Abstract- Indigo dyes for high technical properties are suitable for application in dye-sensitized solar cell. The defect of these components is their aggregation on TiO2 substrate. The wavelength of maximum absorption for selective dye in the presence and absence of anti-aggregation agent are 559 nm and 568.5 nm, respectively. The wavelength of maximum absorption in solvent is 548.5 nm. The reduction of bathochromic effect leads to reduce aggregation dye. The conversion efficiency in the presence and absence of anti-aggregation agent are 3.45% and 3.11%, respectively, that the presence of anti-aggregation agent was improved the conversion efficiency of solar cell.

Keywords: Indigo, solar cell, anti-aggregation agent, conversion efficiency.
1 Introduction

Dye-sensitized solar cells (DSSCs) have been investigated extensively as topic of research in the field of renewable energy resources [1]. Several type dyes such as coumarin dyes, polyene dyes, hemicyanine dyes, thiophene based dyes and indoline dyes have been prepared for DSSCs application [2]. However, the limitations of metal-free organic dyes are reduced in conversion efficiency due to dye aggregation because, dye aggregation inhibit electron transfer from the exited dye to TiO₂ substrate [1]. Therefore, anti-aggregation agents are commonly utilized in dye solution to improve the electron transport resulting in greater DSSCs performance [3]. The results showed that addition of anti-aggregation to dye solution improved DSSCs performance [2].

In this study, we disclose the high efficiency DSSCs with the use of an anti-aggregation agent. The spectrophotometric properties of the indigo dye in solution and on a nano anatase TiO₂ substrate were also examined. The structures of dye molecules and anti-aggregation agents are given in Figure 1.

![Cholic acid](image1)

**Figure 1: Structures of dye molecules and anti-aggregation agents**

2 Experimental

All compounds used in this study were of analytical grade unless otherwise stated. The organic dye was prepared in similar ways as described in the literature [2]. UV-Visible spectrophotometry was carried out on a Dupont 2000DSC instrument and a Cecil 9200 double beam transmission spectrophotometer. The fluorescence spectra of dye solution was obtained by Osean Optics Ush2000flg Fluorometer.

2.1 Dye-sensitized solar cells assembly and photovoltaic characteristics of the resultant solar cells

A nanocrystalline anatase TiO₂ film was coated on a transparent glass support. Each individual dye was adsorbed by dipping a separate coated glass in a 5×10⁻⁵ M ethanolic solution of dye in the absence and presence of anti-aggregation agent such as 3α, 7α, 12α-trihydroxy-5β-cholanic acid (cholic acid) for several hours. The visible bands in the absorption spectrum of the dyes after adsorption on nano TiO₂ film only appeared after the TiO₂ electrodes were dipped in the dye solution for at least 18 hours. Finally, the film was washed with a 1:1 acetonitrile:ethanol mixed solution. tetrabutyl ammonium iodide (0.5 mol dm⁻³) was used as an electrolyte. Each dye-adsorbed TiO₂ electrode, together with a Pt counter electrode and the mentioned electrolyte solution were separately assembled into a sealed sandwich type solar cell [4]. For each solar cell an action spectrum was measured under monochromatic light with a constant photon number (5x10¹⁵ photon cm⁻² s⁻¹). J-V characteristics were measured under illumination with AM 1.5 simulated sun light (100 mW cm⁻²) through a shading mast (5.0 mm×4 mm) by using a Bunko-Keiki CEP-2000 system.

3 Results and Discussion

The structures of the considered organic dye molecules and anti-aggregation agent have been presented in Fig. 1. The wavelength of maximum absorption (λmax) for the synthesized dye in THF is 548.5 nm and λmax of the corresponding dyes adsorbed on a TiO₂ film in the absence and presence of anti-aggregation agents are 559 nm and 568 nm, respectively. Synthesized dyes shows bathochromic shift in the absorption peak as compared to dyes without CN group. This bathochromic shift arises from the fact that one more electron acceptor (-CN) increase the electron withdrawing ability of electron acceptors group and lowers the lower unoccupied molecular orbital, thus reducing the gap between higher and lower unoccupied molecular orbital states [2]. The molar extinction coefficient of dye in THF is also 37383 LM⁻¹cm⁻¹, indicating that dye has good light harvesting abilities. Upon dye adsorption onto a TiO₂ surface, the λmax is bathochromically shifted by 19.5 as compared to the corresponding spectra in solution, implying that dyes adsorbed onto TiO₂ surface contain partial J type aggregates. The λmax...
for dye adsorption onto a TiO$_2$ surface is bathochromically shifted by 10.5 nm in the presence of Cholic acid. The results show that bathochromic shifts in the wavelength of maximum absorption reduced due to presence of the anti-aggregation agent. The wavelength of maximum fluorescent the synthesized dye in THF is 703 nm. In THF solution, dyes depict intense green fluorescence due to the charge transfer from the electron-donating entity to the electron-accepting entity. The oxidation potential (E$_{ox}$) of synthesized dye was measured in acetonitrile by cyclic voltammetry [4]. The oxidation peak potential (E$_{ox}$) for dye can therefore be calculated to be 0.57 vs Fc/Fc$^+$ in acetonitrile. The E$_{red}$ of dye is estimated to be –1.31 vs Fc/Fc$^+$ in acetonitrile. Therefore the synthesized dyes are suitable for use in dye sensitized solar cells.

The photovoltaic properties of dye was attained to clarify effect of anti-aggregation agents. Detailed photovoltaic parameters of dye in the absence and presence of the anti-aggregation agents are also summarized in Table 1. The solar energy to electricity conversion efficiency ($\eta$) of the DSSCs is calculated from the short circuit current ($I_{sc}$), the open-circuit photovoltage ($V_{oc}$), the fill factor (FF), and the intensity of the incident light ($P_{in}$) [5]. Photocurrent–photovoltage (J–V) curves of cells based on dye are illustrated in Fig. 2.

The results carried out under the standard global AM 1.5 solar condition and shown in Table 1. The conversion efficiency of solar energy to electricity of such organic dyes could be improved by using completely different substituted [5] or by addition anti-aggregation agent. Reduced aggregations of dye are directly correlated with faster electron transfer from excited state of dye to TiO$_2$ substrate in solar cell. Therefore designing highly flexible and conjugated organic dye molecules is essential for absolute harvesting of sun light in dye sensitized solar cells. Thus conversion efficiency of dye sensitized solar cells is directly correlated with larger conformational flexibility and diffusion values of organic dye molecules [1].

![Figure 2: Current density-voltage characteristics for dye in the absence and presence of anti-aggregation agents](image)

### 3 Conclusions

Metal-free organic dyes of type (D-π-A) based on indigo as potential sensitizers for DSSCs exhibit suitable conversion efficiency. New metal-free organic dyes based on indigo were synthesized and the spectrophotometric properties of the prepared organic dyes in THF solvent and on TiO$_2$ films in the absence and presence of anti-aggregation agent were examined. In all cases, the absorption maxima of dye applied on the surface of a nanocrystalline TiO$_2$ film gave bathochromic shifts compared to the corresponding dye spectra in THF solution. The results show the dyes from J-type aggregates on the TiO$_2$ substrate but, the amounts of aggregation were reduced in the presence of anti-aggregation agents. Electron transfer process is reduced due to aggregation of molecular dyes. So, anti-aggregation agent is utilized in fabrication of DSSCs. The results show that the conversion efficiencies are improved with reduced aggregation. Synthesized dye indicated 3.45% and 3.87% for conversion efficiency in the absence of anti-aggregation agent and in the presence of cholic acid, respectively. Thus conversion efficiency of dye sensitized solar cells is directly correlated with larger conformational flexibility and diffusion values of organic dye molecules.
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References


