

Synthesis and Characterization of 4-phenyldiazenynaphthalen-1-ol as a Sensitizer for Dye-Sensitized Solar Cells (DSSCs)

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Abstract— The focus of this research is to synthesize and characterize 4-phenyldiazenynaphthalen-1-ol and analyse its optical properties as a sensitizer in Dye-Sensitized Solar Cells (DSSCs). The compound was synthesized and purified by recrystallization. The compound was characterized by an electrothermal melting point apparatus, TLC, UV-Vis Spectroscopy, and Fourier Transform Infrared Spectrometry. The results of the instrumental analysis of the synthesized compound was compared to that of the industrial standard, inorganic ruthenizer 535-bisTBA (N719) dye. The optical band gap of 4-phenyldiazenynaphthalen-1-ol was calculated as 1.95 eV as compared to the literature value of 1.91 eV of the standard N719 dye. The IR spectrum of the compound also showed an indication for N=N stretch for azo bond at 1465 cm^{-1} . Comparing IR spectra of 4-phenyldiazenynaphthalen-1-ol to that of the standard N719 dye, the presence of OH group strong signal around 3326 cm^{-1} is necessary as a feature for dye sensitizers having good anchorage to the TiO_2 surface for better device performance.

Keywords— Azo dyes, DSSC, sensitizers, recrystallization, characterization, solar energy

I. INTRODUCTION

Dyes can be put in various classes and azo dyes are certainly one of the most important classes. Nearly every commercial product, including food, textiles, pigments, and paints, uses dyes. Azo dyes make for almost half of the dyes used in industry. The typical structure of azo dyes is $\text{Ar-N=N-Ar}'$, where Ar and Ar' are two aromatic groups^[1]. Various types of synthetic dyes, including azo dyes, have emerged in textiles [2], leather, aluminum sheets, inkjet printers, paper, and optical equipment^[3]. Energy is an indispensable commodity for economic growth and environmental sustainability. Access to electricity in the West African region varies from 20 % in countries like Sierra Leone, Liberia, Burkina Faso and Niger to 50 % and more in Senegal and more than 70 % in Ghana^[4]

In Ghana and other parts of the African continent, there are major breaches in knowledge and data regarding the use of organic and inorganic materials as solar cells to trap energy from the sun to produce electricity for private and industrial usage. Solar energy is a substitute boundless energy source that can be utilized for electricity production.

The study was focused on the objectives below:

- Synthesize 4-phenyldiazenynaphthalen-1-ol
- Purify the synthesized compound by recrystallization.
- Characterize the compound using electronic melting point apparatus, Ultraviolet-Visible (UV-Vis) spectroscopy and Fourier Transform Infrared (FTIR) spectroscopy.

d. Compare results of characterizations to that of the standard inorganic ruthenizer 535-bisTBA (N719) dye.

Part I of the research comprises a short introduction to the study, Part II accounts for review work that give both theoretical and empirical methods for the study. Part III contains the research materials and methodology that defined the (a) materials, (b) methodology, and (c) instrumentation. The results and discussion of the study are provided in Part IV. Part V and VI detail the conclusion and acknowledgment.

II. RELATED WORK

In 1856 W. H. Perkin discovered Mauveine [5], the first synthetic organic dye. Since then literally thousands of synthetic dyes have been prepared; for example azobenzothiazolyl dyes^[6] and acridine dyes [7]. Unsaturation and conjugation in dyes are essential for light absorption. Chromophoric regions in azo dyes are responsible for absorption and occur normally in a wavelength from 250 nm to 1000 nm^[8]. Electrons are firmly bonded, they will respond and absorb light energy of short wavelength and high frequency. As a result of this the electrons become more mobile with accumulation of conjugated centres of unsaturation in the molecule. Due to their advantages over inorganic solar cells, such as affordability, environmental friendliness, flexibility, and lightness, organic solar cells (OSCs) have emerged as a significant contender in recent years. Also, in solar energy production, excitation in an organic semiconductor can be considered as a tightly coulombically bound electron-hole

pair. It can be described as a mobile excited state due to the electrical neutrality and substantial binding energy between the hole and the electron [9]. Grätzel and his co-workers' research showed that organic substances like azo dyes combine the functions of charge (hole) transfer and light absorption in a single material to produce electrical energy. Due to this fundamental difference, the process of converting photons into electrical energy is different in IPV cells. In this research, we will discuss solar cells whose excitation is generated by the absorption of light (hereafter referred to as organic solar cells).

III. METHODOLOGY

Materials, Reagents and Instrumentation

The following materials and apparatus were used to perform the work: Filter papers, TLC plates, UV-Vis Spectrophotometer, Melting point glass tubes, Electrothermal melting point apparatus, FT-IR (IR Spectrometer), 2 Beakers (250ml), 2 Boiling tubes, Buchner funnel, Aluminum foil, Stirring rod-1, 2 Conical flasks (250ml), Volumetric flask (500ml, 250ml, 100ml), Heating plate with stirrer, ice bath and thermometer Ethanol (96%, Inner Mongolia Pulis chemicals), methanol (99.85%), ethyl acetate(99.5%), acetone(99.5%), salicylic acid (99.5%), dichloromethane (DCM) (99.8%), aniline (99.9%), hydrochloric acid (98%), tetraoxosulphate (VI) acid (98%), 1-naphthol (99%), sodium nitrite (NaNO_2) (97%), sodium acetate (99%), sodium chloride(99%), (all from Fisher Scientific Company, USA). All solvents used were of the analytical grade. UV-Vis Spectrophotometer (Shimadzu Scientific Instruments Inc, Maryland, USA), and Electro thermal melting point apparatus (LabX in Midland, ON, Canada) and FT-IR Spectrometer (Bruker, Massachusetts, United States) were used for analysis. An ice bath was used to provide a temperature range of 0-5°C.

Synthesis

Aniline (4.57 g, 49 mmol) was dissolved in 15 mL of 50% H_2SO_4 which was cooled to reach a temperature range within 0–5 °C. A solution of NaNO_2 (4.0 g, 58 mmol in 15 mL of water) which has been cooled was added dropwise within a temperature range of 0-5 °C to the resulting mixture. A diazonium salt was produced after stirring the mixture for about 30minutes. A previously prepared solution of 1-naphthol (7.2 g, 50 mmol of 1-naphthol in 60 mL of 20 % NaOH) was cooled below 5 °C in alkaline medium and added slowly in drops to the diazonium salt solution. An azo dye was formed which was sticky in nature. Cold water was added dropwise to reduce the sticky mass formation of azo dyes.

The reaction mixture was thoroughly mixed by stirring for about 3 hours and kept at Room Temperature for an hour. Sodium acetate was used to adjust the pH to 7-7.5 range. The dye that was precipitated out of the mixture was filtered. The filtrate was further washed with cold water. It was further recrystallized from an acetone and alcohol ratio mixture of 1:1 and dried in ordinary air resulting in a solid compound.

Thin layer Chromatography

Thin layer Chromatography was used to quantitatively isolate the pure component from several impurities in the compound and to qualitatively find out the number of different compounds present in a synthesized compound. It was also an effective means of testing the purity of the compounds that were synthesized. Plates of size 5cm x10cm were used for preparative TLC and 20cm x 20cm for analytical TLC. The solvent for developing the TLC plates re Acetone/ Petroleum ether (1:1). The solvent was allowed to saturate the developing tank for at least 20-30minutes before developing the TLC plates. After development, the plates were dried and first viewed under a UV lamp before being exposed to the iodine vapour



DYE 1

Figure 1: Tlc Of 4-Phenyldiazenyl naphthalen-1-ol

IV. RESULTS AND DISCUSSION

Table 1: Codes and physical properties of purified dyes.

Code Name	Colour	Nature	Melting point
M1 DYE	Reddish-Brown	Powdery	202-205 °C
N719 dye	Brownish-red	Crystalline powder	250 - 260 °C

The nature of M1 dye was powdery with a reddish-brown colour. The melting point of the dye was between 202-205 °C. As compared to the N719 dye, the colour of the inorganic industrial dye has a brownish-red colour with a crystalline powdery nature. The melting point of the standard dye was measured to be 250-260 °C.

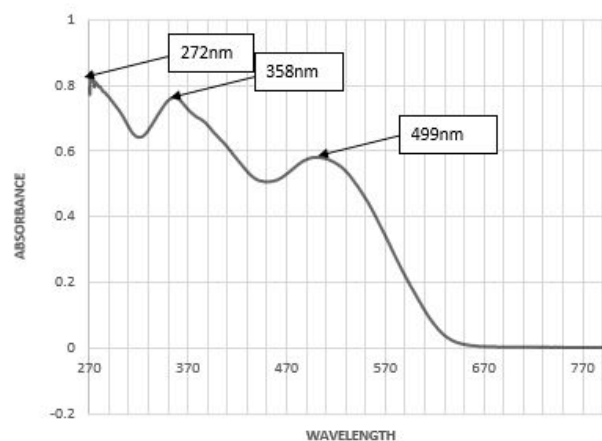


Figure 2 UV-Vis Absorption spectrum of 4-Phenyldiazenyl naphthalen-1-ol

The spectrum of **M1** (Figure 2) shows an intense absorption in the UV region from 270 nm and 650 nm, with a maximum absorption peaks occurring at 272nm, 358nm and 499nm. This absorption 272nm is attributed to a $\pi - \pi^*$ molecular electronic transition. A conjugated pi-electron systems in an aromatic ring act as chromophores and absorb light. The characteristic spectrum of M1 dye, consisting of absorptions in three distinct regions; in the near ultraviolet and in the visible regions suggests Orbital mixing splits these two energy states (358 and 499), producing a high-energy state with high oscillator strength, giving rise to the Q-band in the visible range (490-650 nm). The Q-band is explained by $\pi - \pi^*$ electron transitions. In the Gouterman model, these bands are represented as electronic transitions from two HOMO orbitals (highest occupied molecular orbitals) $a_{1u}(\pi)$ and $a_{2u}(\pi)$ to two LUMO orbitals (lowest unoccupied molecular orbitals). (π^*) orbital [10]. Four Q-bands with weak intensity are produced by a weak transition from the ground state S_0 to the first excited state S_1 [11].

Based on this observation, **M1 dye** should harvest a lot of incident photons as possible in the visible region and hence are possible sensitizer candidates for DSSCs application

Optical Band gap

Table 2. Maximum absorption peaks (λ_{max}), onset of absorption from the longest wavelength absorption edges (λ_{onset}) and calculated optical band gap (E_g) for M1 dye and N719 dye.

Compound	λ_{max} (nm)	λ_{onset} (nm)	E_g (eV)
M1 DYE	272,358,499	635	1.95
N719 DYE	313,393,533	750	1.65

The optical band gaps (E_g) of **M1 DYE** is 1.95 eV and **N719 DYE** is 1.65 eV, in correspond to energy in the visible region. The smaller the E_g value of a molecule, the greater the number of photons they can harvested in the visible region and the better the efficiency of the device. M1 has a lower E_g value than that of the semiconductor (TiO_2 , 3.2 eV) [12]. Therefore, based on their E_g values, **M1** is expected to absorb more photon. The small E_g of **M1** suggests that the distances between their HOMO and LUMO levels is such that the energy in the visible region is enough to cause electron promotion from their valence band into their conduction band.

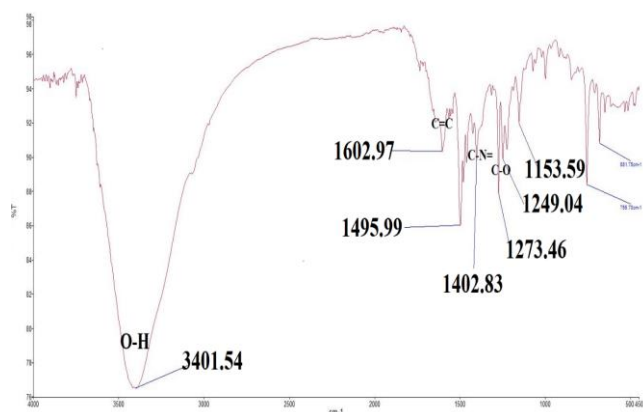


Figure 3 IR spectrum Of 4-Phenyldiazeylnaphthalen-1-ol

Figure 3. depicts the IR spectrum of **DYE 1** and displays characteristic frequency regions of the dye. There was an O-H stretch vibration ranged from 3600 cm^{-1} to 3000 cm^{-1} . The spectrum below shows an O-H stretch vibration of R-OH with a high peak at 3401 cm^{-1} and a C=C stretch of alkenes at 1602 cm^{-1} . Again, a N=N stretch for azo bond was detected at 1495 cm^{-1} . Also, a C-N= bend vibration of amines occurs at 1402 cm^{-1} and C-O stretch for an ester group occurs at 1273 cm^{-1} . The peaks around 756 cm^{-1} and 681 cm^{-1} indicate aromatic regions in the compound which are meta disubstituted aromatic compound.

V. CONCLUSION

The compound synthesized and purified was characterized by melting point apparatus, UV-Vis Spectroscopy and FTIR Spectroscopy. The chemical structure of **M1** was elucidated as 4-phenyldiazeylnaphthalen-1-ol respectively. The optical band gaps (E_g) of 4-phenyldiazeylnaphthalen-1-ol is 1.95 eV which corresponds to energy in the visible region. It was observed that in terms of broader absorptions in the visible region (350 – 800 nm), **M1**, compares closely to the standard **N719** dye. Based on this observation 4-phenyldiazeylnaphthalen-1-ol should harvest a lot of incident photons as possible in the visible region and hence are possible sensitizer candidates for DSSCs application. In all, this work demonstrates that synthetic 4 phenyldiazeylnaphthalen-1-ol is promising possible sensitizers for DSSCs.

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