

Ru(II) and Co(II) Complexes of bis(pyrazolyl)pyridine and pyridine-2,6-dicarboxylic Acid: Synthesis, Photo Physical Studies and Evaluation of Solar Cell Conversion Efficiencies

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We report the synthesis of two nitrogen chelating ligands: 2,6-bis(pyrazolyl)pyridine (L1); 2,6-bis(3,5-dimethylpyrazolyl)pyridine (L2) and their corresponding ruthenium(II) and cobalt(II) complexes formulated as [RuL1L(NCS)₂] (C1), [RuL2L(NCS)₂] (C2), [CoL1L(NCS)₂] (C3) and [CoL2L(NCS)₂] (C4) where L= pyridine-2,6-dicarboxylic acid. The synthesis of the ligands were confirmed by ¹HNMR spectroscopy and FTIR spectra studies confirmed the bonding of the Ru and Co ions to the ligands via the nitrogen atoms. Electronic absorption spectra indicates the geometries around the metal ions are six coordinate octahedral in which L1 or L2 acts as tridentate chelating ligands. In the cyclic voltammetry, cobalt(II) complexes exhibited larger redox potentials as compared to the ruthenium(II) complexes. The conversion efficiencies of the fabricated solar cells using the complexes as sensitizers showed that [RuL2L(NCS)₂], **C2** on TiO₂ semiconductor produced the highest open-circuit photovoltage (V_{oc}) of 87.3 × 10⁻³ mV, short-circuit photocurrent (J_{sc}) of 0.022 mA/cm⁻² and the solar conversion efficiency was 101 × 10⁻⁵ %.

Keywords: Dye-sensitized solar cells, dye sensitizer, photo physical studies, electrochemistry, conversion efficiency

1. INTRODUCTION

Metal complexes containing N-donor ligands have attracted significant interest in recent years for their potential application in catalysis [1], biology [2], molecular electronics [3] and in photochemical conversion of solar energy [4] due to their remarkable photo physical and redox properties [5]. In studies of photochemical conversion of metal complexes bearing nitrogen chelating ligands used as sensitizers for light harvesting in dye sensitized solar cells (DSSCs) have achieved conversion efficiency up to 13% [6]. Ruthenium complexes are among the most effective sensitizers

due to their great charge transfer absorption in the visible region, chemical stability and interesting photo physical properties [7-10].

[Ru(Htcpy)(NCS)₂[TBA]₃ (N749) where Htcpy= 4,4',4''-tricarboxy-2,2',2''-terpyridine has the ability to harvest light near-IR region [11], however the presence of thiocyanate ligands inhibit the long-term stability of the fabricated solar cells [12]. To overcome this, Chou *et. al* [13] designed heteroleptic tridentate sensitizers that consist of terpyridine and 2,6-bis(pyrazolyl)pyridine (TF1-4) with improved conversion efficiency and long-term stability relative to N749 dye, and also the substituents introduced in pyridine enhanced the photo physical properties of the dye.

Ruthenium complexes of 2,6-bis(pyrazolyl)pyridine have been reported to show similar light absorption as terpyridine derivatives with longer lifespan of photostability compared to terpyridine ligands [14, 15]. The photo physical properties of bis(pyrazolyl)pyridine could be enhanced by introducing a substituent into the backbone of pyrazole moiety and the presence of these substituents influences both physical and chemical properties of the corresponding complexes [16-18]. Bis(pyrazolyl)pyridine are more useful in the synthesis of photosensitizers than terpyridine [19] and they act as electron reservoirs due to their π -conjugated aromatic system and they have the ability to photo stabilize the complexes [20, 21].

To the best of our knowledge, there is no report to date about sensitizers of cobalt complexes with 2,6-bis(pyrazolyl)pyridine, which prompted us to use Co(II) complexes as sensitizers as they are relatively cheaper materials. In this paper, we report the synthesis, characterization, photo physical studies, electrochemistry and evaluation of Ru(II) and Co(II) complexes of 2,6-bis(pyrazolyl)pyridine (L1) or 2,6-bis(3,5-dimethylpyrazolyl)pyridine (L2) mixed with pyridine-2,6-dicarboxylic acid and evaluation of their potentials as sensitizers for DSSCs.

2. EXPERIMENTAL

All the reagents and solvents were used as obtained from Sigma-Aldrich. [RuCl₂(DMSO)₄] was synthesized as reported by Evans *et. al* [22] and used as metal precursor. FTIR spectra were obtained as KBr pellets on a Perkin-Elmer Paragon 2000 spectrophotometer in the range 4400-370 cm⁻¹. Electronic absorption and emission spectra were recorded on a Perkin-Elmer Lambda 25 UV-Vis spectrophotometer and Perkin-Elmer Lambda 35 photoluminescence spectrophotometer using 1 cm path length quartz cell. Cyclic voltammetry measurements were obtained using Autolab potentiostat with three electrodes, glassy carbon working electrode, Ag/AgCl reference electrode and Pt counter electrode. The potential range was +1.5 to -1.5 at 100 mVs⁻¹ scan rate. The three electrodes were immersed in 0.5 mM of cobalt(II) and ruthenium(II) solution in water with 0.1 M of phosphate buffer solution (PBS) as a supporting electrolyte. All the experimental procedures were carried out in a nitrogen atmosphere.

2.1. Preparation of 2,6-bis(pyrazol)pyridine (L1)

Pyrazole (1.2 g, 17.6 mmol) was dissolved in 30 mL of DMF in a 100 mL round bottom flask and sodium hydrate (0.422 g, 17.6 mmol) was added to the mixture. The mixture was stirred at 50 °C for 20 minutes followed by the addition of 2,6-dichloropyridine-4-carboxylic acid (1.39 g, 5.86 mmol) and the mixture was refluxed for 24 h at 130 °C. After cooling the mixture, 25 mL of water was added and the product was extracted with dichloromethane. Yield: 0.91 g, 73 %, m.p. 80 °C, IR (KBr pellet) $\nu(\text{cm}^{-1})$: 3365, 2976, 2394, 2364, 1994, 1664, 1395, 1253, 1043, 831, 763, 613. $^1\text{HNMR}$ (D_2O): δ 8.4 (2H, d, Pyr), 8.1 (1H, t, Py), 7.9 (2H, d, Py), 7.8 (2H, d, Py) and 6.4 (2H, t, Pyr).

2.2 Preparation of 2,6-bis(3,5-dimethylpyrazol)pyridine (L2)

2,6-bis(3,5-dimethylpyrazol)pyridine, L2 was prepared using a procedure similar to those used for L1. 3,5-dimethylpyrazole (1.3 g, 13.5 mmol) was dissolved in 30 mL of DMF in a 100 mL round bottom flask, sodium hydrate (0.33 g, 13.5 mmol) was added to the mixture and stirred at 50 °C for 20 minutes, 2,6-dichloropyridine-4-carboxylic acid (1.07 g, 4.5 mmol) was added and refluxed for 24 h. After cooling the reaction mixture, 25 mL of water was added and extracted with diethyl ether. Yield: 0.83 g, 69%, m.p. 82 °C, IR (KBr pellet) $\nu(\text{cm}^{-1})$: 3410, 3198, 2903, 2552, 2366, 1608, 1306, 1161, 1090, 841, 714, 621, 437. $^1\text{HNMR}$ (D_2O): δ 8.4 (1H, t, Py), 8.2 (2H, d, Py).

2.3. Synthesis of $[\text{ML}_1\text{L}(\text{NCS})_2]$ (C1/C3) where M= Ru or Co

$[\text{RuCl}_2(\text{DMSO})_4]$ or CoCl_2 (0.841 mmol) 2,6-bis(pyrazolyl)pyridine (0.841 mmol) were dissolved in 30 mL of DMF/ethanol and refluxed for 4 h. Pyridine-2,6-dicarboxylic acid (0.841 mmol) was added to the mixture and refluxed for 2h. Excess potassium thiocyanate (3.364 mmol) was added and refluxed for 4 h. The reaction mixture was cooled and methanol was removed under vacuum. The obtained after precipitation with diethyl ether was filtered and dried. $[\text{RuL}_1\text{L}(\text{NCS})_2]$, **C1** Yield: 63.8 mg, 52%, m.p. 235 °C, IR (KBr pellet) $\nu(\text{cm}^{-1})$: 3417, 2971, 2971, 2949, 2842, 2368, 2126, 2067, 1869, 1638, 1454, 1397, 1112, 1055, 1016, 619, 477. $[\text{CoL}_1\text{L}(\text{NCS})_2]$, **C3** Yield: 0.27g, 58%, m.p. 250°C, IR (KBr pellet) $\nu(\text{cm}^{-1})$: 3409, 3244, 2340, 2043, 1624, 1447, 1396, 1109, 984, 838, 737, 622, 455.

2.4 Synthesis of $[\text{ML}_2\text{L}(\text{NCS})_2]$ (C2/C4)

2,6-bis(3,5-dimethylzoly)pyridine (0.841 mmol) and $[\text{RuCl}_2(\text{DMSO})_4]$ or CoCl_2 (0.841 mmol) were added and the mixture was refluxed in 30 mL DMF/ethanol for 4h. Pyridine-2,6-dicarboxylic acid (0.841 mmol) was added to the reaction mixture then after 2 h excess potassium thiocyanate was added and refluxed for 8 h. The mixture was cooled at room temperature and DMF was evaporated under vacuum. The product was precipitated with diethyl ether, the product was filtered and dried under vacuum. $[\text{RuL}_2\text{L}(\text{NCS})_2]$, **C2** Yield: 57.7 mg, 43%, m.p. 230°C, IR (KBr pellet) $\nu(\text{cm}^{-1})$: 3424,

2949, 2839, 2365, 2069, 1870, 1646, 1454, 1398, 1113, 1054, 1020, 619, 539. [CoL2L(NCS)₂], **C4**
Yield: 0.31 g, 61%, m.p. 249°C, IR (KBr pellet) $\nu(\text{cm}^{-1})$: 3490, 2949, 2839, 2365, 2067, 1870, 1622, 1433, 1397, 1236, 1112, 1020, 619, 533.

2.5 Solar cell fabrication and evaluation

The dye solutions were prepared in concentration of 0.3 mM in DMF. TiO₂ electrode was dipped into the dye solution for 10 minutes. The TiO₂/dye electrode was washed with fresh ethanol and allowed to dry. Pt plate electrode was put on top of a hot plate at 450 °C for 10 minutes to activate the electrode. The two electrodes were combined and heated at 70 °C for 15 minutes. After cooling, electrode construct was filled with electrolyte. A solar analyzer was used to characterize the cells.

3. RESULTS AND DISCUSSION

3.1 Synthesis of Metal complexes

Ru(II) and Co(II) complexes were synthesized by reacting the respective metal chloride with bis(pyrazolyl)pyridine and pyridine-2,6-carboxylic acid ligands in DMF or ethanol. Molar conductivity measurements indicate that the complexes are non-electrolyte in solution. Spectroscopic studies indicate the metal complexes have octahedral geometries in which the central metal ions are coordinated with nitrogen atoms of the respective ligands as shown in the proposed structure in Figure 1.

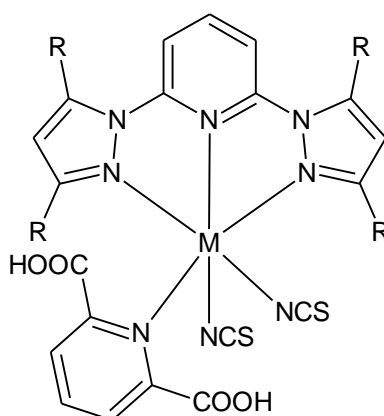


Figure 1. Proposed structure for the metal complexes. (M = Ru or Co and R = H or CH₃)

3.2 FTIR and NMR spectroscopy of the Ru(II) and Co(II) complexes

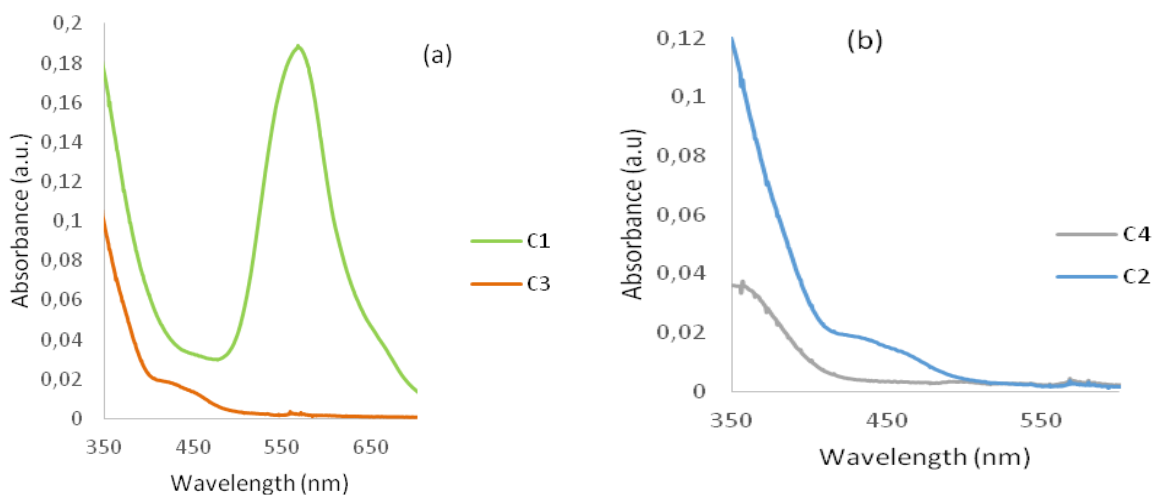
The infra-red spectra of the metal complexes show vibrations at 3490-3409 cm⁻¹ due to O-H present in pyridine-2,6-dicarboxylic acid [23]. The strong vibrational bands observed between 2034

and 2070 cm^{-1} corresponds to $\nu(\text{N}=\text{C}=\text{S})$ stretching vibrations of thiocyanate moiety [24]. The presence of medium band between 1638 and 1646 cm^{-1} could be ascribed to $\nu(\text{C}=\text{O})$ asymmetric stretching vibrations [23]. The weak band observed between 1540 and 1605 cm^{-1} is due to $\nu(\text{C}=\text{C})$ vibration in the spectra of the complexes are blue-shifted relative to their position in the spectra of the ligands [25]. The $\nu(\text{C}=\text{N})$ and $\nu(\text{C}-\text{N})$ stretching vibrations observed in the range 1454 - 1329 cm^{-1} in the spectra of the complexes are observed at lower frequency compared to the free ligands. This could be attributed to coordination of the metal ions and N donor atoms present in the pyrazolyl ligands [13, 25]. The presence of new medium vibrational bands at 619 - 455 cm^{-1} confirms the coordination of the metal ions with nitrogen atoms of the ligands [26, 27].

The ^1H NMR spectra studies of the ligands, L1 in deuterated water (D_2O) show five signals at δ 8.4 (2H, d, Pyr), 8.1 (1H, t, Py), 7.9 (2H, d, Py), 7.8 (2H, d, Py) and 6.4 (2H, t, Pyr). The spectra showed one set of signal for the pyrazole rings indicating that they are equivalent [25]. The spectra of L2 in D_2O solution showed two peaks at δ 8.4 (1H, t, Py), 8.2 (2H, d, Py) but the expected peaks for the aromatic and alkyl groups were not observable and this could be ascribe to the poor solubility of the ligands. ^1H NMR spectroscopy of the metal complexes were not recorded due to their generally poor solubility.

3.3 Electronic and emission spectra studies

The electronic spectra of the complexes, C1-C4 (Figure 2) show two bands in the region 260-340 nm assigned to intraligand π - π^* transitions [28]. Low intensity absorption bands observed at 437-694nm are due to d-d electronic transitions central metal ions and the low energy absorption is due to the presence of carboxylic group that result in low π^* -orbital energy level [29]. Complex, C1 displays a broad band at 588 nm assigned to $^4\text{T}_{2g} \rightarrow ^2\text{T}_{2g}$ transitions [30]. The electronic spectrum of C2 shows two bands at 437 nm ascribed to $^4\text{T}_{2g} \rightarrow ^2\text{T}_{2g}$ and 575 nm assigned to $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_1(\text{P})$ transitions [27, 30]. In the spectra of C3 and C4 two bands observed at 443 and 568 nm respectively correspond to $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_1(\text{P})$ and the second band at 694 and 657 nm due to $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_{2g}(\text{P})$ transitions.



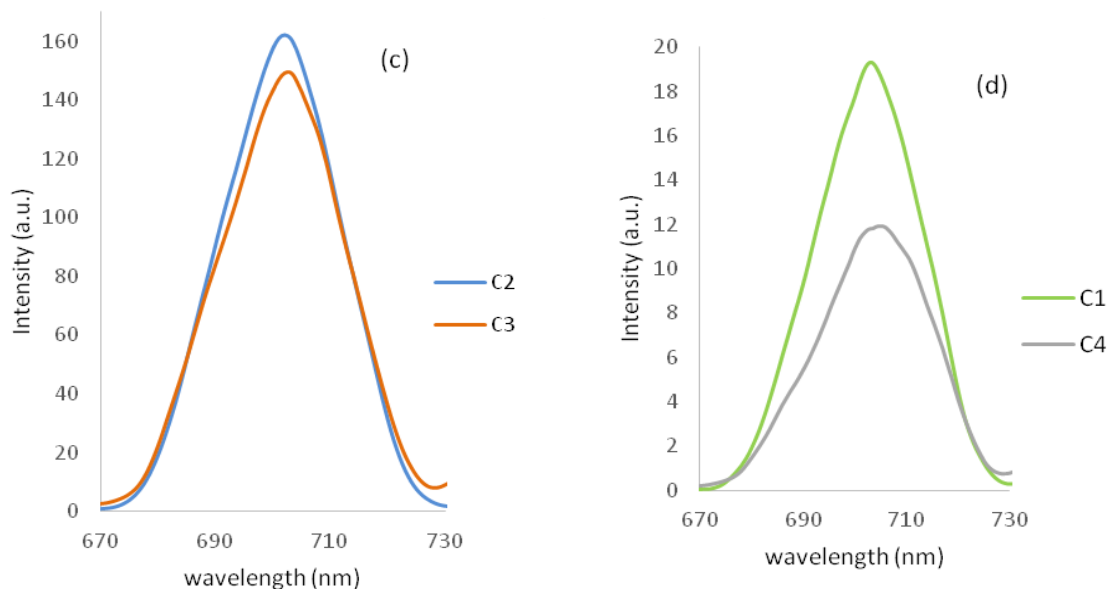


Figure 2. UV-Vis spectra of metal complexes of (a) bis(pyrazolyl)pyridine and (b) bis(3,5dimethylpyrazolyl)pyridine and Emission spectra of complexes of (c) C2 and C3 and (d) C1 and C4

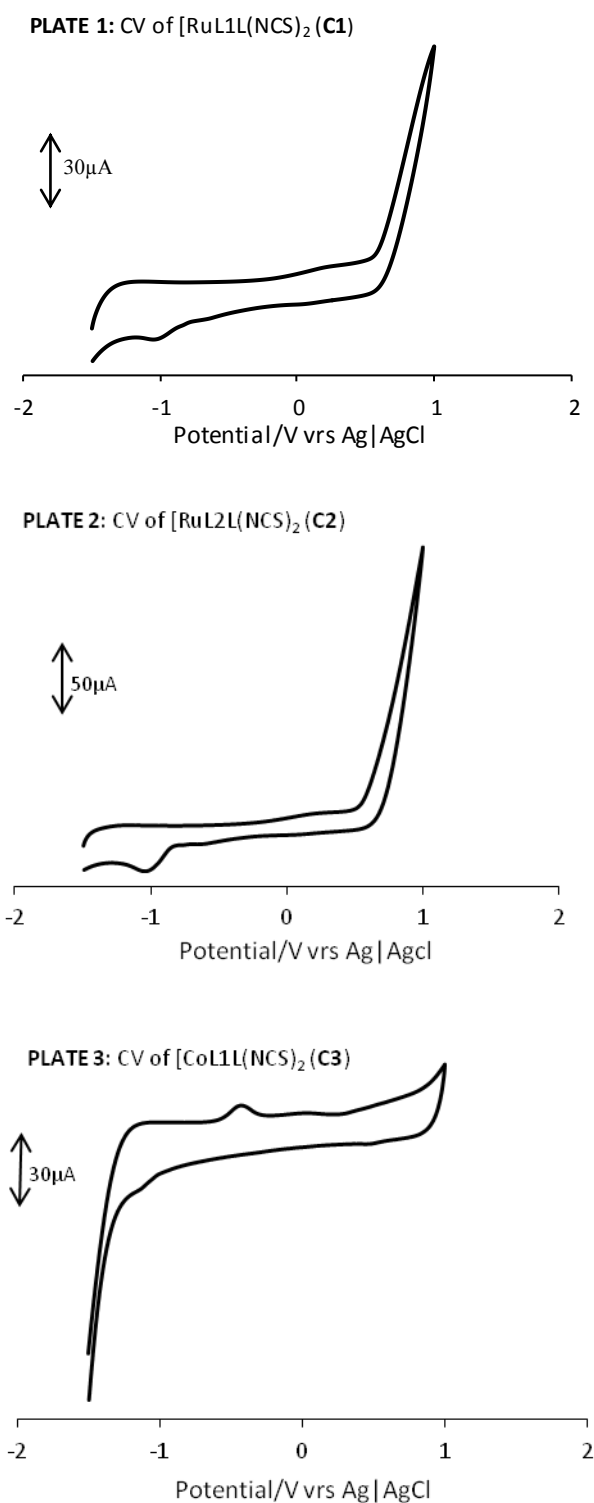
The electronic spectra of Ru(II) and Co(II) complexes confirmed the geometry of the compounds to be octahedral [26, 27].

The emission spectra of the Ru(II) and Co(II) complexes presented in Figure 2 show photo excitation above 400 nm [28, 30]. The complexes were observed to have a broad emission band in the range 703-705 nm. The emission spectra of complex C2 is blue-shifted by 2 nm compared to C1 and this is ascribed to lowering of the intraligand charge transfer transitions that originated from the LUMO due to electron donating group present in intraligand of C2 [31]. Complex, C4 relative to C3 experienced a red-shift by 1 nm, the red-shift is due to the alkyl substituent on pyrazole that enhanced the π -accepting properties of pyrazole and caused increase in HOMO-LUMO charge transfer transitions [21, 31].

3.4 Cyclic voltammetry studies of the complexes

The cyclic voltammograms of complexes C1-C4 shown in Figure 3 (Plates 1-4) were carried out in water containing phosphate buffer solution as a supporting electrolyte. The cyclic voltammogram of ruthenium(II) complexes, C1 and C2 show the Ru(II)/Ru(III) redox couple at positive and negative potentials. Irreversible oxidation peak in the cyclic voltammogram of C1 and C2 was observed at 0.23V and 0.24V respectively. The low oxidation potentials attribute to σ -donor ligand that stabilize the oxidized Ru(II) metal ion [32]. At the anodic potential irreversible reduction peaks were observed at -1.01 V for both C1 and C2 assigned to the contribution of ligands containing pyrazole rings [32, 33].

In the cyclic voltammogram of cobalt complexes C3 and C4, irreversible oxidation peaks were found at 0.41 and 0.77 V respectively, the increase in potential of C4 is due to the coordination of the metal ions to pyrazole causing insufficient electrons in the ligand [34, 35].



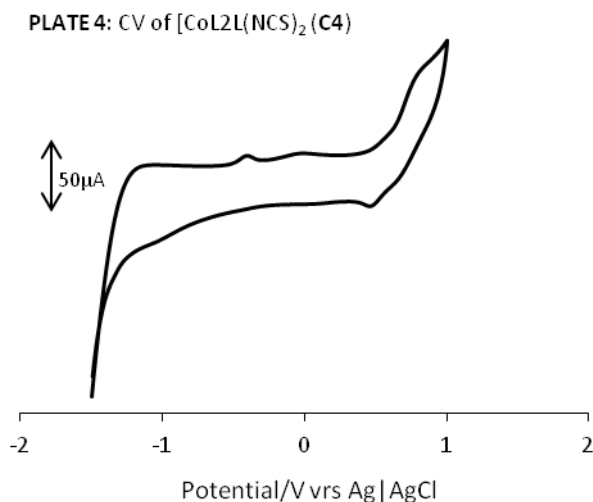


Figure 3. Cyclic voltammograms of C1-C4 at 0.5 mM in water containing 0.1 M of phosphate buffer solution (PBS) as a supporting electrolyte at 100 mVs^{-1} .

The reversible potentials were observed at -1.20 V for C3 and -0.41, -1.20 V for C4. The high reversible peak ascribed to the oxidation of the metal [36]. In the negative reduction potential were C3 and C4 were observed at -1.11V for and -1.03V respectively. The positive reduction observed in the voltammogram of C4 at 0.48 V can be ascribed to the ancillary ligand [37].

3.5 Evaluation of solar cells conversion efficiencies

The solar conversion efficiencies of the fabricated solar cells using the ruthenium and cobalt complexes, (C1-C4) is presented in Table 1 The efficiency of the complexes was between 0.60×10^{-5} and 101×10^{-5} . Complex, C2 show better photovoltaic performance compared to C1, this could be associated with their structural component since C2 contains a substituents that enhance the photostability of the complex. The efficiency of C4 is lower relative to C3 and this could be attributed to the steric structure of C4 that might hinder electronic transitions necessary for enhance photovoltaic performance [35, 36]. The efficiencies of cobalt(II) complexes were very low compared to ruthenium(II) complexes due to the difference in their molecular structures [37] and HOMO-LUMO levels of the complexes [38]. Complex, C2 showed the highest efficiency ($101 \times 10^{-5} \%$). The reason for low efficiencies for the complexes might be ascribed to poor adsorption of the dye onto the surface of the TiO_2 semiconductor. This poor adsorption might be due to the positioning of the anchoring group on the ligands that hinders the carboxylic groups from properly adsorbing onto the surface of the semiconductor. Moreover, the other reason might be steric hindrance that causes low electron transfer [31, 39].

Table 1. I-V characterization of Ru(II) and Co(II) complexes

Complex	J_{sc}	V_{oc}	P_{max}	FF	(η)
C1	0.199	37.0×10^{-3}	0.0442×10^{-3}	0.598	49.1×10^{-5}
C2	0.022	87.3×10^{-3}	0.0908×10^{-3}	0.517	101.0×10^{-5}
C3	0.00347	0.016×10^{-3}	0.001×10^{-3}	11.35	1.5×10^{-5}
C4	0.00119	0.161×10^{-3}	0.005×10^{-3}	1.64	0.60×10^{-5}

4. CONCLUSIONS

Ruthenium(II) and cobalt(II) complexes of bis(pyrazolyl)pyridine and pyridine-2,6-carboxylic acid were synthesized and characterized with the aim of utilizing them as sensitizers in dye sensitized solar cells (DSSCs). The photo physical and redox properties of the complexes show that they can be employed as light-harvesting materials for the fabrication of dyes sensitized solar cells. However, the performance of these complexes were very low. The results obtained from the solar cell of the fabricated complexes show that the solar conversion efficiency depends on their molecular structure. In order to make this compounds efficient materials for dyes sensitized solar cells, it might be necessary to make derivatives of them in form of the black dyes.

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