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Research Article

## Synthesis, Characterization, Photophysical and Electrochemical Properties of Pyridine Based Ruthenium Complexes

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### ABSTRACT

New pyridine based ruthenium complexes with different substituents were synthesized and characterized by Uv-Visible, fluorescence, FTIR and NMR spectroscopies. The substituents and solvent effects of the synthesized compounds on photoluminescence properties have been investigated. The compounds exhibit solvatochromic effect in different solvents. The electrochemical studies of the compounds were performed by cyclic voltammetry. The HOMO and LUMO energy levels are in the range (-5.51)-(-5.52) eV and (-3.04)-(-3.07) eV, respectively. These results indicate that there is no an important effect of side groups on electrochemical properties.

**Keywords:** Pyridine, Ruthenium complex, Electrochemical properties

## Piridin İçeren Rutenyum Komplekslerinin Sentezi, Karakterizasyonu, Fotofiziksel ve Elektrokimyasal Özellikleri

### Öz

Farklı süstitüentlere sahip yeni piridin esaslı rutenyum kompleksleri sentezlendi ve Uv-Visible, floresans, FTIR ve NMR spektroskopileri ile karakterize edildi. Sentezlenen bileşiklerin fotoluminesans özellikleri üzerine süstitüentler ve çözücü etkileri araştırılmıştır. Bileşikler farklı çözücüler içerisinde solvakromatik etki göstermektedir. Bileşiklerin elektrokimyasal çalışmaları döngüsel voltametri ile gerçekleştirildi. HOMO ve LUMO enerji seviyeleri sırasıyla (-5.51)-(-5.52) eV ve (-3.04)-(-3.07) eV aralığındadır. Bu sonuçlar yan grupların elektrokimyasal özellikleri üzerine önemli bir etkisinin olmadığını göstermektedir.

**Anahtar Kelimeler:** Piridin, Rutenyum kompleksi, Elektrokimyasal özellikler

# **I. INTRODUCTION**

Ruthenium complexes have great interest due to their photophysical, stability and electrochemical properties in dye sensitized solar cells, photocatalysis, organic light emitting diodes, and biological applications [1-3]. The oxidation states, ability of binding to DNA, hydrophobicity and lipophilicity properties of ruthenium complexes can be controlled by the use of different ligands. This can allow to alter the biological activities of molecules for the development of anticancer and antibacterial drugs [4,5]. Recently, half-sandwich ruthenium complexes have been widely explored as anticancer and antibacterial drugs because of their low toxicity, high cytotoxicity and high selectivity [6-8]. Half-sandwich ruthenium compounds with 1,3,5-triaza-7-phosphaadamantane, 2,2'-bipyridine and imidazo[4,5-f][1,10]phenanthroline ligands have been shown promising biological activity [7]. Pyridine based ruthenium complexes can be used as a potential agent in the optical imaging of cells [9]. In addition, ruthenium complexes with pyridine can show effective apoptosis in cancer cells and inhibit the formation of bacterial biofilm [10,11].

In this work, we reported the synthesis, characterization, photoluminescence and electrochemical properties of ruthenium compounds bearing pyridine ligands with different substituents (Ru1-Ru3). The effects of side groups of 4-(5-nonyl)pyridine, 4-(2-ethyl-hexyloxy)pyridine and 4-(2-[2-(2-methoxyethoxy)ethoxy]ethoxy)pyridine in the complexes on the photophysical and electrochemical properties have been investigated. The PL bands of Ru2 and Ru3 were red shifted in the presence of C-O-C moiety compared to Ru1. The HOMO and LUMO energy levels are in the range (-5.51)-(-5.52) eV and (-3.04)-(-3.07) eV, respectively. The synthesized compounds are promising candidate for anticancer and antibacterial applications.

## **II. MATERIALS AND METHOD**

### **A. MATERIALS AND METHODS**

4-hydroxypyridine, 2-ethylhexyl iodide, tetrabutyl ammonium hexafluorophosphate (TBAPF<sub>6</sub>) and dichloro(*p*-cymene) ruthenium(II)dimer were provided from Sigma-Aldrich. 4-(5-nonyl)pyridine purchased from ABCR. 4-(2-ethyl-hexyloxy)pyridine and 4-(2-[2-(2-methoxyethoxy)ethoxy]ethoxy)pyridine were synthesized according to literature [12]. Infrared spectra were recorded using Perkin Elmer Spectrum Two FT-IR Spectrometer. NMR spectra were obtained with a Varian Mercury AS400 NMR spectrometer. Spectroscopic studies were performed using a Perkin Elmer LS55 fluorescence and a Shimadzu 1800 UV-Vis spectrophotometers. Electrochemical properties were studied with DropSens mStat 200 bipotentiostat.

#### **A. 1. Synthesis of Ruthenium Complexes**

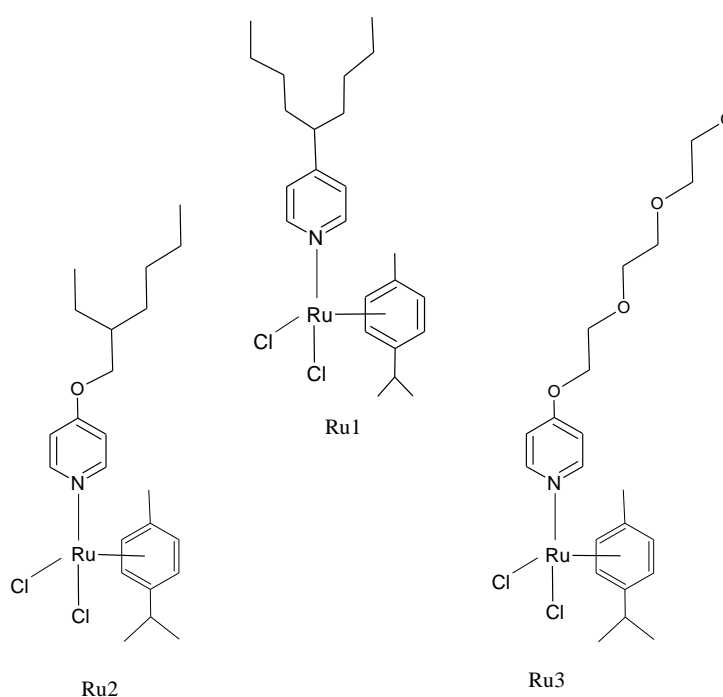
Half sandwich ruthenium complexes (Ru1-Ru3) were synthesized using literature procedure with some modifications [13]. Dichloro(*p*-cymene)ruthenium(II) dimer (0.01 mmol) and corresponding pyridine ligand (4-(5-nonyl)pyridine, 4-(2-ethyl-hexyloxy)pyridine or 4-(2-[2-(2-methoxyethoxy)ethoxy]ethoxy)pyridine) (0.02 mmol) in toluene was stirred at 75 °C for 4 h under argon atmosphere. After cooling to room temperature, the precipitate was filtered. The obtained product was dissolved dichloromethane and precipitated with diethyl ether.

[Ru(4-(5-nonyl)pyridine)(*p*-cymene)Cl<sub>2</sub>]Cl (Ru1): Yellow powder. Yield 86%. FTIR-ATR (cm<sup>-1</sup>): 3114, 2782, 1621, 1465, 1404, 1232, 669. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ<sub>ppm</sub>= 8.87 (d, *J*=6.8 Hz, 2H), 7.08 (d, *J*=6.4 Hz, 2H), 5.43 (d, *J*=5.6 Hz, 2H), 5.22 (d, *J*=6.0 Hz, 2H), 2.98 (m, 1H), 2.51 (m, 1H), 2.08 (s, 3H), 1.68-1.44 (m, 4H), 1.30-1.02 (m, 14H), 0.82 (m, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ<sub>ppm</sub>= 158.3, 154.5, 124.3, 103.7, 96.9, 82.9, 82.6, 45.7, 35.9, 30.9, 29.8, 22.9, 22.5, 18.3, 14.1.

[Ru(4-(2-ethyl-hexyloxy)pyridine)(*p*-cymene)Cl<sub>2</sub>]Cl (Ru2): Yellow powder. Yield 81%. FTIR-ATR (cm<sup>-1</sup>): 3117, 2782, 1637, 1464, 1405, 1232, 1020, 670. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ<sub>ppm</sub>= 8.76 (d, *J*=6.0 Hz, 2H), 6.79 (d, *J*=5.6 Hz, 2H), 5.42 (d, *J*=4.4 Hz, 2H), 5.20 (d, *J*=4.8 Hz, 2H), 3.90 (d, *J*=4.4 Hz, 2H), 2.98 (m, 1H), 2.11 (s, 3H), 1.73-1.30 (m, 15H), 0.91 (m, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ<sub>ppm</sub>= 166.7, 155.6, 111.6, 103.3, 97.2, 82.9, 82.2, 71.4, 39.2, 30.9, 30.5, 29.2, 23.9, 23.2, 22.5, 18.5, 14.2, 11.2.

[Ru(4-(2-[2-(2-methoxyethoxy)ethoxy]ethoxy)pyridine)(*p*-cymene)Cl<sub>2</sub>]Cl (Ru3): Yellow powder. Yield 76%. FTIR-ATR (cm<sup>-1</sup>): 3074, 2924, 1615, 1406, 1231, 1139, 668. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ<sub>ppm</sub>= 8.77 (d, *J*=7.6 Hz, 2H), 6.82 (d, *J*=4.8 Hz, 2H), 5.42 (d, *J*=5.6 Hz, 2H), 5.19 (d, *J*=6.0 Hz, 2H), 4.18 (t, *J*=4.8 Hz, 2H), 3.85 (t, *J*=4.8 Hz, 2H), 3.71-3.60 (m, 6H), 3.55 (m, 2H), 3.37 (s, 3H), 2.95 (m, 1H), 2.09 (s, 3H), 1.29 (dd, *J*=7.2 Hz, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ<sub>ppm</sub>= 166.3, 155.7, 111.7, 103.4, 97.2, 83.0, 82.1, 72.1, 71.1, 70.8, 69.2, 68.3, 59.3, 30.9, 22.5, 22.3, 18.5.

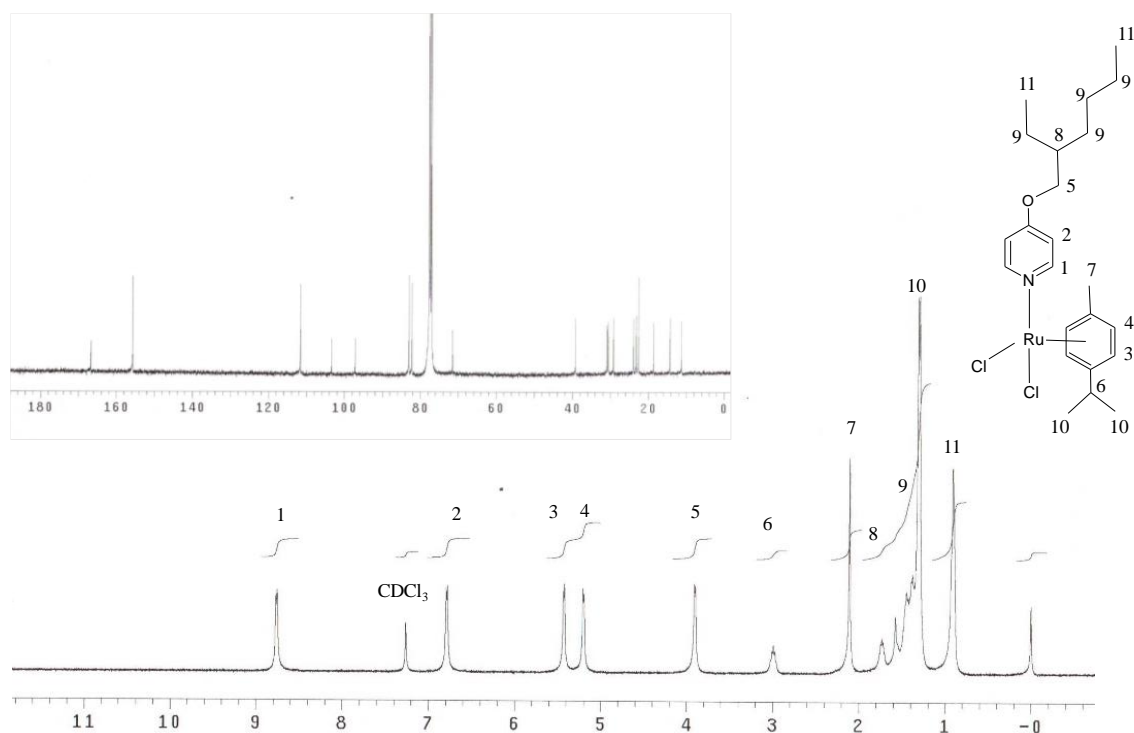
The molecular structures of synthesized complexes (Ru1-Ru3) were given in Figure 1.



**Figure 1.** The molecular structures of Ru1-Ru3.

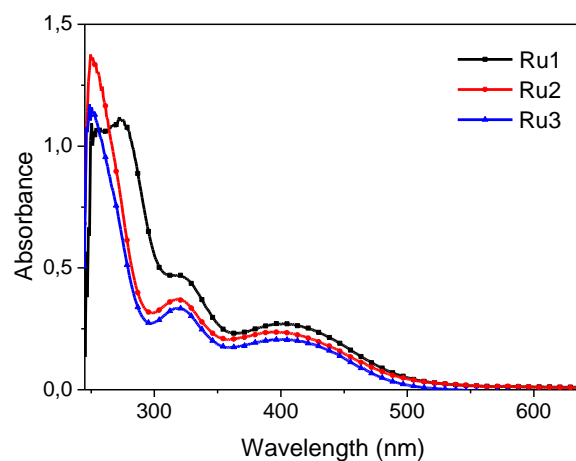
### **III. RESULTS AND DISCUSSION**

The synthesis of ruthenium complexes was confirmed by using FTIR, <sup>1</sup>H NMR and <sup>13</sup>C NMR. The FTIR spectra of Ru1-Ru3 exhibit the characteristic peaks of aliphatic and aromatic C–H bonds between 2782-2924 cm<sup>-1</sup> and 3034-3117 cm<sup>-1</sup>, respectively. The peaks were observed at around 1020 cm<sup>-1</sup> due to the C-O-C stretching bands for Ru2 and Ru3. The <sup>1</sup>H NMR spectra of Ru1-Ru3 show doublet peaks at around 8.77 ppm and 6.82 ppm due to the aromatic proton signals of the pyridine ligands (Figure 2). The two doublet signals at 5.42 ppm and at 5.19 ppm are associated with the aromatic proton signals of the *p*-cymene ligands. The ratios of aliphatic resonance peaks in the range 0.82-4.18 ppm can prove the formation of complexes. The <sup>13</sup>C NMR spectra of Ru1-Ru3 display seven carbon signals in the aromatic region (Figure 2). The signals between 11.2 ppm and 72.1 ppm are assigned to the aliphatic carbons of corresponding ligands and *p*-cymene ligands.



**Figure 2.**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of Ru2 in  $\text{CDCl}_3$ .

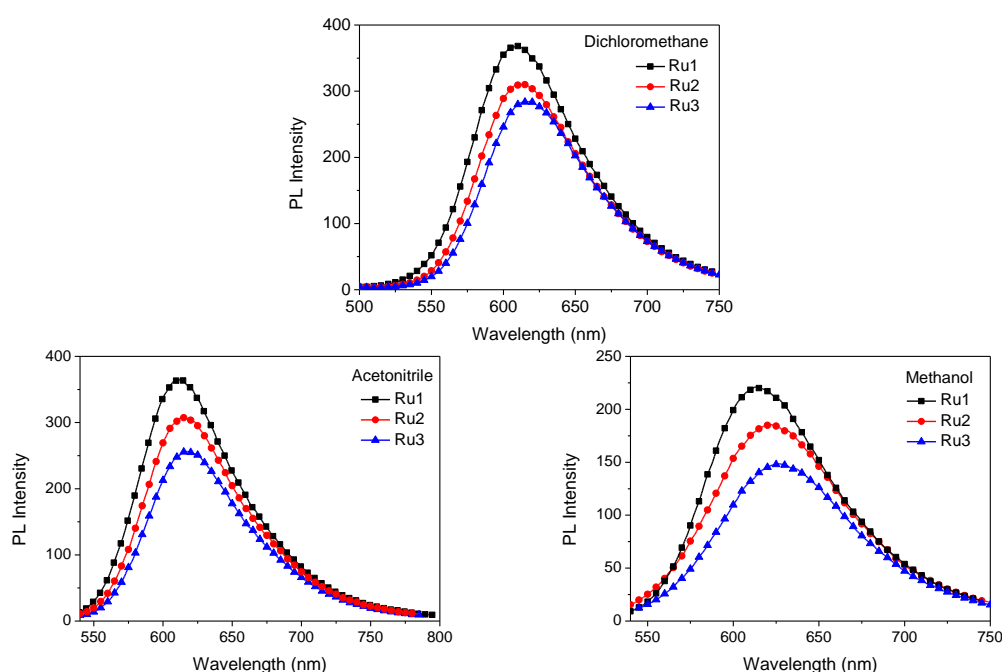
The absorption and photoluminescence (PL) studies of Ru1-Ru3 were performed in acetonitrile and the data are summarized in Table 1. The absorption spectra of Ru1-Ru3 display the bands between 250 nm and 323 nm due to the  $\pi$ - $\pi^*$  transitions due to pyridine and *p*-cymene ligands (Figure 3). The bands at around 405 nm is assigned to metal to ligand charge transfer (MLCT) transitions of the complexes [14,15].



**Figure 3.** The absorption spectra of  $1 \times 10^{-5}$  M solutions of the Ru1-Ru3 in acetonitrile.

PL spectra of Ru1-Ru3 were obtained in different solvents by excitation at 405 nm. The PL spectrum of Ru1 shows orange emission band at 608 nm in dichloromethane (Figure 4). The emission bands of Ru2 and Ru3 were red shifted in the presence of C-O-C moiety compared to Ru1. This is associated with the electron donor properties of 2-ethyl-hexyloxy and -(2-[2-(2-methoxyethoxy)ethoxy]ethoxy)-pyridine ligands [16]. The PL quantum yields of compounds were calculated according to literature [17] using reference material ([Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub>,  $\Phi_{PL} = 0.095$  in acetonitrile). The quantum yields of compounds are found as 0.047 for Ru1, 0.044 for Ru2 and 0.045 for Ru3.

The solvent effect on PL spectra of Ru1-Ru3 have been explored. Ru1 exhibits at 608 nm in dichloromethane, at 611 nm in acetonitrile and at 615 nm in methanol for Ru1. The red shift was observed with the increasing polarity of solvents (dichloromethane < acetonitrile < methanol). This may be related to the more interaction between the solvents and excited molecules which can stabilize the excited state of compounds [18]. Ru2 and Ru3 display similar solvatochromic effect in different solvents. The obtained results indicate that the polarity of solvents and side groups of the compounds can influence the emission spectra.

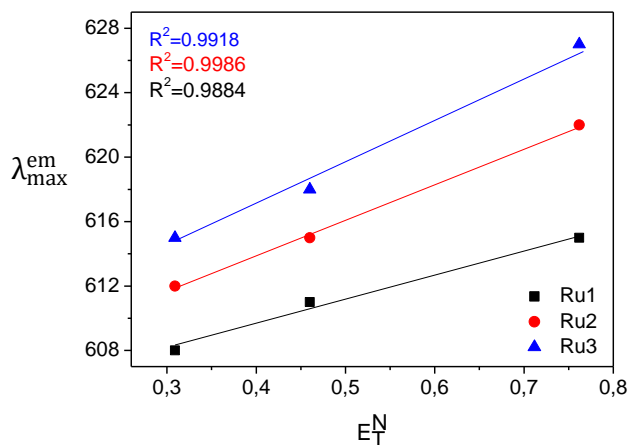


**Figure 4.** The PL spectra of  $1 \times 10^{-5}$  M solutions of the Ru1-Ru3 in different solvents.

**Table 1.** The absorption and emission data of the Ru1-Ru3.

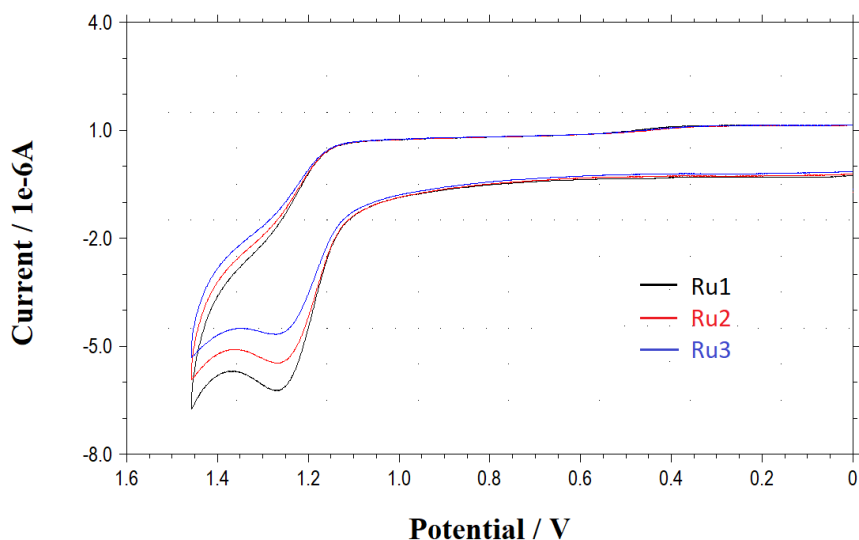
Complex	$\lambda_{\text{mx}}^{\text{abs}}$ (nm) ( $\epsilon/10^5 \text{ M}^{-1} \cdot \text{cm}^{-1}$ )			$\lambda_{\text{mx}}^{\text{em}}$ (nm)	$\lambda_{\text{mx}}^{\text{em}}$ (nm)	$\lambda_{\text{mx}}^{\text{em}}$ (nm)	$\Phi_{PL}$
				(CH <sub>2</sub> Cl <sub>2</sub> )	(CH <sub>3</sub> CN)	(CH <sub>3</sub> OH)	
<b>Ru1</b>	275 (1.11)	323 (0.48)	404 (0.28)	608	611	615	0.047
<b>Ru2</b>	250 (1.37)	319 (0.38)	405 (0.24)	612	615	622	0.044
<b>Ru3</b>	250 (1.15)	320 (0.34)	407 (0.20)	615	618	627	0.045

The PL maximum wavelengths of Ru1-Ru3 as a function of the normalized molar electronic transition energy ( $E_T^N$ ) [19] were given in Figure 5. The linear correlation between PL maxima and  $E_T^N$  for Ru1-Ru3 was observed in polar protic solvent (methanol) and polar aprotic solvents (acetonitrile and dichloromethane). This can allow to predict the solvent effect on PL properties. Figure 5 shows the red shift of PL maxima of the compounds with the increasing polarity of solvents.



**Figure 5.** The PL maximum wavelengths of Ru1-Ru3 as a function of the normalized molar electronic transition energy ( $E_T^N$ ) ( $E_T^N$  (methanol): 0.762,  $E_T^N$  (acetonitrile): 0.460,  $E_T^N$  (dichloromethane): 0.309) [19].

The electrochemical studies were performed by cyclic voltammetry using glassy carbon working electrode, Pt wire counter electrode and Ag wire reference electrode. All compounds exhibit one oxidation peak at around 1.17 V which is associated with Ru(II)/(III) couple (Figure 6) [15]. The HOMO and LUMO energy levels were determined according to literature [20] (ferrocenium/ferrocene couple 0.46 V vs. Ag/ Ag<sup>+</sup>). The HOMO and LUMO energy levels are in the range (-5.51)-(-5.52) eV and (-3.04)-(-3.07) eV, respectively (Table 2). These results indicate that there is no an important effect of side groups on electrochemical properties.



**Figure 6.** Cyclic voltammograms of Ru1-Ru3 in acetonitrile with 0.1 M TBAPF<sub>6</sub>.

*Table 2. The electrochemical data of the Ru1-Ru3.*

<b>Complex</b>	<b>E<sub>ox</sub></b> (V)	<b>HOMO</b> (eV)	<b>LUMO</b> (eV)	<b>Band Gap</b> (E <sub>g</sub> ) (eV)
<b>Ru1</b>	1.17	-5.51	-3.07	2.44
<b>Ru2</b>	1.17	-5.51	-3.05	2.46
<b>Ru3</b>	1.18	-5.52	-3.04	2.48

## **IV. CONCLUSIONS**

In this study, ruthenium complexes bearing pyridine ligands with different substituents were synthesized. The photoluminescence properties of the compounds have been explored. The PL bands of Ru2 and Ru3 were red shifted in the presence of C-O-C moiety compared to Ru1. This is associated with the electron donor properties of 2-ethyl-hexyloxy and -(2-[2-(2-methoxyethoxy)ethoxy]ethoxy)-pyridine ligands. The red shift of PL spectra was observed with the increasing polarity of solvents. The obtained results indicate that the polarity of solvents and side groups of the compounds can influence the emission spectra. The HOMO and LUMO energy levels are in the range (-5.51)-(-5.52) eV and (-3.04)-(-3.07) eV, respectively. An important effect of side groups was not observed on electrochemical properties.

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