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Review

Synthetic light-activated molecular switches and motors on surfaces

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Abstract

Recent advances in synthetic methods and analysis techniques provide a basis for the construction and characterization of organized arrays of molecular switches and motors on surfaces. Among them, molecular systems that can be controlled by light are particularly promising because of their ease of addressability, fast response times and the compatibility of light with a wide range of condensed phases. The aim of this contribution is to highlight selected recent advances in building functional monolayers of light-activated molecules. Special focus is given to monolayers of molecules whose collective switching properties have been harnessed to produce macroscopic effects. The design, structure, and function of monolayers composed of bistable photochromic switches, which can control chirality, wettability, conductivity and self-assembly are described. A recent report on the successful demonstration of light-driven rotary motors functioning while grafted on gold surfaces will also be discussed, followed by a brief conclusion.

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1. Introduction

Molecular photochromic switches are an intriguing class of organic molecules which allow the control of molecular structure and function with light [1]. Consequently, this offers the possibility of effecting dramatic changes to the bulk properties of a system by irradiation. Attractive features of these systems include their short response times, reversibility, clean and tunable energy input, and the ability to convert an optical input into a variety of useful output signals. This is demonstrated by the fact that these molecules have already found commercial application in optical memory devices (including the recordable compact discs, CD-R) [2], light-sensitive sunglasses and ophthalmic lenses [3,4]. More recently, there has been a growing interest in using these materials in new applications such as molecular electronics, smart surfaces, control of supramolecular organization, and nanomachinery. Since many of these require the use of light-sensitive molecules attached to surfaces, the understanding of their individual and collective behaviour when they are organized into monolayers is essential. This highlight review will focus on selected recent examples where photochromic molecular switches and light-driven molecular motors operating on surfaces have been used to generate a change in surface properties, and where key aspects of the switching behaviour of the bistable molecules have been investigated. Section 2 introduces the concept of switches and shuttles and gives a brief description of the classes of molecules discussed throughout. In Section 3 examples of optically controlled wettability and surface free energy modification are treated. Section 4 highlights examples of optically controlled conductivity with a particular emphasis on the potential application to molecular electronics. Section 5 describes the optical control of supramolecular organization by switches which are physisorbed or chemisorbed on surfaces. Finally, Section 6 explores prospects for the use of switchable molecules such as azobenzenes or rotary molecular motors to control motion at the molecular scale.

The overall discussion will focus on light-induced switching of molecular monolayers self-assembled on surfaces. Since some applications require the use of systems beyond the scope of this review such as switchable polymeric, gel, or multilayer systems, we will direct the reader to some leading references on these subjects throughout the text.

1.1. On switches: What is a photochromic molecular switch?

Organic molecular photochromic switches are molecules that can be interconverted reversibly between two (meta)-stable states, **A** and **B**, by stimulus with light (Fig. 1). This change is the result of $cis \rightarrow trans$ photoisomerization, photocyclisation or a combination of the two. For the switch to be useful, it should meet three criteria: (1) it should be thermally stable; (2) the states **A** and **B** should have different properties, such as a large change in molecular geometry, polarity, UV–Vis absorption, etc., and (3) both states of the switch should be separately addressable.

In principle, an ideal photochromic switch would exhibit perfect photocontrol. This means that irradiation at different wavelengths (λ_1 and λ_2) allows quantitative photoconversion to states **A** and **B**, respectively. The ability to address each isomer selectively necessitates that **A** and **B** possess significant differences in their UV–Vis absorption spectra. In many cases this change in absorption is a desirable property in itself [4,5].

Systems with excellent photoequilibria have the obvious advantage that the change in property conveyed by the isomerization is maximized. In practice, however, this is rarely the case. By way of introduction, we will present a brief description of several of the different types of switches discussed in this review, including spiropyrans, azobenzenes, dithienylethenes and other alkenes, i.e., switches based on C=C double bond $cis \rightarrow trans$ isomerization.

1.2. Spiropyrans

Spiropyrans are molecular switches that can undergo reversible photoisomerization between a stable state and a metastable state using UV and/or visible light. They are well suited to control the surface free energy by light, since the relatively hydrophobic 'closed' spirocyclic isomer can be reversibly converted to a highly polar hydrophilic zwitterionic merocyanine isomer that has a much larger dipole moment as sketched in Fig. 2. The thermal conversion from the merocyanine isomer back to the closed spirocyclic form occurs



Fig. 1. Schematic representation of a molecular photochromic switch.



Fig. 2. Schematic representation of the reversible photoisomerization of spiropyran moieties.

typically with a half-life at room temperature of tens of minutes in non-polar media, while the photochemical isomerization with visible light occurs on a much faster timescale [6-8].

1.3. Azobenzenes

Functionalized azobenzenes have received considerable experimental and theoretical attention because they undergo light-driven $trans \rightarrow cis$ isomerization. Their *cis*- and *trans*-isomers have a different spatial arrangement of the aromatic moieties, and consequently show significantly different physical and chemical properties, as shown in Fig. 3 [9]. A major advantage of azobenzene switches is that they are easy to synthesize. However, an important drawback is that, depending on the nature of the substituents on the aromatic groups, these switches often undergo thermal $cis \rightarrow trans$ isomerization at room temperature.

1.4. Dithienylethenes

1,2-Dithienylethenes are reversible molecular switches consisting of conjugated parts connected by a switching element [1,2]. There are two isomers, i.e., a closed form and an open form of the molecule as sketched in Fig. 4. The π -conjugation extends over the



Fig. 3. Reversible photoisomerization of azobenzene moieties upon UV–Vis irradiation. The *trans* isomer is planar and the *cis* isomer is bent and more compact.



Fig. 4. Reversible photocyclisation of 1,2-dithienylethene moieties upon UV-Vis light irradiation.

entire molecule in the closed form whereas it is restricted to each half of the molecule in its open form. As a consequence, the closed form is expected to exhibit intrinsically better electrical conductance properties than the open form. The transition from closed to open form takes place for wavelengths $500 < \lambda < 700$ nm; for the reverse, one requires $300 < \lambda < 400$ nm. Furthermore, dithienylethenes usually exhibit excellent thermal stability.

1.5. Alkenes

The last class of switches dealt with here are olefins which undergo a $cis \rightarrow trans$ photoisomerization schematically shown in Fig. 5, a process which forms the basis for vision [10]. The best-studied group among these systems is the stilbenes, the photochemical isomerization process of which have been reviewed extensively [10,11]. While simple stilbenes also undergo undesired photochemical side reactions making them unattractive as switches, other robust switches have been prepared from olefins including overcrowded alkenes [12] and maleimides [13]. A key advantage of these systems is that they are generally thermally stable and photochemically robust. As with the switches discussed previously, the properties of stilbenes can be highly sensitive to the precise structure, including examples with perfect photocontrol [14]. Additionally, these molecular switches have formed the basis for light-driven molecular rotary motors [15] which will be discussed in the last section of this review.

The photoisomerization of alkenes can also be used to indirectly modulate the strength of association between hydrogen-bonded systems, which form the basis of molecular shuttles constructed from interlocked molecules such as rotaxanes or catenanes [16]. Stimuli-



Fig. 5. General scheme for the photochemical interconversion between the *cis* and *trans* configurations of an alkene.

responsive rotaxanes are molecular shuttles in which the macrocycle is interlocked onto the thread with one, two or more different binding sites ('stations') and terminated with two bulky stoppers [16,17]. The architecture of various types of rotaxanes permit large amplitude motion of the mechanically interlocked subunits in response to an external trigger like light, electrons, temperature, pH, nature of the environment, reversible covalent bond formation, etc. [16–18]. Switchable rotaxanes have been successfully used to vary physical properties such as conductivity [19], induced circular dichroism [20], or fluorescence [21] and are therefore viewed as potential elements for artificial molecular machinery.

2. Switching of wetting properties

Wetting phenomena occurring at the liquid/solid interface depend on the chemical composition and structure of the surface [22–24]. Control of the wettability can be achieved by a gradual modification of the surface free energy and thus changing the affinity of liquid to the surface. The modification of surfaces with molecular switches/molecular motors opens a new way to produce surfaces with well controlled wettability. Although the surface wettability can be controlled thermally [25], chemically [22,26] or electrochemically [27], the precision with which this is done still needs to be improved to meet the stringent requirements imposed by microfluidic systems, performing detection or reactions on a micro- and nano-scale, new types of nanodevices [28] or applications in a high-quality printing. Therefore, applying the energy input in the form of photons to trigger and manipulate the interfacial properties such as wettability is desirable [29]. Recently numerous examples of surfaces with photocontrolled wettability based on molecular switches and machines triggered by light have been developed [30–53].

2.1. Spiropyran functionalized surfaces

Since the two isomers of spiropyrans have dramatically different polarity and dipole moment, they are excellent candidates for application to photoresponsive surfaces with light-switchable wettability as shown in Fig. 6 [6,7,30,31].

The different physical and chemical properties of the two isomers have been exploited in the development of photosensitive membranes that act as a burst valves and allow the control of the passive transport of ions and water across a membrane [32]. These membranes were fabricated by grafting a spiropyran acid chloride on an aminosilane modified nanoporous alumina membrane. While these membranes were observed to switch from non-wetted (closed form of spiropyran) to fully wetted (open form of spiropyran) upon irradiation with UV light [32], the dewetting process was found to be more dramatic (as measured by ion conductance and change in surface free energy) when a hydrophobic molecule, decanoic acid amide, was used in conjunction with the switch with a 1:4 ratio [32]. Interestingly, the conversion of the open form back to the closed isomer with visible light irradiation occurred at all ratios of decanoic acid to spiropyrans but it was not accompanied by dewetting of the nanopores. Dewetting of the membrane was achieved only after drying. Although the light-controlled switching of the spiropyrans from its hydrophobic (closed) isomer to its more hydrophilic (open) form allows the external control of membrane wetting, the influence of the surface roughness and of the nanoscale pore dimensions in the dewetting process cannot be excluded.



Fig. 6. (a) UV–Vis light-induced isomerization of spiropyran from closed (spirocyclic) form to open (merocyanine) form. Two resonance structures of the open form. (b) Examples of water drops deposited on spiropyran functionalized surfaces after visible and UV irradiation. From [7].

Rosario et al. [7] used a sub-monolayer of photoswitchable spiropyrans covalently bound to mixed-monolayers of (3-aminopropyl)triethoxysilane and *tert*-butylchlorosilane to reversibly control water flow in glass capillary tubes. The water meniscus in capillaries coated with the photoresponsive layer of spiropyran rose 2–3 mm when the UV light (366 nm) was switched on, while the control tubes did not exhibit any light-induced capillary rise. The authors also suggested that the rate of the meniscus rise depends on the UV light intensity and the nature of the surface coating – the tubes having a more hydrophilic photoresponsive coating exhibited faster UV-induced capillary rise kinetics than those with a more hydrophobic photoresponsive coating. The light-induced changes in the surface free energy accompanied by changes in wettability were correlated, by means of fluorescence spectroscopy, to the switching between polar and non-polar forms of the surface-bound spiropyran [6].

While the spiropyrans grafted on flat surfaces were successfully used to control surface wettability, the application of spiropyran-coated rough surfaces appeared to be an even more effective tool for amplification of light-induced contact angle switching. Rosario et al. [8] showed that the combination of a rough surface morphology with switchable properties of spiropyrans significantly amplifies the changes of water contact angle with reduced contact angle hysteresis. The authors demonstrated that the low contact angle hysteresis on surfaces, obtained by grafting spiropyran on the silicon wafers covered with silicon nanowires, resulted in advancing contact angles under UV irradiation which were lower than the receding ones under visible irradiation. Hence water droplets can move faster on very rough surfaces than on flat surfaces using gradients in UV and visible light. The surface proposed by Rosario and collaborators may find future application as photonic controllers of water movement in microfluidic devices [7,8].

Another group of spiropyran-based photoresponsive surfaces with controlled nanopatterning and wettability are polymers doped with spiropyran [33,34]. In these systems the light-induced switching of the spiropyrans changes the liquid/air interface of air bubbles trapped in the outermost part of the doped polymer film, and therefore affects the wettability more strongly than the polarity changes of the spiropyrans alone.

2.2. Azobenzene functionalized surfaces

The *trans* \rightarrow *cis* photoisomerization of functionalized azobenzenes induces a change of the dipole moment in these molecules, which in turn determines the hydrophobic and hydrophilic nature of the *trans* and *cis* isomers [35]. Due to specific physico-chemical properties like dipole moment, affinity to polar molecules, etc. [36-50], azobenzene derivatives have been used successfully to control solution properties in bulk solvent (e.g. micelle formation and structure) [37-39] and surface properties including surface free energy, wettability, and liquid crystal alignment [36,40–44]. Surfaces with controlled wettability based on azobenzene derivatives were first demonstrated by Ichimura and co-workers [43] who used aminosilylated silica substrates functionalized with O-carboxylethylated calix[4]resorcinarene with photochromic azobenzene units. The surface free energy gradient necessary to initiate the directed motion of the liquid (olive oil, 1-methyl naphthalene, etc.) was achieved by performing the light-induced *trans* \rightarrow *cis* photoisomerization of the azobenzene moieties in the monolayer in a spatially controlled fashion., which generated a surface energy gradient across the length of the droplet. UV light irradiation (365 nm) resulted in formation of *cis* isomers of the azobenzene units with a larger dipole moment [45]. Therefore, the surfaces with exposed polar *cis*-azobenzene groups had a higher surface energy compared to the *trans* isomer terminated molecules. The spreading of the liquid droplets observed after the *trans* \rightarrow *cis* isomerization was almost complete (before the photostationary state was reached) under UV irradiation. Dewetting phenomena were observed when the *cis*-terminated surface covered with liquid droplets was irradiated with blue light (436 nm). The continuous asymmetric photoirradiation of the surface generated a constant free energy gradient between the advancing and receding edges of the droplets, causing the droplets to advance at constant velocity (35 μ m/s for olive oil), as demonstrated in Fig. 7 [43].

This system has the advantage that the droplets will continue to follow the surface energy gradient (*cis*-rich regions on the surface) without any intrinsic limit to the distance over which they can be transported. The direction and speed of the droplet are tunable by varying the direction and steepness of the gradient in light intensity [43,46]. Recently, Ichimura and co-workers [44] used a silanized silica substrate functionalized with *O*-octacarboxymethylated calix[4]resorcinarene with pendent *p*-octylazobenzene units to prepare a photoresponsive surface with switchable wettability. The wetting/dewetting induced motion of a liquid droplet are caused by the reversible changes of the surface free energy mediated by the reversible *cis* \rightarrow *trans* photoisomerization of the azobenzene molecules. The direction and velocity of the droplet were also in this case tailored by adjusting direction and steepness of the applied light intensity gradient.

A similar approach was used by Delorome et al. [40] and Hamelmann et al. [47] to prepare surfaces with controlled wettability. Contrary to the approach used by Ichimura and co-workers, these authors used a very compact azobenzene sub-monolayer covalently bonded to an alkyl silane monolayer containing an isocyanate group, and they were able to observe the changes in water and oil contact angle resulting from the reversible $trans \rightarrow cis$ isomerization of azobenzene induced with UV–Vis light irradiation. Microstructured surfaces based on azobenzene were also used to produce light-switchable



Fig. 7. Lateral photographs of light-driven motion of an olive oil droplet on a silica plate modified with *O*-carboxylethylated calix[4]resorcinarene photochromic azobenzene units. The olive oil droplet on a *cis*-rich surface moved in a direction of higher surface free energy by asymmetrical irradiation with 436 nm light perpendicular to the surface. The direction of movement of the droplet was controlled by varying the direction of photoirradiation. From [43].

membranes to control the mass transport during the electrochemical processes. Brinker and co-workers [45] used the photoresponsive nanocomposite thin films formed by surfactant-directed self-assembly of an azobenzene-modified silane and tetraethyl orthosilicate to modify the working electrode in an electrochemical cell. This self-assembled inorganic composite acted as a light-switchable nanovalve to control transport of ferrocene dimethanol or ferrocene dimethanol diethylene glycol molecular probes during electrolysis.

The irradiation of the membrane with UV–Vis light caused the $trans \rightarrow cis$ (435 nm) or $cis \rightarrow trans$ (360 nm) isomerization of azobenzene moieties, that enlarge (*cis* isomer) or reduce (*trans* isomer) the pore size and thus control the diffusion rate of the probing molecules to the electrode surface. The mass transport through the photoswitchable membrane was monitored by steady state oxidative currents at constant potential. The remarkable aspect of this system is its complete reversibility.

Azobenzene derivatives were also used to prepare reversible, light-induced micropatterns on surfaces [48,49]. Motschmann and co-workers [48] used UV (350 nm) and visible (455 nm) light in combination with suitable masks to prepare *cis/trans* patterns on a Langmuir–Blodgett monolayer of amphiphilic polymer films with an azobenzene chromophore in a side chain. Such surfaces act as rewritable wetting pattern transducers, and the different wetting behaviour of both interfaces was visualized by the formation of the water microdroplets, after cooling in a humid atmosphere [48]. These surfaces were completely 'erased' (water droplets spread on the surface) under illumination with blue light (455 nm) and a new pattern was created (microdroplets accumulate on the polar *cis* region) by illumination with 350 nm light. These 'smart' surfaces with photoswitchable properties were proposed as templates for high-resolution printing.

Radüge et al. [39] have reported reversible wettability changes upon light irradiation of surfaces functionalized with azobenzene-based polymers. As in the case of the spiropyranbased polymer films, the wettability changes upon light irradiation were attributed mainly to changes of the surface roughness of the film (changes in a polymer film structure due to the *trans* \rightarrow *cis* isomerization) and to the changes in the orientation of the net dipole moment [39]. An influence of temperature was also suggested [50].

2.3. Surfaces of 1,2-dithienylethene-based thin films

Although a number of surfaces with photocontrolled wettability based on spiropyrans and azobenzenes was reported, the number of examples based on dithienylethenes is limited. Contrary to photoresponsive surfaces based on spiropyrans and azobenzenes, dithienylethene-based thin films irradiated with UV–Vis light can exhibit dramatic morphology modifications rather than the changes of surface polarity. These changes can be used to produce superhydrophobic surfaces [51]. Uchida et al. [51] observed reversible changes in surface morphology due to the formation of fine fibril structures of a diameter $\sim 1 \,\mu$ m under irradiation with the UV light (254 nm) of the 20–30 μ m thick dithienylethene film (open form) deposited onto different substrates (e.g. glass, resin, metal) as shown in Fig. 8.

The changes of the surface morphology resulted in dramatic changes in surface wettability that were detected by contact angle measurements. The contact angle of water droplet measured on the open form isomer functionalized surface was 120° as expected for hydrophobic surfaces. Upon irradiation with UV light (254 nm) the colour of the film changed to blue indicating that the open form was transformed into the closed form, and the film became super hydrophobic; the contact angle increased to 163°. The open form was regenerated by irradiation of the 'coloured' film (closed form) with the visible light for 20 min. The authors suggest that the fibril crystals on the surface grow from the crystal lattice of the open form because upon irradiation the open form is converted to the closed form, and different mixtures of open and closed forms have different melting points [51].

2.4. Light-triggered rotaxane-functionalized surfaces

Photoresponsive surfaces based on switchable rotaxanes were recently employed to control surface wettability [52,53]. These surfaces were obtained by grafting the rotaxanes (*E*-isomer) on a 11-mercaptoundecanoic acid self-assembled monolayer on Au(111) by creating hydrogen bonds between the pyridine groups from the macrocycle and the carboxyl end-group of the SAMs as sketched in Fig. 9. In the *E*-isomer of the rotaxane, the macrocycle is positioned at the fumaramide station at the end of the thread, so that the hydrophobic tetrafluorosuccinamide station is exposed. Therefore, the surface prepared using this isomer has a polarophobic nature. Irradiation of such a surface with



Fig. 8. (A) Reversible formation of open and closed forms. (B) Reversible changes in surface morphology of a single crystal of 1,2-dithienylethene (scale bar: 10 μ m); (a) scanning electron microscope (SEM) image of the crystal surface of the open form from a side view (×1000) before UV irradiation (254 nm); (b) SEM image from a side view (×1000) of the surface after UV irradiation (254 nm, 12 W, 10 min) and storage in the dark for 24 h. (c) SEM image from a side view (×1000) of the surface after irradiation with visible light (>500 nm, 500 W, 20 min) and storage in the dark for 24 h. From [51].



Fig. 9. Light-switchable rotaxane with the fluoroalkane station exposed (*E*-isomer) were physisorbed onto a 11-mercaptoundecanoic acid-terminated self-assembled monolayer on Au(111) (hydrophobic surface). Illumination with 240–400 nm light caused the nanometer displacement of the rotaxane thread in the shuttles to shield the fluoroalkane units (*Z*-isomer) leaving a more polarophilic surface.

254–400 nm broad band light causes a photoisomerization of the fumaramide station, generating the maleamide station which has lower affinity for the macrocycle. The macrocycle therefore moves to the tetrafluorosuccinamide station on the thread (Z-isomer). The translocation of the macrocycle causes the shielding of the fluorine atoms, and thus changes the properties of the surface from polarophobic to more polarophilic, and increases the surface free energy. Berná et al. [52] demonstrated that irradiation on one side of the drop was able to generate a surface free energy gradient across the length of the drop large enough to mediate the millimeter-scale directional transport of a microlitre droplet of diiodomethane at speeds up to 1 μ m s⁻¹. In a separate experiment, it was found that the droplet could be moved up a 12° incline. The efficiency in elevating a droplet by biased Brownian motion to store potential energy is at least 50% of the total free energy made available by the nanometer movements of individual machine parts. It has been proposed that this type of liquid transport could be used to perform chemical reactions without vessels simply by bringing together individual drops containing different reagents [53].

Light-controlled changes of the surface properties induced on a single-molecule level allow the precise modification of the surface wettability and therefore are a crucial step for development microreactors, sensors or lab-on-a-chip devices. However, the application of these systems is still limited because fast reversibility has not been achieved [7,31–52]. While various authors give a different explanation of the behaviour of different liquids on the these photoresponsive surfaces, namely hysteresis of the contact angle, gradient of surface free energy or dipole–dipole interactions at the solid/liquid interface, an overall agreement that allows to understand the behaviour of highly-polar liquids like water is still lacking [39–44,52]. Currently, only spiropyran-based surfaces showed sufficiently high surface free energy heterogeneity influenced by the UV–Vis irradiation to create the driving force able to move water [7,24,31]. Despite the fast development of light-controlled surfaces based on molecular machines there is still no photoresponsive system which meets all requirements, i.e., that is employable for reversible control of wettability <u>and</u> applicable to different liquids.

3. Conductivity switching

One of the most widely explored application areas for functional molecular monolayers on surfaces pertains to molecular electronics. A major challenge of molecular electronics is to design devices based on addressable molecular structures and to incorporate these into integrated circuits [54–58]. Their ability to respond an external stimulus places light-triggered molecular switches among the most promising candidates as components for future molecular electronic devices. The utility of these switches as building blocks for molecular electronics is generally judged by what we know of their solution properties [1], or in the case of electrochemical phenomena, their properties when they are in transient contact with the surface of an electrode [59–62]. In the context of the development of molecular electronics, it is crucial to investigate how the properties of photoactive molecular switches are modified, modulated, or degraded when they are chemisorbed on metal surfaces or confined between two electrode surfaces, in a so-called "sandwich configuration". In particular, several phenomena contribute to deactivation of the excited states of light-powered switches once they are grafted on conductive surfaces. For example, the lifetime of the excited state of a chromophore decays as $(z/\lambda)^{-3}$ at short distances, z, from a metal surface whereas charge transfer decays proportional to $exp^{-\beta z}$ where β^{-1} is of the order of a few Ångstroms or less [63]. Yet, appropriate chemical engineering allows optoelectronic

functions of light-powered switches to be maintained on electrodes as shown by the examples described hereafter.

3.1. Reversible switching of azobenzenes on gold

As mentioned above, azobenzenes are well-studied because of their relatively simple structure, containing a nitrogen-nitrogen double bond, which undergoes a reversible $trans \rightarrow cis$ photoisomerization under irradiation. In the context of the development of molecular electronics, it became of particular interest to first achieve reversible switching of metal-bound azobenzene derivatives, and secondly to examine the correlation between the structure of the two azobenzene isomers (*cis* or *trans*) and their charge transport properties.

Investigations on the reversible photoswitching efficiency of azobenzene derivatives have been carried out on monolayers formed by chemisorption on both atomically flat surfaces and on gold nanoparticles.

In one of the first reported experiments correlating photochromic switching and electronic switching, the azobenzene derivatives were grafted through a linker attached to one of its phenyl rings onto Au(111) via a thiol-gold bond. An insulating matrix surrounding the switches was formed by a self-assembled monolayer (SAM) of dodecanethiol. A schematic representation of the switches/dodecanethiol mixed-monolayer which was used is shown in Fig. 10. The tip of a scanning tunneling microscope (STM) was used as a nanoscale probe for the charge transport properties of the switches embedded within the dodecanethiol monolayer. By using the STM apparent height as a switching signature, this experiment provided direct evidence for the photoisomerization of individual azobenzene molecules.

It was first found that azobenzene derivatives grafted on gold exhibit reversible photoswitching, probably facilitated by the use of a short alkyl spacer partially preserving the photoactive azobenzene unit from the influence of the surface [64]. This result highlighted the importance of the chemical structure of the spacer used to connect the photoactive switching units to the considered conductive surface.



Fig. 10. Schematic structures of an azobenzene derivative which can be grafted on a surface through a S–Au bond. (a) *trans* isomer, (b) *cis* isomer [64]. (c) The *trans* isomer was inserted in a SAM of dodecanethiol, forming a mixed azobenzene/dodecanethiol monolayer. The state (open form or closed form) of the embedded azobenzenes was characterized by their apparent height as seen by STM, which measures a convolution of real physical height and of local density of states.

However, investigation of molecular photoswitching in SAMs by STM under ambient conditions is hampered by the fact that prolonged exposure to UV light in air causes irreversible damage to the SAMs by oxidation of the thiol bond [65]. In addition to the in situ study of switching of individual molecules, a statistical investigation of conductance switching was also carried out to confirm that this switching was a light-induced switching – rather than voltage-induced switching [66] or stochastic switching [67].

Moreover, despite their reversible photoswitching, azobenzenes derivatives do not exhibit a clear intrinsic conductivity switching. Indeed, when azobenzenes undergo a $cis \rightarrow trans$ isomerization, the physical height of the molecules is altered, see Fig. 10a and b. This does not significantly change the conductance of the molecule itself but does significantly change its height. The apparent changes in conductivity observed by STM were consequently attributed to the switching of height of the molecules rather than to an internal structural modification leading to a modification of resistance.

3.2. Switching of 1,2-dithienylethenes on electrodes

3.2.1. One-way switching of 1,2-dithienylethenes on gold

In contrast to azobenzenes, dithienylethenes have a similar physical height in both closed and open forms. This allows their charge transport properties to be described without complications or artefacts due to important changes of their physical length. Confirmation of 1,2-dithienylethenes potential for molecular electronics was obtained first by studying the conductivity of a dithienylethene switch with thiophene groups as spacers and functionalized by two thiol functions chemisorbing on each side of a mechanically controllable break junction, as depicted in Fig. 11. I(V) curves revealed that:



Fig. 11. Chemical structures corresponding to closed and open forms of a 1,2-dithienylethene derivative functionalized with two thiophene spacers and having at its extremities two sulphur-based thiol groups which chemisorb on gold (molecule **11**).

(i) switching a molecule from the closed to the open form results in a significant resistance increase of three orders of magnitude;

(ii) once the switch is connected to gold *via* the Au–S bond, it could only be switched from the closed to the open form [68].

The result has been discussed theoretically and although the reasons for one-way switching of the closed form of 1,2-dithienylethene **11** chemisorbed on gold are still under discussion, it appears that the partial disappearance of switching properties is likely due to the fact that HOMO and LUMO levels of **11** are modified by chemisorption [69]. This experimental work with break junctions was followed by studies of the switching process of surface bound molecules using other techniques which give more information about the geometry of the connections to the electrodes, the phenomena which take place during measurement and the number of molecules involved in the junction. Therefore, analogues of **11**, which are functionalized with only one thiol group, were synthesized. In particular, one-way switching of molecule **12** inserted in a dodecanethiol SAM on Au(111) (shown in Fig. 12) was also established by STM [70]. Ultrafast spectroscopy of **12** grafted onto gold colloids finally confirmed the deterioration of the switching properties when a switching 1,2-dithienylethene unit is linked to a conductive surface via a thiophene linker [71].

3.2.2. Reversible switching of 1,2-dithienylethenes on gold

To achieve fully reversible interconversion between the open and closed forms, the photochemistry of monolayer-covered gold nanoparticles was extensively investigated. In the first reports, long alkyl chains were used to isolate the 1,2-dithienylethene photochromic units from the metal surface to some extent [72]. This strategy was also applied successfully in related studies concerning other types of photoswitches, connected to the surface through alkyl chains containing about six carbons [73]. However, using a long alkyl chain spacer to isolate the switching units from the conductive surface also decreases the overall conductivity of the molecules, which is a drawback for possible applications in molecular electronics. Consequently, it appeared more promising to explore the possibility of an adapted spacer which preserves the photochromic properties of the molecules while remaining as short as possible. To expedite the evaluation of a series of tethers through which the switches could be grafted on the surface, the photochromic properties of a series of 1,2-dithienylethenes chemisorbed onto gold nanoparticles were studied as a convenient model system [74].



12 open form

Fig. 12. Chemical structure of dithienylethene 12 in its open form, attached to a gold nanoparticle. The structure of 12 is similar to the structure of 11, with the difference that 12 has only one sulphur-based thiol group. Consequently, 12 can chemisorbed on gold only from one side. After chemisorption, this molecule undergoes only one-way photoswitching.



13 meta linker, open form



13 para linker, open form

Fig. 13. Chemical structure of 1,2-dithienylethenes with phenyl linkers in *meta* and *para* positions, in the open form and attached to a gold nanoparticle. Even grafted on gold nanoparticles, **13** undergo reversible light-induced switching.

This work demonstrated that the linker strongly determines whether the molecules' photoisomerization properties are preserved upon chemisorption or not [74]. As already mentioned, for molecule 12 which is grafted in its open form on gold via a thiophene linker (see Fig. 12), only one-way switching was observed. Alternatively, reversible switching was observed for the switches with phenyl linkers in the *meta* and *para* positions shown in Fig. 13. These findings highlighted that small changes in the molecular structure can have an enormous impact on the overall photochemical properties of hybrid organic molecule/ metal systems. However, the use of UV-Vis spectroscopy on gold nanoparticles in solution left open the possibility that molecules could desorb from the surface, photoisomerize and finally reattach. Therefore, optically transparent films of gold on mica [75] and semi-transparent Au(111) surfaces on mica [76] were prepared. UV-Vis spectroscopy of these surfaces functionalized by monolayers of 1,2-dithienylethenes was carried out at the solid/ gas interface, in order to ensure that the molecular switches remain attached to the surface during photoisomerization processes. These studies confirmed reversible switching for switch 13 with a phenyl linker in the *meta* position, and of a similar switch with one CH₂ group separating the aromatic part from the gold surface. The switching of individual molecules 13 on Au(111), with a linker in the *meta* position, was also investigated by STM [76]. The experimental set-up used was inspired by previous investigations of azobenzenes (Fig. 10): isolated switch molecules 13 were inserted in an insulating monolayer of dodecanethiol. Their switching behaviour was then investigated monitoring the STM apparent height. In its open form, 13 has similar charge transport properties and consequently the same apparent height as dodecanethiol. Therefore, 13 in its open form cannot be distiguished within the SAM of dodecanethiol (Fig. 14a, left panel). On the contrary, despite the fact that the open and closed forms of 13 have similar lengths, the closed form is clearly distinguishable by a higher apparent height (Fig. 14a, right panel). This constitutes an additional indication that closed and open forms are characterized by intrinsiqually different charge transport properties. By using the apparent height of 13 as a switching signature, the authors confirmed reversible photoswitching for 13 on Au(111) (Fig. 14b



Fig. 14. 1,2-Dithienylethene 13 with a *meta* linker is inserted in a SAM of dodecanethiol and chemisorbs through a thiol bond to Au(111). (a) In the open, less conductive form, 13 has the same apparent height as the surrounding dodecanethiol molecules. Alternatively, in the closed form, 13 present a bright contrast which is related to their better charge transport properties. (b) Under appropriate irradiation, molecule 13 switches from open to closed (left) and from closed to open form (right), respectively. (c) Schematic representation of the reversible switching of 13 on Au(111). From [76].

and c). This is drastically different from the behaviour of **11** and **12** and suggests that the reversibility of switching could be directly related to the conjugation between the switching unit and the substrate. To investigate this aspect, further experiments will have to be carried out with a variety of linkers. Understanding the interplay between the chemical structures of 1,2-dithienylethenes and their switching properties will provide a firm basis for creating optoelectronic devices.

3.2.3. Electrochemical readout of photostimulated switching

The development of practical write/read/erase memory devices will ultimately depend on additional functions other than the molecular switching write/erase function (e.g. photochromism). That is, to achieve a write/read/erase memory device a secondary physical signal will be required, to read the state of the switch (in the case of 1,2-dithienylethenes, closed form or open form) non-destructively. Reading and amplification of the signal produced by photostimulated switches were achieved electrochemically, both for chemical and biochemical switches.

In addition to their well-known photoswitching, in solution, 1,2-dithienylethenes switch from open to closed form by irreversible electrochemical oxidation and subsequent reduction of the formed species [59]. When SAMs of 1,2-dithienylethene switches are grafted on conductive surfaces via a long alkyl chain spacer, they are sufficiently isolated from the surface to undergo multi-cyclic photochemical ring-opening and ring-closing. In that way, reversible photoswitching of a 1,2-dithienylethene covered gold surface [77] or ITO surface was achieved and, after photoswitching, the state of the switch (open form or closed form) could be read non-destructively by electrochemical means [78].

Biochemical switches have also been extensively studied. In order to photoactivate redox proteins reversibly, the first reported approach consisted in modifying a photoisomerizable monolayer that acted as a photoactive command surface for the association or dissociation of these redox proteins at the electrode interface [79]. A second method to photostimulate redox enzymes coupled to an electrode surface involved the application of photoisomerizable electron mediators as optical triggers for bioelectrocatalytic transformations [80]. The third approach investigated to photostimulate biocatalysts included chemical modification of redox enzymes by photoisomerizable compounds and immobilization of the photoswitchable biocatalysts on electrode surfaces [81].

4. Controlling supramolecular organization with light-sensitive monolayers

4.1. Photocontrol of supramolecular organization triggered by functional SAMs on flat surfaces

By analogy to molecular electronics in which switches flip between "on" and "off" conductivity states, photoswitchable synthetic or natural biomaterials are systems in which optical signals generate discrete "on" and "off" states of biological functions. For example, vision and other light-triggered biochemical transformations in plants and living organisms are sophisticated biological processes in which optical signals are recorded and turned into chemical events. Then, the information is amplified through physiological processes by surrounding proteins and membranes. The field of photoswitches based on biomaterials has developed extensively in the past decades thanks to the experience gained in manipulating biomaterials through genetic engineering and the fabrication of surfaces modified by biologically active materials [82,83].

Although artificial approaches do not reach these levels of complexity yet, various investigations have focused on transferring information from a SAM of photochromic molecules into the third dimension. Numerous reports describe the use of liquid crystalline phases for signal amplification because of their remarkable ability to change their long-range ordering and optical properties in response to a realtively weak external trigger. In particular, various liquid crystals (LCs) have been deposited on top of photoswitchable SAMs as schematically depicted in Fig. 15. Control of the alignment of LCs driven by photochromic switching of molecules immobilized on a surface was first described by Ichimura et al. [84]. In this work, the molecular orientation of a nematic liquid crystal was switched from homeotropic (main axis of the molecules on average perpendicular to the substrate) to planar (main axis of the molecules on average parallel to the substrate)



Fig. 15. Illustrative representation of the surface-assisted control of the alignment of LC molecules. The surface of which the LC molecules are deposited is functionalized by a monolayer of azobenzenes. When the azobenzene are in their *trans* form, the homeotropic anchoring of the LC molecules drives the orientation of the LCs in the whole LC mesophase. Upon irradiation with UV light, the azobenzenes undergo a *trans* \rightarrow *cis* photoisomerization. Since the azobenzenes from the monolayer isomerize to form the *cis* isomer, the favoured anchoring of the LC molecules on the surface becomes the planar one and the whole alignment of the mesophase is consequently modified. This monolayer-triggerd photoalignment of LC mesophases is reversible [42].

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by $cis \rightarrow trans$ photoisomerization of azobenzene units attached to a quartz surface. Many subsequent investigations have studied the monolayer-mediated photoalignment of liquid crystals [42]. In addition to the alignment of nematics, the orientation of side chain LC polymers, lyotropic LCs, cholesteric LCs, and even highly viscous discotic LCs can be controlled by structural switching of the molecules composing the monolayer [42].

4.2. Photocontrol of supramolecular organization triggered by functional SAMs on metallic nanoparticles

A special case of monolayers formed on surfaces are those formed on metallic nanoparticles. One reason for this is that monolayer-protected gold nanoparticles are expected to strengthen the effect of monolayer-induced organization by taking it into the third dimension. Moreover, their use bridges the gap between measurements in solution and molecular device techniques which demand expensive and time-consuming device fabrication. Connecting photochromic switches to nanoparticles has been used to improve our understanding of how photochemical properties of light-sensitive molecules are affected by quenching from a metallic surface.

For example, competition between $cis \rightarrow trans$ isomerization and [2 + 2] cycloaddition of stilbene derivatives has been described on gold nanoparticles [85]. In contrast to the photochemical reactivity of stilbenylalkyl sulphides when appended as SAMs on planar gold surfaces, the chromophores present on these nanoparticles exhibit efficient $trans \rightarrow cis$ photoisomerization and block [2 + 2] photodimerisation. Also, a number of studies have focused on using SAM-protected nanoparticles as scaffolds for molecular recognition [86]. Photochemical control of molecular recognition between diaminopyridinefunctionalized gold colloids and naphthalimide could be achieved by incorporating azobenzene moieties in the SAM. The enhanced binding observed with the azobenzene moieties in their *trans* form was interpreted in terms of combination of π -stacking effects and better access to binding sites due to reduced steric hindrance [87].

Additionally, capped gold nanoparticles are of particular interest for optoelectronics because of their plasmon absorption in the visible region of the electromagnetic spectrum. These opto-electronic properties of metallic nanoparticle networks can be modulated by various means including interparticle separation [88]. By grafting light-triggered switches on gold nanoparticles it is possible to control this interparticle separation within the network. To do this, a connecting unit containing an azobenzene functional group was grafted onto the surface of different nanoparticles by two thiol groups positioned at the extremities of the linker. Gold nanoparticles thus form a network connected by light-sensitive linkers. The total length of these linkers shrinks from 3 nm in the *trans* form to 2 nm in the *cis* form. Prasad et al. demonstrated by surface plasmon resonance spectroscopy that the interparticle spacing is controlled by the reversible *cis* \rightarrow *trans* photoisomerization of the azobenzene moiety of the linker as shown in Fig. 16 [89].

Another example of how the organization of nanoparticle networks can be controlled reversibly by light-sensitive molecular monolayers is based on the dimerisation of thymine-capped nanoparticles. Thymine bases photodimerise upon irradiation at wavelengths above 270 nm and revert back to thymine again upon irradiation at wavelengths below 270 nm. UV irradiation of a solution of gold nanoparticles modified with the thymine units resulted in the formation of aggregates. Photochemical aggregation of gold nanoparticles was thus achieved by photodimerisation of thymine units [90]. Similarly, sedimentation of



-N=N- azobenzene moiety

Fig. 16. Schematic representation of the photocontrolled interparticle spacing in a gold nanoparticle network. This network was formed by addition of a linker molecule constituted by an azobenzene moiety suitably derivatized on either side with gold surface sensitive groups, into a solution of these gold nanoparticles. The reversible *trans* \rightarrow *cis* isomerization of the azobenzene moiety constituting the link in between the nanoparticles is triggering either a contraction, or reversibly an expansion of the whole network. From [89].

azobenzene-capped nanoparticles by $trans \rightarrow cis$ photoisomerization was observed in toluene where different degrees of solvation between *trans* and *cis* isomers triggered the coagulation of the particles [91].

4.3. Light-induced pattern modification in 2D physisorbed systems studied by STM

Numerous investigations on the reversible photo-addressability of organic compounds on surfaces have been carried out with molecular or (sub)-molecular resolution by STM. Self-organized monolayers formed by physisorption of various molecules from solution have been studied with STM at the interface between a liquid and an atomically flat and conductive surface such as highly oriented pyrolytic graphite (HOPG) [92,93], Au(111) [94] or MoS_2 [95]. The structure of these self-organized monolayers depends on the chemical structure of the molecules used as building blocks, on the chemical properties of the solvent that is used for deposition (in particular polarity), and on the physical and chemical properties of the surface on which the monolayers are formed. Light was recently explored as a possible external stimulus to modify the structure of these self-organized 2D systems and thus of the pattern they form on the surface.

Photoinduced reactions of organic compounds physisorbed at the graphite/liquid interface have been investigated for several systems using STM. They usually induce a modification of the molecular structure which in turn leads to a modification of the self-organized pattern in 2D. Heinz et al. reported the photodecomposition of 10-diazo-2-hexadecylanthrone to 2-hexadecyl-9,10-anthraquinone on HOPG [96]. They were able to identify both the reactant and the product at the HOPG/liquid interface. Moreover, the light-induced *cis* \rightarrow *trans* isomerization of *azobenzene* derivatives has been intensively investigated by STM [97]. Domains of *cis* and *trans* geometries have been simultaneously imaged with submolecular resolution and identified at the HOPG/liquid interface. However, in this example, the *trans* \rightarrow *cis* photoisomerization does not occur within the self-organized monolayer but in the liquid phase on top of HOPG. This transformation in solution is followed by adsorption of the *cis* isomers to the substrate. Since the molecular assemblies of *cis* isomers in azobenzene adlayers are not stable, the *cis* isomer domains disappear quickly and after some time only *trans* isomer domains are observed [98].

The next challenge consisted of achieving structural switching while the switches forming the monolayer remain on the surface. Unequivocal proof of photoinduced reactions at the liquid/HOPG interface, i.e., proceeding only in the monolayer and not in the supernatant solution have been reported only in very few systems. For instance, the photopolymerisation of diacetylene molecules on HOPG has been demonstrated [99]. However, in this example the symmetry of the molecular packing was unchanged before and after reaction, only the STM contrast was altered. In contrast, the [2+2] photochemical dimerisation of cinnamate derivatives triggered a modification of supramolecular ordering: while no photodimerisation was expected to occur in monolayers of long tail cinnamate esters (shown in Fig. 17, left panel), due to the self-assembly of the molecules in an orientation which prevented the necessary orbital overlap, fluctuations in the local geometry of packing allow the reactive centres to approach each other. Thus photodimerisation occurred as shown by the STM image at the HOPG/liquid interface reproduced in Fig. 17, right panel [100]. On the contrary, short tail cinnamate esters (Fig. 17, left panel) form monolayers in which the alkyl chains are interdigitated. No photodimerisation occurred in self-organized monolayers of these short tail cinnamate esters, demonstrating that the interdigitation of monomers limits packing fluctuations and thus switching of structure on the surface. This emphasized the importance of studying the structure of self-organized molecular monolay-



Fig. 17. (left) Chemical structures of the cinnamate esters investigated in Ref. [100]. (right) STM image of the photodimerised long tail cinnamate ester on HOPG. From [100].

ers for the development of future functional molecular systems. A limitation of these types of studies is that reversibility of switching was not achieved.

The study of in situ photoinduced structural transformations in a monolayer is less frequently reported on metal surfaces than on HOPG, despite the fact that the former are of crucial importance in the development of photoresponsive and electronic nanodevices. This might be partially explained by the fact that in some cases molecule/substrate interactions are stronger on silver or gold surfaces than on HOPG. However, Xu et al. have described the photodimerisation of cinnamic acids on Au(111) [101] and Bai et al. have reported the photopolymerisation reaction of diolefins by repeated [2 + 2] photocycloadditions on Au(111) [102]. Lately, in situ *cis* \rightarrow *trans* photoisomerization was demonstrated for stilbene derivatives on Ag/Ge(111) surfaces also [103]. In the latter case, the *cis* isomer domains formed spontaneously and simultaneously along with the *trans* isomer domains from the gas phase. The *cis* isomer domains are metastable and could be transformed to *trans* isomer domains by brief exposure to 248 nm UV light. It should be emphasized that STM observation of a structural transition induced by thermal *trans* \rightarrow *cis* isomerization was achieved only recently [104].

5. Light-driven molecular scale motion in monolayers

A crucial step toward the development of molecular systems operating as nanomachines capable of performing useful work at the nanoscale is the immobilization of these molecular motors on surfaces. Both linear and rotary synthetic molecular motors have been grafted on surfaces. Among them, redox systems have been proven to be very useful in a number of cases, including an impressive application of a switch in a monolayer, which was then used to deflect gold cantilevers in a muscle-like behaviour [105].

5.1. Light-driven linear molecular motors

While in this review we have focused primarily on monolayers of photochromic switches on surfaces and on nanoparticles, elegant examples of light-controlled molecular muscles based on light-driven molecular motors fixed on rigid surfaces appear particularly attractive and interesting. Gaub and coworkers [106] reported the evaluation of the force generated by a single azobenzene–polyamide polymer grafted between a flint glass surface and an AFM tip, as shown schematically in Fig. 18. They found that upon appropriate light stimulus, their photochromic polymer would contract against external force acting along the polymer backbone. The irradiation was performed using total internal reflection (TIR) to avoid light-induced heating of the AFM tip. Interestingly, the polymer (estimated to contain approximately 47 azobenzene subunits) was capable of generating a total contraction of 2.8 nm. This deflection was just less than half of the potential, 6.0 nm, predicted by modelling the total chain contraction generated by the additive *trans* \rightarrow *cis* isomerization processes. This was attributed to incomplete irradiation of the chromophores present at the end of the chain, furthest away from the area of irradiation.

5.2. Light-driven rotary molecular motors

The immobilization of molecular motors on surfaces is especially important for rotary molecular motors, whose rotary motion is very challenging to harness while the system is



Fig. 18. Schematic depiction of the azobenzene polymer grafted onto a glass surface, allowing TIR irradiation of the polymer and not the cantilever. From [106].

overwhelmed by Brownian motion in solution [107]. Despite the fact that unidirectional light-driven rotary motion has been demonstrated in solution [108,109], reports extending this controlled rotary motion to surfaces are still scarce. The first example of light-driven unidirectional rotary motion at the molecular scale on a surface was reported by van Delden et al. [110]. Building on their previous work developing light-driven rotary motion of the upper rotor half of the molecule relative to the lower 'stator' half into *absolute* rotary motion of the rotor relative to the surface of gold nanoparticles (Fig. 19a). Rotary molecular motors were grafted on the surface of gold nanoparticles through two gold–thiol bonds to prevent uncontrolled Brownian rotation. In analogy with the approach described in Sections 3.2.2 and 4.2, the attachment of the motor to gold nanoparticles while allowing the use of stan-dard solution analysis techniques, including UV and circular dichroism (CD) spectroscopy.

In the unidirectional rotation, the motors undergo two energetically uphill photochemical isomerization steps (steps 1 and 3, Fig. 19b), each followed by an energetically downhill irreversible thermal helix inversion step (steps 2 and 4, Fig. 19b) resulting in a full 360° rotation of the rotor half of the molecule with respect to the stator, and with respect to the surface in the surface-grafted system. The direction of rotation is controlled by the configuration at the stereogenic centre.

The rotary process was monitored by CD spectroscopy of the motor-protected nanoparticles in toluene at room temperature. UV irradiation of the surface-grafted motor in its stable form generated a photostationary state, resulting in an approximate inversion of the CD spectrum (solid black to dotted, Fig. 19c). This change in the CD spectrum indicated an inversion of the molecular helicity which occurs when the surface-grafted motors isomerize from a stable to an unstable form (step 1 in Fig. 19). Subsequent heating ($T \ge 50$ °C) of the photostationary state sample containing predominantly the unstable isomer of the motor resulted in the full conversion of unstable motor molecules to stable motor molecules as a result of the thermal helix inversion (step 2, Fig. 19). It was verified by ¹H NMR spectroscopy that the molecule's light-driven rotary motion occurs while the motor molecules remain grafted to the surface throughout the rotary process. Steps 3 and 4 follow in analogy with steps 1 and 2, respectively. The kinetics of the thermal isomerization of the unstable form of the motor molecules to the stable form (steps 2 and 4) were determined by monitoring the change in CD intensity with respect to time at various



Fig. 19. (a) Schematic representation of a rotary molecular motor tethered to a gold nanoparticle through 2 legs, only one motor is shown for clarity. (b) The four-state unidirectional rotation of functionalized nanoparticle *motor on Au* is shown (*hv*: photochemical step; Δ : thermal step). (c) CD spectra of stable-*motor on Au* (solid black), photostationary state when irradiated at ≥ 280 nm (dashed black), and the photostationary state when irradiated at 365 nm (dotted black) samples and after sequential photochemical and thermal isomerization steps. From [110].

temperatures. Using the Eyring equation, it was determined that the Gibbs free energy of activation ($\Delta^{\ddagger}G^{0}$) for the isomerization of the unstable isomer of the motor to the stable isomer while grafted to the gold nanoparticle was $96 \pm 2 \text{ kJ mol}^{-1}$. This value was slightly higher than the barrier that was found for the parent molecule in solution ($\Delta^{\ddagger}G^{0} = 94 \pm 2 \text{ kJ mol}^{-1}$). The authors suggested that this small difference in energy of activation could be due to the reduction in the degrees of freedom of the molecule when grafted onto the surface of the gold nanoparticles.

The functioning of light-driven rotary motors assembled on a gold nanoparticle is a promising step toward investigations aimed at harnessing work from their controlled rotational motion. This work is most interesting because it offers a fundamentally new capability – namely the ability to rotate molecules in a controlled fashion. This ability in concert with modern patterning techniques should allow the "bottom up" manipulation of matter in new ways.

6. Conclusions

A key objective of nanoscience is to create functional systems, smart materials and in general to open new areas of research with small (nanoscale) objects having properties

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which are specific to their size. These fascinating but challenging tasks require the collaboration of specialists from many different fields, from physics to biology. The improvement in chemists' ability to manipulate and synthesize functional and addressable molecules has triggered the development of a whole new area of research concerning the design of molecular switches and molecular machines and their study in solution. In parallel, developments in instrumentation have made it possible to better characterize and consequently to better understand which parameters determine the structure of organic monolayers or thin layers. These combined efforts have resulted in new applications for functional molecular and supramolecular systems, as well as in exciting prospects for their future application in smart materials and in nanotechnology.

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