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Synthesis and Characterization of Novel Schiff Base for Enhanced Dye-Sensitized Solar Cell Photo-Response Mechanism

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Abstract

The efficient photo-response mechanism is one of the key factors in the commercialization of dye-sensitized solar cells in a bid to satisfy renewable energy demands. Progress in green technology has put solar energy on the front burner as a provider of clean and affordable energy for a sustainable society. We report the synthesis of a novel Schiff base with optical transparency in the visible and near IR region of the solar spectrum that can find application in the DSSCs photo-response mechanism. The synthesized crystal exhibited features that could handle some of the shortcomings of dye-sensitized solar cells which include wide band solar spectrum absorption and capability for swift charge transfer within the photoelectrodes. The synthesized Schiff base was characterized using x-ray diffractometer, UV/Visible spectrometer, Frontier transmission infrared spectrometer and conductometer. XRD data revealed the grown crystal to have an average crystallite size of 2.08 nm with average microstrain value of about 269.43. The FT-IR recorded transmission wave ν (CO) at 1207.7 cm^{-1} while dominant wave occurred at ν1654.9 and ν1592.3 cm^{-1} relating to ν (CN) stretching and ν (NH) bending respectively were observed. The IR spectrum revealed the bonding species and a probable molecular structure of 2,6-bis(benzyloxy)pyridine. The UV/Visible spectra convoluted to maximum peak within the near IR region suggesting that 2,6-bis(benzyloxy)pyridine can absorb both the visible and near IR region while its electrical conductivity was determined to be 4.58 μS/cm. The obtained result of the present study revealed promising characteristics of a photosensitizer that can find application in the photo-response mechanism of DSSCs.

Keywords

Dye-Sensitized Solar Cell, Schiff Base, Photosensitizer, Optical Transparency, Benzil, Pyridine

1. Introduction

A promising solution to the world's current energy shortage is viewed as the sun's incident radiation reaching the earth which possesses varying wavelengths available for chemical conversion [1]. The current issues of global warming arising from biosphere degradation have motivated researchers towards viable channels of converting sun's radiation into a suitable energy source. Among renewable energy options available, photosensitizers have exhibited promising characteristics as viable future materials in harvesting and conversion of solar spectrum for third-generation solar cells. Material and medical scientists have engaged photosensitizers as suitable vehicles for chemical fuel which also is valuable for ion recognition [2]. These molecules undergo electronic transition and eventually transfer electrons or energy packs to targeted reactive species. Photosensitizers absorb light energy and chemically altar substrates in photothermal therapy, photodynamic therapy and magnetic hyperthermia in antiviral, antitubercular, anticonvulsant, antihypertensive and anticancer treatments [2] [3] [4]. In dye-sensitized solar cells (DSSCs), they function as electron vehicles in the photo-response mechanism [5]. Traditionally, photosensitizers are either organic dyes or aromatic hydrocarbons which function as the reaction catalyst as they return to the ground state after excitation in repeated routine. Currently, several modifications have been studied to optimize solar cells' output because of fossil fuel environmental pollution. Many efforts being made to verify solar cells as world's future energy are yet to gain popularity and DSSCs amongst others have promising high potential to emerge as sufficient providers of useable energy [6].

DSSCs which belong to the third-generation solar technology are reported to be cheaper, easy to fabricate and reported high theoretical efficiency [5]. However, operational realities challenge this potential in practice such as poor light harvesting efficiency, fast recombination of charges and slow electron transportation within the electrodes [1] [5]. Dye molecules employed in DSSCs possess light absorption capacity that absorbs at wavelengths > 400 nm which is not adequate, while improvement with mesoporous film of nanoparticles that retain adequate dye molecules increased adsorption capacity [1] [7]. However, nanoparticles are reported to be poor harvesters of light due to their smaller wavelength that does not scatter lights of greater wavelength. According to Hou *et al.* [7] high efficiency is observed in DSSC with plasmonic nanocomposites film as compared to conventional TiO_2 nanoparticle but plasmonic nanocomposites have complex fabrication methods and are susceptible to corrosion in practice. Ito *et al.* [8] discussed the use of bilayer electrodes to enhance wider light-harvesting, capacity of DSSCs especially at wavelengths > 700 nm but as light-harvesting is improved, these bilayer particle size reduces power output generation. Kakiage *et al.* [9] discussed the use of common organic dye for DSSCs which has an electron donor/acceptor structure linked through π-conjugated bridge. This π-conjugated bridge had a great influence on the photoelectronic property of the organic dye with the overall cell efficiency proportional to the electron injection efficiency. Kato *et al.* [10] studied DSSCs with solid electrolytes and reported a short circuit current of ~8 $mA \cdot cm^{-2}$ with an open circuit voltage of 0.6 V which is an improvement on liquid electrolytes values. DSSCs have also been researched by inclusion of nanoparticles and band alignment by quantum dots [11], solid-state electrolytes [12], electrocatalytic counter electrodes and semiconductor doping [6] to obtain enhanced performance in practice.

Accordingly, the most critical focus on achieving high efficiency in practice for DSSCs is the photo-response mechanism. The uniqueness of Schiff bases' photophysical properties is an interesting factor in considering sensitizing dyes for photo-response in DSSCs. Schiff bases are known to possess linked carbon, nitrogen double bonds and functional groups that could absorb greater bands of the solar spectrum. Abdel-Shakour *et al.* [13] opined that Schiff bases exhibited enhanced photovoltaic properties for DSSCs due to fast photo-induced electron transfers within their elemental species. The fast electron transfer was ascribed to an overlapping between HOMO and LUMO levels in the functional groups. Schiff bases find applications in disciplines ranging from medicine to biochemistry to material science to coordination chemistry [3]. They exhibit high binding qualities toward charged ions and display profound photophysical properties which can be employed in light harvesting and ion recognition.

Pyridine derived Schiff bases exhibit π-acceptor basic properties with functions as organic ligands owing to the presence of imine nitrogen [3]. In the present study, we focused on synthesis and characterization of a novel Schiff base as an efficient light harvester for the DSSC photo-response mechanism. The synthesis involved a mimicked Michael-type addition with slight modification using pyridine and benzil as raw materials. Herein, the acid-catalyzed reaction was carried out at room temperature using HCl/EtOH protocol. The produced crystal was characterized using UV/Visible spectrometer, Frontier Transmission Infra-Red spectrometer and X-ray diffraction to ascertain the structure and light absorption sensitivity.

2. Experimental

All reagents used in the present study were of analytical grade (AR). Pyridine and absolute ethanol were obtained from JHD Chemicals, benzil and HCl were purchased from Molech Chemicals while double distilled water was collected in our laboratory.

2.1. Preparation of Schiff Base

The acid-catalyzed reaction of pyridine and benzil in the $HCl/EtOH/H_2O$ system was carried out on mild heating and stirring for 330 mins. The approach involved equal molar solutions of pyridine and benzil. For a representative example, 2.0 mmol benzil and 2.0 mmol pyridine were added in a mixture of 100 mL of anhydrous EtOH which was followed by 10 mL of HCl [14]. The reaction mixture was stirred at room temperature for 6 h with mild heating. The resulting mixture was allowed to cool and stored to precipitate which was washed in excess absolute acetone. The resulting crystal was further purified by mild heating with absolute ethanol and allowed to stand. The resultant crystal was stored for further characterization and the molecular structure of the synthesized Schiff base is shown in **Figure 1**.

2.2. Schiff Base Characterization

The UV/Visible spectra were measured with Philips PU 8700 UV/VIS spectrophotometer and electrical conductivity was measured using Jenway conductivity meter. IR spectra were recorded on the FT-IR Agilent Technology Microlab spectrophotometer by ATR technique. The x-ray diffraction spectroscopy (XRD) measurements were performed using Rigaku-binary Mini flex 600 instrument equipped with a monochromatic $\mathrm{CuK}_1\alpha$ (1.5406) x-ray source at step size of 0.01.

3. Results and Discussions

3.1. Optical Transmission Studies

The photo-response mechanism DSSCs amongst other factors is paramount in evaluating the efficiency of DSSC in practice. The sensitizing molecule should be able to possess good absorption capacity in UV/Visible and near IR regions. Accordingly, organic crystal exhibits nonlinear optical characteristics which make the molecular electronic structure adhere strongly to electric fields of applied electromagnetic waves. Regarding Schiff base usage in optical applications, nonlinear optical activity is of utmost importance in which optical frequency and transparency range are considered [15]. **Figure 2** shows the recorded optical transparency of the Schiff base which was scanned in the range between 450 - 850 nm

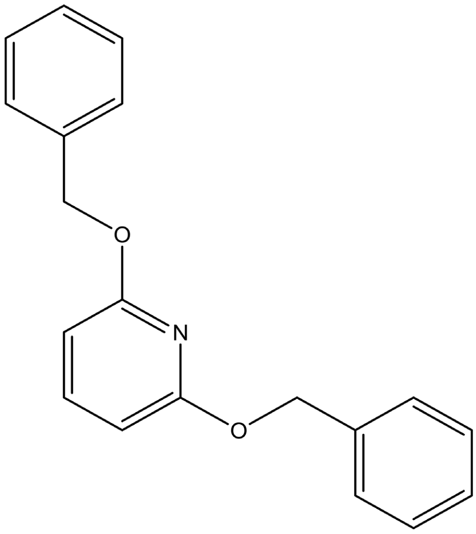

Figure 1. Molecular structure of 2,6-bis(benzyloxy)pyridine.

using PU 8700 UV/VIS spectrometer. As observed from the plot, the crystal exhibited transparency in the visible region with a maximum absorbance at 670 nm but increasing transparency was observed within near IR region. The maximum recorded transparency was recorded at 850 nm which falls in the near IR region where more than 40% of the solar spectrum irradiance is absorbed [1]. This reveals that the Schiff base is a medium for a fine optical transmission of signals beyond the visible into the near IR region. The recorded cut-off transparent value was found to be 437 nm which required rising transmission window observed in the visible region. Electrical conductivity of the synthesized Schiff base was determined to be 4.58 μS·cm^{-1} indicating a large amount of ionic charge on the Schiff base molecular structure. EC of an electrolyte reveals the speed at which charged ions are attracted to the opposite ion [16]. This is necessary for fast electron injection rate and reduces the rate of charge recombination which mitigates DSSCs efficiency in practice. This indicates that the Schiff base can be used effectively for optical applications in the fabrication DSSCs considering the wider band absorbance of the solar spectrum and swift photo-response mechanism.

3.2. FT-IR Analysis

The FT-IR spectra scanned between 4000 - 6500 cm^{-1} revealed the characteristic of surface functional bonds of the Schiff base which is recorded in **Figure 3**. A study of **Figure 3** reveals strong spectra of benzene derivative transmission waves at v715.6 cm^{-1}, v793.9 cm^{-1} and v872.2 cm^{-1}, and reveals the presence of aromatic rings. The spectrum shows transmissions of dominant wave number at v1654.9 and v1592.3 cm^{-1} which points to C=N stretching of imine and N-H

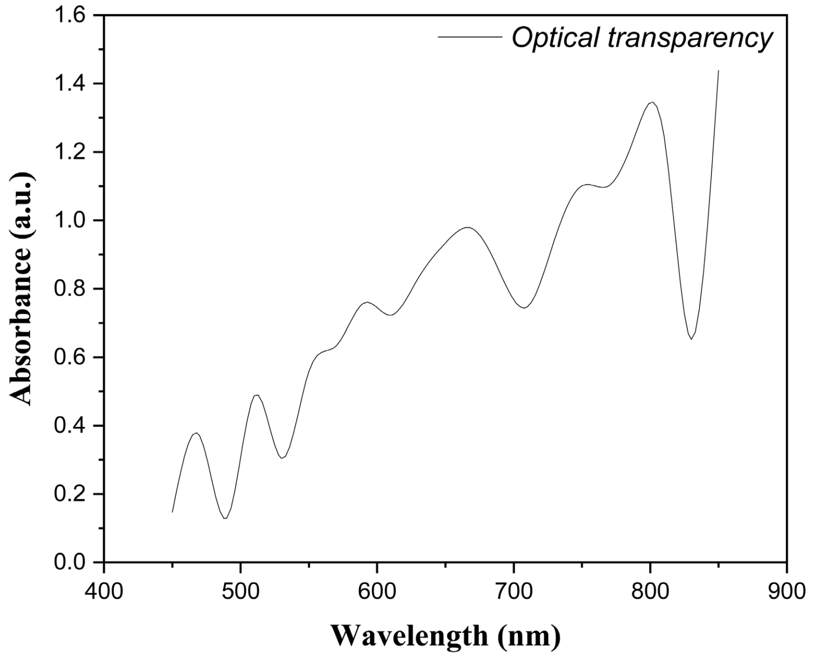

Figure 2. Recorded optical transmission of the synthesized Schiff base.

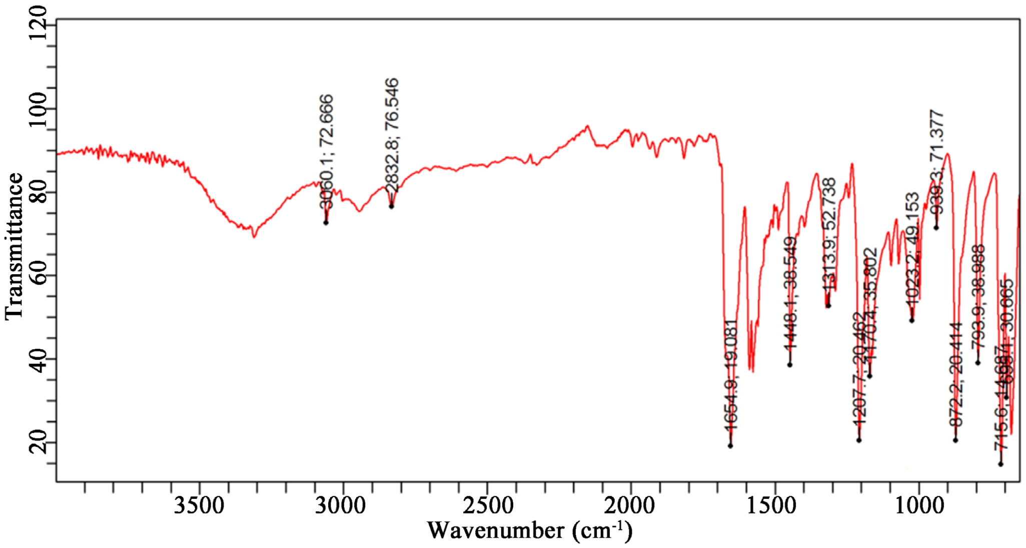

Figure 3. Scanned IR spectra of the synthesized Schiff base.

bending respectively, a feature of Schiff bases [16]. The strong presence of C-O stretching at transmission wave ν1207.7 cm^{-1} and ν1170.4 cm^{-1} signifies the splitting of the benzil structure as observed from FT-IR analysis. The enhanced photo-response mechanism of DSSCs should incorporate anchoring groups such as carboxylic group that enables good attachment of the substrate on photoelectrode surface as expected for fast charge transportation. The presence of medium wave transmission at ν1588.3 cm^{-1} and ν1594.7 cm^{-1} indicates C=C stretching of cyclic alkene analogous to benzil moiety [4]. The weak vibration of C-N stretching regarding aromatic amines was recorded at transmission wave ν1313.9 cm^{-1}, a recognition of withdrawing resonance towards C-O bond. Undoubtedly, the disappearance of transmission wave at ν1666 - 1760 cm^{-1} signifies that C=O group in the benzil molecule was silent, suggesting a splitting. The benzil moiety is attached to the pyridine molecule via the C-O group as wave transmissions at ν1207.7 cm^{-1} and ν1170.4 cm^{-1} are predominant in the spectra. The weak broad band of O-H is observed at 2853.2 - 2985.6 cm^{-1} indicating a hydrogen bond interaction between the species in space. The IR spectrum of the Schiff base as shown in **Figure 3** revealed strong intensity absorption band at ν1654.9 cm^{-1} assigned to C-N stretching mode.

3.3. X-Ray Diffraction

X-ray diffraction study of the Schiff base was performed by using a Rigaku-binary Mini flex 600 diffractometer with Cu Kα (λ = 1.5406 Å). **Figure 4** shows the diffractogram of 2,6-bis(benzyloxy)pyridine crystal as recorded which was scanned over a range between 6˚ - 70˚. The observed peaks existed at approximately 5 angles with the information obtained recorded in **Table 1**. Hossein Alaei *et al.* [17] stated that peak intensity is directly dependent on the array of specific atoms contained within the crystal structure. Perusal of **Figure 4** depicts broadened peak intensity which suggests structural imperfection, as of

Table 1. The calculated data of the diffractogram of 2,6-bis(benzyloxy)pyridine showing Microstrain, Crystallite size and Dislocation density as calculated using FWHM.

2θ (˚)	FWHM (˚)	Height	Integral Breadth	Microstrain ($\varepsilon \times 10^{-3}$)	Crystallite Size (nm)	Dislocation density (1/nm^2)	d-spacing (Å)
17.83965	26.96386	26.96386	42.4832	749.6131	0.29	11.49715933	4.968003602
36.00477	5.09543	5.09543	2.5020	68.4165	1.62	0.380502502	2.492423856
41.92782	17.51351	17.51351	15.6794	199.4488	0.48	4.333657846	2.153000096
54.33985	4.0624	4.0624	1.4455	34.5348	2.17	0.211643389	1.686920064
65.48908	43.49757	43.49757	32.7099	295.1296	0.21	21.68754758	1.424122917

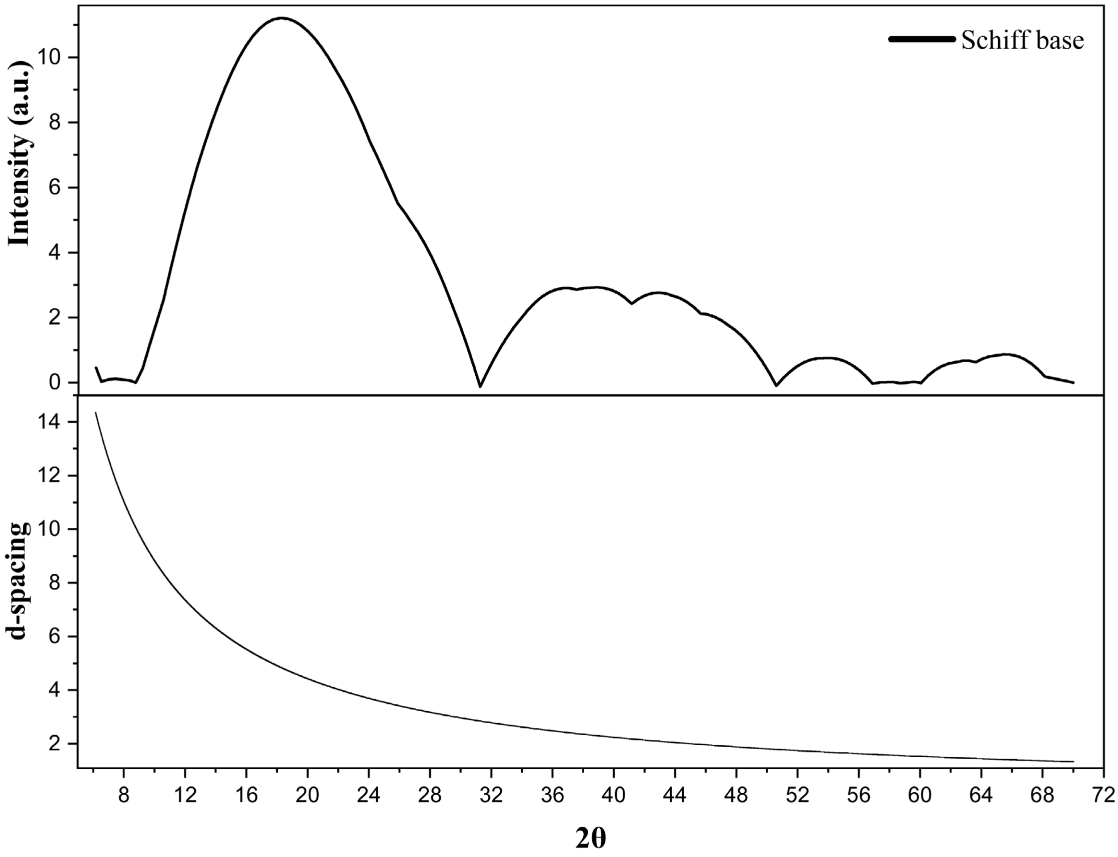

Figure 4. Scanned diffractogram of the synthesized Schiff base showing d-spacing plot.

atoms arranged in a scattered pattern [18]. The diffractogram did not reveal any sharp or visible peak indicating an amorphous nature of the Schiff base. This might suggest that the unit cells do not possess the ordered repetition of atoms hence, we can conclude that the arrangement of atoms in the synthesized Schiff base is random. The crystallite size was calculated using the Scherrer equation:

$$D(\text{nm}) = \frac{K\lambda}{\beta \cos\theta} \tag{1}$$

where k is the Scherrer constant at 0.89, we assumed the crystallite shape to be spherical cubic. λ is the monochromic wavelength (1.5406), β is the FWHM and

θ is the angle of detector position from incident rays.

The calculated average crystallite size was 2.08 nm while values of the d-spacing which depends only on the shape of each unit cell were calculated for observed peak positions and were recorded in **Table 1**. Accordingly, the lack of clear crystalline peak might be the agglomerate formation of small spherulites shaped molecules in scattered formation as contained in the crystal framework. The amorphous percentage index was determined to be 65.81% which was calculated using Equation (2).

$$\% \text{ Amorphous}\left(X_p\right) = \frac{A_p}{A_p + A_d} \tag{2}$$

where A_p is area under the peaks and A_d is area under the diffraction patterns.

As shown in **Table 1**, the d-spacing (Å) decreased with decrease in observed peak volume and increasing angle of detector position from incident rays ($2\mathring{\theta}$). The calculated average microstrain ($\varepsilon \times 10^{-3}$) value for 2,6-bis(benzyloxy)pyridine is 269.4286. This suggests that the crystal accommodates itself in hexagonal family with centrosymmetric space group which is not consistent [19].

4. Conclusion

The present investigation synthesized and characterized novel Schiff bases which could be useful in photo-response mechanism of DSSCs. Synthesis of the grown crystal was achieved in high yields starting from the condensation reaction of pyridine to acid-catalyzed splitting of the benzil molecule. Characterization under UV/Visible studies showed that the grown crystal is transparent within visible and near infrared regions suggesting that it can be utilized for nonlinear optical applications. The observed value of electrical conductivity of the crystal reveals large charged molecular structure that can enhance photo-response mechanism and optical quality of DSSCs. The data recorded from IR spectra revealed vibrations of aromatic transmission and the primary amine (NH) is observed. The absence of transmission wave vibration of C=O groups and C-O transmission wave presence in the IR spectra confirms the splitting of benzil and formation of proposed Schiff base framework. The x-ray diffractogram revealed the crystal to be amorphous with the calculated average dislocation density at 7.622 $n^{-1}\cdot m^{-2}$ suggesting a hexagonal family arrangement but in a random manner with centrosymmetric space group. The synthesized Schiff base in this study possesses these qualities and should be viewed effectively as a photo sensitizer in the photo-response mechanism for DSSCs.

Author Contributions

All authors contributed individually to this work.

Sample Availability

Raw data of samples and synthesized compound sample of the Schiff base is available from the corresponding author at oraphael@atbu.edu.ng.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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