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Bipyridine-coupled Permethylated β-Cyclodextrin

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

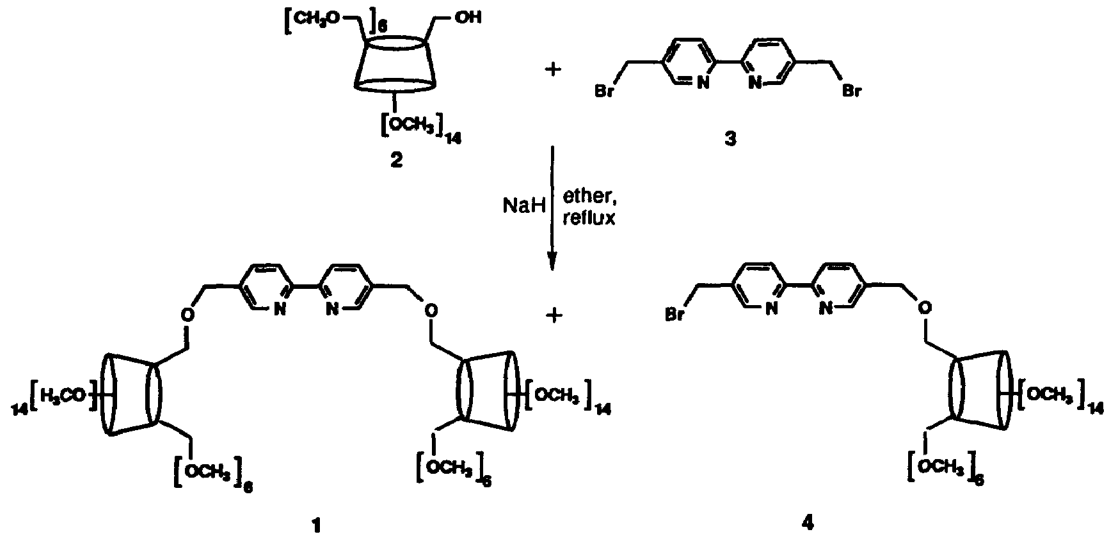
Abstract : The synthesis and characterization of a cyclodextrin dimer, obtained by connecting two permethylated β-cyclodextrins with a 2,2'-bipyridine ligand, and of its luminescent Re(I) metal complex are described. Such a system is of interest to study energy transfer between the active metal center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

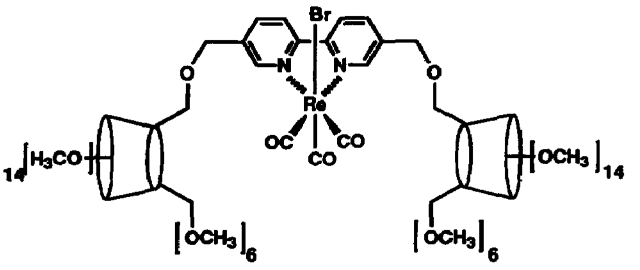
The design and synthesis of multifunctional receptors exhibiting novel properties and functions is a current research area of great importance.[1] The possibility to mimic natural-occuring processes for further exploring and better understanding complex phenomena, such as those associated with electron(s)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

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

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

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





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

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

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

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

Table . Spectroscopic Properties and Electrochemical Data.

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

[a] Measured in MeCN.

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

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

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

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10. Selected analytical data : **1** : $R_f = 0.17$ (silicagel, toluene/isopropanol 1:1) ; Anal. Calc. for $C_{136}H_{228}N_2O_{70}$ (3011.31) : C 54.25, H 7.63, N 0.93 ; found C 53.44, H 7.73, N 0.79 ; PDMS : m/z = 3034.4 $[M+Na]^+$. **4** : $R_f = 0.39$ (silicagel, toluene/MeOH/ether 1:1:7) ; Anal. Calc. for $C_{74}H_{119}Br\ N_2O_{35}$(1976.66) : C 53.01, H 7.15, N 1.67 ; found C 53.41, H 7.48, N 1.25 ; PDMS : m/z = 1678.0 $[M+H]^+$. **5** : $R_f = 0.18$ (silicagel, toluene/MeOH/ ether 1:3:7) ; Anal. Calc. for $C_{139}H_{228}BrN_2O_{73}Re$ (3361.45) :PDMS : m/z = 3361.6 $[M+H]^+$; IR (KBr pellet)ν_{CO} 2022, 1921, 1899 cm^{-1} ; $[\alpha]_D = +83°$ (c = 0.15 in $CHCl_3$).
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