

A STUDY ON THE STRUCTURAL, OPTICAL AND PHOTOVOLTAIC PROPERTIES OF Fe(II) SCHIFF BASE COMPLEX WITH 5 AMINO-2,4-DICHLOROPHENOL-3,5-DITERTBUTHYLSALISYLALDIMINE LIGAND

D. KILINC^a, O. SAHIN^b, S. HOROZ^{c,*}

^a*Siirt University, Faculty of Arts&Sciences, Department of Chemistry, Siirt, 56100, Turkey*

^b*Siirt University, Faculty of Engineering, Department of Chemical Engineering, Siirt, 56100, Turkey*

^c*Siirt University, Faculty of Engineering, Department of Electrical and Electronics Engineering, Siirt, 56100, Turkey*

In our present study, 5 amino-2,4-dichlorophenol-3,5-ditertbuthylsalisylaldimine ligand was synthesized and we used this ligand to prepare its-Fe(II) complex with using the wet chemical method. The structural, optical and electronic properties of Fe(II) Schiff base complex with ligand were characterized using the x-ray diffraction (XRD), optical absorption and Fourier transform-infrared (FT-IR) measurements, respectively. The structure of Fe(II) Schiff base complex with ligand was determined as a monoclinic crystal system. Two absorption bands were observed in the UV-visible region. They are assigned to intraligand and charge transfer transitions, respectively. The FT-IR spectra of Fe(II) Schiff base complex with ligand are similar to the ligand spectra. Despite the similarity, a shift toward higher frequencies was observed in the vibration modes of azomethine groups. Furthermore, Fe(II) Schiff base complex was used as a photosensitizer on TiO₂ film in a DSSC device. Thus, the effect of Fe(II) Schiff base complex on the efficiency of DSSC device was investigated and photovoltaic parameters such as power conversion efficiency (η), open circuit voltage (V_{OC}) and short circuit current density (J_{SC}) were determined. The obtained J_{SC} and V_{OC} value for samples is 3.75mA/cm² and 600 mV, respectively. The η % value was calculated as 0.80. Our result leads to obtain improved conversion efficiency of Fe(II) Schiff base complex with ligand based DSSC device.

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1. Introduction

Schiff bases having the general formula R-NC=N-R include at least one azomethine group which is the most active group as ligands in coordination chemistry (A.G. Imer 2018). Schiff base ligands have a significant position in many technological applications (A.T. Bader 2015) (W. Al Zoubi 2016). Because of this property, Schiff base ligands and their complexes with transition metals have been extensively investigated. These complexes have played important roles in the development of many different scientific fields such as material chemistry (N.K. Chaundary 2017), organo-metallic/bioinorganic chemistry (S. M. Wilkinson 2016), catalysis (K.C. Gupta 2008) and magnetism (M. Machata 2017).

Another application area of metal complexes of Schiff base ligands is solar cells. These materials are used as sensitizers in dye-sensitized solar cells (DSSCs), a type of solar cells (A.W. Jeevadason 2014) (H. Setyawati 2015). Q'Regan et al. (B. O'Regan 1991), Cao et al. (Y. Cao 2017), Al-Ghamdi et al. (A. A. Al-Ghamdi 2014) and Baysal et al. (A. Baysal 2015) mentioned that DSSCs have potential low-cost production processes and high energy conversion efficiency. They have received great interest in recent times owing to their unique characteristics. Numata et al. (Y. Numata 2013) used the ruthenium complex as a sensitizer in a DSSC structure. As it is

*Corresponding author: sabithoroz@siirt.edu.tr

well known, the ruthenium complexes have efficient metal to ligand charge transfer properties (R. Sivakumar 2017). Although ruthenium complexes provide high efficiency, these complexes contain heavy metals that they damage the environment. Because of the disadvantage that the ruthenium has, the researchers have needed new complexes that are easy to synthesize and do not harm the environment (A.G. Imer 2018).

In our present study, 5-amino-2,4-dichlorophenol-3,5-ditertbutylsalicylaldehyde ligand was synthesized and we used this ligand to synthesize 5-amino-2,4-dichlorophenol-3,5-ditertbutylsalicylaldehyde-Fe(II) complex with using the wet chemical method. The synthesized Fe(II) Schiff base complex was characterized by x-ray diffraction (XRD), optical absorption and Fourier transform-infrared (FT-IR) measurements, respectively. Furthermore, Fe(II) Schiff base complex was used as a photosensitizer on TiO₂ film in a DSSC device. Thus, the effect of Fe(II) Schiff base complex on the efficiency of DSSC device was investigated and photovoltaic parameters such as power conversion efficiency (η), open circuit voltage (V_{OC}) and short circuit current density (J_{SC}) were determined.

2. Experimental study

5-amino-2,4-dichlorophenol-3,5-ditertbutylsalicylaldehyde ligand (D. Kilinc 2018) and its Fe complex were synthesized using the wet chemical method. To synthesize ligand; 1 mmol of the amine in ethanol was added to 30 ml of ethanolic solution of 1 mmol of aldehyde. The mixture was then boiled under reflux at 100 °C for 5-6 hours. Yellow-orange ligand particles were observed. As a final step, the ligand was washed sequentially with methanol and chloroform and dried. The ligand's structure is shown in Fig. 1.

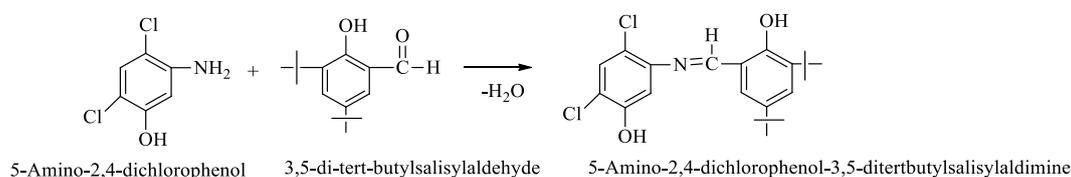


Fig. 1. The synthesis reaction of 5-amino-2,4-dichlorophenol-3,5-ditertbutylsalicylaldehyde ligand.

To synthesize Fe(II) Schiff base complex with ligand; the Fe(OAc)₂ and 5-amino-2,4-dichlorophenol-3,5-ditertbutylsalicylaldehyde ligand were mixed in ethanol. Then, the obtained complex was recrystallized by washing with methanol and chloroform, and then the product was dried. Fig. 2 indicates the synthesis reaction of Fe(II) Schiff base complex with ligand.

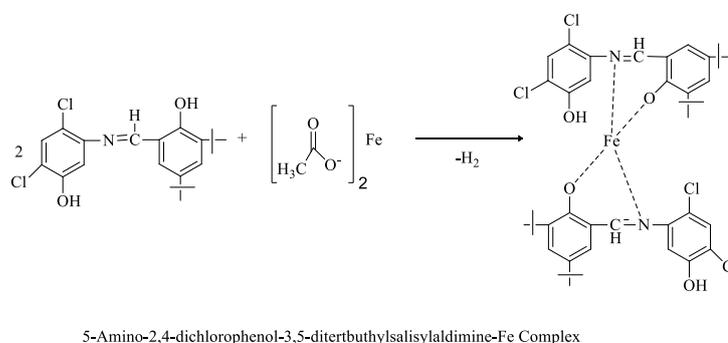


Fig. 2. The synthesis reaction of Fe(II) Schiff base complex.

X-ray diffraction (XRD) on a Rigaku X-ray diffractometer with Cu K α ($\lambda=154,059$ pm) radiation was used to analyze structural properties of Fe(II) Schiff base complex with ligand. The

optical absorption spectrum of complex was obtained with a Perkin-Elmer Lambda 2. Current density (J) versus voltage (V) measurement was performed by using PCE-S20 with a monochromatic light source consisting of a 150-W Xe lamp and a monochromator. For J–V measurement, fluorine-doped tin oxide (FTO, $13\Omega\text{sq}^{-2}$) conductive glass substrates were used as the photoelectrodes. The TiO_2 paste was coated on the FTO substrates using the doctor blade method, then sintered at 450°C for 45 minutes. A certain amount of Fe(II) Schiff base complex with ligand suspensions were dropped on TiO_2 coated on FTO conductive glass substrate. The substrate was dried with N_2 gas and secured against Cu_2S counter electrodes containing polysulfide electrolytes.

3. Results and discussions

Shinde et al. (V.G. Shinde 2015) reported that the XRD spectra of some transition metal complexes display that they are crystalline as well as amorphous in nature. They used a method published by Saxena et al. (N. Saxena 1993) to calculate (hkl) values of reflection. They concluded that the structure of Fe(II) Schiff base complex is a monoclinic crystal system. Fig. 3 shows the recorded XRD patterns for Fe(II) Schiff base complex.

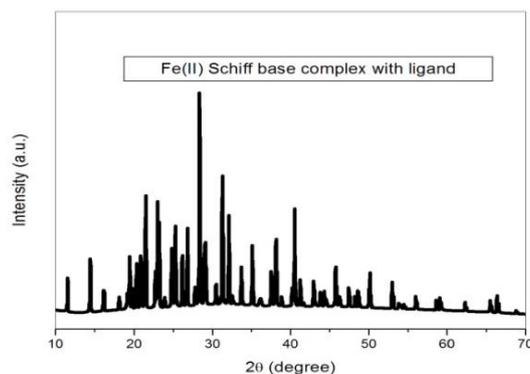


Fig. 3. XRD patterns of Fe(II) Schiff base complex.

Based on the XRD data indicated in Fig. 3, ‘d’ value for Fe(II) Schiff base complex was calculated using the Bragg’s relation given in Equation 1 to determine the structure of sample.

$$n\lambda = 2d\sin\theta \quad (1)$$

Where n is a positive integer, λ is the wavelength of the x-ray, d is the distance between lattice planes and θ is the diffraction angle.

The calculated average ‘d’ value for Fe(II) Schiff base complex is 9.75 \AA . Shinde et al. (V.G. Shinde 2015) mentioned in their study that the ‘d’ value of Fe(II) Schiff base complexes with monoclinic structure is 10.12 \AA . Thus, it can be said that our synthesized Fe(II) Schiff base complex has a monoclinic structure.

The recorded optical absorption spectra for Fe(II) Schiff base complex with ligand are demonstrated in Fig. 4. It was observed high-intensity peaks coming from the electronic transitions are located at 326 and 379 nm, respectively. The observed optical absorption bands in the UV-visible region can be associated with (a) d-d transitions due to ligand field interactions, (b) $\pi\text{-}\pi^*$ (intraligand transitions) owing to molecular orbitals positioned in the ligand and (c) charge transfer transition which is electron transition from the ligand to Fe(II) ion or from Fe(II) ion to ligand, respectively. Thus, it can be said that the band located at 326 nm corresponds to an intraligand transition while the optical band positioned at 379 nm is because of charge transfer transition.

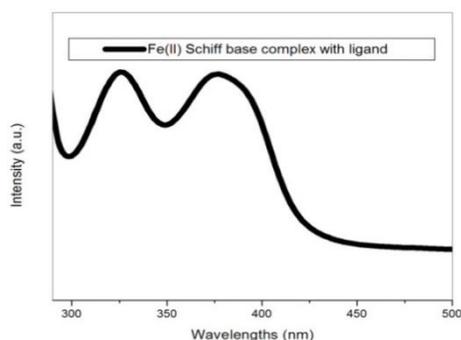


Fig. 4. The recorded optical absorption band in the UV-visible region for Fe(II) Schiff base complex.

The FT-IR spectra for ligand and Fe(II) Schiff base complex are shown in Fig. 5 (a-b).

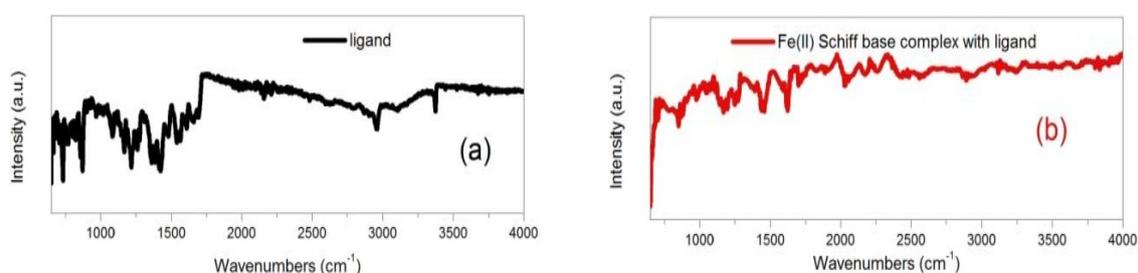


Fig. 5. The recorded FT-IR spectra for (a) ligand and (b) Fe(II) Schiff base complex.

The peaks related to $-\text{CH}_3$ group were observed at 2954 cm^{-1} in Fig. 5a. The observed spectrum at 1669 cm^{-1} can be associated with $-\text{C}-\text{O}$ vibrations. Fernandes et al. (S.A.Fernandes 2013) reported that $-\text{C}=\text{N}-$ (Azomethine) group has vibration mode around 1600 cm^{-1} . The similar peak was observed at 1604 cm^{-1} . Therefore, this peak can correspond to vibration band of the azomethine group. Moreover, the vibration bands for $-\text{C}-\text{O}$ group were observed between $1000\text{--}1200\text{ cm}^{-1}$.

As can be clearly seen in Fig. 5b, the FT-IR spectra of Fe(II) Schiff base complex with ligand are similar to the ligand spectra. Despite similarity, a shift toward higher frequencies was observed in the vibration modes of azomethine group to 1639 cm^{-1} . And also between $3100\text{--}3400\text{ cm}^{-1}$ peak was disappeared on Fe(II) Schiff base complex which was on ligand's spectrum to represent $-\text{OH}$ group. This differences affirms that the Fe(II) metal coordination with ligand.

To investigate photovoltaic properties of Fe(II) Schiff base complex with ligand, Fe(II) Schiff base complex with ligand was used as a photosensitizer on TiO_2 film in a DSSC device. Thus, the effect of Fe(II) Schiff base complex on the efficiency of DSSC device was investigated and photovoltaic parameters such as power conversion efficiency (η), open circuit voltage (V_{OC}) and short circuit current density (J_{SC}) were determined.

The recorded current density (J) versus voltage (V) spectrum for Fe(II) Schiff base complex with ligand is revealed in Fig. 6.

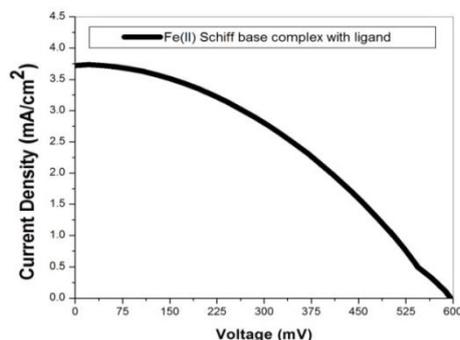


Fig. 6. The recorded J-V spectrum for Fe(II) Schiff base complex with ligand.

The obtained J_{SC} and V_{OC} value for samples is 3.75mA/cm^2 and 600 mV , respectively. The $\eta\%$ value was calculated as 0.80 using the relation is given in Ref. [19]. It is well known that $\eta\%$ value of a DSSC device can be affected by the rate of electron transport in a solar cell structure. The obtained high J_{SC} value for Fe(II) Schiff base complex with ligand shows that there is an effective injection of electrons into TiO_2 conduction band from excited state of complex dye. Thus, this leads to obtain improved conversion efficiency of Fe(II) Schiff base complex with ligand based DSSC device.

4. Conclusions

In our present study, 5 amino-2,4-dichlorophenol-3,5-ditertbutylsalicylaldehyde ligand was synthesized and we used this ligand to synthesis its-Fe(II) complex with using the wet chemical method. The structural, optical and electronic properties of Fe(II) Schiff base complex with ligand were characterized using the x-ray diffraction (XRD), optical absorption and Fourier transform- infrared (FT-IR) measurements, respectively. The structure of Fe(II) Schiff base complex with ligand was determined as monoclinic crystal system. Two absorption bands were observed in the UV-visible region. They are assigned to intraligand and charge transfer transitions, respectively.

The FT-IR spectra of Fe(II) Schiff base complex with ligand are similar to the ligand spectra. Despite similarity, a shift toward higher frequencies was observed in the vibration modes of azomethine groups. Furthermore, Fe (II) Schiff base complex was used as a photosensitizer on TiO_2 film in a DSSC device. Thus, the effect of Fe (II) Schiff base complex on the efficiency of DSSC device was investigated and photovoltaic parameters such as power conversion efficiency (η), open circuit voltage (V_{OC}) and short circuit current density (J_{SC}) were determined. The obtained J_{SC} and V_{OC} value for samples is 3.75mA/cm^2 and 600 mV , respectively. The $\eta\%$ value was calculated as 0.80 . Our result leads to obtain improved conversion efficiency of Fe(II) Schiff base complex with ligand based DSSC device.

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