# Synthesis and Characterization of Ruthenium Complexes with Substituted Pyrazino[2,3-*f*][1,10]-phenanthroline (= Rppl; R = Me, COOH, COOMe)

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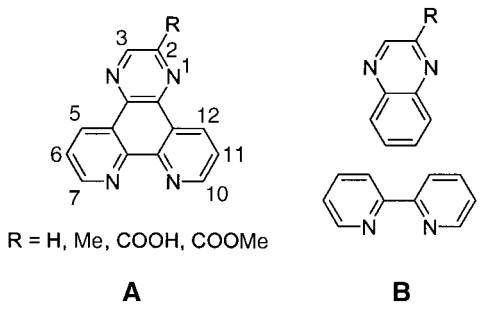
A series of substituted pyrazino[2,3-*f*][1,10]-phenanthroline (Rppl) ligands (with R = Me, COOH, COOMe) were synthetized (see **1**–**4** in *Scheme 1*). The ligands can be visualized as formed by a bipyridine and a quinoxaline fragment (see **A** and **B**). Homoleptic $[Ru(R^1ppl)_3](PF_6)_2$ and heteropleptic $[Ru(R^1ppl)\{(R^2)_2bpy\}_2](PF_6)_2$ ($R^1$ = H, Me, COOMe and $R^2$ = H, Me) metal complexes **5**–**7** and **8**–**13**, respectively, based on these ligands were also synthesized and characterized by conventional techniques (*Schemes 2* and *3*, resp.). In the heteroleptic complexes, the $R^1$-ppl ligand reduces at a less-negative potential than the bpy ligand, reflecting the acceptor property conferred by the quinoxaline moiety. The potentiality of some of these complexes as solar-cell dyes is discussed.

**Introduction.** – Transition-metal complexes with polypyridines have been widely studied in the last decades mainly because of their special photophysical, photochemical, and electrochemical properties [1]. These properties make them potential candidates to be used as dyes in artificial solar-energy-conversion devices, *e.g.*, in photo-electrochemical solar cells [2]. Specifically, (polypyridine)ruthenium(II) complexes have been anchored to semiconductor oxide electrodes, such as $TiO_2$ electrodes, and used to improve the light-to-electricity-conversion yield of the cell. The dye is attached to the semiconductor surface by anchoring groups, such as carboxylates or phosphonates; this anchor is a substituent at a polypyridine ligand of the complex. *Grätzel*'s $[Ru(NCS)_2\{bpy(COOH)_2\}_2]$ dye (bpy = 2,2′-bipyridine), known as N3, is an archetype for this type of complex [2a–d].

The efficiency of the solar cell depends – among other parameters – on the spectroscopic and electrochemical properties of the polypyridine complexes used to sensitize the semiconductor oxide [3]. It is a well known fact that these properties can be tuned by an adequate choice of ligands [1]. This makes the search for new complexes with suitable anchoring ligands one of the most important issues of research on solar-cell dyes.

Functionalized 2,2′-bipyridine has been the main ligand used in [Ru(polypyridine)] dyes. In this work, the synthesis of derivatives **A** of the pyrazino[2,3-*f*][1,10]phenanthraline ligand, Rppl (R = Me, COOH, or COOMe), is reported. This ligand can be visualized as a fusion of a bipyridine and a quinoxaline moiety (see **B**), where the quinoxaline part would also play the role of acceptor group.[1])

[1]) The Rppl ligand with R = H has been reported in the literature with different names, see, *e.g.*, [4].

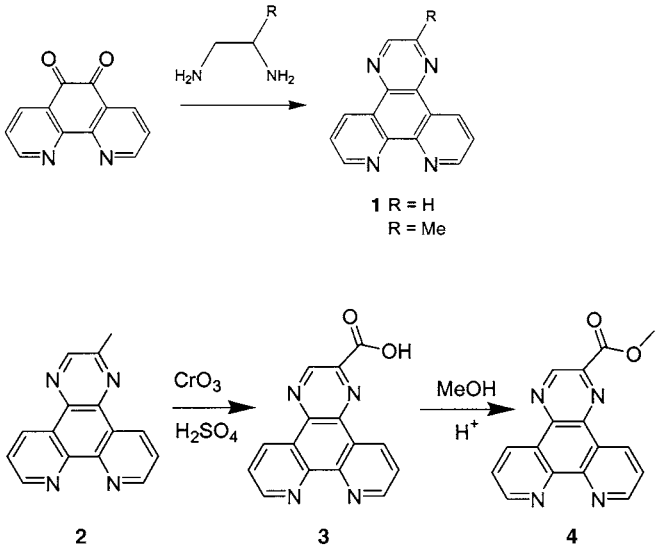



Enhancement of rigidity and aromaticity in the polypyridine ligand should conduct to improvement in the excited-state properties of the complex [5]. In metal complexes, delocalization and rigidity in the acceptor ligand lead to decreased structural changes in the excited state. This, in turn, decreases the nonradiative decay constant and can greatly enhance excited-state lifetimes [5][6].

The synthesis and characterization of homoleptic and heteroleptic ruthenium(II) complexes with these ligands is also reported. Based on the observed properties, the potentiality of the complexes as solar-cell dyes is discussed.

**Results and Discussion.** – *Synthesis.* The synthesis of pyrazino[2,3-*f*][1,10]phenanthroline (**1**) and 2-methylpyrazino[2,3-*f*][1,10]phenanthroline (**2**) was achieved in high yield by a condensation reaction of 1,10-phenanthroline-5,6-dione [7] with ethane-1,2-diamine and propane-1,2-diamine, respectively, in MeOH (*Scheme 1*). The corresponding carboxylic acid ligand **3** was obtained by oxidation of the methyl group of **2** with chromium oxide in concentrated sulfuric acid. Due to the insolubility of this ligand

*Scheme 1*



in most common solvents, **3** was esterified in $MeOH/H_2SO_4$ according to the method of *Garelli* and *Vierling* [8]. The ester **4** obtained is a well and more managable model, suitable to study the behavior of the carboxylate ligand.

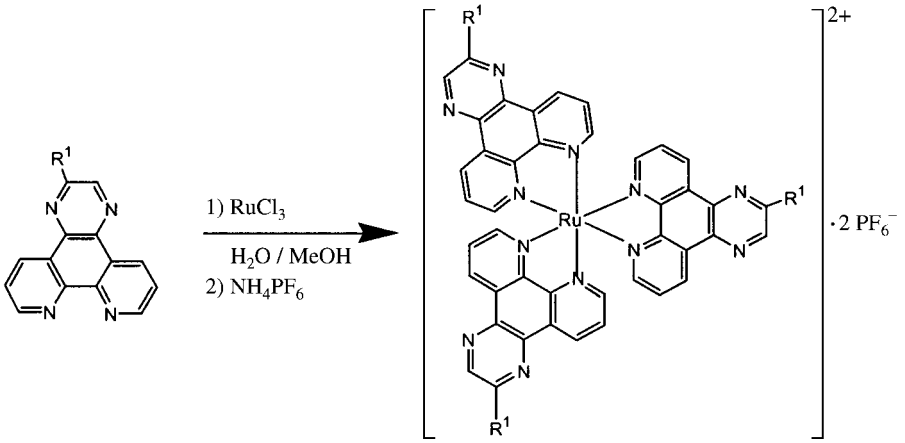
The homoleptic complexes **5**–**6** were generated by reaction of the respective ligand with ruthenium trichloride in $MeOH/H_2O$ in the presence of hydroquinone (*Scheme 2*). The complexes were isolated by precipitation from aqueous solution with ammonium hexafluorophosphate.

The heteroleptic complexes **8**–**13** were obtained by chloro substitution in *cis*-$[RuCl_2\{(R^2)_2bpy\}_2]$ [9] with $R^1$ppl in $MeOH/H_2O$ (*Scheme 3*) and were isolated by the same procedure as described for the homoleptic complexes.

*NMR Spectroscopy.* The $^1$H-NMR spectra of the ligand ppl (**1**) shows the three magnetically nonequivalent protons of the bipyridine moiety and the *s* of the quinoxaline proton, *Fig. 1*,*a*. The lowest-field signal is assigned to H–C(5) and H–C(12) (see **A** for numbering) due to the proximity of the quinoxaline N-atoms that increase the *para* effect of the bipyridine N-atoms [10], shifting this signal to lower field than that of the *ortho* protons H–C(7) and H–C(10) of the bipyridine part. This behavior is not reproduced in the $^{13}$C-NMR spectra, where the chemical shift for C(5) and C(12) appears at higher field than that of C(7), and C(10), according to the order expected for a bipyridine-type ligand [10b]. On the other hand, H–C(6) and H–C(11) as well as C(6) and C(11) of the bipyridine part appear at high field as expected. In the substituted R-ppl ligands, the signal of H–C(5) and H–C(12) as well as that of H–C(7) and H–C(10) split, due to the loss of symmetry in the compound.

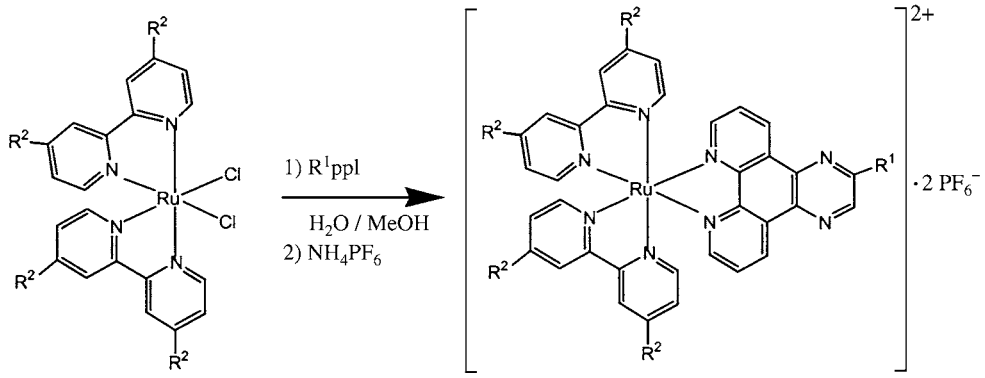
As expected, in the $^1$H-NMR spectra of **2** (R = Me) and **4** (R = COOMe) (*Fig. 1*,*b* and *c*, resp.), the signal corresponding to the quinoxaline proton H–C(3) is strongly affected by the nature of the substituent. In ligand **2**, its shielding is enhanced (0.2 ppm)

*Scheme 2*




**5** $R^1$ = H
**6** $R^1$ = Me
**7** $R^1$ = COOMe

*Scheme 3*




**8** $R^2$ = H, $R^1$ = H
**9** $R^2$ = Me, $R^1$ = H
**10** $R^2$ = H, $R^1$ = Me
**11** $R^2$ = Me, $R^1$ = Me
**12** $R^2$ = H, $R^1$ = COOMe
**13** $R^2$ = Me, $R^1$ = COOMe

compared to the unsubstituted ligand **1**, whereas, for ligand **4**, this proton is manifestly unshielded (0.8 ppm) because of the electron-acceptor properties of the ester group.

In the spectra of the complexes, the complete bipyridine-part pattern remains at almost the same position, except for the signals of H–C(7) and H–C(10), which are shifted to drastically higher field (by *ca.* 0.8 ppm). This effect – due to the electronic current of the heterocycles in an octahedral configuration [11] – is appreciable only in the $^1$H-NMR spectra, since the $^{13}$C-NMR chemical shifts do not suffer major alterations compared to those of the free ligand. The general pattern of the spectra also show the equivalence of the three Rppl ligands in the complex, *Fig. 2, b*.

The $^1$H-NMR spectra of the heteroleptic $[Ru\{(R^2)_2bpy\}_2(R^1ppl)]^{2+}$ type complexes show, in addition to the ppl pattern, two sets of signals for the bpy ligands. When $R^2$ = H, the spectra are converted to a higher order, introducing some uncertainty in the exact chemical-shift value.

*UV/VIS Spectroscopy.* The UV/VIS spectra of the free ligands show a series of low-intensity bands in the 280–350-nm region and a strong band at 260 nm, all assigned to $\pi \rightarrow \pi^*$ transitions. The homoleptic and heteroleptic complexes show UV/VIS spectra quite similar to those of $[Ru(bpy)_3](PF_6)_2$ (*Fig. 3*). The 400–500-nm region is dominated by a MLCT (metal-to-ligand charge transfer) broad manifold. In the case of the ppl complexes, some enhancement of the intensity of the absorption at higher energy is observed. This can be explained by the acceptor properties of ppl that produces a destabilization of the d$\pi$ level of the metal [1c]. The tris(bpy) complex shows two additional bands at 285 and 240 nm; the first one is assigned to a LC band, and the latter to a MLCT [1b]. In the ppl complexes, two bands at *ca.* 290 and *ca.*

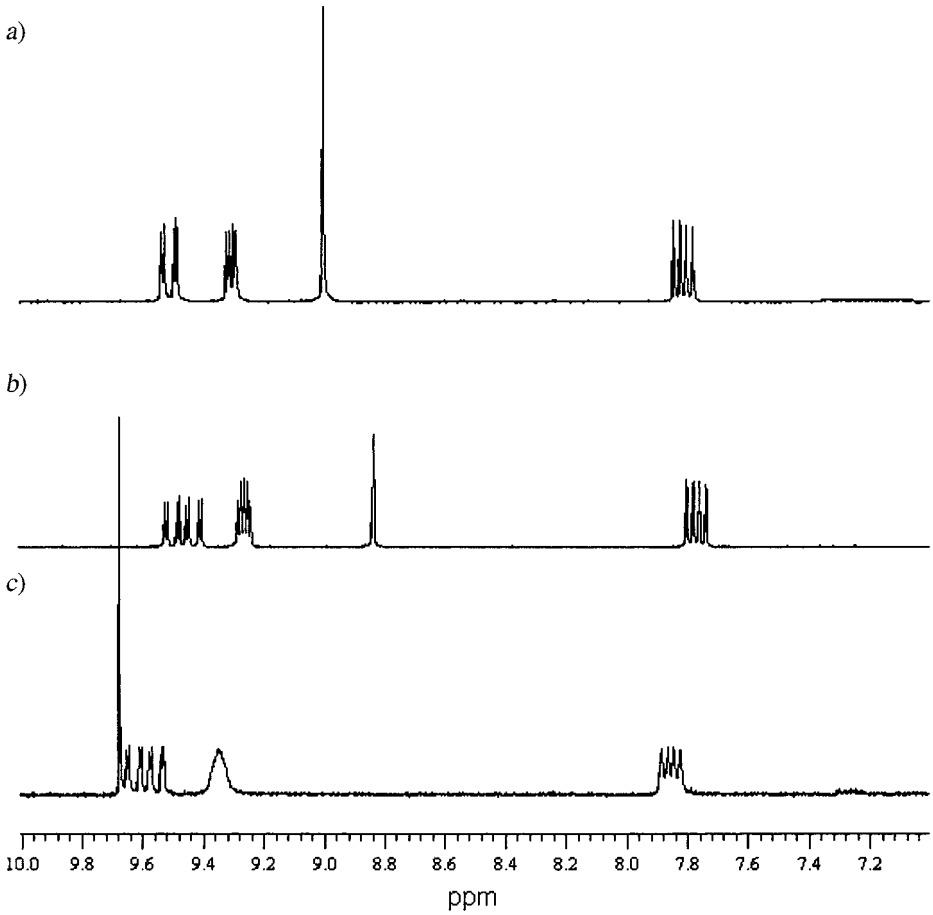



Fig. 1. *$^1$H-NMR Spectra of* a) *ppl* (**1**), b) *(Me)ppl* (**2**), *and* c) *(COOMe)ppl* (**4**) *in* $CDCl_3$

260 nm also appear, but, in this case, they are assigned to LC transitions; the MLCT band probably present in this region is overlapped by the intense LC band.

*Electrochemistry.* The electrochemical data for all the ligands and complexes are shown in the *Table*. In the cyclic voltammogram of the free ligands, the position of the reversible first reduction is very sensible to the substituent group: the less-negative potential is observed for R = COOMe, while the ligand with R = Me shows the most negative potential.

For the homoleptic complexes, a broad reduction peak is observed, followed by a sharp reversible oxidation. Compared to the free ligand, the ligand reduction in the complexes appears at less-negative potentials, due to the coordination effect that lowers the energy of the $\pi^*$ orbitals. Nevertheless, the relative ordering of the ligands remains unaltered. The $Ru^{II}/Ru^{III}$ oxidation potential is relatively constant along the series, evidencing little effect of the substituents on the d-orbital energy of the metal. In the heteroleptic complexes, the reversible-oxidation signal for the $Ru^{II}/Ru^{III}$ couple is

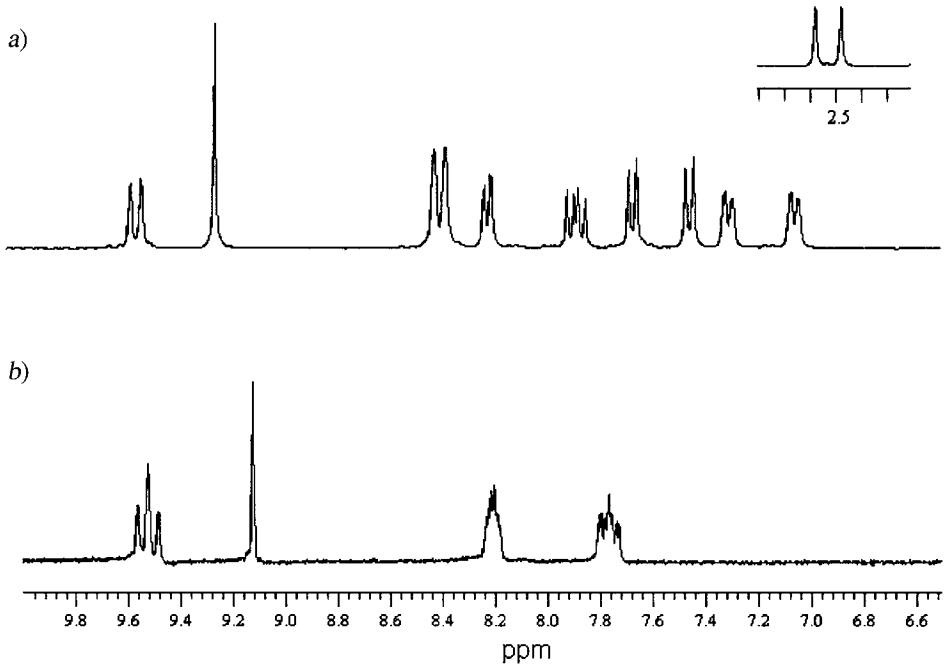



Fig. 2. *$^1$H-NMR Spectra of* a) *[Ru(bpy)$_2$(ppl)](PF$_6$)$_2$* (**8**) *and* b) *[Ru(ppl)$_3$](PF$_6$)$_2$* (**5**) *in CD$_3$CN*

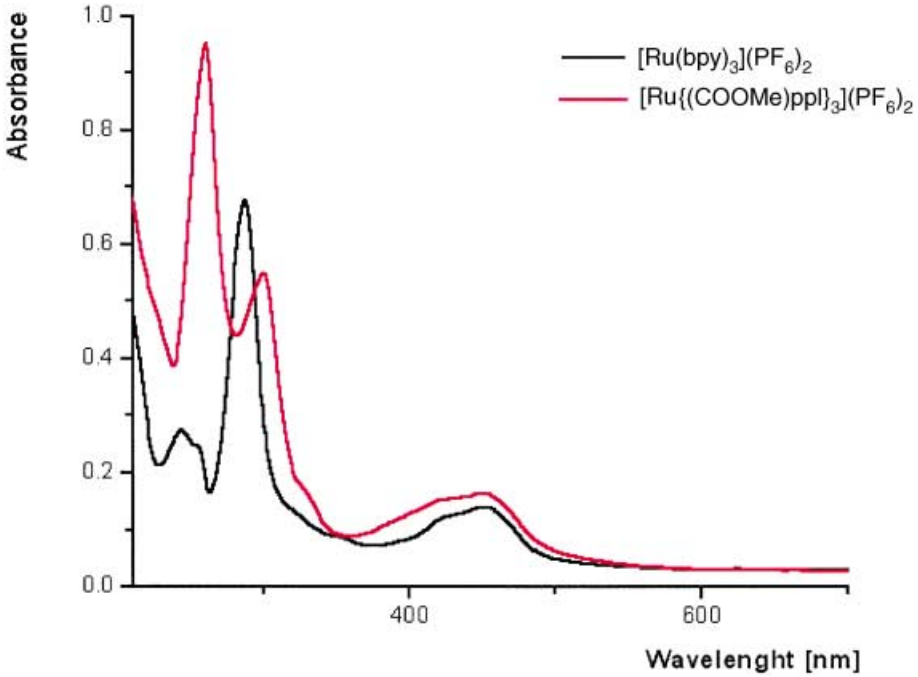



Fig. 3. *UV/VIS Spectra of [Ru{(COOMe)ppl}$_3$](PF$_6$)$_2$* (**7**) *and [Ru(bpy)$_3$](PF$_6$)$_2$ in MeCN*

Table. *Redox Potentials* (V *vs.* Ag/AgCl) *for the Rppl Ligands* (R=H, Me, COOMe) *and Their Corresponding* $Ru^{II}$ *Complexes in MeCN*

| | $E_{1/2}$ ($Ru^{3+}/Ru^{2+}$) | $E_{1/2}$ ($L/L^{-}$) |
|---|---|---|
| **1**[a]) | | −1.50 |
| **2**[a]) | | −1.60 |
| **4**[a]) | | −1.16 |
| **5** | +1.44 | −1.16 |
| **6** | +1.41 | −1.21 |
| **7** | +1.45 | −0.86 |
| **8** | +1.37 | −1.18 |
| **10** | +1.37 | −1.20 |
| **12** | +1.38 | −0.94 |
| **9** | +1.24 | −1.23 |
| **11** | +1.26 | −1.24 |
| **13** | +1.29 | −0.96 |

[a]) DMSO *vs.* saturated calomel electrode (SCE).

observed in the same way as for the homoleptic compounds. Most of the cases show three reductions, as can be seen in *Fig. 4* for the complex $[Ru(bpy)_2\{(COOMe)\text{-}ppl\}](PF_6)_2$ (**12**), the first one assigned to the ppf ligand and the others to bpy. This behavior is a clear evidence for the acceptor properties of ppf. The assignment is based on comparison with the ligand reduction in the homoleptic complexes.

**Conclusions and Outlook.** – A series of ligands derived from pyrazino[2,3-*f*]-[1,10]phenanthroline and their corresponding homo- and heteroleptic complexes were synthetized and characterized. As was previously mentioned, $R^1$-ppl ligands behave as being formed by a 2,2-bipyridine and a quinoxaline moiety. This assumption is supported by theoretical calculations performed with the 'Spartan' package [12]. *Fig. 5*

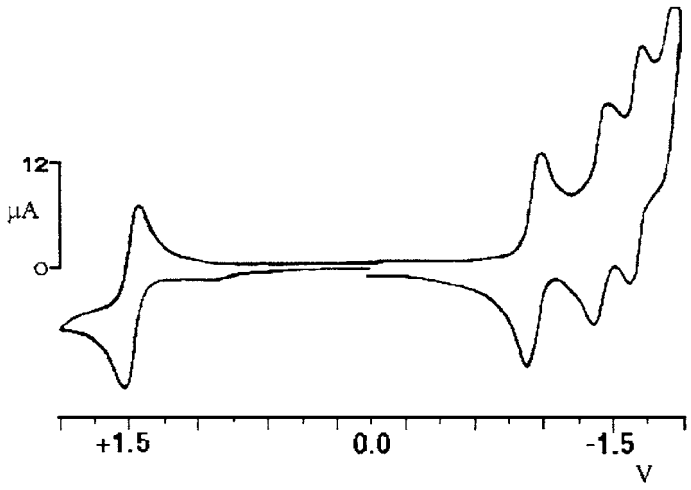



Fig. 4. *Cyclic voltagram of* $[Ru(bpy)_2[(COOMe)ppl]](PF_6)_2$ (**12**) *in MeCN*

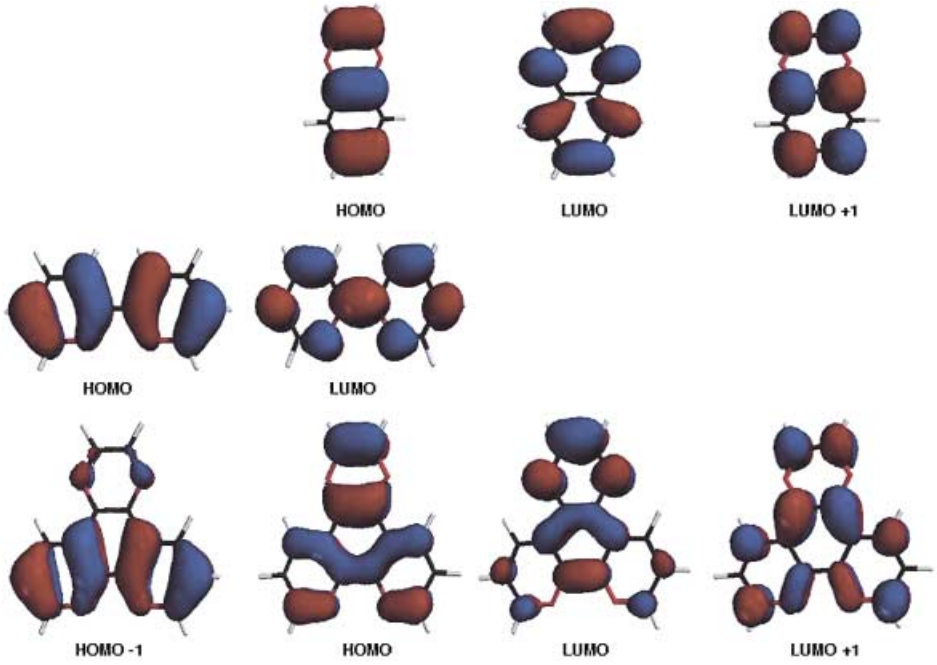



Fig. 5. *Frontier orbitals of ppl and their relationship to 2,2′-bipyridine and quinoxaline orbitals*

shows the electronic-density distributions for the frontier orbitals of ppl and their relationships to the corresponding orbitals for the 2,2′-bipyridine and quinoxaline components. The quinoxaline region dominates the first ligand reduction, as can be concluded from the resemblance of the ppl LUMO and the quinoxaline LUMO. This explains the sensitivity of this region to a change in the R substituent, as observed experimentally.

Interesting to point out is the fact that, in the heteroleptic $[Ru\{(R^2)_2bpy\}_2(R^1ppl)]^{2+}$ type complexes, modification of $R^2$ on the bpy ligands has a strong effect on the metal oxidation potential, evidencing that these ligands have the most marked influence on the metal center.

The capacity to modify the redox potential of the quinoxaline region by substitution with adequate acceptors can be used to introduce directionality to the electron flux after the MLCT absorption. In this way, charge separation in the excited state should be enhanced, and consequently the behavior of the complex as a potential solar-cell dye should be improved. In this context, ligands substituted with an ester group such as **4** are very promising. First, because of their manageability and solubility, the study of their excited-state properties should be straightforward; second, they can be considered good models for the corresponding carboxylated complexes. Moreover, they can be converted by base hydrolysis to the mentioned carboxylated derivatives, and subsequently tested as solar-cell dyes. Both studies, the photophysical behavior of the complexes and their use as solar-cell dyes, are in progress.

## Experimental Part

1. *General.* The 1,10-phenanthroline-5,6-dione and the complexes $[RuCl_2(bpy)_2]$ and $[RuCl_2(Me_2bpy)2]$ were synthesized according to [7][9]. UV/VIS Spectra: *Shimadzu UV-3101PC* spectrophotometer; $\lambda$ in nm. IR Spectra: KBr pellets; *Bruker Vector-22-FTIR* spectrometer; in $cm^{-1}$. $^1$H-NMR Spectra: *Bruker AC/200* (200 MHz) or *Bruker Aspect* 400-MHz spectrometer; in $CD_3CN$ or $CDCl_3$ with $SiMe_4$ as reference; $\delta$ in ppm, $J$ in Hz. NMR spectra were processed with the 'Mestre-C' software package [13]. Cyclic voltammetry: *Bas CV-50W-2.3-MF-9093* equipment.

2. *Theoretical Calculations.* Geometry optimization of ligands were performed by using the semi-empirical methods implemented in the 'Spartan' package [12]. Total energy and molecular surfaces were obtained by using *Hartree-Fock* calculations (6-31G**) on the equilibrium geometry previously obtained.

3. *Syntheses of Ligands. Pyrazino[2,3-*f*][1,10]-phenanthroline* (**1**). Ethane-1,2-diamine (0.5 ml) was added to a suspension of 1,10-phenanthroline-5,6-dione (0.50 g, 2.38 mmol) in MeOH (25 ml). After 5 min, a red soln. appeared, which was stirred overnight at r.t. The solid formed was filtered off and washed with small amounts of MeOH. Recrystallization from toluene gave 0.43 g (79%) of **1**. IR (KBr): 1581, 1467, 1391, 740. $^1$H-NMR ($CDCl_3$): 9.51 (*dd*, $J = 8.2, 1.8$, H–C(5), H–C(12)); 9.30 (*dd*, $J = 4.4, 1.8$, H–C(7), H–C(10)); 9.00 (*s*, H–C(2), H–C(3)); 7.81 (*dd*, $J = 8.2, 4.4$, H–C(6), H–C(11)). $^{13}$C-NMR ($CDCl_3$): 152.71; 147.79; 144.94; 140.983; 133.64; 127.48; 124.40. Anal. calc. for $C_{14}H_8N_4 \cdot 0.5\ H_2O$: C 69.70, H 3.76, N 23.33; found: C 70.09, H 3.37, N 23.54.

*2-Methylpyrazino[2,3-*f*][1,10]phenanthroline* (**2**). To a suspension of 1,10-phenanthroline-5,6-dione (1.00 g, 4.76 mmol) in MeOH (25 ml), propane-1,2-diamine (0.5 ml) was added. The red soln. was stirred overnight at r.t. Evaporation gave an orange tar. The suspension of this tar in $H_2O$ was stirred for 2 days. A white solid was formed, which was filtered off and washed with $H_2O$. Recrystallization from toluene gave 0.93 g (80%) of **2**. IR (KBr): 1581, 1469, 1400, 1366, 744. $^1$H-NMR ($CDCl_3$): 9.5 (*dd*, H–C(12)); 9.41 (*dd*, H–C(5)); 9.26 (*m*, H–C(7), H–C(10)); 8.82 (*s*, H–C(3)); 7.78 (*m*, H–C(6), H–C(11)); 2.9 (*s*, Me). $^{13}$C-NMR ($CDCl_3$): 154.06; 152.09; 151.805; 144.94; 133.15; 132.79; 123.90; 123.81; 22.33. Anal. calc. for $C_{15}H_{10}N_4$: C 73.16, H 4.09, N 22.75; found: C 73.15, H 4.13, N 22.79.

*Pyrazino[2,3-*f*][1,10]phenanthroline-2-carboxylic Acid* (**3**). To **2** (0.9 g, 3.65 mmol) placed in an ice bath, conc. $H_2SO_4$ soln. (10 ml) was slowly added, followed by small portions of chromium oxide (total of 1.2 g, 12 mmol), with vigorous stirring. The resulting mixture was refluxed for 4 h and then stirred overnight at r.t. The green soln. was poured over ice, and the white precipitated formed was filtered off and thoroughly washed with $H_2O$. The product was dried under vacuum: 0.38 g (38% of **3**). IR (KBr): 3500–2250, 1721, 1379, 727.

*Pyrazino[2,3-*f*][1,10]phenanthroline-2-carboxylic Acid Methyl Ester* (**4**). To a suspension of **3** (0.35 g, 1.27 mmol) in MeOH (20 ml), conc. $H_2SO_4$ soln. (1 ml) was added. After refluxing some time, a clear soln. appeared, and refluxing was continued for 24 h. Then $H_2O$ was added and the soln. neutralized with $NaHCO_3$. Finally, the aq. soln. was extracted with $CHCl_3$ ($3 \times 15$ ml), the org. layer dried ($Na_2SO_4$) and evaporated, the white residue re-extracted with $CHCl_3$, and the org. phase dried ($Na_2SO_4$) and evaporated: 0.38 g (98%) of **4**. IR (KBr): 1743, 1723, 1098, 1021, 798. $^1$H-NMR ($CDCl_3$): 9.67 (*s*, H–C(3)); 9.62 (*dd*, H–C(12)); 9.55 (*dd*, H–C(5)); 9.35 (*m*, H–C(7), H–C(10)); 7.85 (*m*, H–C(6), H–C(11)); 4.17 (*s*, MeO). $^{13}$C-NMR ($CDCl_3$): 164.55; 153.26; 152.89; 148.27; 145.11; 142.39; 142.22; 139.66; 133.93; 133.71; 126.62; 126.39; 124.22; 53.28. Anal. calc. for $C_{16}H_{10}N_4O_2 \cdot 3\ H_2O$: C 55.81, H 4.68, N 16.27; found: C 54.62, H 3.25, N 15.55.

4. *Homoleptic Complexes [Ru(R$^1$ppl)$_3$](PF$_6$): General Method:* The appropiate ligand (1.5 mmol), $RuCl_3 \cdot H_2O$ (0.7 mmol), and hydroquinone (0.7 mmol) were dissolved in a MeOH/$H_2O$ 2:1 (25 ml). The soln. was refluxed for 3 h. After filtration, $NH_4PF_6$ was added to precipitated the complex. The solid was filtered off, washed with $H_2O$ and $Et_2O$, and dried under vacuum.

*Tris(pyrazino[2,3-*f*][1,10]phenanthroline-*$\kappa$N$^8$,$\kappa$N$^9$*)ruthenium(2+) Bis[hexafluorophosphate(1–)]* ($[Ru(ppl)_3](PF_6)_2$; **5**). Yield 70%. UV/VIS (MeCN): 253, 290, 448. IR (KBr): 1443, 1383, 840, 557. $^1$H-NMR ($CD_3CN$): 9.5 (*dd*, 6 H); 9.2 (*s*, 6 H); 8.2 (*dd*, 6 H); 7.7 (*m*, 6 H).

*Tris(2-methylpyrazino[2,3-*f*][1,10]phenanthroline-*$\kappa$N$^8$,$\kappa$N$^9$*)ruthenium(2+) Bis[hexafluorophosphate(1–)]* ($[Ru\{(Me)ppl\}](PF_6)_2$; **6**). Yield 69%. UV/VIS (MeCN): 257, 291, 449. IR (KBr): 1408, 1370, 840, 557. $^1$H-NMR ($CD_3CN$): 9.5 (*t*, 6 H); 9.1 (*s*, 3 H); 8.2 (*m*, 6 H); 7.7 (*m*, 6 H); 2.9 (*s*, 9 H).

*Tris(methyl pyrazino[2,3-*f*][1,10]phenanthroline-2-carboxylate-*$\kappa$N$^8$,$\kappa$N$^9$*)ruthenium(2+) Bis[hexafluorophosphate(1–)]* ($[Ru\{(COOMe)ppl\}_3](PF_6)_2$; **7**). Yield 65%. UV/VIS (MeCN): 260, 300, 450. IR (KBr): 1743, 1726, 839, 557. $^1$H-NMR ($CD_3CN$). 9.8 (*s*, 3 H); 9.6 (*m*, 6 H); 8.3 (*t*, 6 H); 7.8 (*m*, 6 H); 4.1 (*s*, 9 H).

5. *Heteroleptic Complexes [Ru{(R$^2$)$_2$bpy}$_2$(R$^1$ppl)](PF$_6$)$_2$: General Method.* A soln. of R$^1$ppl $[RuCl_2\{(R^2)_2bpy\}_2]$ (0.5 mmol), and $H_2O$/MeOH (25 ml) was refluxed for 4 h. The solvent was evaporated

close to dryness, then $H_2O$ was subsequently added. The soln. was filtered off, and $NH_4(PF_6)$ was added to give the desired product. The solid was filtered off and washed with $Et_2O$.

*Bis(2,2′-bipyridine-κN$^1$,κN$^{1'}$)(pyrazino[2,3-f][1,10]phenanthroline-κN$^8$,κN$^9$)ruthenium(2+) Bis[hexafluorophosphate(1−)]* ($[Ru(bpy)_2(ppl)](PF_6)_2$; **8**). Yield 45%. UV/VIS (MeCN): 255, 288, 450. IR (KBr): 839, 557. $^1$H-NMR ($CD_3OD$): 8.1 (*d*, 2 H); 7.7 (*s*, 2 H); 7.2 (*t*, 4 H); 6.8–6.4 (*m*, 6 H); 6.2 (*d*, 2 H); 6.0 (*t*, 2 H); 5.8 (*t*, 2 H).

*Bis(4,4′-dimethyl-2,2′-bipyridine-κN$^1$,κN$^{1'}$)(pyrazino[2,3-f][1,10]phenanthroline-κN$^8$,κN$^9$)ruthenium(2+) Bis[hexafluorophosphate(1−)]* ($[Ru(Me_2bpy)_2(ppl)](PF_6)_2$; **9**). Yield 48%. UV/VIS (MeCN): 256, 285, 450. IR (KBr): 1619, 842, 557. $^1$H-NMR ($CD_3CN$): 9.5 (*d*, 2 H); 9.2 (*s*, 1 H); 8.4 (*s*, 2 H); 8.35 (*s*, 2 H); 8.2 (*d*, 2 H); 7.85 (*m*, 2 H); 7.6 (*d*, 2 H); 7.45 (*d*, 2 H); 7.25 (*d*, 2 H); 7.0 (*d*, 2 H); 2.6 (*s*, 6 H); 2.45 (*s*, 6 H).

*Bis(2,2′-bipyridine-κN$^1$,κN$^{1'}$)(2-methylpyrazino[2,3-f][1,10]phenanthroline-κN$^8$,κN$^9$)ruthenium(2+) Bis[hexafluorophosphate(1−)]* ($[Ru(bpy)_2\{(Me)ppl\}](PF_6)_2$; **10**). Yield 50%. UV/VIS (MeCN): 256, 287, 450. IR (KBr): 840, 557. $^1$H-NMR ($CD_3CN$): 9.5 (*t*, 2 H); 9.1 (*s*, 1 H); 8.5 (*t*, 4 H); 7.8–8.2 (10 H); 7.6 (*d*, 2 H); 7.4 (*t*, 2 H); 7.2 (*t*, 2 H); 2.9 (*s*, 3 H).

*Bis(4,4′-dimethyl-2,2′-bipyridine-κN$^1$,κN$^{1'}$)(2-methylpyrazino[2,3-f][1,10]phenanthroline-κN$^8$,κN$^9$)ruthenium(2+) Bis[hexafluorophosphate(1−)]* ($[Ru(Me_2bpy)_2\{Meppl\}](PF_6)_2$; **11**). Yield 49%. UV/VIS (MeCN): 256, 285, 450. IR (KBr): 1619, 842, 557. $^1$H-NMR ($CD_3CN$): 9.5 (*dd*, 2 H); 9.1 (*s*, 1 H); 8.4 (*s*, 2 H); 8.38 (*s*, 2 H); 8.2 (*t*, 2 H); 7.85 (*m*, 2 H); 7.7 (*d*, 2 H); 7.4 (*m*, 2 H); 7.3 (*d*, 2 H); 7.05 (*d*, 2 H); 2.9 (*s*, 3 H); 2.6 (*s*, 6 H); 2.5 (*s*, 6 H).

*Bis(2,2′-bipyridine-κN$^1$,κN$^{1'}$)(methylpyrazino[2,3-f][1,10]phenanthroline-2-carboxylate-κN$^8$,κN$^9$)ruthenium(2+) Bis[hexafluorophosphate(1−)]* ($[Ru(bpy)_2\{(COOMe)ppl\}](PF_6)_2$; **12**). Yield 45%. UV/VIS (MeCN): 259, 286, 450. IR (KBr): 1744, 1726, 840, 558. $^1$H-NMR ($CD_3CN$): 9.8 (*s*, 1 H); 9.55 (*t*, 2 H); 8.55 (*t*, 4 H); 8.25 (*m*, 2 H); 8.15 (*t*, 2 H); 8.05 (*t*, 2 H); 7.95 (*m*, 2 H); 7.9 (*d*, 2 H); 7.7 (*t*, 2 H); 7.5 (*t*, 2 H); 7.25 (*t*, 2 H); 4.1 (*s*, 3 H).

*Bis(4,4′-dimethyl-2,2′-bipyridine-κN$^1$,κN$^{1'}$)(methyl pyrazino[2,3-f][1,10]phenanthroline-2-carboxylate-κN$^8$,κN$^9$)ruthenium(2+) Bis[hexafluorophosphate(1−)]* ($[Ru(Me_2bpy)_2\{(COOMe)ppl\}](PF_6)_2$; **13**). Yield 50%. UV/VIS (MeCN): 259, 284, 447. IR (KBr): 1744, 1726, 843, 557. $^1$H-NMR ($CD_3CN$): 9.8 (*s*, 1 H); 9.5 (*t*, 2 H); 8.4 (*s*, 2 H); 8.35 (*s*, 2 H); 8.2 (*m*, 2 H); 7.9 (*m*, 2 H); 7.6 (*d*, 2 H); 7.4 (*t*, 2 H); 7.3 (*d*, 2 H); 7.05 (*d*, 2 H); 4.1 (*s*, 3 H); 2.55 (*s*, 6 H); 2.45 (*s*, 6 H).

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