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Reaction Control by Molecular Recognition – A Survey from the Photochemical Perspective

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1.1 Introduction

Molecular recognition through non-covalent interactions between two or more molecules has attracted much attention from a broad spectrum of chemists for a long period of time and has already found many applications in various areas of science and technology. The concept of molecular recognition was first developed for biomolecular systems such as enzyme, antibody and DNA, which can selectively bind the specific target molecules through non-covalent weak interactions, including hydrogen bonding, van der Waals, dipole–dipole, charge–dipole and hydrophobic interactions.[1-3] Recent studies on artificial host–guest systems have revealed that molecular recognition is the essential conceptual basis for supramolecular chemistry and nanotechnology.[4,5]

Reaction control through complexation of substrate by supramolecular host is a relatively new idea compared to the conventional approaches that involve simple collisional attack or coordination of substrate to metal. Multiple non-covalent interactions in supramolecular assembly bind and locate a site-specific substrate in the right position, orientation and conformation near the catalyst or active site, stabilize the high-energy transition state, and eventually make the reaction faster and more selective. Typical examples are found in enzymatic reactions, which proceed with high specificity and efficiency in aqueous solutions under mild conditions. These observations in natural systems have inspired

researchers to develop novel research areas such as supramolecular chemistry, biomimetic chemistry and bio-inspired materials science and technology.[6,7]

Contrary to the thermal counterpart, photochemical reactions in supramolecular system have been less investigated and therefore of current interest. Photochemistry is a powerful tool in synthetic chemistry as a complementary method for achieving compounds that are difficult to obtain through thermal reactions due to high strain, low stability, and orbital symmetry reasons. Unlike thermal reactions, photoreactions deal with excited-state molecules that are usually short-lived but experience much lower energy barriers and exhibit high reactivities even at low temperatures. As a consequence of these features, the precise control of a photoreaction is more difficult to achieve than that of thermal one. This is one of the reasons why most asymmetric photoreactions result in only relatively low enantioselectivities. In this context, supramolecular approaches to the photochemical asymmetric synthesis enable the more precise control of the orientation and conformation of substrates and, as a result, the enantioselectivity of photoproducts, by utilizing the non-covalent interactions in both ground and excited states.

Supramolecular photochemistry is a relatively new interdisciplinary area of science and may be tracked back to the work in early 1980s, where the spectroscopic properties of ions were manipulated by crown ethers.[8–10] The rapid development of supramolecular chemistry in the last two decades accelerated the application of supramolecular systems to organic photochemistry[11,12] and more recently to asymmetric synthesis,[13,14] leading to a great number of publications on reaction control by molecular recognition. Consequently, not all of these areas will be covered, but the concentration will be rather on the representative supramolecular photoreactions conducted primarily in solution. This will help idenitify the crucial concepts, strategies and conclusions as well as the major factors and mechanisms that govern the supramolecular photochemistry in different systems, and also provide the possible applications and future perspectives of this interesting area of supramolecular chemistry.

1.2   Photochemical Reactions Mediated by Macrocyclic Compounds

1.2.1   Supramolecular Photoreactions with Crown Ethers

Crown ethers, a family of cyclic oligomers of ethylene oxide, are artificial macrocyclic hosts which have been synthesized and utilized since the early days of supramolecular chemistry.[15,16] Besides various metal ions that are complexed by crown ethers mainly through ion–dipole interaction, primary and secondary organic ammonium ions also form stable complexes with larger sized crown ethers through ion–dipole and hydrogen-bonding interactions. Stoddart and co-workers used crown ethers that can simultaneously bind two organic ammonium guests to facilitate photodimerization.[17] As illustrated in Scheme 1.1, *trans*-stilbene derivative **2** forms a doubly encircled, doubly threaded 2:2 complex with bis-*p*-phenylene-34-crown-10 **1** to give a centrosymmetric [4]pseudorotaxane in the solid state. In addition to the hydrogen-bonding interactions between **1** and **2**, the complex is also stabilized by π–π stacking interactions between the two *trans*-stilbene units with mean interplanar and centroid-centroid separations of 3.57 and 4.33 Å, respectively. The close arrangement of stilbenes accelerates the photodimerization upon irradiation to
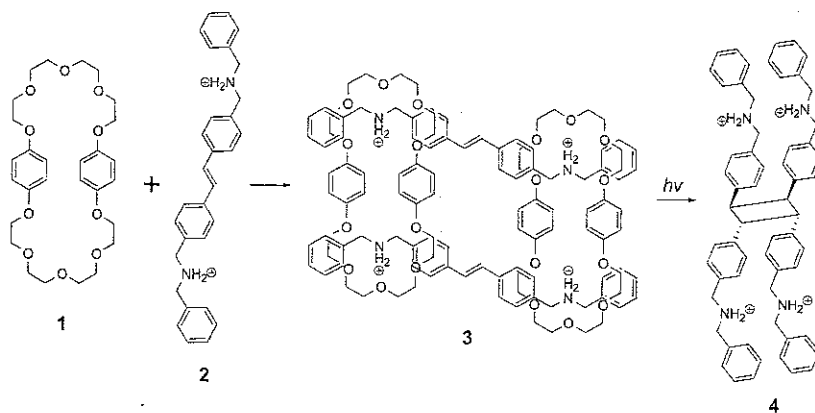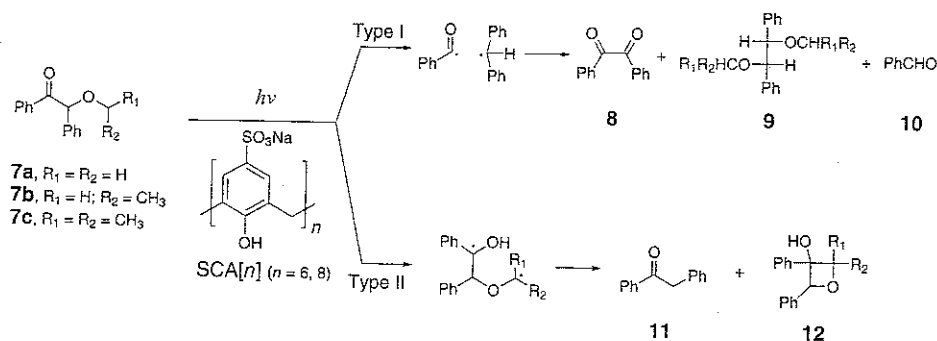
Scheme 1.1
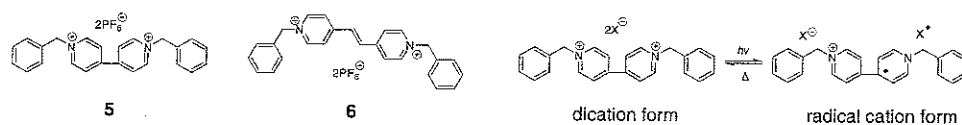
Scheme 1.2

exclusively give a single cyclobutane isomer **4** with a *syn–anti–syn* conformation, as confirmed by X-ray crystallographic analysis. A control experiment showed that no photodimerization but only *trans*-to-*cis* isomerization took place in the absence of crown ether **1**.

The photochromic behavior of viologens is greatly affected upon complexion with crown ether. Viologens show photoinduced colour change in the absence of any additional reagents when dispersed in isotropic thin polymer films.[18] Irradiation of benzylviologen **5** (Scheme 1.2) incorporated in a polymer matrix caused a colour change from colourless to blue as a result of the reduction of **5** from dication to radical cation, which was reverted to dication within 2 h in the dark. Crown ether **1** forms a 1 : 1 complex with **5** and also with **6** in acetone with association constants of *ca.* $200\,M^{-1}$. The charge-transfer (CT) interaction between viologen **5** or **6** and **1** led to the formation of yellow-coloured CT complex with a CT absorption band at 453 nm and 421 nm for **5** and **6**, respectively. The crown ether complexes of photoreduced viologens showed much accelerated bleaching rates than the corresponding free viologen radical cations. A similar phenomenon was observed also for $2 \subset 1$ complex in a polymer matrix.

1.2.2   Supramolecular Photoreactions with Calixarenes

Calix[*n*]arenes are a class of macrocycles that are normally made up of phenol units linked with methylene bridges and possess cavities of various sizes that can accommodate small organic molecules primarily driven by hydrophobic interactions.
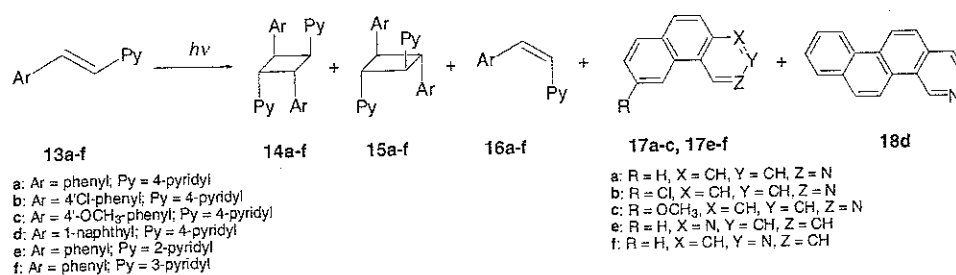
Water soluble *p*-sulfonatocalix[6]arene (SCA[6]) and [8]arene (SCA[8]) (Scheme 1.3) have dimensions of $15.9 \times 11.8\,\text{Å}$ and $20.4 \times 16.7\,\text{Å}$ at the upper rim and $6.5 \times 3.3\,\text{Å}$ and
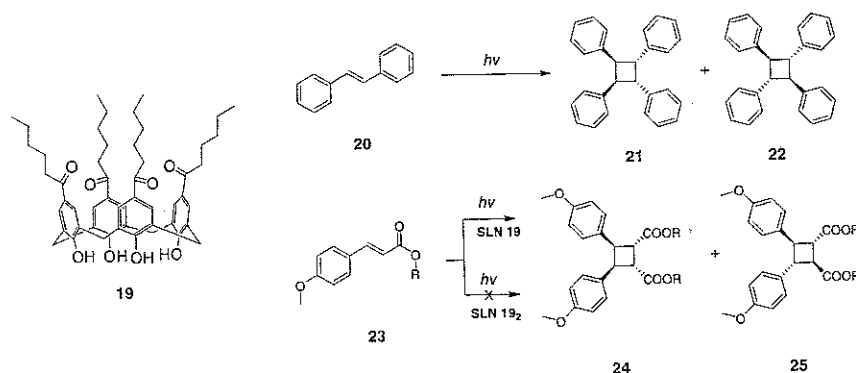
Scheme 1.3

$8.6 \times 5.9\,\text{Å}$ at the lower rim, respectively,[19,20] and provide suitable cavities for accommodating quaternary ammonium ions,[21,22] native amino acids,[23] and small neutral organic molecules.[24] Using SCA[6] and SCA[8][25] as supramolecular hosts, Ramamurthy *et al.* investigated the photochemistry of benzoin alkyl ethers **7a–c**.[26-28] These SCAs formed the corresponding $1:1$ complexes with **7a–c** in aqueous solution, and **7a** showed modest association constants of $137\,\text{M}^{-1}$ and $386\,\text{M}^{-1}$ with SCA[6] and SCA[8], respectively. Upon photolysis, these benzoin alkyl ethers underwent both the Norrish type I (α-cleavage) and type II (γ-hydrogen abstraction) reactions to give photoproducts **8–12** (Scheme 1.3). In the absence of SCAs, pinacol ether **9** was obtained as in 92% relative yield in aqueous solution at pH 7, along with deoxybenzoin **11** (8% relative yield), for which the α-cleavage ($k_\alpha \approx 10^{10}\,\text{s}^{-1}$) faster than the γ-hydrogen abstraction ($k_\gamma \approx 10^9\,\text{s}^{-1}$) is responsible. However, when the photoreaction was performed in the presence of SCA, product **11** became the major product. The relative yield of the type II products **11** and **12** depends critically on the cavity size of hosts and association constants. Photoirradiation of **7a** in the presence of an 8-fold excess amount of SCA[8] or SCA[6] gave **11** and **12** in 96% or 70% combined yield, respectively. The dominant formation of type II products suggests that **7** adopts a conformation favourable for γ-hydrogen absorption in the cavity. Choosing a suitable substrate with higher binding affinity for SCA is likely to be crucial in improving the stereoselectivity of photoreaction.

Photoreaction of stilbazoles **13a–f** (Scheme 1.4) has also been investigated in the presence of SCA[n]. Upon irradiation in dilute aqueous HCl solution without a host, *trans*-stilbazoles **13a–f** gave predominantly *cis*-isomers **16a–f**, along with only small amounts of *anti-head-to-tail* (HT) dimers **14a–f** and *anti-head-to-head* (HH) dimers **15a–f**.[29] In aqueous solution, stilbazoles were found to form $2:1$ complexes with SCA[8] and SCA[6], irradiation of which afforded the corresponding *anti*-HT dimer in 66–86% yield in the presence of SCA[8] and in 60–76% yield in the presence of SCA[6]. The *anti*-HH dimer was given in only 16% yield, which was attributed to the electrostatic repulsion between two pyridinium components. The hydrophobic nature of SCA cavity should be responsible for the inclusion of stilbazoles. It is thus concluded that SCAs control the orientation of stilbazoles through complex formation to eventually enhance the distribution of HT dimer.

a: Ar = phenyl; Py = 4-pyridyl
b: Ar = 4'-Cl-phenyl; Py = 4-pyridyl
c: Ar = 4'-OCH₃-phenyl; Py = 4-pyridyl
d: Ar = 1-naphthyl; Py = 4-pyridyl
e: Ar = phenyl; Py = 2-pyridyl
f: Ar = phenyl; Py = 3-pyridyl

a: R = H, X = CH, Y = CH, Z = N
b: R = Cl, X = CH, Y = CH, Z = N
c: R = OCH₃, X = CH, Y = CH, Z = N
e: R = H, X = N, Y = CH, Z = CH
f: R = H, X = CH, Y = N, Z = CH

Scheme 1.4

Scheme 1.5

Unlike water-soluble calixarenes that encapsulate guests by hydrophobic, electrostatic and van der Waals interactions, amphiphilic calixarenes in solid state form container- or capsule-like structures and include guest molecules predominantly through van der Waals interactions. Photochemical behavior of stilbenes included in amphiphilic molecular capsules of *p*-hexanoylcalix[4]arene **19** (Scheme 1.5) in the solid state was studied by Ananchenko *et al.*[30] Possessing diverse uni- and bimolecular reaction routes, including geometrical isomerization, cyclization and cyclodimerization, stilbenes are good model compounds for examining the effects of calixarene capsules on photoreactivity. In the solid state, two molecules of **19** self-assemble in a head-to-head fashion to form a hydrophobic capsule, which can accommodate two *cis*-stilbene molecules to give a 2:2 complex. This 2:2 complex is not very stable and can release one *cis*-stilbene molecule. On the other hand, *trans*-stilbene **20** is co-included with an ethanol molecule in the capsule to give a 1:1:2 complex. Irradiation of the complex of *cis*-stilbene first gave rise to *trans*-stilbene, and then to [2+2] dimers **21** and **22** in 5:1 ratio upon prolonged irradiation. Irradiation of *trans*-stilbene complex gave *cis*- and *trans*-stilbene in 1:1 ratio, along with a trace amount of dimers **21** and **22**, confirming that the initial capsule is occupied primarily by only one *trans*-stilbene molecule.

Notably, calixarene **19** readily forms solid lipid nanoparticles (SLNs), which can serve as a potential carrier system.[31] 2-Ethylhexyl *trans*-4-methoxycinnamate **23** can be loaded
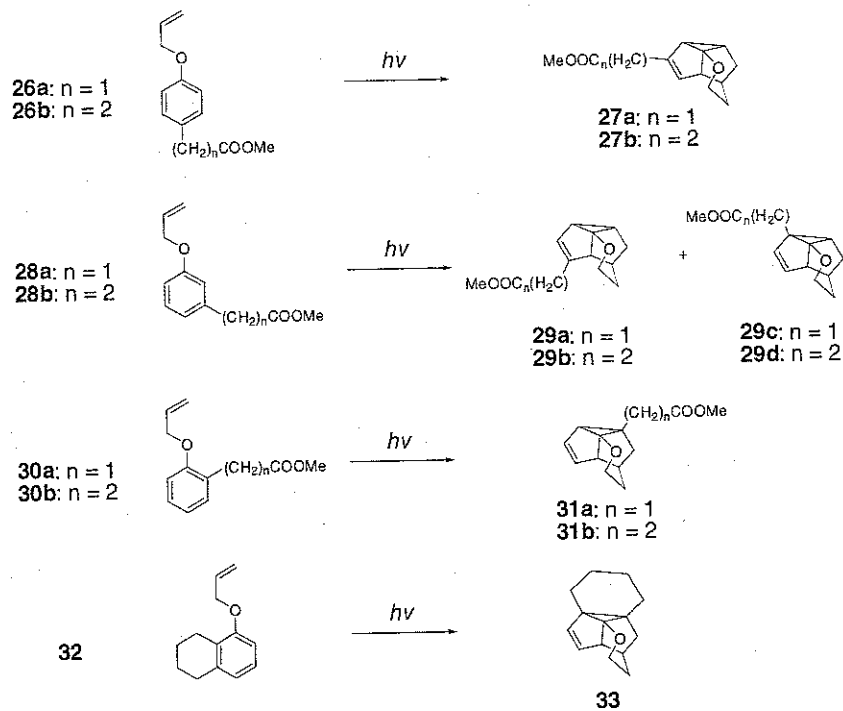
by a solvent displacement method into the SLNs based on **19**. Comparison of the powder X-ray diffraction (XRD) patterns of unloaded SLN and SLN loaded with **23** ([**23**]/[**19**] = 0.6) with that of crystalline complex **23** $\subset$ **19$_2$** revealed that the complexation pattern of the SLN loaded with **23** is similar to that of the crystalline complex. No dimerization product was obtained upon irradiation of **23** loaded in SLN of **19**, and only photoisomerization occurred to give a 4:6 mixture of *cis*- and *trans*-isomer. However, when the stoichiometry was changed to [**23**]/[**19**] = 1.2, photolysis of **23** loaded in SLN yielded HH dimers **24** and **25** in a combined yield of *ca.* 10%. This regioselectivity of cyclodimerization of **23** is attributed to the fact that two **23** molecules preferably align in the **19's** cavity in HH orientation. These results suggest that one can efficiently manipulate the photochemical behavior of **23** by simply adjusting the molar ratio of **23** loaded to the SLNs of amphiphilic **19**.

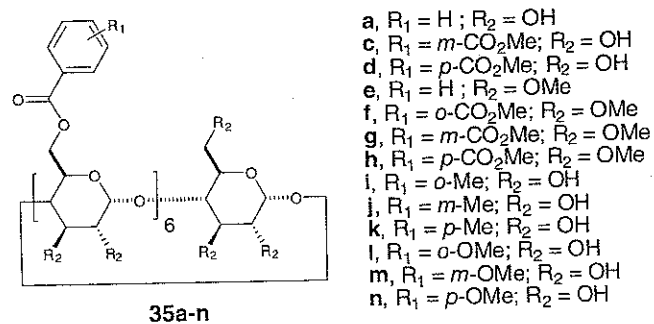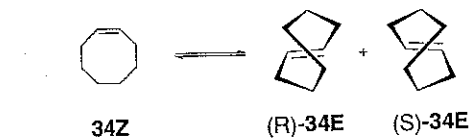### 1.2.3   Supramolecular Photoreactions with Cyclodextrins

Cyclodextrins (CDs) are most frequently employed hosts for supramolecular photoreactions by virtue of the fact that they are readily available, UV-transparent, water-soluble and capable of accommodating a wide range of organic guests in their hydrophobic cavities. Organic guests can form inclusion complexes with α-, β- and γ-CDs in various stoichiometries both in solution and in the solid state.

Unimolecular Reactions   The cavity of β-CD is smaller than that of γ-CD, and normally includes one organic molecule of suitable size to form 1:1, 2:2 or 2:1 host–guest complexes. Asymmetric intramolecular *meta*-photocycloaddition of phenoxyalkenes (Scheme 1.6) has been studied in the presence of β-CD by Eycken and co-workers[32]. The inclusion complexes of **26**, **28**, **30** and **32** with β-CD were collected from the deposit formed in a warm aqueous solution containing β-CD and substrates by centrifugation and decantation. For the complexes of **26a**, **28b**, **30a** and **30b** with β-CD, the host-guest stoichiometries were determined as 2:1 by UV spectroscopy, while the rest of the substrates formed 1:1 complexes. Irradiation of the solid complexes for 24 h led to *ca.* 55–82% conversion, which are appreciably lower than that obtained in the solution-phase photoreactions. In all cases, *meta*-photocycloaddition led exclusively to only one regioisomer of 1,5-bridged dihydrosemibullvalenes **27**, **31** and **33** respectively from **26**, **30** and **32**. On the contrary, irradiation of complex **28** $\subset$ CD afforded two *meta* adducts **29a,b** and **29c,d**. The regioselectivity of adducts **29a** and **29c** is about 1:3 in the presence of β-CD against 1:1 in the absence of β-CD. Photocyclization of 'linear' photosubstrates **26a,b** gave insignificant enantiomeric excess (ee) of less than 3%, which is probably due to the less restricted orientation of *p*-substituted substrate in the cavity. Photocyclization of **28a** afforded minor product **29a** in much better 17% ee but the major product **29c** in only 2% ee. These results may indicate the trade-off relationship between chemical and optical yield: thus, larger steric hindrance leads to low chemical but high optical yield, and vice versa.

It is well documented that direct or sensitized photolysis of (Z)-cyclooctene **34Z** leads to geometrical isomerization to planar chiral (E)-isomer **34E** (Scheme 1.7).[33] Due to the comprehensive work by Inoue *et al.*, the enantiodifferentiating photoisomerization of **34Z** sensitized by optically active benzenecarboxylates has become a benchmark reaction for evaluating chiral photosensitizing system.[34–36] The first supramolecular enantiodifferentiating photoisomerization of **34Z** was examined in direct photolysis of its β-CD complex

26a: n = 1
26b: n = 2

$\xrightarrow{h\nu}$

27a: n = 1
27b: n = 2

28a: n = 1
28b: n = 2

$\xrightarrow{h\nu}$

29a: n = 1
29b: n = 2

+

29c: n = 1
29d: n = 2

30a: n = 1
30b: n = 2

$\xrightarrow{h\nu}$

31a: n = 1
31b: n = 2

32

$\xrightarrow{h\nu}$

33

Scheme 1.6

34Z $\rightleftharpoons$ **(R)-34E**   +   **(S)-34E**

35a-n

a, $R_1 = H$; $R_2 = OH$
c, $R_1 = m\text{-}CO_2Me$; $R_2 = OH$
d, $R_1 = p\text{-}CO_2Me$; $R_2 = OH$
e, $R_1 = H$; $R_2 = OMe$
f, $R_1 = o\text{-}CO_2Me$; $R_2 = OMe$
g, $R_1 = m\text{-}CO_2Me$; $R_2 = OMe$
h, $R_1 = p\text{-}CO_2Me$; $R_2 = OMe$
i, $R_1 = o\text{-}Me$; $R_2 = OH$
j, $R_1 = m\text{-}Me$; $R_2 = OH$
k, $R_1 = p\text{-}Me$; $R_2 = OH$
l, $R_1 = o\text{-}OMe$; $R_2 = OH$
m, $R_1 = m\text{-}OMe$; $R_2 = OH$
n, $R_1 = p\text{-}OMe$; $R_2 = OH$

Scheme 1.7

in the solid state. Photoproduct obtained from this complex was almost racemic with only 0.24% ee, demonstrating that the cavity interior of native β-CD does not possess sufficient enantiodifferentiating ability for the photoisomerization of **34Z**.
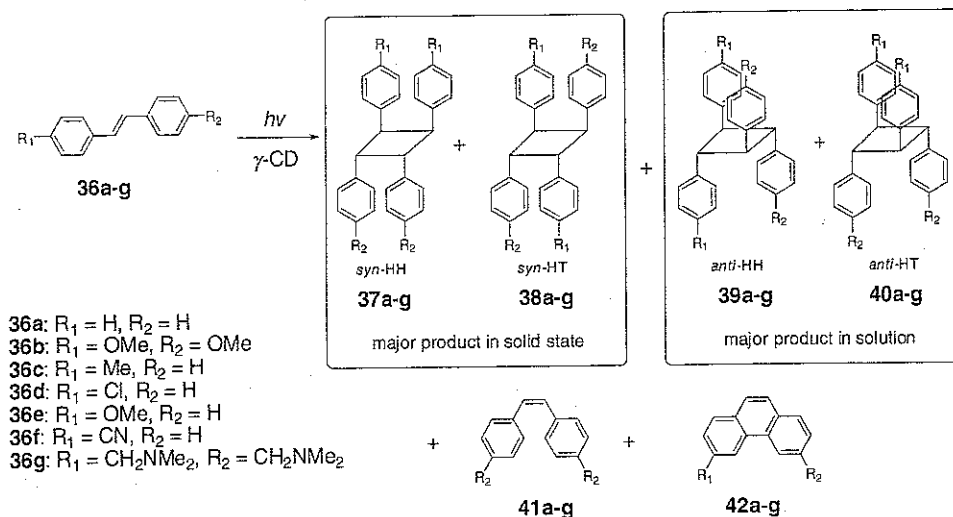
A more sophisticated strategy for achieving higher levels of enantiodifferentiation has been established by performing the photolysis of **34Z** with sensitizing chiral hosts **35** (Scheme 1.7), in which a chromophore is introduced to the primary rim of β-CD. A clear merit of this supramolecular photosensitization system is that the energy of excited sensitizer can be efficiently transferred to **34Z** included in CD cavity, while the undesirable, less-enantiodifferentiating sensitization outside the CD cavity can be prevented. Furthermore, this sensitizing host strategy allows the asymmetric photoreaction to occur with only a catalytic amount of chiral host, achieving photochemical chirality amplification.

In contrast to the small *E/Z* ratios around 0.25 reported for non-supramolecular photosensitizations by conventional alkyl benzoates,[37] an *E/Z* ratio of up to 0.8 were obtained at the photostationary state in 1:1 methanol–water mixture by using **35**. By adjusting the solvent composition, good enantiomeric excesses of up to 24% were obtained upon photosensitization with **35a–d**. The enantioselectivity of **34E** obtained in the photoisomerization of **34Z** with non-methylated CD is in general insensitive to the temperature variations as a result of the insignificant role of entropy in the β-CD-based supramolecular photochirogenesis system. However, the photoisomerization of **34Z** in permethylated CD derivatives **35e–h** turned out to be highly temperature dependent, frequently leading to a switching of the product chirality by changing the reaction temperature.[38] The more flexible skeleton of permethylated CD due to the lack of hydrogen-bonding net at the secondary rim is responsible for the temperature-dependent enantioselectivity.

Recently, further efforts were done to elucidate the effects of chromophore substitution on the ee of **34E**,[39] and much better enantiomeric excesses of up to 46% were reported upon photosensitized isomerization mediated by **35m**. Analogous hosts **35a**, **35l** and **35n** afforded only modest ee's in a range of 4%–10% under optimized conditions.[40] The ee value falls drastically to 1.7% when the *meta*-substituent is altered from methoxy (**35m**) to methyl in **35j**. This result reveals the critical dependence of the efficiency of chirality transfer on the sensitizer structure in the supramolecular photosensitized isomerization system.

Bimolecular Reactions β-CD is known to hinder the [2+2] photodimerization of stilbenes through complexation within its cavity.[41] In contrast, γ-CD can simultaneously include two stilbenes in its larger cavity in both solution and solid phase to significantly facilitate the [2+2] photodimerization reaction.

Wenz and co-workers examined the complexation and photochemical behavior of water-soluble stilbene **36g** with γ-CD in aqueous solution.[41] γ-CD forms 1:2 host–guest complex with **36g** in buffer solution (pH 5.7) at 25 °C with stepwise association constants of $K_1 = 385\,M^{-1}$ and $K_2 = 2730\,M^{-1}$. Photoirradiation of this ternary complex gave cyclobutanes *cis*-**37g** in 19% and *trans*-**39g** in 79% relative yield. The association constants of adducts **37g** and **39g** with γ-CD were $K_{37g \subset \gamma\text{-CD}} = 520\,M^{-1}$ and $K_{39g \subset \gamma\text{-CD}} = 18000\,M^{-1}$, respectively, revealing a great difference in stability between the isomeric complexes of $[\mathbf{36g}]_2 \subset \gamma$-CD.

36a: R_1 = H, R_2 = H
36b: R_1 = OMe, R_2 = OMe
36c: R_1 = Me, R_2 = H
36d: R_1 = Cl, R_2 = H
36e: R_1 = OMe, R_2 = H
36f: R_1 = CN, R_2 = H
36g: R_1 = CH_2NMe_2, R_2 = CH_2NMe_2

Scheme 1.8

The inclusion complexes of **36a–f** with γ-CD were prepared by the co-crystallization method.[42] The host/guest ratio varies from 1:1.60 to 1:1.95, indicating that most of the guests formed 1:2 host–guest complexes. However, the *cis*-isomer **41a** gave only 1:1 complex with γ-CD under the same condition. Photolysis of **36** ⊂ γ-CD for 24 h gave *syn*-dimers **37a–f** and **38a–f** in 59-79% relative yield. This observation is in sharp contrast to the results obtained in the solution-phase photolysis of **37g** mentioned above, and is attributed to the rate-limiting diffusion process prior to the reaction. The large distance and nonparallel orientation of the olefinic double bonds of the stilbenes in crystal lattices prohibit the dimerization of *anti*-isomers.

Tamaki *et al.* reported that water-soluble anthracene derivatives, such as 2-anthracenesulfonate and 2-anthracenecarboxylate, form 2:1 complexes with γ-CD in aqueous solution.[43,44] The [4+4] photodimerization of 2-anthracenecarboxylate (AC) accommodated in γ-CD and its derivatives was investigated in detail.[45] Inoue and co-workers have recently reinvestigated the photodimerization of AC from the chiral point of view by using a variety of chiral hosts. γ-CD forms very stable 1:2 host-guest complex with AC in aqueous buffer solution with association constants of $K_1 = 160 M^{-1}$ and $K_2 = 38500 M^{-1}$.[46]

Photolysis of AC gives four isomeric cyclodimers: *anti*- and *syn*-HT dimers **43** and **44** and *anti*- and *syn*-HH dimers **45** and **46**, of which **44** and **45** are chiral (Scheme 1.9). Irradiation of γ-CD complex of AC at 0°C gives the HT dimers **43** and **44** as major products in 88% combined yield and HH dimers **45** and **46** as minor products in 12% yield. HT dimer **44** is given in a moderate enantioselectivity of 37% ee, while poor enantioselectivity of less than 5% ee is given for HH dimer **45**.

Further efforts to improve the HT/HH and enantioselectivity of the photoreaction were carried out by using modified γ-CDs. Ikeda *et al.* reported that, by using dipyridinio-appended γ-CDs **49a–d** (Scheme 1.10) as chiral hosts, **45** is given in enhanced ee of 13%, which is significantly higher than that obtained with native γ-CD.[47]
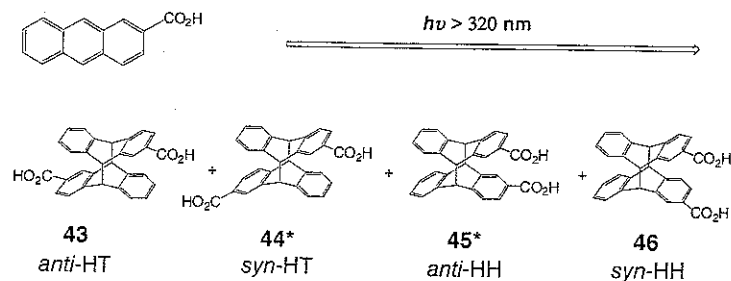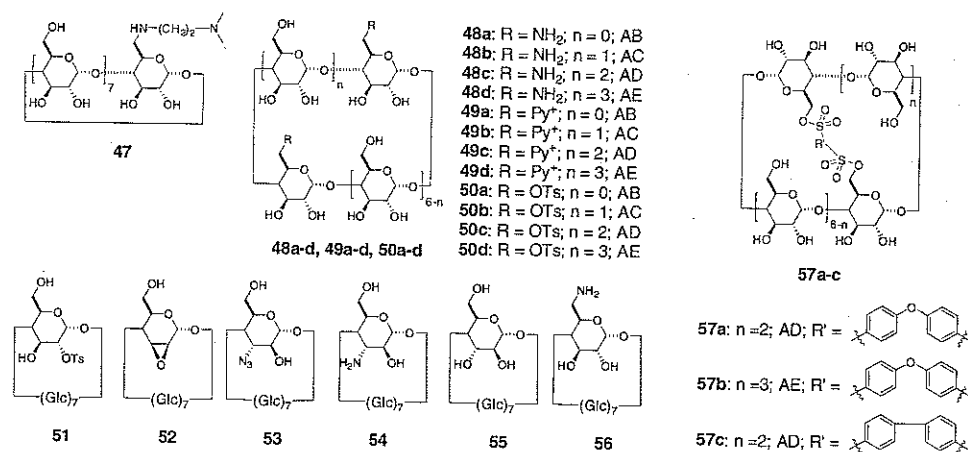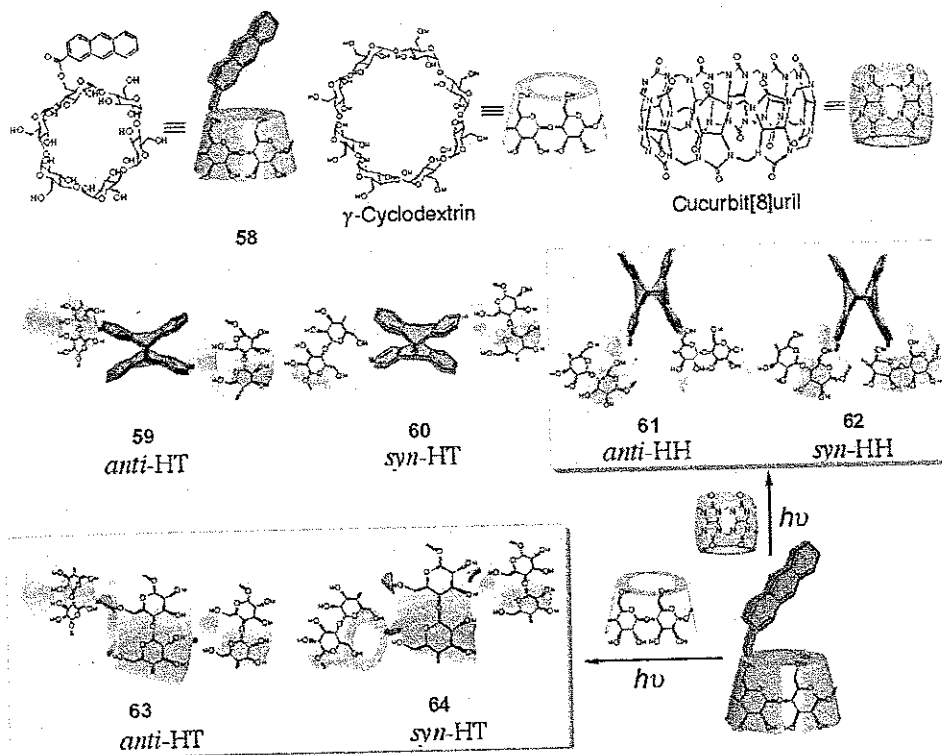
Scheme 1.9

Scheme 1.10

γ-CD derivative **47** that tethered with a flexible dicationic sidearm on the primary rim was also employed for the purpose to improve the chemical and optical yield of HH dimers.[48] In aqueous solution, photoirradiation of AC with **47** gave the cyclodimers in relative yield and ee similar to those obtained with native γ-CD. However, when the photoreaction was performed in a 1 : 1 mixture of water/methanol at −45 °C, the chemical yield of HH dimers was dramatically enhanced to 72% with ee of **45** being significantly improved to 40%. The *anti/syn* (**45/46**) ratio of HH dimers obtained in the photocyclodimerization of AC mediated by regioisomeric 6A,6X-diamino-γ-CDs **48a–d** gradually increased with increasing distance between the two ammonium groups, showing a nice structure–function relationship in supramolecular chirogenesis system.[49] Furthermore, a series of secondary-rim-substituted and skeleton-modified γ-CDs **51–56** were synthesized in order to examine the effect of modification of CD skeleton on the photocyclodimerization of AC.[50] The ee of HT dimer **44** was enhanced up to 71% and the combined yield of HT dimers reached 93% by the use of **54** at 210 MPa and −21.5 °C.

Recently, the effects of flexible and rigid caps introduced to the primary rim of γ-CD (**50a–d, 57a–c**) on the photodimerization of AC were investigated, as capping is known to significantly modify the binding and reaction behavior of native CDs.[51,52] The chemical

γ-Cyclodextrin

Cucurbit[8]uril

58

59
anti-HT

60
syn-HT

61
anti-HH

62
syn-HH

*h*υ

*h*υ

63
anti-HT

64
syn-HT

Scheme 1.11

yield and ee of HH dimer **45** were considerably improved by using capped γ-CDs **57a–c**. The enantioselectivity of HT dimer **44** was found to critically rely on the rigidity of the capping moiety. Thus, flexibly capped γ-CD **50a** afforded **44** in moderate ee around 40%, whereas γ-CD **57c** that has a rigid biphenyl cap gave the antipodal **44** in 58% ee.

The main motif in the photocyclodimerization of AC mentioned above is to enhance the HT/HH and enantioselectivity through modification of γ-CD to provide an optimized microenvironment. An interesting approach has recently been explored to influence the photoreaction inside a host by manipulating the moiety existing outside the cavity.[53] Instead of directly using AC as substrate, 6-*O*-(2-anthracenecarbonyl)-α-CD **58** was employed as a photosubstrate that possesses a bulky α-CD to be located outside the host cavity upon complexation. Two anthracene moieties of **58** can be included in γ-CD cavity to give the stepwise 1 : 1 and 1 : 2 association constants of 270 and 21700 M^{-1}, respectively. Photoirradiation of **58** yielded dimerization products **59–62** in the absence of host, which were hydrolyzed in alkaline solution to give **43–46** for evaluating the yield and enantioselectivity. Direct irradiation of **58** gave HT dimers in 76% combined yield, with low ee's for both HT dimer **44** (5% ee) and HH dimer **45** (16% ee). Photoirradiation of **58** in the presence of γ-CD afforded α-CD-stopped rotaxanes **63** and **64** in a high combined yield of 98%. Furthermore, the ee of HT dimer **44** was greatly enhanced to 91% under a pressure of 210 MPa at −20 °C, suggesting that the α-CD that locates outside the γ-CD

cavity can critically affect the stereo- and enantioselectivity of the [4 + 4] photocyclodimerization of AC occurring inside the cavity.

1.2.4   Supramolecular Photoreactions with Cucurbiturils

Cucurbit[*n*]urils (CB[*n*]s) are a family of macrocyclic compounds comprising 5–10 glycoluril units. CB[6], CB[7] and CB[8] are similar in cavity volume to α-CD, β-CD and γ-CD, respectively. Differing from CDs, CBs are achiral host molecules of D_{nh} symmetry and therefore cannot provide chiral microenvironment.

Although the solubility of CB[7] in water is the highest in the CB family, the relative small cavity, compared to that of CB[8], appears to have limited its application as a template in photochemistry. Up to now, only one work on [4 + 4] photodimerization of a small cationic guest, i.e. protonated 2-aminopyridine **65** (Scheme 1.12), by CB[7] in aqueous solution has been reported by Macartney and co-workers.[54] The [4 + 4] photodimerization of **65** in acidic aqueous solution in the absence of CB[7] gave *anti-* and *syn-trans*-4,8-diamino-3,7-diazatricyclo[4.2.2.2]-dodeca-3,7,9,11-tetraenes **66** and **67** in 4 : 1 ratio. CB[7] can form complex with **65** in 1 : 1 and 2 : 1 stoichiometries, depending on the amount of **65** added. Irradiation of 2 : 1 complex showed a greatly improved reaction rate and gave exclusively *anti-trans*-**66** in 90% yield without accompanying any other products. Such a high stereoselectivity suggests that two **65** molecules in an *anti-trans* alignment are stabilized in CB[7] cavity. Interestingly, the inclusion of photoproduct **66** in the CB[7] cavity efficiently prohibits its thermal re-aromatization.

Kim *et al.* reported that CB[8] could accommodate two aromatic guest molecules to form 1 : 2 host-guest complexes or 1 : 1 : 1 ternary complexes. The solubility of CB[8] is quite poor in water and organic solvents. Fortunately, by adding some metal cations, the solubility of CB[8] could be considerably increased in water. This observation enabled scientists to investigate intermolecular photoreactions in CB[8] cavity.

Stilbene and its derivatives, which had been widely investigated in CDs and CAs, can be included in CB[8] cavity to form 2 : 1 complexes.[55] Two (*E*)-diaminostilbene dihydrochloride **68** (Scheme 1.13) can insert into CB[8] cavity to give a 2 : 1 host-guest complex which has a good solubility in water. Photoirradiation of the complex gave [2+2] photodimerization product 1α,2α,3β,4β-tetrakis(4-aminophenyl)cyclobutane **69** as major product, along with a trace amount of 1α,2β,3α,4β-tetrakis(4-aminophenyl)cyclobutane **70**. No formation of the isomerization product (*Z*)-**68** was observed, which is significantly different from the photoreaction of (*E*)-**68** in the absence of CB[8]. The stereoselectivity of photodimerization in the presence of CB[8] (*syn/anti* = 95/5) is much better than that obtained with γ-CD (*syn/anti* = 80/20).

Scheme 1.12

Scheme 1.13

76a, R = Me
76b, R = Et

77a, R = Me
77b, R = Et
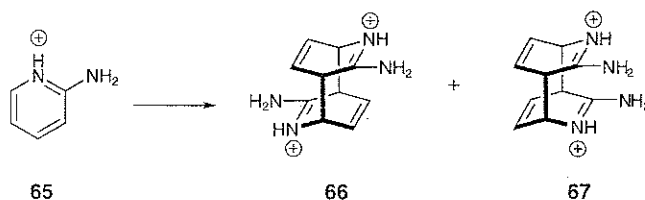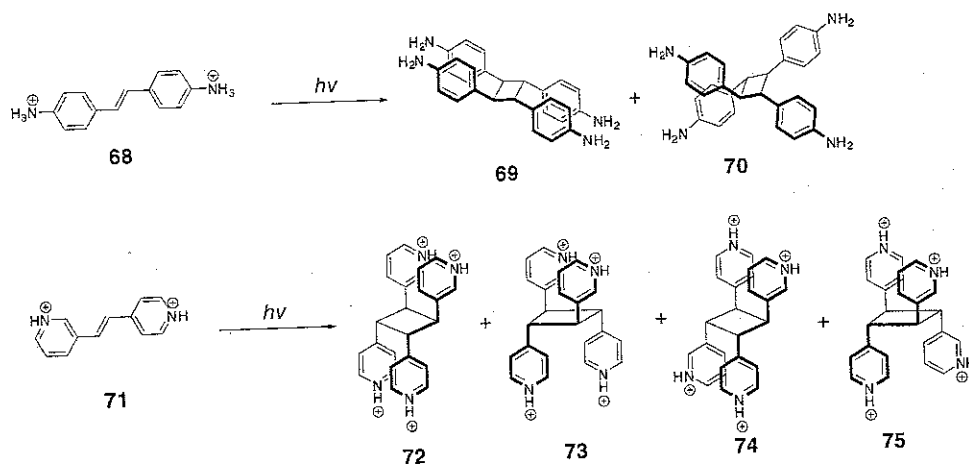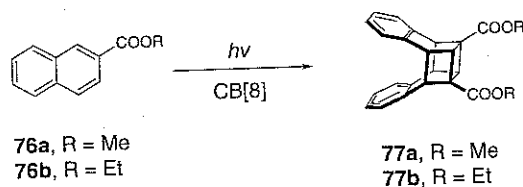
Scheme 1.14

Irradiation of *trans*-1,2-bis(4-pyridyl)ethylene dihydrochloride in the presence of CB[8] also yields the *syn*-dimer as major product in 90% relative yield and *anti*-dimer in only 4% relative yield.[56] However, in the presence of CB[7], no [2+2] dimerization product was obtained and only *cis*-1,2-bis(4-pyridyl)ethylene was formed. This result is attributed to the different complexation stoichiometry of 1,2-bis(4-pyridyl)ethylene with CB[7] (1:1) and CB[8] (2:1).

Recently, photodimerization of unsymmetrical bispyridylethylenes **71** was investigated in the cavity of CB[8].[57] Irradiation of **71** in the absence of CB[8] gave no [2+2] photodimer, and only *trans*-to-*cis* isomerization is observed for the photoreaction in the presence of CB[7]. Interestingly, irradiation of **71** with CB[8] gave exclusively *anti*-HT **74** and *syn*-HH **72** dimers in 80% and 15% relative yield, respectively, among four possible [2+2] dimers of *syn*-HH **72**, *syn*-HT **73**, *anti*-HT **74** and *anti*-HH **75**.

Wu *et al.* investigated the photodimerization of alkyl 2-naphthoates **76a,b** (Scheme 1.14) in the presence of CB[8].[58] The solubility of **76a,b** in water was enhanced upon addition of CB[8]. As a result of 1:2 host–guest complexation between CB[8] and **76**, photodimerization reaction rate was greatly accelerated in aqueous solution to give cubane-like photodimers **77a,b**.

Inoue and co-workers also examined the [4+4] photocyclodimerization of α-CD appended anthracene derivative **58** mediated by CB[8] (Scheme 1.11).[58] Photodimerization

of AC using CB[8] as template gave photodimers in relative yields similar to those obtained in the absence of CB[8]. However, the use of CB[8] as a host for the photo-dimerization of **58** totally inverted the selectivity observed with γ-CD to give HH dimers **45** and **46** in 99% combined yield. The steric repulsion between two α-CD does not appear to play an important role in the determination of the HH/HT ratio but significantly affects the *anti/syn* ratio of HH dimers, revealing a dual role of the bulky α-CD in the stereodif-ferentiation step of the supramolecular photodimerization. On the other hand, α-CD located outside the cavity could even transfer its chiral information to the photodimeriza-tion occurring within the achiral cavity of CB[8] to yield **44** and **45** in modest 17% and 10% ee, respectively.

Large-sized host molecules derived from calixarene and cyclotriveratrylenes have been reported recently. Gibb and co-workers reported some nanoscale host molecules based on resorcinarenes and studied their shape complementarities and the complexation behav-ior with guest molecules.[59-61] Host **78** (Scheme 1.15), which provides a well-defined hydrophobic environment in water, forms a capsular complex [**78**]₂ with a cavity dimen-sion of 1 nm wide and 2 nm long.[59] Ramamurthy *et al.* examined the cage effect of host [**78**]₂ on the photoreaction of 1-phenyl-3-*p*-tolyl-2-propanone,[62] which exhibit significant cage effect comparable to that reported in the solid state.[63,64]

This host molecule can also form 2:2 complex with anthracene (Scheme 1.15)[65]. However, no anthracene dimer was observed even after 10 h irradiation of the complex.
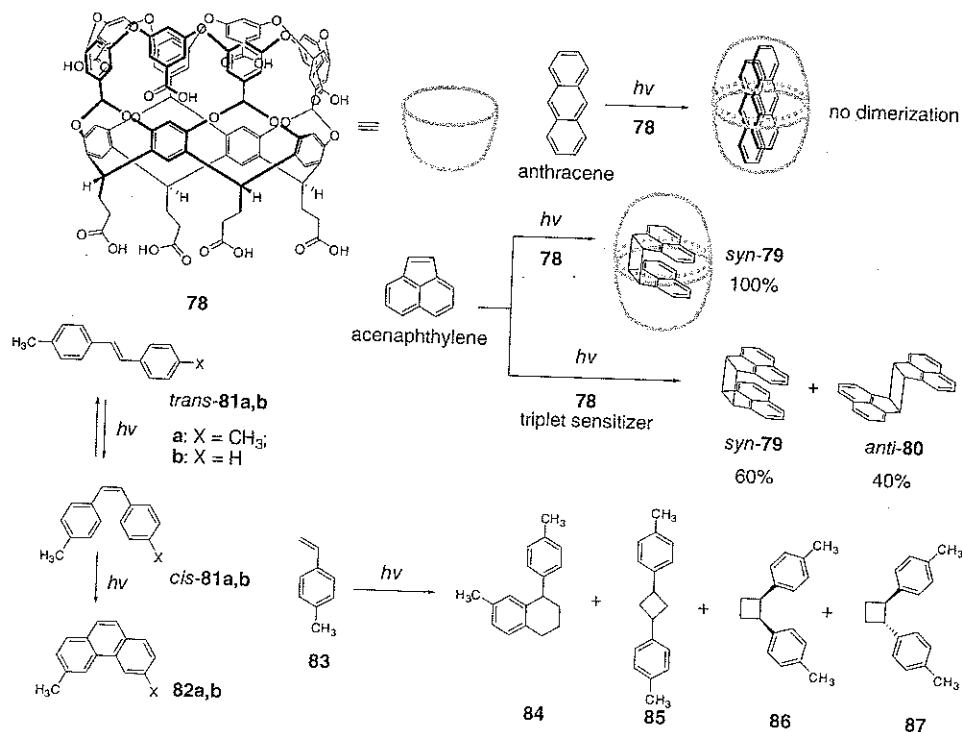
Scheme 1.15

Steady-state fluorescence spectrum of anthracene without **78** was completely different from that in the presence of **78**. Thus, anthracene in aqueous solution showed only monomer fluorescence at 425 nm, but the complex with [**78**]₂ exhibited excimer emission of anthracene with a maximum at 510 nm and a long lifetime of 263 ns. This suggests that the capsule [**78**]₂ confines two anthracene molecules in its cavity in staggered orientation.

Similar to anthracene, acenaphthylene can also be encapsulated by [**78**]₂ to form a 2:2 complex.[66] NMR studies suggested that two acenaphthylene molecules are located in the middle of the capsule cavity and oriented in a parallel fashion. Irradiation of acenaphthylene in the absence of any host yielded *syn-* and *anti*-dimers, with the latter being the major product. Within the [**78**]₂ cavity, only *syn*-dimer **79** was obtained upon irradiation. In the presence of triplet sensitizer eosin-Y, irradiation of the complex gave *syn-* and *anti*-dimers in a ratio 60:40.

Olefins were also examined as guest substrates for this nanocapsule.[67] In borate buffer solution, *trans-* and *cis*-4,4′-dimethylstilbene **81a** formed 1:2 complex with [**78**]₂. Irradiation of *trans*-**81a** ⊂ [**78**]₂ led to very slow isomerization, while *cis*-**81a** ⊂ [**78**]₂ converted to *trans*-isomer very fast. For stilbene **81b** with a smaller size, the *trans*-to-*cis* isomerization became much easier and was almost unaffected by the capsule. Furthermore, 4-methylstyrene **83**, which has a half size of **81a**, was irradiated in the capsule to explore its photochemical behavior. 4-Methylstyrene **83** forms 2:2 complex with **78**. Irradiation of this complex afforded **84** and **85** in 45% and 55% relative yield, respectively.

1.3   Photochemical Reactions with Biomolecules

Biomolecules, such as protein, antibody and DNA, are macromolecules that possess binding sites for organic guests with well-defined three-dimensional geometries and precisely arranged functional groups. As a result of their structural properties, biomolecules are characterized by the significant specificity for complexing and catalyzing their substrates. For example, it is well known that enzyme can accelerate the reaction of its substrate by a factor of one million or even more compared to the control reaction in the absence of enzyme. Their binding sites are highly specific to substrates and can usually catalyze a set of closely related substrates or reactions, but are silent to those mismatched. Since most biomolecules are water-soluble and heat-sensitive, performing a reaction with biomolecules definitely means the use of mild and environmentally benign conditions. On the other hand, light energy is known to be environmentally benign and can be efficiently converted into chemical energy through biophotochemical process, such as photosynthesis. These properties are superior in many aspects to those of artificial hosts and have attracted chemists to pursue efficient and selective chemical reactions in binding sites of biomolecules.

1.3.1   Photochemical Reactions Templated by Deoxyribonucleic Acid (DNA)

DNAs are important molecules that carry the genetic information and are capable of self-replication in living organism. The basic unit of DNA is nucleotide that comprises of a nucleobase (adenine, thymine, cytosine and guanine), deoxyribose, and a phosphate tail (Scheme 1.16). The precise complementarity between adenine and thymine and between cytosine and guanine renders two long chains of nucleotides coiled to give rise to a twisted

Adenine (A)   Guanine (G)   Cytosine (C)   Thymine (T)
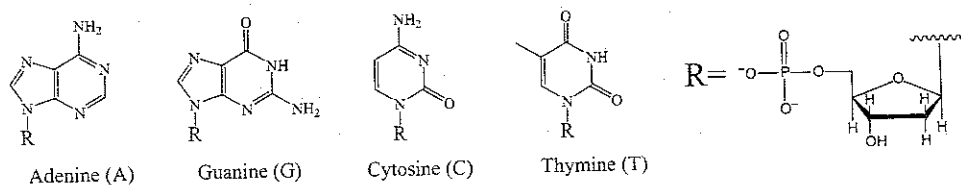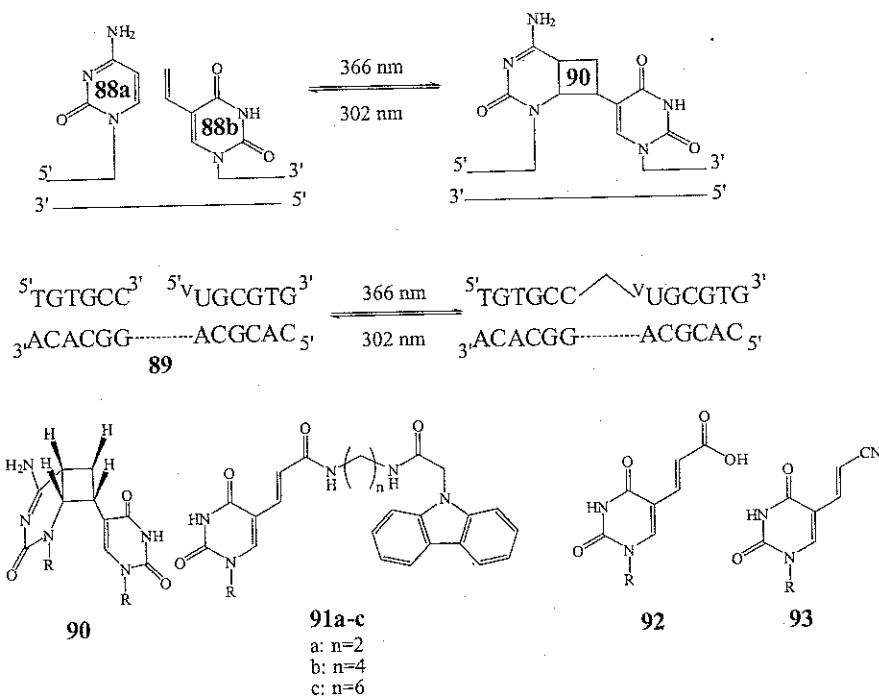
Scheme 1.16

Scheme 1.17

double helix, which is driven predominantly by hydrogen bonding and π π stacking interactions. It is therefore reasonable to anticipate that the DNA chain itself can serve as a good template for precisely positioning the substrates linked to it.

Photoaddition of substrates covalently-linked to DNA at its terminus has been studied for the purpose of exploring photoinduced ligation of oligonucleotides. Photoligation has evident advantages that the ligation can be conducted in water without adding any external reagent in a non-enzymatic fashion and the original DNA can be recovered by wavelength-selective irradiation.

Saito and co-workers investigated a series of photoligation reactions of DNA using native and terminus-functionalized oligonucleotides.[68–76] As illustrated in Scheme 1.17, synthetic oligodeoxynucleotides **88a** and **88b**, which bear a cytosine at the 3'-end and a 5-vinyldeoxyuridine at the 5''-end, are complementary to an oligodeoxynucleotide tem-

plate **89**.[68] In the absence of **89**, no photoadduct was given upon photoirradiation at 366 nm, at which **88b** has only weak absorption of $\varepsilon_{366} = 3.3$. However, photoligated oligodeoxynucleotide **90** was obtained in up to 96% yield when photolysis was carried out for 12 h in the presence of **89**. Only one [2+2] photoadduct that has a *cis-syn* stereochemistry was afforded. The significantly enhanced reactivity and selectivity are attributed to the well-arranged orientation of two oligodeoxynucleotides when complexed with the template **89**. Vinyldeoxyuridine introduced at the 5′-end underwent the same [2+2] photoaddition with thymine at the 3″-end but not with adenine and guanine. The ligated oligodeoxynucleotide can be photodecomposed to give the original 6-mers upon irradiation at 302 nm but better recovered by further irradiation at 366 nm, suggesting photochemical reversibility of the ligation process.

However, the split of ligated DNA with light at 302 nm may also result in damage to DNA due to the dimerization of thymine. To avoid this disadvantage, Fujimoto and coworkers synthesized 3″-terminus-modified oligodeoxynucleotide **91** (Scheme 1.17), in which carbazole is tethered to the 5-carboxyvinyluracil moiety as a sensitizer for photodecomposition.[69] Photolysis of oligodeoxynucleotides with a template gave ligated oligodeoxynucleotide with an efficiency order **91c** > **91b** > **91a**. A *cis-syn* [2+2] adduct was given in 89% yield after the photolysis of **91c** at 366 nm for 6 h at room temperature in the presence of the template. The same reaction performed at 70 °C, where **91c** was decomplexed from the template, afforded no photoligated product, indicative of the importance of preorientation of photosubstrate by supramolecular host. On the other hand, photoirradiation of the isolated adduct in the absence of the template at 366 nm for 6 h afforded **91c** in 90% yield as a result of the photosensitized split.

In order to improve the photoreactivity of template-directed photochemical synthesis of branched oligodeoxynucleotides, the 5-vinyldeoxyuridine component was replaced by 5-carboxyvinyldeoxyuridine **92**, which has a much higher extinction coefficient ($\varepsilon_{366} = 76$).[70] Photoirradiation of **92** for 1 h in the presence of a template gave a *cis-syn* [2+2] adduct in good yield of 93%. Similar [2+2] photocycloaddition between an α-5-cyanovinyldeoxyuridine **93** at the 3′-end and a thymine at the 5′-end also occurred smoothly in the presence of a template.[71] A single mismatch in oligodeoxynucleotide chain led to a great decrease of reaction rate, indicating a critical dependence of photoligation on sequence specificity.

Using **94** as a template DNA, Ihara *et al.* investigated the photodimerization of anthracene tethered to complementary oligodeoxynucleotides **95** and **96** (Scheme 1.18).[77] The reactivity of the photodimerization mediated by **94** was found to be dependent on the distance between oligodeoxynucleotides and anthracene, and decrease in an order of **95a/96a** > **95a/95b** > **95b/96b** > **96a/96b**. The reaction efficiency is also significantly affected by the introduction of an additional or mismatched nucleotide, indicating that this DNA-templated photoligation is highly position- and distance-dependent.

Photodimerization of 1-substituted anthracene derivatives **97a** and **97b** (Scheme 1.19) templated by a full-match DNA **98** selectively afforded only two isomeric dimers among the eight dimers that are possibly formed from the dimerization of **97a** and **97b**. Photoreaction with the full-match template was found to be much more efficient than those with mismatch templates.[78,79]

There are two kinds of grooves in DNA helixes, i.e. major and minor grooves, which can interact with metal ions or organic guests. Since these grooves are well-structured

TTAGGGTTAGCG
94

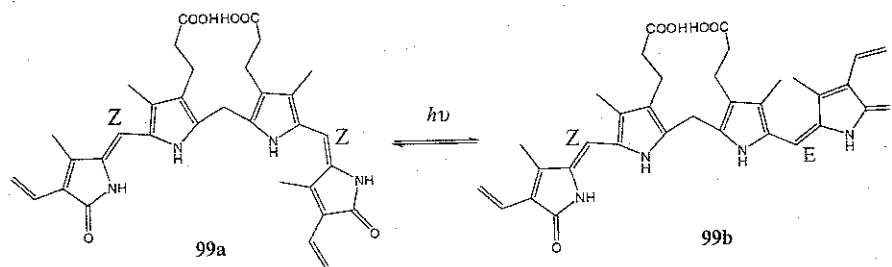*Scheme 1.18*
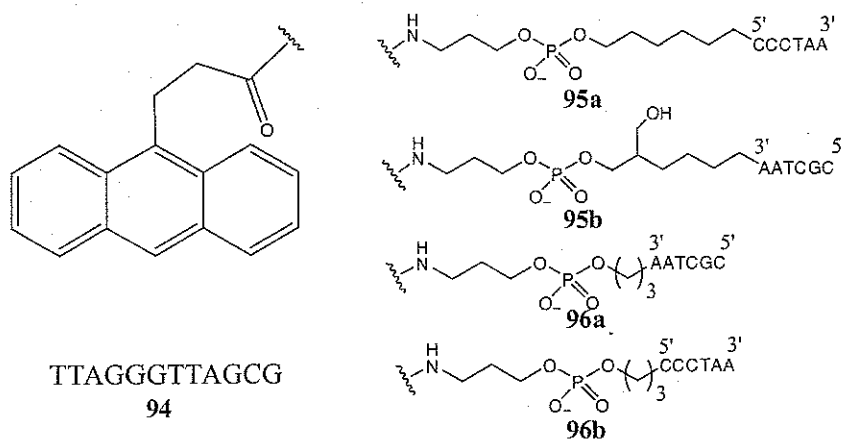
5' CAGTCGTATGCAGGGGGGACGTATGCTGAC 3'
98
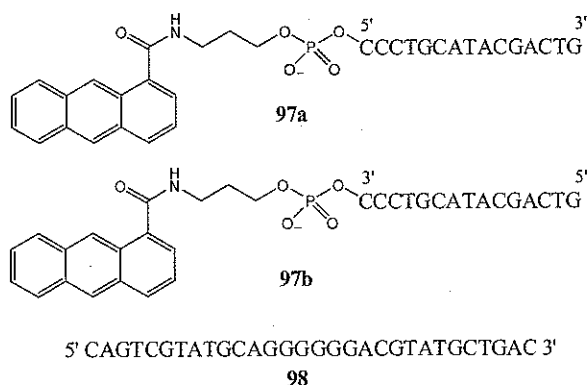
Scheme 1.19

and chiral in nature, they can be used as ideal stereodifferentiating binding sites. Inoue *et al.* performed the enantiodifferentiating photoisomerization of **34Z** (Scheme 1.7) complexed and sensitized by calf thymus DNA (ctDNA).[80] Photosensitized isomerization of **34Z** with pyrimidine nucleosides as chiral sensitizers afforded **34E** in 5.2% ee at the photostationary state. However, much better ee of up to 15.2% was obtained when the photolysis was carried out in the presence of ctDNA in aqueous solution. Supramolecular interaction of **34Z** with hydrophobic minor groove of ctDNA evidently plays an important role in the photochirogenesis, as only negligible ee was obtained for **34E** when the photosensitization was performed in 50% aqueous methanol, in which the supramolecular interaction of **34E** with ctDNA was significantly reduced.

1.3.2 Photochemical Reactions Mediated by Proteins

Proteins, the most abundant and versatile macromolecules in living organisms, are polymers built from about twenty essential L-α-amino acids. Driven by a variety of non-
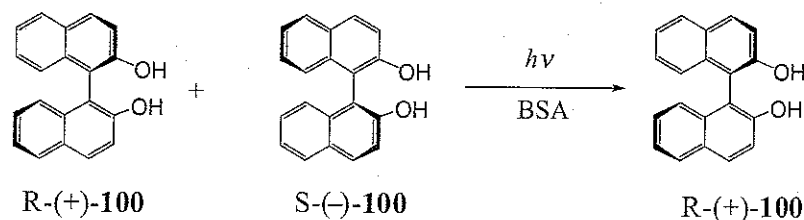
Scheme 1.20

covalent interactions, such as ionic, hydrogen binding, van der Waals and hydrophobic interaction, these biopolymers fold into specific conformations to achieve various biological functions. The binding sites of defined shape and size, as well as the chiral nature, render proteins excellent supramolecular hosts for specific binding and recognition. A series of photochemical reactions have been investigated with various proteins, mainly targeting the photochemical chiral discrimination and generation based on the inherently chiral character of binding sites in protein. Serum albumin is the most abundant protein in plasma which binds and transports not only endogenous but also exogenous compounds, and has therefore been most frequently employed as biosupramolecular host for photochemical reactions.

McDonagh and co-workers investigated the photoisomerization of bilirubin-IIIa **99a,b** (Scheme 1.20) in the presence of human serum albumin (HSA). The *E-Z* photoisomerization between (Z,Z)-**99a** and (E,Z)-**99b** is not inhibited even in the binding cavity of HSA. Bilirubin-IIIa shows intense bisignate circular dichroism spectra in the chiral pocket of HSA.[81,82] The negative exciton coupling signal, which was observed upon irradiation of (Z,Z)-bilirubin-IIIa/HSA complex with a broad-band blue light of $\lambda_{max} = 430\,nm$, was dramatically switched to a positive exciton coupling signal after irradiation with green light at 544 nm.[83] This signal switching, which is controllable by changing the irradiation wavelength, renders the system a potential chiroptical switch.

Zandomeneghi *et al.* reported the enantioselective photoinduced decomposition of 1,1'-binaphthol **100** (Scheme 1.21) included in bovine serum albumin (BSA). Complexation of (R)-(+)- and (S)-(−)-**100** with BSA revealed a remarkable difference in stability between the two diastereomeric complexes, and the BSA complex of (S)-(−)-**100** exhibited a significantly bathochromic shift in the absorption spectrum. By selectively irradiating the (S)-(−)-**100** complex at longer wavelengths, (R)-(+)-**100** of up to 99.5% ee was obtained after 77% of the starting material (racemic **100**) were decomposed.[84–86]

Miranda *et al.* studied the excited-state behavior of chiral drugs bound to BSA and HSA.[87–89] Inclusion of carprofen **101** (Scheme 1.22) in HSA significantly lengthened the triplet-state lifetime of **101** as a result of more rigid surroundings and the suppression of self-quenching of **101**. The complexation of enantiomeric **101** with HSA caused a significant difference in triplet lifetime, and the lifetime of (S)-**101**-HSA complex is 4 times shorter than that of (R)-**101**-HSA complex. Irradiation of **101** alone in aqueous buffer solution led to a polymerization of **101**. However, dechlorinated carprofen **102** was

R-(+)-**100**   S-(–)-**100**   R-(+)-**100**

Scheme 1.21

101   **102**
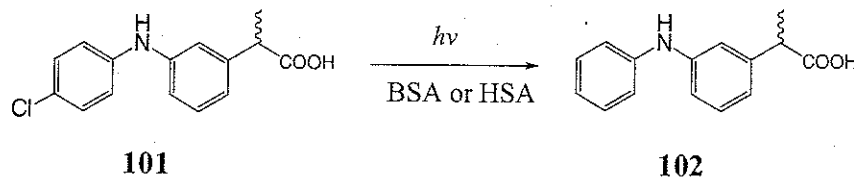
Scheme 1.22

formed in the presence of HSA, and (S)-**101** was 1.5 times more efficient than (R)-**101** in producing the corresponding (S)- and (R)-**102**.

The complexation behavior of organic substrates with proteins is usually very complicated as a consequence of the diversified binding sites with distinctive size, shape, hydrophobicity and binding affinity. Since these binding sites differ in reactivity and selectivity, elucidation of binding behaviour is essential for understanding and manipulating the photoreaction performed in the binding sites of proteins. Inoue and co-workers have comprehensively studied the binding behaviour of 2-anthracenecarboxylate (AC) (Scheme 1.9) to the hydrophobic pockets of BSA and HSA by a combined use of spectroscopic techniques, i.e. UV/Vis, fluorescence and circular dichroism spectroscopy.[90–92] Although HSA and BSA share more than 95% of amino acid residues in common (i.e., 26 out of *ca.* 600 amino acids), the two albumins display entirely different binding, photophysical and photochemical behavior. BSA possesses four binding sites, which accommodate 1, 3, 2 and 3 AC molecules with individual binding constants of $5.3 \times 10^7, 1.3 \times 10^5, 1.4 \times 10^4$ and $3 \times 10^3 M^{-1}$, respectively. In contrast, HSA provides five binding sites that accommodate 1, 1, 3, 5 and >10 AC molecules in the order of reducing binding ability.[93–97] Although multiple AC molecules are bound to sites 2–4 of BSA and sites 3–5 of HSA, they do not appear to be very closely located to each other, since no exciton coupling was seen in the circular dichroism spectrum and no static quenching of fluorescence was detected. AC bound to site 1 of BSA shows highly structured fluorescence with dual lifetimes of 4.8 and 2.1 ns, which are assignable to two kinds of AC that differ in position or orientation in highly hydrophobic environment. However, ACs in site 2 of BSA gave a much longer lifetime of 13.3 ns and the fluorescence spectra became broader; the lifetimes of AC in sites 3 and 4 are practically indistinguishable from that in bulk water (15.9 ns). Almost the same is true for HSA, except for the fact that not only the first but also the second site bind only one AC and are highly hydrophobic.

Each binding site in BSA and HSA exhibits very different photochemical behaviour. Thus, the HT/HH ratio and enantioselectivity obtained in albumin-mediated AC photocyclodimerization are dynamic functions of the AC/BSA or AC/HSA ratio. For example, the HT dimers are produced as the major products in the photodimerization of AC in host-free bulk water and also in the presence of HSA, whereas the HH dimers become the dominant products in the BSA-mediated photodimerization. In the presence of BSA (AC/BSA = 1.3), chiral HT and HH dimers, **44** and **45**, were obtained in 29% and 41% ee, respectively. Interestingly, the ee's for **44** and **45** were further improved up to 38% and 58% by adding nitromethane as a site-selective quencher of AC located in such binding sites that are more accessible but less enantioselective.

In the case of HSA, much higher 79% and 88% ee were reported for **44** and **45**, respectively, at 25 °C and AC/HSA = 3. Temperature was found to have a modest effect on the enantioselectivity to give better ee's of 82% and 90% for **44** and **45**, respectively, by decreasing the temperature to 5 °C.
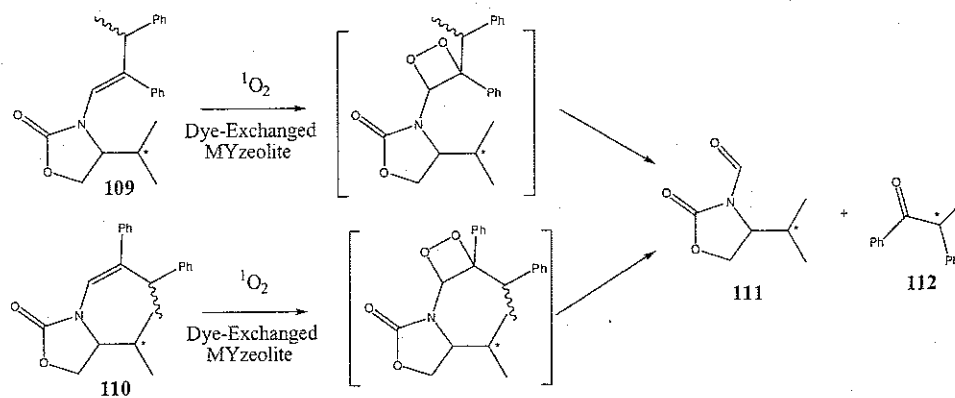
1.4 Photochemical Reactions with Confined Cages Based on Inorganic and Organic–Inorganic Hybrid Materials

1.4.1 Photochemical Reactions with Zeolites

Besides the natural and artificial molecular hosts that are primarily based on organic compounds, photochemical reactions have also been investigated in the confined spaces of inorganic nano- or mesoarchitecture. Zeolites, which are porous crystalline aluminosilicates composed of tetrahedral AlO_4 and SiO_4 building blocks and usually possess cages and channels of 4–14 Å, have been extensively used as hosts for mediating photochemical reactions. The ratio of SiO_4 to AlO_4 can be changed from 1 to infinite, and metal cations are commonly introduced to balance the negative charge of AlO_4 units. The faujasite and pentasil family of zeolites, which form roughly spherical supercages of *ca.* 13 Å and tubular channels with lengths of *ca.* 50 Å, are most commonly used zeolites for catalyzing chemical reactions. Zeolites have a wide UV/Vis transparent region as a result of Al–O–Si framework that is similar to glass and quartz, and therefore are compatible with most organic compounds. The size and free volume zeolite supercages are adjustable by the number and sort of countercations. By virtue of these properties, zeolites have attracted much attention of photochemist as confining media in the last two decades.


a: R_1=H; R_2= CH_3
b: R_1=H; R_2= $(CH_2)_3CH_3$
c: R_1= CH_3; R_2= CH_3
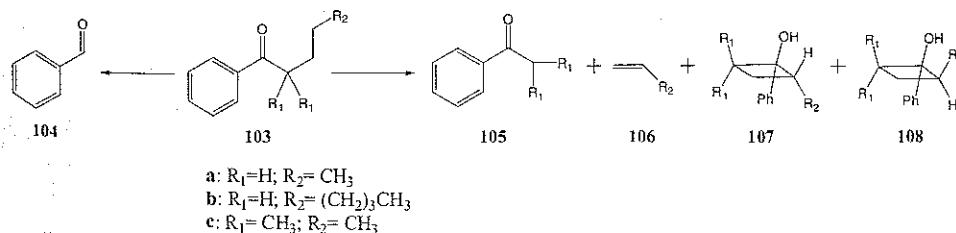
Scheme 1.23

Scheme 1.24

Studies on photochemical reactions within zeolites have already been summarized in several reviews.[98–102] The earliest work in this field appeared in 1980s.[103–106] Turro and co-workers investigated Norrish type I and type II photoreactions of phenyl alkyl ketones **103** in the supercage of faujasite-type zeolites. Photolysis of **103** in solution or solid state was known to give a variety of photoproducts **104–108**, depending on the molecular mobility, conformation and orbital overlap in the excited state. Inclusion of **103** in zeolites can significantly modify the above factors and lead to a switching of reaction selectivity. Photolysis of **103** in supercages of NaY zeolite gave a mixture of products with modest selectivities; **105**/(**107** + **108**) = 0.72–0.83. The ratio was improved to 3.2–3.8 by using NaX zeolite, and was dramatically enhanced up to >50 by using silicalite (S-115) zeolite,[105] suggesting that this photoreaction is highly dependent on the cavity size of zeolite.

Photooxygenation of (*Z*)-enecarbamate **109** (Scheme 1.24) in solution gave methyl deoxybenzoin **112** in only a modest enantioselectivity even at a very low temperature, while a much better optical yield was obtained by starting from the (*E*)-isomer **110**.[107–111] The confinement in zeolite supercage greatly restricts the orientation and conformation of photosubstrate and leads to a significant switching of reaction selectivity from that observed in isotropic media. Thus, singlet oxygenation of (*Z*)-**109** in NaY zeolite loaded with cationic dye sensitizer methylene blue (which is readily introduced into zeolite supercage through cation exchange and generates $^1O_2$ from $^3O_2$ upon irradiation) gave **112** in up to 80% ee. This is possibly due to the restricted space of zeolite supercage that aligns the substrate in an orientation suitable for π-face-selective attack of the C=C bond by $^1O_2$. Compared to the high ee obtained in methylene-blue-exchanged NaY, the same reaction performed in LiY zeolite gave **112** in only 35% ee, for which the larger available volume in the supercage of LiY zeolite is possibly responsible.

Besides the well-confined and rigid framework of zeolites, cation species also plays an important role in manipulating photochemical reaction occurring in the cavity.[112–121] The free volume in zeolite cavity relies on the number and sort of cations located in the cavity. Differing from isotropic media, in which the direction and magnitude of electric field fluctuate around a solvated molecule, cations in zeolite cavity generate a stronger, anisotropic and more stable electric field. Such an electric field can polarize the included
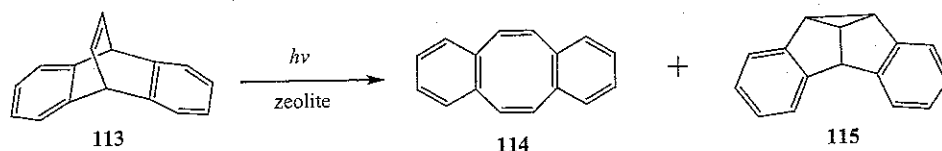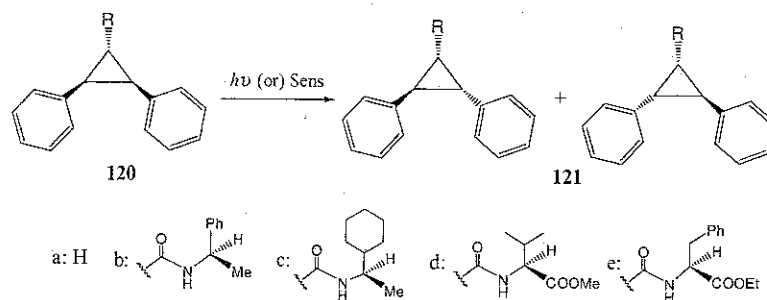
Scheme 1.25
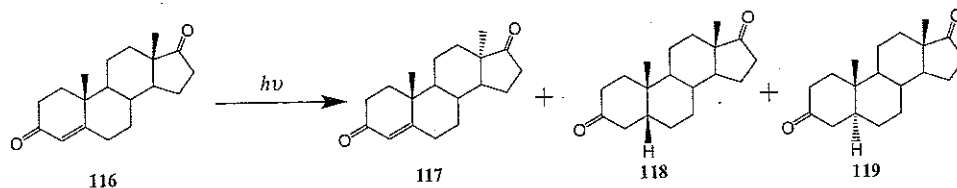
Scheme 1.26

molecules, distort their electron density, and even facilitate heterolytic bond cleavage. Indeed, it has been observed that the intensity and wavelength of absorption and emission of included aromatic compounds were significantly changed in the cavity of zeolite.[122–125] Ramamurthy *et al.* reported that photoreaction of dibenzobarrelene **113** (Scheme 1.25) in Li⁺ and Na⁺ exchanged zeolites resulted in triplet photoproduct **115** in 67% and 62% yield, respectively. This observation indicates that the intersystem crossing is significantly accelerated even by light atoms. However, this effect disappeared when the zeolites were equilibrated with water before use. The electric field of the cations in the cavity, which perturbs the symmetric nature of photosubstrate and facilitates the intersystem crossing, may be responsible for this 'light atom' effect. On the other hand, the heavy atom effect is clearly seen even for hydrated cations, and >99% triplet photoproduct was observed with Tl⁺-incorporated zeolite.[126–129]

Photoreactivity of androstenedione **116** (Scheme 1.26) was demonstrated to be dramatically affected by the electric field of zeolite.[130] The epimerization of **116** to yield **117** is the major reaction in isotropic solution such as hexane, methylene chloride, methanol and cyclohexane. The reduction of the cyclohexenone A-ring can be observed in only propanol, with **118** and **119** being given in 14% combined yield. However, irradiation of **116** in NaY afforded exclusively the reduction products in >85% yield, and no product due to the reaction at the D-ring was observed. This reactivity change observed for the androstenedione included in zeolite cavity was ascribed to the lowering of the π,π^* excited state of the A-ring due to the electric field in zeolite cavity.

Interactions between cation and photosubstrate, such as cation–π, cation–dipole and cation–lone pair interactions, may restrict the mobility and conformation of photosubstrate, and therefore endow the cation with versatile roles in manipulating the reactivity and selectivity of photoreaction in zeolite cavity.[131–142] Ramamurthy and co-workers have studied stereoselective photoisomerization of diphenylcyclopropane derivatives in zeolite supercage. It was found that the photoisomerization of *trans*-diphenylcyclopropane **121a** occurred in the cavity of alkali cation-exchanged Y zeolite to give *cis*-**120a** in high
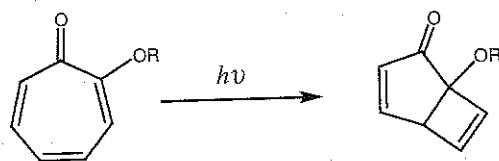
Scheme 1.27

efficiency, while the photolysis of *cis*-**120a** failed to give any *trans*-isomer.[134] This is ascribed to the formation of cation–π complex in which two phenyl groups of *cis*-**121a** sandwich an alkali metal ion. The *cis*-isomer is thus stabilized and the isomerization reaction is inhibited.

However, *trans*-isomers can be given upon photoirradiation of zeolite-mediated *cis*-diphenylcyclopropane derivatives **120b–e** due to the stronger cation–dipole interaction between cation and carboxamide group than cation–π interaction. Photolysis of amide **120b–e** in hexane-methylene chloride solution afforded the corresponding *trans*-isomers in diastereomeric excess (de) less than 2%. In sharp contrast to the result obtained in isotropic solution, photoreaction of **120b–e** adsorbed in zeolite MY gave *trans*-isomers in 20–83% de. The dramatic improvement of de is believed to occur as a result of cation–carbonyl and cation–nitrogen dipolar interactions that fix the conformation of reactants, with asymmetric centres of the chiral amide moiety being located closer to the chirogenic center.[114,132,134,138,143]

Chiral photochemistry in zeolite is an intriguing topic that has attracted intensive attention. Although theoretically zeolites can be chiral, until now no chiral zeolite has been separated in an enantiomerically pure form. Chiral photochemistry in zeolite is conducted primarily through two strategies: the first one is to introduce a chiral auxiliary to photosubstrate and the diastereodifferentiating photoreaction is conducted in intact zeolite, as exemplified in the diastereoselective photoisomerization of diphenylcyclopropane derivatives mentioned above, and the second one is to immobilize optically active compound to chirally modify the zeolite supercage and the enantiodifferentiating photoreaction of prochiral substrate is conducted in this chiral supercage.

Zeolites modified with norephedrine, ephedrine and pseudoephedrine as chiral inductors have been employed for the enantioselective photocyclization of a series of tropolone derivatives **122**.[113,144,145] Photocyclization of **122b** conducted in NaY zeolite modified with (–)-ephedrine gave **123b** in up to 78% ee. The enantioselectivity of the photoreaction was found to be critically controlled by the cationic species and water content in zeolites.

The optical yield of photoreaction in chirally modified zeolite relies on several factors such as cation, chiral inductor and its loading level, which is usually kept at a high level to maximize the number of chiral inductors located around the photosubstrate. An exceptional example may be found in the enantiodifferentiating photoisomerization of **34Z** (Scheme 1.7) sensitized by optically active (poly)alkyl benzoate derivatives immobilized

122

a. R = CH$_3$
b. R = CH$_2$CH$_2$Ph
c. R = CH$_2$COOCH$_3$
d. R = CH$_2$CH$_3$

123

e. R = CH$_2$CH$_2$CH$_3$
f. R = CH$_2$Ph
g. R = CH$_2$CH$_2$CH$_2$Ph

Scheme 1.28

in NaY zeolite reported by Inoue and co-workers.[146] The photoreaction was allowed to occur in the presence of a catalytic amount of sensitizer, and **34E** was obtained in a modest ee of 4.5% upon photosensitization with (–)-methylheptyl benzoate-immobilized NaY zeolite. In contrast, the same sensitizer gave racemic **34E** in homogenous solution.

1.4.2 Photochemical Reactions in Mesoporous Materials

Mesoporous materials have recently attracted considerable attention for the use in photochemical reactions. As defined by the IUPAC nomenclature rules, mesoporous materials have a pore diameter in the range of 2.0–50.0 nm, which is much larger in general than that of zeolite and is certainly beyond the size of normal organic substrates. Therefore, photoreactions can freely proceed without suffering any restriction. In fact, studies on photochemical reaction in mesoporous materials focus more on construction of functional materials rather than the chemical selectivity. For example, azobenzene, which is structurally rigid and has a van der Waals volume of 144 Å^3,[147] requires a large extra volume of 127 Å^3 for the photoisomerization to occur. Taking advantage of this property, azobenzene was loaded into nanocomposite films to be used for and showed a potential application in adjusting the cavity volume of mesoporous materials.[148] Mal *et al.* constructed a photochemically controlled system by anchoring coumarin to the pore openings of MCM-41 for taking up or releasing organic guests by controlling the reversible photodimerization of coumarin.[149]

The size of mesoporous silica MCM-41 can be adjusted by changing the number of carbon atoms in surfactant micelles used in the hydrothermal synthesis. Iwamoto and co-workers have reported photocyclization of diarylethenes **124** in different-sized MCM-41. Only the anti-parallel conformation of open form **124** can undergo cyclization upon irradiation to give closed form **125**. The reaction rate of **124** was found to be remarkably dependent on the amount of **124** loaded as well as the pore diameter of MCM-41s, but be independent of the organic groups on the surface of MCM-41s.[150]

Recently, Inoue and co-workers studied the enantiodifferentiating photocyclodimerization of AC in the channel of mesoporous silica that is modified with γ-CD.[151] Photocyclodimerization of AC with mesoporous without γ-CD gave HH photodimers
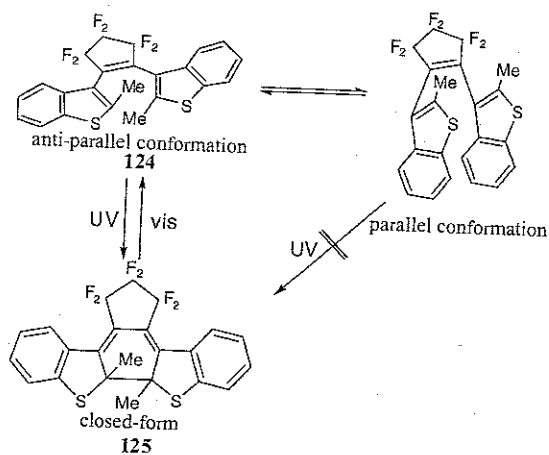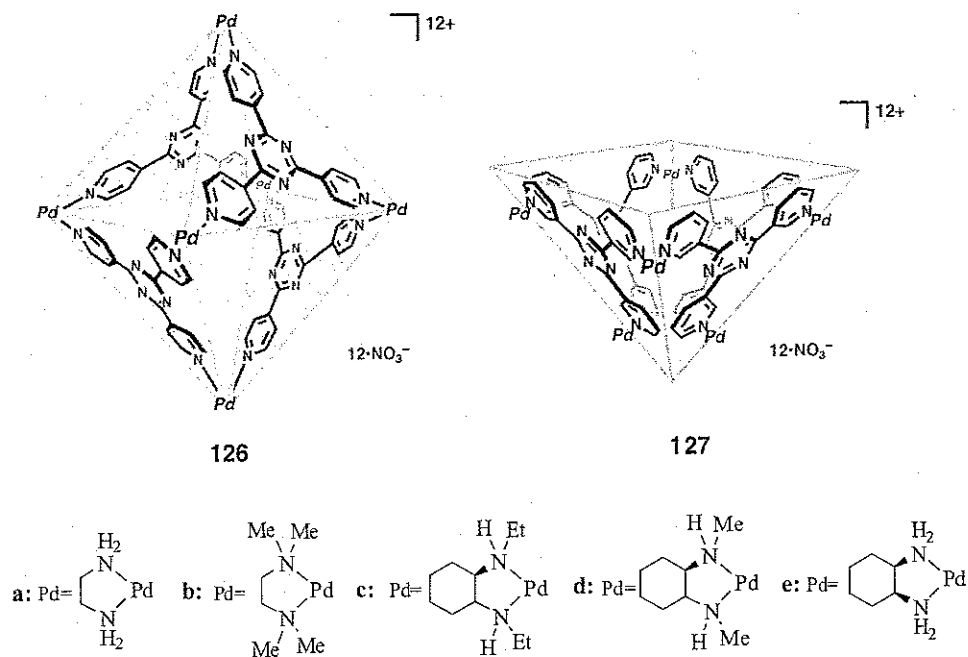
Scheme 1.29

with a low conversion and enantioselectivity. In remarkable contrast to the γ-CD-mediated photoreaction performed in aqueous solution, the photocyclodimerization of AC in γ-CD-modified mesoporous silica led to the major formation of HH photodimers, in particular *anti*-HH dimer **45** in 45% yield and 24.1% ee.
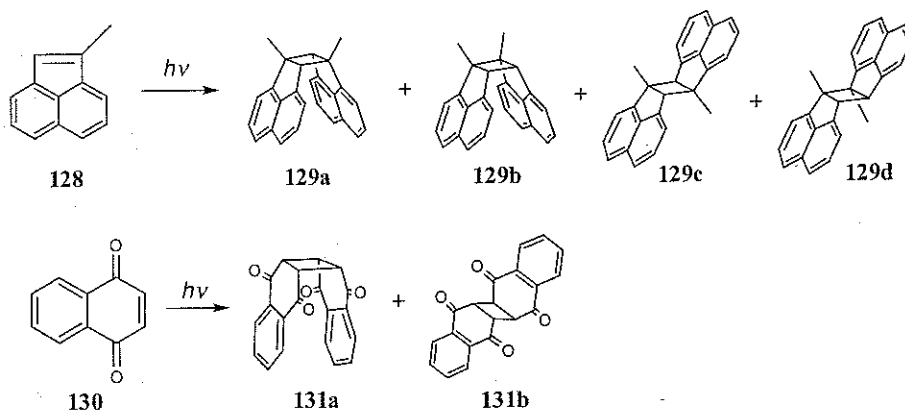
1.4.3 Photochemical Reaction with Self-Assembled Molecular Cages

Organic ligands bearing two or more coordinating sites can form well-structured aggregates upon coordination to metals. Some of these ligand–metal self-assemblies form structurally well-confined cavity that can accommodate organic guests of suitable size. These cages generally have polyhedron structure with rigid skeleton, and the motion of guest(s) included in the cavity is greatly inhibited. Thermal and photochemical reactions conducted in these molecular cages often show remarkably accelerated rates and significantly high selectivities.[152,153]

Compounds **126** and **127** shown in Scheme 1.30 represent two typical coordination cages that are self-assembled from six palladium ions and four tridentate ligands. These coordination cages are well soluble in water and can selectively encapsulate organic substrates in the nano-sized cavity in a well-arranged fashion, mainly through hydrophobic and aromatic interactions. So far, a number of different types of photoreactions have been examined within the cavities of these molecular cages.[154–160] As shown in Scheme 1.31, four stereoisomers **129a-d** are theoretically possible to be formed upon photocyclodimerization of **128**. Strikingly, photocyclodimerization of 0.5 mM **128** in the cavity of **126a** gave the HT *syn*-isomer **129a** as a sole product in >98% yield after 3 h irradiation. On the contrary, photoirradiation of **128** in benzene in the absence of host **126a** gave no adducts even at a high concentration of 150 mM. In the presence of **127a** as a host, photocyclodimerization of **130** in aqueous solution exclusively afforded *syn*-dimer **131a**. This is in sharp contrast to the same photoreaction conducted in benzene without any host, where *anti*-dimer **131b** (21% yield) was favored over *syn*-dimer **131a** (2% yield).

126   **127**

Scheme 1.30

128 $\xrightarrow{h\nu}$ **129a**   +   **129b**   +   **129c**   +   **129d**

130 $\xrightarrow{h\nu}$ **131a**   +   **131b**

Scheme 1.31

The remarkable reactivity and selectivity observed with these molecular vessels are attributed to the greatly increased concentration and the strictly regulated orientation of substrates in the well-confined cavity.

The cavity of molecular cage **126a** is achiral in origin. Interestingly, a chiral cavity can be constructed simply by replacing the peripheral ethylenediamine with optically active diamines, with the original electronic nature, size and T symmetry element being

132   133   134

a: R= H
b: R=CH₃
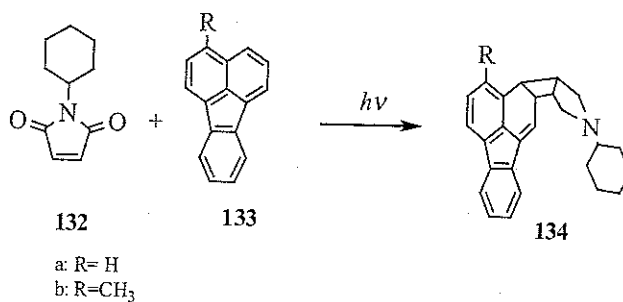
Scheme 1.32

maintained on the whole. Cross addition of **132** and **133** (Scheme 1.32) in the cavity of **126b–e** (Scheme 1.30) gave a single product **134**, which is ascribed to steric control arising from the confined cavity rather than orbital control.[158] The optical yields of this photoaddition reaction increased upon increasing the steric bulk of the *N*-substituent on the chiral diamine and finally gave **134b** in 50% ee with **126c**. This observation is indicative that peripheral chiral auxiliaries, which locate far away from the reaction center and induce only a slight deformation of the triazine panel, are possible to produce considerable asymmetric induction for the photoreaction occurring in the coordinated cages.

1.5   Photochemical Reactions with other Artificial Hosts

1.5.1   Photochemical Reactions with Dendrimers

Dendrimers are highly branched globular molecules which are generally well-defined, effectively monodispersed and highly symmetric.[161–163] A dendrimer is composed of three architectural region: a core moiety, branched repeating units derived from the core and end groups on the periphery of the molecule. Properly designed high-generation dendrimers possess a distinct interior space that is sterically protected from solvent molecules, and therefore dendrimers can serve as container molecules. An elegant 'dendritic box' that can accommodate small organic molecules and control their release by modifying the steric crowding of the dendritic periphery has been described by Meijer *et al.*[164]

Poly(alky aryl ether) dendrimers **135** (Scheme 1.33), possessing carboxylic acid or hydroxyl group at their periphery, were synthesized and used as hosts for several photoreactions.[165] Both **135a** and **135b** are water soluble under the base condition and capable of including organic molecules mainly through hydrophobic interaction. Photolysis of 1-phenyl-3-*p*-tolyl-2-propanone **136** led to α-cleavage to form radical pairs, which after decarbonylation recombine to give diarylethanes **137a**, **137b** and **137c**. The photolysis of **136** in hexane solution gave the product **137a**, **137b** and **137c** in a ratio 2.4 : 1.0 : 1.4, indicating a zero 'cage effect,' where the 'cage effect' was defined as ([**137a**]–[**137b**]–[**137c**])/([**137a**] + [**137b**] + [**137c**]). Interestingly, photoreaction of **136** mediated by G1, G2 and G3 acid dendrimers **135b** showed the gradually increasing cage effects of 0.09, 0.18 and 0.50, respectively, suggesting stronger confinement with increasing dendrimer
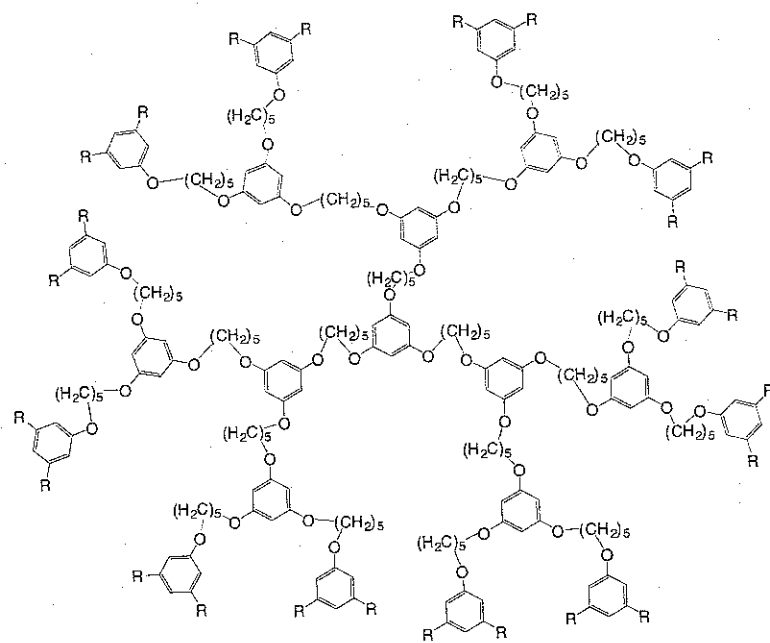
135a: R=OH, b: R=COOH
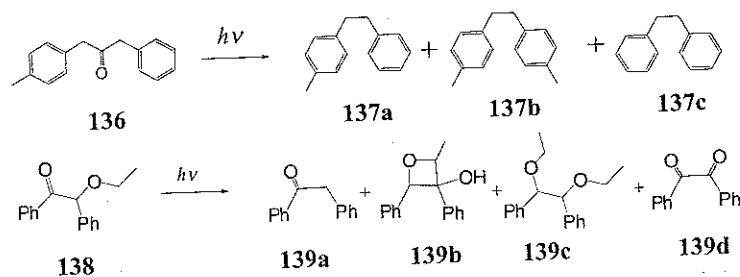
Scheme 1.33

generation. Photolyses of **136** encapsulated by G3 of **135a** gave a larger cage effect of 0.77, revealing that the phenolic dendrimer **135a** is more strongly confining than the acid dendrimer **135b**.

Photolysis of benzoin ethyl ether **138** was demonstrated to be sensitive to the reaction media employed. It affords Norrish type I products **139c** and **139d** in more than 94% combined yield in hexane but type II products **139a** and **139b** in 73% yield in aqueous alkaline solution. Photoreaction of **138** with dendrimer **135b** predominantly gave the type II products, particularly **139a** in 95% yield. However, when the photoreaction was mediated by **135a**, **139a** and **139b** were produced in 21% and 57% yield, respectively, suggesting that the end group plays an important role in dictating the interior character of the dendrimers.

## 1.5.2 Photochemical Reactions with Hydrogen-Bonding Templates

Hydrogen bonding interaction plays vital roles in regulating biochemical processes of proteins and deoxyribonucleic acids, and has been widely utilized for constructing supramolecular architectures. This is due to the largest interaction energy $(5-30 \text{ kJ mol}^{-1})$ among the non-covalent weak interactions as well as the ability to assemble molecules at right distance and angle. As a result of these advantages, a series of photochemical reactions have been investigated using hydrogen-bonding templates.

Bassani and co-workers investigated the complexation behavior of melamine and barbituric acid derivatives, and examined the photodimerization of styrene, stilbene and cinnamate mediated by hydrogen bonding templates.[166–170] Melamine derivatives **140** (Scheme 1.34), which have a hydrogen-bonding motif complementary to barbituric acid derivatives such as **141**, are possible to sequentially form 1:1 and 1:2 hydrogen-bonded complexes with **141**. As illustrated in Scheme 1.35, **140** and **141** can form two kinds of 1:1 complexes and three kinds of 1:2 complexes, among which only complex C is expected to accelerate the photodimerization of **140**. Each of the binding constants K_1 and K_2 should be a sum of these binding constants weighted by their population. A positive cooperativity $(K_2 > K_1)$ was observed upon complexation of **141b** with **140a,b**, presumably as a combined result of allosteric and electronic effects. Photoirradiation of **140** without any template led to a fast *E-to-Z* isomerization to give the *Z/E* ratio of 1.1–5.5 at the photostationary state, although elongated irradiations resulted in a formation of dimers. The existence of barbiturate **141** considerably improved the efficiency and selectivity of the photoreaction. The quantum yields of **142a** and **142b** were increased respectively from 0.7×10^{-3} and 0.1×10^{-3} in the absence of a template to 2.3×10^{-3} and 0.8×10^{-3} in the presence of **141a**.[170] The same strategy was applied to a barbituric acid derivative of fullerene to give a photodimer of fullerene, which could not been obtained without the hydrogen-bonding template.[169]

Bach and co-workers investigated a series of chiral photoreactions that were mediated by Kamp's triacid derivatives **143** working as chiral hydrogen-bonding templates.[171–177] As illustrated in Scheme 1.37, these chiral templates possess an amide (lactam) group to bind an amide substrate through dual hydrogen bonds and also a bulky substituent to shield one of the enantiofaces of substrate when bound to the template. Although these
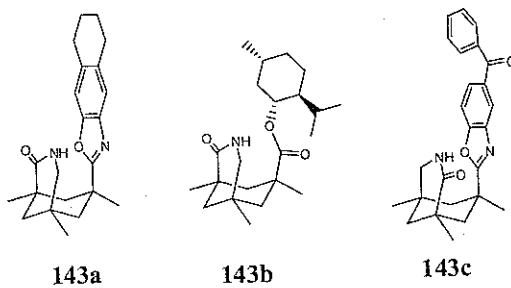

a: R= Me, X=H
140a-c b: R= Me, X=CO₂Me
c: R= Pri, X=C₆H₅

140d

141 a: n=2
b: n=6
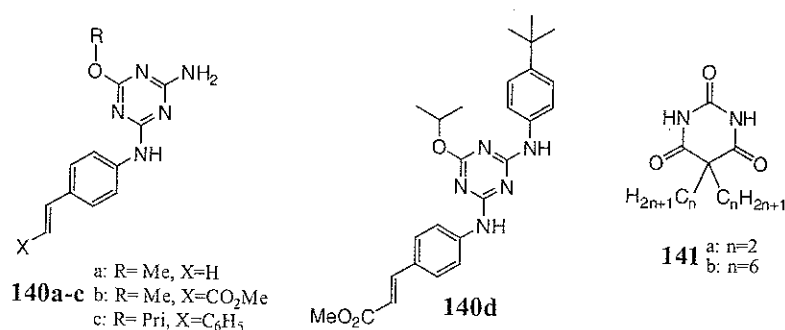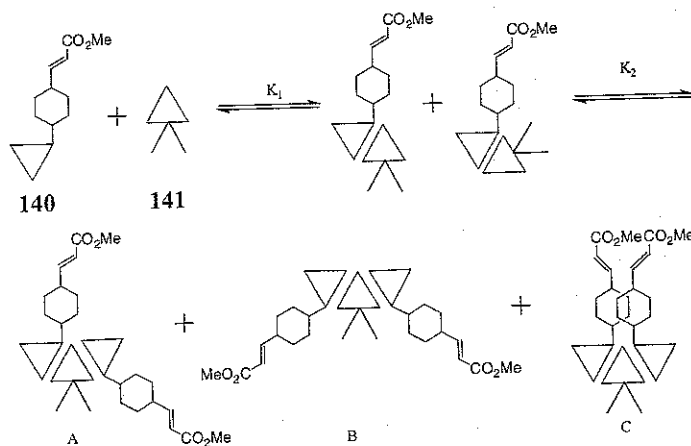
Scheme 1.34
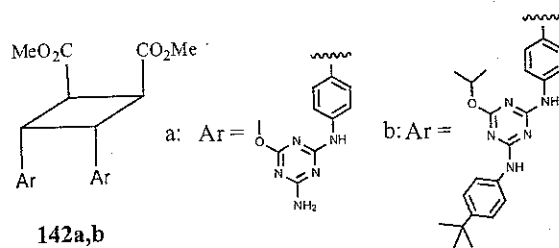
Scheme 1.35

Scheme 1.36

Scheme 1.37

templates can form hydrogen-bonded homodimers, the association constants are low in general due to the steric repulsion between the bulky moieties.

The intramolecular photocycloaddition of prochiral 2-quinolone **144** (Scheme 1.38) was examined in the presence of chiral templates **143a,b**.[178] The amide group of chiral templates forms dual hydrogen bonds with the quinolone moiety of **144**, with the bulky tetrahydronaphthalene moiety preventing the approach of olefinic double bond from the

144 **145**

Scheme 1.38

146 + **147**
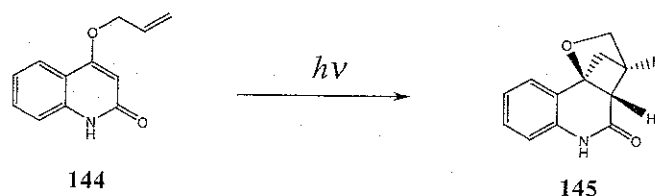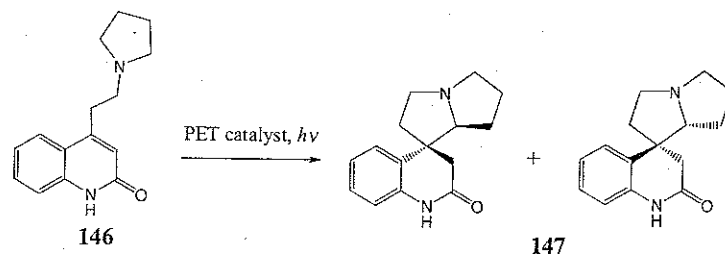
Scheme 1.39

facing side. Increasing the amount of chiral template or lowering the reaction temperature, by which the ratio of bound photosubstrate is greatly increased, significantly improved the enantioselectivity in the photocycloaddition of **144**. By performing the photoreaction in the presence of **143b** at −60 °C, **145** was given in up to 93% ee. In contrast, the same reaction sensitized by a chiral sensitizer lacking the hydrogen-bonding site gave only racemic photoproducts.[179]

Since photoexcitation of free substrate existing in the bulk solution will give racemic photoproducts, at least an equimolar amount of chiral template is necessary in order to obtain photoproduct with good enantioselectivity. A recent report by Bach *et al.* presented a good solution for this shortcoming by covalently grafting a sensitizer to a chiral template. Thus, sensitizing template **143c** (Scheme 1.37) bearing a photoinduced electron transfer sensitizer was synthesized for the use in photosensitized cycloaddition of **146**. Photolysis of **146** in the presence of 0.1 equivalent amount of **143c** afforded **147** in 52-64% yield with up to 70% ee (Scheme 1.39).[180]

1.5.3 Photochemical Reactions Templated by Cationic Ion

Metal ion can form complex through coordination with unsaturated compounds such as olefin. Through coordination with metal ion, two olefins can be positioned in close proximity, and olefin photochemistry may be caused upon irradiation at longer wavelengths by exciting the charge-transfer band of the resultant complex. Evers and Mackor investigated the intramolecular [2+2] photocycloaddition of diene **148**, which is photochemically catalyzed by copper(I) trifluoromethanesulphonate.[181] In the presence of the copper
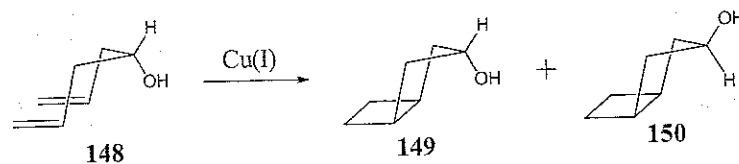
Scheme 1.40
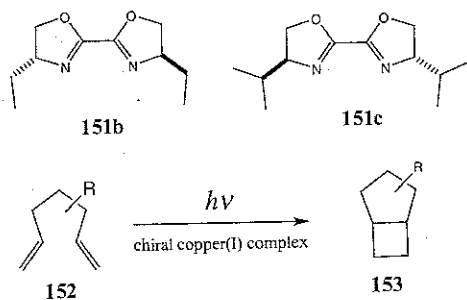
Scheme 1.41
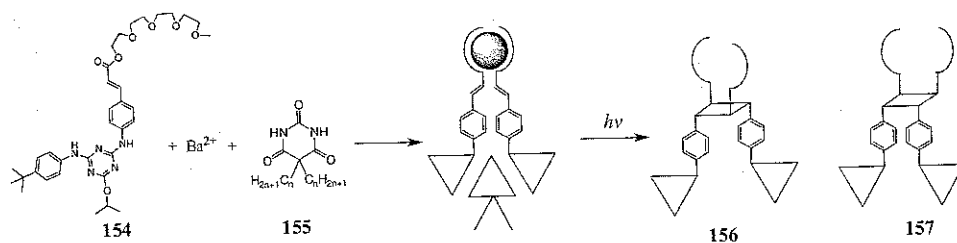
Scheme 1.42

catalyst, irradiation of **148** efficiently gave the *exo-* and *endo-*3-bicyclo[3.2.0]heptanol **149** and **150** in a ratio of 3:2 (Scheme 1.40).

Mattay *et al.* examined the intramolecular [2+2] photocycloadditions of 1,6-dienes **152** catalyzed by copper(I) coordinated to chiral ligands **151** (Scheme 1.41).[182] Photocycloaddition of **152** catalyzed by **151c** gave **153** in up to 5% ee.

Bassani and co-workers studied the photodimerization of **154** using a synergistic effect of hydrogen bonding and metal ion complexation.[183] Photodimerization of **154** was accelerated by a factor of 2 in the presence of one equivalent of KPF_6, and a factor of 5 in the coexistence of KPF_6 and **155**. Among the metal ions examined, Ba^{2+} showed the most significant cooperative effect. While **155** enhanced the photodimerization by a factor of 1.4–1.8, a simultaneous use of **155** and Ba^{2+} gave the quantum yield for the formation of **156** and **157** in more than three orders of magnitude greater than that obtained in the absence of template, and the ratio of **156/157** was greatly improved from 1 to 3.7.

1.6   Photoreaction Control by External Variants

While most studies on supramolecular photochemistry have focused on the design and synthesis of suitable hosts that provide desirable interaction or environment for aimed photosubstrates, recent studies by Inoue *et al.* suggest that the external factors, such as temperature, solvent and pressure, may also play a crucial role in controlling the reactivity and selectivity of photoreactions in supramolecular systems. Changing environmental variants, which is much easier to practice than the optimization of host structure involving tedious syntheses, can provide not only a convenient, yet useful, tool for controlling photochemical outcomes, but also important information regarding the mechanism of supramolecular photochemical reaction.

The effect of temperature has been well established in the photosensitized isomerization of cycloalkenes with conventional sensitizers.[184–187] The change of optical yield upon temperature variation is ascribed to the non-zero differential entropy change for the formation of enantiomeric photoproducts. The entropy effect on supramolecular photochirogenesis systems was found to be closely related to the structural properties of supramolecular hosts. The enantioselectivity shows only small changes with the variation of temperature in photoisomerization of **34Z** sensitized by β-CD-based chromophores.[37] This insignificant effect of temperature is attributed to the low entropy environment in the cavity of β-CD due to its rigid skeleton arising from the hydrogen-bonding network at the secondary rim.

On the contrary, photoisomerization of **158ZZ** with sensitizer-appended γ-CD, which has a more flexible framework than γ-CD, is more sensitive to the temperature alternation. An inversion of product chirality was observed by lowering the temperature in the photoisomerization of **158ZZ** mediated by **159**.[188] Similar phenomenon was observed in photocyclodimerization of AC (Scheme 1.9) included in the cavity of γ-CD derivatives.[189] The enantioselectivity for HH dimer in the photocyclodimerization of AC with diamino- γ -CDs **48** in aqueous methanol solution decreased greatly by lowering the reaction temperature and even showed a dramatic inversion to give the antipodal product. When γ-CD derivatives **50a–d** with flexible caps were used, the ee values obtained for **44** were highly dependent on the temperature. However, in the presence of γ-CD derivatives **57a–c**, which possess a rigid aryldisulfonate cap, the enantiodifferentiation become much less temperature-dependent.[52] On the other hand, when photoisomerization of **34Z** was carried out


158ZZ   R-(–)-**158EZ**   S-(+)-**158EZ**   **159**
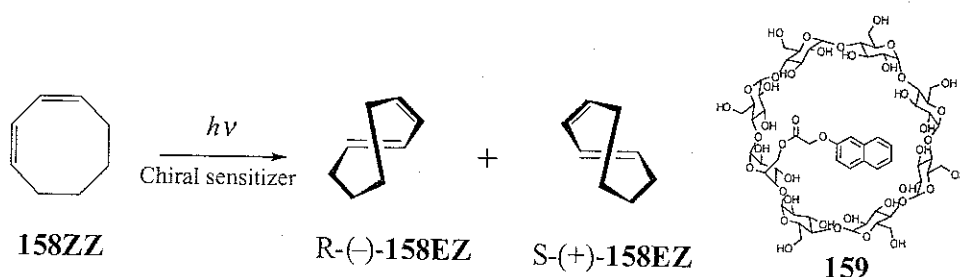
Scheme 1.43

with permethylated β-CD sensitizers **35e–h**, in which the hydrogen bonding network is broken by methylation to give a flexible skeleton, the temperature effect became pronounced to afford a chirality inversion by changing the temperature.

These observations suggest that the entropy effect is a function of the flexibility/rigidity of the skeleton of supramolecular hosts, and is significant for hosts with flexible framework but is insignificant with rigid hosts. Indeed, works of the other research groups have also demonstrated that hosts bearing rigid skeleton such as zeolite show only slight temperature-dependence.

Solvation and desolvation are of paramount importance for molecular recognition in solution. Solvent influences the binding strength of host–guest equilibrium in a diverse way for various host–guest systems. For example, the complexation strength between 18-crown-6 and potassium ion decreases by a factor of $>10^4$ on going from propylene carbonate to water.[190] This significant solvent dependence mainly comes from the difference in desolvation energy of the metal cation in different solvent. In some cases, solvent may play a role of filler upon co-inclusion with the guest substrate to significantly modify the orientation of substrate in the host cavity. It is known that CD bind organic guests mainly through hydrophobic interactions, and addition of methanol to the aqueous solution greatly reduces the binding constant as a result of increased solvation to both of substrate and host. The plot of log Ks for the complexation of **35** and **34Z** against the methanol content showed good straight lines, suggesting that no selective solvation by water or methanol to CD derivatives occurs and water–methanol mixture behaves as a bulk solvent of continuously changing hydrophilicity. The enantioselectivity in photoisomerization of **34Z** with **35** decreases with increasing content of methanol, and appears to be a nice function of host occupancy. On the other hand, addition of methanol decreases the solvent polarity and thus increases the electrostatic interaction of ion pairs. In aqueous solution, the photodimerization of AC mediated by **48a–d** shows only subtle effect of the ammonium cations introduced to the primary rim of γ-CD, but the electrostatic interaction dominates the photodimerization to give the chiral HH dimer as the major product with a greatly enhanced enantioselectivity.

Hydrostatic pressure is also known to play crucial roles in conventional chiral photosensitization of **34Z**, as demonstrated by the fact that product chirality can be manipulated or even inverted by simply changing the pressure when the differential activation volume for the formation of the enantiomeric or diastereomeric pair is not equal to zero. Under high pressure, less volume-demanding structures and processes are absolutely favoured and hence the host-guest association process is advantageous in principle. If there are two or more possible complex structures in a supramolecular system, dramatic equilibrium and selectivity shifts may occur from a shallow, loose and/or bulky complex to a deeper, tighter and compact ones under high pressure. In other words, we acquire an additional tool, that is pressure as an environmental variant, for manipulating the recognition ability and selectivity of a given guest. Another somewhat unexpected great advantage of high pressure applied to supramolecular systems performed in aqueous solutions is the significant lowering of the melting temperature of water, which goes down to $-25\,°C$ at 210 MPa, which enables us to perform photochemical reactions below zero Celsius even in water. Thus, the chemical yield and ee of HT dimer **44** were greatly enhanced in the photocyclodimerization of AC mediated by γ-CD derivatives to reach 53% yield and 71% ee by using host **54** in water at $-22\,°C$ at 210 MPa.

160a   160b
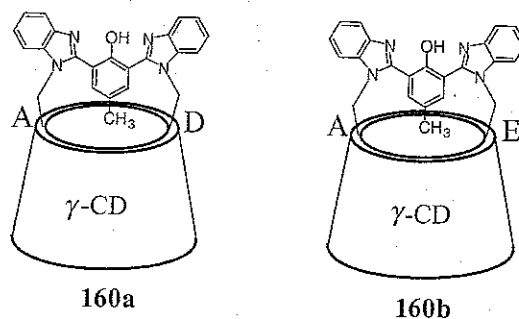
Scheme 1.44

More recently, the effect of pH was investigated in the supramolecular photochirogenic dimerization of AC with *p*-cresolbisbenzimidazole-capped γ-CDs **160a,b**.[191] Thus, photodimerization of AC with AE-capped γ-CD **160b** gave *anti*-HH dimer in 5% ee at pH 11 but the antipodal product in 28% ee at pH 6. The conformational change of the ionizable capping moiety upon the pH variation is responsible for the pH-dependent enantioselectivity.

1.7   Conclusions

Controlling photochemistry through molecular recognition has drawn significant interest from a broad spectrum of scientists and met great progress in recent decades. A number of supramolecular hosts have been successfully exploited for conducting various types of photochemical reactions to reveal the distinct advantages and disadvantages peculiar to each supramolecular system. The multiple non-covalent interactions and the confinement effect operating in host cavity are two major factors that control the supramolecular photochemistry. Successful supramolecular photoreaction requires reasonable design and synthesis of host molecules and a careful selection of suitable photoreaction and substrate. The complementary fitting of size, shape and interaction motif between host and guest substrate are crucially important in choosing a host–guest pair for specific supramolecular photochemistry. In general, supramolecular hosts that have more confined binding sites usually show specific complexation ability and significant reaction selectivity, while those with flexible binding sites are susceptive to the external control by environmental factors.

The supramolecular approach to photochemistry is undoubted a smart efficient way to manipulate and enhance its reactivity and selectivity. In addition to the electronic and orbital properties governing the conventional photoreactions in isotropic media, the steric and conformational effects play heavier roles in supramolecular photochemistry. As a result, photoreactions in supramolecular systems often show unique behavior distinctively different from that of conventional one. On the other hand, the confinement effect of supramolecular hosts can hold two or more photosubstrates in close proximity and consequentially promote bi- and multimolecular photoreactions that are silent in conventional photochemistry under normal conditions.

Despite that supramolecular complexation can crucially affect the steric and/or electronic properties of photosubstrates in both ground and excited state, the stereochemical control of photochemical reaction in supramolecular systems is often considered to be dominated by the prearrangement of photosubstrate in the ground state. A photosubstrate is captured by a host for a period of time that is much longer than the excited-state lifetime. It has been demonstrated that the rate constant for a photosubstrate to get into the cavity of host with a sufficiently large opening is normally in the order 10^{-7}–$10^{-8}\,M^{-1}\,S^{-1}$.[192] An organic guest may stay in the cavity for much longer than $1\,\mu s$ if it has a binding constant of $1000\,M^{-1}$ with the host, which is significantly longer than the lifetime of excited molecules commonly encountered. Therefore, the complexation behaviour of photosubstrate in the ground state is of significant importance in supramolecular photochemistry.

Optimizing the structure and interactions of a supramolecular system still requires sophisticated design, synthesis, and experimental feedback even in the ground state, and should be much more difficult for supramolecular photochemical reactions. In this context, the combined use of external factors, such as temperature, solvent and pressure, provides a versatile and convenient tool for manipulating photochemical reactions in supramolecular system. The role of these external factors is closely correlated with the properties, in particular rigidity, of supramolecular host employed, and the outcomes are often significantly different from those observed in conventional photoreactions, which would be another reason for performing photochemical reaction in supramolecular system.

The number and quality of publications on supramolecular photochirogenesis are rapidly growing in the last decade. Laying in the interdisciplinary area of supramolecular chemistry, photochemistry and asymmetric synthesis, this new area of science is still challenging but appears promising, proposing a novel concept and methodology for overcoming the relatively weak and short-lived interactions in the excited state through multiple supramolecular interactions in both ground and excited states. Indeed, the highest enantioselectivity in solution-phase photoreaction has been achieved by supramolecular photochirogenesis.[193]

In summary, the control of photochemical reactions by molecular recognition becomes one of the most active topics in supramolecular chemistry in recent years. However, supramolecular photochemistry is still conceptually less established, mechanistically less understood, and experimentally less explored compared to the conventional supramolecular chemistry in the ground state. We believe that further comprehensive studies in this area will reveal more intriguing features of supramolecular photochemistry and strength our capability to control photochemical reactions.

Acknowledgements

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