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Supramolecular methods for controlling intermolecular [2 + 2] photocycloaddition reactions of unsaturated compounds in solutions

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This review deals with the methods of supramolecular chemistry used for controlling the efficiency and stereoselectivity of intermolecular [2 + 2] photocycloaddition of olefins and other unsaturated compounds in homogeneous solutions. The best-studied methods are self-assembly through cation – macrocycle interactions, complexation with molecular templates through hydrogen bonding, and confinement of the reactants in supramolecular containers. The possibilities of using anionic templates and combined supramolecular approaches are discussed.
The bibliography includes 107 references.

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I. Introduction

The objects of investigation in supramolecular photochemistry are organic and metal-organic systems self-organizing through noncovalent interactions and containing light-absorbing components (chromophores). Noncovalent interactions and specific spatial organization of the components in supramolecular systems can have a significant impact on the photochemical reactions involving chromophores, such as excitation energy migration, electron transfer, and photoisomerization.[1] An example of supramolecular control of photochemical processes in nature are light-dependent reactions of photosynthesis.

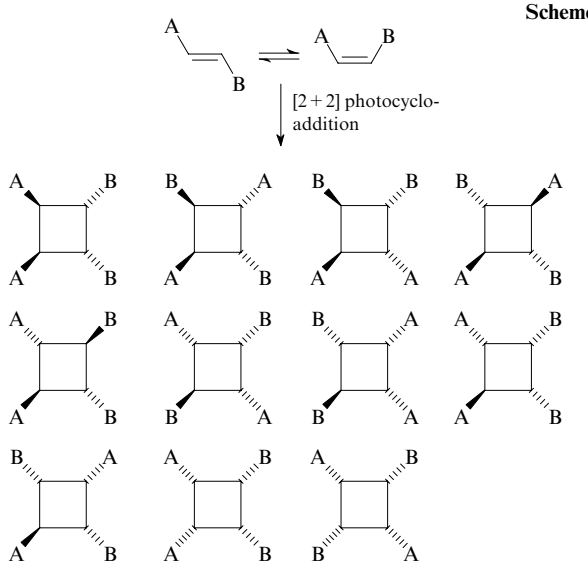
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A classical photoreaction widely used in organic synthesis, including the synthesis of drugs and natural products, is the [2 + 2] photocycloaddition (PCA) of unsaturated compounds.[2, 3] This photoreaction is also used in the chemistry of functional materials and applied physics.[4] Intermolecular [2 + 2] PCA reactions of acyclic unsaturated compounds in homogeneous solutions usually have a very low quantum yield because of the short lifetime of the electronically excited state and lead to a mixture of isomeric cyclobutanes of composition depending on numerous factors. For example, photoirradiation of a solution of 1,2-disubstituted ethylene can lead to formation of 11 isomeric cyclobutanes (Scheme 1).

To initiate an intermolecular [2 + 2] PCA reaction and make it stereospecific, the molecules of an unsaturated compound or two different unsaturated compounds must be combined in pairs with a certain mutual orientation of their C=C double bonds. The assembly can occur spontaneously through noncovalent interactions between the reactants themselves or with the participation of a mediator. To the best of our knowledge, the first examples of self-assembly, resulting in stereospecific [2 + 2] PCA in a homogeneous solution were inclusion complexes of unsaturated compounds with γ-cyclodextrin [5, 6] and supramolecular dimeric complexes of a crown ether styryl dye.[7] Earlier,[8] there has been reported the supramolecular [2 + 2] PCA of a cinnamic acid derivative that forms hydrogen-bonded dimers in nonpolar solvents; however, the reaction in this

Scheme 1



system leads to a mixture of isomeric cyclobutanes in a relatively low yield.

In addition to the self-assembly of the reactants into dimers or heterodimers, there is another supramolecular approach that affords, in specific cases, high selectivity of [2 + 2] PCA.[9] It is applicable mainly to heterocyclic unsaturated compounds with long-lived excited states.

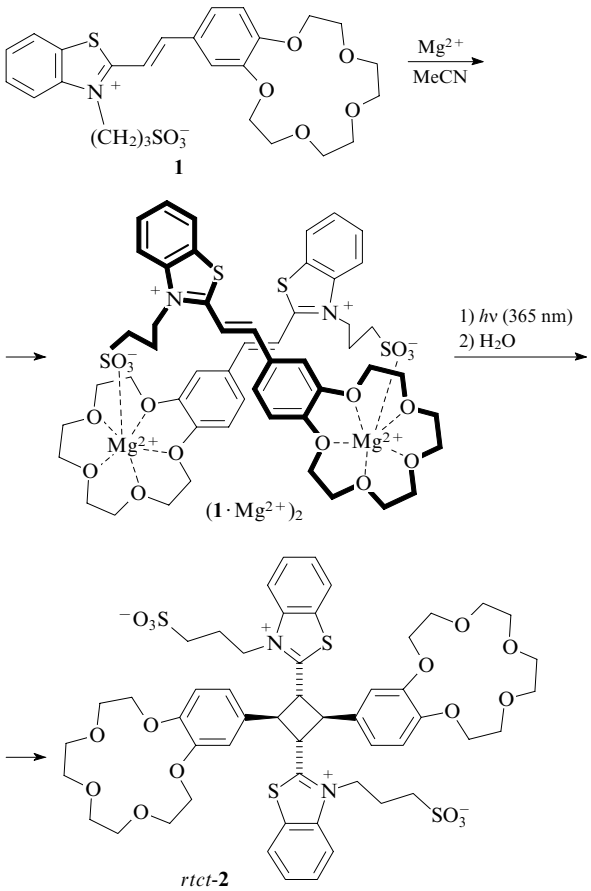
The possibilities of supramolecular chemistry for controlling intermolecular [2 + 2] PCA reactions of unsaturated compounds in homogeneous solutions have been most intensively studied in the past two decades. Some achievements have been already discussed in general reviews [10, 11] dealing with supramolecular photoreactions; however, original developments of Russian scientists have not been presented in full. This review covers all the main achievements in this area of supramolecular photochemistry. Reactions in inhomogeneous fluids, such as micellar solutions, microemulsions and colloids, are not considered.

II. Cation-induced self-assembly

Some crown ether derivatives of unsaturated compounds can assemble in pairs even in very dilute solutions in the presence of Mg^{2+}, Ca^{2+}, Sr^{2+} or Ba^{2+} cations.[12–14] Crown ethers containing a remote ammonium group can dimerize in the absence of metal cations.[15–17] The mutual orientation of the components in supramolecular complexes is determined not only by the topology of coordination bonds responsible for self-assembly but also depends on relatively weak van der Waals interactions and solvent polarity. Various aspects of complexation of crown ether derivatives of unsaturated compounds have been addressed in several reviews.[18–20]

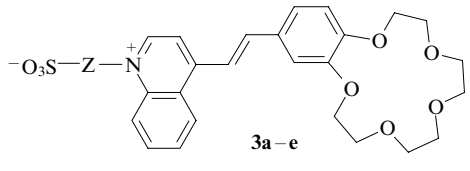
Crown ether styryl dye **1** in MeCN in the presence of $Mg(ClO_4)_2$ can form pseudocyclic dimeric complexes $(\mathbf{1}\cdot Mg^{2+})_2$ due to intermolecular association of the sulfonate group of the *N*-substituent with the metal cation located in the macrocyclic cavity (Scheme 2).[12] It has been revealed [7] that styryl chromophores in the $(\mathbf{1}\cdot Mg^{2+})_2$ dimer are subjected to two competing photoreactions — geometric *E*–*Z* photoisomerization and [2 + 2] PCA. The latter occurs stereospecifically to give cyclobutane **2** as an *rtct* isomer. The structure of *rtct*-**2** corresponds to the concerted cycloaddition of the *anti*-head-to-tail type of two (*E*)-**1** molecules. The yield of compound *rtct*-**2** in photolysis at $\lambda = 365$ nm is >95%. The high yield is due to the following properties of the $\mathbf{1}-Mg^{2+}$ system: (1) complexes containing *Z* photoisomers are not subjected to PCA; (2) *E*–*Z* photoisomerization is reversible when the system is irradiated at $\lambda = 365$ nm; (3) photoadduct **2** does not absorb light at $\lambda = 365$ nm. It should be noted that the lifetime of the excited state of dye **1** in MeCN is only ~140 ps;[12] therefore, without supramolecular assistance, this dye does not undergo PCA even at relatively high concentrations.

Scheme 2



Studies of structure–property relationships have shown that a key role in the supramolecular [2 + 2] PCA of styryl dyes with a betaine structure is played by steric factors.[21–25] For example, the quantum yield of PCA in dimeric complexes of crown ether derivatives of 4-styrylquinoline **3a**–**e** with Mg^{2+} in MeCN varies from 0 (**3e**) to 0.2 (**3a**) depending on the length and conformational flexibility of the *N*-substituent bearing the sulfonate group.[25] The stereospecific PCA in the $\{(\mathbf{3a}-\mathbf{d})\cdot Mg^{2+}\}_2$ complexes gives cyclobutanes **4a**–**d** as *rctt* isomers (Scheme 3). The structure of

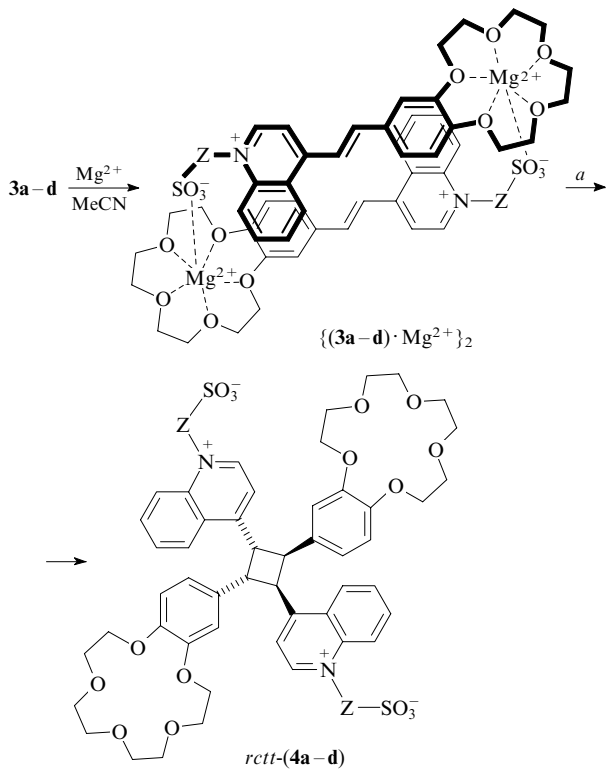
Structures 3



Z = $(CH_2)_2$ (**a**), $(CH_2)_3$ (**b**), $(CH_2)_4$ (**c**), 2-$C_6H_4CH_2$ (**d**), 4-$C_6H_4CH_2$ (**e**)

rctt-**4** corresponds to the concerted cycloaddition of the *syn*-head-to-tail type of two (*E*)-**3** molecules.

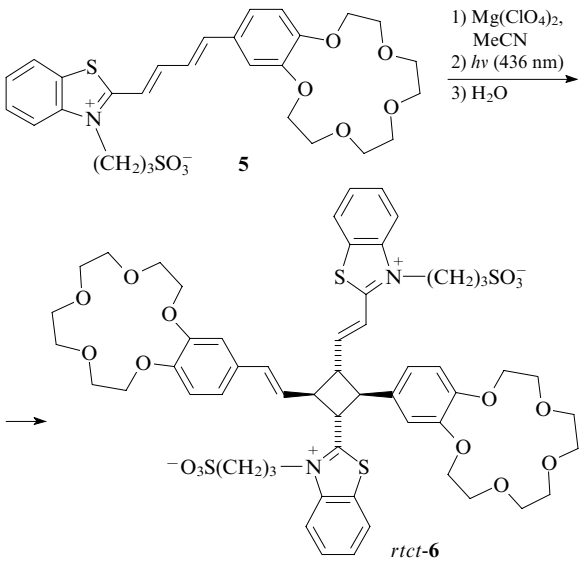
Scheme 3



(*a*) 1) *hv* (405 nm), 2) H_2O

An analogous supramolecular approach has been used to carry out, for the first time, the regio- and stereospecific [2+2] PCA of 1,3-butadiene in a homogeneous solution.[26] It has been found that butadienyl dye **5**, like styryl analogue **1**, can form pseudocyclic dimeric complexes with Mg^{2+} (Scheme 4). Irradiation of the $(\mathbf{5}\cdot Mg^{2+})_2$ complexes in MeCN with visible light initiates the PCA reaction (quantum yield ~0.3), which selectively leads to cyclobutane *rtct*-**6** in quantitative yield (according to NMR data).

Scheme 4

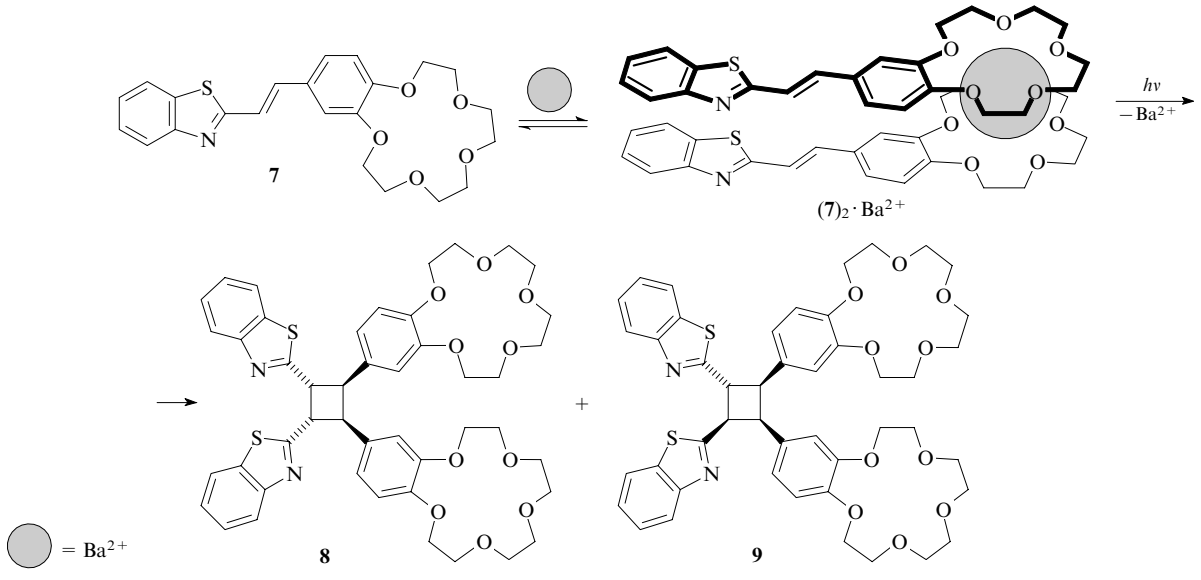


Crown ethers can form sandwich complexes with relatively large metal ions.[27] This property has been used to activate the intramolecular [2+2] PCA of a bis-styryl dye containing two 15-crown-5 moieties.[28] Later, an analogous approach has been used for controlling intermolecular [2+2] PCA reactions of crown ether derivatives of styrylbenzene,[29] stilbene,[30] distyrylbenzobis(thiazole)[31] and distyrylbenzene.[32]

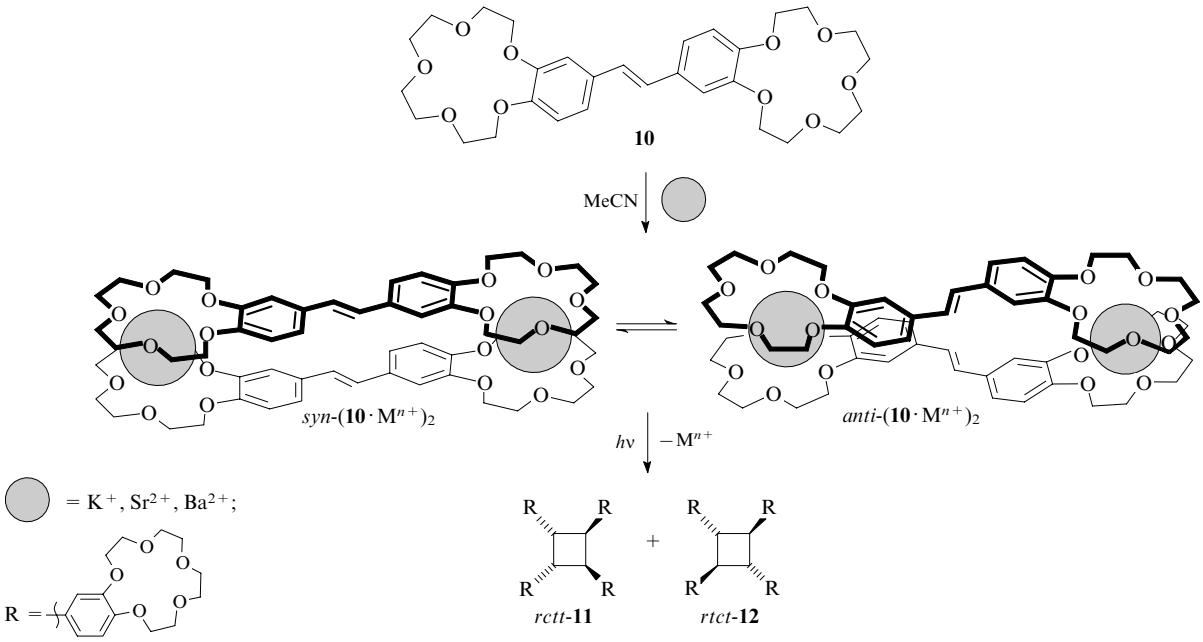
It has been shown that styrylbenzothiazole **7** and Ba^{2+} in MeCN form a 2:1 sandwich complex in which the chromophores are stacked one above the other (Scheme 5).[29] The complex formation induces the [2+2] PCA reaction, which, despite the competing *E*–*Z* photoisomerization, occurs with high quantum yield (~0.13) and gives two isomeric cyclobutanes **8** and **9** in the 3.4:1 ratio. Minor stereoisomer **9** is produced by PCA in sandwich complexes containing *Z* photoisomer of compound **7**. Cyclobutanes **8** and **9** have been isolated in 45% and 5% yields, respectively.

Stilbene **10** with two 15-crown-5 moieties in MeCN can form strong double sandwich complexes of composition 2:2

Scheme 5



Scheme 6

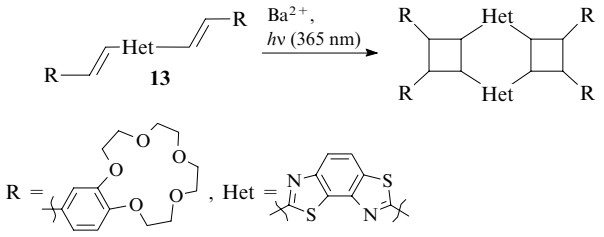


with K^+, Sr^{2+} and Ba^{2+} ions ($\log K_{2:2} > 7$ in MeCN, $K_{2:2} = [(\mathbf{10}\cdot M^{n+})_2]/[(\mathbf{10}\cdot M^{n+})]^2$) (Scheme 6).[30] Self-assembly into $(\mathbf{10}\cdot M^{n+})_2$ dimers led to deactivation of intramolecular $E-Z$ photoisomerization and photocyclization reactions typical of stilbenes and initiated [2+2] PCA, which gave two isomeric 1,2,3,4-tertrasubstituted cyclobutanes — major *rctt*-**11** (relative yield 74%–86% depending on the metal cation) and minor *rtct*-**12**. The overall yield of tetra(crown)cyclobutanes was quantitative (as probed by NMR). According to their structure, isomers **11** and **12** are the products of concerted PCA in the *syn* and *anti* conformers of $(\mathbf{10}\cdot M^{n+})_2$ dimers, respectively.

Distyrylbenzobis(thiazole) **13** contains two 15-crown-5 moieties and, like stilbene **10**, is able to form double sandwich complexes with Ba^{2+} (Scheme 7).[31] It has been demonstrated that complex formation deactivates $E-Z$ photoisomerization of compound **13** and initiates the intermolecular [2+2] PCA reaction. Under certain photolysis conditions, there occurred successive cycloaddition of two pairs of double bonds C=C in the $(\mathbf{13}\cdot Ba^{2+})_2$ complex. The reaction led to a mixture of isomeric bis-cyclobutanes. The exact number of isomers and their structure were not determined.

Bis-crown compounds can self-assemble in the presence of metal cations to form large supramolecular assemblies

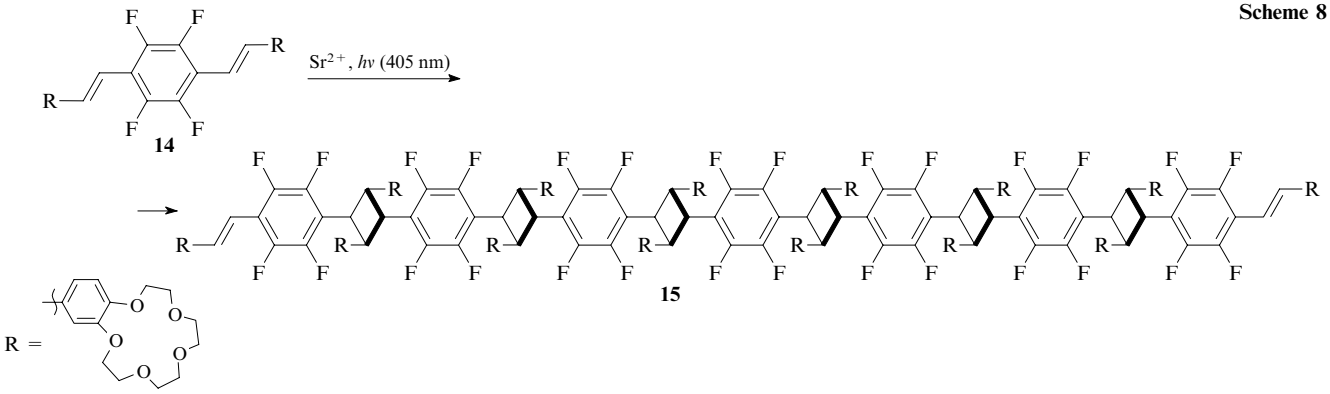
Scheme 7



(coordination polymers) owing to formation of intermolecular sandwich complexes.[33] The following example demonstrates that this feature can be used in photochemical synthesis of nanomaterials.

Complexation of bis-crown-containing distyrylbenzene **14** with K^+, Rb^+, Sr^{2+} and Ba^{2+} ions in MeCN initiated intermolecular [2+2] PCA (Scheme 8).[32] At high concentrations of the ligand (0.01 mol litre^{-1}) and Sr^{2+} (0.1 mol litre^{-1}), the photoreaction afforded cyclobutane oligomers. According to mass spectrometry evidence, the molecular mass of the major photoproduct corresponded to seven molecules of compound **14**. The formation of the high-molecular-mass product (presumably oligomer **15**) is

Scheme 8



explained by the cation-induced self-assembly of bis-crown compound **14** into multidecker sandwiches.

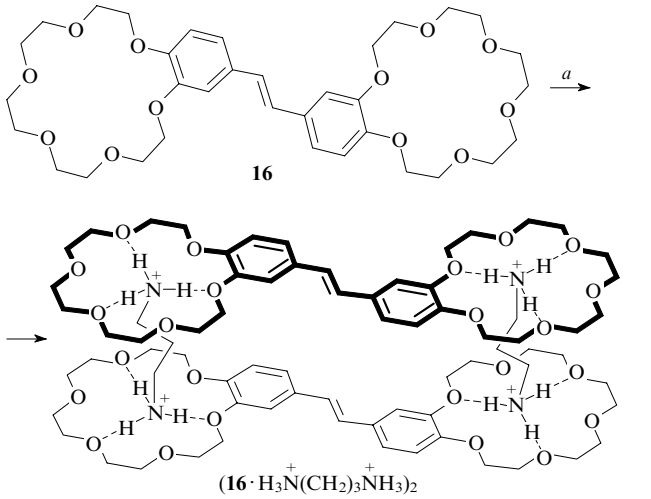
18-Crown-6 ethers are able to form sandwich complexes with dications $H_3N^+(CH_2)_nN^+H_3$.[34, 35] In the case of the 18-crown-6 analogue of stilbene **10** — compound **16** — and short diammonium dications ($n = 2-4$), formation of bis(pseudosandwich) complexes $[\mathbf{16}\cdot H_3N^+(CH_2)_nN^+H_3]_2$ was observed ($\log K_{2:2} > 5$ in MeCN) (Scheme 9).[36] The [2 + 2] PCA reactions in the $\mathbf{16}-H_3N^+(CH_2)_nN^+H_3$ systems, like in the above $\mathbf{10}-M^{n+}$ systems, generated two isomeric cyclobutanes; the relative yield of the *rctt* isomer was as high as 95% (for the 1,3-propanediammonium dication). The *rctt* isomer was isolated as a complex with 1,4-butanediammonium diperchlorate in 79% yield.

Crown compounds containing a remote ammonium group can form pseudocyclic dimers through double intermolecular interaction ammonium cation–macrocycle.[37] This feature has been used for controlling the [2 + 2] PCA reactions of stilbene,[15] 4-styrylpyridine[16, 17] and 4-styrylquinoline[17] derivatives.

Stilbene **17**, containing the 24-crown-8 moiety and the secondary ammonium group, readily dimerizes in CD_2Cl_2 owing to the formation of pseudorotaxane complex **18** (Scheme 10).[15] The stereospecific [2 + 2] PCA reaction in complex **18** gave exclusively *rctt*-cyclobutane **19** in 95% yield.

Styrylpyridine derivative **20**, containing the 18-crown-6 moiety and the primary ammonium group, is also able to form dimeric complexes owing to double intermolecular

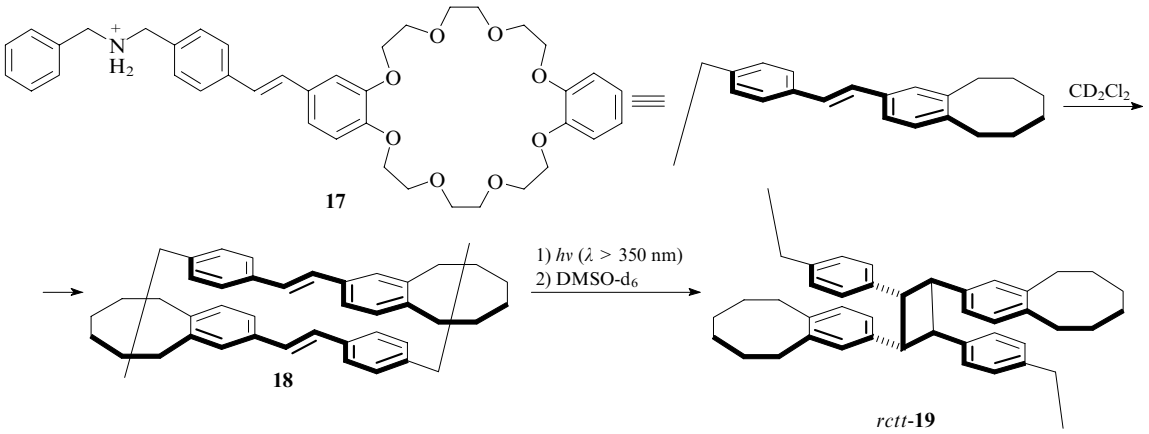
Scheme 9



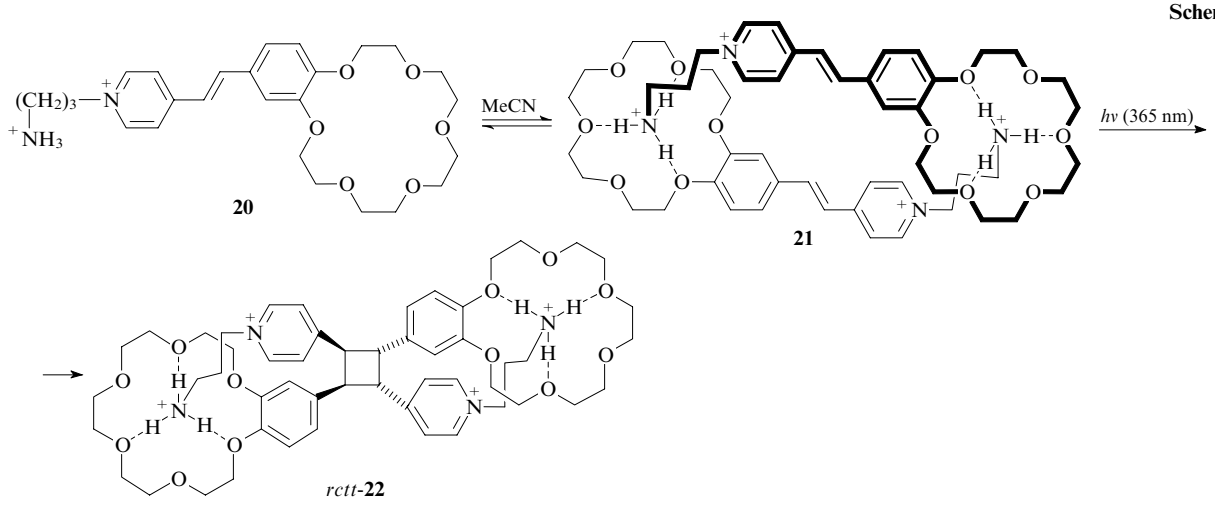
(*a*) $H_3\overset{+}{N}(CH_2)_3\overset{+}{N}H_3$, MeCN

interaction ammonium cation–macrocycle.[16] The dimerization equilibrium constant in MeCN at the ionic strength of 0.01 mol litre^{-1} is $10^{7.3}$ litre mol^{-1} (according to spectrophotometry data). The [2 + 2] PCA reaction in dimeric complexes **21** upon photolysis at $\lambda = 365$ nm occurs stereospecifically (0.38 quantum yield) and gives cyclobutane *rctt*-**22** in quantitative yield. The structure of *rctt*-**22** corre-

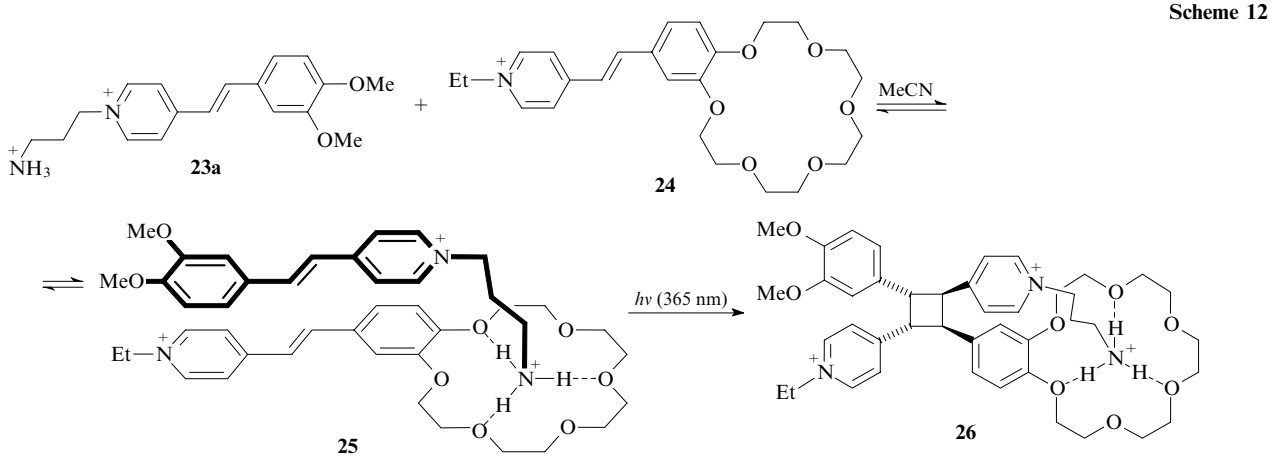
Scheme 10



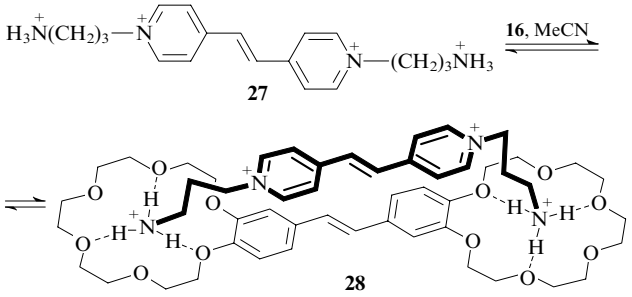
Scheme 11



Scheme 12



Scheme 13



sponds to the concerted cycloaddition of the *syn*-head-to-tail type of two (*E*)-**20** molecules (Scheme 11).

Recently, the synthesis of a large series of ammonioalkyl derivatives of crown ether styryl dyes capable, like compound **20**, of self-assembling into head-to-tail dimers has been reported.[17] It has been found that supramolecular [2+2] PCA reactions of these dyes occur stereospecifically both in solution and in the crystalline state.

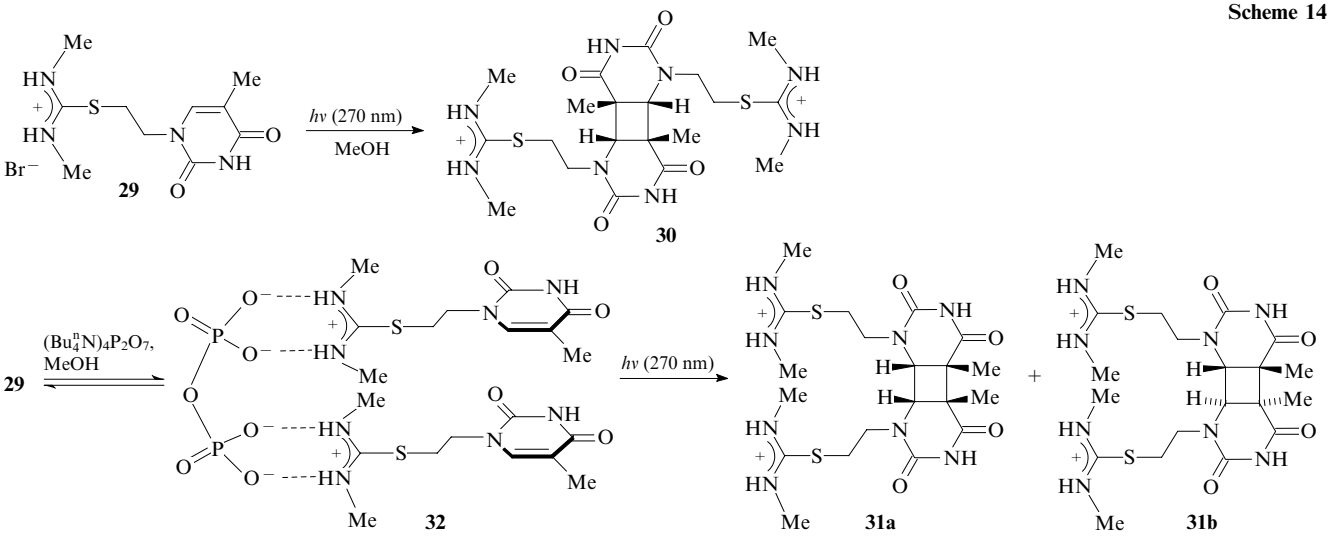
The ability of ammonium cations to form strong complexes with 18-crown-6 ethers has also been used for self-assembly of styrylpyridine derivatives into pseudodimeric complexes.[38, 39] It has been found that compounds **23a** and **24** in MeCN at concentrations $\sim 10^{-3}$ mol litre^{-1} form complex **25**, in which the styrylpyridinium cations are arranged one above the other due to stacking interactions (Scheme 12).[38] In a polar solvent, these interactions are stronger than the Coulomb repulsion between the cations. The dye molecules in pseudodimeric complexes **25** enter into the $E-Z$ photoisomerization and cross [2+2] PCA reactions. The latter is stereospecific and gives cyclobutane **26** as a sole isomer. The Z photoisomers of dyes **23a** and **24** are not subjected to PCA; therefore, under certain conditions of photolysis, cyclobutane **26** can be produced selectively and in high yield (> 50%).

Very stable bimolecular complexes of unsaturated compounds formed through ditopic ammonium cation–macrocycle interaction are known.[40–43] This is exemplified by the complex of bis(18-crown-6)stilbene **16** with the bis-ammonium derivative of dipyridylethylene **27** (Scheme 13). The log$K$ value for complex **28** in MeCN is 9.08.[41] As distinct from dimeric complex **21** and pseudodimeric structure **25**, bimolecular complex **28** is not subjected to [2+2] PCA. Moreover, formation of complex **28** leads to complete quenching of luminescence of the components and deactivates the $E-Z$ photoisomerization and photocyclization reactions.[44] The photoinertness of complex **28** is caused by the fact that local electronic excitation of molecule **16** (π-donor) or **27** (π-acceptor) gives rise to ultrafast electron transfer (τ < 300 fs) followed by excited state deactivation through back electron transfer (τ = 536 fc).[44]

III. Anion-templated self-assembly

Anions are used as templates for self-assembly of diverse supramolecular systems.[45] Experimental data are available

Scheme 14



that demonstrate the possibility of using anionic templates to control [2+2] PCA reactions in solutions.[46] The effect of pyrophosphate anions on the photodimerization of a thymine derivative containing isothiouronium moiety (compound **29**, Scheme 14) has been studied.[46]

UV irradiation of thymine **29** in methanol led to preferred formation of *syn*-head-to-tail cycloadduct **30**. The presence of tetra-n-butylammonium pyrophosphate considerably promoted [2+2] PCA, which mainly gave *syn*-head-to-head **31a** (55%) and *anti*-head-to-tail **31b** (25%) cycloadducts. This effect is due to the fact that one pyrophosphate anion can bind two molecules of **29** to give complex **32** (see Scheme 14). NMR titration experiments support the formation of 1 : 2 complexes.

IV. Control by hydrogen bonding

In this section, we discuss intermolecular [2+2] PCA reactions controlled by hydrogen bonding between the reactants or between the molecular template and reactants.

IV.1. Direct dimerization

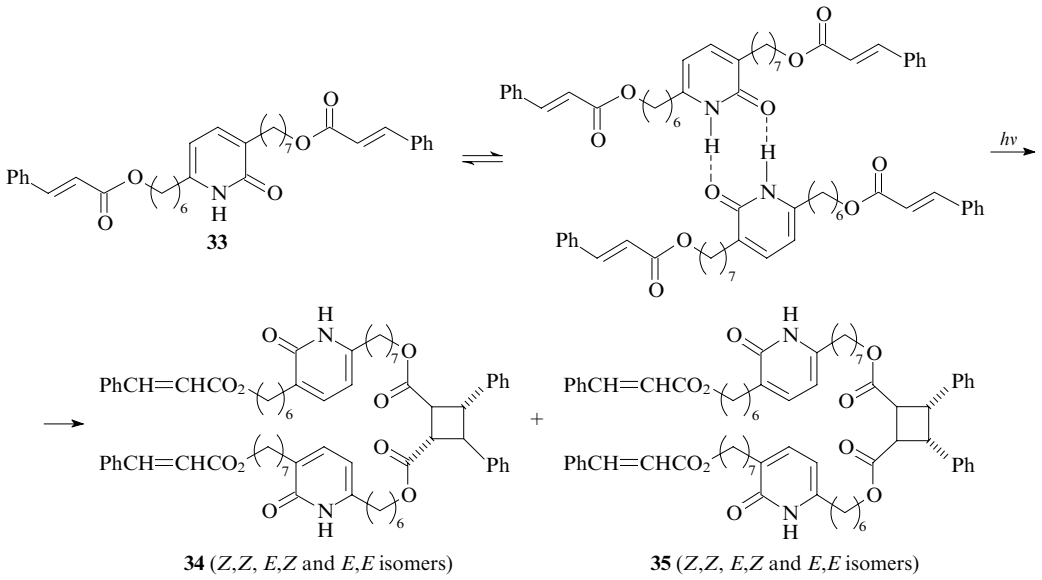
To the best of our knowledge, the first example of using hydrogen bonds for supramolecular assistance of [2+2] PCA of unsaturated compounds in solution was the photochemical synthesis of cyclobutanes from 2-pyridone derivative **33** containing two remote cinnamate moieties.[8] Compound **33** in benzene at a concentration of $\sim$0.005 mol litre^{-1} is nearly completely in the dimer form, which is caused by formation of two hydrogen bonds between the pyridone moieties (Scheme 15). UV irradiation of a solution of pyridone **33** solutions initiated the $E-Z$ photoisomerization of cinnamate moieties, as well as intermolecular [2+2] PCA, which gave cyclobutanes **34** and **35** as mixtures of the E and Z isomers. The overall yield of cyclobutanes after prolonged photolysis was $\sim$37%.

Scheme 16 shows the stereospecific cross [2+2] PCA reaction of thymine **36** with coumarin **37**. These compounds in acetonitrile and benzene form complex **38** through hydrogen bonding and stacking interactions.[47] The supramolecular photoreaction of compounds **36** and **37** in benzene gives cycloadduct **39** with 96% selectivity; however, its yield is no more than 20%.

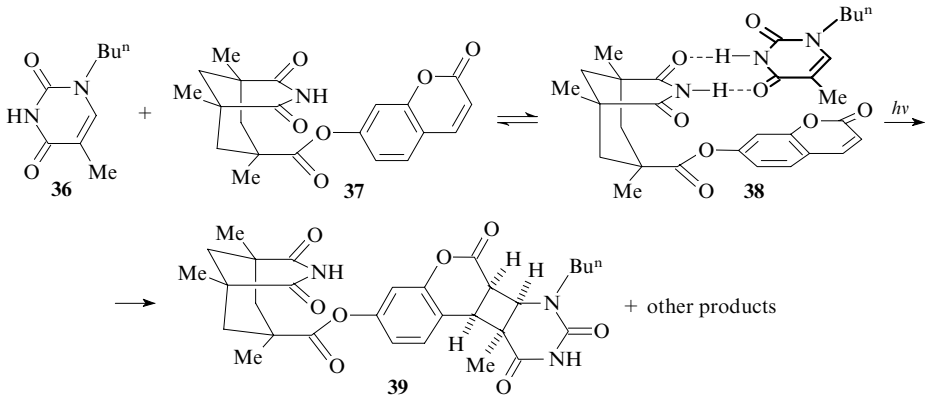
IV.2. Template methods

Molecules prone to form hydrogen bonds can be used as templates for assembling unsaturated compounds containing complementary functional groups in supramolecular complexes with the spatial orientation of the C=C bonds suitable for subsequent [2+2] PCA. Molecular templates are successfully used for controlling solid-phase photoreactions.[48] A good example is the stereospecific synthesis of [5]-ladderane through a three-step intermolecular [2+2] PCA in cocrystals of 1,6-bis(4-pyridyl)-1,3,5-hexatriene

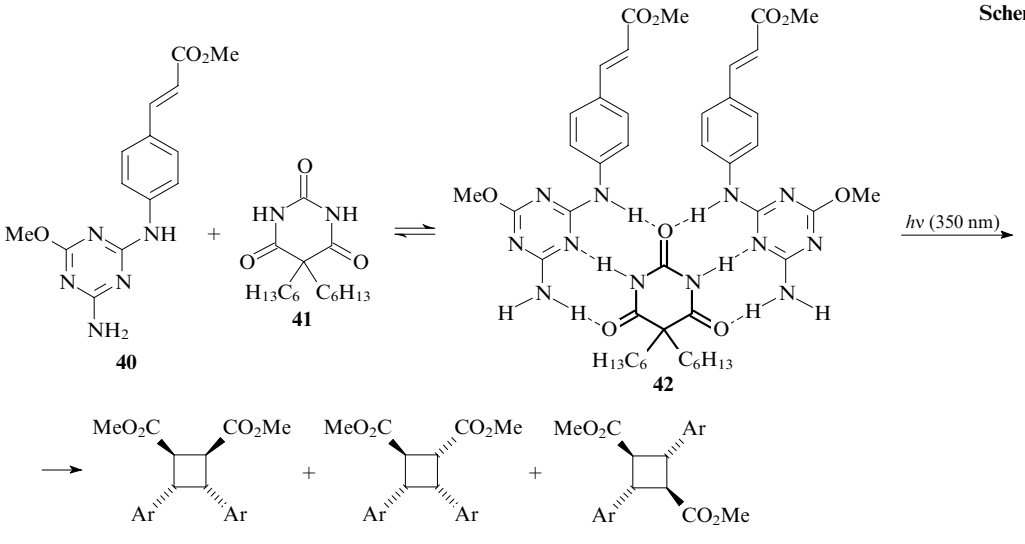
Scheme 15



Scheme 16



Scheme 17



with 5-methoxyresorcinol.[49] In solutions, the use of the template method is complicated by the low stability of multicomponent complexes.

In early studies,[50,51] it has been demonstrated that bimolecular chemical reactions in solutions can be, in principle, controlled by means of molecular receptors possessing two binding sites to add to the substrate through hydrogen bonds. Later, this idea has been used for template control of [2+2] PCA reactions of derivatives of methyl cinnamate,[52] stilbene,[53] styrene,[54] coumarin[55] and thymine.[56]

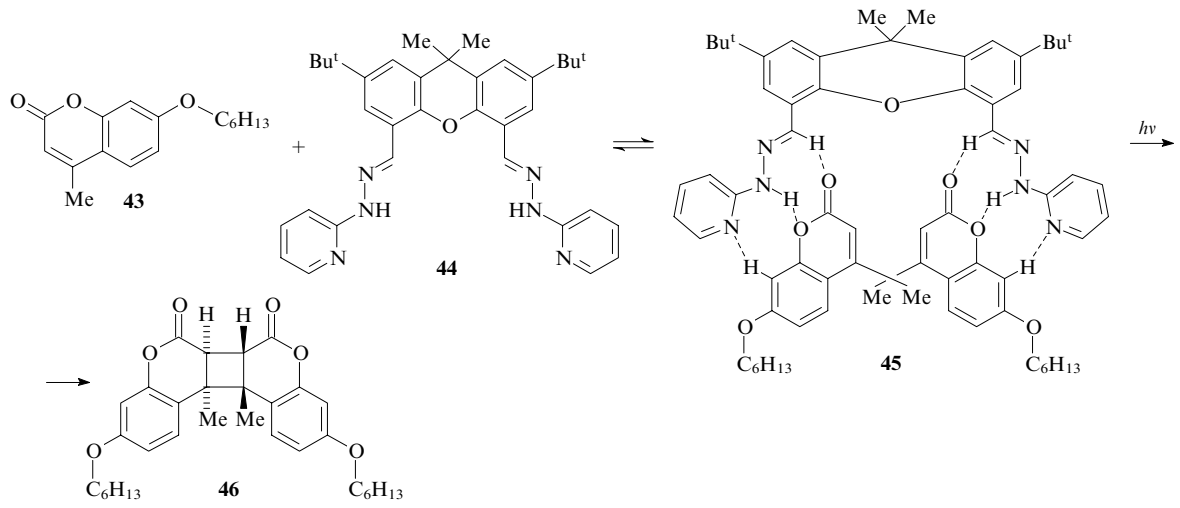
Barbituric acid derivatives have been used as molecular receptors for arylethylenes containing the diaminotriazine moiety.[52–54] Scheme 17 shows the supramolecular [2+2] PCA of methylcinnamate **40**. It has been found that barbiturate **41** can add two molecules of **40** through hydrogen bonding.[52] The stability constant of trimer **42** is ~400 litre mol^{-1} in $CDCl_3$. Complexation has led to a significant increase in the quantum yield of [2+2] PCA of methyl cinnamate **40**. The supramolecular reaction in degassed dichloromethane gave three isomeric cycloadducts in noticeable amounts. The cycloadducts were isolated by preparative HPLC and characterized by NMR and mass spectrometry (the yields of the photoproducts were not reported).

For acyclic unsaturated compounds, the use of molecular templates does not provide strictly stereospecific synthesis of cyclobutanes because of the competing geometric $E-Z$ photoisomerization and a relatively low stability of trimolecular complexes. For cyclic unsaturated compounds, such as coumarin, which are not subject to geometric photoisomerization, the number of theoretically possible isomers of photoadducts is limited, which simplifies the control of the [2+2] PCA selectivity.

Scheme 18 shows the stereospecific [2+2] PCA of coumarin **43** induced by molecular template **44**.[55] Homoditopic receptor **44** can capture two coumarin derivative molecules, arranging them in the head-to-head mode (the stability constant of trimer **45** in $CDCl_3$ is ~150 litre mol^{-1}). Photolysis of a mixture of coumarin **43** with template **44** in deoxygenated acetone led exclusively to *anti*-head-to-head cycloadduct **46**, whereas, in the absence of the template, two photoadducts — *anti*-head-to-head and *anti*-head-to-tail — in the 3 : 2 ratio were observed.

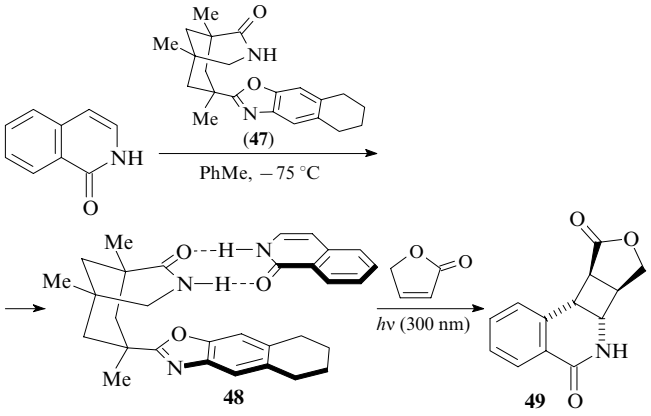
Cyclic unsaturated compounds with long-lived excited states can undergo intermolecular [2+2] PCA reactions even without supramolecular assistance. In these cases, the

Scheme 18



photoreaction selectivity can be controlled by binding the reactant to the molecular template in a 1 : 1 complex. A molecular template, acting as a steric shield, can have an effect on the stereoselectivity of intermolecular reactions of the reactant. An illustrative example of using this approach is enantioselective [2 + 2] PCA of 1(2*H*)-isoquinolone with 2(5*H*)-furanone mediated by chiral molecular receptor **47** (Scheme 19).[57]

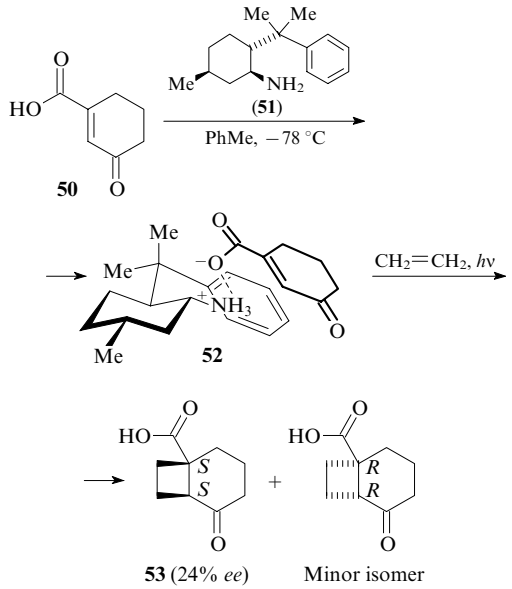
Scheme 19



The formation of two hydrogen bonds between receptor **47** and 1(2*H*)-isoquinolone leads to supramolecular complex **48**. In this complex, the tetrahydronaphtho[2,3-*d*]oxazole unit efficiently shields one face of the substrate molecule so that the cycloaddition reaction can occur only on the other unprotected face. The photoreaction of 1(2*H*)-isoquinolone with 2(5*H*)-furanone in toluene in the presence of template **47** gave cyclobutane **49** as a sole isomer in 95% yield and with high enantioselectivity (98%). The reaction was carried out at low temperature (−75 °C) to enhance the association of 1(2*H*)-isoquinolone with the receptor.

Recently, a six-step synthesis of (−)-pinolinone from 3-acetoxyquinolone has been reported in which the key step is enantioselective intermolecular cross [2 + 2] PCA controlled by receptor **47**.[58]

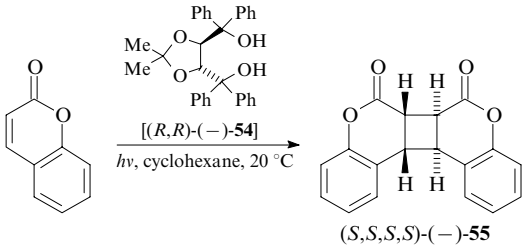
Scheme 20



To control the enantioselectivity of the [2 + 2] PCA of ethylene with 2-cyclohexenone derivative **50**, chiral molecular template **51** was used (Scheme 20).[59] The introduction of compound **51** into a toluene solution containing ketone **50** and ethylene provided moderate enantioselectivity of cross [2 + 2] PCA. This fact is explained by the formation of chiral supramolecular complex **52** in which the benzene ring of receptor **51** creates steric hindrances so that the addition of the ethylene molecule to cyclohexenone **50** can occur only on one side. The highest enantiomeric excess of the *S*,*S* isomer of cyclobutane **53** (24% *ee*, 61% yield) was achieved on photoirradiation in the range where the molar extinction coefficient of complex **52** considerably exceeds the sum of the molar extinction coefficients of individual components.

The enantioselective [2 + 2] PCA reaction of coumarin shown in Scheme 21 represents a specific example of using chiral templates.[60] Prolonged irradiation of an equimolar mixture of coumarin and optically active receptor (*R*,*R*)-(−)-**54** in cyclohexane at 20 °C has led to gradual precipitation of a crystalline complex containing two molecules of (−)-**54** and one molecule of coumarin cyclodimer (*S*,*S*,*S*,*S*)-(−)-**55** (70% yield and ~85% *ee*). The observed selectivity of the reaction has been interpreted in the following way. The photodimerization of coumarin in cyclohexane is photochemically reversible. One of the enantiomers of cyclodimer **55** is protected from the back photoreaction since it is precipitated as a crystalline complex with receptor (−)-**54**. The other enantiomer decomposes into the monomers as a result of retro-PCA in the solution.

Scheme 21

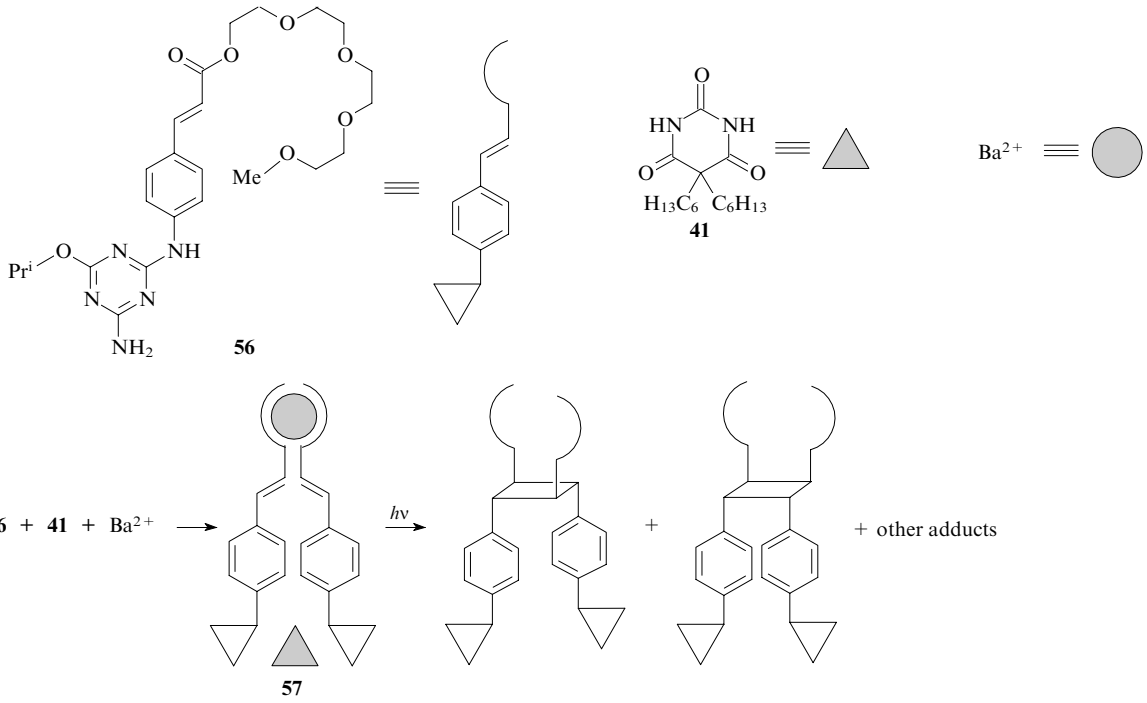


V. Combined approach

Section II presents stereospecific [2 + 2] PCA reactions of unsaturated compounds initiated through self-assembly into dimeric complexes in which the relative orientation of the reactants is fixed due to the double intermolecular interaction (see examples in Schemes 2 and 11). Analogous structures can be assembled by combining different types of interactions, for example, hydrogen bonding and complex formation with a metal ion. Examples of application of this approach are few in number.[29, 61, 62]

Cinnamic acid derivative **56** (Scheme 22) has two independent receptor sites — the oligoether chain capable of binding metal ions and the diaminotriazine moiety which, as mentioned above, can add to barbiturate **41** through hydrogen bonding. It has been reported [61] that the quantum yield of [2 + 2] PCA of free cinnamate **56** at the concentration 0.01 mol litre^{-1} in CH_2Cl_2–MeCN (95 : 5) does not exceed 10^{-4}. In the presence of template **41** (0.005 mol litre^{-1}) and $Ba(ClO_4)_2$ (0.005 mol litre^{-1}), the quantum yield increases by three orders of magnitude and becomes comparable with the quantum yield of geometric *E*–*Z* photoisomerization.

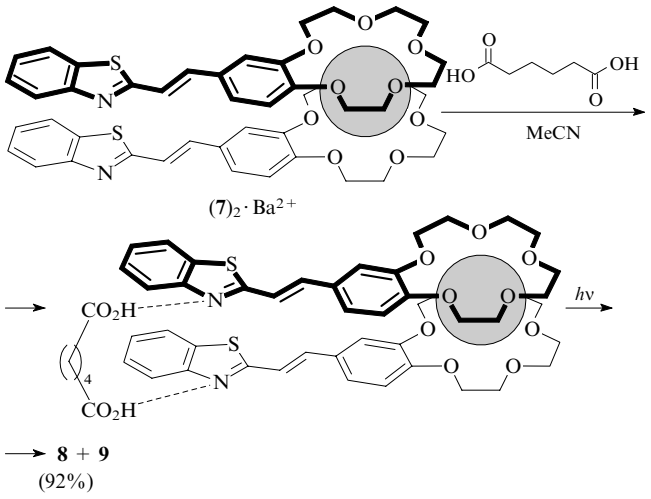
Scheme 22



The observed promotion of [2 + 2] PCA has been attributed to the formation of four-component complex **57**.

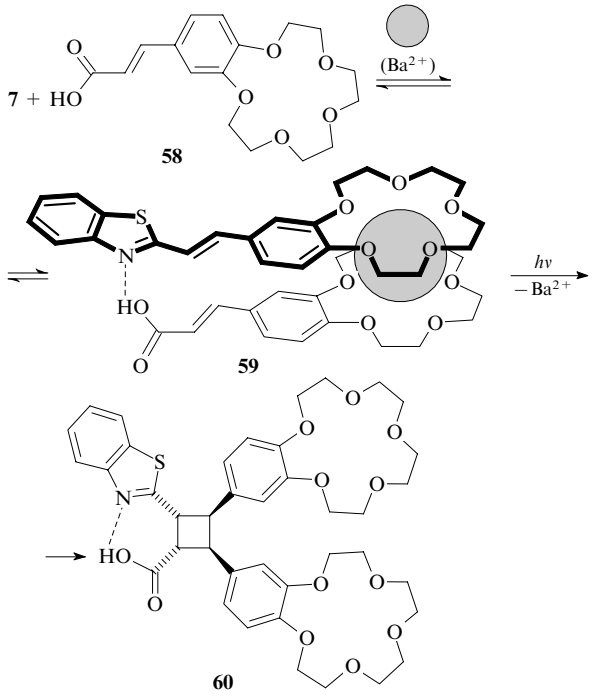
In Section II, there has been discussed the [2 + 2] PCA of styrylbenzothiazole **7** in sandwich complexes $(\mathbf{7})_2 \cdot Ba^{2+}$ (see Scheme 5) leading to two isomeric cyclobutanes **8** and **9** in the 3.4 : 1 ratio. It has been revealed [29] that the introduction of adipic acid into the reaction mixture increases the relative yield of the major isomer by a factor of 3.3. The origin of this phenomenon has not been studied in detail. Presumably, the dicarboxylic acid adds to complex $(\mathbf{7})_2 \cdot Ba^{2+}$ through two hydrogen bonds (Scheme 23), which leads to an increase of the contribution of conformers in which the molecules of **7** have the *syn*-head-to-head arrangement.

Scheme 23



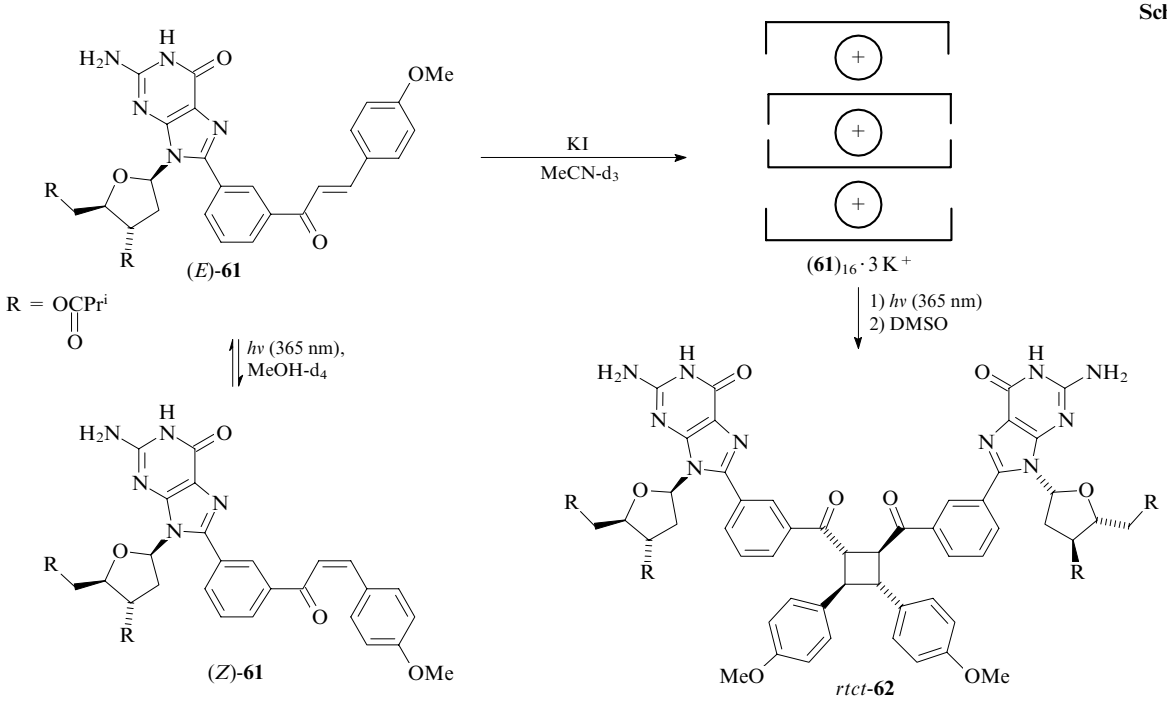
It has been found that styrylbenzothiazole **7** and crown-containing cinnamic acid **58** in MeCN form with Ba^{2+} heterosandwich complex **59** (Scheme 24).[62] Photolysis of an equimolar mixture of compounds **7**, **58** and $Ba(ClO_4)_2$ has led to three cycloadducts: cross-adduct **60** (~43%) as a result of stereospecific PCA in complex **59** and two isomeric cyclobutanes **8** and **9** as a result of PCA in sandwich complex $(\mathbf{7})_2 \cdot Ba^{2+}$. It has been stated that the stereospecificity of the cross PCA in complex **59** is caused by hydrogen bonding between the heterocyclic nitrogen atom of benzothiazole **7** and the carboxylic group of acid **58**; however, no evidence of such an interaction has been received.

Scheme 24



A stereospecific [2 + 2] PCA reaction in a more complex supramolecular structure held by numerous hydrogen

Scheme 25



bonds and complexation with metal ions has been recently described.[63] It is reported that 8-chalconyl-2′-deoxyguanosine derivative **61** in MeCN-d_3 in the presence of a potassium salt forms a supramolecular G-quadruplex composed of four stacked planar tetramers of compound **61** and three potassium ions (Scheme 25). UV irradiation of complex $(\mathbf{61})_{16} \cdot 3\,K^+$ initiates the [2 + 2] PCA reaction of the chalcone moieties to give cyclobutane *rtct*-**62**. It has been concluded[63] that only four of the eight pairs of molecules in complex $(\mathbf{61})_{16} \cdot 3\,K^+$ can be subjected to PCA. Monomer **61** does not enter into the PCA reaction because of the rapid excited state deactivation in the *E*–*Z* photoisomerization reaction.

VI. Confinement in supramolecular containers

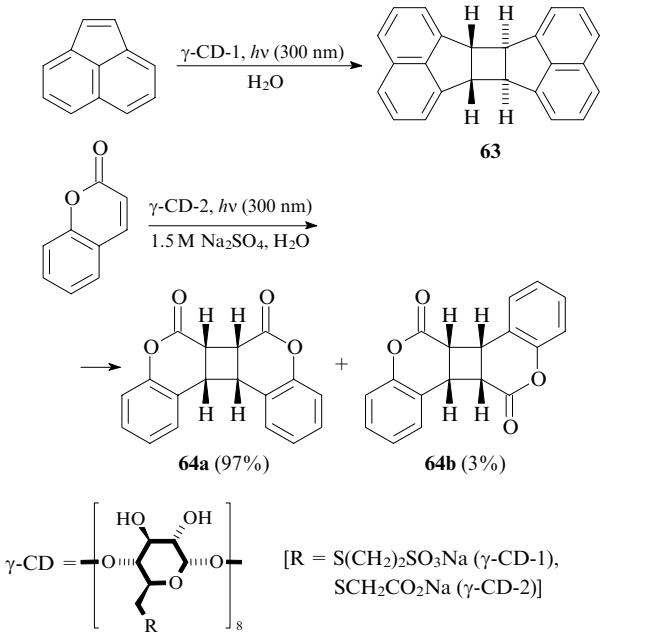
One of the efficient methods of controlling [2 + 2] PCA reactions in solutions is confinement of pairs of unsaturated molecules in the cavities of large macrocyclic molecules. The reaction cavity should be well-structured to ensure the appropriate orientation of guest molecules. A typical way of confinement of reactant pairs is through formation of 1 : 2 host–guest inclusion complexes. Another method implies the formation of 2 : 2 inclusion complexes where two cavitand molecules are combined in a capsule containing two reactant molecules.

Figure 1 shows basic types of supramolecular containers tested as nanoreactors for selective photochemical synthesis of cyclobutanes in solutions: cyclodextrins, cucurbiturils, water-soluble calixarenes, octa acid and coordination nanocages. The results of studies in this field have been discussed in recent reviews;[64, 65] therefore, here we present only some of the latest achievements.

Cyclodextrins are cyclic oligosaccharides composed of α-D-glucopyranose units linked by 1,4-glycosidic bonds. The hydrophobic nature of the cavity imparts cyclodextrins with ability to form inclusion complexes with hydrophobic molecules in aqueous solutions.[66] The γ-CD has a relatively large cavity, which can accommodate two guest molecules. This property of γ-CD has been used for controlling [2 + 2] PCA of acenaphthylene,[5, 67] coumarin,[67] tranilast (a cinnamic acid derivative),[6, 68] stilbenes[69] and stilbazolium salts.[70]

Complexes of native cyclodextrins with hydrophobic reagents are poorly soluble in water, which leads to undesirable heterogeneous reaction conditions. Recently, hydrophilic thioether derivatives of γ-CD have been synthesized, which are able to form readily soluble complexes with different aromatic guest molecules.[71] Thioethers γ-CD-1 and γ-CD-2 have been used for carrying out supramolecular [2 + 2] PCA of acenaphthylene and coumarin, respectively,

Scheme 26



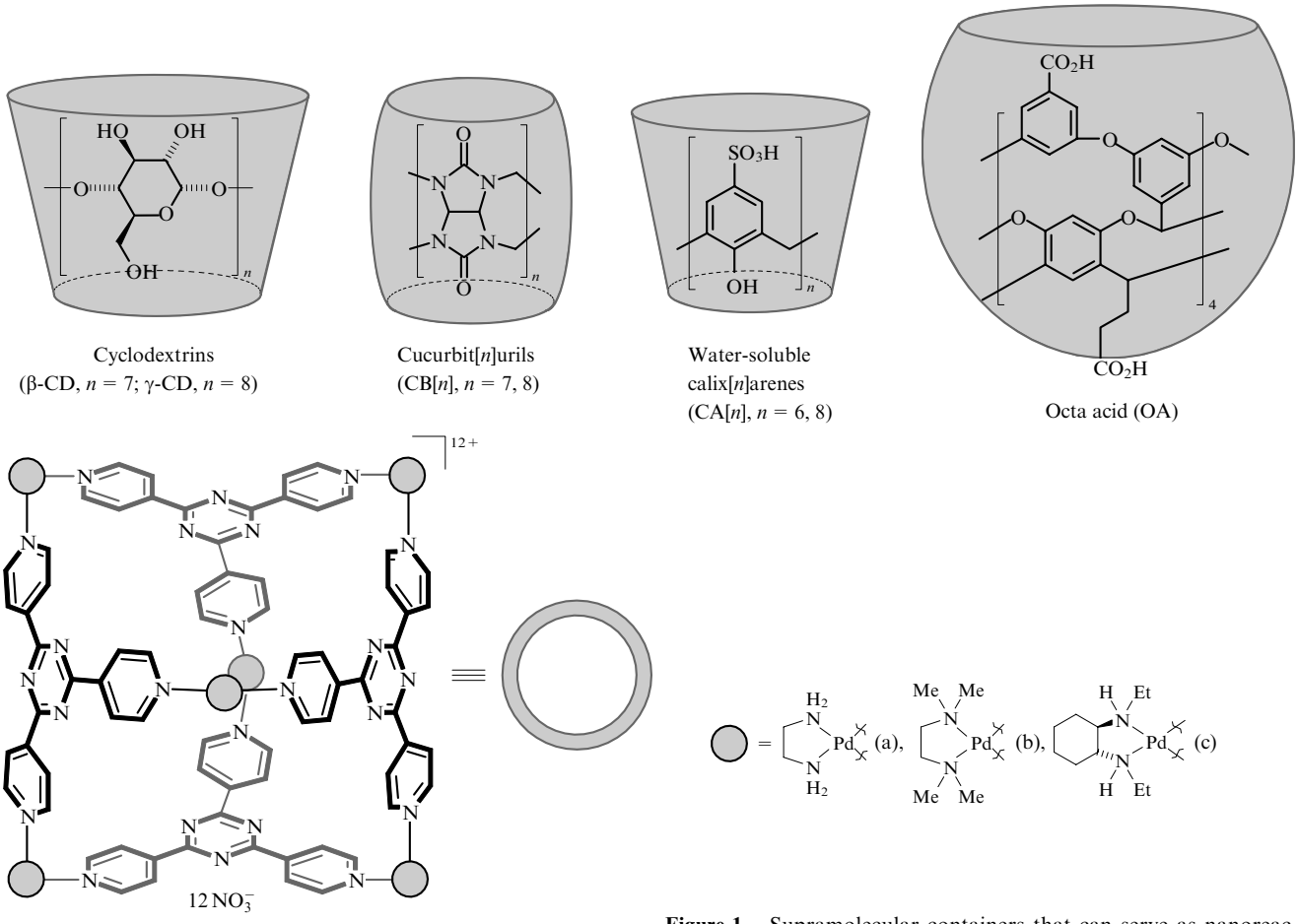


Figure 1. Supramolecular containers that can serve as nanoreactors for photochemical synthesis.

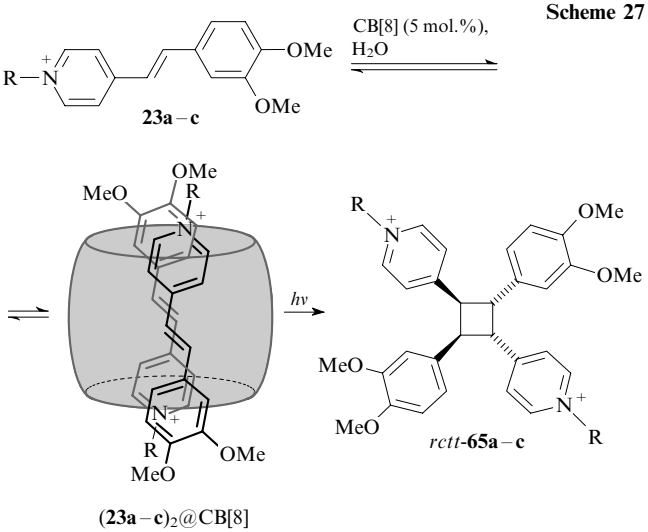
under controlled homogeneous conditions (Scheme 26).[67] The quantum yields of photodimerization of these cyclic unsaturated compounds increased tenfold upon the formation of 1 : 2 host–guest complexes. For acenaphthylene, the supramolecular photoreaction led to the exclusive formation of *anti*-cycloadduct **63** in quantitative yield, which was explained by the antiparallel orientation of two guest molecules in the γ-CD-1 cavity. In the coumarin–γ-CD-2 system, the photoreaction led mainly to *syn*-head-to-head cycloadduct **64a**, while *syn*-head-to-tail cycloadduct **64b** was obtained in only 3% yield.

The [2 + 2] PCA reaction of coumarin is considerably promoted by complexation with modified β-CD in nonpolar solvents.[72] The photoreaction rate in benzene and cyclohexane achieves the highest value at the equimolar receptor-to-substrate ratio. The observed effect is presumably related to the formation of 2 : 2 complexes.

Cucurbiturils are synthetic cyclic oligomers made of glycoluril monomers linked by methylene bridges. The cucurbituril cavity is hydrophobic, while the portals are formed by polar carbonyl groups, which allows these macrocycles to bind both polar and nonpolar organic molecules in aqueous solutions.[73,74] In the cavity size, cucurbiturils are analogous to cyclodextrins with the same number of monomeric units. Oligomer CB[8], which is able, like γ-CD, to form 1 : 2 host–guest inclusion complexes, has been used for controlling [2 + 2] PCA of both hydrophobic and water-soluble unsaturated compounds.[75–87]

Owing to unique receptor properties, cavitand CB[8] can be used in catalytic amounts in supramolecular photochemical synthesis of cyclobutanes from unsaturated compounds that do not undergo the [2 + 2] PCA reaction under common conditions.[84] The effect of CB[7] and CB[8] on the photochemistry of styryl dyes **23** in aqueous solutions has been

Scheme 27

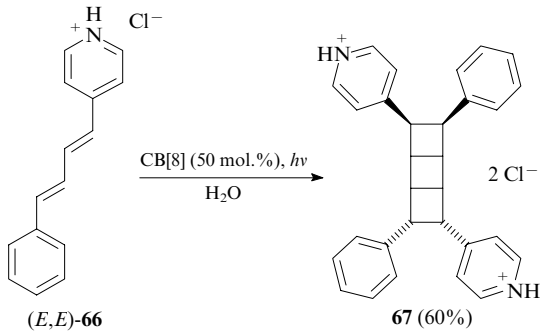


R = $(CH_2)_3NH_3^+ + 2ClO_4^-$ (**a**), $Et + ClO_4^-$ (**b**), $(CH_2)_3SO_3^-$ (**c**)

studied. On irradiation with visible light in the absence of cavitands or in the presence of CB[7], compounds **23** are subjected to reversible $E-Z$ photoisomerization. The introduction of small amounts of CB[8] (5 mol.%) initiates a stereospecific [2+2] PCA reaction (Scheme 27). Prolonged irradiation leads to complete conversion of dyes **23a–c** into corresponding cyclobutanes *rctt*-**65a–c**.

The effect of CB[7] and CB[8] on the photochemistry of diene (*E*,*E*)-**66** has been recently studied.[88] Major photolysis products of compound **66** in water were *E*,*Z*, *Z*,*E* and *Z*,*Z* isomers (radiation source — medium pressure mercury lamp; filter — borosilicate glass). The overall yield of photocycloadducts was insignificant. The introduction of CB[7] (100 mol.%) had no noticeable effect on the distribution of the photoproducts. At the same time, photolysis of compound **66** in the presence of CB[8] (50 mol.%) gave mainly [3]-ladderane **67** (yield 60%) (Scheme 28). Compound **67** is a result of two successive [2+2] PCA reactions. The first reaction gives cyclobutane and, most likely, occurs in inclusion complexes [(*E*,*E*)-**66**]$_2$@CB[8]. Judging by the structure of the end photoproduct, the two guest molecules in these complexes are arranged in a *syn*-head-to-tail mode.

Scheme 28



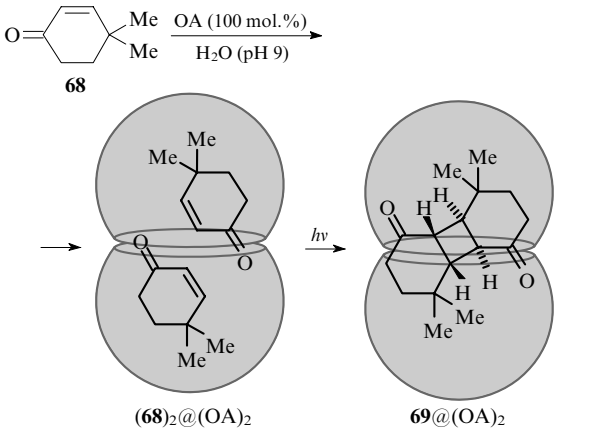
(*E*,*E*)-**66** **67** (60%)

The use of calixarenes[89] as nanoreactors for control of [2+2] PCA of unsaturated compounds in solution has been described only in one original paper.[90] The authors studied the effect of water-soluble calixarenes CA[6] and CA[8] (see Fig. 1) on the photochemistry of several protonated stilbazoles. The introduction of CA[6] or CA[8] into aqueous solutions of stilbazoles activated the [2+2] PCA reaction, which gave, in each case, mainly the *anti*-head-to-tail cycloadduct. The content of this cycloadduct in the photolysate varied from 55% to 86% (according to NMR data at 50%–60% conversion of the reactant). The observed effect has been attributed to the formation of 1:2 host–guest complexes. An essential disadvantage of calixarenes as compared with cucurbiturils is the low stability of complexes with guest molecules. This disadvantage is associated with the conformational flexibility of the hydrophobic cavity of calixarenes.

Octa acid (OA, see Fig. 1) is a synthetic amphiphilic cavitand with a deep hydrophobic cavity and a convex hydrophilic surface.[91] A characteristic property of OA is its ability to form 2:2 inclusion complexes with small organic molecules (<1 nm in length) in weakly basic aqueous solutions (pH ~9).[92] The 2:2 complex is a capsule consisting of two cavitand molecules in which two guest molecules are incarcerated. The OA cavitand has been successfully used for controlling [2+2] PCA reactions of acenaphthylene,[93] 4-methylstyrene,[94] indene and 4,4-dimethylcyclohexenone.[95]

Scheme 29 presents the stereospecific [2+2] PCA of cyclohexenone **68** induced by octa acid.[95] Photolysis of compound **68** (2 mmol litre^{-1}) in a buffer aqueous solution (pH 9) in the presence of OA (2 mmol litre^{-1}) gave cyclobutane **69** as a sole isomer. Irradiation under the same conditions but in the absence of the cavitand did not afford cycloadducts. Photolysis of neat liquid cyclohexenone **68** gave a 3:7 mixture of *anti*-head-to-head and *anti*-head-to-tail cycloadducts. The selectivity of the supramolecular photoreaction is explained by the formation of inclusion complex (**68**)$_2$@(OA)$_2$ in which the guest molecules are arranged in an *anti*-head-to-tail manner.

Scheme 29



68 (**68**)$_2$@(OA)$_2$ **69**@(OA)$_2$

Interestingly that methyl cinnamate encapsulated in OA as a 2:2 complex did not undergo [2+2] PCA.[95] Moreover, encapsulation hindered the $E-Z$ photoisomerization of methyl cinnamate. The authors of this study have arrived at the conclusion that the mutual orientation and reactivity of encapsulated molecules is determined by the available free space around these molecules.

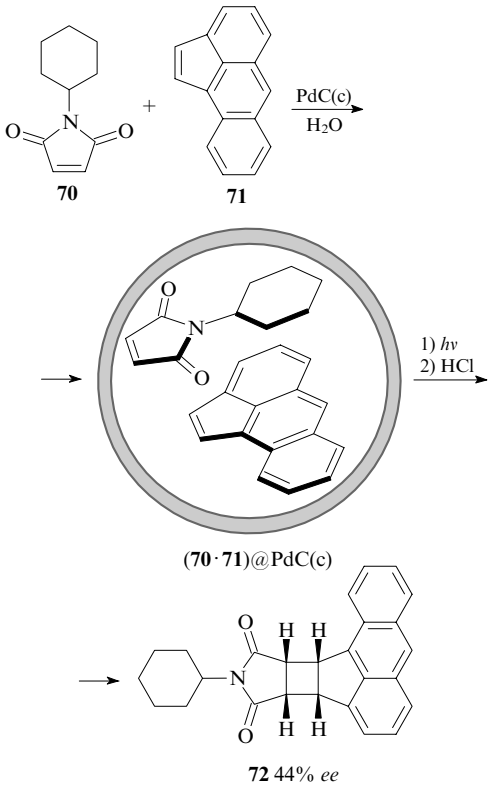
It is worth noting that octa acid is characterized by a broad absorption band with a maximum at about 280 nm and can act as a triplet sensitizer (the triplet state energy for OA is comparable with that for acetophenone).[94] In addition, it can act as an electron donor for excited acceptor molecules.[96] These facts should be taken into account in interpretation of results of photochemical studies of complexes with OA.

Coordination nanocages PdC(a–c) (see Fig. 1) are water-soluble supramolecular structures forming through self-assembly of four tridentate ligands and six Pd^{II} atoms.[97] They possess a large hydrophobic cavity and four portals through which guest molecules can penetrate. The nanocage cavities are roughly spherical.

Nanocage PdC(a) has been used as a nanoreactor for selective photochemical synthesis of cyclobutanes from acenaphthylenes,[98,99] naphthoquinones,[98] coumarins[100] and cinnamates.[101] The ability of nanocages PdC(a–c) to form 1:1:1 inclusion complexes has been used for activation of [2+2] PCA of unsaturated compounds with inert aromatic molecules.[102–106] Cross cycloaddition reactions inside coordination cages proceeded with high regio- and stereoselectivity owing to the predefined mutual orientation of encapsulated reactants.

Nanocage PdC(c) has a chiral cavity, which is due to the presence of peripheral chiral sites.[104] This property has been successfully used for controlling enantioselectivity of cross [2+2] PCA of *N*-cyclohexylmaleimide (**70**) with 3-methylfluoranthene, 1*H*-cyclopenta[*l*]phenanthrene and aceanthrylene (**71**).[106] Scheme 30 presents the photoreaction of compounds **70** and **71** in the cavity of PdC(c).

Scheme 30



Photolysis of ternary complex (**70**·**71**)@PdC(c) in water for 1 h (radiation source — high-pressure mercury lamp) led to cyclobutane **72** as a sole regio- and stereoisomer in ~60% yield with the enantiomeric excess of ~44% (the absolute configuration of enantiomers has not been determined).[106] No other photoproducts have been detected.

It should be noted that coordination nanocages absorb UV light with $\lambda < 310$ nm; therefore, direct excitation of encapsulated reactants that do not absorb in the range > 310 nm is almost impossible. In addition, electronically excited nanocages can act as electron acceptors for guest molecules.[107]

VII. Conclusions

In summary, let us focus on the advantages and disadvantages of supramolecular techniques that are most commonly used to control the [2+2] PCA reaction of unsaturated compounds in homogeneous solutions.

Cation-induced self-assembly of unsaturated compounds modified with crown ethers into dimeric, pseudodimeric and sandwich complexes not only activates [2+2] PCA reactions, but also provides their stereospecificity even in the case of acyclic compounds, which is due to relatively strong noncovalent interactions between the reactants. However, this approach works mainly in organic solvents because crown ether complexes with most cations are characterized by a very low stability in water. Another disadvantage is the necessity to modify the reactants by introducing ligand moieties.

Self-assembly into dimers by means of molecular templates with binding sites for attaching the substrate through hydrogen bonding does not provide a stereospecific synthesis of cyclobutanes from acyclic unsaturated compounds in solution because of the low stability of multicomponent complexes. At the same time, molecular templates are successfully used to control the [2+2] PCA of cyclic unsaturated compounds in organic solvents. In particular, chiral templates providing high enantioselectivity of cross [2+2] PCA reactions involving cyclic unsaturated compounds have been designed.

The control of [2+2] PCA reactions through confinement in supramolecular containers can be carried out in aqueous solutions without any special modification of the reactants. However, to ensure proper mutual orientation of reacting bonds and free space sufficient for the photoreaction to occur, the reactants should be carefully selected by size and other characteristics. Disadvantages of supramolecular containers are their high cost, low solubility in water (γ-CD, CB[8]), interfering UV absorption [OA, PdC(a–c)], and the difficulty to release encapsulated photoproducts.

It should be noted that all advances in this area of supramolecular photochemistry pertain to the reactions of alkenes and 1,3-butadienes. There are almost no examples of efficient control of [2+2] PCA reactions of other unsaturated compounds, such as alkynes and allenes. Control of cross PCA and retro-PCA reactions, the use of anionic templates and combined supramolecular approaches, tailored synthesis of cycloadducts, including structures unavailable by conventional methods (ladderanes, cyclophanes, *etc.*) are still little studied. It is hoped that further progress in the design and synthesis of supramolecular structures will contribute to the solution of these challenges.

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References

1. *Supramolecular Photochemistry: Controlling Photochemical Processes* (Eds V Ramamurthy, Y Inoue) (Hoboken: Wiley, 2011)
2. N Hoffmann *Chem. Rev.* **108** 1052 (2008)
3. T Bach, J P Hehn *Angew. Chem., Int. Ed.* **50** 1000 (2011)
4. Y Sonoda *Molecules* **16** 119 (2011)
5. Z Dong, Z Zhen *Chin. J. Org. Chem.* **6** 44 (1986)
6. F Hirayama, T Utsuki, K Uekama *J. Chem. Soc., Chem. Commun.* 887 (1991)
7. M V Alfimov, S P Gromov, O B Stanislavskii, E N Ushakov, O A Fedorova *Russ. Chem. Bull. (Engl. Transl.)* **42** 1385 (1993) [*Izv. Akad. Nauk, Ser. Khim.* 1449 (1993)]
8. P Beak, J M Zeigler *J. Org. Chem.* **46** 619 (1981)
9. T Bach, H Bergmann *J. Am. Chem. Soc.* **122** 11525 (2000)
10. J Svoboda, B König *Chem. Rev.* **106** 5413 (2006)
11. B Bibal, C Mongin, D M Bassani *Chem. Soc. Rev.* **43** 4179 (2014)
12. A V Barzykin, M A Fox, E N Ushakov, O B Stanislavskii, S P Gromov, O A Fedorova, M V Alfimov *J. Am. Chem. Soc.* **114** 6381 (1992)

13. E N Ushakov, S P Gromov, A V Buevich, I I Baskin, O A Fedorova, A I Vedernikov, M V Alfimov, B Eliasson, U Edlund *J. Chem. Soc., Perkin Trans. 2* 601 (1999)
14. S P Gromov, A I Vedernikov, E N Ushakov, L G Kuz'mina, A V Feofanov, V G Avakyan, A V Churakov, Yu S Alaverdyan, E V Malysheva, M V Alfimov, J A K Howard, B Eliasson, U G Edlund *Helv. Chim. Acta* **85** 60 (2002)
15. D G Amirsakis, A M Elizarov, M A Garcia-Garibay, P T Glink, J F Stoddart, A J P White, D J Williams *Angew. Chem., Int. Ed.* **42** 1126 (2003)
16. S P Gromov, N A Lobova, A I Vedernikov, L G Kuz'mina, J A K Howard, M V Alfimov *Russ. Chem. Bull., Int. Ed.* **58** 1211 (2009) [*Izv. Akad. Nauk, Ser. Khim.* 1179 (2009)]
17. S P Gromov, A I Vedernikov, N A Lobova, L G Kuz'mina, S N Dmitrieva, Yu A Strelenko, J A K Howard *J. Org. Chem.* **79** 11416 (2014)
18. S P Gromov *Russ. Chem. Bull., Int. Ed.* **57** 1325 (2008) [*Izv. Akad. Nauk, Ser. Khim.* 1299 (2008)]
19. E N Ushakov, M V Alfimov, S P Gromov *Russ. Chem. Rev.* **77** 39 (2008)
20. E N Ushakov, M V Alfimov, S P Gromov *Macroheterocycles* **3** 189 (2010)
21. S P Gromov, O A Fedorova, E N Ushakov, A V Buevich, M V Alfimov *Russ. Chem. Bull. (Engl. Transl.)* **44** 2131 (1995) [*Izv. Akad. Nauk, Ser. Khim.* 2225 (1995)]
22. S P Gromov, E N Ushakov, O A Fedorova, A V Buevich, M V Alfimov *Russ. Chem. Bull. (Engl. Transl.)* **45** 654 (1996) [*Izv. Akad. Nauk, Ser. Khim.* 693 (1996)]
23. S P Gromov, O A Fedorova, E N Ushakov, I I Baskin, A V Lindeman, E V Malysheva, T A Balashova, A S Arsen'ev, M V Alfimov *Russ. Chem. Bull. (Engl. Transl.)* **47** 97 (1998) [*Izv. Akad. Nauk, Ser. Khim.* 99 (1998)]
24. O A Fedorova, Yu V Fedorov, A I Vedernikov, S P Gromov, O V Yescheulova, M V Alfimov, M Woerner, S Bossmann, A Braun, J Saltiel *J. Phys. Chem. A* **106** 6213 (2002)
25. S P Gromov, E N Ushakov, O A Fedorova, I I Baskin, A V Buevich, E N Andryukhina, M V Alfimov, D Johnels, U G Edlund, J K Whitesell, M A Fox *J. Org. Chem.* **68** 6115 (2003)
26. E N Ushakov, A I Vedernikov, M V Alfimov, S P Gromov *Photochem. Photobiol. Sci.* **10** 15 (2011)
27. C J Pedersen *J. Am. Chem. Soc.* **92** 386 (1970)
28. S P Gromov, O A Fedorova, E N Ushakov, A V Buevich, I I Baskin, Yu V Pershina, B Eliasson, U Edlund, M V Alfimov *J. Chem. Soc., Perkin Trans. 2* 1323 (1999)
29. S P Gromov, A I Vedernikov, Yu V Fedorov, O A Fedorova, E N Andryukhina, N E Shepel', Yu A Strelenko, D Johnels, U Edlund, J Saltiel, M V Alfimov *Russ. Chem. Bull., Int. Ed.* **54** 1569 (2005) [*Izv. Akad. Nauk, Ser. Khim.* 1524 (2005)]
30. S P Gromov, A I Vedernikov, N A Lobova, L G Kuz'mina, S S Basok, Yu A Strelenko, M V Alfimov, J A K Howard *New J. Chem.* **35** 724 (2011)
31. Yu V Fedorov, O A Fedorova, N E Shepel', S P Gromov, M V Alfimov, L G Kuz'mina, J A K Howard, J Saltiel *Russ. Chem. Bull., Int. Ed.* **54** 2119 (2005) [*Izv. Akad. Nauk, Ser. Khim.* 2056 (2005)]
32. B Strehmel, K B Henbest, A M Sarker, J H Malpert, D Y Chen, M A J Rodgers, D C Neckers *J. Nanosci. Nanotechnol.* **1** 107 (2001)
33. S Fery-Forgues, F Al-Ali *J. Photochem. Photobiol., C: Photochem. Rev.* **5** 139 (2004)
34. A I Vedernikov, E N Ushakov, N A Lobova, A A Kiselev, M V Alfimov, S P Gromov *Russ. Chem. Bull., Int. Ed.* **54** 666 (2005) [*Izv. Akad. Nauk, Ser. Khim.* 656 (2005)]
35. A I Vedernikov, N A Lobova, E N Ushakov, M V Alfimov, S P Gromov *Mendeleev Commun.* 173 (2005)
36. S P Gromov, A I Vedernikov, L G Kuz'mina, N A Lobova, S S Basok, Yu A Strelenko, M V Alfimov *Russ. Chem. Bull., Int. Ed.* **58** 108 (2009) [*Izv. Akad. Nauk, Ser. Khim.* 108 (2009)]
37. S Shinkai, T Yoshida, K Miyazaki, O Manabe *Bull. Chem. Soc. Jpn.* **60** 1819 (1987)
38. A I Vedernikov, S K Sazonov, P S Loginov, N A Lobova, M V Alfimov, S P Gromov *Mendeleev Commun.* **17** 29 (2007)
39. A I Vedernikov, S K Sazonov, L G Kuz'mina, J A K Howard, M V Alfimov, S P Gromov *Russ. Chem. Bull., Int. Ed.* **58** 1955 (2009) [*Izv. Akad. Nauk, Ser. Khim.* 1893 (2009)]
40. S P Gromov, E N Ushakov, A I Vedernikov, N A Lobova, M V Alfimov, Yu A Strelenko, J K Whitesell, M A Fox *Org. Lett.* **1** 1697 (1999)
41. E N Ushakov, S P Gromov, A I Vedernikov, E V Malysheva, A A Botsmanova, M V Alfimov, B Eliasson, U G Edlund, J K Whitesell, M A Fox *J. Phys. Chem. A* **106** 2020 (2002)
42. S P Gromov, A I Vedernikov, E N Ushakov, N A Lobova, A A Botsmanova, L G Kuz'mina, A V Churakov, Yu A Strelenko, M V Alfimov, J A K Howard, D Johnels, U G Edlund *New J. Chem.* **29** 881 (2005)
43. A I Vedernikov, L G Kuz'mina, N A Lobova, E N Ushakov, J A K Howard, M V Alfimov, S P Gromov *Mendeleev Commun.* **17** 151 (2007)
44. E N Ushakov, V A Nadtochenko, S P Gromov, A I Vedernikov, N A Lobova, M V Alfimov, F E Gostev, A N Petrukhin, O M Sarkisov *Chem. Phys.* **298** 251 (2004)
45. R Vilar *Angew. Chem., Int. Ed.* **42** 1460 (2003)
46. Y Kato, S Nishizawa, N Teramae *Org. Lett.* **4** 4407 (2002)
47. K Mori, O Murai, S Hashimoto, Y Nakamura *Tetrahedron Lett.* **37** 8523 (1996)
48. L R MacGillivray *J. Org. Chem.* **73** 3311 (2008)
49. X Gao, T Friščić, L R MacGillivray *Angew. Chem., Int. Ed.* **43** 232 (2004)
50. T R Kelly, C Zhao, G J Bridger *J. Am. Chem. Soc.* **111** 3744 (1989)
51. T R Kelly, G J Bridger, C Zhao *J. Am. Chem. Soc.* **112** 8024 (1990)
52. D M Bassani, V Darcos, S Mahony, J-P Desvergne *J. Am. Chem. Soc.* **122** 8795 (2000)
53. D M Bassani, X Sallenave, V Darcos, J-P Desvergne *Chem. Commun.* 1446 (2001)
54. V Darcos, K Griffith, X Sallenave, J-P Desvergne, C Guyard-Duhayon, B Hasenknopf, D M Bassani *Photochem. Photobiol. Sci.* **2** 1152 (2003)
55. W G Skene, E Couzigné, J-M Lehn *Chem. – Eur. J.* **9** 5560 (2003)
56. W G Skene, V Berl, H Risler, R Khoury, J-M Lehn *Org. Biomol. Chem.* **4** 3652 (2006)
57. S C Coote, T Bach *J. Am. Chem. Soc.* **135** 14948 (2013)
58. F Mayr, C Wiegand, T Bach *Chem. Commun.* **50** 3353 (2014)
59. Y Yanagisawa, Y Nishiyama, H Tanimoto, T Morimoto, K Kakiuchi *Tetrahedron Lett.* **55** 2123 (2014)
60. K Tanaka, T Fujiwara *Org. Lett.* **7** 1501 (2005)
61. Y V Pol, R Suau, E Perez-Inestrosa, D M Bassani *Chem. Commun.* 1270 (2004)
62. O Fedorova, Yu V Fedorov, E Gulakova, N Schepel, M Alfimov, U Goli, J Saltiel *Photochem. Photobiol. Sci.* **6** 1097 (2007)
63. J M Rivera, D Silva-Brenes *Org. Lett.* **15** 2350 (2013)
64. V Ramamurthy, A Parthasarathy *Isr. J. Chem.* **51** 817 (2011)
65. N Vallavoju, J Sivaguru *Chem. Soc. Rev.* **43** 4084 (2014)
66. J Szejtli *Chem. Rev.* **98** 1743 (1998)
67. H M Wang, G Wenz *Beilstein J. Org. Chem.* **9** 1858 (2013)
68. T Utsuki, F Hirayama, K Uekama *J. Chem. Soc., Perkin Trans. 2* 109 (1993)
69. W Herrmann, S Wehrle, G Wenz *Chem. Commun.* 1709 (1997)
70. R Kaliappan, M V S N Maddipatla, L S Kaanumalle, V Ramamurthy *Photochem. Photobiol. Sci.* **6** 737 (2007)

71. H M Wang, G Wenz *Chem. – Asian J.* **6** 2390 (2011)
72. H Asahara, T Iwamoto, T Kida, M Akashi *Tetrahedron Lett.* **54** 688 (2013)
73. J W Lee, S Samal, N Selvapalam, H-J Kim, K Kim *Acc. Chem. Res.* **36** 621 (2003)
74. K I Assaf, W M Nau *Chem. Soc. Rev.* **44** 394 (2015)
75. S Y Jon, Y H Ko, S H Park, H-J Kim, K Kim *Chem. Commun.* 1938 (2001)
76. M Pattabiraman, A Natarajan, R Kaliappan, J T Mague, V Ramamurthy *Chem. Commun.* 4542 (2005)
77. M Pattabiraman, A Natarajan, L S Kaanumalle, V Ramamurthy *Org. Lett.* **7** 529 (2005)
78. M Pattabiraman, L S Kaanumalle, A Natarajan, V Ramamurthy *Langmuir* **22** 7605 (2006)
79. T V Mitkina, D Yu Naumov, N V Kurat'eva, O A Gerasko, V P Fedin *Russ. Chem. Bull., Int. Ed.* **55** 26 (2006) [*Izv. Akad. Nauk, Ser. Khim.* 25 (2006)]
80. M V S N Maddipatla, L S Kaanumalle, A Natarajan, M Pattabiraman, V Ramamurthy *Langmuir* **23** 7545 (2007)
81. N Barooah, B C Pemberton, A C Johnson, J Sivaguru *Photochem. Photobiol. Sci.* **7** 1473 (2008)
82. N Barooah, B C Pemberton, J Sivaguru *Org. Lett.* **10** 3339 (2008)
83. B C Pemberton, N Barooah, D K Srivatsava, J Sivaguru *Chem. Commun.* **46** 225 (2010)
84. S P Gromov, A I Vedernikov, L G Kuz'mina, D V Kondratuk, S K Sazonov, Yu A Strelenko, M V Alfimov, J A K Howard *Eur. J. Org. Chem.* 2587 (2010)
85. B C Pemberton, R K Singh, A C Johnson, S Jockusch, J P Da Silva, A Ugrinov, N J Turro, D K Srivastava, J Sivaguru *Chem. Commun.* **47** 6323 (2011)
86. A Nakamura, H Irie, S Hara, M Sugawara, S Yamada *Photochem. Photobiol. Sci.* **10** 1496 (2011)
87. D A Ivanov, N Kh Petrov, M V Alfimov, A I Vedernikov, S P Gromov *High Energy Chem.* **48** 253 (2014) [*Khim. Vys. Energ.* **48** 295 (2014)]
88. M V S N Maddipatla, M Pattabiraman, A Natarajan, K Srivastav, J T Mague, V Ramamurthy *Org. Biomol. Chem.* **10** 9219 (2012)
89. C D Gutsche *Calixarenes Revisited* (London: Royal Society of Chemistry, 1998)
90. R Kaliappan, L S Kaanumalle, A Natarajan, V Ramamurthy *Photochem. Photobiol. Sci.* **5** 925 (2006)
91. C L D Gibb, B C Gibb *J. Am. Chem. Soc.* **126** 11408 (2004)
92. N Jayaraj, Y Zhao, A Parthasarathy, M Porel, R S H Liu, V Ramamurthy *Langmuir* **25** 10575 (2009)
93. L S Kaanumalle, V Ramamurthy *Chem. Commun.* 1062 (2007)
94. A Parthasarathy, L S Kaanumalle, V Ramamurthy *Org. Lett.* **9** 5059 (2007)
95. A Parthasarathy, S R Samanta, V Ramamurthy *Res. Chem. Intermed.* **39** 73 (2013)
96. P Jagadesan, B Mondal, A Parthasarathy, V J Rao, V Ramamurthy *Org. Lett.* **15** 1326 (2013)
97. M Fujita, D Oguro, M Miyazawa, H Oka, K Yamaguchi, K Ogura *Nature (London)* **378** 469 (1995)
98. M Yoshizawa, Y Takeyama, T Kusukawa, M Fujita *Angew. Chem., Int. Ed.* **41** 1347 (2002)
99. S Karthikeyan, V Ramamurthy *Tetrahedron Lett.* **46** 4495 (2005)
100. S Karthikeyan, V Ramamurthy *J. Org. Chem.* **71** 6409 (2006)
101. S Karthikeyan, V Ramamurthy *J. Org. Chem.* **72** 452 (2007)
102. M Yoshizawa, Y Takeyama, T Okano, M Fujita *J. Am. Chem. Soc.* **125** 3243 (2003)
103. Y Nishioka, T Yamaguchi, M Yoshizawa, M Fujita *J. Am. Chem. Soc.* **129** 7000 (2007)
104. Y Nishioka, T Yamaguchi, M Kawano, M Fujita *J. Am. Chem. Soc.* **130** 8160 (2008)
105. S Horiuchi, Y Nishioka, T Murase, M Fujita *Chem. Commun.* **46** 3460 (2010)
106. T Murase, S Peschard, S Horiuchi, Y Nishioka, M Fujita *Supramol. Chem.* **23** 199 (2011)
107. T Murase, Y Nishijima, M Fujita *Chem. – Asian J.* **7** 826 (2012)