Metal Assembly of Cyclodextrin Recognition Sites

Johanna M. Haider[a][+] **and Zoe Pikramenou***[a][+]

Keywords: Cyclodextrins / Supramolecular chemistry / Receptors / Coordination chemistry / Molecular devices

Cyclodextrin recognition sites are assembled in macromolecular structures by using metal assembly principles. Methylated cyclodextrins are functionalised with bidentate bipyridine and tridentate terpyridine units to give versatile receptor ligands, β-CD–mbpy and β-CD–ttp, respectively, for metal complexation. Tris-cyclodextrin complexes are prepared by reaction of the β-CD–mbpy receptor with iron(II) and by reaction of β-CD–ttp with europium(III). The latter leads to a luminescent complex with three recognition sites around the luminescent metal core. Bis-cyclodextrin complexes are prepared by addition of iron(II) to β-CD–ttp. The characterisation of the compounds and their luminescent properties are reported.

Introduction

Receptors for small molecule recognition are popular building blocks in supramolecular design.[1] Artificial receptors have been developed from either multiple covalent bond synthesis or self-assembly principles for applications that range from biomedical research to the sensor field.[2] The design of optical molecular sensors based on recognition events has attracted much interest for the technological development of molecular devices.[3] Photoactive metal centres have been appended to calixarene[4] or cyclodextrin[5] receptor molecules for sensing ion or molecule recognition events. We are interested in employing cyclodextrins as rigid receptors that bind photoactive guests leading to the spatial organisation of energy or electron donor-acceptor arrays based on transition metals. Cyclodextrins are particularly attractive natural host molecules, water soluble, with a hydrophobic well-defined cavity.[6] Formation of transition metal arrays for photoinduced processes have been previously developed by using covalent bond bridges[7] or hydrogen-bond interfaces[8] to bring the metal centres together in one array. The importance of the cyclodextrin approach is that light-induced processes can be observed between two photoactive units held together by *non-covalent* interactions in aqueous solutions.[9]

The design of cyclodextrin-based organised arrays requires functionalisation of the cyclodextrin glucose units which can be achieved by modifying and using synthetic routes established in carbohydrate chemistry.[10] Metal centres have been attached to both discrete sugar units[11] and functionalised cyclodextrins,[12] primarily for developing models for enzymatic catalysis or sensors. In order to increase the number of guest interaction sites in cyclodextrin recognition systems the design of molecules with more than one cyclodextrin binding sites is attractive. Previous methods to link more than one cyclodextrin have employed covalent bond multi-step synthesis using bridges such as bipyridines,[13] porphyrins,[14] or organoselenium moieties.[15] Such bridged bis-cyclodextrin compounds have shown interesting catalytic properties for ditopic recognition of substrates.[13a] In this paper the assembly of cyclodextrins using coordination principles to yield complexes with multiple cyclodextrin recognition sites around a central metal core is reported. Our approach, using metal centres to assemble receptors, provides metal-directed spatial control of the receptors so that directional intramolecular energy or electron transfer processes between the central metal core and the guest species included in the receptor sites can take place when the metal core is photoactive. Metal centres have been previously employed to bring hydrogen-bonded recognition sites together.[16]

We wish to report the assembly of two or three functionalised cyclodextrins around a metal centre depending on the coordination preference of the metal core; octahedral metal centres and nine-coordinate lanthanide ions are used to spatially organise cyclodextrins functionalised with bidentate (β-CD−mbpy) and tridentate units (β-CD−ttp). Metal coordination properties allow the assembly of three cyclodextrins, which has not previously been investigated via covalent bond synthesis.

Results and Discussion

Synthesis

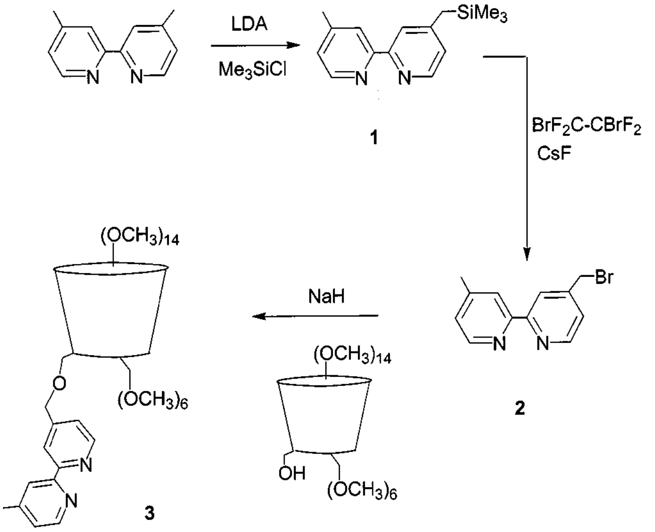
To incorporate a bidentate site on the cyclodextrin rim a new monosubstituted cyclodextrin 2,2′-bipyridine derivative was synthesised by attaching a monohydroxy permethylated cyclodextrin to the 4-position of a 2,2′-bipyridine to give β-CD−mbpy. Bipyridine functionalised cyclodextrins have been previously prepared either by William-

---

[a] Current address: School of Chemistry, University of Birmingham,
Edgbaston, Birmingham B15 2TT, UK
Fax: (internat.) +44-121/414-4403
E-mail: Z.Pikramenou@bham.ac.uk
[+] Previous address: Department of Chemistry, University of Edinburgh,
Kings Buildings, Edinburgh, EH9 3JJ, UK

1434−1948/01/0101−0189 $ 17.50+.50/0

son ether synthesis at the 5,5′- or 6-positions of the bipyridine,[12c] thioether formation at 5,5′-disubstituted bipyridines[13a] or via "phosphinimine" type reactions of 5-methylamino bipyridines.[17] We employed the Williamson ether synthesis as a convenient route to attach the 4-position of a 4,4′-dimethyl 2,2′-bipyridine onto the cyclodextrin. We chose the 4-position both to avoid steric crowding around the metal (a problem with the 6-substituents) and to ensure good electronic coupling for communication of a redox active guest with the metal in photoinduced intramolecular processes. The functionalised cyclodextrin was prepared from the monohydroxy permethylated β-cyclodextrin[18] and 4-bromomethyl, 4′methyl-2,2′-bipyridine. The latter was prepared by modification of a procedure of monosilylation of the dimethyl 2,2′-bipyridine[19] followed by bromination with BrF_2CCF_2Br (Scheme 1).

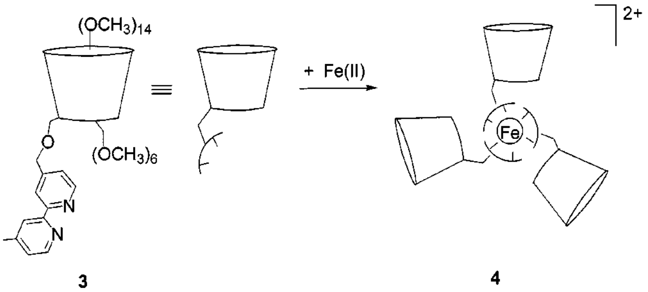


Scheme 1

The 4-substituted bipyridine was shown to be more reactive towards the ether formation under similar conditions than the analogous 6- and 5- substituted bipyridines. The β-CD−mbpy is an attractive ligand due to its versatile solubility in both halogenated solvents and water which is important not only in the handling and purification of the compound but also in the metal complex formation.

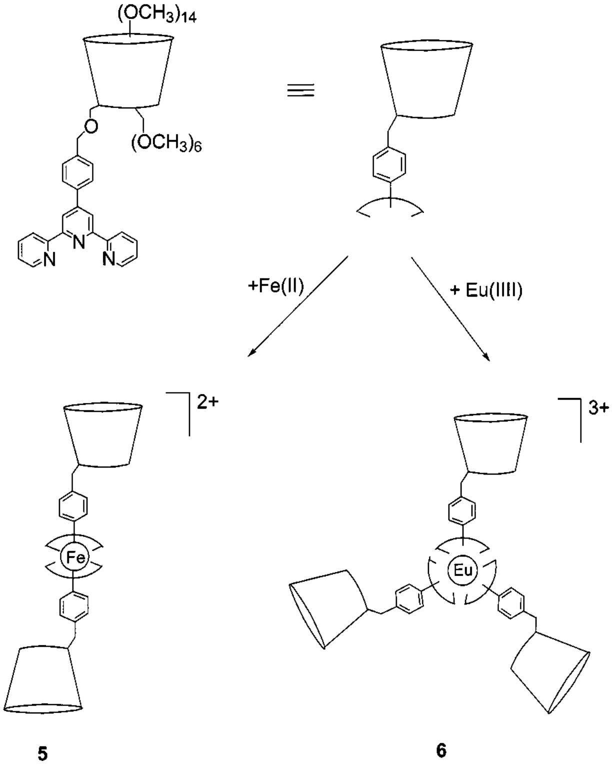
Simple addition of Fe^{II} to a methanolic solution of β-CD−mbpy results in a deep red colour which is attributed to a complex with three cyclodextrins around the iron centre, $[Fe(\beta\text{-CD}-mbpy)_3]^{2+}$ (Scheme 2). Solubility of the complex is enhanced by the presence of the methylated cyclodextrins and chromatographic methods have been more effective for isolation of the complex rather than recrystallization used in the analogous $[Fe(mbpy)_3][PF_6]_2$ complex.

Three cyclodextrins can potentially be assembled around a metal by using a tridentate binding site (such as a tolylterpyridine unit) attached on the cyclodextrin (β-CD−ttp) and a nine coordinate lanthanide, such as europium, (Scheme 3). We have previously reported such a functionalised cyclodextrin β-CD−ttp.[9] Europium(III) ions do not possess strong ligand field preference, adopting high co-



Scheme 2

ordination numbers in solution and they are known to form a tris-complex with 2,2′:6,′2′′ terpyridine. Upon addition of three equivalents of β-CD−ttp in an ethanolic solution of europium chloride the tris-cyclodextrin complex, $[Eu(\beta\text{-CD}-ttp)_3]^{3+}$, is formed.[20]



Scheme 3

When a metal with octahedral geometry is employed with the tridentate functionalised cyclodextrin two cyclodextrins are assembled around the metal; when Fe^{II} is reacted with β-CD−ttp a strong purple coloured complex of $[Fe(\beta\text{-CD}-ttp)_2]^{2+}$ is formed.

Characterisation

NMR, UV/Vis spectroscopy together with mass spectrometric analysis were employed to confirm the identification of the compounds. Electrospray mass spectrometry has proven to be an important technique in the identification of self-assembled polymetallic systems.[21] In our case it has been successfully applied in cyclodextrin systems. In Table 1 the electrospray mass spectrometry data of the complexes

Table 1. Electrospray mass spectrometry data of metallo-cyclodextrins

Metal Complex	*m*/*z*, corresponding fragment
$[Fe(\beta\text{-CD}-mbpy)_3][PF_6]_2$	2422, $\{M-2\ [PF_6]\}^{2+}$ 1717, $\{M-2\ [PF_6] - 1\ CD_f\}^{2+}$[a] 1010, $\{M-2\ [PF_6] - 2\ CD_f\}^{2+}$
$[Eu(\beta\text{-CD}-ttp)_3][PF_6]_3$	1788, $\{M-3\ [PF_6]\}^{3+}$ 1347, $\{M-3\ [PF_6] + Na\}^{4+}$ 1765, $\{M-2\ [PF_6]\}^{2+}$ 1184, $\{M-2\ [PF_6] + Na\}^{3+}$
$[Fe(\beta\text{-CD}-ttp)_2][PF_6]_2$	894, $\{M - 2\ [PF_6] + 2\ Na\}^{4+}$

[a] CD_f = [6-monohydroxy permethylated β-cyclodextrin−H].

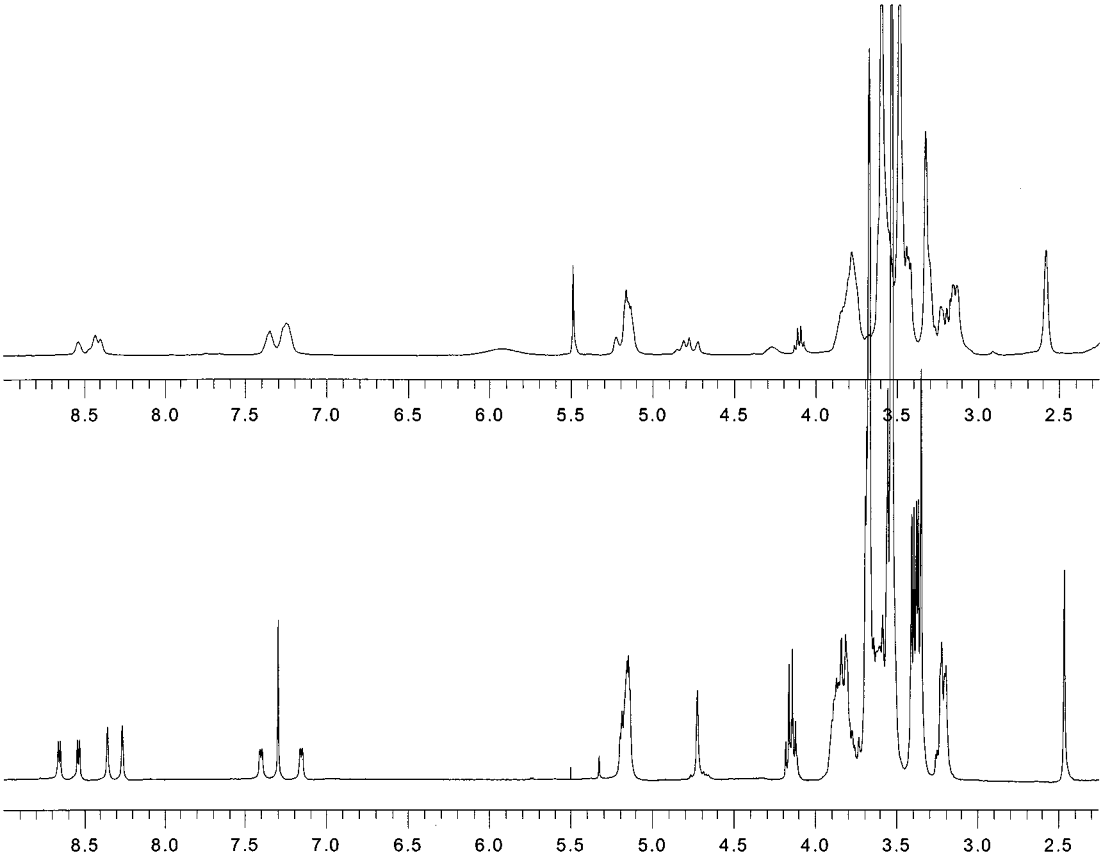


Figure 1. The 360 MHz ^1H NMR spectra of β-CD−mbpy (bottom) in $CDCl_3$ and $[Fe(\beta\text{-CD}-mbpy)_3][PF_6]_2$ (top) in CD_3CN

are presented. The data confirm the formulation of the bis- and tris-cyclodextrin complexes.

In the ^1H NMR spectrum of the β-CD−mbpy ligand, shown in Figure 1, the characteristic anomeric protons of the glucose units are non-equivalent due to the mono-substitution; five of them overlap (multiplet at δ = 5.4) while two separate doublets appear at δ = 5.12 and 5.10 (*J* = 4 Hz).

Substitution of the bipyridine unit is confirmed by the shift of the methylene group from δ = 4.43 in the bromide derivative to δ = 4.66 in β-CD−mbpy. The splitting of the signal as an AB pattern due to the diastereotopic protons upon attachment to the chiral cyclodextrin also confirms this. The rest of the aromatic protons appear as six signals. The H_{Glu}-6,6′ pair of the substituted glucose of the cyclodextrin also becomes diastereotopic, one proton is shifted to δ = 4.06 and shows a cross peak in the 2D TOCSY with the other one at δ = 3.71. Distinct from the cyclodextrin proton manifold are the six primary methoxy groups at δ = 3.34, 3.32, 3.31, 3.30, 3.28, 3.27 and the H_{Glu}-2 glucose protons at δ = 3.18−3.12. Full assignment of the cyclodextrin protons also agrees with previously detailed studies of permethylated cyclodextrins.[22]

The $[Fe(\beta\text{-CD}-mbpy)_3][PF_6]_2$ complex is diamagnetic which indicates that the cyclodextrin substitution does not induce any steric hindrance, which is known to be responsible for spin crossover phenomena in iron complexes.[23] In the ^1H NMR spectrum of the complex (Figure 1), the complexation with the β-CD−mbpy is confirmed by the shift, of the H-6,6′ protons of the bipyridine, to lower frequencies. The aromatic proton peaks are broader than are usually observed which may be due to the presence of the two *fac* and *mer* isomers[24] or to a very small impurity of iron(III)[25] which is difficult to exclude due to the high solubility of the complex. The complex UV/Vis absorption spectrum shows the characteristic MLCT absorption at 530 nm which agrees with the model compound which is a tris-bipyridine iron(II) complex without the cyclodextrin receptor.

The purple bis-cyclodextrin iron complex $[Fe(\beta\text{-CD}-ttp)_2][PF_6]_2$ was characterised by 600 MHz ^1H NMR

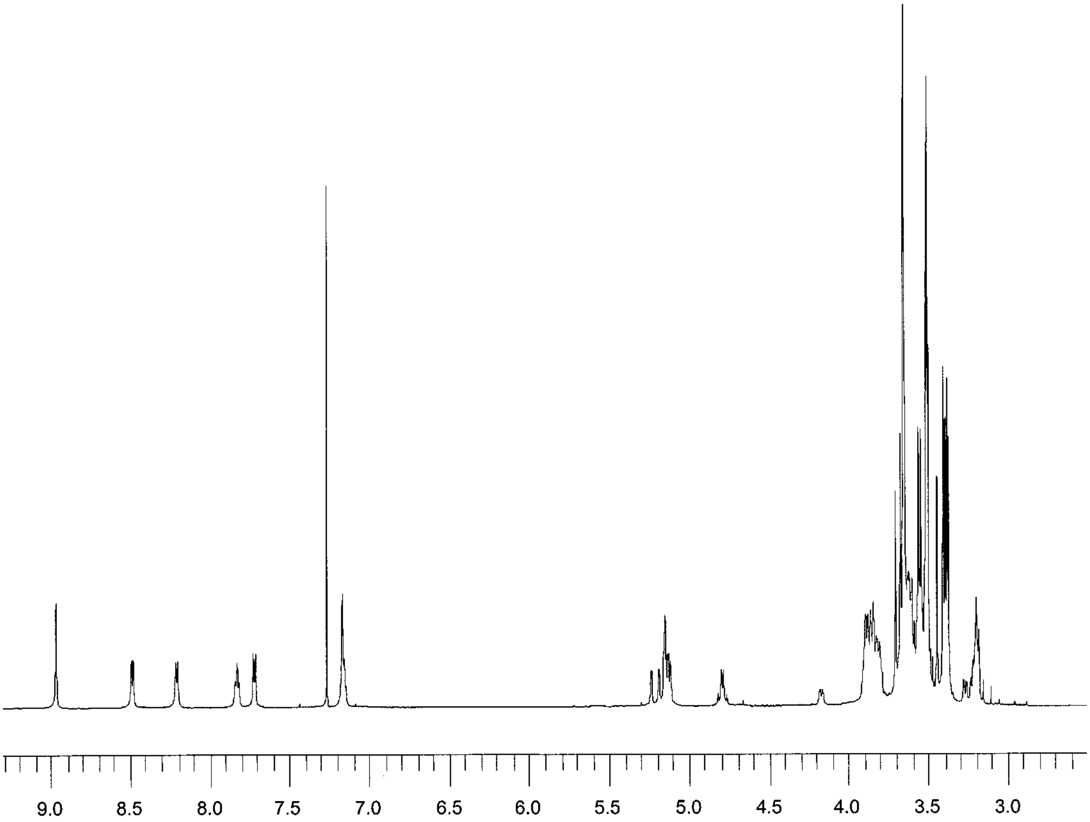


Figure 2. The 600 MHz ^{1}H NMR spectrum of $[Fe(\beta\text{-}CD{-}ttp)_2][PF_6]_2$ in $CDCl_3$

spectroscopy (Figure 2). The H-6 protons of the terpyridine unit show a 1.55 ppm shift at lower frequencies with respect of the chemical shift in the ligand spectrum attributed to metal coordination.[26] The methylene protons on the benzyl ring are diastereotopic appearing as a doublet of doublets at $\delta = 4.75$ where the methylene diastereotopic protons of the substituted glucose ring appear at $\delta = 4.15$ and 3.80, the latter is obscured by the rest of the cyclodextrin protons ($\delta = 3.15{-}3.90$). This was assigned from the ^{1}H-^{1}H COSY contour plot. Acetonitrile solutions of the iron complex display a typical MLCT absorption band at 569 nm. No luminescence was detected upon excitation to the MLCT band for either the bipyridine or the terpyridine cyclodextrin complexes. This is not surprising since both iron(II) bipyridine and terpyridine complexes bear low lying metal-centred states that provide radiationless pathways for luminescence quenching.[27]

Luminescence Spectroscopy

The europium complex was characterised by electrospray mass spectrometry and NMR spectroscopy. In the ^{1}H NMR spectrum of the perchlorate salt of the complex, the observed chemical shifts of the terpyridine protons are consistent with previously reported studies of europium terpyridine complexes.[28] The complex is stable in most organic solvents but dissociates in the presence of water as expected for lanthanide terpyridine complexes.[28] The europium ion was selected as a luminescent probe with well explored photophysical properties. Acetonitrile solutions of the complex exhibit strong red luminescence, characteristic of the europium ion upon excitation at the ligand band (Figure 3). The excitation spectrum upon monitoring the 616 nm europium emission shows a band centred at 320 nm corresponding to the ligand π-π* transition which is in agreement with the absorption spectrum of the complex. The tolyl-terpyri-

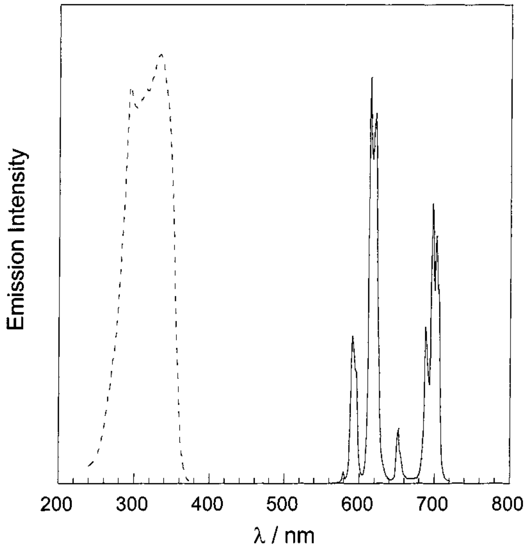


Figure 3. Emission ($\lambda_{exc} = 330$ nm, solid line) and excitation ($\lambda_{em} = 616$ nm, dashed curve) spectra of $[Eu(\beta\text{-}CD{-}ttp)_3]^{3+}$ in acetonitrile corrected for PMT and lamp response, respectively

dine units act as light-harvesting centres for collecting the energy and transferring it to the lanthanide centre.

Conclusions

Metal assembly of polypyridine functionalised cyclodextrins leads to the formation of complexes with two or three cyclodextrin receptor sites around the metal core. The employment of methylated cyclodextrins leads to versatile soluble ligands for metal complex formation. The metallo-receptors developed in this study can take part in photoactive processes occurring in more than one direction in space through the metal core and the guests. We are currently studying the ruthenium(II) analogues of these receptors because of their attractive photophysical properties for inducing energy or electron transfer processes.

Experimental Section

General Procedures and Materials: All starting materials were purchased from Aldrich unless otherwise indicated. β-Cyclodextrin (Acros) was recrystallized from water and dried under vacuum at 80 °C for 8 hours. $RuCl_3 \cdot xH_2O$ was provided from Johnson & Matthey as a loan. Solvents used in synthetic procedures were analytical grade apart from the ones used in size exclusion chromatography and spectroscopic studies where HPLC grade solvents were used. THF was freshly distilled from sodium under nitrogen. All ligand synthetic procedures were carried out under a nitrogen atmosphere. Thin layer chromatography (TLC) analyses were performed on either Merck silica gel 60 glass plates or Merck alumina gel 60 glass plates as indicated. Biobeads SX3 was used as a stationary phase for size exclusion chromatography. Cyclodextrins were detected by an oxidising solution consisting of anisaldehyde/acetic acid/methanol/sulfuric acid in a 2:45:430:22 ratio followed by heating at around 100 °C.

NMR spectra were recorded on Bruker DRX 360 and Varian Inova 600 spectrometers. The protons on the glucose units were indicated as H_{Glu} in the assignments. Fast atom bombardment mass spectrometry was performed on a Kratos MS-50 spectrometer and electrospray on a Quattro instrument at the EPSRC Mass Spectrometry Service Centre in Swansea.

Absorption spectra were recorded on a Perkin−Elmer Lambda 16 UV/Vis spectrometer. Emission and excitation spectra were recorded on a Photon Technology International QM-1 steady state spectrometer described elsewhere.[29]

4′-Methyl-{4-(trimethylsilyl)methyl}-2,2′-bipyridine (1): To a solution of LDA (Fluka, 1.05 g, 9.78 mmol) in freshly distilled THF (20 mL) a solution of 4,4′-dimethyl-2,2′-bipyridine (1.50 g, 8.15 mmol) in the same solvent (50 mL) was added dropwise at −78 °C. The dark brown mixture was kept stirring at that temperature for an hour. Trimethylsilyl chloride (1.06 g, 9.78 mmol) was added under vigorous stirring and after 20 s the reaction was quenched with absolute EtOH (10 mL), where upon the solution turned green. The cold reaction mixture was poured into an aqueous saturated $NaHCO_3$ solution and was left to reach room temperature. The mixture was extracted by dichloromethane (3 × 40 mL) and the combined organic phases were dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvent TLC analysis of the mixture showed the presence of mono- and bis- silyl-substituted products (silica gel deactivated with NH_3, $R_f = 0.68$ and 0.86, respectively). Pure product was obtained after column chromatography (silica gel deactivated by addition of 10% triethylamine to the eluent system: EtOAc/cyclohexane 3:7) (yield: 1.5 g, 72%).

^1H NMR (360 MHz, $CDCl_3$): $\delta = 8.51$ (d, $J = 4.98$ Hz, 1 H, H-6), 8.45 (d, $J = 5.26$ Hz, 1 H, H-6′), 8.21 (s, 1 H, H-3′), 8.04 (s,1 H, H-3), 7.09 (dd, $J = 4.97$ Hz, $J = 1$ Hz, 1 H, H-5′), 6.93 (dd, $J = 5.01$ Hz, $J = 1$ Hz, 1 H, H-5), 2.41 (s, 3 H, 4′-methyl), 2.19 (s, 2 H, 4-methylene), 0.02 (s, 9 H, CH_3-Si).

4-Bromomethyl-4′-methyl-2,2′-bipyridine (2): Caesium fluoride (0.475 g, 3.125 mmol) and $BrF_2C-CBrF_2$ (0.813 g, 3.125 mmol) were added to a solution of **(1)** (0.4 g, 1.56 mmol) in dry DMF (5 mL). The reaction was followed by TLC (deactivated silica, EtOAc/hexane 1:4) (R_f(product) = 0.43). The reaction reached completion after 4−5 h and the mixture was then poured into water (10 mL) and extracted by EtOAc (3 × 50 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and the solvent evaporated. The brown oil was purified by column chromatography (deactivated silica ethyl acetate/cyclohexane 1:4) to give a slightly yellow oil (yield: 0.3 g, 73%).

^1H NMR (360 MHz, $CDCl_3$): $\delta = 8.60$ (d, $J = 4.99$ Hz, 1 H, H-6), 8.49 (d, $J = 4.96$ Hz, 1 H, H-6′), 8.37 (s, 1 H, H-3), 8.19 (s, 1 H, H-3′), 7.29 (dd, $J = 4.95$ Hz, $J = 1$ Hz, 1 H, H-5), 7.11 (dd, $J = 5.03$ Hz, $J = 1$ Hz, 1 H, H-5′), 4.43 (s, 2 H, 4- methylene), 2.39 (s, 3 H, 4′-methyl).

6-Mono[4-methyl(4′-methyl-2,2′-bipyridyl)]-permethylated β-cyclodextrin (β-CD−mbpy) (3): 6-Monohydroxy permethylated β-cyclodextrin (0.8 g, 0.565 mmol) was dissolved in freshly distilled THF (15 mL). NaH (100 mg, 60% suspension in oil, 2.6 mmol) was added and a white precipitate was formed. A solution of (**2**) (208 mg, 0.789 mmol) in THF (5 mL) was added. The mixture was left to reflux for 12 h, quenched with brine (5 mL) and the solvent was evaporated. The residue was treated with brine (10 mL) and extracted with dichloromethane (3 × 40 mL). The combined organic phases were dried over Na_2SO_4, filtered and the solvent was evaporated. The compound was purified through column chromatography (Biobeads SX3, acetone). Yield 0.3 g, 33%.

^1H NMR (600 MHz, $CDCl_3$): $\delta = 8.58$ (d, $J = 5$ Hz, 1 H, H-6), 8.46 (d, $J = 5$ Hz, 1 H, H-6′), 8.28 (s, 1 H, H-3), 8.19 (s, 1 H, H-3′), 7.33 (dd, $J = 5$ Hz, $J = 1$ Hz, 1 H, H-5), 7.09 (dd, $J = 5$ Hz, $J = 1$ Hz, 1 H, H-5′), 5.12 −5.07 (H_{Glu}-1, 7 H), 4.66 (dd, $J = 13.5$ Hz, $J = 19.0$ Hz, 2 H, CH_2 on C-4-bpy), 4.06 (dd, $J = 6.8$ Hz, $J = 3.85$ Hz, 1 H, H_{Glu}-6), 3.83−3.12 (m, H_{Glu}-2,3,4,5,6, $-OCH_{3Glu}$), 2.39 (s, 3 H, $-CH_3$ on C-4′).

$[Fe(\beta\text{-}CD-mbpy)_3][PF_6]_2$ (4): A solution of $[NH_4]_2Fe(SO_4)_2 \cdot 6H_2O$ (12 mg, 0.03 mmol) in water (1 mL) was added to a solution of (**3**) (150 mg, 0.09 mmol) in MeOH (2 mL). The mixture immediately turned dark purple and was left stirring for 30 min. The mixture was treated with a methanolic solution of NH_4PF_6, following extraction with dichloromethane (3 × 20 mL) and column chromatography (Biobeads SX3, acetone) the complex was obtained in 45% yield (70 mg).

^1H NMR (360 MHz, $CDCl_3$): $\delta = 8.55$, 8.42 (2 H, H-3,-3′), 7.35, 7.25 (4 H, H-5,-5′, H-6,-6′), 5.25 −5.10 (7 H, H_{Glu}-1), 4.80 (2 H, CH_2 on C-4-bpy), 4.25 (1 H, H_{Glu}-6), 3.9−3.1 (m, H_{Glu}-2,3,4,5,6, $-OCH_{3Glu}$), 2.6 (3 H, $-CH_3$ on C-4′). − UV/Vis (MeOH) (ε/$M^{-1}cm^{-1}$): $\lambda = 520$ nm (9770), 351 (9700), 297 (83400), 289 (88100). − ESI MS (CH_3CN): $m/z = 2422\{M - 2[PF_6]\}^{2+}$.

[Fe(β-CD−ttp)$_2$][PF$_6$]$_2$ (5): To a solution of β-CD−ttp (50 mg, 0.029 mmol) in methanol (1 mL) a solution of (NH$_4$)$_2$Fe(SO$_4$)$_2$ in the same solvent (5.6 mg, 0.014 mmol) was added. The complex formed immediately giving a strong purple coloured solution. The mixture was heated for a few minutes to 50 °C, cooled to room temperature and a solution of ammonium hexafluorophosphate (4.8 mg, 0.028 mmol) in methanol (1 mL) was added. There was no precipitation due to the high solubility of the methylated cyclodextrin and the complex was isolated following extraction by dichloromethane (74 mg, yield: 73%).

^{1}H NMR (600 MHz, CDCl$_3$): δ = 8.98 (s, 4 H, H-3′), 8.48 (d, J = 7.9 Hz, 4 H, H-3), 8.19 (d, J = 7.7 Hz, 4 H, H$_o$), 7.80 (dd, J = 6.4, 6.8 Hz, 4 H, H-4), 7.71 (d, J = 7.7 Hz, 4 H, H$_m$), 7.19- 7.15 (m, 4 H, H-5,6), 5.24−5.10 (m, 7 H, H$_{\mathrm{Glu}}$-1), 4.78 (dd, J = 7.6 Hz, 4 H, −CH$_2$-benzyl), 4.18 (dd, J = 10.7 Hz, J = 2.9 Hz, 2 H, H$_{\mathrm{Glu}}$-6), 4.0−3.0 (m, H$_{\mathrm{Glu}}$-2,3,4,5,6 −OCH$_{3\mathrm{Glu}}$). − FAB-MS (nitrobenzyl alcohol matrix): m/z = 3674 {M − [PF$_6$]}$^+$, 3530 {M − 2[PF$_6$]}$^+$. − UV/Vis (MeOH) (ε/ M^{-1}cm^{-1}): λ = 568 nm (13800), 313 (37500) 286 (46000).

[Eu(β-CD−ttp)$_3$][PF$_6$]$_3$ (6): 6-Monotolylterpyridine permethylated β-cyclodextrin, β-CD−ttp (100 mg, 57 mmol) was dissolved in absolute EtOH (2 mL) and a hot solution of Eu(NO$_3$)$_3$·5H$_2$O (8.56 mg, 19 mmol) in the same solvent (1 mL) was added. The mixture was refluxed for 3 hours, the volume was reduced and NH$_4$PF$_6$ in EtOH (1 mL) was added. As no precipitate was formed, the mixture was extracted in dichloromethane (2 mL) following evaporation of the solvent. It was filtered through a Millipore column to remove the excess of NH$_4$PF$_6$, to yield 85 mg of the complex after solvent evaporation (yield 79%).

ESI-MS (MeOH/EtOH): m/z = 1788 {M − 3[PF$_6$]}$^{3+}$. − ^{1}H NMR (300 MHz, CD$_3$CN): δ = 16.14 (H-6), 7.18 (H$_{o/m}$), 6.95 (H-4), 6.6 (H$_{o/m}$), 6.3 (H-5), 5.1 (H$_{\mathrm{Glu}}$-1), 4.6 (−CH$_2$-benzyl), 4.0−3.0 (rest of cyclodextrin protons), 2.5−2.4 (H3, 3′). − UV/Vis (CH$_2$Cl$_2$): λ = 280, 330 nm.

Acknowledgments

We are grateful to EPSRC for financial support to J. M. H. (GR/L91788), Drs. N. Spencer, C. M. Hewage and M. Chavarot for obtaining the NMR spectra and Dr. A. M. W. Cargill Thompson for helpful discussions. We also wish to thank Johnson & Matthey for a loan of ruthenium trichloride.

---

[1] F. Vögtle, *Comprehensive Supramolecular Chemistry*; Volume 2, (Exec. Eds. J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle), Elsevier Science, Oxford, **1996**.

[2] [2a] S. H. Gellman, Special Issue on Molecular Recognition, *Chem. Rev.* **1997**, *97*, issue 5. − [2b] D. Gutsche, *Calixarenes, Monographs in Supramolecular Chemistry* (Series Editor: J. F. Stoddart), The Royal Society of Chemistry, Cambridge, **1991**. − [2c] F. Diedrich, *Cyclophanes*, *Monographs in Supramolecular Chemistry*, (Series Editor: J. F. Stoddart), The Royal Society of Chemistry, Cambridge, **1991**.

[3] [3a] A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher, T. E. Rice, *Chem. Rev.* **1997**, *97*, 1515. − [3b] W. K. Hartmann, M. Montellaro, Z. Pikramenou, D. G. Nocera, in *Chemosensors of Ion and Molecule Recognition* (Ed. J.-P. Desvergne and A. W. Czarnik), NATO ASI Series C, 492, Kluwer Academic Publishers, **1997**, 159. − [3c] T. Mizuno, T. Fukumatsu, M. Takeuchi, S Shinkai, *J. Chem. Soc., Perkin Trans. 1* **2000**, 407.

[4] P. D. Beer, Z. Chen, A. J. Goulden, A. Grieve, D. Hesek, F. Szemes, T. Wear, *J. Chem. Soc., Chem. Commun.* **1994**, 1269.

[5] [5a] M. A. Mortellaro, D. G. Nocera, *J. Am. Chem. Soc.* **1996**, *118*, 7414. − [5b] Z. Pikramenou, J.-a Yu, R. B. Lessard, A. Ponce, P. A. Wong, D. G. Nocera, *Coord. Chem. Rev.* **1994,** *132,* 181.

[6] M. V. Rekharsky, Y. Inoue, *Chem. Rev.* **1998**, *98*, 1875.

[7] [7a] E. C. Constable, P. Harverson, C. E. Housecroft, *J. Chem. Soc., Dalton Trans.* **1999**, 3693. − [7b] L. De Cola, P. Belser, *Coord. Chem. Rev.* **1998,** *177*, 301. − [7c] R. Ziessel, M. Hissler, A. El-Ghayoury, A. Harriman, *Coord. Chem. Rev.* **1998,** *180*, 1251. − [7d] F. Barigelletti, L. Flamigni, J.-P. Collin, J.-P. Sauvage, *Chem. Commun.* **1997**, 333.

[8] [8a] T. H. Ghaddar, E. W. Castner, S. S. Isied, *J. Am. Chem. Soc*. **2000**, *122,* 1233. − [8b] M. D. Ward, C. M. White, F. Barigelletti, N. Armaroli, G. Calogero, L. Flamigni, *Coord. Chem. Rev.* **1998,** *171*, 481. − [8c] D. J. Hurley, Y. Tor, *J. Am. Chem. Soc*. **1998**, *120,* 2194. − [8d] E. C. Constable, R. A. Fallahpour, *J. Chem. Soc., Dalton Trans.* **1996**, 2389.

[9] [9a] S. Weidner, Z. Pikramenou, *Chem. Commun.* **1998**, 1473. − [9b] J. M. Haider, M. Chavarot, L. De Cola, Z. Pikramenou, to be submitted.

[10] A. R. Khan, P. Forgo, K. J. Stine, V. T. D'Souza, *Chem. Rev.* **1998**, *98*, 1977**.**

[11] E. C. Constable, S. Mundwiler, *Polyhedron* **1999**, *18***,** 2433.

[12] [12a] E. Rizzarelli, G. Vecchio, *Coord. Chem. Rev.* **1999**, *188*, 343. − [12b] R. Breslow, S. D. Dong, *Chem. Rev.* **1998**, *98*, 1997. − [12c] R. Deschenaux, M. M. Harding, T. Ruch, *J. Chem. Soc., Perkin Trans 2* **1993**, 1251.

[13] [13a] B. Zhang, R. Breslow, *J. Am. Chem. Soc.* **1997**, *119*, 1676. − [13b] R. Deschenaux, A. Greppi, T. Ruch, H.-P. Kriemler, F. Raschdorf, R. Ziessel, *Tetrahedron Lett*. **1994**, *35*, 2165.

[14] [14a] W.-H. Chen, J.-M. Yan, Y. Tagashira, M. Yamaguchi, K. Fujita, *Tetrahedron Lett.* **1999**, *40*, 891. − [14b] R. Breslow, X. Zhang, R. Xu, M. Maletic, R. Merger, *J. Am. Chem. Soc*. **1996**, *118*, 11678. − [14c] Y. Kuroda, M. Ito, T. Sera, H. Ogoshi, *J. Am. Chem. Soc*. **1993**, *115*, 7003.

[15] Y. Liu, C. C. You, Y. Chen, T. Wada, Y. Inoue, *J. Org. Chem.* **1999**, *64*, 7781.

[16] B. Linton, A. D. Hamilton, *Chem. Rev.* **1997**, *97*, 1669.

[17] F. Charbonier, T. Humbert, A. Marsura, *Tetrahedron Lett.* **1999**, *40*, 4047.

[18] Z. Chen, J. S. Bradshaw, M. L. Lee, *Tetrahedron Lett*. **1992**, *33*, 1177.

[19] [19a] S. A. Savage, A. P. Smith, C. L. Fraser, *J. Org. Chem.* **1998**, *63*, 10048. − [19b] U. S. Schubert, C. Eschenbaumer, G. Hochwimmer, *Tetrahedron Lett*. **1998**, *39,* 8643.

[20] [20a] Lanthanide terpyridine complexes have been previously prepared: D. A. Durham, G. H. Frost, F. A. Hart, *J. Inorg. Nucl. Chem.* **1969**, *31*, 833. − [20b] G. H. Frost, F. A. Hart, C. Heath, M. B. Hursthouse, *J. Chem. Soc., Chem. Commun.* **1969**, 1421. − [20c] M. G. Drew, P. B. Iveson, M. J. Hudson, J. O. Liljenzin, L. Spjuth, P. Y. Cordier, A. Enarsson, C. Hill, C. Madic, *J. Chem. Soc., Dalton Trans.* **2000**, 821.

[21] [21a] F. M. Romero, R. Ziessel, A. Dupont-Gervais, A. Van Dorsselaer, *Chem. Commun.* **1996**, 551. − [21b] G. Hopfgartner, F. Vilbois, C. Piguet, *Rapid Communications in Mass Spectrometry* **1999**, *13*, 302.

[22] [22a] J. R. Johnson, N. Shankland, I. H. Sadler, *Tetrahedron* **1985**, *41*, 3147. − [22b] C. M. Spencer, J. F. Stoddart, R. Zarzycki, *J. Chem. Soc., Perkin Trans.2* **1987**,1323.

[23] D. Onggo, J. M. Hook, A. D. Rae, H. A. Goodwin, *Inorg. Chim. Acta* **1990**, *173*, 19.

[24] T. J. Rutherford, D. A. Reitsma, F. R. Keene, *J. Chem. Soc., Dalton Trans.* **1994**, 3659.

[25] E. Sinn, *Inorg. Chim. Acta* **1969**, *3*, 11.

[26] E. C. Constable, A. M. W. Cargill Thompson, D. A. Tocher, M. A. Daniels, *New J. Chem.* **1992**, *16*, 855.

[27] E. Amouyal, M. Mouallem-Bahout, G. Calzaferri, *J. Phys. Chem.* **1991** *95*, 7641.

[28] [28a] R. D. Chapman, R. T. Loda, J. P. Riehl, R. W. Schwartz, *Inorg. Chem.* **1984**, *23,* 1652. − [28b] C. Mallet, R. P. Thummel, C. Hery, *Inorg. Chim. Acta* **1993**, *210,* 223.

[29] N. W. Alcock, P. R. Barker, J. M. Haider, M. J. Hannon, C. L. Painting, Z. Pikramenou, E. A. Plummer, K. Rissanen, P. Saarenketo, *J. Chem. Soc., Dalton Trans.* **2000,** 1447.

Received March 30, 2000
[I00123]