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METALLOCYCLODEXTRINS AND RELATED SPECIES

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Abstract- In first part of the review cyclodextrin (CD) complexes with copper and platinum ions are presented, followed by those with lanthanide ions. Then CD complexes of ferrocenes and of ruthenium ions bound with bipyridine and phenanthroline ligands are described. The next parts of the paper deal with CD complexes with metal ions bound in cyclens or porphyrins. At last some examples of CD-modified nanoparticles are given.

1. Complexes of CDs with copper, gold, silver and platinum ions
2. Complexes of CDs with lanthanide ions
3. Complexes of CDs with various metal ions
4. Complexes of CDs with ferrocenes and half-sandwich molybdenum and manganese species
5. Complexes of CDs with bipyridine and phenanthroline ruthenium compounds
6. Complexes of CDs with metallo-cyclens, -porphyrins and -phthalocyanines
7. CD-modified metal nanoparticles

INTRODUCTION

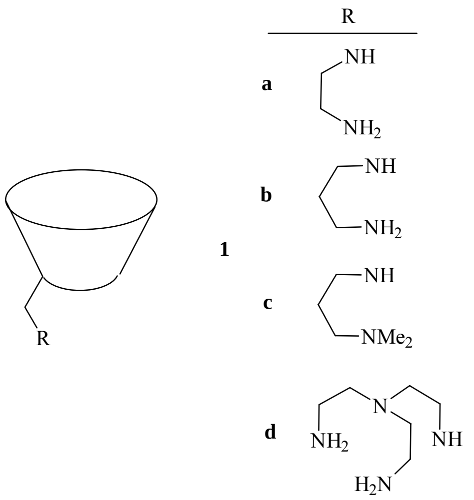
Cyclodextrins (CD) are intensively studied so from theoretical as practical point of view. [1,2] Among them, metallocyclodextrins deserve an attention due to their interesting properties and application possibilities, [3-5] for example as catalysts [6] or NLO materials, [7] in analytical [8] and diagnostic tests [9] and in the construction of molecular switches. [10]

In the continuation of our study concerning cyclodextrins,[11-15] we present here selected examples of metallocyclodextrins and their related species.

1. COMPLEXES OF CDs WITH COPPER, GOLD, SILVER AND PLATINUM IONS

Copper (II) complexes of β-CD derivatives (**1a-d**) have been tested as catalysts for hydrolysis of phosphate triesters.[16] Organophosphates, e.g. paraoxon (**2**) are insecticides and nerve agents; their catalytic breakdown is of importance for the environmental protection.

The triester (**3**) was chosen as the substrate for investigation; in this compound the *tert*-butyl group facilitates the complexation by CD, and the presence of the nitro group enables the detection of the hydrolysis product (**4**). Among copper complexes of **1a-d**, those of **1a,b** are the most efficient catalysts. The hydrolysis of **3** occurring in the CD complex with **1b** proceeds probably by copper-bound hydroxide, as shown in **5**. [16]



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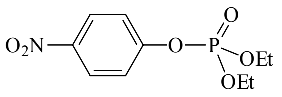

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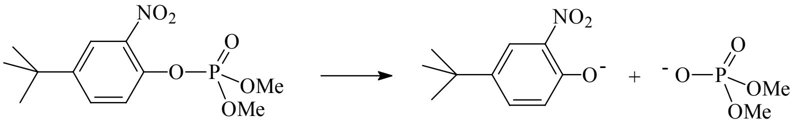
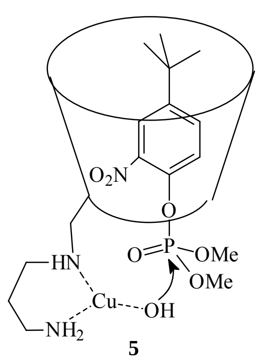


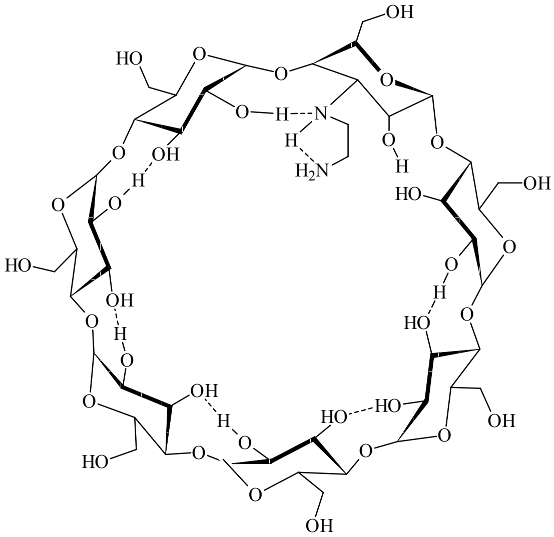
3 **4**



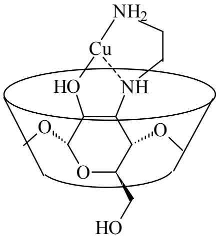
5

Many 6-functionalized CDs have been studied in view of their metal ion binding properties, while works concerning 2- and 3-functionalized CDs are not so numerous. [17] The less extensive investigation of the secondary side of CDs is due to the fact that primary hydroxyl groups are easier modified than the secondary ones. The secondary side of CD is more crowded than the primary one, since the number of hydroxyl groups at secondary side is twice higher. Hydrogen bonds between 2-OH and 3-OH make these hydroxyl groups less flexible than 6-OH groups.

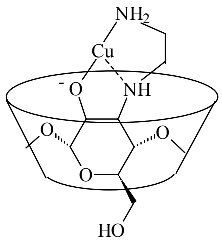
The binding behavior of 3-functionalized β-CD (**L**) containing the modified altrose unit towards Cu(II) ion has been examined in aqueous solutions; the potentiometry and EPR results show that secondary hydroxyl groups, especially 2-OHs take part in the complexation of Cu^{2+} ion. [18] At pH 8 the $[Cu\mathbf{L}]^{2+}$ complex is formed predominantly, and at higher pH the $[Cu\mathbf{L}H_{-1}]^{+}$ deprotonated form is the major species.



L

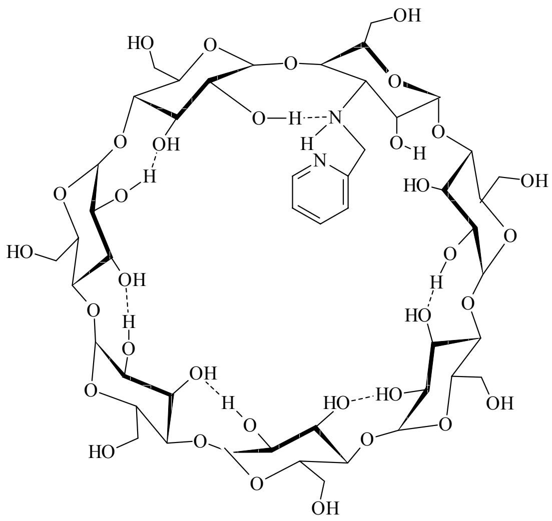


$[CuL]^{2+}$

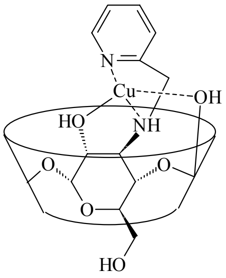


$[CuLH_{-1}]^{+}$

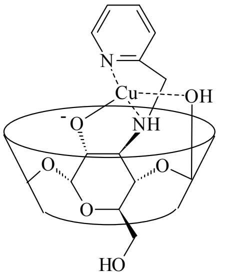
Similar investigations were carried out for the analogous derivative (**L’**). [19] It was established that the copper complex bound in the 2-position has higher stability constant than that bound in the 6-position. The complex [Cu**L**’]$^{2+}$ is the major species at the pH range 3-5, while at higher pH mono- and dideprotonated species [Cu**L**’H$_{-1}$]$^{+}$ and [Cu**L**’H$_{-2}$] , respectively, exist. The formed dimeric species [Cu$_2$**L**’$_2$H$_{-2}$]$^{2+}$ is stabilized by the inclusion of pyridine moieties into CD cavities.



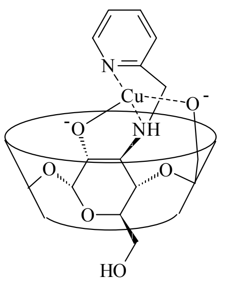
L'



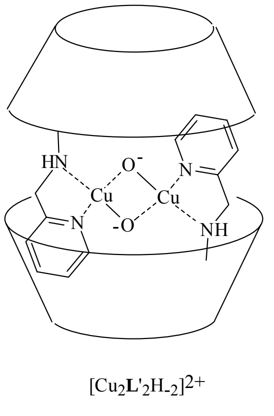
$[CuL']^{2+}$



$[CuL'H_{-1}]^{+}$



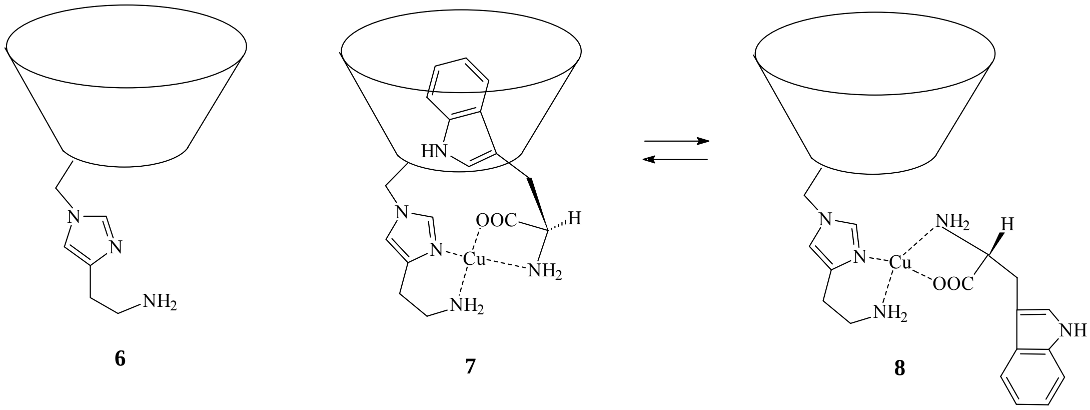
$[CuL'H_{-2}]$



$[Cu_2L'_2H_{-2}]^{2+}$

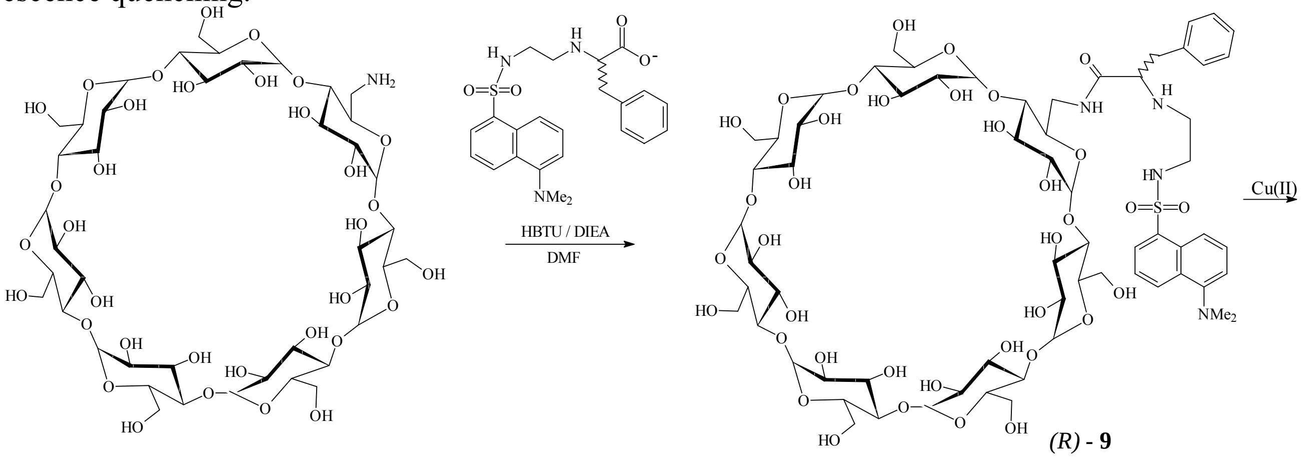
In the study of CDs functionalized with imidazole derivatives, [20] it was found that the copper (II) complexes of β-CD bearing histamine moiety (**6**) bind enantiomeric pairs of amino acidates: alaninate

(AlaO$^-$), phenylalaninate (PheO$^-$) and tryptophanate (TrpO$^-$). [21,22] For the AlaO$^-$ complexes the stability of both diastereomeric ternary complexes with D- and L-AlaO$^-$ is similar. The enantioselectivity was observed however in the case of TrpO$^-$; it was found that the L-TrpO$^-$ complex was favored over that of D-enantiomer. The *cis-trans* equilibrium of the complex of **6** with TrpO$^-$ **7/8** was proposed. [22]



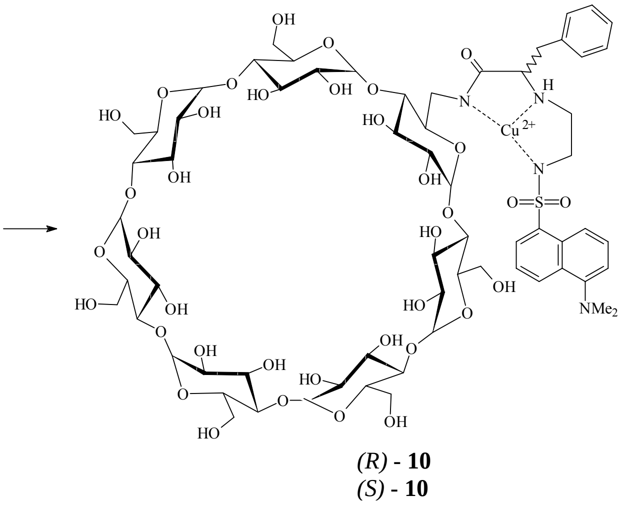
6 **7** **8**

Fluorescent phenylalanine-based CDs (*(R)*-**9**) and (*(S)*-**9**) have been synthesized and converted into Cu(II)complexes (*(R)*-**10**) and (*(S)*-**10**), as shown below; the complexation is accompanied by fluorescence quenching.



(R) - **9**
(S) - **9**

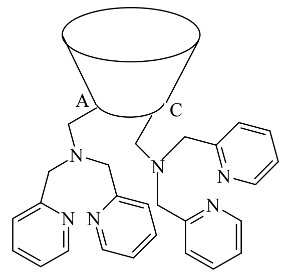
HBTU: *O*-(benzotriazol-1-yl)-*N,N,N',N'*-tetramethyluronium hexafluorophosphate
DIEA: *N,N*-diisopropylethylamine



(R) - **10**
(S) - **10**

Complexes (*(R)*-**10**) and (*(S)*-**10**) contain *R* and *S* stereogenic centers and may serve as enantioselective sensors for amino acids. [23] The addition of amino acids to *(R)*-**10** or *(S)*-**10** induces a "switch on" of fluorescence, which is enantioselective for proline, phenylalanine and tryptophan. This enantioselective fluorescence effect is the highest in the case of proline and may be used for the determination of its optical purity. The above method does not require amino acid derivatization and may be performed on a very low amount of sample.

It is known that many enzymes possess two metal ions in their active center, cooperatively catalyzing the hydrolysis of their substrates. The β-CD-based binuclear metal complexes are more efficient catalysts for the amide hydrolysis than mononuclear complexes, examples are Zn(II) and Cu(II) complexes [Zn_2(**11**)] and [Cu_2(**11**)] with a high catalytic activity for the hydrolysis of **12**. [24] The *ca.* 50 times higher catalytic activity of [Cu_2(**11**)] as compared with that of the mononuclear complex [Cu(**13**)] results from the effective cooperation of both metal centers.



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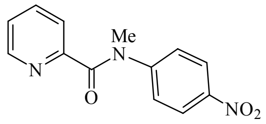

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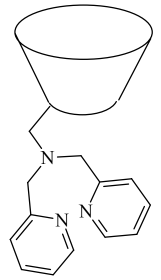
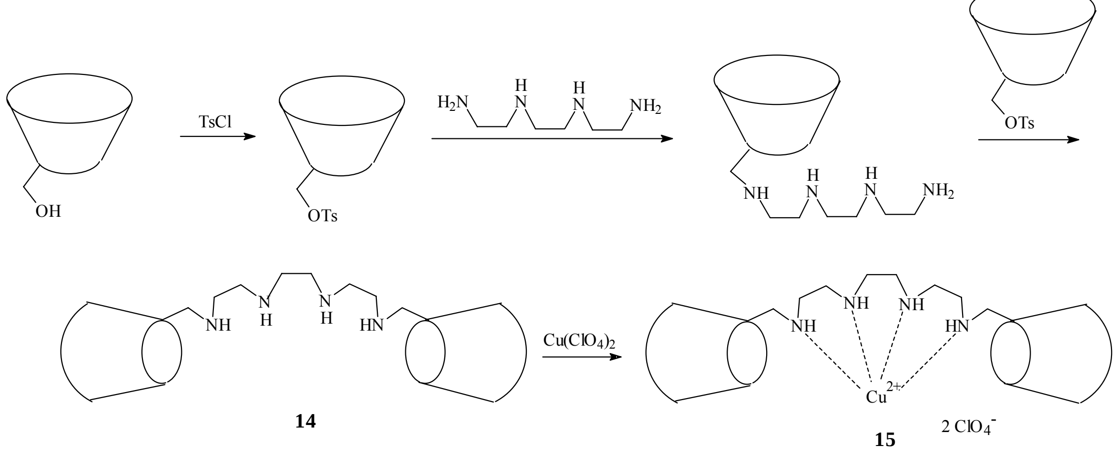


13

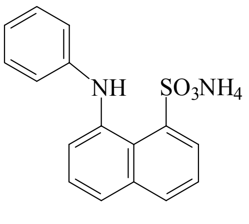
Bridged dimeric CDs attract a special attention due to their increased complexing abilities as compared with that of parent CDs. The linking of two CD moieties by a short spacer enhances their binding properties since one guest-molecule is located in two adjacent CD cavities. [25] Bridged dimeric CDs find application as molecular receptors [26] and may serve as enzyme models. [27,28]

Triethylenetetramine bridged dimeric β-CD (**14**) and its copper (II) complex (**15**) have been synthesized and their recognition of fluorescent dyes ammonium 8-anilino-1-naphthalenesulfonate (ANS) and sodium 6-(*p*-toluidino)-2-naphthalenesulfonate (TNS) examined by spectrofluorometric titrations. [29]

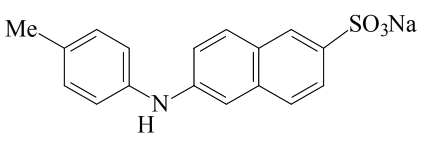


14

15



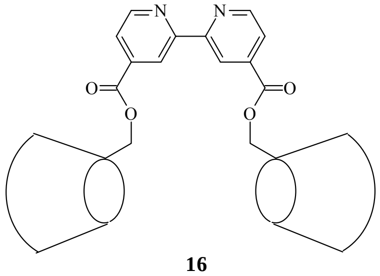
ANS



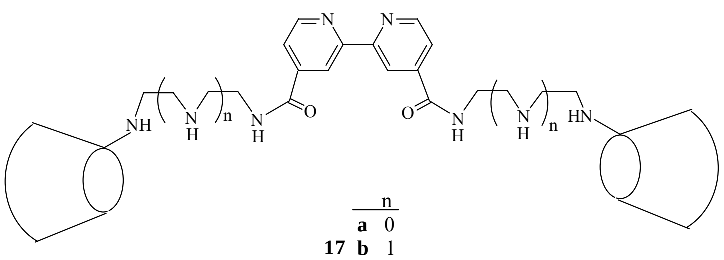
TNS

ANS and TNS show only slight fluorescence in aqueous solutions, in hydrophobic environment, however, e.g. in CD cavity they fluorescence intensively. The binding constant values for host-guest systems of **14** and **15** with ANS and TNS are higher than in the case of the native β-CD due to the cooperative binding by two CD cavities. It was observed that **15** incorporates guests stronger than **14**, this fact being attributed to its triple recognition of the guest by two hydrophobic and one coordination sites.

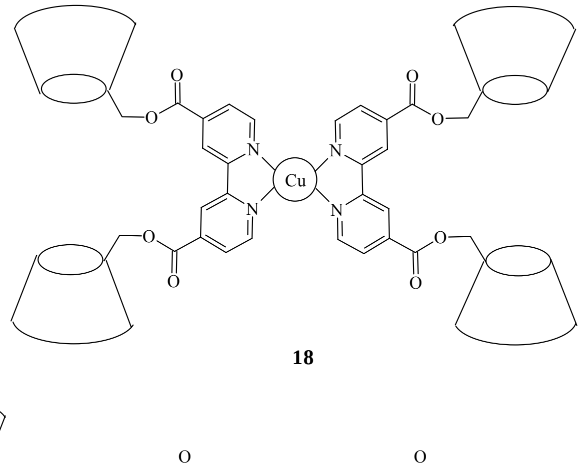
The binding properties of bridged dimeric β-CDs (**16**) and (**17**) and their copper (II) complexes (**18**) and (**19**) for dye guests Methyl Orange (MO), Acridine Red (AR), Rhodamine B (RhB), ANS and TNS have been investigated by UV-VIS, NMR, circular dichroism and fluorescence spectroscopy. [30]



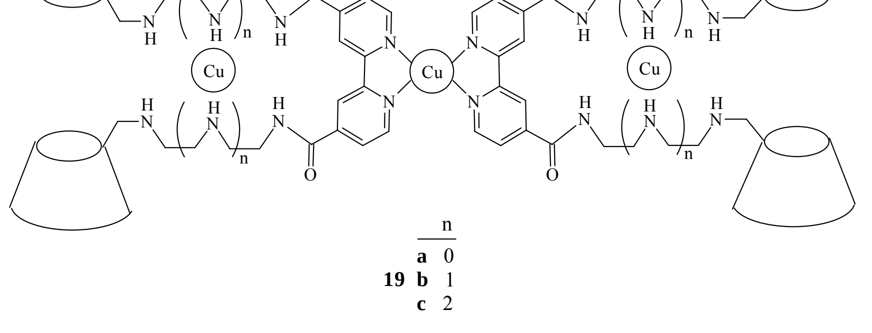
16



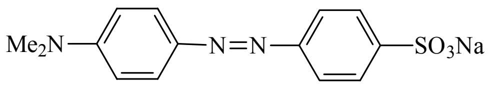
		n
	a	0
17	**b**	1
	c	2



18

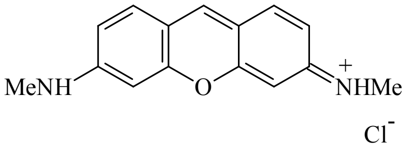


		n
	a	0
19	**b**	1
	c	2



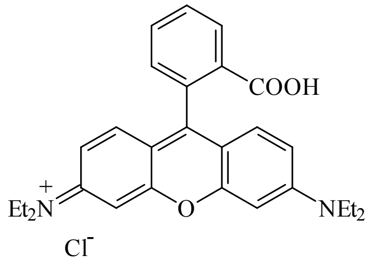
Methyl Orange

MO



Acridine Red

AR



Rhodamine B

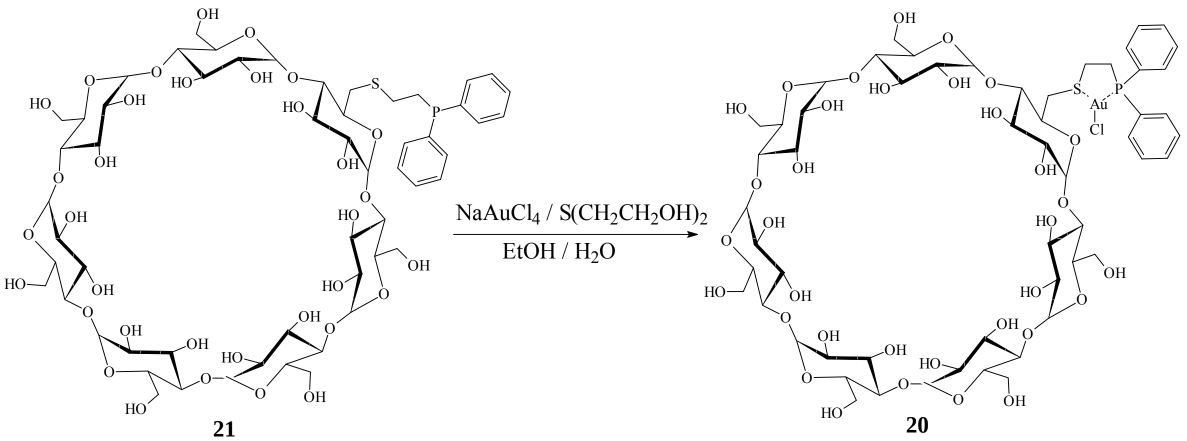
RhB

Complexes (**18**) and (**19**) incorporate two dye molecules forming host-guest systems. In these experiments the molecular multiple recognition between host and guest as well as the shape and size-fit interaction have been taken into account. [29,31] Bridged CDs (**16**) and (**17**) show higher binding abilities than native β-CD due to cooperation of two adjacent CD cavities. Complexes (**18**) and (**19**) display yet stronger binding abilities than bridged dimeric CDs due to the cooperative association of four tethered hydrophobic CD cavities with guests and due to the conformational fixation by metal ions.

In complexes (**18**) and (**19**) the CD cavities and metal coordination centers serve as binding sites. The presence of Cu^{2+} ions changes the conformation of the linking moiety and alters the orientation of two CD cavities, in this way enabling the additional interaction with guest molecule.

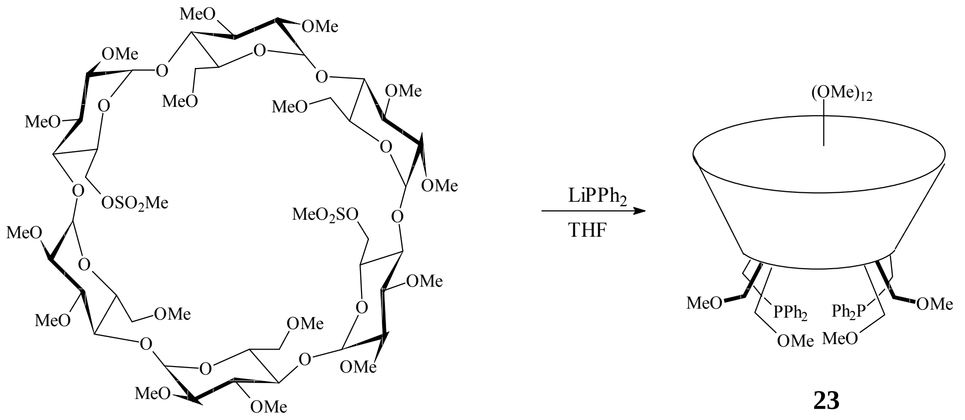
The comparison of stability constants of formed complexes shows that ANS and RhB better exploit the cooperative binding of **18** and **19** than linear guests AR and TNS. The binding of AR, ANS and TNS by short-tethered **18** and **19a** is stronger than in the case of long-tethered **19b,c**; this behavior results from the size-shape matching between host and guest. [30]

Gold complexes with ligands containing phosphorus, nitrogen or sulfur are interesting for their pharmocological activities.[32,33] In this aspect the gold (I) complex (**20**) has been obtained.[34] The synthesis of **20** involves the reaction of thiophosphine modified β-CD (**21**) with AuCl formed *in situ* by reduction of $NaAuCl_4$ with thioglycol.



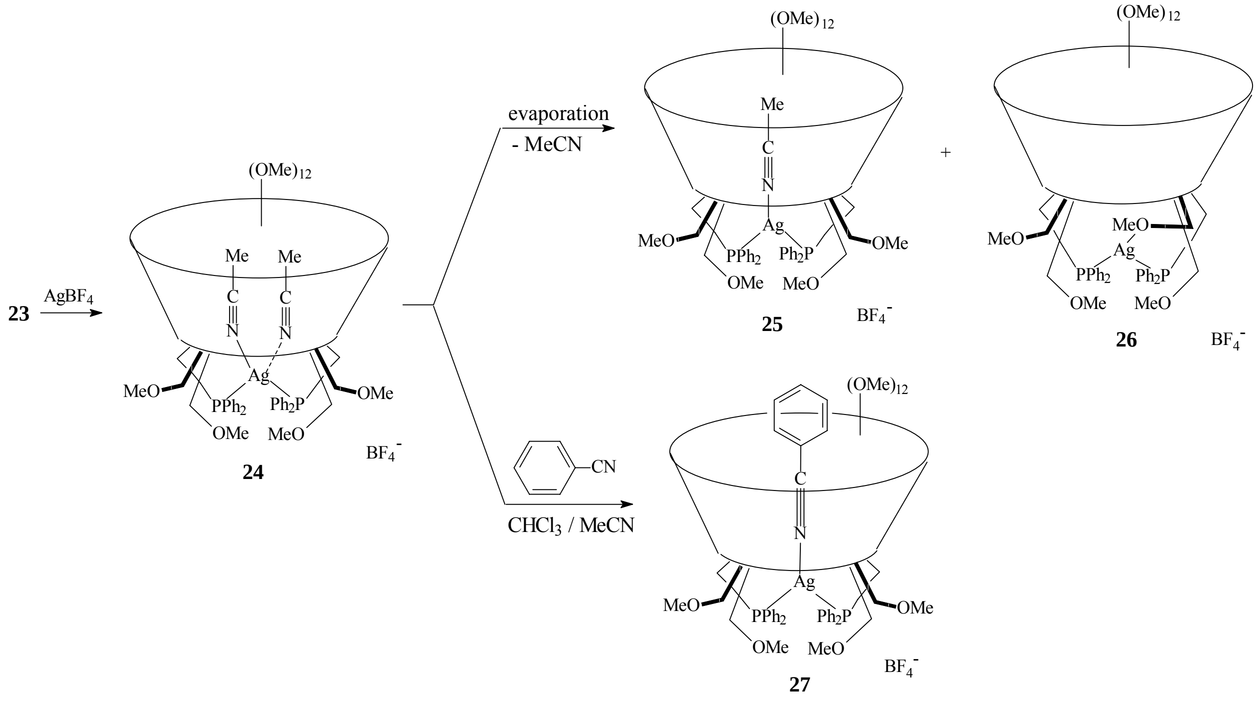
21 **20**

The treatment of the dimesylate of the permethylated α-CD (**22**) with lithium diphenyl phosphide leads to the functionalized α-CD (**23**) . [4,35]



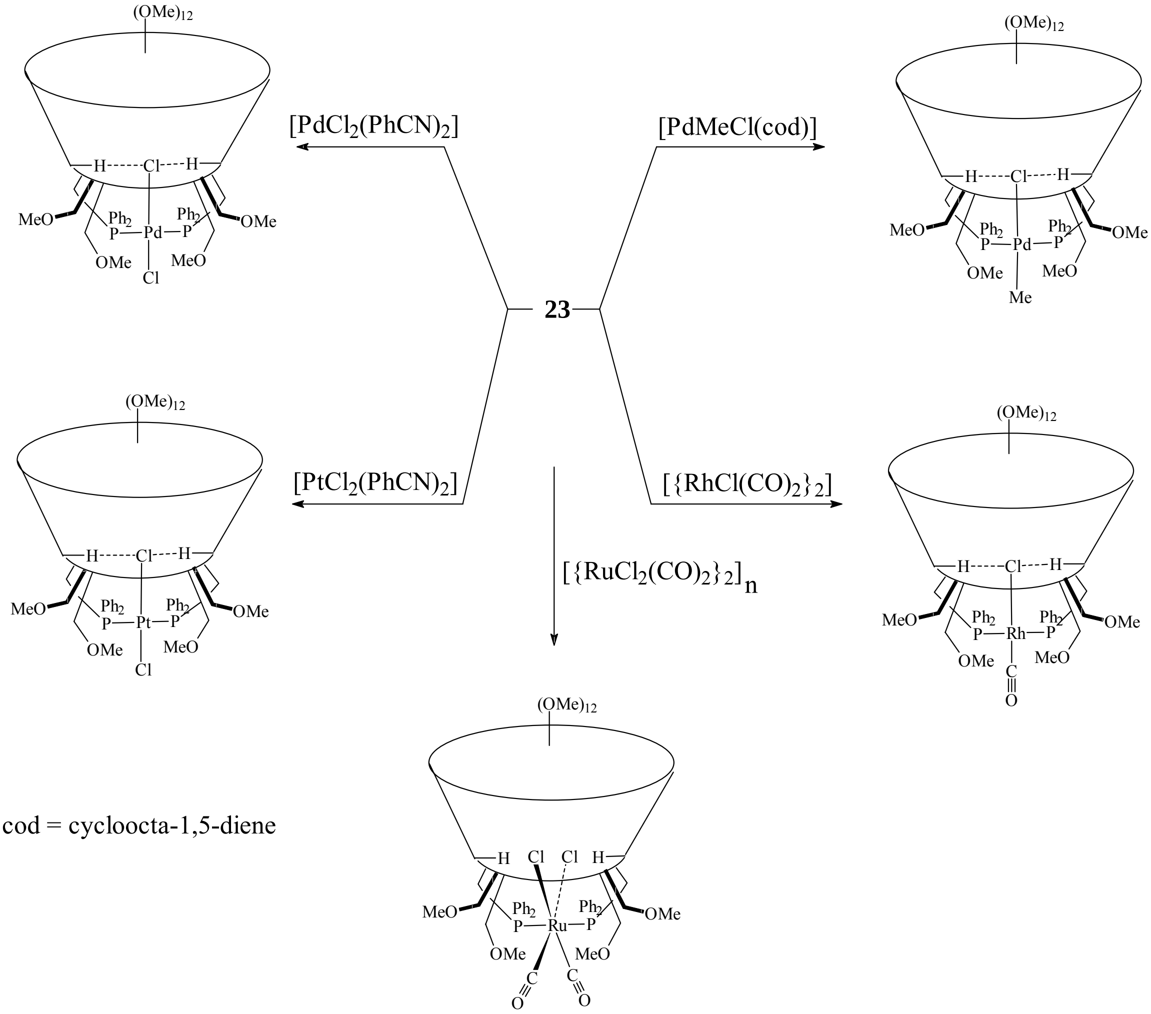
22 **23**

The reaction of **23** with AgBF$_4$ in MeCN affords the complex (**24**) which upon evaporation gives by loss of MeCN the 4:1 mixture of complexes (**25**) and (**26**), and with benzonitrile yields the complex (**27**).



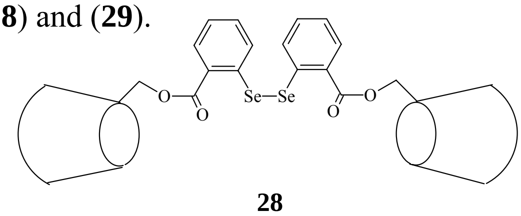
24 **25** **26** **27**

Functionalized α-CD (**23**) has two phosphane units able to form *trans*- chelate complexes with d^8 metals,[36] it incorporates MCl fragments in such a way that chlorine atoms bind noncovalently to inwardly pointing C-H groups of the cavity. The α-CD cavity recognizes a transition metal MCl bond through weak Cl...H5 interactions so in solution as in the solid state.[36] Following complexation reactions of **23** have been performed.



cod = cycloocta-1,5-diene

Bridged dimeric β-CDs (**28**) and (**29**) containing diseleno units were converted into their Pt(IV) complexes (**30-32**) by treatment with $PtCl_4$. [25,37] The host-guest systems of **28** and **29** and of their platinum complexes (**30-32**) with Acridine Red, Rhodamine B, Neutral Red and Brilliant Green have been investigated by UV, fluorescence and circular dichroism spectrometry. [37] As in the case of copper complexes (**18**) and (**19**), [30] platinum complexes (**30-32**) bind dyes stronger than bridged dimeric CDs (**28**) and (**29**).



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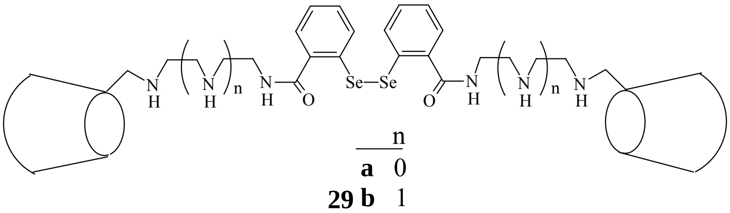
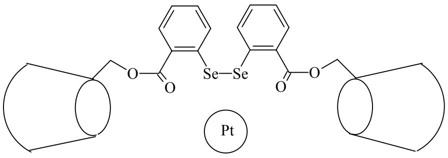


	n
a	0
29 b	1
c	2



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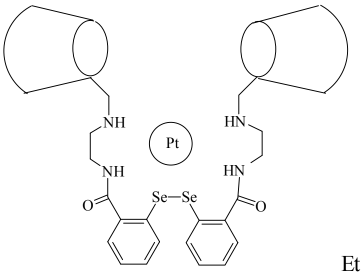

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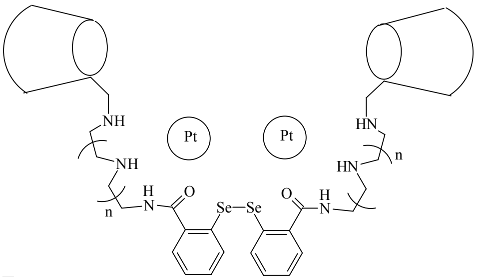
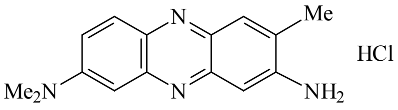
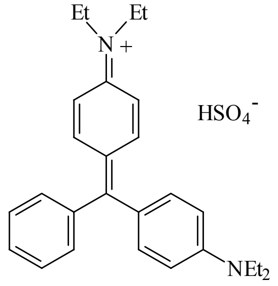


32	n
a	1
b	2

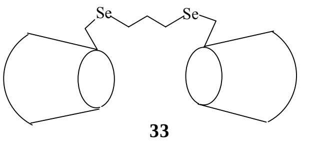


Neutral Red



Brilliant Green

Similar study of the inclusion behavior of organoselenium bridged dimeric β-CDs (**33-35**) and of their platinum (IV) complexes (**36-38**) towards ANS and TNS has been made. [38] As in former examples, [30,37] platinum complexes (**36-38**) bind dyes stronger than bridged dimeric CDs (**33-35**), and much more stronger than native β-CD.



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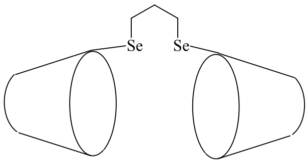
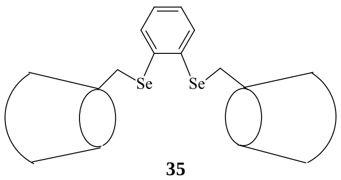
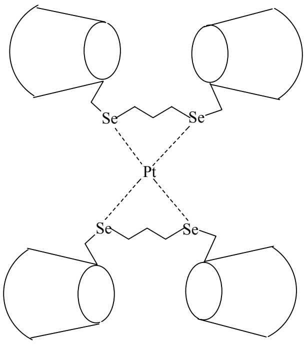


34



35



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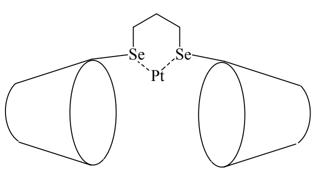

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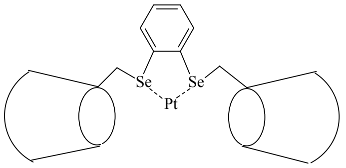
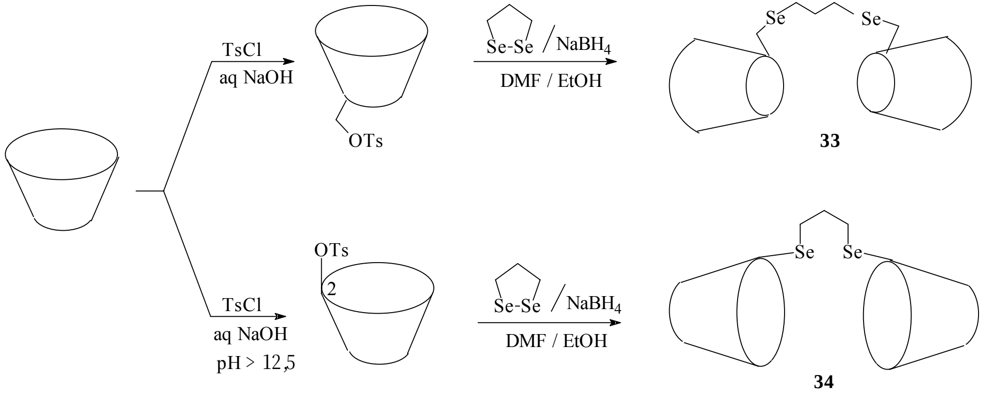


38

The synthesis of **33** and **34** proceeds as follows.

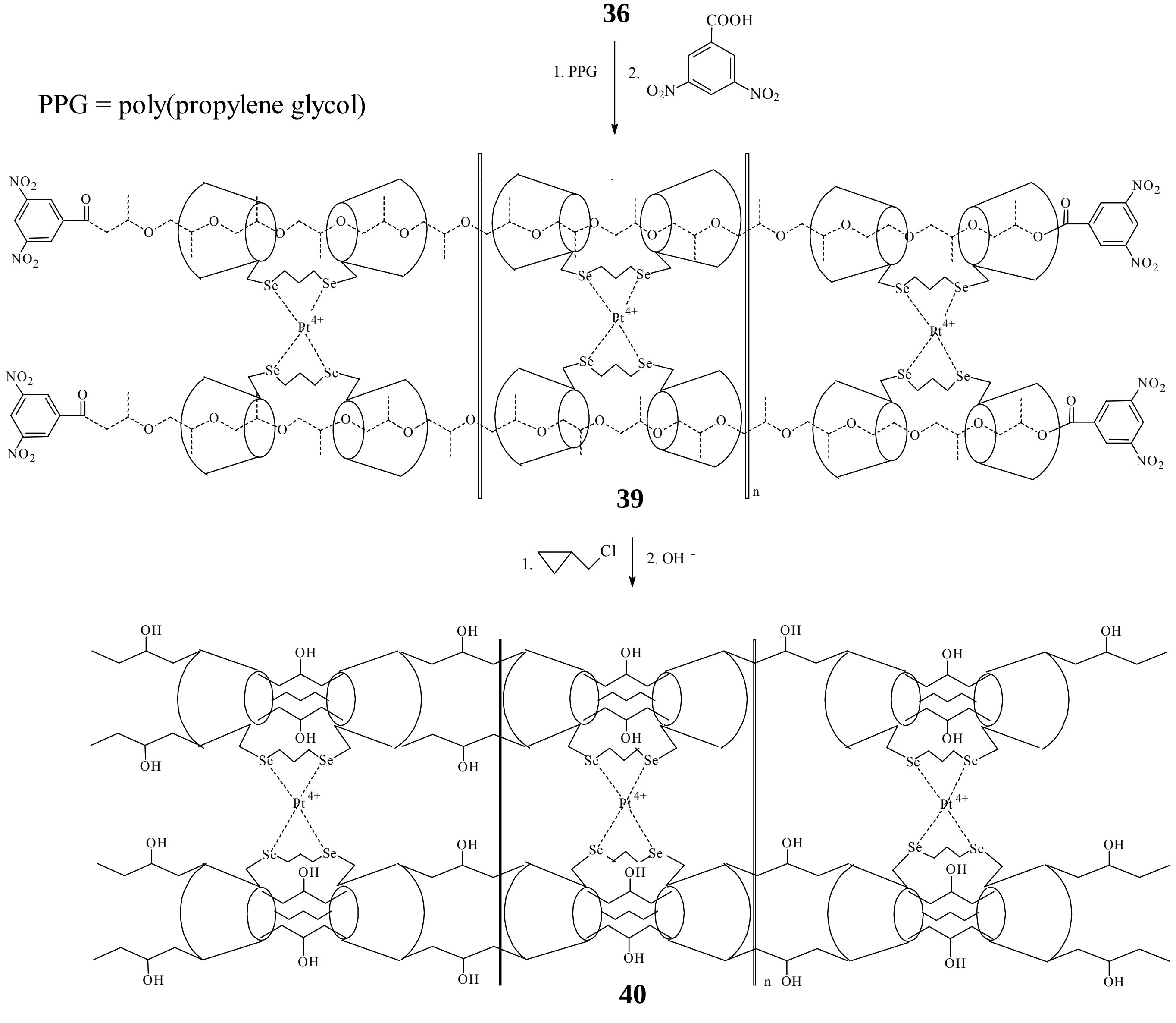


The inclusion of dyes into β-CD and **33-38** results in the strong enhancement of fluorescence intensity. So β-CD as **33-38** form more stable inclusion compounds with TNS than with ANS, since TNS is embedded more deeply in CD cavities than ANS, in which steric hindrance occurs. [38]

It is noteworthy that **34** among **33-35** and **37** among **36-38** show the highest affinities towards ANS, this fact being due to wider openings of 2,2' bridged dimeric CDs than in the case of 6,6'-bridged species. [38]

Bis(molecular tube)s consisting of **36** units have been prepared.[39] Complex (**36**) forms with poly(propylene glycol) a pseudorotaxane, converted by esterification of the terminal hydroxyl groups with 3,5-dinitrobenzoic acid into rotaxane (**39**). The cross-linking of the adjacent CD molecules with epichlorohydrin followed by removal of the polymeric template *via* hydrolysis of the terminal ester groups affords bis(molecular)tubes (**40**), soluble in water and in DMF. The formation of **40** was confirmed by transmission electron spectroscopy (TEM) and atomic force microscopy (AFM) results.

36



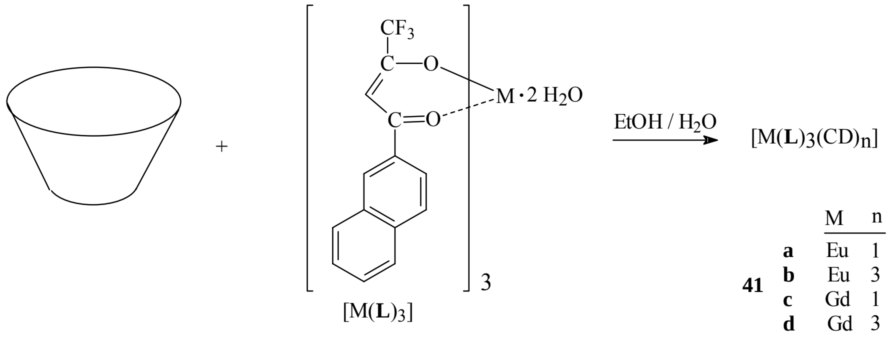
PPG = poly(propylene glycol)

39

40

2. COMPLEXES OF CDs WITH LANTHANIDE IONS

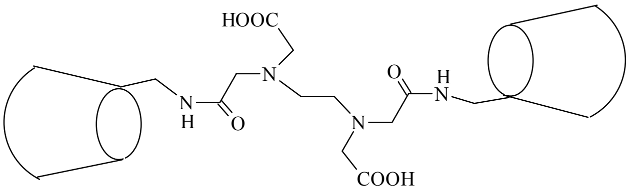
Complexes of β-CD with europium and gadolinium (**41a-d**) have been obtained as follows.[40]



	M	n
a	Eu	1
b	Eu	3
c	Gd	1
d	Gd	3

L = 1-(2-naphthoyl)-3,3,3-trifluoroacetone

CDs are used as molecular recognition sites in the construction of CD-based biomimetic materials [41] and molecular sensors.[42] The molecules incorporated into CD cavity often show changes in photoluminescence, and less frequently in chemiluminescence. An example of the latter behavior is the enzyme model, cerium (IV) complex of the bridged dimeric β-CD (**42**) containing ethylenediamine-tetraacetic acid (EDTA) moiety as a linker, [Ce(**42**)]. [43]



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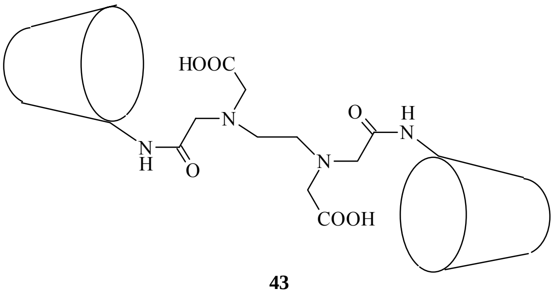
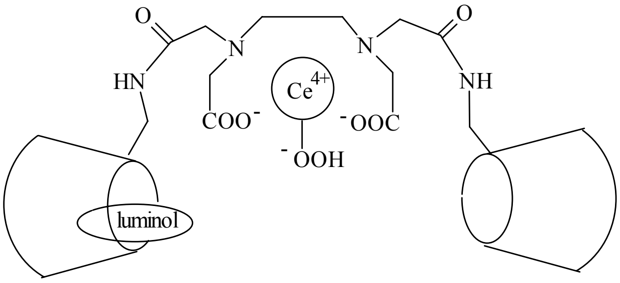


43

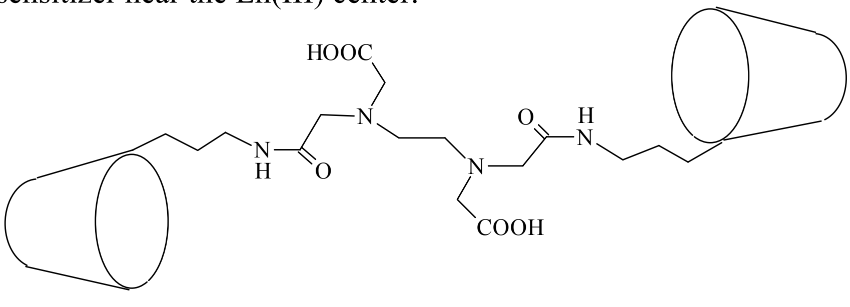
It was found that [Ce(**42**)] catalyzes the chemiluminescent reaction of luminol in the luminol-H_2O_2 system. [43] The cooperation of EDTA-bound cerium ion and β-CD is crucial for the catalytic activity, since individual components do not enhance the chemiluminescence. In this system the catalytic metal complex center and the hydrophobic binding site are localized in one molecule, as it is the case in most metalloenzymes. In the preorganization of luminol and oxidant by the 6-Ce(IV) catalyst, the Ce(IV) center binds the $^-$OOH group, and the CD hydrophobic cavity brings luminol close to the bound -OOH, as shown below, therefore the local concentrations of both luminol and oxidant are considerably increased.

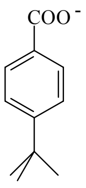


The geometry of the bridged dimeric CD (**42**) is very important for the efficient cooperation of the catalytic Ce(IV) center and the hydrophobic substrate binding site; in the case of the [Ce(**43**)] complex no enhancement of the chemiluminescence of luminol takes place since the CD cavities in **43** are not arranged in such a suitable way as in **42**. [43]

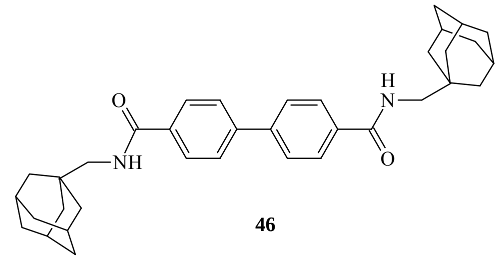
β-CD derivatives covalently functionalized with diethylenetriaminepentaacetate (DPA) or tetra-azacyclododecanetetraacetate (DOTA) may bind Eu(III) or Tb(III); these complexes are used as luminescent sensitizers for the detection of aromatic guests. [44] The encapsulation of a guest sensitizer in the CD cavity enables lanthanide luminescence, and therefore the detection of the guest. Combinations of lanthanide complexes and CDs are interesting for magnetic resonance imaging (MRI).[44,45]

The EDTA-bridged dimeric β-CD (**44**) forms Eu(III) and Tb(III) complexes which bind aromatic sensitizers. [8,9] The sensitizers (**45-47**) are bound in a ditopic way: they have hydrophobic site for CD cavity and a functionality for coordination of Ln(III) ion. Such a ditopic binding mode ensures an efficient energy transfer from the guest to the lanthanide center for sensitized luminescence. The sensitizer (**45**), serving as an antenna chromophore for the sensitization of lanthanide luminescence bears *tert*-butylphenyl moiety for binding to CD, and carboxylate group for coordination of Ln(III) ion. The coordination of the guest carboxylate group and EDTA-bound Ln(III) ion occurs due to the effective concentration of the sensitizer near the Ln(III) center.





45



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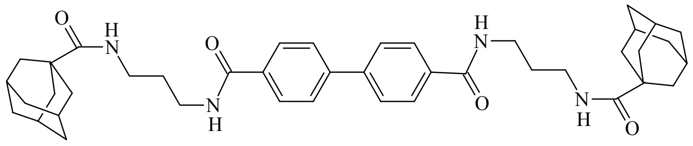
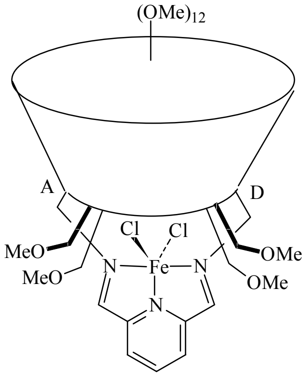


47

The luminescence intensity of [Eu(**44**)] and [Tb(**44**)] in water significantly increases upon addition of **45**. The coordination of the carboxylate group of **45** to Ln(III) ion in [Ln(**45**)$_2$(**44**)] complex was investigated using Gd(III)-induced ^{13}C NMR relaxation rate measurements. [45,46]

3. COMPLEXES OF CDs WITH VARIOUS METAL IONS

It was observed that complexes of methylated α- and β-CDs with Fe(II) ion (**48**) and (**49**) show catalytic activities for the polymerization of ethylene.[47,48]



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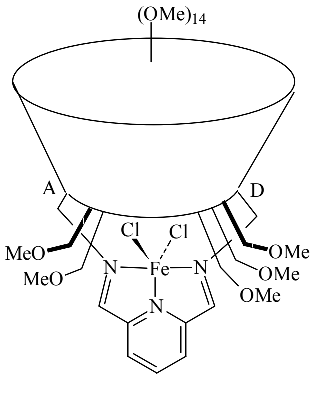
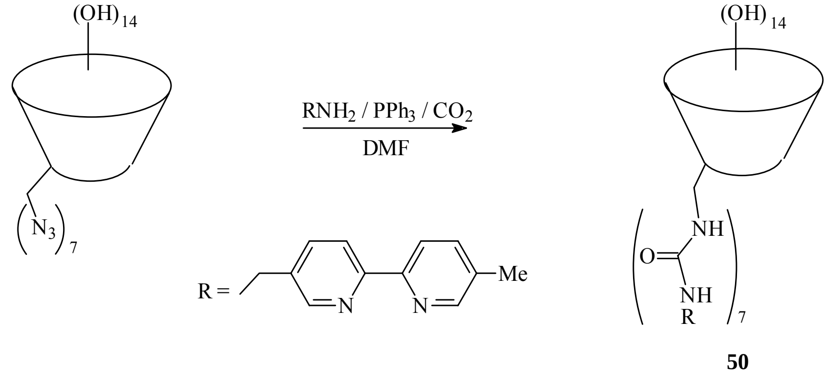
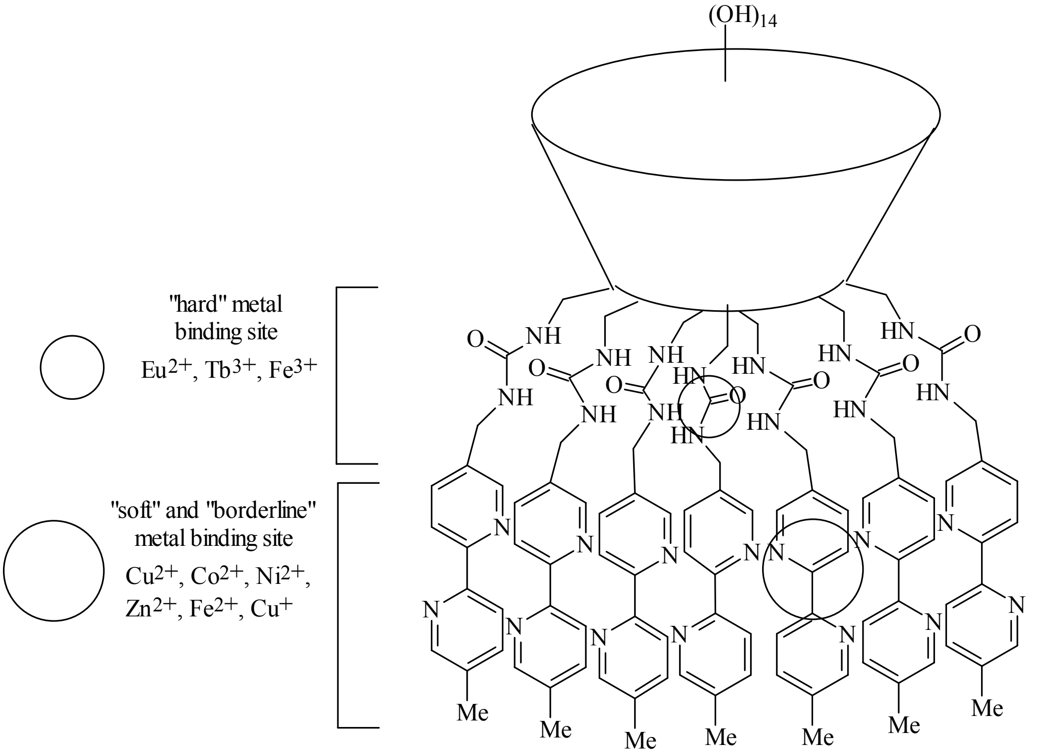


49

The synthesis of bipyridyl-ureido β-CD (**50**) proceeds *via* phosphine imide one-step reaction; the obtained **50** forms complexes with „hard” and „soft” metal ions.[10]

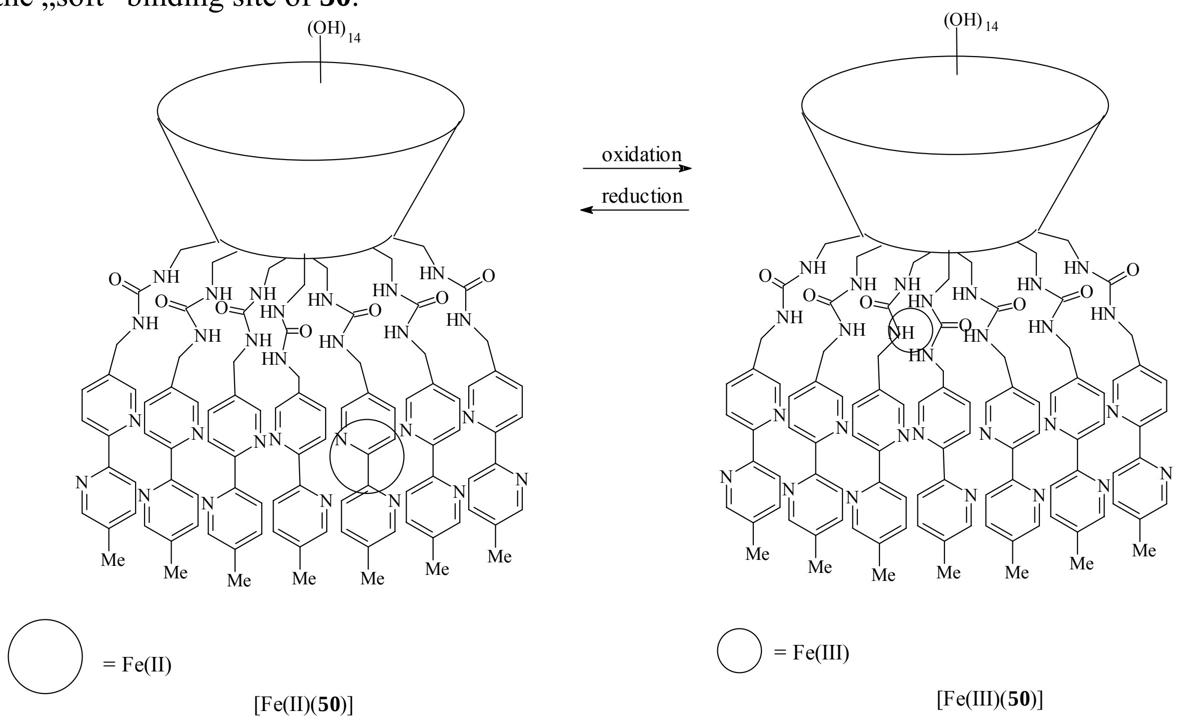


50



complexes of 50

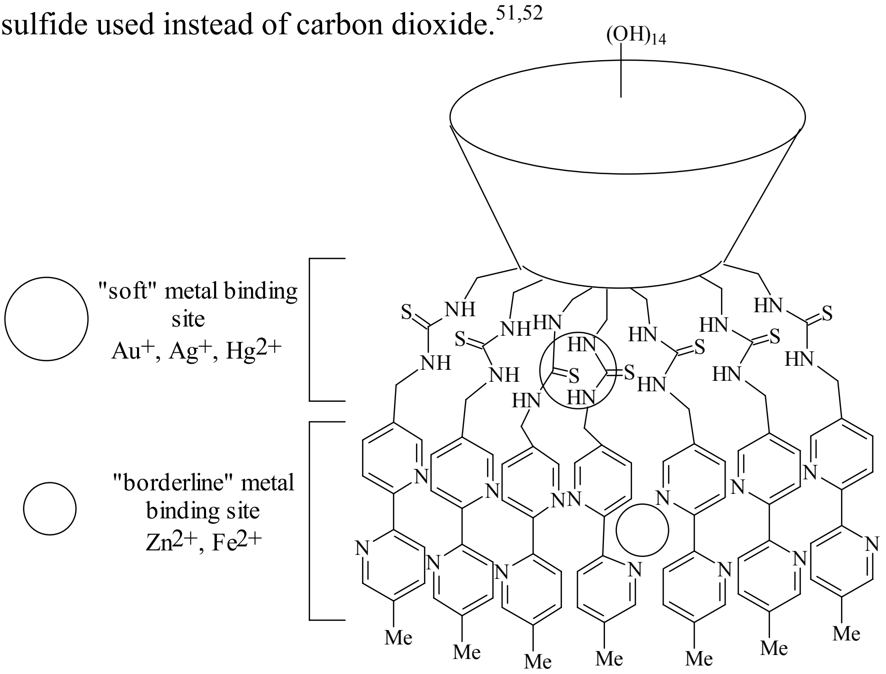
In the search for molecular switches the chemical oxidation and reduction of Fe^{2+}/ Fe^{3+}, accompanied by the reverse translocation of the ion from the „soft" into „hard" cavity of **50** was investigated. [49,50] The treatment of the purple complex ([Fe(II)(**50**)]) with ammonium persulfate leads to the formation of the yellow [Fe(III)(**50**)] complex in which Fe^{3+} ion is situated in the „hard" binding site of **50**. When [Fe(III)(**50**)] reacts with ascorbic acid, the reverse reduction occurs, resulting in the incorporation of Fe^{2+} into the „soft" binding site of **50**. [10]



[Fe(II)(**50**)]

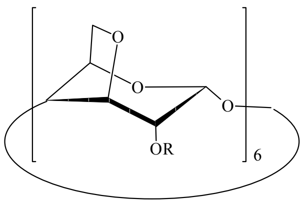
[Fe(III)(**50**)]

The complexation behavior of **51**, i.e. the sulfur analogue of **50** towards metal cations has been studied by UV-VIS spectroscopy.[51] In **51** the urea functions of **50** [10] have been replaced by thiourea groups, therefore **51** binds selectively „soft" metal ions, such as Hg^{2+}, Ag^{+}, Au^{+} and „borderline" metal ions, such as Zn^{2+} and Fe^{2+}, while no inclusion of lanthanide ions occurs. The synthesis of **51** proceeds as in the case of **50**, with carbon disulfide used instead of carbon dioxide.[51,52]

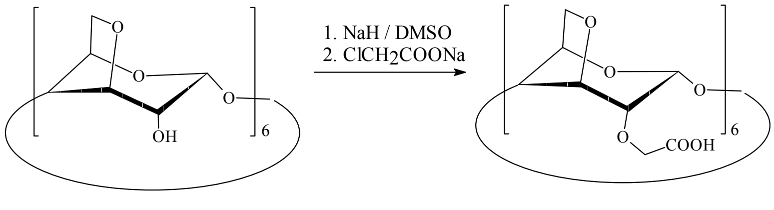


complexes of **51**

Complexing properties of anhydro-CDs (**52a-c**) have been studied. Anhydro-CDs bind cations, in contrast to CDs incorporating hydrophobic guests. In **52a** an affinity for Pb^{2+} ion was observed, **52b** binds Pb^{2+} and Ba^{2+}, and weakly binds physiological cations, especially Ca^{2+}. [53] The affinity of **52c** towards Eu^{3+}, Gd^{3+}, Dy^{3+}, Yb^{3+}, Lu^{3+}, La^{3+}, UO_2^{2+}, Co^{2+}, Cd^{2+}, Pb^{2+}, Ca^{2+}, Cs^{+}, Na^{+} and K^{+} ions has been evaluated by ^1H NMR spectroscopy. [54] It was shown that **52c** has stronger affinity for toxic lanthanides, cobalt and uranyl ions than for sodium, potassium and calcium physiological ions; no affinity of **52c** for Pb^{2+}, Cd^{2+} and Cs^{+} ions has been found. The synthesis of **52c** involves the treatment of **52a** with NaH, followed by sodium chloroacetate. [54]



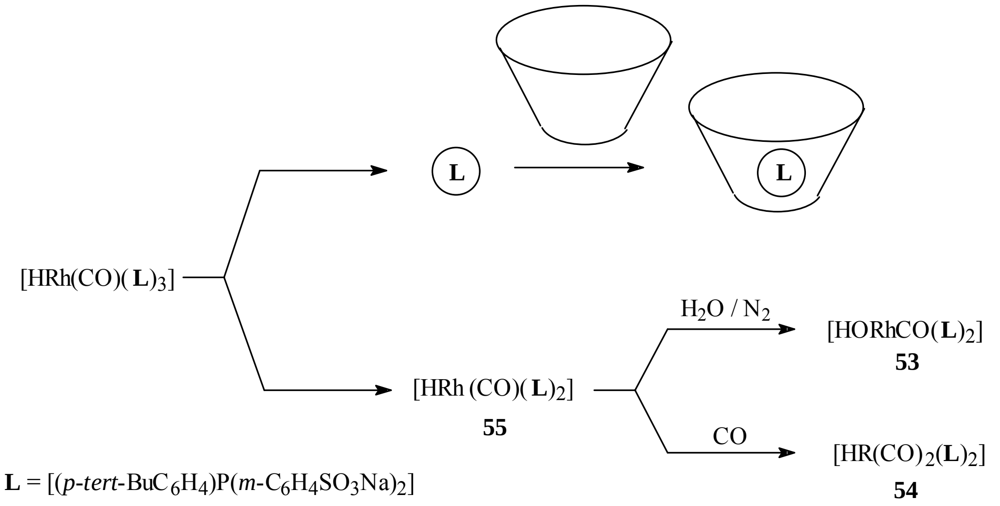
		R
	a	H
52	**b**	Me
	c	CH_2COOH



52a

52c

One should mention here also the effect of β-CD on water-soluble rhodium complex [HRhCO(**L**)$_3$], where **L**= [(*p*-*tert*-BuC$_6$H$_4$) P(*m*-C$_6$H$_4$SO$_3$Na)$_2$]. [55,56] In the presence of β-CD it affords hydroxy complex (**53**) by reaction of water under nitrogen or hydrido complex (**54**) under carbon monoxide. The above conversions proceed *via* the unstable species (**55**) and are promoted by trapping the water soluble ligand (**L**) by β-CD. This behavior is promising for the development of aqueous phase organometallic catalysis. [57,58]

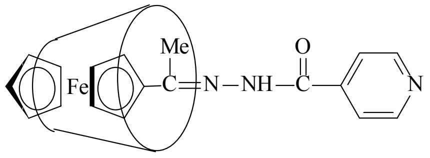


L = [(*p*-*tert*-BuC$_6$H$_4$)P(*m*-C$_6$H$_4$SO$_3$Na)$_2$]

4. COMPLEXES OF CDs WITH FERROCENES AND HALF-SANDWICH MOLYBDENUM AND MANGANESE SPECIES

Numerous CD complexes with ferrocenes are known. [59-62] Acylhydrazones bearing ferrocenyl group are interesting as inhibitors for enzymes, however the water solubility of these compounds is poor. In order to enhance their water solubility and bioavailability, host-guest complexes with β-CD have been synthesized; an example is **56**.[63]

The host-guest binding of α- and β-CDs with ferrocenyl derivatives (**57**) and (**58**) possesing rigid triene chains has been investigated by electrochemical and spectrophotometric measurements.[64] Compounds (**57**) and (**58**) are nearly insoluble in aqueous media, however, in the presence of α- or β-CDs their solubility increases due to the host-guest interaction.



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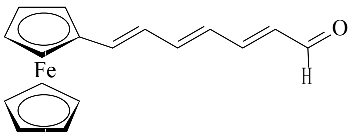

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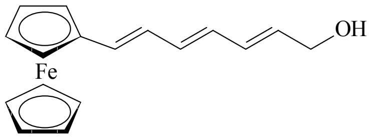
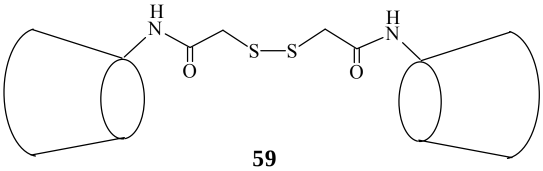


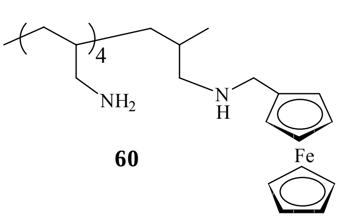
58

Complexes of β-CD with both guests are more stable than those of α-CD. It was observed that α-CD binds mainly the unsaturated chain, while β-CD prefers the ferrocene moiety. This behavior is compatible with similar binding preferencies of α- and β-CDs with ferrocenes bearing aliphatic chains. [64]

The host-guest interaction of bridged dimeric β-CD (**59**) with poly(allylamine) modified with ferrocenyl groups (**60**) results in the formation of layered assemblies, promising for the construction of sensing devices.[65]

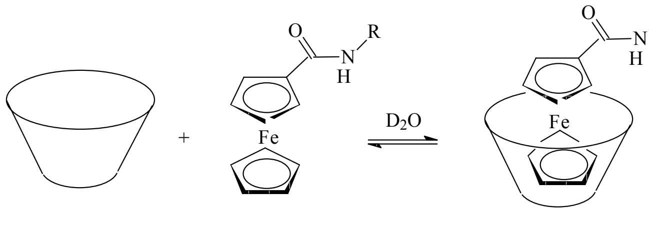


59

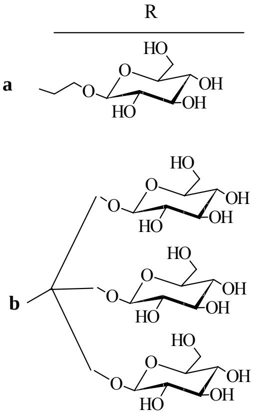


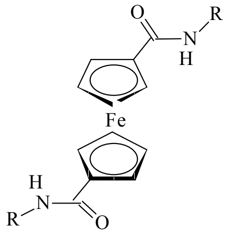
60

β-CD forms with monosubstituted ferrocene derivatives (**61a,b**) the 1:1 complexes (**62a,b**).[66] Since **62b** has a larger substituent than **62a**, the stability constant of the complex β-CD/**62b** is lower than that of the β-CD/**62a** complex. The complexation of β-CD has been observed only for monosubstituted ferrocene derivatives; with **63a,b** in which both cyclopentadienyl rings are substituted, no β-CD complexes are formed.



61a,b **62a,b**

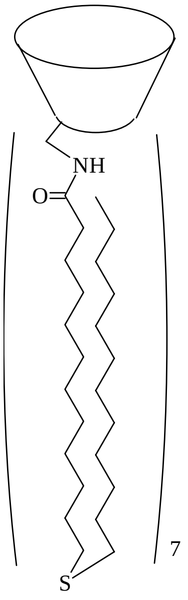




63a,b

Stability constants of 1:1 complexes of α-, β- and γ-CDs with ferrocenium ion have been determined using ^{1}H NMR shift titrations.[60,67] The binding of α-CD is weaker than in the case of β- and γ-CDs. The inclusion of ferrocene and its derivatives into the CD cavities is of interest in the construction of redox switches for nanomolecular sensors. It should be noted that the stability of CD complexes with ferrocenium ion is lower than in the case of the ferrocene molecule.

β-CD modified with seven thioether groups (**64**) and that modified with one thiol group (**65**) form self-assembled monolayers on gold. The monolayers of **64** and **65** were characterized by electrochemistry and wettability experiments. The guest binding of CDs in these monolayers was investigated by surface plasmon resonance (SPR) spectroscopy.[68]



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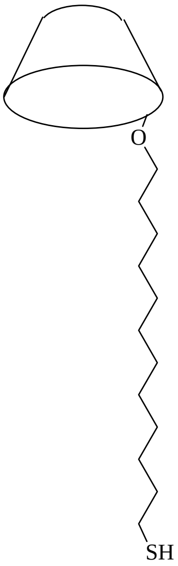
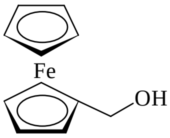


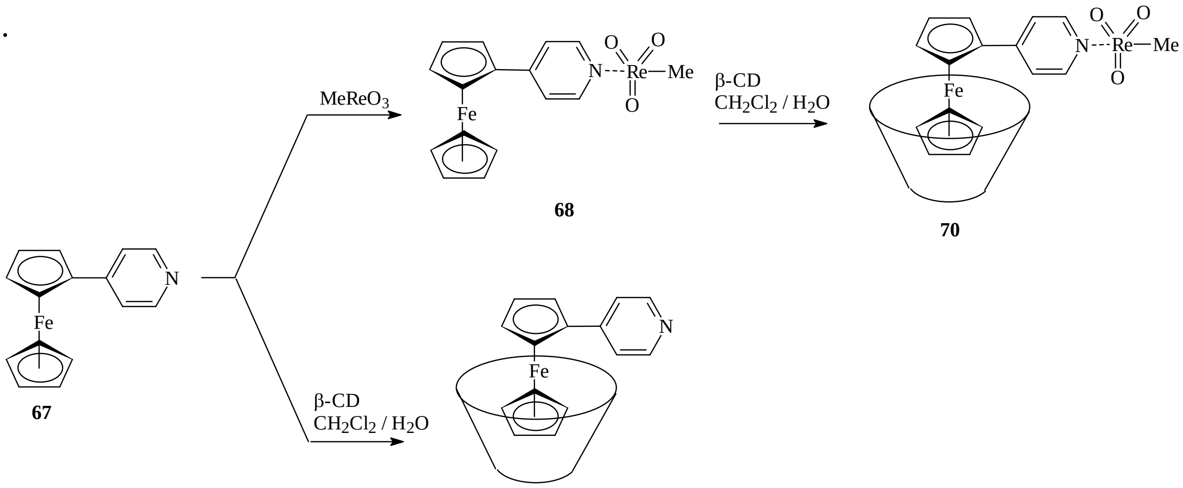
65



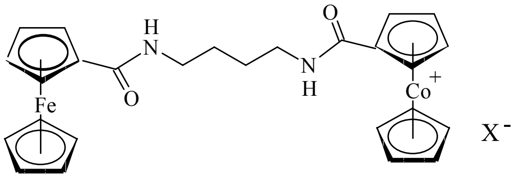
66

Using ferrocenemethanol (**66**) as a guest, its binding by monolayers of **64** on gold and by β-CD in solution were compared. It was found that the binding constants are similar. This observation shows that the perfunctionalization of the primary rim does not affect significantly the cavity interior of β-CD. The charge-transfer resistance towards $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ redox couple in the case of **64** monolayers is higher than in the case of **65** due to the better packing of the former ones.[69]

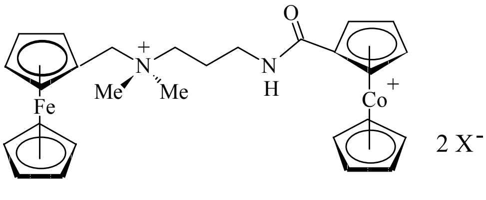
In the study of inclusion complexes of CDs with binuclear organometallics [70] the following reactions have been made. [71] The encapsulation of **67** and **68** in β-CD cavities affording host-guest systems (**69**) and (**70**), respectively, results in their higher thermal stability, as was shown by thermogravimetric analysis.



Investigating ferrocene-cobaltocenium complexes [72,73] the incorporation of **71** and **72** into β-CD has been examined by cyclic voltammetry. [74] It was established that β-CD forms with **71** and **72** stable 1:1 inclusion compounds in which the ferrocene moiety is incorporated into CD cavity. It should be noted that no complexation of β-CD with fc$^+$-cob$^+$ species takes place, while in the case of the fully reduced state fc-cob, having two binding sites, β-CD forms 1:1 and 2:1 complexes (fc = ferrocene, cob = cobaltocene). [74]

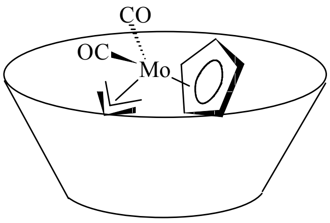


71 X = Cl, PF$_6$



72 X = Cl, PF$_6$

In the study of CD inclusion compounds with half-sandwich complexes of molybdenum, [75] the host-guest systems (**73**) and (**74**) have been synthesized by treatment of the aqueous solution of β-CD with a CH_2Cl_2 solution of MoCp'(η^3-C_3H_5)$(CO)_2$, where Cp' is Cp or indenyl, respectively. [76] The crystalline products (**73**) and (**74**) precipitate at the interface between aqueous and organic solutions. [76]



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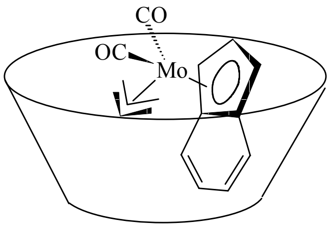
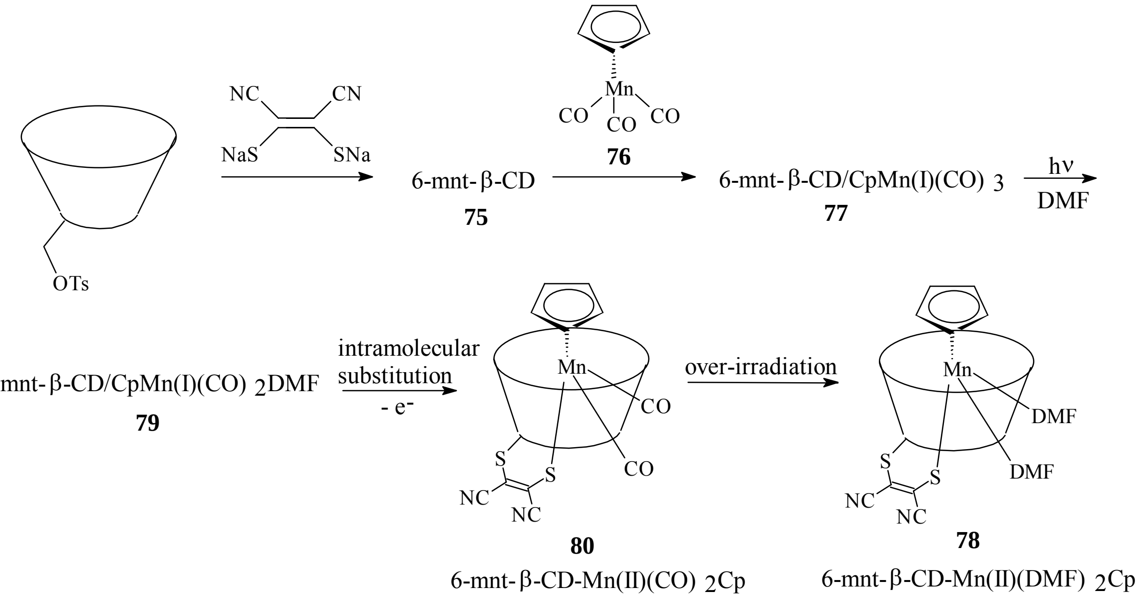


74

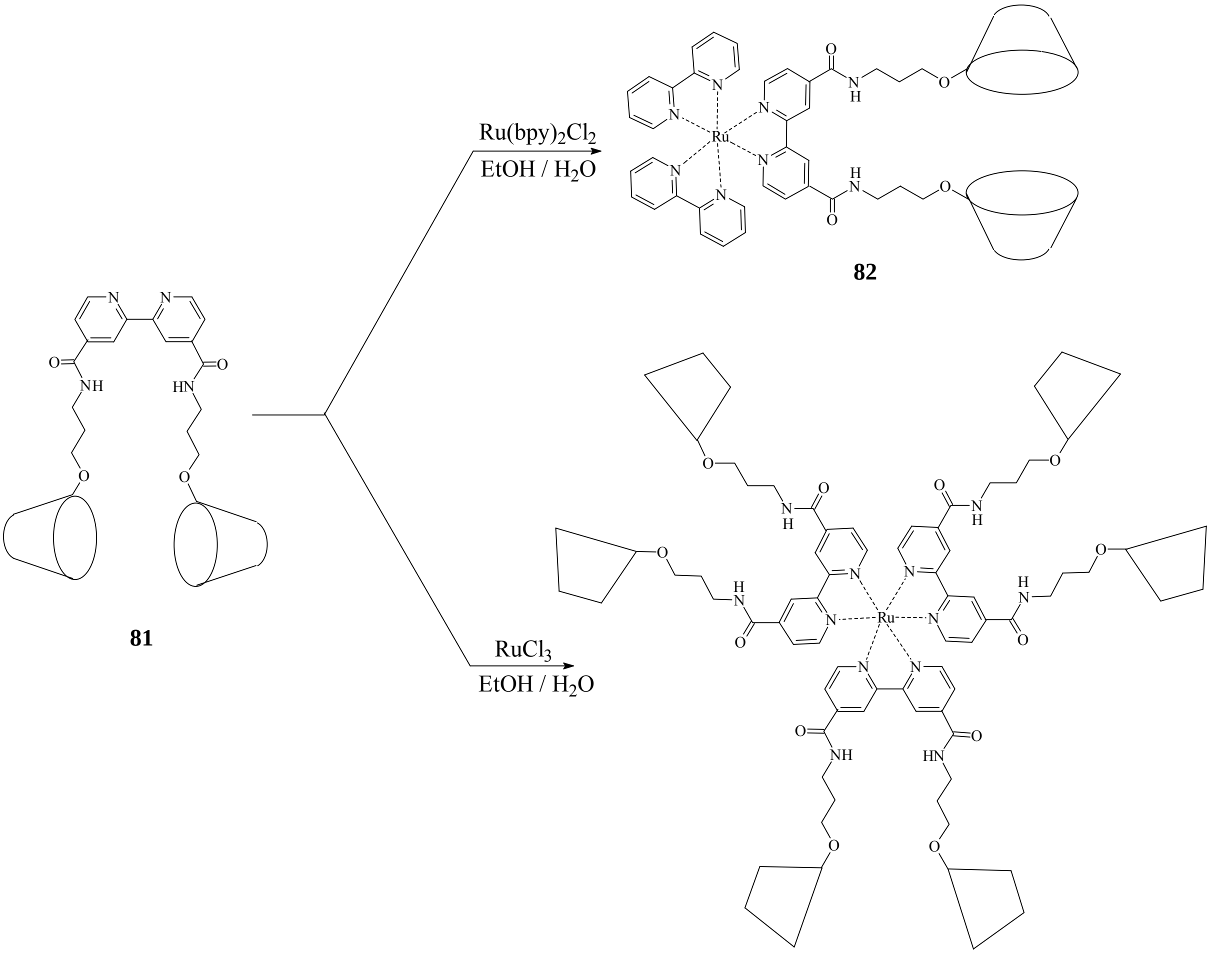
The complexation of 6-mnt-β-CD (**75**) (mnt= maleonitriledithiolate group) with cyclopentadienyl manganese tricarbonyl [CpMn(I)$(CO)_3$] (**76**) has been investigated.[77] The synthesis of **75** involves the reaction of 6-OTs-β-CD with Na_2mnt in water. The treatment of **75** with [CpMn(I)$(CO)_3$] (**76**) leads to the inclusion compound (**77**). [78] The results of the thermogravimetric analysis show that the thermostabilities of both the host and the guest of **77** are significantly increased by the inclusion. In **77** the side-arm interacts with the incorporated guest preventing its liberation and subsequent decomposition by heating.

The irradiation of **77** in DMF solution which results in the unexpected photo-substitution leading to **78** begins with the dissociative loss of CO and the formation of the DMF-solvate (**79**). The intramolecular substitution of coordinated DMF in **79** by strong nucleophilic mnt group, followed by one-electron oxidation affords the self-inclusion compound (**80**) which by over-irradiation gives the compound (**78**). [77] Compound (**78**) is very stable in DMF solution due to a double recognition between the host and the guest, i.e. the binding of mnt to the Mn(II) center and the hydrophobic recognition of organomanganese fragment within the CD cavity.



5. COMPLEXES OF CDs WITH BIPYRIDINE AND PHENANTHROLINE RUTHENIUM COMPOUNDS

Coordination of CDs bearing bipyridine ligands with metal ions has been studied. [9,79-81] It was found that the bipyridine-bridged dimeric β-CD (**81**) forms complexes (**82**) and (**83**) [82] as follows:



81

82

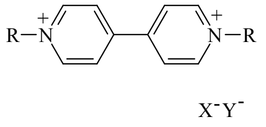
83

The presence of CD units in **82** and **83** protects the luminescent ruthenium center from quenching by oxygen; this behavior enables longer excited state lifetimes and more efficient emission as compared with $[Ru(bpy)_3]^{2+}$. Complex (**83**) shows high quantum yield, promising for its use in sensor devices. [9]

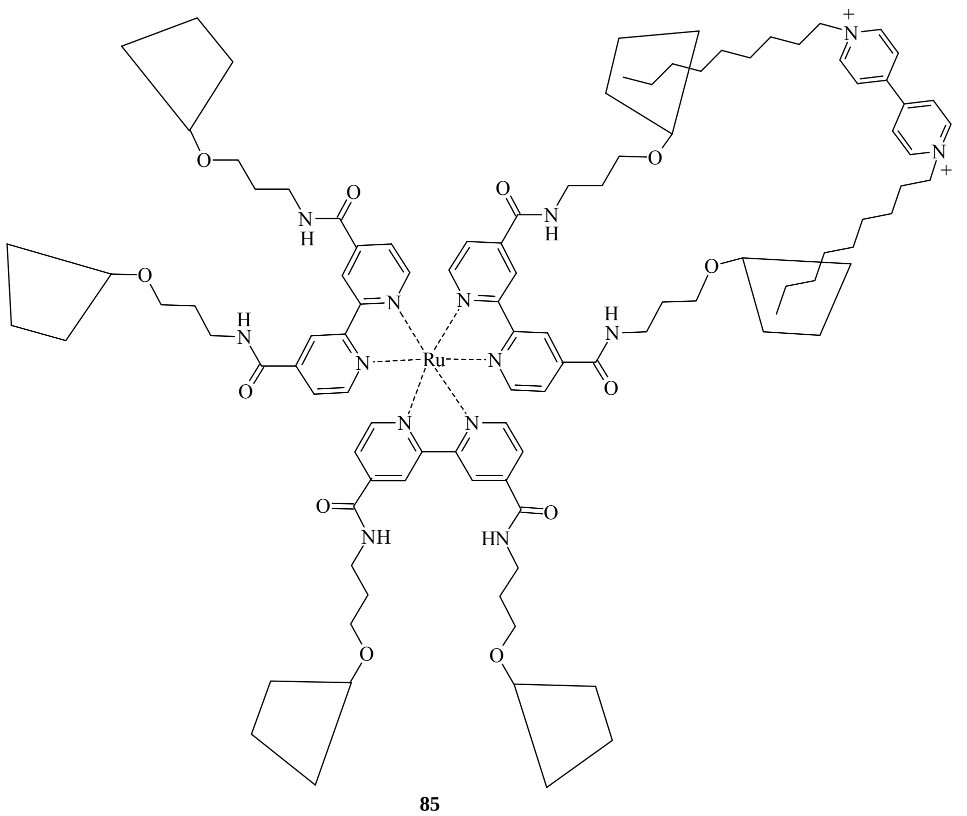
Complexes (**82**) and (**83**) may serve as hosts in supramolecular inclusion systems in which viologens are guests. In **82** and **83** the ruthenium complex acts as an electron donor, while CDs are a binding site for electron acceptors; as those serve dialkyl viologens (**84a-c**). The incorporation of viologens results in the quenching of emission proceeding by a photoinduced electron transfer from the excited ruthenium center to the viologen.

In **81-83** the CD molecules are connected through their secondary rims, enabling the association of ditopic guests. Such cooperative effect leads to higher binding constants and allows to detect photoinduced electron transfer at very low host concentration; these processes have been investigated by steady-state and time-resolved fluorescence spectroscopy. The CD hosts bind viologen guest and bring it close to the luminescent metal center; in this way electron transfer is possible, which otherwise could not proceed in the diluted solutions used for the supramolecular assembly.

Viologens (**84a-c**) served as guests; the long alkyl chains are neccessary for binding to CDs, since the doubly charged bipyridinium ion is too hydrophilic to interact strongly with the CD cavity. The binding of the viologen (**84c**) to **82** and **83** was investigated by fluorimetric and microcalorimetric titrations; **83** forms with viologen (**84c**) the 1:1 host-guest system (**85**) resulting in the decrease of emission intensity.



		R	R1	X	Y
	a	C_5H_{11}	C_5H_{11}	Br	Br
84	**b**	C_9H_{19}	Me	Br	I
	c	C_9H_{19}	C_9H_{11}	Br	Br

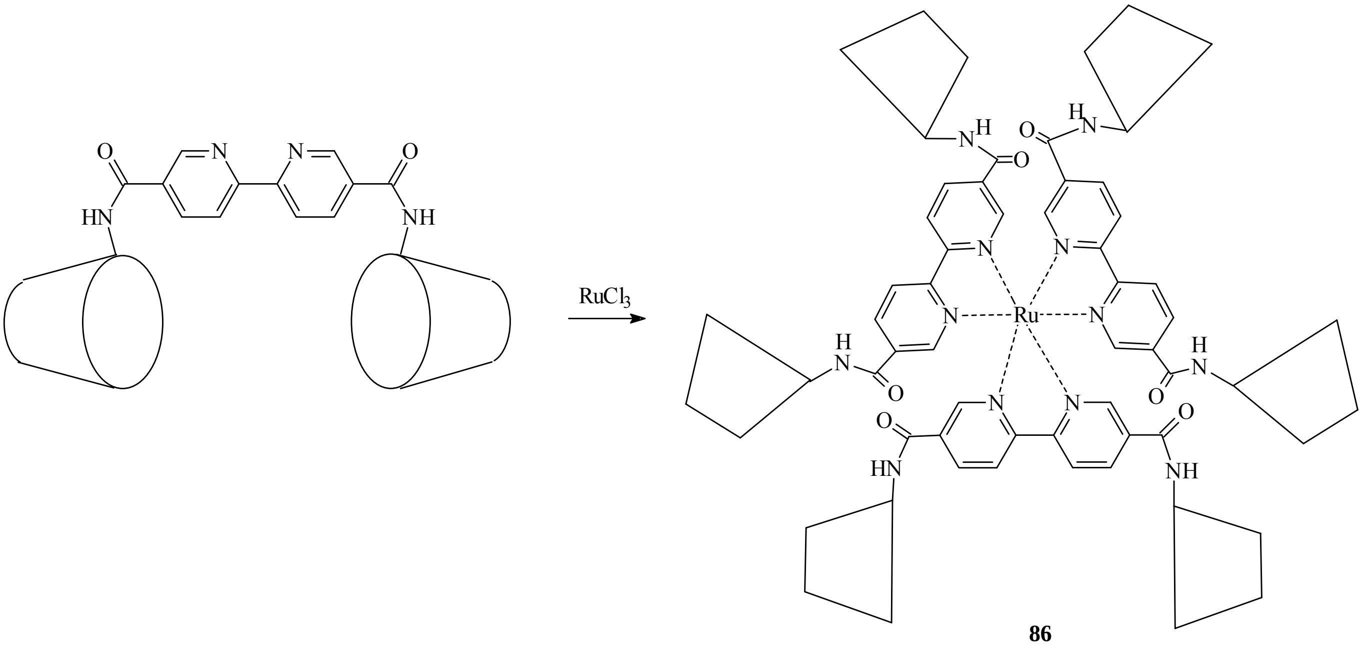


85

When instead of **84c**, the viologen (**84a**) having shorter alkyl chains was used in the experiments, no decrease of the emission intensity of the ruthenium complex (**83**) upon addition of **84a** was observed. The viologen (**84b**), which has one methyl and one nonyl group behaves like a monotopic guest; its binding to **83** is weaker than that of **84c**. [82]

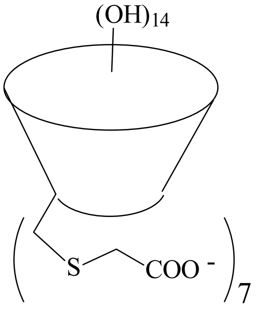
When viologen (**84c**) was added to an aqueous solution of **83**, the emission intensity dropped as a result of the formation of a 1:1 host-guest system (**85)**. Displacement of **84c** by other guests, such as steroids, e.g. ursodeoxycholic acid or lithocholic acid recovers the luminescence of **83**. [9] Due to this behavior **83** may act as a sensor emitting light when a guest, i.e. the compound to be detected is added; such detection of a guest accompanied by the increase in emission intensity is rather rare and allows a sensitive diagnosis. The binding of ursodeoxycholic acid is stronger than in the case of lithocholic acid, i.e. the sensor is able to differentiate between steroids, this fact being of importance for the selective diagnostic test.

It should be mentioned that **86** obtained as follows is, in contrast to **83**, only weakly luminescent since bulky β-CD molecules prevent optimal coordination of the bipyridyl ligands to ruthenium ion. [9]

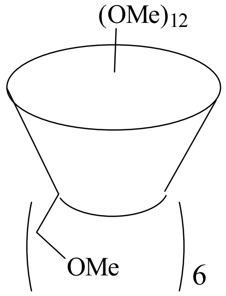


86

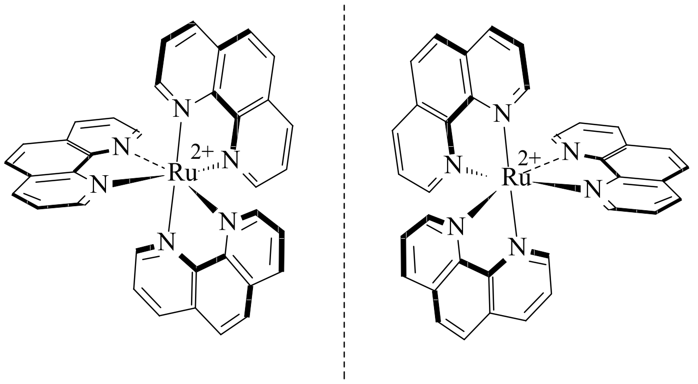
CDs can discriminate between enantiomers of various guests, the origin of the chiral recognition by CD being its asymmetrically twisted cavity. [83-85] Chirality of $[M(phen)_3]^{2+}$ where M=Ru(II), Rh(II), Fe(II), Co(II), and Zn(II) was recognized by derivatives of β- and α-CDs, (**87**) and (**88**), respectively, in D_2O.[86,87]



87



88

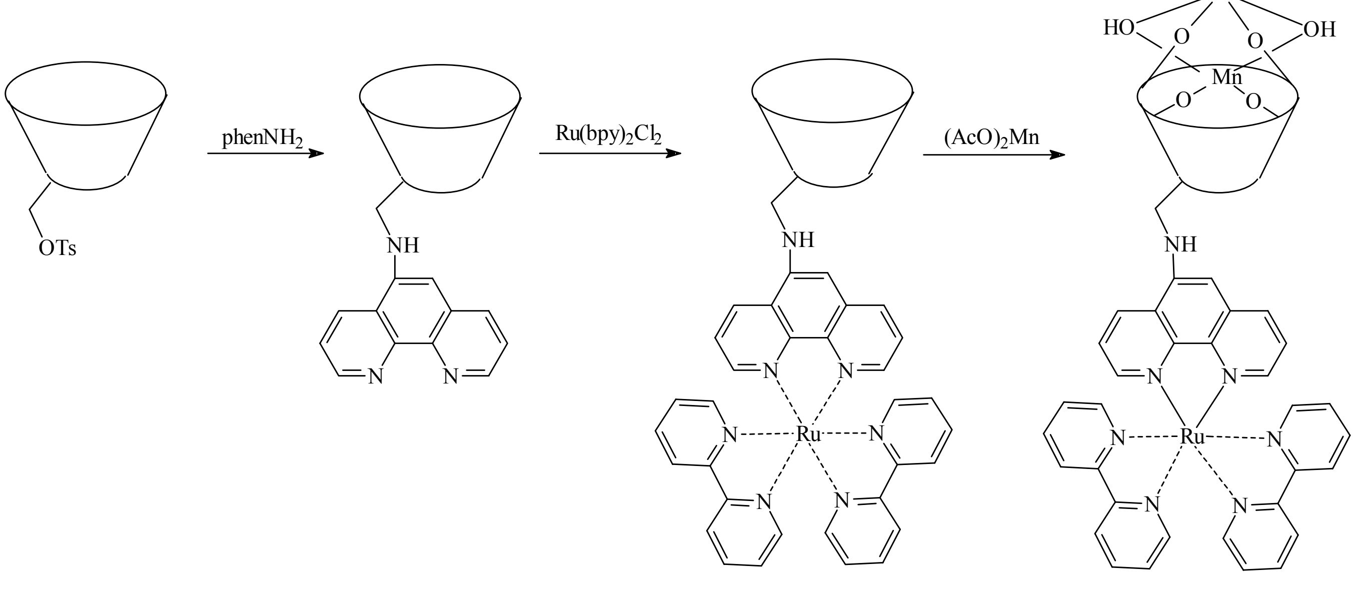


Δ - [Ru (phen)$_3$]$^{2+}$
right - handed
helix configuration

Δ - [Ru (phen)$_3$]$^{2+}$
left - handed
helix configuration

Binding of the anionic **87** with the cationic [Ru(phen)$_3$]$^{2+}$ is promoted by cooperation of Coulomb and van der Waals interactions, as it was shown by positive entropy changes. [88] The binding constant of the complex of **87** with Δ-[Ru(phen)$_3$]$^{2+}$ is higher than in the case of Λ-[Ru(phen)$_3$]$^{2+}$. [87] The neutral **88** recognizes the helicity of the cationic [Ru(phen)$_3$]$^{2+}$; the negative entropy changes, in contrast to **87** suggest that the complex is formed through van der Waals interaction.

In the search for donor-acceptor systems with biomimetic properties, the manganese complex of β-CD bearing Ru(bpy)$_2$ and Ru(phen)$_3$ units (**89**) has been synthesized as follows: [89]

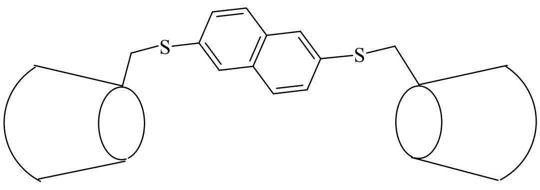


89

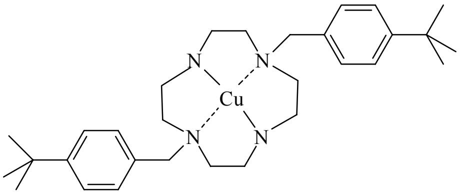
In **89** the donor and acceptor moieties are bridged by the highly rigid CD molecule. The hydroxy-bridged dinuclear Mn site behaves as a donor in an excited state; the photoinduced electron transfer from the Mn (III) centre to Ru^{3+*} leads to the formation of Ru^{2+}.

6. COMPLEXES OF CDs WITH METALLO-CYCLENS, -PORPHYRINS AND -PHTHALOCYANINES

It was observed that bridged dimeric β-CD (**90**) serves as a receptor strongly binding Cu-64-1,7-(4-*tert*-butylphenylmethyl)cyclen (**91**); this receptor/ligand system is promising for tumor pretargeting.[90] The aim of the pretargeting is to maintain a high accumulation of the radiometal at the target site while minimizing nontarget tissue toxicity. In this technique, monoclonal antibodies are covalently bound to a receptor having a high affinity for a radiometal-bearing ligand; an example is **91** containing pendant hydrophobic groups for inclusion into cavity of CDs.

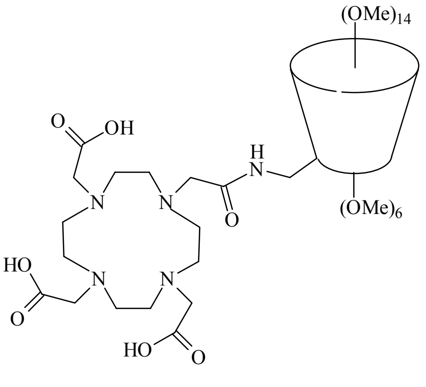


90

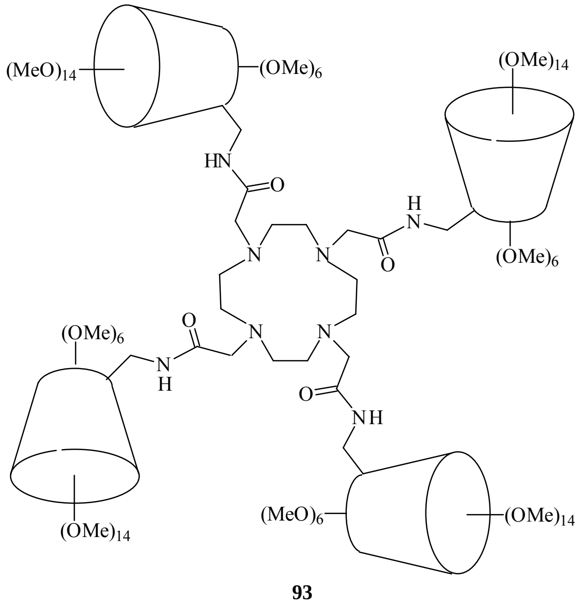


91

Europium, terbium and gadolinium complexes of compounds (**92**) and (**93**) have been investigated.[44] Complexes of **92** and **93** are stable, in the case of **92** neutral, and in the case of **93** triply charged. Complexes of **92** have one bound water molecule, while complexes of **93** are unhydrated, being rare examples of q=0 systems.



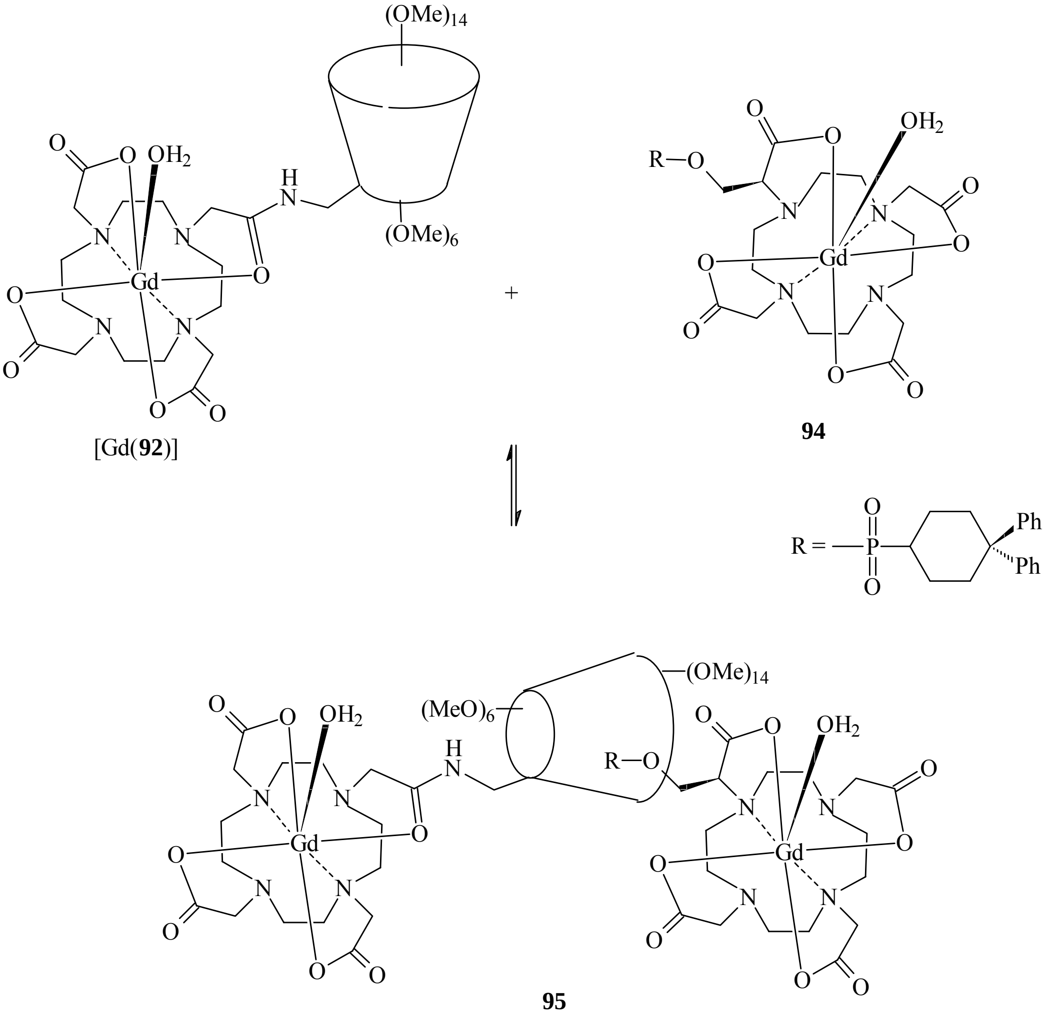
92



93

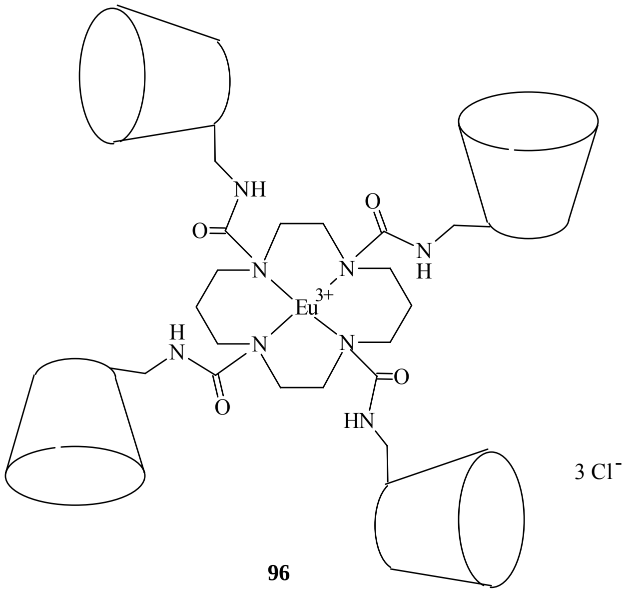
Methyl 4-*tert*-butylbenzoate as well as 1- and 2-methylnaphthalenes and 2-bromonaphthalene have been used as sensitizers of the Ln(III) luminescence of the above complexes. The linking amide carbonyl group serves as a donor to the Ln(III) ion, enabling close proximity of the CD unit to the Ln(III) ion, in this way ensuring the efficient energy transfer from the aryl triplet excited state to the lanthanide ion; as a result the „switching-on" of the lanthanide luminescence, signalling the binding of the aryl chromophore takes place.

Measurement of the relaxivity of a gadolinium complex of **92** as a function of magnetic field strength generates a NMR dispersion profile. In order to achieve the relaxivity enhancement, the [Gd(**92**)] as the host was treated with the gadolinium complex (**94**) serving as a guest affording the inclusion system (**95**).[44]

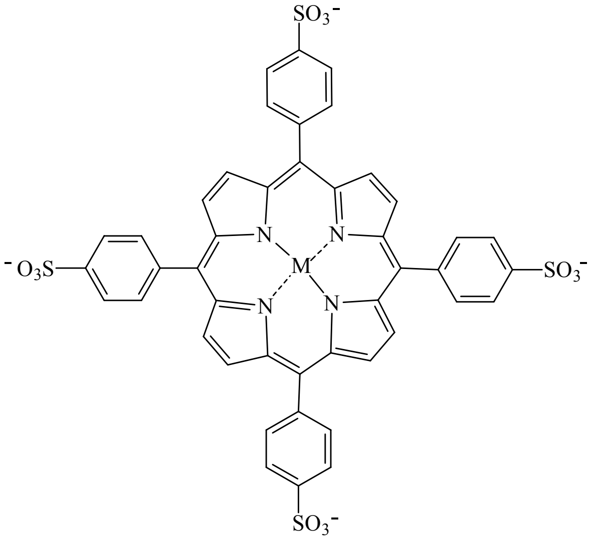


95

One should mention here also the europium complex (**96**) containing four β-CD units [91] and 1:1 complexes of α-, β- and γ-CDs with porphyrin (**97a**). [92]



96

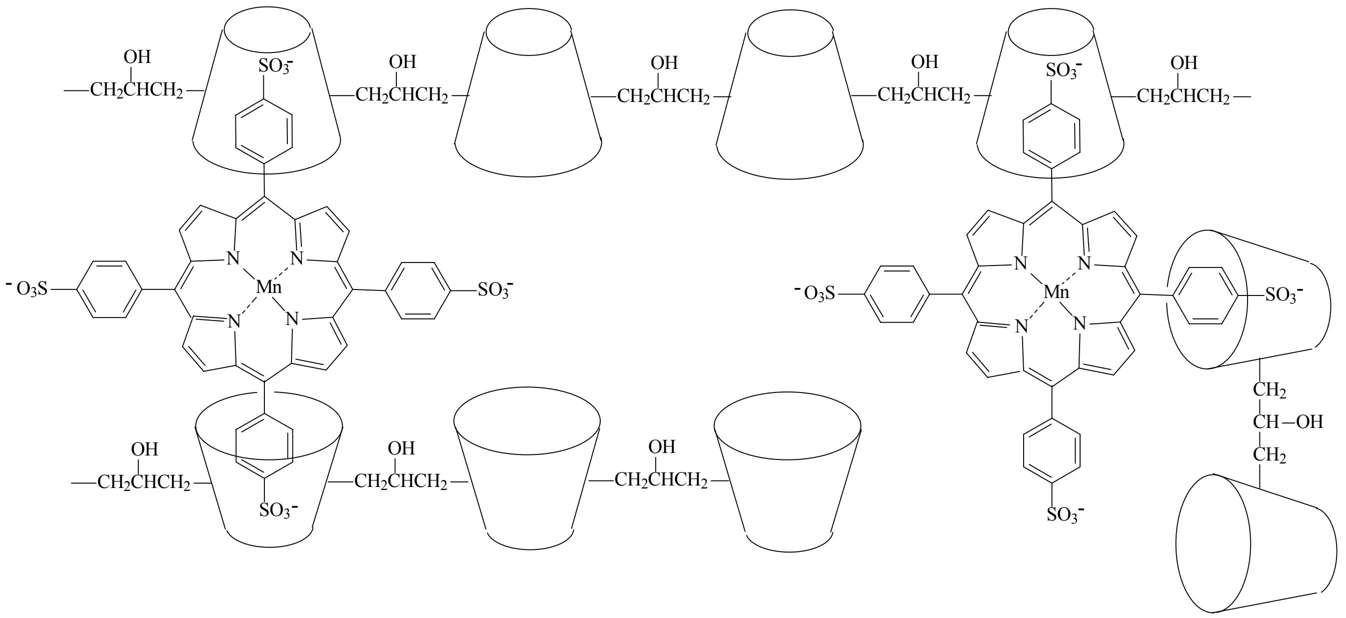


		M
97	**a**	Fe(III)
	b	Mn(III)

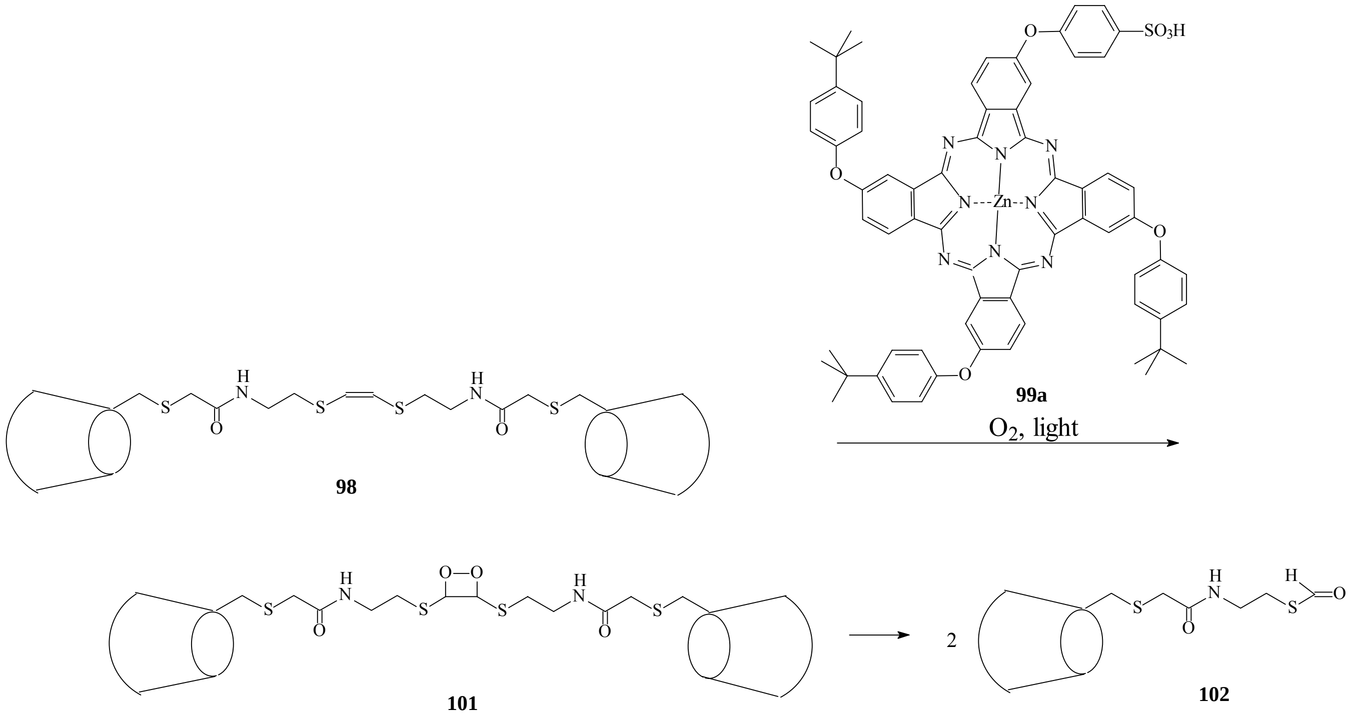
In the search for magnetic resonance imaging (MRI) contrast agents, porphyrin (**97b**) has been investigated.[93] Contrast in MRI involves differences in the relaxation times of protons in tissues, for this purpose coordination compounds of metal ions with several unpaired electrons are suitable. Contrast agents are used in diagnostics; they are paramagnetic complexes with relaxivity dependent on temperature, pH, partial pressure of oxygen $p(O)_2$ and, in some cases, on enzymatic activity.

The partial pressure of oxygen is one among parameters characterizing a biological environment. Contrast agents of the relaxivity dependent upon $p(O_2)$ are promising in various pathological conditions, for example they may be useful in separation of arterial and venous blood. This method is based on the contrast dependent on blood oxygenation levels. A $p(O_2)$ responsive MRI contrast agent is a complex in which the metal ion can switch between two redox states characterized by different relaxation properties.

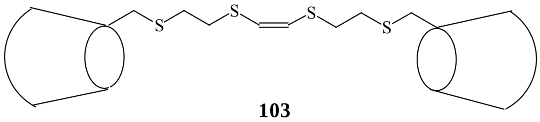
As a model has been taken porphyrin (**97b**) in which the modulation of the redox switch between Mn^{+2}/Mn^{+3} oxidation states is possible; this system shows a high affinity to tumor cells and is promising in photodynamic therapy of cancer (PDT). In order to avoid the dimerization of porphyrins, each complex has been incorporated into CD cavities; for this purpose poly-β-CD containing oligomers of 3-9 CD units has been used, as shown below.[93]



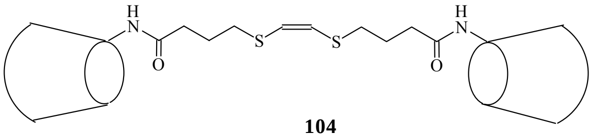
Bridged dimeric CDs, for example **98** bind metallophthalocyanines bearing hydrophobic groups. The resulting complexes are water soluble.[94] The bridged dimeric β-CD (**98**) forms with zinc phthalocyanine (**99a**) the intermediate complex (**100**) undergoing a spontaneous cleavage of the double bond of **98** by single oxygen *via* oxetane (**101**), affording two molecules of CD (**102**). [94]



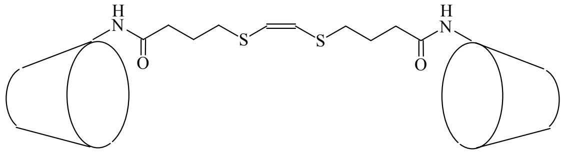
The photosensitizer (**99a**) liberated in this way precipitates and its concentration in the light beam increases allowing binding of proteins at the irradiation site. This process is promising in PDT since it concentrates the sensitizer in the light beam, i.e. localizes it at the tumor site, away from other parts of the body. The bridged dimeric β-CDs (**98**) and (**103-105**) and photosensitizers (**99**) and (**106-110**) were used in experiments.



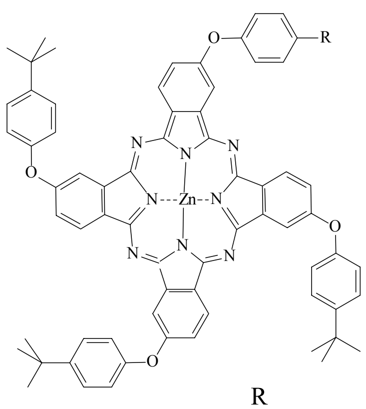
103



104

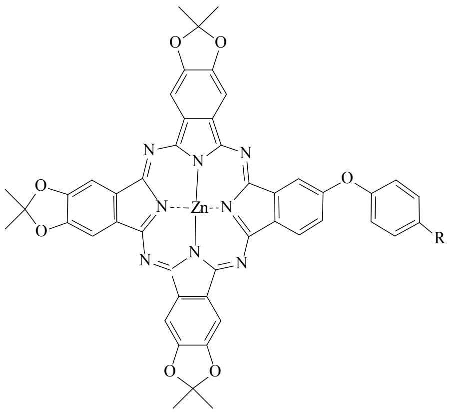


105



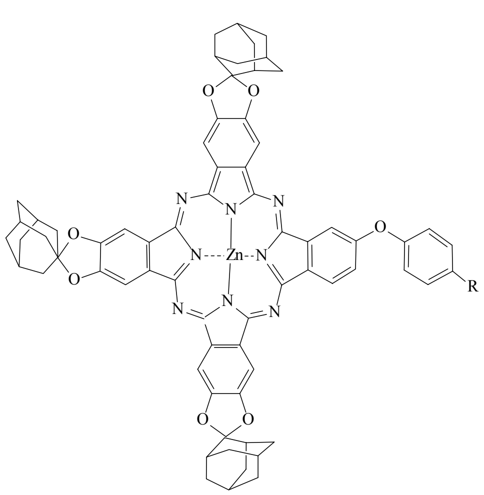
99

	R
a	SO_3H
b	COOH
c	*tert*-Bu



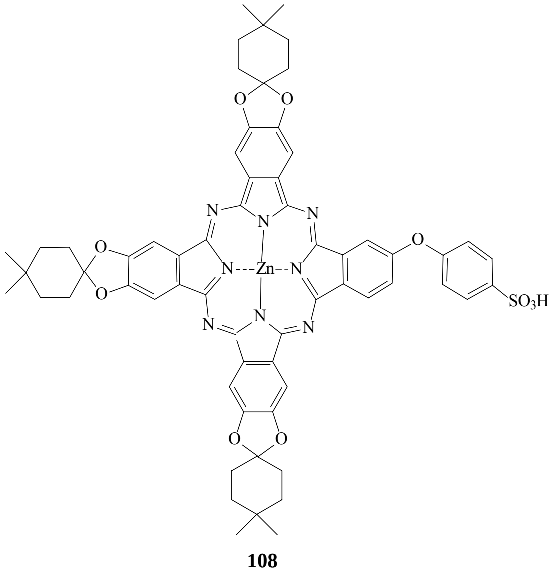
106

	R
a	SO_3H
b	COOH

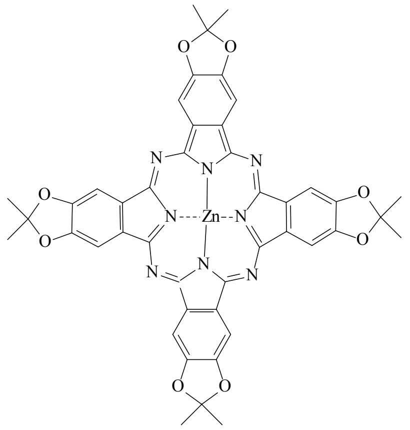


107

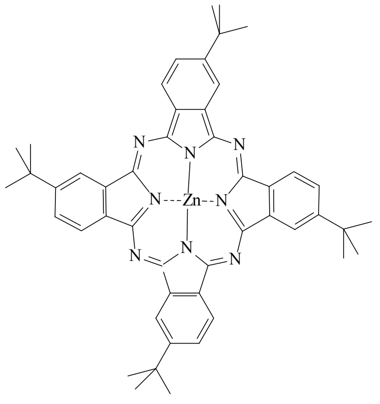
	R
a	SO_3H
b	COOH



108



109



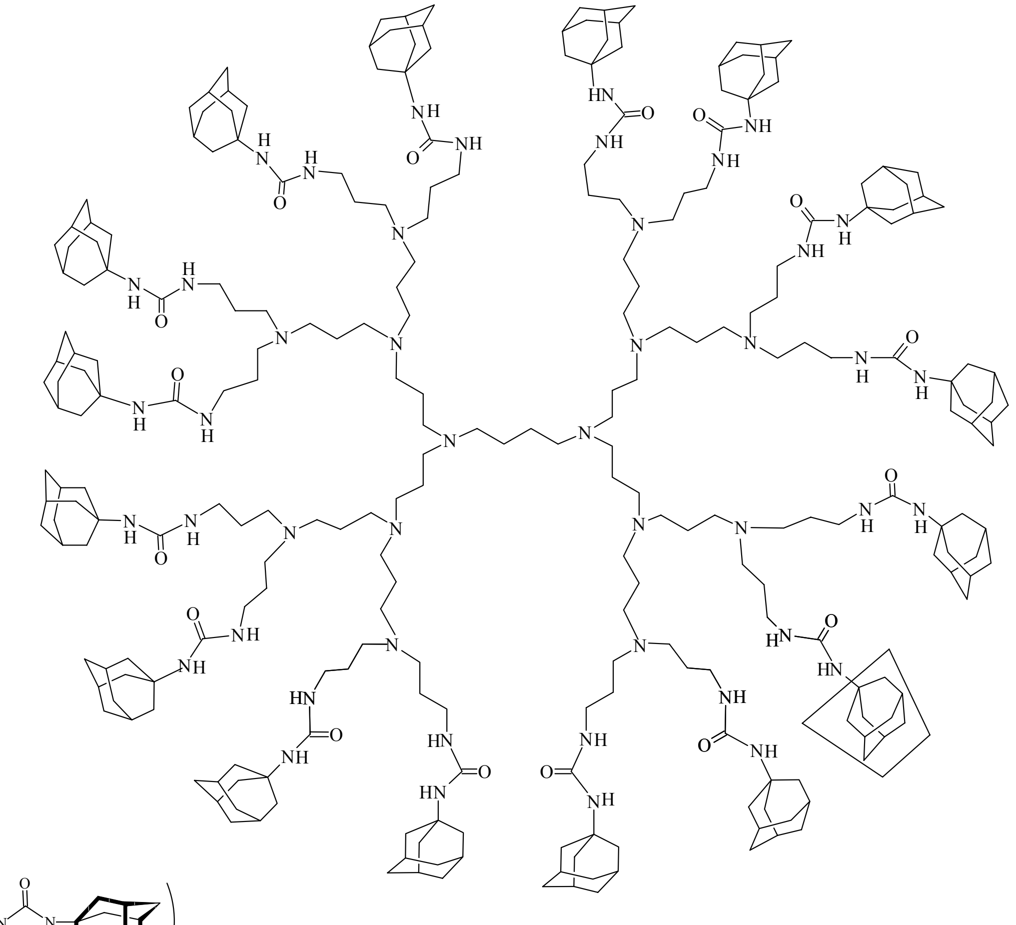
110

It was observed that the photolytic cleavage is most effective in the case of **99a**, **106a**, **107a** and **108** bearing sulfonate solubilizing groups, less effective – in the case of **99b**, **106b** and **107b**, bearing carboxylate solubilizing groups and the least effective in the case of sensitizers (**99c**, **109** and **110**) without solubilizing groups.[94]

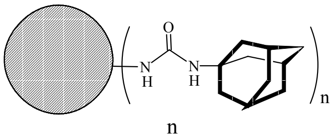
7. CD-MODIFIED METAL NANOPARTICLES

Metal nanoparticles deserve attention for a variety of their application possibilities, e.g. in nanotechnology, construction of molecular devices, catalysis and biological sciences.[95] Modification of metal nanoparticles with organic layers allows to combine properties of metals and of their organic surfaces. [95-98]

Many nanoparticles stabilized by dendrimers are known, e.g. gold [99-101] and silver [102] nanoparticles stabilized by poly(amidoamine) (PAMAM) dendrimers, or palladium nanoparticles [103] stabilized by poly(propyleneimine) (PPI) dendrimers. It was observed that supramolecular assemblies of β-CD with PPI dendrimers (**111d**) and (**111e**) [104,105] may be used as water soluble nanoreactors for the size-selective preparation of modified platinum and gold nanoparticles.[106] These latter are obtained by the reduction of $PtCl_4$ or $HAuCl_4{\cdot}3H_2O$ with aqueous solution of $NaBH_4$ in the presence of **111d**$\cdot$(β-CD)$_{32}$ or **111e**$\cdot$(β-CD)$_{40}$ assemblies. The dense shell of adamantyl-βCD complexes prevents the escape of metal nanoparticles. [106]



111c

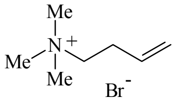


111

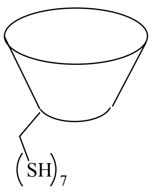
	n
a	4
b	8
c	16
d	32
e	64

Studying modification of gold ,[98] palladium [97] and platinum [97] nanoparticles by CDs, the solutions of Na_2PdCl_4 or Na_2PtCl_4 in DMSO/H_2O were reduced with $NaBH_4$ in the presence of *per*-6-thiol-β-CD (**112**) to give water soluble palladium or platinum nanoparticles.[97,107,108] The chemisorption of **112** on the surface of metal nanoparticles involves the conversion of S-H groups into metal-thiolate bonds. The obtained surface modified palladium and platinum colloidal particles are efficient catalysts for the hydrogenation of allylamine in aqueous solutions.[97]

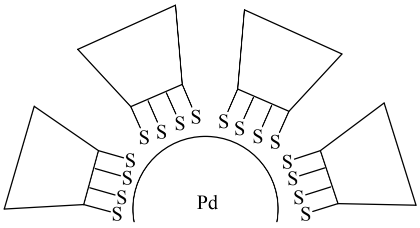
The catalytic activity of such CD-capped palladium nanoparticles (**113**) for the hydrogenation of **114** may be modulated by the presence of appropriate molecules in solution, forming with CDs host-guest systems. [107] For example, the addition of the cationic ferrocene derivative (**115**) inhibits the catalytic activity of CD-capped palladium nanoparticles (**113**) in the hydrogenation of **114**, while the anionic ferrocene derivative (**116**) is a less effective inhibitor than **115**. The inhibiting character of **115** results from its ability to act as a guest and to create Coulombic barriers for the approach of the positively charged substrate (**114**). [107]



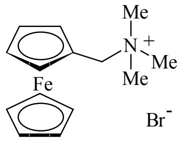
114



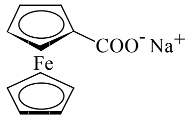
112



113

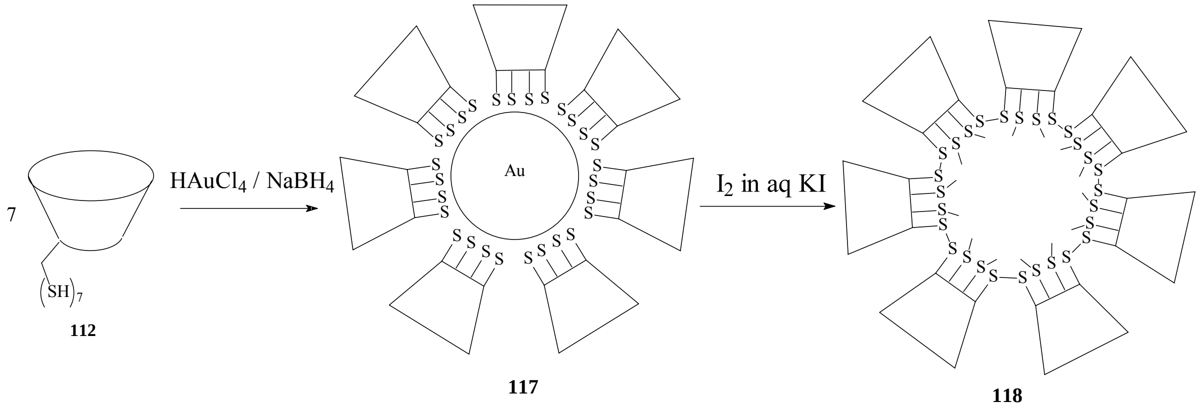


115



116

The CD-modified gold nanoparticles are useful as templates in the synthesis of water soluble CD nanocapsules. [109] Nanometer-sized organic capsules are of interest for application in drug-delivery targeting and as nanoreactors.[110] As an example of the synthesis of CD nanocapsules may serve the reduction of Au(III) compounds in the presence of CD derivative (**112**) leading to gold nanoparticles coated with CD shells (**117**). [98] The subsequent reoxidation of these species by iodine dissolves gold as a mixture of Au(I) and Au(III) complexes and affords monolayer-thick CD nanocapsules (**118**) held together by disulfide bridges. [109,111,112]



CONCLUSION

Numerous works deal with metalloCDs, this fact is a reflection of their interesting properties. [113-116] A special attention is paid to the formation of metalloCDs in the production of catalysts [117] and in the design of iron (II) drugs for human metabolism, a crucial study in the solution of the malnutrition problem. [118] One should also point out that metalloCDs take part in the degradation of organic contaminants, this activity being of a great importance for environmental protection. [119,120]

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