

## CHAPTER I

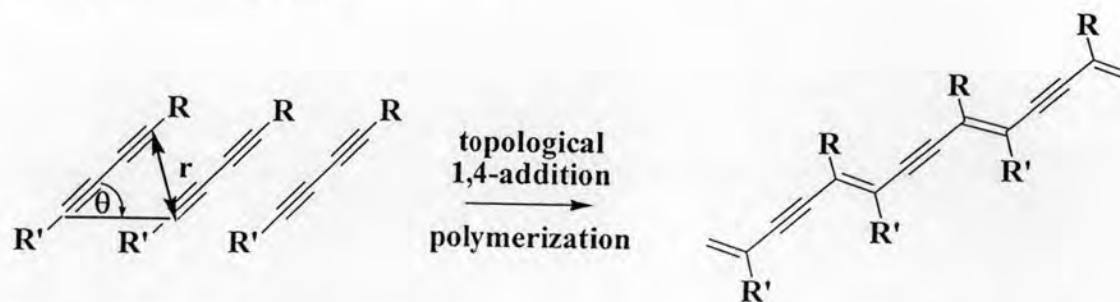
### INTRODUCTION

#### 1.1 Polydiacetylene

Polydiacetylenes (PDAs) are a class of conjugated polymers possessing potential photonic and electronic applications. Photoconductivity [1], third-order optical nonlinearity [2], thermochromism [3], and solvatochromism [4] are well-known interesting properties of PDAs. PDAs are typically obtained from topological polymerization (solid-state polymerization) of appropriate diacetylene (DA) monomers on irradiation by UV light or  $\gamma$  rays [5].

##### 1.1.1 Topological polymerization

Topological polymerizations of diacetylene were first reported by Wegner in 1969 [6]. The mechanism of this kind of polymerization is quite different from that of other polymerization systems which usually take place in solution or liquid state. Like all topological reactions, a polymerization requires precise prealignment of the reactant molecule within a crystal [7]. Diacetylenes are polymerized via a 1,4-addition mechanism where the ideal packing parameters, including the distance between reacting carbons ( $r$ ) of  $\sim 4 \text{ \AA}$  and the inclination angle between the diacetylene and stacking axis of diacetylene ( $\theta$ ) of  $\sim 45^\circ$  relative to the translation axis, can be achieved (Scheme 1.1) [8].



**Scheme 1.1** Packing parameters,  $r = \sim 4 \text{ \AA}$  and  $\theta = \sim 45^\circ$  are required for the topological polymerization of a diacetylene monomer.

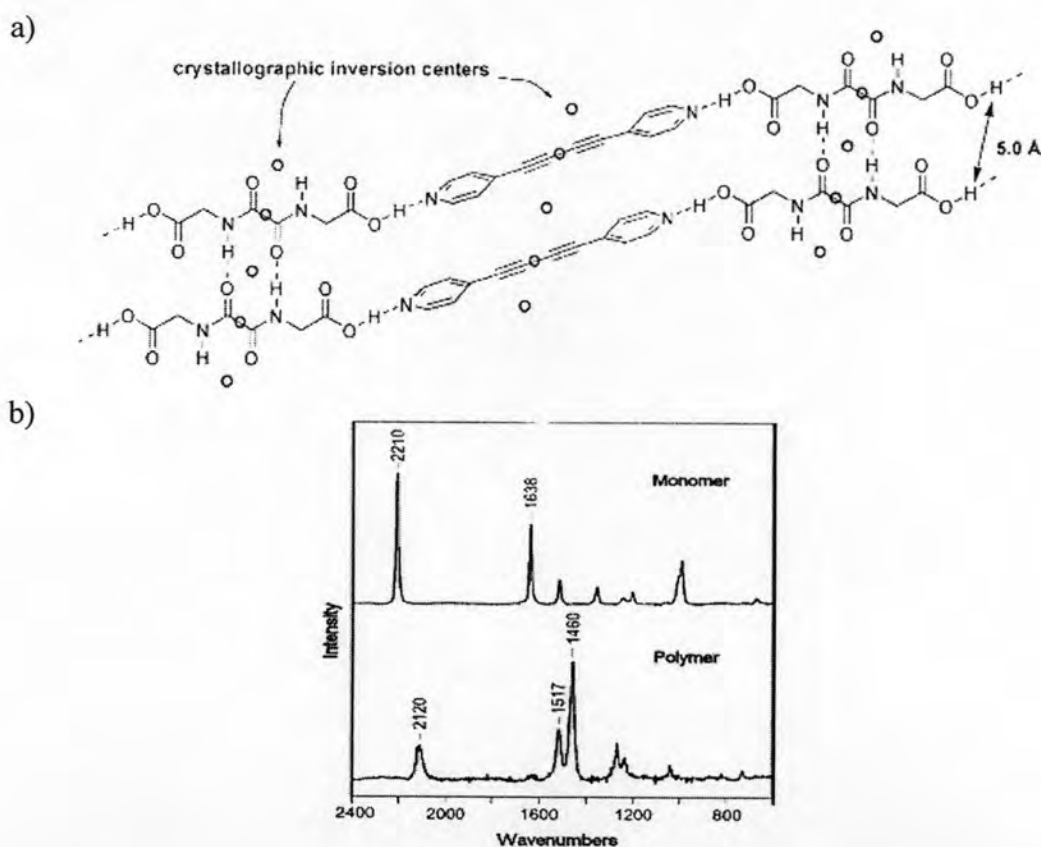
### 1.1.2 Optical and electronic properties

The ene-yne conjugation of PDA backbone is composed of alternating double and triple bonds, and the extent of conjugation depends on its conformation [9]. In an optimal conformation, which is substantially controlled by the side chains, PDAs absorb light at approximately 650 nm, providing a blue appearance that is easily observed by naked eye. Under certain circumstances, the polymer backbone can be distorted from its optimal conformation causing the reduction of its effective conjugation length of the backbone and the absorption maximum of PDAs is shifted lower to about 550 nm corresponding to the appearance of a bright red color. The backbone distortion can be induced by order-disorder transitions in the side chains through environmental perturbation in response to temperature [10], organic solvents [3], pH and salt changes [11], mechanical stress [12], or in the case of biosensors, by the specific interaction between a surface bound ligand and its complementary target [13].

The strong coupling between the electronic structure and the UV-visible absorption of these polymers leading to unique optical and electronic properties leads to tremendous interests in polydiacetylenes for a variety of applications such as chemical sensors [14], biosensors [15], nonlinear optical materials [16], photoresists [17], thermal [18], and mechanical sensors [19].

Many works have been done on the design, syntheses and polymerization of various diacetylene derivatives. For instance, among them, poly(ETDU) [5,7-dodecadiyne-1,12-diol bis(ethylcarbamate)] is typical of the PDAs that exhibit a reversible thermochromic transition between the blue A and red forms [20]. The hydrogen bonding between the carbamate groups plays an important role in the reversible thermochromic behaviors, which have been analyzed by various measurements such as X-ray diffraction, NMR, UV-visible, IR, and Raman spectroscopy [21]. Recently, photoinduced phase transitions between the two forms have also been reported in one of those carbamate-substituted PDAs, a single crystal of poly-4U3[5,7-dodecadiyne-1,12-diol bis(propylcarbamate)] [22].

It is also possible to modify the UV-visible absorption spectrum of neutral conjugated polymers by varying their conformational structure. Controlling the arrangement of polydiacetylenes in crystalline solids remains a challenge for materials chemistry. Chemists have demonstrated that both hydrogen bonding and  $\pi$  stacking can be used as noncovalent controls to prepare crystals with designed structures [23]. Lauher et al. [24] successfully synthesized a series of polydipyridyldiacetylenes and grew cocrystals with oxalamides providing the desired supramolecular structure (Figure 1.1a) in accordance with the structural parameter near the ideal for polymerization confirmed by Raman spectroscopy (Figure 1.1b).

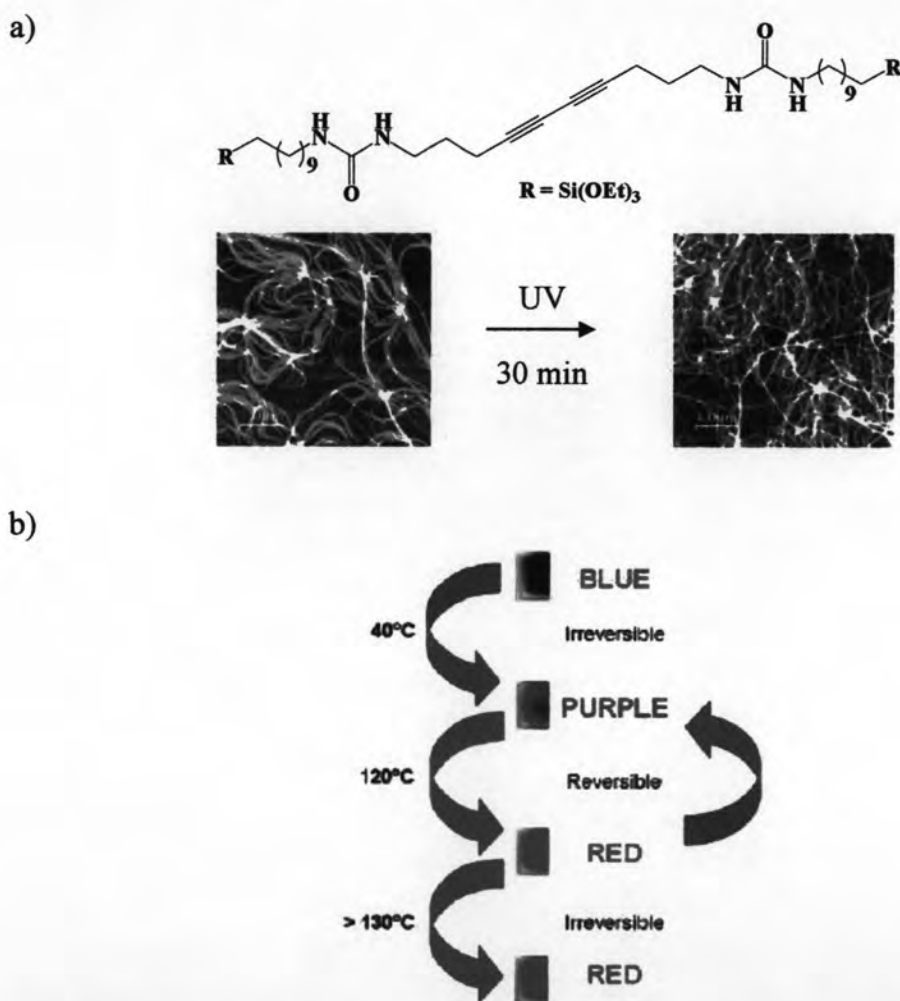


**Figure 1.1** a) Structure of 1,4-di(pyridin-4-yl)buta-1,3-diyne (4-pda) cocrystal with oxalamides b) Raman spectra of monomer and polymer of 4-pda cocrystal [24].

The study of topological polymerization was conducted not only in the crystalline states, the self association of bis(urea) substituted diacetylenes also prepared in cyclohexane organogel form involving much stronger hydrogen bondings than the carbamate and amide groups. The resulting supramolecular assemblies revealed the blue color on a quartz plate and gave conjugated nanofibers upon

exposure to UV-irradiation (Figure 1.2a). Upon heating, the polymer on the quartz plate showed the color change with three chromatic transitions from blue to red with an intermediate purple (Figure 1.2b) [25].

The mechanism of the color change of polydiacetylene has been investigated in detail in the past decade. A variety of analytical techniques, such as electron diffraction, Fourier transform infrared spectroscopy, resonance Raman, fluorescence polarization, and atomic force microscopy, have been employed to identify the molecular orientation of the side chains and backbones [26].

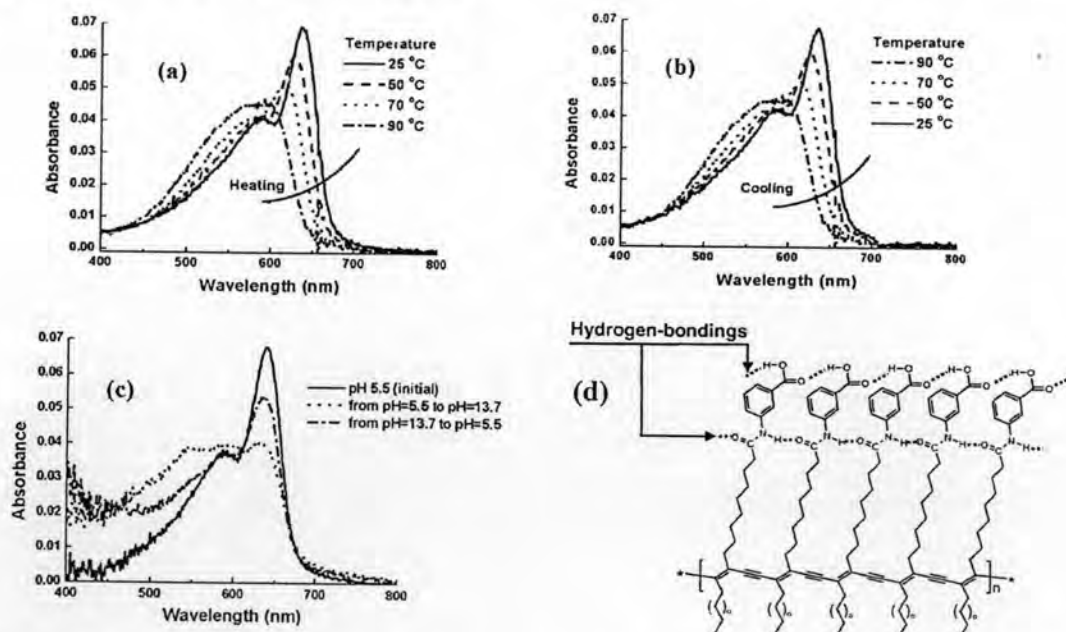


**Figure 1.2** a) AFM image before and 30 min after UV-irradiation b) Diagram of thermochromic phases exhibited by bis(urea) substituted diacetylene dropcast and irradiated on a quartz plate [25].

Recently, diacetylene lipids have also been remerged as one of the most studied class of monomers because they can form nano-structured vesicles uniformly dispersed in an aqueous medium. The vesicle formed in aqueous solution can in turn be polymerized effectively by UV-irradiation. The most commonly used lipid monomers for preparation of vesicles are the derivatives of 10,12-pentacosadiynoic acid (PCDA) that give intense blue-colored solution of poly(PCDA) solution upon photopolymerization.

Ahn and Kim et al. have synthesized a series of new diacetylene monomers and found that, due to the role of enhanced hydrogen bonding, PCDA-mBzA (3-(pentacosadiyno-10,12-diamido)-benzoic acid) showed reversible color change upon thermal and pH stimulus (Figure 1.3a-c). The double hydrogen bonds of PCDA-mBzA provided the supramolecular film with the capability to recover its initial molecular organization, so that the average conjugation length of the  $\pi$  electrons returns to the initial value upon removal of external stimuli (Figure 1.3d).

While 10,12-pentacosadiynoic acid (PCDA) showed irreversible chromism upon the same stimulus as PCDA-mBzA, the result has been reasoned that the single hydrogen-bonding of the carboxylic headgroups of polymerized PCDA is not sufficient for the supramolecules to maintain proper molecular organizations required for the reversible color switching [27].



**Figure 1.3** Reversible colorimetric transitions of LS films (PCDA-mBzA): as a) Heated up, b) Cooled down, c) pH was varied and d) The hydrogen bonding at terminal carboxyl and amide-carbonyl groups [27].



### 1.1.3 Synthesis of diacetylene monomers

Acetylenic coupling has experienced some of the most intensive study of its long history. Rigid and sterically undemanding di- and oligoacetylene moieties, which are frequently encountered in natural products, are finding increasing application as key structural elements in synthetic receptors for molecular recognition. Interesting electronic and optical properties of extensively  $\pi$ -conjugated systems have spurred research into new linear oligoalkynes and acetylenic carbon allotropes [27]. The synthetic challenges associated with these efforts have in turn spawned new methods.

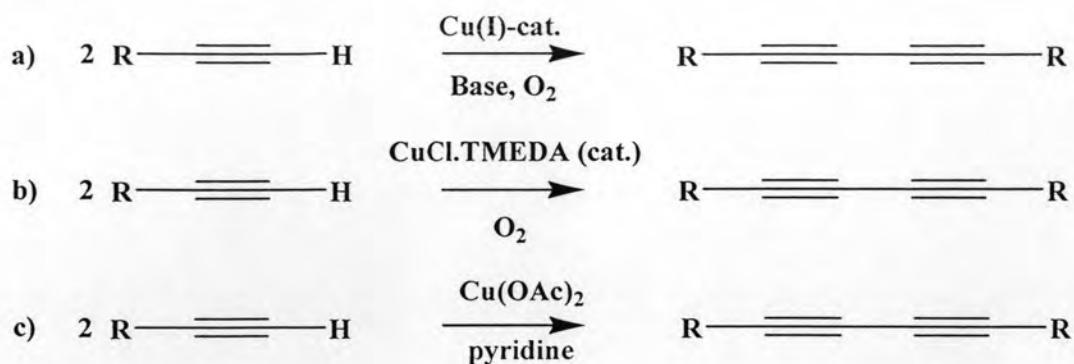
#### - Homocoupling

The classical Glaser coupling reaction of terminal alkynes remains one of the most frequently used methods for synthesis of symmetric or cyclic diacetylenes. The reaction involves the use of catalytic copper(I), which is oxidized in the catalytic cycle by oxygen in the reaction medium (Scheme 1.2a).

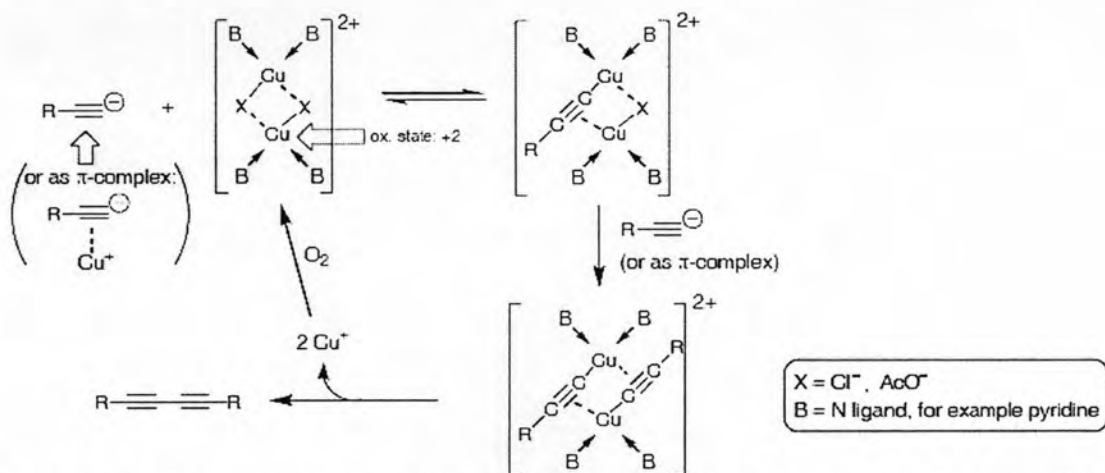
The related Hay coupling reaction has several advantages as compared with the Glaser Coupling. The copper-TMEDA complex used is soluble in a wider range of solvents, so that the reaction is more versatile (Scheme 1.2b).

The Eglinton reaction is also an oxidative reaction of terminal alkynes that widely used to synthesize symmetric diacetylene by using a stoichiometric amount of copper(II) salt in pyridine (Scheme 1.2c). The mechanism of homocoupling involves in catalysis of copper(I or II), which is reoxidized in the catalytic cycle by oxygen in the reaction medium (Scheme 1.2d) [28].

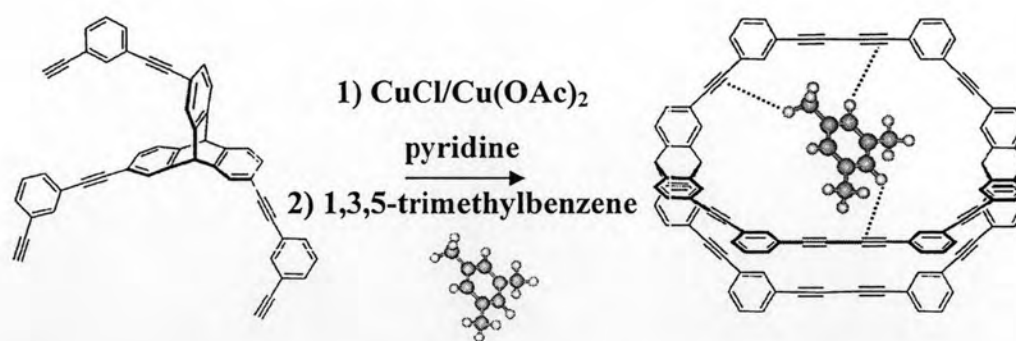
To study a cage molecule for storage and delivery of aromatic compounds, Chen et al. designed new molecular architectures based on the triptycene unit and efficiently synthesized a triptycene-based nanosized molecular cage (Scheme 1.3) by Eglinton-Glaser coupling reaction and they found that this cage molecule could pack into a microporous structure in the solid state and the trimethylbenzene molecules were located in the channels [29].



d) Mechanism



**Scheme 1.2** Homocoupling reaction: a) Glaser coupling reaction, b) Hay coupling reaction and c) Eglinton coupling reaction and d) Mechanism of homocoupling reaction.

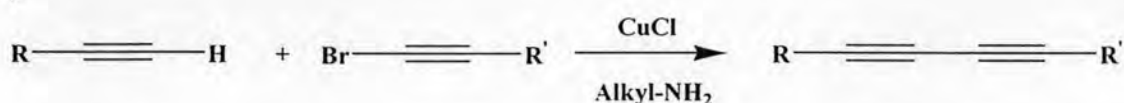


**Scheme 1.3** Synthesis of molecular cage based on the triptycene units [29].

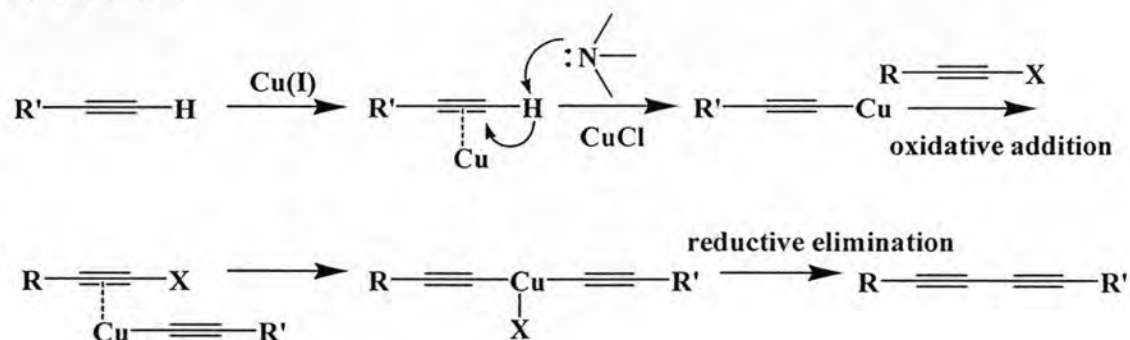
### - Cross-coupling reaction

The Cadiot-Chodkiewicz coupling of 1-bromo alkynes with terminal alkynes in the presence of copper(I) salt and an aliphatic amine has been reported to be a useful route to unsymmetrical 1,3-diynes (Scheme 1.4) [30].

a)



b) Mechanism

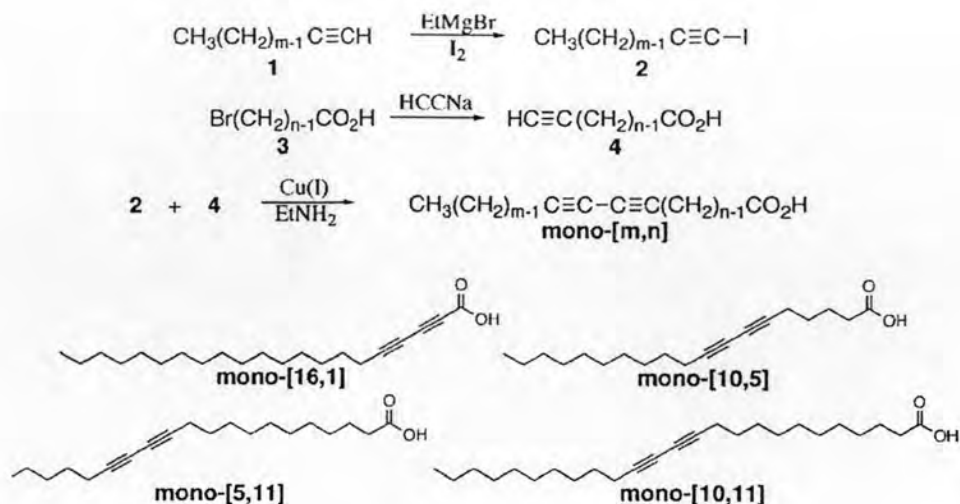


**Scheme 1.4** a) Cadiot-Chodkiewicz coupling reaction and b) Mechanism of cross-coupling.

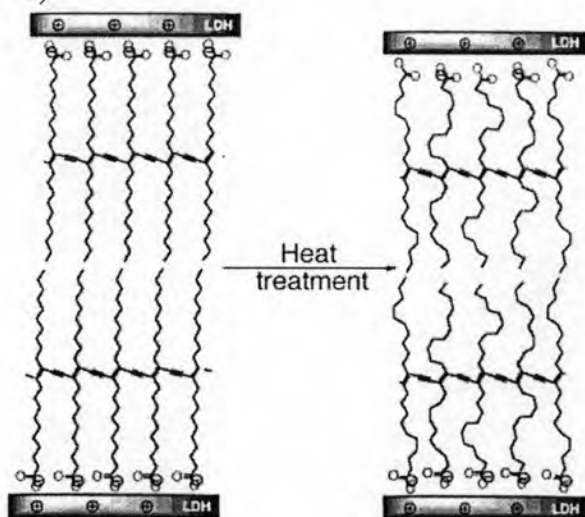
A series of diacetylenecarboxylic monomers (**mono-[m,n]**) were prepared by the condensation of 1-iodo-1-alkynes (**1**) with  $\omega$ -alkyne-1-carboxylic acids (**2**) by Cadiot-Chodkiewicz coupling in the presence of  $\text{Cu(I)}$  and ethylamine (Scheme 1.5a). Layered double hydroxide (LDH) clay hybrids of **poly-[m,n]/LDH** were formed upon polymerization by UV light or  $\gamma$ -ray irradiation [31]. Among the various hybrids investigated, the **poly-[10,11]/LDH** hybrid powder showed the most highly uniform lamella bilayer unit structure as well as the most efficient thermal reversibility, while **poly[10,11]** itself without LDH showed only an irreversible phase transition. This phenomenon was reasoned that poly(diacetylenecarboxylates) lamella sheets were strengthened and stabilized within the rigid sandwich framework of the alumina-magnesia octahedral sheets in the LDH clays (compare Scheme 1.5 b and c).



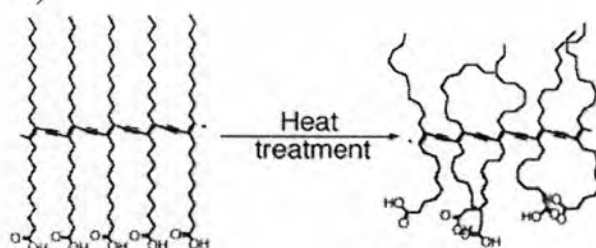
a)



b)



c)



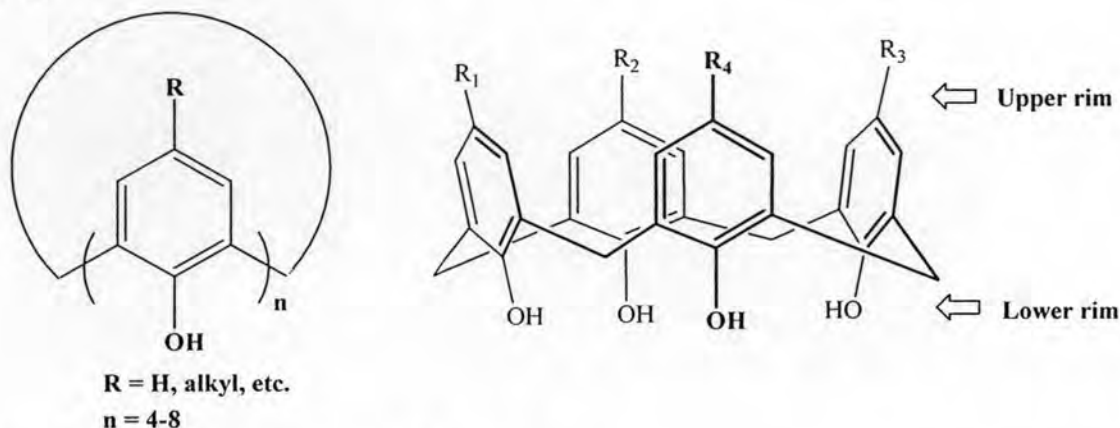
**Scheme 1.5** a) Synthesis of diacetylenecarboxylates or mono-[ $m,n$ ] and proposed drawings of the morphological changes in the lamella unit conformations upon heat treatment: b) Poly-[10,11]/LDH hybrid and c) Poly-[10,11] [31].

## 1.2 Calixarenes

### 1.2.1 Synthesis of calixarenes

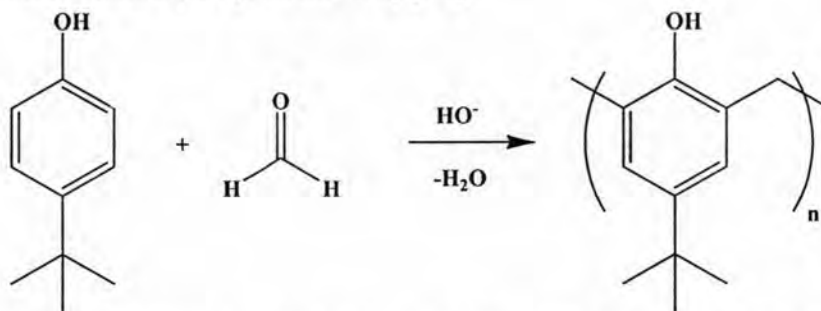
Calixarenes were systematically studied by Gutsche in 1970 and he proposed that these cyclic oligomers be known collectively as “calixarenes”, having recognized in space-filling models of the three-dimensional basket, cup or bucket shape with cavity inner diameter of 3.0, 7.6 and 11.7 Å for calix[4]arene, calix[6]arene and calix[8]arene, respectively [32]. Calixarenes are characterized by the region where the

*tert*-butyl groups are located is called the “upper rim” or “wide rim” and the region where the four hydroxyl groups lie is called the “lower rim” or “narrow rim” (Figure 1.4).



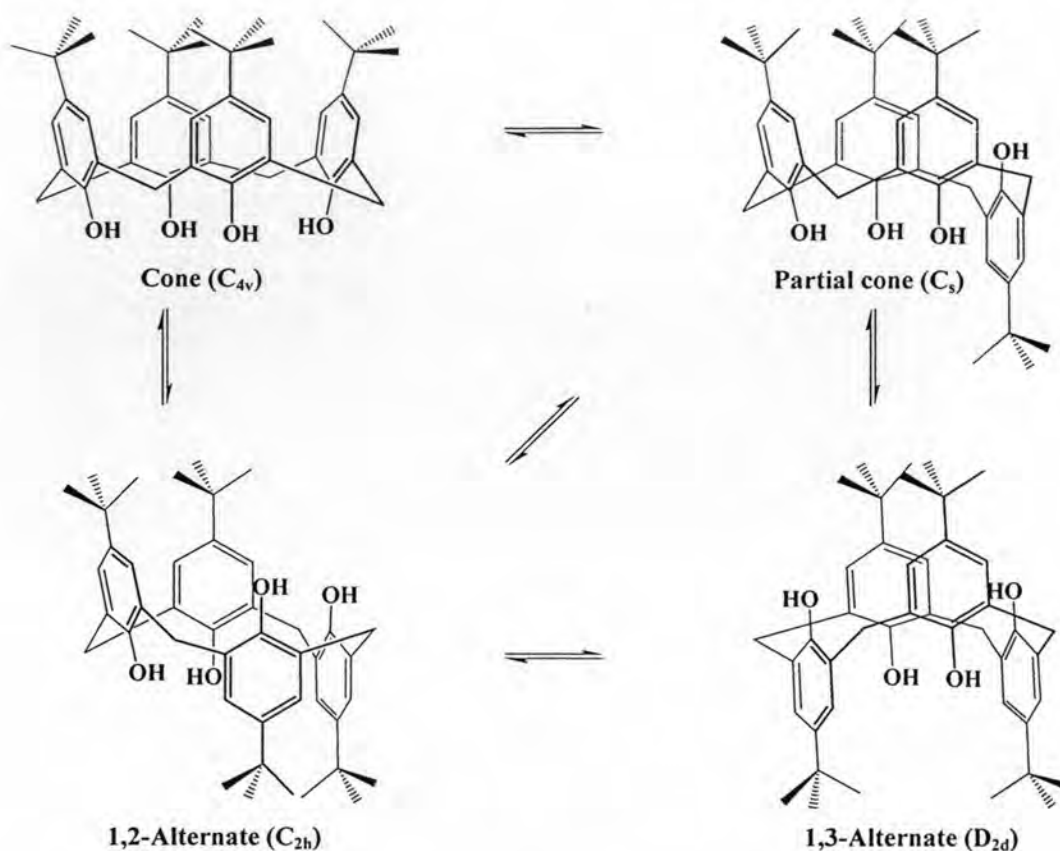
**Figure 1.4** General structures of calixarenes

These cyclic oligomers contain various number of repeating units. The calix[n]arene thus means calixarene that contain n repeating units. Calix[4]arenes are a macrocycle or cyclic oligomer based on a condensation product of a *tert*-butylphenol and formaldehyde (Scheme 1.6) [33].



**Scheme 1.6** Synthesis of calix[n]arene from condensation of phenol and formaldehyde.

The solid-state structure of *tert*-butylcalix[4]arene adopts a vase-like arrangement called the “cone” conformation with idealized structure having  $C_{4v}$  symmetry (Figure 1.5). In this conformation, all four phenolic groups point to the same direction. Rotation of the *tert*-butyl groups through the upper rim is prohibited in calix[4]arenes, but is possible in calixarenes with larger rings. However, rotation of the hydroxyl group through the lower rim is permitted, which results in three other conformations: partial-cone, 1,2-alternate and 1,3-alternate with  $C_s$ ,  $C_{2h}$  and  $D_{2d}$  symmetry, respectively.



**Figure 1.5** Four interchangeable conformations of *tert*-butylcalix[4]arene.

In solid state, calix[4]arene and *tert*-butylcalix[4]arene stay solely in the cone conformation due to the stabilization by four intramolecular hydrogen bonding. In solution, however, the four conformations are interchangeable. The interconversion is generally slow at room temperature but becomes rapid at high temperature, as evidenced by NMR spectroscopy. Since the interconversion among the calix[4]arene conformations originates from the lower rim rotation, bulky substituents on phenolic hydroxyl group can prevent the rotation that locks the conformers into rigid isomers. Experiments were performed to attach groups of different sizes to the hydroxyl group and test the mobility of the calix[4]arenes. It was found that the tetramethyl [34], tetraethyl [35] and tetrakis(cyanomethyl)ethers [36] of calix[4]arene are all conformationally mobile, while the tetrapropyl ether [35] was conformationally rigid even at elevated temperature. Therefore, *O*-substituted groups larger than ethyl can lock the conformation of calix[4]arenes into four stereoisomers. Another interesting point is that partially etherified calix[4]arenes are less flexible than the corresponding fully etherified calix[4]arenes. This is attributed to the existence of intramolecular hydrogen bonding formed between the remaining hydroxyl groups.

### 1.2.2 Chemical modification of calix[4]arene

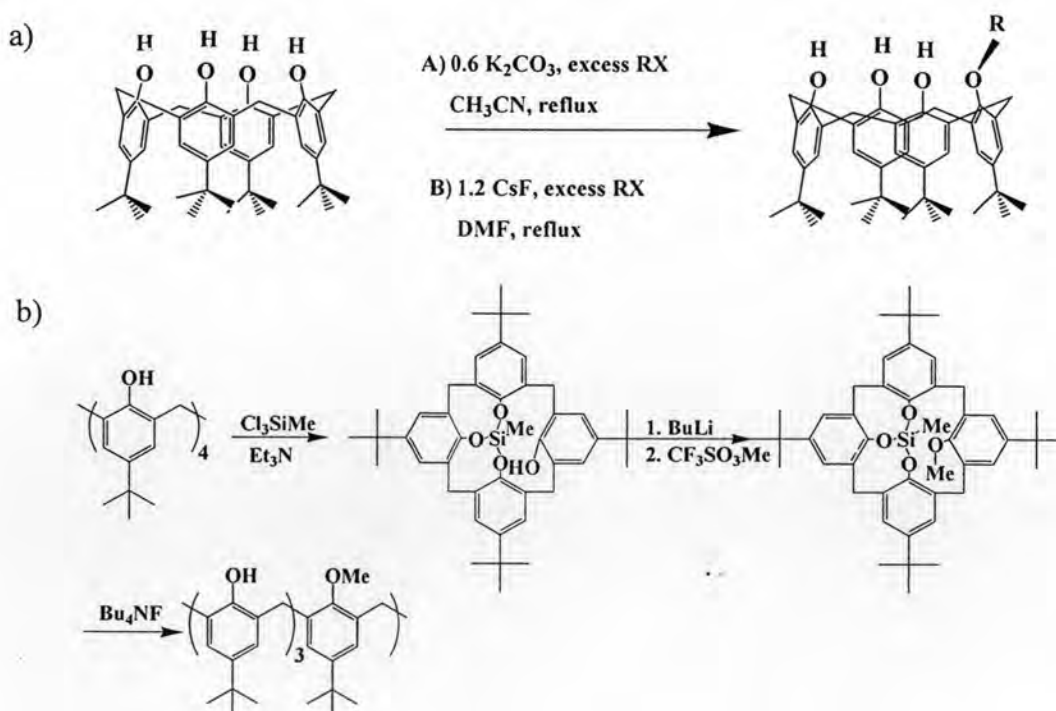
#### - *O*-Alkylation and *O*-acylation of calix[4]arenes

##### Mono-ethers and -ester

Monoethers of calix[4]arenes have been prepared by the reaction with an excess amount of the alkylating agent under controlling equivalent of a weak base such as  $K_2CO_3$  (1.2 equivalent in  $CH_3CN$ ) or  $CsF$  (1-1.2 equivalent in DMF) (Scheme 1.7a) [37]. However, direct *O*-alkylations with  $NaH$  in toluene [38] or  $CH_2Cl_2$  [39] and  $Ba(OH)_2$  in DMF [38, 40] have also been reported.

The controlled cleavage of 1,3-diethers or tetraethers by trimethylsilyl iodide (1 or 3 mol) has also been reported [41]. *O*-alkylation of mono- or triesters and subsequent hydrolysis of the ester groups offers another rational access [42]. Reaction of *tert*-butylcalix[4]arene with tris(dimethylamino)methylsilane or trichloromethyl silane has been used to protect three OH-functions. Methylation of the remaining fourth OH group ( $BuLi/TFA-OMe$ ) and cleavage of the silyltriether gave the mono methylether in 83% over all yield (Scheme 1.7b) [43].

Monoesters have been obtained by direct acylation [44] from 1,3-diethers by reaction with imidazole [45] or from mono- and 1,3-dibenzyl ethers by acylation and subsequent hydrogenolysis of the benzyl protective groups [46].

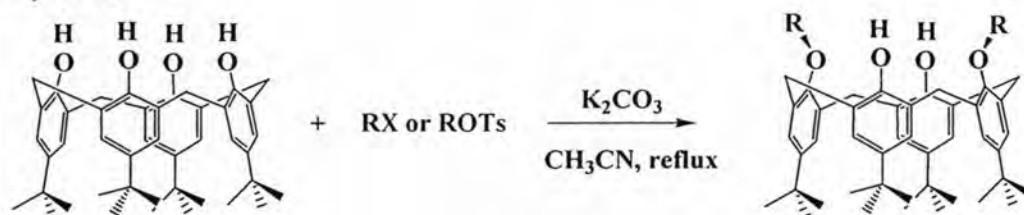


**Scheme 1.7** The synthesis of monosubstituted calix[4]arene [37, 43].

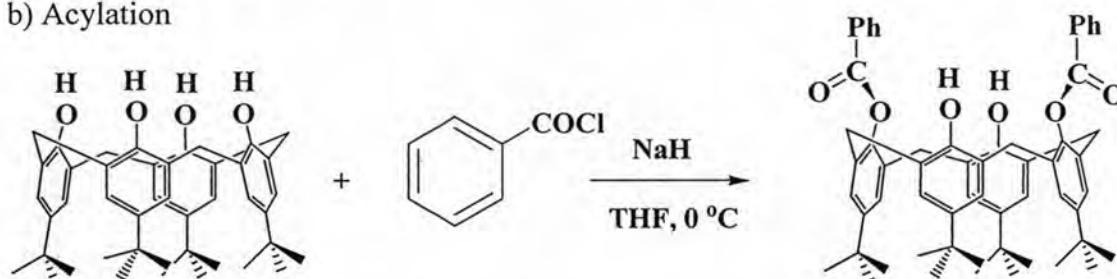
### 1,3-Difunctionalization

Numerous 1,3-diethers with a syn-arrangement of the ether groups have been synthesized, and this derivatization may be considered as one of the standard reactions of calix[4]arenes (Scheme 1.8a) [47]. Usual conditions use sodium or potassium carbonate as a base in refluxing acetone or acetonitrile, but the reaction seems to tolerate many variations of these conditions. The strong tendency for the 1,3-di-*O*-alkylation can be rationalized by the stabilization of the corresponding monoanion of the monoether by two intramolecular hydrogen bonds and by steric reasons. Cone-1,3-diester are easily available for similar reasons, including examples with different ester groups (Scheme 1.8b) [48].

#### a) Alkylation



#### b) Acylation

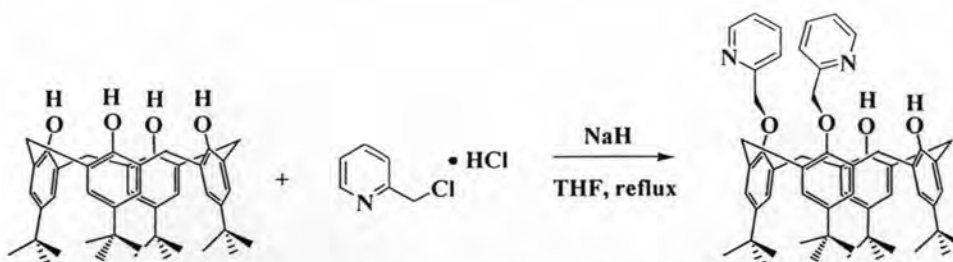


**Scheme 1.8** The synthesis of 1,3-disubstituted calix[4]arene [47, 48].

### 1, 2-Difunctionalization

The *O*-alkylation of two adjacent hydroxyl groups is less favored. Usually it requires a very strong base in excess (e.g. NaH in DMF/THF) to form dianion of the intermediate monoether, in which (most probably) for electrostatic reasons two opposite hydroxyl groups are deprotonated. Even in the trianion the 1,2-diether would be statistically favoured over the 1,3-diether, which in turn might be sterically favoured. The extent of the *O*-alkylation is then stoichiometrically controlled by the equivalents of alkylating agent applied, practically 2.2 equivalents. Various syn-1,2-diethers have been prepared by such direct dialkylation in yields of up to 90% in special case [49] (Scheme 1.9) including 1,2-crown ethers [50].

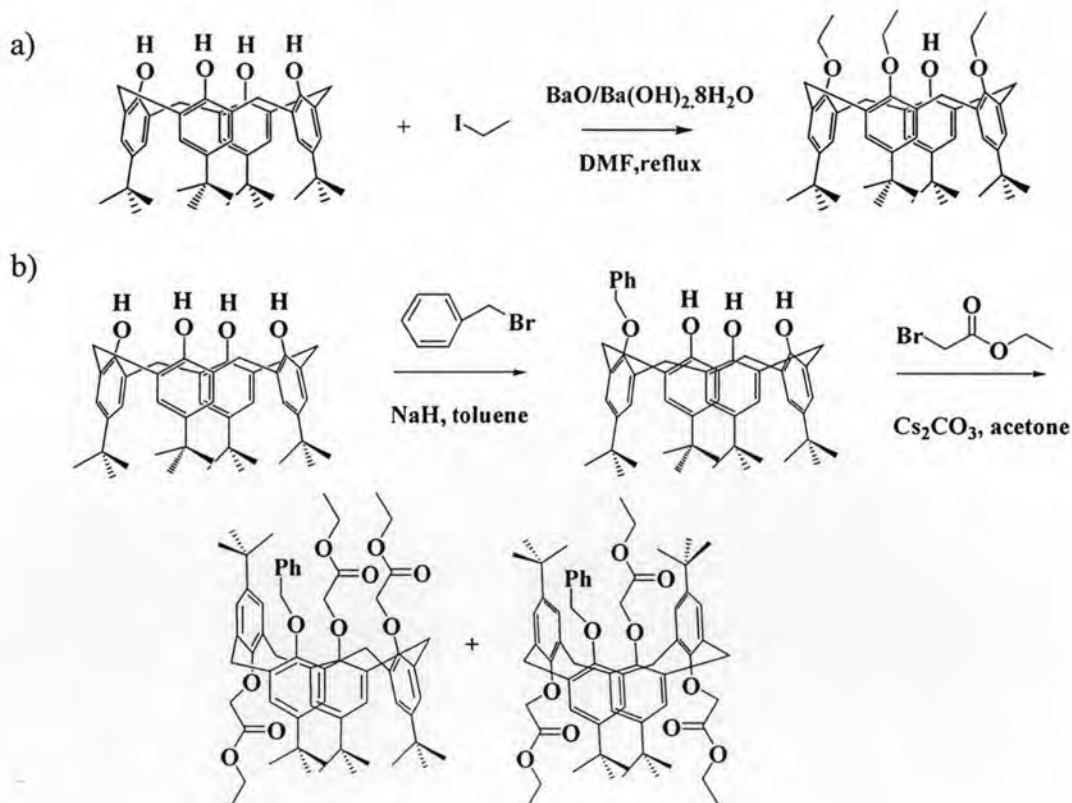




**Scheme 1.9** The synthesis of 1,2-disubstituted calix[4]arene [49].

### Trifunctionalization

Triethers can be easily prepared by *O*-alkylation with alkyl iodides using BaO/Ba(OH)<sub>2</sub> as a base in DMF (Scheme 1.10a) [51]. Tri-*O*-alkylation of *tert*-butylcalix[4]arene with *tert*-butyl-bromoacetate was achieved with using CaH<sub>2</sub> in DMF [52]. The partial cone and 1,3-alternate isomers of triether calix[4]arene have been prepared mainly via tetraether, using the benzylether group as protective group (Scheme 1.10b) [51]. The synthesis of partial cone-tripropylether of *tert*-butylcalix[4]arene can be also achieved by tri-*O*-alkylation of *tert*-butylcalix[4]arene with propyl bromide using Cs<sub>2</sub>CO<sub>3</sub> as a base [51b].

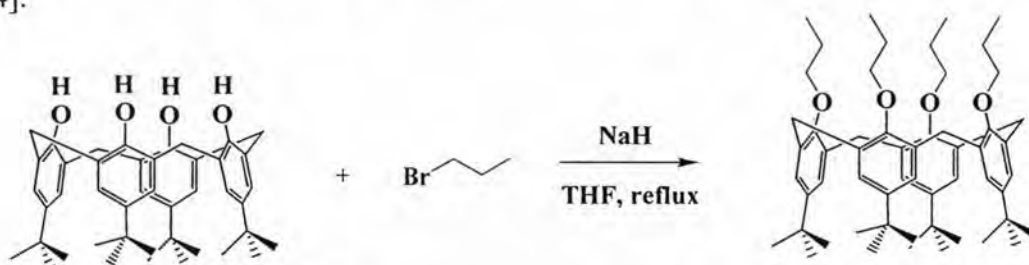


**Scheme 1.10** The synthesis of a) trisubstituted calix[4]arene [51] b) partial cone and 1,3-alternate isomers of triether derivatives via tetraethers [53].

### Tetrafunctionalization

Direct tetra-*O*-alkylation of calix[4]arenes may lead to four stable stereoisomers, if residues longer than ethyl are introduced. Among them derivatives in the cone and in the 1,3-alternate conformation are the most common basic building blocks for more sophisticated structures or self assembled, but all four possible isomers have been prepared in many cases [53]. Often, however, the isolation of a certain conformer requires extensive chromatographic separation techniques.

Usually the cone isomer is formed in the presence of  $\text{Na}^+$  cations.  $\text{Na}_2\text{CO}_3$  in acetone or acetonitrile is often used for reactive alkylating agents such as bromo- or chloro-acetates, -acetamides or -ketones ( $\text{X-CH}_2\text{-CO}_2\text{-R}$ ), while NaH in DMF or THF/DMF is the standard base for alkylbromides, -iodides or tosylates (Scheme 1.11) [54].



**Scheme 1.11** The synthesis of tetrasubstituted calix[4]arene [54].

Although a general set of conditions for each isomer is not available, a general guideline is that a larger alkali cation ( $\text{K}^+$  or  $\text{Cs}^+$ ) favours the formation of partial cone and 1,3-alternate isomers for the *O*-alkylation. For example, replacement of  $\text{Na}_2\text{CO}_3$  by  $\text{Cs}_2\text{CO}_3$  leads to the quantitative formation of the partial cone isomer instead of the cone isomer in the alkylation of *tert*-butylcalix[4]arene with ethylbromoacetate in refluxing acetone [55]. Alkylation of *tert*-butylcalix[4]arene with propyl bromide (*t*-BuOK/benzene/reflux) leads to a 1:1 mixture of the partial cone and 1,3-alternate isomers [54]. Use of  $\text{KOSiMe}_3$  or  $\text{K}_2\text{CO}_3$  gives predominantly the tetrabenzylether in the partial cone isomer [56]. Usually, the 1,2-alternate isomer is the most difficult to obtain [57].

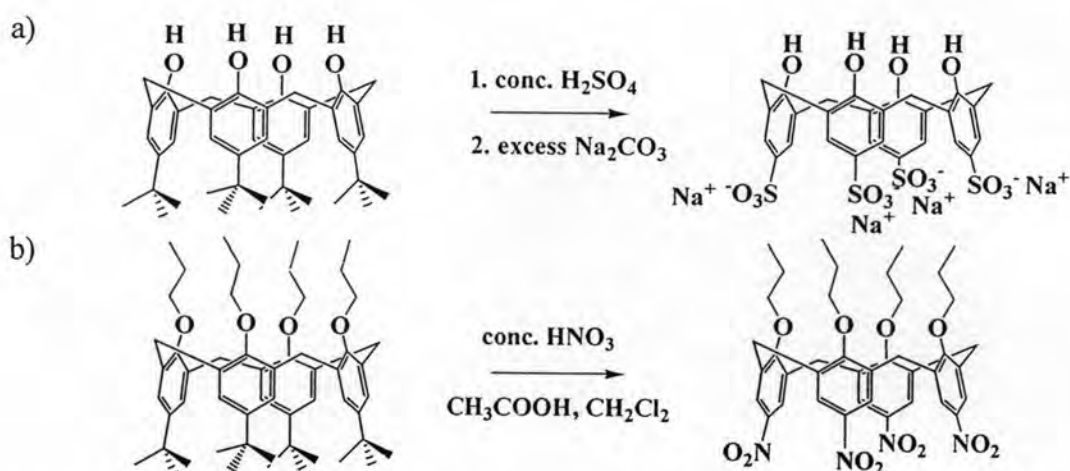
Derivatives in the cone conformation have been also obtained with four rather bulky substituents attached to the oxygen, such as  $\text{R} = \text{P}(\text{C}_6\text{H}_5)_2$  [58] or  $\text{R} = \text{CH}(\text{CO}_2\text{Et})_2$  [59]. Calixarene derived dendrimers of the Frechet-type are probably the most impressive examples for the introduction of four very bulky *O*-alkyl groups in a cone isomer [60].

## - Substitution on the wide rim

### Ipsso substitution of *tert*-butylcalix[4]arene

Atwood [61] synthesized the pentasodium salt of calix[4]arene sulfonate in 80% yield by reacting *tert*-butylcalix[4]arene directly with concentrated sulfuric acid followed by addition of a large excess of  $\text{Na}_2\text{CO}_3$  (Scheme 1.12a). The tetra ipso-acetylation of *tert*-butylcalix[4]arene in  $\text{CH}_2\text{Cl}_2$  with phenol as an acceptor gave the corresponding tetraacetyl calix[4]arene ( $\text{R} = \text{C}(\text{O})\text{CH}_3$ ). Exhaustive nitration of *tert*-butylcalix[4]arene with conc.  $\text{HNO}_3$  or  $\text{KNO}_3/\text{AlCl}_3$  leading to tetranitro calix[4]arene in excellent yield was also reported [62].

The reaction of various tetraethers (cone, partial cone, 1,3-alternate) with 100%  $\text{HNO}_3$  in  $\text{CH}_2\text{Cl}_2/\text{AcOH}$  at room temperature led to the corresponding tetranitro compounds in high yields (Scheme 1.12b) [54].



**Scheme 1.12** The synthesis of a) tetrasulfonic acid [61] b) tetranitro calix[4]arene [54].

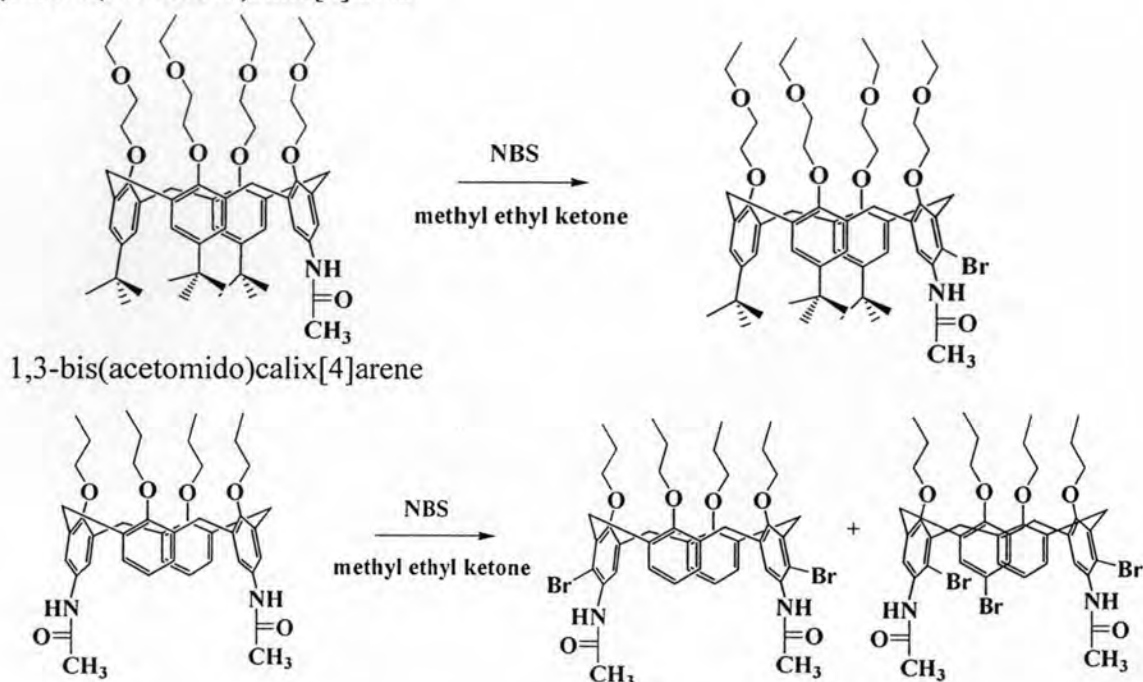
## Electrophilic substitutions of free position on phenyl ring

### Halogenation

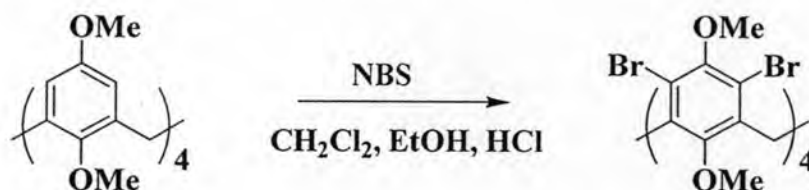
The phenol units in partially *O*-alkylated calix[4]arenes can be selectively brominated. The selective bromination of mono- and 1,3-bis(acetamido)calix[4]arene tetraethers (NBS, methylethylketone, RT) occurs at *m*-position (ortho to the acetamido groups), leading to inherently chiral derivatives (Scheme 1.13a) [63].

Surprisingly the meta-position is preferred even over the para-substitution of free phenoylether units. The exhaustive bromination was reported for the hydroquinone-octamethylether in moderate yields (Scheme 1.13b) [64].

a) mono(acetomido)calix[4]arene



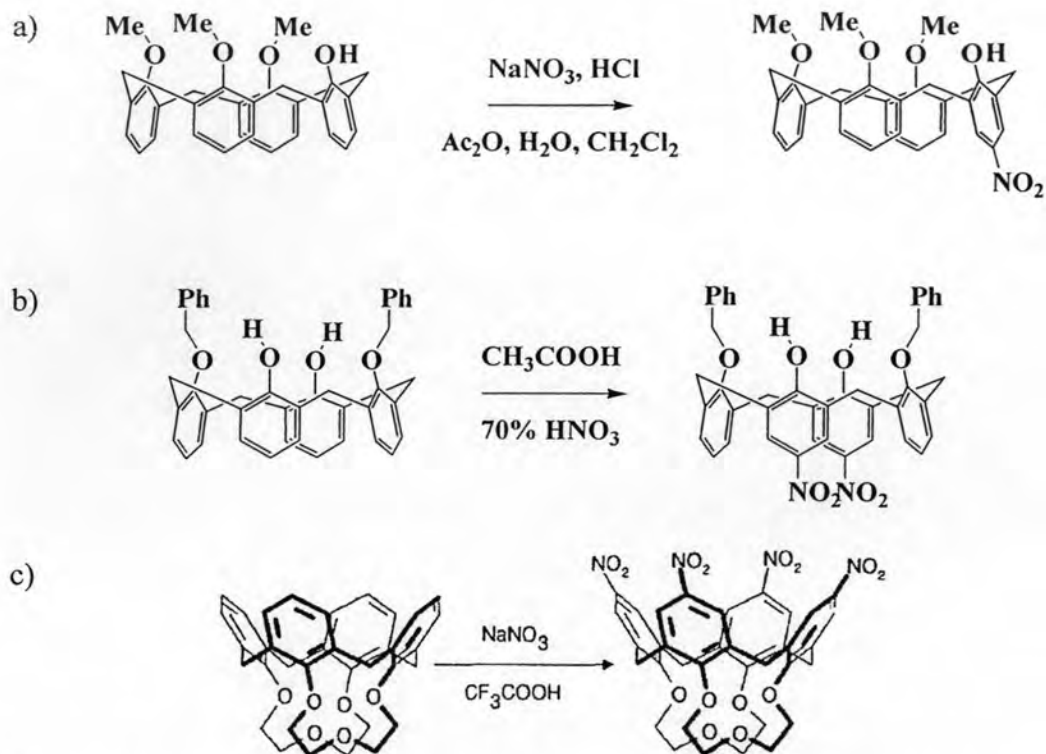
b)



**Scheme 1.13** The bromination of meta-position on phenyl ring substituted with a) acetamido [63] b) methoxy groups [64].

### Nitration

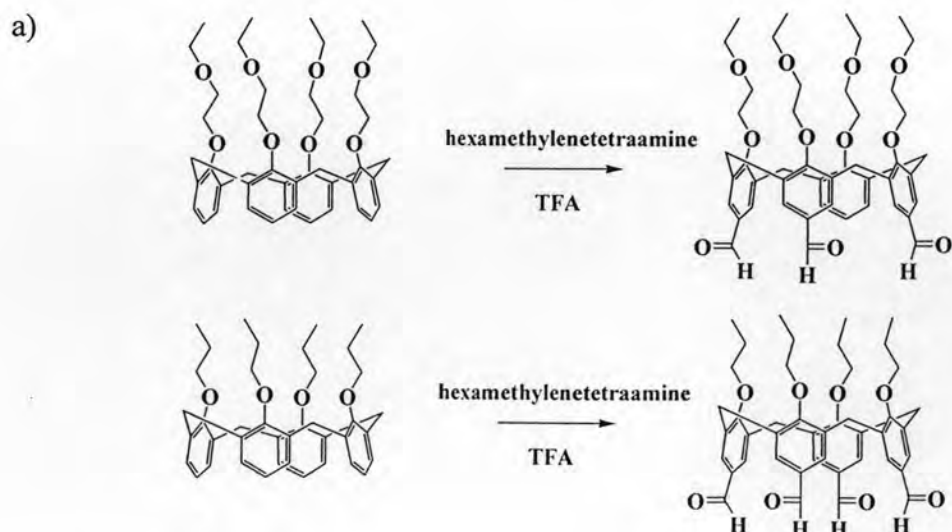
The selective mono-nitration was reported for the trimethyl ether of calix[4]arene (NaNO<sub>3</sub>/HCl) [65] as well as for other triethers and also for various triesters (Scheme 1.14a). Diethers [66] as well as the calix[4]arene dicarbonate and ditosylate [67] have been selectively dinitrated in the para-position of their phenolic units (Scheme 1.14b) and a selective trinitration of mono ethers or esters should also be possible. Ester and carbonate groups can be subsequently cleaved and the deprotected phenolic units can undergo further electrophilic substitution reactions. The tetra-nitration of 1,2;3,4-bis(crownethers) (NaNO<sub>3</sub>/TFA) may be mentioned as an example for the exhaustive nitration (Scheme 1.14c) [68].



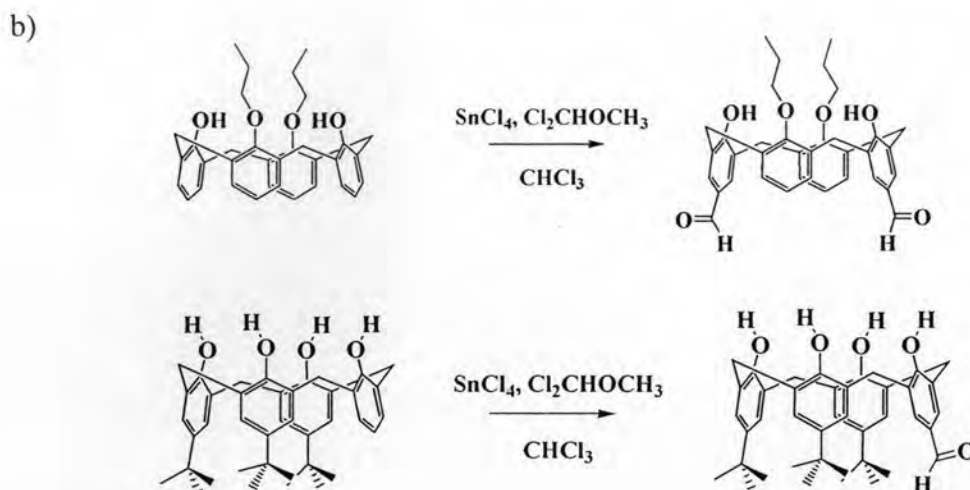
**Scheme 1.14** a) Mono-nitration [65] b) Di-nitration [66] c) Tetra-nitration of calix[4]-arene [68].

### Formylation

The Duff reaction (hexamethylenetetramine/TFA) was used for the triformylation ( $R = (\text{CH}_2)_2\text{OEt}$ ) [69] and the tetraformylation ( $R = \text{C}_3\text{H}_7$ ) (Scheme 1.15a) [70]. The selective diformylation of 1,3-diethers ( $\text{SnCl}_4/\text{Cl}_2\text{CHOCH}_3/\text{CHCl}_3/15\text{ }^\circ\text{C}$ ) was also reported [71], as well as the monoformylation of tris-*tert*-butylcalix[4]arene (Scheme 1.15b) [72].







**Scheme 1.15** a) The formylation of tetraether calix[4]arene [70, 71] b) The selective formylation of dipropyl calix[4]arene and tris(*tert*-butyl)calix[4]arene [72, 73].

### 1.2.3 Calix[4]arene self assembly in solution

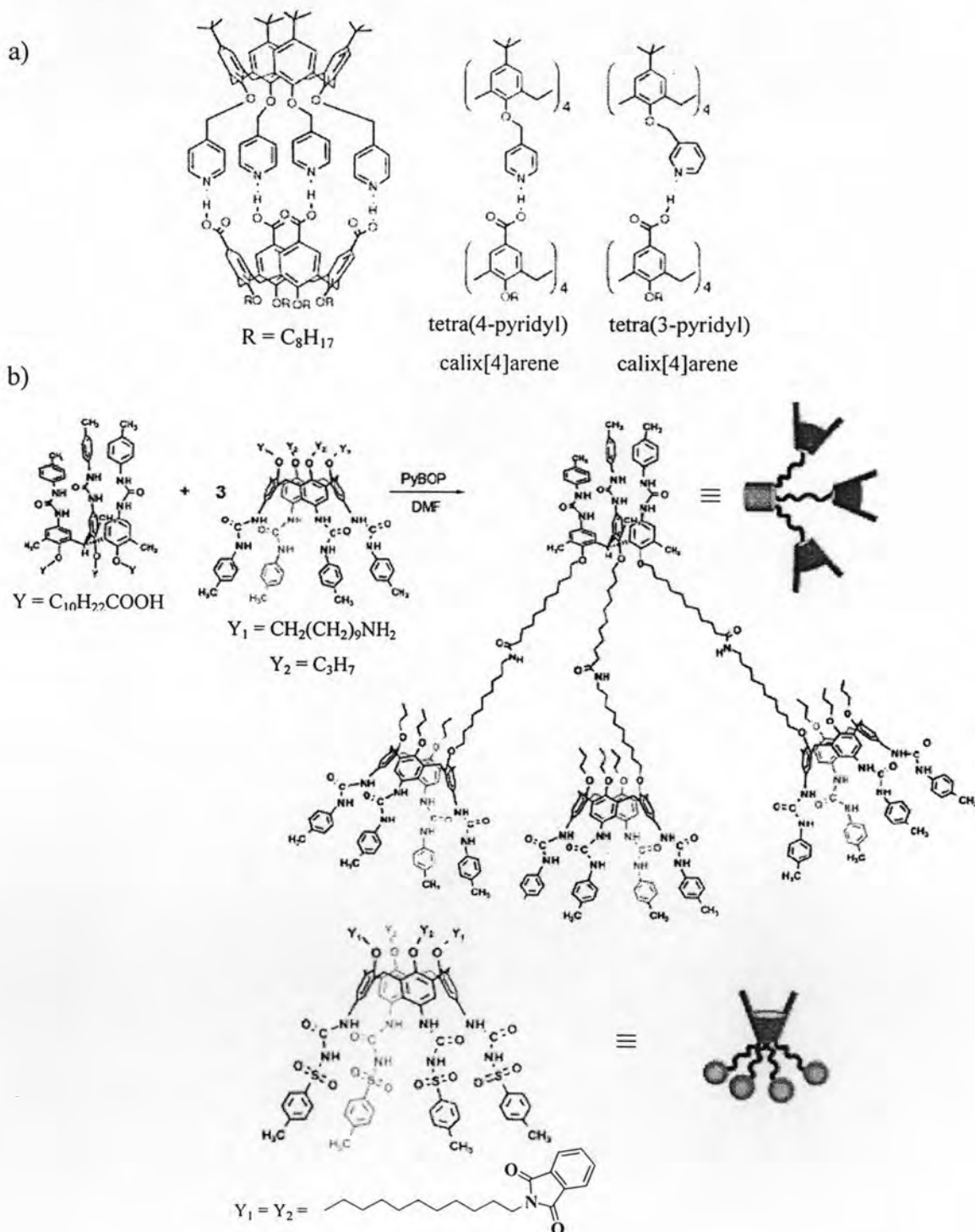
Self-assembly is the spontaneous noncovalent association of two or more molecules under equilibrium conditions into stable, well-defined aggregates [73]. Intermolecular forces are capable of effectively organizing multicomponent supramolecular assemblies in a reversible and accurate fashion using error-correcting mechanisms. Self-assembly provides a novel, rapid way to construct complex nanostructures, receptor systems, catalysts and new materials. Calixarenes, in particular have had a great impact in the history of self-assembly [32]. Their three dimensional concave surface, commercial availability, relatively rigid structure and well-developed synthetic chemistry have made them very attractive platforms for elaboration [74].

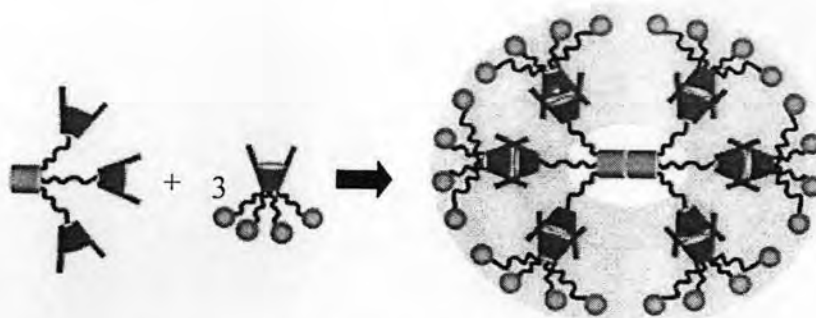
#### - Assembly through hydrogen bonding

##### Dimers without guests

Hydrogen bonding is near-ubiquitous as a force in self-assembly. It is highly directional, specific and, of course, biologically relevant. The interaction between the tetracarboxylic acid calix[4]arene leads to formation of well-defined hydrogen-bonded 1:1 associates with the tetra(4-pyridyl)calix[4]arene and the tetra(3-pyridyl)calix[4]arene (Figure 1.6a). These formations are confirmed by  $^1\text{H}$  NMR and IR spectroscopy, together with VPO (vapor pressure osmometry) measurements [75].

Various attempts to obtain dendrimers via self-assembly have been reported which focus on hydrogen-bonded assemblies. Only recently a first approach was published in which the whole dendritic assembly was built up, shell by shell, in a self-assembly process [76]. It was based on a single complementary pair of hydrogen-bonding motifs -A and B- forming an -AB- assembly. Self-assembled dendrimers are formed by mixing a tripodal core  $A_3$  with a branched linker  $BA_2$  and a capping unit B in the required ratio (Figure 1.6b) [77].

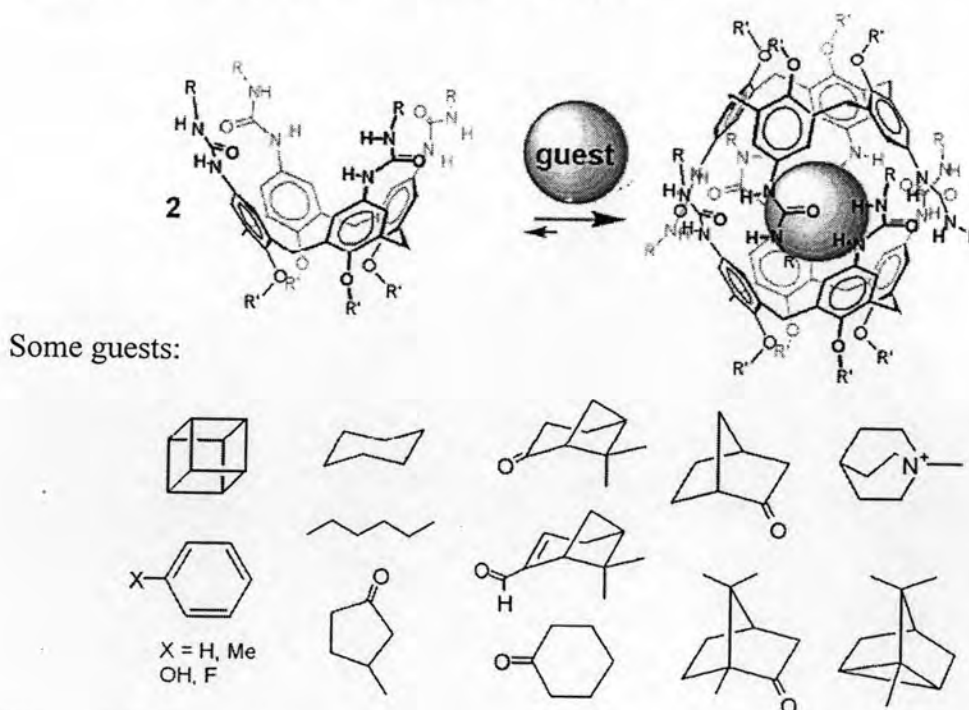




**Figure 1.6** a) The formation of a 1:1 complex of tetracarboxylic acid and tetra-(pyridyl)calix[4]arene [75] b) The representation of a dendrimer self-assembled of two molecules of calixarenes substituted with urea and six molecules of calixarene substituted with phthalimide groups [77].

### Capsules

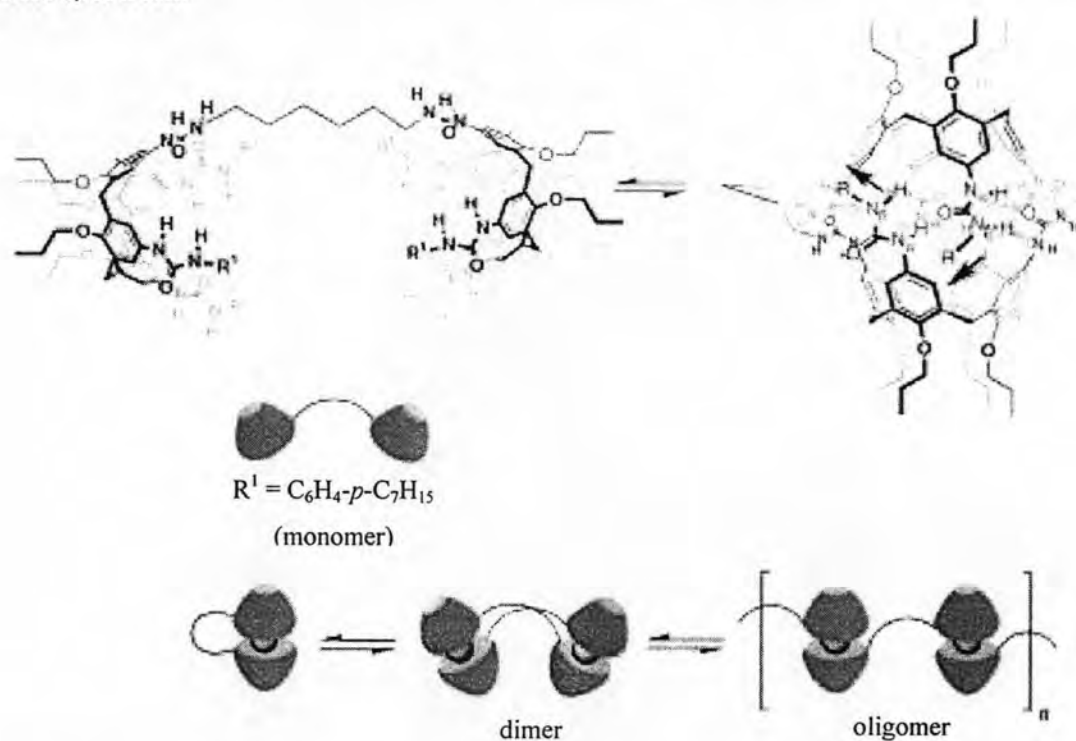
With appropriate curvature and carefully engineered positioning of hydrogen bonding sites, calixarene self-assembling systems generate capsules. By definition, self-assembling capsules are receptors with enclosed cavities which are formed through the reversible noncovalent interactions between two or more subunits [78]. Tetraurea calix[4]arene was found forming hydrogen-bonded dimeric capsules when an appropriated guest is present (Figure 1.7) [79].



**Figure 1.7** The calix[4]arene bearing ureas on the upper rim forms a dimeric capsule when an appropriate guest is present [79].

### Strapped dimers

In unimolecular capsule (Figure 1.8), two calix[4]arene tetraureas are covalently connected via their upper rim [80]. When the linker is short enough to minimize the loss of entropy due to restriction of freely rotating single bonds, stronger dimerization is expected. With the hexamethylene  $-(\text{CH}_2)_6-$  spacer, only the intramolecularly folded capsule **1** was detected by ESI MS. For detection, the *N*-methyl quinuclidinium cation (as its  $\text{BF}_4^-$  salt) was encapsulated and provided a charge for the whole complex in the gas phase. In  $\text{CDCl}_3$  solution, signals for the encapsulated quinuclidinium CH protons appeared upfield at  $\delta = -0.2$  to  $-0.4$  in the  $^1\text{H}$  NMR spectrum.

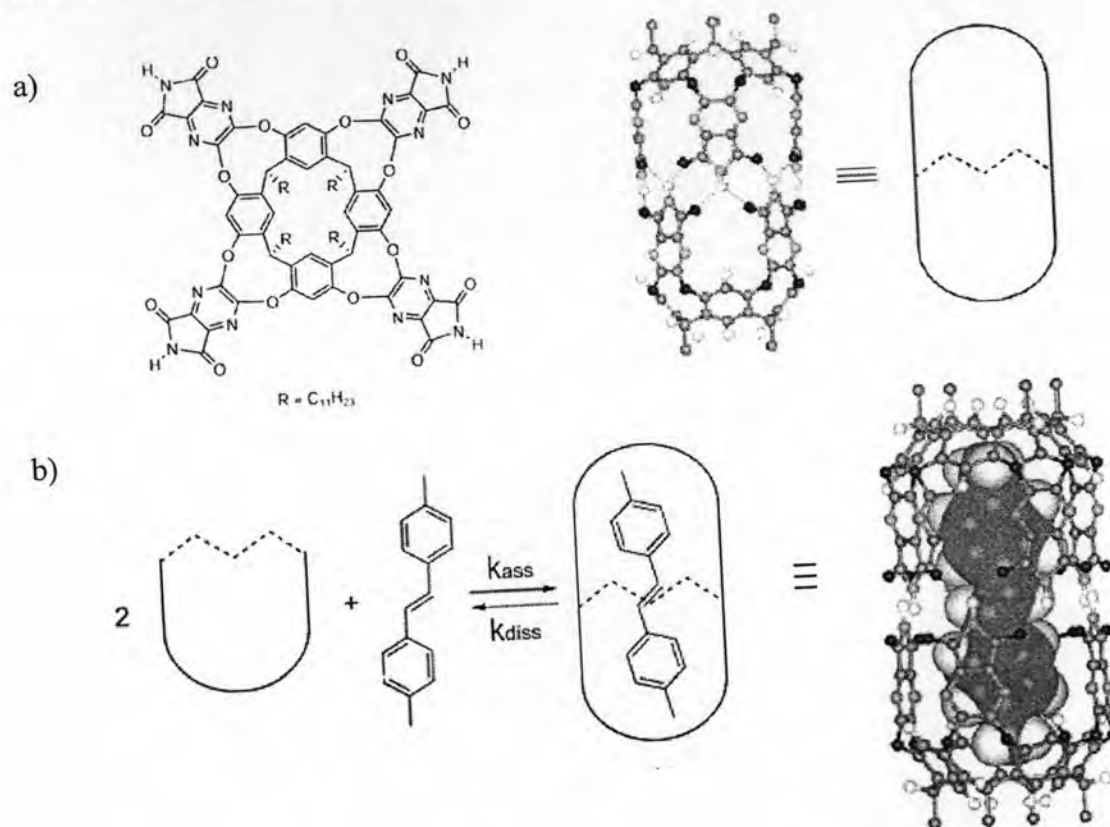


**Figure 1.8** Bridge calix[4]arene dimer and the different options for its self-assembly [80].

### Large dimeric capsules

Self-complementary cyclic tetraimides built on the resorcinarene platform dimerize through hydrogen bonding to afford a cylindrical capsule of tetraimide calix[4]arene (Figure 1.9) [81]. The imides are stabilized by a seam of eight bifurcated  $\text{C}=\text{O}\cdots\text{H}-\text{N}$  hydrogen bonds. 4,4'-Dimethylstilbene was easily encapsulated inside. Only slight dissociation was found in the presence of  $\sim 2500$  equiv of methanol, and

some assembly was seen even in a 50% methanol solution (v/v in mesitylene). From the investigation through conventional  $^1\text{H}$  NMR methods, the encapsulation process is entropy-driven (positive  $\Delta S$ ), even though the two halves of the capsule must come together (must associate), and guest exchange occurs by complete dissociation of the capsule in the presence of protic solvents.



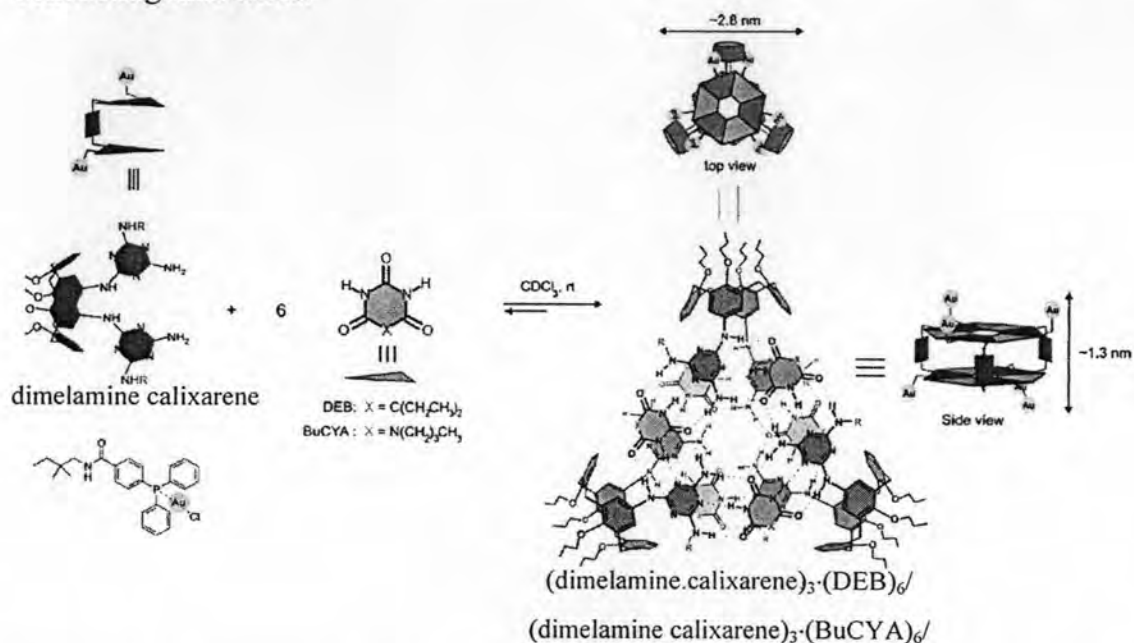
**Figure 1.9** a) The ball-and-stick model of the cylindrical capsule of tetraimide calix[4]arene b) Equilibrium of encapsulation of two molecules of tetraimide calix[4]arene [81].

### Rosettes

The supramolecular assemblies were conformed together by the formation of hydrogen bonding between the donor-acceptor-donor (DAD) array of calix[4]arene dimelamine derivatives and the acceptor-donor-acceptor (ADA) array of the BAR(barbituric acid) or CYA(cyanuric acid) building blocks (Figure 1.1) [82]. Reinhoudt et al. compared hydrogen-bonded assemblies of gold-functionalized rosette assemblies (dimelamine calixarene) $_3$ ·(DEB) $_6$  (DEB = 5,5-diethylbarbituric acid) and (dimelamine calixarene) $_3$ ·(BuCYA) $_6$  (BuCYA = butylcyanuric acid) on highly



oriented pyrolytic graphite (HOPG) surfaces. These systems make them very suitable for many applications in material science due to the structural flexibility. Also, these assemblies containing metal atoms (gold atoms) may function as potential templates for metal alignment leading to new methods for the fabrication of electrically conducting nanowires.

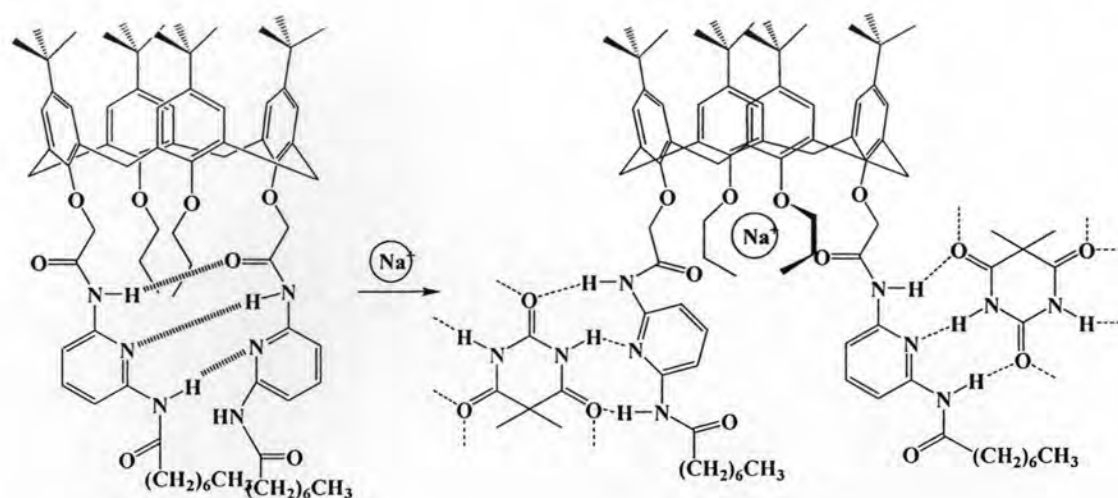


**Figure 1.10** Representation for the formation of the gold-functionalized (dimelamine calixarene) $_3$ ·(DEB) $_6$  and (dimelamine calixarene) $_3$ ·(BuCYA) $_6$  rosette assemblies [82].

### - Metal induced self assembly

#### Assembly of receptors

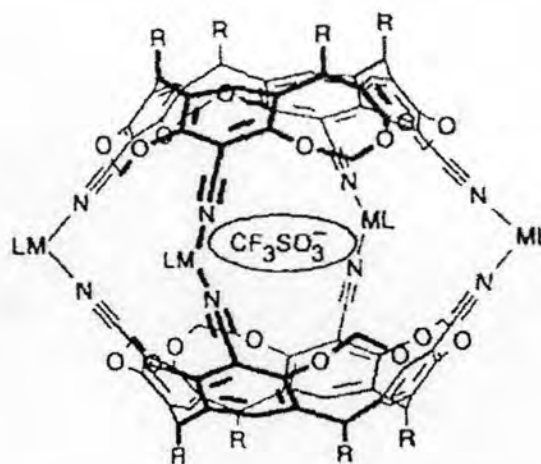
The high affinity of some calixarene receptors towards cations has been effectively used to control the hydrogen bonding assembly processes and switch the equilibrium between the monomer and polymeric self-assembled clusters. Thus, sodium cation (as perchlorate salt) triggers the assembly of bis(2,6-diaminopyridine)calix[4]arene functionalized with two 2,6-diamidopyridine fragments with complementary dialkylbarbiturates in  $\text{CDCl}_3$  and 9:1  $\text{CDCl}_3$ - $\text{CD}_3\text{CN}$  mixture (Figure 1.11) [83]. In the absence of  $\text{Na}^+$ , diaminopyridine moieties are involved in intramolecular hydrogen bonding with the calixarene ether oxygens. Addition of  $\text{Na}^+$  disrupts the intramolecular hydrogen bonding, the carbonyl oxygen atoms turn around to coordinate the cation, thus exposing the diamidopyridine for intermolecular binding.



**Figure 1.11** Hydrogen bonding assemblies of bis(2,6-diaminopyridine)calix[4]arene based receptors [83].

#### Association via coordination

Metal-ligand binding is generally much stronger than hydrogen bonding and very well suited for self-assembly. Metal-induced assemblies are usually robust, although their strength can be controlled by solvent polarity and pH. They can be charged and redox-active. In addition, they may operate in much more polar solution or even in water. Early examples of this type includes tungsten-oxo calix[4]arenes aggregate in a head-to-tail columnar fashion with a W=O group protruding into the cavity of another calixarene [84]. Further progress in this field was probably stimulated by the successful synthesis of hydrogen-bonded capsules. Metal-induced capsular self-assembly tetracyano cavitand (Figure 1.12) of deep cavitands was first described by Jacopozi and Dalcanale [85] Two tetracyano cavitands were connected through four square-planar Pd(II) or Pt(II) entities in  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  and acetone. Evidence of encapsulation of one triflate anion upon dimerization was observed by  $^{19}\text{F}$  NMR. For the Pt (II) case, the assembly process was shown to be reversible:  $\text{Et}_3\text{N}$  dissociated the capsule, while the addition of trifluoroacetic acid restored it.



M = Pd, Pt and L = dppp

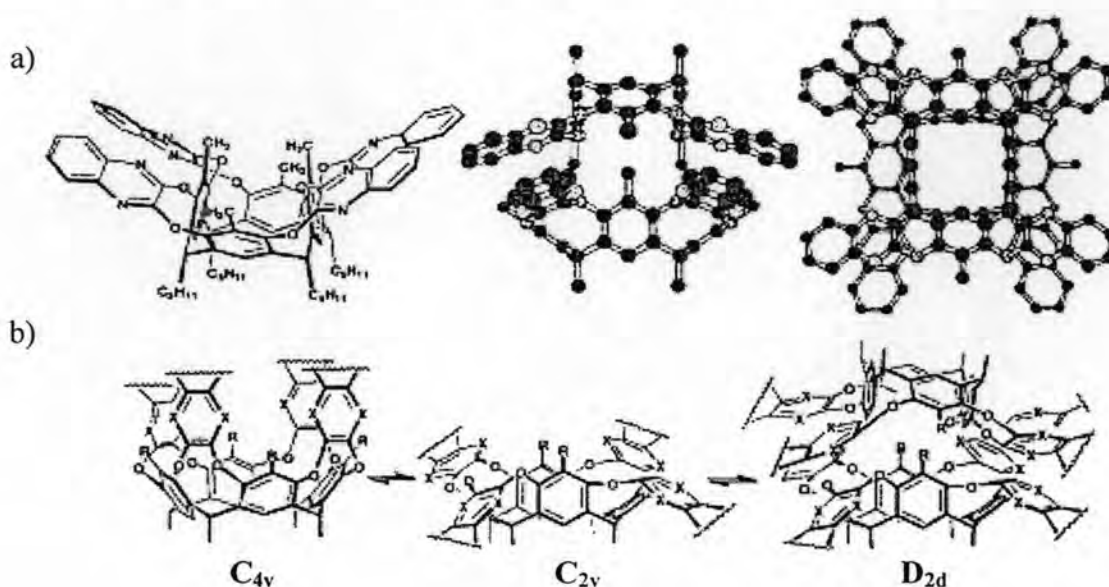
(dppp = 1,3-bis(diphenylphosphino)propane)

**Figure 1.12** Metal-induced self-assembly of capsule of tetracyano cavitand [85].

#### - Assembly through solvophobic forces

Even weaker forces, Van der Waals, CH/ $\pi$  interactions, solvophobic forces, etc. can be used to induce self-assembly. Solvophobic dimerization of Cram's velcrands was perhaps the earliest example of calixarene self-assembly [86]. When the oxygen atoms in 2'-methylresorcinarenes are bridged with heteroarylene units (e.g. pyrazines or quinoxalines), extended structure result (Figure 1.13a). Only the  $C_{2v}$ -symmetrical conformer was observed: the presence of the 2'-methyl substituent sterically destabilized the  $C_{4v}$ -symmetrical vase shape. The kite-shaped  $C_{2v}$ -symmetrical conformer resorcinarene-a velcrand tends to dimerize in organic solution through solvophobic interactions, the  $D_{2d}$ -symmetrical dimers are known as velcraplexes. The two molecules of resorcinarene are rotated  $90^\circ$  with respect to each other to attain extensive surface contacts with 2'-methyl groups filling the holes. Thus two molecules in the dimer share a large preorganized surface composed of four methyls inserted into four complementary cavities and four heteroarylenes in close contact with one another. As a result, the values for  $-\Delta G$  of the dimerization in some cases exceed  $9 \text{ kcal mol}^{-1}$  in solution. Some dimerization processes are entropy driven and enthalpy opposed. The values for  $-\Delta H$  range from  $-5$  to  $8 \text{ kcal mol}^{-1}$  and those for  $\Delta S$  from  $-6$  to  $+40 \text{ cal mol}^{-1} \text{ K}^{-1}$ , respectively. In the  $^1\text{H}$  NMR spectra, separate signals can be seen for both the dimer and the monomer, their ratio is dependent on temperature and concentration. When two different velcrands are mixed together,

their heterodimers can be observed. Velcralex formation was confirmed by FAB-MS and VPO (vapor phase osmometric) measurements and X-ray crystallography.



**Figure 1.13** a) The planar rectangular structure with two protruding up-methyl groups and two methyl-sized holes of velcralex (monomer) and the X-ray structure of the velcralex (dimer) b) The representation of the conformational equilibrium of velcralexes leading to the formation of velcralexes [86].

### Objectives and scope of the thesis

The objectives of this thesis are to synthesize *tert*-butylcalix[4]arene derivatives containing diyne units and carbamate groups linked together with various alkyl chain as a spacer. The synthesized compounds are then studied for their topological polymerization and the molecular self assembly of the resulting polymers. The thermochromic properties of the polymers are also to be investigated.