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NONCOVALENTLY-BOUND CYCLODEXTRIN DIMERS AND RELATED COMPOUNDS. (REVIEW)

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In the review noncovalently-bound cyclodextrin (CD) dimers, i. e., CD host-guest 2:1 complexes as well as CD self-assembled inclusion oligomers, are briefly characterized, showing methods of their investigations; the properties and possible applications of these species are also described.

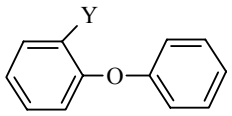
Keywords: cyclodextrin complexes, cyclodextrin dimers host-guest complexes, cyclodextrin dimers inclusion oligomers.

Cyclodextrins (CD) are a topic of intense research due to their ability to form inclusion complexes which find application in a number of industrial fields [1]. In a continuation of our works [2-8] we present here selected examples of CD host-guest 2:1 complexes, *i.e.,* noncovalently-bound CD dimers formed by the templating effect of guest molecules as well as self-assembled inclusion oligomers. CD dimers coordinated by transition metal ions are not included here [9, 10].

The amount of 1:1 host-guest complexes of CDs is enormous [11-13], while 2:1 host-guest complexes are not so common [14, 15]. Besides 2:1 host-guest CD complexes, *i.e.,* noncovalently-bound CD dimers, a great number of covalently linked CD dimers have been synthesized [2]. The first part of the review shows CD host-guest 2:1 complexes containing small and large guest molecules; then covalently-linked CD dimers, including guest molecules, are briefly described. The next part of the review deals with CD self-assembled inclusion oligomers.

1. CD HOST-GUEST 2:1 COMPLEXES WITH SMALL GUEST MOLECULES

The crystal structure of the 2:1 host-guest complex of β-CD with 1,12-dodecanediol has been determined [16]. The host-guest complex forms a [3] pseudorotaxane. Both hydroxy groups of 1,12-dodecanediol protrude from β-CD primary faces and form hydrogen bonds with water molecules. In the study of diphenyl ether derivatives it was found that β-CD gives with **1a** and **1b** crystalline 2:1 host-guest complexes [17].



1a,b

a Y = NO_2, **b** Y = NH_2

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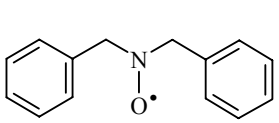
Paramagnetic inclusion complexes between two molecules of β-CD and symmetric dialkyl nitroxides **2** and **3** have been detected by ESR [18]. The ESR spectral analysis of **2** and **3** in the presence of β-CD has shown that with increasing CD concentration at first CD/nitroxide 1:1 complex and then 2:1 complex are formed.



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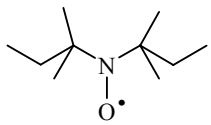
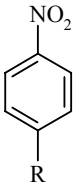


3

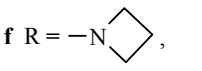
The existence of the 2:1 complex involves the presence of intermolecular hydrogen bonds between two wide faces of both CD molecules. The chemical modifications of the radical guest can lead to the species being able to self-associate. The tendency of CDs to form inclusion complexes and simultaneously to self-associate and form dimers is promising for the production of paramagnetic supramolecular structures useful in the preparation of molecular magnetic materials [19].

It was observed that α-CD forms 2:1 host-guest complexes with nitrobenzene derivatives **4a-i**; among them those with **4b**,**c**,**h**,**i** are weaker than the other ones [20]. The two α-CD molecules assume a head-to-head arrangement in 2:1 complexes.

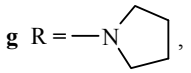


4a–i

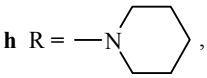
a R = NHMe, **b** R = NMe_2,
c R = NEt_2, **d** R = NHBu,
e R = $NHCH_2COOH$,



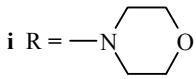
f R =



g R =



h R =



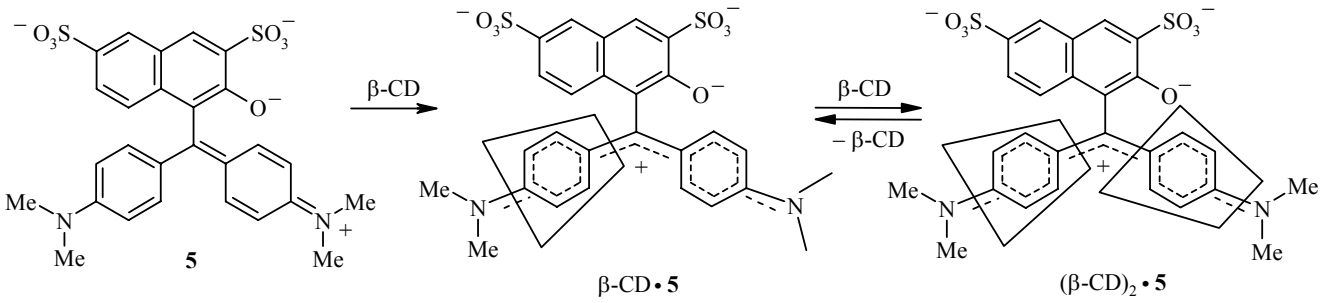
i R =

The oxidation of the dye Green S (**5**) by hydrogen peroxide and by peracetic acid involves attack of the nucleophilic oxygen atom on the central carbon atom of the dye. It is worth noting that the reaction of **5** with hydrogen peroxide carried out in the presence of β-CD first accelerates and then decelerates with the CD concentration [21]. This behavior is explained as follows. The first CD molecule binds to the aryl group of the dye, its narrow face being adjacent to the central carbon atom (β-CD·**5**). The field effect of the CD attracts the nucleophilic oxygen atom of hydrogen peroxide to the central carbon atom and accelerates the reaction. The second CD molecule binds to another aryl group, $(\beta\text{-CD})_2$·**5**, sterically hindering the approach of hydrogen peroxide to the central carbon atom; therefore the rate of the reaction decreases.

The oxidation of **5** with peracetic acid also first accelerates and then slows down with increasing concentrations of CD, similarly to the case of hydrogen peroxide [21]. This is expected, since hydrogen peroxide and peracetic acid attack the central carbon atom of **5**.

However, the effect of β-CD on the oxidation of **5** by Caro's acid is completely different; the reaction is strongly inhibited at lower concentrations of CD, and at higher concentrations no further inhibition is observed [22, 23]. Oxidation of **5** by Caro's acid involves the electrophilic attack of Caro's acid on the nitrogen atoms of $Me_2NC_6H_4$ moieties. The reaction is approximately 50% inhibited by one CD molecule. The second CD molecule, however, does not inhibit the reaction further.

This observation is explained by the fact that in the 1:1 complex, in which the wide face of CD is adjacent to the $Me_2NC_6H_4$ group, the overall dipole of the CD molecule repels the Caro's acid anion and strongly inhibits the reaction. When the second CD molecule is bound by the dimethylamine substituent to the dye, its narrow face being near the $Me_2NC_6H_4$ moiety, then the favorable ion-dipole attraction compensates steric hindrance, and no further inhibition occurs [22].

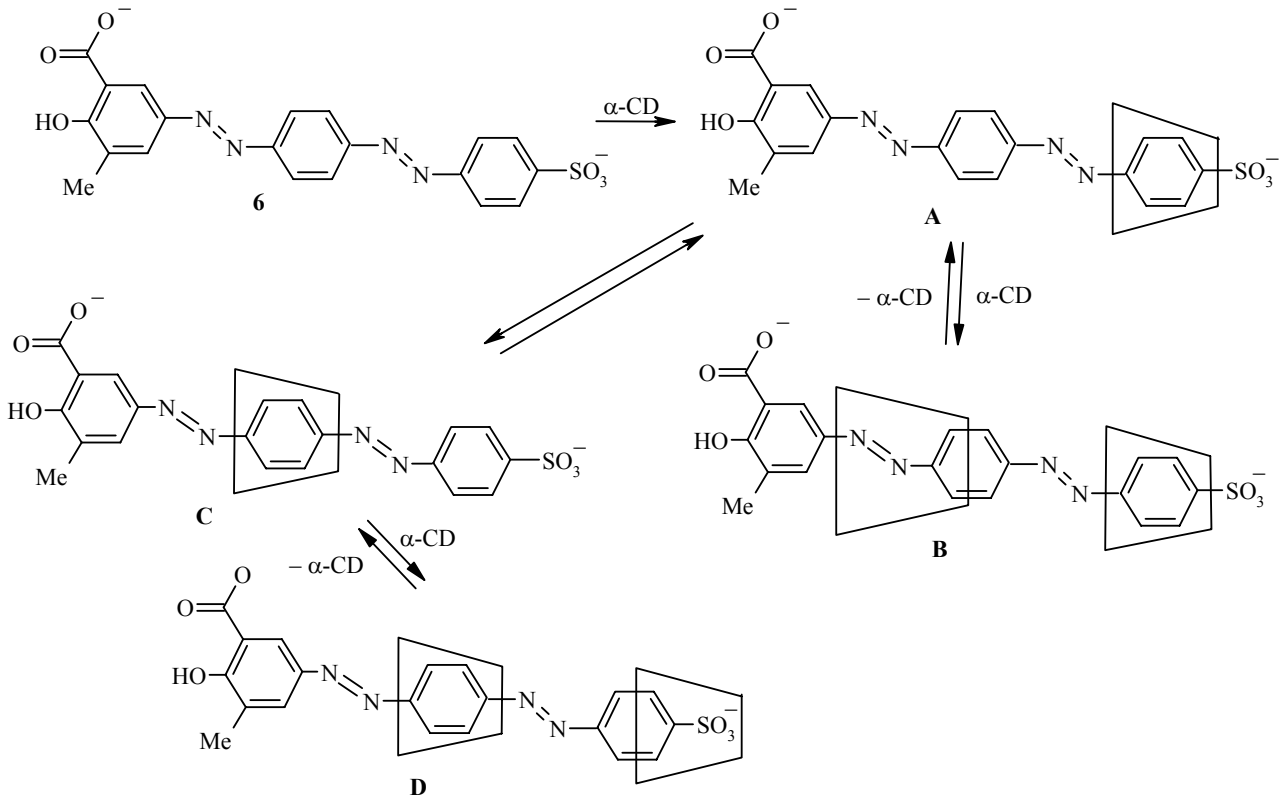


A kinetic and thermodynamic investigation of the sequential threading of α-CD onto the guest dye Mordant Orange 10 (**6**) has been made [24]. In aqueous solution α-CD threads onto **6** to give 1:1 complex **A**, which is in isomeric equilibrium with 1:1 complex **C**, this process being a thermodynamically controlled molecular shuttle.

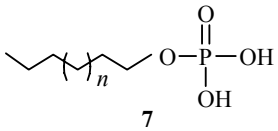
In **A** the **6** molecule is not so deeply incorporated in α-CD as in **C**. When **A** threads a second α-CD molecule, the 2:1 complex **B** is formed, while the threading of the second α-CD molecule by **C** leads to 2:1 complex **D**. These isomeric 2:1 complexes **B** and **D** do not interconvert, as 1:1 complexes **A** and **C** do.

In **A** – **D** the α-CD molecules incorporate **6** from its sulfonate group, which enters into the wide rim. The threading of the second α-CD onto **A** to give **B** is slower than the threading of the first α-CD onto **6**. The threading of the second α-CD onto **C** is faster than in the formation of **B** because in **C** the first α-CD is more distant from the sulfonate group of **5** than in the case of **A**.

Complex **B** is more stable than **D**, since in **B** the **6** molecule is incorporated more deeply in both α-CD molecules than in **D**.



The complexation of β-CD with phosphate esters **7** and **8** as well as with anionic and cationic surfactants **9** and **10**, respectively, has been investigated [25]. The ESI-MS study has shown that β-CD forms with these compounds 1:1 and 2:1 host-guest complexes. The amount of 2:1 complexes is lower than that of 1:1 species.



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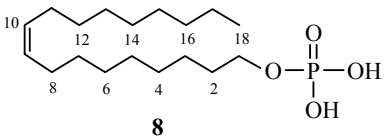
n = 1, 3, 5, 7, 9, 11, 13, 15



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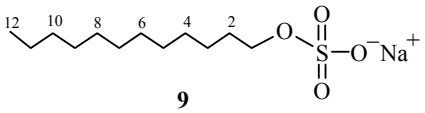

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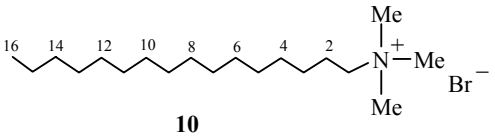
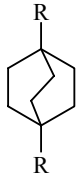


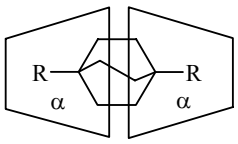
10

The 1:1 and 2:1 complexes of α-CD with 6-bromo-2-naphthol have been obtained. For the 2:1 complex of α-CD with 6-bromo-2-naphthol the thermodynamic properties were determined from measurements of the pulsed laser-induced phosphorescence emanating from the triplet state of 6-bromo-2-naphthol [26]. The higher stability of 2:1 complex as compared with that of the 1:1 complex results from van der Waals interactions and hydrogen-bonding between two host molecules.

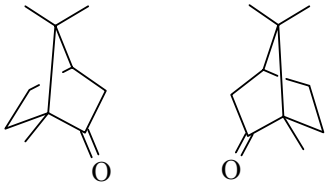
It was established that α-CD forms with bicyclo[2.2.2]octanes **11a**,**b** dynamically stable 2:1 complexes; no 1:1 complexes have been detected [27]. The ΔH and ΔS values of 2:1 complexes of α-CD with camphor enantiomers have been determined by NMR titrations [28]. In the case of (+)-camphor the formation of the 2:1 complex prevails over that of the 1:1 complex [29].



11a,**b**
a R = Me, **b** R = Cl



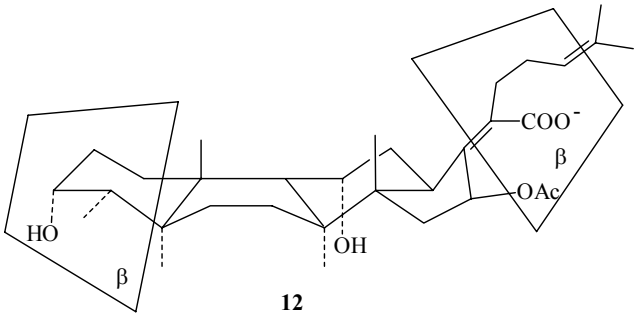
$(\alpha\text{-CD})_2 \cdot$ **11**



(+) 1*R*, 4*R* camphor (–) 1*S*, 4*S*

2. CD HOST-GUEST 2:1 COMPLEXES WITH LARGE GUEST MOLECULES

In the study of steroid antibiotics it was found that β-CD gives with sodium fusidate and potassium helvolate 2:1 complexes **12** and **13**, respectively; their structure has been confirmed by 1D and 2D-NMR analysis [30].



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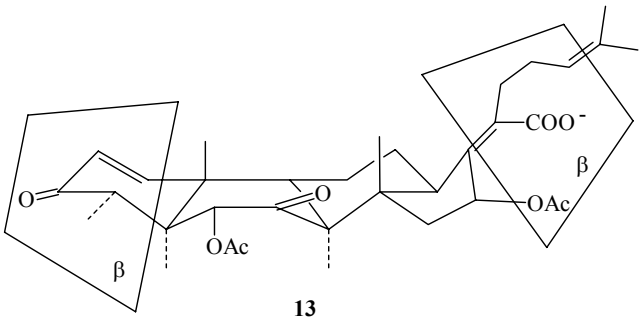
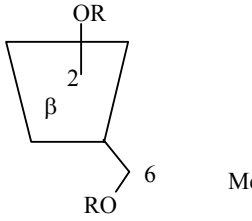


13

The formation of 1:1, 2:1, and 2:2 host-guest complexes of γ-CD with pyrene has been reported. The complexation dynamics was investigated using the stopped-flow technique, where two solutions were rapidly mixed and the relaxation processes toward an equilibrium were followed over time. Changes in the excimer or monomer emission intensities were measured. The dynamics for the 1:1 complex is much faster as compared to those for 2:1 and 2:2 complexes [31].

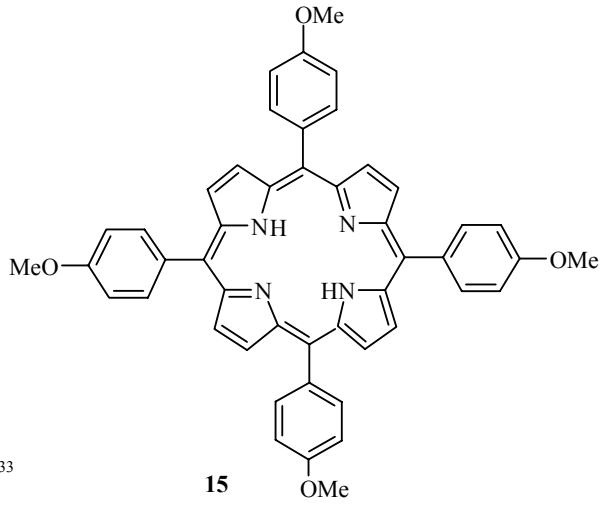
At first the 1:1 complex was formed, then association of two 1:1 complexes, leading to the 2:2 complex, takes place. The subsequent re-equilibration involving the dissociation of the 2:2 complex into two 1:1 complexes and the interaction of a 1:1 complex with a free CD affords the 2:1 complex.

The formation of 2:1 inclusion complexes of β-CD and heptakis(2,6-di-O-alkyl)-β-CD **14** with tetrakis(4-methoxyphenyl)porphyrin (**15**) has been studied by the Rayleigh light scattering technique. In this process two meso methoxyphenyl groups of **15** enter the cavities of CDs from their secondary side; the alkyl substituents of CDs may thread through the cavity, forming co-inclusion complexes. The enhancement of the Rayleigh light scattering decreases in the order of **14b** > **14c** > **14d** > **14a** > β-CD [32].



14a–d

a R = *t*-Bu, **b** R = *n*-C_8H_{17},
c R = *n*-$C_{10}H_{21}$, **d** R = *n*-$C_{16}H_{33}$

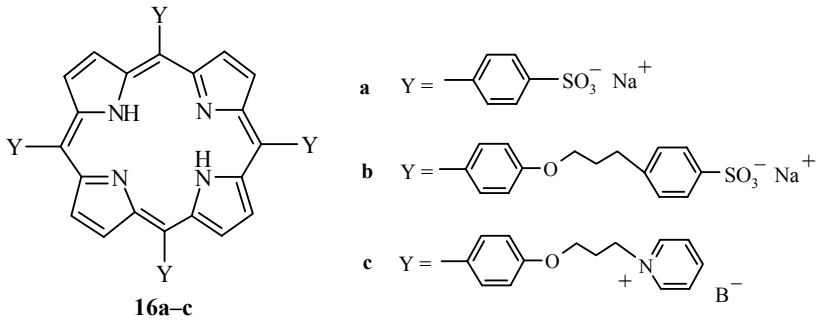


15

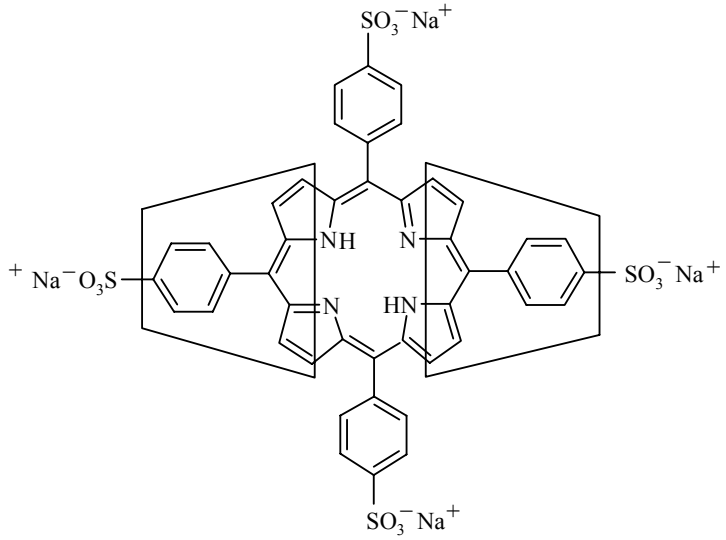
It was found that 2,3,6-tri-O-methyl-β-CD, *i.e.,* TMe-β-CD, forms with 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin **16a** the 2:1 host-guest com-plex, which behaves as a supramolecular sensitizer in water, providing an effici-ent photooxygenation. In this way *L*-methionine methyl ester and uracil may be oxidized; phenol degradation in aqueous solution is also possible [33].

TMe-β-CD includes the peripheral substituent of charged *meso*-tetrasubstituted porphyrins **16** in aqueous ethylene glycol, affording (TMe-β-CD)$_2$·**16** complexes. The binding constants of 1:1 and 2:1 complexes for anionic porphyrins **16a**,**b** are larger than those for cationic porphyrin **16c** [34]. This behavior results from the fact that methyl groups at the rims and the cavity wall of the host are positively polarized due to

the inductive effects of the ethereal oxygen atoms; therefore the penetration of the cationic substituent of **16c** is difficult. The three 2:1 complexes of TMe-β-CD with **16a-c** are very stable in aqueous solutions, strong van der Waals interaction being their main binding force.



16a–c



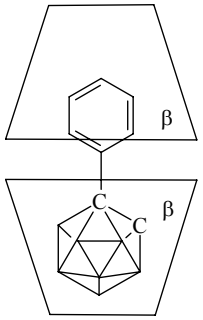
$(TMe–β-CD)_2$ • **16a**

The formation of the 2:1 host-guest complex **17** of β-CD with phenyl-substituted *o*-carborane has been reported [35]. In complexes of unsubstituted *o*-carborane with shallow receptors – calixarenes and cycloveratrylenes – the inclusion is not deep [36], and they are weak. On the contrary, complexes of *o*-carborane with hosts having deeper cavities such as cyclodextrins and cucurbiturils are more robust. The complex **17** is very strong. It is completely undissociated in hot water and in hot toluene, while the complex cucurbit[7]uryl·carborane exists in equilibrium with its components [37].

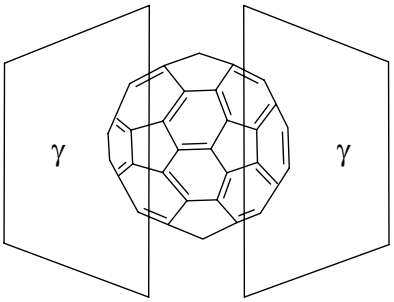
The complexation with phenylcarborane protects β-CD from thermal degradation. The structure of **17** in which carborane and phenyl are incorporated in two CD molecules enables close contact of secondary faces of CDs, resulting in the existence of strong hydrogen bonds.

A water-soluble, stable 2:1 host-guest complex of β-CD with C_{60} has been obtained in DMF/toluene solvent (50/90% DMF, v:v) at room temperature [38]. It was observed that γ-CD forms with C_{60} the 2:1 complex in which the secondary hydroxy groups of γ-CD are connected by hydrogen bonds; in this way the complex is stabilized [39]. The 2:1 complex of γ-CD with C_{60} may undergo hydration, affording species in which water molecules are connected only to γ-CD, or species in which also the included fullerene is hydrated.

The water-soluble 2:1 complex of γ-CD with C_{60}, *i.e.,* γ-CD bicapped C_{60} **18**, was prepared using the ball milling method [40, 41]. It was found that **18** may act as a DNA cleaving reagent in the presence of NADH in an oxygen saturated aqueous solution [41]. The photosensitized reduction of O_2 by NADH produces $O_2^{-\cdot}$ *via* a



17

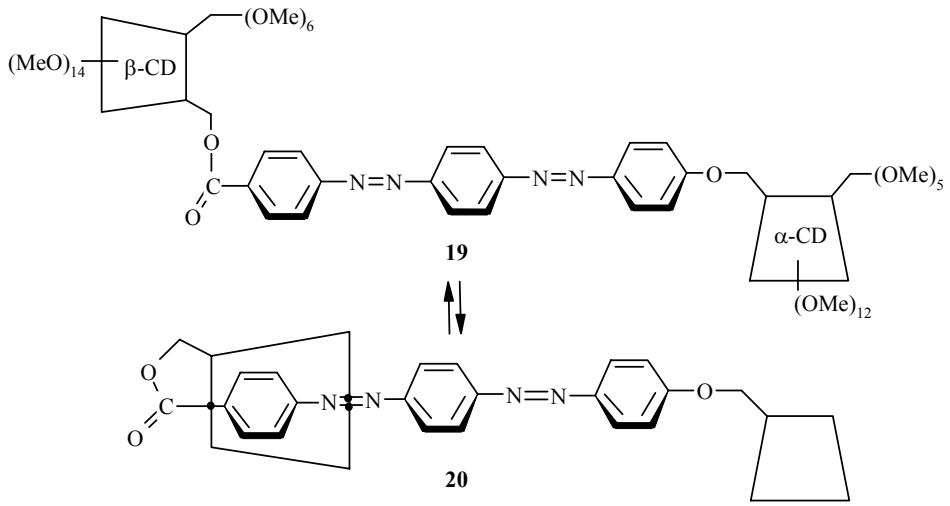


18

photoinduced electron transfer from NADH to γ-CD-bicapped $^3C_{60}$* and *via* electron transfer from NADH to $^1O_2$ formed by energy transfer from γ-CD-bicapped $^3C_{60}$* to O_2. The superoxide $O_2^{-\cdot}$ produced gives H_2O_2, affording the hydroxyl radical responsible for DNA cleavage.

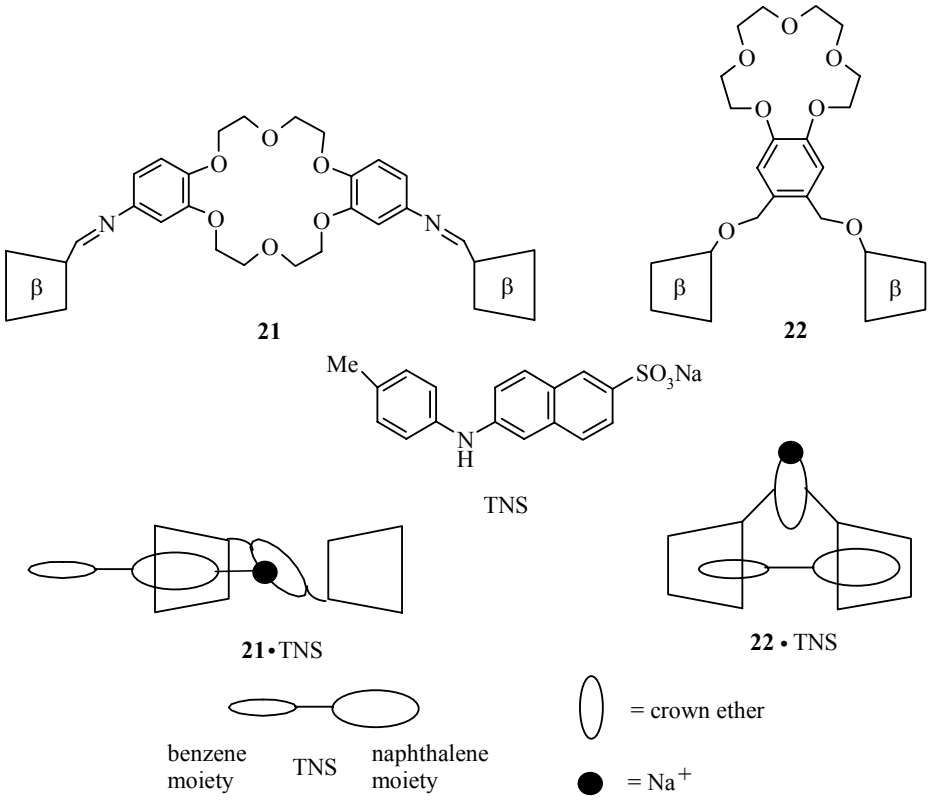
3. COVALENTLY LINKED CD DIMERS INCLUDING GUEST MOLECULES

In the study of covalently linked CD dimers including guest molecules [42, 43] it was found that **19** isomerizes to give a self-inclusion complex **20**. This isomerization results from turning the glucose bearing the guest through 360° ("a somersault mechanism") [44].

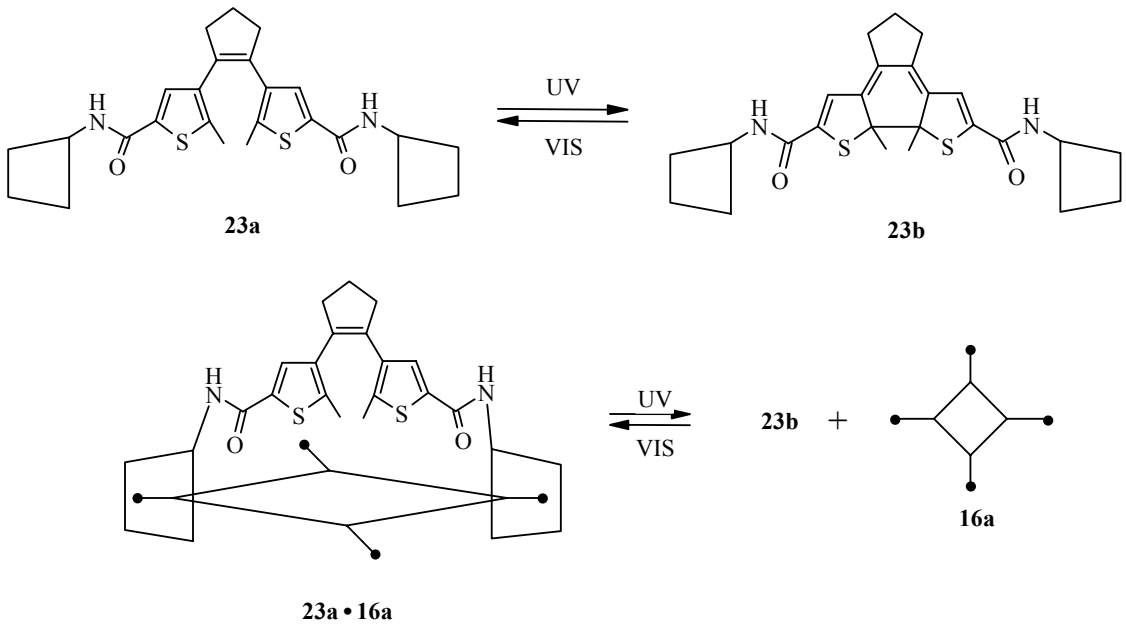


19 ⇄ **20**

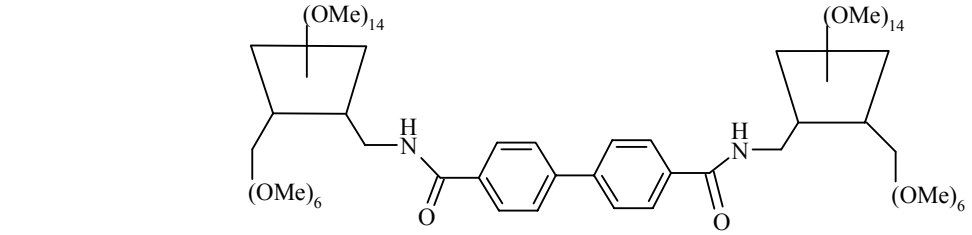
Dimers **21** and **22** covalently bridged by crown ether units may serve as receptors for the fluorescent dye sodium-6-toluidino-2-naphthalenesulfonate (TNS). It was established that in aqueous phosphate NaH_2PO_4/Na_2HPO_4 buffer solution **21** binds TNS to give **21**·TNS, deeply including its anionic naphthalene sulfonate moiety in the CD cavity due to the electrostatic interaction. However, **22** incorporates TNS into both CD cavities, affording **22**·TNS, and this binding is stronger than in the case of **21** [45]. It should be pointed out that **21** and **22** bind TNS more strongly than native β-CD does.



Photoswitchable dithienylethene bridged β-CD dimer **23a** (a flexible open form) when irradiated gives **23b** (a rigid closed form). Compound **23a** serves as a host for porphyrin **16a**; its binding affinity can be photochemically altered. It was observed that **23a** binds porphyrin **16a** more strongly than **23b** does. This binding difference of **23** allows the photocontrolled reversible release and uptake of porphyrin **16a** in solution [46].



In the investigation of CD dimeric assemblies with porphyrins it was established that the aqueous solution of **24**, **25a**, and **25b** shows energy transfer from **25b** to free-base porphyrin **25a**, resulting from the formation of the complex **26** [47].



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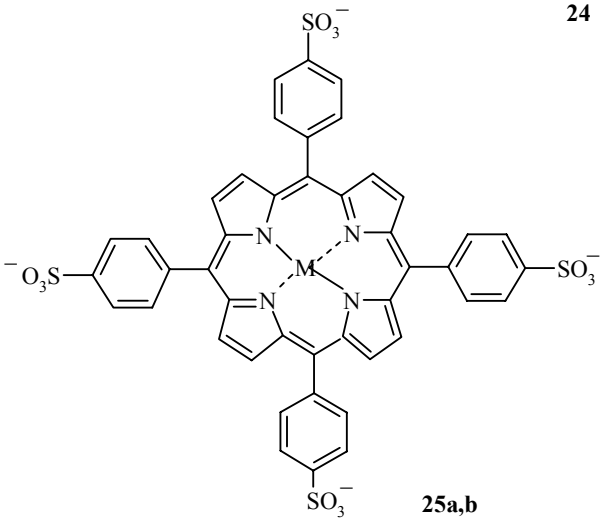
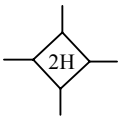
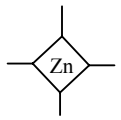


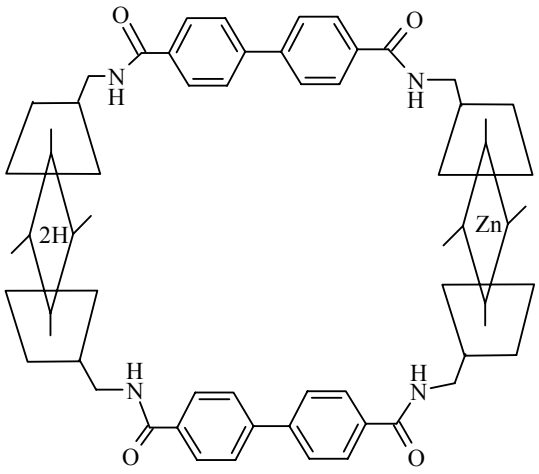
25a,b

a M = 2H



b M = Zn





26

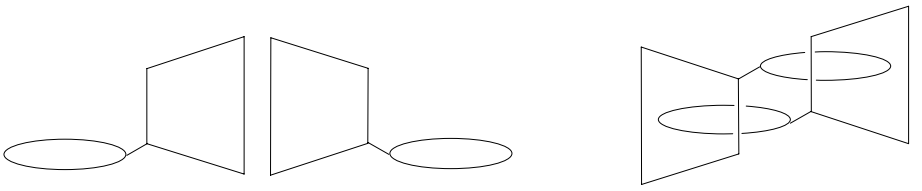
4. CD SELF-ASSEMBLED INCLUSION DIMERS

Chemically modified CDs may form intramolecular self-complexes, in which the appended substituent is self-included in the cavity of its own CD, or they may give intermolecular self-assembled inclusion complexes, *i.e.,* dimers in which the substituent of one CD molecule penetrates into the cavity of the other one [48].

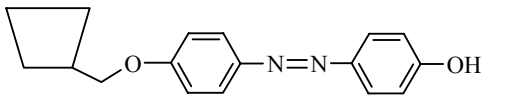
The self-dimerization of permethylated CDs bearing an azobenzene substituent **27-30** (all compounds in *trans*-configuration) has been investigated by ESI-MS (electrospray ionization mass spectrometry). It was shown that two CD molecules form either a contact or an inclusion dimer [49]. The contact dimer is formed by hydrogen bonding of hydroxy groups at the rims of CD molecules while the inclusion dimer forms *via* the hydrophobic interaction between the host CD cavity and the guest-substituent.

For the detection of the inclusion dimer the CD molecules must be permethylated to avoid formation of the contact dimer, and the substituent should be long enough to enter the cavity of the other CD molecule. Amino or hydroxy groups are present at the substituent terminals for protonation and for detection as cations by ESI-MS. Since **27-30** are permethylated species, they cannot form contact dimers, because hydrogen bonding is impossible; therefore inclusion dimers are obtained. However, **31** [50] forms only contact dimer, the tosyl group being too short to enable its inclusion into the cavity of the other CD molecule.

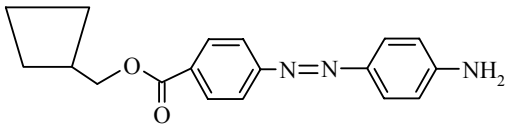
The CD derivative **28a** exists in solution as an equilibrium mixture of the monomer and the inclusion dimer; in order to cap the guest substituents in both the monomer and the dimer, the diazo coupling reaction of this mixture was made. The reaction afforded the capped monomer of **28a**, *i .e.*, **32** and the capped dimer of **28a**, *i. e.*, $\mathbf{32}_2$. The substituent of **32** cannot enter the cavity of the second CD molecule; therefore the formation of the inclusion dimer from the capped monomer would be impossible. CID (collision-induced dissociation) analysis has shown the following stability order of dimers: $(\mathbf{28b})_2 > \mathbf{32}_2 > (\mathbf{28a})_2$.



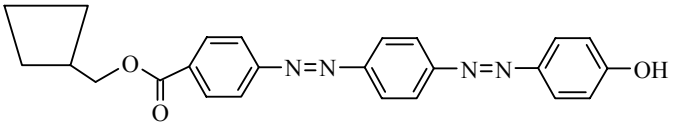
contact dimer inclusion dimer



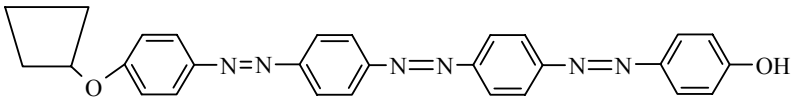
27 α 17 OMe



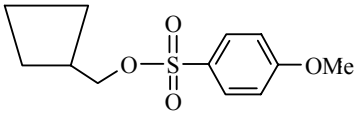
28a,b
a 17 OMe
b 20 OMe



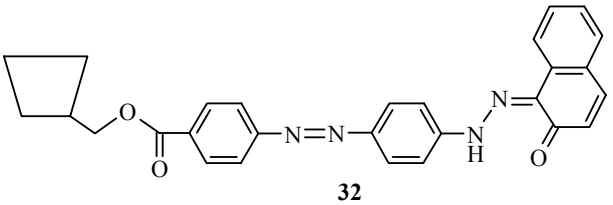
29 β 20 OMe



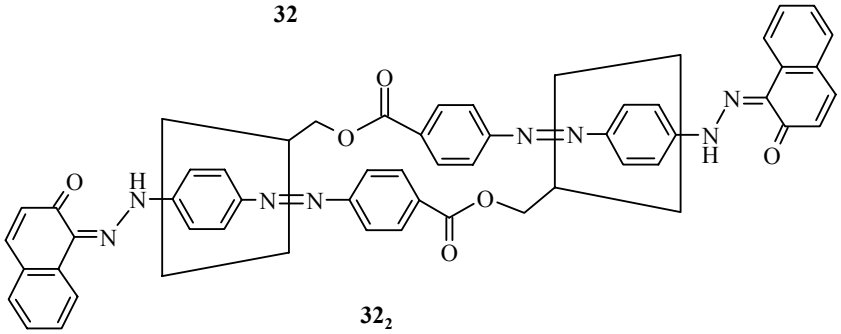
30 α 17 OMe



31 α 17 OMe



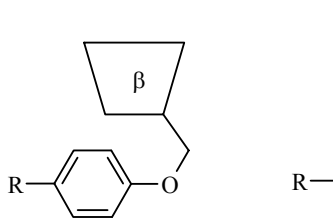
32



32_2

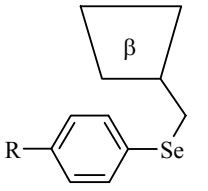
The supramolecular association of **33-35** both in solution and in the solid state has been studied by means of NMR spectroscopy, microcalorimetric titration, STM (scanning tunneling microscopy), and X-ray diffraction [48]. To investigate conformations of **33-35** in aqueous solution, their 2D NMR spectra have been analyzed. These measurements show that the nitrophenyl group of **33b** penetrates into the cavity of other CD from the secondary face to form a head-to-tail dimer $(\mathbf{33b})_2$. However, in **35**, the hydroxyphenyl group penetrates into the cavity of other CD from the primary side, forming a tail-to-tail dimer $\mathbf{35}_2$.

Monomodified β-CDs crystallize in three types: self-inclusion, layer-type packing, and one-dimensional self-assembly. One-dimensional self-assembly is the most frequently observed structure, in which the substituent successively penetrates into the next CD cavity from the secondary side, forming an extended linear polymer. It was observed that modified β-CDs **33** and **34** crystallize in one-dimensional self-assembly. The aromatic rings bearing substituents penetrate deep into the cavities of adjacent β-CDs and align along the screw axis to form head-to-tail helical columnar superstructures. Since the pivot heteroatom through which the aromatic group is tethered to β-CD plays a crucial role in determining the helix structure, control of the self-assembling orientation and helicity in the solid state is possible by tuning this kind of atom and the tether length.

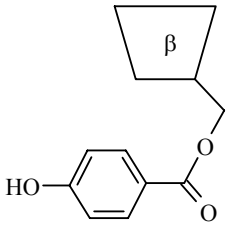


33a–c

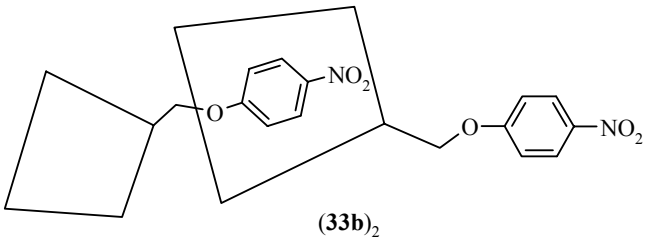
a R = Br, **b** R = NO_2, **c** R = CHO



34

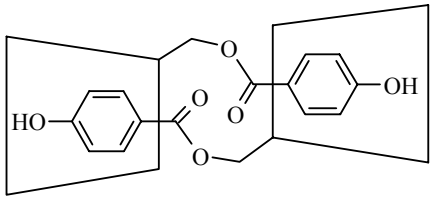


35



$(\mathbf{33b})_2$

Head-to-tail dimer

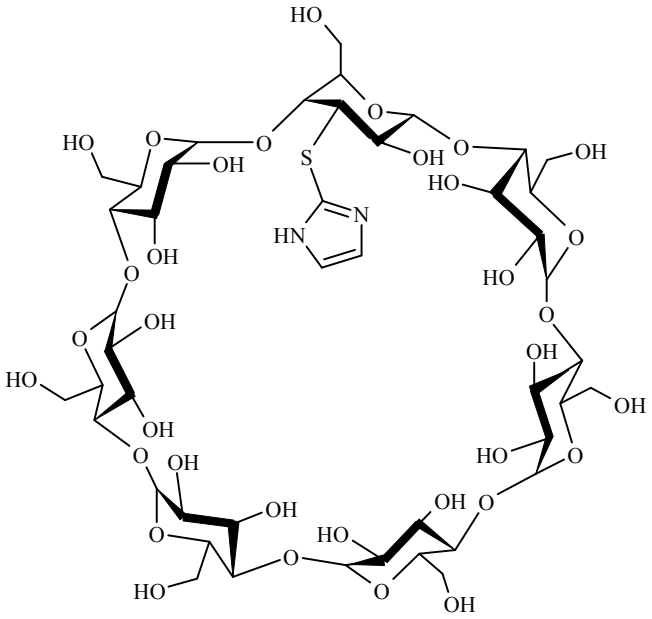


$\mathbf{35}_2$

Tail-to-tail dimer

It should be pointed out that **35** rather unexpectedly crystallizes in a different way. The crystal structure of **35** possesses a C2-symmetric tail-to-tail dimer unit, in which the substituent penetrates the cavity of the adjacent CD from the primary side. Subsequently the dimer self-assembles to form a linear tail-to-tail supramolecular channel structure through hydrogen-bonding of secondary hydroxyls [48]

One should also mention the monosubstituted altro-β-CD **36**; its crystal structure has been determined. It was observed that **36** forms a self-assembled inclusion dimer in which the imidazolyl group of one molecule, situated at its secondary side, enters the secondary side of the other one. This group does not penetrate deep into the counterpart cavity but is localized at its rim. The head-to-head dimers form in crystal four-fold helical columns [51].

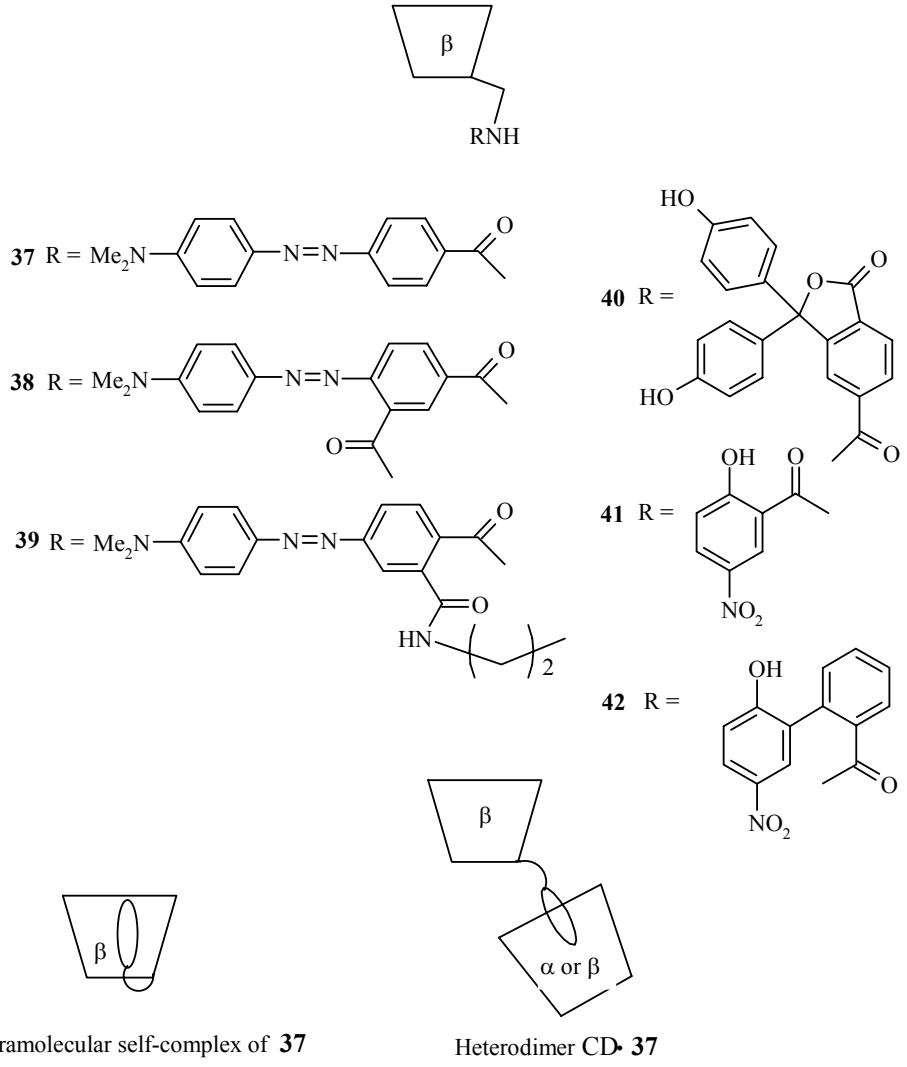


36

Absorption and induced circular dichroism spectroscopy results have shown that dye-modified β-CDs **37**-**42** may form intramolecular self-complexes in which the appended dye moiety is inserted into its own CD cavity or may give heterodimers with native α- or β-CDs by inserting the dye moieties into the CD cavities [52].

It was established that **37** forms an intramolecular self-complex, or a heterodimer CD·**37** with native α- and β-CDs. The formation of the α-CD·**37** heterodimer in acidic medium is accompanied by the disappearance of the red color due to the protonation of azo and dimethylamino groups. The association constant of the α-CD·**37** heterodimer is higher than in the case of the heterodimer β-CD·**37** since the pendant group of **37** better fits to the α-CD than to the β-CD cavity.

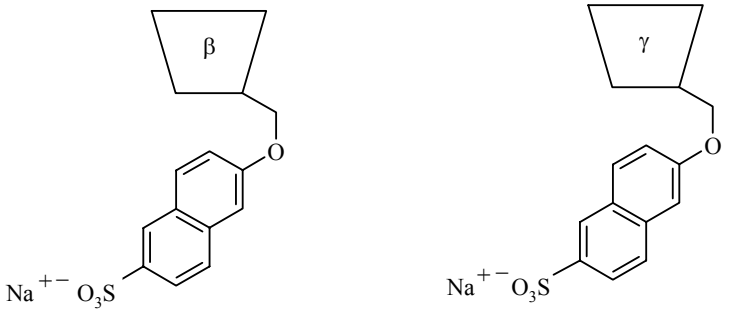
The methyl red-modified β-CD **38** forms only the stable intramolecular self-complex; it does not give heterodimers, neither with α-CD nor with β-CD; no spectral change is observed. Alizarine yellow-modified β-CD **39** forms with α-CD a weak heterodimer α-CD·**39**; only a slight spectral change is observed. The phenolphthalein-modified β-CD **40** exists as a purple dianionic monomer at pH above 10.8. The addition of β-CD causes decoloration due to the formation of the β-CD·**40** heterodimer. The *p*-nitrophenol-modified β-CDs **41** and **42** give heterodimers with α-CD molecules.



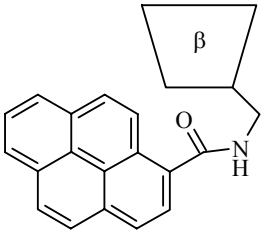
Intramolecular self-complex of **37**

Heterodimer CD• **37**

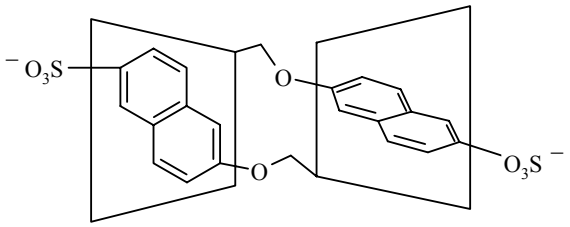
The ^{1}H NMR, circular dichroism, and fluorescence spectroscopy results have shown that **43**, **44**, and **45** form homodimers $\mathbf{43}_2$, $\mathbf{44}_2$, and $\mathbf{45}_2$, respectively. It was also established that **44** gives an associate with β-CD, **45** gives an associate with γ-CD, and **44** forms with **45** a heteroassociate **44**·**45** [53, 54]. Two different CD derivatives can form a heteroassociate when a complementarity between the pendant group of one CD derivative and the cavity of the other CD molecule exists.



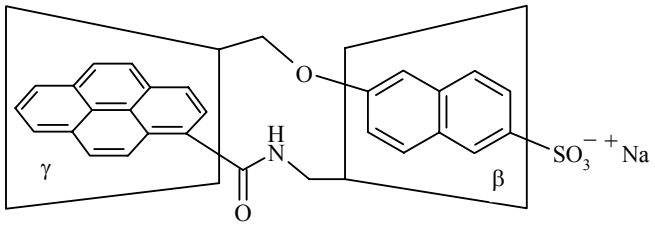
43 **44**



45



43_2

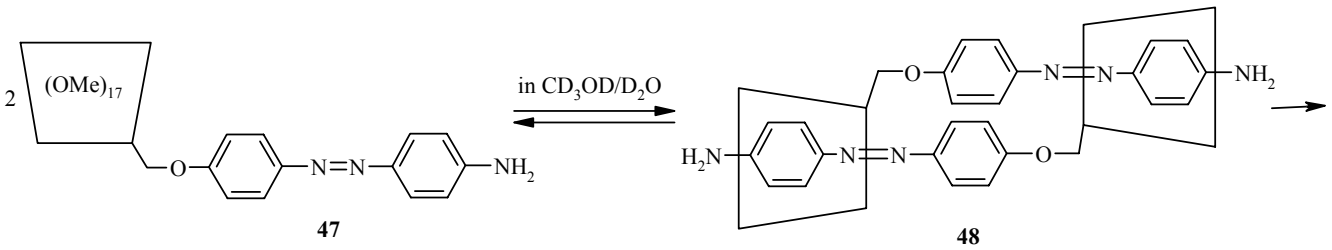


44 • 45

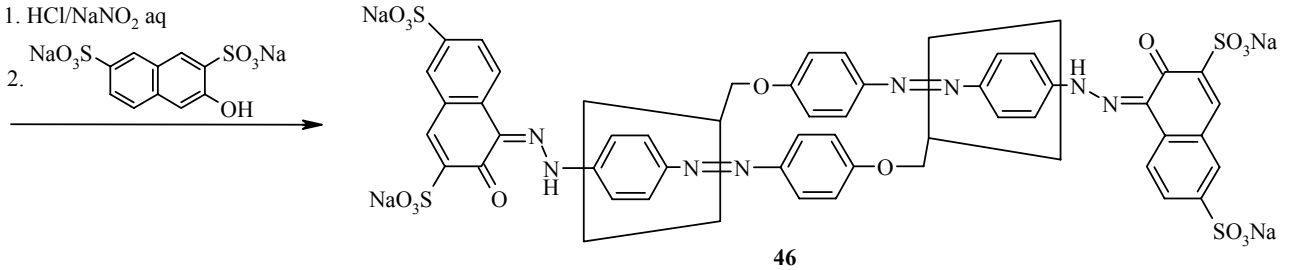
The CD derivatives **43**-**45** were chosen for investigation since naphthalene and pyrene sizes fit well to β- and γ-CD cavities, respectively, and because naphthalene- and pyrene-tethered CDs are widely used as fluorescent receptors. It should be noted that the dimerization constant of $\mathbf{43}_2$ is larger than those of $\mathbf{44}_2$ and $\mathbf{45}_2$ dimers due to better size-matching between the pendant naphthyl group and the cavity of the second **43** molecule than in the case of $\mathbf{44}_2$ or $\mathbf{45}_2$ dimers.

Also, due to the good size-matching of β-CD with naphthalene and γ-CD with pyrene, the association constant **44**·**45** is larger than in the case of their homodimerizations, resulting in $\mathbf{44}_2$ and $\mathbf{45}_2$.

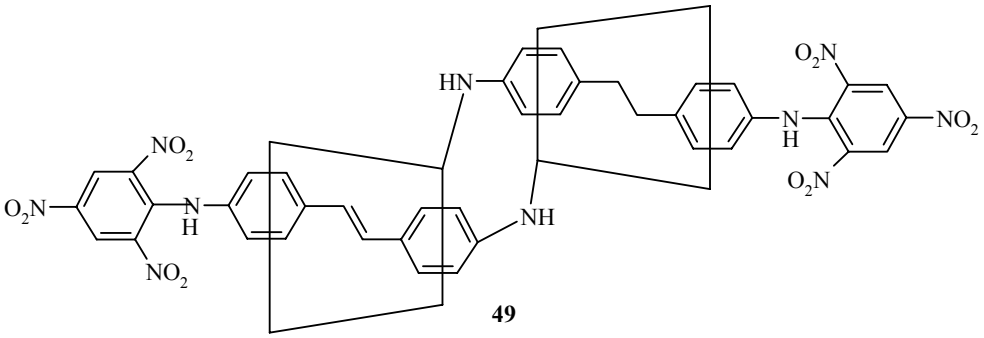
The synthesis of the double [2]rotaxane, called Janus[2]rotaxane **46**, involves dimerization of **47**, affording double [2]pseudorotaxane **48**; its diazotization and bis-azo coupling with 2-naphthol-3,6-disulfonic acid (R-acid) introduces two bulky stoppers to give **46** [55]. Rotaxanes and catenanes, promising in the design of molecular machines and switching devices, are now a topic of growing interest [56]. The double [2]rotaxane **49** is also known [57].



47 **48**



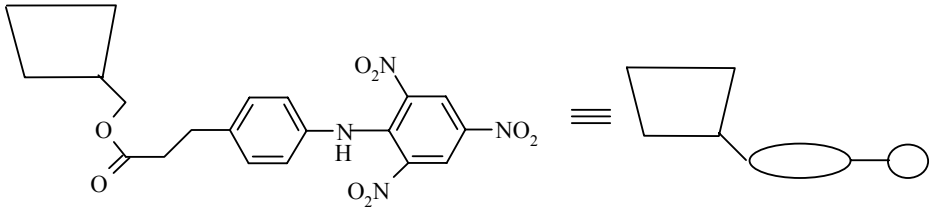
46



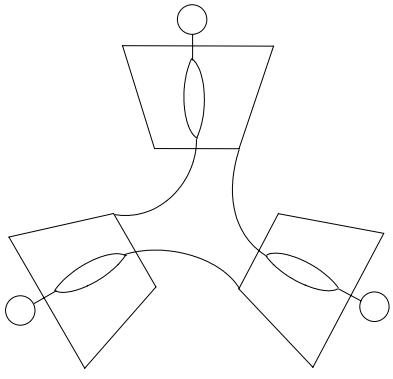
49

5. CD SELF-ASSEMBLED INCLUSION TRIMERS AND TETRAMERS

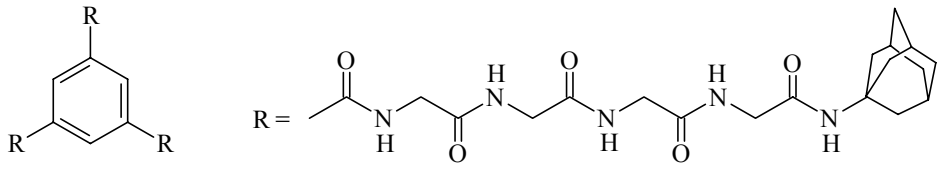
CD self-assembled inclusion trimers [58] and tetramers [59] have been studied. An example of a cyclic noncovalently held trimer of **50** is **50**$_3$ [60]. Complexation of α-, β-, and γ-CDs with dendrimer **51** has been investigated by NMR [58]. The complexation increases the solubility of **51** in water. It was established that the 3:1 complex of β-CD with **51** is considerably stronger than those of α- and γ-CDs due to best size-matching in the case of β-CD.



50

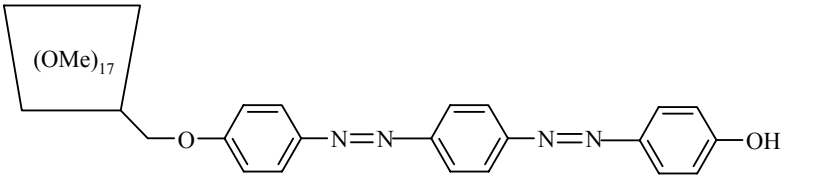


50$_3$

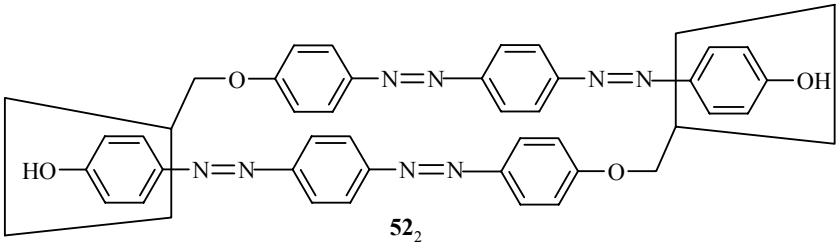


51

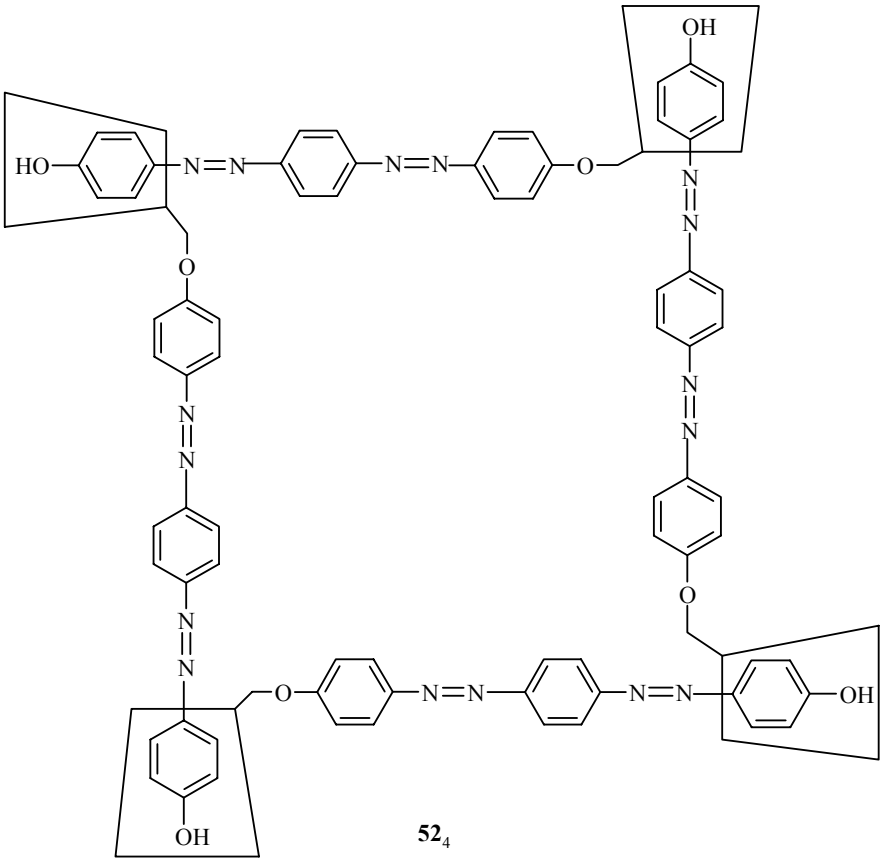
The α-CD derivative **52** containing a bisazophenol tether exists in CD_3OD/D_2O in equilibrium with its inclusion dimer, *i.e.*, the double [2]pseudorotaxane $\mathbf{52}_2$. In a succeeding equilibrium in CD_3OD/D_2O, the existence of $\mathbf{52}_2$ and of the cyclic tetramer $\mathbf{52}_4$ has been observed [59]. It should be noted that the cavity of $\mathbf{52}_4$ is large enough to include a porphyrin molecule.



52



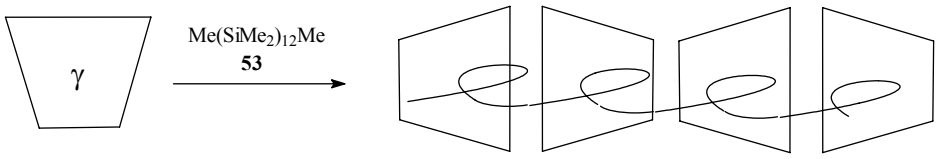
$\mathbf{52}_2$



$\mathbf{52}_4$

Some synthetic polymers can adopt a helical-screw conformation. Such polymers are promising in the design of chiro-optical materials for memory devices. CDs may form inclusion complexes with linear polymers. The CD cavity consists of optically active D-glucose units; therefore the inside of the CD cavity affords a chiral environment for guest molecules.

The mixing of an aqueous solution of γ-CD with permethyldodecasilane $Me(SiMe_2)_{12}Me$ **53** affords the 4:1 complex (γ-CD)$_4$·**53**. The size of the dimethylsilylene units in the main chains fits well to cavities of γ-CD. It is the first example of induced optical activity of oligosilanes within the internal cavity of γ-CD [61]. Oligosilanes are models for polysilanes. Polysilanes substituted with optically active side chains may adopt a preferential helical-sense conformation; the above system leads to such conformation of the oligosilane chain. Polysilanes and oligosilanes with helical structure are interesting due to their photophysical and electronic properties.



(γ-CD)$_4$ · **53**

CONCLUSION

CDs are intensively studied due to their interesting properties; especially CD inclusion abilities have attracted widespread attention. The rapid development of this field of chemistry finds its reflection in numerous works.

Having in view a great number of reports concerning noncovalently-bound CD oligomers [62-66], only their selected examples have been presented. These species are promising for pharmaceutical applications and for the design of molecular devices, their advantage being the environment-friendly approach to parent CDs.

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