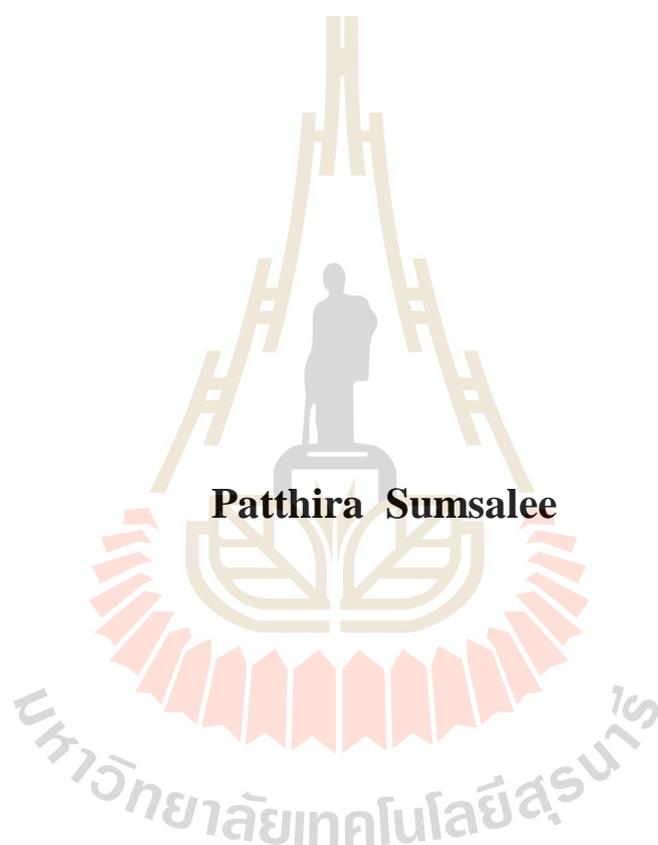


**SYNTHESIS AND CHARACTERIZATION OF NEW
ORGANIC MATERIAL BASED ON ISOINDIGO
DERIVATIVES FOR SOLAR CELLS**



**A Thesis Submitted in Partial Fulfillment of the Requirements for the
Degree of Master of Science in Chemistry
Suranaree University of Technology
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การสังเคราะห์และการวิเคราะห์วัสดุอินทรีย์ตัวใหม่ที่เป็นอนุพันธ์ของไอโซ
อินดิโก สำหรับเซลล์แสงอาทิตย์



วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาเคมี
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งานวิจัยนี้เป็นการสังเคราะห์และวิเคราะห์สารอินทรีย์สีข้อมไวแสงชนิดใหม่สำหรับเซลล์
แสงอาทิตย์ชนิดสีข้อมไวแสงและวัสดุให้อิเล็กตรอนสำหรับเซลล์แสงอาทิตย์ชนิดสารอินทรีย์ของ
สารประกอบไอโซอินดิโกเป็นหลัก โดยที่การสังเคราะห์และวิเคราะห์คุณสมบัติทางแสง ความร้อน
และระดับพลังงาน สารอินทรีย์สีข้อมไวแสงของสารประกอบไอโซอินดิโกเป็นหลักได้ออกแบบ
โมเลกุลให้มีโครงสร้างเพื่อให้สามารถดูดกลืนแสงอาทิตย์ได้ในช่วงกว้างซึ่งได้ทำการเปรียบเทียบ
หมู่ส่งผ่านอิเล็กตรอนระหว่างเบนซีนกับไทโอเฟน สารประกอบไอโซอินดิโกที่ใช้ในเซลล์
แสงอาทิตย์ชนิดสีข้อมไวแสงแสดงการดูดกลืนแสงอาทิตย์ในช่วงความยาวคลื่นที่กว้างมีคุณสมบัติ
ทางความร้อน และไฟฟ้าเหมาะสม ส่วนวัสดุให้อิเล็กตรอนสำหรับเซลล์แสงอาทิตย์ถูกออกแบบ
โมเลกุลให้ดูดกลืนความยาวแสงในช่วงกว้าง โดยทำการเปรียบเทียบหมู่แกนกลางระหว่างแอนทรา
ซีน เบนโซไทโคไดเอโซ และฟลูออรีน วัสดุให้อิเล็กตรอนสำหรับเซลล์แสงอาทิตย์ชนิดสารอินทรีย์
แสดงการดูดกลืนแสงในช่วงกว้าง และยังมีคุณสมบัติทางไฟฟ้า ความร้อนที่เหมาะสม

มหาวิทยาลัยเทคโนโลยีสุรนารี

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PATTHIRA SUMSALEE : SYNTHESIS AND CHARACTERIZATION OF
NEW ORGANIC MATERIAL BASED ON ISOINDIGO DERIVATIVES
FOR SOLAR CELLS. THESIS ADVISOR : ASSOC. PROF. VISIT VAO-
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ORGANIC SOLAR CELLS, DYE SENSITIZED SOLAR CELLS, ORGANIC
MATERIALS, ORGANIC SYNTHESIS, ISOINDIGO

In this research, we synthesized and characterized of organic sensitizers for DSSCs and electron donor materials for OPVs based on isoindigo. The organic sensitizers were designed as D-A- π -A which contained TPA as donor unit, isoindigo as auxiliary acceptor, cyanoacetic acid as acceptor and various thiophene and phenyl as π -spacer while electron donor for OPVs were designed as D-Ar-D which various core moieties (anthracene, benzothiadiazole and fluorene). The chemical structures of these materials were studied by ^1H NMR, ^{13}C NMR, and Mass spectroscopy. The optical, electro chemical and thermal properties of these materials were measured by UV-Vis spectroscopy, cyclicvoltametry and TGA, respectively. Organic materials showed wide absorption range (300-700 nm), high molar extinction coefficient and suitable HOMO and LUMO levels and high thermal stability.

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Patthira Sumsalee

มหาวิทยาลัยเทคโนโลยีสุรนารี

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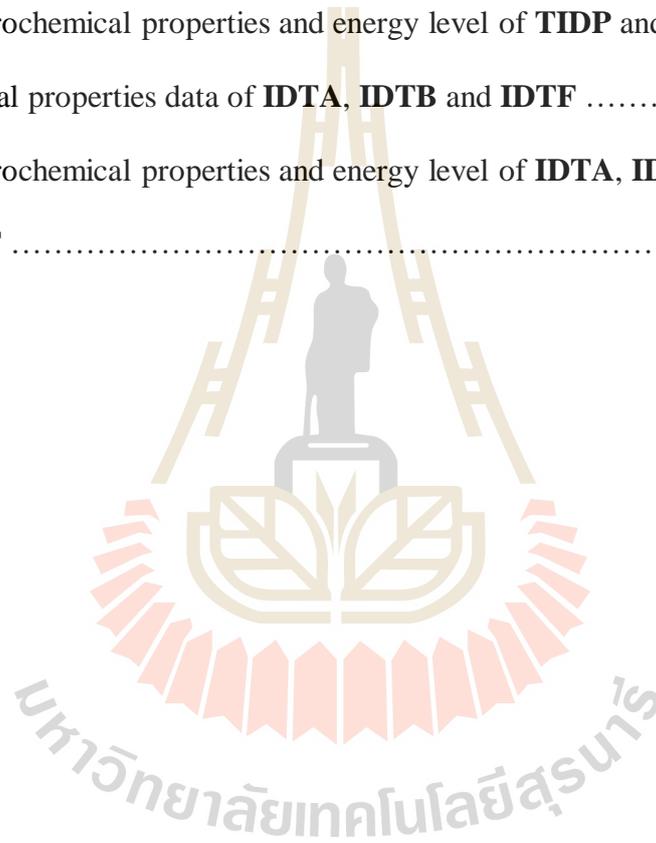
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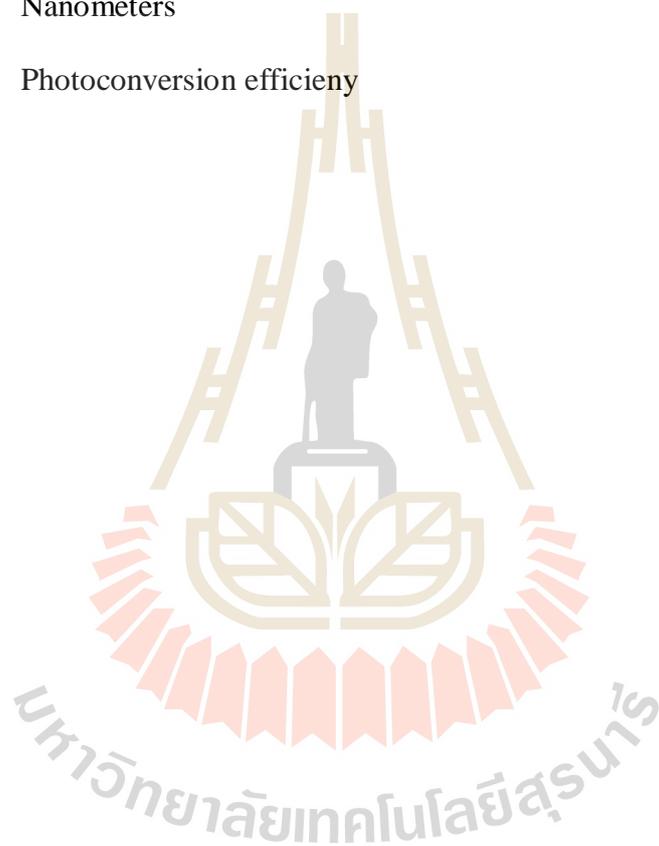
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LIST OF ABBREVIATIONS

OSCs	Organic Solar Cells
DSSCs	Dye Sensitized Solar Cells
OPVs	Organic Photovoltaics
NIS	N-iodosuccinimide
PV	Photovoltaic
ITO	Indium Doped Tin Oxide
ICT	Intramolecular Charge Transfer
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
NMR	Nuclear Magnetic Resonance
δ	Chemical shift in ppm relative to tetramethylsilane
t	Triplet
d	Doublet
m	multiplet
UV	Ultra-violet
n-Bu ₄ NPF ₆	Tetrabutylammonium hexafluorophosphate
CH ₂ Cl ₂	Dichloromethane
THF	Tetrahydrofurane
ϵ	Molar absorption

LIST OF ABBREVIATIONS (Continued)

eV	Electron volt
J	Coupling constant
nm	Nanometers
η	Photoconversion efficiency



CHAPTER I

INTRODUCTION

The global demand for energy is increasing but fossil fuel resources are limited and depleting rapidly. There are many research groups who are interested to find the alternative energy sources. The first choice is carbon based source. It is widely used although it causes the increasing of carbon dioxide in the atmosphere. The second choice is nuclear power which needs to build the power station and generates nuclear fuel wastes. The last one is renewable energy which commonly is wind energy, hydro energy, geothermal energy, biomass energy and solar energy (Bolton and Hall, 1979; Balzani et al., 2007). Solar energy is the best option for alternative energy sources, because the sun is a primary source of clean energy, abundant and environmental friendly.

1.1 Solar cells

Solar cell is an electrical device that converts the energy of light directly into electricity by the photovoltaic effect. The operation of a photovoltaic (PV) cell requires three basic properties:

- The absorption of light, generating either electron-hole pairs or excitons
- The separation of charge carriers of opposite types
- The charge extraction of those carriers to an external circuit

The first generation started with the introduction of silicon-wafer based solar cell. The drawbacks of silicon-wafer are high cost materials and poor capital efficiency because it poor light absorptivity and thickness.

The second generation is thin-film solar cells based. The device based on a stack of layer is thinner than silicon wafers about 100 times which can make a better solar cell. Thin-film approached was handicapped by two issues: (1) the cell's semiconductor was deposited using slow and expensive high-vacuum, (2) the thin-film was deposited directly onto glass as a substrate, eliminating the opportunity using a conductive substrate directly as the electrode.

The third generation is organic solar cell that shows flexible device, cost advantage, light weight and large-scale application. In this work, we have been interested to study materials for organic solar cells.

1.2 Dye sensitized solar cells (DSSCs)

Dye sensitized solar cell (DSSCs) is a class of photoelectrochemical cell. It has been attracted a widespread in both academic and commercial for the conversion of sunlight into electricity.

1.2.1 Component of dye sensitized solar cells

DSSCs contain 5 components: (1) working electrode, (2) semiconductor metal oxide, (3) dye sensitizer (dye), (4) an electrolyte system, and (5) a counter electrode. The key components of dye sensitized solar cells are shown in **Figure 1.1**.

- 1. Working electrode:** anode electrode using indium doped tin oxide (ITO).
- 2. Semiconductor metal oxide:** accept electron from dyes, transmit electron on to external load as well, large surface area for retention of the dye molecule

sensitivity and wide band gap energy (more than 3 eV). Normally, TiO_2 was used for semiconductor.

3. Dye sensitizer: It must show good property for solar absorption, transferred electron to metal oxide particles, had long length optical absorption spectrum in the visible to near infrared (IR). Moreover, it showed high absorption coefficient, high stability in the oxidation state and good adhesive on surface of metal oxide particles. There are many types of dye sensitized solar cell, for example ruthenium complex dye, porphyrin dye and metal free organic dye.

4. Electrolyte system: it can be compensated electron for dye sensitized solar cell or received the positive charge from the cathode electrode and easily to oxidation reaction.

5. Counter electrode: it is usually made of noble-metal platinum or carbon. It can compensate electron to electrolyte system.

1.2.2 Working principle of dye sensitized solar cells

Dye sensitizer anchored on the TiO_2 surface absorbed light and then electrons from the excited dye are injected into the conduction band (CB) of the TiO_2 , generating an electric current. The ground state of the dye is regenerated by the electrolyte to give efficient charge separation. The iodide is regenerated in turn by the reduction of triiodide at the counter electrode and the circuit is completed via electron migration through the external load. The voltage is generated under illumination corresponds to the difference between Fermi level of electron in the solid and redox potential of the electrolyte. Thus, the device generates electricity from light continuously (Liang and Chen, 2013).

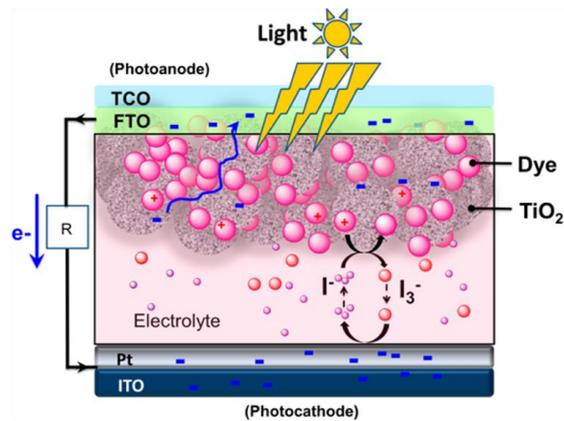


Figure 1.1 Composition of dye sensitized solar cells (Liang and Chen, 2013).

1.2.3 Dye sensitizers

Dye sensitizers are divided into 3 groups: (1) ruthenium metal complex sensitizers, (2) porphyrin sensitizers, and (3) organic sensitizers.

1. Ruthenium metal complex sensitizers

In 1993 Gratzel and coworker reported dye sensitized solar cells with high photo conversion efficiency (η) as shown in **Figure 1.2**. This group reported **N3**, **N719** and **black dye** as high efficiency of 8.2, 10.1 and 11.18% respectively. These dyes sensitized solar cells used TiO_2 as semi-conductor and ruthenium-pyridine complex as sensitizer (Gratzel et al., 1991).

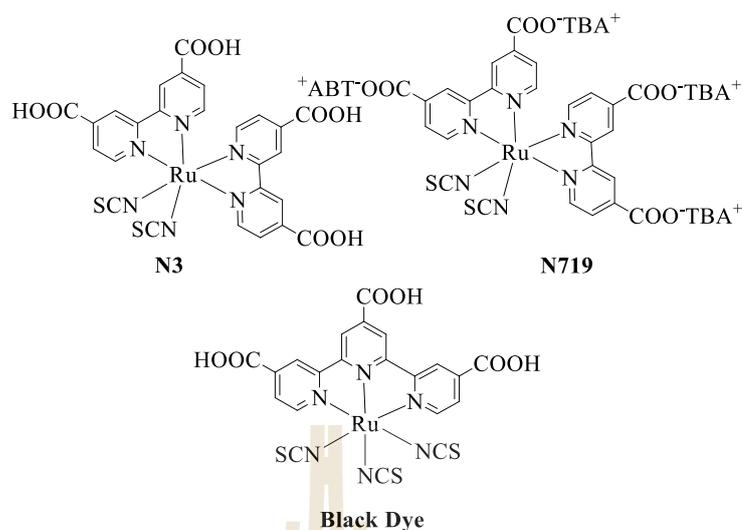


Figure 1.2 Molecular structures of ruthenium complex dyes (Gratzel et al., 1991).

2. Porphyrin Sensitizer

In 2011 Yella and coworkers reported meso-porphyrin dye as shown in **Figure 1.3**, **YD2-o-C8** achieving a η of 11.9%. In conjunction with the cobalt (III/II) tris(2,2'-bipyridine)-based redox electrolyte (Yella et al., 2011).

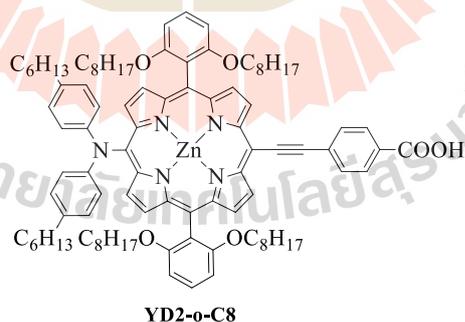


Figure 1.3 The structures of **YD2-o-C8** dye (Gratzel et al., 2011).

In 2014 Mathew and coworker reported **SM315** dye showed **Figure 1.4** achieving an unprecedented IPCE of $\sim 13\%$ (Mathew et al., 2014).

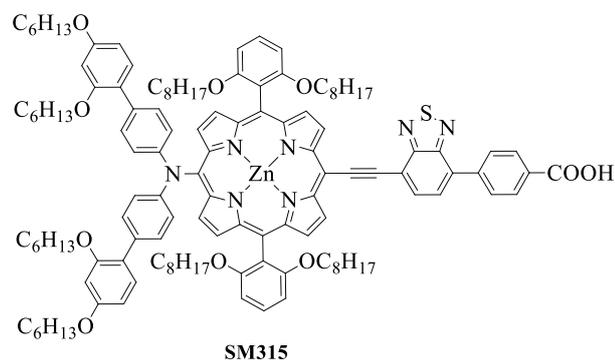


Figure 1.4 Molecular structures of **SM315** (Mathew et al., 2014).

3. Organic sensitizer

All of the ruthenium sensitizers have a narrow absorption range, difficult to synthesize and purify, limited development for large-scale applications and very expensive. As a result, organic dyes are lately stimulating intensive research efforts. The advantages of organic sensitizers in DSSCs include their easily tunable physicochemical properties, suitable molecular design, well established synthetic procedure, along with their ease of purification and high molar absorption coefficient. Metal free organic dyes have obtained great attention for their low cost, high molar absorption coefficient, high efficiency and easy 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 1.5**. This structure can induce the intramolecular charge transfer (ICT) from donor to acceptor via the π -bridge when a dye absorbs light (Zeng et al., 2010).

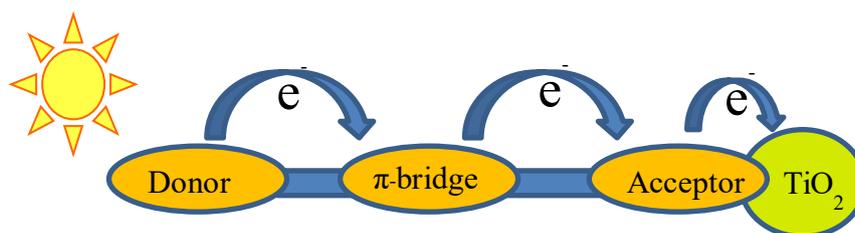


Figure 1.5 The D- π -A structure of metal free organic dye (Zeng et al., 2010).

In recent year, a great deal of research aimed to finding high efficiency organic sensitizers. Arylamine, coumarine and indoline organic sensitizers were investigated, and some of them reached efficiency in the range of 3-8%. The chemical of metal free dyes are shown in **Figure 1.6**. All these organic sensitizers showed sufficient efficiency to represent a visible region, reaching high efficiency.

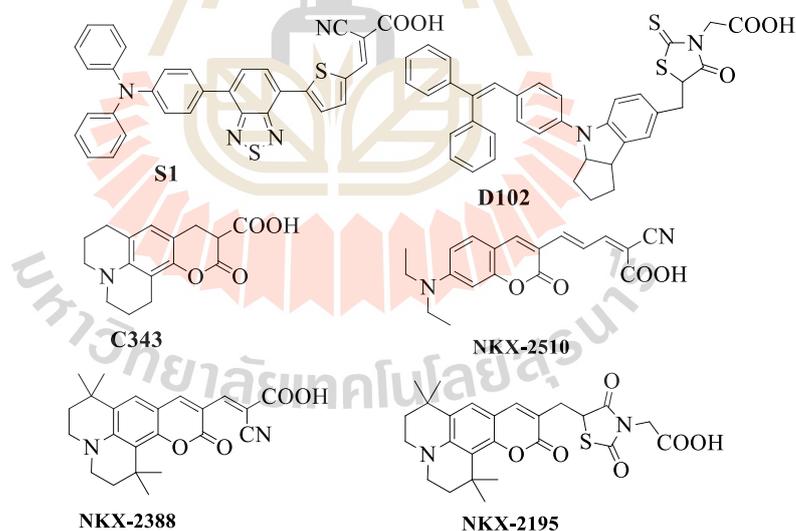


Figure 1.6 Molecular structures of S1, D102, C343, NKX-2510, NKX-2388 and NKX-2195.

1.3 Organic Photovoltaics (OPVs)

Organic photovoltaics (OPVs) cell is a photovoltaic cell that uses organic electronics a branch of electronics that deals with thin film of π - conjugated semiconducting organic molecules, oligomers or polymers for light absorption and charge transport (Kaur et al., 2014). The composition of OPVs was showed in **Figure 1.7**.

1.3.1 Component of Organic Photovoltaics (OPVs)

1. Transparent anode; typically used transparent ITO coated onto a glass or plastic substrate. Transparent anode should be highly conductive materials, good thermal and chemical stability and good transparency.

2. Organic materials; consist of electron donor (D) and electron acceptor (A) for light harvesting. Each material has a highest occupied molecular orbital (HOMO), or ionization potential (IP), and a lowest unoccupied molecular orbital (LUMO), or electron affinity (EA). A band gap is defined as the difference between energy levels of HOMO and LUMO (Yeh N. and Yeh P., 2013).

3. Cathode; The materials such as aluminium, calcium and magnesium have low work function.

1.3.2 Working principle of organic photovoltaics

Donor absorbs light and then the electron from HOMO are excited to LUMO layer and generate electron-hole pairs are called exciton. The excitons diffuse to D-A interface preventing the recombination at ground state. After that, electron is transferred from LUMO of donor to LUMO of acceptor. Next, the electron transfers

through acceptor phase and hole transfer through donor phase. The last step two free charge carriers move to the respective electrode and generate electricity.

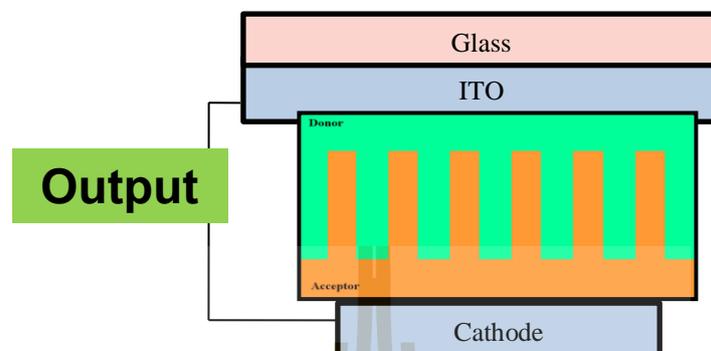


Figure 1.7 Composition of organic photovoltaics.

1.3.3 Organic photovoltaic materials

Organic materials in OPVs consist of electron donor (D) and electron acceptor (A). Electron donor should absorb the light in a maximum range and permit efficient hole transport, such as **P3HT**, **PCPDTBT**, **PPV** and **CN-PPV** shown in **Figure 1.8**. Materials for electron donor used as small organic molecule or polymer (Kaur et al., 2014).

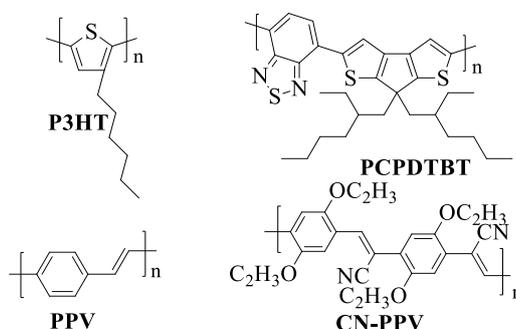


Figure 1.8 Molecular structures of CCTA and CFTA (Kaur et al., 2014).

Electron acceptor materials should be an efficient electron transport such as fullerene and their derivatives. Electron acceptor such as **C₆₀**, **PC₆₁-BM**, **PC₇₁-BM** and **ICMA** as shown in **Figure 1.9** (Kaur et al., 2014).

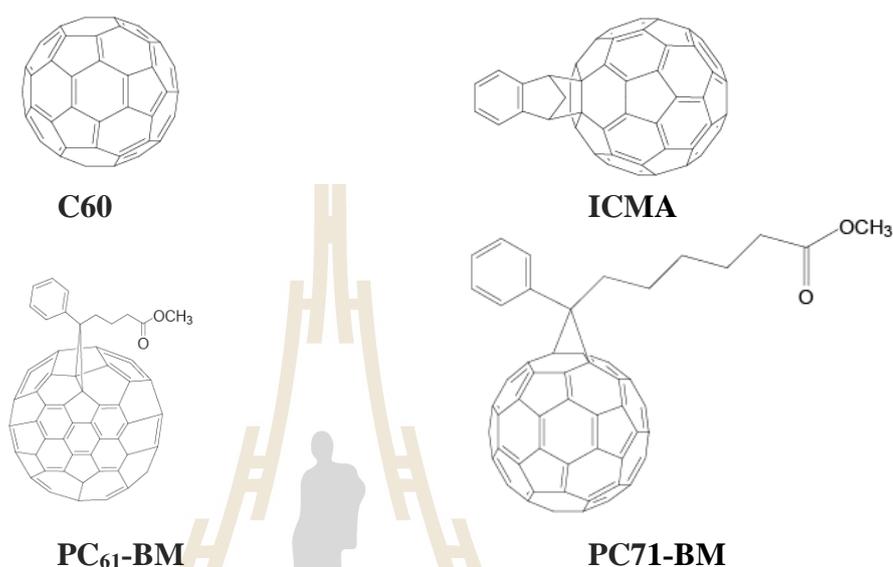


Figure 1.9 The structures of fullerene derivatives (Kaur et al., 2014).

1.4 Isoindigo dyes

Isoindigo has a strong electron-withdrawing character due to the two lactam rings as shown in **Figure 1.10**. It has been widely used in the dye industry and can be obtained easily from various natural sources (Liu, B. et al., 2011). Attaching a bulky and branched alkyl chain to the middle part of the sensitizer is a more effective way to reduce π - π stacking of molecules on the TiO₂ film (Qu et al., 2012).

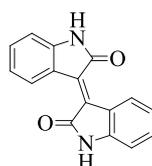


Figure 1.10 Isoindigo structure.

Isoindigo can be synthesized by aldolcondensation reaction of 6-bromooxindole and 6-bromoisatin. This reaction comprises of acid catalyzed condensation of an aromatic ketone. Under these reaction conditions, quantitative yields were obtained. The synthesis of isoindigo according to literature procedures was showed in **Figure 1.11** (Christos et al., 1988).

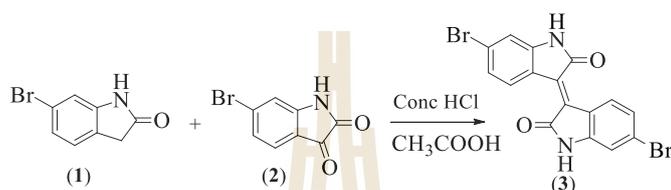


Figure 1.11 The synthesis of isoindigo (Christos et al., 1988).

According to its chemical structure, the large π -conjugated system of isoindigo has the problem of strong π - π stacked aggregation on TiO₂, which may reduce the electron injection efficiency in DSSCs. Therefore, attaching a bulky and branched alkyl chain to the middle part of the sensitizer is a more effective way to reduce π - π stacking of molecules on the TiO₂ film (**Figure 1.12**) (Qu et al., 2012).

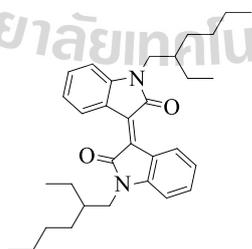


Figure 1.12 Alkyl isoindigo structure (Qu et al., 2012).

CHAPTER II

LITERATURE REVIEWS

2.1 Literature reviews for DSSCs

Kitamura and co-workers first introduced the TPA unit as an electron donor in organic dyes as shown in **Figure 2.1**. TPA based cells gave a PCE of 3.3% and 5.3%. The bathochromic shift of absorption range was achieved by increasing the number of methine units due to higher efficiency (Kitamura et al., 2004).

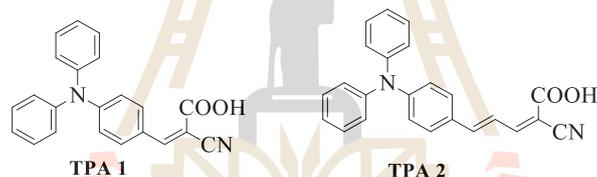


Figure 2.1 Molecular structures of **TPA 1** and **TPA 2** (Kitamura et al., 2004).

Liu and co-workers introduced a series of TPA dyes **TPA15- TPA17** was showed in **Figure 2.2** which contained thiophene derivatives by 3,4-ethylenedioxythiophene (EDOT) and 3,4-bis[2-(2-methoxyethoxy)ethoxy]thiophene (BMEET). Dyes **TPA16** and **TPA17** showed a bathochromic shift compared with **TPA15** due to the strong electron-donating ability of the alkoxy group. The higher PCE of **TPA16** (7.3%) was attributed to a broader spectral response, higher molar absorption coefficient and higher amounts of dye adsorbed on the TiO₂ films (Liu et al., 2011).

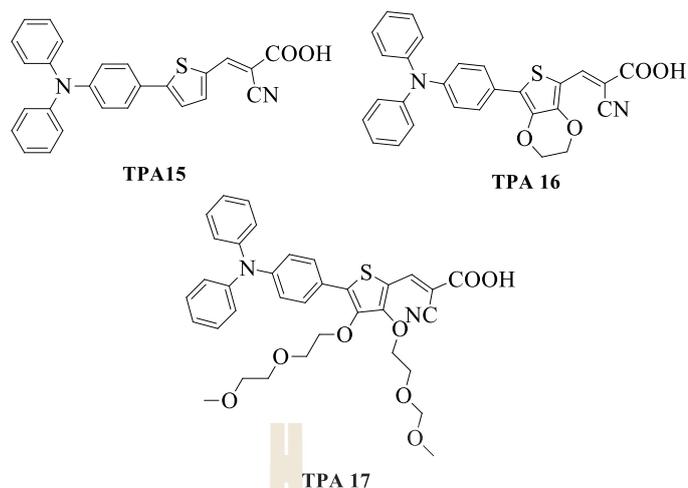


Figure 2.2 The structures of **TPA15- TPA17** (Liu et al., 2011).

To increase the electron-donating ability of TPA Hagberg and co-workers reported organic sensitizer by the introduction of electron-rich groups to adjacent phenyl ring with butoxyl groups **75** and dimethylamine groups **76** as shown in **Figure 2.3**. They found that **75** is the free rotation of the phenyl rings containing four long butoxyl chains in ortho and para positions. The protection by the butoxyl chains produces surface blocking through steric hindrance, preventing electrons in TiO_2 from recombining. **TPA 75** showed high photoconversion efficiency compared to **TPA 76** 6.0% and 4.83% respectively (Hagberg et al., 2009).

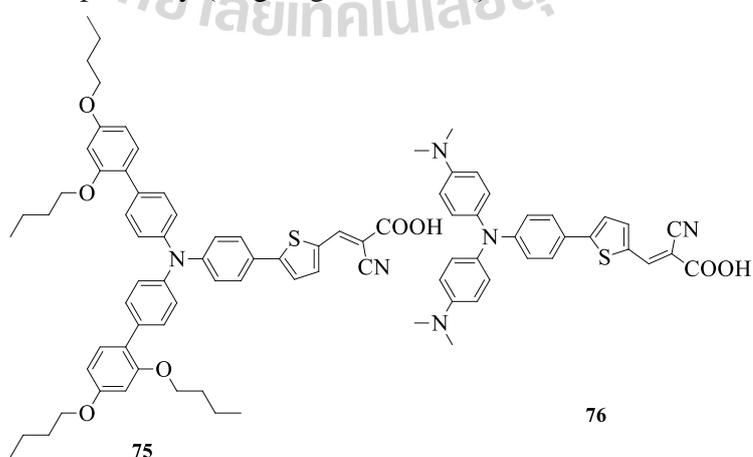


Figure 2.3 The chemical structures of **TPA75** and **TPA76** (Hagberg et al., 2009).

Chang and co-workers introduced Naphthalene based triarylamine dyes showed in **Figure 2.4**. The dipolar compounds containing *N,N*-diphenyl-naphthalen-1-amine as an electron donor. Dyes **131** and **132** showed higher absorptivity and partly to a better resonance effect provided by the naphthalene moiety. Naphthalene based dye showed high photoconversion efficiency **131** gave 7.08% efficiency, and dye **132** showed 5.25% (Chang et al., 2009).

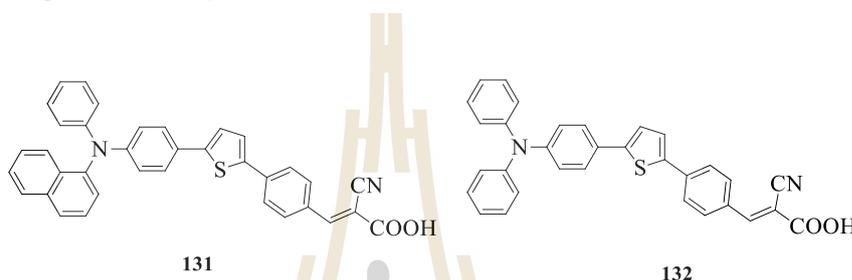


Figure 2.4 Molecular structures of **131** and **132** (Chang et al., 2009).

Ying and co-worker reported six D-A- π -A (**ID10-ID15**) sensitizers based on isoindigo as shown in **Figure 2.5**, with all dyes contained triphenylamine as an electron donor; various π -spacer (thiophene, furan and benzene); cyanoacetic acid as electron acceptor and anchoring group. **ID15** gave high photoconversion efficiency 5.48% compared to **ID11**, **ID12**, **ID13** and **ID14** that showed 3.52, 3.92, 3.22, 4.36 and 4.41% respectively (Ying et al., 2012).

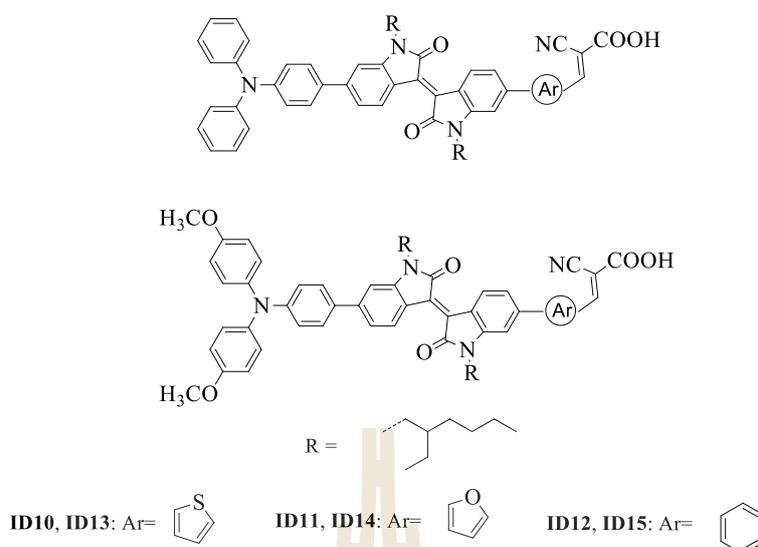


Figure 2.5 The structures of **ID10**, **ID11**, **ID12**, **ID13**, **ID14** and **ID15** (Ying et al., 2012).

In 2014 Wang G. and coworkers reported the D-D- π -A sensitizer, **ID1**, **ID2** and **ID3** based on isoindigo, these molecules contained thiophene as linker and cyanoacetic acid as electron acceptor. The isoindigo dyes was showed in **Figure 2.6**. **ID1** contained triphenylamine and isoindigo as electron donor, **ID2** and **ID3** contains isoindigo as electron donor. Triphenylamine showed good electron donor so **ID1** is the highest photo conversion efficiency 3.33%, **ID2** and **ID3** of 3.00 and 2.57, respectively (Wang, G. et al., 2014).

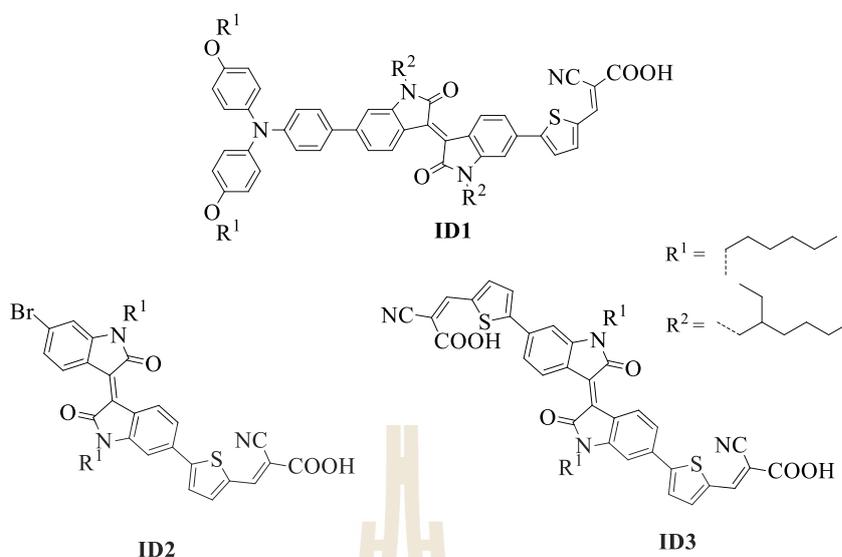


Figure 2.6 Molecular structures of **ID1**, **ID2** and **ID3** (Wang, G. et al., 2014).

In 2015 Wang D. and coworkers introduced organic sensitizers as D-D- π -A, **ID7**, **ID8** and **ID9** based on isoindigo. These dyes were shown in **Figure 2.7**. The desired molecules contained triphenylamine and isoindigo as electron donor, cyanoacetic acid as electron acceptor and various linkers (thiophen, phenyl and furane). **ID7**, **ID8** and **ID9** showed widely absorption spectra and good photoconversion efficiency of 5.50, 3.09 and 5.56, respectively (Wang, D. et al., 2015).

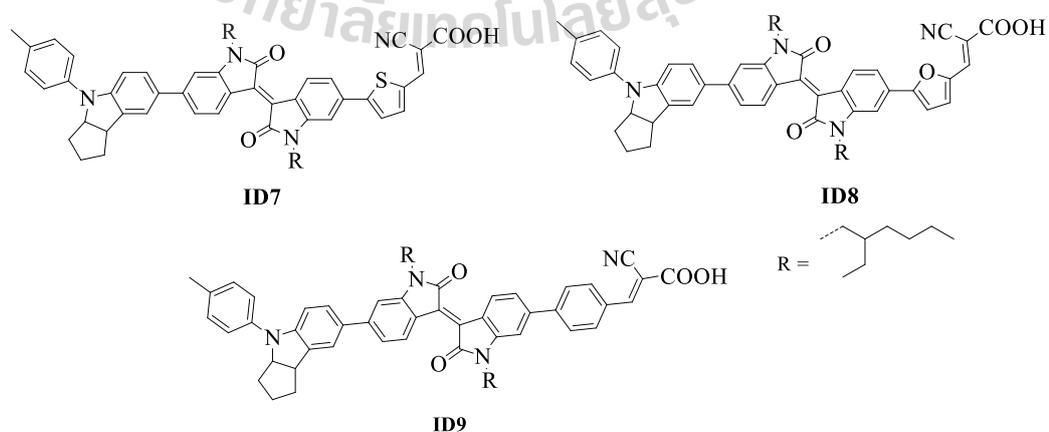


Figure 2.7 Molecular structures of **ID7**, **ID8** and **ID9** (Wang, D. et al., 2015).

2.2 Literature reviews for OPVs

Mei and coworkers investigated a new electron acceptor unit material for organic photovoltaics. The molecules contained D-A-D in **ID9** and A-D-A in **ID10**. Isoindigo unit is used as an electron acceptor to form donor-acceptor-donor (D-A-D) and acceptor-donor-acceptor (A-D-A) isoindigobased oligothiophenes in conjunction with bithiophene as an electron donor as shown in **Figure 2.8**. **ID9** gave efficiency better than devices made from **ID10**. Solar cells made from **ID9** showed a PCE of up to 1.76% while **ID10** had PCEs of up to 0.55% (Mei et al., 2009).

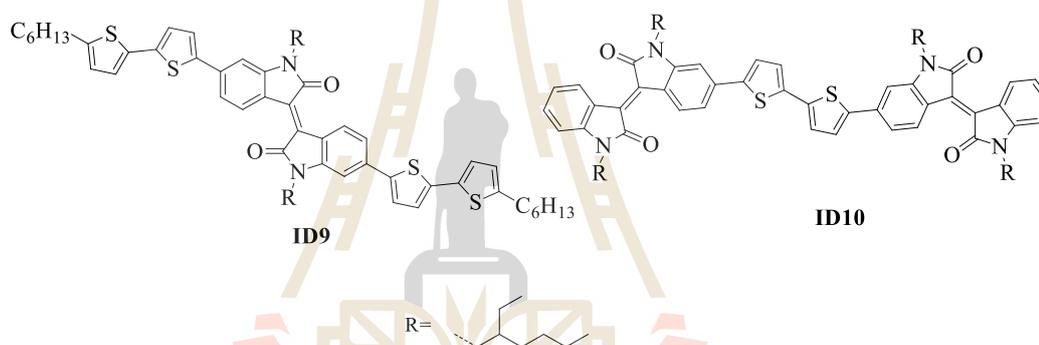


Figure 2.8 The chemical structures of **ID9** and **ID11** (Mei et al., 2009).

In 2013 Wang T. et al. reported an electron acceptor for solution-processable organic solar cells based on isoindigo as shown in **Figure 2.9**. This molecule showed a low band gap (1.5 eV) and HOMO energy level (5.39 eV). The photovoltaic device based on **IDTTT** as the donor and PCBM as the acceptor exhibited a preliminary PCE of up to 1.41% (Wang, T. et al., 2013).

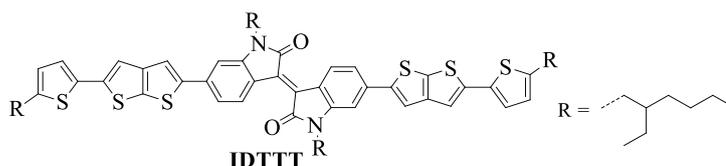


Figure 2.9 Molecular structures of **IDTTT** (Wang, T. et al., 2013).

Yassin and co-workers evaluated electron donor materials for OPVs based on isoindigo which desired molecules as D-A-D. **IDTP** molecule contained dithienopyrrole (DTP) as D unit while **IBF** contained benzofuran (BF) as D unit as shown in **Figure 2.10**. **IBF** based cell showed highest PCE 0.65% compared to **IDTP** which showed 0.19%.

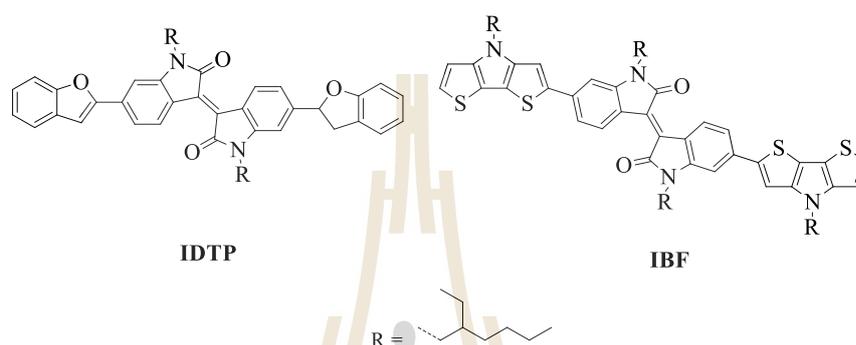


Figure 2.10 Molecular structures of **IDTP** and **IBF** (Yassin and Roncali, 2013).

In 2014 Li, S. and co-workers studied and reported about diketopyrrole and isoindigo based polymers for organic photovoltaics. New polymers based on DPP or ID as electron accepting units and with NDFT as common electron donating units showed in **Figure 2.11**. **PNDFT-ID** showed more absorption efficient than **PNDFT-DPP** in the most of visible region (from 300 to 690 nm) in solution. **PNDFT-ID** showed higher % PCE 2.48 than **PNDFT-DPP** 2.19% (Li et al., 2014).

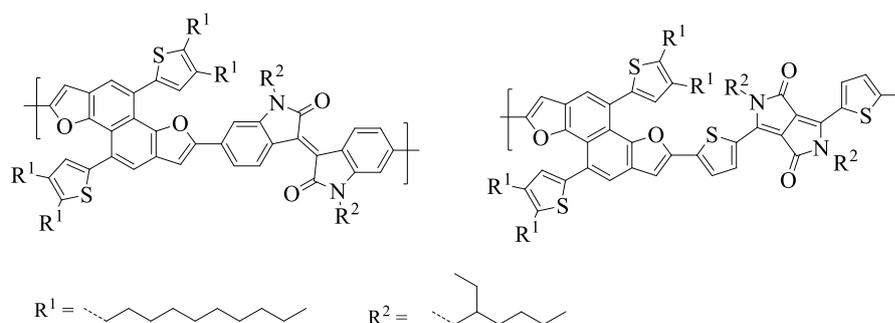


Figure 2.11 The structures of **IDTTT** (Li, S. et al., 2014).

In 2015 Vybornyi and co-workers proposed electron donor based on thienoisindigo as shown in **Figure 2.12**. They introduced acetylene-bridged Donor-Acceptor Donor (D-A-D) type involving triphenylamine or N-phenylcarbazole as donor blocks (D) and thienoisindigo as the acceptor unit (A), **TII-TPA** and **TII-PCz**. The triphenylamine end-capped derivative gave the best power conversion efficiency of 2.20% compared to N-phenylcarbazole end-capped which showed power conversion efficiency of 1.52% (Vybornyi et al., 2015).

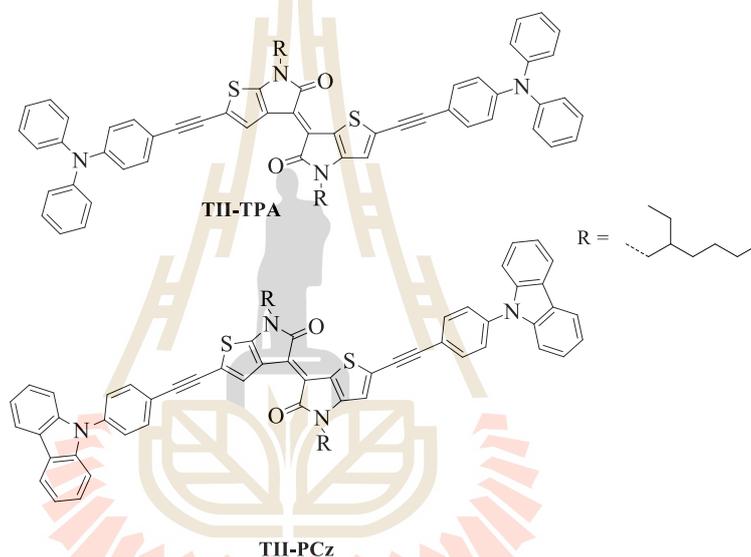


Figure 2.12 Molecular structures of **TII-TPA** and **TII-PCz** (Vybornyi et al., 2015).

Pierre Josse and co-worker evaluated molecular acceptors for organic solar cells based on thienoisindigo (TII) and diketopyrrolopyrrole (DPP) blocks as shown in **Figure 2.13**. **DPP-Pht₂** based device showed best photoconversion efficiency of 3.3% compared to **TII-Thp₂** based device (Josse et al., 2015).

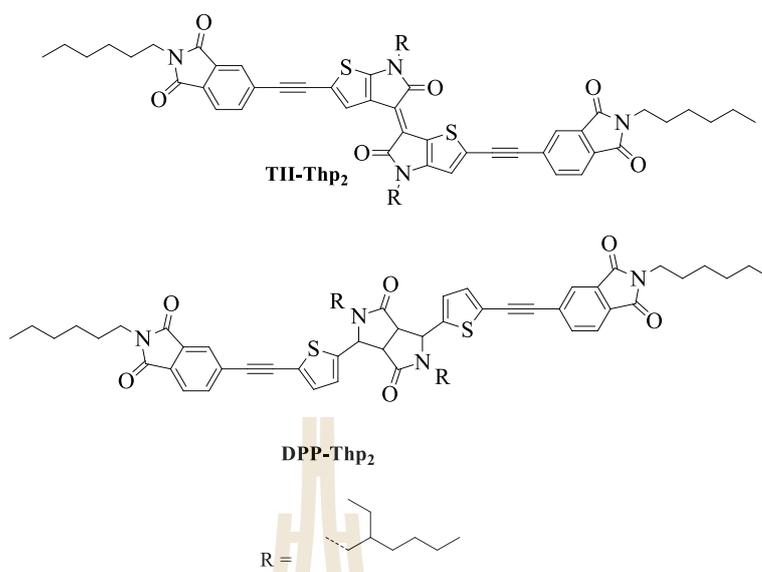


Figure 2.13 Molecular structures of **TII-Thp₂** and **DPP-Pht₂** (Josse et al., 2015).

CHAPTER III

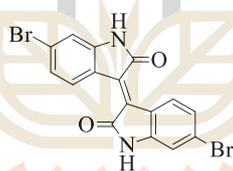
MATERIALS AND METHODES

3.1 Materials

All chemicals and reagents from commercial sources were used without further purification. Reactions were carried out under nitrogen and argon atmosphere unless otherwise stated. Solvents were dried and purified using standard techniques.

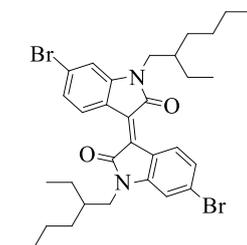
3.2 Methode

Synthesis of 6,6'-Dibromoisindigo



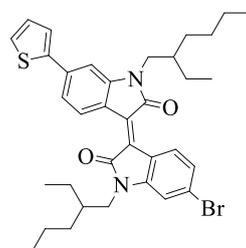
In round-bottom flask 100 ml the mixture of 6-bromooxindole (1.01 g, 4.76 mmol), 6-bromoisatin (1.03 g, 4.55 mmol), Conc. HCl 0.2 ml in CH₃COOH 40 ml were refluxed 24 hr. The reaction was cooled and poured into water after that filtrated to give brown solid 92% yield.

Synthesis of 6,6'-Dibromo-*N,N'*-(2-ethylhexyl)-isoindigo



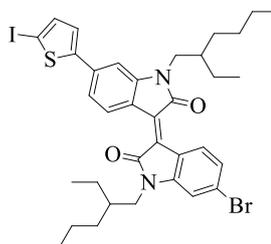
The mixture of 6,6'-Dibromoisoidigo (0.50 g, 1.19 mmol) and 1-bromo-2-ethylhexane (0.85 g, 4.42 mmol) in DMF 50 ml were refluxed 14 hr. The solution was cooled and poured into water. The reaction was extracted with DCM (3x25), washed water (3x25), and brine solution 50 ml dried over Na₂SO₄ anhydrous. The organic layer was evaporated by evaporation. The residue was purified by flash column chromatography using silica gel and DCM: hexane as eluent to give deep-red solid 82% yield. ¹H NMR (δ/ppm, CDCl₃): δ: 9.03 (d, 2H, J=10.0 Hz), 7.15 (d, 2H, J=5.0 Hz), 6.89 (s, 2H), 3.64-3.62 (m, 4H), 1.82 (s, 2H), 1.37- 1.29 (m, 16H), 0.94-0.89 (m, 12H). ¹³C NMR (δ/ppm, CDCl₃): δ: 169.2, 169.2, 146.8, 146.7, 128.8, 127.2, 122.5, 121.7, 120.6, 49.2, 32.1, 23.4 and 14.3 ppm, m/z (MALDI-TOF): 644.15 (required 644.14).

Synthesis of 2-(6'-bromo-*N,N'*-(1-octyl)-isoindigo)-thiophene



The reaction of 6,6'-Dibromo-*N,N'*-(2-ethylhexyl)-isoindigo (0.30 g, 4.22 mmol), 2-thiopheneboronic acid (0.06 g, 5.00 mmol), Pd(PPh₃)₄ (0.0004g, 3.7x10⁻³ mmol) and 2M Na₂CO₃ (17.5 ml, 7.00 mmol) in THF 50 ml was refluxed under nitrogen atmosphere for 24 hr. The mixture was cooled and poured into water. The solution was extracted with DCM (3x25), washed with water (3x25), and brine solution 50 ml dried over Na₂SO₄ anhydrous after that, the organic layer was evaporated. The residue was purified by flash column chromatography using silica gel and DCM: hexane as eluent to give deep-red solid 65%yield. ¹H NMR (δ/ppm, CDCl₃): δ: 9.13 (d, 1H, J=10.0 Hz), 9.06 (d, 1H, J=10.0 Hz), 7.42 (d, 1H, J=5.0 Hz), 7.41 (d, 1H, J=5.0 Hz), 7.28 (d, 1H, J=5.0 Hz), 7.16 (d,1H, J=5.0 Hz), 7.11 (d, 1H, J=5.0 Hz), 6.95 (s, 1H), 6.87 (s, 1H), 3.69-3.57 (m, 4H), 1.83 (s, 2H), 1.37-1.30 (m, 16H), 0.96-0.88 (m, 12H). ¹³C NMR (δ/ppm, CDCl₃): 166.5, 166.2, 145.9, 145.9, 143.9, 138.3, 133.3, 131.2, 131.0, 130.8, 130.4, 128.4, 126.3, 126.1, 125.1, 124.9, 124.4, 120.8, 120.6, 119.4, 111.5, 111.4, 105.1, 44.3, 44.3, 37.7, 37.4, 30.8, 30.6, 28.8, 28.6, 24.2, 24.0, 23.0, 14.1, 14.0, 10.8 and 10.6 ppm, m/z (MALDI-TOF): 647.26 (required 647.71).

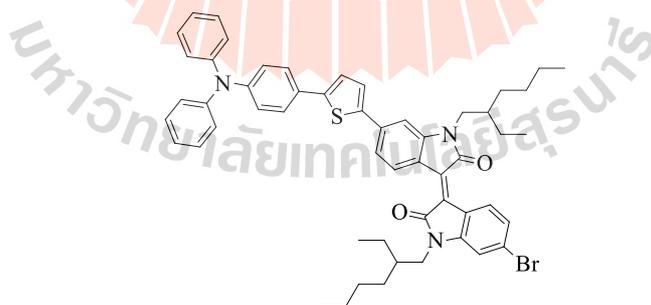
Synthesis of 5-(6'-bromo-*N,N'*-(2-ethylhexyl)-isoindigo)-iodothiophene



A solution of 2-(6'-bromo-*N,N'*-(1-octyl)-isoindigo)-thiophene (0.40 g, 6.31 mmol) in THF 20 ml was stirred. NBS (0.13g, 6.22 mmol) was added into the solution.

Then, CH₃COOH was added 5 ml. The reaction was poured into water and extracted with DCM (3x25), washed with water (3x25), brine solution 50 ml and Na₂S₂O₃ solution 50 ml dried over Na₂SO₄ anhydrous and solvent was removed. The residue was passed through a short silica gel column using DCM: hexane to give red-deep solid 91% yield. ¹H NMR (δ/ppm, CDCl₃): 9.16 (d, 1H, J=10.0 Hz), 9.06 (d, 1H, J=10.0 Hz), 7.19 (d, 1H, J=5.0 Hz), 7.17 (d, 1H, J=5.0 Hz), 7.16 (d, 1H, J=5.0 Hz), 7.07 (d, 1H, J=5.0 Hz), 6.90 (s, 1H) and 6.87 (s, 1H), 3.65 (4H), 1.85 (2H), 1.42-1.39 (16H) and 0.97-0.80 (12H). ¹³C NMR (δ/ppm, CDCl₃): 168.5, 168.2, 149.9, 146.1, 146.0, 138.2, 137.1, 133.0, 131.7, 130.9, 130.5, 126.3, 125.6, 125.0, 121.2, 120.6, 119.2, 111.4, 104.9, 74.3, 44.4, 44.2, 37.7, 37.5, 30.8, 30.6, 28.8, 28.6, 24.2, 24.0, 23.0, 15.9, 14.0, 14.0, 12.9, 10.8, 10.7 and 10.6 ppm, m/z (MALDI-TOF): 774.35 (required 774.12).

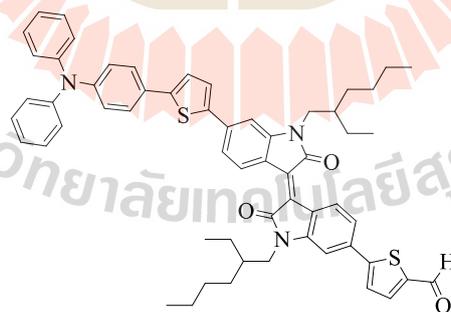
Synthesis of 5-(6'-bromo-*N,N'*-(2-ethylhexyl)-isoindigo)-thiophene-*N,N'*-bisphenylaniline



The reaction of 5-(6'-bromo-*N,N'*-(2-ethylhexyl)-isoindigo)-iodothiophene (0.42 g, 0.34 mmol), 4-diphenylaminophenylboronic acid (0.42 g, 0.39 mmol), Pd(PPh₃)₄ (0.001 g, 0.0004 mmol) 2M Na₂CO₃ (10.0 ml, 20 mmol) in THF was refluxed under N₂ atmosphere for 10 h. The mixture was cooled and poured into water. The solution

was extracted with DCM (3x25), washed with water (3x25), and brine solution 50 ml dried over Na₂SO₄ anhydrous. Organic layer was purified by flash column chromatography using silica gel as stationary phase and DCM: hexane as eluent. The solvent was removed to give purple solid 65% yield. ¹H NMR (δ/ppm, CDCl₃): δ: 9.18 (d, 1H, J= 10.0 Hz), 9.08 (d, 1H, J= 10.0 Hz), 7.54 (d, 2H, J= 5.0 Hz), 7.41 (d, 1H, J= 5.0 Hz), 7.31 (q, 5H), 7.26 (d, 1H), 7.17 (q, 4H), 7.10 (q, 3H), 6.99 (s, 1H), 6.92 (s, 1H), 3.78-3.60 (m, 4H), 1.88 (s, 2H), 1.46-1.28 (m, 16H) and 1.00-0.86 (m, 12H). ¹³C NMR (δ/ppm, CDCl₃): 168.6, 168.2, 147.7, 147.3, 145.9, 145.9, 145.3, 142.0, 138.2, 133.2, 130.7, 130.4, 129.3, 126.5, 124.9, 124.7, 123.4, 123.3, 120.6, 120.6, 118.9, 111.4, 104.6, 44.3, 44.1, 37.7, 37.4, 30.8, 30.6, 28.8, 28.6, 24.2, 24.0, 23.0, 14.1, 14.0, 10.8 and 10.6 ppm, m/z (MALDI-TOF): 891.05 (required 891.33).

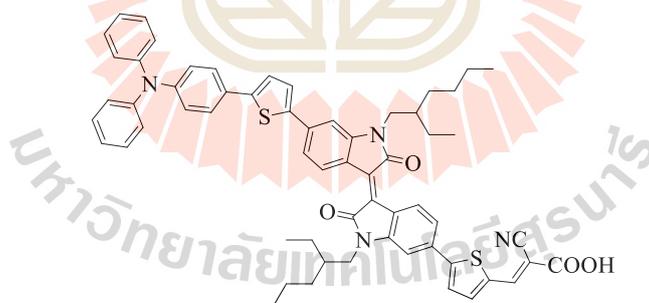
Synthesis of 6-(6'-(4-(Diphenylamino)phenyl)-*N,N'*-(2-ethylhexyl)-isoindigothiophene)-thiophene-5-carbaldehyde



In round-bottom flask 100 ml, 5-(6'-bromo-*N,N'*-(2-ethylhexyl)-isoindigothiophene-*N,N'*-bisphenylaniline (0.30 g, 0.0003 mmol), 5-formyl-2-thiopheneboronic acid (0.0004 g, 0.0630 mmol), Pd(dppf)Cl₂ (0.0005 g, 0.0004x10⁻³ mmol) and 2M Na₂CO₃ (15.5 ml, 0.0065 mmol) in THF 40 ml was refluxed under N₂ atmosphere for 24 hr. The reaction was cooled and poured into water. The mixture was extracted with

DCM (3x25), washed with water (3x25), and brine solution 50 ml dried over Na₂SO₄ anhydrous. Organic layer was purified by flash column chromatography using silica gel as stationary phase and DCM: hexane as eluent. The solvent was removed to give black solid 54%yield. ¹H NMR (δ/ppm, CDCl₃): δ: 10.01 (s, 1H), 9.30 (d, 1H, J= 10.0 Hz), 9.26 (d,1H, J= 10.0 Hz), 7.86 (d, 1H, J= 5.0 Hz), 7.57 (q, 4H), 7.49 (d, 2H), 7.46 (d, 2H), 7.39-7.33 (m, 2H), 7.22 (d, 4H), 7.13 (q, 6H), 7.09 (s, 1H), 3.84-3.81 (m, 4H), 1.98 (s, 2H), 1.51-1.46 (m, 16H), 1.08-0.93 (m, 12H), ¹³C NMR (δ/ppm, CDCl₃): 190.8, 186.4, 186.3, 146.6, 146.3, 145.5, 145.0, 145.7, 145.3, 143.4, 142.5, 139.1, 134.9, 133.2, 131.6, 130.4, 130.4, 130.3, 129.2, 128.3, 127.4, 127.3, 126.8, 125.3, 124.5, 123.4, 122.3, 121.7, 106.6, 104.6, 44.4, 37.8, 30.8, 29.7, 28.8, 24.2, 23.0, 14.4 and 10.6 ppm, m/z (MALDI-TOF): 922.44 (required 922.40).

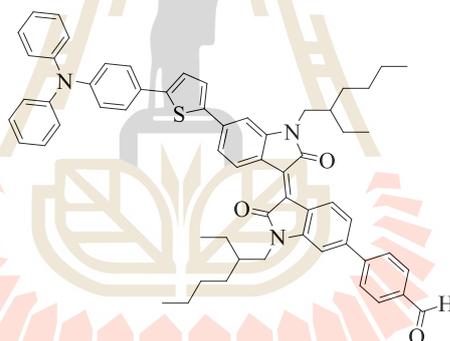
TIDT



A solution of 5-(6'-bromo-*N,N'*-(2-ethylhexyl)-isoindigo)-thiophene-*N,N'*-bisphenylaniline (0.12 g, 0.14 mmol) and ammonium acetate (0.04 g, 0.002 mmol) in CH₃COOH 20 ml was refluxed for 24 h. The solution was cooled and poured into cold water. Recrystallization by dissolving in DCM and layered addition MeOH gave the final product in black solid g, 72%yield. ¹H NMR (δ/ppm, CDCl₃): δ: 9.14 (d, 1H, J= 10.0 Hz), 9.09 (d, 1H, J= 10.0 Hz), 8.21 (s, 1H), 8.03 (d, 2H, J= 5.0 Hz), 7.70 (d, 2H,

$J = 5.0$ Hz), 7.41 (d, 2H, $J = 5.0$ Hz), 7.29 (s, 1H), 7.22 (m, 6H), 7.13 (s, 1H), 7.06 (d, 3H), 7.0 (t, 3H), 6.92 (s, 1H), 6.88 (s, 1H), 3.66 (m, 4H), 1.85 (2H), 1.36 (m, 12), 0.91 (t, 6H) and 0.85 (t, 6H) ppm. ^{13}C NMR (δ /ppm, CDCl_3): 186.6, 186.4, 146.5, 146.4, 145.3, 145.0, 145.9, 145.5, 143.2, 142.4, 139.0, 134.7, 133.1, 131.5, 130.2, 130.4, 130.3, 129.2, 128.3, 127.4, 127.3, 126.8, 125.3, 124.5, 123.4, 122.3, 121.7, 106.6, 104.5, 94.6, 44.4, 37.8, 30.8, 29.6, 28.8, 24.2, 24.0, 14.2 and 10.5 ppm, m/z (MALDI-TOF): m/z 988.91 (required 988.41).

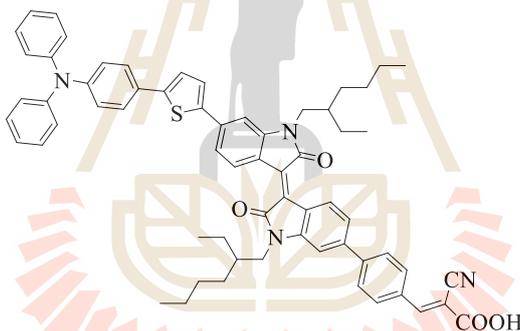
Synthesis of 6-(6'-(4-(Diphenylamino)phenyl)-*N,N'*-(2-ethylhexyl)-isoindigo-thiophene)-phenyl-4-carbaldehyde



5-(6-bromo-*N,N'*-(2-ethylhexyl)-isoindigo)-thiophene-*N,N'*-bisphenylaniline (0.25 g, 0.12 mmol), 4-formylphenylboronic acid (0.02 g, 0.14 mmol), $\text{Pd}(\text{dppf})\text{Cl}_2$ (0.0003 g, 0.41 mmol) and 2M Na_2CO_3 (6.0 ml, 20 mmol) in THF were refluxed under N_2 atmosphere for 24 hr. The mixture was cooled and poured into water. The reaction was extracted with DCM (3x25), washed with water (3x25), and brine solution 50 ml dried over Na_2SO_4 anhydrous. Organic layer was purified by flash column chromatography using silica gel as stationary phase and DCM: hexane as eluent. The solvent was removed to give black solid 79% yield. ^1H NMR (δ /ppm, CDCl_3): δ : 10.07

(s, 1H), 9.22 (d, 1H, d, 2H, J= 10.0 Hz), 9.16 (d, 1H, , J= 10.0 Hz), 7.96 (d, 2H, J= 5.0 Hz), 7.77 (d, 2H, J= 5.0 Hz), 7.48 (d, 2H, J= 5.0 Hz), 7.31-7.22, (m, 8H), 7.15-6.97 (m, 10H), 3.73-3.51 (m, 4H), 1.90 (s, 2H), 1.39-1.25 (m, 16H), 0.99-0.89 (m, 12H). ^{13}C NMR (δ /ppm, CDCl_3): 191.7, 186.6, 186.5, 147.7, 147.3, 146.5, 146.0, 145.7, 145.3, 142.9, 142.1, 138.2, 135.7, 133.1, 131.3, 130.5, 130.3, 130.1, 129.3, 128.0, 127.7, 127.5, 126.5, 125.5, 124.7, 123.4, 122.1, 121.1, 120.7, 118.9, 106.6, 104.6, 44.2, 37.8, 30.8, 29.7, 28.8, 24.3, 23.0, 14.3 and 10.8 ppm, m/z (MALDI-TOF): 915.32 (required 915.44).

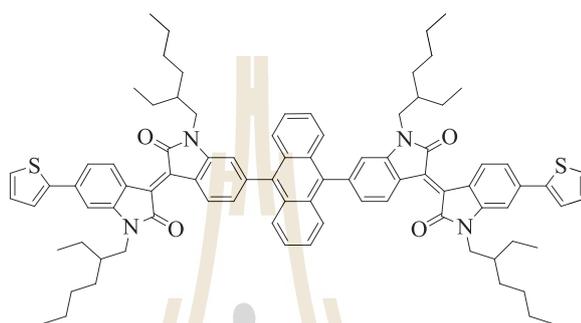
Synthesis of TIDP



A solution of 6-(6'-(4-(Diphenylamino)phenyl)-*N,N'*-(2-ethylhexyl)-isoindigothiophene)-phenyl-4-carbaldehyde (0.15 g, 0.2 mmol) and ammonium acetate (0.04 g, 0.06 mmol) in CH_3COOH 20 ml was refluxed for 24 hr. The solution was cooled and poured into cold water. Recrystallization by dissolving in DCM and layered addition MeOH gave the final product in black solid g, 81%yield. ^1H NMR (δ /ppm, CDCl_3): δ : 9.17 (d, 1H, J= 10.0 Hz), 9.11 (d, 1H, J= 10.0 Hz), 8.24 (s, 1H), 8.05 (d, 2H, J= 5.0 Hz), 7.71 (d, 2H, J= 5.0 Hz), 7.43 (d, 2H, J= 10.0 Hz), 7.33 (d, 1H, J= 10.0 Hz), 7.27-7.17 (m, 6H), 7.07-6.93 (m 10H), 3.69-3.68 (m, 4H), 2.77 (s, 2H), 1.40-1.26 (m, 16H), 0.92-0.85 (m, 12H), ^{13}C NMR (δ /ppm, CDCl_3): 187.5, 186.4, 147.9, 147.7, 146.5,

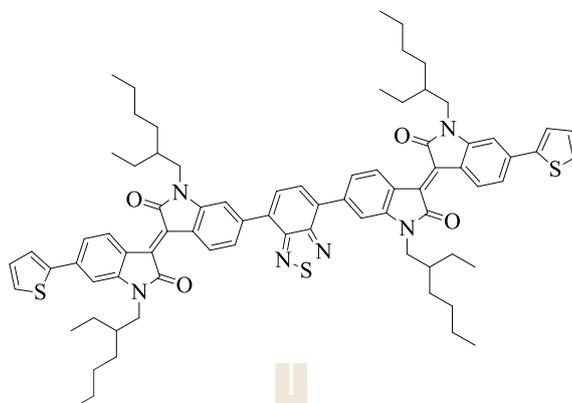
146.0, 145.7, 145.3, 142.9, 142.1, 138.2, 135.7, 133.1, 131.3, 130.5, 130.3, 130.1, 129.3, 128.0, 127.7, 127.5, 126.5, 125.5, 124.7, 123.4, 122.1, 121.1, 120.7, 118.9, 106.6, 104.6, 84.4, 44.1, 37.9, 30.7, 29.4, 28.9, 24.1, 23.1, 14.2 and 10.9 ppm, m/z (MALDI-TOF): m/z 982.68 (required 982.45).

Synthesis of **IDTA**



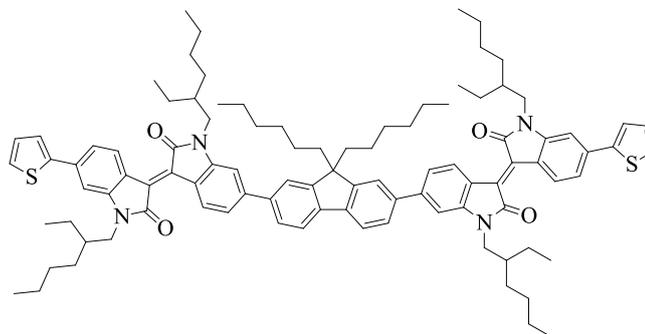
A solution of compound (5) (0.17 g, 2.64 mmol), anthracene-9,10-diboronic acid bis(pinacol) ester (0.05 g, 2.12 mmol) was dissolved in THF 20 ml, Cs_2CO_3 (0.39 g, 1.2 mmol) and $\text{Pd}_2(\text{PPh}_3)_4$ (0.014 g, 0.012 mmol) were added. The reaction was refluxed for 24 h under N_2 atmosphere. The solution was cooled and poured into water. The organic layer was collected and dried over Na_2SO_4 . Solvent were removed by rotary evaporator. The crude product was purified by column chromatography with hexane and dichloromethane (2:1) as eluent to give black solid as 36% yield. ^1H NMR (500 MHz, CDCl_3) δ = 9.17 (4H, d, $J=10.0$ Hz), 8.34 (2H, d, $J=5.0$ Hz), 7.82 (2H, d, $J=5.0$ Hz), 7.44 (3H, s), 7.38 (4H, d), 7.32 (3H, d, $J=5.0$ Hz), 7.14 (4H, d, $J=5.0$ Hz), 7.01 (4H, s), 3.72 (8H, m), 1.90 (4H, s), 1.28 (32H, m) and 0.92 (24H, m). ^{13}C NMR (δ/ppm , CDCl_3): δ 224.9, 223.8, 168.6, 145.7, 144.1, 137.8, 134.1, 132.0, 130.2, 128.3, 127.2, 126.1, 124.2, 121.0, 119.3, 105.1, 77.2, 77.0, 76.7, 44.1, 37.7, 30.8, 29.7, 28.8 ppm, m/z (MALDI-TOF): 1310.68 (required 1310.67).

Synthesis of IDTB



A mixture of compound (5) (0.14 g, 0.22 mmol) and 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) (0.04 g, 0.1 mmol) were dissolved in 20 mL of THF, Pd(PPh₃)₄ (0.012 g, 0.01 mmol) and Cs₂CO₃ (0.33 g, 1.0 mmol) were added into reaction and refluxed for 24 h under N₂ atmosphere. The solution was cooled and poured into water. The solution was extracted with CH₂Cl₂. The combined organic layers were washed with water and dried over anhydrous Na₂SO₄ after that, solvent were removed by rotary evaporator. Crude product was purified using column chromatography with hexane and dichloromethane (2:1) as eluent gave black solid as 32% yield. ¹H NMR (500 MHz, CDCl₃) δ = 9.25 (d, 4H, J=10.0 Hz), 7.51 (d, 4H, J=5.0 Hz), 7.45 (d, 4H, J=5.0 Hz), 7.39 (d, 4H, J=10.0 Hz), 7.22 (t, 4H), 7.09 (s, 4H), 3.82 (m, 8H), 1.98 (s, 4H), 1.50 (m, 32H) and 0.99 (tt, 24H) ppm. ¹³C NMR (δ/ppm, CDCl₃): δ 168.6, 145.7, 144.1, 137.8, 132.0, 130.2, 128.3, 126.1, 124.2, 121.0, 119.4, 105.1, 44.1, 37.8, 30.8, 29.7, 28.8, 24.2, 23.0, 14.1 and 10.84 ppm, m/z (MALDI-TOF): 1268.11 (required 1268.60).

Synthesis of **IDTF**



In 50 mL two-necked flask, (5) (0.12g, 0.2 mmol) and 9,9-dihexylfluorene-2,7-diboronic acid (0.05 g, 0.09 mmol), Pd(PPh₃)₄ (0.01 g, 0.009 mmol) as catalyst Cs₂CO₃ (0.29 g, 0.9 mmol) as base were dissolved in THF 20 ml. The mixture was refluxed for 24 h under nitrogen atmosphere. The reaction mixture was cooled and added 20 ml of water. The reaction was extracted with CH₂Cl₂, washed with water, dried over anhydrous Na₂SO₄ and removed solvent by rotary evaporator. Crude product was purified by column chromatography with hexane and dichloromethane (2:1) as eluent to give black solid as 54% yield. ¹H NMR (500 MHz, CDCl₃) δ = 9.24 (d, 4H, J=10.0 Hz), 7.51 (s, 4H), 7.45 (d, 4H, J=5.0 Hz), 7.41 (d, 4H), 7.22 (s, 4H), 7.09 (s, 4H), 1.98 (s, 4H), 1.49 (m, 40H) and 1.04 (m, 30H) ppm. ¹³C NMR (δ/ppm, CDCl₃): δ 168.6, 145.7, 144.1, 137.87, 132.0, 130.2, 128.3, 126.1, 124.2, 123.9, 121.0, 119.3, 105.1, 44.1, 37.7, 30.8, 30.5, 30.4, 30.1, 30.0, 29.7, 29.2, 29.0, 28.8, 26.7, 24.2, 23.0, 22.7, 19.7, 14.1, 11.1, 10.84 and 10.7 ppm, m/z (MALDI-TOF): 1467.43 (required 1467.86).

CHAPTER IV

RESULTS

4.1 Materials for DSSCs

4.1.1 Synthesis of Isoindigo dyes TIDT and TIDP

The isoindigo dyes (**TIDP** and **TIDT**) were successfully synthesized from aldol condensation, alkylation, Suzuki cross coupling, iodination and Knoevenagel condensation reaction. The retrosynthesis of **TIDP** and **TIDT** is showed in **Figure 4.1**.

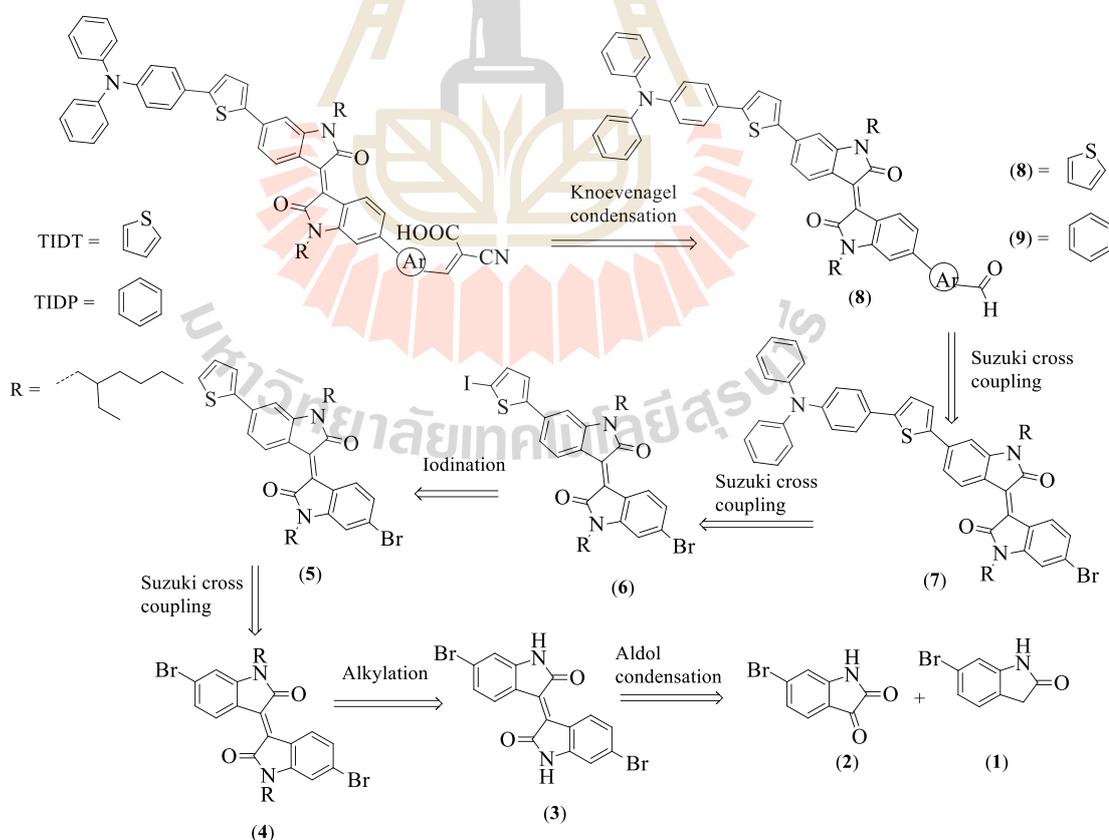


Figure 4.1 The retrosynthesis of **TIDP** and **TIDT**.

First step, 6,6'-Dibromoisoidindigo (**3**) was synthesized from aldolcondensation of 6-bromooxindol (**1**) and 6-bromoisatin (**2**) were dissolved in CH_3COOH followed by the addition of conc. HCl solution. The mixture was heated $80\text{ }^\circ\text{C}$ for 24 h. According to literature review gave brown solid as shown in **Figure 4.2**.

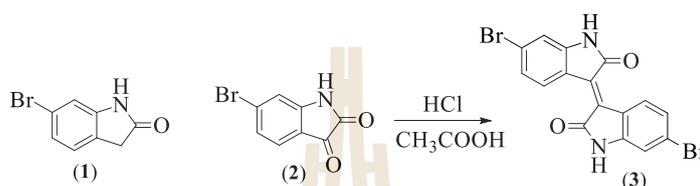


Figure 4.2 Synthesis of 6,6'-Dibromoisoidindigo (**3**) (Christos et al., 1988).

The second step, alkylation reaction of 6,6'-Dibromoisoidindigo (**3**), 1-bromo-2-ethylhexane and K_2CO_3 were dissolved in DMF. The reaction was heated for 18 h gave 6,6'-Dibromo-*N,N'*-(2-ethylhexyl)-isoidindigo (**4**) as shown in **Figure 4.3**.

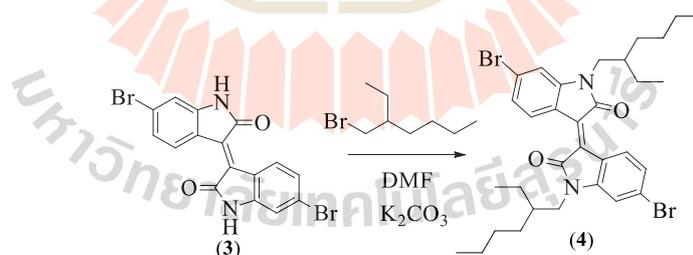


Figure 4.3 Synthesis of 6,6'-Dibromo-*N,N'*-(2-ethylhexyl)-isoidindigo.

The chemical structure of isoidindigo (**4**) was confirmed by ^1H NMR, ^{13}C NMR and Mass spectroscopy. ^1H NMR spectrum of the product showed a new signal of alkyl proton at δ 3.64-3.62 ppm (integration= 4). This signal confirmed as alkyl

proton near nitrogen atom of isoindigo ring. The characteristic proton of isoindigo showed at δ 9.03 ppm (integration = 2). Proton of this position showed high chemical shift because the proton can interact with carbonyl of ketone due to hydrogen bonding according to literature review. ^{13}C NMR spectrum showed a signal of ketone at δ 169.2 ppm. While carbon of CH_3 , CH_2 of alkyl chain showed δ 14.3 and 23.4 ppm, respectively. Mass spectroscopy confirmed molecular mass of product which showed m/z 644.15 (required 644.14).

The third step, synthesis of 2-(6'-bromo-*N,N'*-(2-ethylhexyl)-isoindigo)-thiophene (**5**) from Suzuki cross coupling reaction of 6,6'-Dibromo-*N,N'*-(2-ethylhexyl)-isoindigo (**4**) and 2-thiopheneboronic acid in the present of 2M Na_2CO_3 as base and $\text{Pd}(\text{PPh}_3)_4$ as a catalyst in THF. The mixture was refluxed 24 h as shown in **Figure 4.4**.

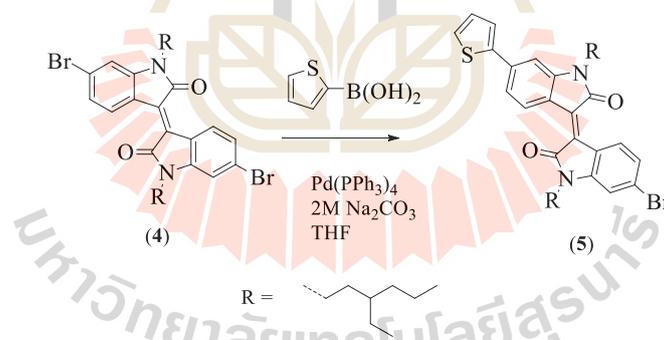


Figure 4.4 Synthesis of 2-(6'-bromo-*N,N'*-(2-ethylhexyl)-isoindigo)-thiophene.

To confirm the structure of compound (**5**) ^1H NMR, ^{13}C NMR and Mass spectroscopy were employed. The ^1H NMR spectrum of product showed a new signal of thiophene proton of 3-position at δ 7.42 (integration= 1, multiplicity= doublet), at δ 7.37 ppm (integration= 1, multiplicity= doublet) belong the 5-position and at δ 7.12 ppm (integration= 1, multiplicity= triplet) revealed proton of 4-position. Peaks region

δ 9.13 and 9.06 ppm (integration ratio 1:1) showed identity proton of isoindigo. The proton of alkyl chain showed at δ 3.69-3.57 ppm (integration= 4) which belong proton of CH₂ near nitrogen atom of isoindigo ring. ¹³C NMR spectrum showed a new carbon of thiophene at δ 128.41 and 126.30 ppm. Mass spectrum revealed m/z 647.26 (required 647.71).

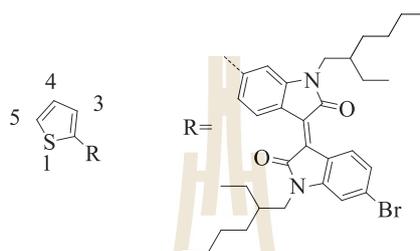


Figure 4.5 Thiophene positions.

The mechanism of Suzuki cross coupling is showed in **Figure 4.6**. Suzuki cross coupling reaction is the organic reaction of an organohalide with boronic acid catalyzed by palladium (0) complex and base. The palladium catalysed mechanism begins with the oxidative addition of the organohalide to the Pd (0) to form a Pd (II) complex. Transmetalation with the organohalide forms the organopalladium species and reductive elimination of product restores the original palladium catalyst.

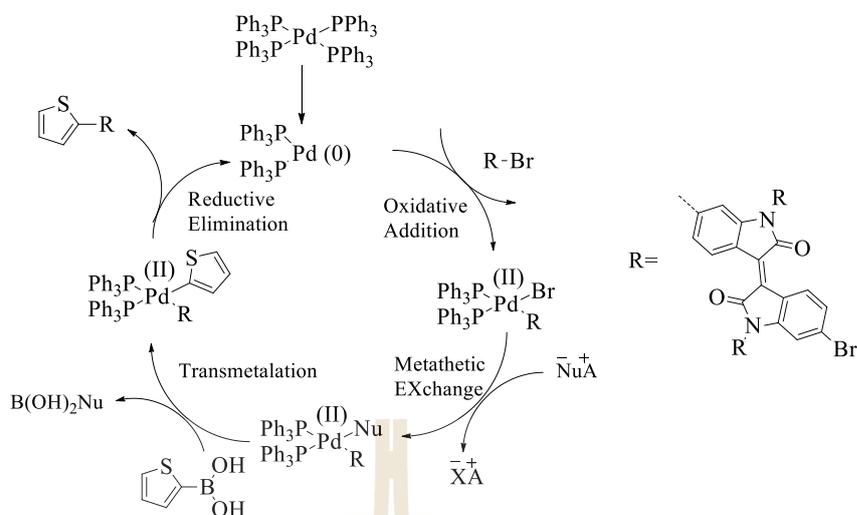


Figure 4.6 Mechanism of Suzuki cross coupling.

5-(6'-bromo-*N,N'*-(2-ethylhexyl)-isoindigo)-iodothiophene (**6**) was obtained from iodination reaction of isoindigothiophene (**5**) reacted with NIS in the mixture of THF: CH₃COOH as shown in **Figure 4.7**.

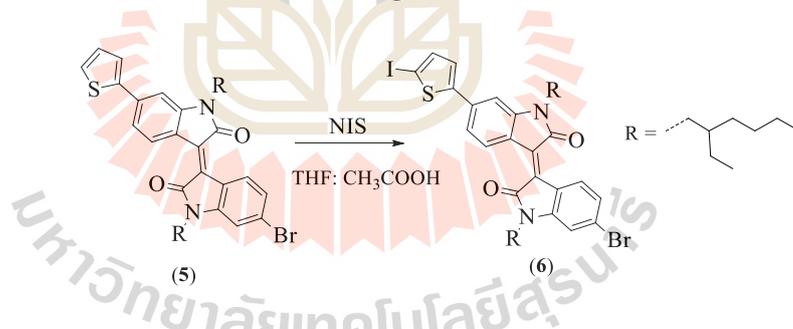


Figure 4.7 Synthesis of 5-(6'-bromo-*N,N'*-(2-ethylhexyl)-isoindigo)-iodothiophene.

Iodoisoindigo (**6**) was confirmed by ¹H NMR, ¹³C NMR and Mass spectroscopy. The ¹H NMR spectrum indicated identity proton of isoindigo at δ 9.16 and 9.06 ppm (integration ratio 1:1). ¹H NMR spectrum signified the proton position 5 disappearing compared to ¹H NMR spectrum of starting. This data confirmed that iodide replaced hydrogen on this position. Substitution reaction of thiophene on 2 and

5- positions are stabilized by charge delocalization to a greater degree than the intermediate from C-3 attack due to gave the product. The proton on other positions still exist which showed at δ 7.17 ppm (integration= 1, multiplicity= doublet) for position 4 and δ 7.16 ppm (integration= 1, multiplicity= doublet) belong position 3. Alkyl region proton present at δ 3.65 ppm (integration=4). ^{13}C NMR spectral of ketone showed peak at δ 168.5 and 168.2 ppm. Carbon peak which contacted with iodide showed δ at 74.3 ppm. Mass spectrum revealed m/z 774.35 (required 774.12). The fifth steps, Suzuki cross coupling of Iodoisoindigo (6) and 4-diphenylaminophenylboronic acid in the present of $\text{Pd}(\text{PPh}_3)_4$ as a catalyst and $2\text{M Na}_2\text{CO}_3$ as base in THF gave 5-(6'-bromo- N,N' -(2-ethylhexyl)-isoindigo)-thiophene- N,N' - bisphenylaniline (7) as shown in **Figure 4.8**.

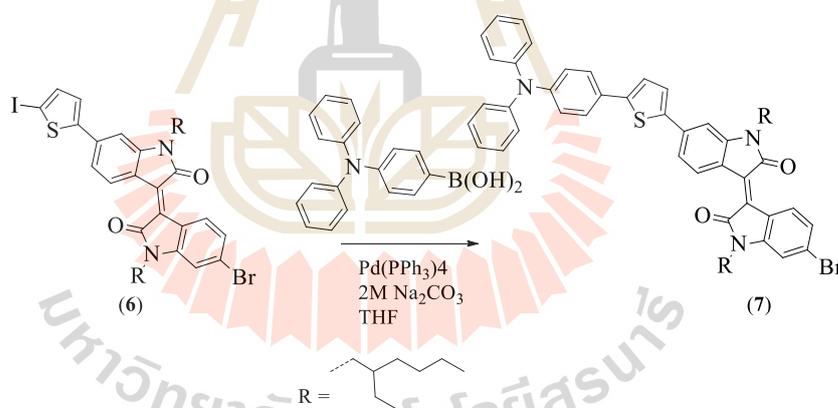


Figure 4.8 Synthesis of 5-(6'-bromo- N,N' -(2-ethylhexyl)-isoindigo)-thiophene- N,N' - bisphenylaniline.

The chemical structure of isoindigo (7) was confirmed by ^1H NMR, ^{13}C NMR and Mass spectroscopy. The ^1H NMR spectrum showed isoindigo characteristic at δ 9.18 and 9.08 ppm (integration= 2). Aromatic proton of TPA revealed around δ 7.54-7.17 ppm indicated that integration increase when compared to ^1H NMR spectrum

of starting. Alkyl proton region showed at δ 3.63 ppm (integration= 4) of CH_2 near nitrogen atom of isoindigo. ^{13}C NMR showed signal peak ketone of isoindigo at 168.6 and 168.2 ppm, carbon peak of TPA showed signal at δ around 147-120 ppm. The product was made sure by Mass spectra which showed m/z 891.05 (required 891.33). Next step, Suzuki cross coupling of isoindigotriphenylamine (7) and 5-formyl-2-thiopheneboronic acid in the present of $\text{Pd}(\text{PPh}_3)_4$ as a catalyst with same manner of isoindigo (7). This condition did not obtain the product. According to the result the changing of catalyst was concerned to $\text{Pd}(\text{dppf})\text{Cl}_2$ and 2M Na_2CO_3 as base in THF which lead to 6-(6'-(4-(Diphenylamino) phenyl) - N,N' -(2-ethylhexyl) - isoindigo-thiophene)-thiophene-5-carbaldehyde (8) as shown in **Figure 4.9**.

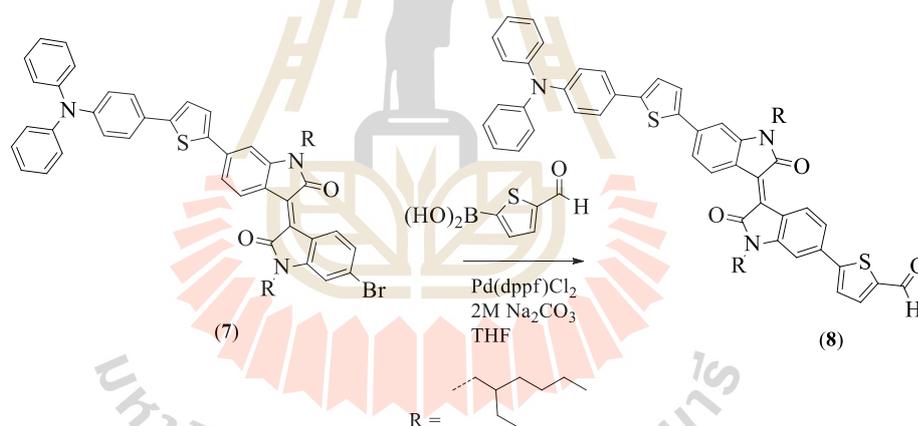


Figure 4.9 synthesis of 6-(6'-(4-(Diphenylamino) phenyl) - N,N' -(2-ethylhexyl) - isoindigo-thiophene)-thiophene-5-carbaldehyde.

To confirm the chemical structure of compound (8) ^1H NMR, ^{13}C NMR and Mass spectroscopy were employed. Peaks present in ^1H NMR spectrum contained a new signal of aldehyde proton at δ 10.01 (1H) which made sure this chemical structure is product. The identity proton of isoindigo indicated at δ 9.30 and 9.26 ppm

(integration ratio 1:1). The proton of thiophene linker unit revealed at δ 7.86 ppm (integration= 1) and 7.57 ppm (integration= 1). Alkyl proton region revealed at δ 3.84-3.81 ppm (integration= 4) which indicated that this region belong proton of CH_2 near nitrogen atom of isoindigo ring. ^{13}C NMR was then used to identify the structure. There are new strong signal of aldehyde carbon indicated at δ 182.42 ppm. Mass spectrum confirmed the product gave m/z 922.44 (required 922.40). The corresponding carbaldehydes were finally converted to **TIDT** dye via Knoevenagel condensation of isoindigothiophene carbaldehyde (**8**) with cyanoacetic acid in the present of ammonium acetate as base in CH_3COOH gave **TIDT** as shown in **Figure 4.10**.

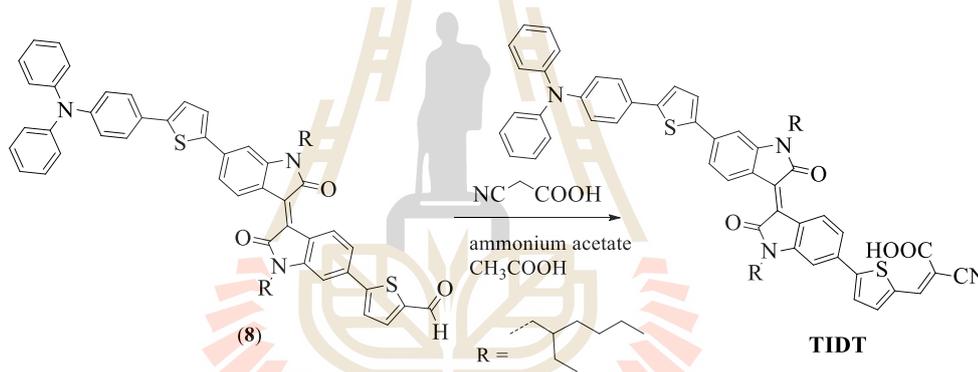


Figure 4.10 Synthesis of **TIDT**.

The chemical structure was confirmed by ^1H NMR, ^{13}C NMR and Mass spectroscopy. ^1H NMR spectrum indicated that identification vinyl proton of **TIDT** dye showed at δ 8.21 ppm as shown in **Figure 4.11**, the identity proton of isoindigo present at δ 9.15 and 9.10 ppm (integration 1:1). The pattern proton of starting illustrated aromatic region at δ 8.04-6.88 ppm. Alkyl proton region still showed at δ 3.67 (integration= 4). ^{13}C Mass spectrum showed carbon peaks of ketone at δ 186.6 and 186.4 ppm. Characteristic carbon peak of CN revealed at δ 96.4 ppm which help us

confirmed this structure is product. Mass spectrum showed m/z 988.91 (required 988.41).

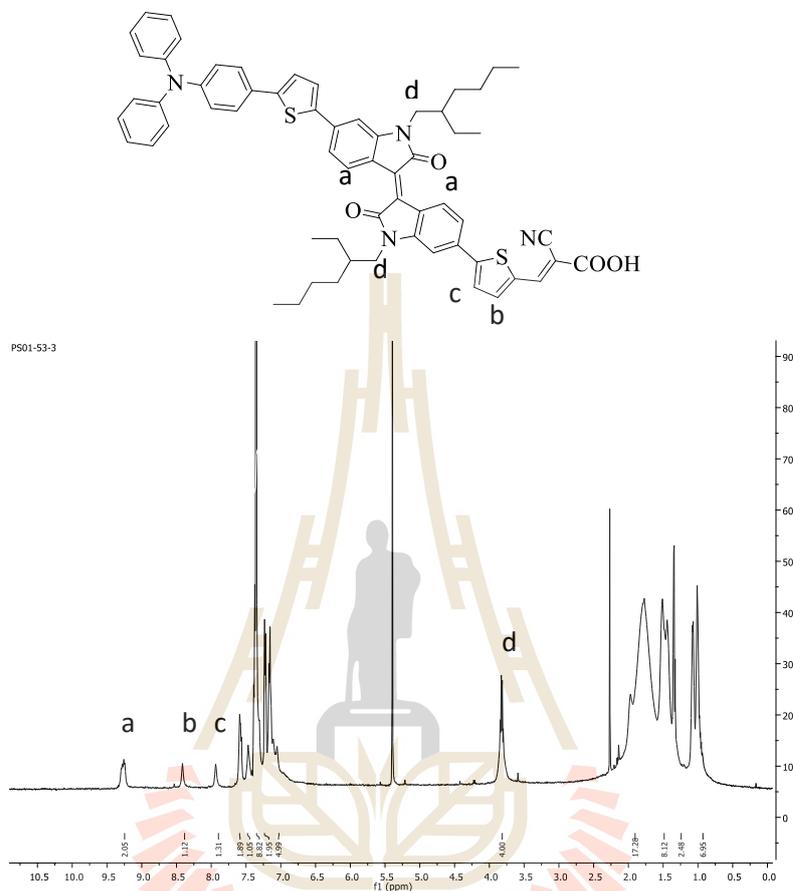


Figure 4.11 $^1\text{H-NMR}$ spectrum of TIDT.

The mechanism of Knoevenagel condensation is showed in **Figure 4.12**.

This reaction is a nucleophilic addition of an active hydrogen compound to a carbonyl group followed by aldehydration reaction in which a molecule of water is eliminated.

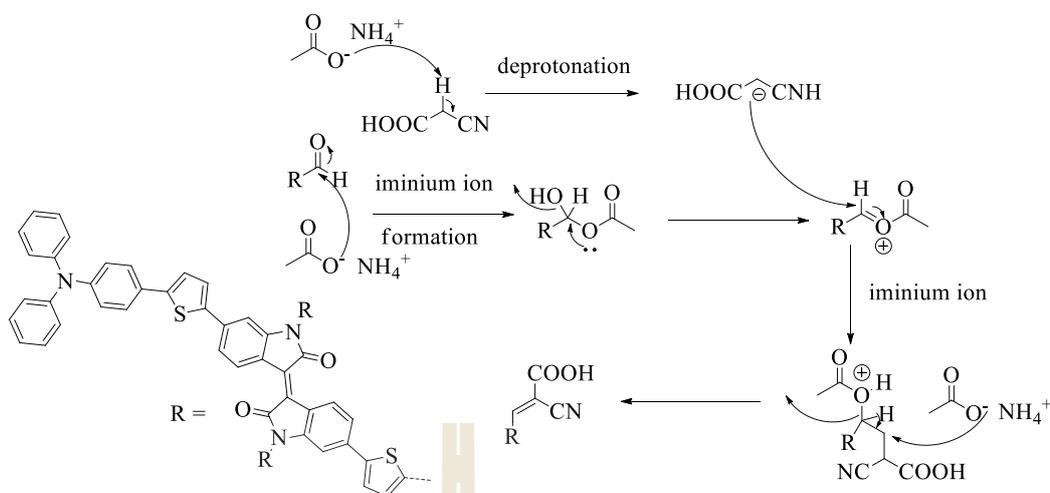


Figure 4.12 Mechanism of Knoevenagel condensation.

Synthesis of 6-(6'-(4-(Diphenylamino) phenyl)-*N,N'*-(2-ethylhexyl)-isoindigo-thiophene)-phenyl-4-carbaldehyde (**9**) from Suzuki cross coupling of isoindigotriphenylamine (**7**) and 4-formylphenylboronic acid in the present of Pd(dppf)Cl_2 as a catalyst and $2\text{M Na}_2\text{CO}_3$ in THF gave isoindigophenylaldehyde (**9**) as shown in **Figure 4.13**.

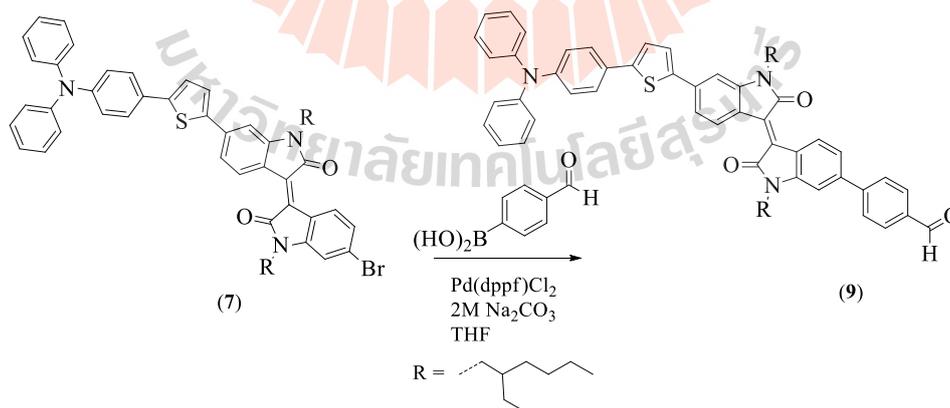


Figure 4.13 Synthesis of 6-(6'-(4-(Diphenylamino) phenyl)-*N,N'*-(2-ethylhexyl)-isoindigo-thiophene)-phenyl-4-carbaldehyde.

Isoindigophenyl benaldehyde (**9**) was synthesized in the same condition of isoindigothiophene carbaldehyde (**8**). The only difference is boronic acid used in the reaction. The structure (**8**) used 2,5-formylthiopheneboronic acid, while the structure (**9**) used 4-phenylaminophenylboronic acid. The chemical structure of isoindigophenyl benaldehyde (**9**) was confirmed by ^1H NMR, ^{13}C NMR and Mass spectroscopy. Peaks present the structure of product which showed aldehyde proton at δ 10.07 (integration=1). This data revealed that Suzuki cross coupling reaction in this condition due to the product. The identity proton of isoindigo illustrated at δ 9.25 and 9.18 ppm (integration ratio 1:1). Proton of phenyl linker unit revealed at δ 7.96 and 7.77 ppm (integration ratio 2:2). ^1H NMR spectrum still showed pattern proton of starting. ^{13}C NMR spectrum revealed signal carbon of aldehyde at δ 191.7 ppm, carbon signal of ketone at δ 186.6 and 186.5 ppm. Mass spectrum confirmed the structure that showed m/z 915.32 (required 915.44).

Finally, the target molecule **TIDP** dye was synthesized via Knoevenagel condensation reaction of isoindigophenylcabaldehyde (**9**) and cyanoacetic acid in the present of ammoniumacetate as base in CH_3COOH gave **TIDP** as in **Figure 4.14**.

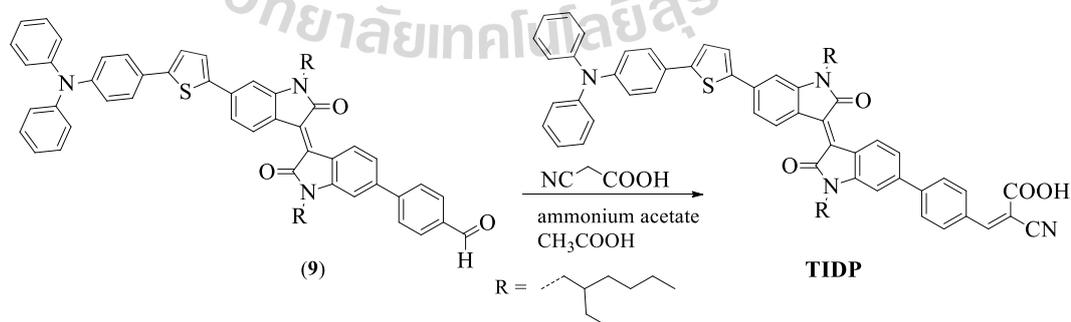


Figure 4.14 Synthesis of **TIDP**.

^1H NMR spectrum of the product is shown in **Figure 4.15**. ^1H NMR spectrum showed characteristic peak of isoindigo at δ 9.17 and 9.14 ppm (integration ratio 1:1). The identity peak of vinyl proton can help us to identify the chemical structure showed at δ 8.24 (integration= 1). Peaks present double peak of phenyl proton of linker unit at δ 8.05 and δ 7.71 ppm (integration ratio 2:2). To identify the structure ^{13}C NMR was used. There are two carbon peaks of ketone showed at δ 187.4 and 187.5 ppm. The identification of **TIDP** was confirmed at δ 84.4 ppm of CN. Mass spectrum help to confirm the structure showed m/z 982.68 (required 982.45).

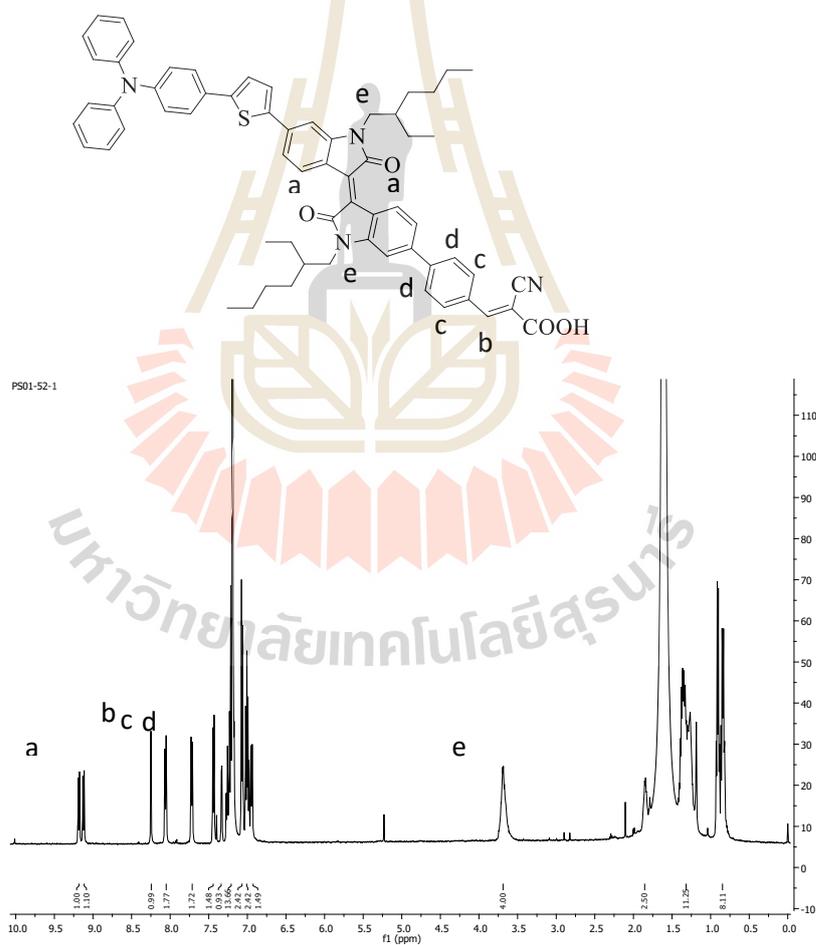


Figure 4.15 ^1H NMR spectrum of **TIDP**.

4.1.2 Optical properties

The optical properties of these dyes have been investigated by UV-Vis absorption in CH_2Cl_2 solution, the absorption spectra of **TIDT** and **TIDP** dyes are shown in **Figure 4.16**. In solution **TIDT** and **TIDP** dyes exhibited two major prominent bands. The strong absorption bands around 325-400 nm corresponds to π - π^* transition of the conjugated aromatic moieties. The absorption around 450-700 nm can be assumed to the intramolecular charge transfer (ICT) between the triphenylamine donor part and the cyanoacetic acceptor moiety. **TIDP** showed higher molar extinction coefficient compared to **TIDT**, while **TIDT** showed broad absorption spectra compared to **TIDP**. **TIDT** showed red shift (27 nm.) compared to **TIDP**. The red shift in absorption can be attributed to the extended conjugation system of the entire structure. These materials showed the wide absorption spectrum which is an advantageous property for light harvesting of the solar spectrum.

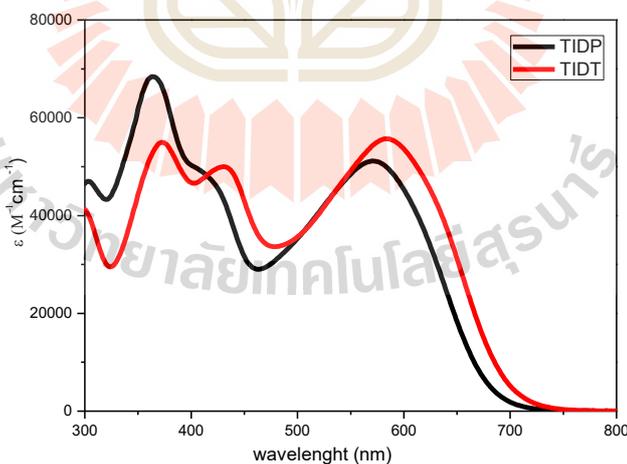


Figure 4.16 Absorption spectra of **TIDP** and **TIDT** measured in CH_2Cl_2 .

Table 1.1 Optical properties data of **TIDT** and **TIDP**.

DYES	$\lambda_{\text{max}}^{\text{abs}} / \text{nm} (\epsilon / \text{M}^{-1} \text{cm}^{-1})$	$\lambda_{\text{onset}}^{\text{abs}}$ (nm) ^a	E_{g} (eV) ^b
TIDT	373 (54,000), 586 (55,000)	700	1.77
TIDP	366 (68,000), 574 (50,000)	675	1.83

^a measured in dichloromethane at room temperature

^b estimated from the onset of absorption ($E_{\text{g}} = 1240 / \lambda_{\text{onset}}$)

4.1.3 Electrochemical properties

Cyclic voltamogram of isoindigo dyes were measured in dichloromethane solution with 0.1 M *n*-Bu₄NPF₆ as a supporting electrolyte illustrated in **Figure 4.17**. The results are shown in **Table 1.2** the CV curves of all dyes exhibited multi quasireversible oxidation. The HOMO of **TIDT** and **TIDP** were calculated to be -5.19 and -5.22 eV, respectively. All dyes were much lower than the redox potential of the I⁻ / I₃⁻ couple (-4.8 eV), therefore, dye regeneration should be thermodynamically favorable and could compete efficiently with the recapture of the injected electrons by the dye radical cation. The LUMO levels of **TIDT** and **TIDP** dyes were calculated from the HOMOs and energy gaps (E_{g}) estimated from the optical absorption edge were higher than the conduction band of the TiO₂ electrode (-4.4 eV) which **TIDT** showed -3.42, while **TIDP** gave -3.39 eV.

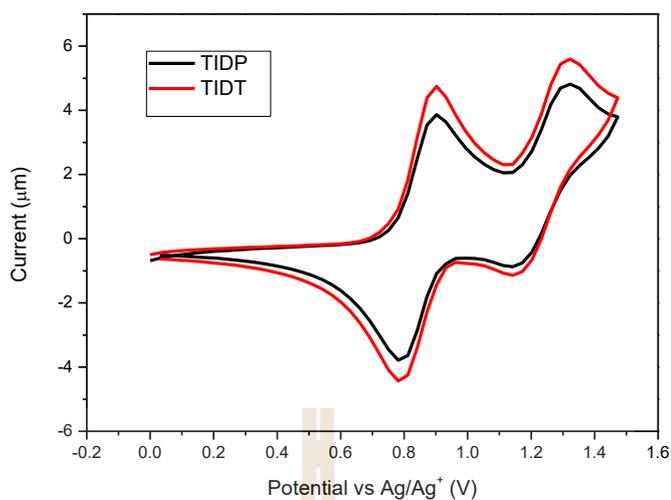


Figure 4.17 cyclic voltammogram of **TIDP** and **TIDT**.

Table 1.2 Electrochemical properties and energy level of **TIDP** and **TIDT**.

DYES	$E^{\text{ox}}_{\text{onset}}$ (V) ^a	E1/2 versus Ag/Ag ⁺ (V) ^b	HOMO (eV) ^c	LUMO (eV) ^d
TIDT	0.75	0.14, 2.18	-5.19	-3.42
TIDP	0.78	0.03, 1.97	-5.22	-3.39

^a measured using glassy carbon electrode as a working electrode, a platinum rod as a counter electrode, and Ag/Ag⁺ as a reference electrode in CH₂Cl₂ solution containing 0.1 M n-Bu₄NPF as supporting electrolyte

^b $E_{1/2} = (E_{c,p} + E_{a,p})/2$: $E_{c,p}$ -peak potential of the cathodic peak: $E_{a,p}$ -peak potential of the anodic peak

^c calculated using the empirical equation: $\text{HOMO} = -(4.44 + E^{\text{ox}}_{\text{onset}})$.

^d calculated from $\text{LUMO} = \text{HOMO} + E_g$

4.1.4 Thermal properties

The thermal stability of **TIDT** and **TIDP** were measured by TGA analysis under atmospheric condition. **Figure 4.18** shows thermogram of these dyes. Those results suggested that the dyes were thermally stable materials with T_{5d} well 100 °C.

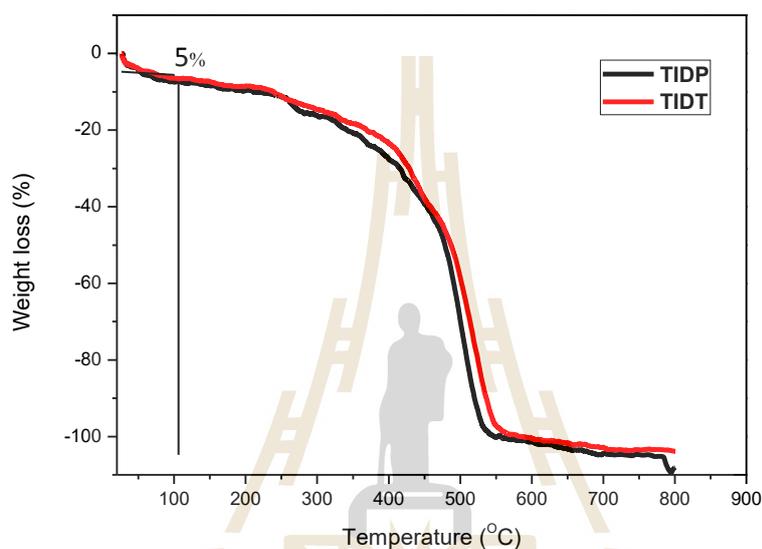


Figure 4.18 Thermogram of **TIDP** and **TIDT**.

4.2 Materials for OPVs

4.2.1 Synthesis of Isoindigo electron donors (**IDTA**, **IDTB** and **IDTF**)

Three electron donor materials for OPVs were synthesized from aldol condensation, alkylation and Suzuki cross coupling reaction. The retrosynthesis of **IDTA**, **IDTB** and **IDTF** was shown in **Figure 4.19**.

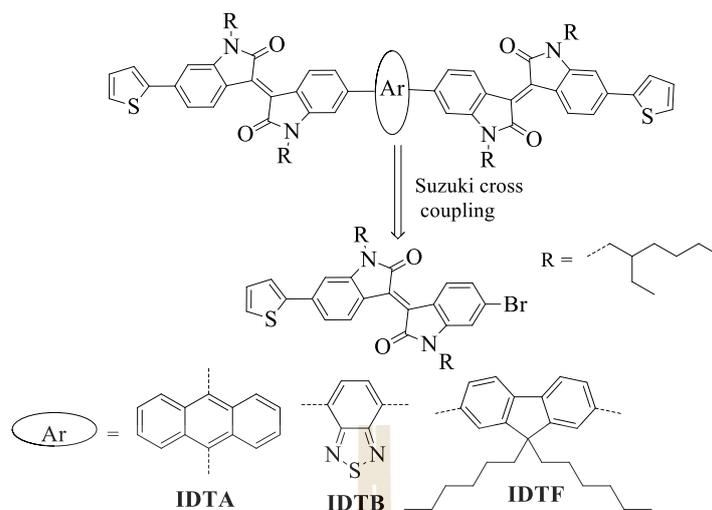


Figure 4.19 The retrosynthesis of **IDTA**, **IDTB** and **IDTF**.

Synthesis of **IDTA** from Suzuki cross coupling reaction of isoindigo (**5**) and anthracene-9,10-diboronic acid bis(pinacol) ester in the present of Cs_2CO_3 as base and $\text{Pd}(\text{PPh}_3)_4$ as a catalyst in THF gave **IDTA** as shown in **Figure 4.20**.

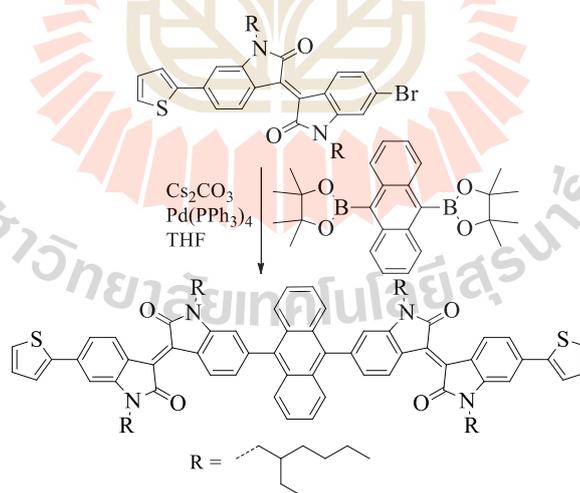


Figure 4.20 Synthesis of **IDTA**.

IDTA was synthesized by Suzuki cross coupling reaction which show in **Figure 4.20**. ^1H NMR spectrum contained identity proton of isoindigo characteristic at δ 9.19 ppm (integration= 2). Aromatic proton of anthracene present at δ 8.36 and 7.35 ppm (integration ratio 4:4). To confirm the structure ^{13}C NMR was used which ^{13}C NMR spectrum present signal peak of ketone at δ 224.9 and 223.8 ppm, carbon signal of anthracene showed δ around 128.3-121.0 ppm. Mass spectroscopy was used to approve molecular weight of the product. Mass spectrum showed m/z 1310.68 (required 1310.67).

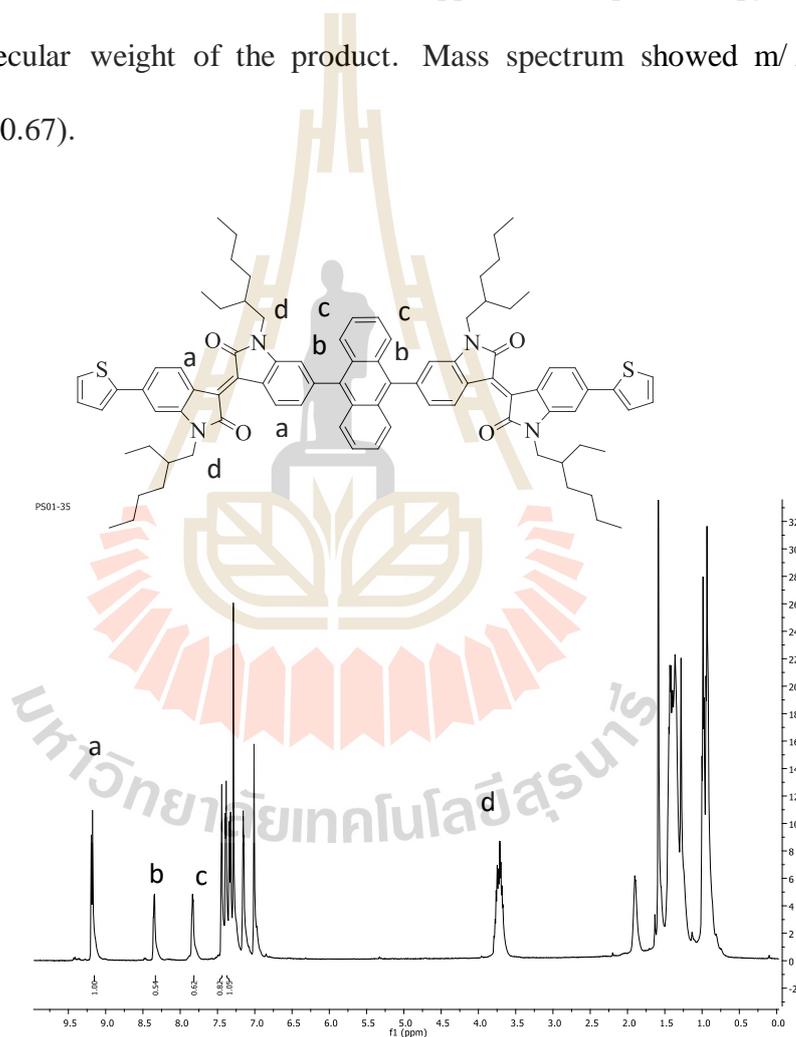


Figure 4.21 ^1H NMR spectrum of **IDTA**.

To synthesize **IDTB** the mixer of isoindigo (**5**) and 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) in the present of Cs_2CO_3 as base and $\text{Pd}(\text{PPh}_3)_4$ as a catalyst in THF were used as shown in **Figure 4.22**.

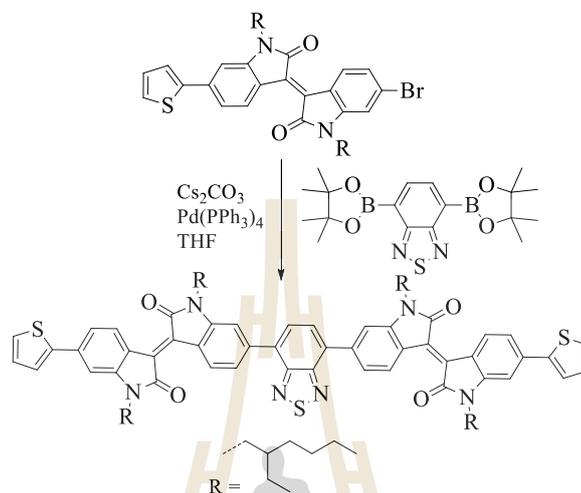


Figure 4.22 Synthesis of **IDTB**.

IDTB was synthesized in the same condition of **IDTA**. The only difference is boronic acid used in the reaction. **IDTB** used 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester). ^1H NMR spectrum represent identification proton of isoindigo at δ 9.27 (2H). The identity proton of benzothiadiazole present at δ 7.41 ppm (integration=2). Aromatic proton pattern of starting showed at δ 7 ppm. Alkyl proton revealed at δ 3.82 ppm (integration+8) which belong proton of CH_2 near nitrogen atom of isoindigoring. ^{13}C NMR was used to assist identify the chemical structure which showed signal peak of ketone at δ 168.6 ppm. Aromatic region of carbon showed at δ 145.7-105.1 ppm and alkyl carbon showed at δ 44.1-10.8 ppm. Mass spectrum showed m/z 1268.11 (required 1268.60).

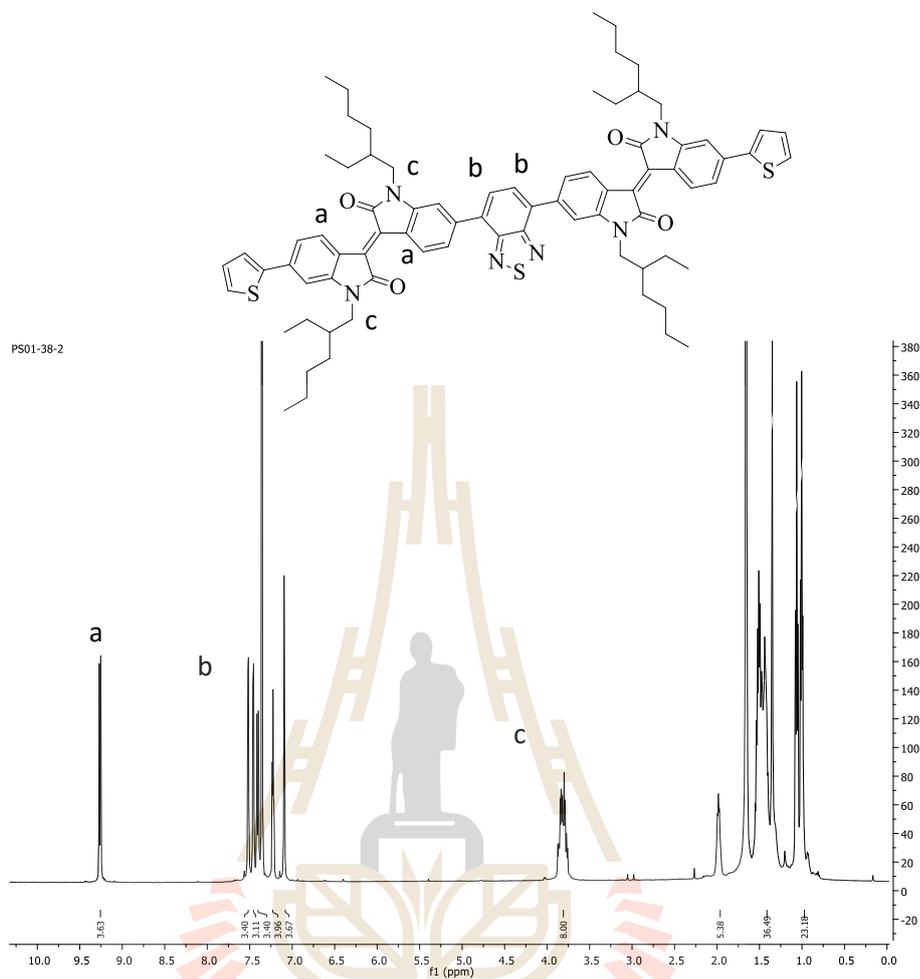


Figure 4.23 ¹H NMR spectrum of IDTB.

Synthesis of **IDTF** using isoindigo (**5**) and 9,9-Dihexylfluorene-2,7-diboronic acid in the presence of Cs₂CO₃ as base and Pd(PPh₃)₄ as a catalyst in THF gave **IDTF** as shown in **Figure 4.24**.

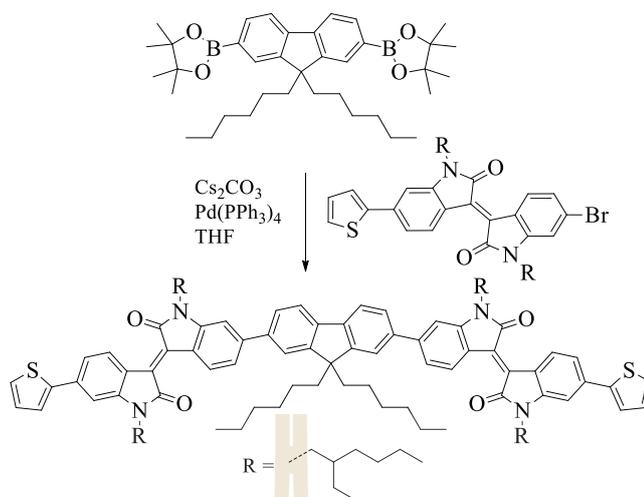
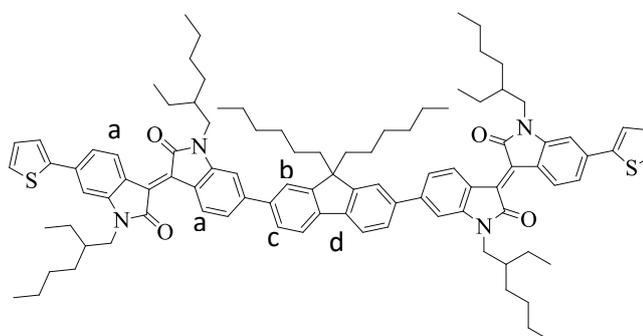


Figure 4.24 Synthesis of **IDTF**.

IDTF was synthesized in the same condition with **IDTA** and **IDTB** which was changed boronic acid as 9,9-Dihexylfluorene-2,7-diboronic acid. **IDTF** was characterized by ^1H NMR, ^{13}C NMR and Mass spectroscopy. The ^1H NMR spectrum showed isoindigo characteristic at δ 9.24 ppm (integration= 4). Aromatic proton of product represents at δ 7.51-7.09 ppm. ^{13}C NMR spectrum showed signal peak of ketone at δ 168.6 ppm, aromatic carbon showed δ at 145.7-105.1 ppm and alkyl carbon at δ 44.1-10.7 ppm. Mass spectroscopy was used to confirm the structure which Mass spectrum showed m/z 1467.68 (required 1467.86).



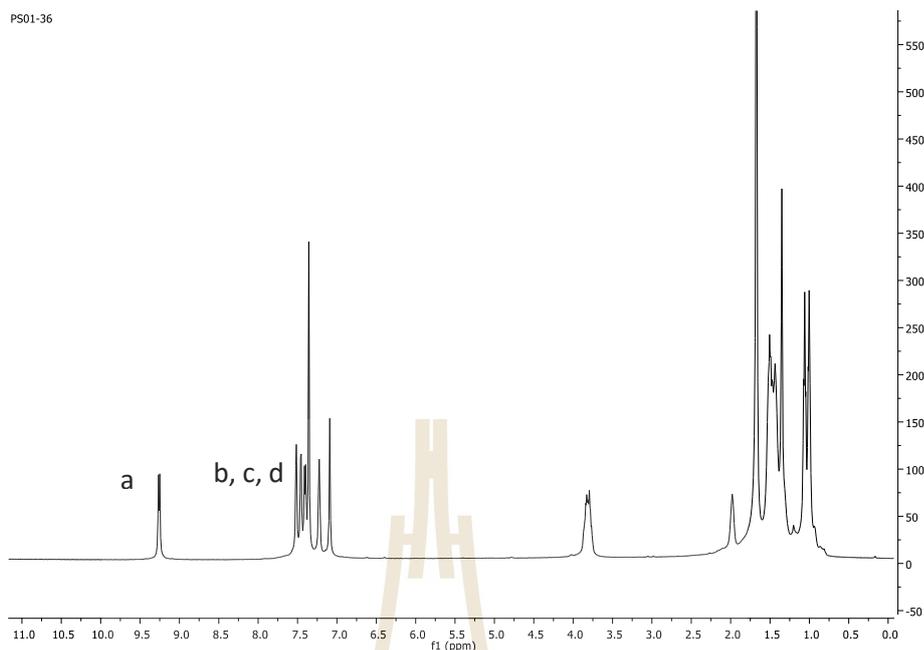


Figure 4.25 ^1H NMR spectrum of **IDTF**.

4.2.2 Optical properties

The UV-Vis absorption spectra of organic photovoltaic materials in dilute CH_2Cl_2 solution are shown in **Figure 4.26**. The absorption spectra of all organic photovoltaic materials showed relative large molar extinction coefficient in visible region (250-650 nm). The strong absorption bands around 250-400 nm corresponds to $\pi\text{-}\pi^*$ transition of transition of the conjugated aromatic moieties. **IDTF** showed highest molar absorptivity relative to **IDTB** and **IDTA**. These materials gave the broad absorption spectra which is suitable to use as light-harvesting in solar cells.

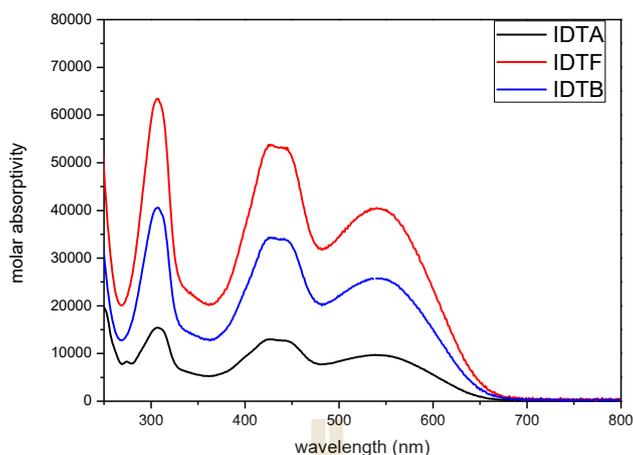


Figure 4.26 absorption spectra of **IDTA** and **IDTF** measured in CH_2Cl_2 .

Table 1.3 optical properties data of **IDTA**, **IDTB** and **IDTF**.

DYES	λ max ^{abs} / nm ($\epsilon/M^{-1} \text{ cm}^{-1}$)	λ onset ^{abs} (nm) ^a	E_g (eV) ^b
IDTA	312 (14,000), 427 (11,000), 548 (42,000)	650	1.91
IDTB	314 (40,000), 412 (34,000), 547 (25,000)	651	1.90
IDTF	318 (64,000), 424 (54,000), 548 (41,000)	652	1.90

^a measured in dichloromethane at room temperature

^b estimated from the onset of absorption ($E_g = 1240/\lambda_{\text{onset}}$).

4.2.3 Electrochemical properties

Cyclic voltamogram of isoindigo dyes were measured in dichloromethane solution with 0.1 M *n*-Bu₄NPF₆ as a supporting electrolyte are illustrated in **Figure 4.27** and all data are listed in **Table 1.4**. The CV curves of all dyes exhibited multi quasireversible oxidation. The HOMO and LUMO levels of **IDTA**, **IDTB** and **IDTF** were calculated to be -5.14 and -3.24, -5.12 and -3.22, -5.11 and -3.21 eV, respectively.

The HOMO and LUMO of these materials revealed suitable HOMO and LUMO levels of an electron acceptor which C₆₀ and their derivatives gave HOMO and LUMO \approx -6.3 and -4.1 eV.

Table 1.4 Electrochemical properties and energy level of **IDTA**, **IDTB** and **IDTF**.

DYES	E ^{ox} _{onset} (V) ^a	HOMO (eV) ^b	LUMO (eV) ^c
IDTA	0.70	-5.14	-3.23
IDTB	0.68	-5.12	-3.22
IDTF	0.67	-5.11	-3.21

^a measured using glassy carbon electrode as a working electrode, a platinum rod as a counter electrode, and Ag/Ag⁺ as a reference electrode in CH₂Cl₂ solution containing 0.1 M n-Bu₄NPF₆ as supporting electrolyte

^b calculated using the empirical equation: HOMO = -(4.44 + E^{ox}_{onset}).

^c calculated from LUMO = HOMO + E_g

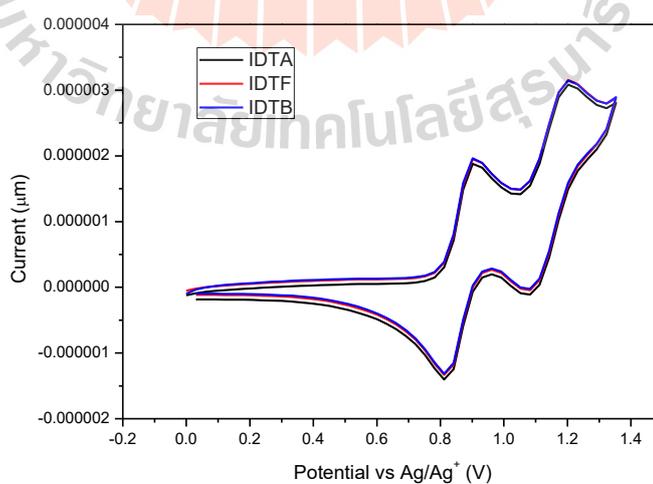


Figure 4.27 cyclicvoltamogram of **IDTA**, **IDTB** and **IDTF**.

4.2.4 Thermal properties

The thermal stability of **IDTA**, **IDTB** and **IDTF** were measured by TGA analysis under nitrogen atmospheric condition. Those results suggested that the dyes were thermally stable materials with T_{5d} well 110 °C which thermogram was showed in **Figure 4.28**. The better thermal stability of the dye is important for the lifetime of the solar cells.

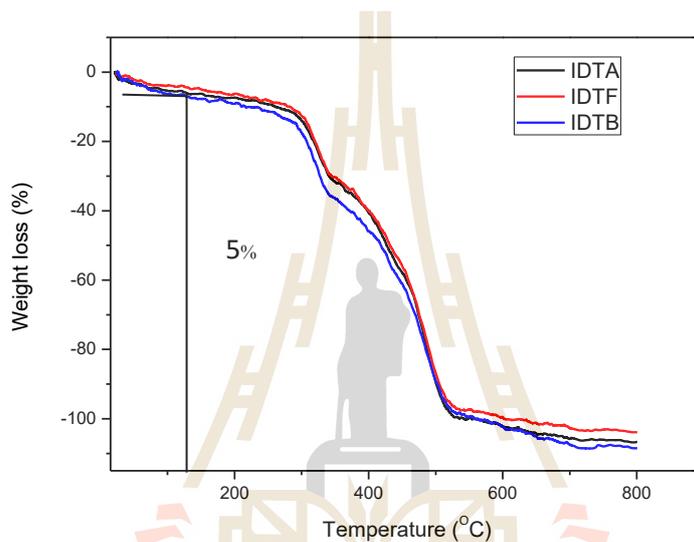


Figure 4.28 Thermogram of **IDTA**, **IDTB** and **IDTF**.

CHAPTER V

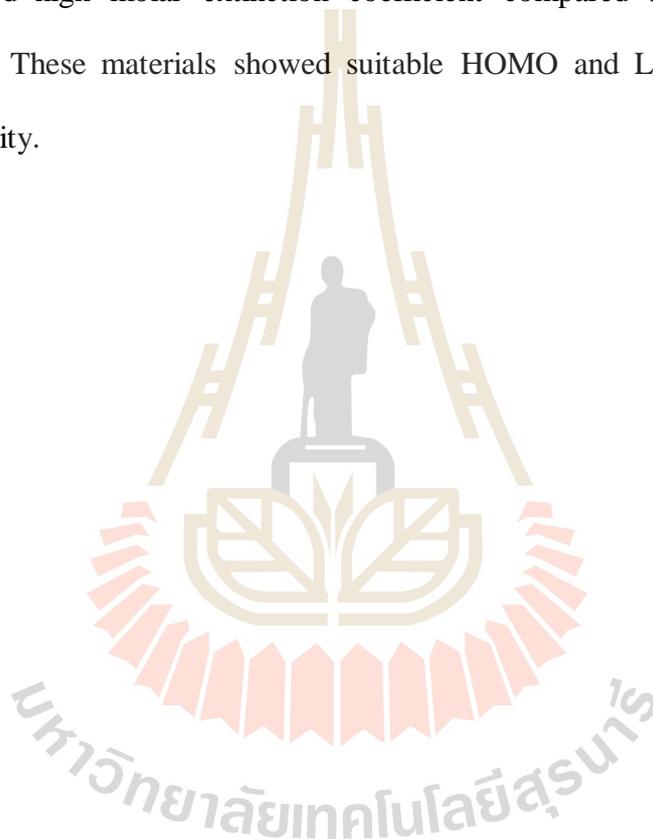
CONCLUSION

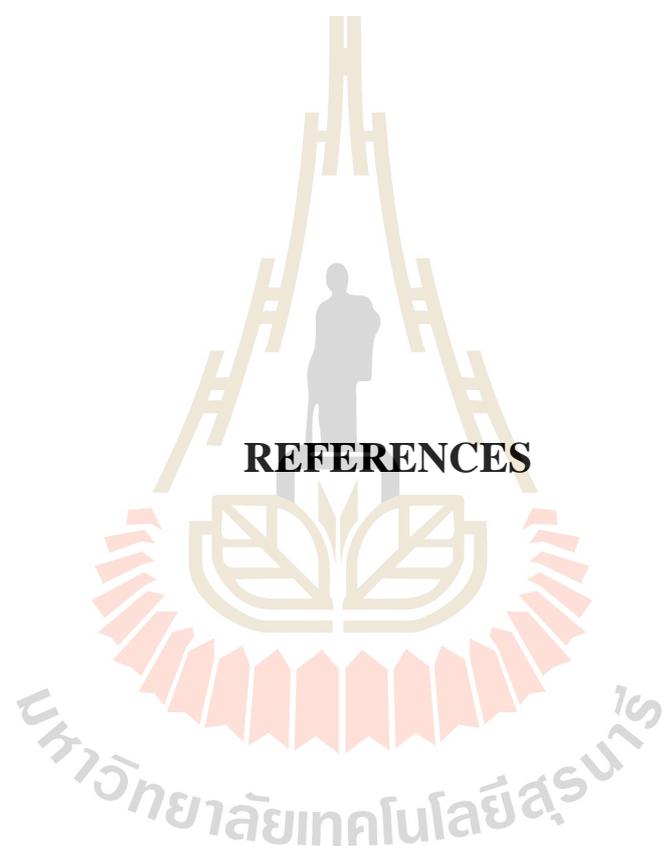
5.1 Dye sensitized solar cells

We have reported synthesis and characterization novel D-A- π -A metal free organic sensitizer **TIDT** and **TIDP** based on isoindigo as sensitizer in dye- sensitized nanocrystalline TiO₂ solar cells (DSSCs). For the two designed dyes, the triphenylamine as electron donor, isoindigo as a auxiliary electron withdrawing unit, various π -spacer (thiophene and phenyl), cyanoacetic acid as an electron acceptor and anchoring group. We found that the introduction of isoindigo based dyes showed wide absorption rang 300-700 nm. **TIDP** showed high molar extinction coefficient compared to **TIDT**. These dyes showed suitable HOMO and LUMO levels and high thermal property.

5.2 Organic photovoltaics

We have successful to synthesize and characterize electron donor materials for organic photovoltaics based on isoindigo. Electron donor materials for OPVs contained isoindigo which various core moieties (anthracene, benzothiadiazole and fluorene). These materials showed wide absorption rang and high molar extinction coefficient. **IDTF** showed high molar extinction coefficient compared to **IDTA** and **IDTB**, respectively. These materials showed suitable HOMO and LUMO level and high thermal stability.





REFERENCES

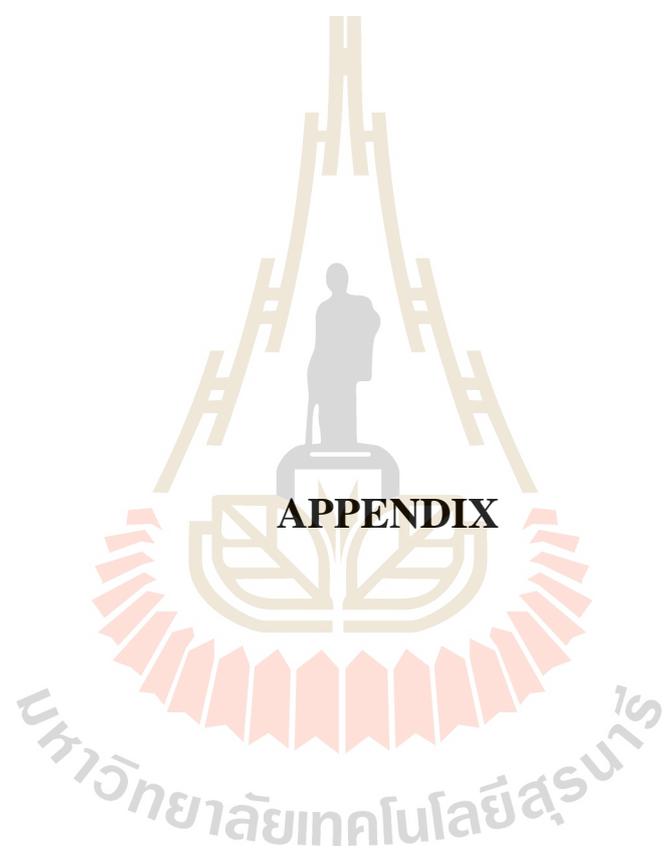
REFERENCE

- Bolton, J. R. and Hall, D. O. (1979). Photochemical conversion and storage of solar energy. **Annual Reviews Energy**. 4: 353–401.
- Chang, Y. J. and Chow, T. J. (2009). Dye-Sensitized solar cell utilizing organic dyes containing triarylene conjugates. **Tetrahedron**. 65: 4726–4734.
- Christos, P. and Xaver, B. (1988). **Helvetica Chimica Acta**. 71: 1079–1083.
- Gratzel, M. (2003). Dye-sensitized solar cells. **Journal of Photochemistry and Photobiology C: Photochemistry Reviews**. 4: 145–153.
- Hagberg, D. P., Jiang, X., Gabrielsson, E., Linder, M., Marinado, T., Brinck, T., Hagfeld, A. and Sun, L. C. (2009). Symmetric and unsymmetric donor functionalization comparing structural and spectral benefits of chromophores for dye sensitized solar cells. **Journal Materials Chemistry**. 19: 7232–7238.
- Josse, P., Dalinot, C., Jaing, Y., Dabos, S., Roncali, J., Blanchard, P. and Cabanetos, C. (2015). Phthalimide end-capped thienoisindigo and diketopyrrolopyrrole as non-fullerene molecular acceptors for organic solar cells. **Journal of Materials Chemistry A**. 4: 250–256.
- Kaur, N., Singh, M., Pathak, D., Wagner, T. and Nunzi, J. M. (2014). Organic materials for photovoltaic applications: review and mechanism. **Synthetic Metals**. 190: 20–26.

- Kitamura, T., Ikeda, M., Shigaki, K., Inoue, T., Anderson, A. N., Ai, X., Lian, Q. T. and Yanagida, S. (2004). Phenyl-conjugated oligoene sensitizers for TiO₂ solar cells. *Chemistry of Materials*. 16: 1806–1812.
- Li, S., Yuan, J., Deng, P., Ma, W. and Zhang, Q. (2014). A comparative study of diketopyrrolopyrrole and isoindigo based polymers for organic photovoltaic applications. *Dyes and Pigments*. 106: 121–127.
- Liang, M. and Chen, J. (2013). Arylamine organic dyes for dye-sensitized solar cells. *Chemical Society Reviews*. 42: 3453–3488.
- Liu, B., Zou, Y., Peng, B., Zhao, B., Huang, K., He, Y. and Pan, C. (2011). Low band gap isoindigo based copolymers: design, synthesis and photovoltaic applications. *Polymer Chemistry*. 2: 1156–1162.
- Liu, W. H., Wu, I. C., Lai, C. H., Lai, C. H., Chou, P. T., Li, Y. T., Chen, C. L., Hsu, Y. Y. and Chi, Y. (2008). Simple organic molecules bearing a 3,4-ethylenedioxythiophene linker for efficient dye-sensitized solar cells. *Chemical Communications*. 41: 5152–5154.
- Mathew, S., Yella, A., Gao, P., Humphry-Baker, R., Curchod, B. F., E., Ashari-Astani, N., Tavernelli, I., Rothlisberger, U., Nazeeruddin, M. K., and Grätzel, M. (2014). **Dye-sensitized solar cells with 13% efficiency achieved through the molecular engineering of porphyrin sensitizers.** *Nature Chemistry*. 6: 242–247.
- Mei, J., Graham, R. K., Stalder, R. and Reynolds, R. J. (2010). Synthesis of isoindigo-based oligothiophenes for molecular bulk heterojunction solar cells. *Organic Letters*. 12: 660–663.

- Qu, S., Qin, C., Islam, A., Wu, Y., Zhu, W., Hua, J., Tian, H., and Han, L. (2012). A novel D-A- π -A organic sensitizer containing a diketopyrrolopyrrole unit with a branched alkyl chain for highly efficient and stable dye-sensitized solar cells. **Chemical Communications**. 55: 6972–6974.
- Wang, D., Ying, W., Zhang, X., Hu, Y., Wu, W. and Hua, J. (2015). Near-infrared absorbing isoindigo sensitizers: Synthesis and performance for dye-sensitized solar cells. **Dyes and Pigments**. 112: 327–334.
- Wang, E., Ma, Z., Zhang, Z., Henriksson, P., Inganäs, O., Zhang, F. and Andersson, M. (2011). An isoindigo-based low band gap polymer for efficient polymer solar cells with high photo-voltage. **Chemical Communications**. 47: 4908–4910.
- Wang, E., Ma, Z., Zhang, Z., Vandewal, K., Henriksson, P., Inganäs, O., Zhang, F. and Andersson, M. (2011). An easily accessible isoindigo-based polymer for high-performance polymer solar cells. **Journal of the American Chemical Society**. 133: 14244–14247.
- Wang, G., Tan, H., Zhang, Y., Wu, Y., Hu, Z., Yu, G. and Pan, C. (2014). Series of D-A system based on isoindigo dyes for DSSC: Synthesis, electrochemical and photovoltaic properties. **Synthetic Metals**. 187: 17–23.
- Wang, T., Chen, Y., Bao, X., Du, Z., Guo, J., Wang, N., Sun, W. and Yang, R. (2013). A new isoindigo-based molecule with ideal energy levels for solution-processable organic solar cells. **Dyes and Pigments**. 98: 11–16.
- Yassin, A. and Roncali, J. (2013). Donor-acceptor-donor (D-A-D) molecules based on isoindigo as active materials for organic solar cells. **New Journal of Chemistry**. 37: 502–507.

- Yeh, N. and Yeh, P. (2013). Renewable and Sustainable energy reviews. **Renewable and Sustainable Energy Reviews**. 21: 421–431.
- Yella, A., Lee, H.-W., Tsao, H. N., Yi, C., Chandiran, A. K., Nazeeruddin, M. K., Diau, E. W.-G., Yeh, C. Y., Zakeeruddin, S. M. And Grätzel, M. (2011). Porphyrin-sensitized solar cells with cobalt (II/III)-based redox electrolyte exceed 12 percent efficiency. **Science**. 334: 629–634.
- Vybornyi, O., Jiang, Y., Baert, F., Demeter, D., Roncali, J., Blanchard., P. and Cabanetos, C. (2015). Solution-processable thienoisindigo-based molecular donors for organic solar cells with high open-circuit voltage. **Dyes and Pigments**. 115: 17–22.
- Zeng, W., Cao, Y., Bai, Y., Wang, Y., Shi, Y., Zhang, M., Wang, F., Pan, Y. and Wang, P. (2010). Efficient dye-sensitized solar cells with an organic photosensitizer featuring orderly conjugated ethylenedioxythiophene and dithienosilole blocks. **Chemistry of Materials**. 22: 1915–1925.



APPENDIX

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SYNTHESIS AND CHARACTERIZATION OF ISOINDIGO DERIVATIVES AS MOLECULAR DONORS FOR ORGANIC PHOTOVOLTAICS

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Abstract: Isoindigo was directly used as the building block for oligomers or polymers, and less attention was paid on the manipulation on its core structure. Still, modification on isoindigo core may have influence on its electric properties. In this work, we design new high performance isoindigo-containing donor molecules employing a novel molecular architecture with two isoindigo chromophores in the conjugated backbone. Three isoindigo derivatives containing aromatic cores were synthesized using a combination of aldol condensation, alkylation and Suzuki cross coupling reactions. The different core moieties, anthracene, benzothiadiazole and fluorene, were used in order to increase molar absorptivity of desired molecules. They were characterized by ¹H NMR, ¹³C NMR, FT-IR and mass spectrometry. The optical properties were studied in dichloromethane solution. The desired compounds exhibited wide absorption spectra in UV-visible region (300-600 nm) with high molar extinction coefficient. The results suggest that the synthesized compounds can be used as donor molecules in organic photovoltaic devices.

1. Introduction

Organic photovoltaics (OPVs) have achieved remarkable progress due to unique advantages such as low cost, light weight and applications in flexible large-area devices. Nitrogen-containing electron-deficient dyes, isoindigo, have attracted an increasing attention as building blocks for organic photovoltaic materials. High charge carrier mobility was obtained for conjugated polymers based on isoindigo derivatives. In this work, we synthesized and characterized the novel isoindigo derivatives as electron donor for organic photovoltaics. The different core moieties, anthracene, benzothiadiazole and fluorene, were used in order to increase molar absorptivity of desired molecules.

2. Materials and Methods

2.1 Materials and instruments

Tetrahydrofuran (THF) was refluxed with benzophenone and Na. Reagent and chemical were purchased from chemical industry. ¹H NMR and ¹³C NMR were record by a Bruker Advance 500 MHz. UV-Vis spectra were measured by Perkin-Elmer UV lambda 25 spectrometer.

2.2 Experimental section

2.2.1 (E)-6,6'-dibromoisindigo (**3**)¹¹

A solution of 6-bromoindole (0.5332 g, 2.21 mmol), 6-bromooxindole (0.5031g, 2.36 mmol) and HCl 0.1 ml

as catalyst were added in 15 ml of acetic acid. The reaction was refluxed for 15 h. The solution was cooled and poured into water to give brown solid as 96% yield.

2.2.2 Isoindigo derivatives (**4**)

(E)-6,6'-dibromoisindigo (**3**) (0.8377g, 5.95mmol) and K₂CO₃ (0.8223 g 5.95 mmol) were dissolved in DMF 40 ml then 1-bromo-2-ethyl hexane 0.5 ml was added. The solution was heated at 100 °C for 15 h. The organic solvent was collected and dried over Na₂SO₄. The crude product was purified by column chromatography with hexane and dichloromethane as eluent (2:1) to give red solid as 84% yield. ¹H NMR (500 MHz, CDCl₃) δ = 9.03 (2H, d, J=10.0 Hz), 7.15 (2H, d, J=10.0 Hz), 6.89 (2H, s), 3.62 (4H, m), 1.82 (2H, s), 1.29 (16H, m) and 0.89 (12H, m) ppm.

2.2.3 (E)-6,6'-dibromoisindigo thiophene (**5**)

A solution of compound (**4**) (0.5 g, 0.75 mmol) and 2-thiopheneboronic acid (0.048 g, 0.38 mmol) were dissolved in THF 20 ml. Catalyzed Pd₂(PPh₃)₄ (0.021 g, 0.02 mmol), 2M Na₂CO₃ 2.58 ml as base were added into solution. The reaction was refluxed for 24 h under N₂ atmosphere. The solution was cooled and poured into water. The organic layer was collected and dried over Na₂SO₄. The crude product was purified by chromatography with hexane and dichloromethane (2:1) as eluent to give red-deep solid as 51% yield. ¹H NMR (500 MHz, CDCl₃) δ = 9.13 (1H, d, J=5 Hz), 9.02 (1H, d J=10.0 Hz), 7.41 (1H, d, J=5.0 Hz), 7.36 (1H, d, J=5.0 Hz) 7.28 (1H, d, J=5.0), 7.16 (2H, d, J=0 Hz), 7.11 (2H, m), 6.95 (1H, s), 6.87 (1H, s), 3.63 (4H, m), 1.83 (2H, t), 1.13 (16H, m) and 0.92 (12H, m) ppm.

2.2.4 IDTA

A solution of compound (**5**) (0.17 g, 2.64 mmol), anthracene-9,10-diboronic acid bis(pinacol) ester (0.05 g, 2.12 mmol) was dissolved in THF 20 ml. Cs₂CO₃ (0.39 g, 1.2 mmol) and Pd₂(PPh₃)₄ (0.014 g, 0.012 mmol) were added. The reaction was refluxed for 24 h under N₂ atmosphere. The solution was cooled and poured into water. The organic layer was collected and dried over Na₂SO₄. The crude product was purified by column chromatography with hexane and dichloromethane (2:1) as eluent to give black solid as 36% yield. ¹H NMR (500 MHz, CDCl₃) δ = 9.17 (4H, d, J=10.0 Hz), 8.34 (2H, d, J=5.0 Hz), 7.82 (2H, d, J=5.0 Hz), 7.44 (3H, s), 7.38 (4H, d), 7.32 (3H, d,

J=5.0 Hz), 7.14 (4H, d, J=5.0 Hz), 7.01 (4H, s), 3.72 (8H, m), 1.90 (4H, s), 1.28 (32H, m) and 0.92 (24H, m) ppm ^{13}C NMR (500 MHz, CDCl_3) δ = 168.6 (4x C=O), 145.7 and 144.1 (Cq), 137.8 (Cq), 134.1 (Cq), 132.0 (Cq), 130.2 (CH), 128.3 (CH), 127.2 (CH), 126.1 (CH), 124.2 (CH), 121.0 (Cq), 119.3 (CH), 44.1 (CH₂), 37.7 (CH), 30.8 (CH₂), 29.7 (CH₂) and 28.88 (CH₂), m/z MALDI-TOF 1310.67

2.2.5 IDTB

A mixture of compound (5) (0.14 g, 0.22 mmol) and 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) (0.04 g, 0.1 mmol) were dissolved in 20 mL of THF. $\text{Pd}(\text{PPh}_3)_4$ (0.012 g, 0.01 mmol) and Cs_2CO_3 (0.33 g, 1.0 mmol) were added into reaction and refluxed for 24 h under N_2 atmosphere. The solution was cooled and poured into water. The solution was extracted with CH_2Cl_2 . The combined organic layers were washed with water, dried over anhydrous Na_2SO_4 . Crude product was purified using column chromatography with hexane and dichloromethane (2:1) as eluent gave black solid as 32% yield. ^1H NMR (500 MHz, CDCl_3) δ = 9.25 (4H, d, J=10.0 Hz), 7.51 (4H, d, J=5.0 Hz), 7.45 (4H, d, J=5.0 Hz), 7.39 (4H, d, J=10.0 Hz), 7.22 (4H, t), 7.09 (4H, s), 3.82 (8H, m), 1.98 (4H, s), 1.50 (32H, m) and 0.99 (24H, tt) ppm. ^{13}C NMR (500 MHz, CDCl_3) δ = 168.6 (C=O), 145.7 (Cq), 144.1 (Cq), 137.7 (Cq), 132.0 (Cq), 130.2 (CH), 128.3 (Cq), 126.1 (CH), 124.2 (CH), 123.9 (CH),

119.4 (CH), 44.1 (CH₂), 37.1 (CH), 31.9 (CH₂), 29.7 (CH₂), 23.8 (CH₂), 14.1 (CH₃), 11.1 (CH₃), m/z MALDI-TOF 1268.60

2.2.2.6 IDTF

In 50 mL two-necked flask, (5) (0.12g, 0.2 mmol) and 9,9-dihexylfluorene-2,7-diboronic acid (0.05 g, 0.09 mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.01 g, 0.009 mmol) as catalyst Cs_2CO_3 (0.29 g, 0.9 mmol) as base were dissolved in THF 20 ml. The mixture was refluxed for 24 h under nitrogen atmosphere. The reaction mixture was cooled and added 20 ml of water. The reaction was extracted with CH_2Cl_2 and washed with water, dried over anhydrous Na_2SO_4 . Crude product was purified by column chromatography with hexane and dichloromethane (2:1) as eluent to give black solid as 54% yield. ^1H NMR (500 MHz, CDCl_3) δ = 9.24 (4H, d, J=10.0 Hz), 7.51 (4H, s), 7.45 (4H, d, J=5.0 Hz), 7.41 (4H, d), 7.22 (4H, s), 7.09 (4H, s), 1.98 (4H, s), 1.49 (40H, m) and 1.04 (30H, m) ppm. ^{13}C NMR (500 MHz, CDCl_3) δ = 168.6 (4x C=O), 145.7 (Cq), 144.1 (Cq), 137.8 (Cq), 132.0 (Cq), 130.2 (Cq), 128.2 (CH), 126.1 (CH), 124.2 (CH), 121.0 (Cq), 44.1 (CH₂), 37.8 (CH), 30.8 (CH₂), 29.7 (CH₂), 28.8 (CH₂), 24.2 (CH₂), 23.0 (CH₂), 14.1 (CH₃), 10.8 (CH₃), m/z MALDI-TOF 1466.86

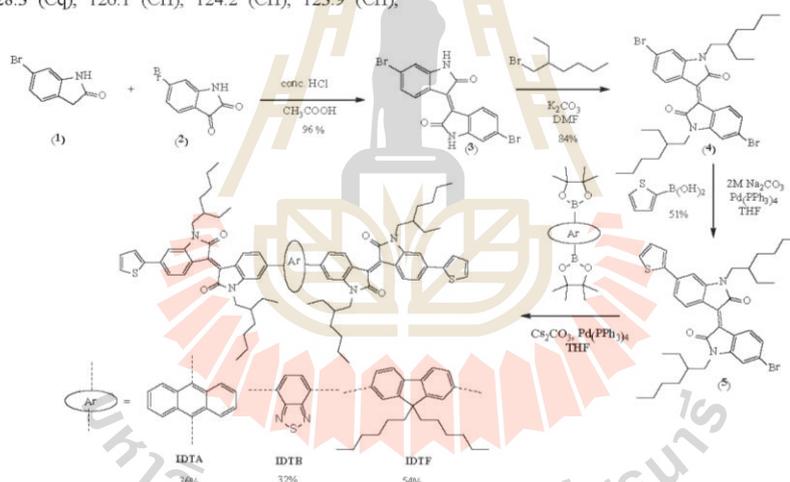


Figure 1. Synthesis pathway of IDTA, IDTB and IDTF

3. Results and Discussion

3.1 Synthesis and Characterization

The synthesis of three organic photovoltaic materials is shown in **Figure 1**. The (E)-6,6'-dibromoisindigo (3) was synthesized by the presence of acid-catalyzed aldol condensation of 6-bromoisindigo and 6-

bromoisatin in acetic acid^[1]. The crude product was purified by column chromatography to give brown solid. Then alkylation reaction of 6,6'-dibromoisindigo using 1-bromo-2-ethylhexane in DMF give isindigo derivatives (4)^[1]. ^1H NMR showed H of alkyl group near nitrogen atom at chemical shift 3.62 ppm (4H) and 1.82-0.89 ppm. Isindigo derivatives were attached by Suzuki cross

coupling reaction of (4) and 2-thiopheneboronic acid in the presence of Pd(PPh₃)₄ as catalyst in THF to give (5). The target molecules were obtained by Suzuki cross coupling reaction of (5) and aryl diboronic ester in THF the presence of Pd(PPh₃)₄ as catalyst and Cs₂CO₃ as base. The ¹H NMR spectra of IDTA, IDTB and IDTF showed in Figure 2. ¹H-NMR spectrum of IDTA showed doublet signal at chemical shift 9.17 ppm (2H) assigning of H atom which carbonyl group. 8.35-1.01 ppm showed the aromatic proton. Multiplet peak at 3.72 ppm (8H) showed protons of alkyl. ¹H NMR spectrum of IDTB showed doublet at 9.25 ppm (2H) which indicated the signal aromatic protons of H-bond and carbonyl group. Chemical shift 7.09-7.52 ppm showed aromatic protons. Chemical shift 3.82 ppm (8H) protons of alkyl groups near nitrogen atom. ¹H NMR spectrum of IDTF showed doublet signal at chemical shift 9.24 ppm (2H) proton assigning as aromatic which is bonding with carbonyl groups. Chemical shift 7.09-7.51 ppm was aromatic proton. Chemical shift 3.81 ppm (8H) showed multiplet which protons of alkyl near nitrogen atom and chemical shift 1-1.98 ppm as proton of alkyl chains.

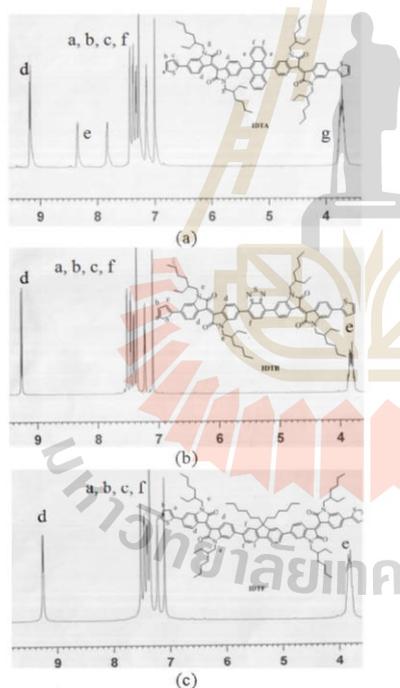


Figure 2. ¹H NMR spectra of (a) IDTA, (b) IDTB and (c) IDTF

The ¹³C NMR of IDTA, IDTB and IDTF showed chemical shift at 168.66 ppm assigning of carbonyl groups. The FT-IR spectra of IDTA, IDTB and IDTF

in Figure 3 showed 3° amine stretching vibration was observed in the region 3500 cm⁻¹ which was the characteristic of lactam. C=O stretching vibration is improved at 1500 cm⁻¹.

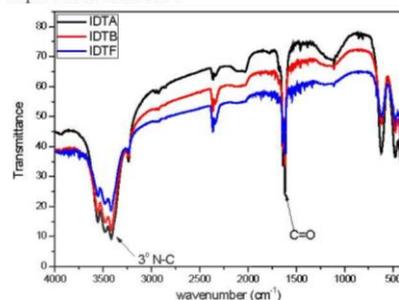


Figure 3. IR spectra of IDTA, IDTB and IDTF

3.2 Optical properties

The UV-Vis absorption spectra of organic photovoltaic materials in dilute CH₂Cl₂ solution are shown in Figure 4. The absorption spectra of all organic photovoltaic materials showed relative large molar extinction coefficient in visible region (300-600 nm). IDTF showed highest molar absorptivity relative to IDTB and IDTA. The synthesized molecules exhibited very low photoluminescence indicating these molecules can be used as donor materials in OPVs.

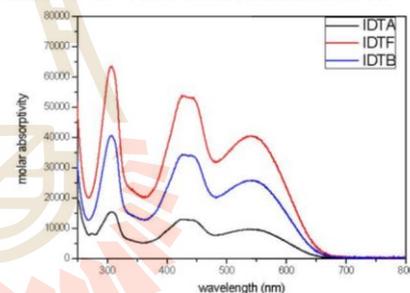


Figure 4. Absorption spectra of IDTA, IDTB and IDTF in CH₂Cl₂ solution.

4. Conclusions

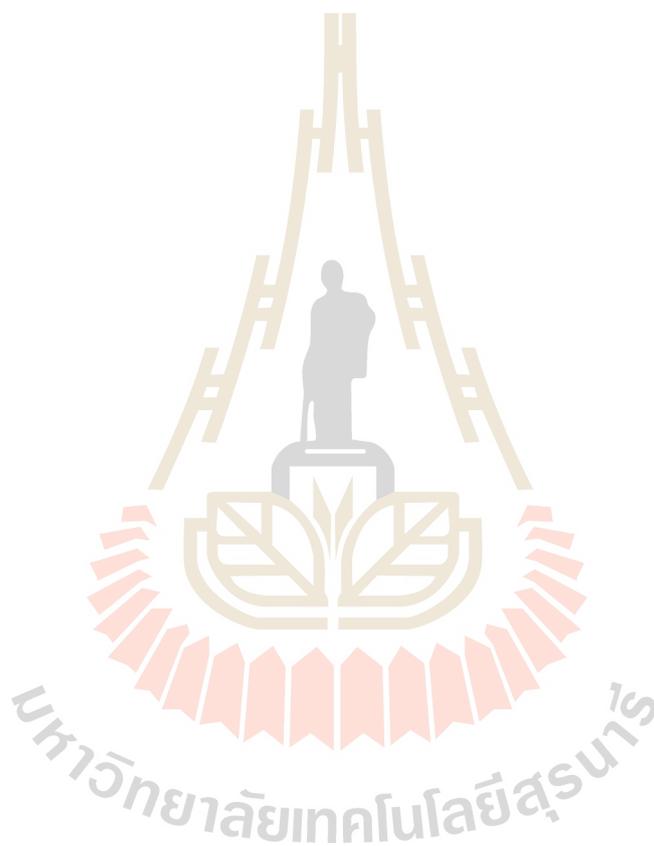
In summary, we have successfully synthesized three organic photovoltaic materials which contained isoindigo bearing various core moieties (anthracene, benzothiadiazole and fluorene) as electron donors. The organic photovoltaic materials showed visible region (300-600 nm) in UV-Vis absorption spectra.

Acknowledgements

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References

- [1] Christos, P., Xaver, P. and Helv, B., 1998, *Chim Acta.*, 71, 1079-1083.
- [2] Wang, D., Ying, W., Zhang, X., Hu, Y., Wu, W. and Hua J., 2015 *Dyes Pigm.*, 112, 327-334.
- [3] Wang, G., Tan, H., Zhang, Y., Wu, Y., Hu, Z., Yu, G. and Pan, C., 2014, *Synth. Met.*, 187, 17-23.
- [4] Zhao, N., Qiu, L., Wang, X., An, Z. and Wan, X., 2014, *Tetrahedron Lett.*, 1040-1044.



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