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

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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]

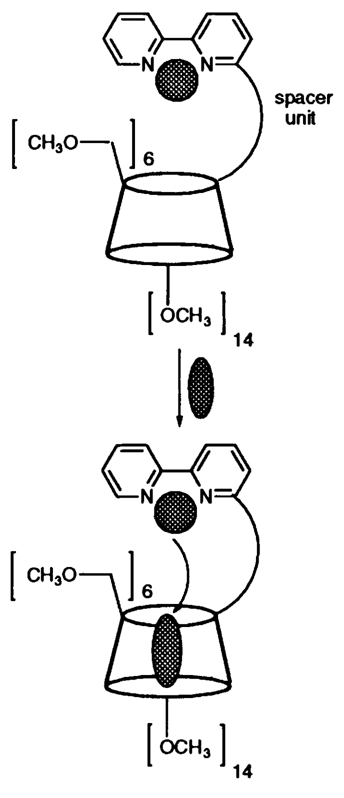
Our approach to the development of new supramolecular photoactive systems has been to combine the recognition properties of cyclodextrins with a photoactive 2,2'-bipyridyl unit. Cyclodextrins have played an important role in the field of supramolecular chemistry,[5,6] notably in the study of enzymatic 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

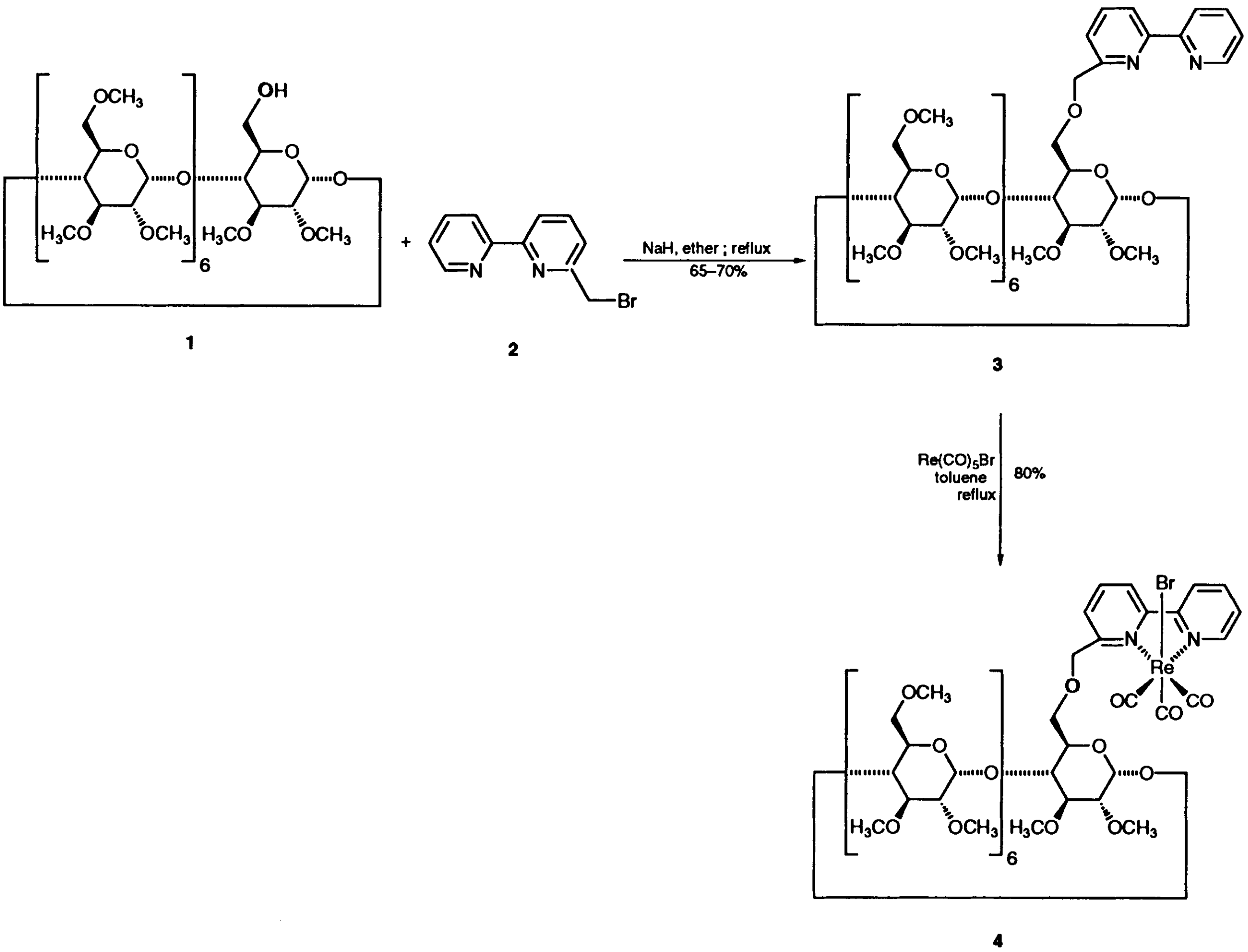


Scheme 1

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

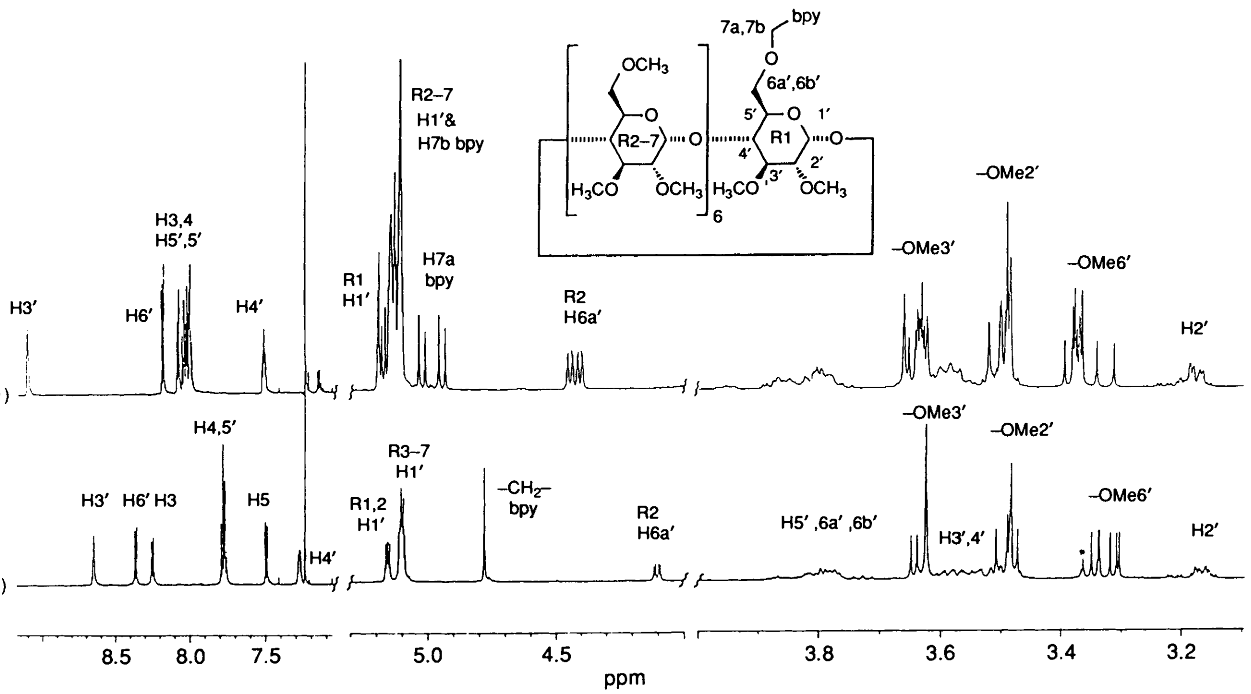


Fig. 1 600 MHz ^1H NMR spectra of (*a*) ligand **3** and (*b*) rhenium complex **4** in $CDCl_3$ at 303 K. Expansions are not plotted to scale. The starred peak is a minor impurity. The aromatic peaks at 7.1 ppm in trace (*b*) are due to residual toluene in the cyclodextrin cavity.

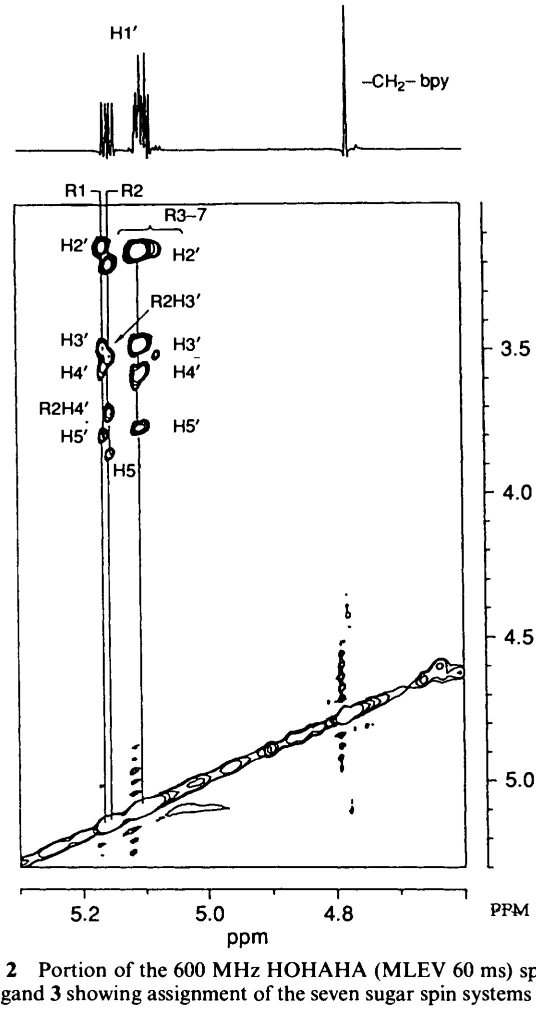


Fig. 2 Portion of the 600 MHz HOHAHA (MLEV 60 ms) spectrum of ligand **3** showing assignment of the seven sugar spin systems

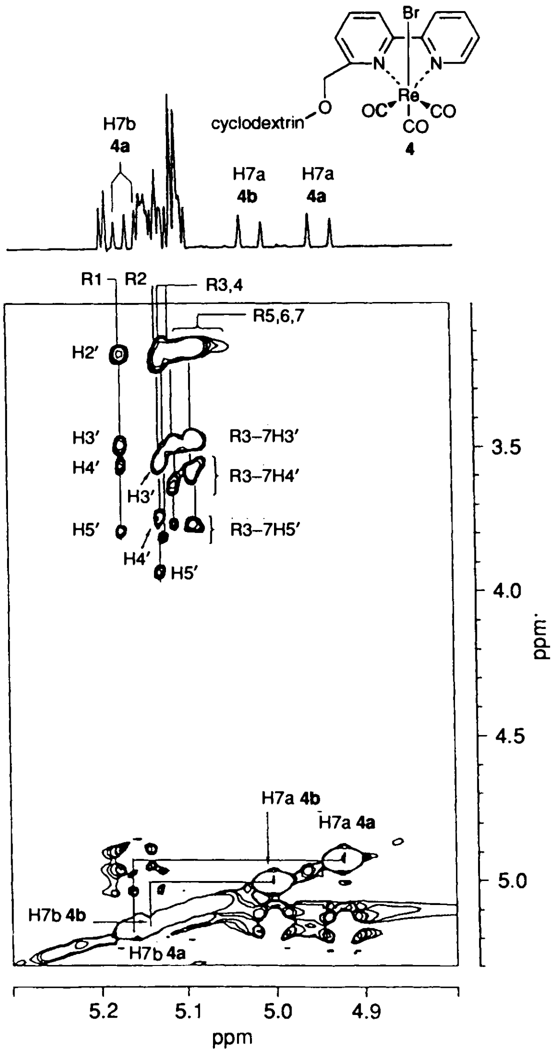


Fig. 3 Portion of the 600 MHz HOHAHA (MLEV 58 ms) spectrum of complex **4** showing assignment of the seven sugar spin systems

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

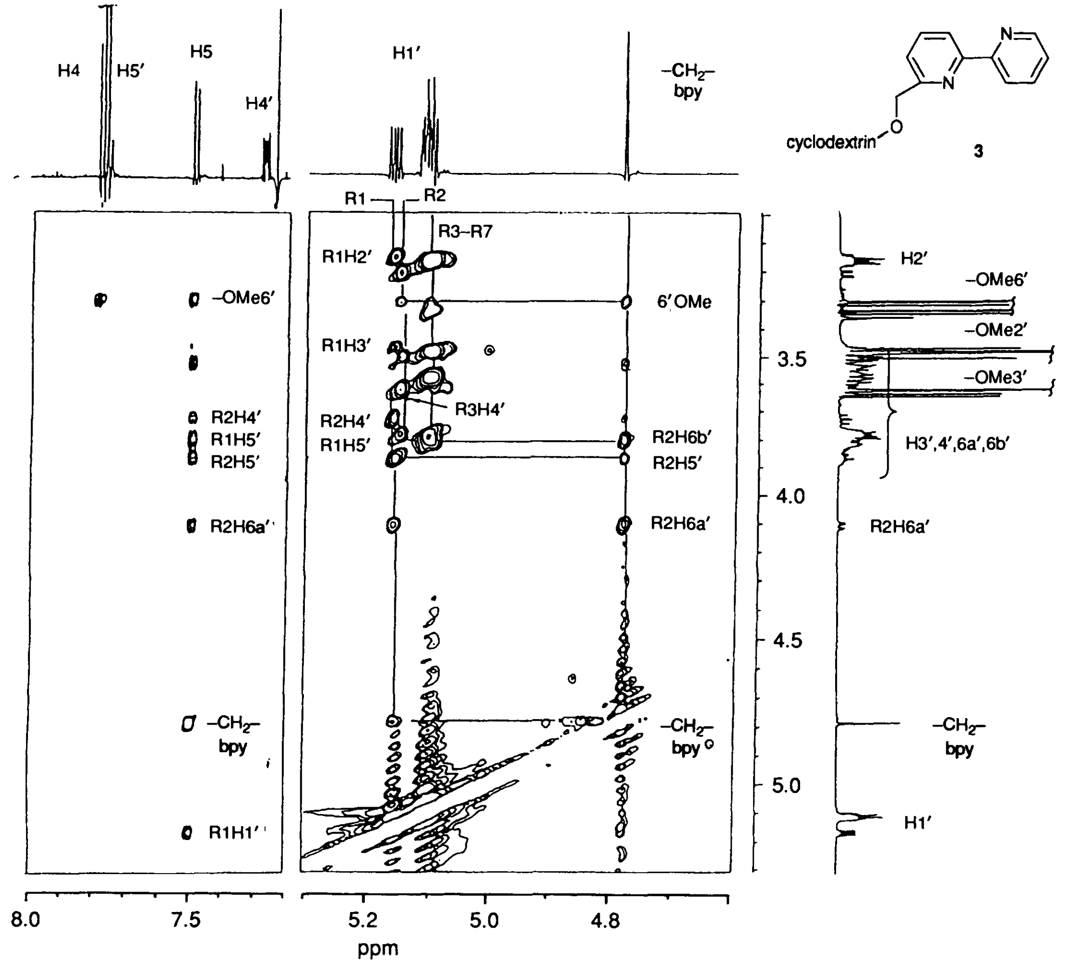


Fig. 4 Portion of the 600 MHz ROESY spectrum of ligand 3 recorded with a mixing time of 250 ms with a 3.5 kHz spin-locking field

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 ^{1}H 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

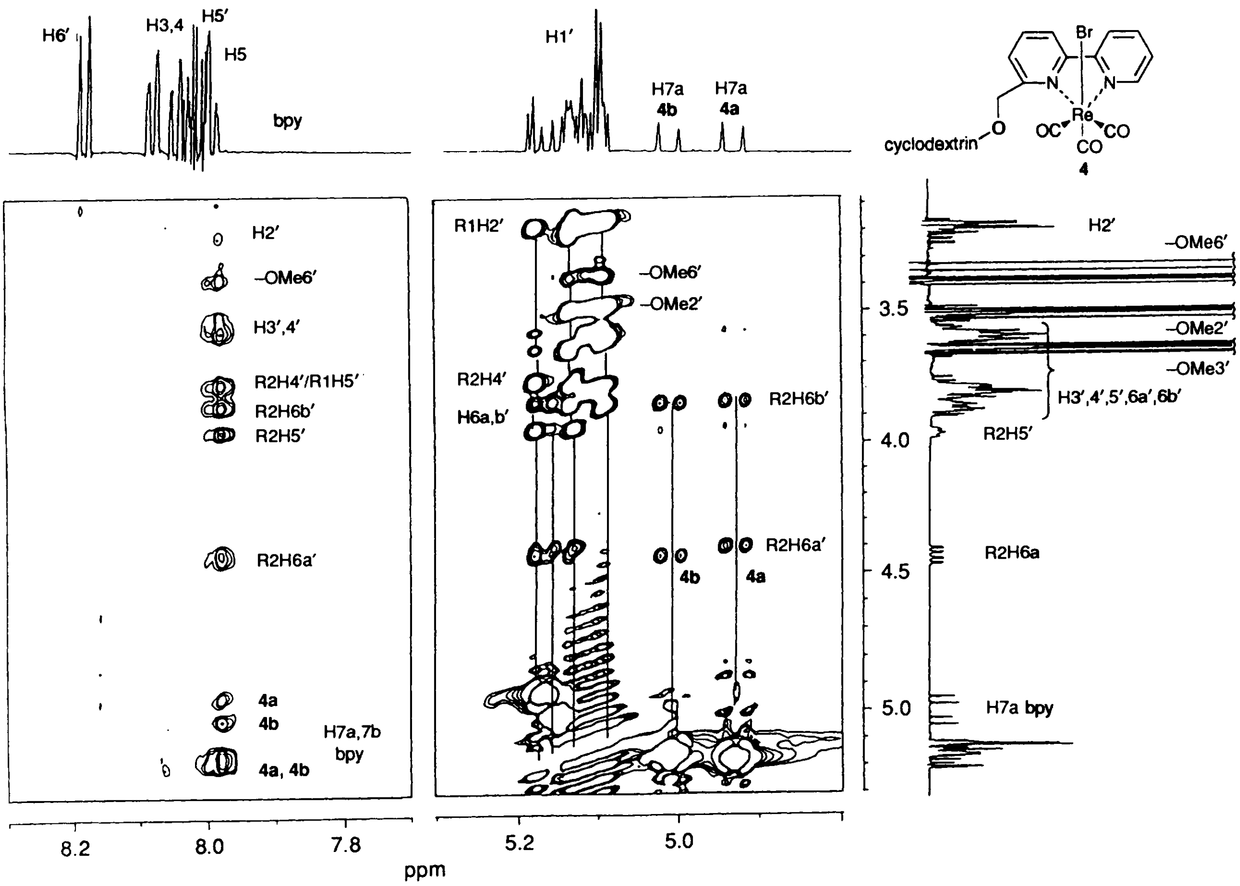


Fig. 5 Portion of the 600 MHz ROESY spectrum of complex **4** recorded with a mixing time of 250 ms and a 3.7 kHz spin-locking field

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 ^1H 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

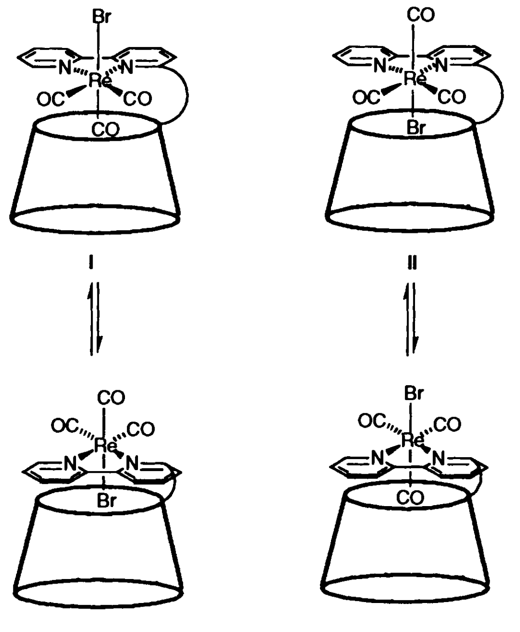
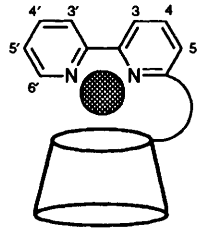
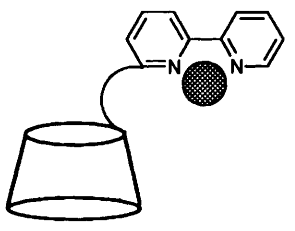


Fig. 6 Schematic representations of diastereomers **I**/**II** and **III**/**IV**



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**),[16d] 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. ^1H 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 subjcted 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 mono-hydroxypermethylated 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%).

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