

Design and spectroscopic study of new ruthenium(II) complexes containing ligands derived from terpyridine and dipyrido[3,2-a:2',3'-c]phenazine: {Ru(4'-Rph-tpy)[dppz(COOH)]Cl}PF₆ with R = NO₂, Br, Cl

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A series of polypyridine ruthenium complexes of the general formula {Ru(Rph-tpy)[dppz(COOH)]Cl}PF₆ with R = Br (1), Cl (2), NO₂ (3) where Rph-tpy is 4'-(4-Rphenyl-2,2':6',2''-terpyridine and dppz(COOH) is dipyrido[3,2-a:2',3'-c]phenazine-2-carboxylic acid were prepared and characterized. These complexes display intense metal-to-ligand charge-transfer (MLCT) bands centered about 500 nm. The effect of pH on the absorption spectra of these complexes consisting of protonatable ligands has been investigated in water solution by spectrophotometric titration. The electrochemistry shows oxidation potentials for the Ru(II)–Ru(III) couple at +0.881 (1), +0.907 (2) and +0.447 V (3), respectively.

KEYWORDS: phenylterpyridine; ruthenium complexes; dipyridophenazine ligand

INTRODUCTION

The design of new ruthenium complexes with polypyridine ligand for their use as catalyst,¹ molecular wires,² and biosensors³ has been a fertile area in the last decades. The application of these complexes as dye-sensitized in solar cell technology is an interesting new area of research.⁴ Scheme 1A shows the molecular orbital of the Ru(II) complex and its relation with the energy levels of a semiconductor, such as TiO₂. If the Ru(II) complex is anchored on the semiconductor surface through a carboxylate group, when an electron jumps from the metal to ligand orbital by visible light absorption, it is injected to the semiconductor empty band, Scheme 1B, thus providing the appropriate charge flow.⁵

In the last years, many groups have been focusing their attention in the design and preparation of new complexes of this type. One the goals of this research is to introduce different functional groups in polypyridine ligand, in order to allow the fine tuning of the redox and spectroscopic properties of the complex.

This work shows the design and the preparation of new metallic complexes with terpyridine 'antenna' functionalized at the 4' position by a phenyl ring, Rph-tpy (R represents a substituent group with different donor or withdrawing capacity; R = Br, Cl or NO₂), and the bidentate planar ligand containing a carboxylic acid group, dipyrido[3,2-f:2',3'-h]phenazine-2-carboxylic acid, dppz(COOH),⁵ which can be used for connection to a TiO₂ surface,⁶ as is known for [Ru(bpy-(COOH))₂(SCN)₂] complexes. Fig. 1 shows these two N-donor ligands and label used in the NMR study.

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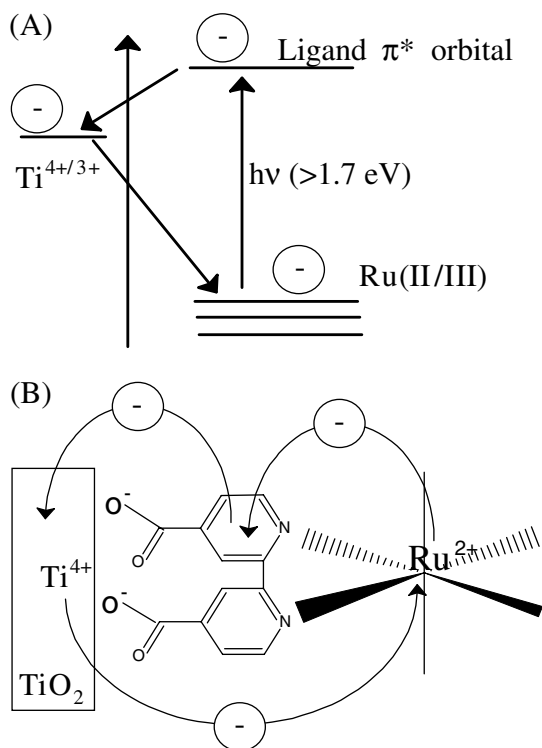
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EXPERIMENTAL SECTION

Instrumentation and measurements

IR spectra were obtained by using a Bruker IFS-66V FT-IR spectrophotometer in the solid state (KBr cell of 0.2 mm



Scheme 1. Mechanism of Ruthenium complexes with bipyridine as dye sensitized solar cell.

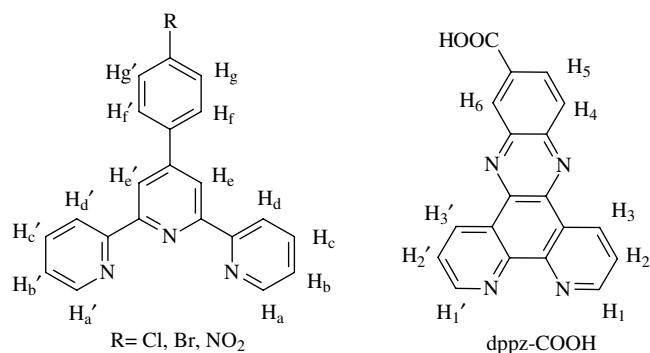


Figure 1. Ligand R-ph-tpy and dppz-COOH scheme proton allocation.

length). $^1\text{H-NMR}$ spectra were recorded on a 350 MHz Bruker spectrometer.

Absorption spectra were measured on a Shimadzu UV-160 spectrophotometer. Values of pH were registered using a Hanna Instrument pH-meter model 211. Electrochemical data were acquired by cyclic voltammetry using a potentiostat/galvanostat, Autolab/PGSTAT30, with Autolab 4.9 software.

The solutions of the complexes for cyclic measurements were prepared in anhydrous acetonitrile using tetra-*n*-butylammonium perchlorate (TBAP, 0.1 M) as supporting

electrolyte. Measurements were made using a three-electrode configuration cell. The working electrode was vitreous carbon; the reference and counter electrodes were Ag–AgCl and a wire platinum, respectively. Potentials were reported as $E_{1/2}$ values determined from $E_{1/2} = 1/2(E_{\text{pa}} + E_{\text{pc}})$, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively. A 100 mV/s sweep rate was used for a complex solution of 8.6×10^{-3} M.

Materials

All chemicals were reagent-grade and used as received unless otherwise specified. 4-Bromobenzaldehyde, 4-nitrobenzaldehyde, 4-chlorobenzaldehyde, 2-acetylpyridine, sodium hydroxide, ammonium acetate, ruthenium trichloride trihydrated, ammonium hexafluorophosphate, chloroform, acetonitrile, ethanol, methanol, methylene chloride, diethylether, chloroform-*d*, acetonitrile-*d*₃ and acetone-*d*₆ were purchased from Aldrich. 4'-(4-Chlorobenzene)-2,2',6',2''-terpyridine (Clph-tpy), 4'-(4-bromobenzene)-2,2',6',2''-terpyridine (Brph-tpy) and 4'-(nitrobenzene)-2,2',6',2''-terpyridine (NO₂ph-tpy) ligands were prepared according to a published procedure.⁷ The [Ru(Brph-tpy)Cl₃], [Ru(Clph-tpy)Cl₃], [Ru(NO₂ph-tpy)Cl₃] complexes were prepared by procedures similar to those used in the preparation of analogs [Ru(tpy)Cl₃].⁸

Synthesis

Synthesis of [Ru(Brph-tpy)(dppzCOOH)Cl]PF₆ (1)

[Ru(Brph-tpy)Cl₃] (0.309 g, 0.516 mmol) and 1,10-phenanthroline-5,6-dione (0.110 g, 0.523 mmol) were added in a round-bottomed flask and dissolved in a solution of ethanol–water (50 mL, 1:1 ratio). After the mixture had been heated at reflux for 3 h, it was cooled to room temperature. Then, 3,4-diaminobenzoic acid (0.100, 0.671 mmol) was added and the mixture was refluxed for an additional 1 h. The red solution was filtrated and the filtrate was concentrated to evaporate ethanol. Then, solid NH₄PF₆ was added to produce dark red precipitated, which was filtered through a glass frit and it was washed with diethylether. The solid was recrystallized in acetonitrile/diethylether and vacuum dried.

Yield: 0.083 g, 16.6%. The $^1\text{H NMR}$ was similar to that obtained for the complex {Ru(Brph-tpy)[dppz(COOH)Cl]PF₆ IR (KBr): ν_{CO} 1706(s), $\nu_{\text{C=C}}$ 1624(m), $\nu_{\text{PF}_6^-}$ 845(s), 560(m) cm⁻¹. Elemental analysis. Calcd (%) for C₄₀H₃₆BrClF₆N₇O₂PRu: C, 43.51; H, 3.29; N, 8.88. Found (%): C, 43.28; H, 3.90; N, 8.70. Complexes 2 and 3 were made by following the same procedure as used for complex 1.

Synthesis of [Ru(Clph-tpy)(dppzCOOH)Cl]PF₆ (2)

From [Ru(Clph-tpy)Cl₃] (0.300 g, 0.542 mmol), 1,10-phenanthroline-5,6-dione (0.110 g, 0.523 mmol) and 3,4-diaminobenzoic acid (0.100 g, 0.671 mmol), the synthesis of 2 was obtained. Yield: 0.410 g, 82%. M.p. 250 °C (d). $^1\text{H NMR}$ (acetone-*d*₆) δ = 7.3 (m, J = 7.7 Hz, H_{c,c'}), 7.6 (m, J = 9.40 Hz, H_{2'}), 7.1 (m, H_{g,g'}, H₄, H₅), 8.0 (m, J = 9.1 Hz, H_{b,b'}), 8.20 (m, J = 8.4 Hz, H₃), 8.26 (d, J = 10, 1, H_{d,d'}), 8.67 (m, J = 10.5, H₂),

8.67 (s, $H_{f,f}$), 8.88 (d, $J = 9.4$ Hz, $H_{a,a'}$), 9.05 (s, H_6), 9.18 (s, $H_{e,e'}$), 9.42 (m, $J = 9.45$ Hz, H_1), 9.99 (m, $J = 9.43$ Hz, H_3), 10.72 (m, $J = 6.5$ Hz, H_1). IR (KBr): ν_{CO} 1706 (s), $\nu_{C=C}$ 1624 (m), $\nu_{PF_6^-}$ 845 (s), 560 (m) cm^{-1} . Elemental analysis, calcd (%) for $C_{40}H_{36}BrClF_6N_7O_2PRu$: C, 45.34; H, 3.42; N, 9.25. Found (%): C, 45.62; H, 2.91; N, 8.83

Synthesis of $[Ru(NO_2ph-tpy)(dppzCOOH)Cl]PF_6$ (3)

From $[Ru(NO_2ph-tpy)Cl_3]$ (0.30 g, 0.534 mmol), 1,10-phenanthroline-5,6-dione (0.11 g, 0.523 mmol) and 3,4-diaminobenzoic acid (0.10 g, 0.671 mmol), compound 3 was obtained. Yield: 0.11 g, 22%. M.p. 300 °C (d). The 1H NMR was similar to that obtained for the $\{Ru(Clph-tpy)[dppz(COOH)Cl]PF_6\}$ complex. IR (KBr) ν_{CO} 1706 (s), $\nu_{C=C}$ 1624 (m), $\nu_{PF_6^-}$ 845 (s), 560 (m) cm^{-1} . Elemental analysis, calcd (%) for $C_{40}H_{36}ClF_6N_8O_4PRu$: C, 44.89; H, 3.39; N, 10.49. Found (%): C, 43.54; H, 2.72; N, 10.46.

RESULT AND DISCUSSION

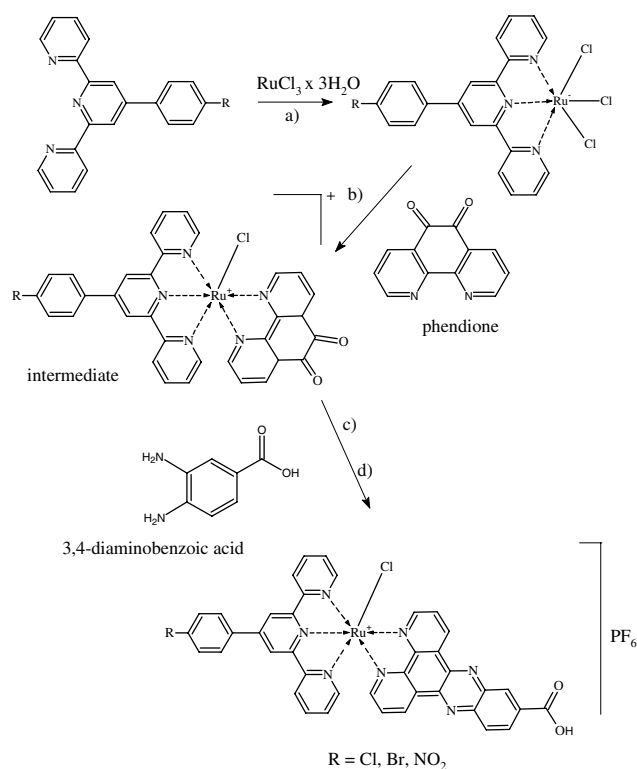
Synthesis

The synthesis of the complexes was carried out following the route shown in Scheme 2. The first step was the coordination of the substituted terpyridine ligand, followed by the incorporation of 1,10-phenanthroline-5,6-dione⁹ to obtain the intermediary complex. *In situ*, by Schiff reaction, the coordination of dppz(COOH) with 1,2-diaminobenzoic acid was obtained.¹⁰ This modified procedure was used in order to overcome the extreme insolubility in mixed solvent shown by the uncoordinated dppz(COOH). Finally, PF_6^- anion was used as a counter ion to precipitate the complexes.

Infrared spectra of the complexes showed the classical $C=C$ and $C=N$ bond signals (cm^{-1}) and the typical pattern for every specific terpyridine. The two signals at 845 and 560 cm^{-1} correspond to PF_6^- ion. The intense signal at 1706 cm^{-1} can be assigned to $\nu(CO)$ from carboxylic acid group.

Absorption spectra

The absorption spectra of the $\{Ru(Rph-tpy)[dppz(COOH)Cl]PF_6\}$ complexes with $R = NO_2, Br, Cl$ were recorded in acetonitrile. The data are listed in Table 1. The compounds display intense bands in the UV region (278 and 360 nm). Considering shape, position and the spectra of the uncoordinated ligands these bands have been assigned as intraligand $\pi \rightarrow \pi^*$ transitions from polypyridine ligand terpyridine and dppz(COOH). The shape of the spectra (Fig. 2) retains most of the features of the components of dppz(COOH), particularly the band centered at 364 nm, which essentially corresponds



Scheme 2. (a) Ethanol, reflux 3 h; (b) ethanol–water (3 : 1), reflux 3 h; (c) ethanol–water (3 : 1), reflux 1 h; (d) NH_4PF_6 .

Table 1. Spectroscopic^a and ground-state pK_a values for Ru complexes determined by means of spectrophotometric titration^b

Compound ^a	λ_{abs} (nm), $\epsilon(10^4, M^{-1} cm^{-1})$			$[Cx] \times 10^5$ ^c	pK_a	Reference
	MLCT	$\pi \rightarrow \pi^*$	$\pi \rightarrow \pi^*$			
$[Ru(bpy)_3]^{2+}$	460					5
$[Ru(ttpy)_3]^{2+}$	490(2.8)					6
$\{Ru(bpy)_2[dppz(COOH)]\}^{2+}$	448(1.9)	364(1.9)	285(12.3)	1.0	5.8	5
$(NEt_3H)\{Ru[tpy-(COOH)_3(SCN)_3]\}$	611(7.3)	344	330	5.0	3.3	11
$\{Ru(Brph-tpy)[dppz(COOH)Cl]\}^+$ (1)	515(5.2)	364(7.1)	278(29)	5.4	4.4	This work
$\{Ru(Clph-tpy)[dppz(COOH)Cl]\}^+$ (2)	517(8.8)	363(9.5)	277(29)	5.6	3.2	This work
$\{Ru(NO_2ph-tpy)[dppz(COOH)Cl]\}^+$ (3)	515(7.4)	360(16.9)	278(47)	5.6	4.7	This work

^a Complexes are PF_6^- salts and the values are obtained in MeCN at room temperature. ^b At room temperature in solutions containing 0.1 M KNO_3 . $ttpy = 4'-(p\text{-tolyl})-2,2'-'6,2'$ -terpyridine. ^c $[Cx]$ = complex concentration used.

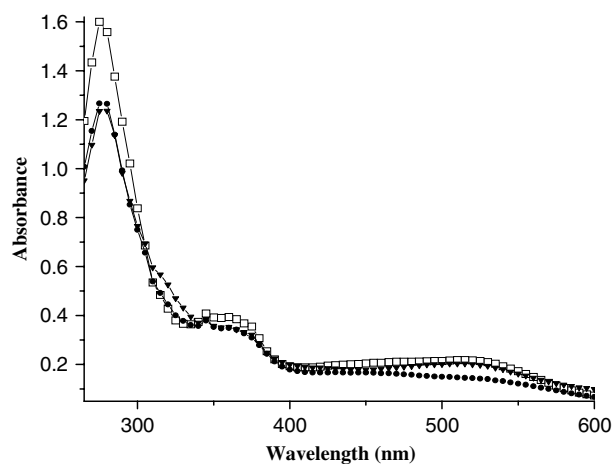


Figure 2. Absorption spectra for $[\text{Ru}(\text{Brph-tpy})[\text{dppz}(\text{COOH})\text{Cl}]\text{PF}_6$ (\blacktriangledown), $[\text{Ru}(\text{NO}_2\text{ph-tpy})[\text{dppz}(\text{COOH})\text{Cl}]\text{PF}_6$ (\bullet), and $[\text{Ru}(\text{Clph-tpy})[\text{dppz}(\text{COOH})\text{Cl}]\text{PF}_6$ (\square).

to the widely studied dppz fragment.¹¹ A broad transition band appears between 400 and 600 nm centered at 515 nm, which is solvent-dependent and can be assigned to a spin-allowed $^1\text{MLCT}$ transition, while at ca. 278 nm and below that wavelength, the intense bands can be attributed to the overlap of Rph-tpy and dppz(COOH) $\pi \rightarrow \pi^*$ transitions. Fig. 2 shows the electronic absorption for the series of complexes $\{\text{Ru}(\text{Rph-tpy})[\text{dppz}(\text{COOH})\text{Cl}]\text{PF}_6$, $\text{R} = \text{Br}, \text{NO}_2, \text{Cl}$. The more intense MLCT band occurs when $\text{R} = \text{Cl}$. All the complexes show higher molar extinction coefficients than those observed in related complexes already reported. For example both $[\text{Ru}(\text{bpy})_2(\text{dppz}(\text{COOH}))]^{2+}$,⁵ and $(\text{NEt}_3\text{H})[[\text{Ru}(\text{tpy}-(\text{COOH})_3)(\text{SCN})_3]$,¹² containing ligands with an uncoordinated carboxylic group displaying MLCT bands centered at λ_{max} 448 nm and 610 nm, with molar extinction

coefficient 1950 and $7320 \text{ M}^{-1} \text{ cm}^{-1}$, respectively. The intensity observed in the last band is attributed to the SCN^- presence.

Measurements of pK_a

The pK_a values for the ruthenium complexes were determined by a conventional pH-metric procedure and simultaneously a spectrophotometric titration was carried out in order to show that the carboxylic group is involved in the deprotonation process. The absorption spectra were less affected (2–3% over a 2–11 pH range), since fully protonated dye is insoluble in water [acetonitrile (16%) was added to prevent precipitation]. A complex solution (0.03–0.05 mM) was prepared in H_2O –acetonitrile (100 mL, 4 : 1) containing KNO_3 (0.1M) in order to maintain an ionic strength constant. The initial pH of the solution was adjusted to 11 by adding NaOH solution (0.2 M).

The UV–visible absorption spectra of each solution were obtained after adding hydrochloric acid and allowing the mixture to equilibrate. The pK_a values are reported in Table 1.

The absorption spectra of the $[\text{Ru}(\text{Brph-tpy})(\text{dppz}(\text{COOH}))\text{Cl}]\text{PF}_6$ complex is only slightly modified by the pH, Figure 3, the major change being on the absorption at 360 nm. This $\pi \rightarrow \pi^*$ absorption was used to determine the pK_a for each complex. The isobestic point at 390 nm represents the equilibrium between the carboxylic/carboxylate species:

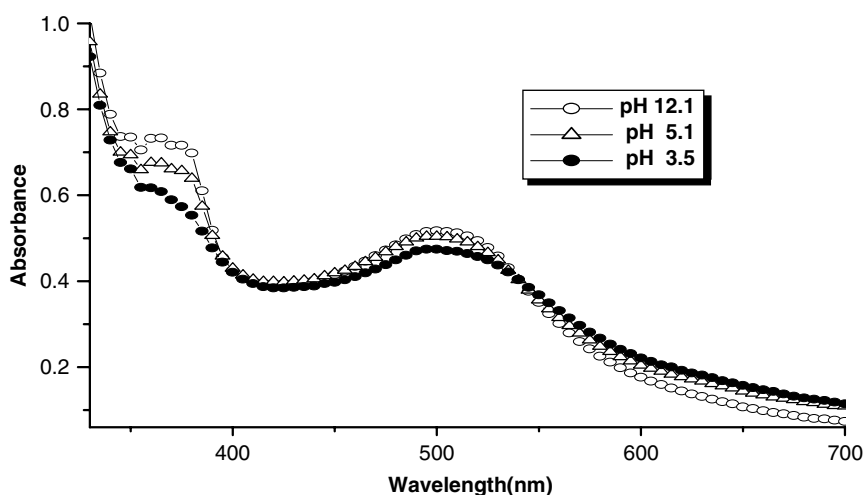
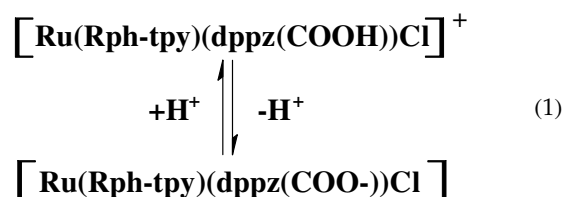


Figure 3. Absorption spectral changes of $[\text{Ru}(\text{Brph-tpy})[\text{dppz}(\text{COOH})\text{Cl}]\text{PF}_6$ as function of pH in an aqueous solution with 16% of acetonitrile (KNO_3 , 0.1 M).

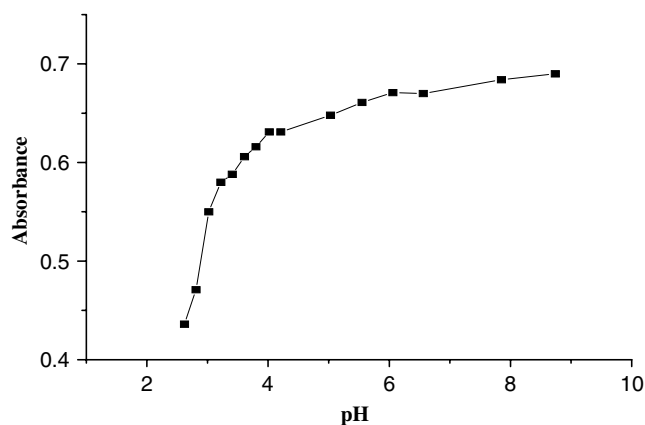


Figure 4. Absorbance changes as a function of pH for the $\{Ru(Clph-tpy)[dppz(COOH)Cl]PF_6\}$ complex at 360 nm.

Fig. 4 shows the absorption changes upon addition of hydrochloric acid to alkaline solutions of $\{Ru(Clph-tpy)[dppz(COOH)Cl]PF_6\}$ complex. An inflection point at pH 3.2 can be observed, which corresponds to ground-state pK_a values.

The results in Table 1 show a unique pK_a value for each complex. The difference in pK_a value in this series of analogous complexes can be understood as a measure of the donor/acceptor properties of the R group on the Rph-tpy ligand.

Electrochemical

Electrochemical data for complexes were measured in acetonitrile solution. In all cases the cyclic voltammogram shows a metal-based reversible couple in the oxidation region, which was assigned for the Ru(II–III) oxidation couple. In addition the cyclic voltammogram shows several events in the reduction region (0 to -2.0 V), which are essentially due to ligand-based reduction (see Fig. 5). The three complexes have the common dppz(COOH) ligand with the same π -electron acceptor characteristics. Then, the position and shift of the oxidation Ru(II–III) couple depend only on the presence of the terpyridine ligand with different substituents, in this case we have Rph-tpy with R = Cl, Br and NO_2 . The data are compiled in Table 2 (Fig. 5).

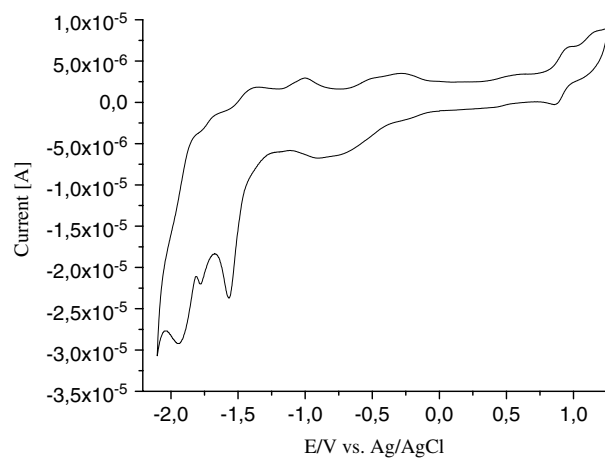


Figure 5. Cyclic voltammogram for the $\{Ru(Clph-tpy)[dppz(COOH)Cl]PF_6\}$ complex.

NMR analysis

Fig. 6 shows the assignments of the protons in NMR spectrum of the NO_2 -ph-tpy ligand. The presence of different substituting ligands (R = Br, Cl) does not shift significantly the signals on the spectrum.

As expected, the 1H -NMR spectra of the complexes $Ru(Rph-tpy)(dppzCOOH)Cl]PF_6$ (R = Br, Cl, NO_2) is very similar. Fig 7 shows the spectrum of the complex with R = Cl, as well as the assignment of all the proton signals. 1H -NMR COSY, Fig. 8, was used for this assignment.

CONCLUSIONS

A new series of Ru(II) complexes $[Ru(Rph-tpy)(dppz(COOH)Cl)PF_6]$, (R = Br, Cl, NO_2), containing an uncoordinated carboxylic group, have been synthesized. These complexes show a very intense MCLT band centered *ca.* 515 nm. We have shown that, by changing the R group on the tpy ligand, a wide range of Ru(II)/Ru(III) redox potentials can be achieved. This fine tuning of the redox potentials, together with the rest of the characteristics mentioned above, make these complexes specially appropriated for their use in solar cell devices.^{12,13}

Table 2. Redox potentials (V) of Ru complexes^a

Compound	$E_{1/2}Ox(\Delta E)$	$E_{1/2} Red(\Delta E)$	Ref	
$[Ru(bpy)_3]^{2+}$	+0.88	-1.69	5	
$[Ru(ttpy)_3]^{2+}$	+1.25		6	
$\{Ru(bpy)_2[dppz(COOH)]\}^{2+b}$	+0.85	-1.40	5	
$(NEt_3H)\{Ru[tpy-(COOH)_3(SCN)_3]\}$	+0.72	-1.10	11	
$\{Ru(Brph-tpy)[dppz(COOH)Cl]^+(1)\}$	+0.88(73)	-1.02(53)	-1.67(i) -1.99(i)	This work
$\{Ru(Clph-tpy)[dppz(COOH)Cl]^+(2)\}$	+0.91(59)	-1.62(i)	-1.78(i) -1.93(i)	This work
$[Ru(NO_2ph-tpy)[dppz(COOH)Cl]^+(3)^c$	+0.45	-0.72(i)	-1.20(i)	This work

^a At room temperature and in CH_3CN solution containing 0.1 M tetra-*n*-butylammonium perchlorate, measured at 100 mV/s. Redox potentials of $[Ru(bpy)_3]^{2+}$ are given for comparison. ^b In DMF. ^c In DMSO. ^d (i) Irreversible; [complex] = 8.6×10^{-3} M.

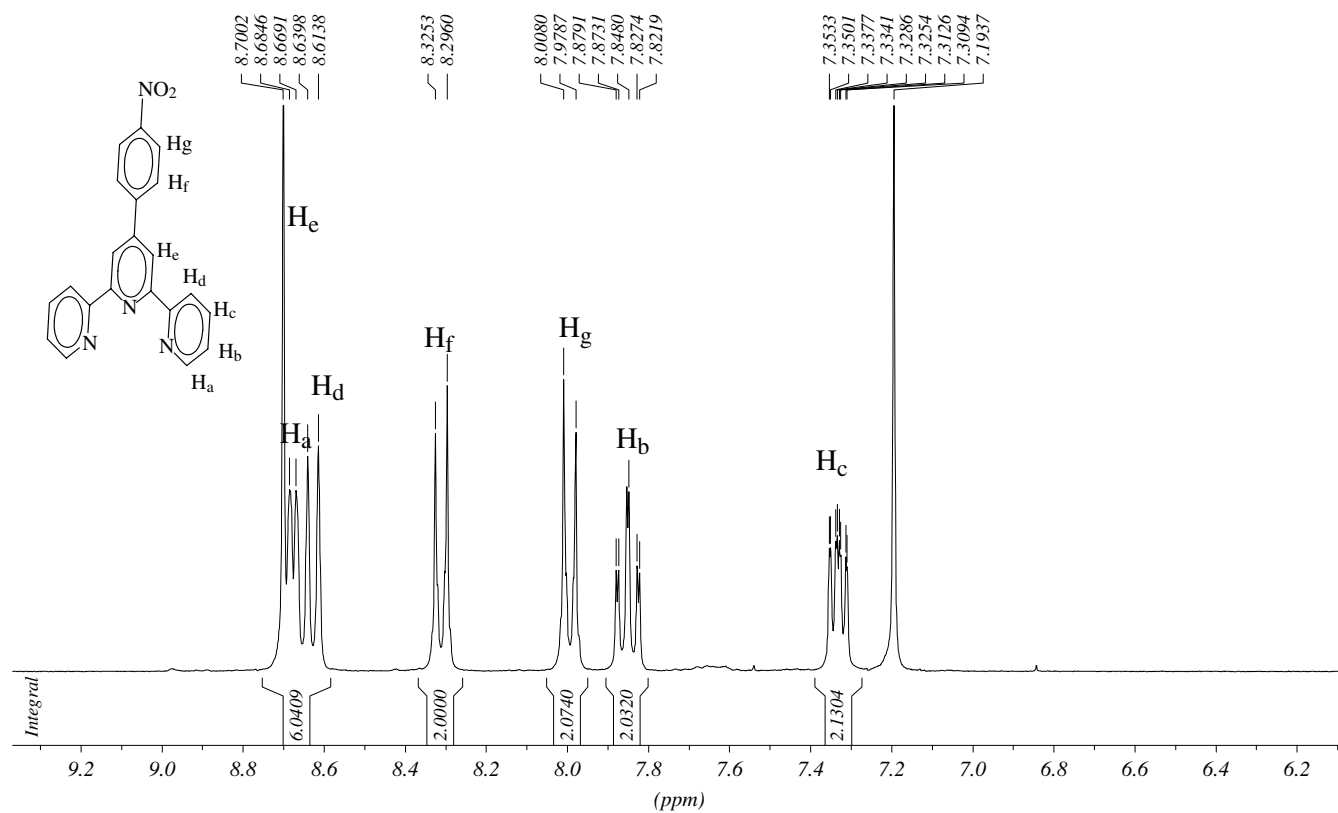


Figure 6. ¹H NMR spectrum for the NO₂-ph-tpy ligand.

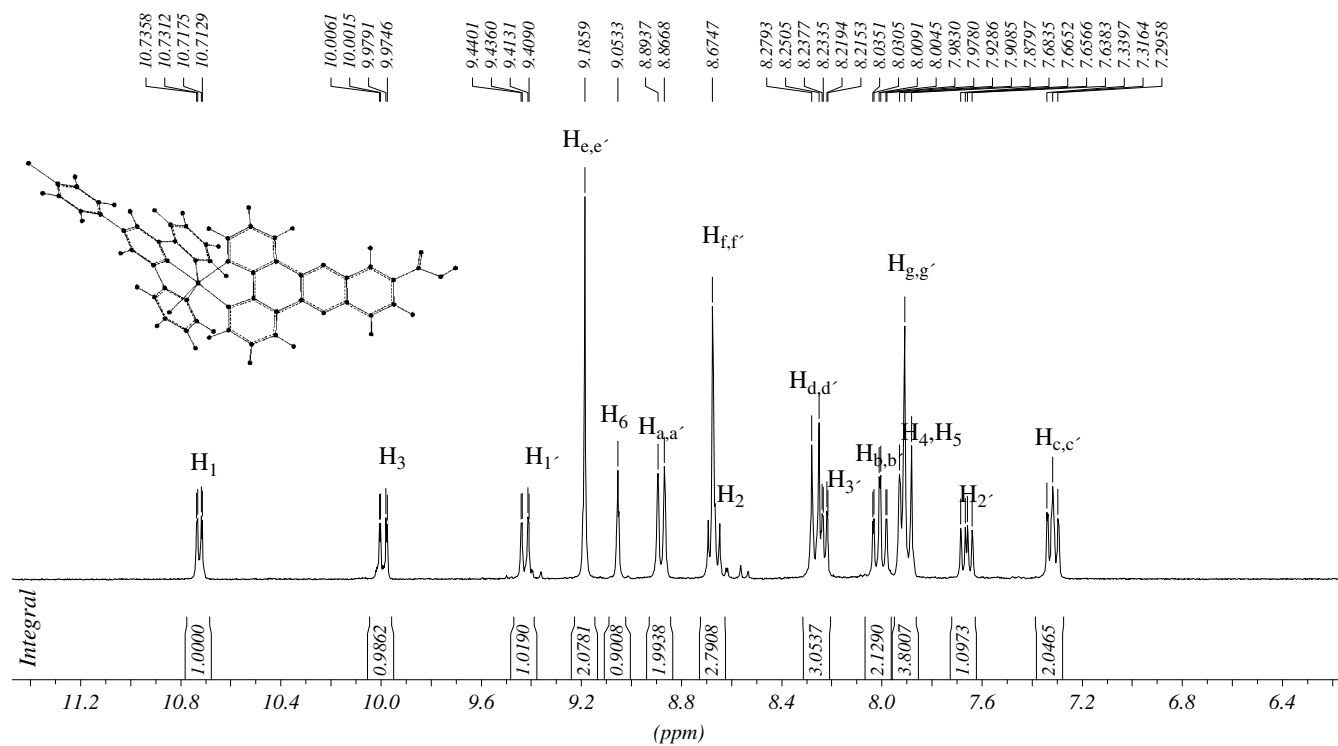


Figure 7. ¹H NMR spectrum for the {Ru(Clph-tpy)[dppz(COOH)Cl]}PF₆ complex.

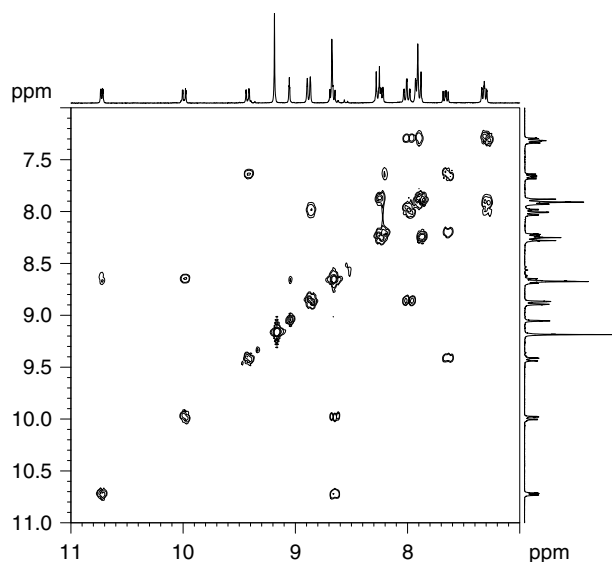


Figure 8. $^1\text{H-NMR}$ COSY spectrum for the $\{\text{Ru}(\text{Clph-tpy})[\text{dppz}(\text{COOH})\text{Cl}]\}\text{PF}_6$ complex.

Additional support for this conclusion arose when we compared our results with those obtained by Grätzel *et al.*,¹² who reported a band centered at 610 nm with a molar extinction coefficient of $7320\text{ M}^{-1}\text{ cm}^{-1}$ for $(\text{NEt}_3\text{H})\{\text{Ru}[\text{tpy}-(\text{COOH})_3(\text{SCN})_3]\}$.

Acknowledgments

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