Recent advances in photoresponsive supramolecular self-assemblies

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Construction of supramolecular self-assemblies whose self-assembling process and self-assembled architectures can be controlled by external stimuli is a fascinating and challenging topic for supramolecular chemists. The modification of photochromic molecules with noncovalent interaction sites or the incorporation of photochromic molecules into self-assembling modules makes light an ideal external input, providing high-performance photoresponsive multicomponent self-assemblies. Among such systems, in this *tutorial review* we deal with several photoresponsive supramolecular self-assemblies showing a unique mechanism and/or type of photoresponse. These examples illustrate that we would be able to produce further new photoresponsive molecular ensembles if one can elaborately hybridize photochromic molecules to specifically-designed supramolecular self-assemblies. We believe that the accumulation of insight into the construction principle, mechanism and concept of such smart supramolecular self-assemblies should realize practical smart functional materials.

Introduction

Supramolecular self-assembly has emerged as a powerful tool for the construction of well-defined nanoarchitectures or for the tailoring of physical properties of polymers from small molecular building blocks.[1–3] The dynamic nature of supramolecular self-assembly due to the reversibility of noncovalent interactions is also a fascinating property,[4] motivating supramolecular chemists to investigate the creation of multicomponent self-assemblies, the degree of aggregation and/or self-assembled nanoarchitectures of which could be regulated by external stimuli. These researches are targeted on the fabrication of smart functional materials where physical properties and functions emerging from large molecular ensembles could be controlled at will.

Dynamic supramolecular self-assembly can be controlled either by changing the external environment or by *in situ* morphological transformation of building blocks. Specifically, the former strategy might be achieved by varying the temperature and the concentration of solutions, or the polarity of medium. On the other hand, the latter strategy requires external input leading to a large mechanical motion of building blocks. The modification of photochromic molecules with noncovalent interaction sites or the incorporation of photochromic molecules into self-assembling modules makes light an ideal external input to establish this strategy. Photoinduced mechanical motion (photoisomerization) of photochromic molecules generally leaves no chemical waste, and furthermore it can be repeated reversibly without addition of any chemical substance. If two photoisomers absorb different wavelengths of light, fully controlled two-state photoswitchable molecular systems and materials can be created.[5–17] Especially for multicomponent self-assemblies, a large number of photoresponsive systems exhibiting a photocontrollable degree of aggregation and/or self-assembled architectures have been successfully created so far.[18]

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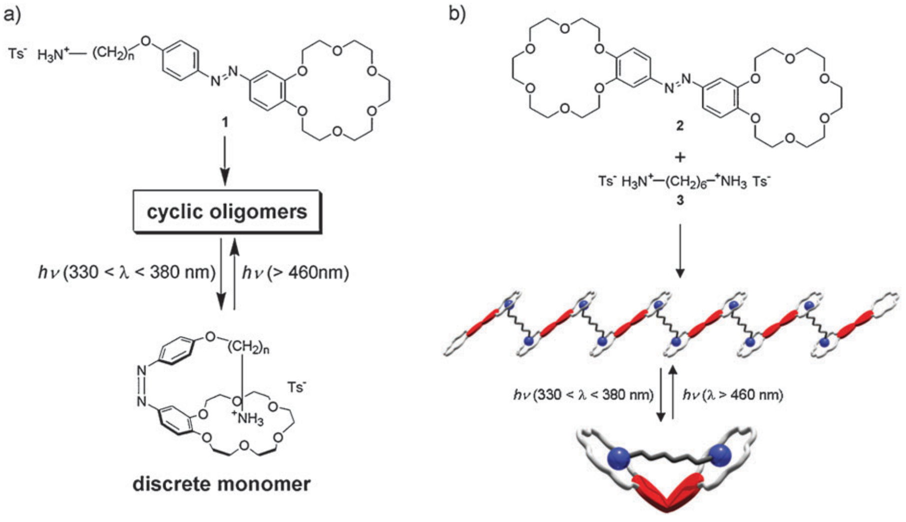

Fig. 1 Photoresponsive self-assemblies established by Shinkai *et al.* (a) One-component system achieved by self-complementary azobenzene **1** functionalized on one end by an ω-ammoniumalkyl and on the other by a crown ether. (b) Two-component system achieved by the mixture of symmetrical azocrown **2** and α,ω-diammoniumalkane **3**.

However, despite the same strategy being employed, several photoresponsive self-assemblies exhibit unique photoresponses upon shedding light. In this tutorial review, we highlight such photoresponsive self-assembling systems whose mechanism and/or type of photoresponse are unique. The systems featured here are: (i) self-assemblies of polymers controlled by photoresponsive host–guest complexation, (ii) photoresponsive self-assemblies affording two distinct extended supramolecular structures, (iii) diversification of photoresponse within a single supramolecular motif, and (iv) photo-manipulation of helical nanostructures. Before introducing these systems, we briefly visit the strategy generally applied for the construction of photoresponsive self-assembling systems.

General strategy

The basic idea for manipulating supramolecular self-assemblies by external light input has already been put forward by Shinkai *et al.* in 1987.[19] They prepared self-complementary azobenzene derivatives **1** functionalized on one end by an ω-ammoniumalkyl and on the other by a crown ether (Fig. 1a). The self-aggregation properties of these molecules in organic media can be controlled by light because their *trans*-isomers favor cyclic oligomerization whereas their *cis*-isomers undergo intramolecular complexation between the two interactive sites, generating a closed monomer. On the other hand, photocontrollable polymeric assemblies were achieved by mixing symmetrically crown-functionalized azobenzene **2** and oligomethylene-α,ω-diammonium cations (Fig. 1b).[20] In both the systems, the bent conformation of *cis*-azobenzene isomer plays an important role as non-aggregative building blocks by forming ''closed'' supramolecular species. The same approach was employed for the construction of photoresponsive self-assemblies of cyclic oligopeptides.[21]

More easily, if the molecular structure or the chemical property of either photoisomer is less aggregative compared to the other, or if we can adjust conditions (*e.g.*, solvent polarity, concentration and temperature) to be unfavorable for the aggregation of either photoisomer, we can make photoresponsive self-assemblies where the degree of aggregation can be controlled by light input. For instance, the *cis*-isomer of azobenzene is morphologically less aggregative because of its bent conformation disadvantageous for dense molecular packing. Moreover, *cis*-azobenzene is more polar compared to the *trans*-isomer,[22] and thereby less aggregative in polar media.[23,24] A variety of photoresponsive self-assemblies have been established based on these principles, which include photoresponsive micelles, supramolecular polymers and organogels.[18,25,26]

Self-aggregation of **4a**[27] and **4b**[28] based on diarylethene photochromic molecules[29] shows contrasting photoresponses (Fig. 2). In the case of **4a**, the flexible 'open' isomer is more aggregative than the rigid 'closed' isomer. In sharp contrast, the 'open' isomer of **4b** is not capable of aggregating and *vice versa*. This might be related to the fact that the hydrogen-bonding interaction of **4b** is more directional and specific, thereby vulnerable to the conformational freedom of the

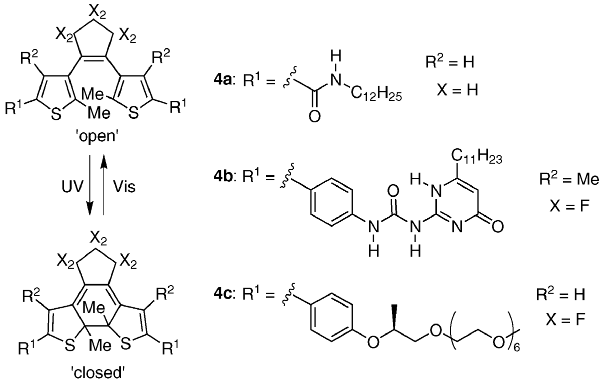

Fig. 2 Self-assembling diarylethene photochromic molecules **4a–c**.

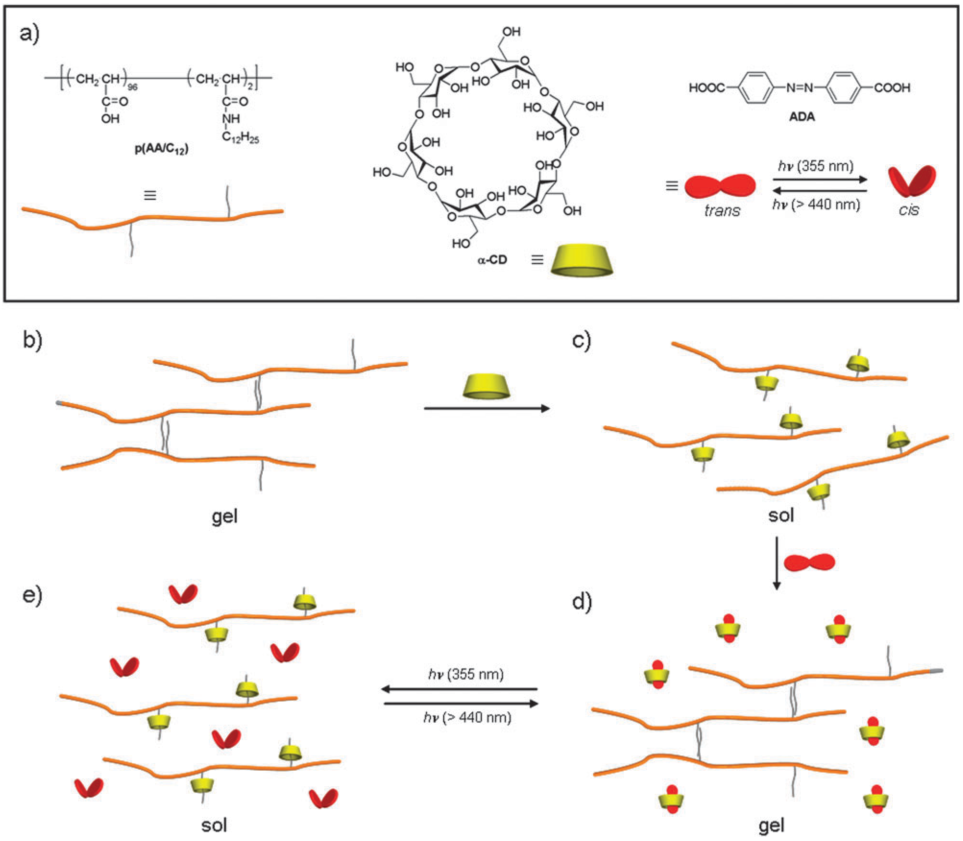

Fig. 3 (a) Structures and cartoon representations of aqueous polymer **p(AA/C$_{12}$)**, azobenzene dicarboxylic acid (**ADA**) and αCD. (b–e) Schematic representation of the self-assembly of aqueous polymer **p(AA/C$_{12}$)** controlled by the photoresponsive complexation between **ADA** and αCD.

building blocks. Analogues of **4a** have recently been applied as building blocks for substantially important photoresponsive self-assemblies where supramolecular chirality of ensembles can be transcribed into molecular chirality by external light input.[30–34] Self-aggregation of diarylethene **4c** occurs in aqueous media through a π–π stacking interaction, which can be controlled photochemically due to the change in molecular planarity upon open (aggregative)–close (dissociative) isomerization.[35]

Thus, the systems introduced in this section exemplify generally employed strategies to obtain photoresponsive smart self-assemblies. In the following sections we introduce those systems that are based on a unique mechanism or that show a unique photoresponse.

Self-assembly of polymers can be controlled by photoresponsive host–guest complexation

Most photoresponsive self-assemblies possess photoswitchable moieties in building blocks in order to induce morphological transformation. From this viewpoint, the photoresponsive self-assemblies of water-soluble polymer **p(AA/C$_{12}$)** reported by Harada *et al.* is unique because the photochromic molecule is used as a 'photoresponsive key'[36] which does not take part in the ensembles (Fig. 3a).[37] They utilized photo-tunable binding affinities of azobenzene dicarboxylic acid (**ADA**) guests with α-cyclodextrin (αCD) host. Similar to the unsubstituted azobenzene,[38] *trans*-**ADA** shows higher binding affinity to αCD compared to the *cis*-isomer.

Poly(acrylic acid)s **p(AA/C$_{12}$)** modified by dodecyl groups self-assemble in water through solvophobic interaction between the aliphatic side chains (Fig. 3b), affording hydrogels. When αCD is added to the gels, sol-to-gel conversion is observed because αCDs capture dodecyl groups, disrupting their solvophobic interactions (Fig. 3b and c). Remarkably, the addition of *trans*-**ADA** to this binary mixture converts the solution to the original gel state since *trans*-**ADA** can predominantly complexes with αCD, thus rendering the dodecyl chains free (Fig. 3c and d). This ternary mixture including **p(AA/C$_{12}$)**, **ADA** and αCD is therefore capable of photoswitching between gel and solution states owing to the photo-tunable binding affinity between **ADA** and αCD. Indeed, irradiation of the gel of the ternary mixture with UV-light resulted in a gel-to-sol conversion as a result of lower binding affinity of photogenerated *cis*-**ADA** to αCD than that of dodecyl group (Fig. 3d and e). Subsequent irradiation of the photogenerated solution with visible light again induced gelation due to preferential complexation of αCD with *trans*-**ADA** (Fig. 3e and d). This system might be categorized as a unique photoresponsive self-assembly driven by a "photoresponsive key". A similar but irreversible photoinduced disaggregation has been reported for supramolecular polymers of quadruple hydrogen-bonding modules.[39]

Other fascinating photoresponsive self-assemblies of polymers have been reported by the same group.[40] They prepared

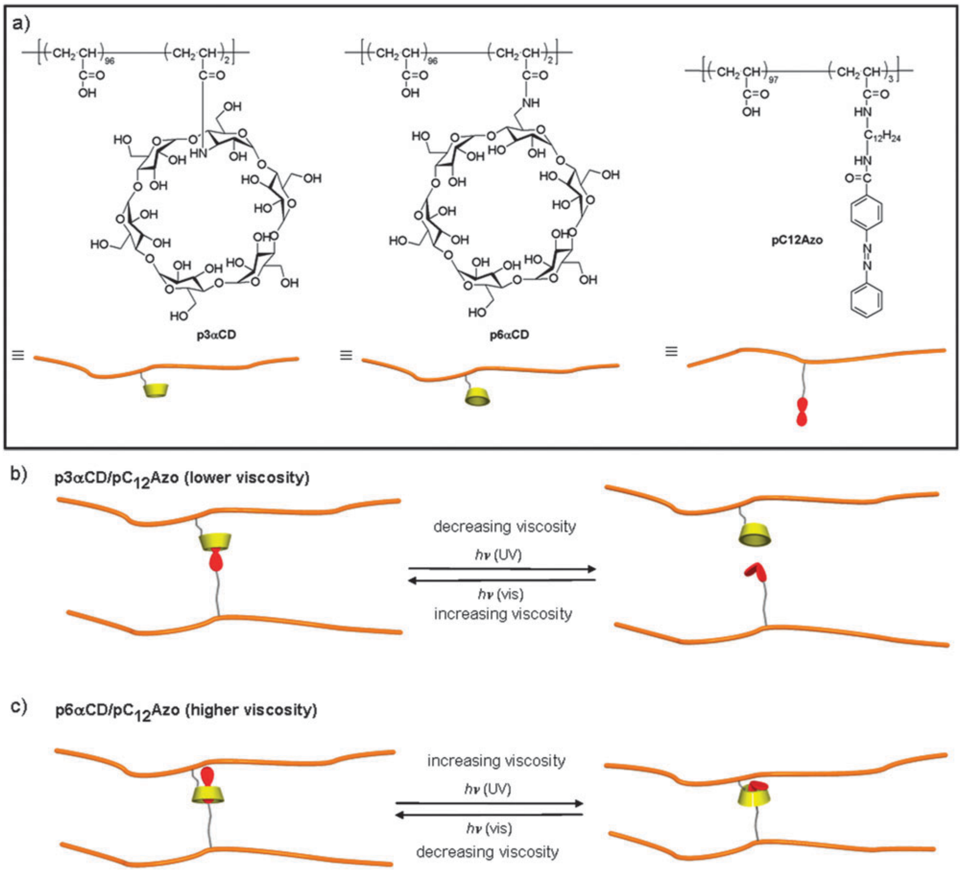

Fig. 4 (a) Structures of crown-appended polymers **p6αCD** and **p3αCD**, and azobenzene-C_{12}-modified polymer **pC_{12}Azo**. (b and c) Schematic representations of photoresponsive self-assemblies of polymer mixtures **p3αCD/pC_{12}Azo** and **p6αCD/pC_{12}Azo**, respectively.

water soluble polymers **p3αCD** and **p6αCD** possessing cyclodextrin pendant groups (Fig. 4a). For **p3αCD**, αCD is connected at the 3-position of a glucose ring whereas for **p6αCD** it is connected at the 6-position. **pC_{12}Azo** is the complementary photoresponsive polymer bearing an azobenzene group on the toe of the dodecamethylene (C_{12}) side chains. The mixtures of these host and guest polymers, *i.e.*, **p3αCD/pC_{12}Azo** and **p6αCD/pC_{12}Azo**, were anticipated to generate cross-linked assemblies through the complexation between azobenzene-C_{12} and αCD moieties. The steady-state viscosity (η) measurements of semidilute solutions showed that these mixtures have dramatically different η values despite the fact that both the assemblies are based on the same host–guest interactions. The η value of **p6αCD/pC_{12}Azo** was two orders of magnitude larger than that of **p3αCD/pC_{12}Azo**. This already suggests that local binding affinities between αCD and azobenzene moieties are different for the two binary mixtures. The mixtures were further investigated by 2-D NMR (NOESY) technique, uncovering different local interaction modes. For **p3αCD/pC_{12}Azo**, interactions were mainly observed between azobenzene and αCD moieties (Fig. 4b, left) whereas for **p6αCD/pC_{12}Azo**, interactions were predominantly observed between C12 and αCD moieties (Fig. 4c, left). Surprisingly, such a small different in local interaction modes causes contrasted η changes for the two binary mixtures upon alternative irradiation with UV and visible light. The mixture **p3αCD/pC_{12}Azo** showed a further decrease in viscosity upon irradiation with UV-light (Fig. 4b, from left to right) whereas **p6αCD/pC_{12}Azo** showed a further increase in viscosity (Fig. 4c, from left to right). When these UV-irradiated mixtures were subsequently irradiated with visible light, reversal changes were observed for each mixture, *i.e.*, increase and decrease in viscosity for **p3αCD/pC_{12}Azo** and **p6αCD/pC_{12}Azo**, respectively (Fig. 4b and c, from right to left). These interesting observations suggest the occurrence of quite different changes in the local interaction modes for the two binary mixtures upon *trans*-to-*cis* isomerization of azobenzene moieties. NOESY measurements of the UV-irradiated mixtures revealed that azobenzene-C_{12} and αCD moieties of **p3αCD/pC_{12}Azo** no longer interact (Fig. 4b, right) whereas C_{12} and αCD moieties of **p6αCD/pC_{12}Azo** interact even after UV-irradiation, suggesting that **p6αCD** and **pC_{12}Azo** are interlocked upon *trans*-to-*cis* isomerization of azobenzene moieties (Fig. 4c, right). The positive effect of *trans*-to-*cis* isomerization of azobenzene on supramolecular assemblies (*i.e.*, enhancement of noncovalent interaction or increase in degree of aggregation) is a unique photoresponse.

Well-defined aggregation of both photoisomers provides self-assemblies where two distinct supramolecular architectures can be guided by light

The use of two distinct conformations of photochromic molecules given by photoisomerization as building blocks

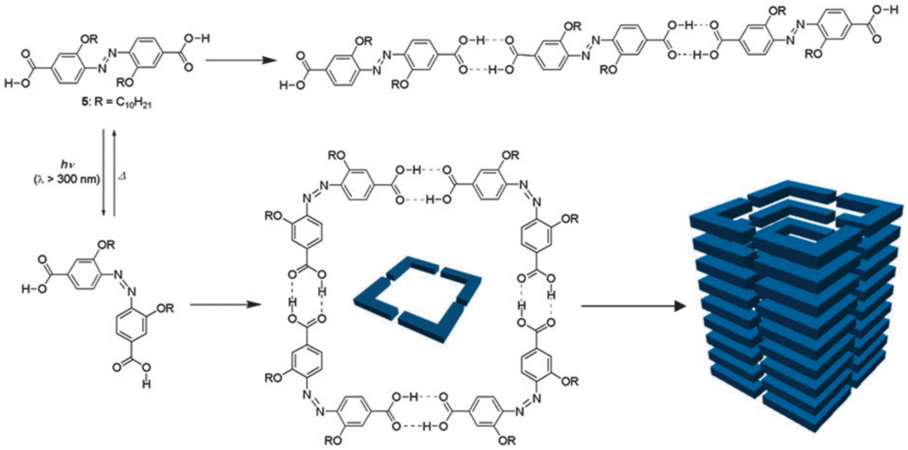

Fig. 5 Photoresponsive self-assemblies of azodibenzoic acid derivative **5**.

for the extended supramolecular polymerization provides self-assemblies where two extended supramolecular architectures can be guided by light input. However, the construction of such systems appears to be extremely difficult because one of the two photoisomers of most photochromic molecules are generally flexible, and thereby unsuitable as building blocks for extended supramolecular architectures. One example of this type of photoresponsive self-assembly has been reported by Sleiman and co-workers. They found that the *trans*- and the *cis*-isomers of azodibenzoic acid derivative **5** self-assemble into distinct higher-order structures (Fig. 5).[41] Vapor pressure osmometry (VPO), NMR, single crystal and powder X-ray measurements and semiempirical calculations demonstrated that the *trans*-isomer forms linear tapelike aggregates whereas the *cis*-isomer generates a discrete tetramer. Remarkably, hierarchically organized rod-like superstructures have been visualized for the *cis*-isomer by using transmission electron microscopy, which was proposed to be constructed through extended π–π stacking of the tetrameric *cis*-isomers. This is a quite rare example where the bent conformation of *cis*-azobenzene is elaborately used as a building block of a well-defined supramolecular edifice. As a result of the tetramerization (and further stacking of the resulting tetramers as suggested by a ^{1}H NMR spectral change), the thermal *cis*-to-*trans* isomerization was significantly suppressed in CH_2Cl_2 compared to the molecularly dissolved state in a hydrogen bond-competing solvent (DMSO).

Introduction of photoswitchable units into a hydrogen-bonded rosette gives cyclic assemblies showing diverse photoresponses

Our group has studied a series of photoresponsive hydrogen-bonded macrocycles so-called rosettes,[42] formed from azobenzene-appended melamines and barbiturates/cyanurates through complementary triple-hydrogen-bonding interactions (Fig. 6). The uniqueness of our photoresponsive rosettes might be the expression of diverse photoresponses even though the same supramolecular motif (hydrogen-bonded rosette) is employed. The type of photoresponse depends on the substituent of the building blocks. The simplest result was observed for rosette I, which is given by mixing **AzoMel1** and **BAR**, both lacking sterically hindered substituents.[43] Rosette I prepared in chloroform is only kinetically stable, giving rise to an irreversible precipitation as a result of transformation into insoluble extended tapelike supramolecular polymers in the timescale of days (Fig. 7a → b). Upon 100 h aging, more than half of the components precipitate.

The azobenzene moieties of rosette I efficiently photoisomerize upon UV-irradiation with maintaining the rosette architectures as evidenced by ^{1}H NMR (Fig. 7a → c). In a photostationary state achieved for the $c = 5$ mM solution upon 1 h irradiation, the *trans* : *cis* ratio was 12 : 88. This result showed that the isomerization of azobenzene moieties has seemingly no impact on the self-assembly of rosette I. However, we noticed that the UV-irradiated solution does not produce any precipitates upon aging over 300 h (Fig. 7c and d), the situation of which is considerably different from the solution without UV-irradiation. This observation clearly demonstrates that the *cis*-azobenzene moieties suppress irreversible denaturation of rosette into tapelike assemblies. We believe that the *cis*-azobenzene moieties of **AzoMel1** increase the solubilities of competing tapelike oligomers, which must always be equilibrated with rosettes to a small extent, preventing their phase-separation (precipitation) by open-ended polymerization.[42,44]

Our next attempt was to induce different types of photoresponse for azobenzene-functionalized rosettes. We considered that the modification of both azobenzene-appended melamines and barbiturates with sterically-demanding substituents such as the tridodecyloxyphenyl (TDP) "wedge" might endow a more direct photoresponse with the self-assembly of a rosette. Thus **AzoMel2** and **BAR-TDP** were prepared and their mixture was shown to form thermodynamically stable rosette II in apolar solvents, which can be detected even by size exclusion chromatography (SEC) without decomposition.[45] As a compensation for the increased thermodynamic stability, however, the azobenzene moieties of rosette II displayed a low photoisomerization efficiency due to the steric crowding within the rosette: the *trans* : *cis* ratio in a photostationary state achieved by the best conditions is only 75 : 25. Statistically,

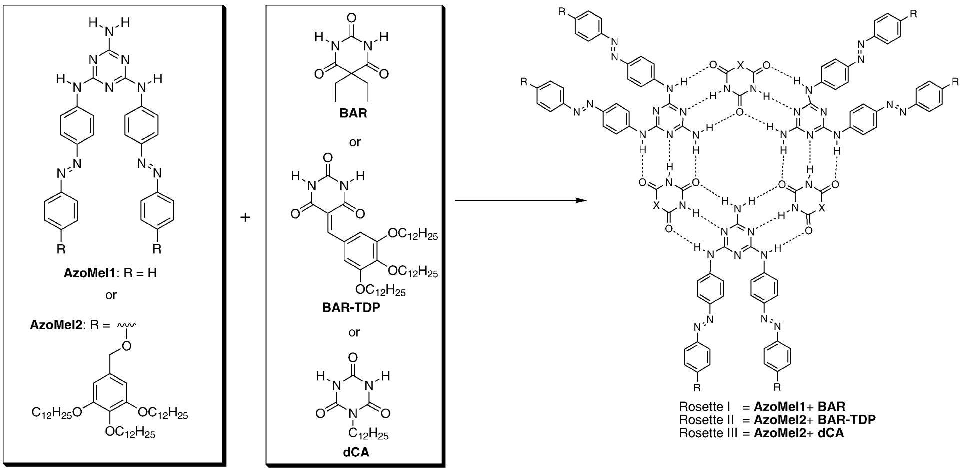

Fig. 6 Supramolecular rosettes I–III formed by mixing azobenzene-appended melamines **AzoMel1** or **AzoMel2** and barbiturates **BAR** or **BAR-TDP** or dodecyl cyanurate **dCA**.

this ratio means that only one or two of the six *trans*-azobenzene moieties in a rosette isomerized to the *cis*-isomer. This seemingly undesired outcome implies that **AzoMel2** possessing two *cis*-azobenzene moieties (*cis*,*cis*-**AzoMel2**) no longer complexes with **BAR-TDP** to construct the rosette architecture. Indeed, the 1 : 1 mixture of preliminary-photo-generated *cis*,*cis*-**AzoMel2** and **BAR-TDP** showed no trace of rosette formation on SEC analysis. Thus, *in situ* generation of aggregative *trans*,*trans*-**AzoMel2** in the *pool of monomers* upon irradiation with visible light triggered the generation of rosettes (Fig. 8), and the amount of rosette II could be quantitatively regulated by visible (increasing the concentration of the rosette) and UV light (keeping the concentration of the rosette).

Despite the low photoisomerization efficiency of the rosette II, we anticipated the expression of a further different type of photoresponse may come true if disk-shaped rosettes hierarchically organize into higher-order columnar structures.[46] This assumption is derived from the idea that the π–π stacking interaction is vulnerable to the perturbation of the aromatic surface, allowing the control over the organization of disc-shaped supramolecules even by a small geometrical change. However, rosette II was found to intrinsically lack the capability to organize into extended columnar superstructures even in the least aliphatic solvent such as cyclohexane, probably due to the bulky TDP wedge in the barbiturate component (**BAR-TDP**), noncoplanar to the hydrogen-bonded core. Thus, rosette III consisting of **AzoMel2** and dodecyl cyanurate (**dCA**) has been prepared, affording columnar assemblies stable in apolar solvents.[47] In a high concentration regime (>10 mM), solvent molecules were confined in the developed fibrous networks composed of bundled rosette columns, giving organogels (Fig. 9a). The *trans*→*cis* photoisomerization of the azobenzene moieties occurred even in the hierarchically organized state, showing a *cis*-content of *ca.* 45% under the

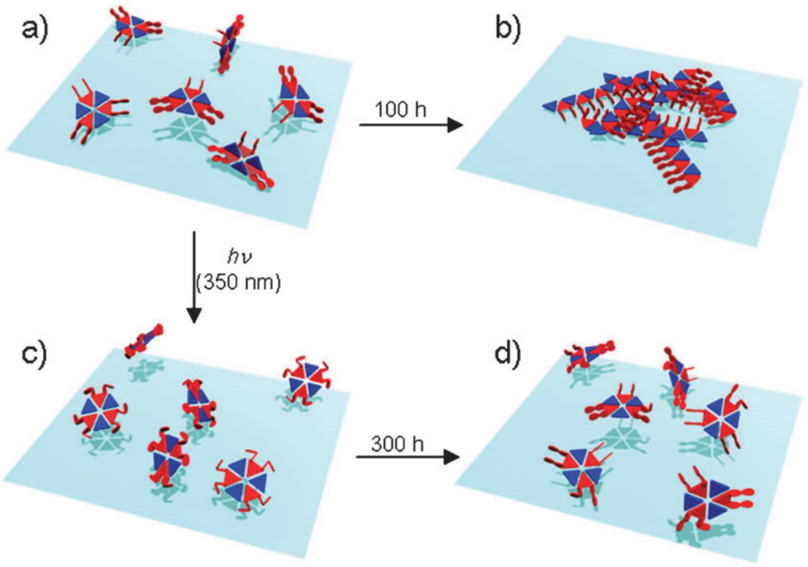

Fig. 7 Schematic representation of the photoinduced stabilization of rosette I.

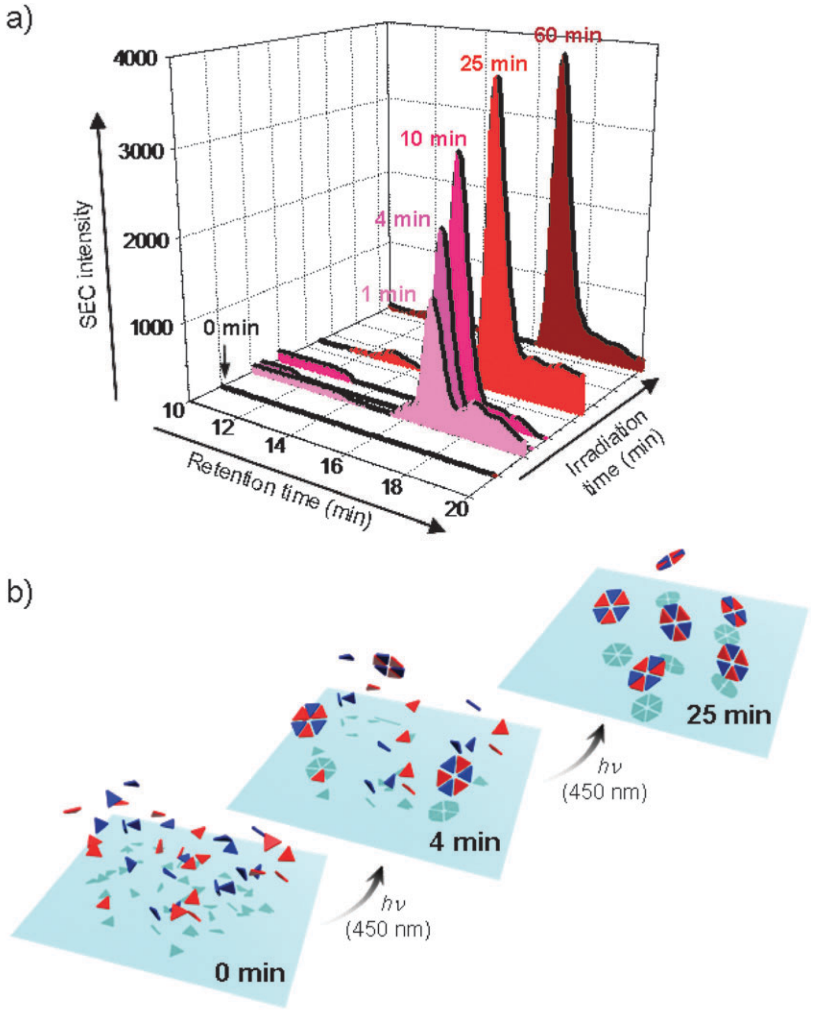

Fig. 8 Phototriggered formation of supramolecular rosette II. (a) Change of size exclusion chromatogram of the mixture of **AzoMel2** and **BAR-TDP** in toluene upon irradiation with 450 nm light, and (b) the corresponding schematic representation of the phototriggered formation of rosettes.

best conditions. The morphological change of rosette III accompanying the isomerization of azobenzene moieties impairs its stacking ability, which was demonstrated by the photoinduced gel-to-sol transition (Fig. 9a and b).[25] The resulting solution could be reconverted to the gel state upon irradiation with visible light and subsequent aging. Thus, by varying the number of the bulky TDP wedges, different types of photoresponse, *i.e.*, photoinduced stabilization, phototriggered formation, and eventually photoregulatable stacking have been achieved for the hydrogen-bonded macrocycles. We are now exploring further new photoresponses using our azobenzene-functionalized rosettes.

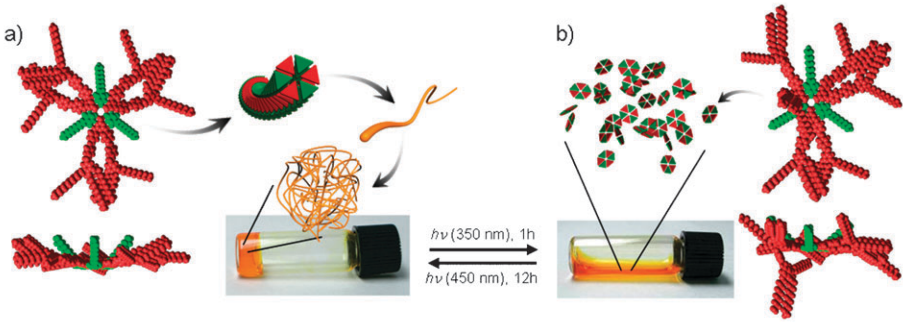

Fig. 9 Photoresponsive hierarchical organization of supramolecular rosette III in cyclohexane. (a) Organization of rosette III possessing all *trans*-azobenzene moieties. (b) Supramolecularly-dissolved rosette III possessing one *cis*-azobenzene moiety.

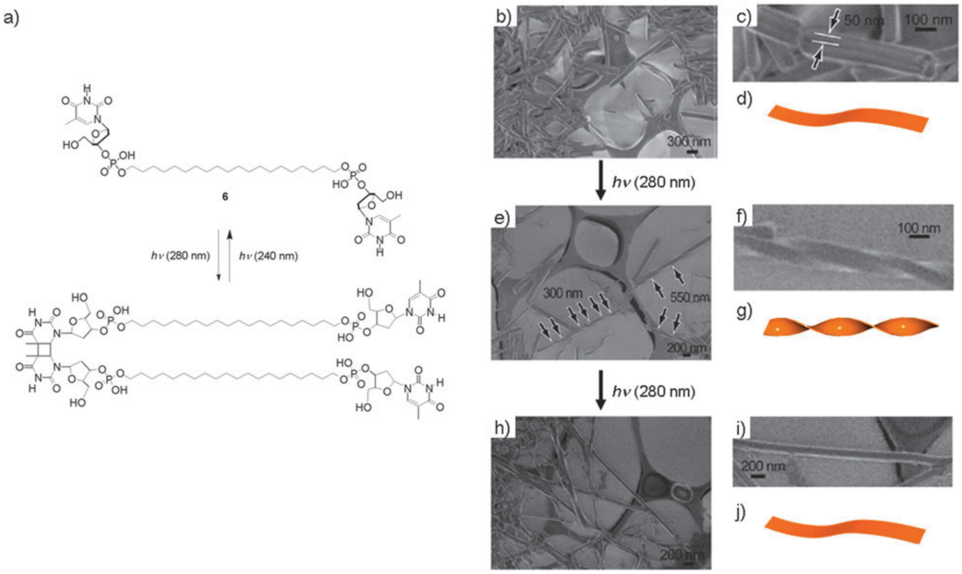

Fig. 10 (a) Photodimerization of thymine-terminated bolaamphiphile **6**. (b,c,e,f,h,i) SEM images of photoinduced helical twisting of self-assembled nanofibers of **6** and (d,g,j) the corresponding schematic representation of the helical twisting of elemental aggregate. (b–d) As-prepared fibers with no helical structure. (e–g) Helically-twisted fibers by 3 h irradiation of 280 nm UV right and (h–j) subsequent depletion of helical structure by 3 h irradiation with 240 nm UV-light. Reproduced with permission from ref. 49. Copyright 2006, Wiley VCH.

Hybridization of photoresponsive units into fiber-forming amphiphiles produces self-assemblies whose helical morphologies can be actuated by light

As a new paradigm of photoresponsive self-assembly, we finally introduce self-assembled nanofibers whose helical morphologies can be transformed by means of external light input. There is a growing interest in self-assembled helical nanoarchitectures because of their potential applications as liquid crystals, nonlinear optics, chiral sensing and separation and templates for inorganic materials.[48] Manipulation of self-assembled helical nanostructures by external light input thus allows us to fabricate smart nanomaterials, chiroptical properties and functions of which could be controlled at will.

One of such systems has been recently reported by Iwaura and Shimizu, who succeeded in the photoinduction/deletion of the helical feature in self-assembled nanofibers, using photo-induced dimerization of thymine nucleobase.[49] Amphiphile **6** terminated by thymidylic acid self-assembles in aqueous media through π–π stacking interactions between bases and solvophobic interactions between oligomethylene chains, forming nanofibers (Fig. 10a–d). Scanning electron microscopic observation revealed that the resulting nanofibers have 10 nm thickness and 80 nm width as typical dimensions and the overall morphology is nonhelical (Fig. 10b–d). Interestingly, when the aqueous solution of **6** was irradiated by 280 nm light for several hours, right-handed helical twisting was induced (Fig. 10e–g). Irradiation for 3 days rendered all the nanofibers

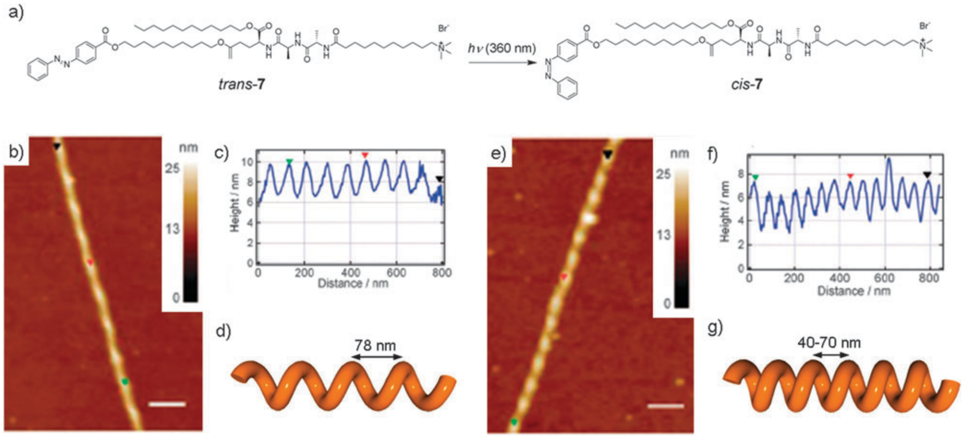

Fig. 11 (a) Photoisomerization of azobenzene-functionalized amphiphile **7**. (b,e) AFM height images and (c,f) the corresponding height profiles and schematic representation of the helical morphologies for the photoinduced actuation of a helical nanofiber of **7** (b–d) before and (e–g) after irradiation of UV-light. Reproduced with permission from ref. 50. Copyright 2007, Wiley VCH.

helical. UV/Vis spectroscopy demonstrated that 63% of the thymine moieties dimerized upon the irradiation, indicating that the helical twisting is indeed induced by the photodimerization of thymine moieties. MALDI-TOF MS measurements of helicity-induced nanofibers showed exclusive generation of dimerized **6** (Fig. 10a), and no oligomeric species even trimer were detected. Thus the torque of the helical twisting is considered to be intermolecular dimerization of two neighboring thymine moieties within nanofibers. Deletion of helicity was subsequently achieved by irradiation with 240 nm light, which reconverts the thymine photodimer to the monomer (Fig. 10h–j).

Another system where helical nanostructures can be manipulated by light stimulus has been reported by Stupp *et al.*[50] Amphiphile **7** (Fig. 11a) possessing terminal *trans*-azobenzene substituents self-organizes in cyclohexyl chloride to form superhelical nanofibers (Fig. 11b). The helical pitch visualized by atomic force microscopy is *ca.* 78 nm and uniform for all the nanofibers (Fig. 11c and d). Interestingly, irradiation of nanofibers dispersed in cyclohexyl chloride at 360 nm diminished the helical pitches to 40–70 nm (Fig. 11e–g). This morphological change can be explained in terms of an increase in the torsional strain upon isomerization of *trans*-azobenzene into the less planar (sterically bulky) *cis*-isomer. The decrease in the helical pitch varied from nanofiber to nanofiber due to the inhomogeneous isomerization efficiency among nanofibers. In contrast, the helical pitch is uniform in each nanostructure, indicating that the photoinduced decrease in the helical pitch is a relaxation process throughout the entire nanostructure.

Conclusions

Numerous research examples have demonstrated that the use of photochromic molecules in supramolecular self-assemblies is the most reasonable method to noninvasively manipulate their degree of aggregation and supramolecular architectures. Here, we have reviewed recently reported supramolecular self-assemblies, some of which could be considered as new paradigms of photoresponsive self-assembling systems. These examples illustrate that there remains a possibility to discover unprecedented photoresponsive molecular ensembles, if one can elaborately combine photochromic molecules with specifically-designed supramolecular building blocks. The incorporation of photoresponsive molecules showing more elaborate mechanical motions[33,51,52] would enhance the quality of photoresponse (*e.g.*, more precise control of aggregation number and supramolecular architecture), enabling the creation of photoresponsive self-assemblies with high sensitivity. On the other hand, the translation of signals emanating from multicomponent self-assemblies by light-stimulus (*i.e.*, changes in aggregation number and supramolecular architecture) to other chemical signals, as seen in light-sensed biological processes such as vision, is a topic that need to be addressed for the creation of further complex systems. We believe that the accumulation of insight into the construction principle, mechanism and concept of such light-driven supramolecular self-assemblies is crucial for the realization of such complex light-driven systems and practical smart functional materials in various fields of science and technology.

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