



Enhancing the Efficiency of Metal Free Based Dye Sensitized Solar Cell from Benzothiazol-2-Yl)Diazenyl]Benzoic Acid

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ABSTRACT

The scientific community's collective efforts over the last 20 years have not only pushed efficiencies higher, but have also produced various novel methods of producing robust and durable DSSC cells at a reasonable cost with good conversion efficiencies. This work centered on enhancing the efficiency of metal free based dye sensitized solar cells from benzothiazol-2-yl)diazenyl]benzoic acid. Two sensitizers A23 and A24 were synthesized and characterized using analytical schemes such as the melting points, FT-IR, GC-MS and NMR spectroscopy to elucidate their structures. The vibrational frequency obtained for the synthesized dyes shows the characteristics absorption peaks due to stretching frequency of the NH-group in the region $3421.7-3459\text{ cm}^{-1}$. The IR spectra of the prepared azo dye also showed an absorption peak in the region $1505.8-1528.2\text{ cm}^{-1}$ attributed to azo chromophoric group (N=N), also the GC-MS analysis dyes showed molecular ion peaks $m/z\ 328.3$ which is consistent with the molecular formula of the dyes. The ^1H and ^{13}C - NMR spectra for the synthesized dye showed eight signals with a highly deshielded signal at 10.39 ppm (1H, singlet) which is attributed to the presence of the OH of the carboxylic group, 7.73 – 8.27 ppm due to the presence of amino (-NH₂) protons. Two signals were observed for two pairs of aromatic proton in the (6.84 – 7.81) ppm range with a coupling constant of 8 – 12 Hz. Also a distinct signal was observed upfield at 3.06 ppm due to the presence of methyl (CH₃) proton. The ^{13}C -NMR spectrum of the Dyes showed the signal at 162.26 ppm for the carbon atom in the COOH group. The photovoltaic parameter of the fabricated cells were characterized via (open circuit voltage (V_{oc}), short circuit current density (J_{sc}), photoelectric conversion efficiencies (η) of the DSSC with active area of 1.0 cm^2 were observed and the comparative results are summarized in figure 1.0 and 2. The open circuit voltage (V_{oc}), and short circuit Current (J_{sc}) of the solar cells were measured under 100 mW/cm^2 at (AM 1.5G solar Condition) and the conversion efficiency of the cells span from 3.86-4.34%. Dye A24 photo-sensitizer demonstrated the higher solar conversion efficiency of 4.34% due to the stronger synergetic effect of D- π -A structural configuration.

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INTRODUCTION

The demand of energy has dramatically increased since the start of the

industrial revolution, in which the transformation of heat into motion began to be applied. This increase is result not only of industrial

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development but also of population growth (Jake, 2011). Nowadays, the majority of the energy sources are non-renewable, such as fossil fuels, coal, oil and natural gas, which provide over 80 % of our energy-plus uranium (Robson et al., 2011). These sources are contaminating, dangerous and produce a strong impact on the environment especially the climate; hence, the world is in search of alternative renewable sources of energy. This includes solar, wind and wave energy, biomass (wood or crops such as sugar), geothermal energy, and hydro power. These alternative sources are fast developing all over the world Chen *et al.*, (2009). Amongst the renewable energy sources, solar energy is one of the most promising. Thus, Ruthenium complex is one of the most effective light harvesting sensitizers reported in DSSCs with an efficiency of 11.5 % (Aghazada *et al.*, 2016), however, the drawbacks of these ruthenium sensitizers are complicated procedure, limited source, high cost, environmentally unsafe, and carcinogenic (Arini *et al.*, 2015). Organic dyes are really promising alternative to the noble ruthenium complexes sensitizers. Indeed, they exhibit many advantages, such as easy tailoring of the structure and properties, higher molar extinction coefficients and less complicated synthesis and purification step with respect to the metal-based ones (Kuang *et al.*, 2007). In addition, concerning cost and environmental issues, they are superior to metal complexes since they are cheaper and without problem of limited source. To date, as a consequence of a lot of work appeared in the literature aimed at the optimization of the design of metal-free dyes, organic sensitizers with higher efficiencies are known (Wang *et al.*, 2005a). Over the years, tremendous efforts have been made to explore natural and organic dye as DSSCs sensitizer due to being nontoxic and environmentally friendly, low cost, and easy modification for functionalization (Bose *et al.*, 2015). However, many efforts have been made to change the different parts of organic dyes for optimizing DSSC performance. Up to now, hundreds of organic dyes, including coumarin, indoline, triarylamine, carbazole, squaraine, perylene, oligothiophene, and natural dyes have

been studied as sensitizers for DSSCs and have showed impressive efficiencies (Campbell *et al.*, 2007). The application of two FTO in a conventional sandwich-type DSSC has often become a major predicament in reducing the total material cost in the fabrication of DSSC. This is primarily because the cost of FTO substrate accounts for approximately 60% of the total materials cost in DSSC (Ellyse *et al.*, 2021). Thus, an alternative configuration so-called "monolithic" is often sought-after to replace the conventional sandwich structure (Seigo and Kaoru, 2012). (Gupta, 2009). Dyes are aromatic compounds that absorb light of wavelength ranging between 700 – 350 nm. The colors of these dyes are originated by absorbing the light in the visible region of the spectrum due to the delocalization of *n*- and π -electrons throughout their structures (Aziz *et al.*, 2009). The use of heterocyclic diazo components is now becoming a prime area of research by dye chemist and remarkable successes have been recorded. The colour range of these dyes extends to blue and blue green, hitherto the exclusive domain of the anthraquinones (Jitender *et al.*, 2010). Although hydroxyl groups are known to be electron donors, they are less efficient in arylazo phenol versus arylazo naphthol structure. This is because the naphthol system does not lose full aromatization when electron delocalization occurs Chen and Ren, (2018). Therefore 3-amino-2-methylbenzoic acid and 3, 5-diaminobenzoic acid couplers generally give dyes that are more bathochromic than phenol-based dyes. The two main thrusts of dyestuffs research have been improved technical excellence and greater cost effectiveness. One long-term aim had been to combine the brightness and high fastness properties of anthraquinone dyes with the strength and economy of azo dyes, (Maradiya and Patel, 2002a).

MATERIALS AND METHODS

Materials

Analytical grade reagents and chemicals from Sigma Aldrich were used for this research work, These include; 4-hydroxyaniline, p-phenylenediamine, 4-methylaniline, N,N-

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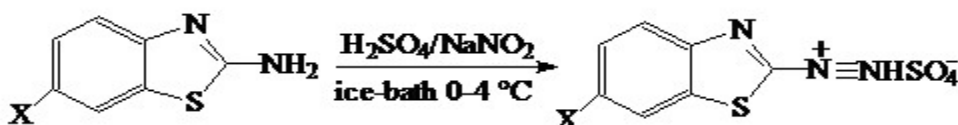
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dimethylbenzene-1,4-diamine, N,N-diethylbenzene-1,4-diamine, dimethylformamide (DMF), sodium nitrite, concentrated sulphuric acid, concentrated hydrochloric acid, acetonitrile, iodine, potassium iodide, absolute ethanol, sodium hydroxide, sodium carbonate, tetrahydrofuran, n-hexane, ethylacetate and ethanol, Gallen-Kemp melting point apparatus, Agilent Uv-visible spectrophotometer, Agilent Fourier transform infra-red spectrophotometer, Agilent GC-MS and ^1H and ^{13}C -NMR spectrometer. These chemicals and reagents were used without further purification

Methods

Diazotizations of 2-aminobenzothiazole Intermediates

A solution of 2-aminobenzothiazole derivatives (0.054 mole) in H_2SO_4 (12 ml) was cooled to 0- 4 °C. To this solution was added a cold solution of sodium nitrite (0.54 mole) drop wise with constant stirring. When the addition was complete, the resultant reaction mixture was left in ice-bath for 1hr. It was used as such for further reaction as shown in the reaction below: (Patel *et al.*, 2003)



2-aminobenzothiazole

diazonium salt of 2-aminobenzothiazole

where X is OH, NH_2

Scheme 1.0: Diazotization of 2-aminobenzothiazole

Coupling Reaction

The coupling component, 3-amino-2-methylbenzoic acid and 3, 5-diaminobenzoic acid couplers was dissolved separately in acetic acid and cooled to 0°C by adding ice. The diazonium solution of the intermediate 1 and 2 that was prepared was then added for 30-40min with vigorous stirring (Maradiya and Patel, 2010). The resulting product was collected by filtration, wash with water and dried. The crude product was purified by recrystallizing it from ethanol and DMF of ratio 9:1.

Characterization of the Intermediates and the Dyes

The physicochemical properties of the intermediates and synthesized dyes were carried out and spectroscopic properties such as FT-IR, GC-MS and NMR

TiO_2 Electrode Preparation and Device Preparation

A monolithic-type DSSC typically consists of a photo-electrode layer, spacer, and

counter electrode that are stacked on a single TCO substrate. The photo-anodes composed of nano-crystalline TiO_2 and counter electrode were prepared using (Wang *et al.*, 2003). Fluorene doped tin oxide (FTO) coated glass (2.2 mm thickness, sheet resistance of 8 Ω/cm^2 , TEC Pilkington) were washed with detergent, water, acetone and ethanol sequentially. After this FTO glass plates were immersed into a 40 mM aqueous TiCl_4 solution at 70 °C for 30 min and washed with water and ethanol. Thin layer of TiO_2 (Solaronix, Ti-Nanoxide D/SP) was deposited (active area, 1.0 cm^2) on transparent conducting glass by screen printing. After drying the electrodes at 120 °C for 6 min, scattering layer TiO_2 particles (Solaronix, Ti-Nanoxide D/SP) were printed.

Photo-Electrochemical Measurement

Photocurrent-voltage characteristics of DSSCs were measured using a Keithly 2400 source meter under illumination of AM 1.5 G solar light from solar simulator (SOL3 A, Oriel)

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equipped with a 450 W xenon lamp (91160. Oriel). The incident light intensity was calibrated using a reference Si solar cell (Newport

Oriel.91150 V) to set 1 Sun (100 mW/cm²). Finally, the J-V curves were recorded by connecting the cells to a Keithley Source Meter.

RESULT AND DISCUSSION

Table 1a: Structures with IUPAC Names of the Synthesized Dyes

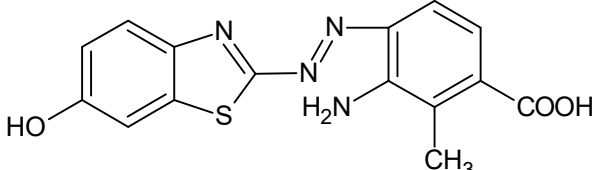
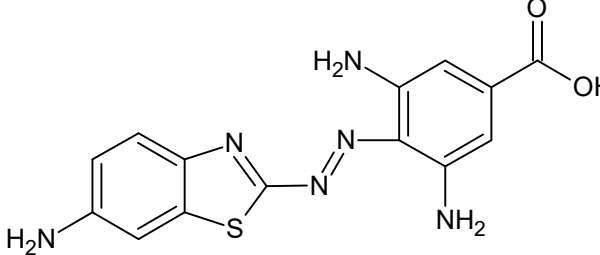
Dyes No	IUPAC Name	Structures of the Synthesized Dyes
A23	3-amino-4-[(E)-(6-hydroxy-1,3-benzothiazol-2-yl)diazenyl]-2-methylbenzoic acid	
A24	3,5-diamino-4-[(E)-(6-amino-1,3-benzothiazol-2-yl)diazenyl]benzoic acid	

Table 1b: Physical Properties of the Synthesized Dyes

Dye no	Molecular formula	Theoretical Molecular Weight (g/mol)	Melting point	Yield (%)	Colour of the crystals
A23	C ₁₄ H ₁₂ N ₆ O ₂ S	328.3	164-165	77	Red brown
A24	C ₁₅ H ₁₂ N ₄ O ₃ S	328.3	143-144	68	Brown

Table 2.0: Spectroscopic properties of the synthesized dyes

Dyes	FT-IR (cm ⁻¹)	GC-MS Mass (m/z)	¹ H and ¹³ C-NMR (400 MHz, DMSO-d ₆)
A23	3421.7, 3267.3 (N-H str.), 1625.1, 1662.4, 1695.9 (C=N), 1505.8, 1539.4 (N=N str.), 797.7, 752.9 (C-S).	57, 207, 253, 119, 91, 328.3	10.37(S, 1H, COOH), 8.25(S, 1H), 8.08(S, 4H, 2NH ₂), 7.71(S, 2H, NH ₂), 7.78(d, 1H, J=12 Hz), 7.71(S, 1H), 6.82(d, 1H, J=8.0 Hz); 166.31, 151.38, 149.27, 148.79, 145.27, 141.85, 139.27, 138.79, 132.09, 130.19, 130.19, 127.50, 121.49, 117.98, 117.01.

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Dyes	FT-IR (cm ⁻¹)	GC-MS Mass (m/z)	¹ H and ¹³ C-NMR (400 MHz, DMSO-d ₆)
A24	3459.0, 3309.9 (OH, N-H str.), 2922.2 (C-H str.), 1695.9, 1666.1, 1606.5 (C=N str.), 1528.2 (N=N str.), 745.5 (C-S).	64, 95.9, 195.9, 225.1, 328.3	10.38(S, 1H, COOH), 10.08(S, 1H, OH), 8.31(S,2H, NH ₂), 8.23(S, 1H), 8.13(S, 1H), 7.8(d, 1H, J=8Hz), 7.11(d, 1H, J=8Hz), 2.24(S, 3H, CH ₃); 168.30, 142.45, 141.10, 140.30, 139.34, 132.94, 131.32, 130.71, 130.04, 129.99, 129.38, 126.74, 125.57, 21.94

Table 3.0 shows the IR-vibrational frequencies, GC-MS and NMR spectroscopy studies of the synthesized dyes absorption peaks in the range 1625.16-1695.9cm⁻¹ due to the presence of C=C and C=N cm⁻¹ and the absorption peaks 1505.8-1528.2 cm⁻¹ is attributed to azo chromophoric group (N=N), while the observed peak in the region 1602.8-1695.9 was due to V_{C=N} as outline in Table 2. Dye 23-24 showed molecular ion peaks at m/z 327.3 and 328.3 respectively which is consistent with the molecular mass of the dyes as indicated in Table 2b. The ¹H and ¹³C- NMR spectra for the synthesized dye showed eight signals with a highly deshielded signal at 10.39 ppm (H,

singlet) which is attributed to the presence of the OH of the carboxylic group, 7.73 – 8.27 ppm due to the presence of amino (-NH₂) protons. Two signals were observed for two pairs of aromatic proton in the (6.84 – 7.81) ppm range with a coupling constant of 8 – 12 Hz. Also a distinct signal was observed upfield at 3.06 ppm due to the presence of methyl (CH₃) proton. The ¹³C-NMR spectrum of the Dyes showed the signal at 162.26 ppm for the carbon atom in the COOH group. Thus a signal at 141.41 ppm for carbon atom in the thiazole ring was also observed while the signal at 140.06 -115.56 ppm for aromatic carbon.

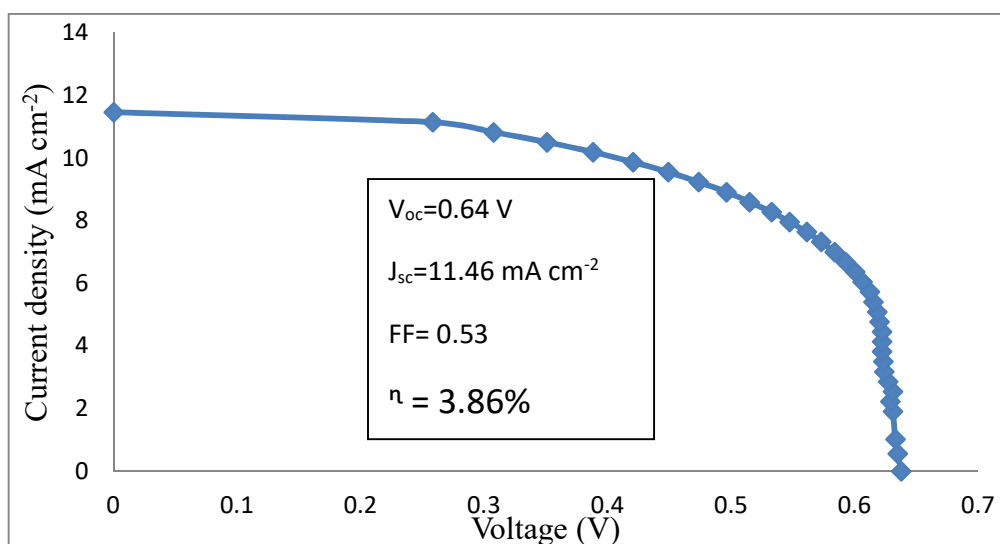


Figure 1.0: Photocurrent-Photovoltage (J–V) Curve for Dye A23

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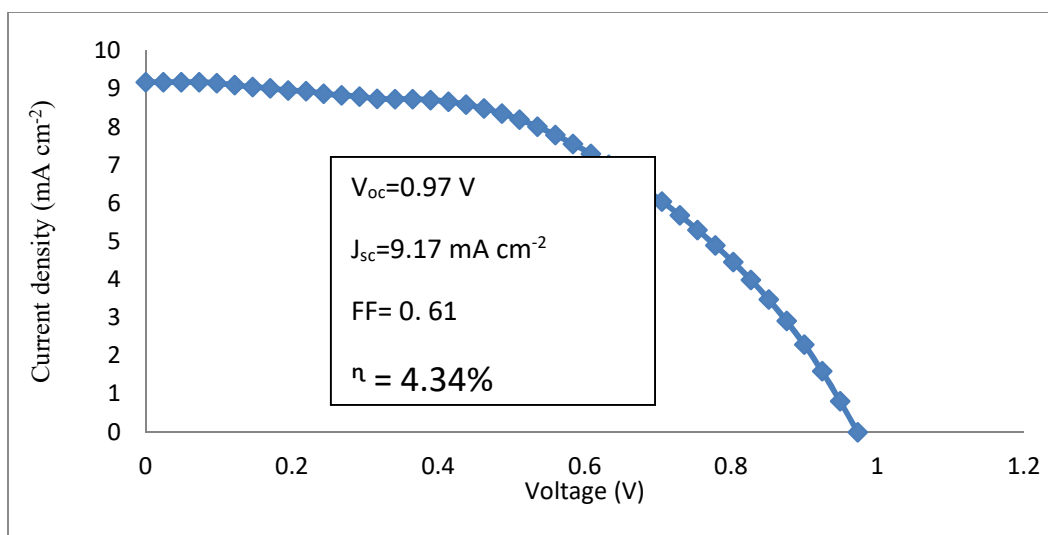


Figure 2.0: Photocurrent-Photovoltage (J–V) Curve for Dye A24

The photovoltaic parameter of the fabricated cells were characterized via (open circuit voltage (V_{oc}), short circuit current density (J_{sc}), photoelectric conversion efficiencies (η) of the DSSC with active area of 1.0cm^2 were observed and the comparative results are summarized in figure 1.0 and 2. The open circuit voltage (V_{oc}), and short circuit Current (J_{sc}) of the solar cells were measured under 100 mW/cm^2 at (AM 1.5G solar Condition). As shown in figure 1.0 and 2 the conversion efficiency of the cells span from 3.86-4.34%. Dye A24 photo-sensitizer demonstrated the higher solar conversion efficiency of 4.34% due to the stronger synergetic effect of D- π -A structural configuration of the dye coupled with the presence of suitable anchoring groups of the respective substituted azo dyes and anti-aggregation agent (Faezeh *et al.*, 2022). Reduce aggregation of dye molecules is directly related with faster electron transfer from the excited state of the dye molecules to the TiO_2 conduction band in the DSSCs (Hosseinnezhad *et al.*, 2014). Thus, absorption spectrum of the dye and the anchorage of the dye to the surface of TiO_2 are important parameters in determining the efficiency of the cell (Oayama and Harima, 2009), therefore anchoring dye molecules is highly critical for absolute absorption of sunlight in DSSCs hence conversion efficiency directly

relies on a suitable dye deposition (Hosseinnezhad *et al.*, 2015). Thus it has been stated that the conversion efficiency of solar cells containing azo dyes is usually higher than 2%. For example three organic dyes with various substituent as the electron donor and carboxylic acid as the electron acceptor were prepared by (Mikroyannidis *et al.*, 2010). Nonetheless, the DSSCs with N719 shows better performance than the DSSCs based on Dye 1 to 8. This is due to the molecular structure of N719 dye, which leads to metal ligand charge transfer (MLCT) effect that reduce the charge recombination at the dye molecules and photoelectrode interface hence providing a higher V_{oc} value. On the other hand, the N719 dye standard contains the expensive ruthenium metal which economically limits its general use (Gurpreet *et al.*, 2016)

CONCLUSION

Two novel azo dyes with a structural configuration of D- π -bridge-A were synthesized and analytical techniques such as FT-IR spectroscopy, GC-MS and ^1H and ^{13}C -NMR spectroscopy were employed to elucidate their structures. Two monolithic DSSCs were successfully fabricated by employing photo-generated light absorbers (sensitizers) made from the synthesized dyes. For the first time, the

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photovoltaic response of monolithic cells containing an active layer of heterocyclic azo dyes is shown. The type of substituent in the active azo layers differed (i.e. electron-donating: NH₂ and OH and electron withdrawing COOH). We demonstrated that changing the substituent in the 2-aminobenzothiazole (diazo component) and the coupling component changes the device's power efficiency. It should be noted that all of the data given demonstrated that heterocyclic azo dyes had a high potential for effective photovoltaic output.

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