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Sakarya University Journal of Science
SAUJS

e-ISSN 2147-835X | Period Bimonthly | Founded: 1997 | Publisher Sakarya University |
<http://www.saujs.sakarya.edu.tr/en/>

Title: 5,6,7-Trimethoxy-2-(methylthio)quinoline with Different Anchoring Groups:
Synthesis and dye-sensitized Solar Cell Applications

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Received: 2020-09-04 16:39:16

Accepted: 2020-11-10 16:55:43

Article Type: Research Article

Volume: 25

Issue: 1

Month: February

Year: 2021

Pages: 83-91

How to cite

Barış Seçkin ARSLAN; (2021), 5,6,7-Trimethoxy-2-(methylthio)quinoline with
Different Anchoring Groups: Synthesis and dye-sensitized Solar Cell
Applications. Sakarya University Journal of Science, 25(1), 83-91, DOI:
<https://doi.org/10.16984/saufenbilder.790573>

Access link

<http://www.saujs.sakarya.edu.tr/en/pub/issue/58068/790573>

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5,6,7-Trimethoxy-2-(Methylthio)Quinoline with Different Anchoring Groups: Synthesis And Dye-Sensitized Solar Cell Applications

Barış Seçkin ARSLAN*¹

Abstract

Two new metal-free organic dyes in D- π -A structure, containing a quinoline π -bridge and malononitrile (**4a**) and cyanoacrylic acid (**4b**) as acceptors, were synthesized for the first time to apply dye-sensitized solar cell (DSSC). The structures of these compounds were elucidated by FT-IR, ¹H NMR, ¹³C NMR techniques. The photophysical and photovoltaic properties of the obtained compounds were investigated and compared by current density–voltage (J–V) graphs. Compound **4b** containing cyanoacrylic acid as an acceptor reached an open–circuit voltage (Voc) of 0.645 V, short–circuit current density (Jsc) of 6.66 mA cm⁻² and fill factor (FF) of 0.70 in the presence of chenodeoxycholic acid (CDCA), showing a power conversion efficiency (PCE) of 3.01%. It is also observed that the incorporation of thiomethyl group to the structure instead of methoxy group increases the PCE.

Keywords: Dye-sensitized solar cells, metal free dyes, quinoline, thiomethyl group.

1. INTRODUCTION

Metal-free dye sensitized solar cells (DSSCs) are a good alternative to silicon-based solar cells thanks to their low manufacture cost, easy production, environment friendly, easily adjustable electrochemical properties [1-5]. A conventional organic dye contains a system (D- π -A) that carries electrons from donor (D) to acceptor (A) via π -bridge (π) [6]. The main

component in these dyes is the aromatic π -bridge that affects absorption capability and intramolecular charge transfer (ICT) [7]. As the π -bridge, especially focused on fused, rigid and planar aromatic structures [8].

Quinolines containing a fused and rigid structure are important compounds of the dye class. The quinoline derivatives found in the structure of natural compounds have applications in various fields such as medicine, organic optoelectronics,

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electronics and polymer chemistry. Besides being used as a light emitting layer in OLEDs owing to their exciting optoelectronic features, they can be used as corrosion inhibitors as they are easily absorbed into metal surfaces. These compounds are promising in DSSC applications due to their described properties [8, 9-14].

In this study, novel two dyes (**4a** and **4b**) containing three methoxy (-OCH₃) and one thiomethyl (-SCH₃) groups as donors, quinoline ring as π -bridge, malononitrile and cyanoacrylic acid as acceptor were synthesized (**Figure 1**). The structures of the obtained compounds were confirmed by FT-IR, ¹H and ¹³C NMR spectra. In addition, DSSC applications of these compounds in D- π -A structure were carried out and their photophysical properties and photovoltaic performances were investigated.

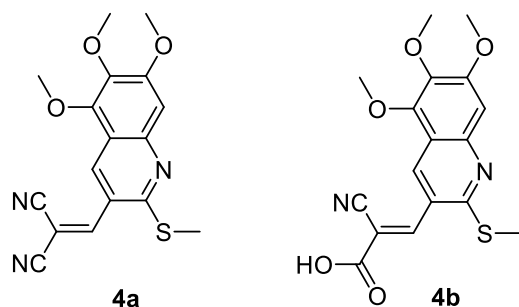


Figure 1. Chemical structures of **4a** and **4b**

2. EXPERIMENTAL

2.1. Materials

Fluorine-doped SnO₂ conducting, TiO₂ paste, platinum paste, sealing film, N719 and redox electrolyte (iodide/triiodide) were purchased from Solaronix. Chenodeoxycholic acid (CDCA), 3,4,5-trimethoxyaniline, dichloromethane (DCM), acetic anhydride, sodium carbonate, *N,N*-dimethylformamide (DMF), phosphoryl chloride, sodium sulfide nonahydrate (Na₂S.9H₂O), methyl iodide, acetonitrile, piperidine, malononitril, cyanoacetic acid were purchased from Sigma-Aldrich. Solvents were highly purified by applying standard methods.

2.2. Synthesis

Compounds **1** and **2** were synthesized in 92% and 87% yields according to the literature, respectively [8]. Synthesis procedure and spectroscopic data of the original compounds (**3**, **4a** and **4b**) are expressed below.

2.2.1. Synthesis of 5,6,7-trimethoxy-2-(methylthio)quinoline-3-carbaldehyde, **3**

DMF (20 mL), sodium sulfide nonahydrate (3.60 g, 15 mmol) and 2-chloro-5,6,7-trimethoxyquinoline-3-carbaldehyde (**2**) (2.82 g, 10 mmol) were added to a 100 mL flask and the mixture was stirred at room temperature for 6 hours. Then, methyl iodide (0.62 mL, 10 mmol) was added to the mixture and the reaction was continued for 12 hours at room temperature. After completion of the reaction, the mixture was extracted with ethyl acetate-water. The organic portion was dried over sodium sulfate and the solvent was removed. It was purified by column chromatography (SiO₂) using hexane/ethyl acetate (19: 1). Beige solid (2.23 g, 76% yield). M.P.: 100-101 °C. IR (cm⁻¹): 3038 (aromatic C-H), 2943 (aliphatic C-H), 2831-2769 (aldehyde C-H), 1682 (C=O), 1609 (C=N), 1586 (C=C), 1114 (C-O-C). ¹H NMR (300 MHz, CDCl₃) δ 10.25 (s, 1H, aldehyde-H), 8.65 (s, 1H, aromatic-H), 7.13 (s, 1H, aromatic-H), 4.12 (s, 3H, -OCH₃), 4.05 (s, 3H, -OCH₃), 3.96 (s, 3H, -OCH₃), 2.68 (s, 3H, -SCH₃). ¹³C NMR (75 MHz, DMSO) δ 191.77, 159.81, 158.87, 148.31, 147.27, 140.17, 139.80, 125.46, 115.17, 103.76, 62.44, 61.63, 57.05, 13.16.

2.2.2. Synthesis of 2-((5,6,7-trimethoxy-2-(methylthio)quinolin-3-yl)methylene)malononitrile, **4a**

The mixture of compound **3** (0.293 g, 1 mmol), malononitrile (0.132 g, 2 mmol) and piperidine (0.2 mL) in acetonitrile (20 mL) was refluxed for 6 hours. After the reaction was completed, the mixture was poured into ice water. The precipitate was filtered off, washed with cold ethanol and finally dried. Orange solid (0.314 g, 92% yield). M.P.: 153-154 °C. IR (cm⁻¹): 3000 (aromatic C-H), 2949 (aliphatic C-H), 2226 (C \equiv N), 1606

(C=N), 1568 (C=C), 1117 (C-O-C). ^1H NMR (300 MHz, CDCl_3) δ 9.01 (s, 1H, alkenyl-H), 8.22 (s, 1H, aromatic-H), 7.10 (s, 1H, aromatic-H), 4.10 (s, 3H, $-\text{OCH}_3$), 4.05 (s, 3H, $-\text{OCH}_3$), 3.97 (s, 3H, $-\text{OCH}_3$), 2.73 (s, 3H, $-\text{SCH}_3$). ^{13}C NMR (75 MHz, DMSO) δ 159.83, 158.62, 156.16, 148.29, 147.28, 140.78, 131.90, 121.79, 115.43, 114.40, 113.65, 104.03, 85.41, 62.78, 61.67, 57.17, 13.63.

2.2.3. Synthesis of 2-cyano-3-(5,6,7-trimethoxy-2-(methylthio)quinolin-3-yl)acrylic acid, **4b**

Compound **4b** was synthesized according to the method used in the synthesis of compound **4a** using cyanoacetic acid (0.170 g) instead of malononitrile. Dark-yellow solid (0.292 g, 81% yield). M.P.: 227-228 °C. IR (cm^{-1}): 3035-2500 (carboxylic acid, O-H), 2994 (aromatic C-H), 2946 (aliphatic C-H), 2225 ($\text{C}\equiv\text{N}$), 1711 (C=O), 1605 (C=N), 1582 (C=C), 1248 (carboxylic acid, C-O), 1116 (C-O-C). ^1H NMR (300 MHz, CDCl_3) δ 8.86 (s, 1H, alkenyl-H), 8.47 (s, 1H, aromatic-H), 6.97 (s, 1H, aromatic-H), 3.94 (s, 3H, $-\text{OCH}_3$), 3.90 (s, 3H, $-\text{OCH}_3$), 3.82 (s, 3H, $-\text{OCH}_3$), 2.57 (s, 3H, $-\text{SCH}_3$). ^{13}C NMR (75 MHz, DMSO) δ 163.42, 159.25, 158.97, 148.53, 148.17, 146.87, 140.67, 131.11, 121.70, 116.36, 115.55, 106.85, 103.96, 62.66, 61.62, 57.05, 13.56.

2.3. Instruments

^1H , ^{13}C NMR measurements were performed on an VARIAN Infinity Plus 300 MHz. The melting points of the compounds were observed using the Schorpp MPM-H1 device. FT-IR spectra were recorded on a Perkin-Elmer FT-IR spectrophotometer. Absorption and fluorescence spectra were obtained in DMSO solution using Shimadzu UV-2600 UV-VIS spectrophotometer and Hitachi F-7000 Fluorescence spectrophotometer, respectively. The J-V features were studied by utilization the potentiostat/galvanostat under AM 1.5 global one sun lighting (100 mW cm^{-2}) from a solar simulator (96000, Newport).

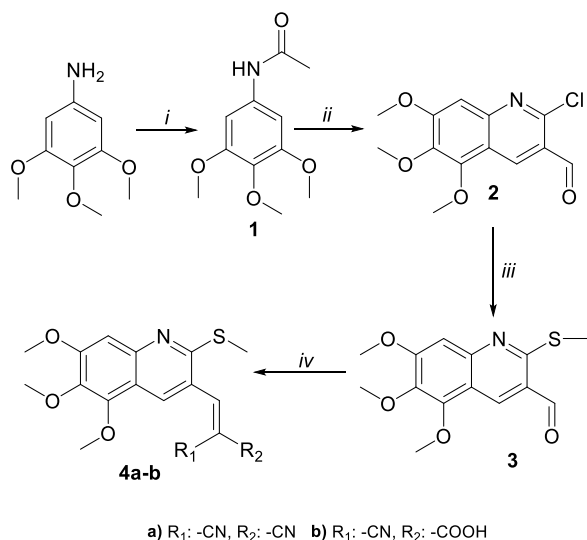
2.4. Production and characterization of DSSCs

DSSCs were prepared pursuant to the Doctor Blade method by applying TiO_2 paste on the FTO substrate [15]. To prepare dye-sensitized photoanodes, FTO substrates were immersed (24 hours for **4a** and 6 hours for **4b**) into a 0.3 mM dye solution in MeOH (both without CDCA and with 5mM CDCA). Platinum counter electrodes were prepared by pouring the platinum paste solution over FTO substrates [16]. Photoanode and counter electrode were combined and sealed with Surlyn and redox electrolyte (I^-/I_3^-) was added through the hole opened in the counter electrode.

3. RESULTS AND DISCUSSIONS

3.1. Synthesis of compounds

Synthesis pathways of compounds **4a** and **4b** are indicated in **Scheme 1**. Primarily, purchased 3,4,5-trimethoxyaniline compound was acetylated with acetic anhydride to obtain the acetanilide derivative (**1**). The acetanilide was converted into the 2-chloro-5,6,7-trimethoxyquinoline-3-carbaldehyde compound (**2**) by the Vilsmeier-Haack reaction [17,18]. Compound **2** was reacted with $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ and then methyl iodide to obtain 5,6,7-trimethoxy-2-(methylthio)quinoline-3-carbaldehyde (**3**) compound [19]. Ultimately, **4a** and **4b** dyes were obtained by Knoevenagel reaction of compound **3** with malononitril and cyanoacetic acid, respectively [15].



(i): DCM, Na₂CO₃, 0°C, Ac₂O, rt, 3 h; (ii): DMF, 0°C, POCl₃, 80 °C, 16 h;
 (iii): Na₂S·9H₂O, DMF, rt, 6 h, MeI, rt, 12 h; (iv): R₁CH₂R₂, piperidine, MeCN, reflux, 6 h.

Scheme 1. Synthetic route for compounds **4a** and **4b**

3.2. Structural Characterization

Compounds **1** and **2** were synthesized according to the literature and their structure was verified by FT-IR, ¹H and ¹³C NMR techniques [8].

FT-IR spectra of the compounds were recorded and compared (**Figure 2**). In FT-IR spectrum of **3**, aromatic C-H, aliphatic C-H, aldehyde C-H, aldehyde C=O, aromatic C=N, aromatic C=C and ether C-O-C stretching vibrations appeared at 3038, 2943, 2831-2769, 1682, 1609, 1586 and 1114 cm⁻¹, respectively. In the **4a** and **4b** FT-IR spectra, aldehyde group stretching vibrations of **3** disappeared. Differently, sharp nitrile stretching vibrations (2226 cm⁻¹ for **4a** and 2225 cm⁻¹ for **4b**) and stretching vibrations belonging to the carboxylic acid group (3035-2500, 1711 and 1248 cm⁻¹ for **4b**) are observed. Other bands are similar for all compounds.

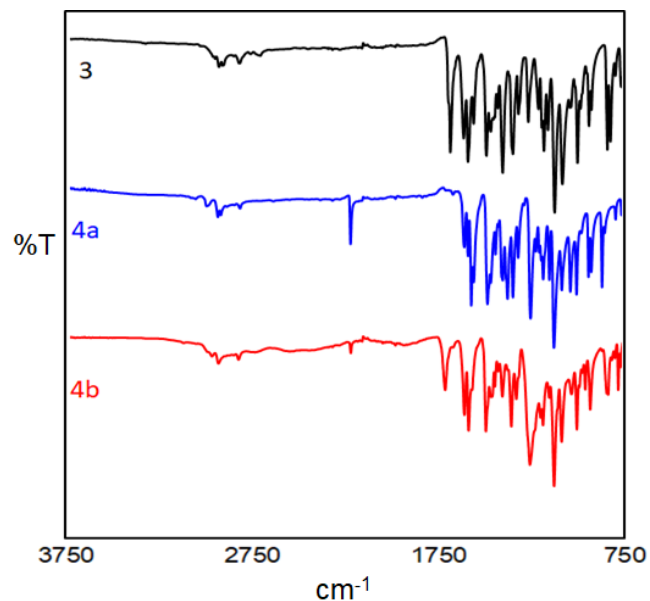


Figure 2. FT-IR spectra of **3**, **4a** and **4b**

¹H NMR spectra (**Figure 3**) of **3**, **4a** and **4b** were taken in CDCl₃ and compared with each other. In ¹H NMR spectrum of compound **3**, one proton of aldehyde group was observed as singlet at 10.25 ppm. Two aromatic protons of the quinoline ring resonated as two singlets at 8.65 and 7.13 ppm. Hydrogens of three different methoxy groups and one thiomethyl group were observed as four singlets of three protons at 4.12, 4.05, 3.96 and 2.68 ppm, respectively. In ¹H NMR spectra of compounds **4a** and **4b**, the aldehyde proton of compound **3** disappeared, replaced by the singlet signals (9.01 ppm for **4a** and 8.86 ppm for **4b**) of alkenyl protons. In addition, two singlets in the aromatic region and four singlet signals in the aliphatic region are observed separately for the two compounds.

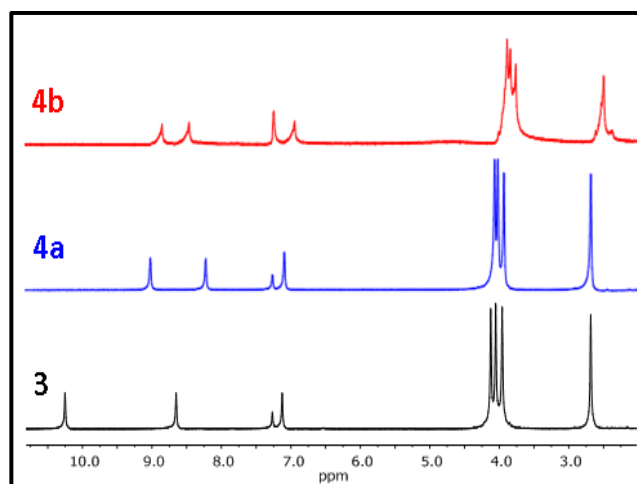


Figure 3. ^1H NMR spectra of **3**, **4a** and **4b**
(300 MHz, CDCl_3)

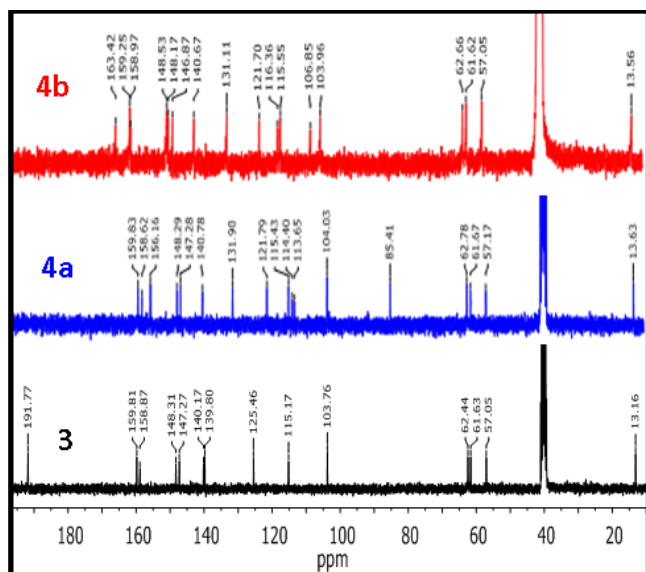


Figure 4. ^{13}C NMR spectra of **3**, **4a** and **4b**
(75 MHz, DMSO-d_6)

^{13}C NMR spectra (Figure 4) of **3**, **4a** and **4b** were taken in DMSO-d_6 and compared with each other. In ^{13}C NMR spectrum of **3**, carbon signal of the aldehyde group is observed at 191.77 ppm. Nine different aromatic carbons appeared at 159.81, 158.87, 148.31, 147.27, 140.17, 139.80, 125.46, 115.17 and 103.76 ppm. Methoxy groups and thiomethyl group carbon peaks are detected at 62.44, 61.63, 57.05 and 13.16 ppm, respectively. In ^{13}C NMR spectrum of **4a**, the signal of the aldehyde carbon has disappeared, instead, signals of two alkenyl carbons and two nitrile carbons are observed. As well as signals of nine aromatic, three methoxy and one thiomethyl carbons are seen. In ^{13}C NMR spectrum of **4b**, one carboxylic acid carbon (163.42 ppm), two alkenyl carbons and one nitrile carbon are observed instead of the aldehyde carbon. As well as signals of nine aromatic, three methoxy and one thiomethyl carbons are seen.

When the FT-IR, ^1H NMR and ^{13}C NMR spectra of the compounds **3**, **4a** and **4b** are examined, it is observed that the proposed compound structures are compatible with the results obtained.

3.3. Photophysical characteristics

The UV-Vis absorption spectra of compounds **3**, **4a** and **4b** in DMSO solution are displayed in Figure 5 and the relevant data are given in Table 1. The λ_{abs} for compounds **3**, **4a** and **4b** are 334, 397 and 380 nm for the intramolecular charge transfer (ICT) band, respectively. As expected, the lowest absorption band belongs to compound **3** with relatively lower conjugation. When compound **4a** containing malononitrile unit and compound **4b** containing cyanoacrylic acid unit were compared, it was observed that the absorption band of **4a** is red shifted (17 nm) [20].

The fluorescence spectra in DMSO solution (Figure 6) were recorded by exciting at the absorption maxima of the compounds. The emission maxima (λ_{em}) for all compounds are parallel to the absorption maxima (λ_{abs}). It demonstrates that the malononitrile moiety similarly affects both light absorption and emission.

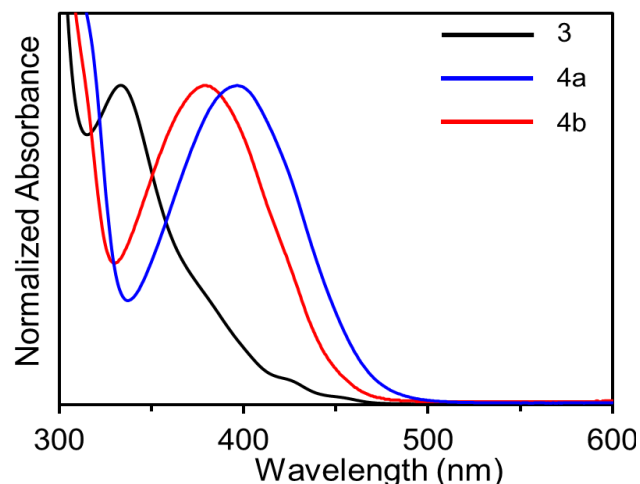


Figure 5. Normalized absorption spectra of **3**, **4a** and **4b** in DMSO solution

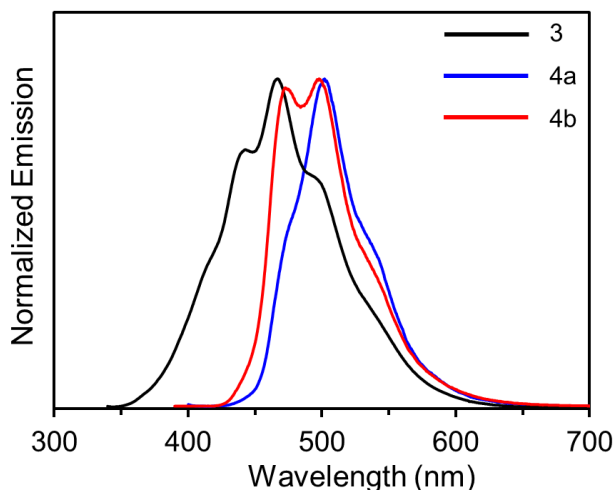


Figure 6. Normalized emission spectra of **3**, **4a** and **4b** in DMSO solution

Table 1.
Optical properties of the compounds

Compound	λ_{abs} [nm] ^a	λ_{onset} [nm] ^b	λ_{em} [nm] ^c	E_{0-0} [eV] ^d
3	334	390	443, 467	3.18
4a	397	470	502	2.64
4b	380	450	473, 498	2.76

^a λ_{abs} : absorption maximum wavelength.

^b λ_{onset} : absorption onset wavelength.

^c λ_{em} : emission maximum wavelength

^d E_{0-0} : band gap, calculated using the equation

$$E_{0-0} = 1240/\lambda_{\text{onset}}$$

3.4. Photovoltaic properties of DSSCs

Due to the low absorption band (334 nm) of compound **3**, only the photovoltaic properties of compounds **4a** and **4b** were investigated. Firstly, the prepared photoanodes were immersed in dye solutions for 6 hours. Because of the weak bonding on TiO₂ surface of the malonitrile group in compound **4a**, there was hardly any coating during this time. Therefore, the immersion time for **4a** was determined as 24 hours.

The current density–voltage (J–V) graph of the DSSCs obtained from dyes **4a** and **4b** are shown in **Figure 7** and the photovoltaic parameters (J_{sc} , V_{oc} , FF and PCE) are given in **Table 2**. When the PCE of the dyes (0.28% for **4a** < 2.73% for **4b**)

are compared, an increase is observed in parallel with the J_{sc} values. There was a more red shift of compound **4a** (397 nm) than **4b** (380 nm) in the absorption spectra. Although this is expected to have an effect on light harvesting ability, it does not appear to be compatible with PCEs [20]. The reason for this is the carboxyl group forms a strong ester bond with the TiO₂ surface, which increases electron conduction [21]. Compound **4b** containing cyanoacrylic acid as an acceptor forms a stronger bond with TiO₂ than compound **4a** containing malonitrile. This results in a higher power conversion efficiency of compound **4b**.

CDCA, which is commonly used as a coadsorbent in DSSC production, prevents aggregation as well as recombination, leading to an increase in J_{sc} and V_{oc} [22]. The J–V curves of the DSSCs of the two dyes containing 5 mM CDCA are shown in **Figure 7** and the associated data in **Table 2**. Two dyes show 0.22–0.40 mA cm⁻² of J_{sc} increase and 12–13 mV of V_{oc} increase. It shows the utility effect of CDCA on performance, the final PCEs lie of **4b** (3.01%) > **4a** (0.44%). When compared to the efficiency of the N719-based device (7.81%) measured under the same conditions, it was determined that compound **4b** (with CDCA) reached approximately 39% of the N719.

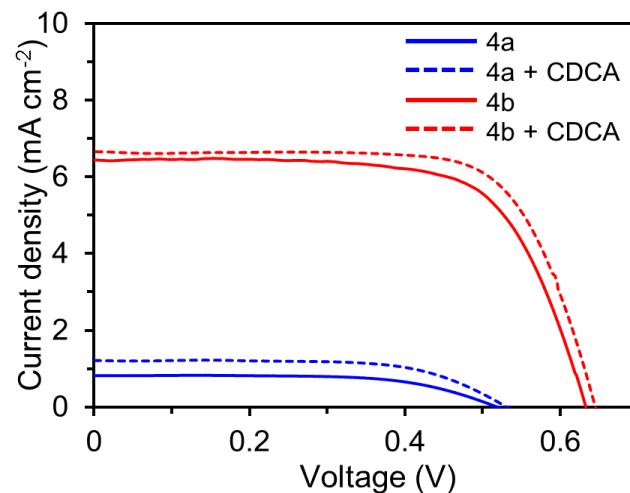


Figure 7. J–V curves of DSSCs based on the dyes in the absence and presence of CDCA

Table 2.
Photovoltaic parameters of the DSSCs

Dye	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	PCE (%)
4a	0.82	0.518	0.66	0.28
4a +CDCA	1.22	0.531	0.68	0.44
4b	6.44	0.633	0.67	2.73
4b +CDCA	6.66	0.645	0.70	3.01
N719 +CDCA	15.16	0.736	0.70	7.81

To understand the effect of the thiomethyl group on PCE, compound **4b** can be compared with structurally similar compound **5b** which is previously synthesized for application in DSSC by our study group [8]. Higher PCE was obtained when the thiomethyl group is incorporation (**Figure 8**) instead of only one methoxy group. The PCEs for the two compounds are 2.62% for **5b** and 3.01% for **4b** in the presence of CDCA. Although the maximum absorbances (380 nm) of these two compounds were the same, due to the different λ_{onset} values (432 nm for **5b** and 450 nm for **4b**), the band gaps (2.87 eV for **5b** and 2.76 eV for **4b**) were changed. This explains why the PCE of compound **4b** is higher than that of compound **5b**.

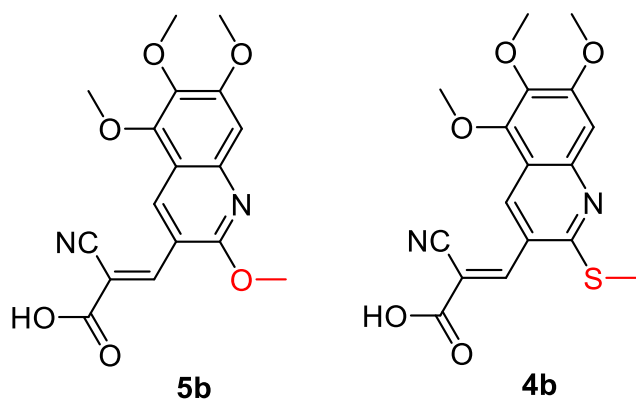


Figure 8. Molecular structures of **5b** in previous work and **4b** in this study

4. CONCLUSIONS

In this study, two novel D- π -A dyes (**4a** and **4b**) containing three methoxy (-OCH₃) and one thiomethyl (-SCH₃) groups as donors, quinoline ring as π -bridge, malononitrile or cyanoacrylic

acid as acceptors were synthesized. The compounds obtained were structurally characterized by FT-IR, ¹H NMR and ¹³C NMR techniques. Two dyes (**4a** and **4b**) were applied on DSSC and the effects of anchoring groups on PCEs were investigated. Compound **4b** demonstrated ($J_{sc} = 6.66$ mA cm⁻², $V_{oc} = 0.645$ V and $FF = 0.70$) the highest power conversion efficiency of 3.01% in the presence of CDCA as a coadsorbent. It also caused a narrowing of the band gap with the introduction of the thiomethyl group into the structure, which positively affects the power conversion efficiency. To sum up, it is determined that the presence of thiomethyl group instead of methoxy group and the better anchoring of cyanoacrylic acid, which forms an ester bond with the TiO₂ surface, increases the PCE.

Funding

The author received no financial support for the research, authorship, and/or publication of this paper.

The Declaration of Conflict of Interest/Common Interest

No conflict of interest or common interest has been declared by the author.

The Declaration of Ethics Committee Approval

The author declares that this document does not require an ethics committee approval or any special permission.

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publication environment other than Sakarya University Journal of Science.

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