

Simple Thiophene Based Organic Dyes as Active Photosensitizers for DSSC Application: from Molecular Design to Structure Property Relationship

Kavya S. Keremane¹, Praveen Naik¹, Airody Vasudeva Adhikari^{2,*}

¹ Department of Chemistry, NITK, 575025 Surathkal, India

² Yenepoya Research Centre, Yenepoya deemed to be University, Deralakatte, 575018 Mangalore, India

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The main objective of our present investigation includes the design synthesis and characterization of two novel D- π -A configured thiophene based dyes C_{1,2}, carrying two different anchors and the same donor system. In the new design, a simple O-alkylated phenyl group as a donor scaffold, cyanovinylene and thiophene group serve as a π -spacer, while cyanoacetic acid, barbituric acid units function as electron acceptor/anchoring units. The newly synthesized compounds were characterized by FTIR, NMR spectroscopic techniques including the elemental analysis. Further, their optical properties were investigated by using UV-visible, fluorescence spectrophotometer. In addition, the Density functional theory (DFT) calculations were performed to get their electron distribution in FMO levels. In order to investigate their photovoltaic characteristics, the synthesized dyes were employed as sensitizers towards the fabrication of DSSC's. The device fabricated with dye C₁ displayed better PCE of 1.2 % with J_{SC} of 3.64 mA cm⁻², V_{OC} of 0.50 V and FF of 65 % than other dye C₂. These experimental results provide a better understanding and deeper insight into the intricacies involved in the design of superior sensitizers to further improve the performance of DSSCs.

Keywords: Thiophene, DSSC, DFT, *J-V* Characteristics, Sensitization.

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1. INTRODUCTION

Dye-sensitized solar cells (DSSCs) have attracted considerable interest, due to their ability of converting direct sunlight into electricity at low fabrication cost, easy manufacturing process compared to conventional *p-n* junction solar cells [1-4]. Typically, DSSCs are composed of sandwich structure: dye-adsorbed wide band gap metal-oxide semiconductor electrode (TiO₂), platinum counter electrode, filled with an electrolyte containing I^-/I_3^- redox couple. Actually, in the working principle of DSSCs, the dyes as sensitizers absorb the photons and get excited and consequently electrons are injected into the conduction band (CB) of the TiO₂ followed by regenerating the dye by the redox electrolyte [2-5]. From the above said mechanism, the photosensitizers (dyes) play as one of the key components to produce high power-conversion efficiency (PCE). The sensitizers with appropriate energy level and light harvesting ability may lead to improved photoelectric conversion efficiency [6, 7]. Till date, the metal-organic complexes have been used to achieve high PCE above 14 % under AM 1.5 irradiation [8, 9]. Due to their high cost, tricky purification steps, and synthetic methods and environmental issues, metal-free organic dyes have been used to replace them. However, the metal-free organic sensitizers overcome all these drawbacks with high molar extinction coefficient, better flexibility for structural control, environmental friendliness, and considerable efficiencies [8, 10]. The overall PCE of fabricated devices are mainly depend on structural properties of the molecules (i.e.) donor (D), acceptor (A) groups and amount of dye molecules adsorbed on TiO₂ surface. Various electrons rich molecules act as electron donor such as triphenylamine, coumarin, thiophene,

indole etc which supply's electron to acceptor groups like carboxylate or phosphonate, firmly grafted on TiO₂ layer [11, 12]. Generally, geometry of the molecules mainly correlates with few factors such as PCE, stability of the molecule, electron injection, dye regeneration and recombination. Among them, the major problem for observed low PCE was mainly due to the dye aggregation and charge recombination. In order to suppress this, introduction of long alkyl chains or a bulky group on donor moiety was found to be useful [13, 14]. The presence of π spacer between donor and acceptor molecules not only helps in enhancing electron conjugation, but also improves the overall stability of the molecule. Thiophene-based polymers, oligomers, and its derivatives have been used as common π -spacer in photovoltaic cells due to their excellent stability, more effective conjugation and electronic tunability [15]. In the literature, the cyanoacetic acid (CA) and barbituric acid (BA) are widely used as electron acceptors due to their excellent electron withdrawing ability [2, 16].

In this paper, we report the synthesis, characterization and photovoltaic investigation of two new D- π -A configured dyes C_{1,2}, carrying O-alkylated phenyl group as an electron donor, cyano vinylene and thiophene group serve as a π -spacer, while cyanoacetic acid, barbituric acid groups act as electron acceptor/anchoring units (Fig. 1). The final molecules were synthesized by simple synthetic methods such as O-alkylation, Vilsmeier-Hack reaction followed by Knoevenagel condensation reactions with high yield as shown in Scheme 1. Structure of all the intermediates and final molecules were characterized using FTIR, and NMR, analysis techniques (Fig. 2 and Fig. 3). The electronic and optical properties of the materials are calculated using UV-Visible and Photoluminance (PL) emission studies. The

* avachem@gmail.com

structural geometry of the molecules were calculated theoretically by density functional theory using Turbomole 7.1 V software. Finally, the dyes C_{1-2} were used as sensitizers towards a fabrication of DSSC to investigate their photovoltaic performance.

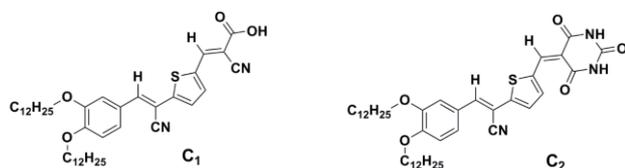
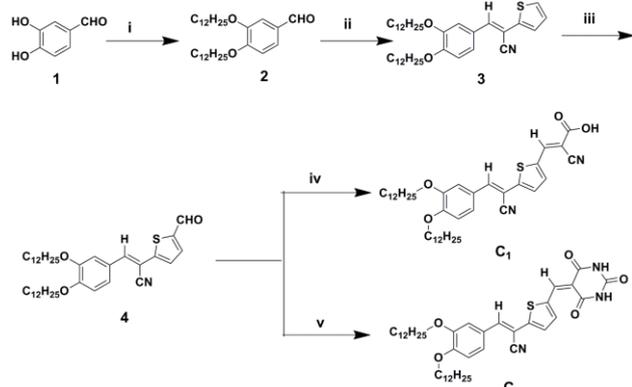


Fig. 1 – Structures of dyes C_1 and C_2



Scheme 1 – Synthetic routes for the chromophores C_{1-2} : (i) 3,4-hydroxybenzaldehyde, potassium carbonate, DMF, 1-bromododecane, RT (ii) thiophene-2-acetonitrile, sodium methoxide, methanol, RT (iii) $POCl_3$, DMF, RT (iv) Cyanoacetic acid, ammonium acetate, glacial CH_3COOH , 110 °C (v) Barbituric acid, Methanol, 60 °C

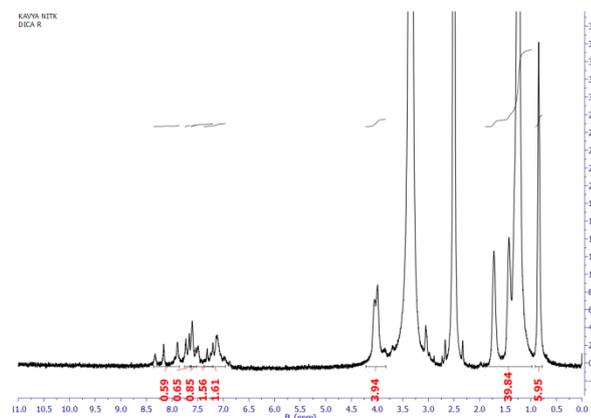


Fig. 2 – 1H NMR spectrum of compound C_1 recorded in DMSO

2. EXPERIMENTAL

2.1 Materials and Methods

The starting materials such as 3,4-dihydroxy benzaldehyde, 1-bromododecane, thiophene-2-acetonitrile, cyanoacetic acid and barbituric acid were procured from Sigma-Aldrich, Alfa Aesar and Spectrochem companies without further purification for the synthesis. The reactions were carried out in inert atmosphere and the progress of reaction was checked by using TLC, and column chromatography technique [3]. The structural characterization of all the intermediates and final molecules were

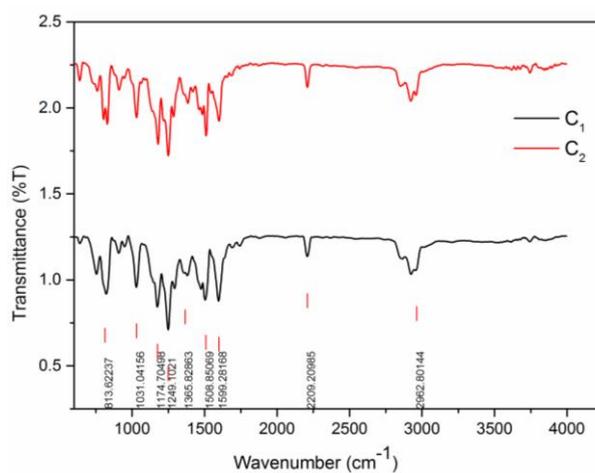


Fig. 3 – FT-IR spectra of C_1 and C_2

done using FTIR (Bruker-Alpha), 1H -NMR (Bruker 400 MHz) [17]. The UV-Vis absorption spectra and PL emission spectra were recorded using SPECORD S600 spectrophotometer and Horiba spectrophotometer [18, 19]. DFT calculations were performed using Turbomole 7.1V software package. Finally, photovoltaic experiments such as JV characteristics and IPCE were carried out using Oriel SOL3A solar simulator connected to Keithley 2400 source meter and QEX10 PV measurement system.

2.1.1 Synthesis of 3,4-bis(dodecyloxy) Benzaldehyde (2)

A mixture of 3,4-hydroxybenzaldehyde (1, 1eq) and potassium carbonate (3 eq) were dissolved in DMF and then added 1-bromododecane (1.2 eq) to the above reaction mixture. The reaction mixture was refluxed at 80 °C for 12 h. Once the reaction completes, mixture was poured into ice cold water, and extracted with dichloromethane. The combined organic layer was dried using sodium sulphate, removed the solvent and the crude product was recrystallized as colourless liquid.

2.1.2 Synthesis of (E)-3-(3,4-bis(dodecyloxy) phenyl)-2-(thiophen-2-yl)acrylonitrile (3)

In a round bottomed flask, Intermediate 2 (1 eq) and thiophene-2-acetonitrile (1.2 eq) were mixed in methanol along with freshly prepared sodium methoxide (1.8eq) solution. The reaction mixture was stirred at room temperature under argon atmosphere for 8 h. The bright yellow precipitate formed was filtered off to give fine yellow solid. Yield 71%,

2.1.3 Synthesis of (E)-3-(3,4-bis(dodecyloxy) phenyl)-2-(5-formylthiophen-2-yl)acrylonitrile (4)

The Vielsmeier salt was prepared by mixing DMF (5 eq) and phosphorous oxychloride (5eq) at -4 °C for 30 minutes. To this salt, intermediate 3 (1eq) in THF (2-3 mL) was added and stirred at room temperature for 12 h. After the completion of reaction, reaction mass was poured into ice cold water and subsequently basified by using 5M NaOH solution. The precipitated solid was filtered and collected. Yield: 60%

2.1.4 Synthesis of (E)-3-(5-((E)-2-(3,4-bis(dodecyloxy)phenyl)-1-cyanovinyl)thiophen-2-yl)-2-cyanoacrylic acid (C₁)

A mixture of intermediate 4, (E)-3-(3,4-bis(dodecyloxy)phenyl)-2-(5-formylthiophen-2-yl)acrylonitrile (1 eq), cyanoacetic acid (1.2 eq), and ammonium acetate (10 eq) and glacial acetic acid (10-15 mL) were taken in a RB flask and refluxed for 12h at 110 °C under argon atmosphere. Once the reaction completes, reaction mixture was poured in ice cold water. The solid obtained was filtered, collected, and washed with cold water to get the pure red colour product. Yield: 74 %

¹H NMR (400 MHz, DMSO-d₆, ppm): 8.31 (s, 1H), 8.16 (s, 1H), 7.70 (s, 1H), 7.60-7.49 (d, 2H), 7.32-7.12 (d, 2H), 4.25-4.00 (t, 4H), 1.75-1.25 (m, 40H), 0.65-0.85 (t, 6H).

2.1.5 Synthesis of (E)-3-(3,4-bis(dodecyloxy) phenyl)-2-(5-((2,4,6-trioxotetrahydropyrimidin-5(2H)-ylidene) methyl)thiophen-2-yl) acrylonitrile (C₂)

A mixture of intermediate 4, (E)-3-(3,4-bis(dodecyloxy)phenyl)-2-(5-formylthiophen-2-yl)acrylonitrile (1 eq), was dissolved in 10-15 mL of absolute methanol and to this 1.2 eq of barbituric acid was added under argon atmosphere and stirred at 60 °C for 10 h. After the completion of reaction, the content was cooled at room temperature and precipitated solid was filtered, washed with cold methanol and collected. It was further recrystallized from absolute methanol to get bright red solid. Yield: 71%.

3. RESULTS AND DISCUSSION

3.1 Photophysical Behavior

The optical behaviour of the molecules C₁ and C₂ (UV-Visible absorption spectra and PL emission spectra) were recorded in 10⁻⁵ M CHCl₃ solution as shown in Fig. 4 and their corresponding data were summarized in Table 1. From the figure we can conclude that the organic sensitizers C₁ and C₂ exhibit absorption maxima at 409 nm and 462 nm, respectively. This is mainly due to the intramolecular charge transfer (ICT)/π-π* transition of the chromophores between donor and acceptor [20]. From the PL spectra results, it is clear that both the dyes exhibit solid luminescence maxima at 522 nm and 575 nm respectively. From the intersection between normalized absorption and emission spectra, the optical band-gap was found [21]. Also, from the data stoke shift values were estimated to be in the range of 113-116 nm. It can be concluded from the data that, C₁ have highest stoke shift value which ultimately results in the superior molar extinction coefficient for the molecule.

3.2 Theoretical Investigation

To understand the electron delocalization of the molecules in depth, DFT calculations were performed using turbomole 7.1 V software package. The dye molecules geometry was optimized using C₁ point group

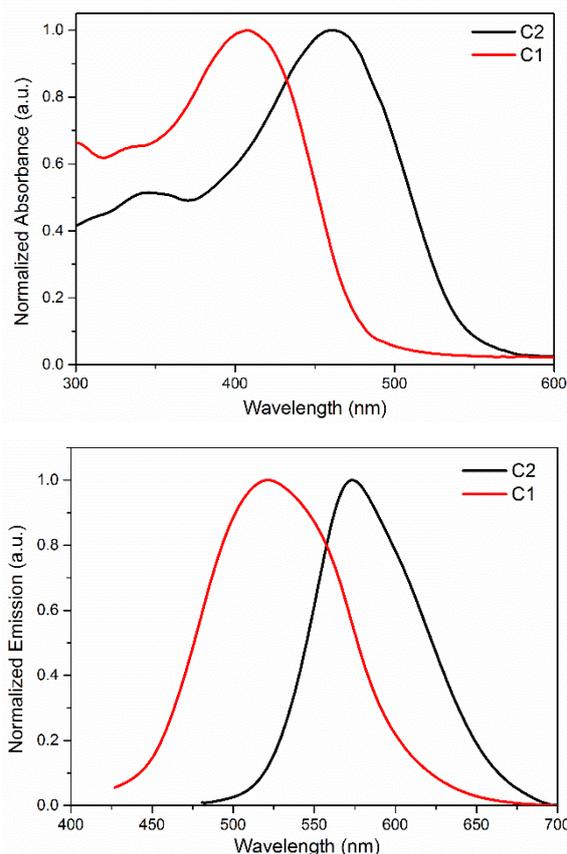


Fig. 4 – Normalized UV-Visible absorption spectra and PL emission spectra of dyes C₁₋₂ in CHCl₃ at 10⁻⁵ M

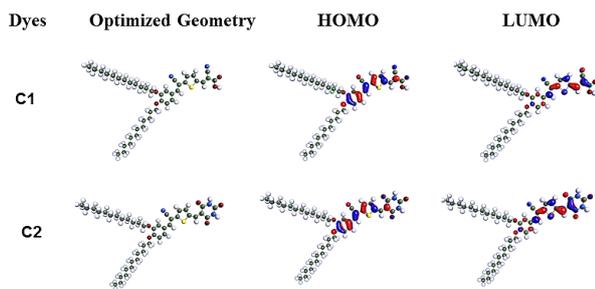
Table 1 – Optical parameters of dyes C₁₋₂

Sample name	Absorption λ_{abs} (nm)	Emission λ_{em} (nm)	Stoke Shift (nm)	Optical band gap $E_{0.0}$ (eV)
C ₁	407	523	116	2.66
C ₂	462	575	113	2.32

symmetry at B3LYP function with def-TZVPP basis set [12, 22]. The optimized molecular geometry along with electronic cloud delocalization in FMO levels along with their parameters are shown in Fig. 5 and Table 2 respectively. From their HOMO energy levels, we can conclude that the electron cloud is predominantly delocalized on O-alkylated phenyl and thiophene rings. However, electron cloud in the LUMO levels were shifted towards electron acceptor groups such as cyanoacetic acid/ barbituric acid and π conjugated spacer. The well-overlapped HOMO and LUMO on molecules gives assured fast photo induced electron transfer from donor to acceptor units.

3.3 Photovoltaic Characterization

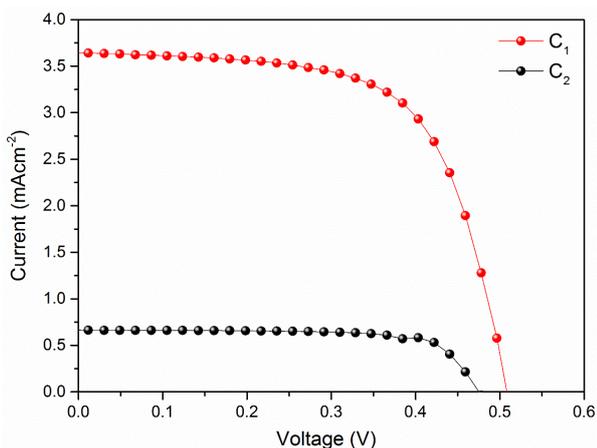
The structure–property relationship of synthesized dyes can be established by fabricating the synthesized dye molecules. The device fabrication of the synthesized molecules were done as per the procedures [10, 23, 24] described in their supplementary information. Keithley 2400 source meter under standard illumination of AM 1.5 G solar light of the solar simulator (SOL3A, Oriel)

Fig. 5 – FT-IR spectra of C_1 and C_2 Table 2 – Theoretical parameters of dyes C_{1-2}

Sample name	E_{LUMO} (eV)	E_{HOMO} (eV)	Band gap E_g (eV)
C_1	- 3.18	- 6.00	2.81
C_2	- 3.26	- 6.01	2.75

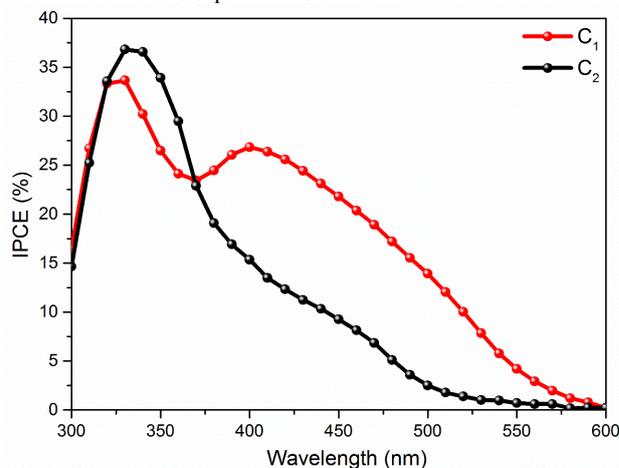
was used to measure the current-voltage (J - V) characteristics of the molecules and corresponding J - V plot is displayed in Fig. 6. Photovoltaic parameters such as open circuit photo voltage (V_{oc}), short-circuit photocurrent density (J_{sc}), fill factor (FF), and power conversion efficiency (PCE) are summarized in Table 3. From the results, it is found that C_1 showed highest PCE of 1.2 %, J_{sc} 3.64 mAcm⁻², and V_{oc} of 0.51 V Compared to that of C_2 (0.23 % PCE, 0.66 mAcm⁻² J_{sc} , 0.47 V V_{oc}). Barbituric acid acts as poor acceptor compared to that of cyano acetic acid may be due to the dye aggregation influencing the molecules electron injection behaviour.

Further, incident photons to electron conversion efficiency (IPCE) experiments were done for the fabricated devices using QEX10, PV measurement system [8, 25, 26] and corresponding plot was displayed in Fig. 7. From the results, it can be concluded that dye C_1

Fig. 6 – J - V characteristics of DSSCs sensitized with dyes C_1 and C_2

displayed broad band in the region of 300-600 nm with the value of 34% compared to that of C_2 . The improved IPCE of C_1 consequently results in the increased JSC

values of C_1 . Thus, dye C_1 with superior π -conjugation has results in the widening of visible absorption spectrum and ultimately leads to the significant improvement in the DSSC performance.

Fig. 7 – IPCE spectra of DSSCs sensitized with dyes C_1 and C_2 Table 3 – Photovoltaic measurement data of dyes C_{1-2}

Dyes	J_{sc} (mA·cm ⁻²)	V_{oc} (V)	FF (%)	η (%)
C_1	3.64	0.51	64.49	1.2
C_2	0.36	0.47	74.63	0.23

4. CONCLUSION

We have successfully designed, synthesized and characterized two novel organic D- π -A architected organic chromophores, C_{1-2} , where in the electron rich donor moiety is linked with two different electron acceptors such as cyanoacetic acid and barbituric acid *via* cyano vinyl thiophene π -spacer. The final molecules were subjected to different characterization such as photophysical, electrochemical, and finally device fabrication studies. From the photophysical studies it is clear that the molecules exhibits good absorption, emission properties and their optical band gap is found to be in the range of 2.32-2.66 eV. From the DFT studies gave the better insight for the electronic distribution in HOMO and LUMO energy levels and the data found was in agreement with the experimental values. The device fabricated using dye C_1 carrying strong electron acceptor cyanoacetic acid shows higher PCE upto 1.2 %, along with superior J_{sc} (3.64 mA·cm⁻²) and V_{oc} (0.51 V) when compared to the dye fabricated using barbituric acid.

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