

Synthesis and Application of an Organic Dye in Nanostructure Solar Cells Device

M. Hoseinnezhad, K. Gharanjig

Abstract—Two organic dyes comprising carbazole as the electron donors and cyanoacetic acid moieties as the electron acceptors were synthesized. The organic dye was prepared by standard reaction from carbazole as the starting material. To this end, carbazole was reacted with bromobenzene and further oxidation and reacted with cyanoacetic acid. The obtained organic dye was purified and characterized using differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FT-IR), proton nuclear magnetic resonance (^1H NMR), carbon nuclear magnetic resonance (^{13}C NMR) and elemental analysis. The influence of heteroatom on carbazole donors and cyano substitution on the acid acceptor is evidenced by spectral and electrochemical photovoltaic experiments. Finally, light fastness properties for organic dye were investigated.

Keywords—Dye-sensitized solar cells, Indoline dye, nanostructure, oxidation potential, solar energy.

I. INTRODUCTION

DONOR-ACCEPTOR (D-A) organic molecules are among the most important conjugated organic materials, and have attracted much academic and technological research interest [1]. The molecules with D- π -A structures have attracted increasing attention since they can serve as electro active and photoactive materials in molecular electronics, such as biochemical fluorescent technology, efficient nonlinear optical (NLO) materials, electro generated chemiluminescence, organic light-emitting diodes (OLEDs), and solar cells [2]. Recently, more and more attention has been directed to the application of metal-free organic dyes in DSSCs. In this work, metal free dye with carbazole sensitizers is reported and its optical, electrochemical, photovoltaic properties and structural relationships is investigated in detail [3]. Gupta et al. investigated the effect of the anchoring group in the performance of carbazole-phenothiazine dyads for dye-sensitized solar cells. The theoretical calculations suggest that the low short current densities might arise from the unfavorable interplay of the dye's optical properties (blue shift of the absorption spectrum) and of the energy alignment between the dye's LUMO and the semiconductor conduction band edge, possibly causing an inefficient electron injection process [4]. Yin et al. synthesized Two conjugated A- π -D- π -A type small molecules having a 4,8-bis(thienyl)-benzo[1,2-b:4,5-b'] dithiophene (TBDT) unit as the donor part, a mono-

thiophene as the p-conjugation bridge, and 2-cyano-3-octyloxy-3-oxo-1-propenyl (COOP) or dicyanovinyl (DCV) as the terminal acceptor unit and investigated. The dye-sensitized solar cells based on prepared dyes showed power conversion efficiency 4.48% and 4.68% [5]. Yan et al. synthesized and characterized a series of linear-conjugated small molecule compounds featured with the acceptor-donor-acceptor-donor-acceptor (A-D-A-D-A) structure. These results indicate that the A-D-A-D-A small molecules with electron-withdrawing dyes as terminals are promising candidates for the high efficiency solution processed organic photovoltaic cells [6]. Wang et al. prepared two D- π -A- π -A organic dyes (YC-1 and YC-2) with 5-phenyl-5H-dibenzo[b,f]azepine derivatives as donor, thiophene as p bridge, and is indigo and cyanoacrylic acid as acceptors. YC-1 and YC-2 show a panchromatic absorption between 300 nm and 800 nm both in solution and neat film. The inferior performance of device based on YC-2 ($\eta=1.46\%$) is ascribed to short electron lifetime as evidenced from electrochemical impedance spectroscopy measurement [7]. Wang et al. reported the synthesis and DSSCs performance of two dye sensitizers XDye1 and XDye2 with D- π -A1- π -A2 structure bearing difluorobenzo[c] [1,2,5]thiadiazole (DFBT) and diketopyrrolopyrrole (DPP)-based as auxiliary acceptor moieties. The effect of DFBT or DPP on the photophysical, electrochemical, and photovoltaic properties of the target dyes were investigated. The investigation of photovoltaic performance of DSSCs indicates that XD1 obtains slightly higher power conversion efficiency (PCE) of 5.04%, but the PCE of the DSSCs based on the dye XD2 with 1 mM CDCA as co-adsorbent is increased to 6.14% [8]. Formo Buene et al. studied the effect of π -linker on new photosensitizers. They designed and prepared eleven new organic dyes and investigated photovoltaic properties in dye-sensitized solar cells devices. The results show that the presence of an additional electron donating group had important effect on the photonic properties of organic dye [9]. Cheng et al. designed and synthesized a series of new organic dyes based on indoline organic dyes. For this end, an aligo-aromatic group namely, 4,5-dihexyl-4,5-dihydrothieno[2'',3'':4',5']pyrrolo [2',3':4,5] thieno[3,2-b]indole (DPTI) has been utilized as π -bridge. The highest power conversion efficiency has been achieved for organic dye, namely M84 about 7.59% [10]. Song et al. prepared porphyrin sensitizers which contain a new acceptor group and studied the effects of steric hindrance and co-sensitization. The presence of benzotriazole in dye structure extended the absorption. Co-adsorption and co-sensitization methods were used for increasing the power conversion efficiency. The results show that the effectiveness

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of incorporating an auxiliary benzotriazole acceptor into porphyrin dyes on achieving extended light-harvesting wavelength ranges and illustrate the importance of avoiding severe torsion within the acceptor part of the porphyrin dyes [11].

In the present work, we aimed at improving the conversion efficiency of DSSCs using organic dyes. To this end, two metal free organic dyes were obtained utilizing cabazol as the electron donating group and cyanoacrylic acid as the fundamental electron acceptor group. The intermediates and synthesized dyes were purified and characterized by analytical techniques. The spectrophotometric properties of the prepared organic dyes in solvent and on a nano anatase TiO₂ substrate were investigated. Fluorometric studies, oxidation potential measurements and density functional theory (DFT) calculation for all dyes were investigated. Dye sensitized solar cells were then assembled utilizing these fluorescent dyes, and their photovoltaic behaviors were determined.

II. EXPERIMENTAL

A. Materials and Instruments

All compounds used in this study were of analytical grade unless otherwise stated, and apparatuses utilized in this research are as follows: UV-visible spectrophotometry was carried out on a Cecil 9200 double beam transmission spectrophotometer. Molar extinction coefficients and absorption maxima were also determined. The ¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker DRX (300/400 MHz) NMR spectrometer. FT-IR measurements were carried out on a Bomene Canada instrument. DSC thermal analysis measurements were carried out on a Dupont 2000 DSC instrument.

B. Synthesis of Dye

9-ethyl-3-formylcarbazole (9 mmol) and cyanoacetic acid (16 mmol) were dried in vacuum. Acetonitrile (40 mL) and piperidine (8 mmol) were surcharged to the mixture of reaction. The suspension was refluxed for 6 h. After the solution was cooled, the organic layer was removed in vacuum. The purification was done by silica gel chromatography using ethylacetate/methanol = 10:1, 83% yield; FT-IR (KBr) (cm⁻¹): 3120: C-H str. Ar., 1657, 1470: C=C str, 1298: C-N str; ¹H-NMR (DMSO-d₆), δ (ppm): 1.35 (t, 3H, CH₃), 4.54 (m, 2H, CH₂), 7.31 (t, 1H), 7.58 (t, 1H), 7.68–7.74 (m, 2H), 8.11 (m, 3H), 8.35 (s, 1H); ¹³C-NMR (CDCl₃) δ (ppm): 107.10, 111.15, 119.13, 120.7, 124.44, 132.73, 138.49, 146.1, 13.2, 27.6, 39.9; Elem. Anal. Calcd. for C₁₈H₁₄N₂O₂: C, 74.47%; H, 4.86%; N, 9.65%. Found: C, 74.16%; H, 4.76%; N, 9.55%.

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 [12].

D. DSSCs Assembly

A nanocrystalline TiO₂ film was coated on a FTO coated glass support. The dye was adsorbed by dipping the coated glass for several hours in a 5×10⁻⁴ M ethanolic solution of the dye containing 7% of 4-tert-butylpyridine and 50 mM of 3α,7β-dihydroxy-5β-cholic acid (cheno). The visible bands in the absorption spectrum of the dyes on nano TiO₂ film only appeared after the TiO₂ 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 solvent. Acetonitrile-ethylenecarbonate (v/v=1:4) containing tetrabutyl ammonium iodide (0.5 mol dm⁻³) was used as an electrolyte. The dye-adsorbed TiO₂ electrode, the Pt counter electrode and the electrolyte solution were assembled into a sealed sandwich type solar cell [13], [14].

An action spectrum was measured under monochromatic light with a constant photon number (5×10¹⁵ 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.

III. RESULTS AND DISCUSSION

TABLE I
ABSORPTION PROPERTIES OF ORGANIC DYES

Properties	λ _{max} (nm) ^a	ε (LM ⁻¹ Cm ⁻¹)	λ _{max} (nm) ^b	λ _F (nm)
Dye 1	435	55232	446	541
Dye 2	452	54123	461	556

a) In solution; b) On TiO₂.

Dye is cyanoacetic acid-based with carbazole unit as the donor. The aldehyde was prepared by a Vilsmeier reaction of N-ethylcarbazole with POCl₃ in DMF [15]. The Knoevenagel reaction as a standard process was utilized for preparation of organic metal free dye. This reaction was done in the presence of piperidine. The UV-Visible absorption of the organic dyes in chloroform are shown in Fig. 1 and the wavelength of maximum absorption (λ_{max}), the molar extinction coefficients (ε_{max}) and λ_F of the corresponding dyes adsorbed on TiO₂ films are listed in Table I. Three different absorption bands at 288 nm, 320 nm and 385 nm were seen in UV-Visible spectrum of organic dye in solution media. The absorption peak in visible area (320 nm) can be defined to an intramolecular charge transfer between the donor group and acceptor group [16], providing efficient charge-separation at the excited state. The fluorescent characteristics of dyes measured in THF are also reported in Table I. In THF solutions, both dyes show intense red fluorescence due to charge transfer to the electron accepting groups.

The oxidation potential (E_{ox}) of synthesized dyes was measured in acetonitrile by cyclic voltammetry to estimate the possibility of electron injection and dye regeneration. There are two distinct redox waves observed in the voltammogram. The first oxidative wave (I) was due to the oxidation of the external standard of Ferrocene, whereas the second wave (II) is due to the electrochemical oxidation of each dye [17]. The oxidation peak potential (E_{pa}), which corresponded to the highest occupied molecular orbital energy (HOMO) of Dye 1 and Dye 2, can be calculated to be +0.93 V and +0.96 V vs Fc/Fc^+ (as an external standard Ferrocene/Ferrocenium redox couple) in acetonitrile, respectively. The energy levels of HOMO of all synthesized dyes are sufficiently positive than the I_3^-/I^- redox potential [(0.42 V (vs. NHE))], indicating that the sufficient thermodynamically driving force for dye regeneration [15]. The E_{red} level of Dye 1 and Dye 2 is calculated to be -1.26 V and -1.35 V, respectively vs Fc/Fc^+ in acetonitrile. The E_{red} level, which corresponded to the lowest unoccupied molecular orbital energy (LUMO) of synthesized dyes, are more negative than the conduction band gap edge of TiO_2 [-0.5 V (vs. NHE)]. Thus, the electron injection process from each excited dye molecule to the TiO_2 conduction band and the subsequent dye regeneration are energetically permissible [18].

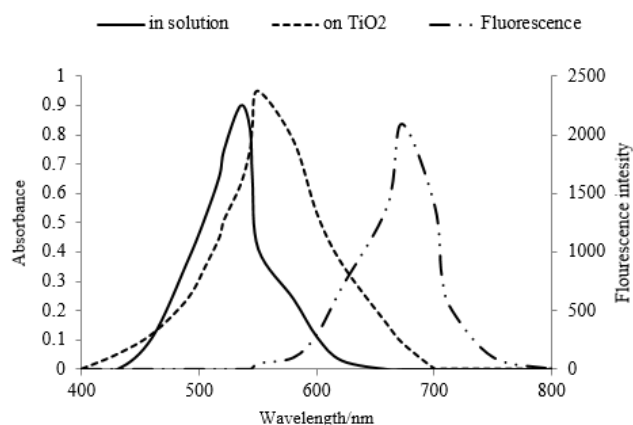


Fig. 1 UV-Vis absorption and fluorescence spectra of Dye 1

DSSCs were prepared and compared to investigate the relationships between the sensitizing behavior of dye molecule and its structures. The organic metal free dyes have been utilized in dye-sensitized solar cells structure as photosensitizers for preparation of electron. The photovoltaic properties of DSSCs device were determined by normalizing the photocurrent density for adventure light and summarized in Table II. Photovoltage properties include: photocurrent density (J_{sc}), photovoltage (V_{oc}) and fill factor (FF). These factors used for calculation of the solar-energy-to-electricity conversion efficiency (η).

TABLE II
PHOTOVOLTAIC PERFORMANCE OF DSSCs BASED ON ORGANIC DYE

Dye source	J_{sc} (mA·cm ⁻²)	V_{oc} (V)	FF (%)	η (%)
Dye 1	8.29	0.56	0.64	2.98
Dye 2	9.44	0.63	0.62	3.66

Commonly, the dye-sensitized solar cells have five components including: substrate, photoanode layer, sensitizer, electrolyte, counter electrode. The electron generation in sensitizer (dye) and injection electron has been followed by five steps.

- (1) Electrons in dye are excited by solar energy adsorption.
- (2) Electrons are transferred from dye to Indium tin oxide (ITO) conducting glass via TiO_2 .
- (3) Electrons get to counter electrode after working at external load.
- (4) $I_3^- + 2e^- \rightarrow 3I^-$ at counter electrode.
- (5) $3I^- \rightarrow I_3^- + 2e^-$ at dye.

The geometrical and electronic properties of dye were studied with density functional theory (DFT) using the Gaussian 03 program package [4], [5]. The location of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of dye molecules are important for repeating the electron production process [19]. The LUMO state should be higher than the conduction band of semiconductor [20].

IV. CONCLUSION

An organic D- π -A dye (metal free dye) by employing carbazole as donor and acrylic acid and cyanoacrylic acid as acceptor unit was designed and prepared as the photosensitizers for dye-sensitized solar cells applications. Absorption and emission spectrum of organic dye contain acrylic acid and cyanoacrylic acid showed that difference manner due to cyanoacrylic acid is stronger acceptor group than acrylic acid. DFT calculation was used for investigation of LUMO and HOMO level. The results show that the synthesized dyes are suitable for using in dye-sensitized solar cells. Finally, organic dyes have been used in DSSCs structure and power conversion efficiency of 2.98% and 3.69% are achieved for Dye 1 and Dye 2, respectively.

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REFERENCES

- [1] M. Hosseinnzhad, R. Jafari, and K. Gharanjig, "Characterization of a green and environmentally friendly sensitizer for low cost dye-sensitized solar cells," *Opto-Electron. Rev.*, vol. 25, pp. 93-98, 2017.
- [2] M. Hosseinnzhad, M. R. Saeb, S. Garshasbi, and Y. Mohammadi, "Realization of manufacturing dye-sensitized solar cells with possible maximum power conversion efficiency and durability," *Sol. Cell*, vol. 149, pp. 314-322, 2017.
- [3] M. Hosseinnzhad, S. Moradian, and K. Gharanjig, "Synthesis and Characterization of Indoline based organic sensitizers for photoelectrochemical cells," *Prog. Color Colorants Coat.*, vol. 10, pp. 43-50, 2017.
- [4] K. S.V. Gupta, J. Zhang, G. Marotta, M. Anil Reddy, S. P. Singh, A. Islam, L. Han, F. De Angelis, M. Chandrasekharan, M. Pastore, "Effect of the anchoring group in the performance of carbazolephenothiazine dyads for dye-sensitized solar cells", *Dye Pigment* vol. 131, pp. 536-545, 2015.
- [5] N.Yin, L. Wang, Y. Ma, Y. Lin, J. Wu, Q. Luo, H. Yang, C. Ma, X. Zhao, "4,8-Bis(thienyl)-benzo(1,2-b:4,5 b')dithiophene based A- π -D- π

- A typed conjugated small molecules with mono thiophene as the π -bridge: Synthesis, properties and photovoltaic performance”, *Dye Pigment* vol. 120, pp. 299-306, 2015.
- [6] W. Yan, Q. Zhang, Q. Qin, S. Ye, Y. Lin, Z. Liu, Z. Bian, Y. Chen, C. Huang, “Design, synthesis and photophysical properties of A-D-A-D-A small molecules for photovoltaic application”, *Dye Pigment* vol. 121, pp. 99-108, 2015.
- [7] Y. Wang, C. Yang, J. Chen, H. Qi, J. Hua, Y. Liu, E. Baranoff, H. Tan, J. Fan, W. Zhu, “Influence of the donor size in panchromatic D- π -A- π -A dyes bearing 5-phenyl-5H-dibenzo-b,f]azepine units for dye-sensitized solar cells”, *Dye Pigment* vol. 127, pp. 204-212, 2016.
- [8] G. Wang, Z. Liu, Y. Deng, L. Xie, S. Tan, “Comparative study on N,N-di-p-tolylaniline-based D- π -A1- π -A2 sensitizers by tuning the auxiliary acceptor for dye-sensitized solar cells”, *Dye Pigment* vol. 145, pp. 427-435, 2017.
- [9] A. Formo Buene, N. Uggerud, S.P. Economopulos, O.R. Gautun, B.H. Hoff, “Effect of π -linkers on phenothiazine sensitizers of dye-sensitized solar cells”, *Dye Pigment*, vol. 151, pp. 263-271, 2018.
- [10] H. Cheng, Y. Wu, J. Su, Z. Wang, R. Prasad Ghimire, M. Liang, Z. Sun, S. Xue, “Organic dyes containing indolodithienopyrrole unit for dye-sensitized solar cells”, *Dye Pigment*, vol. 149, pp. 16-24, 2018.
- [11] H. Song, W. Tang, S. Zhao, Q. Liu, Y. Xie, “Porphyrin sensitizers containing an auxiliary benzotriazole acceptor for dye-sensitized solar cells: effects of steric hindrance and co-sensitization”, *Dye Pigment*, <https://doi.org/10.1016/j.dye.pig.2018.03.054>, 2018.
- [12] M. Hosseinezhad, S. Rouhani, “Synthesis and application of new fluorescent dyes in dye-sensitized solar cells”, *Applied Physics A*, vol. 123, pp. 694-704, 2017.
- [13] M. Hosseinezhad, K. Gharanjig, “Investigation of photovoltaic properties of nanostructure indoline dye-sensitized solar cells using changes in assembling materials”, *Pigment Resin Technol.* vol. 64, No. 5, pp. 393-398, 2017.
- [14] M. Hosseinezhad, “Cosensitization with Vat-Based Organic Dyes for Enhanced Spectral Response of Dye-Sensitized Solar Cells”, *J. Electron. Mater.* Vol. 64, No. 4, pp. 2290-2295, 2017.
- [15] N. A. Ludin, A. M. Al-Alwani Mohmaoud, A.B. Mohamad, A.A.H. Kadhum, K. Sopian, and N.S. Abdul Karim, “Review on the development of natural dye photosensitizer for dye-sensitized solar cells”, *Renew. Sust. Energy Rev.* vol. 31, pp. 386-396, 2014
- [16] A. Torchani, S. Saadaoui, R. Charbi, and M. Fathallah, “Sensitized solar cells based on natural dyes”, *Curr. Appl. Phys.* vol. 15, pp. 307-312, 2015.
- [17] A. Fattori, R. Majer, A. Mazzanti, M. Francesca Ottaviani, A. Modelli, F. Mantellini, S. Santeusano, “N-heterocyclic linkers from 1,2-diazole-1,3-dienes for dye-sensitized solar cells: DFT calculations, synthesis and photovoltaic performance”, *Dye Pigment*, vol. 145, pp. 246-255, 2017.
- [18] L. Martín-Gomis, C. ParejoJulio, C. Álvarez Fernando, F. L. Ángela, S. Santos, “Dye sensitized solar cells (DSSCs) based on bulky *tert*-octylphenoxy-carboxyphenyl substituted phthalocyanine without the presence of co-adsorbents”, *Inorg. Chim. Acta*, vol. 468, pp. 327-333, 2017.
- [19] D. Jin Yun, Y. J. Jeong, H. Ra, J. M. Kim, T. K. An, S. W. Rhee, J. Jang, “Systematic optimization of MWCNT-PEDOT:PSS composite electrodes for organic transistors and dye-sensitized solar cells: Effects of MWCNT diameter and purity”, *Org. Chem.*, vol. 52, pp. 7-16, 2018.
- [20] G. Rajamanickam, S. Narendhiran, S. Pandian Muthu, S. Mukhopadhyay, R. Perumalsamy, “Hydrothermally derived nanoporous titanium dioxide nanorods/nanoparticles and their influence in dye-sensitized solar cell as a photoanode”, *Chem. Phys. Lett.* vol. 689, pp. 19-25, 2015.

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