



EFFICIENCY ENHANCEMENT OF DYE SENSITIZED SOLAR CELLS BY TIN ION CHELATION ON DYE EXTRACTED FROM *Erythrina fusca* FLOWERS

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The use of natural dyes in dye-sensitized solar cells (DSSCs) is a sustainable way to increase the efficiency of solar energy. This work investigates the bathochromic shift that *Erithina fusca* (Erabodu) flower dye exhibits when it chelates with Sn^{2+} ions, providing a novel approach to enhance the performance of DSSCs. To extract the dye, 20g of chopped flower petals and 50ml of ethanol were boiled until the petals took on a pale colour. Subsequently, 2 ml of dye solution were mixed with 0.1 M SnCl_2 solution dropwise till the colour became light purple. After adding Sn^{2+} ions, the pH of Erabodu dye was found to be 4.45 while pH of bare dye was 5.47. The metal chelation and its influence on dye absorption spectra and electron transfer kinetics were chelation and means of spectroscopic observation and electrochemical characterisation. Fluorine-doped tin oxide (FTO) glass plates were coated with a thin layer of TiO_2 nanoparticles before being exposed to the dye. Iodin/triiodide ($\text{I}_2 / \text{I}_3^-$) was used as the electrolyte and FTO glass covered with platinum as the counter electrode. A light source of 100 mW/cm intensity was used to test the solar cell. The efficiency of the Sn^{2+} ion chelated Erabodu dye (1.68 %) was greater than that of the bare dye (0.132 %). This cell's short circuit current density (J_{sc}) was 5.773 mA/cm², its open circuit voltage (V_{oc}) was 458.3 mV, and its fill factor for DSSCs was 0.406. According to the cell's incident photon to current conversion efficiency (IPCE), the action spectrum was widened between 400 and 500 nm, which increased efficiency. Our research opens the door to a viable and environmentally acceptable method of solar energy conversion by demonstrating the potential of Sn^{2+} ion chelated *Erithina fusca* dye as a sensitizer for DSSCs.

Keywords: Bathochromic shift, Dye-sensitized solar cells, Nanoparticles, UVIS spectroscopy, IPEC

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1. INTRODUCTION

The sun provides a vast amount of solar radiation, which can be harnessed to meet our energy demands through technologies like solar panels. Solar radiation, comprising UV, visible, and IR radiation, reaches about 1,368 W/m² at the equator, (Rahman, 2023) amounting to approximately 3.8×10^{22} joules per year globally. Dye-sensitized solar cells (DSSCs), (Rahman, 2023) a type of third-generation photovoltaic cell, utilize organic and synthetic dyes to convert sunlight into electrical energy, with dyes such as ruthenium complexes showing high efficiency (Ayub, 2024). However, natural dyes offer a cost-effective and environmentally friendly alternative. The development of DSSCs, driven by the need for sustainable energy, involves exploring various natural and synthetic dyes to enhance efficiency and reduce environmental impact.

The bathochromic shift observe in dyes is a phenomenon where the absorption spectrum shifts towards longer wavelengths, typically in the red region. This shift occurs due to changes in the molecular structure of the dye, such as the introduction of electron-donating or electron-withdrawing groups, changes in solvent polarity, pH, or molecular interactions. In natural dyes, the bathochromic shift is often observed when the dye is exposed to light, leading to an increase in the absorption of longer wavelengths. (Catur Harsito, 2021)

The industrial applications of bathochromic shifts in natural dyes are diverse and impactful. In the textile and dye industries, these shifts are utilized to create a broad spectrum of colors, enhancing the aesthetic appeal and marketability of fabrics. In the field of renewable energy, bathochromic shifts are pivotal in improving the efficiency of Dye-sensitized Solar Cells (DSSCs) by expanding the range of light absorption, thus boosting solar energy conversion. Additionally, in the food and beverage industry, these shifts assist in quality control by enabling the detection of specific additives or contaminants through color changes. Overall, the strategic use of bathochromic shifts in natural dyes significantly advances product development and performance across various sectors.

The relationship between changing dye color and the bathochromic shift is closely linked. As the dye structure changes, its absorption spectrum shifts, which may result in a color change of the dye. This shift can be exploited to enhance the efficiency of DSSCs by selecting dyes that absorb a broader range of sunlight, including the infrared region. The bathochromic shift caused by ion chelation in natural dyes has been investigated to improve the efficiency of Dye-sensitized Solar Cells (DSSCs), which presents a promising alternative to conventional silicon-based solar cells for capturing sunlight and converting it into electrical energy. (Sigurdson G. , 2015)

The coordination of metal ions with functional groups in natural dyes, such as carboxyl (-COOH) and hydroxyl (-OH) groups, results in the formation of metal-dye complexes (Sigurdson, 2016). These complexes enhance light absorption and promote efficient charge transfer between the dye and the semiconductor material within the solar cell.

Anthocyanins are water-soluble pigments found in many fruits, vegetables, and flowers, giving them their red, purple, and blue colors. Common sources include berries (like blueberries and raspberries), grapes, cherries, plums, red cabbage, eggplants, purple corn, and red onions. In dye-sensitized solar cells, anthocyanins serve as natural dyes that enhance light absorption, particularly in the blue and green parts of the spectrum. They can form complexes with metal ions, causing a bathochromic shift that extends light absorption into the red region. This improves the efficiency of sunlight captured and charge transfer between the dye and the semiconductor. (Sigurdson G. , 2015) Anthocyanins offer a cost-effective, stable, and environmentally friendly alternative to synthetic dyes, (Sigurdson G. , 2015) boosting the performance of DSSCs sustainably.



The bathochromic shift caused by ion chelation with anthocyanins can be advantageous for DSSCs in several ways. Firstly, the expanded absorption range allows for improved light harvesting, enabling the DSSC to capture a wider spectrum of solar radiation. This enhanced light absorption leads to higher photocurrent generation and, consequently, increased power conversion efficiency. Secondly, the chelation-induced bathochromic shift boosts the stability and performance of anthocyanin dyes in DSSCs. The coordination of metal ions with the dye molecule increases the dye's stability, protecting it from degradation due to environmental factors such as light exposure and oxidative reactions. (Erdogan, 2010) This enhanced stability contributes to the long-term efficiency and durability of DSSCs.

Additionally, using anthocyanins from natural sources aligns with the increasing demand for environmentally friendly and sustainable energy technologies. Anthocyanins are plentiful in nature and can be extracted from various plants, making them renewable and eco-friendly alternatives to synthetic dyes in solar cell applications.

Researchers are actively exploring the use of anthocyanins in DSSCs, investigating various metal-dye combinations and optimizing chelation conditions. (Sigurdson G. , 2015) These studies aim to identify the most efficient metal ions and chelation strategies to achieve the maximum bathochromic effect and enhanced performance in DSSCs.

Erythrina fusca, commonly known as "Erabadu," is a species of flowering tree in the legume family, Fabaceae. It produces striking red flowers, with anthocyanin being the primary pigment in its velvety petals (Wickramasinghe, 2019). Dye extracted from "Erabadu" flower petals using ethanol has been employed as a sensitizer for DSSCs. The efficiency of these solar cells is enhanced by the chelation of Sn^{2+} metal ions, which induces a bathochromic shift.

2. METHODOLOGY

2.1 Natural dye extraction

20g of *Erythrina fusca* (Erabadu) flower petals were chopped and boiled in 50 ml of ethanol at a ratio of 1 g to 2.5 ml of ethanol until the petals became pale in color. The resulting, maroon-colored dye was then filtered and collected into a sample bottle covered with aluminium foil. The sealed bottle was stored in a refrigerator at 4°C until use.

2.2 Chelating metal ions to dye

To prepare a 0.1M Sn^{2+} ion solution, 0.1896 g of tin chloride (SnCl_2) was dissolved in 10 ml of distilled water. SnCl_2 3 drops (0.15ml) was added dropwise to 2 ml of the natural Erabadu dye until the dye's color changed from maroon to light purple.

2.3 Preparation of dye-coated film

Fluorine-doped Tin Oxide (FTO) glass plates were cut into 2 cm × 1 cm pieces and cleaned thoroughly. The plates were placed in a small beaker half-filled with distilled water, to which a few drops of washing liquid were added. They were then sonicated for 10 minutes using an ultrasonic bath. After sonication, the beaker was removed, and the plates were rewashed with distilled water containing a few drops of concentrated H_2SO_4 . The FTO glasses were subsequently washed with distilled water and boiled in isopropyl alcohol at 80°C. After boiling, the FTO glasses were dried with mild heat and their conductive side was identified using a conductivity meter.

To prepare the TiO_2 paste, 0.25 g of TiO_2 nanoparticles (20 nm), 0.1 ml of 0.1M HNO_3 , one drop of Triton X-100, and a drop of PEG 400 were mixed. The TiO_2 paste was applied to the conductive surface of the FTO glass plates using the doctor blade method. The film was sintered at 450°C for 45 minutes in a furnace. After sintering, the TiO_2 film was allowed to cool to room temperature. Finally, the TiO_2 -coated FTO glasses were dipped separately in the ion-chelated natural dye solution and the bare dye solution of *Erythrina fusca* flowers for 15 hours in covered test tubes.



2.4 Fabrication of the cell

To prepare the electrolyte for the dye-sensitized solar cells, 0.127 g of iodine (I_2) and 0.83 g of potassium iodide (KI) were dissolved in 10 ml of a mixture of acetonitrile and ethylene carbonate in an 8:2 ratio in a volumetric flask. The solution was then stirred for 5 hours to ensure complete dissolution of the solid particles.

The dye-coated TiO_2 film was used as the anode, while the Pt-sputtered glass plate served as the counter electrode. These were placed side by side and fastened together using crocodile clips to assemble the DSSC. The electrolyte was then filled into the capillary gap between the two plates.

3. RESULTS AND DISCUSSION

Metal chelation leads to larger bathochromic shifts in compounds with more B-ring hydroxyl groups (Sigurdson, 2016). According to published FTIR data, the natural dye extracted from *Erythrina fusca* flower petals contains $-OH$ bonds and $C-O-C$ bonds (Wickramasinghe G. C., 2017). When metal ions chelate with natural dyes that have hydroxyl groups, these functional groups attach with the metal ion, releasing H^+ ions into the medium. This process makes the medium acidic and might change the dye's original color.

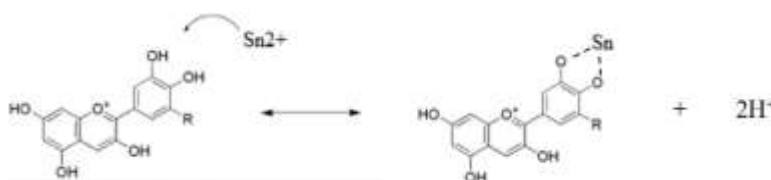


Figure 1: Proposed mechanism of metal ion (M^{n+}) chelation and structural conversion of Anthocyanins (Sigurdson, 2016)

Moreover, the addition of tin chloride to the dye solution may further increase the acidity of the medium due to the presence of trace amount of HCl. However, it is necessary to confirm whether the color change either occurred due to the pH change of the dye solution or due to metal ion chelation.

3.1 Measurement of pH values & color change of dye solutions

The pH value of the maroon-colored bare dye was measured as 5.47, which decreased to 4.49 with the addition of $SnCl_2$ (pH value of original $SnCl_2 = 0.8$) to the dye solution, resulting in a color change to light purple. To confirm whether this color change is solely due to the pH alteration, diluted HCl was added to the dye solution to lower the pH below 5, and diluted NaOH was added to raise the pH above 8. The absorption spectra of the dyes were then measured and compared with those of the pure dye, as depicted in Figure 2.

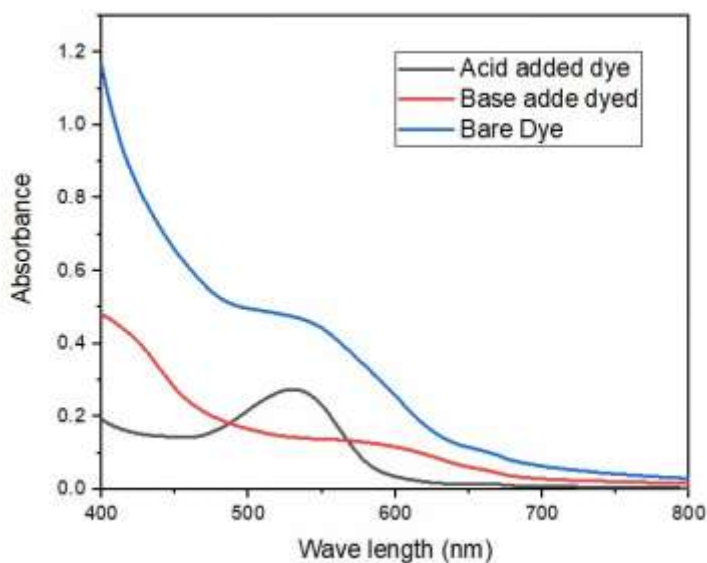


Figure 2: UV visible absorption spectrum after adding acid (pH = 3.3) and base (pH = 9.7) to *Erythrina fusca* dye.

3.2 UV-Visible Absorption Spectrum

The UV-visible absorption spectra clearly indicated that the *Erythrina fusca* flower dye exhibits a hypsochromic shift in acidic media, and the peak disappeared in basic media of the bare dye (figure 2). In contrast, a bathochromic shift was observed in the Sn²⁺ ion-chelated dye solution, as illustrated in Figure 3, confirming the postulate.

Figure 3 displays the UV-Vis absorption spectra of bare dye and Sn²⁺ ion chelated dye extracted from *Erythrina fusca* flower. The absorption measurements were conducted within the wavelength range of 400 nm to 800 nm. Specific peaks were observed at 532 nm for the bare dye and 562 nm for the Sn²⁺ ion-chelated dye. A bathochromic shift, with a peak shift of 30 nm, was observed.

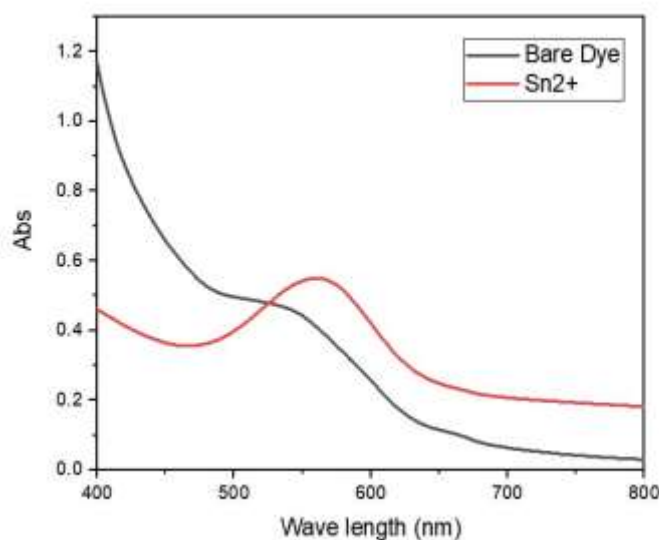


Figure 3: UV-Visible spectrum of *Erythrina fusca* bare dye and Sn²⁺ ion chelated dye solution
A Tauc's plot was obtained with the data from the absorption spectra of the dyes (figure 3)

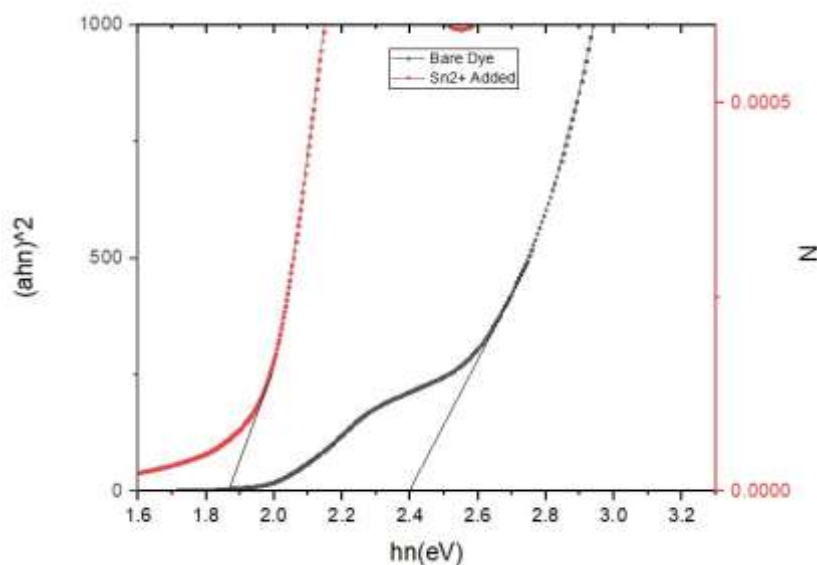


Figure 4: Tauc's plots for bare and Sn²⁺ ion chelated dye extracts of *Erythrina fusca* flowers.

The Tauc relation, as given by the following equation (in which, $A = 1$, $h\nu$ = the photon energy, α = the absorption coefficient, k = absorbance, and E_g = the energy gap between LUMO and HOMO levels), was utilized to determine the energy gap between the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO).

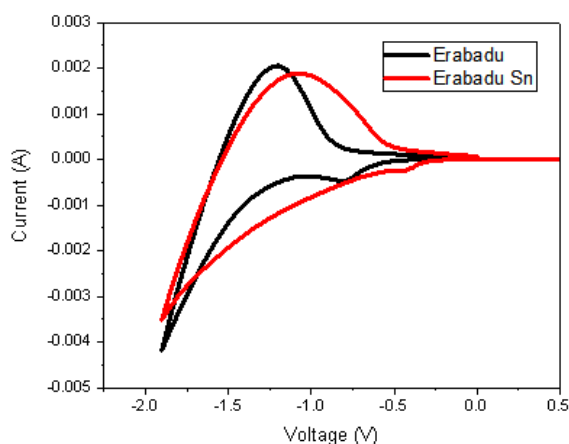
$$(\alpha h\nu)^n = A(h\nu - E_g)$$

$$\alpha = 4\pi k / \lambda, \quad E = Ah\nu$$

2.4 eV and 1.85 eV are the related band gaps for the bare dye and Sn²⁺ ion chelated dye, respectively. Here, $n = 2$ is used because natural dyes have a direct energy gap.

3.3 Cyclic Volta monograms

Figure 5: Cyclic Volta monograms of bare dye and Sn²⁺ ion chelated dye from *Erythrina fusca* flower



The oxidation and reduction potentials of the pigment can be measured using cyclic voltammetry. The oxidation potentials are approximately -1.21V for the *Erythrina fusca* bare dye and -1.1V for the Sn²⁺ ion-chelated dye solution. An Ag/AgCl electrode was used as the reference electrode, and a slight



curvature was observed in the lower segment of the cyclic voltammograms near the oxidation potentials. When the Lowest Unoccupied Molecular Orbital (LUMO) was calculated with respect to the vacuum scale, the oxidation-reduction potential of the dye corresponded to an energy of -3.48 eV for the bare dye and -3.59 eV for the Sn²⁺ chelated dye was observed.

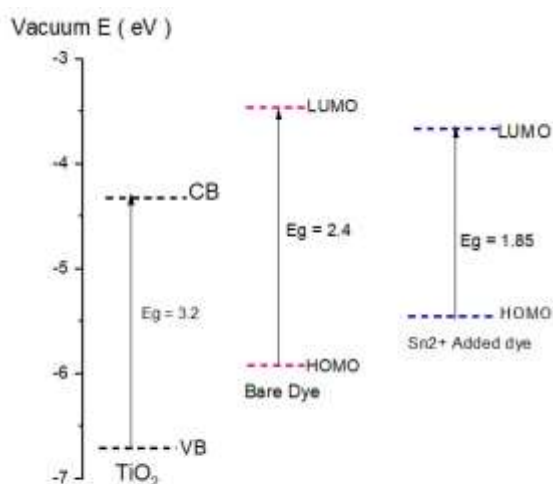


Figure 6 displays the energy band positions of the bare *Erythrina fusca* flower dye and after chelation with Sn²⁺ ions

Figure 6 displays the energy band positions of the bare *Erythrina fusca* flower dye and after chelation with Sn²⁺ ions. The dye's LUMO level moves to a lower energy level because of the chelation with Sn²⁺ ions. Additionally, the band gap energy determined by using Tauc's figure is less. Somehow, the LUMO levels of both dyes are positioned above the conduction band of TiO₂, favouring photoexcited electron injection. Most probably both bare dye and dye chelated with Sn²⁺ ions may be present in the modified dye that adsorbs on to TiO₂. As a result, both dye excitations expand the spectrum to improve DSSC performance.

3.4 J-V characteristics

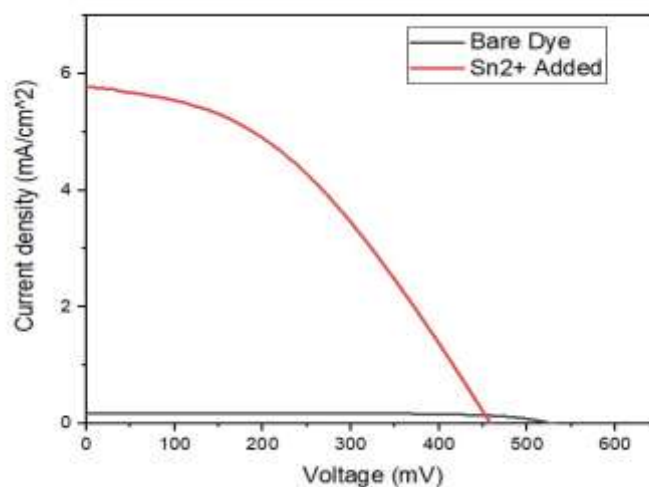


Figure 7: JV Characteristic curve of - Dye-sensitized solar cell sensitized with *Erythrina fusca* flower dye and Sn²⁺ ion chelated dye sensitized solar cell (DSSC) under the Light source of 100 mW/cm²



Table 2 Photovoltaic measurements of the Dye-Sensitized Solar Cell sensitized with *Erythrina fusca* flower dye and Sn²⁺ ion chelated dye sensitized solar cell (DSSC)

Dye solution	Open circuit voltage (VOC) mV	Current density (JSC) mAcm ⁻²	Fill Factor (FF)	Efficiency
Bare Dye	526.7	0.372	0.675	0.132%
Sn ²⁺ chelated dye	458.3	5.773	0.406	1.677%

3.5 IPCE characteristics of the DSSC

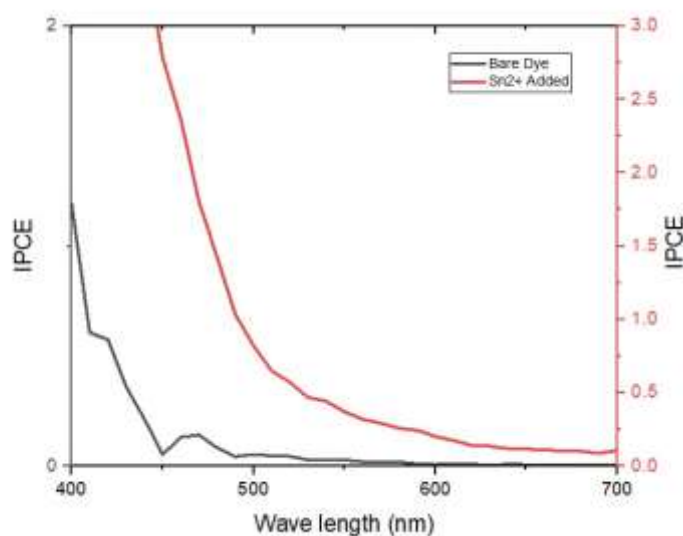


Figure 8 IPCE spectra for *Erythrina fusca* bare dye and Sn²⁺ chelated dye sensitized solar cells.

The incident photon to current efficiency (IPCE) spectra of the Sn²⁺ chelated dye and the bare dye *Erythrina fusca* are displayed in Figure 8. The action spectrum of the dyes and the dye-sensitized solar cell are in the 500–600 nm wavelength range. In comparison, the DSSC with Sn²⁺ ion chelated dye, has a greater photo current conversion efficiency over a wider range of wavelengths.

4. CONCLUSION

Erythrina fusca flowers (Erabadu) were used to extract natural dye for DSSC sensitization. UV-Vis spectra showed a bathochromic shift in the 400–800 nm wavelength range: An absorption peak was seen at 532 nm for bare dye and 562 nm for Sn²⁺ chelated dye. Using the dyes' absorption data, the energy gaps were calculated with the help of tauc's plot. The results showed that the energy gaps for the bare dye was 2.4 eV and the Sn²⁺ chelated dye was 1.85 eV. For bare dye, the solar cell generated an open circuit voltage of 526.7 mV and a short circuit current density of 0.372 mA/cm², with an efficiency of 0.132 % and a fill factor of 0.675. For Sn²⁺ chelated DSSC, the short circuit current density was 5.773 mA/cm², and an open circuit voltage of 458.3 mV with an efficiency of 1.677%. The fill factor of the cell was around 0.406. Since the excited states of both the dyes are located at a



higher energy level with respect to the conduction band of TiO₂, electron transfer from the dyes to the TiO₂ is energetically feasible.

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