

Synthesis and Application of Two Organic Dyes Based on Indoline in Dye-Sensitized Solar Cells

M. Hosseinnzhad¹, S. Moradian^{*2}, K. Gharanjig³

¹ Assistant Professor, Department of Organic Colorants, Institute for Color Science and Technology, P. O. Box 16656118481, Tehran, Iran.

² a) Professor, Faculty of Polymer and Color Engineering, Amirkabir University of Technology, P. O. Box 15875-4413, Tehran, Iran. b) Center of Excellence for Color Science and Technology, Institute for Color Science and Technology, P. O. Box 16656118481, Tehran, Iran.

³ a) Associate Professor, Department of Organic Colorants, Institute for Color Science and Technology, P. O. Box 16656118481, Tehran, Iran. b) Center of Excellence for Color Science and Technology, Institute for Color Science and Technology, P. O. Box 16656118481, Tehran, Iran.

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ABSTRACT

In this paper we sensitized two new organic dyes (Dye 1 and Dye 2) based on indoline with indoxyl as the electron donor group. We used acrylic acid and cyanoacrylic acid as the electron acceptor anchoring group in Dye 1 and Dye 2, respectively. The proposed dyes were sensitized from carbazole as the starting material by standard reactions and characterized by different techniques such as melting point, FTIR, ¹HNMR, elemental analysis and UV-Visible spectroscopy after purification. Spectrophotometric measurements of the synthesized dyes in solution and on a TiO₂ substrate were carried out in order to assess the changes in the status of the dyes. The wavelength of maximum absorption for Dye 1 and Dye 2 in solution are 551.5 nm and 558 nm and on TiO₂ films are 576 nm and 585 nm, respectively. Finally, the proposed dyes were used as sensitizer in a dye solar cell structure and their photovoltaic properties were also investigated. The Conversion efficiency for Dye 1 and Dye 2 were 1.03% and 1.45%, respectively. Prog. Color Colorants Coat. 8 (2015), 309-315 © Institute for Color Science and Technology.

1. Introduction

Dye-sensitized solar cells have engrossed a great deal of interest, as they offer high energy conversion

efficiencies due to low cost and environmentally friendly [1]. Recently, more and more attention has

*Corresponding author: moradian@aut.ac.ir

been directed toward the application of metal-free organic dyes in dye-sensitized solar cells because such organic dyes do not contain expensive ruthenium of limited resource, and have additionally the advantages of relatively facile dye synthesis method and capability of easy molecular tailoring [2]. Coumarine [3], polyene [4], hemicyanine [5], thiophene based [6], and indoline [7] dyes are suitable for application of dye-sensitized solar cells that exhibiting relatively high performances in dye-sensitized solar cells have so far been designed and developed. In such compounds, the electron-donating and electron-accepting groups are connected through a π -conjugated linker (a D- π -A molecular structure) [8]. Their properties can be finely tuned by independently altering, alternating or matching different groups in such D- π -A dyes [9]. In research for high efficiency organic dyes for solar cells, development of new materials offering optimized thermal and photochemical stabilities, as well as appropriate optical and electrical properties is of utmost importance [10].

In the present study, two metal-free organic dyes were obtained utilizing indoxyl as electron donor and cyanoacrylic acid or acrylic acid as electron acceptor groups. The dyes together with their corresponding intermediates were then purified and characterized. The

spectrophotometric properties of the prepared organic dyes in THF solvent and on the nanoanatase TiO₂ substrate were examined. The absorption maxima and the intensities of the resultant dyes were also obtained. Dye sensitized solar cells were then fabricated utilizing these metal-free organic dyes and their photovoltaic behaviors were determined. Schematic representation of the route for synthesis of the prepared metal-free organic dyes is given in Figure 1.

2. Experimental

2.1. Materials and instrumentation

All compounds used in this study were of analytical grade unless otherwise stated. The synthesis route and fully characterization of intermediates (**1**) have been described previously [11, 12]. The FTIR measurements were carried out on a Bomene Canada instrument. NMR measurements were carried out on a 500 MHz Joel instrument. Differential scanning calorimetric (DSC) analyses were carried out on a Dupont 2000DSC instrument. UV-visible spectrophotometry was carried out on a Cecil 9200 double beam transmission spectrophotometer to obtain molar extinction coefficients and absorption maxima.

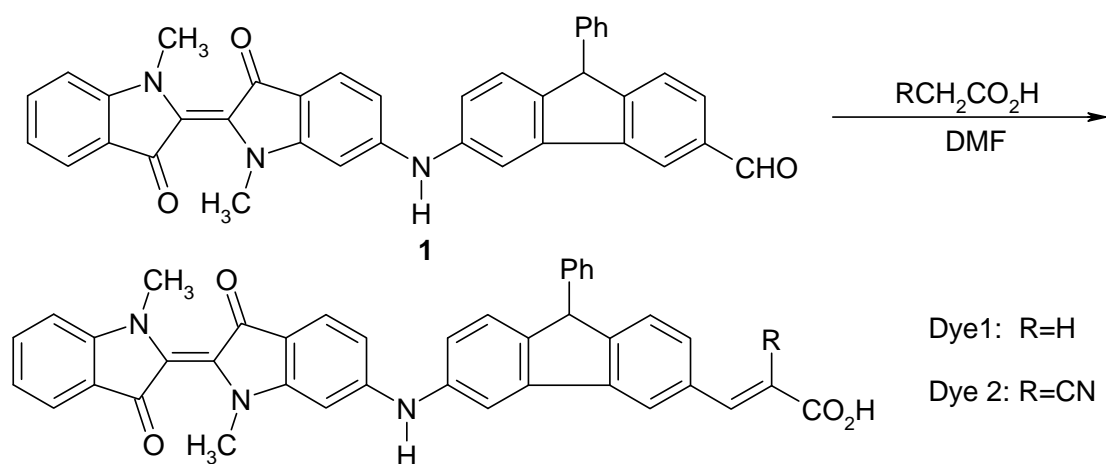


Figure 1: Synthesis route of the dyes.

2.2. Synthesis of Dyes

2.2.1. Synthesis of Dye 1

20 mL acetonitrile were added separately to 17.6 mmol 1 each containing 42 mmol malonic acid and 8 drops of piperidine. Each mixture was stirred at 90 °C for 2 h. After each reaction was completed, the resultant precipitate was filtered and purified by silica gel column chromatography (chloroform:methanol 8:1). Yield: 87%; mp 295.44 °C; FTIR (KBr) (Cm^{-1}): 1711 C=O str., 1499, 1603: C=C str, 1285: C-N str; $^1\text{H-NMR}$ (CDCl_3), δ (ppm): 3.94 (s, 6H), 6.47-6.49 (d, 1H), 6.66-6.68 (d, 2H), 7.14 (s, 3H), 7.22 (t, 3H), 7.37 (d, 2H), 7.87-7.89 (d, 5H), 7.93-7.95 (d, 4H), 8.58 (d, 2H), 9.72 (s, 1H, CO_2H); Elem. Anal. Calcd. for $\text{C}_{37}\text{H}_{28}\text{N}_3\text{O}_4$: C, 75.97%; H, 4.54%; N, 9.09%. Found: C, 75.93%; H, 4.53%; N, 9.11%.

2.2.1. Synthesis of Dye 2

20 mL acetonitrile was added separately to 8 mmol 1 each containing 16 mmol cyanoacetic acid and 9 mmol of piperidine. Each mixture was refluxed for 6 h. After each reaction was completed, it was cooled to room temperature. The resultant precipitate was filtered and purified by silica gel column chromatography (ethylacetate:methanol 10:1). Yield: 87%; mp 304.37 °C; FTIR (KBr) (Cm^{-1}): 1724 C=O str., 1486, 1629: C=C str, 1281: C-N str; $^1\text{H-NMR}$ (CDCl_3), δ (ppm): 4.29 (s, 6H), 7.38-7.40 (d, 2H), 7.44 (s, 3H), 7.47 (t, 3H), 7.58 (t, 2H), 7.70-7.73 (d, 4H), 8.10-8.12 (d, 4H), 8.31 (d, 2H), 9.65 (s, 1H, CO_2H); Elem. Anal. Calcd. for $\text{C}_{38}\text{H}_{27}\text{N}_4\text{O}_4$: C, 74.88%; H, 4.21%; N, 10.92%. Found: C, 74.85%; H, 4.22%; N, 10.90%.

2.3. Electrochemical measurements

Electrochemical measurements of the synthesized dyes were carried out in solution in acetonitrile. The oxidation potential (E_{ox}) was measured using three small-sized electrodes. Ag quasi reference electrode (QRE) was used as the reference. Platinum wires were used as the working and the counter electrodes. All electrode potentials were calibrated with respect to ferrocene(Fc)/ ferrocenium (Fc^+) redox couplet. An acetonitrile solution of each dye containing tetrabutylammonium perchlorate (0.1 mol dm^{-3}) and ferrocene (ca. 1 mmol dm^{-3}) was prepared. The electrochemical measurements were performed at a

scan rate of 100 mV s^{-1} [13].

2.4. Dye-sensitized solar cells (DSSCs) assembly and photovoltaic characteristics of the resultant solar cells

A nanocrystalline TiO_2 film was coated on a transparent glass support. The dye was adsorbed by dipping the coated glass in a $5 \times 10^{-5} \text{ M}$ ethanolic solution of the dye containing 7% 4-tert-butylpyridine and 50 mM 3 α ,7 α -dihydroxy-5 β -cholic acid (cheno) for several hours. The visible bands in the absorption spectrum of the dyes after adsorption on the nano TiO_2 film only appeared after the TiO_2 electrodes were dipped in the dye solution for at least 18 hr. The presence of 4-tert-butylpyridine and cheno is necessary to avoid surface aggregation of the sensitizer (Dye1 or Dye2). Finally, the film was washed with an acetonitrile-ethanol 1:1 mixed solution. Acetonitrile-ethylenecarbonate ($v/v=1:4$) containing tetrabutyl ammonium iodide (0.5 mol dm^{-3}) was used as the electrolyte. The dye-adsorbed TiO_2 electrode, the Pt counter electrode and the electrolyte solution were assembled into a sealed sandwich type solar cell [14, 15].

An action spectrum was measured under monochromatic light with a constant photon number ($5 \times 10^{15} \text{ photon cm}^{-2} \text{ s}^{-1}$). J-V characteristics were measured under illumination with AM 1.5 simulated sun light (100 mW cm^{-2}) through a shading mast ($5.0 \text{ mm} \times 4 \text{ mm}$) by using a Bunko-Keiki CEP-2000 system.

3. Results and discussion

The organic Dye 1 and Dye 2 were synthesized as schematically shown in Figure 1. Component 1 was prepared in a similar way as described in the literature [11, 12]. This material was allowed to react separately with methyl cyanoacetate by the Knoevenagel reaction in the presence of piperidine to give organic dyes [2, 16]. Equimolar solutions of benzaldehyde and ethyl cyanoacetate were mixed in a nitrogen hood to prevent the formation of benzoic acid. A second-order reversible kinetic rate expression was derived assuming that the addition of the enolate anion onto the benzaldehyde is the rate-limiting step in the reaction. Its addition to the benzaldehyde creates a metastable adduct that rapidly transform into the final condensation product with the release of a hydroxyl

anion [9, 11].

The wavelength of maximum absorption (λ_{\max}) and the molar extinction coefficients (ϵ_{\max}) for the two dyes in THF are listed in Table 1 and shown in Figure 2, together with the λ_{\max} of the corresponding dyes adsorbed on the TiO₂ film. The absorption peaks at around 551.5 nm for Dye 1 can be assigned to an intra molecular charge transfer between the donor group and the acrylic acid group [17], providing an efficient charge-separation for the excited state. For the cyanoacetic acid based dyes (Dye 2), when an extra electron acceptor (-CN) was linked to the vinyl bridge, the λ_{\max} had a bathochromic shift from 551.5 nm for Dye 1 to 558 nm for Dye 2. This shift of the maximum absorption peak arises from the fact that more stronger electron acceptor of cyanoacrylic groups intensifies the overall electron withdrawing ability of the system and hence lowering the level of the lower unoccupied molecular orbital (LUMO), thus reducing the gap

between the higher unoccupied molecular orbital (HOMO) and the LUMO states [2]. Upon dye adsorption on TiO₂ surface, the wavelength of maximum absorption is bathochromically shifted by 24.5 and 27 for Dye 1 and Dye 2, respectively, as compared to the corresponding spectra in solution, implying that dyes adsorbed on the TiO₂ surface contain partial J-type aggregates [18-20]. The molar extinction coefficients of Dye 1 and Dye 2 in THF at their respective λ_{\max} are also shown in Table 1, indicating that these novel dyes have good light harvesting abilities [21]. The fluorescent characteristics of dyes measured in THF are represented in Table 1. In THF solution, dyes show intense green fluorescence due to the charge transfer from the electron donating group to the accepting group. The fluorescence emission maxima of the synthesized Dye 1 and Dye 2 in the THF are 615 and 632, respectively.

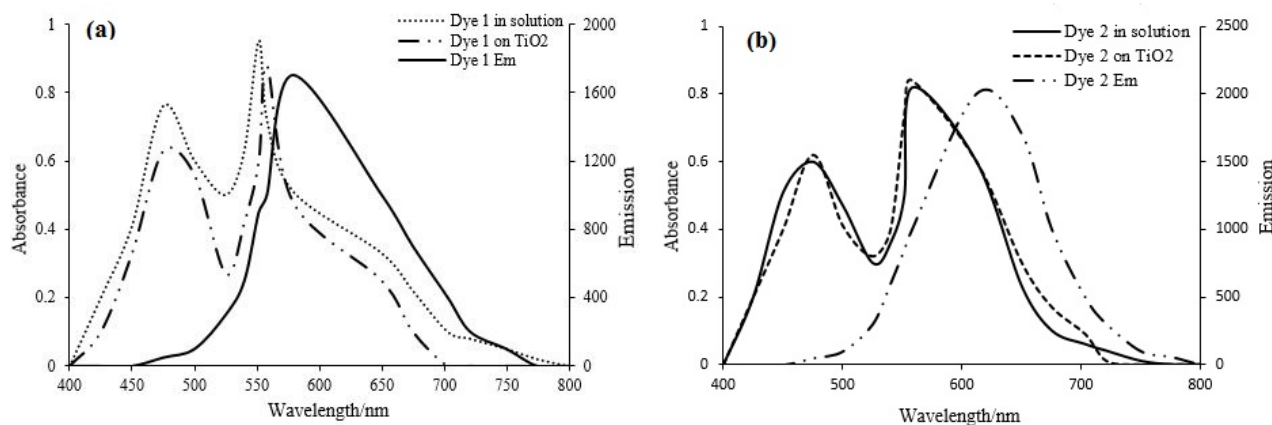


Figure 2: UV-Vis absorption and fluorescence spectra of a) Dye 1 and b) Dye 2.

Table 1: Absorption properties of the synthesized dyes.

Dye	λ_{\max} (nm) (in THF)	ϵ ($M^{-1}cm^{-1}$)	λ_{\max} (nm) (on TiO ₂)	λ_F (nm) (in THF)
1	551.5	29237	576	615
2	558	28447	585	632

The oxidation potential (E_{ox}) of Dye 1 and Dye 2 was measured in acetonitrile by cyclic voltammetry. There are two distinct redox waves observed in the voltammogram. The first oxidative wave (I) was due to the oxidation of the internal standard of ferrocene, whereas the second wave (II) near was due to the electrochemical oxidation of Dyes. The oxidation peak potential (E_{pa}) for Dye 1 and Dye 2 can therefore be calculated to be +1.18 V and +1.06 V vs Fc/Fc^+ in acetonitrile, respectively. Although the standard E_{ox} value is usually not easily obtained experimentally, it can be approximately estimated from the cyclic voltammetric peak potential, which equals it if the electrochemical oxidation is a reversible step [22]. No reduction peak was observed for the synthesized dyes. Therefore, the $E_{ox}-E_{0-0}$ level, where E_{0-0} represents the intersection of normalized absorption and the fluorescence spectra in THF (Figure 2), was calculated. This is considered to correspond to the reduction

potential [20]. The E_{0-0} of Dye 1 and Dye 2 were observed at 582 nm and 612 nm corresponding to 1.93 eV and 1.85 eV, respectively. Therefore, the $E_{ox}-E_{0-0}$ level of Dye 1 and Dye 2 is calculated to be -0.75 V and -0.79 V vs Fc/Fc^+ in acetonitrile.

Dye-sensitized solar cells (DSSCs) were constructed and compared in order to clarify the relationships between the sensitizing behavior of Dye 1 and Dye 2 dye molecules and their structures. The DSSCs utilized these dyes as sensitizers for nanocrystalline anatase TiO_2 . A typical photocurrent-photovoltage (J-V) curve for cells based on Dye 1 and Dye 2 is depicted in Figure 3. The detailed photovoltaic parameters are also summarized in Table 2. The solar energy to electricity conversion efficiency (η) of the DSSCs is calculated from short circuit current (J_{sc}), the open-circuit photovoltage (V_{oc}), the fill factor (FF), and the intensity of the incident light (P_{in}) [22, 23].

Table 2: Photovoltaic performance of DSSCs based on Dye 1 and Dye 2.

Dye	V_{oc} (V)	J_{sc} ($mA \cdot cm^{-2}$)	FF	η (%)
1	0.64	2.47	0.65	1.03
2	0.64	3.38	0.67	1.45

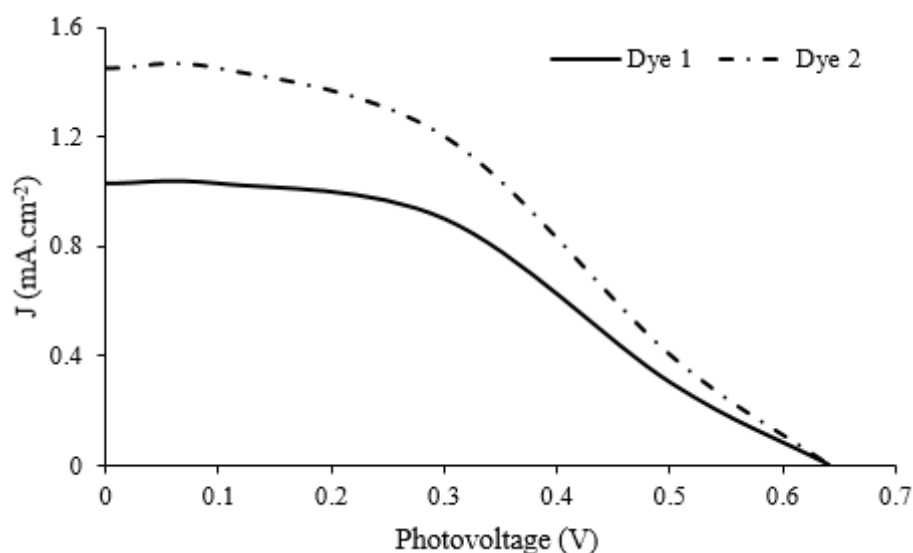


Figure 3: Current density-voltage characteristics for Dye1 and Dye2.

According to the results shown in Table 2, under the standard global AM 1.5 solar condition, the conversion efficiencies of cells containing Dye 1 and Dye 2 are 1.03% and 1.45%, respectively. The larger conversion efficiency of Dye 2 sensitizer is probably due to the stronger electron withdrawal ability of the combination of two cyanoacrylic groups. The conversion efficiency of solar energy to electricity of the present organic dyes could be improved by extending the conjugated length of the organic dyes or by incorporation of a thiophene π -bridge [18, 24-26].

4. Conclusions

Two metal-free organic dyes (D- π -A) to be used as sensitizers in DSSCs were designed and synthesized based on indigo by employing acrylic acid and cyanoacrylic acid as acceptor units. These dyes were identified using FTIR, ^1H NMR, ^{13}C NMR, elemental analysis and UV-Visible spectroscopic techniques. The spectrophotometric properties of the prepared organic dyes in solvent and on TiO_2 films were examined.

According to the results, Dye 2 containing cyanoacrylic acid as the acceptor group showed bathochromic shifts compared to Dye 1. In all cases,

the absorption maxima of Dye 1 and Dye 2 applied on the surface of a TiO_2 film gave a bathochromic effect compared to the corresponding dye spectra in solution. Finally, the prepared dyes were utilized in constructed DSSCs and their photovoltaic behaviors were assessed. A solar energy to electricity conversion efficiency of 1.03 and 1.45 percent were achieved for Dye 1 and Dye 2, respectively. Dye 2 containing cyanoacrylic acid gave higher conversion efficiency than Dye 1 which contains a cyanoacrylic acid as acceptor unit due to its stronger electron withdrawing ability. Detailed experiments and investigation of the interfacial charge transfer processes of these dyes are currently in progress aiming to further increase the overall performances of DSSCs fabricated with this new group of dyes.

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