STUDY OF THE EFFECTS OF FABRICATION METHOD AND DYE MOLECULAR STRUCTURE ON DYE-SENSITIZED SOLAR CELL PERFORMANCE

Kritsada Ronyhut

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การศึกษาผลของวิธีการขึ้นรูปและโครงสร้างทางโมเลกุลของสีย้อมไวแสงที่มีต่อประสิทธิภาพของเซลล์แสงอาทิตย์ชนิดสีย้อมไวแสง

นายกฤษดา รอญยุทธ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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Suranaree University of Technology has approved this thesis submitted in partial fulfillment of the requirements for a Master's Degree.

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กฤษดา รอญยุทธ : การศึกษาผลของวิธีการขึ้นรูปและโครงสร้างทางโมเลกุลของสีย้อมไวแสงที่มีต่อประสิทธิภาพของเซลล์แสงอาทิตย์ชนิดสีย้อมไวแสง (STUDY OF THE EFFECTS OF FABRICATION METHOD AND DYE MOLECULAR STRUCTURE ON DYE-SENSITIZED SOLAR CELL PERFORMANCE) อาจารย์ที่ปรึกษา : ผู้ช่วยศาสตราจารย์ ดร.ธนพร แม่นยำ, 54 หน้า

จุดประสงค์ของวิทยานิพนธ์นี้ เพื่อศึกษาผลเชิงโครงสร้างที่มีผลต่อประสิทธิภาพของเซลล์แสงอาทิตย์ชนิดสีย้อมไวแสงสารอินทรีย์และพัฒนาประสิทธิภาพโดยการเติมสารลดการเกาะกลุ่มของสีย้อมไวแสง เซลล์แสงอาทิตย์ชนิดสีย้อมไวแสงในการศึกษาครั้งประกอบด้วยสีย้อมชนิด C4T3A C12T3A และ C16T3A โดยมีคาร์บาโซลเป็นหมู่ให้อิเล็กตรอนไทโอฟีนเป็นสะพานเชื่อมอิเล็กตรอน และไซยาโนอะซิติค เป็นหมู่รับอิเล็กตรอนและทำหน้าที่ยึดเกาะกับไทเทเนียนไดออกไซด์ที่ขั้วไฟฟ้าใช้งาน รีดอกซ์อิเล็กโทรไลต์ประกอบด้วยคู่รีดอกซ์ไอออนไอโอไดด์/ไตรไอโอไดด์ อนุภาคขนาดนานโนของไทเทเนียมถูกใช้เพื่อเป็นตัวเร่งในปฏิกิริยารีดอกซ์ของอิเล็กโทรไลต์ สีย้อมไวแสงอนุกรมนี้ใช้ศึกษาผลของหมู่อัลคิลที่บนหมู่ให้อิเล็กตรอนคาร์บาโซลตัวที่ 2 โดยมีความยาวของหมู่อัลคิลที่ต่างกัน จากการศึกษาพบ หมู่โดเดคซิล (C12T3A) ทำให้เซลล์แสงอาทิตย์มีประสิทธิภาพสูงสุด สีย้อมไวแสงอนุกรมที่ 2 เพื่อศึกษาผลของหมู่ให้อิเล็กตรอนที่แทนที่ ที่ตำแหน่งเดียวกับหมู่อัลคิลเพื่อเพิ่มความสามารถในการกำเนิดกระแสไฟฟ้า โดยหมู่ให้อิเล็กตรอนผ่านระบบ π-อิเล็กตรอน (C12TSA) และผ่านอิเล็กตรอนคู่โดดเดี่ยว (C4TMA) ผลการศึกษาพบว่า C4TMA ให้ประสิทธิภาพสูงกว่า แต่ยังมีประสิทธิภาพต่ำกว่าเซลล์แสงอาทิตย์ที่ขึ้นรูปจาก C12T3A สีย้อมไวแสงอนุกรมที่ 3 เพื่อศึกษาผลความยาวของระบบ π-อิเล็กตรอนและผลของหมู่อัลคิลที่แทนที่บนสะพานเชื่อมระบบ π-อิเล็กตรอน จากการศึกษาพบ เมื่อเพิ่มความยาวของระบบ π-อิเล็กตรอน โดยการเพิ่มจำนวนหน่วยของไทโอฟีนเป็น 4 หน่วย (C12T4A) สามารถดูดกลืนพลังงานแสงอาทิตย์ในช่วงพลังงานต่ำอย่างมีประสิทธิภาพกว่าสีย้อมไวแสงที่มีไทโอฟีน3 หน่วย (C12T3A) แต่การเพิ่มความยาวของระบบ π-อิเล็กตรอน ทำให้สีย้อมไวแสงง่ายต่อการเกาะกลุ่มแล้วเสมือนตัวกรองแสงทำให้แสงที่ส่องผ่านมายังสีย้อมที่สามารถกำเนิดกระแสไฟฟ้าได้ลดลง ซึ่งเป็นสาเหตุของการลดลงของกระแสไฟฟ้าถึงแม้จะสามารถดูดกลืนพลังงานแสงดีกว่า และเมื่อแทนที่ด้วยหมู่เฮกซิลที่ไทโอฟีน พบว่าประสิทธิภาพของเซลล์แสงอาทิตย์สูงขึ้นเพื่อปรับปรุงประสิทธิภาพเซลล์แสงอาทิตย์ชนิดสีย้อมไวแสง โดยการเพิ่มความสามารถในการกำเนิดกระแสไฟฟ้าด้วยการเติม CDCA พบว่า เมื่อเติม CDCA ลงในสารละลายสีย้อมไวแสง การกำเนิดกระแสไฟฟ้าของเซลล์แสงอาทิตย์เพิ่มขึ้นแต่ต้องพิจารณาถึงขนาดของโมเลกุล ถ้าโมเลกุลมีความ

เกาะสูงการเติม CDCA ในปริมาณที่มากเกินไปจะทำให้ความสามารถในการกำเนิดกระแสไฟฟ้าลดลง เนื่องจากโมเลกุลของสีย้อมไวแสงถูกแทนที่ด้วยโมเลกุล CDCA

สาขาวิชาเคมี
ปีการศึกษา 2561

ลายมือชื่อนักศึกษา________________
ลายมือชื่ออาจารย์ที่ปรึกษา________________
ลายมือชื่ออาจารย์ที่ปรึกษาร่วม________________

KRITSADA RONYHUT : STUDY OF THE EFFECTS OF FABRICATION METHOD AND DYE MOLECULAR STRUCTURE ON DYE-SENSITIZED SOLAR CELL PERFORMANCE. THESIS ADVISOR : ASST. PROF. THANAPORN MANYUM, Ph.D. 54 PP.

DYE SENSITIZED SOLAR CELL/CARBAZOLE

The objectives of this thesis were to study the effect of structural properties of dye sensitizers on dye sensitized solar cell performance efficiency and to improve performance efficiency by aggregation prevention with co-adsorbent. This study used different types of sensitizers, containing carbazole as donor part, oligothiophene as linker and acrylic acid as accepter part. The TiO_2 deposited on FTO was used as working electrode, I^-/I^-_3 redox couple as electron mediator and Pt nanoparticle deposited on FTO as counter electrode. Sensitizer series 1 were used to study the effect of different length of alkyl chain substitution on *N*-secondary carbazole. We found that the dodecyl group had suitable chain for substitution to prevent dye aggregation. Sensitizer series 2 were used to study the effect of different electron donating groups substitution on the same position as alkyl group to increasing of photocurrent generation, since electron donating group via lone pair electron (C4TMA) was more effective than electron donating group via π-conjugated system. Sensitizer series 3 were used to study the effect of π-conjugated system extension and the effect of hexyl group substitution on oligothiophene linker. We found that the longer π-conjugated system dye (C12T4A) could more adsorb longer wavelength photon than the shorter one (C12T3A), resulting in photocurrent generation ability directly, however J_{SC} of C12T3A was higher than J_{SC} of C12T4A, because C12T4A was easy to aggregate on was easy to aggregate on TiO_2 surface, to solve this problem, hexyl group was placed on linker (C12T4HA), C12T4HA J_{SC} achieved the highest value of J_{SC}. To improve the performance of DSSC, chenodeoxycholic acid (CDCA) was used as co-adsorbent to prevent dye aggregation. In order to achieve the highest value of J_{SC}, the suitable number of CDCA mole depend on the steric of dye molecule.

School of Chemistry

Academic Year 2018

Student's Signature__________________

Advisor's Signature__________________

Co-advisor's Signature________________

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Finally, I would also like to express my deep sense of gratitude to my parents for their support and encouragement me throughout the course of this study at Suranaree University of Technology.

Kritsada Ronyhut

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LIST OF ABBREVIATIONS

DSSC	Dye Sensitized Sola Cell
FTO	Fluorine doped Tin oxide
ICE	Internal conversion efficiency
IPCE	Incident photon to current efficiency
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
S	Ground state sensitizer
S^*	Excited state sensitizer
S^+	Oxidative sensitizer
e^-	Electron
η	Over all sunlight to current power
π	Pi bond electron
λ	Wave length

CHARTER I

INTRODUCTION

1.1 Solar energy

Solar energy is the most important energy source for every life. It is one type of renewable energy source, because it has outstanding properties, the first reason, solar is purely clean electrical power generation, it do not have carbon dioxide emission to climate that is the cause of greenhouse phenomena and the second reason it is abundant and free, more than 1.7×10^5 of solar radiation reach to the Earth's surface, to convert solar energy to usable form, photovoltaic cell is the necessary device for electrical power generation process.

1.2 Photovoltaic cell

Photovoltaic cell was first invented since 19th century by Charles Fritts, its sunlight conversion to electrical power can be described by photoelectric effect, reported by Albert Einstein in 1905, the first generation of solar cell. Solar cell can be divided to the main 2 types; solid state solar cell and liquid electrochemical solar cells.

1.2.1 Solid state solar cell

Standard and commercial solid solar cell was fabricated based on silicon material, the outstanding properties of standard silicon was available in sufficient quantities and high efficiency, furthermore, its manufacturing processes do not damage the environment, but its production process was need high technology. The standard silicon solar cell structure is composed with p-type and n-type semiconductor, p-type and n-type semiconductors that are composed of the same material, N-type semiconductors are obtained through the addition of pentavalent impurity atoms (doping), such as phosphorus, arsenic, and antimony, that share free electrons and thereby significantly increase the conductivity of silicon, in the other hand, p-type semiconductor was created by doped trivalent impurity atoms, such as boron, gallium, and aluminum, which have one valence electron less than the silicon atoms. In conclusion, although solid state solar cell based on silicon material show high performance efficiency, its production process is imperative difficult and high technology.

1.2.2 Dye-sensitized solar cells

Dye-sensitized solar cells (DSSC) for the last two decades led to the development of devices that are designed to reduce the cost of production and expand the applications of photovoltaic cells. The composition of DSSC was different from silicon based solar cell following **Figure 1**

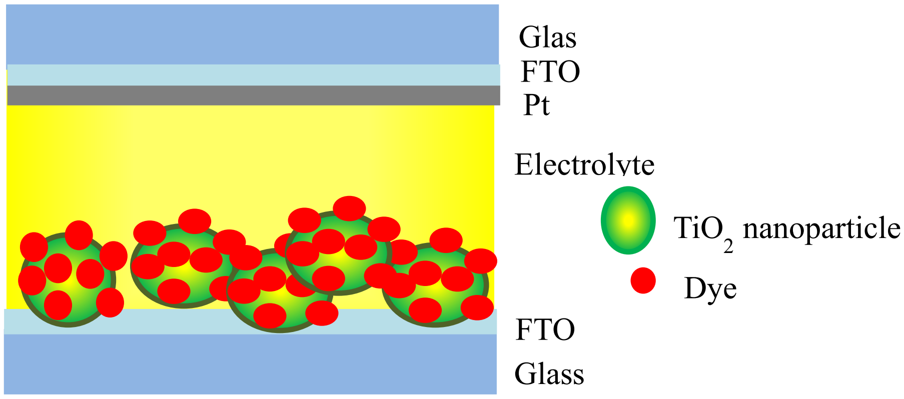


Figure 1 Structures of dye sensitized solar cell.

Working electrode

DSSC working electrode is fabricated from semiconductor thin film deposited on transparent conductive oxide substrate, for example, fluorine doped tin oxide $F:SnO_2$ (FTO) or indium tin oxide (ITO), they are selected to use as electrode substrate, because they allows light to pass through the cell and clear glass substrates were used as electrode substrates because of their low cost, good availability, and high transparency in the visible spectrum. Semiconductor oxide film shows appropriate properties to act as dye sensitized host, because, semiconductor oxide is good chemical stability in solution under visible irradiation, especially, TiO_2 is also a stable photo electrode in electrochemical systems under extreme operating conditions

Sensitized dye

One part of DSSC device which is used to harvest solar radiation and convert to electrical current, to improve performance efficiency ,sensitizer molecule structure is modified to enlarge photon absorption ability to near infrared region of solar radiation, enhance strength of bond between dye molecule and TiO_2 surface and increase stability of dye molecule under oxidative condition.

Redox electrolyte In dye sensitized solar cell, redox electrolyte officiates as electron source to compensate for the oxidized dye, especially, liquid electrolyte is employed widely in DSSC, liquid electrolyte consists of redox couple mediator and additive. The redox couple presents the significant part in charge transfer between the two electrodes and regenerates dye. The redox couple has many essential characteristics, such as, its redox potential must be lower than oxidized energy level of dye molecule, fast electron transfer kinetics to counter electrode, low visible light absorption ability and good stabilities.

Counter electrode To reduce redox couple from working electrode, counter electrode is usually made from platinum (Pt) catalyst, deposited on fluorine doped tin oxide F:SnO_2 (FTO) glass. Platinum has been interesting candidate material for fabricating counter electrodes, because platinum can be fabricated various methods, such as thermal deposition, sputtering coat and it shows high catalytic activity for tri-iodide reduction. Although, platinum has prominent properties for catalytic activity, it has the main disadvantage, such as high cost and rareness. The function of counter electrode is to transfer electron from outer circuit to redox couple and to carry photo current.

1.3 Operation principle of dye sensitized solar cells

Under sun radiation, photon through the front plate of a DSSC, and the incoming photons are absorbed by the layer of sensitized dye molecules, after that, electronic state is turned to excited state (S*) that lies energetically above the conduction band edge (CB) of the TiO_2 particles which can be formulated as follows:

$$S + \text{Photon}\ (hv) \rightarrow S^*$$

The excited dye injects an excited electron into the conduction band of theTiO_2 film working electrode, which results in the oxidation of the photo sensitizer:

$$S^* \rightarrow S^+ + e^- \ TiO_2$$

The redox electrolytes that contain I^-/I_3^-redox couple are used as electron mediator between the counter electrode and the TiO_2photo electrode. Thus, the oxidized dye receives electrons from the I^- ion redox to replace the lost electrons:

$$S^+ + 3I^- \rightarrow 2S + I_3^-$$

The tri-iodide ions reduce back to iodide (regeneration) when they diffuse towards the counter electrode by the electrons that return from the external load:

$$I_3^- + 2e^- \rightarrow 3I^-$$

DSSC operation principle can be displayed following **Figure 2**

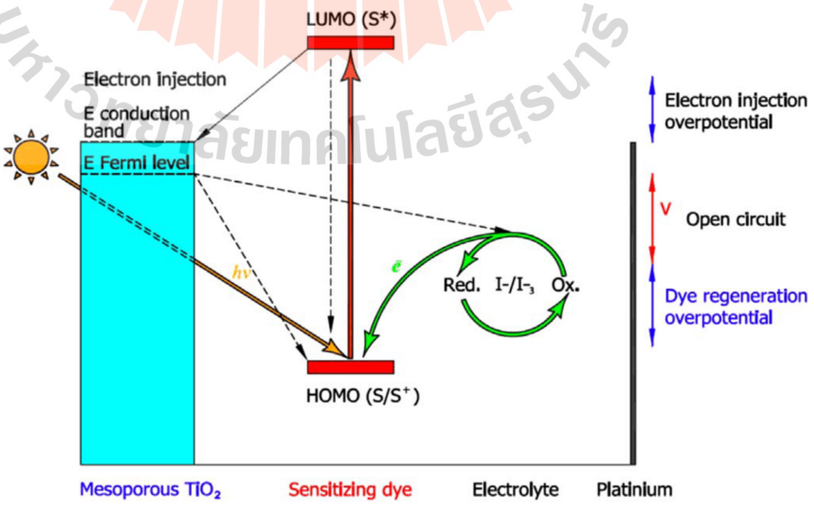


Figure 2 operation principle of dye sensitized solar cell. (Al-Alwani et al., 2016)

1.4 Dye sensitized solar cell characterization

To investigate dye sensitized solar cell properties, the overall sunlight-to-current power (η) and incident photon to current efficiency (IPCE) are used to reveal optical property of dye sensitized solar cell

1.4.1 The overall sunlight-to-current power conversion efficiency

The parameter showed conversion efficiency of dye sensitized solar cell devices. It was derived follow by expression

$$\eta = \frac{P_{max}}{P_{in}} = \frac{J_{SC}\ .\ V_{OC}\ .FF}{P_{in}}$$

Where

J_{SC} (Short circuit current) is the highest current that can be drawn from a solar cell. The cell voltage is at this point zero

V_{OC} (Open circuit voltage) is the highest potential of a solar cell at a given light intensity. It is also the potential where current flow through a solar cell is zero.

FF (Fill factor) is an important parameter to specify the overall abilities of a cell. It describes the quality and idealness of a solar cell. The Fill factor is the ratio of maximum generated power (P_{mp}) to theoretical power maximum (P_{theo}) of a solar cell. The general formula of Fill Factor can be derived from

$$FF = \frac{P_{mp}}{P_{theo}} = \frac{V_{mp}\ .I_{mp}}{V_{oc}\ .I_{sc}}$$

Maximum power voltage (V_{mp})and Maximum power current (I_{mp})are coordinated point on I-V curve which is highest power. Dye sensitized solar cell overall conversion efficiency characterization illustrated information in form of I-V curve following **Figure 3**

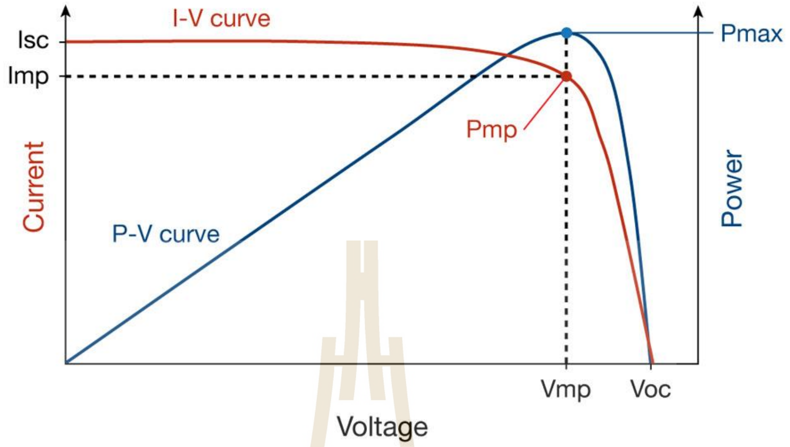


Figure 3 I-V characterization information of DSSC.

http://solarprofessional.com/sites/default/files/articles/ajax/docs/2_SP4_5_pg76_Hernday-3_0.jpg

1.4.2 Incident Photon to Current Efficiency (IPCE)

To study spectral incident photon to collected electron efficiency of DSSCs, incident photon to current efficiency (IPCE) can be used to reveal optical behavior of dye sensitized solar cells. Efficiency can be calculated from

$$IPCE\ (\lambda) = \frac{I_{sc}}{qI_0} = \frac{I_{sc}1240(mAcm^{-2})}{\lambda(nm)P_{in}(mAcm^{-2})}$$

where I_{sc} is short circuit current density of device under single wavelength radiation

q is the elementary charge

I_0 is photon flux

Data from IPCE characterization showed in IPCE curve following **Figure 4**

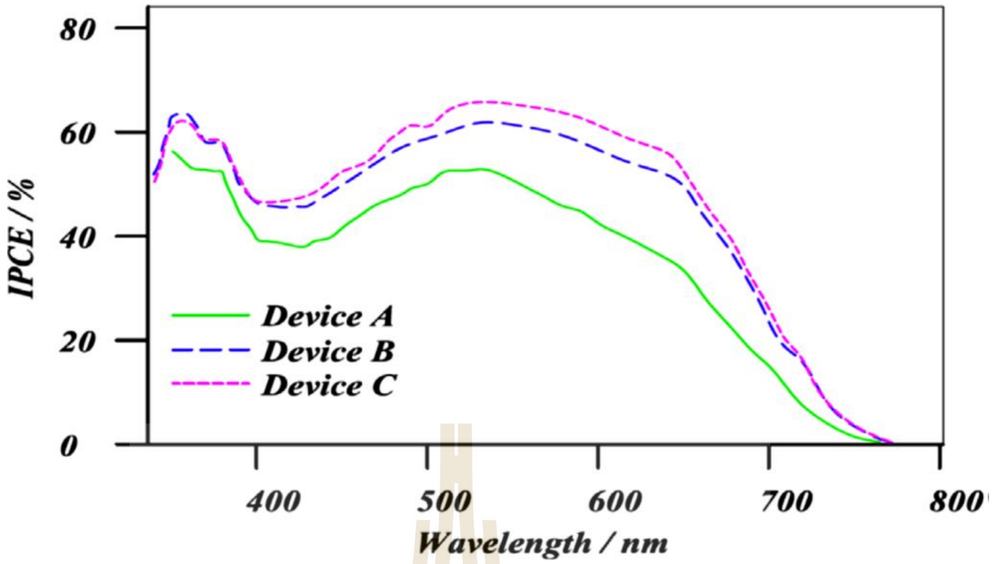


Figure 4 IPCE curve of DSSC. (Al-Alwani et al., 2016)

According IPCE curve, it describes photon harvesting of sensitizer whose it consists of incident photon to current efficiency percentage which show ability of DSSC in photon conversion and photon energy which can excite electron from ground state (HOMO) to exited state (LUMO) of dye molecule.

1.5 Evolution of dye sensitized solar cell

Dye sensitized solar cells can be classified into two classes; 1) metal complexes sensitizers 2) metal-free organic sensitizers.

1) Metal complex sensitizers are first type material to use in DSSCs, it was first reported by Gratzel and coworker in 1991. It consists of central metal and ligand molecule, especially Ruthenium complex sensitizer, their efficiency can achieve more than 8% for example N3, N719 and black dye, there have efficiency 8.2, 10.1 and 11.18% respectively.

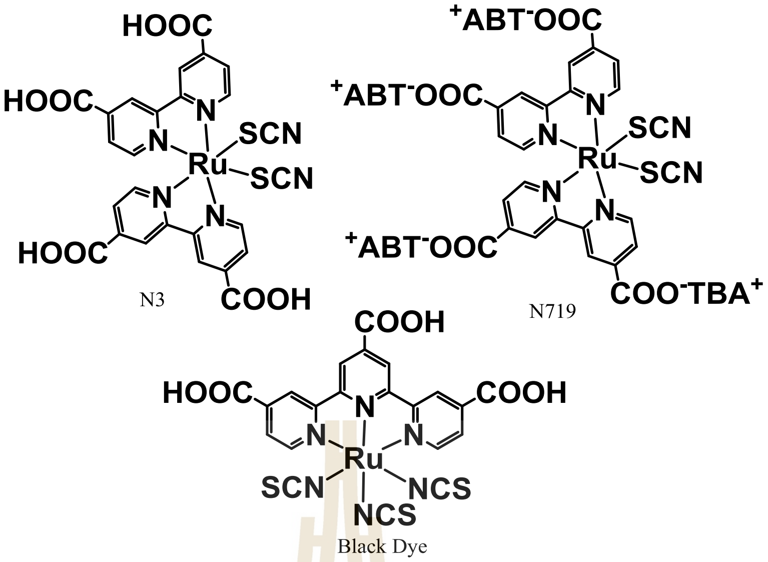
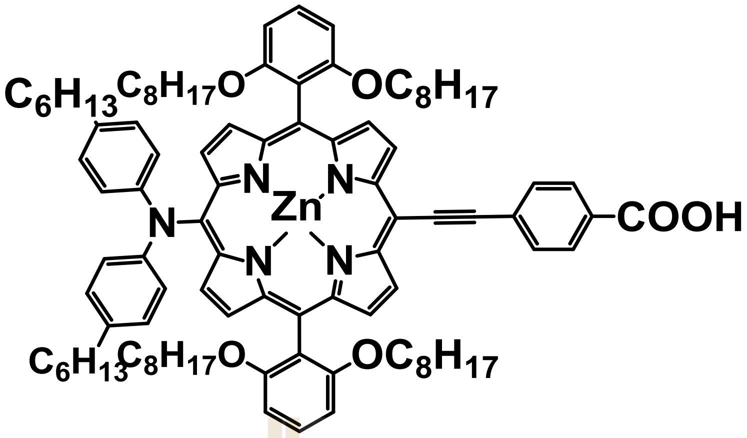


Figure 5 Ruthenium complex dyes structures. (Gratzel et al., 1991)

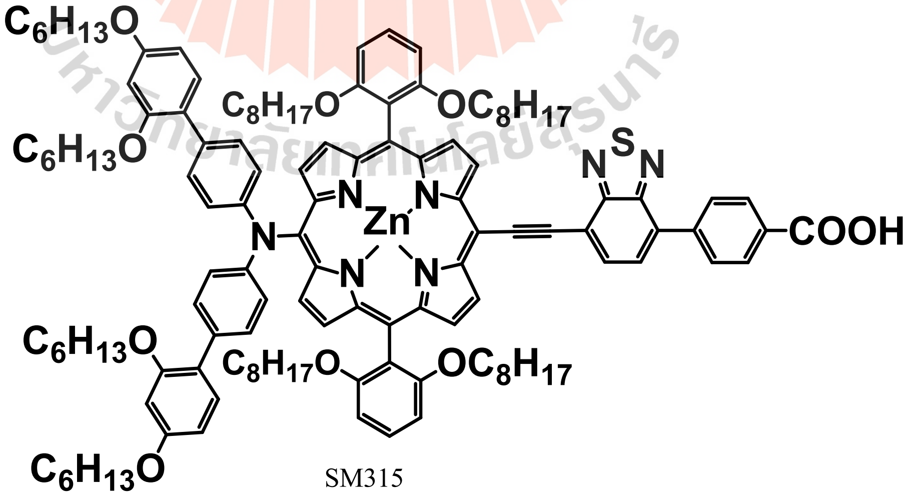
Even though DSSCs based on Ruthenium complex, have high conversion efficiency, but they have some limitation, such as expensive, high toxic metal and difficult to synthesis. So Grätzel and coworkers replaced ruthenium complex sensitizer with meso-porphyrin dye which used Zinc as central metal and porphyrin ring as ligand as show in **Figure 6** YD2-o-C8. They found that DSSCs based on Zinc porphyrin dye achieve 11.9% of overall power conversion efficiency. In addition, Zinc metals have better advantage than Ruthenium metals such as, low cost, non-toxic metal and available in natural. Despite DSSCs based on Zinc porphyrin dye can adjust limitation of Ruthenium complex DSSCs, but Cobalt (III/II) tris (2,2′-bipyridine) redox electrolyte must was used in Zinc porphyrin based DSSCs for raise up overall conversion efficiency to 12.3%, in another hand Cobalt metal in electrolyte has the same property with Ruthenium. (Gratzel et al., 2011).



YD2-o-C8

Figure 6 YD2-o-C8 dye structure.

In 2014 Nazzeruddin and coworker modified Zinc porphyrin dye structure for improve photon harvesting ability by extended conjugated π- electron system and electron donating group substitution following **Figure 7**. As the result overall conversion efficiency of DSSCs, fabricated from modified Zinc porphyrin dye ~13% (Nazzeruddin et al., 2014)



SM315

Figure 7 SM315 structure. (Nazzeruddin et al., 2014)

2) Metal free-organic sensitizers

Although DSSCs based on metal complex dyes achieve high overall conversion efficiency, their photon harvesting behavior cannot absorb photon in infrared region energy, it makes device is low photo current generation ability, complex to synthesis and purification, difficult to produce in industrial scale. As a result, research efforts are focus on organic dyes, because organic sensitizers have advantages, such as, easily tunable physicochemical properties by molecular design, well established synthetic procedure, along with their ease of purification and high molar absorption coefficient. Metal free organic dyes have great attention properties, such as, low cost and variable reagent, high molar absorption coefficient, high efficiency and complicated synthesis. Generally, metal-free organic sensitizers are consisted of donor (D), π-bridge and acceptor (A) moieties, called D-π-A character as shown in **Figure 8** This structure an induce the intramolecular charge transfer (ICT) from donor to accepter via the π-bridge when a dye absorbs light (Zeng W. et al., 2010).

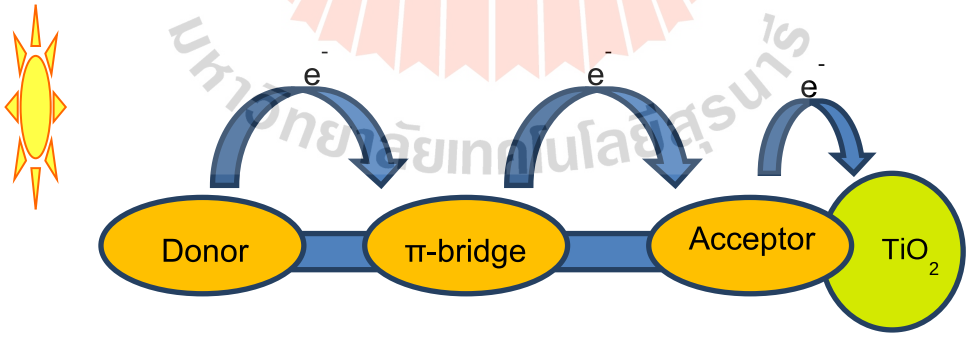


Figure 8 The D-π-A metal free organic dye structure. (Zeng W. et al., 2010).

Dye sensitized solar cells performance efficiency can be improved by 3 pathways

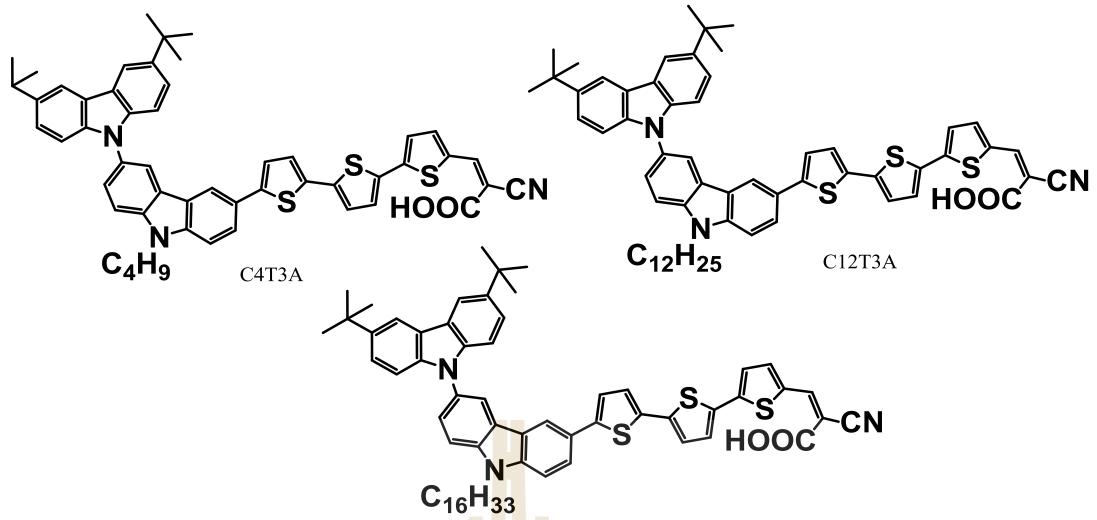
- Dye structure modification to improve photon harvesting ability and power generation
- Working electrode modification
- Redox couple electrolyte improvement

1.6 Research objectives

- To study effect of alkyl chain substituted on carbazole donor group to DSSC performance.
- To study effect of electron donating group substituted on carbazole donor group to DSSC performance.
- To study effect of alkyl chain substituted on thiophene linker to DSSC performance.

1.7 Scope of study

To study effect of dye structure to performance efficiency of DSSC. Dry series 1 have focused on the effect of alkyl chain substituted on N-carbazole donor group. as shown in **Figure 9**



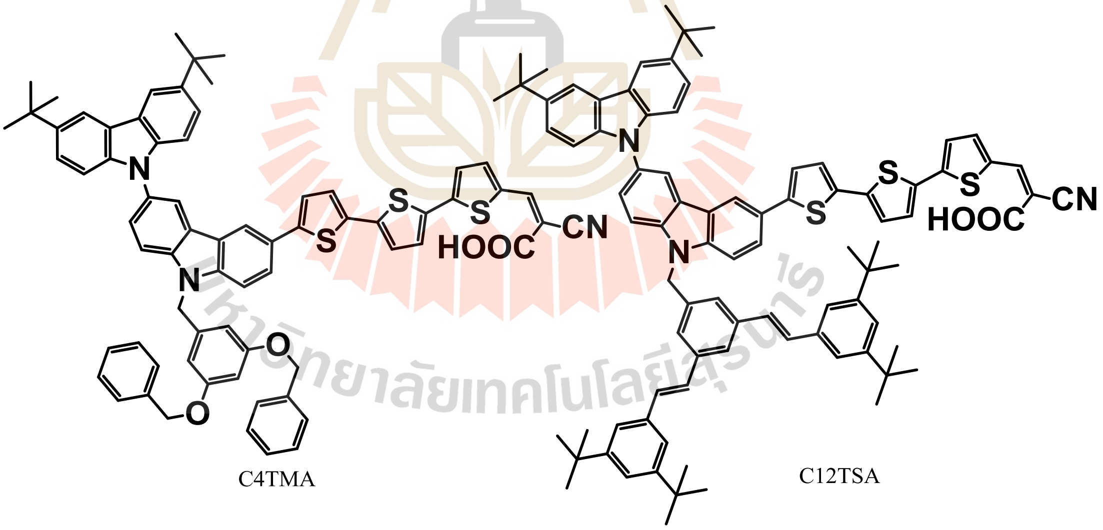
C4T3A

C12T3A

C16T3A

Figure 9 Chemical structures of dyes series I C4T3A, C12T3A and C16T3A.

Dyes series II have focused on the effect of various donor group substituted on carbazole donor moiety as shown as **in Figure 10**.

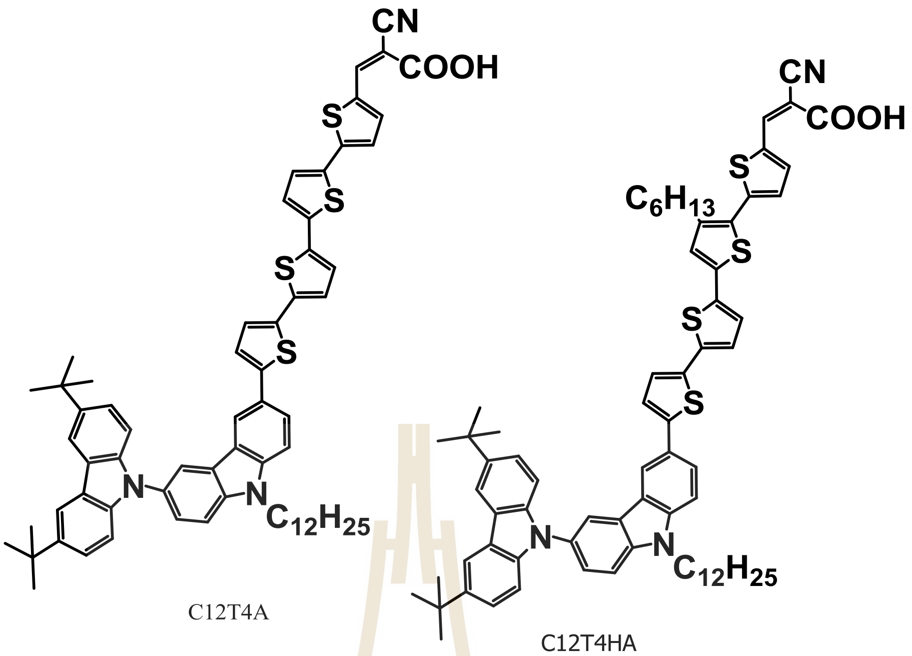


C4TMA

C12TSA

Figure 10 Chemical structures of dyes series II C4TMA and C12TSA.

Dyes series III have focused on the effect of alkyl chain substituted on thiophene linker as shown in **Figure 11**



C12T4A

C12T4HA

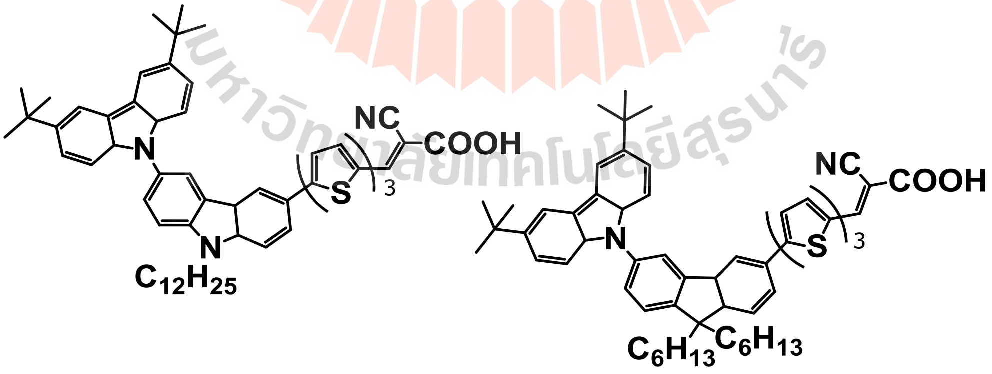
Figure 11 Chemical structures of dyes series III C12T4A and C12T4HA.

CHARPTER II

LITERATURE REVIEWS

2.1 Carbazole donor

In 2013 Sudyoadsuk and coworkers reported organic sensitizer, CCTA and CFTA, having D-D-π-A structure with carbazole-carbazole and carbazole-fluorene as donor moiety, cyanoacetic acid as electron acceptor, thiophene as π-spacer. The CCTA-dyes showed broad and red shifted absorption spectra compared to CFTA. The CCTA-sensitized cell gave an overall conversion efficiency of 5.69% which is higher than power conversion efficiency of DSSCs based on CFTA dye (3.64%). The DSSCs parameters consist of photo current density (J_{sc}) = 11.31 mA cm^{-2}, an open-circuit voltage (V_{oc}) = 0.71 V, and a field factor (FF) = 0.71. (Sudyoadsuk T. et al., 2013).



CCTA

CFTA

Figure 12 Chemical structures of dyes CCTA and CFTA.

In 2014 Venkateswararao and coworker presented effect of π-conjugated linker to optical, electrochemical and photovoltaic properties of dye sensitized solar cell bases on carbazole as donor, thiophene as π-linker and cyaonacetic acid as accepter as shown as **Figure 13** The efficiency of DSSCs utilizing these dyes as sensitizers ranged from 4.22% to 6.04%. They found effect of tert-butyl groups to suppress the recombination of injected electrons which contributed to the increment in the photo current density (J_{SC}) and open circuit voltage (V_{OC}). A dye with carbazole donor functionalized with tert-butyl groups and the conjugation bridge composed of 2,7-disubstituted carbazole and thiophene fragments exhibited higher V_{OC} value. However, the best performance efficiency was achieved by the dye without tert-butyl group substituted carbazole donor and carbazole connect with bithiophene units as π-spacer because of the highest value of dye molecule on surface of working electrode . (Venkateswararao et al., 2014).

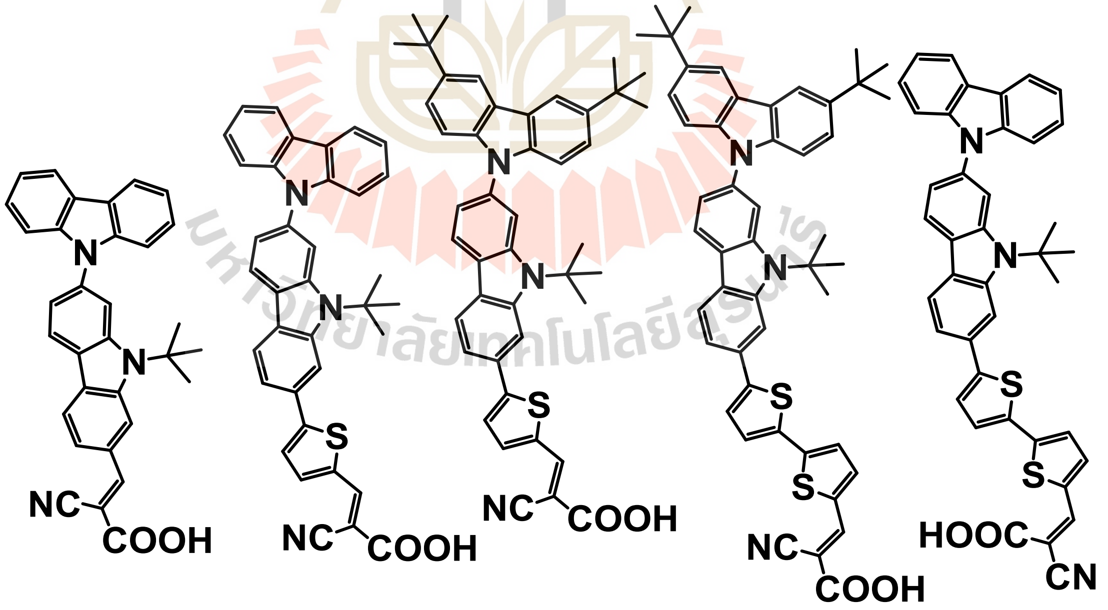


Figure 13 Chemical structures of carbazole donor dyes.

2.2 Effect of π-electron linker

In 2009 Ping and coworker reported effects of alkyl-substituents and π-conjugated thiophene unit to DSSC performance. Sensitizer structure consisted of triphenylamine as donor moiety, cyanoacetic acid as accepter and anchoring group and different thiophene unit π-spacer as shown as **Figure 14** Extended π-electron conjugation by thiophene unit increasing improved low energy photon harvesting, illustrated DSSC based on SD1 and SD5 spectra gradually become broader toward the red region, from SD1, SD3 and SD5 respectively. Open circuit voltage (V_{OC}) increase when introduce hexyl group on thiophene linker, for instance SD2 V_{OC} are 0.76 V which are higher than V_{OC} of SD1

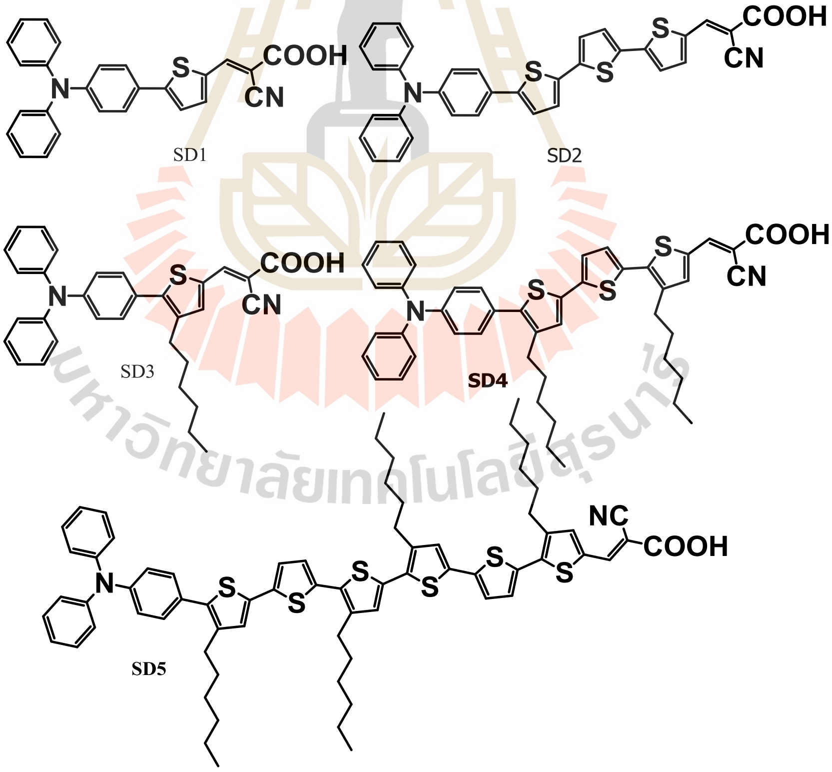


Figure 14 Chemical structures of SD-series sensitizer dyes.

In 2015 Sivanadanam and coworker studied effect of different π-spacer on photo voltaic properties of DSSC based on D-π-A organic sensitizer. Triphenylamine was used to be donor part, cyanoacetic acid as accepter part and benzene, furan and thiophene as π-spacer, coded TPC, TOC and TSC respectively as shown as **Figure 15**. The effect of π-spacer type to optical properties of DSSC based on metal free organic dye was manifested by IPCE spectrum in **Figure 16**. According to IPCE spectrum, DSSC, fabricated from TSC dye, had broader spectrum than device based on TPC and TOC consecutively. Consequently, overall conversion efficiency of TSC device had the highest value because its J_{SC} was higher than TPC and TOC one.

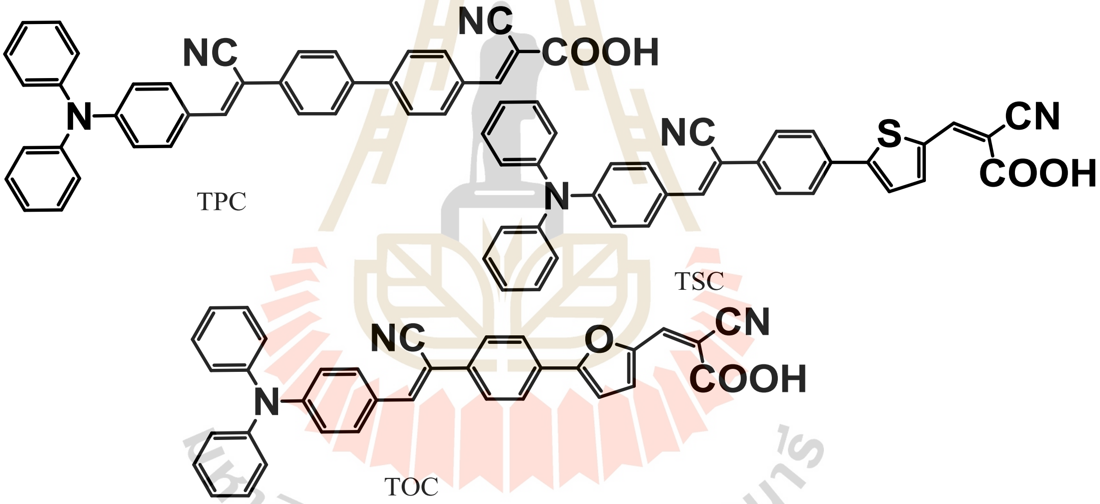


Figure 15 Chemical structure of triphenylamine donor dyes.

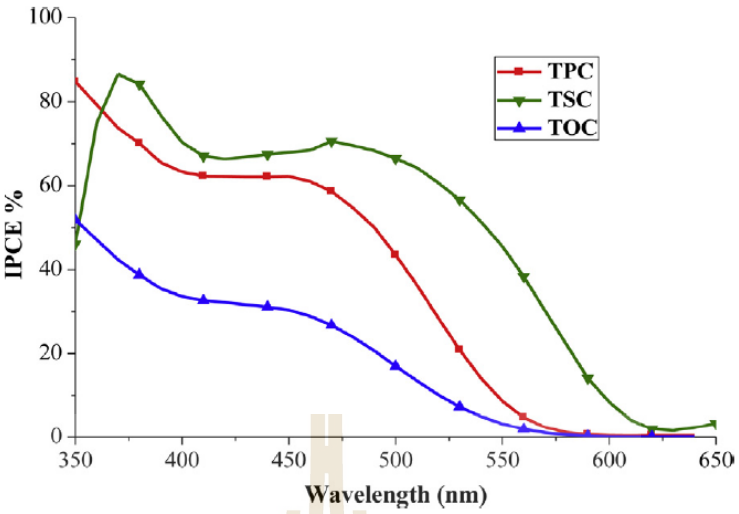


Figure 16 IPCE spectra of DSSCs based on triphenylamine dyes. (Sivanadanam et al., 2015).

In 2016 Roberto and coworker modified metal free organic dyes, based on triphenylamine as donor moiety, thiophene and diathiazole as linker and cyanoacetic acid as accepter part as shown as **Figure 17** n-hexyl group was substituted on linker to prevent recombination reaction between excited electron from dye molecule to TiO_2 electrode and alkoxy substitution on triphenylamine group for increasing of photo current generation. Effect of n-hexyl substitution to sensitizer structure made DSSC V_{OC} was higher than non-substituted n-hexyl and electron donating group: alkoxy and phenyl alkoxy, substitution could raise J_{SC} of DSSC, especially device based on G5 dye which had phenyl alkoxy substituent, afford high photo current.

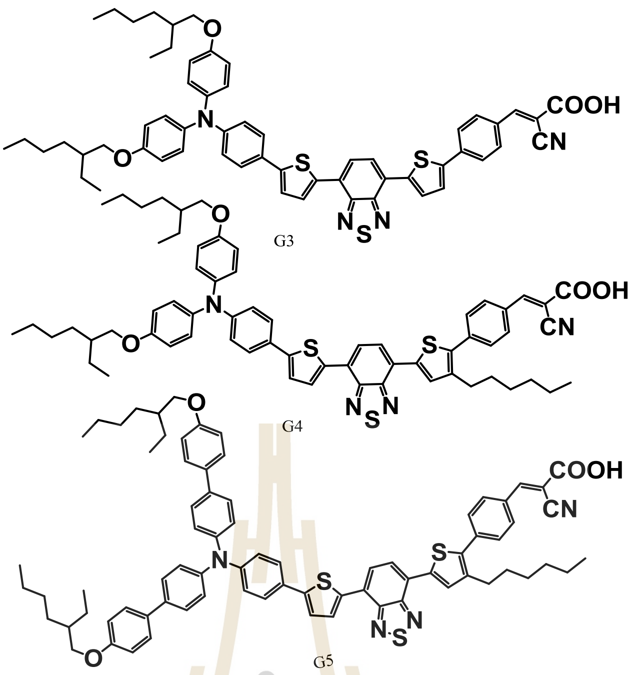


Figure 17 Chemical structure of G-series sensitizer dyes.

2.3 Redox electrolyte

To improve Voc of DSSC, electrolyte based on I^-/I_3^- redox couple with a different cation such as Li^+, tetra-n-butylammonium (TBA^+), or 1,2-dimethyl-3-propylimidazolium ($DMPIm^+$), was added to electrolyte to charge recombination reaction in dye sensitized solar cell. (Shogo, N., et al., 2005) They found open-circuit voltages of DSSCs decreased in the order of $TBA^+ > DMPIm^+ > Li^+$, because the TiO_2 conduction band potential (CBP) were attributed to the positive shift of by the surface adsorption of $DMPIm^+$ and Li^+, in the other hand, tetra-n-butyl ammonium ion is high steric effect ion, so it can prevent Li^+ attribution to surface of TiO_2, so the shift of the conduction band potential back to the negative potential by reducing the amount of adsorbed Li cation.

2.4 Working electrode

To enhance photocurrent generation, larger size particle TiO_2 was composited by screen printing method on surface of working electrode for as light scattering layer. (Wang et al., 2013). Performance efficiency of DSSC with scattering layer is higher than without one, because its photo current is increase, since scattering layer reflect the incident light to dye molecule in transparent layer and extend the traveling distance of the light within the working electrode, so it indicate that performance efficiency can be promoted by scattering layer superimposing

2.5 Effect of chenodeoxycholic acid (CDCA)

One method for photocurrent generation enlargement, chenodeoxycholic acid **Figure 18** (CDCA) is used as a co-adsorbent on the photovoltaic cell to improve performance of dye-sensitized solar cells. (Jing et al., 2013). Two organic dyes, containing phenothiazine and triarylamine segments as donor moiety (P1 and P2) as shown as **Figure 19** were investigated, I-V plot of device based on P2 show characteristic following **Figure 20 - Figure 22,** the DSSCs parameters consists of short-circuit photo current density (J_{SC}) of 9.57 $mAcm^{-2}$, an open-circuit voltage (V_{OC}) of 697 mV, and a fill factor (FF) of 0.66, corresponding to an overall conversion efficiency of 4.42% under the standard global AM 1.5 solar light condition as shown as **Figure 15a**, further more they improved performance efficiency by added CDCA10 mM, overall conversion efficiency increases to 5.31% (Jsc = 10.36 $mAcm^{-2}$, Voc = 0.730 V, FF = 0.70), it indicates that co-absorbent can hinder the formation of dye aggregates and improve electron injection yield and thus leading to an increasing of Jsc in the device photocurrent. In the other hand, increases of the CDCA concentration to 20 mM leads to a decrease in the V_{OC} value, because adsorption of CDCA leaves protons on the TiO_2 surface and hence charges the surface positively shifted by the co-adsorption of CDCA, resulting in Voc loss and CDCA replace sensitizer dye molecule that means photo–current generation molecule decrease, resulting J_{SC} value decrease.

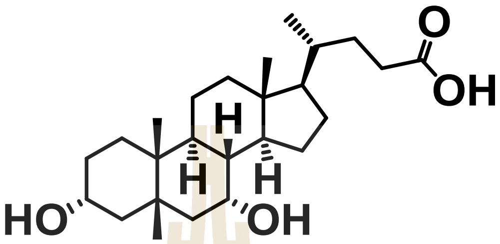


Figure 18 Chemical structure of Chenodeoxycholic acid. (CDCA)

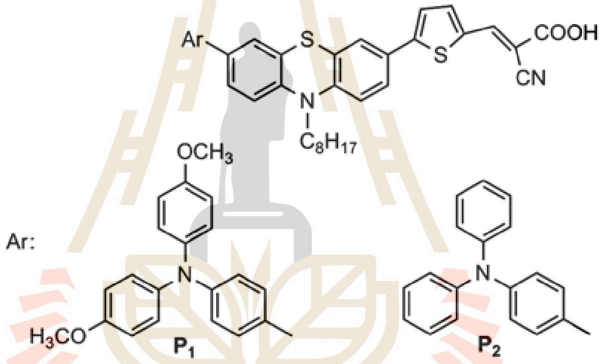


Figure 19 Chemical structures of dyes P1 and P2. (Jing et al., 2013).

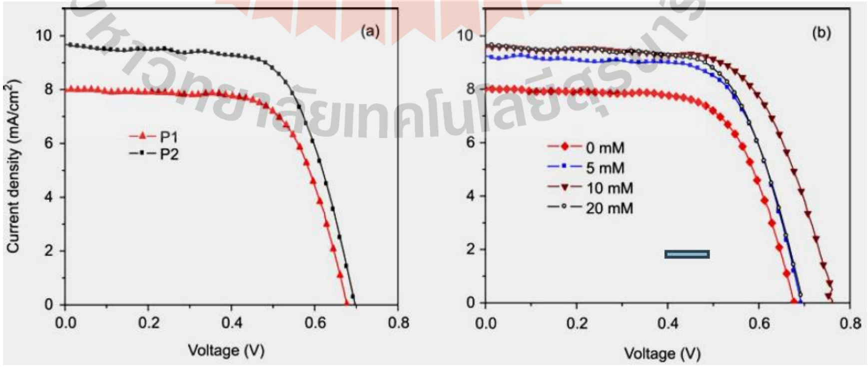


Figure 20 (a) I-V characteristics of DSSCs based on P1 and P2 co-adsorbed without CDC and P1 co adsorbed with CDCA on the concentration of 0, 5, 10, 20 mM. (Jing et al., 2013).

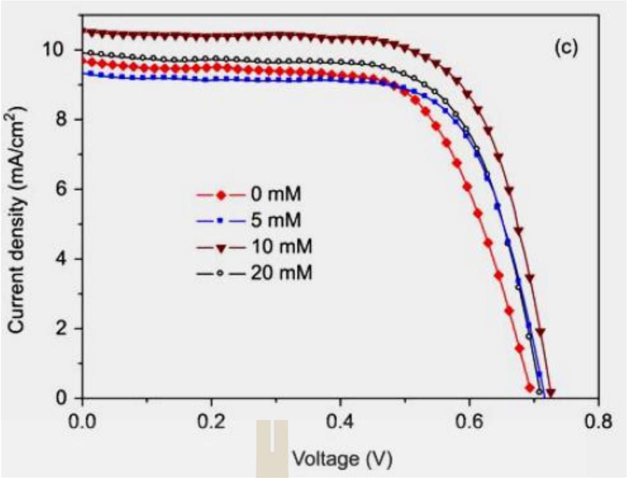


Figure 21 I-V characteristic of P2 with CDCA on the concentration of 0, 5, 10, 20 mM. (Jing et al., 2013).

CHARPTER III

EXERIMENTAL PROCESS AND CHARACTERIZATION METHODS

3.1 Chemical and Materials

Fluorine doped Tin oxide (FTO), 3 mm. of thickness, 8 ohm/sq. of resistivity, 2 mm. of thickness, 15 ohm/sq. of resistivity, scattering TiO_2 and transparent TiO_2 paste were purchased from Solaronix. Robust iodine (I_2) and tertiary butyl pyridine (TBP) were Fluka products, Lithium iodide (LiI) and tertiary propyl ammonium iodide salts (TPAI) were purchased from Sigma-Aldrich, varelonitrile (Merck) and acetonitrile (Merck) were used as electrolyte solvent, ethanol and chloroform, AR grade, were used as solvent in dye solution preparation, N719 dye (Solaronix) was used as standard dye.

3.2 Equipment

New Port Xenon arc lamp was used as light source. Keithley model 2400 was used to measure power conversion efficiency. Keithley 6485 Picoammeter was used to measure power conversion efficiency.

3.3 Working electrode preparation

Fluorine doped tin oxide (FTO) glass: 3 mm thickness, 1.3 cm. of wideness and 2 cm. of length, is used as electrode substrate, it is washed detergent, deionized water, acetone and alcohol step by step 2 times. After step, its conducting side is spin coated with electron blocking solution, anneal at 450ºC for 30 minutes and cool down to room temperature, then transparent TiO_2 paste is screen printed on FTO glass by 90 T mesh screen block, heat 120ºC for 10 minutes and cool down to room temperature, repeat screen printing process 3 times, but the last cycle, transparent TiO_2 paste is replaced by scattering TiO_2 paste. After screen printing process, working electrode is annealed at 500ºC for 30 minutes, then cooled down to 80ºC and immersed in dye solution bath overnight.

Figure 22 Dye bath solution.

Figure 23 Working electrode.

3.4 Counter electrode preparation

Fluorine doped tin oxide (FTO) glass: 3 mm thickness, 1.3 cm. of wideness and 2 cm. of length and drilled, is used as electrode substrate, it is washed detergent, deionized water, acetone and alcohol step by step 2 times. After cleaning process, platinum catalyst is deposited on the conductive side of FTO by dropped 36μL of 7mMH_2PtCl_6 solution in 1:3 of acetyl lactone and methoxy methanol, then remove organic residues counter electrode is heated at 380°C for 30 minutes , then and the last substrate was heated at 480 380°C for 30 minutes by using heat gun and cool down to room temperature.

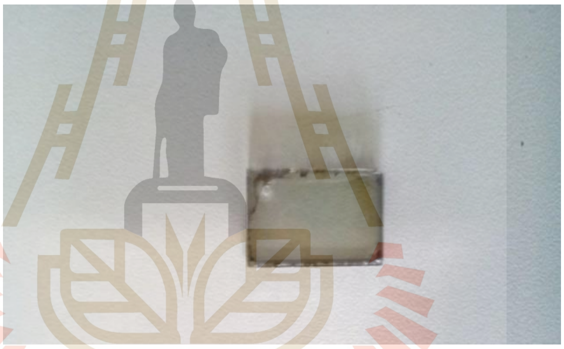


Figure 24 Counter electrode.

3.5 DSSC assembling

Working electrode and counter electrode are assembled into a sandwich-type cell, they are sealed by hot-melt gasket of 25 μm thickness of the ionomer Surlyn on heating stage, then drop electrolyte solution onto the hole, The device is put into a vacuum chamber for electrolyte loading, in the last, the hole is covered by hot-melt ionomer film and covered hot glass. Copper tape attack to the both electrodes, solder with wire for connection to the photovoltaic measurement set up.

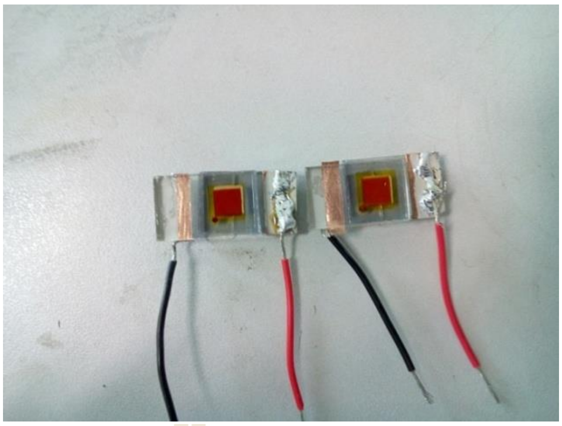


Figure 25 DSSC device.

3.6 Power conversion efficiency measurement

Dye sensitized solar cell parameters: J_{SC}, V_{OC} and FF, were carried out for DSSC overall conversion efficiency calculation. Keithley model 2400 source meter was used to measure photocurrent and open circuit voltage. Light source in measurement, Xenon-arc lamp, was used as photon source in solar simulator under 1.5 AM condition, which 1.5 atmosphere thickness, corresponds to a solar zenith angle of 48.2°

Figure 26 Light source.

3.7 Incident Photon to current efficiency (IPCE)

The key to accurately measuring the IPCE of a solar cell is to quantify the intensity of monochromatic light incident to the device under test and measuring how much current is generated. IPCE test set consist of Xenon-arc lamp, monochromator and picoammeter, all of instruments were driven by COEA DSSC characterization program.

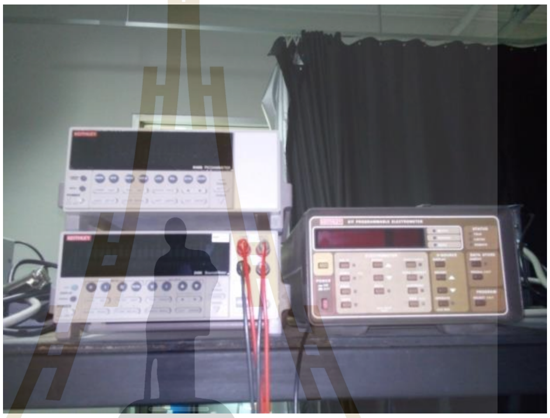


Figure 27 Source meter (below left) and picoammeter. (top left)

CHARPTER IV

RESULTS AND DISCUSSION

4.1 Dye sensitized solar cell fabrication optimization

4.1.1 Effect of transparent TiO_2 component

The number of transparent TiO_2 layer was investigated to study the suitable TiO_2 thickness as working electrode for DSSC. The working electrode consists of different number of transparent TiO_2 layer following 1 layer, 2 layers and 3 layers respectively and 1 layer of scattering TiO_2 0.3 mM of N719 dye solution was used as photosensitizer. E4 redox mediator consisting of 0.05 M of I_2, 0.1 M of LiI, 0.4 M of TBP and 0.6 M of TPAI in mixed solvent between varelonitrile and acetonitrile 15:85 by volume was used as liquid electrolyte. DSSC parameters were measured under 1.5 AM condition and are shown in **Table1**

Table 1 DSSC parameters of different number of transparent TiO_2 layer device.

Device	Number of TiO_2 layer	J_{SC} ($mAcm^{-2}$)	V_{OC} (V)	FF	%PCE
I	1 layer	13.53	0.801	0.725	7.86
II	2 layers	14.50	0.736	0.717	7.64
III	3 layers	16.14	0.740	0.664	7.93

As presented in **Table1** photocurrent densities of the devices (I-III) with different number of transparent TiO_2 layer as working electrode devices are followed 13.53 mAcm^{-2}, 14.50 mAcm^{-2} and 16.14 mAcm^{-2}. This indicates that when number of transparent TiO_2 layer is increased, photocurrent density is changed in the same way directly, because number TiO_2 layer increasing affects to dye loading site on the surface of working electrode, which influence directly photocurrent generation. So, the most suitable number layer of transparent TiO_2 to use as working electrode is 3 layers. Furthermore, V_{OC} value of single layer of transparent TiO_2show the highest value; 0.801 V, it indicates that recombination reaction between iodide/triiodde redox electrolyte and TiO_2 working electrode is prevented by fully dye molecule loading.

4.1.2 Effect of scattering TiO_2 component

To improve photocurrent generation, TiO_2 scattering layer (Vargas and Niklasson, 2001) was superimposed on 3 layers of transparent TiO_2 by doctor blade screen printing method. Number of TiO_2 scattering layer was studied and varied from 0 to 2 layers. 0.3 mM of N719 dye solution in ethanol was used as photosensitizer, E4 redox mediator consisting 0.05 M of I_2, 0.1 M of LiI, 0.4 M of TBP and 0.6 M of TPAI in mixed solvent between varelonitrile and acetonitrile 15:85 by volume. DSSC parameters are shown in **Table 2**

Table 2 DSSC parameters of different number of scattering TiO_2 layer device.

Device	Number of TiO2 scattering layer	J_{SC} (mAcm^{-2})	V_{OC} (V)	FF	%PCE
I	0	11.93	0.741	0.712	6.30
II	1 layer	16.14	0.740	0.664	7.93
III	2 layers	15.12	0.755	0.723	8.25

As shown in **Table2** photocurrent densities of the devices (I-III) with different number of TiO_2 scattering layer as working electrode devices are followed of DSSC are 11.93 $mAcm^{-2}$, 16.14 $mAcm^{-2}$ and 15.12 $mAcm^{-2}$. The photo current density of DSSC increased when TiO_2 scattering layers are coated on top of transparent TiO_2 layer. This is due to the scattering layer reflex incident photon back to sensitizer molecule, therefore it can increase current at working electrode. Especially, 1 layer of scattering TiO_2 showed the highest photo current density to 16.14 $mAcm^{-2}$, that is possible to obtain high performance.

4.2 Effect of electrolyte component

In DSSC fabrication, E4 electrolyte, which composes of 0.05 M of I_2, 0.1 M of LiI, 0.4 M of TBP and 0.6 M of TPAI in mixed solvent between varelonitrile and acetonitrile 15:85 by volume, was used as routine electrolyte. The electrolyte is one of key part in DSSC and help to compensate electron in electron current generation. To illustrate effect of electrolyte components to performance efficiency of dye DSSC, the devices were fabricated with different component electrolyte following, no-TBP, no-TPAI, no-additive and E4 electrolyte. The device was fabricated with N719 dye as sensitizer, 3 layers of transparent TiO_2 and 1 layer of scattering TiO_2 deposited on FTO as working electrode. The DSSC parameters are shown in **Table 3** V_{OC} of No-TBP based device is 0.529 V which is lower than V_{OC} of device based on No-TPAI and E4 electrolyte, because TBP is adsorbed on the photo anode surface, shifting its band edge and acts as a barrier to the recombination at the semiconductor/electrolyte interface. (Yuqiao et al., 2015). In addition, it was found that J_{SC} of device III and IV containing

TPAI in the electrolyte are 16.10 mAcm^{-2}, 16.27 mAcm^{-2}, respectively, that is higher than J_{SC} of devices without TPAI as additive (devices I and II). This indicated that TPAI is very important component in the electrolyte as it encourages electron transfer to conduction band energy level of TiO_2 working electrode (Bandara et al., 2013).

Table 3 DSSC parameters of the DSSC using different electrolyte components.

Device	Electrolyte	J_{SC} (mAcm^{-2})	V_{OC} (V)	FF	%PCE
I	No additive	12.52	0.448	0.648	3.07
II	No TPAI	10.79	0.690	0.548	4.00
III	No TBP	16.10	0.529	0.577	4.91
IV	E4	16.27	0.679	0.640	7.26

4.3 Effect of hexyl chain substitution on secondary carbazole donor

To optimize the performance of D-D-π-A dyes in DSSC, different lengths of alkyl chain substituted on secondary carbazole was investigated and varied following normal butyl chain (C4T3A), normal dodecyl chain (C12T3A), normal hexadecyl chain (C16T3A). Concentrations of dyes C4T3A, C12T3A and C16T3A solution of 0.3 mM in chloroform were used and 0.3 mM of N719 dye solution in ethanol was used as standard material for performance efficiency comparison. DSSCs using 3 lays of transparent TiO_2 and 1 layer of scattering TiO_2 coasted on FTO as working electrode and E4 electrolyte as redox electrolyte were fabricated. DSSC parameters of devices based on different alkyl length groups, substituted on secondary carbazole donor, are shown in **Table 4** and I-V plots are shown in **Figure 28**

As summarised in **Table 4** J_{SC} of the devices fabricated with C4T3A, C12T3A and C16T3A are 13.54 mAcm^{-2}, 13.74 mAcm^{-2} and 13.00 mAcm^{-2}, respectively. The device based on C12T3A showed the highest J_{SC} value. This may result from dodecyl group substituted on secondary carbazole donor which can reduce the dye molecule accumulation on working electrode surface effecting directly to photocurrent generation. In addition, when hexadecyl group is introduced on the same position with dodecyl group (C16T3A), J_{SC} is dropped from 13.74 $mAcm^{-2}$ to 13.00 $mAcm^{-2}$ because hexadecyl group is too high steric effect. This can make number of dye molecule decrease, that reduce photocurrent generation in the same way, as a result, performance efficiency of device based on C12T3A dye is 6.44% [a short circuit current density (Jsc) = 13.74 $mAcm^{-2}$, an open-circuit voltage (Voc) = 0.673 V, and a field factor (FF) = 0.698] reaching > 76% of the reference N719-based device (overall conversion efficiency = 8.42%).

Table 4 DSSC parameters of different of alkyl length substitution on donor and N719 dye devices.

Device	J_{SC} ($mAcm^{-2}$)	V_{OC} (V)	FF	%PCE
C4T3A	13.54	0.657	0.700	6.22
C12T3A	13.74	0.673	0.698	6.44
C16T3A	13.00	0.651	0.644	5.45
N719	15.18	0.789	0.703	8.42

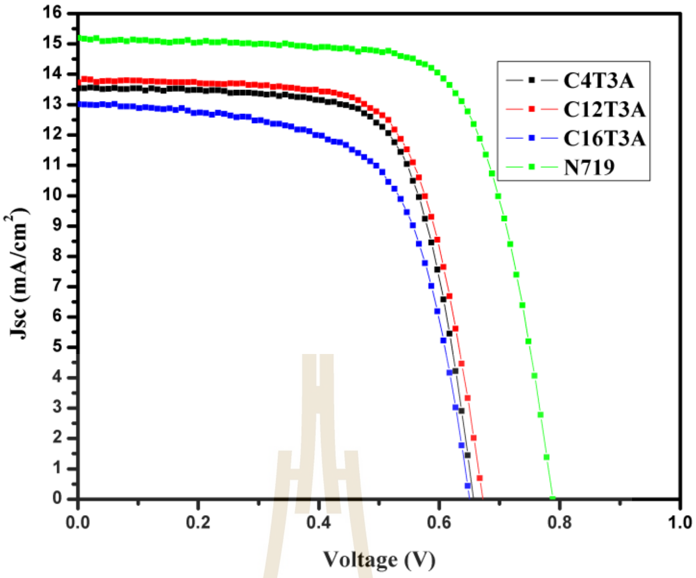


Figure 28 I-V plots of plots of the DSSCs based on C4T3A, C12T3A and C16T3A.

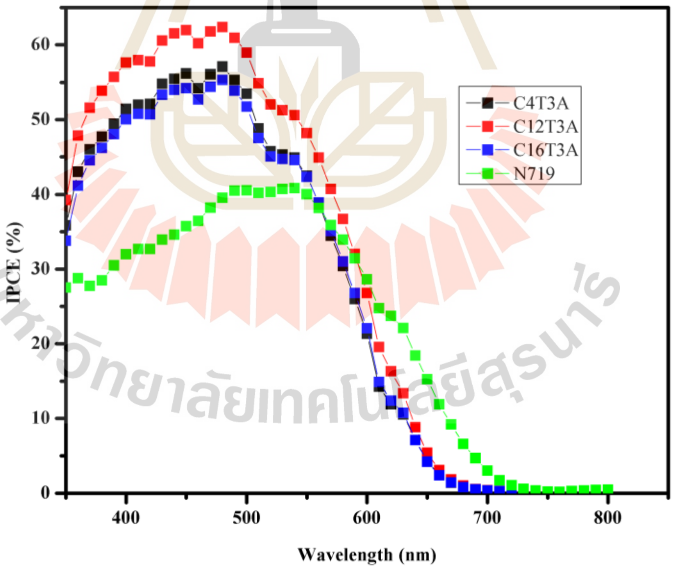


Figure 29 IPCE plots of the DSSCs based on C4T3A, C12T3A and C16T3A.

IPCE plots of the DSSCs based on C4T3A, C12T3A and C16T3A revealed photon absorbed behavior of device. All devices can harvest incident photon in the same region, from 350 nm to 670 nm, but percentage of incident photon to current efficiency (IPCE) of device are different. A maximum IPCE valued of C12T3A based device achieved 63% at 450 nm that is the highest value of series, resulting in a high J_{SC} value. The J_{SC} of C12T3A based showed the best value in the series, it confirmed that photocurrent generation depend on ability of aggregation protection. In the same way, IPCE spectra of N719 cover 350 nm. to 700 nm. that is more red-shifted than organic dye, so, Jsc value of device based on N719 is higher than Jsc of devices based on organic dye.

4.4 Effect of electron donating group substitution on secondary carbazole donor

One way to improve performance of dye sensitizer in DSSC is by introducing different electron donating groups on the same position with alkyl group to increase electron density. There are 2 pathways which is either extended π-conjugated system (C4TMA) or introducing lone paired electron (C12TSA). These dyes contain trithiophene unit as π-conjugated spacer and acrylic acid as accepter.

DSSC devices based on C4TMA and C12TSA were fabricated by using 0.3 mM of C4TMA solution and C12TSA solution in chloroform, 3 lays of transparent TiO_2 and 1 layer of scattering TiO_2 deposited on FTO as working electrode and E4 electrolyte as redox electrolyte. DSSC parameters are summarized in **Table 5** and I-V plots are shown in **Figure 30**

Table 5 DSSC parameters of different of electron donating group substituted on secondary carbazole donor devices.

Device	J_{SC} (mAcm^{-2})	V_{OC} (V)	FF	%PCE
C12T3A	13.74	0.673	0.698	6.44
C4TMA	11.88	0.681	0.703	5.69
C12TSA	10.61	0.669	0.707	5.02

According to **Table 5** J_{SC} of C4TMA device, increased electron density via lone paired electron effect, is 11.88 mAcm^{-2} that is higher than J_{SC} of C12TSA which consist π-conjugated system in structure, but J_{SC} of both devices are lower than J_{SC} of C12T3A, it indicates that electron donating group substitution on secondary carbazole donor cannot promote electron distribution from donor moiety to accepter part, that affect to photocurrent generation directly, because bond between N-atom of carbazole and carbon of electron donating group is not rigid and rotatable that is cause of π-conjugated system breaking.

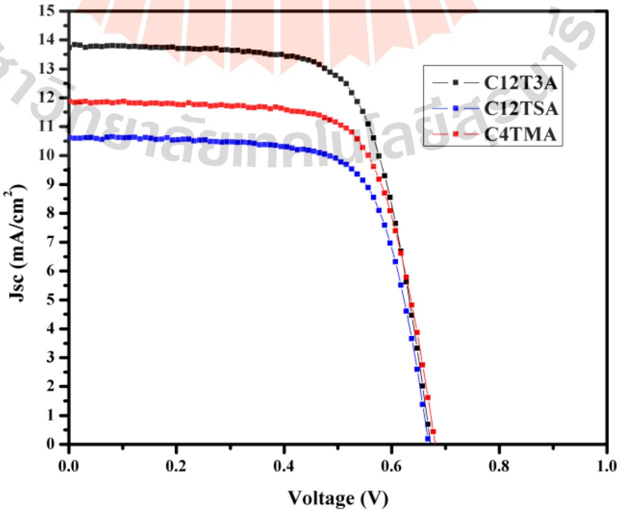


Figure 30 I-V plots of the DSSCs based on C12T3A, C4TMA and C12TSA.

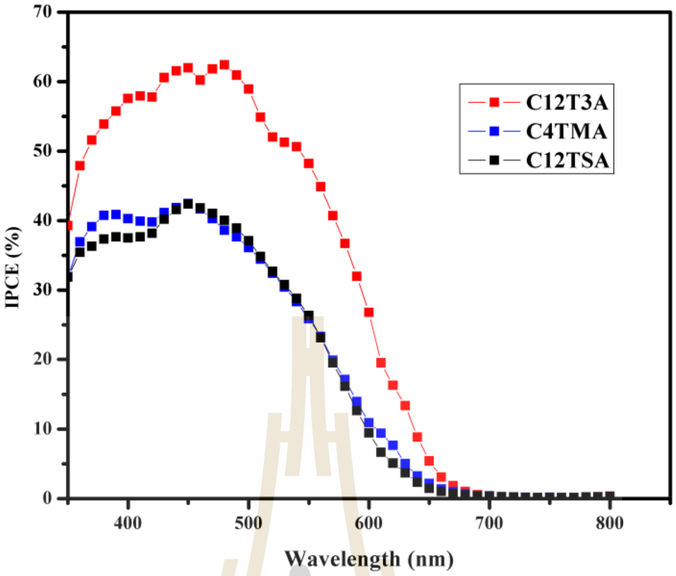


Figure 31 IPCE plots of the DSSCs based on C12T3A, C4TMA and C12TSA.

IPCE plots of the DSSCs based on C4TMA, C12TSA and C12T3A reveal photon absorbed behavior, all of devices can harvest incident photon in the same wavelength; from 350 nm to 670 nm, but IPCE of C12T3A based device achieves higher percentage over both IPCE of C12TSA and C4TMA because, J_{SC} of C12T3A based achieve the best value in sensitized dye series ability. In collusion, incident photon harvesting efficiency depend on π-conjugated system of main structure, electron donating group substituted on secondary carbazole donor cannot encourage photon absorption.

4.5 Effects of extended π -conjugated spacer and hexyl chain substitution on linker

Other way to improve performance of dye sensitized solar cell, π-conjugated linker is extended by thiophene unit increasing to promote incident photon harvesting efficiency in long wavelength region (C12T4A) and π-conjugated linker is substituted by hexyl group (C12T4HA), trithiophene unit is used as π-conjugated spacer and acrylic acid is accepter. DSSC parameters are shown in **Table 6** and I-V plots are shown in **Figure 32**

Table 6 DSSC parameters of extended π-conjugated spacer and hexyl chain substitution on linker devices.

Device	J_{SC} (mAcm^{-2})	V_{OC} (V)	FF	%PCE
C12T3A	13.74	0.673	0.698	6.44
C12T4A	13.95	0.622	0.559	4.85
C12T4HA	13.98	0.663	0.655	6.07
C12T3A	13.74	0.673	0.698	6.44

According to Table 6. J_{SC} of C12T4A device is 13.95 mAcm^{-2} and J_{SC} of C12T3A device is 13.74 mAcm^{-2}, both J_{SC} of C12T4A and C12THA; 4 units of thiophene ring, are higher than C12T3; 3 units of thiophene ring, it indicates that extended π-conjugated spacer contribute photocurrent generation, but V_{OC} of C12T4A ; non alkyl substitution on thiophene linker, decreases form V_{OC} of C12T3A and C12T4HA, since, recombination reaction between TiO_2 and redox electrolyte, alkyl substitution increase hydrophobic property, so I^-/I^-_3 cannot diffuse to TiO_2 surface.

According to I-V plots of the DSSCs based on C12T3A, C12T4A and C12T4HA, Jsc of all devices are the same value, but Voc of devices based on C12T3A and C12T4HA are higher value than Voc of device based on C12T4A, for instance, an overall conversion efficiency of DSSCs based on C12T4HA is 6.07% (Jsc = 11.73 mAcm^{-2}, Voc = 0.673 V, and FF = 0.698)

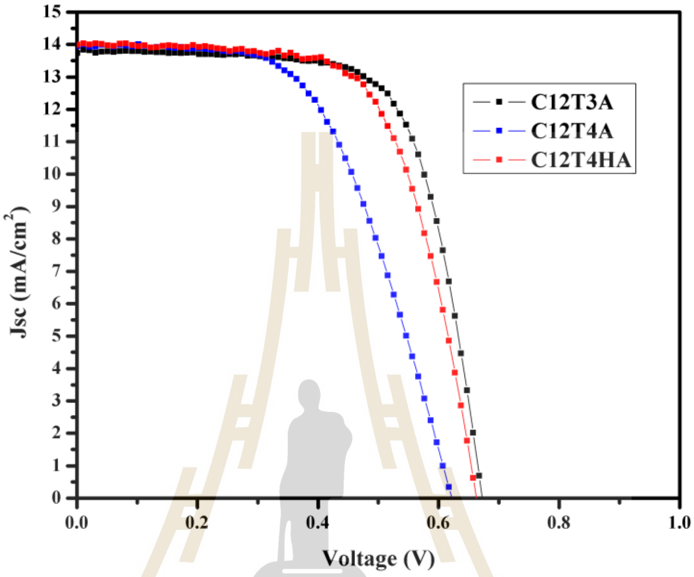


Figure 32 I-V plots of the DSSCs based on C12T3A, C12T4A and C12T4HA.

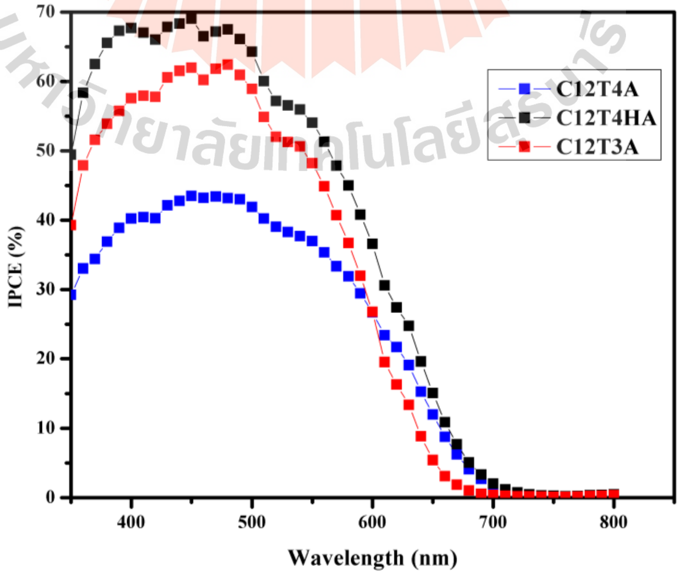


Figure 33 IPCE plots of the DSSCs based on C12T3A, C12T4A and C12T4HA.

According to IPCE plots of C12T4A, C12T4HA and C12T3A, C12T4A and C12T4HA can absorb incident photon from 350 nm to 720 nm, but C12T3A can absorb incident photon only from 350 nm to 680 nm, that mean, C12T4A and C12T4HA is red shift than C12T3A about 40 nm, resulting, J_{SC} of C12T4A and C12THA are higher than C12T3A. So, extended π-conjugated spacer can improve photocurrent generation.

4.6 Effect of CDCA co-absorbent

To suppress dye aggregation, Chenodeoxycholic acid (CDCA) added in 0.3 mM of every dye solution. Mole ratio between sensitized dye and CDCA is 1:10, 1:20 and 1:30 respectively, TiO_2 is used as working electrode, Pt deposited on conductive side of FTO as counter electrode, redox electrolyte consist of 0.05 M of I_2, 0.1 M of LiI, 0.4 M of tert- butyl pyridine (TBP) and 0.6 M of tetrapropyl-ammonium iodidede (TPAI). DSSCs parameters are summarized in **Table 7**- **Table 13** and I-V plots of DSSCs with different CDCA co-adsorbent concentration are shown **Figure 34 - Figure 40**

Table 7 DSSC parameters of devices based on C4T3A with different CDCA ratio additive.

Device	CDCA	J_{SC} ($mAcm^{-2}$)	V_{OC} (V)	FF	%PCE
I	-	13.54	0.657	0.700	6.22
II	1:10	14.08	0.709	0.605	6.03
III	1:20	14.95	0.706	0.701	7.41
IV	1:30	15.05	0.707	0.696	7.40

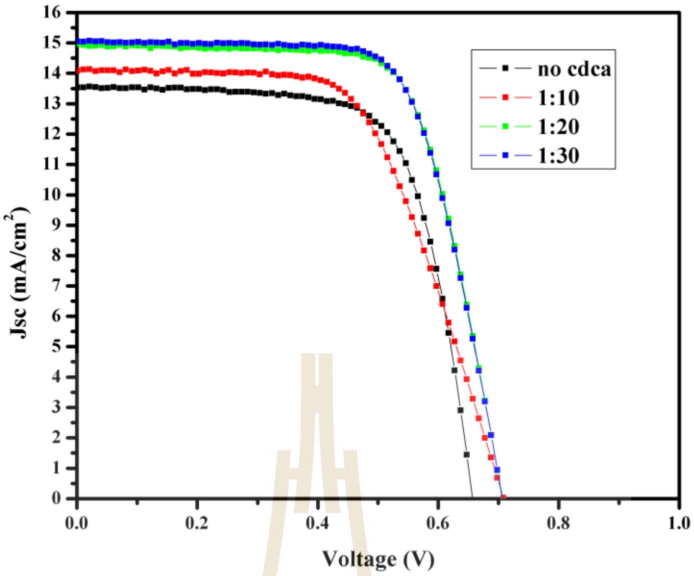


Figure 34 I-V plots of the DSSCs fabricated with C4T3A co-adsorbed with different CDCA concentration.

As present in **Figure 34** and summarized in **Table 7** J_{SC} of C4T3A device increase 14.08 mAcm^{-2}, 14.95 mAcm^{-2} and 15.05 mAcm^{-2} respectively, when mole ratios of dye and CDCA are 1:10, 1:20 and 1:30, J_{SC} of device based on C4T3A increased to 15.05 mAcm^{-2} ,that is the highest value of the series when concentration of CDCA is increased to 1:30 mole ratio between sensitized dye and CDCA, it indicated that dye molecule is facile to aggregate at surface of TiO_2 working electrode, this formation of dye molecule act as light filter, make photon density decrease, that effect to photocurrent generation. Furthermore, CDCA addition improves V_{OC} of device, following V_{OC} of device based on CDCA addition achieves to 0.7 V, but V_{OC} of device based on non-CDCA addition is decreased to 0.65 V, so CDCA addition improve both J_{SC} and V_{OC}

Table 8 DSSC parameters based on C12T3A with different CDCA ratio additive.

Device	CDCA	J_{SC} (mAcm^{-2})	V_{OC} (V)	FF	%PCE
I	-	13.74	0.673	0.698	6.44
II	1:10	14.31	0.713	0.720	7.34
III	1:20	14.82	0.721	0.704	7.52
IV	1:30	13.49	0.713	0.676	6.51

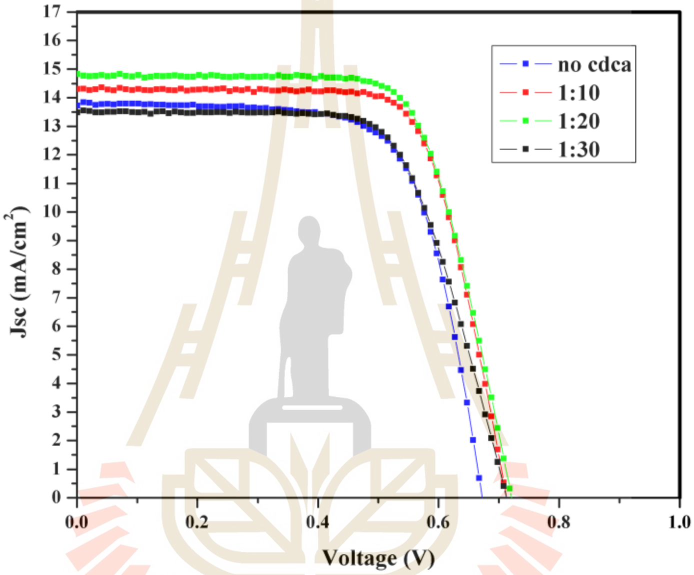


Figure 35 I-V plots of the DSSCs fabricated C12T3A co-adsorbed with different CDCA concentration.

As presented in **Figure 35** and summarized in **Table 8** J_{SC} of C12T3A device is 14.31 mAcm^{-2}, 14.82 mAcm^{-2} and 13.49 mAcm^{-2} respectively, when mole ratios of dye and CDCA are 1:10, 1:20 and 1:30, J_{SC} of device based on C12T3A achieves highest value of 14.82 mAcm^{-2} when mole ratio of CDCA and C12T3A is 1:20, but CDCA is added in mole ratio 1:30 J_{SC} is decreased because dye molecule is too more replaced by CDCA molecule, so to improve the highest performance efficiency, CDCA should be mixed in ratio only 1:20.

Table 9 DSSC parameters based on C16T3A with different CDCA ratio additive.

Device	CDCA	J_{SC} (mAcm^{-2})	V_{OC} (V)	FF	%PCE
I	-	13.00	0.651	0.644	5.45
II	1:10	14.53	0.698	0.671	6.81
III	1:20	14.01	0.711	0.714	7.11
IV	1:30	11.02	0.703	0.730	5.66

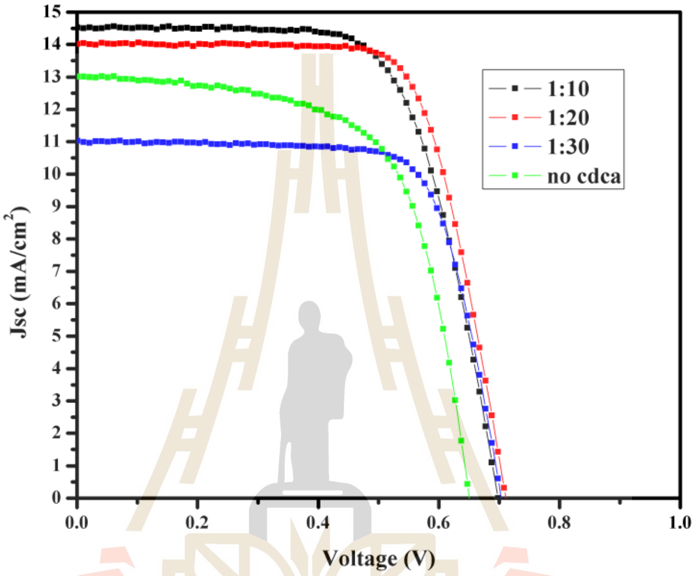


Figure 36 I-V plots of the DSSCs fabricated with C16T3A co-adsorbed with different CDCA concentration.

Following **Figure 36** and **Table 9** , J_{SC} of DSSCs based on 16T3A is 14.31 mAcm^{-2},14.82 mAcm^{-2} and 13.49 mAcm^{-2} respectively, when mole ratios of dye and CDCA are 1:10, 1:20 and 1:30, J_{SC} achieves highest value of 14.50 mAcm^{-2} when mole ratio of C16T3A and CDCA is 1:10, because C16T3A is more steric than C4T3A and C12T3A, resulting, C16T3A is more difficult to form aggregation than C4T3A and C12T3A, so .mole ratio of CDCA is decreased to only 1:10 for reach to the highest value of J_{SC} .

Table 10 DSSC parameters based on C12TSA with different CDCA ratio additive.

Device	CDCA	J_{SC} (mAcm^{-2})	V_{OC} (V)	FF	%PCE
I	-	10.61	0.669	0.707	5.02
II	1:10	12.60	0.682	0.726	6.24
III	1:20	13.41	0.649	0.690	6.01
IV	1:30	10.30	0.684	0.740	5.21

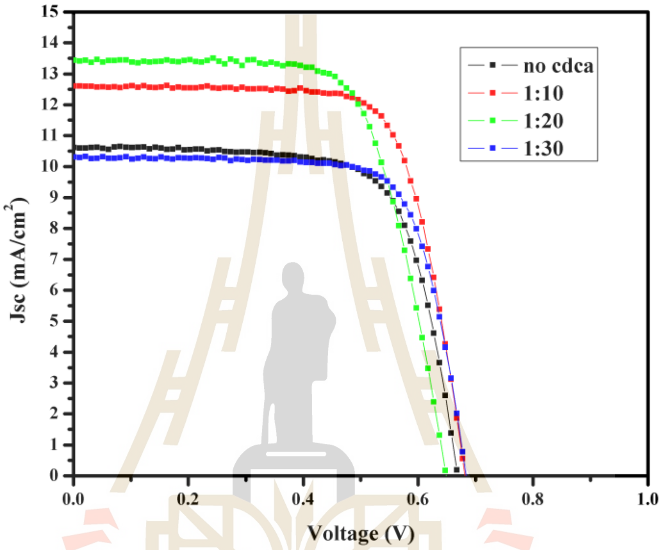


Figure 37 I-V plots of the DSSCs fabricated with C12TSA co-adsorbed with different CDCA concentration.

Following **Figure 37** and **Table 10** J_{SC} of DSSCs based on C12TSA is 12.60 mAcm^{-2}, 13.41 mAcm^{-2} and 10.30 mAcm^{-2} respectively, when mole ratios of C12TSA and CDCA are 1:10, 1:20 and 1:30, C12TSA based device reaches the highest J_{SC} of 13.41 mAcm^{-2} when mole ratio of C12TSA and CDCA is 1:20, so to improve the highest performance efficiency, CDCA should be mixed in ratio only 1:20.

Table 11 DSSC parameters based on C4TMA with different CDCA ratio additive.

Device	CDCA	J_{SC} (mAcm^{-2})	V_{OC} (V)	FF	%PCE
I	-	11.88	0.681	0.703	5.69
II	1:10	12.95	0.691	0.707	6.33
III	1:20	13.62	0.693	0.721	6.80
IV	1:30	12.82	0.705	0.729	6.59

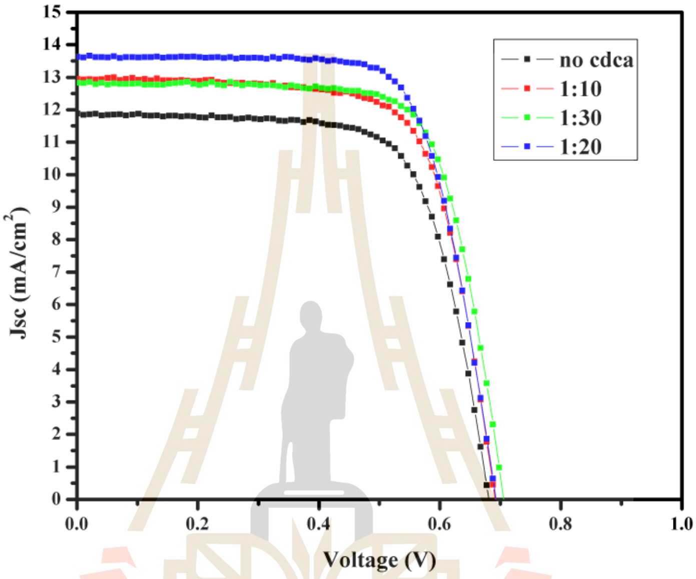


Figure 38 I-V plots of the DSSCs fabricated with C4TMA co-adsorbed with different CDCA concentration.

As presented in **Figure 38** and summarized in **Table 11** J_{SC} of C4TMA device is 12.95 mAcm^{-2}, 13.62 mAcm^{-2} and 12.82 mAcm^{-2} respectively, when mole ratios of C4TMA and CDCA are 1:10, 1:20 and 1:30, C4TMA based device reaches the highest J_{SC} of 13.41 mAcm^{-2} when mole ratio of C4TMA and CDCA is 1:20, for instance, CDCA should be mixed in ratio only 1:20 for the highest performance efficiency.

Table 12 DSSC parameters based on C12T4A with different CDCA ratio additive.

Device	CDCA	J_{SC} (mAcm^{-2})	V_{OC} (V)	FF	%PCE
I	-	13.95	0.622	0.559	4.85
II	1:10	16.64	0.638	0.663	7.04
III	1:20	17.08	0.644	0.671	7.38
IV	1:30	16.83	0.642	0.652	7.05

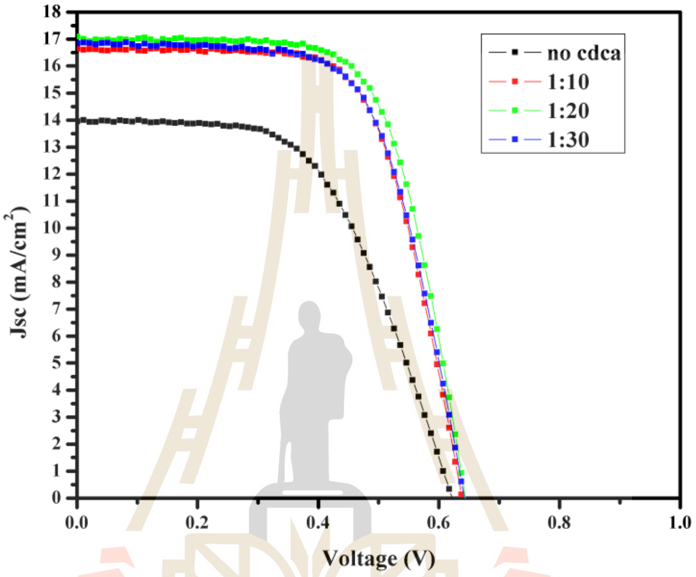


Figure 39 I-V plots of the DSSCs fabricated with C12T4A co-adsorbed with different CDCA concentration.

As presented in **Figure 40** and summarized in **Table 12**, J_{SC} of C12T4A device is 16.64 mAcm^{-2}, 17.08 mAcm^{-2} and 16.83 mAcm^{-2} respectively, when mole ratios of C12T4A are 1:10, 1:20 and 1:30, it C12T4A based device reaches the highest J_{SC} of 17.08 mAcm^{-2} when mole ratio of C12T4A and CDCA is 1:20, for instance, CDCA should be mixed in ratio only 1:20 for the highest performance efficiency.

Table 13 DSSC parameters based on C12T4HA with different CDCA ratio additive.

Device	CDCA	J_{SC} (mAcm^{-2})	V_{OC} (V)	FF	%PCE
I	-	13.98	0.663	0.655	6.07
II	1:10	17.12	0.676	0.667	7.72
III	1:20	16.23	0.669	0.669	7.27
IV	1:30	15.20	0.659	0.677	6.79

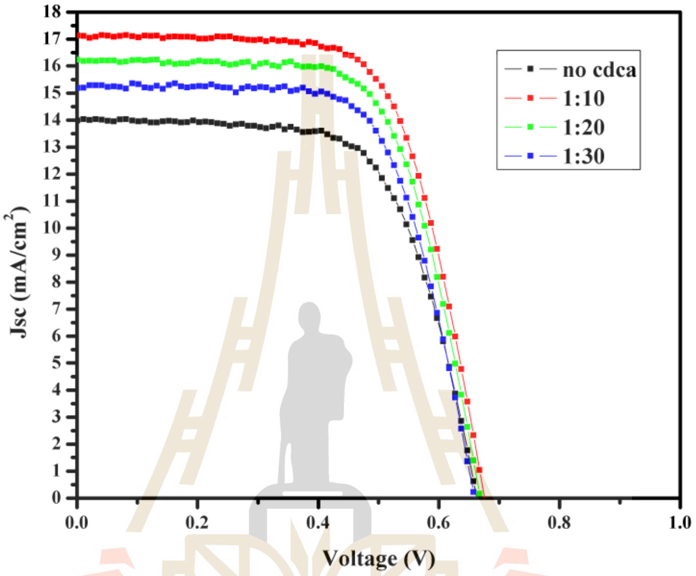


Figure 40 I-V plots of the DSSCs fabricated with C12T4HA co-adsorbed with different CDCA concentration.

As presented in **Figure 41** And summarized in **Table 13,** J_{SC} of C12T4HA device is 17.12 mAcm^{-2}, 16.23 mAcm^{-2} and 15.20 mAcm^{-2} respectively, when mole ratios of C12T4HA are 1:10, 1:20 and 1:30, it C12T4HA based device reaches the highest J_{SC} of 17.12 mAcm^{-2} when mole ratio of C12T4HA and CDCA is 1:10, for instance, CDCA should be mixed in ratio only 1:10 for the highest performance efficiency. To reduce dye aggregation, CDCA is used only 1:10, because C12T4HA is high steric molecule that can prevent dye aggregation by itself.

CHARPTER V

CONCLUSION

Dye sensitized solar cell (DSSC) is one type of several solar cell type, it eliminates reservation of previous solar cell type, for example, solid state solar cell must rely on high and expensive production technology, but dye sensitized solar cell production is not indispensable the same technology, that is why, dye sensitized solar cell have the potential to compete commercially. Working electrode of dye sensitized solar cell is fabricated from TiO_2 with 2 components, the first component is 3 layers of transparent TiO_2 and the last component is 1 layer of scattering TiO_2. Redox electrolyte consists of I^-/I_3^- as redox mediator, tetrapropyl ammonium iodide (TPAI) is used to increase photocurrent density and tert-butyl pyridine (TBP) is used to improve open circuit voltage.

Dye sensitizers are modified by 3 ways. Firstly different length alkyl group is introduced on N atom of secondary carbazole donor, device based on C12T3A dye achieves the highest power conversion efficiency 6.44% (J_{SC} = 13.74 mAcm^{-2}, V_{OC} = 0.673 V and FF = 0.698) because dodecyl group length is effective to prevent dye aggregation that increase J_{SC} of device and reduce recombination reaction that is cause of V_{OC} decreasing. Secondly, electron donating group is introduced on the same position with alkyl group to promote photon harvesting ability of dye molecule, C4TMA; via lone pairs electron, achieves the highest power conversion efficiency 5.69% (J_{SC} = 11.88 mAcm^{-2}, V_{OC} = 0.681 V and FF = 0.703) that higher than efficiency of C12TSA device; π-conjugated electron, both of their efficiency is lower than efficiency of C12T3A. Thirdly, to improve current generation, π-conjugated system is extended by thiophene linker unit increasing, the longer thiophene linker sensitizer (C12T4A) shows better ability of long wave length region photon harvesting than device base on C12T3A dye therefore J_{SC} of C12T4A is 13.95 mAcm^{-2} that is higher than J_{SC} of C12T3A , but power conversion efficiency of C12T3A is still higher, because V_{OC} of C12T3A based device is higher. Although extendedπ-conjugated system improves photon absorption efficiency, it can cause of dye aggregation because of planarity of molecule that decreases J_{SC} of device, to dissolve aggregation of extended linker dye, hexyl group is substituted on thiophene unit (C12T4HA) reaches 13.98 mAcm^{-2} of J_{SC} that is higher than C12T3A J_{SC} and V_{OC} achieves to 0.663 V that is similar to V_{OC} of, it indicate hexyl group substitution improves performance efficiency of DSSC.

One way to prevent dye aggregation, chenodeoxycholic acid (CDCA) is used as co-adsorbent in to dye bath solution. The properties of CDCA consist of strength coordinated covalent bond with TiO_2 likely dye molecule, non photon absorption and high steric effect, especially high steric effect, CDCA reduce dye accumulation, that acts as photon filter, which is cause of decreasing of DSSCs photon current density, so CDCA addition can improve all of photo current density of devices is increasing, but CDCA mixing with the high steric dye molecule should reduce mole ratio.

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