

2,6-Bis[2-(4-pentylphenyl)vinyl]anthracene: A Stable and High Charge Mobility Organic Semiconductor with Densely Packed Crystal Structure

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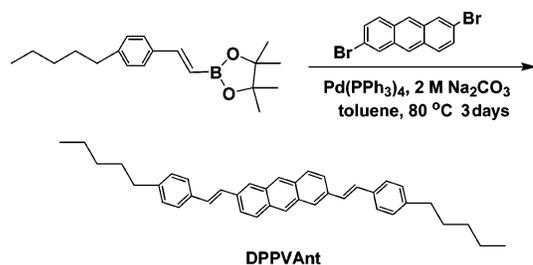
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Interest in organic thin film transistors (OTFTs) and their use in various technological applications has grown significantly in recent years.^{1,2} To realize the full potential of these applications, it is necessary to identify conjugated semiconductors with high mobility and robust environmental stability. Organic oligomers investigated to date include *p*-type, *n*-type, and *p/n*-type bipolar semiconductors.^{3,4} So far, the highest charge carrier mobility in thin film transistors has been observed with pentacene, which has been used as a benchmark *p*-type semiconductor material with a charge mobility over 1.0 cm²/V·s, as reported by several labs.⁵ However, the poor stability and reproducibility of pentacene-based OTFTs may limit pentacene's commercial potential. Recently, Anthony's group reported a series of solution processible pentacene and anthradithioene derivatives with silylethynyl-substituted structures.⁶ The stability and the charge mobility have been improved relative to that of the parent molecules, owing to the enhanced π -stacking crystal packing. This is one of several promising molecular design approaches currently being explored. On the other hand, several strategies have been explored to improve the stability of organic semiconductors through the design of large band gap semiconductor materials, such as anthracene derivatives.^{7–9} However, none of these previously reported large band gap semiconductors has shown device performance comparable to that of pentacene. A recent molecular modeling study of the relationship between the charge mobility and crystal packing of pentacene indicates that the molecular order present in the pentacene crystal structure is not optimal for producing a maximum charge carrier mobility.¹⁰ An even higher charge mobility pentacene molecule was proposed with densely packed crystal structure, but to create such an ideal packing structure with pentacene is impossible.

Here we report our recent discovery of a new semiconductor material, which has a symmetrically substituted phenylenevinylene anthracene backbone pendant with pentyl groups as side chains. To our surprise, the molecule's crystal packing is denser than that of pentacene. The devices incorporating this semiconductor show remarkably high charge carrier mobility, environmental stability, and device repeatability.

Scheme 1 illustrates the synthesis and molecular structure of the new semiconductor, 2,6-bis[2-(4-pentylphenyl)vinyl]anthracene (**DPPVAnt**). The semiconductor was synthesized in high yield (83%) using a Suzuki coupling reaction between 2,6-dibromoanthracene and the commercially available material 4,4',5,5'-tetramethyl-2-[2-(4-pentylphenyl)vinyl]-[1,3,2]dioxaborolane. After purification by thermal gradient zone purification processes, the compound, which was soluble in hot xylene, was characterized by ¹H NMR, ¹³C NMR, high-resolution mass spectrometry, elemental analysis, and X-ray crystallography. The optical band gap, determined at an onset absorption peak of 478 nm is 2.59 eV, which is over 1 eV wider than that of pentacene (702 nm, 1.77 eV). The

Scheme 1. One-Step Synthesis of **DPPVAnt**



large band gap of the compound is consistent with the greater stability of **DPPVAnt** relative to pentacene.¹¹ The stability of **DPPVAnt** was further confirmed by studying its electrochemical behavior. Both the oxidation and reduction potentials of **DPPVAnt** are higher than those of pentacene. The reorganization energy for hole transport in an isolated **DPPVAnt** molecule is 0.143 eV, double that of an isolated pentacene molecule (0.072 eV), but is comparable with most high hole mobility organic semiconductors.¹² Computational results indicate no dipole moment for either molecule.

DPPVAnt crystals were grown in a physical vapor growth process. It should be noted that the quality of the X-ray structure was limited due to the small crystallite size of the crystals. Single crystals of **DPPVAnt** pack in a herringbone geometry, similar to pentacene.¹³ However, compared to pentacene and our previous reported anthracene derivative DHTAnt,⁷ **DPPVAnt** is more densely packed (see Figure 1). This could explain the relatively

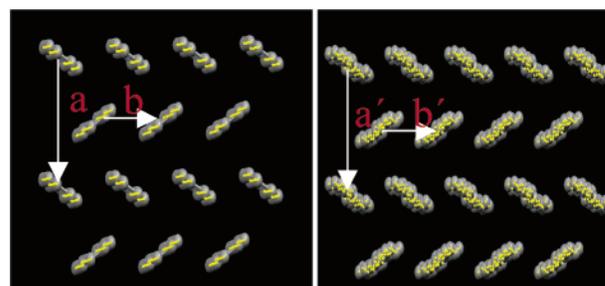


Figure 1. Crystal packing of pentacene molecule ($a = 7.79 \text{ \AA}$, $b = 6.27 \text{ \AA}$) (left) and **DPPVAnt** molecule ($a' = 7.23 \text{ \AA}$, $b' = 5.85 \text{ \AA}$) (right).

high mobility of the molecule as predicted by the molecular modeling.¹⁰ Such a dense packing structure is at least partially due to the molecule's extended conjugation length and intermolecular van der Waals interactions between flexible alkyl side chains and planar aromatic rings in neighboring molecular layers.

OTFT devices were fabricated in a "top contact" geometry as we reported previously.⁷ The mobility of the semiconductor, in the range of 0.1–1.28 cm²/V·s, is dependent on the substrate temper-

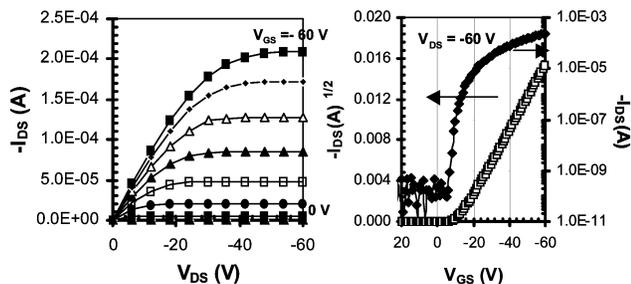


Figure 2. Characteristics of DPPVAnt OFET devices ($L = 60 \mu\text{m}$, $W = 600 \mu\text{m}$) fabricated at $T_{\text{sub}} = 60 \text{ }^\circ\text{C}$ with a saturated charge mobility of $1.28 \text{ cm}^2/\text{V}\cdot\text{s}$ and on/off ratio of 1.6×10^7 , sub-threshold swing of $1.9 \text{ V}/\text{dec}$ with a threshold voltage of -13 V .

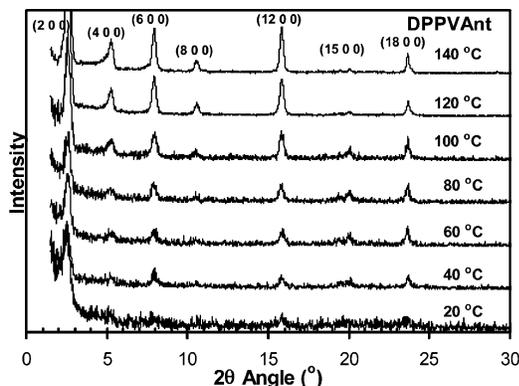


Figure 3. XRD DPPVAnt at different substrate temperatures.

atures. On/off current ratios are excellent with orders of 10^6 – 10^7 (see Supporting Information). Maximum charge mobility is observed in the range of 60 – $80 \text{ }^\circ\text{C}$, possibly due to the well-ordered thin films grown in this temperature regime. All OTFTs showed very well-defined linear- and saturation-regime output characteristics (see Figure 2).

To understand the observed substrate temperature-dependent mobility, thin films (40 nm) of DPPVAnt, prepared at different substrate temperatures, were investigated using X-ray diffraction (XRD) (Figure 3). In general, it is clear that the films are successively more ordered with temperature, and reflections correspond well with the $(h 0 0)$ reflections from single-crystal data. Interestingly, we observed that the peak intensities increase when h is an even number at all substrate temperatures. When h is an odd number, such as $(15 0 0)$, the peak intensity increases until it reaches a maximum at $100 \text{ }^\circ\text{C}$, then it decreases at higher substrate temperatures. These subtle peak intensity variations indicate that there is a change in orientation of the thin films when the substrate temperature changes. A possible explanation is that, below $40 \text{ }^\circ\text{C}$, the order of the thin films is poor. When the substrate temperature is around 60 – $80 \text{ }^\circ\text{C}$, the orientation of the molecules is optimal, favoring charge transport. From 100 – $140 \text{ }^\circ\text{C}$, there is annealing of the films, giving rise to a new orientation and subsequent growth of the films about the new orientation. Such subtle changes may explain why the charge mobility value has a peak around 60 – $80 \text{ }^\circ\text{C}$ and decreases when the substrate temperature goes either

direction. As for the thin film morphology, AFM images of all the thin films show a well-connected, worm-like texture (see Supporting Information).

Under similar device fabrication conditions, highly purified pentacene showed maximum charge mobility around $1.05 \text{ cm}^2/\text{V}\cdot\text{s}$. However, the stability of pentacene OTFTs is far less than that of DPPVAnt semiconductor OTFTs. When the devices were stored at an ambient condition for 1 month, pentacene OTFTs displayed an average charge mobility of $0.03 \text{ cm}^2/\text{V}\cdot\text{s}$ with on/off ratios below 10^2 . In contrast, DPPVAnt devices retained high charge mobility of $0.95 \text{ cm}^2/\text{V}\cdot\text{s}$ with on/off ratios above 10^6 after storage of over 20 months under ambient conditions.

In conclusion, we have synthesized a novel, high charge mobility and stable organic semiconductor. We envision that the high charge mobility of the new semiconductor is due to its densely packed crystal structure along with its well-ordered thin film morphology. These findings, combined with our earlier studies, provide additional structure–property understanding needed to create new high stability, high mobility organic semiconductors.

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Supporting Information Available: Details of experimental procedures, UV–vis, electrochemistry spectra of DPPVAnt, table content of OTFT device data, and X-ray crystal structure cif file. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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