

SYNTHESIS AND CHARACTERIZATION OF NOVEL ORGANIC

MATERIALS FOR OPTOELECTRONIC DEVICES

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY MAJOR IN CHEMISTRY FACULTY OF SCIENCE UBON RATCHATHANI UNIVERSITY YEAR 2012 COPYRIGHT OF UBON RATCHATHANI UNIVERSITY



THESIS APPROVAL UBON RATCHATHANI UNIVERSITY DOCTOR OF PHILOSOPHY MAJOR IN CHEMISTRY FACULTY OF SCIENCE

TITLE SYNTHESIS AND CHARACTERIZATION OF NOVEL ORGANIC MATERIAL FOR OPTOELECTRONIC DEVICES

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บทคัดย่อ

ชื่อเรื่อง	: การสังเคราะห์และพิสูจน์เอกลักษณ์ของวัสดุอินทรีย์ชนิดใหม่
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ศัพท์สำคัญ : หมู่ให้ หมู่รับ ไพ-คอนจูเกต เซลล์แสงอาทิตย์ชนิคสีย้อมไวแสง ไคโอคเรืองแสงสารอินทรีย์

้ในงานวิจัยนี้รายงานการสังเคราะห์และพิสูจน์เอกลักษณ์ของสารอินทรีย์ที่เป็นสีย้อมไว แสงทั้งหมด 4 กลุ่ม ประกอบด้วยสีข้อมไวแสงกลุ่ม 2D-D-**π**-A กลุ่ม D-D-**π**-A กลุ่ม ไพแรนมาโล โนไนไตร และกลุ่ม A-D-A และสารเรื่องแสงอินทรีย์กลุ่ม D-A-D พบว่าวัสคุอินทรีย์ทั้งหมด แสคง คุณสมบัติทางแสงและทางเคมีใฟฟ้าที่สัมพันธ์กับโครงสร้างความยาวของระบบคอนจูเกชันภายใน ์ โมเลกุล เช่น แสคงแถบการดูคกลื่นแสงและการเรื่องแสงที่ความยาวคลื่นมากขึ้น (เข้าใกล้คลื่นแสง สีแคง) เมื่อจำนวนหมู่ไทโอฟีนเพิ่มขึ้น หรือแสคงก่าศักย์ไฟฟ้าออกซิเคชันที่ลคลงเมื่อจำนวนหมู่ ไทโอฟีนเพิ่มขึ้น นอกจากนี้ ขนาคของหมู่ให้อิเล็กตรอน ก็ส่งผลต่อปริมาณสีย้อมไวแสงที่ถูกดูดซับ บนอนุภาคไททาเนียมออกไซค์เป็นผลมาจากความเกะกะของหมู่ที่มีขนาคใหญ่ ทำให้ประสิทธิภาพ ของเซลล์แสงอาทิตย์ชนิคสีข้อมไวแสงมีก่าน้อยลงด้วย สีข้อมไวแสงกลุ่มไพแรนมาโลโนไนไตร แสดงคุณสมบัติทางแสงและทางเคมีไฟฟ้าที่คีด้วยการขยายความยาวคอนจูเกชันและการเพิ่มหมู่ดึง อิเล็กตรอนในระบบไพ-คอนจูเกต และสี่ย้อมไวแสงกลุ่มที่มีหมู่ให้อิเล็กตรอนหนึ่งหมู่ หมู่รับ อิเล็กตรอนสองหมู่ แสดงคุณสมบัติทางแสงและทางเคมีไฟฟ้าที่คีด้วยการเพิ่มหมู่จับกับอนุภาค ไททาเนียมออกไซค์เป็นสองหมู่ ซึ่งเป็นการเพิ่มประสิทธิภาพการส่งผ่านอิเล็กครอนไปยังอนุภาค ไททาเนียมออกไซค์ จากสีย้อมไวแสงทั้งหมด 12 ชนิด พบว่า สีย้อมไวแสง DPA3 ที่มีหมู่ให้ อิเล็กตรอนสองหมู่คือ คาร์บาโซลและไคฟีนิลเอมีน มีหมู่ไทโอฟีนสามหมู่เป็นสะพานคอนจูเกชัน และมีหมู่ไซยาโนอะคริลิกแอซิดเป็นหมู่รับอิเล็กตรอน ให้ค่าประสิทธิภาพการเปลี่ยนพลังงานแสง เป็นพลังงานไฟฟ้ามากที่สุคคือร้อยละ 5.12 ในขณะที่สีย้อมไวแสง CFPA ที่ประกอบค้วยหมู่ คาร์บาโซลและฟลูออรีนเป็นหมู่ให้อิเล็กตรอน หมู่ฟินิลลืน ไพแรนมาโลโนไนไตร และไทโอฟีน

สองหมู่ เป็นระบบ ไพ-กอนจูเกต และมีหมู่อะกริลิกแอซิคเป็นหมู่รับอิเล็กตรอน ให้ก่าประสิทธิภาพ การเปลี่ยนพลังงานแสงเป็นพลังงานไฟฟ้าน้อยที่สุคคือร้อยละ 0.82

สำหรับกลุ่มวัสคุเรืองแสงสารอินทรีย์ จากการศึกษาพบว่า โครงสร้างแบบ D-A-D ที่มี หมู่ให้อิเล็กตรอนสองหมู่และมีแกนกลางที่มีสมบัติเป็นหมู่รับอิเล็กตรอน สามารถถูกปรับปรุง คุณสมบัติการดูคกลืนแสง การเรืองแสง และคุณสมบัติทางเคมีไฟฟ้า ด้วยการปรับเปลี่ยนความยาว ของระบบคอนจูเกชันและความแรงของหมู่รับอิเล็กตรอนแกนกลาง และพบว่า สารเรืองแสง DTBTD ที่มีแกนกลางเป็นอนุพันธ์เบนโซไทเอไคเอโซลที่ต่ออยู่กับหมู่ไทโอฟีนสองหมู่ เรืองแสงที่ ความยาวคลื่นแสงสีแดง เนื่องจากมีระบบคอนจูเกชันที่ยาวที่สุดและมีหมู่ดึงอิเล็กตรอนที่แรงที่สุด ในขณะที่สารเรืองแสง DND เรืองแสงที่ความยาวคลื่นแสงสีน้ำเงิน เนื่องจากไม่มีหมู่แกนกลางที่มี ความสามารถในการดึงอิเล็กตรอนและเป็นสารที่มีคอนจูเกชันสั้นที่สุด

ABSTRACT

TITLE	: SYNTHESIS AND CHARACTERIZATION OF NOVEL ORGANIC
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ORGANIC LIGHT-EMITTING DIODES

This thesis deals with synthesis and characterization of four series organic materials including 2D-D- π -A TPA dyes, D-D- π -A DPA dyes, pyranemalononitrile dyes and A-D-A dyes, as well as D-A-D emitting materials. The compounds exhibit optical and electrochemical characteristic that relate to the conjugation length in molecules such as red shift in absorption and emission or lower in oxidation potentials as the number of thiophene increases. A large side of donor moiety prevents dyes aggregation and also reduces dyes among adsorbed on TiO₂ resulting in lower in DSSCs efficiency. Pyranemalononitrile dyes exhibit good photophysical and electrochemical properties with the expanded absorption spectra by introducing the electron withdrawing moiety, pyranemalononitrile, into π -conjugated bridge. Single donor double accepter dyes show good optical and electrochemical properties as well due to the increasing anchoring group, increasing the possibility of electron injection from dyes to TiO₂ electrode. Among 12 dyes in this work, DPA3 with carbazole encapped-diphenylamine double electron donor, tertthiophene π -conjugated bridge, and cyanoacrylic acid accepter exhibit the highest power conversion efficiency (η) of 5.12%, whereas CFPA with carbazole-fluorene donor phenylene-(pyran-4-yilidine)malononitrile-bisthiophene spacer and acrylic acid accepter exhibits lowest η of 0.82%.

For OLEDs materials, D-A-D type organic emitting materials exhibit the absorption, emission, and electrochemical characteristic that can be tuned by the conjugation system and electronic nature of the central core. DTBTD with benzothiadiazole core extended with two thiophene moiety shows fluorescence in red region due to the longest conjugation length and strongest electron affinity core. On the other hand DND without electron affinity core exhibits the emission in blue region due to the shortest conjugation length.

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CONTENTS

PAGES

ACKNOWLEDGMENTS	I
THAI ABSTRACT	II
ENGLISH ABSTRACT	IV
CONTENTS	VI
LIST OF TABLES	IX
LIST OF FIGURES	XI
LIST OF ABBREVIATIONS	XVI

.

CHAPTER

-

1 INTRODUCTION

1.1 Optoelectronic devices	1
1.2 Dye sensitized solar cells (DSSCs)	1
1.2.1 Component and working principles	1
1.2.2 Overall efficiency of the photovoltaic cell (η_{cell})	3
1.2.3 Sensitizers	4
1.3 Organic Light Emitting Diodes (OLEDs)	9
1.3.1 Device structure and operation	9
1.3.2 Types of devices	9
1.3.3 Previous organic electroluminescent materials	12
1.3.4 Hole transport materials	17
1.4 Motivation and aims	19
2 SYNTHESIS AND CHARACTERIZATION OF CARBAZOLE-	
TRIPHENYLAMINE DYES FOR DYE-SENSITIZED SOLAR CELLS	
2.1 Introduction	20
2.2 Target dyes and Aims	22

2.3	Results and discussion	23
2.4	Conclusion	39

CONTENTS (CONTINUED)

PAGES

3 SYI	NTHESIS AND CHARACTERIZATION OF CARBAZ	OLE-
DII	PHENYLAMINE DYES FOR DYE-SENSITIZED SOL	AR CELLS
	3.1 Introduction	40
	3.2 Target dyes and Aims	42
	3.3 Results and discussion	42
	3.4 Conclusion	59
4 SY	NTHESIS AND CHARACTERIZATION OF (PYRANE	-4-YLIDENE)
MA	ALONONITRILE DYES FOR DYE-SENSITIZED SOLA	AR CELLS
	4.1 Introduction	61
	4.2 Target dyes and Aims	62
	4.3 Results and discussion	63
	4.4 Conclusion	80
5 SY	INTHESIS AND CHARACTERIZATION OF CARBAZ	OLE DONOR
DI	ACCEPTER (A-D-A) DYES FOR DYE-SENSITIZED S	OLAR CELLS
	5.1 Introduction	81
	5.2 Target dyes and Aims	83
	5.3 Results and discussion	83
	5.4 Conclusion	95
6 SY	INTHESIS AND CHARACTERIZATION OF D-A-D EM	IITTING
MA	TERIALS FOR ORGANIC LIGHT EMITTING DIOD	ES
	6.1 Introduction	96
	6.2 Target molecules and aims	98
	6.3 Results and discussion	100
	6.4 Conclusion	115
7 SU	MMARY	116

-

CONTENTS (CONTINUED)

8 EXPERIMENT 8.1 General procedures and instruments 118 8.2 Synthesis 120 REFERENCES APPENDICES 120

VITAE

.

VIII

PAGES

190

LIST OF TABLES

TABLE		PAGES
2.1	Optical properties data of TPA1-TPA3	29
2.2	Electrochemical properties and energy level of carbazole-triphenylamine dyes	31
2.3	Calculated HOMO and LUMO gab	34
2.4	T _{sd} of TPA dyes	35
2.5	Performance parameters of DSSCs constructed using TPA dyes	38
3.1	Photophysical data of DPA1-DPA3	47
3.2	Maximum absorption of DPA1 measured in various solvents	48
3.3	Electrochemical properties and energy level of carbazole-diphenylamine dyes	51
3.4	Dihedral Angles (deg) between moieties for the ground state of the dyes	
	optimized by B3LYP/6-31G(d,p) in CH ₂ Cl ₂	53
3.5	Energy Level, HOMO-LUMO energy gab ($\Delta_{\text{H-L}}$), and electron contribution	
	of the HOMO and LUMO of DPA dyes calculated by B3LYP/6-31G(d,p)	54
3.6	T _{sd} of DPA1-DPA3	55
3.7	Performance parameter of DSSCs constructed using DPA1-DPA3 as sensitizen	^a 59
4.1	Optical data of CFP dyes	72
4.2	Electrochemical property and energy level of CFP dyes	74
4.3	The selected bond distances and dihedral angles of CFPA and CFPC by	
	B3LYP/6-31G(d.p)	75
4.4	Summarized energy and characteristic of Frontier Orbitals of CFP dyes	
	calculated by B3LYP/6-31G(d.p)	77
4.5	T _{sd} of CFPA and CFPC	77
4.6	Performance parameter of DSSCs constructed using CFPA and CFPC as sensi	tizer ^a 79
5.1	Optical properties data of CB01-CB22 dyes	91
5.2	Electrochemical data and energy level of carbazole diaccepter dyes	92
5.3	T _{sd} of CB dyes	93
5.4	Performance parameter of DSSCs constructed using CB dyes as sensitizer ^a	95

LIST OF TABLES (CONTINUED)

TABLE		PAGES
6.1	Photophysical data of D-A-D emitting materials	110
6.2	Electrochemical properties and energy level of carbazole diaccepter dyes	112
6.3	The half-wave oxidation potential of multi-oxidation process	113
6.4	Thermal properties of D-A-D compounds	115

LIST OF FIGURES

FIGURE	IGURE	
1.1	Schematic representation of the construction and the operational principle of	
	DSSCs	3
1.2	<i>J-V</i> curve	4
1.3	Chemical structures of N3, N719 and black dyes	5
1.4	Chemical structures of K19, K73, K77 and Ru-1 dyes	6
1.5	Chemical structures of C343, NKX-2311, NKX-2753 and NKX-2677 dyes	6
1.6	Chemical structures of D102 and D149 dyes	7
1.7	Chemical structures of JK-1 and JK-2 dyes	7
1.8	Chemical structures of JK-24 and JK-25 dyes	8
1.9	Possible binding modes for carboxylic acid groups on TiO ₂	8
1.10	Cross-sectional representation of an OLEDs with both ETL and HTL	9
1.11	Structure (left) and energy level diagram (right) of single-layer OLEDs	11
1.12	Structure (left) and energy level diagram (right) of multi-layer OLEDs	11
1.13	Chemical structures of conducting polymers	12
1.14	Molecular electroluminescence materials	12
1.15	The example of low molecular weight electroluminescent materials	14
1.16	Some example of light-emitting dendrimer	16
1.17	Example of efficient hole transporting materials	18
2.1	The structure of some triphenylamine dyes	21
2.2	TPA dyes with extended π -spacer cyclohexylene linker	22
2.3	Chemical structure of target dyes (TPA1-TPA3)	23
2.4	H ¹ -NMR spectrum of intermediate 26 in CDCl ₃	24
2.5	Expanded aromatic region H ¹ -NMR spectrum of intermediate 31 in CDCl ₃	26
2.6	H ¹ -NMR spectrum of TPA1 in DMSO-d6	27
2.7	Absorption spectra of TPA1-TPA3 ; (A) measured in CH ₂ Cl ₂ (B) dyes adsorbe	ed on
	TiO ₂ film	28

·

LIST OF FIGURES (CONTINUED)

FIGURE

PAGES

2.8	(A) Fluorescence spectra of TPA1-TPA3 measured in CH_2Cl_2 solution	
	(B) Absorption and emission spectra of TPA1 indicated stroke shift	29
2.9	(A) Cyclic voltamogram of TPA1-TPA3 in dry CH_2Cl_2 with scan rate of 0.05	
	V/s and 0.1 M $n-Bu_4NPF_6$ as electrolyte. (B), (C) and (D) Multiple scan Cyclic	
	voltamogram of TPA1, TPA2 and TPA3, respectively	31
2.10	Energy diagram indicated HOMO/LUMO levels of TPA1-TPA3	32
2.11	Schematic views of the ground state structures for TPA3	33
2.12	Molecular orbital of TPA dyes relevant ground state and excited state	34
2.13	TGA thermograms of TPA1-TPA3 dyes	35
2.14	(a) The adsorption data for the dyes onto TiO_2 films measured over a period	
	of 50 h at room temperature, (b), (c) and (d) the absorption spectra of TPA1,	
	TPA2 and TPA3 in various time	36
2.15	The space-filling molecular models of the optimized conformation of the dyes	36
2.16	IPCE spectra (A) and <i>I-V</i> characteristic (B) of TPA1-TPA3	37
3.1	Structure of diphenylamine encaped-cabazole (33) and biscabazole (34)	40
3.2	Structure of 4,4-(diphenylamino)diphenylamine (35) and	
	4,4-dicarbazolediphenylamine (36)	41
3.3	Structure of D-A compound with Diphenylamine donor	42
3.4	The structure of target dyes (DPA1-DPA3)	43
3.5	Absorption spectra of DPA dyes: (A) CH_2Cl_2 , (B) adsorbed on TiO_2 film	46
3.6	PL spectra of DPA1-DPA3 in CH ₂ Cl ₂	47
3.7	The absorption spectra of DPA dyes in various solvent	48
3.8	Cyclic voltamogram of DPA1-DPA3 in dry CH_2Cl_2 with scan rate of 0.05 V/s	
	and 0.1 M n-Bu ₄ NPF ₆ as electrolyte at 25 $^{\circ}$ C	49
3.9	Multiscan cyclic voltamogram of DPA1 (A), DPA2 (B) and DPA3 (C) in dry	
	CH_2Cl_2 with scan rate of 0.05 V/s and 0.1 M n-Bu ₄ NPF ₆ as electrolyte at 25 °C	50

LIST OF FIGURES (CONTINUED)

FIGURE

.....

3.10	Energy diagram of HOMO/LUMO of DPA1-DPA3	51
3.11	Schematic view of the ground-state (S0) structure for DPA3	52
3.12	Molecular orbital of DPA dyes relevant ground state and excited state	53
3.13	TGA thermograms of DPA1-DPA3 dyes	54
3.15	(A) dyes uptakes onto TiO_2 films measured over a period of 50 h at room	
	temperature, (B), (C) and (D) the absorption spectra of DPA1, DPA2 and	
,	DPA3 in various concentration	55
3.16	FT-IR spectra of the DPA1 adsorbed in TiO ₂ films	56
3.17	IPCE spectra of DPA and N3 dyes	57
3.18	I-V characteristic of DPA1-DPA3 and N3 reference dye	58
4.1	The structure of DCM and DCM derivatives; red-light emitter for OLEDs	62
4.2	DSSCs dyes from fluorene derivatives	62
4.3	Structure of (pyrane-4-ylidene)malononitrile dyes (CFP dyes)	63
4.4	H ¹ -NMR of aldehyde intermediate 55	65
4.5	H ¹ -NMR of malononitrile intermediate 56	66
4.6	H ¹ -NMR of malononitrile intermediate 58	67
4.7	H ^I -NMR of CFPA	68
4.8	H ¹ -NMR of CFPC	69
4,9	Absorption spectra of CFPA and CFPC dyes collected in CH ₂ Cl ₂	70
4.10	Absorption spectra of CFPA and CFPC adsorbed on TiO_2 film	71
4.11	Photoluminescent spectra of CFPA and CFPC measured in CH ₂ Cl ₂ solution	72
4.12	Cyclic voltamogram of CFPA and CFPC	73
4.13	The energy diagram of CFP dyes	74
4.14	Optimized structure of CFPA and CFPC	75
4.15	Frontier molecular orbital of CFPA and CFPC calculated by B3LYP/6-31G(d,p)	76
4.16	TGA thermograms of CFPA and CFPC	77

PAGES

LIST OF FIGURES (CONTINUED)

FIGURE		PAGES
4.17	IPCE spectra of CFP dyes and N719	78
4.19	I-V characteristic of CFPA and CFPC	79
5.1	Structure of example A-D-A dyes	82
5.2	Structure of target A-D-A dyes (CB01-CB22).	83
5.3	H ¹ -NMR spectrum of compound 68	85
5.4	H ¹ -NMR spectrum of compound 70	85
5.5	H ¹ -NMR spectrum of compound 69	86
5.6	Expanded H ¹ -NMR spectrum of compound 71	86
5.7	Expanded H ¹ -NMR spectrum of compound CB22	87
5.8	Absorption spectra of CB01-CB22 (A) E plot; (B) Normalized intensity plot	90
5.9	Absorption spectra and PL spectra of BCFnT $(n = 0, 2, 4, 6, 8)$ in thin film	91
5.10	Cyclic voltamogram of CB dyes in dry DMF	92
5.11	The energy diagram of CB dyes	93
5.12	TGA thermograms of CB dyes	94
5.13	IPCE spectra and I-V curves of DSSCs based on CB dyes as sensitizer	95
6.1	Example of red emitting materials based on BTD central core	97
6.2	Example of full color emitting materials based on A-D-A structure	8
6.3	Structure of taget D-A-D emitting materials	99
6.4	Structure of starting materials	100
6.5	H ⁱ -NMR spectra of DND	104
6.6	H ¹ -NMR spectra of DT2D	104
6.7	H ¹ -NMR spectra of DBD	106
6.8	H ¹ -NMR spectra of DPBPD	106
6.9	UV-visible spectra of DAD emitting materials in CH ₂ Cl ₂	108
6.10	UV-visible spectra of DAD emitting materials in thin film	108

-

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FIGURE		PAGES
6.11	Photoluminescent spectra of DAD emitting materials in CH_2Cl_2 (A),	
	and thin film, (B) excited at 350 nm	109
6.12	Cyclic voltamograms of D-A-D emitter in dry CH ₂ Cl ₂	111
6.13	Multi-scan cyclic voltamograms of DFD and DBD in dry CH_2Cl_2	113
6.14	DCS (second heating) and TGA traces of D-A-D series	114

LIST OF ABBREVIATIONS

ABBREVIATION FULL WORD

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CH ₂ Cl ₂	Dichloromethane
THF	Tetrahydrofuran
DMSO	Dimethylsulphoxide
RT	Room temperature
d	Doublet
dd	Doublet of doublets
td	Triplet of doublets
з	Molar absorption
eV	Electron volt
h	Hour/hours
НОМО	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
IPCE	Incident photon to current efficiency
η	Overall light-to-electric power conversion efficiency
ΙΤΟ	Indium-tin oxide
FT-IR	Fourier transform Infrared
J	Coupling constant
М	Molar concentration
MHz	Megahertz
min	Minutes
μΑ	Microamperes
μm	Micrometers
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
<i>n</i> -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°	Original state
AM 1.5	Air Mass 1.5
K	Kilo
W	Watt
v	Voltage (V)
s	second
I	Current (ampere)
$V_{ m oc}$	Open circuit voltage
$J_{ m sc}$	Short circuit current
ff	Fill factor
J-V	Current density-voltage

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CHAPTER 1

GENERAL INTRODUCTION

1.1 Optoelectronic devices

Electronic and optoelectronic devices impact many areas of society, from simple household appliances and multimedia systems to communications, computing, and medical instruments [1]. Optoelectronic device is the technology that combined optics and electronics, or called electrical-to-optical or optical-to-electrical transducers, or instruments that use such devices in their operation [2]. The development of electroactive and photoactive materials has been greatly progressed due to their potentials in optoelectronic devices, such as electroluminessence (EL) devices, photovoltaic devices, thim film transistors, and solid state lasers [3]. Among the optoeleclectronic materials, organic optoelectronic materials have received a great deal of attention for their application over inorganic ones because their ease of processing and the tunability of their properties through simple chemical modification [4]. Extensively studies have shown that conjugated organic materials exhibit a variety of interesting optical, electrical, photoelectric, and magnetic properties in solid state [5]. Thus this thesis has focused on development of novel organic materials for organic optoelectronic devices such as organic photovoltaic cells or dye sensitized solar cells and organic light emitting diodes.

1.2 Dye sensitized solar cells (DSSCs)

Photovoltaic devices are based on the concept of charge separation at an interface of two materials of different conduction mechanism. To date this field has been dominated by solidstate junction devices, usually made of silicon, and profiting from the experience and material availability resulting from the semiconductor industry. The dominance of the photovoltaic field by inorganic solid-state junction devices is now being challenged by the emergence of a third generation of cells, based, for example, on nanocrystalline and conducting polymers films. These offer the prospective of very low cost fabrication and present attractive features that facilitate market entry. It is now possible to depart completely from the classical solid-state junction device, by replacing the contacting phase to the semiconductor by an electrolyte, liquid, gel or solid, thereby forming a photo-electrochemical cell. The phenomenal progress realized recently in the fabrication and characterization of nanocrystalline materials has opened up vast new opportunities for these systems. Contrary to expectation, devices based on interpenetrating networks of mesoscopic semiconductors have shown strikingly high conversion efficiencies, which compete with those of conventional devices. The prototype of this family of devices is the dye-sensitzed solar cells (DSSCs), which realize the optical absorption and the charge separation processes by the association of a sensitizer as light-absorbing material with a wide band gap semiconductor of naaocrystalline morphology [6-8].

1.2.1 Component and working principles

Conventional DSSCs typically contain five components [9]: 1) a photoanode, 2) a mesoporous semiconductor metal oxide film, 3) a sensitizer (dye), 4) an electrolyte/hole transporter, and 5) a counterelectrode. In DSSCs, the incoming light is absorbed by the sensitizer, which is anchored to the surface of semiconducting TiO_2 nanocrystals. Charge separation takes place at the interface through photoinduced electron injection from the excited dye into the conduction band of the TiO_2 . Holes are created at the dye ground state, which is further regenerated through reduction by the hole-transport material (HTM), which itself is regenerated at the counterelectrode by electrons through an external circuit. In principle, for efficient DSSCs the regeneration of the sensitizer by a hole transporter should be much faster than the recombination of the conduction band electrons with the oxidized sensitizer. Additionally, the highest occupied molecular orbital (HOMO) of the dye should lie below the energy level of the holetransporter, so that the oxidized dyes formed after electron injection into the conduction band of TiO_2 can be effectively regenerated by accepting electrons from the HTM. The general operating principle of a dye-sensitized solar cell is depicted in Figure 1.1 [10].

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Figure 1.1 Schematic representation of the construction and the operational principle of DSSCs.

The research area dealing with DSSCs is expanding very rapidly and attracting scientist from different disciplines: 1) Chemists to design and synthesize suitable donor-acceptor dyes and study structure-property relationships; 2) physicists to build solar cell devices with the novel materials, to characterize and optimize their performances, and to understand the fundamental photophysical processes; and 3) engineers to develop new device architectures. The synergy between all the disciplines will play a major role for future advancements in this area [9].

1.2.2 Overall efficiency of the photovoltaic cell (η_{cell})

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 DSSCs 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.

The solar energy to electricity conversion efficiency under white-light irradiation (e.g., AM1.5G) can be obtained from the following equation [11]:

$$\eta_{\text{cell}} = \frac{J_{\text{sc}} \cdot V_{\text{oc}} \cdot \text{ff}}{I_0}$$
(1)

Where I_0 (mW/cm²) is the photon flux (e.g., ca. 100 mW/cm² for AM 1.5 G), J_{sc} (mW/cm²) 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 squareness of the *J-V* curve (Figure 1.2).



Figure 1.2 J-V curve.

1.2.3 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. 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- and ground-state redox processes, in order to minimize free energy losses in primary and secondary electron transfer steps [12].

1.2.3.1 Metal complex sensitizers

Sensitizer 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 10.0, 11.2 and 10.8%, respectively (Figure 1.3) [13]. The high efficiencies of the ruthenium(II)-polypyridyl DSSCs can be attributed to their wide absorption range from the visible to the near-infrared (NIR) regime. In addition, the carboxylate groups attached to the bipyridyl moiety lower the energy of the ligand π orbital. Since the electronic transition is a metal-to-ligand charge transfer (MLCT), excitation energy is effectively channeled to the carboxylate group, from which electron injection into the conduction band of the semiconductor takes place. However, the molar extinction coefficients of these dyes are moderate (20000 M⁻¹cm⁻¹ for the longest wavelength MLCT transition) [9].



Figure 1.3 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 [14]) 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.

1.2.3.2 Metal-Free Organic sensitizers

Recently, performances of DSSCs based on metal-free organic dyes have been remarkably improved by several groups. The first transient studies on a coumarin dye in DSSCs was performed in 1996, when Gratzel et al. found injection rates of 200 fs from C**343** into the conduction band of TiO₂. Since C**343** has a narrow absorption spectrum, the conversion

5

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 [15]. 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 [16].





Figure 1.4 Chemical structures of K19, K73, K77 and Ru-1 dyes.



Figure 1.5 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** [17].



Figure 1.6 Chemical structures of D102 and D149 dyes.

In 2007, Yuanzuo Li et al. [18] reported 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%.



Figure 1.7 Chemical structures of JK-1 and JK-2 dyes.

In 2007, Duckhyun Kim et al. [19] 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 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 DSSCs.



Figure 1.8 Chemical structures of JK-24 and JK-25 dyes.

1.2.3.3 Anchoring groups

Most of the dyes employed in DSSCs have carboxylic acid groups to anchor on the TiO₂-surface. The binding is reversible with high binding equilibrium constants $(K = 10^5 \text{ M}^{-1})$. At a pH > 9 the equilibrium is typically shifted to the reactant side and the dye molecules desorbed. 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 [20] 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 TiO₂ semiconductor. Some of the possible modes of chelation/derivatization, ranging from chemical bonding (chelating or bridging mode) to H-bonding, are shown in Figure 1.9 [21].



Figure 1.9 Possible binding modes for carboxylic acid groups on TiO₂.

1.3 Organic Light Emitting Diodes (OLEDs)

Organic light emitting Diodes (OLEDs) have recently received a great deal of attention for their application as full color, flat-panel displays as well as from the standpoint of scientific interest. They are attractive because of low voltage driving, high brightness, capability of multicolor emission by the selection of emitting materials and easy fabrication of large-area and thin film devices [22].

1.3.1 Device structure and operation

The basic OLEDs structure is shown in **Fig.1.10**. The OLEDs structure is similar to inorganic LEDs: an emitting layer between an anode and a cathode. Holes and electron are injected from the anode and cathode. However, there is sometimes difficulty in injecting carriers into the organic layer from the usually inorganic contacts. To solve this problem, often the structure includes an electron transport layer (ETL) and/or a hole transport layer (HTL), which facilitate the injection of charge carriers. The hole transporting layer (HTL) can transport holes from the anode to the emitting layer (EML). The electron transporting layer (ETL) is used to transport electrons from the metal cathode to the EML [23]. The mobility of electrons and holes is different in organic compounds. The key point to operate OLEDs is to control the excitons (electron and hole pairs), so that holes and electrons meet in the emissive layer in equal quantities.



Figure 1.10 Cross-sectional representation of an OLEDs with both ETL and HTL.

1.3.2 Types of devices

The typical structure of molecule OLEDs consists of single or multiple layers of organic thin films sandwiched normally between the transparent indium tin oxide (ITO) glass and vacuum-evaporated metals with low work function such as magnesium/silver (Mg/Ag) or aluminium (Al) [24].

1.3.2.1 Single layer devices

The simplest form of OLEDs is shown in **Figure 1.11**. It consists of a thin film of an organic electroluminescent material a sandwiched between two conducting electrodes upon a substrate. The cathode is usually made from a low work-function metal such as calcium or aluminium. A higher work-function material is used as the anode. For light to leave the device, one of the electrodes must be transparent to the emitted light. Hence materials that are transparent to the desired frequency range of visible light such as polyaniline, indium-tin oxide (ITO) are chosen as the anode [25-27].

When a bias is applied across the device, electrons are injected into the light emitting material near to the cathode to form radical anions. Material near the anode is oxidised, giving radical cations, this is known as hole injection. These charges migrate across the device under the applied electric field where they recombine forming an unstable, neutral, excited state (exciting). The exciton is formed either as a singlet or a triplet spin state, the singlet being the same as the singlet excited state involed in photoluminescence. Radiative relaxation of the singlet exciton ($\sim 10^{-9}$ s) gives photons with a frequency given approximately by the HOMO-LUMO gap of the emissive material. If relaxation of the exciton occurs by a non-radiative pathway, the efficiency of the device is reduced and the resultant heating may cause breakdown of the device and reduct its working lifetime.

The ratio of the number of photons produced to the number of electrons injected into the device is the internal efficiency of the OLEDs. Not all of the emitted photons leave the device, hence the external efficiency, by a factor 2n, where n is the refractive index of the layers. For a material with a typical refractive index of 1.4 [25], the external efficiency is smaller than internal efficiency by a factor of four [26]. Currently, external efficiencies of devices lie within the range 0.1-10%. It is also noteworthy that because of spin statistics, the maximum internal efficiency of an OLEDs decaying from the singlet excited state is restricted to only 25% of the photoluminescence quantum yield of the emissive material [26]. Hence some groups are working on phosphorescent OLEDs materials, where intersystem crossing to and decay from a triplet state is encouraged by the presence of heavy atom.



Figure 1.11 Structure (left) and energy level diagram (right) of single-layer OLEDs

1.3.2.2 Multi-layer devices

In order to attain optimal efficiency for a single-layer device, electrons must be injected by the cathode at the same rate as holes are injected by the anode [26, 28]. For this to be so, the respective barriers to charge injection at the electrons must be either the same or zero. This is normally not the case. For organic electroluminescent materials, for example poly(1, 4-phenylene vinylene), (PPV), hole injection is often predominant and therefore radical cation are the majority charge carriers. Electron injection must be improved to enhance device efficiency. This can be achieved by using a cathode with the lowest possible work-function, so calcium would be a better electron injector than aluminium. Alternatively, incorporation of an additional layer (Fig. 1.12) with an electron affinity equal to or greater than PPV can promote electron injection from the cathode and at the same time provide a barrier to the motion of holes, promoting exciton formation in the light emitting layer. This type of layer is known as an electron-conducting/holeblocking (ECHB) layer [24].



Figure 1.12 Structure (left) and energy level diagram (right) of multi-layer OLEDs.

When the efficiency of a device is limited by hole injection, the inclusion of a suitable hole injection layer can be beneficial. One of the widely used polymers for promoting the hole injection is poly(3,4-ethylenedioxythiophene)–poly(styrene) known as the PEDOT :PSS which has been found to be useful in a hybrid OLED architecture combining both the advantages of polymer LED (PLED) and multi-layered small molecule OLED [25].



Figure 1.13 Chemical structures of conducting polymers.

1.3.3 Previous organic electroluminescent materials

Electroluminescence from organic materials was first discovered in the 1960s when crystals of anthracene were seen to fluoresce when placed under a large (ca. 100 V) potential difference between two metal electrodes [30]. At this time the operating voltages were too high and brightness too low for commercial application, so organic materials could not complete with the recently available inorganic LED.

In following years, much work was done on the electroluminescence of evaporated thin films of molecular materials. In 1985, Tang accomplished electroluminescence from a thin of vapor deposited aluminium tris-8-hydroxyquinoline (Alq₃) in a two layer device with an external efficiency of 1% [31].

In 1990 electroluminescence was reported from the conjugated polymer PPV [31]. This discovery gave fresh impetus to the development of new materials for use in LEDs, and of LED displays themselves, as a feasible and attractive alternative to the existing display technologies.





1.3.3.1 Low molecular weight materials

Since the first report of multi-layered organic light-emitting diodes (OLEDs) using low molecular weight molecules by Tang and Van Slyke [32] electroluminescent (EL) devices have been developed remarkably because they have applications in full-color flatpanel displays [33–35]. Many studies focused on improving device efficiency and enhancing the durability of OLEDs. High-performance EL devices are composed of thin organic multi-layers, viz. the hole-transporting layer (HTL), electron-transporting layer (ETL) and emission layer (EML). For the fabrication of highly stable OLEDs, low molecular weight materials with specific optical and electronic properties, such as fluorescence, energy levels, charge mobility, etc., and high morphologic stability are required [36-38]. The thermal stability of materials used in OLEDs, particularly hole-transporting material, is one of the significant factors of the device durability. Under thermal stress, most organic materials tend to turn into the thermodynamically stable crystalline state, which leads to device failure [39, 40]. A considerable amount of evidence indicates that an amorphous thin film with a high glass transition temperature (T_g) is more stable to heat damage [41–45]. For the hole-transport layer, high thermal stability, especially high T_g of above 100 °C, good hole-transport ability, excellent film formability are essentially needed.

Amorphous molecular materials or molecular glasses are of interest because of the following aspects. They are in a thermodynamically non-equilibrium state and hence may exhibit glass-transition phenomena usually associated with amorphous polymers. The T_g of molecular glasses is understood as the temperature at which molecular motions of a group of molecules, which are caused by intramolecular bond rotations, start to take place, resulting in a change in the position of the gravity of molecules. It is thought that they assume a variety of states such as the amorphous glass, supercooled liquid, and crystal. They may be characterized by the presence of free volume and by the disorder of both intermolecular distance and orientation. They may form uniform, transparent amorphous thin films by vapor deposition and spin-coating methods. In contrast to single crystals and liquid crystals, which show anisotropic properties, amorphous molecular materials may exhibit isotropic properties as well. The example of low molecular weight electroluminescent materials are depicted in Figure 1.15 [46-49].



Figure 1.15 The example of low molecular weight electroluminescent materials.

1.3.3.2 Conjugated organic polymers

In the late 1970s, conjugated polymers were proclaimed as futuristic new materials that would lead to the next generation of electronic and optical devices. It now appears with the discoveries of, for example, organic transistors [50], polymer light-emitting diodes (OLEDs) and solar cells that new technologies are imminent. It has become apparent, from this large body of work, that extensive delocalization of electrons along the polymer backbone is necessary for a polymer to behave as semiconductor or even as an electrical conductor. This delocalization of electrons may occur through the interaction of π -electrons in a highly conjugated chain or by a similar interaction of π -electrons with non bonded electrons of atoms such as sulphur and nitrogen in the backbone. In that way electrochemical polymerization of aromatic compounds such as thiophene [51], furan, indole [52], carbazole, azulene, pyrene [53], and benzene [54]. Conjugation has been rapidly extended. Polypyrrole, polyaniline and their derivatives are the most commonly used conjugated polymers because of their relatively superior stability [55]. Other examples include poly(p-phenylene vinylene)s (PPVs), polyfluorenes and polyalkylthiophenes. For some time the application of conjugated polymers has been limited due to their intractability and insolubility, especially in the doped state. This problem was overcome by

the use of substituted monomers [56, 57], which not only produced processable polymers, but also allowed the polymers obtained to be fully characterized by chemical and physical methods. Conjugated polymers are also widely exploited because of their special characteristics such as low densities, mechanical strength, ease of fabrication, flexibility in design, stability, resistance to corrosion and low cost.

The performance of OLEDs is related to three main technological issues: 1) color range, 2) electroluminescence efficiency, 3) realiability or stability. The color of OLEDs depends on the molecular compositions of the organic interface. The luminance efficiency can be improved by incorporating phosphorescent dyes as dopants in an emitting layer and, thus, exploiting the energy transfer from the singlet state of the host to the triplet state of the phosphorescent emitter to obtain electrophosphorescence [58]. But this concept demands the use of additional layers/components of host and blocking materials and the realization of an almost perfect match of energy levels in the various materials involved in order to guarantee a high degree of energy transfer to the triplet emitter. Moreover, phosphorescent emitter has to be doped into a host material to avoid any triplet-triplet annihilation and the recombination zone has to be confined to the doped layer. This has been successfully demonstrated in devices prepared by vapor deposition of low molar mass compounds as well as doped systems in polymer blends [59, 60]. This is, at present, one of the most attractive strategies to obtain highly efficient devices with emission in the green to red region. The reliability of OLEDs and other electro-optical devices, is a key source for the sceptical approach in the photonics community. The main cause of the reliability problem is the degradation of organic molecules. Many groups are addressing this issue and one solution is to introduce stabilizing agents and efficient sealing methods. Another reliability problem relates to deterioration of the active cathode. Engineering tools have been used to deal with this issue.

For the fabrication of high-performance OLEDs, an understanding of basic processes, such as charge injection from the electrodes, charge transport, recombination of charge carriers to generate the electronically excited-state molecule as well as development of new materials with high performance and judicious choice of the combination of emitting and charge transporting materials and the combination of emitting and luminescent dopant molecules, are of vital importance. For this purpose, not only emitting materials but also charge transporting

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materials are also required. Both polymers and small molecules are candidates for materials in OLEDs.

The materials for OLEDs should meet the following requirements [61]: possess a suitable ionization potential and electron affinity in order to match energy levels for the injection of charge carriers at electrode/organic material and organic material/organic material interfaces, permit the formation of a uniform film without pinholes, morphological stability, thermal and electrochemical stability, and also high luminescence for emitting materials. In addition, doping of luminescent compounds has been shown to be an effective method for attaining high brightness and desirable emission color.

1.3.3.3 Dendrimer

Dendrimers are now an important class of light-emitting material for use in organic light-emitting diodes (OLEDs). Dendrimers are branched macromolecules that consist of a core, one or more dendrons, and surface groups. The different parts of the macromolecule can be selected to give the desired optoelectronic and processing properties. The first light-emitting dendrimers were fluorescent but more recently highly efficient phosphorescent dendrimers have been developed. The solubility of the dendrimers opens the way for simple processing and a new class of flat-panel displays. The dendrimer comprises a core to which one or more dendrons (branched structures) are attached. The dendrons themselves can have two components, the branching units and linking moieties. The number of levels of branching is called the generation of the dendrimer. To improve the solubility and processability, surface groups are often attached to the distal (outer) ends of the dendrons. The emissive chromophores of the dendrimers can be located at the core of the dendrimer, within the dendrons, and/or at the surface of the dendrimers. All these strategies have been investigated with the most successful approach being where the core is the light emitting component. OLEDs containing light-emitting dendrimers have been reported to have external quantum efficiencies of up to 16 %. Some light-emitting dendrimers are depicted in Figure 1.15 [62, 63].



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1.3.4 Hole transport materials

The Hole Transporting Material (HTL) is very common in small-molecule-based OLED devices but are less common in polymer-based devices because conjugated polymers are usually good hole conductors themselves. They serve to provide a hole-conductive (via charge hopping) pathway for positive charge carriers to migrate from the anode into the EML. On the basis of this requirement, HTMs are usually easily oxidized and are fairly stable in the one-electron oxidized (radical-cation) form. This further translates into the materials having a fairly shallow HOMO energy level-preferably isoenergetic with the anode/HIL WF and somewhat lower in energy than the HOMO energy level of the EML. This latter property improves the chances of charge flow into the EML with minimal charge trapping. As the main function of the HTL is to conduct the positive charge carrier holes, hole-traps (higher energy HOMO materials) should be avoided either in the bulk of the material (i.e., hole-trapping impurity levels <<0.1% are typically required) or at interfaces. Another, perhaps less commonly appreciated, function of the HTL is that it should act as an EBL to prevent the flow of electrons from the EML and ultimately to the anode. For this purpose, a very shallow LUMO level is desirable. Some favorable HTL are given in Figure 1.17 [64, 65].



Tg: 95 °C HOMO: -5.70 eV; LUMO: -2.60 eV



 $T_g:$ 152 °C HOMO: -XXX eV; LUMO: -XXX eV

Tg: 65 °C HOMO: -5.50 eV; LUMO: -2.30 eV



m-MTDATA: Tg: 75 °C HOMO: -5.10

Figure 1.17 Example of efficient hole transporting materials.

1.4 Motivation and aims

The development of novel organic materials for optoelectronic applications has attracted a lot of interest both industry and academic. Especially in the area of organic light emitting diodes (OLEDs) and dye sensitized solar cells (DSSCs), hugs process has been made. One of main technology attractions of organic electronics that the active layers can be deposited at low temperatures by liquid phase techniques. This makes organic semiconductors ideal candidates for low-cost, large-area electronic applications on flexible substrates. The creation of novel photo and electro-active organic materials and their structures, reactions, properties, functions and applications for electronic and optoelectronic devices have widely been investigated. Therefore this thesis reports the development of the synthesis and characterization of novel organic materials for application in organic light emitting diodes (OLEDs) and dye sensitized solar cells (DSCs). The aims of this thesis are follows:

1.4.1 To synthesize the new series of carbazole-triphenylamine dyes, carbazolediphenylamine dyes, carbazole donor diaccepter dyes as well as (pyrane-4-ylidine)malononitrile derivatives as organic dye sensitizer for dye-sensitized solar cell.

1.4.2 To synthesize the novel Donor-Accepter-Donor type emitting materials for organic light emitting diodes

1.4.3 To characterize and study the elctronic, photophysical, electrochemical and thermal properties of the target molecules.

1.4.4 To investigate their device performance as in DSSCs and OLEDs application.

CHAPTER 2

SYNTHESIS AND CHARACTERIZATION OF CARBAZOLE-TRIPHENYLAMINE DYES FOR DYE-SENSITIZED SOLAR CELLS

2.1 Introduction

Due to its excellent properties in elctron donating ability, triphenylamine (TPA) have been widely used in organic material field such as hole transporting material in OLEDs or dyesensitizer in DSSCs [66]. Among the recently developed metal free organic dyes, triphenylamine dyes have displayed promising performance in the development of photovoltaic devices. Theoretical and experimental studies have demonstrated that TPA can be used as the efficient dye sensitizers due to its non-planar structure that can suppress the dye aggregation or its optical properties that can increase the light harvesting ability [67]. Various types of TPA derivatives were reported in term of molecular structure development related to their performance in DSSCs. For example the simple structure of TPA dyes (11-14) were first reported as dye sensitizer by Jun Chen in 2007 [68]. The structure of previous TPA dyes are shown in Figure 2.1. The dyes were designed with TPA as electron donor, rhodanine-3-acetic acid as electron accepter and allylene group as π -spacer. The dyes with short and simple structure show promising cell performance when the conjugation of the molecule was extended by introducing more double bond. One year later then, they reported TPA dyes (15 and 16) with different electron accepter cyanoacrylic acid group replacing rhodanine-3-acetic acid [69]. Compound 16 with cyanoacrlic acid accepter exhibits better conversion efficiency compared to compound 14 which has the same chromophore.

After then TPA dyes have been attracted an attention as efficient dye sensitizer evidenced by many reports in TPA dyes development. Chul hee Kim and co-worker [70] report an efficient TPA dye with structure of TPA as donor, thiophene and phenylene as π -conjugated linker and cyanoacrylic as electron accepter (17 and 18) and the dyes exhibit excellent overall solar-toelectricity conversion efficiency of 9.1% equivalent to 90% of N3 dye (η 10.1%). At the same period Pi-Tai Chou and Yun Chi [71] reported modified TPA dyes by using thiophene derivatives, 3,4-ethylenedioxythiophene and bis[2-(2-methoxyethoxy)ethoxy]thiophene as π -spacer (19 and 20) and found that the introduction of ester moieties in π -spacer increase the spectral response and renders a better degree of charge separation, resulting in a leap in photovoltaic performance in comparison to its parent compound (Fig. 2.1) More over the two different electron accepters, cyanoacrylic acid and rhodanine-3-acetic acid, were investigated. Although the rhodanine-3-acetic acid dye exhibits good spectral features and large molar extinction coefficient, the photovoltaic performance are smaller than that of cyanoacetic acid dyes. This results can confirmed that rhodanine-3-acetic acid is poor anchor in comparison to cyanoacrylic acid.



Figure 2.1 The structure of some triphenylamine dyes.

21

The molecular engineering of dyes is the main effort to get the excellent dyes with excellent optical and electrical properties of the dyes. He Tian and his coworker [72] reported starburst triphenylamine based dyes with double donor moiety (D-D- π -A); modified triphenylamine as donor, 5,5-dimethylcyclohexenyl-2,4-diene as π -spacer and cyanoacrylic acid as accepter (Fig. 2.2) and found that the introduction of starburst carbazole-triphenylamine group as double electron donor (23) brought about improved photovoltaic performance comparing with the single triphenylamine unit (21). It might be described as the steric starburst carbazole-triphenylamine donor suppress the dye aggregation which decrease the DSSCs performance.



Figure 2.2 TPA dyes with extended π -spacer cyclohexylene linker.

2.2 Target dyes and Aims

Due to the promising donor ability of triphenylamine, we have designed the target dyes with TPA donor co-operate with two carbazole for the purpose of prevent dye aggregation and increasing donor ability. Therefore the objectives of this chapter are:

2.2.1 To synthesize dyes containing carbazole-triphenylamine as double electron donor, oligothiophene (thiophene 1-3 units) as π -conjugated bridge and cyanoacrylic acid as electron accepter.

2.2.2 To study the effect of π -conjugation in the spacer to optical, electrochemical and thermal properties of the dyes by varying thiophene unit.

2.2.3 To fabricate DSSCs devices based on the synthesized dyes and investigate their device performance.



Figure 2.3 Chemical structure of target dyes (TPA1-TPA3).

2.3 Results and discussion

2.3.1 Synthesis

The Carbazole-Triphenylamine dyes **TP1-TPA3** have been synthesized using a combination of Bromination, Suzuki coupling, Ullmann coupling and Knoevanegel reaction as depicted in scheme 2.1, 2.2 and 2.3.





The carbazole-triphenylamine donor (26) was synthesized by Ullmann coupling reaction between 3,6-di-*tert*-butylcarbazole (25) and tris(4-iodophenyl)amine (24) using copper

iodide as catalyst, (\pm) -*trans*-1,2-diaminocyclohexane as co-catalyst, potassium phosphate as base in toluene under reflux condition (Scheme 2.1). The mole equivalent of 3,6-di-*tert*-butylcarbazole and tris(4-iodophenyl)amine was used to be 2:1 to control the substitution of carbazole moiety in product. In this condition, di-substituted triphenylamine was obtained as major product in 48% yield, whereas the mono- and tri-substituted triphenylamine were obtained as by product in 31% and 27% yield, respectively.

The structure of compound 26 was confirmed by NMR, IR and mass data (see chapter 8). The H¹-NMR spectrum of intermediate 26 exhibits the strong singlet signal at chemical shift 8.37 ppm (4H) which was assigned as the proton at position 4 and 5 of carbazole moiety (proton c). Whereas the doublet signal at chemical shift 7.80 ppm (2H, J = 7.2 Hz) was assigned as two protons in phenyl iodide ring (proton a). The doublet signal at chemical shift 7.20 ppm (2H, 7.2 Hz) that couplet with proton (a) was assigned to proton (b) due to their equal coupling constant of 7.2 Hz. The overlapping peaks at chemical shift around 7.50-7.68 ppm are assigned as other protons in carbazole and TPA moieties. The protons of four t-butyl groups was clearly located at chemical shift 1.68 (s) equivalent to 36 protons can be confirmed the introduction of two carbazole moiety to TPA. Moreover the successful synthesis of this donor moiety was also confirmed by HRMS which indicated the molecular ion of the product at m/z 926.3902.



Figure 2.4 H¹-NMR spectrum of intermediate 26 in CDCl₁.

To extend the conjugation of the dyes, oligothiophene was introduced to TPA donor using combination reaction of Suzuki coupling and bromination. Monothiophene intermediate (27) was prepared by coupling reaction between triphenylamine donor (26) and 2-thiopheneboronic acid using Tetrakis(triphenylphosphine)Palladium(0) as catalyst, sodium carbonate as base in THF/H₂O at reflux. The product was obtained in this condition in good yield. Next step, *N*-bromosuccinamide bromination of the resultant thiophene intermediate (27) in THF afforded bromothiophene intermediate (28) in excellent yield. To introduce more thiophene, the repeating step of Suzuki coupling and bromination were incorporated.



Scheme 2.2 Synthetic route to olithiophene intermediate (mono and bisthiophene (27, 28), and brominated thiophene (29, 30).

The structures of all thiophene intermediate (27-30) were confirmed by NMR, IR and mass data. Although the H¹-NMR spectra of compounds elongated with thiophene units are quite more complicated than compound 26. The singlet signal at chemical shift around 8.3 ppm (4H) of proton c of carbazole moiety was clearly shown. But the other aromatic signals were overlap with each other that make it difficult to assign. However the protons of four t-butyl groups were still present at chemical shift 1.68 ppm. Therefore the structures of thiophene intermediate were confirmed by HRMS which indicate the molecular ion of compound 27, 28, 29 and 30 at m/z 882.4819, 964.4637, 961.3908 and 1044.3773, respectively. The aldehyde intermediate **31**, **32** and **33** were then formed in reasonable yield by Suzuki coupling condition of corresponding halide **26**, **29**, **30** with 5-formyl-2-thiophene boronic acid as described above. The successful introduction of aldehyde functional group was clearly confirmed by NMR and IR spectra. The singlet signal of aldehyde proton (measured in CDCl₃) was located at chemical shift 9.89, 9.87 and 9.88 for aldehyde protons of compound **31**, **32**, **33**, respectively. The dominant IR peaks of C=O stretching of aldehyde was also observed at wavenumber 1670, 1665 and 1665 cm⁻¹ for compound **22-24**. From spectroscopic data, the aldehyde groups were successfully incorporated to the molecules.



Scheme 2.3 Suzuki coupling reaction of aldehyde intermediate (22, 23, 24).





Final step in synthesis of target dyes, Knoevenagel condensation of resultant aldehydes (**31-33**) with 2-cyanoacetic acid in the presence of piperidine as base in chloroform gave desired organic dyes **TPA1-TPA3** as orange, red and dark red solids, respectively in moderate yield. The structures of target dyes were confirmed by NMR, IR and mass spectra. The IR spectra of all dyes exhibit C=N stretching of cyanoacrylic acid as sharp peaks at wavenumber 2200 cm⁻¹ indicate the cyanoacrylic acid group in the dye molecules. The H¹-NMR spectra measured in DMSO-d6 show singlet signal of allylic proton of acrylic acid group at chemical shift 8.17, 8.00 and 8.05 ppm for **TPA1**, **TPA2** and **TPA3**, respectively. The other protons that indicate the chemical structure of donor and thiophene spacer of this series such as four protons of carbazole moieties, doublet protons of phenyl ring and 36 protons of four t-butyl groups are still be observed.



Scheme 2.4 Synthesis of target dyes (TPA1-TPA3) by Knoevanegel reaction.



Figure 2.6 H¹-NMR spectrum of TPA1 in DMSO-d6.

2.3.2 Optical Properties

The absorption spectra of carbazole-triphenylamine dyes measured in dichloromethane solution and adsorbed on TiO₂ thin film are shown in Figure 2.7. In solution, all three dyes show similar characteristic of donor-accepter arylamine dyes which show strong absorption bands around 290-350 nm corresponds to π - π * transition and broad absorption bands around 400-550 nm corresponds to Intramolecular Charge transfer Transition (ICT) of donor-accepter compound [73]. The bathochromic shifted (red shifted) absorption spectra and larger molar extinction coefficient (ϵ) (Table 2.1) were observed when more thiophene units were introduced. The red shift in absorption can be attributed to the extended conjugation system of the entire structure. Moreover, the ϵ values of the ICT bands of these dyes are considerably larger than that of the Ru dye (N3, $\lambda_{s30 \text{ nm}} = 14500 \text{ M}^{-1} \text{ cm}^{-1}$), indicating good light harvesting ability.

On the other hand, comparing to their absorption spectra in solution, the dyes adsorbed on TiO₂ exhibit slightly hypsochromic shifted or blue shifted (13-20 nm) which indicate strong interactions between dyes and semiconductor surface. Such phenomenon is commonly observed in the spectral response of other organic dyes, which may be ascribed to the H-aggregation of the dye molecules on the TiO₂ surface and/or the interaction of the anchoring groups of the dyes with the surface of TiO₂ [74]. The blue shift absorption of the dyes bonded to TiO₂ film can be observed in general type of acrylic anchoring group [21]. From absorption spectra of dyes in dichloromethane solution, the energy gab of all dyes can be calculated from λ_{onset} from formula $E_g = 1240/\lambda_{onset}$ and the calculated data are shown in Table 2.1.



Figure 2.7 Absorption spectra of TPA1-TPA3; (A) measured in CH₂Cl₂ (B) dyes adsorbed on TiO₂ film.

The fluorescence emission spectra of the dyes in CH_2Cl_2 (Fig. 2.8) showed a red-shift upon increased number of thiophene units in the molecule, which is roughly parallel to the trend of the absorption spectra (Figure 2.7(A)). The stroke shift between absorption and emission spectra range between 60-100 nm.



Figure 2.8 (A) Fluorescence spectra of TPA1-TPA3 measured in CH₂Cl₂ solution.
(B) Absorption and emission spectra of TPA1 indicated stroke shift.

l'able 2.1	Optical	properties data	of TPA1-TPA3.
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compound	λ_{max}^{abs}/r	$\lambda_{_{onset}}^{_{abs}}$	λ_{max}^{em}	Eg	
	solution [*]	Adsorbed on TiO ₂ ^b	(nm) ^a	(nm) ^{a,c}	(eV) ^d
TPA1	331 (33,059)	437	553	585	2.24
	458 (22,860)				
TPA2	339 (32,319)	440	564	595	2.20
	455 (26,500)				
TPA3	339 (32,318)	449	587	584	2.11
	464 (30,900)				

^a measured in dichloromethane solution at room temperature.

^b measured dyes adsorbed on TiO_2 film.

 $^{\circ}$ excited at maximum absorption in solution.

 d estimated from the onset of absorption (E $_{g}$ =1240/ λ_{onset}).

2.3.3 Electrochemical properties

The electrochemical properties of the dyes were studied by CV in CH_2Cl_2 solution with 0.1 M n-Bu₄NPF₆ as a supporting electrolyte. The results are shown in Figure 2.9 and all data are listed in Table 2.2. The CV curves of all dyes exhibited multi quasireversible oxidation and one irreversible reduction processes. The reduction wave was attributed to the reduction of the cyanoacrylic acid acceptor moiety, which was in the range of -1.55 to -1.86 V. The first oxidation wave of TPA dyes corresponded to the removal of electrons from the peripheral carbazole donor moieties to give radical cation. The first oxidation potentials decreased from 0.88, 0.83 to 0.78 V when a number of thiophene units in the molecule or length of the π -conjugated spacers increased from TPA1, TPA2 to TPA3, respectively, as observed in other oligothiophenes [75]. The multiple CV scans of TPA dyes revealed identical CV curves with no additional peak at lower potential on the cathodic scan (E_{pc}) being observed. This indicates that no oxidative coupling at the 3,6 positions of the peripheral carbazole led to electro-polymerization was taken place. This is due to the present of 3,6-di-tert-butyl groups. This type of electrochemical coupling reaction can be detected in some carbazole derivatives with unsubstituted 3,6-positions and might be occurred upon charge separation, which hampers the dye regeneration [76]. Therefore, it is important that the dyes are electrochemically stable molecules.

The HOMO and LUMO energy levels of the dyes calculated from the onset potential of the CV curves are summarized in Table 2.2. The HOMO of **TPA1** (-5.22 eV) was lower than those of both **TPA2** (-5.20 eV) and **TPA3** (-5.16 eV), but all were much lower than the redox potential of the I/I_3 couple (-4.8 eV), therefore, dye regeneration should be thermodynamically favorable and could compete efficiently with the recapture of the injected electrons by the dye radical cation. The LUMOs (-2.97 - -3.03 eV) of these dyes calculated from the HOMOs and energy gaps (E_g) estimated from the optical absorption edge were less negative than the conduction band of the TiO₂ electrode (-4.4 eV *vs* vacuum) [77] and the LUMO of **N3** dye (-3.84 eV) [78]. To ensure efficient charge injection the LUMO level of dye should be >0.3 eV above the conduction band of the TiO₂. Therefore, all dyes have sufficient driving force for electron injection from the excited dyes to the conduction band of TiO₂. As a result, **TPA** dyes have enough energetically driving force for efficient DSSCs using a nanocrystalline titania photocatalyst and the I/I_3 redox couple.



Fugure 2.9 (A) Cyclic voltamogram of TPA1-TPA3 in dry CH_2Cl_2 with scan rate of 0.05 V/s and 0.1 M n-Bu₄NPF₆ as electrolyte. (B), (C) and (D) Multiple scan Cyclic voltamogram of TPA1, TPA2 and TPA3, respectively.

Dyes	E ^{ox} _{onset} (V) ^a	HOMO (eV) ^c	LUMO (eV) ^d
TPA1	0.88	-5.22	-2.79
TPA2	0.83	-5.20	-2.96
TPA3	0.78	-5.16	-3.03

 Table 2.2 Electrochemical properties and energy level of carbazole-triphenylamine dyes.

^a measured using glassy carbon electrode as a working electrode, a platinum rod as a counter electrode, and Ag/Ag^{+} as a reference electrode in CH_2Cl_2 solution containing 0.1 M n-Bu4NPF as supporting electrolyte.

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

^c calculated from LUMO = HOMO + E_g .



Figure 2.10 Energy diagram indicated HOMO/LUMO levels of TPA1-TPA3.

2.3.4 Quantum chemical calculation

To gain insight into the geometrical, electronic and optical structures of the dyes, quantum chemical calculation was performed using TDDFT/B3LYP6-31G (d.p) method. The results are shown in Figure 2.11 and 2.12. A major factor for low conversion efficiency of many organic dyes in DSSCs is the formation of dye aggregation on the semiconductor surface. We therefore designed bulky donor moiety making up of two 3,6-di-tert-butylcarbarzole units connected to triphenylamine unit to perform steric hindrance part (starburst donor) of the molecule. The optimized structures of TPA3 revealed that the dihedral angles formed between carbazole (D1) and phenyl (Ph) planes in all molecules were as large as 54.34-55.63° resulting bulky structure, which could help to prevent the close π aggregation effectively between the dye molecules. The non-coplanar geometry can also reduce contact between molecules and enhance their thermal stability. The aromatic rings of the π -conjugated spacers adopted more planar conformation with the dihedral angles of the benzene and thiophene (T1) planes ranging from 19.60 to 22.80°, and the thiophene (T_1) and thiophene (T_2, T_3) planes (TPA2 and TPA3) ranging from 4.23 to 10.54°, whereas the thiophene (T_3) and acrylic acid (A) planes were nearly coplanar (dihedral angle $< 0.15^{\circ}$). This suggests that π -electrons from the donor moiety can delocalize effectively to the acceptor moiety, which subsequently transfer to the conduction band of TiO_2 .



Figure 2.11 Schematic views of the ground state structures for TPA3.

The molecular orbital distribution is very important in determining the chargeseparated states of organic dyes. The electron distributions of the HOMO and LUMO of **TPA** dyes are shown in Figure 2,12. To create an efficient charge-transfer transition, HOMO must be localized on the donor unit and LUMO on the acceptor unit. The HOMOs of these compounds were delocalized over the donor moiety. In **TPA1-TPA3** dyes, the major contribution of the donor moiety comes from both triphenylamine and each peripheral carbazole. The LUMOs were delocalized across the oligothiophenes and cyanoacrylic acid acceptor. The results indicate that the distribution of the HOMO and LUMO of all dyes is well-separated suggesting the HOMO-LUMO transition and can be considered as an ICT transition.

As expected, the calculated HOMOs, LUMOs and energy gaps (E_g cal) of TPA dyes decrease when increasing a number of thiophene units in the molecule, in agreement with experimental absorption spectra and electrochemical results. These E_g cal values were slightly higher than those estimated from the optical absorption edge (E_g) (Table 2.3). There are factors responsible for the errors because the orbital energy difference between HOMO and LUMO is still an approximate estimation to the transition energy since the transition energy also contains significant contributions from some two-electron integrals. The real situation is that an accurate description of the lowest singlet excited state requires a linear combination of a number of excited configurations.



Figure 2.12 Molecular orbital of TPA dyes relevant ground state and excited state.

Table 2.3 Calculated HOMO and LUMO g	ab.
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		Gas			DCM	<u></u>
Compounds	НОМО	LUMO	Eg	НОМО	LUMO	Eg
	(eV)	(eV)	(eV)	(eV)	(eV)	(eV)
TPA1	-5.24	-2.73	2.51	-5.05	-2.67	2.38
TPA2	-5.16	-2.83	2.33	-4.97	-2.78	2.19
TPA3	-5.10	-2.88	2.22	-4.91	-2.83	2.09

2.3.5 Thermal Properties

For optoelectronic applications, the thermal stability of organic materials is crucial for device stability and lifetime. The degradation of organic optoelectronic devices depends on morphological changes resulting from the thermal stability of the amorphous organic materials [79]. Figure 2.13 and Table 2.4 show TGA thermograms and T_{sd} of **TPA1-TPA3** dyes investigated by TGA analysis under nitrogen atmospheric condition. Those results suggested that the dyes were thermally stable materials with temperature at 5% weight loss (T_{sd}) well over 285 °C. The better thermal stability of the dye is important for the lifetime of the solar cells.



Figure 2.13 TGA thermograms of TPA1-TPA3 dyes.

2.3.6 Dye Adsorption Kinetic on TiO₂

The performance of a DSSC is not only based on the absorption of the harvesting dye but also on the total amount of dye present. Therefore, the dye uptake was determined using spectrophotometric measurements of UV-Vis absorption according to the reported method [80]. Figure 2.14 shows the dye uptake profiles as a function of time and absorption spectra in different concentration for **TPA1-TPA3** dyes. In all cases, dye uptake markedly increased at the beginning until it reached a plateau at about 30 h. These profiles are typical for organic adsorbates into nanoporous inorganic matrices [81]. It was found that at the equilibrium maximum uptakes of each dye were 44.44×10^{15} , 50.65×10^{15} , and 53.90×10^{15} molecules cm⁻² for **TPA1, TPA2** and **TPA3**, respectively. In view of the lower dye uptake of **TPA1** dye on the TiO₂ film compared to others, such a result can be rationalized by steric hindrance of the donor moiety around the carboxylic acid anchoring group, which arises from a considerably shorter π -spacer of **TPA1** as shown in Figure

2.15. As a result, **TPA2** and **TPA3** dyes with longer π -conjugated spacers have more space to accommodate the donor moiety allowing larger dye uptake.



Figure 2.14 (A) The adsorption data for the dyes onto TiO₂ films measured over a period of 50 h at room temperature, (B), (C) and (D) the absorption spectra of TPA1, TPA2 and TPA3 in various time.



Figure 2.15 The space-filling molecular models of the optimized conformation of the dyes.

2.3.7 Cell performance

Typical DSSCs devices with effective area of 0.25 cm² were fabricated using **TPA1-TPA3** 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 I₂ (0.1 M), LiI (0.1 M) and t-butyl-pyridine (0.5 M) in acetonitrile solution was used as an electrolyte system. The photovoltaic parameters under a solar condition (AM 1.5) are summarized in Table 2.5. *I-V* curves of all dyes are shown in Figure 2.16 (B) whereas plots of Incident Photon-to-current conversion efficiency (IPCE) at various wavelengths are given in Figure 2.16(A). The IPEC spectra of the dyes lie in blue/green regions implied by their absorption spectra and show maximum IPCE larger than N3. TPA2 based device with 2 thiophene units exhibit the best maximum IPCE of 86%, whereas TPA3 dyes exhibit the broadest spectra among three dyes. Comparing to the N3 reference dye, it shows very broad IPEC spectrum almost reach 750 nm which indicate the high performance of photon absorption which is normally observed in Ru complex dyes.

Under continuous visible-light irradiation (AM 1.5G, 100 mWcm⁻²), the **TPA3**sensitized DSSCs showed the highest η among three dyes and gave a short-circuit photocurrent density (J_{sc}) of 9.98 mAcm⁻², open-circuit voltage (V_{∞}) of 0.70 V, and fill factor (*FF*) of 0.67, corresponding to a η of 4.62%. The J_{sc} and η values of the DSSCs were in the order of **TPA3** (9.98 mA cm⁻², 4.62%) > **TPA2** (9.02 mA cm⁻², 4.34%) > **TPA1** (7.53 mA cm⁻², 3.70%). The larger J_{sc} and η of **TPA3** cell demonstrates the beneficial influence of the red-shifted absorption spectrum and the broadening of the IPCE spectrum of **TPA3** on TiO₂ film. Whereas the lower efficiency of the **TPA1**-based cell could be attributed to both the poorer spectral response and the lower dye content on TiO₂ film. The use of *tert*-butyl groups as the substituents on the peripheral carbazole might also play the role in shielding the TiO₂ surface from $1/I_3$ in the electrolyte and thus reduce the charge recombination or dark reaction. The efficiency of **TPA3**-sensitized DSSC reaches 89% of the reference N3-based cell ($\eta = 5.20\%$). Interestingly, **TPA1**-based cell also has efficiency reaching >71% of the N3-based cell even though **TPA1** dye had a lower IPCE value and narrower IPCE spectrum than those of both **TPA2** and **TPA3**.



Figure 2.16 IPCE spectra (A) and *I-V* characteristic (B) of TPA1-TPA3.

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 Table 2.4
 Performance parameters of DSSCs constructed using TPA dyes.

Dye	Dye uptake ^a	IPCE	J_{sc}	V _{oc}	FF	η
	(x10 ¹⁵ molecule.cm ⁻²)	(%)	(mA.cm ⁻²)	(V)		(%)
TPA1	44.44 ± 1.95	78	7.53	0.72	0.69	3.70
TPA2	50.65 ± 1.81	86	9.02	0.71	0.68	4.34
TPA3	53.90 ± 0.50	80	9.98	0.70	0.67	4.62
N3	55.13 ± 1.02	68	12.18	0.65	0.66	5.20

2.4 Conclusion

We report here on the synthesis and photophysical/electrochemical properties of a series of novel starburst 2D-D- π -A carbazole-triarylamine based organic dyes (TPA1-TPA3) as well as their application in dye-sensitized nanocrystalline TiO₂ solar cells (DSSCs). For the three designed dyes, the carbazole-triarylamine, thiophene and the cyanoacetic acid take the role as electron donor, π -spacer and anchoring group, respectively. It was found that the introduction of two carbazole moieties to form the 2D-D- π -A configuration brought about superior performance, in terms of bathochromically extended absorption spectra, enhanced molar extinction coefficient, dye aggregation prevention and better thermo-stability. Moreover, the HOMO and LUMO energy levels tuning can be conveniently accomplished by alternating the donor moiety, which was confirmed by electrochemical measurements and theoretical calculations. The DSSCs based on the dye TPA3 showed the best photovoltaic performance: a maximum monochromatic incident photon-to-current conversion efficiency (IPCE) of 80%, a short-circuit photocurrent density (J_{sc}) of 9.98 mA cm², an open-circuit photovoltage (V_{oc}) of 0.70 V, and a fill factor (FF) of 0.67, corresponding to an overall conversion efficiency (η) of 4.62% under 100 mWcm⁻² irradiation. This work suggests that the dyes based on 2D-D- π -A structure are promising candidates for improvement of the performance of the DSSCs.

CHAPTER 3

SYNTHESIS AND CHARACTERIZATION OF CARBAZOLE-DIPHENYLAMINE DYES FOR DYE-SENSITIZED SOLAR CELLS

3.1 Introduction

Although the diphenylamine moiety have not much gained popularity on field of organic optoelectronic devices comparing to triphenylamine, the diphenylamine unit have attracted our consideration because of its donor ability and its non-planar structure. There are some reports that study the properties of diphenylamine encaped-carbazole (**33**) and biscarbazole (**34**) as hole transporting materials (Figure 3.1) [83, 84]. Compounds show glass-forming characteristic with glass-transition temperatures in the range of 72–128 °C characterized by differential scanning calorimetry. The electron photoemission spectra of the materials have been recorded and the ionisation potentials of 5.25–5.30 eV have been established. Room temperature hole-drift mobility in the amorphous film of 6,6-di(*N*-dimethylphenylamino)-9,9-butyl-3,3-bicarbazole (**34**) established by the time-of-flight technique approaches 10^{-6} cm²/Vs at an applied electric field of 6.4×10^{5} V/cm.



Figure 3.1 Structure of diphenylamine encaped-cabazole (33) and biscabazole (34).

The low molecular weight organic compounds called molecular glasses from carbazole encaped-diphenylamine (35) and ((diphenyl)amino)phynylamine (36) were reported as hole-transporting materials by J.V. Grazulevicius and co-worker [85]. The compound are found to be

good amorphous hole transporting molecules with hole drift mobility in the range of 10^{-4} - 10^{-6} cm²/Vs at the applied field of 3×10^{5} V/cm.



Figure 3.2 structure of 4,4-(diphenylamino)diphenylamine (35) and

4,4-dicarbazolediphenylamine (36)

T.K. Kinstle and co-worker [86] reported novel series of donor-accepter molecules having diphenylamine/triphenylamine donor, phenyl-ethynyl-carbazole linkers attached to a terminal malononitrile acceptor (**37** and **38** in Fig. 3.3). The compounds incorporated with diphenylamine donor showed characteristic of donor-accepter such as the ICT absorption band in UV-visible and fluorescence spectra, HOMO and LUMO levels and the low energy gab revealed the good electron donor properties of diphynylamine.



Figure 3.3 Structure of D-A compound with Diphenylamine donor.

From the literature study above, we have ensured that the diphenylamine moiety can be used as electron donor for DSSCs materials. More over the non-planar structure of arylamine can promote the steric hindrance of the dyes molecules.

3.2 Target dyes and aims

3.2.1 To synthesize three dyes containing diphenylamine-encabed with 3,6-di-*tert*butylcarbazole as double donor, oligothiophene (thiophene unit = 1-3) as π -conjugated linker and cyanoacrylic acid as electron accepter as sensitizer in DSSCs.

3.2.2 To study the optical, electrochemical and thermal properties of the dyes due to the extension of conjugation system by varying thiophene unit.

3.2.3 To compare the diphenylamine dyes with triphenylamine dyes (chapter 2) in term of photo/electrochemical properties and steric effect between the different donor moiety.

3.2.4 To fabricate DSSCs devices based on the synthesized dyes and investigate the device performance.



Figure 3.4 The structure of target dyes (DPA1-DPA3).

3.3 Results and discussion

3.3.1 Synthesis

The carbazole-diphenylamine dyes (**DPA1-DPA3**) were synthesized by stepwise synthetic protocol similar to the TPA synthesis which start from donor synthesis, molecular elongation by increasing the thiophene unit and end-up with incorporation of accepter.

The synthesis of donor part starting with diphenylamine starting material was iodinated in the mixture of potassium iodide and potassium iodate in acetic acid/ethyl acetate (1:1) at 80°C resulting in diiododiphenylamine 2 in poor yield (scheme 3.1). The unidentified sticky adduct occurred during reaction may cause the low quantitative amount of di(4-iodophenyl)amine (**39**). The structure of iodinated product was confirmed by ¹H-NMR spectra (measured in CDCl₃) which exhibit very clear doublet signal of aromatic proton at chemical shift at 6.80 and 7.53 ppm with coupling constant of 8.7 Hz. The N-H starching of free amine was also observed in IR

spectrum of compound **39**. Alkylation of **39** in the presence of 1-bromododecane, sodium hydroxide in dimethyl sulfoxide at room temperature gave n-dodecyl-bis(4-iodophenyl)amine (**40**) in excellent yield. The Alkyl peaks were observed in ¹H-NMR spectrum of compound **40** to confirm successful introduction of alkyl group to N position of diphenylamine (see chapter 8).



Scheme 3.1 Synthesis of N-dodecyl-4-iodo-N-(4-iodophenyl)aniline (40).

The 3,6-di-*tert*-butylcarbazole-endcapped-diphenylamine donor part was prepared by Ullmann coupling reaction between 3,6-di-*tert*-butylcarbazole and excess amount of alkylated iododiphenylamine (**40**) yielded mono-substituted diphenylamine (DPA, **41**) as major product and di-substituted DPA as minor product. The tertiary butyl group at position 3 and 6 of carbazole were introduced in purpose of steric hindrance and oxidative coupling protection which is commonly observed in arylamine materials. The successful coupling between carbazole and diphenylamine was confirmed by ¹H-NMR spectrum. The singlet signal at chemical shift 8.13 ppm was observed which contribute to the proton at position 4 and 5 of carbazole moiety.



Scheme 3.2 Synthesis of 3,6-di-tert-butylcarbazole-endcapped-diphenylamine donor (41).

To elongate the conjugation of the molecules, mono and dithiophene was introduced to donor using combination reaction of Suzuki coupling and bromination. Monothiophene intermediate (42) was prepared by coupling reaction between donor (41) and 2thiopheneboronic acid using Tetrakis(triphenylphosphine)Palladium(0) as catalyst, sodium carbonate as base in THF/H_2O at reflux and obtained in good yield. NBS bromination of the resultant thiophene intermediate in THF at room temperature afforded bromothiophene intermediate (44) in moderate yield. To introduce more thiophene, the repeating step of Suzuki coupling and bromination was proceed.



Scheme 3.3 Synthesis of oligothiophene intermediate.

The extended carboxaldehyde functionalized thiophene intermediate (46-48) were achieved by Suzuki condition as well. The coupling reaction between corresponding aryl halide (41, 44 and 45) and 5-formyl-2-thiopheneboronic acid (scheme 3.4) yielded the aldehyde 46, 47 and 48 in 54, 57 and 51%, respectively. This moderate yield are commonly observed in Suzuki coupling of 5-formyl-2-thiopheneboronic acid due to its unstable thiophene carboxaldehyde intermediate. The successful introduction of aldehyde functional group was confirmed by H¹ NMR and IR spectra. The singlet signal of aldehyde proton in CDCl₃ was located at chemical shift 9.85, 9.85 and 9.84 for aldehyde protons of compound 46, 47 and 48, respectively. The IR peaks of C=O stretching of aldehyde was also observed at wavenumber 1664, 1665 and 1659 cm⁻¹. Finally the dyes were obtained by Knoevenagel reaction of corresponding aldehyde (46-48) with cyanoacetic acid. All dyes were obtained as orange, red and dark red amorphous solid. The color of dyes are

intended to be darker comparing to the carbazole-triphenylamine series (Chapter 2) which are good signed for good absorption property. The solubility of dyes in common organic solvent is pretty excellent owing to the long alkyl chain attached to N position of arylamine.



Scheme 3.4 Synthesis of DPA1-DPA3.

3.3.2 Optical Properties

The absorption spectra of DPA dyes both measured in dichloromethane solution and adsorbed on anatase phase TiO_2 particle as well as their emission spectra are displayed in Figure 3.5. The dyes show similar UV-vis characteristic comparing to TPA dyes (Chapter 2) including π to π^* transition at 290-350 nm and intramolecular charge transfer transition (ICT) at 400-550 nm because of their very similar chromophores, but the DPA dyes exhibit little red shifted in ICT band. The difference between maximum absorption wavelengths of the two series are 8, 20 and 17 nm for *single*, *bis* and *tert*-thiophene, respectively. It can be described in term of During DPA dyes, the molar absorptivity of ICT band is moderately high, ranging from 25,174 to 30,102 M⁻¹cm⁻¹. As a number of thiophene units in the molecules increases from **DPA1** to **DPA3**, the ICT bands show bathochromic shift and increase in molar absorptivity. It should be noted that absorption spectrum of D-D- π -A compared to D- π -A structure, bathochromically shifts in the ICT peak together with significant increases in molar extinction coefficient were improved. The molar absorptivity of DPA dyes are considerably larger than that of the standard ruthenium dye N3 at 518 nm ($\lambda = 13000 \text{ M}^{-1}\text{cm}^{-1}$), indicating excellent light harvesting ability of our DPA dyes. Moreover, the greater maximum absorption coefficients of the organic dyes allow a correspondingly thinner nanocrystalline film so as to avoid the decrease of the film mechanical strength. This also benefits the electrolyte diffusion in the film and reduces the recombination possibility of the light-induced charges during transportation [86].

The absorption spectra of DPA dyes adsorbed on the TiO_2 films (Figure 3.5 (b) are broadened overing the region of 350–600 nm and slightly blue shifted (20–28 nm) compared to their solution spectra. The former is ascribed to H-aggregation and the interaction of the anchoring groups of the dyes with the surface of TiO_2 which commonly observed in the spectral response of other organic dyes [74, 87]. The latter can be explained by non-planar structure of tert-butylcarbazole unit of dyes preventing aggregation via molecular stacking.



Figure 3.5 Absorption spectra of DPA dyes: (A) CH₂Cl₂, (B) adsorbed on TiO₂ film.

The photoluminescent spectra of DPA dyes measured in CH_2Cl_2 are depicted in Figure 3.6. It shows red shift when the thiophene unit in the molecule is increasing similar to their absorption and the PL spectra of TPA dyes in chapter 2 due to the elongation of the conjugation in molecules.



Figure 3.6 PL spectra of DPA1-DPA3 in CH₂Cl₂.

	λ_{max}^{abs} /1	λ_{onset}^{abs}	λ_{max}^{em}	Eg	
сотроила	solution [°]	Adsorbed on TiO ₂ ^b	(nm) ^a	(nm) ^{a,c}	(eV) ^d
DPA1	298 (28,911)	408	561	597	2.21
	331 (18,395)				
	458 (25,110)				
DPA2	298 (30,611)	409	584	626	2.12
	350 (19,086)				
	463 (27,435)				
DPA3	298 (29,802)	409	604	625	2.05
	464 (30,900)				
	472 (30,102)				

Table 3.1 Photophysical data of DPA1-DPA3.

^a measured in dichloromethane solution at room temperature.

^b measured dyes adsorbed on TiO_2 film.

^c excited at maximum absorption in solution.

 d estimated from the onset of absorption (E $_{g}$ =1240/ λ_{onset}).

The effect of solvent polarity on the absorption spectra of **DPA1** dyes was also studied (Figure 3.7 and Table 3.2). The absorption was measured in five different solvents (dimethylformamide (DMF), ethanol (EtOH), dimethylsulfoxide (DMSO), tetrahydrofurane (THF) and dichloromethane (DCM)). We assigned the absorption bands at 298 nm as **B1**, at 331 nm as **B2** and at 410-458 nm as **B3**, respectively. There is only **B3** band that be effected by solvent polarity change. These **B3** bands therefore are assigned as ICT bands of donor-accepter molecule which can be generally observed in most sensitizer. The absorption spectra show blue shift when the polarity of solvents are increasing. **DPA1** in DMF exhibited lowest maximum absorption at 410 nm (4.85×10^{-19} J), whereas **DPA1** in dichloromethane exhibited the highest at 459 nm (4.33×10^{-19} J). These results can be considered as the negative solvatochromism-physical intermolecular solute-solvent interaction forces-which tend to alter the energy difference between ground and excited state of chromophore of the dyes [88]. The polar solvents are good support solvent to the excited state dye species more than non-polar solvents resulting in close molecular orbital, which tends to absorb light at high energy region (low wavelength).



Figure 3.7 The absorption spectra of DPA dyes in various solvent.

Table 3.2 Maximum absorption of DPA1 measured in various solvents.

solvent	DMF	EtOH	DMSO	THF	DCM
$\lambda_{max}(nm)$	410	421	430	441	458
$E^{a}(10^{-19} J)$	4.85	4.72	4.62	4.51	4.33

^a calculated from $E = h\nu/\lambda$

3.3.3 Electrochemical properties

Cyclic voltamogram of DPA dyes measured in dicloromethane solution are illustrated in Figure 3.8 and the multiple scan are shown in Figure 3.9 (A), (B) and (C) for DPA1, DPA2 and DPA3, respectively. From CV curves, DPA2 and DPA3 with two and three thiophene moieties exhibit three reversible oxidation peaks whereas DPA1 with one thiophene moiety show only two oxidation process. The first two oxidation peaks in low potential are contributed to the oxidation of Nitrogen atom in carbazole and diphenylamine units, whereas the third one in higher oxidation potential are attributed to the oxidation of the conjugation backbone which have thiophene moities. The oxidation onset of DPA1, DPA2 and DPA3 are 0.78, 0.70 and 0.64, respectively (Table 3.3) indicated that increasing in conjugation length of the dyes shifted the oxidation potential in a negative direction [89].



Fugure 3.8 Cyclic voltamogram of DPA1-DPA3 in dry CH_2Cl_2 with scan rate of 0.05 V/s and 0.1 M n-Bu₄NPF₆ as electrolyte at 25 °C.

Their multiple CV scans reveal identical CV curves with no additional peak at lower potential on the cathodic scan being observed signifying no oxidative coupling at the 3,6positions of the peripheral carbazole due to the tert-butyl substituents and they are electrochemically stable molecules. This type of electrochemical coupling reaction can be detected in some carbazole derivatives with unsubstituted 3,6-positions occurred upon charge separation, which could suppress the dye regeneration resulting in lower the efficiency of the DSSCs performance [76].



Fugure 3.9 Multiscan cyclic voltamogram of DPA1 (A), DPA2 (B) and DPA3 (C) in dry CH_2Cl_2 with scan rate of 0.05 V/s and 0.1 M n-Bu₄NPF₆ as electrolyte at 25 °C.

The lowest unoccupied molecular orbital (LUMO) levels of the dyes were estimated by the value of E_{onset}^{ox} and E_g (from Table 3.1), whereas the highest occupied molecular orbital (HOMO) levels were obtained at λ_{onset} of absorption spectra. The examined HOMO and LUMO levels are listed in Table 3.3. To get an efficient electron injection, LUMO of the dye has to be sufficiently more negative than conduction band edge of TiO₂ (-4.4 eV), and the HOMO has to be more positive than redox potential of Iodide/triiodide (-4.8 eV). As results in Table 3.3, the introduction of more thiophene moiety into the molecule shifts the HOMO levels negatively, which decrease the gap between HOMO level and redox potential of iodide/triiodide. This might reduce the efficiency of regeneration of the oxidized dye by I and the overall solar to electricity conversion efficiency at the same time [90].

Comparing to HOMO and LUMO levels of TPA dyes, HOMO of DPA series are close to redox potential of Iodide/triiodide more than TPA series and LUMO of DPA dyes also line nearly conduction band of TiO_2 more than TPA dyes. Moreover the energy gab of DPA dyes are slightly lower than TPA dyes. These results are agreeably with the absorption band of DPA dyes which exhibit more red shift in absorption than TPA dyes. It may indicate that the DPA series may show higher DSSCs performance than that of TPA series due to their good optical and electrical properties.

Dyes	$E_{onset}^{ox}(V)^{a}$	HOMO (eV) ^c	LUMO (eV) ^d
DPA1	0.78	-5.18	-2.97
DPA2	0.70	-5.09	-2.97
DPA3	0.64	-5.04	-2.99

 Table 3.3 Electrochemical properties and energy level of carbazole-diphenylamine dyes.

^a measured using glassy carbon electrode as a working electrode, a platinum rod as a counter electrode, and Ag/Ag^{+} as a reference electrode in CH_2Cl_2 solution containing 0.1 M n-Bu4NPF as supporting electrolyte

^b calculated using the empirical equation: HOMO = -(4.44 + E_{onst}^{ox}) ^c calculated from LUMO = HOMO + E_{g}



Figure 3.10 Energy diagram of HOMO/LUMO of DPA1-DPA3.

3.3.4 Quantum chemical calculation

In all the computations, the tertiary butyl groups substituted at carbazole and dodecyl side chain substituted at DPA are replaced by hydrogen atoms. The ground-state (S0) geometries of **DPA1-DPA3** were optimized by the B3LYP/6-31G(d,p) [91] method in CH_2Cl_2 solvent of the conductor-like polarizable continuum model (C-PCM) [92, 93]. The optimized S0 state structures of **DPA3** are shown in Figure 3.11. Table 3.4 shows the dihedral angles between the connecting moieties denoted in Figure 3.11. The molecules have a bent structure due to the N atom of the diphenylamine unit. The conjugation holds across this N atom trough lone pair electron of Nitrogenatom. Although the tert-butyl and dodecyl groups may affect the planarity of the molecules, this conjugation provides a significant factor for the strong photoabsorption of dyes molecules. As we have expected, the nonplanarity exists at carbazole and the phenyl of DPA (D1-D2) due to steric repulsion between the H atoms with a dihedral angle of -63°. Another phenyl group of DPA (D2), the thiophene (π -spacer), and the accepter moieties (A) are nearly planar. The thiophene units have a zigzag structure which maintains the near planarity of the molecules. We expect the planarity in the D2- π -A moieties would contribute to the high absorption coefficient for efficient light harvesting ability.



Figure 3.11 Schematic view of the ground-state (S0) structure for DPA3.

Dihedral angle	DPA1	DPA2	DPA3
D1-D2	-63.12	-63.34	-63.20
Ph-Ph	41.87	40.10	40.55
D2-T1	-8.82	-17.62	-20.67
T1-T2	-1.28	5.09	-
T2-T3	-0.96	-	-
Т3-А	1.27	0.25	0.38

Table 3.4 Dihedral Angles (deg) between moieties for the ground state of the dyes optimized byB3LYP/6-31G(d,p) in CH,Cl,.

D1 = carbazole unit;

D2 = diphenylamine unit;

A = cyanoacrylic acid;

T1, T2, and T3 = thiophene units;

Ph-Ph = dihedral angle between two phenylene rings of the diphenylamine moiety.

Orbital density analysis using the GaussSum program38 was carried out for the HOMO and LUMO of all dyes, and the contribution from each moiety is summarized in Table 3.5 and Figure 3.12. The orbital densities of the HOMO are distributed over the D-D moiety, which are 91%, 73%, and 62% for **DPA1**, **DPA2**, and **DPA3**, respectively. The orbital densities of the LUMO, on the other hand, are delocalized across the π -spacer and accepter, which are decomposed as 38% (π -spacer) and 47% (A) for **DPA1**, 53% (π -spacer) and 41% (A) for **DPA2**, and 60% (π -spacer) and 38% (A) for **DPA3**. These values show that the distributions of the HOMO and LUMO of the dyes are well separated, suggesting that the HOMO \rightarrow LUMO transition can be regarded as an intramolecular charge transfer (ICT), which is a major characteristics of D- π -A based dyes. This feature also enables the desirable efficient electron transfer with strong photoabsorption for DSSCs.


Figure 3.12 Molecular orbital of DPA dyes relevant ground state and excited state.

Table 3.5. Energy Level, HOMO-LUMO energy gab (Δ_{H-L}), and electron contribution of the HOMO and LUMO of DPA dyes calculated by B3LYP/6-31G(d,p).

Dye		Energy	Δ _{II-L}	E	lectron contr	ibution (%)	
		(eV)	(eV)	D1	D2	Т	Α
DPA1	LUMO	-2.71	2.46	0	15	38	47
	НОМО	-5.17		57	34	6	3
DPA2	LUMO	-2.76	2.26	0	6	53	41
	НОМО	-5.02		29	44	22	4
DPA3	LUMO	-2.90	2.04	0	2	60	38
	НОМО	-4.94		20	42	35	3

3.3.5 Thermal properties

The thermal properties of **DPA1-DPA3** dyes were evaluated using thermogravimetric analysis. Figure 3.13 displays the TGA thermograms of the dyes which has good thermal stability, i.e., it is stable up to around 280 °C [T_{sd} (degradation temperature at 5% weight loss)] in a nitrogen atmosphere. As can be seen in Figure 3.13, the dyes undergo a three-step degradation. The weight loss during the first step (around 400 °C) or around 20% weight loss equivalent to the weight of accepter moiety, and the weight losses during the second and third steps (440-610 °C) may correspond to the weight fractions of the aromatic parts of the two side groups [94].



Figure 3.13 TGA thermograms of DPA1-DPA3 dyes.

3.3.6 Dye adsorption on TiO₂ film

The performance of a DSSC also depends on the total amount of dye present [94]. Therefore, the dye uptake was determined using UV-vis absorption technique [80]. In all case, the rate of dye adsorption is initially rapid and eventually reaches a plateau. These profiles are typical for organic adsorbates into nanoporous inorganic matrixes [95]. The chemisorption of all dyes onto the surface of TiO₂ films was confirmed by FT-IR spectroscopy (Fig. 3.15), which showed absorption peaks of dyes on TiO₂ at lower energy (1577 cm⁻¹), whereas the free acrylic acid locate at 1598 cm⁻¹ indicated the vibration of carboxylate group. The characteristic vibration modes of the carboxylate group of all dyes are identical to those reported for other dyes [96, 97]. This indicates that all dyes bind in the same way to TiO₂. Therefore, the difference observed in performance can be directly related to the effect of the molecular volume and how much dye is

absorbed. The dye uptakes depend on the steric hindrance of the donor moiety around the carboxylic acid anchoring group; such steric hindrance can be reduced in **DPA3** with longer π -conjugated spacers. At equilibrium, maximum uptakes of each dye are $(84.4 \pm 3.8) \times 10^{15}$, $(97.5 \pm 2.0) \times 10^{15}$, and $(104.3 \pm 1.8) \times 10^{15}$ molecules cm⁻² for **DPA1**, **DPA2**, and **DPA3**, respectively. Under this dye-loading result, the light-harvesting efficiency of **DPA1** is expected to be less than those of the other dyes leading to a small incident monochromatic photon to current conversion efficiency for the **DPA1** based cell.

Comparing dye uptakes of TPA series (44.44 x 10^{15} , 50.65 x 10^{15} , and 53.90 x 10^{15} molecules cm⁻² for **TPA1**, **TPA2** and **TPA3**, respectively), DPA dye can adsorbed on TiO₂ film more than TPA dyes. This because the TPA dyes have two carbazole unit (2D-D- π -A dyes) that increase the steric hindrance whereas DPA dyes (D-D- π -A) have less steric effect from one carbazole moiety resulting in more dye uptake.



Figure 3.14 (A) dyes uptakes onto TiO₂ films measured over a period of 50 h at room temperature, (B), (C) and (D) the absorption spectra of DPA1, DPA2 and DPA3 in various concentration.



Figure 3.15 FT-IR spectra of the DPA1 adsorbed in TiO_2 films.

3.3.5 Cell performance

DPA1-DPA3 Dyes were used as the sensitizers for dye-sensitized nanocrystalline anatase TiO_2 solar cells. The corresponding IPCE plots and current density-voltage (*J-V*) characteristics are shown in Figure 3.16, and the resulting photovoltaic parameters (average values) are summarized in Table 3.7. The IPCE spectra of **DPA1-3** sensitizers plotted as a function of the excitation wavelength are broadened and red-shifted as the number of thiophene units in the molecule increases, which is coincident with the result of the absorption spectra. The IPCE spectrum of **DPA3** shows a high maximum value of 83%, which is slightly higher than the IPCE values of both **DPA1** (81%) and **DPA2** (82%). The higher IPCE value of **DPA3** is probably due to its \mathcal{E} , which enhances the electron-injection yield in comparison with those of the other dyes. Because of their larger molar extinction coefficients, the IPCE values of dyes **DPA1-DPA3** are higher than that of the N3 dye; the N3 dye shows a broader IPCE spectrum, which is consistent with its wide absorption spectrum.

Under standard AM 1.5G 100 mW cm⁻² illumination, the **DPA3**-sensitized cell shows the highest overall efficiency among the three dyes and gives a short-circuit photocurrent density (J_{sc}) of 10.89 mA cm⁻², open-circuit voltage (V_{oc}) of 0.70 V, and fill factor (*FF*) of 0.67, corresponding to an overall conversion efficiency (η) of 5.12%. The short-circuit photocurrent densities and efficiencies of the DSSCs are in the order **DPA3** (10.89 mA cm⁻², 5.12%) > **DPA2** (8.88 mA cm⁻², 4.10%) > **DPA1** (7.19 mA cm⁻², 3.52%). The better solar cell performance of the **DPA3**-based cell than that of the other dyes in this series can be explained by the red shift of the absorption spectrum of **DPA3** compared to **DPA1** and **DPA2**. This is better for the light harvesting efficiency in DSSCs. While the lower efficiency of the **DPA1**-based cell can be attributed to both the poorer spectral property and the lower dye content on the TiO_2 film.



Figure 3.16 IPCE spectra of DPA and N3 dyes.



Figure 3.17 *I-V* characteristic of DPA1-DPA3 and N3 reference dye.

The efficiency of the **DPA3**-based device reaches 90% of the efficiency of the standard ruthenium dye **N3**-based cell ($\eta = 5.71\%$). The efficiency of the **DPA1**-based cell also reaches >62% of the efficiency of the **N3**-based cell even though **DPA1** has a lower IPCE value and narrower IPCE spectrum than both **DPA2** and **DPA3**. The η/η_{N3} values of **DPA3** are competitive with or higher than those of the D- π -A-type sensitizers containing carbazole or diphenylamine as the donor (49-90%, which shows that the use of D-D- π -A type sensitizers improves the energy harvesting of the DSSCs by decreasing aggregation and increasing the molar

extinction coefficients. This relative efficiency (η/η_{N3}) enables the comparison of the solar cell performance in different experimental conditions.

Dye	Dye uptake ^b	$J_{\rm sc}$	V _{oc}	FF	η
	(x10 ¹⁵ molecule/cm ²)	(mA/cm ²)	(V)		(%)
DPA1	88.4±3.8	7.19	0.73	0.67	3.52
DPA2	97.5±2.0	8.88	0.70	0.66	4.10
DPA3	104.3±1.8	10.89	0.70	0.67	5.12
N3	55.1±1.0	11.54	0.71	0.70	5.71

Table 3.7 Performance parameter of DSSCs constructed using DPA1-DPA3 as sensitizer^a.

^aexperiments were conducted in identical condition using TiO₂ photonode with approximately 11 μ m thickness and 0.25 cm² working area on the FTO (8 Ω /A) substrate. ^bobtained from dye adsorption measurement.

3.4 Conclusion

We have developed new D-D- π -A type organic sensitizers using 3,6-di-*tert*butylcarbazol-9-ylphenyl-*N*-dodecylaniline as double electron donor moiety (D-D), oligothiophenes as π -conjugated spacers (π) and cyanoacrylic acid as the electron acceptor (A) for DSSCs. These dyes exhibit high thermal and electrochemical stability. HOMO and LUMO energy level tuning is achieved by varying the conjugation between the carbazole-diphenylamine donor and the cyanoacetic acid acceptor. The dyes show similar UV-vis characteristic comparing to TPA dyes including π transition at 290-350 nm and ICT bands at 400-550 nm because of their similar chromophores. But the DPA dyes exhibit little red shifted in ICT band which can be described in term of aggregation. The red shift absorption can be observed when the number of thiophene unit are increasing due to the elongation of conjugation length.

The ground state geometry, dihedral angle, and electronic structure both in ground state and exited state of the dye molecules were investigated by the DFT method. The D-D moiety has non-planar structure that may inhibit unfavorable dye aggregation yet to keep the conjugation in D- π -A moiety; the conjugation in D- π -A moiety is important for high intensity of

photoabsorption. The electron distribution of ground state (HOMO) and excited state (LUMO) shows that, even though the dihedral angle between D-D moiety are quite high (60°) the electron can distribute between donor and accepter very well (from donor 57% to accepter 47% in case of **DPA1** dye).

The results suggest that the organic dyes based on double donor moiety are promising candidates for improvement of the performance of the DSSCs. DSSCs devices using these dyes exhibit efficiencies ranging from 3.52-5.12% under AM 1.5G illumination. The best performance among these dyes was found in **DPA3**, which shows a maximal IPCE value of 83%, J_{sc} value of 10.89 mA cm⁻², V_{oc} value of 0.70 V, and *FF* value of 0.67, that correspond to an overall conversion efficiency of 5.12% (89.6% of the **N3**-based cell).

CHAPTER 4

SYNTHESIS AND CHARACTERIZATION OF (PYRANE-4-YLIDENE)MALONONITRILE DYES FOR DYE-SENSITIZED SOLAR CELLS

4.1 Introduction

The molecular structure of the dye plays an important role in DSSCs. The performance of DSSCs generally depends on the relative energy levels of the sensitizers and the kinetics of the electron-transfer processes at the interface between the dye bound to the semiconductor surface. One general principle to construct an efficient dye and efficient DSSCs is the absorption spectra of the dye should cover the whole visible and some of the near-infrared region, and its molar extinction coefficient must be as high as possible to enable efficient light harvesting ability [98]. Therefore, the introduction of accepter in π -spacer may expand the absorption spectra of the dye to near IR region.

Donor-acceptor (D-A) pyran-4-ylidene derivatives have attracted much attention because of their interesting optical properties. Thus, 4-dicyanomethylene-2-methyl-6-(4dimethylaminostyryl)-4H-pyran (**DCM**) is a well known laser dye, and many of its derivatives are useful red dopants for organic light-emitting diodes (OLED). Figure 4.1 show the structures of DCM derivatives as the examples of red dopant materials using in both NLO and OLEDs application [99-102].

The UV-Visible and fluorescence spectra of DCM derivatives, as expected, show the red-shift absorption, and all exhibit a charge transfer (CT) absorption band in solution cover the region 400-600 nm. The HOMO and LUMO levels of the DCM derivatives range between -5.4 - (-5.7) eV and -2.3 - (-3.2) eV, respectively. This results show that it is possible to incorporate this DCM type in the molecules to expand the absorption spectra of the target dyes.



Figure 4.1 The structure of DCM and DCM derivatives; red-light emitter for OLEDs.

Fluorene is well known as a promising optical and thermally stable material and is widely used as emitting materials in OLEDs application and optoelectronic materials. The high molar extinction coefficient of fluorene derivatives can be observed in various reports [103]. Beside used as OLEDs materials there are many studies reported fluorene derivative as donor or π -spacer part in DSSCs to enhance the absorption ability of the sensitizer [104-107].



Figure 4.2 DSSCs dyes from fluorene derivatives.

With arylamine donor, fluorene π -bridge dyes (56, 57 and 58) exhibited longer wavelength absorption due to π -conjugated elongation in the bridge and the significant lowering of the LUMO level when compared to the dyes without fluorene moiety have high molar extinction coefficient ranged around 33,000 - 37,000 M⁻¹cm⁻¹. The dyes with the same donor without fluorene spacer exhibits lower the molar extinction coefficient around 22,000 M⁻¹cm⁻¹ which ensured that fluorene unit in π -spacer enhance the absorption ability of the dyes.

In dye 58, fluorene unit was introduced as part of donor group (directly introduced at N-atom of arylamine). The bis-dimethylfluoreneaniline moiety (acting as electron donor) ensure greater resistance to degradation when exposed to light and high temperatures as compared to simple arylamines. Also, the non-planar structure of bis-dimethylfluoreneaniline suppresses aggregation, disfavoring molecular stacking. The dye show red-shifted absorption and very strong molar extinction coefficient of 44,000 M^{-1} cm⁻¹ which indicate that the bis-dimethylfluoreneaniline moiety influence the optical characteristic of the dyes in the promising way to enhance the \mathcal{E} .

Therefore in this series we designed the dyes molecules with carbazole-fluorene donor pyran-4-ylidinemalononitrile conjugated with bisthiophene unit as spacer and acrylic acid or cyanoacrylic acid accepter used as sensitizer in DSSCs.

4.2 Target dyes and aims

From mentions above, the new series of dye-sensitizer was designed. The carbazole moiety was used as electron donor due to its electron donating ability and thermal properties, the fluorene was introduced to increase the ε value, whereas the (pyrane-4-ylidene)malononitrile moiety was incorporated into the molecule to expand the absorption spectra cover to red region. The aims of this chapter are:

4.2.1 To synthesize 2 dyes containing carbazole-fluorene as electron donor, (pyrane-4ylidene)malononitrile plus bithiophene as π -conjugated linker and cyanoacrylic acid or acrylic acid as electron accepter.

4.2.2. To investigate the different anchoring group (cyanoacrylic acid and acrylic acid); effect of electron withdrawing moiety (-CN) to optical and electrochemical properties and HOMO-LUMO levels.

4.2.3 To investigate the DSSCs performance based on the (pyrane-4-ylidene)malononitrile dyes as dye-sensitizer.



Figure 4.3 Structure of (pyrane-4-ylidene)malononitrile dyes (CFP dyes).

4.3 Results and discussion

4.3.1 Synthesis

The synthesized strategy of pyrane dyes is the same as TPA and DPA dyes which are constructing the dye from donor, followed by introducing the linker and then attached the accepter in the last step. The synthesis of CFP dyes are illustrate in Figure 4.1. The carbazole fluorene donor (54) were synthesized by Ullmann coupling reaction between 3,6-di-*tert*-butylcarbazole and 5,7-bromo-9,9-dihexylfluorene as described in previous reports [108, 109]. The aldehyde intermediate (55) was prepared from Suzuki coupling between aryl bromide donor (54) and 4-formylphenylboronic acid to give aldehyde (55) in good yield. The ¹H-NMR and IR data were confirmed the successful introduction of aldehyde functional group. IR spectrum of aldehyde 55 shows the vibration of C=O stretching of aldehyde at 1646 cm⁻¹ and C=C stretching of aromatic compound at 1562 cm⁻¹. The rest of IR signal are assigned as C-H stretching of aromatic ring (3042 cm⁻¹), C-H stretching of aliphatic chain in fluorene moiety and *tert*-butyl group in carbazole (2800-2900 cm⁻¹) and C-C stretching of aliphatic chain at 1416 cm⁻¹ and more. ¹H-NMR spectrum (in CDCl₃) reveals singlet signal of aldehyde proton (1H) at chemical shift 10.1 ppm and singlet signal of two protons of 4,5-carbazole moiety at chemical shift 8.25 ppm (2H).

The synthetic scheme and the expanded ¹H-NMR in aromatic region of compound **55** are shown in Scheme 4.1 and Figure 4.4, respectively.



Scheme 4.1 Synthesis of aldehyde intermediate 55.



Figure 4.4 H¹-NMR of aldehyde intermediate 55.

The introduction of (pyran-4-ylidine)malononitrile moiety was proceed under Knoevenagel reaction between the corresponding aldehyde (55) and 2,6-dimethylpyrane-4ylidenemalononitrile using piperdine as base in chloroform at reflux to give malononitrile product (56) in poor yield. Although we have tried to improve the reaction yield by increasing the mole percent of 2,6-dimethylpyrane-4-ylidenemalononitrile, the low amount of desired product was still obtained. Due to the introduction of accepter malononitrile moiety in the molecules, the yellowishorange product was obtained.



Scheme 4.2 Synthesis of malononitrile intermediate 56.

The chemical structure of malononitrile intermediate (56) was also confirmed by ¹H-NMR and IR spectra. IR spectrum of aldehyde 55 shows the vibration of C \equiv N stretching of malononitrile moiety at wavenumber 2210 cm⁻¹, C=O stretching of aldehyde at 1652 cm⁻¹ and C=C stretching of aromatic compound at 1563 cm⁻¹, whereas ¹H-NMR spectrum measured in CDCl₃ as solvent reveals singlet signal of two protons of carbazole moiety and three methyl protons of methyl group in malononitrile at chemical shift 2.44 ppm as singlet.



Figure 4.5 H¹-NMR of malononitrile intermediate 56.

Next step the thiophenyl substituted (pyrane-4-ylidene)malononitrile (57) was also prepared by Knoevenagel reaction. The reaction of 5-bromothiophene-2-carbaldehyde and corresponding methyl malononitrle (56) under piperidine condition gave compound 57 in good yield. Although the NMR and IR characteristic of reactant (56) and product (57) are similarly because of their similar chromophore, the disappearance of methyl proton of malononitrile moiety can confirm the success of this reaction.

To extend the conjugation length, another thiophene unit was introduced through Suzuki coupling reaction between compound **57** and 5-formylthiopheneboronic acid under $Pd(PPh_3)_4$ catalyst condition as depicted in scheme 4.3. The reddish-orange solid was obtained. The successful introduction of aldehyde functional group was confirmed by IR peak of C=O stretching of aldehyde at 1658 cm⁻¹ and H¹ NMR signal of aldehyde (singlet, 1H) at chemical shift 9.85 ppm.



Scheme 4.3 Synthesis of compound 57 and 58.



Figure 4.6 H¹-NMR of malononitrile intermediate 58.

Final target dyes **CFPA** and **CFPC** were prepared by Knoevanegel reaction between corresponding aldehyde **58** and malonic acid or cyanoacetic acid in piperidine condition. The reaction yielded 60% and 72% for CFPA and CFPC, respectively as shown in scheme 4.4. The products were achieved as dark red solid which are good sign for absorption spectra in near IR region. Both dyes can dissolve in common organic solvents such as dichloromethane, chloroform and THF. This good solubility may be due to the two hexyl groups in fluorene.



Scheme 4.4 Synthesis of CFPA and CFPC dyes.

The structure of **CFPA** and **CFPC** were confirmed by ¹H-NMR and IR spectra. They show similar vibrational mode of O-H stretching at 3394 and 3421 cm⁻¹, C=N stretching at wavenumber 2210 and 2201 cm⁻¹, C=O stretching of carboxylic acid at 1637 cm⁻¹ and C=C stretching of aromatic compound at 1547 and 1537 cm⁻¹. ¹H-NMR spectrum of both dyes measured in CDCl₃ show singlet signal of two protons of carbazole (position 4 and 5) moiety, while the rest of aromatic protons (including protons in both anchoring groups) overlap with each other that make it difficult to identify. However the mass spectrum of **CFPA** and **CFPC** are used to confirm the structure of the dyes.





69



Figure 4.8 H¹-NMR of CFPC.

4.3.2 Optical Properties

The absorption spectra of CFPA and CFPC dyes measured in dichloromethane solution and adsorbed on TiO₂ thin film and emission spectra measured in dichloromethane solution are shown in Figure 4.9, 4.10 and 4.11 and the corresponding data are summarized in Table 4.1. In solution, two dyes show similar absorption feature which show two absorption bands (x and y) around 290-350 nm corresponds to π - π * transition and strong absorption bands around 400-550 nm (z) corresponds to Intramolecular Charge transfer Transition (ICT) of donor-accepter dyes. The bathochromic shifted (red shifted) absorption spectra were observed in CFPC dye which can ascribe as the stronger electron withdrawing ability of cyanoacrylic acid moiety in CFPC than acrylic acid moiety in CFPA [110]. This red-shifted can be found in the report of malonic acid anchoring group comparing to cyanoacrylic acid as well [104 and 111]. From absorption spectra of dyes in dichloromethane solution, the energy gab of all dyes can be calculated from λ_{onset} from formula Eg = 1240/ λ_{onset} and the calculated data are shown in Table 4.1. The molar extinction coefficient (ϵ) of ICT bands CFPA and CFPC dyes are 47,341 and 60,911 M⁻¹cm⁻¹ which are the highest value in this thesis. The promising ϵ value may probably be due to the fluorene moiety in donor part as expectation. This may indicate a better ability of light harvesting of the CFP dyes compared to those of TPA and DPA dyes without fluorine moiety (\mathcal{E} range between 20,000 – 35,000 M⁻¹ cm⁻¹).



Figure 4.9 Absorption spectra of CFPA and CFPC dyes collected in CH₂Cl₂.

The absorption maxima of CFP dyes adsorbed on TiO_2 film are illustrated in Figure 4.10. Comparing to their absorption spectra in solution, the dyes adsorbed onto surface of TiO_2 film exhibit broader and little hypsochromic shift or blue shift in absorption spectra (11 and 18 nm for CFPA and CFPC, respectively), which indicate strong interactions between dyes and semiconductor surface. The blue shift in absorption were also observed in TPA and DPA dyes reported in previous chapter and a blue shift absorption of the dyes bonded to TiO_2 film can be observed in general type of acrylic anchoring group [21, 74, 87].



Figure 4.10 Absorption spectra of CFPA and CFPC adsorbed on TiO_2 film.

The photoluminescent spectra of CFP dyes measured in CH_2Cl_2 solution are depicted in Figure 4.11. Among two dyes, CFPC exhibit little red shift in emission (2 nm) compared to CFPA due to the strong electron withdrawing anchoring group of CFPC. Moreover CFPA and CFPC show stroke shift at 173 and 164 nm





	λ_{max}^{abs} /nm	$(E/M^{-1}cm^{-1})$	$\lambda_{_{onset}}^{_{abs}}$	λ_{max}^{em}	Eg
compound	solution ^a	Adsorbed on	(nm) ^a	(nm) ^a	(eV) ^c
		TiO ₂ ^b			
CFPA	297 (41,434)	444	574	628	2.16
	353 (40,595)				
	455 (47,341)				
CFPC	297 (44,869)	448	579	630	2.14
	351 (39,657)				
	466 (60,911)				

 Table 4.1 Optical data of CFP dyes.

^a measured in dichloromethane solution at room temperature.

^b measured dyes adsorbed on TiO_2 thin film.

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

4.3.3 Electrochemical properties

To evaluate the possibility of electron transfer from the excited dye to conductive band of TiO₂, the electrochemical properties were measured by cyclic voltametry in CH₂Cl₂ solution at room temperature using 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte as shown in Figure 4.12 and the electrochemical characteristics of CFPA and CFPC are summarized in Table 4.2. CFPA and CFPC exhibit irreversible oxidation process. The oxidation onset of CFPA and CFPC appeared nearly the same position at 1.03 and 1.04 V due to the same molecular structure. This first oxidation potential is attributed to the oxidations of Nitrogen atom of *tert*-butylcarbazole, whereas the rest oxidation waves indicated the removal of electrons from the backbone. The reduction processes of these dyes are not observed. The difference anchoring group has less influence to the oxidation potential. Comparing to TPA and DPA dyes, CFPA and CFPC exhibit higher oxidation potential (E^{ox}_{onsel} of TPA and DPA dyes range around 0.66-0.88 V). This is probably due to the stronger electron withdrawing ability of (pyrane-4-ylidine)malononitrile moiety in the spacer, which delocalizes electron density from donor toward accepter segment and makes it less prone to oxidation [104].



Fugure 4.12 Cyclic voltamogram of CFPA and CFPC.

The lowest unoccupied molecular orbital (LUMO) of CFPA and CFPC were estimated by the value of E_{onset}^{ox} and E_g , whereas the highest occupied molecular orbital (HOMO) levels were obtained from λ_{onset} of absorption spectra. The examined HOMO and LUMO levels are listed in Table 4.2. To get an efficient electron injection, LUMO of the dye has to be sufficiently more negative than conduction band edge of TiO₂ (-4.4 eV), and the HOMO has to be

more positive than redox potential of Iodide/triiodide (-4.8 eV). As results in Table 4.2, The HOMO of the dyes are very proximal and the LUMO levels are not noticeably different. However the estimated LUMO of DFPA and CFPC are lined below conduction band of TiO_2 and HOMO of the dyes are lined negatively than redox couple potentials which indicate the enough driving force for electron injection and regeneration process.

Dyes	E ^{ox} _{onset} (V) ^a	HOMO (eV) ^b	LUMO (eV) ^c
CFPA	1.03	-5.47	-3.31
CFPC	1.04	-5.48	-3.34

 Table 4.2 Electrochemical property and energy level of CFP dyes.

^a measured using glassy carbon electrode as a working electrode, a platinum rod as a counter electrode, and Ag/Ag^{+} as a reference electrode in CH_2Cl_2 solution containing 0.1 M n-Bu₄NPF as supporting electrolyte.

^b calculated using the empirical equation: HOMO = -(4.44 + E_{onset}^{ox}). ^c calculated from LUMO = HOMO + E_{g} .



Figure 4.13 The energy diagram of CFP dyes.

4.3.4 Quantum chemical calculation

In the investigation of donor-accepter systems, the molecular structure of the ICT states is an important point of discussion. Herein, theoretical calculations were performed to study the ground-state structures of CFP dyes calculated by B3LYP/6-31G(d.p) level of theory implemented in Gaussian 09 program. The dihedral angle between carbazole and fluorene of CFPA and CFPC were calculated to be -54.03 degree and -54.72 degree, respectively indicate that N-linked carbazole and fluorine are twist out of plane which is the uniform of the carbazole component [112, 113]. The T-A dihedral angle are calculated to be -0.18 degree and -0.01 degree allowed the electron delocatization into the whole molecules. Moreover the cyanoacrylic acid group was found to be located in co-planar with the thiophene ring. From the calculated results indicate that the linker and acceptor moieties are fully conjugated as demonstrated by the co-planarity of the linker and acceptor groups.



Figure 4.14 Optimized structure of CFPA and CFPC.

Table 4.3 The selected bond distances and dihedral angles of CFPA and CFPC by

Dyes		C-F	F-P	P-E1	E1-Py	Py-E2	E2-T1	T1-T2	T2-A
CFPA	Dihedral(Φ)	-54.03	34.67	-0.62	2.93	-2.79	-0.79	1.90	-0.18
	Distance (r)	1.42	1.48	1 .46	1.44	1.45	1.43	1.43	1.44
Dyes CFPA CFPC	Dihedral(Φ)	-54.72	34.90	-1.46	-2.50	2.14	0.32	0.72	-0.01
	Distance (r)	1.42	1.48	1. 46	1.44	1.45	1.44	1.43	1.43

B3LYP/6-31G(d.p).

Note: C is Carbazole, F is Fluorene, P is phenyl, E is ethene, Py is pyran, T is thiophene, A is accepter.

To gain insight into the geometrical electronic structures of the dyes, molecular orbital and density of state were performed by using B3LYP/6-31G(d,p) level of theory. The frontier molecular orbitals of the CFPA and CFPC dyes are shown in Figure 4.15. The HOMO are localized over the carbazole and fluorene unit with percentage decomposition of 80 and 49% respectively, while the LUMO are localized in pyran unit, thiophene and accepter. At ground state, the electron in carbazole and fluorene does not distribute distinctively to phenyl ring (P) due to the large twist angle between fluorene and phenyl. This may reduce electron transport process from donor to accepter which low the efficiency of the dyes. The electron density distribution of LUMO state for CFPA at accepter moiety (12%) are less than in CFPC (25%). This can be attributed to the less electron withdrawing ability of acrylic acid than that of cyanoacrylic acid which indicate the possibility of electron in accepter unit of CFP dyes are quite less than in DPA dyes which show percentage composition in accepter between 38-47%. This is probably due to the strong electron withdrawing ability of pyrane unit.



Figure 4.15 Frontier molecular orbital of CFPA and CFPC calculated by B3LYP/6-31G(d,p).

Dvac	Molecular	Percentage composition					
	orbital	С	F-P	Py	Т	Α	
CEDA	LUMO	0	2	44	43	12	
CITA	НОМО	80	19	1	0	0	
OFDO	LUMO	0	0	28	47	25	
	НОМО	80	19	1	0	0	

 Table 4.4
 Summarized energy and characteristic of Frontier Orbitals of CFP dyes calculated by

 B3LYP/6-31G(d.p).

Note: C is Carbazole, F is Fluorene, P is phenyl, Py is pyran, T is thiophene, A is accepter

4.3.5 Thermal Properties

The thermal degradation of CFPA and CFPC were studied by thermogravimetric analysis under nitrogen atmospheric condition. TGA thermograms of the dyes are displayed in Figure 4.16 and T_{5d} are listed in Table 4.5. The dyes exhibit 5% weight loss at 286 and 302 °C suggested that the dyes were thermally stable materials with temperature over 286 °C which is good for long term stability of DCCCs devices.



Dyes	T _{5d} (°C)
CFPA	286
CFPC	302

Figure 4.16 TGA thermograms of CFPA and CFPC.

3.3.5 Cell performance

Typical DSCs devices with effective area of 0.25 cm² were fabricated using CFPA and CFPC as sensitizer. Nanocrystalline anatase TiO_2 coated on FTO substrate were use as working electrode whereas pt layer 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. The photovoltaic parameters under a solar condition (AM 1.5) are summarized in Table 4.6. *I-V* curves of the dyes are shown in figure 1 and plots of Incident Photon-to-current conversion efficiency (IPCE) at various wavelengths are given in figure 2. The IPEC spectra of the **CFPA** and **CFPC** are broad cover whole UV regions that almost reach 650 nm implied by their absorption spectra. But the maximum IPEC of CFP dyes are much lower than that of N719 reference dyes and lower than TPA and DPA dyes. The maximum IPCE values of CFP dyes are 31% and 34% for CFPA and CFPC, respectively. This low photo to current conversion of this series is probably due to the low electron density distributed at accepter as described in theoretical study by quantum calculation. Although the electron withdrawing moiety ((pyralne-4-ylidine)malononitrile) expand the absorption spectra into the red region, it take a role of decreasing the electron delocalization between donor and accepter. This may decrease the IPCE value of the dyes.



Figure 4.17 IPCE spectra of CFP dyes and N719.

The current density-voltage (J-V) curves of the DSSCs based on CFPA and CFPC under simulated AM1.5G irradiation (100 mW cm⁻²) are displayed in Figure 4.18, where short-circuit photocurrent (J_{sc}) , open-circuit photovoltage (V_{oc}) , fill factor (*FF*), and power conversion efficiency (η) can be determined. The DSSC based on CFPC produces η of 1.35%

 $(J_{sc} = 3.68 \text{ mA cm}^{-2}, V_{oc} = 0.55 \text{ V}, FF = 0.67)$ which are higher than its analog CFPA that produces η of 0.82% ($J_{sc} = 2.63 \text{ mA cm}^{-2}, V_{oc} = 0.55 \text{ V}, FF = 0.57$). The low over all conversion efficiency of the dyes are relative to their low IPCE values. However CFPC shows better cell performance than CFPA due to its good photophysical, electrochemical properties and its IPCE value indicated that the cyanoacrylic acid is the better anchoring group than acrylic acid accepter.



Figure 4.18 *I-V* characteristic of CFPA and CFPC.

Table 4.6 Performance parameter of DSSCs constructed using CFPA and CFPC as sensitizer^a.

Dye	J _{sc}	V _{oc}	FF	η
	(mA/cm ²)	(V)		(%)
CFPA	2.63	0.55	0.57	0.82
CFPC	3.68	0.55	0.67	1.35
N719	12.04	0.70	0.70	5.90

^a experiments were conducted in identical condition using TiO₂ photonode with approximately 11 μ m thickness and 0.25 cm² working area on the FTO (8 Ω /A) substrate.

3.4 Conclusion

A series of organic chromophores with the structure of donor- π -accepter- π -accepter (D- π -A- π -A) have been synthesized and characterized in order to approve optical and electrochemical properties as well as the DSSCs performance. The carbazole-fluorene take a role as electron donor, phenylene, bisthiophene and (pyrane-4-ylidine)malononitrile functionalized as π -conjugated bridge which has accepter property, and the two anchoring group, cyanoacetic acid and acrylic acid, were incorporated. The absorption spectra of the dyes exhibit broad and red shift due to the introduction of accepter moiety ((pyrane-4-ylidine)malononitrile) into the spacer which help to extend the spectra cover the red region. The HOMO and LUMO levels of the dyes are lined positively than iodide/triiodide potential and conduction band edge of TiO₂ which are driving force for electron regeneration and electron injection process. The optimized structure of the dyes at ground state and the calculated electron distribution between donor and accepter indicated the possibility of charge separation in excited dyes. Although the dyes exhibit the low in IPCE value, the dye **CFPC** show the overall conversion efficiency (η) of 1.35% ($J_{sc} = 3.68$ mA cm⁻², $V_{oc} = 0.55$ V, FF = 0.67) which are higher than its analog **CFPA**. This result ensures that the cyanoacrylic acid is better anchoring group than acrylic acid group.

CHAPTER 5

SYNTHESIS AND CHARACTERIZATION OF CARBAZOLE DONOR DIACCEPTER (A-D-A) DYES FOR DYE-SENSITIZED SOLAR CELLS

5.1 Introduction

There are numerous dyes with common structural compositions; an electron donor with a high absorption band in the visible range, π -bridgee or π -spacer and an electron acceptor (most notably cyanoacrylic acid), which facilitate vectorial charge transfers upon light absorption as well as assist the dye to anchor on the TiO₂ surface has been reported to enhance the charge carrier mobilities with effective intramolecular charge transfers [114]. However, researches on DSSCs have led to a greater understanding of the key dye characteristics like, possessing high molar extinction coefficients [115, 116], low band gaps and capable of absorbing the entire solar spectrum that make dyes to achieve high power conversion efficiencies [117]. Most importantly, the structural configurations of dyes that containing multiple electron acceptors followed by anchoring groups can generate photoinduced intramolecular charge transfer (ICT), which can provide efficient electron injection to the TiO₂ conduction band [118]. Therefore in this chapter, it is involved the investigation of low band gap dye sensitizer with the structure of Donor-Diaccepter or Accepter-Donor-Accepter (A-D-A) for enhancement charge separation in excited dye and for improvement the photo harvesting ability.

There are few works that have reported the multiple anchoring group (cyanoacrylic acid) with various donor such as fluorene, carbazole, dithieno[3,2-b:2',3']pyrole and triphenylamine[119, 120]. The structures of A-D-A dyes sensitizer are shown in Figure 5.1. In case of fluorene and dithieno[3,2-b:2',3']pyrole dyes, the dyes with fluorene donor (**59, 60**) show very strong molar extinction coefficients ranged from $9.2 \times 10^4 - 11.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at their correspondent absorption maxima which are higher than those of **61** (7.46 $\times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and **62** (7.90 $\times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) which are the dithieno[3,2-b:2',3']pyrole dyes. This can be attributed to the fused phenyl rings of fluorene cores as the higher molar extinction coefficients indicate, **59** and **60** dyes earing fluorene cores have facilitated higher light harvesting efficiencies than **61** and **62**

containing dithieno[3,2-b:2',3']pyrole cores. The fluorene-based 60 cell exhibited the best energy conversion efficiencies (η 4.73%) among 4 dyes, with $V_{\rm oc}$ 0.61 V, $J_{\rm sc}$ 12.27 mA/cm², and *FF* 0.59. As described above, due to the largest molar extinction coefficient, 60 dye has the highest light harvesting efficiency and consequently promoted 60 to have the best photovoltaic performance among four dyes [119].

In case of carbazole donor, 3,6-carbazole and 2,7-carbazole moiety have been investigated. Two sets of symmetrical A-D-A organic sensitizers (Fig.5.1) with electron donating carbazole cores functionalized at two different positions (3,6- and 2,7-substituted) and linked through π -conjugated thiophene bridges (to broaden the absorption range of the dyes) to two electron-accepting cyanoacrylic acid units acting as terminal anchoring groups. The UV spectra reveals that 2,7-substituted carbazole exhibited red-shifted absorption comparing to 3,6-substituted carbazole. Furthermore, substitution of the alkyl side chains in the thiophene moieties, led to intramolecular ring twisting, thereby inducing larger band gap energies and associated blue shifts in the UV-Vis spectra. Although the 2,7-substituted exhibit the promising optical properties, compound 62 with 3,6-disubstituted carbazole exhibit the best efficiency (η 4.82%) with $V_{\rm oc}$ 0.61 V, $J_{\rm sc}$ 12.66 mA/cm², and *FF* 0.62 [120].



Figure 5.1 Structure of example A-D-A dyes.

82

5.2 Target dyes and Aims

From the introduction above, we have designed a series of Accepter-Donor-Accepter (A-D-A) dyes with 3,6-disubstituted carbazole donor and symmetric and asymmetric π -conjugated thiophene linker. The aims of this chapter are:

5.2.1 To synthesize symmetric and asymmetric A-D-A dyes containing carbazole moiety as electron donor, oligothiophene as π -conjugated bridge and dicyanoacrylic acid group as double electron accepter.

5.2.2 To investigate the π -conjugated bridge system; symmetric and asymmetric arms to the absorption spectra and also the molar extinction coefficient.

5.2.3 To investigate the DSSCs performance of the synthesized dye-based devices.



Figure 5.2 Structure of target A-D-A dyes (CB01-CB22).

5.3 Results and discussion

5.3.1 Synthesis

The carbazole donor diaccepter (or A-D-A) dyes (**CB01-CB22**) were synthesized by stepwise synthetic protocol illustrated in scheme 5.3.1. 3,6-dibromo-N-(2-ethylhexyl)carbazole (67) was used as starting material. The preparation of (67) was described in previous report [121]. The strategy that was used to prepare the difference moiety of thiophene was shown in Scheme 5.1 and 5.2. The Suzuki coupling reaction between 3,6-dibromo-N-(2-ethylhexyl)carbazole (67) and 2thiopheneboronic acid was performed as the same condition in previous chapter including Tetrakis(triphenylphosphine)Palladium(0) as catalyst, sodium carbonate as base in THF/H₂O (scheme 5.1). The condition control to obtained mono and di-substituted thiophene unit in one step was using 1.5 equivalent of 2-thiopheneboronic acid. This step provided mono- and di-substituted carbazole in over all yield of 91% (23% for mono-substituted carbazole (68) and 68% for di-substituted carbazole (69)). The mono and di-thiophene substituted carbazole were further brominated using NBS in THF at room temperature to give brominated adduct (70) and (71) in excellent yield.



Scheme 5.1 Synthesis of bromothiphene intermediate (70 and 71)

The structures of compounds were confirmed by NMR and IR spectra. For example, the H¹-NMR in CDCl₃ of compound **68** show singlet signal at chemical shift 8.25 ppm of two protons at position 4 and 5 in carbazole moiety (Figure 5.3), doublet signal at 7.75 ppm (1H, J = 8.4 Hz) and 6.59 ppm (1H, J = 8.7 Hz) are assigned to H^c of thiophene ring and H^b of carbazole moiety, respectively. The rest of aromatic protons are overlap with each other which is difficult to identify. Moreover aliphatic protons of 2-ehtylhexyl side chains (proton d) were observed at chemical shift 3.93 (2H, d, J = 6.7 Hz) indicate that this alkyl group connected to N-position of carbazole moiety. The IR spectrum of compound 68 reveals C=C stretching of aromatic ring at 1625 and 1598 cm⁻¹. C-H stretching of aromatic compound at 3092 cm⁻¹ and C-H stretching of aliphatic side chain at 2956, 2921, 2855 cm⁻¹.



Figure 5.3 H^{1} -NMR spectrum of compound **68**.

 H^{1} -NMR and IR spectra of thiophene intermediate compound 69, 70 and 71 are quite similar due to their similar backbone and functional group. In compound 70 proton H^{c} was replaced by Bromine atom led to the disappearance of H^{c} signal at 7.75 ppm as shown in Figure 5.4.



Figure 5.4 H¹-NMR spectrum of compound 70.



Figure 5.5 H¹-NMR spectrum of compound 69.

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Figure 5.6 Expanded H¹-NMR spectrum of compound 71.

86

To elongate the thiophene unit in linked arms, re-step of Suzuki coupling of aryl halide intermediate dibromothiophene (71) and 2-thiophene boronic acid was proceed under the same condition as shown in scheme 5.2. The mole ratio between boronic compound/aryl halide still be 1.5 to gave mono- and di-substituted bis-thiophene in 27 and 45% yield, respectively followed by NBS bromination to give brominated adduct in good yield. The structure elucidation of bisthiophene intermediate are also based on the interpretation of IR and NMR spectra and the spectral data of each compound are listed in chapter 8.



Scheme 5.2 Synthetic route of bisthiophene intermediate 74 and 75.

To introduce the aldehyde functional group, Suzuki coupling reaction between corresponding aryl halide intermediate (70, 71, 74 and 75) and 4-formylphenylboronic acid was performed under similar condition as describe in previous. Although many reports review that the cyanoacrylic acid should connect directly onto the thiophene unit to reduce dihedral angle between the conjugated bridge and cyanoacrylic acid group, we chose 4-formylphenyl moiety instead of 5-formylthiophene due to the more stable of 4-formylphenylboronic acid than 2-formylthiopheneboronic acid. We have tried to introduce 2-thiophenecarboxaldehyde to the molecules but the reaction yield was very unpleasant (2-5%). The major product was only mono-

87

substituted formylthiophene. It is probably due to the unstable of 5-formylthiopheneboronic acid its self. The reaction yield for this step are 93, 82, 74 and 82% for aldehyde 76 to 79, respectively. The aldehyde functional groups in the molecules were confirmed by IR and NMR spectra which show C=O stretching of aldehyde between 1686-1694 cm⁻¹ and singlet signal of aldehyde proton at 10.00-10.08 ppm, clearly confirmed that the aldehyde moiety was successfully introduced to the molecules.

Finally the four target dyes was obtained by Knoevanegel reaction between the corresponding aldehyde (76 - 79) and cyanoacetic acid using piperidine as base in chloroform at reflux condition. The dyes were obtained as red-orange to dark red. The more thiophene units were introduced, the more dark color was gained. Unfortunately the dyes do not show good solubility in common organic solvent such as dichloromethane and chloroform. It can be dissolved little in DMF and THF. This poor solubility of the dyes can be consideration as the planar structure of the carbazole core inducing the dye aggregation led to the difficult isolation of the dye product by chromatographic method. Therefore the yield of this step is rather small.



Scheme 5.3 Synthesis of diaccepter dyes CB01-CB22.



Figure 5.7 Expanded H¹-NMR spectrum of compound CB22.

5.3.2 Optical Properties

The UV-visible absorption spectra of dyes in DMF solutions are displayed in Figure 5.8 (A) and (B), respectively, and their corresponding data are listed in Table 5.1. Owing to their similar structure, all the **CB** dyes exhibit similar absorption pattern located in the range of 260-500 nm which distinguish into two dominant peaks. The first one located at 280 nm was assigned as π - π * transition band, whereas the second one (the stronger one) that ranges around 390-420 nm can be attribute to the ICT band of donor-accepter molecule.

As expected, CB22 with the longest symmetric conjugated system exhibits more red shift absorption (λ_{max} 423 nm, ICT band) comparing to the shortest symmetric CB11 dyes. Whereas an asymmetric dye (CB01) exhibits the most blue shift (396 nm) due to the less π conjugation length. Comparing to the other dyes in this thesis (Chapter 2, 3 and 4), the carbazole dyes exhibit the most blue shift in absorption spectra. The absorption maxima (ICT band) of TPA (chapter 2), DPA (chapter 3) and CFP (chapter 4) dyes range between 450 – 470 nm, whereas λ_{max} of ICT band of CB dyes range around 390 – 420 nm. It can be consider as most of CB dyes have less chromophore (one carbazole donor) than other series which have double donor. Another possible reason that can describe the blue shift spectra of CB series is that the absorption spectra were collected in polar solvent (DMF). The effect of solvent polarity on ICT band of donoraccepter compound was clearly investigated in chapter 3. The ε value of CB11 and CB21 are
noticeably higher than that of CB01 and CB02. This is clearly the effect of more conjugated length of thiophene chromophore in CB11 and CB22.



Figure 5.8 Absorption spectra of CB01-CB22 (A) E plot; (B) Normalized intensity plot.

The absorption spectra of CB dyes adsorbed on TiO_2 thin film are displayed in Figure 5.9(A). The absorption spectra adsorbed on TiO_2 film are broader than the spectrum in DMF (Figure 5.8). It is suggested that the broadening of the absorption spectrum is due to an interaction between the dyes and TiO_2 led to the dyes aggregation because of the planarity of carbazole cores [120, 122]. It has been also observed that when the dyes are adsorbed onto the TiO_2 surface the absorption spectrum of the dyes becomes broad and blue shift [123]. Although the broader absorptions of the dyes on the TiO_2 films are favorable for light harvesting, their absorption maxima were shifted to shorter wavelengths. We attribute these blue shifts to the formation of H-type aggregates or deprotonation of the carboxylic acid units [74, 124], indicating that the carboxylic acid moieties are stronger electron acceptors compared with the carboxylatetitanium units. Similar phenomena have been observed for several other organic dyes [125-127].

The photoluminescence spectra of CB dyes are depicted in Figure 5.9(B). Compared to their absorption spectra in DMF solution (Figure 5.8), PL spectra exhibit red shift with the stroke shift value between 113-120 nm.





Table 5.1 Optical properties data of CB01-CB22 dyes.

Dyes	λ^{abs}_{onset}	λ^{abs}_{max}	ε at λmax	λ ^{em} max	λ^{abs}_{max}	Stroke
	(solution)	(solution)	(solution)	(solution)	(on TiO ₂)	shift
	(nm) ^a	(nm) ^a	(M ⁻¹ cm ⁻¹) ^a	(nm) ^{a, b}	(nm) ^c	(nm)
CB01	456	396	24,669	515	396	119
CB11	466	405	21,230	522	416	117
CB12	486	413	25,723	533	433	120
CB22	492	423	27,870	536	450	113

^a measured in dimethylformamide (DMF) solution at 25 °C

^b excited at maximum absorption in solution

 $^{\circ}$ measured dyes adsorbed on TiO₂ thin film

5.3.3 Electrochemical properties

Cyclic voltamogram of carbazole dyes measured in dimethylformamide solution are illustrated in Figure 5.10 and the electrochemical data, HOMO and LUMO levels are summarized in Table 5.2. Owing to the presence of central electron donating moieties (carbazole donor core), CB dyes exhibit dominant irreversible oxidation peaks at higher voltage and the smaller on at lower voltage, whereas the reduction process of the dyes are not observed. The dyes with more thiophene unit exhibit lower oxidation onset indicate easier losing electron due to the increasing electron density in the backbone. The oxidation onset of **CB01**, **CB11**, **CB12** and **CB22** are 0.78, 0.70 and 0.64, respectively indicated that increasing in conjugation length of the dyes shifted the oxidation potential in a negative direction. The HOMO levels of the dyes were in the range -5.39 to -5.25 eV with respect to I/I_3 redox couple (-4.8 eV), thus the low energy levels of dyes ensured negative Gibb's energies and thus provided enough driving forces for the charge regenerations [128]. The deduced LUMO levels were in the range of ca. -2.67 to -2.73 eV, which are higher than the conduction band edge (-4.4 eV), thus indicating that the electron injection process is energetically favorable [129].



Fugure 5.10 Cyclic voltamogram of CB dyes in dry DMF.

Dyes	$\mathbb{E}_{onset}^{0x}(V)^{a}$	E _g (eV) ^b	HOMO (eV) ^c	LUMO (eV) ^d
DB01	0.95	2.72	-5.39	-2.67
DB 11	0.93	2.66	-5.37	-2.71
DB12	0.83	2.55	-5.27	-2.72
DB22	0.81	2.52	-5.25	-2.73

 Table 5.2 Electrochemical data and energy level of carbazole diaccepter dyes.

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

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

^c calculated using the empirical equation: HOMO = -(4.44 + E_{onset}^{ox})

^d calculated from LUMO = HOMO + E_{g}



Figure 5.11 The energy diagram of CB dyes.

5.3.3 Electrochemical properties

The thermal decomposition of **CB** dyes was studied by thermogravimetric analysis under nitrogen atmospheric condition. TGA thermograms of the dyes are displayed in Figure 5.12 and T_{sd} are listed in Table 5.3. The dyes exhibit 5% weight loss between 160 and 244 °C. The low thermal properties are parallel to its small molecular weight.



Figure 5.12 TGA thermograms of CB dyes.

5.3.4 Cell performance

The photovoltaic properties of DSSCs containing CB dyes were measured under simulated AM 1.5 irradiation condition (100 mW/cm²), where TiO_2 photoelectrodes with approximately a thickness of 12 mm and a working area of 0.25 cm² were utilized. The incident photon-to-current conversion efficiency (IPCE) and photocurrent voltage (*J-V*) curves of DSSCs

based on CB dyes and N719 refference dyes are shown in Figure 5.13 (A) and (B), respectively, and the details of photovoltaic parameters, such as the open-circuit photovoltage ($V_{\rm OC}$), short-circuit photocurrent density ($J_{\rm SC}$), fill factor (*FF*), and solar-to-electrical energy conversion efficiency (η) are listed in 5.4.



Figure 5.13 IPCE spectra (A) and I-V curves (B) of DSSCs based on CB dyes as sensitizer.

Dye	$J_{\rm sc}$	V _{oc}	FF	η
 ,	(mA/cm ²)	(V)		(%)
CB01	9.54	0.72	0.69	4.70
CB 11	8.67	0.68	0.73	4.29
CB12	7.26	0.61	0.73	3.21
CB22	5.35	0.56	0.74	2.23
N719	12.04	0.70	0.70	5.90

Table 5.4 Performance parameter of DSSCs constructed using CB dyes as sensitizer^a.

^aexperiments were conducted in identical condition using TiO₂ photonode with approximately 11 μ m thickness and 0.25 cm² working area on the FTO (8 Ω /A) substrate.

Due to the large molar extinction coefficient and red shift in absorption spectra, the cell based on CB22 sensitizer should show the better IPCE spectra among four dyes, but the results show that the IPCE value of CB22 exhibits the lowest in maximum IPCE value of 22%, whereas CB01 based device show the highest IPCE performance at 64%. This is because of the low solubility of the dye when more thiophene units are introduced. Base on the fact that bisthiophene moiety provide planar structure, incorporating with planarity of 3,6-disubstituted carbazole, the dyes CB12 and CB22 are less soluble which cause a problem in the cell fabrication process. Therefore the best overall conversion efficiency comes from CB01 based cell with η of 4.70 % ($J_{sc} = 9.54$ mA cm⁻², $V_{oc} = 0.72$ V, FF = 0.69) which is equivalent to 79% compared to N719 reference cell.

5.4 Conclusion

We have synthesized a series of organic sensitizers with functionalized 3,6-carbazole (donor) connected to two anchoring cyanoacrylic acid (acceptor) termini via symmetrical and asymmetrical conducting thiophene linkers. In this A-D-A configuration, the dyes show the optical properties influenced from the number of thiophene unit as observed in previous study in chapter 2 and 3. The absorption and emission spectra are more red shift when the number of thiophene ring are increasing. The dye **CB22** containing symmetric bisthiophene as spacer show the best optical characteristic. The HOMO and LUMO levels of four dyes indicate the driving force for electron injection and regeneration process. From optical and electrochemical characteristic of CB dyes indicate the good sign for using CB dyes as sensitizer in DSSCs. Unfortunately, the DSSCs from CB dyes based device exhibit the cell performance during η 2.23-4.7%. The best performance comes from **CB01** based cell with 4.70 % ($J_{sc} = 9.54$ mA cm⁻², $V_{oc} = 0.72$ V, FF = 0.69).

CHAPTER 6

SYNTHESIS AND CHARACTERIZATION OF D-A-D EMITTING MATERIALS FOR ORGANIC LIGHT EMITTING DIODES

6.1 Introduction

Although the first generation organic light emitting diodes (OLEDs) displays has now been produced in consumer electronics such as digital cameras and mobile phones, it is still interesting to be investigated to develop more efficient and stable phosphorescent materials to simplify or improve device performance and stability. The device performance of OLEDs depends on the charge balance of the injected holes and electrons as well as the exciton confinement in a device [130]. As π -conjugated emissive materials often exhibit better hole injection and transport than electrons, the charge balance of an OLED device is often optimized by sequential deposition of functional layers to differentially perform the charge injection, charge transport, and light emission [131]. Multifunctional emissive materials with a dipolar character, which transport holes and electrons more or less equally, may be used to simplify the fabrication and structure of a multilayer device [132].

Many Donor-Accepter (D-A) molecules have been employed as emitters in OLEDs, but the nature of the emissive states has not always been established or clear, neither are the factors governing the EL efficiency and thus the choice of the D and A moieties [133-135]. Systematic studies of the effects of factors such as the electron-donating strength of the donor moiety, the electron-accepting strength of the acceptor moiety, and the molecular geometry on the EL of D–A molecules have been lacking but are essential for a rational molecular design of nextgeneration emissive materials for OLEDs [136]. The emission from such D–A molecules, in principle, can originate from intramolecular charge-transfer (ICT) excited states formed by reaction between the donor radical cations and the cceptor radical anions [137]. Thus, a choice of the D and A units could facilitate simultaneous manipulation of the highest occupied molecular orbital/lowest unoccupied molecular orbital (HOMO/LUMO) levels and the emission color of the D–A molecule [138].

Donor-Accepter-Donor (D-A-D) type organic emissive materials have been largely unexplored in field of OLED application even though this is typical structure for two-photon absorbing dyes. Depending on the electronic nature of the central aryl donor moiety, this type of materials will emit light cover visible spectrum by tuning the conjugation length and type of central aryl core. There are few reports that investigated the D-A-D OLED materials based on thiophene, benzothiadiazole, benzoazadiazole and fluorenone. The charge transfer from donor to accepter of this OLED type provide the materials in low band gap and tuning color to red region.

Benzothiadiazole (BTD) core with arylamine donor based on D-A-D type were reported as red emitting materials by Shuntaro Mataka and co-workers [139]. The examples of BTD emitters are given in Figure 6.1. The photon absorbing and the fluorescent quantum yield of this materials were investigated and found that the BTD derivatives exhibit orange to red photoluminescent and the length and the planarity of the p-conjugated spacers between the benzothiadiazole unit and the amino groups play an important role in increasing the two-photon absorption activity.



A series of D-A-D bis-dipolar emissive oligoarylfluorenes, bearing an electron affinitive core, 9,9-dibutylfluorene as conjugated bridges, and diphenylamino as end-caps were reported by Ye Tao and co-workers [140]. The materials modified by the use of various electron affinitive central aryl cores that included dibenzothiophene, phenylene, oligothiophenes, 2,1,3-benzothiadiazole, 4,7-dithien-2-yl-2,1,3-benzothiadiazole, thiophene *S*,*S*¢-dioxide, and dibenzothiophene*S*,*S*¢-dioxide exhibit the full UV-vis spectrum cover from 412 to 656 nm. Most of materials can form morphologically stable amorphous thinfilms (*T*g) 88-127 °C with a high decomposition temperature, $T_{dec} > 450$ °C. The multilayer OLEDs based on these emitters exhibit good to excellent device performance with emission colors spanning the full UV-vis spectrum. The emitter bearing oligothiophene core based devices exhibit a maximum luminance of 5000-12500 cd m⁻² and luminous efficiency up to 3.6-4.0 cd A⁻¹.



Figure 6.2 Example of full color emitting materials based on A-D-A structure.

6.2 Target molecules and aims

Based on literatures review above, we have interested in the emitting materials with the basic structure of Donor-Accepter-Donor type. We have designed the molecules with carbazole-triphenylamine as donor moiety due to the non-planar structure of TPA and the thermal stability of carbazole moiety as well as the electron donating ability of both arylamine derivatives. For the accepter core, we varied the selected core to form the full color emitting materials from blue (phenyl, fluorine), green (oligothiophene) to red (benzothiadiazole) and expected that the large electron donor moiety will display the importance role for improving the OLEDs performance of D-A-D type emitting materials.

Therefore, the aims of this chapter are:

6.2.1 To synthesize D-A-D type emitting materials with carbazole-triphenylamine as donor and Fluorene, oligothiophene and benzothiadiazole as accepter core as shown in Figure 6.3.

6.2.2 To investigate the optical and electrochemical properties of the materials: how the electron affinity core effect the absorption, emission, the molar extinction coefficient as well as the HOMO-LUMO levels of the materials

6.2.3 To investigate the OLEDs performance based on the emitter from target molecules.



Figure 6.3 Structure of taget D-A-D emitting materials.

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6.3.1 Synthesis

The synthesis of D-A-D emitting materials were proceed by double coupling reaction including double Suzuki coupling of halide of arylamine donor compound **26**, **29**, **30** and **94** with the corresponding boronic acid; 9,9-dipropylfluorene-2,7-bis(boronic acid pinacol ester) (95), 2,5-thiophenediboronic acid (96) and 2,1,3-Benzothiadiazole-4,7-bis(boronic acid pinacol ester) (97), or Stille homo coupling of two arylamine. The structure of corresponding halide donor and boronic acid derivatives are given in Figure 6.4 and the synthetic scheme are illustrated in scheme 6.1-6.2.





The synthesis of **DND**, **DT2D** and **DT4D** were performed using Stille coupling reaction between halide donor 26, 29 and 30 under $Pd(PPh_3)_4$ and hexabutyldistananne condition, gave **DND**, **DT2D** and **DT4D** in 11, 39 and 39% respectively.

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Scheme 6.1 Synthesis of DND, DT2D and DT4D by Stille coupling reaction.

The synthesis of **DFD** and **DT1D** were performed using Suzuki coupling reaction between halide donor 26 and corresponding boronic acid; 9,9-dipropylfluorene-2,7-bis(boronic acid pinacol ester) (95) for **DFD**, and 2,5-thiophenediboronic acid (96) for **DT1D** under $Pd(PPh_3)_4$, 2M Na₂CO₃ in THF, gave **DFD** and **DT1D** in 37 and 15% respectively.



Scheme 6.2 Synthesis of DFD and DT1D by Suzuki coupling reaction.

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The synthesis of **DBD**, **DTBTD** and **DPBPD** were performed using Suzuki coupling reaction between halide donor 26, 27 and 94 with 2,1,3-Benzothiadiazole-4,7-bis(boronic acid pinacol ester) (97 under Pd(PPh₃)₄ and 2M Na₂CO₃ in THF, gave **DBD**, **DTBTD** and **DPBPD** in 49, 36 and 38% respectively.





All products were obtained as solid and can be dissolved very well in common organic solvent such as dichloromethane and chloroform due to the steric non-planar structure of donor TPA moiety, except **DTBTD** and **DPBPD** that have less solubility than other because of their planar benzothiadiazole core, led to the aggregation in solid state. **DND** and **DFD** were obtained as white solid, **DT1D** and **DT2D** were obtained as greenish-yellow, while **DT4D** was orange solid. The BTD core series were achieved as orange to dark red solid. The color becomes darker when the conjugation in the accepter core is extended.

The chemical structures of products were identified by NMR and IR techniques. Because of similar functional groups, IR spectra of D-A-D compounds show very similar features composed of C=C stretching around 1600 cm⁻¹, C-C stretching at 1450 cm⁻¹, and C-H stretching of aliphatic and aromatic. H¹-NMR spectra of the compounds exhibit dominant singlet signal at chemical shift 8.10-8.25 ppm collected in CDCl₃ represent 8 protons of carbazole at position 4 and 5 and very strong singlet signal at chemical shift 1.5 ppm represent 72 protons of 24 methyl groups in carbazole moiety, whereas the peaks appeared overlapped each other at 7.0-7.5 ppm were the proton of aromatic segment in the whole molecules. Figure 6.5, 6.6 and 6.5 displayed the selected H¹-NMR spectra of **DND**, **DT2D** and **DBD** represent the H¹-NMR spectra of compound without core, oligothiophene core and benzothiadiazole core, respectively and the spectroscopic data are given in chapter 8.



Figure 6.5 H¹-NMR spectra of DND.

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Figure 6.6 H¹-NMR spectra of DT2D.

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Figure 6.7 H¹-NMR spectra of DBD.



Figure 6.8 H¹-NMR spectra of DPBPD.

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6.3.2 Optical Properties

The absorption spectra in solution of all D-A-D emitting materials were collected in dichloromethane and thin film prepared by spin coating of the emitting materials on glass substrate. The spectra of compound in solution and thin film are displayed in Figure 6.9 and 6.10, and the corresponding data are listed in Table 6.1. The D-A-D compounds can be divided into three groups based on the aryl core type which are: group 1 (G1) composed of DND and DFD, group 2 (G2) refer to the thiophene compounds which are DT1D, DT2D and DT4D, and group 3 refer to the benzothiadiazole core (DBD, DPBPD and DTBTD). Absorption spectra of G1 exhibit two distinguish peaks located at 295 and 350 nm. The spectra of G2 and G3 show three dominant peaks. The first two peaks located at 295, 350 nm, and the third band range between 400-600 nm. The first two peaks are assigned to π - π * transition of aromatic compounds, whereas the third band are assigned to ICT band of donor-accepter compounds. The molar extinction coefficient of the band at 350 nm (70,000-100,000 M^{-1} cm⁻¹) are rather higher than the ε of ICT band (20,000-70,000 M⁻¹cm⁻¹). For G1, the incorporation of Fluorene core just affects only the absorption wavelength shifted a bit into red region (24 nm), but does not affects to the molar absorptity (E 99,854 M⁻¹ cm⁻¹ for DND and 101,360 M⁻¹ cm⁻¹ for DFD). Based on our knowledge, the introduction of fluorene moiety into the molecules will increase the molar absorptivity [104-107]. For G2, the increasing of thiophene unit, as expected, shifts the absorption of ICT band into lower energy (396, 418 and 450 nm for DT1D, DT2D and DT3D) and also increases the molar absorptivity (44,160, 54,895 and 70,616 M⁻¹ cm⁻¹ for DT1D, DT2D and DT3D). This result is related to their observed color. For G3, DTBTD exhibit the most red shift in absorption due to the longer in conjugation system. Comparing to DPBPD, DTBTD exhibits more red shift than DPBPD because of the more planarity of thiophene than phenyl ring, which has repulsion between two H at adjacent ring [141].

The absorption spectra of D-A-D compounds measured in thin film are displayed in Figure 6.10. Among thin film, the compounds are exhibit red shift in absorption when the conjugation in the molecules is increasing as observed in solution. The absorption in film exhibits broad and little red shift compared to its spectra in solution [142]. This is probably due to the aggregation in solid state of the compounds.



Figure 6.9 UV-visible spectra of DAD emitting materials in CH_2Cl_2 .

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Figure 6.10 UV-visible spectra of DAD emitting materials in thin film.

The fluorescence spectra of D-A-D series measured in dilute dichloromethane solution (A) and in thin film (B) excited at 350 nm are shown in Figure 6.11. The compounds exhibit red shift in emission as increased the electron affinity of the aryl core and extended the conjugation length of the molecules. All compounds in G1 and G2 series were strongly fluorescent in solution with color-tuning from deep blue to bright orange as the number of thiophene units increased, whereas G3 with BTD core exhibit lesser fluorescent. We also investigated the effect of excitation wavelength to emission spectra and found that the excitation at absorption maxima of ICT band reduced the fluorescence intensity, while excitation at absorption of donor (350 nm) exhibit better in fluorescence. This indicate that the energy can transfer from donor to accepter in D-A-D molecules.

From fluorescence spectra both in solution and thin film, the spectra of all compounds can span cover the UV-visible region from blue to red due to the extension of conjugation length and the incorporation of electron affinity core provided the full color emitting materials from one series.



Figure 6.11 Photoluminescent spectra of DAD emitting materials in CH₂Cl₂ (A), and thin film (B) excited at 350 nm.

	λ_{max}^{abs} (nm)(E/M ⁻¹ cm ⁻¹)		$\lambda_{_{onset}}^{_{abs}}$	λ _{max} em (nm	_{nax} ^{em} (nm) ^c Stroke		es shift E _g ^e	
	solution ^a	solid ^b	(nm) ^a	Solution ^a	Solid ^b	(nm) ^d	(eV)	
DND	349 (99,854)	348	396	422	426	73	3.13	
DFD	346	348	414	443	433	70	2.99	
	(101,369)							
	373 (85,524)							
DT1D	339 (56,125)	348, 403	447	465	488	69	2.77	
	396 (44,160)							
DT2D	337 (61,110)	347, 421	481	494	517	76	2.58	
	418 (54, 895)							
DT4D	334 (74,537)	348, 456	521	529	545	79	2.39	
	450 (70,616)							
DPBPD	334 (93,595)	349, 444	489	513	528	91	2.53	
	422 (25,407)							
DBD	331 (93,002)	350, 467	534	600	599	138	2.32	
	462 (20,993)							
DTBTD	348 (93,496)	348, 537	613	636	647	108	2.02	
	528 (43,096)		•					

 Table 6.1 Photophysical data of D-A-D emitting materials.

^a measured in dichloromethane solution at 25 $^{\circ}$ C.

^b measured in thin film spin coated on glass substrate.

^c excited at 350 nm.

 $^{d} \ \lambda_{\max}^{em} - \lambda_{\max}^{abs} \text{ of ICT band.}$

^e estimated from the onset of absorption (E_g =1240/ λ_{onset}).

6.3.3 Electrochemical properties

To probe the redox properties of these D-A-D series, cyclic voltammetry performed in a three-electrode cell setup with 0.1 M Bu_4NPF_4 as a supporting electrolyte in CH_2Cl_2 was carried out. The Cyclic voltamogram of all compounds are shown in Figure 6.11 and the results are tabulated in Table 6.2 and 6.3. All compounds exhibit reversible oxidation wave with $E_{1/2}$ in the range of 0.66-1.67 V and E_{onset} of 0.31-0.42 V, G1 (DND and DFD) and G3 (BTD) series exhibit three dominant oxidation peaks, corresponding to three arylamine (two carbazole and one triphenylamine) on both side of donor groups, where as G2 (thiophene core) series exhibit four or more (DT4D) oxidation peaks. This more oxidation process may come from the loss of electron in aryl core.





The conjugation length and the strength of electron affinity core significantly affect the oxidation potentials of compounds. For example the emitting materials with BTD core exhibit highest oxidation potential among 3 groups. The first oxidation potential of BTD core range between 0.8 V, while the orther series are between 0.6-0.7 V. This higher in oxidation potential of BTD series are attribute to the electron withdrawing ability of benzothiadiazole core. In general, the stronger the electronic withdrawing strength, which holds electrons more strongly, the higher the (first/second) oxidation potential is. On the other hand, the longer the conjugated aryl core, which can better stabilize the radical cation(s), the lower the oxidation potential is. Therefore, **DT4D** exhibit lower oxidation potential than **DT2D** and **DT1D**.

Compound	E ^{ox} onset (V) ^a	HOMO (eV) ^b	LUMO (eV) ^c
DND	0.69	-5.13	-2.00
DFD	0.73	-5.17	-2.18
DT1D	. 0.67	-5.11	-2.34
DT2D	0.66	-5.10	-2.52
DT4D	0.63	-5.07	-2.68
DPBPD	0.76	-5.20	-2.67
DBD	0.76	-5.20	-2.88
DTBTD	0.72	-5.16	-3.14

Table 6.2 Electrochemical properties and energy level of D-A-D emitting materials.

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

^b calculated using the empirical equation: HOMO = $-(4.44 + E_{onset}^{ox})$

^c calculated from LUMO = HOMO + E_g

The LUMO determined by the difference of HOMO and optical energy gap was tabulated in Table 6.2. The electron withdrawing nature of the aryl central core and the conjugation length affect the HOMO and LUMO levels as well as the energy gap. Consistently, the stronger the electron withdrawing strength, the more stabilized is the LUMO (-2.67 to -3.14 eV). These results further support that the LUMO, HOMO, and energy gap of these D-A-D series can easily be modified or tuned by the use of various central aryl cores.

Compound	E ^{0x1} 1/2	E ^{0x2} 1/2	E ^{ox3} 1/2	E ^{0x4} 1/2	E ^{°x5} 1/2	E ^{0x6} 1/2
	(V)	(V)	(V)	(V)	(V)	(V)
DND	0.75	0.88	1.11	1.47	-	-
DFD	0.81	1.11	1.37	1.67	-	-
DT1D	0.74	0.82	1.16	1.40	-	-
DT2D	0.75	1.13	1.32	1.61	-	-
DT4D	0.66	0.79	0.96	1.13	1.24	1.50
DPBPD	0.83	1.13	1.45	1.75	-	-
DBD	0.83	1.13	1.48	-	-	-
DTBTD	0.80	1.12	1.33	1.53	-	-

Table 6.3 The half-wave oxidation potential of multi-oxidation process.

During double scan of the oxidation process of D-A-D emitting materials, there is no new oxidation wave (Figure 6.13). This indicates the electrochemical reaction is not taken place, due to radical at C-3 and C-6 position of periperyl carbazole. This can contribute to a tertbutyl substituent and C-3 and C-6 position of carbazole provided more steric hindred. From these results, the carbazole radical cation cannot occur oxidative coupling at the surface of glassy electrode. This result indicates that radical cation for this molecule is stable to an oxidative coupling.

6.3.4 Thermal Properties

For OLED applications, thermal stability of organic materials is crucial for device stability and lifetime. The degradation of organic electroluminescent devices depends on morphological change resulting from the thermal instability of the amorphous organic layer. The phase-transition properties of D-A-D emitting materilas were determinedd by differential scanning calorimetry (DSC) in nitrogen atmosphere at heating rate of 10 °C/min, the results are shown in **Figure 6.14**. DSC measurements show that all D-A-D compounds are amorphous. The crystallization behavior does not observe in this series. This can be attributed to the bulky donor group which suppressed the flexibility of compound. Glass transition state of this D-A-D compound range bwtween 220-250 °Cwhich indicate the good thermal property of this series. It has been reported that the life time of OLEDs is directly related to the T_g values and thermal stability [143].



Figure 6.13 Multi-scan cyclic voltamograms of DFD and DBD in dry CH₂Cl₂.



Figure 6.14 DCS (second heating) and TGA traces of D-A-D series.

Compound	DND	DFD	DT1D	DT2D	DT4D	DPBPD	DBD	DTBTD
$T_g (^{\circ}C)$	223	234	242	-	247	243	243	255
$T_m (°C)$	-	-	-	324	372	363	343	368
T_{5d} (°C)	227	252	228	239	231	278	229	339

 Table 6.4 Thermal properties of D-A-D compounds.

6.4 Conclusion

A series of organic light-emitting materials with Donor-Accepter-Donor type were successfully synthesized and characterized. The key step to successfully synthesize the compounds is convergent approach using double Suzuki coupling and Stille coupling reaction. The compounds show absorption and emission cover from blue to red region, which shown that the absorption, emission, and electrochemical properties are significantly affected by the electronic nature of the electron affinitive central core, provided an effective tool to tune/modify these functional properties leading to success in the full color emission tuning. Most of compound show high thermal stabilities with a decomposition temperature of $T_{sd} > 250$ °C and form morphologically stable amorphous thin films (Tg) 220-250 °C. From photophysical and electrochemical data show that this type of emitting materials can be used as efficient emitting materials for OLEDs application.

CHAPTER 7

SUMMARY

In this work, we have successfully synthesized and characterized five series of DSSCs sensitizer and OLEDs materials for optoelectronic devices including: starburst TPA dyes, DPA dyes, (pyrane-4-ylidine)malononitrile dyes, single donor double accepter dyes as well as full color emissive materials based on donor-accepter-donor type. The combination of Knoevanegel reaction, Suzuki coupling reaction, Ullmann coupling reaction, bromination and alkylation were used to prepare intermediate and target molecules. The structure elucidation of all compounds was based on spectroscopic methods including NMR, IR and MS techniques. UV-visible and fluorescence spectrometry and cyclic voltammetry were used to characterize the optical and electrochemical properties and thermal properties were studied by DSC and TGA. The quantum calculation was used to estimate the optimized structure and the possibility of electron distribution for further understanding what's going on inside the molecules. A series of novel starburst 2D-D- π -A carbazole-triarylamine-based organic dye (**TPA1-TPA3**) and D-D- π -A (**DPA1-DPA3**) exhibit the promising photophysical, electrochemical and thermal properties related to the donor and π -spacer type. The optical characteristic of the dyes can be tuned by the number of thiophene unit in the bridge, and also donor type. The more number of thiophene unit, the more red shift in absorption spectra. The more in conjugation length, the smaller in oxidation potential. The large side of donor moiety of the dyes resulting in less dyes aggregation which affective the efficiency in good way, but provide less dye uptakes onto the surface of mesoporous metal oxide resulting in lower efficiency. Therefore the efficient DSSCs device could come from the optimized all parameter in DSSCs. For CFP dyes, the two exhibit good characteristic of optical and electrical data, which are broad absorption spectra, high molar extinction coefficient, suitable HOMO-LUMO level for good light harvesting ability and electron injection/regeneration process. Moreover the dyes also show good thermal stability. Unfortunately the DSSCs based devices exhibit rather small overall conversion efficiency compared to the first two series (TPA and DPA dyes). This may consider as due to the incorporation of the accepter into π -spacer, the electron cannot distribute to accepter as much as it could be. Additionally a large side of the molecules may reduce the dye uptake onto TiO_2 film.

The one donor-double accepter (A-D-A) dyes based on carbazole moiety were investigated. The optical and electrochemical properties of the dyes were also tuned by increasing the number of thiophene unit as observed in TPA and DPA dyes. The bisthiophene arms exhibits more red shift than monothiophene and symmetric thiophene exhibits more red shift than asymmetric dyes due to the elongation of conjugation. Due to the planar structure of the carbazole core, it causes the dyes aggregation which decrease the power conversion efficiency of A-D-A dyes.

Among four series of the dyes sensitizer, DPA dyes exhibit best characteristic in optical and electrochemical properties such as most red shift in absorption and lowest in oxidation potentials which indicate the efficient light harvesting ability and charge separation process. DPA dye with three thiophene units (**DPA3**) shows most red shift absorption spectra (λ_{max} 472 nm) and lowest energy gab (2.05 eV) related to the best overall power conversion efficiency (η) of 5.12 % (a short-circuit photocurrent density (J_{sc}) of 10.89 mA cm⁻², open-circuit voltage (V_{oc}) of 0.70 V, and fill factor (*FF*) of 0.67) which almost reach to 90% compared to **N3** reference dyes.

Finally, the full color emissive materials based on donor-accepter-donor type were also investigated. The absorption, emission, and electrochemical properties are significantly affected by the electronic nature of the electron affinitive central core, provided an effective tool to tune/modify these functional properties leading to success in the full color emission tuning. The emissive materials show good thermal stabilities with high value of T_g and T_{5d} up to 250 °C. From photophysical and electrochemical data show that this type of emitting materials can be used as efficient full color emitting materials for OLEDs.

CHAPTER 8

EXPERIMENT

8.1 General procedures and instruments

¹H-NMR spectra were recorded on Brüker AVANCE (300 MHz) spectrometer. ¹³C NMR spectra were recorded on Brüker AVANCE (75 MHz) spectrometer and were fully decoupled. Chemical shifts (δ) are reported relative to the residual solvent peak in part per million (ppm). Coupling constants (*J*) are given in Hertz (Hz). Multiplicities are quoted as singlet (s), broad (br), doublet (d), triplet (t), quartet (q), AA'BB' quartet system (AA'BB'), AB quartet (ABq) and multiplet (m).

The IR spectra were recorded on a Perkin-Elmer FT-IR spectroscopy as KBr disks or neat liquid between two NaCl plates. The absorption peaks are quoted in wavenumber (cm⁻¹). 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 /dm³mol⁻¹cm⁻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.

UV-Visible and fluoreacence spectra were recored on Perkin-Elmer UV-Visible spectrophotometer LAMDA 35 and fluorescence spectrophotometer LS-45. The absorption and emission in solution were measured in distilled dicloromethane and dimethylformamide. The absorbtion and emission in thin film were measured compounds coated on glass substrate by spin coating technique. The dyes adsorbed on TiO_2 films were prepared by dipping dyes solution on TiO_2 substrate for 24 h and then rinced to removed the unadsorbed dyes, and dried over air flow for 24 h.

Dichloromethane was distilled from calcium hydride. Tetrahydrofuran (THF) was heated at reflux under nitrogen over sodium wire and benzophenone until the solution became blue and was freshly distilled before use.

Analytical thin-layer chromatography (TLC) was performed with Merck aluminium plates coated with silica gel 60 F254. 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.

The electrochemistry was performed using a AUTOLAB spectrometer. All measurements were made at room temperature on sample dissolved in freshly distilled dichloromethane, 0.1 M tetra-n-butylammonium hexafluorophosphate as electrolyte. The solutions were degassed by ubbling with nitrogen. Dichloromethane was washed with concentrated sulfuric acid and distilled from calcium hydride. A glassy carbon working electrode, platinum wire counter electrode, and a Ag/AgCl/NaCl (Sat.) reference electrode were used. The ferrocenium/ferrocene couple was used 74 as standard, and the ferrocene was purified by recrystallization from ethanol and then dried under high vacuum and stored over P_2O_5 .

Differential scanning calorimetric (DSC) analysis was performed on a METTLER DSC823e thermal analyzer using a heating rate of 10 $^{\circ}$ C/min and a cooling rate of 50 $^{\circ}$ C/min under a nitrogen flow. Samples were scanned from 25 to 250 $^{\circ}$ C and then rapidly cooled to 25 $^{\circ}$ C and scanned for the second time at the same heating rate to 350 $^{\circ}$ C.

Thermal gravimetric analysis (TGA) was performed on a TG8120 thermoPlus, Rigaku, Japan thermal analyzer. Samples were scanned from 25 °C to 700 °C using a heating rate of 10 °C/min and a cooling rate of 70 °C/min under a nitrogen flow.

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

The dyes adsorption kinetic were measured dyes adsorded on TiO_2 films by study the UV-visible absorption spectra and adsorbed time of the dyes in dichloromethane solution. The cuvettes were sealed to prevent solvent leaking. The adsorbed area was 0.25x0.25 cm².

DSSCs fabrication: Fluorine-doped SnO₂ conducting glasses (8 Ω /sq TCO30-8, Solaronix) were used for transparent conducting electrodes. The double nanostructure thick film (1 μ m thickness) consisting of a transparent (Ti-Nanoxide 20T/SP, Solaronix) and a scattering (Ti-Nanoxide R/SP, Solaronix) TiO₂ layers were screen-printed on TiCl₄ treated FTO. Prior to dye sensitization, the TiO₂ electrode with cell geometry of 0.5 × 0.5 cm² were treated with an aqueous solution of 4 ×10⁻² M TiCl₄ at 70°C in a water saturation atmosphere, heated to 450°C for 30 min and then cooled to 80°C. The TiO₂ electrodes were immersed in the dye solution (3 ×10⁻⁴ M N3 in ethanol, and 5 ×10⁻⁴ M organic dyes in CH₂Cl₂) in the dark at room temperature for 24 hours to

stain the dye onto the TiO_2 surfaces. The dye-adsorbed TiO_2 photoanode and Pt counter electrode were assembled into a sealed cell by heating a gasket Meltonix 1170-25 film (25 µm thickness, Solaronix) as a spacer between the electrodes. An electrolyte solution of 0.6 M LiI, 0.03 M I₂, 0.1 M guanidinium thiocyanate, and 0.5 M *tert*-butylpyridine in 15/85 (v/v) mixture of benzonitrile and acetonitrile was filled through the predrilled hole by a vacuum back filling method. For each dye, six devices were fabricated and measured for consistency and the averaged cell data was reported. The reference cells with the same device configuration based on N3 dye, as the sensitizer, were also fabricated for comparison. The measured current density-voltage data were averaged from forward and backward scans with a bias step and a delay time of 10 mV and 40 ms, respectively. Incident photon to electron conversion efficiency (IPCE) of the device under shortcircuit condition were performed by mean of an Oriel 150W Xe lamp fitted with a CornerstoneTM 130 1/8 m monochromator as a monochromatic light source, a Newport 818-UV silicon photodiode as power density calibration and a Keithley 6485 picoammeter. All measurements were performed using a black plastic mask with an aperture area of 0.180 cm² and no mismatch correction for the efficiency conversion data.

8.2 Synthesis



N,N-bis(4-(3,6-di-*tert*-butylcarbazol-N-yl)phenyl)-4-iodoaniline (26)

To a 100 ml round bottom flask, tris(4-iodophenyl)amine (3.0 g, 4.8 mmol), 3,6-ditert-butylcarbazole (2.7 g, 9.6 mmol), CuI (0.9 g, 4.8 mmol), K_3PO_4 (3.3 g, 24.1 mmol), and (±)trans-1,2-diaminocyclohexane (0.6 ml, 4.8 mmol) in 60 ml of toluene were added. The resulting mixture was degassed for 5 min and then refluxed under N₂ atmosphere for 24 h. After cooling, the solid residue was filtered out. The filtrate was washed with water (200 ml x 2) and brine (200 ml), dried over anhydrous sodium sulphate and evaporated to dryness. The pure compound was obtained by silica gel column chromatography using DCM/Hexane (1:9) as eluent. Yield: 1.9 g (48%). Light gray solid. m.p. > 250 $^{\circ}$ C, FT-IR (KBr, cm⁻¹): 3042, 2955, 1507, 1483, 810. ¹H NMR (CDCl₃): 8.37 (4H, s), 7.80 (2H, d, J = 7.2 Hz), 7.50-7.68 (16H, m), 7.20 (2H, d, J = 7.2 Hz), 1.68 (s, 36H). ¹³C NMR (CDCl₃): 147.2, 145.9, 145.6, 142.6, 139.4, 133.3, 130.9, 128.7, 127.8, 126.8, 125.3, 124.5, 123.6, 123.3, 122.7, 116.3, 110.8, 109.2, 34.8, 32.0. HRMS m/z: 926.3902 [M+H]

N,N-bis(4-(3,6-di-tert-butylcarbazol-N-yl)phenyl)-4-(thiophen-2-yl)aniline (27)

To a 100 ml round bottom flask, **26** (2.0 g, 1.9 mmol), 2-thiopheneboronic acid (0.27 g, 1.9 mmol), Pd(PPh₃)₄ (0.05 g, 0.04 mmol), 2 M Na₂CO₃ aqueous (16 ml) and 40 ml of THF were placed. The resulting mixture was degassed for 5 min and then refluxed under N₂ atmosphere for 24 h. After cooling, DCM (100 ml) was added and the organic layer was washed with water (100 ml x 2) and brine (100 ml), dried over anhydrous sodium sulphate and evaporated to dryness. The pure compound was obtained by silica gel column chromatography using DCM/Hexane (1:9) as eluent. Yield: 1.3 g (72%). Colorless solid. m.p. > 250 °C, FT-IR (KBr, cm⁻¹): 3041, 2958, 1507, 1473, 809. ¹H NMR (CDCl₃): 8.11 (4H, d, J = 5.4 Hz), 7.59 (2H, s), 7.24-7.48 (19H, m), 7.05 (1H, s), 1.68 (s, 36H). ¹³C NMR (CDCl₃): 146.6, 145.9, 143.6, 142.7, 139.1, 132.7, 129.5, 128.5, 127.7, 121.1, 125.2, 124.9, 123.8, 123.1, 116.5, 109.5, 34.8, 32.2 HRMS m/z: 882.4819 [M+H]



4-(5-bromothiophen-2-yl)-N,N-bis(4-(3,6-di-tert-butylcarbazol-N-

yl)phenyl)aniline (29)



N-Bromosuccinamide (0.35 g, 2.0 mmol) was added in small portions to a solution of **27** (1.7 g, 1.9 mmol) in THF (30 ml). The mixture was stirred at room temperature under N₂ for 1 h. Water (30 ml) and DCM (100 ml) were added. The organic phase was separated, washed with water (100 ml x 2), brine solution (100 ml), dried over anhydrous Na₂SO₄, filtered, and the solvent was removed to dryness. Purification by silica gel column chromatography eluting with DCM/Hexane (1:9) gave brominated product. Yield: 1.5 g (91%). Colorless solid. m.p. > 250 °C, FT-IR (KBr, cm⁻¹): 3041, 2959, 1507, 1473, 809. ¹H NMR (CDCl₃): 8.15 (4H, d, J = 1.2 Hz), 7.26-7.52 (21H, m), 7.03 (1H, s), 1.68 (s, 36H). ¹³C NMR (CDCl₃): 147.3, 145.7, 142.9, 139.3, 138.5, 133.4, 127.7, 126.2, 125.2, 123.6, 123.3, 116.3, 109.2, 86.3, 34.7, 32.0 HRMS m/z: 961.3908 [M+H]

4-([2,2'-bithiophen]-5-yl)-*N,N*-bis(4-(3,6-di-*tert*-butylcarbazol-*N*-yl)phenyl)aniline





Compound 28 was prepared from 29 with a method similarly to that described above

for 27 and obtained as yellowish green solid. Yield: 1.8 g (63%). Light yellow green solid. m.p. >

250 °C, FT-IR (KBr, cm⁻¹): 3041, 2953, 1507, 1472, 808. ¹H NMR (CDCl₃): 8.16 (4H, s), 7.04-7.62 (24H, m), 1.68 (s, 36H). ¹³C NMR (CDCl₃): 146.7, 145.9, 142.8, 139.4, 133.2, 129.2, 127.8, 127.7, 126.7,125.1, 124.6, 124.6, 124.6, 124.2,123.9, 123.3, 123.2, 116.2, 109.2, 34.8, 32.0 HRMS m/z: 964.4637 [M+H]

4-(5'-bromo-[2,2'-bithiophen]-5-yl)-*N,N*-bis(4-(3,6-di-*tert*-butylcarbazol-*N*-yl)phenyl)aniline (30)



30 was prepared from **28** with a method similarly to that described above for **29**. Yield: 1.3 g (87%). Light yellow green solid. m.p. > 250 $^{\circ}$ C, FT-IR (KBr, cm⁻¹): 3041, 2959, 1507, 1473, 808. ¹H NMR (CDCl₃): 8.16 (4H, s), 7.26-7.60 (20H, m), 7.18 (1H, d, J = 3.6 Hz), 7.09 (1H, d, J = 3.9 Hz), 6.98 (1H, d, J = 3.6 Hz), 6.94 (1H, d, J = 3.9 Hz), 1.68 (s, 36H). ¹³C NMR (CDCl₃): 147.0, 145.8, 143.3, 142.8, 139.3, 139.0, 135.0, 133.2, 130.6, 127.7, 126.8, 125.2, 124.9, 124.4, 123.5, 123.3, 123.1, 116.2, 109.2, 34.7, 32.0 HRMS m/z: 1044.3773 [M+H]

5-(4-(bis(4-(3,6-di-tert-butylcarbazol-N-yl)phenyl)amino)phenyl)thiophene-2-

carbaldehyde (31)



To a 100 ml round bottom flask, **26** (1.5 g, 1.8 mmol), 5-formyl-2-thiopheneboronic acid (0.15 g, 1.1 mmol), Pd(PPh₃)₄ (0.02 g, 0.01 mmol), 2 M Na₂CO₃ aqueous solution (12 ml) and 25 ml of THF were placed. The resulting mixture was refluxed under N₂ atmosphere for 24 h. After cooling, DCM (100 ml) was added and the organic layer was washed with water (100 ml x 2) and brine (100 ml), dried over anhydrous sodium sulphate and evaporated to dryness. The pure compound was obtained by silica gel column chromatography using DCM/Hexane (1:5) as eluent. Yield: 0.75 g (75%). Light yellow solid. m.p. > 250 °C, FT-IR (KBr, cm⁻¹): 3042, 2958, 1670, 1599, 1507, 1446, 808. ¹H NMR (CDCl₃): 9.89 (1H, s), 8.17 (4H, s), 7.74 (1H, d, J = 3.9 Hz), 7.66 (2H, d, J = 8.4 Hz), 7.42-7.56 (17H, m), 7.37 (1H, d, J = 3.8 Hz), 7.30 (2H, d, J = 8.1 Hz), 1.68 (s, 36H). ¹³C NMR (CDCl₃): 182.5, 154.1, 148.7, 145.4, 142.9, 141.7, 139.3, 137.5, 133.9, 127.8, 127.6, 127.3, 125.8, 123.6, 123.4, 123.4, 123.2, 116.2, 109.2, 34.7, 32.0 HRMS m/z: 909.4761 [M+H]

5'-(4-(bis(4-(3,6-di-*tert*-butylcarbazol-*N*-yl)phenyl)amino)phenyl)-[2,2'bithiophene]-5-carbaldehyde (32)



32 was prepared from **29** with a method similarly to that described above for **31**. Yield: 0.64 g (70%). Yellow solid. m.p. > 250 °C, FT-IR (KBr, cm⁻¹): 3042, 2959, 1665, 1601, 1507, 1456, 808. ¹H NMR (CDCl₃): 9.87 (1H, s), 8.18 (4H, d, J = 1.3 Hz), 7.67 (1H, d, J = 3.9 Hz), 7.61 (2H, d, J = 8.6 Hz), 7.25-7.55 (24H, m), 1.68 (s, 36H). ¹³C NMR (CDCl₃): 182.3, 147.7, 147.2, 145,9, 145.7, 142.8, 141.4, 139.3, 137.3, 134.5, 133.4, 128.2, 127.8, 127.2, 127.0, 125.4, 124.1, 123.8, 123.5, 123.3, 116.2, 109.2, 34.7, 32.0 HRMS m/z: 991.4728 [M+H] 5''-(4-(bis(4-(3,6-di-*tert*-butylcarbazol-*N*-yl)phenyl)amino)phenyl)-[2,2':5',2''terthiophene]-5-carbaldehyde (33)



33 was prepared from **30** with a method similarly to that described above for **31**. Yield: 0.72 g (60%). Yellow solid. m.p. > 250 °C, FT-IR (KBr, cm⁻¹): 3041, 2957, 1665, 1601, 1508, 1460, 808. ¹H NMR (CDCl₃): 9.88 (1H, s), 8.17 (4H, d, J = 1.5 Hz), 7.70 (1H, d, J = 4.2 Hz), 7.61 (2H, d, J = 8.4 Hz), 7.23-7.55 (23H, m), 7.17 (1H, d, J = 3.9 Hz), 1.68 (s, 36H). ¹³C NMR (CDCl₃): 182.3, 147.2, 146.8, 145.8, 144.0, 142.8, 141.6, 139.3, 139.3, 137.2, 135.0, 134.3, 133,3, 128.7, 127.7, 126.9, 125.5, 124.3 124.0, 123.5, 123.3, 116.2, 109.2, 34.7, 32.0 HRMS m/z: 1074.4470 [M+H]

(E)-3-(5-(4-(bis(4-(3,6-di-*tert*-butylcarbazol-N-yl)phenyl)amino)phenyl)thiophen-



A mixture of **31** (0.3 g, 0.3 mmol), cyanoacetic acid (0.038 g, 0.4 mmol) piperidine (2 drops) and chloroform (20 ml) was placed to 50 ml round bottom flask and refluxed under N_2 atmosphere for 18 h. After cooling, the reaction was quenched with 2 ml of water and 50 ml of DCM was added. The organic layer was washed with water (50 ml x 2) and brine (50 ml), dried
over anhydrous Sodium sulphate, filtered and evaporated to dryness. The pure compound was obtained by silica gel column chromatography eluting with MeOH:DCM (2:98). Yield: 0.16 g (58%). Light orange solid. m.p. > 250 °C, FT-IR (KBr, cm⁻¹): 3422, 3042, 2958, 2211, 1582, 1508, 1473, 808. ¹H NMR (DMSO): 8.28 (4H, s), 8.17 (1H, s), 7.75 (3H, d, J = 8.4 Hz), 7.61 (2H, d, J = 8.4 Hz), 7.23-7.55 (13H, m), 7.27 (2H, d, J = 8.4 Hz), 1.68 (s, 36H). ¹³C NMR (DMSO): 164.3, 150.1, 148.0, 145.5, 142.8, 139.0, 138.0, 135.5, 133.2, 127.9, 127.8, 125.9, 124.2 124.0, 123.5, 123.3, 116.8, 109.6, 34.9, 32.2 HRMS m/z: 976.717 [M+H]

(*E*)-3-(5'-(4-(bis(4-(3,6-di-*tert*-butylcarbazol-*N*-yl)phenyl)amino)phenyl)-[2,2'bithiophen]-5-yl)-2-cyanoacrylic acid (TPA2)



TPA2 was prepared from **32** with a method similarly to that described above for **TPA1**. Yield: 0.12 g (57%). Orange solid. m.p. > 250 °C, FT-IR (KBr, cm⁻¹): 3422, 3042, 2958, 2213, 1610, 1508, 1473, 809. ¹H NMR (DMSO): 8.27 (4H, d, J = 1.2 Hz), 8.00 (1H, s), 7.73 (3H, d, J = 8.4 Hz), 7.35-7.63 (20H, m), 7.26 (2H, d, J = 8.4 Hz), 1.68 (s, 36H). ¹³C NMR (DMSO): 163.8, 147.2, 145.7, 144.1, 142.8, 141.7, 139.0, 136.1, 134.7, 133.0, 128.4, 127.9, 127.2 125.6, 124.7 124.5, 124.0, 123.1,119.6, 116.8, 109.6, 34.8, 32.2 HRMS m/z: 1059.350 [M+H]

(*E*)-3-(5''-(4-(bis(4-(3,6-di-*tert*-butylcarbazol-*N*-yl)phenyl)amino)phenyl)-[2,2':5',2''-terthiophen]-5-yl)-2-cyanoacrylic acid (TPA3)



TPA3 was prepared from **33** with a method similarly to that described above for **TPA1**. Yield: 0.19 g (48%). Dark red solid. m.p. > 250 °C, FT-IR (KBr, cm⁻¹): 3419, 3042, 2960, 2212, 1609, 1508, 1473, 808. ¹H NMR (DMSO): 8.27 (4H, s), 8.05 (1H, s), 7.70 (2H, d, J = 8.4 Hz), 7.64 (1H, d, J = 4.2 Hz), 7.57 (4H, d, J = 8.4 Hz), 7.32-7.47 (16H, m), 7.25 (2H, d, J = 8.4 Hz), 1.68 (s, 36H). ¹³C NMR (DMSO): 164.5, 147.0, 145.7, 143.2, 142.8, 142.3, 141.8, 139.0, 137.7, 137.2, 135.8, 134.8, 134.5, 132.9, 128.5, 127.8, 127.1, 127.0, 126.2, 125.5, 125.3, 124.8 124.4, 123.9, 123.1, 118.9, 116.7, 109.5, 34.9, 32.2 HRMS m/z: 1040.50 [M+H]

bis(4-iodophenyl)amine



A mixture of diphenylamine (5.0 g, 29.5 mmol), KI (5.8 g, 35.4 mmol), KIO₃ (6.9 g, 32.5 mmol) in glacial acetic acid (250 ml) was heated at 70 $^{\circ}$ C for 12 h. The temperature was cooled and DCM (200 ml) was added. The organic phase was thoroughly washed with water (200 ml x 4), 0.2 M aqueous Na₂SO₃ (200 ml x 2) and aqueous NaHCO₃ (200 ml), brine solution (200 ml), dried over anhydrous Na₂SO₄ and filtered. After solvent evaporation, the pure compound was obtained by recrystallization from DCM/hexane mixture as light gray solids (4.2 g, 34%). m.p. 122-123 $^{\circ}$ C, FT-IR (KBr, V, cm⁻¹): 3420 (N-H), 3075 (=C-H), 1585 (C=C), 1499, 1307, 815. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 7.53 (4H, d, *J* = 8.7 Hz), 6.80 (4H, d, *J* = 8.7 Hz). ¹³C NMR

N-dodecyl-4-iodo-N-(4-iodophenyl)aniline (40)

A mixture of *bis*(4-iodophenyl)amine (6.0 g, 14.2 mmol), 4-bromododecane (4.3 ml, 17.1 mmol), NaOH (4.6 g, 113.6 mmol) in 50 ml of DMSO was stirred at room temperature for 24 h. The solid residue was filtered out. Water (50 ml) was added to filtrate and then extracted with ethyl acetate. The organic phase was washed with water (100 ml x 2), aqueous HCl (2 M, 50 ml) and brine (50 ml), dried over anhydrous Na₂SO₄, filtered and evaporated to dryness. Purification by silica gel column chromatography using hexane as eluent gave colorless oil (7.6 g, 90%). FT-IR (NaCl, V, cm⁻¹): 3061 (=C-H), 2922 (-C-H), 1585, 1575 (C=C), 1486, 1361, 1245, 1006, 810. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 7.51 (4H, d, *J* = 8.7 Hz), 6.76 (4H, d, *J* = 8.7 Hz), 3.61 (2H, t, *J* = 7.5 Hz), 1.60 (2H, q, *J* = 6.3 Hz), 1.26 (18H, m), 0.89 (3H, t, *J* = 6.3 Hz). ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 147.3, 138.2, 123.1, 52.3, 32.0, 29.7, 29.6, 29.4, 27.3, 27.0, 22.7, 14.2. HRMS calcd for C₂₄H₃₃I₃N: *m/z* 589.07; found: *m/z* [MH⁺]

4-(3,6-di-*tert*-butylcarbazol-N-yl)-N-dodecyl-N-(4-iodophenyl)aniline (41)



A mixture of 40 (8.9 g, 15.2 mmol), 3,6-di-*tert*-butylcarbazole (1.0 g, 3.8 mmol), CuI (0.4 g, 1.9 mmol), K_3PO_4 (2.0 g, 9.4 mmol), and (±)trans-1,2-diaminocyclohexane (0.2 ml, 1.9 mmol) in toluene (70 ml) was degassed with N_2 for 5 min and then heated at reflux under N_2 atmosphere for 24 h. After cooling, the solid residue was filtered out and washed with DCM (50 ml). The organic filtrate was washed with water (100 ml x 2) and brine solution (100 ml), dried over anhydrous Na_2SO_4 and evaporated to dryness. Purification by silica gel column

chromatography using DCM/hexane (1:9) as eluent gave light gray wax (1.3 g, 46%). FT-IR (NaCl, V, cm⁻¹): 3042 (=C-H), 2956 (-C-H), 1583, 1513 (C=C), 1487, 1363, 1262, 810. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 8.13 (2H, d, J = 1.5 HZ), 7.56 (2H, d, J = 9.0 Hz), 7.33-7.47 (6H, m), 7.16 (2H, d, J = 8.7 Hz), 6.83 (2H, d, J = 9.0 Hz), 3.83 (2H, s), 1.60 (2H, s), 1.27 (18H, m), 0.86 (3H, t, J = 6.6 Hz). ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 147.6, 146.3, 142.6, 139.5, 138.1, 131.7, 127.7, 123.4, 123, 122.9, 122.6, 122.2, 119.9, 116.1, 109.1, 83.3, 52.5, 34.7, 32.0, 31.9, 29.6, 29.6, 29.4, 29.3, 27.4, 27.0, 22.6, 14.1. HRMS calcd for C₄₄H₅₇IN₂: *m/z* 740.36; found: *m/z* [MH⁺]

4-(3,6-di-tert-butylcarbazol-N-yl)-N-dodecyl-N-(4-(thiophen-2-yl)phenyl)aniline

(42)



4-(5-bromothiophen-2-yl)-N-(4-(3,6-di-*tert*-butylcarbazol-N-yl)phenyl)-N-

dodecylaniline (44)



N-Bromosuccinamide (0.56 g, 3.2 mmol) was added in small portions to a solution of **42** (2.1 g, 3.0 mmol) in THF (30 ml). The mixture was stirred at room temperature under N₂ for a further 1 h. Water (30 ml) and DCM (100 ml) were added. The organic phase was separated, washed with water (100 ml x 2), brine solution (100 ml), dried over anhydrous Na₂SO₄, filtered, and the solvents were removed to dryness. Purification by silica gel column chromatography eluting with DCM/hexane (1:9) gave brominated product as colorless sticky gum (1.5 g, 66%). FT-IR (NaCl, V, cm⁻¹): 3036 (=C-H), 2923 (-C-H), 1676, 1486 (C=C), 1362, 1253, 810. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 8.17 (2H, s), 7.45-7.51 (H, m), 7.37 (2H, d, *J* = 8.4 Hz), 7.21-7.26 (3H, m), 7.01 (2H, d, *J* = 8.4 Hz), 6.96 (2H, dd, *J* = 8.4, 5.6 Hz), 3.77 (2H, t, *J* = 7.5 Hz), 1.77 (2H, m), 1.13-1.57 (18H, m), 0.87 (3H, t, *J* = 6.2). ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 147.5, 146.4, 146.0, 142.6, 139.5, 131.7, 130.7, 127.7, 126.7, 126.5, 123.5, 122.4, 120.5, 116.2, 110.5, 52.5, 37.1, 34.7, 32.7, 32.0, 31.9, 30.0, 29.7, 29.6, 29.4, 29.3, 27.5, 27.1, 22.7, 19.7, 14.1 HRMS calcd for C₄₈H₅₉BrN₂S: *m/z* 774.36; found: *m/z* [MH⁺]

4-([2,2'-bithiophen]-5-yl)-N-(4-(3,6-di-*tert*-butylcarbazol-N-yl)phenyl)-Ndodecylaniline (43)



Compound **43** was prepared from **44** with a method similarly to that described above for **42** and obtained as light green sticky gum (1.7 g, 73%). FT-IR (NaCl, V, cm⁻¹): 3036 (=C-H), 2924 (-C-H), 1602, 1512 (C=C), 1499, 1363, 1262, 809. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 8.14 (2H, d, J = 1.2 Hz), 7.54 (2H, d, J = 8.7 Hz), 7.01-7.49 (17H, m), 3.78 (2H, t, J = 7.2 Hz), 1.77 (2H, m), 1.26-1.47 (18H, m), 0.83 (3H, t, J = 6.2). ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 147.3, 146.6, 143.3, 142.6, 139.6, 131.4, 127.8, 127.8, 127.3, 126.7, 124.6 124.1, 123.5, 123.4, 123.2, 122.6, 121.9, 121.1, 116.2, 109.3, 52.6, 37.2, 34.8, 32.1, 32.0, 30.1, 29.8, 29.7, 29.7, 29.5, 29.4, 27.6, 27.2, 22.8, 14.2. HRMS calcd for C₅₂H₆₂N₂S₂: *m/z* 778.44; found: *m/z* [MH⁺]

4-(5'-bromo-[2,2'-bithiophen]-5-yl)-*N*-(4-(3,6-di-*tert*-butylcarbazol-*N*-yl)phenyl)-*N*-dodecylaniline (45)



Compound 45 was prepared from 43 with a method similarly to that described above for 44 and obtained as light yellow-green sticky gum (1.1 g, 72%). FT-IR (NaCl, V, cm⁻¹): 3029 (=C-H), 2923 (-C-H), 1589, 1576 (C=C), 1486, 1362, 1245, 810. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 8.15 (2H, d, J = 1.8 Hz), 7.36-7.55 (8H, m), 7.21 (2H, d, J = 6.3 Hz), 7.06-7.14 (4H, m), 6.92 (2H, dd, J = 3.8, 12.6 Hz), 3.81 (2H, t, J = 7.2 Hz), 1.77 (2H, s), 1.27-1.55 (18H, m), 0.86 (3H, s). ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 147.4, 146.7, 143.8, 142.6, 139.5, 139.1, 134.5, 131.6, 130.6, 127.7, 126.7, 124.9, 123.5, 123.3, 123.1, 122.5, 120.6, 110.5, 109.2, 52.5, 34.7, 32.0, 31.9, 29.6, 29.6, 29.4, 29.3, 27.5, 27.1, 22.7, 14.1. HRMS calcd for C₅₂H₆₁BrN₂S₂: *m/z* 856.30; found: *m/z* [MH⁺]

5-(4-((4-(3,6-di-*tert*-butylcarbazol-*N*-yl)phenyl)(dodecyl)amino)phenyl)thiophene-2-carbaldehyde (46)



A mixture of 41 (0.6 g, 0.9 mmol), 5-formyl-2-thiopheneboronic acid (0.1 g, 0.6 mmol), $Pd(PPh_3)_4$ (0.016 g, 0.013 mmol), 2 M Na_2CO_3 aqueous solution (7 ml) in THF (20 ml) was degassed with N_2 for 5 min and then heated at reflux under N_2 atmosphere for 24 h. After cooling, DCM (50 ml) was added and the organic layer was washed with water (50 ml x 2) and

brine solution (50 ml), dried over anhydrous Na₂SO₄, filtered and evaporated to dryness. Purification by silica gel column chromatography using DCM/hexane (1:4) as eluent gave yellow sticky gum (0.47 g, 54%). FT-IR (NaCl, V, cm⁻¹): 3036 (=C-H), 2918 (-C-H), 1664 (C=O), 1600, 1510 (C=C), 1446, 1362, 1225, 805. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 9.85 (1H, s), 8.15 (2H, s), 7.70 (2H, d, *J* = 3.8 Hz), 7.58 (2H, d, *J* = 8.6 Hz), 7.26-7.53 (10H, m), 6.99 (2H, d, *J* = 8.6 Hz), 3.82 (2H, t, *J* = 7.5 Hz), 1.77 (2H, s), 1.26-1.54 (18H, m), 0.85 (3H, s). ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 182.5, 155.1, 149.1, 145.6, 142.8, 140.9, 139.3, 137.8, 133.5, 127.8, 127.5, 125.0, 124.2, 123.5, 123.3, 122.3, 117.9, 116.2, 109.1, 52.5, 34.7, 32.0, 31.9, 29.6, 29.6, 29.4, 29.3, 27.5, 27.0, 22.6, 14.0. HRMS calcd for C₄₉H₆₀N₂OS: *m/z* 724.44; found: *m/z* [MH⁺]

5'-(4-((4-(3,6-di-*tert*-butylcarbazol-*N*-yl)phenyl)(dodecyl)amino)phenyl)-[2,2'bithiophene]-5-carbaldehyde (47)



Compound 47 was prepared from 44 with a method similarly to that described above for 46 and obtained as light yellow-green sticky gum (0.3 g, 57%). FT-IR (NaCl, V, cm⁻¹): 3038 (=C-H), 2919 (-C-H), 1664 (C=O), 1607, 1511 (C=C), 1454, 1361, 1227. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 9.85 (1H, s), 8.17 (2H, s), 7.65 (2H, d, *J* = 3.8 Hz), 7.18-7.51 (13H, m), 7.09 (2H, d, *J* = 8.6 Hz), 3.82 (2H, t, *J* = 7.5 Hz), 1.79 (2H, s), 1.29-1.49 (18H, m), 0.85 (3H, m). ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 182.3, 148.0, 147.5, 146.6, 146.2, 142.7, 141.2, 139.5, 137.4, 133.7, 132.3 127.8, 127.2, 126.9, 125.7, 123.6, 123.5, 123.3, 123.2, 122.8, 119.7, 116.2, 109.2, 52.5, 34.7, 32.0, 31.9, 29.6, 29.6, 29.4, 29.3, 27.6, 27.1, 22.7, 14.1. HRMS calcd for C₅₃H₆₂N₂OS₂: *m/z* 806.43; found: *m/z* [MH⁺]



Compound **48** was prepared from **45** with a method similarly to that described above for **46** and obtained as yellow-orange solid (0.28 g, 51%). m.p. > 250 °C, FT-IR (KBr, V, cm⁻¹): 3059 (=C-H), 2914 (-C-H), 1659 (C=O), 1597, 1509 (C=C), 1454, 1356, 1225, 1046, 809, 791. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 9.84 (1H, s), 8.26 (2H, s), 7.09-7.58 (18H, m), 3.82 (2H, s), 1.83 (2H, s), 1.36-1.63 (18H, m), 0.95 (3H, s). ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 182.2, 147.6, 146.8, 146.3, 144.5, 142.7, 141.5, 139.6, 139.5, 137.3, 134.4, 134.1, 132.0, 127.8, 127.0, 126.7, 126.4, 125.5, 124.1, 123.9, 123.6, 123.3, 123.2, 122.7, 120.3, 116.3, 109.3, 52.5, 34.8, 32.1, 32.0, 29.7, 29.7, 29.5, 29.4, 27.6, 27.2, 22.8, 14.2. HRMS calcd for C₅₇H₆₄N₂OS₃: *m/z* 888.42; found: *m/z* [MH⁺]

(E)-2-cyano-3-(5-(4-((4-(3,6-di-*tert*-butylcarbazol-N-yl)phenyl)(dodecyl)amino) phenyl)thiophen-2-yl)acrylic acid (DPA1)



A mixture of 46 (0.16 g, 0.2 mmol), cyanoacetic acid (0.04 g, 0.4 mmol) and piperidine (2 drops) in chloroform (20 ml) was degassed with N₂ for 5 min and then heated at reflux under N₂ atmosphere for 8 h. After cooling, the reaction was quenched with water (5 ml) and extracted with DCM (50 ml x 2). The combined organic layer was washed with water (50 ml x 2) and brine (50 ml), dried over anhydrous sodium sulphate, filtered and evaporated to dryness. Purification by silica gel column chromatography eluting with MeOH:DCM (1:9) afforded orange solids (0.11 g, 61%). m.p. >250 °C, FT-IR (KBr, V, cm⁻¹): 3421 (O-H), 3042 (=C-H), 2925 (-C- H), 2213 (C=N), 1598 (C=O), 1512 (C=C), 1363, 1225, 808. ¹H NMR (300 MHz, DMSO, δ , ppm): 8.22 (3H, s), 7.77 (1H, s), 7.62 (2H, d, J = 8.1 Hz), 7.29-7.52 (9H, m), 7.04 (2H, d, J = 8.4 Hz), 3.81 (2H, s), 1.67 (2H, s), 1.19-1.40 (18H, m), 0.80 (3H, s). ¹³C NMR (75 MHz, DMSO, δ , ppm): 164.4, 148.6, 145.8, 142.7, 139.2, 134.5, 132.4, 127.8, 127.5, 124.7, 124.4, 123.9, 123.2, 123.2, 123.1, 119.1, 116.7, 109.5, 52.0, 34.8, 32.2, 31.7, 29.5, 29.4, 29.4, 29.2, 29.1, 27.4, 26.8, 22.5, 14.3. HRMS calcd for C₅₂H₆₁N₃O₂S: *m/z* 791.45; found: *m/z* [MH⁺]

(E)-2-cyano-3-(5'-(4-((4-(3,6-di-*tert*-butylcarbazol-N-yl)phenyl)(dodecyl)amino) phenyl)-[2,2'-bithiophen]-5-yl)acrylic acid (DPA2)



Compound **DPA2** was prepared from **47** with a method similarly to that described above for **DPA1** and obtained as orange-red solid (0.12 g, 59%). m.p. > 250 °C, FT-IR (KBr, V, cm⁻¹): 3420 (O-H), 3041 (=C-H), 2925 (-C-H), 2213 (C=N), 1598 (C=O), 1512 (C=C), 1363, 1225, 809. ¹H NMR (300 MHz, DMSO, δ , ppm): 8.14 (1H, s), 8.04 (2H, s), 7.87 (1H, s), 7.15-7.50 (13H, m), 6.97 (2H, d, J = 7.8 Hz), 3.71 (2H, s), 1.65 (2H, s), 1.17-1.37 (18H, m), 0.75 (3H, s). ¹³C NMR (75 MHz, DMSO, δ , ppm): 167.0, 147.6, 146.1, 145.3, 143.8, 142.5, 139.2, 135.1, 133.8, 131.6, 127.5, 126.7, 125.8, 123.8, 123.6, 123.1, 120.0, 116.1, 109.3, 52.2, 34.7, 32.3, 31.7, 29.5, 29.4, 29.4, 29.2, 29.1, 27.4, 26.8, 22.5, 14.2. HRMS calcd for C₅₆H₆₃N₃O₂S₂: *m/z* 791.45; found: *m/z* [MH⁺]

(E)-2-cyano-3-(5''-(4-((4-(3,6-di-*tert*-butylcarbazol-*N*-yl)phenyl)(dodecyl)amino) phenyl)-[2,2':5',2''-terthiophen]-5-yl)acrylic acid (DPA3)



Compound **DPA3** was prepared from **48** with a method similarly to that described above for **DPA1** and obtained as dark red solid (0.18 g, 47%). m.p. > 250 °C, FT-IR (KBr, V, cm⁻¹): 3421 (O-H), 3036 (=C-H), 2924 (-C-H), 2212 (C=N), 1602 (C=O), 1512 (C=C), 1363, 1225, 808. ¹H NMR (300 MHz, DMSO, δ , ppm): 8.02 (1H, s), 7.75 (1H, s), 7.73 (3H, s), 7.07-7.51 (14H, m), 6.99 (2H, d, J = 8.4 Hz), 3.73 (2H, s), 1.66 (2H, s), 1.16-1.37 (18H, m), 0.75 (3H, s). ¹³C NMR (75 MHz, DMSO, δ , ppm): 167.0, 147.6, 146.1, 145.3, 143.8, 142.5, 139.2, 135.1, 133.8, 131.6, 127.5, 126.7, 125.8, 123.8, 123.6, 123.1, 120.0, 116.1, 109.3, 52.2, 34.7, 32.3, 31.7, 29.5, 29.4, 29.4, 29.2, 29.1, 27.4, 26.8, 22.5, 14.2. HRMS calcd for C₆₀H₆₅N₃O₂S₃: *m/z* 955.42; found: *m/z* [MH⁺]

4-(7-(3,6-di-*tert*-butylcarbazol-N-yl)-9,9-dihexylfluoren-2-yl)benzaldehyde (55)



A mixture of **54** (2.0 g, 3.0 mmol), 4-formylphenylboronic acid (0.4 g, 2.7 mmol), Pd(PPh₃)₄ (0.095 g, 0.082 mmol), and 2 M Na₂CO₃ aqueous solution (40 ml) in THF (60 ml) was degassed with N₂ for 5 min. The reaction mixture was stirred at reflux under N₂ for 24 h. After being cooled to room temperature, water (100 ml) was added and extracted with CH₂Cl₂ (80 ml x 2). The combined organic phase was washed with water (80 ml), brine solution (80 ml), dried over anhydrous Na₂SO₄, filtered, and the solvents were removed to dryness. Purification by column chromatography over silica gel eluting with a mixture of CH₂Cl₂ and hexane (1:4) followed by recrystallization from Hexane afforded 1 as colorless solid (1.3 g, 69%). m.p. >250 °C, FT-IR (KBr, V, cm⁻¹): 3048 (C-H), 2954, 2926, 2856 (C-H), 1646 (C=O), 1562 (C=C, Ar), 1487, 1363, 1262, 925, 808. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 10.12 (1H, s), 8.25 (2H, s), 8.04 (2H, d, *J* = 8.1 Hz), 7.95 (1H, d, *J* = 7.3 Hz), 7.43-7.92 (11H, m), 2.11 (4H, t, *J* = 7.3 Hz), 1.56 (18H, s), 1.19 (16H, m), 0.85 (6H, t, *J* = 5.5 Hz), ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 191.8, 152.8, 151.9, 147.5, 142.9, 141.0, 139.3, 139.1, 138.6, 137.3, 135.1, 130.3, 127.7, 126.5, 125.4, 123.5, 123.4, 121.7, 121.4, 121.0, 120.2, 116.3, 109.2, 55.5, 40.3, 34.7, 32.0, 31.5, 29.6, 23.9, 22.5, 14.0. HRMS calcd for C₃₂H₆₁NO: *m/z* 695.79; found: *m/z* 696.826 [MH⁺].

(*E*)-2-(2-(4-(7-(3,6-di-*tert*-butylcarbazol-*N*-yl)-9,9-dihexylfluoren-2-yl)styryl)-6methylpyran-4-ylidene)malononitrile (56)



A mixture of **55** (1.13 g, 1.58 mmol), 2-(2,6-dimethylpyran-4-ylidene)malononitrile (1.36 g, 7.90 mmol) and piperidine (2 drops) in chloroform (20 ml) was heated at reflux under N₂ atmosphere for 18 h. After cooling to room temperature, the reaction was quenched with water (5 ml) and extracted with CH₂Cl₂ (50 ml x 2). The combined organic layer was washed with water (50 ml x 2) and brine (50 ml), dried over anhydrous sodium sulphate, filtered and evaporated to dryness. Purification by silica gel column chromatography eluting with CH₂Cl₂:Hexane (1:4) afforded yellowish-orange solids (0.46 g, 39%). m.p. >250 °C, FT-IR (KBr, V, cm⁻¹): 3042 (=C-H), 2926, 2856 (-C-H), 2210 (C=N), 1652, 1563 (C=C, Ar), 1472, 1416, 1361, 1295, 1178, 925, 808. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 8.17 (2H, s), 7.93 (1H, d, *J* = 8.4 Hz), 7.85 (1H, d, *J* = 8.3 Hz), 7.77 (2H, d, *J* = 8.1 Hz), 7.39-7.70 (10H, m), 6.81 (1H, s), 6.74 (2H, m), 6.57 (1H, s), 2.44 (3H, s), 2.02 (4H, t, *J* = 7.2 Hz), 1.48 (18H, s), 1.11 (16H, m), 0.79 (6H, t, *J* = 6.3 Hz). ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 161.9, 159.1, 156.2, 152.7, 151.9, 143.5, 142.8, 141.5, 139.3, 138.8, 137.6, 137.2, 133.3, 128.3, 127.7, 126.1, 125.6, 123.5, 123.4, 121.4, 121.3, 120.9, 120.2, 117.9, 116.3, 115.0, 109.2, 107.3, 106.5, 59.5, 55.5, 40.3, 34.7, 32.0, 31.5, 29.6, 23.9, 22.5, 20.0, 14.0. HRMS calcd for C₆₂H₆₇N₃O: *m/z* 873.08; found: *m/z* 874.104 [MH⁺].



A mixture of **56** (1.00 g, 1.14 mmol), 5-bromothiophene-2-carbaldehyde (0.24 g, 1.26 mmol) and piperidine (2 drops) in chloroform (20 ml) was heated at reflux under N₂ atmosphere for 18 h. After cooling, the reaction was quenched with water (5 ml) and extracted with CH₂Cl₂ (50 ml x 2). The combined organic layer was washed with water (50 ml x 2) and brine (50 ml), dried over anhydrous sodium sulphate, filtered and evaporated to dryness. Purification by silica gel column chromatography eluting with CH₂Cl₂:Hexane (1:4) afforded dark orange solids (0.87 g, 73%). m.p. >250 °C, FT-IR (KBr, V, cm⁻¹): 3052 (=C-H), 2952, 2926, 2856 (-C-H), 2207 (C≡N), 1637, 1600, 1547 (C=C, Ar), 1491, 1473, 1416, 1362, 1294, 1201, 1179, 943, 808. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 8.19 (2H, s), 7.93 (1H, d, *J* = 8.7 Hz), 7.41-7.87 (15H, m), 7.10 (2H, m), 6.83 (1H, d, *J* = 15.9 Hz), 6.73 (1H, s), 6.68, (1H, s), 6.48 (1H, d, *J* = 15.6 Hz), 2.07 (4H, m), 1.50 (18H, s), 1.13 (16H, m), 0.79 (6H, t, *J* = 6.9 Hz). ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 158.1, 157.5, 155.4, 152.7, 151.9, 143.6, 142.8, 141.6, 140.6, 139.3, 139.2, 138.8, 137.5, 133.3, 131.4, 130.8, 129.5, 128.4, 127.8, 126.2, 125.4, 123.5, 123.4, 121.4, 120.9, 120.2, 118.2, 117.8, 116.5, 116.3, 115.0, 109.2, 107.2, 59.6, 55.6, 40.3, 34.7, 32.0, 31.5, 29.6, 23.9, 22.5, 14.0. HRMS caled for C₆, H₆₈N₃OSBr: m/z 1041.43; found: m/z 1042.4395 [MH⁺].

2-(2-((E)-4-(7-(3,6-di-tert-butylcarbazol-N-yl)-9,9-dihexylfluoren-2-yl)styryl)-6-

((E)-2-(5'-formyl-[2,2'-bithiophen]-5-yl)vinyl)pyran-4-ylidene)malononitrile (58)



A mixture of 57 (1.12 g, 0.91 mmol), 5-formyl-2-thiopheneborobic acid (0.16 g, 0.76 mmol), $Pd(PPh_3)_4$ (0.022 g, 0.016 mmol), and 2 M Na_2CO_3 aqueous solution (20 ml) in THF (30 ml) was degassed with N_2 for 5 min. The reaction mixture was heated to reflux under N_2 for 24 h. After being cooled to room temperature, water (50 ml) was added and extracted with CH₂Cl₂ (50 ml x 2). The combined organic phase was washed with water (50 ml), brine solution (50 ml), dried over anhydrous Na2SO4, filtered, and evaporated under vacuum to dryness. Purification by column with a mixture of CH_2Cl_2 and hexane (1:1) afforded 7 as reddish-orange solid (0.39 g, 44%). FT-IR (KBr, V, cm⁻¹): 3055 (=C-H), 2953, 2860 (-C-H), 2211 (C=N), 1658 (C=O), 1638, 1601, 1504, 1473 (C=C, Ar), 1362, 1294, 1261, 944, 807. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 9.85 (1H, s), 8.23 (2H, s), 7.92 (2H d, J = 8.0 Hz), 7.31-7.83 (18H, m), 6.80 (1H, d, J = 15.8 Hz), 6.68 (2H, s), 6.58 (2H, d, J = 15.7 Hz), 2.11 (4H, s), 1.55 (18H, s), 1.18 (16H, m), 0.85 (6H, t, J = 6.3 Hz). ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 182.4, 158.2, 157.5, 155.3, 152.8, 152.0, 145.5, 143.5, 142.9, 142.7, 141.4, 140.6, 139.3, 139.2, 138.8, 137.2, 137.0, 136.9, 133.4, 131.5, 129.5, 128.5, 127.7, 127.0, 126.5, 126.2, 125.4, 123.6, 123.4, 121.3, 120.3, 118.8, 118.1, 116.4, 115.2, 109.2, 107.2, 107.2, 60.1, 55.6, 40.3, 34.8, 32.1, 31.6, 29.7, 24.0, 22.6, 14.1. HRMS calcd for $C_{72}H_{71}N_3O_2S_2$: m/z 1073.50; found: m/z 1074.5119[MH⁺].

(E)-3-(5'-((E)-2-(6-((E)-4-(7-(3,6-di-*tert*-butylcarbazol-N-yl)-9,9-dihexylfluoren-2-

yl)styryl)-4-(dicyanomethylene)pyran-2-yl)vinyl)-[2,2'-bithiophen]-5-yl)acrylic acid (CFPA)



A mixture of 57 (0.20 g, 0.18 mmol), malonic acid (0.027 g, 0.27 mmol) and piperidine (2 drops) in chloroform (20 ml) was heated at reflux under N₂ atmosphere for 18 h. After cooling, the reaction was quenched with water (5 ml) and extracted with CH₂Cl₂ (50 ml x 2). The combined organic layer was washed with water (50 ml x 2) and brine (50 ml), dried over anhydrous sodium sulphate, filtered and evaporated to dryness. Purification by silica gel column chromatography eluting with 2% MeOH:CH₂Cl₂ afforded red solid (0.12 g, 60%). m.p. >250 °C, FT-IR (KBr, V, cm⁻¹): 3394 (O-H), 3042 (C-H, Ar), 2926, 2856 (C-H), 2210 (C≡N), 1637 (C=O), 1600, 1547 (C=C), 1490, 1473, 1363, 1250, 944, 807. ¹H NMR (300 MHz, DMSO, δ , ppm): 8.31 (2H, s), 7.30-8.16 (24H, m), 7.21 (1H, d, *J* = 15.7 Hz), 6.95 (1H, d, *J* = 16.5 Hz), 2.08 (4H, s), 1.41 (18H, s), 1.05 (16H, s), 0.72 (6H, m). ¹³C NMR (75 MHz, DMSO, δ , ppm): 159.8, 157.0, 152.0, 151.8, 142.8, 139.1, 129.4, 129.1, 123.8, 123.2, 121.3, 116.6, 109.3, 107.6, 55.6, 34.8, 32.2, 31.7, 31.4, 29.4, 23.9, 22.5, 22.4 14.2. HRMS calcd for C₇₄H₇₃N₃O₃S₂: *m/z* 1115.51

(E)-2-cyano-3-(5'-((E)-2-(6-((E)-4-(7-(3,6-di-*tert*-butylcarbazol-N-yl)-9,9dihexylfluoren-2-yl)styryl)-4-(dicyanomethylene)pyran-2-yl)vinyl)-[2,2'-bithiophen]-5yl)acrylic acid (CFPC)



139

A mixture of **57** (0.25 g, 0.23 mmol), cyanoacetic acid (0.029 g, 0.35 mmol) and piperidine (2 drops) in chloroform (20 ml) was heated at reflux under N₂ atmosphere for 18 h. After cooling, the reaction was quenched with water (5 ml) and extracted with CH₂Cl₂ (50 ml x 2). The combined organic layer was washed with water (50 ml x 2) and brine (50 ml), dried over anhydrous sodium sulphate, filtered and evaporated to dryness. Purification by silica gel column chromatography eluting with 2% MeOH:CH₂Cl₂ afforded red solid (0.17 g, 72%). m.p. >250 °C, FT-IR (KBr, V, cm⁻¹): 3421 (O-H), 3052 (C-H, Ar), 2926, 2856 (C-H), 2201 (C \equiv N), 1637 (C=O), 1600, 1537 (C=C, Ar), 1490, 1473, 1418, 1363, 1250, 1203, 994, 807. ¹H NMR (300 MHz, DMSO, δ , ppm): 8.23 (2H, s), 7.26-8.06 (24H, m), 7.07 (1H, d, *J* = 15.6 Hz), 6.85 (1H, d, *J* = 14.4 Hz), 2.09 (4H, s), 1.39 (18H, s), 1.02 (16H, s), 0.70 (6H, m). ¹³C NMR (75 MHz, DMSO, δ , ppm): 164.4, 159.0, 158.5, 156.0, 152.8, 151.8, 142.8, 142.7, 142.3, 140.2, 139.5, 139.1, 138.8, 137.6, 137.0, 136.7, 134.4, 133.1, 131.5, 130.3, 129.1, 127.7, 127.5, 126.3, 126.5, 125.8, 125.4, 123.9, 123.2, 121.7, 121.4, 121.3, 120.9, 119.3, 116.8, 115.7, 115.7, 109.3, 107.6, 57.9, 55.6, 34.8, 32.2, 31.3, 29.3, 23.9, 22.4, 14.2. HRMS calcd for C₇₅H₇₂N₄O₃S₂: m/z 1140.50.

3,6-dibromo-N-(2-ethylhexyl)carbazole (67)



N-Bromosuccinamide (2.22 g, 12.51 mmol) was added in small portions to a solution of *N*-ethylhexylcarbazole (1.66 g, 5.95 mmol) in THF (30 ml). The mixture was stirred at room temperature under N₂ for a further 1 h. Water (30 ml) and DCM (50 ml) were added. The organic phase was separated, washed with water (50 ml x 2), brine solution (50 ml), dried over anhydrous Na₂SO₄, filtered, and the solvents were removed to dryness. Purification by silica gel column chromatography eluting with hexane gave brominated product as colorless sticky gum (1.51 g, 91%). FT-IR (NaCl, V, cm⁻¹): 2961, 2923, 2873 (C-H), 1600 (C=C), 1483, 1213, 777. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 8.03 (2H, s), 7.52 (2H, dd, *J* = 9.5, 1.8 Hz), 7.15 (2H, d, *J* = 8.7 Hz), 3.93 (2H, d, *J* = 6.9 Hz), 1.97 (1H, m), 1.32 (8H, m), 0.89 (6H, t, *J* = 7.2). ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 139.6, 128.9, 123.9, 123.0, 111.9, 110.5, 47.5, 39.3, 31.0, 28.7, 24.0, 23.3, 14.0, 10.9. HRMS calcd for C₂₀H₂₃Br₂N: *m/z* 435.02; found: *m/z* 436.0272 [MH⁺]

3-bromo-*N***-(2-ethylhexyl)-6-(thiophen-2-yl)carbazole** (68) and *N***-(2-ethylhexyl)-3,6-di(thiophen-2-yl)carbazole** (69)



A mixture of 67 (2.28 g, 5.21 mmol), 2-thiopheneboronic acid (1.40 g, 10.95 mmol), Pd(PPh₃)₄ (0.12 g, 0.10 mmol), 2 M Na₂CO₃ aqueous (34 ml) in THF (57 ml) was degassed with N₂ for 5 min and then heated at reflux under N₂ atmosphere for 24 h. After cooling, dichloromethane (100 ml) was added and the organic layer was washed with water (100 ml x 2) and brine solution (100 ml), dried over anhydrous Na₂SO₄, filtered and evaporated to dryness. Purification by silica gel column chromatography using hexane as eluent gave colorless sticky gum 3-bromo-9-(2-ethylhexyl)-6-(thiophen-2-yl)carbazole (68) (0.52 g, 23%) and 9-(2ethylhexyl)-3,6-di(thiophen-2-yl)carbazole (69) (1.61 g, 68%), respectively.

Compound **68**; FT-IR (NaCl, V, cm⁻¹): 2956, 2921, 2855 (C-H), 1625, 1598 (C=C), 1481, 1448, 1216, 789. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 8.25 (2H, s), 7.75 (1H, dd, J = 8.4, 1.2 Hz), 7.59 (1H, dd, J = 8.7, 1.5 Hz), 7.18-7.42 (5H, m), 3.93 (2H, d, J = 6.7 Hz), 1.91 (1H, m), 1.38 (8H, m), 0.99 (6H, m). ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 145.5, 140.6, 139.9, 128.9, 128.5, 128.1, 126.1, 124.8, 124.5, 123.8, 123.1, 117.7, 111.9, 110.6, 109.5, 47.4, 39.4, 31.1, 28.9, 24.5, 23.2, 14.2, 11.0. HRMS calcd for C₂₄H₂₆BrNS: *m/z* 439.10; found: *m/z* 440.1051 [MH⁺]

Compound **69**; FT-IR (NaCl, V, cm⁻¹): 2961, 2923, 2873 (C-H), 1601 (C=C), 1483, 1213, 777. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 8.49 (2H, s), 7.84 (2H, d, J = 8.4 Hz), 7.52 (2H, d, J = 3.3 Hz), 7.42 (2H, d, J = 5.1 Hz), 7.29 (2H, t, J = 4.2 Hz), 4.02 (2H, d, J = 5.7 Hz), 2.14 (1H, m), 1.46 (8H, m), 1.07 (6H, m). ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 145.7, 140.9, 128.1, 125.9, 124.5, 123.7, 123.2, 122.1, 117.9, 109.5, 47.5, 39.5, 31.0, 28.9, 24.9, 23.1, 14.2, 11.0. HRMS calcd for C₂₈H₂₉NS₂: *m/z* 443.17; found: *m/z* 444.1822 [MH⁺]



Compound **70** was prepared from **68** with a method similarly to that described above for **44** and obtained as colorless solid or colorless sticky gum (0.34 g, 88%). FT-IR (NaCl, V, cm ¹): 2961, 2923, 2873 (C-H), 1630, 1601 (C=C), 1483, 1213, 777. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 8.14 (1H, s), 8.05 (1H, s), 7.51-7.58 (2H, m), 7.28 (1H, d, J = 8.1 Hz), 7.20 (1H, d, J = 8.7Hz), 7.03 (2H, m), 3.99 (2H, d, J = 1.5 Hz), 1.96 (1H, m), 1.30 (8H, m), 0.90 (6H, m). ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 146.9, 140.7, 139.9, 130.8, 128.6, 125.5, 124.3, 123.1, 122.1, 117.4, 111.9, 110.6, 110.0 109.5, 47.5, 39.4, 31.0, 28.8, 24.4, 23.0, 14.1, 10.9. HRMS calcd for $C_{24}H_{25}Br_2NS: m/z 517.01$; found: m/z 518.0154 [MH⁺]

3,6-bis(5-bromothiophen-2-yl)-N-(2-ethylhexyl)carbazole (71)



Compound **71** was prepared from **69** with a method similarly to that described above for **44** and obtained as colorless solid or colorless sticky gum (0.57 g, 76%). FT-IR (NaCl, V, cm⁻¹): 2961, 2923 (C-H), 1630, 1601 (C=C), 1483, 1213, 777. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 8.21 (2H, d, J = 1.5 Hz), 7.61 (2H, dd, J = 8.4, 1.5 Hz), 7.35 (2H, d, J = 8.7 Hz), 7.06 (4H, dd, J = 8.7, 3.9 Hz), 4.10 (2H, d, J = 1.5 Hz), 2.05 (1H, m), 1.25-1.40 (8H, m), 0.86-0.95 (6H, m). ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 147.0, 141.1, 130.8, 125.5, 124.3, 123.0, 122.2, 117.6, 109.9, 109.6 47.6, 39.4, 31.0, 28.8, 24.3, 23.0, 14.0, 10.8. HRMS calcd for C₂₈H₂₇Br₂NS₂: *m/z* 599.00; found: *m/z* 600.0031 [MH⁺] 3-([2,2'-bithiophen]-5-yl)-6-(5-bromothiophen-2-yl)-N-(2-ethylhexyl)carbazole (72) and 3,6-di([2,2'-bithiophen]-5-yl)-N-(2-ethylhexyl)carbazole (73)



Compound 72 and 73 were prepared from 71 with a method similarly to that described above for 68 and 69 and obtained as colorless solid.

Compound 72; yield 27% (0.72 g), FT-IR (NaCl, V, cm⁻¹): 2956, 2923, 2855 (C-H), 1625, 1598 (C=C), 1481, 1216, 789, 685. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 8.24 (1H, s), 8.17 (1H, s), 7.70 (1H, d, J = 8.4 Hz), 7.60 (1H, d, J = 8.4 Hz), 7.04-7.31 (9H, m), 3.98 (2H, d, J = 1.5 Hz), 2.05 (1H, s), 1.30 (8H, m), 0.89 (6H, m). ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 147.1, 144.3, 141.0, 140.9, 137.7, 135.5, 130.8, 127.8, 125.5, 125.1, 124.6, 124.3, 124.2, 124.1, 123.2, 123.1, 123.0, 122.6, 122.2, 117.6, 117.5, 109.9, 109.6 47.6, 39.4, 31.0, 28.8, 24.3, 23.0, 14.0, 10.8. HRMS calcd for C₃₂H₃₀BrNS₃: *m/z* 603.07; found: *m/z* 603.0721 [M⁺]

Compound 73; yield 45% (1.08 g), FT-IR (NaCl, V, cm⁻¹): 2957, 2926, 2856 (C-H), 1627, 1599 (C=C), 1484, 1452, 1218, 791. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 8.30 (2H, d, J =1.2 Hz), 7.69 (2H, dd, J = 8.4, 1.5 Hz), 7.33 (2H, d, J = 8.7 Hz), 7.18 (8H, m), 7.04-7.07 (2H, m), 4.13 (2H, d, J = 1.4 Hz), 2.03 (1H, m), 1.27-1.44 (8H, m), 0.99-1.09 (6H, m). ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 144.4, 140.9, 137.8, 135.5, 127.8, 125.5, 124.3, 124.2, 124.0, 123.2, 123.0, 122.6, 117.6, 109.6, 47.6, 39.4, 31.0, 28.8, 24.3, 23.0, 14.0, 10.8. HRMS calcd for C₃₆H₃₃NS₄: m/z607.15; found: m/z 607.1497 [M⁺], 608.1569 [MH⁺].

3-(5'-bromo-[2,2'-bithiophen]-5-yl)-6-(5-bromothiophen-2-yl)-*N*-(2-

ethylhexyl)carbazole (74)



Compound 74 was prepared from 72 with a method similarly to that described above for 44 and obtained as colorless solid (1.78 g, 79%) FT-IR (KBr, V, cm⁻¹): 2956, 2916, 2855 (C-H), 1612, 1598 (C=C), 1484, 1451, 1216, 778. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 8.16 (1H, s), 8.12 (1H, d, J = 1.5 Hz), 7.61 (1H, dd, J = 8.4, 1.2 Hz), 7.56 (1H, dd, J = 8.4, 1.5 Hz), 7.24 (2H, dd, J = 9.6, 1.2 Hz), 7.17 (1H, d, J = 3.6 Hz), 7.05 (3H, m), 6.98 (1H, d, J = 3.9 Hz), 6.91 (1H, d, J = 3.9 Hz), 3.92 (2H, d, J = 1.5 Hz), 2.00 (1H, s), 1.30-1.38 (8H, m), 0.89-0.94 (6H, m). ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 147.1, 144.8, 140.0, 139.3, 134.2, 132.1, 131.8, 131.5, 130.8, 130.1, 129.9, 129.5, 126.0, 125.8, 125.2, 124.6, 124.3, 124.2, 124.1, 123.2, 123.1, 123.0, 122.6, 122.2, 117.6, 117.5, 109.9, 109.6 47.6, 39.4, 31.0, 28.8, 24.3, 23.0, 14.0, 10.8. HRMS calcd for $C_{32}H_{29}Br_2NS_3$: *m/z* 680.98; found: *m/z* 680.9786 [M⁺]

3,6-bis(5'-bromo-[2,2'-bithiophen]-5-yl)-N-(2-ethylhexyl)carbazole (75)



Compound 75 was prepared from 73 with a method similarly to that described above for 44 and obtained as colorless solid (1.62 g, 74%) FT-IR (KBr, V, cm⁻¹): 2956, 2916, 2855 (C-H), 1612, 1598 (C=C), 1484, 1451, 1216, 778. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 8.31 (2H, d, J = 1.2 Hz), 7.70 (2H, dd, J = 8.7, 1.2 Hz), 7.37 (2H, d, J = 8.7 Hz), 7.26 (2H, d, J = 3.9 Hz), 7.12 (2H, d, J = 3.6 Hz), 7.00 (2H, d, J = 3.6 Hz), 6.96 (2H, d, J = 3.9 Hz), 4.15 (2H, d, J = 6.6Hz), 2.05 (1H, m), 1.28-1.44 (8H, m), 0.87-0.99 (6H, m). ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 144.9, 141.0, 139.2, 134.4, 130.6, 125.3, 124.9, 124.2, 123.2, 123.1, 122.6, 117.6, 109.6 47.6, 39.4, 31.0, 28.8, 24.4, 23.0, 14.0, 10.8. HRMS calcd for C₃₆H₃₁Br₂NS₄: *m/z* 762.97; found: *m/z* 762.9727 [M⁺]

144

4-(5-(N-(2-ethylhexyl)-6-(4-formylphenyl)carbazol-3-yl)thiophen-2-

yl)benzaldehyde (76)



A mixture of 70 (0.70 g, 1.34 mmol), 4-formylphenylboronic acid (0.40 g, 2.68 mmol), Pd(PPh₃)₄ (0.062 g, 0.054 mmol), 2 M Na₂CO₃ aqueous solution (10 ml) in THF (30 ml) was degassed with N₂ for 5 min and then heated at reflux under N₂ atmosphere for 24 h. After cooling, dichloromethane (50 ml) was added and the organic layer was washed with water (50 ml x 2) and brine solution (50 ml), dried over anhydrous Na₂SO₄, filtered and evaporated to dryness. Purification by silica gel column chromatography using dichloromethane/hexane (1:1) as eluent gave yellow solid (0.66 g, 93%). FT-IR (KBr, V, cm⁻¹): 2925, 2852 (C-H), 1690 (C=O), 1594 (C=C), 1482, 1437, 1167, 794. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 10.07 (1H, s), 10.00 (1H, s), 8.39 (2H, m), 7.76 (10H, m), 7.36-7.48 (4H, m), 4.16 (2H, d, *J* = 6.0 Hz), 2.09 (1H, m), 1.27-1.41 (8H, m), 0.87-0.97 (6H, m). ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 192.00, 191.42, 147.8, 147.2, 141.5, 141.2, 140.4, 140.2, 134.7, 134.5, 130.8, 130.6, 130.4, 127.4, 126.2, 125.6, 124.4, 125.3, 124.3, 123.3, 119.3, 117.7, 109.8, 109.7, 47.6, 39.4, 31.0, 28.8, 24.4, 23.0, 14.0, 10.9. HRMS calcd for C₃₈H₃₃NO₂S: *m/z* 569.24; found: *m/z* 570.2470 [MH⁺]

4,4'-(5,5'-(N-(2-ethylhexyl)carbazole-3,6-diyl)bis(thiophene-5,2-

diyl))dibenzaldehyde (77)



Compound 77 was prepared from 71 with a method similarly to that described above for 76 and obtained as yellow-orange solid (0.44 g, 82%). FT-IR (KBr, V, cm⁻¹): 2916 (C-H), 1686 (C=O), 1592 (C=C), 1436, 1163, 791. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 9.97 (2H, s), 8.30 (2H, s), 7.72-7.81 (10H, m), 7.26-7.45 (6H, m), 4.09 (2H, d, *J* = 5.4 Hz), 2.04 (1H, m), 1.30-1.36 (8H, m), 0.87-0.92 (6H, m). ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 191.3, 147.2, 141.1, 140.4, 140.1, 134.8, 130.4, 126.1, 125.6, 124.4, 124.3, 123.1, 117.7, 109.6, 47.6, 39.4, 31.0, 28.8, 24.4, 23.0, 14.0, 10.9. HRMS calcd for C₄₂H₃₇NO₂S₂: *m/z* 651.23; found: *m/z* 651.2276 [M⁺], 652.2340 [MH⁺]

4-(5-(N-(2-ethylhexyl)-6-(5'-(4-formylphenyl)-[2,2'-bithiophen]-5-yl)carbazol-3yl)thiophen-2-yl)benzaldehyde (78)



Compound 78 was prepared from 74 with a method similarly to that described above for 76 and obtained as yellow-orange solid (0.59 g, 74%). FT-IR (KBr, V, cm⁻¹): 2946, 2916 (C-H), 1691 (C=O), 1595 (C=C), 1441, 1163, 783. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 10.08 (1H, s), 10.01 (1H, s), 8.41 (2H, s), 7.78-8.01 (10H, m), 7.39-7.50 (4H, m), 4.20 (2H, d, *J* = 6.9 Hz), 2.10 (1H, m), 1.25-1.56 (8H, m), 0.86-0.97 (6H, m). ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 192.00, 191.42, 147.8, 147.2, 141.5, 141.2, 140.4, 140.2, 134.7, 134.5, 130.8, 130.6, 130.4, 127.4, 126.2, 125.6, 124.4, 125.3, 124.3, 123.3, 119.3, 117.7, 109.8, 109.7, 47.6, 39.4, 31.0, 28.8, 24.4, 23.0, 14.0, 10.9. HRMS calcd for C₃₈H₃₅NO₂S: *m/z* 569.24. 4,4'-(5',5'''-(N-(2-ethylhexyl)carbazole-3,6-diyl)bis([2,2'-bithiophene]-5',5-

diyl))dibenzaldehyde (79)



Compound 79 was prepared from 75 with a method similarly to that described above for 76 and obtained as orange solid (0.43 g, 82%). FT-IR (KBr, V, cm⁻¹): 2924, 2854 (C-H), 1694 (C=O), 1597 (C=C), 1445, 1166, 788. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 10.01 (2H, s), 8.34 (2H, d, *J* = 1.5 Hz), 7.89 (4H, d, *J* = 8.4 Hz), 7.73-7.78 (6H, m), 7.24-7.43 (10H, m), 4.16 (2H, d, *J* = 6.9 Hz), 2.09 (1H, m), 1.27-1.41 (8H, m), 0.87-0.97 (6H, m). ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 191.3, 145.2, 141.0, 140.6, 139.8, 139.3, 134.9, 134.9, 130.5, 129.9, 125.9, 125.5, 125.4, 124.3, 123.2, 123.1, 122.8, 117.6, 109.6, 47.6, 39.4, 31.0, 28.8, 24.4, 23.0, 14.0, 10.9. HRMS calcd for C₅₀H₄₁NO₂S₄: *m/z* 815.20; found: *m/z* 815.2031 [M⁺], 816.2098 [MH⁺]

(E)-3-(4-(5-(6-(4-((E)-2-carboxy-2-cyanovinyl)phenyl)-N-(2-ethylhexyl)carbazol-3yl)thiophen-2-yl)phenyl)-2-cyanoacrylic acid (CB01)



A mixture of 76 (0.42 g, 0.73 mmol), cyanoacetic acid (0.31 g, 3.65 mmol) and piperidine (2 drops) in chloroform (40 ml) was heated at reflux under N_2 atmosphere for 24 h.

After cooling, the reaction was quenched with water (5 ml) and extracted with dichloromethane (50 ml x 2). The combined organic layer was washed with water (50 ml x 2) and brine (50 ml), dried over anhydrous sodium sulphate, filtered and evaporated to dryness. Purification by silica gel column chromatography eluting with gradient methanol/dichloromethane (1-50%) afforded the dye as orange solids (0.10 g, 19%). FT-IR (KBr, V, cm⁻¹): 3384 (O-H), 2927 (C-H), 2212 (C \equiv N), 1623 (C=O), 1590 (C=C), 1345, 1188, 789. ¹H NMR (300 MHz, DMSO, δ , ppm): 8.75 (1H, s), 8.68 (1H, s), 7.59-7.98 (16H, m), 4.30 (2H, d, *J* = 6.6 Hz), 2.02 (1H, m), 1.26-1.34 (8H, m), 0.76-0.88 (6H, m). ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 139.8, 134.9, 134.9, 130.5, 129.9125.4, 124.3, 123.2109.6, 47.6, 39..8, 24.4, 23.0, HRMS calcd for C₄₄H₃₇N₃O₄S: *m/z* 703.25.

(2E,2'E)-3,3'-((5,5'-(N-(2-ethylhexyl)carbazole-3,6-diyl)bis(thiophene-5,2-diyl))bis(4,1-phenylene))bis(2-cyanoacrylic acid) (CB11)



Compound **CB11** was prepared from 77 with a method similarly to that described above for **CB01** and obtained as red-orange solid (0.14 g, 23%). FT-IR (KBr, V, cm⁻¹): 3384 (O-H), 2925 (C-H), 2212 (C=N), 1624 (C=O), 1591 (C=C), 1350, 1189, 787. ¹H NMR (300 MHz, DMSO, δ , ppm): 8.69 (2H, s), 7.92-7.96 (6H, m), 7.82 (6H, d, J = 8.1 Hz), 7.72 (2H, d, J = 3.6 Hz), 7.61-7.64 (4H, m), 4.30 (2H, d, J = 6.6 Hz), 2.00 (1H, m), 1.20-1.31 (8H, m), 0.78-0.89 (6H, m). ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 141.0, 140.61130.5, 129.9, 125.9, 125.5, 125.4, 124.3, 123.2, 123.1.6, 47.6, 39.4, 31.0, 28.8, 24.4, 23.0, 14.0, 10.9. HRMS calcd for C₄₈H₃₉N₃O₄S₂: *m*/z 785.24.

(E)-3-(4-(5-(6-(5'-(4-((E)-2-carboxy-2-cyanovinyl)phenyl)-[2,2'-bithiophen]-5-yl)-

N-(2-ethylhexyl)carbazol-3-yl)thiophen-2-yl)phenyl)-2-cyanoacrylic acid (CB12)



Compound **CB12** was prepared from 78 with a method similarly to that described above for **CB01** and obtained as red solid (0.094 g, 17%). FT-IR (KBr, V, cm⁻¹): 3364 (O-H), 2924 (C-H), 2212 (C=N), 1616 (C=O), 1594 (C=C), 1353, 1189, 779. ¹H NMR (300 MHz, DMSO, δ , ppm): 8.68 (1H, s), 8.64 (1H, s), 7.26-7.94 (20H, m), 4.29 (2H, m), 1.13-1.30 (8H, m), 0.75-0.87 (6H, m). ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 140.6, 134.9, 130.5, 125.5, 125.4, 123.1, 122.8, 117.6, 109.6, 47.6, 39.4, 31.0, 28.8, 24.4, 23.0, 14.0. HRMS calcd for C₅₂H₄₁N₃O₄S₃: *m/z* 867.23.

(2E,2'E)-3,3'-((5',5'''-(N-(2-ethylhexyl)carbazole-3,6-diyl)bis([2,2'-bithiophene]-5',5-diyl))bis(4,1-phenylene))bis(2-cyanoacrylic acid) (CB22)



Compound CB22 was prepared from 79 with a method similarly to that described above for CB01 and obtained as red solid (0.12 g, 18%). FT-IR (KBr, V, cm⁻¹): 3383 (O-H), 2921 (C=H), 2211 (C=N), 1623 (C=O), 1597 (C=C), 1370, 1081, 784. ¹H NMR (300 MHz, DMSO, δ ,

ppm): 8.67 (2H, s), 7.94 (6H, d, J = 7.5 Hz), 7.80 (6H, d, J = 7.8 Hz), 7.68 (2H, d, J = 3.9 Hz), 7.62 (1H, s), 7.59 (1H, s), 7.57 (2H, d, J = 3.6 Hz), 7.44 (2H, d, J = 3.6 Hz), 7.41 (2H, d, J = 3.9 Hz), 4.29 (2H, m), 2.08 (1H, m), 1.21-1.33 (8H, m), 0.76-0.89 (6H, m). ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 139.3134.9, 129.9, 125.5, 125.4, 124.3, 123.2, 123.1, 122.8, 117.6, 109.6, 47.6, 39.4, 31.0, 28.8, 24.4, 10.9. HRMS calcd for C₅₆H₄₃N₃O₄S₄: *m/z* 949.21.

4,4'-(*N*,*N*-bis(4-(3,6-di-tert-butylcarbazol-*N*-yl)phenyl)amino)-1,1'-biphenyl (DND)



A degassed solution of 26 (0.71 g, 0.76 mmol), hexabutyldistananne (0.21 g, 0.37 mmol) and Pd(PPh₃)₄ (0.018g, 0.015 mmol) in toluene (25 ml) was heat at 80 $^{\circ}$ C under N₂ atmosphere for 24 h. After the reaction mixture was cooled to room temperature, water (10 ml) was added. The mixture was extracted with dichloromethane (50 ml x 2). The combined organic phase was washed with water (50 ml), brine solution (50 ml), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. Purification by silica gel column chromatography using dichloromethane/hexane (1:6)as eluent followed bγ recrystallization with dichloromethane/hexane afforded 2 as colorless solid (0.063 g, 11%); m.p. >250 °C; FT-IR (KBr, V, cm⁻¹): 2958 (C-H), 1505 (C=C), 1474, 1261, 793. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 8.16 (8H, s), 7.64 (4H, d, J = 8.1 Hz), 7.42-7.52 (36H, m), 1.54 (72H, s). ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 145.2, 141.0, 140.6, 139.8, 139.3, 134.9, 134.9, 130.5, 129.9, 125.9, 125.5, 125.4, 124.3, 123.2, 123.1, 122.8, 117.6, 109.6, 47.6, 34.4, 31.0. HRMS calcd for C₁₁₆H₁₂₀N₆: m/z 1596.96; found: *m/z* 1598.429 [MH₂⁺]

2,5-Bis{N,N-bis[4-(3,6-di-tert-butylcarbazol-N-yl)phenyl]4-aminophenyl}-9,9-

dipropylfluorene (DFD)



A mixture of 26 (0.50 g,0.54 mmol), 9,9-dipropylfluorene-2,7-bis(boronic acid pinacol ester) (0.12 g, 0.24 mmol), $Pd(PPh_3)_4$ (0.012 g, 0.009 mmol), 2 M Na_2CO_3 aqueous solution (15 ml) in THF (25ml) was degassed with N_2 for 5 min and then heated at reflux under N_2 atmosphere for 24 h. After cooling, dichloromethane (50 ml) was added and the organic layer was washed with water (50 ml x 2) and brine solution (50 ml), dried over anhydrous Na_2SO_4 , filtered and evaporated to dryness. Purification by silica gel column chromatography using dichloromethane/hexane (1:6)as eluent followed by recrystallization with dichloromethane/hexane gave yellow solid (0.30 g, 37%). m.p. > 250 $^{\circ}$ C, FT-IR (KBr, V, cm⁻¹): 2952 (C-H), 1507 (C=C), 1493, 1262, 807. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.23 (8H, s), 7.48-7.84 (46H, m), 2.13 (4H, m), 1.54 (74H, s), 0.78 (6H, m). ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 151.8, 146.6, 146.2, 142.8, 139.4, 139.4, 139.3, 136.8, 133.0, 128.3, 127.7, 125.7, 125.0, 123.3, 121.1, 120.1, 116.3, 109.3, 55.5, 43.0, 34.8, 32.1, 29.7, 17.4, 14.6. HRMS calcd for $C_{135}H_{140}N_6$: *m/z* 1845.11; found: *m/z* 1845.289 [M⁺]

2,5-Bis{N,N-bis[4-(3,6-di-tert-butylcarbazol-N-yl)phenyl]4-aminophenyl}

thiophene (DT1D)



A mixture of **26** (0.80 g,0.86 mmol), 2,5-thiophenediboronic acid (0.006 g, 0.34 mmol), Pd(PPh₃)₄ (0.015 g, 0.013 mmol), 2 M Na₂CO₃ aqueous solution (15 ml) in THF (25ml) was degassed with N₂ for 5 min and then heated at reflux under N₂ atmosphere for 24 h. After cooling, dichloromethane (50 ml) was added and the organic layer was washed with water (50 ml x 2) and brine solution (50 ml), dried over anhydrous Na₂SO₄, filtered and evaporated to dryness. Purification by silica gel column chromatography using dichloromethane/hexane (1:6) as eluent followed by recrystallization with dichloromethane/hexane gave yellow solid (0.086 g, 15%). m.p. > 250 °C, FT-IR (KBr, V, cm⁻¹): 2952 (C-H), 1507 (C=C), 1491, 1260, 786. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 8.16 (8H, s), 7.17-7.65 (42H, m), 1.48 (72H, s). ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 151.8, 146.6, 146.2, 142.8, 139.4, 139.4, 139.3, 136.8, 133.0, 128.3, 127.7, 125.7, 125.0, 123.3, 121.1, 120.1, 116.3, 109.3, 34.8, 32.. HRMS calcd for C₁₂₀H₁₂₂N₆S: *m/z* 1678.95; found: *m/z* 1679.564 [MH⁺].

5,5'-Bis{*N*,*N*-bis[4-(3,6-di-tert-butylcarbazol-*N*-yl)phenyl]4-aminophenyl}-2,2'bithiophene (DT2D)



152

Compound **DT2D** was prepared from **29** with a method similarly to that described above for **DND** and obtained as green solid (0.17 g, 39%). m.p. >250 °C; FT-IR (KBr, V, cm⁻¹): 2952 (C-H), 1507 (C=C), 1493, 1262, 807. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 8.16 (8H, d, J = 0.9 Hz), 7.61 (4H, d, J = 8.7 Hz), 7.40-7.53 (36H, m), 7.30 (4H, d, J = 8.4 Hz), 7.22 (2H, d, J = 3.6 Hz), 7.19 (2H, d, J = 3.6 Hz), 1.49 (72H, s). ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 146.8, 145.9, 142.8, 139.3, 136.3, 133.2, 129.1, 127.7, 126.7, 125.1, 124.4, 123.5, 116.2, 109.2, 34.5, 32.0. HRMS calcd for C₁₂₄H₁₂₄N₆S₂: *m/z* 1760.93; found: *m/z* 1761.703 [MH⁺]

5,5^{***}-Bis{*N*,*N*-bis[4-(3,6-di-tert-butylcarbazol-*N*-yl)phenyl]4-aminophenyl}-2,2^{*}:5^{*},2^{***}-guaterthiophene (DT4D)



Compound **DT4D** was prepared from **30** with a method similarly to that described above for **DND** and obtained as orange solid (0.17 g, 39%). m.p. >250 °C; FT-IR (KBr, V, cm⁻¹): 2952 (C-H), 1507 (C=C), 1491, 1260, 808. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 8.16 (8H, d, J = 1.2 Hz), 7.60 (4H, d, J = 8.4 Hz), 7.40-7.53 (32H, m), 7.29 (4H, d, J = 8.4 Hz), 7.22 (2H, d, J = 3.7 Hz), 7.19 (2H, d, J = 3.7 Hz), 7.11 (4H, m), 1.49 (72H, s). ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 146.9, 145.9, 143.0, 142.8, 139.3, 136.4, 133.2, 129.1, 127.7, 126.7, 125.2, 124.4, 123.5, 116.2, 109.2, 34.7, 32.0. HRMS calcd for C₁₃₂H₁₂₈N₆S₄: *m/z* 1924.91; found: *m/z* 1928.359 [MH₂⁺]

4,7-Bis{N,N-bis[4-(3,6-di-tert-butylcarbazol-N-yl)phenyl]aminophen-4-yl}-2,1,3-

benzothiadiazole (DBD)



A mixture of 26 (0.90 g,0.97 mmol), 2,1,3-Benzothiadiazole-4,7-bis(boronic acid pinacol ester) (0.012 g, 0.32 mmol), Pd(PPh₃)₄ (0.015 g, 0.013 mmol), 2 M Na₂CO₃ aqueous solution (15 ml) in THF (25ml) was degassed with N_2 for 5 min and then heated at reflux under N_2 atmosphere for 24 h. After cooling, dichloromethane (50 ml) was added and the organic layer was washed with water (50 ml x 2) and brine solution (50 ml), dried over anhydrous Na_2SO_4 , filtered and evaporated to dryness. Purification by silica gel column chromatography using dichloromethane/hexane (1:6)as eluent followed by recrystallization with dichloromethane/hexane gave red solid (0.27 g, 49%). m.p. > 250 °C, FT-IR (KBr, V, cm⁻¹): 2955 (C-H), 1505 (C=C), 1474, 1261, 808. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.16 (8H, s), 8.04 (4H, d, J = 8.4 Hz), 7.86, (2H, s), 7.43-7.55 (36H, m), 1.48 (72H, s). ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 154.2, 147.6, 146.0, 142.8, 139.4, 132.2, 132.1, 130.3, 127.8, 127.7, 125.4, 123.9, 123.6, 123.3, 116.2, 109.2, 34.7, 32.0. HRMS calcd for $C_{122}H_{122}N_8S$: m/z 1730.95; found: m/z 1731.719 $[MH^{\dagger}]$

4,7-Bis{5-(*N*,*N*-bis[4-(3,6-di-tert-butylcarbazol-*N*-yl)phenyl]aminophenyl)-thien-2-yl}-2,1,3-benzothiadiazole (DTBTD)



Compound **DTBTD** was prepared from **29** with a method similarly to that described above for **DBD** and obtained as dark red solid (0.19 g, 36%). m.p. >250 °C; FT-IR (KBr, V, cm ¹): 2958 (C-H), 1505 (C=C), 1474, 1261, 814, 793. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 8.17 (8H, s), 7.90 (2H, s), 7.71 (4H, d, J = 8.2 Hz), 7.40-7.55 (36H, m), 7.32 (4H, d, J = 8.2 Hz), 1.49 (72H, s). ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 152.6, 147.1, 145.9, 145.2, 142.8, 139.4, 133.2, 129.1, 128.7, 127.8, 127.0, 125.4, 125.2, 124.4, 123.9, 123.3, 123.3, 116.2, 109.2, 34.7, 32.0. HRMS calcd for C₁₃₀H₁₂₆N₈S₃: *m/z* 1894.93; found: *m/z* 1895.577 [MH⁺]

4,7-Bis{4,4'-(N,N-bis[4-(3,6-di-tert-butylcarbazol-N-yl)phenyl]amino)-1,1'biphenyl}-2,1,3-benzothiadiazole (DPBPD)



Compound **DPBPD** was prepared from **94** with a method similarly to that described above for **DBD** and obtained as dark red solid (0.19 g, 38%). m.p. >250 °C; FT-IR (KBr, V, cm⁻¹): 2958 (C-H), 1505 (C=C), 1474, 1261, 814, 793. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 8.16 (8H, d, J = 0.9 Hz), 8.10 (4H, d, J = 8.1 Hz), 7.90 (2H, s), 7.82 (4H, d, J = 8.1 Hz), 7.71 (4H, d, J = 8.4 Hz), 7.40-7.54 (36H, m), 1.49 (72H, s). ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 154.2, 142.8, 139.3, 136.0, 133.2, 132.8, 129.7, 128.2, 127.7, 127.0, 125.1, 124.6, 123.5, 123.3, 123.3, 116.2, 109.2, 34.7, 32.0. HRMS calcd for C₁₃₄H₁₃₀N₈S₁: *m/z* 1883.0.1

4'-bromo-*N,N*-bis(4-(3,6-di-*tert*-butylcarbazol-9-yl)phenyl)-[1,1'-biphenyl]-4amine (94)



A mixture of **26** (1.0 g, 1.07 mmol), 4-bromophenylboronic acid (0.072 g, 0.36 mmol), Pd(PPh₃)₄ (0.005 g, 0.007 mmol), 2 M Na₂CO₃ aqueous solution (10 ml) in THF (15ml) was degassed with N₂ for 2 min and then heated at reflux under N₂ atmosphere for 24 h. After cooling, dichloromethane (50 ml) was added and the organic layer was washed with water (50 ml x 2) and brine solution (50 ml), dried over anhydrous Na₂SO₄, filtered and evaporated to dryness. Purification by silica gel column chromatography using dichloromethane/hexane (1:6) as eluent followed by recrystallization with dichloromethane/hexane gave color less solid (0.26 g, 76%). m.p. m.p. > 250 °C, FT-IR (KBr, V, cm⁻¹): 2955 (C-H), 1505 (C=C), 1474, 1261, 808. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 8.16 (4H, s), 7.43-7.59 (21H, m), 1.48 (36H, s). ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 142.85, 139.30,131.90, 128.36, 127.70, 125.24, 123.34, 116.22, 109.31, 34.72, 32.06. HRMS calcd for C₆₄H₆₄N₃Br: *m/z* 955.12.

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APPENDIX

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Synthesis and Characterization of 2D-D-π-A-Type Organic Dyes Bearing Bis(3,6-di-tert-butylcarbazol-9-ylphenyl)aniline as Donor Moiety for Dye-Sensitized Solar Cells

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Keywords: Donor-acceptor systems / Dyes / Sensitizers / Conjugation

A series of novel 2D-D-π-A-type organic dyes, namely CCTTnA (n = 1-3), bearing bis(3,6-di-tert-butylcarbazol-9-CUTINA (n = 1-3), beating 0.5(3, 0-4)-cutivation of 0.5(3, 0-4), 0.5(3, 0Ħ thiophene segments with a number of thioph one to three units as π -conjugated spacers (\mathbf{x}), and cyano-acrylic acid as the electron acceptor (A) were synthesized nd characterized as dye sensitizers for dye-sensitized solar cells (DSSCs). These compounds exhibit high thermal and electrochemical stability. Detailed investigations of these dyes reveal that both peripheral carbazole donors (2D) have heneficial influence on the red-shifted absorption spectrum of the dye in solution and dye adsorbed on TiO_2 film, and the

broadening of the incident monochromatic photon-to-current broadening of the incident monocaromatic photon-to-current conversion efficiency (IPCE) spectra of the DSSCs, leading to enhanced energy conversion efficiency (n). Among these dyes, CCTT3A shows the best photovoltaic performance, and a maximal incident monochromatic photon-to-current con-version efficiency (IICCE) while of 640 % actuatic their is photoa matunal increment monocurron are product-to-current conversion efficiency (IPCE) value of 80% a short-circuit photo-current density (J_{sc}) of 9.98 mA cm⁻², open-circuit voltage (V_{oc}) of 0.70 V, and fill factor (FF) of 0.67, corresponding to $\{V_{sd} \mid 0 \ 0.70 \ v, \text{ and rul lattor} (1+) \ 0 \ 0.67, \ corresponding to an overall conversion efficiency <math>\eta \ 04.6\%$ were achieved. This work suggests that organic dyes based on this type of donor molecy or donor molecular architecture are promising candidates for improved performance DSSCs.

efficiency of more than 9.9% was fabricated by Sony.^[3] Al-

though there is still room for improvement of the efficiency

of Ru-based DSSCs,^[4] Ru dyes are nevertheless costly, difficult to attain, and normally have only moderate absorption intensity.^[5] Enormous effort is also being dedicated to the

development of new and efficient dyes that are suitable with

respect to their modest cost, case of synthesis and modifica-

tion, large molar extinction coefficient, and long-term sta-

bility. Organic dyes meet all these criteria. Thus, there have

been remarkable developments in organic dye-based DSSCs

in recent years,^[9] and efficiencies exceeding 10% have been

achieved by using dyes that have broad, red-shifted, and intense spectral absorption in the visible light region.^[7] Although remarkable progress has been made in the development of organic dyes as sensitizers for DSSCs, their chemical structures still require optimization for further improvement in performance. Most of the developed organic dyes are composed of donor, x-conjugation, and acceptor moleties, thereby forming a D-R-A structure, and broad ranges of conversion efficiencies have been achieved [6-8] Most of the highly efficient DSSCs based on organic dyes have long n-conjugated spacers between the donor and acceptor, resulting in broad and intense absorption spectra, aromatic amines as donor moieties, a strong electron-withdrawing group (cyanoacrylic acid) as acceptor, and anchoring moleties. However, the introduction of long π -conjugated seg-

Introduction

Since the report by O'Reagan and Grätzel in 1991 on dye-sensitized solar cells (DSSCs) with dramatically in-creased light harvesting efficiency,^[1] this type of solar cell has attracted considerable and sustained attention because it offers the possibility of low-cost conversion of photoenergy.^[7] To date, DSSCs with a validated efficiency record of more than 11% have been obtained with Ru complexes such as the black dye.[3] More recently, a DSSC submodule of 17 cm² consisting of eight parallel cells with a conversion

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71

ments results in rod-like molecules, which can lead to recombination of the electrons to the triiodide and magnify aggregation between molecules.^[9] The close π - π aggregation can not only lead to self-quenching and reduction of electron injection into TiO2, but can also result in instability of the organic dyes due to the formation of excited triplet states and unstable radicals under light irradiation.^[10] On the basis of these criteria, recently, organic dyes with 2D-n-A structures have been reported by several groups [11] Their

- 76 studies suggest that good performance for organic dyes based on 2D-n-A structure over the simple D-n-A configuration could be achieved by the molecular design.
- We anticipated that further improvements could be made 81 by introducing an additional donor moiety into the aromatic amine to form a 2D-D-n-A structure, and envisaged that such architectures would extend the absorption region, enhance the molar extinction coefficient, reduce the tendency to aggregate, and lead to better thermal stability
- compared with simple D-R-A structures. To this end, we prepared a set of new, simple 2D-D-π-A-type organic dyes In our design (Figure 1), triphenylamine and carbazole moieties were employed as the aromatic and additional donors, respectively, thereby forming a bis(3,6-di-tert-butyl-
- carbazol-9-ylphenyl)aniline donor moiety (2D-D). The cya-91 noacrylic acid and oligothiophenes were incorporated as acceptor (A) and simple π -spacer (π), respectively. Recently, efficient DSSCs that incorporate various triphenylamine and carbazole-based dyes have been reported, indicating the
- importance of their further investigation in DSSCs (124 In addition, it has been found that by incorporating an electron-donor group into the dye molecule, the physical separation of the dye cation from the electrode surface can be increased, which facilitates a high rate of charge separation
- 101 and collection compared with interfacial charge-recombination processes [13] Furthermore, the use of triphenylamine and carbazole have aroused great interest because of their excellent hole-transport capability, and their derivatives have become classic hole-transporting materials.[14] Moreover, the bulky, nonplanar structure of this 2D-D moiery may prove to be important for solving the intractable problems associated with close π - π aggregation of the dye molecules. The inclusion of tert-butyl substituents can increase the solubility of the dye, and also form a hydrophobic 111
- blocking layer on the TiO2 surface to suppress the approach of iodide/triiodide $(1^{-}/1_{3}^{-})$ electrolyte to the TiO₂, consequently leading to an improvement in the open-circuit voltage. Herein, we report a detailed synthesis and the physical and photophysical properties of these 2D-D-n-A-type dyes (CCTTnA). Furthermore, their use as dye sensitizers in
- DSSCs in comparison with N3 dye and D-R-A-type dye (TT2A),^[15] having triphenylamine as a donor, are also reported.

Results and Discussion

Synthesis and Characterization 121

> The dyes were synthesized as outlined in Scheme 1. First, a key intermediate, N.N-bis[4-(3,6-di-ten-butylcarbazoi-9-



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Figure 1. Molecular structures of the designed dyes

yl)phenyl]-4-iodoaniline (3), was synthesized from Ullmann coupling of tri(p-iodophenyl)amine (1) with 3,6-di-tert-butylcarbazole (2) obtained from directed iodination of triphenylamine with I2, and from an alkylation of carbazole with tert-butyl chloride, respectively. A stoichiometric reaction of 1 (2 equiv.) and 2 (1 equiv.) under a catalytic system of Cul as catalyst, (±)-trans-1,2-diaminocyclohexane as cocatalyst, and K3PO4 as base in toluene, afforded intermedi-134 ate 3 in moderate yield (44%). From 3, intermediates 5 and 7 were synthesized by using a combination of Suzuki crosscoupling and bromination reactions in an iterative manner. Suzuki cross-coupling reaction with 2-thiophene boronic acid catalyzed by [Pd(PPh3)4]/Na2CO3 (aq.) in tetra-136 hydrofuran (THF) was employed to achieve an increased number of thiophene units in the molecule, whereas bromination with N-bromosuccinimide (NBS) in THF selectively introduced a bromo function to the a-position of the terminal thiophene ring, allowing a further Suzuki cross-cou-141 pling reaction to be performed. The Suzuki coupling of 3 and 5 with 2-thiophene boronic acid afforded thiophene compounds 4 and 6 in good yields, whereas bromination of 4 and 6 with NBS yielded bromo intermediates 5 and 7 in 91 and 87%, respectively. Subsequent coupling of interme-140 diates 3, 5 and 7 with 5-formylthiophene-2-boronic acid under the same Suzuki coupling conditions gave 8, 9, and 10 in yields of 75, 70, and 60%, respectively. Final Knoevenagel condensation of these aldehydes with cyanoacrylic acid in the presence of a catalytic amount of piperidine in CHCl3 151 heated at reflux for 18 h gave (E)-3-[5-(4-{bis[4-(3,6-di-tertbutylcarbazol-9-yl)phenyljamino | phenyl)thiophen-2-yl]-2-cyanoacrylic acid (CCTT1A), (E)-3-15'-(4-{bis[4-(3,6-di tert-butylcarbazol-9-yl)phenyl]amino}phenyl)-(2,2'-bithiophen)-5-yi]-2-cyanoacrylic acid (CCTT2A) and (E)-3-[5"-156 (4-{bis[4-(3,6-di-tert-butylcarbazol-9-yl)phenyl]amino}phenyl)-(2,2':5',2''-terthiophen)-5-yl]-2-cyanoacrylic acid (CCTT3A) in yields of 58, 57, and 48%, respectively. All dyes can be crystallized to give intensely colored solids. The colors of these solid products varied from orange to dark-161

Date: 04-03-13 10:15:18 Pages: 14



Scheme I. Synthesis of CCTTnA ($n \approx 1-3$) and TT2A dyes

red as the number of thiophene units in the molecule in-creased from CCTTIA, CCTT2A to CCTT3A. In the synthesis of (E)-3-{5'-[4-(diphenylamino)phenyl]-2,2'-bithiophen-5-yl}-2-cyanoacrylic acid (TT2A), intermediate thiophen-5-yl}-2-cyanoacrylic acid (TT2A), intermediate 2,2'-bithiophene-5-carbaldehyde (11) was first selectively iodinated at the a-position of the terminal thiophene ing with NIS in THF to give 5'-iodo-2,2'-bithiophene-5-carb-aldehyde (12) in 83% yield. Subsequently, Suzuki coupling of 12 with 4-(diphenylamino)phenylboronic acid(¹⁶⁾ af-forded 5'-[4-(diphenylamino)phenyl]-2,2'-bithiophene-5-carbaldehyde (13) in a yield of 82%. Knowenagel conden-sation of this aldehyde with cyanoacrylic acid catalyzed by piperidine produced TT2A in 79% yield. The structures of

171 piperidine produced TT2A in 79% yield. The structures of

all dye molecules were characterized unambiguously on the basis of FTIR, ¹H NMR, and ¹³C NMR spectroscopy as 176 well as high-resolution mass spectrometry. These compounds show good solubility in organic solvents, presum-

Eur. J. Org. Chem. 0000, 0-0

166

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3

18

ably as a result of their steric bulk and the presence of terrbutyl substituents, allowing dye adsorption on TiO_2 film and fabrication of DSSCs.

Optical Properties

UV/Vis absorption spectra of CCTTnA and TT2A in CH_2Cl_2 are shown in Figure 2 and the characteristic data are summarized in Table I. The spectra of CCITnA exhibited three strong absorption bands at 297-298, 330-340, 18 and 455-464 nm, respectively (Figure 2, a). The first and second absorption bands were attributed to localized π - π^* transitions of the carbazole and triphenylamine donors (2D-D), respectively. The third band was ascribed to intramolecular charge transfer (ICT) transition from the 2D-D 19 moiety to the cyanoacrylic acid acceptor. This was con-



FULL PAPER



Figure 2. UV/Vis absorption spectra of dyes (a) in CH₂Cl₂ solution and (b) adsorbed on TiO₂ film. (c) UV/Vis absorption spectra of CCTT1A in different solvents. (d) PL spectra of dyes in CH₂Cl₂ solution.

Table 1. Optical, thermal, electrochemical, and electronic properties of the dyes.

Dye	Abs _{enal} isi [nm]	€ [44 ⁻¹ cma ⁻¹]	Abs. ^[4]	Em. _{ma} tel (am)	t [ns] (%) ^{jei}	x ™	E1/2 VS Ag/ Ae*#4 177	بي 191	E,M	E, cafe	HOMO/
CCTTIA	458	25225	416	646		· · · ·		19		144	LOWO
			400	040	1.14 (74.6)	0.60	-1.61, 0.81, 1.08,	284	2.25	2.38	-5 77/-7 97
CCT12A	455	30133					1.40				1.1
		29322	44.2	658	0.88 (61.0)	0.73	-1.86, 0.81, 1.08,	285	2 21	710	6 70/ 2 00
COTTA							1.35.1.50			2.0	-3.207-2.99
COLIDA	404	33926	450	672	0.85 (80.5)	1.12	-1.61 0.78 0.99	353	1 1 2	3.00	
-							106 1 11 1 17	222	215	208	-5.16/3.03
I IZA	405	20206	422	651	130 (97.6)	6.00	1.56 0.02 1.37		-		
N309	530	14500	-	_	1.50 (11.0)	V. 70	-1.35, 0.92, 1.35	29 0	2.25	2.38	-5.28/-3.03
					-	-	-	-	1.86	1.86	-5 52/-3 84

[a] Absorption and emission measured in CH₂Cl₂ solution. [b] Absorption of the dyes adsorbed on TiO₂ film. [c] Fluorescence lifetime measured in CH₂Cl₃ solution at 25 °C. [d] Measured by CV using a glassy carbon working electrode, Pi counter electrode and Ag/Ag^{*} N₂. [f] Estimated from the absorption onset: $E_{g} = 1240/L$ [g] Calculated by at the TDDFT/B3LYP/6-31G (d,p) level. [h] Calculated from oxidation onset potential: HOMO = $-(E_{onset}^{oot} + 4.44)$; UUMO = HOMO - E_{g} .

firmed by a negative solvatochromic shift, i.e., hypsochromics of a negative solution one sum, i.e. hypocu-romic shift of maximum wavelength (λ_{max}) of the peaks at longer wavelength in more polar solvents, whereas the posi-

bathochromic shifts and increased e values. The absorption spectra and the ε values of conjugated chromophores increase as the degree of conjugation is extended.[17]

tions of the first and second absorption bands were nearly Comparison of the absorption spectra and ε values of 2D-D- π -A dyes CCTTIA and CCTT2A to those of (E)-3independent of solvent polarity (Figure 2, c). The molar ex-tinction coefficients (ε) of the first and second absorption $\{5, [4, (diphenylamino)phenyl]thiophen-2-yl\}-2-cyanoacrylic$ $acid (<math>\lambda_{ICT} = 379$ nm, $\epsilon = 17000$ m⁻¹ cm⁻¹ in CHCl₃)¹¹⁸¹ and 211 bands of all compounds were nearly identical ($\varepsilon = 42326$ and 33061 M^{-1} cm⁻¹, respectively), as they have the same do-TT2A (λ_{tCT} = 405 am, ϵ = 20206 m⁻¹ cm⁻¹), having simple nor. The ε values of the ICT bands of CCTTnA were mod-D- π -A structures, revealed significant bathochromic shifts (50-79 nm) of the ICT peaks and increases in the ε values erate to high, ranging from 25225 to $33926 \text{ M}^{-1} \text{ cm}^{-1}$. As the number of thiophene units in the molecules increase from (1.45-1.48 fold). These results suggest that the use of carba-CCTTIA, CCTT2A to CCTT3A, the ICT bands showed zole as an additional or secondary donor to triphenylamine

4 www.eurjoc.org

196

201

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206

Job/Unit: 021479 /KAP1 Date: 04-03-13-1-13-18 Pages: 14

2D-D-n-A-Type Organic Dyes

donor to form a 2D-D-n-A structure dye may be an effective way to bathochromically shift and enhance the ϵ value of the dye's absorption spectra, which is desirable for harvesting more solar light. Moreover, the e values of the ICT

- 221 peaks of these dyes are considerably larger than that of the Ru dye (N3, $a_{30 \text{ nm}} = 14500 \text{ M}^{-1} \text{ cm}^{-1}$),^[19] indicating good light harvesting ability. The higher ϵ values of the dyes allow a correspondingly thinner nanocrystalline film to be used, so avoiding a decrease in the mechanical strength of the
- film. This is also advantageous for electrolyte diffusion in 226 the film and reduces the possibility of recombination of the light-induced charges during transportation.[20] The absorption spectra of CCITnA adsorbed on TiO2 films are shown in Figure 2 (b). The spectra were slightly blueshifted (13-
- 231 22 nm) compared with spectra measured in CH2Cl2. Such a phenomenon is commonly observed in the spectral response of other organic dyes, and may be ascribed to the H-aggregation of the dye molecules on the TiO2 surface and/or the interaction of the anchoring groups of the dyes with the surface of TiO2 [21] The fluorescence emission spec-236
- tra of the dyes in CH2Cl2 were redshifted with increasing numbers of thiophene units in the molecule, which was roughly parallel to the trend of the absorption spectra (Figure 2, d). The fluorescence decay curves of the dyes were measured in CH_2Cl_2 at 25 °C and their decay parameters
- 24 i giving the best fit are summarized in Table 1. As the number of thiophene units in the molecule increased from CCTT1A, CCTT2A to CCTT3A, the major relaxation time decreased from 1.14, 0.88 to 0.83 ns, respectively.

246 **Electrochemical and Thermal Properties**

251

The electrochemical properties of the dyes were studied by cyclic voltammetry (CV) in CH2Cl2 solution with 0.1 M "Bu, NPF6 as a supporting electrolyte. The results are shown in Figure 3 (a) and all data are listed in Table 1. The CV curves of all dyes exhibited multi quasireversible oxidation events and one irreversible reduction process. The reduction wave was attributed to the reduction of the cyanoacrylic acid acceptor moiety, which was in the range of -1.55 to -1.86 V. The first oxidation wave of TT2A

agreed with the removal of electrons from the tri-25 phenylamine donor to give the corresponding radical cation, whereas those of CCTTnA corresponded to removal of electrons from the peripheral carbazole donor moieties to give the radical cation. The first oxidation potentials of CCTTnA decreased from 0.88, 0.83 to 0.78 V when the 26 number of thiophene units in the molecule or the length of the π -conjugated spacers were increased from CCTTIA, CCTT2A to CCTT3A, respectively, as observed in other oligothiophenes^[22] These values were lower than that of TT2A (0.92 V), indicating the advantage of having periph-26 eral carbazoles as extra donors. The multiple CV scans of CCITInA revealed identical CV curves, with no additional peak at lower potential on the cathodic scan (E_{pe}) being observed. This indicates that no oxidative coupling at the 3 or 6 positions of the peripheral carbazole, leading to elec-27 tropolymerization, took place, presumably due to the presence of the 3,6-di-tert-butyl groups. This type of electrochemical coupling reaction can be detected in some carbazole derivatives with unsubstituted 3,6-positions^[23] and might occur upon charge separation, which hampers the 270 dye regeneration. Therefore, importantly, it is clear that the dyes are electrochemically stable molecules

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The HOMO and LUMO energy levels of the dyes calculated from the onset potential of the CV curves are summarized in Table I. The HOMO of CCTTIA (-5.22 eV) was 28 lower than those of both CCTT2A (-5.20 eV) and CCTT3A (-5.16 eV), but all were much lower than the redox potential of the $1^{-}/I_{3}^{-}$ couple (-4.8 eV), therefore, dye regeneration should be thermodynamically favorable and should compete efficiently with the recapture of the injected 28 electrons by the dye radical cation. The LUMOs (-2.97 to -3.03 eV) of these dyes calculated from the HOMOs and energy gaps (E_g) estimated from the optical absorption edge were less negative than the conduction band of the TiO_2 electrode (-4.00 eV vs. vacuum)¹²⁴ and the LUMO of N3 29 dye (-3.84 eV).1191 To ensure efficient charge injection, the LUMO level of the dye should be more than 0.3 eV above the conduction band of the TiO2. Therefore, all dyes have sufficient driving force for electron injection from the excited dyes to the conduction band of TiO2. As a result, 29



Figure 3. (a) CV curves measured in CH_2Cl_2 solution with nBu_4NPF_6 as supporting electrolyte at a scan rate of 100 mV/s. (b) TGA thermograms measured at a heating rate of 10 °C/min under N₂.

Eur. J. Org. Chem. 0000, 0-0

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Date: 04-03-13 10-15-18

FULL PAPER

CCTTnA have sufficient energetic driving force for efficient DSSCs using a nanocrystalline titania photocatalyst and the 1-713 redox couple. Moreover, having high LUMO potentials, these dyes become very attractive for other metal 301 oxide semiconductors with higher conduction bands than that of TiO2 such as ZnO, Nb2O3, SrTiO3 and their composites^[25] to achieve high open-circuit voltage (V_{oc}) DSSCs.

The thermal properties were investigated by thermogravimetric analysis (TGA), and the results suggested that dyes CCTTnA were thermally stable materials, with temperature

at 5% weight loss (T_{5d}) well over 285 °C (Figure 3, b). The better thermal stability of the dye is important for the life-time of the solar cells^[26]

Quantum Chemical Calculations

311 To gain insight into the geometrical, electronic, and optical structures of these new dyes, quantum chemistry calculations were performed at the TDDFT/B3LYP/6-31G (d,p) level: [27] the results are summarized in Figure 4 and detailed in the Supporting Information. A major factor leading to

low conversion efficiencies of many organic dyes in DSSCs 316 is the formation of dye aggregation on the semiconductor surface.[10] We therefore included a bulky donor moiety equipped with two 3,6-di-tert-butylcarbazole units con-

- nected to a triphenylamine unit to increase the steric bulk 321 of the molecule. The optimized structures of CCTTnA revealed that the dihedral angles formed between carbazole (D1) and phenyl (Pb) planes in all molecules were as large as 54.34-55.63° due to the steric bulk of the structure, which could help to prevent close π - π aggregation effec-
- tively between the dye molecules. The noncoplanar geome-326 try can also reduce contact between molecules and enhance their thermal stability [28] The aromatic rings of the π -conjugated spacers adopted more planar conformations, with the dihedral angles between the benzene and thiophene (T_1)

331 planes ranging from 19.60 to 22.80°, and the thiophene (T_1) and thiophene (T_{25} T_{3}) planes (CCTT2A and CCTT3A) ranging from 4.23 to 10.54°, whereas the thiophene (T_{3}) and acrylic acid (A) planes were nearly coplanar (dihedral angle of less than 0.15°). This suggests that π -electrons from the donor moiety can delocalize effectively to the acceptor 336

moiety, which can subsequently transfer to the conduction band of TiO2.



Figure 4 CCT3A matic views of the ground state structures for

Figure 5. The HOMO and LUMO orbitals of TT2A (top) and CCTT2A (bottom).

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V. Promarak et al.

The molecular orbital distribution is very important in determining the charge-separated states of organic dyes. The electron distributions of the HOMO and LUMO of CCTTnA and TT2A are shown in Figure 5 and in the Sup-341 porting Information. To create an efficient charge-transfer transition, the HOMO must be localized on the donor unit and the LUMO on the acceptor unit.^[29] The HOMOs of these compounds are calculated to delocalize over the donor moiety. In CCTTnA dyes, the major contribution of the 346 donor moiety comes from both triphenylamine and each peripheral carbazole. The LUMOs are delocalized across the oligothiophene groups and cyanoacrylic acid acceptor. The results indicate that the distribution of the HOMO and 351 LUMO of all dyes is well-separated, suggesting that the HOMO-LUMO transition and can be considered as an ICT transition. The lowest transition $(S_{\sigma} \rightarrow S_{11}^* > 93\%$ HOMO→LUMO) of CCTTbA dyes corresponds to a charge-transfer excitation from the carbazole-triphenyl-356 amine donor to the oligothiophene π -spacer and cyanoacrylic acid acceptor (see the Supporting Information). The S_2 transition state (S₀ \rightarrow S_2 ; > 88%) is related to a HOMO-I->LUMO transition and has a charge shift mainly from the two peripheral carbazole moieties to the oligothiophene π-spacer and cyanoacrylic acid acceptor, which is reflected 361 in the molecular orbital involved in the transition as well as in the low oscillator strength due to the long-range charge shift. For the S₃ transition state (S₀ \rightarrow S₃; > 88% HOMO-2→LUMO), a charge shift mainly originates from the do-360 nor moiety and oligothiophene π-spacer to the oligothiophene n-spacer and cyanoacrylic acid acceptor with moderate to high oscillator strengths. This means that these additional carbazole donor units may cause a cascade effect that aids charge separation. Therefore, it is believed that 371-



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FULL PAPER_



Figure 7. Space-filling molecular models of the optimized conformation of the dyes.

Photovoltaic Properties of CCTFnA

CCTTnA and TT2A dyes were used as sensitizers for dye-sensitized nanocrystalline anatase TiO₂ solar cells (DSSCs). Cells with an effective area of 0.25 cm^2 (0.5 cm) × 0.5 cm) were fabricated with 11 µm (9.5 µm transparent + 1.5 µm scattering) thick TiO₂ working electrode, platinum (Pt))

(Pt) counter electrode, and an electrolyte composed of 436 0.03 M 1₂/0.6 M Lit/0.1 M guanidinium thiocyanate/0.5 M tert-butylpyridine in a 15:85 (v/v) mixture of benzonitrile/ acetonitrile solution. The reference cell with the same structure based on N3 dye as the sensitizer, was made for comparison. To assess photovoltaic performance, five cells were

- 441 prepared and measured under the standard conditions. The corresponding current density-voltage (*J-V*) characteristics and the incident monochromatic photon-to-current conversion efficiency (IPCE) plots are shown in Figure 8, and the resulting photovoltaic parameters (average values) are summarized in Table 2. The IPCE spectra of CCTTnA-sensi-
- tized DSSCs plotted as a function of excitation wavelength were broadened and redshifted as the number of thiophene units in the molecule increased, which is coincident with the absorption spectra. The IPCE action spectra for DSSC
 451 based on CCTT2A were considerable with the
- 451 based on CCTT2A were considerably redshifted in comparison with that of a DSSC with TT2A as a result of baving additional donors in CCTT2A; which is consistent with the UV/Vis absorption spectra of the dye-loaded TiO₂ films. The photocurrent response of CCTT2A-sensitized DSSC 4150 had a higher value, exceeding 76% between 435 and

504 nm, compared with the other dyes. The maximum

1PCE (80%) occurred at 475 nm, which is higher than the IPCE values of both CCTTIA- (70%) and CCTT3A (76%)-sensitized DSSCs. This observation deviates from our expectation on the basis of the e values of their absorp-461 tion spectra, but is also observed in other types of organic dyes.^[33] In all devices, we observed a decrease in the IPCE above 600 nm in the long-wavelength region that can be attributed to a decrease in the light-harvesting efficiency of these dyes. The slightly lower IPCE value of CCTT3A-sensitized DSSC compared with that of CCTT2A-sensitized DSSC is probably due to extended π -conjugation elong-ation of CCTT3A, which may lead to decreased electroninjection yield relative to that of the CCTT2A dye.[34] This suggests that the structural modification of the dyes 471 strongly influences electron-injection and the collection efficiencies, which, in turn, has a significant effect on the IPCE and overall conversion efficiency (η) of the devices. Moreover, the IPCE values of all synthesized dyes were higher than that of the N3 dye due to the larger molar extinction 476 coefficients of these dyes, however, the N3 dye showed a broader IPCE spectrum, which is consistent with its wider absorption spectrum.

Under continuous visible-light irradiation (AM 1.5G, 100 mW cm⁻²), the CCTT3A-sensitized DSSC showed the 481 highest q among these dyes and gave a short-circuit photocurrent density (J_{sc}) of 9.98 mA cm⁻², open-circuit voltage (Voc) of 0.70 V, and fill factor (FF) of 0.67, corresponding to a η of 4.62%. The J_{sc} and η values of the DSSCs were in the order: CCTT3A (9.98 mA cm⁻², 4.62%) > CCTT2A 480 $(9.02 \text{ mA cm}^{-2}, 4.34\%) > \text{CCTTIA} (7.53 \text{ mA cm}^{-2}, 3.70\%) > \text{TT2A} (6.89 \text{ mA cm}^{-2}, 3.38\%). The measured <math>J_{sc}$ values of these solar cells were also cross-checked with the J_{sc} values calculated from integration of their corresponding IPCE spectra (Cal. Jsc), thus supporting the reported effi-491 ciency, with the results being in agreement to within 5% (Table 2). The larger J_{sc} and η of the CCTT2A (2D-D- π -A)-sensitized solar cell compared with that of a solar cell based on TT2A (D-π-A) demonstrates the beneficial influence of the redshifted absorption spectrum of CCTT2A on TiO₂ film and the broadening of the IPCE spectrum of CCTT2A-sensitized solar cell. This could result from cascading electron transfer from the additional carbazole do-



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V. Promarak et al.

FULL PAPER

ness. Purification by silica gel column chromatography (MeOH/

Date: (04-63-13-10-15:18

- ness. Purification by silica get column chromatography (MeOH/ CH₂Cl₂, 2:98) afforded the product (0.16 ¢, 5.8%) as an orange so-lid (m.p. 2:50°C). FTR (KBr); č = 3422 (O−H), 3042, 2958, 2214 (C=N), 1582 (C=O), 1508, 1316, 1294, 1263, 808 cm⁻¹, 1H NMR (300 MHz, CDCI₄/D₂|DMSO); å = 8.28 (s, 4 H), 8.17 (s, 1 H), 7.75 (d, J = 8.4 Hz, 2 H), 151 (s, 2 H), 723-755 (m, 12 H), 727 (d, J = 8.4 Hz, 2 H), 141 (s, 36 H) pm⁻¹² CMR (75 MHz, CDCI₄/D₄]DMSO); å = 164,3, 150, 148,0, 1455, 142,8, 139,0 1380 1355 1337 (7.79 1778) 1558 1317 (140, 0.000) 866 139.0, 138.0, 135.5, 133.2, 127.9, 127.8, 125.9, 124.2, 124.0, 123.5, 123.3, 116.8, 109.6, 34.9, 32.3 ppm. HRMS: *mlz* calcd. for 871
 - CscH64N4O2S [M*] 976.4750; found 976.7170. (E)-3-15'-(4-{Bis[4-(3,6-di-rerr-butylcarbazol-9-yl)pbeayljamino}-

- (E)-3-45'-(4-{Bisl4-(3.6.di-terr-butylcarbazol-9-yl)pbeaylJauino]-phenyl)-(2,2'-bittiaphen)-5-yl|-2-cyanoaccytic Acid (CCTT2A): Compound CCTT2A (0.12 g. 57%) was prepared from 9 by using a similar method to that described abwee for CCTT1A, as a red solid (m.p. > 259°C). FTIR (KBr): v̄ = 3422 (0-H), 3042, 2958, 2211 (C=N), 1610 (C=O), 1508, 1363, 1317, 1294, 1263, 809 cm⁻¹. ¹ NMR (300 MHz, CDC1/JoL]DMSO: δ̄ = 8.27 (d. J = 12 Hz, 4 H), 8.00 (s, 1 H), 7.73 (d. J = 8.4 Hz, 2 H), 7.35-7.63 (m, 20 H), 7.26 (d. J = 8.4 Hz, 2 H), 1.40 (s, 36 H) ppm. ¹¹C NMR (75 MHz, CDCIy[D4]DMSO): δ̄ = 16.38, 1472, 1457, 1442, 1417, 1320, 1321, 1196, 1163, 1096, 348, 322 ppm. HRMS: mizaled. for CmJHa,NQ55 (MH⁻¹) 1058, 4627; cond 1059, 3502. 881
- 886 (E}-3-[5''-{4-{Bis|4-(3,6-di-tert-butylcarbazol-9-yi}phenyljamino}-(2)-5)-74-(1034-(3,6-d)-cert-butylc2r0a201-9-y1)pbcsyljanuso)-pbcsyl)-(2,2'5',2''-terthinphen)-5-y1]-2-cyua0acrylic Acid (CCTT3A Compound CCTT3A (0.19 g, 48 %) was prepared from 10 by using a similar method to that described above for CCTT1A as a dark-red solid (m.p. > 250 %). FTIR (KBr): $\bar{v} = 3419$ (O-H),
- as a dark-red solid (m.p. > 259 °C). FTIR (KBr): $\overline{v} = 3419$ (O–H), 3042, 2960, 2213 (C=N), 1609 (C=O), 1508, 1364, 1317, 1294, 1263, 808 cm⁻¹. ¹H NMR (300 MHz, CDC/JDB/DMSO): $\delta = 8.27$ (s, 4 H), 8.05 (s, 1 H), 7.70 (d, J = 8.4 Hz, 2 H), 7.64 (d, J = 4.2 Hz, 1 H), 7.57 (d, J = 8.4 Hz, 4 H), 7.32–7.47 (m, 17 H), 7.25 (d, J =891
- 1 H), 7.57 (d, J = 8.4 Hz, 4 H), 7.32-7.47 (m, 17 H), 7.25 (d, J = 8.4 Hz, 2 H), 1.39 (s, 36 H) ppm. ¹⁴C NMR (75 MHz, CDCly [D₄]DMSO; *b* = 164.5, 1470, 1457, 1432, 1428, 1423, 1418, 1390, 137.7, 137.2, 1358, 134.8, 134.5, 132.9, 128.5, 127.8, 127.1, 127.0, 126.2, 125.5, 125.3, 124.8, 124.4, 123.9, 123.1, 118.9, 116.7, 116.5, 132.9, 123.5, 116.5, 896 109.5, 34.9, 32.2 ppm. HRMS: m/z calcd. for C74H66NeO2S3 [M*] 1140,4504; found 1140.5029.
- (E)-3-{5'-{4-{Diphenylamino}phenyl}-2,2'-bithiophen-5-yl}-2-901
- (E)-3-{5'-{4-(Diphenylamiao)phenyl[-2,2'-bithiophen-5-y]-2-cynaescrylic Acid (TTZA): Compound TTZA (0.20 g, 79%) was prepared from 13 by using a similar method to that described above for CCTT1A, as a red-orange solid (m, p. > 250 °C). FTIR (KBr): v = 3418 (O-H), 3044, 2964, 2211 (C=N), 1611 (C=O), 1512, 1364, 1315, 1284, 1260, 808 cm⁻¹. 'H NMR (300 MHz; [DgIDMSO): δ = 8.00 (s, 1 H), 7.58-7.62 (m, 3 H), 7.40-7.45 (m, 3 H), 7.30-7.35 (m, 4 H), 7.04-7.10 (m, 6 H), 6.93 (d, J = 8.4 Hz, 2 H) ppn. ¹/² C NMR (75 MHz; [DgIDMSO): δ = 147.72, 147.19, 144.32, 141.53, 140.20, 136.56, 136.18, 134.32, 130.15, 127.29, 127.19, 126.97, 124.96, 124.62, 124.55, 124.10, 123.13, 119.80 ppn. HKMS: m/z caled. for C=sHash/0.55, [M⁻¹] 300.0966; found 504.0983. 906
- 911

Supporting Laformation (see footnote on the first page of this arti-cle): Quantum chemical calculations, multiple CV scans, FTIR spectra, and UV/Vis absorption spectra of dyes adsorbed on TiO₂. 916 and ¹H and ¹³C NMR spectra of the dyes and intermediates.

Acknowledgments

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12 www.curjoc.org

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V. Promarak et al.

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Article

D–D– π –A-Type Organic Dyes for Dye-Sensitized Solar Cells with a Potential for Direct Electron Injection and a High Extinction Coefficient: Synthesis, Characterization, and Theoretical Investigation

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G Supporting Information

ABSTRACT: A series of organic sensitizers with the direct electron injection mechanism and a high molar extinction coefficient comprising double donors, a π -spacer, and to interim comprising accube conors, a π -spacer, and anchoring acceptor groups $(D-D-\pi-A$ type) were synthe-sized and characterized by experimental and theoretical methods for dye-sensitized solar cells. (E)-2-Cyano-3-(5^{*}, 4, ((4-(3.6-di-tert-butylcarbaze)-9, yi)phenyi)dodecylamino)-phenyi)-(2,2':5',2'-terthiophene]-5-yi]acrylic acid showed performance with a maximal incident photon to electron



formance with a maximal incident photon to election conversion efficiency of 83%, J_w value of 10.89 mA (m⁻², Ve value of 0.70 V, and full factor of 0.67, which correspond to an overall conversion efficiency of 5.12% under AM 1.5G illumination. The molecular geometry, electronic structure, and excited states were investigated with density functional theory, in the molecular geometry electronic structure, and excited states were investigated with density functional theory. illumination. The molecular geometry, electronic structure, and excited states were investigated with density functional theory, time-dependent density, functional theory, and the symmetry-adapted cluster-configuration interaction method. The double donor molecules and prevent iodide/triodide in the electron-donating ability, but also inhibit aggregation between dye molecules and prevent iodide/triodide in the electrolyte from recombining with injected electrons in TiO, Detailed assignments of the UV-vis spectra below the ionization threshold are given. The low-lying light-harvesting state has intramolecular charge transfer character with a high molar extinction coefficient because of the long π spacer. Our experimental and theoretical findings support the potential of direct electron injection from the dye to TiO₂ in one step with electronic excitation for the present D- π -A sensitizers. The direct electron injection, inhibited aggregation, and high molar extinction coefficient may be the origin of the observed high efficiency. This type of $D-D-\pi-A$ structure with direct electron injection would simplify the strategy for

25653

■ INTRODUCTION

Since the report on dye-sensitized solar cells (DSSCs) with a dramatic increase in the light-harvesting efficiency by O Reagan and Grätzel in 1991, this type of solar cell has attracted considerable and sustained attention as it offers the possibility of low-cost conversion of the photoenergy.⁵ To date, a DSSC with a validated efficiency (η) record of >11% has been obtained with rathenium complex dyes such as the black dye.³ Though there is still room for inprovement of the efficiency of ruthenium-based DSSCs.⁴ ruthenium dyes are nevertheless costly and hardly attained and normally have a moderate absorption intensity.⁵ Enormous effort is also being dedicated to developing efficient dres suitable for their modest cost, case

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of synthesis and modification, large molar extinction coefficient, and long-term stability. Rathenium-free dyes or organic dyes meet all these criteria; therefore, there has been remarkable development in organic dye-based DSSCs in recent years," and efficiencies exceeding 12% have been achieved using dyes which have broad, red-shifted, and intense spectral absorption in the visible light region, 400-800 nm.

Although remarkable progress has been made in the organic dyes as sensitizers for DSSCs, optimization of their chemical

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The Journal of Physical Chemistry C

UB3-dye-based cell was 5.12%; it reaches 89.7% of the efficiency of an N3-dye-based cell. We also performed calculations of a model of dve adsorption on TiO₂; the DFT/TDDFT calculations of a $(TiO_2)_{3k}$ —dye cluster soggested that the electron injection proceeds directly from the dye to TiO₂ by photoabsorption. The direct injection caused by intense absorption of visible light may be the origin of the high efficiency of the present dyes. The present theoretical elucidations for the experimental findings contain several new physical insights. We showed the rational design in which theoretical and experimental techniques cooperate is important to improve the performance of organic DSSCs.

EXPERIMENTAL AND COMPUTATIONAL METHODS

Experimental Methods. Fluoring-doped SnO2 conducting glasses (8 $\Omega/sq,$ TCO30-8, Solaronix) were used for trans parent conducting electrodes. The double nanostructure thick film (~1 μ m thickness) consisting of a transparent (Ti-Manoxide 2017/SP, Solaronia) and a scattering (Ti-Nanoxide R/SP, Solaronia) and a scattering (Ti-Nanoxide R/SP, Solaronia) TiO₂ layer were screen printed on TiCl. treated fluorine-doped tin oxide (FTO). Prior to dye sensitization, the TiO₂ electrode with a cell geometry of 0.5 \times 0.5 cm² was treated with an aqueous solution of 4 \times 10⁻¹ M TiCl, at 70 °C in a water saturation atmosphere, heated to 450 °C for 30 min, and then cooled to 80 °C. The TiO₂ electrodes were immersed in the dye solution (3 × 10⁻⁴ M N3 in ethanol and 5×10^{-4} M organic dyes in CH₂Cl₂) in the dark at room temperature for 24 h to stain the dye onto the TiO₂ surfaces. The dye-adsorbed TiO₂ photoanode and Pt counter electrode were assembled into a sealed cell by heating a gasket Meltonix 1170-25 film (25 µm thickness, Solaronix) as a spacer between the electrodes. An electrolyte solution of 0.6 M Lil, 0.03 M $\mathrm{I_2}$ 0.1 M guanidinium thiocyanate, and 0.5 M tort-butylpyridine in a 15/85 (v/v) mixture of benzonitrile and acetonitrile was filled through the predrilled hole by a vacuum backfilling method. For each dye, six devices were fabricated and measured for consistency, and the averaged cell data were reported. The reference cells with the same device configuration based on the N3 dye, as the sensitizer, were also fabricated for comparison. The measured current density-voltage data were averaged from forward and backward scans with a bias step and a delay time of 10 mV and 40 ms, respectively.⁴¹ The incident photon to electron conversion efficiency (IPCE) of the device under to the definite the second se 818-UV silicon photodiode for power density calibration, and a Keithley 6485 picoammeter. All measurements were performed using a black plastic mask with an aperture area of 0.130 cm² and no mismatch correction for the efficiency conversion data. The experimental details are described in the Supporting Information.

Computational Details. In all the computations, the t-Bu groups substituted at CAZ and dodecyl side chain substituted at DPA are replaced by hydrogen atoms. The ground-state (S_0) geometries of UB1-3 were optimized by the B3LVP/6 JIG(d,p)³³ method in CH₂Cl₂ solvent of the conductor-like polarizable continuum model (C-PCM).³³ The UV-vis absorption spectra were calculated by SAC-Cl with a double- ζ plus polarization (DZP) class basis.³⁴ These computations were performed by CAUSSIAN 09.³⁵ As a model of the DSSC prototype system, we studied the cluster model (TiO₂)₁₆-dye

25655

systems with the TD CAM-B3LYP method and fully relaxed geometries that were optimized by the PBE/DNP method³⁶ with DMoH^{3,7} The full details of the computation are given in the Supporting Information. The adsorption energy was calculated as

 $E_{ass} = E[(TiO_1)_{38} - dye] - E[(TiO_1)_{38}] - E[dye]$ (1)

where $E[(TiO_2)_{35}-dye]$ is the total energy of the $(TiO_2)_{16}-dye$ system and $E[(TiO_2)_{36}]$ and E[dye] are the total energies of the $(TiO_2)_{36}$ cluster and dye molecule, respectively.

RESULTS AND DISCUSSION

Synthesis and Characterization. The synthesis noutes to prepare dyes UB1-3 are shown in Scheme S1 in the Sepporting Information, and the detailed synthetic proceedares and characterization data are provided therein as well. All dyes can be crystallized in deep colored solids. The colors of these solid products changed from orange to dark real as the number of thiophene units in the molecule increased from UB1, UB2, to UB3.

Ground-State Geometry and Molecular Orbitals. The optimized S_0 state structures of UB1–3 are shown in Figure S1 in the Supporting Information. Table 1 shows the dihedral

Table 1. Dihedral Angles (deg) between Moieties for the Ground State of the Dyes Optimized by B3LYP/6-31G(d,p) in CH_1Cl_2

UBI	UB2	UB3
-63.12	-6334	65.18
41.87	40.10	48.55
-8.82	-17.62	~20.67
	-1.28	5.09
		-0.05
1.37	0.25	0.36
	UB1 -63.12 41.87 -8.82	UB1 UB2 -63.12 -63.34 41.67 40.10 -8.82 -17.62 -12.8 1.27 0.25

"D₄ = carbazole unit; D₂ = diphenylamine unit; T₁, T₂, and T₄ = thiophene unit; A = cyanoacrylic acid. "Ph=Ph = dihedral angle between two phenylene rings of the diphenylamine molety.



Figure 1. Schematic view of the ground-state (S_0) structure for UB3.

angles between the connecting moleties denoted in Figure 1. The molecules have a bent structure due to the N atom of the diphenylmine unit, yet the conjugation holds across this N atom. Although the t-Bu and dodecyl groups may affect the planarity of the molecules, this conjugation provides a significant factor for the strong photoabscoption of these molecules as seen later in the oscillator strength. As we have expected, the nonplanarity exists at CAZ and the phenyl molecules with a dihedral angle of ~63°. Another phenyl group of DPA (D₂-D₂) due to steric repulsion between the H atoms with a dihedral angle of ~63°. Another phenyl group of DPA (D₂), the thiophene (a spacer), and the A moletiles are nearly planar. In UR2 and UB3, the thiophene units have a zigzag

diadolorg/10.2021/jp302269412 Phys. Chem. C 2012, 116, 25653–25663

The Journal of Physical Chemistry C

may be caused by some error cancellations, orbital relaxation and reorganization effects are relatively small for organic molecules in comparison with those for transition-metal compounds, where orbital relaxation is significant even for vertical detachment processes. The observed $E_{n=0}$ also agreed well with the calculated $\Delta_{M=1}$; therefore, the experimentally predicted LUMO energy levels agreed well with the calculated one. Figure 2 shows that the HOMO has a large coefficient at



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Figure 2. Hartree-Fock MOs of UB1 relevant to the excited states.

the 3,6-positions of CAZ. On the basis of frontier orbital theory, the 3,6-positions of CAZ are active in the exidired (cationic) form of the dye. The protection of these positions by 1-Bu groups is favorable for stability of the exidired form of the dye according to the theoretical prediction.

By according to the theoremical prediction. The thermal properties were investigated by thermogravimetric analysis (TGA). Those results suggest that dyes UB1-3are thermally stable materials with a temperature at 5% weight loss (T_{Sd}) well over 284 °C (Figure 58 in the Supporting Information). The better thermal stability of the dye is important for the lifetime of the solar cells.^{19,49}

UV-Vis Spectra. UV-vis absorption spectra of UB1-3 in a dilute solution of CH_1Cl_2 and on TiO₂ films are shown in Figure 3, and the characteristic data are summarized in Table 4.



Figure 3. (a) Absorption spectra of the dyes in CH₂CL solution and (b) absorption spectra of the dyes on TiO₂ films. UB1 (black squares), UB2 (red circles), and UB3 (blue inverted triangles).

In solution, all the dyes display three strong absorption bands appearing at 450–600, 330–340, and 297–300 nm, respec-

Table 4. Optical Properties of the Dyes

dye 2..." (nm) €¹² (M⁺¹ am⁺¹) λ_{A}^{F} (rem) 081 1. " (nm) Engl (eV) 457 25 174 420 UB2 598 463 2.31 27 460 435 UB3 630 472 2.36 30 103 453 635 2.24

"Measured in CH₂Cl₂ solution. ¹⁰Dyes adsorbed on a TiO₂ film. "The 0–0 transition energy, E₀₋₁₀ estimated from the intercept of the normalized absorption and emission spectra of the dyes in CH₂Cl₂: $E_{0-10} = 1239.84 / \lambda_{intercept}$.

25657

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twely. We denote these bands as B1, B2, and B3, B1 shows a negative solvatochromic shift, i.e., a hypsochromic shift of nazimum wavelength (λ_{max}), in more polar solvents (Figure S6, Supporting Information). The positions of B2 and B3 are nearly independent of the solvent polarity. This indicates that B1 is ascribed to an ICT transition from the D–D moiety to the A moiety, while the ICT character is small for B2 and B3; these bands can be assigned as localized $\pi \to \pi^*$ transitions of CAZ and DPA.

e of B1 of these dyes is moderately high, ranging from 25 174 to 30 102 M⁻¹ cm⁻¹. As the number of thiophene units in the molecules increases from UB1 to UB2 and UB3, the B1 bands show a bathochromic shift and increased e. It should be noted that the absorption spectrum of UB1 compared to that of (E)-3 (5 (4 (diphenylamino)phenyl)thiophene-2-yl)-2-cyanoacrylic acid ($\lambda_{1c} = 379 \text{ mn}, r = 17000 \text{ M}^{-1} \text{ cm}^{-1}$ in CHCL)⁴³ having a $D - \pi - A$ structure bathochromically shifts in the ICF peak together with significant increases in the molar extinction coefficient (about 1.48-fold). The D-D- π -A structure is effective for a bathochromic shift in the absorption spectrum and enhances ε . Moreover, ε of all dyes at the ICT band is considerably larger than that of the standard ruthenium dye N3 at 518 nm ($\varepsilon = 13\,000$ M⁻³ cm⁻¹),⁴⁴ indicating excellent lightharvesting ability. The greater maximum absorption coefficients of the organic dyes allow a correspondingly thinner nanocrystalline film so as to avoid the decrease of the film mechanical strength. This also benefits the electrolyte diffusion inclusions strength that has been been as the recording contained in the film and reduces the recombination possibility of the light induced charges during transportation.¹⁵ The absorption spectra of UB1-3 adsorbed on the TiO, films (Figure 3b) are broadened, covering the region of 350-600 nm, and slightly blue-shifted (20-28 nm) compared to their solution spectra. The former is ascribed to the interaction of the anchoring groups of the dyes with the surface of TiO_2 and is commonly observed in the spectral response of other organic dyes.²⁺⁴⁶ The latter can be explained by the nonplanar structure of the t-Ba-CAZ unit of the dyes preventing aggregation via molecular stacking.

Theoretical Absorption Spectra of the Dyes. The theoretical absorption spectra calculated by SAC-CI are shown in Figures 4–6 for UB1–3 with the experimental spectra. SAC-CI reproduced the UV-wis spectrum satisfactorily to provide reliable assignment and characterization of the electronic spectrum. The TDDFT calculations shown in Tables S1–S3 in the Supporting Information suffered severe functional dependence, and it was difficult to assign the spectra by TDDFT calculations only. We concluded that the long-range correction is at least necessary for studying these compounds by TDDFT. The related excitation energy, oscillator strength, dipole mement, and transition character for UB1 calculated by SAC-CI are summarized in Table 5, where the states with f >0.05 are shown; the complete lists are given in the Supporting Information (Tables S4–57).



Figure 4. (a) Experimental and (b) SAC-C1 absorption spectra of UB1. The SAC-C1 results were convoluted with a Gaussian envelope: the folum was 0.4 eV for the lowest state and 0.2 eV for the other states.



Figure 5. (a) Experimental and (b) SAC-CI absorption spectra of UB2. The SAC-CI results were convoluted with a Gaussian envelope: the 5whm was 0.4 eV for the lowest state and 0.3 eV for the other states.

Our findings obtained by the SAC-CI calculations can be summarized briefly as follows: the lowest absorption that corresponds to the HOMO \rightarrow LUMO transition with ICT character shifts to lower energy with increasing length of the thiophene chain. This can be simply explained by the decrease of the HOMO-LUMO energy gap. The lowest absorption in the visible light region contains only one electronic transition, while other absorption bands are composed of several electronic transitions. The higher excitations relate to the contributions of local $\pi \rightarrow \pi^*$ transitions or a mixture of ICT and $\pi \rightarrow \pi^*$ characters. The details of the absorption spectra can be analyzed using the computational results.

In the experimental UV-vis spectrum, four absorption bands, B1, B2, B3, and B4, with two shoulders, S1 and S2, can be identified for UB1 at 600-260 nm. below the ionization threshold. The SAC-CI calculation can consistently assign these

25658



Figure 6. (a) Experimental and (b) SAC-CI absorption spectra of UB3. The SAC-CI results were convoluted with a Gaussian envelope: the fishin was 0.4 eV for the lowest state and 0.2 eV for the other state.

structures of the absorption spectrum, although the first absorption band is the most relevant in the present DSSC molecules. The absorption center of B1 was observed at 2.71 eV (457 nm). The lowest excited state was calculated at 2.72 eV (455 nm) by SAC-CI, in excellent agreement with experiment and characterized as a HOMO \rightarrow LUMO transition that is ICT as explained in the previous section. This excitation is responsible for the electron transfer from CAZ and DPA to point to the thiophene π -spacer and cyanoucrylic acid acceptor. The B2 band observed corresponds to the second state calculated at 4.02 eV. The fifth and sixth states correspond to the observed B3 band. The S1 shoulder observed around 4.3 eV may be assigned to the 11th state calculated at 4.81 eV. Then the next, 12th, state calculated corresponds to the S2 shoulder. The B4 band observed at \$.15 eV may be assigned to the 19th and 20th states calculated at 6.11 and 6.34 eV, respectively; however, the present computational conditions are insufficient for quantitative agreement of excited states in the higher energy region. For the characterization of the excited states, we also evaluated the dipole moment (μ) for the ground and excited states, which are included in Table 5. From μ and $\Delta \mu_i$ the excited states with considerable oscillator strength are assigned to ICT in the low-energy region and the mixture of π $\rightarrow \pi^*$ and ICT in the high-energy region. The band structures of the absorption spectra of UB2 and UB3 shown in Figures S and 6 are very similar to that of UB1. The spectra can be assigned in a similar manner. Within 20 states solved, we could not obtain high-intensity states around 6.0 eV, which may correspond to the B4 band of UB2 and UB3. Our SAC-CI and TD CAM-B3LYP calculations showed that

Our SAC-CI and TD CAM-B3LYP calculations showed that UB1-3 have only one ICT excited state in the visible light region. This feature seems to be common to many other D-a-A-type dyes: consequently, it yields a narrow absorption band. For efficient light-harvesting properties, this can be a serious disadvantage. The broadness of the ICT band of UB1-3 is attributed to the Franck-Condon factor: the effects of molecular vibrations and solute-solvent interactions. In this sense, very ngld a/fameworks, such as conjugated macrocyclic compounds, are not favorable because molecular vibrations are

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The Journal of Physical Chemistry C

Table 5. Absorption Energy (ΔE , eV (nm)), Dipole Moment (μ , D), Dipole Moment Change ($\Delta \mu$, D), Oscillator Strength (f), and Transition Character of the Singlet Excited States of US1 Calculated by SAC-Ct⁴

	Sec. 1				<u> </u>	SACIC	A CARLER AND A CARLE
DIACE	sibu vrs' ev (nur)		$\Delta E_{eV} (nm)$	μ (D)	$\Delta \mu^{b}(0)$	1	amplitude (arbital manual)
1	2.71 (457)	81	2.72 (455)	19.62	5:41	1.074	a contract (contacts cransicolity)
2	3.75 (331)	B2	4.62 (3:39)	7.19	-: 12	0.060	(n) $(n - 1)$
÷			4.45 (279)	13.52	536	0.009	$0.00 (H \rightarrow L + 5) + 0.31 (H - 1 \rightarrow L + 12)$
5	4.16 (298)	83	4.55 (273)	4 20	1.44	0.485	$0.70 (H - S \rightarrow L)$
6			4.56 (272)	ù n a	1.32	G.1.5.7	$9.50 (H - 1 \rightarrow L + 5) + 0.32 (H - 5 \rightarrow L)$
11	4.3 (288)	SI.	4.81 (258)	14.00	0.76	0.287	0.70 (H - 4 - 4 + 5)
12	4.7 (264)	S2	5.36 (231)	12.32	10.61	0.192	$0.44 (H \rightarrow L + 4) + 0.28 (H \rightarrow L)$
19	5.13 (241)	84	6.13 (2013)	12.23 T 45	3.51	0.191	$0.43 (H - 2 \rightarrow L + 1) = 0.36 (H - L + 4)$
20			534 (195)	6.00	-986	0.453	0.76 (H - 1 - L + 12)
The states	with f > 0.05 are show	n brat	an alian at t	0.99	-1.52	0.945	$0.60 (H \rightarrow L + 12) + 0.43 (H - 4 \rightarrow L + 5)$
$-\mu_{\rm GS}$, and	I the ground state dip	ole mor	es show the change went is \$331 D	is in the dip.	ste moments fr	on the gro	and state (GS) to excited states (ESs), $\Delta \mu = l \mu_{ss}$

Table 6. Performance Parameters of DSSCs Constructed Using Dyes"

			* *				
aye	dye uptake" (1023 molecules cm ⁻¹)	J_{sc} (mA cm ⁻²)	$V_{n}(V)$	FF	a (5.5	ate Fins	
CB:	84.수 士 3.8	7.16	2.53		4 (4)	97485 (%)	called J_{R} (mA cm ⁻²)
UB2	97.5 ± 2.0	6.20	V-73	0.07	3.52	62	6,98
UB3	1043 + 18	2.02	9.7 0	0.66	4.10	72	8.61
N3	55 T. A. F.O.	59	0.70	5.67	5.12	90	10.56
Konneinen		13.54	0.71	0.70	5.74	100	11.70
Lapennien	IS WE'R COnstanted in idantical words						4 4 7

"Experiments were conducted in identical conditions using a TiO, photoanode with an approximately 11 μ m thickness and a 0.25 cm² working area on the PTO (§ Ω /sa) substrates. "Obtained from dye adsorption measurements. "Relative η compared with the reference N3 value, relative η of corresponding IPCE spectra."

25659

restricted and such compounds usually show sharp absorption bands. Flexibility of the present $D-D-\pi-A$ framework could contribute to the broadness of the ICT band. The largest dye, UB3, showed the broadest absorption. If the excited-state geometry of the molecule is significantly different from the geometry in the ground state, the Franck-Condon overlap becomes small and the absorption coefficient decreases. Therefore, moderate rigidness is also required for a high absorption coefficient and also stability of the dyes.

Dye Adsorption on a TIO2 Film. The performance of a DSSC also depends on the total amount of dye present; therefore, the dye uptake was determined.⁶ In all case, the rate of dye adsorption is initially rapid and eventually reaches a plateau (see Figure S7 in the Supporting Information). These profiles are typical for organic adsorbates into nanoporous inorganic matrixes.⁴⁶ The chemisorption of all dyes onto the surface of TiO, films was confirmed by FT-IR spectroscopy, which showed absorption peaks of both the dyes and TiO2 (Figure S8 in the Supporting Information). The cheracteristic ubration modes of the carboxylate group of all dyes are identical to those reported for other dyes.⁴⁵⁵⁰ This indicates that all dyes bind in the same way to TiO2; therefore, the difference observed in performance can be directly related to the effect of the molecular volume and how much dye is absorbed.

The dye uptakes depend on the steric hindrance of the donor moiety around the carboxylic acid enchoring group: such steric hindrance can be reduced in UB3 with longer π conjugated spacers. At equilibrium, maximum uptakes of each dye are (64.4 3.8) × 10¹⁵, (97.5 ± 2.0) × 10¹⁵, and (104.3 ± 1.8) × 10¹⁵ molecules cm⁻² for UB1, UB2, and UB3, respectively (Table 6). Under this dye-loading result, the light-harvesting efficiency of UB1 is expected to be less than those of the other dyes, leading to a small incident monochromatic photon to current conversion efficiency for the UB1-based cell.

Photovoltaic Properties. Dyes UB1-3 were used as the sensitizers for dye-sensitized nanocrystalline anatase TiO₂ solar cells. The corresponding IPCE plots and current density-voltage (J-V) characteristics are shown in parts a and b, respectively, of Figure 7, and the resulting photovoltaic





parameters (average values) are summarized in Table 6. The IPCE spectra of UB1-3 sensitizers plotted as a function of the excitation wavelength are broadened and red-shifted as the number of thiopiene units in the molecule increases, which is coincident with the result of the absorption spectra. The IPCE spectrum of UB3 shows a high maximum value of 83%, which is slightly higher than the IPCE values of both UB1 (81%) and UB2 (82%). The higher IPCE value of UB3 is probably due to its *e*, which enhances the electron-injection yield in comparison with those of the other dyes.⁵⁰ Because of their larger molar extinction coefficients, the IPCE values of dyes UB1-3 are higher than that of the N3 dye; the N3 dye shows a breader IPCE spectrum, which is consistent with its wide absorption

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The Journal of Physical Chemistry C

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spectrum. Under standard AM 1.SG 100 mW cm⁻² illumination, the UB3-sensitized cell shows the highest overall efficiency among the three dyes and gives a short-crucit photocurrent density (j_{cc}) of 10.89 mA cm⁻², open-circuit voltage (V_{cc}) of 0.70 V, and fill factor (FF) of 0.67, corresponding to an overall conversion efficiency (j_1) of the bott-circuit photocurrent densities and efficiencies of the DSSCs are in the order UB3 (10.89 mA cm⁻², 5.12%) > UB2 (B.38 mA cm⁻², 4.10%) > UB1 (7.19 mA cm⁻², 5.25%). The measured j_{cc} values of these solar cells were also crosschecked with the j_{cc} values calculated from integration of their corresponding IPCE spectra (calcd j_{cc}), parity verifying the reported efficiency and the results found to be in agreement te within 3% (Table 6).

The better solar cell performance (highest η and J_{sc}) of the UB3-based cell than that of the other dyes in this series can be explained by the red shift of the absorption spectrum of UB3 compared to UB1 and UB2: this is better for the light-harvesting efficiency. While the lower efficiency of the UB1based cell compared to the UB2- and UB3-based cells can be attributed to both the poorer spectral property and the lower dye content on the TiO2 film. The efficiency of the UB3-based device reaches 90% of the efficiency of the standard ruthenium dye N3-based cell ($\eta = 5.71\%$). The efficiency of the UB1based cell also reaches >62% of the efficiency of the N3-based cell even though UB1 has a lower IPCE value and narrower IPCE spectrum than both UB2 and UB3. The η/η_{N3} values of UB1-3 (Table 6) are competitive with or higher than those of the D- π -A-type sensitizers containing carbazole or diphenylamine as the donor (49–90%) see Table S8 in the Supporting Information for details), which shows that the use of $D-D-\pi$ -A-type sensitizers improves the energy harvesting of the DSSC by decreasing aggregation and increasing the molar extinction coefficients. This relative efficiency (η/η_{N3}) enables the comparison of the solar cell performance in different experimental conditions.

 $\epsilon~(mM^{-1}~cm^{-1})$ multiplied by dye uptake (mol cm^{-2}) leads to a dimensionless value. This value corresponds to the absorbance of lue optical spectra. For the present dyes, this $\epsilon.x$ dye uptake value shows excellent linear correlation with the observed J_{κ} as shown in Figure 8, where the intercept is approximately zero; the zero intercept implies that no current density is observed for zero absorbance. If we assume the ϵ value of free dyes is directly proportional to that ϵ addes dyes, the amount of excited dyes is proportional to this $\epsilon \times dye$ uptake value and also linearly correlates with J_{μ} . This linear



Figure 8. Linear relation between J_{sc} and $e \times dye$ uptake. The linear regression line is $J_{sc} = 2.056(e \times dye uptake) = 0.04$ with $R^2 = 0.999$.

25660

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correlation states that $f_{\rm sc}$ is determined only by the absorbance of a photon. The length of the thicphene chain does not affect the efficiency of electron injection, although the LUMO energy level and $E_{\rm sc}$ * depend on the chain length. This length independence of the injection mechanism strongly suggests the direct injection mechanism (SUB1-3) because such a mechanism may not explicitly involve the electronic states of the thiophene units. This is the experimental evidence for direct injection. CT bands are not clearly observed in Figure 3 for the adsorbed system; therefore, the potential for direct injections for the dye=TiO₁ duster model system in the next section. Model of the Dye/Semiconductor Prototype. To

obtain a further understanding of the electronic structure involved in the dye/semiconductor charge transfer process in the prototype system, we model the prototype system with the dye adsorbed on the anatise $(TiO_2)_{35}$ cluster. Our dyes chemiserb on the T_1O_2 surface as suggested by TT-IRspectroscopy: thus, we calculated only the chemisorption configuration which is formed by the two carboxplate oxygen itorus bonded with the two T i atoms of the TiO_surface, while a proton of the dye forms a hydroxyl group with a surface oxygen. Two Ti=O bonds form, with the Ti=O bond distances ranging from 2.07 to 2.02 Å, indicating bidentate chemisorption.³² The calculated adsorption energies of UB1, UB2, and UB3 on the $(TiO_3)_{35}$ cluster are -10.3, -13.9, and -13.1kcal/mol, respectively, indicating strong interactions between the dyes and TiO_2 surface.

It is well-known that the mechanism of electron injection from the dye to the semiconductor can be theoretically elucated by the study of the electronic structure of the dye adsorbed on the semiconductor, which can be classified into two types.¹¹ The first mechanism, indirect injection, involves photoexcitation to a dye excited state, and then an electron is transferred to the semiconductor. The second is a direct mechanism, a one-step electron injection from the ground state of the dye to the conduction band of the semiconductor by photoexcitation.

The electronic structure and excitation energies in the present (TiO1)18-dye model systems were examined by the TDDFT calculations at the optimized geometries. The absorption peaks were characterized in the gas phase using TD CAM-B3LYP⁵² with the 3-21G(d) basis.⁵⁵ The results are shown in Table 59 in the Supporting Information. In $(TiO_{2})_{34}$ -UB1, the excitation from the HOMO - 1 to the LUMO + 12 and LUMO + 21 contributed to the strong absorption in the visible light region. The MOs relevant to this transition and conduction band are shown in Figure 9. The HOMO = 1 is delocalized over the dye, while the LUMO + 12 and LUMO + 21 are distributed at the $(TiO_2)_{38}$ -dye interface, indicating the strong coupling between the dye excited state and the conduction band states of TiO₂. This result indicates that the direct injection mechanism is identified in the present dyes, and this is one origin of their excellent performance as sensitizers. For the $(TiO_2)_{38}$ -UB2 and $(TiO_2)_{38}$ -UB3 complexes, a similar picture was obtained (see Figures S10 and S11 in the Supporting Information). These transition characters and MOs of the $(TiO_2)_{38}$ -dye model system show that the sensitization mechanism in the prototypes is an interfacial direct charge transfer process corresponding to electron injection from the excited dyes to the conduction band of the TiO_2 surface. This theoretical and experimental evidence altogether supports the direct injection mechanism for the

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