New Scaffolds for Supramolecular Chemistry: Upper-Rim Fully Tethered 5-Methyleneureido-5′-methyl-2,2′-bipyridyl Cyclodextrins

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Abstract: Seven upper-rim fully tethered cyclodextrins (URFT-CDs) have been synthesised in a good average coupling yield using the one-step "phosphine imide" approach and their metal complexation behaviour with lanthanides and transition metals was explored. We observed that the A-TE-E light conversion process (antennae effect) occurs in the URFT-CD lanthanide complexes. A molecular redox switch based on the corresponding iron complexes is also reported. A reversible intramolecular translocation of the Fe^{II} and Fe^{III} ions, between two distinct binding cavities has been monitored spectroscopically and achieved by chemical triggering. Finally, a negative allosteric control of ion recognition through the formation of a CD pseudocryptand is discussed.

Keywords: allosterism · 2,2′-bipyridine · cyclodextrins · molecular devices · molecular switches

Introduction

Cyclodextrins (CDs), a class of oligosaccharides with six, seven or eight D-glucose units linked by α-1,4-glycosidic bonds, are well known to accommodate various guest molecules into their hydrophobic cavity in aqueous solution.[1] The natural cyclodextrins are themselves of great interest as molecular hosts, but much of their utility in supramolecular chemistry is derived from their structural modification. From another point of view, natural CDs may be viewed as molecular scaffolds on which functional groups and other substituents of increasing sophistication can be assembled with controlled geometry. Thus, metallocyclodextrins, rotaxanes, catenanes or surface monolayers of these modified cyclodextrins are now accessible.[2] Here, metallocyclodextrins are considered as coordination compounds or metal complexes in which the modified CD acts as a ligand platform. The majority of metallocyclodextrins are formed from functionalised CDs which incorporate one or more metal ion coordinating groups of varying degrees of complexity.[3] In the following discussion, some of these CDs are presented along with their more interesting properties.

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Results and Discussion

The new devices introduced here are based on upper-rim bisheterocyclic (2,2′-bipyridyl) fully functionalised CDs, which accommodate one single or two different metal ions in their internal "hard" binding cavity and external "soft" binding cavity, leading to lanthanide and transition metal complexes (Figure 1).

The present work describes these molecular devices with respect to the nature of the complexing ions involved.

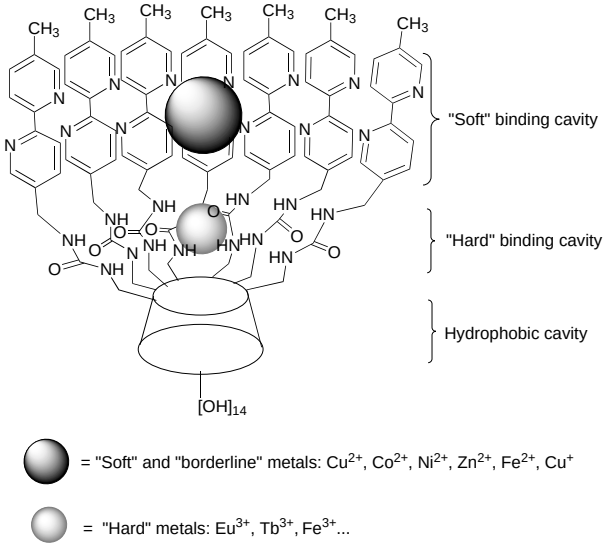

Figure 1. Schematic representation of an upper-rim fully tethered CD binuclear complex with "hard" and "soft" binding cavities.

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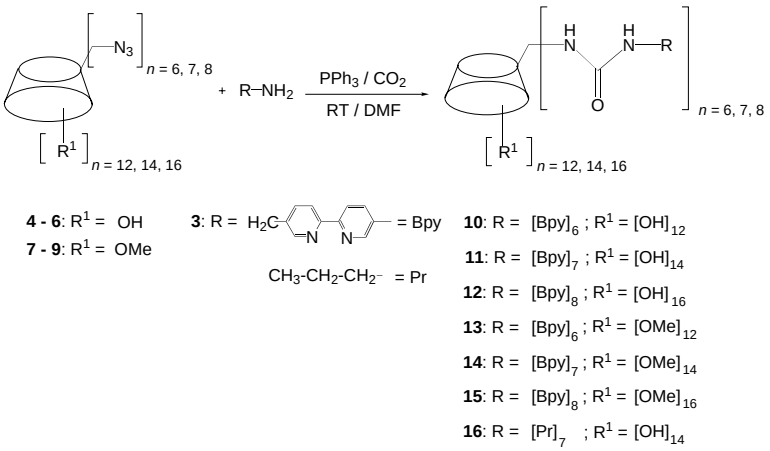
Synthesis of the devices required the preparation of the hexakis to octakis azido-cyclodextrins **4**–**9**,[4, 5] and their condensation with 5-methylamino-5′-methyl-2,2′-bipyridine (**3**) or *n*-propylamine, using the so called "phosphine imide" one-pot reaction,[6–7] to give directly the URFT-CDs **10**–**16** in moderate to good yields (30–60%) (Scheme 1). This reaction has also been extended to other heterocycles such as 2,2′-bithiazole[8a] and thiourea derivatives, using carbon disulphide in place of carbon dioxide as reagent and solvent.[8b] Recently, we published the scope and limitations of this methodology, allowing the synthesis of symmetrical versus unsymmetrical cyclodextrin carbodiimides under mild conditions, or isocyanates of complex and sensitive molecules without the use of hazardous reagent (e.g. phosgene).[9a]



Scheme 1. Synthesis of URFT-CDs **10**–**16**.

All new compounds were characterised by FTIR, NMR, CpMAS-NMR, MALDI-FTICR-MS, UV/Vis spectroscopies and elemental analysis. The spectroscopic FTIR, ^{1}H NMR, ^{13}C NMR and MS data were all in agreement with the assigned structures. As expected, the IR spectra exhibited strong characteristic frequencies for the carbonyl urea functions ν_{CO-NH} at around 1650 cm^{-1}, and intense aromatic double bonds $\nu_{C=C}$ at around 1550 cm^{-1} that corresponded to the bipyridine units. Characteristic ^{13}C NMR spectra of **10**–**16** in solution (DMSO) indicated that the C_2 ligand symmetry was conserved. Signals corresponding to NH–*C*O–NH carbonyl carbons at $\delta = 156-160$, and intense sharp signals corresponding to the bipyridyl carbons at $\delta = 155-120$ were detected. Analyses of the ^{13}C NMR spectra, revealed that the glycosyl carbon signals of the upper-rim persubstituted bipyridyl compounds (e.g. compound **14** in Figure 2) were highly broadened and of lower intensities than the aromatics. This effect was not found under the same conditions with **16** (propyl substituents). The ^{1}H NMR spectra (e.g. for compound **14**) recorded in solution (10^{-2} M) and in two solvents (e.g. MeOH and DMSO), exhibited broad and unresolved resonance signals (like a polymer) in both the regions expected for cyclodextrins and bipyridines and therefore their assignment was rendered uncertain. In our opinion, this phenomenon may be interpreted in terms of polymeric-like aggregates formed by self-organisation of the polyaromatic cyclodextrins in solution. Broadening of signals disappeared at the highest dilution (10^{-4} M in MeOH), indicating a dissociation of the proposed aggregates, but no evidence of a characterised dimer could be ascertained. This effect was not observed with DMSO. Nevertheless, the integration ratio (6:1) observed between the aromatic part and a broad singlet at $\delta = 5.10$, attributed to H(1) of CD, and the ratio (3:1) observed between the methyl singlet of bipyridines at $\delta = 2.40$ and the same CD H(1) singlet, were consistent with the assigned *per*-substitution. Broadening of signals was not found in alkyl derivative **16**, and thus proton resonances could easily be assigned. Owing to the limit of ligand solubility, the carbon NMR signal-to-noise ratios were improved by recording the Cp-MAS NMR spectrum. Spectra of **14** and its Eu^{III} complex **17** are shown in Figure 3. The NMR spectrum of ligand **14** in the solid phase was correlated to those in solution and clearly

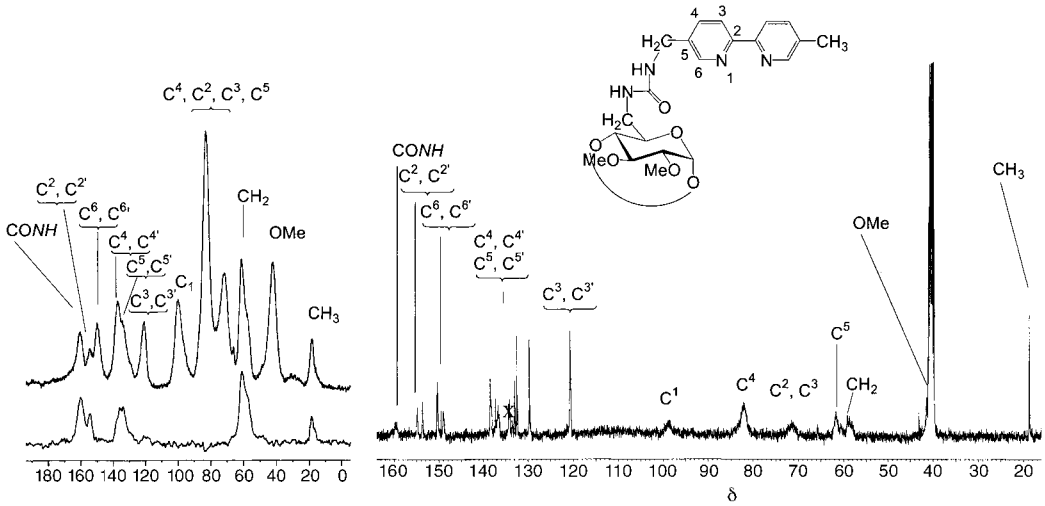


Figure 2. ^{13}C CpMAS NMR spectrum (8 KHz) and SPT of odd carbons (left) and ^{13}C NMR spectrum in solution (right) of ligand **14**.

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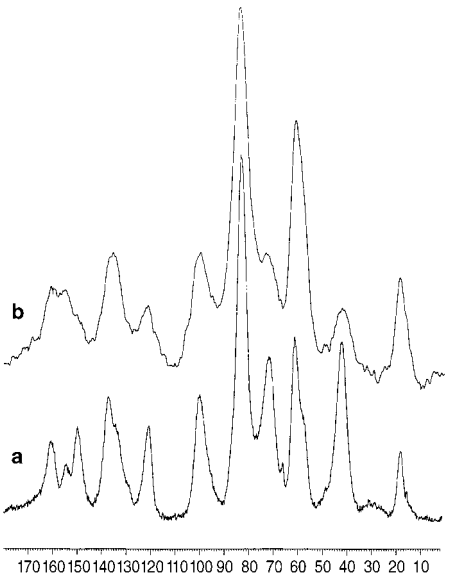

Figure 3. ^{13}C CpMAS NMR spectra of (a) ligand **14** and (b) [Eu^{III}(**14**)] complex **17**.

exhibited the best signal-to-noise ratios, particularly for the carbons signals of glucosyl units and the urea carbonyl. The lack of bipyridine carbon signals on complexation with the Eu^{3+} ion, confirms that the bypyridine units are not involved.

Positive mode FABMS showed the presence of the desired compound with a base peak at *m/z* 2705 corresponding to $[\mathbf{11}+H]^+$, accompanied by a fragment $[M-$ bipyridyl$]^+$ at *m/z* 2522. It should be noted that characterisation of the $[M+H]^+$ ion was obtained only in the case of the lower-rim unsubstituted β-CD derivatives. This result was attributed to the greater stability of the β-CD core towards ionisation, relative to α- and γ-CDs or their methylated derivatives. With these last cases, the cyclodextrin cores are probably broken first and give a set of oligomeric fragments as observed in the mass spectra of polymers. It should be noted that so far, all attempts to characterise this family of ligands by ESMS have failed. Elemental analyses were consistent with the presence of an additional number of associated water molecules owing to cyclodextrin hydration.

From a conformational point of view, previous results obtained with a ureido-cyclam ligand family by molecular dynamics computations, indicated that the molecules adopted a spatial "calix" form, which essentially arises from the presence of strong intramolecular hydrogen bonds between urea functions.[9a] Preliminary computations (molecular mechanics) with **11**, suggest a spatial "tubular" organisation of the ligand (Figure 4).[9b] The molecular geometry of **11** was optimised using the DISCOVER III programme of INSIGHT II (Biosym/MSI) and the AMBER force field. Minimisation was performed at 298 K using "steepest descent". "Conjugate gradients" and "Newton–Raphson" methods were then applied to complete the minimisation which converged for a maximum derivative of 0.01 kcal mol^{-1} Å or for 1000 steps of 1 ps. However, in the absence of full molecular dynamics computations, or other information such as X-ray analyses, one should treat these preliminary results with care.

Treatment of **14** and **16** with $EuCl_3 \cdot 6H_2O$ afforded the complexes **17** and **18** in 71 and 90% yield, respectively. These were obtained as pink powders, by diffusion of diethyl ether into a methanol solution of **14** and **16** at room temperature. The europium complex of **16** was characterised by positive mode MALDI FTICR-MS which had the desired mononuclear complex with an ion peak $[\mathbf{16} \subset Eu^{III},Cl_2]^+$ at *m/z* 1946 (36%), accompanied by characteristic fragments $[\mathbf{16} \subset Eu^{III},Cl]^{2+}$, $[\mathbf{16} \subset Eu^{III}]^{3+}$, and $[\mathbf{16} \subset Eu^{III}-$propyl$-NH-CO]^{3+}$ at *m/z* 1911 (45%), 1876 (40%) and 1790, respectively. Recent papers have reported efficient antennae effects for Eu^{III} or Tb^{III} complexes of β-cyclodextrins bearing amino carboxylates[3c] or ureido cyclam derivatives.[10] In a recent paper, our group presented preliminary results on luminescence properties and an efficient antennae effect (A-TE-E) of Eu^{3+} and Tb^{3+} complexes of ligand **11**.[11] The luminescence excitation of $[\mathbf{11} \subset Eu^{III}Cl]^-$ at 288 nm, and of $[\mathbf{16} \subset Lb^{III},PF_6)]^-$ at 280 nm, cause standard

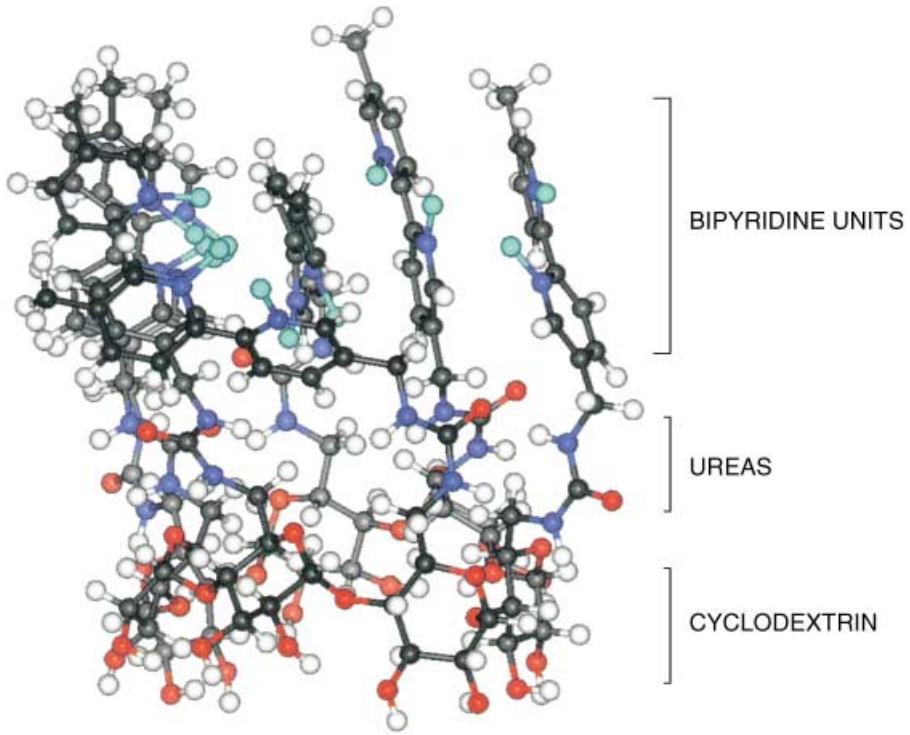

Figure 4. Ball-and-stick structure of ligand **11** [printed from the Insight II molecular modelling program and obtained by molecular mechanics minimization at 298 K, until a maximum derivative of 0.01 kcal mol^{-1} Å (done with AMBER force field and DISCOVER III, program from (Biosym/MSI)].

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emission of the Eu^{III} and Tb^{III} lanthanide ions by an absorption–energy transfer–emission light conversion process. Thus, the transitions corresponding to $^5D_0-{}^7F_j$ (Eu^{III}) and $^5D_4-{}^7F_j$ (Tb^{III}) are observed (Figure 5). Lifetime measurements recorded in the time resolved mode for the two complexes gave: $\tau = 0.7$ ms and 3.5 ms for the $[\mathbf{11} \subset Eu^{III}Cl]^-$ and $[\mathbf{16} \subset Lb^{III},PF_6)]^-$ complexes, respectively. This antennae effect also occurs with all the investigated ligands **10**–**16** and an extensive study of their steady-state photophysical properties will be described in a forthcoming paper.

Cation complexation—UV/Vis absorption spectra: As shown in Figure 1, upper-rim fully substituted bipyridyl-ureido-CDs **10**–**15** accommodate two potential complexation sites inside their structures and one in **16** (the internal, hydrophobic cavity of the CD core is not taken into account). In this section, the cation complexation behaviour of two representative ligands [**11** (non-methylated) and **14** (lower-rim permethylated)] is illustrated by UV/Vis spectroscopy; the results were similar for other molecules except **16** (owing to a lack of the bipyridine units). Titrations of the ligands **10**–**16** with lanthanides (Eu^{3+}, Tb^{3+}, Sm^{3+} and Dy^{3+}) and other "hard" HSAB-classified cations (e.g. Fe^{3+}) followed by "soft" or "borderline" metals were monitored by UV/Vis spectroscopy.

The electronic spectra of the free ligands **10**–**15** were recorded in MeOH and had two absorption maxima in the UV region at $\lambda_{max} = 250$ nm and 284–288 nm ($\pi-\pi^*$ and n–π^* of bipyridines and urea carbonyl). Molar extinction coefficients of 55080–110830 $mol^{-1}L^{-1}cm^{-1}$ were obtained for the bipyridyl derivatives; these gave an estimated extinction average of about 12500 $mol^{-1}L^{-1}cm^{-1}$ per bipyridine unit which is in the expected range of values measured for 2,2-bipyridine. In the case of the propyl derivative **16**, the absorption maximum was at $\lambda_{max} = 260$ nm with a molar extinction coefficient of 603 $mol^{-1}L^{-1}cm^{-1}$ as a result of the urea-carbonyl chromophores.

The titrations of **10**–**15** by lanthanides (Figure 6) had an isobestic point at 305 nm, a slight red shift of the 288 nm absorption to 292 nm and appearance of a LMCT band at 320 nm owing to efficient metal coordination and according to conformational changes occurring in the ligands. The complexes of **10**–**16** had a stoichiometry of 1:1 and this was also confirmed by plasma torch titration of Eu^{III} in **17** (see Experimental Section). A stability constant of $6.02 \times 10^5\,M^{-1}$ was calculated for the $[\mathbf{11} \subset Eu^{III}Cl]^-$ complex. [11] In these complexes, lanthanides or "hard" metals are coordinated to the urea carbonyl oxygen atoms; this is in accordance with their coordination preference observed in our previous results obtained with **11**,[12] MALDI-FTMS of **18**, and literature reports.[13]

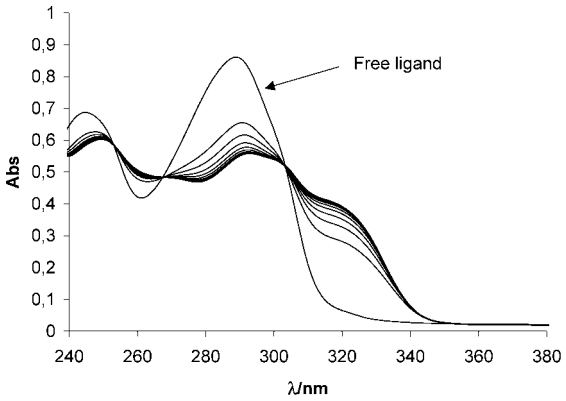

Figure 6. Spectrophotometric titration of **11** ($c = 1.0 \times 10^{-5}$ mol L^{-1}) in MeOH with $TbCl_3 \cdot 6H_2O$; $Tb^{3+} = 0.2-2$ equiv.

Titration of **14** by Fe^{III} was an exception because in this case two isobestic points were determined: one, with 1 equivalent and the second with 2 equivalents of Fe^{III} added to the ligand, indicating a new $[(Fe)_2(\mathbf{14})]$ binuclear complex [2M:1L] formation (Figure 7). Looking at the absorbance evolution, coordination with bipyridine units could be excluded and formation of a stable, six-coordinate complex is suggested[14] in which the CD lower-rim methyl ether oxygen atoms of **14** act as a crown ether macrocycle "hard" binding cavity.[15] This effect was not observed in the presence of an excess of lanthanide ions.

In contrast, titrations of the free ligands **10**–**15** by addition of "borderline" or "soft" metals (Co^{II}, Ni^{II}, Fe^{II}, Cu^{II} and Cu^{I}) gave another isobestic point at 292 nm, along with a strong red shift (and a hyperchromic effect) of the 288 nm absorption band to 305 nm (Figure 8). The complexes had a stoichiometry of 1:1. In the case of Fe^{II}, a new MLCT band at $\lambda_{max} = 520$ nm was observed, along with the appearance of the characteristic purple [Fe^{II}-bipyridyl] complex colour.

Addition of transition metals (e.g. Cu^{I}) to the mononuclear lanthanide complex, reveals a second isobestic point at 308 nm, with a new strong red-shift of the 292 nm absorption maximum to 310 nm and a hyperchromic effect as result of the second metal coordination and conformational change occurring in the complex (Figure 9). The resulting new

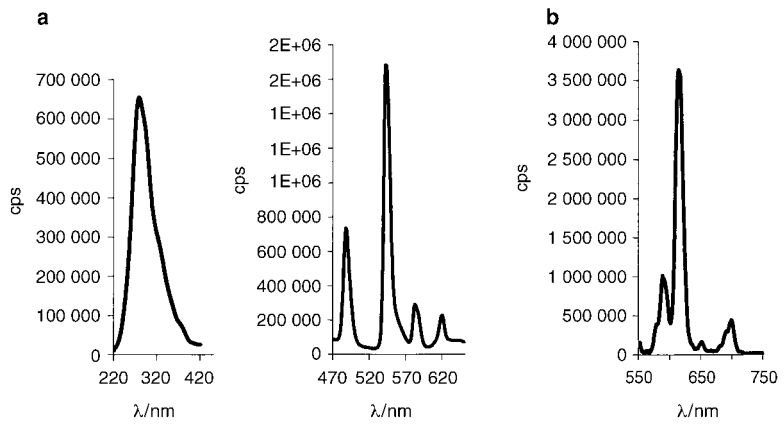

Figure 5. a) Excitation and emission spectra of $[Tb(\mathbf{16})(PF_6)]^-$ ($c = 1.06$ mmol L^{-1}); b) emission spectrum of $[Eu(\mathbf{11})(Cl)]^-$ ($c = 2.65 \times 10^{-6}$ mol L^{-1}) in MeOH at 300 K.

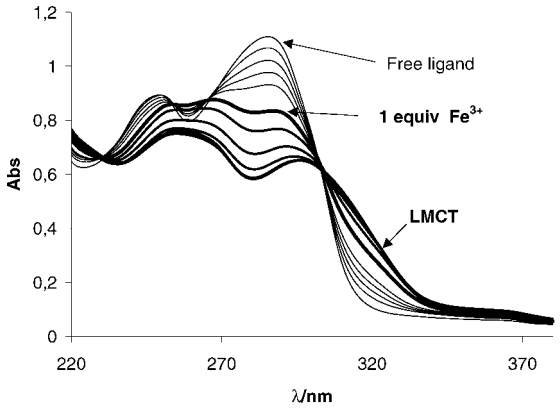

Figure 7. Spectrophotometric titration of **14** ($c = 1.0 \times 10^{-5}$ mol L^{-1}) in MeOH with $Fe_2(SO_4)_3$; $Fe^{3+} = 0.2 - 2.2$ equiv.

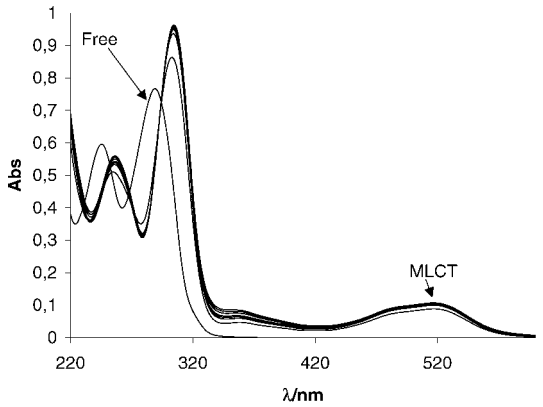

Figure 8. Spectrophotometric titration of **11** ($c = 1.0 \times 10^{-5}$ mol L^{-1}) in MeOH with $FeSO_4 \cdot 7H_2O$; $Fe^{2+} = 0.2 - 1.0$ equiv.

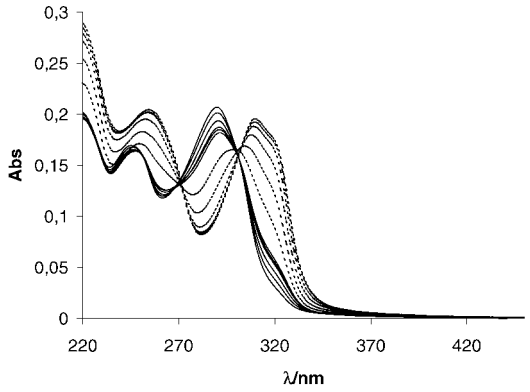

Figure 9. Spectrophotometric titration of **11** ($c = 2.4 \times 10^{-6}$ mol L^{-1}) in MeOH with $TbCl_3 \cdot 6H_2O$ (solid line), then $[Cu(CH_3CN)_4]^+ PF_6^-$ (dashed line); $Tb^{3+} = 0.2 - 1$ equiv and $Cu^+ = 0.2 - 1.2$ equiv.

heterobinuclear complexes were found to have a 1:1 stoichiometry for the second metal. In these complexes, the "soft" metal is coordinated to the bipyridyl units according to their coordination preference reported recently.[13c] The resulting absorption spectrum for the heterobinuclear complex is a superposition of the individual mononuclear complexes without the appearance of any supplementary charge-transfer bands.

Finally, negative allosteric control of cation recognition was also observed when europium ion was added to a preformed mononuclear "borderline" metal complex (for example [**11** $\subset$ Co^{II}]). In this case, formation of the Co^{II} complex with terminal bipyridines probably induced a dramatic conformational change in the "hard" recognition site by formation of a pseudo-cryptand, therefore inhibiting the lanthanide ion access to the cavity. This feature is supported by the absence of the corresponding isobestic point and LMCT absorption band (shoulder at 320 nm) of the Eu^{3+} ion coordination process (Figure 10). Similarly, allosteric control of ion recognition through formation of pseudo-cryptands was explored a few years ago by Nabeshima's group.[16] The authors showed in particular, that for a designed triple-stranded helix with three polyether chains and terminal 2,2′-bipyridyl groups as "hard" and "soft" metal coordination sites, that the corresponding iron(II) complex induced an allosteric control on the second metal (alkali cation) complexation and transport.

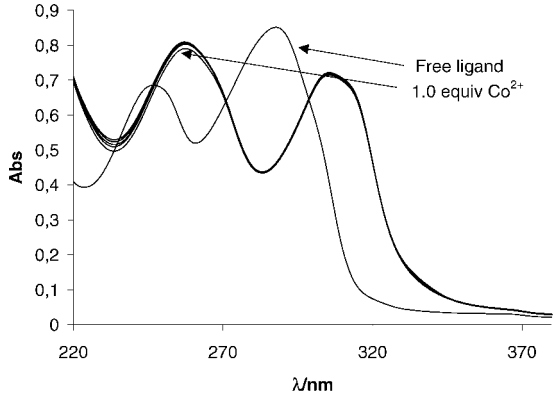

Figure 10. Allosteric negative effect of Co^{2+} on the coordination of Eu^{3+} ion in MeOH; ligand **11** $c = 1.0 \times 10^{-5}$ mol L^{-1}; $Co^{2+} = 1.0$ equiv and $Eu^{3+} = 0.2 - 1$ equiv.

It was evident, with respect to the transition metal coordination number, that participation of the six, seven or eight ureido-bipyridyl arms was not necessary for the formation of stable mononuclear transition metal complexes. A maximum of two (e.g. Cu^{I}) or three (e.g. Fe^{II}) ureido-bipyridyl units were necessary to complete the desired number of coordination sites, leaving the supplementary units free of complexation.

Iron translocation by chemical triggering: The growing interest in the miniaturisation of electronic components is stimulating research on molecular assemblies with device-like functionalities.[17] One of these functionalities could be a redox molecular switch based on chemical triggering, as published in the case of a triple-stranded helical iron complex.[18] Attempts to reproduce such a functionality with **11** have been achieved with iron, which can occupy one of the two distinct binding cavities in the CD structure. Reversible intramolecular translocation of the metal ion between the "hard" and "soft" cavities was achieved by chemical oxidation and reduction, owing to the different coordination preferences of the Fe^{II} and Fe^{III} states (see Figure 12). UV/Vis titration of **11** with Fe^{III} (Figure 11), indicates formation of the expected [**11** $\subset$ Fe^{III}-urea] complex [1M:1L]] with a light

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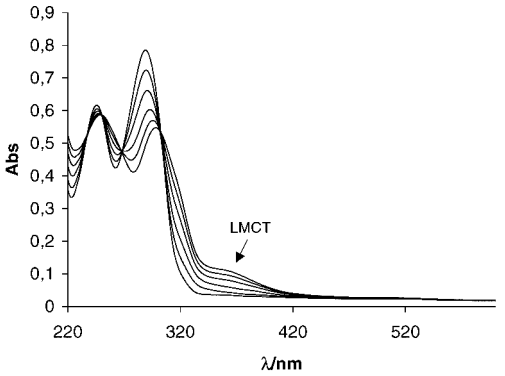

Figure 11. Spectrophotometric titration of ligand **11** ($c = 1.0 \times 10^{-5}$ mol L^{-1}) in MeOH with $Fe_2(SO_4)_3$; $Fe^{3+} = 0.2-1.0$ equiv.

brown colour and a stability constant of 1.28×10^5 M^{-1}. Titration of **11** with Fe^{II} gave a [1M:1L], characteristically light purple coloured, [**11** ⊂ Fe^{II}-bipyridyl] complex with a stability constant of 2.80×10^5 M^{-1}; correspondingly, a new MLCT band appeared at $\lambda_{max} = 520$ nm (Figure 8). To verify the occurrence of metal–metal interaction, we prepared the dinuclear Fe^{III}/Fe^{II} complex by treatment of **11** with one equivalent of $FeCl_3$ followed by one equivalent of $FeSO_4$. The resulting absorption spectrum is a superposition of the individual mononuclear complexes without any supplementary charge-transfer bands. Treatment of the mononuclear complex [**11** ⊂ Fe^{III}-urea] with ascorbic acid resulted in a rapid reduction, as evidenced by the appearance of the purple-red absorption of the bipyridyl complex, and identical spectral features of the latter with those of the bipyridyl complex previously obtained by treatment of **11** with $FeSO_4$ (Figure 8). Reversal of the reduction process was achieved by heating the [**11** ⊂ Fe^{II}-bipyridyl] complex for a few minutes at 70 °C with excess ammonium persulphate; this was evidenced by the disappearance of the purple-red colour and regeneration of the light yellow colour of the [Fe^{III}(**11**)] urea complex (Figure 13).

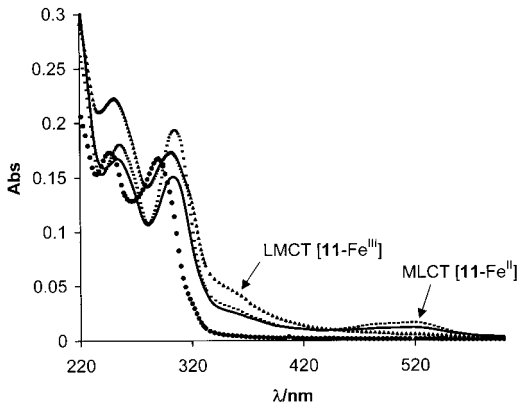

Figure 13. UV/Vis spectra of the ligand **11** ($c = 2.4 \times 10^{-6}$ mol L^{-1}) in MeOH. Fe^{II}/Fe^{III} reduction then re-oxidation is triggered by ascorbic acid and $(NH_4)_2S_2O_8$ present in tenfold excess. ● Ligand **11**; ▲ [**11** ⊂ Fe^{III}]; - - - - [**11** ⊂ Fe^{II}]; —— [**11** ⊂ Fe^{III}].

Conclusion

The new molecular devices introduced here are intended to contribute to the future development of nanotechnologies based on cyclodextrins. The challenges that remain to be met include isolating homo- and heterometallic complexes, developing means of immobilising Langmuir–Blodgett films of these amphiphilic URFT-CDs and their complexes on conducting or non-conducting surfaces (actually in progress), to stimulate the switching functionality by electrochemical or photochemical techniques and to explore potentialities of other redox couples. Photophysical properties of lanthanide complexes are also under investigation. Their evaluation as pinpoint sources of light, after self-assembling monolayers on surfaces, to give photosensitive chips is underway. Elsewhere, modifications of structures, by chemically-controlled introduction of a designed number of other bis-heterocyclic systems and new functional groups, investigations into cations and organic compound recognition modulation or catalysis, are planned for the construction of molecular machines and general systems for the amplification and modulation of molecular information.

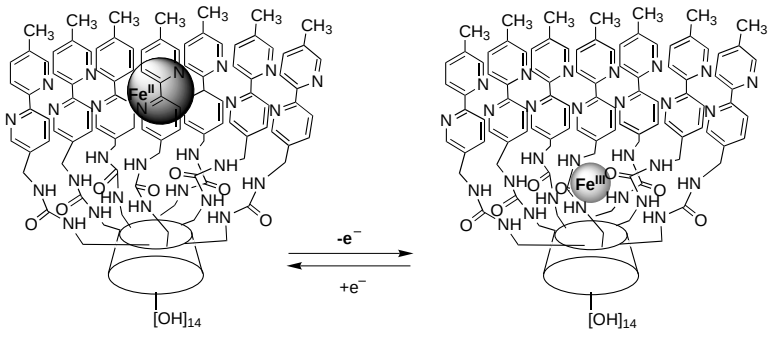

Figure 12. Schematic representation of the URFT-CD metal complex-based molecular switches that function on exposure to reducing and oxidizing chemical agents through the interconversion and translocation of iron.

Experimental Section

Structures of all compounds were assigned by ^{1}H and ^{13}C NMR spectra recorded on a Bruker DRX-400 or DRX-300 (MAS) spectrometer. FTIR spectra were recorded on a Perkin–Elmer 1600 apparatus. UV/Vis spectra were done on a Safas UVmc^2. Luminescence experiments were performed on a Spex Fluorolog II photon counting spectrofluorimeter equipped with a 450 W xenon continuous-wave irradiation source. Mass spectra were recorded in FAB positive mode on a ZAB-SEQ mass spectrometer and on a Thermo-Finnigan Mat. MALDI-FTICR-MS used a Nd/Yag laser (355 nm). All new compounds gave satisfactory spectroscopic data. DMF was dried over $CaSO_4$, filtered off and flushed with argon to eliminate dimethylamine. Retention factors were measured on TLC aluminium plates coated with silica gel unless stated otherwise. Column chromatography was also performed with silica gel unless otherwise stated. NH_3 refers to a 28% solution of ammonia in water.

5-Monobromomethyl-5′-methyl-2,2′-bipyridine (1): NBS (0.03 mol, 5.30 g) and a catalytic quantity of AIBN was added to a solution of 5,5′-dimethyl-

2,2′-bipyridine (0.03 mol, 5.0 g) in CCl_4 (250 mL). The mixture was stirred and heated at reflux under argon for 90 min. The reaction was monitored by TLC. The hot solution was then filtered off and the filtrate concentrated to dryness. The dibromomethyl derivative was precipitated from CH_2Cl_2 and separated by filtration. The filtrate was purified by column chromatography (CH_2Cl_2) to afford **1** (2.86 g, 0.01 mol, 40%) as a white powder. $R_f = 0.7$ (CH_2Cl_2/MeOH 98:2); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.68$ (s, 1H; H6-bpy), 8.62 (s, 1H; H6′-bpy), 8.37 (d, 1H, $^3J(H,H) = 8.2$ Hz; H3-bpy), 8,30 (d, 1H, $^3J(H,H) = 8.2$ Hz; H3′-bpy), 7.85 (d, 1H, $^3J(H,H) = 8.2$ Hz; H4-bpy), 7,64 (d, 1H, $^3J(H,H) = 8.2$ Hz; H4′-bpy), 4.55 (s, 2H; CH_2Br), 2.41 (s, 3H; CH_3).

5-Azidomethyl-5′-methyl-2,2′-bipyridine (2): 5-Monobromomethyl-5′-methyl-2,2′-bipyridine (**1**) (2.0 g, 0.08 mol) was added in small portions to a solution of sodium azide (3.0 g, 46.1 mol, 6 equiv) in DMSO (40 mL). The solution was stirred at 70 °C for 2 h and then cooled to RT. Distilled water (80 mL) was added and the product was extracted with toluene (5 × 30 mL). The organic layer was dried over $MgSO_4$ and evaporated to dryness. The residue was purified by column chromatography (CH_2Cl_2) to give **2** (1.5 g, 0.07 mol, 88%) as a white powder. $R_f = 0.55$ (CH_2Cl_2/MeOH 90:10); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.63$ (s, 1H; H6-bpy), 8.53 (s, 1H; H6′-bpy), 8.43 (d, 1H, $^3J(H,H) = 8.2$ Hz; H3-bpy), 8.31 (d, 1H, $^3J(H,H) = 8.2$ Hz; H3′-bpy), 7.80 (d, 1H, $^3J(H,H) = 8.2$ Hz; H4-bpy), 7.66 (d, 1H, $^3J(H,H) = 8.2$ Hz, H4′-bpy), 4,45 (s, 2H; CH_2N_3), 2.42 (s, 3H; CH_3).

5-Aminomethyl-5′-methyl-2,2′bipyridine (3): 5-Azidomethyl-5′-methyl-2,2′-bipyridine (**2**) (0.88 g, 4.0 mmol) was dissolved in a CH_2Cl_2/EtOH solution (100 mL, 1:1), and Pd/C (10%, 0.16 g) was then added. The mixture was stirred under H_2 pressure for 21.3 h. The reaction medium was filtered through Celite and washed with a mixture CH_2Cl_2/EtOH (1:1). The filtrates were evaporated to dryness and diethylether was added to the residue. The precipitate was then filtered over a sintered glass to give **3** (0.51 g, 2.5 mmol, 65%) as a white powder. $R_f = 0.52$ (CH_2Cl_2/MeOH 9:1, on Al_2O_3); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.59$ (s, 1H; H6-bpy), 8.49 (s, 1H; H6′-bpy), 8.32 (d, 1H, $^3J(H,H) = 8.2$ Hz; H3-bpy), 8.26 (d, 1H, $^3J(H,H) = 8.2$ Hz; H3′-bpy), 7.77 (d, 1H, $^3J(H,H) = 8.2$ Hz; H4-bpy), 7.61 (d, 1H, $^3J(H,H) = 8.2$ Hz; H4′-bpy), 3.94 (s, 2H; CH_2), 2.38 (s, 3H; CH_3), 1.62 (s, NH_2).

Hexakis-[6-deoxy-6-(5-methyleneureido-5′-methyl-2,2′-bipyridyl)]-cyclomaltohexaose (10): Triphenylphosphane (2.63g, 10.0 mmol, 70 equiv) was added to hexakis-(6-deoxy-6-azido)-cyclomaltohextaose (**4**) (0.16 g, 0.14 mmol) in distilled DMF (25 mL). A solution of 5-aminomethyl-5′-methyl-2,2′-bipyridine (0.20 g, 1.0 mmol, 7 equiv) in distilled DMF (15 mL) was added dropwise to the mixture and a stream of dry CO_2 was simultaneously bubbled through the solution. The mixture was stirred for 16 h at RT under the stream of CO_2. The solution was concentrated to dryness. Diethyl ether was added to the residue and the precipitate was filtered and washed thoroughly with diethyl ether. The solid was purified by column chromatography (NH_3/dioxan 43:57) to give **10** (0.11 g, 0.05 mmol, 33%). ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta = 8.41$ (d, unresolved, 2H; bipy), 8.16 (d, unresolved, 2H; bipy), 7.73 (m, 2H; bpy), 5.60–5.52 (br m, 3H; N*H*, CH_2-bpy), 4.87 (br s, 6H; H1-CD), 4.16–3.36 (m, 48H; H2 to H-6 CD, O*H*-CD), 2.32 (s, 21H; CH_3-bpy); ^{13}C NMR (100 MHz, [D$_6$]DMSO): $\delta = 155.0$ (CONH), 153.0 (C_2, $C_{2'}$), 150.1 (C_6), 148.5 ($C_{6'}$), 138.3 (C_4), 136.5 ($C_{4'}$), 134.5 (C_5, C_3), 130.4 ($C_{3'}$), 120.7 (CH_2), 102.5 (C_1), 84.0 (C_4), 73.5–72.7 (C_2, C_3, C_5), 18.6 (CH_3); IR (KBr): $\tilde{\nu} = 3400-3152$ (NH, OH), 1648 (*CO*NH), 1556 cm^{-1} (C=C aromatics); UV/Vis (MeOH): λ_{max} (ε) = 288 (58660 mol^{-1} dm^3 cm^{-1}); FAB-MS (thioglycerol): *m*/*z*: 2354 [*M*+HCl+H]$^+$, 2171 [*M*+HCl+H − bipyridyl]$^+$; elemental analysis calcd (%) for $C_{114}H_{132}N_{24}O_{30}\cdot 9H_2O$ (2480.5): C 55.20, H 6.10, N 13.56; found: C 55.60, H 6.43, N 12.96.

Heptakis-[6-deoxy-6-(5-methyleneureido-5′-methyl-2,2′-bipyridyl)] cyclomaltoheptaose (11): Triphenylphosphane (1.3 g, 5.0 mmol, 70 equiv) was added to heptakis-(6-deoxy-6-azido)-cyclomaltoheptaose (**5**) (0.095 g, 0.07 mmol) in distilled and argon degassed DMF (25 mL). A solution of 5-aminomethyl-5′-methyl-2,2′-bipyridine (0.13 g, 0.65 mmol, 9 equiv) in distilled DMF (20 mL) was then added dropwise whilst a stream of dry CO_2 was simultaneously bubbled through the solution. The mixture was stirred for 15 h at RT under the stream of CO_2. The solution was concentrated to dryness to give an orange oil. Diethyl ether was then added to the residue, and the resulting red-orange precipitate was filtered and washed with diethyl ether to give a solid that was purified by crystallisation in hot absolute ethanol to afford **11** (0.12 g, 0.04 mmol, 61%). $R_f = 0.5$ (NH_3/dioxan 1:10); ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta = 8.28$ (d, 2H; bpy), 7.99 (d, 2H; bpy), 7.50 (m, 2H; bpy), 6.93 (br s, 1H; N*H*), 6.36 (br s, 1H; N*H*), 5.92 (m, 2H; CH_2-bpy), 4.88 (s, 7H; H1-CD), 4.22–3.58 (m, 56H, H2 to H6-CD, O*H*-CD), 2.24 (s, 21H; CH_3-bpy); ^{13}C NMR (100 MHz, [D$_6$]DMSO): $\delta = 159.8$ (CONH), 154.8 (C_2), 153.4 ($C_{2'}$), 150.0 (C_6), 148.5 ($C_{6'}$), 137.9 (C_4), 136.2 ($C_{4'}$), 133.8 (C_5), 120.6 (C_3), 120.4 ($C_{3'}$), 103.2 (C_1), 84.8 (C_4), 73.2 (C_2), 71.1 (C_3), 68.2 (C_5), 18.6 (CH_3); IR (KBr): $\tilde{\nu} = 3352-2923$ cm^{-1}, (NH, OH), 1643 cm^{-1} (NHC=O); UV/Vis (MeOH): λ_{max} (ε) = 288 nm (88560 mol^{-1} dm^3 cm^{-1}); FAB-MS (thioglycerol): *m*/*z*: 2705 [*M*+H]$^+$, 2522 [*M* − bipyridyl]$^+$; elemental analysis calcd (%) for $C_{133}H_{154}N_{28}O_{35}\cdot 10H_2O$ (2884.9): C 55.37, H 6.08, N 13.59; found: C 55.31, H 5.69, N 12.81.

Octakis-[6-deoxy-6-(5-methyleneureido-5′-methyl-2,2′-bipyridyl)]-cyclomaltooctaose (12): A solution of 5-aminomethyl-5′-methyl-2,2′-bipyridine (0.20g, 1.0 mmol, 9 equiv) in distilled DMF (55 mL) was added dropwise to a mixture of triphenylphosphane (2.05 g, 8.0 mmol, 70 equiv) and octakis-(6-deoxy-6-azido)-cyclomaltooctaose (**6**) (0.17 g, 1.0 mmol) in DMF (25 mL). A stream of dry CO_2 was simultaneously bubbled through the solution. The mixture was stirred for 16 h at RT under CO_2, then concentrated to dryness and diethyl ether was added to the residue. The precipitate was then filtered and thoroughly washed with diethyl ether. The solid was purified by column chromatography (NH_3/dioxan 33:67) to give **12** (0.12 g, 0.04 mmol, 35%). ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta = 8.38$ (d, unresolved, 2H; bipy), 8.08 (d, unresolved, 2H; bipy), 7.63 (m, 2H; bpy), 5.97 (m, 2H; CH_2-bpy), 4.89 (br s, 8H; H1-CD), 4.20–3.35 (m, 64H; H2 to H6-CD, O*H*-CD), 2.29 (s, 24H; CH_3-bpy); ^{13}C NMR (100 MHz, [D$_6$]DMSO): $\delta = 159.0$ (*CO*NH), 154.8 (C_2), 153.5 ($C_{2'}$), 150.2 (C_6), 148.8 ($C_{6'}$), 138.1 (C_4), 136.5 ($C_{4'}$), 133.9 (C_5), 130.5 (C_3, $C_{3'}$), 120.6 (CH_2), 102.9 (C_1), 84.0 (C_4), 73.3 (C_2, C_3), 65,8 (C_5), 57.0 (C_6), 18.6 (CH_3); IR (KBr): $\tilde{\nu} =$ 3351 (NH, OH), 1647 (*CO*NH), 1557 cm^{-1} (C=C aromatics); UV/Vis (MeOH): λ_{max} (ε) = 286 (97100 mol^{-1} dm^3 cm^{-1}); elemental analysis calcd (%) for $C_{151}H_{174}N_{32}O_{40}\cdot 8H_2O$ (3221.3): C 56.30, H 5.95, N 13.91; found: C 55.95, H 6.10, N 13.52.

Hexakis-[2,3-di-*O*-methyl-6-deoxy-6-(5-methyleneureido-5′-methyl-2,2′-bipyridyl)]-cyclomaltohexaose (13): 5-Aminomethyl-5′-methyl-2,2′-bipyridine (0.16 g, 0.80 mmol, 7 equiv) was added in small portions to a mixture of triphenylphosphane (2.11 g, 8.04 mmol, 70 equiv) and hexakis-(2,3-di-*O*-methyl-6-dexy-6-azido)-cyclomaltohexaose (**7**) (0.15 g, 0.11 mmol) in DMF (60 mL); a stream of dry CO_2 was bubbled through the solution simultaneously. The mixture was stirred at RT under CO_2 for 16 h. The solution was concentrated to dryness, and diethyl ether was added to the residue. The resulting precipitate was filtered and washed thoroughly with diethyl ether. The solid was purified by column chromatography (NH_3/dioxan 11:89) to give **13** (0.10 g, 0.04 mmol, 35%). ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta = 8.79$ (s, 1H; bpy), 8.53 (s, 1H; bpy), 8.32 (d, 1H; bpy), 8.29 (d, 1H; bpy), 8.11 (d, 1H; bpy), 7.76 (d, 1H; bpy), 5.10 (br s, 6H; H1-CD), 4.12–3.00 (m, 72H; H2 to H6-CD, CH_3O-CD), 2.36 (s, 18H; CH_3-bpy); ^{13}C NMR (100 MHz, [D$_6$]DMSO): $\delta = 159.6$ (*CO*NH), 154.8 (C_2), 153.5 ($C_{2'}$), 150.2 (C_6), 148,9 ($C_{6'}$), 138.2 (C_4), 136.6 ($C_{4'}$), 134.1 (C_5), 132.4 (C_3), 129.7 ($C_{3'}$), 120.6 (CH_2), 100.1 (C_1), 83.6–81.5 (C_4, C_3), 72.2–71.7 (C_2), 61.9 (C_5), 58.0 (C_6), 18.6 (CH_3); IR (KBr): $\tilde{\nu} = 3391$ (NH), 1654 (*CO*NH), 1560 cm^{-1} (C=C aromatics); UV/Vis (MeOH) λ_{max} (ε) = 289 (55080 mol^{-1} dm^3 cm^{-1}); elemental analysis calcd (%) for $C_{126}H_{156}N_{24}O_{30}\cdot 10H_2O$ (2666.9): C 56.75, H 6.65, N 12.61; found: C 56.95, H 6.52, N 12.15.

Heptakis-[2,3-di-*O*-methyl-6-deoxy-6-(5-methyleneureido-5′-methyl-2,2′-bipyridyl)]-cyclomaltoheptaose (14): A solution of 5-aminomethyl-5′-methyl-2,2′-bipyridine (0.16 g, 0.8 mmol, 8 equiv) in distilled CH_2Cl_2 (55 mL) was added dropwise to a mixture of triphenylphosphane (1.84 g, 7.0 mmol, 70 equiv) and heptakis-(2,3-di-*O*-methyl-6-dexy-6-azido)-cyclomaltoheptaose (**8**) (0.15 g, 0.1 mmol) in dry distilled CH_2Cl_2 (25 mL). A stream of dry CO_2 was bubbled through the solution simultaneously. The mixture was stirred at RT under CO_2 for 15 h. The solution was then concentrated to dryness and diethyl ether was added to the residue. The resulting precipitate was filtered and washed thoroughly with diethyl ether. The solid was purified by column chromatography (NH_3/dioxan 25:75) to give **14** (0.15 g, 0.05 mmol, 52%). ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta =$ 8.50 (d, unresolved, 2H; bpy), 8.25 (d, unresolved, 2H; bpy), 7.70 (m, 2H; bpy), 5.11 (s, 7H; H1-CD), 4.30–3.07 (m, 42H; H2 to H6-CD), 3.57 (s, 21H; CH_3O-CD), 2.32 (br s, 21H; CH_3-bpy); ^{13}C NMR (100 MHz, [D$_6$]DMSO): $\delta = 159.3$ (*CO*NH), 154.8 (C_2), 153.6 ($C_{2'}$), 150.3 (C_6), 149.0 ($C_{6'}$), 138.4 (C_4), 136.7 ($C_{4'}$), 134.1 (C_5), 132.3 (C_3), 129.6 ($C_{3'}$), 120.6 (CH_2),

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99.7 – 98.6 (C_1), 82.2 (C_4), 71.5 (C_2, C_3), 61.7 – 60.6 (C_5), 59.1 – 58.7 (C_6), 18.6 (CH_3); ^{13}C CPMAS NMR (75 MHz, *rs* = 8 KHz): δ = 160, 154 ($C_{2'}$, $C_{2''}$), 150($C_{6'}$, $C_{6''}$), 138 ($C_{4'}$, $C_{4''}$, $C_{5'}$, $C_{5''}$), 121 ($C_{3'}$,$C_{3''}$), 100 (C_1), 84 (C_4), 70 (C_2, C_3, C_5), 60 (CH_2), 42 (OCH_3), 19 (CH_3); IR (KBr): $\tilde{\nu}$ = 3366 – 2929 (NH, OH), 1654 (*CO*NH), 1554 cm^{-1} (C=C aromatics); UV/Vis (MeOH) λ_{max} (ε) = 286 (110830 mol^{-1} dm^3 cm^{-1}); elemental analysis calcd (%) for $C_{147}H_{182}N_{28}O_{34}\cdot 10H_2O$ (3081.3): C 57.30, H 6.61, N 12.73; found: C 57.02, H 6.31, N 12.30.

Octakis-[2,3-di-*O*-methyl-6-deoxy-6-(5-methyleneureido-5′-methyl-2,2′-bipyridyl)]-cyclomaltooctaose (15): 5-Aminomethyl-5′-methyl-2,2′-bipyridine (0.13 g, 0.65 mmol, 9 equiv) was added in small portions to a mixture of triphenylphosphane (1.33 g, 5.07 mmol, 70 equiv) and octakis-(2,3-di-*O*-methyl-6-dexy-6-azido)-cyclomaltooctaose (**9**) (0.12 g, 0.72 mmol) in DMF (60 mL). A stream of dry CO_2 was simultaneously bubbled through the solution. The mixture was then stirred at RT under CO_2 for 16 h. The workup procedure was the same as above and the crude precipitate was purified by column chromatography (NH_3/dioxan 15:85) to give **15** (0.10 g, 0.03 mmol, 43 %). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 8.40 (br s, 2H; bpy), 8.22 (br s, 2H; bpy), 7.63 (m, 2H; bpy), 5.11 (s, 8H; H1-CD), 4.40 – 3.08 (m, 96H; H2 to H6-CD, C*H*$_3$O-CD), 2.30 (br s, 24H; C*H*$_3$-bpy); ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 159.5 (*CO*NH), 154.8 (C_2), 153.6 ($C_{2'}$), 150.1 (C_6), 148.8 ($C_{6'}$), 138.2 (C_4), 136.6 ($C_{4'}$), 134.1 (C_5), 132.4 (C_3), 129.6 ($C_{3'}$), 120.6 (CH_2), 98.8 (C_1), 82.1 (C_4), 70.8 – 69.3 (C_2, C_3), 61.1 (C_5), 59.1 (C_6), 18.6 (CH_3); IR (KBr): $\tilde{\nu}$ = 3367 (NH, OH), 1656 (*CO*NH), 1555 cm^{-1} (C=C aromatics); UV/Vis (MeOH): λ_{max} (ε) = 289 (79460 mol^{-1} dm^3 cm^{-1}); elemental analysis calcd (%) for $C_{167}H_{206}N_{32}O_{40}\cdot 12H_2O$ (3517.8): C 57.02, H 6.59, N 12.74; found: C 56.93, H 6.31, N 12.30.

Heptakis-(6-deoxy-6-propyl)-cyclomaltoheptaose (16): Propylamine (3.0 mmol, 0.2 g, 8 equiv) was added dropwise to a mixture of triphenylphosphane (26.6 mmol, 7.0 g, 70 equiv) and heptakis-(6-deoxy-6-azido)-cyclomaltoheptaose (**5**) (0.5 g, 0.4 mmol) in DMF (45 mL). The solution was flushed with CO_2 and stirred at RT for 17 h. The product was then precipitated with diethyl ether, filtered off and washed with diethyl ether. The crude product was then dissolved in boiling methanol, cooled to RT and re-precipitated with diethyl ether to give **16** (0.245 g, 37 %). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 6.50 (t, unresolved, 1H; N*H*), 6.10 (t, unresolved, 1H; N*H*), 4.84 (s; H1-CD), 3.62 – 2.93 (m, 56H; H2 to H6-CD, O*H*-CD), 1.34 (m, 14H; C*H*$_2$ propyl), 0.83 (m, 21H; C*H*$_3$ propyl); ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 159.2 (CONH), 103.1 (C_1), 84.8 (C_4), 73.3 (C_3), 71.9 (C_2), 59.0 (C_5), 41.9 (C_6), 23.9 (CH_2), 12.1 (CH_3); IR (KBr): $\tilde{\nu}$ = 3367 (NH, OH), 2961 – 2875 (C–H propyl), 1637 cm^{-1} (*CO*NH); UV/Vis (MeOH): λ_{max} (ε) = 260 nm (603 mol^{-1} dm^3 cm^{-1}); MALDI (FTICR) MS (*para*-nitroaniline): *m*/*z* (%): 1746 [*M*+Na]$^+$ (58), 1660 [*M*+Na – 86]$^+$; elemental analysis calcd (%) for $C_{70}H_{126}N_{14}O_{35}\cdot 7H_2O$ (1849.9): C 45.45, H 7.63, N 10.60; found: C 45.77, H 7.15, N 10.20.

{Heptakis-[2,3-di-*O*-methyl-6-deoxy-6-(5-methyleneureido-5′-methyl-2,2′-bipyridyl)]-cyclomaltoheptaose} europium(III) chloride (17): A solution $EuCl_3$ (0.024 g, 0.06 mmol, 1.1 equiv) in MeOH (5 mL) was added to a solution of heptakis-(2,3-di-*O*-methyl-6-deoxy-6-(5-methyleneureido-5′-methyl-2,2′-bipyridyl)]-cyclomaltoheptaose (**14**) (0.15 g, 0.05 mmol) in MeOH (10 mL).The mixture was stirred at RT for 24 h. The solution was then concentrated under reduced pressure. The product was precipitated with diethyl ether, filtered off and washed several times with diethyl ether. Pure **17** (0.116g, 71 %) was obtained as a pink powder. ^{1}H NMR (400 MHz, CD_3OD, $-4\,^\circ$C): δ = 8.77 (s, 1H; H6-bpy), 8.56 (s, 1H; H6′-bpy), 8.38 (s, 1H; H3-bpy), 8.30 (s, 1H; H3′-bpy), 8.07 (s, 1H; H4-bpy), 7.85 (s, 1H; H4′-bpy), 5.16 (br s, 7H; H1-CD), 4.27 (br s, 7H), 3.33 (br s, 42H; C*H*$_3$O-CD), 2.46 (br s, 21H; C*H*$_3$-bpy); ^{13}C CPMAS (75 MHz, rs = 8 KHz): δ = 160 (*CO*NH), 154 ($C_{2'}$, $C_{2''}$), 150($C_{6'}$, $C_{6''}$), 138 ($C_{4'}$, $C_{4''}$, $C_{5'}$, $C_{5''}$), 121 ($C_{3'}$, $C_{3''}$), 100 (C_1), 84 (C_4), 70 (C_2, C_3, C_5), 60 (OCH_3), 42 (CH_2), 19 (CH_3); IR (KBr): $\tilde{\nu}$ = 3401 (NH), 1654 (*CO*NH), 1560 cm^{-1} (C=C aromatics); UV/Vis (MeOH): λ_{max} (ε) = 284 nm (90904 mol^{-1} dm^3 cm^{-1}); plasma torch analysis calcd for a solution of **17** ($c = 3.4\times10^{-4}$ mol L^{-1}): equiv (Eu^{3+}): 53 mg L^{-1}; found: 72 mg L^{-1}.

[Heptakis-(6-deoxy-6-propyl)-cyclomaltoheptaose] europium(III) chloride (18): A solution of $EuCl_3$ (0.02 g, 0.06 mmol, 1.1 equiv) in MeOH (15 mL) was added to a solution of heptakis-(6-deoxy-6-propyl)-cyclomaltoheptaose (**16**) (0.095 g, 0.055 mmol) in MeOH (10 mL). The mixture was stirred at RT for 24 h. The solution was then evaporated to dryness, and the final product was precipitated with diethyl ether, filtered off and washed with diethyl ether to give **18** (0.10 g, 90 %) as a powder. IR (KBr): $\tilde{\nu}$ = 3338 (NH, OH), 1628 cm^{-1} (*CO*NH); UV/Vis (MeOH): λ_{max} (ε) = 260 nm (760 mol^{-1} dm^3 cm^{-1}); MALDI (FTICR) MS (*para*-nitroaniline) *m*/*z* (%): 1946 (35) [*M*+Eu+(Cl)$_2$]$^+$, 1911 (45) [*M*+Eu+Cl]$^{2+}$, 1876 (40) [*M*+Eu]$^{3+}$, 1790 (68) [*M*+Eu – 86]$^{3+}$.

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