

## Using light to control physical properties of polymers and surfaces with azobenzene chromophores\*

Rola H. El Halabieh, Ozzy Mermut, and Christopher J. Barrett<sup>‡</sup>

Department of Chemistry, McGill University, 801 Sherbrooke Street West,  
Montreal, Quebec, H3A 2K6 Canada

*Abstract:* Azobenzene chromophores can be switched between two geometric isomers using visible light. This photoisomerization is rapid, reversible, and of high quantum yield, and the wavelengths effecting the transformation can be tuned synthetically with substituent groups to the chromophores. Upon isomerization, there can be significant changes to the optical, geometric, mechanical, and chemical properties of azobenzene molecules, and these photo-switchable properties can often be transferred to large host systems into which azobenzene is incorporated. This review describes polymers and surfaces that have been prepared recently that incorporate azobenzene groups, and some of the interesting physical and chemical properties that can be switched reversibly as a result.

### INTRODUCTION

Azobenzene, with two phenyl rings separated by an azo ( $-N=N-$ ) bond, serves as the parent molecule for a broad class of aromatic azo compounds. These chromophores are versatile molecules and have received much attention in research areas both fundamental and applied. The strong electronic absorption maximum can be tailored by ring substitution to fall anywhere from the ultraviolet to red-visible regions, allowing chemical fine-tuning of color. This, combined with the fact that these azo groups are relatively robust and chemically stable, has prompted extensive study of azobenzene-based structures as dyes and colorants [1,2]. The rigid mesogenic shape of the molecule is well suited to spontaneous organization into liquid-crystalline (LC) phases, and hence polymers doped or functionalized with azobenzene-based chromophores (azo polymers) are common as LC media [3,4]. With appropriate electron donor/acceptor ring substitution, the  $\pi$  electron delocalization of the extended aromatic structure can yield high optical nonlinearity, and azo chromophores have seen extensive study for nonlinear optical applications as well [5,6]. One of the most interesting properties of these chromophores, however, and the subject of this review, is the readily induced and reversible isomerization about the azo bond between the *trans* and the *cis* geometric isomers [7,8], and the geometric changes that result when azo chromophores are incorporated into biopolymers and other polyelectrolytes. This light-induced interconversion allows systems incorporating azobenzenes to be used as photoswitches, effecting rapid and reversible control over a variety of chemical, mechanical, electronic, and optical properties.

Perhaps of a range as wide as the interesting phenomena displayed by azo aromatic compounds, is the variety of molecular systems into which these chromophores can be incorporated. In addition to LC media and amorphous glasses, azobenzenes can be incorporated into self-assembled monolayers and superlattices [9], sol-gel silica glasses [10], and various biomaterials [11–13]. The photochromic or

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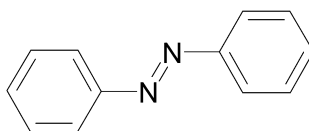
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<sup>‡</sup>Corresponding author

photoswitchable nature of azobenzenes can also be used to control the properties of novel small molecules, using an attached aromatic azo group. Molecules of this type include azobenzenes attached to crown-ethers [14], cyclodextrins [15,16], organometallic ferrocene polymers [17], dendrimers [18,19], 3-d polycyclics such as cubane [20] or adamantane [21], proteins such as bacteriorhodopsin [22], and azo-functionalized  $C_{60}$  buckminsterfullerenes [23,24]. A review will be presented here of the photochemical and photophysical nature of chromophores in host polymers, the geometric and orientational consequences of this isomerization, and some of the interesting ways in which these phenomena have been exploited recently to exert control over solution and biochemical properties using light.

## AZOBENZENE CHROMOPHORES

For purposes of classification of geometrical photoswitching, the nature and behavior of an azobenzene-based chromophore can be described well by three variables: the electronic absorbance maximum  $\lambda_{\max}$ ; the dipole moment  $\mu$ ; and the shape, which can be roughly quantified by the aspect ratio  $r_a$  and the effective occupied volume, OV. Each of these variables can be controlled synthetically with the introduction of appropriate ring substituents, or in the case of  $r_a$  also by linking together additional phenyl rings with azo bonds to form dis- and tris-azobenzene dyes [25–27]. For the wide range of  $\lambda_{\max}$  values displayed by various azo chromophores (and hence the wide range of colors and properties) a useful classification scheme was introduced by Rau. Azo aromatic chromophores can be considered to belong to one of three spectral types based on the energetic ordering of their  $(\pi^*, n)$  and  $(\pi^*, \pi)$  electronic states as that of azobenzene type, aminoazobenzene type, or pseudo-stilbene type [7]. Azobenzene-type molecules (shown in Fig. 1), display a low-intensity  $\pi^* \leftarrow n$  absorption band in the visible region and a high-intensity  $\pi^* \leftarrow \pi$  band in the UV. *Ortho*- or *para*-substitution with an electron-donating group (such as an  $-\text{NH}_2$  amino) leads to the aminoazobenzene type where the  $\pi^* \leftarrow n$  and  $\pi^* \leftarrow \pi$  bands are very close or overlapped in the violet or near-visible UV, due to an increase in the  $\pi$  orbital energy and a decrease in the energy of the  $\pi^*$  orbital. This effect is enhanced with the 4 and 4' position substitution of electron donor and electron acceptor (push/pull) substituents (such as an amino and  $-\text{NO}_2$  nitro group, respectively), which shifts the  $\pi^* \leftarrow \pi$  transition band toward the red (past that of the  $\pi^* \leftarrow n$ ) to assume a reverse order, and places the molecule in the pseudo-stilbene spectral class. The three classes then exhibit colors of yellow, orange, and red, respectively, they will isomerize with characteristic rates and to characteristic extents, and hence in general they will interact differently with light of a given wavelength when incorporated into polymers.



**Fig. 1** The structure of azobenzene.

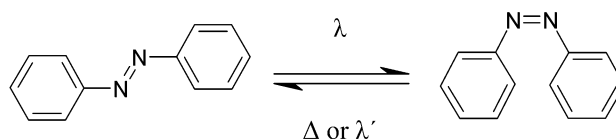
Substitution with electron donor and/or electron acceptor groups increases the electric dipole moment ( $\mu$ ) of the chromophore as well [28]. Azo chromophores both respond to an external electric field and generate one, which contributes to the local EM environment, and can influence neighboring dipoles as well. The result of this is a tendency toward directional alignment of the chromophores with an applied external field (poling), which is used extensively in nonlinear optical (NLO) studies and applications. The rates and extent of this alignment (if it can be induced at all) depend strongly on the local viscosity of the matrix. In general, one needs to bring a system to the rubbery or melt phase for an appreciable response. The geometrical shape descriptions of azo chromophores are less easily quantified, but in general can be described by the aspect ratio and the occupied volume. The aspect ratio  $r_a$ , of interest mainly to LC systems, is the ratio of the length of the rigid portion to the average diameter,

approximating the mesogen to be cylindrical. In general, the larger the  $r_a$  value, the greater the tendency to organize into LC phases, though the LC phase structure (if any) also depends strongly on the mobility of the mesogens. If there is a link connecting the mesogen to a polymeric backbone that is too short to allow sufficient motion (generally fewer than six ethylene spacers), LC phases will be prevented from organizing, and the material will be isotropic and amorphous. The occupied volume of an azo chromophore can be defined as the volume enclosed by the van der Waals electrostatic surface, but for purposes of geometric transformations, it is often of more use to define the effective occupied volume, OV. This is equal to the sum of the occupied volume of the molecule proper and the room necessary for it to stretch and rotate due to excited-state vibration, and represents the volume necessary to undergo this transformation (known as the free-volume requirement).

These chromophores can be either doped or functionalized into a variety of host matrices for casting as thin films. Early work on azo films concentrated on easy-to-prepare host/guest systems, which could load the chromophore to moderate content. Dyes attached to the polymer backbone through covalent bonds (functionalized systems) are now generally considered to be preferable to host/guest doping for most applications, as they avoid the inherent problem of phase separation or microcrystallization. Though often more time-consuming and difficult to prepare, the increased chromophore content and enhanced thermal and temporal stability of functionalized polymers are of great advantage as well to most systems or devices studied. In these functionalized systems, dye loading of up to one chromophore per two backbone atoms can easily be achieved, or even higher in the case of bi-pendant functionalization [29]. The chromophores can be functionalized in the main chain of the polymer [30–32], but it is side chain functionalized systems which comprise the vast majority of the literature reports, owing to an advantage of increased stability, available functionality, chromophore content, and ease of preparation and processing. Most recent reports concentrate on these more stable systems for some of the most pronounced isomerization effects [33–52].

## PHOTOCHEMISTRY OF AZOBENZENE

Key to some of the most interesting applications of azobenzene polymers is the readily induced and reversible isomerization about the azo bond between the *trans* (*E*) and *cis* (*Z*) geometrical isomers, which can be interconverted by light and heat.



**Fig. 2** *Trans* (left) and *cis* (right) geometrical isomers of azobenzene.

The *trans*-isomer can be photoisomerized to the *cis*-isomer, which can be converted back to the *trans* form again either photochemically or thermally. The isomerization is completely reversible, free from side reactions, and according to Rau [7], one of the cleanest photoreactions known. This applies to azobenzenes in solution, liquid crystals, sol-gel systems, monolayer films, dispersed in polymers, and bound in polymers, though with marked differences in kinetics and quantum yields. It is important to note that the composition of the photostationary state, the equilibrium state of the three conversion processes under irradiation, is unique to each system and can depend on irradiation intensity, temperature, quantum yields, free volume, and substituents. The *trans* form of azobenzene is the more stable isomer, with a difference in ground-state energies of *cis* and *trans* of 50 kJ/mol [53]. Unlike the planar *trans* form, *cis*-azobenzene assumes a geometry with the phenyl rings twisted at right angles to the C–N=N–C plane [54]. The literature on isomerization of azobenzenes was reviewed in 1955 by

Wyman [55], in 1971 by Ross and Blanc [56], and more recently by Kumar in 1989 [57], and by Rau in 1990 [7].

For purposes of azobenzene isomerization, the nature of the light that is used to induce isomerization can be defined simply by three properties: wavelength, intensity, and polarization. The irradiation used in most experimental work with azo polymers can be generated by low-power gas lasers (such as Ar<sup>+</sup> or HeNe) or solid-state (such as YAG or GaAs) lasers, as they produce light which is of more than sufficient intensity, and of the appropriate frequency [58,59]. The wavelengths of light produced by these readily available lasers can address usual  $\lambda_{\text{max}}$  values of a wide range of substituted azo chromophores, from the UV (Ar<sup>+</sup> line at 350 nm), through blue (Ar<sup>+</sup> line at 488 nm) and green (Ar<sup>+</sup>, YAG, HeNe lines at 514, 532, 545 nm), to the red (HeNe, GaAs lines at 633, 675 nm). The rates and extent of isomerization of azobenzenes depend on the irradiation intensity, the quantum yields for the two processes ( $\Phi_{\text{trans}}$  and  $\Phi_{\text{cis}}$ ), and the rate constant  $k$  which governs the thermal relaxation from the *cis* back to the *trans* form. The net effect of these competing processes can be summarized by the *cis* concentration [*cis*] in the photostationary state (PSS), representing the extent of isomeric conversion achieved under irradiation. In general,  $k$  for the spectral classes of azobenzene, aminoazobenzene, and pseudo-stilbene is observed to be on the order of hours, minutes, and seconds, respectively, and the isomeric ratio in the PSS is observed to be predominantly *cis*, near unity, and predominantly *trans* respectively under usual irradiation levels [7]. In the dark, [*cis*] usually lies below the limit of detection, and the system can be considered to be comprised of 100 % *trans* molecules.

The mechanism of isomerization of azobenzene is still unclear. Early suggestions [56] of a rotation about the –N=N– double bond axis were in disagreement with later work suggesting an inversion mechanism through a linear transition state [60], though further work with substituent dependencies of thermal relaxation again suggested a rotation mechanism [61]. The range of results suggests that there may not be one general mechanism, but a competition between the two, depending on the spectral class of the chromophore and the local environment. In thin films of polymers functionalized with pseudo-stilbene azo chromophores, the dominant pathway appears to be an in-plane inversion of the phenyl ring most distant from the polymer backbone [62], in agreement with recent ab initio and density functional studies [63,64].

In thin films of pseudo-stilbene materials, both *trans*- and *cis*-isomers can be pumped with the same wavelength in the blue or green to induce rapid *trans* → *cis* and *cis* → *trans* photoisomerizations, with a timescale on the order of picoseconds [65,66]. In the absence of light, there is a thermal relaxation from the *cis*-containing photostationary state to the *trans*-only state, which has been well studied [67–71,76] and is observed to occur on the order of seconds [72–76]. The amount of *cis* present in these systems at the photostationary state can be measured indirectly by spectroscopic methods [77,78], and can range from the limit of detection to over 40 % [79,80], depending on the thermal rate constant (which can be determined from absorbance measurements) [81–86], and on the quantum yields for the two photochemical processes (which can be determined by indirect spectroscopy) [87–89].

## PHOTOPHYSICS OF AZOBENZENE

The geometrical change associated with *trans*- to *cis*-isomerization of azobenzenes is significant, and can be used to destroy or rearrange the order in a wide variety of organized media. The conversion from *trans*- to *cis*-azobenzene decreases the distance between the 4 and 4' ring positions from 9.0 to 5.5 Å [90], increases the average free-volume requirement [44], and can produce a substantial change in many of the observable properties of azo-containing systems. Azobenzenes can thus be used as efficient, reversible, and high-resolution photoswitches, and have been well studied for these applications, especially in the areas of photoinduced phase transitions in LC media, surface properties of Langmuir–Blodgett and self-assembled monolayer films, and “command surfaces” which can communicate photoinduced changes to their surroundings. The three main criteria for a useful phototrigger are

reversibility, large geometrical or electrical change, and high quantum yield for the process [7]. Azobenzenes meet the first two conditions inherently, and can be optimized to meet the third.

In addition to mechanical or electrical changes which can be induced by irradiation, systems in which function is moderated by surface properties are also well suited to photoswitching by incorporation of azobenzene groups. This class of systems includes azo-modified surfactants which were observed to destabilize and phase-separate upon irradiation [91,92], and azo-functionalized polypeptides and cellulose polymers whose aqueous solubility could be switched on and off with UV irradiation [93,94]. There have also been studies reported of azo-functionalized gelatin films that can crystallize upon photoinduced isomerization [95], and liposome membranes incorporating azobenzene whose transport properties can be controlled by light [96]. As well, azobenzenes functionalized with metal-chelating ligands have been shown to display markedly different metal extraction abilities depending on the isomeric ratio [97], and an azo-functionalized synthetic template was demonstrated to be successful at light-induced catalysis [98], where the template is formed (and hence the catalytic activity initiated) only when photoisomerization to the *cis* conformation assembles the active surface. Other interesting properties which have been shown to be photoswitchable by azo-functionalization include the chirality of optically active polymers [99,100], the viscosity of azo polymers in solution [101], the luminescence of organometallic azo-palladium complexes [102], and the redox potential and ionic conductivity of some azobenzene-functionalized systems [103–109]. Incorporation of azobenzene has also been shown to give photocontrol to the twisting and chirality of both natural and synthetic helical polymers such as polypeptides [110–112] and polyisocyanates [113–115].

The geometric change induced by isomerization can be substantial enough to overcome the thermodynamically favored alignment and organization of LC phases, as irradiation of an azobenzene-containing LC film has been shown to change both the orientational axis of the aligned mesogens [116–120], or to induce isothermal LC phase transitions as well upon irradiation [121–126]. Since the transparency of many LC devices is sensitive to the LC phase and orientation vector, this effect has been used to produce azobenzene-mediated photoswitching of display devices [127]. It has also been demonstrated that the spontaneous polarization of ferroelectric liquid crystals can be light-modulated after incorporation of azobenzene into the matrix [128–131].

Similarly, with organized monolayer films, where a single layer of molecules is anchored to a substrate or otherwise assembled, incorporation of azobenzene can produce measurable changes in a variety of properties upon irradiation and isomer conversion. In addition to photocontrol of the dimension, structure, and morphology of these ultrathin films [132–136], the orientation axis of the material can change with isomerization [137–143], which can be used for optical device applications [144–146]. Indirect changes which can be photoinduced through isomerization in these films include conductivity [147,148], reflectivity [149,150], and surface thermodynamics [151,152], as evidenced by changes in water contact angle [153]. In addition to control of the matrix hosting the azobenzene, geometric changes can be transferred from some photoisomerized systems to their surroundings, as is the case with azo-functionalized monolayer films covered with (or sandwiching) a liquid crystal cell. In these command surfaces, the induced geometrical change in the underlying azo monolayer can be sufficient to change the orientation of the overlying LC layer as an indirect photoswitch, over a thickness of many micrometers [154–156].

Of greatest relevance to this review however, is the structural or geometric change which can be photoinduced through azobenzene isomerization in biopolymers or other polyelectrolytes. As thin films, this isomerization and expansion relationship has been studied in organized monolayer films [157–159], where up to a 3-fold increase in surface area has been observed upon irradiation [159]. In thick films, geometric changes in the glassy state are usually less pronounced. The larger free-volume requirement of the photogenerated *cis*-isomer has been shown to result in the expansion of irradiated azo films, however [160–165], observed as either an increase in film thickness in the presence of light as measured by ellipsometry [160], or by a decrease in the density as measured by total attenuated reflection [161–165]. Both of these methods are sensitive to small changes in film thickness and can de-

tect this in situ isomerization-induced expansion, which has been termed the “photoelastic” or “elasto-optic” effect [165]. In both cases, the expansion was attributed to the large free-volume requirement of the *cis* form on irradiation. In one instance, a net contraction of an azo film was observed under irradiation [164]. In this case, the chromophore was a large bis-azo dye, which folds up into a more compact *cis* form on isomerization. The authors attribute this contraction anomaly to the free volume change of this chromophore being negative, strongly suggesting that the pressure driving this often-observed expansion is due to the positive free-volume requirement on isomerization inherent to most systems. A review of other photochemical processes that require a free volume greater than that initially afforded in a matrix has also been published [166].

### THIN FILMS INCORPORATING AZOBENZENES

While standard approaches for thin film preparation can be applied to fabricate azobenzene-functionalized surfaces such as the Langmuir–Blodgett method [167–172] spin-coated films [173–178], and using self-assembly to produce monolayer films [179,180], a new and facile technique for incorporating these photoreactive moieties has come to receive much attention in the last decade. Originally reported by Decher et. al in 1991 [181,182], the sequential assembly of oppositely charged polymers (polyelectrolytes) in an alternating layer-by-layer (LbL) fashion has recently become a useful tool for the controlled fabrication of various organic multilayered structures and modification of surfaces in aqueous media. Specifically, the multilayer is achieved by first immersing a negatively charged or hydrophilic substrate in a dilute positively charged polymer solution followed by thorough rinsing of the surface in an aqueous bath to remove unadsorbed polymer. The resulting polycation-coated surface is subsequently immersed in the oppositely charged polyion solution, and then followed with another aqueous wash. The cycle is then repeated until the desired number of layers is achieved. Recently, it has also been demonstrated that physisorbed multilayer films can similarly be achieved by alternately spinning solutions of polycation and polyanion using a standard spin coater [183]. This LbL ionic self-assembly of multilayers (ISAMs) is highly advantageous from the point of view of developing optically functionalized polymer films over broad length scales ranging from only a few angstroms to several microns [184]. Research of dye-containing ISAMs has demonstrated that the technique is also versatile in terms of adsorption onto various metal and inorganic substrates and is not restricted to flat adsorption geometries [185–190]. LbL films that contain azobenzenes have been shown to exhibit high resistance to heat, harsh solvents, and extended mechanical sonication [191].

Of particular importance to the LbL technique is the ability to achieve fine chemical control over the physical properties of these films either by adjusting the ionic strength of the adsorption baths [192–195] or by using weakly charged polymers, whose charge density can be altered through pH adjustments of the polyelectrolyte solutions [196–199]. Extensive studies of the later procedure have been performed to reveal the high sensitivity of physical properties such as layer thickness [200,201], permeability, morphology [202,203], and density [204,205] to the degree ionization of the polyelectrolytes that contain the azo-photochromic units. As such, there has been an increasing interest in this thin film technique as demonstrated by the significant rise in the number of papers produced on the subject of multilayers since its introduction in 1991.

To date, there have been more than 800 papers which have examined the multilayer coating technique, particularly from the standpoint of its versatile nature with respect to incorporation of secondary functionalities in the polyions assembled. Corresponding to the initial investigations of the multilayer method, one has also seen a dramatic increase in the number of LbL systems incorporating azobenzenes, particularly those that address their photoisomeric properties. Major contributors in the field of the ISAM technique applied to optically responsive azobenzene chromophores have been Advincula [206–210], Kumar and Tripathy [211–213], Tiede [214–217], Heflin [218], and Barrett [219–221]. In general, either the polycation or polyanion can bear substituted azobenzene chromophores along the side chain. The capability of high efficiency and fully reversible photoswitching with irradiation across

a varying range of UV–vis light has prompted investigations into the synthesis of azo-polyelectrolytes which contain hydrophilic functional groups on the chromophores [222–225]. These studies have demonstrated that the photoresponsive *cis*–*trans*-isomerization rates of the azobenzenes in the layers are highly dependent on the functional groups attached to the chromophores. An additional level of versatility in this method is given by the fact postassembly functionalization of reactive precursor polyions is amenable to the LbL technique to achieve substituted azobenzene moieties across several polymer layers [212].

The degree of photoorientation and alignment of the chromophores upon irradiation in ISAM optical films has also been investigated using azobenzene-containing bolaamphiphiles or ionenes. For example, Tieke et al. have recently demonstrated the induction of significant in-plane dichroism due to the photo-orientation of the photochromic unit, where the long axis becomes perpendicularly oriented to the electric field of the incident light [215]. Aggregation, orientational order and/or electrostatic interactions of the charged groups within the polyelectrolyte matrix can cause restricted mobility of the azobenzene units, inducing weak anisotropy in such systems, which varies with irradiation conditions. Advincula et al. have also demonstrated that when a non-azo-containing polycation is combined with an azo-bearing polyanion, the molecular orientation of the azobenzene groups in the film and the photoisomerization kinetics are significantly influenced by the chemical structure of the polycation [207]. Recent discovery of a solvato-chromic influence on the photoisomerization kinetics of self-assembling amphiphilic azo-copolymers in aqueous-organic solutions also suggests that these photochromes can serve as excellent probes for the local polymer environment in stacked multilayer surfaces [226]. For example, incorporation of a highly dense array of azobenzenes in multilayers can serve as pH sensors of the local solvent through measurement of the rate of photoswitching in the multilayers [191].

## AZOBENZENES AS PHOTOSWITCHES

The basic requirement of a successful molecular switch is the presence of two distinct forms of the molecule that can be interconverted reversibly by means of an external stimulus, such as light, heat, pressure, magnetic or electric fields, pH change, or chemical reaction. Irradiation of azobenzene-containing materials induces reversible isomerization between the two isomers making azobenzenes light-switchable molecules (photoswitches). As described earlier, the photoisomerization of azobenzenes is accompanied by significant changes in the absorption spectra, structure, and dipole moment of the molecule. These changes can thus alter properties of the surrounding environment by switching them “on” or “off”. The following sections review physical properties that can be modulated by light, with emphasis on structural changes, surface properties, binding affinity, catalytic activity, conductivity, permeability, complexation behavior, and stereochemistry.

### Reversible structural changes

Langmuir–Blodgett (LB) films incorporating azobenzene chromophores have been extensively studied. The cross-sectional area of the *cis*-azobenzene is larger than that of the *trans* form, and photoconversion in these systems can be accompanied by especially pronounced geometric consequences. Several reports indicate that the surface occupied by the Langmuir monolayers having azobenzenes in their *trans* form are much smaller than when they isomerize to the *cis* form [227–237]. Reports of isomerization in densely packed LB films have also been made [232,233], where the two-dimensional structure is destroyed by protrusions from the films to release the photoinduced stress that is applied on the film surface. Systems showing larger photoinduced morphological changes have also been characterized. Ghadiri et al. [234,235] studied a peptide system in which the isomerization of the azobenzenes results in photoswitchable hydrogen bonding, which allows the controlled conversion between inter- and intra-molecularly assembled cylindrical structures, both in solution and in thin films at the water–air surface. Rotello et al. [236] investigated the conformational changes of a polystyrene back-

bone with photoswitchable azobenzenes on the side chains. The isomerization of the side chain to the more compact *cis*-isomer can relax the polymer structure, allowing enhancement of the side chain aromatic stacking and dipole–dipole interactions. Finally, polymers having azobenzene cross-links have also been studied [237], where a change in dilation volume is measured as a result of photoisomerization, and a reversible change in the pore volume of the network polymer was achieved.

Layered species like clay minerals, graphite, silicates, and micas offer two-dimensional interlayer spaces for organizing guest species. The insertion of guest materials into these layered species does not affect the structural features of the host, except for the interlayer space which is expanded upon intercalation of the guest species [238]. Frequently, dialkyldimethyl ammonium is incorporated into the interlayer gallery before the insertion of the guest species in order to facilitate the introduction of the latter into the system [239,240]. Several other attempts to intercalate azobenzene derivatives into layered inorganic hosts have also been reported [238–246]. The expected result is that the photoisomerization of the azobenzene will induce changes in the basal space, and Fujita et al. [241,244,245] have reported a successful reversible change in this basal spacing upon isomerization. The azobenzenes introduced in the host system must be in large amounts, however (>66 %), and the interlayer gallery needs to be free of any impurities. Furthermore, a perpendicular intercalation of the azobenzenes is ultimately necessary and is best achieved when the host material has a pseudo-trimolecular structure. In this case, the alkylammonium makes the surface of the interlayer uneven, presenting periodic hollows, where the phenyl rings fit well [244]. Under these conditions only, the photoisomerization of the azobenzenes induces a reversible decrease (4 %) in the basal spacing due to the contraction of the long axis of the chromophores. Recently, Ogawa et al. [246] reported an increase (2 %) in the basal spacing of a silicate (host)-azobenzene (guest) system upon isomerization. The orientation of the azobenzene within the interlayer space was not perpendicular to the interlayer surface due to the absence of the anchoring alkyl ammonium.

Azobenzenes have been incorporated at various locations in dendrimers, such as the central or peripheral sections of the large molecules [247–249]. The expectation is that the placement of the photochromic moieties within a dendrimer's central core would lead to reversible photoinduced configurational changes. However, only a few studies reported the isomerization effect on the large-scale morphology of the dendrimers [249]. <sup>1</sup>H NMR studies suggest however that the isomerization of the azobenzene units present at the center of the dendrimers induces a structural transition from a spherical to a semi-spherical configuration [249]. Furthermore, the photomodulation of dendrimer's hydrodynamic volume was found to be sensitive to the relative placement of the azobenzenes within the structure. Dendrimers with peripheral azobenzenes experienced a larger change in their hydrodynamic volume than the dendrimers having the azobenzenes in the internal section. Investigations have also been conducted on the characterization of azo dendrimers in Langmuir and Langmuir–Blodgett films [250,251], where the total surface area of the monolayer increases when the azobenzenes isomerize because the *cis*-azobenzenes assume bulkier conformations and occupy more volume than the *trans* form, especially when long alkyl chains are attached to them.

### Switchable surface and binding properties

Interfacial phenomena such as wettability can be reversibly switched by photoisomerization. A few studies report the photocontrol of wettability of LB films of azobenzene polymers containing fluorinated end chains [252–254], where upon isomerization the contact angle decreases due to the formation of the polar form of the *cis*-isomer. Furthermore, Ichimura et al. [255] used the photoinduced wettability changes of calix[4]resorcinarenes, cyclic bowl-shaped macromolecules. Dipole moment changes can also induce changes in the surface potential of SAM films [256,257], where the surface potential was observed to increase upon isomerization due to the presence of the more polar *cis*-azobenzene. Perhaps one of the most striking effects of azobenzene's photoisomerization is the controlled motion of a neighboring photoinactive substance. Ichimura reported that spatial control of the UV-irra-



diation of a photoresponsive film of calix[4]resorcinarenes generates a gradient in the surface tension enabling the net mass transport of liquid drops on that surface [251,258].

The binding activity of crown ethers containing azobenzene with alkali metal surfaces was extensively studied by Balzani [259]. More recently, several groups have synthesized crown ethers having intra-annular azobenzene moieties for similar photoswitching of binding activity [260–267]. Shinkai also reported sugar recognition using phenylboronic acids functionalized with azobenzene [268]. One very interesting report of photocontrolled binding activity is with calix[n]arenes, cavity-shaped cyclic compounds built from four to eight phenol rings linked by methylene bridges into a macrocyclic arrangement. Calix[n]arenes and their substituted derivatives have been well studied for their inclusion and complexation properties known to depend on the geometry of the extractant between the complexation and the decomplexation steps. Introduction of an azobenzene entity within the calix[n]arenes brings about some photocontrol of the binding properties of these molecules. In fact, several studies have shown that some ions are better extracted by one isomer than the other [269–274]. However, very little work was done using light as a trigger for the isomerization. Vicens et al. [269] do describe an interesting system (Fig. 3) where the binding activity of the calix[4]crown ether is photosensitive. In fact,  $\text{Na}^+$  is preferentially extracted by the *trans*-isomer of the system, while the *cis* form extracts better the  $\text{Rb}^+$  and  $\text{Cs}^+$ . This selection behavior was rationalized in terms of the position of the lone pairs of the oxygen atoms attached to the azobenzene group. These atoms have an  $sp^2$  configuration leading to a “flattening effect” of the glycolic chain, making the polyether loop act like tweezers for the cation with the lone pairs directed toward the cavity of the loop, in the *cis* form. On the other hand, the *trans*-isomer has a relatively small number of coordination sites as all the lone pairs of the oxygen atoms attached to the azobenzene group are pointing outside the cavity of the loop, allowing only small cations like  $\text{Na}^+$  to be extracted in the *trans* form. This effect is due to the structural position of the phenyl rings in the *trans*-azobenzene.

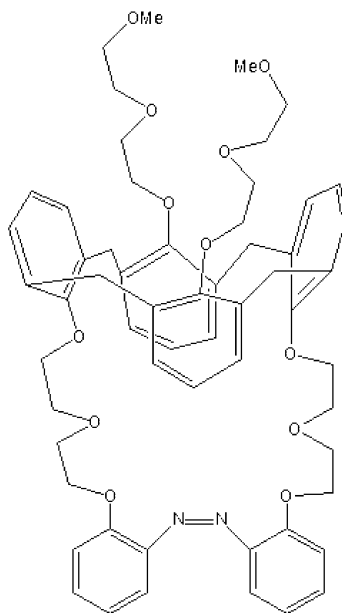
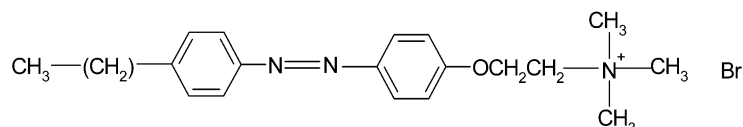


Fig. 3 Calix[4]crown ether reported to be photosensitive.

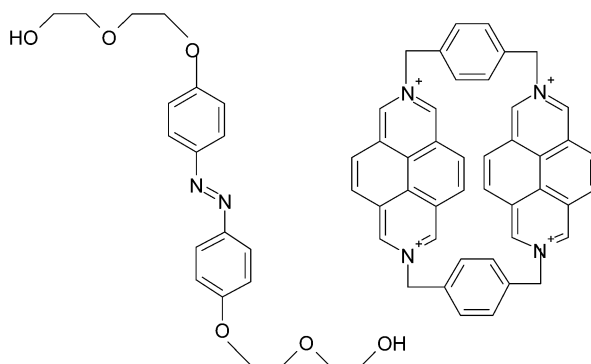
### Complexation and self-assembly

Incorporation of azobenzene moieties into macromolecular structures can allow control over the formation of complexes. Several reports have shown photocontrol of the formation of inclusion complexes, micelles, and oligonucleotides complexes; the association of polymers with eosin; and the dethreading of rotaxanes [275–280]. Cyclodextrins have attracted a great deal of attention because of their ability to bind to hydrophobic species in their cavities to form noncovalent host/guest inclusion complexes. The guest in question could be a polymer chain bearing an azobenzene function making the system photoresponsive, and allow regulation of the inclusion complexation between the azobenzene and the cyclodextrins. Several studies have reported the photocontrol of cyclodextrin complexation [276–280]. For example, Shirahama et al. [278] investigated the stability of the complex formed between the three native cyclodextrin forms and the azo structure shown in Fig. 4. The affinity of the 1:1 inclusion complex formed increases from the  $\alpha$ -cyclodextrin to the  $\beta$ -cyclodextrin to the  $\gamma$ -cyclodextrin. This result is predicted, with the smaller cavity of the  $\alpha$ -cyclodextrin providing a stronger interaction with the azobenzene molecule than the interaction present in the large cavities of  $\beta$ -cyclodextrin and  $\gamma$ -cyclodextrin. When UV-light is introduced to the system, the *trans*-azobenzene isomerizes to the bulkier *cis* form.



**Fig. 4** Azobenzene guest molecule to photoregulate cyclodextrin complexation.

Azobenzenes have also been incorporated into catenanes and rotaxanes, of interest as simple organic logic devices by Stoddart et al. [281–283] who reported photocontrol of dethreading and rethreading of a pseudorotaxane that is formed between the azo chromophore thread and a ring (Fig. 5). The two molecules self-assemble in an acetonitrile solution to form a pseudorotaxane superstructure through donor–acceptor stabilizing interactions. Fluorescence and absorption studies show that photoisomerization of the azobenzene component from the *trans* form to the *cis* form is accompanied by reversible dethreading of the thread and ring component, representing a simple molecular machine.



**Fig. 5** Azobenzene pseudorotaxane system.

Azobenzenes units introduced in linear amphiphilic molecules have been used to control micelle formation with light. These photosurfactants were added to a variety of polymers [284–289], to investigate photocontrol over the formation of micelles or vesicles. For example, a change in the cmc value

upon photoisomerization has been reported for micelles, which also adopt much smaller size when the solution is irradiated with UV-light, due to the more polar nature of the *cis* form of the surfactant [285]. Komiyama et al. have reported the photocontrol of oligonucleotide self-assembly by introducing azobenzene units into the chains [290–296]. The azobenzene's presence has been shown not to disrupt the stability of either the backbone or the nucleic acid bases, but the duplexes containing a *trans*-azobenzene are more stable than those containing a *cis*-azobenzene, with marked difference in melting curves for the *trans* and *cis* complexes. In all cases, the melting point ( $T_m$ ) of the duplexes decreases significantly upon isomerization, reaching a maximum difference between *trans*- and *cis*-isomer of 40 °C [293]. Circular dichroism studies show that the nonplanar structure of the *cis*-azobenzene is unfavorable for intercalation into oligonucleotide duplexes, making the duplex unstable due to steric hindrance. Triple-helix complex formation has also been reported [293,297], to show the same general characteristic behavior as the duplexes. Hence, photosensitive oligonucleotides have been successfully synthesized, and regulation of the complex formation and dissociation was achieved by irradiation. Similarly, photocontrol of the association and assembly of various aromatic systems bearing azobenzene moieties with fluorescent eosin has been investigated [298–299]. For example, bipyridinium functionalized with azobenzene exhibits an association constant with eosin in the *cis* form that is 12 times greater than in the *trans* form [298]. In fact, absorption measurements show that the isomerization can even cause the formation of the complex; the larger dipole moment of the *cis*-azobenzene participates in the stabilization of the charge-transfer complex between eosin and the bipyridium unit.

### Photoregulation of biochemical activity

Polypeptides are appealing candidates for azobenzene incorporation, to try and gain photocontrol over their  $\alpha$ -helix and  $\beta$ -sheet structures [300]. Several studies have reported the reversible destruction of order in this secondary structure [300–302], the reversible switching between left- and right-handed helices [303,304] or the reversible control of the excess of one-handedness over the other [305–308]. Reversible chiro-optical properties have also been reported in low-molecular-weight azo species [309], where *trans*- to *cis*-isomerization of the azobenzene unit led to an optical activity switching efficiency of 90 %. Incorporating azobenzene moieties into various selective membranes has proved to be a successful method to photomodulate the opening and closing of the pores, and has provided a good control over the ionic fluxes through them [310,313]. Sata et al. observed that changes in the polarity upon isomerization of an azobenzene moiety incorporated within a membrane caused changes in the pore size of the membrane [314]. The transport number of various ions across this membrane also increased significantly when photoisomerization occurred. Kokube et al. [315] used the planar bilayer lipid membrane of soybean lecithin as their system. Compared to a full activity of *trans*-azobenzene, the *cis*-azobenzene system produced no detectable current, which indicated obstruction of the channel. The fact that the ion permeation can be highly dependent on subtle changes in supramolecular assemblies was also demonstrated by Hurst et al. [316]. The *trans*- to *cis*-photoisomerization caused a five-fold increase in the transmembrane diffusion of  $K^+$  ions at 40 °C due to disruption of the bilayer membrane and opening of an ion-gate channel.

The ionic flux dependence on the transition temperature was extensively investigated by Yonezawa et al. [317–319]. They incorporated 8A5 molecules (Fig. 6) into liposomes membranes and studied the  $K^+$  permeation changes upon isomerization at different temperatures. The permeation coefficient was highest in the *cis* form near the transition temperature. The *cis*-isomer of the 8A5 molecules

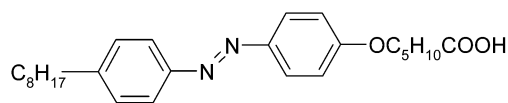


Fig. 6 8A5 azobenzene amphiphile used to photoregulate liposome membranes.

occupies more volume than the *trans* form and increases the phase-separation boundaries at the transition temperatures, expanding the pores within the membrane and enhancing the  $K^+$  permeation.

Finally, gramicidin A ion channels were photomodulated when azobenzene moieties were introduced (Fig. 7). Gramicidin A is a naturally occurring 15 amino acid polypeptide consisting of an alternating sequence of D- and L-amino acids. In an ordered amphiphilic environment like micelles, lipid vesicles, or lipid bilayers, it adopts a single helical dimer structure [320]. This dimer has the shape of a cylinder large enough to accommodate the passage of ions such as  $Na^+$  or  $K^+$ , constituting an ion channel. Controlling the gating of gramicidin A by the photoisomerization of azobenzenes covalently attached at the mouth of this ion channel provided control over the ion flux passing through the membrane. The *cis*-azobenzene, having a larger dipole moment than the *trans* form, increases the conductance of the channel [321,322]. Photomodulation of gramicidin A channel formation was also achieved [323]. Isomerization studies of photoswitchable gramicidin A were investigated before and after incorporation of the ion channel into the bilayer lipid membranes. The more polar *cis*-isomer of the azobenzene moiety increases the  $Na^+$  ion concentration enhancing the conductance of the membrane. If irradiation was carried out before introducing the ion channel into the membrane, the *cis*-azogramicidin A is far more conducting than the *trans* form [323]. Hence, the combination of an azobenzene with these ion channels proved successful in photoswitching the ion permeability across lipid membranes.

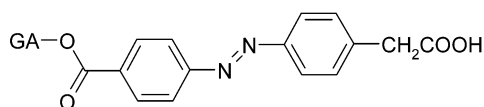


Fig. 7 Azobenzene-containing gramicidin protein as a photoswitchable ion channel.

Lastly, photocontrol of enzyme activity is also available, as there exist several methods to photo-regulate an enzyme's activity by acting as inhibitors for the enzyme active site in one of their conformations. Willner recently published a comprehensive review of the photocontrol of enzyme properties [324]. Generally speaking, azobenzene modified enzymes can be divided into two classes: inhibitors and catalysts. Abell showed that the *cis*-isomer of azobenzene  $\alpha$ -chymotrypsin is more inhibiting than the *trans* form [325,326]. This activity difference was suggested to be due to differences in the polarity between the two isomers. The modulation of proteolytic enzyme activity by means of a photochromic inhibitor was also investigated [327], where the *cis* form inhibits the enzyme activity less than the *trans* form. This observation was accounted for by the fact that the two amino groups are closer to each other in the *cis*-isomer than they are in the *trans*-isomer. This configurational state hampers the inhibiting activity of the enzyme. The incorporation site of the azobenzene moiety in a particular enzyme plays an important role in the effect that photomodulation has on enzyme activity. Hamachi et al. [328] varied the position of the azobenzene moiety in ribonuclease and observed that the closer the azobenzene is to the active site of the enzyme, the more efficient is the control over the photoresponse. This observation was also reported by Sisido et al. [329] for the photocontrol of horseradish peroxidase activity. Similarly to inhibitors, catalytic enzymes are affected by the shape and polarity changes of the azobenzene part upon photoisomerization. Configurational changes of the  $\alpha$ -chymotrypsin make the *cis* form less active than the *trans* form toward hydrolysis of *p*-nitrophenyl acetate [330].

## CONCLUSION

Azobenzene chromophores can be incorporated successfully into a variety of interesting systems (poly-electrolytes, inorganics, surfaces, and biopolymers) to allow reversible control of a variety of physical and chemical properties with light. In many cases, large changes can be effected quickly with light after

even a modest incorporation of the chromophore, as the geometric effects of the isomerization can be amplified in the host, or set off a cascade of secondary photochemical and photophysical response.

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