

DOCTORAL THESIS

Synthesis and characterization Naphtho[2,1-b:3,4-b']dithiophene-based organic semiconducting molecules for organic electronics

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Abstract

Thienoacenes represent an intriguing class of organic semiconducting molecules with potential applications in organic electronics. Some of thienoacenes have been reported with high charge carrier mobility in organic field-effect transistors (OFET). OFETs based on naphtho[2,1-*b*:3,4-*b'*]dithiophene (**NDT**) exhibited moderate device performance and low-band gap donor-acceptor copolymers based on **NDT** showed a promising solar power conversion efficiency.

In this thesis, four novel series of thienoacenes based on naphtho[2,1-*b*:3,4-*b'*]dithiophene backbone were designed and synthesized for OFET applications. Firstly, a novel series of *p*-type semiconducting naphthodithieno[3,2-*b*]thiophene derivatives (**NDTT-n**) composed of six-fused aromatic rings were designed and synthesized (**Figure 1**). The OFETs based on **NDTT-10**, and **NDTT-12** fabricated by vacuum deposition showed a hole mobility of 0.22 and 0.13 cm²/(Vs), respectively with I_{on}/I_{off} above 10⁷ after annealing at 80 °C.

Secondly, the derivatives of **NDT** fused with benzene rings at the flanks of thiophene, namely **NBBT-n** (**Figure 2**) were also designed and synthesized. OFETs based on **NBBTF-10** fabricated by vacuum deposition exhibited a hole mobility of 0.35 cm²/(Vs) with a current on/off ratio of 10⁶ – 10⁷ after annealing at 160 °C. Further extension of π -conjugation of **NDTT** by incorporating with fused

thiophenes leading to a new **NBTBT-n** series was also developed (**Figure 3**). The OFETs fabricated by **NBTBT-10** showed the hole mobility up to $0.25 \text{ cm}^2/(\text{Vs})$ with a current on/off ratio of $10^5 - 10^6$ after annealing at 220°C .

Lastly, two dimensionally π -extended, butterfly-shaped thienoacenes (**Figure 4**) were also synthesized. The OFETs based on **SMB-10** fabricated by spin-coating showed the best performance in this series with an average mobility of $0.027 \text{ cm}^2/(\text{Vs})$ for five devices and the highest mobility of $0.038 \text{ cm}^2/(\text{Vs})$ with a current on/off ratio of $10^6 - 10^7$ by from chloroform.

Key words: organic semiconducting molecules, organic field-effect transistor, thienoacene, charge carrier mobility.

The molecule structures of four novel series are shown as below.

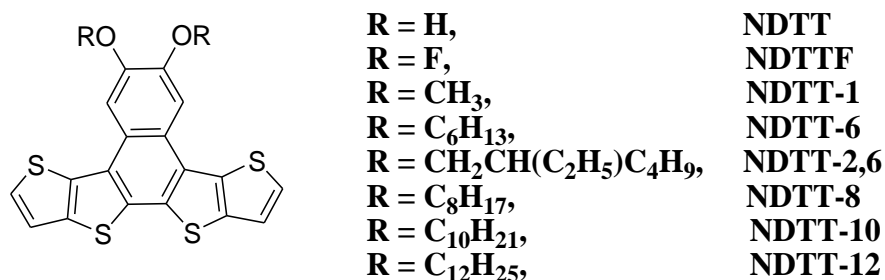
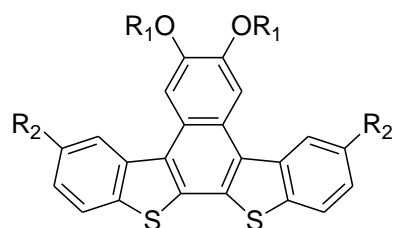
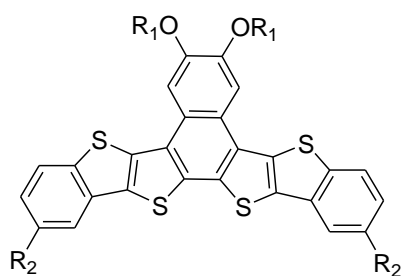


Figure 1. The molecular structure of **NDTT** and its derivatives.



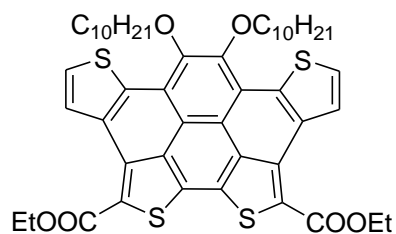
$R_1 = C_{10}H_{21}$, $R_2 = H$, **NBBT-10**
 $R_1 = C_8H_{17}$, $R_2 = F$, **NBBTF-8**
 $R_1 = C_{10}H_{21}$, $R_2 = F$, **NBBTF-10**
 $R_1 = C_{12}H_{25}$, $R_2 = F$, **NBBTF-12**

Figure 2. The molecular structure of **NBBT-n** series.

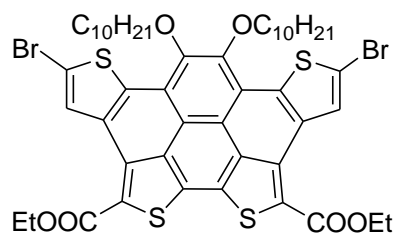


$R_1 = C_6H_{13}$, $R_2 = H$, **NBTBT-6**
 $R_1 = CH_2CH(C_2H_5)C_4H_9$, $R_2 = H$, **NBTBT-2,6**
 $R_1 = C_8H_{17}$, $R_2 = H$, **NBTBT-8**
 $R_1 = C_{10}H_{21}$, $R_2 = H$, **NBTBT-10**
 $R_1 = C_{12}H_{25}$, $R_2 = H$, **NBTBT-12**
 $R_1 = C_{10}H_{21}$, $R_2 = F$, **NBTBTF-10**

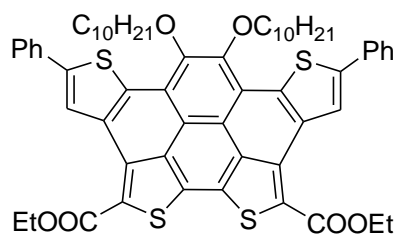
Figure 3. The molecular structure of **NBTBT-n** series.



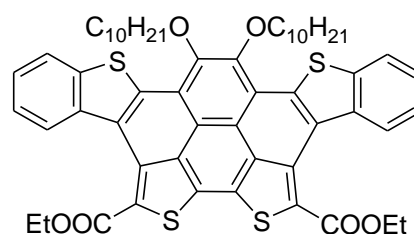
SM-10



SMB-10



SMP-10



SMBZ-10

Figure 4. Two-dimensional thienoacenes in butterfly-shaped structure.

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