



Novel photo-switching using azobenzene functional materials

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Abstract

Azobenzene (azo) chromophores have been incorporated into a wide variety of materials and molecular architectures, including polymers, dendrimers, and molecular glasses. Azobenzene exhibits a uniquely clean and efficient photochemistry, with facile geometric isomerization about the azo bond, converting the molecule from *trans* to *cis*. This review discusses the extensive number of investigations of azobenzene photo-switching and photo-modulation. In particular, azos can be used to alter material behaviour with light, switching both molecular and macroscopic properties. A large number of photobiological studies have shown that interfacing the azo chromophore with enzymes and biopolymers is feasible and useful. The all-optical surface patterning unique to azobenzenes is also reviewed. Lastly, azobenzene photomechanical effects are discussed. © 2006 Elsevier B.V. All rights reserved.

Keywords: Azobenzene; isomerization; Surface patterning; Photomechanical; Photo-switching

1. Introduction

Photochemistry has evolved from an academic curiosity to a major component of modern technology over the last century. The production of now-ubiquitous microelectronics relies on optical lithography and a wide range of photochemical tricks crafted for that purpose. Similarly, the backbone of modern international communication is optical, and the materials required for the related devices are exploiting ever-more-exotic photochemical phenomena. Though these technologies are now well established, there is nevertheless intense effort into designing new photochemical materials with enhanced photo-response. The azobenzene chromophore has been studied for over 70 years, yet it continues to present new and unique optical effects. Due to its clean photochemistry, and substantial change in material properties during light irradiation, it has been investigated as an active component for a variety of applications, from lithography, to non-linear optical devices, to all-optical switches, and even data storage. It has also served as an invaluable photochemical model system, enabling greater insight into a wide range of systems. Furthermore, the azobenzene chromophores have been invaluable as scientific tools, enabling a large number of

unique and truly elegant investigations. Specifically, by acting as a photo-switch, the azobenzene unit allows one to modulate a desired property or elicit conversion of a species or phase, on command.

This review discusses some of the photo-switching and photomechanical aspects of the rich azobenzene photochemistry, as well as the many unique photofunctional azobenzene materials that have been prepared. In particular, we shall attempt to highlight experiments where the use of azobenzene switching has enabled unique types of studies to be realized. The azobenzene class of chromophores is characterized by the azo linkage ($-N=N-$) that bridges two phenyl rings. This extended aromatic structure gives rise to azobenzene's intense optical absorption and related optical properties. Strictly, 'azobenzene' refers only to the parent molecule, though the term is now frequently used to refer to the entire class of substituted azo molecules. The unique commonality among the azobenzene molecules (azos) is the clean and efficient photochemical isomerization that can occur about the azo linkage when the chromophore absorbs a photon. The two states are a thermally stable *trans* (also denoted E), and a meta-stable *cis* configuration (the Z state). Light anywhere within the broad *trans-azo* absorption band will elicit photochemical isomerization (with high quantum efficiency near the λ_{max}). The *cis* configuration will then typically relax thermally back to the *trans* state with a lifetime that depends sensitively upon the particular azo's substitution pattern, as well as on local conditions. Irradiation of the *cis* form with light within its (possibly distinct) absorption band can

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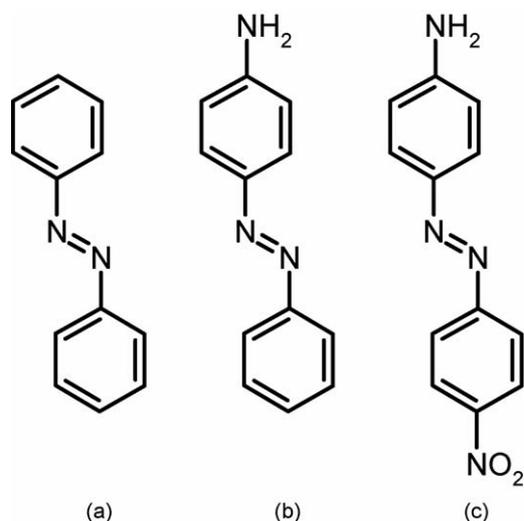


Fig. 1. Examples of azobenzene molecules that fall into the three spectroscopic classes: (a) azobenzenes (b) aminoazobenzenes, and (c) pseudo-stilbenes.

also elicit the photochemical *cis*-to-*trans* isomerization. This simple and clean photochemistry gives rise to the innumerable photo-switching and photo-conversion capabilities that have been discovered in this novel system.

2. Azobenzene photochemistry

The azos are typically divided into three classes, distinguished by their spectral and photophysical response, which is intimately tied to their substitution patterns. These categories are [1]: the azobenzene-type molecules, the aminoazobenzene-type, and the pseudo-stilbenes (Fig. 1). The azobenzene-type molecules are similar to the parent (unsubstituted) azobenzene molecule, and have their most prominent absorption features in the UV. The aminoazobenzenes are substituted at the ortho- or para- position with an electron donating group (typically an amino, $-\text{NH}_2$), and exhibit strong absorption features in the visible-blue region. Lastly, the pseudo-stilbenes are characterized by a strongly asymmetric electron distribution, which results from being substituted at the 4 and 4' positions with electron-donating and electron-withdrawing groups (called a 'push/pull' substitution pattern). The pseudo-stilbenes have a strong and broad absorption feature throughout the visible, have non-linear optical properties (owing to the asymmetric electron distribution), and often have the best photo-switching response, making them ideal candidates for a variety of applications and studies. For instance, the dipole of the pseudo-stilbenes can be oriented in an electric field, and the higher order moments of the electron distribution give rise to a significant non-linear response [2,3].

Without a doubt the most interesting feature of the azobenzenes is their ability to undergo fast, efficient, and fully reversible photo-isomerization (Fig. 2). Absorption of a photon leads to movement of the phenyl rings about the azo bond, converting the molecule from the *trans* (E) state to the *cis* (Z) state. The isomerization is one of the cleanest photoreactions known, not generating side-products even with innumerable isomeriza-

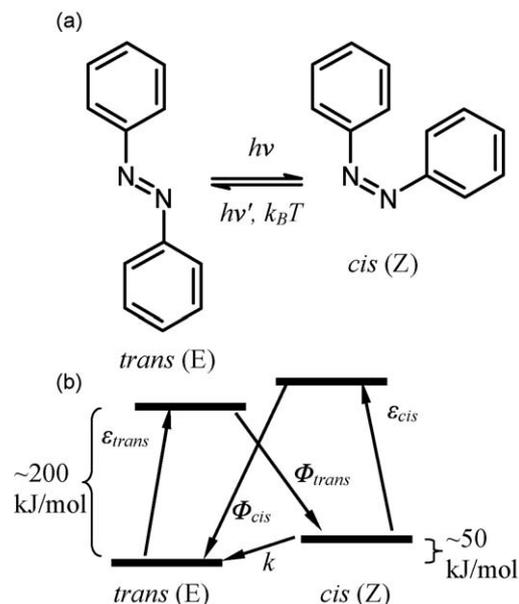


Fig. 2. (a) Azobenzene can be converted from the *trans* to the *cis* state photochemically, and will revert back to the stable *trans* state thermally. Alternately, the *cis* to *trans* conversion can be effectuated with a distinct wavelength of light. (b) Simplified state model for azobenzene chromophores. The extinction coefficients are denoted ϵ , whereas the quantum yields for the photoisomerizations are labelled Φ . The rate of thermal relaxation is denoted by k . Competition between these pathways determines the composition of the photo-stationary state.

tion cycles [1]. At a molecular scale, the isomerization leads to extremely large changes in conformation and size. The *trans* isomer is nearly always the thermodynamically favoured isomer, being more stable by approximately 50 kJ/mol [4,5]. The energy barrier to the photo-excited state is on the order of 200 kJ/mol [6]. As a result, in the dark (or under typical ambient illumination), the azobenzenes are found predominantly in the *trans* form. Absorption of a photon in the *trans* absorption band causes isomerization to the *cis* state with high quantum yield. A photon in the *cis* absorption band can then be used to elicit the *cis* to *trans* back-isomerization. These photo-isomerization reactions have timescales on the order of picoseconds [7,8]. Even without illumination, however, a population of azo *cis* isomers will thermally reconvert back to the more stable *trans* state, with a timescale that depends greatly on the azo's substitution pattern. Lifetimes are typically on the order of hours, minutes, and seconds, for azobenzenes, aminoazobenzenes, and pseudo-stilbenes, respectively. The energy barrier for this thermal isomerization is on the order of 90 kJ/mol [9,10]. Even in the case of the parent azobenzene, the *cis* lifetime is not long enough for the molecule to be treated as a stable two-state system. Considerable research has gone into elongating the *cis* lifetime, which would then allow the two states to be selected without unwanted interconversion (useful in applications that require two stable states, such as data storage). Typically, bulky substituents have been used to hinder the thermal back reaction. For instance, a polyurethane with the azo chromophore in the main-chain exhibited a lifetime of 4 days (thermal rate-constant of $k = 2.8 \times 10^{-6} \text{ s}^{-1}$, at 3 °C) [11], and an azo substituted with bulky pendants had a lifetime of 60

days ($k < 2 \times 10^{-7} \text{ s}^{-1}$, at room temperature) [12]. The inherent conformational strain of macrocyclic azobenzene compounds has been used to create a much more stable *cis* populations, with lifetimes of 20 days ($k = 5.9 \times 10^{-7} \text{ s}^{-1}$) [13], 1 year (half-life 400 days, $k = 2 \times 10^{-8} \text{ s}^{-1}$) [14,15], or even a lifetime of 6 years ($k = 4.9 \times 10^{-9} \text{ s}^{-1}$) [16]. Similarly, using the hydrogen-bonding of peptide segments, a *cis* lifetime of ~ 40 days ($k = 2.9 \times 10^{-7} \text{ s}^{-1}$) was achieved [17]. In extreme cases, the *cis* species can be stabilized by completely preventing isomerization: by attachment to a surface [18], synthesis of ring-like molecules [19], or even, in the case of the parent azobenzene, crystallization of the *cis* form [20,21]. These experiments again emphasize that the azo isomerization requires a large geometric change in molecular configuration. The thermal back-relaxation is generally first-order, although the distribution of highly constrained configurations that arise in a glassy polymer matrix can lead to anomalously fast decay components [22–25]. Accordingly, higher matrix crystallinity increases the decay rate [26]. Again, the relationship between molecular size constraint and kinetic processes points to the highly geometric nature of the isomerization. In fact, the decay rate can be used to probe the local environment and molecular conformation [27,28].

Under irradiation, a bulk azo sample will achieve a photo-stationary state, whose steady-state composition of *trans* and *cis* species is based upon the competition between photo-isomerization (in one or both directions) and constant thermal relaxation back into the *trans* state. Thus, the steady-state composition is unique to each system, depending upon the quantum yields for the two isomerization processes (Φ_{trans} and Φ_{cis}), and the thermal relaxation rate constant (k). Moreover, the composition is affected by irradiation intensity and wavelength, temperature, and the host matrix (be it solution, liquid crystal mixture, monolayer, polymer matrix, etc.). Upon irradiation, an azo sample's spectrum will change (as the proportion of *cis* to *trans* molecules changes), making the system photochromic. Because of this, the composition of the steady-state, and the isomerization kinetics, are usually monitored using absorption spectroscopy [29,30], although NMR methods have also been successfully applied [31]. The ring substitution pattern influences both the *trans* and the *cis* absorption spectra. In the case of the pseudo-stilbenes, the two absorption spectra overlap significantly, meaning that a single wavelength of light can be used to effectuate both the forward and reverse photo-isomerizations, which leads to a mixed photo-stationary state, with molecules being constantly interconverted between the two isomers. This, in part, explains why the pseudo-stilbenes give rise to the most efficient photo-response, especially in cases where motion of the azo chromophore is required. In cases where the azo isomerization is being used as a switch, or where a two-state system is desired, this overlap of the spectra is obviously undesirable. Azobenzene units are extremely sensitive to packing and aggregation, with π - π stacking causing shifts in the absorption spectra, and changes in photophysical properties. When the azos are aligned in a parallel fashion (head-to-head), they are called J-aggregates, and give rise to a red-shift (bathochromic) compared to the well-isolated chromophore spectrum. If the dipoles are instead antiparallel (head-to-tail), they are called H-aggregates,

and one observes a blue-shift (hypsochromic). The local packing can be influenced, of course, by solvent conditions and molecular architecture. For instance, local water concentration in THF solutions can markedly change the azo isomerization behaviour [32]. In fact, even a small water fraction (a few percent) was found to be sufficient to give rise to measurable differences [27]. In these cases, as water content increases, the azo units are driven to aggregate. This aggregated population necessarily exhibits a hindered isomerization.

3. Photoinduced motion and switching

The photochemical isomerization of azobenzene creates a geometric change of molecular dimensions. This molecular motion can give rise to much larger-scale and even coordinated motion. The type and extent of induced response of course depends upon the system. In some cases the molecular motion enables switching of a macroscopic material property. The azobenzene moiety is robust and versatile, having been incorporated into a wide variety of different system types, including: small molecules, doped into polymeric systems, supramolecular assemblies, liquid crystals, and covalently bonded to crystalline or amorphous polymers. Although doping is an easy and convenient way to include azobenzene in a matrix of choice, it is usually found that mobility leads to aggregation and crystallization of the azo molecules, making the resultant films heterogeneous and optically cloudy. Thus, by far the most often-employed incorporation strategy is to covalently bind the azo chromophore to a polymer backbone [33]. More recently, however, there has been much success with creating azobenzene dendrimers [34–36] and even molecular glasses [37,38]. These monodisperse systems appear to maintain the desirable photomotions and photo-switching properties, while allowing precise control of molecular architecture and thus material properties [39]. Thin films are typically prepared by spin-coating, although there are many examples of solvent evaporation, Langmuir–Blodgett films, and self-assembled monolayers. The following describes the various types of photoinduced motion observed in various azo systems, starting from the smallest-scale and working towards larger-scale effects.

3.1. Molecular motion

Fundamentally, the isomerization of an azobenzene chromophore is a photo-induced molecular motion. Isomerization involves rotation or inversion about the azo bond, with concerted twisting of the phenyl rings, with these rings twisted at an angle of 90° (relative to the C–N=N–C plane) in the final *cis* state [40,41]. The conversion from *trans* to *cis* reduces the distance between the ends of the moiety (between the 4 and 4' positions): from 0.99 nm in the *trans* state to 0.55 nm in the *cis* state [42–44]. This change in geometry results in a change in the molecular dipole, increasing it from essentially zero in the *trans* state to 3.1 D in the *cis* form (for the parent azobenzene) [20]. The free volume requirement of the *cis* is larger than the *trans* [45], with estimates of approximately 0.12 nm^3 required for isomerization to proceed via an inversion of the azo

bond [23,40], and 0.28 nm^3 for a rotation about the azo bond [11]. This large molecular change generates a nanoscale force, which has been successfully measured in single-molecular force spectroscopy experiments [46,47]. In such an experiment, illumination causes the azobenzene-polymer to contract, exerting piconewton molecular forces on demand. Careful analysis and modelling of this microscopic photo-generated force were able to show that pulling on *cis* azobenzene molecule does not alter its lifetime (thermal relaxation rate constant) [48]. This molecular motion was used to reversibly thread and dethread a pseudo-rotaxane, creating a simplistic molecular machine [49,50]. In another case, an azo bridging two porphyrin rings allowed photo-control of electron transfer [51]. The tantalizing prospect is that the azo motion could be used to drive molecular-scale machines, on demand. Light is well suited to power and actuate molecular devices since it avoids the limitations of diffusion or wiring at small size-scales, while being extremely fast, clean, and specific.

3.2. Photo-orientation

The molecular motion of azobenzenes can give rise to a unique form of photo-orientation, shown schematically in Fig. 3. The process is statistical, occurs when irradiating with polarized light, and is enhanced in systems where repeated isomerizations

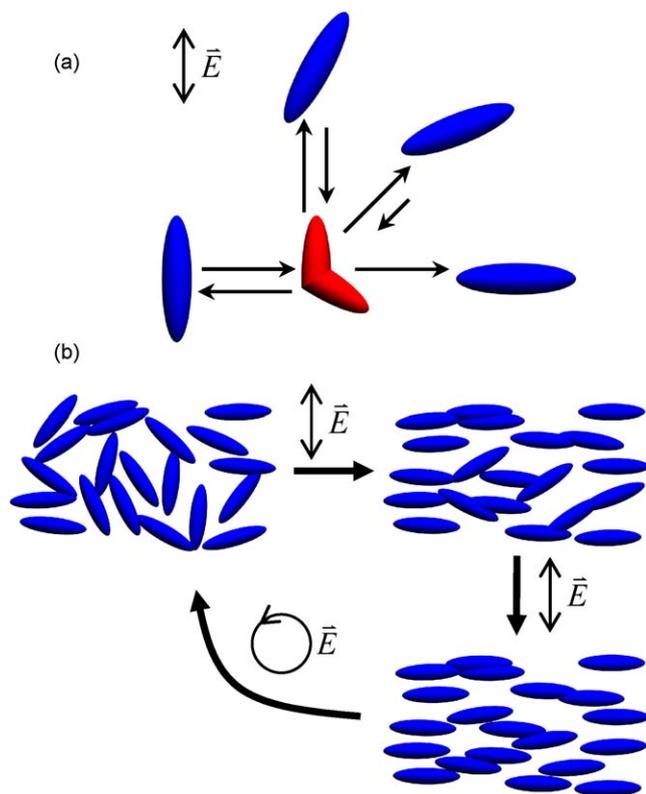


Fig. 3. The mechanism of statistical photo-orientation of azo molecules. (a) The molecules aligned along the polarization direction of the incident light will isomerize, and take on a new random orientation. The molecules that lie perpendicular to the polarization of light cannot absorb a photon and remain fixed. (b) An initially isotropic distribution of chromophores will become progressively aligned with polarized irradiation. Irradiation with circularly polarized light can restore isotropy.

are facilitated (i.e. the pseudo-stilbenes). An azo molecule will preferentially absorb light polarized along its transition dipole axis (long axis of the molecule). More specifically, the probability of photon absorption varies as $\cos^2\varphi$, where φ is the angle between the light polarization and the azo dipole axis. Azos oriented along the polarization will absorb light with high probability, whereas those oriented at 90° to the incident polarization will absorb far less light. Each time a chromophore undergoes a *trans* to *cis* to *trans* isomerization cycle, its position will vary in a small and random way. Thus, starting from an initial uniform angular distribution of chromophores, those that lie along the polarization direction will absorb and reorient, whereas those that lie against the polarization direction will not move. The result is a statistical depletion of the population of chromophores oriented in the polarization direction, with a concomitant enrichment of the perpendicular population (i.e. orientation hole burning). The photo-orientation is reversible: isotropy can be restored using circularly polarized light, or a new orientation direction can be selected by irradiation with a new polarization. This statistical reorientation is remarkably fast, and gives rise to very strong birefringence (anisotropy in refractive index) and dichroism (anisotropy in absorption spectrum) due to the large inherent anisotropy of the azo electronic system [52,53]. The process is no doubt facilitated by the mesogen-like cooperative motion of the azobenzene groups, even in amorphous samples below the glass-transition temperature (T_g) [54]. Oriented azo samples can also have strong non-linear optical (NLO) properties, if the azo molecules have strongly asymmetric electron distributions (as the pseudo-stilbenes do) [3]. An NLO material requires not merely anisotropy, but non-centrosymmetry. Thus, the azo dipoles must typically be aligned with an electric field, although photo-orientation has proved to be useful in aligning azo materials at lower field strength and temperature [55–58]. However, by using polarized light and its harmonics, a directional electric field results, and a net non-centrosymmetry can be produced entirely optically [59,60].

The azobenzene moiety is anisotropic and rigid. It is therefore no surprise that it exhibits many liquid crystalline properties, and that many azobenzene systems (both small molecule and polymeric) have liquid crystalline (LC) mesophases. In LC systems, the azo photo-isomerization takes on a new character: the isomerization can control the LC phase, and the photo-orientation can be used to reorient the LC director [61–63]. Even when doped in small quantity in a LC matrix, the orientation of the azo mesogen can be used to orient the entire sample [64,65]. This has also been applied to the creation of ‘command surfaces,’ where azos tethered to the surface control the phase of a liquid crystal solution in contact [66–68]. With proper choice of irradiation geometry, one can produce a large number of different LC phase orientations, including creating in-plane order (director parallel to the surface), homeotropic alignment (director perpendicular to the surface), tilted or even biaxial [69]. The isomerization itself elicits phase changes, since, while the *trans* state is an excellent mesogen, the *cis* state is not and will destroy LC order [70], which permits fast photo-activated phase changes [71–74]. It is also possible to create chiral domain structures in liquid crystalline [75] or preoriented amorphous samples [76]. An incident

circularly polarized beam becomes elliptically polarized due to the initial oriented layer. This induced ellipse reorients chromophores deeper in the film, which in turn modify the ellipticity of the beam at the point in the film. This reorientation of chromophores, which subsequently modifies the ellipticity of the beam, continues throughout the film, leading to a corkscrew-like arrangement of the chromophores [77]. One can even switch between right- and left-handed helices at will, simply by changing the handedness of the input light beam. These phase controls are excellent examples of the azo molecular motion being amplified to much larger size-scales. In the case of liquid crystals, entire domains can be oriented, and in fact a macroscopic sample can be homogeneously oriented in this way.

3.3. Photo-switching

In addition to photo-switching bulk material properties [78], the azo isomerization can be used to alter domains and supramolecular structures. This is similar to the case of liquid crystalline systems, since the azo switching is being amplified into conversions on much larger length-scales. On irradiation, one can induce a phase change [79], a solubility change [80,81], crystallization [82], reverse phase separation [83], or alter the critical micelle concentration (cmc) and surface activity [84]. Experiments on methacrylates [85,86] and polyamides [87] showed that the polymer's chiral helix could be reversibly suppressed on irradiation. In polyisocyanate polymers, it could be selected whether irradiation would suppress or increase chirality [88,89].

There is a growing body of literature analyzing how self-assembled systems can be altered with light. In many cases, the effect is for azobenzene isomerization to disrupt a supramolecular organization. For instance, in an amphiphilic polypeptide system, self-assembled micelles were formed in the dark, and could be disaggregated with light [90]. When assembled as a transmembrane structure, the reversible formation and destruction of the aggregate allowed for photo-switching of ion transport [91]. In an elegant example of photo-control of self-assembled order, cyclic peptide rings connected with an azo unit exhibited different hydrogen bonding networks depending on the azo's isomeric state (Fig. 4) [17,92]. In the *trans* state, the subunits organized into extended linear chains, whereas in the *cis* state, they participated in intra-molecular hydrogen bonding, forming discrete subunits. Another unique system involved hydrogen-bonding azobenzene rosettes that could be hierarchically organized by irradiation [93]. When mixed with H-bonding linker molecules, the liquid-crystalline azo molecules organized into rosettes, which stacked into columns. The columns then intertwined to form fibres. UV irradiation could be used to destroy the ordering, progressively disrupting the higher-order structures. In this system, the hierarchical organization led to a highly viscous phase, and finally an essentially solid organogel. UV irradiation restores fluidity, making this system a photo-reversible solid–liquid phase-transition material. In related work, binary organogels self-assembled into nanofibres, which significantly restricted the azo isomerization [94]. An azobenzene surfactant in aqueous solution also showed reversible fluidity, where irradiation

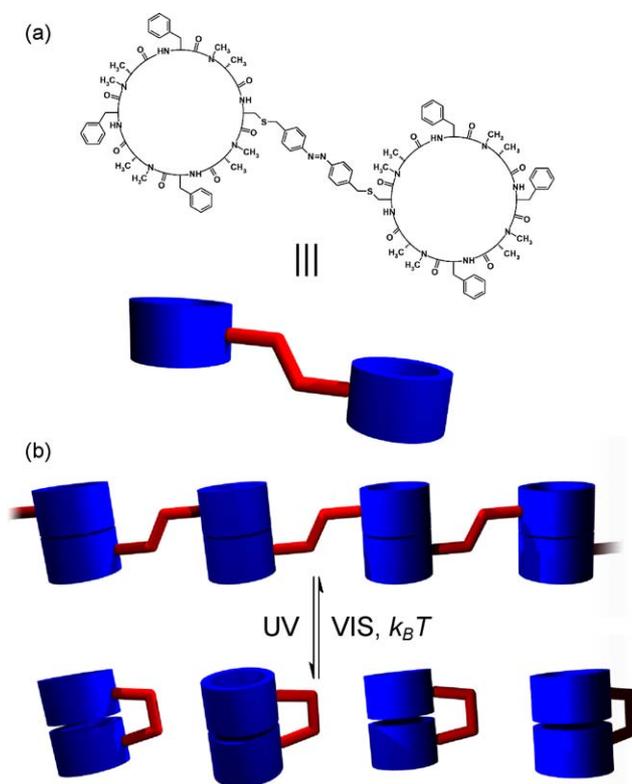


Fig. 4. (a) Two cyclic peptides joined by an azo group can act as a photo-responsive material. (b) In the thermally stable *trans* state, the molecules self-assemble via hydrogen-bonding into an extended network. With UV irradiation, the molecules preferentially self-associated, disrupting the extended network.

ation destroyed self-assembled order, transforming a solid-like gel into a fluid [95]. Similarly, the association of an azo polyacrylate and the protein bovine serum albumin could be controlled with light, which also created a 40-fold change in the viscosity during irradiation [96]. Photo-reduction of azo solution viscosity has been established [97–99], resulting from changes in hydrodynamic size and aggregation. Using dendrimers to amplify this effect has also been successful, with very large changes in hydrodynamic volume [100]. The systems involving large-scale self-assembly, however, show a much more dramatic photo-control of viscosity (and even phase), with orders-of-magnitude different viscosities in the two states, due to the amplification that self-assembly enables.

The isomerization of azobenzene has been applied to self-assembly in block-copolymer films. In this case, the microphase separation of the azo block-copolymer could be controlled with light [101]. In solution, azo block-copolymers can be used to create photo-responsive micelles [102–106] and vesicles [107]. Since light can be used to disrupt the encapsulating vesicle, this has been investigated for pulsatile drug delivery [108]. Careful attention to the self-assembly behaviour, and the change in azo dipole moment upon irradiation in particular, is required to optimize the photo-control of vesicle formation/destruction [109]. Azo colloids have also been prepared, and used as photo-responsive monolayers [32,110], exhibiting all the usual photo-physical phenomena (such as photo-orientation). Azo colloids

have been shown to photo-deform into ellipsoids under irradiation [111,112]. Photonic crystals can also be created with azo materials. For instance, an inverse opal structure with infiltrated azobenzene liquid crystal could have its optical properties photo-modulated [113]. By creating a photonic crystal from azobenzene colloids, on the other hand, one can anisotropically deform the regular colloidal array, providing a unique way to tune photonic properties [114]. In another experiment, an azo-containing multilayer was embedded as a defect in a (silica colloid) photonic crystal [115]. In essence, there is no limit to the ways in which the azo photo-switching can be amplified to create larger scale modulation in material properties.

3.4. Photobiological experiments

The bridging of biology and physical chemistry is an ever-expanding research domain. It is no surprise that the clean and unique azo photochemistry has been applied to switching biological systems [116]. One of the earliest investigations of azobenzene in a biological context involved embedding azobenzene molecules into a model membrane system [117]. Upon isomerization, the lamella were disrupted and rearranged, which also changed the enzymatic activity of membrane-bound proteins. The catalytic activity of a cyclodextrin with a histidine and azobenzene pendant was photo-controllable because the *trans* version of the azo pendant can bind inside the cyclodextrin pocket, whereas the *cis* version liberated the catalytic site [118]. Photo-regulation of polypeptide structure has been an active area of research [119], with the azobenzenes making significant contributions. Azo-modified poly(L-alanine)[120,121], poly(L-glutamic acid)[122,123] and poly(L-lysine)[124], among others, have been prepared. Depending on the system, photo-isomerization may cause no change [123], or can induce a substantial conformational change, including transitions from ordered chiral helix to disordered achiral chain [125–127], changes in the α -helix content, or even reversible α -helix to β -sheet conversions [128]. Also, owing to the change in local electrostatic environment, the pK_a of the polypeptides can be controlled in these systems.

Covalent attachment of azobenzene units to enzymes can modify protein activity by distorting the protein structure with isomerization. This was used to control the enzyme activity of papain [129,130] and the catalytic efficiency of lysozyme [131]. A different methodology is to immobilize the protein of interest inside a photo-isomerizable copolymer matrix, which was used to control α -chymotrypsin [130,132,133]. The azobenzene need not be directly incorporated into an enzyme of interest. In one case, the activity of tyrosinase could be modified by isomerization of small-molecule azo inhibitors [134]. The photo-selective binding of short peptide fragments into enzymes can be used to inhibit, thus control, activity [135,136]. Similarly, the binding of an azo-peptide with a monoclonal antibody was found to be photo-reversible [137]. The photo-response of azobenzene can thus be used to control the availability of key biomolecules. In one case, NAD^+ was modified with an azobenzene group, and introduced into a mixture with an antibody that binds to the *trans* form [138]. This binding makes NAD^+ unavailable,

whereas irradiation of the solution with UV light induces the *trans* to *cis* isomerization, and thereby liberates NAD^+ .

Bioengineering has more recently been broadened by expanding the natural protein alphabet with artificial amino acids. This enables novel and non-natural protein sequences to be created, while still exploiting the highly efficient natural synthesis machinery. Chiral azobenzene amino acids have been synthesized, and incorporated into protein sequences [139]. The introduction of artificial photoactive residues opens the possibility of photo-control of biological processes. For instance, *E. coli* variants were selectively evolved that would incorporate azobenzene amino acids into proteins, which enabled photo-control of protein binding in that organism [140]. Photo-control of the binding affinity of a transcription factor to its promoter, allowed for, in essence, light-control of gene expression in the organism. In another case, a (negatively charged) hydrophilic azobenzene amino acid was incorporated into a restriction enzyme, and enabled control of activity with light [141,142]. Specifically, the *trans* azo residue was positioned at the dimer interface, and disrupted association, whereas in the *cis* state, the proteins could aggregate and exhibit normal biological activity. It has also been suggested that the rapid switching of azobenzene could be used as a ‘molecular shuttle’ for electron transduction in enzyme systems [143]. In effect, this would mean that light could be efficiently used to alter behaviour in yet another class of enzymes. Incorporation of azobenzene into DNA is another interesting way to control biological systems. In one case, the duplex of modified DNA could be reversibly switched [144], since the *trans* azobenzene intercalates between base pairs, and helps bind the two strands of the double helix together, whereas the *cis* azobenzene disrupted the duplex [145]. By incorporating an azobenzene unit into the promoter region of an otherwise normal DNA sequence, it was possible to photo-control gene expression [146]. In this case, the *trans* versus *cis* states of the azo unit have different interactions with the polymerase enzyme.

These experiments suggest an overall strategy to control biological systems using light. A complex biochemical pathway can be controlled by photo-regulating the activity or availability of a key biomolecule. This allows one to turn a biological process on and off at will, using light. The use inside living organisms is obviously more complicated, but one can reasonably easily apply these principles to control biological processes in industrially relevant settings. The ability to quickly and cleanly switch biological activity using a short light pulse may find application in new microfluidic devices, which need to be able to address specific device regions, and may rely upon natural molecular machinery to carry out certain tasks. Azobenzenes present unique opportunities in the biological sciences for studying complex biological systems, in addition to controlling them. A bacteriorhodopsin analogue with a central azobenzene molecule, rather than the retinal, was prepared as a model system for studying rhodopsin [147]. As expected, the azobenzene molecule did not interact as favourably with the protein host as strongly as the natural retinal. Despite this, the azo molecules could be coupled into the protein (in the absence of retinal), and led to significant shifts in the physicochemical properties of the complex. Moreover, the azo molecule could

be used as a probe of the inner protein domain (sensing pH, for instance). A particularly elegant experiment involved using azobenzenes to monitor protein folding [148,149]. Femtosecond two-dimensional infrared (2D IR) spectroscopy was used as a gauge of the distances between carbonyl groups in the peptide. An azobenzene chromophore, incorporated inside the polypeptide chain, acted as the photoswitch, initiating a conformational change, hence initiating protein folding, on demand. Simultaneous time-resolved measurements of the azo spectra allowed determination of the folding dynamics. This unique measurement of protein folding behaviour was possible because of the photo-triggering nature of the azo unit. Ultrafast laser pulse experiments are being used to study a large number of chemical reactions, providing detail not before possible. This technique is, however, obviously limited to systems where the chemical events can be photo-triggered. By incorporating azobenzene units into new systems, one can generate a photo-triggerable system from an otherwise photo-inactive one. This strategy can thus be applied to a wide range of problems in chemical dynamics, with biological systems being obvious targets.

3.5. Surface mass transport

A remarkable and unprecedented micron-scale photophysical motion was discovered in thin films of the azo-polymer poly(disperse red 1) in 1995 [150,151] (see Fig. 5). What was found was that the free surface of the thin film would deform in response to an incident light field, in effect reproducing the incident variation in light intensity (or polarization) as a surface relief structure. This spontaneous optical patterning was found to occur at low power and was not ablative or destructive. Rather,

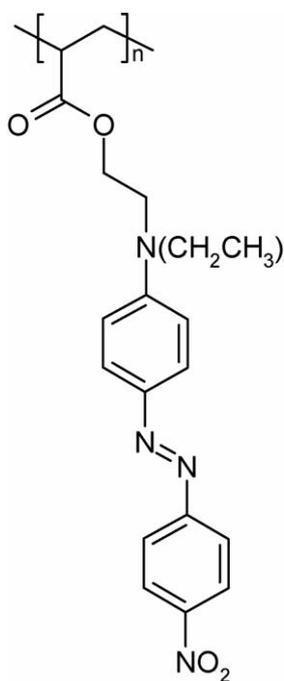


Fig. 5. Chemical structure of the poly(disperse red 1) acrylate, a pseudo-stilbene side-chain azo-polymer material that was found to generate high-quality surface-relief structures when exposed to light gradients.

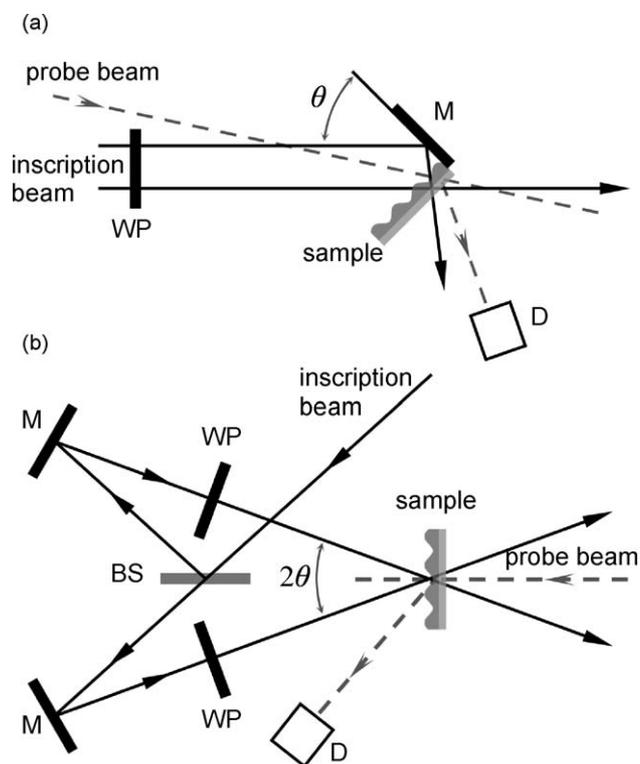


Fig. 6. Typical experimental setup for the inscription of surface relief gratings. In the diagrams, M refers to mirrors that control the incident beams, WP are polarization-controlling wave-plates, BS is a beam-splitter, and D is a detector used to measure the diffraction efficiency of a probe laser beam (often a HeNe 633 nm). (a) In a one-beam setup, a single beam is reflected off of a mirror adjacent to the sample. (b) A two-beam experiment allows for independent control of the polarization state of the two interfering beams.

polymer material was being moved over nanometer to micron length scales, at temperatures well below the material's glass-to-rubber transition temperature (T_g). The prototypical experiment for demonstrating this effect is shown in Fig. 6: two coherent laser beams interfere at the sample surface, giving rise to a sinusoidal variation in light intensity and/or polarization, which is then encoded in the surface as a sinusoidal surface relief grating (SRG). These topographical gratings were found to be very large, up to hundreds of nanometers in height (Fig. 7). The process absolutely requires the presence of azobenzene chromophores, and that these chromophores undergo repeated isomerization cycles. Despite intensive investigation into this system since its discovery, some questions remain unanswered. Notably, there is still some ambiguity as to the nature of the driving force. This subject area has been reviewed numerous times before, as experimental results became available [2,33,152,153].

3.5.1. Experimental observations

The surface mass patterning process is optical in nature; that is, the surface topography is a holographic reproduction of the incident light-field. In addition to the formation of prototypical sinusoidal SRGs, experiments have used focused Gaussian laser spots to induce localized Gaussian 'dents' or extended trenches in surfaces [154]. Multiple gratings (or other topographic holograms) can be induced in the same sample, with their

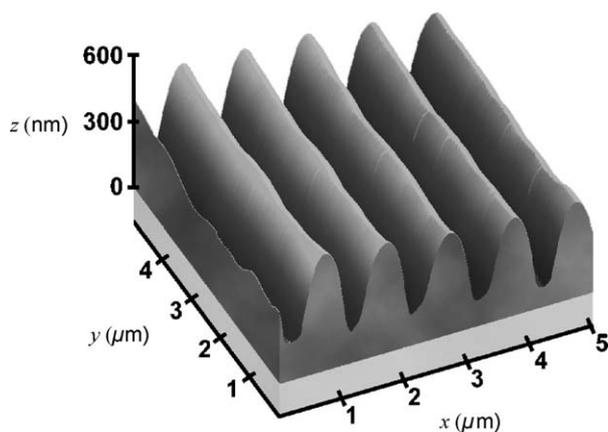


Fig. 7. Atomic force microscopy (AFM) image of a typical surface relief grating (SRG) inscribed on an azo-polymer film. The grating height is several hundred nanometers, comparable to the film thickness.

topographies adding on top of one another. Thus, arbitrary complex surface structures can be formed using multiple exposures or by scanning a laser spot [153]. The extent of mass transport (usually characterized by the grating height or, equivalently, the grating diffraction efficiency) increases with irradiation power, up to a saturation limit. It should be emphasized, however, that significant (albeit slow) surface deformation is observed even at extremely low laser power (even 1 mW/cm^2), as long as the inscription wavelength is within the azo absorption band. In the amorphous azo-polymer systems, the surface pattern is 180° out of phase with respect to the light field. That is, light intensity maxima lead to valleys in the surface relief, with material building up in the dark regions. Different polarization combinations lead to different extents of mass transport. Firstly, an optical field vector component in the direction of light modulation (hence mass transport) is necessary [154]. Thus, in the case of interfering two *s*-polarized beams, very little mass transport is observed. Pure polarization patterns can, in fact, give rise to significant grating heights, although the highest quality gratings are obtained by interfering right- and left-handed circularly polarized light. This combination gives rise to a spatial variation of both light intensity and light polarization at the sample surface, which evidently enhances the photo-motion considerably [155].

From the materials standpoint, a wide variety of azo-containing materials have been found to exhibit the surface-patterning phenomenon. The inclusion of an azo moiety, and its ability to undergo repeated isomerization cycles, appears crucial. The process appears most reproducible and efficient in polymer systems. Doping azos into a polymer matrix is not generally effective. Conversely, very high molecular weight polymers (or cross-linked systems) are unable to undergo the photo-induced motion [156]. Despite these general trends, there are numerous interesting examples of both high and low molecular weight azo systems showing mass transport. For instance, high molecular weight polypeptides [157] ($\text{MW} \sim 10^5$) and azo-cellulose polymers [158,159] ($\text{MW} \sim 10^7$) were found to generate gratings. Recent progress with molecular glasses has shown that the surface patterning phenomenon appears in these systems too [37]. In fact, the molecular version formed gratings more quickly than

its corresponding polymer system [160]. Molecular glasses offer fine control over molecular architecture and hence material properties. Moreover, the inherently smaller size of such a molecule, compared to a conventional polymer chain, is attractive from the standpoint of high-resolution photolithography. Surface patterning can also be accomplished with dendrimers of sufficient generation [161]. Surface gratings have also been demonstrated in liquid crystalline systems [162,163], albeit sometimes requiring higher power than in amorphous systems. In LC systems, the grating inscription shows clear signs of requiring cooperative motion.

The topographical surface patterning is accompanied by other types of patterning. The fact that numerous types of gratings are superimposed during a typical inscription experiment complicates analysis of the diffraction efficiency. As already described, polarized light photo-orientates chromophores, and this necessarily inscribes a birefringence grating into the material bulk when a spatially varying incident polarization pattern is used. The exact orientation of chromophores in the peaks and valleys of an SRG has been measured by Raman confocal microspectrometry [164–166], where it was confirmed that the azo chromophores will statistically align against the polarization direction at that grating position. More surprisingly, the anisotropy grating within the azo material gives rise to a density grating under appropriate treatment. It was found that the oriented chromophores acted as seeds that underwent microcrystallization with thermal treatment [167,168]. The topographical, birefringence, and density gratings are stable. During irradiation, a transient refractive index grating will also be established, due to the different refractive index of the *trans* and *cis* chromophores.

The formation of surface topography in the azo systems requires considerable material motion over micron length-scales. In amorphous systems, the inscription occurs well below the glass-to-rubber transition temperature (T_g), in defiance to conventional wisdom. It has been established that cycling of the azo chromophores between isomeric states is crucial to the observed mass transport, which has led to the suggestion that the material becomes somehow ‘photo-softened’ or ‘photo-plasticized’ during irradiation, enhancing material mobility by orders of magnitude. Although compelling, this suggestion has not been borne out by experiments. Attempts to measure photo-softening have involved quartz crystal microbalance [169] and electromechanical spectroscopy [170,171]. These results show a small effect, with less than 10% change in compliance during irradiation. This is much smaller than the change one would observe past T_g , where material motion becomes unfrozen. While bulk material properties remain largely unaffected, it is clear that isomerization is greatly increasing molecular motion, as demonstrated by segregation of some material components to the free surface [172], and the optical erasure of SRGs [173–175]. Thus, the photo-induced motion appears to be a highly local effect, large enough to allow migration of polymer chains, but not as significant on macroscopic scales.

3.5.2. Mechanism

Several mechanisms have been formulated to explain the microscopic origin of the driving force in azobenzene surface

patterning. Thermal effects would appear to be the most natural explanation, since absorption of the incident light could cause local thermal gradients. Thermal mechanisms, however, cannot account for the polarization-dependence, nor the extremely low laser power that is sufficient to generate the effect. In a detailed modeling analysis [176], it was shown that the temperature gradient typically induced is on the order of 10^{-4} K, much too small for any significant spatial variation of material properties. Moreover, the absolute temperature increase for typical irradiation conditions was predicted to be on the order of 5 K, which suggests that photo-heating effects (such as thermally-induced softening) are negligible. On the other hand, high-intensity pulsed experiments are undoubtedly thermally driven, and do not operate by the same mechanism. An asymmetric diffusion model [177,178] was formulated, wherein the photo-isomerization of chromophores leads to biased motion along their molecular axis. Thus, material motion is controlled by the statistical (and polarization-dependent) orientation of molecules. However, this diffusion would presumably be hindered by attachment to a polymer chain, whereas experimentally this attachment is crucial. A mean-field theory [179,180] considered that oriented chromophores would tend to attract one another. Although this fits naturally with the data on photo-induced micro-crystallization, it predicts material accumulation in the illuminated regions, rather in the dark regions, in contrast to experiments on amorphous systems (although data on liquid crystalline systems is consistent with this model). Models based on the interaction between the electric field of the incident light, and the polarization grating that the light induces in the material, have been presented [155,181–183]. Although these models naturally describe the polarization behaviour, calculations indicate that the expected force density is much too small [184]. Lastly, an assumption of a gradient in pressure induced in the material [156,185] (due to the light gradient) can be used to model the observed mass transport. This theory only partially accounts for the polarization dependence. However, it fits in extremely well with the increasing number of reports of photomechanical effects in azo systems. It has not yet been fully established which of the competing theories is correct, and it may indeed be that various effects contribute to varying extents.

3.6. Macroscopic motion

An area of increasing interest is the use of azobenzenes to generate photomechanical effects or even macroscopic motion. The most direct demonstration of macroscopic motion is the mechanical bending and unbending of freestanding azo-polymer LC thin films [186,187]. This effect is attributed to photo-contraction of the free surface, with correspondingly less contraction deeper in the film (where, due to absorption, the light intensity falls off). The fact that the direction of bending can be controlled with the polarization of the incident light (since this polarization controls azobenzene orientation) means that the azobenzene materials enable full directional photo-mechanical control [188]. Furthermore, the photomechanical effect can be heavily optimized [189] and may turn out to be a highly efficient photo-actuator.

Recent ellipsometry measurements of amorphous azo-polymers showed an expansion of the material during irradiation [190] (up to 4% expansion). The expansion has both a reversible and irreversible component, suggesting both elastic expansion and viscoelastic flow. That contraction is observed in LC materials, whereas expansion is observed in amorphous polymers is consistent with other macroscopic investigations. Specifically, for a thin film floating on a water surface, a contraction in the direction of polarized light was seen for LC materials, whereas an expansion was seen for amorphous materials [191]. Although the photomechanical effect is relatively small, it can be amplified to larger scale motion, as the bending of freestanding films demonstrates. Similarly, the photo-induced bending of a micro-cantilever coated with an azobenzene monolayer that expanded upon irradiation [192] shows how azo photo-expansion can be applied to device structures. Similar experiments with more than a monolayer of material may yield even greater response. Thus, it appears possible that azo materials could act as photo-actuators or even artificial muscles in some carefully chosen applications.

4. Conclusions

Azobenzene materials have been actively investigated ever since the initial discovery of their unique and clean photo-isomerization. Many new phenomena, related to this photo-isomerization, have been discovered as a result, including photo-orientation of materials, photo-switching of material properties, and even an all-optical surface patterning phenomenon. These effects have been suggested for a wide variety of applications, from lithographic patterning, to all-optical switches, to photo-actuation, and many others. Whether or not these applications become industrially significant, one must appreciate the contribution that azobenzene photochemistry has made in the sciences. Azobenzene photochemistry has not only provided deeper insight into fundamental issues of photochemistry and photophysics, but offers a uniquely simple and efficient switch for photo-triggering in a wide variety of scientific investigations.

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