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Soluble and Easily Crystallized Anthracene Derivatives: Precursors of Solution-Processable Semiconducting Molecules

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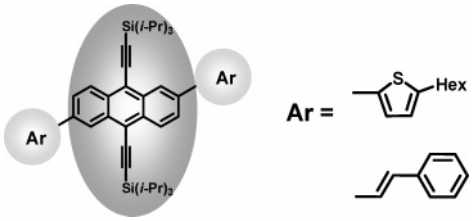
ABSTRACT



New soluble anthracene derivatives containing thiophene and phenylenevinylene derivatives were synthesized via well-known synthetic routes. TIPS derivatives were added at the 9,10-positions of anthracene for the solubility and crystallinity. Both of the molecules were found to be promising for high charge mobility and stable organic semiconductors. The soluble anthracene core (TIPSAnt) is a potential precursor for the synthesis of novel semiconducting materials.

The identification of new organic semiconducting molecules has been a crucial factor driving improvements in organic thin-film transistors (OTFTs) and great achievements have been reported.[1] Recently there has been increased interest in the stability and processability of OTFT devices, in addition to the conventional focus on device performances. Organic molecules soluble in organic solvents are promising materials for inexpensive device fabrication since they can be processed by simple solution techniques such as spin-coating, drop-casting, or inkjet-printing.[2] To date, most efforts to synthesize soluble semiconducting molecules have focused on polymeric conjugated systems.[3] Compared to polymers, however, oligomeric semiconducting molecules have several advantages including well-defined structure and ease of synthesis, purification, and structural modification.

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Among the soluble oligomers reported to date, the functionalized pentacene has one of the greatest potentials as a semiconducting material.[4] Adding bulky triisopropylsilylethynyl (TIPS) groups at the 6,13-positions of the pentacene not only improves the π-orbital overlap but also enhances the solubility and the oxidative stability of the material. Moreover, solution-deposited OTFT device properties with use of functionalized pentacene and anthradithiophene were reported.[5] To modify the chemical structure of TIPS pentacene, Anthony et al. synthesized various new oligomers based on tetracene, pentacene ethers, and so on.[6]

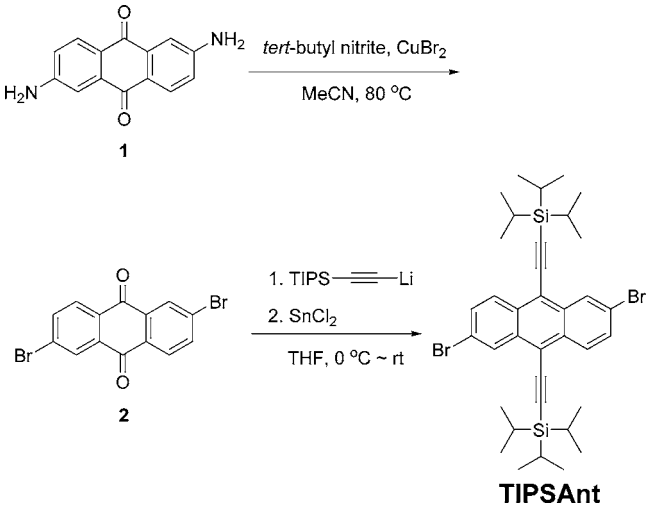
Among the oligomeric systems for OTFTs, anthracene is one of the most important fused aromatics.[7] In 2005 and 2006, Meng et al. reported novel anthracene−oligomer-based semiconductors that showed high field-effect mobilities with excellent stability.[8] In addition, attempts to develop soluble oligomers with use of anthracene moieties have also been reported recently.[9]

Our approach is to introduce bulky TIPS groups at the 9,10-positions of 2,6-dibromoanthracene molecules to create a soluble oligomer core. The resulting functionalized dibromo anthracene can be coupled with various aromatic boronic acids or esters via the well-known Suzuki coupling reaction.

The target soluble oligomer core 2,6-dibromo-9,10-bis(triisopropylsilylethynyl)anthracene (**TIPSAnt**) was synthesized according to the procedure discribed in Scheme 1. Commercially available 2,6-diaminoanthraquinone **1** was converted into 2,6-dibromoanthraquinone **2**[10] by using the Sandmeyer reaction and then TIPS was introduced at the 9,10-positions of the anthracene via synthetic routes similar to that used for TIPS pentacene.[5a] TIPS groups make anthracene highly soluble in common organic solvents such as chloroform, chlorobenzene, and toluene. (cf. 2,6-dibromoanthraquinone **2** is insoluble in such solvents.)

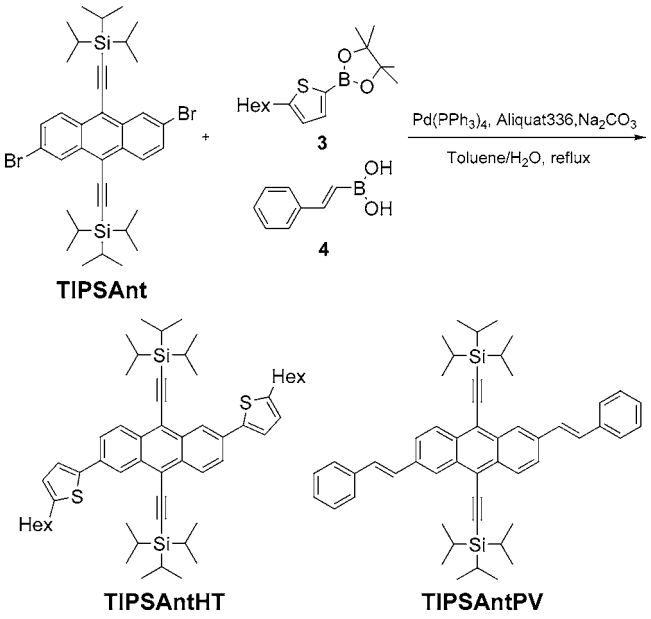
The bromo groups of **TIPSAnt** enable coupling of the molecules with various borolanylaryl molecules, for example, acene, thiophene, and fluorene derivatives. In the present work we chose hexylthiophene and phenylenevinylene as

Scheme 1. Synthesis of the Soluble Oligomer Core (**TIPSAnt**)



counterparts of **TIPSAnt**. 2,6-Bis(5′-hexyl-thiophene-2′-yl)-9,10-bis(triisopropylsilylethynyl)anthracene (**TIPSAntHT**) and 2,6-bis(2′-phenylvinyl)-9,10-bis(triisopropylsilylethynyl)-anthracene (**TIPSAntPV**) were synthesized via a Suzuki coupling reaction as shown in Scheme 2.

Scheme 2. Synthesis of **TIPSAntHT** and **TIPSAntPV**



The products were bright orange, highly crystalline solids. Similar to **TIPSAnt**, **TIPSAntHT** and **TIPSAntPV** also show good solubility in common organic solvents due to the TIPS groups and especially **TIPSAntHT** shows higher solubility due to hexyl groups on the thiophenes. The compounds were characterized by ^{1}H NMR and ^{13}C NMR, as well as elemental analysis. (See the Supporting Information.)

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The thermal transitions of the oligomers have been studied by differential scanning calorimetry (DSC) under a nitrogen atmosphere. We found that **TIPSAntHT** exhibits a major melting endotherm at 192 °C and a corresponding crystallization exotherm upon cooling at 160 °C. These two peaks are very significant and reversible without any extra thermal transitions. **TIPSAntPV** exhibits liquid crystalline property showing the first endothermal peak at 63 °C and the second endothermal peak at 242 °C, and corresponding exothermal peaks at 50 and 188 °C. From these thermal responses, we concluded that **TIPSAntHT** and **TIPSAntPV** are highly crystalline and should form well-ordered thin films when deposited on a substrate. (TGA and DSC results can be seen in the Supporting Information.)

Due to their solubility and well-ordered thin film forming property, we successfully prepared thin films of the compounds on quartz plates by spin-coating a solution of **TIPSAntHT** and **TIPSAntPV** in chloroform (20 mg/1 mL, 1500 rpm for 40 s). We could confirm that simple solution deposition techniques are feasible for depositing layers of the oligomers during device fabrication. The UV−vis absorption and photoluminescence (PL) spectra of the oligomers were recorded both in solution (chloroform) and in film form, as shown in Figure 1. Both of the oligomers show good absorption and emission properties in both solution and film state. Specifically, they exhibit slightly red-shifted absorption and significantly red-shifted PL emission in the film state relative to the solution state. Interestingly, in the PL spectra, the differences in emission maxima between the solution and film states of **TIPSAntPV** and **TIPSAntHT** are 70 and 100 nm, respectively, which correspond to the extremely high intermolecular interactions in the film state. The existence of strong interactions in π-conjugated systems between neighboring molecules in the solid state is desirable for good TFT device performances.

To investigate the electrochemical stability as well as the charge-transport property of the oligomers, we carried out cyclic voltammetry (CV) measurements on thin films of the oligomers, as summarized in the Supporting Information. The oligomers show reversible waves for both p-doping and n-doping processes. The oxidation potential E_{ox} (p-doping) for **TIPSAntHT** and **TIPSAntPV** was 0.96 and 0.98 V, respectively. The relatively high oxidation potentials of the oligomers compared to TIPS pentacene (380 mV)[6c] resulted in better oxidation stability of the materials. The HOMO levels of the **TIPSAntHT** and **TIPSAntPV** were estimated as −5.36 and −5.38 eV, respectively, using the previously reported empirical equation.[11] It is worth noting that the HOMO levels of both materials match well with the work function of gold metal.[11c] As a result, the hole injection from the gold source electrode in p-type thin-film transistors is expected to be efficient.

Single crystals of **TIPSAntHT** and **TIPSAntPV**, easily grown from hexane and methylene chloride, were analyzed by X-ray crystallography. Figure 2 shows π-interactions between neighboring molecules in the solid state. The conjugated unit, along the anthracene core, is planar for both oligomers. (Alkyl chains on the thiophenes are coplanar with the conjugation unit.) This planar characteristic is favorable for intermolecular close packing, resulting in a good charge carrier transport in the solid state of the materials.[9b] Two molecules parallel to each other engage in face-to-face interactions for both oligomers. The interplanar distances for

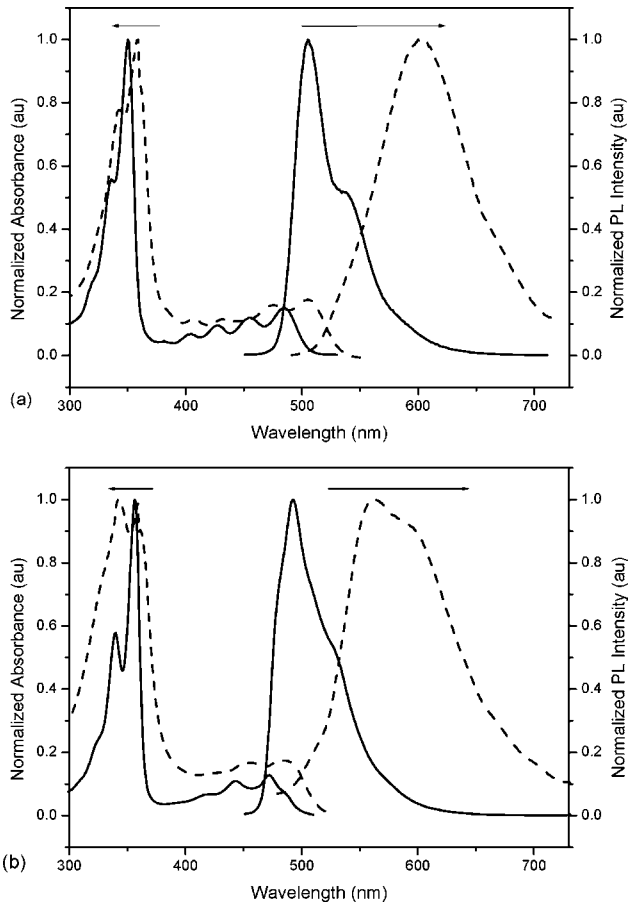

Figure 1. Optical properties. UV−vis absorption and PL emission spectra of (a) **TIPSAntHT** and (b) **TIPSAntPV** in chloroform solution (solid line) and film form (dotted line).

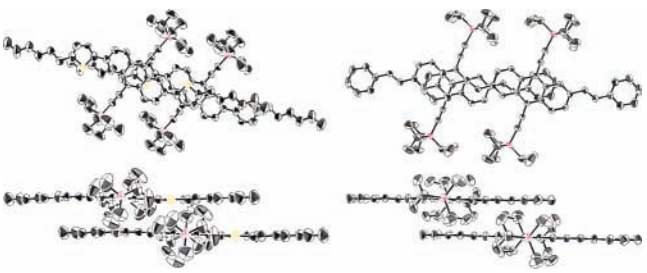

Figure 2. X-ray crystal structures of **TIPSAntHT** (left) and **TIPSAntPV** (right): top view (top) and side view (bottom).

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TIPSAntHT and **TIPSAntPV** in the single crystal were 3.49 and 3.44 Å, respectively, similar to the value for functionalized pentacene, which indicates excellent surface overlap of the adjacent molecules.[4a] Superior π-stacking is also confirmed in Figure 3. The oligomers stack in a two-

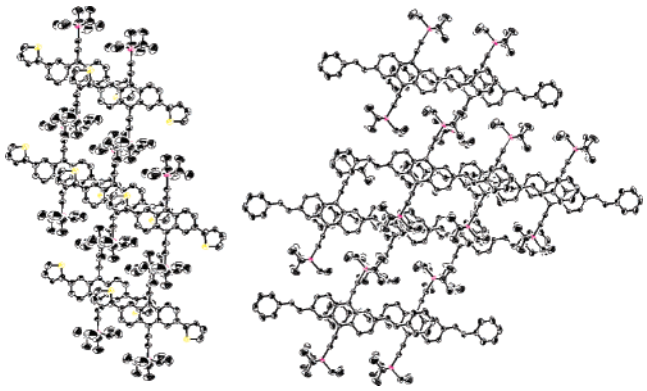

Figure 3. X-ray crystal structures of **TIPSAntHT** and **TIPSAntPV** stacks: view normal to the plane of the conjugated units. Hexyl groups are omitted for clarity.

dimensional columnar array with efficient π-orbital overlap by face-to-face molecular interactions, whereas **DHTAnt**[8a] and **DPPVAnt**,[8b] which lack TIPS groups, pack in the herringbone geometry. Similar to the case of TIPS pentacene, the bulky TIPS groups improve face-to-face interactions and discourage edge-to-face molecular interactions for the anthracene derivatives.

To test the potential of the oligomers as organic semiconductors, field-effect transistors (FETs) of **TIPSAntHT** and **TIPSAntPV** were fabricated by solution processing, preliminarily. Top-contact OFETs were fabricated on a common gate of highly n-doped silicon with a 300 nm thick thermally grown SiO_2 dielectric layer. Substrates were modified with octyltrichlorosilane from a toluene solution for 2 h at room temperature and films of organic semiconductors were spin-coated at 2000 rpm from 0.7 wt % chloroform solution, with a thickness of 45 nm. As shown in Figure 4, the FET device of **TIPSAntHT** shows typical p-channel responses and the output curve shows very good saturation behavior. Remarkably, the drain off-current of **TIPSAntHT** in the transfer curve was less than 10^{-12} A, indicating the electrochemical stability and high purity of **TIPSAntHT**. The field-effect mobility of the **TIPSAntHT**-based device was 4×10^{-3} cm^2/(V·s) ($I_{on}/I_{off} = 10^6$) calculated in the saturation regime. In case of TIPSAntPV, the field-effect mobility was 3×10^{-4} cm^2/(V·s) ($I_{on}/I_{off} = 10^5$). We are currently investigating the OFET devices of **TIPSAntHT** and **TIPSAntPV** to improve the performances,

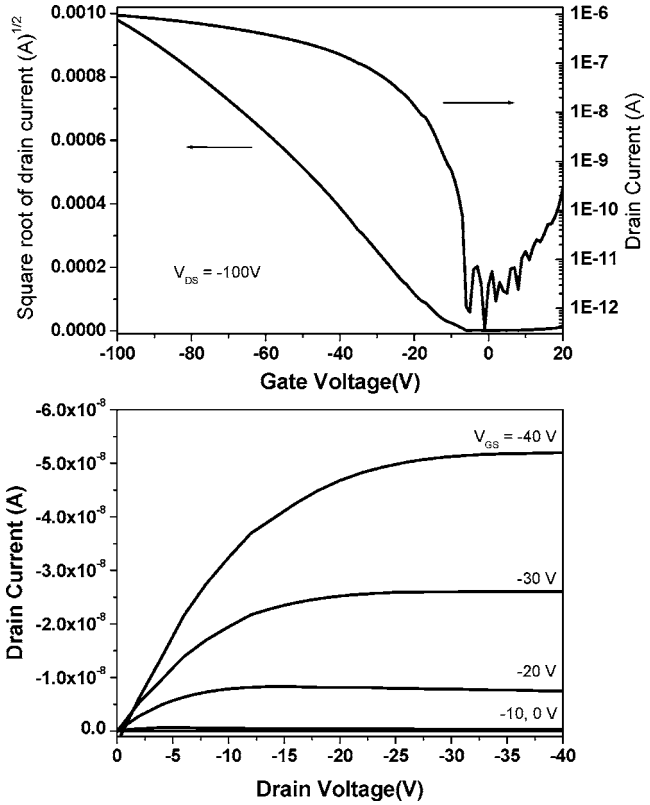

Figure 4. Characteristics of **TIPSAntHT** OFET devices.

and introducing other kinds of aromatic counterparts to **TIPSAnt** for the synthesis of new soluble oligomers.

In conclusion, we propose **TIPSAnt** as a precursor of a new class of semiconducting molecules with desirable properties: solubility, high crystallinity in single-crystal and thin-film form, solution-technique processability, good optical properties, and electrochemical stability. **TIPSAntHT** and **TIPSAntPV** show promising properties and potentialities for solution-processable semiconductors.

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Supporting Information Available: Experimental procedures, characterizations for all compounds, and TGA, DSC, CV, AFM, and single-crystal X-ray crystallographic data for **TIPSAntHT**. This material is available free of charge via the Internet at http://pubs.acs.org.

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