

Synthesis and Evaluation of Photovoltaic Properties of an Organic Dye for Dye-Sensitized Solar Cells

M. Hosseinejad, K. Gharanjig

Abstract—In the present study, metal free organic dyes were prepared and used as photo-sensitizers in dye-sensitized solar cells. Double rhodanine was utilized as the fundamental electron acceptor group to which electron donor aldehyde with varying substituents was attached to produce new organic dye. This dye was first purified and then characterized by analytical techniques. Spectrophotometric evaluations of the prepared dye in solution and on a nano anatase TiO₂ substrate were carried out in order to assess possible changes in the status of the dyes in different environments. The results show that the dye form j-type aggregates on the nano TiO₂. Additionally, oxidation potential measurements were also carried out. Finally, dye sensitized solar cell based on synthesized dye was fabricated in order to determine the photovoltaic behavior and conversion efficiency of individual dye.

Keywords—Conversion efficiency, dye-sensitized solar cell, photovoltaic behavior, sensitizer.

I. INTRODUCTION

IN the past two decades the dye-sensitized solar cell (DSSCs) has attracted remarkable attention as one of the most promising technologies toward cost-effective solar energy exploitation [1]. Recently, more attention has been directed toward the application of metal-free organic dyes in DSSCs because such organic dyes do not contain the expensive ruthenium and have additionally, the advantages of relatively facile dye synthesis and capability of easy molecular tailoring [2]. Many organic dyes exhibiting relatively high performances in DSSCs have so far been designed and developed [3]. Due to the ever increasing energy crisis, many researches has been focused in recent years, on the synthesis of new sensitizers and/or on the study of the mechanism of energy conversion. In such compounds, the electron-donating and electron-accepting groups are connected through a π -conjugated linker (i.e. 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 optimized thermal and photochemical stabilities, as well as appropriate optical and electrical properties is of utmost importance [4].

In the present investigation, metal-free donor acceptor π -conjugated organic dyes based on indoline as the electron donor, a simple naphthyl residue, as part of the π -conjugated

system and double rhodanine as the electron withdrawing (acceptor) anchoring groups are proposed and investigated. The dye was purified and characterized. The spectrophotometric properties of the prepared organic dye in solvent and on a nano anatase TiO₂ substrate was also examined. Dye sensitized solar cell was then fabricated utilizing this metal-free organic dye and its photovoltaic behavior was determined. Schematic representation of the route for synthesis of the prepared metal-free organic dye is given in Fig. 1.

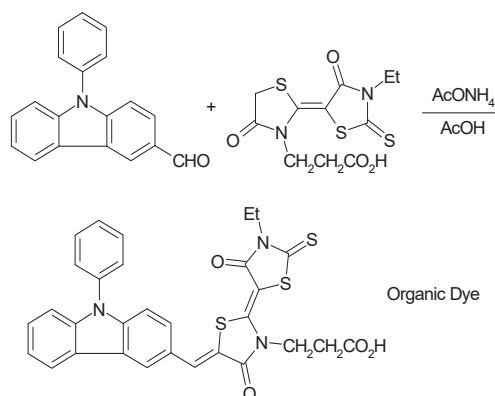


Fig. 1 Synthesis route of organic dye

II. EXPERIMENTAL

A. Materials and Instrumentation

All compounds used in this study were of analytical grade unless otherwise stated. The substituted aldehyde component [3] together with double rhodanine were prepared in similar ways as described in the literature [5]. The FT-IR measurements were carried out on a Bomem Canada instrument. NMR measurements were carried out on a 500 MHz Joel instrument. Differential scanning calorimetry (DSC) and UV-Visible spectrophotometry were carried out on a Dupont 2000DSC instrument and a Cecil 9200 double beam transmission spectrophotometer, respectively. The fluorescence spectra of dye solution were obtained by Oseaan Optics Usb2000flg Fluorometer. Fluorescence quantum yield was determined on the basis of the absorption and fluorescence spectra, using fluorescein as standard ($\Phi_{\text{ref}} = 0.95$).

B. Synthesis of Dye

A substituted aldehyde compound (1.0 mmol), together with double rhodanine (1.0 mmol) and ammonium acetate

M. Hosseinejad is with the Institute for Color Science and Technology, Tehran, Iran (corresponding author, phone: 98-21-22944184; Fax: 98-21-22947537; e-mail: hosseinezhad-mo@icrc.ac.ir).

K. Gharanjig is with the Institute for Color Science and Technology, Tehran, Iran (email: gharanjig@icrc.ac.ir)

(1mg) were added separately to acetic acid (20 ml). The mixture was refluxed for 1 hour. After the reaction was complete which was checked by TLC; water was added to the mixture. The resulting precipitate was filtered and purified by silica gel column chromatography (chloroform: methanol = 8:1). In this way a dye was obtained, the physical and spectral data of which is as follows: Yield = 72%; mp: 284 °C; FTIR (KBr) (Cm^{-1}): 3011: CH str. Ar, 1698: C=O str. Acid, 1617, 1455: C=C str.; $^1\text{H-NMR}$ (CDCl_3), δ (ppm): 1.33 (3H, CH_3), 2.74 (t, 2H, CH_2), 3.75-3.77 (m, 1H), 4.11 (t, 2H, N- CH_2), 4.21 (t, 2H, N- CH_2), 7.11 (t, 3H, ArH), 7.22 (t, 2H, ArH), 7.37-7.40 (d, $J=7.5$ Hz, 2H, ArH), 7.55 (s, 1H, ArH), 7.75-7.77 (d, $J=7.7$ Hz, 4H, ArH), 9.82 (s, 1H, CO_2H); $^{13}\text{C-NMR}$ (CDCl_3), δ (ppm): 54.12 (2C), 57.32 (2C), 110.12, 112.58, 115.47, 116.56 (2C), 118.22, 123.16 (3C), 124.95, 127.84 (2C), 128.28, 129.19, 130.03 (4C), 132.14, 135.77, 144.00, 146.47, 149.19 (4C), 163.85 (C=O, Acid), 205.14, 208.53 (C=O); Elem. Anal. Calcd. for $\text{C}_{30}\text{H}_{23}\text{S}_3\text{O}_4\text{N}_2$: C, 63.04%; H, 4.02%; N, 4.90%. Found: C, 63.08%; H, 4.08%; N, 4.93%.

C. 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 (2 ml) of dyes 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} [2].

D. DSSCs Assembly

A nanocrystalline anatase TiO_2 film was coated on a transparent glass support. Organic dye was adsorbed by dipping a separate coated glass in a $5 \times 10^{-5} \text{ M}$ ethanolic solution of each dye containing 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 nano TiO_2 film only appeared after the TiO_2 electrodes were dipped in the dye solution for at least 8 hours. Finally, the film was washed with a 1:1 acetonitrile:ethanol solution. Acetonitrile: ethylenecarbonate (1:4) containing tetrabutyl ammonium iodide (0.5 mol dm^{-3}) was used as an electrolyte. Dye-adsorbed TiO_2 electrode, together with a Pt counter electrode and the mentioned electrolyte solution were separately assembled into a sealed sandwich type solar cell [2].

For solar cell 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.

III. RESULTS AND DISCUSSION

An organic dye was synthesized based on double rhodanine as schematically shown in Fig. 1. The aldehyde component [3] and double rhodanine were prepared in a similar way as described in the literature [5]. Finally, aldehydes were allowed to react separately with active methylene containing double rhodanine in the presence of a base to give organic dye. This dye was purified and characterized to have the structures given in Fig. 1. The yield of reaction for these dye varied in the 72 percent. Table I depicts the wavelength of maximum absorption (λ_{max}) together with the respective molar extinction coefficient in dimethyl sulfoxide (DMSO) for individual dye as well as the corresponding λ_{max} on nano TiO_2 films. The wavelength of maximum fluorescence (λ_{F}) for dye is also given in Table I.

TABLE I
ABSORPTION PROPERTIES OF ORGANIC DYE

Properties	λ_{max} (nm) ^a	ϵ ($\text{LM}^{-1}\text{Cm}^{-1}$)	λ_{max} (nm) ^b	λ_{F} (nm)
Dye	542	55232	554	675

a In solution; b On TiO_2 .

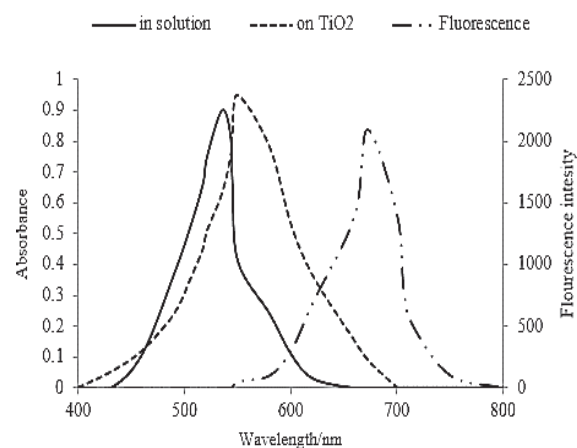


Fig. 2 UV-Vis absorption and fluorescence spectra of dye

Fig. 2 shows the adsorption and fluorescence curves of synthesized dye. However, the dye shows bathochromic shifts on nano TiO_2 compared to their corresponding λ_{max} in solution. These facts suggest the formation of a partial j-type aggregation on nano TiO_2 . The suitable absorption of dye can be attributed to an intramolecular charge transfer between the donor to acceptor groups [6] which provides an efficient charge separation for the excited state. This is assigned to two electron donating substituents on the aldehyde component, which in turn lowers, the level of the lower unoccupied molecular orbital (LUMO) thus reducing the gap between the higher unoccupied molecular orbital (HOMO) and the corresponding LUMO states [3].

The fluorescent characteristics of dyes measured in THF are also reported in Table I. In THF solutions, synthesized dye shows intense blue fluorescence due to charge transfer to the electron accepting groups. The fluorescence emission maxima of indigo dyes are higher than indole-based dyes for example,

HY1-HY2 (548-553 nm) [7] due to presence carbonyl groups in structure indigo organic dyes.

The oxidation potential (E_{ox}) of organic dye 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 the Dye. The oxidation peak potential (E_{pa}) for organic dye can therefore be calculated to be 0.65 vs Fc/Fc^+ in acetonitrile. 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 [6]. No reduction peak was observed for the synthesized dye. Therefore, the $E_{ox}-E_{0.0}$ level, where $E_{0.0}$ represents the intersection of normalized absorption and the fluorescence spectra in DMSO (Fig. 2), was calculated. This is considered to correspond to the reduction potential [1]. The $E_{0.0}$ of organic dye was observed at 618 nm corresponding to 2.01 eV, respectively. Therefore, the $E_{ox}-E_{0.0}$ level of organic dye is calculated to be -1.7 V vs Fc/Fc^+ in acetonitrile.

The photovoltaic properties of organic dye were attained. Typical photocurrent–photovoltage ($J-V$) curves of cell based on organic dye is illustrated in Fig. 3. Detailed photovoltaic parameters of organic dye are also summarized in Table II. The solar energy to electricity conversion efficiency (η) of the DSSCs is calculated from the short circuit current (J_{sc}), the open-circuit photovoltage (V_{oc}), the fill factor (FF), and the intensity of the incident light (P_{in}) [2].

TABLE II
PHOTOVOLTAIC PERFORMANCE OF DSSCs BASED ON ORGANIC DYE

Properties	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	η (%)
Dye	0.65	9.01	0.64	3.75

The results carried out under the standard global AM 1.5 solar condition and shown in Table II demonstrate that a maximum value of 3.75% for the conversion efficiency of cells containing organic dye was achieved. The large conversion efficiency of sensitizer is probably due to the stronger electron donating ability of the respective substituted aldehyde component. The conversion efficiency of solar energy to electricity of such organic dyes could be improved by addition of further electron donating groups on the aldehyde component, extending the conjugated length of these organic dyes, incorporation of a thiophene π -bridge [3] or by using completely different aldehyde components.

Fig. 4 shows that the maximum Incident Photo-to Current Efficiency (IPCE) values for the synthesized dyes are: organic dye (72.1). This is also true for J_{sc} (mA/cm^2) values organic dye (9.01), thus the conversion efficiency (%) is large: D1 (3.75). In fact, the maximum IPCE value mainly affects the conversion efficiency value.

IV. CONCLUSION

A metal-free organic dye of type (D- π -A) as potential

sensitizers for DSSCs were designed and synthesized by employing double rhodanine as the acceptor unit. This dye was synthesized and their structures were identified by the use of FTIR, 1H NMR, elemental analysis and UV-Visible spectroscopic techniques. The spectrophotometric properties of the prepared organic dye in DMSO solvent and on TiO_2 films were examined. The absorption maxima of organic dye applied on the surface of a nano anatase TiO_2 film gave bathochromic shifts compared to the corresponding dye spectra in DMSO solution. Finally, the prepared dye was utilized in constructed DSSCs and their photovoltaic behaviors were assessed. A solar energy to electricity conversion efficiency of 3.75% was achieved for organic dye containing double rhodanine with a methine chain and one donating substituents on the aldehyde component which seems to act as the best donor/acceptor combination for electron transfer in this series. 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 dye.

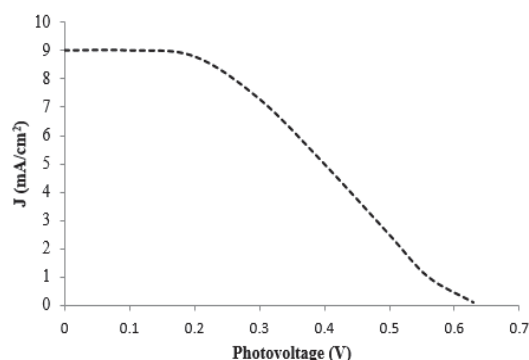


Fig. 3 Current density-voltage Characteristics for organic dye

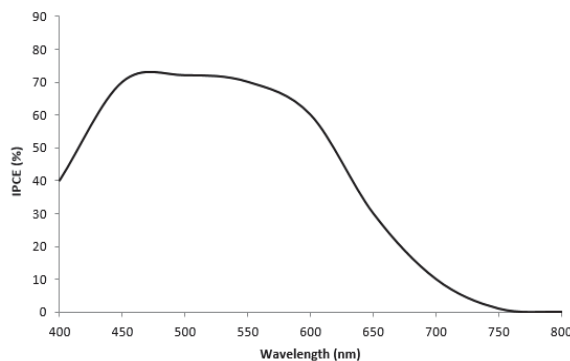


Fig. 4 Photo-to-current action spectra of synthesized dye

ACKNOWLEDGMENT

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

REFERENCES

- [1] M. Hosseinnzhad, S. Moradian, K. Gharanjig, "Synthesis and Application of Two Organic Dyes for Dye-Sensitized Solar Cells", *Prog. Color Colorants Coat.* Vol. 6, pp. 109-117, 2013.
- [2] M. Hosseinnzhad, S. Moradian, K. Gharanjig, "Investigation of effect of anti-aggregation agent on the performance of nanostructure dye-sensitized solar cells", *Opto-electron. Rev.*, vol. 23, pp. 126-130, 2015.
- [3] M. Hosseinnzhad, S. Moradian, K. Gharanjig, F. Afshar Taromi, "Synthesis and Characterization of Eight Organic Dyes for Dye-Sensitized Solar Cells", *Mater. Technol.*, vol. 29, pp. 112-117, 2014.
- [4] J. Chang, C. Lee, D. Kumar, P. Chen, L. Lin, K.R. Thomas, K. Ho, "Co-sensitization promoted light harvesting for dye-sensitized solar cells using unsymmetrical squaraine dye and novel pyrenoimidazole-based dye", *J. Power Sources.*, vol. 240, pp. 779-785, 2013.
- [5] 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 Pigments.*, vol. 80, pp. 233-238, 2009.
- [6] M. Hosseinnzhad, S. Moradian, K. Gharanjig, "Novel organic dyes based on thioindigo for dye-sensitized solar cells", *Dye Pigments.* Vol. 123, pp. 147-153, 2015.
- [7] Hsiu-Yi Yang, Yung-Sheng Yen, Ying-Chan Hsu, Hsien-Hsin Chou, and Jiann T. Lin, "Organic Dyes Incorporating the Dithieno(3,2-b:2',3'-d)thiophene Moiety for Efficient Dye-Sensitized Solar Cells", *Org. Lett.*, Vol. 12, No. 1, 2010, 16-19.

M. Hosseinnzhad was born in 1984 in Tehran, Iran, and received her B.Sc. from K.N. Toosi university of technology in 2008 and her M.Sc. from the Amirkabir university of technology in 2010. After this, she studied and received her Ph.D. from Amirkabir university of technology in 2014 under the direction of professor Siamak Moradian, on a thesis entitled "the synthesis of organic dyes based on indoline for dye-sensitized solar cells". After her doctoral degree, she was appointed as an assistant professor at the Institute for Color Science and Technology in 2014. Her current research interests include the design and synthesis of organic dyes and dye sensitizers for dye-sensitized solar cells.