SYNTHESIS AND CHARACTERIZATION OF CARBAZOLE DERIVATIVES FOR ORGANIC LIGHT-EMITTING DIODE AND INDOLE DERIVATIVES FOR DYE-SENSITIZED SOLAR CELL

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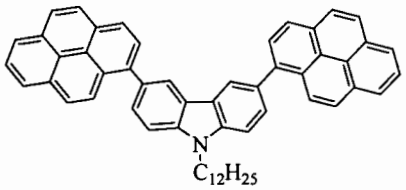
บทคัดย่อ

เรื่อง	:	การสังเคราะห์และพิสูจน์เอกลักษณ์อนุพันธ์คาร์บาโซลสำหรับอุปกรณ์ไดโอดเรืองแสง สารอินทรีย์และอนุพันธ์อินโดลสำหรับอุปกรณ์เซลล์แสงอาทิตย์ชนิดสีย้อมไวแสง
ผู้วิจัย	:	ธิติมา ศิริเริ่ม
ชื่อปริญญา	:	วิทยาศาสตรมหาบัณฑิต
สาขาวิชา	:	เคมี
อาจารย์ที่ปรึกษา	:	ผู้ช่วยศาสตราจารย์ ดร. ทินกร แก้วอินทร์
คำสำคัญ	:	ไดโอดเรืองแสงอินทรีย์, สารส่งผ่านประจุ, สารเรืองแสง ปฏิกิริยาซูซูกิ ครอส-คับปลิง, อินโดล, เซลล์แสงอาทิตย์ชนิดสีย้อมไวแสง

ในงานวิจัยนี้ได้ทำการสังเคราะห์อนุพันธ์คาร์บาโซลที่มีหมู่ปิดท้ายด้วยโมเลกุลของไพรีน (**CP2**) และแอนทราซีน (**CA2**) โดยใช้ปฏิกิริยาโบรมิเนชัน และปฏิกิริยา Suzuki cross-coupling และพิสูจน์เอกลักษณ์ด้วยเทคนิค ^{1}H NMR, ^{13}C-NMR, FT-IR, UV-Vis, fluorescence และ mass spectroscopy และ cyclic voltammetry โดย 9-dodecyl-3,6-di(pyren-1-yl)carbazole (**CP2**) และ 9-dodecyl-3,6-di(anthracen-1-yl)carbazole (**CA2**) ให้สเปกตรัมการคายแสงในช่วงสีน้ำเงินเข้มที่ 430 nm และ 442 nm และมีความเสถียรทางไฟฟ้าที่สูง สารเหล่านี้จึงน่าจะเป็นอีกทางเลือกหนึ่งสำหรับใช้เป็นสารเรืองแสงสีน้ำเงินในไดโอดเรืองแสงอินทรีย์



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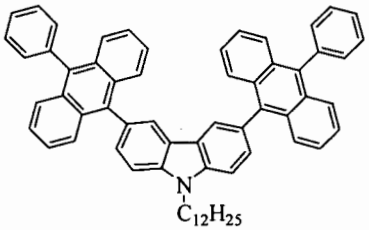
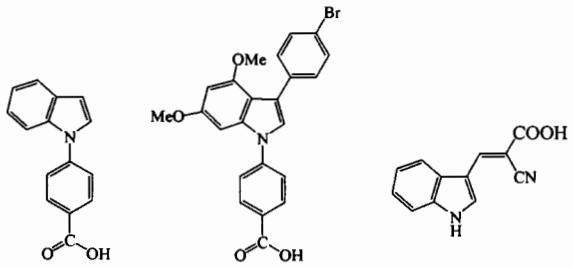


(CA2)

นอกจากนี้ยังได้ทำการสังเคราะห์อนุพันธ์อินโดลชนิดใหม่ **In1-In5** ที่โมเลกุลประกอบด้วยอนุพันธ์อินโดลเป็นหมู่ให้อิเล็กตรอน พันธะคู่หรือหมู่ฟีนิลเป็นสายโซ่เชื่อมต่อและหมู่คาร์บอกซิลเป็นหมู่รับอิเล็กตรอนและยึดจับเพื่อใช้เป็นโมเลกุลสีย้อมไวแสงในเซลล์แสงอาทิตย์ชนิดสีย้อมไวแสง โมเลกุลเป้าหมายสังเคราะห์ได้จากปฏิกิริยา Ullman coupling, ปฏิกิริยาไฮโดรไลซิส, ปฏิกิริยา Knoevenagal condensation และ ปฏิกิริยา Vilsmeier–Haack โดยคาดหวังว่าโมเลกุลเป้าหมาย In1-In5 จะถูกนำไปใช้เป็นสีย้อมในเซลล์แสงอาทิตย์ชนิดสีย้อมไวแสงได้อย่างมีประสิทธิภาพ



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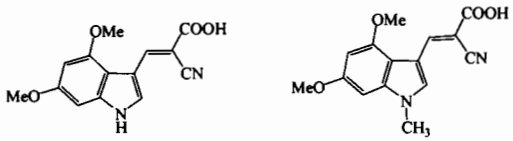

(In4) (In5)

สุดท้ายนี้โมเลกุลเป้าหมาย **In1-In5** ถูกพิสูจน์เอกลักษณ์โดยใช้เทคนิค ^{1}H-NMR, ^{13}C-NMR, FT-IR และ mass spectroscopy.

ABSTRACT

TITLE : SYNTHESIS AND CHARACTERIZATION OF CARBAZOLE DERIVATIVES FOR ORGANIC LIGHT-EMITTING DIODE AND INDOLE DERIVATIVES FOR DYE-SENSITIZED SOLAR CELL

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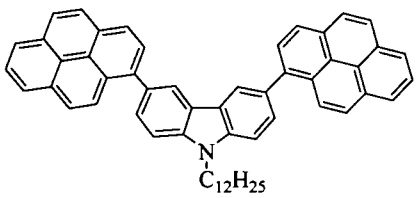
KEYWORDS : CARBAZOLE, ORGANIC LIGHT-EMITTING DIODES, SUZUKI CROSS-COUPLING REACTION, INDOLE, DYE-SENSITIZED SOLAR CELL

In this research, carbazole derivatives end-capped with pyrene (**CP2**) and anthracene **(CA2)** have been synthesized using bromination and Suzuki cross-coupling reaction and characterized by ^{1}H NMR, ^{13}C-NMR, FT-IR, UV-Vis, fluorescence and mass spectroscopy and cyclic voltammetry. Compound 9-dodecyl-3,6-di(pyren-1-yl)carbazole (**CP2**) and 9-dodecyl-3,6-di(anthracen-1-yl)carbazole (**CA2**) showed the PL spectra in deep blue region at 430 nm and 442 nm and exhibited high electrochemical stability. These compounds could be alternative materials for using as blue light-emitters in organic light emitting diodes.



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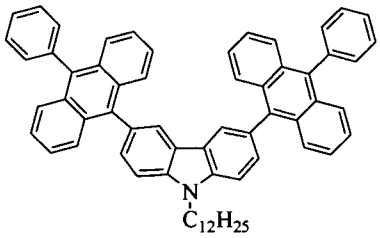
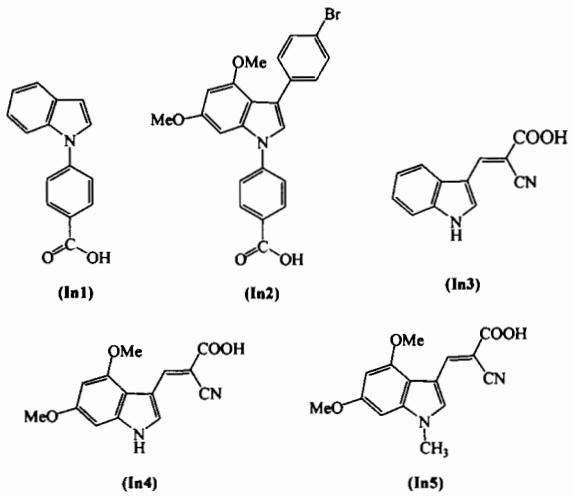


(CA2)

Moreover, a new series of indole derivatives **In1-In5**, containing indole derivatives as electron donating, double bond or phenyl group as π-spacer and carboxyl group as electron acceptor and anchor, for using as dye molecules in DSSCs were successfully synthesized. The target molecules were synthesized by using Ullman coupling, hydrolysis reaction, Knoevenagal condensation and Vilsmeier–

Haack reaction. The target compound **In1-In5** could be promising candidates for improvement of the performance dye of the DSSCs.



Finally, target molecules, **In1-In5** were characterized by using ^{1}H-NMR, ^{13}C-NMR, FT-IR and mass spectroscopy.

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LIST OF ABBREVIATIONS

ABBREVIATION	FULL WORD
OLED	Organic light-emitting diode
LCD	Liquid crystal display
ITO	Indium tin oxide
HIL	Hole-injection layer
HIM	Hole-injection material
HTL	Hole-transporting layer
HTM	Hole-transporting material
EML	Emissive layer or emitting layer
ETL	Electron-transporting layer
ETM	Electron-transporting material
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
EL	Electroluminescence
PL	Photoluminescence
TLC	Thin-layer chromatography
NMR	Nuclear magnetic resonance
^{1}H-NMR	Proton nuclear magnetic resonance
^{13}C-NMR	Carbon nuclear magnetic resonance
FT-IR	Fourier transform Infrared
UV	Ultra-violet
CV	Cyclic voltammetry
DSC	Differential scanning calorimetry
δ	Chemical shift in ppm relative to tetramethylsilane
s	Singlet
d	Doublet
dd	Doublet of doublets

LIST OF ABBREVIATIONS (CONTINUED)

ABBREVIATION	FULL WORD
t	Triplet
ε	Molar absorption coefficient
eV	Electron volt
h	Hour/hours
rt	Room temperature
J	Coupling constant
MHz	Megahertz
V	Voltage
M	Molar concentration
μA	Microamperes
μm	Micrometer
nm	Nanometers
mmol	Milimoles
mol	Moles
ppm	Part per million
min	minutes
Ω	Ohm
DCM	Dichloromethane
THF	Tetrahydrofuran
n-Bu_4NPF_6	Tetrabutylammonium hexafluorophosphate
DFT	Density functional theory
ΔE_h	Hole energy barriers
ΔE_e	Electron energy barriers
EA	Electron affinity
E_g	Energy gap
E_{onset}	Energy onset

LIST OF ABBREVIATIONS (CONTINUED)

ABBREVIATION	FULL WORD
Φ_F	Fluorescent quantum yield
λ	Wavelength
λ_{abs}	Wavelength absorption
λ_{em}	Wavelength emission
λ_{max}	Wavelength maximum
λ_{onset}	Wavelength onset
λ_{el}	Wavelength electroluminescent
T_g	Glass transition temperature
T_c	Crystallization temperature
T_d	Decomposition temperature
T_m	Melting temperature

CHAPTER 1

SYNTHESIS AND CHARACTERIZATION OF CARBAZOLE DERIVATIVES FOR ORGANIC LIGHT-EMITTING DIODE

1.1 INTRODUCTION

1.1.1 Organic light emitting diodes (OLEDs)

In the former time, many exhibited technologies, for example, cathode ray tube (CRT), liquid crystal displays (LCDs), light emitting diodes (LEDs) were inducing to show in the market. However, there are lots of limitations of the displays such as bulkiness, low viewing angle, color purity, etc [1]. Furthermore, the current demand generation displays are the brightness reproduction, pure color, high resolution, light weight, thin screen, and decreasing of cost and low power consumption, which was set in these OLED devices.

Organic light-emitting diodes (OLEDs) are relatively technology for light sources in which the emissive electroluminescent layer is a film of organic compound that emits light in response to an electric current [2]. First proposed by Ching W. Tang in 1987 [3], OLEDs have attracted significant attention from the scientific community due to their optical potential properties for future flat-panel displays and lighting applications [2]. OLEDs have high potential electronic and optical properties, for example, low voltage driving, high brightness, ability of multicolor emission selected by emitting materials, easy large-area fabrication, and thin-film devices which they have no added backlight required for brightness of the screen [4]. According to the varieties of report on improving OLEDs properties, there are witness that is significant advancement related to brightness, multi- or full-color emission, and OLEDs endurance and thermal stability.

In addition, organic light emitting diodes are more attended recently because they have a wide range of display applications. The application of OLED technology is thin solid films of organic molecules that use electricity to generate light. There are various devices found consist of mobile phones, computer monitors, car radios, digital cameras and large TV screen, and etc [5]. The movable applications

help OLEDs high light output to read easily in sunlight, and it helps create brighter, especially wavy images in the devices. OLEDs using accompany with various prominent advantage included lower and better power used since it lacks of backlight effects and a faster reaction in view of its high speed. Also, the diodes are really lightweight and flexible. The OLEDs is the basis technology in the present time, but it tends to be the most needed in the future because of effective devices.

Figure 1.1 Organic light emitting diodes (OLEDs) display applications [6]

1.1.2 Organic light emitting diodes structure

The OLEDs structure consist of four part including substrate, anode, organic layers and cathode [7] as shown in **Figure 1.2**.

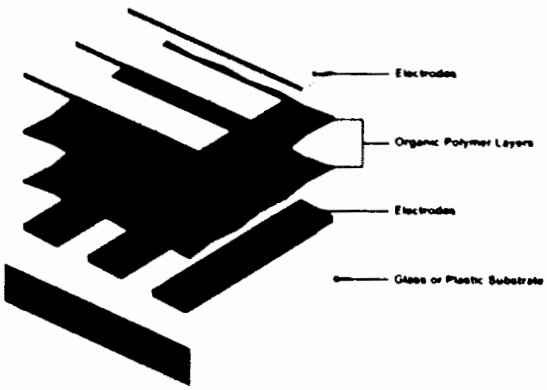


Figure 1.2 Organic light emitting diodes (OLEDs) structure [8]

1.1.2.1 Substrate layer–It supports OLED and is made up of transparent plastic or glass film.

1.1.2.2 Anode layer–It is a transparent layer that removes electrons. Indium tin oxide is commonly used as the anode material.

1.1.2.3 Organic layer–Layer formed of organic molecules or polymers

1) Conductive layer–Transports holes from anode made up of organic plastic. Polymer light-emitting diodes: PLED, also light-emitting polymers: LEP, are used in electroluminescent conductive polymer. Typical polymers used in PLED displays include derivatives of poly (*p*-phenylene vinylene) and polyfluorene.

2) Emissive layer–Transports electrons from the cathode layer. It is made up of organic plastic.

1.1.2.4 Cathode layer–Injects electrons. It may be transparent or not. Metals such as aluminium and calcium are often used in the cathode

1.1.3 Working principle of organic light emitting diodes

The working principle of OLEDs was shown in **Figure 1.3**. When electrical current is applied to the electrodes anode and cathode the charges and electron start moving in the device under the influence of the electric field. Electrons leave the cathode, giving electrons to emissive layer and electrons remove form conducting layer to anode, giving holes (h^+) at conducting layer. The holes jump to the emissive layer and recombine with the electrons. The recombination of this charges leads to the creation of a photon with a frequency given by the energy gap ($E = h\nu$) between the LUMO and HOMO levels of the emitting molecules. Therefore, the electrical power applied to the electrodes is transformed into light [2].

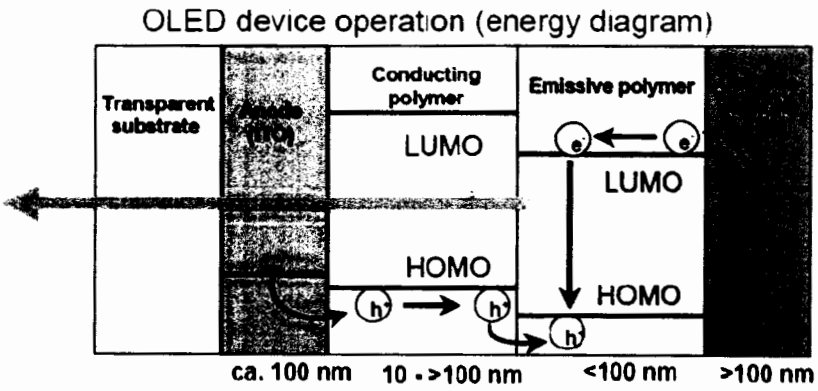


Figure 1.3 Working principle of OLEDs [9]

1.1.4 Literature reviews of OLEDs

In this part, the publications of synthesis and study optical properties of organic light emitting diodes would be described. For example:

In 2012, a highly fluorescent bis (4-diphenylaminophenyl) carbazole end-capped fluorine, **TCF**, was synthesized and characterized by D. Meunmart and co-workers. This material showed greater ability as a solution processed blue emitter and hole-transporter for OLEDs than commonly used NPB. High-efficiency deep-blue and Alq3-based green devices with luminance efficiencies and CIE coordinates of 0.93 cd/A, (0.16, 0.09), and 3.78 cd/A and (0.29, 0.45) were achieved, respectively. The use of the triphenylamine-carbazole substituent might be an effective method to prepare amorphous molecules with excellent electrochemical, thermal, and morphological stabilities for OLEDs by forming dendritric structures with other fluorescent or non-fluorescent core units [10].

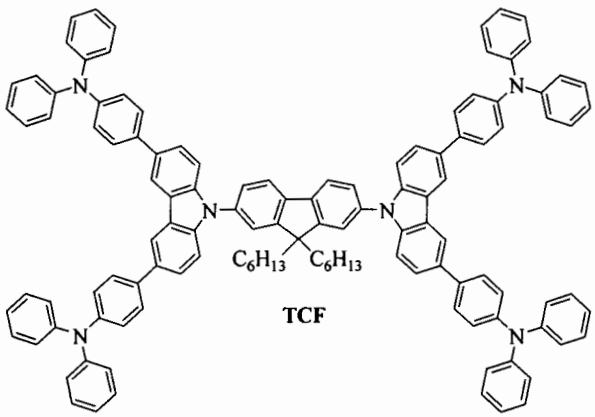


Figure 1.4 Chemical structure of TCF

In 2012, Sukrawee Pansay et al. [11] designed and synthesized four benzo[b]thien-2-yl derivatives **4a-4d** (**Figure 1.5**). The properties of **4a -4d** as a blue emissive layer (EML) in OLED were investigated. Under an applied voltage, the devices (**4b–d**) emitted a bright deep-blue light with maximum peaks (λ_{EL}) centered at 416, 428, and 436 nm, respectively. The electroluminescence (EL) spectra of all diodes matched their corresponding PL spectra indicating that the EL emission originates from the singlet-excited states of the EML materials. However, **4a** did not show any EL property in the device. This may be due to its very small, planar structure

leading to fluorescence quenching in the solid state. Carbazole **4d** bearing four benzo[b]thiophene substituents had the best EML properties among these four materials. The **4d**-based device exhibited a high maximum brightness of 582 cd m^{-2} for blue OLED at 8.6 V, a turn-on voltage of 4.1 V.

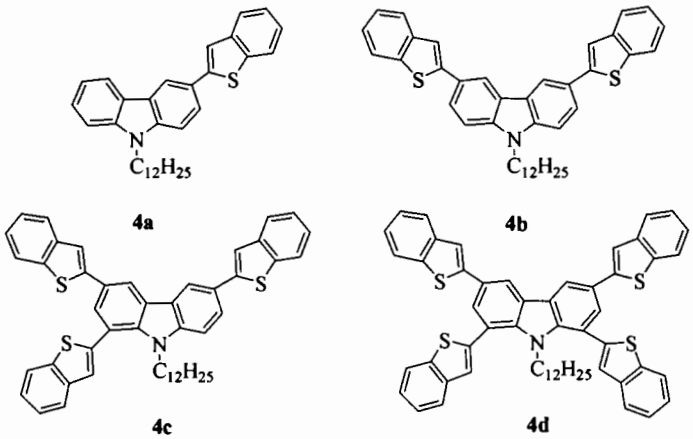


Figure 1.5 Structure of benzo[b]thien-2-yl derivatives.

In 2016, bis-(4-benzenesulfonyl-phenyl)-9-phenyl-9H-carbazoles were designed and synthesized by Bin Huang and co-workers [12]. The nondoped devices using 3,6-bis-(4-benzenesulfonyl-phenyl)-9-phenyl-9H-carbazoles **2a** and 2,7-bis-(4-benzenesulfonyl-phenyl)-9-phenyl-9H-carbazoles **2b** as the emitters show deep blue emission color with EL spectra peaks at 424 and 444 nm and the Commission Internationale de l'Eclairage (CIE) coordinates of (0.177, 0.117) and (0.160, 0.117), respectively. Furthermore, these materials based devices have high color-purity with small width at half-maximum (FWHM) of 65 and 73 nm, respectively. The results provide a novel approach for the design of deep blue emitter for high-color-purity nondoped OLEDs.

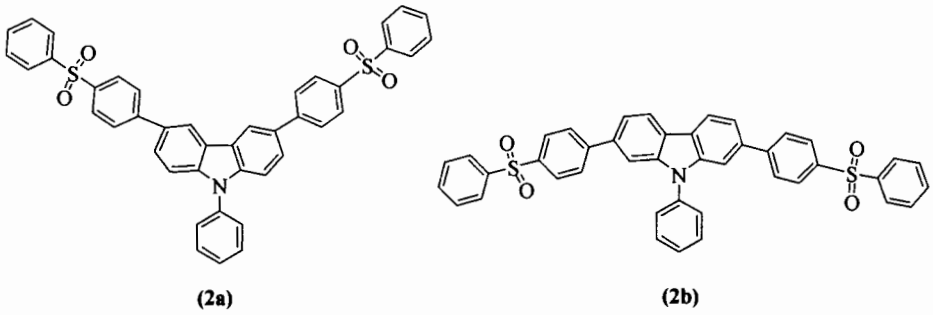


Figure 1.6 Structure of bis-(4-benzenesulfonyl-phenyl)-9-phenyl-9H-carbazoles.

In 2016, **DPACz1**, **DPACz2** and **DPACz3** were synthesized and characterized by Shahid Ameen *et al* [13]. Diphenylamine substituents at 1- or 1,8-positions of carbazoles show increasing of the band-gap compared with the previously reported 3,6- or 2,7-substituted ones. In addition, all materials indicated high triplet energy levels of 2.68, 2.60 and 2.45 eV, respectively. Based on suitable HOMO levels and high triplet energies, they were investigated for their potential as host materials for green phosphorescent OLEDs with the device configuration, [ITO/ PEDOT:PSS/Emitting layer/TPBi/CsF/Al]. Moreover, the devices of all materials shown emitted typical green light with high luminance and had low turn-on voltages along with good luminous efficiencies. These results indicated the usefulness of new materials and kind of 1-/1,8-substitution of carbazole would open a new way of materials design.

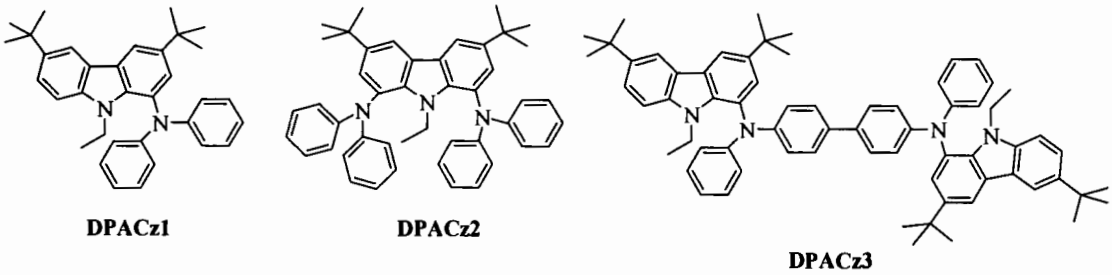


Figure 1.7 Structure of DPACz1, DPACz2 and DPACz3

In 2016, Shi H. et al [14] presented two novel phenylethene-carbazole derivatives containing dimesitylboron groups, 3-(dimesitylboryl)-9-ethyl-6-(1,2,2-triphenylvinyl)-9H-carbazole **DETPCZ** and 1,2-bis(6-(dimesitylboryl)-9-ethyl-9H-carbazol-3-yl)-1,2-diphenylethene **DECZDEP**. The electrochemical thermal and photophysical properties were reported. Both compounds show excellent thermal stability (Td up to 254 °C) and high electrochemical stability. Moreover, the multi-layer EL devices illustrated the sky blue-green emitting EL with high maximum luminance and maximum luminance efficiency of 15,780 cd m^{-2} and 6.90 cd A^{-1} at CIE of (0.20, 0.28) and (0.23, 0.41), respectively. The results provide a novel way for the design and application of novel AIE-luminophores.

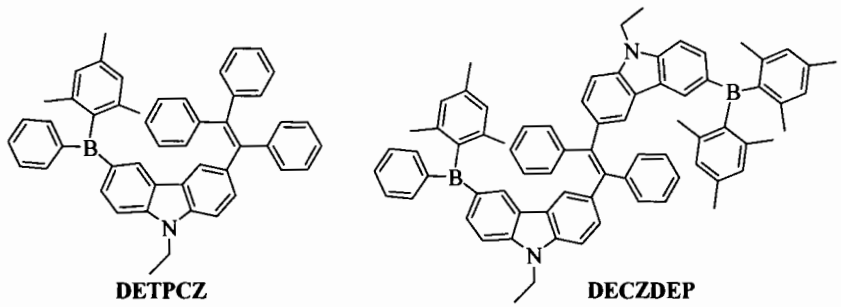


Figure 1.8 Structure of DETPCZ and DECZDEP

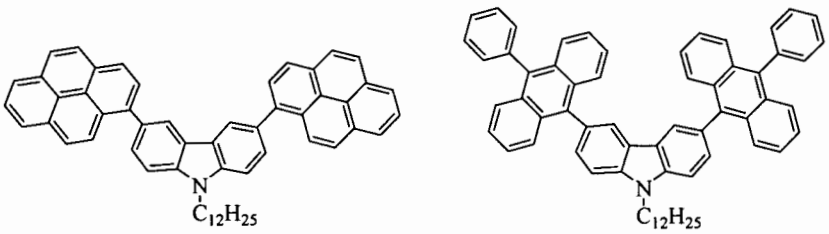
Due to a variety of organic materials of OLED have been reported. We are particularly interested in synthesize organic compounds for OLEDs.

1.1.5 Aim of the thesis

Initally proposed by Ching W. Tang in 1987 [3], organic light-emitting diodes (**OLEDs**) have attracted significant attention from the scientific community due to their potential for future flat-panel displays and lighting applications [15]. Today, the developments of OLED technologies mainly focus on the optimization of device structures and on developing new emitting materials. Clearly, new materials emitting pure colors of red, green, and blue (**RGB**) with excellent emission efficiency and high stability, are the key point of OLED development for full-color flat displays. The performance of blue OLEDs is usually inferior to that of green and red OLEDs due to poor carrier injection into the emitters [16] and electroluminescent (**EL**)

properties of the blue OLEDs need to be improved. Therefore, one area of continuing research in this field is the pursuit of a stable-blue emitting material [17]. Although many fluorescent blue emitters have been reported such as pyrene derivatives [18], carbazole derivatives [19], anthracene derivatives [20], fluorene derivatives and aromatic hydrocarbons [21], there is still a clear need for further developments in terms of efficiency and color purity compared to red and green emitters.

In this research, we synthesize and characterize of a series of emissive materials based on carbazole derivatives. In addition, we synthesize the following a carbazole derivatives containing two pyrenyl and two anthracene endgroup of carbazole unit as core, whose chemical structure of target molecules, **CP2** and **CA2** are shown in **Figure 1.9**. They are used as light-emitting materials in OLEDs.



(CP2) **(CA2)**

Figure 1.9 The target molecules CP2 and CA2

Objectives of this research

(1) To synthesize pyrene and anthracene-substituted carbazole derivatives as both emitting and hole-transporting materials for OLEDs.

(2) To characterize and identify the target product during the synthesis steps

(3) To study optical property and potential of the target molecules

1.2 RESULTS AND DISCUSSION

In this research, organic compounds, carbazole derivatives, were designed for studied OLEDs properties. The target molecules **CP2** and **CA2**, pyrene and anthracene-substituted carbazole derivatives, were designed synthesized, characterized and studied optical property. Structure of **CP2** and **CP1** are shown in **Figure 1.10**.

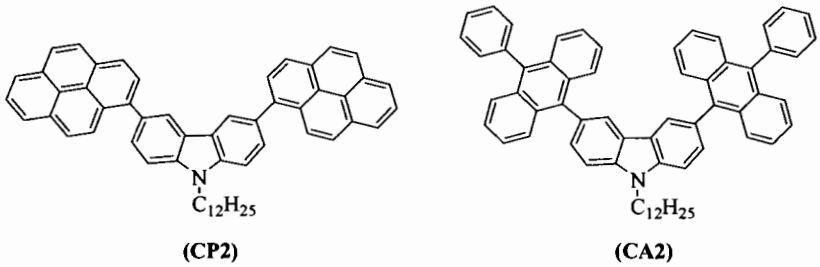


Figure 1.10 Structure of CP2 and CP1

1.2.1 Synthesis and characterization of CP2 and CA2

The target carbazole **CP2** and **CA2** were successfully synthesized by bromination and Suzuki cross coupling. The target carbazole were synthesized from Suzuki cross coupling of dibromocarbazole **3** with pyrene-1-boronic acid and 10-phenyl-9-anthraceneboronic acid. The dibromocarbazole **3** was synthesized alkylation of carbazole **1** with 1-bromododecane and following by bromination with *N*-bromosuccinamine (NBS) as shows in **Figure 1.11**.

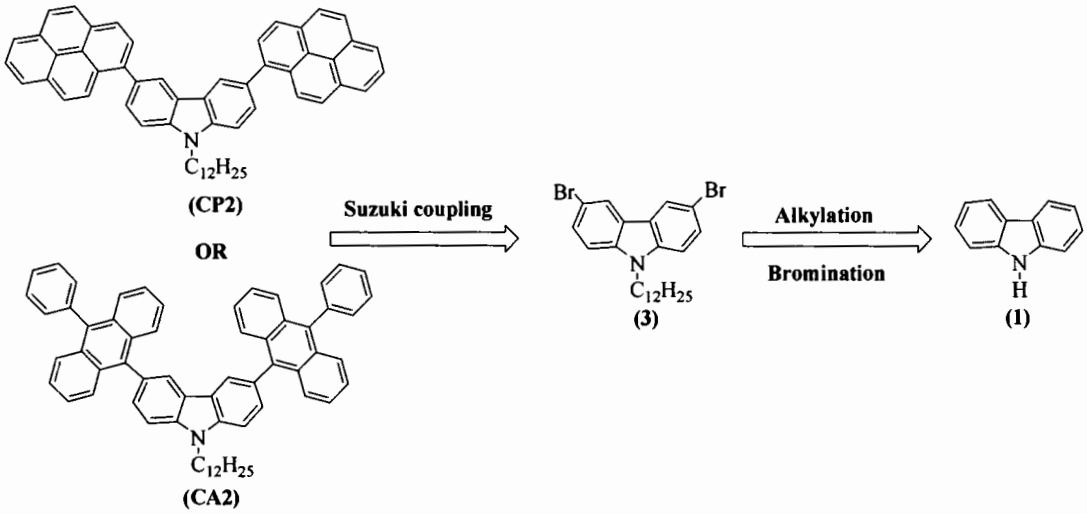


Figure 1.11 Retrosynthesis of carbazole CP2 and CA2

First step, 9-dodecylcarbazole **2** was synthesized by alkylation reaction at the N-position of carbazole **1** with 1-bromododecane. The treatment of carbazole with

sodium hydride (NaH) and 1-bromododecane in DMF at 0 °C to room temperature overnight gave 9-dodecylcarbazole **2** in 97% yield as shows in **Figure1.12**.

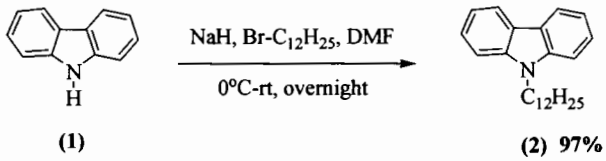


Figure1.12 Synthesis of 9-dodecylcarbazole 2

The 9-dodecylcarbazole **2** was confirmed by ^{1}H-NMR and ^{13}C-NMR [11]. ^{1}H-NMR spectra of 9-dodecylcarbazole **2** still show eight aryl proton in the same region of carbazole and shows new triplet peak of N-C$\underline{H}_2$- proton at δ = 4.36 (2H) and peak of alkyl protons at δ = 1.96 (2H), 1.41-1.37 (18H) and δ = 1.05 (3H) ppm. Remarkable, the NH proton of carbazole was absented. Moreover, ^{13}C-NMR spectrum shows new signal of N-$\underline{C}H_2$- at δ = 43.2 ppm and new ten peaks of 11 alkyl carbons. These results confirmed that product was compound **2.**

The mechanism of alkylation reaction was purposed *via* nucleophilic substitution reaction as shows in **Figure1.13**. Nitrogen anion intermediate **[A]** were generated by reaction of carbazole with hydride of NaH. Then, nitrogen anion attacked at C-1 position of 1-bromododecane to give 9-dodecylcarbazole **2**.

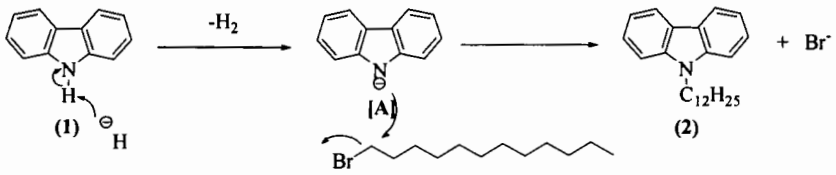


Figure 1.13 Mechanisms of alkylation reaction of carbazole

Next step, selective bromination of 9-dodecylcarbazole **2** at C-3 and C-6 position were investigated. The treatment of compound **2** with NBS in THF at room temperature for 3h afforded 3,6-dibromo-9-dodecylcarbazole **3** in 91% yields as shows in **Figure1.14**.

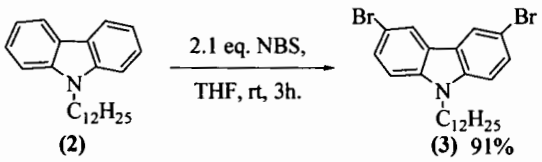


Figure 1.14 Bromination of 9-dodecylcarbazole 2

The compound **3** was confirmed by ^{1}H-NMR and ^{13}C-NMR [11]. ^{1}H-NMR spectra of 3,6-dibromo-9-dodecylcarbazole **3** shows six aromatic protons at δ = 8.15 (2H), 7.55 (2H) and 7.29 (2H) and shows twenty five alkyl protons in the same region of dodecyl group. The absented of two protons of carbazole was believe that bromination on carbazole **2** was appeared. Moreover, ^{13}C-NMR spectrum shows CH aromatic carbon of carbazole only three signals at δ = 129.0 (2 x CH), 123.5 (2 x CH), 123.3 (2 x CH). Therefore, NMR results confirm that two protons of carbazole were substituted by two bromine atoms. These results confirmed that product was compound **3.**

The mechanism of bromination was purposed *via* electrophilic aromatic substitution as shows in **Figure1.15**. Firstly, carbon C-3 position of carbazole as a nucleophile attacked at bromine atom of *N*-bromosuccinimide to give carbazole intermediate **[B]**. The aromatization of intermediate **[B]** *via* deprotonation gave intermediate compound **[C]**. Then, bromination at C-6 position of carbazole **[C]** in the same mechanisms gave intermediate **[D]** and 3,6-dibromo-9-dodecylcarbazole **3,** respectively.

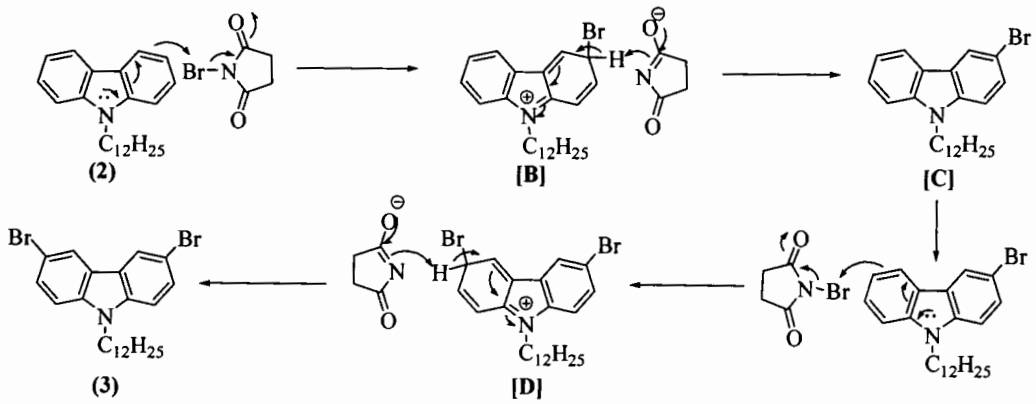


Figure 1.15 Mechanisms of bromination of 9-dodecylcarbazole (2)

Then, target molecules **CP2** was synthesized by Suzuki cross coupling reaction. The treatment of compound **3,** pyrene-1-boronic acid, $Pd(PPh_3)_4$ as the catalyst and aqueous Na_2CO_3 as the base in THF at reflux afforded target molecules **CP2** in 53 % yields as shows in **Figure1.16**.

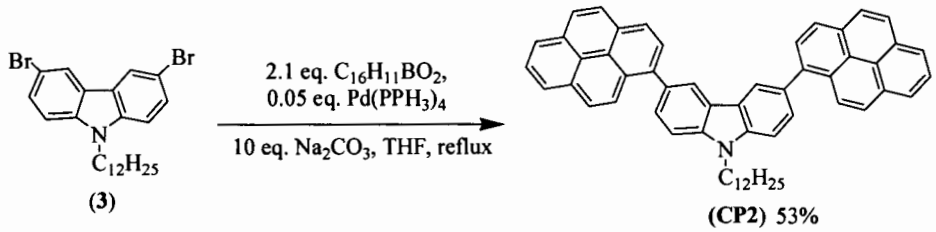


Figure 1.16 Synthetic of target molecules CP2

The target compound **CP2** was confirmed by ^{1}H-NMR and ^{13}C-NMR. ^{1}H-NMR spectra of compound **CP2** show 24 aromatic protons (new more 18 aromatic protons from compound **3**) and show twenty five alkyl protons in the same region of dodecyl group. The increasing of new 18 aromatic protons were believe that bromine atom were substituted by pyrenyl group. In addition, ^{13}C-NMR spectra shows new 18 CH aromatic carbons and new 14 Cq aromatic carbons of pyrenyl group. Therefore, NMR results confirm that two bromine atoms were substituted by two pyrenyl groups. Moreover, the high resolution mass spectrometry (MALDI-TOF) of compound **CP2** found 735.2981 (calcd for $C_{56}H_{49}N$: *m/z* 735.3865). These results confirmed that product was compound **CP2**.

The mechanism of Suzuki coupling reaction follows a three-step mechanism cycle, oxidative addition, transmetallation and reductive elimination as described in **Figure 1.16**. The oxidative addition at C-Br bond of compound **3** with Pd(0) gave organopaladium complex **[E]**. The reaction of complex **[E]** with Na_2CO_3 gave complex **[F]**. Transmetallation of complex **[F]** with organoboron species **[G]**, preparing from reaction of boronic acid and Na_2CO_3, gave complex **[H]**. Finally, reductive elimination of complex **[D]** gave molecules **[I]**. Then, Suzuki coupling reaction at C-6 position of carbazole **[I]** in the same mechanisms gave target compound **CP2**.

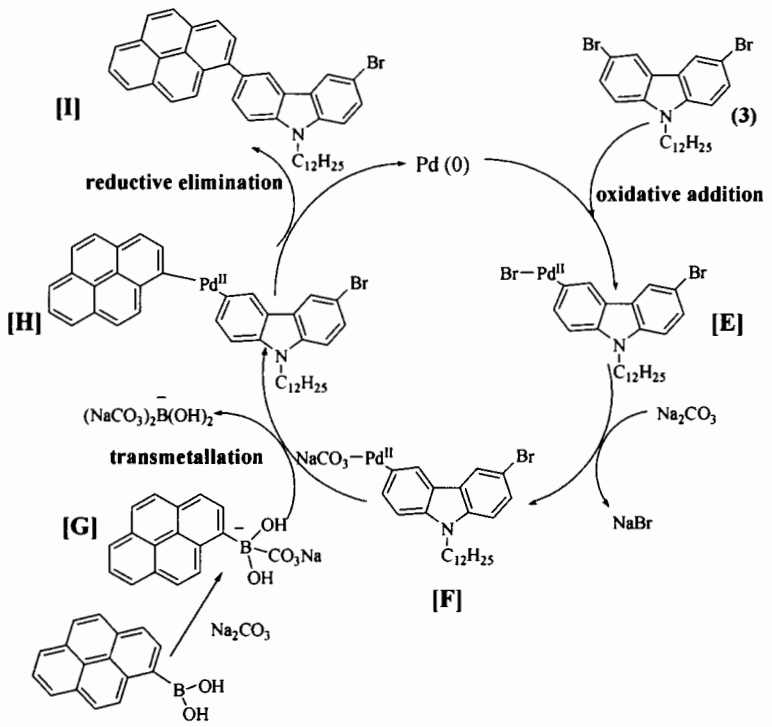


Figure 1.17 The proposed mechanism of Suzuki coupling reaction

Finally, the target molecules **CA2** was synthesized by Suzuki cross coupling reaction. The treatment of compound **3**, 10-phenyl-9-anthracene boronic acid, $Pd(PPh_3)_4$ as the catalyst and K^tOBu as the base in THF at reflux afforded target molecules **CA2** in 68 % yields as shows in **Figure 1.18**.

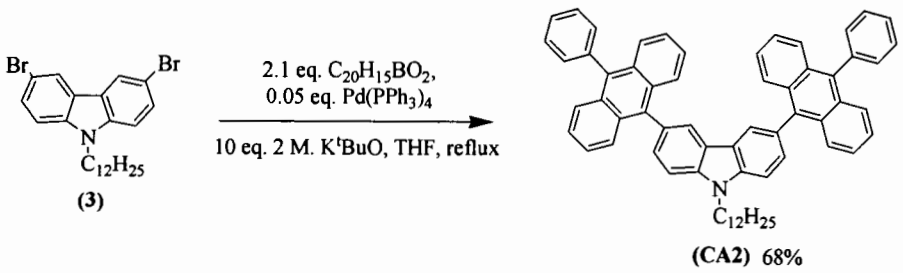


Figure 1.18 Synthetic of target molecules CA2

The target compound **CA2** was confirmed by ^{1}H-NMR and ^{13}C-NMR. ^{1}H-NMR spectra of compound **CA2** shows 32 aromatic protons (new more 26 aromatic protons from compound **3**) and shows twenty five alkyl protons in the same region of

dodecyl group. The increasing of new 26 aromatic protons were believe that bromine atom were substituted by 10-phenyl-9-anthracenyl group. In addition, ^{13}C-NMR spectrum shows new 26 CH aromatic carbon and new 14 Cq aromatic carbon of 10-phenyl-9-anthracenyl group. Therefore, NMR results confirm that two bromine atoms were substituted by 10-phenyl-9-anthracenyl group. Moreover, the high resolution mass spectrometry (MALDI-TOF) of compound **CA2** found 839.3175 (calcd for $C_{64}H_{57}N$: *m/z* 839.4491). These results confirmed that product was compound **CA2**.

The mechanism of Suzuki coupling of compound **CA2** similar to mechanism of Suzuki coupling reaction as described in **Figure 1.17**.

1.2.2 Optical properties of CP2 and CA2

The optical properties of the organic materials were investigated by UV-Vis and fluorescence spectrophotometer in dry dichloromethane (DCM). The UV-Vis absorption and photoluminescence spectra of the target molecules **CP2** and **CA2** were measured as shown in **Figure 1.19** and the corresponding data summarized in Table 1.1. In solution absorption spectra, the UV-Vis spectra of the target molecules **CP2** and **CA2** exhibited two major absorption bands. The first absorption band of compounds **CP2** and **CA2** were assigned in terms of the strong absorption band in the region of 200-275 nm corresponding to the π-π^* local electron transition of the carbazole moieties and the second absorption bands at longer wavelength around 350-400 nm corresponding to intermolecular charge transfer (ICT) transition between the carbazole and conjugated substituted dipyrene and dianthracene. However, the substitution dipyrene **CP2** to substituted anthracene **CA2** of carbazole increased the conjugation length of compounds resulting a red-shift and broad in absorption spectra. Therefore, the ICT of **CA2** was stronger than ICT of **CP2**.

These compounds in solution show fluoresce in the blue region (430–442 nm) with featureless photoluminescence (PL) spectra. The emission spectra display maxima at 430 and 442 nm, for **CP2** and **CA2**, respectively. From the substitution dipyrene **CP2** to substituted anthracene **CA2**, the PL spectra also show a gradual red-shife, concomitant with the increasing conjugation length (**Figure 1.19**).

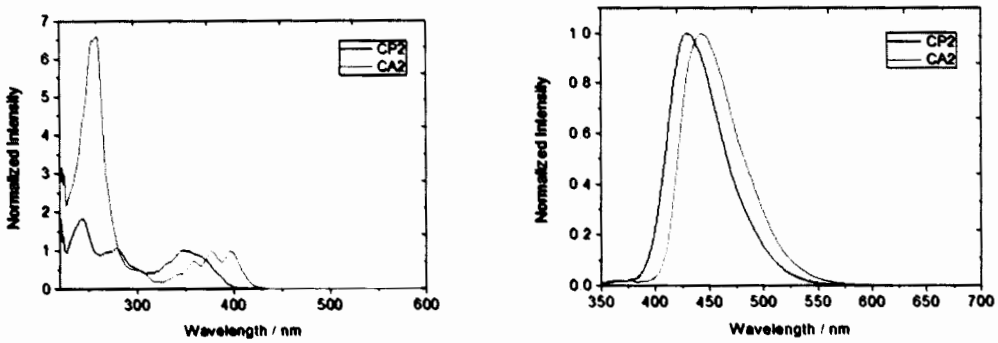


Figure 1.19 Normalized absorption spectra (left) and normalized emission spectra (right) in CH_2Cl_2 of CP2 and CA2

Table 1.1 Physical data of CP2 and CA2

Compound	λ_{abs}(log ε)[a] (nm $M^{-1}cm^{-1}$)	λ_{em}[a] (nm)	Eg[b] (eV)
CP2	279 (5.37), 348 (2.35)	430	3.10
CA2	305 (3.93), 359 (4.09), 377 (4.24), 397 (4.23)	442	2.95

[a] Measured in dilute CH_2Cl_2 solution.

[b] Calculated from the absorption edge, Eg = 1240 per onset

The energy gaps (E_g) of the target molecules from the absorption edge were nearly identical (2.95-3.10 eV), despite the somewhat different molecular sizes and substance groups.

Conclusion of optical properties, compound **CA2** has longer conjugate and stronger intermolecular charge transfer than **CP2** from result of UV absorption spectra. Moreover, emission spectra conclude that compound **CP2** and **CA2** emit in the blue region but **CA2** spectra showed peak shift of up to 12 nm from compound **CP2**.

1.2.3 Electrochemical properties of CP2 and CA2

The electrochemical properties of materials were performed using the cyclic voltammeter (CV). All measurements were made at room temperature on sample dissolved in freshly distilled dichloromethane and 0.1 M tetra-*n*-

butylammonium hexafluorophosphate (n-Bu_4NPF_6) as electrolyte. The solutions were degassed by bubbling with argon. A typical electrochemical cell consists of three electrodes; a glassy carbon working electrode, platinum wire counter electrode, and Ag/AgCl/NaCl (Sat.) reference electrode, controlled by a potentiostat. The potential difference was applied between the working and counter. The third electrode was the reference electrode, through which no current flows, and from which the potentials of the other electrodes were measured. A part from the solutions, the solute in this work contained an electrolyte to decreases the resistivity.

The electrochemical stability of materials was performed by multiple-scan CV curves. The HOMO energy levels of materials were calculated from the oxidation onset potentials (E_{onset}) with empirical equation of HOMO = - (4.44 + E_{onset}) while LUMO energy levels were calculated by subtracting the E_g from HOMO levels.

Electrochemical behaviors of **CP2** and **CA2** investigated by cyclic voltammetry (CV), and resulting data are shown in **Figure 1.20**.

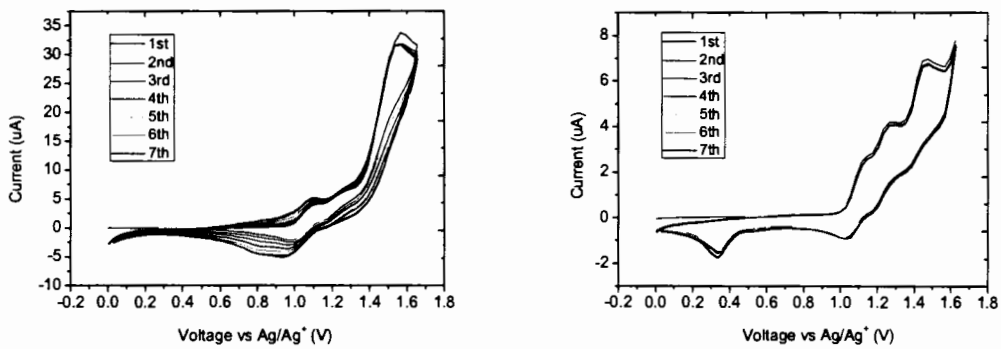


Figure 1.20 Cyclic voltammograms of CP2 (left) and CA2 (right) in dry CH_2Cl_2 with scan rate of 0.05 V/s and 0.1 M n-Bu_4NPF_6 as electrolyte, muti scan.

Multiple CV scans of **CA2** revealed identical CV curves with no additional peak at lower potentials on the cathodic scan (Epc) being observed. This suggests no electrochemical coupling at either the carbazole or anthracene peripheries, indicating electrochemically stable molecules. However, the target molecule **CA2** more stable than target molecule **CP2**. The CV curve of **CP2** shows three irreversible oxidation processes. The first oxidation is assigned to the removal of electrons from the

carbazole moiety resulting in carbazole radical cations (CBZ.$^+$). In all cases, during the cathodic scan additional peaks at lower potentials are observed, indicating electrochemical coupling reactions of the radical cations formed were taking place. As proposed in **Figure 1.21**, the generated CBZ.$^+$ is stabilized by electron delocalization through 1,8-substituted electron rich pyrene rings to form a pyrene radical cation (Py.$^+$) which is relatively less stable compared with the CBZ.$^+$. The Py.$^+$ readily undergoes a radical–radical dimerization coupling to form a stable neutral pyrene dimer as indicated by the presence of the cathodic peaks (Epc) around 0.61-0.94 V in their first CV scan and an increasing change in the CV curves under the repeated CV scans 10 **Figure 1.20**.

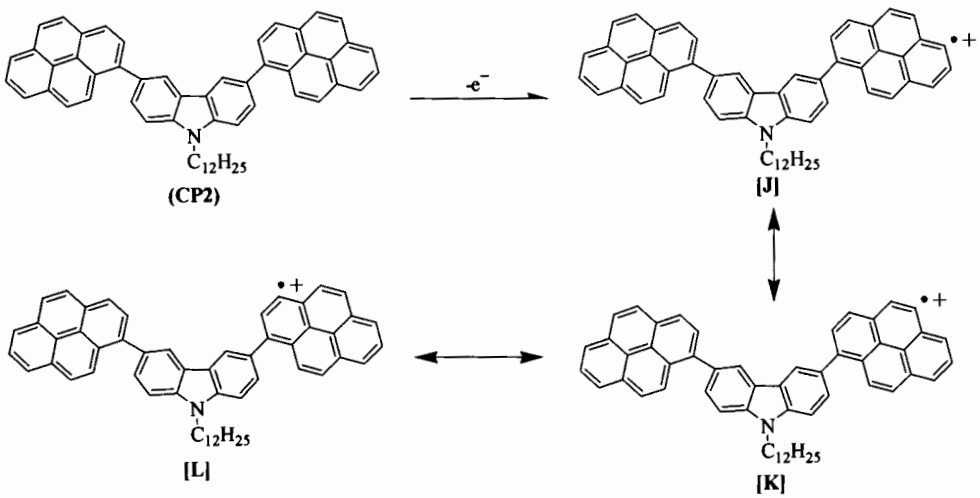


Figure 1.21 Oxidation process of pyrene

Moreover, they also showed similar wave in different scans, no distinct a slight shift of the CV curves. During in order oxidation cycle of all compounds, the oxidation progressively shifted to higher energy with increasing the aromatic unit. This might be the first example of pyrene and anthracene derivatives that undertake an electrochemical oxidation coupling reaction.

The HOMO energy levels of pyrene and anthracene derivatives were estimated to be -5.41 and -5.45 eV respectively. The LUMO energy levels of pyrene and anthracene derivatives were estimated to be -2.31 and -2.50 eV respectively (**Table 1.2**).

Table 1.2 Physical data of CP2 and CA2

Compound	Eg[b] (eV)	HOMO[c] (eV)	LUMO[d] (eV)
CP2	3.10	-5.41	-2.31
CA2	2.95	-5.45	-2.50

[b] Calculated from the absorption edge, Eg = 1240 per onset

[c] Estimated from HOMO = $-(4.44 + E^{ox}_{onset})$

[d] Estimated from LUMO = HOMO + E_g

1.2.4 HOMO and LUMO frontier orbitals of CP2 and CA2

To gain insights into the geometrical and electronic properties of these multiple substituted carbazoles, quantum chemistry calculations were performed using the DFT/B3LYP/6-31G(d,p) method. The optimized structures of **CP2** reveal that the attached pyrene units twist out of the plane of the carbazole forming bulky substituents around the carbazole. This would facilitate the formation of amorphous materials. In all cases **CP2** and **CA2**, π-electrons in the HOMO orbitals delocalize only over the carbazole and two substituents at the 3,6-positions substituted carbazole backbone, whereas after light irradiation (LUMO), the excited electrons are delocalized largely over the pyrene and anthracene plane.

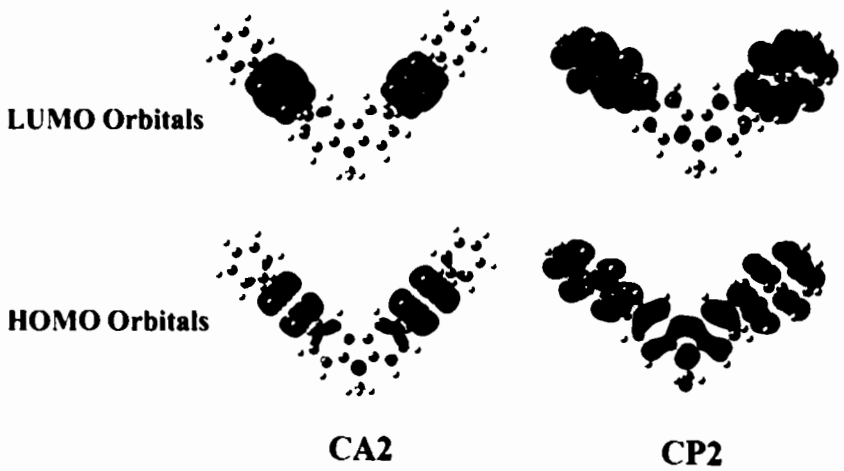
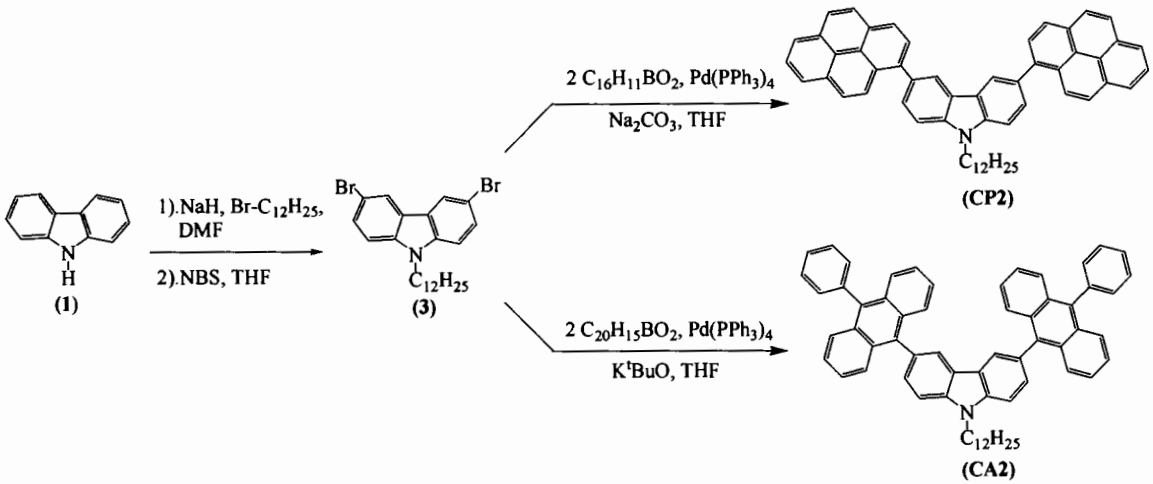


Figure 1.22 The HOMO (bottom) and LUMO (top) orbitals of CP2 and CA2 calculated by DFT/B3LYP/6-31G(d,p) method.

1.3 CONCLUSION

In conclusion, we have successfully synthesized pyrene and anthracene-substituted carbazole (**CP2**, **CA2**) by the Suzuki-cross coupling reaction of dibromo intermediates with pyrene-1-boronic acid and 10-phenyl-9-anthraceneboronic acid, respectively. The target molecules were characterized by using melting points, ^{1}H-NMR and ^{13}C-NMR spectroscopy, FT-IR spectroscopy and mass spectrometer.



The optical and electrochemical properties of both compounds can be tuned by varying the substituted on carbazole ring. The substitution dipyrene **CP2** to substituted anthracene **CA2** of carbazole increased the conjugation length of compounds resulting a red-shift and broad in absorption spectra. These compounds were emissive of blue light with high thermal stability which is potentially useful for applications in electroluminescent devices. Optimize structure and electron density of HOMO and LUMO have been performed by DFT/B3LYP/6-31G(d,p) method.

1.4 EXPERERIMENTAL

1.4.1 GENERAL EXPERIMENT

All solvents and reagents were purchased from Aldrich, Acros and Fluka received unless otherwise stated. Analytical thin-layer chromatography (TLC) was performed with Merck aluminium plates coated with silica gel 60 F_{254}. Column chromatography was carried out using gravity feed chromatography with Merck silica gel mesh, 60 Å. Where solvent mixtures are used, the portions are given by volume.

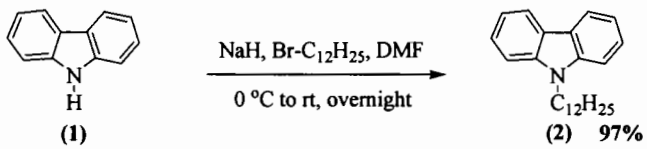
Melting points was measured by BUCHI 530 model in open capillary method and are uncorrected and reported in degree Celsius.

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Brüker AVANCE 300 MHz spectrometer. Chemical shifts (δ) are reported relative to the residual solvent peak in part per million (ppm). Coupling constants (J) are given in Hertz (Hz). Multiplicities are quoted as singlet (s), broad (br), doublet (d), triplet (t), quartet (q), and multiplet (m).

The IR spectra were recorded on Perkin-Elmer FT-IR spectrum RXI spectrometer. The absorption peaks are quoted in wavenumber (cm^{-1}). MALDI-TOF mass spectra were recorded on Bruker Daltonics (Bremen, Germany) Autoflex II Matrix-Assisted Laser Desoprtion/Ionization-Time of Flight Mass Spectrometer (BIFEX) using α-cyano-4-hydroxycin-namic acid as matrix. UV–Vis spectra were recorded on a Perkin–Elmer UV Lambda 25 spectrometer.

The electrochemistry was performed using a AUTOLAB spectrometer. All measurements were made at room temperature on sample dissolved in freshly distilled dichloromethane, 0.1 M tetra-*n*-butylammonium hexafluorophosphate as electrolyte. The solutions were degassed by bubbling with argon. Dichloromethane was distilled from calcium hydride. A glassy carbon working electrode, platinum wire counter electrode, and a Ag/AgCl/NaCl (Sat.) reference electrode were used.

1.4.2 Synthesis of 9-Dodecylcarbazole (2)



To a solution of carbazole (10.1021 g, 59.80 mmol) in DMF (93 mL) was added NaH (2.3540g, 89.58 mmol) and then 1-bromododecane (15.0000 g, 89.70 mmol). The reaction mixture was stirred at 0 °C to rt for 20 h. Water (100 mL) was added and the mixture was extracted with ethyl acetate (50 mL x 3). The combined organic phases were washed with a dilute HCl solution (50 mL x 2), water (100 mL), and brine solution (50 mL), dried over anhydrous Na_2SO_4, evaporated and purified by column chromatography to give a pale yellow viscous oil (19.7825 g, yield 97%) [11].

$C_{24}H_{33}N$;

^{1}H-NMR (300 Hz, $CDCl_3$):

δ = 8.24 (2H, d, J = 7.8 Hz), 7.79-7.49 (4H, m), 7.36 (2H, d, J = 14.4 Hz), 4.36 (2H, t, J = 6.9 Hz), 1.96 (2H, t, J = 6.6 Hz), 1.41-1.37 (18H, m) and 1.05 (3H, t, J = 5.4 Hz) ppm.

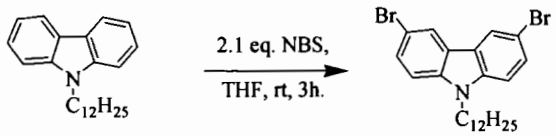
^{13}C-NMR (75 Hz, $CDCl_3$):

δ = 140.6 (2 x Cq), 125.7 (2 x CH), 123.0 (2 x Cq), 120.5 (2 x CH), 118.8 (2 x CH), 108.8 (2 x CH), 43.2 (N-$\underline{C}H_2$), 32.1 (CH_2), 29.8 (2 x CH_2), 29.75 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.1 (CH_2), 27.4 (CH_2), 22.9 (CH_2), 14.3 (CH_3) ppm.

IR (KBr):

ν_{max} = 3052, 2922, 2851, 1597, 1484, 1451, 1324, 1152, 746, 720 cm^{-1}.

1.4.3 Synthesis of 3,6-Dibromo-9-dodecylcarbazole(3)



(2) (3) 91%

In the flask, covered with aluminum foil, to a solution of 3-monobromo-9-dodecylcarbazolen **2** (0.5184 g, 1.54 mmol) in THF (15 mL) was added NBS (0.5772 g, 3.24 mmol) in small portions at 0°C. After stirred 0 °C to rt for 3 h, the reaction mixture was poured into water. The mixture was extracted with methylene chloride (20 mL x 3), washed with water (20 mL x 3), dried over anhydrous Na_2SO_4, evaporated and purified by column chromatography to give a white pearl solid (0.6951 g, yield 91%). [11]

$C_{24}H_{31}Br_2N$; m.p. = 50-52 °C

^{1}H-NMR (300 Hz, $CDCl_3$):

δ = 8.15 (2H, s), 7.55 (2H, d, J = 8.7 Hz), 7.29 (2H, d, J = 8.7 Hz), 4.25 (2H, t, J = 7.0 Hz), 1.85 (2H, s), 1.30-1.21 (18H, m), 0.88 (3H, t, J = 6.3 Hz)

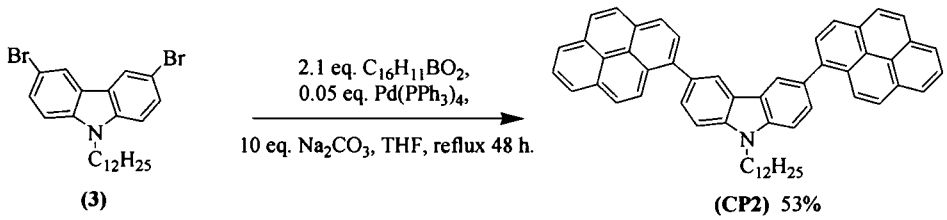
^{13}C-NMR (75 Hz, $CDCl_3$):

δ = 139.4 (2 x Cq), 129.0 (2 x CH), 123.5 (2 x CH), 123.3 (2 x CH), 111.9 (2 x Cq), 110.4 (2 x CH), 43.4 (N-CH_2), 31.8 (CH), 29.6 (2 x CH), 29.5 (CH), 29.4 (CH), 29.3 (2 x CH), 28.8 (CH), 27.2 (CH), 22.7 (CH), 14.1 (CH_3) ppm.

IR (KBr):

ν_{max} = 2950, 2918, 2848, 1592, 1469, 1289, 1224, 1057, 802, 720 cm^{-1}.

1.4.4 Synthesis of 9-Dodecyl-3,6-di(pyren-1-yl)carbazole (CP2)



To a stirred solution of 3,6-dibromo-9-dodecyl carbazole **3** (0.2000 g, 0.34 mmol) and $Pd(PPh_3)_4$ (0.0303 g, 0.02 mmol) in tetrahydrofuran (20 mL) were added pyrene-1-boronic acid (0.1759 g, 0.71 mmol) and an aqueous Na_2CO_3 solution (0.5576 g, 5.26 mmol). The mixture was refluxed for 48 h. After cooling, the mixture was extracted with dichloromethane (30 mL x 3), washed with water (30 mL x 3), dried over anhydrous, evaporated and purified by column chromatography to give a white pearl solids (0.2506 g, yield 53%).

$C_{56}H_{49}N$; m.p. = 170-173 °C

^{1}H-NMR (300 Hz, $CDCl_3$):

δ = 8.40 (2H, s), 8.34 (2H, d, J = 9.30 Hz), 8.25 (2H, d, J = 7.80 Hz), 8.20-8.10 (10H, m), 8.06-7.97 (4H, m), 7.80 (2H, d, J = 8.40 Hz), 7.65 (2H, d, J = 7.64), 4.47 (2H, t, J = 7.20 Hz), 2.10 (2H, t, J = 6.90 Hz), 1.57-1.30 (18H, m) and 0.91 (3H, t, J = 6.90 Hz)

^{13}C-NMR (75 Hz, $CDCl_3$):

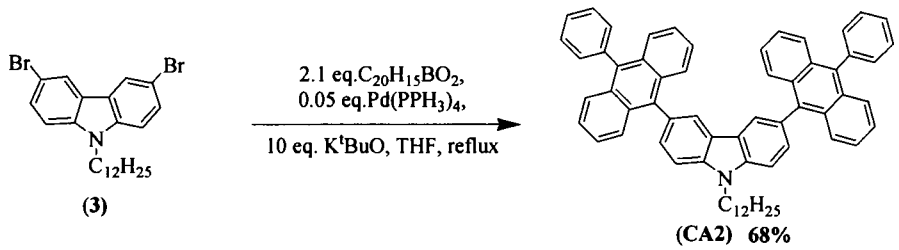
δ = 140.3 (2 x Cq), 138.7 (2 x Cq), 132.1 (2 x Cq), 131.6 (2 x Cq), 131.1 (2 x Cq), 130.3 (2 x Cq), 128.9 (2 x Cq), 128.7 (2 x CH), 128.2 (2 x CH), 127.5 (2 x CH), 127.3 (2 x CH), 127.1 (2 x CH), 125.9 (2 x CH), 125.7 (2 x CH), 125.1 (2 x Cq), 125.0 (2 x Cq), 124.9 (2 x CH), 124.6 (4 x CH), 123.1 (2 x Cq), 122.5 (2 x CH), 108.7 (2 x CH), 43.6 (N-$\underline{C}H_2$), 31.9 (CH_2), 29.7 (3 x CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.2 (CH_2), 27.5 (CH_2), 22.7 (CH_2), 14.1 (CH_3) ppm.

IR (KBr):

ν_{max} = 3038, 2919, 2849, 1600, 1480, 1347, 1279, 1153, 849, 817 cm^{-1}

MALDI-TOF (*m/z*) calcd for $C_{56}H_{49}N$: 735.3865; found 735.2981 (M^+).

1.4.5 Synthesis of 9-Dodecyl-3,6-di(anthracen-1-yl)carbazole (CA2)



To a stirred solution of 3,6-dibromo-9-dodecyl carbazole **3** (0.2507g, 0.42 mmol) and $Pd(PPh_3)_4$ (0.0246 g, 0.02 mmol) in tetrahydrofuran (25 mL) were added 10-phenyl-9 anthraceneboronic acid (0.2672 g, 0.89 mmol) and an aqueous *t*-BuOK solution (0.4789, 4.26 mmol). The mixture was refluxed for 48 h. After cooling, the mixture was extracted with dichloromethane (30 mL x 3), washed with water (30 mL x 3), dried over anhydrous, evaporated and purified by column chromatography to give a white pearl solids (0.3986 g, yield 68%).

$C_{64}H_{57}N$; m.p. = >200 °C

^{1}H-NMR (300 Hz, $CDCl_3$):

δ = 8.19 (2H, s), 7.84-7.80 (4H, m), 7.74-7.68 (6H, m), 7.63-7.48 (12H, m), 7.33-7.26 (8H, m), 4.57 (2H, t, *J* = 6.9 Hz), 2.15 (2H, t, *J* = 7.5 Hz), 1.50-1.20 (18H, m) and 0.86 (3H, t, *J* = 6.3 Hz)

^{13}C-NMR (75 Hz, $CDCl_3$):

δ = 140.4 (2 x Cq), 139.2 (2 x Cq), 137.9 (2 x Cq), 136.8 (2 x Cq), 131.42 (4 x CH), 131.36 (2 x CH),130.6 (4 x Cq), 129.9 (4 x Cq), 129.5 (2 x Cq), 129.4 (2 x CH), 128.4 (4 x CH), 127.4 (4 x CH), 126.9 (4 x CH), 124.9 (4 x CH), 124.8 (4 x CH), 123.3(2 x CH), 122.8 (2 x Cq), 108.8 (2 x CH),43.7 (N-$\underline{C}H_2$), 31.9 (CH_2), 29.69 (3 x CH_2), 29.66 (CH_2), 29.57 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 27.6 (CH_2), 22.7 (CH_2), 14.1 (CH_3) ppm.

IR (KBr):

ν_{max} = 2921, 2851, 1599, 1492, 1440, 1388, 1281, 1232, 1025, 767, 700 cm^-

MALDI-TOF (*m/z*) calcd for $C_{64}H_{57}N$: 839.4491; found 839.3175 (M^+).

CHAPTER 2

SYNTHESIS AND CHARACTERIZATION OF INDOLE DERIVATIVES FOR DYE-SENSITIZED SOLAR CELL

2.1 INTRODUCTION

2.1.1 Dye-sensitized solar cells (DSSCs)

Actually, the capability of human is to extent dependently on the available energy sources. In the developing countries, energy consumption has reached a level of over 4 x 1018 J already in the present annual worldwide and it is foresighted to multiply swiftly accompany with the increasing of world population and demand of energy [22]. As to the rising energy demand and more reduced fossil fuel reserves, the damaged environment and the improved greenhouse effect, affected by the combustion of fossil fuels, can out of control [23]. In other words, if the demands of energy have a chance to use renewable energy sources, the cost of environment could be decreased. Yearly, the sun could provide energy 3 x 1024 J to the earth [24]. This is about 750000 times greater than the present consumption of global population. The expectation to absorb the sunlight and turn it into electric power or to generate chemical fuels, for example, hydrogen, is become reality in the last two decades. Colloids and nanocrystalline films of various semiconductor systems have been manipulated in form of transform the solar energy directly to be the chemical or electrical energy. The traditional photovoltaic which is based on the solid-state connection devices, such as crystalline or amorphous silicon, has exception of changing solar energy approximately 20% to become electricity efficiencies. To invent the photovoltaic, however, is extravagant because it has to use intensive high temperature energy and high vacuum processes.

In 1991, O'Regan and Gratzel distributed a progress of an option solar harvesting device, dye-sensitized solar cell (DSSCs), [25]. The device supplies 7% of altering a solar energy to electricity, based on a mesoscopic inorganic semiconductor. Then 2.5% of energy proficiency had been reached in this research field. Moreover, the some semiconductor surfaces such as TiO_2 or ZnO is stimulated by an optical

absorbing chromophore with properties of charge disunion that can absorb the solar light and its excited state inject electrons into the semiconductor [26].

2.1.2 Dye-sensitized solar cells structure

The dye-sensitized solar cell is a low-cost solar cell belonging to the group of thin film solar cells. It is based on a semiconductor formed between a photo-sensitized anode and an electrolyte, a photoelectrochemical system. Therefore, the DSSCs structure consist of 4 part including organic sentitizer coating, electrolyte solution, counter electrode and dye sensitizer [27] as shown in **Figure 2.1**.

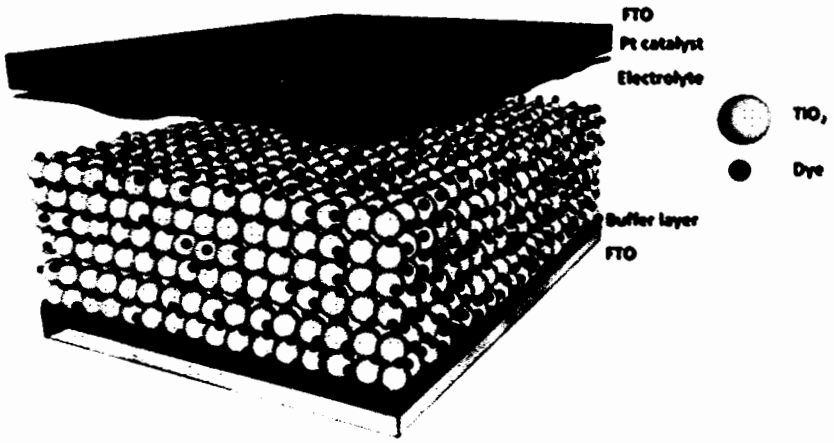


Figure 2.1 Dye-sensitized solar cells structure (DSSCs) structure [28]

2.1.2.1 Organic sensitizer coating with wide band gab semiconductor which is placed in contact with a redox electrolyte, the material of choice has been TiO_2 (anatase).

2.1.2.2 An electrolyte solution containing redox couple such as I^-/I_3^-, the regeneration of the sensitizer by iodide intercepts the recapture of the conduction band electron by the oxidized dye.

2.1.2.3 A counter electrode which is a platinized conductive glass substrate such as fluorine-doped tin oxide glass (FTO).

2.1.2.4 Dye sensitizer serve as the solar energy absorber in DSSC, whose proprieties will have much effect on the light harvesting efficiency and the overall photoelectric conversion efficiency. The ideal sensitizer for dye-sensitized solar cells should absorb all light below a threshold wavelength of about 920 nm. In addition, it

should be firmly grafted to the semiconductor oxide surface and inject electrons to the conduction band with a quantum yield of unity. Its redox potential should be sufficiently high that it can be regenerated rapidly via electron donation from the electrolyte or a hole conductor. Finally, it should be stable enough to sustain at least 108 redox turnovers under illumination corresponding to about 20 years of exposure to natural light.

2.1.3 Principle of Dye-sensitized solar cells

The working principle of DSSCs was shown in **Figure 2.2**. Dye in dye-sensitized solar cells discharges electrons when hit by sunlight. Discharged electrons move toward a transparent anode (negative electrode) through titanium dioxide (titania particles). Electrons that have reached the transparent anode (negative electrode) move toward counter electrode (positive electrode) through an external circuit. Iodide electrolyte receives electrons from the positive electrode. Electrolyte provides received electrons to dye, thanks to the working of iodide ions. Dye received electrons returns to their original condition. Dye-sensitized solar cells generate power by repeating the cycle [29].

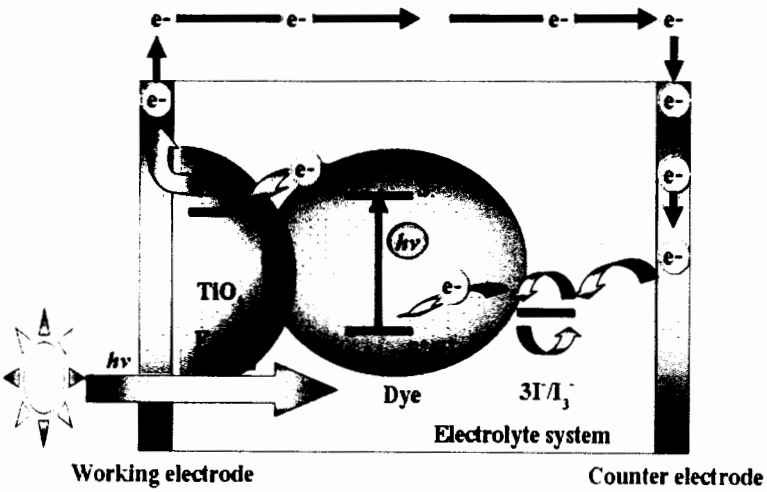


Figure 2.2 Working principle of DSSCs [30]

2.1.4 Literature reviews

In this part, the publications of synthesis and study optical properties of dye-sensitizer for DSSCs application would be described. For example:

In 2007, Kim, D et al. [31] investigated that the organic dyes (**JK-24, JK-25** and **JK-28**) containing *N*-(9,9-dimethylfluoren-2-yl)carbazole or *N*-(4-(2,2-diphenylvinyl)phenyl)carbazole as electron donor and cyanoacrylic acid as electron acceptor bridged by thiophene units, gave an overall conversion efficiency (η) of 3.87-5.15%. Although many structure frameworks such as coumarin, aniline and indoline have been employed as good electron donor unit, the small molecular organic dyes containing the *N*-substituted carbazole structural have been little explored for DSSCs.

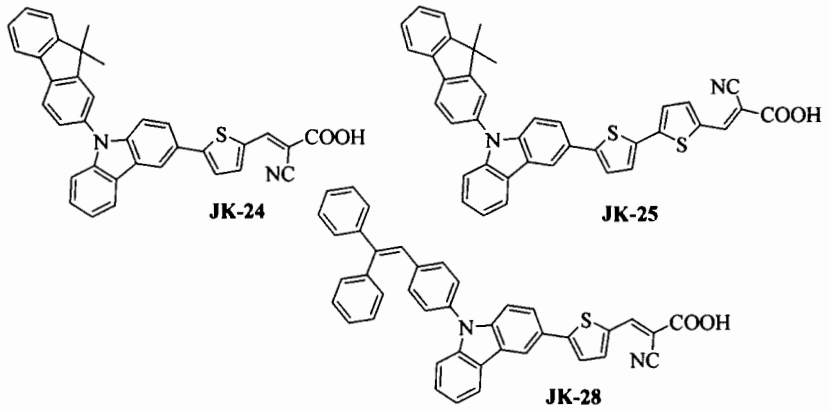


Figure 2.3 Chemical structures of JK-24, JK-25 and JK-28 dyes

In 2009, Chang, Y J. et al. [32] reported that the highly efficient and stable organic dyes (**1P-PSP** and **1N-PSP**) composed of triphenylamine or *N,N*-diphenylnaphthalen-1-amine moiety as the electron donor and cyanoacrylic acid moiety as the electron acceptor with an overall conversion efficiency of 5.25-7.08%.

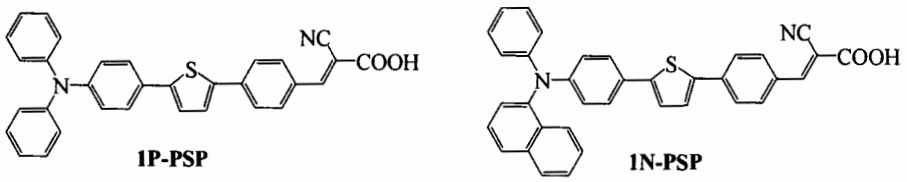


Figure 2.4 Chemical structures of 1P-PSP and 1N-PSP dyes

In 2012, Wan, Z. et al. [33] investigated that the organic dyes (**CBZ, WD-5**, and **DTA**) containing carbazole, phenothiazine or diphenylamine as electron donor and cyanoacrylic acid as electron acceptor bridged by phenyl units, gave an overall conversion efficiency of 1.77-2.03%.

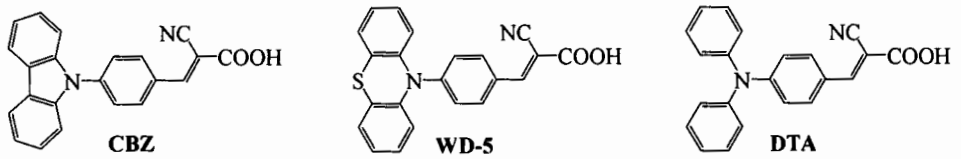


Figure 2.5 Chemical structures of CBZ, WD-5, and DTA dyes

In 2009, Jaejung, K. et al. [34] designed and synthesize organic dye benzo[*cd*]indole **JK51**. Firstly, benzoindole aldehyde **10JK** were synthesized from 2, 6, 7, 8-tetrahydro-1-phenylbenzo[*cd*]indole **1JK** *via* four steps reactions. Then aldehyde **10JK** were reacted with cyanoacetic acid and piperidine to gain the substance **JK51** as shown in **Figure 2.6**. The benzo[*cd*]indole **JK51** show conversion conversion efficiency at 8.42%, short circuit at 17.43 mA/cm^2, open circuit voltage at 0.680 V, and fill factor at 0.71.

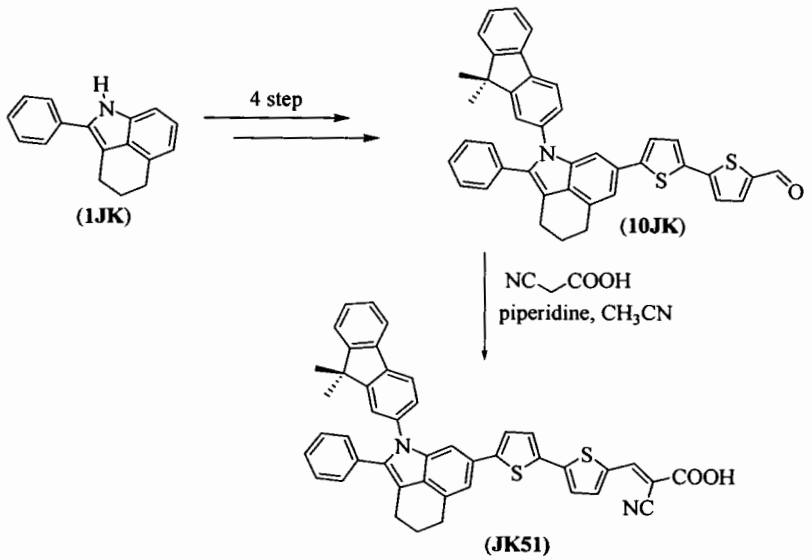


Figure 2.6 Dye-organic synthesis included of benzo[*cd*]indole group

In 2012, Shingo, K. et al. [35] synthesized new type of organic dying included of carbazole (**MK75, MK79, MK80**), indole (**MK81-83**), and indoline (**MK84-86**) as electron donors. These substances had cyanoacrylic acid which was electron acceptors and they were joined together with bi-3-*n*-hexylthiophene as shown in **Figure 2.7.** As for bringing this to study about conversion efficiency, carbazole **MK75, MK79** and **MK80** was valued from 5.1 to 5.4%, indole **MK81-83** was valued between 3.5 to 3.9%, and indoline **MK84-86** was valued from 3.0 to 3.7%.

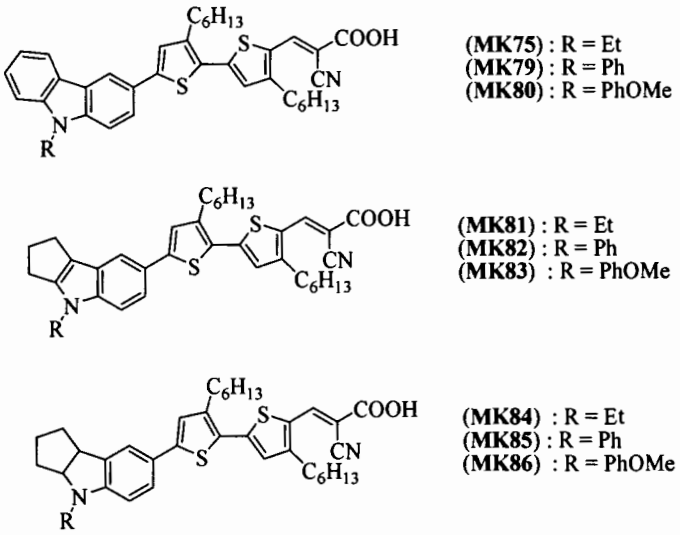


Figure 2.7 The structure of dye molecules included of carbazole (MK75, MK79, MK80), indole (MK81-83) and indoline (MK84-86)

In 2014, Gang, W. et al. [36] studied about the property of electricity and dye-sensitized which had a system of D-π-A in form of isoindigo group. The study was done by synthesizing **ID1**, **ID2**, and **ID3** as shown in **Figure 2.8.** The finding indicated that **ID1** had extended range of absorption and energy conversion efficiency (η). Moreover, **ID1** was the utmost value at 3.33% under 100 mW/cm^2 simulated AM 1.5 G solar irradiation.

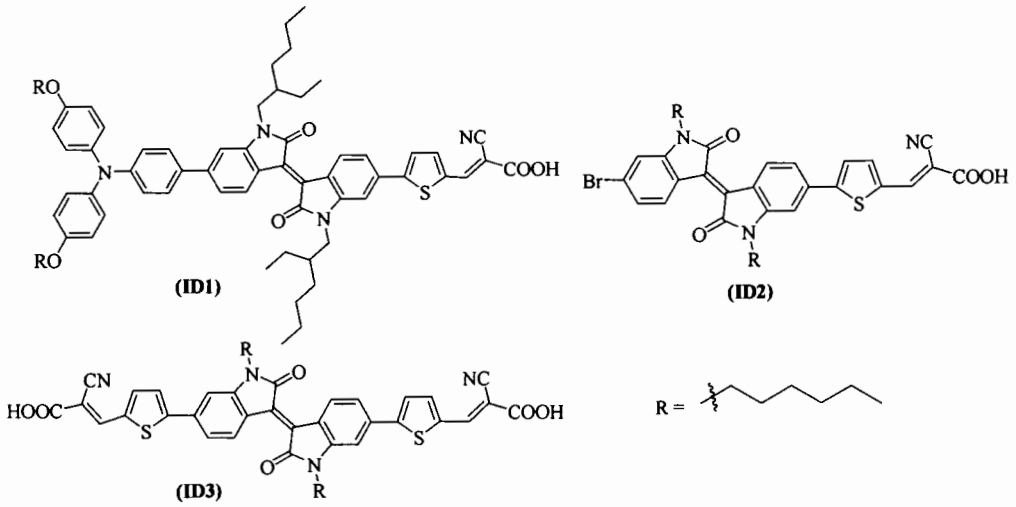


Figure 2.8 The structure of ID1-ID3 dye-sensitized molecules

In 2008, the efficiency and stability of organic dye **JK79**, improveing working's quality of dye-sensitized solar cells, were studied by Kim, D. et al [37]. The improvement could be done by combining of bis-dimethylfluorenyl amino and indole group to target dye-sensitized molecule for increasing pi bond conjugation. The target molecule **JK79** was synthesized from indole substance **10JK**. The four reaction steps of compound **10JK** gave aldehyde **13JK**, and then it was reacted with cyanoacetic acid and piperidine to be Knoevenagel consideration to gain the target compound **JK79** as shown in **Figure 2.9.** The result of photo properties show that compound **JK79** gave short circuit at 13.62 mA/cm^2, open circuit voltage at 0.705 V, fill factor at 0.74 and conversion efficiency at 7.18%

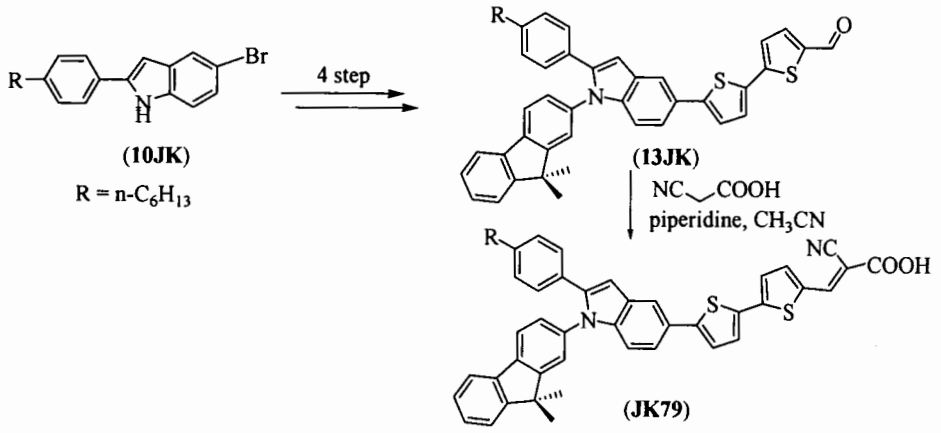


Figure 2.9 Dye-organic synthesis (8)

In 2013, Kim, B. H. et al. [38] synthesized organic dying (**DP-T**) and (**DP-P**) which included thiophene and *N*-methyl pyrrole as the connective between electron donors and electron acceptors respectively. The targets molecules were synthesized by Knoevenagel condensation of aldehyde (**1c**) and (**2d**) with cyanoacetic acid as shown in **Figure 2.10.** For bringing this to study about conversion efficiency, the result revealed that a thiophene derivative **DP-T** had the highest value as 3.53% and a methyl pyrrole derivative **DP-P** had the utmost value as 3.03%. It was clear that a thiophene derivative **DP-T** was more efficient than a methyl pyrrole derivative **DP-P**. This affected from thiophene captured and absorbed solar energy better than *N*-methyl pyrrole, so it was more conversion efficiency than *N*-methyl pyrrole.

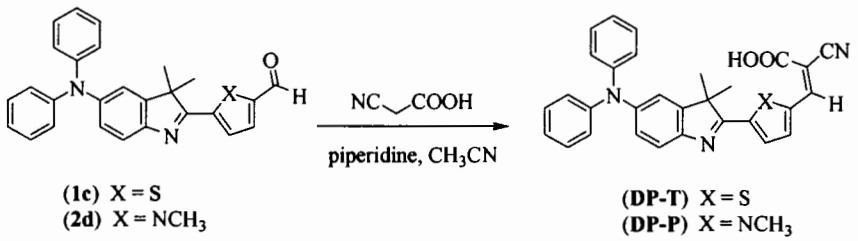
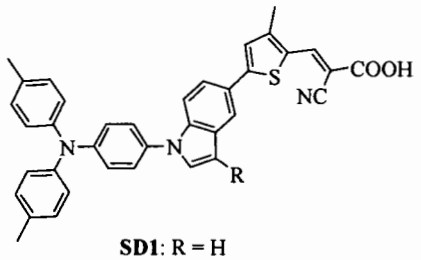


Figure 2.10 The synthesis of organic dying included of thiophene and *N*-methyl pyrrole as the connectors

In 2014, dye-sensitized type D-D-π-A, indole **SD1** and **SD2** (**Figure 2.11**), were synthesized and studied by Liu, X. et al [39]. The synthesis compounds included triphenylamine and indole as electron donors. The results of conversion efficiency indicated that the conversion efficiency (η) of dye-sensitized type **SD2** at 6.74% higher than the conversion efficiency (η) at 5.53% of **SD1**. It was believe that donated effective of SCN group of **SD2** stronger than H aton of **SD1**.



SD1: R = H
SD2: R = SCN

Figure 2.11 structure of SD1 and SD2

In 2015, new D-π-A type indole dye-sensitized **D1**, **D2** and **D3** (**Figure 2.12**), were synthesized and studied by BaBu, D. D. et al [40]. The target dyes included indole as electron donor and cyanoaceticacid, rhodanine-3-acetic acid and 4-aminobenzoic acid as electron acceptor, respectively. The dye **D1**, **D2** and **D3** gave conversion efficiency at 1.04, 0.35 and 1.18%. Interestingly, the absorption maximum red shifted in the order **D3<D<D2** but the device sensitized by **D3** displayed the highest efficiency.

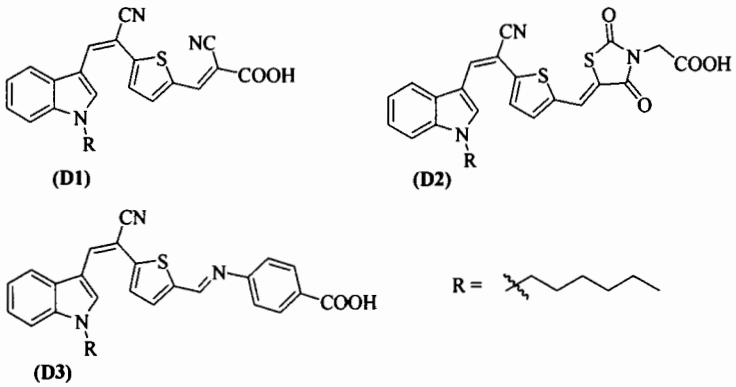


Figure 2.12 structure of D1, D2 and D3

2.1.5 Aim of the thesis

According to literature reviews, dye-sensitized molecule consist of major three parts [41]. The first part is electron donating group (D) which is electron rich funaction such as hetroaromatic group; carbazole, coumarins, triphenylamines and indolines. The second part is electron acceptor (A) which is electron withdrawing and polar group such as carboxyl group and sulfonyl group. The final part of dye is π-

spacer (π) which is conjugation linker betaween electron donating and electron acceptor group such as double bond and phenyl group.

In this research, we synthesized and characterized a new series of indole derivatives for dye-sensitized solar cells (DSSCs). The indole derivatives as electron donating group, containing double bond and phenyl group as π-spacer and benzoic and cyanoacetic acid group as electron acceptor, were designed, synthesized and characterized. The chemical structure of **In1-In5** are shown in **Figure 2.13**.

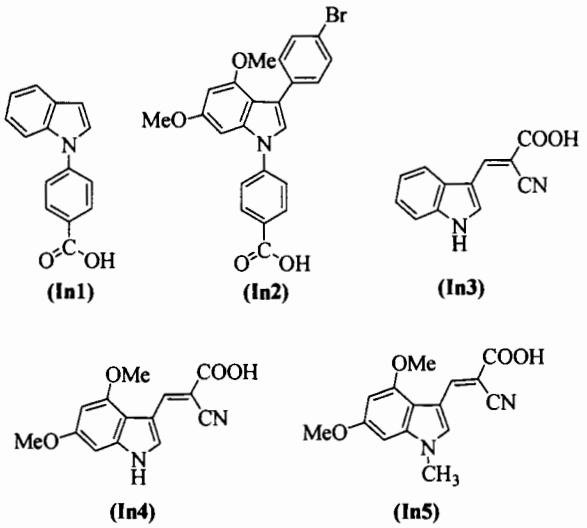


Figure 2.13 The target molecules In1-In5

2.1.5.1 Objectives of this research

To synthesize a series of aromatic or double bond and carboxyl-substituted indole derivatives as dye sensitizer for dye-sensitized solar cells.

To characterize and identify the target product during the synthesis steps.

2.2 RESULTS AND DISCUSSION

In this research, we synthesize and characterize a new series of dye-sensitized molecule for dye-sensitized solar cells (DSSCs) based on indole derivatives as electron donating group. Moreover, we designed and synthesized the following a indole containing double bond and phenyl group as π-spacer and benzoic and

cyanoacetic acid group as electron acceptor. The chemical structure of target molecules, **In1-In5**, are shown in **Figure 2.14**.

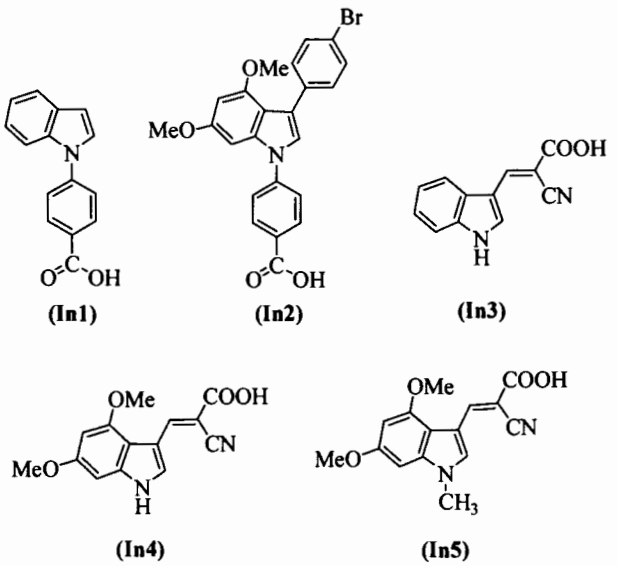


Figure 2.14 Structure of In1-In5

The target carbazole **In1-In5** were successfully synthesized by Ullman coupling, hydrolysis reaction and Knoevenagal condensation. The targets **In1** and **In2** were synthesized from Ullman coupling of indole with iodoarylester following by hydrolysis reaction. In addition, The indoles **In3-In5** was synthesized *via* Knoevenagal condensation of indolealdehyde with cycanoacetic acid as shows in **Figure 2.15**.

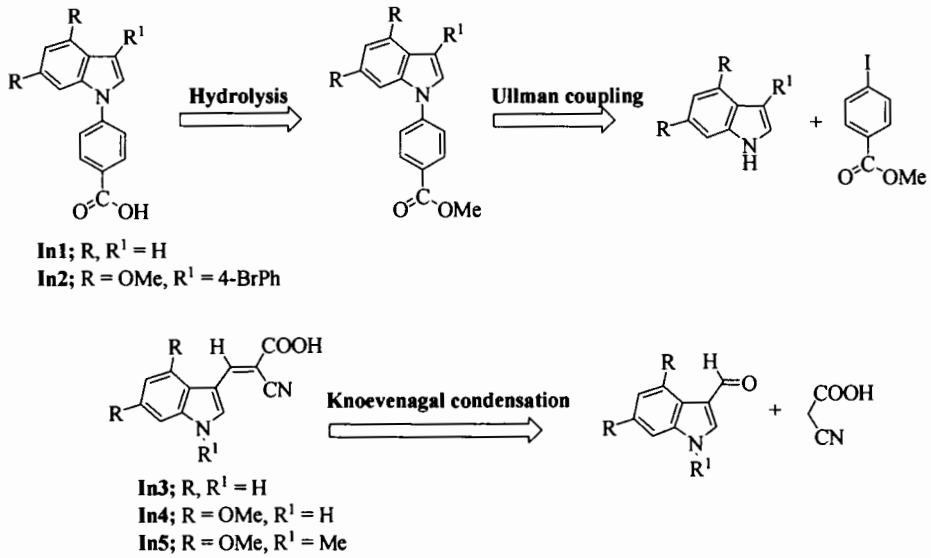


Figure 2.15 Retrosynthesis of carbazole In1-In5

2.2.1 Synthesis and characterization of 4-(indol-1-yl)benzoic acid (In1)

The target dye **In1**, containing indole as electron donating group, phenyl as π-spacer at *N*-position of indole and carboxyl group as electron acceptor was designed. The 4-(indol-1-yl)benzoic acid **(In1)** was successfully synthesized by Ullman coupling and hydrolysis reaction. First step, compound **4** was synthesized by Ullman coupling reaction of indole with methyl 4-iodobenzoate. The treatment of indole and methyl 4-iodobenzoate in the presence of copper iodide and trans-1,2-diaminocyclohexane as catalyst and K_3PO_4 as a base in toluene at reflux for 48 h led to compound **4** in 94% as show in **Figure 2.16**.

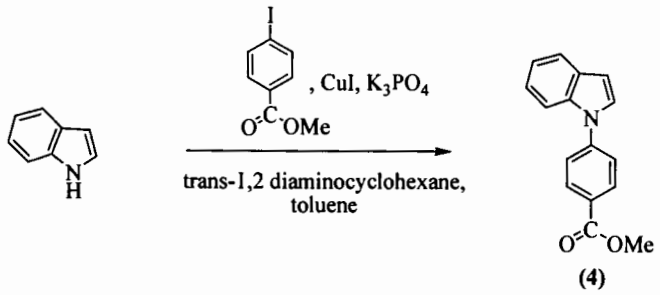


Figure 2.16 Synthesis of methyl 4-(indol-1-yl) benzoate 4

The compound **4** was confirmed by ^{1}H-NMR and ^{13}C-NMR. ^{1}H-NMR spectra of compound **4** shows new peak of four protons of aryl group and the singlet peak of O-CH_3 protons at δ = 3.98 (3H) ppm. Remarkable, the NH proton of indole was absented. Moreover, ^{13}C-NMR spectrum shows peck of C = O carbons at δ = 166.4 ppm, new peak of six carbons of aryl carbon and new signal of O-$\underline{C}H_3$- at δ = 52.2 ppm. These results confirmed that product was methyl 4-(indol-1-yl) benzoate **4.**

The mechanism of Ullman coupling reaction follows a three-step mechanism cycle as described in **Figure 2.17**. The reaction of CuI, indole and K_3PO_4 afforded intermediate **[M].** The oxidative addition at C-I bond of methyl 4-iodobenzoate with intermediate **[M]** gave organocopper complex **[N]**. Then, reductive elimination of complex **[N]** releases the coupling product **4** and the active CuI catalyst is regenerated.[42]

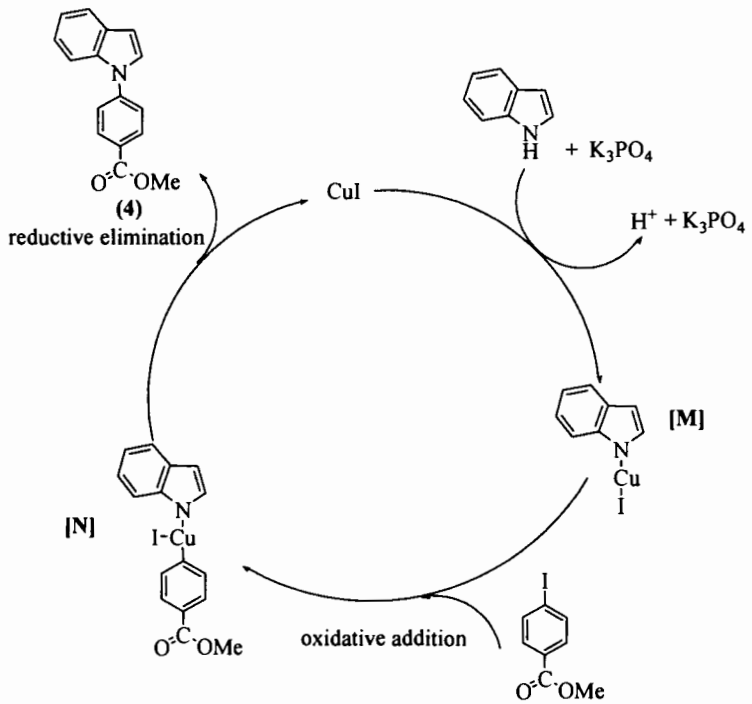


Figure 2.17 The proposed mechanism of Ullmann coupling rection

Finally, the target molecule **In1** was synthesized by hydrolysis reaction. The treatment of methyl 4-(indol-1-yl)benzoate **4** and KOH as the base in THF and IPA at reflux for 2 h afforded target molecules **In1** in 64% yields as shows in **Figure 2.18**

Figure 2.18 Hydrolysis reaction of methyl 4-(indol-1-yl)benzoate 4

The compound **In1** was confirmed by ^{1}H-NMR and ^{13}C-NMR. ^{1}H-NMR spectra of compound **In1** still show ten proton of aryl group but peak of O-C$\underline{H}_3$ disappeared. Remarkable, ^{13}C-NMR spectrum of **In1** disappeared carbon peck of O-CH_3 group. Moreover, the high resolution mass spectrometry (MALDI-TOF) of compound **In1** found 237.1056 (calcd for $C_{15}H_{11}NO_2$: *m/z* 237.0790). These results confirmed that product was 4-(indol-1-yl) benzoic acid **In1**.

The mechanism of hydrolysis reaction was proposed *via* three-step as show in **Figure 2.19**[22]. First step, the hydroxide nucleophiles attacks at the electrophilic C=O of ester breaking the π bond and creating the intermediate **[O]**. The intermediate **[O]** collapses, reforming the C=O results in the loss of the leaving group the alkoxide, MeO^-, leading to the carboxylic acid. Finally, A very rapid equilibrium where the alkoxide, MeO^- functions as a base deprotonating the carboxylic acid, RCO_2H, (an acidic work up would allow the carboxylic acid **In1** to be obtained from the reaction).

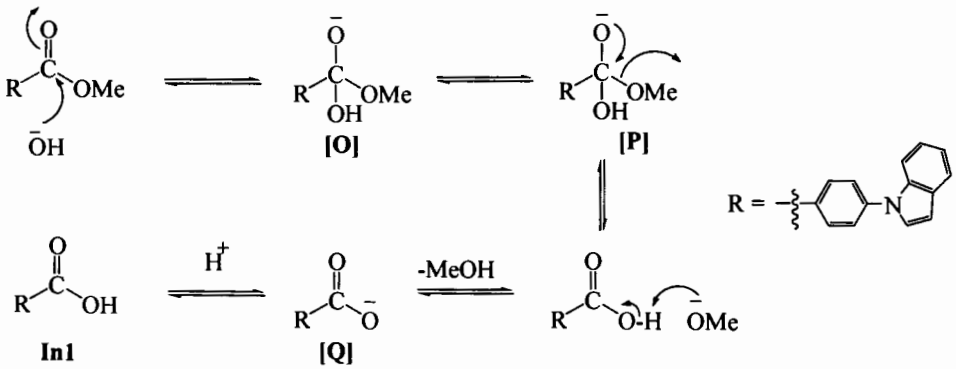


Figure 2.19 The proposed mechanism of hydrolysis reaction

2.2.2 Synthesis and characterization 4-(3-(4-bromophenyl)-4,6-dimethoxyindol-1-yl)benzoic acid (In2)

The target dye **In2**, containing 4,6-dimethoxyindole as electron donating group, phenyl as π-spacer at *N*-position of indole and carboxyl group as electron acceptor was designed. The 4-(3-(4-bromophenyl)-4,6-dimethoxyindol-1-yl) benzoic acid **(In2)** was synthesized *via* Ullman coupling and hydrolysis reaction similar to **In1** synthetic partway. First step, methyl 4-(3-(4-bromophenyl)-4,6-dimethoxyindol-1-yl) benzoate **6** was synthesized by Ullman coupling reaction of indole **5** with methyl 4-iodobenzoate. The treatment of indole **5** and methyl 4-iodobenzoate in the presence of copper iodide and trans-1,2-diaminocyclohexane as catalyst and K_3PO_4 as a base in toluene at reflux for 48 h led to ester **6** in 41% as show in **Figure 2.20**.

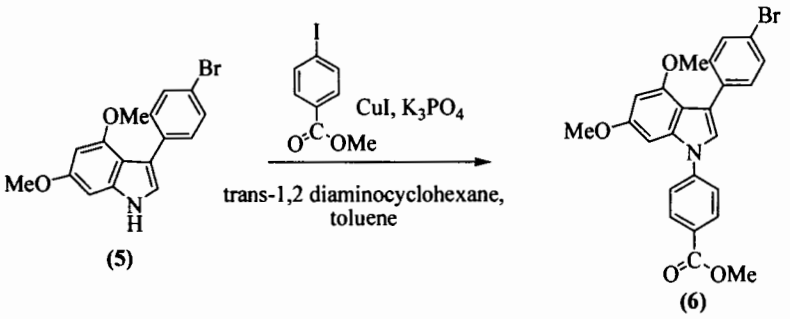


Figure 2.20 Synthesis of methyl 4-(3-(4-bromophenyl)-4,6-dimethoxyindol-1-yl) benzoate 6

The compound **6** was confirmed by ^{1}H-NMR and ^{13}C-NMR. ^{1}H-NMR spectra of compound **6** show new peak of four protons of aryl group and new peak of three protons of O-CH_3 group. Remarkable, the N-H proton of indole **5** was absented. Moreover, ^{13}C-NMR spectrum shows peck of O=C carbons at δ = 166.3 ppm, new peak of six carbons of aryl carbon and new peak of one carbon of O-$\underline{C}H_3$ group. These results confirmed that product was of methyl 4-(3-(4-bromophenyl)-4,6-dimethoxyindol-1-yl)benzoate **6**.

The mechanism of Ullmann coupling of compound **6** similar to mechanism of Ullmann coupling of compound **4** as shown in **Figure 2.17**.

Finally, the target molecules **In2** was synthesized by hydrolysis reaction. The treatment of methyl 4-(3-(4-bromophenyl)-4,6-dimethoxyindol-1-yl)benzoate **6**

and KOH as the base in THF and IPA at reflux for 2 h afforded target molecules **In2** in 46% yields as shows in **Figure 2.21.**

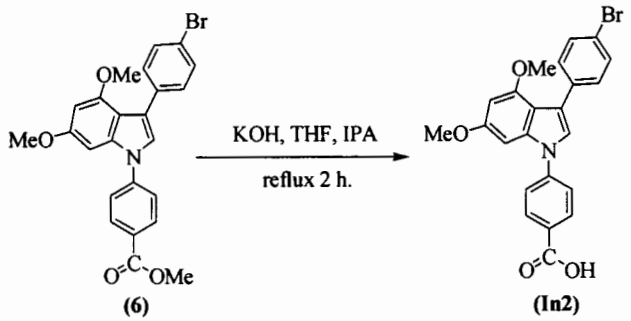


Figure 2.21 Hydrolysis reaction of methyl 4-(3-(4-bromophenyl)-4,6-dimethoxy indol-1-yl)benzoate 6

The compound **In2** was confirmed by ^{1}H-NMR and ^{13}C-NMR. ^{1}H-NMR spectra of compound **In2** still show eleven protons of aryl group but proton of O-CH_3 reduced to six protons. Remarkable, ^{13}C-NMR spectrum of **In2** shown two carbon peck of O-CH_3 group. Moreover, the high resolution mass spectrometry (MALDI-TOF) of compound **In2** found 451.0924 (calcd for $C_{23}H_{18}BrNO_4$: *m/z* 451.0419). These results confirmed that product was 4-(3-(4-bromophenyl)-4,6-dimethoxyindol-1-yl) benzoic acid **(In2)**.

The mechanism of hydrolysis of compound **6** similar to mechanism of hydrolysis of compound **4** as shown in **Figure 2.19**.

2.2.3 Synthesis and characterization of 2-cyano-3-(indol-3-yl)acrylic acid (In3)

The target dye **In3**, containing indole as electron donating group, double bond as π-spacer at C3-position of indole and cyanoacetic acid as electron acceptor was designed. The 2-cyano-3-(indol-3-yl)acrylic acid **(In3)** was easy synthesized by Knoevenagal condensation. The commercial indole-3-carbaldehyde **7** was reacted with cyanoacetic acid and piperidine in chloroform at reflux for 48 h led to 2-cyano-3-(indol-3-yl)acrylic acid **In3** in 24% as show in **Figure 2.22**.

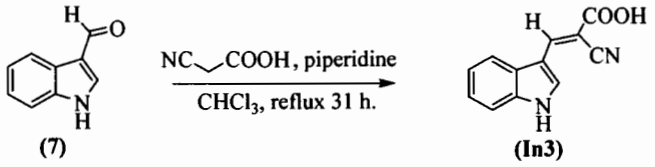


Figure 2.22 Knoevenagal reaction of indole-3-carbaldehyde 7

The 2-cyano-3-(indol-3-yl)acrylic acid **In3** was confirmed by ^{1}H-NMR and ^{13}C-NMR. ^{1}H-NMR spectra of compound **In3** still show five protons of aryl and one protons of N-H group and new one proton peak of C=C-H group. Remarkable, the formyl proton (–CHO) of indole-3-carbaldehyde **7** was absented. In addition, ^{13}C-NMR spectrum shows new peck of carboxyl carbons (COOH) at δ = 165.9 ppm, new peak of CN carbons at δ = 110.6 ppm and new two carbon peak of alkene group. Moreover, the high resolution mass spectrometry (MALDI-TOF) of compound **In3** found 212.0361 (calcd for $C_{12}H_8N_2O_2$: *m/z* 212.0586). These results confirmed that product was 2-cyano-3-(indol-3-yl)acrylic acid **(In3)**.

The mechanism of Knoevenagal reaction follows a step mechanism as described in **Figure 2.23**.[44]. In the first step, deprotonation of the cyanoacetic acid by piperidine afforded carbanion intermediate **[R].** On the other hand, aldehyde **7** reacted with piperidine to give intermediate **[S]** and then release OH^- to give intermediate **[T]**. Next step, carbanion **[R]** attack at C=N of intermediate **[T]** gave intermediate **[U]**. Finally, elimination of piperidine afford target molecule **In3**.

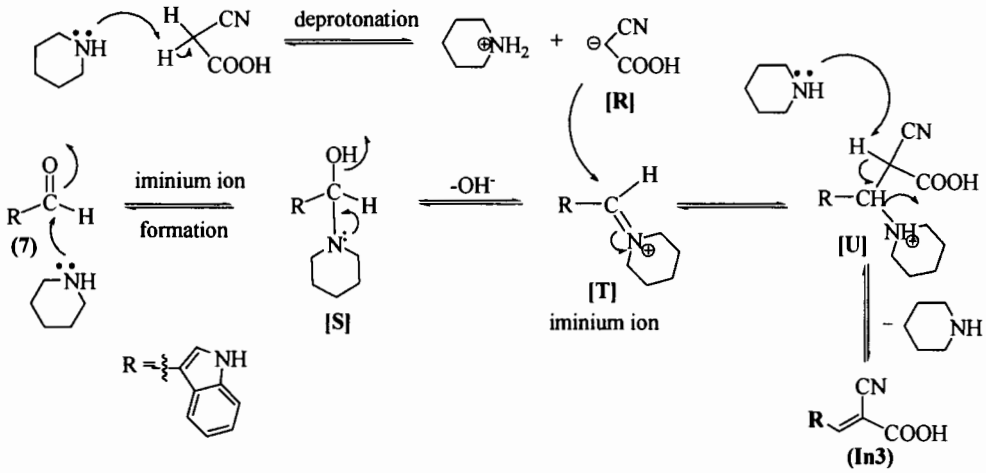


Figure 2.23 The proposed mechanism of Knoevenagal reaction

2.2.4 Synthesis and characterization of 2-cyano-3-(4,6-dimethoxyindol-3-yl)acrylic acid (In4)

The target dye **In4**, containing 4,6 dimethoxyindole as electron donating group, double bond as π-spacer at C3-position of indole and cyanoacetic acid as electron acceptor was designed. The 2-cyano-3-(4,6-dimethoxyindol-3-yl)acrylic acid (**In4**) was successfully synthesized by Vilsmeier–Haack reaction and Knoevenagal condensation. First step, aldehyde **9** was synthesized by Vilsmeier–Haack reaction of 4,6-dimethoxyindole **8** [45]. The treatment of compound **8** with phosphoryl chloride in *N,N*-dimethylformamide stirred at 0 °C to room temperature for 1 h led to compound **9** in 58% as show in **Figure 2.24**.

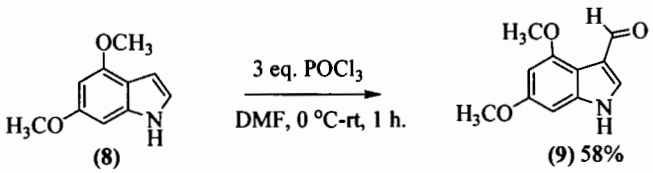


Figure 2.24 Vilsmeier–Haack reaction of 4,6-dimethoxyindole 8

The compound **9** was confirmed by ^{1}H-NMR and ^{13}C-NMR. ^{1}H-NMR spectra of compound **9** show new one peak proton of CHO group at 10.36 ppm, still show six protons of O-CH_3 and one peak of N-H proton but protons of aryl group reduced to three proton. Moreover, ^{13}C-NMR spectrum shows new peck carbon of CHO group at δ = 188.3 ppm and one C-H carbon peak was absented compare to ^{13}C-NMR of starting material. These results confirmed that product was 3-formyl-4,6-dimethoxyindole **9**.

The mechanism of Vilsmeier–Haack reaction follows a step mechanism as described in **Figure 2.25**. In the first step, reaction of DMF and $POCl_3$ gave intermediate **[V]** and then then release $PCl_2O_2^-$ afforded intermediate **[W]**. Next step, reaction C3 of indole **8** attack at C=N of intermediate **[W]** gave intermediate **[X]** and Cl^-. Deprotonation of intermediate **[X]** gave intermediate **[Y]**. Finally, imminium hydrolysis of intermediate **[Y]** afford indole aldehyde [46] **9**.

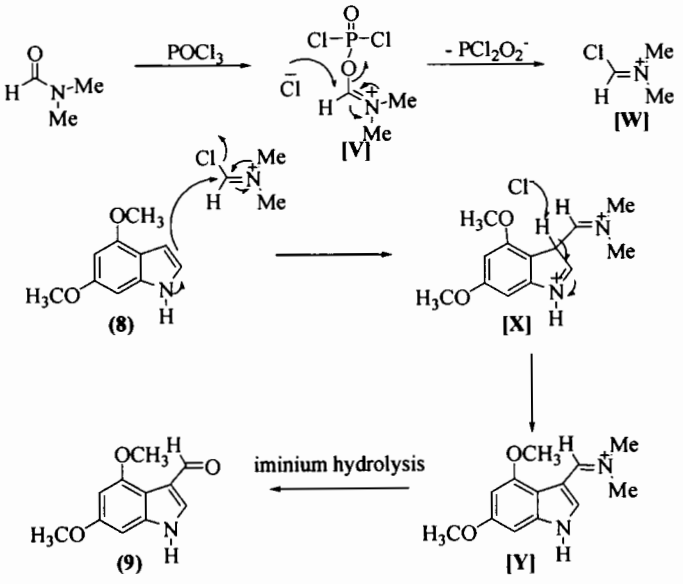


Figure 2.25 The proposed mechanism of Vilsmeier–Haack reaction

Finally, the target molecule **In4** was synthesized by Knoevenagal reaction. The 3-formyl-4,6-dimethoxyindole **9** reacted with cyanoacetic acid and piperidine in chloroform at reflux for 48 h led to 2-cyano-3-(4,6-dimethoxyindol-3-yl) acrylic acid **In4** in 27% as show in **Figure 2.26**.

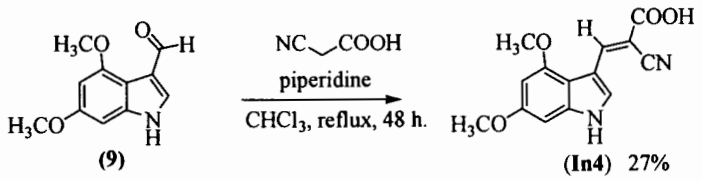


Figure 2.26 Knoevenagal reaction of 3-formyl -4,6-dimethoxyindole 9

The 2-cyano-3-(4,6-dimethoxyindol-3-yl)acrylic acid **In4** was confirmed by ^{1}H-NMR and mass spectrometry. ^{1}H-NMR spectra of compound **In4** still show three protons of aryl, one protons of N-H group and new one proton peak of C=C-H group. Remarkable, the formyl proton (–CHO) of 3-formyl -4,6-dimethoxyindole **9** was not appeared. Moreover, the high resolution mass spectrometry (MALDI-TOF) of compound **In4** found 272.0978 (calcd for $C_{14}H_{12}N_2O_4$: *m/z* 272.0797). These results confirmed that product was 2-cyano-3-(4,6-dimethoxyindol-3-yl)acrylic acid **In4**.

The mechanism of Knoevenagal reaction of compound **In4** similar to mechanism of Knoevenagal reaction of compound **In3** as shown in **Figure 2.23**.

2.2.5 Synthesis and characterization of 2-cyano-3-(4,6-dimethoxy-*N*-methylindol-3-yl) acrylic acid (In5)

The target dye **In5**, containing 4,6dimethoxy-*N*-methylindole as electron donating group, double bond as π-spacer at C3-position of indole and cyanoacetic acid as electron acceptor was designed. The 2-cyano-3-(4,6-dimethoxy-*N*-methylindol-3-yl)acrylic acid (**In5**) was successfully synthesized by methylation and Knoevenagal reaction. First step, 3-formyl-4,6-dimethoxyindole **9** was synthesized by methylation reaction at the *N*-position. Treatment of 3-formyl -4,6-dimethoxyindole **9** with sodium hydride (NaH) and methyl iodide in DMF for 1.5 h under N_2 gas gave 3-formyl-4,6-dimethoxy-*N*-methylindol **10** in 97% as show in **Figure 2.27**.

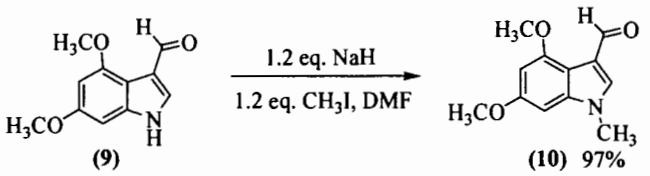


Figure 2.27 Methylation of 3-formyl -4,6-dimethoxyindole 9

The 3-formyl-4,6-dimethoxy-*N*-methylindol **10** was confirmed by ^{1}H-NMR and ^{13}C-NMR [25]. ^{1}H-NMR spectra of 9-dodecylcarbazole **2** still show proton of –CHO, aryl and OCH_3 group and shows new singlet peak of N-C$\underline{H}_3$- proton at δ = 3.96 ppm. Remarkable, NH proton of 3-formyl-4,6-dimethoxyindole **9** was absented. Moreover, ^{13}C-NMR spectrum shows new signal of N-$\underline{C}H_3$- at δ = 39.2 ppm. These results confirmed that product was compound **10.**

The mechanism of methylation reaction of compound **10** similar to mechanism of alkylation reaction of carbazole **1** as shown in chapter 1 **Figure 1.13**.

Finally, the target molecules **In5** was synthesized by Knoevenagal reaction. The 3-formyl-4,6-dimethoxy-*N*-methylindol **10** reacted with cyanoacetic acid and piperidine in chloroform at reflux for 24 h led to 2-cyano-3-(4,6-dimethoxy-*N*-methylindol-3-yl)acrylic acid **In5** in 79% as show in **Figure 2.28**.

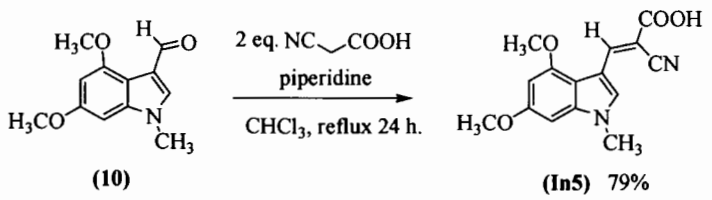


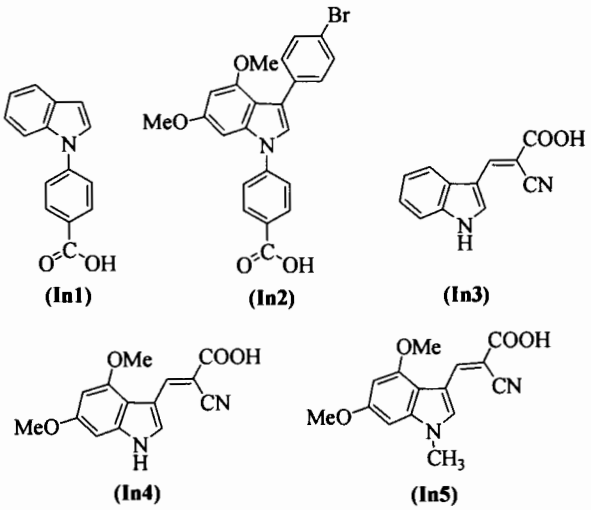
Figure 2.28 Knoevenagal reaction of 3-formyl-4,6-dimethoxy-*N*-methylindol 10

The 2-cyano-3-(4,6-dimethoxy-*N*-methylindol-3-yl) acrylic acid **In5** was confirmed by ^{1}H-NMR and ^{13}C-NMR. ^{1}H-NMR spectra of compound **In5** still show three protons of aryl, three protons of N-CH_3 group, six protons of O-CH_3 and new one proton peak of C=C-H group. Remarkable, the formyl proton (–CHO) of 3-formyl-4,6-dimethoxy-*N*-methylindol **10** was not appeared. ^{13}C-NMR spectrum shows new peck of carboxyl carbons (COOH) at δ = 165.4 ppm, new peak of CN carbons at δ = 114.5 ppm and new two carbon peak of alkene group. Moreover, the high resolution mass spectrometry (MALDI-TOF) of compound **In5** found 286.1352 (calcd for $C_{15}H_{14}N_2O_4$: *m/z* 286.0954). These results confirmed that product was 2-cyano-3-(4,6-dimethoxy-*N*-methylindol-3-yl)acrylic acid **In5**.

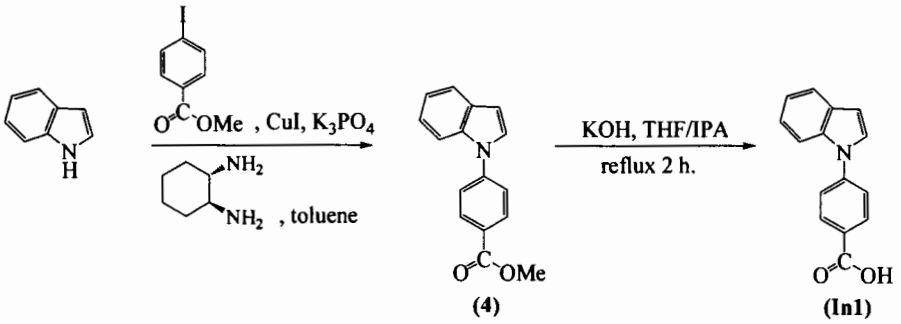
The mechanism of Knoevenagal reaction of compound **In5** similar to mechanism of Knoevenagal reaction of compound **In3** as shown in **Figure 2.23**.

2.3 CONCLUSION

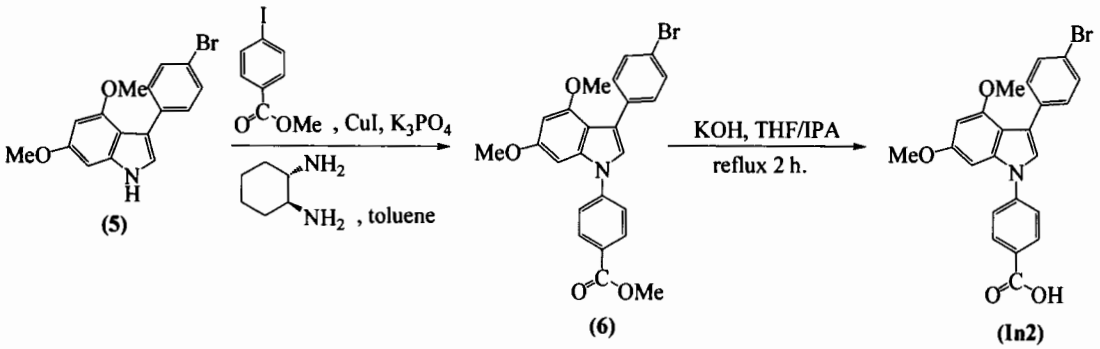
In this reserch, a new series of indole derivatives **In1-In5**, containing varies electron donating, π-spacer and electron acceptor, for using as dye molecules in DSSCs were successfully synthesized. The target molecules were synthesized by using Ullman coupling, hydrolysis reaction, Knoevenagal condensation and Vilsmeier–Haack reaction.



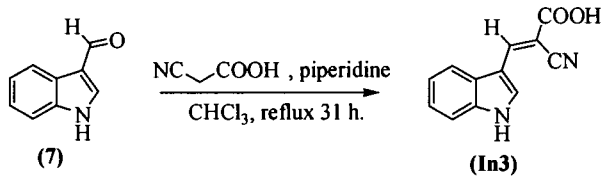
In the first, the target molecule **In1** was synthesized by Ullman coupling reaction of indole with methyl 4-iodobenzoate led to ester **4** in 94% and then hydrolysis of ester **4** with KOH to afforded 2-cyano-3-(indol-3-yl)acrylic acid **In1** in 64% yields.



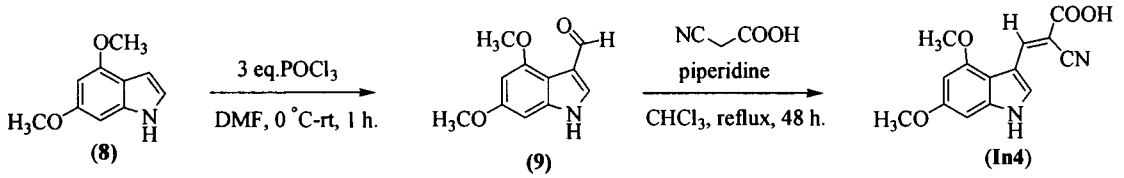
In the same way, the target molecule **In2** was synthesized by Ullman coupling reaction of 3-(4-bromophenyl)-4,6-dimethoxyindole **5** with methyl 4-iodobenzoate led to ester **6** in 41% and following by hydrolysis reaction of ester **6** with KOH afforded 4-(3-(4-bromophenyl)-4,6-dimethoxyindol-1-yl)benzoic acid **In2** in 46%.



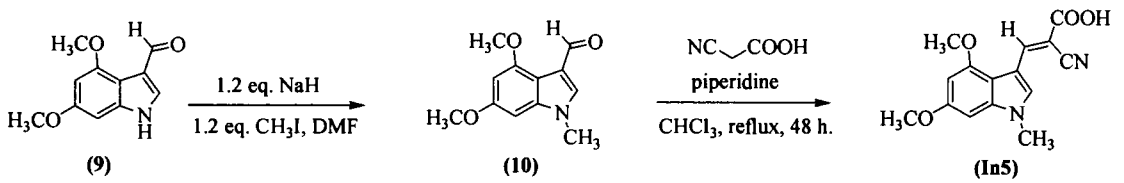
The target molecule **In3** was easy synthesized by Knoevenagal condensation, The commercial indole-3-carbaldehyde **7** was reacted with cyanoacetic acid led to 2-cyano-3-(indol-3-yl)acrylic acid **In3** in 24%.



The target molecule **In4** was successfully synthesized by Vilsmeier–Haack reaction and Knoevenagal condensation. First step, Vilsmeier–Haack reaction of 4,6-dimethoxyindole **8** led to aldehyde **9** in 58%. Next, Knoevenagal reaction of aldehyde **9** with cyanoacetic acid led to 2-cyano-3-(4,6-dimethoxyindol-3-yl)acrylic acid **In4** in 27%.



The final target molecule **In5** was successfully synthesized by methylation and Knoevenagal reaction. First step, methylation of aldehyde indole **9** gave 3-formyl-4,6-dimethoxy-*N*-methylindol **10** in 97%. Finally, Knoevenagal reaction of aldehyde **10** with cyanoacetic acid led to 2-cyano-3-(4,6-dimethoxy-*N*-methylindol-3-yl)acrylic acid **In5** in 79%.



All target molecules were characterized by using melting points, ^{1}H-NMR and ^{13}C-NMR spectroscopy, FT-IR spectroscopy and mass spectrometer. Unfortunately we have no time for fabrication of solar cell all of them but we will complete it in the

future. Moreover, we believe that the target compound **In1-In5** are promising candidates for improvement of the performance of the DSSCs.

2.4 EXPERERIMENTAL

2.4.1 General experiment

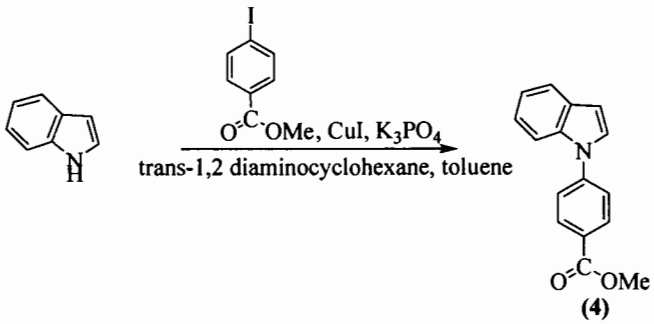
All solvents and reagents were purchased from Aldrich, Acros and Fluka received unless otherwise stated. Analytical thin-layer chromatography (TLC) was performed with Merck aluminium plates coated with silica gel 60 F_{254}. Column chromatography was carried out using gravity feed chromatography with Merck silica gel mesh, 60 Å. Where solvent mixtures are used, the portions are given by volume.

Melting points was measured by BUCHI 530 model in open capillary method and are uncorrected and reported in degree Celsius.

^{1}H and ^{13}C NMR spectra were recorded on a Brüker AVANCE 300 MHz spectrometer. Chemical shifts (δ) are reported relative to the residual solvent peak in part per million (ppm). Coupling constants (J) are given in Hertz (Hz). Multiplicities are quoted as singlet (s), broad (br), doublet (d), triplet (t), quartet (q), and multiplet (m).

The IR spectra were recorded on Perkin-Elmer FT-IR spectrum RXI spectrometer. The absorption peaks are quoted in wavenumber (cm^{-1}). UV–Vis spectra were recorded on a Perkin–Elmer UV Lambda 25 spectrometer. MALDI-TOF mass spectra were recorded on Bruker Daltonics (Bremen, Germany) Autoflex II Matrix-Assisted Laser Desoprtion/Ionization-Time of Flight Mass Spectrometer (BIFEX) using α-cyano-4-hydroxycin-namic acid as matrix.

2.4.2 Synthesis of methyl 4-(indol-1-yl)benzoate



General Procedure of Ullman coupling:

A mixture of indole (0.1023 g, 0.8737 mmol), methyl 4-iodobenzoate (0.1908 g, 0.7281 mmol), CuI (0.0693 g, 0.3640 mmol), and K_3PO_4 (0.4636 g, 2.1843 mmol) in round bottom flask were added toluene (20 mL) and trans-1,2-diaminocyclohexane (0.0414 g, 0.3640 mmol). The mixture was degassed and stirred at reflux under N_2 for 48 h. After being cooled to room temperature, water (50 mL) was added and extracted with CH_2Cl_2 (50 mL x 3). The combined organic phases were washed with water (50 mL) and brine solution (70 mL), dried over $MgSO_4$ and evaporated under reduce pressure. Purification of crude reaction by column chromatography eluting with 1:3 v/v ethyl acetate/hexane gave methyl 4-(indol-1-yl)benzoate **4** (0.1719 g, 94%).

$C_{16}H_{13}NO_2$; m.p. = 50-52 °C

^{1}H-NMR (300 Hz, $CDCl_3$):

δ = 8.21 (d, 2H, ArH, J = 7.8 Hz), 7.72-7.55 (m, 4H, ArH), 7.39 (d, 1H, ArH, J = 2.4 Hz), 7.30-7.13 (m, 2H, ArH), 6.74 (d, 1H, ArH, J = 1.8 Hz), 3.98 (s, 3H, OCH_3) ppm.

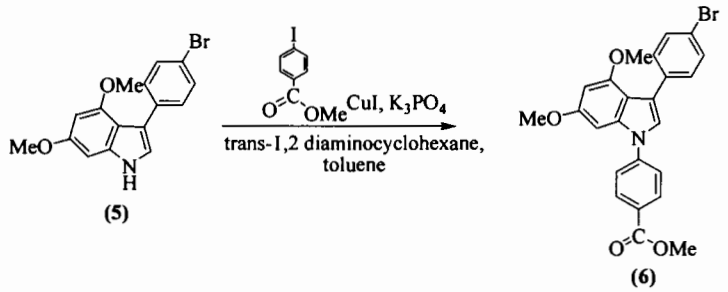
^{13}C-NMR (75 Hz, $CDCl_3$):

δ = 166.4 (C=O), 143.8 (Cq), 135.5 (Cq), 131.3 (2 x CH), 129.8 (Cq), 127.6 (Cq), 127.4 (CH), 123.3 (2 x CH), 122.9 (CH), 121.4 (CH), 121.0 (CH), 110.6 (CH), 104.9 (CH), 52.2 (OCH_3) ppm.

IR (KBr):

ν_{max} = 3050, 2948, 1706, 1602, 1453, 1431, 1279, 1210, 1095, 745 cm^{-1}.

2.4.3 Synthesis of methyl 4-(3-(4-bromophenyl)-4,6-dimethoxyindol-1-yl)benzoate



According to general procedure of Ullman coupling, treatment of 3-(4-bromophenyl)-4,6-dimethoxyindole **5** (0.4000 g, 1.20 mmol), methyl 4-iodobenzoate (0.2629 g, 1.00 mmol), CuI (0.0094 g, 0.04 mmol), trans-1,2-diaminocyclohexane (0.0570 g, 0.50 mmol), K_3PO_4 (0.4473 g, 2.10 mmol) and toluene (40 mL) gave yellow oil methyl 4-(3-(4-bromophenyl)-4,6-dimethoxyindol-1-yl)benzoate **6** (0. 1918 g, 41%).

$C_{24}H_{20}BrNO_4$;

^{1}H-NMR (300 Hz, $CDCl_3$):

δ = 8.21 (d, 2H, J = 8.1 Hz), 7.71-7.50 (m, 6H), 7.14 (s, 1H), 6.69 (s, 1H), 6.33 (s, 1H), 3.97 (s, 3H), 3.82 (s, 6H) ppm.

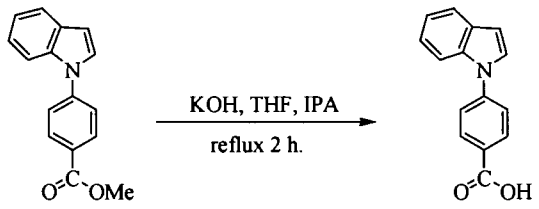
^{13}C-NMR (75 Hz, $CDCl_3$):

δ = 166.3 (O=C), 158.4 (Cq), 155.0 (Cq), 143.5 (Cq), 138.0 (Cq), 136.7 (Cq), 134.3 (Cq), 131.3 (2 x CH), 131.1 (2 x CH), 130.7 (2 x CH), 128.1 (Cq), 123.8 (CH), 123.7 (2 x CH), 120. 2 (Cq), 119.8 (Cq), 93.27 (CH), 86.6 (CH), 55.7 (OCH_3), 55.2 (OCH_3), 52.3 (OCH_3) ppm.

IR (KBr):

ν_{max} = 2996, 2946, 2843, 1718, 1602, 1433,1274, 1206, 1174, 1085, 730 cm^{-1}.

2.4.4 Synthesis of 4-(indol-1-yl)benzoic acid



(4) (In1)

General Procedure of Hydrolysis reaction:

Methyl 4-(indol-1-yl)benzoate **4** (0.1500 g, 0.5969 mmol) and KOH (0.0610 g, 1.1938 mmol) were dissolved in THF(10 mL) and IPA (10 mL). The reaction mixture was stirred at reflux for 2 h and monitored by TLC until it was complete. Acid H_3PO_4 2M (50 mL) was added, and the reaction was extracted with DCM (20 mL x 2), washes with water (20 mL x 2) and bine solution (20 mL x 2), and then dried over Na_2SO_4 anhydrous, followed by recrystallization by hexane/EtOH to give 4-(indol-1-yl)benzoic acid **In1** (0.0905 g, 64%).

$C_{15}H_{11}NO_2$; m.p. > 200 °C

^{1}H-NMR (300 Hz, $CDCl_3$):

δ = 8.29 (d, 2H, J = 8.1 Hz), 7.72 – 7.64 (m, 4H), 7.41 (d, 1H, J = 3.0 Hz), 7.31-7.19 (m, 2H), 6.75 (d, 1H, J = 2.4 Hz) ppm.

^{13}C-NMR (75 Hz, $CDCl_3$):

δ = 169.9 (O=C), 144.5 (Cq), 135.4 (Cq), 132.0 (2 x CH), 129.9 (Cq), 127.3 (CH), 126.5 (Cq), 123.3 (2 x CH), 123.0 (CH), 121.4 (CH), 121.1 (CH), 110.6 (CH), 105.2 (CH) ppm.

IR (KBr):

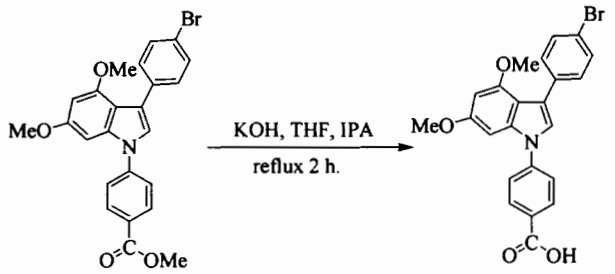
ν_{max} = 1666, 1599, 1452, 1426, 1315, 1291, 933, 822, 775, 721 cm^{-1}.

UV-vis spectroscopy (in CH_2Cl_2 at 5x10^{-6} M):

λ_{max} = 320 nm (ε = 1.11 x 10^5 cm^{-1} M^{-1}), 273 nm (ε = 9.20 x 10^4 cm^{-1} M^{-1}), 228 nm (ε = 1.27 x 10^5 cm^{-1} M^{-1})

MALDI-TOF (*m/z*) calcd for $C_{15}H_{11}NO_2$: 237.0790; found 237.1056(M$^+$).

2.4.5 Synthesis of 4-(3-(4-bromophenyl)-4,6-dimethoxyindol-1-yl)benzoic acid



(6) (In2)

According to general procedure of hydrolysis reaction, treatment of methyl 4-(3-(4-bromophenyl)-4,6-dimethoxyindol-1-yl) benzoate **6** (0.1227 g, 0.26 mmol), KOH (0.0268 g, 0.52 mmol), THF (10 mL) and IPA (10 mL) at reflux for 2 h gave 4-(3-(4-bromophenyl)-4,6-dimethoxyindol-1-yl) benzoic acid **In2** (0.0549 g, 46%).

$C_{23}H_{18}BrNO_4$; m.p. > 200°C

^{1}H-NMR (300 Hz, $CDCl_3$):

δ = 8.29 (d, 2H, *J* = 8.4 Hz), 7.66 (d, 2H, *J* = 8.4 Hz), 7.51 (s, 4H), 7.16 (s, 1H), 6.72 (s, 1H), 6.35 (s, 1H), 3.84 (s, 3H), 3.83 (s, 3H) ppm.

^{13}C-NMR (75 Hz, $CDCl_3$):

δ = 170.0 (O=C), 158.5 (Cq), 155.1 (Cq), 144.3 (Cq), 138.0 (Cq), 134.2 (Cq), 132.0 (2 x CH), 131.1 (2 x CH), 130.7 (2 x CH), 126.9 (Cq), 123.7 (2 x CH), 123.7 (Cq), 120.2 (Cq), 120.0 (Cq), 111.7 (Cq), 93.4 (CH), 86.7 (CH), 55.7 (OCH_3), 55.2 (OCH_3), ppm.

IR (KBr):

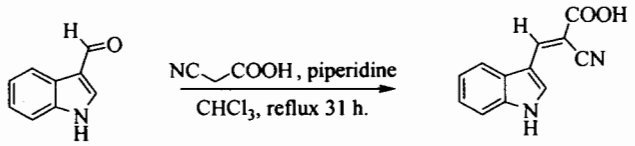
ν_{max} = 1689, 1594, 1429, 1318, 1293, 1240, 1208, 1174, 1083, 815, 769 cm^{-1}.

UV-vis spectroscopy (in CH_2Cl_2 at $5x10^{-6}$ M):

λ_{max} = 339 nm (ε = 3.50 x 10^4 cm^{-1} M^{-1}), 281 nm (ε = 7.28 x 10^4 cm^{-1} M^{-1}), 231 nm (ε = 1.07 x 10^5 cm^{-1} M^{-1})

MALDI-TOF (*m/z*) calcd for $C_{23}H_{18}BrNO_4$: 451.0419; found 451.0924 (M^+).

2.4.6 Synthesis of 2-cyano-3-(indol-3-yl)acrylic acid



(7) (In3)

General Procedure of Knoevenagal condensation:

To solution of indole-3-carbaldehyde **7** (0.200 g, 1.38 mmol) and cyanoacetic acid (0.386 g, 4.54 mmol) in chloroform 20 mL was added piperidine (1 mL) and stirred at reflux for 48 h under N_2 gas. The mixture was extracted with ethyl acetate, washed with water, dried over $MgSO_4$ and evaporated under reduce pressure. The crude product was separated by column chromatography eluting with 1:9 v/v methanol/ethyl acetate to give 2-cyano-3-(indol-3-yl)acrylic acid **In3** (0.0696 g, 24%).

$C_{12}H_8N_2O_2$; m.p. > 200°C

^{1}H-NMR (300 Hz, $CDCl_3$):

δ = 8.61 (s, 1H), 8.55 (s, 1H), 7.81–7.78 (m, 1H), 7.54 (s, 1H), 7.48-7.46 (m, 1H), 7.29-7.22 (m, 2H) ppm.

^{13}C-NMR (75 Hz, $CDCl_3$):

δ = 165.9 (O=C), 147.0 (CH), 136.3 (Cq), 131.5 (CH), 127.6 (Cq), 123.6 (CH), 122.1 (CH), 118.4 (Cq), 117.8 (CH), 112.4 (CH), 110.6 (CN), 93.3 (Cq) ppm.

IR (KBr):

ν_{max} = 3296, 3063, 2925, 2208, 1606, 1398, 1113, 956, 742, 608 cm^{-1}.

UV-vis spectroscopy (in CH_2Cl_2 at $1x10^{-5}$ M):

λ_{max} = 389 nm (ε = 2.83 x 10^4 cm^{-1} M^{-1}), 276 nm (ε = 1.40 x 10^4 cm^{-1} M^{-1}), 229 nm (ε = 2.28 x 10^4 cm^{-1} M^{-1})

MALDI-TOF (*m/z*) calcd for $C_{12}H_8N_2O_2$: 212.0586; found 212.0361 (M^+).

2.4.7 Synthesis of 3-formyl -4,6-dimethoxyindole (9)

To a stirred and ice cooled solution of 4,6-dimethoxyindole **8** (0.5059 g, 2.86 mmol) in *N,N*-dimethylformamide (5 mL) was added dropwise an ice cooled solution of phosphoryl chloride (1.3159 g, 8.58 mmol) in *N,N*-dimethylformamide (5 mL). After stirred at 0 °C for 1 h, solution was allowed to come to room temperature and then was made strongly basic with 6 M sodium hydroxide solution (5 ml). The mixture was extracted with dichloromethane, washed with water, dried over $MgSO_4$ and evaporated under reduce pressure. The crude product was separated by column chromatography eluting with 3:2 v/v ethyl acetate/hexane to give 3-formyl -4,6-dimethoxyindole **9** (0.3391 g, 58%).

$C_{11}H_{11}NO_3$; m.p. = 148-153 °C

^{1}H-NMR (300 Hz, $CDCl_3$):

δ = 10.36 (s, 1H, CHO), 10.31 (brs, 1H, NH) 7.07 (t, 1H, ArH, J = 2.6 Hz), 6.56 (t, 1H, ArH, J = 2.6 Hz), 6.17 (s, 1H, ArH), 4.05 (s, 3H, OCH_3), 3.99 (s, 3H, OCH_3) ppm.

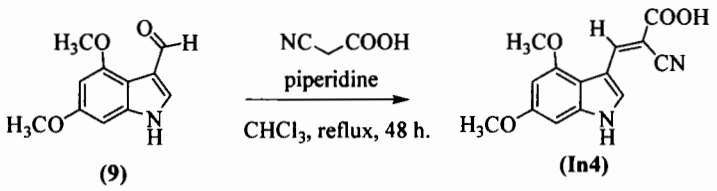
^{13}C-NMR (75 Hz, $CDCl_3$):

δ = 188.3 (CHO), 163.1 (Cq), 160.2 (Cq), 136.7 (Cq), 122.7 (CH), 105.0 (Cq), 99.7 (Cq+CH), 86.8 (CH), 56.5 and 55.7 (2xOCH_3) ppm.

IR (KBr):

ν_{max} = 3368, 2850, 1630, 1500, 1218 cm^{-1}.

2.4.8 Synthesis of 2-cyano-3-(4,6-dimethoxyindol-3-yl)acrylic acid



According to general procedure of Knoevenagal condensation, treatment of 3-formyl-4,6-dimethoxyindole (**9**) (0.0819 g, 0.40 mmol), cyanoacetic acid (0.0683 g, 0.80 mmol) and piperidine (0.10 mL) in chloroform 20 mL gave 2-cyano-3-(4,6-dimethoxyindol-3-yl)acrylic acid **In4** (0.0290 g, 27%).

$C_{14}H_{12}N_2O_4$; m.p. = 171-174 °C

^{1}H-NMR (300 Hz, $CD_3OD + CDCl_3$):

δ = 8.49 (s, 1H, NH), 7.80 (d, 1H, ArH, J = 3.6 Hz), 6.96 (d, 1H, ArH, J = 3.6 Hz), 6.37 (s, 1H, CH), 5.30 (s, 1H, CH), 4.16 (s, 3H, OCH_3), 4.05 (s, 3H, OCH_3) ppm.

IR (KBr):

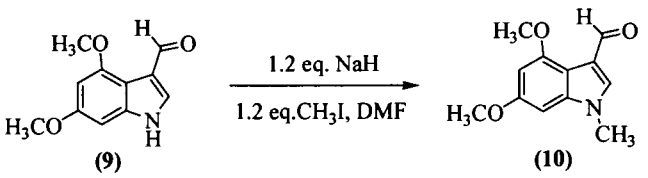
ν_{max} = 3100, 2921, 1633, 1603, 1264, 1070, 1050, 1032, 968, 719 cm^{-1}.

UV-vis spectroscopy (in CH_2Cl_2 at $5x10^{-6}$ M):

λ_{max} = 394 nm (ε = 4.90 x 10^4 cm^{-1} M^{-1}), 269 nm (ε = 2.24 x 10^4 cm^{-1} M^{-1}), 235 nm (ε = 2.08 x 10^4 cm^{-1} M^{-1})

MALDI-TOF (*m/z*) calcd for $C_{14}H_{12}N_2O_4$: 272.0797; found 272.0978 (M^+).

2.4.9 Synthesis of 3-formyl-4,6-dimethoxy-*N*-methylindol



To a suspension of sodium hydride (NaH) (0.0145 g, 0.60 mmol) in *N,N*-dimethylformamide (DMF) 5 mL was added dropwise of 3-formyl-4,6-dimethoxyindole **9** (0.1022 g, 0.50 mmol) in DMF 5 mL. After stirred for 1 h, methyl iodide (0.0869 g, 0.60 mmol) was added into the reaction mixture and stirred for 1.5 h under N_2 gas. The mixture was neutralized with 6 M HCl, extracted with dichloromethane, washed with water, dried over $MgSO_4$ and evaporated under reduce pressure. The crude product was separated by column chromatography eluting with 1:4 v/v dichloromethane/hexane to give 3-formyl-4,6-dimethoxy-*N*-methylindol **10** (0.1055 g, 97%)

$C_{12}H_{13}NO_3$; m.p. = 100-106 °C

^{1}H-NMR (300 Hz, $CDCl_3$)

δ = 10.47 (s, 1H, CHO), 6.83 (d, 1H, H2, *J* = 3.0 Hz), 6.53 (d, 1H, H7, *J* = 3.0 Hz), 6.22 (s, 1H, H5), 4.05 (s, 3H, OCH_3), 4.01 (s, 3H, OCH_3), 3.96 (s, 3H, N-CH_3) ppm

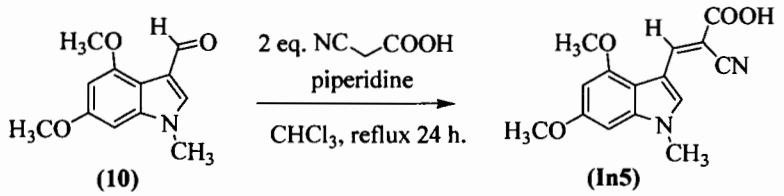
^{13}C-NMR (75 Hz, $CDCl_3$)

δ = 188.0 (CHO),165.0 (Cq),159.2 (Cq_3), 130.3 (CH), 115.8 (Cq), 107.2 (Cq), 99.1 (CH), 87.9 (CH), 57.2 (OCH_3), 39.2 (NCH_3)

IR (KBr):

ν_{max} = 2944, 2921, 2848, 1653, 1561, 1514, 1459, 1362, 1246, 1207, 727 cm^{-1}.

2.4.10 Synthesis of 2-cyano-3-(4,6-dimethoxy-*N*-methylindol-3-yl)acrylic acid



According to general procedure of Knoevenagal condensation, treatment of 3-formyl-4,6-dimethoxy-*N*-methylindol (**10**) (0.7500 g, 3.43 mmol), cyanoacetic acid (0.582 g, 6.85 mmol) and piperidine (2.0 mL) in chloroform 20 mL gave 2-cyano-3-(4,6-dimethoxy-*N*-methylindol-3-yl)acrylic acid **In5** (0.770 g,79%).

$C_{15}H_{14}N_2O_4$; m.p. = 170-174 °C

^{1}H-NMR (300 Hz, $CDCl_3$)

δ = 8.55 (s, 1H, COOH), 6.61 (d, 1H, H-alkene, *J* = 3Hz), 6.27 (d, 1H, H2, *J* = 3Hz), 6.10(s, H, H5), 3.78 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 3.65 (s, 3H, N-CH_3) ppm

^{13}C-NMR (75 Hz, $CDCl_3$)

δ =165.4 (C=O),157.8 (Cq),157.7 (Cq), 149.0 (CH), 135.9 (Cq), 129.0 (Cq), 116.2(Cq), 114.5 (CN), 103.7 (Cq), 100.2 (Cq), 98.8 (Cq), 87.1 (Cq), 55.2 (OCH_3), 55.1 (OCH_3), 36.8 (NCH_3).

IR (KBr)

ν_{max} = 2923, 2848, 1667, 1573, 1557, 1393, 1159, 1061, 1011, 708 cm^{-1}.

UV-vis spectroscopy (in CH_2Cl_2 at $5x10^{-6}$ M):

λ_{max} = 426 nm (ε = 5.30 x 10^4 cm^{-1} M^{-1}), 277 nm (ε = 7.90 x 10^4 cm^{-1} M^{-1}), 229 nm (ε = 1.36 x 10^5 cm^{-1} M^{-1})

MALDI-TOF (*m/z*) calcd for $C_{15}H_{14}N_2O_4$: 286.0954; found 286.1352 (M^+).

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APPENDICES

APPENDICES A

^{1}H NMR, ^{13}C NMR and UV-Vis absorption spectrum of compounds

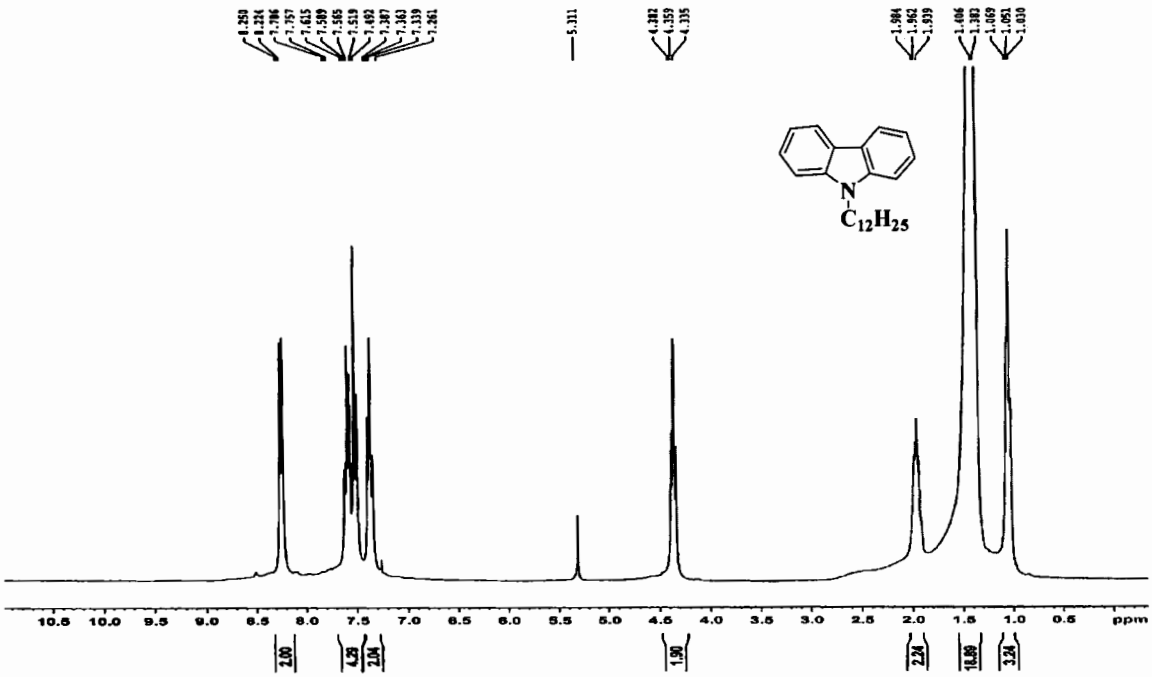

Figure A.1 The ^{1}H NMR (in $CDCl_3$) spectrum of 9-dodecylcarbazole 2

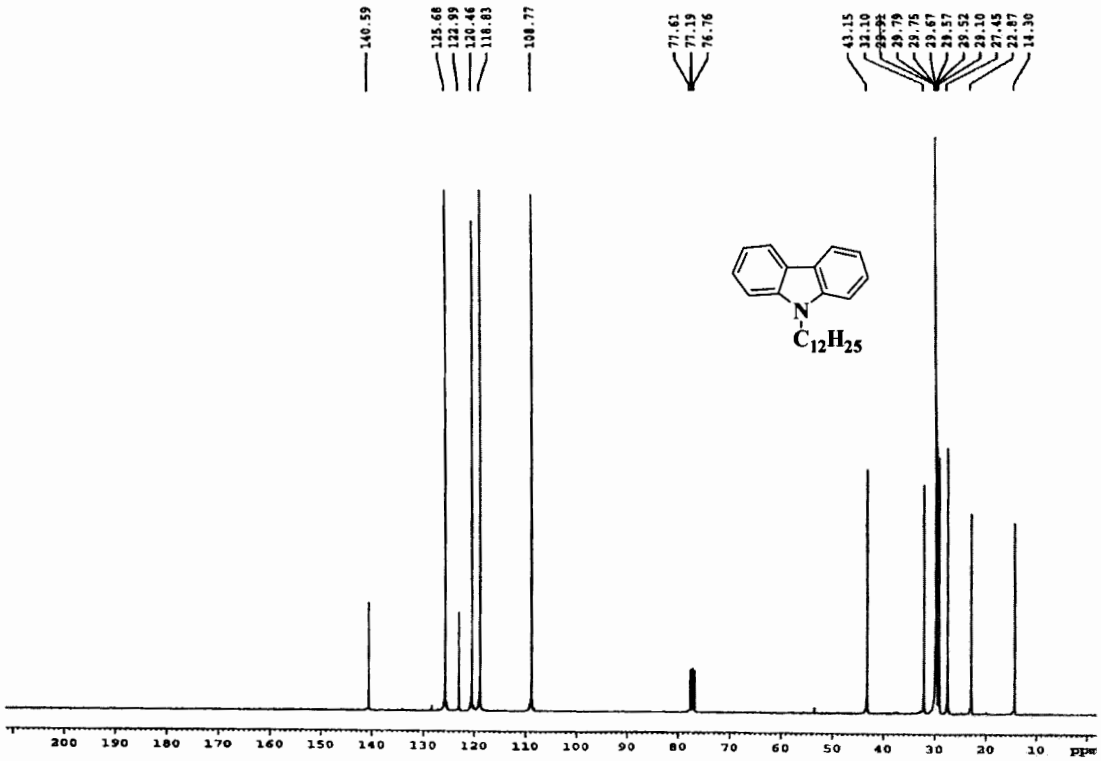

Figure A.2 The ^{13}C NMR spectra of 9-dodecylcarbazole 2

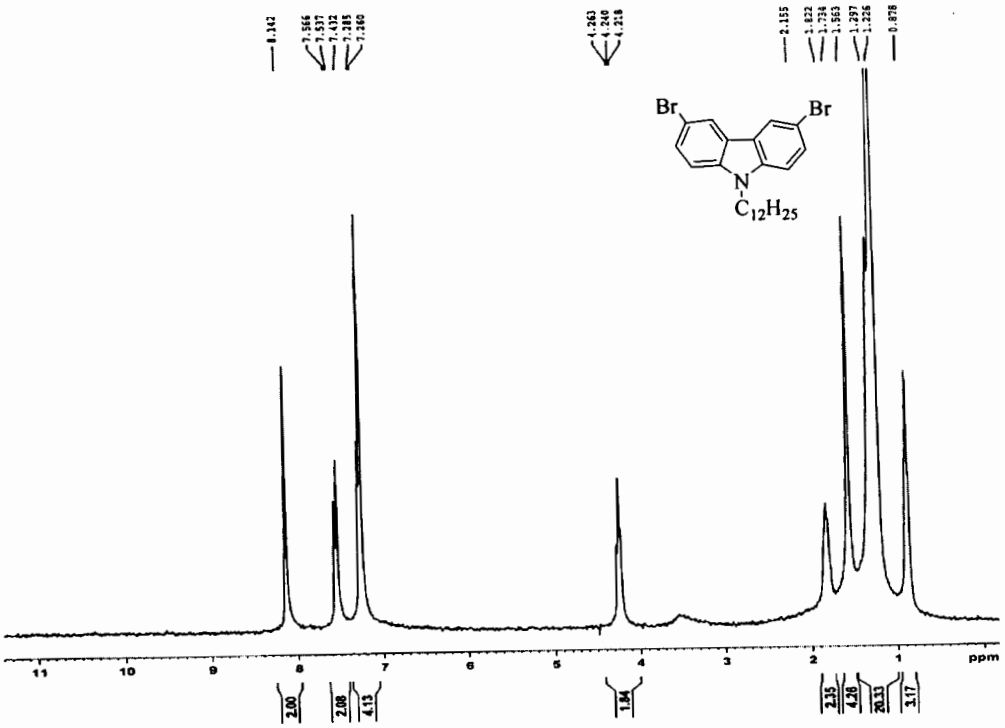

Figure A.3 The ^{1}H NMR (in $CDCl_3$) spectrum of 3,6-Dibromo-9-dodecylcarbazole

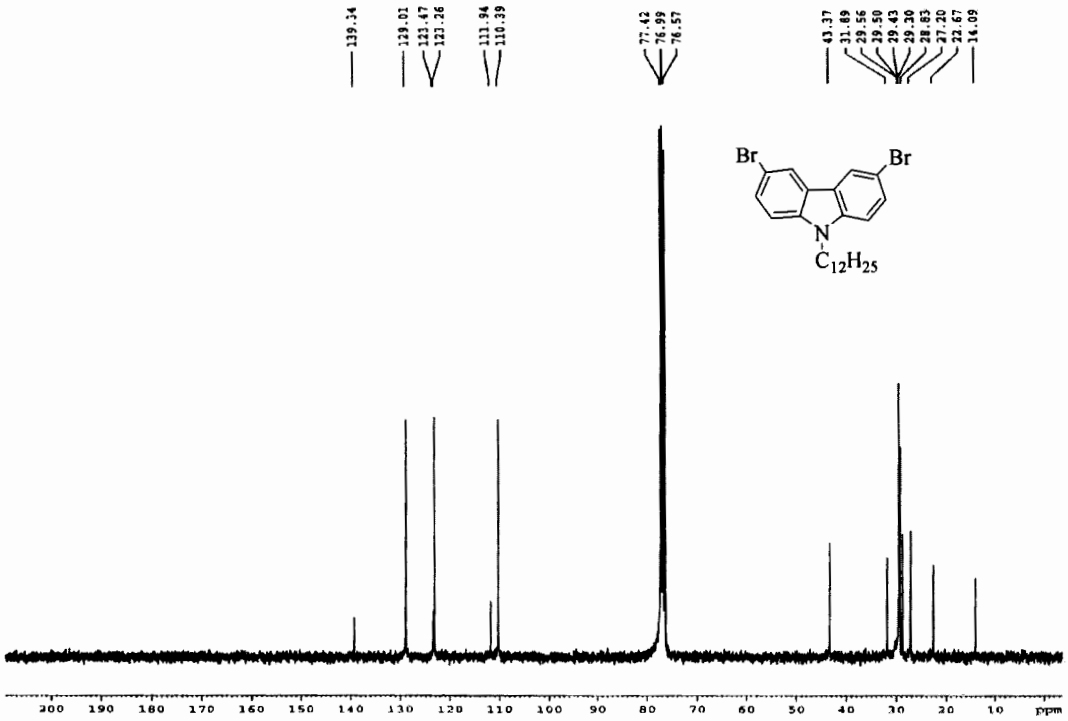

Figure A.4 The ^{13}C NMR spectra of 3,6-Dibromo-9-dodecylcarbazole

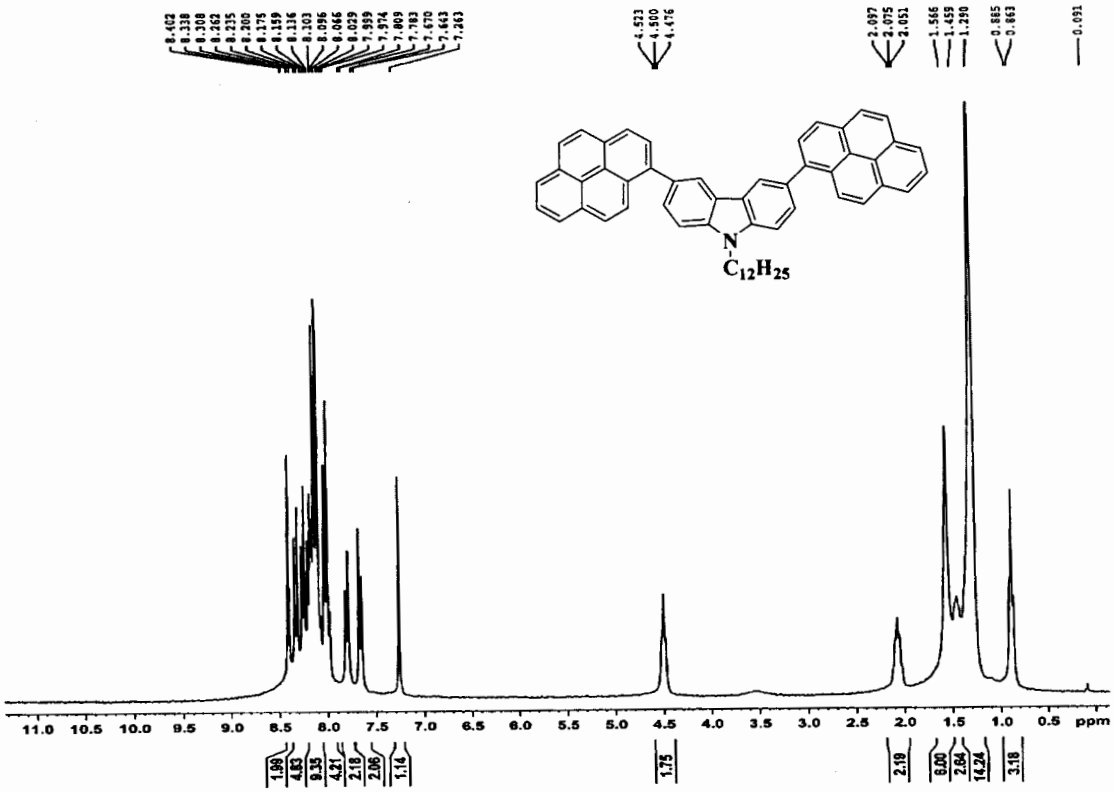

Figure A.5 The ^{1}H NMR (in $CDCl_3$) spectrum of CP2

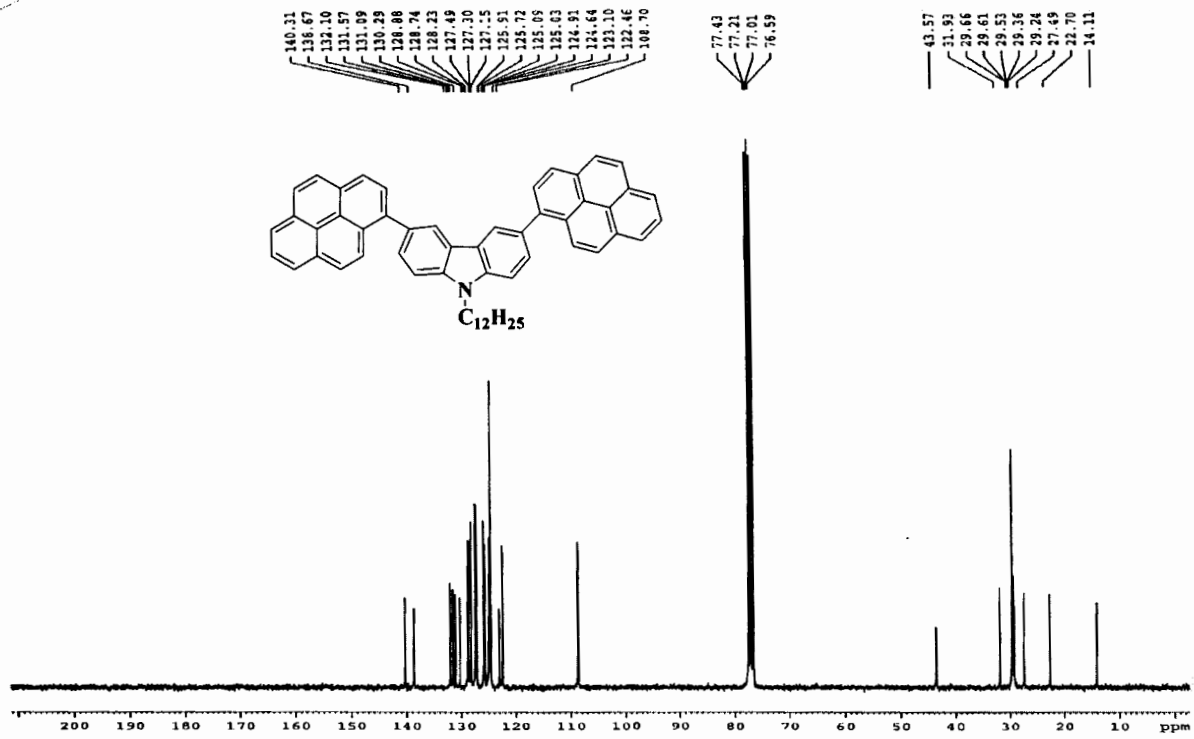

Figure A.6 The ^{13}C NMR spectra of CP2

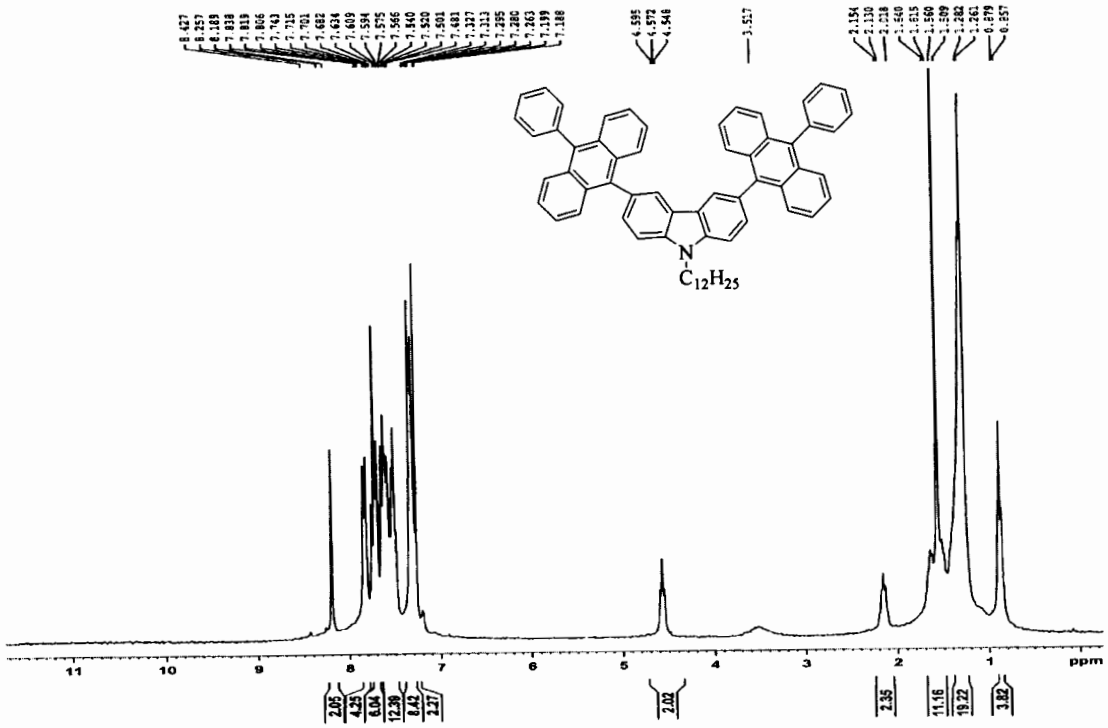

Figure A.7 The ^{1}H NMR (in $CDCl_3$) spectrum of CA2

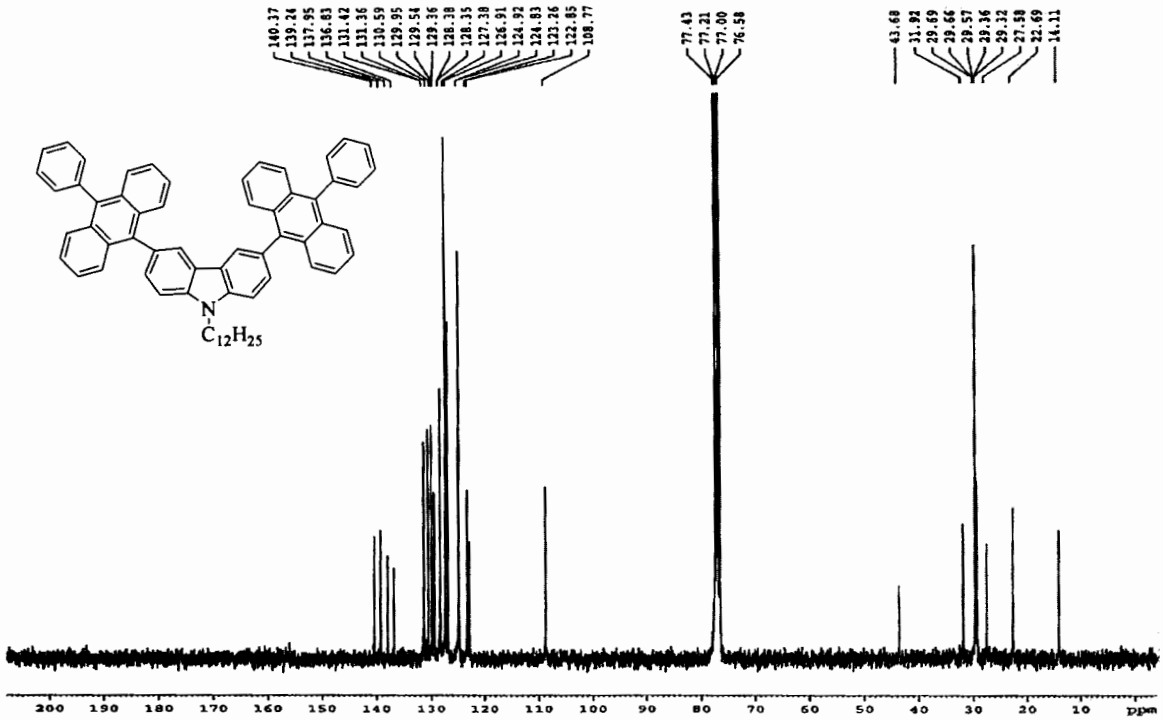

Figure A.8 The ^{13}C NMR spectra of CA2

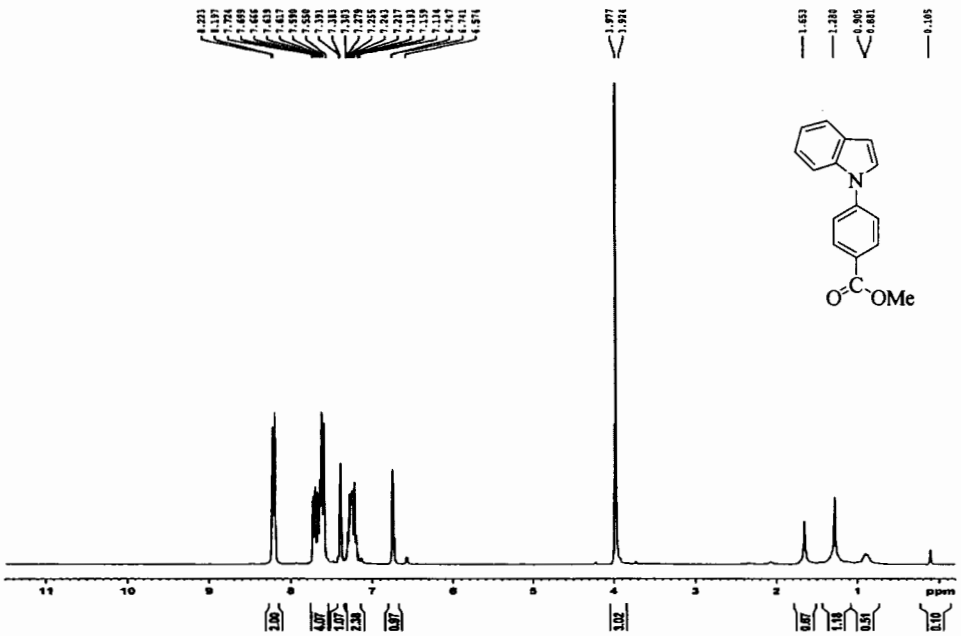

Figure A.9 The ^{1}H NMR (in $CDCl_3$) spectrum of methyl 4-(indol-1-yl) benzoate 4

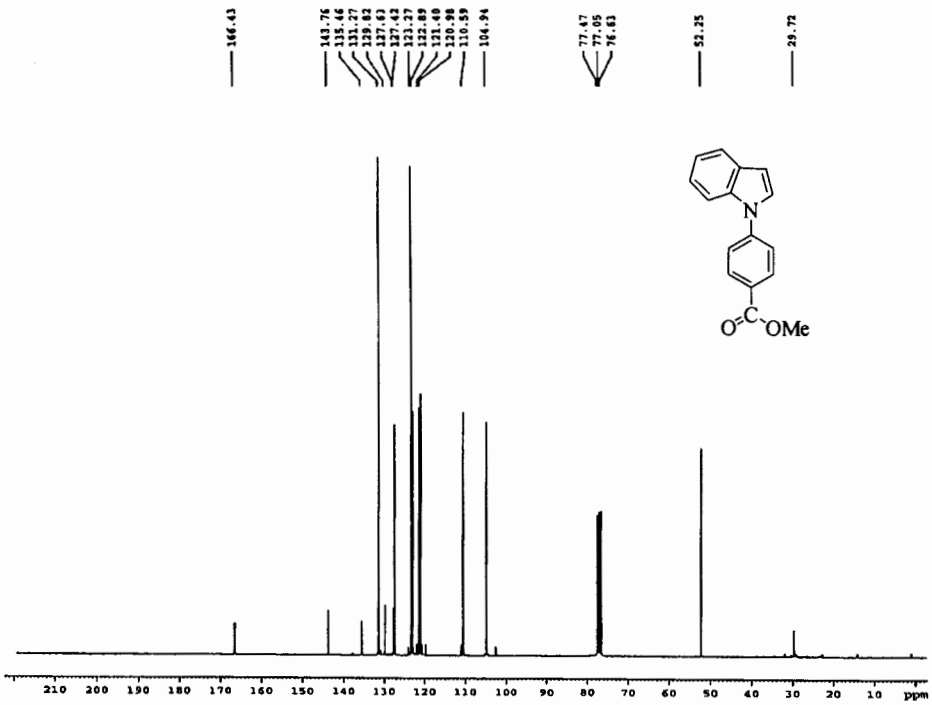

Figure A.10 The ^{13}C NMR spectra of methyl 4-(indol-1-yl) benzoate 4

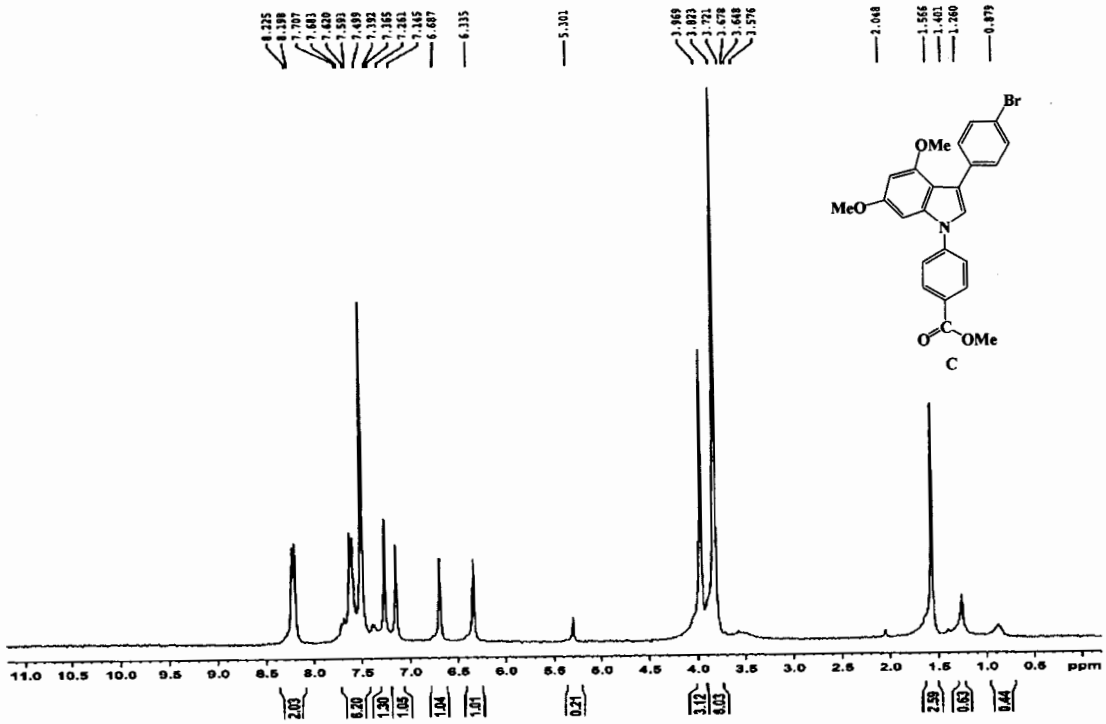

Figure A.11 The ^{1}H NMR (in $CDCl_3$) spectrum of methyl 4-(3-(4-bromophenyl)-4,6-dimethoxyindol-1-yl)benzoate 6

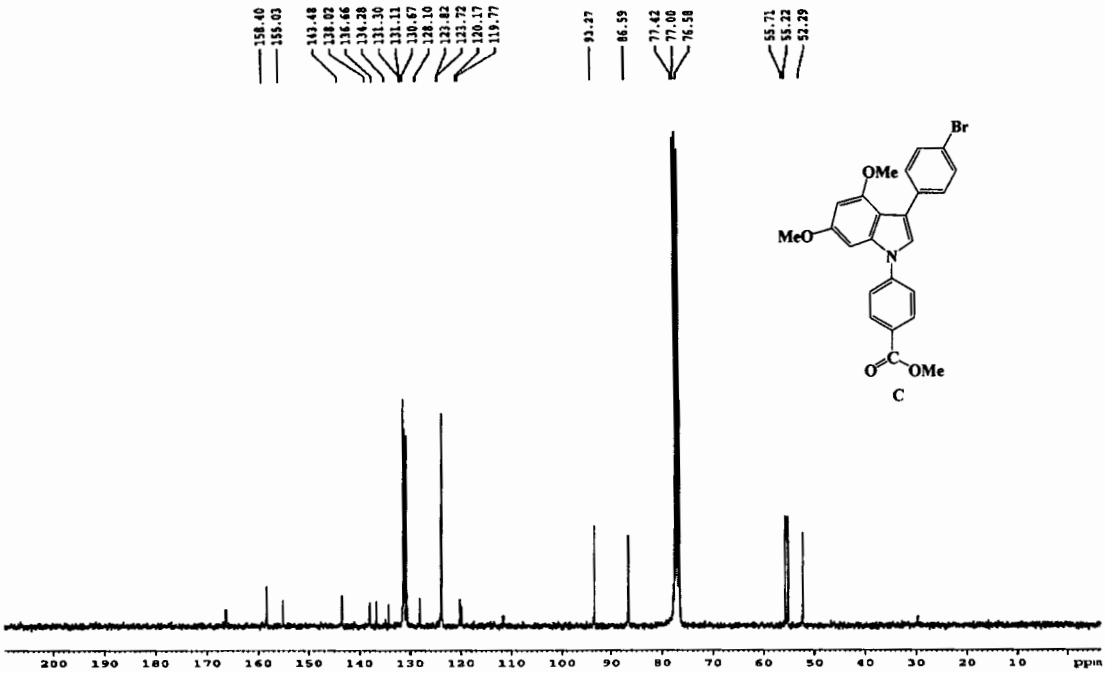

Figure A.12 The ^{13}C NMR spectra of methyl 4-(3-(4-bromophenyl)-4,6-dimethoxyindol-1-yl)benzoate 6

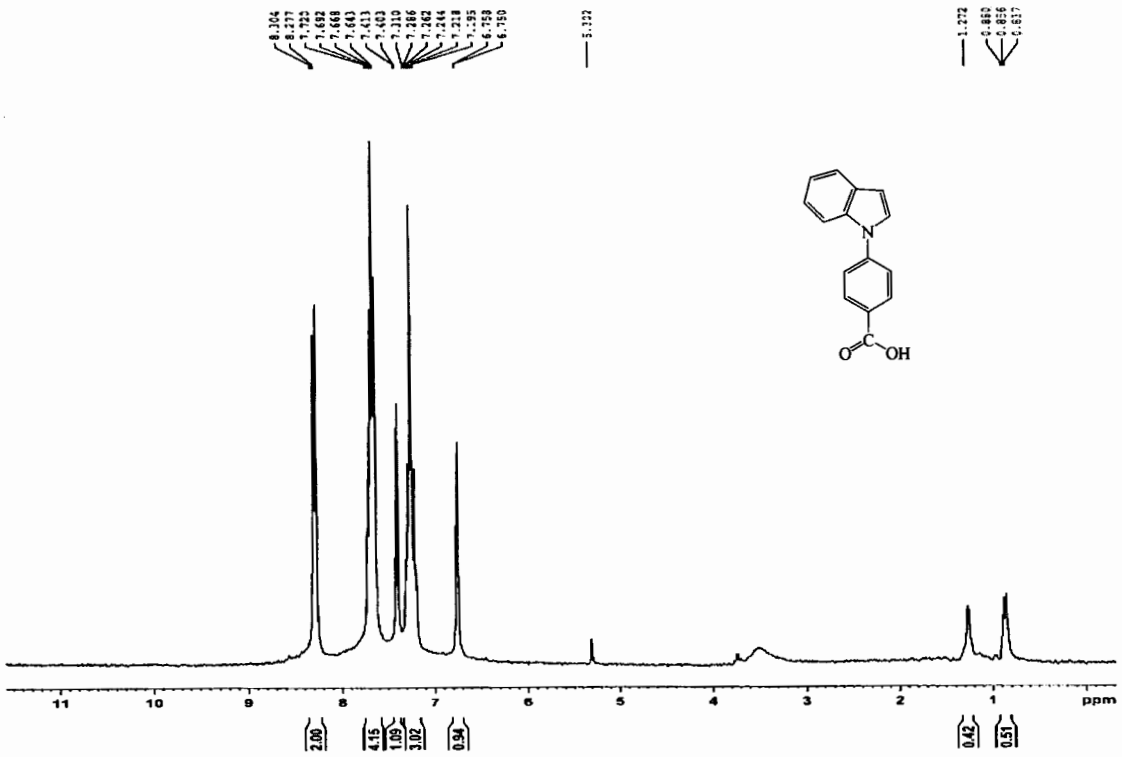

Figure A.13 The ^{1}H NMR (in $CDCl_3$) spectrum of In1

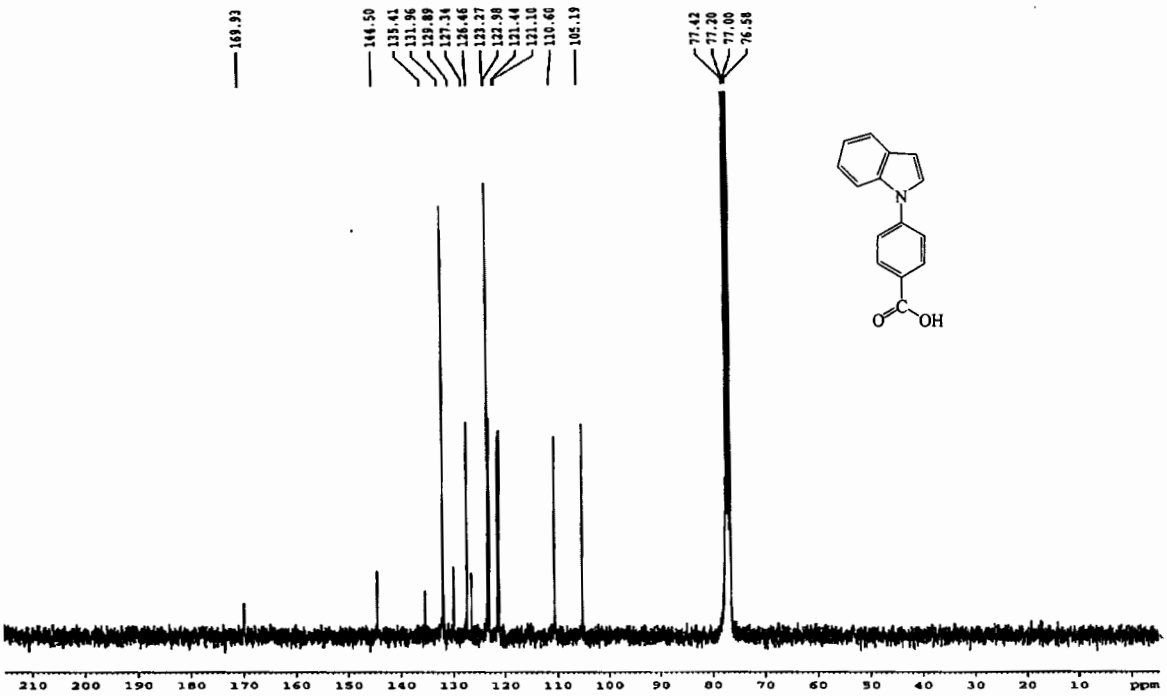

Figure A.14 The ^{13}C NMR spectra of In1

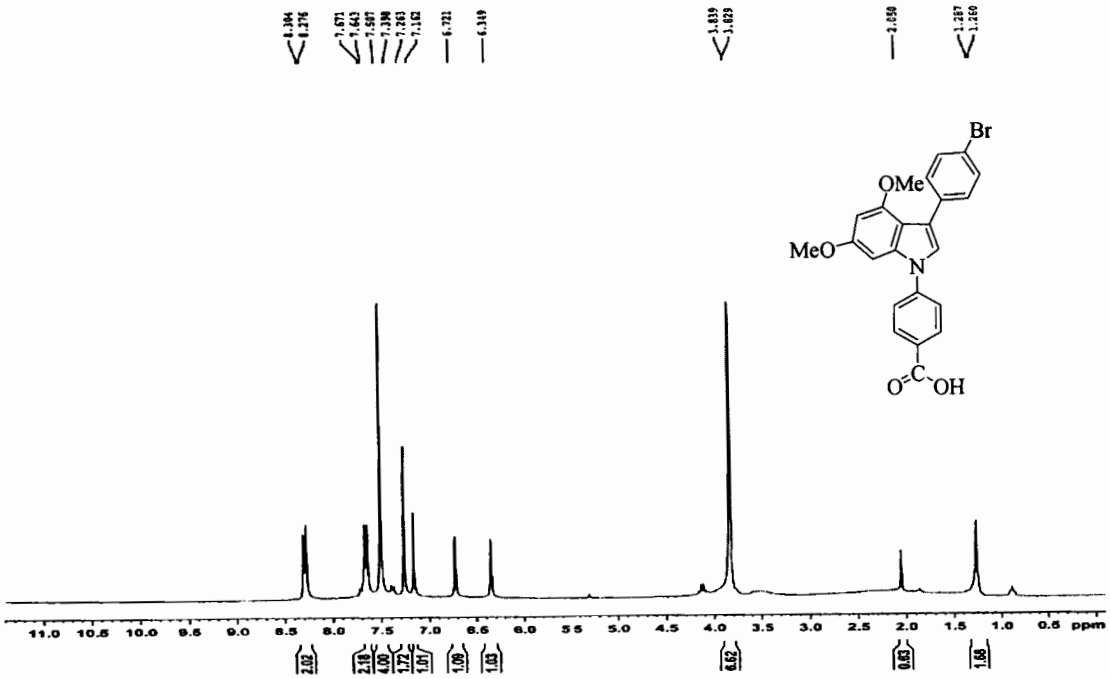

Figure A.15 The ^{1}H NMR (in $CDCl_3$) spectrum of In2

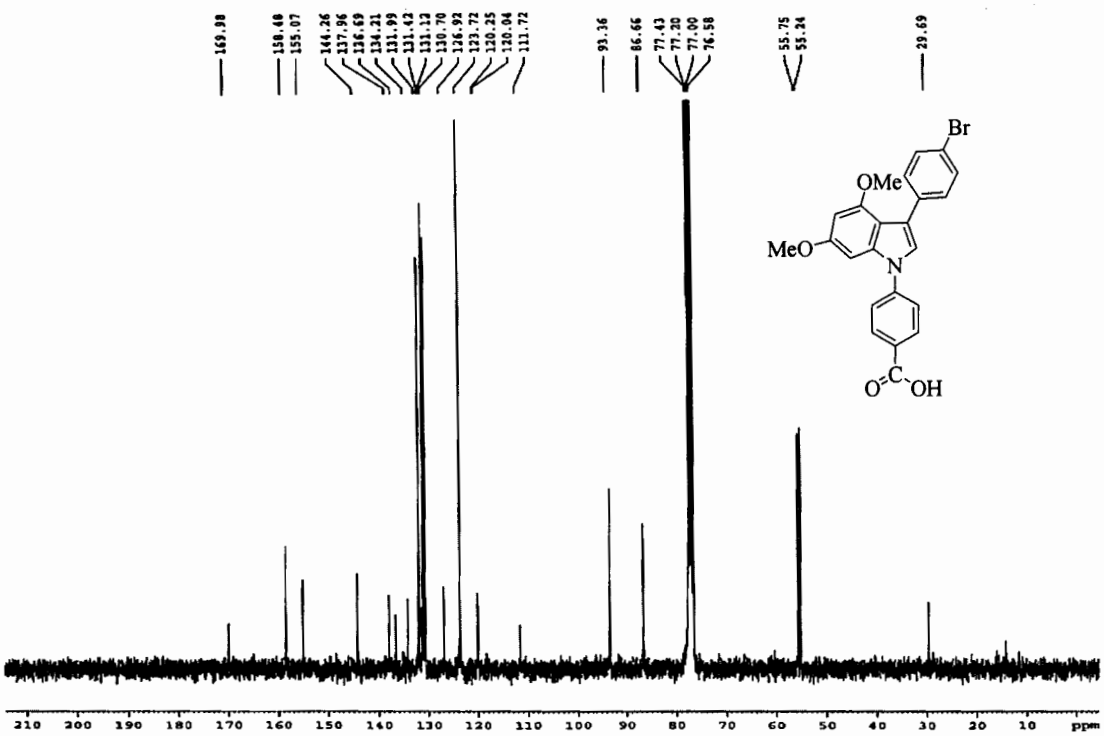

Figure A.16 The ^{13}C NMR spectra of In2

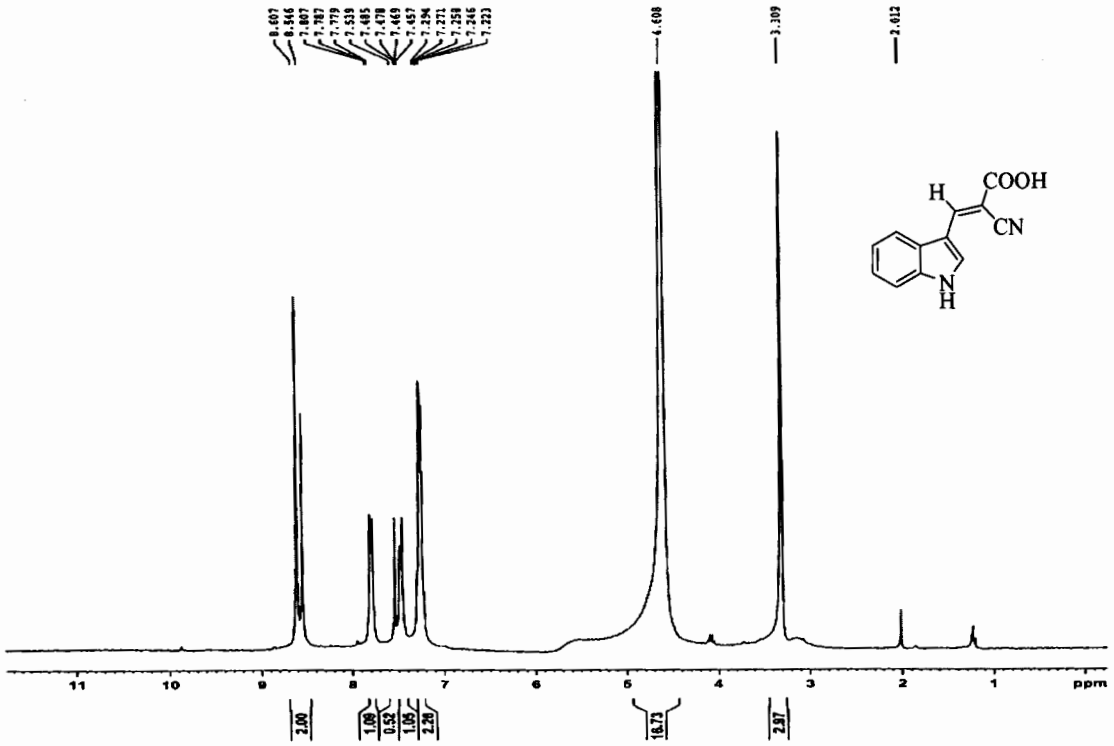

Figure A.17 The ^{1}H NMR (in $CDCl_3$) spectrum of In3

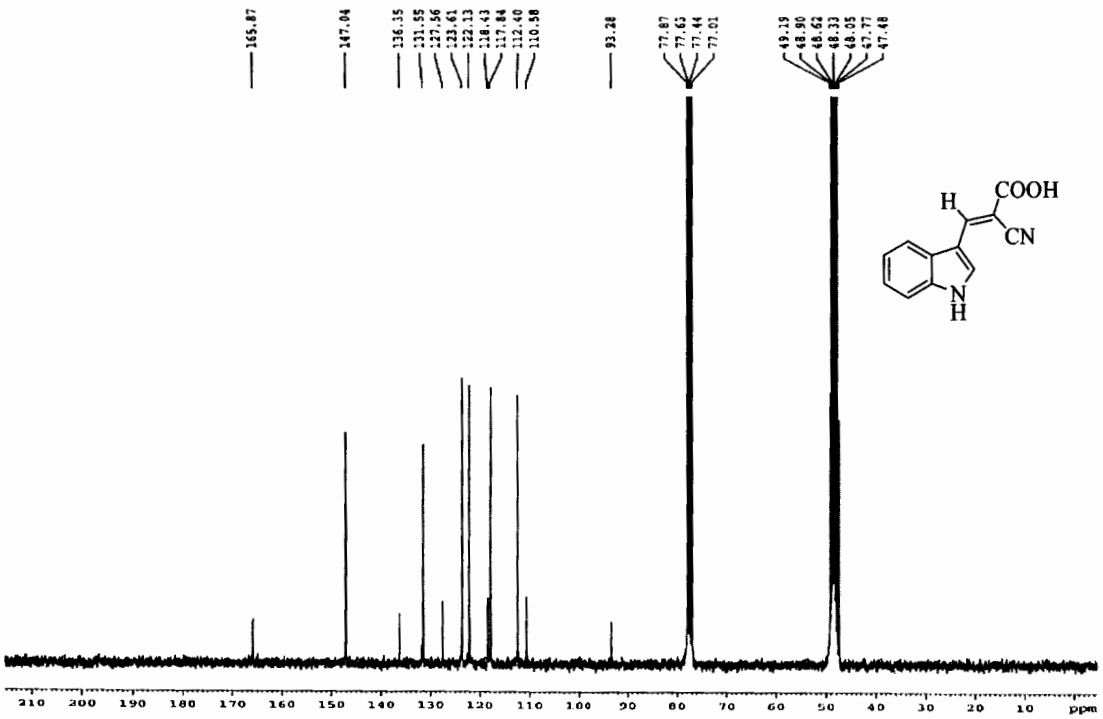

Figure A.18 The ^{13}C NMR spectra of In3

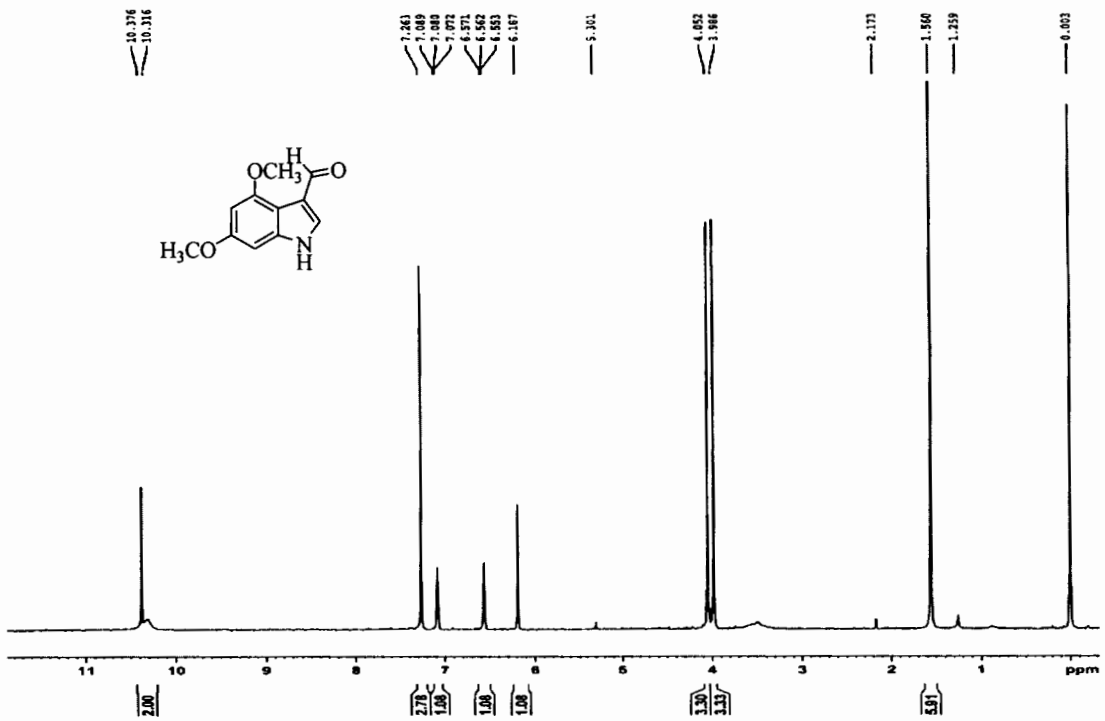

Figure A.19 The ^{1}H NMR (in $CDCl_3$) spectrum of 3-formyl-4,6-dimethoxyindole 9

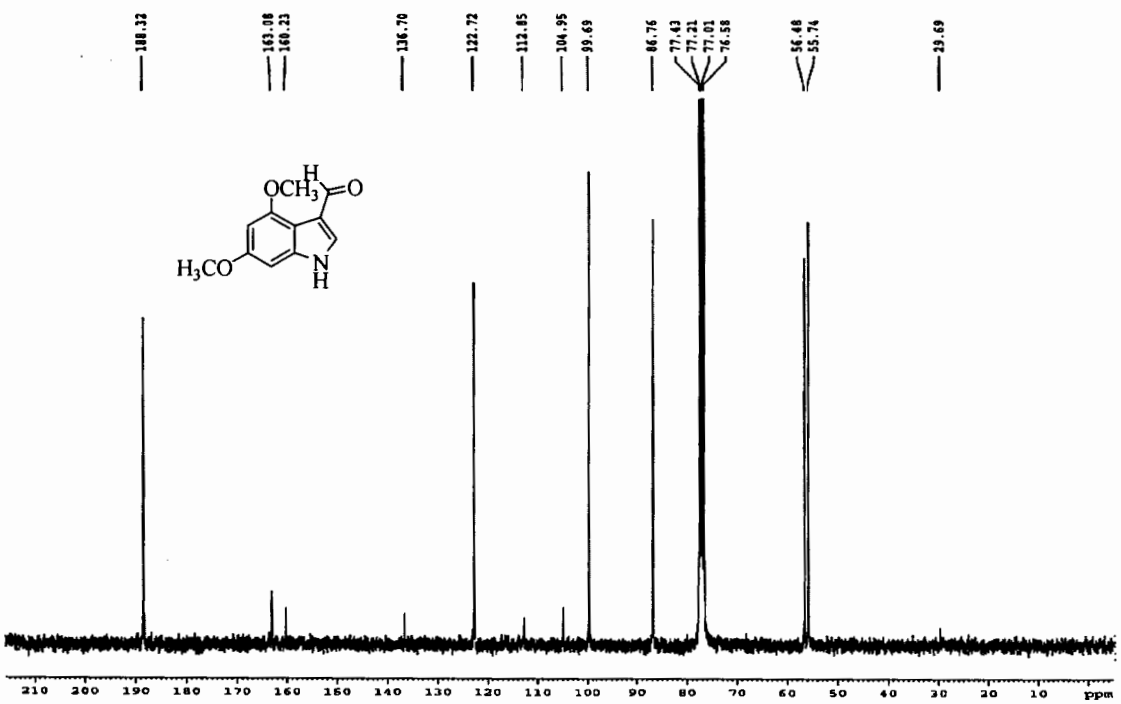

Figure A.20 The ^{13}C NMR spectra of 3-formyl -4,6-dimethoxyindole 9

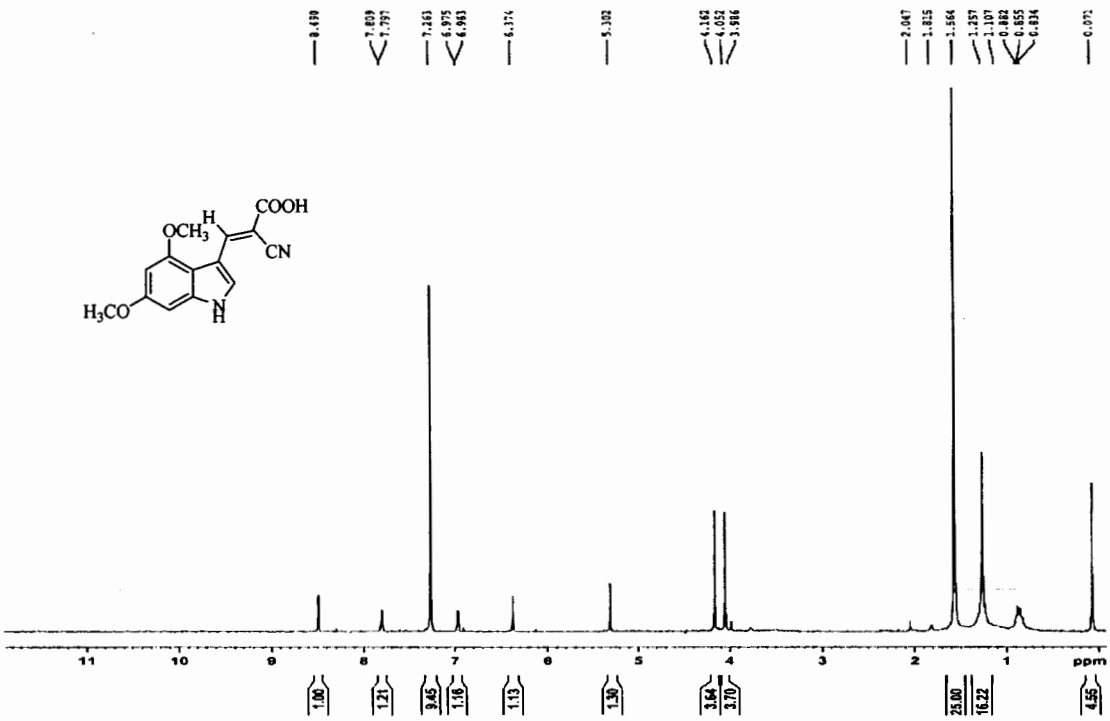

Figure A.21 The ^{1}H NMR (in $CDCl_3$) spectrum of In4

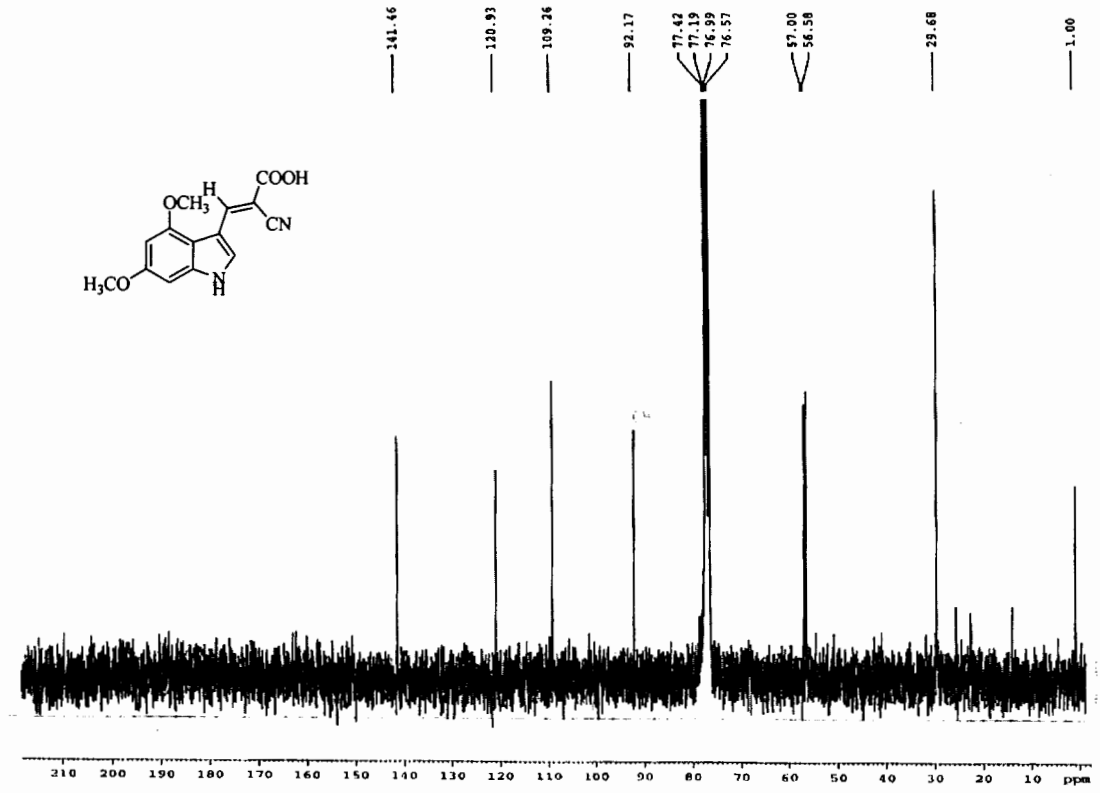

Figure A.22 The ^{13}C NMR spectra of In4

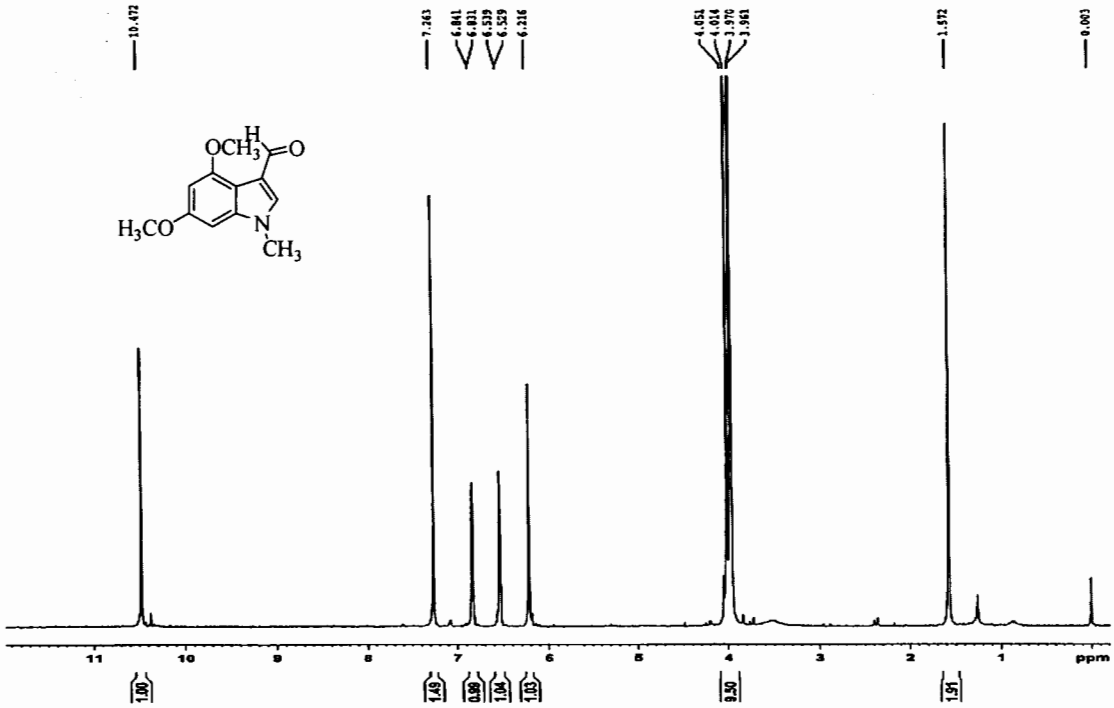

Figure A.23 The ^{1}H NMR (in $CDCl_3$) spectrum of 3-formyl-4,6-dimethoxy-*N*-methylindol 10

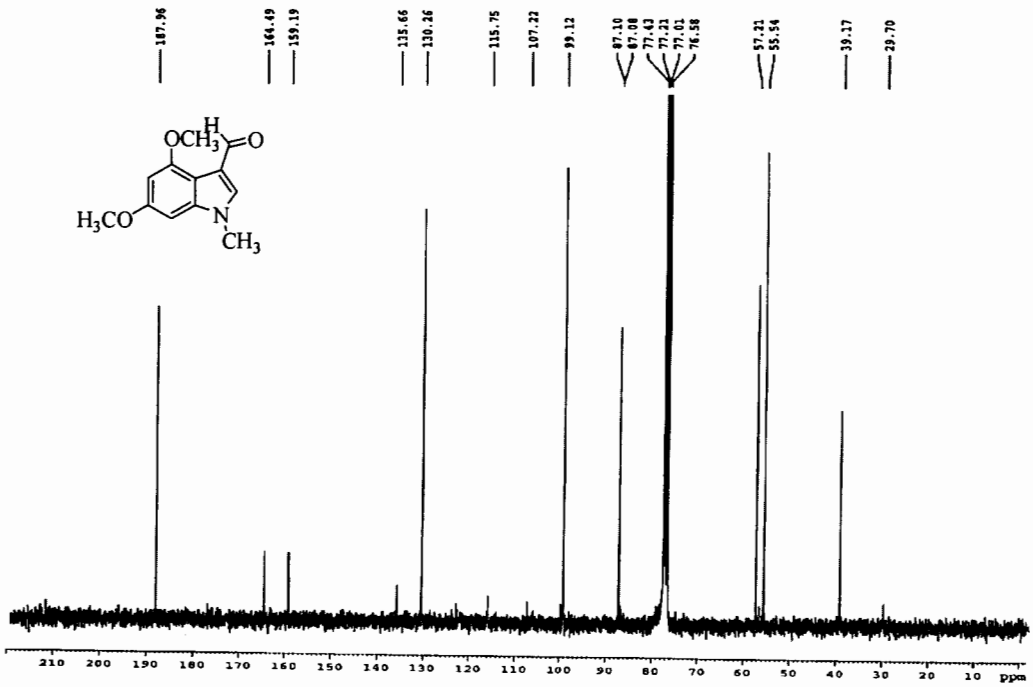

Figure A.24 The ^{13}C NMR spectra of 3-formyl-4,6-dimethoxy-*N*-methylindol 10

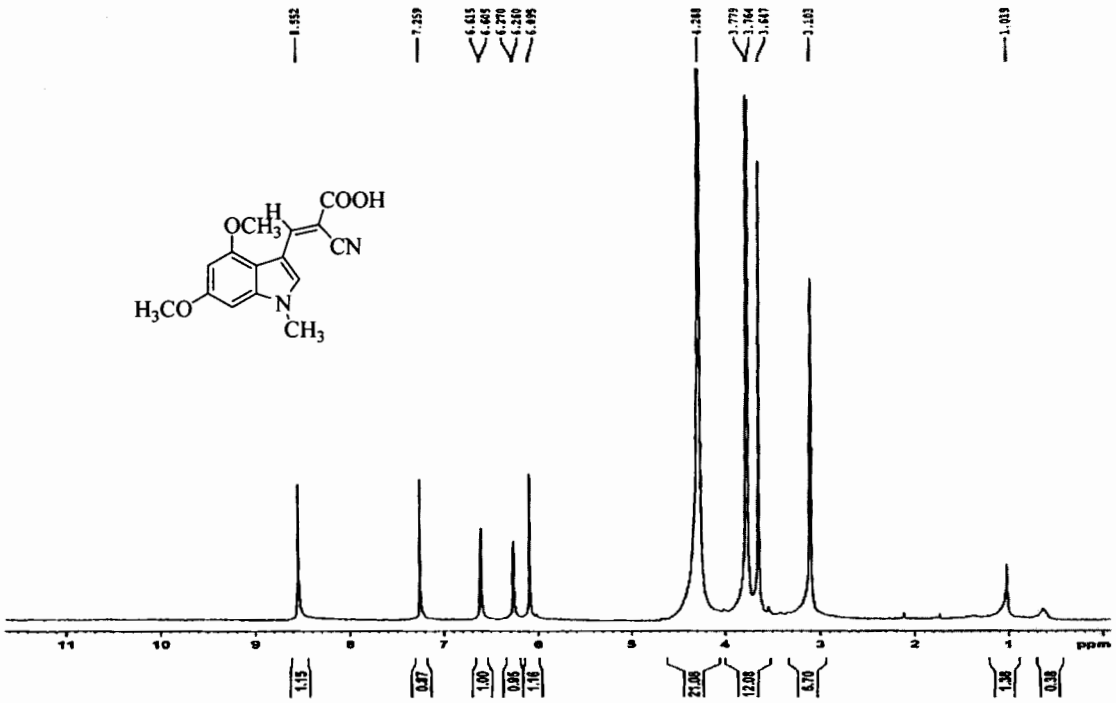

Figure A.25 The ^{1}H NMR (in $CDCl_3$) spectrum of In5

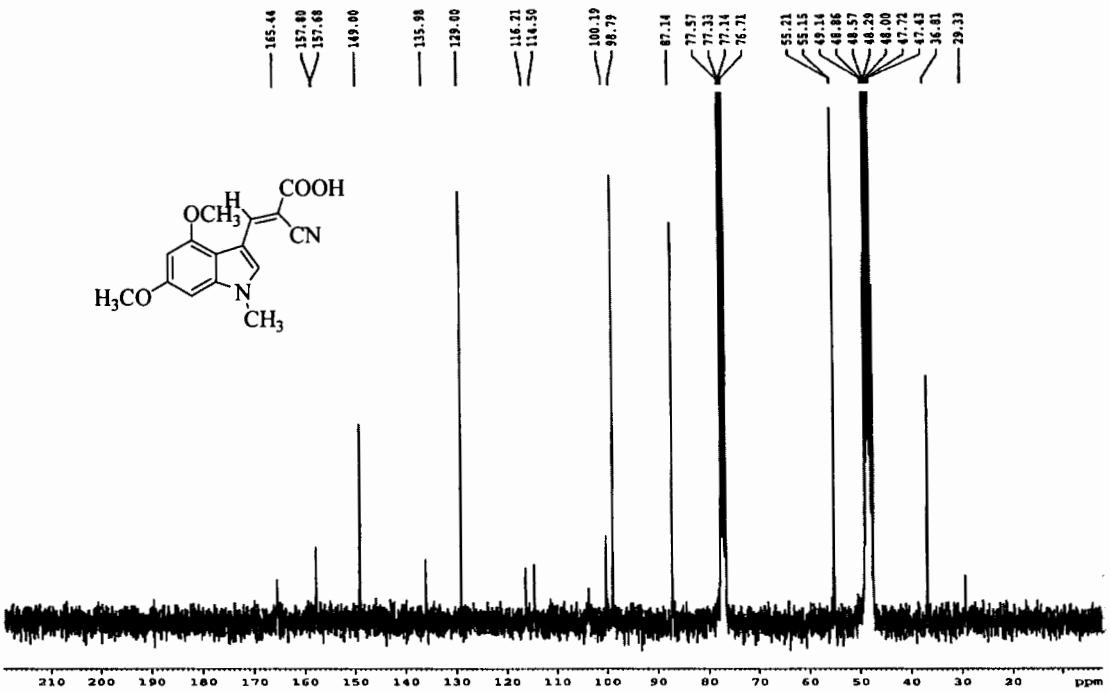

Figure A.26 The ^{13}C NMR spectra of In5

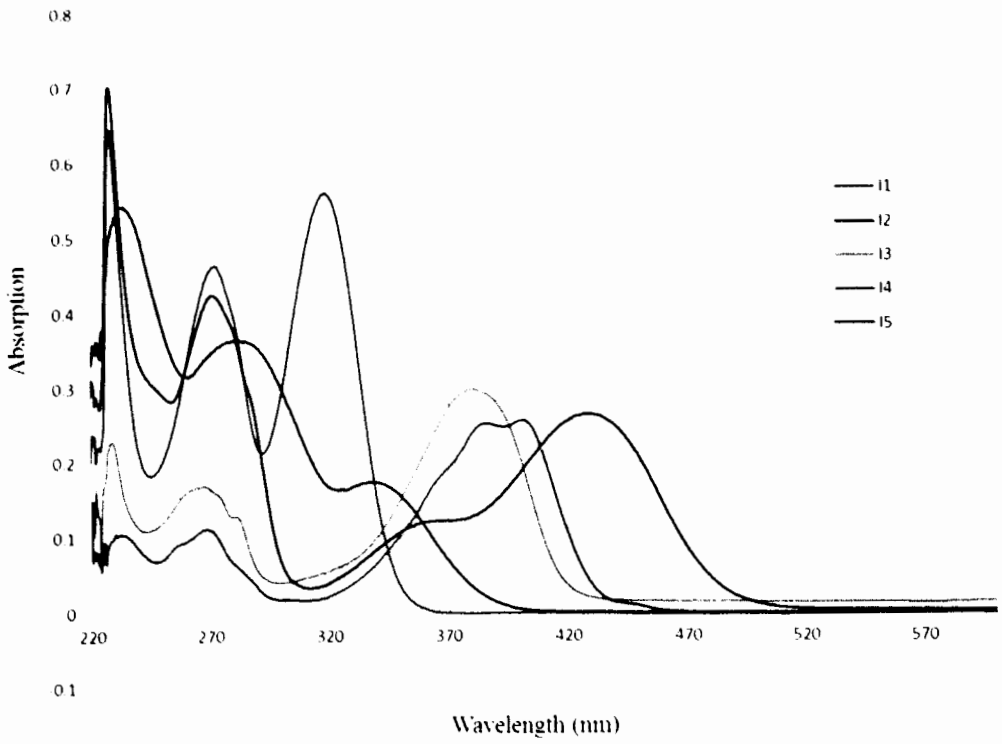

Figure A.27 UV-Vis absorption spectra of In1-In5 in DCM at $5x10^{-6}$ M.

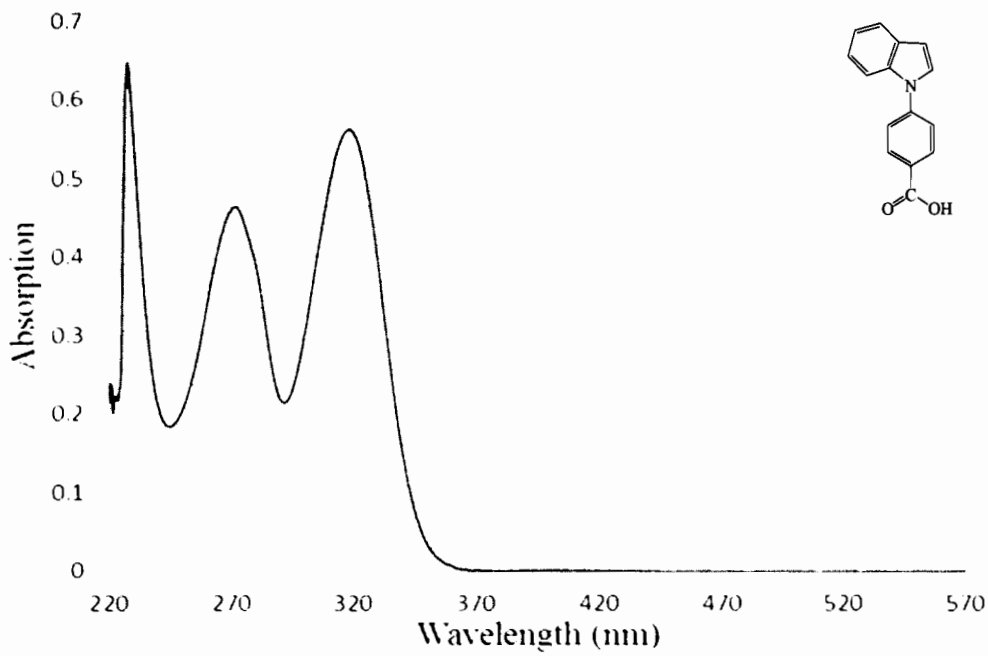

Figure A.28 UV-Vis absorption spectra of In1 in DCM at $5x10^{-6}$ M.

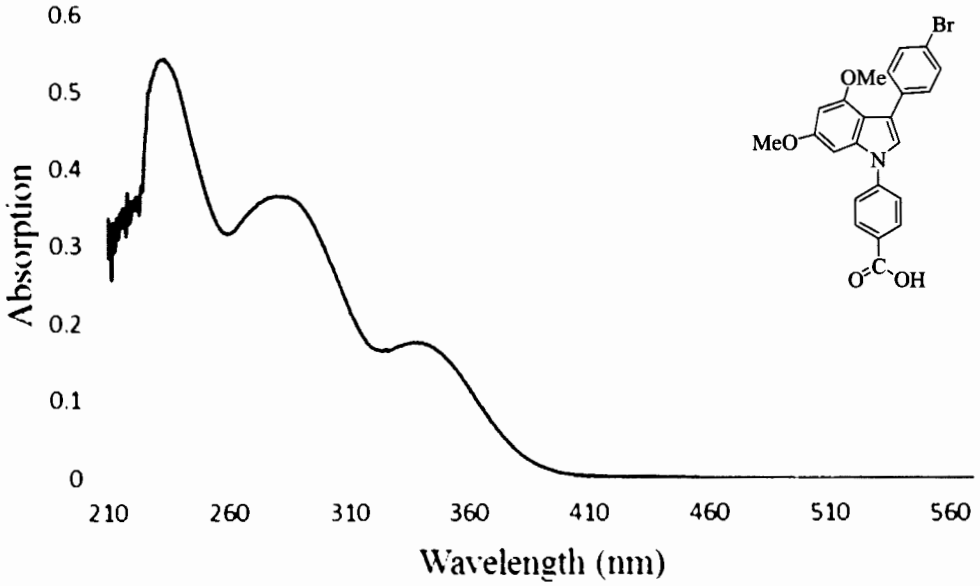

Figure A.29 UV-Vis absorption spectra of In2 in DCM at $5x10^{-6}$ M.

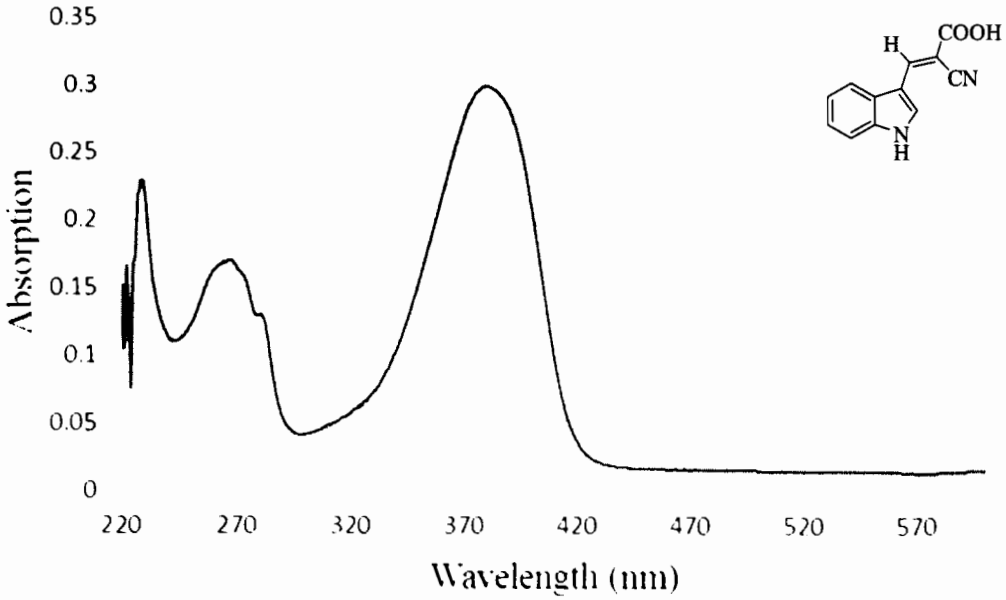

Figure A.30 UV-Vis absorption spectra of In3 in DCM at $1x10^{-5}$ M.

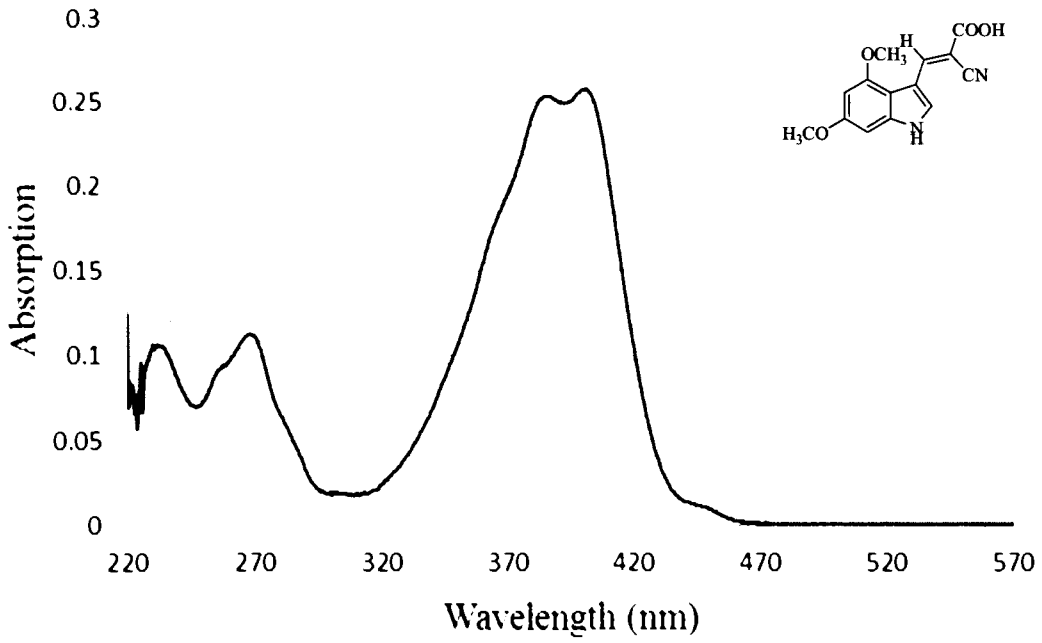

Figure A.31 UV-Vis absorption spectra of In4 in DCM at $5x10^{-6}$ M.

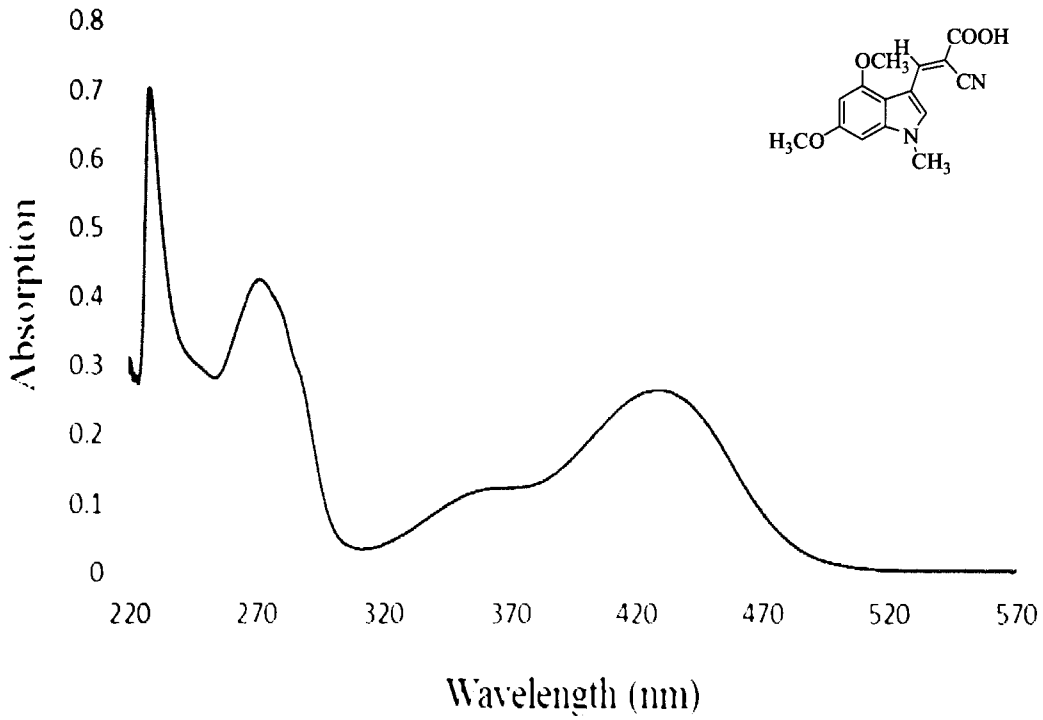

Figure A.32 UV-Vis absorption spectra of In5 in DCM at $5x10^{-6}$ M.

APPENDICES B

Publication

ประชุมวิชาการ มอบ. วิจัย ครั้งที่ 8

17 - 18 กรกฎาคม 2557

อาคารเทพรัตนสิริปภา มหาวิทยาลัยอุบลราชธานี

การสังเคราะห์และพิสูจน์เอกลักษณ์ของอนุพันธ์คาร์บาโซลเพื่อเป็นสารเรืองแสงสีน้ำเงินสำหรับอุปกรณ์ไดโอดเรืองแสงสารอินทรีย์

Synthesis And Characterization Of Carbazole Derivatives As Blue Light-Emitters For Organic Light Emitting Diodes (OLEDs)

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บทคัดย่อ

อนุพันธ์คาร์บาโซลที่มีหมู่ปิดท้ายด้วยโมเลกุลของไพรีนและแอนทราซีนถูกสังเคราะห์ขึ้นโดยใช้ปฏิกิริยาโบรมิเนชัน และปฏิกิริยา Suzukicross-coupling และพิสูจน์เอกลักษณ์ด้วยเทคนิค ^{1}H NMR, UV-Vis, Fluorescence spectroscopy และ เทคนิค cyclic voltammetry โดย 9-Dodecyl-3,6-di(pyren-1-yl)carbazole (CP2) และ 9-Dodecyl-3,6-di (anthracen-1-yl) carbazole (CA2) ให้เสปกตรัมการคายแสงในช่วงสีน้ำเงินเข้มที่ 430 และ 442 nm และมีความเสถียรทางไฟฟ้าที่สูง สารเหล่านี้จึงน่าจะเป็นอีกทางเลือกหนึ่งสำหรับใช้เป็นสารเรืองแสงสีน้ำเงินในไดโอดเรืองแสงอินทรีย์

คำสำคัญ : คาร์บาโซล ไดโอดเรืองแสงที่มีชั้นสารเรืองแสงเป็นสารอินทรีย์ ปฏิกิริยา Suzuki cross-coupling

Abstract

Carbazole derivatives containing pyrene and anthracene substituents were synthesized using bromination and Suzuki cross-coupling reactions, and their chemical structure were characterized by ^{1}H NMR, UV-Vis, fluorescence spectroscopy and cyclic voltammetry. Compound 9-dodecyl-3,6-di(pyren-1-yl)carbazole (CP2) and 9-dodecyl-3,6-di(anthracen-1-yl)carbazole (CA2) showed the PL spectra in deep blue region at 430 and 442 nm and exhibited high electrochemical stability. These compounds could be alternative materials as blue light-emitters in organic light emitting diodes.

Keywords: Carbazole, Organic light-emitting diodes, Suzuki cross-coupling reaction

Introduction

Initally proposed by Ching W. Tang in 1987[1], organic light-emitting diodes (OLEDs) have attracted significant attention from the scientific community due to their potential for future flat-panel displays and lighting applications.[2] Today, the developments of OLED technologies mainly focus on the optimization of device structures and on developing new emitting materials. Clearly, new materials emitting pure colors

of red, green, and blue (RGB)with excellent emission efficiency and high stability, are the key point of OLED development for full-color flat displays. The performance of blue OLEDs is usually inferior to that of green and red OLEDs due to poor carrier injection into the emitters[3] and electroluminescent (EL) properties of the blue OLEDs need to be improved. Therefore, one area of continuing research in this field is the pursuit of a stable-blue emitting material.[4] Although many fluorescent blue emitters have been reported such as pyrene derivatives,[5] carbazole derivatives,[6] anthracene derivatives,[7] fluorene derivatives, and aromatic hydrocarbon,[9] there is still a clear need for further developments in terms of efficiency and color purity compared to red and green emitters.

Therefore, in this work, we reported the synthetic route and properties of 9-dodecyl-3,6-di(pyren-1-yl)carbazole (CP2) and 9-dodecyl-3,6-di(anthracen-1-yl)carbazole (CA2) (end-capped carbazole with pyrene and anthracene groups, respectively as solution processed blue emitters for OLEDs.

Objective

To synthesize and characterize the pyrene and anthracene-substituted carbazole derivatives as blue emitting materials for OLEDs.

Methodology and Experimental

1. General procedures

^{1}H NMR spectra were recorded on Brüker AVANCE (300 MHz) spectrometer. Chemical shifts (δ) are reported relative to the residual solvent peak in part per million (ppm). Coupling constants (*J*) are given in Hertz (Hz). UV-Visible spectra were recorded in CH_2Cl_2 on a Perkin-Elmer UV Lambda 25 spectrometer. Fluorescence spectra were recorded in CH_2Cl_2 on a Perkin-Elmer L S 50B Luminescence spectrometer. Analytical thin-layer chromatography (TLC) was performed with Merck aluminium plates coated with silica gel 60 F_{254}. Column chromatography was carried out using gravity feed chromatography Merck silica gel mesh, 60 Å. Solvent mixture were used and the portions are given by volume.

2. Synthetic procedures

2.1 Synthesis of 9-dodecylcarbazole (2)

To a solution of carbazole (10.0000 g, 59.80 mmol) in DMF (93 mL) was added NaH (2.1500 g, 89.58 mmol). Then, 1-Bromododecane (15.0000 g, 89.70 mmol) was added. The reaction mixture was stirred at 0°C-rt for 20 h. Water (100 mL) was added and the mixture was extracted with ethyl acetate (50 mL x 3). The combined organic phases were washed with a diluted HCl solution (50mL x 2), water (100 mL), and brine (50 mL), dried over anhydrous Na_2SO_4, evaporated and purified by column chromatography to give a pale yellow viscous oil (25.3776 g,97%) ; 1H NMR (300 MHz, $CDCl_3$): δ 8.09 (2H, d, *J* = 2.4 Hz), 7.44 (4H, m), 7.25 (2H, d, *J* = 2.4 Hz, 4.3 (2H, t, *J* = 2.1 Hz), 1.88 (2H, t, *J* = 2.1 Hz), 1.33 (18H, m) and 0.89 (3H, t, *J* = 2.1 Hz)

2.2 Synthesis of 3,6-dibromo-9-dodecylcarbazole(3)

In the round bottom flask, covered with aluminum foil, a stirred solution of 9-dodecylcarbazole (**2**) (0.0700 g, 0.16 mmol) in THF (15 mL) was added NBS (0.0400 g, 0.19 mmol) in small portions. The reaction mixture was poured into ice-cold water. The mixture was allowed to warm to room temperature overnight. The mixture was extracted with methylene chloride (20 mL x 3), washed with water (20 mL x 3), dried over anhydrous Na_2SO_4, evaporated and purified by column chromatography to give a white pearl solid (0.0719 g,91%); 1H NMR (300 MHz, $CDCl_3$) δ8.15 (2H, d, J = 1.5 Hz), 7.56 (2H, dd, J_1 = 0.9 Hz, J_2 = 0.6 Hz), 7.26 (2H, d, J = 0.9 Hz), 4.24 (2H, t, J = 0.9 Hz), 1.82 (2H, t, J = 0.9 Hz), 1.43 (18H, m), 0.87 (3H, t, J = 2.1 Hz)

2.3 Synthesis of 9-dodecyl-3,6-di(pyren-1-yl)carbazole (CP2)

To a stirred solution of 3,6-dibromo-9-dodecyl carbazole (**3**) (0.4000 g, 0.81 mmol) and $Pd(PPh_3)_4$ (0.0400 g, 0.04 mmol) in tetrahydrofuran (30mL) was added pyrene-1-boronic acid (0.41g, 1.70mmol), and an aqueous Na_2CO_3 solution (0.8500 g, 8.10 mmol). The mixture was refluxed for 48 h. After cooling, the mixture was extracted with dichloromethane (30 mL x 3), washed with water(30mL x 3), dried over anhydrous, evaporated and purified by column chromatography to give a white pearl solids (0.3195 g, 53%); 1H NMR (300 MHz, $CDCl_3$) δ 8.41 (2H, s), 8.34 (2H, d, J = 9.30 Hz), 8.25 (2H, d, J = 7.80 Hz), 8.20-8.10 (10H, m), 8.06-7.97 (4H, m), 7.80 (2H, d, J = 8.4 Hz), 7.64 (2H, d, J = 7.64 Hz), 4.47 (2H, t, J = 7.2 Hz), 1.10 (2H, t, J = 6.9 Hz), 1.57-1.30 (18H, m) and 0.91 (3H, t, J = 6.9 Hz)

2.4 Synthesis of 9-dodecyl-3,6-di(anthracen-1-yl)carbazole (CA2)

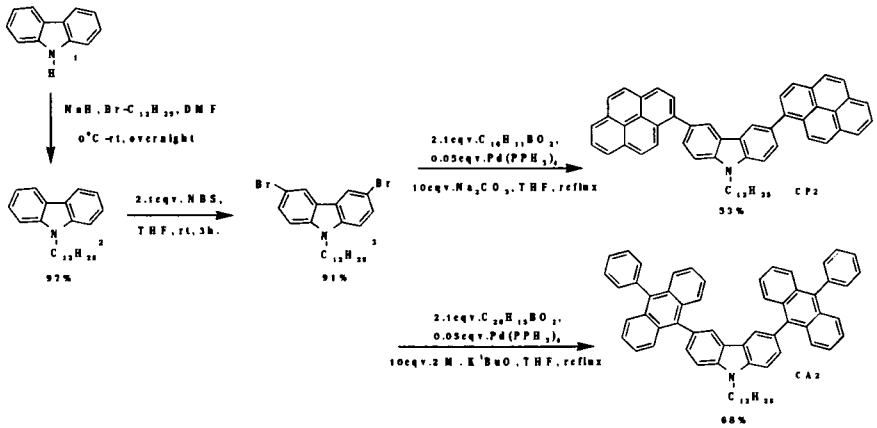
To a stirred solution of 3,6-dibromo-9-dodecyl carbazole (**3**) (0.2500g, 0.42 mmol) and $Pd(PPh_3)_4$ (0.02g, 0.05 mmol) in tetrahydrofuran (25 mL) were added 10-phenyl-9 anthraceneboronic acid (0.26g, 0.89 mmol), and an aqueous ^{t}BuOK solution (0.47 g, 4.26 mmol). The mixture was refluxed for 48 h. After cooling, the mixture was extracted with dichloromethane (30 mL x 3), washed with water (30mL x 3), dried over anhydrous, evaporated and purified by column chromatography to give a white pearl solids (0.2440 g,68%);1H NMR (300 MHz, $CDCl_3$) δ 8.18 (2H, s), 7.83-7.80 (5H, m), 7.74-7.68 (7H, m), 7.63-7.50 (12H, m), 7.32-7.26 (12H, m), 4.56 (2H, t, J = 6.9 Hz),2.15 (2H, t, J = 7.5 Hz), 1.57-1.28 (18H, m) and 0,86 (3H, t, J = 6.3 Hz

Results and Discussion

1. Synthesis of CP2 and CA2

The target molecules **CP2** and **CA2** were successfully synthesized as shown in scheme 1. The 9-dodecylcarbazole was first synthesized by nucleophilic substitution reaction at the 9-position of carbazole (**1**) with 1-bromododecane. Then, selective bromination of compound 2 at 3 at the 6-position with NBS in THF afforded compound 3 in 91% yields. The target molecule CP2, dipyrene substituted carbazole, was synthesized by Suzuki cross coupling of **3** with pyrene-1-boronic acid using $Pd(PPh_3)_4$ as catalyst and Na_2CO_3 as base in THF at reflux for 48 h. Dianthracene substituted carbazole (**CA2**) was

synthesized by Suzuki cross coupling reaction of **3** and 10-phenyl-9-anthraceneboronic acid with $Pd(PPh_3)_4$ as a catalyst and ^{t}BuOK as a base in THF at reflux for 48 h. (Scheme 1.) All compounds were characterized by ^{1}H NMR analysis. The data are presented in the experimental section.



Scheme 1. Synthesis of carbazole derivatives

2. Optical properties

The spectroscopic properties of CP2 and CA2 were measured in dichloromethane (CH_2Cl_2) as shown in Figure 1. The solution absorption spectra exhibited two major absorption bands. The first absorption bands at around 200-275 nm could be attributed to the π-π^* transition of the carbazole moieties and the second absorption bands at longer wavelength around 350-400nm corresponded to the π-π^* transition of the carbazole-pyrene and carbazole-antracene cores. These compounds in solution fluoresced in the blue region (430–442 nm) with featureless photoluminescence (PL) spectra. The emission spectra displayed maxima at 430 and 442 nm, for **CP2** and **CA2**, respectively. From the substituted dipyrene **CP2** to substituted anthracene**CA2**, the **PL** spectra also showed red-shifted absorption and in PL spectra, concomitant with the increasing conjugation length (Figure 1).

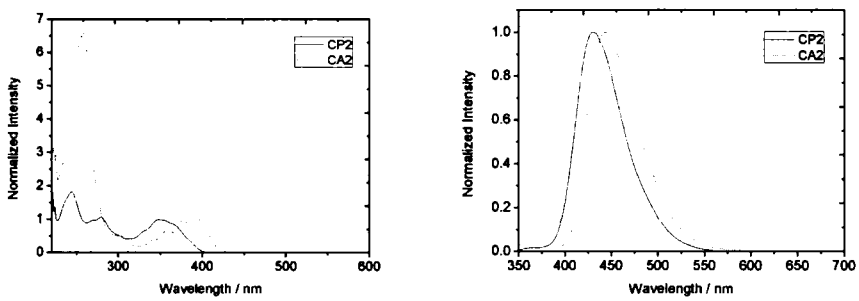


Figure 1. Normalized absorption spectra (left) and normalized emission spectra (right) of CP2 and CA2 in CH_2Cl_2

3.Electrochemical properties

Electrochemical behaviors of **CP2** and **CA2** were investigated by cyclic voltammetry **(CV)**, and the results were shown in Figure 2. Multiple cyclic voltammetry (CV) scans of **CA2** revealed identical cyclic voltammograms with no additional peak at lower potentials on the cathodic scan (E_{pc}). This suggested no electrochemical coupling at either the carbazole or anthracene peripheries, indicating electrochemically stable molecules.

The CV curve of **CP2** showed three irreversible oxidation processes.The first oxidation is assigned to the removal of electrons from the carbazole moiety resultingin carbazole radical cations **($CBZ^{\cdot+}$)**. In the case of CP2, during additional peaks at lower potentials were observed during the cathodic scan indicating electrochemical coupling reactions of the radical cations. The generated $CBZ^{\cdot+}$ is stabilized by electron delocalization through 1,8-substituted electron rich pyrene rings to form a pyrene radical cation **($Py^{\cdot+}$)** which is relatively less stable compared with the $CBZ^{\cdot+}$. The $Py^{\cdot+}$ readily undergoes a radical–radical dimerization coupling to form a stable neutral pyrene dimer as indicated by the presence of the cathodic peaks **(E_{pc})** around 0.61–0.94 V in their first CV scan and an increasing change in the CV curves under the repeated CV scans (Figure 2).[10] This might be the first example of pyrene derivatives that undertook an electrochemical oxidation coupling reaction. The HOMO energy levels were estimated to be -5.41 and -5.45 eV, respectively **(Table 1)**.

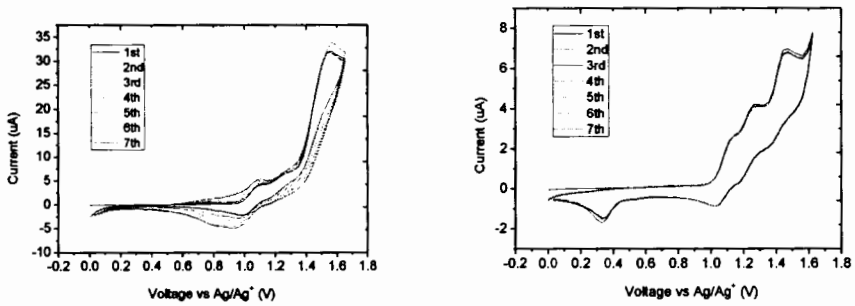


Figure 2. Cyclic voltammograms of **CP2** (left) and **CA2** (right) in dry CH_2Cl_2 with scan rate of 0.05 V/s and 0.1 M n-Bu_4NPF_6 as electrolyte

Table 1 Physical data of CP2 and CA2

Compound	λ_{abs}(log ε)[a](nm $M^{-1}cm^{-1}$)	λ_{em}[a](nm)	Eg[b] (eV)	HOMO[c] (eV)	LUMO[d] (eV)
CP2	279 (5.37),348 (2.35)	430	3.10	-5.41	-2.31
CA2	305 (3.93),359 (4.09), 377 (4.24),397 (4.23)	442	2.95	-5.45	-2.50

[a]Measured in dilute CH_2Cl_2

[b] Calculated from the absorption edge, $E_g = 1240/\lambda_{onset}$

[c]Estimated from HOMO = $-(4.44 + E^{ox}_{onset})$

[d]Estimated from LUMO = HOMO + E_g

3. HOMO and LUMO frontier orbitals

To gain insights into the geometrical and electronic properties of these multiple substituted carbazoles, quantum chemical calculations were performed using the DFT/B3LYP/6-31G(d,p) method. The optimized structures of **CP2**and **CA2** revealed that the attached pyrene and anthracene units twisted out of the plane of the carbazole forming bulky substituents around the carbazole. This would facilitate the formation of amorphous morphology. In all cases for **CP2** and **CA2**, π-electrons in the HOMO orbitals delocalized only over the carbazole and two substituents at the 3,6-positions substituted carbazole backbone, whereas after light irradiation (**LUMO**), the excited electrons were delocalized largely over the pyrene and anthracene plane.

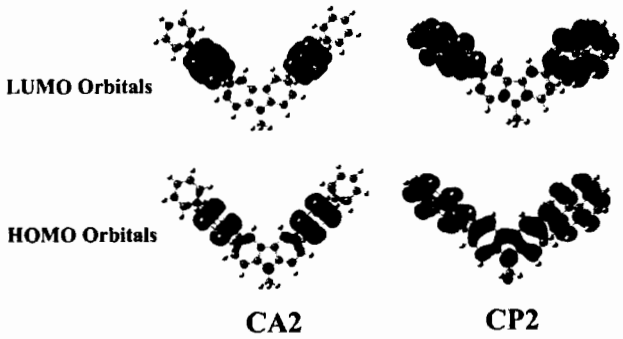


Figure 3. The HOMO (bottom) and LUMO (top) orbitals of CP2 and CA2 calculated by DFT/B3LYP/6-31G(d,p) method.

Conclusion

In conclusion, we have successfully synthesized pyrene and anthracene-substituted carbazole (**CP2, CA2**) by the Suzuki-cross coupling reaction of dibromo intermediates with pyrene-1-boronic acid and 10-phenyl-9-anthraceneboronic acid, respectively. The electronic and electrochemical properties of both compounds could be tuned by varying the substituents on carbazole ring. The substitution of dipyrene **CP2** by substituted anthracene **in CA2** increased the conjugation length of compounds resulting in a red-shift and broad in absorption spectra. These compounds emitted blue light with high thermal stability, which is potentially useful for applications in electroluminescent devices. Optimize structures and electron density of HOMO and LUMO have been performed by DFT/B3LYP/6-31G(d,p) method.

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