

## MASTER'S THESIS

### Synthesis and characterization of substituted poly(dibenzofulvenes) and some novel fluorescent dyes

Wong, Yin

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**Synthesis and characterization of substituted  
Poly(dibenzofulvenes) and some novel  
fluorescent dyes**

WONG Yin

A thesis submitted in partial fulfillment of the requirements for  
the degree of  
Master of Philosophy

Principal Supervisor: Dr. Leung M. Louis

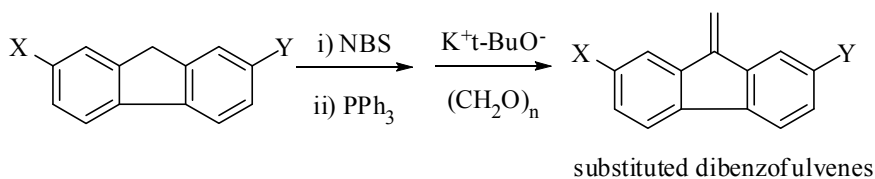
Hong Kong Baptist University

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## Abstract

Conventional conducting polymers are known effective organic semiconductors. The extensively lengthened conjugation along the polymer backbone, however, gives rise to numerous undesirable properties. The significantly reduced band gap rendered the polymers colored and prone to photo-oxidation. Also, installation of long insulating alkyl solubilizing groups is necessary to make the polymers soluble. In this study, a series of novel substituted poly(dibenzofulvene)s (poly(DBF)s) have been synthesized. The pi-stacked poly(DBF)s have limited conjugation length compared with traditional organic semi-conducting polymers (e.g. polyacetylene) but yet possessed high charge mobility ( $3 \times 10^{-4} \text{cm}^2(\text{Vs})^{-1}$ ) and thus may serve as a new generation of organic semiconductor.

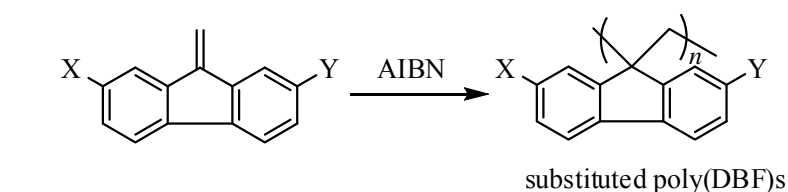
In Chapter 2, a series of novel mono-substituted and di-substituted dibenzofulvenes have been prepared from the corresponding fluorenes with fair to very good overall yields (35.7%~66.7%) based on the Wittig chemistry. Comparing to the traditional lithiation and oxidation routes, the advantages of the Wittig approach have been its simplicity and ease of handling.



(X,Y)=	(H,H)	(Br,OMe)
	(OMe,H)	(Br,OPr)
	(NO <sub>2</sub> ,H)	(Br,OHex)
	(Br,H)	(NO <sub>2</sub> ,OPr)
	(I, H)	(NO <sub>2</sub> ,OHex)
	(CN, H)	(Br,Br)
	(Ac,H)	

In Chapter 3, a series of novel substituted poly(DBF)s have been synthesized by free-radical initiated polymerization for the monomers prepared in Chapter 2. The solubility of the substituted poly(DBF)s depended on the type of the substituents. High molecular weights were achieved when the polymers have high solubility. Upfield shifts observed in the <sup>1</sup>H NMR spectra of the substituted poly(DBF)s supported the presence of  $\pi$ - $\pi$  stacking conformation in the polymers. The absorption and photoluminescence spectra of the polymers investigated also strongly supported the presence of  $\pi$ - $\pi$  stacking. The photoluminescence spectra of all the polymers consisted of both excimer and defect emissions. In general, the excimer wavelength of the substituted poly(DBF)s increased with the emission maximum of their corresponding fluorenes. The oxidation potentials of the polymers were found to be lower than their corresponding fluorenes as the  $\pi$ - $\pi$  stacking conformation assisted the stabilization of the resulting hole. The reduction in the ionization potentials of the

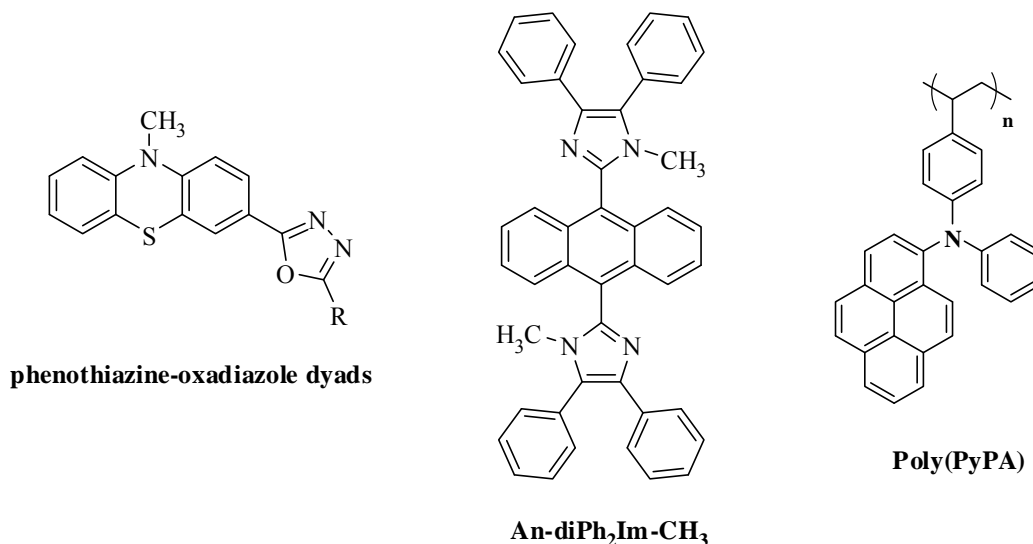
substituted poly(DBF)s depended on both the molecular weights and the substituent nature of the polymers. The substituted poly(DBF)s also exhibited moderate thermal stabilities with degradation onset temperatures ranging from 254°C to 342°C. The majority of the polymers showed an endothermic peak which was suggested to be the result of depolymerization in the range 170-240°C.



X	Y	
H	H	Poly(dibenzofulvene) <b>Poly(DBF)</b>
MeO	H	Poly(2-methoxydibenzofulvene) <b>Poly(2-MeO-DBF)</b>
NMe <sub>2</sub>	H	Poly(2-dimethylaminodibenzofulvene) <b>Poly(2-NMe<sub>2</sub>-DBF)</b>
F	H	Poly(2-fluorodibenzofulvene) <b>Poly(2-F-DBF)</b>
Br	H	Poly(2-bromodibenzofulvene) <b>Poly(2-Br-DBF)</b>
I	H	Poly(2-iododibenzofulvene) <b>Poly(2-I-DBF)</b>
CN	H	Poly(2-cyanodibenzofulvene) <b>Poly(2-CN-DBF)</b>
NO <sub>2</sub>	H	Poly(2-nitrodibenzofulvene) <b>Poly(2-NO<sub>2</sub>-DBF)</b>
NO <sub>2</sub>	OPr	Poly(2-nitro-7-propoxydibenzofulvene) <b>Poly(2-NO<sub>2</sub>-7-PrO-DBF)</b>
NO <sub>2</sub>	OHex	Poly(2-nitro-7-hexoxydibenzofulvene) <b>Poly(2-NO<sub>2</sub>-7-HexO-DBF)</b>
Br	OMe	Poly(2-bromo-7-methoxydibenzofulvene) <b>Poly(2-Br-7-MeO-DBF)</b>
Br	OPr	Poly(2-bromo-7-propoxydibenzofulvene) <b>Poly(2-Br-7-PrO-DBF)</b>
Br	OHex	Poly(2-bromo-7-hexoxydibenzofulvene) <b>Poly(2-Br-7-HexO-DBF)</b>
Br	Br	Poly(2,7-dibromodibenzofulvene) <b>Poly(2,7-diBr-DBF)</b>

In Chapter 4, some miscellaneous fluorescent small molecules and polymer have been prepared and characterized. The first was a series of novel bluish green dyes based on phenothiazine-oxadiazole dyads. They are efficient dyes with high quantum yields in the range of 0.50-0.72. The photophysical, thermal and electrochemical of the dyes have been investigated and the results have shown that they have potential

for electroluminescent application. The second series was two sky-blue dyes, 9,10-bis(4,5-diphenyl-1-methyl-imidazol-2-yl)anthracene (An-diPh<sub>2</sub>Im-CH<sub>3</sub>) and 9-(4,5-Ddiphenyl-1-methyl-imidazol-2-yl)anthracene (An-Ph<sub>2</sub>Im-CH<sub>3</sub>), with their photophysical, thermal and electrochemical properties reported. Finally, a novel pyrene-containing polymer, Poly(*N*-phenyl-*N'*-(1-pyrenyl)-*N''*-(4-vinylphenyl)amine) (Poly(PyPA)), has been synthesized via cationic polymerization with  $M_n$  and  $M_w$  of 57,500 and 187,800 respectively. The photophysical, thermal and electrochemical properties of Poly(PyPA) have been investigated and reported. A single layer PLED of Poly(PyPA) emitted in sky-blue color with maximum luminance and current efficiency of the single-layer Poly(PyPA) device were 933cd/m<sup>2</sup> and 0.057cd/A respectively with a low turn-on voltage of 4.0V.



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