

## MASTER'S THESIS

### Synthesis and structure-property relationships of novel multi-[pi] conjugated molecular systems

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# **Synthesis and Structure-Property Relationships of Novel Multi- $\pi$ -Conjugated Molecular Systems**

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

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**Hong Kong Baptist University**

**July 2006**

## Abstract

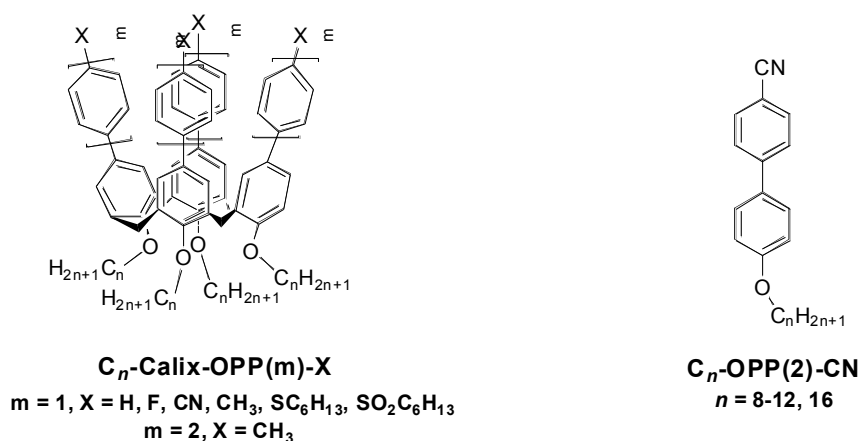
Several novel series of monodisperse, well-defined  $\pi$ -conjugated oligomers, which included the *cone*-conformed end-functionalized oligophenylene (OPP) substituted calix[4]arenes, **C<sub>n</sub>-Calix-OPP(*m*)-X**,  $n = 8-16$ ,  $m = 1$  or  $2$ ,  $X = H, F, CH_3, CN, SC_6H_{13}$  and  $SO_2C_6H_{13}$ ; cyano-substituted biphenyl monomer derivatives, **C<sub>n</sub>-OPP(2)-CN**,  $n = 9-12$  and  $16$ ; zig-zag multi-dipolar oligoaryleneethynylenes **DA(*n*)**,  $n = 2, 4, 6$ , and their extended analogous **D-Ar-A(*n*)**,  $n = 2, 4$ , Ar = phenylethynyl, fluorenylethynyl, and bifluorenylethynyl, bithienylethynyl, and terthienylethynyl as well as two analogous of zig-zag oligoaryleneethynylenes **DD(*n*)** and **AA(*n*)**,  $n = 4, 6$ , have been designed and successfully synthesized in good to excellent yields using either palladium-catalyzed Suzuki cross-coupling or palladium-catalyzed Sonogashira cross-coupling as the key reactions. All the newly synthesized  $\pi$ -conjugated oligomers were fully characterized with  $^1H$  NMR,  $^{13}C$  NMR, MS and high resolution mass spectroscopy analysis (HRMS) and found to be in good agreement with the expected structures.

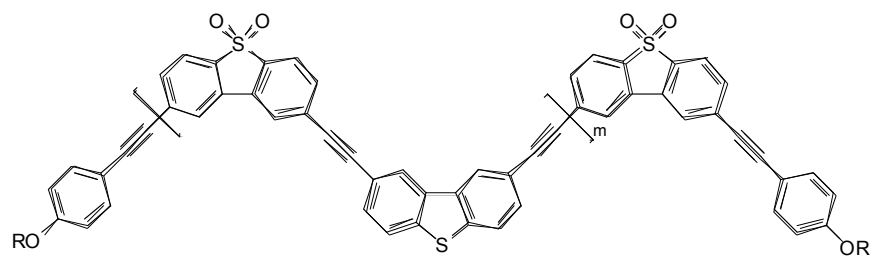
The mesomorphic properties of the end-functionalized oligophenylene (OPP) substituted calix[4]-arenes, **C<sub>n</sub>-Calix-OPP(*m*)-X** and the cyano-substituted biphenyl monomer derivatives, **C<sub>n</sub>-OPP(2)-CN** were examined by differential scanning calorimetry (DSC), polarized optical microscopy (POM) and X-ray diffraction (XRD) measurements. The structure-liquid crystalline property correlation for

$C_n$ -Calix-OPP(1)-CN was established.

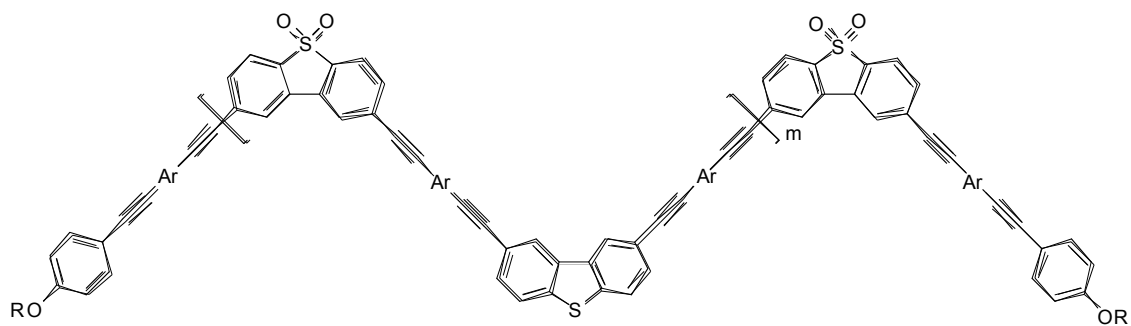
In addition, the photophysical, thermal and nonlinear optical (two-photon absorption) properties of the zig-zag type multi-dipolar oligoaryleneethynylenes **DA(n)** and their extended type **D-Ar-A(n)** molecular materials were investigated by UV-vis spectroscopy and fluorescence spectroscopy, thermogravimetric analysis (TGA), and two-photon induced fluorescence method using 800 nm femtosecond pulsed lasers as an excitation source, respectively. Furthermore, the optical properties of the two homologous series of **DD(n)** and **AA(n)** were examined. The structure-property relationships of these zig-zag oligoaryleneethynylenes were also studied and discussed.

The structure of these newly synthesized  $\pi$ -conjugated oligomers were shown below:

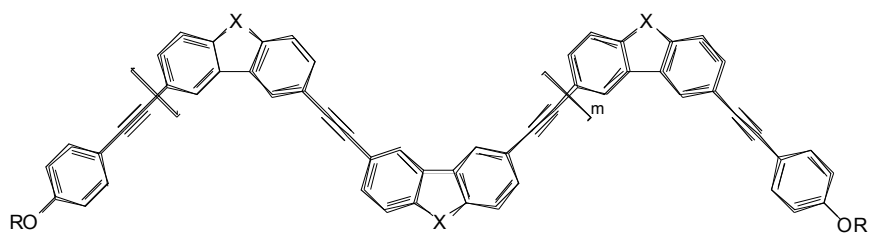




**DA(2) m = 0**  
**DA(4) m = 1**  
**DA(6) m = 2**



**D-Ar-A(2) m = 0**  
**D-Ar-A(4) m = 1**      **Ar = Ph, MF, DF, DTP, TTP**



**m = 1, 2    n = 2m+2**

**DD-(n) : X = S,    n = 4, 6**  
**AA-(n) : X = SO<sub>2</sub>, n = 4, 6**

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