SYNTHESIS AND CHARACTERIZATION OF CARBAZOLE-BASED DONOR ORGANIC DYES FOR DYE SENSITIZED SOLAR CELLS

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บทคัดย่อ

ชื่อเรื่อง : การสังเคราะห์และพิสูจน์เอกลักษณ์ของโมเลกุลสีย้อมไวแสงอินทรีย์ที่มีหมู่คาร์บาโซลเป็นหมู่ให้อิเล็กตรอนสำหรับเซลล์แสงอาทิตย์ชนิดสีย้อมไวแสง
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ศัพท์สำคัญ : ดี-ไพ-เอ ดี-ดี-ไพ-เอ คาร์บาโซล เซลล์แสงอาทิตย์ชนิดสีย้อมไวแสง

ในงานวิจัยนี้รายงานการสังเคราะห์และพิสูจน์เอกลักษณ์ของสารอินทรีย์ที่มีหมู่คาร์บาโซลเป็นหมู่ให้อิเล็กตรอน โดยออกแบบโมเลกุลสีย้อมประเภท D-π-A ที่มีหมู่ไพ-คอนจูเกตและหมู่รับอิเล็กตรอนที่แตกต่างกัน โมเลกุลสีย้อมประเภท D-D-π-A ที่มีหมู่ไพ-คอนจูเกตที่แตกต่างกัน สำหรับใช้เป็นโมเลกุลสีย้อมไวแสงในเซลล์แสงอาทิตย์ชนิดสีย้อมไวแสง โมเลกุลเป้าหมายที่สังเคราะห์ได้พิสูจน์เอกลักษณ์โดยใช้เทคนิค ^{1}H-NMR ^{13}C-NMR และ FT-IR โมเลกุลเป้าหมายที่สังเคราะห์ได้ ทำการวัดการดูดกลืนแสงด้วยเทคนิคยูวีและวิสิเบิลสเปคโตรสโคปีพบว่า โมเลกุลเป้าหมายมีการดูดกลืนแสงในช่วงของความยาวคลื่นแสงยูวีและวิสิเบิล เมื่อทำการทดสอบคุณสมบัติทางความร้อนพบว่า โมเลกุลเป้าหมายมีความเสถียรทางความร้อน จึงคาดว่าโมเลกุลเหล่านี้สามารถนำไปใช้เป็นโมเลกุลสีย้อมไวแสงในเซลล์แสงอาทิตย์ชนิดสีย้อมไวแสงได้อย่างมีประสิทธิภาพ

ABSTRACT

TITLE : SYNTHESIS AND CHARACTERIZATION OF CARBAZOLE-BASED
DONOR ORGANIC DYES FOR DYE SENSITIZED SOLAR CELLS
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DEGREE : MASTER OF SCIENCE
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This thesis deals with synthesis and characterization of carbazole-based donor organic dyes. The designed D-π-A organic dyes containing different linker and acceptor units and designed D-D-π-A organic dyes containing different linker units for using as dye molecules in dye-sensitized solar cell. The target molecules were characterized by ^{1}H-NMR ^{13}C-NMR and FT-IR. The target molecules exhibit a adsorption band cover UV and visible region. All compounds show good thermal properties. The photovoltaic performance of DSCs using these materials as dyes is under investigation and will be reported in the future.

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LIST OF ABBREVIATIONS

ABBREVIATION	FULL WORD
DMF	Dimethylformamide
THF	Tetrahydrofuran
DMSO	Dimethylsulphoxide
RT/rt	Room temperature
d	Doublet
dd	Doublet of doublets
td	Triplet of doublets
ε	Molarabsorption
eV	Electron volt
h	Hour/hours
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
IPCE	Incident photon to current efficiency
η	Overall light-to-electric power conversion efficiency
ITO	Indium-tin oxide
FT-IR	Fourier transform Infrared
J	Coupling constant
M	Molar concentration
MHz	Megahertz
min	Minutes
mol	Moles
mmol	Milimoles
m	unresolved multiple
N	Normal concentration
nm	Nanometers

LIST OF ABBREVIATIONS (CONTINUED)

ABBREVIATION	FULL WORD
NMR	Nuclear magnetic resonance
δ	Chemical shift in ppm relative to tetramethylsilane
ppm	Parts per million
s	Singlet
t	Triplet
TLC	Thin-layer chromatography
UV	Ultra-violet
n-Bu$_4$NPF$_6$	Tetrabutylammonium hexafluorophosphate
TD-DFT	Time-dependent density functional theory
GBL	Gamma-butyrolactone
NMP	*N*-methyl-2-pyrrolidone
S$^+$	Excited dye
S^0	Original state
AM 1.5	Air Mass 1.5
K	Kilo
W	Watt
V	Voltage (V)
s	second
I	Current
(A) A	Ampere
V_{oc}	Open circuit voltage
J_{sc}	Short circuit current
ff	Fill factor
J-V	Current density-voltage

CHAPTER 1

INTRODUCTION

1.1 Dye Sensitized Solar cells

1.1.1 Introduction

The quality of human life is to a large extent dependent on the availability of energy sources. The present annual worldwide energy consumption has already reached a level of over 4 x 10^{18} J and is predicted to increase rapidly with the increasing world population and the rising demand of energy in the developing countries. By meeting this energy demand with further depletion of fossil fuel reserves, the environmental damages followed by the enhanced green house effect, caused by the combustion of fossil fuels, could get out of hand. If, on other hand, this energy demand could be met by the use of renewable energy sources the environmental cost could be decreased. The sun could annually supply the earth with 3 x 10^{24} J, which is about 750000 times more than the global population currently consumes [1]. The dream to capture the sunlight and turn it into electric power or to generate chemical fuels, such as hydrogen, has in the last couple of decades become reality.

Solar cells are the devices that are able to convert solar energy into electrical energy. The aim of solar cell research is to increase the solar energy conversion efficiency at low cost to provide a cost- effective sustainable energy source. There are various types of solar cells and some of them will be mentioned here. Crystalline silicon solar cells are the most widely used solar cells and dominate the market at present. Stable devices and the possibility to use knowledge and technologies from the microelectronics industry have given crystalline solar cells a leading role among other types of solar cells. To meet the demand of reducing material and purification costs thin film solar cells have been developed. Thin film solar cells are based on thin layers of various semiconductor materials such as amorphous silicon, cadmium telluride (CdTe), copper indium gallium diselenide (CIGS). Even though the thin film solar cell requires less material, the complex production processes of the different combinations of rare materials are expensive and may limit a future large-scale production.

An alternative solar cell technology is the dye-sensitized solar cell (DSCs). DSCs consist of a dye-sensitized semiconductor material, often titanium dioxide (TiO_2), where dyes molecules attached onto the semiconductor act as light absorbers. This is in contrast to the solar cells mentioned above where the light is absorbed by the semiconductor material itself.

Dye solar cells (DSCs) have been actively studied since Grätzel and co-workers reported high solar energy to electricity conversion efficiencies of up to 12% with a DSCs based on ruthenium complex photosensitizer. However, the use of ruthenium dyes will limit the large-scale application of such complexes in the future due to the problem of high and unfriendly environmental issues. In the meantime, metal free organic dyes are being increasingly studies in DSCs due to good performance, simple preparation and low cost. Recently, a metal-free sensitizer, an indoline dye, gave an impressive high efficiency of 9% for DSCs [2]. However, organic dyes have often presented the low conversion efficiency and low operation stability compared to metal complexes. The major factors for low conversion efficiency for the DSCs based on organic dyes are the formation of dye aggregation on the semiconductor surface and recombination of conduction band electrons with triiodide in the electrolyte.

Organic dye containing an electron donor, π-conjugation and π-electron acceptor, which is called the D-π-A structure. The π-conjugated unit as an electron spacer to connect the donor and accepter.

1.1.2 Principle of Dye Sensitized Solar Cells

The DSCs, or the Grätzel cell, is a complex system where three different components, the semiconductor, the chromophore and the electrolyte are brought together to generate electric power from light without suffering any permanent chemical transformation (Figure 1.1) [3].

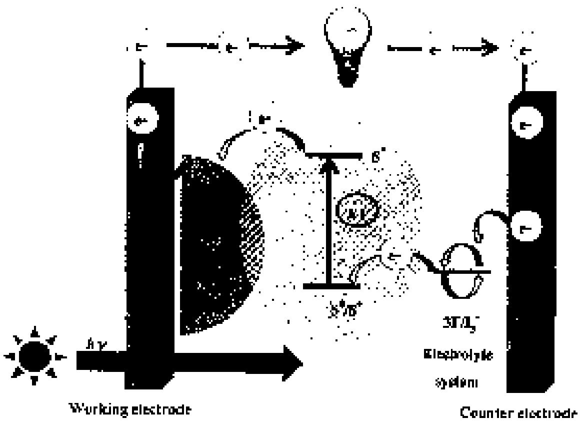


Figure 1.1 Schematic picture of the dye sensitized solar cell

The nanocrystalline semiconductor is usually the anatase TiO_2, although alternative wide band gap oxides such as ZnO can be used. A monolayer of the chromophore, i.e. the sensitizer, is attached to the surface of the semiconductor. Photoexcitation of the chromophore results in the injection of an electron into the conduction band of the semiconductor (Figure 1.2). The chromophore is regenerated by the electrolyte, usually an organic solvent containing a redox couple, such as iodide/triiodide. The electron donation to the chromophore by iodide is compensated by the reduction of triiodide at the counter electrode and the circuit is completed by iodide is compensated by the reduction of triiodide at the counter electrode and the circuit is completed by electron migration through the external load. The overall voltage generated corresponds to the difference between the Fermi level of the semiconductor and the redox potential of the electrolyte [4].

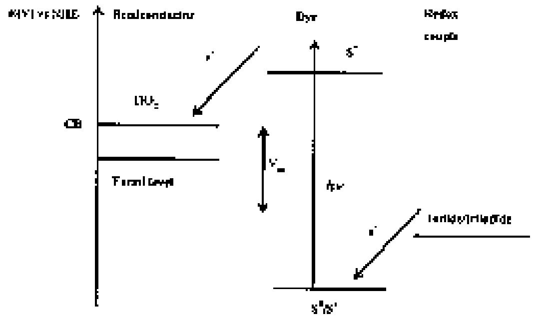


Figure 1.2 Schematic picture of the electron flow in the DSCs

The performance of the solar cell can be quantified with parameters such as incident photon to current efficiency (IPCE), open circuit photovoltage (V_{oc}) and the overall efficiency of the photovoltaic cell (η_{cell}). The efficiency of the DSC is related to a large number of parameters. This thesis will only focus on the development of efficient sensitizers and their synthesis, even so, it is important to have the general concepts in mind.

1.1.3 Overall Efficiency of the Photovoltaic Cell (η)

The solar energy to electricity conversion efficiency under white-light irradiation (e.g., AM1.5 G) can be obtained from the following equation:

$$\eta = \frac{J \cdot V \cdot ff}{I_0}$$

Where I_0 (mW/cm^2) is the photon flux (e.g., ca. 100 mW/cm^2 for AM 1.5 G), J_{sc} (mW/cm^2) is the short-circuit current density under irradiation, V_{oc} (V) is the open-circuit voltage, ff represents the cell fill factor. The fill factor is defined by the ratio of the current and the voltage at the maximum power point to the short circuit current and the open circuit voltage. The fill factor measures the square ness of the I-V curve (Figure 1.3) [5].

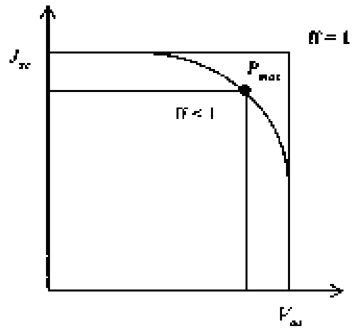


Figure 1.3 I-V curve

1.1.4 Sensitizers

The efficiencies of the sensitizers are related to some basic criteria. The HOMO potential of the dye should be sufficiently positive compared to the electrolyte redox potential for efficient dye regeneration.10 The LUMO potential of the dye should be sufficiently negative to match the potential of the conduction band edge of the TiO_2 and the light absorption in the visible region should be efficient. However, by broadening the absorption spectra the difference in the potentials of the HOMO and the LUMO energy levels is decreased. If the HOMO and LUMO energy levels are too close in potential, the driving force for electron injection into the semiconductor or regeneration of the dye from the electrolyte could be hindered. The sensitizer should also exhibit small reorganization energy for excited-state and ground-state redox processes, in order to minimize free energy losses in primary and secondary electron transfer steps [6, 7].

1.1.4.1 Ruthenium sensitizers

Sensitizers of ruthenium complexes such as the **N3**, **N719** and black dyes have been intensively investigated and show record solar energy-to-electricity conversion efficiencies (η) of 10, 11.2 and 10.8%, respectively (Figure 1.4) [8].

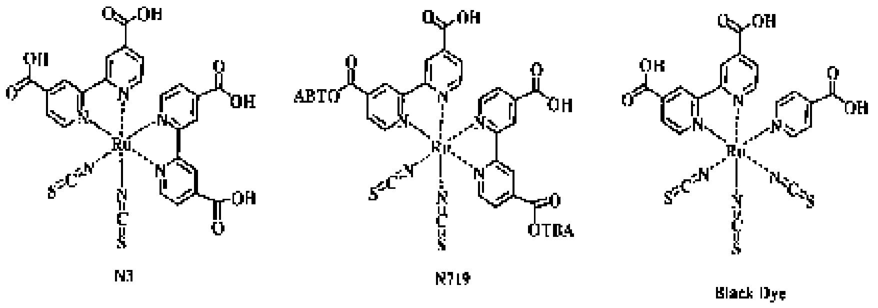


Figure 1.4 Chemical structures of **N3**, **N719** and black dyes

A large number of different ruthenium based sensitizers have been investigated in order to improve the photovoltaic performance and stability of the DSCs. Amongst them especially four (**K19**, **K73**, **K77** and **Ru-1**) [6], have shown interesting properties in that they are competing in efficiency and have higher molar extinction coefficients than the three former. The enhanced absorption observed is expected from the extended conjugated system [9].

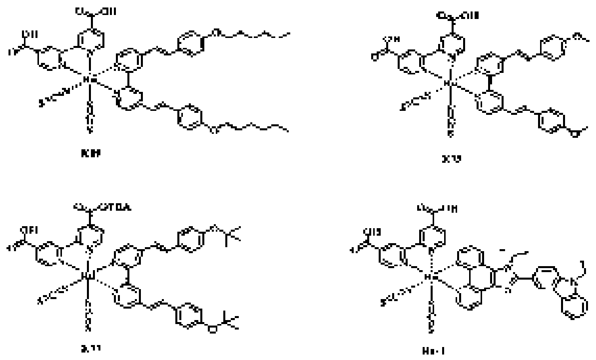


Figure 1.5 Chemical structures of **K19**, **K73**, **K77** and **Ru-1** dyes

1.1.4.2 Organic sensitizers

Recently, performances of DSCs based on metal-free organic dyes have been remarkably improved by several groups. The first transient studies on a coumarin dye in DSCs was performed in 1996, when Gratzel et al. found injection rates of 200 fs from **C343** into the conduction band of TiO_2. Since **C343** has a narrow absorption spectrum, the conversion efficiency of this specific compound was low. By introduction of a methine unit, the π-system could be expanded and in 2001 a respectable efficiency of 5.6% was obtained with **NKX-2311** [7]. Adding more methine units (up to three) and introducing bulky substituents to prevent dye-aggregation could push the efficiency to 6.7% in 2005 (**NKX-2753**). Currently other building blocks like thiophene are tested, which are believed to give a higher stability. First results of 7.4% for **NKX-2677** are encouraging [10]

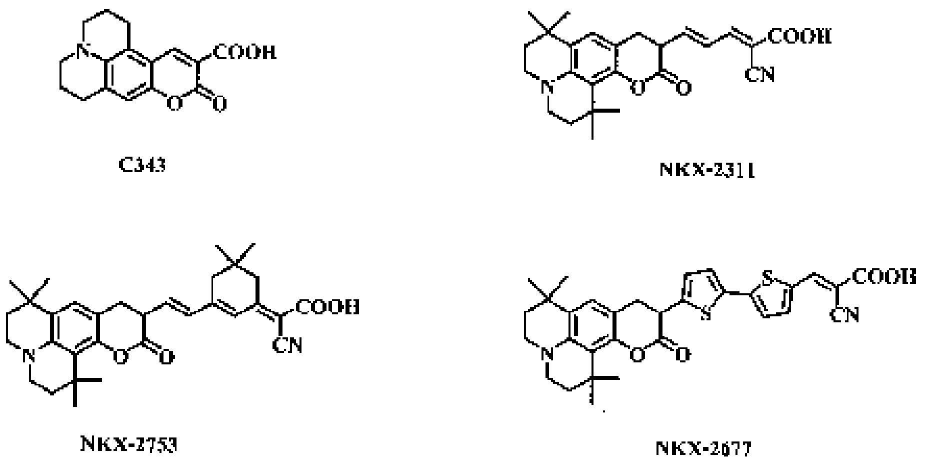
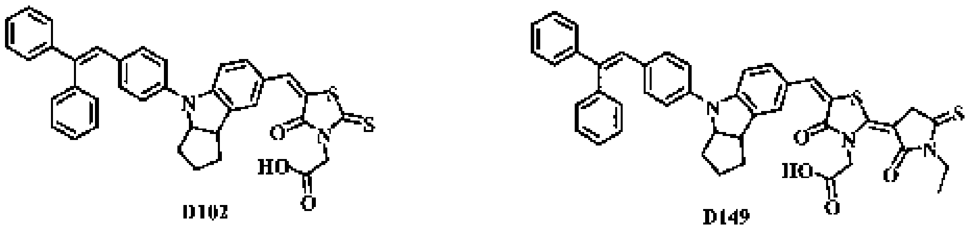


Figure 1.6 Chemical structures of **C343**, **NKX-2311**, **NKX-2753** and **NKX-2677** dyes

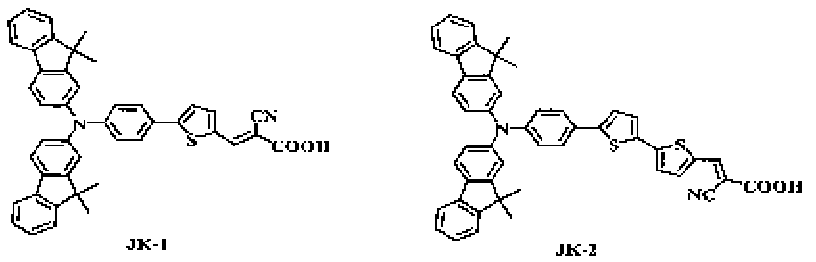
In 2003, an indoline dye **D102** and **D149** discovered by Ito et al. These indoline dyes gave solar-to-electrical energy conversion efficiency of 6.1 and 9%, respectively, in full sunlight. A highest efficiency for organic dyes has been achieved by an indoline dye **D149** [11].



D102 D149

Figure 1.7 Chemical structures of **D102** and **D149** dyes

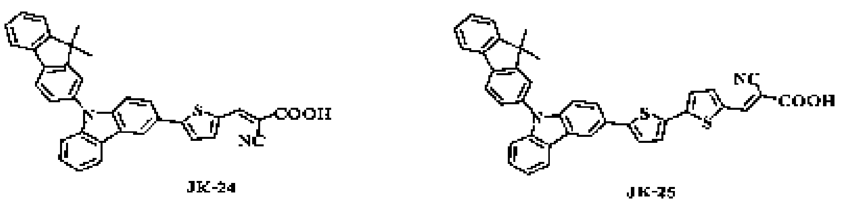
In 2007, Yuanzuo Li et al. [12]. reported that the highly efficient and stable organic dyes **JK-1** and **JK-2** composed of bis-dimethylfluoreneaniline moiety as the electron donor and cyanoacrylic acid moiety as the electron acceptor with an overall conversion efficiency of 8.01%.



JK-1 JK-2

Figure 1.8 Chemical structures of **JK-1** and **JK-2** dyes

In 2007, Duckhyun Kim et al. [13]. investigated that the organic dyes **JK-24** and **JK-25** containing N-(9,9-dimethylfluoren-2-yl)carbazole as electron donor and cyanoacrylic acid as electron acceptor bridged by thiophene units, gave an overall conversion efficiency (η) of 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 motif have been little explored for DSCs.



JK-24 JK-25

Figure 1.9 Chemical structures of **JK-24** and **JK-25** dyes

In 2009, Ping Shen et al. [14]. investigated that the organic dyes **SD1** and **SD2** containing triphenylamine, both with and without an n-hexyl-substituted oligothiophene as π-conjugated linker. These triphenylamone dyes gave solar-to-electrical energy conversion efficiency of 3.06 and 4.02%, respectively, under simulated AM 1.5 G solar irradiation (100 mW/cm^2).

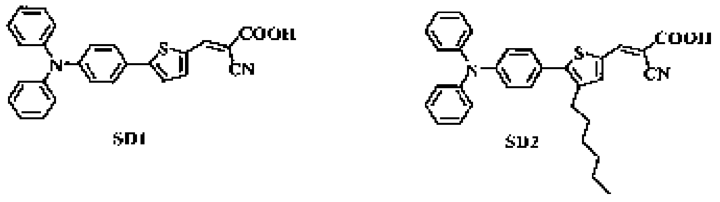


Figure 1.10 Chemical structures of **SD1** and SD2 dyes

1.1.4.3 Anchoring groups

Most of the dyes employed in DSCs have carboxylic acid groups to anchor on the TiO_2-surface. The binding is reversible with high binding equilibrium constants (K = 10^5 M^{-1}). At a pH > 9 the equilibrium is typically shifted to the reactant side and the dye molecules desorb. This somewhat fragile linkage triggered the development of dyes with different anchoring groups. In general the binding strength to a metal oxide surface decreases in the order phosphonic acid > carboxylic acid > ester > acid chloride > carboxylate salts > amides [15]. due to its strong electronic withdrawing properties, the most widely used and successful to date being the carboxylic acid and phosphonic acid functionalities. The carboxylic acid groups, while ensuring efficient adsorption of the dye on the surface also promote electronic coupling between the donor levels of the excited chromophores and the acceptor levels of the TiO_2 semiconductor. Some of the possible modes of chelation/derivatization, ranging from chemical bonding (chelating or bridging mode) to H-bonding, are shown in Figure 1.10 [16].

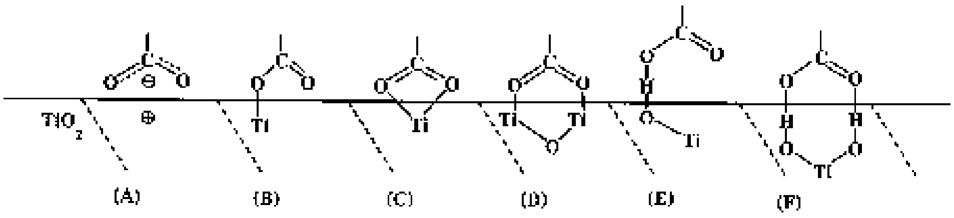


Figure 1.11 Possible binding modes for carboxylic acid groups on TiO_2

CHAPTER 2

SYNTHESIS AND CHARACTERIZATION OF TRIPHENYLAMINE-BASED DONOR DYES WITH DIFFERENT ACCEPTORS

2.1 Introduction

Organic sensitizers were divided into three parts; donor, linker and acceptor. This is a convenient method to systematise the sensitizers. There are several basic criteria that an efficient sensitizer should fulfill, and these criteria can be used when designing a new chromophore. First of all, light excitation should be associated with vectorial electron flow from the light harvesting moiety of the dye, i.e. the donor and the linker, towards the proximity of the semiconductor, i.e. the acceptor/ anchoring group of the dye. This can be seen as the HOMO is located over the donor and the linker, while the LUMO is located over the acceptor, i.e. a pronounced push-pull effect. Second, the HOMO potential of the dye should be sufficiently positive compared to the electrolyte redox potential for efficient dye regeneration. Third, the LUMO potential of the dye should be sufficiently negative to match the potential of the conduction band edge of the TiO_2. Fourth, a strong conjugation and electronic coupling across the donor and the acceptor to ensure high electron transfer rates. Finally, to obtain a dye with efficient photocurrent generation, π-stacked aggregation on the semiconductor should be avoided [17]. Aggregation may lead to intermolecular quenching or molecules residing in the system not functionally attached to the semiconductor surface and thus acting as filters.

2.1.1 Triphenylamine donor

In photovoltaic cells the interest of using triphenylamine based sensitizers has increased in recent years. Triphenylamine have some very investigating electronic and optical properties and been lately investigated as advanced molecular optoelectronic materials due to their thermal stability and tunability of physical properties through chemical modification.

Organic dyes derived from triphenylamine (TPA) with TPA as the electron donor, which showed that expansion of π-electron systems conjugated with phenyl ring of TPA had obvious effect on the performance of DSCs and gave high power conversion efficiency [17]. Among the donor groups, triphenylamine (TPA) and its derivatives have displayed promising properties in the development of DSCs, because the TPA unit suppresses the aggregation of the dye due to its nonplanar structure [18]. Cause the overall conversion efficiency of DSCs based on **D5** was 5.94% (J_{sc} = 12.00 mA/cm^2, V_{oc} = 688 mV, ff = 0.72).

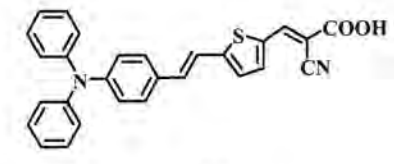

D5

Figure 2.1 Examples of dye D5

2.1.2 Oligothiophenes as π-conjugated linker

Expansion of the π-conjugated C=C backbone to extend the absorption spectrum and broaden it to the red region, is one way to decrease the HOMO/LUMO energy level differences and thereby increase the solar cell performance. This would, however, complicate the synthetic procedure and affect the stability of the dye due to photoinduced *trans* to *cis* isomerisation. The introduction of different π-conjugated ring moieties, such as thiophene, benzene or pyrrole is an elegant way of extending the π-conjugated system without affecting the stability of the dye. In 2003 Hara et al. reported a series of coumarine dyes with different linker units (Figure 2.2) [19].

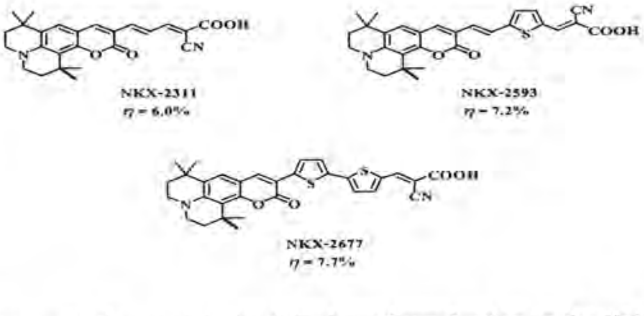


Figure 2.2 π-conjugated extension by thiophene introduction in the linker

Broadened toward the red region when the dyes are adsorbed on the surface of TiO$_2$, leading to an increase of the photocurrent. **NKX-2593** and **NKX-2677** both show efficiencies over 7% and have almost identical absorption spectra. From a synthetic point of view, **NKX-2593** requires a slightly shorter synthetic route than **NKX-2677** to obtain approximately the same efficiency.

2.1.3 Cyanoacrylic acid and Cyanoacrylamide as Acceptor and Anchoring Groups

The dyes are bonded to the TiO_2 surface through an anchoring group. The anchoring group should provide close contact between the dye acceptor unit and the TiO_2 surface for efficient electron injection and in general a strong bond is desired to avoid dye desorption over time. The former requisite is achieved by designing dyes with anchoring groups also acting acceptor group upon dye excitation.

Anchoring to TiO_2 has been achieved through a number of functional groups. In general the binding strength to a metal oxide surface decreases in the order phosphonic acid > carboxylic acid > ester > acid chloride > carboxylate salts > amides [15] due to its strong electronic withdrawing properties.

2.2 Aim of the Study

We designed a novel donor π-conjugate acceptor (D-π-A) organic materials based on triphenylamine as the donor group, with a thiophene linker and a cyanoacrylamide or cyanoacrylic acid moiety as acceptor/anchoring group (**TpSSA3** and **TpSSA4**). The synthetic strategy included well-known methodology, such as Ullmann coupling, Suzuki cross coupling and the last step where cyanoacrylamide or cyanoacrylic acid was coupled to the chromophore according to the Knoevenagel condensation reaction.

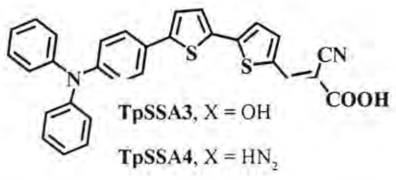
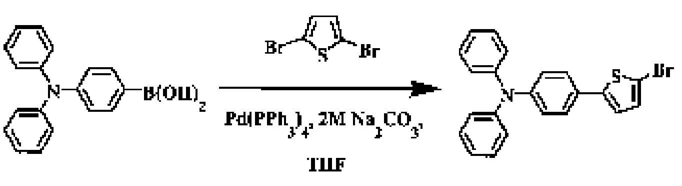


Figure 2.3 Organic dye structures of **TpSSA3** and **TpSSA4** organic dyes

2.3 Results and Discussion

2.3.1 Synthesis

For the synthesis of triphenylamine based dyes, (*E*)-2-cyano-3-(5-(5-(4 (diphenylamino)phenyl)thiophen-2-yl)thiophen-2-yl)acrylic acid (**TpSSA3**), first 4-(5-bromothiophen-2-yl)-*N*,*N*-diphenylbenzenamine (**TpS1**) was prepared from triphenylamine boronic acid precursor and commercially available 2, 5-dibromothiophene under Suzuki cross coupling reaction in the presence of Pd(PPh$_3$)$_4$ as catalyst and 2M Na$_2$CO$_3$ as a base in THF as a solvent for 24 h to directly yield 4-(5-bromothiophen-2-yl)-*N*,*N*-diphenylbenzenamine (**TpS1**). The residue was purified by column chromatography on silica gel eluting with hexane to afford a white solid in 26% as shown in Figure 2.4.



TpS1, 26%

Figure 2.4 Suzuki cross coupling reaction to form 4-(5-bromothiophen-2-yl)-*N*,*N*-diphenyl benzenamine (**TpS1**).

The mechanism of Suzuki cross coupling as shown in Figure 2.5

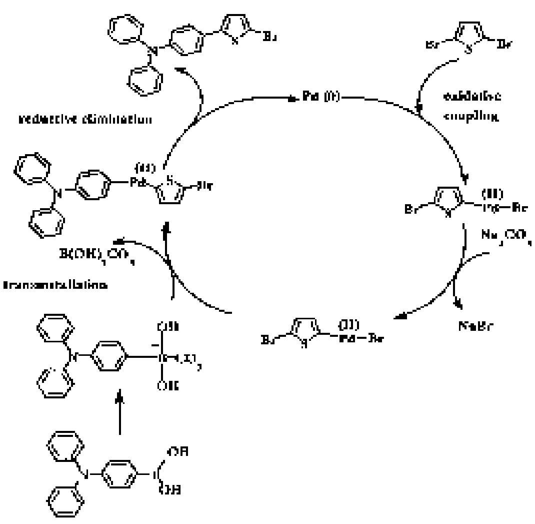


Figure 2.5 The proposed mechanism of Suzuki coupling reaction.

Suzuki cross coupling reaction of 4-(5-bromothiophen-2-yl)-*N,N*-diphenyl benzenamine **(TpS1)** with 5-Formyl-2-thiophene boronic acid in the presence of $Pd(PPh_3)_4$ as catalyst and 2M Na_2CO_3 as a base in THF as a solvent for 24 h to directly yield 5-(5-(4-(diphenyl amino)phenyl)thiophen-2-yl)thiophene-2-carbaldehyde **(TpS2)**. The residue was purified by column chromatography on silica gel eluting with hexane increasing gradually to Hexane:CH_2Cl_2 (6:1) to afford a yellow solid in 82% as shown in Figure 2.6.

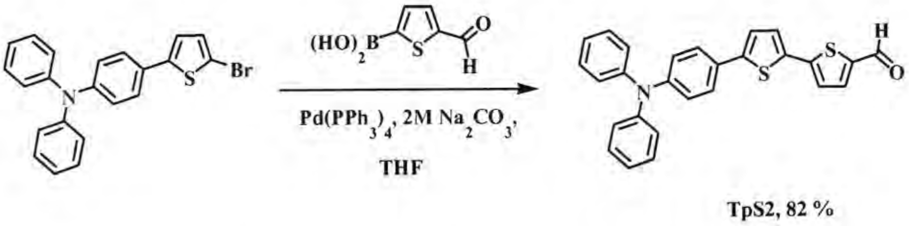


Figure 2.6 Suzuki cross coupling reaction to form 5-(5-(4-(diphenylamino)phenyl)thiophen-2-yl) thiophene-2-carbaldehyde **(TpS2)**.

The mechanism of Suzuki cross coupling of 5-(5-(4-(diphenylamino)phenyl) thiophen-2-yl)thiophene-2-carbaldehyde **(TpS2)** is shown in Figure 2.7

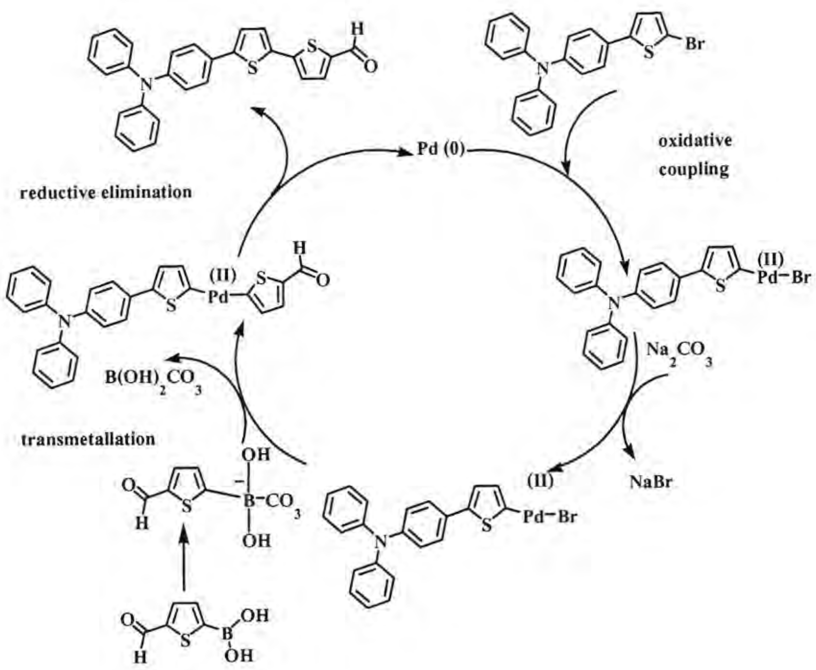


Figure 2.7 The proposed mechanism of Suzuki coupling reaction.

Knoevenagel condensation reaction of 5-(5-(4-(diphenylamino)phenyl)thiophen-2-yl)thiophene-2-carbaldehyde (**TpS2**) with 2-cyanoacetic acid in the presence of acetic acid as catalyst and ammonium acetate as co-catalyst gave *(E)*-2-cyano-3-(5-(5-(4-(diphenylamino) phenyl) thiophen-2-yl)thiophen-2-yl)acrylic acid (**TpSSA3**) in good yield.

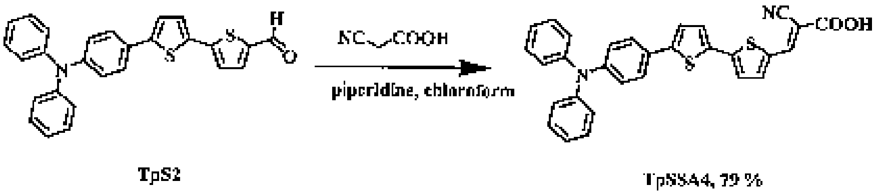


Figure 2.8 Knoevenagel condensation reaction to form *(E)*-2-cyano-3-(5-(5-(4-(diphenylamino) phenyl)thiophen-2-yl)thiophen-2-yl)acrylic acid (**TpSSA3**).

The mechanism of *(E)*-2-cyano-3-(5-(5-(4-(diphenylamino)phenyl)thiophen-2-yl)thiophen-2-yl)acrylic acid (**TpSSA4**) is shown in Figure 2.9

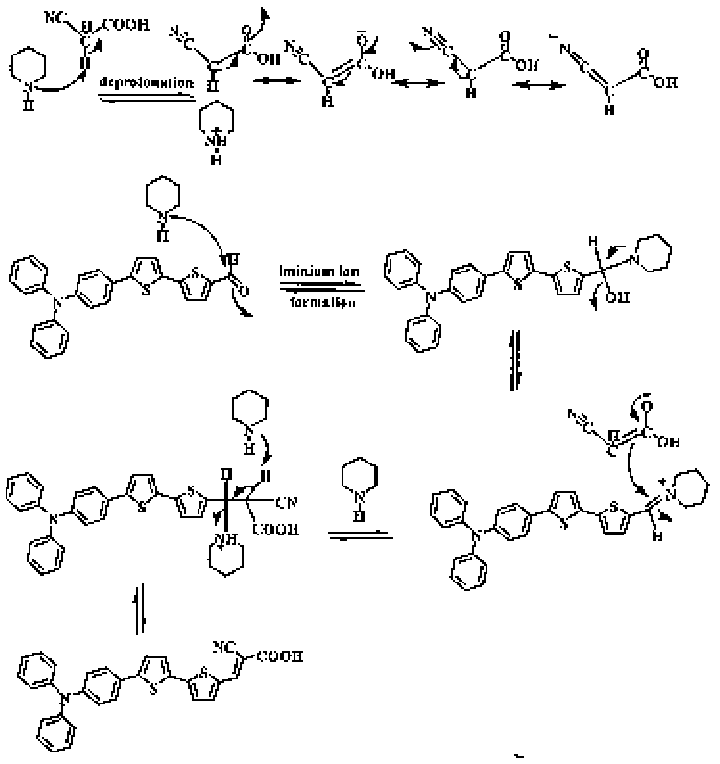
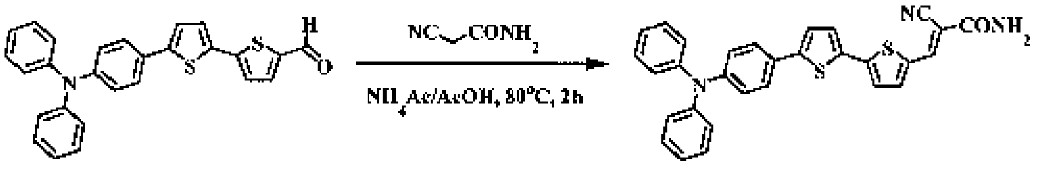


Figure 2.9 The proposed mechanism of Knoevenagel condensation reaction of *(E)*-2-cyano-3-(5-(5-(4-(diphenylamino)phenyl)thiophen-2-yl)thiophen-2-yl)acrylic acid (**TpSSA4**).

Knoevenagel condensation reaction of 5-(5-(4-(diphenylamino)phenyl)thiophen-2-yl)thiophene-2-carbaldehyde **(TpS2)** with 2-cyanoacetamide in the presence of acetic acid as catalyst and ammonium acetate as co-catalyst gave (*E*)-2-cyano-3-(5-(5-(4-(diphenyl amino) phenyl)thiophen-2-yl)thiophen-2-yl)acrylamide **(TpSSA3)** in good yield.



TpS2 **TpSSA3, 77 %**

Figure 2.10 Knoevenagel condensation reaction to form (*E*)-2-cyano-3-(5-(5-(4-(diphenylamino) phenyl)thiophen-2-yl)thiophen-2-yl)acrylamide **(TpSSA3)**.

The reaction mechanism involves acid-catalyzed tautomerization of the carbonyl compound to the enol is shown in Figure 2.11.

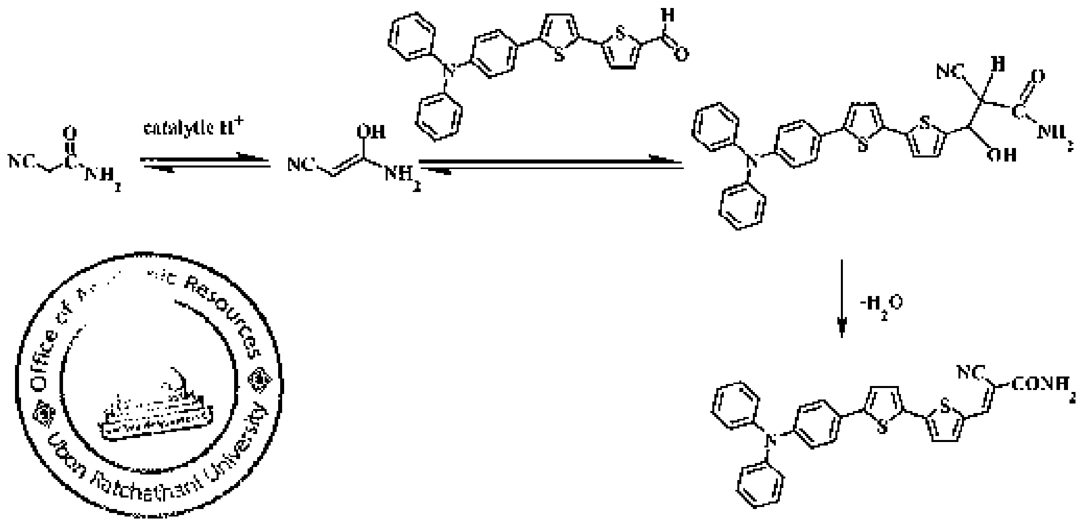


Figure 2.11 The proposed mechanism of Knoevenagel condensation reaction of (*E*)-2-cyano-3-(5-(5-(4-(diphenylamino)phenyl)thiophen-2-yl)thiophen-2-yl)acrylamide **(TpSSA4)**.

2.3.2 Optical properties

UV–vis and fluorescence spectra of **TpSSA3** and **TpSSA4** dye in dry CH_2Cl_2 are shown in Figure 2.12 and listed in Table 2.1, together with the UV–vis spectrum of the corresponding dye absorbed on TiO_2 nanoparticle. The absorption spectrum of **TpSSA3** displayed three major absorption bands with absorption maxima at 295, 350 and 479 nm295 and **TpSSA4** displayed three major absorption bands with absorption maxima at, 352 and 482 nm. The former corresponds to the π–π^* transition of the later corresponds to the π–π^* transition of the π-conjugated system of dye through the phenyl ring to acceptor group. The bathochromic shifted (red shifted) absorption spectra were observed in **TpSSA4** has dye which can ascribe as the stronger electron withdrawing ability of cyanoacrylic acid moiety in **TpSSA3** than cyanoacrylamide moiety in **TpSSA4** [20]. The absorption spectrum of **TpSSA3** on TiO_2 nanoparticle shown in Figure 2.13. It is broadened when compared to that in solution due to the interaction of the anchoring group with the surface titanium ions.

The fluorescence emission spectra of the **TpSSA4** and **TpSSA3** dyes in CH_2Cl_2 (**Figure 2.12** (right)) showed a red-shift from 595 to 622 nm, indicating that the cyanoacrylic acid moiety are stronger electron acceptors compared with the cyanoacrylamide moiety.

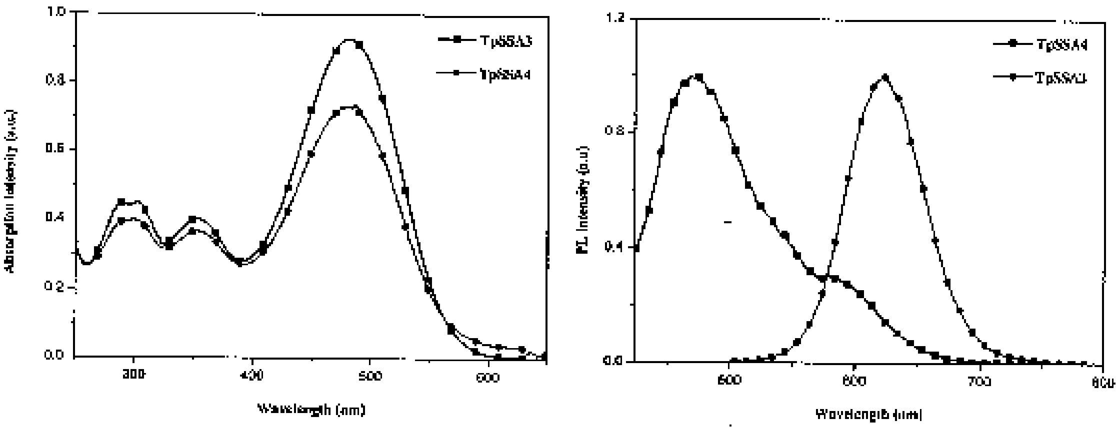


Figure 2.12 Absorption (left) and emission (right) spectra of **TpSSA3** and **TpSSA4** dyes in dichloromethane.

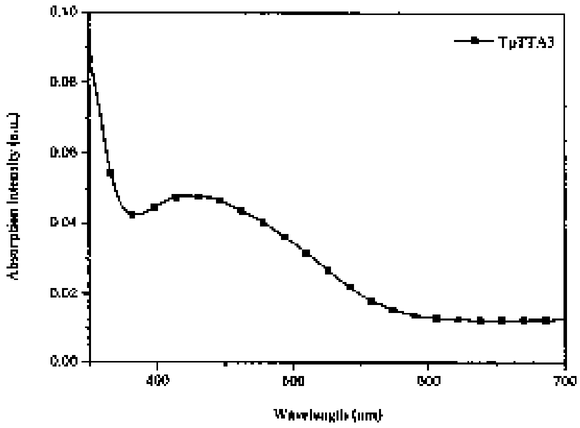


Figure 2.13 Absorption spectra of TiO_2 films sensitized by **TpSSA3**.

Table 2.1 The absorption and fluorescence data of **TpSSA3** and **TpSSA4** dyes.

Compound	**λ_{max} (nm) and ε (10^4 M^{-1} cm^{-1})**	**λ_{max} on TiO_2 (nm)**	**λ_{max} of emission in CH_2Cl_2 (nm)**
TpSSA3	482 (2.00)	-	622
TpSSA4	479 (1.92)	426	595

2.3.3 Thermal properties

For optoelectronic applications, the thermal stability of organic material is crucial for device stability and lifetime [21]. The degradation of organic optoelectronic devices depends on morphological changes resulting from the thermal stability of the amorphous organic materials [22]. Figure 2.14 and Table 2.2 show TGA thermograms and temperature at 5% weight loss (T_{5d}) of **TpSSA3** and **TpSSA4** dyes investigated by TGA analysis under nitrogen atmospheric condition. Those results suggested that the dyes were thermally stable materials with T_{5d} well over 290°C which is good for long stability of DSCs devices.

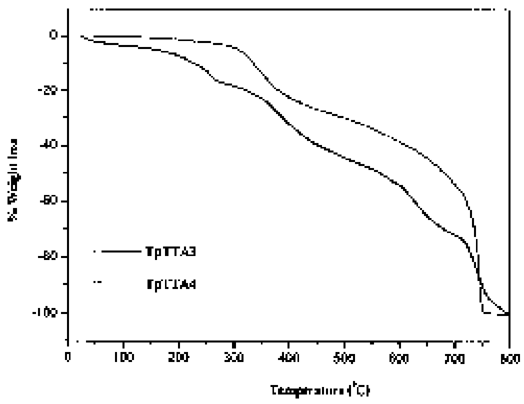


Figure 2.14 TGA thermograms of **TpSSA3** and **TpSSA4** dyes.

Table 2.2 Thermal properties of **TpSSA3** and **TpSSA4** dyes

Compound	T_{5d} (°C)
TpSSA3	291
TpSSA4	355

2.3.4 Cell performance

Typical DSSCs devices with effective area of 0.25 cm^2 were fabricated using **TpSSA3** as sensitizer. Nanocrystalline anatase TiO_2 coated on FTO substrate were use as working electrode whereas Pt layer coated on ITO substrate were employed as counter electrode. The mixture of I_2 (0.1 M), LiI (0.1 M) and t-butyl-pyridine (0.5 M) in acetonitrile solution was used as an electrolyte system. *I-V* curves of dyes are shown in Figure 2.15 (right) whereas plots of Incident Photon-to-current conversion efficiency (IPCE) at various wavelengths are given in Figure 2.15 (**left**). The action spectra of monochromatic incident photon-to-current conversion efficiencies (IPCE) for DSCs based on **TpSSA3** and **N3**. The IPCE spectra of **TpSSA3** show maxima at 429 nm, efficiencies about 81%. The IPCE value of **TpSSA3** is higher but shaper than that of **N3** as commercial dye.

Under continuous visible-light irradiation (AM 1.5G, 100 mWcm^{-2}), the **TpSSA3**-sensitized DSSCs showed the highest η among three dyes and gave a short-circuit photocurrent density (J_{sc}) of 10.92 mAcm^{-2}, an open circuit voltage (V_{oc}) of 0.68 V, a fill factor (FF) of 0.63 and a power conversion efficiency (PCE) of 4.76%. Device made of a commercial dye **N3** under the same condition was compared as a reference.

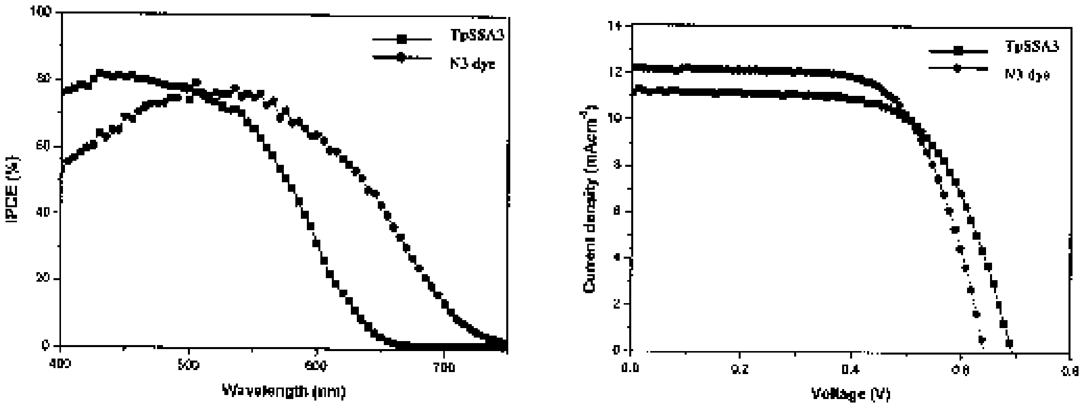


Figure 2.15 IPCE spectra (left) and *I-V* characteristic (right) of **TpSSA3**

2.4 Conclusion

The designed dye compounds **TpSSA3** and **TpSSA4** were synthesized using a combination of bromination, Suzuki cross-coupling and Knoevenagel condensation reactions. The optical and thermal properties of these compounds can be tuned by varying the acceptor group. The number of thiophene increased the conjugation length of compounds resulting a red-shift and broad in absorption solution spectra. Under standard global AM 1.5 solar condition, the **TpSSA3** based cell give a short circuit photocurrent density of 10.92 mA cm^{-2}, an open circuit voltage of 0.68 V, a fill factor of 0.63, corresponding to a power conversion efficiency (PCE) of 4.76%, and the maximum incident monochromatic photon-to-current conversion efficiency (IPCE) of 81% at 429 nm. The performance of DSCs using these materials as dyes is under investigation and will be reported in the future.

CHAPTER 3

SYNTHESIS AND CHARECTERIZATION OF CARBAZOLE-BASED DONOR

3.1 Introduction

The molecules with D–π–A structures have attracted increasing attention since they can serve as electroactive and photoactive materials in molecular electronics, such as biochemical fluorescent technology, efficient nonlinear optical (NLO) materials, ganic light-emitting diodes (OLEDs) or electrogenerated chemiluminescence, and solar cells [23].

Oligo(p-phenylenes) have some very investigating electronic and optical properties and been lately investigated as advanced molecular optoelectronic materials due to their high photoluminescence efficiency, good charge transportation, thermal stability and tunability of physical properties through chemical modification [24].

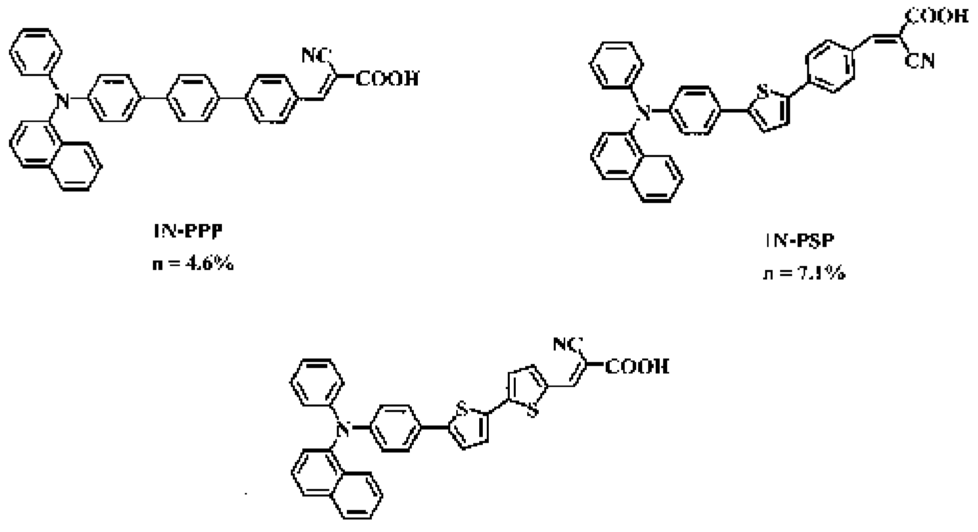
One way to increase the efficiency of the DSCs is to prevent recombination of electrons from the semiconductor to the electrolyte. This can be achieved by introducing alkyl chains in the linker part of the dye, forming an insulating layer yielding an increased electron lifetime in the DSCs (Figure 3.1, **MK-1**) [25, 26]. The alkyl chains are also believed to prevent aggregate formation on the surface of the TiO_2. However, in 2007 Kim et al. reported a negative influence of the efficiency when introducing alkyl chains in the linker part of the dye [27].

3.1.1 Carbazole as donor

Due to the electron-donating nature of carbazoles, they have been widely used as hole-transporting materials for a number of applications, such as xerography, organic field-effect transistors, photorefractive systems, light emitting diodes, etc. Long-lived charge separate states and multiphoton absorbing abilities have been reported for some of these carbazole based materials. In photovoltaic cells the interest of using carbazole based sensitizers has increased in recent years. Studies of the ruthenium complexes with carbazole as electron donor moiety showed especially improved photophysical properties and interesting electrochemical properties, included in some cases relatively long synthetic procedures which would have yielded high production costs and their efficiencies in the DSC was relatively low (η = 5.15-8.30%) compared to for instance some indoline sensitizers [28, 29,30].

3.1.2 Thiophenes-phenylene as π-Conjugated Linker

The function of a bridge group is twofold, i.e. acting both as a part of the light absorbing chromophore and also as a channel for transporting charges. A good bridge group should promote the absorption of light over a wide wavelength region, yet retards the rate of internal charge recombination. Linearly connected arylenes serve both purposes quite well. The flexible dihedral angles between adjacent aryl groups are twisted to a greater extend upon excitation to the CT state, while the electronic resonance is reduced and the rate of charge recombination slows down. In 2009 Tahsin J.Chow et al. reported a series of naphthyl phenylamine dyes with different linker units (Figure 3.1) [31].



1N-PPP
η = 4.6%

1N-PSP
η = 7.1%

1N-PSS
η = 6.1%

Figure 3.1 π-conjugated extension by thiophene-phenylene introduction in the linker

The triarylene bridges consist of phenyl and/or thiophenyl groups linked together in a linear fashion. These compounds exhibited a high absorptivity in the blue/green region of solar light. **1N-PSP** and **1N-PSS** both show efficiencies over 6% and have almost identical absorption spectra. From a synthetic point of view, **1N-PSS** quires a slightly shorter synthetic route than **1N- PSP** to obtain approximately the same efficiency.

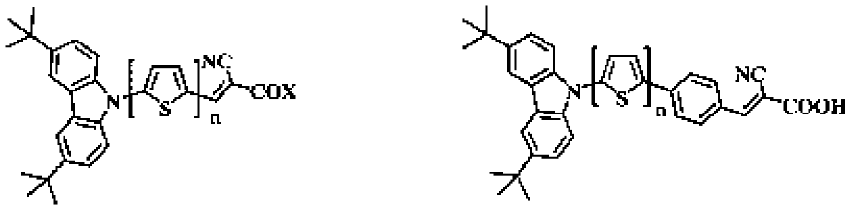
3.1.3 Cyanoacrylic acid and Cyanoacrylamide as Acceptor and Anchoring Groups

The carboxylic acid group is by far the most employed group for attachment of the sensitizers to the semiconductor surface. The binding modes have been investigated by Galoppini and co-workers [32].

When it comes to the slightly wider term acceptor groups, cyanoacrylic acid is by far most commonly used due to its strong electronic withdrawing properties. There is a number of different acceptor groups reported and some show promising results. In some cases, the ending of the linker and the beginning of acceptor lie in the eye of the beholder, since the increased conjugation that some acceptor groups provided will broaden the absorption spectra. However, in this thesis a synthetic point of view will be used to differentiate the linker and the acceptor depending on the reactants used [28, 33, 34].

3.2 Aim of study

We designed an organic chromophore based on carbazole as the donor group, with a oligothiophene and oligothiophene-phenylene linker and a cyanoacrylic acid or cyanoacrylamide moiety as acceptor/anchor group that would be an interesting starting point for further modifications (Figure 3.2). The D-π-A type organic dyes were synthesized using a combination of alkylation, bromination, Ullmann coupling, Suzuki cross-coupling and Knoevenagel condensation reactions.



CSSA9, n = 2, X = NH2
CSSA10, n = 2, X = OH
CSSSA11, n = 3, X = OH

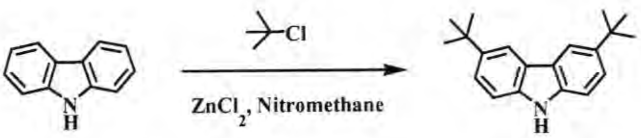
CSPA12, n = 1
CSSPA13, n = 2

Figure 3.2 organic dye structures of D-π-A type organic dyes

3.3 Results and Discussion

3.3.1 Synthesis

The synthesis of **CSSA9**, **CSSA10**, **CSSA11**, **CSPA12** and **CSSPA13**, first, Friedel-Craft reaction of carbazole with *tert*-butylchloride in the presence of zinc chloride as a catalyst in nitromethane as a solvent gave 3,6-di-*tert*-butylcarbazole **(G1)** as white powder in 86% as shown in Figure 3.3.



G1, 92%

Figure 3.3 Synthesis of 3,6-di-*tert*-butylcarbazole **(G1)**

The reaction mechanism *via* stable carbocation is shown in Figure 3.4.

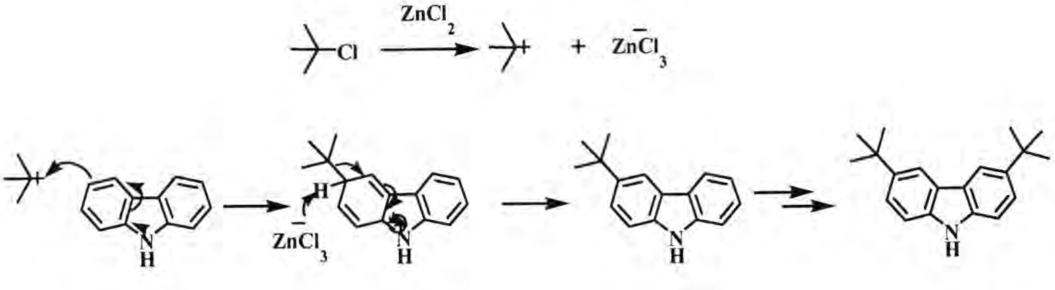


Figure 3.4 The propose mechanism of Friedel-Craft reaction

Ullmann coupling reaction of 3,6-di-*tert*-butylcarbazole (G1) with 2,5-dibromo thiophene in the presence of copper iodide as a catalyst, (±)-*trans*-1,2-diaminocyclohexane as a co-catalyst, and potassium phosphate as a base in toluene as a solvent at reflux for 24 h led to 3,6-di-*tert*-butyl-9-(5-bromothiophen-2-yl)-9*H*-carbazole **(CS2)** as white solid in 50% yield as outlined in Figure 3.5.

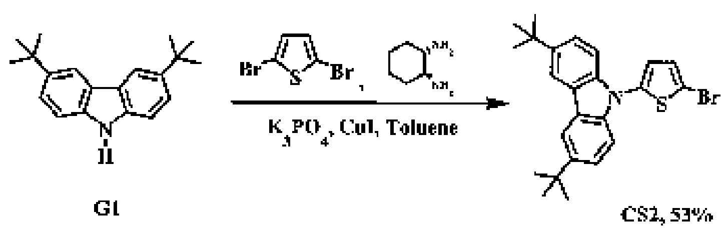


Figure 3.5 Synthesis of 3,6-di-*tert*-butyl-9-(5-bromothiophen-2-yl)-9*H*-carbazole **(CS2)**

Ullmann coupling mechanism is shown in Figure 3.6. The active species is a copper (I) iodide which undergoes oxidative addition with the second equivalent of halide, followed by reductive elimination and the formation of the thiophene-carbazole carbon bond.

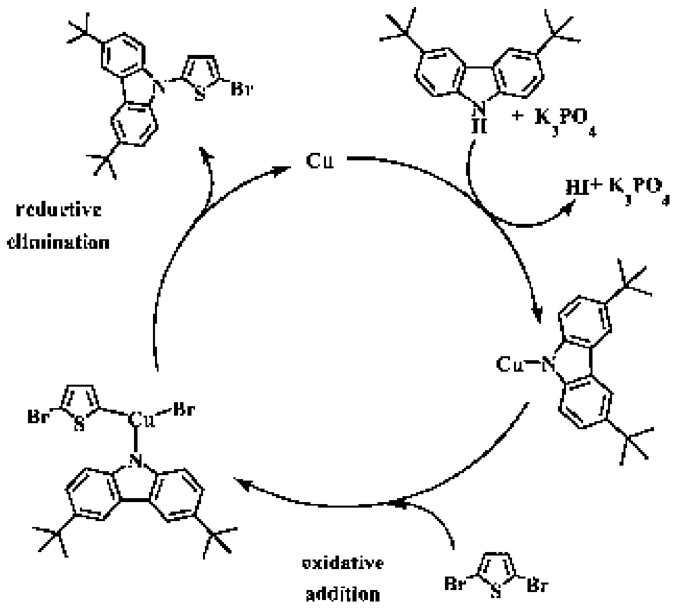


Figure 3.6 The proposed mechanism of Ullmann coupling rection

Suzuki cross coupling reaction of 3,6-di-*tert*-butyl--5)-bromothiophen-2-yl)-9*H*-carbazole **(CS2)** with 5-Formyl-2-thiophene boronic acid in the presence of $Pd(PPh_3)_4$ as catalyst and 2M Na_2CO_3 as a base in THF as a solvent for 24 h to directly yield 5-(5-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)thiophen-2-yl)thiophene-2-carbaldehyde **(CSS5)** as yellow solid in 60% yield as shown in Figure 3.7.

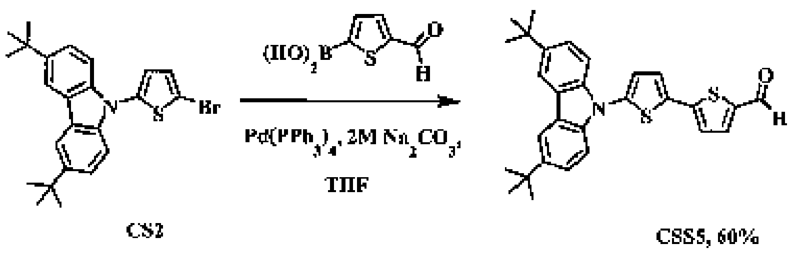


Figure 3.7 Suzuki cross coupling reaction to form 5-(5-(3,6-di-*tert*-butyl-9H-carbazol-9-yl) thiophen-2-yl)thiophene-2-carbaldehyde (**CSS5**)

The proposed mechanism of Suzuki cross coupling reaction is show in Figure 3.8. The Suzuki reaction ie the coupling of an aryl or vinyl boronic acid with an aryl or vinyl or vinyl halide using a palladium catalyst to form C-C bond. Thus, base activation of organoboron reagents as boronate intermediates facilitated the transfer of the organic group from boron to palladium (transmetallation). The reaction has later been extended to also include couplings with alkyl groups [35].

$$\mathrm{RM} + \mathrm{RX} \longrightarrow \mathrm{R\text{-}R'} + \mathrm{MX}$$

R, R' = aryl, vinyl, alkyl
X = halide
M = B(OH)$_2$

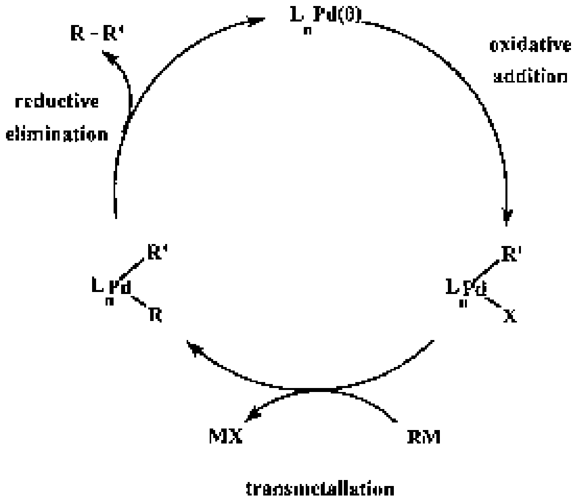
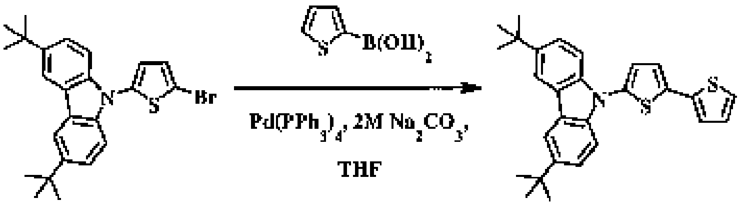


Figure 3.8 The proposed mechanism of Suzuki coupling rection

For dyes having extended π-conjugation was synthesized by Suzuki coupling reaction of bromo intermediate compound **CS2** with 2-thiopheneboronic acid to give 3,6-di-*tert*-butyl-9-(5-(thiophen-2-yl)thiophen-2-yl)-9*H*-carbazole (**CSS3**) as white solid in 88% yield as shown in Figure 3.9.



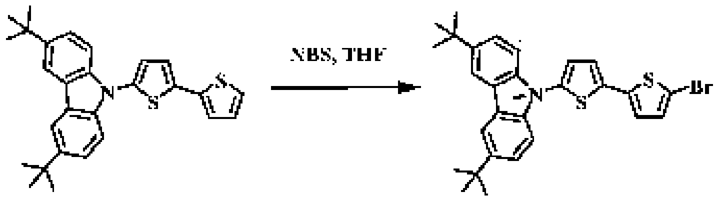
CS2

CSS3, 88%

Figure 3.9 Suzuki cross coupling reaction to form 3,6-di-*tert*-butyl-9-(5-(thiophen-2-yl) thiophen-2-yl)-9*H*-carbazole (**CSS3**)

The Suzuki cross coupling reaction follows a three-step mechanism cycle, oxidative addition, transmetallation and reductive elimination as described in Figure 3.12.

3,6-di-tert-butyl-9-(5-(thiophen-2-yl)thiophen-2-yl)-9H-carbazole (**CSS3**) was brominated with NBS in tetrahydrofuran gave 3,6-di-*tert*-butyl-9-(5-(5-bromothiophen-2-yl) thiophen-2-yl)-9*H*-carbazole (**CSS4**) as white solid in 100% yield (Figure 3.10).



CSS3

CSS4, 100%

Figure 3.10 Bromination reaction to form 3,6-di-*tert*-butyl-9-(5-(5-bromothiophen-2-yl) thiophen-2-yl)-9*H*-carbazole (**CSS4**)

The reaction mechanism involved bromination reaction as described in Figure 3.11.

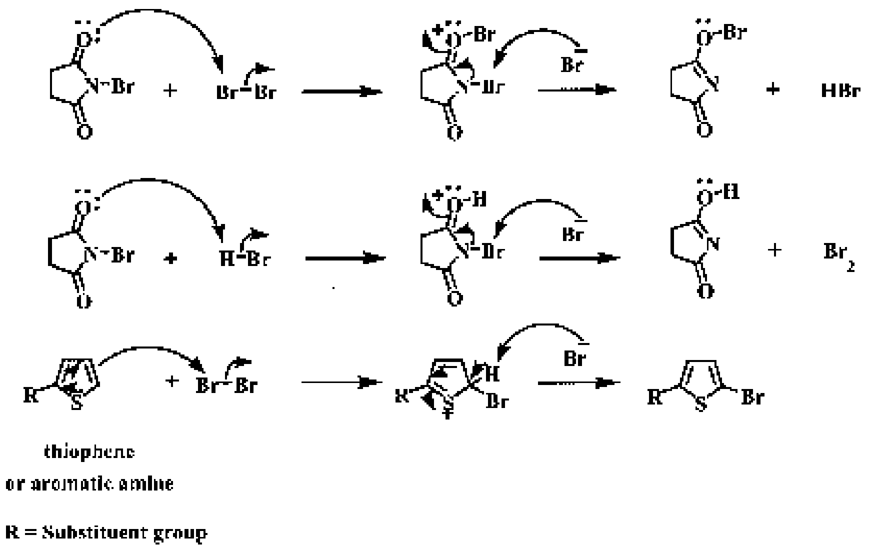


Figure 3.11 The proposed mechanism of Bromination reaction

The Suzuki coupling reaction was performed with the bromo intermediate and 5-formyl thiopheneboronic acid was carried out using $Pd(PPh_3)_4$ as a catalyst and Na_2CO_3 as a base in THF as a solvent for 24 h to directly yield 5-(5-(5-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)thiophen-2-yl)thiophen-2-yl)thiophene-2-carbaldehyde (**CSSS6**) as yellow solid in 72% yield as shown in Figure 3.12.

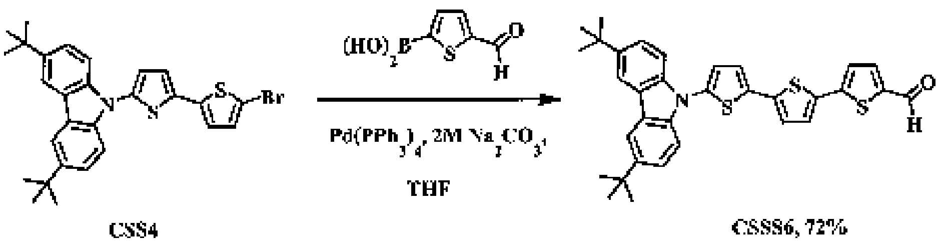


Figure 3.12 Suzuki cross coupling reaction to form 5-(5-(5-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)thiophen-2-yl)thiophen-2-yl)thiophene-2-carbaldehyde (**CSSS6**)

For dye with thiophene-phenyl as linker and cyanoacrylic acid as an acceptor was synthesized. Suzuki cross coupling reaction of 3,6-di-*tert*-butyl-9-(5-bromothiophen-2-yl)-9*H*-carbazole (**CS2**) with 4-formylphenylboronic acid in the $Pd(PPh_3)_4$ as a catalyst and Na_2CO_3 as a base in THF as a solvent for 24 h to directly yield 4-(5-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl) thiophen-2-yl)benzaldehyde **(CSP8)** as yellow solid in 99% yield as shown in Figure 3.13.

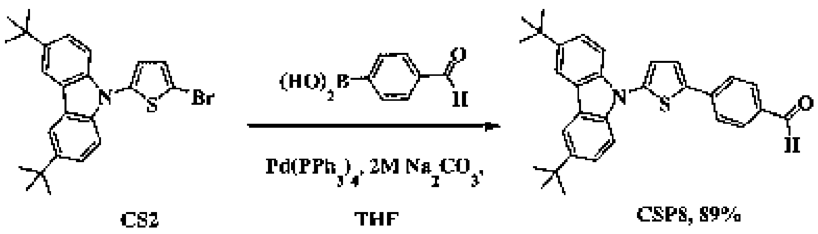


Figure 3.13 Suzuki coupling reaction of 4-(5-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)thiophen-2-yl)benzaldehyde **(CSP8)**

Suzuki cross coupling reaction of **CSS4** with 4-formylphenylboronic acid in the $Pd(PPh_3)_4$ as a catalyst and Na_2CO_3 as a base in THF as a solvent for 24 h to directly yield 4-(5-(5-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)thiophen-2-yl)thiophen-2-yl)benzaldehyde **(CSSP7)** as yellow solid in 89% yield as shown in Figure 3.14.

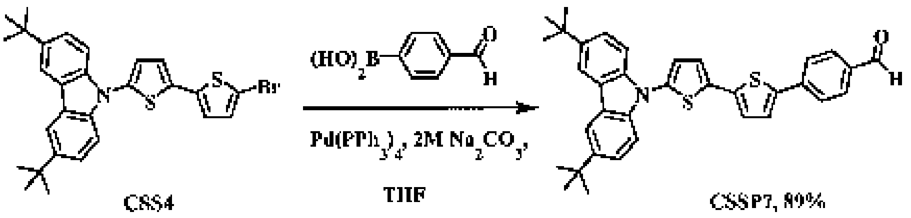


Figure 3.14 Suzuki cross coupling reaction to form 4-(5-(5-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl) thiophen-2-yl)thiophen-2-yl)benzaldehyde **(CSSP7)**

The dye with cyanoacetamide as an acceptor was synthesized Knoevenagel condensation reaction of **CSS5** with 2-cyanoacetamide in the presence of acetic acid as catalyst and ammonium acetate as co-catalyst gave the target *(E)*-3-(5-(5-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl) thiophen-2-yl)thiophen-2-yl)-2-cyanoacrylamide **(CSSA9)** as red solid in 78% yield as shown in Figure 3.15.

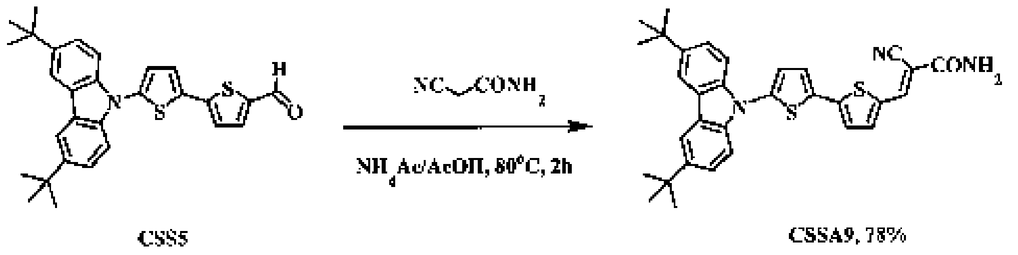


Figure 3.15 Synthesis of target *(E)*-3-(5-(5-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)thiophen-2-yl) thiophen-2-yl)-2-cyanoacrylamide **(CSSA9)**

Knoevenagel condensation mechanism involves acid-catalyzed tautomerization of the carbonyl compound to the enol is shown in Figure 3.16.

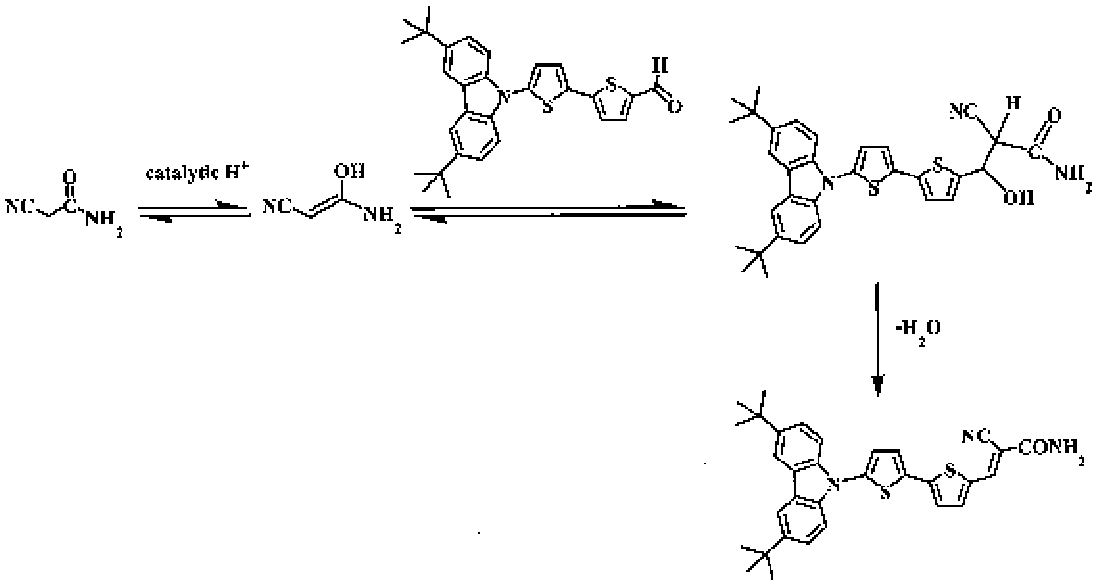


Figure 3.16 The proposed mechanism of Knoevenagel condensation reaction

The dye with cyanoacrylic acid as an acceptor was synthesized. Knoevenagel condensation reaction of **CSS5 with** cyanoacetic acid in the presence of piperidine as base and chloroform as solvent gave *(E)*-3-(5-(5-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)thiophen-2-yl)thio phen-2-yl)-2-cyanoacrylic acid **(CSSA10)** in good yield as shown in Figure 3.17.

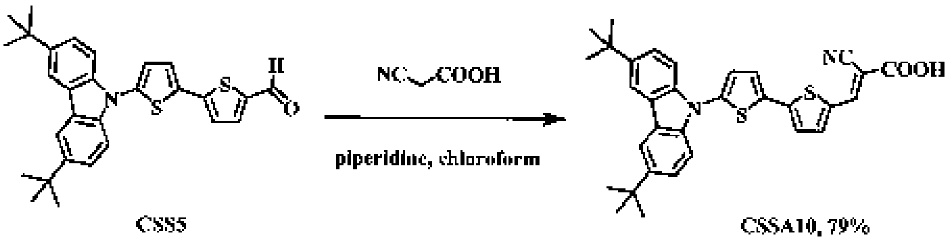


Figure 3.17 Synthesis of *(E)*-3-(5-(5-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)thiophen-2-yl) thiophen-2-yl)-2-cyanoacrylic acid (**CSSA10**)

Knoevenagel condensation is addition reaction of the methylene components, activated with two electronwithdrawing groups, to aldehyde can be performed with secondary amines. A reasonable variation of the mechanism, in which piperidine acts as organocatalyst, involves the corresponding iminium intermediate as the acceptor is shown in Figure 3.18.

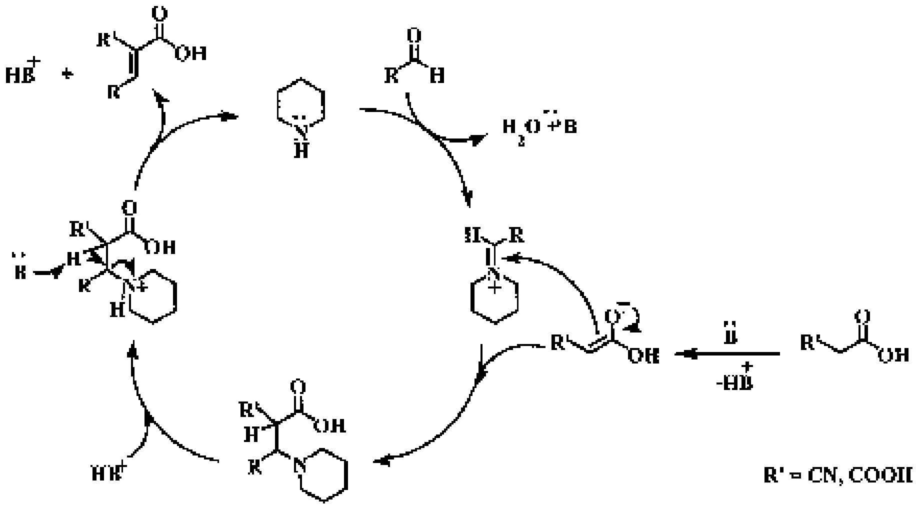


Figure 3.18 The proposed mechanism of Knoevenagel condensation reaction.

The dye with cyanoacrylic acid as an acceptor was synthesized. Knoevenagel condensation reaction of 10 with cyanoacetic acid in the presence of piperidine as a base and and chloroform as solvent to directly yield *(E)*-3-(5-(5-(5-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)thio phen-2-yl)thiophen-2-yl)thiophen-2-yl)-2-cyanoacrylic acid (**CSSSA11**) as yellow solid in 82% yield as shown in Figure 3.19.

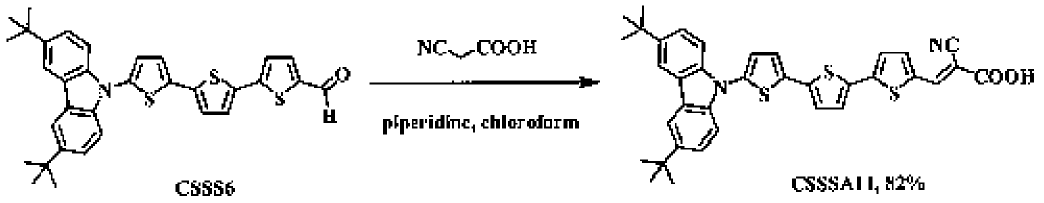


Figure 3.19 Knoevenagel condensation reaction to form CSSSA11

Knoevenagel condensation reaction of **CSP8** with cyanoacetic acid in the presence of piperidine as base and chloroform as solvent gave *(E)*-3-(5-(5-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)thiophen-2-yl) thiophen-2-yl)-2-cyanoacrylic acid **(CSPA12)** in 52% yield as show in Figure 3.20.

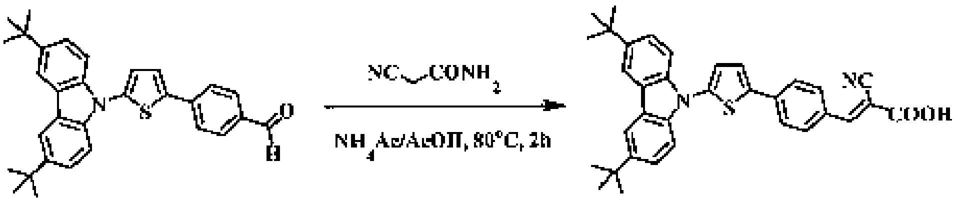


Figure 3.20 Knoevenagel condensation reaction to form *(E)*-3-(4-(5-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)thiophen-2-yl)phenyl)-2-cyanoacrylic acid **(CSPA12)**

Knoevenagel condensation reaction of 4-(5-(5-(3,6-di-*tert*-butyl-9H-carbazol-9-yl)thiophen-2-yl)thiophen-2-yl)benzaldehyde **(CSSP7)** with cyanoacetic acid in the presence of piperidine as base and chloroform as solvent gave *(E)*-3-(4-(5-(5-(3,6-di-tert-butyl-9*H*-carbazol-9-yl)thiophen-2-yl)thiophen-2-yl)phenyl)-2-cyanoacrylic acid **(CSSPA13)** in 39% yield as show in Figure 3.21

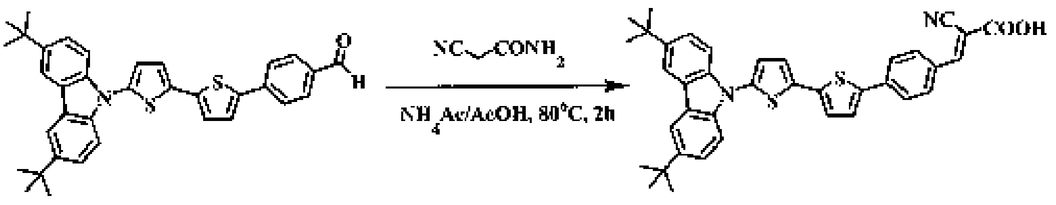


Figure 3.21 Knoevenagel condensation reaction to form *(E)*-3-(4-(5-(5-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)thiophen-2-yl)thiophen-2-yl)phenyl)-2-cyanoacrylic acid **(CSSPA13)**

3.3.2 Optical properties

UV–vis and fluorescence spectra of **CSSA9, CSSA10, CSSSA11, CSPA12** and **CSSPA13** dyes in dry CH_2Cl_2 are shown in Figure 2.12 and listed in Table 2.1, together with the UV–vis spectrum of the corresponding dye absorbed on TiO_2 nanoparticle. UV–vis and fluorescence spectra of **CSSA9, CSSA10, CSSSA11, CSPA12** and **CSSPA13**dyes in dry CH_2Cl_2 are shown in Figure 2.12 and listed in Table 2.1, together with the UV–vis spectrum of the corresponding dye absorbed on TiO_2 nanoparticle. In solution, all five compounds exhibits a three major absorption bands. Which show absorption bands around 290-350 nm corresponds to π-π^* transition and broad absorption bands around 400-600 nm corresponds to Intramolecular Charge transfer Transition (ICT) of donor-accepter compound [36]. Comparition between the **CSSA9** and **CSSA10** dyes, which has the same electron donor and π-conjugate, but different acceptor moiety. It can be seen that the maximum absorption of the visible regioñ bathochromic shifted (red shifted) from 441 to 428 nm. Comparition between the **CSSA10, CSSSA11, CSPA12** and **CSSPA13,** which has the same electron donor and acceptor moiety, but different π-conjugating systems. It can be seen that the maximum absorption of the visible region red-shifts from 397, 412, 428 to 449 nm for **CSPA12, CSSPA13, CSSA10** and **CSSSA11**, respectively. The dyes have linker containing more thiophene moiety displayed a greater bathochromic shift and the π orbital in thiophene is located at a higher potential level than in phenyl ring, there for is delocalized more extensively than the later. A better conjugation in the former is also supported by a more planar comformation [37].

The fluorescence emission spectra of the dyes in CH_2Cl_2 (Fig. 3.22 (right)) showed a red-shift upon increased number of thiophene units in the molecule, which is roughly parallel to the trend of the absorption .

When the **CSSA10, CSSSA11, CSPA12** and **CSSPA13** dyes are attached to TiO_2 surface, the absorption spectra of these dyes are broadened are blue-shifted as compared to that in solution (Figure 3.23), indicating strong interactions between the dyes and the semiconductor surface.

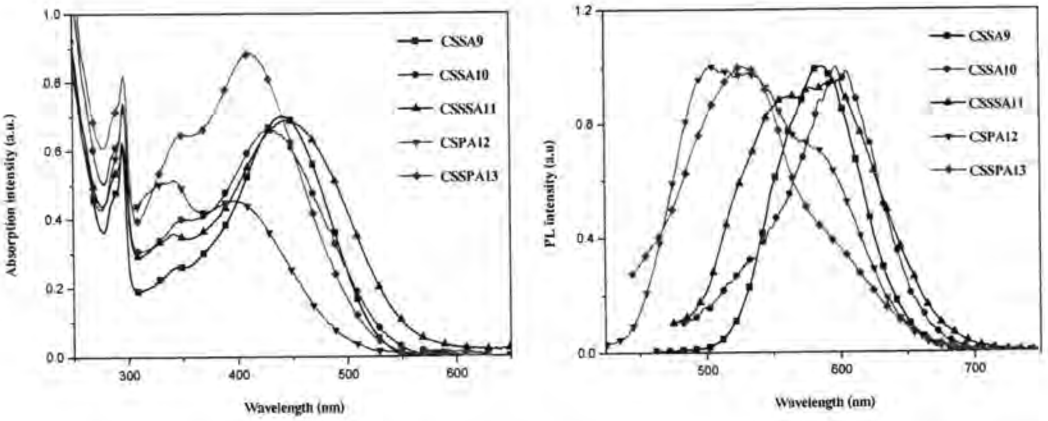


Figure 3.22 Absorption (left) and emission (right) spectra of **CSSA9, CSSA10, CSSSA11, CSPA12** and **CSSPA13**dyes in dichloromethane

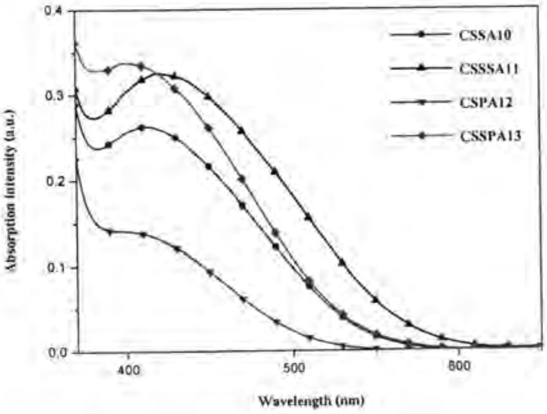


Figure 3.23 Absorption spectra of TiO_2 films sensitized by **CSSA9, CSSA10, CSSSA11, CSPA12** and **CSSPA13**

Table 3.1 The absorption and fluorescence data of **CSSA9, CSSA10, CSSSA11, CSPA12** and **CSSPA13** dyes

Compound	**λ_{max} (nm) and ε (10^4 M^{-1} cm^{-1})**	**λ_{max} on TiO_2 (nm)**	**λ_{max} of emission in CH_2Cl_2 (nm)**
CSSA9	295 (3.32), 345 (4.24), 441 (3.18)	-	587
CSSA10	296 (3.34), 348 (4.11), 428 (3.51)	413	590
CSSSA11	295 (3.74), 341 (4.25), 449 (3.57)	421	593
CTPA12	296 (2.94), 341 (3.50), 397 (3.71)	395	505
CSSPA13	296 (2.90), 3.50 (3.34), 412 (2.73)	400	527

3.3.3 Thermal properties

For optoelectronic applications, the thermal stability of organic material is crucial for device stability and lifetime [21]. The degradation of organic optoelectronic devices depends on morphological changes resulting from the thermal stability of the amorphous organic materials [22]. Figure 3.24 and Table 3.2 show TGA thermograms and temperature at 5% weight loss (T_{5d}) of **CSSA9, CSSA10, CSSSA11, CSPA12** and **CSSPA13**dyes investigated by TGA analysis under nitrogen atmospheric condition. Those results suggested that the dyes were thermally stable materials with T_{5d} well over 290°C which is good for long stability of DSCs devices.

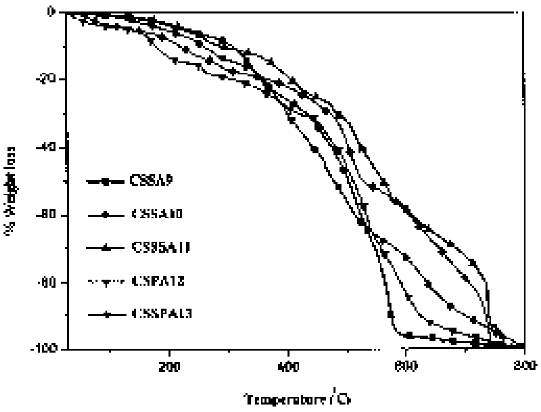


Figure 3.24 TGA thermograms of **CSSA9, CSSA10, CSSSA11, CSPA12** and **CSSPA13** dyes

Table 3.2 Thermal properties of **CSSA9, CSSA10, CSSSA11, CSPA12** and **CSSPA13** dyes

Compound	**T_{5d}(°C)**
CSSA9	324
CSSA10	295
CSSSA11	383
CSPA12	238
CSSPA13	252

3.4 Conclusion

The designed dye compounds **CSSA9, CSSA10, CSSSA11, CSPA12** and **CSSPA13** were synthesized using a combination of Bromination, Ullmann coupling, Suzuki cross-coupling and Knoevenagel condensation reactions. The target molecules exhibit a absorption band cover UV and visible region. The optical and thermal properties of these compounds can be tuned by varying the linker and acceptor group. The number of thiophene increased the conjugation length of compounds resulting a red-shift and broad in absorption solution spectra. The dyes have oligothiophene and oligothiophene-phenylene linker. These compounds as oligothiophene linker exhibited a high absorptivity more oligothiophene-phenylene linker. The performance of DSCs using these materials as dyes is under investigation and will be reported in the future.

CHAPTER 4

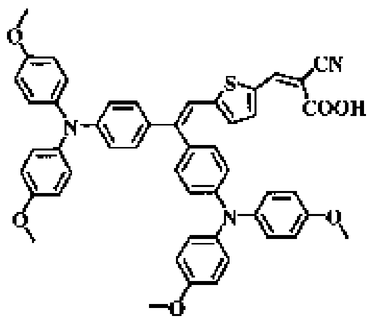
SYNTHESIS AND CHARECTERIZATION OF D-D-π-A TYPE ORGANIC DYES HAVING CARBAZOLE-N-YL-DODECYLOXYPHENYL CARBAZOLE AS A DONOR

4.1 Introduction

Organic dipolar compounds containing an electron donor (D), electron acceptor (A) and an π-conjugated linker have found wide applications on the new generation of optoelectronic device. Electron transfer from D to A happens rapidly upon photoexcitation to generate a charge-seperated spicies [28]. Subsequent charge recombination may proceed within the molecule to generate a charge-transfer (CT) emission in certain cases, or it may beguided to proceed though an external circuit such as the design in dye-sensitized solar cells (DSCs). Because the efficiency of the solar cell competes with the internal charge recombination, the life time of the CT state become the major concern the design the dyes.

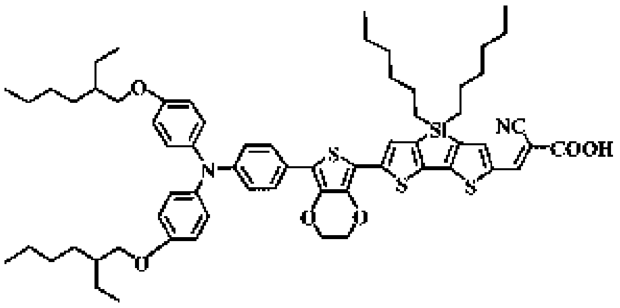
The advantage of organic dyes is the ease of tuning their photophysical properties through the structural modification. D-D-π-A organic molecules are among the most important conjugated organic materials [29]. Organic dyes with D–D–π-A structure over the simple D–π-A configuration, introducing a secondary electron donor into the dye molecule can increase electron-density of donor and enhance molar extinction coefficient, which resulted in high overall conversion efficiency [30].

In 2008 Daniel P. et al reported D11-sensitized solar cells yield overall conversion efficiency of 7.20% under standard AM 1.5 sun light. In 2009 Zeng. W and others reported a C219 as the sensitizer exhibited an impressive efficiency of 8.9% under a low light intensity of 14.39 mW cm^{-2} [38].



D11

$\eta = 7.20\ \%$



C219

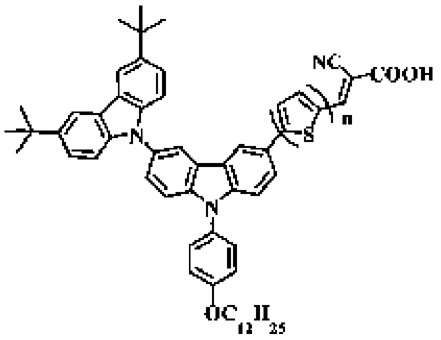
$\eta = 8.9\%$

Figure 4.1 D-D-π-A organic dyes

Furthermore, the bulky alkylphenyl groups could suppress the aggregation due to the disturbance of the π-π stacking, which should always be avoided for efficient photocurrent generation because aggregation may lead to intermolecular quenching or affect the light absorption by the filtering effect [39].

4.2 Aim of study

We designed D-D-π-A type organic dyes based on carbazole (G1)as the primary donor group, carbazole connected with dodecyloxyphenyl group as the secondary donor, with a oligothiophene linker and a cyanoacrylic acid moiety as acceptor/anchor group that would be an interesting starting point for further modifications (Figure 4.2). The D-D-π-A type organic dyes were synthesized using a combination of alkylation, bromination, Ullmann coupling, Suzuki cross-coupling and Knoevenagel condensation reactions.



G1CSA12, n = 1
G1CSSA12, n = 2
G1CSSSA13, n = 3

Figure 4.2 organic dye structures of D-D-π-A type organic dyes

4.3 Results and Discussion

4.3.1 Synthesis

The synthesis of D-D-π-A type organic dyes based on carbazole (G1)as the primary donor group, carbazole connected with dodecyloxyphenyl group as the secondary donor, with a oligothiophene linker and a cyanoacrylic acid moiety as acceptor/anchor group, first, Alkylation reaction of phenol with bromododecane in the presence of potassium hydroxyde as a base in DMSO as a solvent stirred for 24 h led to 1-(dodecyloxy)benzene (**PO**) as oil in 75% yield a outlined in Figure 4.3.

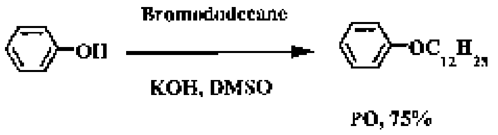


Figure 4.3 Alkylation reaction to form 1-(dodecyloxy)benzene (PO)

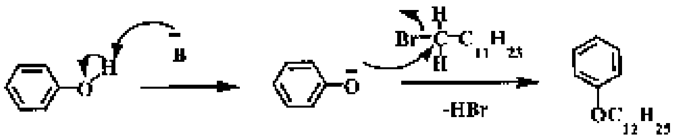


Figure 4.4 The proposed mechanism of nucleophilic substitution reaction

1-(dodecyloxy)benzene (**PO**) was brominated with NBS in ammonium acetate and acetonenitrile as solvent gave 3,6-di-tert-butyl-9-(5-(5-bromothiophen-2-yl) thiophen-2-yl)-9H-carbazole (**PO2**) as oil in 100% yield (Figure 4.5).

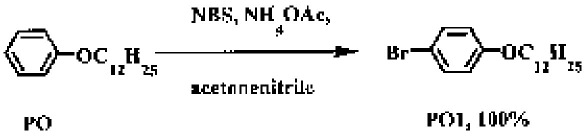


Figure 4.5 Bromination reaction to form 1-bromo-4-(dodecyloxy)benzene (**PO**)

Ullmann coupling reaction of 1-bromo-4-(dodecyloxy)benzene (**PO**) with carbazole in the presence of copper iodide as a catalyst, (±)-*trans*-1,2-diaminocyclohexane as a co-catalyst, and potassium phosphate as a base in toluene as a solvent at reflux for 24 h led 9-(4-(dodecyloxy) phenyl)-9*H*-carbazole (**CPO2**) as white solid in 95% yield a outlined in Figure 4.7.

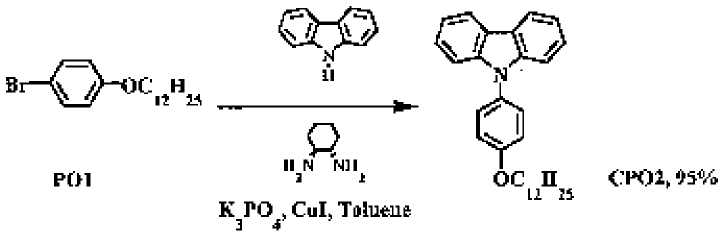


Figure 4.6 Ullmann coupling reaction to form 9-(4-(dodecyloxy) phenyl)-9*H*-carbazole (**CPO2**)

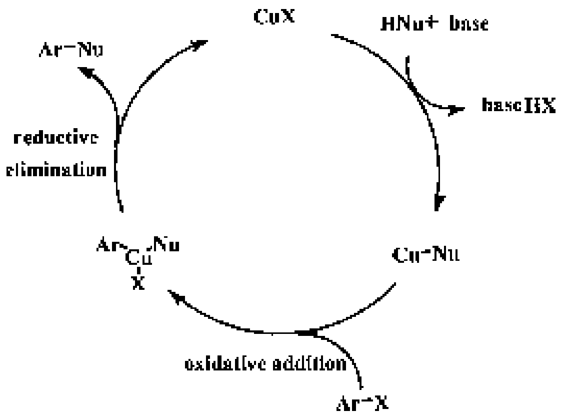


Figure 4.7 The proposed mechanism of Ullmann coupling reaction

Ullmann coupling mechanism is shown in Figure 4.8. The active species is a copper (I) iodide which undergoes oxidative addition with the second equivalent of halide, followed by reductive elimination and the formation of the thiophene-carbazole carbon bond.

9-(4-(dodecyloxy) phenyl)-9H-carbazole (**CPO2**) was brominated with NBS in tetrahydrofuran as solvent gave 3,6-dibromo-9-(4-(dodecyloxy)phenyl)-9*H*-carbazole (**CPO3**) as white solid in 71% yield yield a outlined in Figure 4.8.

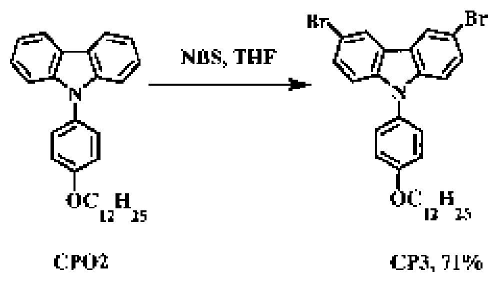


Figure 4.8 Bromination reaction to form 3,6-dibromo-9-(4-(dodecyloxy)phenyl)-9*H*-carbazole (CPO3)

The reaction mechanism involved bromination reaction as described in Figure 3.11.

Ullmann coupling reaction of 3,6-dibromo-9-(4-(dodecyloxy)phenyl)-9*H*-carbazole (**CPO3**) with 3,6-di-*tert*-butyl-9*H*-carbazole (G1) in the presence of copper iodide as a catalyst, (±)-*trans*-1,2-diaminocyclohexane as a co-catalyst, and potassium phosphate as a base in toluene as a solvent at reflux for 24 h led to 3,6-di-*tert*-butyl-9-(3-bromo-9-(4-(dodecyloxy) phenyl)-9*H*-carbazol-6-yl)-9*H*-carbazole (**G1C4**) in 36% yield yield a outlined in Figure 4.9 and the mechanism of Ullmann coupling reaction as described in Figure 4.7.

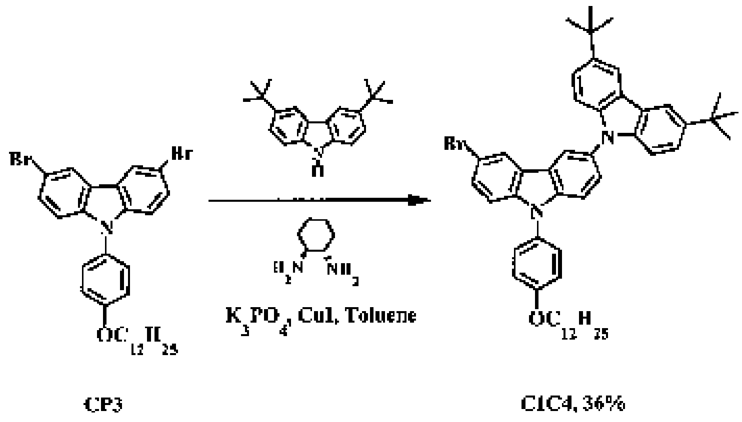
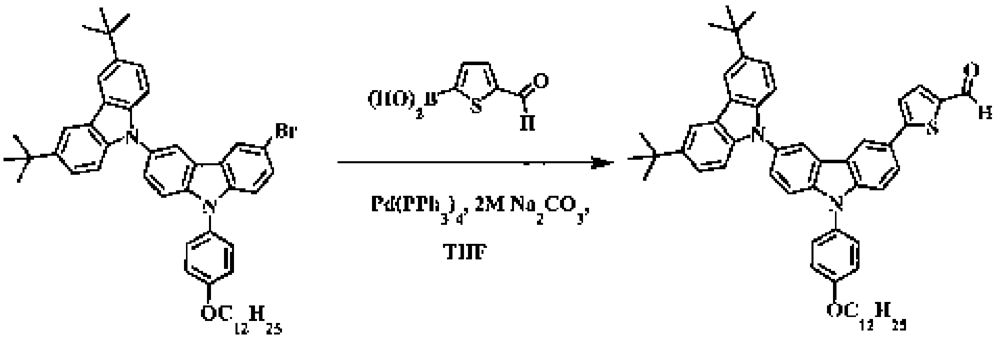


Figure 4.9 Ullmann coupling reaction to form 3,6-di-*tert*-butyl-9-(3-bromo-9-(4-(dodecyloxy) phenyl)-9*H*-carbazol-6-yl)-9*H*-carbazole (**G1C4**)

The Suzuki coupling reaction was performed with the bromo intermediate and 5-formyl thiopheneboronic acid was carried out using Pd(PPh$_3$)$_4$ as a catalyst and Na$_2$CO$_3$ as a base in THF as a solvent for 24 h to directly 5-(3-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-9-(4-(dodecyl oxy)phenyl)-9*H*-carbazol-6-yl)thiophene-2-carbaldehyde as yellow (**G1CS6**) solid in 78% yield as shown in Figure 4.10.



C1C4 **G1CS6, 78%**

Figure 4.10 Suzuki coupling reaction to form 5-(3-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-9-(4-(dodecyl oxy)phenyl)-9*H*-carbazol-6-yl)thiophene-2-carbaldehyde (**G1CS6**)

The mechanism of Suzuki coupling reaction follows a three-step mechanism cycle, oxidative addition, transmetallation and reductive elimination as described in Figure 3.12

The Suzuki coupling reaction was performed with the bromo intermediate and 2-thiopheneboronic acid was carried out using Pd(PPh$_3$)$_4$ as a catalyst and Na$_2$CO$_3$ as a base in THF as a solvent for 24 h to directly yield 3,6-di-*tert*-butyl-9-(9-(4-(dodecyloxy)phenyl)-3-(thiophen-2-yl)-9*H*-carbazol-6-yl)-9*H*-carbazole (**G1CS5**) as yellow solid in 73% yield as shown in Figure 4.11.

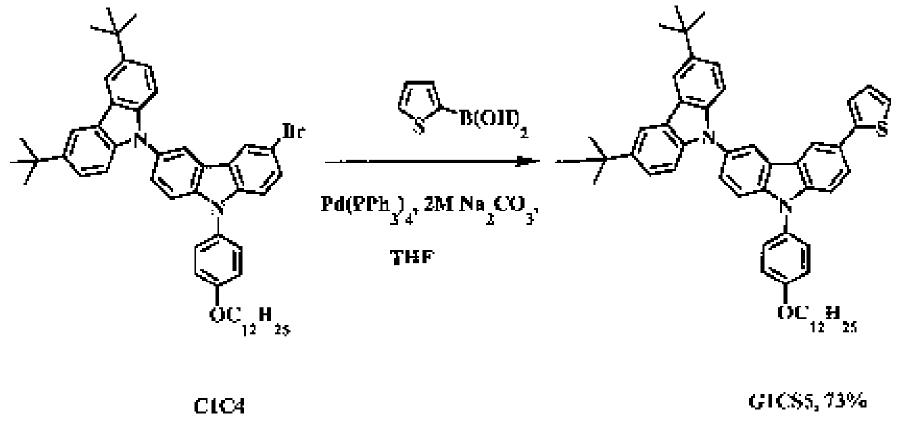


Figure 4.11 Suzuki coupling reaction to form 3,6-di-*tert*-butyl-9-(9-(4-(dodecyloxy)phenyl)-3-(thiophen-2-yl)-9*H*-carbazol-6-yl)-9*H*-carbazole **(G1CS5)**

The mechanism of Suzuki coupling reaction follows a three-step mechanism cycle, oxidative addition, transmetallation and reductive elimination as described in Figure 3.12.

Bromination reaction of 3,6-di-*tert*-butyl-9-(9-(4-(dodecyloxy)phenyl)-3-(thiophen-2-yl)-9*H*-carbazol-6-yl)-9*H*-carbazole in the presence(**G1CS5**) of NBS with tetrahydrofuran as a solvent gave 3,6-di-*tert*-butyl-9-(3-(5-bromothiophen-2-yl)-9-(4-(dodecyloxy)phenyl)-9*H*-carbazol -6-yl)-9*H*-carbazole **(G1CS7)** as white solid in 98% yield as shown in Figure 4.14.

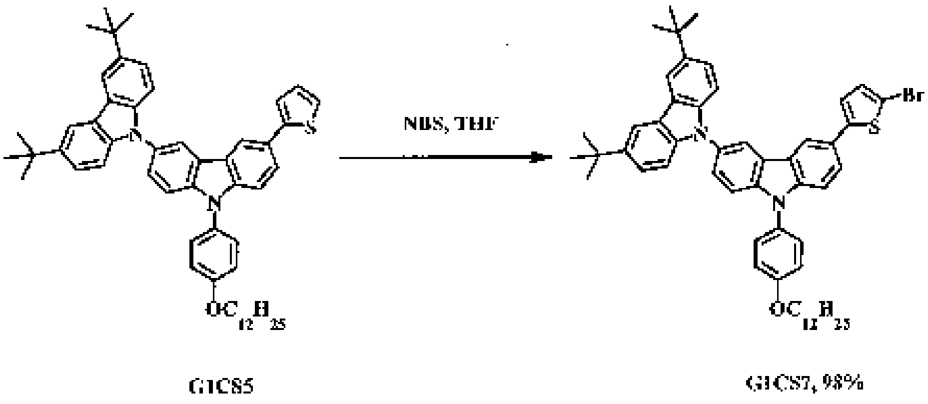


Figure 4.12 Bromination reaction to form 3,6-dibromo-9-(4-(dodecyloxy)phenyl)-9*H*-carbazole **(G1CS7)**

The reaction mechanism involved bromination reaction as described in Figure 3.11.

The Suzuki coupling reaction was performed with the bromo intermediate and 5-formyl thiopheneboronic acid was carried out using $Pd(PPh_3)_4$ as a catalyst and Na_2CO_3 as a base in THF as a solvent for 24 h to directly 5-(5-(3-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-9-(4-(dodecyloxy)phenyl)-9*H*-carbazol-6-yl)thiophen-2-yl)thiophene-2-carbaldehyde as **(G1CSS10)** yellow solid in 75% yield as shown in Figure 4.15

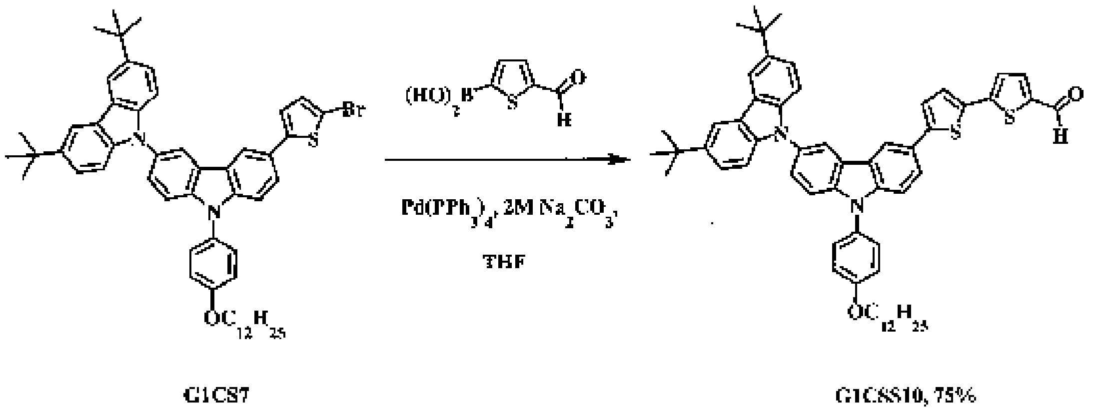
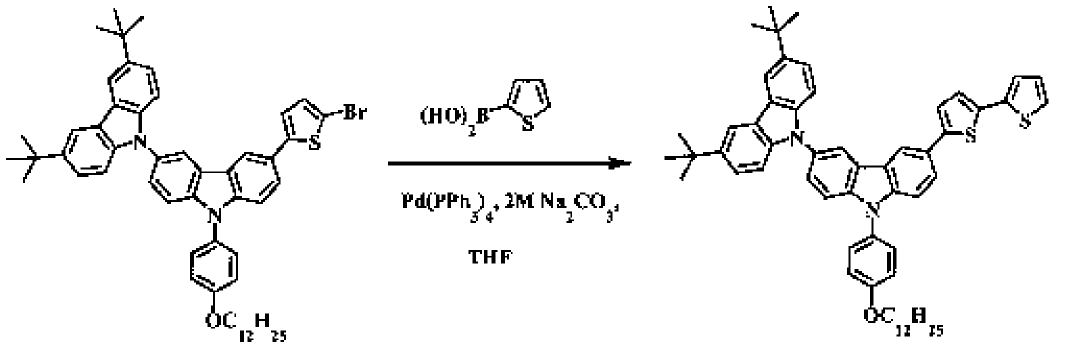


Figure 4.13 Suzuki coupling reaction to form 5-(5-(3-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-9-(4-(dodecyloxy)phenyl)-9*H*-carbazol-6-yl)thiophen-2-yl)thiophene-2-carbaldehyde **(G1CSS10)**

The mechanism of Suzuki coupling reaction follows a three-step mechanism cycle, oxidative addition, transmetallation and reductive elimination as described in Figure 3.12.

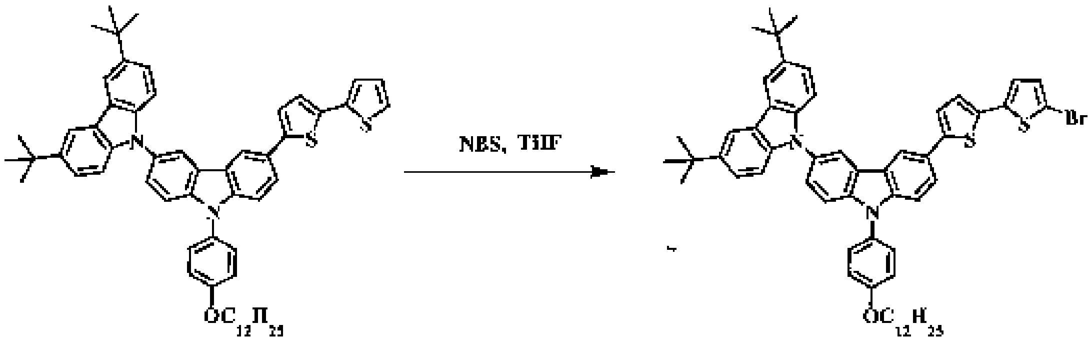
The Suzuki coupling reaction was performed with the bromo intermediate and 2-thiopheneboronic acid was carried out using $Pd(PPh_3)_4$ as a catalyst and Na_2CO_3 as a base in THF as a solvent for 24 h to directly yield 3,6-di-*tert*-butyl-9-(9-(4-(dodecyloxy)phenyl)-3-(5-(thiophen-2-yl)thiophen-2-yl)-9*H*-carbazol-6-yl)-9*H*-carbazole **(G1CSS8)** as yellow solid in 86% yield as shown in Figure 4.16.



G1CS7 **G1CSS8, 86%**

Figure 4.14 Suzuki coupling reaction to form 3,6-di-*tert*-butyl-9-(9-(4-(dodecyloxy)phenyl)-3-(5-(thiophen-2-yl)thiophen-2-yl)-9*H*-carbazol-6-yl)-9*H*-carbazole (G1CSS8)

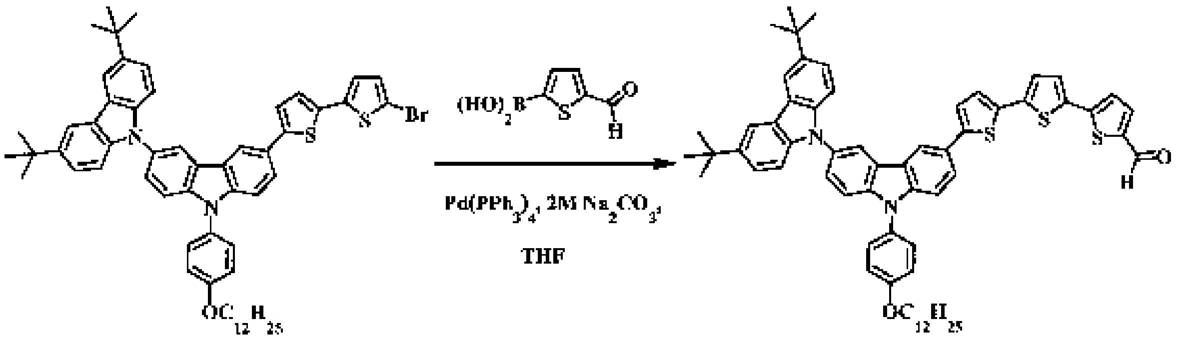
3,6-di-*tert*-butyl-9-(9-(4-(dodecyloxy)phenyl)-3-(5-(thiophen-2-yl)thiophen-2-yl)-9*H*-carbazol-6-yl)-9*H*-carbazole (**G1CSS8**) was brominated with NBS in tetrahydrofuran as solvent gave 3,6-di-*tert*-butyl-9-(3-(5-(5-bromothiophen-2-yl)thiophen-2-yl)-9-(4-(dodecyloxy) phenyl)-9*H*-carbazol-6-yl)-9*H*-carbazole (**G1CSS9**) as white solid in 77% yield a outlined in Figure 4.15.



G1CSS8 **G1CSS9, 77%**

Figure 4.15 Suzuki coupling reaction to form 3,6-di-*tert*-butyl-9-(3-(5-(5-bromothiophen-2-yl)thiophen-2-yl)-9-(4-(dodecyloxy)phenyl)-9*H*-carbazol-6-yl)-9H-carbazole (G1CSS9)

The Suzuki coupling reaction was performed with the bromo intermediate and 5-formyl thiopheneboronic acid was carried out using Pd(PPh$_3$)$_4$ as a catalyst and Na$_2$CO$_3$ as a base in THF as a solvent for 24 h to directly 5-(5-(5-(3-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-9-(4-(dodecyloxy)phenyl)-9*H*-carbazol-6-yl)thiophen-2-yl)thiophen-2-yl)thiophene-2-carbaldehyde (**G1CSSS11**) as yellow solid in 79% yield as shown in Figure 4.19.

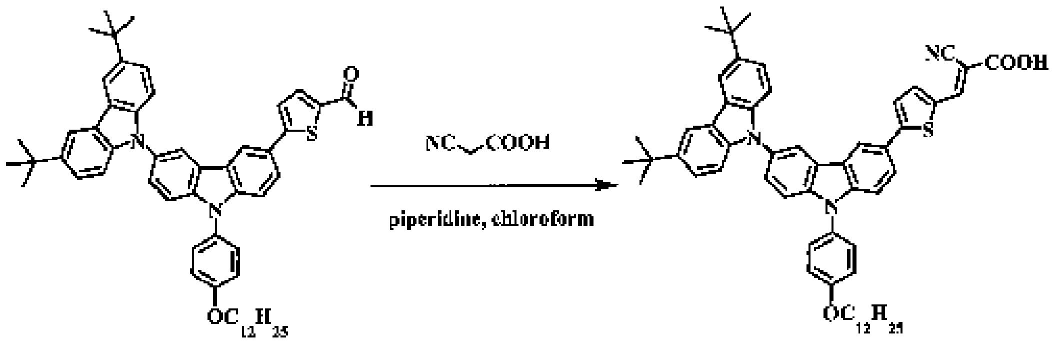


G1CSS9

G1CSSS11, 79%

Figure 4.16 Suzuki coupling reaction to form 5-(5-(5-(3-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-9-(4-(dodecyloxy)phenyl)-9*H*-carbazol-6-yl)thiophen-2-yl)thiophen-2-yl)thiophene-2-carbaldehyde (**G1CSSS11**)

The dye with cyanoacrylic acid as an acceptor was synthesized. Knoevenagel condensation reaction of aldehyde compound with cyanoacetic acid in the presence of piperidine as a base and and chloroform as solvent to directly yield *(E)*-3-(5-(3-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-9-(4-(dodecyloxy)phenyl)-9*H*-carbazol-6-yl)thiophen-2-yl)-2-cyanoacrylic acid (**G1CSA12**) as red solid in 62% yield as shown in Figure 4.17.

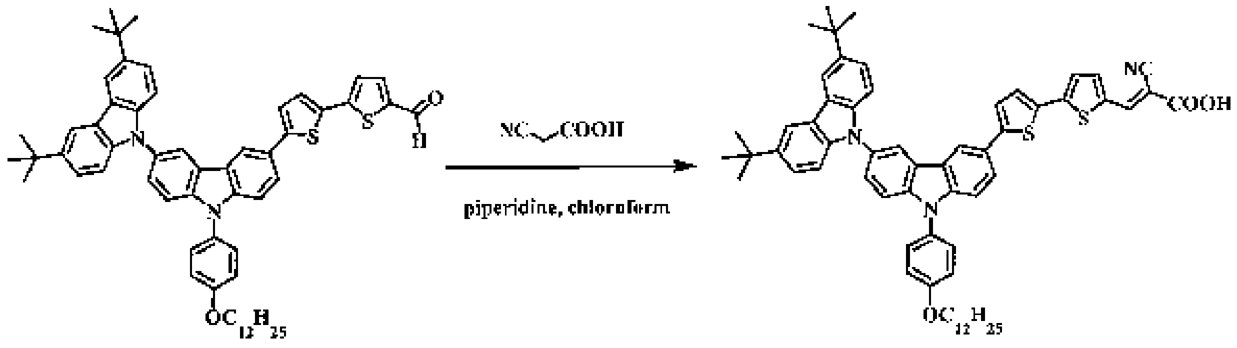


G1CS6

G1CSA12, 62%

Figure 4.17 Knoevenagel condensation reaction to form *(E)*-3-(5-(3-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-9-(4-(dodecyloxy)phenyl)-9*H*-carbazol-6-yl)thiophen-2-yl)-2-cyanoacrylic acid (**G1CSA12**)

Knoevenagel condensation reaction of aldehyde compound with cyanoacetic acid in the presence of piperidine as a base and and chloroform as solvent to directly yield *(E)*-3-(5-(5-(3-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-9-(4-(dodecyloxy)phenyl)-9*H*-carbazol-6-yl) thiophen-2-yl) thiophen-2-yl)-2-cyanoacrylic acid (G1CSSA13) as red solid in 61% yield as shown in Figure 4.18.

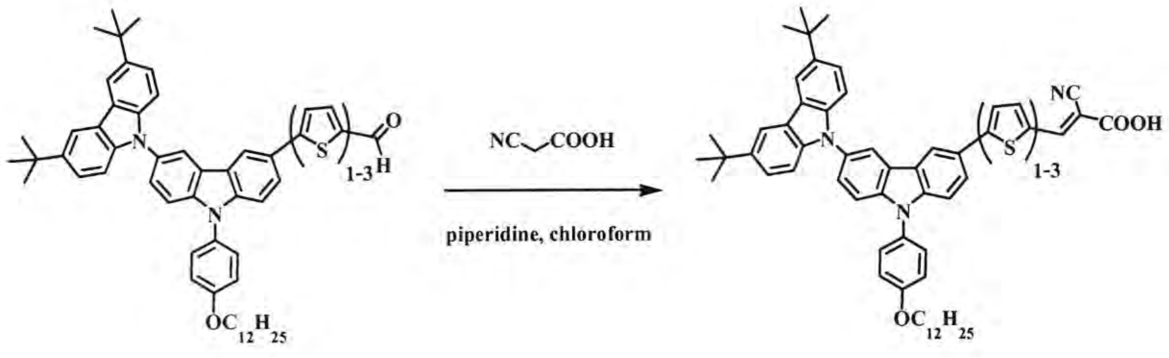


G1CSS9

G1CSSA13, 61%

Figure 4.18 Knoevenagel condensation reaction to form *(E)*-3-(5-(5-(3-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-9-(4-(dodecyloxy)phenyl)-9*H*-carbazol-6-yl)thiophen-2-yl)thiophen-2-yl)-2-cyanoacrylic acid (G1CSSA13)

Knoevenagel condensation reaction of aldehyde compound with cyanoacetic acid in the presence of piperidine as a base and and chloroform as solvent to directly yield *(E)*-3-(5-(5-(5-(3-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-9-(4-(dodecyloxy)phenyl)-9*H*-carbazol-6-yl) thiophen-2-yl)thiophen-2-yl)thiophen-2-yl)-2-cyanoacrylic acid (**G1CSSSA14**) as red solid in 65% yield as shown in Figure 4.19.



G1CSSS11

G1CSSSA14, 65%

Figure 4.19 Knoevenagel condensation reaction to form *(E)*-3-(5-(5-(5-(3-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-9-(4-(dodecyloxy)phenyl)-9*H*-carbazol-6-yl)thiophen-2-yl)thiophen-2-yl)thiophen-2-yl)-2-cyanoacrylic acid (**G1CSSSA14**)

Knoevenagel condensation is addition reaction of the methylene components, activated with two electronwithdrawing groups, to aldehyde can be performed with secondary amines. A reasonable variation of the mechanism, in which piperidine acts as organocatalyst, involves the corresponding iminium intermediate as the acceptor is shown in Figure 3.18.

4.3.2 Optical properties

UV–vis and fluorescence spectra of **G1CSA12, G1CSSA13** and **G1CSSSA14** dyes in dry CH_2Cl_2 are shown in Figure 4.20 and listed in Table 4.1, together with the UV–vis spectrum of the corresponding dye absorbed on TiO_2 nanoparticle. In solution, all three dyes show similar characteristic of donor-accepter. Dyes **G1CSA12, G1CSSA13** and **G1CSSSA14** exhibited broad absorption spectra ranging from 250 to 600 nm. The spectra exhibit three major absorption bands. The absorption band at around 298 nm can be attributed to the π-π^* transition of the carbazole moieties and the absorption bands at longer wavelength around 450 nm corresponding to the intramolecular charge transfer (ICT) transition between the donor and the acceptor. This indicates that the molecules have a D-D-π-A character. As the number of thiophene units in the molecules increase, the spectra bathochromic shifted (red shifted) and the molar extinction coefficients (ε) increase. The broad absorption spectra and high ε value are the key requirments for best sentisizer for efficient DSC.

As expected, **G1CSSSA14** with the dodecyloxyphenyl exhibits more red shift absorption (λ_{max} 450 nm, ICT band) comparing to the **CCT3A** dyes (λ_{max} 443 nm, ICT band) [40]. The red shifted in the absorption can be attributed to the dodecyloxyphenyl moiety as electron withdrawing group and long conjugated system. Furthermore, the bulky alkylphenyl groups could suppress the aggregation due to the disturbance of the π-π stacking [31].

The UV-vis absorption spectra of the **G1CSA12, G1CSSA13** and **G1CSSSA14** dyes adsorped on TiO_2 film show a hypsochromic shifted or blue shifted and broader spectra when compare to their corresponding absorption spectra in solution (Figure 4.21). The broadending of the dyes absorption on the surface of the TiO_2 films and blue shifted of the peak maxima is belived to result from the formation of partial H-aggregate [41].

The fluorescence emission spectra of the dyes in CH_2Cl_2 (Fig. 4.20 (right)) a red-shift upon increased number of thiophene units in the molecule, which is roughly parallel to the trend of the absorption spectra.

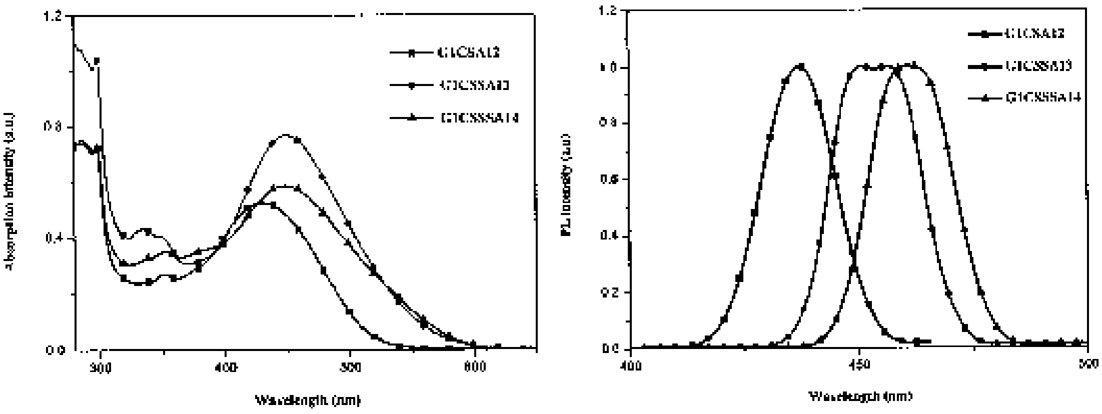


Figure 4.20 Absorption (left) and emission (right) spectra of **G1CSA12, G1CSSA13** and **G1CSSSA14** dyes in dichloromethane.

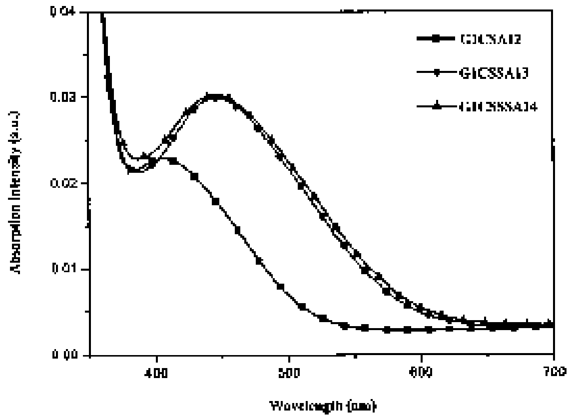


Figure 4.21 Absorption spectra of TiO_2 films sensitized by **G1CSA12**, **G1CSSA13** and **G1CSSSA14** dyes.

Table 4.1 The absorption and fluorescence data of **G1CSA12**, **G1CSSA13** and **G1CSSSA14**

Compound	**λ_{max} (nm) and ε (10^4 M^{-1} cm^{-1})**	**λ_{max} on TiO_2 (nm)**	**λ_{max} of emission in CH_2Cl_2 (nm)**
G1CSA12	297 (2.30), 352 (4.00), 430 (3.06)	407	406
G1CSSA13	298 (1.10), 348 (3.22), 448 (3.86)	444	451
G1CSSSA14	298 (3.74), 353 (4.39), 450 (3.98)	445	461

4.3.3 Thermal properties

For optoelectronic applications, the thermal stability of organic material is crucial for device stability and lifetime [21]. The degradation of organic optoelectronic devices depends on morphological changes resulting from the thermal stability of the amorphous organic materials [22]. Figure 3.23 and Table 3.2 show TGA thermograms and temperature at 5% weight loss (T_{5d}) of **G1CSA12**, **G1CSSA13** and **G1CSSSA14** dyes investigated by TGA analysis under nitrogen atmospheric condition. Those results suggested that the dyes were thermally stable materials with T_{5d} well over 170 °C which is good for long stability of DSCs devices.

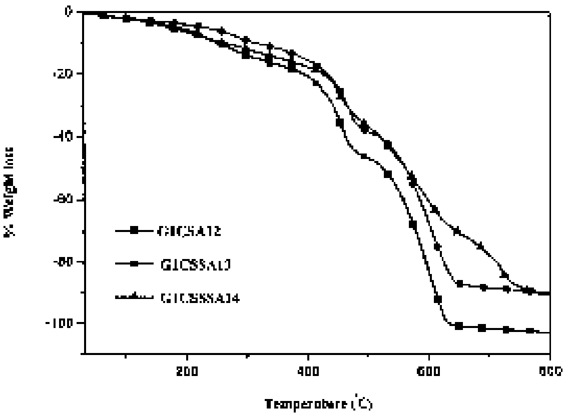


Figure 4.22 TGA thermograms of **G1CSA12, G1CSSA13** and **G1CSSSA14** dyes.

Table 4.2 Thermal properties of **G1CSA12, G1CSSA13** and **G1CSSSA14** dyes

Compound	T_{5d}(°C)
G1CSA12	176
G1CSSA13	187
G1CSSSA14	233

4.4 Conclusion

The designed dye compounds **G1CSA12, G1CSSA13** and **G1CSSSA14** were synthesized using a combination of Alkylation, Bromination, Ullmann coupling, Suzuki cross-coupling and Knoevenagel condensation reactions. The target molecules exhibit a absorption band cover UV and visible region.. The number of thiophene increased the conjugation length of compounds resulting a red-shift and broad in absorption solution spectra. Furthermore, the bulky alkylphenyl groups could suppress the aggregation due to the disturbance of the π-π stacking, which should always be avoided for efficient photocurrent generation because aggregation may lead to intermolecular quenching or affect the light absorption by the filtering effect. The performance of DSCs using these materials as dyes is under investigation and will be reported in the future.

CHAPTER 5

SYNTHESIS AND CHARECTERIZATION OF D-D-π-A TYPEORGANIC DYES HAVING CARBAZOLE DENDRON-CARBAZOLE AS DONOR

5.1 Introduction

Organic dyes with D–D–π-A structure over the simple D-π-A configuration, introducing a secondary electron donor into the dye molecule can increase electron-density of donor and enhance molar extinction coefficient, which resulted in high overall conversion efficiency [42]. Carbazole has strong absorption in the near-UV region and a low redox potential. The electrochmical and spectroscopic properties of carbazole and its derivative have been extensively investigated. Chemically, carbazole can be easily functionallized at its 3-, 6- or 9-positions and covalently liked to other molecular moieties [43, 44]. Due to its unique optical, electrical, and chemical properties, carbazole has been used widely as a funtional building block or substituent in the construction of organic molecules for use as active componants in solar cells. Morever, the thermal stability and glassy state durability of the organic molecules were found to be signification improved upon incorporation of a carbazole moiety in to the structure [45].

π-Conjugated oligothiophene molecules have attracted much attention in the area of organic chemistry and material sciences. They possess very interesting electronic and optical properties and have been investigated as advanced molecular electronic materials.

The carboxylic acid group is by far he most employed group for attachment of the sensitizers to the semiconductor surface. The binding modes for dye sensitizers with carboxylic acid anchoring groups have been investigated by Galoppini [46]. Phosphonic acid also strongly to metal oxide but are not frequently used, derivative of carboxylic acids has also been employed, such as esters and carboxylic salts [47].

5.2 Aim of the Study

We designed a novel D D π-A organic materials based on G1 and G2 as primary donor, carbazole with phenyloxyalkylation as the secondary donor group, thiophene linker and cyanoacrylic acid moiety as acceptor/anchoring group (**G1CSSA13** and **G2CSSA5**). The synthetic strategy included well-known methodology, such as Ullmann coupling, Suzuki cross coupling and the last step where cyanoacrylamide or cyanoacrylic acid was coupled to the chromophore according to the Knoevenagel condensation reaction.

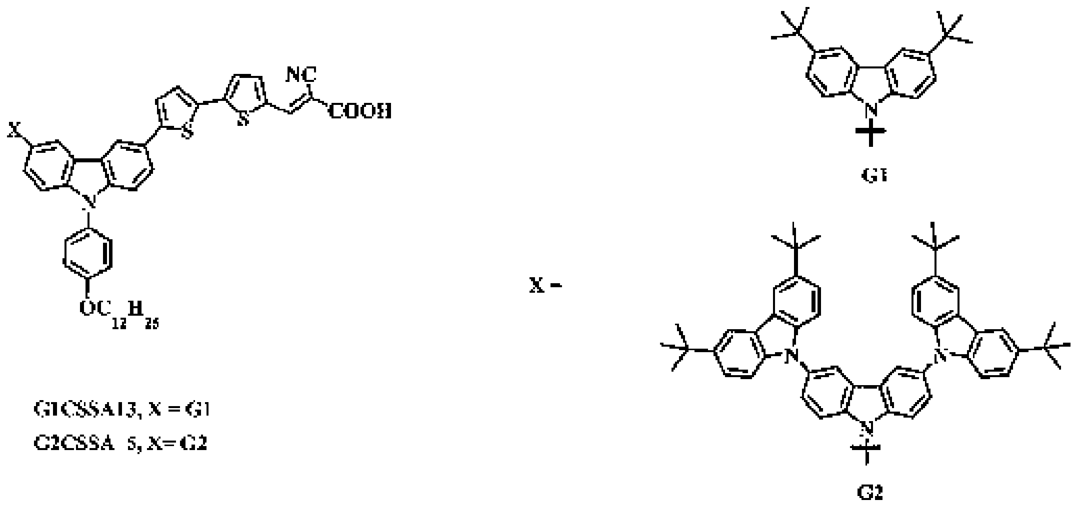


Figure 5.1 Organic dye structures of **G1CSSA13** and **G2CSSA5** organic dyes

5.3 Results and Discussion

5.3.1 Synthesis

For the synthesis of *(E)*-3-(5-(5-(3-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-9-(4-(dodecyloxy) phenyl)-9*H*-carbazol-6-yl)thiophen-2-yl)thiophen-2-yl)-2-cyanoacrylic acid (**G1CSSA13**) as shown in chapter 4.

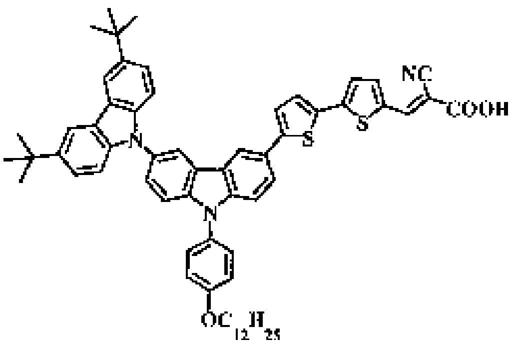


Figure 5.2 (*E*)-3-(5-(5-(3-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-9-(4-(dodecyloxy)phenyl)-9*H*-carbazol-6-yl)thiophen-2-yl)thiophen-2-yl)-2-cyanoacrylic acid **(G1CSSA13)**

The synthesis of 3,6-bis(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-9-(3-bromo-9-(4-(dodecyloxy) phenyl)-9*H*-carbazol-6-yl)-9*H*-carbazole was prepared from 3,6-dibromo-9-(4-(dodecyloxy)phenyl)-9*H*-carbazole **(CP3)** with 3,6-di-*tert*-butyl-9-(3-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-9*H*-carbazol-6-yl)-9*H*-carbazole **(G2)** under Ullmann coupling reaction in the presence of copper iodide as a catalyst, (±)-*trans*-1,2-diaminocyclohexane as a co-catalyst, and potassium phosphate as a base in toluene as a solvent at reflux for 24 h as white solid in 65% yield as outlined in Figure 5.3.

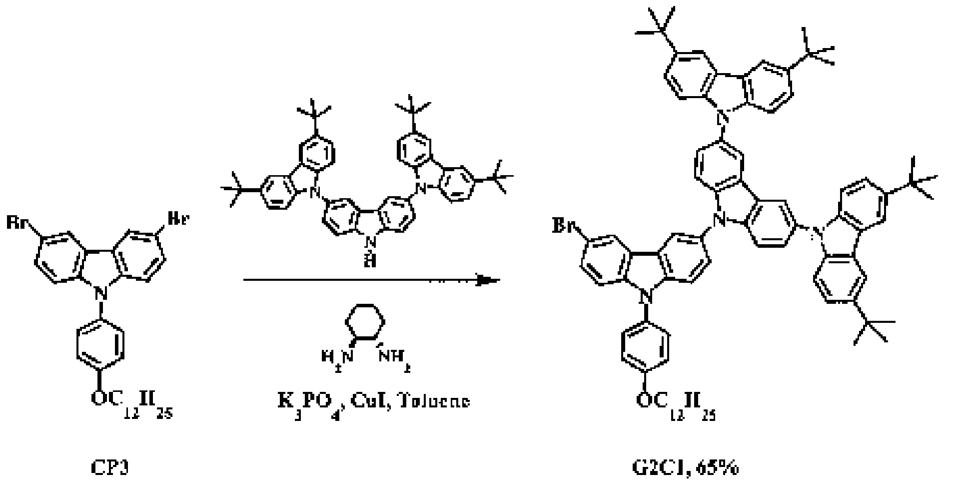
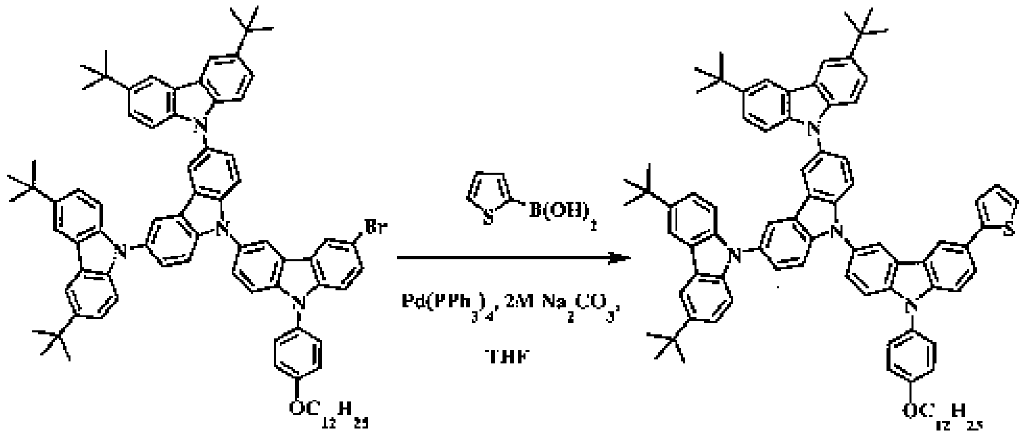


Figure 5.3 Ullmann coupling reaction to form 3,6-bis(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-9-(3-bromo-9-(4-(dodecyloxy)phenyl)-9*H*-carbazol-6-yl)-9*H*-carbazole (G2C1)

Ullmann coupling mechanism is shown in Figure 4.8. The active species is a copper (I) iodide which undergoes oxidative addition with the second equivalent of halide, followed by reductive elimination and the formation of the thiophene-carbazole carbon bond.

Suzuki cross coupling reaction of 3,6-bis(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-9-(3-bromo-9-(4-(dodecyloxy)phenyl)-9*H*-carbazol-6-yl)-9*H*-carbazole **(CP3)** with 2-thiophene boronic acid in the presence of $Pd(PPh_3)_4$ as catalyst and 2M Na_2CO_3 as a base in THF as a solvent for 24 h to directly yield 53,6-bis(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-9-(9-(4-(dodecyloxy) phenyl)-3-(thiophen-2-yl)-9*H*-carbazol-6-yl)-9*H*-carbazole **(G2CS2)** as a white solid in 60% as shown in Figure 5.4.



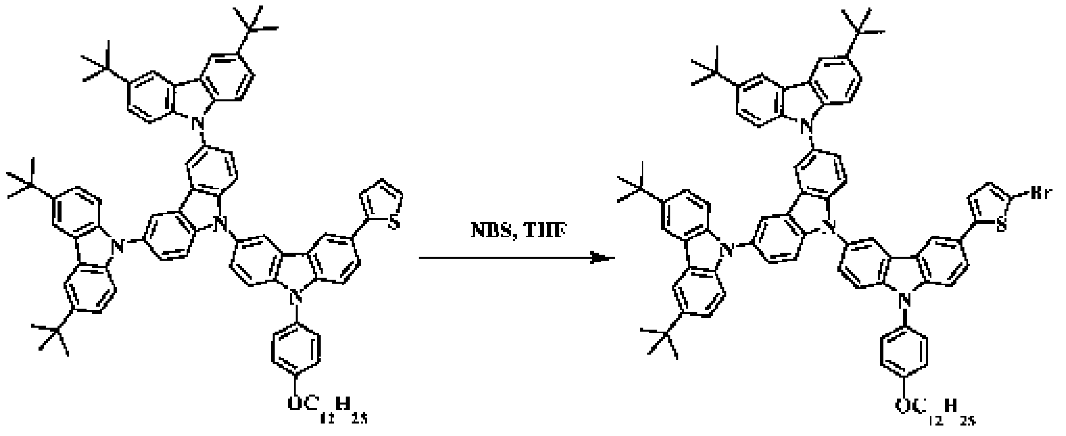
G2C1

G2CS2, 93%

Figure 5.4 Ullmann coupling reaction to form 3,6-bis(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-9-(9-(4-(dodecyloxy)phenyl)-3-(thiophen-2-yl)-9*H*-carbazol-6-yl)-9*H*-carbazole **(G2CS2)**

The proposed mechanism of Suzuki cross coupling reaction is show in Figure 3.8. The Suzuki reaction is the coupling of an aryl or vinyl boronic acid with an aryl or vinyl or vinyl halide using a palladium catalyst to form C-C bond. Thus, base activation of organoboron reagents as boronate intermediates facilitated the transfer of the organic group from boron to palladium (transmetallation). The reaction has later been extended to also include couplings with alkyl groups.

Bromination reaction of 3,6-bis(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-9-(9-(4-(dodecyloxy)phenyl)-3-(thiophen-2-yl)-9*H*-carbazol-6-yl)-9*H*-carbazole **(G2CS2)** with NBS in THF as solvent to directly yield 3,6-bis(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-9-(3-(5-bromo thiophen-2-yl)-9-(4-(dodecyloxy)phenyl)-9*H*-carbazol-6-yl)-9*H*-carbazole **(G2CS3)** as white solid in 88% yield as outlined in Figure 5.5.



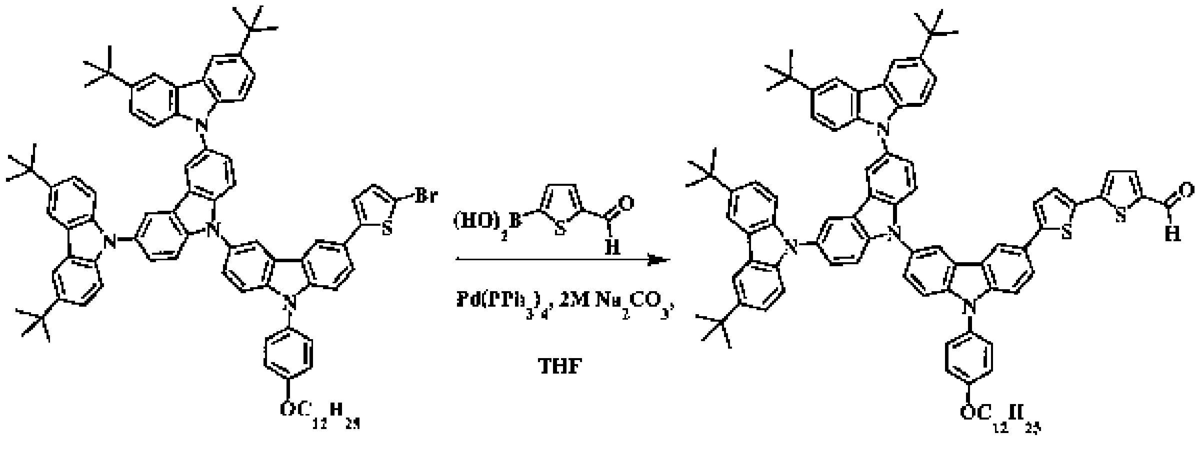
G2CS2

G2CS3, 88%

Figure 5.5 Bromination reaction to form 3,6-bis(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-9-(3-(5-bromothiophen-2-yl)-9-(4-(dodecyloxy)phenyl)-9*H*-carbazol-6-yl)-9*H*-carbazole (G2CS3)

The reaction mechanism involved bromination reaction as described in Figure 3.11.

Suzuki cross coupling reaction of 3,6-bis(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-9-(3-(5-bromothiophen-2-yl)-9-(4-(dodecyloxy)phenyl)-9*H*-carbazol-6-yl)-9*H*-carbazole **(G2CS3)** with 5-formyl thiophene boronic acid in the presence of $Pd(PPh_3)_4$ as catalyst and 2M Na_2CO_3 as a base in THF as a solvent for 24 h to 5-(5-(3-(3,6-bis(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-9*H*-carbazol-9-yl)-9-(4-(dodecyloxy)phenyl)-9*H*-carbazol-6-yl)thiophen-2-yl)thiophene-2-carbaldehyde **(G2CSS4)** as a yellow solid in 72% as shown in Figure 5.6.

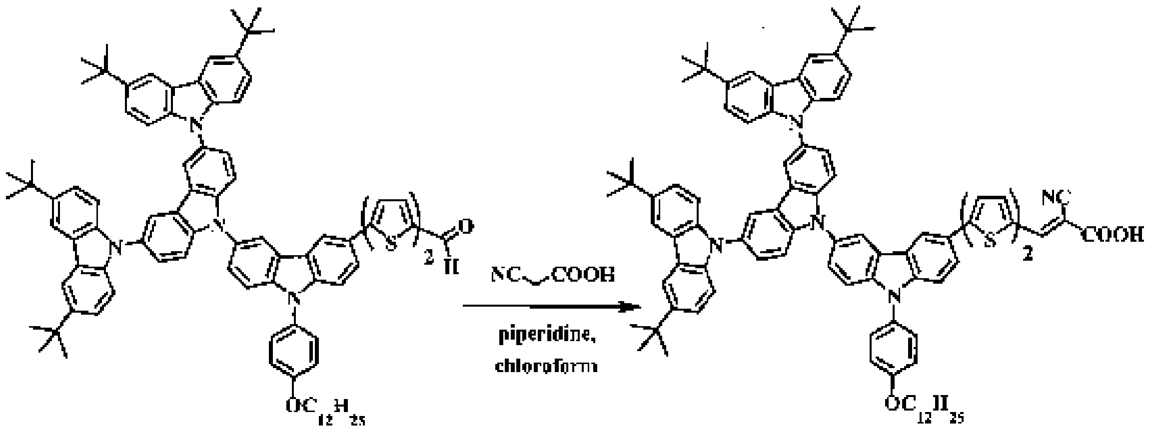


G2CS3

G2CSS4, 72%

Figure 5.6 Suzuki cross coupling reaction to form 5-(5-(3-(3,6-bis(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-9*H*-carbazol-9-yl)-9-(4-(dodecyloxy)phenyl)-9*H*-carbazol-6-yl)thiophen-2-yl) thiophene-2-carbaldehyde **(G2CSS4)**

Knoevenagel condensation reaction of aldehyde compound with cyanoacetic acid in the presence of piperidine as a base and and chloroform as solvent to directly yield **G2CSSA5** as red solid in 65% yield as shown in Figure 5.7.



G2CSS4

G2CSSA5, 69%

Figure 5.7 Knoevenagel condensation reaction to form **G2CSSA5**

5.3.2 Optical properties

UV–vis and fluorescence spectra of **G1CTTA13** and **G2CTTA5** dyes in dry CH_2Cl_2 are shown in Figure 5.8 and listed in Table 5.1, together with the UV–vis spectrum of the corresponding dye absorbed on TiO_2 nanoparticle. The **G2CTTA5** dye showed the maximum absorption wavelength (λ_{max}) 456 nm (molar absorption coefficient (ε) = 28,800 $M^{-1}cm^{-1}$) with the longest symmetric conjugated system exhibits more red shift absorption comparing to the shortest symmetric **G1CTTA13** dyes (Chapter 4). The absorption maxima of **G2CTTA5** dyes adsorbed on TiO_2 film are illustrated in Figure 5.9. Comparing to their absorption spectra in solution, the dyes adsorbed onto surface of TiO_2 film exhibit broader and hypsochromic shift or blue shift in absorption spectra, which indicate strong interactions between dyes and semiconductor surface. The blue shift in absorption were also observed in three dyes reported in chapter 4 and a blue shift absorption of the dyes bonded to TiO_2 film can be observed in general type of acrylic anchoring group [48, 49, 50].

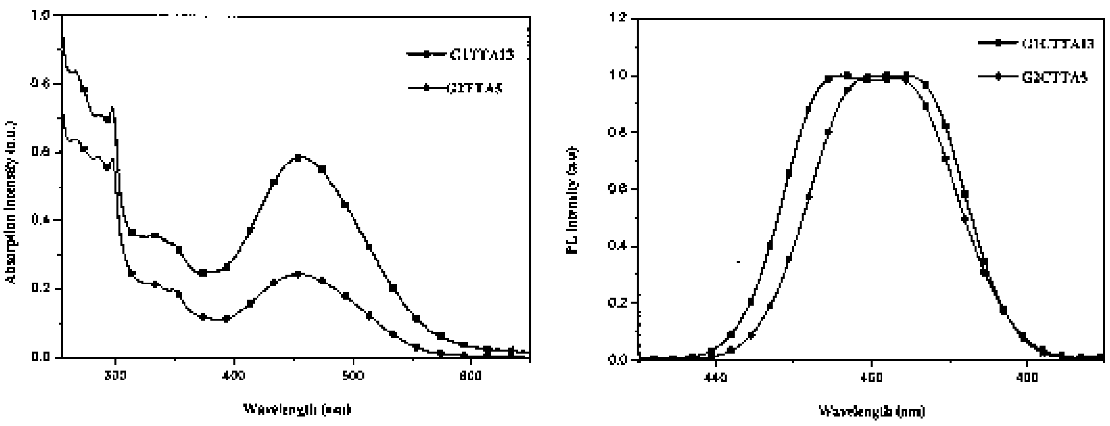


Figure 5.8 Absorption (left) and emission (right) spectra of **G1CTTA13** and **G2CTTA5** dyes in dichloromethane.

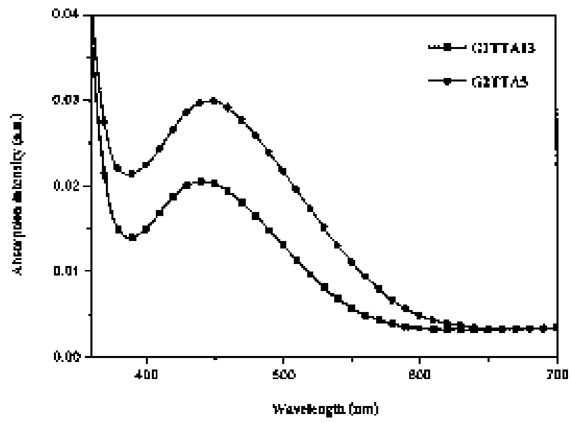


Figure 5.9 Absorption spectra of TiO_2 films sensitized by **G1CTTA13** and **G2CTTA5 dyes**

Table 5.1 The absorption and fluorescence data of **G1CTTA13** and **G2CTTA5** dyes

Compound	**λ_{max} (nm) and ε (10^4 M^{-1} cm^{-1})**	**λ_{max} on TiO_2 (nm)**	**λ_{max} of emission in CH_2Cl_2 (nm)**
G1CTTA13	298 (1.10), 348 (3.22), 448 (3.86)	444	451
G2CTTA 5	298 (0.06), 349 (3.27), 456 (2.88)	449	461

5.3.3 Thermal properties

For optoelectronic applications, the thermal stability of organic material is crucial for device stability and lifetime [21]. The degradation of organic optoelectronic devices depends on morphological changes resulting from the thermal stability of the amorphous organic materials [22]. Figure 5.10 and Table 5.2 show TGA thermograms and temperature at 5% weight loss (T_{5d}) of **G1CSSA13** and **G2CSSA5** dyes investigated by TGA analysis under nitrogen atmospheric condition. Those results suggested that the dyes were thermally stable materials with T_{5d} well over 180 °C which is good for long stability of DSCs devices.

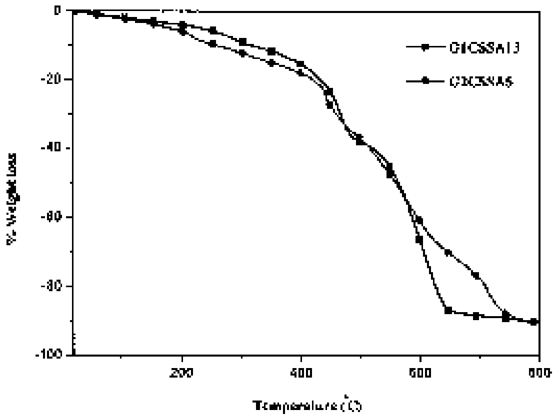


Figure 5.10 TGA thermograms of G1CSSA13 and G2CSSA5 dyes

Table 5.2 Thermal properties of G1CSSA13 and G2CSSA5 dyes

Compound	**T_{5d} (°C)**
G1CSSA13	187
G2CSSA 5	233

5.4 Conclusion

The designed dye compounds **G1CSSA13** and **G2CSSA5** were synthesized using a combination of Alkylation, Bromination, Ullmann coupling, Suzuki cross-coupling and Knoevenagel condensation reactions. The target molecules exhibit a absorption band cover UV and visible region. The number of thiophene increased the conjugation length of compounds resulting a red-shift and broad in absorption solution spectra. Furthermore, the bulky alkylphenyl groups could suppress the aggregation. The performance of DSCs using these materials as dyes is under investigation and will be reported in the future.

CHAPTER 6

SUMMARY

The designed D-π-A type organic dyes **TpSSA3** and **TpSSA4** based on triphenylamine as the donor group, with a thiophene linker and a cyanoacrylamide or cyanoacrylic acid moiety as acceptor/anchoring group, The dyes **CSSA9, CSSA10, CSSA11, CSPA12** and **CSSPA13** with carbazole as the donor group, oligothiophene and oligothiophene-phenylene linker and a cyanoacrylic acid or cyanoacrylamide moiety as acceptor/anchor group.

The designed D-D-π-A type organic dyes **G1CSA12, G1CSSA13, G1CSSSA14** and **G2CSSA5** composed of three parts: (1) cabarzole donating groups (D); (2) an oligothiophene (π); and (3) an cyanoacrylic acid anchoring groups (A). They were synthesized using a combination of alkylation, bromination, Ullmann coupling, Suzuki cross-coupling and Knoevenagel condensation reactions. The electronic and thermal properties of these compounds can be tuned by varying the number of thiophene rings and anchoring group. These compounds exhibited a high molar absorptivity in the blue/green region of solar light. The number of thiophene increased the conjugation length of compounds resulting a red-shift and broad in absorption solution spectra.

CHAPTER 7

EXPERIMENT

7.1 General procedures and instruments

^{1}H-NMR spectra were recorded on Brüker AVANCE (300 MHz) spectrometer. ^{13}C NMR spectra were recorded on Brüker AVANCE (75 MHz) spectrometer and were fully decoupled. Chemical shifts (d) 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), $AA'BB'$ quartet system ($AA'BB'$), AB quartet (ABq) and multiplet (m).

The UV-visible spectra were measured in spectrometric grade dichloromethane on a Perkin-Elmer UV Lambda 25 spectrometer. The absorption peaks are reported as in wavelength (nm) (log ε /dm^{3}mol^{-1}cm^{-1}) and sh refers to shoulder. Fluorescence spectra were recorded as a dilute solution in spectroscopic grade dichloromethane on a Perkin-Elmer LS 50B Luminescence Spectrometer.

Dichloromethane was washed with conc. H_2SO_4 and distilled twice from calcium hydride. Tetrahydrofuran (THF) was heated at reflux under nitrogen over sodium wire and benzophenone until the solution became blue and freshly distilled before use. All reagents and solvents were purchased from Aldrich, Acros, Fluka or Thai Supplies and received unless otherwise stated.

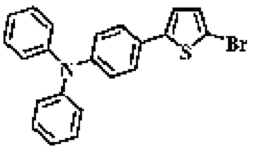
Analytical thin-layer chromatography (TLC) was performed with Merck aluminium plates coated with silica gel 60 F_{254}. Column chromatography was carried out using gravity feed chromatography with Merck silica gel mesh, 60 Å. Where solvent mixtures are used, the portions are given by volume.

Thermogravimetric measurements were carried out using a thermoanalysis apparatus TGA/SDTA851 from Mettler Toledo. Samples for the measurements were prepared by filling alox crucibles. Measurements were performed at a heating rate of 10 °C /min under a nitrogen flow rate of 75 cm^3/min in the temperature range from 25 to 800 °C.

Melting points was measured by BIBBY Stuart Scientific melting point apparatus SMP3 in open capillary method and are uncorrected and reported in degree celsius.

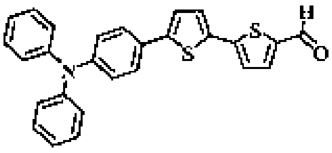
7.2 Synthesis and characterization

4-(5-bromothiophen-2-yl)-N,N-diphenylbenzenamine (TpS1)



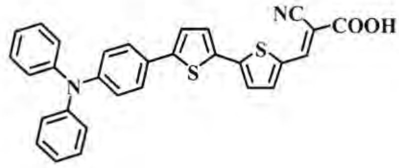
The a stirred solution of bromo compound (0.01 g, 0.36 mmol) and $Pd(PPh_3)_4$ (0.0003 g, 0.0003 mmol) in tetrahydrofuran (15 ml) were added 2,5-thiopheneboronic acid (0.10 g, 0.36 mmol), and an aqueous Na_2CO_3 solution (0.38 g, 3.66 mmol). The mixture was refluxed for 48 h. After an cooling the solution, H_2O (50 ml) was added to the solution and extracted by dichloromethane (50 ml x 3). The organic layer was separated and dried in Na_2SO_4. The solvent was removed in vacuo. Purification by column chromatographyl over silica gel eluting with a mixture of methylene chloride and n-hexane (1:6) followed by recrystallization with a mixture of methylene chloride and methanol afforded orange solids (yield 26 %). $C_{22}H_{16}BrNOS$; m.p. 123 °C; ^1H NMR (300 MHz, CDCl) : δ 7.37 (2H, d, J = 8.62 Hz), 7.28 (4H, t, J = 7.57 Hz), 7.13 (4H, d, J = 7.67 Hz), 7.08-7.05 (4H, m), 7.00 (1H, d, J = 3.38 Hz), 6.96 (1H, d, J = 3.83 Hz) ppm.

5-(5-(4-(diphenylamino)phenyl)thiophen-2-yl)thiophene-2-carbaldehyde (TpS2)



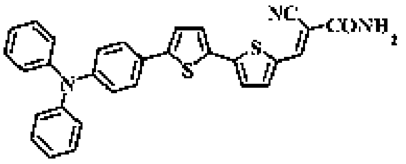
The a stirred solution of bromo compound (0.01 g, 0.36 mmol) and $Pd(PPh_3)_4$ (0.0003 g, 0.0003 mmol) in tetrahydrofuran (15 ml) were added 5-formyl-2-thiopheneboronic acid (0.10 g, 0.36 mmol), and an aqueous Na_2CO_3 solution (0.38 g, 3.66 mmol). The mixture was refluxed for 48 h. After an cooling the solution, H_2O (50 ml) was added to the solution and extracted by dichloromethane (50 ml x 3). The organic layer was separated and dried in Na_2SO_4. The solvent was removed in vacuo. Purification by column chromatographyl over silica gel eluting with a mixture of methylene chloride and n-hexane (1:6) followed by recrystallization with a mixture of methylene chloride and methanol afforded orange solids (yield 82 %). $C_{27}H_{19}NOS_2$; m.p. 138 °C; ^{1}H NMR (300 MHz, CDCl) : δ 9.85 (1H, s), 7.67 (1H, s), 7.47 (2H, d, J = 7.5 Hz), 7.28 (6H, m), 7.12 (9H, m) ppm; ^{13}C NMR, (300 MHz, CDCl) : 182.37, 148.07, 147.44, 147.27, 146.29, 141.30, 137.41, 134.08, 129.41, 127.24, 127.10, 126.63, 124.83, 123.74, 123.48, 123.19, 123.14, 77.45, 77.03, 76.61 and 29.71.

(*E*)-2-cyano-3-(5-(5-(4-(diphenylamino)phenyl)thiophen-2-yl)thiophen-2-yl) acrylic acid (TpSSA3)



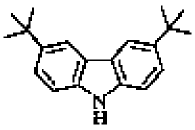
A mixture of 5-(5-(4-(diphenylamino)phenyl)thiophen-2-yl)thiophene-2-carbaldehyde (0.2 g, 0.45 mmol) and cyanoacetic acid (0.05 g, 0.68 mmol) was vacuum-dried and chloroform (25 ml) and piperidine (0.11 ml, 1.37 mmol) were added. The solutionwas refluxed for overnight. After cooling the solution, the organic layer was removed in vacuo. Purification by column chromatographyl over silica gel eluting with a mixture of methylene chloride and methanol (3:1) followed by recrystallization with a mixture of methylene chloride and methanol afforded a red solids (yield 79 %). $C_{30}H_{20}N_2O_2S_2$; m.p. 240 °C; ^{1}H NMR (300 MHz, DMSO-d_6) : δ 8.02 (1H, s), 7.63-7.57 (3H, m), 7.44-7.40 (3H, m), 7.32 (4H, t, J = 7.5 Hz), 7.10-7.03 (6H, m), 7.08 (2H, d, J = 7.8 Hz), 7.04 (2H, d, J = 7.5 Hz), 6.94 (2H, d, J = 8.4 Hz) ppm; ^{13}C NMR, (300 MHz, DMSO-d_6) : 147.72, 147.19, 144.32, 141.53, 136.56, 136.18, 134.32, 130.15, 127.29, 127.19, 126.97, 124.96, 124.62, 124.55, 124.10, 123.13, 40.78,40.50, 40.23, 39.95, 39.67, 39.39 and 39.11.

(*E*)-2-cyano-3-(5-(5-(4-(diphenylamino)phenyl)thiophen-2-yl)thiophen-2-yl) acrylamide (TpSSA4)



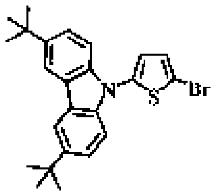
A mixture of aldehyde compound (0.30 g, 0.69 mmol) and cyanoacrylamide (0.06 g, 0.82 mmol) in ammonium acetate (0.26 g, 3.42 mmol) and acetic acid (30 ml). The solution was refluxed for overnight. After cooling the solution, water (100 ml) was added and the mixture was extracted with dichloromethane (50 ml x 2). The combined organic phases were washed water (50 ml x 2), and brine solution (100 ml), dried over anhydrous Na_2SO_4, filtered and the solvents were removed to dryness. Purification by column chromatographyl over silica gel eluting with of methylene chloride followed by recrystallization with a mixture of methylene chloride and methanol afforded a red solids (77 % yield). $C_{30}H_{21}N_3OS_2$; m.p. 218 °C; ^1H NMR (300 MHz, DMSO-d_6) : δ 8.36 (1H, s), 7.64 (1H, d, *J* = 4.2 Hz), 7.48 (2H, d , *J* = 1.8 Hz), 7.36 (1H, d, *J* = 3.9 Hz), 7.33-7.28 (4H, t, *J* = 1.8 Hz), 7.24 (1H, d, *J* = 3.9 Hz), 7.22 (1H, d, J = 3.9 Hz), 7.16-7.13 (4H, m), 7.10-7.08 (4H, m) ppm; ^{13}C NMR, (300 MHz, DMSO-d_6) : 162.46, 148.13, 147.27, 147.23, 146.64, 145.31, 139.11, 134.06, 133.79, 129.41, 127.54, 126.98, 126.62, 124.86, 123.96, 123.52, 123.33, 123.07, 117.51, 97.47, 77.45, 77.22, 77.02, 76.60 and 29.70.

3,6-di-*tert*-butyl-9*H*-carbazole (G1)



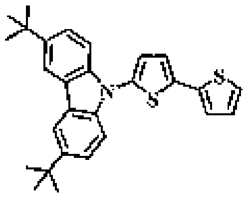
Carbazole (10 g, 59.80 mmol) and $ZnCl_2$ (24.45 g, 179.41 mmol) were dissolved in nitromethane (150 ml), then *t*-butyl chloride was slowly added to the mixture. The reaction mixture was stirred at room temperature under N_2 for 5 h. The reaction mixture was poured into water and extracted with CH_2Cl_2 (100 ml x 3). The combined organic phase was washed with water (100 ml), brine solution (100 ml), dried over sodium sulfate anhydrous, filtered and the solvent was remove in vacuum. The residue was purified by recrystallization with hexane, to give 3,6-di-*tert*-butylcarbazole (15.37 g, 92%) as white powder. $C_{20}H_{25}N$; m.p. 223-224 °C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.09 (2H, s), 7.85 (1H, s), 7.48 (2H, dd, *J* = 8.5 Hz, *J* = 1.6 Hz), 7.34 (2H, d, *J* = 8.5 Hz), and 1.47 (18H, s) ppm; FT-IR (KBr) 3411, 3059, 2959, 2903, 2864, 1628, 1577, 1492, 1466, 880, and 815 cm^{-1}.

3,6-di-*tert*-butyl-9-(5-bromothiophen-2-yl)-9*H*-carbazole (CS2)



To a mixture of CuI (0.01 g, 0.08 mmol), K_3PO_4 (0.08 g, 0.41 mmol), and **G1** (0.04 g, 0.16 mmol) in toluene (10 ml) were added 2,5-dibromothiophene (0.1 g, 0.41 mmol) and (+/-)-*trans*-1,2-diaminocyclohexane (0.009 g, 0.08 mmol). The reaction mixture was stirred at 110 °C under nitrogen. After 24 h, water (100 ml) was added until the two phases mixed. The solution was extracted with CH_2Cl_2 (100 ml x 3), washed with water (100 ml), brine solution (100 ml) and dried with Na_2SO_4, filtered, and the solvents removed to dryness. After the solvent was evaporated. The crude product was purified by column chromatography on silica gel with hexane as eluent to yield **CT2** (53 % yield). $C_{24}H_{26}BrNS$; m.p. 146 °C; ^{1}H NMR (300 MHz, CDCl) : δ 8.10 (2H, s), 7.50 (2H, dd, *J* = 1.79 Hz, *J* = 7.17 Hz), 7.34 (2H, d, *J* = 8.61 Hz), 7.15 (1H, d, *J* = 3.91 Hz), 6.95 (1H, d, *J* = 3.93 Hz) ppm; ^{13}C NMR, (300 MHz, CDCl) : 143.94, 140.13, 128.90, 125.08, 124.03, 123.59, 116.29, 109.49, 77.45, 77.02, 76.60, 34.79 and 31.99.

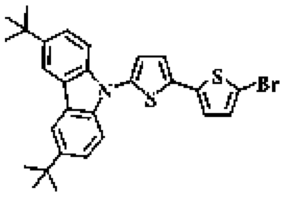
3,6-di-*tert*-butyl-9-(5-(thiophen-2-yl)thiophen-2-yl)-9*H*-carbazole (CSS3)



To a stirred solution of **CTT2** (1.86 g, 4.23 mmol) and $Pd(Phh_3)_4$ (0.09 g, 0.08 mmol) in tetrahydrofuran (30 ml) were added 2-thiopheneboronic acid (0.59 g, 4.65 mmol), and an aqueous

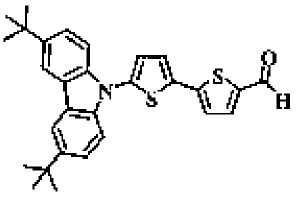
Na_2CO_3 solution (8.97 g, 84.65 mmol). The mixture was refluxed for 48 h. After cooling the solution, H_2O (50 ml) was added to the solution and extracted by dichloromrthane (50 ml x 3). The organic layer was separated and dried in Na_2SO_4. The solvent was removed in vacuo. Purification by column chromatography over silicagel eluting with n-hexane followed by recrystallization with a mixture of methyilene chloride and methanol afforced white solids (88 % yield). $C_{28}H_{29}NS_2$; m.p. 156 °C; ^{1}H NMR (300 MHz, CDCl) : δ 8.21 (2H, s), 7.59 (4H, m), 7.30-7.25 (3H, m), 7.13-7.07 (2H, m) ppm; ^{13}C NMR, (300 MHz, CDCl) : 143.74, 140.19, 137.99, 135.22, 127.91, 124.78, 124.71, 123.96, 123.88, 123.59, 122.31, 116.24, 109.69, 77.445, 77.03, 76.60, 34.79, 32.01 and 29.72.

3,6-di-*tert*-butyl-9-(5-(5-bromothiophen-2-yl)thiophen-2-yl)-9*H*-carbazole (CSS4)



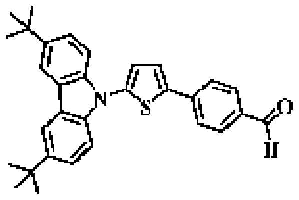
In a flask, covered with aluminum foil, stirred solution CSS4 (1.56 g, 3.53 mmol) in THF (15 ml) was added NBS (0.65 g, 3.70 mmol), was added in small portions. Water (50 ml) was added and the mixture was extracted with methylene chloride (50 ml x 3). The organic layer was separated and dried in Na_2SO_4. The solvent was removed in vacuum. Purification by column chromatographyl over silica gel eluting with a n-hexane afforded white solid (yield 100%). $C_{28}H_{28}BrNS_2$; m.p. 164 °C; ^{1}H NMR (300 MHz, CDCl) : δ 8.11 (2H, s), 7.51 (2H, dd, J = 1.2 Hz), 7.42 (2H, d, J = 8.7 Hz), 7.15 (1H, d, J = 3.9 Hz), 7.08 (2H, d, J = 3.6 Hz), 7.01 (1H, d, J = 3.6 Hz), 6.95 (1H, d, J = 3.6 Hz) ppm; ^{13}C NMR, (300 MHz, CDCl) : 143.86, 140.07, 138.68, 134.04, 130.73, 124.72, 123.99, 123.95, 123.64, 122.64, 116.28, 111.31, 109.64, 77.44, 77.02, 76.60, 34.79, 31.99 and 29.57.

5-(5-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)thiophen-2-yl)thiophene-2-carbaldehyde (CSS5)



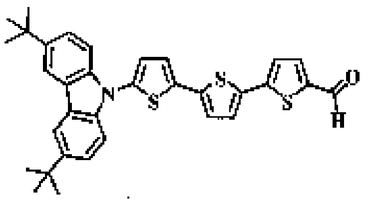
To a stirred solution of bromo compound (0.8 g, 1.81 mmol) and Pd(PPh$_3$)$_4$ (0.002 g, 0.002 mmol) in tetrahydrofuran (15 ml) were added 5-formyl-2-thiopheneboronic acid (0.28 g, 1.81 mmol), and an aqueous Na$_2$CO$_3$ solution (1.92 g, 18.16 mmol). The mixture was refluxed for 48 h. After cooling the solution, H$_2$O (50 ml) was added to the solution and extracted by dichloromethane (50 ml x 3). The organic layer was separated and dried in Na$_2$SO$_4$. The solvent was removed in vacuum. Purification by column chromatographyl over silica gel eluting with a mixture of methylene chloride and n-hexane (1:4) followed by recrystallization with a mixture of methylene chloride and methanol afforded orange solids (yield 60 %). C$_{28}$H$_{29}$NOS$_2$; m.p. 186 ^{o}C; ^{1}H NMR (300 MHz, CDCl) : δ 9.90 (1H, s), 8.10 (2H, s), 7.71 (1H, d, *J* = 3.9 Hz), 7.51 (2H, m), 7.48 (2H, d, *J* = 8.7 Hz), 7.42 (1H, d, *J* – 3.9 Hz), 7.27 (1H, d, *J* = 6.0 Hz), 7.15 (1H, d, *J* = 3.9 Hz) ppm; ^{13}C NMR, (300 MHz, CDCl) : 146.86, 144.18, 141.87, 140.93, 139.78, 137.31, 133.17, 125.04, 124.66, 124.18, 124.11, 123.82, 116.38, 109.65, 77.45, 77.03, 76.60, 334.81 and 31.97.

4-(5-(3,6-di-*tert*-butyl-*9H*-carbazol-9-yl)thiophen-2-yl)benzaldehyde (CSP8)



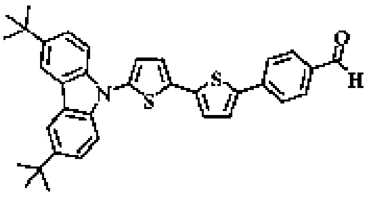
To a stirred solution of **CS2** (0.50 g, 1.13 mmol) and Pd(PPh$_3$)$_4$ (0.01 g, 0.01 mmol) in tetrafuran (30 ml) were added 4-formylphemylboronic acid (0.11 g, 0.76 mmol), and an aqueous Na$_2$CO$_3$ solution (1.53 g, 14.47 mmol). The mixture was refluxed for 48 h. After cooling the solution, H$_2$O (50 ml) was added to the solution and extracted by dichloromethane (50 ml x 3). The organic layer was separated and dried in Na$_2$SO$_4$. The solvent was removed in vacuo. Purification by column chromatographyl over silica gel eluting with a n-hexane followed by recrystallization with a mixture of methylene chloride and methanol afforded yellow solids (yield 89%). C$_{31}$H$_{31}$NOS; m.p. 214 ^{o}C; ^{1}H NMR (300 MHz, CDCl) : δ 8.13 (2H, s), 7.95 (2H, d, *J* = 8.1 Hz), 7.81 (2H, d, *J* = 8.1 Hz), 7.55-7.53 (4H, m), 7.28 (1H, d, *J* = 0.9 Hz), 7.22 (1H, d, *J* – 3.9 Hz) ppm.

5-(5-(5-(3,6-di-*tert*-butyl-*9H*-carbazol-9-yl)thiophen-2-yl)thiophen-2-yl) thiophene-2-carbaldehyde (CSSS6)



To a stirred solution of bromo compound (0.20 g, 0.36 mmol) and Pd(PPh$_3$)$_4$ (0.004 g, 0.004 mmol) in tetrahydrofuran (10 ml) were added 5-formyl-2-thiopheneboronic acid (0.06 g, 0.43 mmol), and an aqueous Na_2CO_3 solution (0.77 g, 7.32 mmol). The mixture was refluxed for 48 h. After cooling the solution, H_2O (50 ml) was added to the solution and extracted by dichloromethane (50 ml x 3). The organic layer was separated and dried in Na_2SO_4. The solvent was removed in vacuum. Purification by column chromatographyl over silica gel eluting with a mixture of methylene chloride and n-hexane (1:5) followed by recrystallization with a mixture of methylene chloride and methanol afforded orange solids (yield 72%). $C_{33}H_{31}NOS_3$; m.p. 192 °C. ; ^{1}H NMR (300 MHz, CDCl) : δ 8.97 (1H,s), 8.12 (2H, s), 7.68 (2H, d, J =0.013 Hz), 7.53-7.46 (4H, m), 7.31-7.26 (3H, m) and 7.18-7.11 (2H, m). ^{13}C NMR, (300 MHz, CDCl): 182.41, 146.65, 143.97, 139.98, 139.11, 138.88, 137.33, 134.80, 133.91, 126.96, 125.98, 124.71, 124.19, 124.04, 123.77, 123.70, 123.16, 116.32, 109.66, 77.45, 77.23, 77.02, 76.60, 34.80 and 31.99.

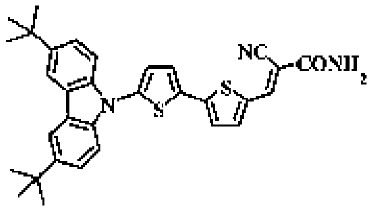
4-(5-(5-(3,6-di-*tert*-butyl-*9H*-carbazol-9-yl)thiophen-2-yl)thiophen-2-yl) benzaldehyde (CSSP7)



To a stirred solution of CSS4 (0.40 g, 0.72 mmol) and Pd(PPh$_3$)$_4$ (0.008 g, 0.008 mmol) in tetrafuran (15 ml) were added 4-formylphemylboronic acid (0.11 g, 0.76 mmol), and an aqueous Na_2CO_3 solution (1.53 g, 14.48 mmol). The mixture was refluxed for 48 h. After cooling the solution, H_2O (50 ml) was added to the solution and extracted by dichloromethane (50 ml x 3). The organic layer was separated and dried in Na_2SO_4. The solvent was removed in vacuo.

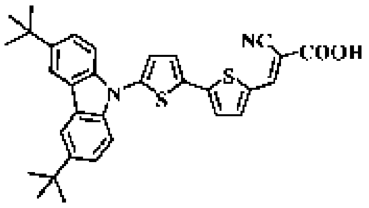
Purification by column chromatographyl over silica gel eluting with a n-hexane followed by recrystallization with a mixture of methylene chloride and methanol afforded yellow solids (yield 89 %). $C_{31}H_{31}NOS$; m.p. 218 °C; ^1H NMR (300 MHz, CDCl) : δ 10.03 (1H, s), 8.13 (2H, s), 7.93 (2H, d, *J* = 8.4 Hz), 7.79 (2H, d, *J* = 8.4 Hz), 7.52-7.51 (4H, m), 7.44 (1H, d, *J* = 3.9 Hz), 7.30 (1H, d, *J* = 8.4 Hz), 7.24 (1H, d, *J* = 3.9 Hz), 7.14 (1H, d, *J* = 3.9 Hz) ppm; ^{13}C NMR, (300 MHz, CDCl) : 143.92, 141.45, 140.04, 139.63, 138.77, 135.17, 134.45, 130.54, 125.90, 125.71, 124.94, 124.76, 124.02, 123.57, 122.86, 116.31, 109.67, 77.45, 77.23, 77.02, 76.60, 34.80 and 31.99.

(*E*)-3-(5-(5-(3,6-di-*tert*-butyl-*9H*-carbazol-9-yl)thiophen-2-yl)thiophen-2-yl)-2-cyanoacrylamide (CSSA9)



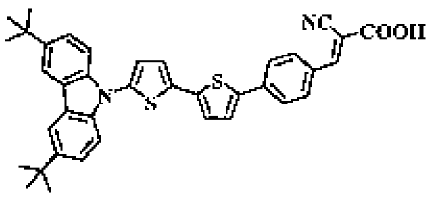
A mixture **CSS5** (0.20 g, 0.42 mmol) and cyanoacrylamide (0.04 g, 0.51 mmol) in ammonium acetate (0.16 g, 2.14 mmol) and acetic acid (10 ml). The solution was refluxed for overnight. After cooling the solution, water (100 ml) was added and the mixture was extracted with dichloromethane (50 ml x 2). The combined organic phases were washed water (50 ml x 2), and brine solution (100 ml), dried over anhydrous Na_2SO_4, filtered and the solvents were removed to dryness. Purification by column chromatographyl over silica gel eluting with a mixture of methylene chloride and n-hexane (1:2) followed by recrystallization with a mixture of methylene chloride and methanol afforded red solids (yield 78%). $C_{32}H_{31}N_3OS_2$; m.p. 212 °C; ^1H NMR (300 MHz, CDCl) : δ 8.40 (1H, s), 8.13 (2H, s), 7.67 (1H, d, *J* = 3.9 Hz), 7.39-7.53 (4H, t, *J* = 1.2 Hz), 7.43 (1H, d, *J* = 3.9 Hz), 7.2 (1H, d, *J* = 3.9 Hz), 7.18 (1H, d, *J* = 3.9 Hz) ppm; ^{13}C NMR, (300 MHz, CDCl) : 162.43, 145.28, 144.25, 141.22, 139.67, 138.88, 134.60, 132.72, 125.30, 124.51, 124.37, 123.87, 117.36, 116.39, 109.70, 98.28, 77.47, 77.05, 76.62, 34.82, 31.97 and 29.71.

(*E*)-3-(5-(5-(3,6-di-*tert*-butyl-*9H*-carbazol-9-yl)thiophen-2-yl)thiophen-2-yl)-2-cyanoacrylic acid (CSSA10)



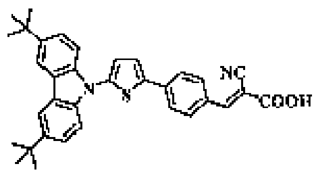
A mixture of **CSS5** (0.25 g, 0.53 mmol) and cyanoacetic acid (0.06 g, 0.79 mmol) was vacuum-dried and chloroform (25 ml) and piperidine (0.13 ml, 1.59 mmol) were added. The solution was refluxed for overnight. After cooling the solution, the organic layer was removed in vacuo. Purification by column chromatographyl over silica gel eluting with a mixture of methanol and methylene chloride (1:10) followed by recrystallization with a mixture of methylene chloride and methanol afforded a red solids (yield 97%). $C_{32}H_{30}N_2O_2S_2$; m.p. 220 °C; ^{1}H NMR (300 MHz, DMSO-d_6) : δ 8.18-8.06 (4H, m), 7.61 (1H, d, J = 0.01 Hz), 7.79-7.38 (5H, m), 7.26 (1H, d, J = 0.01 Hz) ppm; ^{13}C NMR, (300 MHz, DMSO-d_6) : 143.65, 139.21, 137.09, 135.68, 132.81, 123.73, 123.49, 118.73, 115.93, 109.37, 105.22, 77.83, 77.40, 76.97, 40.13, 39.85, 39.58, 39.29, 34.46, 31.71, 31.66, 29.27 and 13.89.

(*E*)-3-(4-(5-(5-(3,6-di-*tert*-butyl-*9H*-carbazol-9-yl)thiophen-2-yl)thiophen-2-yl) phenyl)-2-cyanoacrylic acid (CSSPA13)



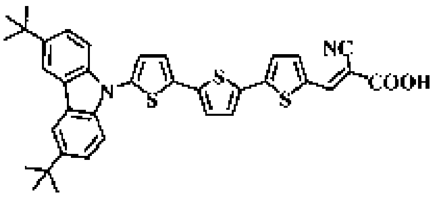
A mixture of **CSSP7** (0.35 g, 0.65 mmol) and cyanoacetic acid (0.11 g, 1.30 mmol) was vacuum-dried and chloroform (15 ml) and piperidine (0.16 ml, 1.95 mmol) were added. The solution was refluxed for overnight. After cooling the solution, the organic layer was removed in vacuo. Purification by column chromatographyl over silica gel eluting with a mixture of methanol and methylene chloride (1:20) followed by recrystallization with a mixture of methylene chloride and methanol afforded a red solids (yield 39%). $C_{38}H_{34}N_2O_2S_2$; m.p. 238 °C; ^{1}H NMR (300 MHz, DMSO-d_6) : δ 8.13 (1H, s), 7.95 (2H, s), 7.78 (1H, d, J = 6.9 Hz), 7.45-7.34 (5H, m), 7.29 (3H, m), 7.21 (1H, s), 7.07 (2H, d, J = 13.80 Hz), 6.92 (1H, s) ppm; ^{13}C NMR, (300 MHz, DMSO-d_6) : 151.35, 143.67, 141.77,139.74, 138.23, 136.59, 134.29, 131.51, 130.85, 128.68, 125.25, 125.15, 124.69, 124.39, 123.86, 123.46, 122.48, 118.27, 116.06, 109.54, 77.63, 77.41, 77.21, 76.78, 6-.03, 40.85, 40.57, 40.29, 40.01, 39.74, 39.46.39.18, 38.64, 34.59, 31.82, 30.26, 28.81, 23.66, 22.84, 13.94 and 10.87.

(*E*)-3-(4-(5-(3,6-di-*tert*-butyl-*9H*-carbazol-9-yl)thiophen-2-yl)phenyl)-2-cyano acrylic acid (CSPA12)



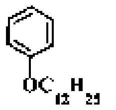
A mixture of **CSP8** (0.30 g, 0.77 mmol) and cyanoacetic acid (0.13 g, 1.54 mmol) was vacuum-dried and chloroform (15 ml) and piperidine (0.19 ml, 2.31 mmol) were added. The solution was refluxed for overnight. After cooling the solution, the organic layer was removed in vacuo. Purification by column chromatographyl over silica gel eluting with a mixture of methylene chloride and hexane (1:10) followed by recrystallization with a mixture of methylene chloride and methanol afforded a orang solid (yield 52%). $C_{34}H_{32}N_2O_2S$; m.p. 250 °C; ^1H NMR (300 MHz, DMSO-d_6): δ 8.12 (1H, s), 7.86 (2H, s), 7.71 (2H, s), 7.34 (2H, d, *J* = 7.5 Hz), 7.16-7.10 (5H, m), 6.77 (1H, s) ppm; ^{13}C NMR, (300 MHz, DMSO-d_6): 168.27, 150.94, 143.64, 139.71, 139.60, 139.54, 136.65, 131.65, 131.10, 125.26, 124.51, 123.82, 123.41, 123.17, 118.19, 116.01, 109.51, 106.58, 77.77, 77.54, 77.34, 76.91, 40.74, 40.47, 40.19, 39.91, 39.63, 39.35, 39.07, 34.53 and 31.78.

(*E*)-3-(5-(5-(5-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)thiophen-2-yl)thiophen-2-yl) thiophen-2-yl)-2-cyanoacrylic acid (CSSSA11)



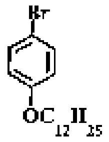
A mixture of CSSS6 (0.30 g, 0.54 mmol) and cyanoacetic acid (0.09 g, 1.08 mmol) was vacuum-dried and chloroform (15 ml) and piperidine (0.13 ml, 1.62 mmol) were added. The solution was refluxed for overnight. After cooling the solution, the organic layer was removed in vacuo. Purification by column chromatographyl over silica gel eluting with a mixture of methanol and methylene chloride (1:10) followed by recrystallization with a mixture of methylene chloride and methanol afforded a red solids (yield 82%). $C_{36}H_{32}N_2O_2S_3$; m.p. 249 °C; ^1H NMR (300 MHz, DMSO-d_6): δ 8.33 (1H, s), 7.84 (2H, s), 7.72-7.46 (2H, m), 7.01 (4H, m), 7.60-7.49 (5H, m) ppm.

1-(dodecyloxy)benzene (PO)



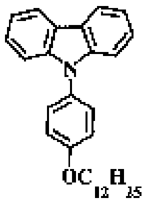
To a solution of phenol (1.00 g, 10.62 mmol) in DMF 10 ml) was added followed by KOH (5.10 g). 1-Bromododecane (10.00 g, 41.86 mmol) was added. The reaction mixture was stirred at room temperature for 48 h. Water (100 ml) was added and the mixture was extracted with methylene chloride (50 ml x 3). The 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, filtered and the solvents were removed to dryness. Purification by column chromatography over silica gel eluting with hexane gave a pale white viscous oil (75%). $C_{18}H_{30}O$; ^{1}H NMR (300 MHz, CDCl): δ 7.31-7.26 (2H, m), 6.96-6.89 (3H, m), 3.98-3.94 (2H, m), 1.83-1.28 (2H, m), 1.56-1.28 (18H, m), 0.91-0.87 (3H, m) ppm. ^{13}C NMR, (300 MHz, CDCl): 7.309, 7.284, 7.259, 6.958, 6.933, 6.920, 6.893, 3.981, 3.959, 3.937, 3.437, 3.415, 3.392, 1.910, 1.888, 1.864, 1.839, 1.815, 1.792, 1.767, 1.745, 1.572, 1.456, 1.436, 1.384, 1.279, 0.917, 0.897, 0.875 and 0.016.

1-bromo-4-(dodecyloxy)benzene (PO1)



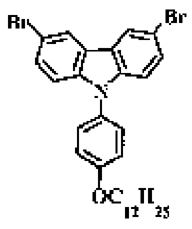
In a flask, covered with aluminum foil, stirred solution of **PO** (3.00 g, 11.43 mmol), amonium acetare (0.09 g, 1.18 mmol) in acetonenitrile (50 ml) was added NBS (2.22 g, 11.43 mmol), was added in small portions. The reaction mixture was poured into ice-cold water. The mixture was allowed to warm to room temperature overnight. Water (15 ml) was added and the mixture was extracted with methylene chloride (20 ml x 3). The organic layer was separated and dried in Na_2SO_4. The solvent was removed in vacuum. The pure product was obtained by column chromatography over silica gel eluting with hexane as an eluent a white pearl solid (yield 100 %). $C_{18}H_{29}BrO$; m.p. 37 °C; ^{1}H NMR (300 MHz, CDCl): δ 7.35 (2H, d, J = 0.03 Hz), 6.67 (2H, d, J = 0.03 Hz), 3.93-3.89 (2H, m), 1.85-1.72 (2H, m), 1.44-1.27 (18H, m), 0.90-0.86 (3H, m) ppm; ^{13}C NMR, (300 MHz, CDCl): 158.27, 132.18, 116.31, 112.54, 77.43, 77.01, 76.59, 68.28, 31.92, 29.65, 29.63, 29.58, 29.56, 29.36, 29.35, 29.17, 25.99, 22.69 and 14.11.

9-(4-(dodecyloxy)phenyl)-9H-carbazole (CPO2)



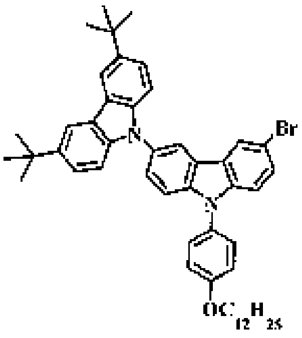
To a mixture of CuI (0.27 g, 1.46 mmol), K_3PO_4 (1.55 g, 7.32 mmol), and carbazole (1.00 g, 2.92 mmol) in toluene (70 mL) were added **PO1** (0.58 g, 3.51 mmol) and (+/-)-*trans*-1,2-diaminocyclohexane (0.16 g, 1.46 mmol). The reaction mixture was stirred at 110 °C under nitrogen. After 24 h, water (100 ml) was added until the two phases mixed. The solution was extracted with CH_2Cl_2 (100 ml x 3), washed with water (100 ml), brine solution (100 ml) and dried with Na_2SO_4, filtered, and the solvents removed to dryness. Purification by column chromatographyl over silica gel eluting with a hexane followed by recrystallization with a mixture of methylene chloride and methanol afforded a white solids (yield 95 %). $C_{30}H_{37}NO$; m.p. 40 °C; ^{1}H NMR (300 MHz, CDCl): δ 8.15 (2H, d, J = 7.8 Hz), 7.46-7.26 (8H, m), 7.11 (2H, d, J = 8.7 Hz), 3.98-3.94 (2H, m), 1.83-1.28 (2H, m), 1.56-1.28 (18H, m), 0.91-0.87 (3H, m) ppm.

3,6-dibromo-9-(4-(dodecyloxy)phenyl)-9H-carbazole (CP3)



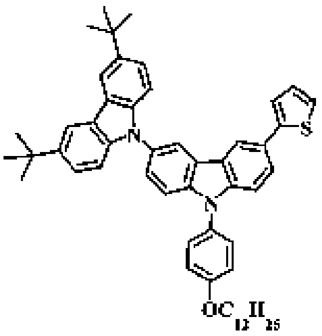
In a flask, covered with aluminum foil, stirred solution of **CPO2** (0.05 g, 0.11 mmol) in THF (10 ml) was added NBS (0.04 g, 0.24 mmol), was added in small portions. Water (15 ml) was added and the mixture was extracted with methylene chloride (20 ml x 3). The organic layer was separated and dried in Na_2SO_4. The solvent was removed in vacuum. The pure product was obtained by column chromatography over silica gel eluting with hexane as an eluent a white solid (yield 71 %). $C_{30}H_{35}Br_2NO$; m.p. 49 °C; ^{1}H NMR (300 MHz, CDCl): δ 8.18 (2H, d, J = 1.5 Hz), 7.49 (2H, dd, J = 1.8 Hz), 7.36 (2H, d, J = 8.7 Hz), 7.17 (2H, d, J = 8.7 Hz), 7.09 (2H, d, J = 8.7 Hz), 3.98-3.94 (2H, m), 1.83-1.28 (2H, m), 1.56-1.28 (18H, m), 0.91-0.87 (3H, m) ppm; ^{13}C NMR, (300 MHz, CDCl): 158.93, 158.70, 141.73, 140.38, 140.06, 129.53, 129.28, 129.02, 128.49, 128.35, 126.56, 124.82, 123.68, 123.14, 122.96, 122.03, 120.41, 120.03, 115.78, 112.78, 112.37, 111.48, 111.22, 109.97, 77.44, 77.22, 77.02, 76.59, 68.44, 31.93, 29.69, 29.66, 29.63, 29.42, 29.37, 29.29, 26.09, 22.70 and 14.13.

3,6-di-*tert*-butyl-9-(3-bromo-9-(4-(dodecyloxy)phenyl)-*9H*-carbazol-6-yl)-*9H*-carbazole (G1C4)



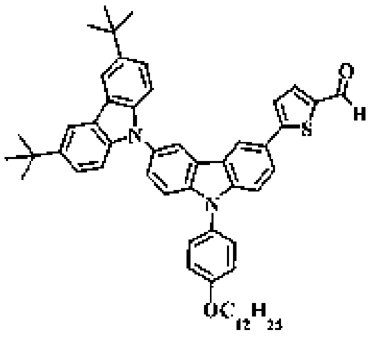
To a mixture of CuI (0.02 g, 0.08 mmol), K_3PO_4 (0.09 g, 0.42 mmol), and **CP3** (0.10 g, 0.17 mmol) in toluene (15 ml) were added G1 (0.04 g, 0.17) and (+/-)-*trans*-1,2-diaminocyclohexane (0.01 g, 0.08 mmol). The reaction mixture was stirred at 110 °C under nitrogen. After 24 h, water (100 ml) was added until the two phases mixed. The solution was extracted with CH_2Cl_2 (100 ml x 3), washed with water (100 ml), brine solution (100 ml) and dried with Na_2SO_4, filtered, and the solvents removed to dryness. After the solvent was evaporated. The pure product was obtained by column chromatography over silica gel eluting with with a mixture of methyilene chloride and n-hexane (1:30) as an eluent a white solid (yield 36 %). $C_{50}H_{59}BrN_2O$; m.p. 160 °C; ^1H NMR (300 MHz, CDCl): δ 8.24-8.07 (2H, m), 7.57-7.38 (6H, m), 7.34-7.08 (8H, m), 3.98-3.94 (2H, m), 1.83-1.28 (2H, m), 1.56-1.28 (18H, m), 0.91-0.87 (3H, m) ppm; ^{13}C NMR, (300 MHz, CDCl): 158.95, 142.57, 140.74, 140.58, 140.16, 130.62, 129.29, 129.16, 128.47, 125.96, 124.46, 123.55, 123.21, 123.13, 122.90, 119.12, 116.22, 115.84, 112.75, 111.58, 110.99, 109.98, 109.11, 77.44, 77.01, 76.59, 68.50, 34.75, 32.70, 31.94, 29.69, 29.66, 29.63, 29.43, 29.37, 29.29, 26.10, 22.70 and 14.12.

3,6-di-*tert*-butyl-9-(9-(4-(dodecyloxy)phenyl)-3-(thiophen-2-yl)-*9H*-carbazol-6-yl)-*9H*-carbazole (G1CS5)



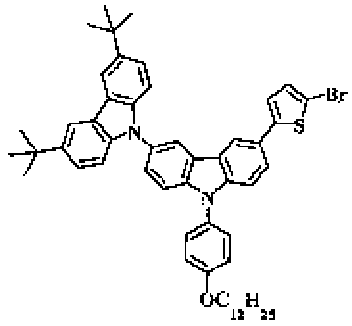
To a stirred solution of **G1C4** (1.50 g, 1.91 mmol) and Pd(Phh$_3$)$_4$ (0.04g, 0.04 mmol) in tetrahydrofuran (20 ml) were added 2-thiopheneboronic acid (0.26 g, 2.1 mmol), and an aqueous Na$_2$CO$_3$ solution (4.05 g, 38.26 mmol). The mixture was refluxed for 48 h. After cooling the solution, H$_2$O (50 ml) was added to the solution and extracted by dichloromrthane (50 ml x 3). The organic layer was separated and dried in Na$_2$SO$_4$. The solvent was removed in vacuo. Purification by column chromatography over silicagel eluting with a mixture of methyilene chloride and n-hexane (1:30) by recrystallization with a mixture of methylene chloride and methanol afforded white solids (yield 73 %). C$_{54}$H$_{62}$N$_2$OS; m.p. 104 °C; ^{1}H NMR (300 MHz, CDCl): δ 8.31 (2H, dd, *J* = 1.5 Hz, *J* = 1.8 Hz), 8.20 (2H, d, *J* = 1.5 Hz), 7.72 (1H, dd, *J* = 1.5 Hz), 7.58-7.47 (6H, m), 7.40-7.34 (4H, m), 7.26 (1H, d, J = 3.0 Hz), 7.18-7.09 (3H, m), 4.11-4.07 (2H, m), 1.90-1.85 (2H, m), 1.56-1.29 (18H, m), 0.92-0.87 (3H, m) ppm; ^{13}C NMR, (300 MHz, CDCl): 158.83, 145.37, 142.50, 141.55. 140.77, 140.25, 130.45, 129.60, 128.46, 128.03, 126.94, 125.58, 125.10, 123.96, 123.52, 123.24, 123.11, 122.32, 119.20, 117.91, 116.22, 115.79, 110.90, 110.43, 109.18, 77.44, 77.02, 76.60, 68.49, 34.76, 32.09, 31.94, 29.70, 29.67, 29.64, 29.44, 29.38, 29.32, 26.12, 22.71 and 14.13.

5-(3-(3,6-di-*tert*-butyl-*9H*-carbazol-9-yl)-9-(4-(dodecyloxy)phenyl)-*9H*-carbazol-6-yl) thiophene-2-carbaldehyde (G6CS1)



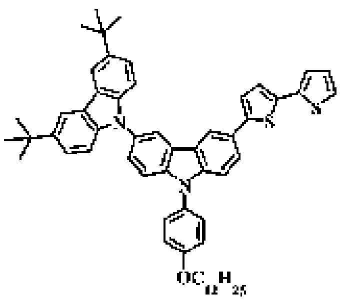
To a stirred solution of bromo compound (0.50 g, 0.63 mmol) and Pd(PPh$_3$)$_4$ (0.007 g, 0.007 mmol) in tetrahydrofuran (20 ml) were added 5-formyl-2-thiopheneboronic acid (0.10 g, 0.66 mmol), and an aqueous Na$_2$CO$_3$ solution (1.35 g, 12.75 mmol). The mixture was refluxed for 48 h. After cooling the solution, H$_2$O (50 ml) was added to the solution and extracted by dichloromethane (50 ml x 3). The organic layer was separated and dried in Na$_2$SO$_4$. The solvent was removed in vacuum. Purification by column chromatographyl over silica gel eluting with a mixture of methylene chloride and n-hexane (1:30) followed by recrystallization with a mixture of methylene chloride and methanol afforded orange solids (yield 78%).

3,6-di-*tert*-butyl-9-(3-(5-bromothiophen-2-yl)-9-(4-(dodecyloxy)phenyl)-*9H*-carbazol-6-yl)-*9H*-carbazole (G1CS7)



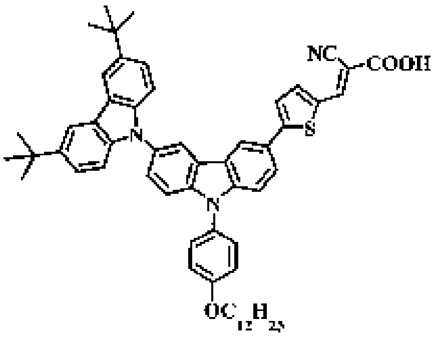
In a flask, covered with aluminum foil, stirred solution **G1CS5** (0.15 g, 0.19 mmol) in THF (10 ml) was added NBS (0.03 g, 0.20 mmol), was added in small portions. Water (50 ml) was added and the mixture was extracted with methylene chloride (50 ml x 3). The organic layer was separated and dried in Na_2SO_4. The solvent was removed in vacuum. Purification by column chromatographyl over silica gel eluting with with a mixture of methyilene chloride and n-hexane (1:30) followed by recrystallization with a mixture of methylene chloride and methanol afforded white solid (yield 98%). $C_{50}H_{59}BrN_2O$; m.p. 118 °C; ^1H NMR (300 MHz, CDCl): δ 8.28 (1H, d, J = 1.5 Hz), 8.21 (3H, dd, J = 1.2 Hz, J = 1.5 Hz), 7.01 (1H, dd, J = 1.5 Hz, J = 1.8 Hz), 7.56-7.48 (6H, m), 7.36 (3H, dd, J = 3.3 Hz), 7.16 (2H, d, J = 8.7 Hz), 7.06 (2H, dd, J = 3.9 Hz, J = 3.6 Hz), 4.11-4.07 (2H, m), 1.90-1.85 (2H, m), 1.56-1.29 (18H, m), 0.92-0.87 (3H, m) ppm; ^{13}C NMR, (300 MHz, CDCl): 158.89, 146.87, 142.55, 141.72, 140.80, 140.22, 130.85, 129.45, 128.45, 126.14, 125.72, 124.70, 123.83, 123.54, 123.28, 123.13, 122.41, 119.17, 117.68, 116.24, 115.82, 110.99, 110.57, 110.22, 109.15, 77.45, 11.03, 16,60, 68.50, 34.76, 32.09, 31.95, 29.70, 29.67, 29.64, 29.45, 29.38, 29.38, 29.31, 26.12, 22.72 and 14.14.

3,6-di-tert-butyl-9-(9-(4-(dodecyloxy)phenyl)-3-(5-(thiophen-2-yl)thiophen-2-yl)-9H-carbazol-6-yl)-9H-carbazole (G1CSS8)



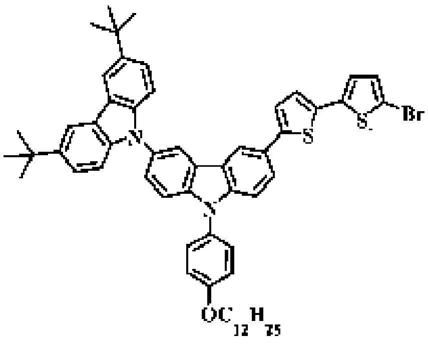
To a stirred solution of **G1C4** (0.93 g, 1.08 mmol) and $Pd(Phh_3)_4$ (0.02 g, 0.02 mmol) in tetrahydrofuran (10 ml) were added 2-thiopheneboronic acid (0.17 g, 1.13 mmol), and an aqueous Na_2CO_3 solution (2.29 g, 21.66 mmol). The mixture was refluxed for 48 h. After cooling the solution, H_2O (50 ml) was added to the solution and extracted by dichloromrthane (50 ml x 3). The organic layer was separated and dried in Na_2SO_4. The solvent was removed in vacuo. Purification by column chromatography over silicagel eluting with a mixture of methyilene chloride and n-hexane (1:30) followed by recrystallization with a mixture of methyilene chloride and methanol affored white solids (yield 86 %). $C_{58}H_{64}N_2OS_2$; m.p. 122 °C; ^1H NMR (300 MHz, CDCl): δ 8.30 (2H, s), 8.19 (2H, S), 7.71 (1H, d, J = 8.4 Hz), 7.54-7.47 (6H, m), 7.39-7.34 (4H, m), 7.24 (1H, d, J = 5.7 Hz), 7.21-7.15 (4H, s), 7.02 (1H, t, J = 4.2 Hz), 4.11-4.07 (2H, m), 1.90-1.85 (2H, m), 1.56-1.29 (18H, m), 0.92-0.87 (3H, m) ppm.

(*E*)-3-(5-(3-(3,6-di-*tert*-butyl-*9H*-carbazol-9-yl)-9-(4-(dodecyloxy)phenyl)-*9H*-carbazol-6-yl)thiophen-2-yl)-2-cyanoacrylic acid (G1CSA12)



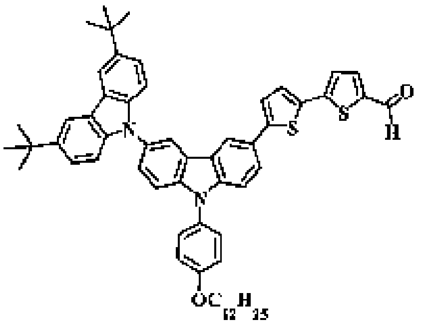
A mixture of **G1CS6** (1.00 g, 1.22 mmol) and cyanoacetic acid (0.21 g, 2.45 mmol) was vacuum-dried and chloroform (20 ml) and piperidine (0.31 ml, 3.68 mmol) were added. The solution was refluxed for overnight. After cooling the solution, the organic layer was removed in vacuo. Purification by column chromatographyl over silica gel eluting with a mixture of methanol and methylene chloride (1:10) followed by recrystallization with a mixture of methylene chloride and methanol afforded a red solids (yield 62%). $C_{58}H_{64}N_2OS_2$; m.p. 122 °C; ^1H NMR (300 MHz, DMSO-d_6): δ 8.23 (2H, s), 8.05 (4H, d, J – 0.03 Hz), 7.45-7.28 (6H, m), 7.17-7.10 (4H, m), 6.87 (3H, m), 3.86 (2H, s), 1.69 (2H, s), 1.34-1.17 (18H, m), 0.79-0.75 (3H, m) ppm; ^{13}C NMR, (300 MHz, DMSO-d_6): 158.51, 152,45, 144.45, 142.28, 141.62, 140.69, 139.66, 137.45, 134.77, 130.32, 128.66, 127.83, 125.16, 124.74, 123.43, 122.77, 118.66, 118.42, 117.86, 115.87, 110.81, 110.10, 108.98, 103.22, 77.92, 77.69, 77.49, 77.06, 68.14, 40.69, 40.41, 40.13, 39.85, 39.58, 39.30, 39.02, 34.48, 31.86, 31.84, 29.34, 29.15, 29.07, 29.00, 25.79, 22.41 and 13.95.

3,6-di-*tert*-butyl-9-(3-(5-(5-bromothiophen-2-yl)thiophen-2-yl)-9-(4-(dodecyloxy)phenyl)-*9H*-carbazol-6-yl)-*9H*-carbazole (G1CSS9)



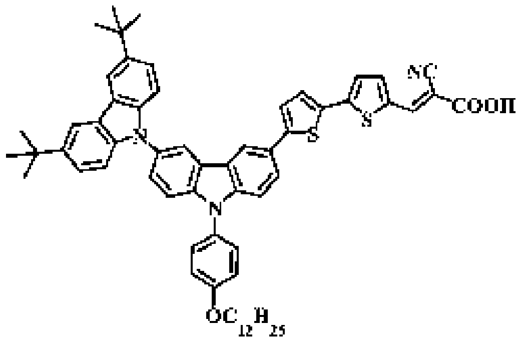
In a flask, covered with aluminum foil, stirred solution **G1CSS8** (0.65 g, 0.73 mmol) in (30 ml) was added NBS (0.13 g, 0.77 mmol), was added in small portions. The mixture was allowed to warm to room temperature for 3 h. Water (50 ml) was added and the mixture was extracted with methylene chloride (50 ml x 3). The organic layer was separated and dried in Na_2SO_4. The solvent was removed in vacuum. Purification by column chromatographyl over silica gel eluting with a mixture of methylene chloride and n-hexane (1:30) followed by recrystallization with a mixture of methylene chloride and methanol afforded green solid (yield 77 %). $C_{58}H_{63}BrN_2OS_2$; m.p. 130 $^{\circ}$C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.30 (2H, s), 8.19 (2H, d, J = 0.04 Hz), 7.67 (1H, d, J = 0.02 Hz), 7.59-7.48 (6H, m), 7.38 (3H, d, J = 0.02 Hz), 7.22-7.08 (4H, m), 6.66 (2H, d, J = 0.04 Hz), 4.08 (2H, s), 1.88 (2H, s), 1.56-1.31 (18 H, m), 0.91 (3H, s) ppm. ^{13}C NMR, (300 MHz, CDCl): 158.87, 144.73, 142.54, 141.68, 140.78, 140.20, 134.66, 130.65, 130.56, 129.46, 126.29, 125.68, 124.96, 124.71, 123.87, 123.54, 123.29, 123.12, 122.87,119.17, 117.65, 116.24, 115.80, 110.98, 110.55, 1.0.16, 77.45, 77.03, 76.60, 68.49, 34.76, 3209, 32.03, 31.95, 29.71, 29.68, 29.65, 29.45, 29.39, 29.31, 26.12, 22.71 and 14.15.

5-(5-(3-(3,6-di-*tert*-butyl-*9H*-carbazol-9-yl)-9-(4-(dodecyloxy)phenyl)-*9H*-carbazol-6-yl)thiophen-2-yl)thiophene-2-carbaldehyde (G1CSS10)



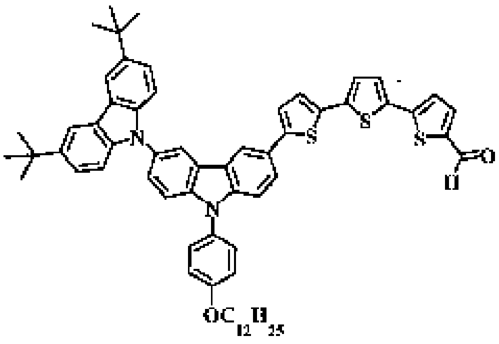
To a stirred solution of **G1CS7** (0.54 g, 0.63 mmol) and Pd(PPh$_3$)$_4$ (0.10 g, 0.66 mmol) in tetrahydroforan (10 ml) were added 5-formyl-2-thiophene boronic acid (0.10 g, 0.60 mmol), and an aqueous Na$_2$CO$_3$ solution (1.34 g, 12.69 mmol). The mixture was refluxed for 48 h. After cooling the solution, H$_2$O (50 ml) was added to the solution and extracted by dichloromethane (50 ml x 3). The organic layer was separated and dried in Na$_2$SO$_4$. The solvent was removed in vacuum. Purification by column chromatographyl over silica gel eluting with a mixture of methylene chloride methanol and (1:10) followed by recrystallization with a mixture of methylene chloride and methanol afforded orange solids (yield 75%). C$_{58}$H$_{63}$BrN$_2$OS$_2$; m.p. 130 ^{o}C; ^{1}H NMR (300 MHz, DMSO-d$_6$): δ 8.31 (2H, s), 8.19 (2H, d, *J* = 1.2 Hz), 7.72-7.67 (2H, m), 7.60-7.46 (6H, m), 7.41-7.34 (4H, m), 7.30 (2H, d, *J* = 3.9 Hz), 7.17 (2H, d, *J* = 8.7 Hz), 4.11-1.07 (2H, m), 1.90-1.85 (2H, m), 1.48-1.37 (18 H, m), 0.91-0.86 (3H, m) ppm. . ^{13}C NMR, (300 MHz, CDCl): 158.76, 144.68, 142.50, 141.54, 141.42, 140.48, 139.86, 137.68, 136.28, 136.03, 134.45, 130.31, 129.15, 128.46, 126.69, 126.04, 125.91, 124.79, 124.50, 123.97, 123.91, 123.35, 122.96, 119.58, 118.25, 116.57, 116.13, 111.26, 110.73, 109.49, 79.64, 79.40, 78.76, 70.32, 68.32, 54.88, 40.89, 40.62, 40.34, 40.06, 39.78, 39.50, 39.23, 34.86, 32.28, 31.80, 29.55, 29.50, 29.31, 29.22, 29.20, 26.03 and 22.88.

(*E*)-3-(5-(5-(3-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-9-(4-(dodecyloxy)phenyl)-9*H*-carbazol-6-yl)thiophen-2-yl)thiophen-2-yl)-2-cyanoacrylic acid (G1CSSA13)



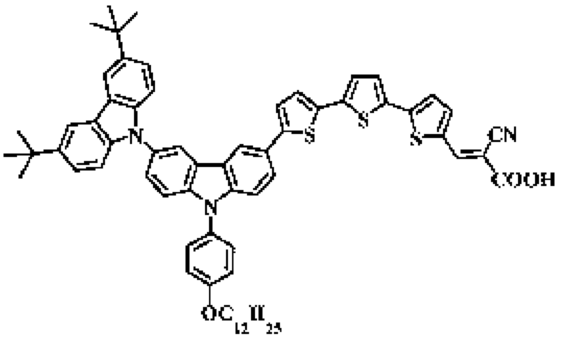
A mixture of **G1CS7** (0.25 g, 0.28 mmol) and cyanoacetic acid (0.04 g, 0.57 mmol) was vacuum-dried and chloroform (20 ml) and piperidine (0.07 ml, 0.86 mmol) were added. The solution was refluxed for overnight. After cooling the solution, the organic layer was removed in vacuo. Purification by column chromatographyl over silica gel eluting with a mixture of methanol and methylene chloride (1:5) followed by recrystallization with a mixture of methylene chloride and methanol afforded a red solids (yield 61%). $C_{62}H_{65}N_3O_3S_2$; m.p. 194 °C; ^1H NMR (300 MHz, DMSO-d_6): δ 8.78 (1H, s), 8.64 (1H, s), 8.29 (2H, s), 8.05 (1H, s), 7.81-7.78 (2H, m), 7.64-7.32 (12H, m), 7.21(2H, d, *J* = 0.02 Hz), 4.07 (2H, m), 1.76 (2H, m), 1.41-1.23 (18 H, m), 0.98-0.83 (3H, m) ppm.

5-(5-(5-(3-(3,6-di-*tert*-butyl-*9H*-carbazol-9-yl)-9-(4-(dodecyloxy)phenyl)-*9H*-carbazol-6-yl)thiophen-2-yl)thiophen-2-yl)thiophene-2-carbaldehyde (G1CSSS11)



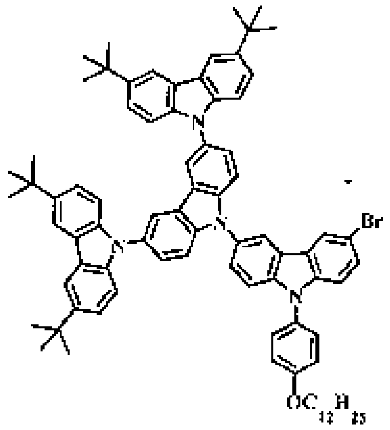
To a stirred solution of **G1CSS10** (0.48 g, 0.51 mmol) and $Pd(PPh_3)_4$ (0.005 g, 0.005 mmol) in tetrahydrofuran (20 ml) were added 5-formyl-2-thiopheneoronic acid (0.08 g, 0.54 mmol), and an aqueous Na_2CO_3 solution (1.09 g, 10.29 mmol). The mixture was refluxed for 48 h. After cooling the solution, H_2O (50 ml) was added to the solution and extracted by dichloromethane (50 ml x 3). The organic layer was separated and dried in Na_2SO_4. The solvent was removed in vacuum. Purification by column chromatographyl over silica gel eluting with a mixture of methanol and methylene chloride (1:3) followed by recrystallization with a mixture of methylene chloride and methanol afforded orange solids (yield 79%). $C_{63}H_{66}N_2O_2S_3$; m.p. 140 °C; ^1H NMR (300 MHz, DMSO-d_6): δ 9.85 (1H, s), 8.30 (2H, s), 8.19 (2H, s), 7.72-7.66 (2H, m), 7.55-7.46 (6H, m), 7.40-7.34 (3H, m), 7.28-7.23 (5H, m), 7.17-7.15 (2H, m), 4.11-1.07 (2H, m), 1.90-1.85 (2H, m), 1.58-1.48 (18 H, m), 0.89-0.86 (3H, m) ppm. ^{13}C NMR, (300 MHz, CDCl): 182.39, 158.89, 146.97, 145.43, 142.55, 141.75, 140.79, 140.18, 139.52, 137.39, 134.63, 134.07, 130.59, 129.42, 128.45, 127.04, 126.17, 125.71, 125.52, 124.69, 124.19, 123.93, 123.84, 123.53, 123.31, 123.12, 123.07, 119.05, 117.70, 116.24, 115.81, 111.01, 110.58, 109.14, 7.44, 77.22, 77.01, 76.59, 68.50, 34.76, 32.08, 31.94, 29.70, 29.66, 29.63, 29.44, 29.37, 29.30, 26.11, 22.71 and 14.13.

(*E*)-3-(5-(5-(5-(3-(3,6-di-*tert*-butyl-*9H*-carbazol-9-yl)-9-(4-(dodecyloxy)phenyl)-*9H*-carbazol-6-yl)thiophen-2-yl)thiophen-2-yl)thiophen-2-yl)-2-cyanoacrylic acid (G1CSSSA14)



A mixture of **G1CSSS11** (0.30 g, 0.31 mmol) and cyanoacetic acid (0.05 g, 0.62 mmol) was vacuum-dried and chloroform (20 ml) and piperidine (0.07 ml, 0.93 mmol) were added. The solution was refluxed for overnight. After cooling the solution, the organic layer was removed in vacuo. Purification by column chromatographyl over silica gel eluting with a mixture of methanol and methylene chloride (1:4) followed by recrystallization with a mixture of methylene chloride and methanol afforded a red solids (yield 65%). $C_{66}H_{67}N_3O_3S_3$; m.p. 210 °C.

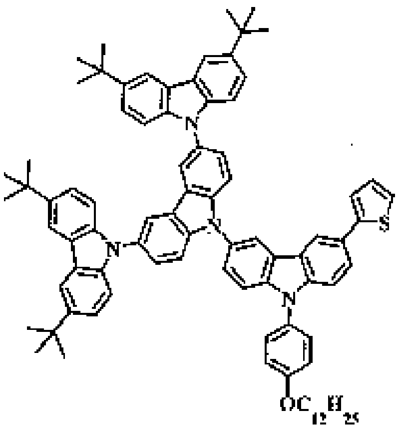
3,6-bis(3,6-di-*tert*-butyl-*9H*-carbazol-9-yl)-9-(3-bromo-9-(4-(dodecyloxy)phenyl)-9H-carbazol-6-yl)-*9H*-carbazole (G2C1)



To a mixture of CuI (0.05 g, 0.28 mmol), K_3PO_4 (0.30 g, 1.42 mmol), and **CP3** (1.96 g, 7.00 mmol) in toluene (60 ml) were added **G2** (0.41 g, 0.56 mmol) and (+/-)-*trans*-1,2-

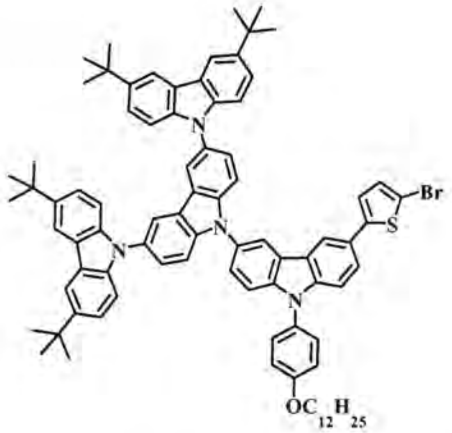
diaminocyclohexane (0.03 g, 0.28 mmol). The reaction mixture was stirred at 110 °C under nitrogen. After 24 h, water (100 ml) was added until the two phases mixed. The solution was extracted with CH_2Cl_2 (100 ml x 3), washed with water (100 ml), brine solution (100 ml) and dried with Na_2SO_4, filtered, and the solvents removed to dryness. After the solvent was evaporated. The pure product was obtained by column chromatography over silica gel eluting with a mixture of methylene chloride and hexane (1:10) as an eluent a white solid (yield 65%). $C_{82}H_{89}BrN_4O_3$; m.p. 140 °C; ^{1}H NMR (300 MHz, CDCl): δ 8.40 (2H, d, J = 1.2 Hz), 8.32 (2H, d, J = 1.5 Hz), 8.27 (2H, s), 8.17 (4H, s), 7.72 (1H, d, J = 1.5 Hz), 7.61 (5H, m), 7.54-7.46 (6H, m), 7.38-7.31 (4H, m), 7.27 (2H, d, J = 5.7 Hz), 7.18 (2H, d, J – 9 Hz), 4.12-4.07 (2H, m), 1.88 (2H, m), 1.55-1.26 (18H, m), 0.91-0.87 (3H, m) ppm; ^{13}C NMR, (300 MHz, CDCl): 159.12, 142.52, 141.39, 141.15, 140.93, 140.25, 130.69, 129.52, 129.10, 128.53, 126.00, 124.32, 123.74, 123.56, 123.36, 123.18, 123.12, 119.66, 119.35, 116.20, 115.93, 113.03, 111.77, 111.45, 111.14, 109.16, 77.45, 77.02, 76.60, 34.74, 32.07, 31.94, 29.70, 29.67, 29.64, 29.44, 29.38, 29.30, 26.11, 22.71 and 14..

3,6-bis(3,6-di-*tert*-butyl-*9H*-carbazol-9-yl)-9-(9-(4-(dodecyloxy)phenyl)-3-(thiophen-2-yl)-*9H*-carbazol-6-yl)-*9H*-carbazole (G2CS2)



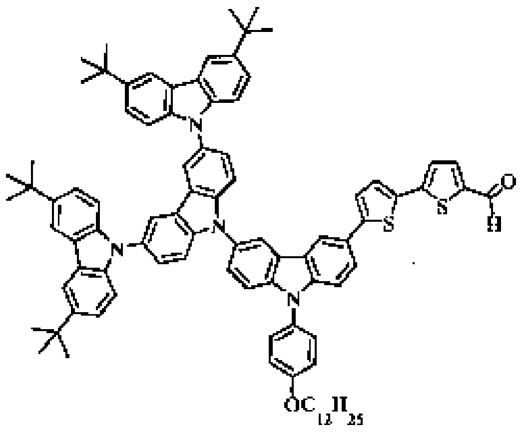
To a stirred solution of **G2S1** (0.58 g, 0.47 mmol) and $Pd(PPh_3)_4$ (0.005 g, 0.005 mmol) in tetrahydrofuran (20 ml) were added 2-thiopheneboronic acid (0.07 g, 0.56 mmol), and an aqueous Na_2CO_3 solution (1.00 g, 9.46 mmol). The mixture was refluxed for 48 h. After cooling the solution, H_2O (50 ml) was added to the solution and extracted by dichloromrthane (50 ml x 3). The organic layer was separated and dried in Na_2SO_4. The solvent was removed in vacuo. Purification by column chromatography over silicagel eluting with a mixture of methyilene chloride and n-hexane (1:10) followed by recrystallization with a mixture of methyilene chloride and methanol affored white solids (yield 93%). $C_{86}H_{92}N_4OS$; m.p. 140 °C; ^1H NMR (300 MHz, CDCl): δ 8.46 (2H, d, J = 0.07 Hz), 8.23 (6H, d, J = 0.10 Hz), 7.75 (2H, t, J = 0.03 Hz), 7.63-7.55 (7H, m), 7.50-7.37 (10H, m), 7.29-7.12 (4H, m), 4.13-4.09 (2H, m), 1.92-1.87 (2H, m), 1.30-1.27 (18H, m), 0.90 (3H, m) ppm; ^{13}C NMR, (300 MHz, CDCl): 158.99, 145.25, 142,50, 141.73, 141.51, 140.27, 130.62, 129.42, 149.34, 128.53, 128.09, 127.22, 125.998, 125.68, 125.44, 124.26, 124.09, 123.70, 123.56, 123.12, 122.47, 119.74, 119.34, 118.04, 116.20, 115.88, 111.34, 111.23, 110.62, 109.18, 77.45, 77.03, 76.61, 68.53, 34.75, 32.08, 31.95, 29.71, 29.68, 29,65, 29.46, 29.39, 29.33, 26.13, 22.72 and 14.15.

3,6-bis(3,6-di-*tert*-butyl-*9H*-carbazol-9-yl)-9-(3-(5-bromothiophen-2-yl)-9-(4-(dodecyloxy)phenyl)-*9H*-carbazol-6-yl)-*9H*-carbazole (G2CS3)



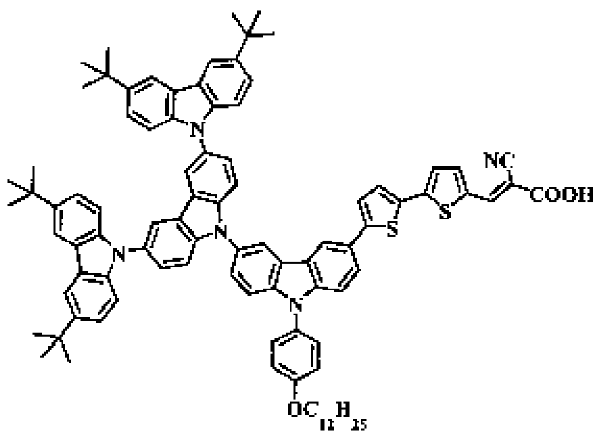
In a flask, covered with aluminum foil, stirred solution **G2CS2** (0.44 g, 0.36 mmol) in THF (15 ml) was added NBS (0.06 g, 0.37 mmol), was added in small portions. The mixture was allowed to warm to room temperature for 3 h. Water (50 ml) was added and the mixture was extracted with methylene chloride (50 ml x 3). The organic layer was separated and dried in Na_2SO_4. The solvent was removed in vacuum. Purification by column chromatographyl over silica gel eluting with a mixture of methylene chloride and n-hexane (2:10) followed by recrystallization with a mixture of methylene chloride and methanol afforded green solid (yield 88%). $C_{86}H_{91}BrN_4O_3S$; m.p. 210 °C.

5-(5-(3-(3,6-bis(3,6-di-*tert*-butyl-*9H*-carbazol-9-yl)-*9H*-carbazol-9-yl)-9-(4-(dodecyloxy)phenyl)-*9H*-carbazol-6-yl)thiophen-2-yl)thiophene-2-carbaldehyde (G2CSS4)



To a stirred solution of **G2CS3** (0.41 g, 0.31 mmol) and Pd(PPh$_3$)$_4$ (0.003 g, 0.003 mmol) in tetrahydrofuran (20 ml) were added 5-formyl-2-thiopheneoronic acid (0.05 g, 0.33 mmol), and an aqueous Na$_2$CO$_3$ solution (0.67 g, 6.39 mmol). The mixture was refluxed for 48 h. After cooling the solution, H$_2$O (50 ml) was added to the solution and extracted by dichloromethane (50 ml x 3). The organic layer was separated and dried in Na$_2$SO$_4$. The solvent was removed in vacuum. Purification by column chromatographyl over silica gel eluting with a mixture of methylene chloride and n-hexane (3:10) followed by recrystallization with a mixture of methylene chloride and methanol afforded orange solids (yield 72%). $C_{91}H_{94}N_4O_2S_2$; m.p. 210 °C; ^{1}H NMR (300 MHz, CDCl): δ 9.86 (1H, s), 8.50 (1H, s), 8.43 (1H, s), 8.28 (2H, s), 8.18-8.17 (4H, m), 7.77-7.73 (2H, m), 7.68-7.53 (6H, m), 7.59-7.54 (2H, m), 7.49-7.45 (5H, m), 7.42-7.33 (7H, m), 7.15 (2H, d, J = 8.7 Hz), 4.13-4.09 (2H, m), 1.92-1.87 (2H, m), 1.56-1.29 (18H, m), 0.90-0.86 (3H, m) ppm; ^{13}C NMR, (300 MHz, CDCl):182.39, 159.11, 147.44, 147.22, 142.54, 142.12, 141.44446, 141.32, 140.26, 137.45, 134.28, 130.69, 129.59, 129.19, 128.51, 127.32, 126.15, 125.99, 125.10, 124.11, 123.57, 123.48, 123.22, 123.13, 119.75, 118.02, 116.02, 115.93, 111.50, 111.18, 110.84, 109.16, 77.45, 77.23, 77.03, 76.61, 68.55, 34.75, 32.07, 31.95, 29.71, 29.67, 29.65, 29.45, 29.38, 29.32, 26.13, 22.72 and 14.14.

(E)-3-(5-(5-(3-(3,6-bis(3,6-di-*tert*-butyl-9H-carbazol-9-yl)-*9H*-carbazol-9-yl)-9-(4-(dodecyloxy)phenyl)-*9H*-carbazol-6-yl)thiophen-2-yl)thiophen-2-yl)-2-cyanoacrylic acid (G2CSSA5)



A mixture of **G2CSS4** (0.23 g, 0.17 mmol) and cyanoacetic acid (0.02 g, 0.34 mmol) was vacuum-dried and chloroform (20 ml) and piperidine (0.04 ml, 0.51 mmol) were added. The solution was refluxed for overnight. After cooling the solution, the organic layer was removed in vacuo. Purification by column chromatographyl over silica gel eluting with a mixture of methylene chloride and hexane (3:10) followed by recrystallization with a mixture of methylene chloride and methanol afforded a red solids (yield 69%). $C_{94}H_{95}N_5O_3S_2$; m.p. 194 ^{o}C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.21-8.01 (9H, m), 7.44-7.18 (17H, m), 7.03-6.82 (8H, m), 3.76 (2H, s), 1.62 (2H, s), 1.30-1.14 (18 H, m), 0.78-0.74 (3H, m) ppm; ^{13}C NMR, (300 MHz, DMSO-d_6): 168.82, 158.70, 145.80, 144.34, 142.43, 141.34, 141.16, 140.87, 139.99, 134.99, 134.43, 130.40, 129.19, 128.80, 126.49, 126.06, 125.71, 124.72, 123.93, 122.94, 119.42, 119.08, 118.67, 117.33, 1166.06, 116.63, 111.14, 110.25, 109.14, 104.39, 103.37, 78.14, 77.92, 77.29, 32.00, 31.82, 29.57, 29.54, 29.52, 29.49, 29.31, 29.25, 29.15, 29.95, 25.95, 22.59 and 14.13.

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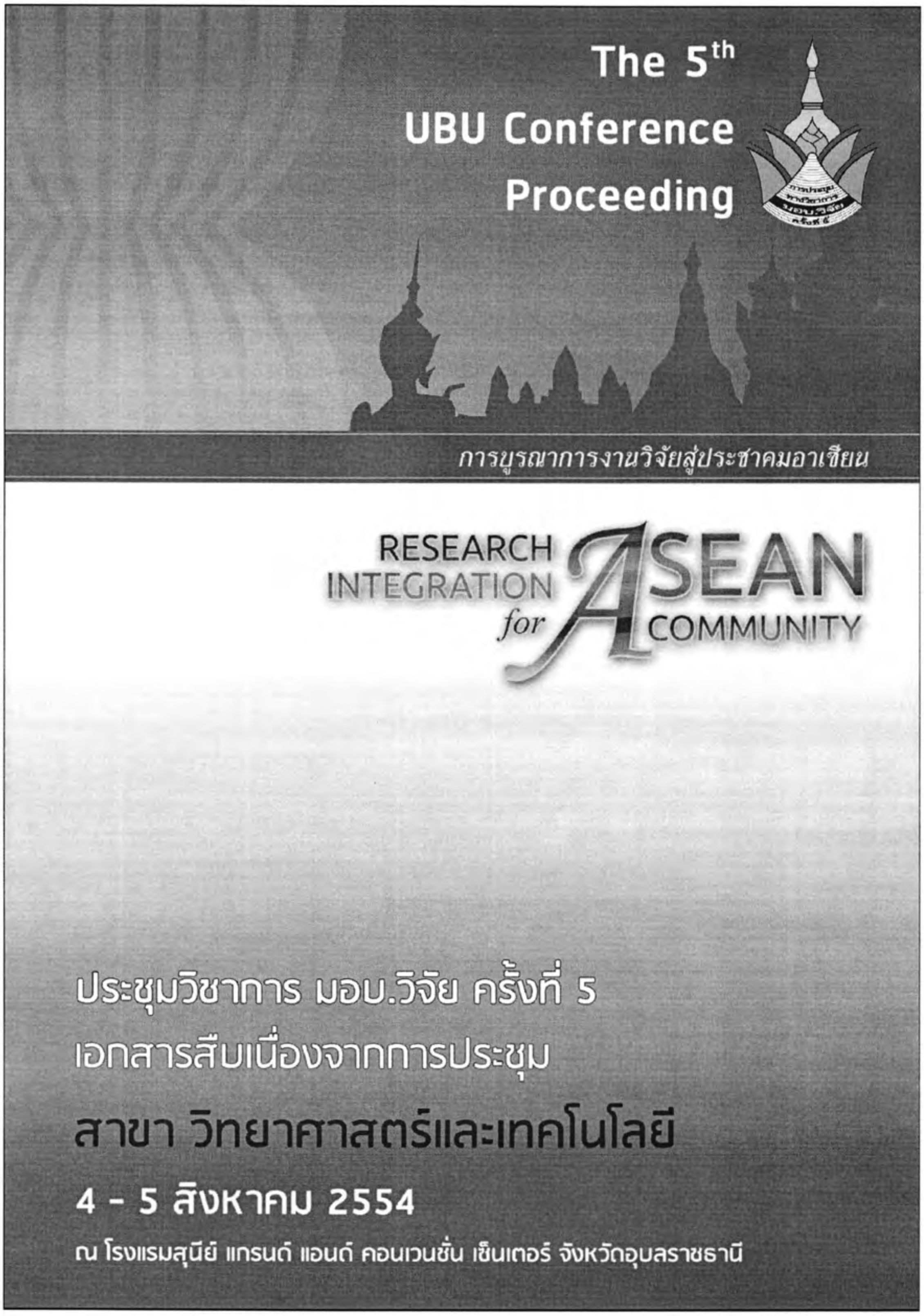
APPENDIX



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สาขา วิทยาศาสตร์และเทคโนโลยี

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ณ โรงแรมสุนีย์ แกรนด์ แอนด์ คอนเวนชั่น เซ็นเตอร์ จังหวัดอุบลราชธานี

การสังเคราะห์และพิสูจน์เอกลักษณ์ของอนุพันธ์ไตรฟีนิลเอมีน สำหรับเซลล์แสงอาทิตย์ชนิดสีย้อมไวแสง

Synthesis and Characterization of Triphenylamine Derivative for Dye Solar Cells

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บทคัดย่อ

เซลล์แสงอาทิตย์ชนิดสีย้อมไวแสงกำลังได้รับความสนใจเป็นอย่างมาก เนื่องจากสามารถเตรียมได้ง่าย และมีราคาถูก ในงานวิจัยนี้ได้ทำการพัฒนาโมเลกุลสีย้อมไวแสงอินทรีย์ประเภท D-π-A คือ **NJ01-6** ที่มีหมู่ไบไทโอฟีนเป็นหมู่พาย-คอนจูเกต มีหมู่ไตรฟีนิลเอมีนเป็นหมู่ให้อิเล็กตรอน และมีหมู่ไซยาโนอะคริลิกแอซิดเป็นหมู่รับอิเล็กตรอน โดยทำการสังเคราะห์โมเลกุลสีย้อมไวแสงด้วยปฏิกิริยาซูซูกิ ครอส-คับปลิง, โบรมิเนชัน และปฏิกิริยาโนเวเนเกล คอนเดนเซชัน เมื่อนำโมเลกุลสีย้อมไวแสง **NJ01-6** ไปขึ้นรูปเป็นอุปกรณ์เซลล์แสงอาทิตย์ชนิดสีย้อม ไวแสงให้ค่าประสิทธิภาพการเปลี่ยนพลังงานแสงเป็นพลังงานไฟฟ้าสูงสุด (IPCE) เท่ากับ 81% ที่ความยาวคลื่น 429 นาโนเมตร โดยมีค่า PCE = 5.07%, V_{oc} = 0.69 V, J_{sc} = 11.18 mA cm^{-2} และ FF = 0.66 ภายใต้การฉายแสงจำลอง 100 mW cm^{-2}

คำสำคัญ : เซลล์แสงอาทิตย์ชนิดสีย้อมไวแสง สีย้อมไวแสงสารอินทรีย์ D-π-A ไตรฟีนิลเอมีน

Abstract

Dye solar cells (DSCs) have attracted much attention, due to their prospects of simple preparation and low cost. In this work, we developed D-π-A type organic dye, namely **NJ01-6** having the bithiophene as their π-conjugated bridge, triphenylamine as donor and cyanoacrylic acid as acceptor. The organic dye was synthesized using Suzuki cross-coupling, bromination and Knoevenagel condensation reactions. Under standard global AM 1.5 solar condition, the **NJ01-6**-based cell give a short circuit photocurrent density (J_{sc}) of 11.18 mA cm^{-2}, an open circuit voltage (V_{oc}) of 0.69 V, a fill factor (FF) of 0.66, corresponding to a power conversion efficiency (PCE) of 5.07%, and the maximum incident monochromatic photon-to-current conversion efficiency (IPCE) of 81% at 429 nm.

Keywords : Dye solar cells (DSCs), Organic dye, D-π-A, Triphenylamine

Introduction

Dye solar cells (DSCs) have been actively studied since Grätzel and co-workers reported high solar energy to electricity conversion efficiencies of up to 12% with a DSCs based on ruthenium complex photosensitizer. However, the use of ruthenium dyes will limit the large-scale application of such complexes in the future due to the problem of high and unfriendly environmental issues. In the meantime, metal free organic dyes are being increasingly studies in DSCs due to good performance, simple preparation and low cost [1]. Recently, a metal-free sensitizer, an indoline dye, gave an impressive high efficiency of 9% for DSCs [2]. However, organic dyes have often presented the low conversion efficiency and low operation stability compared to metal complexes. The major factors for low conversion efficiency for the DSCs based on organic dyes are the formation of dye aggregation on the semiconductor surface and recombination of conduction band electrons with triiodide in the electrolyte.

Organic dye containing an electron donor, π-conjugation and electron acceptor, which is called the D-π-A structure. The π-conjugated unit as an electron spacer to connect the donor and accepter. Oligothiophenes are usually used as the π-conjugated system because of their chemical and environmental stability as well as their electronic tenability [3]. The triphenylamine can improve the hole-transporting ability of the materials, and the non polar structure of triphenylamine can also prevent the formation of dye aggregate [4]. In this work, we investigated on the synthesis and characterizations of D-π-A type organic dye with the oligothiophene as their π-conjugated system, triphenylamine as donor and cyanoacrylic acid as acceptor, and applied them successfully to sensitize nanocrystalline TiO_2 based on solar cells.

Objective

1. To synthesize novel donor acceptor π-conjugated (D-π-A) organic material
2. To study their optical and electrochemical properties
3. To investigate the performance of dye based device

Methodology

1. General methods

^{1}H NMR spectra were recorded on Bruker AVANCE (300 MHz) spectrometer. ^{13}C NMR spectra were recorded on Bruker AVANCE (75MHz) spectrometer and were fully decoupled. Chemical shifts (δ) are reported relative to the residual solvent peak part per million (ppm). Coupling constants (J) are given in Hertz (Hz). UV-Visible spectra were measured in CH_2Cl_2 on a Perkin-Elmer UV Lambda 25 spectrometer. Fluorescence spectra were measured in CH_2Cl_2 on a Perkin-Elmer L S 50B Luminescence spectrometer. Analytical thin-layer chromato- graphy (TLC) was performed with Merck aluminium plates coated with silica gel 60 F_{254}. Column chromato- graphy was carried out using gravity feed chromatography Merck silica gel mesh, 60 Å, where solvent mixture were used and the portions are given by volume.

Preparation DSC electrodes

To prepare the DSC working electrodes, the FTO glass used as current collector (FTO 3 mm thickness, 15 Ω/cm^2, Solaronix, Switzerland) was first cleaned in a detergent solution using an ultrasonic bath for 15 min, and then rinsed with water and ethanol. The FTO glass plates were immersed into a 40 mm aqueous $TiCl_4$ aqueous solution at 70°C for 30 min and washed with water and ethanol.

The commercial available TiO_2 paste (20T/SP and R/SP, Solaronix) and modified paste was deposited on SnO_2:F glass for fabricated photo anode electrodes by screen-printing method. This screen-printing procedure (with coating, storing and drying) was repeated to change the thickness of the nanocrystalline-TiO_2 working electrode. The electrodes coated with the TiO_2 pastes were gradually heated under an airflow at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 5 min and 500°C for 30 min. After sintering, the surface area of the TiO_2 electrodes was measured precisely with camera and followed integration of the resulting image by Image J software.

After the size measurement, the TiO_2 film was re - treatment with $TiCl_4$ and sintered again, as described above. At 80 °C in the cooling, the TiO_2 electrode was immersed into a 3×10^{-4} M N-3 dye solution in Ethanolic solution and kept at room temperature for 20–24 h to complete the sensitizer uptake.

To prepare the counter electrode, a hole was drilled in the FTO glass by 1 mm diamonds driller. The perforated sheet was washed with H_2O as well as with a 0.1 M HCl solution in ethanol and cleaned by ultrasound in an acetone bath for 10 min. After removing residual organic contaminants by heating in air for 15 min at 450 °C, the Pt catalyst was deposited on the FTO glass by coating with a drop of H_2PtCl_6 solution (7 mM in Isopropanal) and repeating the heat treatment at 385 °C for 20 min.

DSC assembling

The dye-covered TiO_2 electrode and Pt-counter electrode were assembled into a sandwich type cell and sealed with a hot-melt gasket of 30 µm thickness made of the ionomer Surlyn 1702 (Dupont). The aperture of the Surlyn frame was 1mm square larger than that of the TiO_2 area and its width was 1 mm.

A drop of the electrolyte, a solution 0.60M LiI, 0.03M I_2, 0.10M guanidinium thiocyanate and 0.50M 4-tert-butylpyridine in the mixture of acetonitrile and benzonitrile (volume ratio: 85:15)) was put on the hole in the back of the counter electrode. The electrolyte was introduced into the cell via vacuum backfilling. The cell was placed in a small vacuum chamber to remove inside air. Exposing it again to ambient pressure causes the electrolyte to be driven into the cell. Finally, the hole was sealed using a hot-smelt ionomer film (Surlyn 1702, 30 µm thickness, Du-Pont) and hot cover glass (1mm thickness).

Photovoltaic measurements employed an AM 1.5 solar simulator. The power of the simulated light was calibrated to be 100 $mWcm^{-2}$ by using a reference Si photodiode equipped with an IR-cutoff filter (KG-3, Schott). *I-V* curves were obtained by applying an external bias to the cell and measuring the generated photocurrent with a Keithley model 2400 digital source meter. The voltage step and delay time of photocurrent were 0.2 V and 40 ms, respectively. Light reflection losses were eliminated using a solid mask.

2. Synthetic procedures

Synthesis of 2

To a mixture of **1** (0.10 g, 0.34 mmol), 2, 5-dibromothiophene (0.21 g, 0.86 mmol) and $Pd(PPh_3)_4$ (0.0039 g, 0.0034 mmol) in THF (20 ml) were added 2M Na_2CO_3 (0.36 g, 0.34 mmol). The reaction mixture was heated at reflux under N_2 atmosphere for 24 h. After being cool to room temperature, the mixture was extracted with CH_2Cl_2 (50 mlx2). The combined organic layer was washed successively with water (20 mlx3), brine solution (20 mlx2), dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue was purified by column chromatography on silica gel eluting with Hexane to afford a white solid (0.03 g, 26%). ^1H NMR ($CDCl_3$): δ 7.37 (d, 2H, *J* = 8.62 Hz), 7.28 (t, 4H, *J* = 8.02, 7.57 Hz), 7.13 (d, 4H, *J* = 7.67 Hz), 7.08 (m, 4H), 7.00 (d, 1H, *J* = 3.83 Hz), 6.96 (d, 1H, *J* = 3.83 Hz).

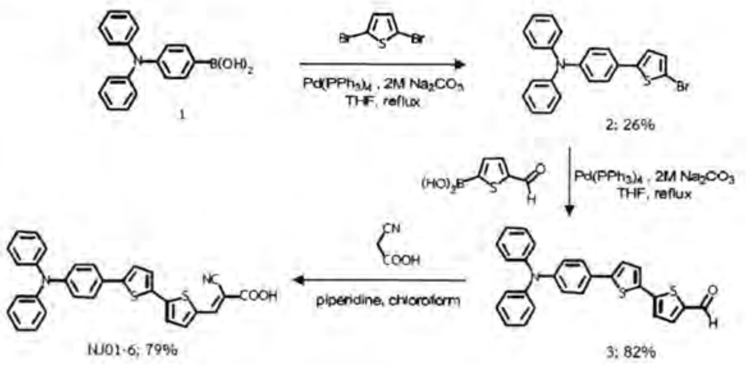
Synthesis of 3

To a mixture of **2** (0.21 g, 0.51 mmol), 5-Formyl-2-thiophene boronic acid (0.08 g, 0.51 mmol) and $Pd(PPh_3)_4$ (0.05 g, 0.051 mmol) in THF (20 ml) was added 2M Na_2CO_3 (1.08 g, 0.1020 mmol). The reaction mixture was heated at reflux under N_2 atmosphere for 24 h. After being cool to room temperature, the mixture was extracted with CH_2Cl_2 (50 mlx2). The combined organic layer was washed successively with water (20 mlx3), brine solution (20 mlx2), dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue was purified by column chromatography on silica gel eluting with hexane increasing gradually to Hexane:CH_2Cl_2 (6:1) to afford a yellow solid (0.71 g, 82%). ^1H NMR ($CDCl_3$): δ 7.76 (d, 1H, *J* = 3.9 Hz), 7.46 (d, 2H, *J* = 8.7 Hz), 7.32 (d, 1H, *J* = 3.9 Hz), 7.28 (t, 4H, *J* = 8.4, 7.2 Hz), 7.24 (d, 1H, *J* = 3.9 Hz), 7.18 (d, 1H, *J* = 3.6 Hz), 7.13 (d, 4H, *J* = 7.5 Hz), 7.08-7.04 (m, 4H).

Synthesis of NJ01-6

To a mixture of **3** (0.20 g, 0.45 mmol) and cyanoacetic acid (0.03 g, 0.68 mmol) was added piperidine (0.12g, 1.37 mmol) in chloroform. The reaction mixture was heated at reflux under N_2 atmosphere for 6 h. After being cool to room temperature, the mixture was extracted with CH_2Cl_2 (50 mlx2). The combined organic layer was washed successively with water (20 mlx3), brine solution (20 mlx2), dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue was purified by column chromatography on silica gel eluting with CH_2Cl_2 increasing gradually to CH_2Cl_2:CH_3OH (3:1) to afford a red solid (0.71 g, 82%). ^1H NMR (DMSO-d_6): δ 8.02 (s, 4H), 7.63–7.54 (m, 3H), 7.44–7.40 (m, 3H), 7.32 (t, 4H, *J* = 7.5 Hz), 7.10–7.03 (m, 6H), 7.08 (d, 2H, *J* = 7.8 Hz), 7.04 (d, 2H, *J* = 7.5 Hz), 6.94 (d, 2H, *J* = 3.9 Hz)

Results and Discussion



Scheme 1. The structures and preparation of NJ01-6

The target **NJ01-6** was successfully prepared as outline in Scheme 1. Intermediate **2** was first synthesized by Suzuki cross coupling of **1** with 2, 5-dibromothiophene with Pd(PPh$_3$)$_4$ as catalyst and 2M Na$_2$CO$_3$ as base in THF/H$_2$O as solvent at reflux for 48 h. The aldehyde intermediate **3** were then formed by cross coupling of the obtained aryl bromide **2** with 5-formyl-2-thiophene boronic acid under the same Suzuki cross coupling reactions. Knoevenagel condensation of the resultant aldehyde **3** with cyanoacetic acid in chloroform as solvent and piperidine as base gave the organic dye **NJ01-6** as red solid in good yield.

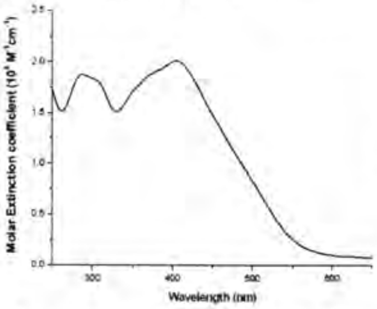


Figure 1. Absorption spectra of **NJ01-6** in CH$_2$Cl$_2$ solution (10^{-5} M) at 25 °C

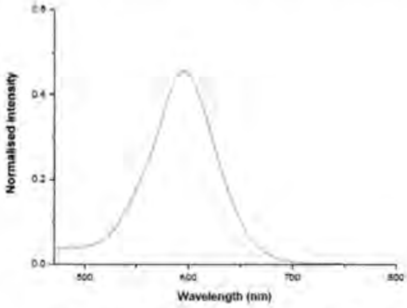


Figure 2. Emission spectra of **NJ01-6** in CH$_2$Cl$_2$ solution (10^{-4} M) at 25 °C

The absorption and emission spectra of the organic dye **NJ01-6** in dilute solution are shown in Figure 1. The dye exhibit two distinct absorption bands at around 288 nm corresponding to the π–π^* electron transition of the conjugated molecule and at around 405 nm corresponding to an intramolecular charge transfer transition (ICT) between the triphenylamine donating unit and the cyanoacrylic acid anchoring moiety. The molar extinction coefficient (ε) of the **NJ01-6** is 20,000 $M^{-1}cm^{-1}$. The dye shows the maximum emission at 595 nm as show in Figure 2.

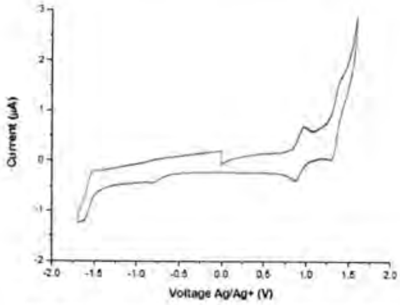


Figure 3. CV curve of **NJ01-6** in CH_2Cl_2 solution with n-Bu_4NPF_6 as supporting electrolytes, scan rate of 50 mVs^{-1}

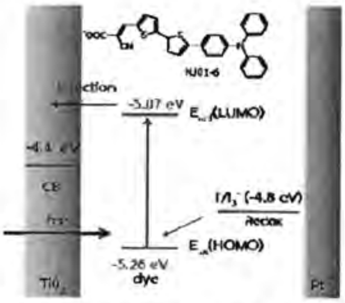


Figure 4. Schematic energy diagram for DSCs based on NJ01-6, a nanocrystalline TiO_2 electrode, and I^-/I_3^- redox couple.

CV curve of **NJ01-6** show the oxidation process of triphenylamine and conjugated thiophene moieties, while the irreversible reduction can be assigned to the reduction process of cyanoacrylic acceptor. The HOMO and LUMO energy levels of this dye were determined using the onset position of the oxidation and energy gab (E_g). The determinated LUMO level is -3.07 eV, which matches well the conduction band of TiO_2 favoring electron jumping from dye to TiO_2. The determinated HOMO level is -5.26 eV, which matches well with redox potential of the I^-/I_3^- redox electrolytes favoring electron jumping from electrolyte to dye.

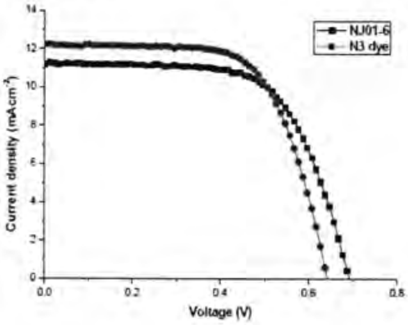


Figure 5 Current density-voltage (*J-V*) characteristic for DSCs from the **NJ01-6** and **N3** dye

Figure 5 shows current density-voltage (*J-V*) characteristic of device based on the **NJ01-6** giving a short circuit photocurrent density (J_{sc}) of 11.18 $mAcm^{-2}$, an open circuit voltage (V_{oc}) of 0.69 V, a fill factor (FF) of 0.66 and a power conversion efficiency (PCE) of 5.07%. Device made of a commercial dye **N3** under the same condition was used as a reference.

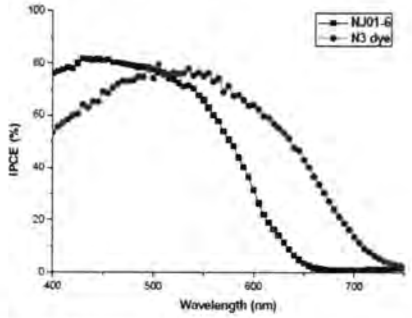


Figure 5 IPCE action spectra for DSCs based on NJ01-6 and N3 dye-sensitized transparent TiO_2 films

Figure 6, show action spectra of monochromatic incident photon-to-current conversion efficiencies (IPCE) for DSCs based on **NJ01-6** and **N3**. The IPCE spectrum of NJ01-6 shows maxima efficiency about 81% at 429 nm. The IPCE value of **NJ01-6** is higher but shaper than that of **N3** dye.

Conclusion

In summary, we have synthesized and characterized of **NJ01-6** dye with triphenylamine as donor, thiophene linker and cyanoacrylic acid accepter. The organic dye was synthesized using Suzuki cross coupling, bromination and Knoevenagel condensation reactions. Under standard global AM 1.5 solar condition, the **NJ01-6** based cell give a short circuit photocurrent density of 11.18 mA cm^{-2}, an open circuit voltage of 0.69 V, a fill factor of 0.66, corresponding to a power conversion efficiency (PCE) of 5.07%, and the maximum incident monochromatic photon-to-current conversion efficiency (IPCE) of 81% at 429 nm.

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