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Effect of pH in the Photoluminescence of a Ruthenium Complex Featuring a Derivative of the Ligand pyrazine[2,3-f][1,10]-phenanthroline

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Abstract

A new ruthenium complex, $[Ru(bpy)_2(dbe\text{-}ppl)](PF_6)_2$ (bpy = 2,2'-bipyridine and dbe-ppl = dimethyl 4,4'-(pyrazino[2,3-f][1,10]phenanthroline-2,3-diyl)dibenzoate, has been synthesized and characterized by ^{1}H-NMR spectroscopy, UV-Vis, IR, and cyclic voltammetry.

Irradiation on the MLCT band results in photoluminescence in both protic and aprotic solvents. The photoluminescence in water is pH dependent, it shows a behavior which can be described by the Henderson-Hasselbalch assuming the protonation/deprotonation of the excited state with a pKa of 2.40 ± 0.01.

Introduction

The synthesis of ruthenium diimine complexes possessing redox and photoactive residues remains an active research area due to their diverse applications as solar cell dyes[1–3], anion sensors[4,5] or as probes for DNA binding[6–8].

Complexes possessing ligands with extended π systems, as pyrazino[2,3-f][1,10]phenanthroline, ppl, and dipyrido[3,2-a:2',3'-c]phenazine, dppz, (figure 1) are of special interest. These ligands could be analyzed as the fusion of a bipyridine moiety with a quinoxaline or phenazine moiety.

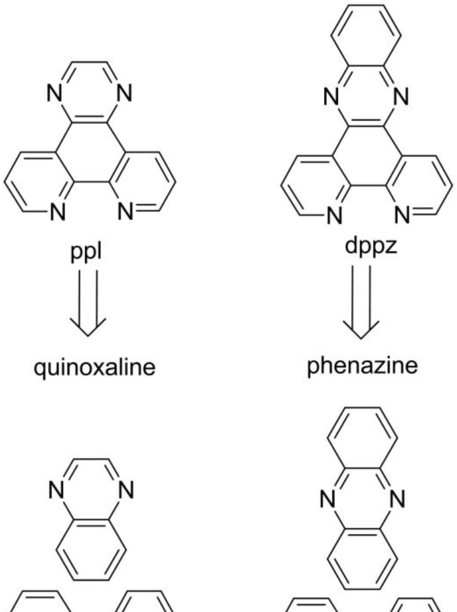


Figure 1. Schematic representation of the fragments constituting the ligands and dppz ppl

This configuration gives origin to a distinctive photophysical behavior of their complexes, e.g. [Ru(bpy)$_2$(dppz)]$^{2+}$ is nonemissive in aqueous solution but have long-lived photoluminescent excited states in aprotic environments or when intercalated to DNA. This behavior is known as the “light switch effect”[9]

Hydrogen bonding between solvent and the nitrogen atoms of the phenazine region (phz) has been claimed to explain the quenching of photoluminescence[10,11]. Also, it has been reported that the emission can be dominated by temperature, due to the presence of two different, close in energy, charge transfer states in the dppz ligand. In this model, photoluminescence is observed when the “bright state” on the bipyridine region of the dppz ligand is populated, while the emission is quenched by the population of the lowest energy state, the “dark state” located on the phenazine region of the dppz ligand[12,13]. Similar observations have been made when the ppl or dppz ligands are functionalized with electron acceptor groups[14].

Although compounds having this type of effect are interesting as cellular probes, its use in photoelectrochemical solar cells may be limited. It has been reported that electron injection quantum yield of dppz type compounds into the titanium dioxide conduction band is influenced by the presence of water in the semiconductor/solvent interface[15]. Therefore, in order to prepare new sensitizers with these types of ligands is desirable that the excited states of its complexes show no quenching by water.

In this work we report the synthesis and characterization of a new ppl derivative functionalized with benzoic methylesters groups, which potentially could be used as sensitizer in photoelectrochemical solar cells, their photophysical properties in aqueous solution are described and discussed.

Experimental

Apparatus and reagents

All reagents were of analytical grade and were used as received without further purification. Thiamine hydrochloride and 4-formyl benzoate were purchased from Aldrich. Ammonium nitrate, methanol and acetic acid were purchased from Merck.

5,6-diamine-1,10-phenanthroline[16], *cis*-$Ru(bpy)_2Cl_2$[17] were prepared accorded to procedures described elsewhere

The absorption spectra were obtained using a Jasco 530 UV–visible spectrophotometer. The photoluminescence emission spectra were recorded on a Shimadzu RF-5301 PC. Electrochemical measurements were performed using a Princeton Applied Research PG 580 potentiostat and a classical three-electrode setup consistent on Pt flat disk working electrode, a Pt wire auxiliary electrode and an Ag/AgCl reference electrode. IR spectra were obtained using a Brucker Vector 22 FT using KBr. NMR spectra were recorded on a Brucker AVANCE 400 MHz spectrometer using DMSO-d^6 with TMS as internal reference.

pKa determination

The pKa was determined by fitting the obtained data to the Henderson-Hasselbalch equation:

$$pK_a = pH + \log\left[\frac{PLI_{max} - PLI}{PLI - PLI_{min}}\right] \quad \text{(Equation 1)}$$

Where PLI_{max} and PLI_{min} are, respectively, the maximum and minimum of photoluminescence intensity of the base and conjugated acid species and PLI is the photoluminescence intensity as function of the pH. The goodness of the fit was judged by the R^2 parameter, which was greater than 0.996.

Photoluminescence quantum yield measurements, ϕ_{PL}, were performed using the optically dilute technique with $[Ru(bpy)_3](PF_6)_2$ in acetonitrile as the actinometer:

$$\emptyset_{PL} = (A_r/A_s)(I_s/I_r)(n_s/n_r)^2\emptyset_r \qquad \text{(Equation 2)}$$

A_r and A_s were the absorbances of the actinometer and sample, respectively, I_r and I_s were the integrated photoluminescence of the actinometer and sample, respectively, n_r and n_s were the refraction indexes for the solvents used for the actinometer and sample, respectively, and Φ_r was the quantum yield for $[Ru(bpy)_3](PF_6)_2$ in acetonitrile (Φ_r = 0.062).

The excited state reduction potentials, $E_{1/2}(Ru^{III/II}*)$, were calculated from the ground state potentials and from the free energy stored in the thermally equilibrated MLCT excited state, ΔG_{es}:

$$E_{1/2}(Ru^{III/II*}) = E_{1/2}(Ru^{III/II}) - \Delta G_{es} \qquad \text{(equation 3)}$$

ΔG_{es} was estimated by drawing a tangent line to the high-energy side of the photoluminescence spectra

Synthesis

dimethyl 4,4'-(2-hydroxyacetyl)dibenzoate (1).

Thiamine hydrochloride (1.80 g, 5.35 mmol) was dissolved in 20 mL of 1:3 water/methanol mixture and cooled down using an ice bath, and then 5 mL of a 2M NaOH solution was added dropwise for a period of 10 minutes. To the resulting solution 4-formyl benzoate (14.9 g, 91 mmol) was added and then the mixture was heated to 60 °C for 15 minutes and afterward at reflux conditions for 1 hour. The resulting suspension was cooled to room temperature and the white solid was filtered off, washed with water, methanol and ethyl ether, then was dried on air. Yield: 12.3 g (82.2%). ^{1}H NMR (400 MHz, DMSO-d6) δ 8.11 (d, J = 8.5 Hz, 2H), 8.01 (d, J = 8.5 Hz, 2H), 7.91 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.3 Hz, 2H), 6.18 (s, 1H), 3.85 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d6) δ 198.57 (s), 165.94 (s), 165.47 (s), 144.56 (s), 138.33 (s), 133.28 (s), 129.33 (s), 129.31 (s), 129.22 (s), 129.03 (s), 127.50 (s), 75.70 (s), 52.50 (s), 52.12 (s).

dimethyl 4,4'-oxalyldibenzoate (2)

A mixture of dimethyl 4,4'-(2-hydroxyacetyl)dibenzoate **(1)** (10,02 g, 32,96 mmol), copper acetate (II) (0.1 g, 0.5 mmol), ammonium nitrate (5.0 g 62.5 mmol) and 35 mL of an acetic acid-water 80% solution was refluxed until formation of a yellow precipitate. The mixture was cooled to room temperature, the solid collected by filtration, washed with water, methanol and ethyl ether and then dried under vacuum. Yield: 8.84 g (88.8%). The solid obtained was used without further purification.

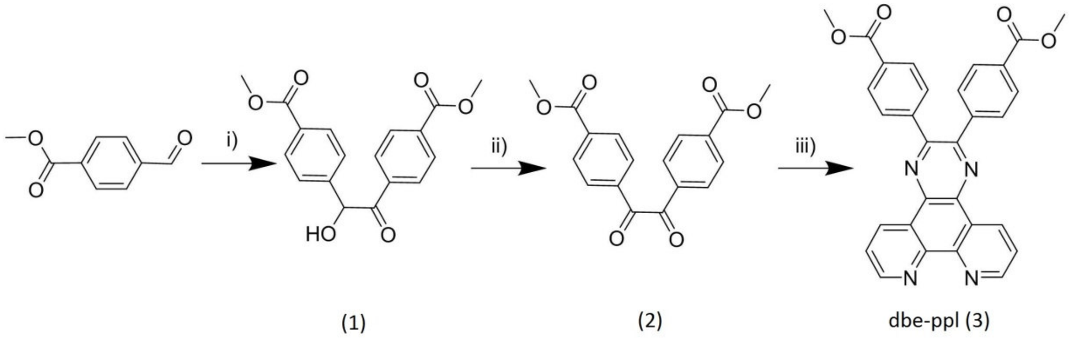
dimethyl 4,4'-(pyrazino[2,3-f][1,10]phenanthroline-2,3-diyl)dibenzoate (dbe-ppl). A mixture of 5,6-diamino-1,10-phenanthroline (0,100 g, 0.5 mmol) with dimethyl 4,4'-oxalyldibenzoate (0.163 g, 0.5 mmol) and 25 mL of methanol were refluxed for 12 hrs. The resulting solid was filtered off and washed with water and methanol. Yield: 0.21 g (84 %). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.44 (dd, J = 8.1, 1.5 Hz, 2H), 9.24 (dd, J = 4.3, 1.6 Hz, 2H), 8.00 (d, J = 8.3 Hz, 4H), 7.95 (dd, J = 8.1, 4.4 Hz, 2H), 7.78 (d, J = 8.3 Hz, 4H), 3.88 (s, 6H).

[Ru(bpy)$_2$(dbe-ppl)](PF$_6$)$_2$. Ru(bpy)$_2$Cl$_2$ 0.110 g, (0.23 mmol) with 0.115 g (0.23 mmol) of dbe-ppl ligand were dissolved in MeOH/H_2O 2 : 1 (25 ml). The solution was refluxed for 3 h. After filtration, NH_4PF_6 was added to precipitate the complex. The solid was filtered off, washed with H_2O and Et_2O, and dried under vacuum. Yield: 0.20 g (67 %). ^{1}H NMR (400 MHz, DMSO) δ 9.60 (d, J = 8.3 Hz, 1H; H3), 8.87 (m, 2H; H6, H7), 8.29 (d, J = 5.3 Hz, 1H; H1), 8.23 (t, J = 8.0 Hz, 1H; H7), 8.14 (t, J = 7.8 Hz, 1H; H11), 8.04 (m, 3H; H5, H3), 7.86 (d, J = 5.5 Hz, 1H; H9), 7.83 (d, J = 8.4 Hz, 1H; H4), 7.73 (d, J = 5.5 Hz, 1H; H13), 7.64 – 7.58 (m, 1H; H8), 7.43 – 7.33 (m, 1H; H12), 3.89 (s, 3H; CH3).

Results and discussion

Synthesis

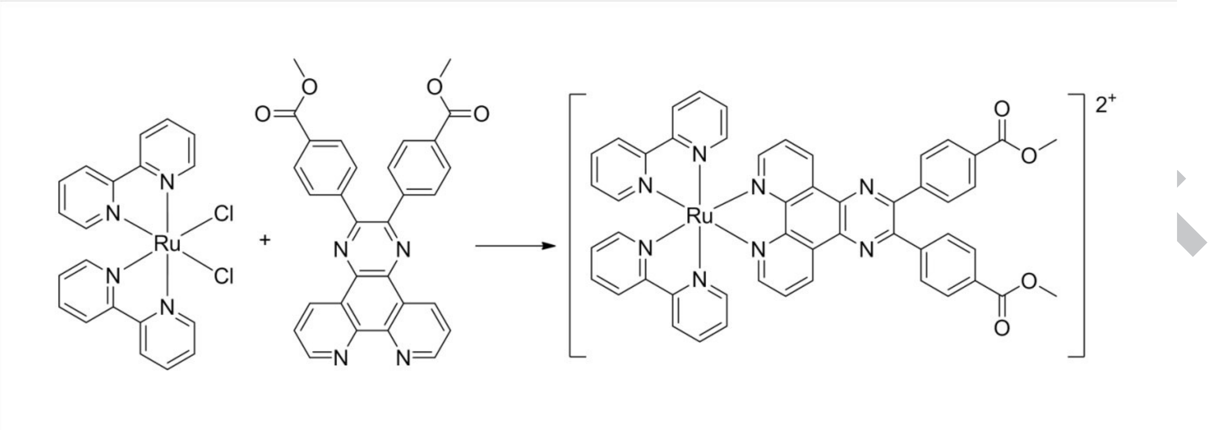
The ligand dimethyl 4,4'-(pyrazino[2,3-f][1,10]phenanthroline-2,3-diyl)dibenzoate, **dbe-ppl**, was synthesized in a sequence of three steps as depicted in scheme 1, the first step consists in a benzoin type condensation of 4-formyl benzoate with thiamine hydrochloride as catalyst[18], the second step correspond to the catalytic oxidation to the respective benzyl **(1)** using copper acetate and ammonium nitrate in acetic acid. Finally, the condensation of **(2)** with 5,6-diamino-1,10-phenanthroline leads to the ligand of interest which to our knowledge is reported for the first time.



Scheme 1. Synthetic route for the synthesis of the dbe-ppl ligand. i) thyamine hydrochloride, NaOH 2 eq ii) $Cu(OAc)_2$, NH_4NO_3, iii) 5,6-diamine-1,10-phenanthroline

This synthetic approach seems to be more convenient for the synthesis of substituted pyrazino[2,3-f][1,10]phenanthroline than the condensation of diamines with 5,6-dione-1,10-phenanthroline[19].

The synthesis of the complex of interest was accomplished in one step as depicted in scheme 2. Its synthesis was achieved by direct reaction of $Ru(bpy)_2Cl_2$ with (dbe-ppl) in a water ethanol mixture and a subsequent isolation by precipitation from aqueous solution with ammonium hexafluorophosphate.



Scheme 2. Synthetic route to the synthesis of the [Ru(bpy)$_2$(dbe-ppl)](PF$_6$)$_2$ complex

Electrochemistry

The electrochemical properties of [Ru(bpy)$_2$(dbe-ppl)](PF$_6$)$_2$ in CH_3CN were investigated using cyclic voltammetry (CV). The electrochemical and spectroscopic data are summarized in Table 1, together with those of reference compounds for comparison.

In Figure 2 is shown the cyclic voltammetry of the complex of interest. It can be observed three quasi-reversible waves at +1.29 V, -1.21 V and -1.44 V vs. Ag/AgCl respectively. The first wave is assigned to the ruthenium (III/II) couple while the other two waves are attributed to ligand reductions. This electrochemical behavior agrees with those reported for similar ligand complexes[19].

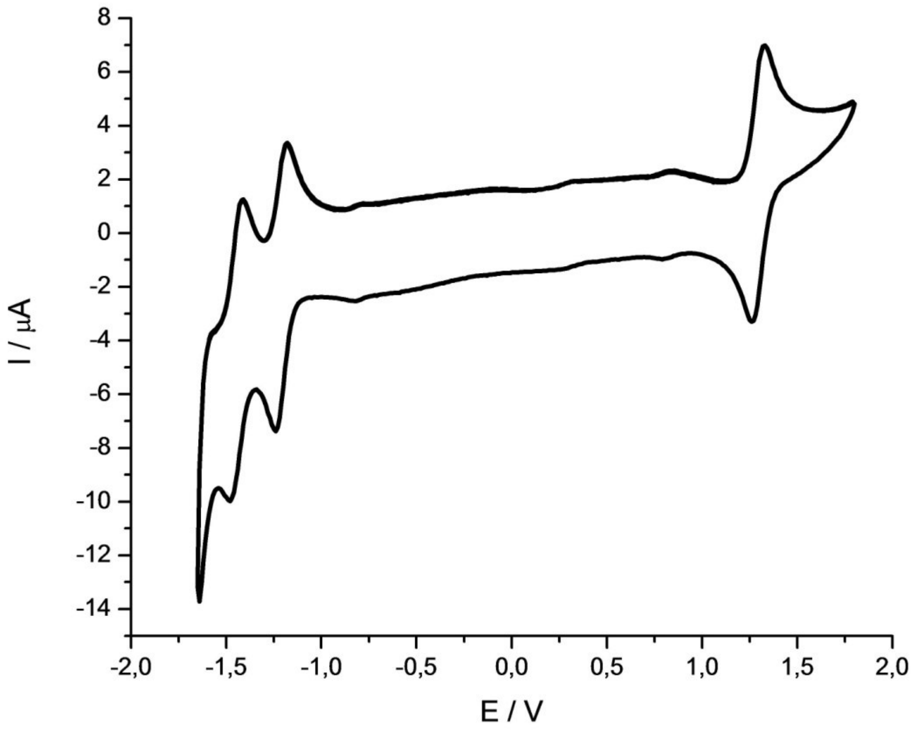


Figure 2. Cyclic voltammogram of [Ru(bpy)$_2$(dbe-ppl)](PF$_6$)$_2$ at a platinum electrode in CH$_3$CN 0.1 M TBAH at a scan rate of 100 mVs^{-1}

Absorption and Emission Spectroscopy

The absorption and emission spectra of [Ru(bpy)$_2$(dbe-ppl)](PF$_6$)$_2$ at room temperature in acetonitrile solution are plotted in Figure 3. In the ultraviolet region, its absorption is dominated by intense ligand centered (LC) ππ* transitions. The visible part of the spectra is dominated by $(d(\pi)^6) \rightarrow (d(\pi)^5(\pi)^1)$ metal-to-ligand charge-transfer (MLCT) bands which are characteristic of the polypyridinic ruthenium complexes [7].

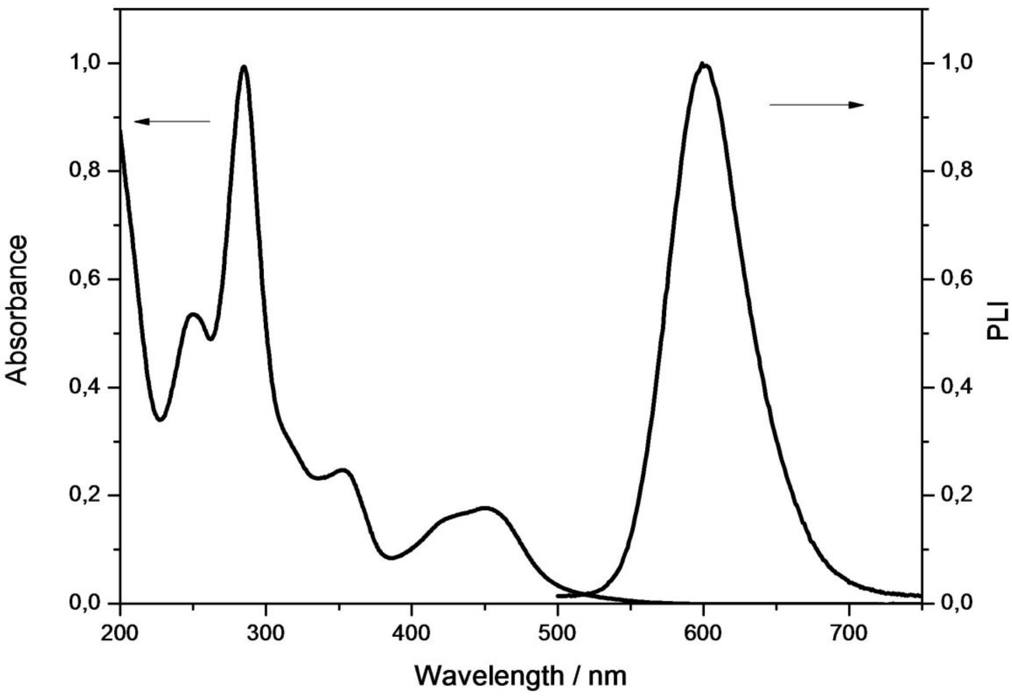


Figure 3. Normalized Absorption spectrum (left axis) and Emission spectrum (right axis) of $[Ru(bpy)_2(dbe\text{-}ppl)](PF_6)_2$ in CH_3CN solution.

Irradiation on the MLCT band results in photoluminescence, Figure 3 shows the steady-state photoluminescence spectrum recorded in acetonitrile. The emission quantum yield, calculated by comparative actinometry, was found to be 0.05 in acetonitrile solution.

It has been reported that other structurally related ligands, which like the ligand dbe-ppl have electron withdrawing groups, show a "light switch" effect similar to that presented in dppz ligand complexes.[14]. Therefore, we expected that the interaction of protic solvents with the nitrogen atoms of the quinoxaline region would lead to the quenching of the photoluminescence. Interestingly this compound emits both in protic and aprotic solvents.

Effect of the solution pH on the spectroscopic properties

To learn more about the behavior of the photoluminescence in water, we conducted experiments varying the pH in the range from 0.7 to 10.3 at constant ionic strength. Figure 4 shows the absorption and emission spectra of the complex as a function of pH.

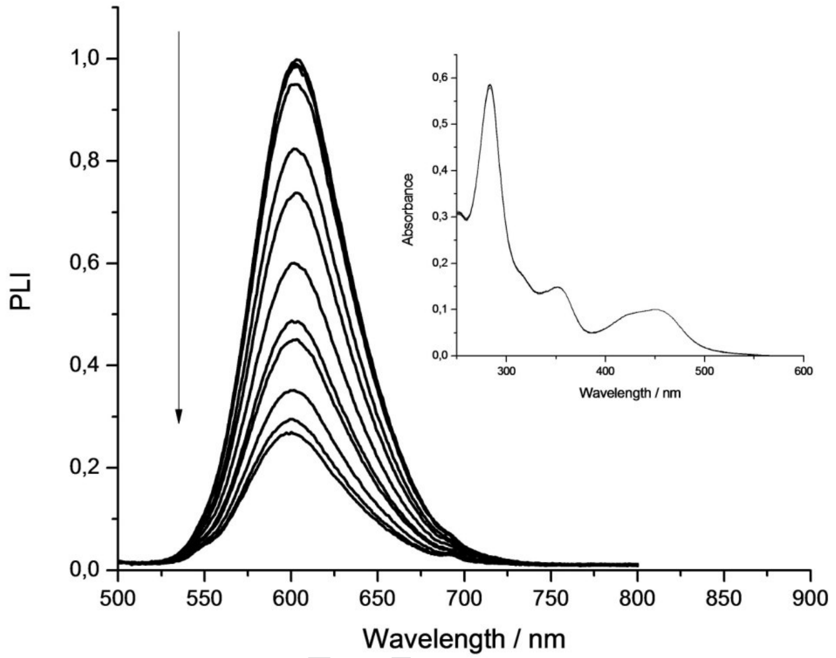


Figure 4. Emission spectra of $[Ru(bpy)_2(dbe\text{-}ppl)]^{2+}$ in water as function of pH. The pH values in order of decreasing photoluminescence intensity are: 10.3, 5.0, 3.5, 3.0, 2.8, 2.6, 2.3, 2.2, 2.0, 1.9, 1.8. The inset show the absorption spectra registered at the same pH values.

A different behavior was observed between the absorption and emission spectroscopy: whereas the modification of the solution pH produces no change in the MLCT band in the emission spectra is observed a clear decrease in the photoluminescence intensity.

The profile of emission intensities versus pH is shown in Figure 5, the sigmoidal shape of the curve suggests the existence of just one process of protonation / deprotonation of the excited state of the complex. Fitting the deprotonated fraction to the Henderson-Hasselbalch equation (eq 1) yielded a pKa of 2.40 ± 0.01.

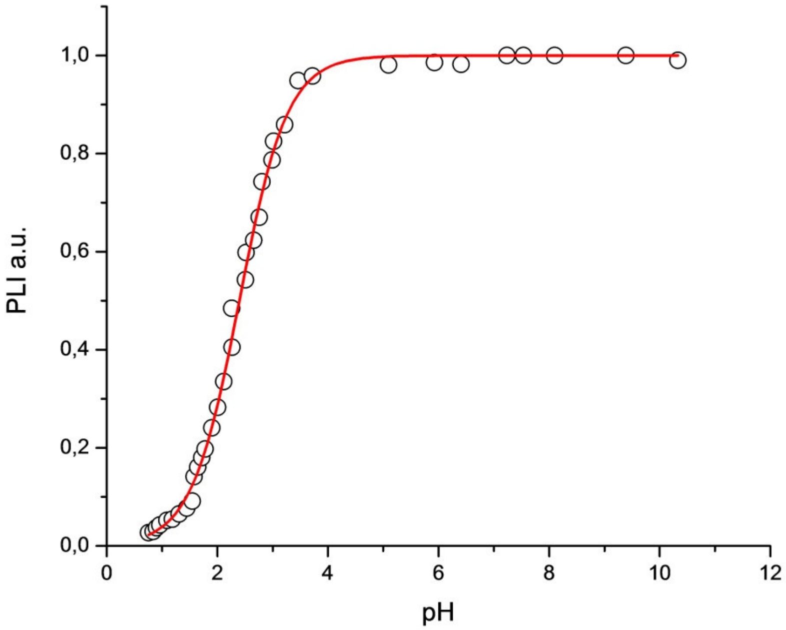


Figure 5. Normalized photoluminescence intensity at 600 nm as function of pH. The solid line represents the fitting of the data to the Henderson-Hasselbalch equation.

The fact that there was no change in the MLCT band absorbance when the pH of the solution is altered can be interpreted in terms of the presence of close low lying π* unoccupied orbitals related to distinct regions of the ligand molecule. In the dppz and ppl type ligands, the lowest unoccupied molecular orbital, the "redox orbital" is ascribed to the quinoxaline region and is populated by the first added electron from electrochemical reduction. Higher in energy is located the "optical orbital" related to the bipyridine region of the ppl ligand and it is involved in the electronic transitions[20]. Protonation of the nitrogen atoms on the pyrazine region should lower the energy of the redox orbital leading to a non-emissive pathway for excited state decay.

The electrochemical and spectroscopic data are in agreement with this model. The maximum MLCT wavelength in polypyridinic ruthenium compounds can be roughly estimated by the energy related to the oxidation of the metal and the first reduction of the ligands[21]. According to the electrochemical data the maximum MLCT wavelength for this complex should be observed at ca. ~500 nm, but experimentally the maximum of this band is observed at 454 nm. If the calculation is made with the second reduction process the maximum wavelength should be observed at ~450 nm.

Table 1. Electrochemical and spectroscopic data for $[Ru(bpy)_2(dbe\text{-}ppl)]^{2+}$.

Compound	$E_{1/2}$ $Ru^{III/II}$ (V)	$E_{1/2}$ $Ru^{2+/+}$ (V)	λ_{abs} (nm)	λ_{em} (nm)	Φ_{em}	$E_{1/2}$ $Ru^{III/II*}$ (V)
$[Ru(bpy)_2(dbe\text{-}ppl)]^{2+}$	1.29	-1.21	454	600	0.050	-0.99
[d] $[Ru(bpy)_3]^{2+}$	1.29	-1.33	452	620	0.062	-1.00
[e] $[Ru(bpy)_2dppz]^{2+}$	1.24	-0.86[a]	448	610	0.021	
		-0.77[b]				
[d,c] $[Ru(bpy)_2ppl]^{2+}$	1.37	-1.18	454	630	0.022	-0.95

[a] In DMF, [b] In ethanol. [c] data taken from reference [19], [d] data taken from reference [22], [e] data taken from reference [23]

Implications for photoelectrochemical solar cells.

The ligand dbe-ppl have adequate functional groups to be adsorbed on metal oxide surfaces, which opens the possibility to employ compounds of this ligand in applications as photoelectrochemical solar cells or photocatalyst in supramolecular processes.

The calculated reduction potential in the thermal equilibrated excited state for this compound is -0.99 V vs. Ag/AgCl, this value stands near the calculated electrochemical potential of the conduction band edge on titanium dioxide (-0.90 V MeCN Li+ 0.1 M)[24] which indicates that a photoinduced interfacial electron injection to titanium dioxide is possible.

It has been shown that related complexes injects efficiently electrons on the conduction band of nanocrystallytes of titanium dioxide in the absence of water, but as its concentration increases in the solution, the injection quantum yield decreases in about 60 %[15], a possible reason to that behavior could be the quenching of the excited state by water or adsorbed protons on the titanium dioxide surface. As we have shown, the excited state of $[Ru(bpy)_2(dbe\text{-}ppl)]^{2+}$ it is not quenched by water at neutral pH values so we expect this complex should be a good sensitizer even in the presence of small amounts of water.

Conclusions and outlook

In summary, a new Ru(II) complex has been synthesized and characterized. This compound shows photoluminescence both in protic and aprotic solvents. In water, a diminution of the photoluminescence intensity is only observed at pH values below 4.

Since the ligand dbe-ppl posses the methyl ester functional groups it could be employed as a sensitizer in photoelectochemical solar cells.

Acknowledgements

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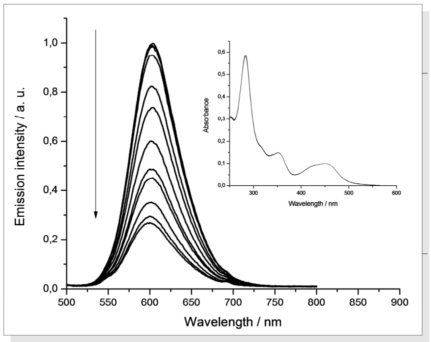
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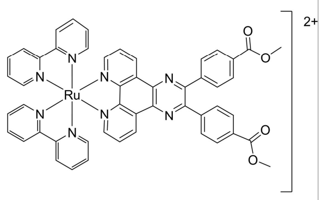
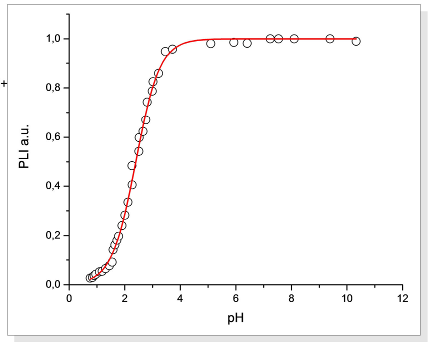
600
Wavelength / nm


N
Ru
O
2+


PLI a.u.
1,0
0,8
0,6
0,4
0,2
0,0
0
2
4
6
8
10
12
pH

Highligths

- The synthesis and characterization of a new ruthenium complex is reported.
- The complex shows photoluminescence in both protic and aprotic solvents.
- Photoluminiscence is quenched in water at low pH.