48. Synthesis, Characterization, and Electrochemical and Photophysical Properties of Rhenium(I) and Ruthenium(II) Complexes of 2,2′-Bipyridine Ligand Functionalized β-Cyclodextrins

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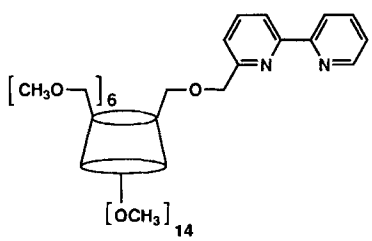
The synthesis, characterization, and electrochemical and photophysical properties of the Re^{I} and Ru^{II} complexes of permethylated β-cyclodextrins, functionalized on the primary face by a 2,2′-bipyridine ligand, are reported. For comparison, model compounds, in which the cyclodextrin was replaced by a Me group, were also prepared and their properties investigated.

Introduction. – The design and synthesis of photo- and electroactive receptors exhibiting novel properties are among the current challenges in supramolecular chemistry. Beautiful systems and interesting studies have been described. The readers are referred to, *e.g.*, the following outstanding references [1].



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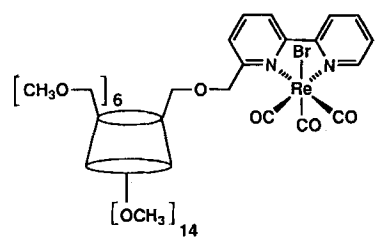

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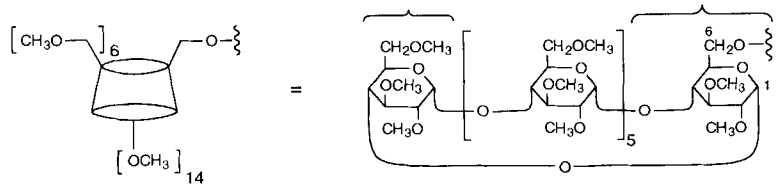


[1]) Part of Ph.D. Thesis of *T. R.*

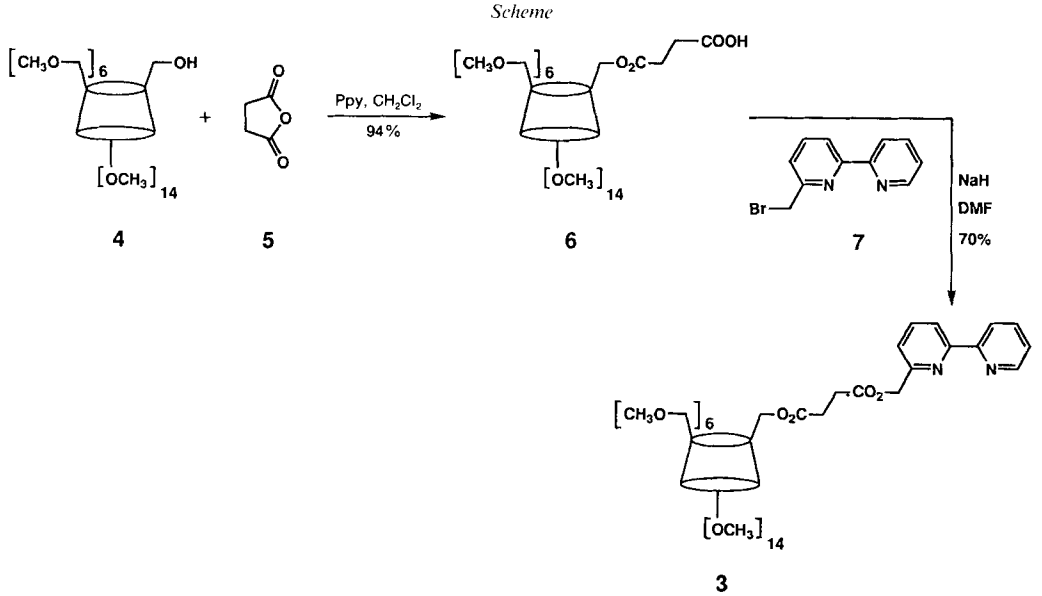
Recently, we reported a novel family of receptors based on the rich host-guest chemistry of the cyclodextrins (CD's) and on the unique complexation features of the 2,2′-bipyridine ligand (bpy) [2]. Compound **1** [2a, b], the first member of the series, was synthesized in good yield from monohydroxylated permethylated β-CD [3] and 6-(bromomethyl)-2,2′-bipyridine [4]. The neutral Re^{I}-complex $[Re(\mathbf{1})(CO)_3Br]$ (**2**) [2a, b] was easily prepared from **1** and $[Re(CO)_5Br]$. High-field NMR studies and fast-atom-bombardment mass spectrometry (FAB-MS) were performed to confirm the structure and purity of **1** and **2**. A dimeric species, obtained by connecting two permethylated β-CD's at the 5,5′-positions of a 2,2′-bipyridine derivative, and its Re^{I} complex were also synthesized [2c]. The latter species are expected to have strong affinity towards ditopic substrates [5].

Pikramenou and *Nocera* [6] reported a β-CD substituted by a macrocyclic ligand and its Eu^{III} complex. Energy transfer was shown to occur between the photoactive lanthanide complex and an encapsulated benzene molecule. This constitutes an elegant example of molecular communication within a supramolecular assembly. It is well-known that $[Re(bpy)(CO)_3Cl]$ is luminescent in solution and at room temperature [7]. Therefore, structures of type **2** should be ideal candidates to investigate energy transfer between the transition-metal complex and a substrate included in the CD cavity. Furthermore, owing to the wide complexation capability of the bipyridine ligand, a large variety of photoactive metal complexes can be prepared.

To fully understand the mechanism of energy transfer, the physicochemical properties of the receptor must be known. We describe, herein, the synthesis of the new bipyridine-modified cyclodextrin **3**, the preparation of the bipyridinerhenium(I) and -ruthenium(II) complexes of **1** and **3** as well as their electrochemical and photophysical properties.

Results and Discussion. – *Syntheses.* Treatment of monohydroxylated permethylated β-CD **4** [3] with succinic anhydride (**5**) (CH_2Cl_2, room temperature, 48 h) gave intermedi-

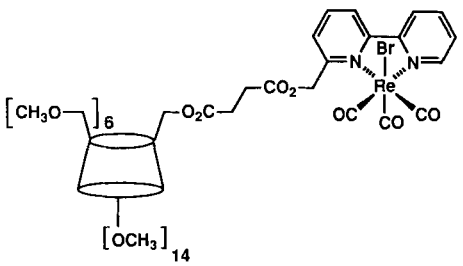
Scheme



4 **5** **6** **7** **3**

ate **6** in 94% yield (*Scheme*). Monoacid **6** was then reacted with 6-(bromomethyl)-2,2′-bipyridine (**7**) [4] (DMF, 80–90°, 14 h) in the presence of NaH. Purification by column chromatography (CC; silica gel, toluene/i-PrOH 4:1) yielded the target receptor **3** (70%).

The rhenium complex of receptor **3**, *i.e.*, compound **8**, was prepared analogously to [Re(**1**)(CO)$_3$Br] (**2**) [2b] from **3** and [Re(CO)$_5$Br] (toluene, reflux, 3 h). After purification by CC (silica gel, toluene/i-PrOH 4:1), the neutral species [Re(**3**)(CO)$_3$Br] (**8**) was obtained in 65% yield. As for complex **2**, the facial geometrical isomer of complex **8** was exclusively formed [7]. The ruthenium complex of receptor **1**, [Ru(**1**)(bpy)$_2$]Cl$_2$ (**9**), was obtained in 71% yield by reacting [Ru(bpy)$_2$Cl$_2$] and **1** (H$_2$O/EtOH 1:1, 80°, 14 h), followed by purification by CC (*RP-18*, THF and then EtOH). For comparison, model compounds **10** and **11**, in which the CD moiety was replaced by a Me group, were also prepared (see *Exper. Part*).



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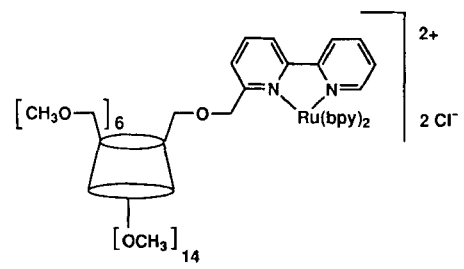

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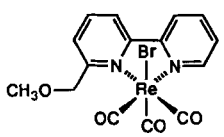

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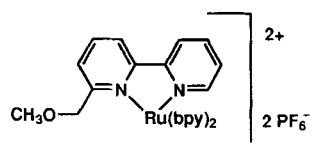

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Photophysical Properties. The investigated compounds are thermally inert, and their absorption spectra show no change within 2–3 days. *Table 1* summarizes data concerning absorption spectra (293 K), emission spectra (77 and 293 K), emission lifetime (77 and 293 K), and emission quantum yields (293 K). Spectra of compounds **2** and **8–10** are

Table 1. *Spectroscopic and Photophysical Properties of* **1–3** *and* **8–10**. Data at room temperature in MeCN solution and at 77 K in EtOH/MeOH 1:4 glass.

	Abs. λ_{max} [nm]	ε [l·mol^{-1}·cm^{-1}]	$Em_{r.t.}$ [nm]	$\tau_{r.t.}$[a]) [ns]	$\Phi_{r.t.}$[a])·10^3	Em_{77K} [nm]	τ_{77K} [μs]	k_r[b]) [μs^{-1}]	k_{nr}[c]) [μs^{-1}]
1	284	15900	376		0.2	433[d])	$1.1 \cdot 10^6$		
	237	11800							
3	283	16100	374		0.3	431[d])	$9.8 \cdot 10^5$		
	237	11500							
2	366	2300	608	28.5	5.47	528	3.18	0.192	34.9
	323	9530							
	298	12300							
	244	17900							

Table 1 (cont.)

	Abs. λ_{max} [nm]	ε [l·mol^{-1}·cm^{-1}]	$Em_{r.t.}$ [nm]	$\tau_{r.t.}$[a]) [ns]	$\Phi_{r.t.}$[a])·10^3	Em_{77K} [nm]	τ_{77K} [μs]	k_r[b]) [μs^{-1}]	k_{nr}[c]) [μs^{-1}]
8	369	2480	610	27.5	5.55	532	2.85	0.202	36.2
	322	8510							
	298	12300							
	244	16900							
9	445	9650	615	8.8	0.86	583	5.17	0.098	110
	288	54700							
	245	21600							
10	367	2610	614	24.0	4.31	530	2.55	0.180	41.5
	322	9170							
	297	11700							
	244	18400							
$[Ru(bpy)_3]^{2+}$	451	14600	611	890[e])	59[e])	585	4.86	0.066	1.06

[a]) In degassed solution. [b]) Calculated as $k_r = \Phi_{r.t.}/\tau_{r.t.}$. [c]) Calculated as $k_{nr} = 1/\tau_{r.t.} - k_r$. [d]) Phosphorescence emission, see text. [e]) See [8].

shown in *Fig. 1* (absorption) and *Fig. 2* (emission). The corrected excitation spectra (not shown) indicate that the intensity of the luminescence band is independent of the excitation wavelength. Data for $[Ru(bpy)_3]^{2+}$ are also added in *Table 1* for comparison.

Receptors **1** and **3** have absorption spectra very similar to that of the bpy ligand [2a]. The absorption spectra of complexes **2** and **8**–**10** are similar to those of the respective cyclodextrin-free analogues, *i.e.*, $[Re(bpy)(CO)_3Br]$ and $[Ru(bpy)_3]^{2+}$. The lowest-energy absorption band (*Table 1*) is assigned to the metal-to-ligand charge transfer (MLCT) transition: $M \rightarrow {}^*\pi(bpy)$. The more intense bands in the UV region at higher energy are of intraligand (IL) origin, as can be seen by comparison with the absorption spectra of the respective uncomplexed ligands **1**, **3**, and bpy.

Receptors **1** and **3** luminescence at room temperature, analogously to the bpy ligand (λ_{em} 350 nm in 3-methylpentane) [9] and to other substituted bipyridine derivatives (λ_{em} 350–360 nm in cyclohexane) [10]. At 77 K, no fluorescence is observed for **1** and **3**: the data in *Table 1* refer to phosphorescence emission, which is very similar to the one observed for the bpy ligand (λ_{em} 433 nm, $\tau = 0.955$ s) [11].

The rhenium and ruthenium complexes **2** and **8**–**10** luminesce both in fluid solution (293 K) and in glass (77 K). The Re^I complexes **2** and **8** feature emission characteristics which are very similar to those exhibited by the model compound **10**. In these three species, the luminescence properties are indicative of a charge-transfer nature of the emitting state. This conclusion can be drawn by usual considerations [7]: *i*) the position and the shape of the emission band are consistent with those previously reported for other polypyridinerhenium(I) complexes, *ii*) the emission band at 77 K is devoid of vibrational structure and blue-shifted with respect to the 293 K emission band, and *iii*) the emission lifetime is in the ns range at 293 K and in the μs range at 77 K.

As far as the blue shift of the emission band on lowering the temperature is concerned, one can note that this blue shift is much more pronounced for the Re complexes ($\Delta \approx 2400$ cm^{-1}) than for the Ru one ($\Delta \approx 900$ cm^{-1}). This appears to be a common phenomenon [7b] [12] and can be explained with the change in solute-solvent interactions which occur on going from the ground state to the excited one. For Re complexes

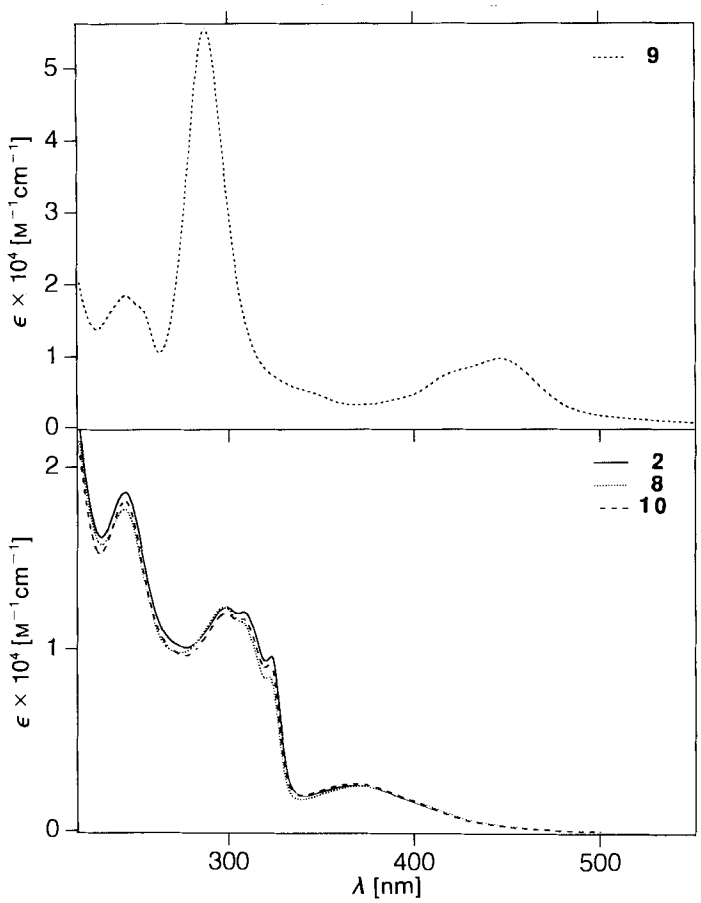

Fig. 1. *Absorption spectra of compounds* **2** *and* **8**–**10** *in acetonitrile solution at room temperature*

(uncharged species), it can be expected that MLCT excitation (Re→bpy) changes considerably the molecular dipole moment: the electron moved is formally localized on the only bpy ligand present. In a frozen matrix (77 K), the solvent molecules cannot undergo dipole reorientation, and the excited complex experiences the solvation environment of the ground-state complex in an energy-demanding situation. The same reasoning could, in principle, also be applied to the Ru-complex **9**, as it is commonly accepted that in $[Ru(bpy)_3]^{2+}$, the MLCT state can be described with the excited electron localized on a single bpy ligand [12] [13]. However, one has to take into account that the charge (2+) of the ruthenium complex dictates the solvation environment and masks the change in dipole moment that occurs on going from the ground state to the excited one.

From the $\Phi_{r.t.}$ and $\tau_{r.t.}$ values, it is possible to evaluate k_r and k_{nr}, *i.e.*, the radiative- and nonradiative-decay rate constants, respectively, of the excited state. One can see that the presence of the CD cup does not influence significantly the k_r and k_{nr} values of the Re complexes. This observation suggests that the bpy arm holding the metal is most

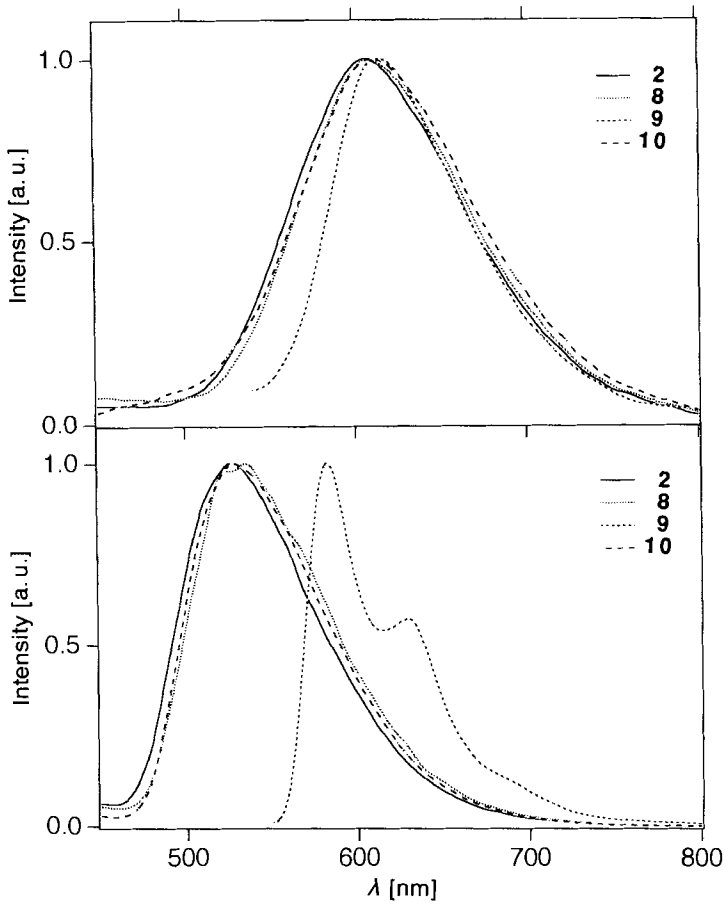

Fig. 2. *Emission spectra of compounds* **2** *and* **8–10** *in acetonitrile solution at room temperature* (top) *and in ethanol/methanol 1:4 glass at 77 K* (bottom)

likely swung away form the base of the CD cup, so that the medium surrounding the metal complex is essentially the same in the presence or in the absence of the CD unit.

For **9**, the emitting level can also be assigned to a MLCT state by analogy to the $[Ru(bpy)_3]^{2+}$ complex [7a] [12]. The only difference with $[Ru(bpy)_3]^{2+}$ deals with the emission quantum-yield and lifetime values at room temperature which are both much smaller for **9**. This finding is undoubtedly due to the fact that the bpy ligand is connected to the CD unit through the 6-position. This is sterically demanding for the Ru complex, so that the bite of the ligands around the metal is no longer optimal. In turn, this causes a weaker ligand-field splitting of the d-orbitals on the metal with a lowering of the ^{3}MC state, which facilitates a nonradiative conversion to the ground state. Indeed, it can be seen from *Table 1* that the k_{nr} value for **9** is two orders of magnitude greater than that of $[Ru(bpy)_3]^{2+}$. Increase of k_{nr} due to sterically hindering ligands is a well known phenomenon [14]. Interestingly, the same steric effect is not observed with the Recomplexes **2** and **8**: molecular models clearly show that around the Re complex, there is enough

room to fit the 6-position of the substituted bpy unit, as the remaining ligands (three CO and one Br) are much less bulky that the two bpy molecules which complete the coordination sphere of the Ru complex **9**.

Electrochemical Properties. The results are collected in *Table 2*. We will first consider the reduction potentials. Scanning cathodically from 0 to −2.1V *vs.* a saturated-calomel electrode (SCE), the cyclovoltammogram showed one (for the rhenium) or three (for the ruthenium) steps as described in previous studies [16] [17]. The reversible waves observed for these complexes correspond to one or three successive one-electron ligand-based reduction processes. The redox potentials determined for the cyclodextrin-containing rhenium (**2** and **8**) and ruthenium (**9**) complexes are very close to the redox potentials of the parent cyclodextrin-free compounds **10** and **11**, respectively, and to those reported for $[Re(bpy)(CO)_3Cl]$ [16] and for $[Ru(bpy)_3]^{2+}$ [17], indicating that the interaction between the complex and the CD cup is very weak. This finding is in agreement with the results obtained from the photophysical investigations (see above).

Table 2. *Electrochemical Data* (Cyclic Voltammetry)

	$E_{1/2}$/V[a]) (ΔE/mV[b]))
2	+1.41 (60), −1.33 (70)
8	+1.41 (60), −1.29 (60)
10	+1.34 (80), −1.34 (70)
$[Re(bpy)(CO)_3Cl]$	+1.37 (irr)[c]), −1.34 (60)
9	+1.29 (80), +1.03 (qr)[d]), −1.23 (60), −1.42 (70), −1.69 (70)
11	+1.28 (80), −1.22 (60), −1.41 (70), −1.68 (90)
$[Ru(bpy)_3]^{2+}$	+1.27 (100), +1.03 (qr)[d]), −1.26 (70), −1.43 (80), −1.70 (80)

[a]) Measured in anhydrous MeCN in 0.1M TBAP (for the rhenium complexes **2**, **8**, **10**, and $[Re(bpy)(CO)_3Cl]$), and in anhydrous dimethylformamide in 0.1M TBAH (for the ruthenium complexes **9**, **11**, and $[Ru(bpy)_3]^{2+}$), under Ar, at room temperature (reference electrode SCE, internal reference $Fc/Fc^+ + 0.39$ V), at 200 mV/s.

[b]) Separation between anodic and cathodic peak potentials ΔE_p (Fc/Fc^+ 80 mV), under the same experimental conditions. No compensation was made for internal cell resistance.

[c]) Anodic peak potential.

[d]) Quasi-reversible oxidation of the Cl^- anion (see [15]).

The behavior of complexes **2**, **8**, and **9** on oxidation can be easily rationalized with the behavior of **10** and **11**. Scanning from 0 to +1.7 V (*vs.* SCE) shows an anodic and a cathodic peak for both the cyclodextrin-containing rhenium (**2** and **8**) and ruthenium (**9**) complexes, with a peak potential separation of 60 mV (**2** and **8**) and 80 mV (**9**). Coulometric oxidation (*vs.* SCE) of these three complexes is monoelectronic ($n = 0.98$ e at +1.51 V for **2** and **8**, and $n = 0.95$ e at 1.40 V for **9**), and no degradation of the oxidized complexes is observed after exhaustive coulometric back-reduction (*vs.* SCE) at +1.30 V for **2** and **8**, and at +1.17 V for **9**. The results of the rhenium(I) complexes are of interest since $[Re(bpy)(CO)_3Cl]$ gave an irreversible oxidation peak (at the same potential) as previously described [7] [16]. This stabilization effect being also observed in compound **10**, it is likely to conclude that the Re^{II} oxidation state is more stable in complexes **2**, **8**, and **10** due to a weak interaction between the metallic centre and the O-atom present in the β-position of the linker. When the O-atom is anchored further apart from the metal (*e.g.* in the 5,5′-positions) this effect is less significative, as indeed observed [2c].

Conclusions. – The synthesis and characterization of new receptors obtained by substituting the primary face of a permethylated β-cyclodextrin with 2,2′-bipyridine-ligand derivatives are described. The Re^{I} and Ru^{II} transition-metal complexes were prepared in good yield. The electrochemical and photophysical properties of these systems were examined and found to be similar to those of the parent cyclodextrin-free materials. These results are of prime importance as they show that the combination of a cyclodextrin with a bipyridine framework does not alter neither the remarkable coordination properties of the bipyridine ligand nor the physicochemical characteristics of the transition-metal complexes. Such supramolecular structures are interesting candidates to investigate electron and/or photon transfer between an encapsulated guest molecule and an active metal centre.

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Experimental Part

General. Column chromatography (CC): silica gel *60* (70–230 mesh, ASTM, *Merck*), if not stated otherwise. TLC: aluminium sheets precoated with 0.2 mm silica gel $60F_{254}$ (*Merck*). Melting points: *Büchi-510* instrument (uncorrected). Optical rotations: *Perkin-Elmer-241* polarimeter. UV/VIS Spectra (λ_{max} in nm (ε in $l \cdot mol^{-1} \cdot cm^{-1}$)): in MeCN with a *Uvikon-810* spectrometer. IR Spectra (KBr pellet; in cm^{-1}): *Perkin-Elmer-FTIR-1720* spectrophotometer. ^1H- and ^{13}C-NMR Spectra: *Bruker-AMX-400* spectrometer at 400.13 (^1H) and 100.62 MHz (^{13}C); $SiMe_4$ as internal reference; signal assignment was made by comparison with the spectra of **1** [2b] and **2** [2b] (Glc = glucose unit). MS (in m/z): fast-atom-bombardment ionization (FAB), THGL = thioglycerol matrix; desorption chemical ionization (DCI).

Materials. The synthesis and characterization of receptor **1** [2a,b] and of its Re^{I}-complex **2** [2a,b] were reported. Monohydroxylated permethylated β-cyclodextrin **4** [3] and 6-(bromomethyl)-2,2′-bipyridine (**7**) [4] were prepared following the literature procedures. Solvents were dried prior to use: Et_2O ($MgSO_4$, NaH, $LiAlH_4$), CH_2Cl_2 ($CaCl_2$, P_2O_5), DMF (3 Å molecular sieves). [$Re(CO)_5Br$] was obtained from *Strem Chemicals Inc.* and used as provided. Cyclodextrin derivatives were dried under vacuum at 40° in the presence of P_2O_5.

Photophysical Measurements. Spectrophotometric-grade solvents were used. Measurements were performed with freshly prepared solns. Absorption spectra: *Perkin-Elmer-λ-6* spectrophotometer. Emission spectra: *Perkin-Elmer-LS-50* spectrofluorometer equipped with a *Hamamatsu-R-928* photomultiplier. Emission lifetimes: *Edinburgh-199* single-photon-counting equipment. Emission quantum yields were measured at 20° with the optically diluted method [18] calibrating the spectrofluorometer with a standard lamp. $[Ru(bpy)_3]^{2+}$ in aerated aq. soln. was used as a quantum-yield standard assuming a value of 0.028 [19]. When necessary, samples were degassed by freeze-pump-thaw cycles.

Electrochemistry. Electrochemical measurements were carried out on a classical three-electrode potentiostatic setup composed of a potentiostat, a pilot scanner, a current-potential converter (*EDT-ECP 133*), and an *xy* recorder (*IFELEC IF 3802*). The working electrode was a platinum rotating disk electrode (*SOLEA Tacussel EDI* type, area 3.14 mm^2) used without rotation for cyclic voltammetry. The reference electrode (saturated-calomel electrode = SCE) was connected to the electrolysis cell by a bridge filled with the same solvent and supporting electrolyte as the solution. Measurements were carried out under an Ar flow in anh. MeCN +0.1M tetrabutylammonium perchlorate (TBAP) for the rhenium complexes and in anh. DMF +0.1M tetrabutylammonium hexafluorophosphate (TBAH). The ferrocene/ferrocenium (Fc/Fc^+) couple was used as internal reference.

*6-Deoxy-icosa-*O*-methyl-β-cyclodextrin-6-yl Hydrogen Butanedioate* (**6**). A mixture of monohydroxylated permethylated β-CD **4** (1.0 g, 0.7 mmol), succinic anhydride (**5**; 0.71 g, 7 mmol), Et_3N (5 drops), and pyrrolidinopyridine (21 mg, 0.14 mmol) in dry CH_2Cl_2 (10 ml) was stirred at r.t. for 48 h. The solvent was evaporated and the solid residue treated with toluene and filtered off to remove insoluble compounds. Evaporation of the solvent yielded **6** (1.0 g, 94%) which was used without further purification. R_f 0.14 (toluene/i-PrOH 1:1; H_2SO_4). IR: 1740,

1195, 1163, 1109, 1039. ^{1}H-NMR ($CDCl_3$): 5.16–5.08 (*m*, 7H, H–C(1)(Glc)); 4.55–4.52 (br. *dd*, H_b–C(6)(Glc^1)); 4.20–4.15 (br. *dd*, H_a–C(6)(Glc^1)); 3.97 (*m*, H–C(5)(Glc^1)); 3.80–3.6 (*m*, 18H, H–C(5), H–C(6)(Glc)); 3.66 (*m*, 21H, MeO–C(3)(Glc)); 3.66–3.50 (*m*, 14H, H–C(4), H–C(5)(Glc)); 3.50 (*s*, 21H, MeO–C(2)(Glc)); 3.38–3.41 (4*s*, 18H, MeO–C(6)(Glc)); 3.19 (*m*, 7H, H–C(2)(Glc)); 2.66 (*s*, CH_2COOH); 2.64 (*s*, CH_2COO). FAB-MS (negative mode, THGL): 1513 ([*M* – H]$^-$).

*2,2′-Bipyridine-6-methyl 6-Deoxy-icosa-*O*-methyl-β-cyclodextrin-6-yl Butanedioate* (**3**). To a soln. of **6** (0.200 g, 0.13 mmol) in dry DMF (8 ml), NaH (40 mg, 0.16 mmol) was added and the mixture stirred at r.t. for 1 h. Then 6-(bromomethyl)-2,2′-bipyridine (**7**; 40 mg, 0.16 mmol) was added and the mixture stirred at 100–110° for 14 h. The mixture was cooled to r.t. and hydrolized with H_2O. The aq. phase was extracted with Et_2O (3 × 10 ml), the combined org. phase dried ($MgSO_4$) and evaporated, and the residue purified by CC (toluene/i-PrOH 4:1): 156 mg (70%) of **3**. White solid. M.p. 86°. $[\alpha]_D = +129$ (*c* = 0.152, $CHCl_3$). R_f 0.43 (toluene/i-PrOH 1:1; H_2SO_4 and UV). UV/VIS: 237 (11500), 283 (16100). IR: 1742, 1162, 1110, 1074, 1039. ^{1}H-NMR ((D$_6$)acetone): 8.68 (*m*, H–C(bpy)); 8.50 (*m*, H–C(bpy)); 8.43 (*d*, H–C(bpy)); 8.00 (*t*, H–C(bpy)); 7.93 (*m*, H–C(bpy)); 7.5 (*d*, H–C(bpy)); 7.42 (*m*, H–C(bpy)); 5.36 (*s*, CH_2–C(6)(bpy)); 5.12 (*m*, 7H, H–C(1)(Glc)); 4.58 (*dd*, H_b–C(6)(Glc^1)); 4.37 (*dd*, H_a–C(6)(Glc^1)); 3.90–3.60 (*m*, 19H, H–C(5), H–C(6)(Glc)); 3.61–3.57 (series of *s*, 21H, MeO–C(3)(Glc)); 3.57–3.50 (*m*, 7H, H–C(4)(Glc)); 3.49–3.47 (series of *s*, 21H, MeO–C(2)(Glc)); 3.46–3.40 (*m*, 7H, H–C(3)(Glc)); 3.31 (series of *s*, 18H, MeO–C(6)(Glc)); 3.09–3.08 (*dd*, 7H, H–C(2)(Glc)); 2.80 (*m*, CH_2CH_2). ^{13}C-NMR ($CDCl_3$): 172.5, 172.4 (C=O); 156.5, 155.8, 149.8, 138.3, 137.6, 124.5, 122.0, 121.9, 120.7 (bpy); 100.4–99.6 (5*s*, C(1)(Glc)); 82.7–82.2 (5*s*, C(2)(Glc)); 81.44–80.8 (5*s*, C(3), C(4)(Glc)); 72.1–71.9 (4*s*, C(6)(Glc)); 71.6, 70.0, 67.9 (C(5)(Glc^1)); 64.8, 64.4 (C(6)(Glc)); 62.2–62.1 (*Me*O–C(3)(Glc)); 59.7–59.1 (*Me*O–C(2), *Me*O–C(6)(Glc)); 29.7, 29.6 (CH_2).

Complexes **8** *and* **10**. The Re-complexes **8** and **10** were obtained in 65% yield from **3** and 6-(methoxymethyl)-2,2′-bipyridine (prepared by treatment of **7** with MeONa/MeOH for 2 h at r.t. followed by CC purification (CH_2Cl_2/MeOH 98:2)), resp., and [Re(CO)$_5$Br] following the procedure used to synthesize **2** [2b].

Data of (2,2′-Bipyridine-6-methyl-κ^2N,N′ *6-Deoxy-icosa-*O*-methyl-β-cyclodextrin-6-yl Butanedioate)bromotricarbonylrhenium(I)* **8**: M.p. 103–106°. $[\alpha]_D = +100$ (*c* = 0.140, $CHCl_3$). R_f 0.26 (toluene/i-PrOH 1:1; H_2SO_4 and UV). UV/VIS: 244 (16900), 298 (12300), 322 (8510), 369 (2480). IR: 2024, 1920, 1903, 1742, 1607, 1164, 1110, 1037. ^{1}H-NMR ((D$_6$)acetone): 9.21 (*d*, H–C(bpy)); 8.73 (*d*, H–C(bpy)); 8.69 (*d*, H–C(bpy)); 8.34 (2*t*, 2H–C(bpy)); 7.97 (*d*, H–C(bpy)); 7.82 (*m*, H–C(bpy)); 5.66 (*m*, CH_2–C(bpy)); 5.15–5.09 (*m*, 7H, H–C(1)(Glc)); 4.45–4.39 (*m*, H_b–C(6)(Glc^1)); 3.97–3.79 (*m*, H–C(5), H_b–C(6)(Glc)); 3.61–3.59 (series of *s*, 21H, MeO–C(3)(Glc)); 3.48–3.47 (series of *s*, 21H, MeO–C(2)(Glc)); 3.58–3.35 (*m*, 20H, H–C(3), H–C(4), H_a–C(6)(Glc)); 3.46–3.35 (*m*, 7H, H–C(3)(Glc)); 3.33–3.28 (series of *s*, 18H, MeO–C(6)(Glc)); 3.10 (*dd*, 7H, H–C(2)(Glc)); 2.83 (*m*, CH_2CH_2). FAB-MS (positive mode, THGL): 2032 (M^+), 1953 ([*M* – Br]$^+$). Anal. calc. for $C_{80}H_{122}BrN_2O_{41}Re \cdot$ toluene (2126.11): C 49.15, H 6.16, N 1.32; found: C 49.31, H 6.55, N 1.30.

Data of Bromotricarbonyl[6-(methoxymethyl)-2,2′-bibpyridine-κ^2N,N′*]rhenium(I)* (**10**): R_f 0.47 (toluene/i-PrOH 1:1). UV/VIS: 244 (18400), 297 (11700), 322 (9170), 367 (2610). IR: 2020, 1921, 1905. ^{1}H-NMR ((D$_6$)acetone): 9.30 (*d*, H–C(3′)); 8.83 (*d*, H–C(6′)); 8.74 (*d*, H–C(3)); 8.44 (*AB*, 2H, H–C(4), H–C(5′)); 8.09 (*d*, H–C(5)); 7.92 (*t*, H–C(4′)); 5.02 (*s*, MeOCH_2); 3.67 (*s*, MeO). ^{1}H-NMR ($CDCl_3$): 9.15 (*d*, H–C(3′)); 8.21 (*d*, H–C(6′)); 8.03–8.12 (*m*, H–C(3), H–C(4), H–C(5′)); 7.94 (*d*, H–C(5)); 7.54 (*m*, H–C(4)); 5.01, 4.98, 4.93, 4.89 (*AB*, MeOCH_2); 3.67 (*s*, MeO). DCI-MS (NH_3): 568 ([*M* + NH_3]$^+$), 550 (M^+), 522 ([*M* – CO]$^+$), 471 ([*M* – Br]$^+$). Anal. calc. for $C_{15}H_{12}BrN_2O_4Re$ (550.38): C 32.73, H 2.20, N 5.09; found: C 31.88, H 2.26, N 4.81.

Bis(2,2′-bipyridine-κ^2N,N′*){6-[(icosa-*O*-methyl-β-cyclodextrin-6-*O*-yl)methyl]-2,2′-bipyridine-*κ^2N,N′*}-ruthenium(II) Dichloride* **9**. An equimolar amount of **1** and [Ru(bpy)$_2$Cl$_2$] in H_2O/EtOH 1:1 was stirred at 80° for 14 h. The soln. was evaporated and the solid residue first washed with Et_2O and then purified by CC (*RP-18*, THF, then EtOH): **9** (71%). UV/VIS: 245 (21600), 288 (54700), 445 (9650). IR: 1636, 1606, 1194, 1163, 1142, 1108, 1088, 1071, 1038. ^{1}H-NMR ((D$_6$)acetone): 8.87–8.74, 8.35–8.17, 8.10–8.09, 7.99–7.76, 7.62–7.56, 7.52–7.49 (series of *m*, 23H, bpy); 5.28, 5.21 (2*s*, CH_2–bpy); 5.16–5.09 (*m*, 7H, H–C(1)(Glc)); 4.86–4.72 (*dd*, H_b–C(6)(Glc^2)); 4.45–4.32 (*dd*, 1H, H_a–C(6)(Glc)); 3.89–3.66 (*m*, 13H, H–C(5), H_b–C(6)(Glc)); 3.59 (*m*, 21H, MeO–C(3)(Glc)); 3.61–3.36 (*m*, 20H, H–C(3), H–C(4), H_a–C(6)(Glc)); 3.48 (*m*, 21H, MeO–C(2)(Glc)); 3.33–3.25 (*m*, 18H, MeO–C(6)(Glc)); 3.18 (*m*, 7H, H–C(2)(Glc)). FAB (positive mode, THGL): 1998, 1996 ([*M* – Cl]$^+$).

Bis(2,2′-bipyridine-κ^2N,N′*)[6-(methoxymethyl)-2,2′-bipyridine-*κ^2N,N′*]ruthenium(II) Hexafluorophosphate* **11**. A soln. of 6-(methoxymethyl)-2,2′-bipyridine (25 mg, 0.12 mmol) and [Ru(bpy)$_2$Cl$_2$] (62 mg, 0.12 mmol) in H_2O/EtOH 1:1 (2 ml) was heated at 80° for 3 h. The mixture was evaporated and the solid residue dissolved in H_2O and then treated with a sat. aq. soln. of NH_4PF_6 (5 ml). The precipitate was filtered, washed with cold H_2O,

and dried: 70 mg (63%) of **11**. ^{1}H-NMR ((D$_6$)acetone): 9.90–8.91, 8.42–8.29, 8.06–7.89, 7.74–7.62 (series of *m*, 23H, bpy); 4.38 (*d*, 1H, C*H*$_2$–bpy); 3.69 (*d*, 1H, C*H*$_2$–bpy); 2.93 (*s*, MeO, in CD_2Cl_2). Anal. calc. for $C_{32}H_{28}F_{12}N_6OP_2Ru$ (903.59): C 42.54, H 3.12, N 9.30; found: C 42.24, H 3.31, N 9.05.

REFERENCES

[1] 'Frontiers in Supramolecular Organic Chemistry and Photochemistry', Eds. H.-J. Schneider and H. Dürr, VCH Verlagsgesellschaft, Weinheim, 1991; V. Balzani, F. Scandola, 'Supramolecular Photochemistry', Horwood, Chichester, 1991.

[2] a) N. Brügger, R. Deschenaux, T. Ruch, R. Ziessel, *Tetrahedron Lett.* **1992,** *33,* 3871; b) R. Deschenaux, M.M. Harding, T. Ruch, *J. Chem. Soc., Perkin Trans. 2* **1993,** 1251; c) R. Deschenaux, A. Greppi, T. Ruch, H.-P. Kriemler, F. Raschdorf, R. Ziessel, *Tetrahedron Lett.* **1994,** *35,* 2165.

[3] M. Tanaka, Y. Kawaguchi, T. Niinae, T. Shono, *J. Chromatogr.* **1984,** *314,* 193.

[4] R. Ziessel, J.-M. Lehn, *Helv. Chim. Acta* **1990,** *73,* 1149.

[5] R. Breslow, B. Zhang, *J. Am. Chem. Soc.* **1994,** *116,* 7893; B. Zhang, R. Breslow, *ibid.* **1993,** *115,* 9353; R. Breslow, B. Zhang, *ibid.* **1992,** *114,* 5882; F. Venema, C.M. Baselier, E. van Dienst, B.H.M. Ruël, M.C. Feiters, J.F.J. Engbersen, D.N. Reinhoudt, R.J.M. Nolte, *Tetrahedron Lett.* **1994,** *35,* 1773.

[6] Z. Pikramenou, D.G. Nocera, *Inorg. Chem.* **1992,** *31,* 532.

[7] a) K. Kalyanasundaram, 'Photochemistry of Polpyridine and Porphyrin Complexes', Academic Press, London, 1992; b) D.J. Stufkens, *Comments Inorg. Chem.* **1992,** *13,* 359.

[8] K. Nakamaru, *Bull. Chem. Soc. Jpn.* **1982,** *55,* 1639.

[9] E. Castellucci, L. Angeloni, G. Marconi, E. Venuti, I. Baraldi, *J. Phys. Chem.* **1990,** *94,* 1740.

[10] E. Castellucci, L. Angeloni, A. Juris, G. Marconi, R. Ziessel, *J. Photochem. Photobiol., A* **1992,** *67,* 311.

[11] M.K. De Armond, J.E. Hillis, *J. Chem. Phys.* **1971,** *54,* 2247.

[12] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. von Zelewski, *Coord. Chem. Rev.* **1988,** *84,* 85.

[13] W.K. Smothers, M.S. Wrighton, *J. Am. Chem. Soc.* **1983,** *105,* 1067.

[14] K. Araki, M. Fuse, N. Kishii, S. Shiraishi, *Bull. Chem. Soc. Jpn.* **1992,** *65,* 1220, and ref. cit. therein.

[15] G. Cauquis, A. Deronzier, B. Sillion, B. Damin, J. Garapon, *J. Electroanal. Chem. Interfacial Electrochem.* **1981,** *117,* 139.

[16] J.C. Luong, L. Nadjo, M.S. Wrighton, *J. Am. Chem. Soc.* **1978,** *100,* 5790.

[17] N.E. Tokel-Takvoryan ,R.E. Hemingway, A.J. Bard, *J. Am. Chem. Soc.* **1973,** *95,* 6582.

[18] J.N. Demas, G.A. Crosby, *J. Phys. Chem.* **1971,** *75,* 991.

[19] K. Nakamaru, *Bull. Chem. Soc. Jpn.* **1982,** *55,* 2697.