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Study of the effect of aliphatic and π -conjugated systems on the photophysical properties of polypyridinic Ruthenium II complexes as potential semiconductor materials for iTMC type LEC

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Abstract

The photophysical properties of polypyridinic Ruthenium complexes, as potential semiconductor materials for iTMC (ionic transition metal complex) type LECs have been studied. Substituted 2,2'-bipyridine ligands were used to study the effects of conjugated and aliphatic chains on the properties of the complexes, especially on the photophysical properties. Specifically, the N^N type ligands 4,4'-bis[2-hydroxy-2-(phenyl)ethyl]-2,2'-bipyridine (1), 4,4'-bis(α -styrene)-2,2'-bipyridine (2) and 4,4'-diphenylethyl-2,2'-bipyridine (3) were synthesized, and used to prepare the corresponding [Ru^{II}(bpy)₂(N^N)](PF₆)₂ complexes. All three ligands contain a phenyl group as substituent for bpy, but with different residues as bridges between both: ligands 1 and 3 have free rotating connecting groups, while 2 is more rigid due to the styryl double bond. From the achieved results it was observed that, as expected, a conjugation on the ligand produces complexes with bands shifting toward lower energy regions, due to the electronic communication between the phenyl and bipyridine groups. On the contrary, in the absence of this conjugation, as is the case of the complexes with ligands 1 and 3, absorptions and emissions bands are very similar to the corresponding complex with unsubstituted bpy. Therefore, complexes with

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ligands 1 and 3 seem to be promising for LEC devices, due to the free rotations of the connecting aliphatic chain. This should preserve the properties as emission color, and advantages of $Ru(bpy)_3^{2+}$ photoluminescence, but increasing the efficiency when used in a device, avoiding crystallization and diminishing self-quenching processes.

Keywords: ruthenium, polypiridinc complex, iTMC, LEC

1. Introduction

Since the first successful report by Tang and Van Slyke [1], in the last decades, organic light emitting diodes (OLEDs) have concentrated lots of attention. In a second stage, the use of transition metal complexes as semiconductor materials on OLEDs reached broad attention due to their potential higher emission quantum efficiency. In regard to the emission properties of transition metal compounds, ruthenium stands out among others, as corroborated by the extensive research studying its photophysical processes [2]. One of the main characteristics that make the use of ruthenium compounds interesting is the large number of excited states these molecules may assume, together with a significant spin-orbit coupling which allows rapid internal conversion and intersystem crossings processes. The process of populating the excited state belongs to a $d-\pi^*$ transition, also named ¹MLCT (Metal-Ligand Charge Transfer). The deactivation of the ¹MLCT state has two main paths to follow, the radiative deactivation from the singlet state, generating a fluorescent emission, or the intersystem crossing process to a lower energy ³MLCT state, from where phosphorescence can occur [3].

In the search of a simpler device fabrication process, solid-state light-emitting electrochemical cells (LECs) have been developed as promising flat lighting devices [4, 5]. Traditionally, the reported design for OLED devices were based on multilayer organic semiconductor materials deposited by vacuum thermal evaporation on indium tin oxide (ITO), covered by a low work-function cathode. From Rubner's seminal work [6], introducing a device with a ruthenium polypyridyl complex film deposited trough spin-coating, to Malliaras *et al.* [7, 8] progress on efficiency, lifetime and desired emission, the

ionic Transition Metal Complexes (iTMC) type LECs have received increased attention [9-11]. The following requirements are necessary to be considered when designing iTMC materials, in order to improve the performance of LEC devices:

- The size of the complex and its effect of the quantum yield; more specifically the distance between the metallic centers in order to avoid self-quenching.
- Film crystallization induced by the molecular structure. Amorphous films have shown ideal morphology to avoid degradation and film defects in organic semiconductor devices.

The aim of this study is to provide some insight and understanding of the physicalchemical properties that a complex should possess in order to be used in iTMC-LECs. The goal is to understand the effect of steric and electronic effects over the color of the emission, and over the potential performance of a device based on these complexes. This would permit to predict the behavior of a substance in an LEC before preparing the device. Based on this, the synthesis of a series of ruthenium complexes were prepared, together with a full characterization with different tools (UV-Vis and FT-IR Spectroscopies, Multi nuclear NMR, Elemental Analysis, Emission studies, Cyclic Voltammetry). Specifically, three polypyridinic ligands of the type 2,2'-bipyridine are proposed, in order to study the effect of branched highly conjugated substituents, such as styrene, and how would the presence and absence of these conjugations affect the chemical and physical properties. The ligands 4,4'-bis[2-hydroxy-2-(phenyl)ethyl]-2,2'-bipyridine (1), 4,4'-bis(α -styrene)-2,2'bipyridine (2) and 4,4'-diphenylethyl-2,2'-bipyridine (3) were synthesized (Fig. 1), as well as their corresponding $[Ru(bpy)_2(N^N)](PF_6)_2$ complexes. Although similar molecules have been reported, complexes with ligands 1 and 3, to our knowledge, have not yet been previously reported [10, 12]. Complex with ligand 2 was used for comparison reasons, related to the study of the effect of the presence and absence of conjugation in the ligand. Considering the color of the emission, it is expected that a high conjugation, as in ligand 2, would allow absorption and emission processes at low energy values, compared to systems with less delocalization. On the other hand, the presence of substituents with aliphatic chains directly bound to bpy, as in ligands 1 and 3, should displace absorption and emission

of the corresponding complexes to higher energy values compared with complexes with ligand **2** [2, 13, 14].

Figure 1

2. Materials and methods

2.1.Materials

The reagents used in the synthesis of the precursors, ligands and complexes, were acquired from Aldrich and Merck. The solvents were used with no prior treatment, with the exception of THF and acetonitrile, being used in the synthesis of the ligands, and in the cyclic voltammetry and emission studies, respectively. The first was dried using sodium wires and the second with phosphorus pentoxide.

2.2.Equipment

The hydrogenation equipment used for the synthesis of ligand **3** was a Shaker Type Hydrogenation Apparatus, Model 2915, Parr Instrument Company. The equipments employed for the NMR experiments were the BRUKER Avance 200 MHz or BRUKER Avance 400 MHz spectrometers. The infrared spectra were recorded in a BRUKER spectrometer, Model Vector 22 with a Fourier Transformation Module, on KBr pellets. The Elemental Analyses were carried out on Fisons - EA-1108 CHNS-O Element Analyzer. The absorption spectra were recorded on a Shimadzu UV-Vis-NIR 3101 PC spectrophotometer. The cyclic voltammograms were recorded using a BAS CV-50W, using a BAS Model MF-2013 platinum disc working electrode with an area of 0.02 cm², a Ag/AgCl reference electrode (BAS Model MF-2062) and a platinum wire as auxiliary electrode, with an area of 0.57 cm². All measurements were made at 100 mV/s sweep rate. The samples were prepared at a concentration of 10^{-4} M. The emission spectra were recorded with a PERKIN ELMER L55 spectrometer.

2.3.Ligand Synthesis.

2.3.1. 4,4'-bis[2-hydroxi-2-(phenyl)ethyl]-2,2'-bipyridine (1): In a round flask of 250 mL, 0.50 g (2.71 mmol) of 4,4'-dimethyl-2,2-bipyridine were added to 20 mL of dry THF, in a N₂ atmosphere and in an ethanol/liquid N₂ bath, until the complete solubility of the reagent was achieved. Next, 3.5 mL of lithium diisopropylamide (LDA) was dropwise added, stirring the solution for 75 min. 0.55 mL (5.42 mmol) of benzaldehyde were then incorporated, and the mixture allowed to react with vigorous stirring for 5 hours. Later, the reaction mixture was deactivated with 1 mL of methanol and 10 mL of distilled water. Following this, the organic phase was extracted with three portions of 25 mL of chloroform, and the organic solution dried with MgSO₄, and left under vacuum. To the dry product, 25 mL of a 1:1 mixture of acetic acid/water was added, and the solution refluxed for 2 hours. After cooling the mixture in an ice bath, the formed precipitate was filtered off. The obtained yield was 70%. FT-IR, cm⁻¹, (Ker): 3356 (stretching O-H, OH unit); 1597 (stretching C=C pyridine); 1555 (stretching C=N pyridine); 700 (bending, monosubstitued aromatic unit). ¹H-NMR 200 MHz, δ ppm, (CDCl₃): 8.52 (d, H₁, H₁'), 8.31 (s, H₃, H₃'), 7.13 (d, H₂, H₂'), 5.05 (t, H₆, H₆'), 3.10 (d, H₄, H₄', H₅, H₅'), 2.44 (s, H₇, H₇').

2.3.2. 4,4'-bis(*a*-styrene)-2,2'-bipyridine (2): To a 100 mL round flask, 0.60 g (1.51 mmol) of **1** and 60 mL of acetic acid were added, and refluxed for 18 hours. After that, half the solvent was removed in a rotary evaporator system and the precipitate was filtered and washed with ether. The obtained yield was 66%. FT-IR, cm⁻¹, (Ker): 1634 (stretching C=C, alkene unit); 1585 (stretching C=C, pyridine); 1541 (stretching C=N pyridine); 692 (bending, monosubstitued aromatic unit). ¹H-NMR 200 MHz, δ ppm, (CDCl₃): 8.67 (d, H₁,H₁'), 8.56 (s, H₃, H₃'), 7.48 (d, H₄, H₄'), 7.37 (d, H₂, H₂'), 7.15 (d, H₅, H₅').

2.3.3. 4,4'-diphenylethyl-2,2'-bipyridine (**3**): The ligand 4,4'-bis(α -styrene)-2,2'-bipyridine (**2**) underwent hydrogenation with stirring, adding 0.18g (0.50 mmol) of it to a mixture of 0.1 g of 10% palladium over active charcoal and 25 mL of an ethanol/acetic acid 4:1 mixture. The solution was hydrogenated for 24 hours, till no further consumption of

hydrogen was noticeable. Afterwards, the resulting solution was filtered to remove the catalyst. The solution was neutralized with a 1M solution of NaOH, to later continue with an extraction with three portions of 25 mL of chloroform. The organic phase was dried with MgSO₄, and the solvent removed under vacuum. The obtained yield was 22%. ¹H-NMR 200 MHz, δ ppm, (CDCl₃): 8.57 (d, H₁,H₁'), 8.30 (s, H₃, H₃'), 7.11 (d, H₂, H₂'), 3.01 (s, H₄, H₄', H₅, H₅', H₆, H₆', H₇, H₇').

2.4.Synthesis of Complexes

2.4.1. cis-[Ru(bpy)₂(1)](PF₆)₂: In a two-necked round flask, 0.20 g (0.38 mmol) of cis-Ru(bpy)₂Cl₂ and 0.19 g (0.76 mmol) of AgPF₆ were added, together with 35 mL of DMF. In a second round 100 mL flask, 0.15 g (0.38 mmol) of 1 in 40 mL of benzene were added and stirred until the reagent was completely dissolved. The solution was added to the former mixture, refluxing the system for 4 hours, protected from light. The flask was dried under vacuum and acetone added until all substances were dissolved. The mixture was filtered over celite, to remove the insoluble AgCl formed. The solution was then concentrated to precipitate the complex with ether. The obtained yield was 71%. Anal. C₄₆H₄₀N₆RuO₂F₁₂P₂x0.6H₂O (%) calc: C 49.75; H 3.74; N 7.57. Exp. C 49.30; H 4.20; N 7.69. FT-IR, cm⁻¹, (Ker): 3417 (stretching O-H, OH unit); 1618 (stretching C=C pyridine); 1604 (stretching C=N pyridine); 841, 557 (stretching P-F); 703 (bending, monosubstitued aromatic unit). ¹H-NMR 400 MHz, δ ppm, (C₃D₆O): 8.82 (t, H₁'), 8.52 (d, H₃), 8.21 (m, H₂'), 8.00 (m, H₄'), 7.83 (d, H₁), 7.60 (m, H₃'), 7.40 (t, H₂), 5.06 (s, H₆), 4.64 (s, H₇), 3.20 (d, H₄, H₅). ¹³C-NMR 400 MHz, δ ppm, (C₃D₆O): 152.789 (C₄'), 151.626 (C₁), 138.920 (C₂'), 128.802 (C₃'), 128.321 (C₂), 128.417 (C₃), 125.406 (C₁'), 74.039 (C₆), 45.082 (C₄₋₅).

2.4.2. cis-[Ru(bpy)₂(2)](PF₆)₂: The procedure was carried out similarly than for complex [Ru(bpy)₂(1)](PF₆)₂. The obtained yield was 60%. Anal. C₄₆H₃₆N₆RuF₁₂P₂ x0.5H₂O (%) calc: C 51.50; H 3.48; N 7.83. Exp. C 51.45; H 3.89; N 7.85. FT-IR, cm⁻¹, (Ker): 1631 (stretching C=C, alkene unit); 1609 (stretching C=C, pyridine); 1577 (stretching C=N pyridine); 839, 557 (stretching P-F); 692 (bending, monosubstitued

aromatic unit). ¹H-NMR 400 MHz, δ ppm, (C₃D₆O): 9.05 (s, H₃), 8.82 (d, H₁'), 8.19 (m, H₂'), 8.06 (d, H₄'), 7.94 (d, H₁), 7.80 (d, H₄), 7.71 (d, H₂), 7.59 (m, H₃'), 7.45 (d, H₅). ¹³C-NMR 400 MHz, δ ppm, (C₃D₆O): 152.784 (C₄'), 152.391 (C₁), 139.010 (C₂'), 137.559 (C₄), 130.449 (C₅), 129.948 (C₃'), 128.875 (C₂), 125.343 (C₁'), 122.209 (C₃).

2.4.3. *cis*-[**Ru**(**bpy**)₂(**3**)](**PF**₆)₂: The procedure was carried out similarly than for complex [Ru(bpy)₂(1)](PF₆)₂, but using benzene as solvent to precipitate the complex. The obtained yield was 76%. C₄₆H₄₀N₆RuF₁₂P₂x1.75 H₂O (%) cal: C 50.26; H 3.99; N 7.64. **Exp. C 50.62; H 4.99; N 7.54**. ¹H-NMR 400 MHz, δ ppm, (C₂D₃N): 8.49 (dd, H₁'), 8.21 (s, H₃), 8.05 (m, H₂'), 7.68 (dd, H₄'), 7.50 (d, H₁), 7.40 (dt, H₃'), 7.25 (d, H₂), 3.10 (d, H₄, H₅), 2.99 (d, H₆, H₇). ¹³C-NMR 400 MHz, δ ppm, (C₃D₆O): 152.774 (C₄'), 152.435 (C₁), 138.896 (C₂'), 129.347 (C₃'), 128.992 (C₂), 125.553 (C₃), 125.369 (C₁'), 37.583 (C₄₋₅), 36.816 (C₆₋₇).

2.4.4. $[Ru(bpy)_3](PF_6)_2$: The synthesis of this complex was carried out following procedures previously reported in the literature [15]. The obtained yield was 68%.

3. Results and Discussion

3.1.Synthesis

The ligands 1, 2 and 3 were synthesized carrying out modifications to the procedures described by Juris *et al.* [16]. Amongst these modifications, there is the use of acetic acid as a dehydration agent instead of sulfuric acid, to convert 1 to 2. This was done considering that the first one is a weaker acid; therefore, it is expected to prevent better than sulfuric acid the possible decomposition of the ligands. The synthetic procedure for ligand 3 reported indicated the need of applying temperature to carry out effectively the reaction. As the hydrogenation equipment used did not possess a heating system, the reaction was left to react for a longer period of time, with satisfactory results, although with lower yield than the reported procedure.

Concerning the synthesis of the complexes, the procedure described by Nazeeruddin [17] was mainly followed. In all cases, DMF was used as solvent rather than ethanol. The advantage DMF presents is its high boiling point, permitting to carry out the reactions at higher temperatures, and therefore decreasing significantly the reaction time (from 6 to 3 hours). Also, DMF may behave as a reducing agent for the reduction of Ru(III) to Ru(II), avoiding the need of an additional reducing agent such as a hydroquinone.

3.2.UV-Visible Spectroscopy

The Absorption maxima for ligands and complexes are reported in Table 1, while Figure 2 shows the experimental spectra for all synthesized complexes. Concerning the ligands, a two bands characteristic pattern in the region between 230 and 280 nm was observed, ascribed to π - π * transitions. The pattern is analogous to the bpy ligand that was used as a comparison reference. The position of the lower energy band for **2** at 312 nm is rather anomalous when compared to the other ligands in the series. A deeper analysis of the UV spectra of this last ligand has been previously reported by the group [18].

Table 1

Figure 2

Regarding the complexes, two bands are observed as a general trend, one in the 400-500 nm region, where mainly MLCT (metal ligand charge transfer) bands should be observed, and a second, in the region of 250-300 nm, expected to be ILCT (Intra Ligand Charge Transfer) bands [9]. Analyzing these last transitions, their comparison to the maximum absorptions of the corresponding free ligands is remarkably interesting, as the shift between them is minimal, allowing to demonstrate the predominant ILCT character of these bands in the complexes; therefore these transitions are only slightly affected by the coordination of the ligands to the metallic center. Just like the free ligands, the complex containing ligand 2, is singled out for presenting a shift in the MLCT band, of *ca* 20 nm to lower energies, with respect to the other complexes of the series. It should be mentioned

that for similar complexes it has been proposed that the origin of the lower energy band is due the sum of several transitions originated from different fragments of the ligands, and that it may possess a mixed MLCT-ILCT character [18].

3.3.Emission Spectroscopy

The emission measurements of the synthesized complexes are presented in Figure 2. Their corresponding emission maxima are summarized in Table 1. When analyzing the obtained emission for the three complexes in regard to $[Ru(bpy)_3](PF_6)_2$, there is a slight shift to the red region for complexes with ligands 1 and 3, and a more marked shift for the complex with ligand 2. This tendency is analogous to the one analyzed above for the UV absorptions. Specifically, the property of absorbing and emitting at lower energies for the complex with ligand 2, is ascribed to the electronic communication between the bipyridyl and phenyl groups because of the linking double bonding. This increase of conjugation is reflected in a lower difference of the energy between the HOMO d and LUMO π^* levels, and in a lower difference between the triplet state and the singlet ground state for emission, as observed in Table 1.

It is noteworthy to mention that for complexes with ligands 1 and 3, the absence of electronic communication between the bipyridyl and phenyl groups reflects both, in the UV and emission spectra, by a similar position of the corresponding bands, when compared to $[Ru(bpy)_3]^{2+}$.

3.4.Cyclic Voltammetry

In Table 2, the half-wave potentials for the oxidation and reduction processes of the complexes are shown, while in Figure 3 the voltammogram for the $[Ru(bpy)_21](PF_6)_2$ complex is shown. Concerning the $Ru^{2+/3+}$ oxidation potentials, although all complexes present half wave potential values of the same order of magnitude than complex $[Ru(bpy)_3](PF_6)_2$, a slight displacement to lower potential values is consistently observed, suggesting that a substitution on the bipyridinic groups has a rather low influence over the charge density on the metal. All the reduction processes showed an irreversible behavior. It

is possible to observe that the complex with ligand 2 presents the less negative reduction potential, which reflects more delocalized character of this ligand, and agrees with the results obtained in the photophysical experiments. Moreover, calculating the difference between the half-wave potentials of the first reduction and oxidation, $\Delta E^{1/2}$, the same trend than observed for the absorption and emission data is observed, permitting to relate this difference to the HOMO - LUMO energy gap. Moreover, the relation between $\Delta E_{1/2}$ and the emission energy is lineal, supporting the idea that the emission in all complexes has the same origin. ANS

Figure 3

Table 2

4. Conclusion

The effects of branched substituents ligands with high and low conjugation degree were studied, along with the physical and chemical properties of the corresponding polypyridinic Ru (II) complexes for potential use as iTMC for LECs. To carry out this study, different ligands were synthesized. Compared to the unsubstituted bpy ligand and its corresponding *tris* complex, ligand 2 and complex $[Ru(bpy)_22](PF_6)_2$ present a shift to lower energy in their absorption and emission bands. Therefore, our results corroborate the importance of using highly conjugated branched substituents if the aim is to achieve low energy emissions. On the contrary, the introduction of heavier metals such us osmium and iridium, would increase the HOMO-LUMO energy gap, reaching higher energy emissions [12].

On the other hand, the use of complexes with ligands with branched substituents with free rotating aliphatic groups, produce negligible color shifting when compared to their analogues with unsubstituted bpy. Therefore, complexes with ligands 1 and 3 are particularly interesting, considering that the employment of these large sized ligands, and specially the presence of a significant rotation degree of freedom in them, should reduce the possibilities of contact between metallic centers, diminishing self-quenching and therefore

increasing the yield when forming part of a device. That is to say, complexes $[Ru(bpy)_21](PF_6)_2$ and $[Ru(bpy)_23](PF_6)_2$ would be good candidates to be tested in LEC devices, as they preserve the emission color of the $[Ru(bpy)_3](PF_6)_2$, but at the same time, they should show enhanced luminescence. Therefore, it would be interesting to evaluate the performance of these complexes in a device, keeping in mind their size and free rotation of the connecting aliphatic chain.

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Figure Captions

5924.

Figure 1. Scheme of the synthesized complexes

Figure 2. Absorption (solid lines) and Emission (dashed lines) Spectra for the Ru complexes

Figure 3. Voltammogram of [Ru(bpy)₂1](PF₆)₂

Tables

		293 K	293 K		
	Compound	λ_{abs} , nm	λ_{em} , nm ^a	-	
	1	241, 282 ^a	360		
	2	227, 312 ^a	370		
	3	241, 283 ^a	-		
	bpy	236, 281 ^a	-		
	$[Ru(bpy)_21](PF_6)_2$	288, 450 ^b	605		
C)	$[Ru(bpy)_22](PF_6)_2$	294, 470 ^b	645		
	$[Ru(bpy)_23](PF_6)_2$	290, 457 ^b	605		
	$[Ru(bpy)_3](PF_6)_2$	285, 450 ^b	598		
	^a Results in Aceto	onitrile, ^b Results	in DMF		

Table 1. Absorption and Emission Spectral Data of

ligands and complexes

	$E_{1/2}$ (Ru), ev	$E_{1/2}$ (L ^{0/2}), eV	$E_{1/2}$ (L ^{-/2-}), eV	∆E¼, eV
$[Ru(bpy)_21](PF_6)_2$	0,85	-1,75	-1,95	2,60
$[Ru(bpy)_22](PF_6)_2$	0,84	-1,64	-1,90	2,48
$[Ru(bpy)_23](PF_6)_2$	0,84	-1,76	-1,95	2,60
$[Ru(bpy)_3](PF_6)_2$	0,89	-1,73	-1,92	2,62
			50	

Table 2. Electrochemical Data of the Complexes









The photophysical properties of Ruthenium complexes with substituted 2,2'-bipyridine (bpy) ligands, as potential semiconductor materials for iTMC type LEC have been studied. The absence of conjugation in the bpy substitution permits to retain the emission color of a $Ru(bpy)_{3}^{2+}$ type moiety, while avoiding self ordering when used in a device. Acceleration

The photophysical properties of polypyridinic Ruthenium complexes have been studied.

Potential application for LEC was evaluated.

Compounds with free rotation ligands should be promising for iTMC LECs.

Diminishing of solid-state ordering and self-quenching are expected.