

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

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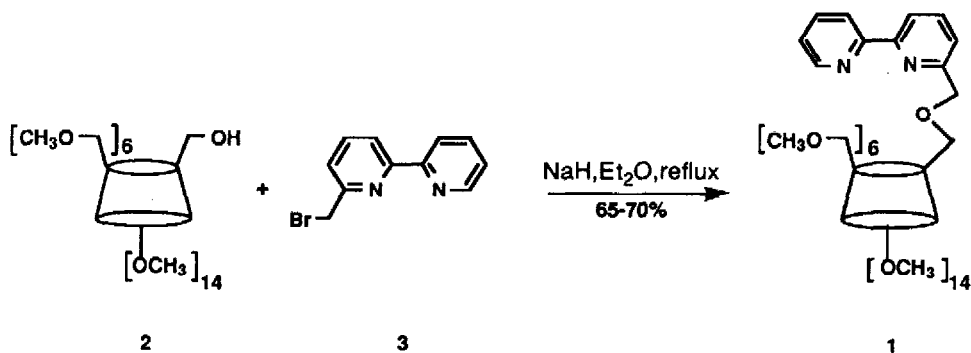
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**Abstract :** A  $\beta$ -cyclodextrin substituted with a 2,2'-bipyridine (abbreviated to CD(per-OMe)-bpy) and the complexes [(CD(per-OMe)-bpy)Ir( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Cl]Cl, [(CD(per-OMe)-bpy)Rh( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Cl]Cl and (CD(per-OMe)-bpy)Re(CO)<sub>3</sub>Br have been synthesized, and their properties examined.

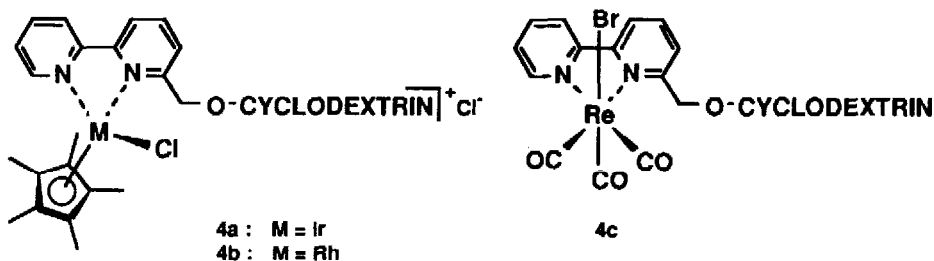
Supramolecular photochemistry is currently a field of intense activity, and interesting results have been obtained.<sup>1</sup> The principal motivation of the studies is the possibility of obtaining fundamental information for the better understanding of photobiological processes. The design, synthesis,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

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

Compound **1** was synthesized by reacting the monohydroxy- $\beta$ -cyclodextrin **2**<sup>4</sup>, 6-bromomethyl-2,2'-bipyridine **3**<sup>5</sup> and NaH in dry Et<sub>2</sub>O, at reflux. Purification by column chromatography (silicagel, toluene/methanol/isopropanol 15:1:1) resulted in pure CD(per-OMe)-bpy<sup>6</sup> (white solid, 65-70%). A positive circular dichroism band at 280 nm (MeCN,  $c = 7.8 \times 10^{-5} \text{M}$ ) due to the  $\pi$ - $\pi^*$  transition would seem to indicate that the bipyridine is oriented towards the cavity, resulting in a capped conformation.<sup>7</sup> This is supported by space-filling models. Such orientations have already been observed for other modified cyclodextrins.<sup>1c</sup>



The metal complexes **4a-c** were prepared from **1** by treatment with [Ir( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Cl<sub>2</sub>]<sub>2</sub>, [Rh( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Cl<sub>2</sub>]<sub>2</sub> and Re(CO)<sub>5</sub>Br, respectively, adapting literature procedures.<sup>8</sup> Purification by column chromatography and crystallization yielded the cationic complexes **4a**<sup>6</sup> (87%), **4b**<sup>6</sup> (77%) and the neutral complex **4c**<sup>6</sup> (90%).



The receptor, CD(per-OMe)-bpy, has an absorption maximum,  $\lambda_{\max}$ , at 285 nm ( $\epsilon=15\ 900$ ) [bpy :  $\lambda_{\max}$  280 nm,  $\epsilon=16\ 300$ ].<sup>9</sup> The Ir<sup>III</sup>, Rh<sup>III</sup> and Re<sup>I</sup> complexes, **4a-c**, show absorption bands comparable with those reported for the corresponding [(bpy)Ir( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Cl]Cl,<sup>8a</sup> [(bpy)Rh( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Cl],<sup>8a</sup> and (bpy)Re(CO)<sub>3</sub>Cl<sup>5</sup> analogues. It is well known that Re(I)-bipyridine complexes are luminescent<sup>8b</sup>, and indeed a strong emission at 603 nm was observed at room temperature when a MeCN solution of **4c** was excited at 390 nm. The emission efficiency was comparable to that of the parent (bpy)Re(CO)<sub>3</sub>Cl complex when both species were excited under the same conditions.

The electrochemical properties of **4c** were investigated by cyclic voltammetry. In addition to a reversible reduction at  $E_{1/2} = -1.34$  V [(bpy)Re(CO)<sub>3</sub>Cl :  $E_{1/2} = -1.37$  V],<sup>5</sup> a reversible oxidation wave was obtained at  $E_{1/2} = +1.38$  V. This is interesting since (bpy)Re(CO)<sub>3</sub>Cl gives an irreversible oxidation peak at the same potential.<sup>5</sup> This result indicates in fact that the Re(II) oxidation state is more stable in **4c** than in the cyclodextrin-free analogue. The origin of this stabilization could be the consequence of an interaction between the metallic centre and the cyclodextrin.

**Table.** Spectroscopic Properties and Electrochemical Data

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

<sup>a</sup> Measured in MeCN.

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

<sup>c</sup> Separation between anodic and cathodic peak potentials.  $\Delta E_p$  for Cp<sub>2</sub>Fe, under the same conditions was 70 mV. No compensation was made for internal cell resistance.

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

## References and Notes

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6. Selected analytical data :  
**1** : m.p.= 98-101°C ;  $R_f = 0.42$  (silicagel, toluene/isopropanol 1:1) ;  $[\alpha]_D = +143$  (c = 0.15 in  $\text{CHCl}_3$ ) ;  
 Anal. Calc. for  $\text{C}_{73}\text{H}_{118}\text{O}_{35}\text{N}_2$  (1583.73) : C 55.36, H 7.51, N 1.77 ; found : C 55.10, H 7.43, N 1.43.  
**4a** :  $[\alpha]_D = +114$  (c = 0.15 in  $\text{CHCl}_3$ ) ; FAB : m/z = 1945.8 [M]<sup>+</sup>. **4b** :  $[\alpha]_D = +119$  (c = 0.15 in  $\text{CHCl}_3$ ) ;  
 FAB : m/z = 1855.7 [M]<sup>+</sup>. **4c** :  $R_f = 0.28$  (silicagel, toluene/isopropanol 1:1) ;  $[\alpha]_D = +122$  (c = 0.15 in  $\text{CHCl}_3$ ) ; IR (KBr pellet)  $\nu_{\text{CO}}$  2022, 1920, 1901  $\text{cm}^{-1}$ . Anal. Calc. for  $\text{C}_{76}\text{H}_{118}\text{O}_{38}\text{N}_2$  BrRe (1933.89) :  
 C 47.20, H 6.15, N 1.45 ; found : C 47.90, H 6.16, N 1.15.
7. No circular dichroism signal was observed in a mixture of one equivalent of permethylated  $\beta$ -cyclodextrin and one equivalent of bipyridine under the same conditions.
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