

**SYNTHESIS AND CHARACTERIZATION OF
CARBAZOLE-BASED CONJUGATED POLYMER
VIA DIRECT ARYLATION POLYMERIZATION**



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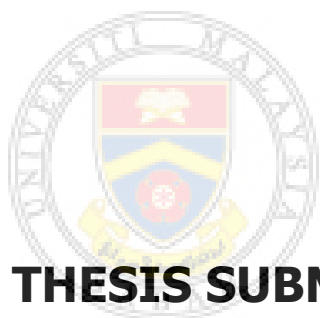


(Dr. Mohd Sani Bin Sarjadi)
Penyelia

Tarikh : 25 March 2020

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UMS

**THESIS SUBMITTED IN FULFILLMENT FOR
THE MASTER OF SCIENCE**

**FACULTY OF SCIENCE AND NATURAL
RESOURCES
UNIVERSITI MALAYSIA SABAH
2020**

DECLARATION

I hereby declare that this thesis is my own work except for the quotations and references which have been properly acknowledged.

16 August 2019



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ABSTRACT

Conjugated polymers, with excellent optical and electrical properties, have appeared as promising operative materials for a diverse range of applications. Donor-Acceptor (D-A) framework, which copolymerizes electron-donors and electron- acceptors alternatively in conjugated backbones, has proven to be the most effective strategy for obtaining low bandgap polymers that desirable for optoelectronic applications. The synthesis of conjugated polymers is primarily relied on conventional cross-couplings, in particularly, Suzuki and Stille couplings, which involve the use of costly toxic organometallic reagents for monomers' functionalization. Despite robust and effective, these protocols produce stoichiometric quantities of toxic byproducts. Direct arylation polymerization (DAP) is a newly established synthetic strategy that provides a clean and low cost pathway towards conjugated polymers. It allows direct coupling of aryl halides and aromatic compounds without preactivation of Carbon-Hydrogen (C-H) bonds. In this research, an alternating D-A type copolymer based on N-9-hexadecyl-2,7-dibromocarbazole and 4,7-di(2-thienyl)benzothiadiazole was synthesized by DAP. This structure is modified from the classical low bandgap copolymer poly[N-9'-heptadecanyl-2,7-carbazole-alt -5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) which exhibited excellent devices performance. One-pot DAP reaction was carried out under phosphine-free condition with palladium (II) acetate as the catalyst, pivalic acid as the additive, and potassium carbonates as the base. The resulting copolymer, poly[(9-hexadecyl-2,7-carabzole-alt-4,7-di(2-thienyl)-2,1,3-benzothiadiazole)] (P1) was obtained in 44%. It showed good solubility in organic solvents and has been satisfactorily characterized by FTIR and NMR. UV-Vis absorption spectra show the presence of inter-chain interaction and aggregation in the solid state. The optical bandgap of the copolymer was found to be in between 1.77 – 1.81 eV, which is slightly lower than that of the PCDTBT (1.88 eV).

ABSTRAK

SINTESIS DAN PENCIRIAN BAGI POLIMER BERKONJUGAT ASAS-KARBAZOL MELALUI PEMPOLIMERAN ARIILASI LANGSUNG

Polimer konjugasi, dengan sifat optik dan elektrik yang sangat baik, telah muncul sebagai bahan pengendali yang menjanjikan untuk pelbagai aplikasi. Kerangka Donor-Acceptor (D-A), yang mengkopolimerkan penyumbang elektron dan penerima elektron secara alternatif dalam tulang belakang konjugat, telah terbukti sebagai strategi yang paling berkesan untuk mendapatkan polimer bandgap yang rendah yang diinginkan untuk aplikasi optoelektronik. Sintesis polimer konjugasi ini terutamanya bergantung kepada penyambung silang konvensional, terutamanya, gandingan Suzuki dan Stille, yang melibatkan penggunaan reagen organik organometalit yang mahal untuk kegunaan monomer. Walaupun kuat dan berkesan, protokol ini menghasilkan kuantiti stoikiometrik produk sampingan toksik. Polimerisasi arilasi langsung (DAP) adalah strategi sintetik yang baru ditubuhkan yang menyediakan laluan kos yang bersih dan rendah ke arah polimer konjugat. Ia membolehkan gandingan langsung aril halida dan sebatian aromatik tanpa preaktivasi bon Carbon-Hydrogen (C-H). Dalam hal ini, kopolimer jenis D-A berselang-seling berdasarkan benzothiadiazole N-9-heksadecil-2,7-dibromocarbazole dan 4,7-dalam (2-siyenyl) disintesis oleh DAP. Struktur ini diubahsuai daripada kopolimer rendah band klasik [N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thenyenyl-2',1'3'-benzothiadiazole)] (PCDTBT) yang mempamerkan prestasi peranti yang sangat baik. Reaksi DAP satu periuk dijalankan di bawah keadaan bebas fosfin dengan palladium (II) asetat sebagai pemangkin, asid pivalik sebagai aditif, dan karbonat kalium sebagai bes. Kopolimer yang dihasilkan, poli [(9-heksadecil-2,7-carabzole-alt-4,7-di (2-thenyenyl) -2,1,3-benzothiadiazole)] (P1) diperolehi dalam 44%. Ia menunjukkan keterlarutan yang baik dalam pelarut organik dan telah dicirikan oleh FTIR dan NMR dengan memuaskan. Spektra penyerapan UV-Vis menunjukkan kehadiran interaksi antara rantaian dan pengagregatan dalam keadaan pepejal. Penumpukan optik kopolimer didapati berada di antara 1.77 - 1.81 eV, yang sedikit lebih rendah daripada PCDTBT (1.88 eV).

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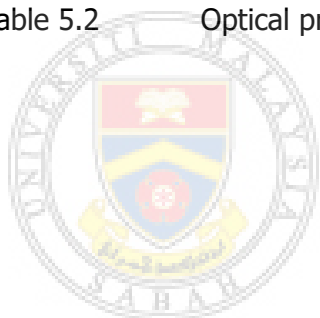
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LIST OF SYMBOLS AND ABBREVIATIONS

%	Percentage
*	Multiplication
~	Similarity
°C	Degree celsius
Π	Pi
α	Alpha
β	Beta
δ	Delta
λ	Lambda
(<i>o</i> -MeOPh) ₃ P	Tris(2-methoxyphenyl)phosphine
BHJ	Bulk heterojunction
brs	Broad singlet
C-Br	Carbon-bromine bond
Cbz	Carbazole
C-H	Carbon-hydrogen bond
CHCl ₃	Chloroform
C-I	Carbon-iodine bond
CMD	Concerted metalation-deprotonation
Cs ₂ CO ₃	Cesium carbonates
DArP	Direct arylation polymerization
DBrBT	4,7-dibromo-2,1,3-benzothiadiazole

DMAc	Dimethylacetamide
DMF	Dimethylformamide
DTBT	4,7-di(2-thienyl)-2,1,3-benzothiadiazole
E_g^{opt}	Optical band gap
eV	Electronvolt
FF	Fill factor
FTIR	Fourier Transform Infrared
g	Grams
GPC	Gel permeation chromatography
H₂SO₄	Sulphuric acid
HOMO	Highest occupied molecular orbital
HPCy₃BF₄	Tricyclohexylphosphine tetrafluoroborate
ITO	Indium tin oxide
J_{sc}	Short circuit current
K₂CO₃	Potassium carbonates
KOAc	Potassium acetate
LUMO	Lowest unoccupied molecular orbital
M_n	Number average molecular weight
Na₂SO₄	Sodium sulphate
NBS	N-bromosuccinimide
NDA	Neodecanoic acid
nm	Nanometer
NOE	Nuclear overhauser enhancement