



## Synthesis and Characterization of Indoline-based Organic Sensitizers for Photoelectrochemical Cells

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### ABSTRACT

**I**n this paper we designed and prepared three free-metal organic dyes (Dye 1, Dye 2 and Dye 3) based on indoline with *n*-phenyl substituted iminodibenzyl as the electron donor group. We used cyanoacrylic acid substituent as the electron acceptor anchoring group in organic dyes. The proposed dyes were prepared from iminodibenzyl as the starting material by standard reactions and characterized by different techniques such as melting point, FT-IR, <sup>1</sup>HNMR, elemental analysis and UV-Visible spectroscopy after purification. Spectrophotometric measurements of the organic dyes in solution and on a photoanode substrate were carried out in order to assess status changes of the dyes. The wavelengths of maximum absorption for Dye 1 to Dye 3 in solution are 416 nm, 421 nm and 409 nm and on photoanode substrate are 437 nm, 440 nm and 421 nm, respectively. Finally, the proposed dyes were used as sensitizer in a photoelectrochemical cell structure and their photovoltaic properties were also investigated. The conversion efficiency for Dye 1 to Dye 3 is 2.84%, 3.11% and 2.12%, respectively. *Prog. Color Colorants Coat. 10 (2017), 43-50* © Institute for Color Science and Technology.

### 1. Introduction

Dye-sensitized solar cells (DSSCs) are a suitable source for the generation of green, clean and low cost energy [1]. Dyes are important components in dye-sensitized solar cells due to preparation electricity with absorption of light photons. Application of metal-free organic dyes in various structures, for example coumarine [2], polyene [3], hemicyanine [4], thiophene based [5], and indoline [6] in DSSCs have attracted board attention due to easy production, good reproducibility and the absence of expensive ruthenium

[7]. In photovoltaic organic dyes, as optical materials, the electron-donating and electron-accepting groups are connected through a  $\pi$ -conjugated linker (a D- $\pi$ -A molecular structure) [8]. The quality of photovoltaic properties can be improved by alternating or matching different groups in organic dyes in acceptor, donor or conjugated linker components [9].

The investigation of new substitutes and offering are processed to achieve high power conversion efficiency improvement of optical and electrical properties of dye-sensitized solar cells [10-12].

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Iminodiphenyl is a good starting material due to its suitable cost and conjugated system [13, 14]. Wu et al. [15] presented an organic dye containing ethyliminodibenzyly for DSSCs. The results show that the synthesized dye is suitable for dye-sensitized solar cells and power conversion efficiency of 3.49% has been achieved. There are many papers on the organic dye contain iminodibenzyl substituent application in new technologies as sensor design [16, 17] and preparation of new drugs [18] but, there are few reports on the application of these photovoltaic materials in DSSCs.

In the present study, three metal-free organic dyes were synthesized utilizing *n*-substituted iminodibenzyl as the electron donor and cyanoacrylic acid as the electron acceptor groups. The dyes together with their corresponding intermediates were then purified and characterized. The spectrophotometric properties of the synthesized dyes in solution and on the photoanode substrate were examined. Dye sensitized solar cells were then fabricated utilizing these synthesized 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 (**1-3**) have been described previously [19]. The FT-IR 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.

### 2.2. Synthesis of Dyes

Acetonitrile (20 mL) was added separately to 8 mmol **1**, **2** and **3** each containing 16 mmol cyanoacetic acid and 9 mmol piperidine. Each mixture was refluxed for 6 h. After each reaction was complete, it was cooled to room temperature. The resultant precipitate was filtered and purified by silica gel column chromatography (ethylacetate/methanol=10:1).

#### 2.2.1. Dye 1

Yield: 84%; mp 235.7 °C; FT-IR (KBr) ( $\text{Cm}^{-1}$ ): 1655 C=O str., 1476, 1601: C=C str, 1502: C-N str;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ),  $\delta$  (ppm): 4.15 (3H,  $\text{OCH}_3$ ), 6.88-6.93 (d, 4H), 7.17-7.22 (dd, 1H), 7.36-7.45 (d, 2H), 7.52 (t, 2H), 7.63 (s, 1H), 7.84-7.89 (d, 2H), 8.11-8.16 (d, 4H), 9.63 (s, 1H, OH);  $^{13}\text{CNMR}$  ( $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ): 59.77, 90.74, 110.17, 112.45, 114.67, 115.11, 116.44, 118.47, 119.82, 120.12, 121.17, 122.26, 123.32, 125.19, 126.31, 127.42, 128.19, 129.56, 130.78, 131.44, 132.91, 134.27, 135.62, 139.22, 140.14, 168.12; Elem. Anal. Calcd. for  $\text{C}_{25}\text{H}_{20}\text{N}_2\text{O}_3$ : C, 75.75%; H, 5.05%; N, 3.53%. Found: C, 75.61%; H, 4.85%; N, 3.12%.

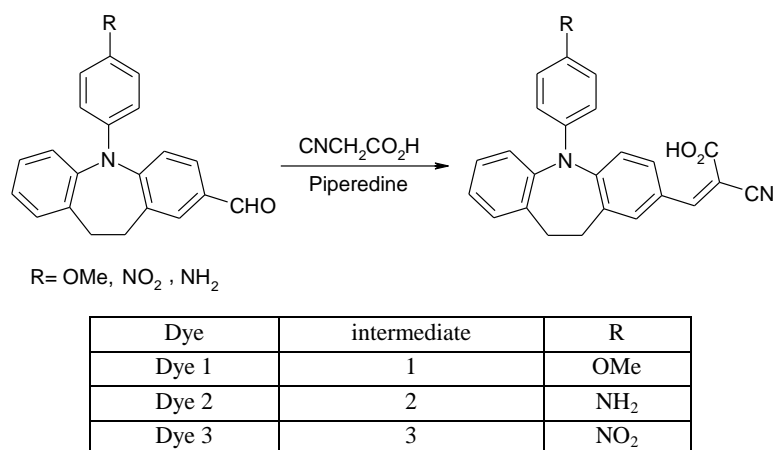


Figure 1: Synthesis route of the dyes.

### 2.2.2. Dye 2

Yield: 85%; mp 229.11 °C; FT-IR (KBr) ( $\text{Cm}^{-1}$ ): 1707 C=O str., 1482, 1611: C=C str, 1410: C-N str;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ),  $\delta$  (ppm): 5.89 (2H,  $\text{NH}_2$ ), 6.92-6.97 (d, 4H), 7.11-7.19 (dd, 1H), 7.41-7.46 (d, 2H), 7.49 (t, 2H), 7.58 (s, 1H), 7.77-7.81 (d, 2H), 8.02-8.07 (d, 4H), 9.54 (s, 1H, OH);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ): 55.11, 93.47, 110.17, 111.14, 112.32, 112.93, 115.71, 118.26, 119.47, 120.23, 121.16, 122.46, 123.43, 125.11, 127.32, 129.34, 130.11, 132.46, 133.51, 134.78, 135.21, 137.58, 139.36, 163.32; Elem. Anal. Calcd. for  $\text{C}_{24}\text{H}_{19}\text{N}_3\text{O}_2$ : C, 75.59%; H, 4.98%; N, 11.02%. Found: C, 75.32%; H, 4.62%; N, 10.83%.

### 2.2.3. Dye 3

Yield: 88%; mp 214.73 °C; FT-IR (KBr) ( $\text{Cm}^{-1}$ ): 1675 C=O str., 1453, 1604: C=C str, 1416: C-N str;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ),  $\delta$  (ppm): 6.83-6.89 (d, 4H), 7.15-7.21 (dd, 1H), 7.39-7.44 (d, 2H), 7.62 (t, 2H), 7.71 (s, 1H), 7.82-7.87 (d, 2H), 8.17-8.23 (d, 4H), 9.59 (s, 1H, OH);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ): 60.32, 92.48, 110.77, 112.14, 113.33, 115.41, 116.71, 118.24, 119.21, 120.14, 121.42, 122.17, 124.21, 125.36, 127.41, 129.34, 130.71, 131.23, 132.26, 133.59, 134.52, 137.63, 138.27, 165.41; Elem. Anal. Calcd. for  $\text{C}_{24}\text{H}_{17}\text{N}_3\text{O}_4$ : C, 70.07%; H, 4.14%; N, 10.02%. Found: C, 70.21%; H, 3.98%; N, 9.82%.

## 2.3. Electrochemical measurements

Electrochemical measurements of the synthesized dyes were carried out in acetonitrile solution. The oxidation potential ( $E_{\text{ox}}$ ) 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 ( $\text{Fc}$ )/ferrocenium ( $\text{Fc}^+$ ) redox couplet. An acetonitrile solution of each dye containing tetrabutylammonium perchlorate ( $0.1 \text{ mol dm}^{-3}$ ) and ferrocene (ca.  $1 \text{ mmol dm}^{-3}$ ) was prepared. The electrochemical measurements were performed at a scan rate of  $100 \text{ mV s}^{-1}$  [20, 21].

## 2.4. Photoelectrochemical cell assembly and characterization

A nanocrystalline  $\text{TiO}_2$  film was coated on a transparent glass support. The dye was absorbed by dipping the coated glass in a  $5 \times 10^{-5} \text{ M}$  ethanolic dye solution containing 7% 4-tert-butylpyridine and 50 mM

3 $\alpha$ ,7 $\alpha$ -dihydroxy-5 $\beta$ -cholic acid (cheno) for several hours. The visible bands in the absorption spectrum of the dyes after adsorption on the nano  $\text{TiO}_2$  film only appeared after the  $\text{TiO}_2$  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 (Dye 1, Dye 2 and Dye 3). Finally, the film was washed with an acetonitrile-ethanol 1:1 mixed solution. Acetonitrile-ethylene carbonate (v/v=1:4) containing tetrabutyl ammonium iodide ( $0.5 \text{ mol dm}^{-3}$ ) was used as the electrolyte. The dye-adsorbed  $\text{TiO}_2$  electrode, the Pt counter electrode and the electrolyte solution were assembled into a sealed sandwich type solar cell [22-24].

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 ( $100 \text{ mW cm}^{-2}$ ) through a shading mast (5.0 mm $\times$ 4 mm) by using a Bunko-Keiki CEP-2000 system.

## 3. Results and Discussion

As shown in Figure 1, Dye 1 to Dye 3 were prepared with N-substituted iminodibenzyl unit as the donor groups and cyanoacrylic acid as the acceptor group. The dye reaction was the condensation of the respective aldehyde with cyanoacetic acid by the Knoevenagel reaction in the presence of piperidine [15, 25]. The Knoevenagel condensation reaction is a useful transformation in organic synthesis [26]. The Knoevenagel condensations between carbonylic compounds and methylene malonic esters produce several important key products that include nitriles used in anionic polymerization and the  $\alpha,\beta$ -unsaturated ester intermediates employed in the synthesis of several therapeutic drugs and pharmacological products [27].

The wavelength of maximum absorption ( $\lambda_{\text{max}}$ ) and the molar extinction coefficients ( $\epsilon_{\text{max}}$ ) for the synthesized dyes in acetonitrile are listed in Table 1 and shown in Figure 2, together with the  $\lambda_{\text{max}}$  of the corresponding dyes adsorbed on the  $\text{TiO}_2$  film. The absorption peaks for synthesized dyes can be assigned to an intra-molecular charge transfer between the donor group and acceptor group [28], providing an efficient charge-separation for the excited state. The wavelength of maximum absorption has been achieved around 421 nm for Dye 2. This of the maximum absorption peak arises for Dye 2 from the fact that more stronger electron acceptor of two acceptor groups intensifies the

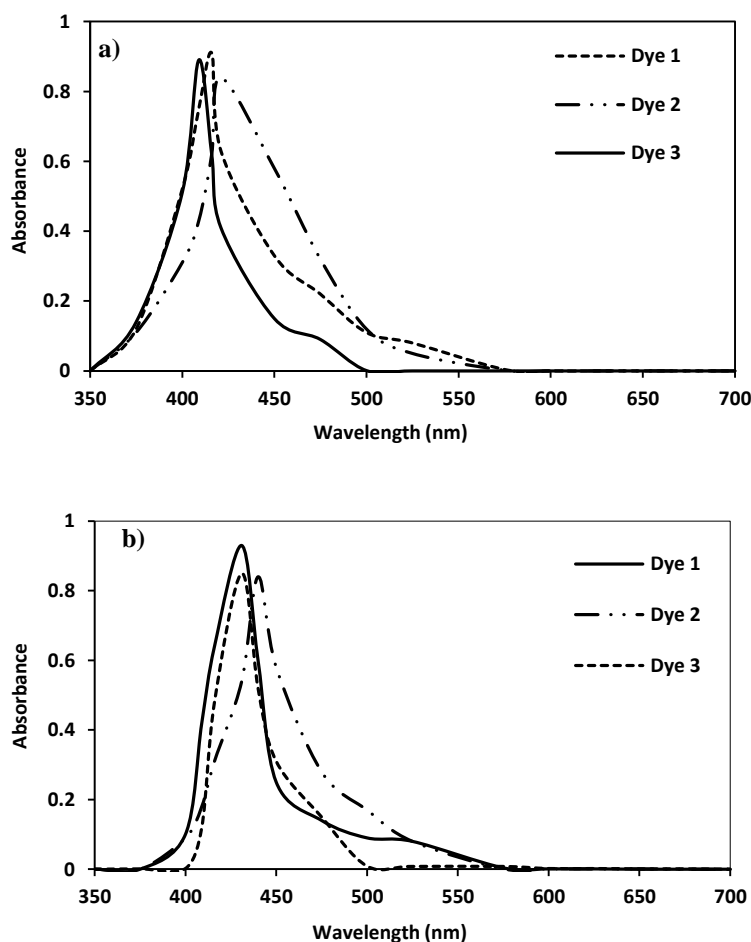
overall electron withdrawing ability of the system and hence lowering the level of the lower unoccupied molecular orbital (LUMO), thus reducing the gap between the higher unoccupied molecular orbital (HOMO) and the LUMO states [2, 29]. Upon dye adsorption on to a photo-anode surface, the wavelength of maximum absorption is bathochromically shifted by 21, 19 and 22 for Dye 1, Dye 2 and Dye 3, respectively, as compared to the corresponding spectra in solution, implying that dyes adsorbed on to the TiO<sub>2</sub> surface contain partial J-type aggregates [30-32].

The molar extinction coefficients of Dye 1 to Dye 3 in acetonitrile at their respective  $\lambda_{\max}$  are also shown in Table 1, indicating that these novel dyes have good light harvesting abilities [33]. The fluorescent characteristics of dyes measured in acetonitrile are studied. The results show that Dye 2 has been shown intense red fluorescence due to the charge transfer from the electron donating group (NH<sub>2</sub>) to the accepting group. The fluorescence emission maxima of the synthesized Dye 2 in the acetonitrile are 621nm.

**Table 1:** Absorption properties of the synthesized dyes

Dye	$\lambda_{\max}(\text{nm})^a$	$\epsilon (\text{M}^{-1}\text{cm}^{-1})$	$\lambda_{\max}(\text{nm})^b$	$\lambda_{\text{F}}(\text{nm})^a$
1	416	25364	437	506
2	421	25487	440	621
3	409	25421	421	523

a) Acetonitrile solution, b) on photoanode substrate



**Figure 2:** UV-Vis absorption spectra of a) in solution and b) on TiO<sub>2</sub> substrate.

The oxidation potential ( $E_{ox}$ ) of Dye 1 to Dye 3 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, Dye 2 and Dye 3 can therefore be calculated to be +1.17 V, +1.19 V and +1.15 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 method, which they are the same if the electrochemical oxidation is a reversible reaction [34, 35]. The  $E_{ox}-E_{0,0}$  level of Dye1, Dye2 and Dye3 is calculated to be -0.65 V, -0.72 V and -0.74 V vs  $Fc/Fc^+$  in acetonitrile.

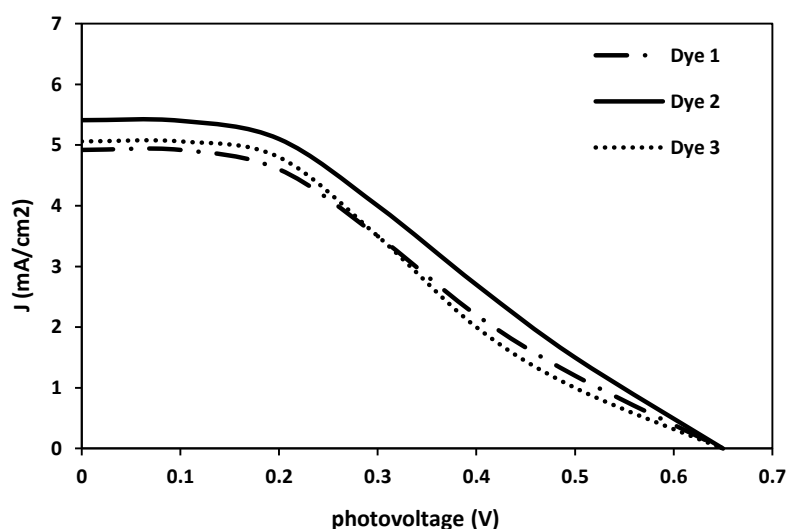
Dye-sensitized solar cells (DSSCs) were constructed and compared in order to clarify the relationships between the sensitizing behavior of Dye1 to Dye3 molecules and their structures. The DSSCs

utilized the synthesized organic dyes as sensitizers for nanocrystalline anatase  $TiO_2$ . A typical photocurrent–photovoltage ( $J-V$ ) curve for cells based on Dye1 to Dye 3 is depicted in Figure 3. The detailed photovoltaic parameters are also summarized in Table 2. The solar energy to electricity conversion efficiency ( $\eta$ ) 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 ( $P_{in}$ ) [34, 36].

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, Dye 2 and Dye 3 are 2.84%, 3.11% and 2.12%, respectively. The larger conversion efficiency of Dye 2 sensitizer is probably due to the stronger electron donating ability of the amino groups. The conversion efficiency of solar energy to electricity for the present organic dyes could be improved by extending the conjugated length of the organic dyes or by incorporation of a  $\pi$ -bridge [37, 38].

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

Dye	$V_{oc}$ (V)	$J_{sc}$ ( $mA \cdot cm^{-2}$ )	FF	$\eta$ (%)
1	0.63	7.77	0.58	2.84
2	0.62	9.12	0.55	3.11
3	0.63	6.12	0.55	2.12



**Figure 3:** Current density-voltage characteristics for Dye 1, Dye 2 and Dye 3.

## 4. Conclusions

Three metal-free organic dyes (D- $\pi$ -A) to be used as sensitizers in DSSCs were designed and synthesized based on indoline by employing cyanoacrylic acid as acceptor units. These dyes were identified by the use of FT-IR,  $^1\text{H}$ NMR,  $^{13}\text{C}$ NMR, elemental analysis and UV-Visible spectroscopic techniques. The spectrophotometric properties of the prepared organic dyes in solvent and on  $\text{TiO}_2$  films were examined. According to the results, Dye 2 containing amino group as the donor group showed bathochromic shifts compared to Dye 1 and Dye 3. In all cases, the absorption maxima of Dye 1, Dye 2 and Dye 3 applied on the surface of a  $\text{TiO}_2$  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 2.84, 3.11 and 2.12 percent were achieved for Dye 1, Dye 2 and Dye 3, respectively. Due to stronger electron donating ability of amino group, Dye 2 gave higher conversion efficiency than Dye 1 and Dye 3 containing a nitro and methoxy unit. 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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