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Immobilized azobenzenes for the construction of photoresponsive materials*

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Abstract: The immobilization of molecular switches onto inorganic supports has recently become a hot topic as it can give rise to novel hybrid materials in which the properties of the two components are mutually enhanced. Even more attractive is the concept of "transferring" the switchable characteristics of single layers of organic molecules onto the underlying inorganic components, rendering them responsive to external stimuli as well. Of the various molecular switches studied, azobenzene (AB) has arguably attracted most attention due to its simple molecular structure, and because its "trigger" (light) is a noninvasive one, it can be delivered instantaneously, and into a precise location. In order to fully realize its potential, however, it is necessary to immobilize AB onto solid supports. It is the goal of this manuscript to comprehensively yet concisely review such hybrid systems which comprise AB forming well-defined self-assembled monolayers (SAMs) on planar and curved (colloidal and nanoporous) inorganic surfaces. I discuss methods to immobilize AB derivatives onto surfaces, strategies to ensure efficient AB isomerization, ways to monitor the switching process, properties of these switchable hybrid materials, and, last but not least, their emerging applications.

Keywords: azobenzene; hybrid materials; nanoparticles; photoswitches; surfaces.

INTRODUCTION

The integration of molecular switches with inorganic surfaces has recently become a hot topic as it can give rise to novel hybrid materials in which the properties of the two components are mutually affected or even enhanced in a reversible fashion [1]. Even more attractive is the concept of "transferring" the switchable characteristics of single layers of organic molecules onto the underlying inorganic components, rendering them responsive to external stimuli as well. Of the various molecular switches studied, photoswitches attracted the most attention because their "trigger"—light—is a noninvasive one, it can be delivered instantaneously, and into a precise location. Due to its simple molecular structure and unique characteristics, azobenzene (AB) [2–7] (IUPAC name: diphenyldiazene) has arguably been the most studied photoswitch ever since its reversible isomerization was first reported some eight decades ago [8]. When the thermodynamically stable *trans* (or *E*; from the German *entgegen*, opposite) isomer of AB is exposed to UV ($\lambda \approx 365$ nm) light, it isomerizes [9,10] to the *cis* (or *Z*; from the German *zusammen*, together) form (Fig. 1). The latter isomer is metastable—that is, it spontaneously reverts back to the *trans* form once the UV source is removed. Although this thermal re-isomerization is slow,

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Fig. 1 (a) Geometrical and electronic changes accompanying the AB isomerization process. (b) Fast and reversible changes in spectral properties of an AB (here, 4-(11-mercaptoundecanoxyazobenzene)) exposed to UV and visible light (intensity $\approx 1.0 \text{ mW/cm}^2$ each). The band centered at $\lambda_{max} \approx 365 \text{ nm}$ originates from the π - π * transition in *trans*-AB. The band centered at $\lambda_{max} \approx 445 \text{ nm}$ originates from the n- π * transition in *cis*-AB. It is important to emphasize that the UV-irradiated sample is not a pure *cis* isomer but a photostationary state comprising the *cis* form (usually up to ~90 %) and the *trans* form because of the constant thermal relaxation of the former to the latter.

it can be greatly accelerated by heating or by exposure to visible ($\lambda \approx 430$ nm) light—in fact, both *trans–cis* and *cis–trans* reactions can be complete within picoseconds [11–13]. Moreover, they proceed with high quantum yields and are fully reversible. Most importantly in the context of our discussion, however, the two isomers differ markedly in their molecular geometries and electronic properties, making AB an attractive component of photoswitchable architectures and materials.

First, AB isomerization—from the extended *trans* configuration to the more bulky *cis* one entails a significant change in molecular shape by causing one phenyl ring to move with respect to the other (Fig. 1a). This large-amplitude motion decreases the distance between any additional substituents at the two rings. The effect is most pronounced in 4.4'-disubstituted ABs, where the distance between the two substituents can reversibly be modulated between ~ 9 and ~ 6.5 Å [14,15] (Fig. 1a). In some materials incorporating AB moieties, this change in molecular geometry can manifest itself even at the macroscale, as has been shown in AB-incorporating polymers [16–19] and molecular crystals [20], making these materials capable of converting light into mechanical energy. Second, AB isomerization is accompanied by a significant change in the polarity of the molecule. While the lone electron pairs on the nitrogen atoms are pointing in opposite directions in the *trans* configuration, rendering it effectively nonpolar, their mutual arrangement in the cis isomer gives rise to a significant increase in the dipole moment of the molecule (typically ~0-1.2 D for the trans configuration of AB, and ~3.1-4.4 D for the *cis* isomer [21-26], depending [25] on the substitution pattern). This effect has widely been used in supramolecular systems-for example, Fujita et al. demonstrated the possibility of switching the polarity of the interior of a self-assembled capsule covalently modified with AB groups [27]. Finally, these two effects can act cooperatively to induce motion in supramolecular switches, where the *trans-cis* isomerization can lead to the expulsion of AB guests from cavities of macrocyclic hosts such as cyclophanes [28,29] or cyclodextrins (CDs) [30-34].

In order to fully realize its potential—with the ultimate goal of fabricating functional photoresponsive materials—it is necessary to immobilize AB onto solid supports. It is the goal of this paper to review hybrid systems which comprise ABs forming well-defined self-assembled monolayers (SAMs) on planar and curved (colloidal and nanoporous) inorganic surfaces (due to space limitations, the discussion is focused mostly on covalently bound SAMs and does not include, for example, AB-incorporating Langmuir–Blodgett (LB) layers or surface-adsorbed polymers). I discuss methods used to immobilize AB derivatives onto surfaces, strategies to ensure efficient AB isomerization, ways used to monitor the switching process, properties of these switchable hybrid materials, and, last but not least, their emerging applications.

AZOBENZENE IMMOBILIZED ON PLANAR SURFACES

Most research has focused on the preparation of SAMs [35-38] of AB ligands on noble metals and on silicon due to the technological importance of these substrates as well as the well-established monolayer formation techniques on their surfaces. While the formation of SAMs on noble metals relies on the use of sulfur-based ligands (usually thiols) [39], various approaches have been employed to covalently attach AB-terminated ligands to silicon [40-43]. One has to keep in mind, however, that once immobilized, the AB groups require enough space to isomerize-it has been estimated that the volume required for trans-to-cis switching of the parent AB unit amounts to ~127 A³ [44]. While the isomerization is not a problem for molecules moving around freely in solution, it can be suppressed significantly in densely packed monolayers—a problem which has been studied extensively in SAMs on Au. Packing characteristics of simple alkyl AB thiols in monolayers on Au(111) were investigated by several groups in the mid-1990s (e.g., [45-47]). Indeed, scanning probe microscopy (SPM) studies show particularly dense packing of these molecules on the surface, with an average surface area of ~0.187 nm² occupied by a single molecule [46]. Strikingly, this value is even lower than an average surface area occupied by a single alkyl thiol molecule on Au (0.215 nm² determined by scanning tunneling microscopy (STM) [48]; this dense packing is also manifested by the significant (~50 nm) blue shift of the π - π * band at $\lambda \approx 347$ nm—compare to a ~30-nm blue shift for AB single crystals). Indeed, it has been shown that the packing of the monolayer is mostly influenced by the interactions between the AB groups, and not by the commensurability with the underlying Au(111) substrate [49]. In addition to the very dense packing, AFM and STM studies reveal that the AB units within the SAMs are arranged in a herringbone pattern, with their short axes roughly parallel to each other [45,50]. Taken together, it is not surprising that, until relatively recently, SAMs of AB thiols on Au were considered photochemically inactive [51,52].

Consequently, much research has focused on generating free volume necessary for AB isomerization. Analyzing multiple literature examples of switching success as a function of the surface area occupied by a single AB ligand (Table 1) allows one to conclude that an AB group has to enjoy at least ~0.40 nm² of conformational freedom to be able to isomerize [53,54] (of course, this condition only applies to ABs on *planar* substrates—surface area requirements are higher for AB attached to surfaces with negative curvatures (i.e., inside nanopores, e.g., [55]), and lower for AB attached to surface with positive curvatures (i.e., on NPs, e.g., [56]), as we will see further in the text). With this key criterion established, we will now talk about strategies undertaken to engineer sweep volume necessary for the isomerization to take place.

Surface area occupied by a single molecule	Switching observed?	Ref.
0.19 nm ²	No	[46]
0.25 nm ²	No	[57]
0.26 nm ²	No	[49]
0.30 nm ²	No	[58]
0.31 nm ²	No	[59]
0.39 nm ²	No	[60]
0.41 nm ²	Yes	[61]
0.43 nm ²	Yes	[21]
0.50 nm ²	Yes	[62]
0.66 nm ²	Yes	[63]
0.75 nm ²	Yes	[64]
0.87 nm ²	Yes	[65]

Table 1 Average surface areas occupied by a single ABmolecule and isomerization success in selectedmonocomponent SAMs of various AB thiols.

Toward efficient photoswitching in SAMs

One way to create free volume for isomerization is to create bicomponent (mixed) self-assembled monolayers (*m*SAMs) comprising an AB-functionalized thiol and a shorter, background ligand acting as a spacer (e.g., see Fig. 5a). The *m*SAMs are usually fabricated by co-adsorbing a mixture of the two thiols [66–68]. Unfortunately, the ratio of the thiols in solution used for surface functionalization does not necessarily reflect their ratio within the resulting *m*SAM [69]—this discrepancy originates from the difference in intermolecular interactions between the ligand molecules in solution and within SAMs. Another problem associated with *m*SAMs is a slow phase separation of the initially homogeneous film into phase-segregated domains [70–74]—a process that occurs even faster in AB-containing SAMs due to the strong π - π intermolecular interactions. Since AB isomerization in phase-segregated films is limited to molecules located at phase boundaries, the switching performance of the bicomponent monolayers slowly deteriorates.

Accordingly, alternative—sometimes very clever—strategies have been devised to engineer free volume necessary for AB isomerization without the need to prepare mixed SAMs. The use of mixed (unsymmetrical) disulfides (such as 1 in Fig. 2) is analogous to adsorbing a 1:1 mixture of an AB and an alkyl thiol, except that the ratio is inevitably retained in the surface-absorbed monolayer. The average surface area occupied by one dialkyl disulfide molecule is ~0.43 nm², which is just about the space (~0.40 nm²) needed for AB to isomerize. As a result, the inherent 50 % dilution brought about by the use of an unsymmetrical disulfide is sufficient to create photoswitchable surfaces [21,75–78]. Unfortunately, the phase separation problem remains when working with disulfides—upon adsorption onto Au, a disulfide molecule is cleaved [79–81] into a pair of thiolates, which, as we already know, have a propensity to phase-segregate. Tamada et al. subjected 1 (see Fig. 2)-functionalized Au to heating at various temperatures and found that the photoreactivity of the samples decreased to a level of single-component SAMs of the corresponding AB thiol, indicating a complete phase separation [76]. To avoid the problem of disulfides (e.g., 2 in Fig. 2) [82–84] can be used instead, however, sulfide SAMs have not been characterized as extensively as those derived from thiols and disulfides.

Another way to "dilute" ABs on surfaces is to increase the lateral bulkiness of individual thiol molecules. This goal can be accomplished either by installing alkyl substituents on the parent AB moiety, or by placing a bulky group elsewhere in the molecule. Interestingly, placing just one methyl group at the *meta* position rendered densely packed thiolate monolayers photoresponsive, although the surface



Fig. 2 Structural formulas of AB ligands illustrating the different approaches devised to ensure free volume for AB isomerization. Examples selected here include an unsymmetrical disulfide **1** [21], unsymmetrical sulfide **2** (Hex = *n*-hexyl) [82], an AB with its phenyl rings substituted with bulky alkyl groups **3** [62], a *para*-carborane-incorporating AB **4** [85], a ligand encircled by α -CD **5** [86], a lipoic acid *cis*-AB ester **6** (SAMs prepared from the *trans* isomer were not switchable) [87], an asparagusic acid ester **7** [88], an adamantane-based tripodal ligand **8** [89], a calix[4]resorcinarene-based ligand **9** (X = CH₂COOH; R = *n*-octyl) [90], and a TATA-based ligand **10** (R = *n*-propyl) [91].

was "congested"—that is, the *trans*-to-*cis* reaction proceeded slower, while the back-isomerization proceeded faster compared to the same AB in a diluted monolayer [76]. The size and number of alkyl substituents increases the bulkiness of the chromophore. For example, Han et al. found that the surface areas occupied by photoswitchable thiols based on the 3-methyl-3'-*sec*-butylazobenzene and the 2,6-diethyl-3'-*sec*-butylazobenzene (**3** in Fig. 2) cores increase to 0.50 nm² [62] and 0.55 nm² [92], respectively. These subtle structural changes have a significant impact on the isomerization yield (~51 and ~88 %, respectively). The bulkiness of the ligands can also be increased without the need to modify the AB moiety, as was demonstrated by inserting a *para*-carborane cluster between an AB and a thiolated alkyl chain (**4** in Fig. 2) [85], by encircling the ligand with an α -CD ring prior to the formation of an SAM (**5** in Fig. 2) [86], or simply by adsorbing pre-UV-irradiated AB (e.g., **6** in Fig. 2) (ref. [87], but also [58,93–95]) (although the photoreactivity in the last case may rapidly deteriorate due to the migration and clustering of the ligands when in their *trans* states).

Surface concentration of ABs can also be decreased by immobilizing each chromophore unit through more than one surface "anchor". A simple illustration of this strategy is the use of asparagusic acid derivatives (e.g., 7 in Fig. 2) [88], which bind to gold via two sulfur "handles". Attachment of the AB group to the 4-position of the 1,2-dithiolane ring seems to play an important role—in fact, analogous SAMs prepared from lipoid acid derivatives did not show any switching. More sophisticated

molecular designs have employed the rigid adamantane moiety (e.g., **8** in Fig. 2; see also Fig. 8a)—a scaffold that makes it possible to keep the AB unit away from and normal to the underlying metal substrate, and to ensure that the chromophores do not interact with one another [89,96]. Analogously, Ichimura et al. prepared a series of calix[4]resorcinarene-based AB ligands with eight carboxylate anchors (e.g., **9** in Fig. 2) for their attachment to hydrophilic surfaces such as silica [90,97]. Finally, Herges, Magnussen et al. have proposed a conceptually novel "platform" approach to ensure efficient isomerization of AB [91,98,99]. The method is based on the use of flat, highly stabilized triazatriangulenium (TATA) carbocations. When applied onto a surface, the molecules lie flat and self-assemble into hexagonal close-packed arrays, and can then be conveniently alkylated with organolithium reagents, e.g., with the corresponding AB [91]. Moreover, the distances between the perpendicularly aligned AB units can easily be manipulated by the choice of side-chains on the TATA moiety (see **10** in Fig. 2). The longer the alkyl chains, the larger the "footprints" of the molecules on the surface—for example, intermolecular distances were increased from ~1.1 to ~1.3 nm upon substituting a propyl chain (R = n-C₃H₇ in **10**) with an octyl (R = n-C₈H₁₇ in **10**) one.

It is important to emphasize that the above considerations concerning free volume only hold for ABs *strongly* bound to the underlying surface. We will illustrate this issue with a recent example of AB monolayers physisorbed on mica [100]. In contrast to the strongly bound SAMs discussed above, these ligands (**11** and **12** in Fig. 3) lacked any headgroups and their interaction with the mica surface was negligible—still, they formed well-defined monolayers stabilized by strong lateral van der Waals (vdW) interactions between the long (oleyl) alkyl chains. Atomic force microscopy (AFM) has shown that SAMs of **11** had a well-defined thickness of 3.1 ± 0.2 nm (in agreement with the calculated length of the molecule), which decreased to 2.6 ± 0.2 nm upon exposure to UV light, and then returned to the original values upon standing (Fig. 3b). The importance of the lateral diffusion for efficient isomerization is supported by the study of **12**-derived monolayers, which were stabilized by intermolecular H-bonding suppressing the movement of ligand molecules with respect to one another. Indeed, while the SAM changed the thickness reversibly (from 3.5 ± 0.2 to 3.0 ± 0.2 to 3.5 ± 0.2 nm), the process was accompanied by formation of multiple defects (Fig. 3c, *right*). In sum, this study has demonstrated that the free volume requirement does not apply for *physisorbed* close-packed monolayers.



Fig. 3 Efficient photoisomerization in densely packed monolayers physisorbed on mica [100]. (a) Structural formulas of oleyl derivatives of AB incapable (11) and capable (12) of forming intermolecular H-bonds. (b) AFM images of SAM formed by 11 upon exposure to UV and visible light. (c) AFM images of SAM formed by 12 upon exposure to UV and visible light. Blue arrows indicate the locations of defects formed as a result of UV irradiation. The formation of the defects is attributed to enhanced intermolecular interactions between molecules of 12. Adapted with permission from ref. [100] (copyright © 2010 American Chemical Society).

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Finally, we will discuss another exception to the free volume rule—this time in an SAM of *covalently* bound molecules. One might imagine that switching in densely packed monolayers of simple AB thiols would be possible if the short axes of the AB groups were arranged parallel to another—in this case, free volume needed for isomerization of one molecule would be created by the switching of neighboring molecules. Unfortunately, as we saw above, the chromophores are arranged roughly perpendicular to one another and isomerization is severely hampered. Rampi, Mayor, Samorì et al. extended the aromatic system of AB by installing additional phenyl groups at the 4- and 4'-positions and found that when in SAMs, these molecules indeed packed parallel to one another in order to maximize the π - π interactions [101,102]. These SAMs consisted of 2D crystalline domains with diameters ranging between 10 and 20 nm (Fig. 8d) and when exposed to UV light, they readily isomerized in a collective fashion—in fact, the *trans*-*cis* conversion in the monolayers (94–100 %) was even higher than in solution (88 %)! This cooperative effect can be rationalized by the fact that the π - π stacking interactions between the neighboring AB groups are maximized when they are in the same (either *cis* or *trans*) configurations—for example, isomerization of a *trans*-AB moiety is thought to occur faster if it is surrounded by the already isomerized *cis*-AB groups.

Monitoring of azobenzene switching

A number of methods listed below have been employed or devised to monitor the switching of surfaceimmobilized ABs. Some of them are discussed in more detail in the subsequent paragraphs.

- (i) UV-vis spectroscopy has been routinely used by many workers (e.g., [62,82,102,103]). Given the necessity to deal with single layers of molecules, the more intense peak at $\lambda \approx 365$ nm are usually monitored.
- (ii) *Ellipsometry* can provide information about the average thickness of the sample. Real-time measurements on AB monolayers on Au [87,88] showed that the thickness decreases by 0.4–0.5 nm reversibly upon UV light irradiation [67,104], in fair agreement with the calculated geometries of the molecules.
- (iii) *Surface plasmon resonance spectroscopy* is another technique that has been used to monitor switching in real time and under ambient conditions [66,75,76,85].
- (iv) *Contact angle measurements*: See "Azobenzene switching controls wetting of surfaces" further in the text.
- (v) Adsorption of molecules/particles from solution: See "Azobenzene switching controls adsorption on surfaces" further in the text.
- (vi) Atomic force microscopy: We have already mentioned the use of AFM to image switching in densely packed SAMs (Fig. 3). Remarkably, AFM in the non-contact mode has also been used to observe switching in individual molecules [96]. For example, a molecular tripod with a reversibly switching "apex" (see Fig. 8a) was assembled on Au and imaged as either ~3.2 or ~2.8 nm protrusions, depending on the type of irradiation applied. These values are in fair agreement with the estimated physical heights of the *trans* (~3.6 nm) and the *cis* (~3.0 nm) isomers of the tripod. More examples of imaging single molecules switching are discussed in the context of their electrical properties (see "Azobenzene switching controls electrical properties of SAMs" further in the text).
- (vii) Kelvin probe measurements have been used to monitor changes in the work function, $\Delta \Phi$, of AB-functionalized surfaces [78]. $\Delta \Phi$ is inversely proportional to the dipole moment normal to the surface (D_⊥)—therefore, *trans-cis* isomerization is normally accompanied by an increase in $\Delta \Phi$. 4-Cyanosubstituted AB is one exception where the isomerization is accompanied by an *increase* in D_⊥ due to the strongly electron-withdrawing CN group—this is indeed manifested by higher values of $\Delta \Phi$ [77,78]. It is worth mentioning that changes in work function can impact a range of material properties—for example, photoisomerization of AB in SAMs has been used to manipu-

late magnetic and superconducting properties of thin layers of Au [105] and Nb [106], respectively.

- (viii) Measurements of electrical properties: They have been studied in various experimental designs including the solid/liquid Hg-drop junction, STM, conductive AFM, as well as electrochemical STM—see "Azobenzene switching controls electrical properties of SAMs" further in the text.
- (ix) *Electrochemical methods*: The extent of AB isomerization can be evaluated quantitatively by cyclic voltammetry (CV) owing to the fact that cis-AB is less stable thermodynamically than the trans isomer, and can be reduced at a less negative potential [107]. Specifically, the trans isomer remains electrochemically inactive when the potential is swept from -0.5 to +0.7 V (vs. standard calomel electrode; SCE), while *cis*-AB is reduced to hydrazobenzene. The reduction is fully reversible, and regeneration of AB can be observed as an anodic current at +0.28 V. Fujishima et al. have used CV to monitor photoisomerization in their densely packed monolayers and found, not surprisingly, that few (up to 5 %) of the molecules isomerized, even upon prolonged UV irradiation [46]. AB isomerization can also be followed indirectly by looking at mass transport through AB-incorporating monolayers. These designs take advantage of the fact that the crosssectional area of cis-AB [108] is approximately 1.5–2.0 times that of the trans isomer [109] and the photoswitch can act as a molecular "gate". Mirkin et al. prepared SAMs terminated with such gates controlling the access of redox-active species from the solution to the electrode surface [93]. The monolayers encouraged and inhibited the diffusion of ferrocyanide anions when exposed to visible and UV light, respectively. Other workers prepared AB thiols incorporating the redoxactive ferrocene moiety and observed the effect of light on the diffusion of charge-compensating counterions through the monolayer [58,65]. Overall, the above studies provide a consistent picture of the effect of AB configuration on the diffusion of molecular species through SAMs. Finally, Willner et al. proposed [63] a state-of-the-art supramolecular system comprising a ferrocene-functionalized β -CD macrocyclic ring threaded onto a Au electrode-immobilized AB functionalized with a long alkyl chain terminated with a bulky anthracene stopper [63], and used it to follow AB isomerization by monitoring the interfacial electron transfer rates (k_{et}) . Depending on the configuration of the switch, β -CD resided preferentially on the *trans*-AB ring (close to the electrode), or on the alkyl chain (when AB was in the *cis* form; further away from the electrode). The position of the ferrocene probe with respect to the electrode determined electron transfer rates—indeed, k_{et} values fluctuated between ~65 and ~15 s⁻¹ when the system was exposed to visible and UV light, respectively.
- (x) Surface-enhanced Raman spectroscopy: AB's strong Raman cross-section [110] and the ability to enhance the signal by the adjacent Au surface have made it possible to characterize thiolate SAMs prepared from various trans- and cis-ABs [111]. The spectra varied depending on the wavelength of light applied during SAMs preparation—in fact, the spectra recorded on cis-AB SAMs showed distinct differences between those of trans-AB in solution and on the surfaces—the two latter ones, on the other hand, were very similar to each other. While the study did not report switching of the immobilized ABs, it does confirm that the two molecular configurations have different surface-enhanced Raman spectroscopy (SERS) signatures and the technique can, in principle, be used to monitor isomerization on the surface.

Azobenzene switching controls wetting of surfaces

Contact angle measurements provide perhaps the simplest way to monitor switching of surface-immobilized ABs and have been routinely used by many workers. It is usually the case that UV irradiation of a *trans*-AB-covered surface with a water droplet resting on it leads to the spreading of the liquid. The increased wettability is usually attributed to the higher dipole moment of the *cis* isomer, as has been confirmed by elegant experiments involving an AB bearing a cyano group at the *para* position [21]. In this case, the highly polar CN group gives rise to a high (4.93 D) dipole moment in the *trans* configu-

ration of the photoswitch. Upon isomerization, however, the cyano and the *cis*-AB groups render the molecule polarized in two opposing directions, decreasing its dipole moment to 2.77 D; as a result, UV irradiation led to an *increase* in the contact angle [21].

The contact angle decrease, however, is not limited to polar solvents—in fact, *all* liquids reported in the literature [112,113], ranging from water to diiodomethane to olive oil, spread more readily on *cis*-modified surfaces. In the case of nonpolar liquids, the surface's free energy is lowered due to the formation of dipole-induced dipole interactions between *cis*-AB and the liquid molecules [113].

Unfortunately, the difference in the contact angle on *trans*- and *cis*-AB-covered *smooth* surfaces does not usually exceed 10° [40,41,82,114]. Larger differences would be beneficial as far as the development of new photoswitchable surfaces is concerned. It is well known, however, that increasing the roughness of hydrophilic and hydrophobic surfaces can turn them into superhydrophilic and superhydrophobic ones, respectively [115,116], an observation that leads us to the hypothesis that AB switching on *rough* surfaces might result in higher contact angle changes. In an elegant study aimed to address this question, Cho et al. used the layer-by-layer deposition technique to fabricate amino-modified surfaces of various porosities, and covalently attached to them AB **13** (Fig. 4a) [117,118]. As expected, the difference between the water contact angle before and after UV irradiation increased gradually (Fig. 4b) with the number of deposition cycles, and reached an astonishing value of ~150° for a surface which had been subjected to nine deposition cycles (Figs. 4c,d; compare to ~5° for an unmodified surface), thus giving rise to light-induced switching between superhydrophobic and superhydrophilic surfaces.



Fig. 4 Photocontrolled wetting of surfaces. (a) Structural formula of AB **13** attached to amino-functionalized surfaces of different porosities. (b) Dependence of water contact angle on the surface porosity. *X*-axis indicates the number of layer-by-layer deposition cycles. (c) Reversible wettability of a smooth (empty squares) and rough (filled squares) surface. The rough surface was prepared by a series of nine layer-by-layer deposition cycles. (d) Demonstration of switchable wettability on a patterned and selectively UV-irradiated substrate [117]. (e) Structural formula/schematic representation of a supramolecular complex **14** comprising *trans*-AB and α -CD used to prepare SAMs on smooth and rough Au surfaces. (f) Schematic representation (*left*) and contact angle changes (*right*) accompanying light-induced isomerization of **14** on the surface of Au. AB isomerization entails reversible translocation of the α -CD ring. (g) Reversible wettability changes of **14**-modified smooth Au (green traces), **14**-modified rough Au (pink traces) and rough surfaces modified with AB thiol **14** lacking the CD ring (orange traces) [86]. Adapted with permission from ref. [117] (copyright © 2006 American Chemical Society) and ref. [86] (copyright © 2008 Royal Society of Chemistry).

Similarly, contact angle variation was increased from ~2° up to ~66° when a flat silicon surface modified with an AB-incorporating polymer was replaced with one having thin pillars placed perpendicular to the surface and covered with the same polymer [119]. The effect of roughness was also studied with an AB-incorporating supramolecular switch (Fig. 4e) [86]. Here, the monolayer is terminated with the strongly hydrophilic α -CD ring before, and *cis*-AB after UV irradiation—as a result, UV light causes water droplets to assume more spherical shapes (Fig. 4f). Again, the use of a rough (prepared by electrodeposition; ~50° contact angle switching) Au surface instead of a smooth one (~2° switching) led to a 25-fold increase in contact angle fluctuation (Fig. 4g). This enhancing effect of surface roughness has been attributed to the trapping of air in the pores of a *trans*-AB-terminated surface—upon photoisomerization, however, water can penetrate the pores by capillary action.

Given the different contact angles and wettabilities before and after exposure to UV light, some authors have considered the possibility of guiding the motion of liquids using light [90,112,113,120]. For a motion of the droplet to occur, the hysteresis in the contact angles, $\Delta \theta_{h}^{trans} = \theta_{adv}^{trans} - \theta_{rec}^{trans}$, must be greater that the difference between the advancing contact angles, $\Delta \theta_{s} = \theta_{adv}^{trans} - \theta_{adv}^{crans}$, where θ_{adv} and θ_{rec} indicate advancing and receding contact angles, respectively (see Fig. 5a). It follows that a minimum requirement for a photoinduced droplet movement is that $\theta_{rec}^{trans} > \theta_{adv}^{cis}$ [90]. This requirement is satisfied for about 60 % of the systems reported in the literature [90,113], however, no photoinduced motion of water has yet been achieved. An example of a light-guided movement of a droplet (of olive oil) is shown in Fig. 5b, where the *cis*-AB-decorated surface is exposed to blue light with a gradient of intensity, thus creating surface free energy gradients. It would be interesting to investigate light-induced droplet movement on *rough* surfaces with the aim of saturating the spectrum of liquids whose photocontrolled movement can be achieved.



Fig. 5 Light-driven motion of liquids on photoresponsive surfaces. (a) Requirement for the motion of a droplet to occur: the advancing contact angle on a *cis*-AB surface should be larger than the receding contact angle on a *trans*-AB surface: $\theta_{\text{rec}}^{trans} > \theta_{\text{adv}}^{cis}$. (b) Light-induced motion of an olive oil droplet on a 9-modified silica surface. The surface was uniformly exposed to UV light followed by irradiation with $\lambda = 436$ nm (blue) light with a gradient of intensity. The droplet moves in the direction of higher surface energy. The movement is stopped by a uniform exposure to blue light. Adapted with permission from ref. [112] (copyright © 2002 Royal Society of Chemistry).

Azobenzene switching controls adsorption on surfaces

Reversible changes in the water contact angle discussed in the previous paragraphs are a macroscopic manifestation of the different affinities of water molecules to the *cis*- and *trans*-AB moieties. Likewise, larger molecules and their complexes—all the way up to living cells—can potentially experience switchable interactions with the underlying AB-coated surface—an assumption that could pave a way to the development of "smart" surfaces capturing and releasing these entities on-demand. One strategy

to achieve high selectivity of these interactions would be to hide and expose recognition units in a reversible fashion—and AB fits this purpose well because the large-amplitude motion it undergoes causes the rotation of the pendant phenyl ring by 120°, thus "burying" the originally exposed 4'-substituent inside the monolayer (assuming that the molecules comprising the monolayer are relatively well-packed and oriented normal to the surface) (Fig. 6a). In one example, Russell et al. investigated axial ligation of metallated porphyrins (cobalt and zinc tetraphenylporphyrin; CoTPP and ZnTPP, respectively) to a photoswitchable surface prepared from a 4-(4-pyridyl)azophenoxy disulfide (15 in Fig. 6b). In the *trans* configuration of AB, the pyridine group was exposed to solution and available to bind the porphyrin molecules-indeed, these surfaces could accommodate ~4 and >6 times more CoTPP and ZnTPP, respectively, than the corresponding *cis*-AB-functionalized surfaces [121,122]. Moreover, the ability to reversibly capture and release the TPPs was demonstrated over at least several cycles. Sortino et al. have employed the same strategy to control the adsorption of a negatively charged porphyrin onto platinum modified with positively charged sulfide monolayers (packing density in an SAM, $\rho_{SAM} = 1.0$ molecules/nm²), whereby the positive charges originated from the tetraalkylammonium group placed at the 4'-position of AB (16 in Fig. 6c) [83]. Indeed, the positively charged groups became less accessible after the samples were UV-irradiated—as supported by the *increase* in water contact angle (Fig. 6c, top right) —and the surfaces released as much as ~80 % of the originally bound porphyrin (Fig. 6c, bottom right). Of course, the possibility to "turn" the electrostatic interactions "on" and "off" could be applied to other negatively charged molecules as well, and the same team has used their surfaces to demonstrate the possibility of binding both single- and double-stranded DNA in a reversible fashion [84].



Fig. 6 Reversible adsorption on photoswitchable surfaces. (a) Reversible masking and exposing a recognition group attached to the 4'-position of the AB moiety [83,84,123,124]. (b) Structural formula of a photoswitchable 4-pyridylazophenoxy-terminated disulfide with a metal ion-coordinating group **15**. (c) *Left*: structural formula of a photoswitchable AB sulfide with a positively charged recognition group **16**. *Top right*: Reversible changes in water contact angle (empty circles) and absorbance maximum (due to the *trans*-AB band; solid circles) of the sulfide monolayers. *Bottom right*: Changes in absorbance at $\lambda = 424$ nm (Soret band of the negatively charged porphyrin probe) as the monolayers capturing the probe are kept in the dark (squares), exposed to light of $\lambda = 424$ nm (triangles), and to light of $\lambda = 360$ nm (circles). (d) *Left*: Structural formula of a photoswitchable AB thiol with the RGD peptide sequence **17**. *Right*: Micrographs of NIH 3T3 fibroblast cells resting on a RGD thiol-modified Au surface after exposure to UV and visible light. Adapted with permission from ref. [83] (copyright © 2007 Royal Society of Chemistry) and ref. [123] (copyright © 2009 Wiley-VCH Verlag GmbH & Co. KgaA).

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The concept of reversibly displaying a recognition unit has also been used to construct surfaces capable of controlling the attachment of cells [123,125]. In this case, the tripeptide sequence arginine-glycine-aspartate (RGD)—well known to bind to cell membrane receptors and to promote cell adhesion [126]—was used as the surface-bound recognition element. In the original study, several RGD-AB constructs differing in chain lengths were synthesized and grafted on PMMA surfaces via acrylamide linkers [125]. As expected, UV irradiation of all the surfaces reduced cell adhesion (by ~30 %), with one of these surfaces, remarkably, decreasing the adhesion to the level of unmodified poly(methyl methacrylate) (PMMA). Unfortunately, even bare PMMA adsorbed a substantial amount of cells due to non-specific adsorption. To eliminate this problem, Shao, Jiang et al. prepared [123] *m*SAMs of an RGD-AB-terminated thiol (**17** in Fig. 6d) and a hexaethylene glycol ((EG)₆)-terminated thiol, with the (EG)₆ group suppressing [127] non-specific cell adhesion. The monolayers were carefully engineered so as to preferentially expose RGD before, and (EG)₆ after exposure to UV light, thus giving rise to highly specific cell adhesion; in fact, UV irradiation of surfaces covered with an *m*SAM containing 0.1 % of **17** reduced the number of cells adsorbed by a factor of 12. Importantly, subsequent exposure to visible light induced cell reattachment, restoring the original number of cells at the surface (Fig. 17d, *right*).

One could also imagine a situation where the interactions between surface-bound ABs and solution molecules are governed directly by the molecular structure (*trans* vs. *cis*) of the AB unit—as opposed to the exposure of any recognition unit attached to the AB core. Let us consider, for example, AB with two metal-ion complexing, iminodiacetic groups strategically placed at the *para* positions (**18** in Fig. 7a)—while each of these two groups can bind metal ions independently in the *trans* geometry of the photoswitch, they can act cooperatively in the *cis* isomer, thus giving rise to greatly increased binding constants, and to the ability of regulating ion binding using light [128,129]. Such a photoresponsive ion complexing entity has indeed recently been attached to Au surfaces via the lipoic acid linker, and its Cu(II) binding properties were investigated [130]. The amounts of Cu²⁺ bound were monitored by CV; as expected, *cis*-AB interacted with copper more readily than the *trans* isomer, and visible light irradiation led to the release of some of the ions to the solution. Interestingly, an "inverse" system for metal ion complexation, whereby the *trans* configuration binds metal (Ni²⁺, Co²⁺) cations preferentially, has also been reported [131]. This design is based on a 2-(phenyldiazenyl)pyridine motif (**19** in Fig. 7a) whose *trans* configuration features two nitrogen atoms arranged in a way that makes bidentate chelation of metal (Ni²⁺, Co²⁺) cations possible.



Fig. 7 Reversible photocontrolled capture and release of metal ions by AB-immobilized ligands. (a) An iminodiacetic group-based ligand binding Cu^{2+} ions strongly in its *cis* configuration. (b) A 2-(phenyldiazenyl)pyridine-based ligand binding Zn^{2+} ions strongly in its *trans* configuration.

The difference in molecular geometries between the two isomers of immobilized ABs can also be used to adsorb and release biomolecules. Abell et al. prepared a series of AB-incorporating phenylalanine-based transition-state analogues (inhibitors) of chymotrypsin. They have found that the inhibitors bound to the enzyme more tightly when in their *cis* configurations [132], with moderate (up to ~5 times [133]) changes in the inhibition constants. The photoswitchable peptides were then immobilized onto the Au surface, which provided a means to study photocontrolled adsorption of chymotrypsin with surface plasmon resonance (SPR). Similarly, RNA aptamers against a synthetic photoswitchable peptide lysine-arginine-AB-arginine (where AB = 4,4'-bifunctionalized *trans*-AB) were generated by in vitro selection from a pool of random nucleotides [134]. While the aptamers interacted strongly with the Au-immobilized *trans*-peptide (as monitored by SPR), 5 min of UV irradiation was enough to desorb more than 90 % of the aptamer molecules from the surface. It should be kept in mind, however, that these and other binding experiments were performed not on pure *trans* or *cis* isomers, but on photostationary mixtures *enriched* in one of the two isomers, which inevitably leads to lower selectivities of binding.

Azobenzene switching controls electrical properties of SAMs

Because of the large electronic and geometric changes associated with its isomerization, AB is an attractive light-driven molecular switch for molecular electronic devices. Theoretical studies have demonstrated [135,136] that the conductance of the two isomers varies significantly. Due to the non-planar arrangement of the two phenyl rings in the *cis* isomer, orbitals on the two rings have different configurations, making the *cis* isomer less conductive ("off" state) than the highly polarizable *trans* form ("on" state). Several research groups have used STM to observe photoswitching of individual AB molecules [68,101,137,138]. When interpreting the STM data, one has to keep in mind that the STM images are a convolution of electronic structure as well as physical height of the molecules. In the case of AB, UV irradiation gives rise to the *cis* isomer, which is both shorter and less conductive than the highly polarizable *trans* form ("on" state); therefore, the isomerization should lead to a pronounced decrease of the apparent height of the molecules.

Pioneering work in this field comes from the Shikawa's group, who worked with mSAMs shown in Fig. 8b. Interestingly, AB molecules successfully isomerized despite being embedded in a matrix of thiols as long as the trans-AB ligands themselves, as shown in Fig. 8b, right. More vivid changes might be expected when the AB units protrude above the background monolayer. Weiss, Tour et al. prepared an mSAM composed of decanethiol and a thiolated AB (see Fig. 8c, left) and imaged isolated trans-AB moieties as ~2.1 nm protrusions from the background monolayer [68]. These protrusions are observed as high-contrast spots in the STM images in Fig. 8c. The apparent height of the cis-AB molecules, on the other hand, was estimated at ~ 0.7 nm above the decanethiol matrix, and they were barely discernible by STM (note that the difference in the physical height of the molecules should amount to only ~0.65 nm—as opposed to ~1.4 nm). A series of images in Fig. 8c shows that prolonged UV light irradiation leads to the disappearance of most of the high-contrast spots, and their subsequent reappearance upon exposure to visible light (indicated with black squares). Interestingly, some cis-to-trans reisomerization events were also observed under continuous UV irradiation (marked with a blue arrow); in fact, this seemingly counterintuitive result is in agreement with the metastable nature of cis-AB. In another example, Rampi, Mayor, Samori et al. have used STM to observe switching of the entire crystalline domains in their π - π stacked azobiphenyl (Fig. 8d, *left*) SAMs [101]. In this case, the presence of an additional phenyl group on the "wagging" end of the molecule might have contributed to an increase in the contrast of the STM images (Fig. 8d, right). Finally, Song et al. have used both STM [94] and conductive atomic force microscopy (cAFM) [95] to show a higher conductance of trans-AB within monolayers on silicon.

On the other hand, the *cis* isomer is more compact than the *trans* form and UV-irradiation is expected to reduce the distance between the two electrodes, thereby decreasing the tunneling barrier

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Fig. 8 Imaging of reversible photoisomerization of individual AB molecules covalently attached to surfaces. (a) Switching of AB in a single molecule monitored by non-contact AFM. (b,c) Switching in *m*SAMs observed by STM. See text for details. (d) Isomerization in a single-component SAM of azobiphenyl thiols. In the STM image, a border between the *cis*- (low contrast; *top*) and the *trans*- (high contrast; *bottom*) AB domains can be seen. A single *cis*-AB molecule is marked with an oval. Lines indicated as I and II are profiles traced along the directions of the unit cell axes in the two domains (note the different scales on the *y*-axes). Adapted with permission from ref. [96] (copyright © 2010 Royal Society of Chemistry), ref. [137] (copyright © 2003 American Chemical Society), ref. [68] (copyright © 2008 American Chemical Society), and ref. [101] (copyright © 2007 National Academy of Sciences USA).

length and *increasing* conductance. For example, Rampi, Mayor, Samorì et al. studied conductance through their azobiphenyl-incorporating molecular junction between Au and Hg electrodes and found a ~1.4 order of magnitude difference in the currents, with the *cis* isomer-based monolayers being more conductive. This value could be quantitatively accounted for by the equation describing a through-bond tunneling mechanism [139]. The same authors subsequently studied the conductivity of their mono-layers by means of cAFM [140] (Fig. 8a). Depending on the size of the tip used, ~30 or ~90 AB molecules could be probed at a time. Current switching ratios of ~30 were strikingly similar to the values (~25-fold difference) obtained using the Hg-drop set-up. Moreover, this small discrepancy was explained by the fact that while the Hg-drop experiment is a macroscopic measurement over a large ensemble of molecules, the AFM tip is more likely to probe single-crystalline domains comprising *trans*-AB only.

The π -conjugated systems attached directly to the surface of Au, however, might suffer from low isomerization quantum yields. It is well known that in order to ensure AB isomerization with high yields, the chromophore should be spatially separated from the noble metal surface—otherwise, the excited state of the *trans* isomer will be quenched by the metal surface prior to isomerization. The

length of the linker, however, cannot be too long if potential applications in molecular electronics are considered—otherwise, electron transfer rates become too slow and the resistance increases. To satisfy both conditions, Vuillaume et al. have replaced the traditionally used alkyl chain linker with a π -conjugated bithiophene unit (**20** in Fig. 9b) and studied the electrical properties of **20**-derived SAMs on Au by means of cAFM [61,104]. Remarkably high values (up to 7000—compare with up to 30 in the previous examples) of the on/off conductance switching ratios were observed in these monolayers (Fig. 9b). To explain these results, the authors have performed first-principles density functional theory (DFT) calculations and concluded that both delocalization of frontier orbitals as well as electronic coupling of **20** to the electrode were more favorable in the case of the *cis* isomer [104]. These electronic factors along with the decreased molecular length of *cis*-**20** accounted for the record-breaking conductance switching values. Finally, Kontturi et al. have used scanning electrochemical microscopy to investigate electron transfer through *m*SAMs comprising a short AB thiol on Au—once again, electron transfer rates were higher in *cis*-AB-enriched monolayers [67].



Fig. 9 Photoswitchable conductive monolayers. (a) *Left*: A cAFM-based set-up used to probe the conductance of azobiphenyl monolayers. *Right*: representative *I*–*V* curves measured on azobiphenyl-functionalized Au after exposure to UV (blue) and visible (red) light. (b) *Left*: structural formula of a bithiophene-incorporating AB thiol **20**. *Right*: representative *I*–*V* curves measured on **20**-functionalized Au after exposure to UV (blue) and visible (red) light. Compare the *y*-axes (on/off ratios) in the two *I*–*V* curves. Adapted with permission from ref. [140] (copyright © 2008 American Chemical Society) and ref. [104] (copyright © 2010 American Chemical Society).

We can conclude the last two paragraphs with a well-known paradox: some authors have associated the "on" state of AB with the *trans* configuration (e.g., [68,95,136,141]), while others with the *cis* state (e.g., [67,139,140,142]). The bottom line here is that the conductance changes can be used to monitor the photoswitching events, or, in other words, AB isomerization can give rise to (sometimes pronounced) conductance changes, making it a feasible element of future molecular electronic devices.

AZOBENZENE ATTACHED TO THE PORES OF MESOPOROUS MATERIALS

We will now focus our discussion on porous materials whose pores are covalently functionalized with AB groups. According to the IUPAC definition, porous solids are classified according to their pore sizes as *nano-*, *meso-*, and *macroporous* if the pore diameters are smaller than 2 nm, fall in the range 2–50 nm, and are bigger than 50 nm, respectively [143,144]. In the context of AB immobilization, <2-nm pores are too narrow to provide a convenient platform for the attachment and isomerization of the photoswitch—in fact, nanoporous materials covalently modified with AB have not been reported. On the other hand, the relatively large (>50 nm) pores of macroporous solids provide a very large volume as far as the change in the molecular length of AB is concerned. One might argue that the most interesting phenomena arise when the photoisomerization process (associated with a ~0.35-nm decrease in the molecular length) results in large variations of the accessible volume inside the pores. It is for this reason that most work has focused on the immobilization and isomerization of AB inside mesoporous materials with pore diameters in the range 2–8 nm.

Mesoporous materials have revolutionized the field of materials science during the past two decades. Mesoporous silicas [144–146] have been studied in the most detail and have found numerous applications in, for example, catalysis, membrane separations, adsorption, and chemical sensing [147,148]. One can hypothesize that the covalent attachment of AB to the internal walls of mesoporous materials might enable external control of all of these properties using light. Several types of nano-composites incorporating AB molecules noncovalently associated with the nanostructured inorganic component have been reported [149–155]. These materials exhibited photocontrol of ion flux through a synthetic ion channel [150], basal spacing in a layered silicate [153], as well as gas permeation through a zeolite [154]. In order to develop robust functional materials, however, it is essential to attach AB to the underlying scaffold in a covalent fashion.

The preparation of ordered mesoporous silicas is routinely achieved by surfactant-directed selfassembly [145,156,157]—thermally induced condensation of silane precursors (typically, tetraethyl orthosilicate; TEOS) co-organized with ordered surfactant micelles in aqueous solution. A range of surfactants ranging from cationic [145,158] to neutral [159,160] to anionic [161,162] and differing in chain lengths have been employed—the latter variable determining pore diameters of the resulting mesostructures [163]. In addition, mesoporous materials can be synthesized in the form of various morphologies [164], including monoliths [145], 2D films [156,165], as well as spherical nanoparticles (NPs) [166,167]. Once the framework has been formed, the surfactant molecules need to be removed to vacate the pores—this is usually achieved by solvent extraction of the organic molecules, or their combustion during calcination (~350–450 °C).

When a silylated AB is added to the reaction mixture, it undergoes co-condensation with TEOS, leading to a covalent incorporation of the photoswitch into the silica framework (Fig. 10e, *top*). The advantage of this approach is a uniform distribution of AB in and a precise control of the composition of the final material. Of course, the surfactant templates need to be removed from the pores they have templated; in the case of hybrid inorganic–organic materials, this goal can only be achieved by solvent extraction. Alternatively, AB can be grafted onto presynthesized silica framework (postsynthetic modification; Fig. 10e, *bottom*). Facile surface functionalization requires activation of either the silica matrix or the AB, typically achieved with isocyanatopropyltriethoxysilane [168,169].

The concept of covalent functionalization of mesoporous materials with AB was first realized by Brinker et al. [170]. In their strategy, TEOS was co-condensed with a triethoxysilyl-functionalized AB (10 % of the total silane content) in the presence of a nonionic surfactant. Pores in these frameworks had diameters of ~3.2 nm (roughly equal to twice the length of their *trans*-AB ligand—18.2 Å). It is worth emphasizing that the immobilized AB groups must have had enough free volume to isomerize; no detectable photoisomerization was observed prior to solvent extraction of the surfactant molecules, or in a microporous material obtained from the same mixture of silanes, but in the absence of the surfactant templates. Likewise, AB incorporated in a framework obtained using a longer surfactant (and



Fig. 10 (a,b) TEM images of ordered mesoporous silicas in the form of monoliths prepared using nonionic block copolymer P123 as the surfactant [171]; (c,d) TEM images of ordered mesoporous silicas in the form of nanosized spheres prepared using cetyltrimethylammonium bromide (CTAB) as the surfactant [172]. The images in (a) and (c) were taken in the direction parallel to the pore channels. The images in (b) and (d) were taken in the direction perpendicular to the pore channels. (e) Co-condensation (*top*) and postsynthetic modification (*bottom*) as two approaches to the preparation of AB-functionalized silicas. (f) Preparation of photoresponsive silica framework with AB-crosslinked pores by the co-condensation method. Adapted with permission from ref. [171] (copyright © 2005 Elsevier, Ltd.) and ref. [172] (copyright © 2008 Elsevier, Ltd.).

having larger pores of \sim 6.5 nm in diameter) enjoyed more conformational freedom, and, not surprisingly, its isomerization proceeded faster and with higher yield (approaching isomerization kinetics of free molecules in solution).

In an example illustrating the postsynthetic modification method, Maeda et al. have described [173] a two-step functionalization strategy involving (i) modification of the surface silanol groups with 3-aminopropyltriethoxysilane and (ii) attachment of an alkyl bromide-terminated AB through quaternary ammonium salt formation. AB anchored in 7.6-nm pores of a 2D hexagonal mesoporous silica exhibited a very efficient photoresponse, swiching between the *trans* and the *cis* forms upon irradiation (for only several minutes at 10 °C) with $\lambda_{UV} = 365$ nm and $\lambda_{Vis} = 436$ nm, respectively. In order to measure the accessible pore volumes for both isomers, the authors performed liquid-phase adsorption experiments using a bulky (octabutoxyphthalocyanine; OBPc) molecular probe and found, perhaps

unexpectedly, that the probe adsorbed more readily (by a factor of 5-10 %) on silica covered with the *extended*, *trans* isomer of AB (for all the 4'-alkylazobenzenes studied). The authors hypothesize that this observation reflected the strength of the attractive vdW forces between the alkyl chains attached to the AB moiety (these chains are more exposed in the *trans* isomer) and the OBPc's butyl chains, rather than the actual physical space available inside the nanopores (which would be expected to be larger in the case of *cis*-AB). This hypothesis is supported by experiments with unfunctionalized AB, which showed identical amounts of the probe absorbed irrespective of the configuration of the switch.

One reason behind the lack of effect of AB isomerization on the physical space inside the nanopores might have been the relatively long and flexible linker [173] these researchers have used to connect the photoswitch to the silica framework. Indeed, when AB was attached *directly* to the pore walls, reversible changes in pore diameters have been observed [55]. In that study, MCM-41 was postsynthetically modified by heating with various amounts of 4-triethoxysilyl-AB, such that the surface concentrations ranged from $\rho = 0.3$ to 1.1 AB/nm². These surface densities had a pronounced effect on the degree of *trans*-to-*cis* conversion—while the isomerization proceeded smoothly for ρ < 0.9 AB/nm², the AB groups were too congested above this value of ρ , and the conversion yields dropped precipitously. For both MCM-41 materials studied (pore diameters prior to UV irradiation 2.75 and 3.75 nm, respectively), pore diameters (at $\rho = 0.9$ AB/nm²) decreased by ~1 nm—in agreement with the calculated [55] change of 1.1 nm associated with photoisomerization of this AB. Once again, the importance of a bulky probe (here, 4-(N,N-dimethylamino)benzylidenemalonitrile) molecule should be stressed: no significant differences between the adsorption isotherms of small molecule probes (N_2, CCl_4) are seen in these systems, thus suggesting that these molecules are too small to discriminate between the two isomers of the AB group, and demonstrating the importance of a careful choice of probe molecules to obtain meaningful results [170].

One potential application of these photoswitchable mesoporous frameworks could be in optically mediated control of mass transport through AB-functionalized pores. To show the proof of concept, Brinker et al. have performed chronoamperometry experiments on indium tin oxide (ITO) electrodes modified with thin films of their photoswitchable mesoporous silica [170], with the pores aligned in a direction perpendicular to the electrode (Fig. 11) [22]. Reversible changes in mass transport were probed via measurements of the steady-state oxidative currents of two polar ferrocene-based probe molecules. As might have been expected, UV irradiation induced a rapid (and reversible over several cycles) current increase, associated with an encouraged diffusion of ferrocene dimethanol (FDM in Fig. 11c) molecules through the AB-decorated pores to the electrode surface (Figs. 11b,c). When a more bulky (ferrocene dimethanol diethylene glycol; FDMDG in Fig. 11c) probe was used, lower values of and analogous variations (~40 % in both cases) in oxidative current were detected. Although this study has clearly demonstrated reversible mass transport through photoresponsive nanopores, the mechanism of the diffusion control seems to remain unresolved-the proposed explanation based on optical switching of pore sizes should be contrasted with an alternative explanation based on polarity switching—in fact, it is well known [3,27,174,175] that polar molecules have a higher affinity toward the cis isomer of AB.

We have so far discussed examples of mesoporous materials having their pores functionalized with *pendant* AB groups, whereby photoisomerization affects the polarity and/or accessible volume inside the pores. The attachment of the photoswitch in the *bridging* mode could allow one to create materials with *stretchable pores*, in which the AB groups would act as molecular muscles (Fig. 10f). In a study that seems to challenge the common perception of silica mesostructures as structurally rigid materials, Garcia et al. have reported co-condensation of TEOS with two different 4,4'-bis(silylated)azobenzenes, and described light-switchable properties of the resulting materials [168]. They have demonstrated photochange in pore diameters by means of powder X-ray diffraction, as well as absorption studies. In the latter experiments, a polydisperse batch of Au NPs was allowed to diffuse into the AB-bridged silica exposed to both visible and UV light. UV–vis spectroscopy has shown that the materials exposed to UV light soaked up much fewer NPs than the non-irradiated (*trans*) ones and

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Fig. 11 Optical switching of mass transport through AB-functionalized nanoporous silica membrane. (a) Scheme of the experimental set-up. CE = counterelectrode; RE = reference electrode; WE = working electrode. (b) Reversible isomerization of AB anchored in the pores of the silica film. (c) Reversible changes of current for the two probe molecules used. Adapted with permission from ref. [22] (copyright © 2004 American Chemical Society).

that the UV-irradiated silicas slowly regained their ability to absorb larger quantities of the NPs upon standing in the dark. At the same time, UV–vis as well as parallel transmission electron microscopy (TEM) studies have demonstrated, not surprisingly, that the average diameter of the NPs remaining in solution increased, with the smaller NPs being absorbed more readily in the nanosized pores.

The traditional underlying principle of creating new photoswitchable materials has been to create contrasting macroscale material properties endowed by the two isomers of AB. An obvious way to enhance this contrast is to maximize the population of molecules in either *cis* or *trans* configuration achieved by exposure to light of wavelengths at which a given isomer absorbs most photons ($\lambda \approx$ 365 nm for *trans*- and $\lambda \approx 450$ nm for *cis*-AB). New applications can emerge, however, as a result of irradiating with a wavelength at which *both* isomers absorb equally (isosbestic point; $\lambda_{iso} \approx 413$ nm for AB). In this case, the molecules become "frustrated", continuously photoisomerizing between the two configurations. The groups of Zink [169,176–181] and Fujiwara [182,183] have pioneered the concept of "nanoimpeller"—tethered AB irradiated at λ_{iso} and acting as a single-molecule "stirrer" [182] imparting the motion of untethered molecules around it (Fig. 12a). In their original report, the latter team has shown that mesoporous silica with pores functionalized with AB and soaked with cholesterol (probe) accelerated the release of the probe molecules readily when irradiated simultaneously with UV and visible light, with as much as ~ 97 % of the probe liberated after 1 h (compare with ~ 52 , ~ 56 , and ~64 % release in the dark, under visible, and under UV light irradiation, respectively) [182]. The same group has subsequently come up with a curious demonstration of the nanoimpeller concept in thin plate and column chromatography [183]. Having attached AB to commercially available silica gels, they have investigated the effect of photoirradiation on the rate of elution. While UV or visible light irradiation had little or no effect on the elution rates, exposure to both types of light at the same time accelerated solvent development by up to ~13 %. Inside a matrix of relatively large (diameters ~7 nm) and irregular pores, the small change in the molecular length of the photoswitch is unlikely to affect the diffusion



Fig. 12 Immobilized ABs as nanoimpellers. (a) When exposed to simultaneous irradiation with UV and visible light (or to light of wavelength corresponding to the isosbestic point of AB), AB groups perform an impeller-like movement, increasing the mobility of surrounding molecules. (b) Photodriven release of a probe (Coumarin 540A) from AB-functionalized mesoporous silica nanospheres. The arrow indicates when the irradiation was started. Adapted with permission from ref. [172] (copyright © 2008 Elsevier, Ltd.) and ref. [176] (copyright © 2007 American Chemical Society).

of the developing solvent molecules—instead, the authors argue that it is the continuous photoisomerization that increases fluidity of the eluent.

While the acceleration of the effluent rate remains in the realm of appealing demonstrations, lightactivated release of drug molecules from mesoporous carriers might have the potential to revolutionize the field of controlled drug delivery. Zink et al. have worked with nanosized silica spheres with AB groups tethered to the pore interiors (Fig. 12a) [176,178]. Luminescence spectroscopy has demonstrated that particles filled with a luminescent probe (Coumarin 540A) hold the cargo prior to photostimulation, and release it upon exposure to light ($\lambda = 457$ nm; Fig. 12b), thus confirming photoinduced expulsion of the probe from the particles. No probe was released upon exposure to red ($\lambda = 647$ nm) light a wavelength at which AB does not absorb (and the "impellers" are not activated). It is worth stressing here that with its biocompatibility, membrane permeability, optical transparency, and straightforward functionalization, nanosized silica provides an ideal platform for the development of light-stimulated carriers for drug molecules [172]. Indeed, it was recently demonstrated that mesoporous silica particles can deliver the anticancer drug camptothecin into cancer cells and release it on-demand upon exposure light of $\lambda = 413$ nm, leading to cell death [177].

AZOBENZENE ATTACHED TO NANOPARTICLE SURFACES

A recent explosion of interest in nanosized inorganic crystals derives to a large extent from the fact that a host of fascinating material properties emerge at this length scale. For example, size-dependent optical [184–187], electronic [188–191], catalytic [192–194], and magnetic [195,196] properties of NPs have been widely investigated and led to numerous commercial applications. These and other properties could be modulated reversibly by rendering the NPs responsive to external stimuli through surface modification with molecular switches responding to these stimuli, which has been the main motivation behind the interest in the integration of NPs with molecular switches [1,197–200]. In this context, AB has attracted most attention because its isomerization—and potentially the modulation of NP properties—can be affected by light. For an efficient isomerization, however, several preconditions have to be met, and the following paragraphs are devoted to the discussion of the steric and energetic factors concerning the isomerization process.

Strategies employed to ensure efficient switching on NPs

Initial studies on NPs functionalized with well-defined monolayers of ABs date back to 1998, when Evans et al. attempted to follow the photoisomerization process spectroscopically [66]. After attempts to collect data from planar substrates proved unsuccessful (because of the extremely low concentrations when dealing with monolayers of molecules on planar surfaces), small (2 nm) Au NPs were employed as supports for mixed monolayers comprising an AB-terminated thiol and *p*-mercaptophenol. The *trans*-AB band at $\lambda \approx 350$ nm and its reversible decrease were clearly visible. Unfortunately, the NPs irreversibly agglomerated and precipitated after only a few cycles-most likely because the background monolayer was too short to effectively stabilize the particles. Likewise, it is important that the AB ligand itself is long enough to provide a sufficient separation of the chromophore from the metal surface otherwise, isomerization might be inefficient because of quenching of the excited state of the chromophore by the underlying metal surface (resonance energy transfer [201–204]). To investigate such a possibility, Whitesell et al. functionalized 2.5-nm Au NPs with a series of thiolated ABs (Fig. 13a) [205]. When present freely in solution, these molecules had almost identical values of isomerization quantum yields ($\Phi_i \approx 0.1$). When bound to NPs, however, the Φ_i values gradually decreased (down to $\Phi_i \approx 7 \cdot 10^{-4}$) as the separation between the chromophore and the Au surface decreased (Fig. 13a), thus highlighting the importance of spatial separation of the two moieties [206-209].

At the same time, this study has shown that as far as AB isomerization is concerned, steric hindrance is not an issue, even for single-component monolayers, if the NP diameter is small enough (and the curvature large enough; Fig. 13b). In another example, 4-(7-mercaptoheptanoxy)azobenzene photoswitched efficiently on the surfaces of 2.0 nm Au NPs [56]. Remarkably, both *trans-cis* and



Fig. 13 Importance of energetic and steric factors in the photoswitching of AB on metal NPs. (a) Effect of linker length on AB isomerization quantum yield, Φ_i . Shortening the chain length from C₁₂ to C₄ reduces Φ_i by nearly two orders of magnitude. (b–d) Strategies used to create free volume required for isomerization: (b) Decreasing NP size: shown here is a single-component monolayer of mercaptobutanoxyazobenzene on a 1.74-nm Au NP [210]. The very small NP size (and its large curvature) makes isomerization possible. (c) Mixed monolayer approach exemplified by a 5.6-nm Au NP covered with 25 % of a long-chain AB thiol and 75 % of dodecylamine [211]. (d) Thiolate ligands on a 13-nm Au NP rendered bulky by encircling with an α -CD host [212].

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cis–trans isomerizations were reported to be *faster* on NPs than in solution of free molecules, the reaction rates being larger by a factor of 2.9 and 2.3, respectively. This cooperative effect can probably be rationalized by the fact that the π – π stacking interactions between the neighboring AB groups are maximized when they are in the same (either *cis* or *trans*) configurations—for example, isomerization of a *trans*-AB moiety would occur faster if it was surrounded by *cis*-AB groups. This behavior could be attributed to a cooperative switching effect discussed above for azobiphenyl-based SAMs [101].

For NPs of larger (> ~5.0 nm) diameters, it becomes necessary to create free volume by diluting the AB ligands with other, shorter ones. In their seminal work on optimizing photoisomerization on colloidal surfaces, Tamada et al. functionalized 5.2-nm Au NPs with an unsymmetrical disulfide [213,214] (corresponding to 50 % dilution) and observed no deviations from first-order kinetics for both UV- and visible light-induced reactions, indicative of no steric hindrance during the process [213]. A more general approach is based on the preparation of *m*SAMs (Fig. 13c) [211,215–217], either by co-adsorbing a mixture of two thiols, or by a partial exchange of weakly bound ligands (usually alkylamines). Finally, an elegant strategy to increase average surface areas occupied by individual thiolate ligands involves the preparation of supramolecular inclusion complexes prior to adsorption on NPs. By encircling the ligands with bulky macrocyclic hosts (such as α -CD here), their lateral sizes become significantly increased (Fig. 13d; compare **5** in Fig. 2). UV–vis studies on NPs shown in Fig. 13d have indicated the absence of π – π stacking between the neighboring AB groups, and switching kinetics were identical to those of free molecules [212].

Photoisomerization accompanied by reversible NP aggregation

Having discussed some steric and electronic aspects of AB isomerization in systems where the solvents (DCM, DMF) stabilized NPs covered with *both* isomers of the photoswitch, we will now focus on several examples where isomerization is followed by NP aggregation. The isomerization is accompanied by a significant change in the polarity of the molecule—it therefore does not come as a surprise that AB-decorated NPs can undergo reversible coagulation and redispersion when exposed to the different wavelengths of light. The possibility to reversibly address the NP aggregation state could lead to the development of nanomaterials whose structure and properties would be affected and adjusted by light. Moreover, the thermally induced (spontaneous) re-isomerization of *cis*-AB could be employed to render not only the NPs, but also their properties (optical, magnetic, catalytic, etc.) metastable—as we will see in an example below.

UV irradiation of trans-AB-coated Au NPs in nonpolar solvents (toluene, cyclohexane) leads to their aggregation and sedimentation [211,213,215,218]. The solution of NPs prior to irradiation is stable due to strong solvation of the hydrophobic *trans* isomer by the solvent molecules. Exposure to UV light, however, generates the hydrophilic *cis* isomer and disrupts the solvation shell around the NPs, leading to their aggregation. This solvophobic effect probably operates in tandem with direct dipolar interactions between cis-AB groups on different NPs [215]. UV-induced aggregation also took place in chloroform, although the higher dielectric constant of the solvent discriminated between differently substituted ABs [219]. For example, NPs terminated with *cis*-4-alkoxy-4'-alkylazobenzene remained soluble both before and after UV irradiation, however, when a more polar *cis*-4,4'-alkoxyazobenzene was used instead, reversible aggregation has successfully been carried out [219], thus demonstrating the importance of the substitution pattern on the AB group for the properties of the NPs. Overall, these results indicate that nonpolar solvents stabilize trans- (but not cis-) AB-coated NPs, and suggest that the opposite effect—that is, stabilization cis- (but not trans-) AB-coated NPs—might occur in more polar solvents. Interestingly, such a system has indeed been reported in a study that surveyed a variety of solvent mixtures [220]. Fine-tuning of the polarity of various chloroform (dielectric constant, ε_r = 4.81)-ethanol (ε_r = 24.3) mixtures led to the finding that a 1:3 chloroform-ethanol mixture provided a suitable environment for an "inverse" light-induced aggragation of AB-coated NPs, in which the ther-

mally equilibrated NPs formed an insoluble precipitate, but were dispersed in the "metastable" state of the ligands.

Another "inverse" system is based on NP-functionalized 4,4'-diphenylazobenzene (azobiphenyl) and dispersed in toluene [221]. In this case, the extended aromatic system of the ligand molecule encouraged favorable π - π stacking interactions between *trans*-ABs anchored to different NPs, leading to interdigitation and formation of large NP aggregates. Interestingly, π - π stacking interactions between *cis*-ABs were reduced to the extent that the NPs dissolved following UV irradiation. The latter example highlights the importance of various types of interparticle interactions and demonstrates that light-controlled self-assembly properties of NPs can be engineered by subtle changes in the molecular structure of the photoswitch.

The ability to reversibly self-assemble NPs using light was recently combined with the fact that the aggregation process is accompanied [184,222] by pronounced color changes to develop novel rewritable information storage media, in which writing and erasing can be performed using light [211]. The main challenge on the way to this goal was the ability to carry out NP aggregation in a semi-permeable organogel rather than in solution—fortunately, the AB-coated NPs did not loose their switching or aggregation properties when dispersed in syndiotactic PMMA matrices (Fig. 14a). Upon exposure to UV light, thin films containing Au NPs changed color from red to purple to blue, depending on the aggregate size (determined by the irradiation time; Fig. 14b, *left*). Likewise, the originally yellow films based on Ag NPs [223] turned orange-red and then purple (Fig. 14b, right). When the irradiation was administered locally (e.g., through a transparency mask) inducing NP aggregation in the exposed areas, images (such as those in Fig. 14d) could be created. A unique feature of this technique is that multicolor images could be created using only one type of "ink" by irradiating different areas of the same film for different periods of time. Owing to the dynamic [224] nature of the NP aggregates, the messages persisted only as long as ABs remained in their *cis* configuration—that is, they disappeared quickly when exposed to intense visible light, or "self-erased" slowly under ambient conditions or in the dark. It is worth emphasizing that the process was completely reversible (Fig. 14c) and once a message was erased, a new one could be written (Fig. 14d). Moreover, the films could be preprogrammed



Fig. 14 Writing messages on a self-erasing paper [211]. (a) Schematic representation of a reversible NP selfassembly process and TEM images of individual (*left*) and aggregated (*right*) NPs. (b) Self-assembly of AB-modified Au (*left*) and Ag (*right*) NPs followed by UV–vis spectroscopy. t_{irr} s indicate UV irradiation times and the colors of the traces correspond to those of the original samples. (c) Reversible color changes of an Au NP film exposed alternately to UV and visible light. (d) Writing and erasing multiple messages in the same Au NP film. Adapted with permission from ref. [211] (copyright © 2009 Wiley-VCH Verlag GmbH & Co. KgaA).

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so as to keep the messages for prescribed periods of time [211]. This strategy was based on functionalizing the NPs with predefined numbers of ABs—not surprisingly, increasing AB coverages on NPs made writing more rapid, and the images took more time to fade. Overall, the self-erasing paper is a vivid demonstration of the unique possibilities created by a combination of NPs and photoswitchable molecules.

UV-triggered irreversible NP aggregation

The examples covered so far described AB-functionalized NPs undergoing reversible changes in structure and/or properties. Although AB isomerization itself is a fully reversible reaction, it could also be used to trigger other, irreversible processes. For example, AB-induced aggregation of NPs coupled with the formation of covalent crosslinks between the NPs in the aggregated state could be developed into a way of organizing NPs into irreversible NP assemblies using light. To achieve this goal, a thiolated AB compound bearing an additional thiol group at the 4'-position ("azobenzene dithiol"; ADT in Fig. 15a) was synthesized [215]. Au NPs functionalized with this ligand were metastable in toluene solution most likely because a good solvation of *trans*-AB molecules rendered the unbound thiol groups effectively unreactive. UV irradiation, however, induced *trans*-to-*cis* isomerization followed by NP aggregation. Only in this aggregated state were the free thiol groups able to "find" other NPs and form covalent bridges between the neighboring NPs (the proposed mechanism of light-induced self-assem-



Fig. 15 Light-induced self-assembly (LISA) of NPs [215]. (a) Structural formula and schematic representation of *trans*-bis(11-mercaptoundecanoxy)azobenzene (*trans*-ADT). (b) Proposed mechanism of LISA: UV irradiation of *trans*-ADT NPs induces photoisomerization and NP aggregation. Only in this aggregated state covalent crosslinking between the neighboring NPs can take place. Attached photographs show vials containing solutions of NPs before (*left*) and after (*right*) UV-induced self-assembly. (c) Plot of ADT surface coverage on NPs vs. diameters and λ_{max} values of the resulting spherical aggregates. (d) Scanning electron microscopy (SEM) image of covalently crosslinked, spherical aggregates of NPs obtained when LISA was conducted in pure toluene. (e) SEM image of a covalently crosslinked, crystalline assembly of NPs obtained when LISA was conducted in a 4:1 toluene-methanol mixture. Adapted with permission from ref. [215] (copyright © 2007 National Academy of Sciences USA) and ref. [1] (copyright © 2010 Royal Society of Chemistry).

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bly (LISA) of NPs [215] is shown in Fig. 15b). When the process took place in pure toluene, the relatively polar NP aggregates tended to minimize contact with the solvent and assumed spherical shapes ("supraspheres"; Fig. 15d). The formation of the supraspheres followed the nucleation-and-growth mechanism, whereby surface concentrations of AB determined the number of particles which acted as "seeds"—for example, high AB coverages gave rise to large numbers of seeds, and therefore small aggregate diameters. This relation has made it possible to precisely regulate the suprasphere dimensions in the 50–300 nm diameter range (Fig. 15c). In more polar environments (e.g., toluene-methanol mixtures), *cis*-ABs were better solvated, and the NPs had enough time to adjust their positions within the aggregates before the irreversible, covalent crosslinking took place. As a result, formation of regular, 3D crystals, such as the one shown in Fig. 15e, was observed. It is worth pointing out that of the two well-defined NP superstructures obtained, the spherical ones have so far proven more useful as versatile precursors of different classes of materials, including mesoporous metal sponges [225], novel heterodimeric NPs [226], as well as anisotropic NP assemblies [227].

In the LISA mechanism described above, photoisomerization of surface-bound ABs was followed by the spontaneous aggregation of NPs. One way to *decouple* these two processes and to stabilize the metastable *cis*-ADT NPs could be based on photoisomerizing ABs on NPs "trapped" in a solid, transparent medium (Fig. 16a)—with the assumption that spatial constraints imposed by the solid medium would not prevent AB isomerization, but preclude NP aggregation (rendering the *cis*-ADT NPs (liter-



Fig. 16 NP-based temperature sensors. (a) Photoisomerization of ABs on NPs immobilized in a frozen solvent is used as a way to stabilize the metastable *cis*-ADT NPs. Aggregation is triggered by bringing the sample above the solvent melting point, $T_{\rm M}$. Because the aggregation is irreversible, subsequent freezing results in a pale red (as opposed to the original bright red) solid. Therefore, the NPs "remember" that the sample has been brought up above $T_{\rm M}$. (b) UV–vis spectra accompanying the aggregation process. (c) Samples of ADT NPs in solvents of varying $T_{\rm M}$ s UV-irradiated at ~ -80 °C, warmed up to 0 °C, and cooled down again. (d) The use of a cone-shaped, transparent template can provide information about the time the sample was above $T_{\rm M}$. Adapted with permission from ref. [228] (copyright © 2010 Wiley-VCH Verlag GmbH & Co. KgaA).

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ally) "frozen" in the solid state; diffusion of NPs in a solid medium is negligible). Moreover, if the solid medium is a frozen solvent, its melting would trigger irreversible aggregation of NPs. Because the aggregation process is accompanied by a pronounced color change (Fig. 16b), these metastable NPs could serve as temperature probes "remembering" the temperature history of the sample [228]. This concept is illustrated by experimental samples (shown in Fig. 16c) containing ADT-functionalized Au NPs in various aromatic solvent (benzene-toluene-xylene) mixtures differing in their melting points, $T_{\rm M}$. All of these samples were UV-irradiated at a low (~ -80 °C) temperature, then momentarily warmed up to an unknown temperature $T_{\rm X}$, and cooled down again. Only the samples whose $T_{\rm M} < -7.7$ °C turned pale—indicating that the solvent had melted, inducing NP aggregation. This observation leads one to the conclusion that 6.5 °C < $T_{\rm X} < -7.7$ °C—in fact, $T_{\rm X}$ was 0 °C. Moreover, encasing the metastable NPs samples inside a cone-shaped elastomer template (Fig. 16d) enables the construction of sensors which not only "remembered" whether, but could also indicate *how long* the sample was above $T_{\rm X}$. This type of geometry enforces directional melting (and NP aggregation) starting at the bottom of the sample, the precipitation front proceeding upwards. For example, the sensor shown in Fig. 16d allows one to visually distinguish between samples raised above $T_{\rm M}$ for 8 and 10 min.

CONCLUSIONS

Although AB has been around for a long time, the recent interest in stimuli-responsive materials ensures that the field of AB-incorporating systems is advancing rapidly—in fact, almost half of the literature references in this review come from the past five years. Despite these recent achievements, much remains to be done. For example, (i) the possibility of adjusting the AB isomerization wavelength (the *trans* absorption band can be shifted from $\lambda \approx 365$ nm (near UV) all the way up to $\lambda \approx 520$ nm (green light) with the substitution pattern of the parent AB rings [229]) remains pretty much [230] unexplored despite the fact that the ability of a given system to respond to multiple wavelengths of light might represent an interesting contribution to the evolving field of systems chemistry [231]. (ii) The metastable nature of cis-AB is a fascinating feature that gives rise to new types of dynamic materials [211], however, certain applications (e.g., optical data storage) require thermal stability of both states—in this context, the combination of ABs with other types of photoswitches in which both isomers are thermally stable (e.g., diarylethenes [232,233]) seems attractive. (iii) The elegant research of Einaga et al. have demonstrated the possibility of reversibly modulating magnetic properties of various solids using light via AB monolayers [210,234,235]—a strategy that could in principle be used to control a range of other material properties. ABs assembled on the surfaces of catalytic metals, for example, could be used to modify the catalytic activity, either by blocking access of substrates to the metal surface or via electronic communication with the underlying catalytic surface. Another way to tune the catalytic properties of surfaces by light is to immobilize predesigned photoswitchable organic catalysts—one such catalyst has recently been reported by Hecht et al. [236], but its switching is still to be demonstrated. (iv) As far as NPs are concerned, practically all examples of AB-functionalized materials reported to date are limited to spherical NPs. Although one example of nanorods uniformly covered with ABs has been reported [237], strategies to place the photoswitches selectively on given crystallographic planes of these and other anisotropic NPs still need to be developed. (v) Finally, in the field of nanoporous materials, a grand challenge remains to develop AB-based systems capable of absorbing and releasing gas molecules reversibly by using light—a goal that could also be achieved using NP networks covalently crosslinked with AB-incorporating bridges [238,239].

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