

Synthesis and Photophysical Studies of Ru(II) and Co(II) Complexes of bis(benzimidazolyl)pyridine and Evaluation of Their Potential as Sensitizers for Dyes Sensitized Solar Cells

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We report the synthesis of ruthenium(II) and cobalt(II) complexes of bis(benzimidazolyl)pyridine based ligands formulated as $[\text{RuL}_1\text{L}_n(\text{NCS})_2]$ (**C1**), $[\text{RuL}_2\text{L}_n(\text{NCS})_2]$ (**C2**), $[\text{CoL}_3\text{L}_n(\text{NCS})_2]$ (**C3**), $[\text{CoL}_1\text{L}_n(\text{NCS})_2]$ (**C4**), $[\text{RuL}_2\text{L}_n(\text{NCS})_2]$ (**C5**) and $[\text{RuL}_3\text{L}_n(\text{NCS})_2]$ (**C6**) where $\text{L}_1 = 2,6$ -bis(benzimidazolyl)pyridine, $\text{L}_2 = 2,6$ -bis(butylbenzimidazolyl)pyridine, $\text{L}_3 = 2,6$ -bis(benzylbenzimidazolyl)pyridine and $\text{L}_n =$ pyridine-2,6-dicarboxylic acid. The ligands and complexes were characterized by FTIR and NMR spectroscopy. The complexes exhibited some photoluminescence properties and their photophysical property was influenced by the presence of electron donating group. The cyclic voltammogram of the complexes show high negative reduction potentials ascribed to the increased π conjugation in the ligands. Three complexes were evaluated as sensitizers for dyes sensitized solar cells with ruthenium(II) complexes of bis(butylbenzimidazolyl)pyridine showing better performance while cobalt(II) complex shows the lowest efficiency.

Keywords: Dye-sensitized solar cells; bis(benzimidazolyl)pyridine ligands, photo-electrochemical studies, Ru(II); Co(II).

1. INTRODUCTION

Energy crisis is one of the major challenges the world is facing at present due to increase in demand for fossil fuels and negative environment impacts associated with the production and use of fossil fuels [1-3]. The current situation has led to the search and development of alternative sources of energy that is renewable and environmentally friendly [4,5]. Solar energy is considered as one perfect renewable energy source that has unlimited and pollution free characters [6-9]. The sunlight can be harvested and converted directly into electricity by means of photovoltaic devices [10]. Energy from

the sun is a clean, abundant and cheap energy source able to play an important role in human society [11, 12]. Among solar cells, dye sensitized solar cells (DSSCs) are very attractive choice for energy due to their low production cost and promising power conversion efficiency of up to 13% [13].

Ruthenium(II) complexes containing polypyridine ligands such as N3, N719 and N749 or black dye are the best ruthenium(II) complexes that have been employed as sensitizers in dye sensitized solar cells [14,15]. Black dyes have drawn attention in the application of dyes due to their ability to harvest light energy in the red and near infrared region [16]. In general ruthenium(II) complexes bearing N-N-N-donor ligands are known to have good photochemical and photophysical properties, nitrogen tridentate ligands are being investigated because they are inexpensive, easy to prepare and have low toxicity [17]. Bis(benzimidazolyl)pyridine ligands are considered as terpyridine in nature because they have similar structure and both ligands are tridentate nitrogen donor atoms with similar photophysical characteristics [18]. The polarity and increase of π -system in the bis(benzimidazolyl)pyridine ligand is attributed to the two imidazole rings system [19,20]. It also possess hydrogen bonds which are both H-bond donor and H-bond acceptor in the imidazole ring, therefor are excellent ligands for the synthesis of light emitting devices [21]. In this paper, we report the synthesis, spectroscopic, photo-electrochemistry studies and evaluation of the potential of Ru(II) and Co(II) bis(benzimidazolyl)pyridine complexes as sensitizers for DSSCs.

2. EXPERIMENTAL

All the reagents and solvents were of analytical grade and used as obtained without any further purification. The FTIR spectra were obtained as KBr pellets on a Perkin-Elmer Paragon 2000 spectrophotometer. ¹HNMR spectra were recorded on a Varian Unity Spectrometer in D₂O at room temperature. Electronic absorption and emission spectra of ligands were recorded on a 1 cm path length quartz cell on a Perkin-Elmer Lambda 25 UV-Vis spectrophotometer and Perkin-Elmer Lambda 35 Photoluminescence spectrophotometer. Cyclic voltammetry was carried out on a Autolab potentiostat with three equipped electrodes (glassy carbon working electrode, Ag/AgCl reference electrode and Pt counter electrode) in 0.5 water solution with 0.1 M of phosphate buffer solution (PBS) as a supporting electrolyte. All synthesis related to air sensitive compounds were carried out under nitrogen atmosphere.

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

Pyridine-2,6-dicarboxylic acid (1.7 g, 13 mmol) and 1,2-phenylenediamine (2.13 g, 26.4 mmol) were added to 3.9 g of polyphosphoric acid. The mixture was refluxed while stirring at 150 °C for 6 h. The mixture was cooled to 90°C and poured into 50 mL of water. Subsequently, the mixture was neutralized to pH 8 with ammonium solution. The resultant white solid was collected by filtration and repeatedly washed with methanol. Yield: 3.23g, 79%, m.p. 180°C, IR (KBr pellet); $\nu(\text{cm}^{-1})$: 3208, 3105, 2822, 2364, 2208, 1945, 1716, 1675, 1725, 1517, 1462, 1206, 1067, 896, 533.

2.2 Preparation of 2,6-bis(butylbenzimidazol-2-yl)pyridine (L₂)

2-chlorobutane (1.2 g, 7.71 mmol), 2,6-bis(benzimidazolyl)pyridine (L₁) (1.2 g, 3.85 mmol) and KOH (0.28 g, 4.98 mmol) were dissolved in 30 mL of acetone and refluxed for 4 h at 35°C. After cooling an equal amount was added to the mixture, which was extracted by dichloromethane, the organic layer was dried over MgSO₄ and evaporated to dryness. Yield 1.11g, 68%, m.p. 180°C, IR (KBr pellet) $\nu(\text{cm}^{-1})$: 3235, 2370, 2270, 2201, 1937, 1622, 1460, 1091, 791, 618.

2.3 Preparation of 2,6-bis(benzylbenzimidazolyl)pyridine (L₃)

The preparation of 2,6-bis(benzylbenzimidazolyl)pyridine (L₃) was similar to the method reported for L₂. Bromobenzene (0.71 g, 7.71 mmol), 2,6-bis(benzimidazolyl)pyridine (1.2 g, 3.85 mmol) (L₁) and KOH (0.28 g, 4.98 mmol) were dissolved in 30 mL of acetone and refluxed for 4 h. The product obtained was dried over MgSO₄ and evaporated to dryness. Yield: 1.22g, 68%, m.p. 172°C, IR (KBr pellet) $\nu(\text{cm}^{-1})$: 3237, 2983, 2904, 1924, 1623, 1400, 1069, 883, 757, 622, 555.

2.4 Synthesis of [RuL₁L_n(NCS)₂] (C1)

2,6-bis(benzimidazolyl)pyridine (L₁) (0.12 g, 0.206 mmol) and [RuCl₂(DMSO)₄] (0.2 g, 0.206 mmol) were dissolved in 25 mL of DMF. The mixture was refluxed in the dark for 4 h, pyridine-2,6-dicarboxylic acid (0.069 g, 0.206 mmol) was added to the mixture and refluxed for 2 h. After 2h excess potassium thiocyanate was added to the mixture and refluxed for 8 h. The reaction mixture was cooled at room temperature, the DMF was evaporated under vacuum. The residue was suspended in diethyl ether, the brown solid was filtered under vacuum, rinsed with diethyl ether and dried under vacuum. Yield: 89 mg, 62%, m.p. 220°C, IR (KBr pellet) $\nu(\text{cm}^{-1})$: 3409, 3244, 2839, 2374, 2122, 2084, 1620, 1464, 1400, 1397, 1308, 1109, 1068, 818, 622.

2.5 Synthesis of [RuL₂L_n(NCS)₂] (C2)

The synthesis of C2 was carried out in a similar method used for C1. 2,6-bis(butylbenzimidazolyl)pyridine (0.175 g, 0.206 mmol) and [RuCl₂(DMSO)₄] (0.2 g, 0.206 mmol) were placed in 25 mL of DMF. Yield: 106 mg, 64%, m.p. 212°C, IR (KBr pellet) $\nu(\text{cm}^{-1})$: 3424, 2821, 2366, 2343, 2068, 1869, 1635, 1400, 1291, 1117, 1015, 839, 758, 618, 536, 472.

2.6 Synthesis of [RuL₃L_n(NCS)₂] (C3)

The synthesis of C3 was carried out using method similar to the one used for C1 (section 2.2.1). 2,6-bis(benzylbenzimidazolyl)pyridine (0.191 g, 0.206 mmol) and [RuCl₂(DMSO)₄] (0.2g, 0.206 mmol) were placed in 25 mL of DMF. Yield: 47 mg, 27%, m.p. 210°C, IR (KBr pellet) $\nu(\text{cm}^{-1})$: 3429, 2955, 2819, 2359, 2124, 2067, 1978, 1646, 1510, 1377, 1116, 1019, 618, 538.

2.7 Synthesis of $[CoL_1L_n(NCS)_2]$ (**C4**).

$[CoCl_2 \cdot 6H_2O]$ (0.2 g, 0.841 mmol) and 2,6-bis(benzimidazolyl)pyridine (0.262 g, 0.841 mmol) were dissolved in a minimal amount of ethanol. The solution was left to stir at reflux for 3 h. After 3 h pyridine-2,6-dicarboxylic acid (0.140 g, 0.841 mmol) was added to the mixture then excess potassium thiocyanate (0.327 g, 3.364 mmol) was added after 2 h. The mixture was refluxed for 4 h, after cooling down the reaction medium at room temperature, ethanol was evaporated under vacuum and diethyl ether was added to the solution to precipitate the compound. The product was then filtered, washed with ethanol, and diethyl ether and dried under vacuum. Yield: 0.4g, 74%, m.p. 240°C, IR (KBr pellet) $\nu(cm^{-1})$: 3415, 3235, 2839, 2374, 2122, 2067, 1634, 1464, 1398, 1308, 1115, 1058, 1017, 618, 540, 473.

2.8 Synthesis of $[CoL_2L_n(NCS)_2]$ (**C5**).

The complex, **C5** was prepared in a similar method as reported for **C4**. $[CoCl_2 \cdot 6H_2O]$ (0.2 g, 0.841 mmol) and 2,6-bis(butylimidazolyl)pyridine (0.356 g, 0.841 mmol) were dissolved and refluxed for 3 h. Yield: 0.46g, 72%, m.p. 242°C, IR (KBr pellet) $\nu(cm^{-1})$: 3418, 2839, 2374, 2170, 2068, 1869, 1623, 1427, 1304, 1291, 1102, 1015, 839, 750, 618, 536, 422.

2.9 Synthesis of $[CoL_3L_n(NCS)_2]$ (**C6**)

The synthesis of **C6** was carried out using similar method reported for **C4**. $[CoCl_2 \cdot 6H_2O]$ (0.2 g, 0.841 mmol) and 2,6-bis(butylbenzimidazolyl)pyridine (0.389 g, 0.841 mmol) were added and refluxed for 3 h. Yield: 0.42g, 62%, m.p. 240°C, IR (KBr pellet) $\nu(cm^{-1})$: 3415, 3235, 2496, 2368, 1622, 1394, 1283, 1075, 917, 776, 733, 619, 541.

2.10 Preparation of solar cell device

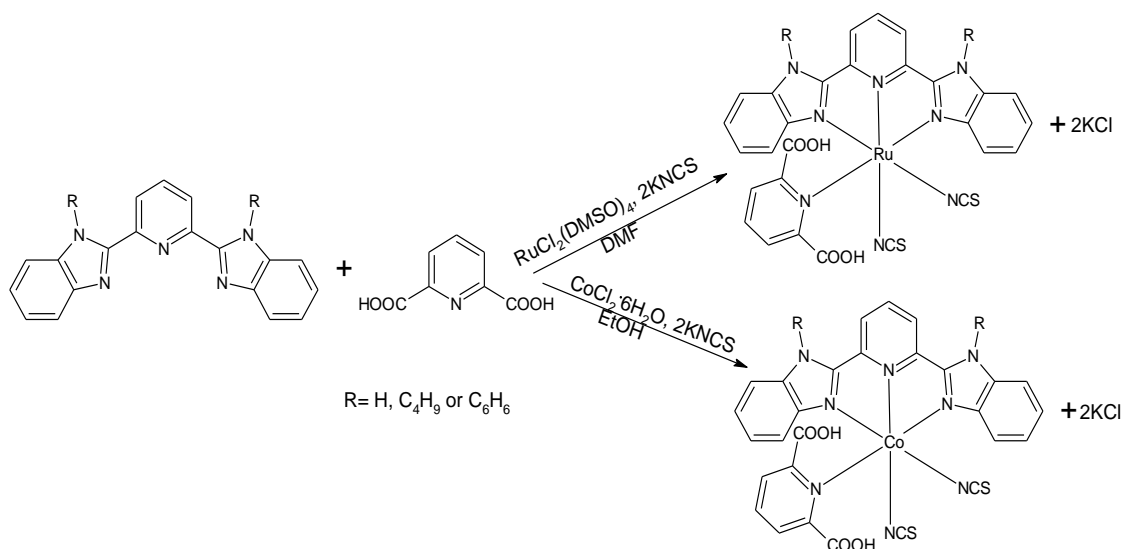
The solar cell assembly was carried out as follows: The dye solution was prepared in a concentration of 0.3 mM in DMF. TiO_2 electrode was dipped into the dye solution for 10 minutes, Pt plate electrode with a hole was put on top of a hot plate at 450 °C for 10 minutes to activate the electrode. The TiO_2 /dye electrode was taken out from the dye solution and washed with fresh ethanol and allowed to dry. The two electrodes were combined and a sealer was placed between the two electrodes and clipped with a blinder then heated at 70 °C for 15 minutes. After cooling, electrode construct was filled with electrolyte and the hole was sealed with a cap sealer.

3. RESULTS AND DISCUSSION

3.1 Synthesis

The complexes were synthesized by reacting $RuCl_2(DMSO)_4$ or $CoCl_2 \cdot 6H_2O$ with one equivalent amount of the corresponding ligand (L_1 - L_3) in DMF or ethanol as shown in Scheme 1. The

molar conductance of the ligands and the complexes are in the range of 0.1- 28.5 $\mu\text{Scm}^2\text{mol}^{-1}$ indicating all the compounds are non-electrolyte in solution [22].



Scheme 1. Synthesis of Ru(II) and Co(II) bis(benzimidazole)pyridine complexes

3.2 Infrared spectroscopy of the complexes

The IR spectra of the ligands and the complexes were compared in order to confirm the coordination of the N atom in the ligands to Ru or Co ions. The spectra of free ligands (L_1 , L_2 and L_3) show bands at 3208, 3235 and 3237 cm^{-1} respectively which are due to N-H group present in benzimidazole moiety. The absorption bands in the range 1675 and 1400 cm^{-1} due to C=C and C=N stretching vibrations are characteristic bands of benzimidazole group, while in spectra of the complexes (**C1-C6**), these bands shifted to confirm the coordination of nitrogen atoms and the Ru or Co atom [23,24]. The absorption bands in the range 1206-1069 cm^{-1} due to $\nu(\text{C-N})$ for L_1 - L_3 shift to lower frequencies between 1377-1307 cm^{-1} in complexes indicating the coordination is through the N atom of pyridine group [25]. In the spectra of complexes **C1** and **C4**, the $\nu(\text{N-H})$ stretching bands appeared at 3244-3235 cm^{-1} and these are attributed to uncoordinated N-H group of benzimidazole group. The shift could be ascribed to the involvement of the N-H in intermolecular hydrogen bond [26]. The strong and broad vibrational bands observed between 3429 and 3209 cm^{-1} for **C1-C6** are due to $\nu(\text{O-H})$ bending vibrations, present in 2,6-pyridinedicarboxylic acid [27]. The medium vibrational band between 1646 and 1620 cm^{-1} ascribed to the $\nu(\text{C=O})$ asymmetric stretching vibrations [27]. The presence of $\nu(\text{C-O})$ vibration at 1291-1113 cm^{-1} is due to the carbonyl group of pyridine-2,6-dicarboxylic acid. The vibrational bands around 2100 cm^{-1} are due to $\nu(\text{N=C=S})$ stretching vibrations of the thiocyanate moiety [20]. The disappearance of the $\nu(\text{N-H})$ stretching bands disappearing in the complexes shows that the NH is deprotonated and new $\nu(\text{N-H})$ vibrational bands at 622-540 ascribed to coordination between ligand and metal [19].

3.3 $^1\text{H-NMR}$ spectroscopic studies

The ^1H NMR spectra of some of the compounds were obtained in D_2O solution. The $^1\text{H-NMR}$ of the ligands and complexes (**C3-C6**) could not be recorded due to poor solubility. The $^1\text{H-NMR}$ spectrum of **C1** in D_2O solution, shows four signals at δ 8.57 (2H, s, L_n), 8.38 (1H, s, Py), 8.10 (1H, s, Py) and 7.93 (4H, m, Py). The spectrum showed one set of signal for the benzimidazole rings indicating that they are equivalent [19]. Three peaks observed for 2,6-bis-(benzimidazolyl)pyridine are similar to the $^1\text{H-NMR}$ of the same ligand reported in literature [19,28] for benzimidazole, but the peak position are slightly different from the expected peaks. The peak around δ 7.30 ppm for Ph-H (4H) multiplet was not visible and the one for N-H singlet was not expected due to D_2O exchange [27]. The $^1\text{H-NMR}$ spectrum for **C2** was similar to the spectrum for **C1** but **C2** contains additional peaks that are assigned to butyl groups. The spectrum of **C2** in D_2O solution showed 10 peaks at δ 8.57 (2H, d, L_n), 8.39 (1H, s, Py), 8.10 (1H, s, Py), 7.94 (4H, m, Py), 3.25-2.87 (18H, s, butyl) and 3.02-2.75 (18H, s, butyl). The expected peak around δ 9.00 ppm assigned for 2H, t, Pdca and peak around δ 7.30 ppm assigned for Ph-H (4H) multiplet were not visible.

3.4 Photophysical studies of the complexes.

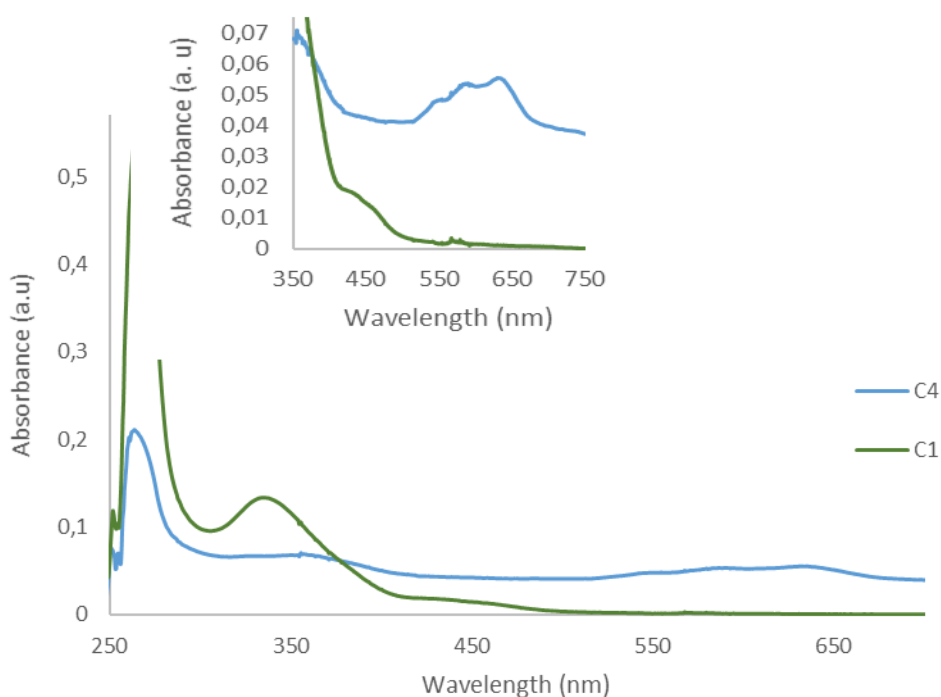


Figure 1. UV-Vis spectra of Ru(II) (**C1**) and Co(II) (**C4**) complexes

The electronic spectra of the ligands show bands at 239-355 nm region assigned to $\pi \rightarrow \pi^*$ transitions but in the spectra of the complexes (Figure 1-3) strong bands observed at 257-375 nm are ascribed to $\pi \rightarrow \pi^*$ transitions. Two weak bands in the region 435-638 nm in the electronic spectra of the

complexes are assigned ascribed to d-d transition, this indicates the coordination of the ligands (L₁-L₃) to the metal center with octahedral geometry [28]. The two bands in the visible region of ruthenium(II) complexes (C1-C3) at 446-720 nm assigned to $^4T_{2g} \rightarrow ^2T_{2g}$ and $^4T_{1g}(F) \rightarrow ^4T_1(P)$ transitions [29]. In the electronic spectra of cobalt(II) complexes (C4-C6), two bands of weak intensity are observed at 435-638 nm region ascribed to $^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$ and $^4T_{1g}(F) \rightarrow ^4T_1(P)$ of an octahedral Co(II) complexes [29-31]. The electronic spectra of ruthenium(II) complexes were observed at higher intensity compared to that of cobalt(II) which may be due to the molecular weight of the complexes.

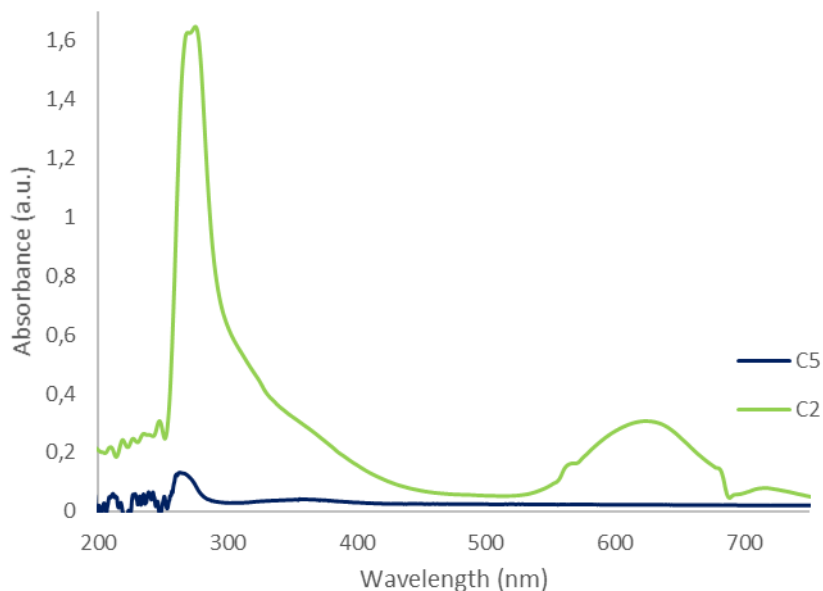


Figure 2. UV-Vis spectra Ru(II) (C2) and Co(II) (C5) complexes

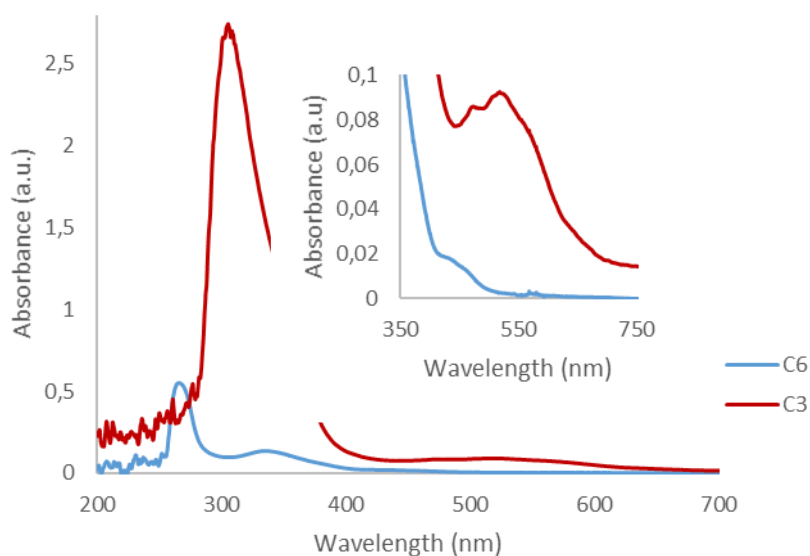


Figure 3. UV-Vis spectra of Ru(II) (C3) and Co(II) (C6) complexes.

The emission spectra of the complexes (figure 4) were observed to have a broad emission bands between 660 and 704 nm. The emission of ruthenium(II) complexes (C1-C3) show triplet

excited state and metal-to-ligand charge transfer transitions ($^3\text{MLCT}$) character with excited electrons localized in bis-(benzimidazolyl)pyridine [31]. The emission for **C3** relative to **C1** and **C2** is red-shifted by 1 nm, the red-shift emission is due π -conjugation of L_3 which stabilizes the $^3\text{MLCT}$ state [32]. The emission intensity gradually increased with decrease in the molecular weight of the ruthenium(II) complexes in the order **C1**>**C2**>**C3**. In cobalt(II) complexes, **C5** relative to **C4** and **C6** is blue-shifted by 41 nm, the blue-shift is due to π^* orbital in the ligand. The electronic absorption of **C5** d-d transition was not observed therefore **C5** has high π^* orbital energy hence lower emission is obtained compared to **C4** and **C6** [33]. Complex **C4** relative to **C6** is blue-shifted by 3 nm, the shift is due to N-H group present in bis(benzimidazolyl)pyridine in which it acts as H^+ donor, the intermolecular H-bond is responsible for the change in emission of the complexes. The π -conjugated substituent present on L_3 enhanced the electronic stabilization of excitation of the complex [33, 34].

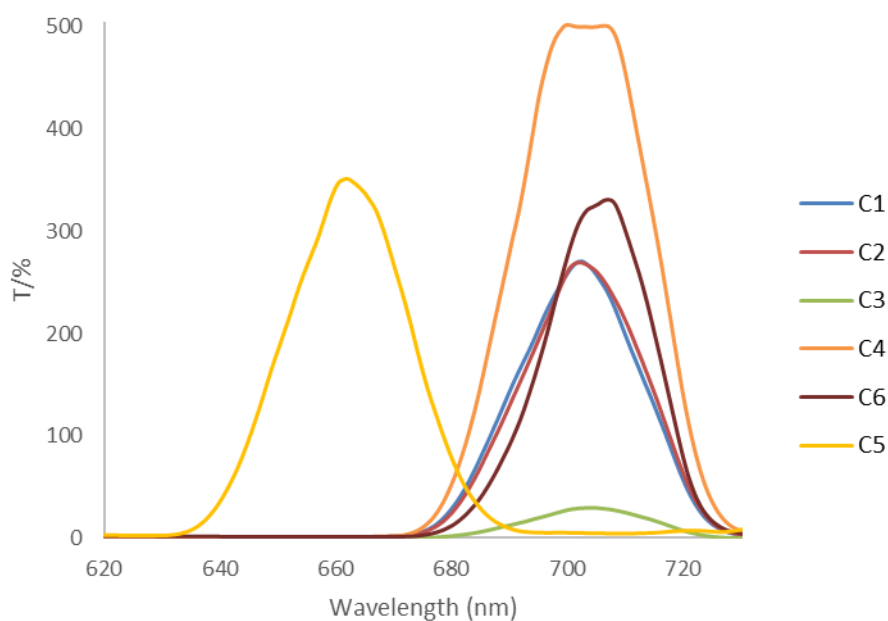


Figure 4. Emission spectra of Ru(II) and Co(II) complexes (**C1-C6**)

3.5 Cyclic voltammetry studies of the complexes

The cyclic voltammogram of **C1-C6** (Figures 5) was carried out in water containing phosphate buffer solution as a supporting electrolyte. The oxidation peaks were not visible in the cyclic voltammogram of **C1**, **C2** and **C3**. At the cathodic potential, irreversible peaks were observed at -1.01, -1.00 and -0.99 V for **C1**, **C2** and **C3** respectively but the assignment of these peaks is not certain since the solution is aqueous these peaks might be due to water or to benzimidazole ring. In the cyclic voltammogram of **C4**, irreversible oxidation peak was observed at -0.42 V ascribed to oxidation of electron withdrawing group from uncoordinated NH group of benzimidazole [35], while the reversible oxidation for **C5** and **C6** was observed at -0.38 and -0.29 respectively attributed to the oxidation of ligand. The irreversible oxidation peaks observed at +0.55, +0.12V for **C4**, +0.58, 0.10V for **C5** and

+0.83, +0.17 for **C6**, the oxidation potential that are more positive correspond to absorption of an electron from t_{2g} metal center, highest molecular orbital (HOMO) [36]. The positive reduction peaks observed at +0.46, +0.46 and +0.48V for **C4**, **C5** and **C6** respectively, the potentials are assigned to ancillary group that result in reduction of the cobalt(II) metal ion [37]. The increase in potential in **C6** due to π -electron system of L_3 . The negative potential at -0.48 for **C4** is due high π^* orbital energy shown in the electronic absorbance spectra (Figure 2), thus ligand-base reduction is observed [35]. High reduction potentials observed at -1.11, -1.09 and -1.02 V for **C4**, **C5** and **C6** might be ascribed to benzimidazole or water since the complexes were prepared in aqueous solution and the H-bond in benzimidazole group does not affect the reduction process [28].

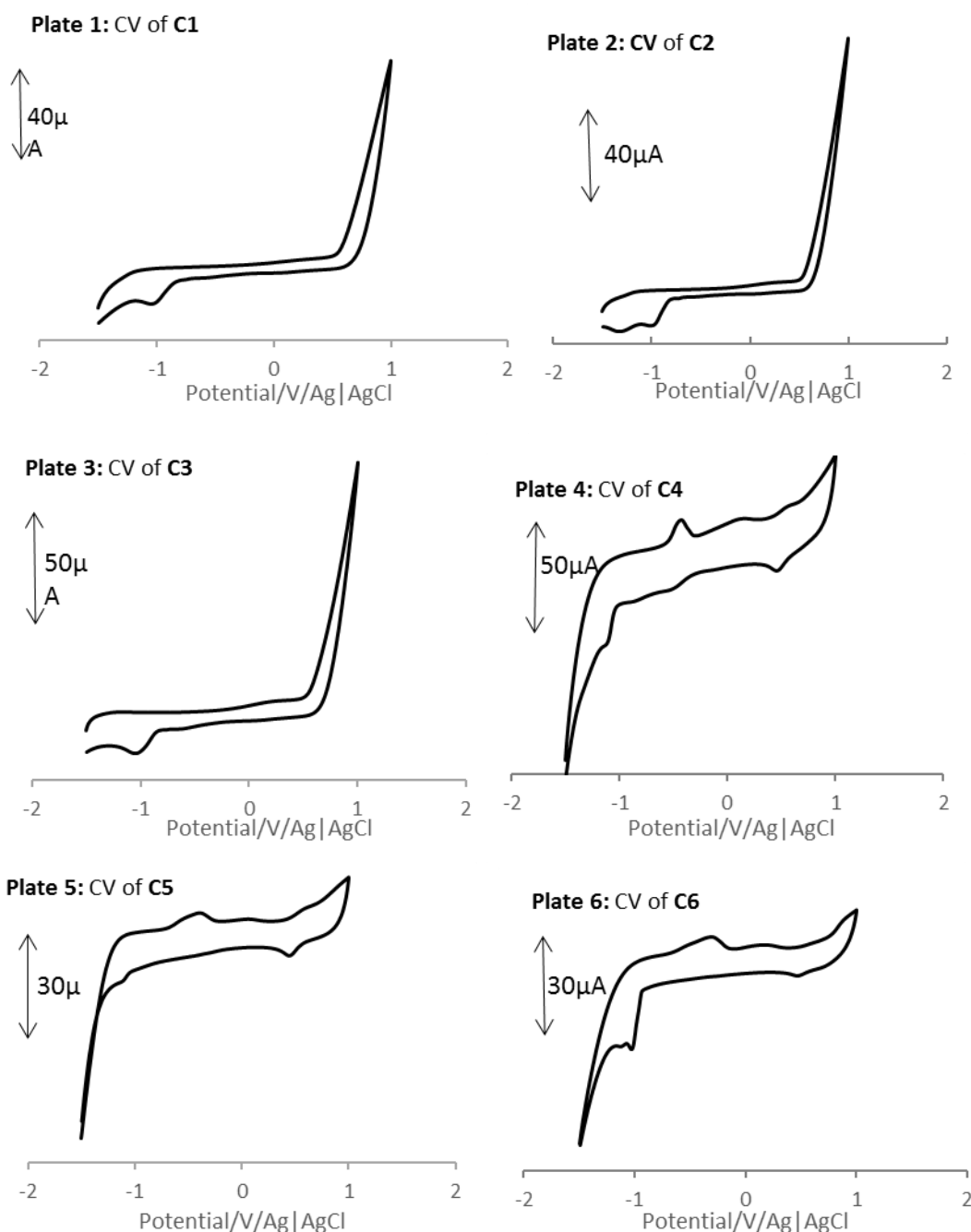


Figure 5. Cyclic voltammetry of **C1- C6** H_2O containing 0.1 M of phosphate buffer solution

3.6 Evaluation of Solar cell performance efficiency

The solar conversion efficiencies of the dyes, **C1**, **C2** and **C6** are presented in Table 1. **C3**, **C4** and **C5** were not characterized because **C3** have low yield, **C4** was not characterized because the d-d transition was not obtained in the visible region and **C5** was lighter in colour, the pigment of the dye was not visible when coated onto TiO₂ semiconductor. The efficiency obtained for **C1**, **C2** and **C6** at 9.8×10^{-5} , 19.0×10^{-5} % and 1.0×10^{-5} respectively. The solar cell with **C2** was observed to show highest efficiency (19.0×10^{-5}) indicating the presence of methyl group has effect on the dye sensitized solar cell performance. The electron withdrawing group on benzimidazole is expected to tune the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) levels in a favourable way [29].

Table 1. Photovoltaic parameter of solar cells fabricated with **C1**, **C2** and **C6**

Complex	J_{sc}/ mAcm^{-2}	V_{oc}/ mV	P_{max}	FF	(η)
C1	0.191	5.93×10^{-3}	0.09×10^{-3}	0.787	9.8×10^{-5}
C2	0.0176	14.3×10^{-3}	0.0171×10^{-3}	0.679	19.0×10^{-5}
C6	0.00283	0.049×10^{-3}	0	2.93	1.0×10^{-5}

The values of open circuit potential (V_{oc}), short circuit current (J_{sc}) and fill factor (FF) are shown in Table 1. The photovoltaic parameters were very low and the solar conversion efficiency is dependent on three factors [37]. The poor values of these factors tend to decrease efficiency of cells. The use of pyridine-2,6-dicarboxylic acid was to provide grafting of Ru(II) or Co(II) complexes onto the semiconductor to ensure the flow of electrons from the sensitizer to semiconductor. In these complexes, the carboxylic groups are too close to the metal ion and the electrons could not freely move through the semiconductor which led to poor values of efficiency. In the cyclic voltammetry of Ru(II) complexes the oxidation potentials were not visible and the reduction potential were more negative than expected. The reduction and oxidation respond to LUMO and HOMO levels of the complexes [28] resulted in poor photovoltaic values. The leaking of the solar cell during the experiment also affected the performance of the DSSC as the I_3/I^- strongly affect the performance of the solar cells [38].

4. CONCLUSIONS

2,6-bis-(benzimidazolyl)pyridine (L_1) and its two derivatives (L_2 and L_3), their Ru(II) and Co(II) complexes were successfully synthesized. All the compounds were characterized by molar conductivity measurements and FTIR spectroscopy. Spectroscopic studies were used to confirm the proposed structure of the synthesized ligands and the metal complexes. FTIR and electronic spectra of the complexes confirmed the coordination of the metal ions through the nitrogen atoms, except for **C5** as d-d transition was not visible in the UV spectra. The cyclic voltammogram of the complexes have

more reduction potentials which could be ascribed to the increased π -conjugation in the ligands. The increase in π -system of the ligands improved the photo-electrochemical properties of the complexes. The efficiency of the complexes was observed to increase with increasing molar weight of the ligand. The complexes show good photophysical properties, cobalt(II) were not promising sensitizers but they can be utilized in photo-electrochemical application.

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