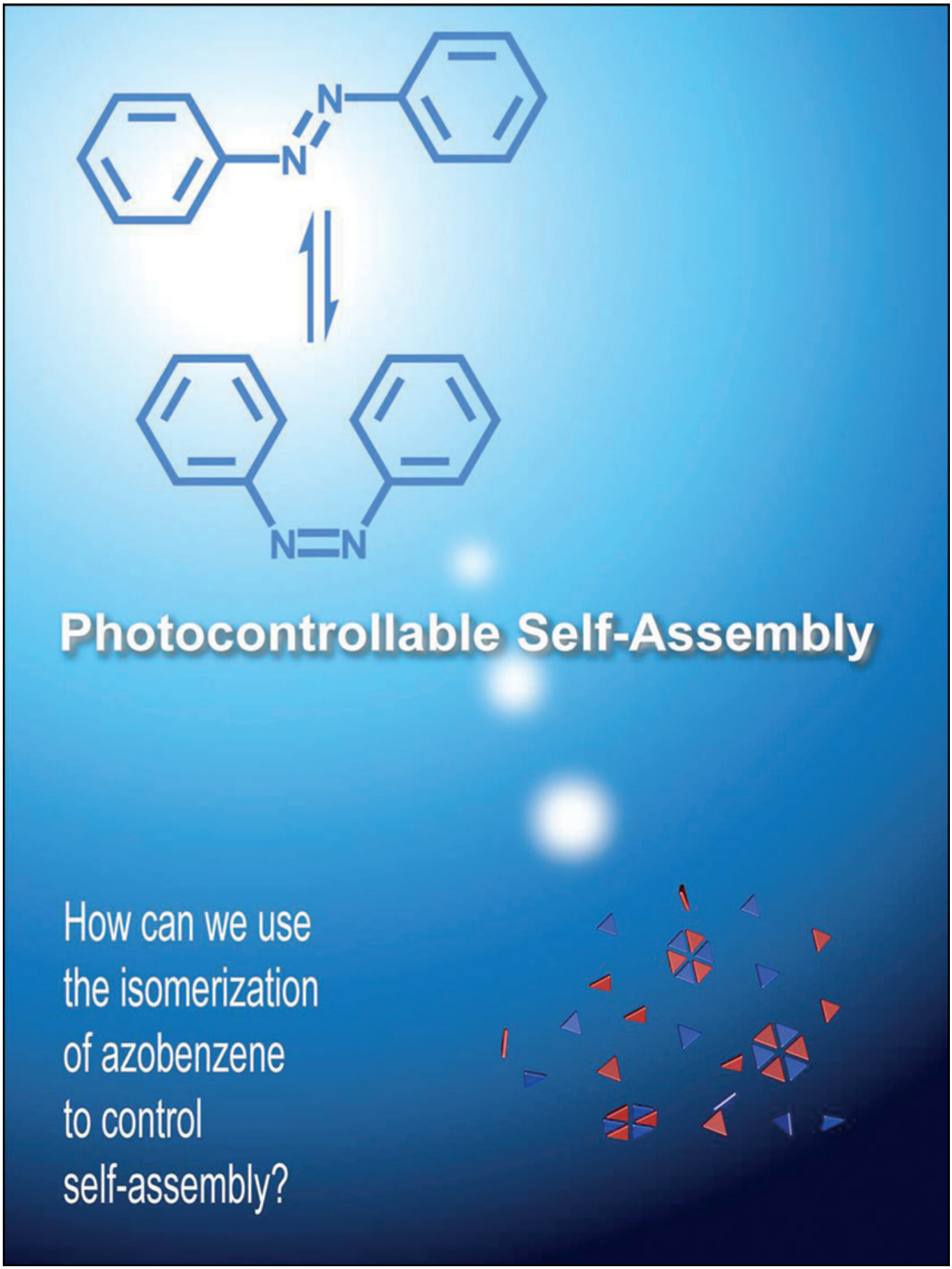


DOI: 10.1002/chem.200401323 *Chem. Eur. J.* **2005**, *11*, 4054 – 4063

Photocontrollable Self-Assembly

Shiki Yagai,* Takashi Karatsu, and Akihide Kitamura[a]

Abstract: The incorporation of photoswitching molecules into molecular building blocks creates the possibility of photoresponsive self-assemblies in which the self-assembled architecture or self-assembling process can be controlled by external light stimulus. Among the photoswitching molecules, azobenzene has been used most widely by virtue of the large photoinduced changes in its molecular geometry and physical properties. This article reviews how azobenzene can be effectively used to construct the self-assemblies in which supramolecular structure and formation/dissociation can be altered by light.

Keywords: azobenzene · isomerization · photochemistry · self-assembly · supramolecular chemistry

Introduction

Beyond scientific curiosity, molecular self-assembly is currently recognized as the most powerful strategy in the development of new functional materials requiring nanometer-scaled molecular manipulation that is not achievable by a conventional top-down approach.[1] Synthetically well-programmed molecular building blocks, with respect to the position of the noncovalent interactive sites, molecular shape, rigidity, and amphiphilicity, provide sophisticated self-assemblies through noncovalent interactions.[2]

One ultimate goal for supramolecular chemists may be to control molecular self-assembly under ambient conditions by external inputs such as electricity, pH, redox potential, magnetic field, and light. Control of the molecular self-assembly by external light stimulus is advantageous, because photochemical reactions occur very rapidly and thereby a fast response can be obtained. Light is also advantageous in view of its ready availability as a mild energy source.[3] As epitomized by the vision, the use of the light-powered isomerization of organic molecules is the most reliable strategy to convert photochemical energy to reversible physical motion without waste.[4] Pertinent molecular design of the building blocks, especially focusing on the orthogonal function of the binding sites and the photoresponsive units, results in smart self-assemblies with large photoresponses in the structures and the assembling process. In this article, we describe how we can use photoswitching molecules to control the self-assemblies with several illustrations of the azobenzene-introduced systems.

[a] Dr. S. Yagai, Prof. Dr. T. Karatsu, Prof. Dr. A. Kitamura
Department of Applied Chemistry and Biotechnology
Faculty of Engineering, Chiba University
1-33 Yayoi-cho, Inage-ku, Chiba 263-8522 (Japan)
Fax: (+81) 43-290-3039
E-mail: yagai@faculty.chiba-u.jp

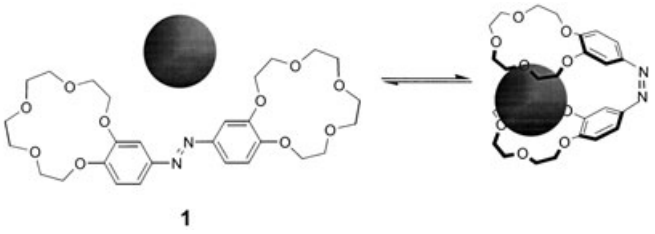
Photoresponsive Molecular Recognition Systems Guide the Design Strategy toward the Creation of Photocontrollable Self-Assemblies

The primary requirement for the power unit in photoresponsive supramolecular systems is the presence of large changes in its molecular geometry or physical properties as a result of the photochemical reaction. Synthetic accessibility is also quite important. Azobenzene fulfills the above requirements and is the most widely employed power unit in photoresponsive supramolecular systems. Since self-assembly is the accumulation of the molecular recognition events between the building blocks, the design strategies employed in photoresponsive molecular recognition systems can be directly applied to create photocontrollable self-assembly. With the following examples we describe how the isomerization of azobenzene can be applied to construct smart photoresponsive molecular recognition systems.

Strategy 1: If the two phenyl rings of the azobenzene molecule are modified with noncovalent binding sites, the relative position of the two binding sites is altered dramatically by *trans–cis* isomerization. This strategy has been widely applied in photoresponsive molecular recognition systems,[5] and is exemplified by the azobenzene/crown ether molecule

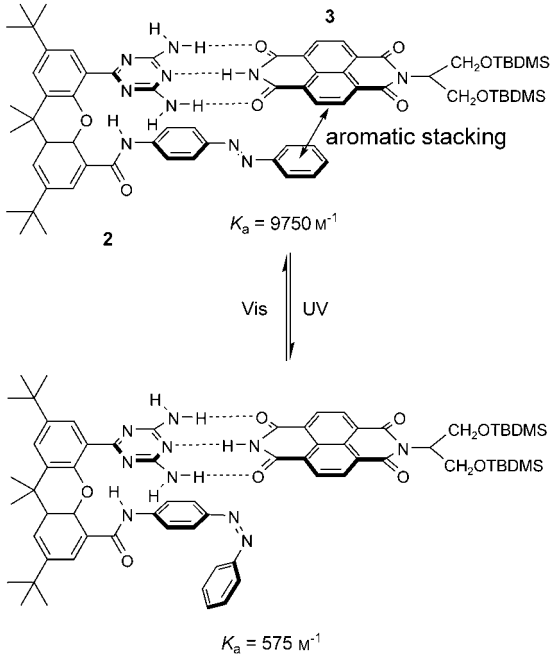
 DOI: 10.1002/chem.200401323

1 used in the pioneering work of Shinkai (Scheme 1).[5a] Molecule **1** shows butterfly-like motion accompanying the *trans–cis* isomerization, in which only the *cis* isomer captures large alkali-metal cations by the formation of sandwich-type 1:1 complex.



Scheme 1. Butterfly-like motion of the azobenzene-crown ether **1**. A large alkali-metal cation is selectively captured by the *cis* isomer.

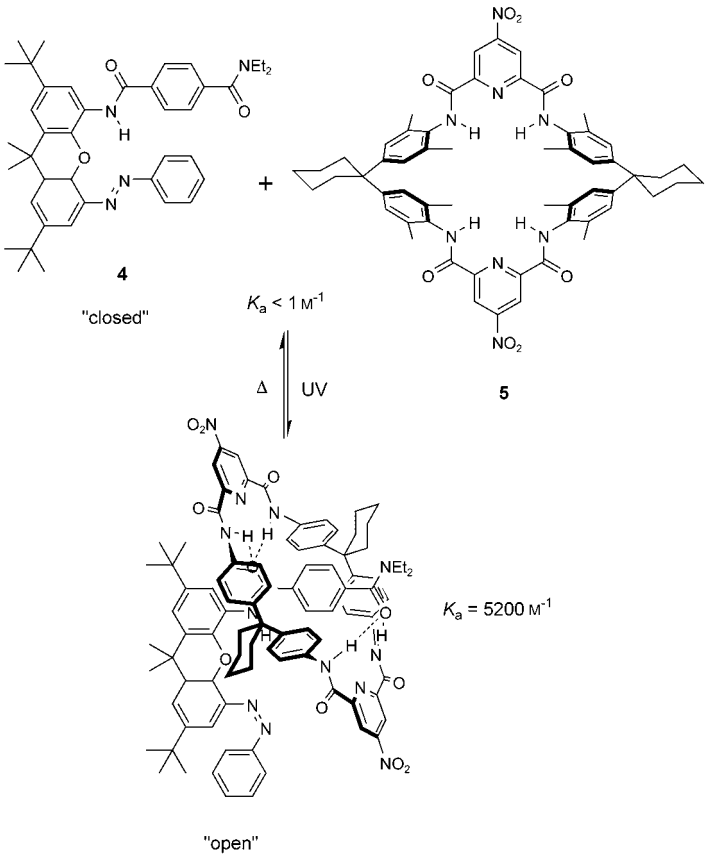
Strategy 2: The second strategy is the use of aromatic stacking interactions that occur favorably in the planar *trans* isomer. A good example based on this strategy is the photocontrolled hydrogen-bond-directed molecular recognition system by Rotello et al. (Scheme 2).[6] Naphthaldiimide de-



Scheme 2. Photocontrolled molecular recognition between **2** and **3**.

rivative **3** complexes with photoresponsive receptor **2**, which contains *trans*-azobenzene. A relatively high association constant ($K_a = 9750\,M^{-1}$ in $CDCl_3$) indicates the cooperation of DAD·ADA (D = donor, A = acceptor) hydrogen-bonding and aromatic-stacking interactions between the *trans*-azobenzene moiety and naphthaldiimide **3**. When the complex is irradiated with UV-light, K_a decreases 16-fold due to the depletion of the effective aromatic stacking interaction between the two chromophores.

Strategy 3: If azobenzene can be incorporated into the position neighboring the binding site, its large morphological changes in isomerization will control the degree of steric crowding around the binding site. The photoresponsive pseudorotaxane system shown in Scheme 3 is a good exam-



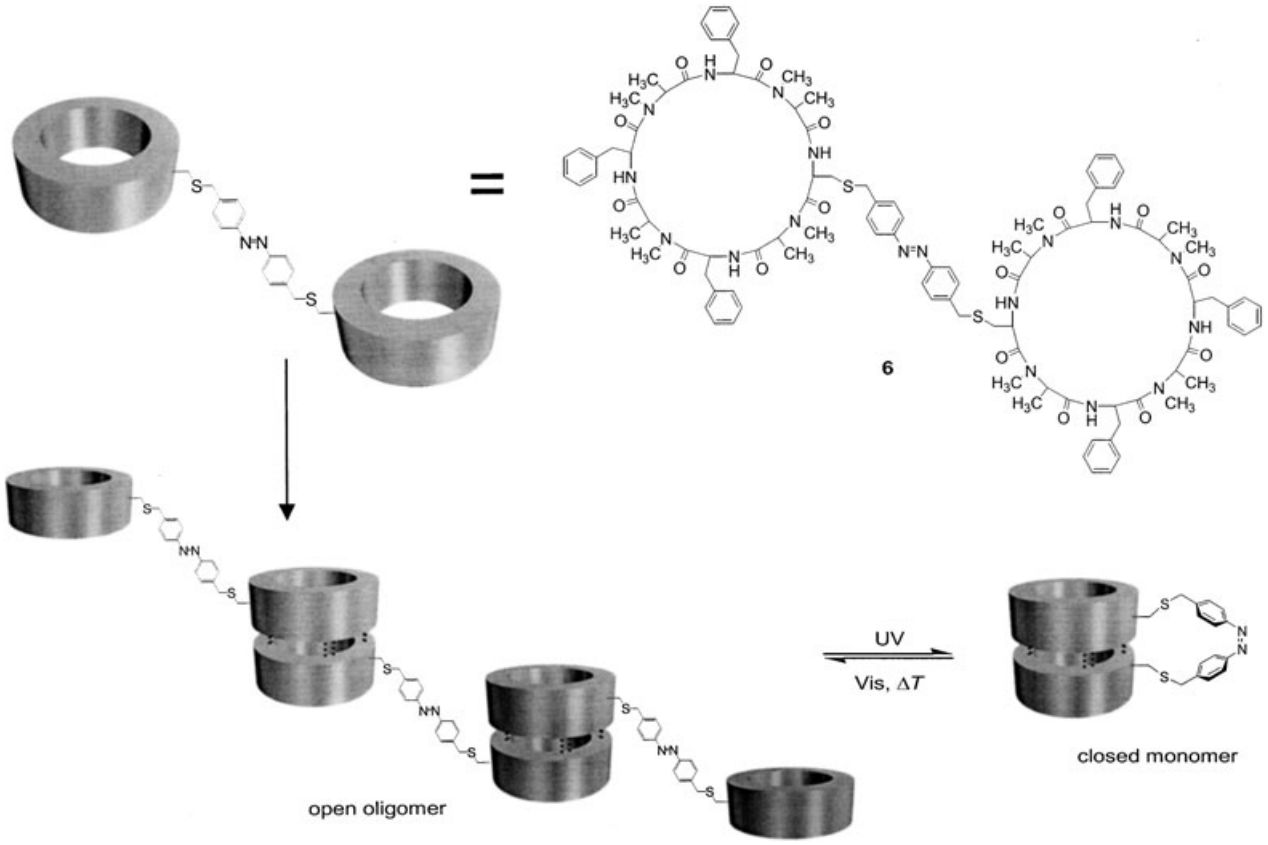
Scheme 3. Photocontrolled pseudorotaxane formation between **4** and **5**.

ple based on this strategy.[7,8] Xanthene derivative **4**, featuring *trans*-azobenzene, cannot function as a host molecule for the lactam guest **5** ($K_a < 1\,M^{-1}$ in $CDCl_3$), because the azobenzene moiety sterically blocks the amide binding sites of **4**. Upon irradiation with UV-light, **4** converts to a suitable host molecule for **5** ($K_a = 5200\,M^{-1}$), because the amide binding sites are now in an "open" state concomitantly with the *trans*→*cis* photoisomerization of the azobenzene moiety. In contrast to this example, careful molecular design makes it possible to construct photoresponsive molecular recognition systems, in which the *trans* isomer acts as a sterically favorable substituent and the *cis* isomer as an unfavorable one. In both the cases, the introduction of sterically demanding substituents at the end of azobenzene may enhance the difference of steric crowding between the *trans* and *cis* states.

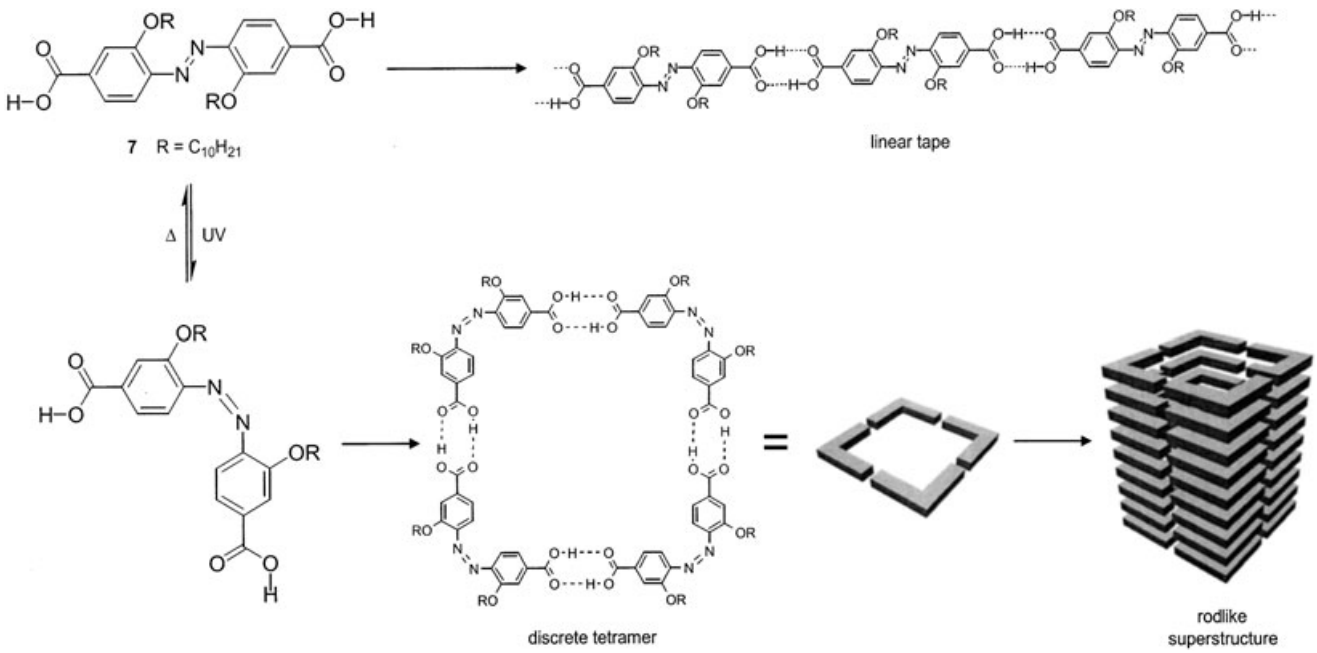
Photocontrollable Self-Assemblies Based on Strategy 1: Photoswitchable Self-Assembling Architecture

Under the ambient conditions, well-designed molecular building blocks usually self-assemble into one supramolecular architecture. Alteration of the supramolecular architecture requires modification of the building blocks. If two (or more) geometrical isomers of a photoresponsive molecular building block are capable of forming distinct supramolecular structures, then strategy 1 enables the creation of specific self-assemblies, the supramolecular structures of which are photochemically switchable. Ghadiri et al. established a prominent photoswitchable self-assembly based on this strategy.[9] Azobenzene derivative **6** tethering two cyclic octapeptides as multiple hydrogen-bonding sites was designed and synthesized (Scheme 4). The *trans* isomer of **6** forms linear and polydisperse hydrogen-bonded assemblies in chloroform. UV-light irradiation of the solution of the linear species resulted in switching to the intramolecularly hydrogen-bonded closed species with butterfly-like motion of the molecule, as evidenced by NMR studies. Interestingly, photogenerated closed species showed remarkable resistence to *cis*→*trans* thermal isomerization, owing to the multiple intramolecular hydrogen-bonding interactions. An analogous effect was found in the photochemistry of **1**.[5a]

Sleiman and co-workers also established an excellent photoswitchable self-assembly based on strategy 1, yet the molecular building block is very simple (Scheme 5).[10] In this system, two geometrical isomers of azobenzene dicarboxylic acid derivative **7** form dramatically different superstructures by using intermolecular hydrogen-bonding as well as aromatic stacking interactions. In noncompeting solvents such as chloroform and dichloromethane, the *trans* isomer forms linear tapelike aggregates. In contrast, the photogenerated *cis* isomer was found to form discrete tetramer, which hierarchically associates into rodlike superstructures through effective aromatic stacking. The rodlike superstructures were visualized by transmission electron microscopy. This is a rare example in which the bent conformation of *cis*-azobenzene is dexterously utilized to construct a well-defined self-assembly that can persist in solution.[11] As a consequence of the formation of the hydrogen-bonded tetramer, thermal *cis*→*trans* isomerization of **7** in noncompeting solvents showed large enthalpic barriers in comparison with those in competing solvents such as dimethylsulfoxide and methanol. It should be emphasized that thermally unstable *cis*-azobenzene derivatives can be stabilized if they are successfully embedded in self-assembled scaffolds.



Scheme 4. Schematic representation for the photoswitchable self-assembly of azobenzene/cyclic octapeptide **6**.

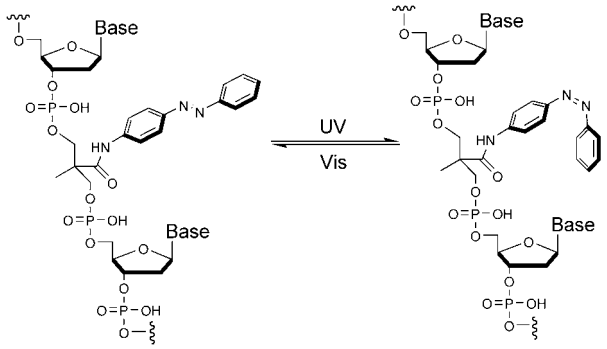


Scheme 5. Schematic representation for the photoswitchable self-assembly of azobenzene dicarboxylic acid derivative **7**.

Photocontrollable Self-Assemblies Based on Strategy 2: Photoregulated Formation of Biomolecular Assemblies and Synthetic Extended Assemblies

Strategy 2 has been effectively utilized to photocontrol the association and dissociation of biomolecular aggregates. In 1985, Pieroni et al. reported photocontrolled aggregation of poly(L-glutamic acid) containing azobenzene side chains.[12] The polypeptide undergoes intermolecular aggregation in aqueous solution by means of hydrophobic interactions between the planar, nonpolar *trans*-azobenzene side chains as the main driving force. UV-light irradiation induces the isomerization of side chains to the bent, polar *cis* isomers, dissociating the polypeptide aggregates through the decrease of solvophobicity as well as the depletion of the effective aromatic stacking interaction.

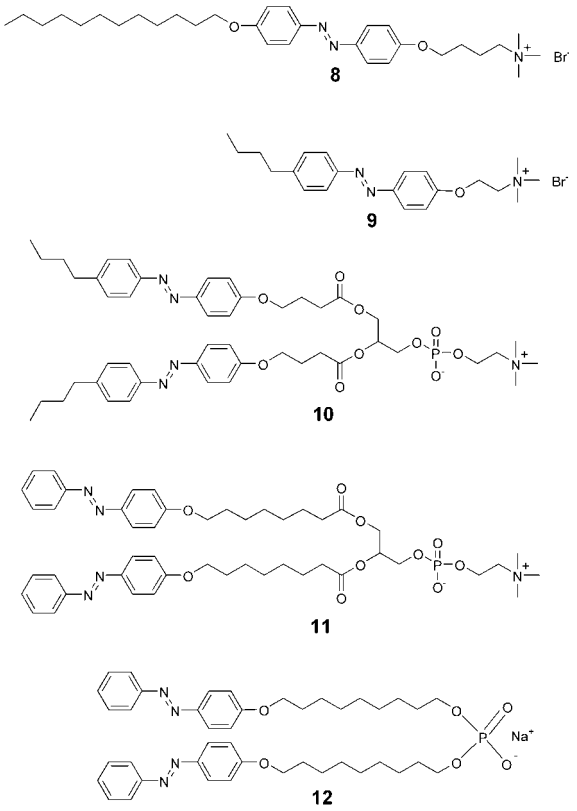
As a related example, Asanuma and Komiyama established the photocontrolled self-assembly of DNA duplex[13a] and triplex[13b] using synthetic oligonucleotides featuring azobenzene side chains (Scheme 6). In the case of the duplex system, they showed that the melting temperature (T_m) of the duplex between the oligonucleotide 5′-AAAXAAAA-3′ (X denotes the residue bearing azobenzene side chain) and the complementary strand 5′-TTTTTTTT-3′ changed drastically accompanying the *trans–cis* photoisomerization of the azobenzene moiety (T_m = 24.8 °C in *trans* and 15.9 °C in *cis*). It was suggested that the absence of sufficient aromatic stacking interaction between the *cis*-azobenzene with the adjacent DNA bases destabilizes the duplex. Based on this observation, phototriggered dissociation/reconstitution of the duplex was realized at the temperature between T_m (*trans*) and T_m (*cis*).



Scheme 6. Photoisomerization of azobenzene-incorporated DNA.

The linear and planar morphology of *trans*-azobenzene is compatible with the molecular requirements for the amphiphilic molecules, creating membranous assemblies such as micelles and vesicles. The introduction of amphiphilic azobenzene derivatives into membranous systems thus offers the possibility to photochemically control the structure and destruction/reconstitution of membranous assembly based on strategy 2; *trans*-azobenzene amphiphiles stabilize the membrane by the effective aromatic stacking interaction, while bent morphology of *cis*-azobenzene amphiphiles is unfavorable for regular alignment required for the formation of membrane.

Several groups have reported azobenzene-containing amphiphilic molecules as exemplified in Scheme 7.[14–18] Amphiphile **8** forms membranous globular aggregates, which can be observed by electron microscope measurements.[14] Upon irradiation of UV-light, globular aggregates were transformed to the short rodlike aggregates accompanying the *trans*→*cis* photoisomerization. The globular aggregates were

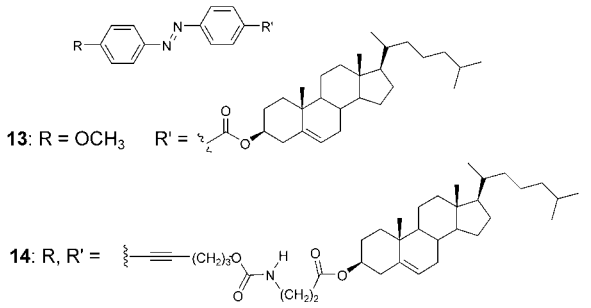


Scheme 7. Molecular structures of the azobenzene-containing amphiphilic molecules **8** by Kunitake,[14] **9** by Sakai,[15] **10** by Yianni,[16] **11** by Whitten,[17] and **12** by Engberts.[18]

recovered by subsequent visible-light irradiation (or thermal isomerization).

Amphiphiles **9**–**12** were used by mixing in vesicles composed of nonchromophoric amphiphiles in the aim of photoregulation of vesicle destruction and reconstitution.[15–18] In all cases, UV-light-induced destruction of the vesicles was confirmed by a leakage experiment of the entrapped molecules. In the cases of **9**–**11**, photoinduced destruction of the vesicles was visually observed in electron microscopic measurements. The authors who studied amphiphiles **11** and **12** suggested that the photoresponse of the azobenzene amphiphiles in the vesicles are strongly dependent on their aggregated state.[17,18]

As counterparts of the self-assembly of azobenzene amphiphiles in aqueous conditions, self-assemblies of the azobenzenes **13**[19] and **14**[20] (Scheme 8) possessing crystallization-avoiding aliphatic side chains in organic solvents afford photoresponsive organogels.[21] In these systems, the photoresponse of the assemblies was visibly discernible by the reversible gel–sol transition upon the irradiation of UV (gel→sol) and visible light (sol→gel). In both **13** and **14**, CD studies revealed that the *cis* isomers cannot regularly align. Interestingly, in the case of **14**, photoinduced hydrogen-bond breaking (gel→sol) and reforming (sol→gel) of the amide groups was confirmed by IR measurements.

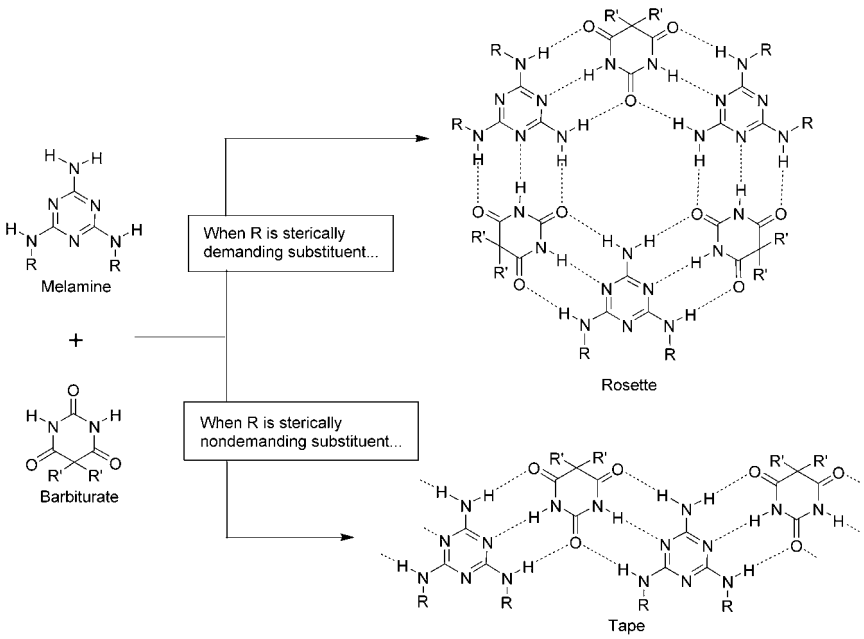


Scheme 8. Molecular structures of the photoresponsive organogelators **13** by Shinkai[19] and **14** by Tamaoki.[20]

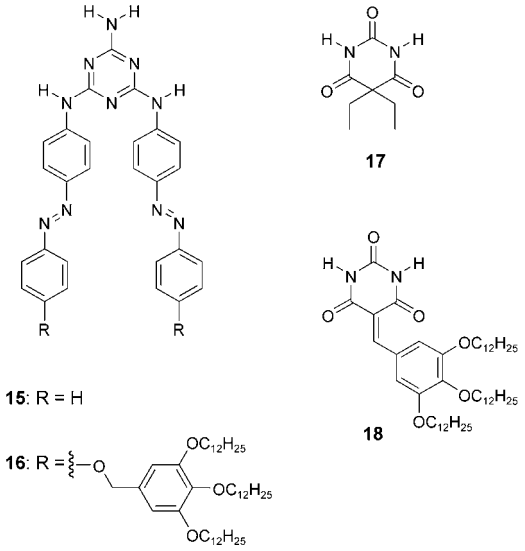
Photocontrollable Self-Assemblies Based on Strategy 3: Photoregulated Formation of Discrete Aggregates

In spite of the successful photocontrol of the polydisperse extended self-assemblies described above, studies on the photocontrol of monodisperse discrete self-assembly with well-defined shape, such as dendritic architecture, have not appeared so far except for our examples described below.[22,23] Indeed, it seems difficult to construct discrete self-assemblies with azobenzene as a main molecular scaffold. In this context, for discrete systems, strategy 3 is reliable, because azobenzene can be introduced to the already-established self-assemblies as a "substituent". To effectively transduce the photoinduced motion of azobenzene to the change of steric information in the molecular recognition event, self-assemblies that are under the control of severe substituent effects are desired. From this viewpoint, hydrogen-bonded self-assembly between melamine and barbiturate (or cyanurate) is a reasonable system to fulfill such a requirement (Scheme 9). This system shows interesting substituent effect on the aggregate formation, which was intensely studied by Whitesides and co-workers.[24] Briefly, the introduction of sterically demanding substituents to melamine (R′ in Scheme 9) leads to the preferential formation of the cyclic hexamer (rosette) over the competing linear tapelike aggregates (tape). The mechanism of this substituent effect remains controversial.[25] It is possible to photocontrol the aggregate species if azobenzene is introduced as a steric-crowding-controllable substituent.

Thus, azobenzene-appended melamine **15** was prepared and its co-aggregation with 5,5′-diethylbarbituric acid (**17**) in $CDCl_3$ was investigated (Scheme 10).[22] For **15**, steric crowding of the *N*-substituents increases with *trans*→*cis* isomerization in the aggregated state (Scheme 11). When two azobenzene moieties were in the *trans* conformation, formation of rosette $\mathbf{15}_3\cdot\mathbf{17}_3$ was confirmed by NMR investigation. Rosette $\mathbf{15}_3\cdot\mathbf{17}_3$ was found to be thermodynamically unstable and slowly transformed into insoluble tapelike aggregates, giving rise to irreversible precipitation. The 100 h aging resulted in the transformation of 80% of rosette into tapes. This observation demonstrates that the steric crowding of the *trans*-azobenzene moiety in **15** is not enough to retain



Scheme 9. Two supramolecular architectures formed from the coaggregation between *N*,*N*′-disubstituted melamine and barbiturate.

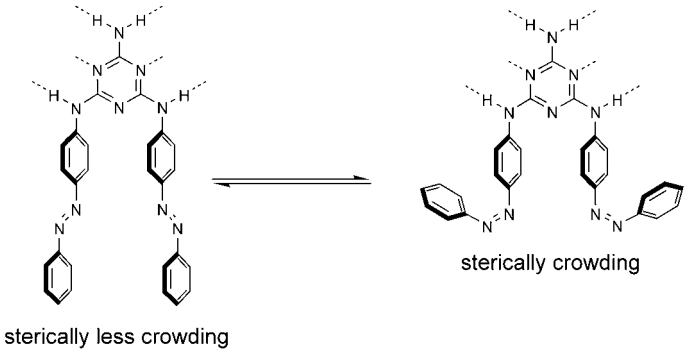


Scheme 10. Molecular structures of azobenzene-appended melamines **15** and **16** and barbiturates **17** and **18**.

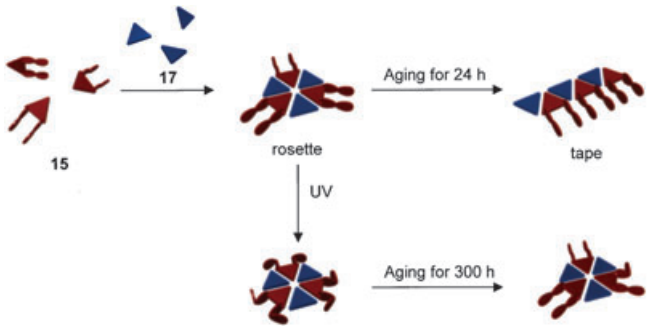
the rosette structure in the solution, allowing the formation of linear tapes as thermodynamic products.

In the conventional synthetic approach, this irreversible rosette→tape transformation can be avoided by the introduction of more sterically demanding substituents such as a 4-*tert*-butylphenyl group into the amino groups of melamines.[24a] For melamine **15**, however, the steric crowding of the substituents can be increased by external light input even after the preparation of the assembly. UV-light irradiation of the freshly prepared solution of $\mathbf{15}_3\cdot\mathbf{17}_3$ converted 80% of *trans*-azobenzene into the *cis* isomer at the photostationary state, without sacrificing the rosette structure. The resulting *cis*-azobenzene thermally isomerized to the *trans* isomer with a half decay period of 70 h. Remarkably, no precipitation was observed over 300 h after the UV-light irradiation. This result strikingly demonstrates that the *cis*-azobenzene moiety in **15** acts as a sterically demanding substituent, avoiding the irreversible rosette→tape transformation (Scheme 12).

Having established the fact that the isomerization of the azobenzene introduced to the melamine component indeed affects its aggregation with its complementary partner, our



Scheme 11. Isomerization of azobenzene-appended melamine **15**.



Scheme 12. Schematic illustration of the photoresponsive aggregation between **15** and **17**.

study was directed toward more direct photocontrol of the hydrogen-bonded assembly. The discrete nature of the rosette assembly is quite intriguing from its applicability to the

core of self-assembling dendrimers.[26] Since dendrimers act as hosts for guest encapsulation,[27] the stimuli-induced formation and deformation[28] of the dendritic architectures have significant meaning. Self-assembling dendrimers are capable of achieving such functions in an effective manner, that is, formation/dissociation of the dendrimers from/into the dendrons. With the achievement of the stimuli-induced formation of dendrimers in our mind as a final goal, we introduced tris(dodecyloxy)phenyl (TDP) wedges into the melamine and barbiturate components (**15**→**16** and **17**→**18**). The introduction of this bulky substituent enhances the effect of the azobenzene isomerization on their aggregation based on strategy 3. On the one hand, *trans*-azobenzene in **16** directs the TDP wedge toward the opposite side of the hydrogen-bonding site (Figure 1, left), thereby allowing the formation of the rosette with complementary **18**. On the other hand, bent *cis*-azobenzene in **16** inhibits the complexation with **18** by directing the bulky TDP wedge toward the interactive site (Figure 1, right).

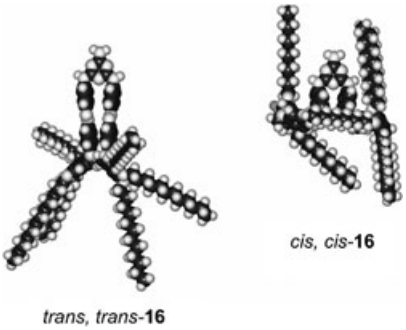


Figure 1. Morphological change of **16** on the *trans–cis* isomerization of the azobenzene moieties (energy-minimized by MM+ force-field calculation).

When the two azobenzene moieties were the *trans* isomer, melamine **16** aggregated with **18** to form remarkably stable rosette $\mathbf{16}_3\cdot\mathbf{18}_3$ in chloroform, toluene, and methylcyclohexane as confirmed by ^{1}H NMR spectroscopy, size-exclusion chromatography (SEC), dynamic light scattering, and UV-visible measurements. In sharp contrast to the rosette $\mathbf{16}_3\cdot\mathbf{18}_3$, no irreversible rosette→tape transformation was observed over a period of one month. In sharp contrast to rosette $\mathbf{15}_3\cdot\mathbf{17}_3$, *trans*→*cis* isomerization of azobenzene arms in $\mathbf{16}_3\cdot\mathbf{18}_3$ upon irradiation of UV-light (370 nm) is drastically suppressed; the *trans*/*cis* ratio was only 76:24 at the photostationary state. The solvent and the concentration had no effect on the *trans*/*cis* ratio as long as the stoichiometric formation of the rosette was established. This indicates that the suppression of the *trans*→*cis* isomerization comes from intrinsic steric crowding in a rosette accommodating a total of 27 of the exterior dodecyl side chains.

The above results suggests that when compound **16** possesses two *cis*-azobenzene (*cis*,*cis*-**16**) moieties, it cannot aggregate with **18**. Thus, preliminary photogenerated *cis*,*cis*-**16** (94% isomeric purity) was mixed with **18** in toluene and the formation of rosette species was analyzed by SEC. As expected, no peak corresponding to the rosette was detected, indicating *cis*,*cis*-**16** and **18** existed in a monomeric pool. The formation of the rosette is supposed to be hampered by the severe intermolecular steric interaction between the TDP wedges. This result closely relates to the self-assembling dendrimer systems in which increasing generation of dendrons destabilizes the stability of dendrimers by steric interaction between the dendrons.[26b,c] The monomeric pool of *cis*,*cis*-**16** and **18** could be retained by keeping the solution at 0°C, which suppresses the thermal *cis*→*trans* isomerization.

The high (SEC-detectable) stability of the rosette $\mathbf{16}_3\cdot\mathbf{18}_3$ enable us to chase the phototriggered formation of the rosette by SEC. Figure 2 shows the SEC data obtained upon irradiation of the monomeric pool of *cis*,*cis*-**16** and **18** with visible light (450 nm). The concentration of the rosette in the solution is completely controlled by the irradiation of the visible light. Owing to this large photoinducible morphological change of **16**, phototriggered self-assembly of discrete aggregates could be achieved (Scheme 13).

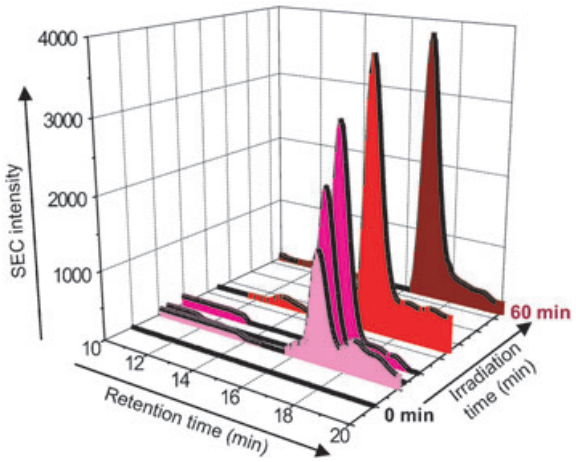
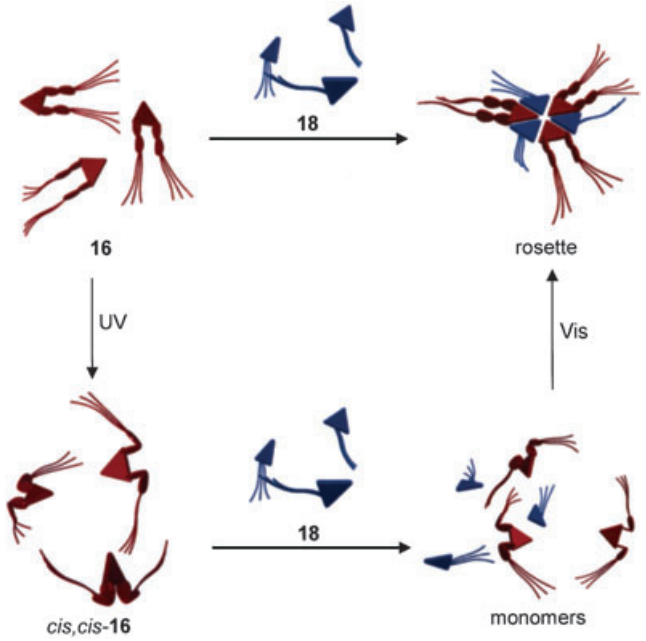


Figure 2. Phototriggered self-assembly of the rosette $\mathbf{16}_3\cdot\mathbf{18}_3$ detected by SEC.

Perspectives

Given the desire to control dynamic molecular self-assembly by facile external input, creation of photoresponsive supramolecular systems is emerging as an active research topic. Careful incorporation of photoswitching molecules, one of which was described in this article, imparts great photoresponse to the self-assemblies without spoiling their intrinsic association ability. If we can impart some function to the self-assembled state, the desired function can be achieved in a controlled manner.



Scheme 13. Schematic illustration of the photocontrolled self-assembly of the rosette $\mathbf{16}_3 \cdot \mathbf{18}_3$.

Recently, molecular-level tools have been fabricated from photoswitching molecules. As examples of azobenzene use, molecular scissors[29] and hinges[30] have been exploited. In these molecular-size tools, the geometrical changes in the isomerization of azobenzene are converted to more precise mechanical motions by covalent modification. Use of these molecular tools as photoresponsive units may facilitate more precise photochemical control of self-assemblies.

Our further interest is in imparting the wavelength-dependent photoresponse (more than three wavelength regions) to the assembly, so that stimulation by one specific wavelength moves the assembly to a specific state. Such a "multi-input" function requires 1) self-assemblies capable of forming diverse supramolecular structures or superstructures (including hierarchical association) and 2) conjugation of different photoswitching molecules stimulated by different light energy.[31] Moreover, sequential signal transfer initiated by phototriggered self-assembly, mimicking the principle of vision, is a target and will be exploited in the foreseeable future.

Acknowledgements

We deeply thank Mr. Toshiharu Nakajima of Chiba University and Prof. Dr. Hitoshi Tamiaki of Ritsumeikan University for their experimental assistance and helpful discussions of our work.

[1] J. M. Lehn, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 4763–4768.
[2] a) D. S. Lawrence, T. Jiang, M. Levett, *Chem. Rev.* **1995**, *95*, 2229–2260; b) D. Philp, J. F. Stoddart, *Angew. Chem.* **1996**, *108*, 1242–1286; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1154–1196; c) L. Brunsveld, B. J. B. Folmer, E. W. Meijer, R. P. Sijbesma, *Chem. Rev.* **2001**, *101*, 4071–4097.
[3] R. Ballardini, V. Balzani, A. Credi, M. T. Gandolfi, M. Venturi, *Acc. Chem. Res.* **2001**, *34*, 445–455.
[4] C. Dugave, L. Demange, *Chem. Rev.* **2003**, *103*, 2475–2532.
[5] a) S. Shinkai, T. Nakaji, T. Ogawa, K. Shigematsu, O. Manabe, *J. Am. Chem. Soc.* **1981**, *103*, 111–115; b) F. Würthner, J. Rebek, Jr., *Angew. Chem.* **1995**, *107*, 503–505; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 446–448; c) R. Cacciapaglia, S. D. Stefano, L. Mandolini, *J. Am. Chem. Soc.* **2003**, *125*, 2224–2227; d) I. A. Banerjee, L. Yu, H. Matsui, *J. Am. Chem. Soc.* **2003**, *125*, 9542–9543; e) C. A. Hunter, M. Togrul, S. Tomas, *Chem. Commun.* **2004**, 108–109.
[6] A. Goodman, E. Breinlinger, M. Ober, V. M. Rotello, *J. Am. Chem. Soc.* **2001**, *123*, 6213–6214.
[7] K.-S. Jeong, K.-J. Chang, Y.-J. An, *Chem. Commun.* **2003**, 1450–1451.
[8] Balzani and Stoddart et al. also reported a photoresponsive pseudorotaxane system based on strategy 2. See: V. Balzani, A. Credi, F. Marchioni, J. F. Stoddart, *Chem. Commun.* **2001**, 1860–1861.
[9] M. S. Vollmer, T. D. Clark, C. Steinem, M. R. Ghadiri, *Angew. Chem.* **1999**, *111*, 1703–1706; *Angew. Chem. Int. Ed.* **1999**, *38*, 1598–1601.
[10] F. Rakotondradany, M. A. Whitehead, A.-M. Lebuis, H. F. Sleiman, *Chem. Eur. J.* **2003**, *9*, 4771–4780.
[11] Yamaguchi et al. reported *cis*-azobenzene-based extended assemblies persistent in solution. See: Y. Saiki, H. Sugiura, K. Nakamura, M. Yamaguchi, T. Hoshi, J. Anzai, *J. Am. Chem. Soc.* **2003**, *125*, 9268–9269.
[12] a) O. Pieroni, A. Fissi, J. L. Houben, F. Ciardelli, *J. Am. Chem. Soc.* **1985**, *107*, 2990–2991; b) O. Pieroni, A. Fissi, N. Angelini, F. Lenci, *Acc. Chem. Res.* **2001**, *34*, 9–17.
[13] a) H. Asanuma, T. Ito, T. Yoshida, X. Liang, M. Komiyama, *Angew. Chem.* **1999**, *111*, 2547–2549; *Angew. Chem. Int. Ed.* **1999**, *38*, 2393–2395; b) X. Liang, H. Asanuma, M. Komiyama, *J. Am. Chem. Soc.* **2002**, *124*, 1877–1883.
[14] T. Kunitake, N. Nakashima, M. Shimomura, Y. Okahata, K. Kano, T. Ogawa, *J. Am. Chem. Soc.* **1980**, *102*, 6644–6646.
[15] H. Sakai, A. Matsumura, S. Yokoyama, T. Saji, M. Abe, *J. Phys. Chem. B* **1999**, *103*, 10737–10740.
[16] C. G. Morgan, E. W. Thomas, S. S. Sandhu, Y. P. Yianni, A. C. Mitchell, *Biochim. Biophys. Acta* **1987**, *903*, 504–509.
[17] a) X. Song, J. Perlstein, D. G. Whitten, *J. Am. Chem. Soc.* **1997**, *119*, 9144–9159; b) D. G. Whitten, L. Chen, H. Cristina Geiger, J. Perlstein, X. Song, *J. Phys. Chem. B* **1998**, *102*, 10098–10111.
[18] J. M. Kuiper, J. B. F. N. Engberts, *Langmuir* **2004**, *20*, 1152–1160.
[19] a) K. Murata, M. Aoki, T. Nishi, A. Ikeda, S. Shinkai, *J. Chem. Soc. Chem. Commun.* **1991**, 1715–1718; b) K. Murata, M. Aoki, T. Suzuki, T. Harada, H. Kawabata, T. Komori, F. Ohseto, K. Ueda, S. Shinkai, *J. Am. Chem. Soc.* **1994**, *116*, 6664–6676.
[20] N. Koumura, M. Kubo, N. Tamaoki, *Langmuir* **2004**, *20*, 9897–9900.
[21] Other examples of photoresponsive organogel or supramolecular polymers: a) B. J. B. Folmer, E. Cavini, R. P. Sijbesma, E. W. Meijer, *Chem. Commun.* **1998**, 1847–1848; b) L. N. Lucas, J. van Esch, R. M. Kellogg, B. L. Feringa, *Chem. Commun.* **2001**, 759–760; c) J. Eastoe, M. Sánchez-Dominguez, P. Wyatt, R. K. Heenan, *Chem. Commun.* **2004**, 2608–2609.
[22] S. Yagai, T. Karatsu, A. Kitamura, *Chem. Commun.* **2003**, 1844–1845.
[23] S. Yagai, T. Nakajima, T. Karatsu, A. Kitamura, *J. Am. Chem. Soc.* **2004**, *126*, 11500–11508.
[24] G. M. Whitesides, E. E. Simanek, J. P. Mathias, C. T. Seto, D. N. Chin, M. Mammen, D. M. Gordon, *Acc. Chem. Res.* **1995**, *28*, 37–44.
[25] a) J. P. Mathias, E. E. Simanek, G. M. Whitesides, *J. Am. Chem. Soc.* **1994**, *116*, 4326–4340; b) A. G. Bielejewska, C. E. Marjo, L. J. Prins, P. Timmerman, F. de Jong, D. N. Reinhoudt, *J. Am. Chem. Soc.* **2001**, *123*, 7518–7533; c) I. Ghiviriga, D. C. Oniciu, *Chem. Commun.* **2002**, 2718–2719.

[26] a) A. W. Freeman, R. H. Vreekamp, J. M. J. Fréchet, *Polym. Mater. Sci. Eng.* **1997**, *77*, 138–139; b) W. T. S. Huck, R. Hulst, P. Timmerman, F. C. J. M. van Veggel, D. N. Reinhoudt, *Angew. Chem.* **1997**, *109*, 1046–1049; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1006–1008; c) Y. Ma, S. V. Kolotuchin, S. C. Zimmerman, *J. Am. Chem. Soc.* **2002**, *124*, 13757–13769.

[27] a) F. Zeng, S. C. Zimmerman, *Chem. Rev.* **1997**, *97*, 1681–1712; b) A. W. Bosman, H. M. Janssen, E. W. Meijer, *Chem. Rev.* **1999**, *99*, 1665–1688; c) D. Astruc, F. Chardac, *Chem. Rev.* **2001**, *101*, 2991–3024; d) S. M. Grayson, J. M. J. Fréchet, *Chem. Rev.* **2001**, *101*, 3819–3867.

[28] a) D. Seebach, G. F. Herrmann, U. D. Lengweiler, B. M. Bachmann, W. Amrein, *Angew. Chem.* **1996**, *108*, 2969–2972; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2795–2797; b) M. Smet, L.-X. Liao, W. Dehaen, D. V. McGrath, *Org. Lett.* **2000**, *2*, 511–513.

[29] T. Muraoka, K. Kinbara, Y. Kobayashi, T. Aida, *J. Am. Chem. Soc.* **2003**, *125*, 5612–5613.

[30] Y. Norikane, N. Tamaoki, *Org. Lett.* **2004**, *6*, 2595–2598.

[31] K. Higashiguchi, K. Matsuda, M. Irie, *Angew. Chem.* **2003**, *115*, 3661–3664; *Angew. Chem. Int. Ed.* **2003**, *42*, 3537–3540.

Published online: March 7, 2005

