Exciting Supramolecular Architectures: Light-Induced Processes and Synthetic Transformations in Noncovalent Assemblies

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Dedicated to Prof. H. Bouas-Laurent on occasion of his 72nd birthday

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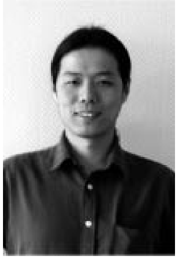
This review outlines recent advances in the area of supramolecular photochemistry, particularly with respect to the use of noncovalent interactions to direct and control excited-state processes in the solid phase and in solution.

Light is a versatile tool in modern science. The growing momentum of nanotechnology has rekindled interest in photochemical processes, which play an important role in numerous applications in which light is used as a source of energy or to transmit information to and from molecular components. The latter are frequently arranged in a constrained environment, which imparts new – though at times unexpected – behavior. This microreview is focused on the recent work in this growing area, which, interestingly, is not necessarily the dominion of photochemists. It is immediately obvious that design and synthesis play a leading role in the development of some of the more interesting systems reported. Photoinduced processes frequently encountered include fluorescence, $E \rightarrow Z$ isomerization of conjugated double bonds, energy and electron transfer, and cyclodimerization reactions. Their behavior, and at times their outcome, can be influenced by the presence of noncovalent interactions that impart structural order or rigidity to the



Chih-Hao Huang was born in Taiwan and received a B.S. degree (in 1996) and an M.S. degree (in 1998) in Chemistry from National Taiwan University, Taiwan. After spending one year as a research and teaching assistant in Professor T.-Y. Luh's group at NTU, he undertook a Ph. D. degree with Dr. D. Bassani at Bordeaux University, where he is currently is in his third year as a graduate student in organic chemistry. His thesis work explores the self-assembly of supramolecular materials applied to photonic devices.

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MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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components. This microreview presents recent advances in this area, accompanied by selected older work when necessary to better illustrate the direction the field is moving in. The more specialized reviews referenced herein will guide the interested reader toward previous work in the field. The first examples described are from crystal-based systems, which may seem to be a rather dated approach. However, much of our understanding of supramolecular chemistry in solution comes from solid foundations built on our growing understanding of intermolecular forces gleaned from examining crystal structures, and recent advances in this specialized field amply justify continued interest.

I. Supramolecular Photochemistry in the Solid State

The effect of intermolecular order on photochemical transformations was first rationalized by Schmidt, Cohen and coworkers in the early 1970s,[1] though the propensity of cinnamates to crystallize into polymorphs possessing different photoreactivities had been recognized before that. Since then, examples of lattice-controlled solid-state photoreactions have steadily increased, and molecular engineering of purposefully designed systems has burgeoned into an attractive means of controlling and understanding photoreactivity. Because the crystal environment provides a haven from solvent–solute interactions, which lower the persistence of multicomponent assemblies in solution, intermolecular forces that are too weak to lead to sufficiently high association constants in solution can be used.[2] Also, in cases where the photoreaction takes place within the crystal lattice and not only in the vicinity of a defect or on the surface, quantitative conversion with high stereo- and regioselectivity can be expected. Despite the inherent difficulty in obtaining mixed crystals of suitable quality and the generally low efficiency of solid-state transformations, the breadth of this approach is exemplified in the examples that follow.

The elegant synthesis of extended ladderanes by MacGillivray and coworkers (Figure 1) represents a convincing example of what can be achieved by molecular design.[3] Hydrogen-bonding (H-B) interactions are used to induce the crystallization of assemblies in which extended polyene structures are constrained within a critical distance (<4.2 Å) in a coplanar orientation. Upon irradiation, stepwise cyclodimerization of the double bonds leads to the efficient stereospecific synthesis of the corresponding ladderane. Interestingly, the large molecular transformation that occurs takes place with minimal atom movement. Because the crystal lattice is not destroyed in the process,[4] quantitative yields of strained photoproducts, including cyclophanes,[5] can be obtained. Numerous other examples[6] of the use of hydrogen bonds to construct photoactive crystalline assemblies serve to demonstrate the utility of this leitmotif.

The use of intermolecular forces to direct the assembly of solid-state architectures is, of course, not limited to hydrogen bonds. Metal-ligand coordination,[7] hydrophobic interactions,[8–10] and ionic forces[11] have also been used with success. In the solid state, the latter are a powerful directing tool due to the strong nature of Coulombic interactions. For example, the crystalline diamine double salts of cinnamic acid efficiently steer the photodimerization reaction such that a switch in selectivity is observed between salts formed using *cis*- and *trans*-1,2-diaminocyclohexanes (Figure 2).[11e] Because of their propensity to photodimerize in the solid state, cinnamate derivatives have been widely used in demonstrating supramolecular topochemical reaction control in the solid state, including asymmetric induction and chirogenesis.[12]

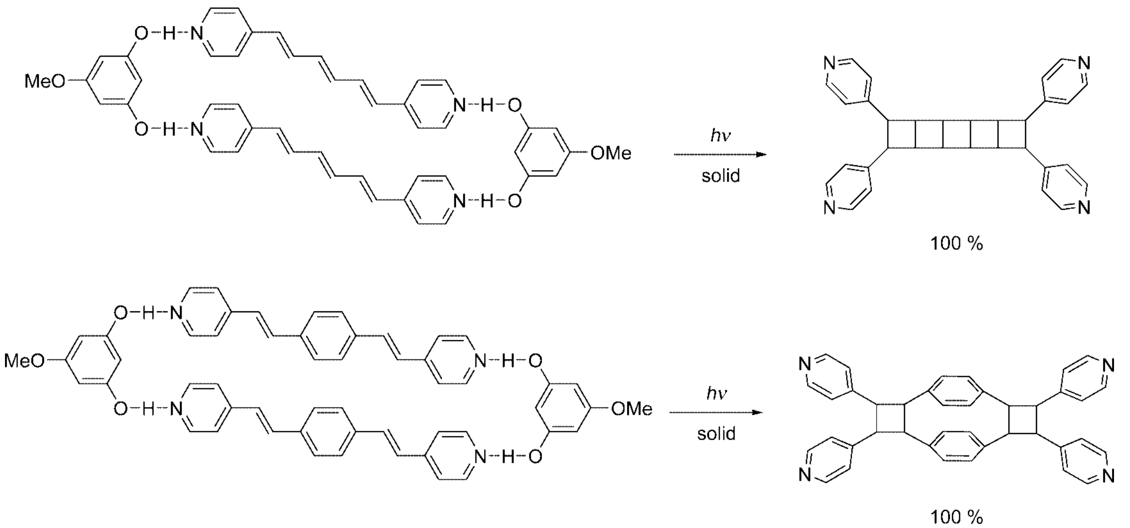

Figure 1. Hydrogen bonding between complementary subunits is used to steer the orientation of photoactive polyenes in the solid state. Upon irradiation, these architectures are quantitatively transformed to the corresponding laderanes[3] and cyclophanes.[5] Reproduced from ref.[3] by permission from Wiley-VCH and from ref.[5] by permission from the Royal Society of Chemistry.

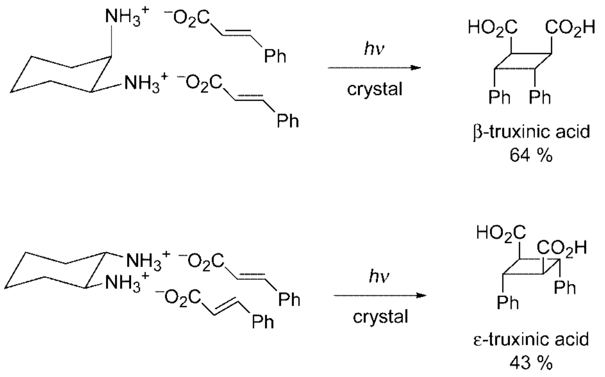

Figure 2. *Cis* and *trans* diamines form salts in the presence of cinnamic acid, which then crystallize into photosensitive double salts that are predisposed for the formation of specific photodimers.[11e]

II. Supramolecular Photochemistry in Solution

The design of solution-based, photoactive supramolecular systems is somewhat complicated by the presence of solvent–solute interactions. Whereas in the solid state one has to contend with the uncertainties of crystal packing forces, in solution it is the delicate balance between having sufficient intermolecular forces to maintain an assembled architecture and preserving solubility that is difficult to achieve. In solution, the directionality and predictability of H-B interactions causes them to be favored over other intermolecular forces to direct the formation of discrete assemblies. Whereas most architectures are geared toward either solid state or solution, the homocomplementary stilbene derivative shown in Figure 3, which possesses crown ether and ammonium ion binding sites, was recently shown to form a noncovalent dimer that possesses the unusual property of being photoactive in both the solid state and solution.[6g] Because of the relatively weak nature of H-B architectures in solution, complex multicomponent architectures exist in dynamic equilibrium with partially assembled precursors unless there is a strong positive allosterism to generate a specific structure.[13]

Supramolecular control of excited-state reactivity goes beyond merely increasing the local concentration of reactants.[14] Although the effective molarity within a self-assembled architecture can be quite high,[15] it is frequently the orientational parameters that exert the most influence on which of several reaction coordinates is favored upon excitation. The formation of H-B pyridone dimers was first used by Beak and Ziegler to enhance the photodimerization of distant cinnamates in solution.[16] More recently, similar interactions formed the basis of the enantioselective dimerization of pyrimidones[17] (Figure 4) and their cycloaddition to aromatic aldehydes and ketones.[18] By exerting enantiotopic control over photochemical reactions, their usefulness in organic synthesis can be expanded significantly.[19]

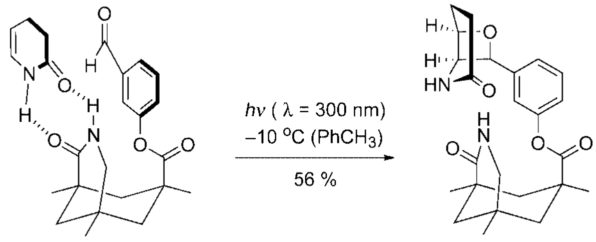

Figure 4. Hydrogen bonding can successfully be used in asymmetric synthesis by assembling a prochiral guest and a chiral host to induce enantiocontrol over a photochemical transformation. Reproduced with permission from ref.[17]. Copyright 2001 American Chemical Society.

A promising area in supramolecular photochemistry is the capture of dynamic assemblies for the purpose of molecular recognition, where the use of light as an external trigger is an attractive alternative to metal binding or olefin metathesis. The concept is illustrated in Figure 5, and it is easy to see how a guest or host may be prepared photochemically by irradiating a mixture of photoactive subunits. For such systems to be effective, the choice of an excitation

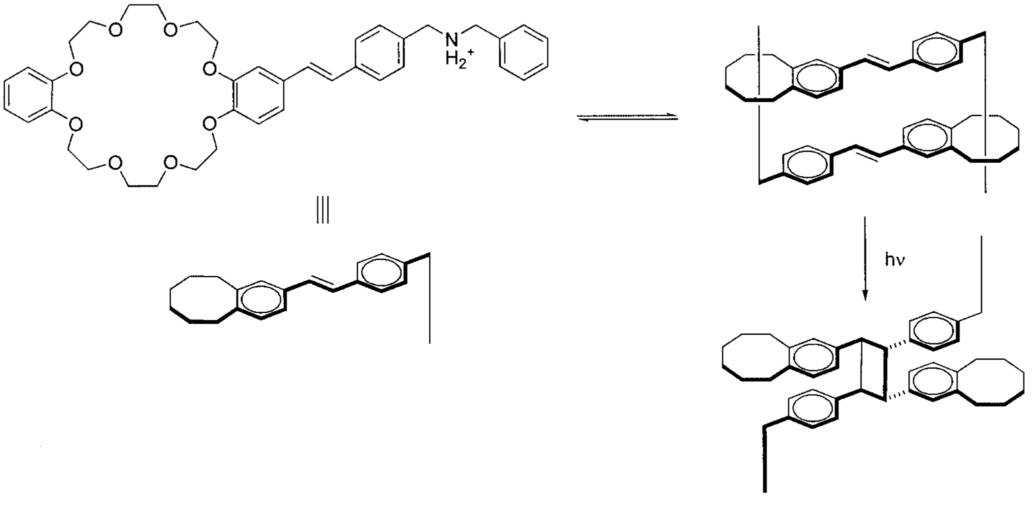

Figure 3. A daisy chain formed from two complementary stilbene derivatives undergoes stereospecific photodimerization both in solution and in the solid state. Reproduced from ref.[6g] by permission from Wiley-VCH.

wavelength where the template or photoproducts do not absorb light is important to achieve high conversions with minimal side products. Light can be used directly to imprint molecular recognition sites on Au-supported monolayers, which leads to the rapid construction of highly selective electrode arrays.[20] Another example is the irradiation of aminotriazine-appended cinnamic esters, which, when performed in the presence of a complementary barbiturate derivative, is conducive to the formation of photodimers that bind to the template.[21] The observed switch in regioselectivity and reaction mechanism is reminiscent of the principle of least-atom-motion observed in solid-state transformations, albeit applied to solution-based noncovalent architectures. The barbiturate receptors prepared by photochemically-driven, substrate-induced receptor synthesis are comparable to conventional barbiturate receptors, and show promise in differentiating nucleic acid derivatives.[22] Similarly, Skeen et al. extended this approach to promote the *trans–syn* photodimerization of a coumarin derivative using an extended ditopic receptor.[23] The incorporation of two or more independent binding sites and a photoactive moiety leads to systems in which different inputs can be used to control the outcome of a reaction.[24] The scope of the template approach is not limited to directing reaction pathways of well-known photochemical transformations. It may also serve to induce photoreactions not otherwise observed

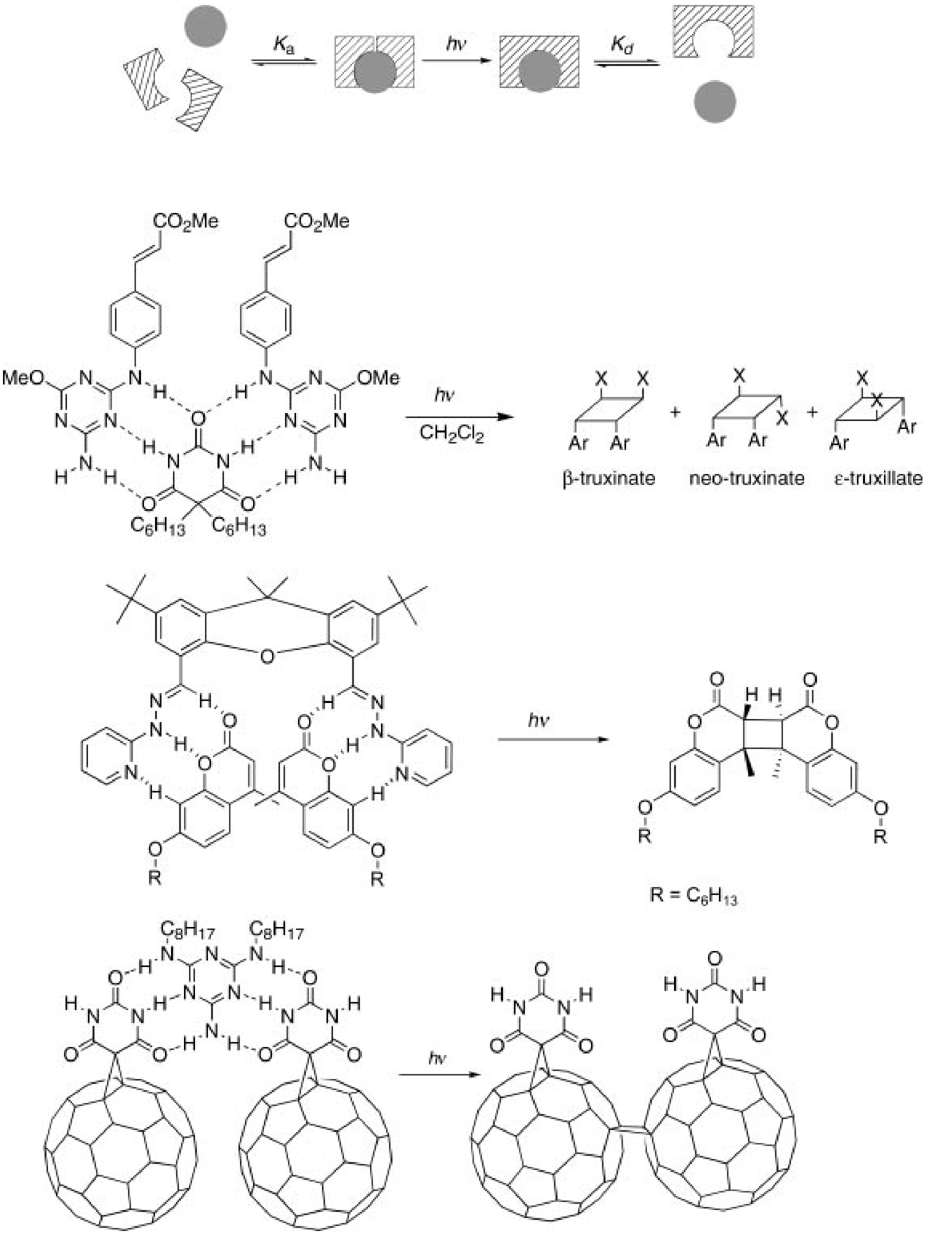

Figure 5. Covalent capture of a dynamic assembly around a given template often leads to the formation of a receptor for the template – a process of substrate-induced receptor synthesis.[21] Barbituric acid derivatives make convenient templates, as they possess two non-self-complementary binding sites that can be used to assemble photoactive chromophores, including coumarins[23] and fullerenes.[25] Reproduced with permission from ref.[25]. Copyright 2003 American Chemical Society.

in solution. An example of this is the template-assisted photodimerization of fullerene,[25] which was previously thought to be photochemically inert in solution at the low concentrations at which it is soluble. It is proposed that the anticipated supramolecular assembly mimics the distance and orientation found in crystalline C_{60}, which is known to undergo facile [2 + 2] photopolymerization.[26]

An alternative strategy to spatially constrain reactants during the course of a photoinduced reaction is to position them inside a cagelike structure. Despite the inherent difficulty in designing host systems of proportions sizeable enough to accommodate two chromophores, many successful examples are known. Whereas the use of cyclodextrin[27] or zeolites[10,28] to direct photoreactions is well established, the use of imprinted polymers,[29] dendrimers,[8,30] and self-assembled supramolecular cages is less frequent. A particularly elegant example is a palladium cage described recently by Fujita and coworkers (Figure 6). This cage self-assembles from four tritopic ligands and six metal ions to afford a structure that can accommodate acenaphthenes or naphthoquinones and direct their ensuing photodimerization.[31] Interestingly, direct excitation of the metallocage using short-wavelength UV light leads instead to the oxidation of enclosed hydrocarbon guests.[32] Cucurbituril (Figure 6) has been recently reported to also encapsulate cinnamate chromophores and efficiently direct their photo-

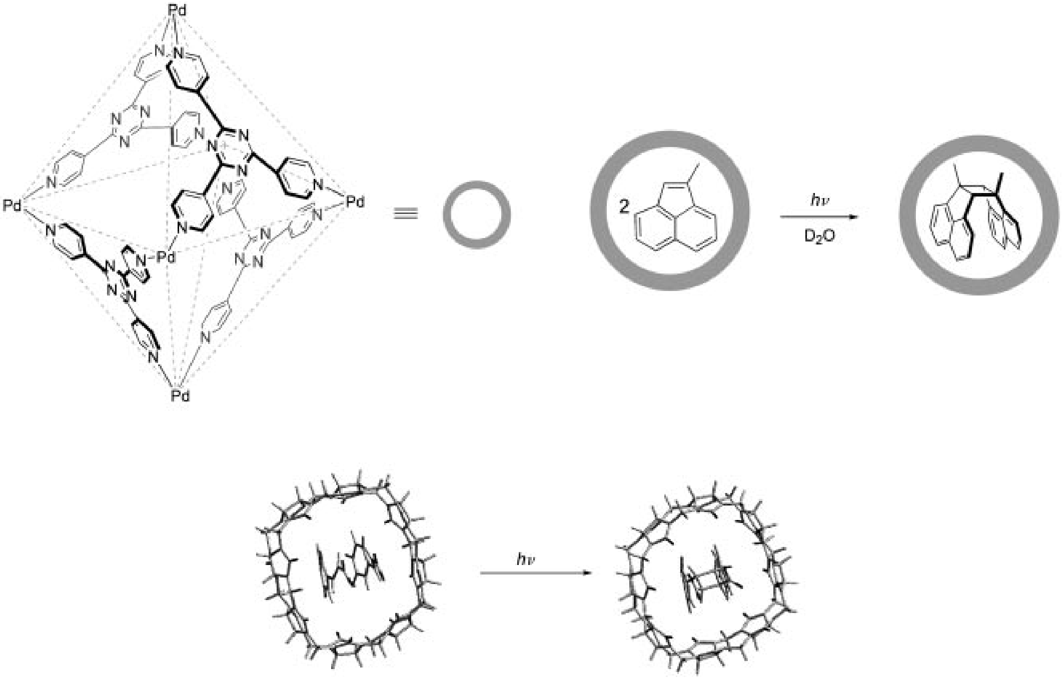

Figure 6. Examples of supramolecular cages to direct photochemical reactions. Top: A multicomponent self-assembled cage that serves as a host to two acenaphthene molecules, which then selectively photodimerize into a *syn* head-to-tail dimer.[31b] Bottom: Cucurbituril has recently been reported to act as an efficient promoter of otherwise non- or poorly photoreactive cinnamate derivatives by encapsulating and maintaining two chromphores in close proximity.[33] Reproduced from ref.[31b] with permission of Wiley-VHC and from reference[33] by permission of the American Chemical Society. Copyright 2005 American Chemical Society.

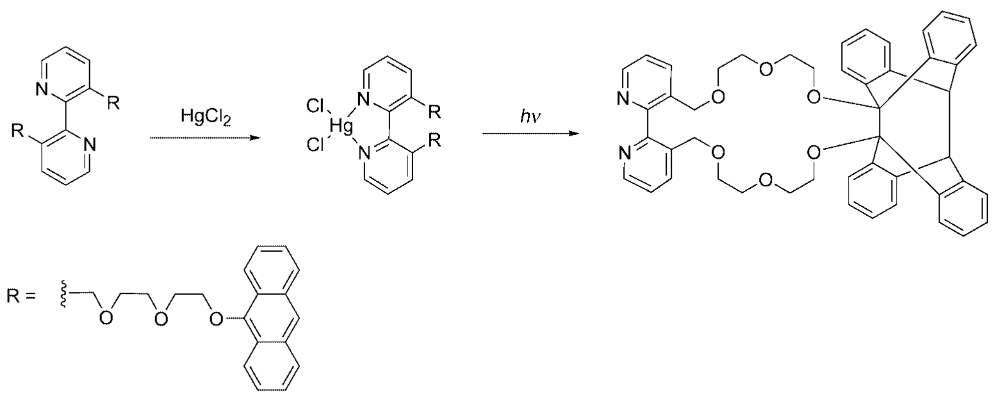

Figure 7. Photochromic systems responding to two or more chemical inputs can be built by combining independent binding sites with photoactive molecules. In the above example, binding of a transition-metal ion to the bipyridine moiety provokes a confromational change to the *cisoid* structure. The latter is apt to bind alkali metal ions and to promote photodimerization of the pendant anthracene chromophores. Reproduced from ref.[35d] with permission from Wiley-VCH.

dimerization, even in cases where the latter are reticent to undergo dimerization in solution.[33]

III. Photochemical Control of Supramolecular Architectures

The binding of metal ions can exert control over photochemical processes even when the binding site is remotely located from a chromophore.[34] Of course, the binding process itself can be modulated photochemically, which makes these systems interesting in several aspects, from sensing[35] to the phototriggered release[36] (or capture) of metal ions. For example, the photodimerization of pendant anthracene units has been used to modify the binding properties of various metal complexation sites (Figure 7) and, more recently, of a Hamilton receptor for barbituric acid derivatives. In the latter case, the photoinduced conformational change was sufficient to induce the expulsion of the bound guest upon irradiation.[37] Surface-bound systems suited for photo- or electrochemical sensing are accessible by immobilization of a receptor or host onto a substrate.[38]

Upon irradiation, nitrophenols are known to undergo facile intramolecular H-atom transfer that leads to the release of protected alcohols, amines or carboxylic acids.[39] This and other photolabile protecting groups, such as dithianes,[40] have been employed to induce the collapse of supramolecular assemblies. The strategy relies on the incorporation of the photocleavable unit in a key location so that, upon irradiation, the ensuing light-induced bond scission leads to the dissociation of a central unit into ineffective sub-units. This approach has been applied to amphiphiles,[41] rosettes,[42] and cyclodextrins,[43] as well as to the release of masked biochemical substrates[44] or guests that compete for binding sites in supramolecular polymer architectures.[45]

Light-induced conformational changes in one or more components of a supramolecular architecture can be used to significantly alter the global properties or the structure of the ensemble. In cases where the photoactive units are oriented or aligned, the photoinduced conformational changes are additive, and sub-nanometer molecular motion

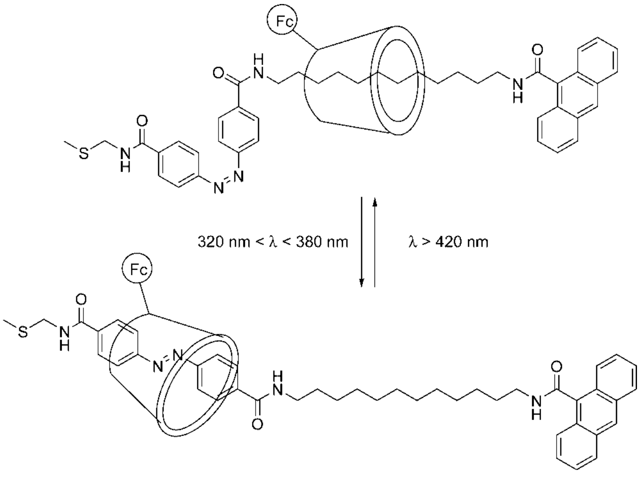

Figure 8. Light-induced isomerization of the azobenzene chromophore drives the motion of a cyclodextrin shuttle threaded onto a surface-bound alkyl chain. The ferrocene moiety provides a convenient electrochemical signal indicating the location of the shuttle.[52a]

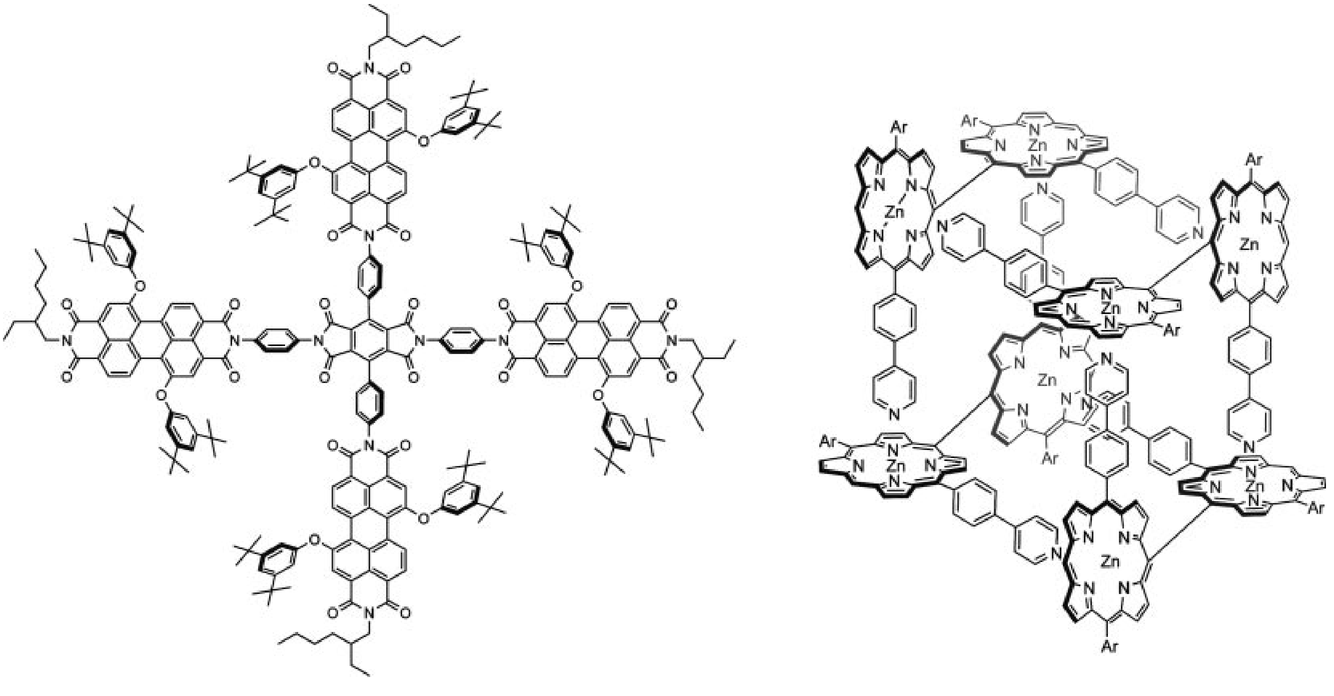

Figure 9. Two recent examples of extended or three-dimensional chromophore arrays incorporating perylenedimides[59a] (left) or porphyrins[59b] (right). Both are particularly well suited for absorption of light in the visible region of the spectrum. Reproduced from refs.[59a,b] with permission. Copyright 2004 American Chemical Society.

can lead to macroscopically visible changes. In this area, $E \rightarrow Z$ isomerization of conjugated double bonds is a versatile means to provoke reversible structural variations. In view of its high photostability and resistance to fatigue,[46] it is no surprise that the azobenzene chromophore has been widely used for such applications relative to related stilbene derivatives, which are prone to undergo electrocyclization from the Z-isomer. Azobenzenes have thus been incorporated into a wide variety of supramolecular assemblies, including catenanes and rotaxanes,[47] dendrimers,[48] and polymers.[49] Hydrogen-bonded assemblies can be rendered photoresponsive by the incorporation of pendant or inserted azobenzenes, which can then be used to induce light-triggered morphological variations.[50] These can in turn be used to control subsequent events such as molecular recognition[51] and even electronic interactions at electrode surfaces (Figure 8).[52] Azobenzene isomerization has also been used to prepare photoresponsive membranes,[53] microemulsions,[54] and vesicles,[55] as well as to control ion transport[56] and catalysis.[57]

A particularly active area of research located at the intersection of supramolecular chemistry and photochemistry is the construction of complex ordered architectures for the purpose of light-energy collection and conversion. This research endeavor may be mimicking what is already found in nature, where the distribution of light-conversion machinery is, in fact, nonrandom.[58] Recent examples[59] of extended or three-dimensional light-harvesting arrays are particularly impressive, (Figure 9), and self-organization is a viable tool to direct energy- and/or electron-transfer processes in such assemblies.[60] This area has been reviewed recently, and shall not be discussed further.[61] The possibility of converting incident radiation, once collected, into chemical or electrical energy holds promise for the future development of organic photovoltaic devices. In this field, recent work has focused on the incorporation of fullerenes into conjugated polymers, and considerable progress has been made in understanding the photoinduced energy- and electron-transfer processes that immediately follow the absorption of light. For this purpose, well-defined covalent or

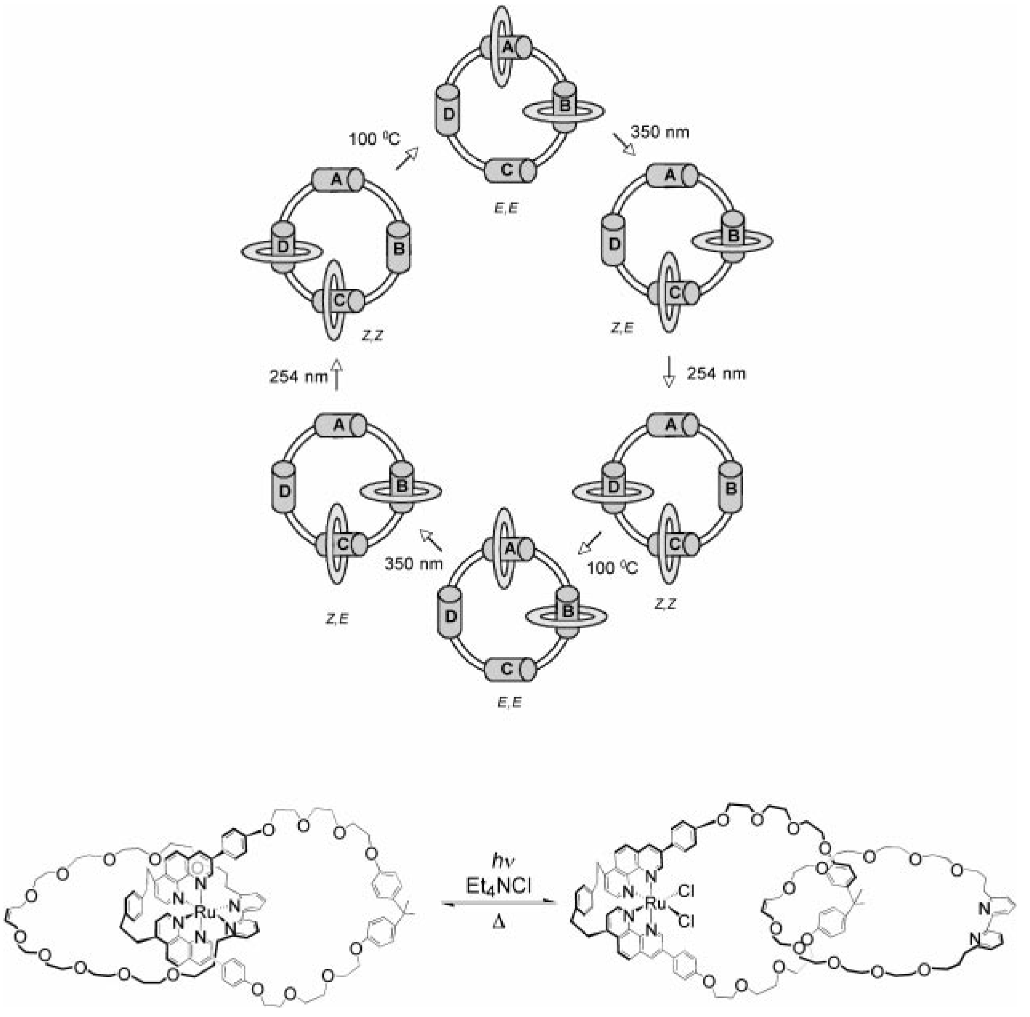

Figure 10. Top: Example of light- and heat-driven unidirectional motion in a triple catenane.[68] Bottom: When the excitation of a coordination complex populates a dissociative excited state, the ensuing photodissociation provides a novel means of unlocking motion in a supramolecular assembly.[70]

supramolecular systems are desirable, and the many systems prepared to date combine functionality, aesthetic pleasure, and synthetic challenge. In such assemblies, distant chromophores become photocontrollable units to gate electron- or energy transfer.[62] Assembly/disassembly of multicomponent architectures conducive to electron transfer evokes images of electrical extension cables.[63] Photovoltaic devices built using supramolecular assembly of photoactive organic subunits offer an interesting approach to inducing long-range ordering in molecular materials.[64] Compared to their covalent counterparts, these assemblies could present advantages such as increased modularity and ease of synthesis.[65] However, as in most other all-organic devices, issues of low durability and efficiency remain difficult to solve.

IV. Light in the Design of Molecular Machines

This short tour could not be complete without mentioning the fascinating area of molecular machines.[66] Fact or fiction, they have stimulated the imagination of scientists and the general public in many ways, and carry with them dreams of ultimate miniaturization. Many biological examples of purpose-directed molecular movement exist, and there is no reason to believe that synthetic analogues cannot be built one day and find future use. Light, once again, makes a convenient source of energy for such devices, as it leaves no side products that need to be evacuated.[67] It also provides the possibility of signaling to, from, or between photoactive subunits. Light was recently used by Leigh et al. to enable the translocation of a catenane between four different base stations.[68] In this example, precisely controlled $E \rightarrow Z$ isomerization of distinct olefinic double bonds within one architecture is achieved using monochromatic irradiation at specific wavelengths. This isomerization, in turn, provokes variations in the binding constants of the smaller catenane unit for each station, which then slides toward the station exhibiting the highest affinity. Unidirectional rotation was obtained by inserting a third catenane unit, as shown in Figure 10. The introduction of chirality can be used to impart chiro-optical switching in supramolecular assemblies and in liquid crystals.[69] A novel means of inducing molecular movement in supramolecular assemblies, providing an alternative to double bond isomerization, is the use of photoinduced cleavage reactions. Recent examples of this approach are based on metal–ligand complexes[70] or photochromic compounds[71] characterized by a dissociative excited state and a thermally allowed back-reaction.

As these examples demonstrate, our capacity to imagine wonderfully elegant systems is commensurate with our ability to construct complex three-dimensional molecular architectures endowed with specific functionalities. For this, synthetic organic chemistry remains a cornerstone in the edifice of supramolecular chemistry, even though it is sometimes relegated to the sidelines. We hope that this brief tour of photoactive supramolecular architectures will spark the imagination and pride of the organic chemistry community: so much has been achieved thanks to recent advances in synthetic methodology.

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