

SYNTHESIS OF F AND Cl CONTAINING NOVEL QUINOXALINE-BASED
CONJUGATED POLYMERS FOR ORGANIC SOLAR CELL

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY



BY
SEVGİ AYDIN

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
CHEMISTRY

JANUARY 2025

Approval of the thesis:

SYNTHESIS OF F AND Cl CONTAINING NOVEL QUINOXALINE-BASED CONJUGATED POLYMERS FOR ORGANIC SOLAR CELL

submitted by **SEVGİ AYDIN** in partial fulfillment of the requirements for the degree of **Master of Science in Chemistry, Middle East Technical University** by,

Prof. Dr. Naci Emre Altun

Dean, **Graduate School of Natural and Applied Sciences**

Prof. Dr. Ayşen Yılmaz

Head of the Department, **Chemistry**

Prof. Dr. Ali Çırpan

Supervisor, **Chemistry, METU**

Assist. Prof. Dr. Erol Yıldırım

Co-Supervisor, **Chemistry, METU**

Examining Committee Members:

Prof. Dr. İrem Erel Göktepe

Chemistry, METU

Prof. Dr. Ali Çırpan

Chemistry, METU

Assist. Prof. Dr. Erol Yıldırım

Chemistry, METU

Prof. Dr. Görkem Günbaş

Chemistry, METU

Prof. Dr. Atilla Cihaner

Chemical Engineering, Atılım University

Date: 09.01.2025



I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name Last name: Sevgi Aydın

Signature:

ABSTRACT

SYNTHESIS OF F AND Cl CONTAINING NOVEL QUINOXALINE-BASED CONJUGATED POLYMERS FOR ORGANIC SOLAR CELL

Aydın, Sevgi
Master of Science, Chemistry
Supervisor: Prof. Dr. Ali Çırpan
Co-Supervisor: Assist. Prof. Dr. Erol Yıldırım

January 2025, 167 pages

In this study, the benzodithiophene-based donor molecules and selenophene π -bridged quinoxaline-based novel acceptor molecules were polymerized by a Stille Cross-coupling reaction to produce nine donor-conjugated polymers. (P1F, P2F, PCL, P1FD2, P2FD2, PCID2, P2FS, PCLS). Six different polymers were synthesized (P1F, P2F, PCL, P1FD2, P2FD2, and PCID2) to produce organic solar cell devices. In addition, the other three polymers (P0F, P2FS, and PCLS) were synthesized only to study and compare the optical and electrochemical properties of the polymers. Polymers were characterized by gel permeation chromatography (GPC), thermal gravimetric analysis (TGA), UV-Vis spectrometry, and differential pulse voltammetry (DPV). The optical bandgap (E_g^{opt}) values, calculated from the thin-film onset values of the polymers, were determined to be 1.62, 1.70, 1.72, 1.73,

1.76, 1.90, 1.72, 1.74, and 1.97 eV, respectively, in the order of P1F, P2F, PCl, P1FD2, P2FD2, PCID2, P0F, P2FS, and PCIS. The HOMO/LUMO energy levels of the polymers were found to be -5.56/-3.87, -5.65/-3.87, -5.86/-3.82, -5.79/-3.91, -5.67/-3.63, -5.84/-3.76, -5.82/-3.78, -5.40/-3.66, and -5.64/-3.64 eV, respectively, in the same order. Devices were constructed using the structure ITO/PEDOT: PSS/Donor: Acceptor/PDINN/Ag, where the active layer consisted of polymers as donor materials blended with fullerene and non-fullerene acceptors. The current-voltage characteristics of the fabricated devices were evaluated using a solar simulator illuminated with AM 1.5G light. The performance of the best devices was recorded as 7.54%, 3.87%, 3.71%, 2.36%, 1.62%, and 1.57% respectively, in the order of polymers used in the active layer: P2F, PCl, P1F, P2FD2, PCID2, and P1FD2.

Keywords: Quinoxaline, BDT, Halogen, Organic Solar Cell, Conjugated Polymers

ÖZ

F VE Cl İÇEREN YENİ KİNOKSALİN TABANLI KONJÜGE POLİMERLERİN ORGANİK GÜNEŞ PİLİ İÇİN SENTEZİ

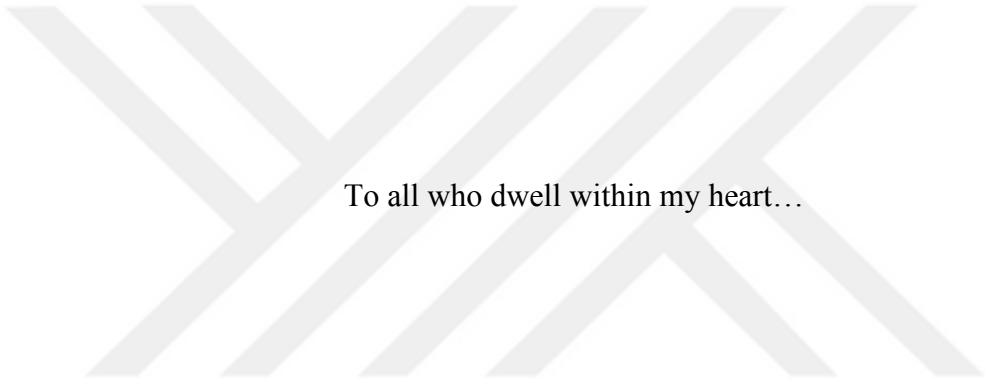
Aydın, Sevgi
Yüksek Lisans, Kimya
Tez Yöneticisi: Prof. Dr. Ali Çırpan
Ortak Tez Yöneticisi: Assist. Prof. Dr. Erol Yıldırım

Ocak 2025, 167 sayfa

Bu çalışmada, benzoditiyofen bazlı elektron verici moleküller ve selenofen π -köprülü kinoksalin bazlı yeni electron alıcı moleküller, Stille polikondensasyon tepkimesi ile polimerize edilerek dokuz elektron verici konjuge polimer (P1F, P2F, PCL, P1FD2, P2FD2, PCID2, P2FS, PCLS) üretildi. Organik güneş pili cihazlarının üretimi için altı farklı polimer (P1F, P2F, PCL, P1FD2, P2FD2 ve PCID2) sentezlendi. Ayrıca, diğer üç polimer (P0F, P2FS ve PCLIS) yalnızca polimerlerin optik ve elektrokimyasal özelliklerini incelemek ve karşılaştırmak amacıyla sentezlendi. Polimerler jel geçirgenlik kromatografisi (GPC), termal gravimetrik analiz (TGA), UV-Vis spektrometrisi ve diferansiyel darbe voltametrisi (DPV) ile karakterize edildi. Polimerlerin ince film başlangıç değerlerinden hesaplanan E_g^{opt} değerleri sırasıyla P1F, P2F, PCL, P1FD2, P2FD2, PCID2, P0F, P2FS ve PCLIS sırasıyla 1.62, 1.70, 1.72, 1.73, 1.76, 1.90, 1.72, 1.74 ve 1.97 eV olarak belirlendi. Polimerlerin aynı

sırayla HOMO/LUMO enerji seviyeleri -5.56/-3.87, -5.65/-3.87, -5.86/-3.82, -5.79/-3.91, -5.67/-3.63, -5.84/-3.76, -5.82/-3.78, -5.40/-3.66 ve -5.64/-3.64 eV olarak tespit edildi. Cihaz, aktif katmanın fulleren ve fulleren olmayan alıcılarla harmanlanmış donör polimerlerden oluştuğu ITO/PEDOT: PSS/Donör:Akseptör/PDINN/Ag yapısı kullanılarak inşa edildi. Üretilen cihazların akım-gerilim özellikleri, AM 1.5G ışığıyla aydınlatılan bir güneş simülatörü kullanılarak değerlendirildi. Aktif tabakada P2F, PCl, P1F, P2FD2, PCID2 ve P1FD2 polimerleri içeren en iyi cihazların performansı sırasıyla %7,54, %3,87, %3,71, %2,36, %1,62 ve %1,57 olarak kaydedildi.

Anahtar Kelimeler: Kinoksalin, BDT, Halojen, Organik Güneş Pili, Konjuge Polimerler



To all who dwell within my heart...

ACKNOWLEDGMENTS

I would like to thank Prof. Dr. Ali ırpan for allowing me to work at ırpan Research Group Solar Laboratory and for leading me to my first experience in my academic life. The three years I spent in the laboratory provided me with a much more different and valuable experience than I had anticipated, both in the field of research and in my stepping into the adult world.

I would like to thank Assist. Prof. Dr. Erol Yıldırım for guiding me with his knowledge and always making me feel his consultancy.

I am grateful to Dr. Gönül Hızalan Özsoy for sincerely answering all my questions, guiding me correctly, and facilitating my studies.

I would like to thank Dr. Elif Demir Arabacı for the valuable support she provided me during the thesis writing process, as well as for the incredible emotional support and knowledge she provided me about everything.

I would like to thank Oğuzhan Karakurt for inspiring me with his analytical thinking skills, planned and willful work habits, and for patiently answering every question I asked by sharing his experiences.

I would like to express my heartfelt gratitude to Cem Maraşlıoğlu for his invaluable assistance and for being a supportive labmate who made brainstorming sessions both productive and enjoyable.

I would like to thank Elif Pınar Yılmaz for her harmonious and open communication attitude and for making my work easier with her quick responses.

I am grateful to my dear friend Meltem Türkatar for always being there for me, doing her best to reduce my stress, and giving me strength during difficult times. This process would have been much more difficult without you my lovely friend.

I would like to thank all my teammates in the lab for supporting me, being patient and helping me throughout these three years. I have learned a lot from all of you.

I would like to express my gratitude to my family for always being there for me and supporting me in all my decisions.

And I adore my little Otto for being such a loving, docile, and perfect baby. You are the best choice in my life.

This study is supported by the Scientific and Technological Research Council of TURKEY (TUBITAK) with project number 222ZA151.

I would also thank METU Central Laboratory, for TGA, UPS, AFM, and TEM analysis.

TABLE OF CONTENTS

ABSTRACT	v
ÖZ	vii
ACKNOWLEDGMENTS	x
TABLE OF CONTENTS	xii
LIST OF TABLES	xvii
LIST OF FIGURES	xviii
LIST OF ABBREVIATIONS	xxv
LIST OF SYMBOLS	xxxi
CHAPTERS	
1 INTRODUCTION	1
1.1 Polymer	1
1.2 Conjugated Polymers	2
1.3 Low Bandgap Conjugated Polymers	3
1.4 Palladium-catalyzed Cross-Coupling Reactions	4
1.4.1 Stille Cross-Coupling Reaction	5
1.4.2 Mechanism	6
1.5 The Role of Conjugated Polymers in Modern Technology	7
1.6 Organic Solar Cells	8
1.6.1 Architecture of Organic Solar Cells	9
1.6.2 Deposition Methods	13
1.6.3 Working Principle	14
1.6.4 Characterization of OSCs	16

1.6.5	Important Parameters of OSCs.....	17
1.7	Active Layer	18
1.7.1	Morphology of the Active Layer.....	18
1.7.2	Fullerene as an Acceptor	19
1.7.3	Non-Fullerene Acceptor	20
1.7.4	Molecular Engineering of the Donor Polymer	21
1.8	Literature Review	30
1.9	Aim of the Study	32
2	RESULTS AND DISCUSSION	35
2.1	Gel Permeation Characterization.....	35
2.2	Thermogravimetric Analysis.....	36
2.3	Optical Characterization.....	37
2.4	Electrochemical Characterization	44
2.5	Ultraviolet Photoemission Spectroscopy Characterization	50
2.6	Photovoltaic Characterizations.....	51
2.6.1	P2F-based Device.....	51
2.6.2	Comparison of P1F-based and P2F-based Device	58
2.6.3	Comparison of PCl-based and P2F-based Device.....	62
2.6.4	Comparison of the P1FD2-based and P1F-based devices.....	66
2.6.5	Comparison of the P2FD2-based and P2F-based devices.....	68
2.6.6	Comparison of the PCID2-based and PCl-based devices.....	70
2.6.7	Summary of the Six Devices	72

3	EXPERIMENTAL	75
3.1	Materials	75
3.2	Methods and Instruments.....	75
3.3	Synthesis of Monomers	76
3.3.1	Synthesis of Molecule 2 (1,2-bis(octyloxy)benzene)	76
3.3.2	Synthesis of Molecule 3 (1,2-bis(3,4-bis(octyloxy)phenyl)ethane-1,2-dione).....	77
3.3.3	Synthesis of Molecule 7 (4-fluorobenzene-1,2-diamine)	78
3.3.4	Synthesis of Molecule 8 (4,5-difluorobenzene-1,2-diamine)	78
3.3.5	Synthesis of Molecule 9 (4,5-dichlorobenzene-1,2-diamine).....	79
3.3.6	Synthesis of Molecule 10 (5-fluorobenzo[c][1,2,5]thiadiazole).....	80
3.3.7	Synthesis of Molecule 11 (5,6-difluorobenzo[c][1,2,5]thiadiazole).....	81
3.3.8	Synthesis of Molecule 12 (5,6-dichlorobenzo[c][1,2,5]thiadiazole)	82
3.3.9	Synthesis of Molecule 13 (4,7-dibromo-5-fluorobenzo[c][1,2,5]thiadiazole).....	83
3.3.10	Synthesis of Molecule 14 (4,7-dibromo-5,6-difluorobenzo[c][1,2,5]thiadiazole).....	84
3.3.11	Synthesis of Molecule 15 (4,7-dibromo-5,6-dichlorobenzo[c][1,2,5]thiadiazole)	85
3.3.12	Synthesis of Molecules 19, 20 and 21	85
3.3.13	Synthesis of Molecule 23 (tributyl(selenophen-2-yl)stannane).....	92
3.3.14	Synthesis of Molecule 24 (2,3-bis(3,4-bis(octyloxy)phenyl)-6-fluoro-5,8-di(selenophen-2-yl)quinoxaline)	93

3.3.15	Synthesis of Molecule 25 (2,3-bis(3,4-bis(octyloxy)phenyl)-6,7-difluoro-5,8-di(selenophen-2-yl)quinoxaline).....	94
3.3.16	Synthesis of Molecule 26 (2,3-bis(3,4-bis(octyloxy)phenyl)-6,7-dichloro-5,8-di(selenophen-2-yl)quinoxaline).....	95
3.3.17	Synthesis of Acceptor Monomer 1 (2,3-bis(3,4-bis(octyloxy)phenyl)-5,8-bis(5-bromoselenophen-2-yl)-6-fluoroquinoxaline)	96
3.3.18	Synthesis of Monomer 2 (2,3-bis(3,4-bis(octyloxy)phenyl)-5,8-bis(5-bromoselenophen-2-yl)-6,7-difluoroquinoxaline)	97
3.3.19	Synthesis of Acceptor Monomer 3 (2,3-bis(3,4-bis(octyloxy)phenyl)-5,8-bis(5-bromoselenophen-2-yl)-6,7-dichloroquinoxaline)	98
3.3.20	Synthesis of Molecule 28 (3,6-dibromobenzene-1,2-diamine).....	99
3.3.21	Synthesis of Molecule 29 (2,3-bis(3,4-bis(octyloxy)phenyl)-5,8-dibromoquinoxaline).....	100
3.3.22	Synthesis of Molecule 30 (2,3-bis(3,4-bis(octyloxy)phenyl)-5,8-di(selenophen-2-yl)quinoxaline).....	101
3.3.23	Synthesis of Acceptor Monomer 4 (2,3-bis(3,4-bis(octyloxy)phenyl)-5,8-bis(5-bromoselenophen-2-yl)quinoxaline)	102
3.3.24	Synthesis of Molecule 32 (2-(2-ethylhexyl)thieno[3,2-b]thiophene).....	103
3.3.25	Synthesis of Molecule 34 (4,8-bis(5-(2-ethylhexyl)thieno[3,2-b]thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene)	104
3.3.26	Synthesis of Donor Monomer 1 ((4,8-bis(5-(2-ethylhexyl)thieno[3,2-b]thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane))	105
3.3.27	Synthesis of Donor Monomer 2	106

3.3.28	Synthesis of Molecule 35 (2-((2-ethylhexyl)thio)thieno[3,2-b]thiophene)	107
3.3.29	Synthesis of Molecule 36 (4,8-bis(5-((2-ethylhexyl)thio)thieno[3,2-b]thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene)	108
3.3.30	Synthesis of Donor Monomer 3	109
3.4	Synthesis of Polymers	112
3.4.1	Synthesis of P1F	112
3.4.2	Synthesis of P2F	114
3.4.3	Synthesis of PCl	115
3.4.4	Synthesis of P1FD2	117
3.4.5	Synthesis of P2FD2	118
3.4.6	Synthesis of PCID2	119
3.4.7	Synthesis of P2FS	120
3.4.8	Synthesis of PCIS	121
3.4.9	Synthesis of P0F	122
3.5	Construction of the Organic Solar Cell Devices	123
4	CONCLUSIONS	125
	REFERENCES	127
	APPENDICES	
A.	Spectra	139

LIST OF TABLES

TABLES

Table 1.1. Comparison of PTB7Th and PTTBDT-FFT	27
Table 1.2. Photovoltaic properties of the literature analogues.....	32
Table 2.1. The molecular weight characteristics of the polymers	35
Table 2.2. Thermal characteristics of the polymers	36
Table 2.3. Optical properties of the polymers in CHCl ₃ and thin film.....	38
Table 2.4. Optical properties of the P0F, P1F, and P2F with literature analogs (Yang et al., 2014)	41
Table 2.5. Optical properties of the P2FD2 with literature similar(Lenaerts et al., 2020)	43
Table 2.6. Electrochemical properties of the polymers	45
Table 2.7. HOMO level of the polymers which determined by UPS	50
Table 2.8. Summary of the device performance of the P2F-based device.....	52
Table 2.9. Summary of the device performance of the P1F and P2F-based device	58
Table 2.10. Summary of the device performance of the PCl and P2F-based device	62
Table 2.11. Summary of the device performance of the P1FD2 and P1F-based device	66
Table 2.12. Summary of the device performance of the P2FD2 and P2F-based device	68
Table 2.13. Summary of the device performance of the PCID2 and PCl-based device	71
Table 3.1. Optimization of the synthetic route of the D3	111

LIST OF FIGURES

FIGURE

Figure 1.1. Structure of some conjugated polymers.....	3
Figure 1.2. Backbones of the donor and acceptor on the thesis	4
Figure 1.3. Stille cross-coupling reactions scheme	6
Figure 1.4. Design of the single layer OSC.....	9
Figure 1.5. Design of the bilayer OSC device.....	10
Figure 1.6. Design of the commercial bulk heterojunction OSC	11
Figure 1.7. Design of the bulk heterojunction OSC in the thesis study	13
Figure 1.8. Scheme of the working principle of the OSC	14
Figure 1.9. J-V characteristics of OSC under dark and illuminated conditions (Gu et al., 2007).....	17
Figure 1.10. Structure of the ITIC and Y6	21
Figure 1.11. Main parts of donor polymers (H. Zhou et al., 2012)	22
Figure 1.12. Structure of the acceptor material and BDT containing donor polymer	23
Figure 1.13. Structure of the acceptor material and quinoxaline-containing donor polymer.....	24
Figure 1.14. Structure of the PTB7-Th and PTTBDT-FTT	26
Figure 1.15. Structure of the literature polymers	31
Figure 1.16. Structures of the synthesized nine polymers.....	34
Figure 2.1. Normalized absorbance spectrum of the first six polymers in CHCl ₃ and thin film	39
Figure 2.2. Normalized absorbance spectrum of the P0F, P2FS and PCIS in CHCl ₃ and thin film	40

Figure 2.3. Differential pulse voltammogram of the first six polymers in 0.1 M TBAPF ₆ /ACN	46
Figure 2.4. Differential pulse voltammogram of the polymers in 0.1 M TBAPF ₆ /ACN	47
Figure 2.5. Energy level diagram of the P2F-based device	51
Figure 2.6. J-V characteristics of the a) P2F:Y6(1:1.2) with 0.6% CN and b) P2F:ITIC-Th (1:1.3) with 1% DIO	52
Figure 2.7. J-V characteristics of the P2F:Y6(1:1.3) with no additives and P2F:Y6(1:1.3) with 1% CN	53
Figure 2.8. EQE spectra of the a) P2F:Y6(1:1.3) with no additives and b) P2F:Y6(1:1.3) with 1% CN	54
Figure 2.9. TEM images of the blend films based on a) P2F:Y6(1:1.3) with no additives and b) P2F:Y6(1:1.3) with 1% CN	55
Figure 2.10. Tapping mode of AFM height images of the blend film of a) P2F:Y6(1:1.3) with no additives and b) P2F: Y6(1:1.3) with 1% CN, respectively	56
Figure 2.11. J-V characteristics of the best device P2F:Y6(1:1.3) with 1% CN	57
Figure 2.12. Energy level diagram of the P1F-based and P2F-based device	58
Figure 2.13. J-V characteristics of the a) P1F:Y6(1:1.2) and b) P1F:Y6(1:1.3) with 1%CN	59
Figure 2.14. EQE spectra of the P1F:Y6(1:1.2) with 1% CN	60
Figure 2.15. a) TEM and b) tapping mode AFM height images of the blend film of P1F: Y6 (1:1.2)	60
Figure 2.16. Energy level diagram of the PCl-based and P2F-based device	62
Figure 2.17. J-V characteristics of the a) PCl: Y6(1:1.2) and b) PCl: Y6:PC ₇₁ BM(1:1.2:0.2)	63
Figure 2.18. EQE spectra of the PCl: Y6:PC ₇₁ BM(1:1.2:0.2)	64

Figure 2.19. a) TEM and b) tapping mode AFM height images of the blend film of PCl: Y6:PC ₇₁ BM (1:1.2:0.2)	64
Figure 2.20. Energy level diagram of the P1FD2-based and P1F-based device	66
Figure 2.21. J-V characteristics of the P1FD2:Y6: P ₇₁ BM(1:1.2:0.1) with 1% CN67	
Figure 2.22. Energy level diagram of the P2FD2-based and P2F-based device	68
Figure 2.23. J-V characteristics of the P2FD2:Y6(1:1.2) with 1% CN.....	69
Figure 2.24. Energy level diagram of the PCID2-based and PCl-based device	70
Figure 2.25. J-V characteristics of the PCID2:Y6(1:1.2) with 1% CN	71
Figure 3.1. Synthetic route of molecule 2	76
Figure 3.2. Synthetic route of molecule 3	77
Figure 3.3. Synthetic route of molecule 7	78
Figure 3.4. Synthetic route of molecule 8	78
Figure 3.5. Synthetic route of molecule 9	79
Figure 3.6. Synthetic route of molecule 10	80
Figure 3.7. Synthetic route of molecule 11	81
Figure 3.8. Synthetic route of molecule 12	82
Figure 3.9. Synthetic route of molecule 13	83
Figure 3.10. Synthetic route of molecule 14	84
Figure 3.11. Synthetic route of molecule 15	85
Figure 3.12. Synthetic route of molecule 16	86
Figure 3.13. Synthetic route of molecule 17	87
Figure 3.14. Synthetic route of molecule 18	88
Figure 3.15. Synthetic route of molecule 19	89
Figure 3.16. Synthetic route of molecule 20	90
Figure 3.17. Synthetic route of molecule 21	91
Figure 3.18. Synthetic route of molecule 23	92
Figure 3.19. Synthetic route of molecule 24	93

Figure 3.20. Synthetic route of molecule 25	94
Figure 3.21. Synthetic route of molecule 26	95
Figure 3.22. Synthetic route of A1	96
Figure 3.23. Synthetic route of A2	97
Figure 3.24. Synthetic route of A3	98
Figure 3.25. Synthetic route of molecule 28	99
Figure 3.26. Synthetic route of molecule 29	100
Figure 3.27. Synthetic route of molecule 30	101
Figure 3.28. Synthetic route of molecule A4	102
Figure 3.29. Synthetic route of molecule 32	103
Figure 3.30. Synthetic route of molecule 34	104
Figure 3.31. Synthetic route of molecule D1	105
Figure 3.32. Structure of D2	106
Figure 3.33. Synthetic route of molecule 35	107
Figure 3.34. Synthetic route of molecule 36	108
Figure 3.35. Most successful synthetic route of D3	110
Figure 3.36. Unsuccessful synthetic route of P1F	112
Figure 3.37. Successful synthetic route of P1F	113
Figure 3.38. Successful synthetic route of P2F	114
Figure 3.39. Unsuccessful synthetic route of PC1	115
Figure 3.40. Successful synthetic route of PC1	116
Figure 3.41. Successful synthetic route of P1FD2	117
Figure 3.42. Successful synthetic route of P2FD2	118
Figure 3.43. Successful synthetic route of PCID2	119
Figure 3.44. Successful synthetic route of P2FS	120
Figure 3.45. Successful synthetic route of PCIS	121
Figure 3.46. Successful synthetic route of P0F	122

Figure A.1. ^1H NMR spectrum of compound 2 in CDCl_3	139
Figure A.2. ^{13}C NMR spectrum of compound 2 in CDCl_3	140
Figure A.3. ^1H NMR spectrum of compound 3 in CDCl_3	140
Figure A.4. ^{13}C NMR spectrum of compound 3 in CDCl_3	141
Figure A.5. ^1H NMR spectrum of compound 13 in CDCl_3	141
Figure A.6. ^{13}C NMR spectrum of compound 13 in CDCl_3	142
Figure A.7. ^1H NMR spectrum of compound 14 in CDCl_3	142
Figure A.8. ^{13}C NMR spectrum of compound 13 in CDCl_3	143
Figure A.9. ^1H NMR spectrum of compound 14 in CDCl_3	143
Figure A.10. ^{13}C NMR spectrum of compound 13 in CDCl_3	144
Figure A.11. ^1H NMR spectrum of compound 19 in CDCl_3	144
Figure A.12. ^{13}C NMR spectrum of compound 19 in CDCl_3	145
Figure A.13. ^1H NMR spectrum of compound 20 in CDCl_3	145
Figure A.14. ^{13}C NMR spectrum of compound 20 in CDCl_3	146
Figure A.15. ^1H NMR spectrum of compound 21 in CDCl_3	146
Figure A.16. ^{13}C NMR spectrum of compound 20 in CDCl_3	147
Figure A.17. ^1H NMR spectrum of compound 23 in CDCl_3	147
Figure A.18. ^{13}C NMR spectrum of compound 23 in CDCl_3	148
Figure A.19. ^1H NMR spectrum of compound 24 in CDCl_3	148
Figure A.20. ^{13}C NMR spectrum of compound 24 in CDCl_3	149
Figure A.21. ^1H NMR spectrum of compound 25 in CDCl_3	149
Figure A.22. ^{13}C NMR spectrum of compound 25 in CDCl_3	150
Figure A.23. ^1H NMR spectrum of compound 26 in CDCl_3	150
Figure A.24. ^{13}C NMR spectrum of compound 26 in CDCl_3	151
Figure A.25. ^1H NMR spectrum of A1 in CDCl_3	151
Figure A.26. ^{13}C NMR spectrum of compound A1 in CDCl_3	152
Figure A.27. ^1H NMR spectrum of A2 in CDCl_3	152

Figure A.28. ^{13}C NMR spectrum of compound A2 in CDCl_3	153
Figure A.29. ^1H NMR spectrum of A3 in CDCl_3	153
Figure A.30. ^{13}C NMR spectrum of compound A3 in CDCl_3	154
Figure A.31. ^1H NMR spectrum of 29 in CDCl_3	154
Figure A.32. ^{13}C NMR spectrum of compound 29 in CDCl_3	155
Figure A.33. ^1H NMR spectrum of 30 in CDCl_3	155
Figure A.34. ^{13}C NMR spectrum of compound 30 in CDCl_3	156
Figure A.35. ^1H NMR spectrum of A4 in CDCl_3	156
Figure A.36. ^{13}C NMR spectrum of compound A4 in CDCl_3	157
Figure A.37. ^1H NMR spectrum of 32 in CDCl_3	157
Figure A.38. ^{13}C NMR spectrum of compound 32 in CDCl_3	158
Figure A.39. ^1H NMR spectrum of 34 in CDCl_3	158
Figure A.40. ^{13}C NMR spectrum of compound 34 in CDCl_3	159
Figure A.41. ^1H NMR spectrum of D1 in CDCl_3	159
Figure A.42. ^{13}C NMR spectrum of compound D1 in CDCl_3	160
Figure A.43. ^1H NMR spectrum of 35 in CDCl_3	160
Figure A.44. ^{13}C NMR spectrum of compound 35 in CDCl_3	161
Figure A.45. ^1H NMR spectrum of 36 in CDCl_3	161
Figure A.46. ^{13}C NMR spectrum of compound 36 in CDCl_3	162
Figure A.47. ^1H NMR spectrum of D3 in CDCl_3	162
Figure A.48. UPS spectrum of the P1F and P2F with 7 eV bias	163
Figure A.49. UPS spectrum of the PCl and P1FD2 with 7 eV bias	163
Figure A.50. UPS spectrum of the PCID2 with 7 eV bias	164
Figure A.51. Thermogram of P1F	164
Figure A.52. Thermogram of P2F	165
Figure A.53. Thermogram of PCl	165
Figure A.54. Thermogram of P1FD2	166

Figure A.55. Thermogram of P2FD2	166
Figure A.56. Thermogram of PCID2.....	167



LIST OF ABBREVIATIONS

ABBREVIATIONS

GPC	Gel Permeation Chromatography
TGA	Thermal Gravimetric Analysis
UV-Vis	Ultraviolet-visible spectroscopy
DPV	Differential Pulse Voltammetry
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
ITO	Indium Tin Oxide
PEDOT: PSS	Poly(2,3-dihydrothieno-1,4-dioxin)-poly(styrenesulfonate)
PDINN	N,N'-Bis{3-[3-(Dimethylamino)propylamino]propyl} perylene-3,4,9,10-tetracarboxylic diimide
AM	Air Mass
BDT	Benzo[1,2-b:4,5-b'] dithiophene
PA	Polyacetylene
PPV	Poly(Phenylene Vinylene)
PANI	Polyaniline

PPy	Polypyrrole
PT	Polythiophene
ECL	Effective Conjugation Length
D	Donor
A	Acceptor
OLED	Organic Light-emitting Diodes
NIR	Near Infrared
OSC	Organic Solar Cell
FF	Fill Factor
PCE	Power Conversion Efficiency
J_{sc}	Short Circuit Current
V_{oc}	Open Circuit Voltage
EQE	External Quantum Efficiency
BHJ	Bulk Heterojunction
ZnO	Zinc Oxide
PC ₆₁ BM	[6,6]-phenyl-C ₆₁ -butyric acid methyl ester
PC ₇₁ BM	[6,6]-phenyl-C ₆₁ -butyric acid methyl ester
L_D	Exciton Diffusion Length

J	Current
V	Voltage
STC	Standard Test Conditions
R_s	Low Series Resistance
R_{sh}	High Shunt Resistance
J_m	Maximum Current
V_m	Maximum Voltage
P_{max}	Maximum Produced Power Output
P_{in}	Power Input
DIO	1,8-Diiodooctane
CN	Chloronaphthalene
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
AFM	Atomic Force Microscopy
NFA	Non-Fullerene Acceptor
eV	Electron Volt
TT	thieno, [3,2-b]thiophene
M_n	Number Average Molecular Weight
M_w	Weight Average Molecular Weight

PDI	Polydispersity Indices
Da	Dalton
nm	Nanometre
mL	Millilitre
TBAPF ₆	Tetrabutylammonium Hexafluorophosphate
ACN	Acetonitrile
M	Molar
UPS	Ultraviolet Photoemission Spectroscopy
CV	Cyclic Voltammetry
ITIC-Th	3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone))-5,5,11,11-tetrakis(5-hexylthienyl)-dithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene
CHCl ₃	Chloroform
R _q	Square Surface Roughness
TCI	Tokyo Chemical Industry
TMS	Trimethylsilane
PPM	Parts per Million
NMR	Nuclear Magnetic Resonance
TLC	Thin Layer Chromatography

Da	Dalton
P1F	Poly(5-(5-(4,8-bis(5-(2-ethylhexyl)thieno[3,2-b]thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophen-2-yl)selenophen-2-yl)-alt-2,3-bis(3,4-bis(octyloxy)phenyl)-6-fluoro-8-(selenophen-2-yl)quinoxaline)
P2F	Poly(5-(5-(4,8-bis(5-(2-ethylhexyl)thieno[3,2-b]thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophen-2-yl)selenophen-2-yl)-alt-2,3-bis(3,4-bis(octyloxy)phenyl)-6,7-difluoro-8-(selenophen-2-yl)quinoxaline)
PC1	Poly(5-(5-(4,8-bis(5-(2-ethylhexyl)thieno[3,2-b]thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophen-2-yl)selenophen-2-yl)-alt-2,3-bis(3,4-bis(octyloxy)phenyl)-6,7-dichloro-8-(selenophen-2-yl)quinoxaline)
P1FD2	Poly(5-(5-(4,8-bis(4-chloro-5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophen-2-yl)selenophen-2-yl)-alt-2,3-bis(3,4-bis(octyloxy)phenyl)-6-fluoro-8-(selenophen-2-yl)quinoxaline)
P2FD2	Poly(5-(5-(4,8-bis(4-chloro-5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophen-2-yl)selenophen-2-yl)-alt-2,3-bis(3,4-bis(octyloxy)phenyl)-6,7-difluoro-8-(selenophen-2-yl)quinoxaline)
PCID2	Poly(5-(5-(4,8-bis(4-chloro-5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophen-2-yl)selenophen-2-yl)-alt-2,3-bis(3,4-bis(octyloxy)phenyl)-6,7-dichloro-8-(selenophen-2-yl)quinoxaline)

P0F	Poly(5-(5-(4,8-bis(5-(2-ethylhexyl)thieno[3,2-b]thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophen-2-yl)selenophen-2-yl)-alt-2,3-bis(3,4-bis(octyloxy)phenyl)-8-(selenophen-2-yl)quinoxaline)
P2FS	Poly(5-(5-(4,8-bis(5-((2-ethylhexyl)thio)thieno[3,2-b]thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophen-2-yl)selenophen-2-yl)-alt-2,3-bis(3,4-bis(octyloxy)phenyl)-6,7-difluoro-8-(selenophen-2-yl)quinoxaline)
PCIS	Poly(5-(5-(4,8-bis(5-((2-ethylhexyl)thio)thieno[3,2-b]thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophen-2-yl)selenophen-2-yl)-alt-2,3-bis(3,4-bis(octyloxy)phenyl)-6,7-dichloro-8-(selenophen-2-yl)quinoxaline)



LIST OF SYMBOLS

SYMBOLS

η_{abs}	the fraction of photons absorbed
η_{diss}	the fraction of electron-hole pairs that are dissociated
η_{coll}	the fraction of charges that reach the electrodes().
E_{g}^{op}	optical bandgap
E_{g}^{el}	electronic bandgap
λ	lambda
$E_{\text{ox}}^{\text{onset}}$	oxidation onset
$E_{\text{red}}^{\text{onset}}$	reduction onset
J	coupling constant

CHAPTER 1

INTRODUCTION

1.1 Polymer

The word "polymer" comes from the Greek words "polus," which means "many, much," and "meros," which means "part." A polymer is a material or substance made up of many repeating subunits that are formed from one or more species of monomers to form macromolecules. The modern concept of polymers first surfaced in the 1920s after an ongoing dispute due to H. Staudinger's paper titled "Über Polymerization". The macromolecular theory mentioned in the paper was a revolutionary idea at the time. The theory argues that polymers are long chains of repeating units. He was awarded the 1953 Nobel Prize in Chemistry for his achievement. (Feldman, 2008) Furthermore, Paul J. Flory proposed the chain transfer mechanism in radical polymerization in 1937 when working at Du Pont with W.H. Carothers. He was awarded the Nobel Prize in 1974. Afterward, Carothers succeeded in the commercial development of polyamide (nylon) fiber and neoprene rubber in the 1930s. In 1938, commercial production of polystyrene was started. Moreover, in 1939, low-density polyethylene was started to produce. In the 1950s, the coordination polymerization of olefins using the complex metal-organic catalyst of aluminum alkyl/titanium chloride was discovered by Karl Ziegler and Giulio Natta. Numerous studies of the stereochemistry of polymer chains and the novel area of stereoregular polymers of different monomers have been prompted by the significant discovery of the Ziegler-Natta catalysts for stereospecific polymerization

of olefins (Y. Ito, S. Okamura, 1937). Industrial polymers developed quickly between the 1950s and 1980s, finding new application areas in construction, electronics, and medicine (Gedde & Hedenqvist, 2019). Today, polymers are one of the largest fields of study in the world.

1.2 Conjugated Polymers

Conjugated polymers are a class of polymers which has consecutive single and double bonds that cause delocalized π electrons in the main chain (Palumbo & Yang, 2022). The most basic conjugated organic polymer, polyacetylene (PA), was initially synthesized in 1958 as a linear, high molecular weight, polyconjugated polymer with a regular structure and high crystallinity. However, it initially gained little interest due to manufacturing techniques that rendered PA an insulator. Furthermore, the vast majority of polymers were considered as an electric insulator nature with similar electrical and optical properties, which possess no mobile charges and no photoabsorption in the UV spectral region, until 1977 when MacDiarmid, Heeger, and Shirakawa proposed a straightforward technique for creating film samples that showed highly electrical conductivity upon treatment with oxidizing agents like halogens (Feast et al., 1996). It was a breakthrough for the polymer field and earned them the Nobel Prize in Chemistry in 2000 (Huang et al., 2020). Subsequently, interest in conductive polymers like polyphenylene, poly(phenylene vinylene) (PPV), polyaniline (PANI), polypyrrole (PPy), polythiophene (PT), and conjugated monomers like fluorene, carbazole, thiophene, and its fused derivatives, benzothiadiazole grows over time which results in the development of novel electronic materials according to the requirements of certain applications (Guo et al., 2013). In this thesis study, benzodithiophene (BDT) and quinoxaline-based complex conjugated polymers were synthesized to construct an organic solar cell.

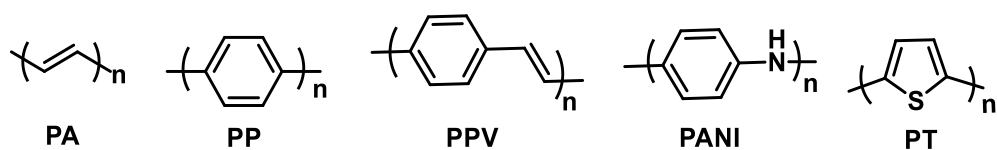


Figure 1.1. Structure of some conjugated polymers

1.3 Low Bandgap Conjugated Polymers

Organic materials capture a smaller range of the solar spectrum than inorganic semiconductors due to their wider bandgaps. Consequently, reducing the bandgap of the conjugated polymer is essential for optimizing photon harvesting in organic solar cell (OSC) devices, as it enhances the overlap with the solar spectrum (Bundgaard & Krebs, 2007). The band gap of a conjugated polymer is identified by the onset of the polymer's optical absorption spectrum. Furthermore, to get a low bandgap, polymers must absorb in the near-infrared (long wavelength) range. However, for conjugated polymers, the optical absorption achieves its maximum value after a specific conjugation length, known as the effective conjugation length (ECL). Providing the repeating units with the quinonoid structure can be an effective way to increase the ECL. D–A type systems where the ‘D’ unit has strong electron-donating and the ‘A’ unit has strong electron-withdrawing moieties strengthen the double bond character between the repeating units that stabilizes the low band gap quinonoid-like forms within the polymer backbones by producing an internal push-pull effect. Consequently, a conjugated polymer can cause a decrease in its band gap energy by alternating the proper donor and acceptor units in the main chain (Ajayaghosh, 2003)(Wu et al., 2015). In this thesis study, BDT main core is used as the donor unit and the quinoxaline main core is used as the acceptor unit of the donor polymers.

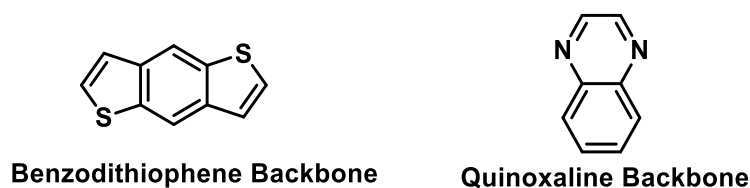


Figure 1.2. Backbones of the donor and acceptor on the thesis

1.4 Palladium-catalyzed Cross-Coupling Reactions

Cross-coupling reactions are a synthetic approach that involves combining an organohalide ($\text{Ar}_1\text{--X}$) with an organometallic compound ($\text{Ar}_2\text{--M}$) reagent and employing metal catalysts to create C–C bonds (Majhi & K. Jash, 2023). Recognition of the importance of this broad class of reactions started with the work of Richard Heck, Eiichi Negishi, and Akira Suzuki which rewarded the Nobel Prize in Chemistry (Jana et al., 2011). Palladium-catalyzed cross-coupling processes for organo-compounds are extensively employed as prevalent synthetic methods for the development of novel, efficient conjugated donor-acceptor polymers. Pd is the preferred metal for cross-coupling reactions due to its redox properties, efficiency, ability to use a wide variety of ligands, and mild working conditions. Stille, Sonogashira, Suzuki, and Heck can be considered as the most commonly used Pd-catalyzed cross-coupling polymerizations, in which several nucleophilic reagents, including aryl stannanes, terminal alkynes, aryl boronic acids or esters, and alkenes, are employed, respectively. (Murad et al., 2020) In addition to that, Suzuki and Stille coupling reactions are commonly preferred due to the high efficiency of the synthesized conjugated polymers used in OSC devices (Al-Azzawi et al., 2023).

1.4.1 Stille Cross-Coupling Reaction

Stille cross-coupling reaction is a widely used synthetic route for forming a C-C bond, utilizing a Pd (0) catalyst in addition to organotin chemicals. With the presence of a catalytic amount of Pd complex, the reaction between organostannanes and halides is known as the Stille cross-coupling reaction. The history of the reaction begins with the research conducted by Eaborn and colleagues in 1976, followed by the investigations of the Kosugi–Migita group in 1977 (Majhi & K. Jash, 2023). However, the reaction gained recognition with the work of John Kenneth Stille involving the coupling of a diverse array of alkyl tin reagents with various aryl and acyl halides and achieving much-improved yields under milder conditions (Stille, 1986). An appealing feature of the Stille reaction is the ease of synthesis of organotin reagents. Furthermore, air stability and withstanding various functional groups on the two counterparts without using any protection or deprotection methods, such as sensitive groups like ester and alcohol are the other favorable properties of the reaction (Farina & Krishnan, 1991). The properties are mostly attributable to the low polarity of the Sn-C bond. Regarding this, the Stille reaction is distinct from other cross-coupling reactions which utilize more polar organometallic reagents (Espinete & Echavarren, 2004).

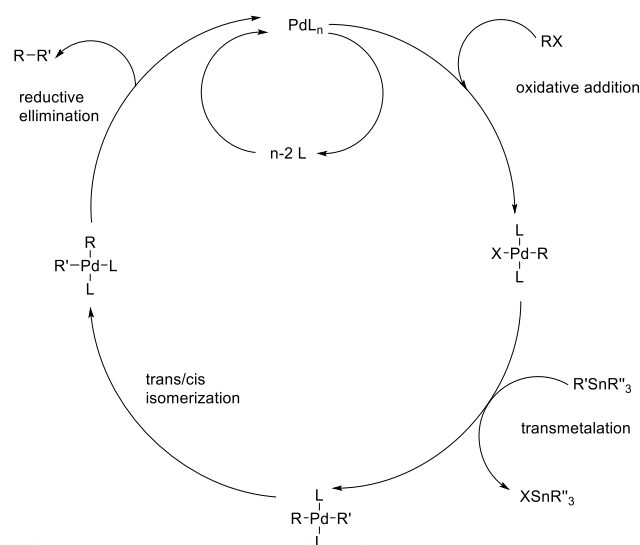


Figure 1.3. Stille cross-coupling reactions scheme

1.4.2 Mechanism

The mechanism of the Stille cross-coupling reaction contains three primary steps;

1. Oxidative-addition
2. Transmetalation
3. Reductive elimination

The cycle starts with the activation of the Pd(II) to Pd(0)L₂ by arylstannane monomer, it permits entry of the Pd into the catalytic cycle. Both Pd(II) and Pd(0) can be selected as catalysts, with examples including Pd(OAc)₂ and Pd(PPh₃)₂Cl₂ for Pd(II) or Pd(PPh₃)₄ and Pd₂(dba)₃ for Pd(0), according to the condition and yield of the reaction (Murad et al., 2020). The first primary step initiates with the oxidative addition of the aryl halide (**R-X**), which is the rate-determining step, to form a cis-palladium complex (**X-Pd(II)L₂-R**). After that, the complex underwent cis/trans isomerization to provide a trans intermediate to increase the stability. The second step is transmetalation which includes organic group (**R'**) transfer between the organo-stannane reagent (**R'-SnR''₃**) and the Pd (II) complex to produce cis Pd (II)

complex that is composed of two organic groups (**R-Pd (II)-R'**). According to Stille's review in 1986, while oxidative-addition and reductive-elimination sequences are understood, the transmetalation phase has not yet been fully comprehended (Stille, 1986). Currently, ongoing research continues to understand the transmetalation mechanism. Finally, Pd(II) returns to its starting position, Pd(0), after reductive elimination has produced a C-C bond between two organic compounds (**R-R'**) and the final product obtained (Espinet & Echavarren, 2004).

1.5 The Role of Conjugated Polymers in Modern Technology

Conjugated polymers were first used in the fabric dye industry in the 1800s. Subsequently, with the discovery of their conductive characteristics, initial applications started in batteries. To expand their employment in sophisticated electrical and optoelectronic devices, applications gradually changed from utilizing the polymers' conductive qualities to investigating their semiconducting properties. Conjugated polymers gained a lot of attention, especially in the 1980s, when they were first used in solar cells and later in field-effect transistors. Following the discovery of electroluminescence in conjugated polymers in the 1990s, organic light-emitting diodes (OLEDs) were developed using conjugating polymers (Rasmussen et al., 2023). Moreover, conjugated polymers have been used in a wide range of commercial applications. Today, organic photovoltaic devices, NIR photodetectors, organic light-emitting diodes, nonlinear optical devices, energy storage photodetectors, chemo- and bio-sensors, organic field-effect transistors, electrochromic devices, memory storage devices, and various sensors are examples of modern technological applications of conjugated polymers (X. Fan et al., 2013)(Murad et al., 2020). The thesis study focuses on the conjugated polymers used in the active layer of the organic solar cells. Therefore, emphasis will be placed on OSC.

1.6 Organic Solar Cells

The growing global population has resulted in a substantial increase in energy demand. Furthermore, the environmental damage caused by fossil fuels, along with their declining sustainability, has intensified interest in clean and renewable energy sources. Among these, solar energy has emerged as one of the most widely preferred options (Cheng et al., 2009). Organic solar cell technology has been in development for over 30 years. However, significant attention towards this technology has surged with advancements in power conversion efficiency. These improvements are primarily attributed to research focused on the integration of novel materials, modifications to device architecture, and innovative strategies in molecular engineering (Hoppe & Sariciftci, 2004). Generally, small molecules and conjugated polymers are used in OSCs. When compared with the inorganic ones, organic solar cells have lower charge-carrier mobility (Dimitrakopoulos & Mascaro, 2001) and relatively high exciton binding energy. Latter property limits the thickness of the device to equal or smaller than 100 nm. However, both drawbacks can be compensated due to the strong absorption coefficient of OSC which shows high absorbance even equal to or lower than 100 nm. OSC generally has a higher bandgap than inorganic ones which can affect the light-harvesting (Gregg & Hanna, 2003). Despite this, it has very attractive features that can be listed as: large-scale production properties, mechanical flexibility, low cost, lightweight, and easy processability (Hoppe & Sariciftci, 2004). Furthermore, since the turn of the twenty-first century, there has been a notable improvement in both the efficiency of polymer photovoltaic devices and the understanding of the physical mechanisms underlying OSCs (Yeh & Yeh, 2013). The numerous advantages and increasing power conversion efficiencies of these devices make OSCs promising candidates for solar cell applications in both academia and industry.

1.6.1 Architecture of Organic Solar Cells

1.6.1.1 Single Layer Devices

The most basic kind of organic solar cell device is a single-layer cell, which has just one organic layer sandwiched between two electrodes. The device is composed of an anode layer (typically indium tin oxide, or ITO), a cathode layer (metals such as magnesium or aluminum), and an organic layer (Nelson, 2002). The operating principle of this device relies on the work function difference between the electrodes to overcome the exciton binding energy, which is typically higher than 0.5 eV for conjugated polymers. However, a single material in the organic layer is generally insufficient for effective exciton dissociation into holes and electrons. The dependence of the photovoltaic properties of single layer devices on the nature of the electrode results in a low fill factor (FF). Other factors affecting FF include the high series resistance of the organic layer and the field-dependent generation of charges (Tang, 1986). In 1994, Marks et al. were employed in single-layer solar cells using PPV, yielding a minimal external quantum efficiency (EQE) of approximately 1% and a power conversion efficiency (PCE) of 0.1% (Marks et al., 1994).

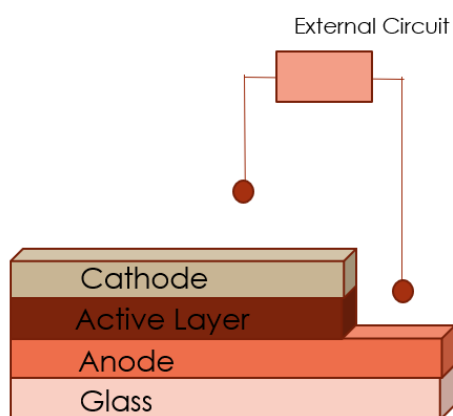


Figure 1.4. Design of the single layer OSC

1.6.1.2 Bilayer Devices

A bilayer device consists of two organic layers sandwiched between electrodes. The interface region between these layers is predominantly accountable for the photogeneration of charges and has a lower dependence on external electric fields compared to single-layer devices. In bilayer systems, the properties of the organic interface play a greater role in determining the amplitude and polarity of the open-circuit voltage (V_{oc}) than the electrode-organic interfaces (Tang, 1986). The exciton diffusion length in conjugated polymers, typically ranging from 4 to 20 nm, significantly limits the performance of bilayer devices, as only excitons generated within 10–20 nm of the interface can reach the donor-acceptor interface (Winder & Sariciftci, 2004). Furthermore, due to this limitation, the thickness of the organic layer also has a significant influence on device performance (Gu et al., 2007). In 1986, Tang and his colleagues constructed a device using perylene tetracarboxylic derivative as an acceptor material and copper phthalocyanine (CuPc) as a donor material. PCE of the device was reported to be 1%. Consequently, such a device often results in a higher FF and PCE than that of single-layer devices (Tang, 1986).

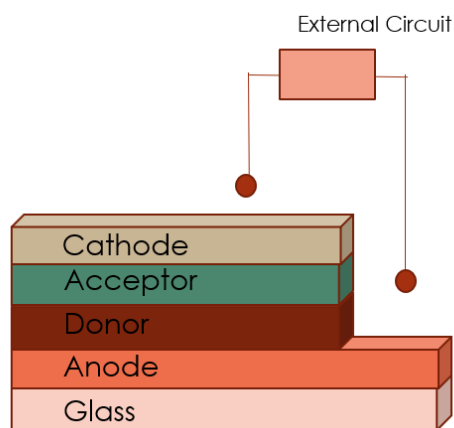


Figure 1.5. Design of the bilayer OSC device

1.6.1.3 Bulk Heterojunction Devices

In 1995, Yu and his coworkers constructed an OSC device with an active layer containing a blend of conjugated polymer and fullerene derivatives to increase the donor-acceptor interface and reduce the exciton migration distance. It is concluded that by controlling the morphology of phase separation into an interpenetrating network, a larger interfacial area in the bulk material can be achieved (Yu et al., 1995). Unlike the previous architecture, where the A and D materials were stacked one on top of the other and could make selective contact with the cathode and anode electrodes, the BHJ has two routes to transport electrons and holes to the electrodes. Furthermore, the D and A domains should form a bicontinuous network with a nanoscale shape for efficient charge transfer and collection after exciton dissociation (Dennler et al., 2009)(Po et al., 2010). Consequently, in bulk heterojunction, the photogenerated excitons are more effective in dissociating into free holes and electrons compared to the prior architectures, which improves charge separation efficiency and results in increased PCE.

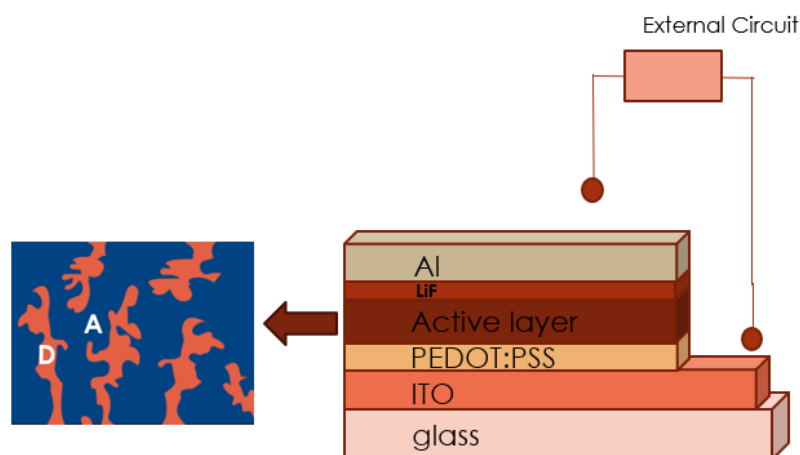


Figure 1.6. Design of the commercial bulk heterojunction OSC

1.6.1.3.1 Device Engineering of Bulk Heterojunction

BHJ solar cells constructed in the theses study consist of six layers which are sequentially glass substrate, transparent anode, an ultra-thin layer of N, N'-Bis{3-[3-(Dimethylamino)propylamino]propyl}perylene-3,4,9,10-tetracarboxylic diimide (PDINN), an active layer, a thin layer of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT: PSS) and silver cathode (H. Zhou et al., 2012). The work function of the electrodes is an important parameter in identifying if the contact with the organic material is ohmic or blocking, and the difference in work functions provides charge carriers the potential needed to reach the electrodes. To create an ohmic contact low work function metals like aluminum or silver are used as cathode material and high work function materials are used as anode material. It is necessary for one electrode to be transparent to effectively harvest sunlight. Since achieving transparency with metals is challenging, transparent conductive oxides, such as indium-tin oxide (ITO) or zinc oxide (ZnO), are typically used as the anode material. Subsequently, PDINN and PEDOT: PSS are used as buffer layers which help charges to collect on electrodes and increase efficiency. PDINN, spin coated as a thin layer beneath the silver cathode, enhances the contact and reduces the work function of the silver. Conversely, PEDOT: PSS which is a transparent material deposited above the ITO increases the work function of the electrode, behaves as an electron-blocking layer, and can elevate the surface properties of the ITO (Po et al., 2010). Furthermore, the active layer, located in the middle of the device, consists of both donor and acceptor materials. The acceptor material can consist of fullerene derivatives, such as PC₆₁BM and PC₇₁BM, or non-fullerene acceptors (H. Zhou et al., 2012). The donor material can be either a small molecule or a polymer; however, in this thesis study, a polymer donor material was utilized, and devices incorporating both NFA (non-fullerene acceptor) and fullerene-based acceptors were fabricated.

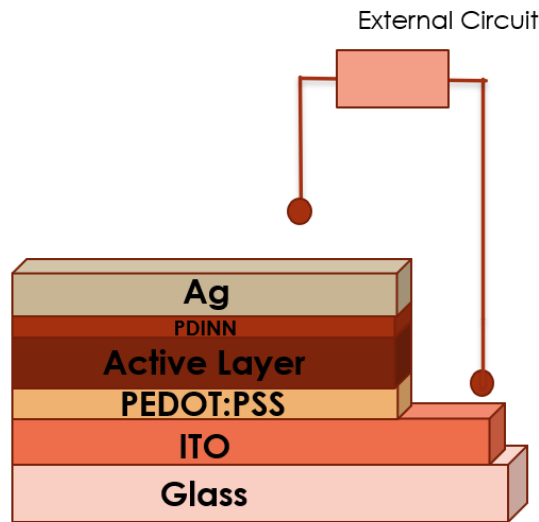


Figure 1.7. Design of the bulk heterojunction OSC in the thesis study

1.6.2 Deposition Methods

Organic solar cells can be constructed using various deposition methods, depending on the materials used. Typically, the metal cathode is deposited through thermal evaporation, and the transparent conductive oxide is applied via sputtering. The PEDOT: PSS buffer layer and the photoactive layer are deposited using wet techniques, such as spin-coating, doctor blading, screen-printing, and inkjet printing (Po et al., 2010). While the high molar mass and low decomposition temperature of polymers make evaporation impossible, good solution processability enables their application through wet techniques (Hoppe & Sariciftci, 2004). Even though many new techniques have been developed in this regard, with the advantages of high efficiency and low costs, spin coating is still the most preferred technique (Vak & Kim, 2007).

1.6.3 Working Principle

The working principle of an OSC device includes 4 steps. In the initial step, exciton formation occurs upon photon absorption. Subsequently, the exciton diffuses through the material until it reaches the donor-acceptor (D–A) interface, where the electric field facilitates its dissociation into free holes and electrons. At the interface, electrons are transferred to the cathode, while holes move toward the anode, ultimately generating the current. The quantity of generated charges that are gathered at the electrodes controls the electric current a photovoltaic solar cell produces. Overall photocurrent efficiency is determined by 3 parameters; a fraction of photons absorbed (η_{abs}), the fraction of electron-hole pairs that are dissociated (η_{diss}), and finally the fraction of charges that reach the electrodes (η_{coll}) (Hoppe & Sariciftci, 2004).

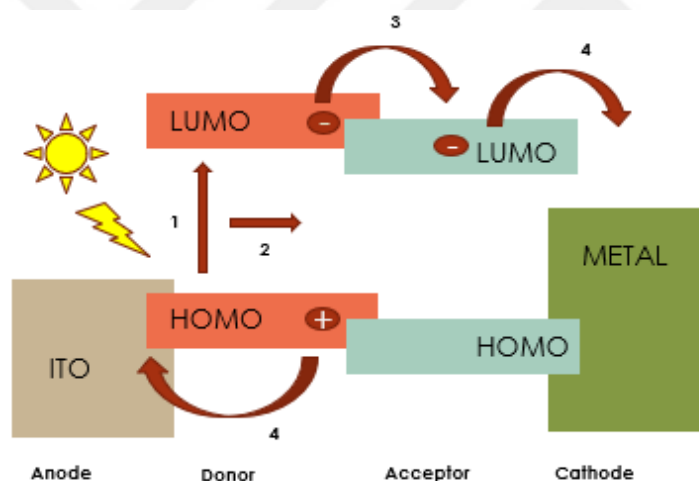


Figure 1.8. Scheme of the working principle of the OSC

1.6.3.1 Light Absorption

Matching the absorption spectrum of the polymer with the solar spectrum is essential for achieving high absorption efficiency. Thus, low absorption efficiency reduces

photocurrent generation and limits the efficiency of the device which is driving the search for new materials with energy levels better overlap to capture photons at longer wavelengths. Furthermore, one strategy to overcome this limitation is to lower the band gap of the donor material (lower than 2 eV defined as low bandgap polymer), which increases photon absorption and enhances current generation, ultimately leading to a higher PCE (Brabec et al., 2002). Consequently, the absorption spectrum, absorption coefficient, layer thickness, and internal multiple reflections are the common parameters that affect the fraction of absorbed photons (η_{abs}) (Hoppe & Sariciftci, 2004).

1.6.3.2 Exciton Diffusion

The factor that limits the diffusion of the electron through the interface is called the exciton diffusion length (L_D). Since the exciton diffusion length of polymers generally ranges from 4 nm to 20 nm, only photons that have enough distance to interface can participate in the current formation. Minimizing the layer thickness can be considered an effective method that shortens diffusion distance to the donor-acceptor contact and enhances the probability of the exciton reaching the interface (Yeh & Yeh, 2013).

1.6.3.3 Charge Dissociation

The energy difference between the HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) levels of the donor and acceptor materials creates an electric field at the interface. When an exciton arrives at the interface, if the energy difference between the HOMO and LUMO levels is greater than the exciton binding energy, the exciton efficiently dissociates into free electrons

and holes (Yeh & Yeh, 2013). The fraction of dissociated exciton (η_{diss}) is highly dependent on the diffusion of the exciton to the interface (Hoppe & Sariciftci, 2004).

1.6.3.4 Charge Transport

After exciton separation into electrons and holes, electrons are accepted by the cathode electrode, which has a higher electron affinity, while holes are accepted by the anode electrode, which has a lower ionization potential, resulting in current formation. However, recombination or charge trapping in a disordered interpenetrating organic material, resulting from low charge mobility, can lead to reduced η_{coll} and efficiency of the device (Yeh & Yeh, 2013).

1.6.4 Characterization of OSCs

The performance of an organic solar cell device is determined by the current (J)–voltage (V) graph. Generally, in the literature, the power conversion efficiency (PCE) which serves as a comprehensive measure of device efficiency is used to quantify the performance of the device. The measurement depends on mainly three parameters; short circuit current density (J_{sc}), open circuit voltage (V_{oc}), and fill factor (FF). A general J-V characteristic measurement takes place in both dark and illumination states using the standard test conditions (STC) that include a solar spectrum intensity of 100 mW/cm², an AM 1.5 with an incoming spectral angle of approximately 48° and a constant room temperature of 25 °C (Benanti & Venkataraman, 2006). Using STC is crucial for advancing the literature by standardizing measurements globally, thereby enabling consistent and reliable comparisons (Gu et al., 2007).

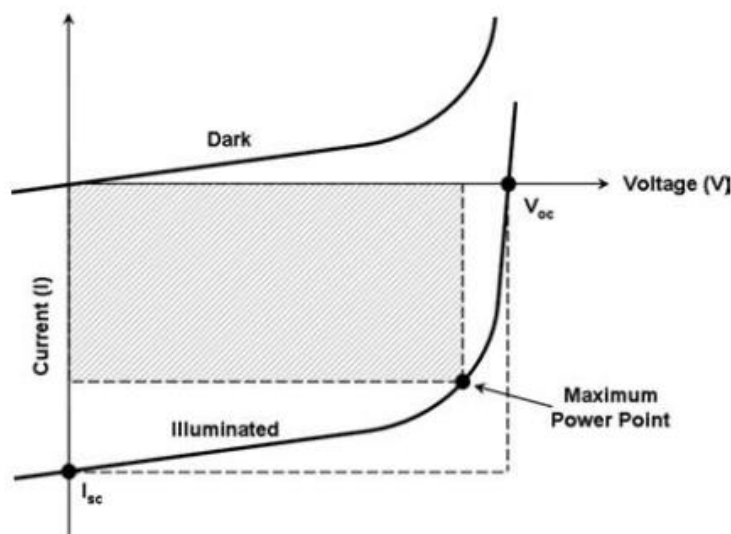


Figure 1.9. J-V characteristics of OSC under dark and illuminated conditions (Gu et al., 2007)

1.6.5 Important Parameters of OSCs

The power conversion efficiency (PCE) is primarily established by three important parameters: open circuit voltage (V_{oc}), short circuit current (J_{sc}), and fill factor (FF).

Open Circuit Voltage (V_{oc}): It refers to the maximum voltage throughout the device when the current flow is zero (Bian et al., 2012). It has a linear correlation with the energy difference between the HOMO of the donor and the LUMO of the acceptor. Considering this principle, for instance, lowering the HOMO level of the donor causes an increase in the V_{oc} . However, it can also widen the bandgap of the polymer, resulting in a reduced J_{sc} (H. Zhou et al., 2012).

Short Circuit Current (J_{sc}): It is defined as the maximum current flow measured without applied voltage. J_{sc} is highly dependent on light absorption; therefore, factors

that enhance light absorption, such as using narrow-bandgap polymers, also contribute to an increase in J_{sc} (H. Zhou et al., 2012).

Fill Factor (FF): It can be defined as the proportion of the maximum actual power output of the cell to its theoretical power output. It indicates how easily charge carriers can travel through the solar device to the electrodes. It has a direct relationship with the squareness of the J-V characteristics, as a higher degree of squareness corresponds to an increase in FF (Qi & Wang, 2013). Furthermore, for high FF values, low series resistance (R_s) and high shunt resistance (R_{sh}) are required which depend on the morphology of the active layer (H. Zhou et al., 2012). In conclusion, the parameter is highly affected by charge mobility, active layer thickness, and active layer morphology (Gupta et al., 2010).

$$FF = \frac{P_{max}}{J_{sc}V_{oc}} = \frac{J_m V_m}{J_{sc}V_{oc}} \quad \text{Equation 1.1}$$

Power Conversion Efficiency (PCE): It can define as the ratio of maximum produced power output (P_{max}) of OSC device to the power input (P_{in}) of the incident light. P_{in} value generally accepted as 100 mW/cm² under AM 1.5G illumination conditions. The PCE of an organic solar cell is calculated by equation 1.2:

$$PCE = \frac{P_{max}}{P_{in}} = \frac{FF J_{sc}V_{oc}}{P_{in}} \quad \text{Equation 1.2}$$

1.7 Active Layer

1.7.1 Morphology of the Active Layer

Morphology optimization is an important factor in improving the PCE of organic solar cells (Huang et al., 2014). The morphology of BHJ can be modified by changing the molecular structure of the D-A blend and the processing methods. There have been several approaches presented in previous years that allow for the

modification of the film nano-morphology (Pivrikas et al., 2011). Which can be listed as;

1. Post-production treatment such as thermal annealing, polar solvent treatment, using a buffer layer between the active layer and electrode, etc.
2. Matching of the solubility of the materials
3. Using suitable solvents according to boiling point to optimize the solvent evaporation rate
4. The application of spin-coated films with a slower drying rate
5. Chemical additives such as 1,8-diiodooctane (DIO), chloronaphthalene (CN)

Morphology of the active layer can be characterized by X-ray scattering, electron microscopies such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), and scanning probe microscopies such as atomic force microscopy (AFM) (Huang et al., 2014) (Pivrikas et al., 2011).

1.7.2 Fullerene as an Acceptor

Over the decade, molecular engineering of donor polymer has been mostly responsible for the elevation of the PCE of OSCs due to little progress in modifying the acceptor materials. Until the major improvement of NFAs in 2015, fullerene-based acceptors dominated the organic solar cell (OSC) field as the primary acceptor material by limiting the PCE of devices to around 10%. The use of modified fullerene such as [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) and PC₇₁BM, a C₇₀ analogue of PC₆₁BM, has been preferred instead of the buckminsterfullerene (C₆₀) itself due to low solubility of the molecule (H. Zhou et al., 2012). Advantages of the fullerene-based acceptors include their 3D character, delocalized LUMOs, high electron mobilities, and the capacity to establish interpenetrating networks with donors. However, low tunability, limited absorption in the visible and near-infrared

regions, low thermal and photochemical stability, long purification time, and high-cost properties led to a search for new acceptor materials in the field (C. Yan et al., 2018).

1.7.3 Non-Fullerene Acceptor

NFAs have been utilized in the OSC for more than 20 years, however, the working field received little attention due to the performance of NFA devices in the past. Rylene monoimides, tetracyanobutadiene derivatives, pentacene derivatives, twisted acene-imides, and phthalocyanines are some examples of used NFA which mostly resulted in lower PCE values than fullerene-based ones (C. Yan et al., 2018). In 2015, Zhan et al., synthesized the molecule ITIC by incorporating the indacenodithiophene (IDT), acceptor unit, and 2-(3-oxo-2,3-dihydroinden-1-ylidene) malononitrile (INIC), donor units, on the same molecule which opened a new path for the design of NFAs. In 2016, Zhao et al. constructed a device using PBDB-T: ITIC-based NFA blend yielding 11% PCE while the PBDB-T: PC₇₁BM blend yielding 7.45 % (W. Zhao et al., 2016). Furthermore, a wide range of ITIC-based NFAs were synthesized by modifying the end group or backbone to take advantage of the characteristics of the molecule (Yuan & Zou, 2022). It is essential to consider matching energy levels of donor and acceptor unit when designing the NFA which has a high PCE. In this context, In 2017, Feng et al. reported an A-DA'D-A molecule (BZIC) that framework an electron-deficient (A') segment into the middle of the central D conjugated building block to form a fused DA'D backbone (Feng et al., 2017). Afterward, In 2019, Yuan et al. designed the Y6 acceptor which is another A-DA'D-A type molecule that yields 15% PCE (Yuan et al., 2019). Overall, NFAs are an appealing research field when compared to fullerene-based acceptors, for boosting PCE due to their significant absorptions in visible and near-infrared spectrum, high electron mobility, high chemical and thermal stability, and high tunability (Yuan &

Zou, 2022). Currently, 19% PCE has been achieved using a non-fullerene acceptor with a ternary blend for single-junction organic solar cells (Cui et al., 2021). In the thesis study, ITIC and Y6 were used as NFA in the active layer blend.

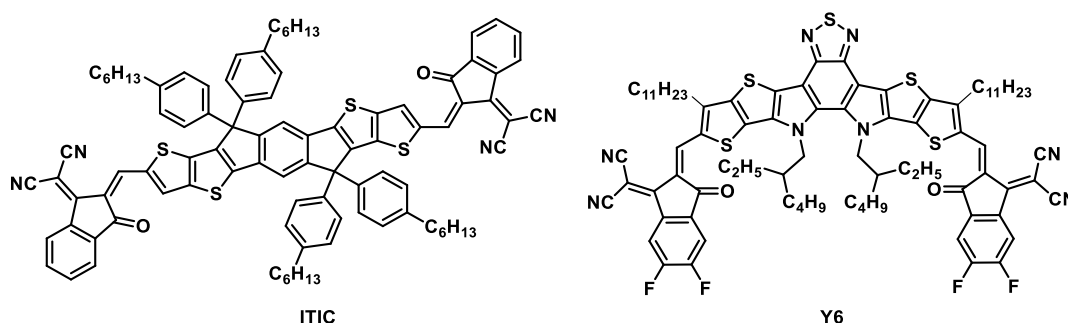


Figure 1.10. Structure of the ITIC and Y6

1.7.4 Molecular Engineering of the Donor Polymer

Modification of the donor polymer is a vital section of the OSC research. As discussed earlier, the donor polymer includes donor and acceptor units which use the push-pull effect to provide a low band gap (Wu et al., 2015). In this regard, there are certain key points for selecting appropriate donor-acceptor units and creating the donor polymer. To increase the photovoltaic performance of the device, the donor polymer needs to be engineered by following guidelines.

1. The absorption spectrum of the donor polymer needs to overlap with the solar spectrum to result in high J_{sc} . Thus, the polymer that has a high extinction coefficient and narrow bandgap must be synthesized. Furthermore, lowering the LUMO of the polymer is a common strategy to achieve a narrow bandgap (Bundgaard & Krebs, 2007). The difference between the LUMO of the acceptor and donor polymer needs to be 0.3 - 0.5 eV for effective charge separation (Scharber et al., 2006).
2. The polymer needs to exhibit a high hole mobility (Zhan & Zhu, 2010).

3. The polymer should dissolve effectively in organic solvents (Scharber et al., 2006).
4. The polymer has to establish a good morphology with an acceptor in the active layer to increase the charge separation (Dang et al., 2013).

Conjugated polymers can be investigated to separate four sections which include the backbone, π -bridge, the side chain, and the substituents (H. Zhou et al., 2012).

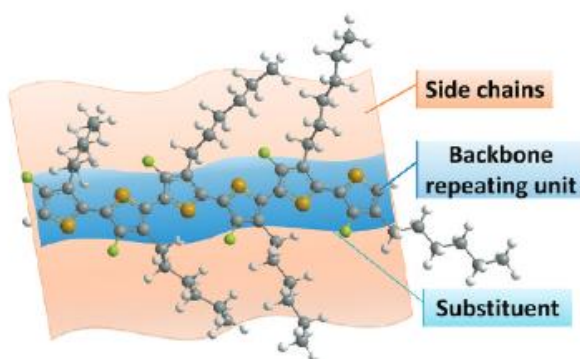


Figure 1.11. Main parts of donor polymers (H. Zhou et al., 2012)

1.7.4.1 Backbone Repeating Units

1.7.4.1.1 Benzodithiophene as a Donor Unit

Benzo[1,2-b:4,5-b'] dithiophene (BDT) unit is regarded as a highly promising monomer candidate for building high-performance photovoltaic materials. Due to its rigid, planar, and electron-rich character, it offers highly tunable molecular energy levels, optical band gaps, and high hole mobilities. Determined by years of investigations, developing BDT with two-dimensional side groups can be considered to be a practical and effective way to maximize the photovoltaic performance of the conjugated polymers (Yao et al., 2016). Furthermore, using an alkylated aromatic

ring as a side chain on the BDT core to increase the 2-D character is a very common strategy to increase the charge transport and the bulk heterojunction morphology (An & Hou, 2022). In 2021, Cui et al. produced a low-bandgap non-fullerene acceptor (NFA) **eC9-2Cl** and a large-bandgap polymer donor **PBQx-TF** for OSC. According to the literature, so far highest PCE of devices that use BDT as donor monomer (**PBQx-TF**), without considering the ternary blends and tandem devices, was reported as 17.7 % with a V_{oc} of 0.868 V by Cui and coworkers (Cui et al., 2021).

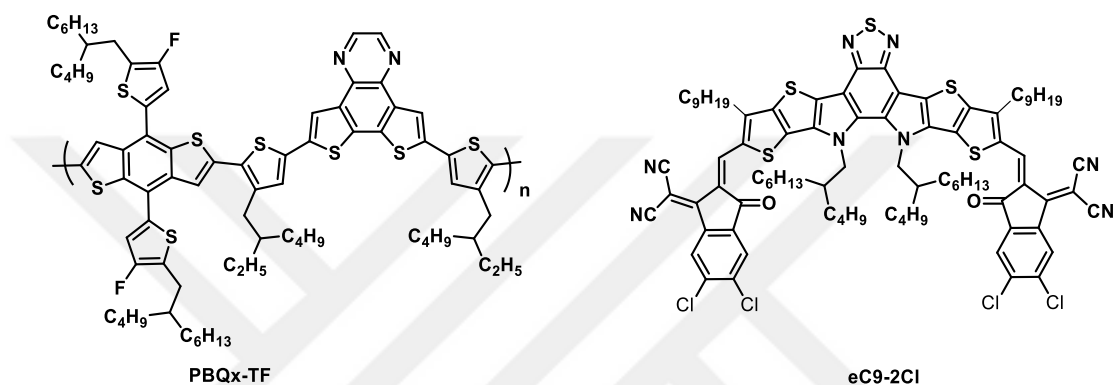


Figure 1.12. Structure of the acceptor material and BDT containing donor polymer

1.7.4.1.2 Quinoxaline as an Acceptor Unit

One of the most widely used building blocks for the synthesis of D–A conjugated polymers is quinoxaline and its derivatives. With containing two nitrogen atoms, quinoxaline exhibits electron-deficient properties, making it a commonly used acceptor in donor-acceptor type polymers for OSCs (M. Liu et al., 2017). To increase the efficiency of the OSC, the properties of donor and acceptor molecules need to be tuned very delicately. Hence, easy modification of the quinoxaline gives the molecule finely tunable properties. For instance, quinoxaline can be modified using an electron-withdrawing or donating group and using an aromatic ring to increase the molecule's ECL. In addition to that, easy modification properties can be used to

improve the solubility and processibility of the synthesized polymer (Gedefaw et al., 2017). In 2021, Zhu et al., constructed an OSC based on **PBQ6:Y6** accomplishes a high fill factor of 77.91% and a PCE of 17.62%. Currently, in OSC which contains quinoxaline-based polymer in the active layer around 18% PCE has been seen (Zhu et al., 2021).

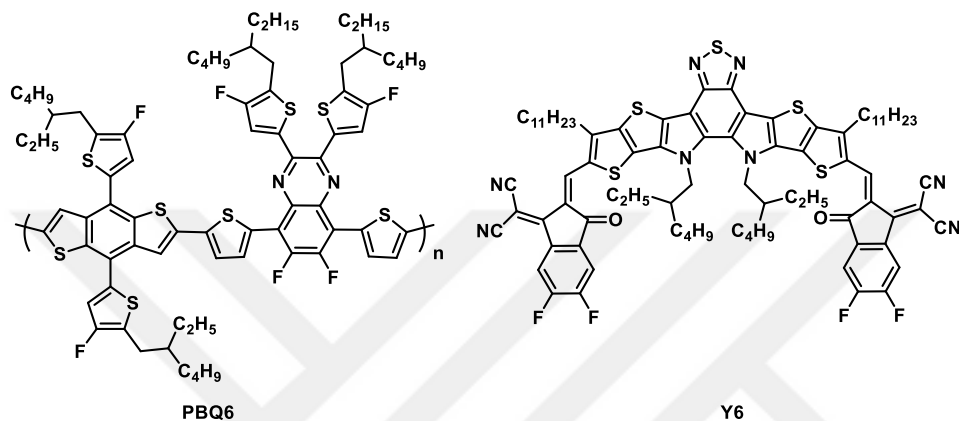


Figure 1.13. Structure of the acceptor material and quinoxaline-containing donor polymer

1.7.4.2 Affect of the Π – Bridges on Polymer

π -bridge can be employed to optimize the donor-acceptor unit by extending the external conjugation length and enhancing molecular planarity, both of which contribute to increased electron delocalization, improved light absorption, and more efficient charge transport (B. Zhou et al., 2023).

1.7.4.2.1 Selenophene π -Bridges

Selenophene is a common π -bridge which used in donor polymer design. The fact that selenium is a larger atom than sulfur leads to low aromaticity which results from

inefficient overlap with the π -system. Subsequently, selenophene has an increasing effect on the quinoidal resonance which elongates the absorption spectra to the longer wavelength region (Near-Infrared region). Furthermore, the Se molecule can boost charge carrier mobility with increasing intermolecular Se-Se interaction, which is attributed to the Se atom's greater polarizability than the S atom (Cuesta et al., 2019). Equally important, the use of selenium atoms, due to their lower ionization potential compared to sulfur, can stabilize the LUMO level and lowered its energy. This modification reduces the bandgap without affecting the V_{oc} of the device (Heeney et al., 2007).

1.7.4.3 Affect of Side Chains on Polymer

Molecular weight, solubility, and processability primarily depend on side chains. Side chains should be adjusted carefully, as improper configurations can increase steric hindrance, disrupt morphology, reduce the effective conjugation length by resulting in significant twisting, cause a wider bandgap, and ultimately, lower the power conversion efficiency of the device (H. Zhou et al., 2012). Meanwhile, side-chain engineering is indeed an essential and widely spread technique used to tune the physical properties of a conjugated polymer and achieve high-performance OSCs, including absorption, energy level, molecular packing, and charge transport (Qunping Fan et al., 2016).

1.7.4.3.1 Thiophene and Thienothiophene Side Chain on BDT

Side chain engineering of BDT-based polymers has gained momentum after it was realized that the use of conjugated side chains contributes to electron delocalization and provides promising photovoltaic performance (Q. Fan et al., 2015). Thiophene side chain substitution on BDT, the earliest method to synthesize 2D conjugated

BDT unit (Yao et al., 2016), which is used to increase the intermolecular π - π interactions by increasing the effective conjugation length of BDT-based polymers (Kim et al., 2015). The thienyl substitution on BDT can lower the HOMO level of the polymer by increasing the donating ability of the donor unit, which is attributed to the electron-rich structure of the thiophene molecule. (Peng et al., 2011) Similarly, due to the rigid, planar, and electron-rich structure of thieno, [3,2-b]thiophene (TT), its substitution to the BDT unit resulted in improved π - π interaction, molecular ordering, and hole mobility (Kim et al., 2015). Furthermore, the TT side chain was widely employed in low-bandgap polymers (Yao et al., 2016). Consequently, thiophene and thieno[3,2-b]thiophene side chains have been utilized to enhance the photovoltaic characteristics of BDT-based polymers (Kim et al., 2015). However, the effect of the side chains on the photovoltaic performance is highly dependent on its interaction with the donor and acceptor; thus, there are no common rules for selecting side chains. To compare the performance of thiophene and thieno[3,2-b]thiophene side chain substituted BDT acceptor units, Table 1.1 provides the literature data of PTB7-Th and PTTBDT-FTT (Figure 1. 14) (Yao et al., 2016).

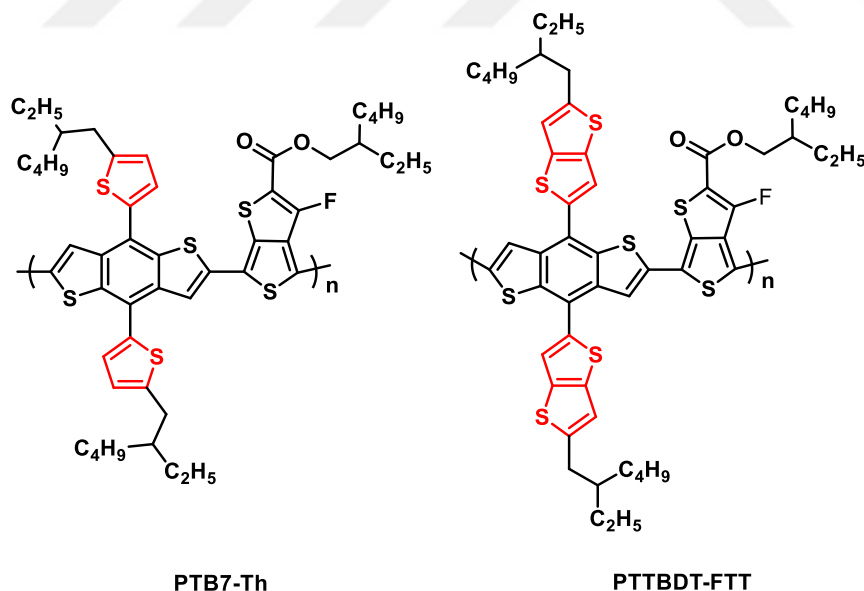


Figure 1.14. Structure of the PTB7-Th and PTTBDT-FTT

Table 1.1. Comparison of PTB7Th and PTTBDT-FFT

Device	E_g^{opt}	HOMO (eV)	LUMO (eV)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
PTB7-Th: PC₇₁BM	1.58	-5.22	-3.22	0.80	15.73	74.3	9.35
PTTBDT-FFT: PC₇₁BM	1.55	-5.31	-3.76	0.77	14.70	68	7.71

1.7.4.3.2 Benzene Side Chain on Quinoxaline

The benzene group exhibits weak electron-donating characteristics, a large π -conjugated area, and good planarity (Yao et al, 2016). Because of these properties, it is widely used as a side chain in the quinoxaline core to enhance vertical conjugation. Furthermore, it can broaden the absorption spectrum of the polymer (Jiang et al., 2018). The most significant feature of benzene substitution is that its five free positions allow for facile tuning of the polymer properties. On the other hand, quinoxaline-based polymers with two pendant freely rotating benzene groups on the quinoxaline rings may inhibit the intermolecular packing and influence electron mobility (J. Zhang et al., 2011). Therefore, alkoxy group substitution may be preferred as it can slightly help intermolecular interaction over only alkyl substitution (Kitazawa et al., 2012).

1.7.4.3.3 Alkyl Chains

One of the favorable attributes of the organic solar cell is its solution processability, which is able to be attained by adjusting the flexible side chains on the polymer backbone. Long and branched alkyl side chains increase solubility by reducing π - π interactions on the polymer backbone attributed to enhancing steric hindrance.

However, reducing π - π interaction also lowers the electron mobility. Alkyl rearrangements must be carefully designed to ensure optimal balance between solubility and π - π interactions (Yao et al., 2016). Adjusting the substituent position can influence the main chain planarity, film morphology, interchain structure, and electronic structure. Furthermore, the length of the alkyl chain must be limited to a certain length to avoid bending, which reduces the steric effect and adversely lowers the solubility (D. Zhou et al., 2024). It is a common strategy to substitute "O" and "S" heteroatoms on the alkyl chain to alter the optical and electrical characteristics of the polymer and balance the π - π interaction. Alkyloxy-substituted polymers exhibit higher HOMO levels than their alkyl-substituted analogs due to stronger electron-donating properties of the alkoxy group. Consequently, the alkoxy substituent has a narrower optical band gap than alkyl-substituted analogs (Yao et al., 2016). Moreover, it shows lower steric hindrance than the alkyl group. Conversely, alkylthio substitution can lower the HOMO and LUMO levels of polymer compared with the alkoxy substitution due to the lower electron donating ability of the S atom than the O atom (Wang et al., 2016). Additionally, when compared with their alkoxy analog, alkylthio substitution can increase the electron mobility by inducing ordered π - π packing and exhibiting a narrow bandgap (Yao et al., 2016) which leads to improvement in the FF value of the device (Wang et al., 2016).

1.7.4.4 Substituents

Substituents such as halogen groups primarily affect the electronical properties of the polymer and are frequently utilized to tune the band gap and energy levels of donor material (H. Zhou et al., 2012).

1.7.4.4.1 Halogen Substitution

The fluorine atom is the most electron-withdrawing substituent and the smallest electron-withdrawing group and the introduction of F into the conjugated backbone would lower both the LUMO and HOMO levels of the conjugated polymers, with minimal steric hindrance (Gao et al., 2014). Furthermore, the fluorine atom may result in greater intermolecular interaction and alter the rotation barriers between adjacent conjugated components, which may result in more ordered aggregation morphologies, increased carrier mobilities, and superior photovoltaic performance of the OSC device. On the other hand, the chlorine atom has a lower electronegativity than fluorine and has a higher dipole moment due to its larger atomic size. The larger size can cause stronger steric hindrance that can affect the aggregation according to the position of the chlorine atom. For instance, chlorine substitution on conjugated side chains, such as thiophene, can lead to a higher dihedral angle between the two pendant side chains that freely rotate, increasing steric hindrance and reducing aggregation behavior yet, the meta position can be selected to minimize the effect of side chain rotation on twisting of the backbone. However, chlorine atoms substituted onto the backbone have a direct effect on polymer conformation, which can significantly influence the aggregation behavior. Furthermore, the higher dipole moment increases the electron delocalization into the chlorine atom which stabilizes the HOMO level of the polymer more than the fluorine atom. It can cause lower HOMO and LUMO levels of chlorine-substituted polymers compared with the fluorine counterparts (Zhang et al., 2018). To conclude, incorporating halogen atoms such as F and Cl into the polymer may cause a decrease in HOMO and LUMO levels which ultimately promote high V_{oc} and highly influence the morphology according to the position of the substituent (D. Zhou et al., 2024).

1.8 Literature Review

In this thesis, nine polymers were synthesized to be used as donor polymers in the active layer of bulk heterojunction organic solar cells. P2FD2 has the most similar design to the polymer counterparts in the literature; the main differences are the alkyl chain and the usage of a different π -bridge (Lenaerts et al., 2020). Although used donor and acceptor units are separately found in the literature, polymers in the thesis study can be considered new because most of them are not coupled with the same donor or acceptor, and contain different π bridges, alkyl chains, or heteroatoms compared with literature counterparts. Table 1.2. summarizes the photovoltaic output of the polymers according to the literature. The photovoltaic properties of **PBDTCIT-TQxT** and **PBCl-Qx** highlight the effects of chlorine substitution on BDT and quinoxaline units. **P1F** and **P2F** allow for a comparison of the impact of the position and quantity of fluorine atoms. Similarly, **P3** and **P4** facilitate the evaluation of the π -bridge effect, while **PTTBDT-FT** and **PSTTBDT-FT** are used to study thienothiophene substitution and compare the influence of alkyl versus alkylthio groups.

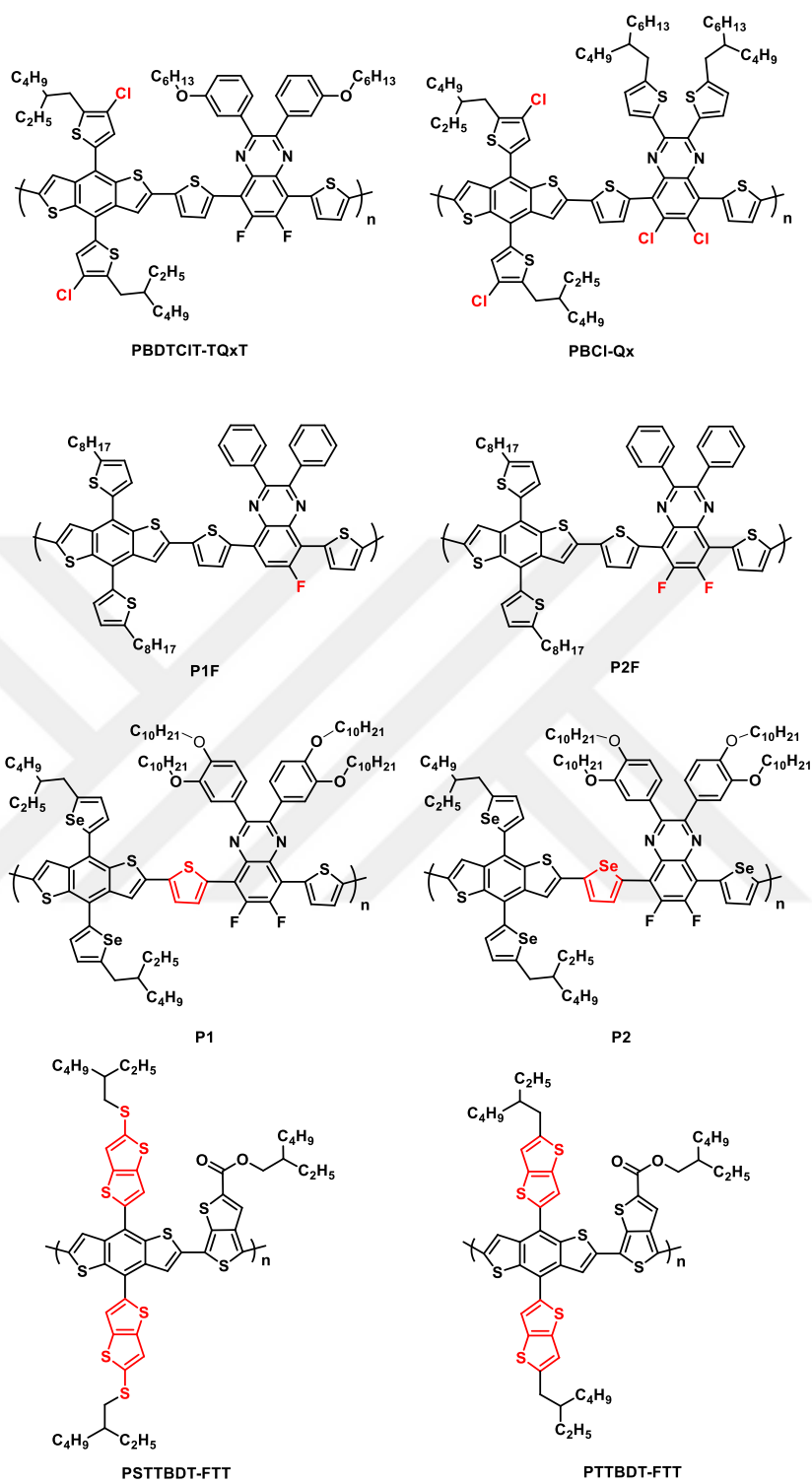


Figure 1.15. Structure of the literature polymers

Table 1.2. Photovoltaic properties of the literature analogues

Polymers	D-A	V_{oc}	J_{sc}	FF	PCE	References
Blend	Ratio	(V)	(mA/cm²)	(%)	(%)	
PBDTCIT-TQxT: ITIC	1:1	0.94	14.61	0.60	8.22	(Lenaerts et al., 2020)
PBCI-Qx: Y6	1:1	0.76	26.32	62.1	12.44	(Lee et al., 2022)
P1F:PC₆₁BM	1:3	0.87	6.52	55	3.1	(Yang et al., 2014)
P2F:PC₆₁BM	1:3	0.91	6.84	59	3.7	(Yang et al., 2014)
P1:PC₇₁BM	1:2	0.80	8.39	60.8	4.10	(Arslan et al., 2022)
P2:PC₇₁BM	1:2	0.75	9.51	48.3	3.44	(Arslan et al., 2022)
PSTTBDT-FT: PC₇₁BM	1:1.5	0.80	15.38	70	8.61	(Kim et al., 2015)
PTTBDT-FT: PC₇₁BM	1:1.5	0.77	14.70	68	7.71	(Kim et al., 2015)

1.9 Aim of the Study

The main goal of the study is to enhance the photovoltaic properties of organic solar cells by synthesizing nine new polymer donor units. Additionally, the study aims to investigate the effect of the different side chains and halogen substitution on polymer

donor units for organic bulk heterojunction solar cells by analyzing the bandgap, HOMO-LUMO level, solubility, film-making ability, and morphology of polymers. In this study, benzodithiophene and quinoxaline-based nine new donor-conjugated polymers were synthesized by using the Stille cross-coupling reaction. Four distinct acceptor units, three halogen-substituted and one non-halogenated, were coupled with three donor units which had thiophene, thienothiophene, and alkylthio substituted thienothiophene side chain. To proceed, BDT-based monomers were selected as donor units due to their fused and electron-rich nature, and quinoxaline-based monomers were selected as acceptor units due to containing two nitrogen atoms which provide an electron-deficient nature to the monomer. BDT and quinoxaline coupled copolymers are the common low-bandgap polymers that are widely used in OSC devices. According to the literature, halogen substitution typically decreases both the HOMO and LUMO energy levels. Similarly, thiophene or thienothiophene substitution can lower the HOMO level of the polymer by extending the conjugation length and enhancing π - π interactions, while a selenophene π -bridge specifically lowers the LUMO level. Therefore, synthesizing polymers with deep HOMO and LUMO energy levels, which enable a high V_{oc} and J_{sc} , is a key strategy to improve the photovoltaic performance of the device. **P1F**, **P2F**, **PCl**, **P1FD2**, **P2FD2**, and **PCID2** are the six synthesized polymers for the TUBİTAK Project. Three polymers, **P1F**, **P2F**, and **PCl** contain thienothiophene-substituted BDT core while the other three, **P1FD2**, **P2FD2**, and **PCID2**, contain chlorinated thiophene-substituted BDT as a donor monomer to compare the side chain effect on the BDT. Furthermore, both side chains containing donor monomer coupled with the three quinoxaline-based acceptor which contain one fluorine, two fluorine, and two chlorine atoms to investigate the effect of the halogen substitution. Additionally, three polymers, **P2FS**, **PCIS**, and **P0F** were synthesized, the first pair was synthesized to investigate the effect of the change in the alkyl chain, and the third polymer which contains a non-halogenated quinoxaline core was synthesized

to be used as a reference, respectively. To illustrate, the first pair, **P2FS** and **PCIS**, was synthesized to observe alkylthio substitution on thienothiophene which polymers contain the original donor in the project that had to be replaced with thiophene containing donor due to purification problems of the **D3** monomer and the third polymer, **P0F** was synthesized to use as reference to understand the effect of the halogenation. Consequently, nine donor polymers were synthesized, and optical, electrical properties and mechanical properties were characterized. Furthermore, conventional OSCs were fabricated by using the first six polymers to investigate photovoltaic characterization and by optimizing the device to reach the highest PCE of the synthesized polymers.

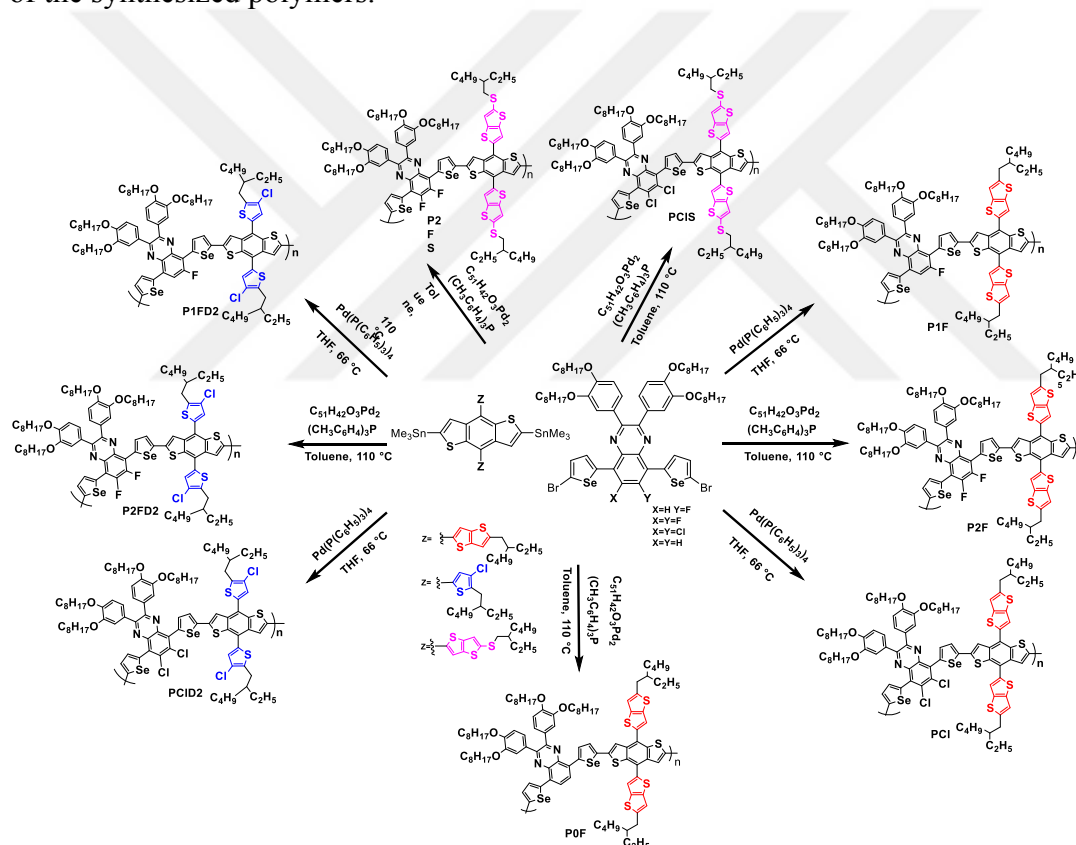


Figure 1.16. Structures of the synthesized nine polymers

CHAPTER 2

RESULTS AND DISCUSSION

2.1 Gel Permeation Characterization

Table 2.1. The molecular weight characteristics of the polymers

Polymer	M_n (Da)	M_w (Da)	PDI
P1F	7736	10554	1.36
P2F	22676	27812	1.23
PCL	13152	28312	2.15
P1FD2	12584	17256	1.37
P2FD2	85955	169104	1.97
PCID2	46115	84937	1.84
P0F	9002	13281	1.48
P2FS	2021	2271	1.12
PCIS	2738	3201	1.17

The number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity indices (PDI) of the polymers were established using gel permeation chromatography by using chloroform as the eluent and polystyrene as the standard. The molecular weight of the polymers can be affected by many

parameters, including polymerization time, used catalyst solvent pair, and reactivities of the monomers. The first seven polymers, **P1F**, **P2F**, **PCI**, **P1FD2**, **P2FD2**, **PCID2**, and **P0F** have appropriate molecular weights to satisfy the polymer definition. P1F has the lowest M_n value with 7736 Dalton (Da), among the seven polymers due to the low reactivity of mono-fluorine substitution when compared to two fluorine or chlorine containing ones. Moreover, **P1FD2** and **P0F** also have lower M_n values, 12584 Da and 9002 respectively, which lends further weight to the argument. Low reactivity can result from the reduced electron-accepting ability of the polymers, which affects the oxidative addition step of the Stille coupling reaction (Espinet & Echavarren, 2004). However, the last two polymers, **P2FS** and **PCIS**, with M_n values of 2021 and 2738 Da can be considered as oligomers. Due to the impurity of the **D3** monomer, which contained a mixture of bis-stannylated, mono-stannylated, non-stannylated molecules, the mono-stannylated species acted as an end-capping agent. This resulted in shorter chain lengths and lower molecular weight. They were synthesized only to compare their optical and electrochemical characteristics with the first seven polymers, as outlined in the aim of the study (Wang et al., 2016).

2.2 Thermogravimetric Analysis

Table 2.2. Thermal characteristics of the polymers

Polymers	T_d (°C)
P1F	413.05
P2F	423.83
PCI	417.38
P1FD2	441.04
P2FD2	427.93
PCLD2	424.39

Table 2.2 presents the temperature at the starting point of the 5% weight loss for the six polymers. Thermogravimetric analysis was performed in a nitrogen atmosphere with a heating rate of 10°C/min, ranging from 25°C to 800°C. The TGA thermograms revealed that the polymers were thermally stable, with onset decomposition temperatures corresponding to 5% weight loss at 413.05, 423.83, 417.38, 441.04, 427.93, and 424.39°C, respectively, in the order shown in the table. Td temperatures are closely related to the Mn of the polymers, and Td of the **P1F**, **P2F**, **PCI**, **P2FD2**, and **PCID2** follow the same order as their Mn values, where lower molecular weight polymers decompose more easily than higher molecular weight polymers. However, despite the lower molecular weight of **P1FD2**, the highest Td of the polymer can be attributed to its higher molecular interactions compared to polymers containing the same side chain on the BDT (Ohring, 1995). Further information can be found in section 2.3, **P1FD2** part. The results show that all polymers are stable enough for OSC applications. Thermograms of the polymers are available in Appendix C.

2.3 Optical Characterization

The optical characterization of the polymers was performed using UV-Vis spectroscopy in both chloroform solution and thin-film form. Thin films are prepared by spray coating with 0.5 mg/mL chloroform/polymer solution. The optical bandgap of the polymers was calculated based on the λ_{onset} of the polymer in the thin-film state, as the polymers are coated on the active layer in thin-film form.

$$E_g^{\text{opt}} = hc/\lambda = 1241 / \lambda_{\text{onset}} \quad \text{Equation 2.1}$$

Table 2.3. Optical properties of the polymers in CHCl₃ and thin film

Polymers	Solution	Thin Film	Thin Film	E _g ^{opt} (eV)
	$\lambda_{\text{max}}(\text{nm})$	$\lambda_{\text{max}}(\text{nm})$	$\lambda_{\text{onset}}(\text{nm})$	
P1F	554	559	765	1.62
P2F	585	642	730	1.70
PCL	360	553	720	1.72
P1FD2	436	532	716	1.73
P2FD2	599	634	704	1.76
PCID2	475	511	652	1.90
P0F	361/422	382	723	1.72
P2FS	377	392	714	1.74
PCIS	366	388	630	1.97

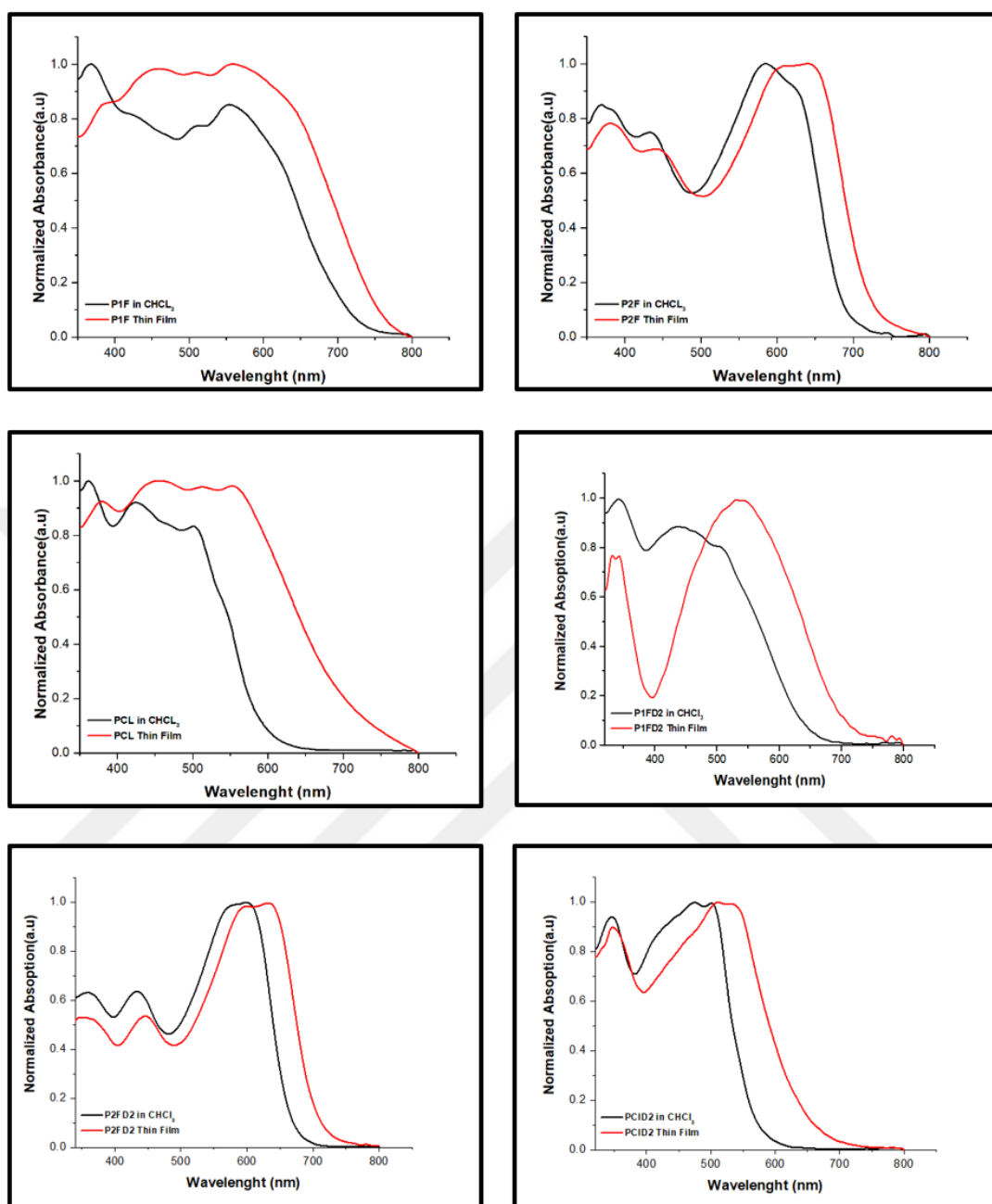


Figure 2.1. Normalized absorbance spectrum of the first six polymers in CHCl_3 and thin film

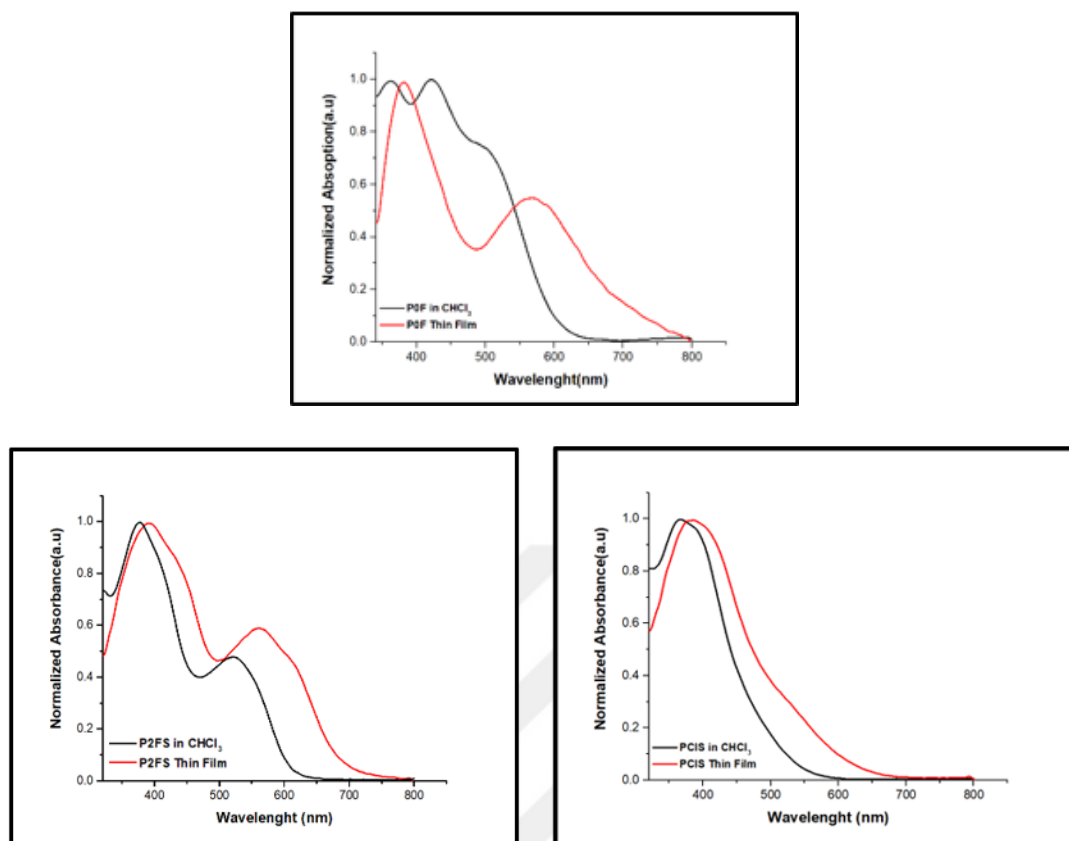


Figure 2.2. Normalized absorbance spectrum of the P0F, P2FS and PCIS in CHCl_3 and thin film

In most of the UV-Vis spectra, the bands observed between 300 and 500 nm are attributed to π - π^* transitions, while those between 500 and 800 nm correspond to the intermolecular charge transfer of the polymers. The polymers exhibit an increasing optical bandgap trend from mono-fluorine to chlorine substitution on quinoxaline by increasing the electron-withdrawing effect of the substituents which is consistent with the results reported in previous work of Qiao et al in 2015 (Qiao et al., 2015).

In the absorption spectrum of **P1F** in solution form, the π - π^* band exhibits higher intensity than the ICT band. The polymer shows a very weak redshift, which can be attributed to its low M_n value, leading to reduced aggregation. The broad ICT band

observed in the thin film of **P1F** may result from the asymmetry of the polymer, as the position of the mono-fluorine substitution varies along the chain. This causes different polymer chains to exhibit slightly different absorption spectra. **P2F** and **PCI** both exhibit a redshift, indicating strong π - π interactions and enhanced aggregation. The broad ICT band observed in **PCI** may result from its high PDI value (2.15). The broadness of the ICT band leads to an overlap with the π - π^* band, reducing the distinctness of the bands.

P0F, **P1F**, and **P2F** are compared with similar molecules that differ in the substitution of thiophene instead of thienothiophene on BDT, featuring a thiophene π -bridge and the absence of alkoxy groups on quinoxaline. The absorption spectrum of **P2F** closely resembles its literature counterparts, however, **P1F** is different due to its much broader ICT band. **P0F**, **P1F**, and **P2F** exhibit lower bandgaps compared to similar polymers reported in the literature, attributed to the higher π - π interaction of thienothiophene (Yao et al., 2016b).

Table 2.4. Optical properties of the P0F, P1F, and P2F with literature analogs (Yang et al., 2014)

Polymers	Thin Film $\lambda_{\text{max}}(\text{nm})$	$E_{\text{g}}^{\text{opt}}(\text{eV})$
P0F	382	1.72
Literature similar P0F	580	1.80
P1F	559	1.62
Literature similar P1F	575	1.80
P2F	642	1.70
Literature similar P2F	588	1.81

P1FD2 demonstrates a broader ICT band with a more pronounced π - π^* interaction band, evident from its greater red shift compared to **P1F**, with minimal overlap between the bands. Therefore, **P1FD2** can exhibit higher π - π interaction and aggregation. The absorption spectrum of **P2FD2** is quite similar to that of **P2F**, while **PCID2** exhibits a more pronounced π - π^* interaction band and a broad ICT band similar to **PCI**. Since **PCID2** has a lower PDI value, its ICT band is not as broad as that of **PCI**. Additionally, **P2F** and **PCI** exhibit a higher redshift than **P2FD2** and **PCID2**. This behavior can indicate the higher planarity of **P2F** and **PCI**, attributed to the thienothiophene substitution, which enhances π - π interactions more effectively than the chlorine-substituted thiophene side chain (Zhang et al., 2015)(Yao et al., 2016b).

Additionally, **P1FD2**, **P2FD2**, and **PCID2** exhibit higher optical bandgaps compared to their thienothiophene-substituted counterparts which are discussed further in the electrochemical characterization part (section 2.4). **P2FD2** shows a similar absorption band to its literature counterparts, which differ by using thiophene instead of selenophene as the π -bridge. **P2FD2** also has a slightly higher λ_{max} value than **PBDTCIT-TQxT**, likely due to the increased conjugation length facilitated by the selenophene π -bridge, which enhances quinoidal resonance. Differences in the π bridge have not been reflected in optical results which can be observed by the very close E_g^{opt} of the two polymers.

Table 2.5. Optical properties of the P2FD2 with literature similar(Lenaerts et al., 2020)

Polymers	Thin Film $\lambda_{\text{max}}(\text{nm})$	$E_{\text{g}}^{\text{opt}}(\text{eV})$
P2FD2	634	1.76
Literature similar PBDTCIT-TQxT	627	1.78

P0F exhibits a higher optical bandgap than **P1F**, which is inconsistent with the literature, where the electron-withdrawing properties of substituents are generally expected to increase the bandgap (Qiao et al., 2015). This discrepancy may arise from the lower donor-acceptor interaction in **P0F**, as the reduced accepting ability of the acceptor fails to balance the strong donor properties of the thienothiophene-containing BDT core. The lower ICT intensity in the absorption spectra further supports the evidence of deficient donor-acceptor interaction in **P0F**.

P2FS and **PCIS** contain an alkylthio group on the thienothiophene, which is substituted onto the BDT core, polymers only differ from the first three polymers with sulfur atoms. These polymers can be considered as oligomers due to their low M_n values. The low intensity of the ICT band is attributed to the short polymer chains, which cause lower π - π interaction and aggregation. However, in 2016, Wang et al. synthesized difluorobenzothiadiazole and indacenodithiophene (IDT)-based polymers with varying chain lengths, starting from the smallest oligomers up to an 11 kDa polymer, to investigate the effect of chain length on the properties of the polymers. The optical and electrochemical results of these polymers and oligomers were similar. Oligomers exhibit slightly higher optical and electronic bandgaps, as well as lower HOMO and higher LUMO levels, due to the reduced influence of halogen atoms in the chain caused by the shorter chain length. For instance, while

dimers have four halogen groups substituted, trimers have eight, resulting in a stronger electron-withdrawing effect for trimers than for dimers. This effect continues progressively with increasing chain length, up to a molecular weight of 10 kilodaltons (kDa). Due to the significantly short chain length of the **P2FS** and **PCIS**, making comparisons with other polymers is not deemed reasonable further discussed below. **P2FS** exhibits stronger π - π interaction and aggregation behavior than **PCIS**, as evidenced by the higher intensity of the ICT band of the **P2FS**. Furthermore, both **P2FS** and **PCIS** exhibit higher optical bandgaps compared to **P2F** and **PCI**, which can be attributed to the low M_n values of the oligomers. The shorter conjugation length in oligomers typically results in higher bandgap values than those of their polymer counterparts (Wang et al., 2016). Moreover, the significantly greater difference between the optical bandgaps of **PCIS** and **PCI** further supports this observation. This is likely due to the very low intensity of the ICT band in **PCIS**, which contributes to its substantially higher optical bandgap. Since the M_n values of two polymers are very small, the optical bandgap calculation can be affected by overly broad spectra, making the onset misleading and too large. The electronic and optical bandgaps are nearly identical, whereas normally the electronic bandgap is higher than the optical bandgap, which suggests that the optical bandgap can be overestimated (Baran et al., 2010).

2.4 Electrochemical Characterization

The electrochemical characterization of the polymers was performed using Differential Pulse Voltammetry (DPV) in 0.1 M of TBAPF₆/ACN at N₂ atmosphere on a Pt counter electrode vs. Ag/AgCl reference electrode with step size 5 mV, sample period 0.1 s, pulse time 0.05 s and pulse size 10 mV. Thin films are prepared by spray coating with 0.5 mg/mL chloroform/polymer solution on the ITO surface. ACN was selected as the solvent due to its strong ionic conductivity and its ability

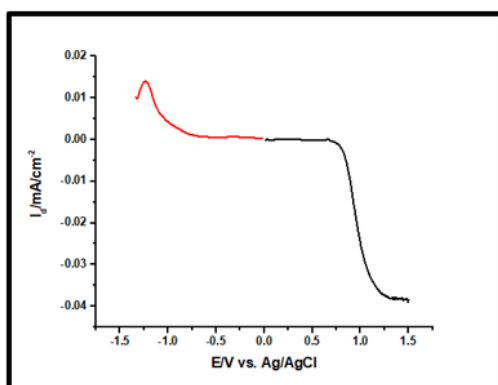
to provide a stable polymer film without dissolving the polymer on the ITO surface. DPV was used due to its higher sensitivity. By delivering a series of voltage pulses, DPV offers higher resolution than cyclic voltammetry (CV), making it possible to detect oxidation and reduction peaks more precisely, especially for materials that take a longer time to completely oxidize or reduce. This is important since polymers in the study react electrochemically more slowly and higher sensitivity of DPV makes it possible to characterize the redox processes more accurately (Vilas-Boas et al., 2019).

$$\text{HOMO} = -(4.75 + E_{\text{ox}}^{\text{onset}}), \text{LUMO} = -(4.75 + E_{\text{red}}^{\text{onset}}) \quad \text{Equation 2.2}$$

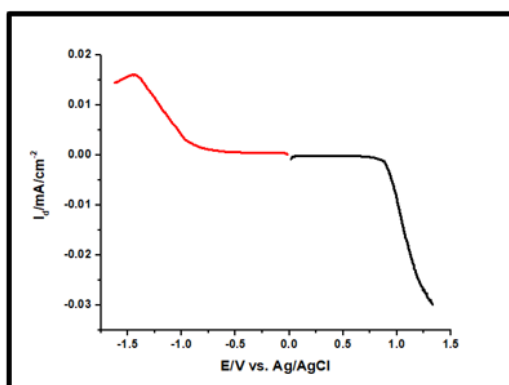
$$E_{\text{g}}^{\text{el}} = \text{HOMO} - \text{LUMO} \quad \text{Equation 2.3 (Baran et al., 2010)}$$

Table 2.6. Electrochemical properties of the polymers

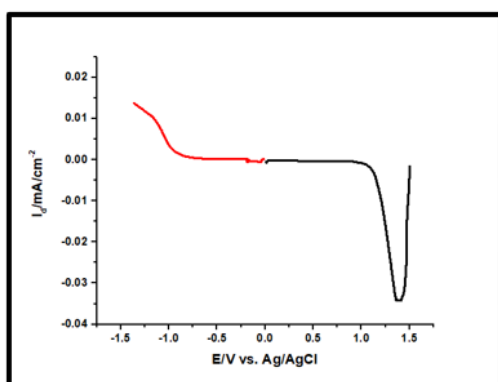
Polymers	$E_{\text{ox}}^{\text{onset}}$ (V)	$E_{\text{red}}^{\text{onset}}$ (V)	HOMO (eV)	LUMO (eV)	E_{g}^{el} (eV)
P1F	0.81	-0.88	-5.56	-3.87	1.69
P2F	0.9	-0.88	-5.65	-3.87	1.78
PCL	1.11	-0.93	-5.86	-3.82	2.04
P1FD2	1.04	-0.84	-5.79	-3.91	1.88
P2FD2	0.92	-1.12	-5.67	-3.63	2.04
PCID2	1.09	-0.99	-5.84	-3.76	2.08
P0F	1.07	-0.97	-5.82	-3.78	2.04
P2FS	0.65	-1.09	-5.4	-3.66	1.74
PCLS	0.89	-1.11	-5.64	-3.64	2



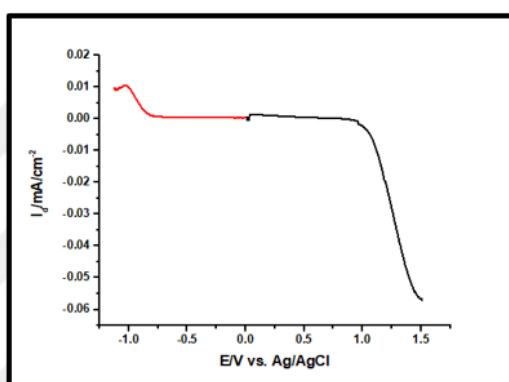
P1F



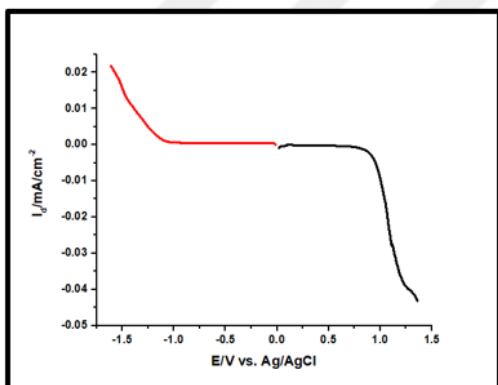
P2F



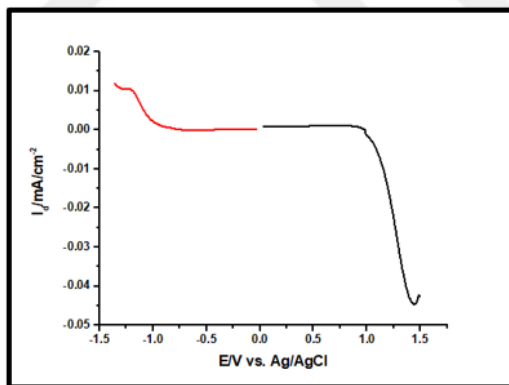
PCI



P1FD2



P2FD2



PCID2

Figure 2.3. Differential pulse voltammogram of the first six polymers in 0.1 M TBAPF₆/ACN

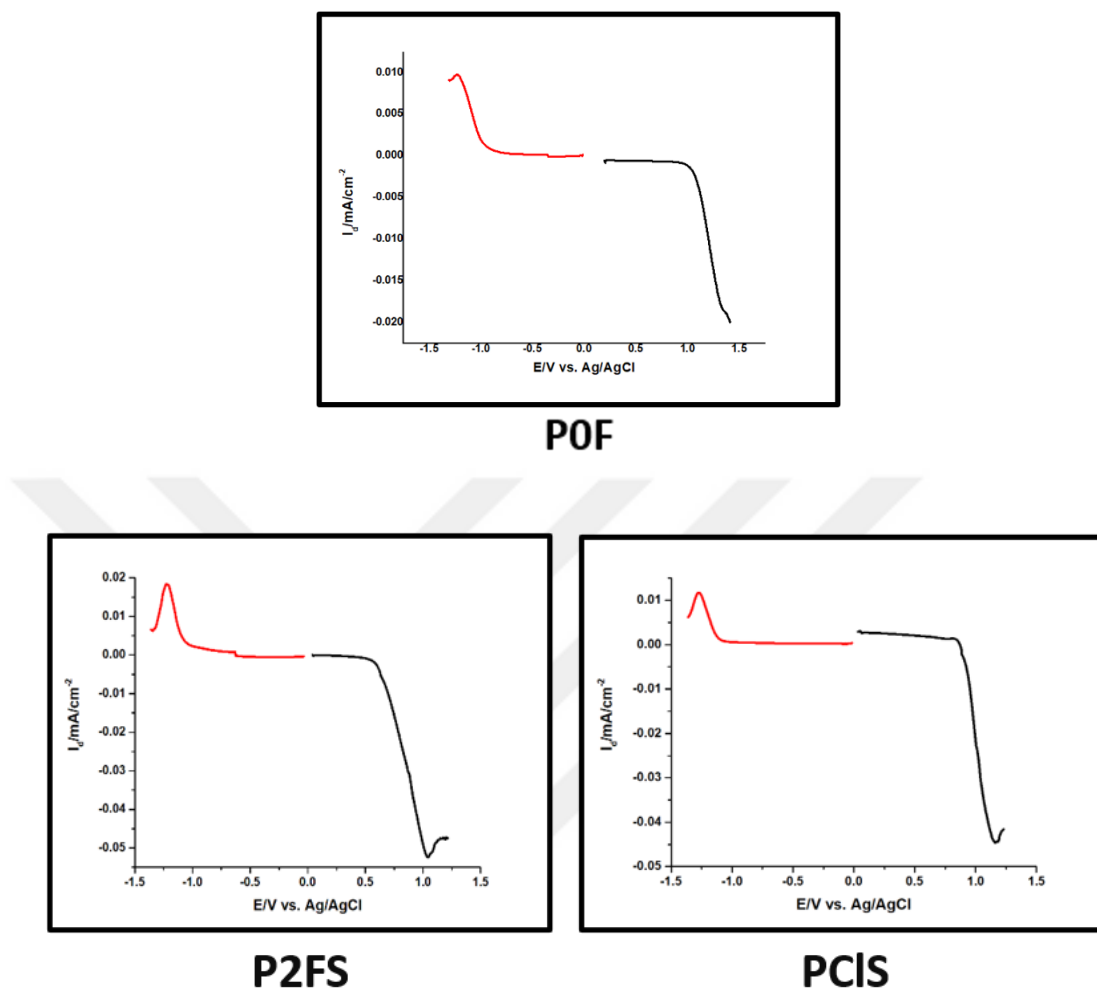


Figure 2.4. Differential pulse voltammogram of the polymers in 0.1 M TBAPF₆/ACN

Electronic bandgaps of the polymers are consistent with the optical bandgap. Moreover, electronic bandgaps of the polymers are higher than optical bandgaps due to the generation of free ions in the electrochemical characterization while optical characterization measures the neutral excited state (Baran et al., 2010).

The first three polymers exhibit a decrease in HOMO level, **P1F** has a higher HOMO level when the **PCI** has the lowest due to the higher electron affinity of the chlorine atom. A higher electron affinity by enhancing electron delocalization, stabilizes the HOMO level (Zhang et al., 2018). However, the effect of the halogens on the LUMO level is subtle. The results align with earlier literature on polymers which has similar structures, indicating that fluorine has no significant effect on the LUMO levels of the resultant polymer systems, though it does reduce the HOMO level. The increased bandgap observed with electron-withdrawing substituents can be attributed to their strong influence on the HOMO and only a minor influence on the LUMO (Qiao et al., 2015).

PCID2 exhibits lower HOMO and LUMO levels compared to **P2FD2**, likely due to the stronger electron affinity of the chlorine atom on the quinoxaline unit. On the other hand, the lower HOMO and LUMO levels of **P1FD2** may result from the reduced steric hindrance of the mono-fluorine substitution on the acceptor, which facilitates better donor-acceptor interaction compared to polymers with the same side chain substituted on the BDT core. Consequently, the effect of electron-withdrawing groups on the BDT unit, which according to the literature lowers both HOMO and LUMO levels, is observed more prominently (Lenaerts et al., 2020) (D. Liu et al., 2015).

Chlorine-substituted thiophene-containing polymers exhibit higher electronic bandgaps compared to thienothiophene-containing ones. This is due to the electron-withdrawing chlorine substitution on the BDT unit, which reduces the donating ability of the BDT core (Lenaerts et al., 2020). Additionally, chlorine substitution on thiophene can increase the dihedral angle between the two pendant side chains that can freely rotate, leading to greater steric hindrance and reduced planarity compared to thienothiophene-containing polymers (Zhang et al., 2015). Both of these effects can decrease the donor-acceptor interaction, resulting in a higher bandgap for

polymers containing **D2**. **P2FD2** and **PCID2** exhibit higher LUMO levels compared to **P2F** and **PCI**, while the HOMO levels of all four polymers are relatively remained unaffected with the change of the side chain of the donor. This effect may result from the stronger π - π interaction of thienothiophene, which enhances donor-acceptor interaction and leads to relatively lower LUMO levels. On the other hand, the chlorine-substituted thiophene on BDT may exhibit reduced donor-acceptor interaction compared to thienothiophene counterparts due to the steric hindrance introduced by the chlorine atom.

P0F has a higher bandgap, lower HOMO level, and higher LUMO level compared to **P1F**. This unexpected result may arise from the weaker donor-acceptor interaction in **P0F** compared to **P1F**, as discussed in the optical characterization section (2.2). The lower electron-accepting ability of the non-halogenated quinoxaline results in a higher LUMO level than **P1F** and fails to stabilize the strong donor properties of the thienothiophene-substituted BDT. This leads to reduced electron delocalization and a localized HOMO primarily on the BDT unit, resulting in a lower HOMO level and very high bandgap comparing the **P1F**.

P2FS and **PCLS** have the alkylthio group substituted on thienothiophene rather than the alkyl group. HOMO of the **PCLS** is lower than **P2FS** due to the higher electron affinity of the chlorine atom. The increased bandgap observed with electron-withdrawing substituents can be attributed to their strong influence on the HOMO and only a minor influence on the LUMO (Qiao et al., 2015). According to the literature, alkylthio groups generally lower the HOMO and LUMO levels of polymers due to an increase in donating ability of the donor. However, due to the lower Mn value of the polymers, the contribution of halogens on the quinoxaline core is lower compared to the long polymer chain, which can result in higher HOMO and LUMO levels for the **P2FS** and **PCIS** (B. Zhou et al., 2023)(Wang et al., 2016).

2.5 Ultraviolet Photoemission Spectroscopy Characterization

Table 2.7. HOMO level of the polymers which determined by UPS

Polymers	HOMO
P1F	-5.6
P2F	-5.93
PCI	-6.06
P1FD2	-5.68
PCID2	-5.95

$$E_{\text{kin}} = |E_{1 \text{ onset}} - E_{2 \text{ onset}}| \quad \text{Equation 2.4}$$

$$\text{HOMO} = E_{\text{kin}} - 21.22 \text{ eV} \quad (\text{Andrade et al., 2005})$$

HOMO results of five polymers which were determined by Ultraviolet Photoemission Spectroscopy (UPS) are consistent with the DPV characterization. Furthermore, due to the image charge effect, UPS characterization generally reports lower HOMO levels compared to CV measurements. The UPS spectrum of the first five polymers is provided in Appendix B (Andrade et al., 2005). The UPS characterization of **P2FD2** will be obtained in the future.

2.6 Photovoltaic Characterizations

The main optimizations were performed using the P2F-based device, and other devices were constructed accordingly in light of these optimizations. The colored texts correspond to the best organic solar cell devices in the tables.

2.6.1 P2F-based Device

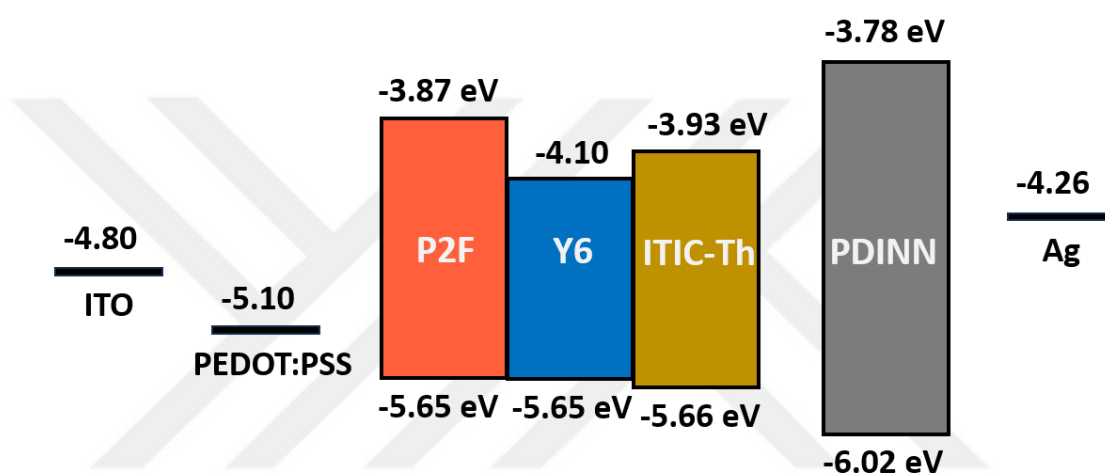


Figure 2.5. Energy level diagram of the P2F-based device

Table 2.8. Summary of the device performance of the P2F-based device

Polymer Blend	Solvent	D: A Ratio	Coating Rate	Additive	Ag Thickness (nm)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
P2F:Y6	CHCl ₃	1:1.2	2500	0.6% CN	100nm	0.79	16.16	45.24	5.65
P2F: ITIC-Th	CHCl ₃	1:1.3	3000	1% DIO	100nm	0.78	7.70	58.39	3.51
P2F:Y6	CHCl ₃	1:1.3	2500	1% CN	100nm	0.69	16.37	59.88	6.76
P2F:Y6	CHCl₃	1:1.3	3000	1% CN	100nm	0.70	17.23	62.51	7.54
P2F:Y6	CHCl ₃	1:1.3	2500	-	100nm	0.78	18.45	43.54	6.27

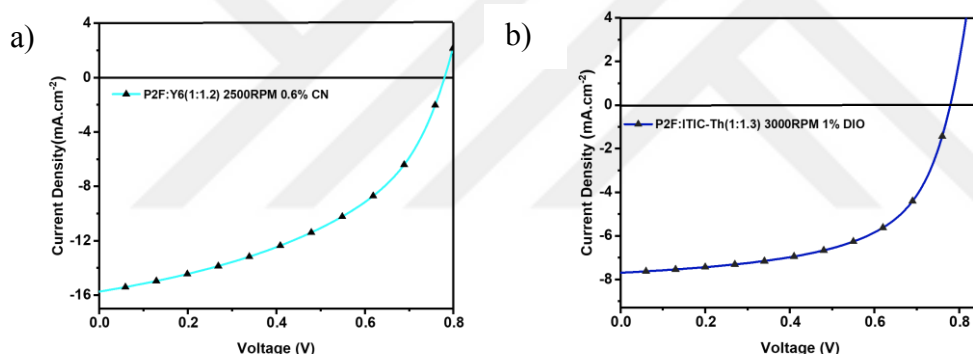


Figure 2.6. J-V characteristics of the a) P2F:Y6(1:1.2) with 0.6% CN and b) P2F:ITIC-Th (1:1.3) with 1% DIO

The **P2F: ITIC-Th** device exhibits the lowest J_{sc} value among all the optimizations, while its V_{oc} value remains relatively high. This is because the absorption band of ITIC-Th (500–800 nm) is similar to that of **P2F**, resulting in limited complementary absorption. In contrast, Y6 has a broader absorption range of 400–1000 nm, which complements the absorption of **P2F**, leading to enhanced light harvesting and a higher J_{sc} for the device compared to ITIC-Th (Mahadevan et al., 2024).

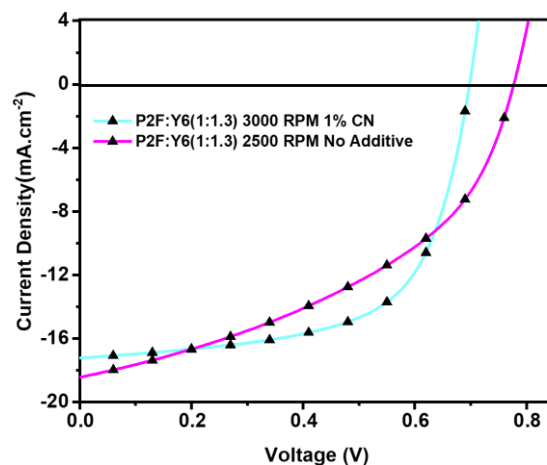


Figure 2.7. J-V characteristics of the P2F:Y6(1:1.3) with no additives and P2F:Y6(1:1.3) with 1% CN

Additives are selected based on the properties of the donor and acceptor materials. DIO is a commonly used additive with ITIC-Th, as it reduces π - π stacking while increasing the purity of the domains. Conversely, CN is widely used with Y6 non-fullerene acceptors, as it enhances π - π stacking and balances crystallization. However, both CN and DIO typically reduce V_{oc} by influencing crystallization and aggregation (Chen et al., 2024). The addition of 0.6% and 1% CN has shown a positive effect on the morphology of the device. When the Y6 ratio was increased from 1.2 to 1.3, the weight of the CN additive was also increased to further enhance the device morphology. The device with a 1:1.2 (D: A) ratio and 1% CN additive exhibits the highest FF value, benefiting from an increased η_{diss} due to its optimal morphology with well-defined phase separation and domain size that reduces recombination (F. Zhao et al., 2018). Additionally, the broad absorption spectrum of the Y6 enhances η_{abs} , contributing to improved device performance.

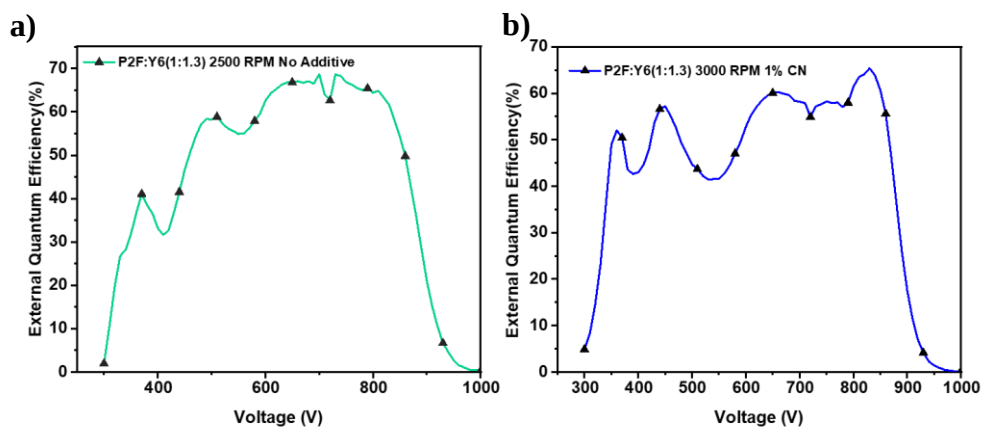


Figure 2.8. EQE spectra of the a) P2F:Y6(1:1.3) with no additives and b) P2F:Y6(1:1.3) with 1% CN

The external quantum efficiency (EQE) spectra of the **P2F: Y6** blend were measured to validate the J_{sc} values of the devices. The J_{sc} values obtained from the EQE curves were $19.30 \text{ mA} \cdot \text{cm}^{-2}$ for the no-additive device with a peak of 69% EQE at 740 nm and $17.67 \text{ mA} \cdot \text{cm}^{-2}$ for the 1% CN device with a peak of 65% EQE at 830 nm. The EQE curves closely paralleled the J_{sc} values calculated from the device measurements. The EQE graph of the device without additives shows a higher intensity around 650 nm. However, after the addition of 1% CN, the EQE in the near-UV and near-IR regions increases.

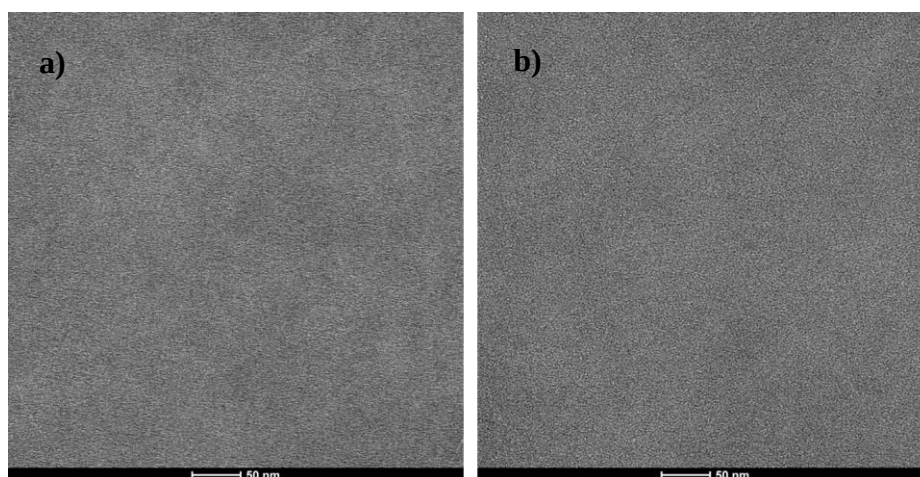


Figure 2.9. TEM images of the blend films based on a) P2F:Y6(1:1.3) with no additives and b) P2F:Y6(1:1.3) with 1% CN

Figure 2.9 exhibits the transmission electron microscopy (TEM) analysis of the **P2F:Y6** (1:1.3) blend with no additive and 1% CN, showing the sizes of 50 nm respectively. Electron-rich domains appear white, while electron-deficient materials appear dark in the TEM analysis. The surface morphology of both devices is similar and uniformly dispersed and distinct phase dissociation was not observed between the polymer donor and Y6 in either film (Lee et al., 2022). Furthermore, optimizes the phase separation and enhances charge dissociation by increasing the donor-acceptor interface and obtaining interpenetrating networks (Hoppe et al., 2006). Since the FF value is closely related to the active layer morphology, the higher FF value observed in both devices can be explained by the improved morphology of the active layer, as observed in the TEM results (F. Zhao et al., 2018).

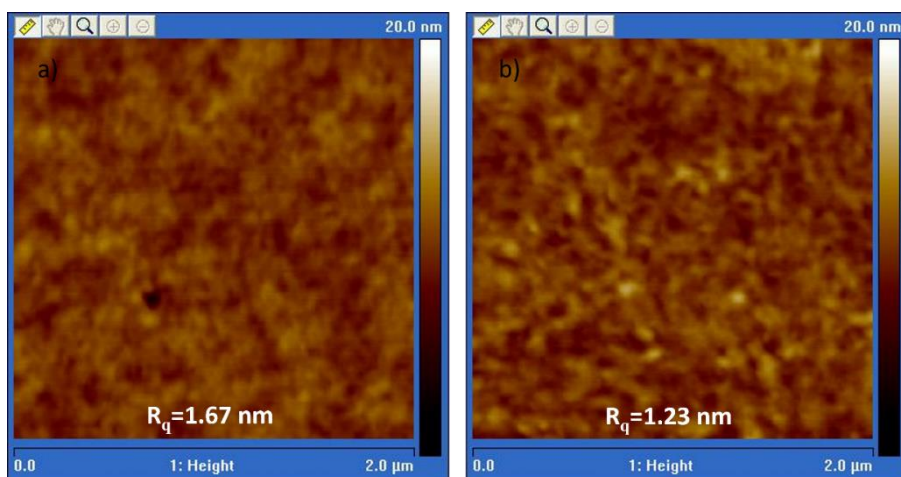


Figure 2.10. Tapping mode of AFM height images of the blend film of a) P2F: Y6(1:1.3) with no additives and b) P2F: Y6(1:1.3) with 1% CN, respectively

Figure 2.10 shows the atomic force microscopy (AFM) results of the **P2F: Y6** with no additive and 1% CN. Square surface roughness (R_q) of no additive is 1.67 nm when the R_q of the 1% CN-containing device is 1.23 nm with the thickness of 131.91 nm and 106.69 nm respectively. Thickness differences emerged from the changing coating rate that no additive-containing device coated at 2500 rpm and % 1 CN coated at 3000 rpm. The addition of CN smoothed the surface of the blend film, reducing the R_q from 1.67 nm to 1.23 nm, enhancing the packing of the active layer, and resulting in smaller aggregate sizes (Chen et al., 2024).

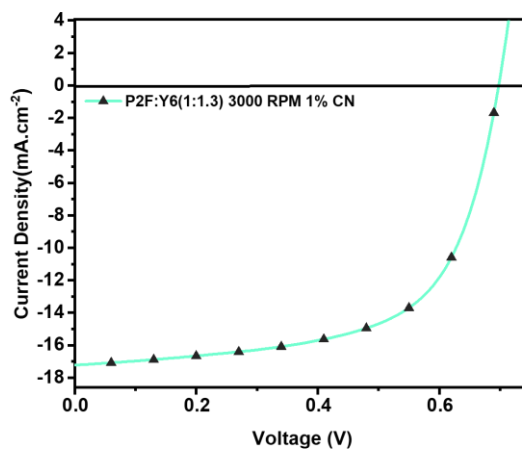


Figure 2.11. J-V characteristics of the best device P2F:Y6(1:1.3) with 1% CN

To summarize, **P2F: Y6** (1:1.3) with 1 % CN is the best device among the six donor polymers, with a 0.70 V V_{oc} , 17.23 mA/cm² J_{sc} , 62.51 % FF, and a 7.54 % PCE. (Figure 2.11) This performance is attributed to the good complementarity of the absorption spectra of Y6 and **P2F**, improved morphology with optimized domain size, and better alignment of the HOMO-LUMO energy levels between Y6 and **P2F**.

2.6.2 Comparison of P1F-based and P2F-based Device

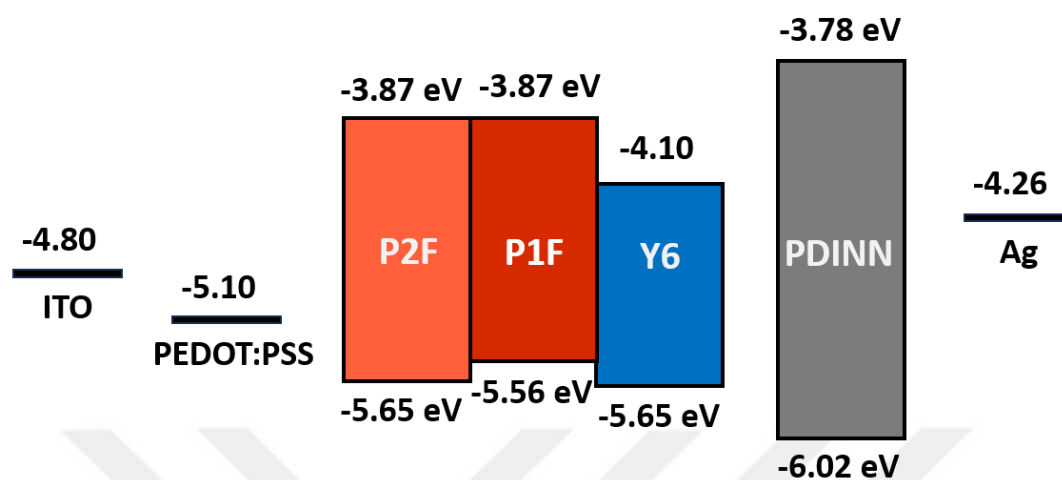


Figure 2.12. Energy level diagram of the P1F-based and P2F-based device

Table 2.9. Summary of the device performance of the P1F and P2F-based device

Polymer Blend	Solvent	D: A Ratio	Coating Rate	Additive	Ag Thickness (nm)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
P1F:Y6	CHCl ₃	1:1.2	2500	1% CN	100nm	0.66	12.11	41.81	3.34
P1F:Y6	CHCl ₃	1:1.2	3000	1% CN	100nm	0.66	12.39	45.38	3.71
P1F:Y6	CHCl ₃	1:1.3	2500	1% CN	100nm	0.65	10.68	41.68	2.89
P1F:Y6	CHCl ₃	1:1.3	3000	1% CN	100nm	0.66	9.50	40.53	2.54
P2F:Y6	CHCl ₃	1:1.3	3000	1% CN	100nm	0.70	17.23	62.51	7.54

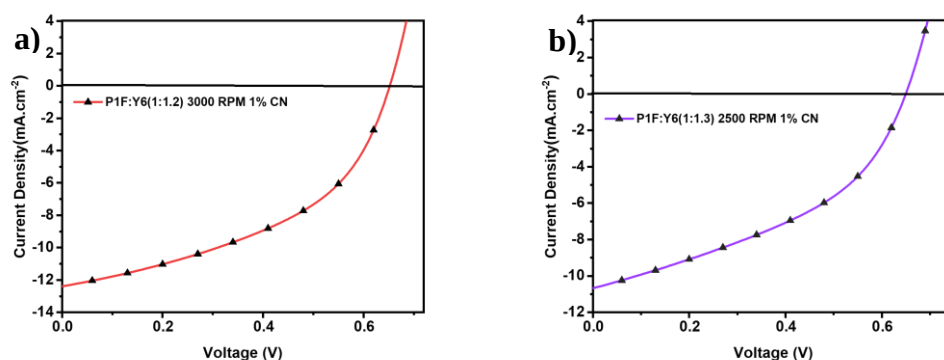


Figure 2.13. J-V characteristics of the a) P1F:Y6(1:1.2) and b) P1F:Y6(1:1.3) with 1%CN

Compared with the **P2F**-based device, cascade-like energy levels of the **P1F: Y6** device combined with the lower bandgap of the **P1F** with a very broad absorption spectrum make the **P1F**-based device a better candidate for enhancing the PCE of the OSC. However, the **P1F**-based device exhibits a lower V_{oc} and J_{sc} value than the **P2F**-based device with a %3.71 PCE. Lower V_{oc} and J_{sc} of the **P1F**-based device mainly result from the high-lying HOMO level of the polymer compare to **P2F**. Since FF represents the diode behavior of the device and is related to the charge transport and recombination processes in the active layer, fast charge transport and low charge recombination depend mainly on morphological properties. Therefore, a lower FF value can be mainly related to the morphology of the active layer (F. Zhao et al., 2018). Furthermore, in between the 2–40 kD Mw value, charge mobility is highly affected by the molecular weight. Low molecular weight can cause a lowering of the charge mobility of the device by the formation of disordered grain boundaries and traps due to the higher density of chain ends of the polymers. Therefore, the lower molecular weight of the **P1F** ($M_n=7736$ Da $M_w=10554$ Da) can also contribute to the lower PCE of the device (Wadsworth et al., 2018).

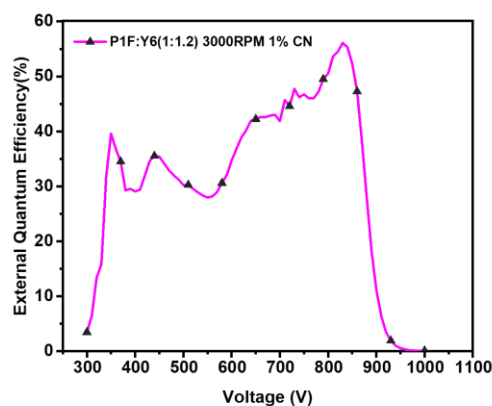


Figure 2.14. EQE spectra of the P1F:Y6(1:1.2) with 1% CN

Figure 2.14 depicts the EQE spectra of the P1F-based device, which shows a photoresponse across the 300-900 nm wavelength range, with a peak of 55% EQE at 860 nm, when the P2F-based device achieves 65% EQE at 830 nm. The integrated current density is 12.98 mA/cm², which closely matches the J-V readings. However, the EQE values in the 300-500 nm range are rather small compared to P2F-based devices even if P1F has a broader and intense absorption band than P2F in that region. Furthermore, improving light utilization in this region has the potential to boost the J_{sc} (Cui et al., 2021).

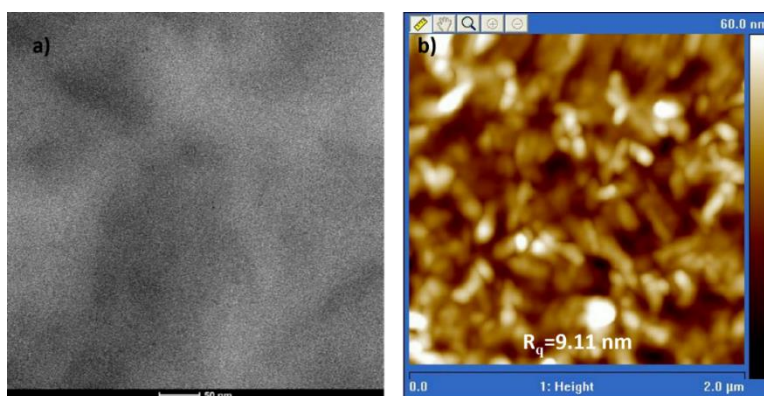


Figure 2.15. a) TEM and b) tapping mode AFM height images of the blend film of P1F: Y6 (1:1.2)

Figure 2.15.a exhibits the TEM analysis of the **P1F:Y6** (1:1.2) blend, showing the sizes of 50 nm. When large-scale phase separation with a continuous light phase embedded with discrete large-size dark domains is seen in the **P1F** film due to poor miscibility in between **P1F** and Y6 compared to the **P2F: Y6**. In the **P2F** film, processed with CN due to better miscibility, creating uniformly dispersed interpenetrating networks without distinct phase dissociation (Lee et al., 2022). A larger domain size of **P1F: Y6** may reduce charge dissociation by decreasing the donor-acceptor interface, leading to lower FF and PCE compared to **P2F: Y6**. Since the FF value is closely related to the active layer morphology, the lower FF value observed in the **P1F: Y6** device can be explained by the relatively poor morphology of the active layer compared to **P2F: Y6**, as observed in the TEM results (F. Zhao et al., 2018)(Hoppe et al., 2006). Figure 2.15.b shows the AFM results of the **P1F: Y6** blend with 1% CN. The R_q of the device is 9.11 nm, with a thickness of 113.30 nm. Both **P2F** (active layer thickness= 106.69 nm) and **P1F** blends have similar active layer thicknesses due to the use of a 3000 rpm coating rate. The root mean square surface roughness (R_q) of **P1F: Y6** is much higher compared to **P2F: Y6** ($R_q = 1.23$ nm), which also contributes to the lower FF value and overall poor PCE of the device.

2.6.3 Comparison of PCl-based and P2F-based Device

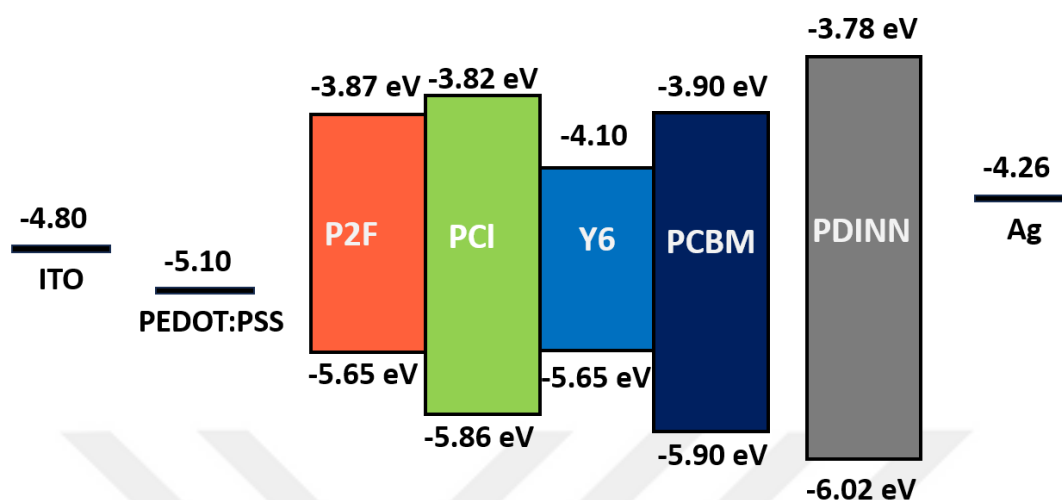


Figure 2.16. Energy level diagram of the PCl-based and P2F-based device

Table 2.10. Summary of the device performance of the PCl and P2F-based device

Polymer Blend	Solvent	D: A Ratio	Coating Rate	Additive	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
PCl: Y6	CHCl ₃	1:1.2	2500	1% CN	0.77	10.17	37.17	2.91
PCl: Y6	CHCl ₃	1:1.2	3000	1% CN	0.79	10.30	37.82	3.08
PCl: Y6: PC ₇₁ BM	CHCl ₃	1:1.2: 0.2	2500	1% CN	0.81	12.87	37.16	3.87
PCl: Y6: PC ₇₁ BM	CHCl ₃	1:1.2: 0.2	3000	1% CN	0.79	11.42	36.41	3.28
P2F: Y6	CHCl ₃	1:1.3	3000	1% CN	0.70	17.23	62.51	7.54

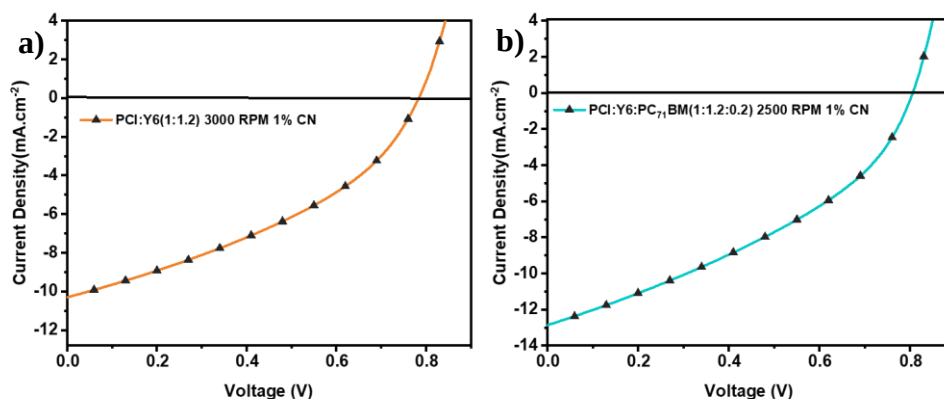


Figure 2.17. J-V characteristics of the a) PCI: Y6(1:1.2) and b) PCI: Y6:PC₇₁BM(1:1.2:0.2)

The **PCI: Y6** (1:1.2) device has lower V_{oc} and J_{sc} values due to the lower HOMO level of PCI compared to the HOMO level of Y6, which creates a blocking current further affects the device properties. Furthermore, this mismatch can lead to increased charge recombination and decreased effective charge transport, ultimately resulting in a low PCE. For efficient device performance, the energy levels of the materials need to be arranged in a cascade-like manner (Lee et al., 2022). The **PCI: Y6:PC₇₁BM** (1:1.2:0.2) device demonstrates higher V_{oc} , J_{sc} , and PCE (3.87%) due to a better alignment of the HOMO levels in the ternary blend of **PCI**, Y6, and PC₇₁BM, where PC₇₁BM has a lower HOMO level than **PCI**. The higher V_{oc} of the **PCI: Y6:PC₇₁BM** device compared to **P2F: Y6** results from a larger difference between the HOMO of the polymer and the LUMO of the acceptor. However, while this effect increases V_{oc} , it reduces the J_{sc} of the device. The lower J_{sc} value of the **PCI: Y6:PC₇₁BM** device is attributed to the higher bandgap of **PCI**. Additionally, the lower FF value of the **PCI: Y6:PC₇₁BM** device is attributed to low parameters and an unevenly dispersed surface morphology (F. Zhao et al., 2018). To summarize, lower V_{oc} , J_{sc} , and FF values contribute to the lower PCE of the **PCI: Y6:PC₇₁BM** device compared to **P2F: Y6**.

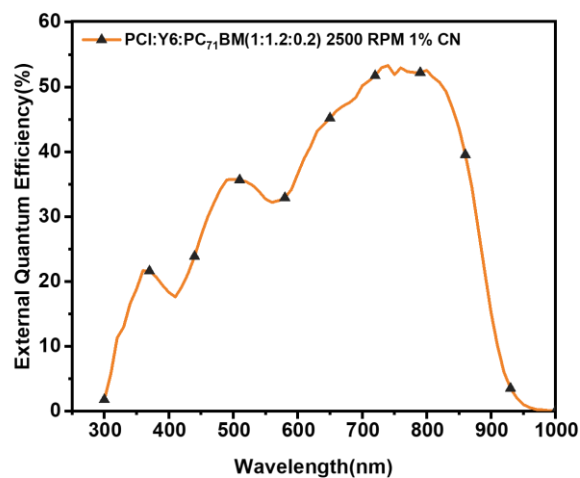


Figure 2.18. EQE spectra of the PCI: Y6:PC₇₁BM(1:1.2:0.2)

Figure 2.18. depicts the EQE spectra of the PCI-based device, which shows a photoresponse across the 300-1000 nm wavelength range, with a peak of 53% EQE at 745 nm, when the P2F-based device achieves 65% EQE at 830 nm. The integrated current density is 13.31 mA/cm², which closely matches the J-V readings.

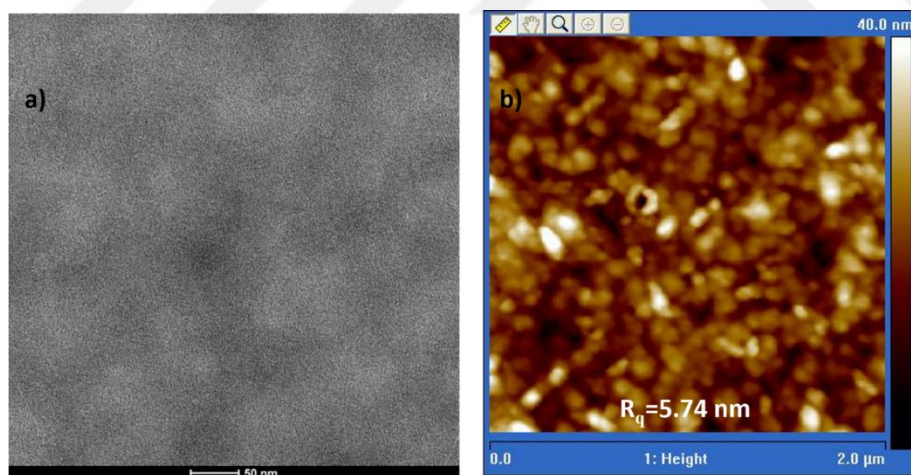


Figure 2.19. a) TEM and b) tapping mode AFM height images of the blend film of PCI: Y6:PC₇₁BM (1:1.2:0.2)

Figure 2.19. a. exhibits the TEM analysis of the **PCI: Y6:PC₇₁BM** (1:1.2:0.2) blend, showing the sizes of 50 nm. **PCI: Y6:PC₇₁BM** has a larger domain size and lower miscibility than **P2F: Y6** which can cause larger phase separation. Moreover, it can lead to a lower J_{sc} value due to reduced charge dissociation. On the other hand, in the **P2F** film, due to better miscibility between **P2F** and Y6, creating uniformly dispersed interpenetrating networks without distinct phase dissociation (Lee et al., 2022). The lower FF value observed in the **PCI: Y6:PC₇₁BM** device can be explained by the relatively poor surface morphology of the active layer compared to **P2F: Y6**, as observed in the TEM results (F. Zhao et al., 2018). Figure 2.17. b shows the AFM results of the **PCI: Y6: PC₇₁BM**. The R_q of the device is 5.74 nm, with a thickness of 171.14 nm. The AFM results confirm the TEM findings, showing an unevenly dispersed surface morphology (F. Zhao et al., 2018). The root mean square surface roughness (R_q) of **PCI: Y6:PC₇₁BM** is much higher compared to **P2F: Y6** ($R_q = 1.23$ nm), which also supports the lower FF value and overall poor PCE of the device.

2.6.4 Comparison of the P1FD2-based and P1F-based devices

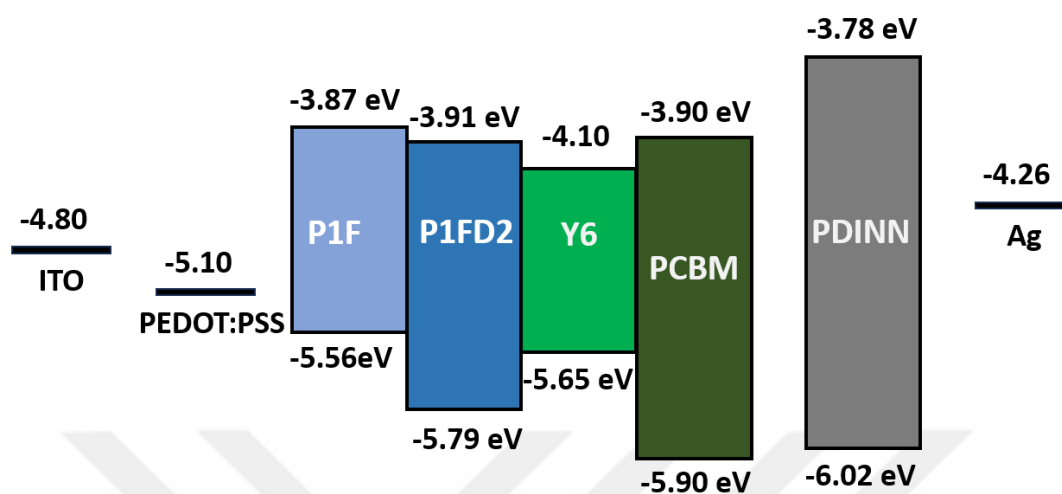


Figure 2.20. Energy level diagram of the P1FD2-based and P1F-based device

Table 2.11. Summary of the device performance of the P1FD2 and P1F-based device

Polymer Blend	Solvent	D: A Ratio	Coating Rate	Additive	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
P1FD2:								
Y6:	CHCl₃	1:1.2:	3000	1% CN	0.66	7.10	33.74	1.57
PC₇₁BM		0.1						
P1F:Y6	CHCl₃	1:1.2	3000	1% CN	0.66	12.39	45.38	3.71

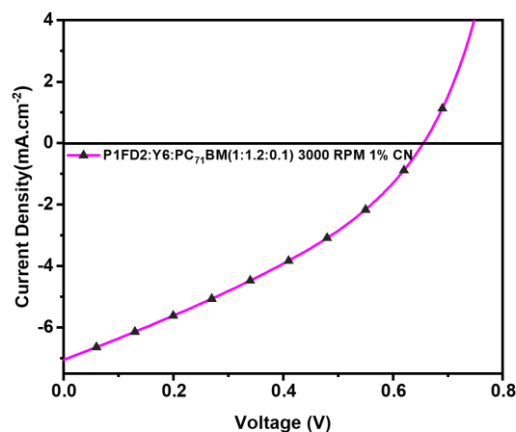


Figure 2.21. J-V characteristics of the P1FD2:Y6: P₇₁BM(1:1.2:0.1) with 1% CN

P1F and **P1FD2** have very similar HOMO energy levels; however, **P1FD2** exhibits a slightly lower HOMO level compared to **P1F** and Y6. To achieve cascade-like energy levels, **P1FD2** was blended with Y6 and PC₇₁BM. The V_{oc} of both devices is the same, despite the lower HOMO level of **P1FD2**. This could be attributed to the fact that the Y6 and PC₇₁BM blend (1.2:0.1) is insufficient to create cascade-like manner energy levels. Consequently, the blocking contact formed by the energy levels at the donor-acceptor interface leads to a lower V_{oc} for **P1FD2**. (Lee et al., 2022) However, the low miscibility of PC₇₁BM with the blend limits the amount of PC₇₁BM that can be added. **P1FD2** demonstrates a lower J_{sc} than **P1F**, which can be attributed to the higher bandgap of **P1FD2**, leading to reduced light absorption (H. Zhou et al., 2012). Additionally, the low J_{sc} and V_{oc} , combined with the low solubility of the polymer and poor miscibility within the blend, contribute to a reduced FF. This results in defects in the active layer's surface morphology and the active layer had poor film making quality, which is visibly noticeable (F. Zhao et al., 2018). Device optimizations will continue to improve the morphology and increase the PCE.

2.6.5 Comparison of the P2FD2-based and P2F-based devices

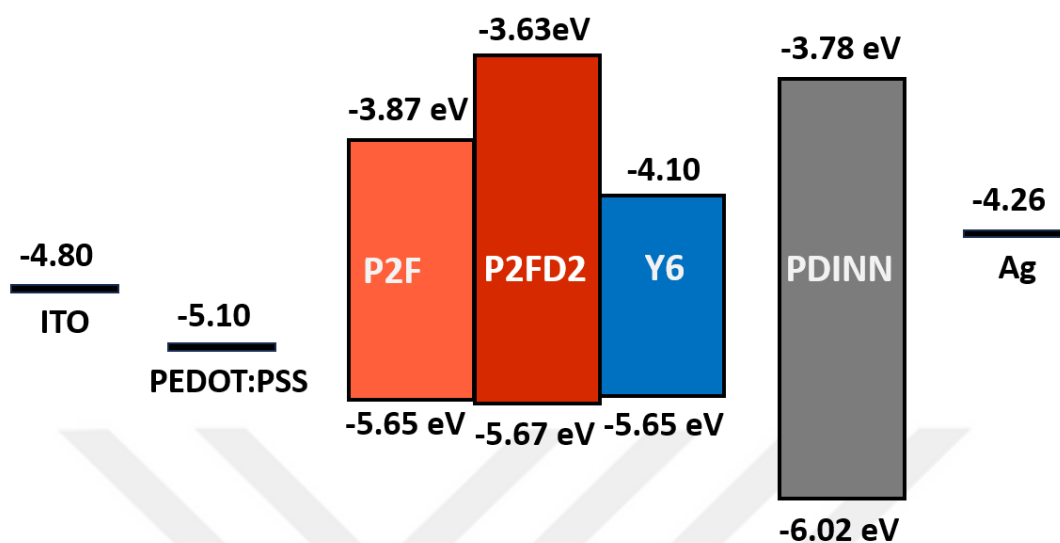


Figure 2.22. Energy level diagram of the P2FD2-based and P2F-based device

Table 2.12. Summary of the device performance of the P2FD2 and P2F-based device

Polymer Blend	Solvent	D: A Ratio	Coating Rate	Additive	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
P2FD2:Y6	CHCl₃	1:1.2	3000	1% CN	0.84	8.36	33.65	2.36
Literature								
PBDTCIT-TQxT: ITIC	CB	1:1		1% DIO	0.94	14.61	0.60	8.22
P2F:Y6	CHCl₃	1:1.3	3000	1% CN	0.70	17.23	62.51	7.54

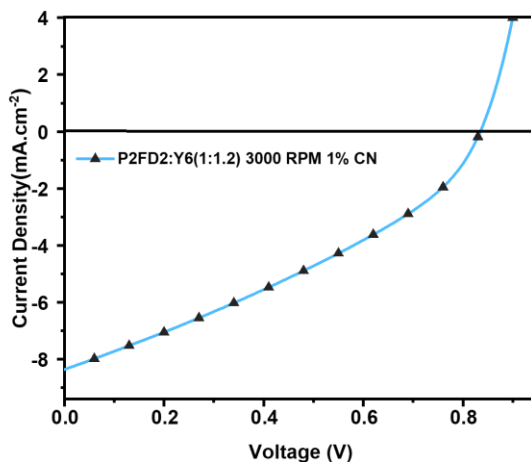


Figure 2.23. J-V characteristics of the P2FD2:Y6(1:1.2) with 1% CN

The **P2FD2:Y6** device exhibits a higher open-circuit voltage (V_{oc}) compared to the **P2F:Y6** device, even though **P2F** and **P2FD2:Y6** have very similar HOMO values. This can be attributed to the larger difference (0.47 eV) between the LUMO of **P2FD2** and **Y6**, which facilitates easier charge dissociation and reduces energy loss (Y. Yan et al., 2022)(Azzouzi et al., 2019). On the other hand, the higher bandgap of **P2FD2** results in a lower J_{sc} . The very high molecular weight of **P2FD2** ($M_n = 85955$ Da $M_w = 169104$ Da) may be responsible for the lower FF value of the device, as the longer chain lengths of the polymers can exhibit reduced packing ability due to chain entanglement (Wadsworth et al., 2018). When compared to **PBDTCIT-TQxT:ITIC**, which differs from **P2FD2** in the incorporation of a thiophene π -bridge and fewer alkoxy groups on the quinoxaline, **PBDTCIT-TQxT** has higher HOMO and LUMO levels and a lower bandgap than **P2FD2**. The higher V_{oc} of the **PBDTCIT-TQxT:ITIC** device arises from the cascade-like energy level alignment, compared to the **P2FD2:Y6** device, where the HOMO levels of the donor and acceptor are very close. The higher J_{sc} value of the **PBDTCIT-TQxT:ITIC** device results from the lower bandgap of **PBDTCIT-TQxT** compared to **P2FD2** (Lenaerts et al., 2020). In

summary, the mismatch in energy levels between the donor and acceptor, along with the higher bandgap of **P2FD2**, likely contributed to its lower PCE compared to the literature counterpart. A ternary blend with PC₇₁BM will be constructed in future work, which could be useful for optimizing the energy levels of the device and improving the PCE.

2.6.6 Comparison of the PCID2-based and PCI-based devices

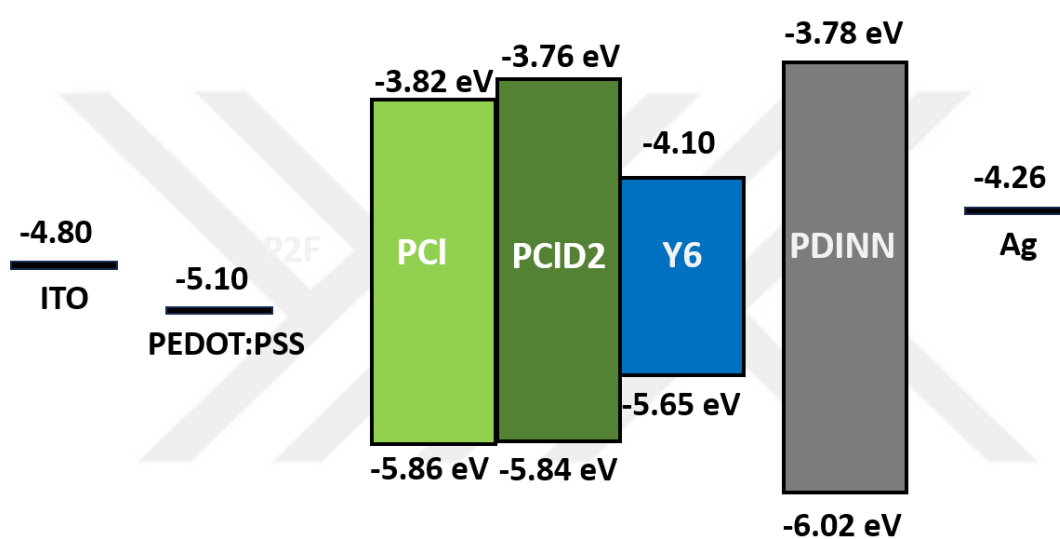


Figure 2.24. Energy level diagram of the PCID2-based and PCI-based device

Table 2.13. Summary of the device performance of the PCID2 and PCI-based device

Polymer Blend	Solvent	D: A Ratio	Coating Rate	Additive	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
P2CID2: Y6	CHCl₃	1:1.2	2500	1% CN	0.69	6.63	35.39	1.62
P2CID2: Y6	CHCl ₃	1:1.2	3000	1% CN	0.72	6.16	34.35	1.52
Literature PBCl-Qx: Y6	CHCl ₃	1:1	2000	1% DIO	0.76	26.32	62.1	12.44
PCI: Y6	CHCl₃	1:1.2	3000	1% CN	0.79	10.30	37.82	3.08

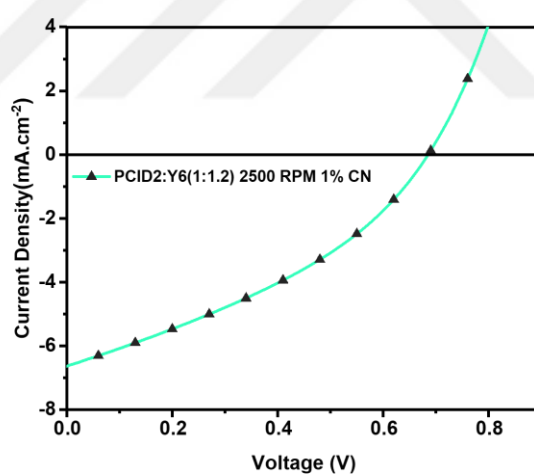


Figure 2.25. J-V characteristics of the PCID2:Y6(1:1.2) with 1% CN

PCID2:Y6 was compared with **PCI: Y6** rather than the best-performing **PCI**-based device, **PCI: Y6:PC₇₁BM**, for a more direct comparison. **P2CID2:Y6** exhibited a

lower V_{oc} than **PCI: Y6**, despite their very similar HOMO levels. This may be attributed to the higher molecular weight of **P2CID2** ($M_n = 46.115$ Da, $M_w = 84.937$ Da). To provide a clearer explanation, high molecular weight exceeding 40 kDa can disrupt the morphology, leading to higher bimolecular recombination losses and reduced charge mobility, which negatively impacts both the V_{oc} and the FF of **P2CID2:Y6** (Azzouzi et al., 2019; Wadsworth et al., 2018). The lower J_{sc} of **P2CID2:Y6** is attributed to the higher bandgap of **P2CID2** compared to **PCI**. These combined effects result in the overall lower efficiency of **P2CID2:Y6** relative to **PCI: Y6**. **PCI: Y6** can also be compared to its literature counterpart (**PBCI-Qx: Y6**), where **PBCI-Qx** shares a similar structure with **P2CID2**, differing in its thiophene side chain on the quinoxaline and its thiophene π -bridge (Lee et al., 2022). Moreover, **PBCI-Qx** has higher HOMO and LUMO levels compared to **P2CID2**, which are better matched with **Y6** and the poor energy level matching of **P2CID2** is responsible for the significant V_{oc} differences between the two devices. Despite the fact that **PBCI-Qx** has a higher electronic bandgap, higher HOMO and LUMO levels, and a similar absorption spectrum compared to **P2CID2**, **P2CID2** shows a lower J_{sc} . This may also result from the poor energy level alignment in **P2CID2:Y6**, making it more prone to bimolecular recombination and reducing the J_{sc} . A ternary blend with PC₇₁BM will be constructed for future work, which could be useful for improving the energy level alignment in the device and consequently can result in higher efficiency.

2.6.7 Summary of the Six Devices

The **P2F**-based device exhibited the highest PCE of 7.54 % among the six devices due to its better surface morphology and good alignment with the energy levels of **Y6**. The **PCI**-based device had the second-highest PCE value, at 3.87%, resulting from the better surface morphology of the blend and a higher V_{oc} than the **P1F**-based

device. The outcome can be attributed to the good miscibility of the blend and the lower HOMO of **PCI**, respectively. **P1F** exhibited the lowest PCE among the **D1**-containing polymers, with a value of 3.71%, due to its lower V_{oc} , which is caused by its higher HOMO, and its relatively poor surface morphology compared to the first three polymers. A similar PCE trend was observed for the **D2**-containing polymers. **P2FD2** had the highest PCE at 2.36%, followed by **PCID2** at 1.62%, and **P1FD2** with the lowest PCE at 1.57%. Parallel to the first polymers set, **P2FD2** achieved the highest device parameters due to better energy level alignment with Y6. Additionally, **PCID2** exhibited a higher V_{oc} than **P1FD2**, which can be ascribed to its lower HOMO level, potentially contributing to the higher PCE of the device. Furthermore, **D2**-containing polymers showed lower PCE values than their **D1** counterparts despite similar V_{oc} values. This effect can be attributed to the higher bandgap and lower planarity of the polymers, which reduce light absorption and decrease the J_{sc} .



CHAPTER 3

EXPERIMENTAL

3.1 Materials

Chemicals were supplied by Merck, Tokyo Chemical Industry (TCI), and Solarmer. Unless otherwise specified, all reactions were performed under a nitrogen atmosphere. A solvent drying system (Mbraun MBSPS5) was used to obtain dry solvents. Triethylamine is distilled using calcium hydride as a drying agent. Four-inch molecular sieves were also immersed in liquids to absorb moisture and humidity. Silica gel 60 (230–400 mesh) from Merck was used as the stationary phase for column chromatography, and commercial 0.25 mm silica gel plates (TLC Merck Silica Gel 60) were used for thin-layer chromatography.

3.2 Methods and Instruments

The ^{13}C and ^1H NMR spectra were determined by using a Bruker Spectrospin Avance DPX-400 MHz spectrometer. Trimethylsilane (TMS) served as the internal standard, and chemical shifts are indicated in parts per million (ppm). Deuterated solvents, CDCl_3 were used for the ^1H and ^{13}C NMR analyses. The molecular weight distribution of the produced polymers was determined by gel permeation chromatography (Shimadzu-20A) using polystyrene as an external standard. Solutions were prepared by using chloroform. Thermal analysis of the polymers was performed using a thermogravimetric analyzer (Pyris 1 TGA). Electrochemical characterizations were performed by using differential pulse voltammetry (DPV) with a Gamry 600 Potentiostat. Optical characterizations were performed using a

Varian Carry 5000 model spectrometer with UV-Vis spectroscopy. Photovoltaic characterizations were conducted using Keithley 2400 under 1.5 G illumination and 100 mW cm⁻².

3.3 Synthesis of Monomers

3.3.1 Synthesis of Molecule 2 (1,2-bis(octyloxy)benzene)

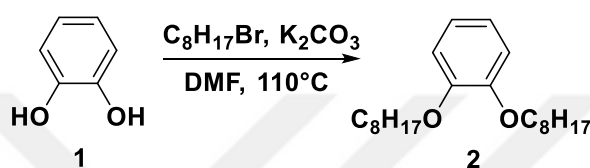


Figure 3.1. Synthetic route of molecule 2

2.00 g catechol (**molecule 1**) (18.16 mmol), 10.04 g K_2CO_3 (72.65 mmol), and 60 mL dry dimethylformamide (DMF) were added to a 250 mL two-mouth reaction flask. The mixture was heated to 60°C and stirred at this temperature for 30 minutes. Then, 12.28 g (63.57 mmol) $\text{C}_8\text{H}_{17}\text{Br}$ was added to the mixture, and the temperature was increased to 110°C and the reaction continued under N_2 gas. After 3 days, the reaction was terminated under the thin-layer chromatography (TLC) control. The solid remaining in the reaction was filtered with filter paper. The DMF solvent in the resulting filtrate was evaporated under reduced pressure and the remaining materials were extracted 3 times using dichloromethane (DCM) and brine. In the next stage, the organic phase was dried with sodium sulfate (Na_2SO_4) and filtered. The filtered organic phase was evaporated under reduced pressure. The resulting crude product was purified using column chromatography (silica, hexane) to obtain **molecule 2** as a colorless liquid. (5.52 g, 90.8% yield). ^1H NMR (400 MHz, CDCl_3) δ 6.87 (m, 4H), 4.05 – 3.90 (m, 4H), 1.87 – 1.74 (m, 4H), 1.45 (m, 4H), 1.36 – 1.24 (m, 16H), 0.98

– 0.72 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 149.2, 121.0, 114.0, 69.3, 31.86, 29.4, 29.4, 29.3, 26.1, 22.7, 14.1.

3.3.2 Synthesis of Molecule 3 (1,2-bis(3,4-bis(octyloxy)phenyl)ethane-1,2-dione)

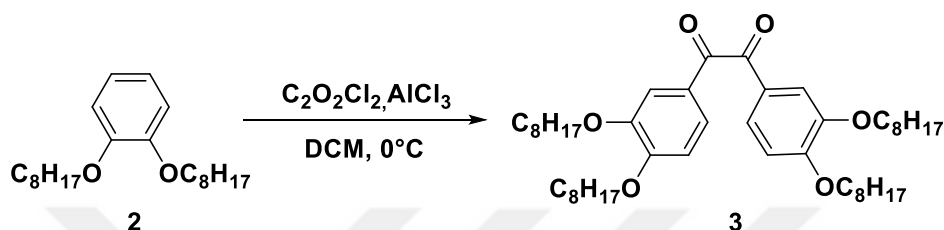


Figure 3.2. Synthetic route of molecule 3

5.95 g of **molecule 2** (17.79 mmol) was added to a 250 mL two-mouth reaction flask. It was exposed to the vacuum to remove air and moisture for 10 minutes. Under N_2 gas, 1.35 g (10.74 mmol) AlCl_3 and 10 mL DCM were mixed in the reaction flask and brought to 0 °C in an ice bath. 10 mL DCM and 0.930 mL (10.85 mmol) oxalyl chloride ($\text{C}_2\text{O}_2\text{Cl}_2$) were mixed and added to the reaction dropwise. After 1 hour, the reaction was taken to room temperature to continue for 18 hours. At the end of 18 hours, the reaction was terminated under TLC control. The reaction was poured into 1 M HCl solution and stirred for 1 hour. DCM and distilled water were used to extract the mixture three times. The organic phase was then filtered and dried using Na_2SO_4 . Reduced pressure was used to evaporate the filtered organic phase. After crystallizing with ethanol, **molecule 3** was obtained as a pure white solid. (3.12 g, 48.5% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.56 (s, 2H), 7.42 (d, J = 8.5 Hz, 2H), 6.84 (d, J = 8.5 Hz, 2H), 4.05 (m, 8H), 1.84 (m, 8H), 1.53 – 1.43 (m, 8H), 1.43 – 1.16 (m, 32H), 0.89 (m, 12H). ^{13}C NMR (100 MHz, CDCl_3) δ (100 MHz, CDCl_3) δ 192.1, 153.2, 147.6, 124.4, 110.5, 109.8, 67.4, 30.01, 27.6, 27.12, 24.3, 21.0, 12.4.

3.3.3 Synthesis of Molecule 7 (4-fluorobenzene-1,2-diamine)

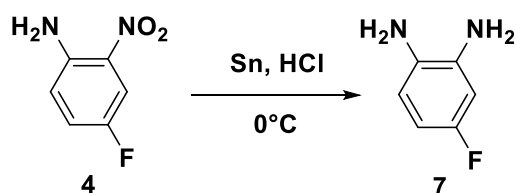


Figure 3.3. Synthetic route of molecule 7

2.00 g of 4-fluoro-2-nitroaniline (**molecule 4**) (11.49 mmol) and 60 mL 37% HCl were added to the 250 mL flask accompanied by N₂ gas. After waiting for the reactant to dissolve in HCl, it was brought to 0 °C in an ice bath. 6.60 g (55.60 mmol) tin (Sn) was added to the reaction in 3 portions for 20 minutes. After the reaction was stirred for 3 hours at 0 °C, air was released with a syringe and kept in the freezer overnight. The pH value of the product was increased to 10 by adding 8 M NaOH solution. The mixture was extracted three times using ethyl acetate and water. The organic phase was dried using Na₂SO₄, filtrated to separate from Na₂SO₄, and evaporated under low pressure. **Molecule 7**, 1.62 g of white solid, was obtained. (1.62g, 75.0% yield). Since amine groups are extremely sensitive to moisture and oxygen in the air, the material was used directly in the next reaction without further purification.

3.3.4 Synthesis of Molecule 8 (4,5-difluorobenzene-1,2-diamine)

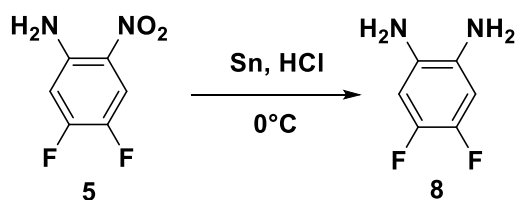


Figure 3.4. Synthetic route of molecule 8

2.00 g of 4,5-difluoro-2-nitroaniline (**molecule 5**) (11.49 mmol) and 60 mL 37% HCl were placed in a 250 mL reaction flask under N₂ gas. After the reactant dissolved, the flask was placed in an ice bath and brought to 0 °C. 6.60 g (55.60 mmol) Sn was added to the reaction in 3 portions over 20 minutes. After the reaction was stirred for 3 hours at 0 °C, the air was released with a syringe and kept in the freezer overnight. The pH of the product was increased to 10 by adding 8 M NaOH solution. The resulting mixture was extracted three times using ethyl acetate and water. The organic phase was dried using Na₂SO₄ and filtrated to separate from Na₂SO₄. The organic phase was evaporated under low pressure. **Molecule 8**, a white solid, was obtained. (1.44g, 86.7% yield) Since amine groups are extremely sensitive to moisture and oxygen in the air, the material was used directly in the next reaction without further purification.

3.3.5 Synthesis of Molecule 9 (4,5-dichlorobenzene-1,2-diamine)

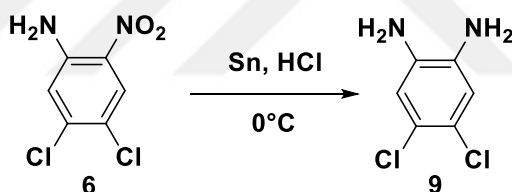


Figure 3.5. Synthetic route of molecule 9

1.00 g of 4,5-dichloro-2-nitroaniline (**molecule 6**) (11.49 mmol) and 60 mL 37% HCl were added to the 250 mL flask accompanied by N₂ gas. As a result of the dissolution of the reactant, the reaction flask was brought to 0°C in the ice bath. 2.78 g (23.38 mmol) Sn was added to the reaction in 3 portions, lasting 20 minutes. After the reaction was stirred for 3 hours at 0 °C, air was released with a syringe and kept in the freezer overnight. The pH of the mixture was increased to 10 by adding 8 M NaOH solution. The mixture was extracted three times using ethyl acetate and water.

The organic phase was dried using Na₂SO₄ and filtrated to separate from Na₂SO₄. The organic phase was evaporated under low pressure. **Molecule 9** was obtained as a white solid. (845 mg, 98.8% yield). Since amine groups are extremely sensitive to moisture and oxygen in the air, the material was used directly in the next reaction without further purification.

3.3.6 Synthesis of Molecule 10 (5-fluorobenzo[c][1,2,5]thiadiazole)

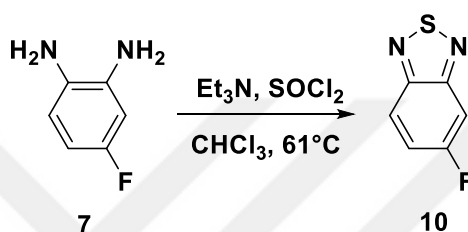


Figure 3.6. Synthetic route of molecule 10

1.62 g of **molecule 7** (9.99 mmol) was placed in a 100 mL schlenk tube and after vacuuming for 5 minutes, 25 mL of dry chloroform was added under N₂ gas. Then, 5.31 mL of dry triethylamine (38.08 mmol) was added to the reaction medium. After molecule 7 was dissolved in the resulting mixture, the reaction tube was brought to 0 °C in an ice bath and 1.39 mL of SOCl₂ (19.04 mmol) was added dropwise to the reaction medium. Afterwards, the reaction was refluxed for 1 day at 61 °C. The next day, after observing that the reaction was completed by TLC control, the mixture was extracted with chloroform. After washing the organic phase with water 3 times, it was dried using Na₂SO₄, and the organic phase was separated by filtration, and an orange solid was obtained by evaporating the solvents under reduced pressure. The resulting orange solid was purified using column chromatography (silica, hexane: DCM – 1:3) to obtain an orange solid (**molecule 10**). (1.47 g, 65.9% yield) Since the material sublimated at room temperature, it was quickly used in the next reaction.

3.3.7 Synthesis of Molecule 11 (5,6-difluorobenzo[c][1,2,5]thiadiazole)

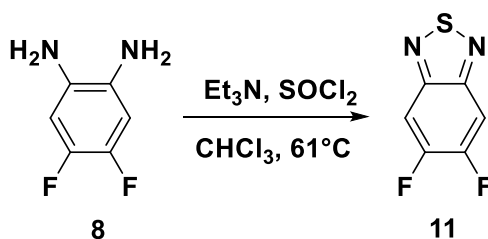


Figure 3.7. Synthetic route of molecule 11

1.44 g of **molecule 8** (9.99 mmol) was added to a 100 mL schlenk tube and vacuumed for 5 minutes. Then, 25 mL of dry chloroform was added to the schlenk tube using N₂ gas. Then, 5.57 mL of dry triethylamine (39.97 mmol) was added to the reaction medium. After dissolution was observed, the reaction tube was brought to 0°C in an ice bath and 1.46 mL of SOCl₂ (19.98 mmol) was added dropwise to the reaction. Afterwards, the reaction was refluxed for 1 day at 61 °C. The next day, after observing that the reaction was completed by TLC control, the mixture was extracted with chloroform. After washing the organic phase with water 3 times, it was dried with Na₂SO₄ and the organic phase, separated by filtration, was evaporated under reduced pressure to obtain an orange solid. The resulting orange solid was purified using column chromatography (silica, hexane: DCM – 1:3) to obtain an orange solid (**molecule 11**). (1.32 g, 76.7% yield) Since the material sublimated at room temperature, it was quickly used in the next reaction.

3.3.8 Synthesis of Molecule 12 (5,6-dichlorobenzo[c][1,2,5]thiadiazole)

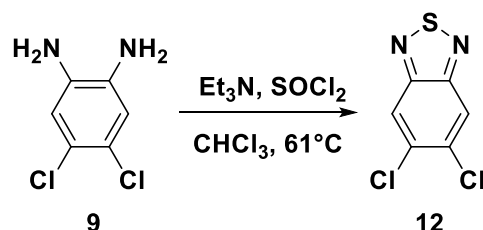


Figure 3.8. Synthetic route of molecule 12

845 mg of **molecule 9** (4.77 mmol) was placed in a 100 mL schlenk tube and after applying a vacuum for 5 minutes, 25 mL of dry chloroform was added under N₂ gas. Then, 2.18 mL of dry triethylamine (15.61 mmol) was added to the reaction medium. After dissolution, the schlenk tube was brought to 0 °C using an ice bath, and 0.568 mL of SOCl₂ (7.78 mmol) was added dropwise to the reaction medium. Then, Afterwards, the reaction was refluxed for 1 day at 61 °C. The next day, the completion of the reaction was observed by TLC control, and the mixture was extracted using chloroform. After washing the organic phase with water 3 times, it was dried by adding Na₂SO₄ and filtrated to separate from Na₂SO₄. The organic phase was evaporated under reduced pressure to obtain an orange solid. The resulting orange solid was purified with the help of column chromatography (silica, hexane: DCM – 1:3), and an orange solid (**molecule 12**) was obtained. (665 mg, 67.9% yield). Because the material sublimated at room temperature, it was quickly used in the next reaction.

3.3.9 Synthesis of Molecule 13 (4,7-dibromo-5-fluorobenzo[c][1,2,5]thiadiazole)

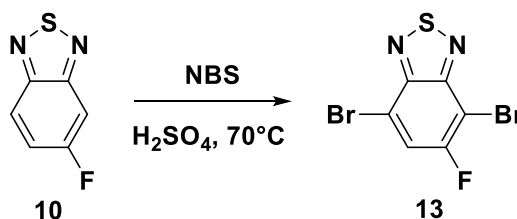


Figure 3.9. Synthetic route of molecule 13

1.47 g of **molecule 10** (7.67 mmol), 6.05 g of n-bromo succinimide (NBS) (33.96 mmol), and 30 mL of sulfuric acid (H₂SO₄) were added to a 250 mL 2-necked reaction flask and connected to a reflux condenser. NBS was preferred instead of Br₂ for the bromination to avoid the toxicity associated with Br₂ and the reaction was performed in acidic media to increase the electrophilicity of the Br in NBS. Then, the reaction was continued overnight by bringing the ambient temperature to 70°C and the reaction was terminated after TLC control. Then, the mixture in the reaction flask was added to a 400 mL ice-filled beaker and stirred at room temperature until the ice melted, then washed with cold water and filtered. The resulting solid was crystallized using methanol and a white solid (**molecule 13**) was obtained. (1.31 g, 52.4% yield) ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, J = 8.3 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 160.4, 157.8, 149.3, 126.3, 123.0, 112.9. (97.3 fluorine signal)

3.3.10 Synthesis of Molecule 14 (4,7-dibromo-5,6-difluorobenzo[c][1,2,5]thiadiazole)

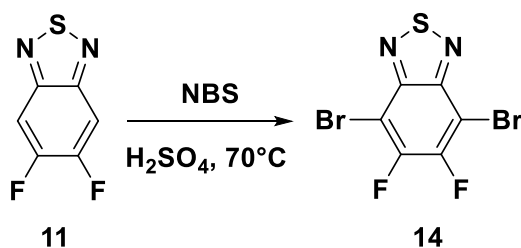


Figure 3.10. Synthetic route of molecule 14

1.32 g of **molecule 11** (7.67 mmol), 5.46 g of NBS (30.67 mmol), and 30 mL of H₂SO₄ were placed in a 250 mL 2-necked reaction flask and connected to the reflux condenser. NBS was preferred instead of Br₂ for the bromination to avoid the toxicity associated with Br₂ and the reaction was performed in acidic media to increase the electrophilicity of the Br in NBS. The reaction was continued overnight by bringing the ambient temperature to 70°C and the reaction was terminated by TLC control. Then, the reaction was poured into a beaker filled with ice up to 400 mL and stirred at room temperature until the ice melted, then washed with cold water and filtered. The resulting solid was crystallized with methanol and a white solid (**molecule 14**) was obtained. (1.50 g, 59.3% yield) ¹H (400 MHz, CDCl₃) δ ¹³C NMR (100 MHz, CDCl₃) δ 150.7, 148.3, 146.6. (97.1 fluorine signal)

3.3.11 Synthesis of Molecule 15 (4,7-dibromo-5,6-dichlorobenzo[c][1,2,5]thiadiazole)

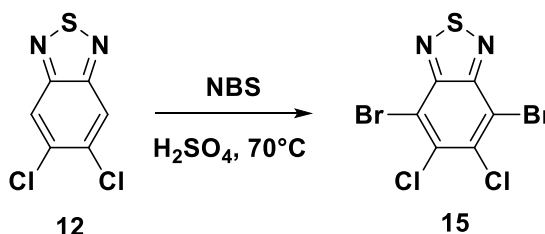


Figure 3.11. Synthetic route of molecule 15

665 mg **molecule 12** (3.24 mmol), 2.31 g NBS (12.97 mmol), and 40 mL H₂SO₄ were added to a 250 mL, 2-necked reaction flask and connected to a reflux condenser. NBS was preferred instead of Br₂ for the bromination to avoid the toxicity associated with Br₂ and the reaction was performed in acidic media to increase the electrophilicity of the Br in NBS. The temperature was brought to 70°C and the reaction was continued for 1 day and terminated after TLC control. Then, the mixture in the reaction flask was added to a beaker filled with 400 mL ice and stirred at room temperature until the ice melted, then washed with cold water and filtered. The resulting solid was crystallized with the help of methanol and a white solid (**molecule 15**) was obtained. (1.00 g, 84.7% yield) ¹H (400 MHz, CDCl₃) δ ¹³C NMR (100 MHz, CDCl₃) δ 151.2, 136.2, 114.8.

3.3.12 Synthesis of Molecules 19, 20 and 21

3.3.12.1 First Trial

The **molecules 13, 14, and 15** and the required amount of zinc (Zn) were placed into a 100 mL schlenk tube and dissolved with 25 mL of acetic acid under N₂ atmosphere. After 1 day at 80°C, the reaction was filtered to separate the zinc from the media.

Then, filtered organic solution which contained reduced organic product and acetic acid was placed in a 100 mL schlenk tube without any purification and 15 mL of acetic acid was added. Then, **molecule 3** was added to the media and the reaction was heated to 80°C for another 24 hours. The reaction was terminated the next day and extraction was performed with chloroform. Then, the solvents in the filtered organic phase were evaporated under reduced pressure to obtain a yellow solid. The obtained yellow solid was purified in 2 steps using column chromatography (silica, hexane: EtOAc – 25:1), (silica, hexane: DCM – 5:1), and a yellow solid was obtained. With the synthesis route in the first attempt, 60.8%, 55.6%, and 65.3% yields were obtained for **molecule 19**, **molecule 20**, and **molecule 21**, respectively. To increase these efficiencies and reduce the material cost, it was decided to apply a second attempt. Thus, the new efficiencies were successfully increased to 70.2% for **molecule 19**, 91.3% for **molecule 20**, and 80.1% for **molecule 21**.

3.3.12.2 Second Trial

3.3.12.2.1 Synthesis of Molecule 16 (3,6-dibromo-4-fluorobenzene-1,2-diamine)

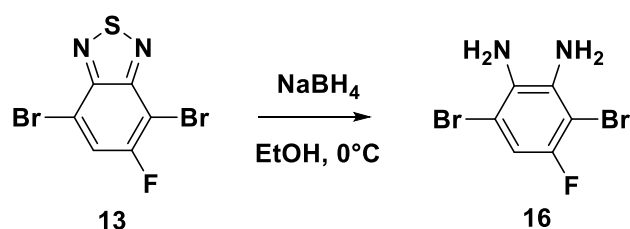


Figure 3.12. Synthetic route of molecule 16

500 mg of **molecule 13** (1.60 mmol) was placed in a 250 mL double-necked flask and after vacuuming for 15 minutes, 50 mL of ethanol was added under nitrogen atmosphere. After the temperature was brought to 0 °C, 2.32 g of NaBH₄ (61.28

mmol) was added to the reaction flask and the reaction was continued for one day. The next day, after TLC control, the reaction was terminated and extraction was performed with diethyl ether. The organic phase was washed with water 3 times and dried using Na₂SO₄ and the solvents in the organic phase separated by filtration were evaporated under vacuum to obtain a white solid, **molecule 16** (458 mg, 91.6% yield). Since amine groups are extremely sensitive to moisture and oxygen in the air, the material was used directly in the next reaction without further purification.

3.3.12.2.2 Synthesis of Molecule 17 83,6-dibromo-4,5-difluorobenzene-1,2-diamine)

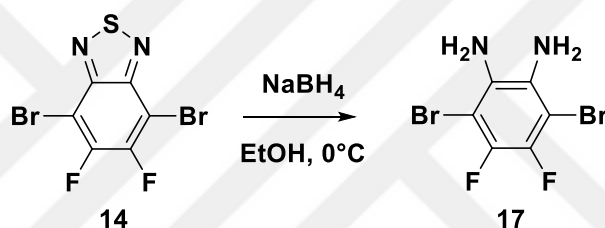


Figure 3.13. Synthetic route of molecule 17

300 mg of **molecule 14** (909.24 μ mol) was placed in a 250 mL two-necked reaction flask and after applying vacuum for 15 minutes, 50 mL of ethanol was added under the nitrogen atmosphere. The temperature was brought to 0 °C with an ice bath and 1.32 g of NaBH₄ (34.76 mmol) was added to the reaction flask and the reaction was continued for one day. The next day, the reaction was terminated by TLC control, and extraction was performed with diethyl ether. The organic phase was washed 3 times with water and dried with Na₂SO₄ and the organic phase separated by filtration was evaporated under reduced pressure to obtain a white solid, **molecule 17**. (252 mg, 91.3% yield) Since amine groups are extremely sensitive to moisture and oxygen in the air, the material was used directly in the next reaction without further purification.

3.3.12.2.3 Synthesis of Molecule 18 (3,6-dibromo-4,5-dichlorobenzene-1,2-diamine)

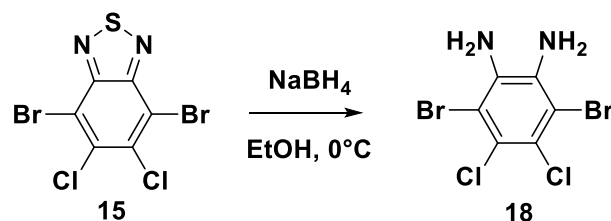


Figure 3.14. Synthetic route of molecule 18

471 mg of **molecule 15** (1.3 mmol) was placed in a 250 mL double-mouthed flask and after applying a vacuum for 15 minutes, 50 mL of ethanol was added to the reaction under a nitrogen atmosphere. Then, the temperature was brought to 0 °C with an ice bath, and 1.88 g of NaBH₄ (49.63 mmol) was added to the reaction flask and the reaction was continued for one day. The reaction was terminated by TLC control the next day and extraction was performed with diethyl ether. After washing the organic phase 3 times with water, it was dried using Na₂SO₄, and the solvents in the organic phase separated by filtration were evaporated under reduced pressure to obtain a white solid, **molecule 18**. (252 mg, 57.7% yield) Since amine groups are extremely sensitive to moisture and oxygen in the air, the material was used directly in the next reaction without further purification.

3.3.12.2.4 Synthesis of Molecule 19 (2,3-bis(3,4-bis(octyloxy)phenyl)-5,8-dibromo-6-fluoroquinoxaline)

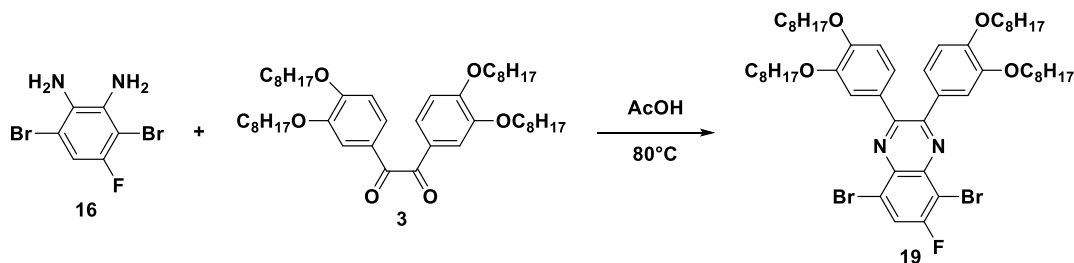


Figure 3.15. Synthetic route of molecule 19

458 mg of **molecule 16** and 1.22 g mg of molecule 3 (863.68 μmol) were placed into a 250 mL schlenk tube and dissolved with 25 mL of acetic acid (AcOH) under N_2 atmosphere. The reaction was continued for 1 day at 80°C. The reaction was terminated with TLC control and extraction was performed with chloroform. The organic phase was washed 3 times with water and dried with Na_2SO_4 , then Na_2SO_4 was filtered and removed from the organic phase. The solvents in the filtered organic phase were evaporated under reduced pressure to obtain a yellow solid. The obtained yellow solid was purified in 2 steps using column chromatography (silica, hexane: EtOAc – 25:1), (silica, hexane: DCM – 5:1), and a yellow solid (**molecule 19**) was obtained. (560 mg, 70.2% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.87 (s, 1H), 7.27 (d, $J = 8.8$ Hz, 2H), 7.23 (s, 2H), 6.84 (d, $J = 8.8$ Hz, 2H), 4.01 (t, $J = 6.6$ Hz, 4H), 3.86 (t, $J = 6.6$ Hz, 4H), 1.82 (dd, $J = 14.4, 7.0$ Hz, 4H), 1.77 – 1.68 (m, 4H), 1.46 – 1.27 (m, 40H), 0.90 – 0.85 (m, 12H). ^{13}C NMR (100 MHz, CDCl_3) δ 157.9, 155.5, 151.9, 150.6, 148.5, 148.3, 146.4, 136.9, 133.7, 128.1, 127.9, 121.6, 121.2, 121.0, 120.4, 120.2, 113.2, 110.6, 105.7, 105.5, 66.9, 29.6, 27.1, 27.0, 26.8, 23.8, 20.5, 11.9.

3.3.12.2.5 Synthesis of Molecule 20 (2,3-bis(3,4-bis(octyloxy)phenyl)-5,8-dibromo-6,7-difluoroquinoxaline)

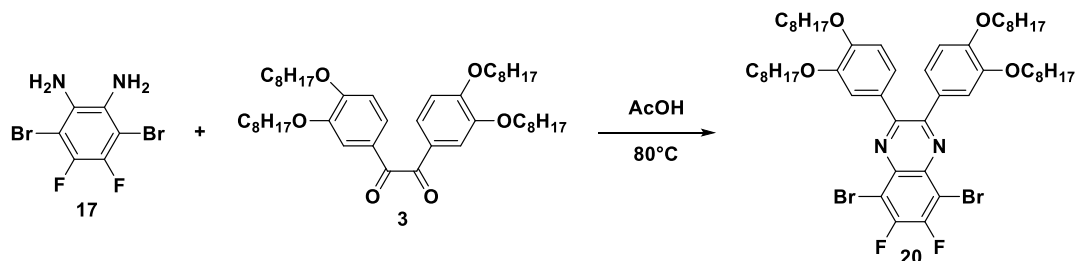


Figure 3.16. Synthetic route of molecule 20

252 mg of **molecule 17** and 625 mg of molecule 3 (864 μmol) were placed into a 250 mL schlenk tube and dissolved with 25 mL of acetic acid under N_2 atmosphere. The reaction was continued for 1 day at 80°C. Then, the reaction was terminated with TLC control, and extraction was performed with chloroform. The organic phase, which was washed with water 3 times, was dried with Na_2SO_4 and filtered, and the solvents in the filtered organic phase were evaporated under reduced pressure to obtain a yellow solid. The yellow solid obtained was purified 2 times using column chromatography (silica, hexane: EtOAc – 25:1), (silica, hexane: DCM – 5:1), and a yellow solid (**molecule 20**) was obtained. (610 mg, 75.4% yield) ^1H NMR (400 MHz, CDCl_3) δ 7.28 (d, $J=8.1$ Hz, 2H), 7.26 (s, 2H), 6.86 (d, $J=8.1$ Hz, 2H), 4.04 (t, $J=6.6$ Hz, 4H), 3.88 (t, $J=6.6$ Hz, 4H), 1.88 – 1.83 (m, 4H), 1.79 – 1.73 (m, 4H), 1.35 (m, 40H), 0.91 (dd, $J=6.6, 4.5$ Hz, 12H). ^{13}C NMR (100 MHz, CDCl_3) δ 152.0, 149.9, 149.1, 147.0, 134.0, 128.5, 121.7, 113.8, 111.2, 107.6, 67.5, 30.2, 27.7, 27.6, 27.4, 24.4, 21.0, 12.5.

3.3.12.2.6 Synthesis of Molecule 21 (2,3-bis(3,4-bis(octyloxy)phenyl)-5,8-dibromo-6,7-dichloroquinoxaline)

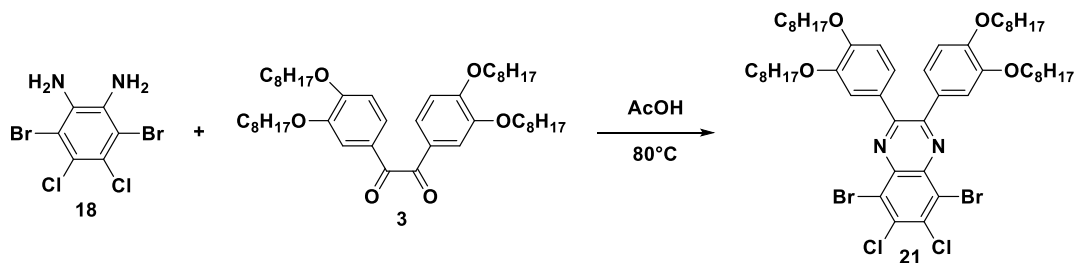


Figure 3.17. Synthetic route of molecule 21

350 mg of **molecule 18** and 732 mg of **molecule 3** (1.01 mmol) were placed into a 250 mL schlenk tube and dissolved with 25 mL of acetic acid under N₂ atmosphere. The reaction was continued for 1 day at 80°C and terminated with TLC control. Then, extraction was performed with chloroform. The organic phase was washed with water 3 times and dried with Na₂SO₄. Na₂SO₄ was filtered and removed from the organic phase and the solvents in the filtered organic phase were evaporated under reduced pressure to obtain a yellow solid material. The material was purified in 2 steps by column chromatography (silica, hexane: EtOAc – 25:1), (silica, hexane: DCM – 5:1), and a yellow solid (**molecule 21**) was obtained. (1.06 g, 93.8% yield) ¹H NMR (400 MHz, CDCl₃) δ 7.27 (d, J=8.25 Hz, 2H), 7.25 (s, 2H), 6.83 (d, J = 8.25 Hz, 2H), 4.01 (t, J = 8.7, 4.4 Hz, 4H), 3.86 (t, J = 8.7, 4.4 Hz, 4H), 1.85 – 1.80 (m, 4H), 1.77 – 1.71 (m, 4H), 1.43 – 1.27 (m, 40H), 0.89 – 0.84 (m, 12H). ¹³C NMR (100 MHz, CDCl₃) δ 151.7, 148.6, 146.4, 135.4, 132.7, 127.7, 122.6, 121.2, 113.0, 110.4, 66.9, 66.8, 29.6, 27.1, 26.8, 23.7, 20.4, 11.9.

3.3.13 Synthesis of Molecule 23 (tributyl(selenophen-2-yl)stannane)

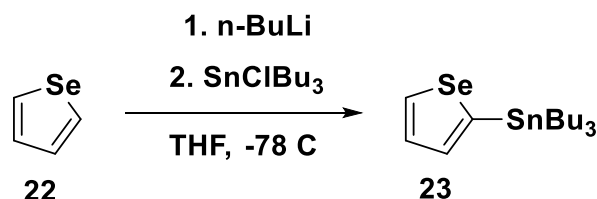


Figure 3.18. Synthetic route of molecule 23

1.00 g of selenophene (**molecule 22**) (7.63 mmol) was placed in a 100 mL schlenk tube and dissolved with 25 mL of dry THF under nitrogen gas. The reaction temperature was brought to -78°C and 3.36 mL of n-BuLi (8.39 mmol in 2.5 M hexane) was added dropwise over approximately 20 min. The reaction mixture was allowed to stir for 1 h and then brought to room temperature and stirred for 1 h at this temperature. The mixture was then brought to -78°C again and 2.59 mL of SnBu₃Cl (9.16 mmol) was added dropwise at this temperature. The reaction was allowed to stir for 24 hours at room temperature. After 24 hours, excess n-BuLi was deactivated with pure water, and extraction was carried out with chloroform. The organic phase, which was washed with water 3 times, was dried by adding Na₂SO₄. In the next step, Na₂SO₄ was filtered and the solvents were evaporated under reduced pressure to obtain a transparent yellow liquid (**molecule 23**). (2.50 g, 77.9% yield) The obtained material was used in subsequent syntheses without needing further purification. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.36 (dd, *J* = 4.8 Hz, 1H), 7.51 (d, *J* = 1.3 Hz, 1H), 7.49 (t, *J* = 4.8, 1.3 Hz, 1H), 1.63 – 1.53 (m, 6H), 1.51 – 1.42 (m, 6H), 1.32 (m, 16H), 1.15 – 1.06 (m, 6H), 0.90 (td, *J* = 7.3, 2.4 Hz, 25H), 0.83 – 0.76 (m, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 136.0, 133.4, 128.7, 27.4, 27.1, 26.0, 25.6, 25.4, 25.3, 25.0, 15.7, 11.9, 11.8, 9.3, 6.9.

3.3.14 Synthesis of Molecule 24 (2,3-bis(3,4-bis(octyloxy)phenyl)-6-fluoro-5,8-di(selenophen-2-yl)quinoxaline)

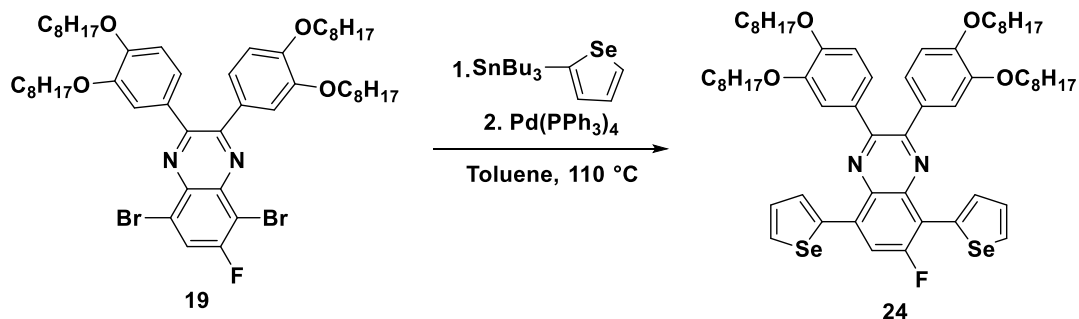


Figure 3.19. Synthetic route of molecule 24

500 mg **molecule 19** (515 μmol) and 1.08 g molecule 25 (2.57 mmol) were placed in a 100 mL schlenk tube. After vacuuming for 10 minutes, 20 mL dry toluene was added to the schlenk tube under N_2 atmosphere. After degassing the reaction for 10 minutes, 54 mg bis(triphenylphosphine)palladium (II) dichloride $\text{PdCl}_2(\text{PPh}_3)_2$ (77 μmol) was added to the mixture. The reaction was heated to 100°C for 24 hours. The reaction, which was terminated by TLC, was evaporated under reduced pressure and purified by column chromatography (silica, hexane: chloroform – 4:1). Red solid (**molecule 24**) was obtained. (120 mg, 21.8% yield) ^1H NMR (400 MHz, CDCl_3) δ 8.34 (d, $J = 3.7$ Hz, 1H), 8.25 (d, $J = 4.6$ Hz, 1H), 8.23 (s, 1H), 8.05 (s, 1H), 8.03 (s, 1H), 7.50 – 7.44 (m, 2H), 7.33 (d, $J = 10.6$ Hz, 2H), 7.20 (d, $J = 8.2$ Hz, 2H), 6.85 (d, $J = 8.2$ Hz, 2H), 4.03 (t, $J = 6.6$ Hz, 4H), 3.92 (t, $J = 6.6$ Hz, 4H), 1.85 (d, $J = 7.3$ Hz, 4H), 1.79 – 1.74 (m, 4H), 1.44 – 1.29 (m, 40H), 0.89 (d, $J = 5.1$ Hz, 12H). ^{13}C NMR (100 MHz, CDCl_3) δ 157.4, 154.9, 150.0, 148.7, 147.9, 147.7, 146.3, 138.1, 134.7, 133.6, 133.4, 131.4, 130.7, 129.6, 128.4, 128.3, 127.1, 126.7, 125.9, 125.4, 121.6, 121.5, 115.9, 115.8, 113.7, 112.8, 112.5, 110.3, 66.9, 39.8, 29.6, 27.2, 27.1, 23.8, 20.5, 11.8.

3.3.15 Synthesis of Molecule 25 (2,3-bis(3,4-bis(octyloxy)phenyl)-6,7-difluoro-5,8-di(selenophen-2-yl)quinoxaline)

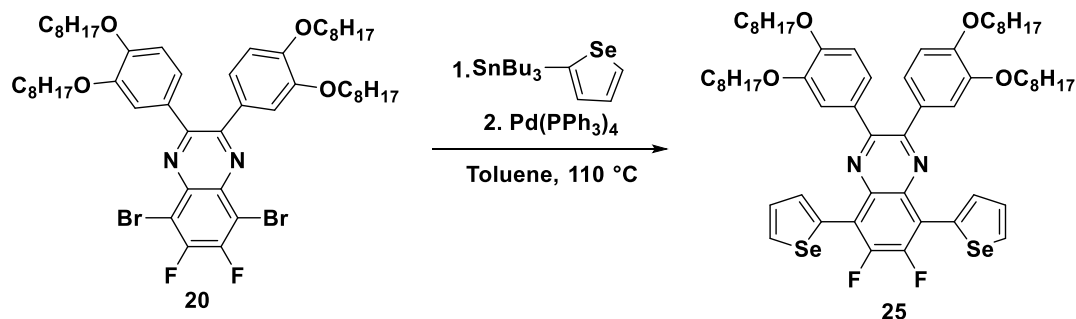


Figure 3.20. Synthetic route of molecule 25

590 mg **molecule 20** (0.59 mmol) and 550 mg molecule 25 (1.30 mmol) were placed in a 100 mL schlenk tube. After vacuuming for 10 minutes, 20 mL dry toluene was added to the schlenk tube under N₂ atmosphere. After degassing the reaction for 10 minutes, 30 mg PdCl₂(PPh₃)₂ (40 μmol) was added to the mixture. The reaction was heated to 100°C for 24 hours. The reaction, which was terminated by TLC, was evaporated under reduced pressure and purified by column chromatography (silica, hexane: chloroform – 4:1). The red solid (**molecule 25**) was obtained pure. (420 mg, 64.6% yield) ¹H NMR (400 MHz, CDCl₃) δ 8.36 (d, J = 3.9 Hz, 2H), 8.30 (d, J = 5.8 Hz, 2H), 7.50 (dd, J = 5.8, 3.9 Hz, 2H), 7.31 (s, 2H), 7.19 (d, J = 8.4 Hz, 2H), 6.85 (d, J = 8.4 Hz, 2H), 4.04 (t, J = 6.7 Hz, 4H), 3.91 (t, J = 6.7 Hz, 4H), 1.89 – 1.83 (m, 4H), 1.79 – 1.74 (m, J = 7.6 Hz, 4H), 1.37 – 1.28 (m, 40H), 0.91 – 0.87 (m, 12H). ¹³C NMR (100 MHz, CDCl₃) δ 150.5, 149.1, 147.5, 146.7, 135.8, 133.4, 132.8, 131.5, 129.2, 128.4, 122.8, 117.9, 114.9, 111.5, 68.2, 30.8, 28.3, 28.3, 28.2, 25.0, 21.7, 13.1.

3.3.16 Synthesis of Molecule 26 (2,3-bis(3,4-bis(octyloxy)phenyl)-6,7-dichloro-5,8-di(selenophen-2-yl)quinoxaline)

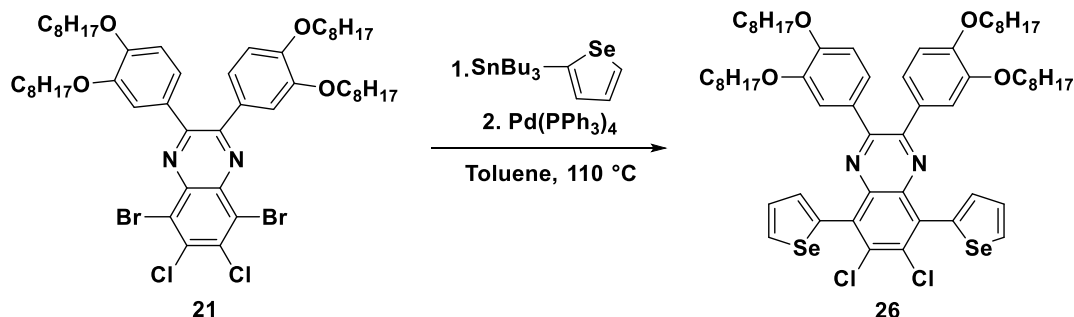


Figure 3.21. Synthetic route of molecule 26

350 mg **molecule 21** (342 μmol) and 475 mg molecule 25 (1.13 mmol) were placed in a 100 mL schlenk tube. After vacuuming for 10 minutes, 20 mL dry toluene was added to the schlenk tube under N_2 atmosphere. After degassing the reaction for 10 minutes, 17 mg $\text{PdCl}_2(\text{PPh}_3)_2$ (24 μmol) was added to the mixture. The reaction was heated to 100°C and stirred for 24 hours. The reaction, which was terminated by TLC, was evaporated under reduced pressure and purified by column chromatography (silica, hexane: chloroform – 4:1). A red solid (**molecule 26**) was obtained. (300 mg, 78.1% yield) ^1H NMR (400 MHz, CDCl_3) δ 8.33 (d, $J = 5.5$ Hz, 2H), 7.74 (d, $J = 3.5$ Hz, 1H), 7.47 (dd, $J = 5.5, 3.5$ Hz, 1H), 7.32 (s, 1H), 7.11 (d, $J = 8.4$ Hz, 2H), 6.74 (d, $J = 8.4$ Hz, 2H), 3.97 (t, $J = 6.6$ Hz, 4H), 3.83 (d, $J = 6.6$ Hz, 4H), 1.84 – 1.79 (m, 4H), 1.77 – 1.72 (m, 4H), 1.42 – 1.28 (m, 40H), 0.90 – 0.86 (m, 12H). ^{13}C NMR (100 MHz, CDCl_3) δ 149.3, 148.2, 146.5, 138.2, 135.3, 132.2, 132.0, 131.1, 130.9, 128.6, 126.6, 121.3, 113.2, 110.3, 66.9, 29.8, 27.3, 27.2, 27.1, 23.9, 20.7, 12.1.

3.3.17 Synthesis of Acceptor Monomer 1 (2,3-bis(3,4-bis(octyloxy)phenyl)-5,8-bis(5-bromoselenophen-2-yl)-6-fluoroquinoxaline)

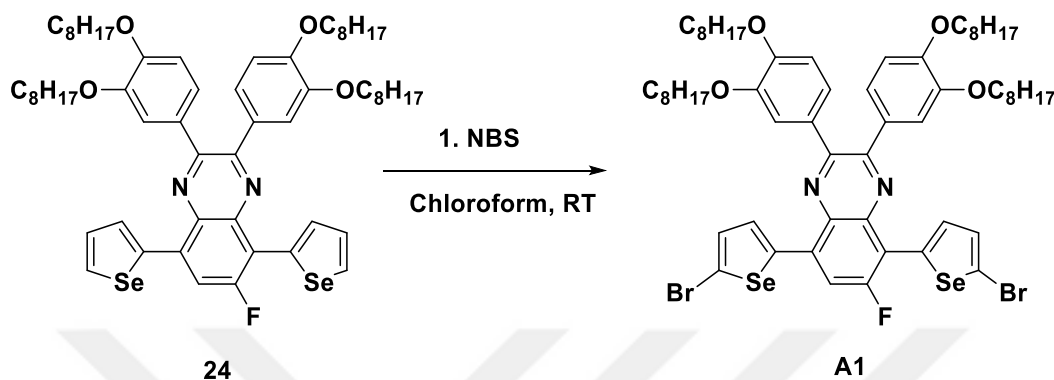


Figure 3.22. Synthetic route of A1

120 mg **molecule 24** (112 μmol) was added to a 250 mL of two-mouthed reaction flask. After 10 minutes of vacuum, 50 mL chloroform and 44 mg (246 μmol) NBS were added in the presence of N_2 atmosphere. After the addition process was completed, the reaction mixture was stirred at room temperature for 24 hours and the reaction was terminated by TLC control. Extraction of the product was performed with chloroform. The organic phase was washed with water 3 times and dried with Na_2SO_4 , then Na_2SO_4 was filtered and removed from the organic phase. The solvents in the filtered organic phase were evaporated under reduced pressure and purified using column chromatography. (silica, hexane: chloroform – 3:1). A red solid (**A1**) was obtained. (100 mg, 73.0% yield) ^1H NMR (400 MHz, CDCl_3) δ 7.99 (d, J = 4.3 Hz, 1H), 7.89 (s, 1H), 7.66 (d, J = 4.1 Hz, 1H), 7.42 (s, 1H), 7.37 (d, J = 4.43 Hz, 1H), 7.36 (s, 1H), 7.35 (d, J = 4.1 Hz, 1H), 7.03 (d, J = 8.3 Hz, 2H), 6.82 (d, J = 8.3 Hz, 2H), 4.03 (dd, J = 14.6, 7.8 Hz, 8H), 1.86 (dd, J = 14.5, 7.3 Hz, 8H), 1.52 – 1.44 (m, 8H), 1.29 (m, 32H), 0.91 – 0.86 (m, 12H). ^{13}C NMR (100 MHz, CDCl_3) δ 157.7, 155.1, 150.7, 149.3, 148.1, 147.9, 146.7, 138.9, 135.0, 130.9, 130.4, 129.9, 129.9,

129.5, 129.3, 127.9, 127.7, 124.5, 122.1, 121.7, 121.5, 115.5, 115.4, 113.6, 111.8, 111.5, 111.5, 110.2, 67.2, 66.8, 29.7, 27.3, 27.1, 23.9, 20.5, 11.9.

3.3.18 Synthesis of Monomer 2 (2,3-bis(3,4-bis(octyloxy)phenyl)-5,8-bis(5-bromoselenophen-2-yl)-6,7-difluoroquinoxaline)

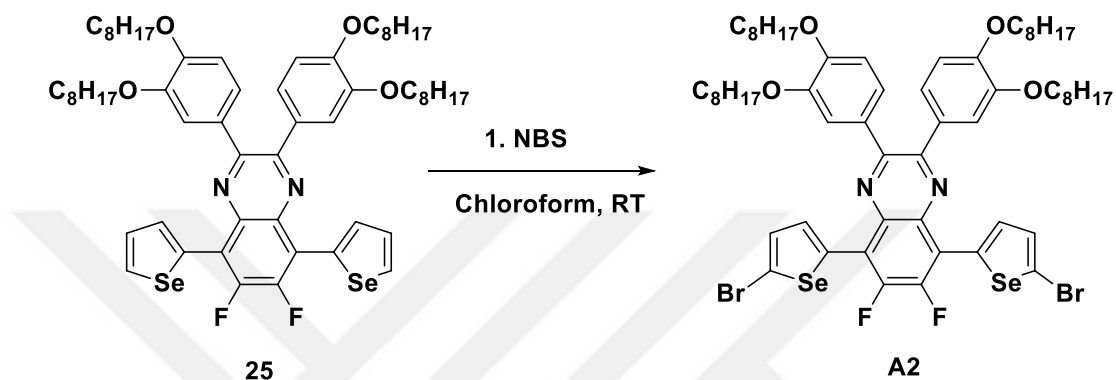


Figure 3.23. Synthetic route of A2

420 mg **molecule 25** (390 μmol) was added to a 250 mL of two-mouthed reaction flask. After 10 minutes of vacuum, 50 mL chloroform and 170 mg (960 μmol) NBS were added in the presence of N_2 atmosphere. After the addition process was completed, the reaction mixture was stirred at room temperature for 1 day and the reaction was terminated by TLC control. Extraction of the product was performed with chloroform. The organic phase was washed with water 3 times and dried with Na_2SO_4 , then Na_2SO_4 was filtered and removed from the organic phase. The solvents in the filtered organic phase were evaporated under reduced pressure and purified using column chromatography. (silica, hexane: chloroform – 3:1). A red solid (**A2**) was obtained. (320 mg, 66.7% yield) ^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, $J = 4.4$ Hz, 2H), 7.36 (s, 2H), 7.34 (d, $J = 4.4$ Hz, 2H), 7.00 (d, $J = 8.2$ Hz, 2H), 6.81 (d, $J = 8.2$ Hz, 2H), 4.02 (m, 8H), 1.89 – 1.79 (m, 8H), 1.53 – 1.46 (m, 8H), 1.37 – 1.20 (m, 32H), 0.91 – 0.84 (m, 12H). ^{13}C NMR (100 MHz, CDCl_3) δ 151.3, 149.6, 148.2,

147.1, 135.3, 132.5, 131.9, 131.5, 128.9, 124.4, 123.1, 117.5, 115.0, 111.7, 68.6, 68.3, 31.1, 28.7, 28.5, 25.3, 21.9, 13.4.

3.3.19 Synthesis of Acceptor Monomer 3 (2,3-bis(3,4-bis(octyloxy)phenyl)-5,8-bis(5-bromoselenophen-2-yl)-6,7-dichloroquinoxaline)

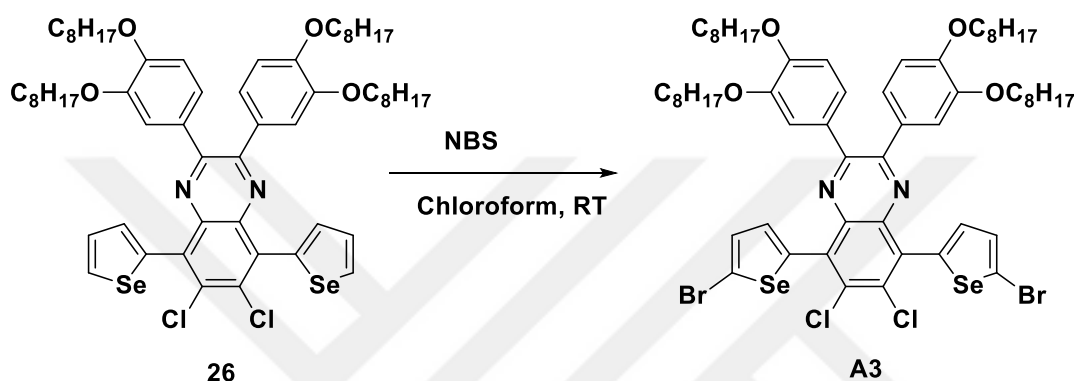


Figure 3.24. Synthetic route of A3

229 mg **molecule 26** (204 μmol) was added to a 250 mL of two-mouthed reaction flask. After vacuum application for 10 minutes, 50 mL chloroform and 80 mg (408 μmol) NBS were added under N_2 atmosphere. After the addition process was completed, the reaction mixture was allowed to stir for 24 hours at room temperature and the reaction was terminated by TLC control. Extraction of the product was performed with chloroform. The organic phase was washed with water 3 times and dried with Na_2SO_4 , then Na_2SO_4 was filtered and removed from the organic phase. The solvents in the filtered organic phase were evaporated under reduced pressure and purified using column chromatography. (silica, hexane: chloroform – 3:1). A red solid (**A3**) was obtained. (210 mg, 80.5% yield) ^1H NMR (400 MHz, CDCl_3) δ 7.64 (d, $J = 4.3$ Hz, 2H), 7.37 (s, 2H), 7.32 (d, $J = 4.3$ Hz, 2H), 6.97 (d, $J = 8.4$ Hz, 2H), 6.68 (d, $J = 8.4$ Hz, 2H), 3.91 (dd, $J = 13.2, 5.8$ Hz, 8H), 1.77 – 1.72 (m, 8H), 1.42 –

1.37 (m, 8H), 1.27 – 1.20 (m, 32H), 0.83 – 0.79 (m, 12H). ^{13}C NMR (100 MHz, CDCl_3) δ 150.4, 149.1, 147.5, 139.6, 134.9, 132.0, 131.6, 131.2, 130.6, 128.7, 122.2, 120.2, 113.8, 110.9, 67.7, 30.5, 28.1, 27.9, 24.8, 24.7, 21.4, 12.8.

3.3.20 Synthesis of Molecule 28 (3,6-dibromobenzene-1,2-diamine)

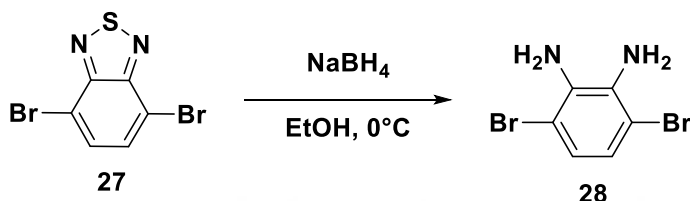


Figure 3.25. Synthetic route of molecule 28

1 g of **molecule 27** (1.3 mmol) was placed in a 250 mL double-mouthed flask and after applying a vacuum for 15 minutes, 50 mL of ethanol was added to the reaction under a nitrogen atmosphere. Then, the temperature was brought to 0°C with an ice bath, and 4.92 g of NaBH_4 (130.07 mmol) was added to the reaction flask and the reaction was continued for one day. The reaction was terminated by TLC control the next day and extraction was performed with diethyl ether. After washing the organic phase 3 times with water, it was dried using Na_2SO_4 , and the solvents in the organic phase separated by filtration were evaporated under reduced pressure to obtain a white solid, **molecule 28**. (720 mg, 79 % yield) Since amine groups are extremely sensitive to moisture and oxygen in the air, the material was used directly in the next reaction without further purification.

3.3.21 Synthesis of Molecule 29 (2,3-bis(3,4-bis(octyloxy)phenyl)-5,8-dibromoquinoxaline)

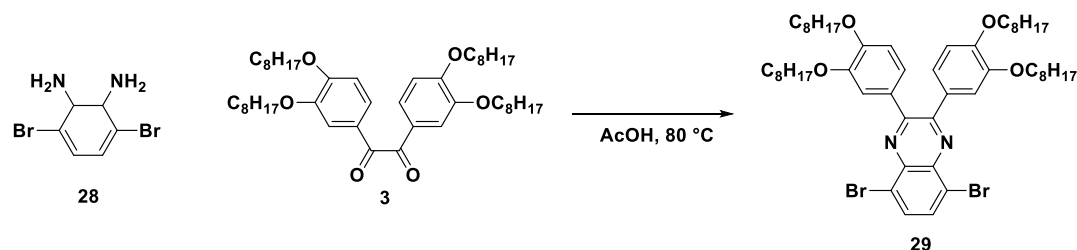


Figure 3.26. Synthetic route of molecule 29

720 mg of **molecule 28** (2.69 mmol) and 2.04 mg of **molecule 3** (2.82 mmol) were placed into a 250 mL schlenk tube and dissolved with 25 mL of acetic acid under N₂ atmosphere. The reaction was continued for 1 day at 80°C and terminated with TLC control. Then, extraction was performed with chloroform. The organic phase was washed with water 3 times and dried with Na₂SO₄. Na₂SO₄ was filtered and removed from the organic phase and the solvents in the filtered organic phase were evaporated under reduced pressure to obtain a yellow solid material. The material was purified by column chromatography (silica, hexane: DCM – 3:1), and a yellow solid (**molecule 29**) was obtained. (1.54 g, 60.2% yield) ¹H NMR (400 MHz, chloroform-*d*) δ 7.86 (d, *J* = 1.3 Hz, 2H), 7.27 (s, 2H), 6.84 (d, *J* = 8.9 Hz, 4H), 4.01 (t, *J* = 6.7 Hz, 4H), 3.86 (t, *J* = 6.7 Hz, 4H), 1.83 (t, *J* = 7.4 Hz, 4H), 1.74 (t, *J* = 7.4 Hz, 4H), 1.47 – 1.23 (m, 20H), 0.89 (dt, *J* = 6.9, 3.5 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 146.9, 132.9, 130.8, 128.2, 127.8, 127.2, 126.4, 124.3, 124.1, 121.7, 67.3, 30.1, 27.7, 27.4, 21.0, 19.6, 19.2, 12.4.

3.3.22 Synthesis of Molecule 30 (2,3-bis(3,4-bis(octyloxy)phenyl)-5,8-di(selenophen-2-yl)quinoxaline)

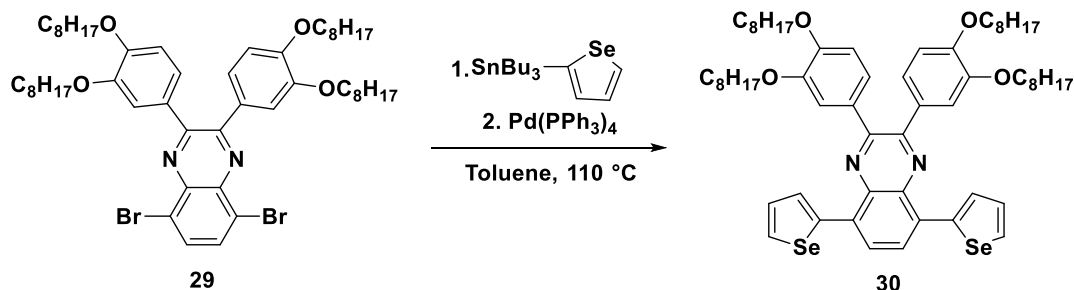


Figure 3.27. Synthetic route of molecule 30

493 mg **molecule 29** (517.31 μmol) and 1.09 mg molecule 25 (2.59 mmol) were placed in a 100 mL schlenk tube. After vacuuming for 10 minutes, 20 mL dry toluene was added to the schlenk tube under N_2 atmosphere. After degassing the reaction for 10 minutes, 54.47 mg $\text{PdCl}_2(\text{PPh}_3)_2$ (77.60 μmol) was added to the mixture. The reaction was heated to 110°C and stirred for 24 hours. The reaction, which was terminated by TLC, was evaporated under reduced pressure and purified by column chromatography (silica, hexane: chloroform – 4:1). A red solid (**molecule 30**) was obtained. (500 mg, 91.8% yield) ^1H NMR (400 MHz, chloroform-*d*) δ 8.21 (d, $J = 2.3$ Hz, 2H), 8.20 (d, $J = 6.1$ Hz, 2H), 8.04 (dd, $J = 4.0$ Hz, 2H), 7.44 (dd, $J = 6.1$, 4.0 Hz, 2H), 7.36 (s, 2H), 7.22 (d, $J = 8.3$ Hz, 2H), 6.85 (d, $J = 8.3$ Hz, 2H), 1.90 – 1.82 (m, 4H), 1.78 (m, 4H), 1.52 – 1.26 (m, 40H), 0.90 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 149.6, 147.7, 146.3, 139.6, 134.1, 133.6, 129.9, 128.7, 126.6, 124.6, 122.6, 121.5, 113.7, 110.3, 67.0, 29.7, 27.0, 24.6, 23.9, 20.5, 15.1, 11.9.

3.3.23 Synthesis of Acceptor Monomer 4 (2,3-bis(3,4-bis(octyloxy)phenyl)-5,8-bis(5-bromoselenophen-2-yl)quinoxaline)

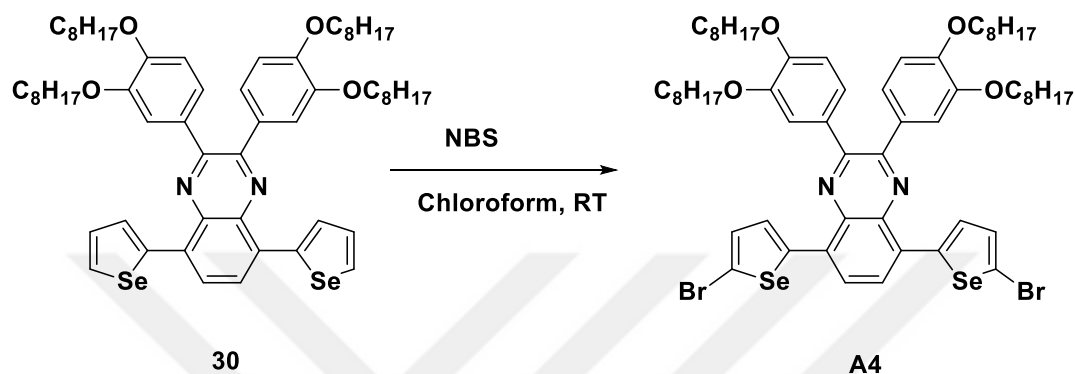


Figure 3.28. Synthetic route of molecule A4

500 mg **molecule 30** (474.72 μmol) was added to a 250 mL of two-mouthed reaction flask. After vacuum application for 10 minutes, 50 mL chloroform and 337.97 mg (1.9 mmol) NBS were added under N_2 atmosphere. After the addition process was completed, the reaction mixture was allowed to stir for 24 hours at room temperature and the reaction was terminated by TLC control. Extraction of the product was performed with chloroform. The organic phase was washed with water 3 times and dried with Na_2SO_4 , then Na_2SO_4 was filtered and removed from the organic phase. The solvents in the filtered organic phase were evaporated under reduced pressure and purified using column chromatography. (silica, hexane: chloroform – 3:1). A red solid (**A4**) was obtained. (430 mg, 82.3% yield) ^1H NMR (400 MHz, chloroform- d) δ 8.65 (d, $J = 2.1$ Hz, 2H), 7.44 (d, $J = 2.0$ Hz, 2H), 7.39 (d, $J = 2.0$ Hz, 2H), 7.26 (s, 2H), 7.07 (dd, $J = 8.4$ Hz, 2H), 6.79 (d, $J = 8.4$ Hz, 2H) 4.00 (m, 8H), 1.83 (m, 8H), 1.48 (m, 8H), 1.41 – 1.25 (m, 32H), 0.89 (tt, $J = 4.9, 2.5$ Hz, 12H). ^{13}C NMR (100

MHz, CDCl₃) δ 151.8, 150.6, 149.1, 137.0, 137.0, 136.8, 131.8, 130.5, 128.4, 124.0, 121.1, 115.7, 112.6, 109.3, 69.3, 32.2, 29.7, 29.7, 29.5, 26.5, 23.0, 14.4.

3.3.24 Synthesis of Molecule 32 (2-(2-ethylhexyl)thieno[3,2-b]thiophene)

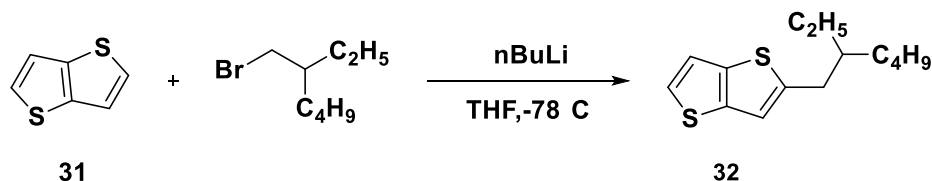


Figure 3.29. Synthetic route of molecule 32

Under a nitrogen atmosphere, 1.00 g of **molecule 31** (7.13 mmol) and dry THF were added to a 100 mL of schlenk tube. Then, 4.28 mL of 2.5 M n-BuLi (10.7 mmol) was added dropwise to the reaction medium at -78°C. It was stirred for half an hour at -78°C and half an hour at room temperature. Then, 2.07 g of 1-bromo-2-ethylhexane (10.7 mmol) was added dropwise to the schlenk tube at -78°C. The reaction was brought to room temperature again and stirred for 1 day. The excess n-BuLi was quenched with distilled water and the mixture was extracted with ethyl acetate and brine pair. The organic phase was washed with water 3 times, dried with Na₂SO₄, and filtrated to separate from Na₂SO₄. The organic phase was evaporated under reduced pressure to obtain a colorless liquid. The resulting colorless solid was purified using column chromatography (hexane) to give a colorless liquid (**molecule 32**) (1.3 g, 72.2% yield.) ¹H NMR (400 MHz, chloroform-*d*) δ 7.27 (d, *J* = 5.2 Hz, 1H), 7.19 (d, *J* = 5.2 Hz, 1H), 6.94 (s, 1H), 2.82 (d, *J* = 6.8 Hz, 2H), 1.62 (q, *J* = 5.8 Hz, 1H), 1.45 – 1.24 (m, 8H), 1.03 – 0.80 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 147.3, 138.7, 137.6, 125.2, 119.5, 117.2, 41.4, 35.2, 32.4, 29.0, 25.5, 23.1, 14.2, 10.8.

3.3.25 Synthesis of Molecule 34 (4,8-bis(5-(2-ethylhexyl)thieno[3,2-b]thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene)

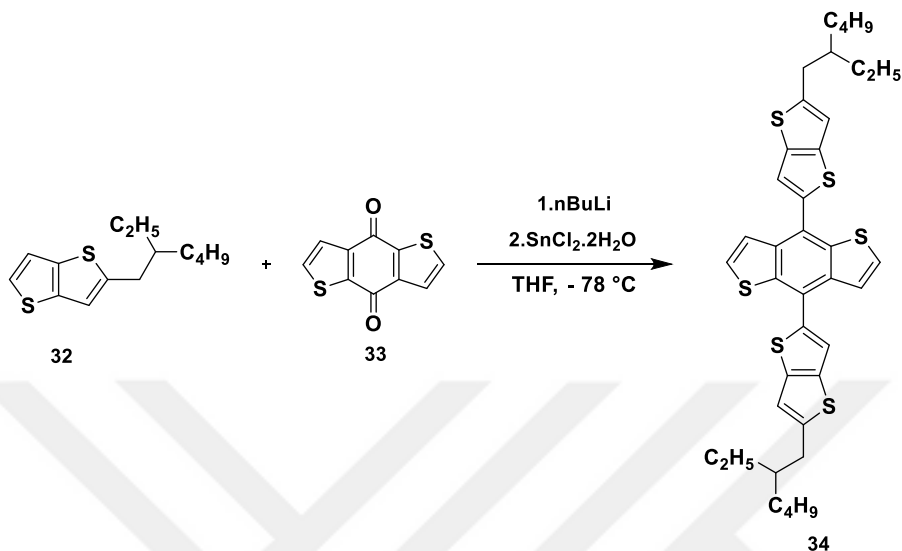


Figure 3.30. Synthetic route of molecule 34

Under nitrogen gas, 1.00 g **molecule 32** (3.96 mmol) and dry THF were added to a 100 mL Schlenk tube. Then, 1.74 mL of 2.5 M nBuLi (4.36 mmol) was added dropwise to the reaction medium at -78°C. It was stirred for half an hour at -78°C and then for half an hour at room temperature. Then, 567.15 mg **molecule 33** (2.57 mmol) was added to the Schlenk tube again at -78°C. The reaction refluxed at 60°C for 2 hours. The reaction was poured into SnCl₂(H₂O)₂ (1.52 mg, 6.73 mmol) in a 10% HCl mixture. After the mixture was stirred for another 2 hours, it was poured onto ice and extracted with diethyl ether. The organic phase was washed with water 3 times and dried with Na₂SO₄, and the separated organic phase was evaporated under reduced pressure and crystallized with ethanol. A yellow solid (**molecule 34**) was obtained. (1.00 g, 73% yield). ¹H NMR (400 MHz, chloroform-*d*) δ 7.70 (dd, *J* = 5.7, 1.0 Hz, 1H), 7.57 (s, 1H), 7.48 (dd, *J* = 5.7, 1.0 Hz, 1H), 7.03 (s, 1H), 2.89 (d, *J* = 5.8 Hz, 2H), 1.68 (q, *J* = 6.2 Hz, 1H), 1.50 – 1.28 (m, 8H), 0.98 – 0.87 (m, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 146.6, 138.2, 138.1, 136.4, 135.6, 126.8, 123.1, 122.2, 119.3, 116.2, 40.3, 34.1, 31.2, 27.7, 24.3, 21.9, 13.1, 9.7.

3.3.26 Synthesis of Donor Monomer 1 ((4,8-bis(5-(2-ethylhexyl)thieno[3,2-b]thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane))

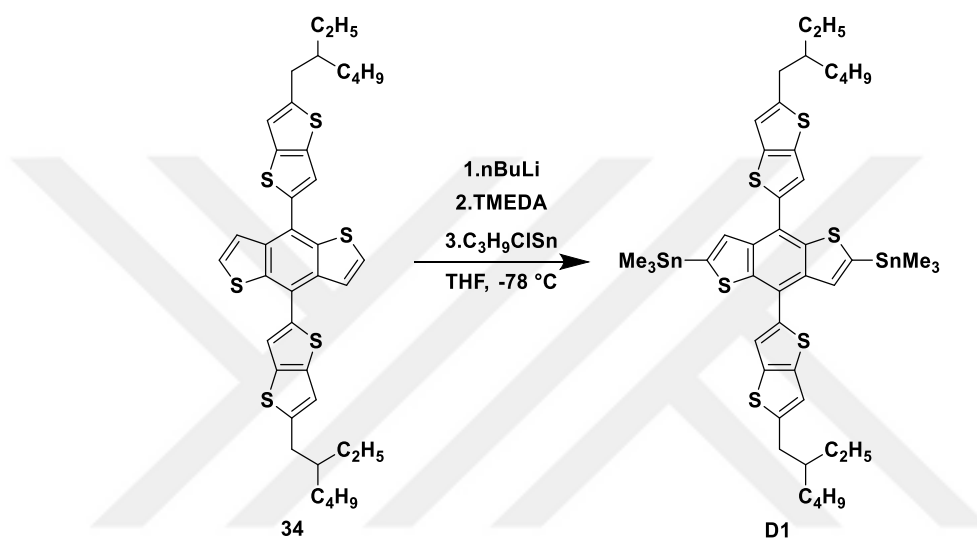


Figure 3.31. Synthetic route of molecule D1

Under nitrogen gas, 1.00 g of **molecule 34** (1.45 mmol) and 0.7 mL tetramethylethylenediamine (TMEDA) (4.34 mmol) were dissolved by 25 mL of dry THF in a 100 mL Schlenk tube. Then, 1.45 mL of 2.5 M n-BuLi (3.62 mmol) was added dropwise to the reaction medium at -78°C . After stirring for 1 hour at -78°C , it was stirred for 1 hour at room temperature. Then, 4.34 mL of 1.0 M trimethyltin chloride ($\text{C}_3\text{H}_9\text{ClSn}$) (4.34 mmol) was added dropwise to the schlenk tube again at -78°C . The reaction was brought to room temperature again and terminated after 24 hours. The excess n-BuLi was quenched with distilled water and the mixture was extracted with diethyl ether and brine pair. The organic phase was washed 3 times

with water and dried with Na₂SO₄ and the organic phase separated by filtering was evaporated under reduced pressure to obtain a yellow solid. The obtained yellow solid was purified by crystallization with dry acetone and a yellow solid (**D1**) was obtained. (1.18 g, 80.27% yield) ¹H NMR (400 MHz, CDCl₃) δ 7.74 (s, 1H), 7.59 (s, 1H), 7.04 (s, 1H), 2.89 (dd, J = 6.5, 2.5 Hz, 2H), 1.71 – 1.66 (m, 1H), 1.41 – 1.34 (m, 8H), 0.96 – 0.93 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 145.5, 141.8, 141.1, 138.2, 137.3, 135.6, 129.1, 120.6, 118.3, 115.5, 39.5, 33.3, 30.5, 26.9, 23.5, 21.1, 12.3, 8.9.

3.3.27 Synthesis of Donor Monomer 2

The commercial donor monomer (**D2**) was utilized in the synthesis of three polymers.

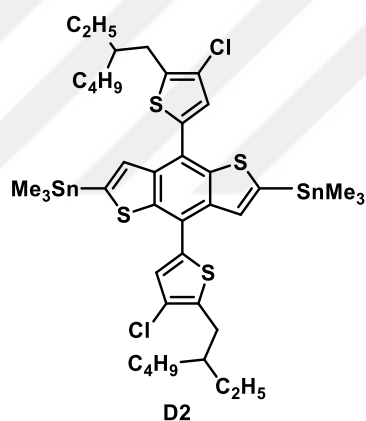


Figure 3.32. Structure of D2

3.3.28 Synthesis of Molecule 35 (2-((2-ethylhexyl)thio)thieno[3,2-b]thiophene)

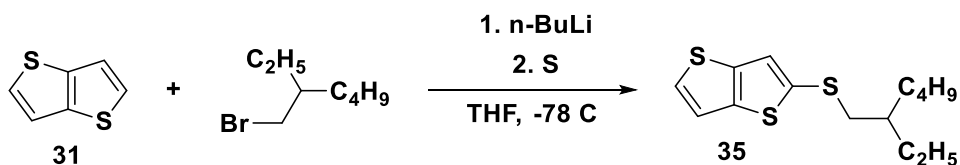


Figure 3.33. Synthetic route of molecule 35

Under nitrogen gas, 1.00 g of **molecule 31** (7.13 mmol) and dry THF were added to the 100 mL schlenk tube. Then, 4.28 mL of 2.5 M n-BuLi (10.7 mmol) was added dropwise to the reaction medium at -78°C. After stirring for half an hour at -78°C, it was stirred for half an hour at room temperature. Then, 342.92 mg of sulfur powder (10.7 mmol) was added at 0°C, and after stirring for 2 hours, 2.07 g of 1-bromo-2-ethylhexane (10.7 mmol) was added dropwise to the Schlenk tube again at 0°C. The reaction was brought to room temperature again and terminated after 24 hours. The excess n-BuLi was quenched with distilled water and the mixture was extracted with ethyl acetate and brine pair. The organic phase was washed 3 times with water and dried with Na₂SO₄ and the organic phase separated by filtering was evaporated under reduced pressure to obtain a colorless liquid. The obtained colorless solid was purified using column chromatography (hexane) and a colorless liquid (**molecule 35**) was obtained. (1.2 g, 59.11% yield) ¹H NMR (400 MHz, CDCl₃) δ 7.40 (d, J = 5.3 Hz, 1H), 7.30 (s, 1H), 7.19 (d, J = 5.3 Hz, 1H), 2.86 (d, J = 6.4 Hz, 2H), 1.57 – 1.56 (m, 1H), 1.44 – 1.24 (m, 8H), 0.89 – 0.84 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 140.0, 136.8, 136.6, 125.8, 123.8, 117.9, 42.5, 37.6, 30.5, 27.2, 23.7, 21.6, 12.6, 9.2.

3.3.29 Synthesis of Molecule 36 (4,8-bis(5-((2-ethylhexyl)thio)thieno[3,2-b]thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene)

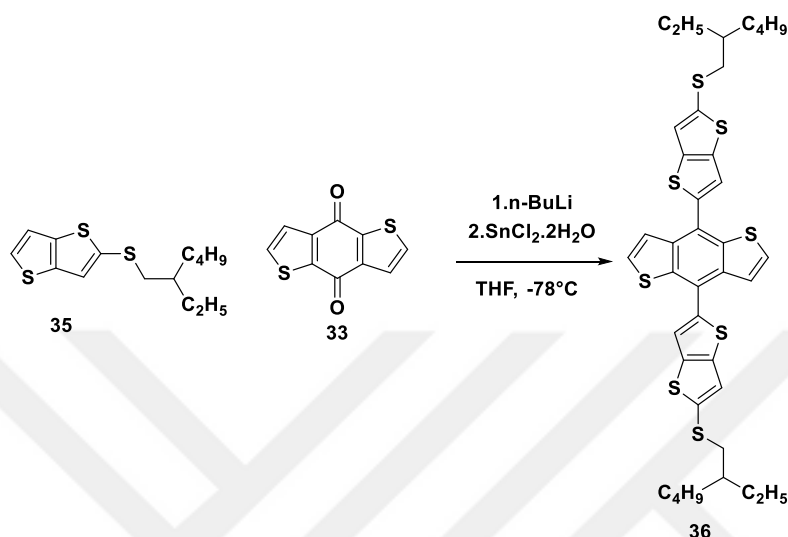


Figure 3.34. Synthetic route of molecule 36

Under nitrogen gas, 1.12 g of **molecule 35** (3.94 mmol) and dry THF were added to a 100 mL Schlenk tube. Then, 1.73 mL of 2.5 M nBuLi (4.33 mmol) was added dropwise to the reaction medium at -78°C. It was stirred for half an hour at -78°C and then for half an hour at room temperature. Then, 563.63 mg of **molecule 33** (2.56 mmol) was added to the Schlenk tube again -78°C. The reaction refluxed at 60°C for 2 hours. The reaction was poured into the SnCl₂·2H₂O (1.51 mg, 6.69 mmol) in a 10% HCl mixture. After the reaction was stirred for another 2 hours, it was poured onto ice and extracted with diethyl ether. The organic phase was washed with water 3 times and dried with Na₂SO₄, and the filtered organic phase was evaporated under reduced pressure and crystallized with ethanol. A yellow solid (**molecule 36**) was obtained. (1.3 g, 87.2% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, J = 5.7 Hz, 2H), 7.57 (s, 2H), 7.50 (d, J = 5.7 Hz, 2H), 7.38 (s, 2H), 2.93 (d, J = 6.4 Hz, 4H),

1.69 – 1.61 (m, 4H), 1.54 – 1.40 (m, 8H), 1.35 – 1.25 (m, 8H), 0.94 – 0.88 (m, 12H).
¹³C NMR (100 MHz, CDCl₃) δ 141.3, 141.1, 139.3, 139.0, 138.8, 136.7, 128.1, 125.0, 124.0, 123.1, 120.3, 44.0, 39.0, 32.0, 28.7, 25.2, 23.0, 14.1, 10.7.

3.3.30 Synthesis of Donor Monomer 3

3.3.30.1 Unsuccessful Trials

Relevant purification and reaction optimization studies are listed below.

- a. Considering the literature, in the trial conducted using 2.5 equivalents of n-BuLi, 2.5 equivalents of SnMe₃ and 500 mg of **molecule 36**, molecule synthesis was unsuccessful (Kan et al., 2015).
- b. Considering that the amount of starting material used in the reaction affects the reaction efficiency, the amount of material used was increased. 1 g of starting material was used, and other variables were kept constant. The trial failed.
- c. Considering the literature, in addition to 2.5 equivalents of n-BuLi and 2.5 equivalents of SnMe₃, 2.5 equivalents of TMEDA were added to increase the stability of the intermediate compound formed by n-BuLi. In this experiment, 1 g of the starting material (**molecule 36**) was used. In the ¹H NMR spectrum, signals belonging to **D3** were observed, but the by-product signal (single-sided tinned) and signals belonging to the starting material were also observed. Purification experiments of the target material were started using the precipitation method. The materials were tried to be precipitated using acetone, ethanol, methanol, hexane, and isopropyl alcohol (IPA), but no successful results were obtained (Kan et al., 2015) (Ye et al., 2014).
- d. The material with ¹H NMR signals belonging to molecule **D3** in three trials was reacted again without purification using 3.5 equivalents of n-BuLi, 2.5 equivalents

of SnMe_3 , and 2.5 equivalents of TMEDA. Purification processes were performed using alumina column chromatography (Hexane). It was observed that the target material was degraded in alumina column chromatography. Original signals related to the material could not be detected in the ^1H NMR result. The trial failed.

e. Considering the literature, 3 equivalents of $n\text{-BuLi}$, 3 equivalents of SnMe_3 , and 3.5 equivalents of TMEDA were added. 1.3 g reactant was used. It was not re-reacted and was purified from the excess tin by a rapid alumina column chromatography (10 hexane:1 chloroform) to prevent deterioration. The material could not be separated from the initial and single-sided tin substituted materials (Kan et al., 2015) (Ye et al., 2014).

3.3.30.2 Most Successful Trial (Trial 3) ((4,8-bis(5-((2-ethylhexyl)thio)thieno[3,2-b]thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane))

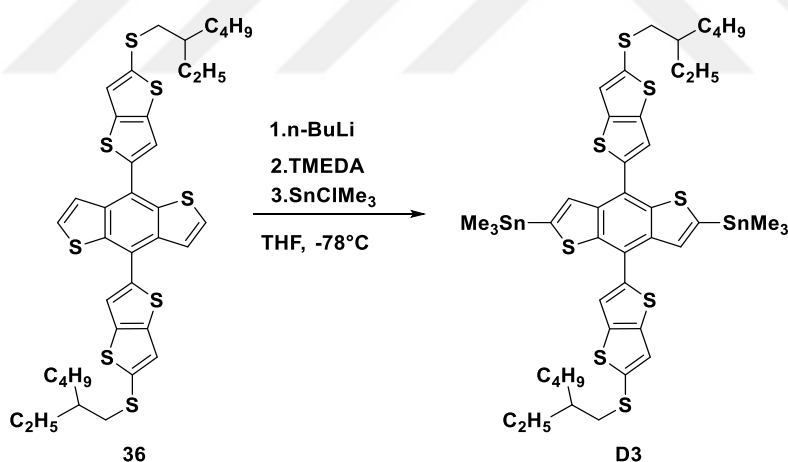


Figure 3.35. Most successful synthetic route of D3

Under nitrogen gas, 1.33 g of **molecule 36** (1.76 mmol) was dissolved by 25 mL of dry THF into the 100 mL Schlenk tube. Then, 924.21 mL (6.16 mmol) of

Tetramethylethylenediamine (TMEDA) was added dropwise at room temperature. Then, 2.64 mL of 2.5 M n-BuLi (5.28 mmol) was added dropwise to the reaction medium at -78°C. After stirring for 1 hour at -78 °C, it was stirred for 1 hour at room temperature. Then, 5.28 mL of 1.0 M trimethyltin chloride (5.28 mmol) was added dropwise to the Schlenk tube at -78 °C. The reaction was stirred at room temperature again and terminated after 24 hours. The excess n-BuLi was quenched with distilled water and the mixture was extracted with diethyl ether and brine. The organic phase was washed 3 times with water and dried with Na₂SO₄ and the organic phase separated by filtering was evaporated under reduced pressure to obtain the product. The product was purified from excess tin by a rapid alumina column chromatography (20 hexane:1 chloroform) to prevent deterioration. The product could not be separated from the initial and single-sided tin substituted products. An unpure yellow solid (**D3**) was obtained. ¹H NMR (400 MHz, CDCl₃) δ 7.70 (s, 1H), 7.58 (s, 1H), 7.39 (s, 1H)

Table 3.1. Optimization of the synthetic route of the D3

Trial	n-BuLi	SnClMe ₃	TMEDA	Gram of the Reactant	Purification
1	2.5	2.5	x	500 mg	Crystallization
2	2.5	2.5	x	1.00 g	Crystallization
3	2.5	2.5	2.5	1.00 g	It was used in the 4th trial without any purification.
4	3.5	2.5	2.5	1.00 g	Alumina Column Chromatography (hexane)
5	3	3	3.5	1.30 g	Alumina Column Chromatography (10 hexane:1 chloroform)

3.4 Synthesis of Polymers

3.4.1 Synthesis of P1F

3.4.1.1 Unsuccessful Synthesis

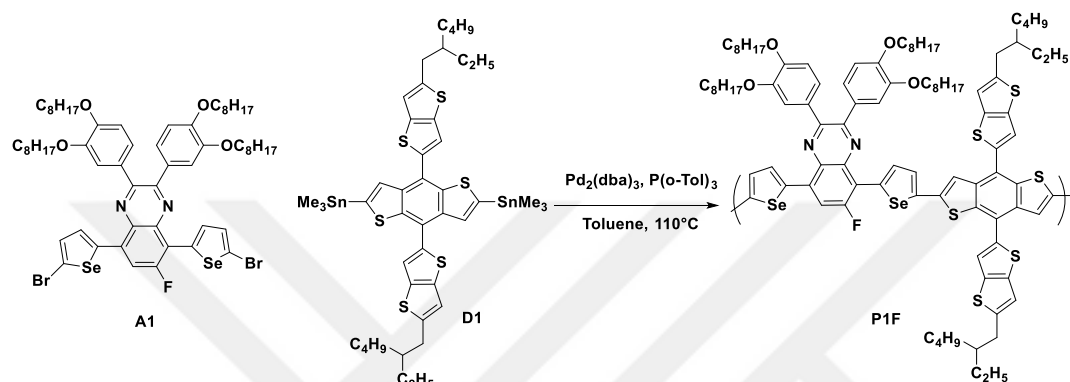


Figure 3.36. Unsuccessful synthetic route of P1F

139.40 mg monomer **A1** (113.42 μmol) and 115.32 mg (113.42 μmol) monomer **D1** were added to a 50 mL of schlenk tube and a vacuum was performed for half an hour. Under nitrogen gas, 10 mL dry toluene was added to the schlenk tube. Then, 4.39 mg (14.43 μmol) tris(o-tolyl) phosphine ($\text{P}(\text{o-Tol})_3$) and 5.51 mg (6.01 μmol) tris(dibenzylideneacetone)dipalladium (0) ($\text{Pd}_2(\text{dba})_3$) were added rapidly and heated in an oil bath at 110 °C, respectively. The reaction was terminated at 7 hours when the formation of insoluble particles was noticed. The reaction was brought to room temperature and poured into 50 mL of cold methanol which contain 5 mg of palladium scavenger and stirred for 1 hour. Then, it was filtered and air-dried. The polymer underwent purification through Soxhlet extraction with a sequence of solvents: methanol, acetone, hexane, and chloroform. The chloroform extract was then concentrated under reduced pressure, and the resulting solid was precipitated

using methanol. Since very little chloroform fraction was obtained, it was decided to change the catalyst and solvent.

3.4.1.2 Successful Synthesis

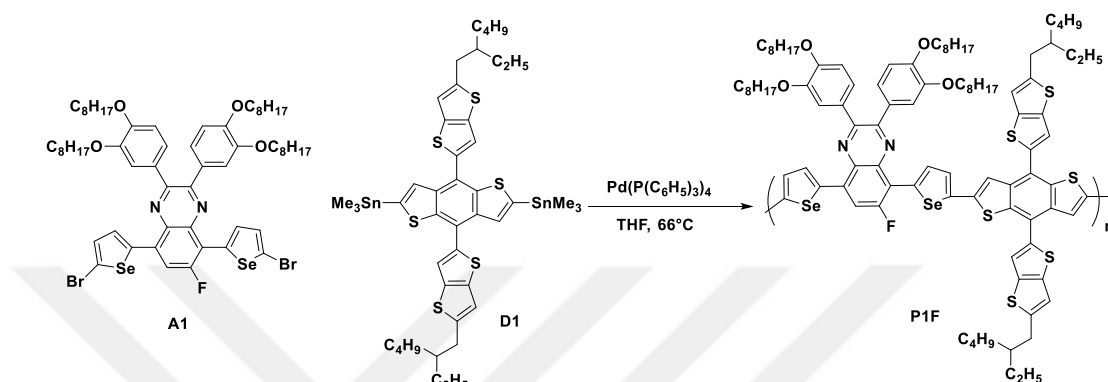


Figure 3.37. Successful synthetic route of P1F

135.40 mg molecule **A1** (110.17 μmol) and 112.01 mg (110.17 μmol) molecule **D1** were added to a 50 mL schlenk tube and a vacuum was performed for half an hour. Under nitrogen gas, 10 mL dry THF was added to the schlenk tube. Then, 8.91 mg (7.71 μmol) tetrakis(triphenylphosphine)palladium (0) ($\text{Pd}(\text{PPh}_3)_4$) was added rapidly and heated in an oil bath at 66°C . The reaction was terminated in 10 hours by TLC control. The reaction was brought to room temperature and poured into 50 mL cold methanol that 5 mg palladium scavenger was added and stirred for 1 hour. At the end of 1 hour, it was filtered and air-dried. The polymer underwent purification through Soxhlet extraction with a sequence of solvents: methanol, acetone, hexane, and chloroform. The chloroform extract was then concentrated under reduced pressure, and the resulting solid was precipitated using methanol. The solid was dried under a vacuum to obtain polymer **P1**. (130 mg, 66% yield)

3.4.2 Synthesis of P2F

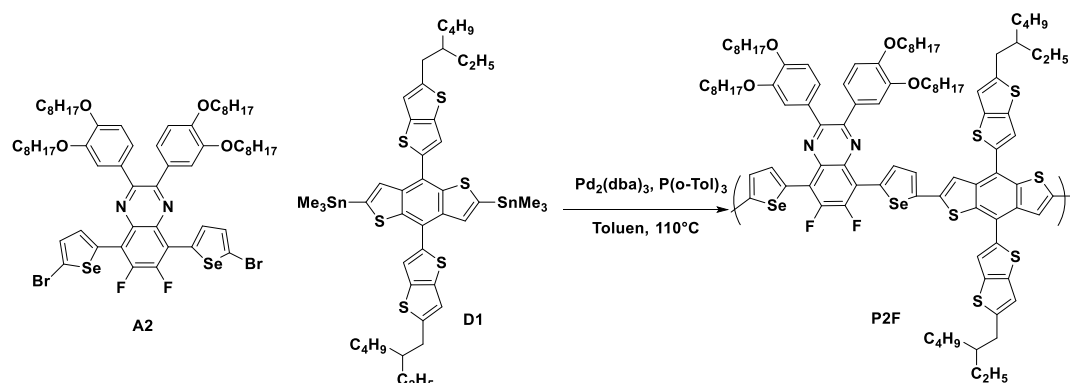


Figure 3.38. Successful synthetic route of P2F

150 mg monomer **A2** (120.29 μmol) and 122.30 mg (120.29 μmol) monomer **D1** were added to a 50 mL schlenk tube and a vacuum was performed for half an hour. Under nitrogen gas, 10 mL dry toluene was added to the schlenk tube. Then, 4.39 mg (14.43 μmol) $\text{P}(\text{o-Tol})_3$ and 5.51 mg (6.01 μmol) $\text{Pd}_2(\text{dba})_3$ were added rapidly and heated in an oil bath at 110°C . The reaction was terminated after 9 hours with TLC control. The reaction was brought to room temperature and poured into 50 mL of cold methanol. 5 mg of palladium scavenger was added and stirred for 1 hour. After 1 hour, it was filtered and air-dried for 24 hours. Then, the polymer underwent purification through Soxhlet extraction with a sequence of solvents: methanol, acetone, hexane, and chloroform. The chloroform extract was then concentrated under reduced pressure, and the resulting solid was precipitated using methanol. The solid was then dried under a vacuum to obtain **P2F** polymer. (200 mg, 92.2 % yield)

3.4.3 Synthesis of PCI

3.4.3.1 Unsuccessful Synthesis

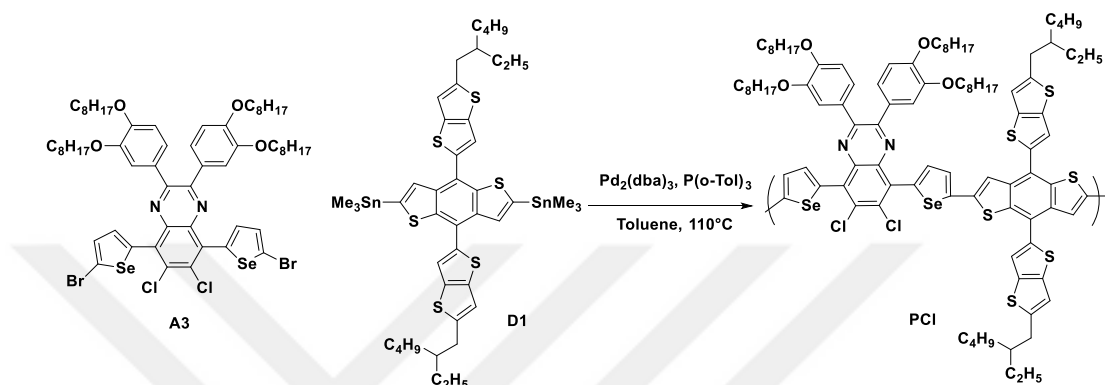


Figure 3.39. Unsuccessful synthetic route of PCI

153.60 mg of molecule **A3** (120.01 μmol) and 122.01 mg (120.01 μmol) of molecule **D1** were added to a 50 mL schlenk tube and vacuumed for half an hour. Under nitrogen gas, 10 mL of dry toluene was added to the schlenk tube. Then, 4.38 mg (14.40 μmol) of $\text{P}(\text{o-Tol})_3$ and 5.49 mg (6.00 μmol) of $\text{Pd}_2(\text{dba})_3$ were quickly added and heated in an oil bath at 110°C . The reaction was terminated when the formation of insoluble particles was noticed in 2 hours and 30 minutes. The reaction was brought to room temperature and poured into 50 mL of cold methanol. 5 mg of palladium scavenger was added and stirred for 1 hour. After 1 hour, it was filtered and air-dried. Then, the polymer underwent purification through Soxhlet extraction with a sequence of solvents: methanol, acetone, hexane, and chloroform. The chloroform extract was then concentrated under reduced pressure, and the resulting solid was precipitated using methanol. Since very little chloroform fraction was obtained, it was decided to change the catalyst and solvent.

3.4.3.2 Successful Synthesis

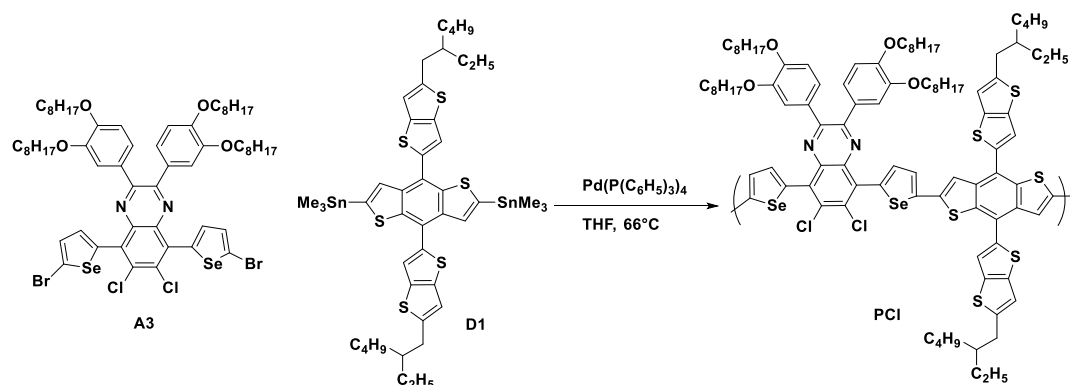


Figure 3.40. Successful synthetic route of **PCI**

149.50 mg molecule **A3** (116.80 μmol) and 118.76 mg (116.80 μmol) molecule **D1** were added to a 50 mL schlenk tube and a vacuum was performed for half an hour. Under nitrogen gas, 10 mL dry THF was added to the schlenk tube. Then, 9.45 mg (8.18 μmol) $\text{Pd}(\text{PPh}_3)_4$ was added rapidly and heated in an oil bath heated to 66°C . The reaction was terminated in 7 hours and 40 minutes by TLC control. The reaction was brought to room temperature and poured into 50 mL cold methanol. 5 mg palladium scavenger was added and stirred for 1 hour. At the end of 1 hour, it was filtered and air-dried. Then, the polymer underwent purification through Soxhlet extraction with a sequence of solvents: methanol, acetone, hexane, and chloroform. The chloroform extract was then concentrated under reduced pressure, and the resulting solid was precipitated using methanol. The solid was then dried under a vacuum to obtain polymer **PCI**. (160 mg, 75% yield)

3.4.4 Synthesis of P1FD2

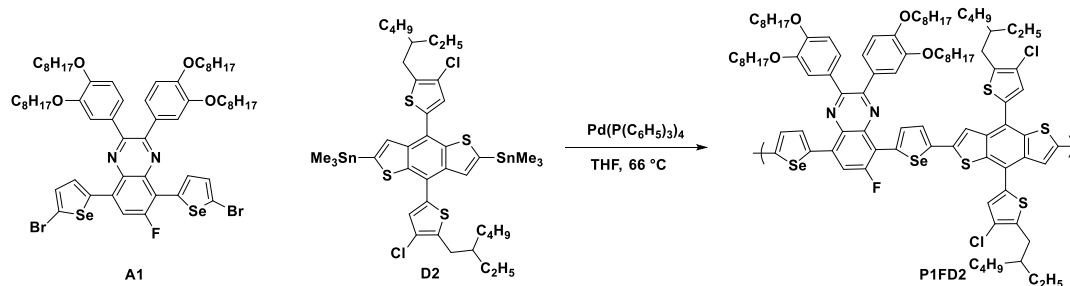


Figure 3.41. Successful synthetic route of P1FD2

101 mg molecule **A3** ($82.18\ \mu\text{mol}$) and 80 mg ($82.18\ \mu\text{mol}$) molecule **D1** were added to a 50 mL schlenk tube and a vacuum was performed for half an hour. Under nitrogen gas, 10 mL dry THF was added to the schlenk tube. Then, 6.65 mg ($5.75\ \mu\text{mol}$) $\text{Pd}(\text{PPh}_3)_4$ was added rapidly and heated in an oil bath heated to 66°C . The reaction was terminated in 13 hours and 40 minutes by TLC control. The reaction was brought to room temperature and poured into 50 mL cold methanol. 5 mg palladium scavenger was added and stirred for 1 hour. At the end of 1 hour, it was filtered and air-dried. Then, the polymer underwent purification through Soxhlet extraction with a sequence of solvents: methanol, acetone, hexane, and chloroform. The chloroform extract was then concentrated under reduced pressure, and the resulting solid was precipitated using methanol. The solid was then dried under a vacuum to obtain polymer **P1FD2**. (60 mg, 41.8% yield)

3.4.5 Synthesis of P2FD2

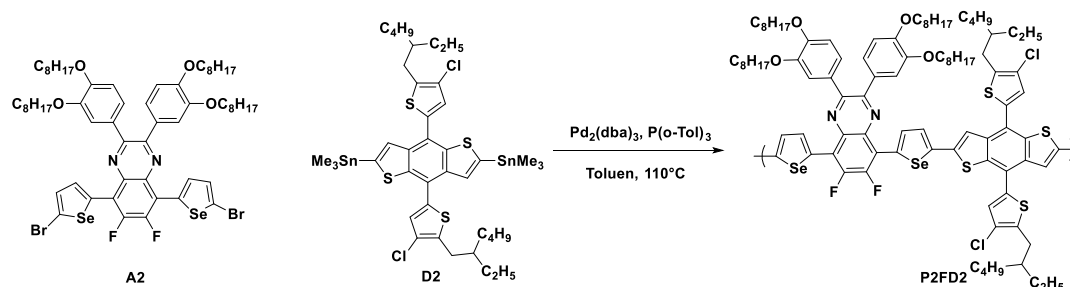


Figure 3.42. Successful synthetic route of P2FD2

100 mg of molecule **A2** (80.19 μmol) and 78.06 mg (80.19 μmol) of molecule **D2** were added to a 50 mL schlenk tube and vacuumed for half an hour. Under nitrogen gas, 10 mL of dry toluene was added to the schlenk tube. Then, 2.93 mg (9.62 μmol) of $\text{P}(\text{o-Tol})_3$ and 3.67 mg (4.01 μmol) of $\text{Pd}_2(\text{dba})_3$ were quickly added and heated in an oil bath at 110°C . The reaction was terminated after 5 hours and 20 minutes with TLC control. The reaction was brought to room temperature and poured into 50 mL of cold methanol. 5 mg of palladium scavenger was added and stirred for 1 hour. After 1 hour, it was filtered and air-dried for 24 hours. Then, the polymer underwent purification through Soxhlet extraction with a sequence of solvents: methanol, acetone, hexane, and chloroform. The chloroform extract was then concentrated under reduced pressure, and the resulting solid was precipitated using methanol. The solid was then dried under a vacuum to obtain **P2FD2** polymer. (120 mg, 84.9 % yield)

3.4.6 Synthesis of PCID2

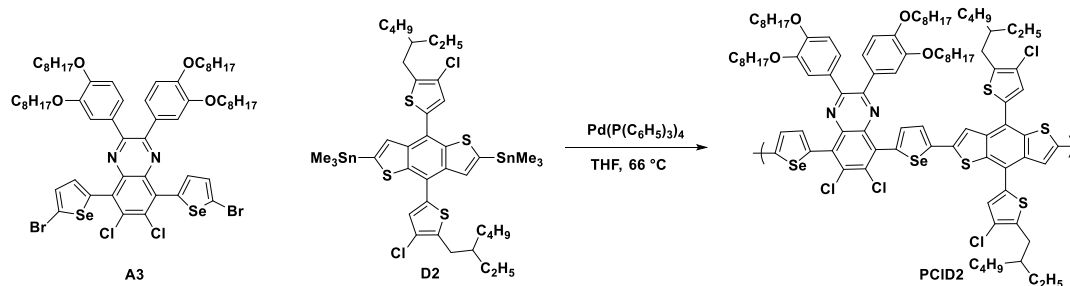


Figure 3.43. Successful synthetic route of PCID2

104.70 mg molecule **A3** (79.63 μmol) and 112.01 mg (81.80 μmol) molecule **D2** were added to a 50 mL schlenk tube and a vacuum was performed for half an hour. Under nitrogen gas, 10 mL dry THF was added to the schlenk tube. Then, 6.62 mg (5.73 μmol) $\text{Pd}(\text{PPh}_3)_4$ was added rapidly and heated in an oil bath at 66°C. The reaction was terminated after 30 hours and 50 minutes by TLC control. The reaction was brought to room temperature and poured into 50 mL cold methanol that 5 mg palladium scavenger was added and stirred for 1 hour. At the end of 1 hour, it was filtered and air-dried. The polymer underwent purification through Soxhlet extraction with a sequence of solvents: methanol, acetone, hexane, and chloroform. The chloroform extract was then concentrated under reduced pressure, and the resulting solid was precipitated using methanol. The solid was dried under a vacuum to obtain polymer **PCID2**. (120 mg, 81.7 % yield)

3.4.7 Synthesis of P2FS

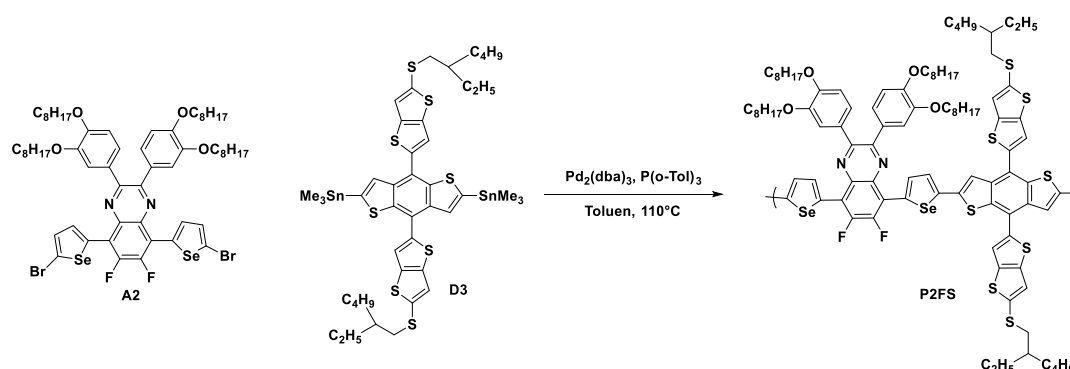


Figure 3.44. Successful synthetic route of P2FS

70 mg of molecule **A2** (56.13 μmol) and 168.53 mg (56.13 μmol) of molecule **D3** were added to a 50 mL schlenk tube and vacuumed for half an hour. Under nitrogen gas, 10 mL of dry toluene was added to the schlenk tube. Then, 5.13 mg (16.84 μmol) of $\text{P}(\text{o-Tol})_3$ and 5.14 mg (5.61 μmol) of $\text{Pd}_2(\text{dba})_3$ were quickly added and heated in an oil bath at 110°C . The reaction was terminated after 8 hours 40 minutes with TLC control. The reaction was brought to room temperature and poured into 50 mL of cold methanol. 5 mg of palladium scavenger was added and stirred for 1 hour. After 1 hour, it was filtered and air-dried for 24 hours. Then, the polymer underwent purification through Soxhlet extraction with a sequence of solvents: methanol, acetone, hexane, and chloroform. The chloroform extract was then concentrated under reduced pressure, and the resulting solid was precipitated using methanol. The solid was then dried under a vacuum to obtain **P2FS** polymer. (68 mg, 66.7% yield)

3.4.8 Synthesis of PCIS

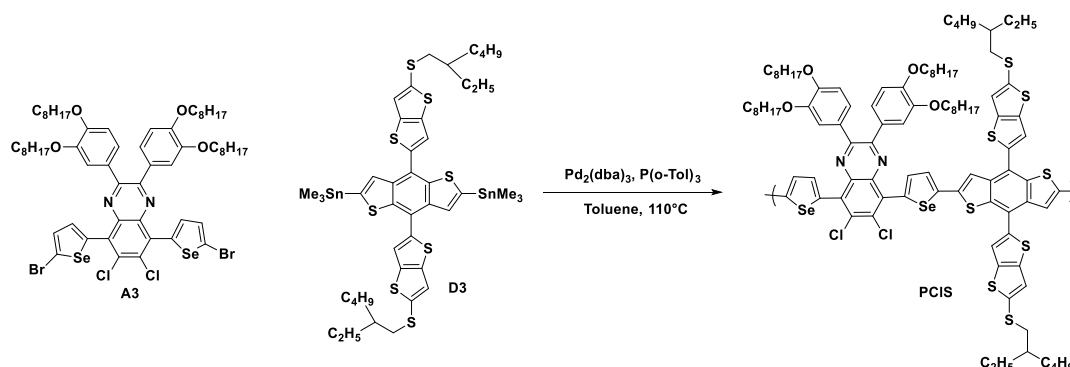


Figure 3.45. Successful synthetic route of PCIS

70 mg of molecule **A3** (56.13 μmol) and 168.53 mg (56.13 μmol) of molecule **D3** were added to a 50 mL schlenk tube and vacuumed for half an hour. Under nitrogen gas, 10 mL of dry toluene was added to the schlenk tube. Then, 5.13 mg (16.84 μmol) of $\text{P}(\text{o-Tol})_3$ and 5.14 mg (5.61 μmol) of $\text{Pd}_2(\text{dba})_3$ were quickly added and heated in an oil bath at 110°C . The reaction was terminated after 10 hours and 30 minutes with TLC control. The reaction was brought to room temperature and poured into 50 mL of cold methanol. 5 mg of palladium scavenger was added and stirred for 1 hour. After 1 hour, it was filtered and air-dried for 24 hours. Then, the polymer underwent purification through Soxhlet extraction with a sequence of solvents: methanol, acetone, hexane, and chloroform. The hexane fraction was collected under reduced pressure and the solid was precipitated using methanol. The solid was then dried under a vacuum to obtain **PCIS** polymer. (70 mg, 76.1% yield)

3.4.9 Synthesis of P0F

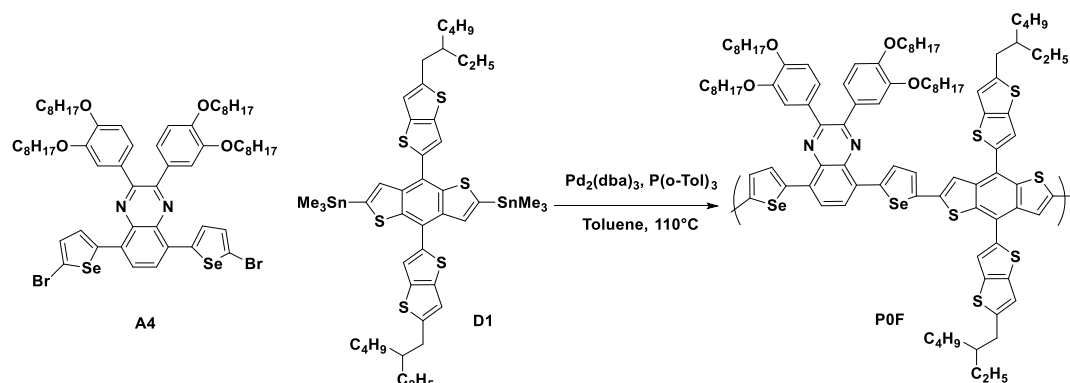


Figure 3.46. Successful synthetic route of P0F

61 mg of molecule **A4** (50.37 μmol) and 51.21 mg (50.37 μmol) of molecule **D1** were added to a 50 mL schlenk tube and vacuumed for half an hour. Under nitrogen gas, 10 mL of dry toluene was added to the schlenk tube. Then, 1.84 mg (6.04 μmol) of $\text{P}(\text{o-Tol})_3$ and 2.31 mg (2.52 μmol) of $\text{Pd}_2(\text{dba})_3$ were quickly added and heated in an oil bath at 110°C . The reaction was terminated after 10 hours with TLC control. The reaction was brought to room temperature and poured into 50 mL of cold methanol. 5 mg of palladium scavenger was added and stirred for 1 hour. After 1 hour, it was filtered and air-dried for 24 hours. Then, the polymer underwent purification through Soxhlet extraction with a sequence of solvents: methanol, acetone, hexane, and chloroform. The chloroform extract was then concentrated under reduced pressure, and the resulting solid was precipitated using methanol. The solid was then dried under a vacuum to obtain **P0F** polymer. (22 mg, % 24.7 yield)

3.5 Construction of the Organic Solar Cell Devices

First 2.5 cm wide ITO-coated glass strips are cut into long, thin pieces and the middle of the strips are taped. To remove the ITO layer from the edges, zinc (Zn) powder is sprinkled on the area remaining on the outside of the strip, then a 1:3 ratio HCl: water solution is poured with a glass pasteur pipette. The glass strip is first cleaned with water, then the tape is removed and washed with acetone. After drying, it is cut into 2.5 cm x 2.5 cm dimensions and subjected to ultrasonic cleaning for 15 minutes in a 1% Hellmanex detergent and water mixture, pure water, acetone, and isopropyl alcohol, respectively. Then, the ITO-coated glasses which are dried with a nitrogen gun are subjected to oxygen plasma treatment for 5 minutes. PEDOT: PSS is filtered with a PES filter with a pore size of 0.45 μm and statically coated in a spin coating device at a speed of 3500 rpm. After the coating process, annealing is performed on a heating stirrer at 160°C in the dark for 15 minutes. Chloroform was preferred as the solvent in the active layer mixture. Active layer solutions are prepared based on the 7 mg/mL donor concentration. As a solvent additive, chloronaphthalene (CN) was added at a volumetric rate of 0.6% in some experiments and diiodoctane (DIO) at a volumetric rate of 1% in other experiments. The additive was added to the active layer solution in a nitrogen atmosphere glove box and this mixture was mixed for 1 hour at 45°C, 300 rpm, in a heater mixer. Then, the active layer was coated with a spin coater on PEDOT: PSS coated ITO surfaces which were cleaned with a nitrogen gun in a nitrogen atmosphere glove box. The effect of the active layer thickness on the device efficiency was investigated by changing the coating speed. Finally, the coated active layers were subjected to thermal annealing at 100°C for 5 or 10 min. After the cells cooled, the PDINN solution was coated on the active layer. The concentration of this solution was prepared as 1 mg/mL in methanol and applied at 3000 rpm. In the last step, the cathode layer was evaporated 100 nm thick silver under 10^{-7} torr pressure in a nitrogen atmosphere glove box. Measurements are

performed with a Keithley 2400 electrometer device under the A.M. 1.5G solar simulator (100 mW/cm^2) in the glove box system.



CHAPTER 4

CONCLUSIONS

Nine different novel polymers were successfully synthesized using the Stille cross-coupling reaction. Six polymers were synthesized to construct organic solar cell devices (**P1F**, **P2F**, **PCl**, **P1FD2**, **P2FD2**, and **PCID2**), while the other three polymers (**P0F**, **P2FS**, and **PCIS**) were only used for investigating and comparing the optical and electrochemical properties of the polymers. The polymerization reaction was performed using four different acceptor monomers and three different donor monomers, one of which was commercially purchased. The M_n values of the polymers were determined to be 7.7 kDa, 22.7 kDa, 13.2 kDa, 12.6 kDa, 86.0 kDa, 46.1 kDa, 9 kDa, 2.0 kDa, and 2.7 kDa, respectively, in the order of **P1F**, **P2F**, **PCl**, **P1FD2**, **P2FD2**, **PCID2**, **P0F**, **P2FS**, and **PCIS**. The polymers effectively absorbed light in the visible region and exhibited appropriate E_g^{opt} for constructing organic solar cells (OSCs). The E_g^{opt} values, calculated from the thin-film onset values of the UV-Vis spectra of the polymers, were determined to be 1.62, 1.70, 1.72, 1.73, 1.76, 1.90, 1.72, 1.74, and 1.97 eV, respectively, in the order of **P1F**, **P2F**, **PCl**, **P1FD2**, **P2FD2**, **PCID2**, **P0F**, **P2FS**, and **PCIS**. Electrochemical characterizations were performed using differential pulse voltammetry, and the HOMO/LUMO energy levels of the polymers were found to be -5.56/-3.87, -5.65/-3.87, -5.86/-3.82, -5.79/-3.91, -5.67/-3.63, -5.84/-3.76, -5.82/-3.78, -5.40/-3.66, and -5.64/-3.64 eV, respectively, in the same order. A primary goal of the study which is lowering the HOMO and LUMO energy levels, was successfully achieved, and the energy levels of the polymers are suitable for constructing OSCs. Six polymers were used to construct organic solar cell (OSC) devices. The device exhibiting the highest power

conversion efficiency (PCE) was **P2F: Y6 (1:1.3)** with a PCE of 7.54%. Moreover, the performance of the best devices was recorded as 7.54%, 3.87%, 3.71%, 2.36%, 1.62%, and 1.57% respectively, in the order of **P2F: Y6**, **PCl: Y6:PC₇₁BM**, **P1F: Y6**, **P2FD2:Y6**, **PClD2:Y6**, and **P1FD2:Y6:PC₇₁BM**. **P2F: Y6** demonstrated optimal domain size and efficient miscibility, along with better morphology compared to **PCl: Y6:PC₇₁BM** and **P1F: Y6**, as confirmed by TEM and AFM analyses.

Device optimization will continue to further increase the PCE. To achieve cascade-like energy levels that facilitate better charge dissociation and transfer, a ternary blend of Y6 with PC₇₁BM or another non-fullerene acceptor featuring a lower HOMO level than Y6 will be utilized.

REFERENCES

- Ajayaghosh, A. (2003). Donor-acceptor type low band gap polymers: Polysquaraines and related systems. *Chemical Society Reviews*, 32(4), 181–191. <https://doi.org/10.1039/b204251g>
- Al-Azzawi, A. G. S., Aziz, S. B., Dannoun, E. M. A., Iraqi, A., Nofal, M. M., Murad, A. R., & M. Hussein, A. (2023). A Mini Review on the Development of Conjugated Polymers: Steps towards the Commercialization of Organic Solar Cells. *Polymers*, 15(1), 1–38. <https://doi.org/10.3390/polym15010164>
- An, C., & Hou, J. (2022). Benzo[1,2-b:4,5-b']dithiophene-Based Conjugated Polymers for Highly Efficient Organic Photovoltaics. *Accounts of Materials Research*, 3(5), 540–551. <https://doi.org/10.1021/accountsmr.2c00020>
- Andrade, B. W. D. Ö., Datta, S., Forrest, S. R., Djurovich, P., Polikarpov, E., & Thompson, M. E. (2005). Relationship between the ionization and oxidation potentials of molecular organic semiconductors. *Organic Electronics*, 6, 11–20. <https://doi.org/10.1016/j.orgel.2005.01.002>
- Arslan, Y., Taskaya, S., Alemdar, E., Yıldırım, E., & Cirpan, A. (2022). Investigation the effect of π bridge and side chain on photovoltaic properties of benzodithiophene and quinoxaline based conjugated polymers. *European Polymer Journal*, 169, 1–14. <https://doi.org/10.1016/j.eurpolymj.2022.111141>
- Azzouzi, M., Kirchartz, T., & Nelson, J. (2019). Factors Controlling Open-Circuit Voltage Losses in Organic Solar Cells. *Trends in Chemistry*, 1(1), 49–62. <https://doi.org/10.1016/j.trechm.2019.01.010>

- Baran, D., Balan, A., Celebi, S., Meana Esteban, B., Neugebauer, H., Sariciftci, N. S., & Toppare, L. (2010). Processable multipurpose conjugated polymer for electrochromic and photovoltaic applications. *Chemistry of Materials*, 22(9), 2978–2987. <https://doi.org/10.1021/cm100372t>
- Benanti, T. L., & Venkataraman, D. (2006). Organic solar cells: An overview focusing on active layer morphology. *Photosynthesis Research*, 87(1), 73–81. <https://doi.org/10.1007/s11120-005-6397-9>
- Bian, L., Zhu, E., Tang, J., Tang, W., & Zhang, F. (2012). Recent progress in the design of narrow bandgap conjugated polymers for high-efficiency organic solar cells. *Progress in Polymer Science*, 37(9), 1292–1331. <https://doi.org/10.1016/j.progpolymsci.2012.03.001>
- Brabec, C. J., Winder, C., Sariciftci, N. S., Hummelen, J. C., Dhanabalan, A., van Hal, P. A., & Janssen, R. A. J. (2002). A Low-Bandgap Semiconducting Polymer for Photovoltaic Devices and Infrared Emitting Diodes. *Advanced Functional Materials*, 12(10), 709–712. [https://doi.org/10.1002/1616-3028\(20021016\)](https://doi.org/10.1002/1616-3028(20021016))
- Bundgaard, E., & Krebs, F. C. (2007). Low band gap polymers for organic photovoltaics. *Solar Energy Materials & Solar Cells*, 91(11), 954–985. <https://doi.org/10.1016/j.solmat.2007.01.015>
- Cheng, Y. J., Yang, S. H., & Hsu, C. S. (2009). Synthesis of conjugated polymers for organic solar cell applications. *Chemical Reviews*, 109(11), 5868–5923. <https://doi.org/10.1021/cr900182s>
- Cuesta, V., Vartanian, M., Malhotra, P., Biswas, S., De La Cruz, P., Sharma, G. D., & Langa, F. (2019). Increase in efficiency on using selenophene instead of thiophene in π -bridges for D- π -DPP- π -D organic solar cells. *Journal of Materials Chemistry A*, 7(19), 11886–11894. <https://doi.org/10.1039/c9ta02415h>

- Cui, Y., Xu, Y., Yao, H., Bi, P., Hong, L., Zhang, J., Zu, Y., Zhang, T., Qin, J., Ren, J., Chen, Z., He, C., Hao, X., Wei, Z., & Hou, J. (2021). Single-Junction Organic Photovoltaic Cell with 19% Efficiency. *Advanced Materials*, 33(41), 1–8. <https://doi.org/10.1002/adma.202102420>
- Dang, M. T., Hirsch, L., Wantz, G., & Wuest, J. D. (2013). Controlling the morphology and performance of bulk heterojunctions in solar cells. Lessons learned from the benchmark poly(3-hexylthiophene):[6,6]-phenyl- C61-butyric acid methyl ester system. *Chemical Reviews*, 113(5), 3734–3765. <https://doi.org/10.1021/cr300005u>
- Dennler, G., Scharber, M. C., & Brabec, C. J. (2009). Polymer-fullerene bulk-heterojunction solar cells. *Advanced Materials*, 21(13), 1323–1338. <https://doi.org/10.1002/adma.200801283>
- Dimitrakopoulos, C. D., & Mascaró, D. J. (2001). Organic thin-film transistors: A review of recent advances. *IBM Journal of Research and Development*, 45(1), 11–27. <https://doi.org/10.1147/rd.451.0011>
- Espinet, P., & Echavarren, A. M. (2004). The mechanisms of the Stille reaction. *Angewandte Chemie International Edition*, 43(36), 4704–4734. <https://doi.org/10.1002/anie.200300638>
- Fan, Q., Liu, Y., Yang, P., Su, W., Xiao, M., Chen, J., Li, M., Wang, X., Wang, Y., Tan, H., Yang, R., & Zhu, W. (2015). Benzodithiophene-based two-dimensional polymers with extended conjugated thienyltriphenylamine substituents for high-efficiency polymer solar cells. *Organic Electronics*, 23, 124–132. <https://doi.org/10.1016/j.orgel.2015.04.013>
- Fan, X., Zhang, M., Wang, X., Yang, F., & Meng, X. (2013). Recent progress in organic-inorganic hybrid solar cells. *Journal of Materials Chemistry A*, 1(31), 8694–8709. <https://doi.org/10.1039/c3ta11200d>

- Farina, V., & Krishnan, B. (1991). Large Rate Accelerations in the Stille Reaction with Tri-2-furylphosphine and Triphenylarsine as Palladium Ligands: Mechanistic and Synthetic Implications. *Journal of the American Chemical Society*, 113(25), 9585–9595. <https://doi.org/10.1021/ja00025a025>
- Feast, W. J., Tsibouklis, J., Pouwer, K. L., Groenendaal, L., & Meijer, E. W. (1996). Synthesis, processing and material properties of conjugated polymers. *Polymer*, 37(22), 5017–5047. [https://doi.org/10.1016/0032-3861\(96\)00439-9](https://doi.org/10.1016/0032-3861(96)00439-9)
- Feldman, D. (2008). Polymer history. *Designed Monomers and Polymers*, 11(1), 1–15. <https://doi.org/10.1163/156855508X292383>
- Feng, L., Yuan, J., Zhang, Z., Peng, H., Zhang, Z. G., Xu, S., Liu, Y., Li, Y., & Zou, Y. (2017). Thieno[3,2-b]pyrrolo-Fused Pentacyclic Benzotriazole-Based Acceptor for Efficient Organic Photovoltaics. *ACS Applied Materials and Interfaces*, 9(37), 31985–31992. <https://doi.org/10.1021/acsami.7b10995>
- Gedde, U. W., & Hedenqvist, M. S. (2019). *Fundamental Polymer Science, Second Edition*. <https://doi.org/10.1007/978-3-030-29794-7>
- Gedefaw, D., Prosa, M., Bolognesi, M., Seri, M., & Andersson, M. R. (2017). Recent Development of Quinoxaline Based Polymers/Small Molecules for Organic Photovoltaics. *Advanced Energy Materials*, 7(21), 1–38. <https://doi.org/10.1002/aenm.201700575>
- Gregg, B. A., & Hanna, M. C. (2003). Comparing organic to inorganic photovoltaic cells: Theory, experiment, and simulation. *Journal of Applied Physics*, 93(6), 3605–3614. <https://doi.org/10.1063/1.1544413>
- Gu, S., Neugebauer, H., & Sariciftci, N. S. (2007). Conjugated Polymer-Based Organic Solar Cells. *Chemical Reviews*, 107(1), 1324–1338. [https://doi.org/10.1016/s0927-0248\(03\)00137-5](https://doi.org/10.1016/s0927-0248(03)00137-5)
- Gupta, D., Mukhopadhyay, S., & Narayan, K. S. (2010). Fill factor in organic solar

- cells. *Solar Energy Materials & Solar Cells*, 94(8), 1309–1313.
<https://doi.org/10.1016/j.solmat.2008.06.001>
- Heeney, M., Zhang, W., Crouch, D. J., Chabinyc, M. L., Gordeyev, S., Hamilton, R., Higgins, S. J., McCulloch, I., Skabara, P. J., Sparrowe, D., & Tierney, S. (2007). Regioregular poly(3-hexyl)selenophene: A low band gap organic hole transporting polymer. *Chemical Communications*, 47, 5061–5063.
<https://doi.org/10.1039/b712398a>
- Hoppe, H., & Sariciftci, N. S. (2004). Organic solar cells: An overview. *Journal of Materials Research*, 19(7), 1924–1945.
<https://doi.org/10.1557/JMR.2004.0252>
- Hoppe, H., Sariciftci, N. S., & Hoppe, H. (2006). Morphology of polymer / fullerene bulk heterojunction solar cells. *Journal of Materials Chemistry*, 16(1), 45–61. <https://doi.org/10.1039/b510618b>
- Huang, Y., Kramer, E. J., Heeger, A. J., & Bazan, G. C. (2014). Bulk heterojunction solar cells: Morphology and performance relationships. *Chemical Reviews*, 114(14), 7006–7043. <https://doi.org/10.1021/cr400353v>
- Jana, R., Pathak, T. P., & Sigman, M. S. (2011). Advances in transition metal (Pd,Ni,Fe)-catalyzed cross-coupling reactions using alkyl-organometallics as reaction partners. *Chemical Reviews*, 111(3), 1417–1492.
<https://doi.org/10.1021/cr100327p>
- Jiang, H., Wu, Y., Islam, A., Wu, M., Zhang, W., Shen, C., Zhang, H., Li, E., Tian, H., & Zhu, W. (2018). Molecular Engineering of Quinoxaline-Based D – A – π – A Organic Sensitizers: Taking the Merits of a Large and Rigid Auxiliary Acceptor. *ACS Applied Materials and Interfaces*, 10, 13635–13644.
<https://doi.org/10.1021/acsami.8b02676>
- Kan, B., Zhang, Q., Liu, F., Wan, X., Wang, Y., & Ni, W. (2015). Bin Kan, Qian

- Zhang, Feng Liu, Xiangjian Wan, Yunchuang Wang, Wang Ni, Xuan Yang, Mingtao Zhang, Hongtao Zhang, Thomas P. Russell, Yongsheng Chen. *Chemistry of Materials*, 27, 8414–8423.
<https://doi.org/10.1021/acs.chemmater.5b03889>
- Kim, J. H., Park, J. B., Jung, I. H., Yoon, S. C., Kwak, J., & Hwang, D. H. (2015). New alkylthio-thieno[3,2-b]thiophene-substituted benzodithiophene-based highly efficient photovoltaic polymer. *Journal of Materials Chemistry C*, 3(17), 4250–4253. <https://doi.org/10.1039/c5tc00627a>
- Kitazawa, D., Watanabe, N., Yamamoto, S., & Tsukamoto, J. (2012). Conjugated polymers based on quinoxaline for polymer solar cells. *Solar Energy Materials & Solar Cells*, 98, 203–207.
<https://doi.org/10.1016/j.solmat.2011.11.010>
- Lee, S. W., Shin, H. J., Park, B., Shome, S., Whang, D. R., Bae, H., Chung, S., Cho, K., Ko, S. J., Choi, H., & Chang, D. W. (2022). Effect of Electron-Withdrawing Chlorine Substituent on Morphological and Photovoltaic Properties of All Chlorinated D-A-Type Quinoxaline-Based Polymers. *ACS Applied Materials and Interfaces*, 14(17), 19785–19794.
<https://doi.org/10.1021/acsami.2c00764>
- Lenaerts, R., Devisscher, D., Pirotte, G., Gielen, S., Mertens, S., Adriaenssens, P., Verstappen, P., Vandewal, K., & Maes, W. (2020). The effect of halogenation on PBDTT-TQxT based non-fullerene polymer solar cells – Chlorination vs fluorination. *Dyes and Pigments*, 181, 1–9.
<https://doi.org/10.1016/j.dyepig.2020.108577>
- Liu, D., Zhao, W., Zhang, S., Ye, L., Zheng, Z., Cui, Y., Chen, Y., & Hou, J. (2015). Highly Efficient Photovoltaic Polymers Based on Benzodithiophene and Quinoxaline with Deeper HOMO Levels. *Macromolecules*, 48(15), 5172–5178. <https://doi.org/10.1021/acs.macromol.5b00829>

- Liu, M., Gao, Y., Zhang, Y., Liu, Z., & Zhao, L. (2017). Quinoxaline-based conjugated polymers for polymer solar cells. *Polymer Chemistry*, 8(32), 4613–4636. <https://doi.org/10.1039/c7py00850c>
- Mahadevan, S., Liu, T., Pratik, S. M., Li, Y., Ho, H. Y., Ouyang, S., Lu, X., Yip, H. L., Chow, P. C. Y., Brédas, J. L., Coropceanu, V., So, S. K., & Tsang, S. W. (2024). Assessing intra- and inter-molecular charge transfer excitations in non-fullerene acceptors using electroabsorption spectroscopy. *Nature Communications*, 15(1), 1–10. <https://doi.org/10.1038/s41467-024-46462-x>
- Majhi, S., & K. Jash, S. (2023). Recent developments of nanocatalysts for Stille coupling reaction. *Synthetic Communications*, 53(24), 2061–2087. <https://doi.org/10.1080/00397911.2023.2269585>
- Marks, R. N., Halls, J. J. M., Bradley, D. D. C., Friend, R. H., & Holmes, A. B. (1994). The photovoltaic response in poly(p-phenylene vinylene) thin-film devices. *Journal of Physics: Condensed Matter*, 6(7), 1379–1394. <https://doi.org/10.1088/0953-8984/6/7/009>
- Murad, A. R., Iraqi, A., Aziz, S. B., Abdullah, S. N., & Brza, M. A. (2020). Conducting polymers for optoelectronic devices and organic solar cells: A review. *Polymers*, 12(11), 1–47. <https://doi.org/10.3390/polym12112627>
- Ohring, M. (1995). Polymers, Glasses, Ceramics, and Nonmetallic Mixtures. *Engineering Materials Science*, 135–188. <https://doi.org/10.1016/b978-012524995-9/50028-3>
- Peng, Q., Liu, X., Su, D., Fu, G., Xu, J., & Dai, L. (2011). Novel Benzo[1,2- b :4,5- b'] dithiophene – Benzothiadiazole Derivatives with Variable Side Chains for High-Performance Solar Cells. *Advanced Materials*, 23(39), 4554–4558. <https://doi.org/10.1002/adma.201101933>
- Pivrikas, A., Neugebauer, H., & Sariciftci, N. S. (2011). Influence of processing

- additives to nano-morphology and efficiency of bulk-heterojunction solar cells: A comparative review. *Solar Energy*, 85(6), 1226–1237.
<https://doi.org/10.1016/j.solener.2010.10.012>
- Po, R., Maggini, M., & Camaioni, N. (2010). Polymer solar cells: Recent approaches and achievements. *The Journal of Physical Chemistry C*, 114(2), 695–706. <https://doi.org/10.1021/jp9061362>
- Qi, B., & Wang, J. (2013). Fill factor in organic solar cells. *Physical Chemistry Chemical Physics*, 15(23), 8972–8982. <https://doi.org/10.1039/c3cp51383a>
- Qiao, Z., Wang, M., Zhao, M., Zhang, Z., Li, Y., Li, X., & Wang, H. (2015). Effect of fluorine substitution on the photovoltaic performance of poly(thiophene-quinoxaline) copolymers. *Polymer Chemistry*, 6(47), 8203–8213.
<https://doi.org/10.1039/c5py01193k>
- Qunping Fan, H. J., Yu Liu, W. S., Hua Tan, Y. W., & , Renqiang Yang, W. Z. (2016). Efficient polymer solar cells based on a new quinoxaline derivative with fluorinated phenyl side chain. *Journal of Materials Chemistry C*, 4(13), 2606–2613. <https://doi.org/10.1039/C6TC00353B>
- Rasmussen, S. C., Gilman, S. J., & Wilcox, W. D. (2023). Conjugated Polymers : Synthesis & Design Individual sales Institutional sales. *American Chemical Society*. <https://doi.org/10.1021/acsinfocus.7e7026>
- Scharber, M. C., Mühlbacher, D., Koppe, M., Denk, P., Waldauf, C., Heeger, A. J., & Brabec, C. J. (2006). Design rules for donors in bulk-heterojunction solar cells - Towards 10 % energy-conversion efficiency. *Advanced Materials*, 18(6), 789–794. <https://doi.org/10.1002/adma.200501717>
- Stille, J. K. (1986). The Palladium-Catalyzed Cross-Coupling Reactions of Organotin Reagents with Organic Electrophiles. *New Synthetic Methods*, 25(6), 508–524. <https://doi.org/10.1002/anie.198605081>

- Tang, C. W. (1986). Two-layer organic photovoltaic cell. *Applied Physics Letters*, 48(2), 183–185. <https://doi.org/10.1063/1.96937>
- Vak, D., & Kim, S. S. (2007). Fabrication of organic bulk heterojunction solar cells by a spray deposition method for low-cost power generation. *Applied Physics Letters*, 91(8), 1–3. <https://doi.org/10.1063/1.2772766>
- Vilas-Boas, Â., Valderrama, P., Fontes, N., Geraldo, D., & Bento, F. (2019). Evaluation of total polyphenol content of wines by means of voltammetric techniques: Cyclic voltammetry vs differential pulse voltammetry. *Food Chemistry*, 276, 719–725. <https://doi.org/10.1016/j.foodchem.2018.10.078>
- Wadsworth, A., Hamid, Z., Bidwell, M., Ashraf, R. S., Khan, J. I., Anjum, D. H., Cendra, C., Yan, J., Rezasoltani, E., Guilbert, A. A. Y., Azzouzi, M., Gasparini, N., Bannock, J. H., Baran, D., Wu, H., de Mello, J. C., Brabec, C. J., Salleo, A., Nelson, J. McCulloch, I. (2018). Progress in Poly (3-Hexylthiophene) Organic Solar Cells and the Influence of Its Molecular Weight on Device Performance. *Advanced Energy Materials*, 8(28), 1–15. <https://doi.org/10.1002/aenm.201801001>
- Wang, J. L., Liu, K. K., Yan, J., Wu, Z., Liu, F., Xiao, F., Chang, Z. F., Wu, H. Bin, Cao, Y., & Russell, T. P. (2016). Series of Multifluorine Substituted Oligomers for Organic Solar Cells with Efficiency over 9% and Fill Factor of 0.77 by Combination Thermal and Solvent Vapor Annealing. *Journal of the American Chemical Society*, 138(24), 7687–7697. <https://doi.org/10.1021/jacs.6b03495>
- Wu, J. S., Cheng, S. W., Cheng, Y. J., & Hsu, C. S. (2015). Donor-acceptor conjugated polymers based on multifused ladder-type arenes for organic solar cells. *Chemical Society Reviews*, 44(5), 1113–1154. <https://doi.org/10.1039/c4cs00250d>
- Y. Ito, S. Okamura, B. R. (1937). *Macromolecular Concept and Strategy for*

- Humanity in Science, Technology and Industry* (first edit). Springer-Verlag Berlin. <https://doi.org/10.1007/978-3-642-61036-3>
- Yan, C., Barlow, S., Wang, Z., Yan, H., Jen, A. K. Y., Marder, S. R., & Zhan, X. (2018). Non-fullerene acceptors for organic solar cells. *Nature Reviews Materials*, 3, 1–19. <https://doi.org/10.1038/natrevmats.2018.3>
- Yan, Y., Zhang, Y., Liu, Y., Shi, Y., Qiu, D., Deng, D., Zhang, J., Wang, B., Adil, M. A., Amin, K., Memon, W. A., Wang, M., Zhou, H., Zhang, X., & Wei, Z. (2022). Simultaneously Decreasing the Bandgap and Voc Loss in Efficient Ternary Organic Solar Cells. *Advanced Energy Materials*, 12(20), 1–9. <https://doi.org/10.1002/aenm.202200129>
- Yang, P., Yuan, M., Zeigler, D. F., Watkins, S. E., Lee, J. A., & Luscombe, C. K. (2014). Influence of fluorine substituents on the film dielectric constant and open-circuit voltage in organic photovoltaics. *Journal of Materials Chemistry C*, 2(17), 3278–3284. <https://doi.org/10.1039/c3tc32087a>
- Yao, H., Ye, L., Zhang, H., Li, S., Zhang, S., & Hou, J. (2016). Molecular design of benzodithiophene-based organic photovoltaic materials. *Chemical Reviews* 116(12), 7397–7457. <https://doi.org/10.1021/acs.chemrev.6b00176>
- Ye, L., Zhang, S., Zhao, W., Yao, H., & Hou, J. (2014). Highly Efficient 2D-Conjugated Benzodithiophene-Based Photovoltaic Polymer with Linear Alkylthio Side Chain. *Chemistry of Materials*, 26, 3603–3605. <https://dx.doi.org/10.1021/cm501513n>
- Yeh, N., & Yeh, P. (2013). Organic solar cells: Their developments and potentials. *Renewable and Sustainable Energy Reviews*, 21, 421–431. <https://doi.org/10.1016/j.rser.2012.12.046>
- Yu, G., Gao, J., Hummelen, J. C., Wudi, F., & Heeger, A. J. (1995). Polymer Photovoltaic Cells: Enhanced Efficiencies via Network of Internal Donor-

- Acceptor Heterojunctions. *Science*, 270(5243), 1789–1792.
<https://doi.org/10.1126/science.270.5243.1789>
- Yuan, J., Zhang, Y., Zhou, L., Zhang, G., Yip, H. L., Lau, T. K., Lu, X., Zhu, C., Peng, H., Johnson, P. A., Leclerc, M., Cao, Y., Ulanski, J., Li, Y., & Zou, Y. (2019). Single-Junction Organic Solar Cell with over 15% Efficiency Using Fused-Ring Acceptor with Electron-Deficient Core. *Joule*, 3(4), 1140–1151.
<https://doi.org/10.1016/j.joule.2019.01.004>
- Yuan, J., & Zou, Y. (2022). The history and development of Y6. *Organic Electronics*, 102, 1–5. <https://doi.org/10.1016/j.orgel.2022.106436>
- Zhan, X., & Zhu, D. (2010). Conjugated polymers for high-efficiency organic photovoltaics. *Polymer Chemistry*, 1(4), 409–419.
<https://doi.org/10.1039/b9py00325h>
- Zhang, Y., Gao, X., Li, J., & Tu, G. (2015). Highly selective Palladium-catalyzed Suzuki coupling reaction toward chlorine-containing electroluminescence polymers. *Dyes and Pigments*, 120, 112–117.
<https://doi.org/10.1016/j.dyepig.2015.03.031>
- Zhao, F., Wang, C., & Zhan, X. (2018). Morphology Control in Organic Solar Cells. *Advanced Energy Materials*, 8(28), 1–34.
<https://doi.org/10.1002/aenm.201703147>
- Zhao, W., Qian, D., Zhang, S., Li, S., Inganäs, O., Gao, F., & Hou, J. (2016). Fullerene-Free Polymer Solar Cells with over 11% Efficiency and Excellent Thermal Stability. *Advanced Materials*, 28(23), 4734–4739.
<https://doi.org/10.1002/adma.201600281>
- Zhou, B., Dai, T., Zhou, J., Chen, Y., Geng, Y., Lei, P., Zheng, G., Zeng, Q., & Zhou, E. (2023). Conjugated D- π -A photovoltaic polymers containing thieno[3,2-b]thiophene π -bridge. *Materials Chemistry Frontiers*, 8(6), 1563–

1590. <https://doi.org/10.1039/d3qm00849e>

Zhou, H., Yang, L., & You, W. (2012). Rational design of high performance conjugated polymers for organic solar cells. *Macromolecules*, 45(2), 607–632. <https://doi.org/10.1021/ma201648t>

Zhu, C., Meng, L., Zhang, J., Qin, S., Lai, W., Qiu, B., Yuan, J., Wan, Y., Huang, W., & Li, Y. (2021). A Quinoxaline-Based D–A Copolymer Donor Achieving 17.62% Efficiency of Organic Solar Cells. *Advanced Materials*, 33(23), 1–9. <https://doi.org/10.1002/adma.202100474>



APPENDICES

A. Spectra

Bruker Spectrospin Avance DPX-400 Spectrometer was employed to analyze each chemical. TMS and CDCl_3 , a deuterated solvent, were employed as internal standards.

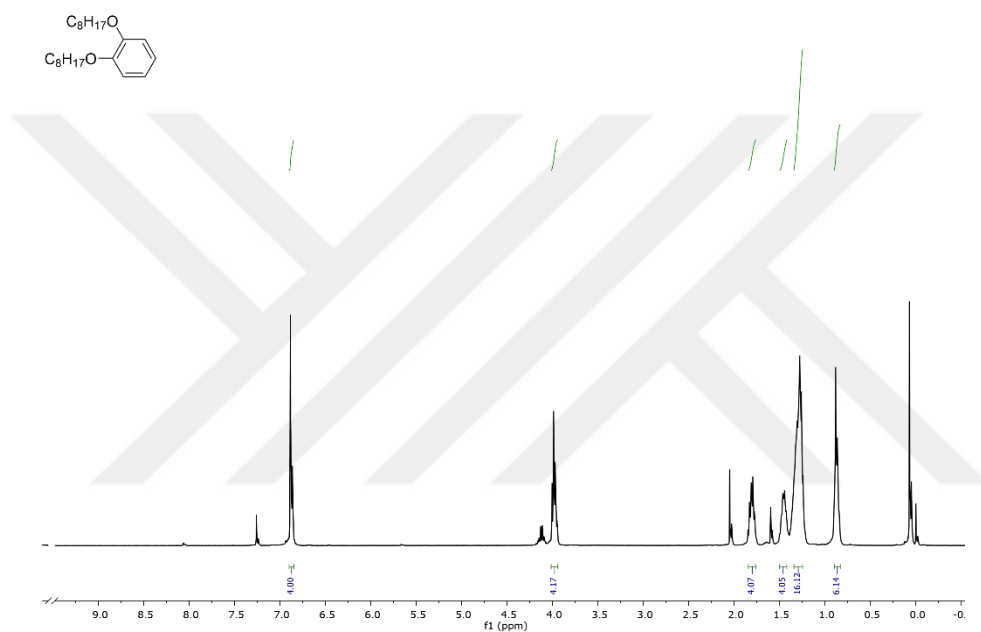


Figure A.1. ^1H NMR spectrum of **compound 2** in CDCl_3

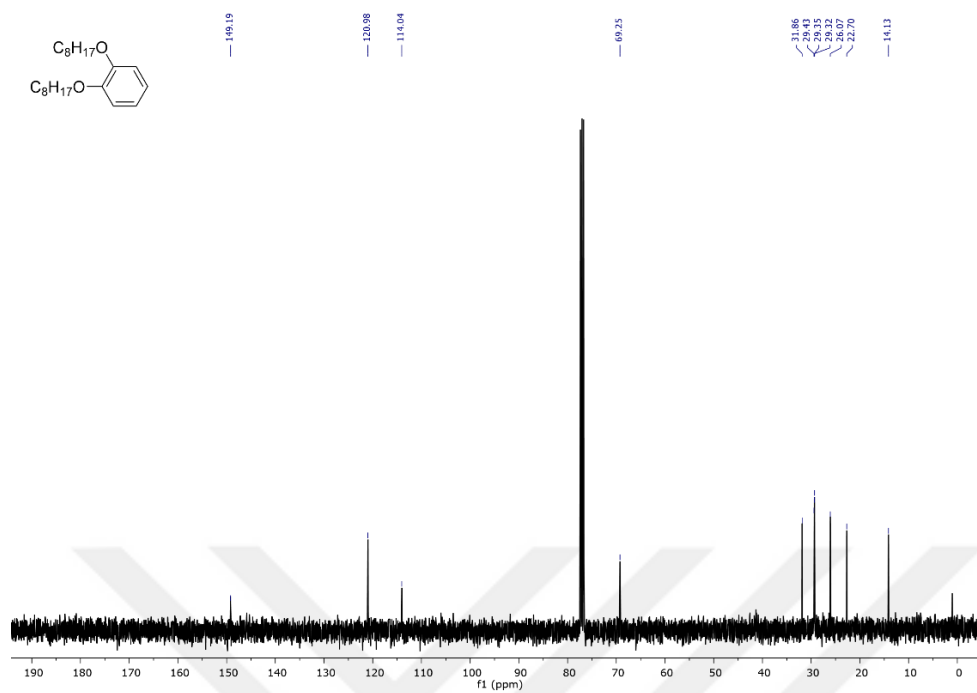


Figure A.2. ^{13}C NMR spectrum of compound 2 in CDCl_3

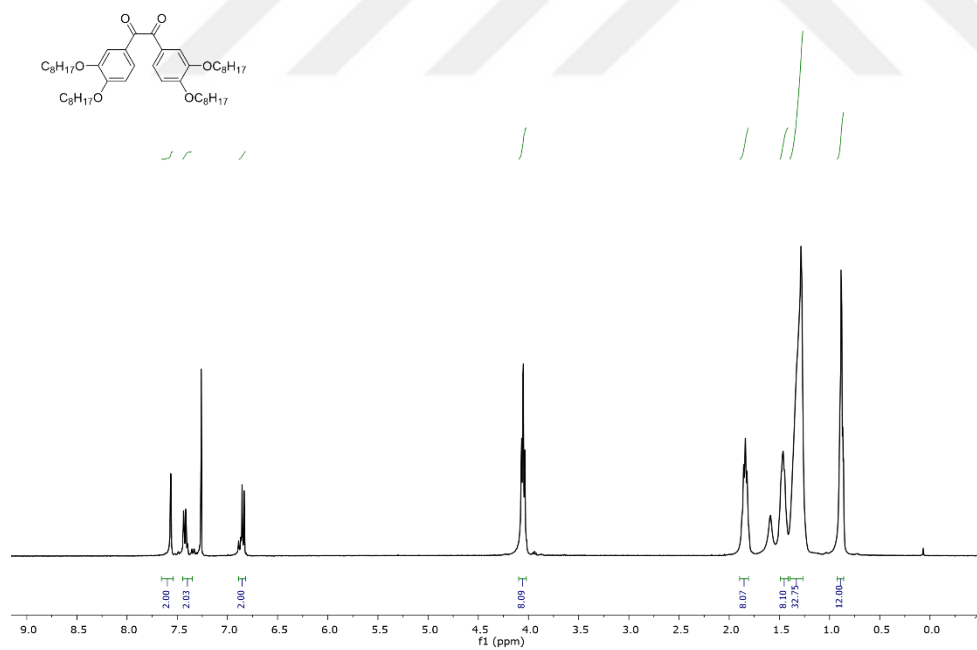


Figure A.3. ^1H NMR spectrum of compound 3 in CDCl_3

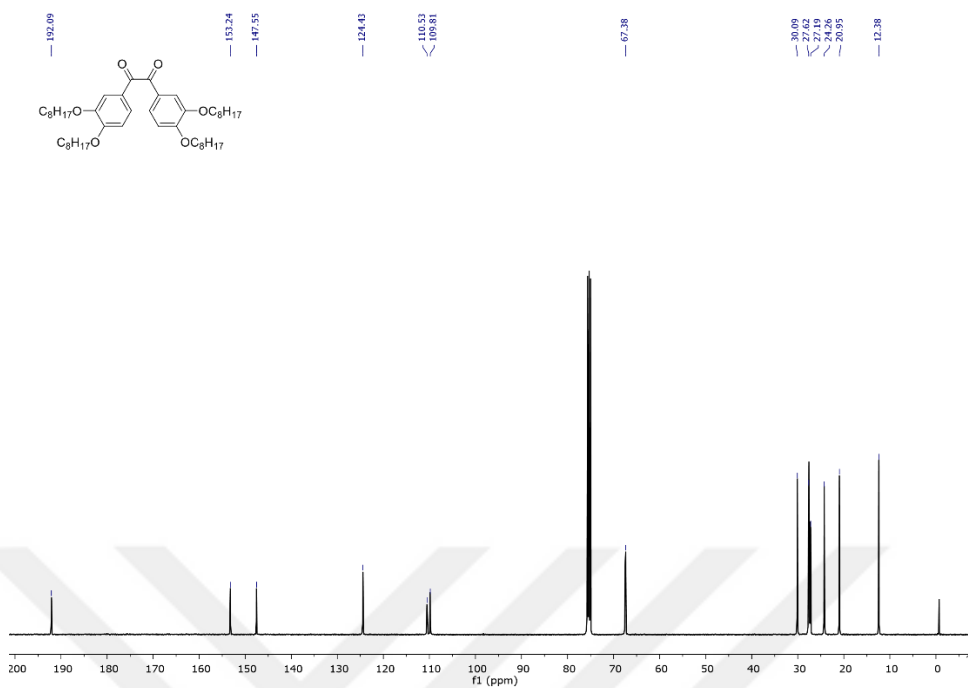


Figure A.4. ¹³C NMR spectrum of compound **3** in CDCl₃

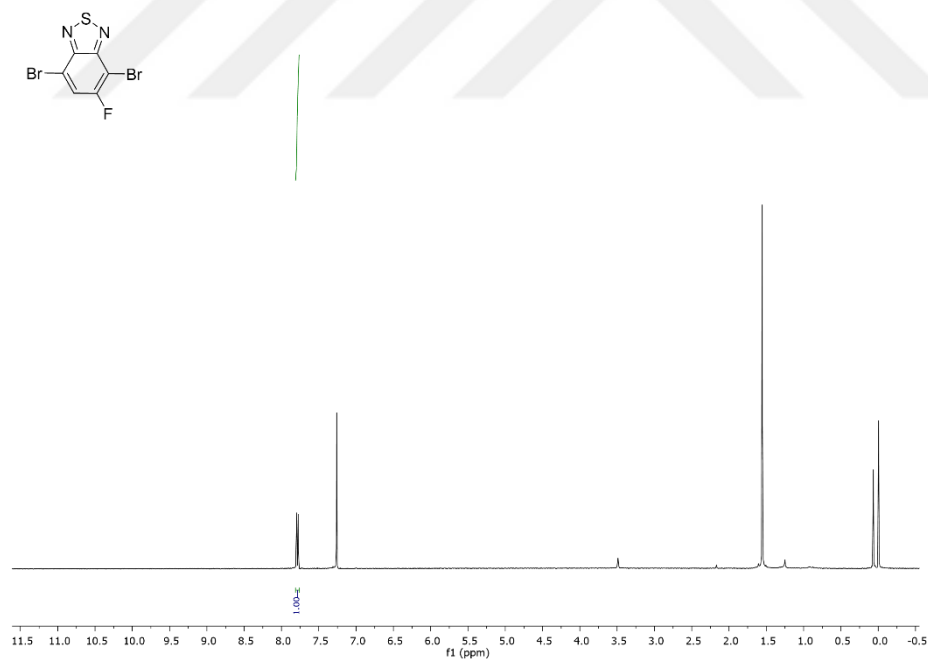


Figure A.5. ¹H NMR spectrum of compound **13** in CDCl₃

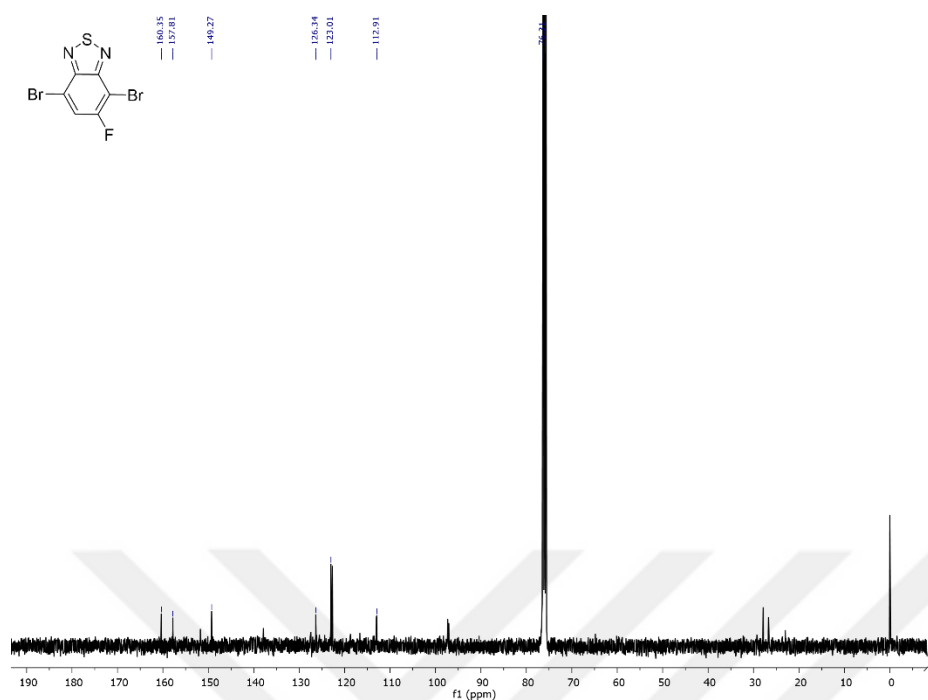


Figure A.6. ^{13}C NMR spectrum of compound **13** in CDCl_3

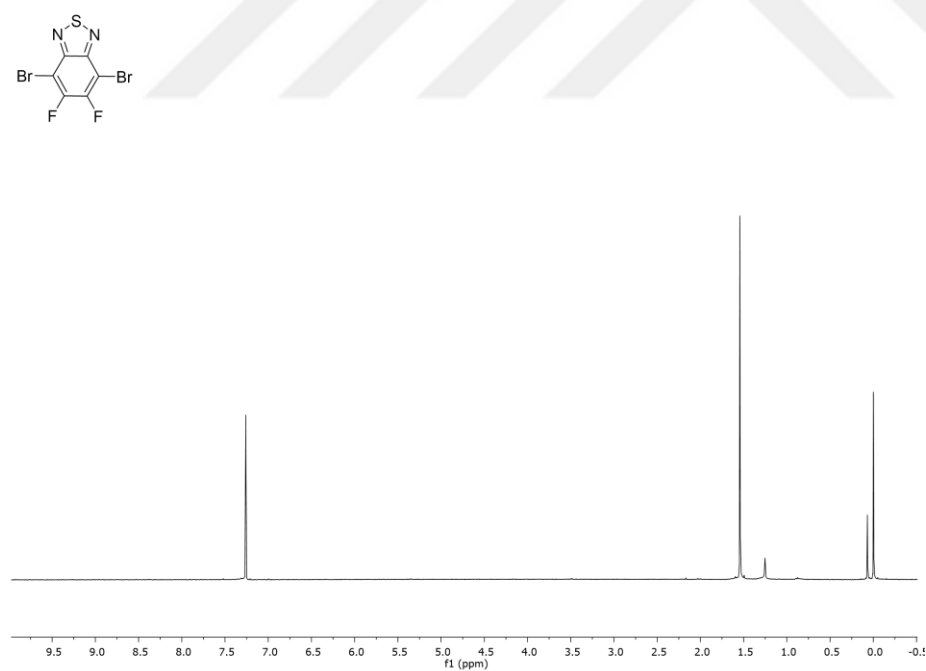


Figure A.7. ^1H NMR spectrum of compound **14** in CDCl_3

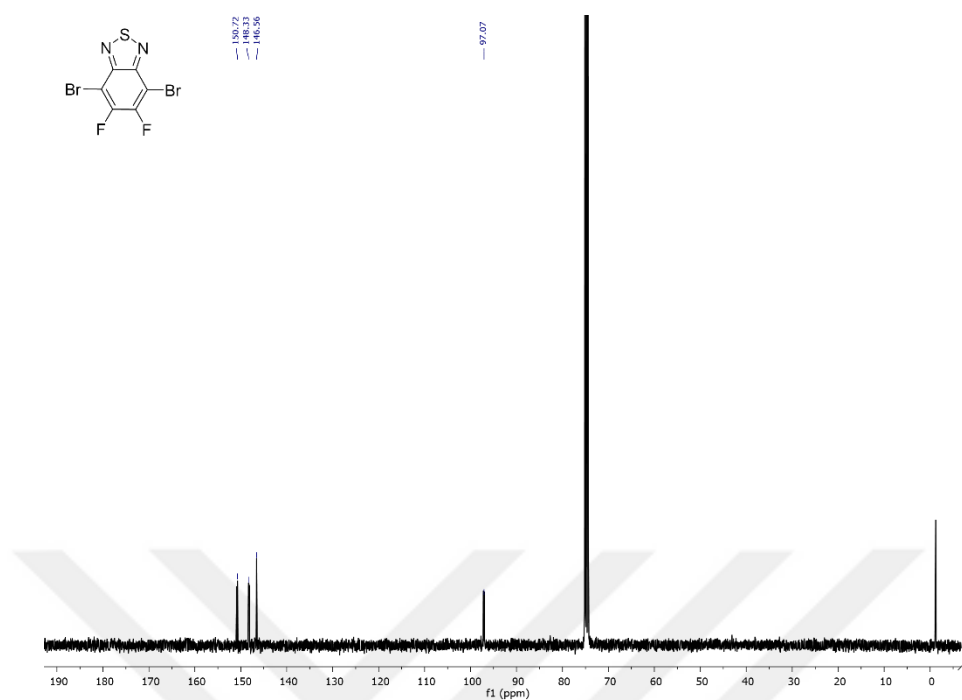


Figure A.8. ^{13}C NMR spectrum of compound **13** in CDCl₃

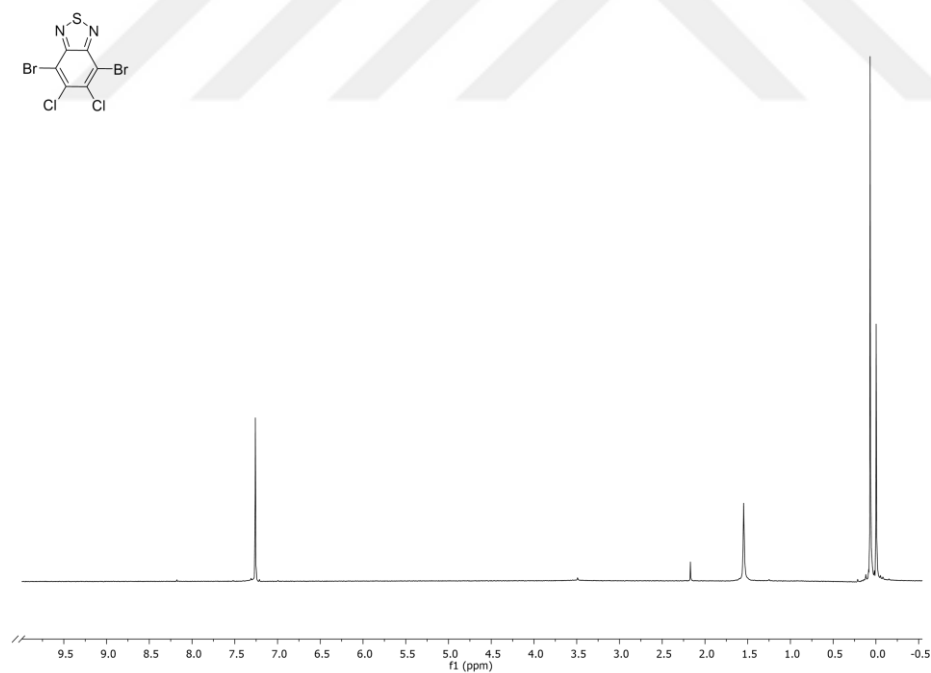


Figure A.9. ^1H NMR spectrum of compound **14** in CDCl₃

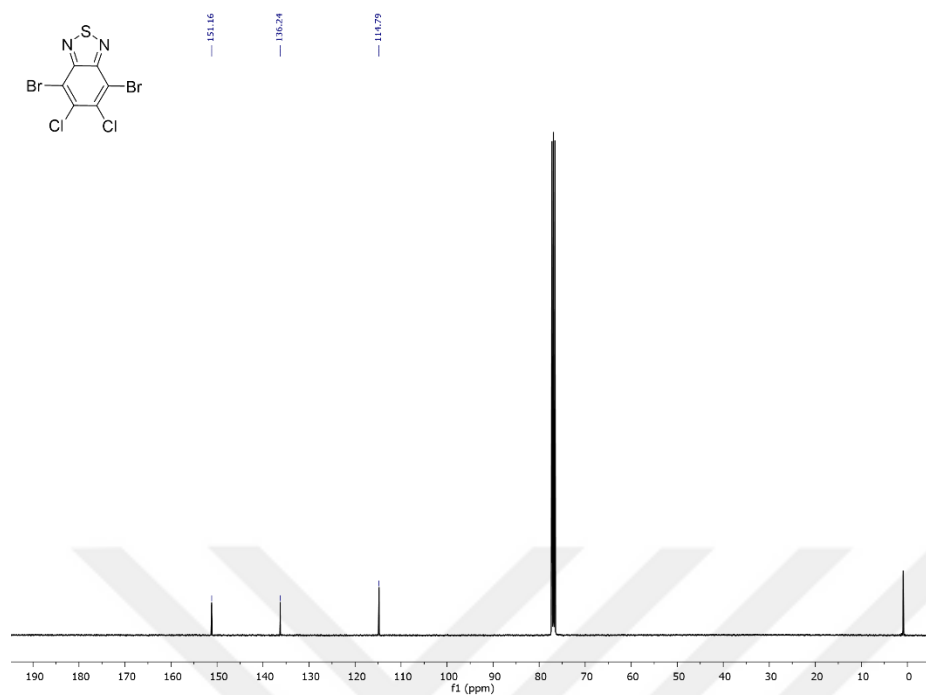


Figure A.10. ^{13}C NMR spectrum of compound **13** in CDCl_3

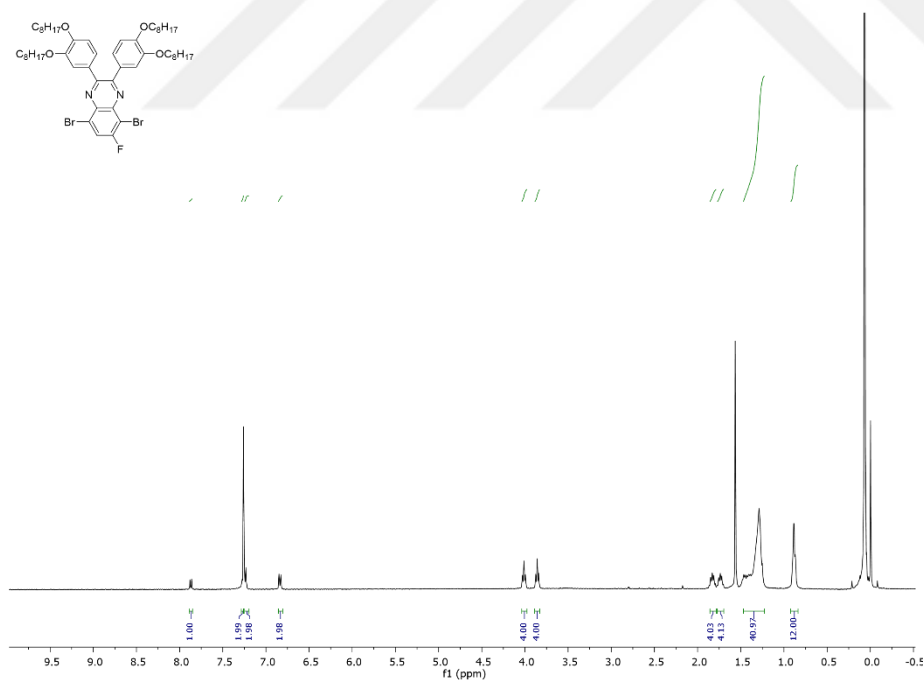


Figure 4.11. ^1H NMR spectrum of compound **19** in CDCl_3

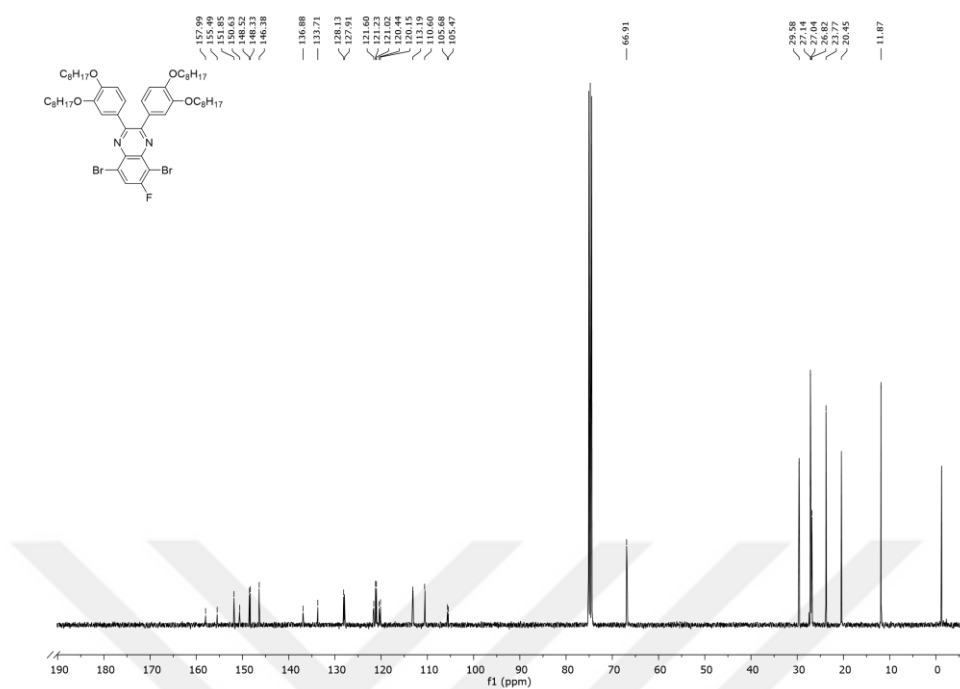


Figure A.12. ¹³C NMR spectrum of compound **19** in CDCl₃

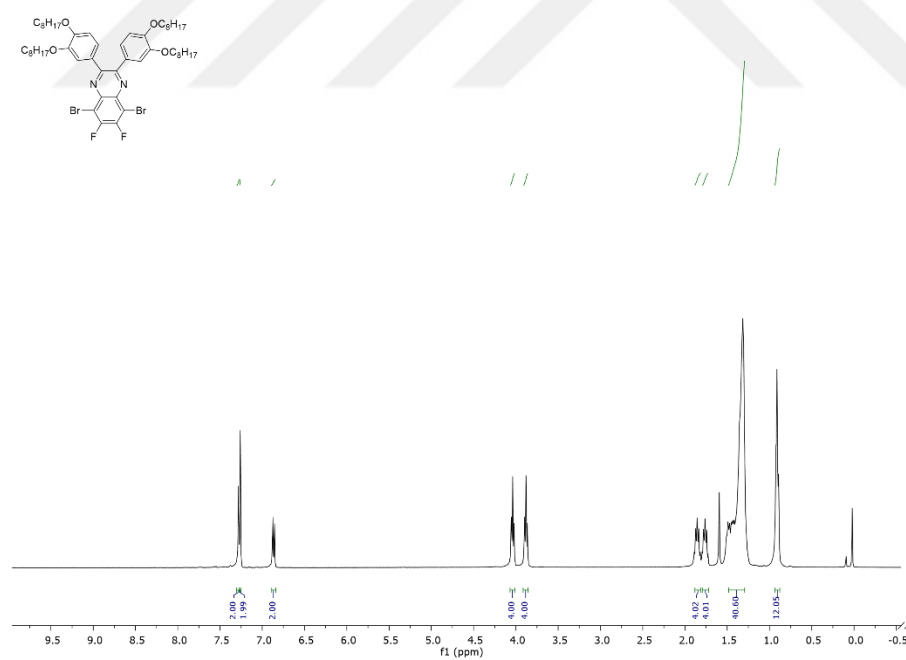


Figure A.13. ¹H NMR spectrum of compound **20** in CDCl₃

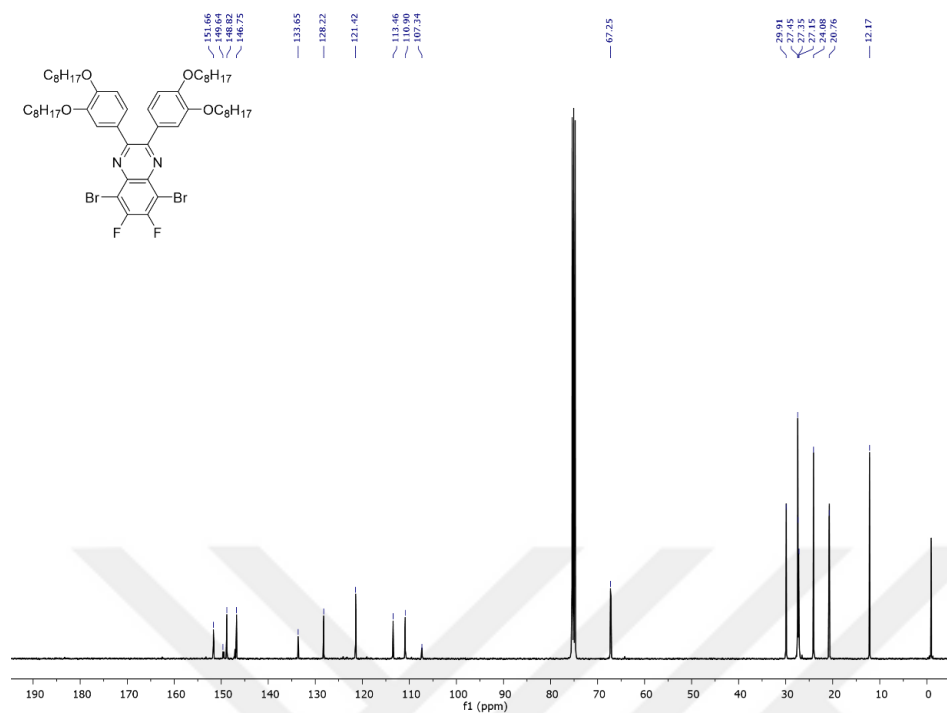


Figure A.14. ^{13}C NMR spectrum of compound **20** in CDCl_3

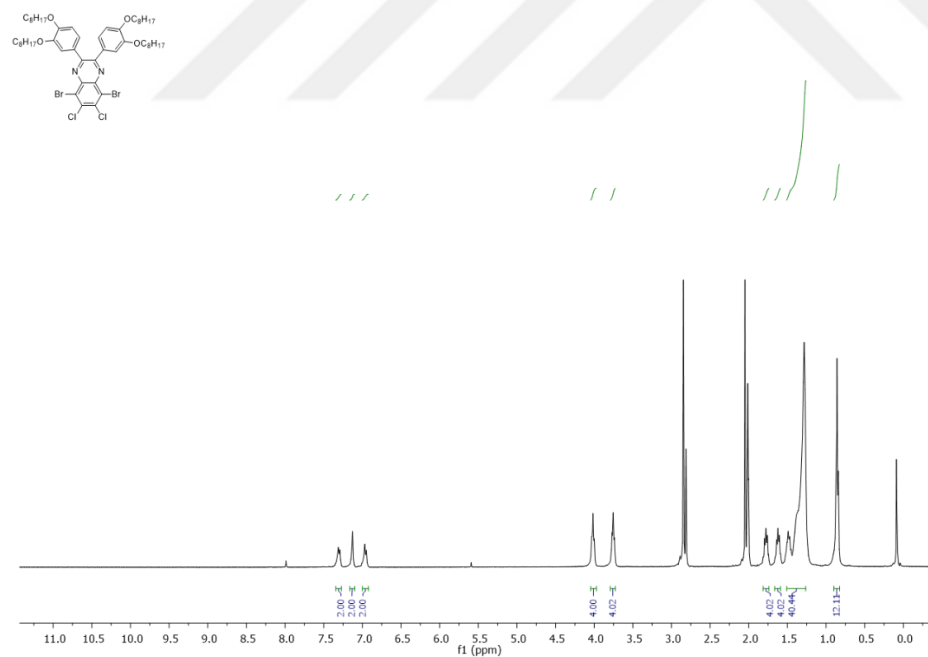


Figure A.15. ^1H NMR spectrum of compound **21** in CDCl_3

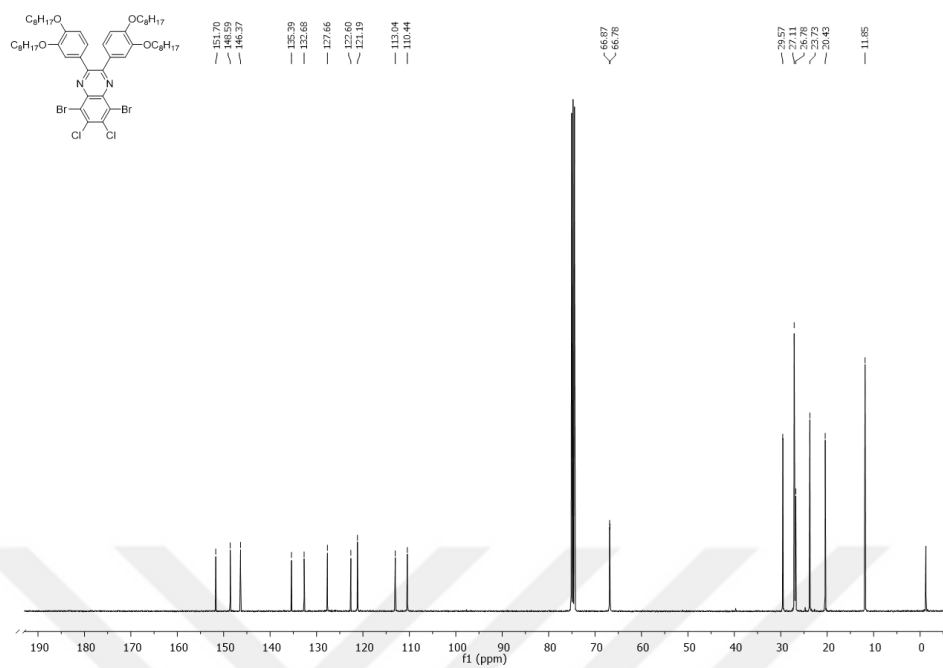


Figure A.16. ^{13}C NMR spectrum of compound **20** in CDCl_3

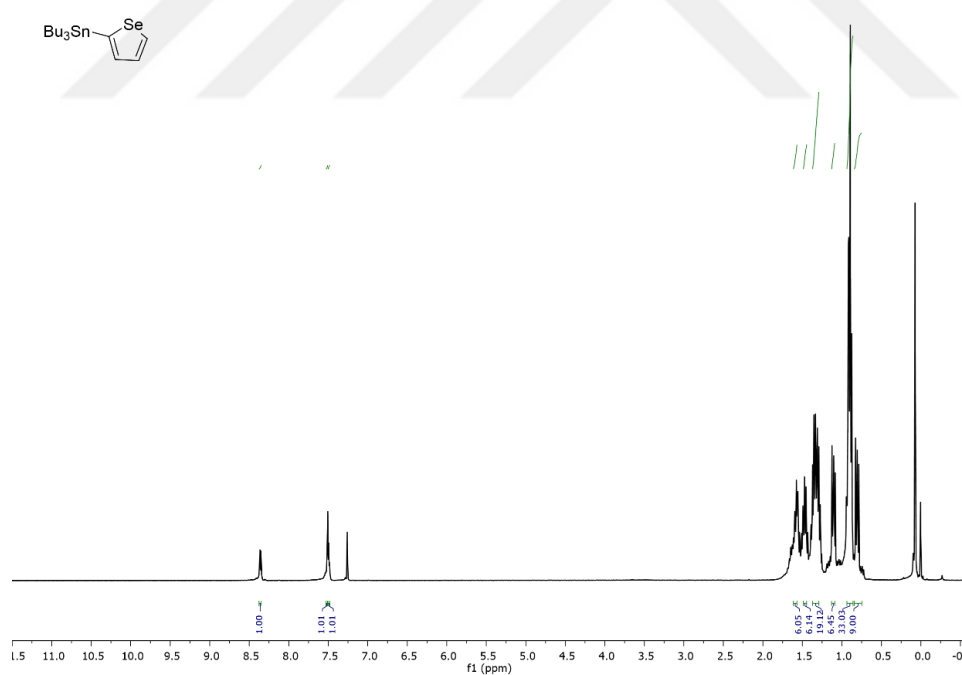
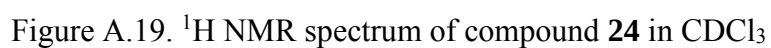
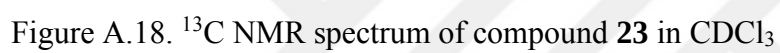


Figure A.17. ^1H NMR spectrum of compound **23** in CDCl_3



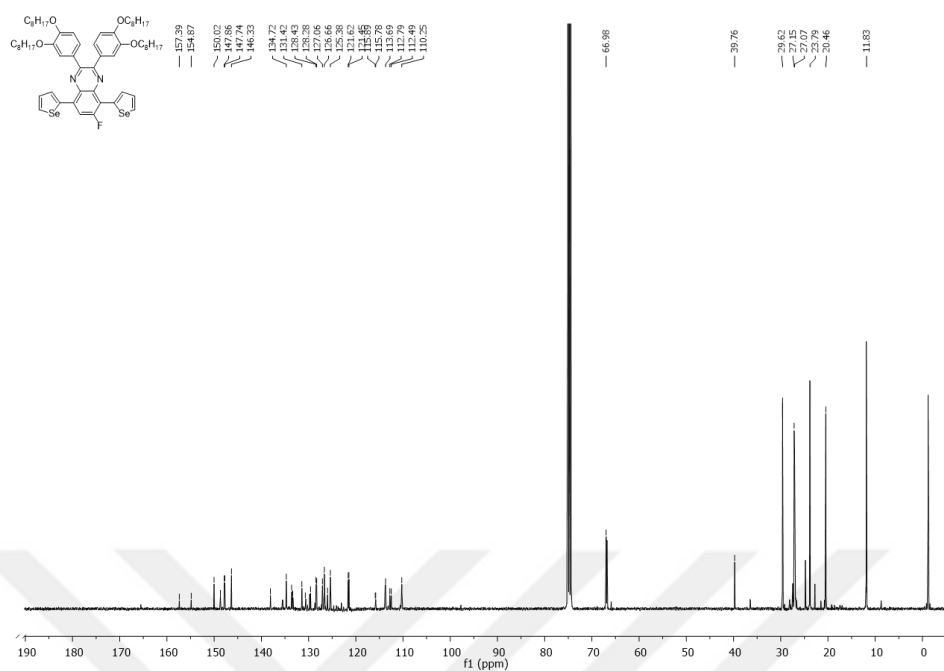


Figure A.20. ¹³C NMR spectrum of compound **24** in CDCl₃

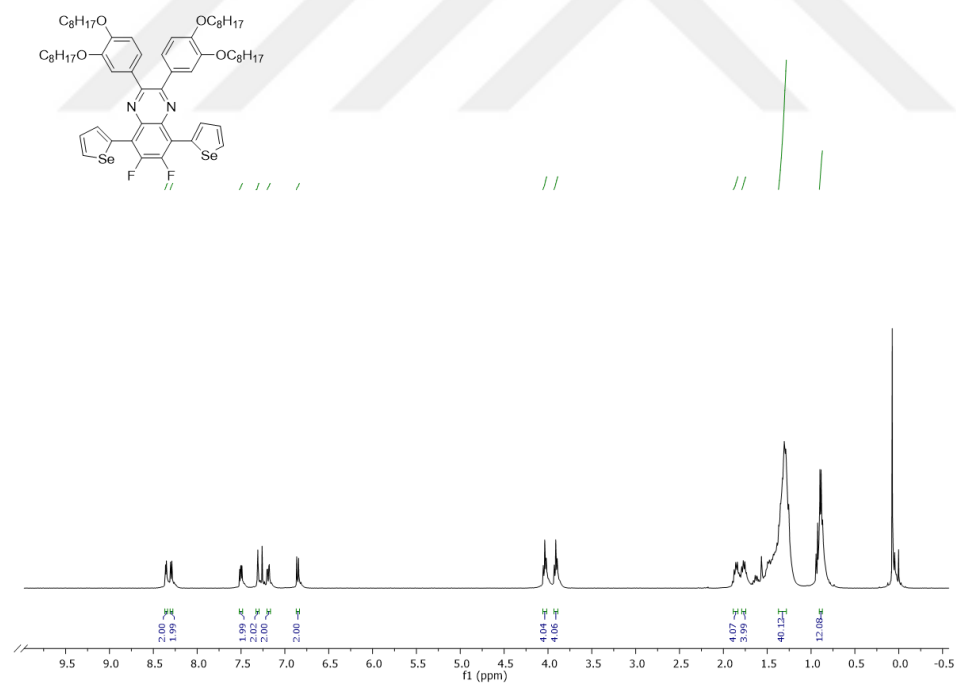


Figure A.21. ¹H NMR spectrum of compound **25** in CDCl₃

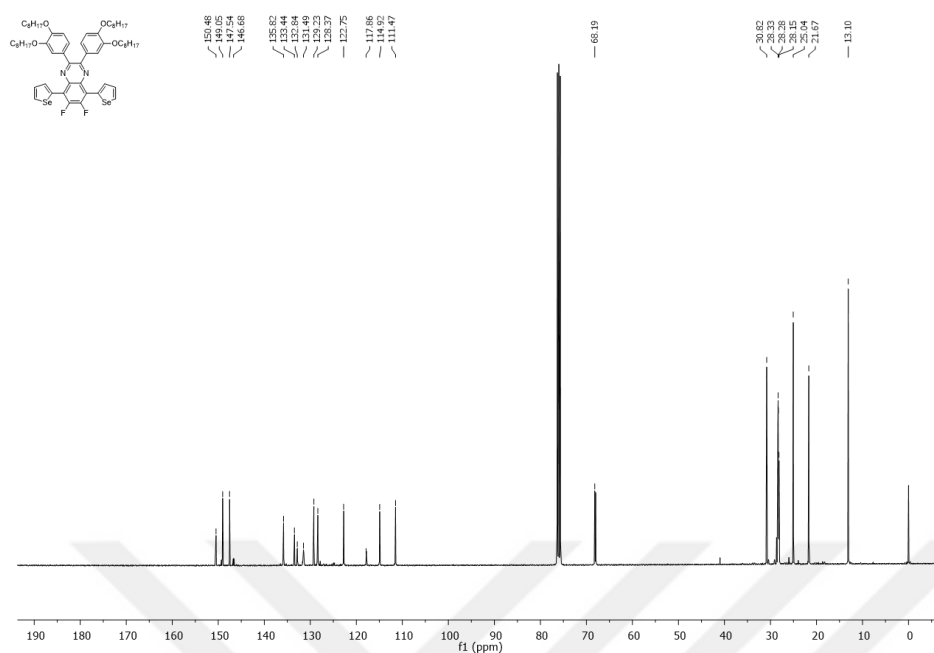


Figure A.22. ¹³C NMR spectrum of compound **25** in CDCl₃

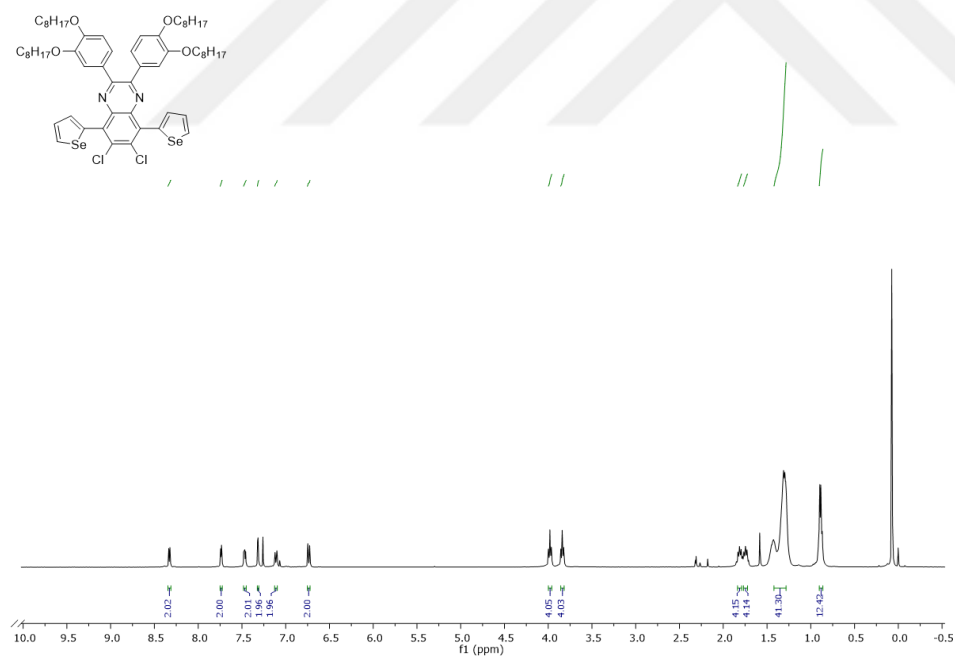


Figure A.23. ¹H NMR spectrum of compound **26** in CDCl₃

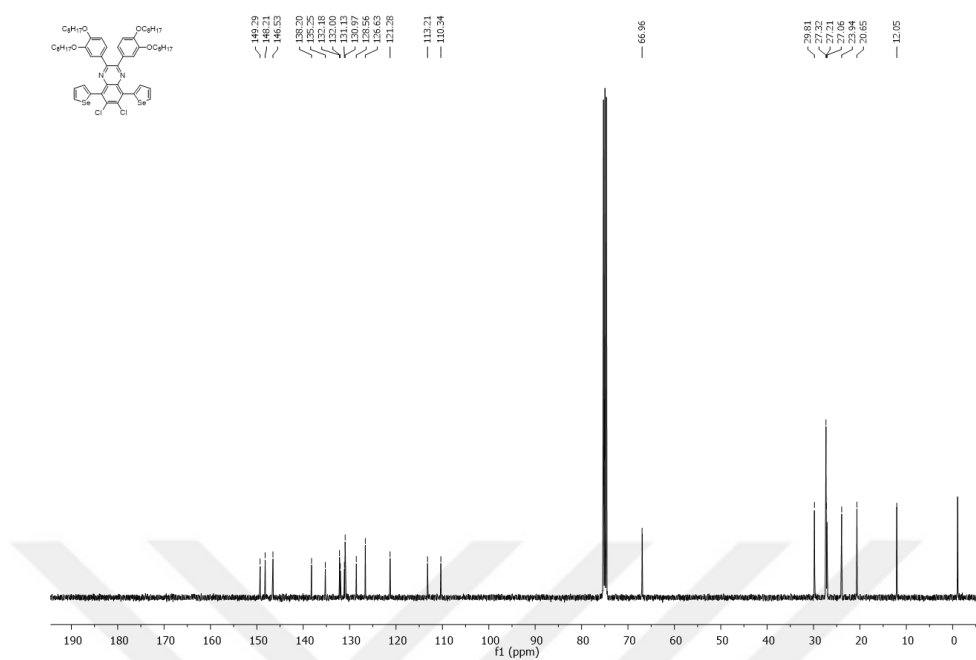


Figure A.24. ^{13}C NMR spectrum of compound **26** in CDCl_3

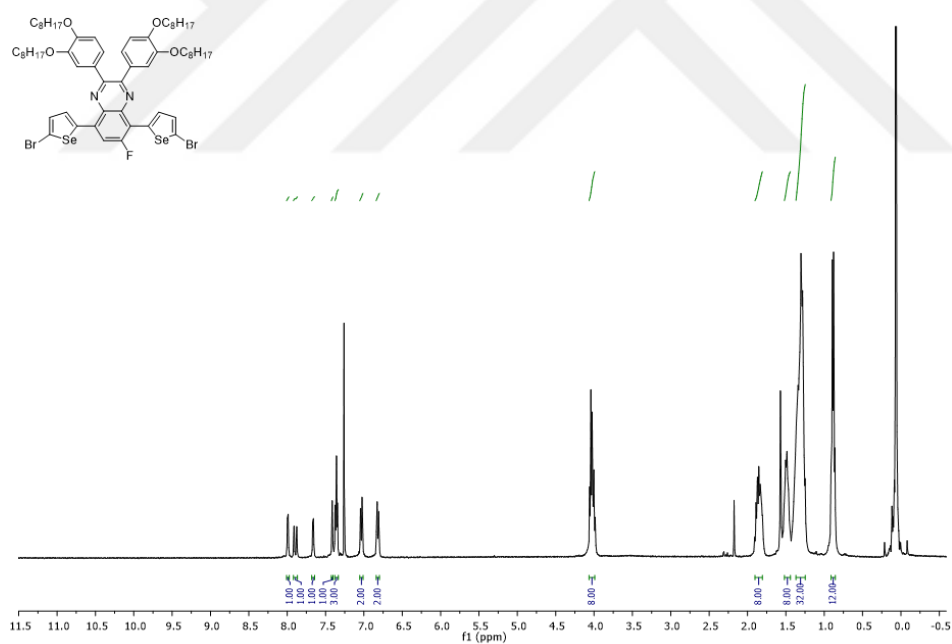
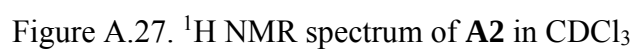


Figure A.25. ^1H NMR spectrum of **A1** in CDCl_3



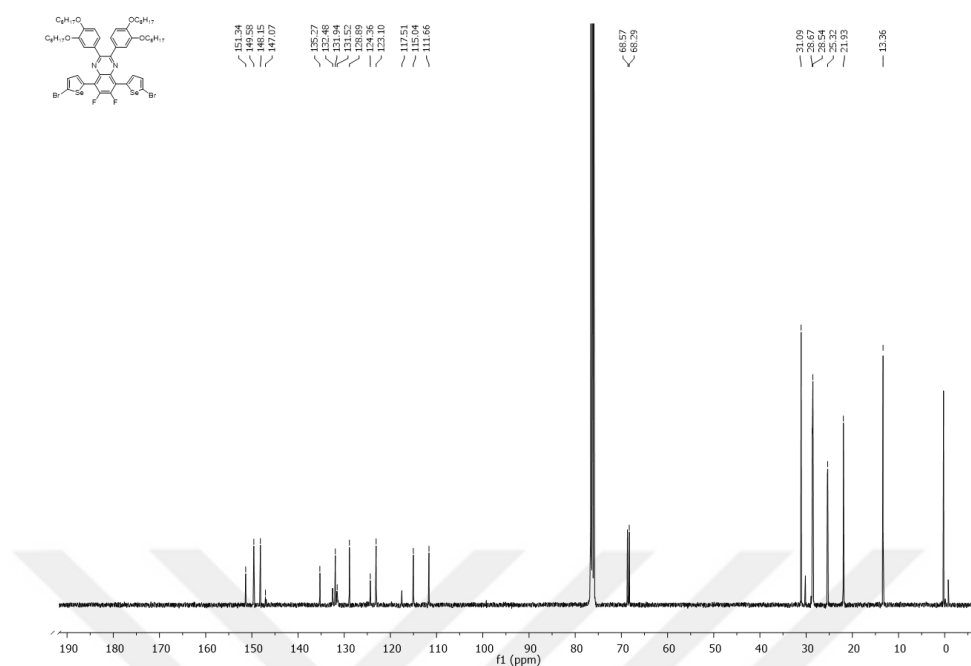


Figure A.28. ^{13}C NMR spectrum of compound **A2** in CDCl_3

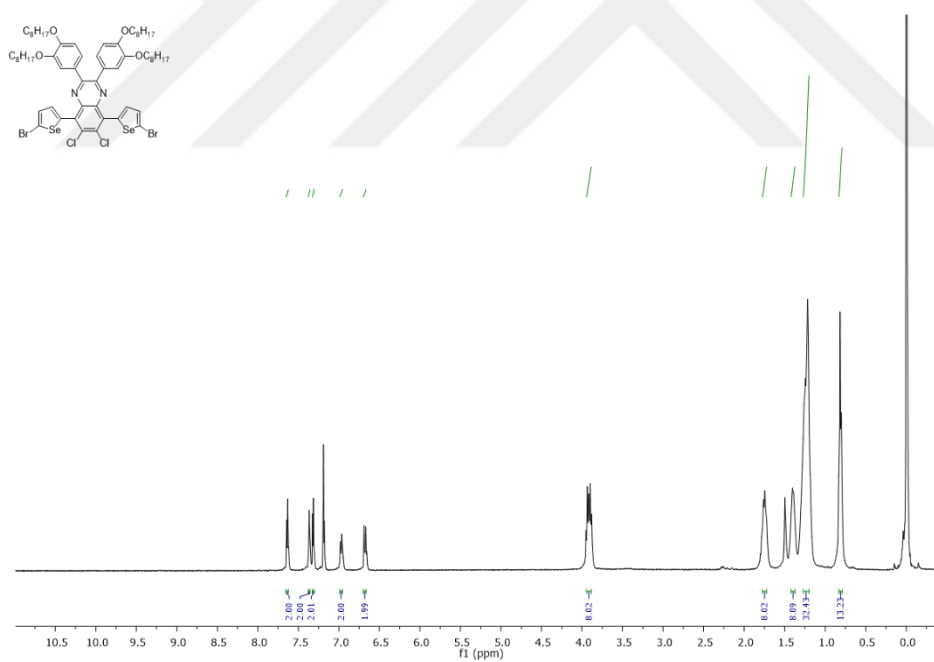
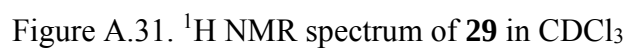


Figure A.29. ^1H NMR spectrum of **A3** in CDCl_3



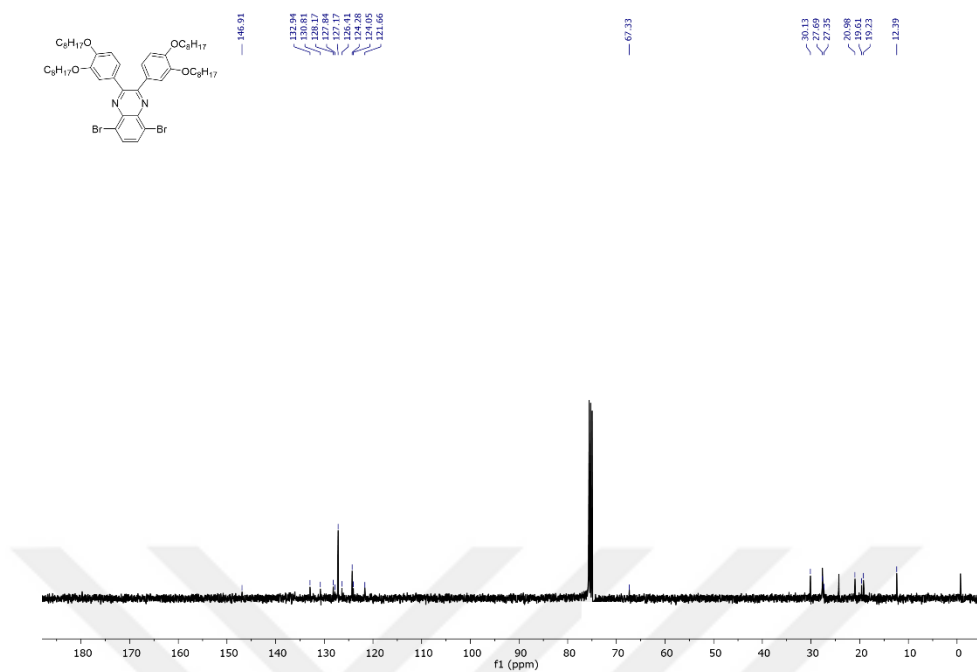


Figure A.32. ^{13}C NMR spectrum of compound **29** in CDCl_3

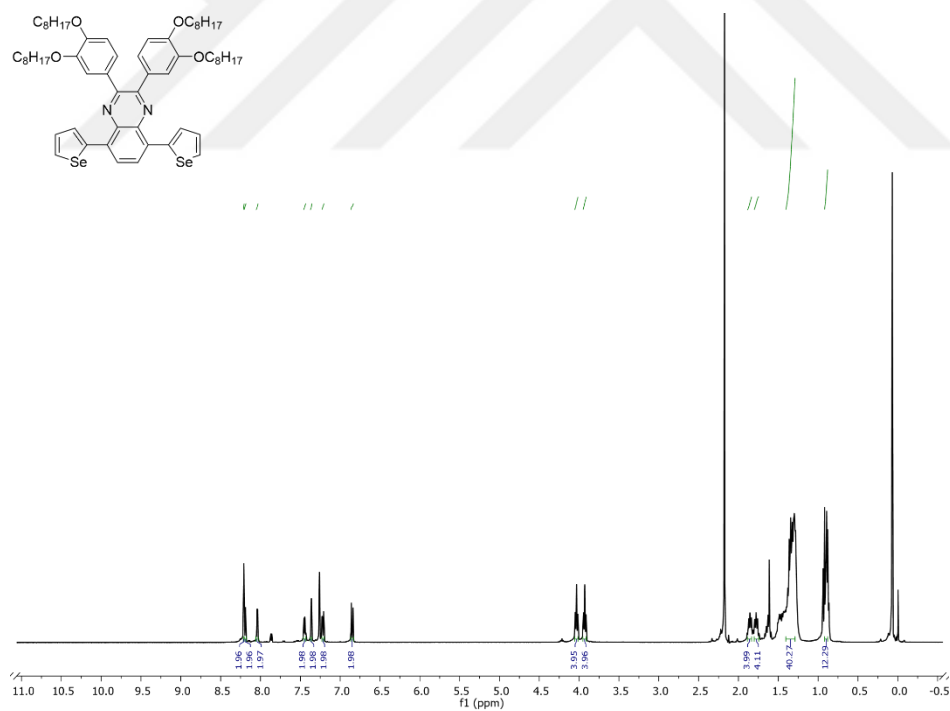


Figure A.33. ^1H NMR spectrum of **30** in CDCl_3

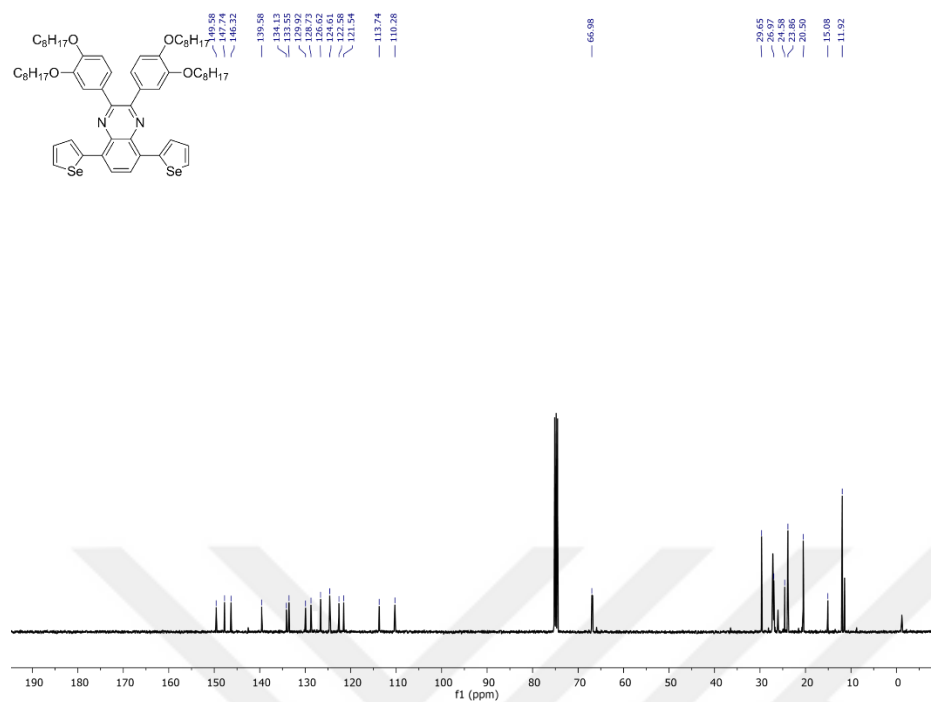


Figure A.34. ^{13}C NMR spectrum of compound **30** in CDCl_3

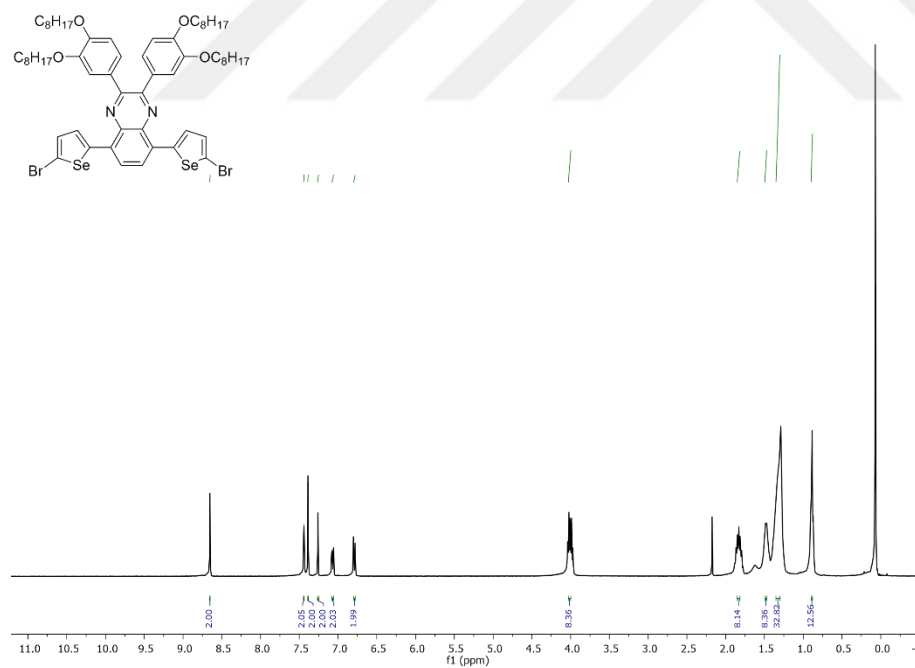


Figure A.35. ^1H NMR spectrum of **A4** in CDCl_3

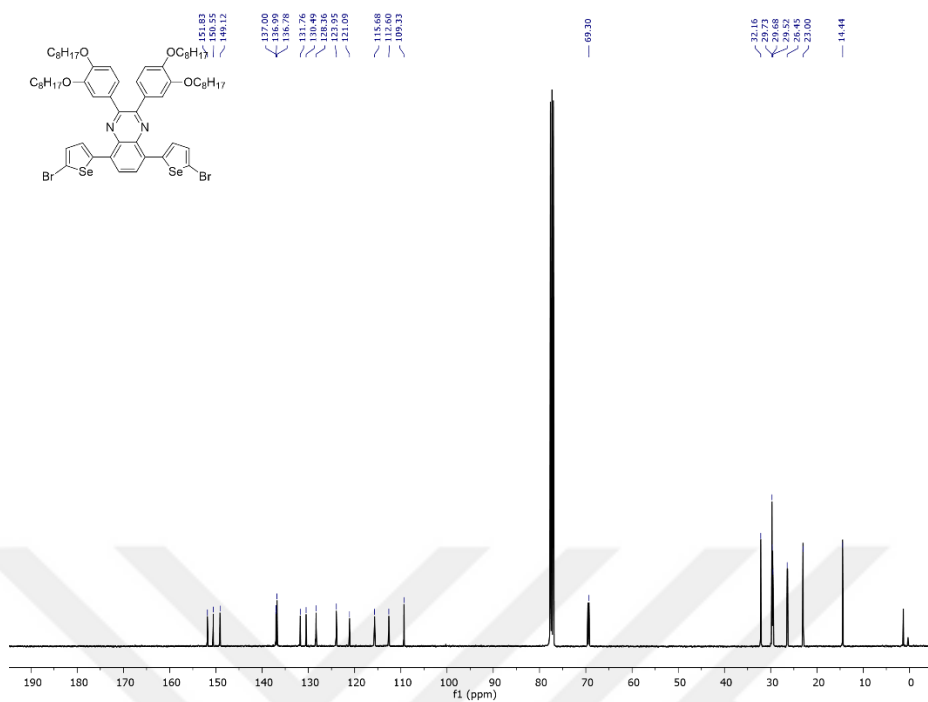


Figure A.36. ¹³C NMR spectrum of compound **A4** in CDCl₃

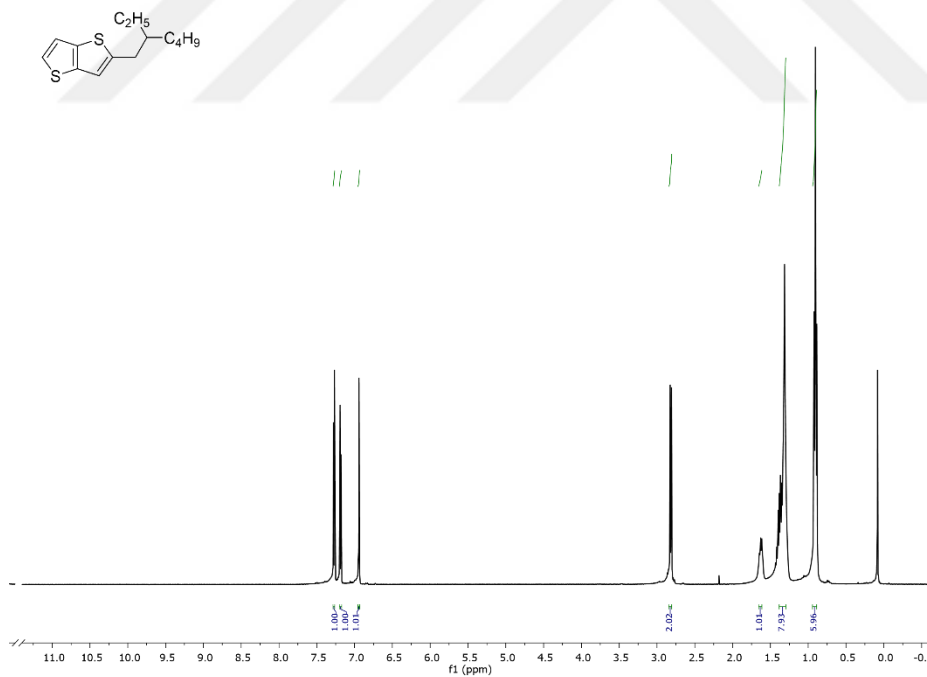


Figure A.37. ¹H NMR spectrum of **32** in CDCl₃

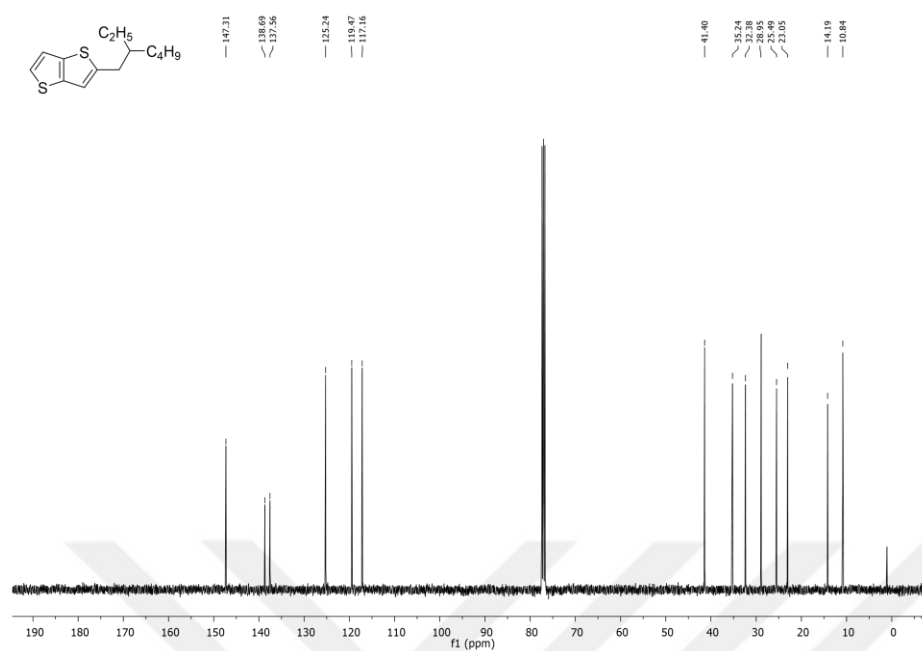


Figure A.38. ^{13}C NMR spectrum of compound **32** in CDCl_3

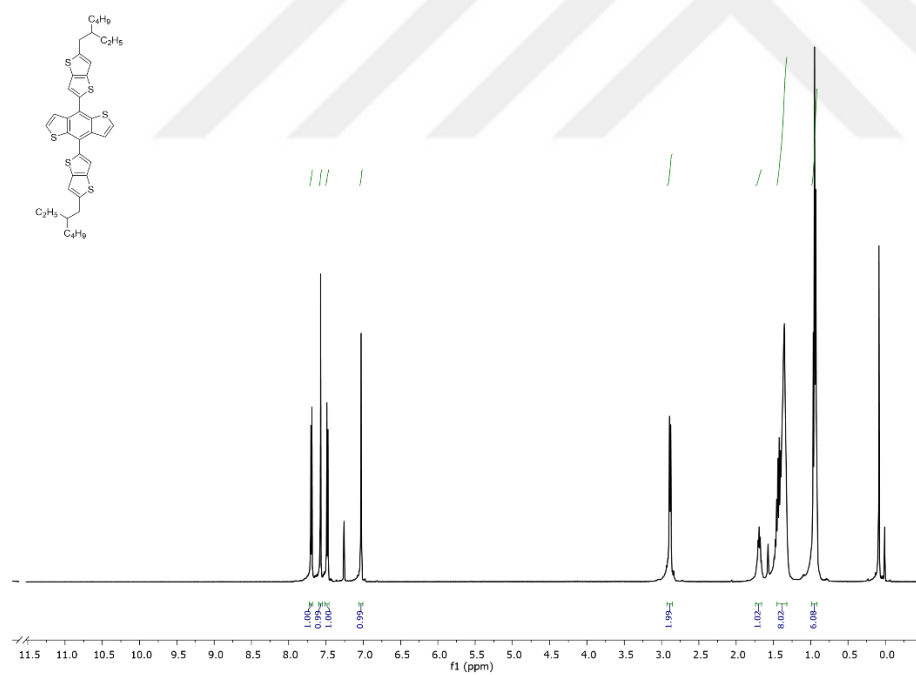


Figure A.39. ^1H NMR spectrum of **34** in CDCl_3

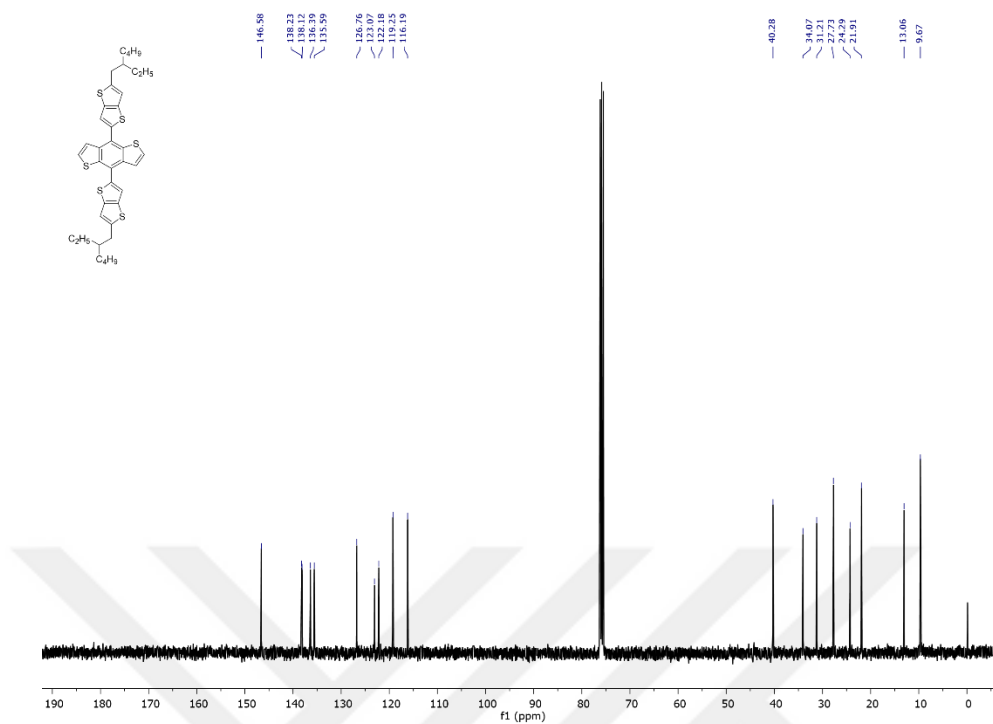


Figure A.40. ^{13}C NMR spectrum of compound **34** in CDCl_3

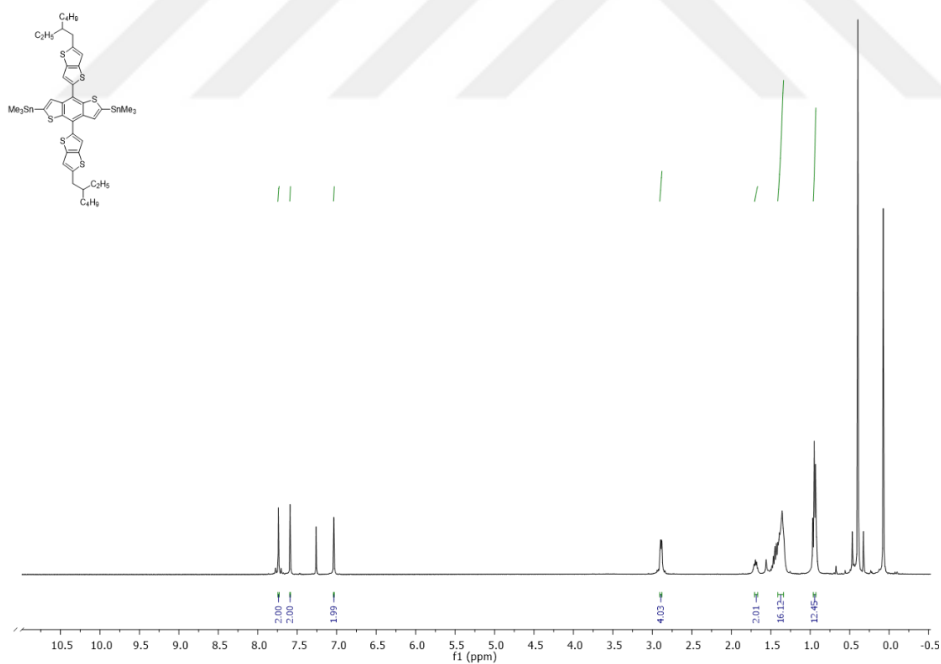


Figure A.41. ^1H NMR spectrum of **D1** in CDCl_3

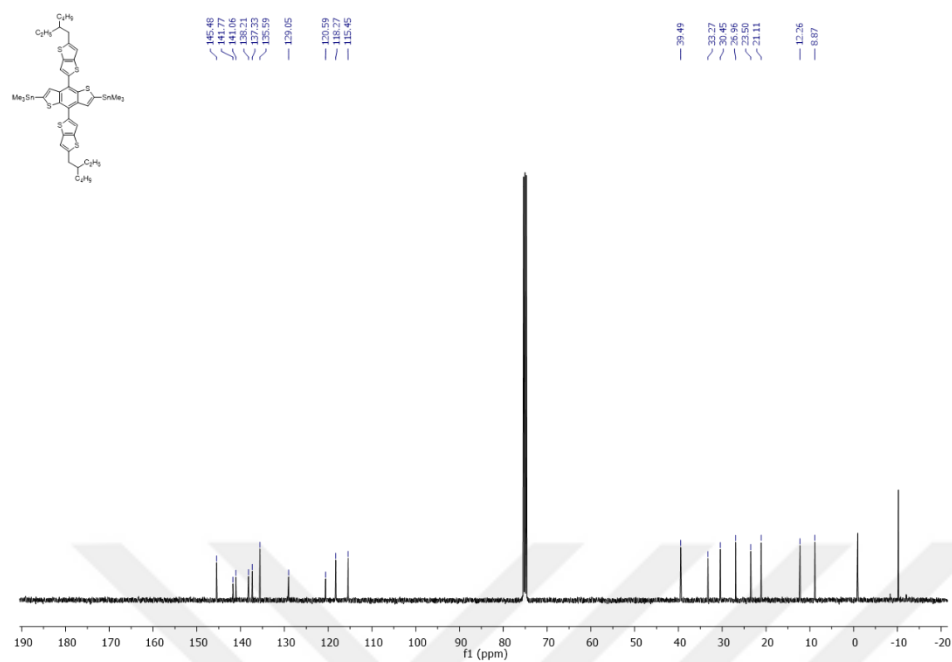


Figure A.42. ^{13}C NMR spectrum of compound **D1** in CDCl_3

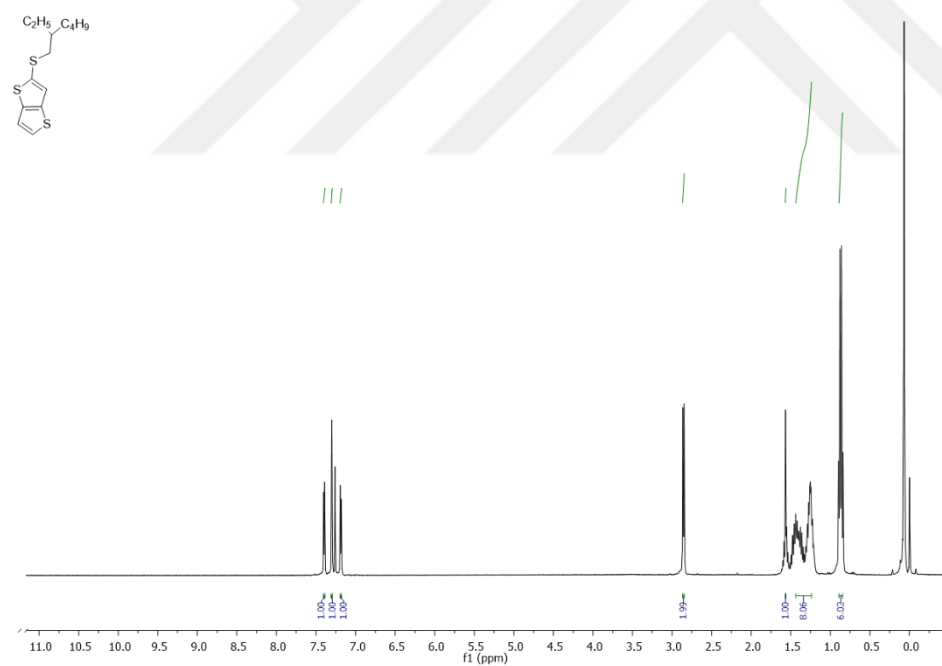


Figure A.43. ^1H NMR spectrum of **35** in CDCl_3

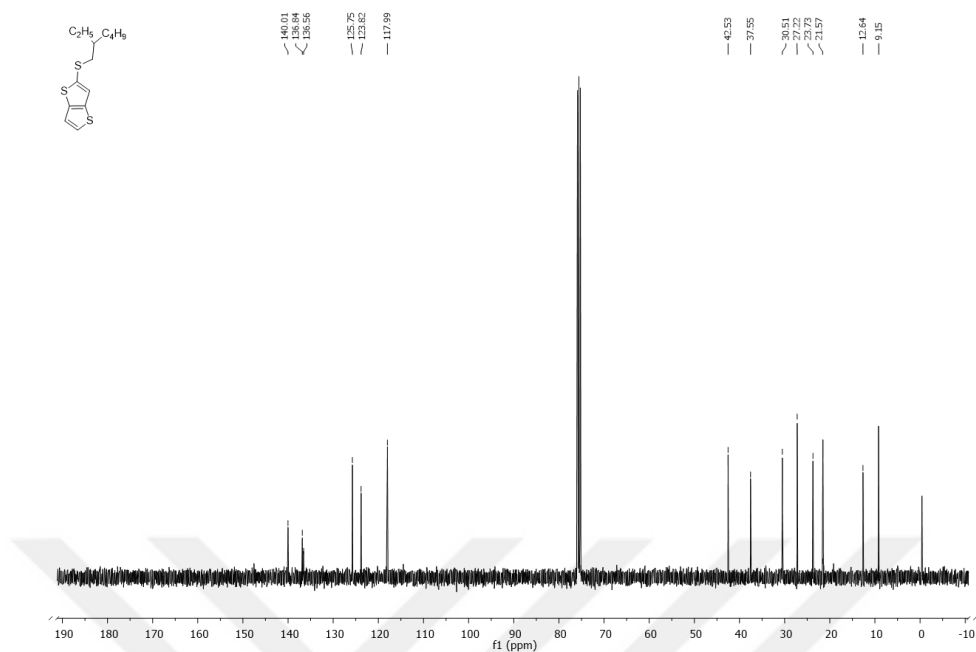


Figure A.44. ¹³C NMR spectrum of compound 35 in CDCl₃

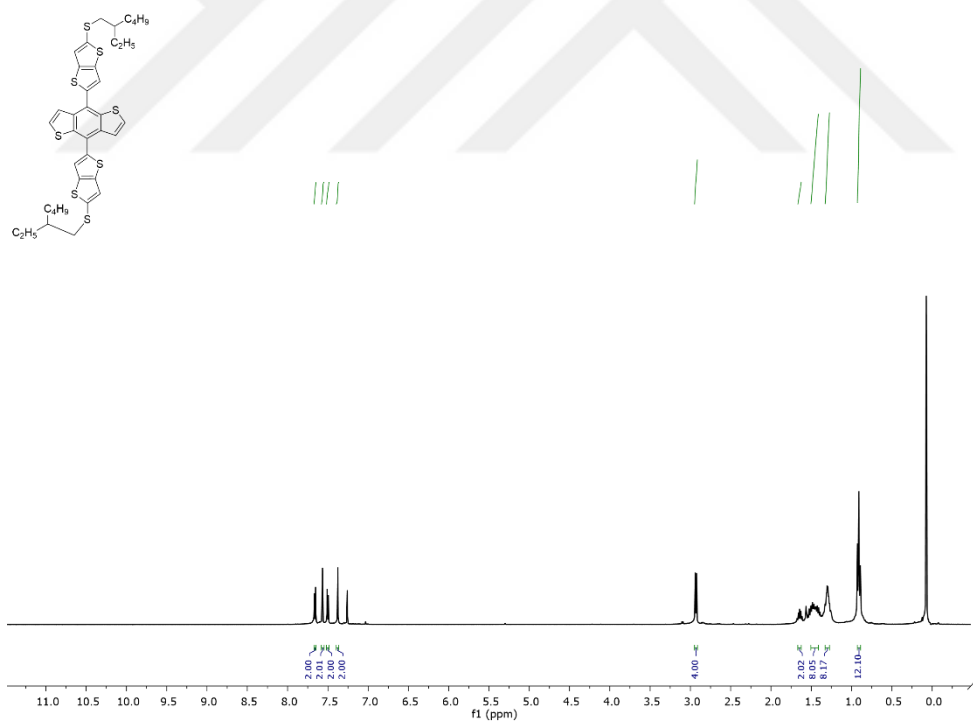


Figure A.45. ¹H NMR spectrum of **36** in CDCl₃

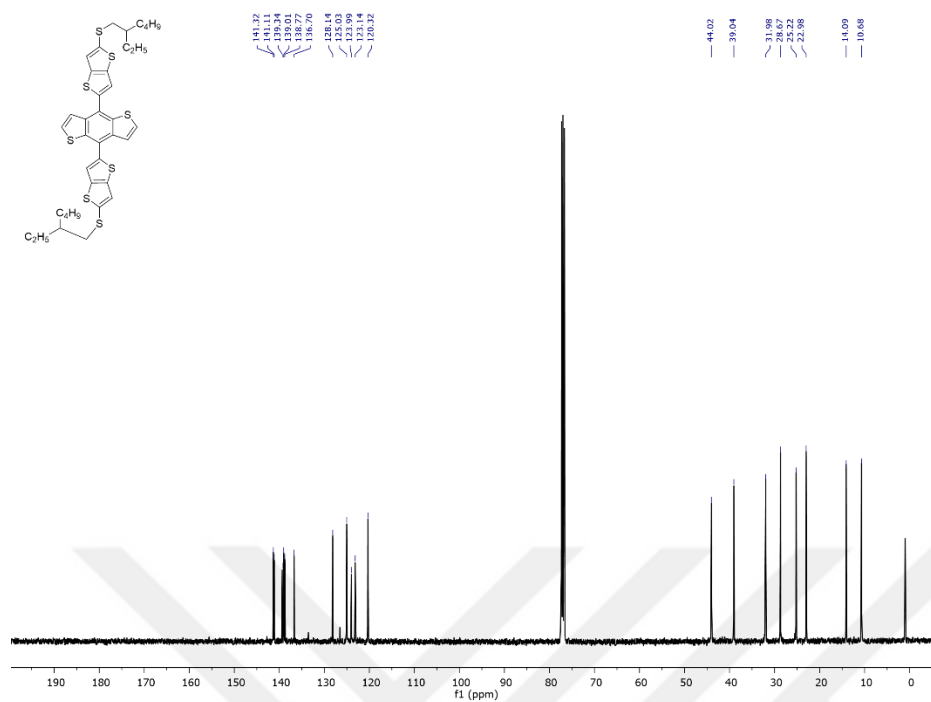


Figure A.46. ^{13}C NMR spectrum of compound **36** in CDCl_3

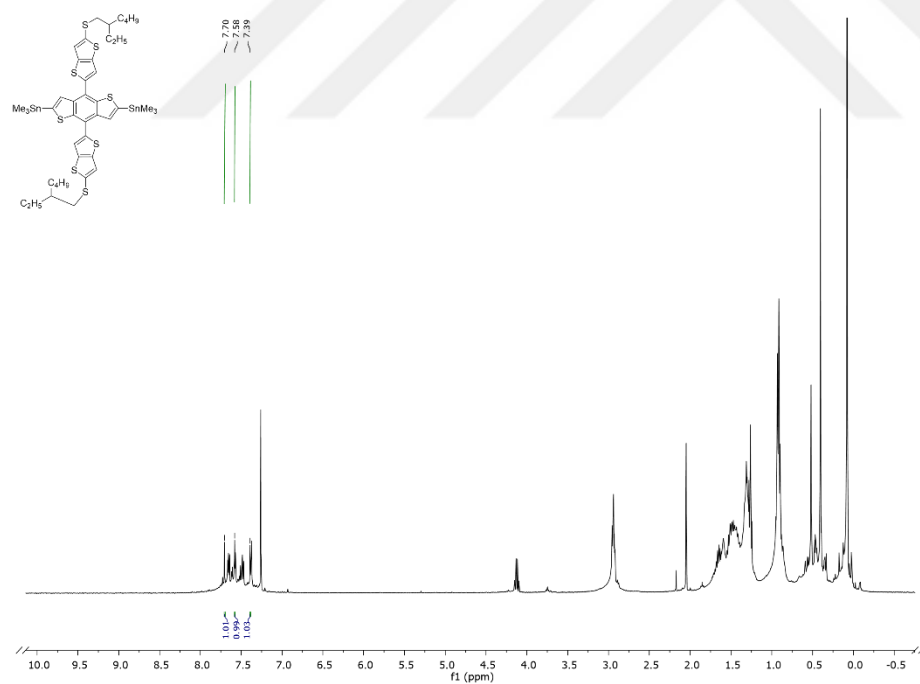


Figure A.47. ^1H NMR spectrum of **D3** in CDCl_3

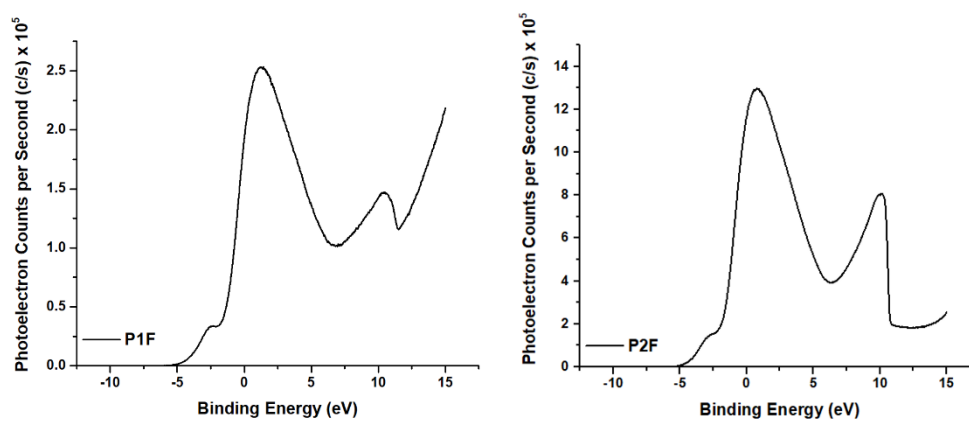


Figure A.48. UPS spectrum of the **P1F** and **P2F** with 7 eV bias

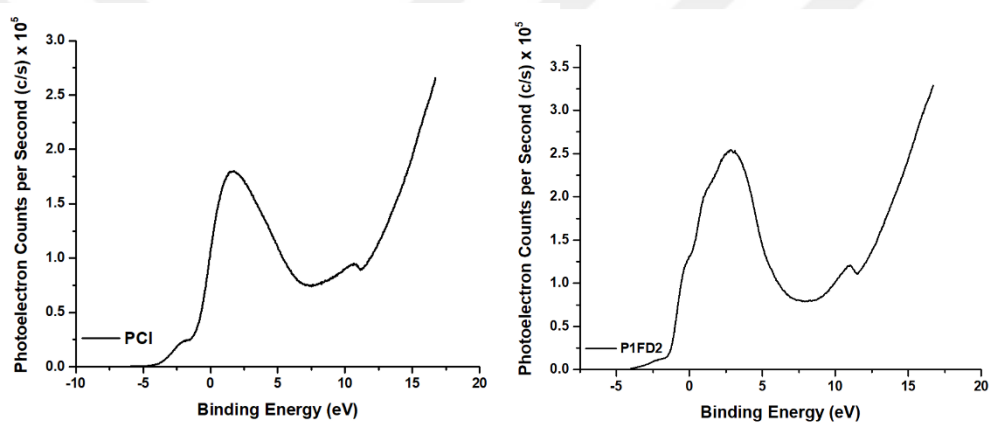


Figure A.49. UPS spectrum of the **PCl** and **P1FD2** with 7 eV bias

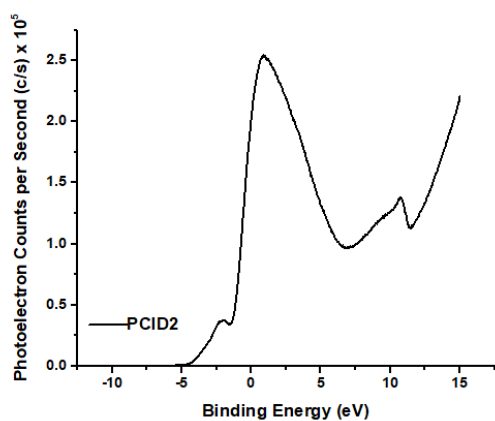


Figure A.50. UPS spectrum of the **PCID2** with 7 eV bias

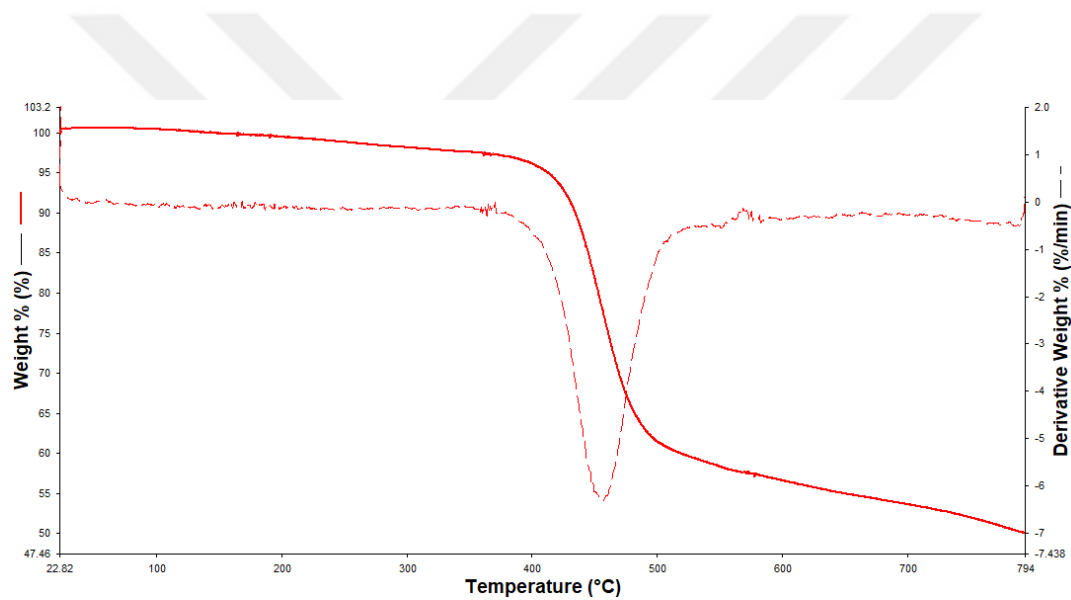


Figure A.51. Thermogram of P1F

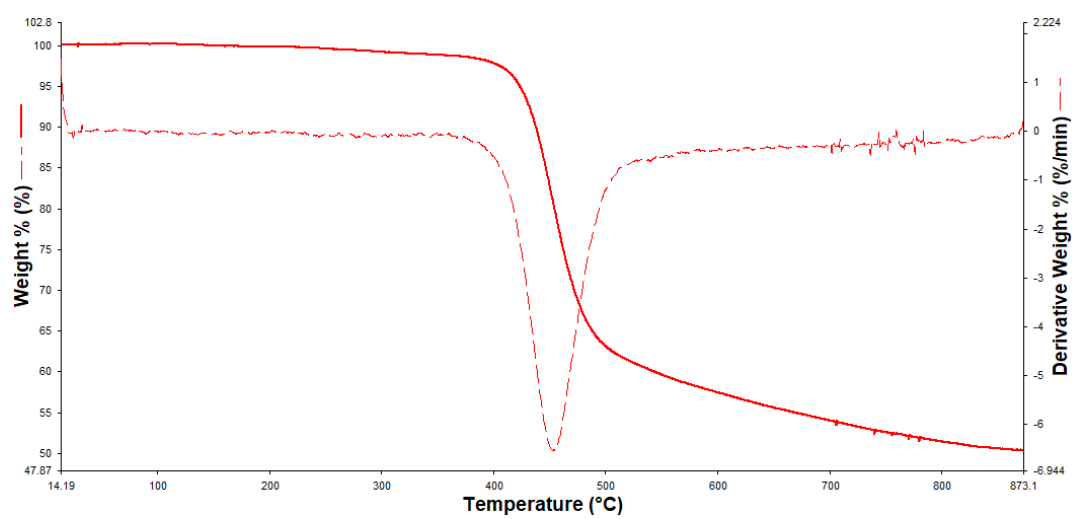


Figure A.52. Thermogram of P2F

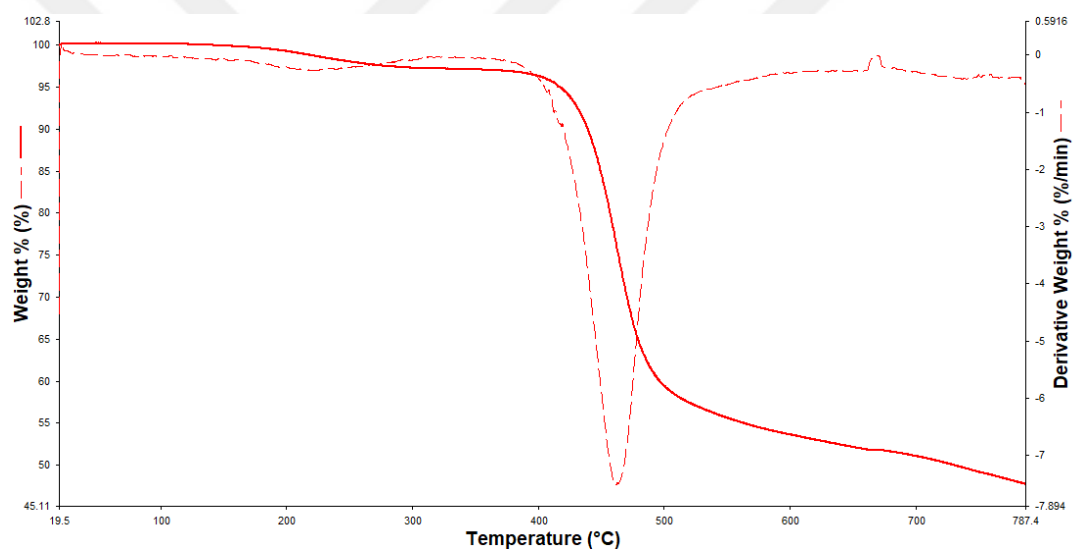


Figure A.53. Thermogram of PCl

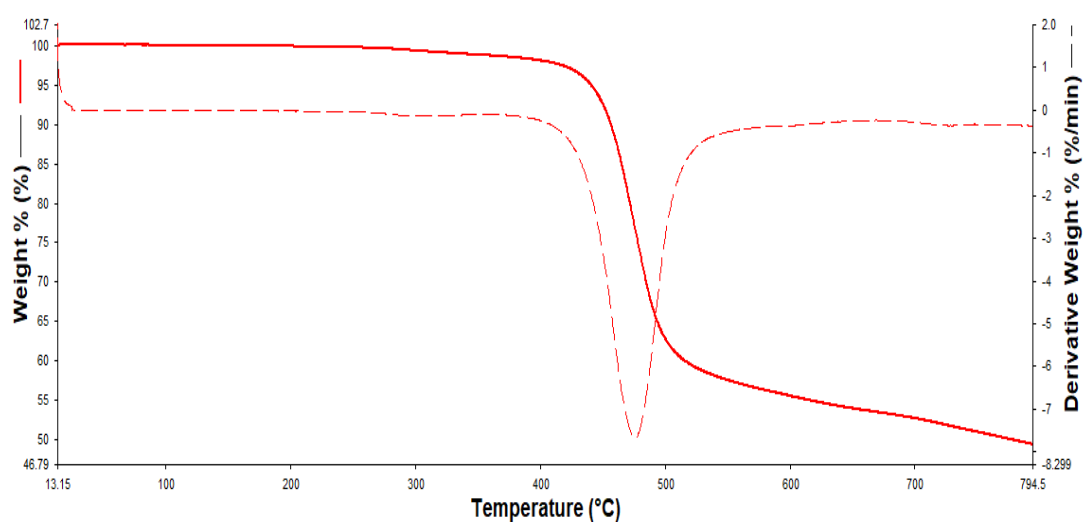


Figure A.54. Thermogram of P1FD2

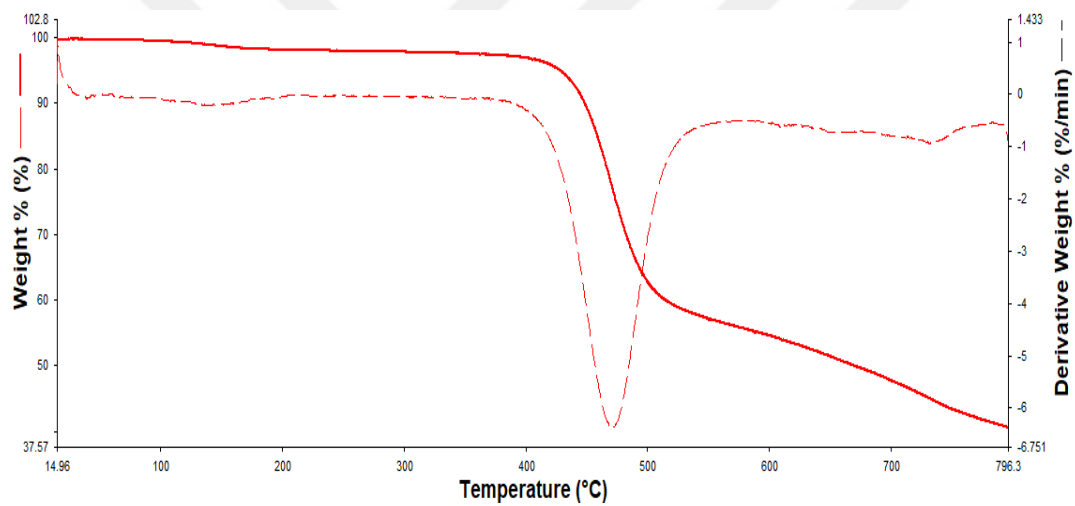


Figure A.55. Thermogram of P2FD2

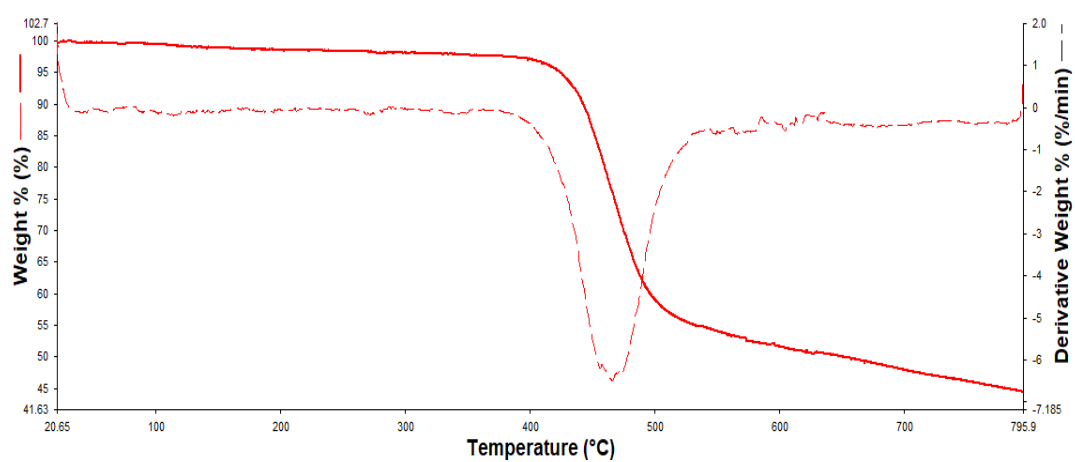


Figure A.56. Thermogram of PCID2