



Synthesis and Application of Two Organic Dyes for Dye-Sensitized Solar Cells

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

¹ Ph.D. Student, Faculty of Polymer and Color Engineering, Amirkabir University of Technology, P.O.Box 15875-4413, Tehran, Iran.

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

³ Associate Professor, (a) Center of Excellence for Color Science and Technology and (b) Department of Organic Colorants, Institute for Color Science and Technology (ICST), P.O. Box: 16765-654, Tehran, Iran.

ARTICLE INFO

Article history:

Received: 04-03-2013

Final Revised: 30-04-2013

Accepted: 13-05-2013

Available online: 13-05-2013

Keywords:

Indigo

Dye-sensitized solar cells

Sensitizers

Photovoltaic materials

Conversion efficiencies

Photocurrent-photovoltage curves

ABSTRACT

In the present study, two new organic dyes based on indigo were prepared and used as sensitizers in dye-sensitized solar cells. To this end, indoxyl was utilized as the electron donor and cyanoacrylic acid as the electron acceptor anchoring groups. These dyes together with their corresponding intermediates were purified and characterized by FTIR, ¹HNMR, ¹³CNMR, elemental analysis and UV-Visible analytical techniques. Spectrophotometric evaluations of the prepared dyes in solution and on a TiO₂ substrate were carried out in order to assess changes in the status of the dyes. The results show that the dyes form j-type aggregates on the TiO₂ substrate. Finally, dye sensitized solar cells were fabricated in order to determine the current density/ photovoltage curves and conversion efficiencies of each dye. Prog. Color Colorants Coat. 6(2013), 109-117. © Institute for Color Science and Technology.

1. Introduction

Dye-sensitized solar cells (Grätzel cells) have attracted a great deal of interest, as they offer high energy conversion efficiencies at low cost [1]. Recently, more and more attention has been directed toward the application of metal-free organic dyes in dye-sensitized solar cells because such organic dyes do not contain the expensive ruthenium of limited resource, and have additionally, the advantages of relatively facile dye synthesis and capability of easy molecular tailoring [2]. Many organic dyes inclusive of coumarine [3], polyene

[4], hemicyanine [5], thiophene based [6], and indoline [7] dyes 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). Their properties can be finely tuned by independently altering, alternating or matching different groups in such D- π -A dyes. In research for high efficiency organic dyes for solar cells, development of new materials offering

*Corresponding author: moradian@aut.ac.ir

optimized thermal and photochemical stabilities, as well as appropriate optical and electrical properties is of utmost importance [8].

In the present study, two metal-free organic dyes were obtained utilizing indoxyl as the electron donor and cyanoacrylic acid or acrylic acid as the 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 nano anatase TiO_2 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.

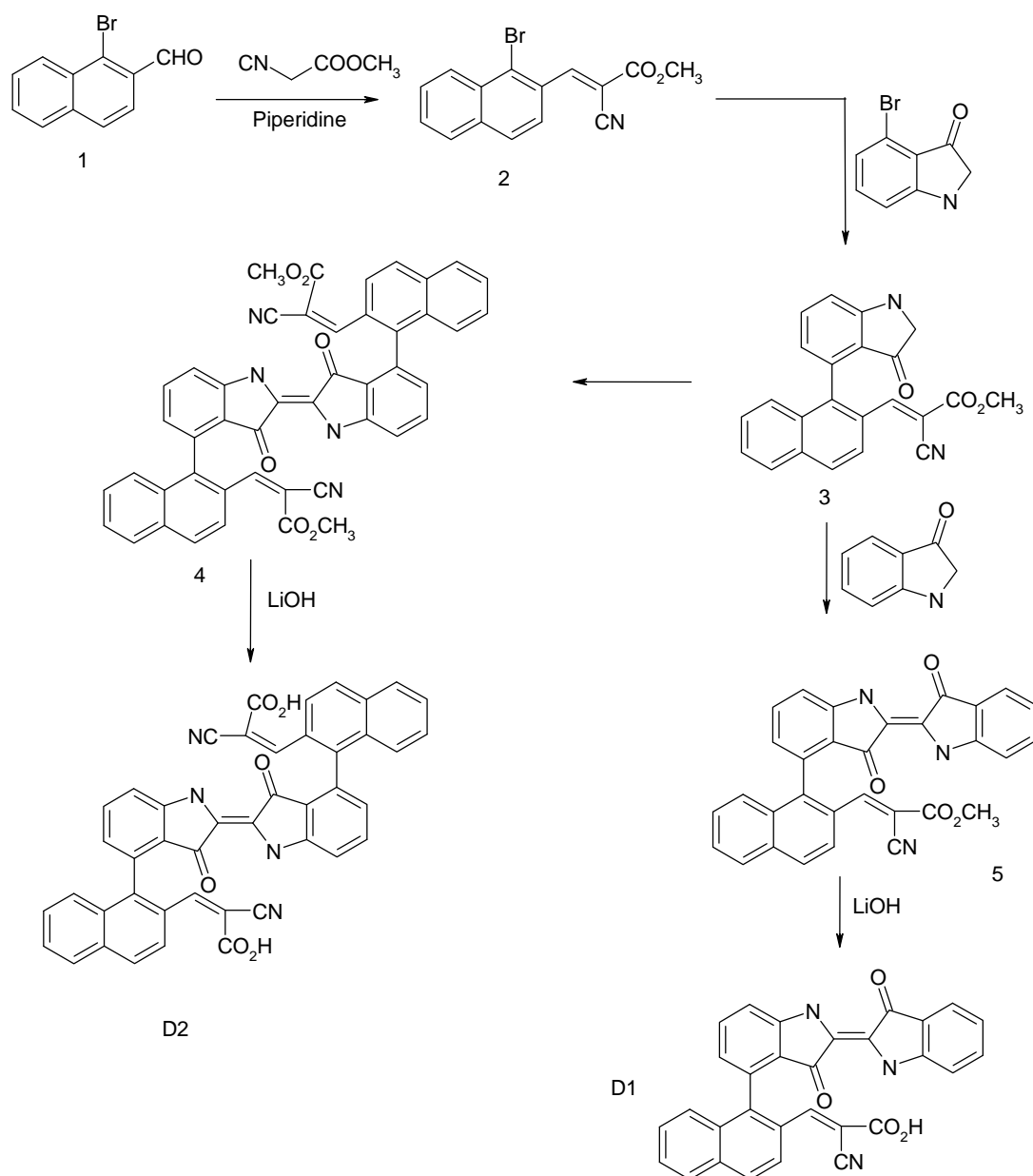


Figure 1: Synthesis route of the dyes.

2. Experimental

2.1. Materials and instrumentation

All compounds used in this study were of analytical grade unless otherwise stated. The FTIR measurements were carried out on a Bomem 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 intermediates

2.2.1. 2-Cyano-2-(1-bromonaphthalene)-carboxylate (2)

8 mmol 1-Bromo-2-naphthaldehyde (1), 16 mmol methyl cyanoacetate and 9 mmol of piperidine were added to 20 ml of acetonitrile. The mixture was refluxed for 6 hr. After the reaction was complete, the mixture was cooled to room temperature. The resulting precipitate was filtered and purified by silica gel column chromatography (ethyl acetate/hexane =1/5) (Yield=77%). mp 122–125 °C, FTIR (KBr) (Cm⁻¹): 3113: CH str. Ar, 1711: C=O str. Acid, 1609, 1455: C=C str; ¹H-NMR (CDCl₃), δ (ppm): 1.11 (s, 3H, CH₃), 6.89 (s, 1H, C9), 7.22-7.24 (d, 3H, C3, C4, C5), 7.35 (t, 2H, C6, C7), 7.66-7.67 (d, 1H, C8); Elem. Anal. Calcd. for C₁₅H₁₀BrNO₂: C, 56.98%; H, 3.16%, N, 4.43%;. Found: C, 56.95%; H, 3.18%, N, 4.46%.

2.2.2. 2-Cyano-2-(indoxyle)-carboxylate (3)

To [Pd(PPh₃)₄] (0.194 mmol) was added a deoxygenated solution of **2** (1.94 mmol) in DME (10 ml). This was followed by a deoxygenated solution of 3-boromoindoxyl (2.91 mmol) in ethanol (5 ml), and then a deoxygenated solution of aqueous sodium carbonate (16.5 mmol in 8.2 ml water). The resultant mixture was refluxed under nitrogen for 46 h over which time it turned deep blue. After cooling to room temperature, the mixture was quenched with 50 ml water. The resultant organic extracts were combined filtered; the resulting precipitate was filtered and purified by silica gel column chromatography (ethyl acetate/hexane =1/3) (Yield=77%). mp 159–161 °C, FTIR (KBr) (Cm⁻¹): 3117: CH str. Ar, 1709: C=O str. Acid, 1598, 1448: C=C str; ¹H-NMR (CDCl₃), δ (ppm): 0.82 (s, 3H, CH₃), 1.26 (s, 2H, CH₂), 7.04 (s, 1H, C9), 7.11-7.13 (d, 3H, C3, C4, C5), 7.24-7.26 (d, 3H, C8, C5', C7'), 7.49 (t, 1H, C6'), 7.56 (t,

2H, C6, C7); Elem. Anal. Calcd. for C₂₃H₁₅N₂O₃: C, 75.20%; H, 4.08%, N, 7.62%;. Found: C, 75.23%; H, 4.11%, N, 4.06%.

2.2.3. 4, 4'-(2-Cyano-2-naphthalene-carboxylate) indigo (4)

Under an inert atmosphere of argon, a solution of 2-Cyano-2-(indoxyle)-carboxylate (**3**) (9 mmol) in methanol (15 ml) was vigorously stirred with Na₂CO₃. After 1 h under stirring at 45 °C, the dark violet residue was filtered and intensively washed with methanol and cold water. The resulting precipitate was filtered and purified by silica gel column chromatography (ethyl acetate/hexane =1/2) (Yield=82%). mp 226–228 °C, FTIR (KBr) (Cm⁻¹): 3119: CH str. Ar., 1714: C=O str. Acid, 1605, 1455: C=C str; ¹H-NMR (CDCl₃), δ (ppm): 1.12 (s, 6H, 2CH₃), 6.72 (s, 2H, C16, C16'), 7.08-7.10 (d, 6H, C5, C7, C10, C5', C7', C10'), 7.30-7.33 (d, 6H, C11, C12, C15, C11', C12', C15'), 7.56 (t, 6H, C6, C13, C14, C6', C13', C14'); Elem. Anal. Calcd. for C₄₆H₂₆N₄O₆: C, 75.61%; H, 3.56%, N, 7.67%;. Found: C, 75.64%; H, 3.54%, N, 7.66%.

2.2.4. 4-(2-Cyano-2-naphthalene-carboxylate) indigo (5)

Under an inert atmosphere of argon, a solution of 2-Cyano-2-(indoxyle)-carboxylate (**3**) (9 mmol), indoxyl (5 mmol) in methanol (15 ml) was vigorously stirred with Na₂CO₃. After 1 h under stirring at 45 °C, the dark violet residue was filtered and intensively washed with methanol and cold water. The resulting precipitate was filtered and purified by silica gel column chromatography (ethyl acetate/hexane =1/2) (Yield=85%). mp 186–188 °C, FTIR (KBr) (Cm⁻¹): 3116: CH str. Ar., 1706: C=O str. Acid, 1600, 1452: C=C str; ¹H-NMR (CDCl₃), δ (ppm): 1.35 (s, 3H, CH₃), 6.84 (s, 1H, C16), 7.16-7.18 (d, 6H, C5, C7, C15, C12, C11, C10), 7.24-7.26 (d, 2H, C4', C7'), 7.56 (t, 5H, C6, C13, C14, C5', C6'); Elem. Anal. Calcd. for C₃₁H₁₇N₃O₄: C, 75.15%; H, 3.43%, N, 8.48%;. Found: C, 75.14%; H, 3.47%, N, 8.46%.

2.3. Synthesis of Dyes

To a solution of (4) or (5) (5mmol) in DMSO (3.5 ml), 0.8 ml of 1M LiOH was added at 0 °C. The mixture was stirred overnight at room temperature, and the reaction quenched by addition of 30 ml of H₂O. The resulting precipitate was collected by filtration, re-dissolved in

acetone, and concentrated in vacuo to give the corresponding dye D1 or D2. The dyes were then purified by silica gel column chromatography (ethyl acetate/hexane =1/2).

2.3.1. 4-(2-Cyano-2-naphthalene-acrylic acid) indigo (D1)

(Yield = 82%); mp 165–167 °C, FTIR (KBr) (cm^{-1}): 3110: CH str. Ar, 1705: C=O str. Acid, 1611, 1458: C=C str.; $^1\text{H-NMR}$ (CDCl_3), δ (ppm): 6.88 (s, 1H, C16), 7.22–7.24 (d, 6H, C5, C7, C15, C12, C11, C10), 7.32–7.34 (d, 2H, C4', C7'), 7.61 (t, 5H, C6, C13, C14, C5', C6'), 10.86 (s, 1H, CO_2H); $^{13}\text{CNMR}$ (CDCl_3) δ (ppm): 219.73 (C=O, Ket), 152.31 (C=O, Acid), 110.32, 110.87, 111.46, 112.13, 112.84, 113.72, 114.63, 115.92, 116.09, 116.73, 118.55, 119.92, 120.31, 121.83, 122.21, 123.48, 124.32, 125.76, 126.54, 127.49, 129.37, 129.99, 130.11, 131.45, 132.53 (Ar.), 60.38, 58.71 (Aliphatic); Elem. Anal. Calcd. for $\text{C}_{30}\text{H}_{15}\text{N}_3\text{O}_4$: C, 74.84%; H, 3.11%, N, 8.73%; Found: C, 74.80%; H, 3.13%, N, 8.75%.

2.3.2. 4, 4'-(2-Cyano-2-naphthalene-acrylic acid) indigo (D2)

(Yield = 78.5%); mp 211–215 °C, FTIR (KBr) (Cm^{-1}): 3116: CH str. Ar, 1711: C=O str. Acid, 1603, 1449: C=C str.; $^1\text{H-NMR}$ (CDCl_3), δ (ppm): 6.81 (s, 2H, C16, C16'), 7.15–7.17 (d, 6H, C5, C7, C10, C5', C7', C10'), 7.36–7.38 (d, 6H, C11, C12, C15, C11', C12', C15'), 7.59 (t, 6H, C6, C13, C14, C6', C13', C14'), 10.55 (s, 1H, CHO_2); $^{13}\text{CNMR}$ (CDCl_3) δ (ppm): 221.48 (C=O, Ket.), 155.72 (C=O, Acid), 109.43, 109.82, 110.11, 110.77, 111.82, 112.08, 112.88, 113.67, 114.52, 115.17, 115.83, 116.82, 117.00, 117.48, 118.74, 119.11, 119.90, 120.26, 120.47, 121.32, 121.94, 122.22, 122.75, 123.24, 124.44, 124.74, 125.83, 126.36, 126.82, 127.13, 129.37, 129.80, 130.42 (Ar.), 59.42, 57.86 (Aliphatic); Elem. Anal. Calcd. for $\text{C}_{44}\text{H}_{22}\text{N}_4\text{O}_6$: C, 75.21%; H, 3.13%, N, 7.97%; Found: C, 75.24%; H, 3.14%, N, 7.95%.

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 5×10^{-5} M ethanolic solution of the dye containing 7% 4-tert-butylpyridine and 50 mM $3\alpha,7\alpha$ -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 (D1 or D2). 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 [10, 11].

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 mm \times 4 mm) by using a Bunko-Keiki CEP-2000 system.

3. Results and discussion

3.1. Synthesis

The organic dyes D1 and D2 were synthesized as schematically shown in Figure 1. Component 1 was prepared in a similar way as described in the literature [9, 12]. This material was allowed to react separately with methyl cyanoacetate by the Knoevenagel reaction in the presence of piperidine to give compound 2 [2, 13]. Equimolar solution 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. The enolate anion is formed after removing a proton from the methylenic group of the ethyl cyanoacetate. 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]. Compound 2 was allowed to react with indoxyl to give compound 3. This type of coupling procedure was first reported in 1901 by Ullmann as a reaction that generates a carbon-carbon bond between two aromatic nuclei. It involves heating the mixture of the aryl halides with copper powder or copper bronze at 100–360 °C either with or without any solvent. Products of this reaction are the desired biaryl(s) and the corresponding copper(I) halide. In this study, bromonaphthaldehyde (from part one) was converted into binaphthaldehyde using excess copper powder in DMF at 150 ° [9–14]. Compound 3 was made to react firstly with indoxyl and secondly by itself to give compounds 4 and

5, respectively. Finally, D1 and D2 were synthesized through the reaction between compounds 4 and 5 with LiOH, respectively.

3.2. UV-Visible absorption and fluorescence spectra

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 545.5 nm for D1 can be assigned to an intra molecular charge transfer between the donor group and the acrylic acid group [14], providing an efficient charge-separation for the excited state. For the cyanoacetic acid based dyes (D2), when an extra electron acceptor (-CN) was linked to the vinyl bridge, the λ_{\max} had a bathochromic shift from 545.5 nm for D1 to 573.6 nm for D2. The shift in the maximum

absorption peak arises from the fact that more stronger electron acceptor of two 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 onto a TiO₂ surface, the wavelength of maximum absorption is bathochromically shifted by 22.5 and 24 for D1 and D2, respectively as compared to the corresponding spectra in solution, implying that dyes adsorbed onto the TiO₂ surface contain partial J-type aggregates [15-17]. The molar extinction coefficients of D1 and D2 in THF at their respective λ_{\max} are also shown in Table 1, indicating that these novel dyes have good light harvesting abilities [18].

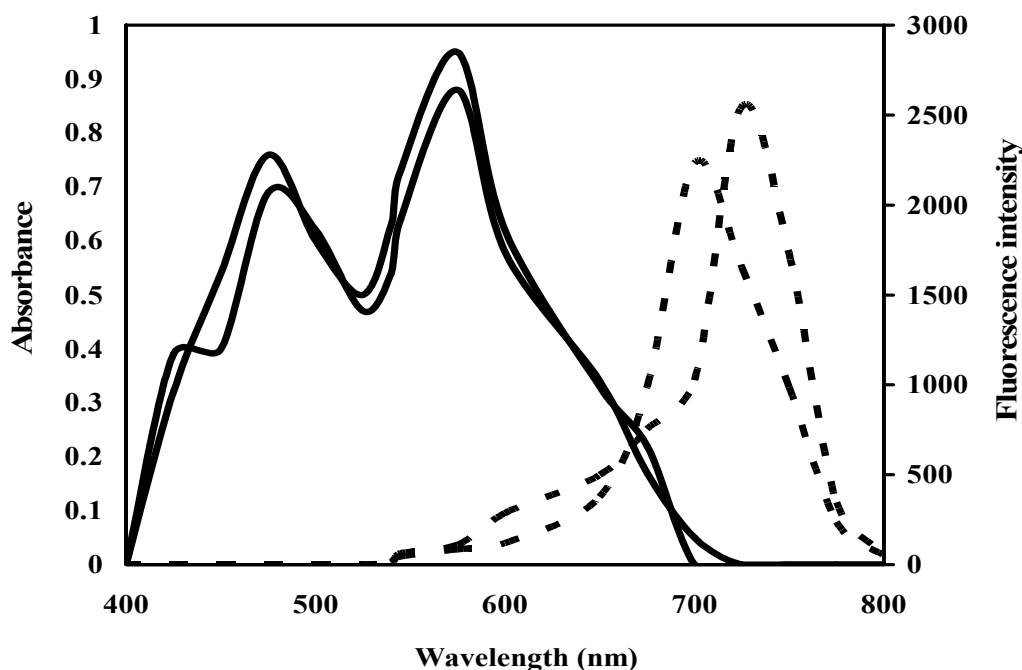


Figure 2: UV-Vis absorption and fluorescence spectra of D1 and D2 dyes.

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)
D1	545.5	36383	568	700
D2	573.6	36429	597.6	712

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 dyestuffs D1 and D2 in the THF is 700 and 712 nm, respectively.

3.3. Photovoltaic performance

Dye-sensitized solar cells (DSSCs) were constructed and compared in order to clarify the relationships between the sensitizing behavior of D1 and D2 dye molecules and their structures. The DSSCs utilized these dyes as sensitizers for nanocrystalline anatase TiO₂. A typical photocurrent–photovoltage (J–V) curve for cells based on D1 and D2 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_m) according to equation 1 [19, 20]:

$$\eta = \frac{[J_{sc}(\text{mAcm}^{-2})][V_{oc}(\text{V})][FF]}{P_m(\text{mW.cm}^{-2})} \quad (1)$$

According to the results shown in Table 2, under the standard global AM 1.5 solar conditions, the conversion efficiencies of cells containing D1 and D2 are 3.11% and 3.45%, respectively. The larger conversion efficiency of D2 sensitizer is probably due to the stronger electron withdrawal ability of the combination of two cyanoacrylic groups.

Table 2: Photovoltaic performance of DSSCs based on D1 and D2 dyes.

Dye	V_{oc} (V)	J_{sc} (mA.cm ⁻¹)	FF	η (%)
D1	0.64	7.47	0.65	3.11
D2	0.63	8.55	0.64	3.45

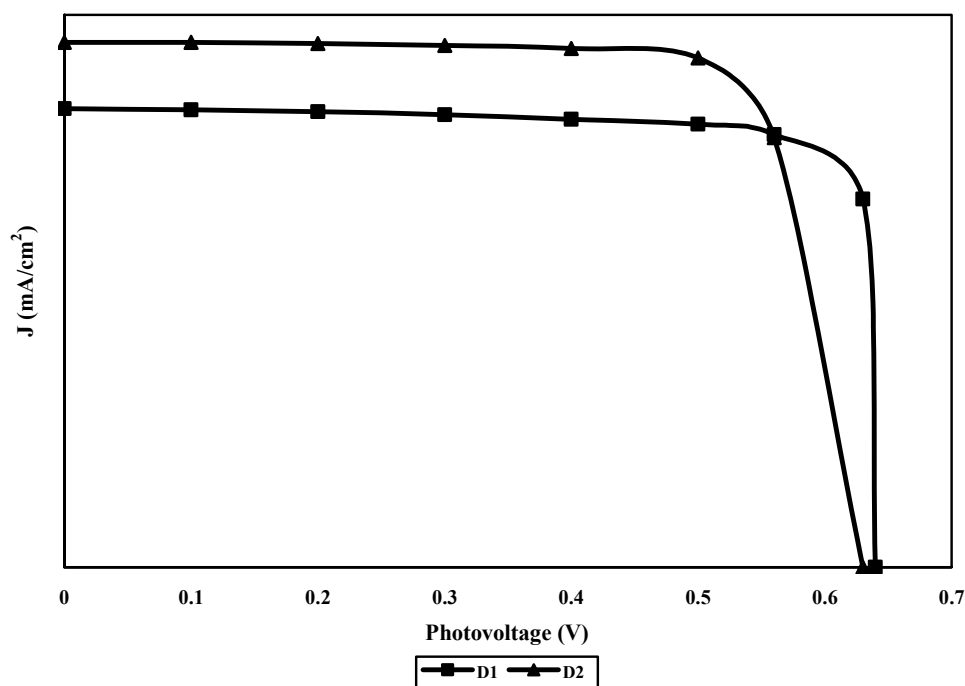


Figure 3: Current density-voltage characteristics for D1 and D2 dyes.

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, 21-23].

3.4. Electrochemical properties

The oxidation potential (Eox) of D1 and D2 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) was due to the electrochemical oxidation of Dyes. The oxidation peak potential (Epa) for D1 and D2 can therefore be calculated to be +0.40 V and +0.44 V vs Fc/Fc⁺ in acetonitrile, respectively. Although the standard Eox

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 [19]. No reduction peak was observed for the synthesized dyes. Therefore, the Eox-E0-0 level, where E0-0 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 E0-0 of D1 and D2 were observed at 660 nm and 672 nm, respectively corresponding to 1.87 eV and 1.81 eV, respectively. Therefore, the Eox-E0-0 level of D1 and D2 is calculated to be -1.47 V and -1.3V vs Fc/Fc⁺ in acetonitrile. A typical cyclic voltammetric curve for cells based on D1 and D2 is depicted in Figure 4.

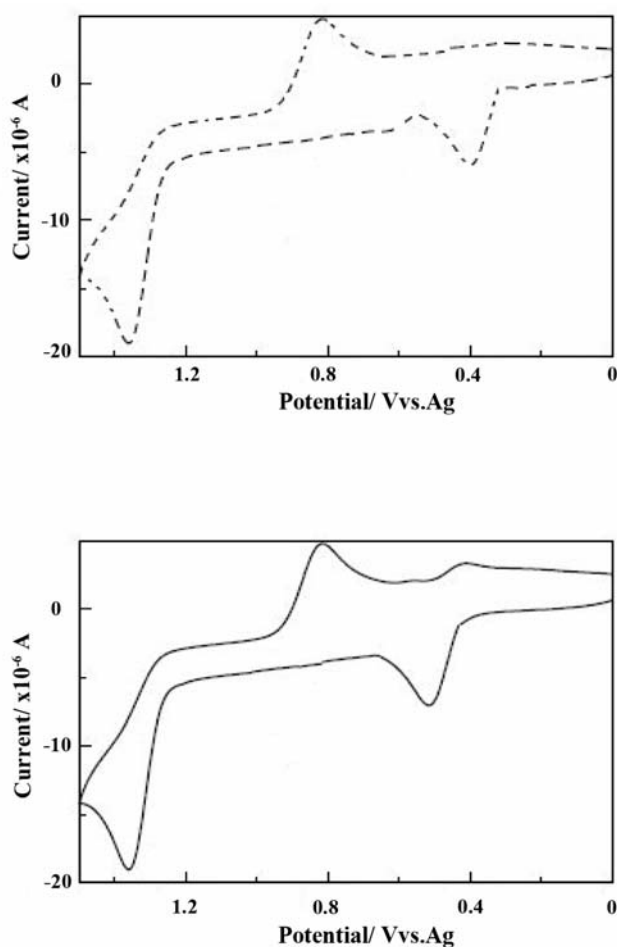


Figure 4: cyclic voltammetric curve for D1 and D2 dyes (---- D1, —D2)

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 cyanoacrylic acid as acceptor units. These dyes were synthesized and their structures together with the structures of their corresponding intermediates were identified by the use of 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, D2 containing two cyanoacrylic acid as the acceptor group showed bathochromic shifts compared to D1. In all cases, the absorption maxima of D1 and D2 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 3.11 and 3.45 per cent were achieved for D1 and D2, respectively. D2 containing two cyanoacrylic acid gave higher conversion efficiency than the dye D1 containing a cyanoacrylic acid as acceptor unit attributable 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.

Acknowledgement

The authors sincerely thank the Center of Excellence for Color Science and Technology for making this investigation possible.

5. References

1. B. O'Regan, M. Grätzel, A low cost, high efficiency solar cell based on dye-sensitized colloidal TiO_2 films, *Nature*, 353(1991), 737-740.
2. T. Wu, M. Tsao, F. Chen, S. Su, C. Chang, H. Wang, Y. Lin, W. Yang, I. Sun, Synthesis and characterization of organic dyes containing various donors and acceptors, *Int. J. Mol. Sci.*, 11(2010), 329-353.
3. (a) K. Hara, K. Sayama, Y. Ohga, A. Shinpo, S. Suga, H. Arakawa, A coumarin derivative dye sensitized nanocrystalline TiO_2 solar cell having a high solar energy conversion efficiency up to 5.6%, *Chem Commun.*, 2001, 569-570; (b) K. Hara, T. Sato, R. Katoh, A. Furude, Y. Ohga, A. Shinpo, S. Suga, K. Sayama, H. Sugihara, H. Arakawa, Molecular design of coumarin dyes for efficient dye-sensitized solar cells, *J. Phys. Chem. B*, 107(2003), 597-606; (c) A. Furube, R. Katoh, K. Hara, T. Sato, S. Murata, H. Arakawa, M. Tachiya, Lithium ion effect on electron injection from a photoexcited coumarin derivative into a TiO_2 nanocrystalline film investigated by visible to IR ultrafast spectroscopy, *J. Phys. Chem. B*, 109(2005), 16406-16414; (d) Z. Wang, Y. Cui, K. Hara, Y. Danoh, C. Kasada, A. Shinpo, A high light harvesting efficiency coumarin dye for stable dye-sensitized solar cells, *Adv. Mater.*, 19(2007), 1138-1141.
4. (a) K. Hara, M. Kurashige, S. Ito, A. Shinpo, S. Suga, K. Sayama, H. Arakawa, Novel polyene dyes for highly efficient dye-sensitized solar cells, *Chem. Commun.*, 2003, 252-253; (b) M. Velusamy, K. Thomas, J. Lin, Y. Hsu, K. C. Ho, Organic dyes incorporating low-band-gap chromophores for dye-sensitized solar cells, *Org. Lett.*, 7(2005), 1899-1902; (c) S. Li, K. Jiang, K. Shao, L. Yang, Novel organic dyes for efficient dye-sensitized solar cell, *Chem. Commun.*, 2006, 2792-2794; (d) R. Chen, X. Yang, H. Tian, L. Sun, Tetrahydroquinoline dyes with different spacers for organic dye-sensitized solar cells, *J. Photochem. Photobiol., A*, 189(2007), 295-300; (e) P. Qin, X. Yang, R. Chen, L. Sun, Influence of π -conjugation units in organic dyes for dye-sensitized solar cells, *J. Phys. Chem. C*, 111(2007), 1853-1860.
5. (a) Z. Wang, F. Li, C. Huang, Highly efficient sensitization of nanocrystalline TiO_2 films with styryl benzothiazolium propylsulfonate, *Chem. Commun.*, 2000, 2063-2064; (b) Z. Wang, F. Li, C. Huang, Photocurrent enhancement of hemicyanine dyes containing RSO_3^- group through treating TiO_2 films with hydrochloric acid, *J. Phys. Chem. B*, 105(2001), 9210-9217; (c) Q. Yao, L. Shan, F. Li, D. Yin, C. Huang, An expanded conjugation photosensitizer with

- two different adsorbing groups for solar cells, *New J. Chem.*, 27(2003), 1277-1283.
6. (a) N. Koumura, Z. Wang, S. Mori, M. Miyashita, E. Suzuki, K. Hara, Alkyl-functionalized organic dyes for efficient molecular photovoltaics, *J. Am. Chem. Soc.*, 128(2006), 14256-14257; (b) Z. Wang, N. Koumura, Y. Cui, M. Takahashi, H. Sekiguchi, A. Mori, T. Kubo, A. Furube, K. Hara, Hexylthiophene functionalized carbazole dyes for efficient molecular photovoltaics: tuning of solar-cell performance by structural modification, *Chem. Mater.*, 20(2008), 3993-4003.
 7. S. Ito, H. Miura, S. Uchida, M. Takata, K. Sumioka, P. Liska, P. Comte, P. Péchy, M. Grätzel, High-conversion-efficiency organic dye-sensitized solar cells with a novel indoline dye, *Chem. Commun.*, (2008), 5194-5196.
 8. A. Khazaji, S. Hotchandani, S. Das, P. Kamat, Controlling dye (merocyanine-540) aggregation on nanostructured TiO₂ films: an organized assembly approach for enhancing the efficiency of photosensitization, *J. Phys. Chem. B*, 103(1999), 4693-4700.
 9. T. Kanti Pradhan, A. De, J. Mortier, Application of directed metalation in synthesis. Part 8: Interesting example of chemoselectivity in the synthesis of thioaurones and hydroxy ketones and a novel anionic ortho-Fries rearrangement used as a tool in the synthesis of thienopyranones and thiafluorenones, *Tetrahedron*, 6(2005), 9007-9017.
 10. M. Matsui, T. Fujita, Y. Kubota, K. Funabiki, J. Jin, T. Yoshida, H. Miura, The use of indoline dyes in a zinc oxide dye-sensitized solar cell, *Dyes Pigm.*, 80(2009), 233-238.
 11. M. Nazeeruddin, A. Kay, I. Rodicio, R. Humpbry-Baker, E. Miiller, P. Liska, N. Vlachopoulos, M. Grätzel, Conversion of light to electricity by cis-X₂bis(2,2'-bipyridyl-4,4'-dicarboxylate) ruthenium(II) charge-transfer sensitizers (X = Cl⁻, Br⁻, I⁻, CN⁻, and SCN⁻) on nanocrystalline titanium dioxide electrodes, *J. Am. Chem. Soc.*, 115(1993), 6382-6390.
 12. P. Sommeling, B. Oregan, R. Haswell, H. Smit, N. Bakker, T. Smits, J. Kroon, J. Roosmalen, Influence of a TiCl₄ post-treatment on nanocrystalline TiO₂ films in dye-sensitized solar cells, *J. Phys. Chem. B*, 110(2006), 19191-19197.
 13. M. Tabatabaee, H. Bagheri, M. Shahvazian, Application of thionine dye for highly sensitive and selective catalytic kinetic determination of Osmium, *Prog. Color Colorants Coat.*, 3(2010), 33-40.
 14. M. Liang, W. Xu, F. Cai, P. Chen, B. Peng, J. Chen, Z. Li, New triphenylamine-based organic dyes for efficient dye-sensitized solar cells, *J. Phys. Chem. C*, 111(2007), 4465-4472.
 15. S. Kim, J. Lee, S. Kang, J. Ko, J. Yung, S. Fantacci, F. DeAngelis, M. DiCenco, K. Nazeeruddin, M. Gratzel, Molecular engineering of organic sensitizers for solar cell applications, *J. Am. Chem. Soc.*, 128(2006), 16701-16707.
 16. L. Schmidt Mende, U. Bach, R. Baker, T. Horiuchi, H. Miura, S. Ito, S. Uchida, M. Gratzel, Organic dyes for highly efficient solid-state dye-sensitized solar cells, *Adv. Mater.*, 17(2005), 813-815.
 17. D. Hagberg, J. Yum, H. Lee, F. Angelis, T. Marinado, K. Karlsson, R. Humphry Baker, L. Sun, A. Hagfeldt, M. Gratzel, M. Nazeeruddin, Molecular engineering of organic sensitizers for dye-sensitized solar cell applications, *J. Am. Chem. Soc.*, 130(2008), 6259-6266.
 18. S. Park, Y. Won, Y. Choi, J. Kim, Molecular design of organic dyes with double electron acceptor for dye-sensitized solar cell, *Energy Fuels*, 23(2009), 3732-37326.
 19. G. Boschloo, A. Hagfeldt, Activation energy of electron transport in dye-sensitized TiO₂ solar cells, *J. Phys. Chem. B*, 109(2005), 12093-12098.
 20. M. Matsui, T. Fujita, Y. Kubota, K. Funabiki, J. Jin, T. Yoshida, H. Miura, Substituent effects in a double rhodanine indoline dye on performance of zinc oxide dye-sensitized solar cell, *Dyes Pigm.*, 86(2010), 143-148.
 21. A. Khosravi, K. Gharanjig, S. Moradian, M. Hosseinnezhad, A Kinetic study on the dissolution of tqwo naphthalimide based synthesized disperse dyestuffs in the presence of dispersing agent, *Prog. Color Colorants Coat.*, 4(2011), 107-112.
 22. K. Hara, T. Sato, R. Katoh, A. Furube, Y. Ohga, A. Shinpo, Molecular design of coumarin dyes for efficient dye-sensitized solar cells, *J. Phys. Chem. B*, 107(2003), 597-606.
 23. F. Dolatzadeh, S. Moradian, M. M. Jalili, Effect of nano silica on moisture absorption of polyurethane clear coat as studied by EIS and gravimetric methods, *Prog. Color Colorants Coat.*, 3(2010), 92-100.