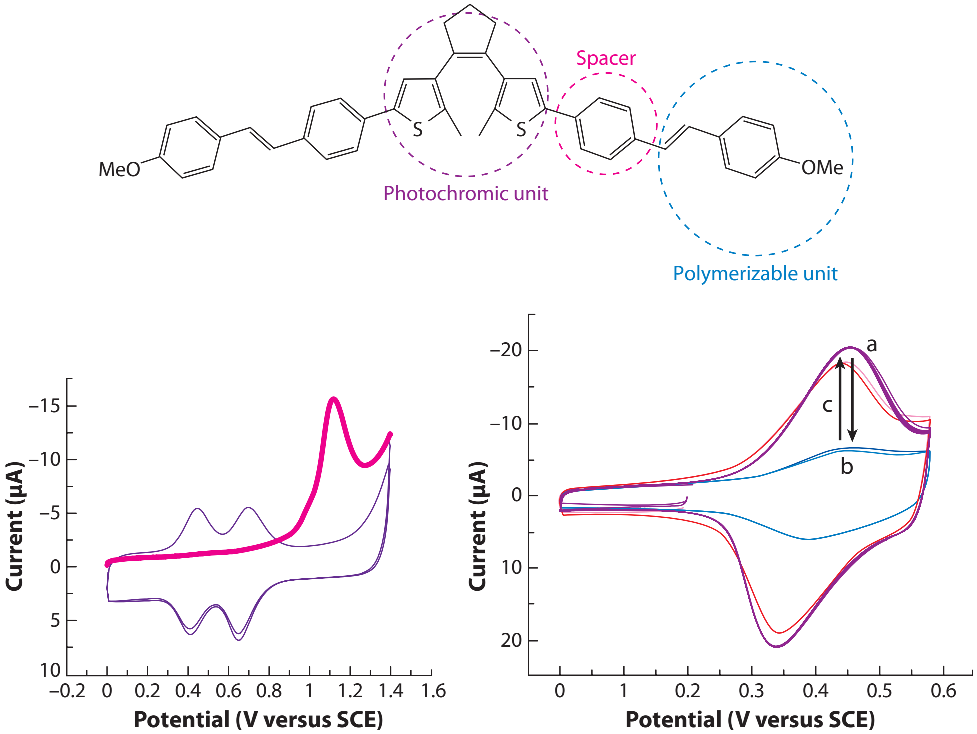

Figure 12

(*Top panel*) A bifunctional molecule with a photo/electrochromic dithienylethene and two electropolymerizable methoxystyryl units. (*Lower left panel*) Cyclic voltammetry of the open-state polymer on a glassy carbon electrode prepared by visible irradiation (>420 nm) of a closed-state polymer in monomer-free solution at 0.1 V s^{-1} in DCM (0.1 M $TBAClO_4$). The initial cycle is indicated as a heavier line. (*Lower right panel*) Cyclic voltammetry of the polymer in the closed state on a glassy carbon electrode at 0.75 V s^{-1} in CH_2Cl_2 (0.1 M $TBAClO_4$) before (*a*) and after (*b*) photochemical ring opening by visible irradiation (>420 nm) of the closed-state polymer in monomer-free solution and after (*c*) oxidative ring closure. SCE, saturated calomel electrode. Figure reproduced from Reference 74. Copyright ACS 2008.

6. PHOTOSWITCHABLE MOLECULAR SELF-ASSEMBLED MONOLAYERS IN ELECTRONIC DEVICES

As mentioned above, a key goal of molecular switching on surfaces is to use changes in molecular conductance as a control element in electronic devices. Perhaps the most basic of molecular devices is a molecule that can be switched (81–84) between states of low and high conductivity (i.e., on and off). Indeed, Stoddart, Heath, and coworkers' (85) system, which has a 160-kb memory based on wired-up organic molecular switches, has demonstrated the viability of the bottom-up approach to constructing molecular components in electronic circuitry. This system uses redox stimulation to drive changes in the molecular state and hence the transport properties through the junction. Following this work, Bloom and coworkers (86) reported a fully light-driven, solid-state molecular-switching device based on monolayers of photochromic molecules. With this photoswitchable device, they made an important breakthrough regarding the critical problem of short circuits in molecular-based devices and in achieving unprecedented changes in conductivity. Their approach was to immobilize a dithienylethene photochromic switch on a gold surface. In earlier systems (such as those described above), the second electrode is brought into direct contact

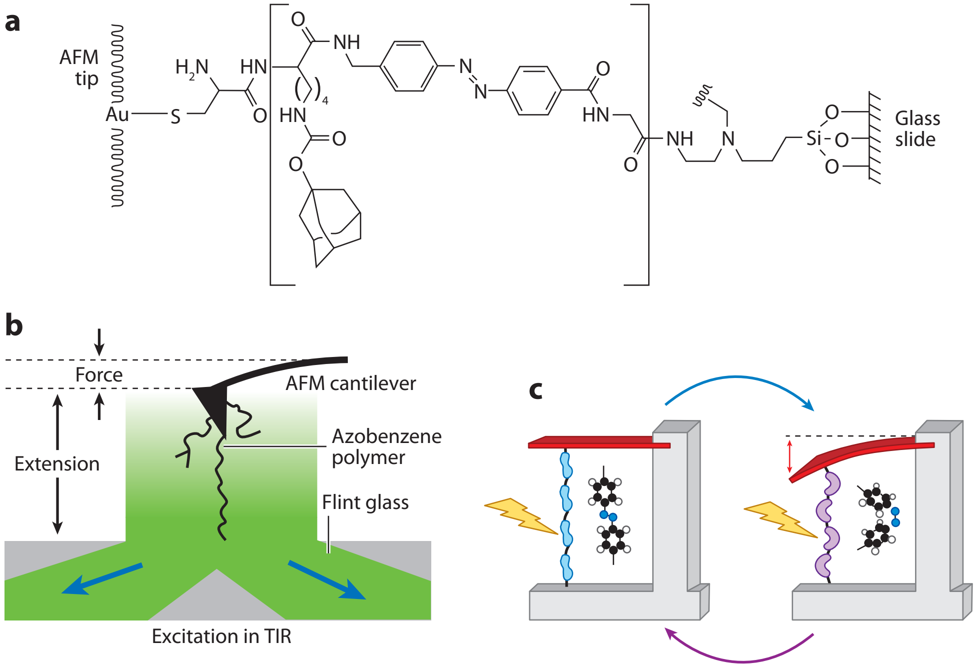

Figure 13

(*a*) A photochromic azobenzene-based polymer attached to an atomic force microscope (AFM) tip and a surface. (*b*) Irradiation with UV and visible light results in a contraction and relaxation of the polymer, respectively. (*c*) Schematic diagram showing changes to the tip upon irradiation using total internal reflectance (TIR). Figure reproduced from Reference 75. Copyright AAAS 2002.

with the SAM, which causes a high probability of defects and short circuits affecting the results. In Bloom and coworkers' system, the SAM was first coated with a conducting polymer layer, which provided the electronic connection to the second metallic electrode, thereby avoiding the formation of defects.

Irie and coworkers (87) recently reported a macroscopic switching device based on diarylethene photochromic molecules. In this device, a conductive polymer based on diarylethenes is

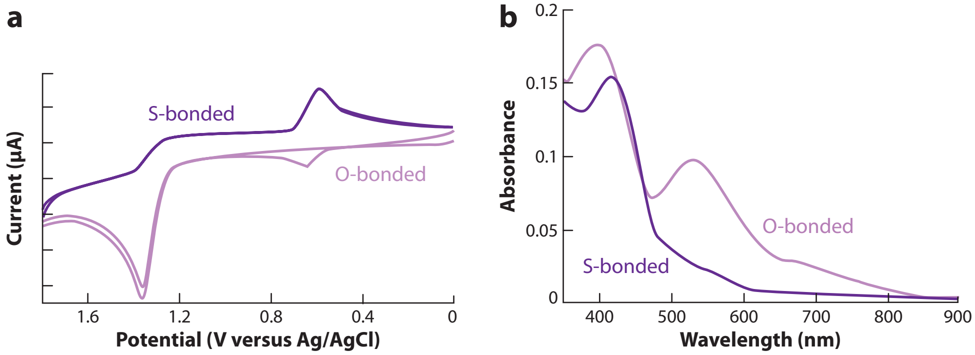

Figure 14

Cyclic voltammetry and UV/visible absorption spectra of two forms of a light-/redox-switchable complex $[Ru^{II}(tpy)(pic)(DMSO)]^{+}$. Figure taken from Reference 80, copyright ACS 2003.

sandwiched between various metallic and ITO electrodes. This study highlighted the importance of the type of metallic electrode employed on device performance. With aluminum and the open form of the diarylethene switch, they observed a rectifying behavior owing to the significant junction barrier at the aluminum/polymer interface. This contrasts with the ohmic characteristics of the gold/polymer interface, which in combination with the ohmic polymer/ITO interface provides for symmetric I-V characteristics for the device. This difference in the junction behavior was ascribed to aluminum's lower work function. In the ring-closed state (induced by UV light irradiation), higher currents and symmetric I-V curves were observed for both devices, which was attributed to the loss of the junction barrier at the aluminum/polymer interface owing to the presence of electronic states at the previously energetically forbidden region in the original polymer. The overall reversibility of current switching was poor, although this did not result directly from a loss in the reversibility of photochemical switching (characterized by the reversible changes in the intensity of fluorescence emission). Instead, it was attributed to the instability of the junction or interface structure upon irradiation. This is unsurprising considering that the shape of single crystals of diarylethenes can be changed following photoswitching (66); hence the polymer would be expected to undergo switching-related mechanical stresses. One can overcome this instability through the use of a nonphotochromic polystyrene polymer doped with diarylethene molecules (88).

More recently micrometer-sized devices based on a network of nanoparticles deposited between interdigitated nanogold electrodes (**Figure 15**) were reported (89). The nanoparticles were coated with switchable diarylethenes that provided bridges between the nanoparticles. Conductance switching by a sequence of UV and visible irradiation cycles was fully reversible, albeit with long switching times (10 h for the maximum on/off ratio).

Nuckolls and coworkers (90) reported recently a field-effect transistor based on an isolated single-walled carbon nanotube functionalized with spiropyran photochromic molecules. Pyrene- or alkane-tethered spiropyran molecules self-assembled on a single-walled carbon nanotube, which contacted with gold electrodes on each side. Alternating irradiation with UV and visible light switched the device between low and high conductance reversibly. The reversible switching in the functionalized single-walled carbon nanotube field-effect transistor was attributed to the photoswitching of the tethered molecules owing to one of two possible reasons: (*a*) The charge-separated state of merocyanine introduces scattering sites for the carriers by creating localized dipole fields around the nanotubes, or (*b*) the proximal phenoxide ion quenches the *p*-type carriers in the tubes and behaves as a charge trap.

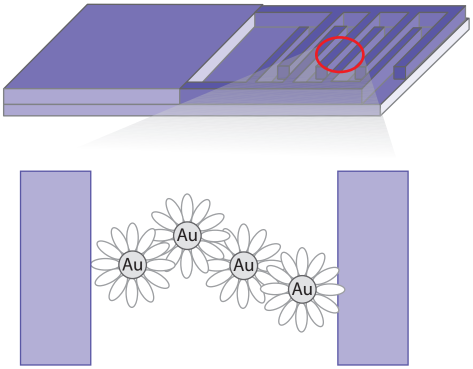

Figure 15

A diarylethene-gold nanoparticle network deposited on an interdigitated nanogap gold electrode. Figure reproduced with permission from Reference 89. Copyright RSC 2007.

7. PROSPECTS FOR MOLECULAR-BASED PHOTOSWITCHABLE SYSTEMS ON SURFACES

The immobilization of organic and inorganic photoswitchable molecules on conductive surfaces, in particular, allows one to tune the response in applications from dye-based solar cells to sensors (91, 92) and molecular electronics (5). In any application, however, the change in molecular properties induced by immobilization on a surface, such as the quenching of electronically excited states, clearly may be less important than the effect immobilization has on excited-state relaxation kinetics and especially on the conformational freedom required for isomerization, in terms of both photochemical switching times and quantum yields. Indeed, perhaps these latter considerations ultimately define the suitability of an approach in forming photoswitchable SAMs. Despite the sometimes troublesome effects of the surface confinement of photoswitchable molecules on their photochromic behavior, these effects can be viewed positively as an additional tool over and above the tuning of molecular structure in achieving control over molecular properties. The challenge still remains to develop surfaces and molecular anchoring methods that allow for increased spatial and electronic control over the interactions between molecules and bulk materials.

DISCLOSURE STATEMENT

The authors are not aware of any biases that might be perceived as affecting the objectivity of this review.

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