

Synthesis and OFET Performance of Functionalized Pentacene Derivatives

Michelle L. Senatore, Toshihiro Okamoto, Abhijit Basu Mallik, Ming Lee Tang, Mang-Mang Ling and Zhenan Bao, Department of Chemical Engineering, Stanford University, 381 North-South Mall, Stanford, CA 94305-5025*

Introduction

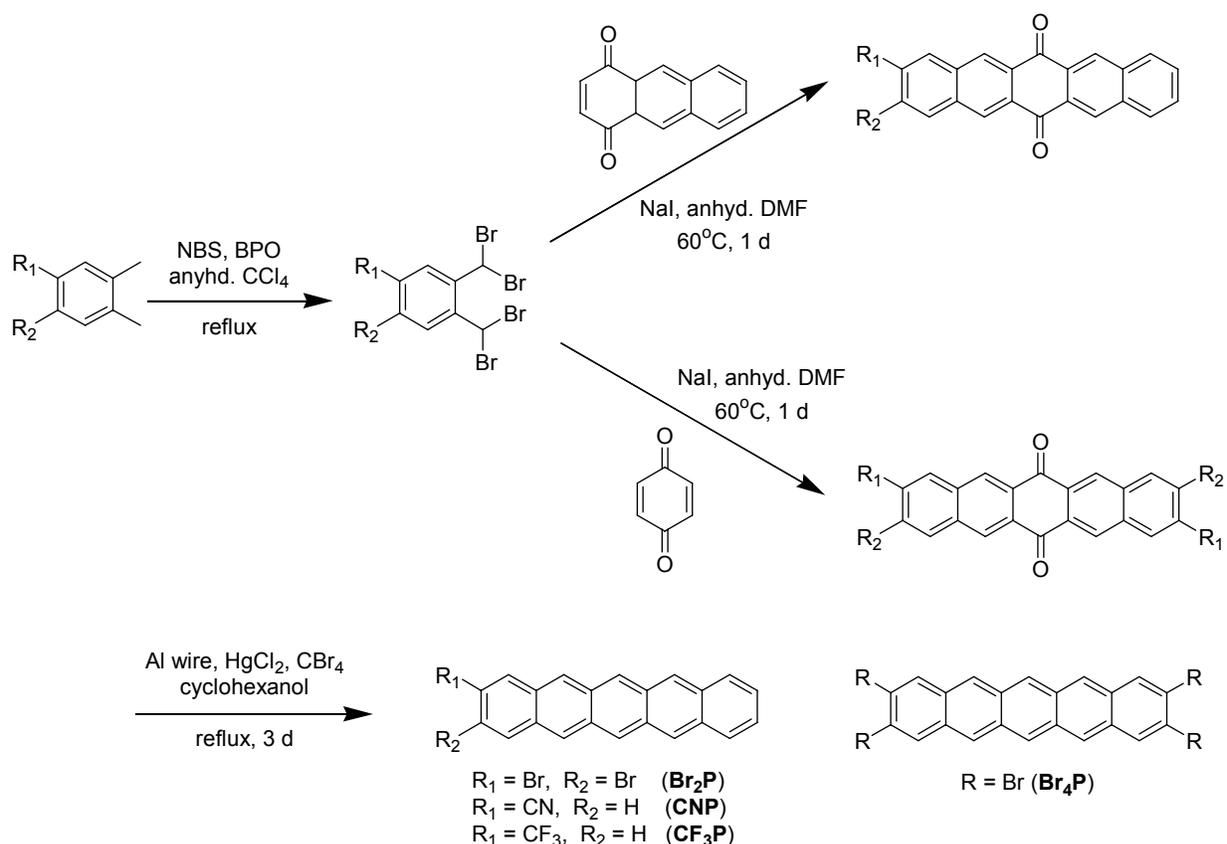
Organic thin-film field-effect transistors (OFETs) are of great interest to researchers because of their potential to offer light-weight, flexible, low-cost alternatives to devices currently utilizing the traditional silicon-based transistor. The semiconducting organic materials can often be solution processed, which would allow for deposition via inkjet or reel-to-reel printing onto flexible, plastic substrates.¹ Further, the synthesis of organic materials is versatile in that the molecules can be functionalized to promote desired changes in solubility, stability, and electronic properties.

Pentacene was among the first molecules to show high field-effect performance.² Although pentacene has demonstrated great promise in this field, its derivatives have yet to be widely studied. A few groups have investigated the functionalization of pentacene at the central and terminal rings. Wudl, Bao, and coworkers³ substituted the hydrogen atoms in the 2, 3, 9, and 10 positions with methyl groups. Anthony et al.⁴ and Neckers et al.⁵ reported the synthesis of 6,13-substituted pentacene derivatives with either electron-withdrawing or trialkylsilylethynyl groups substituted on the terminal rings. Functionalization of the pentacene core has the potential to improve electronic properties by adjusting the HOMO and LUMO levels of the molecule, altering the size and shape of the molecule and thus changing the packing mode, and possibly improving stacking.

We report the synthesis of four new functionalized pentacene derivatives based on symmetrical and asymmetrical substitutions, as illustrated in Scheme 1. Thin film transistors have been fabricated for two of the molecules, and their device performance is also reported.

Results and Discussion

Synthesis of the pentacene derivatives was performed in a multi-step reaction scheme as shown in Scheme 1.



Scheme 1: Synthetic Scheme

The tetrabrominated starting materials were synthesized in moderate yields using a method similar to literature procedures.⁶ These compounds underwent a Diels-Alder cyclization reaction to produce the substituted pentacene precursors. In a procedure similar to what is reported in literature,^{7,8} the reaction of the tetrabrominated compounds with 1,4-anthraquinone in the presence of NaI and anhydrous DMF at 60°C afforded asymmetric quinones in 60-88% yields while reaction with *p*-benzoquinone under the same conditions gave symmetric quinones in slightly lower yields. The quinones were then converted to the corresponding pentacene derivatives in 38-71% yields by reduction in the presence of aluminum wire, cyclohexanol, and catalytic amounts of HgCl₂ and CBr₄. The crude products were purified via sublimation prior to device fabrication.

In order to determine the stability of the molecules, thermal gravimetric analysis (TGA) was performed for pentacene derivatives under a stream of nitrogen gas at a heating rate of 10°C/min. The decomposition temperature was defined as the temperature at which a 5% weight loss takes place. We found that the decomposition temperature of 2,3-dibromopentacene (**Br₂P**) was 15 °C higher than that of 2,3,9,10-tetrabromopentacene (**Br₄P**), even though **Br₂P** has a smaller molecular weight. As a result, **Br₂P** could be purified by multi-sublimation to give enough pure compounds for the measurement of device performance; however, it was difficult to obtain pure **Br₄P**.

Top-contact thin-film transistors were fabricated on octadecyltrimethoxysilane (OTS) treated SiO₂/Si substrates. **Br₂P** and 2-cyanopentacene (**CNP**) were thermally evaporated at different substrate temperatures. All devices operated as *p*-type transistors. The field-effect mobility was calculated using the *I*_{DS} values in the saturation regions, as summarized in Table

1. **Br₂P** devices yielded a mobility of 0.21 cm²V⁻¹s⁻¹ at substrate temperatures ranging from 80-90°C, while **CNP** devices exhibited mobility near 10⁻² cm²V⁻¹s⁻¹. The field-effect mobility of **Br₂P** increased with increasing T_D, which is attributed to better ordered thin films and larger grain sizes at elevated T_D. As shown in Figure 1, the AFM images also showed sharper grain boundaries and larger crystal size for higher T_D thin films. Thus, the grain sizes for **Br₂P** was on the order of 250-400 nm at T_D = 25 °C, while its sizes became bigger at 90 °C, on the order of 500-750 nm. Ongoing research of the synthesis and device performance of other pentacene derivatives is currently being conducted.

Compound	Surface Treatment	Deposited Temperature (°C)	Mobility μ (cm ² V ⁻¹ s ⁻¹)	On/Off ratio I _{on} /I _{off}
Br₂P	OTS	25	0.11	2.8 x 10 ⁵
		70	0.17	1.2 x 10 ⁵
		80	0.21	2.2 x 10 ⁵
CNP	OTS	25	0.0019	2.9 x 10 ²
		70	0.0087	5.6 x 10 ²
		80	0.0092	6.5 x 10 ²

Table 1. Field-effect mobilities of transistors prepared at different substrate temperature (T_D) using top-contact geometry.

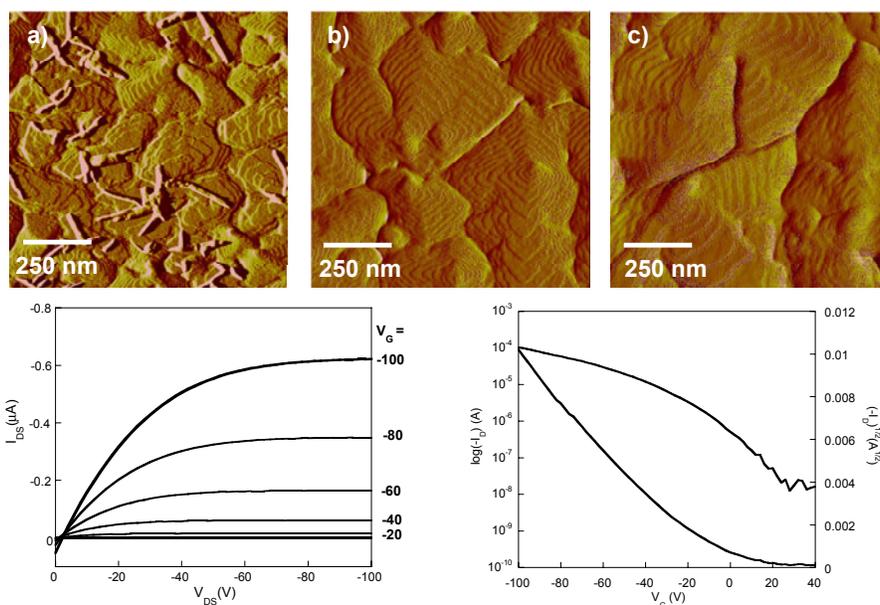


Figure 1 [Upper]. AFM (phase) of **Br₂P** deposited at a) 25 °C b) 70 °C and c) 90 °C. **[Bottom]** a) I_{DS} vs V_{DS} characteristic of **Br₂P** (90 °C) at different gate voltages prepared at elevated substrate temperature with channel length L = 200 μm and channel width W = 4000 μm, b) I_{DS} vs V_G characteristics of **Br₂P** thin film transistors.

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