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The Novel Ru(II) Complexes for Dye-Sensitized Solar Cells

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Ru(II) polypyridine complexes are widely used in application areas such as photochemistry, photophysics, photocatalysis, electrochemistry, electron and energy transfer process. In addition, Ru(II) complexes are the most commonly used metal complexes as photosensitizer in Dye Sensitized Solar Cells (DSSCs). The molar absorption coefficient of the complex in DSSC dyes can be increased by increasing π-conjugation. For this purpose, two new ruthenium complexes containing pyridinyl carboxylate ligands were synthesized and characterized by NMR, FT-IR, UV-Vis spectroscopic techniques. The I/V characteristics and the DSSC efficiencies of the synthesized Ru(II) complexes were investigated.

*Keywords:*Ru(II) polypridine complexes, DSSCs, Photosensitizer, Pyridinyl carboxylate ligand, DSSC efficiency

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1. Introduction

There is great attention to the production of dye-sensitized solar cells (DSSC) due to are relatively much safest and cheaper than other kinds of solar cells [1, 2]. An vital part of DSSC is the sensitizer layer which ruthenium complexes containing anchor ligands bearing free carboxylic acid group are generally used. In this work, we synthesized two new ruthenium complexes containing pyridinyl carboxylate ligands an ancillary ligand and [2,2'-bipyridine]-4,4'-dicarboxylic acid as an anchor ligand and tested their I-V characteristics in DSSC.

2. Experimental details

A Jeol JNM-ECX400II was used for NMR spectra at 297 K. A Thermo Scientific Evolution 201 system was used for UV–Vis spectra. Optical band gaps were calculated using literature method from UV-Vis spectra [3].A Perkin Elmer Spectrum One FTIR system was used for the infrared spectra. Cyclic voltammogram (CV) was monitored with a MTI–BST8–STAT–EIS–LD instrument. DSSC was prepared according to literature method [4].

2.1. Syntheses of the new Ru(II) complexes

The pyridine-2-carboxylic acid (0.2 mmol) or quinoline-2-carboxylic acid (0.2 mmol) and KOH (0.2 mmol) was dissolved in DMF and continuously stirred at room temperature for a 1 h. Then, [RuCl$_2$(p–cymene)]$_2$ complex (0.1 mmol) was added this solution and stirred at 60 °C for 4 h. At the end of this time, [2,2'-bipyridine]-4,4'-dicarboxylic acid (0.2 mmol) and NH$_4$SCN (0.2 mmol) was added above solution and stirred for further 12 h at 160 °C. Then, the volatiles were removed under vacuum and the precipitate was washed with cold water, MeOH and diethyl ether.

3. Results and discussion:

The complexes was synthesized from the reaction of [RuCl$_2$(p-cymene)]$_2$, potassium salt of pyridine-2-carboxylic acid or quinoline-2-carboxylic acid, [2,2'-bipyridine]-4,4'-dicarboxylic acid and NH$_4$SCN using Schlenck techniques. The reaction scheme was given Fig. 1. The various spectroscopic and analytic techniques were used for characterization of compounds such as NMR, FT-IR, UV-

Vis.

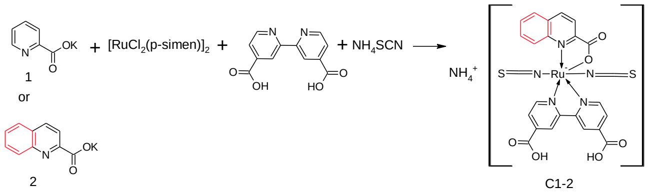
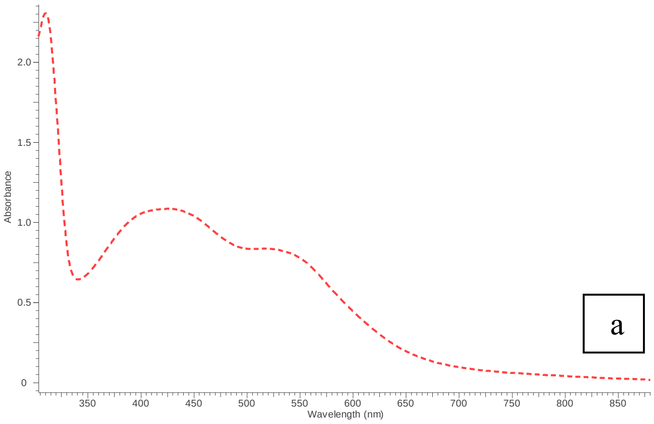


Fig.1.*Synthesis of Ru(II) complexes*

The aromatic protons of complexes were observed between 7.0 and 9.5 ppm as multiplet for C1 and between 7.3 –9.2 ppm as multiplet for C2 in ^{1}H-NMR spectra. The peaks are very complex for the assignment of hydrogen because a mixture of isomers may be formed. ^{13}C-NMR spectra could not be recorded because of the low solubility caused from carboxylate groups. The precipitate was used as obtained as a sensitizer in DSSC.

At the FT-IR spectra of C1, while -OH stretching bands were observed at 3398 cm^{-1}, vibration of thiocyanate ligands were monitored 2101$cm^{-1}$and 2052 cm^{-1} as double bands. Additionally, C=O stretching band was observed at 1708 cm^{-1}. On the other hand, while -OH stretching bands were observed at 3406 cm^{-1}, vibration of thiocyanate ligands were monitored 2109$cm^{-1}$and 2071 cm^{-1} as double bands and C=O stretching band was observed at 1708 cm^{-1}at the FT-IR spectra of C2.

The electronic spectra of the complexes in DMF were given Fig. 2. While the huge bandsunder 350 and the broad peak between 350-450 nm are $\pi \rightarrow \pi^*$ transitions for C1 and C2, the broad band between around 450-600 nm was attributed to the metal to ligand charge transfer bands. Optical band gap (Ebg) of the C1-2 obtained from absorption spectra are 1.77 and 2.00 eV, respectively.



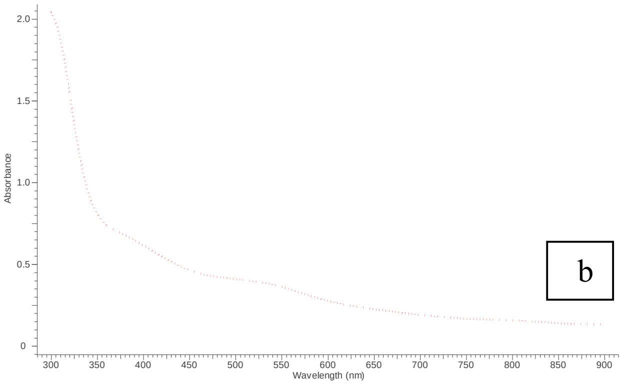
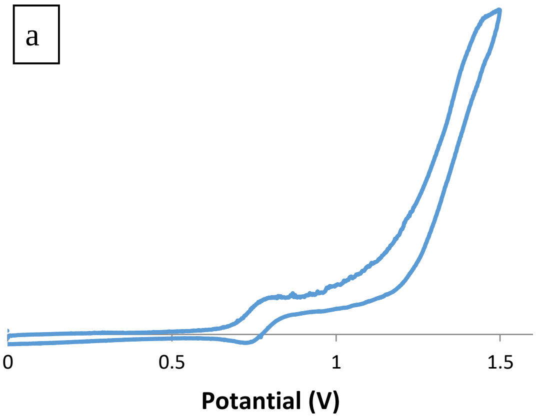


Fig.2. *The absorption spectra of complexes (1x10^{-5} M in DMF) for C1 (a) and C2 (b).*

The electrochemical properties of the complexes were examined with cyclic voltammetry technique (Fig. 3). The voltammogram of the complex was displayed an irreversible oxidation peak in DMF solution including 0,1 M $LiClO_4$ (supporting electrode). The HOMO energy level of the complex was calculated $E_{HOMO} = -(E_{ox}-E_{Fc/Fc+})^{+}$ (–4.8), and the energy level of LUMO was calculated from $E_{LUMO} = E_{HOMO} + E_{bg}$ [5, 6]. The calculated E_{HOMO} and E_{LUMO} values are -5.47 and -3.70 eV for C1 and -5.42 and -3.42 eV for C2, respectively. The result reveals that the complex is fully compatible to use as sensitizers in DSSC. While the LUMO level of the complex is under the energy level of the I^-/I_3^- redox couple, the HOMO level of the complex is over the energy level of the TiO_2 conduction band [4].



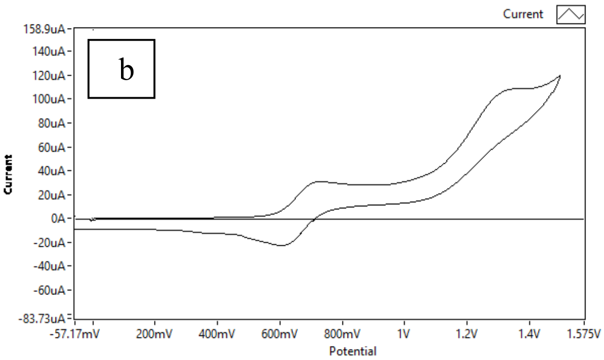


Fig.3. *Cyclic voltammograms were measured in DMF solution (1x10^{-3}) at scan rate of 100 mVs^{-1} for C1 (a) and C2 (b).*

The synthesized complexes were tested in DSSC as sensitizer. DSSC was prepared according to literature method [4]. The current density–voltage (J–V) curves of prepared DSSC were monitored under 100 mW/cm^2 (Fig. 4). The I-V characteristics of prepared DSSC were given in Table 1.

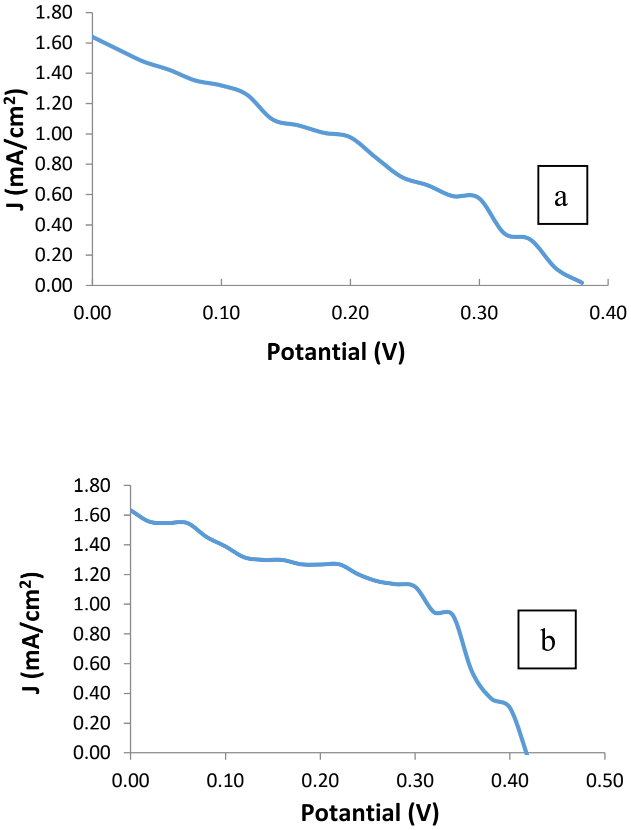


Fig.4. *The current density–voltage curves of DSSCs under 100 mW/cm^2 light intensitie for C1 (a) and C2 (b).*

Table 1. The I-V characteristics of prepared DSSCs using the C1-2

Complex	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η%
C1	1.64	0.38	0.31	0.20
C2	1.63	0.42	0.49	0.34

Conclusions

In this paper, we synthesized a new Ru(II) complexes containing 2-pyridinylcarboxylate ligands as an ancillary ligand and [2,2'-bipyridine]-4,4'-dicarboxylic acid as an anchor ligand andcharacterized with structural-, spectral- and electrochemical methods. The I-V characteristics of complexes tested in DSSC. The result show that the increasing conjugation at ancillary ligand backbone increase power conversation yield (n%).

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