

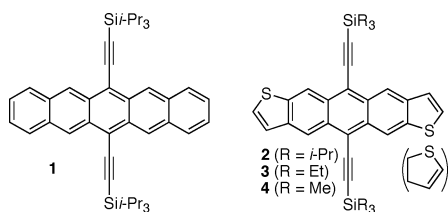
Organic Field-Effect Transistors from Solution-Deposited Functionalized Acenes with Mobilities as High as 1 cm²/V·s

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Organic field-effect transistors (OFETs) are a cornerstone in the development of organic electronic devices,¹ with a simple device structure allowing detailed studies of the effects of crystalline order and interface modifications on device performance. Along with the basic science that can be extracted from OFET devices, there are many potential applications for OFETs, including control elements for displays, RFID tags, and sensors.² High-performance OFETs typically require vacuum deposition of the organic layer.³ Realization of organic electronics' potential for simple processing requires the ability to form devices by solution deposition methods, preferably using simple, inexpensive, easily purified materials. Several research programs have addressed this issue by preparing soluble precursor molecules that can be deposited by solution methods, with the desired semiconductor generated by thermal annealing of the film.⁴ Such methods have yielded OFETs with mobilities as high as 0.9 cm²/V·s, although a 200 °C annealing step is required. An alternative approach uses molecules with small, soluble aromatic surfaces where deposition involves crystallization of the molecules on the substrate. While this approach yields devices with good hole mobility (1 cm²/V·s), it relies on the serendipitous growth of crystals across the source and drain electrodes and is not amenable to large-area production.⁵



We recently reported syntheses and properties of functionalized pentacene (**1**)⁶ and anthradithiophene (**2**)⁷ derivatives designed to exhibit enhanced π -stacking interactions. The materials are easily prepared in one or two high-yielding steps from commercial starting materials, and derivative **1** showed a hole mobility of 0.4 cm²/V·s in an OFET prepared by vacuum deposition.⁸ The high solubility of these functionalized materials (> 100 mg/mL in chloroform) led us to investigate the fabrication of OFETs by solution deposition.

Silylethynylated pentacenes typically adopt either a 1-D “slipped-stack” or 2-D “bricklayer” arrangement in the solid state.⁹ The only derivatives that have so far produced acceptable performance in OFETs have been those that have adopted the latter arrangement, exemplified by pentacene derivative **1**. The crystal order of this material is represented at the top of Figure 1.

Anthradithiophenes functionalized on the thiophene ring were reported to yield good hole mobility from vapor-deposited films (on the order of 0.1 cm²/V·s)¹⁰ and moderate mobility from solution-

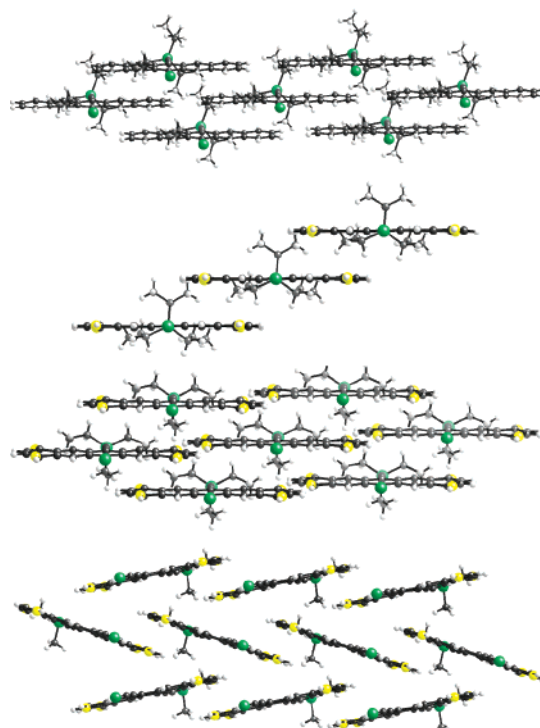


Figure 1. Crystalline order of compounds **1–4** (top–bottom), as viewed along the short-axis of the acene. Alkyl groups on front-most silicon atoms omitted for clarity.

deposited films (~ 0.01 cm²/V·s).^{10c} As with pentacene,⁶ placing substituents on the central aromatic ring of the anthradithiophenes **2–4** both improves the solubility and tunes the intermolecular order to favor π -stacking in the solid state. Unlike similar pentacene derivatives, small changes in the size of the substituent have a dramatic effect on the solid-state order of these molecules, as shown in Figure 1. Triisopropylsilyl derivative **2** packs in a 1-D slipped-stack arrangement, with an average distance of 3.46 Å between π -faces. Triethylsilyl derivative **3** adopts a 2-D π -stacking arrangement similar to that of compound **1**, except for a decrease in π -face separation (from 3.43 Å for **1** to ~ 3.25 Å for **3**), and increased short-axis displacement (see Table 1). Trimethylsilyl derivative **4** shows a molecular order dominated by edge-to-face interactions, leading to a herringbone arrangement with no π -stacking. For molecules **1–3**, the distance of lateral (short-axis) slip is given in Table 1 (values for all nearest neighbors are given for materials exhibiting 2-D π -stacking), along with the total π -overlap area for these derivatives. As with the materials prepared in the original anthradithiophene studies,¹⁰ compounds **2–4** were prepared as inseparable mixtures of *syn*- and *anti*-isomers.

The substrate for the field-effect transistors consisted of a heavily doped Si wafer with a thermally grown oxide layer (370 nm),

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Table 1. Device Parameters for Functionalized Pentacene and Anthradithiophene OFETs (1–4) and Degree of π -Overlap for 1–3

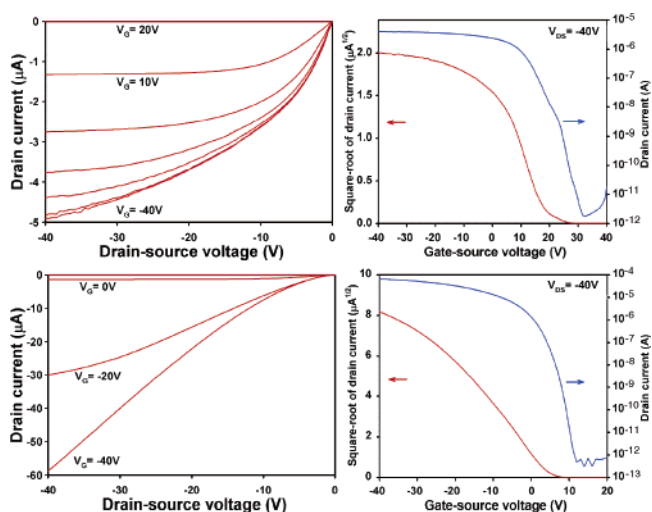
	μ ($\text{cm}^2/\text{V}\cdot\text{s}$)	$I_{\text{on}}/I_{\text{off}}$	π -overlap (\AA^2)	lateral slip (\AA)
1	0.17	10^5	7.73	0.9, 1.7
2	$<10^{-4}$	10^3	2.23	1.2
3	1.0	10^7	1.57	2.75, 1.76
4	NA	NA	(no overlap)	(no π -overlap)

serving as gate electrode and dielectric. Gold source and drain contacts were evaporated to yield devices with a channel length of $22\ \mu\text{m}$ and a channel width of $340\ \mu\text{m}$. The gold electrodes were then treated with pentafluorobenzenethiol to improve the electrode interface.¹¹ A 1–2 wt % solution of the acene in toluene was spread across the device surface using a plastic blade, and the solvent was allowed to evaporate. The devices were then heated in air at $90\ ^\circ\text{C}$ for 2 min to drive off residual solvent. All measurements were performed in air at room temperature, and mobilities were calculated from the saturation currents.

Pentacene **1** yielded devices with hole mobility of $0.17\ \text{cm}^2/\text{V}\cdot\text{s}$ and an on/off current ratio of 10^5 . These values are similar in magnitude to those obtained from a vapor-deposited film of the same material, likely due to the strong templating effect of the silyl group. The anthradithiophene derivatives present an excellent study of how subtle changes in functionalization lead to significant differences in device performance. Triisopropylsilyl derivative **2** formed uniform thin films from solution, but they were amorphous: the best mobility measured was $<10^{-4}\ \text{cm}^2/\text{V}\cdot\text{s}$. In contrast, triethylsilyl compound **3** formed uniform films of excellent quality, yielding hole mobility of $1.0\ \text{cm}^2/\text{V}\cdot\text{s}$ with an excellent on/off current ratio (10^7). The performance of this material is likely due to the close π -stacked interactions in the crystal.^{10b} Trimethylsilyl derivative **4** formed needlelike crystals on the substrate, leading to poor coverage and no transistor action. Clearly, the ability to form high-quality films is essential to device performance, and the strength of π -stacking interactions in the solid may influence the uniformity of the solution-cast film.

Apparent in the $I_{\text{D}}-V_{\text{DS}}$ plots for both **1** and **3** (Figure 2) is that the performance of these devices is strongly contact-limited. High source contact resistance is common in OFETs and can cause current compression of I_{D} for small V_{DS} and high V_{G} .¹² Charge injection limited by space charges near the source may also result in the concave-down nonlinearity of I_{D} for small V_{DS} (as is seen for **3**).¹³ Addition of the silylethynyl groups to the aromatic core increases the oxidation potential (and thus the HOMO energy level) of these molecules by $>300\ \text{mV}$ versus the parent hydrocarbons. While this increase may play a role in the improved oxidative stability of the molecules, it also hampers hole injection into the film.

On/off current ratios for all of these materials are high, on the order of 10^5 – 10^7 . Compound **3**, in particular, has very low conductivity in the “off” state, which speaks to the purity of the material, as well as the absence of oxidative doping of the films. The majority of OFET materials attain the required level of purity from repeated sublimation, which can be a loss-type process. The materials presented here were purified by recrystallization, which is a simple and scalable purification process. This combination of simple synthesis, easy purification, and ability to form high-quality devices from solution-deposited films is an important step in the

**Figure 2.** Electrical characterization for OFETs of functionalized pentacene **1** (top) and anthradithiophene **3** (bottom). Left: plot of drain current (I_{D}) versus drain-source voltage (V_{DS}). Right: plot of I_{D} and $I_{\text{D}}^{1/2}$ versus gate-source voltage (V_{GS}).

development of new materials for organic electronics. We are currently investigating modifications of **1** and **3** to improve the efficiency of charge injection.

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Supporting Information Available: Experimental details and cif files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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