UNIVERSITE DE NEUCHATEL
Faculté des Sciences
Institut de Chimie

CYCLODEXTRINES SUBSTITUEES PAR L'ENTITE BIPYRIDINE :

SYNTHESE, COMPLEXATION ET ETUDE DE PROPRIETES PHYSICO-CHIMIQUES

Version réduite de la thèse
présentée à la Faculté des Sciences par

Thomas RUCH

Chimiste diplômé de l'Université de Neuchâtel
pour l'obtention du grade de docteur ès sciences

Novembre 1993

IMPRIMATUR POUR LA THÈSE

Cyclodextrines substituées par l'entité bipyridine:
Synthèse, complexation et études de propriétés
physico-chimiques

de M. Thomas Ruch

UNIVERSITÉ DE NEUCHÂTEL

FACULTÉ DES SCIENCES

La Faculté des sciences de l'Université de Neuchâtel sur le rapport des membres du jury,

Messieurs R. Deschenaux, R. Neier, A. Coleman (Paris)
et A. Juris (Bologne)

autorise l'impression de la présente thèse.

Neuchâtel, le 19 mai 1995

Le doyen:

H.-H. Nägeli

Version réduite de la thèse présentée sous forme de quatre publications.

Le texte complet de la thèse est déposé chez Monsieur le Professeur R. Deschenaux, à l'Institut de Chimie de l'Université de Neuchâtel.

Publications

N. Brügger, R. Deschenaux, T. Ruch, R. Ziessel, " A New Class of Photo- and Electro-active Receptors : Synthesis of a 2,2'-Bipyridyl Ligand Functionalized β-Cyclodextrin", *Tetrahedron Lett.* **1992**, *33*, 3871.

R. Deschenaux, M.M. Harding, T. Ruch, " Synthesis and a High Field NMR Study of a 2,2'-Bipyridyl Substituted β-Cyclodextrin and its Luminescent Re^{I} Metal Complex", *J. Chem. Soc. Perkin ,Trans. 2* **1993**, 1251.

R. Deschenaux, A. Greppi, T. Ruch, H.-P. Kriemler, F. Raschdorf, R. Ziessel, " Bipyridine-coupled Permethylated β-Cyclodextrin", *Tetrahedron Lett.* **1994**, *35*, 2165.

R. Deschenaux, T. Ruch, P.-F. Deschenaux, A. Juris, R. Ziessel " Synthesis, Characterization, and Electrochemical and Photophysical Properties of Rhenium(I) and Ruthenium(II) Complexes of 2,2'-Bipyridine Ligand Functionalized β-Cyclodextrins", *Helv. Chim. Acta* **1995**, *78*, 619.

Tetrahedron Letters, Vol. 33, No. 27, pp. 3871-3874, 1992
Printed in Great Britain

0040-4039/92 $5.00 + .00
Pergamon Press Ltd

A New Class of Photo- and Electro-active Receptors : Synthesis of a 2,2'-Bipyridyl Ligand Functionalized β-Cyclodextrin and its Ir(III), Rh(III) and Re(I) Complexes

Nadia Brügger,[a] Robert Deschenaux,*[a] Thomas Ruch [a] and Raymond Ziessel[b]

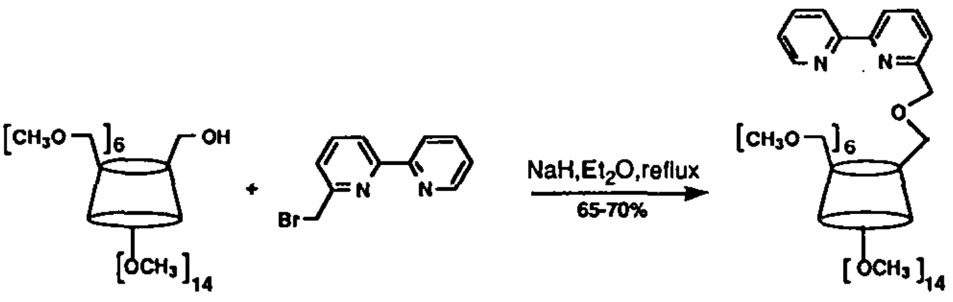
[a]Université de Neuchâtel, Institut de Chimie, Av. de Bellevaux 51, 2000 Neuchâtel, Switzerland.
[b]Ecole Européenne des Hautes Etudes des Industries Chimiques de Strasbourg, 1 rue Blaise Pascal, 67008 Strasbourg, France.

Abstract : A β-cyclodextrin substituted with a 2,2'-bipyridine (abbreviated to CD(per-OMe)-bpy) and the complexes [(CD(per-OMe)-bpy)Ir(η^5-C_5Me_5)Cl]Cl, [(CD(per-OMe)-bpy)Rh(η^5-C_5Me_5)Cl]Cl and (CD(per-OMe)-bpy)Re$(CO)_3$Br have been synthesized, and their properties examined.

Supramolecular photochemistry is currently a field of intense activity, and interesting results have been obtained.[1] The principal motivation of the studies is the possibility of obtaining fundamental information for the better understanding of photobiological processes. The design, synthesis, and study of new receptors constitute a challenge for the further development of complex supramolecular assemblies exhibiting specific photochemical and photophysical properties.

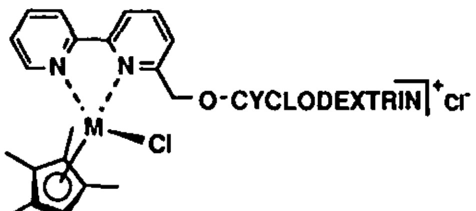
We report herein : i) the synthesis of CD(per-OMe)-bpy, **1**, which represents the first example of a new family of receptors based on the rich host-guest chemistry of the cyclodextrins[2] and on the unique complexation features of 2,2'-bipyridine[3], ii) the preparation and characterization of the (CD(per-OMe)-bpy)-transition metal complexes **4a-c**, and iii) preliminary physicochemical properties of **1** and **4a-c** (Table). All compounds were characterized by ^{1}H, ^{13}C{^{1}H}-NMR, mass, electronic and infra-red spectroscopies and elemental analysis. The data are consistent with the proposed structures.

Compound **1** was synthesized by reacting the monohydroxy-β-cyclodextrin **2**[4], 6-bromomethyl-2,2'-bipyridine **3**[5] and NaH in dry Et_2O, at reflux. Purification by column chromatography (silicagel, toluene/methanol/isopropanol 15:1:1) resulted in pure CD(per-OMe)-bpy[6] (white solid, 65-70%). A positive circular dichroism band at 280 nm (MeCN, $c = 7.8\times10^{-5}$M) due to the π-π* transition would seem to indicate that the bipyridine is oriented towards the cavity, resulting in a capped conformation.[7] This is supported by space-filling models. Such orientations have already been observed for other modified cyclodextrins.[1c]

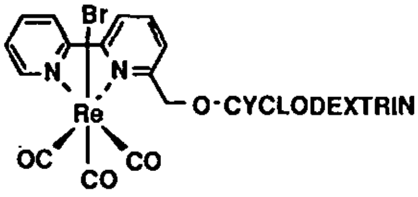


2 **3** **1**

The metal complexes **4a-c** were prepared from **1** by treatment with $[Ir(\eta^5\text{-}C_5Me_5)Cl_2]_2$, $[Rh(\eta^5\text{-}C_5Me_5)Cl_2]_2$ and $Re(CO)_5Br$, respectively, adapting literature procedures.[8] Purification by column chromatography and crystallization yielded the cationic complexes **4a**[6] (87%), **4b**[6] (77%) and the neutral complex **4c**[6] (90%).



4a : M = Ir
4b : M = Rh



4c

The receptor, CD(per-OMe)-bpy, has an absorption maximum, λ_{max}, at 285 nm (ε=15 900) [bpy : λ_{max} 280 nm, ε=16 300].[9] The Ir^{III}, Rh^{III} and Re^{I} complexes, **4a-c**, show absorption bands comparable with those reported for the corresponding $[(bpy)Ir(\eta^5\text{-}C_5Me_5)Cl]Cl$,[8a] $[(bpy)Rh(\eta^5\text{-}C_5Me_5)Cl$,[8a] and $(bpy)Re(CO)_3Cl$[5] analogues. It is well known that Re(I)-bipyridine complexes are luminescent[8b], and indeed a strong emission at 603 nm was observed at room temperature when a MeCN solution of **4c** was excited at 390 nm. The emission efficiency was comparable to that of the parent $(bpy)Re(CO)_3Cl$ complex when both species were excited under the same conditions.

The electrochemical properties of **4c** were investigated by cyclic voltammetry. In addition to a reversible reduction at $E_{1/2}$= -1.34 V [$(bpy)Re(CO)_3Cl$: $E_{1/2}$= -1.37 V],[5] a reversible oxidation wave was obtained at $E_{1/2}$= +1.38 V. This is interesting since $(bpy)Re(CO)_3Cl$ gives an irreversible oxidation peak at the same potential.[5] This result indicates in fact that the Re(II) oxidation state is more stable in **4c** than in the cyclodextrin-free analogue. The origin of this stabilization could be the consequence of an interaction between the metallic centre and the cyclodextrin.

Table. Spectroscopic Properties and Electrochemical Data

Compound	λ / nm (ε / l mol^{-1} cm^{-1})[a]	$E_{1/2}$ / V[b](ΔE/mV[c])
1	237 (11 800), 244 (10 700), 285 (15 900)	
4a	246 (13 900), 299 (13 500), 310 (sh), 324 (10 100), 360 (sh)	
4b	237 (27 800), 311 (12 000), 320 (12 400), 380 (2 330)	
4c	246 (17 900), 300 (12 300), 310 (11 900), 324 (9 350), 370 (2 300)	-1.34 (70), +1.38(70)

[a] Measured in MeCN.

[b] Obtained from cyclic voltammetry on platinum in dry MeCN (reference electrode : saturated calomel ; supporting electrolyte : 0.1 M TBAP ; internal reference : ferrocene), at room temperature under argon, at 0.1 Vs^{-1} scan rate.

[c] Separation between anodic and cathodic peak potentials. ΔEp for Cp_2Fe, under the same conditions was 70 mV. No compensation was made for internal cell resistance.

The synthesis of other highly fluorescent complexes and their use as optical sensors for chiral molecules are currently under investigation.

References and Notes

1. a) *Frontiers in Supramolecular Organic Chemistry and Photochemistry*, Schneider H.-J.and Dürr H., eds; VCH Verlagsgesellschaft, Weinheim, 1991 ; b) Balzani V. and Scandola F., *Supramolecular Photochemistry,* Harwood, Chichester, England, 1991 ; c) Fukushima H., Osa T. and Ueno A., *J. Chem. Soc., Chem.. Commun.* **1991**, 15-17 and references therein ; d) Pikramenou Z., Nocera D.G., *Inorg. Chem.* **1992**, *31*, 532-536
2. a) *Inclusion Phenomena and Molecular Recognition*, Atwood J.L., ed., Plenum Press, New York, 1990. b) Tabushi I., Kuroda Y. and Mizutami T., *Tetrahedron*, **1984**, *40*, 545-552 ; c) Breslow R., *Chemistry in Britain*, **1983**, 126-131.
3. Balzani V., Bolletta F., Gandolfi M.-T. and Maestri M., *Topics Curr. Chem.* **1978**, *75*, 1-64 ; Kalyanasundaram K., *Coord. Chem. Rev.*, **1982**, *46*, 159-244.
4. Tanaka M., Kawaguchi Y., Niinae T. and Shono T., *J. Chromatogr.*, **1984**, *314*, 193-200.
5. Ziessel R. and Lehn J.-M., *Helv. Chim. Acta*, **1990**, *73*, 1149-1162
6. Selected analytical data :

   1 : m.p.= 98-101°C ; R_f = 0.42 (silicagel, toluene/isopropanol 1:1) ; $[\alpha]_D$= +143 (c = 0.15 in $CHCl_3$) ; Anal. Calc. for $C_{73}H_{118}O_{35}N_2$ (1583.73) : C 55.36, H 7.51, N 1.77 ; found : C 55.10, H 7.43, N 1.43. **4a** : $[\alpha]_D$= +114 (c = 0.15 in $CHCl_3$) ; FAB : m/z = 1945.8 $[M]^+$. **4b** : $[\alpha]_D$= +119 (c = 0.15 in $CHCl_3$) ; FAB : m/z = 1855.7 $[M]^+$. **4c** : R_f = 0.28 (silicagel, toluene/isopropanol 1:1); $[\alpha]_D$= +122 (c = 0.15 in $CHCl_3$) ; IR (KBr pellet) ν_{CO} 2022, 1920, 1901 cm^{-1}. Anal. Calc. for $C_{76}H_{118}O_{38}N_2$ BrRe (1933.89) : C 47.20, H 6.15, N 1.45 ; found : C 47.90, H 6.16, N 1.15.
7. No circular dichroism signal was observed in a mixture of one equivalent of permethylated β-cyclodextrin and one equivalent of bipyridine under the same conditions.
8. (a) Youinou M.-T. and Ziessel R., *J. Organomet. Chem.*, **1989**, *363*, 197-208 ; (b) Juris A., Campagna S., Bidd I., Lehn J.-M. and Ziessel R., *Inorg. Chem.*, **1988**, *27*, 4007-4011 and references therein.
9. De Armond M.K. and Hillis J.E., *J. Chem. Phys.*, **1971**, *54*, 2247-2253.

(Received in France 8 April 1992)

Synthesis and a High Field NMR Study of a 2,2'-Bipyridyl Substituted β-Cyclodextrin and its Luminescent Re^I Metal Complex[1]

Robert Deschenaux,*[a] **Margaret M. Harding***[b] **and Thomas Ruch**[a]
[a] *Université de Neuchâtel, Institut de Chimie, Avenue de Bellevaux 51, 2000 Neuchâtel, Switzerland*
[b] *Department of Organic Chemistry, The University of Sydney, NSW 2006, Australia*

The synthesis and an NMR spectroscopic study of the substituted β-cyclodextrin derivative β-CD(per-OMe)bpy **3**, and the metal complex β-CD(per-OMe)bpyRe(CO)$_3$Br **4** are reported. The ligand **3** was prepared by condensation of monohydroxypermethylated β-cyclodextrin **1** with 6-bromomethyl-2,2'-bipyridine **2** under standard Williamson reaction conditions. The neutral complex, β-CD(per-OMe)bpyRe(CO)$_3$Br **4**, was obtained by treatment of the ligand **3** with Re(CO)$_5$Br. 600 MHz two-dimensional NMR experiments (DQF-COSY, HOHAHA, ROESY) were used to establish the purity and structure of the ligand **3** and complex **4** in CDCl$_3$. The two diastereotopic bipyridyl methylene protons (H7a, H7b) in ligand **3** appear as a singlet at 4.82 ppm. The protons H3', H4', H5', and H6a',6b' on the adjacent ring R2 are shifted downfield compared to the protons on the other six sugar rings. In the complex **4**, the bipyridyl methylene protons (H7a, H7b) appear as 2 AX systems, R2H6a' appears as a doublet of doublets and the aromatic protons appear as complex multiplets, consistent with the formation of two diastereomeric complexes **4a** and **4b**. While circular dichroism measurements suggest that the metal is directed over the cavity, NOE connectivities between the bipyridyl protons and the surface of the cyclodextrin cavity were not detected in ROESY experiments. Preorganized assemblies based on **4**, in which the metal is directed over the cavity, provide ideal systems in which to study photochemical communication between the photoactive unit and a guest molecule encapsulated in the cyclodextrin cavity.

The field of supramolecular photochemistry has been a subject of intense activity in recent years, owing to the potential of supramolecular assemblies containing photoactive components to allow access to new tunable processes.[2,3] Numerous examples of photoactive supramolecular systems that have allowed the study of processes such as photoinduced energy transfer, charge separation effected by electron or proton transfer, and perturbation of optical transitions and polarizations, have been reported in recent years, and have been summarized by Balzani and Scandola.[3]

The design and synthesis of photochemical supramolecular architectures that possess new and useful properties remains a challenge. An elegant way to obtain such systems is to functionalize a receptor with a photoactive unit, and several examples of this type have been reported.[4] The choice of both the receptor and the photoactive unit in this case, and how they are connected into one component, is of critical importance as the properties of these individual units will control the photochemical and photophysical behaviour of the supramolecular structure.[3]

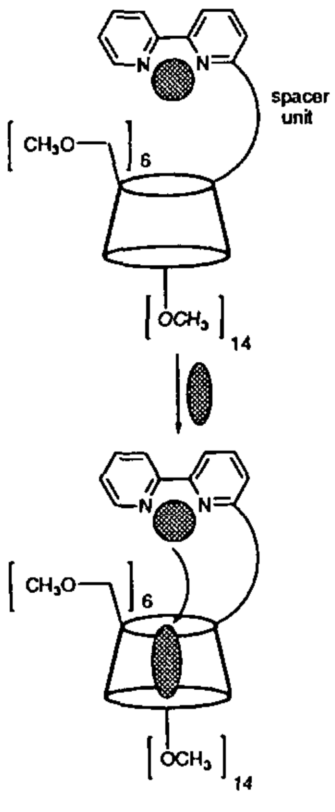
Our approach to the development of new supramolecular photoactive systems has been to combine the recognition properties of cyclodextrins with a photoactive 2,2'-bipyridyl unit. Cyclodextrins have played an important role in the field of supramolecular chemistry,[5,6] notably in the study of enzymatic reactions,[6] owing to their ability to form inclusion complexes with a large variety of organic[6] and organometallic[7] guest molecules. In addition, photoprocesses in a range of supramolecular systems that incorporate cyclodextrins in their structures have been studied.[8] The unique complexation[9] and photophysical[10] properties of bipyridines, when covalently attached to a cyclodextrin receptor, should allow access to systems with new physicochemical properties.

Examination of CPK models indicated that a cyclodextrin substituted on the primary face by a metal bipyridyl coordination complex placed in close proximity to the cyclodextrin cavity has the potential to give a molecular framework that allows communication (transfer of electrons, photons) between a substrate in the cyclodextrin cavity and a photoactive metal bipyridyl unit (Scheme 1). Efficient communication requires ideally that the metal centre is located over the cyclodextrin cavity as depicted in Scheme 1. With one exception,[11] there are no previous reports of cyclodextrin systems in which a metal binding site has been covalently attached to the cyclodextrin periphery in order to facilitate communication between a photoactive metal binding unit and a bound molecule in the cyclodextrin cavity. The one exception is a recent study where electron transfer in a cyclodextrin capped by a crown ether complexing a europium cation and a molecule of benzene in the cyclodextrin, was reported.[11]

This paper reports the synthesis and an NMR study of the ligand β-CD(per-OMe)bpy **3**, and the metal complex β-CD(per-OMe)bpyRe(CO)$_3$Br **4**. Preliminary electrochemical and spectroscopic properties of the complex **4** have been reported.[12] A single atom linker was used to connect the bipyridine to the cyclodextrin system, in order to constrain the metal binding site in close proximity to the cavity, and to allow the placement of a metal centre over the cyclodextrin cavity (Scheme 1). 600 MHz ^{1}H NMR spectroscopy (DQF-COSY,[13] HOHAHA,[14] ROESY)[15] has been used to establish unequivocally the structure of the ligand **3** and the complex **4** and to study the solution conformation of the complex **4**. The results of this work are important in the design of new, related systems that incorporate features with the potential to allow supramolecular photochemical processes to be developed and studied.

Results and Discussion

Synthesis.—The synthesis of several monosubstituted cyclodextrin derivatives has been reported in the literature.[16] The required bipyridyl ligand **3** was prepared by treatment of monohydroxypermethylated β-cyclodextrin **1**[16d] with sodium

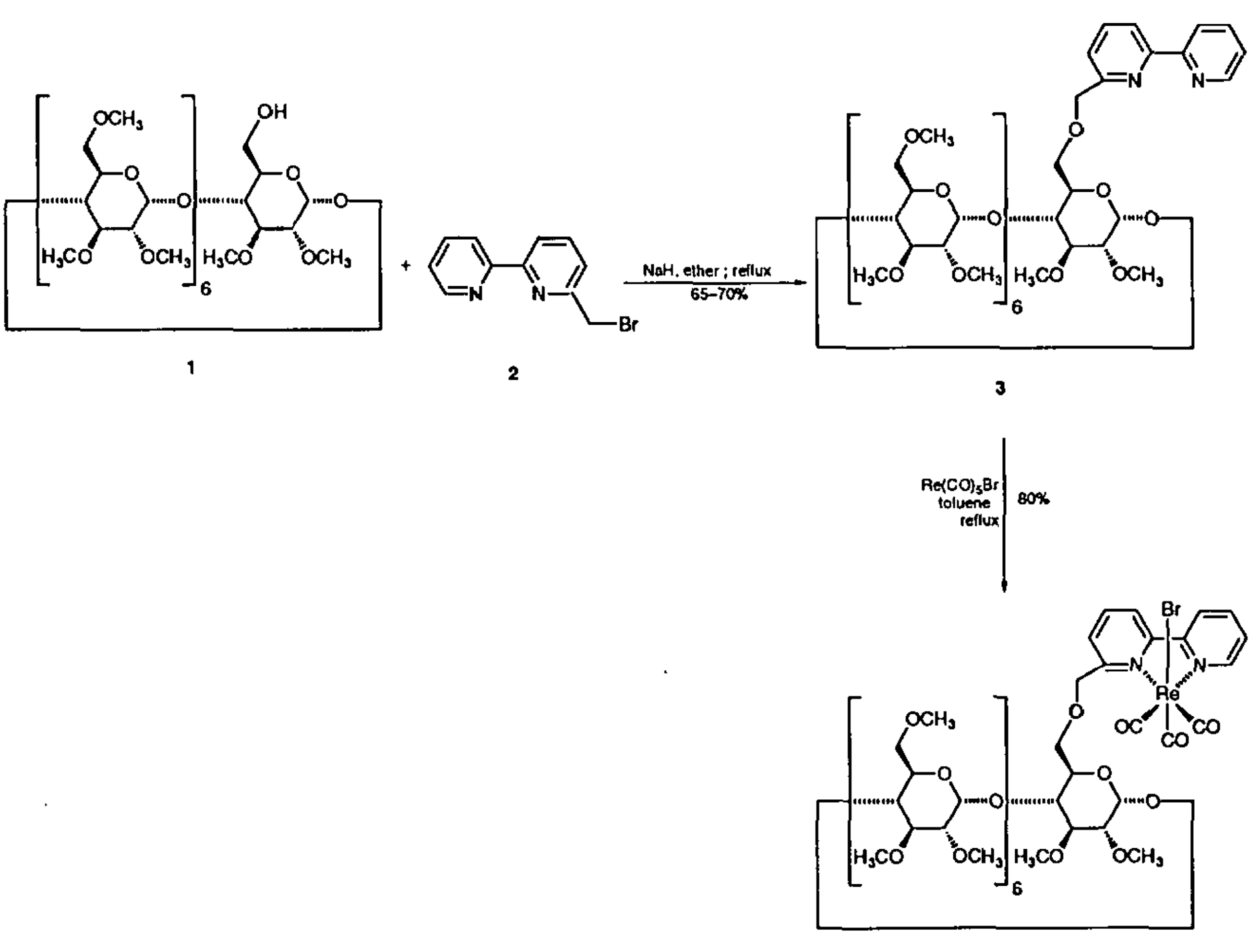


Scheme 1

hydride in dry ether, at reflux, followed by condensation with 6-bromomethyl-2,2′-bipyridine **2**[17] under standard Williamson reaction conditions (Scheme 2). Purification by column chromatography afforded β-CD(per-OMe)bpy **3** in 65–70% yield. The neutral complex β-CD(per-OMe)bpyRe(CO)$_3$Br **4** was obtained in 80% yield by reacting equimolar quantities of the ligand **3** and Re(CO)$_5$Br in refluxing toluene. FAB mass spectra gave the expected molecular ion peaks for **3** and **4** and microanalytical data were in agreement with the proposed structures.

Assignment of NMR Spectra.—NMR Spectroscopy was used to confirm the structure and purity of the ligand **3**, and the complex **4**. Both compounds are soluble in a range of organic solvents. One-dimensional proton NMR spectra of the ligand **3** were recorded at 400.13 MHz in $CDCl_3$, CD_2Cl_2, CD_3CN, CD_3OD and C_6D_6. On the basis of these spectra, $CDCl_3$ was chosen as the solvent in which to carry out 2D experiments, as the best signal dispersion in both the aromatic and aliphatic regions of the spectrum was observed in this solvent.

Fig. 1 shows expanded regions of the 600 MHz ^{1}H NMR spectra of the ligand **3** and the complex **4**. Assignment of these spectra is non-trivial owing to the asymmetry of the compounds. In each case, there are seven chemically non-equivalent sugar rings, each of which, in principle, gives rise to a distinct set of signals for the sugar ring protons. While the assignment and solution conformation(s) of β-cyclodextrin,[18] permethylated β-cyclodextrin,[19] and other *symmetrically* substituted cyclodextrins[20] has been reported, there is only limited NMR data[21] available concerning spectral parameters that may be used to



Scheme 2

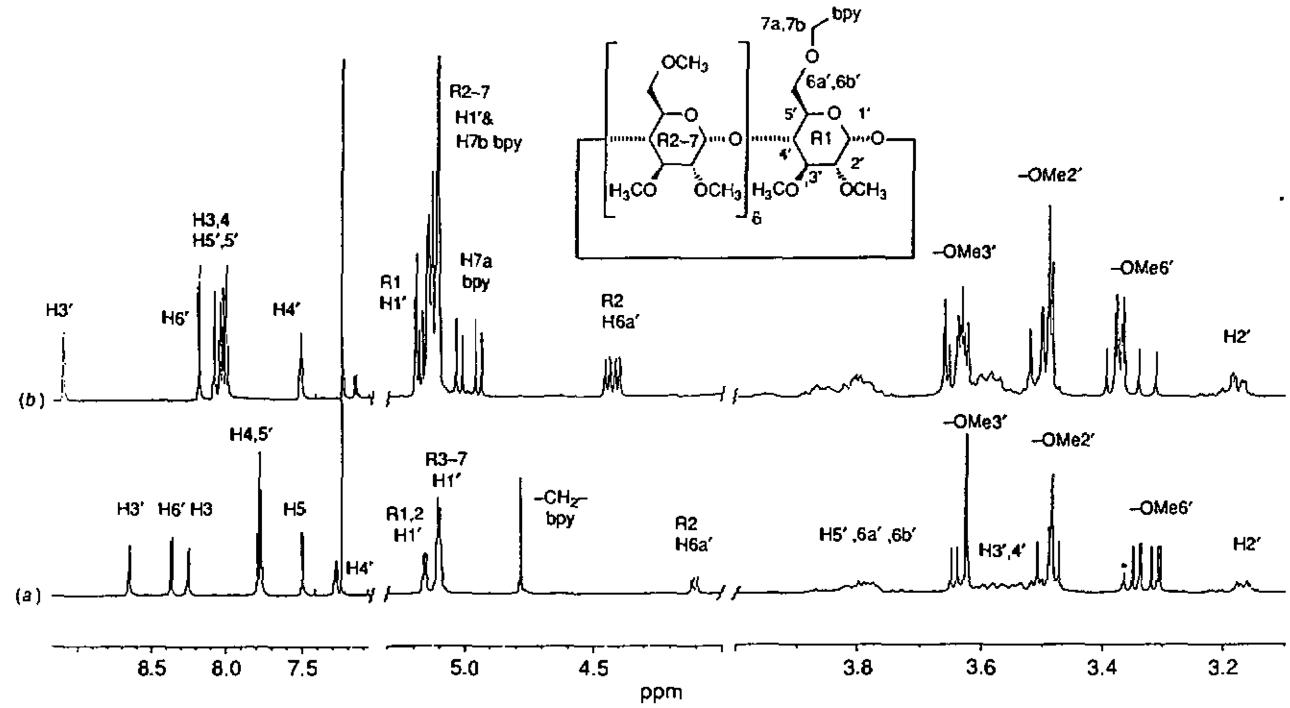


Fig. 1 600 MHz ^1H NMR spectra of (*a*) ligand 3 and (*b*) rhenium complex 4 in $CDCl_3$ at 303 K. Expansions are not plotted to scale. The starred peak is a minor impurity. The aromatic peaks at 7.1 ppm in trace (*b*) are due to residual toluene in the cyclodextrin cavity.

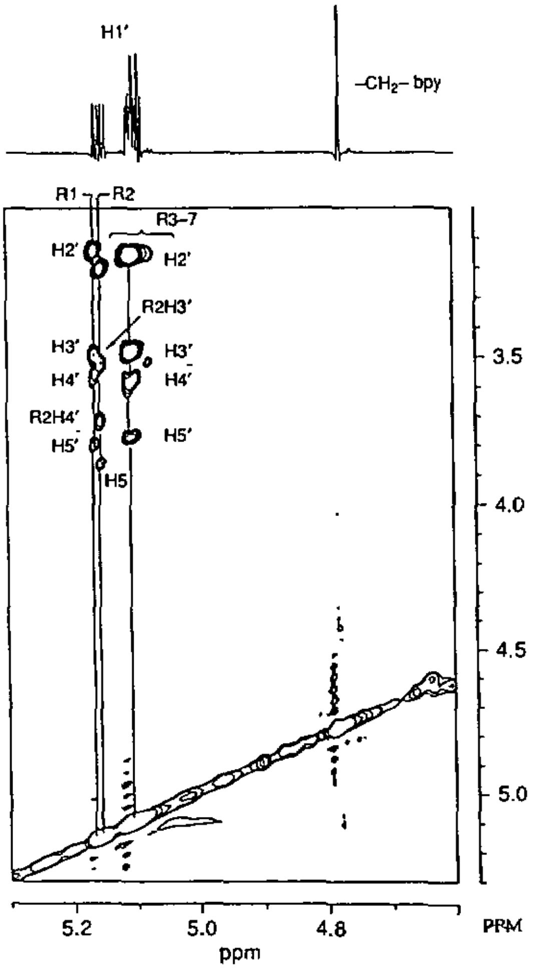


Fig. 2 Portion of the 600 MHz HOHAHA (MLEV 60 ms) spectrum of ligand 3 showing assignment of the seven sugar spin systems

characterize monofunctionalized β-cyclodextrins. In principle, as each sugar contains a distinct spin system, then starting from the anomeric H1' proton, which resonates downfield, typically

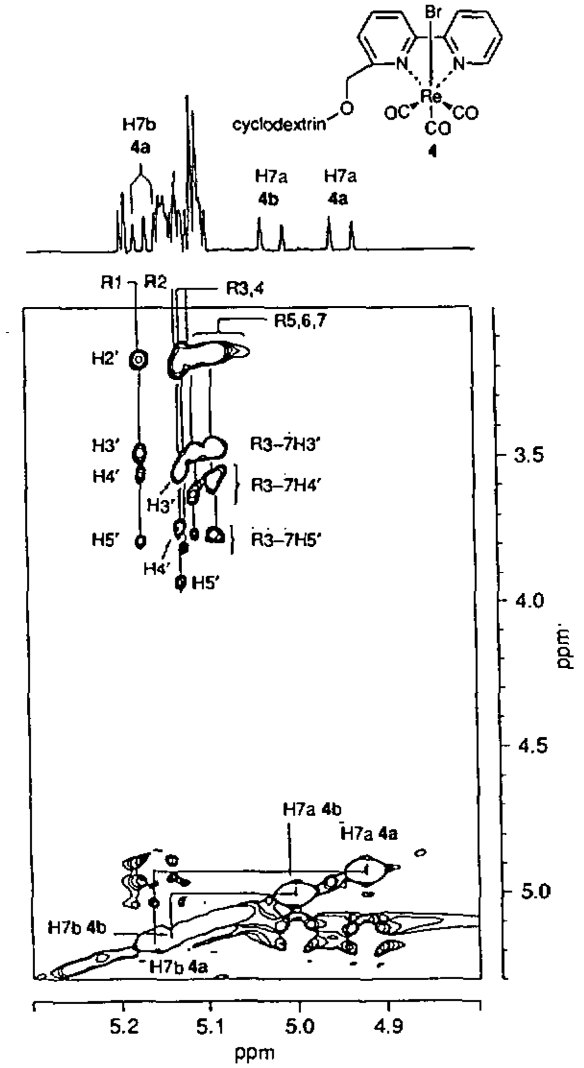


Fig. 3 Portion of the 600 MHz HOHAHA (MLEV 58 ms) spectrum of complex 4 showing assignment of the seven sugar spin systems

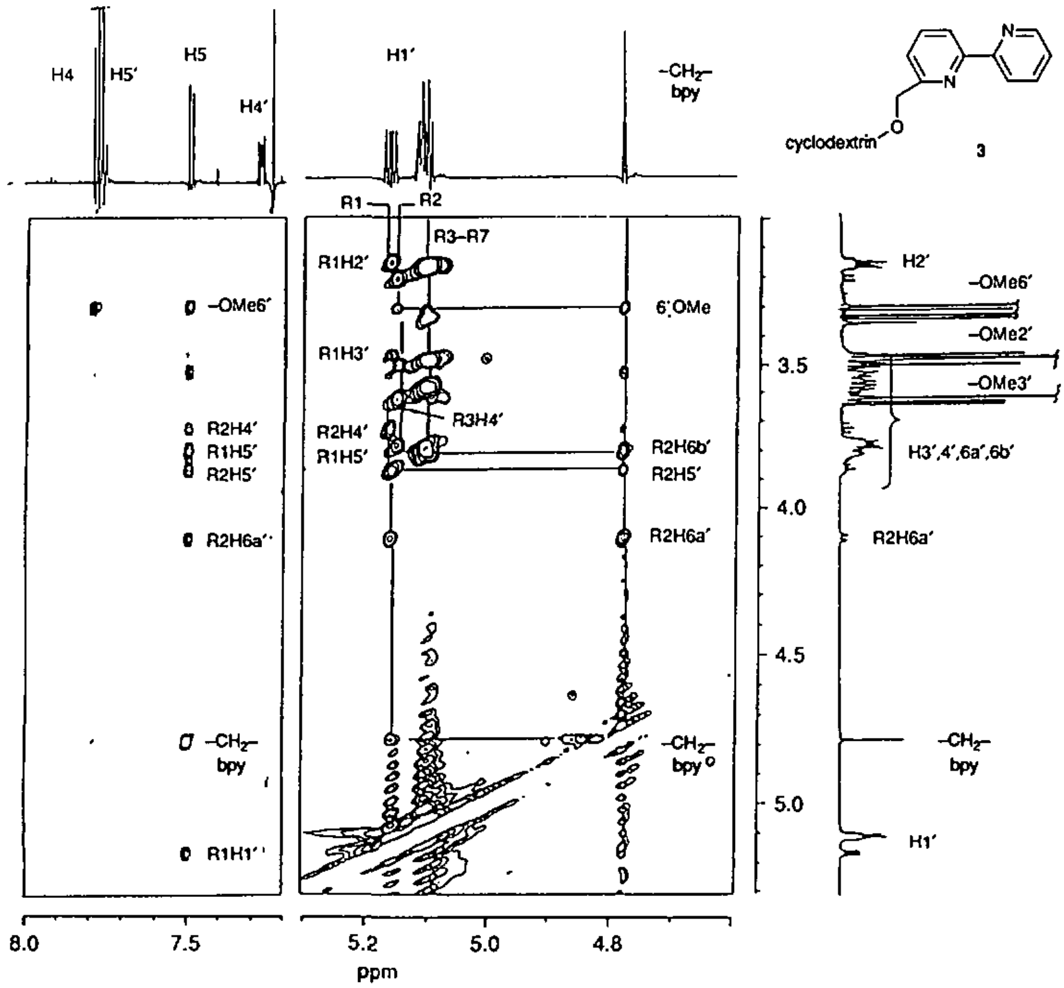


Fig. 4 Portion of the 600 MHz ROESY spectrum of ligand 3 recorded with a mixing time of 250 ms with a 3.5 kHz spin-locking field

at *ca.* 5 ppm, one should be able to assign sequentially the protons in a given sugar from a COSY spectrum. However, severe spectral overlap in the region 3–4 ppm in the present system did not allow the identification of unambiguous connectivity patterns. In order to overcome this problem, HOHAHA[14] experiments were performed and proved to be extremely useful in allowing the spin systems to be assigned (Figs. 2 and 3). Two-dimensional NOE experiments were used to establish the position of substitution of the bipyridyl group, and to assign the spin systems to the seven sugar rings R1–7 (Figs. 4 and 5). Initially, NOESY[22] experiments were carried out, but only weak peaks were detected. As the rotational correlation time of compounds of this size typically is in the region where minimal NOE enhancements are observed, the corresponding rotating frame (ROESY)[15] experiment was therefore used to obtain NOE data.

(a) *β-CD(per-OMe)bpy* 3. The one-dimensional ^1H NMR spectrum of the ligand 3 is presented in Fig. 1(*a*). The bipyridyl aromatic protons resonate between 7.3 and 8.8 ppm and the bipyridyl methylene protons appear as a sharp singlet at 4.8 ppm. Due to the chirality of the cyclodextrin ring, the bipyridyl methylene protons are diastereotopic but in the ligand 3 the chemical shifts of these two protons are equivalent and they both resonate at 4.8 ppm in $CDCl_3$. Starting from the seven anomeric protons, (H1'R1–7), which resonate between 5.05–5.20, protons H2'R1–7 were assigned from the DQF-COSY spectrum as they resonate upfield of all other sugar resonances at *ca.* 3.15 ppm. By integration, all remaining 95 protons, *i.e.* H3', H4', H5' and H6a',b' as well as the methoxyl protons at positions 2', 3' and 6' resonate between 3.3 and 3.9 ppm. The high degree of spectral overlap in this region is not unexpected given the similarity of the chemical environments of the seven sugar rings in the cyclodextrin system, and is more severe than the observed chemical shifts in related cyclodextrins containing free hydroxy groups.[21]

The anomeric H1' protons at 5.0–5.2 ppm were used as a starting point to assign the sugar spin systems of R1–7 using a HOHAHA experiment (Fig. 2). The most downfield proton in this multiplet was assigned to H1' of R1, the ring that contains the bipyridyl group, as an NOE was observed between H6a',6b' of this spin system and the bipyridyl methylene protons. Starting from this doublet at 5.18 ppm, transfer of magnetisation to H2'–H5' was observed in the HOHAHA spectra, defining the spin system of ring R1. Tentative assignments of H3' to H5' were made by comparison of the chemical shifts of the observed peaks with those observed in the unsubstituted permethylated β-cyclodextrin,[19] and were confirmed, in some cases, in the DQF-COSY spectrum.

The second doublet at 5.16 ppm was assigned to H1' of the spin system of ring R2, confirmed by a R1H1' ↔ RXH4' NOE between the two rings (Fig. 4). Protons H4', H5', H6a', H6b' in R2 are all shifted downfield, the most significant change being observed for H6a' which resonates at 4.14 ppm [Fig. 1(*a*)]. Protons R2H6a',6b' were assigned due to strong coupling to R2H5', and hence HOHAHA transfer to H5' was observed. This connectivity was also observed in the COSY spectrum. Examination of CPK models shows that the bipyridyl ring has rotational flexibility and is in close proximity to R2 as it rotates. This is consistent with the observed changes in chemical shifts for the protons on R2.

The protons on the five sugar rings R3–7 all had similar chemical shifts and appeared as overlapping multiplets. The

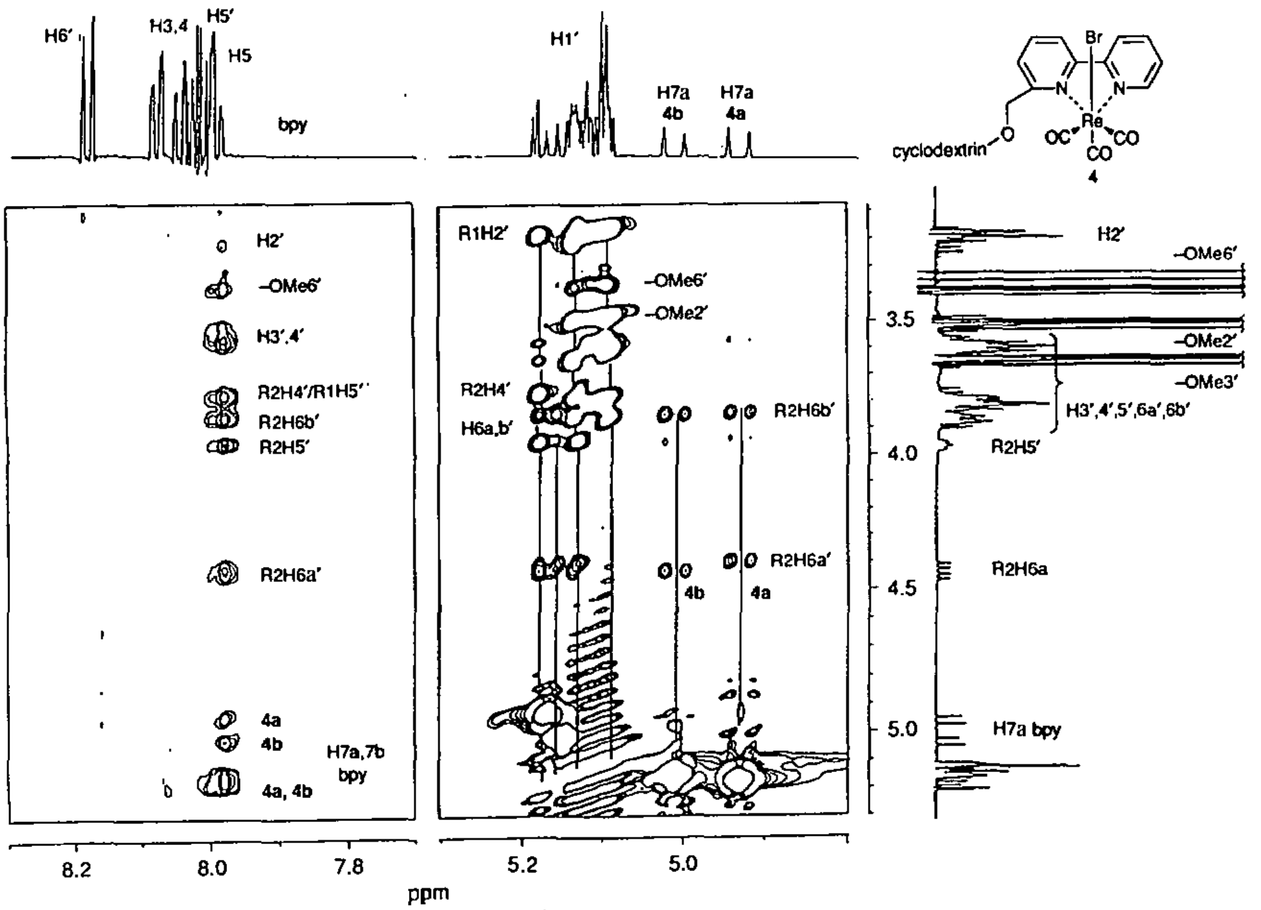


Fig. 5 Portion of the 600 MHz ROESY spectrum of complex 4 recorded with a mixing time of 250 ms and a 3.7 kHz spin-locking field

spin system H1'-H5' for rings R3-R7 is indicated in Fig. 2. Further assignment was not possible owing to the high degree of overlap observed. The methoxy protons at carbons 2', 3' and 6' in the sugar rings (-OMe2', -OMe3', -OMe6') appeared at distinct chemical shifts and appeared as five singlets, three singlets (intensities 1:1:5), and six singlets respectively [Fig. 1(*a*)]. These peaks were assigned to positions 2', 3' and 6' respectively, by comparison with the reported data for 2,3,6-tri-*O*-methyl-β-cyclodextrin.[19]

(b) *β-CD(per-OMe)bpyRe(CO)$_3$Br* 4. The one-dimensional NMR spectrum of the rhenium tricarbonyl complex 4 is presented in Fig. 1(*b*). Comparison of the spectrum with the ligand 3 shows several significant changes. The rhenium atom introduces a new chiral centre and hence two diastereomers, 4a and 4b are formed. Thus, the two diastereotopic bipyridyl methylene protons (H7a,b) are shifted downfield to *ca.* 5 ppm and change from a sharp singlet in the ligand to two sets of AX doublets (*J* 14.9 Hz). In addition, proton R2H6a', which appears as a doublet of doublets at 4.1 ppm in the ligand 3 [Fig. 1(*a*)], is shifted downfield to 4.4 ppm in the complex 4 and appears as two doublets of doublets. The presence of two diastereomers is also indicated by the appearance of two sets of aromatic resonances in the ^{1}H and ^{13}C spectra. The protons, H7a and H7b in 4 appear at significantly different chemical shifts compared to the ligand 3 owing to their close proximity to the rhenium centre. The appearance of these protons as a singlet or an AX system in each diastereomer appears to be solvent dependent; in the model system in which a -CH_2OCH_3 group is substituted at position 6 of the bipyridyl system (as opposed to β-cyclodextrin in the present study), H7a and H7b appear as an AB quartet in $CDCl_3$ but as a singlet in [$^2H_6$]acetone.

From the DQF-COSY and HOHAHA spectra, the sugar spin systems of 4 were assigned in a similar manner to that described in detail above for the assignment of the spectrum of 3. Fig. 3 shows a section of the HOHAHA spectrum, summarizing these assignments. The anomeric H1' protons were dispersed in the ratio 1:1:1:4. The most downfield doublet in this multiplet at 5.21 was assigned to H1' of ring R1, the ring bearing the bipyridyl substituent. The next most downfield doublet at 5.17 was assigned to the adjacent ring R2, and the expected R1H1' ↔ R2H4' NOE between the rings was observed (Fig. 5). The chemical shifts of the protons in this ring showed the same trend as for the ligand, *i.e.* H4', H5', H6a', H6b' were shifted downfield compared to these protons in R1 and R3-7. Discrete spin systems for two other rings were observed in the HOHAHA spectrum (Fig. 3), but the overlap in this region of the spectrum did not allow unequivocal assignment of these spin systems to individual rings.

Solution Conformation of Rhenium Complex 4.—The disposition of the complexed bipyridyl unit in the complex 4 is of particular importance if the photochemical and electrochemical properties of the complex are to be fully understood and exploited in the design of new and/or modified assemblies based on 4. Analysis of the COSY and HOHAHA experiments show that complex 4 exists as a mixture of two diastereomers 4a and 4b, but these experiments give no information about the orientation of the complex with respect to the cavity.

Circular dichroism measurements have previously indicated[12] that there is a preferred orientation of the metal centre over the cavity, **A**, as opposed to other conformations in which the rhenium complex is oriented away from the cavity, **B**. The existence of complexes **A** in which the metal centre is directed over the cyclodextrin cavity, was therefore considered. In this case, the situation is complex, as formation of diastereomeric complexes is possible, in which the coordinated bromine is

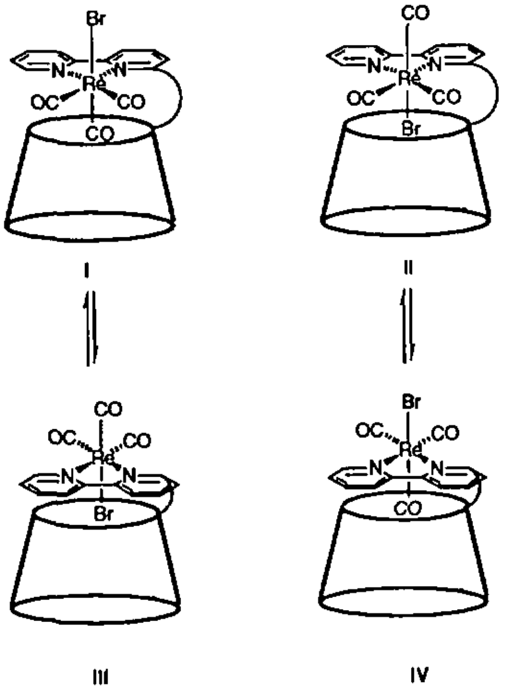
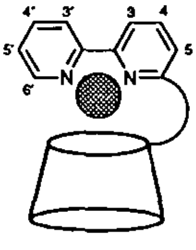
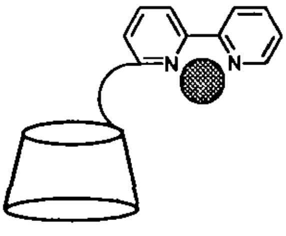


Fig. 6 Schematic representations of diastereomers I/II and III/IV



A



B

directed either over the cavity or away from the cyclodextrin cavity (Fig. 6). Complexes I/II and III/IV are diastereomers, as well as I/IV and II/III. Complexes I/III and II/IV are rotamers and may be interconverted by rotation about the linker bonds. Hence, if only complexes of type A are formed, then on statistical grounds, one would expect that the four complexes I, II, III, IV would be formed in equal amounts. As only signals corresponding to two diastereomers were observed, then if the metal is indeed directed over the cavity, it is most likely that I/III and II/IV are in rapid exchange giving rise to two species on the NMR time scale.

ROESY spectra were recorded to see if NOE connectivities between the bipyridyl aromatic protons and protons on sugar rings other than R1, R2 could be observed (Fig. 5) in support of I–IV. Examination of CPK models shows that the surface of the cyclodextrin is effectively covered by the 6'-OMe groups that project upwards from the sugar rings. If complexes I–IV are present, then the bipyridyl aromatic protons will lie over the surface of the cyclodextrin and may be in close proximity to the 6'-OMe groups. Good evidence for the existence of such complexes would be the detection of an NOE between any of the bipyridyl protons H3, 4, 3', 4', 5', 6' and the 6'-OMe groups. On the basis of the assigned resonances, no such long range connectivities were detected in ROESY experiments. The failure to detect these NOEs does not exclude the presence of species I–IV; the coordinated complex is quite bulky and when positioned over the cavity, the bipyridyl protons may be too far (> 3.5 Å) from the 6'-OMe groups to be detected in a ROESY experiment.

Thus, while the NMR spectra show the presence of two diastereomers, NOESY data does not provide supporting evidence for circular dichroism studies which suggested the complex is directed over the cavity.[12] Apart from X-ray crystallography (which in the present case will be difficult owing to the presence of diastereomers), there is no other technique that will provide conclusive data in support of the circular dichroism measurements. Work is underway towards the preparation of β-cyclodextrins functionalized on the same face by two bipyridyl ligands. Complexation of the two bipyridyl ligands to a transition metal in this receptor provides direct entry into transition metal capped cyclodextrins.

Conclusions

The development of a new class of molecules in which a photoactive bipyridyl unit is connected to permethylated β-cyclodextrin, is reported. A detailed NMR spectroscopic study has been carried out on the ligand β-CD(per-OMe)bpy 3, and the metal complex β-CD(per-OMe)bpyRe(CO)$_3$Br 4, in which the photoactive unit and the cyclodextrin receptor are separated by a one atom spacer. The complex 4 exists as a mixture of two diastereomers; conformations in which the complex is directed over the cavity result in four diastereomers depending on whether the coordinated bromine is pointing into or away from the cavity. Preorganized assemblies based on 4, in which the metal is directed over the cavity, provide ideal systems in which to study photochemical communication between the photoactive unit and a guest molecule encapsulated in the cyclodextrin cavity.

Experimental

General.—Melting points were recorded on a Büchi 510 instrument and are uncorrected. IR spectra (KBr pellet) were recorded on a Perkin-Elmer FTIR 1720 spectrophotometer. UV–VIS spectra were measured in MeCN with a Uvikon 810 spectrometer. Optical rotations were recorded on a Perkin-Elmer 241 polarimeter. Column chromatography was performed on silica gel (Kieselgel 60, 70–230 mesh, ASTM, Merck). TLC was performed on aluminium sheets precoated with 0.2 mm silica 60 F_{254} (Merck).

Materials.—Monohydroxypermethylated β-cyclodextrin (1),[16a] and 6-bromomethyl-2,2'-bipyridine (2),[17] were prepared following the literature procedures. Diethyl ether (Et_2O) was dried over $MgSO_4$ and distilled first from NaH and then from $LiAlH_4$ prior to use. Re(CO)$_5$Br was obtained from Strem Chemicals, Inc and was used as provided. Compounds 3 and 4 were dried under vacuum at 40 °C in the presence of P_2O_5 for two days to remove solvent molecules in the cyclodextrin cavity.

NMR Spectroscopy.—NMR samples were prepared as 10 mol dm^{-1} solutions in deuteriochloroform and were referenced to the residual solvent protons. *J*-Values are in Hz. ^{1}H NMR spectra were recorded on a Bruker AMX600 spectrometer operating at 600.14 MHz over a spectral width of 5500 Hz with quadrature detection employed throughout. Two-dimensional spectra were acquired in the phase sensitive mode using time-proportional phase incrementation (TPPI).[23] Data sets resulting from 400–512 increments of t_1 were acquired and zero filled to 1024 points, with each free induction decay composed of 2048 data points. Typically 64 transients were recorded for each increment of t_1 with a recycle delay of 1.0–1.3 s. Double quantum filtered COSY (DQF-COSY)[13] spectra were acquired using the standard pulse sequence. HOHAHA[14] spectra were acquired using a 9–10 kHz spin locking field with an MLEV-17 sequence of 35–65 ms. ROESY[15] spectra were acquired using a

3–4 kHz spin locking field with mixing times of 250 and 400 ms. Data were subjected to shifted sine-bell weighting functions in f1 and f2 and were base line corrected where required using Bruker software on an X32 data station. Inverse detection proton–carbon correlation experiments were carried out on an AMX400 with GARP[24] decoupling over 4K data points with 64 scans per increment, over 256 increments. Proton decoupled ^{13}C NMR spectra were recorded at 100.6 MHz (3) and 125.7 MHz (4) with WALTZ[25] decoupling of the proton frequencies. Assignments follow the numbering shown in Fig. 1 and structure A.

β-CD(per-OMe)-bpy (3).—To a solution of monohydroxypermethylated β-cyclodextrin **1** (1.0 g, 0.70 mmol) in dry Et_2O (10 cm^3), NaH (17 mg, 0.70 mmol) was added, and the mixture stirred at reflux for 1 h. A solution of 6-bromomethyl-2,2′-bipyridine **2** (0.20 g, 0.80 mmol) in dry Et_2O (10 cm^3) was added, and the mixture stirred at this temperature for a further four days. The mixture was cooled to room temperature, and hydrolysed with brine (10 cm^3). The aqueous phase was extracted with Et_2O (3 × 10 cm^3), the organic phases combined, dried over $CaSO_4$, and evaporated to give an oily residue (1.13 g). This residue was purified by chromatography over silica (toluene/methanol/isopropanol 15:1:1) and the major band was collected. Evaporation of the solvent yielded 0.73 g (66%) of **3** as a white solid: m.p. 98–101 °C; R_f 0.42 (toluene/isopropanol 1:1); $[\alpha]_D$ +143 (*c* 0.15 in $CHCl_3$); $\lambda_{max}(\varepsilon)$/nm 237 (11 800), 244 (10 700), 285 (15 900); FAB MS *m/z* 1583 ($M + H^+$); δ_H Hbpy: 8.65 (m, H3′), 8.36 (dt, *J* 8.0, 1.1, H6′), 8.25 (d, *J* 7.7, H3), 7.78 (dd, *J* 7.8, H4), 7.68 (dt, *J* 7.7, 1.8, H5′), 7.50 (dd, *J* 7.7, 1.0, H5), 7.28 (ddd, *J* 7.3, 4.8, 1.2, H4′), 4.82 (s, H7,7′); Hsugars R1: 5.20 (d, *J* 3.67, H1′), 3.14 (H2′), 3.49 (H3′), 3.57 (H4′), 3.80 (H5′), 3.80 (H6a′); R2: 5.19 (d, *J* 3.7, H1′), 3.21 (H2′), 3.52 (H3′), 3.72 (H4′), 3.86 (H5′), 4.14 (dd, *J* 4.06, 10.82, H6a′), 3.83 (H6b′); R3–7: 5.10 (m, H1′), 3.15 (H2′), 3.47 (H3′), 3.59 (H4′), 3.76 (H5′); 3.68, 3.67, 3.65 (3s, 1:1:5, –OMe2′), 3.542, 3.524, 3.521, 3.518, 3.508 (5s, –OMe3′), 3.33, 3.34, 3.35, 3.371, 3.374 and 3.38 (6s, –OMe6′); δ_C(100.6 MHz) 128 (C3), 146 (C4), 130 (C5), 83.5 (C7), 158 (C3′), 132.5 (C4′), 146 (C5′) and 130 (C6′) (Found: C, 55.1; H, 7.45; N, 1.45. Calc. for $C_{73}H_{118}O_{35}N_2$: C, 55.36; H, 7.51; N, 1.77%).

β-CD(per-OMe)bpyRe(CO)$_3$Br (4).—A solution of ligand **3** (100 mg, 6.3 × 10^{-5} mol) and $Re(CO)_5Br$ (26 mg, 6.4 × 10^{-5} mol) in toluene (4 cm^3) was stirred at reflux for 3 h. The mixture was cooled to room temperature, the solvent removed under vacuum, and the resultant residue purified by chromatography over silica (toluene/isopropanol 1:1) to give 0.096 g (79%) of **4**: m.p. 105 °C (decomp.); R_f 0.28 (toluene/isopropanol 1:1); $[\alpha]_D$ +122 (*c* 0.15 in $CHCl_3$); ν/cm^{-1} 2022, 1920, 1901 (CO); $\lambda_{max}(\varepsilon)$/nm 246 (17 900), 300 (12 300, 310 (11 900), 324 (9350), 370 (2300); FAB MS *m/z* 1932 $[M - H]^+$, 1853 $[M - H - Br]^+$; δ_H Hbpy: 9.10 (m, H3′), 8.18 (m, *J* 8.5, 1.0, H6′), 8.08 (dd, *J* 7.7, 2.1, H3), 8.04 (2t, *J* 7.8, H4), 8.02 (dd, *J* 8.0, H5′), 7.94 (dd, *J* 7.7, 1.6, H5), 7.51 (m, H4′), 5.17, 4.95 and 5.15, 5.02 (2AX systems, *J* 14.9, H7a,b); Hsugars R1: 5.19 (d, *J* 3.86, H1′), 3.18 (H2′), 3.49 (H3′), 3.57 (H4′), 3.79 (H5′); R2: 5.12 (H1′), 3.19 (H2′), 3.57 (H3′), 3.75 (H4′), 3.93 (H5′), 4.44, 4.40 (2dd, *J* 2.90, 11.4, H6a′), 3.91, 3.92 (2d, H6b′); R3 5.12 (H1′), 3.17 (H2′), 3.56 (H3′,4′), 3.81 (H5′); R4: 5.11 (H1′), 3.16 (H2′), 3.50 (H3′), 3.63 (H4′), 3.77 (H5′); R5–7: 5.19 (H1′), 3.16 (H2′), 3.48 (H3′), 3.58 (H4′), 3.78 (H5′); 3.658, 3.651, 3.641, 3.638, 3.633, 3.629, 3.626, 3.621 (8s, –OMe2′), 3.50–3.62 (m, H3′, H4′R1–7), 3.519, 3.501, 3.500, 3.493, 3.489, 3.480 (6s, –OMe3′), 3.394, 3.379, 3.376, 3.373, 3.369, 3.364, 3.34 and 3.313 (8s, –OMe6′); δ_C(125.7 MHz) 197.2, 197.1 (CO), 196.8, 196.7 (CO), 188.5, 188.3 (CO), 163.7, 163.6 (C3′), 156.8, 156.7, 156.7 (2 Cbpy), 153.7, 153.6 (Cbpy), 140.0, 139.8 (Cbpy), 127.6 (Cbpy), 125.2, 125.0 (Cbpy), 124.0 (bpy), 122.11 (Cbpy), 99.7 (m), 83.2 (m), 80.9 (m), 72.0 (m), 59.3 (m) (Found: C, 47.9; H, 6.15; N, 1.15. Calc. for $C_{76}H_{118}O_{38}N_2BrRe$: C, 47.20; H, 6.15; N, 1.45%).

Acknowledgements

Financial support from the Australian Research Council is gratefully acknowledged by M. M. H. The authors would like to thank the referees for helpful comments.

References

1 Presented in part at The Sixth International Cyclodextrin Symposium, Chicago, April 21–24, 1992.
2 *Frontiers in Supramolecular Chemistry and Photochemistry*, eds. H.-J. Schneider and H. Dürr, VCH Verlagsgesellschaft, Weinheim, 1991.
3 V. Balzani and F. Scandola, *Supramolecular Photochemistry*, Harwood, Chichester, England, 1991.
4 Ref. 3, ch. 10, pp. 267–318 and references therein.
5 *Inclusion Phenomena and Molecular Recognition*, ed. J. L. Atwood, Plenum Press, New York, 1990.
6 (*a*) R. Breslow, *Science*, 1982, **218**, 532; (*b*) R. Breslow, *Chemistry in Britain*, 1983, 126; (*c*) I. Tabushi, *Acc. Chem. Res.*, 1982, **15**, 66; (*d*) I. Tabushi, Y. Kuroda and T. Mizutani, *Tetrahedron*, 1984, **40**, 545; (*e*) V. T. D'Souza and M. L. Bender, *Acc. Chem. Res.*, 1987, 20, 146.
7 (*a*) H. M. Colquhoun, J. F. Stoddart and D. H. Williams, *Angew. Chem. Int. Ed. Engl.*, 1986, **25**, 487; (*b*) A. Harada and S. Takahashi, *J. Chem. Soc., Chem. Commun.*, 1986, 1229; (*c*) A. Harada, K. Saeki and S. Takahashi, *Organometallics*, 1989, **8**, 730.
8 See for example: (*a*) A. Ueno, F. Moriwaki, T. Osa, F. Hamada and K. Murai, *J. Am. Chem. Soc.*, 1988, **110**, 4323; (*b*) G. A. Reitz, J. N. Demas, B. A. DeGraff and E. M. Stephens, *J. Am. Chem. Soc.*, 1988, **110**, 5051; (*c*) J. I. Cline III, W. J. Dressick, J. N. Demas and B. A. DeGraff, *J. Phys. Chem.*, 1985, 89, 94; (*d*) R. A. Bissell and A. P. de Silva, *J. Chem. Soc., Chem. Commun.*, 1991, 1148; (*e*) A. Ueno, T. Kuwabara, A. Nakamura and F. Toda, *Nature*, 1992, **356**, 136.
9 *Supramolecular Chemistry*, ed. E. Vögtle, Wiley, New York, 1991.
10 (*a*) V. Balzani, F. Bolletta, M.-T. Gandolfi and M. Maestri, *Topics Curr. Chem.*, 1978, 75, 1; (*b*) K. Kalyanasundaram, *Coord. Chem. Rev.*, 1982, **46**, 159.
11 Z. Pikramenou and D. G. Nocera, *Inorg. Chem.*, 1992, **31**, 532.
12 N. Brügger, R. Deschenaux, T. Ruch and R. Ziessel, *Tetrahedron Lett.*, 1992, 33, 3871.
13 U. Piantini, O. W. Sorensen and R. R. Ernst, *J. Am. Chem. Soc.*, 1982, **104**, 6800.
14 (*a*) L. Braunschweiler and R. R. Ernst, *J. Magn. Reson.*, 1983, **53**, 521; (*b*) A. Bax and D. G. Davis, *J. Magn. Reson.*, 1985, 65, 355; (*c*) P. L. Weber, L. C. Sieker, T. S. A. Samy, B. R. Reid and G. P. Drobny, *J. Am. Chem. Soc.*, 1987, **109**, 5842.
15 (*a*) A. A. Bothner-By, R. L. Stephens, J.-M. Lee, C. D. Warren and R. W. Jeanloz, *J. Am. Chem. Soc.*, 1984, **106**, 811; (*b*) A. Bax and D. G. Davis, *J. Magn. Reson.*, 1985, **63**, 207.
16 See for example: (*a*) E. Akkaya and A. W. Czarnik, *J. Am. Chem. Soc.*, 1988, **110**, 8553; (*b*) I. Tabushi, T. Nabeshima, K. Fujita, A. Matsunaga and T. Imoto, *J. Org. Chem.*, 1985, **50**, 2638; (*c*) R. P. Bonomo, V. Cucinotta, F. D'Alessandro, G. Impellizzeri, G. Maccarrone, G. Vecchio and E. Rizzarelli, *Inorg. Chem.*, 1991, 30, 2708; (*d*) M. Tanaka, Y. Kawaguchi, T. Niinae and T. Shono, *J. Chromatogr.*, 1984, **314**, 193.
17 R. Ziessel and J.-M. Lehn, *Helv. Chim. Acta*, 1990, 73, 1149.
18 A. P. Croft and R. A. Bartsch, *Tegrahedron*, 1983, 39, 1417.
19 J. R. Johnson, N. Shankland and I. H. Sadler, *Tetrahedron*, 1985, 15, 3147.
20 See for example: (*a*) P. R. Ashton, P. Ellwood, I. Staton and J. F. Stoddart, *J. Org. Chem.*, 1991, **56**, 7274; (*b*) P. Ellwood, C. M. Spencer, N. Spencer, J. F. Stoddart and R. Zarzycki, *J. Inclusion Phenom. Mol. Recog. Chem.*, 1992, **12**, 121.
21 (*a*) W. Saka, Y. Yamamoto, Y. Inoue, R. Chujo, K. Takahashi and K. Hattori, *Bull. Chem. Soc. Jpn.*, 1990, 63, 3175; (*b*) H. Ideka, Y. Du, A. Nakamura and F. Toda, *Chem. Lett.*, 1991, 1495; (*c*) H. Ikeda, Y. Nagano, Y. Du, T. Ikeda and F. Toda, *Tetrahedron Lett.*, 1990, 5045; (*d*) M. J. Pregel and E. Buncel, *Can. J. Chem.*, 1991, 69, 130; (*e*) C. S. Lai, G. J. Moody, J. D. R. Thomas, D. C. Mulligan, J. F. Stoddart and R. Zarzycki, *J. Chem. Soc., Perkin Trans. 2*, 1988, 319.
22 (*a*) J. Jeener, B. H. Meier, P. Bachmann and R. R. Ernst, *J. Chem. Phys.*, 1979, 71, 4546; (*b*) A. Kumar, R. R. Ernst and K. Wütrich,

Biochem. Biophys. Res. Commun., 1980, 95, 1; (*c*) A. Macura and R. R. Ernst, *Mol. Phys.*, 1980, **41**, 95.
23 D. Marion and K. Wütrich, *Biochim. Biophys. Res. Commun.*, 1983, **113**, 967.
24 A. J. Shaka, P. B. Barker and R. Freeman, *J. Magn. Reson.*, 1985, **64**, 547.
25 A. J. Shaka, J. Keeler and R. Freeman, *J. Magn. Reson.*, 1983, **53**, 313.

Paper 3/01734F
Received 25*th March* 1993
Accepted 31*st March* 1993

Pergamon

Tetrahedron Letters, Vol. 35, No. 14, pp. 2165-2168, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $6.00+0.00

0040-4039(94)E0271-X

Bipyridine-coupled Permethylated β-Cyclodextrin

Robert Deschenaux,*[a] **Alain Greppi**,[a] **Thomas Ruch**,[a] **Hans-Peter Kriemler**,[b] **Fritz Raschdorf**[b] **and Raymond Ziessel**.[c]

[a]Université de Neuchâtel, Institut de Chimie, Av. de Bellevaux 51, 2000 Neuchâtel, Switzerland.
[b]Research Services Physics Department, Spectroscopy, Ciba-Geigy Ltd, 4002 Basel, Switzerland.
[c]Ecole Européenne des Hautes Etudes des Industries Chimiques de Strasbourg, 1 rue Blaise Pascal, 67008 Strasbourg, France.

Dedicated to Prof. K. Bernauer on the occasion of his 60th birthday

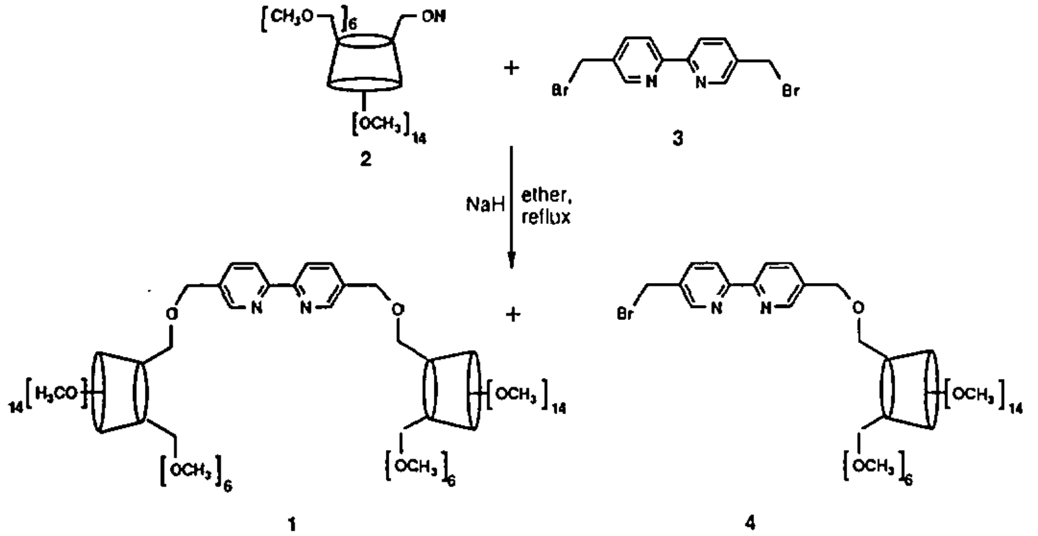
Abstract : The synthesis and characterization of a cyclodextrin dimer, obtained by connecting two permethylated β-cyclodextrins with a 2,2'-bipyridine ligand, and of its luminescent Re(I) metal complex are described. Such a system is of interest to study energy transfer between the active metal center and a bound ditopic substrate.

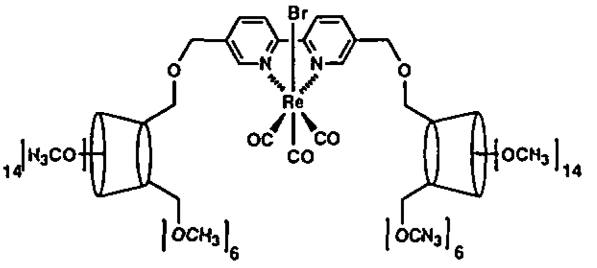
The design and synthesis of multifunctional receptors exhibiting novel properties and functions is a current research area of great importance.[1] The possibility to mimic natural-occuring processes for further exploring and better understanding complex phenomena, such as those associated with electron(s) or photon(s) transfer, strongly motivated these investigations.[2]

We reported the synthesis, characterization, solution behaviour and physico-chemical properties of a permethylated β-cyclodextrin substituted on the primary face by a 2,2'-bipyridine ligand and of its Re(I) transition metal complex.[3] This latter species is of particular interest to study electron and/or photon transfer between the complexed active metal center and an encapsulated guest : energy transfer was recently studied between a β-cyclodextrin derivatized with an europium aza crown and a benzene molecule included in the cyclodextrin cavity.[4]

Our interest in the bipyridyl ligand functionalized cyclodextrins[3,5] led us to extend our investigations to dimeric structures 1 and 5. Such receptors were specially designed for binding ditopic guest molecules.[6] The structure of all new compounds were confirmed by ^{1}H-, ^{13}C{^{1}H}-NMR, plasma desorption mass spectrometry (PDMS),[7] electron and infrared spectroscopy and elemental analyses.

Cyclodextrin dimer **1** was prepared by reacting the monohydroxy-β-cyclodextrin 2[8] with 5,5'-bis-(bromomethyl)-2,2'-bipyridine 3.[9] The synthesis was carried out in dry ether, at reflux, in the presence of NaH. Purification by column chromatography (silicagel, toluene/MeOH/ether 1:1:7, v/v) yielded the desired compound **1**[10] as a white solid (15-20%). Cyclodextrin 4,[10] which eluted first, was also isolated from the reaction mixture (10%). Interestingly, the unreacted bromine atom of 4, upon further substitution, opens the way to supramolecular constructions in which two different receptors are connected by the bipyridine ligand. Such systems would exhibit strong affinity towards heteroditopic substrates.





5

The neutral transition metal complex 5[10] was obtained in 70% yield by reacting the free ligand 1 with $Re(CO)_5Br$ in toluene, at reflux, followed by purification by column chromatography (silicagel, toluene/MeOH/ether 1:3:7, v/v). As expected (see IR bands[10]) the facial isomer of complex 5 formed during the reaction.

The dimeric cyclodextrin **1** presented absorption bands comparable with those of 5,5'-dimethyl-2,2'-bipyridine [245 nm (14 700), 288 nm (18 000)]. This result is important as it indicates that the two cyclodextrin units do not modify markedly the spectroscopic characteristics of the bridging bipyridine ligand. Related to the above observation, the Re(I)-complex **5** showed a UV-spectrum similar to the one exhibited by the cyclodextrin-free analogue fac-[Re(bpy)$(CO)_3$Cl].[11]

The electrochemical properties of **5** were investigated by cyclic voltammetry. Two reversible waves were determined : a reduction peak at $E_{1/2}$ = -1.30 V, and an oxidation one at $E_{1/2}$ = +1.40V. These data are in agreement with the results obtained for the Re(I)-complex of the previously reported 2,2'-bipyridyl ligand functionalized permethylated-β-cyclodextrin.[3b]

Finally, when a MeCN solution of **5** ($c = 1.01 \cdot 10^{-4}$M) was irradiated at 376 nm (room temperature) a strong luminescence was observed at 609 nm. Interestingly, the intensity of this emission was comparable to that obtained for fac-[Re(bpy)$(CO)_3$Cl][11] when irradiated under identical conditions.

Table. Spectroscopic Properties and Electrochemical Data.

Compound	λ/nm (ε/l·mol^{-1}·cm^{-1})^{a}	$E_{1/2}$/V^{b} (ΔE/mV^{c})
1	244 (10 650), 290 (15 370)	
5	250 (20 000), 300 (16 140), 325 (12 480), 376 (2400)	-1.30 (70), +1.40 (80)

[a] Measured in MeCN.

[b] Obtained from cyclic voltammetry on platinum in dry MeCN (reference electrode : saturated calomel; supporting electrolyte : 0.1M TBAP; internal reference : ferrocene, +0.40 V), at room temperature, under argon, at 0.1 Vs^{-1} scan rate.

[c] Separation between anodic and cathodic peak potentials. ΔEp for ferrocene under the same conditions was 70 mV. No compensation was made for internal cell resistance.

In conclusion, the first electron- and photo-active cyclodextrin dimer as well as preliminary physico-chemical investigations have been reported. Such supramolecular assemblies are of particular interest to study communication (electron and/or photon transfer) between a metal active center and a bound ditopic guest molecule.

References and Notes

1. Vögtle F., *Supramolecular Chemistry*, Wiley, Chichester, 1991.
2. Lehn J.-M., in *Frontiers in Supramolecular Organic Chemistry and Photochemistry*, Schneider H.-J. and Dürr H. (eds), VCH Verlagsgesellschaft, Weinheim, 1991, 1-28.
3. (a) Deschenaux R., Harding M.M., Ruch T., *J. Chem. Soc., Perkin Trans. 2* **1993**, 1251-1258.
   (b) Brügger N., Deschenaux R., Ruch T., Ziessel R., *Tetrahedron Lett.* **1992**, *33*, 3871-3874.

4. Pikramenou Z., Nocera D.G., *Inorg. Chem.* **1992**, *31*, 532-536.
5. Deschenaux R., Harding M.M., Ruch T., Ziessel R. in *Proceedings of the Sixth International Symposium on Cyclodextrins*, Editions de Santé, Paris, France, 1992, 101-105.
6. The Cu(II)-complex of a cyclodextrin dimer obtained by connecting two native β-cyclodextrins with a 5,5'-bipyridine derivative exhibited significant catalysis for hydrolysis of bound ditopic substrates : a) Zhang B., Breslow R., *J. Am.Chem. Soc.* **1993**, *115*, 9353-9354; b) Breslow R., Zhang B., *J. Am.Chem. Soc.* **1992**, *114*, 5882-5883.
7. Cotter R.J., *Anal. Chem.* **1988**, *60*, 781-795.
8. Tanaka M., Kawaguchi Y., Niinae T., Shono T., *J. Chromatogr.* **1984**, *314*, 193-200.
9. Ebmayer F., Vögtle F., *Chem. Ber.* **1989**, *122*, 1725-1727.
10. Selected analytical data : **1** : $R_f = 0.17$ (silicagel, toluene/isopropanol 1:1) ; Anal. Calc. for $C_{136}H_{228}N_2O_{70}$ (3011.31) : C 54.25, H 7.63, N 0.93 ; found C 53.44, H 7.73, N 0.79 ; PDMS : m/z = 3034.4 $[M+Na]^+$. 4 : $R_f = 0.39$ (silicagel, toluene/MeOH/ether 1:1:7) ; Anal. Calc. for $C_{74}H_{119}Br\ N_2O_{35}$(1976.66) : C 53.01, H 7.15, N 1.67 ; found C 53.41, H 7.48, N 1.25 ; PDMS : m/z = 1678.0 $[M+H]^+$. 5 : $R_f = 0.18$ (silicagel, toluene/MeOH/ether 1:3:7) ; Anal. Calc. for $C_{139}H_{228}BrN_2O_{73}Re$ (3361.45) :PDMS : m/z = 3361.6 $[M+H]^+$; IR (KBr pellet)ν_{CO} 2022, 1921, 1899 cm^{-1} ; $[\alpha]_D = +83°$ (c = 0.15 in $CHCl_3$).
11. Juris A., Campagna S., Bidd I., Lehn J.-M., Ziessel R., *Inorg. Chem.* 1988, 27, 4007-4011 and references therein.

(*Received in France* 14 *January* 1994; *accepted* 2 *February* 1994)

48. Synthesis, Characterization, and Electrochemical and Photophysical Properties of Rhenium(I) and Ruthenium(II) Complexes of 2,2′-Bipyridine Ligand Functionalized *β*-Cyclodextrins

by **Robert Deschenaux***, **Thomas Ruch**[1]), and **Pierre-François Deschenaux**

Université de Neuchâtel, Institut de Chimie, Av. de Bellevaux 51, CH-2000 Neuchâtel

and **Alberto Juris***

Università degli Studi di Bologna, Dipartimento di Chimica 'G. Ciamician', Via Selmi 2, I-40126 Bologna

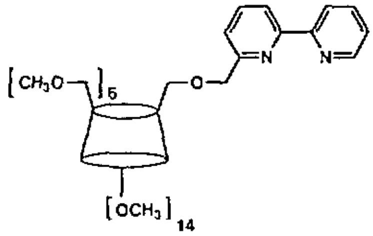
and **Raymond Ziessel***

Ecole Européenne des Hautes Etudes des Industries Chimiques de Strasbourg, URM 46 du CNRS,
1, rue Blaise Pascal, F-67008 Strasbourg

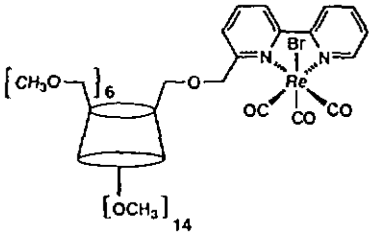
(17.XI.94)

The synthesis, characterization, and electrochemical and photophysical properties of the Re^I and Ru^{II} complexes of permethylated *β*-cyclodextrins, functionalized on the primary face by a 2,2′-bipyridine ligand, are reported. For comparison, model compounds, in which the cyclodextrin was replaced by a Me group, were also prepared and their properties investigated.

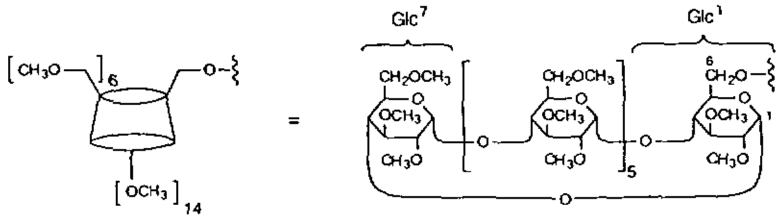
Introduction. – The design and synthesis of photo- and electroactive receptors exhibiting novel properties are among the current challenges in supramolecular chemistry. Beautiful systems and interesting studies have been described. The readers are referred to, *e.g.*, the following outstanding references [1].



1



2



---

[1]) Part of Ph.D. Thesis of *T. R.*

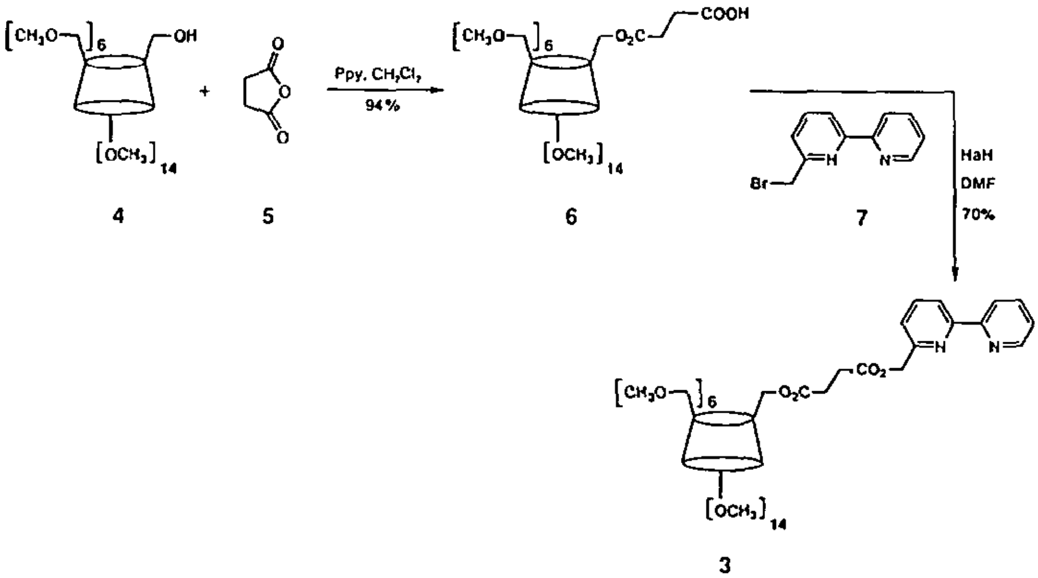
Recently, we reported a novel family of receptors based on the rich host-guest chemistry of the cyclodextrins (CD's) and on the unique complexation features of the 2,2'-bipyridine ligand (bpy) [2]. Compound **1** [2a,b], the first member of the series, was synthesized in good yield from monohydroxylated permethylated β-CD [3] and 6-(bromomethyl)-2,2'-bipyridine [4]. The neutral Re^I-complex $[Re(1)(CO)_3Br]$ (**2**) [2a,b] was easily prepared from **1** and $[Re(CO)_5Br]$. High-field NMR studies and fast-atom-bombardment mass spectrometry (FAB-MS) were performed to confirm the structure and purity of **1** and **2**. A dimeric species, obtained by connecting two permethylated β-CD's at the 5,5'-positions of a 2,2'-bipyridine derivative, and its Re^I complex were also synthesized [2c]. The latter species are expected to have strong affinity towards ditopic substrates [5].

Pikramenou and *Nocera* [6] reported a β-CD substituted by a macrocyclic ligand and its Eu^{III} complex. Energy transfer was shown to occur between the photoactive lanthanide complex and an encapsulated benzene molecule. This constitutes an elegant example of molecular communication within a supramolecular assembly. It is well-known that $[Re(bpy)(CO)_3Cl]$ is luminescent in solution and at room temperature [7]. Therefore, structures of type **2** should be ideal candidates to investigate energy transfer between the transition-metal complex and a substrate included in the CD cavity. Furthermore, owing to the wide complexation capability of the bipyridine ligand, a large variety of photoactive metal complexes can be prepared.

To fully understand the mechanism of energy transfer, the physicochemical properties of the receptor must be known. We describe, herein, the synthesis of the new bipyridine-modified cyclodextrin **3**, the preparation of the bipyridinerhenium(I) and -ruthenium(II) complexes of **1** and **3** as well as their electrochemical and photophysical properties.

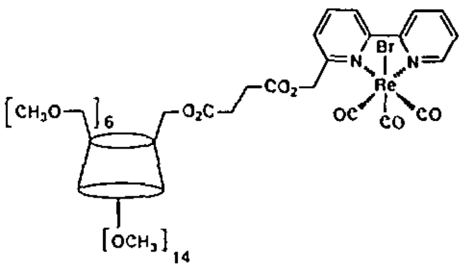
Results and Discussion. – *Syntheses.* Treatment of monohydroxylated permethylated β-CD **4** [3] with succinic anhydride (**5**) (CH_2Cl_2, room temperature, 48 h) gave intermedi-

Scheme

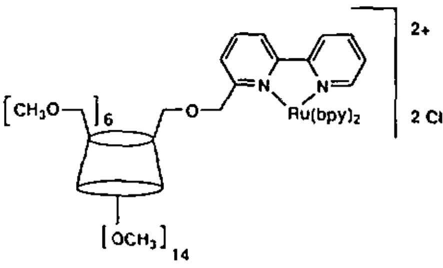


ate 6 in 94% yield (*Scheme*). Monoacid 6 was then reacted with 6-(bromomethyl)-2,2'-bipyridine (7) [4] (DMF, 80–90°, 14 h) in the presence of NaH. Purification by column chromatography (CC; silica gel, toluene/i-PrOH 4:1) yielded the target receptor 3 (70%).

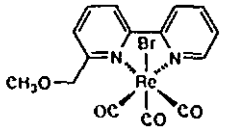
The rhenium complex of receptor 3, *i.e.*, compound 8, was prepared analogously to [Re(1)(CO)$_3$Br] (2) [2b] from 3 and [Re(CO)$_5$Br] (toluene, reflux, 3 h). After purification by CC (silica gel, toluene/i-PrOH 4:1), the neutral species [Re(3)(CO)$_3$Br] (8) was obtained in 65% yield. As for complex 2, the facial geometrical isomer of complex 8 was exclusively formed [7]. The ruthenium complex of receptor 1, [Ru(1)(bpy)$_2$]Cl$_2$ (9), was obtained in 71% yield by reacting [Ru(bpy)$_2$Cl$_2$] and 1 (H$_2$O/EtOH 1:1, 80°, 14 h), followed by purification by CC (*RP-18*, THF and then EtOH). For comparison, model compounds 10 and 11, in which the CD moiety was replaced by a Me group, were also prepared (see *Exper. Part*).



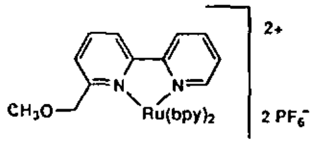
8



9



10



11

Photophysical Properties. The investigated compounds are thermally inert, and their absorption spectra show no change within 2–3 days. *Table 1* summarizes data concerning absorption spectra (293 K), emission spectra (77 and 293 K), emission lifetime (77 and 293 K), and emission quantum yields (293 K). Spectra of compounds 2 and 8–10 are

Table 1. *Spectroscopic and Photophysical Properties of* 1–3 *and* 8–10. Data at room temperature in MeCN solution and at 77 K in EtOH/MeOH 1:4 glass.

	Abs. λ_{max} [nm]	ε [l·mol^{-1}·cm^{-1}]	Em$_{r.t.}$ [nm]	$\tau_{r.t.}$^{a}) [ns]	$\Phi_{r.t.}$^{a})·10^3	Em$_{77K}$ [nm]	τ_{77K} [µs]	k_r^{b}) [µs^{-1}]	k_{nr}^{c}) [µs^{-1}]
1	284	15900	376		0.2	433^d)	1.1·10^6		
	237	11800							
3	283	16100	374		0.3	431^d)	9.8·10^5		
	237	11500							
2	366	2300	608	28.5	5.47	528	3.18	0.192	34.9
	323	9530							
	298	12300							
	244	17900							

Table 1 (cont.)

	Abs. λ_{max} [nm]	ε [$l \cdot mol^{-1} \cdot cm^{-1}$]	$Em_{r.t.}$ [nm]	$\tau_{r.t.}$[a]) [ns]	$\Phi_{r.t.}$[a]) $\cdot 10^3$	Em_{77K} [nm]	τ_{77K} [μs]	k_r[b]) [μs^{-1}]	k_{nr}[c]) [μs^{-1}]
8	369	2480	610	27.5	5.55	532	2.85	0.202	36.2
	322	8510							
	298	12300							
	244	16900							
9	445	9650	615	8.8	0.86	583	5.17	0.098	110
	288	54700							
	245	21600							
10	367	2610	614	24.0	4.31	530	2.55	0.180	41.5
	322	9170							
	297	11700							
	244	18400							
$[Ru(bpy)_3]^{2+}$	451	14600	611	890[e])	59[e])	585	4.86	0.066	1.06

[a]) In degassed solution. [b]) Calculated as $k_r = \Phi_{r.t.}/\tau_{r.t.}$. [c]) Calculated as $k_{nr} = 1/\tau_{r.t.} - k_r$. [d]) Phosphorescence emission, see text. [e]) See [8].

shown in *Fig. 1* (absorption) and *Fig. 2* (emission). The corrected excitation spectra (not shown) indicate that the intensity of the luminescence band is independent of the excitation wavelength. Data for $[Ru(bpy)_3]^{2+}$ are also added in *Table 1* for comparison.

Receptors **1** and **3** have absorption spectra very similar to that of the bpy ligand [2a]. The absorption spectra of complexes **2** and **8–10** are similar to those of the respective cyclodextrin-free analogues, *i.e.*, $[Re(bpy)(CO)_3Br]$ and $[Ru(bpy)_3]^{2+}$. The lowest-energy absorption band (*Table 1*) is assigned to the metal-to-ligand charge transfer (MLCT) transition: M → *π(bpy). The more intense bands in the UV region at higher energy are of intraligand (IL) origin, as can be seen by comparison with the absorption spectra of the respective uncomplexed ligands **1**, **3**, and bpy.

Receptors **1** and **3** luminescence at room temperature, analogously to the bpy ligand (λ_{em} 350 nm in 3-methylpentane) [9] and to other substituted bipyridine derivatives (λ_{em} 350–360 nm in cyclohexane) [10]. At 77 K, no fluorescence is observed for **1** and **3**: the data in *Table 1* refer to phosphorescence emission, which is very similar to the one observed for the bpy ligand (λ_{em} 433 nm, τ = 0.955 s) [11].

The rhenium and ruthenium complexes **2** and **8–10** luminesce both in fluid solution (293 K) and in glass (77 K). The Re^I complexes **2** and **8** feature emission characteristics which are very similar to those exhibited by the model compound **10**. In these three species, the luminescence properties are indicative of a charge-transfer nature of the emitting state. This conclusion can be drawn by usual considerations [7]: *i*) the position and the shape of the emission band are consistent with those previously reported for other polypyridinerhenium(I) complexes, *ii*) the emission band at 77 K is devoid of vibrational structure and blue-shifted with respect to the 293 K emission band, and *iii*) the emission lifetime is in the ns range at 293 K and in the μs range at 77 K.

As far as the blue shift of the emission band on lowering the temperature is concerned, one can note that this blue shift is much more pronounced for the Re complexes ($\Delta \approx 2400\ cm^{-1}$) than for the Ru one ($\Delta \approx 900\ cm^{-1}$). This appears to be a common phenomenon [7b] [12] and can be explained with the change in solute-solvent interactions which occur on going from the ground state to the excited one. For Re complexes

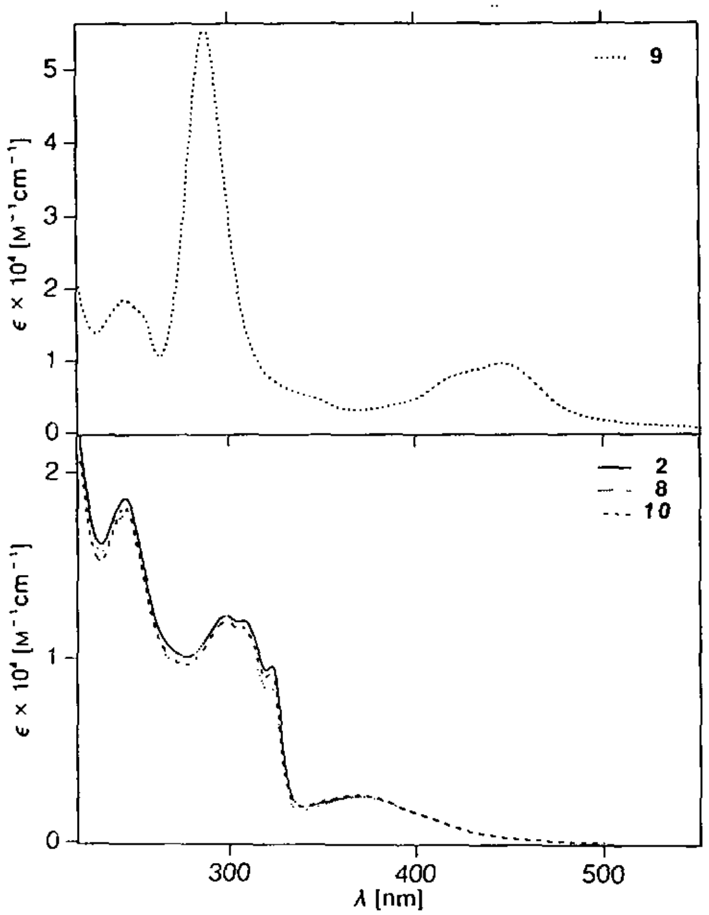


Fig. 1. Absorption spectra of compounds **2** *and* **8**–**10** *in acetonitrile solution at room temperature*

(uncharged species), it can be expected that MLCT excitation (Re→bpy) changes considerably the molecular dipole moment: the electron moved is formally localized on the only bpy ligand present. In a frozen matrix (77 K), the solvent molecules cannot undergo dipole reorientation, and the excited complex experiences the solvation environment of the ground-state complex in an energy-demanding situation. The same reasoning could, in principle, also be applied to the Ru-complex **9**, as it is commonly accepted that in $[Ru(bpy)_3]^{2+}$, the MLCT state can be described with the excited electron localized on a single bpy ligand [12] [13]. However, one has to take into account that the charge (2+) of the ruthenium complex dictates the solvation environment and masks the change in dipole moment that occurs on going from the ground state to the excited one.

From the Φ_{rt} and τ_{rt} values, it is possible to evaluate k_r and k_{nr}, *i.e.*, the radiative- and nonradiative-decay rate constants, respectively, of the excited state. One can see that the presence of the CD cup does not influence significantly the k_r and k_{nr} values of the Re complexes. This observation suggests that the bpy arm holding the metal is most

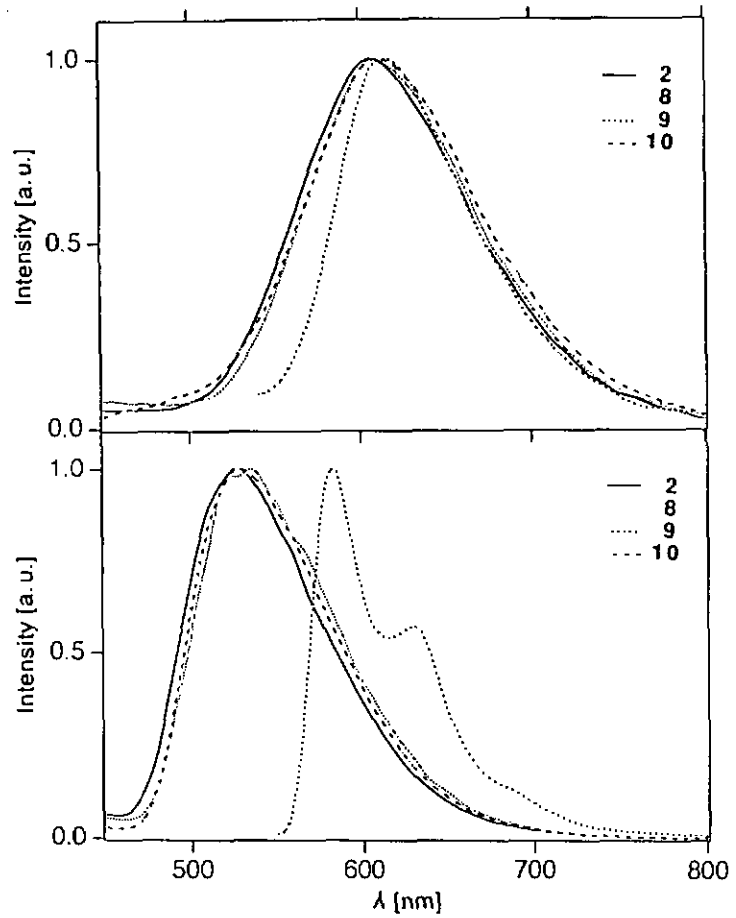


Fig. 2. *Emission spectra of compounds* **2** *and* **8**–**10** *in acetonitrile solution at room temperature* (top) *and in ethanol/methanol 1:4 glass at 77 K* (bottom)

likely swung away form the base of the CD cup, so that the medium surrounding the metal complex is essentially the same in the presence or in the absence of the CD unit.

For **9**, the emitting level can also be assigned to a MLCT state by analogy to the $[Ru(bpy)_3]^{2+}$ complex [7a] [12]. The only difference with $[Ru(bpy)_3]^{2+}$ deals with the emission quantum-yield and lifetime values at room temperature which are both much smaller for **9**. This finding is undoubtedly due to the fact that the bpy ligand is connected to the CD unit through the 6-position. This is sterically demanding for the Ru complex, so that the bite of the ligands around the metal is no longer optimal. In turn, this causes a weaker ligand-field splitting of the d-orbitals on the metal with a lowering of the ^{3}MC state, which facilitates a nonradiative conversion to the ground state. Indeed, it can be seen from *Table 1* that the k_{nr} value for **9** is two orders of magnitude greater than that of $[Ru(bpy)_3]^{2+}$. Increase of k_{nr} due to sterically hindering ligands is a well known phenomenon [14]. Interestingly, the same steric effect is not observed with the Re complexes **2** and **8**: molecular models clearly show that around the Re complex, there is enough room to fit the 6-position of the substituted bpy unit, as the remaining ligands (three CO and one Br) are much less bulky that the two bpy molecules which complete the coordination sphere of the Ru complex **9**.

Electrochemical Properties. The results are collected in *Table 2.* We will first consider the reduction potentials. Scanning cathodically from 0 to −2.1 V *vs.* a saturated-calomel electrode (SCE), the cyclovoltammogram showed one (for the rhenium) or three (for the ruthenium) steps as described in previous studies [16] [17]. The reversible waves observed for these complexes correspond to one or three successive one-electron ligand-based reduction processes. The redox potentials determined for the cyclodextrin-containing rhenium (**2** and **8**) and ruthenium (**9**) complexes are very close to the redox potentials of the parent cyclodextrin-free compounds **10** and **11**, respectively, and to those reported for $[\mathrm{Re(bpy)(CO)_3Cl}]$ [16] and for $[\mathrm{Ru(bpy)_3}]^{2+}$ [17], indicating that the interaction between the complex and the CD cup is very weak. This finding is in agreement with the results obtained from the photophysical investigations (see above).

Table 2. *Electrochemical Data* (Cyclic Voltammetry)

	$E_{1/2}$/V[a]) (ΔE/mV[b]))
2	+1.41 (60), −1.33 (70)
8	+1.41 (60), −1.29 (60)
10	+1.34 (80), −1.34 (70)
$[\mathrm{Re(bpy)(CO)_3Cl}]$	*+1.37 (irr)[c]), −1.34 (60)*
9	+1.29 (80), +1.03 (qr)[d]), −1.23 (60), −1.42 (70), −1.69 (70)
11	+1.28 (80), −1.22 (60), −1.41 (70), −1.68 (90)
$[\mathrm{Ru(bpy)_3}]^{2+}$	+1.27 (100), +1.03 (qr)[d]), −1.26 (70), −1.43 (80), −1.70 (80)

[a]) Measured in anhydrous MeCN in 0.1M TBAP (for the rhenium complexes **2**, **8**, **10**, and $[\mathrm{Re(bpy)(CO)_3Cl}]$), and in anhydrous dimethylformamide in 0.1M TBAH (for the ruthenium complexes **9**, **11**, and $[\mathrm{Ru(bpy)_3}]^{2+}$), under Ar, at room temperature (reference electrode SCE, internal reference $\mathrm{Fc/Fc^+}$ + 0.39 V), at 200 mV/s.

[b]) Separation between anodic and cathodic peak potentials ΔE_p ($\mathrm{Fc/Fc^+}$ 80 mV), under the same experimental conditions. No compensation was made for internal cell resistance.

[c]) *Anodic peak potential.*

[d]) Quasi-reversible oxidation of the $\mathrm{Cl^-}$ anion (see [15]).

The behavior of complexes **2**, **8**, and **9** on oxidation can be easily rationalized with the behavior of **10** and **11**. Scanning from 0 to +1.7 V (*vs.* SCE) shows an anodic and a cathodic peak for both the cyclodextrin-containing rhenium (**2** and **8**) and ruthenium (**9**) complexes, with a peak potential separation of 60 mV (**2** and **8**) and 80 mV (**9**). Coulometric oxidation (*vs.* SCE) of these three complexes is monoelectronic (n = 0.98 e at +1.51 V for **2** and **8**, and n = 0.95 e at 1.40 V for **9**), and no degradation of the oxidized complexes is observed after exhaustive coulometric back-reduction (*vs.* SCE) at +1.30 V for **2** and **8**, and at +1.17 V for **9**. The results of the rhenium(I) complexes are of interest since $[\mathrm{Re(bpy)(CO)_3Cl}]$ gave an irreversible oxidation peak (at the same potential) as previously described [7] [16]. This stabilization effect being also observed in compound **10**, it is likely to conclude that the $\mathrm{Re^{II}}$ oxidation state is more stable in complexes **2**, **8**, and **10** due to a weak interaction between the metallic centre and the O-atom present in the β-position of the linker. When the O-atom is anchored further apart from the metal (*e.g.* in the 5,5′-positions) this effect is less significative, as indeed observed [2c].

Conclusions. – The synthesis and characterization of new receptors obtained by substituting the primary face of a permethylated β-cyclodextrin with 2,2'-bipyridine-ligand derivatives are described. The Re^I and Ru^{II} transition-metal complexes were prepared in good yield. The electrochemical and photophysical properties of these systems were examined and found to be similar to those of the parent cyclodextrin-free materials. These results are of prime importance as they show that the combination of a cyclodextrin with a bipyridine framework does not alter neither the remarkable coordination properties of the bipyridine ligand nor the physicochemical characteristics of the transition-metal complexes. Such supramolecular structures are interesting candidates to investigate electron and/or photon transfer between an encapsulated guest molecule and an active metal centre.

R. D. acknowledges the Research Services Physics Department, Spectroscopy, *Ciba-Geigy Ltd.*, Basel, for the FAB-MS analyses.

Experimental Part

General. Column chromatography (CC): silica gel *60* (70–230 mesh, ASTM, *Merck*), if not stated otherwise. TLC: aluminium sheets precoated with 0.2 mm silica gel *60F₂₅₄* (*Merck*). Melting points: *Büchi-510* instrument (uncorrected). Optical rotations: *Perkin-Elmer-241* polarimeter. UV/VIS Spectra (λ_{max} in nm (ε in $l \cdot mol^{-1} \cdot cm^{-1}$)): in MeCN with a *Uvikon-810* spectrometer. IR Spectra (KBr pellet; in cm^{-1}): *Perkin-Elmer-FTIR-1720* spectrophotometer. ^1H- and ^{13}C-NMR Spectra: *Bruker-AMX-400* spectrometer at 400.13 (^1H) and 100.62 MHz (^{13}C); $SiMe_4$ as internal reference; signal assignment was made by comparison with the spectra of **1** [2b] and **2** [2b] (Glc = glucose unit). MS (in *m/z*): fast-atom-bombardment ionization (FAB). THGL = thioglycerol matrix; desorption chemical ionization (DCI).

Materials. The synthesis and characterization of receptor **1** [2a, b] and of its Re^I-complex **2** [2a, b] were reported. Monohydroxylated permethylated β-cyclodextrin **4** [3] and 6-(bromomethyl)-2,2'-bipyridine (**7**) [4] were prepared following the literature procedures. Solvents were dried prior to use: Et_2O ($MgSO_4$, NaH, $LiAlH_4$), CH_2Cl_2 ($CaCl_2$, P_2O_5), DMF (3 Å molecular sieves). $[Re(CO)_5Br]$ was obtained from *Strem Chemicals Inc.* and used as provided. Cyclodextrin derivatives were dried under vacuum at 40° in the presence of P_2O_5.

Photophysical Measurements. Spectrophotometric-grade solvents were used. Measurements were performed with freshly prepared solns. Absorption spectra: *Perkin-Elmer-λ-6* spectrophotometer. Emission spectra: *Perkin-Elmer-LS-50* spectrofluorometer equipped with a *Hamamatsu-R-928* photomultiplier. Emission lifetimes: *Edinburgh-199* single-photon-counting equipment. Emission quantum yields were measured at 20° with the optically diluted method [18] calibrating the spectrofluorometer with a standard lamp. $[Ru(bpy)_3]^{2+}$ in aerated aq. soln. was used as a quantum-yield standard assuming a value of 0.028 [19]. When necessary, samples were degassed by freeze-pump-thaw cycles.

Electrochemistry. Electrochemical measurements were carried out on a classical three-electrode potentiostatic setup composed of a potentiostat, a pilot scanner, a current-potential converter (*EDT-ECP 133*), and an *xy* recorder (*IFELEC IF 3802*). The working electrode was a platinum rotating disk electrode (*SOLEA Tacussel EDI* type, area 3.14 mm^2) used without rotation for cyclic voltammetry. The reference electrode (saturated-calomel electrode = SCE) was connected to the electrolysis cell by a bridge filled with the same solvent and supporting electrolyte as the solution. Measurements were carried out under an Ar flow in anh. MeCN +0.1M tetrabutylammonium perchlorate (TBAP) for the rhenium complexes and in anh. DMF +0.1M tetrabutylammonium hexafluorophosphate (TBAH). The ferrocene/ferrocenium (Fc/Fc^+) couple was used as internal reference.

6-Deoxy-icosa-O-methyl-β-cyclodextrin-6-yl Hydrogen Butanedioate (**6**). A mixture of monohydroxylated permethylated β-CD **4** (1.0 g, 0.7 mmol), succinic anhydride (**5**; 0.71 g, 7 mmol), Et_3N (5 drops), and pyrrolidinopyridine (21 mg, 0.14 mmol) in dry CH_2Cl_2 (10 ml) was stirred at r.t. for 48 h. The solvent was evaporated and the solid residue treated with toluene and filtered off to remove insoluble compounds. Evaporation of the solvent yielded **6** (1.0 g, 94%) which was used without further purification. R_f 0.14 (toluene/i-PrOH 1:1; H_2SO_4). IR: 1740, 1195, 1163, 1109, 1039. ^{1}H-NMR (COCl$_3$): 5.16–5.08 (*m*, 7 H, H–C(1)(Glc)); 4.55–4.52 (br. *dd*, H$_b$–C(6)(Glc^1)); 4.20–4.15 (br. *dd*, H$_a$–C(6)(Glc^1)); 3.97 (*m*, H–C(5)(Glc^1)); 3.80–3.6 (*m*, 18 H, H–C(5), H–C(6)(Glc)); 3.66 (*m*, 21 H, MeO–C(3)(Glc)); 3.66–3.50 (*m*, 14 H, H–C(4), H–C(5)(Glc)); 3.50 (*s*, 21 H, MeO–C(2)(Glc)); 3.38–3.41 (4*s*, 18 H, MeO–C(6)(Glc)); 3.19 (*m*, 7 H, H–C(2)(Glc)); 2.66 (*s*, C*H*$_2$COOH); 2.64 (*s*, CH$_2$COO). FAB-MS (negative mode, THGL): 1513 ([*M* – H]$^-$).

*2,2'-Bipyridine-6-methyl 6-Deoxy-icosa-*O*-methyl-β-cyclodextrin-6-yl Butanedioate* (3). To a soln. of 6 (0.200 g, 0.13 mmol) in dry DMF (8 ml), NaH (40 mg, 0.16 mmol) was added and the mixture stirred at r.t. for 1 h. Then 6-(bromomethyl)-2,2'-bipyridine (7; 40 mg, 0.16 mmol) was added and the mixture stirred at 100–110° for 14 h. The mixture was cooled to r.t. and hydrolized with H_2O. The aq. phase was extracted with Et_2O (3 × 10 ml), the combined org. phase dried ($MgSO_4$) and evaporated, and the residue purified by CC (toluene/i-PrOH 4:1): 156 mg (70%) of 3. White solid. M.p. 86°. $[\alpha]_D = +129$ ($c = 0.152$, $CHCl_3$). R_f 0.43 (toluene/i-PrOH 1:1; H_2SO_4 and UV). UV/VIS: 237 (11500), 283 (16100). IR: 1742, 1162, 1110, 1074, 1039. ^{1}H-NMR ((D$_6$)acetone): 8.68 (*m*, H–C(bpy)); 8.50 (*m*, H–C(bpy)); 8.43 (*d*, H–C(bpy)); 8.00 (*t*, H–C(bpy)); 7.93 (*m*, H–C(bpy)); 7.5 (*d*, H–C(bpy)); 7.42 (*m*, H–C(bpy)); 5.36 (*s*, CH$_2$–C(6)(bpy)); 5.12 (*m*, 7 H, H–C(1)(Glc)); 4.58 (*dd*, H$_b$–C(6)(Glc^1)); 4.37 (*dd*, H$_a$–C(6)(Glc^1)); 3.90–3.60 (*m*, 19 H, H–C(5), H–C(6)(Glc)); 3.61–3.57 (series of *s*, 21 H, MeO–C(3)(Glc)); 3.57–3.50 (*m*, 7 H, H–C(4)(Glc)); 3.49–3.47 (series of *s*, 21 H, MeO–C(2)(Glc)); 3.46–3.40 (*m*, 7 H, H–C(3)(Glc)); 3.31 (series of *s*, 18 H, MeO–C(6)(Glc)); 3.09–3.08 (*dd*, 7 H, H–C(2)(Glc)); 2.80 (*m*, CH$_2$CH$_2$). ^{13}C-NMR (CDCl$_3$): 172.5, 172.4 (C=O); 156.5, 155.8, 149.8, 138.3, 137.6, 124.5, 122.0, 121.9, 120.7 (bpy); 100.4–99.6 (5*s*, C(1)(Glc)); 82.7–82.2 (5*s*, C(2)(Glc)); 81.44–80.8 (5*s*, C(3), C(4)(Glc)); 72.1–71.9 (4*s*, C(6)(Glc)); 71.6, 70.0, 67.9 (C(5)(Glc^1)); 64.8, 64.4 (C(6)(Glc)); 62.2–62.1 (*Me*O–C(3)(Glc)); 59.7–59.1 (*Me*O–C(2), *Me*O–C(6)(Glc)); 29.7, 29.6 (CH$_2$).

Complexes 8 and 10. The Re-complexes 8 and 10 were obtained in 65% yield from 3 and 6-(methoxymethyl)-2,2'-bipyridine (prepared by treatment of 7 with MeONa/MeOH for 2 h at r.t. followed by CC purification (CH_2Cl_2/MeOH 98:2)), resp., and [Re(CO)$_5$Br] following the procedure used to synthesize 2 [2b].

*Data of (2,2'-Bipyridine-6-methyl-κ^2*N,N' *6-Deoxy-icosa-*O*-methyl-β-cyclodextrin-6-yl Butanedioate)bromotricarbonylrhenium(I)* 8: M.p. 103–106°. $[\alpha]_D = +100$ ($c = 0.140$, $CHCl_3$). R_f 0.26 (toluene/i-PrOH 1:1; H_2SO_4 and UV). UV/VIS: 244 (16900), 298 (12300), 322 (8510), 369 (2480). IR: 2024, 1920, 1903, 1742, 1607, 1164, 1110, 1037. ^{1}H-NMR ((D$_6$)acetone): 9.21 (*d*, H–C(bpy)); 8.73 (*d*, H–C(bpy)); 8.69 (*d*, H–C(bpy)); 8.34 (2*t*, 2 H–C(bpy)); 7.97 (*d*, H–C(bpy)); 7.82 (*m*, H–C(bpy)); 5.66 (*m*, CH$_2$–C(bpy)); 5.15–5.09 (*m*, 7 H, H–C(1)(Glc)); 4.45–4.39 (*m*, H$_b$–C(6)(Glc^1)); 3.97–3.79 (*m*, H–C(5), H$_b$–C(6)(Glc)); 3.61–3.59 (series of *s*, 21 H, MeO–C(3)(Glc)); 3.48–3.47 (series of *s*, 21 H, MeO–C(2)(Glc)); 3.58–3.35 (*m*, 20 H, H–C(3), H–C(4), H$_a$–C(6)(Glc)); 3.46–3.35 (*m*, 7 H, H–C(3)(Glc)); 3.33–3.28 (series of *s*, 18 H, MeO–C(6)(Glc)); 3.10 (*dd*, 7 H, H–C(2)(Glc)); 2.83 (*m*, CH$_2$CH$_2$). FAB-MS (positive mode, THGL): 2032 (M^+), 1953 ([*M* – Br]$^+$). Anal. calc. for $C_{80}H_{122}BrN_2O_{41}Re \cdot$ toluene (2126.11): C 49.15, H 6.16, N 1.32; found: C 49.31, H 6.55, N 1.30.

*Data of Bromotricarbonyl[6-(methoxymethyl)-2,2'-bibpyridine-κ^2*N,N'*]rhenium(I)* (10): R_f 0.47 (toluene/i-PrOH 1:1). UV/VIS: 244 (18400), 297 (11700), 322 (9170), 367 (2610). IR: 2020, 1921, 1905. ^{1}H-NMR ((D$_6$)acetone): 9.30 (*d*, H–C(3')); 8.83 (*d*, H–C(6')); 8.74 (*d*, H–C(3)); 8.44 (*AB*, 2 H, H–C(4), H–C(5')); 8.09 (*d*, H–C(5)); 7.92 (*t*, H–C(4')); 5.02 (*s*, MeOC*H*$_2$); 3.67 (*s*, MeO). ^{1}H-NMR (CDCl$_3$): 9.15 (*d*, H–C(3')); 8.21 (*d*, H–C(6')); 8.03–8.12 (*m*, H–C(3), H–C(4), H–C(5')); 7.94 (*d*, H–C(5)); 7.54 (*m*, H–C(4)); 5.01, 4.98, 4.93, 4.89 (*AB*, MeOC*H*$_2$); 3.67 (*s*, MeO). DCI-MS (NH$_3$): 568 ([*M* + NH$_3$]$^+$), 550 (M^+), 522 ([*M* – CO]$^+$), 471 ([*M* – Br]$^+$). Anal. calc. for $C_{15}H_{12}BrN_2O_4Re$ (550.38): C 32.73, H 2.20, N 5.09; found: C 31.88, H 2.26, N 4.81.

*Bis(2,2'-bipyridine-κ^2*N,N'*){6-[(icosa-*O*-methyl-β-cyclodextrin-6-*O*-yl)methyl]-2,2'-bipyridine-κ^2*N,N'*}ruthenium(II) Dichloride* 9. An equimolar amount of 1 and [Ru(bpy)$_2$Cl$_2$] in H_2O/EtOH 1:1 was stirred at 80° for 14 h. The soln. was evaporated and the solid residue first washed with Et_2O and then purified by CC (*RP-18*, THF, then EtOH): 9 (71%). UV/VIS: 245 (21600), 288 (54700), 445 (9650). IR: 1636, 1606, 1194, 1163, 1142, 1108, 1088, 1071, 1038. ^{1}H-NMR ((D$_6$)acetone): 8.87–8.74, 8.35–8.17, 8.10–8.09, 7.99–7.76, 7.62–7.56, 7.52–7.49 (series of *m*, 23 H, bpy); 5.28, 5.21 (2*s*, C*H*$_2$–bpy); 5.16–5.09 (*m*, 7 H, H–C(1)(Glc)); 4.86–4.72 (*dd*, H$_b$–C(6)(Glc^2)); 4.45–4.32 (*dd*, 1 H, H$_a$–C(6)(Glc)); 3.89–3.66 (*m*, 13 H, H–C(5), H$_b$–C(6)(Glc)); 3.59 (*m*, 21 H, MeO–C(3)(Glc)); 3.61–3.36 (*m*, 20 H, H–C(3), H–C(4), H$_a$–C(6)(Glc)); 3.48 (*m*, 21 H, MeO–C(2)(Glc)); 3.33–3.25 (*m*, 18 H, MeO–C(6)(Glc)); 3.18 (*m*, 7 H, H–C(2)(Glc)). FAB (positive mode, THGL): 1998, 1996 ([*M* – Cl]$^+$).

*Bis(2,2'-bipyridine-κ^2*N,N'*)[6-(methoxymethyl)-2,2'-bipyridine-κ^2*N,N'*]ruthenium(II) Hexafluorophosphate* 11. A soln. of 6-(methoxymethyl)-2,2'-bipyridine (25 mg, 0.12 mmol) and [Ru(bpy)$_2$Cl$_2$] (62 mg, 0.12 mmol) in H_2O/EtOH 1:1 (2 ml) was heated at 80° for 3 h. The mixture was evaporated and the solid residue dissolved in H_2O and then treated with a sat. aq. soln. of NH_4PF_6 (5 ml). The precipitate was filtered, washed with cold H_2O, and dried: 70 mg (63%) of **11**. ^{1}H-NMR ((D_6)acetone): 9.90–8.91, 8.42–8.29, 8.06–7.89, 7.74–7.62 (series of *m*, 23 H, bpy); 4.38 (*d*, 1 H, C*H*$_2$–bpy); 3.69 (*d*, 1 H, C*H*$_2$–bpy); 2.93 (*s*, MeO, in CD_2Cl_2). Anal. calc. for $C_{32}H_{28}F_{12}N_6OP_2Ru$ (903.59): C 42.54, H 3.12, N 9.30; found: C 42.24, H 3.31, N 9.05.

REFERENCES

[1] 'Frontiers in Supramolecular Organic Chemistry and Photochemistry', Eds. H.-J. Schneider and H. Dürr, VCH Verlagsgesellschaft, Weinheim, 1991; V. Balzani, F. Scandola, 'Supramolecular Photochemistry', Horwood, Chichester, 1991.

[2] a) N. Brügger, R. Deschenaux, T. Ruch, R. Ziessel, *Tetrahedron Lett.* **1992**, *33*, 3871; b) R. Deschenaux, M. M. Harding, T. Ruch, *J. Chem. Soc., Perkin Trans. 2* **1993**, 1251; c) R. Deschenaux, A. Greppi, T. Ruch, H.-P. Kriemler, F. Raschdorf, R. Ziessel, *Tetrahedron Lett.* **1994**, *35*, 2165.

[3] M. Tanaka, Y. Kawaguchi, T. Niinae, T. Shono, *J. Chromatogr.* **1984**, *314*, 193.

[4] R. Ziessel, J.-M. Lehn, *Helv. Chim. Acta* **1990**, *73*, 1149.

[5] R. Breslow, B. Zhang, *J. Am. Chem. Soc.* **1994**, *116*, 7893; B. Zhang, R. Breslow, *ibid.* **1993**, *115*, 9353; R. Breslow, B. Zhang, *ibid.* **1992**, *114*, 5882; F. Venema, C. M. Baselier, E. van Dienst, B. H. M. Ruël, M. C. Feiters, J. F. J. Engbersen, D. N. Reinhoudt, R. J. M. Nolte, *Tetrahedron Lett.* **1994**, *35*, 1773.

[6] Z. Pikramenou, D. G. Nocera, *Inorg. Chem.* **1992**, *31*, 532.

[7] a) K. Kalyanasundaram, 'Photochemistry of Polpyridine and Porphyrin Complexes', Academic Press, London, 1992; b) D. J. Stufkens, *Comments Inorg. Chem.* **1992**, *13*, 359.

[8] K. Nakamaru, *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1639.

[9] E. Castellucci, L. Angeloni, G. Marconi, E. Venuti, I. Baraldi, *J. Phys. Chem.* **1990**, *94*, 1740.

[10] E. Castellucci, L. Angeloni, A. Juris, G. Marconi, R. Ziessel, *J. Photochem. Photobiol., A* **1992**, *67*, 311.

[11] M. K. De Armond, J. E. Hillis, *J. Chem. Phys.* **1971**, *54*, 2247.

[12] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. von Zelewski, *Coord. Chem. Rev.* **1988**, *84*, 85.

[13] W. K. Smothers, M. S. Wrighton, *J. Am. Chem. Soc.* **1983**, *105*, 1067.

[14] K. Araki, M. Fuse, N. Kishii, S. Shiraishi, *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1220, and ref. cit. therein.

[15] G. Cauquis, A. Deronzier, B. Sillion, B. Damin, J. Garapon, *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *117*, 139.

[16] J. C. Luong, L. Nadjo, M. S. Wrighton, *J. Am. Chem. Soc.* **1978**, *100*, 5790.

[17] N. E. Tokel-Takvoryan ,R. E. Hemingway, A. J. Bard, *J. Am. Chem. Soc.* **1973**, *95*, 6582.

[18] J. N. Demas, G. A. Crosby, *J. Phys. Chem.* **1971**, *75*, 991.

[19] K. Nakamaru, *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2697.