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The I-V Characteristics of a New Ru(II) Complex for Different Devices

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Dye Sensitized Solar Cells (DSSCs) have become very popular for the last decades because of their superior electrical properties, low-cost, conductivity, high molecular weight, and the possibility to modify the structure with different chromophore groups. Ru complexes containing bi- and tri- dentate benzimidazole type ligands are very important in DSSC technology. In this study, L1 ligand was synthesized by derivation of 2,2'-(pyridine-2,6-diyl)bis(5,6-dimethyl-1H-benzimidazole) ligand and Ru-L1 complex was prepared by using isonicotinic acid and isothiocynate as ancillary ligands. The synthesized Ru(II) complex was characterized by NMR, FT-IR, UV-Vis spectroscopic techniques, HOMO-LUMO energy levels were determined and compared with the theoretical calculations. DSSC efficiency of the Ru(II) complex was investigated under various light intensities and the I/V characteristic of the diode that produced with Ru(II) complex was examined.

Keywords: DSSCs, Ru complex, Benzimidazole type ligands, HOMO-LUMO energy, Diode

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1. Introduction

There is great attention to the production of Solar cells both in laboratory and industry. Dye-sensitized solar cells (DSSC) are relatively much safest and cheaper than other kinds of solar cells[1, 2]. For this, there is much ongoing research in the literature to obtain a good DSSC. An important part in DSSC is the dye layer which ruthenium complexes containing anchor ligands are generally used. In this work, we synthesized a new ruthenium complex containing 2,6-bisbenzimidazole ligands as an ancillary ligand and isonicotinic acid as an anchor ligand and tested their I-V characteristics in DSSC. Additionally, a diode was produced using synthesized Ru(II) complex and its I-V characteristics were analyzed. Recently, many diodes prepared in the literature using Ru(II) complexes.

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 CHNS–932 (LECO) instrument was used for the CHN analyses of complex.A Perkin Elmer Spectrum One FT-IR system was used for the infrared spectra. Cyclic voltammogram (CV) was monitored with a MTI–BST8–STAT–EIS–LD instrument The Al/Ru(II)-L1/n-Si/Al diode was fabricated according to literature method using Al for thermal evaporation source [4]. DSSC was prepared according to literature method[5].

2.1. Synthesis of Ligands

The L1 ligand was synthesized according to literature method using 2,3,5,6-tetramethylbenzyl chloride and 2,2'-(pyridine-2,6-diyl)bis(5,6-dimethyl-1H-benzimidazole)[5].

^{1}H-NMR (400 MHz, $CDCl_3$) d ppm 1.98 (s, 12 H), 2.13 (s, 6 H), 2.15 (s, 12 H), 2.31 (s, 6 H), 6.13 (s, 4 H), 6.37 (s, 2 H), 6.92 (s, 2 H), 7.55 (s, 2 H), 8.02 (t, 1 H), 8.39 (d, 2 H). ^{13}C-NMR (101 MHz, CDCl3) d ppm 15.57, 20.43, 24.15, 29.81, 46.57, 111.90, 119.85, 125.23, 129.72, 131.30, 131.66, 131.69, 131.85, 132.38, 133.34, 133.99, 134.84, 137.89, 141.53, 149.69, 150.29. FT–IR (cm^{-1}): 3029, 2966, 2918, 1624, 1576, 1507, 1474, 1449, 1409, 1384, 1355, 1325, 1262, 1218, 1160, 1131, 1083, 1040, 1002, 960, 904, 868, 834, 771, 739, 708, 668, 650, 598, 554, 509, 457, 433.

2.2. Synthesis of the new Ru(II) complex

The L1 ligand (0.684mmol) and [$RuCl_2$(p–cymene)]$_2$complex (0.326mmol) were mixed in DMF (10mL) at 80°C for 4h. Then, isonicotonic acid (ina) (0.684mmol) and ammoniumthiocyanate (1.304mmol) were added and stirred at 160°C for further 24 h. At the end of this time, the reaction volume was distilled approximate 2mL and Et_2O was added to obtain a dark-brown solid. The crude product was filtered off and washed with H_2O, EtOH and Et_2O, respectively.

Anal. Calc. For [(L1)$(SCN)_2$(ina)Ru].EtOH: C, 63.1; H, 5.8; N, 10.7 % found : C, 63.0; H, 5.9; N, 10.3 %. ^{1}H–NMR (400 MHz, DMSO–d6) d ppm 2.10 (d, J=3.21 Hz, 12 H) 2.35 (s, 6 H) 2.49 (s, 4 H) 6.18 (s, 4 H) 6.21 (s., 2 H) 6.46 (s, 2 H) 7.01 (s, 2 H) 7.23 (d, J=5.50 Hz, 2 H) 7.80 (t, J=7.8 Hz, 1 H) 7.86 (d, J=5.50 Hz, 2 H) 8.42 (d, J=7.8Hz, 2 H). ^{13}C–NMR (101 MHz, DMSO–d6) d ppm 15.61, 15.81, 20.60, 34.80, 47.70, 113.09, 118.49, 123.57,130.25, 131.50, 132.48, 134.03, 134.43, 135.30, 139.95, 140.58, 141.24, 151.03, 152.01, 153.82, 154.70, 158.61, 162.39, 169.25. FT–IR (cm^{-1}): 3396, 2989, 2972, 2902, 2102, 1686, 1595, 1472, 1436, 1408, 1394, 1382, 1250, 1242, 1229, 1075, 1066, 1057, 1028, 892, 879, 800, 772, 738, 696, 674, 603, 581, 538, 458, 434.

2.3. Computational procedure

The theoretical calculations were carried out by using the Gauss-View graphical user interface [6] and Gaussian 03 software package [7] with LANL2DZ basis set for metal ion and 6-311g(d,p) for remaining atoms.

3. Results and discussion:

The L1 was synthesized from the reaction of 2,2'-(pyridine-2,6-diyl)bis(5,6-dimethyl-1H-benzimidazole), KOH and 2,3,5,6-tetramethylbenzyl chloride in acetone under reflux conditions. The complex was synthesized from the reaction of [$RuCl_2$(p-cymene)]$_2$, ina and NH_4SCN using Schlenck techniques. The complex reaction scheme was given Figure 1. The various spectroscopic and analytic techniques were used for characterization of compounds such as NMR, FT-IR, UV-vis.

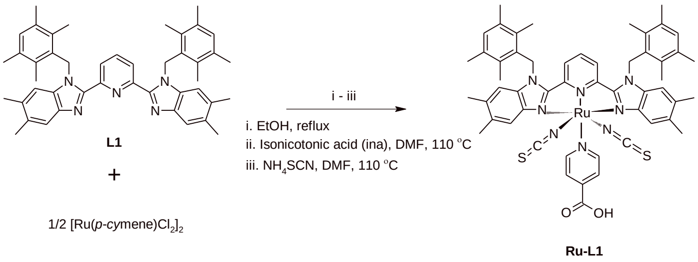

Fig.1: *Synthesis of Ru(II)-L1*

The data of NMR and FT-IR spectra were given in the experimental section, and the data supports the proposed structure formulas.

The electronic spectra of the Ru(II)-L1 complex in DMF were given Figure 2(a). The absorption spectra of complex were compatible with literature [8]. While the three huge bandsbetween 300 nm and 400 nm are $\pi \rightarrow \pi^*$ transitions, the broad band between around 450-600 nm was attributed to the metal to ligand charge transfer bands. Optical band gap (Ebg) of the Ru(II)-L1 complex obtained from absorption spectra is 1.93 eV.

The electrochemical properties of the Ru(II)-L1 complex were examined with cyclic voltammetry technique (Fig. 2b). The voltammogram of the complex was displayed an irreversible oxidation peak in DMF solution including 0,1 M $LiClO_4$ (supporting electrode)at scan rate of 100 mV.s^{-1}. 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 $E_{LUMO} = E_{HOMO} + E_{bg}$ [9, 10]. The Fig. 3. shows an energy level diagram of the Ru(II)-L1 complex together with TiO_2 and I^-/I_3^- levels. Fig. 3. 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.

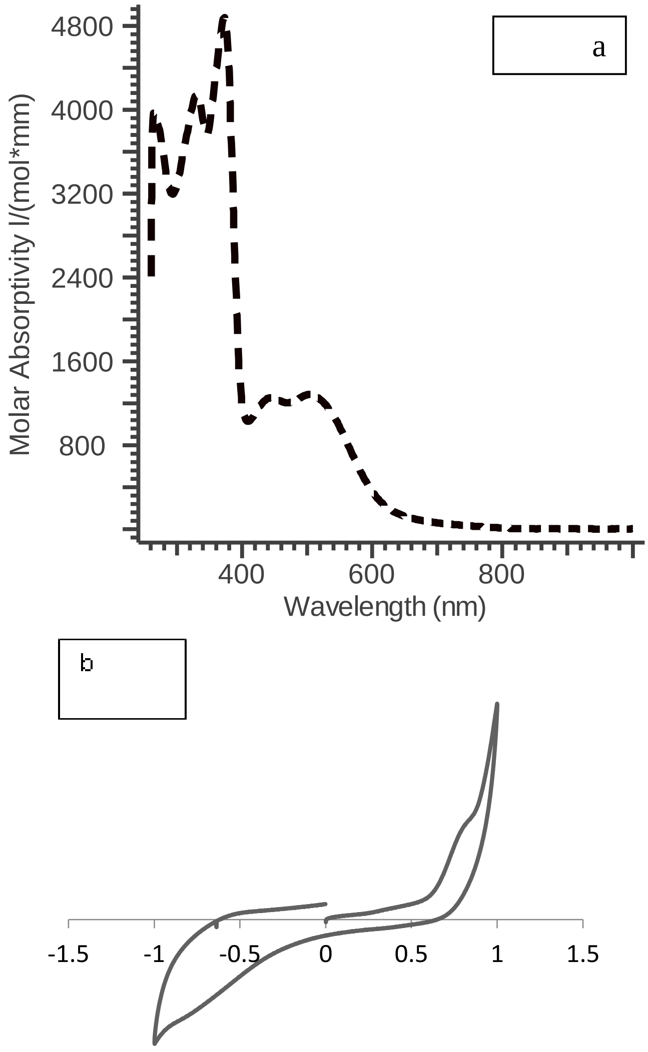

Fig.2: *The absorption spectra of Ru(II)-L1 complex (1x10^{-5} M in DMF) (a) and Cyclic voltammograms of Ru(II)-L1 (b) complex were measured in DMF solution (1x10^{-3}) at scan rate of 100 mVs^{-1}.*

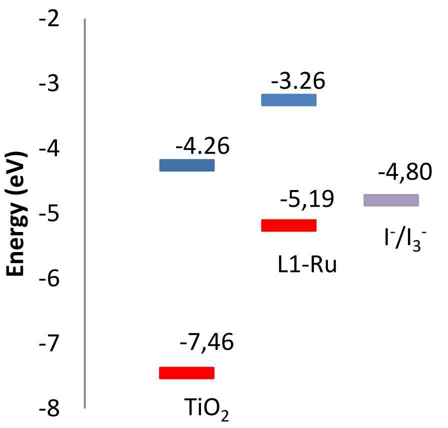

Fig.3: *HOMO (-) and LUMO (-) energy levels of the complex together with TiO_2 and I^-/I_3^- levels*

The optimized molecular structures and calculated molecular orbitals of Ru(II)-L1 were calculated with energy levels in vacou (Fig. 4). The results show that HOMOs and HOMO–1s fully settle down located at the metal and NCS$^-$ ligands while LUMOs locate at the ina ligand.

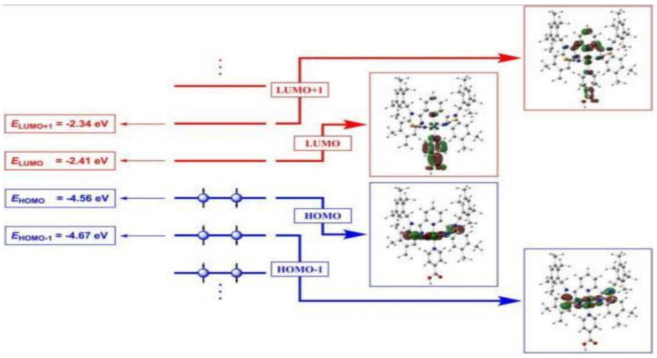

Fig.4: *Optimal molecular structure and isodensity surface plots of the first two frontier molecular orbitals*

The synthesized complex was tested in DSSC as sensitizer. The current density–voltage (J–V) curves of prepared DSSC were monitored under various illumination intensities (Fig. 5).The I-V characteristics of prepared DSSC were given in Table 1. The data show that increasing light intensity generally increases the short circuit current and the open circuit voltage.

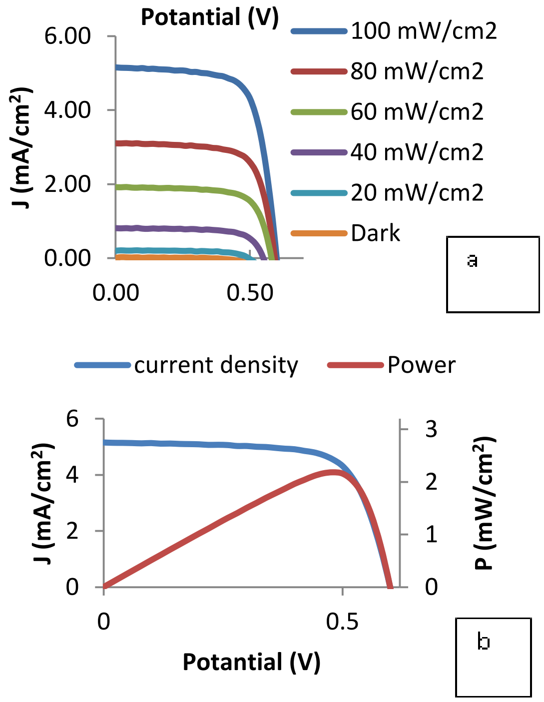

Fig.5: *a) The current density–voltage curves of DSSC under various light intensities. b) The power–voltage and current density–voltage overlapped curves of DSSC under 100 mW/cm^2 light intensities.*

Table 1. The I-V characteristics of prepared DSSC using the Ru(II)-L1 complex under various incoming light intensity

L2-Ru	Incoming Light Intensity				
	100 mW/cm^2	80 mW/cm^2	60 mW/cm^2	40 mW/cm^2	20 mW/cm^2
J_{sc} (mA/cm^2)	5,153	3,099	1,917	0,817	0,201
V_{oc} (V)	0,620	0,600	0,600	0,560	0,500
FF	0,684	0,707	0,687	0,684	0,697
η%	2,183	1,642	1,316	0,782	0,350

Additionally, a diode was prepared using Ru(II)-L1 complex and tested its I-V characteristics at room temperature under dark conditions. In I-V curve of diode was given in Fig 6. The ideality factor of prepared diode was determined with literature method as 4.0 [11]. This value is very large for ideal diode. This observation is related with interface conditions and nature of diode.

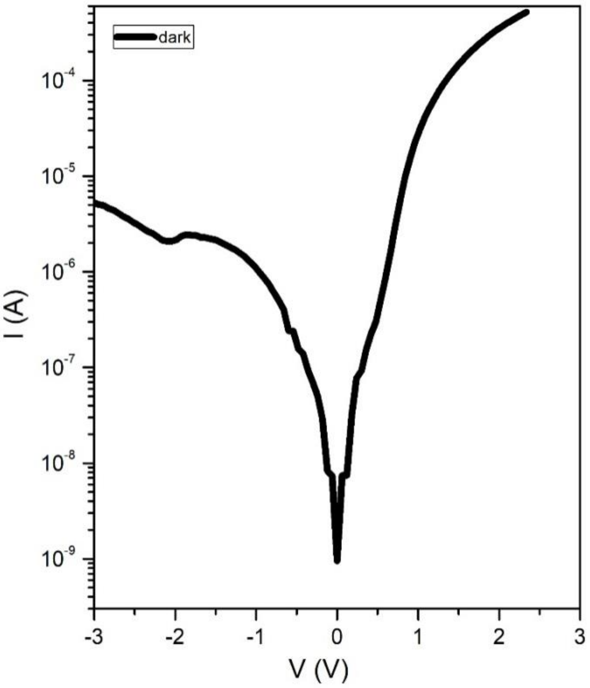

Fig.6: *In(I)-V curve of Al/Ru(II)-L1/n-Si/Al*

Conclusions

In this paper, we synthesized a new Ru(II) complex containing 2,6-bisbenzimidazole ligands as an ancillary ligand and isonicotinic acid as an anchor ligand andcharacterized with structural-, spectral- and electrochemical methods. The theoretical properties of complex were computed using DFT method. The complex tested their I-V characteristics in DSSC and diode devices. The result show that the DSSC device has moderate power conversation yield (n%) and the prepared diode ideality factor is 4.0. For better devices, the ligands around Ru(II) may slightly be changed using similar groups.

Acknowledgements

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