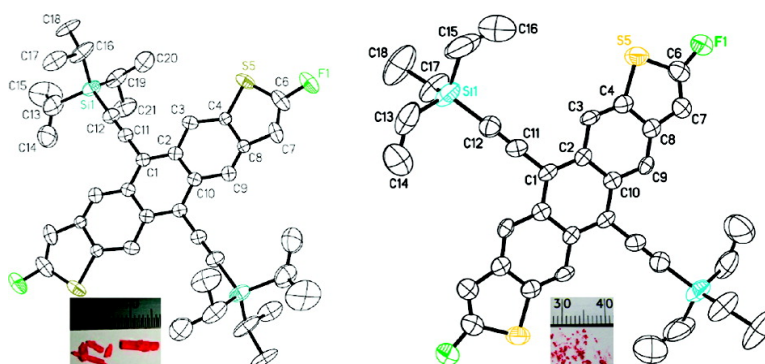


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Chromophore Fluorination Enhances Crystallization and Stability of Soluble Anthradithiophene Semiconductors

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The field of organic electronics often struggles with the tradeoff between the high performance but costly processing of small-molecule semiconductors and the generally lower performance of solution-deposited polymers.¹ While some small molecules can be deposited from solution to yield high-performance field-effect transistors (FETs), they typically require either high-temperature annealing steps or deposition methods involving slow solvent evaporation to yield high crystallinity, precluding the use of low-cost, high-throughput processing techniques.² To utilize common fabrication methods such as spin-coating, substitution strategies that accelerate small-molecule semiconductor crystallization are needed. Our prior work on anthradithiophenes involved manipulation of simple geometrical factors to induce the necessary π -stacking for high carrier mobility, yielding high performance devices from slowly crystallized films. Spin-coating, however, gave only amorphous films with poor device performance.³ This report describes partial fluorination as a method to accelerate the crystallization and improve the stability of these soluble semiconductors.

Noncovalent interactions such as H-bonding have been used to control the growth of organic optoelectronic materials,⁴ but such forces might interfere with the weaker π -stacking that drives self-assembly in silylthynyl heteroacenes. Weaker halogen-based interactions have been exploited in tetrathiafulvalene materials to improve crystallization,⁵ and fluorine interactions in particular are promising supramolecular synthons in crystal engineering.⁶ For functionalized anthradithiophenes, we envisioned that both F–F and F–S interactions (Figure 1), as well as the known interactions between fluorinated and non-fluorinated aromatic surfaces,⁷ should enhance the crystallization of these soluble materials.

Fluorinated anthradithiophenes **1F** and **2F** are easily prepared, like all anthradithiophenes reported to-date, as an inseparable mixture of *syn*- and *anti*-isomers (in Figure 1, only the *anti*-isomer is shown for clarity; in Figure 2, the disorder is readily apparent). Fluorine substitution of this chromophore significantly changed a number of molecular properties, inducing a blue-shift in absorption and a 100 mV increase in oxidation potential vs **1H** and **2H**. More significant is the dramatic increase in thermal and photostability of the fluorinated derivatives. **1F** and **2F** are now stable in the melt, and while films of **2H** bleached under laboratory lighting with $t_{1/2} < 30$ min, films of **2F** exhibited minimal decomposition over several weeks of study (Figure S1). Under bright light, **2F** decomposed with $t_{1/2} > 2000$ h. This stabilization arises from both substitution of the most reactive position of the anthradithiophene and electronic changes induced by the electron-deficient fluorine substituent.⁸ Crystallographic analysis of **1F** and **2F** showed

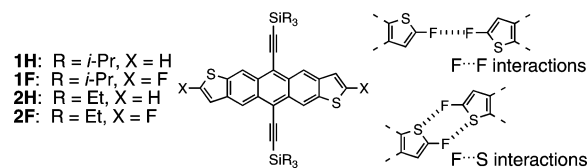


Figure 1. Substituted anthradithiophenes **1H**, **1F**, **2H**, and **2F** and expected F···F and F···S interactions.

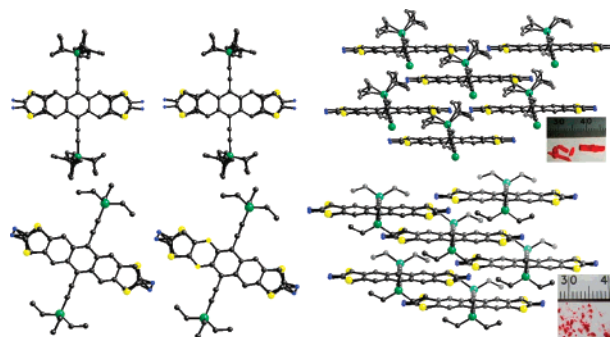


Figure 2. Crystal packing of **1F** (top, some alkyl groups on Si removed for clarity) and **2F** (bottom), along with images of their crystals.

π -stacked arrangements with interplanar spacings ranging from 3.27 to 3.40 Å. In **1F** (F···F contacts as close as 2.6 Å) the crystal packing changed dramatically from **1H**'s 1-D "slipped" π -stack (Figure S2) to a 2-D π -stacking arrangement. In **2F** (S···F contacts as close as 3.16 Å) the differences from **2H** are more subtle but include a 0.3 Å long-axis shift between neighboring molecules in the π -stacks (Figure S3). Although this difference is small, such long-axis movements are predicted to yield significant changes in transport properties.⁹

Unlike non-fluorinated **1H**, we were unable to prepare uniform films of **1F**, which instead formed large block-like crystals on the substrate. In contrast, **2F** exhibited two-dimensional film growth yielding uniform, crystalline films even from spin-cast solutions. The difference in film growth may arise from the longitudinal tilt of the **2F** chromophore in the unit cell allowing interaction between the fluorinated chromophore and the substrate (compared to **1F**, which would interact strictly through the silyl substituents).¹⁰ Successful device fabrication with **2F** also required treatment of the Au electrodes with pentafluorothiophenol. While such treatments are common in the fabrication of organic FETs, they typically serve to alter the work function of the electrode to facilitate charge injection.¹¹ Here, the surface treatment appears to induce nucleation and rapid crystal growth of **2F** on the gold electrodes, yielding large, plate-like crystallites that grow from the electrodes and span the channel region (Figure S4). Without this treatment, crystalline films still formed but with significantly lower uniformity and device

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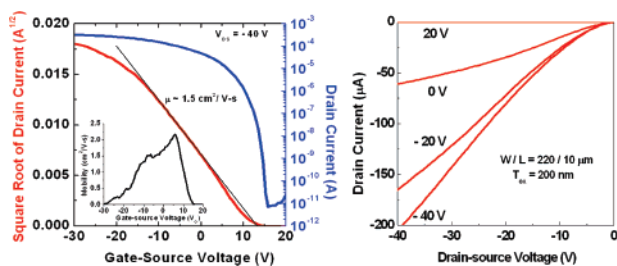


Figure 3. $\text{Log}(I_D)$ and $\sqrt{I_D}$ versus V_{GS} with mobility versus V_{GS} inset (left) and I_D versus V_{DS} for several values of V_{GS} (right) for a FET fabricated from a spin-cast thin film of **2F**. $W/L = 220/10 \mu\text{m}$, $T_{\text{ox}} = 200 \text{ nm}$.

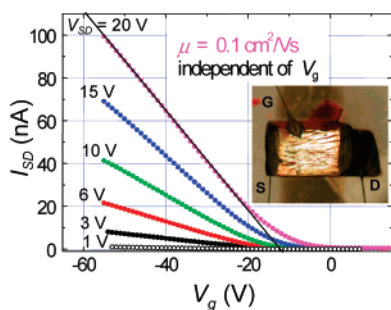


Figure 4. Single-crystal FET device performance of **1**. The inset is a photograph of the device, where a rough top surface of the solution-grown crystal can be seen under the gate.

performance. The degree of crystallinity in the films is remarkable considering their speed of formation (1200 rpm/2 min), conditions under which **2H** yielded only amorphous films. The nature of the interaction between **2F** and the surface treatment is currently being investigated.¹⁰ Because of the improved crystallization induced by the electrode treatment, device performance and uniformity of spin-cast films of **2F** are significantly improved over those of **2H**. In devices with a channel length of 5–10 μm , hole mobility greater than $1 \text{ cm}^2/\text{V s}$ was measured, and average mobility for 50 devices was $0.7 \pm 0.15 \text{ cm}^2/\text{V s}$. Figure 3 shows an example of a high mobility ($>1.5 \text{ cm}^2/\text{V s}$) $10 \mu\text{m}$ channel device. All devices were fabricated in air with a maximum process temperature of $90 \text{ }^\circ\text{C}$. The significant contact problems shown in Figure 3 are typical for the high mobility spin cast devices even with the contact treatment.

Although the thin film transport properties of **1F** could not be evaluated, the large solution-grown crystals of **1F** allowed fabrication of free-standing single-crystal FETs (Figure 4). An aqueous suspension of colloidal graphite formed the source and drain electrodes, parylene-*N* ($1 \mu\text{m}$ thick) was used as the insulator, and thermally evaporated silver was used as the gate electrode.¹² The conformal nature of the parylene coating allows fabrication of leakage-free devices even on these rough crystal surfaces. The devices showed a gate-voltage independent mobility of $0.1 \text{ cm}^2/\text{V s}$. Mobility in these devices was likely limited by the rough surface of the solution-grown crystals (inset Figure 4), leading to trapping and scattering sites at the crystal/dielectric interface. An observation of threshold voltage dependence on crystal growth solvent similarly indicates that changes in the crystal surface have a significant impact on device performance. Crystallization methods that reduce surface roughness (e.g., vapor transport) will likely improve the performance of these devices.

The perfluorination or perfluoroalkyl substitution of aromatic compounds is a well-known technique to alter the electronic properties of p-type semiconductors, creating high performance n-type materials.¹³ We demonstrate here that the strategic addition of a few fluorine substituents does not alter p-type behavior but dramatically improves thermal and photostability and induces solid-state interactions that accelerate crystallization. Fluorine-substituted **2F** in particular is a robust semiconductor that easily and reproducibly forms stable, high quality thin films, allowing detailed studies not possible with non-fluorinated **2H**. This partial fluorination strategy should also be suitable for use on other heteroaromatic semiconductors.¹⁴ We are currently exploiting the increased volatility of fluorinated aromatic systems^{13b} to form high quality single crystals by vapor transport methods, which will allow further study of the transport properties of these materials.

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Supporting Information Available: Synthesis of **1F** and **2F**, and their corresponding CIF files, as well as details describing device fabrication and characterization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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