A Novel Organometallic Polymer of Osmium(0), $[Os(2,2'\text{-bipyridine})(CO)_2]_n$: Its Electrosynthesis and Electrocatalytic Properties Towards CO_2 Reduction

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A new kind of organometallic polymer of osmium(0) $[Os^0(bpy)(CO)_2]_n$ (bpy = 2,2′-bipyridine) has been prepared as a thin film on an electrode surface by electrochemical reduction of the mononuclear *trans*(Cl)-$[Os^{II}(bpy)(CO)_2Cl_2]$ precursor complex. This modified electrode proves to be a good electrocatalyst for the reduction of CO_2 in aqueous media.

Introduction

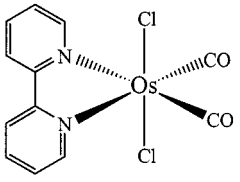
It is now well established that the two-electron reduction of a mononuclear ruthenium(II) complex precursor such as *trans*(Cl)-$[Ru(bpy)(CO)_2Cl_2]$ (bpy = 2,2′-bipyridine) leads to the facile formation of thin films of $[Ru(bpy)(CO)_2]_n$ on conductive electrode surfaces.[1,2] This new kind of organometallic polymer, containing Ru−Ru chains, proved to be a highly selective and efficient catalyst for the electroreduction of carbon dioxide in aqueous media[3,4] and for the water-gas shift (WGS) reaction.[5] It also exhibits interesting photochemical properties.[6] We could reasonably expect formation of an analogous Os^0 organometallic polymer by the electrochemical reduction of the parent mononuclear osmium(II) complex *trans*(Cl)-$[Os(bpy)(CO)_2Cl_2]$ (**1**), which has recently been synthesized but only superficially characterized.[7]

We present here a preliminary electrochemical study of **1** which confirms that films of the $[Os(bpy)(CO)_2]_n$ polymer can indeed be prepared effectively. Their capability to act as an electrocatalyst for CO_2 reduction has been briefly evaluated.

Results and Discussion

Synthesis of Complex 1

The complex *trans*(Cl)-$[Os(bpy)(CO)_2Cl_2]$ (**1**) was synthesized in two steps according to a modified literature procedure[7] (see Experimental Section). The ^1H NMR spectroscopic data reveal that the bpy ligand coordinates in a symmetrical environment, with the chloride ligands occupying the axial positions as schematically depicted in Figure 1.



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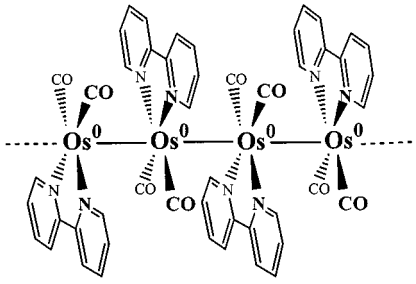

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Figure 1. Schematic molecular structures of **1** and **2**

The IR spectrum of **1** displays two intense CO-stretching bands (2022 and 1943 cm^{-1}) shifted to lower frequencies relative to the corresponding *trans*(Cl)-$[Ru(bpy)(CO)_2Cl_2]$ complex.[8] It is noteworthy that the ν(CO) band shifts of 41/56 cm^{-1} in the solid state (CsI pellet or nujol) are much larger than the values of 23/31 cm^{-1} in CH_3CN and 24/33 cm^{-1} in THF. The lower ν(CO) frequencies for **1** reflect a stronger Cl→Os σ- and, in particular, π-donation inducing a stronger Os→CO π-back-donation. At the same time the Os−Cl bonds in **1** are stronger and less readily split upon electrochemical reduction than in the Ru derivative, as shown by the radical anion $[Os(bpy^{\cdot-})(CO)_2Cl_2]^-$ detectable by cyclic voltammetry (CV) in THF at moderate scan rates (see below). A similar difference in ν(CO) frequencies and stability of the M−Cl bond was observed, for example,

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in the [M(bpy)(CO)$_3$Cl] complex series (M = Re[9] and Mn[10]).

Electrochemical Behaviour of Complex 1

The CV of **1** in CH_3CN (with added 0.1 M TBAP) exhibits an irreversible nearly two-electron cathodic peak at $E_{pc} = -1.61$ V[11] along with small anodic peaks between -0.80 V and 0 V on the reverse scan [Figure 2(a)]. This behaviour is typical of an electrodeposition-redissolution phenomenon, as previously observed for the parent mononuclear Ru^{II} complex.[1,2]

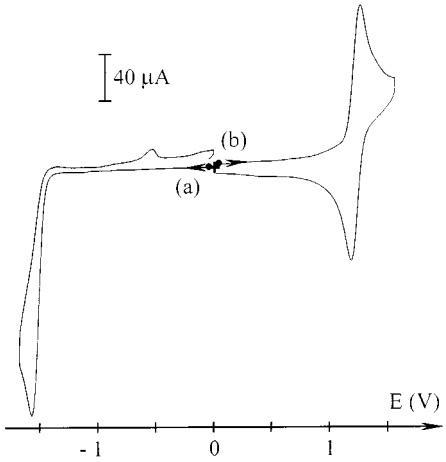

Figure 2. Cyclic voltammograms (ν = 100 mV s^{-1}) of **1** (2.2 mM) in CH_3CN + 0.1 M TBAP at a Pt disc electrode (r = 2.5 mm) recorded between: (a) 0 V and -1.70 V, and (b) 0 V and 1.60 V vs. Ag/Ag$^+$

The negative potential shift observed for the reduction of **1** compared to the corresponding Ru^{II} complex ($\Delta E_{pc} = -0.11$ V)[8] is in agreement with the stronger Os→bpy π-back-donation induced by the Cl→Os donation along with the increased Os→CO π-back-donation, as revealed by the IR ν(CO) data (see above).

The reductive electrochemical polymerization of **1**, monitored by iterative CV or by applied potential electrolysis, leads to a dark green-blue coloured electroactive polymer [Os^0(bpy)(CO)$_2$]$_n$ (**2**) adherent to the working electrode surface. Equation (1) summarizes the overall process of electropolymerization.

$$n\,[Os^{II}(bpy)(CO)_2Cl_2] + 2n\,e^- \rightarrow [Os^0(bpy)(CO)_2]_n + 2n\,Cl^- \quad (1)$$

The electroactivity and electropolymerization properties of the osmium complex **1** are consistent with the mechanism proposed for the electropolymerization of *trans*(Cl)-Ru(bpy) equivalent complex in acetonitrile.[12] The electroreduction of **1** produces ultimately the polymer **2** by an electrochemical propagation process [Equation (2)−(5)]. The initial formation of the one-electron reduced [Os(bpy$^{\bullet-}$)(CO)$_2$Cl$_2$]$^-$ (**1**$^-$) species containing the 2,2′-bipyridine radical anion [Equation (2)] is followed by rapid loss of one chloride ligand to give an Os^I complex [Equation (3)]. This formally 17e$^-$ species readily dimerizes [Equation (4)]. Details of this step will be published in a forthcoming article. The similar or even more facile reducibility of the dimer, and further tetramer and oligomer intermediates compared to that of **1**, allows the growth of a polymeric chain [Equation (5)].

$$[Os^{II}(bpy)(CO)_2Cl_2] + e^- \rightarrow [Os^{II}(bpy^{\bullet-})(CO)_2Cl_2]^- \quad (2)$$

$$[Os^{II}(bpy^{\bullet-})(CO)_2Cl_2]^- \rightarrow [Os^{I}(bpy)(CO)_2Cl] + Cl^- \quad (3)$$

$$2\,[Os^{I}(bpy)(CO)_2Cl] \rightarrow [Os^{I}(bpy)(CO)_2Cl]_2 \quad (4)$$

$$n/2\,[Os^{I}(bpy)(CO)_2Cl]_2 + n\,e^- \rightarrow \text{dimers} \rightarrow \text{oligomers} \rightarrow [Os^0(bpy)(CO)_2]_n + n\,Cl^- \quad (5)$$

Experiments conducted in a less dissociating and coordinating solvent like THF support this overall mechanism. In this solvent the electrogenerated radical anion [Os(bpy$^{\bullet-}$)(CO)$_2$Cl$_2$]$^-$ is remarkably stable, the cyclic voltammogram exhibiting now a nearly reversible one-electron couple at $E_{1/2} = -1.64$ V ($\Delta E_p = 0.17$ V; $I_{pa}/I_{pc} = 0.93$) at a scan rate of 100 mVs^{-1} (Figure 3). However, decreasing the scan rate to 20 mVs^{-1} turns the reduction of **1** almost totally irreversible; an exhaustive electrolysis carried out at -1.80 V then furnished the polymer **2** after two electrons per precursor **1** had been passed (see below). In addition, some UV/Vis, IR and EPR spectroelectrochemical experiments, conducted at low temperatures, are in progress and confirm the localization of the odd electron in the radical anion of **1** on the bpy ligand.

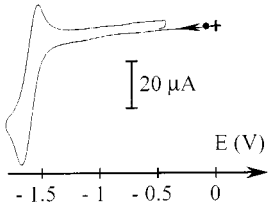

Figure 3. Cyclic voltammogram (ν = 100 mV s^{-1}) of **1** (1.6 mM) in THF + 0.2 M TBAP at a Pt disc electrode (r = 2.5 mm) recorded between 0 V and -1.85 V vs. Ag/Ag$^+$

The growth of the electroactive Os^0 polymeric film **2** can be more conveniently documented by iterative CV carried out in CH_3CN (+ 0.1 M TBAP). Two clear reversible redox systems, characteristic of the polymer electroactivity, appear at $E_{1/2} = -0.80$ V (anodic) and -1.55 V (cathodic) and increase in size continuously as the potential is repeatedly scanned from -0.60 to -1.75 V (Figure 4A). When the resulting modified electrode is transferred into a fresh electrolyte solution in the absence of **1** [Figure 4B(a)], the electroactivity persists and remains unaffected, provided the potential scan is limited to -0.60 V.

The redox properties of **2**, immobilized on the electrode surface, strongly resemble those of [Ru(bpy)(CO)$_2$]$_n$.[2] Their comparison allows us to attribute the reversible anodic system to oxidation of the osmium centre ($Os^{I/0}$) and the reversible cathodic system to the reduction of the bpy ligand (bpy$^{0/\bullet-}$) in the polymer **2**. The complete electropolymerization of **1** (2 mM) can be achieved by its exhaustive controlled-potential electrolysis at a large-surface working electrode at -1.60 V. A quantitative electrical yield (two mol of electron are needed for one mol of precursor complex) is obtained. During this electropolymerization experiment

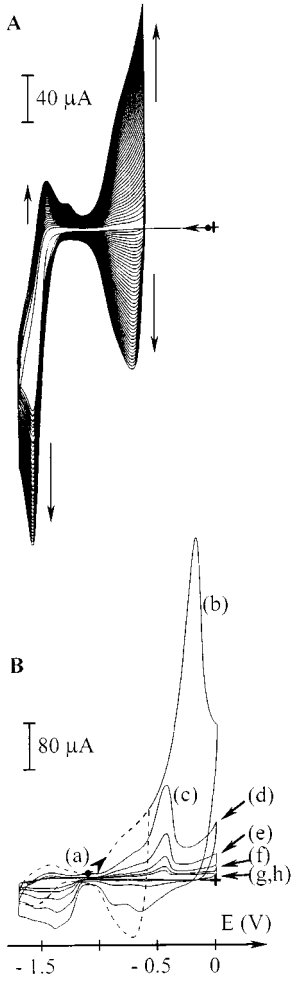

Figure 4. (A) Cyclic voltammograms (ν = 100 mV s^{-1}) of **1** (2.2 mM) in CH_3CN + 0.1 M TBAP at a Pt disc electrode (r = 2.5 mm) from the 1st to the 40th successive scans between −0.60 V and −1.75 V; (B) cyclic voltammograms recorded with the same Pt working electrode modified with surface-deposited **2**, transferred into neat CH_3CN +0.1 M TBAP; scan range: (a) −0.6 V and −1.75 V; (b) − (h) 0 V and −1.75 V vs. Ag/Ag^+

two molar equivalents of chloride ligand were liberated in solution, as revealed by voltammetry on a rotating disk electrode.[13] A comparison of the intensity of the wave at $E_{1/2}$ = 0.60 V (Cl^- oxidation system) with that of a standard solution of chloride confirms the overall stoichiometry of the polymerization process [Equation (1)]. It should be noted that a large anodic peak located at −0.21 V is observed when the potential is scanned back to 0 V [Figure 4B(b)]. This peak corresponds to the oxidation-desorption of the polymer **2** that induces cleavage of the Os−Os bonds, as was also demonstrated for the corresponding Ru^0(bpy) polymer.[8] In fact, successive potential scans in this range of potentials induce the complete disappearance of the polymer film electroactivity [Figure 4B(b)-(h)].

A full physicochemical characterization of the $[Os(bpy)(CO)_2]_n$ polymeric film is not easy to achieve since it is unstable at potentials higher than −0.40 V and cannot be handled in air. However, the molecular structure of **2** presented in Figure 1 is strongly supported by the close resemblance of the physicochemical properties of **2** with those of the corresponding Ru^0 polymer as well as by the following arguments:[2] (a) The insolubility of **2** is in favour of a polymeric structure; (b) The electronic absorption spectrum of the film deposited on optically transparent electrode (OTE) doped with indium tin oxide (ITO) exhibits two broad and intense absorption bands in the visible region (λ_{max} = 554 and 664 nm), consistent with a polymeric structure containing metal−metal bonds and possessing an Os→bpy charge transfer transition;[4] (c) Electropolymerization of **1** consumes exactly two electrons per Os(bpy) moiety and results in decoordination of both Cl^- ligands; (d) The ν(CO) wavenumbers and band pattern of **2** [1958 (vs), 1900 (m) and 1872 (s) cm^{-1}], recorded in THF at 293 K during in situ IR spectroelectrochemical experiments, are close to those of the Ru^0 polymer [1966 (vs), 1908 (s) and 1885 (vs)]. The smaller difference in the ν(CO) wavenumbers between the Os and Ru polymers observed for the parent dichloro complexes (see above), is understandable, as the Cl^- ligands are already dissociated and the metal→CO π-back-donation is therefore not affected.

In the positive potential region, the CV of **1** exhibits a reversible one-electron anodic wave (I_{pa}/I_{pc} = 1) formally corresponding to the Os^{II}/Os^{III} redox couple [Figure 2(b)]. The lower oxidation potential of **1** ($E_{1/2}$ = 1.23 V) than for the corresponding Ru^{II} dichloro complex ($E_{1/2}$ = 1.45 V),[14] again reflects the stronger Cl→Os σ/π-donation. The absence of any associated peak on the reverse cathodic scan on the scale of the CV indicates the stability of the oxidized osmium(III) cationic complex. However, bulk electrolysis at 1.30 V, consuming one electron per mol of **1**, produces a new species which is soluble in the electrolyte and reversibly reducible at a lower potential ($E_{1/2}$ = 0.47 V). Investigation of this novel complex is in progress.

Electrocatalytic Reduction of CO_2 with $[Os(bpy)(CO)_2]_n$ (2)

The electrocatalytic properties of the $[Os(bpy)(CO)_2]_n$ polymer, deposited on the cathode surface as described above, were investigated with CV experiments carried out in CO_2-saturated organic solvents containing ca. 10% water, and pure aqueous media. The initial electroactivity of the polymer in pure CO_2-saturated organic electrolyte [Figure 5(a)] completely changed after addition of 5% water [Figure 5(b)]. In particular, a strong enhancement of the cathodic current at −1.30 V was observed. In addition, repeated voltammetric scanning between −0.70 V and −1.50 V shows that this catalytic effect is persistent. Preparative scale electrolyses, using carbon felt electrodes (10 × 10 × 4 mm^3) modified with electrodeposited $[Os(bpy)(CO)_2]_n$ ($\tau_{Os} = 5 \times 10^{-7}$ mol cm^{-2}), confirm the catalytic activity of this molecular cathode towards CO_2 electroreduction. For instance, preliminary experiments have revealed that electrolysis conducted at −1.23 V vs. SCE in pure aqueous electrolyte (H_2O + 0.1 M $LiClO_4$) produces $HCOO^-$ and CO with 10% and 60% current efficiency, respectively, after 60 C had been consumed. The difference between the $[M(bpy)(CO)_2]_n$ (M = Ru^0 or Os^0) catalysts in the selectivity of the product formation towards formate is noteworthy. It should be recalled that under the same elec-

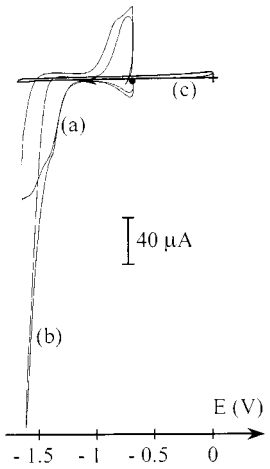

Figure 5. Cyclic voltammograms (ν = 100 mV s^{-1}) in CO_2-saturated CH_3CN + 0.1 M TBAP recorded with a vitreous carbon working electrode (r = 1.5 mm) pre-modified with **2**, deposited during electrolysis of **1** (1.2 mM) at −1.60 V (Q = 5 mC), conditions: (a) before addition of water; (b) after addition of 5% water; (c) zero electroactivity of the naked VC electrode after addition of 5% water

trocatalytic conditions the Ru(bpy) polymer conducts almost quantitative transformation of CO_2 into CO with a current efficiency higher than 97%, whereas the yield of $HCOO^-$ is less than 1%.[3] These results nicely correspond with the different electrocatalytic properties of related mononuclear $[M(bpy)_2(CO)H]^+$ complexes (M = Os^{II} [15] and M = Ru^{II}).[16] In CO_2-saturated CH_3CN with added water the latter Os and Ru complexes act as homogeneous catalysts for the electrochemical reduction of CO_2 to formate with 22% and 17% yield, and to CO with 46% and 57% yield, respectively. Further research to improve the stability and catalytic performance of **2** is in progress.

Conclusion

The strong Cl→Os σ/π-donation makes the axial Os−Cl bonds in *trans*(Cl)-[Os(bpy)$(CO)_2Cl_2$] (**1**) less prone to cleavage upon reduction than the Ru−Cl bonds in the corresponding Ru^{II} complex. Nevertheless, dissociation of the Cl^- ligands is still rapid and produces ultimately the same kind of insoluble, redox-active polymer $[Os^0(bpy)(CO)_2]_n$ (**2**) as reported for Ru. Electrocatalytic reduction of CO_2 in aqueous media, initiated by reduction of **2** deposited on the cathode surface, results in a higher yield of formate production than achieved previously with $[Ru^0(bpy)(CO)_2]_n$. Further investigation of **1**, **2** and closely related complexes is in progress to understand the catalytic mechanism and to improve the catalyst performance.

Experimental Section

General Remarks: K_2OsCl_6 (Alfa) and NH_4Cl (Fluka), formaldehyde and formic acid (both Acros) were used as received. Acetone, hexane, 2-propanol, THF and dichloromethane (all purchased from Acros) were dried by conventional procedures. All syntheses and measurements were performed under an atmosphere of dry nitrogen or argon, using standard Schlenk techniques. Silica gel (kieselgel 60, Merck, 70−230 mesh) for column chromatography was dried and activated by heating in vacuo at 160 °C overnight. The solutions of slightly light-sensitive *trans*(Cl)-[Os(bpy)$(CO)_2Cl_2$] were kept in the dark to avoid photochemical decomposition.

Electrochemical measurements were carried out using an EG & G Princeton Applied Research Model 173 potentiostat-galvanostat equipped with a Sefram TGM 164 X-Y recorder. The cyclic voltammograms were obtained in a conventional three-electrode cell under an argon atmosphere in a dry box (Jaram). The working electrodes for cyclic voltammetry were platinum or vitreous carbon discs (0.19 or 0.07 cm^2) polished with a 2 μm diamond paste (Mecaprex Presi). All potentials are reported relative to Ag|10 mM Ag^+ in CH_3CN + 0.1 M nBu_4NClO_4 (TBAP).[11] The supporting electrolyte, from Fluka, was dried under vacuum at 80° C for 3 days before use. Acetonitrile from Rathburn (HPLC grade) was used as received. THF was freshly distilled from Na/benzophenone.

All preparative-scale electrocatalytic experiments were run under a CO_2 atmosphere on carbon felt pieces (RVC 2000 from Le Carbone Lorraine) modified by a polymer film in a conventional three-electrode cell made air-tight with vacuum grease (M. Apiezon). All experiments were stopped after a predetermined number of coulombs had been passed. The current efficiency corresponds to the theoretical number of mol calculated from the experimental number of coulombs (100% yield)/calculated number of mol after analysis (CO_2 reduction into CO or $HCOO^-$ is a two-electron reduction process). CO was analysed on a Delsi Model 30 gas chromatograph with a FID, with a 120-cm long 5 Å molecular sieve column, followed by a catalytic oven. H_2 was used as carrier gas. Formate ions were analysed on a Waters Associate HPLC with a Bio-Rad HPX-87H cation exchange resin column eluted with 10^{-2} M H_2SO_4 solution. A UV detector at 224 nm was used.

Electronic absorption spectra were recorded with a Hewlett-Packard HP 8452 A diode array spectrophotometer controlled with a Compaq 286 computer. UV/Vis spectroelectrochemical experiments were conducted in a dry box under an argon atmosphere. The cells were inserted into an optical translator connected to the spectrophotometer by an optical fibre system (Photonetics spectrofip system). The optical fibres pass through the wall of the dry box by means of seals. UV/Vis spectroelectrochemical measurements on polymer films were made by using a conventional sandwich-type cell.[17] The optical transparent electrode (OTE) (1.1 cm diameter) was doped with indium tin oxide (ITO) (Balthracon Z 20 from Balzers).

IR spectra were recorded with Perkin−Elmer Spectrum GX FTIR or Bio-Rad FTS-7 FTIR spectrometers. IR spectroelectrochemical experiments at room temperature were carried out with a previously described OTTLE cell equipped with a Pt minigrid working electrode (32 wires/cm) and with CaF_2 windows.[18]

^1H NMR spectra were recorded at room temperature on Bruker AMX 300 or AC-250 spectrometers; the chemical shifts (in ppm) are relative to the solvent $CDCl_3$ (δ = 7.25) or CD_3CN (δ = 1.96).

Synthesis of *trans*(Cl)-[Os(bpy)$(CO)_2Cl_2$] (1) $[Os(CO)_2Cl_2]_n$: K_2OsCl_6 (1 g; 2.1 mmol) was added to an N_2-purged (20 min.) mixture of formaldehyde (15 mL) and formic acid (90%, 50 mL) and refluxed for 3 days. The colour changed from red to green within 3 h and ultimately to light yellow (NB: further reflux produces a brownish solution presumably due to organic decomposition products). Next, the solution was cooled to room temperature and the solvents evaporated. The brownish residue was

extracted with acetone to remove KCl. After evaporation of the acetone the solid was washed with CH_2Cl_2/hexane (1:1) to remove any organic side products. The product was obtained with a yield in the range of 800−900 mg and is a white, occasionally pinkish/yellowish powder. − IR (THF): ν(CO) = 2116 cm^{-1} (m) and 2022 (vs).

***trans*(Cl)-[Os(bpy)(CO)$_2$Cl$_2$] (1):** Polymeric $[Os(CO)_2Cl_2]_n$ (200 mg) and an excess of bpy (5 equiv.) were dissolved in 2-propanol (50 mL) and heated at reflux temperature until the IR spectra showed complete conversion [two intense ν(CO) bands arose at 2040 and 1972 cm^{-1}]. In order to obtain exclusively the desired dichloro complex, the crude product was redissolved in NH_4Cl-saturated CH_2Cl_2 and stirred overnight. The solution was filtered and the resulting complex **1** was purified by column chromatography (activated silica, using CH_2Cl_2/hexane gradient elution) to yield a light yellow powder. Yield: 100 mg (50%). The use of *n*-propanol instead of 2-propanol should be avoided, as it results in significantly lower yields (ca 20%). − IR (THF): ν(CO) = 2032 cm^{-1}(vs), 1962 (vs); in *n*PrOH: ν(CO) = 2041 (vs), 1972 (vs); in CH_2Cl_2: ν(CO) = 2040 (vs), 1971 (vs); in CH_3CN: ν(CO) = 2038 (vs), 1968 (vs); in CsI pellet: ν(CO) = 2022 (vs), 1943 (vs), ν(Os−Cl) 317 (w). − ^{1}H NMR ($CDCl_3$): δ = 9.13 (d, ^3J = 7.2 Hz, 2 H, $H_{6,6'}$), 8.23 (d, ^3J = 10.8 Hz, 2 H, $H_{3,3'}$), 8.13 (t, ^3J = 10.8 Hz, 2 H, $H_{4,4'}$), 7.67 (t, ^3J = 8.0 Hz, 2 H, $H_{5,5'}$). − UV/Vis (THF): λ_{max} = 362 nm; in CH_3CN: λ = 350. − MS (FD^+): *m*/*z* = 474 [M + H]$^+$; (FAB^+): *m*/*z* = 474 [M + H]$^+$, 446 [M + H − CO]$^+$, 439 [M + H − Cl]$^+$, 418 [M + H − 2CO]$^+$, 411 [M + H − 2Cl]$^+$, 383 [M + H − CO − 2Cl]$^+$.

Acknowledgments

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