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Versatile α , ω -Disubstituted Tetrathienoacene Semiconductors for High Performance Organic Thin-Film Transistors

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Facile one-pot [1 + 1 + 2] and [2 + 1 + 1] syntheses of thieno[3,2-b]thieno[2',3':4,5]thieno[2,3-d]thiophene (tetrathienoacene; TTA) semiconductors are described which enable the efficient realization of a new TTA-based series for organic thin-film transistors (OTFTs). For the perfluorophenyl endfunctionalized derivative DFP-TTA, the molecular structure is determined by single-crystal X-ray diffraction. This material exhibits n-channel transport with a mobility as high as $0.30 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and a high on-off ratio of 1.8×10^7 . Thus, DFP-TTA has one of the highest electron mobilities of any fused thiophene semiconductor yet discovered. For the phenyl-substituted analogue, DP-TTA, p-channel transport is observed with a mobility as high as $0.21 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. For the 2-benzothiazolyl (BS-) containing derivative, DBS-TTA, p-channel transport is still exhibited with a hole mobility close to $2 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. Within this family, carrier mobility magnitudes are strongly dependent on the semiconductor growth conditions and the gate dielectric surface treatment.

1. Introduction

Organic semiconductors have attracted growing attention over the past decade due to their potential application in organic thin-film transistors (OTFTs) for low cost/printable electronics, such as flexible displays, RF-ID components, and e-papers.^[1-12] Compared with well-known organic semiconductors, such as pentacenes^[13–15] and anthradithiophene derivatives,^[16–18] fused-thiophenes^[19–21] offer the attraction of relatively higher ambient stability originating from large band gaps, and good

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charge transport properties, reflecting extensive molecular conjugation and strong intermolecular S---S interactions which promote close molecular packing. Several fused thiophene derivatives have already been demonstrated to have good p-type charge transport performance (Figure 1). For example, those with three fused thiophene units, compounds 1^[22] and 2,^[23] and those with four thiophenefused units, **3**.^[19] **4**.^[24] **5**.^[25] and **6**^[26] exhibit hole mobilities up to 0.42, 0.89, 0.14, 0.06, 0.70, and 2.75 cm² V⁻¹ s⁻¹, respectively. Furthermore, five-ring fused pentacene analogs 7^[27] and 8^[28] achieve hole mobilities of 0.51, and 1.7 cm² V⁻¹ s⁻¹, respectively. Relative to p-type fused thiophenes, the potential of n-type fused thiophene-based semiconductors has not been fully explored until recently, and

then only for a limited range of materials.^[29–31] One approach to realizing electron transport in organic semiconductors is to functionalize p-type semiconductors with strong electronwithdrawing substituents, such as perfluorophenyl,^[32] carbonyl^[33] groups. Previously we investigated perfluorophenyl substituted dithieno[2,3-b:3',2'-d]thiophene (**DFP-DTT**; **9**) and perfluorobenzoyl (C₆F₅CO) substituted DTTs (**FBB-DTT**; **10** and **DFB-DTT**; **11**). All three of these new DTTs exhibit decent electron mobilities, as high as 0.07, 0.03, and 0.003 cm² V⁻¹ s⁻¹, respectively, for vapor-deposited films.

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Figure 1. Several examples of fused thiophene organic semiconductors.

Following a molecular design strategy analogous to DTTs, the fused tetrathiophene-based tetrathienoacene (TTA) system, end-functionalized with electron-withdrawing groups, is investigated in this contribution to better understand correlations between molecular structure and n-type TFT performance (Figure 2). To the best of our knowledge, the first example of a TTA-based small molecule semiconductor with a p-channel mobility of 0.14 cm² V⁻¹ s⁻¹ was reported by Y. Liu et al. in 2009.^[19] The second TTA, endcapped with styrenyl groups, was reported by the same team in 2010 with a mobility of 0.06 cm² V⁻¹ s^{-1.[24]} Recently a dicyanomethylene substituted fused tetrathienoquinoid was reported with a good mobility of 0.9 cm² V⁻¹ s⁻¹ after solution processing.^[34] Since then, no other TTA-based small molecules have been reported, due to synthetic difficulties in accessing the tetrathiophene core, which was obtained in only 15 ~ 26% overall yield from reaction of 3-bromothiophene and 3-bromothieno[3,2-b]thiophene.^[19]

To address this issue, we report here facile "one-pot" [1 + 1 + 2] and [2 + 1 + 1] syntheses of TTA. Compared to the previous synthetic routes, this one-pot synthesis offers a more

efficient route to obtain tetrathiophene cores at a low cost. Furthermore, we show that TTA can also be generated in a reverse [2 + 1 + 1] order, unprecedented in TTA chemistry. With the help of electron-withdrawing groups, this TTA core is shown to achieve good n-type charge transport in OTFT devices. The perfluorophenyl end-functionalized derivative DFP-TTA exhibits n-channel transport with a mobility as high as $0.30 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, rendering it one of the highest performing n-type semiconductors among fused thiophenes reported to date. Two other TTA derivatives are synthesized to better understand molecular structure-device performance relationships. Phenyl-substituted derivative DP-TTA and the 2-benzothiazolyl (BS-) containing derivative DBS-TTA exhibit p-channel transport with mobilities as high as 0.21 cm² V⁻¹ s⁻¹ and 0.002 cm² V⁻¹ s⁻¹, respectively. Materials properties such as crystal structure, HOMO-LUMO localization/energetics, and film microstructure are discussed and compared/contrasted with the DTT analogs (Figure S1). In addition, film growth conditions including substrate temperature, and dielectric surface treatment are investigated and shown to strongly influence TFT device response in a readily understandable way.



Figure 2. Chemical structures of the tetrathienoacene (TTA) derivatives synthesized in this study.

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Scheme 1. One-pot [1 + 1 + 2] and [2 + 1 + 1] synthetic routes to the **TTA** core.

2. Results and Discussion

In this section we first describe the synthesis of the new semiconductors, followed by molecular characterization. Next, we examine details of the solid state packing, and the microstructure of the vapor-deposited films based on X-ray diffraction data. Finally, we discuss thin-film transistor characterization and correlate the results with semiconductor film morphology, such as crystalline domain size, surface coverage, and nucleation density at the semiconductor-dielectric interfacial region.

2.1. Synthesis

Since the key building block in this investigation is the tetrathiophene-fused core, a one-pot [1 + 1 + 2] synthesis of TTA was first explored. Our new approach originates from inexpensive, commercially available materials and dispenses with the requirement of expensive bis(phenyl-sulfonyl)sulfide, which is conventionally used in the fused-thiophene syntheses,^[35–37] and the results for TTA derivatives are much shorter synthetic times with comparable yields. For this one-pot synthesis, 3-bromothiophene is first lithiated with *n*-BuLi, followed first by S₈ and then by TsCl addition, as shown in **Scheme 1**. Next, the mixture is treated with 3-lithiumthienothiophene,



generated in situ from 3-bromothienothiophene, synthesized as shown in Scheme S1.^[37,38] Without product isolation, the crude mixture is subsequently dilithiated with *n*-BuLi and ring closure is achieved with CuCl₂ to afford TTA in >27% yield. An alternative/reversed one-pot [2 + 1 + 1] synthesis of TTA was also explored and offers a comparable yield (~22%).^[39] For comparison, TTA was prepared following the known fused thiophene synthetic route in which 3-bromothiophene is first ring-fused,^[40] and then brominated to give 2,3,5,6-tetrabromothieno[3,2-*b*]thiophene, then double ring-fused, following a known TTA synthetic route,^[41] to afford tetrathienoacene in an total yield

of 16% (**Scheme 2**). Undoubtedly, the latter route is much more time-consuming and labor-intensive compared to the one-pot synthetic route developed here.

Since perfluorophenyl functionalization is likely to result in good candidates for n-channel semiconductors, the synthesis of C_6F_5 -functionalized TTA (**DFP-TTA**) was explored and achieved in a yield of 75% via Stille coupling (**Scheme 3**). For comparison, **DP-TTA** was also prepared via Stille coupling and the yield is comparable to the Suzuki coupling approach (Scheme 3). More conjugated benzothiazolyl substituents, in addition to contributing the electron-withdrawing capacity of the carbonyl group (C = O), tend to form planar molecular structures,^[42] thus possibly resulting in lower-lying LUMOs, and hence possible n-channel transport. Therefore, 2-benzothiazolyl (BS-) end-capped **DBS-TTA** was prepared and achieved in a yield of ~51% by refluxing 2-aminobenzenethiol with **TTA**-(COCH)₂^[41] with SOCl₂ in situ as shown in **Scheme 4**.

2.2. Semiconductor Thermal and Optical Properties

The three TTA-based materials synthesized in this study are thermally stable and lack any detectable phase transitions at low



Scheme 2. Synthesis of tetrathienoacene from 3-bromothiophene.



Scheme 3. Synthetic route to DFP-TTA and DP-TTA.

temperatures, indicating they are suitable for TFT fabrication. As might be expected, the highest molecular weight compound, **DBS-TTA**, exhibits the highest melting point and TGA weight loss temperature. For **DFP-TTA** and **DP-TTA**, differential scanning calorimetry (DSC) does not reveal obvious endothermic features at temperatures below 280 °C. The thermogravimetric analysis data indicate weight loss (5%) only on heating above 330 °C, as summarized in **Table 1**. Note that the present TTA compounds have significantly higher melting points and higher weight loss temperatures in comparison to their DTT analogs, **DFP-DTT**, **DP-DTT**, and **DBS-DTT** (Figure S1). Interestingly, with perfluorophenyl groups end-capping the TTA core, **DFP-TTA** has a lower melting point and a lower weight loss temperature than its nonfluorinated analogue, **DP-TTA**, and exhibits higher volatility, doubtless due to the perfluoroaryl substituents.^[30,31]

The optical absorption spectra of the TTA compounds in $o-C_6H_4Cl_2$ are significantly red-shifted versus their DTT analogs as shown in **Figure 3**, verifying the smaller band gaps of TTA compounds than their DTT analogs. As expected, the benzothiazolyl-substituted derivative, **DBS-TTA**, exhibits the smallest energy gap among the compounds in this study, arguing that the

delocalization extends from the TTA (or DTT) core to the two benzothiazolyl substituents. Interestingly, derivatives with C₆F₅- substituents exhibit slightly blue-shifted absorptions versus those with C₆H₅ substituents in both the TTA and DTT series, as seen in **DFP-TTA** ($\lambda_{max} \sim 384$ nm) vs. **DP-DTT** ($\lambda_{max} \sim 389$ nm) and **DFP-DTT** ($\lambda_{max} \sim 367$ nm) vs. **DP-DTT** ($\lambda_{max} \sim 373$ nm). The HOMO-LUMO energy gaps calculated from the onset of the optical absorption (2.6–3.1 eV) increase in the order: **DBS-TTA** < **DP-TTA** < **DFP-TTA** as well as **DBS-DTT** < **DP-DTT** < **DFP-DTT**, as shown in Table 1.

R = H; DP-TTA

These results seem contradictory at first glance considering well-known electron-withdrawing group (EWG) effects that typically red-shift absorption maxima in optical spectra.^[43–50] However, the present DPV and DFT studies (See more below) reveal that the electron-withdrawing C_6F_5 group lowers both the HOMO and LUMO, also consistent with known EWG effects. Moreover, the HOMO levels of **DFP-TTA** and **DFP-DTT** are lowered versus **DP-TTA** and **DP-DTT** with respect to their LUMOs. Consequently, the energy gaps for C_6F_5 - substituted derivatives **DFP-TTA** and **DFP-DTT** become slightly larger, thereby explaining the slightly blue-shifted absorption maxima.



Scheme 4. Synthetic route to DBS-TTA.

Table 1. Thermal, optical, and electrochemical comparison of the properties of TTA and DTT compounds.

Compound	DSC Tm(°C)	TGA	UV-vis ^{b)} λmax (nm)	Reduction Potential	Oxidation Potential	Δ Egap(eV)	
		(°C, 5%)		(V) ^{c)}	(V) ^{c)} —	(Optical) ^{b)}	(DPV) ^{c)}
DFP-TTA	280	330	384	-1.66	1.46	2.93	3.12
DP-TTA	280 ^{a)}	371	389	-1.94	1.15	2.87	3.09
DBS-TTA	442	443	426,451	-1.48	1.35	2.60	2.83
DFP-DTT	258	270	367	-1.62	1.64	3.06	3.26
DP-DTT	290	394	373	-1.95	1.21	3.02	3.16
DBS-DTT	262	388	417,441	-1.46	1.47	2.69	2.93

^{a)}see ref. 19; ^{b)}in o-C₆H₄Cl₂; ^{c)}by DPV in o-C₆H₄Cl₂ at 25 °C (using ferrocene/ferrocenium as internal standard, set at +0.60 V).





Figure 3. Optical spectra of TTA compounds (solid lines) and DDT compounds (dashed lines) in o-C₆H₄Cl₂ solution.

The photooxidative stability of the present TTA derivatives was investigated by monitoring the absorbance decay at λ_{max} in aerated CHCl₃ solutions exposed to white light (fluorescent lamp) at room temperature. Under these conditions over the course of 3 days, no decomposition is observed for any of these compounds, demonstrating the photo-oxidative stability of these materials.

2.3. Electrochemical Characterization

Differential pulse voltammograms (DPVs) of the TTA compounds were recorded in dichlorobenzene at 25 °C, and the resulting reductive and oxidative potential data are summarized in Table 1.^[51] The electrochemically-derived HOMO levels of the TTAs are significantly up-shifted versus their DTT analogs as shown in **Figure 4**. More π -electron delocalization is observed for the fused-tetrathiophene TTA system than for the DTTs, and the HOMO-LUMO energy gaps of the TTAs obtained from the DPV data are smaller than those of their DTT analogs. For C₆F₅- substituted DFP-TTA, the electron affinity increases with the larger number of fluoroaryl rings, and fluoroaryl substitution in DFP-TTA strongly lowers both the HOMO and LUMO energies versus those in DP-TTA. Similar trends are observed for DFP-DTT compared to its nonfluorinated derivative DP-DTT. The DPV of DFP-TTA exhibits an oxidative peak at +1.46 V and a reductive peak at -1.66 V (using ferrocene/ferrocenium as the internal standard, set at +0.60 V). For comparison, the oxidation and reduction potentials of DP-TTA ($E_{ox} = +1.15$ V, $E_{red} = -1.94$ V) are shifted to more negative values, which can be attributed to the electronwithdrawing effects of the perfluorophenyl substituents. Similarly, the benzothiazolyl substitution in compound DBS-TTA (E_{ox} = +1.35 V, $E_{\rm red}$ = -1.48 V) strongly shifts the HOMO and LUMO energies to higher values compared to DP-TTA, and induces the most extensive π -electron delocalization within the TTA series, and also has the smallest band gap. The HOMO-LUMO energy gaps obtained from the DPV data are 3.12 eV for DFP-TTA, 3.09 eV for DP-TTA, and 2.83 eV for DBS-TTA (assuming ferrocene/ferrocenium oxidation at 4.8 eV).^[52,53] Overall, the electrochemically-derived HOMO-LUMO energy gaps can be ranked in

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Figure 4. The electrochemically-derived HOMO and LUMO energy levels of TTA and DTT molecules.

the order **DBS-TTA** < **DP-TTA** < **DFP-TTA** (as well as **DBS-DTT** < **DP-DTT** < **DFP-DTT**; Table 1, Figure 4), which is consistent with the values obtained from optical spectroscopy.

It is interesting to highlight the different effects of the two electron-deficient end-groups on the HOMO and LUMO energies. While the perfluorophenyl substituents lower both frontier orbital energies due to almost identical contribution of the perfluorophenyl units to both HOMO and LUMO orbitals (Figure S2), benzothianolyl substitution lowers the LUMO energy to a far greater extent than the HOMO. Note that despite the fact that both substituents are formally electron-withdrawing groups, the nature of their effects differs substantially; for the perfluorophenyl substituents a σ -(-I) isomeric effect is expected versus a π -mediated mesomeric (-M) electron-withdrawing effect for the benzothianolyl substitution.^[54] These different effects explain the rather different modulations of the frontier MO energies, and may result in very different electrical behavior. Furthermore, if we analyze the theoretical charge distributions on both neutral DFP-TTA and DBS-TTA molecules (see Figure S2 in Supporting Information) we observe that the atoms bearing the greatest negative charge in DBS-TTA are the nitrogen atoms, with negative charges of -0.518 e. each. Furthermore, the sulfur atoms in the benzothianolyl group bear a much less positive charge than in the corresponding thiophene rings (Figure S2), underscoring the electron-deficient character of the lateral substituent sulfur atoms. These two electron-deficient atoms are involved to a greater extent in the LUMO (as evidenced in the frontier orbital topologies in Figure S2) than in the HOMO, which explains the unequal destabilization of both frontier orbitals as discussed above. In contrast, the negative charge on the electron-withdrawing perfluorophenyl substituents is localized on the fluorine atoms, which are equally involved in both the HOMO and LUMO topologies (Figure S2), in agreement with the equal stabilization of both orbitals discussed above.

2.4. Semiconductor Solid State and Thin-Film Structure

Thin films of the new semiconductors were vapor-deposited with the goal of investigating the thin-film microstructure



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and morphology for TFT device fabrication. The morphology/ TFT properties of the TTA films were investigated on doped Si (gate)/SiO₂ (gate insulator) substrates with several different gate dielectric surface treatments. Hexamethyldisilazane (HMDS)modified substrates were prepared by exposing the Si/SiO₂ substrates to HMDS vapor for 7 days in a nitrogen atmosphere to yield a trimethylsilyl-coated surface. Octadecyltrichlorosilane (OTS)-modified substrates were fabricated by immersion of the Si/SiO₂ substrates in 3.0 mM hexane solutions of the silane reagent in air for 1 hour after 10 hours of solution aging under 55-60% of relative humidity. All substrates were characterized by advancing aqueous contact angle measurements, which indicate increasing hydrophobicity in the order: SiO_2 (28°) < HMDS (95°) < OTS (104°) . Additionally, the surface roughnesses were evaluated by tapping mode atomic force microscopy (AFM), revealing a root-mean square (RMS) roughness of 0.15 nm for SiO₂, 0.20 nm for HMDS, and 0.35 nm for OTS. All semiconductor films (~50 nm thick) were vapor-deposited while maintaining the substrates at the temperatures (T_{DS}) of 25, 50, and 110 °C, and with a film growth rate of 0.1 Å/s. All films were characterized by θ -2 θ X-ray diffraction (XRD) scans and tapping mode AFM.

Before discussing the XRD results for the TTA films, it is useful to begin by correlating film X-ray θ - 2θ scan data with a compound of known crystal structure. This initial examination allows a much more thorough analysis of the molecular ordering in the solid film. The perfluorinated TTA derivative DFP-TTA crystallizes in the monoclinic space group P2₁/c. The unit cell packing viewed perpendicular to the molecular stacking direction is illustrated in **Figure 5**B, and along the *c*-axis in Figure 5C.

Similar to other fused thiophenes, the unit cell of **DFP-TTA** exhibits a commonly observed herringbone packing motif with

Δ

B

С

19.7Å

DFP-TTA

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cell parameters, a = 28.500 Å, b = 3.9449 Å, c = 11.3467 Å, $\alpha = 90.00^{\circ}$, $\beta = 91.014^{\circ}$, $\gamma = 90.00^{\circ}$, and Z = 2 (Figure 5). The fluorinated phenyl moiety is slightly twisted from the plane of the fused tetrathiophene core, with a dihedral angle of 10.2° (Figure 5B). The cofacial stacking distance between TTA cores is 3.59 Å (Figure 5B), and the shortest intermolecular sulfur---sulfur contact is 3.58 Å (Figure 5C). This planar molecular structure, short packing distances, and high crystal density (2.086 gcm⁻³) suggest ideal conditions to achieve significant charge transport in solid films. In general, DFP-DTT^[30] exhibits a very similar crystal structure to DFP-TTA. This latter molecule also has a typical herringbone packing with cell parameters, a =11.7702 Å, b = 37.048 Å, c = 3.8830 Å, $\alpha = 90.00^{\circ}$, $\beta = 90.000^{\circ}$, $\gamma =$ 90.00°, and Z = 4 (Figure S3) and the perfluorophenyl groups are slightly twisted by 11.1° from the DTT core plane (Figure S3B). The stacking distance between planar DTT cores is 3.60 Å (Figure S3B) with a shortest intermolecular sulfur-to-sulfur distance of 3.48 Å (Figure S3C). In addition, the slipping angle of the DFP-DTT stack is 68° similar to 65° in DFP-TTA. It is well known that the herringbone motif is the result of pulling two adjacent molecular stacks together with a roll angle in the opposite direction.^[55] When the slipping angle is larger, the overlap of the π -conjugated cores is substantially increased along the stacking direction. Since their slipping angle is almost identical, the degree of spacial overlap between adjacent π -conjugated cores depends on the core sizes of molecules. The effect of the greater core size in the DFP-TTA versus that in DFP-DTT is reflected in more efficient charge transport properties for the corresponding thin film transistors (see more below).

With the crystal structure data in hand, it is straightforward to simulate the XRD powder pattern and therefore assign the reflections observed in the thin film XRD measurements. Thus, d spacings calculated from the XRD data, and the molecular

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Figure 5. Crystal structure of DFP-TTA (A) molecular length of DFP-TTA = 19.7 Å, (B) slipping angle of adjacent TTA cores = 65° ; cofacial distance between TTA cores = 3.59 Å; torsion angle between core and perfluorophenyl plane = 10.2° (C) the shortest intermolecular sulfur - sulfur distance = 3.58 Å.

10.2°

3.59Å

65°

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Compound	Substrate	2θ (°)	d-spacing (A)	Molecular length (A)		
	temperature (°C)		Film XRD	DFT calc.	Single crystal data	
DFP-TTA	25,50	4.3	20.7	19.8	19.7	
DP-TTA	25,50	4.6	19.4	17.3	NA ^{a)}	
DBS-TTA	25, 50, 110	3.8	23.3	22.8	NA	
DFP-DTT	25,50	4.7	18.8	17.5	17.4	
DP-DTT	25,70	2.6	16.9	17.0	NA	
DBS-DTT	25, 70, 90	4.2	21.0	20.5	NA	

^{a)}Not available

lengths computed from the geometry optimization and the single-crystal structure analysis are summarized in Table 2. Figure 6 shows a graphical comparison of the experimental and simulated data, with a 2θ scan of a **DFP-TTA** film grown at $T_D = 50$ °C on an OTS-coated substrate, and a powder pattern generated from the single-crystal data. The (h 0 0) reflection family is particularly pronounced, from $(1 \ 0 \ 0)$ to $(6 \ 0 \ 0)$. The (1 0 0) reflection in the film XRD is observed at $2\theta = 4.25^{\circ}$, corresponding to a d spacing of 20.7 Å (Table 2), approximately the length of the unit cell *a* axis. This indicates that the films are highly textured and that DPF-TTA molecules in the films are predominantly aligned with their long molecular axes along the substrate normal; that is, film growth is favored in the a direction. It is also apparent that higher deposition temperatures (T_D) make this *a*-directional alignment even more favorable, as indicated by sharpening and increased intensity of the (*h* 0 0) reflections in the θ -2 θ scans of the corresponding films of the same thickness (Figure S4, Supporting Information).

Table 2. Film microstructural parameters for TTA and DTT molecular systems.

In general, both TTA and DTT molecular types appear to be aligned approximately vertically at the semiconductor-dielectric interface since none of the d spacings is smaller than molecular lengths (Table 2). The slight estimated size difference between TTA and DTT may reflect the intrinsic inaccuracies of the method. This edge-on type molecular arrangement is well known to promote optimum charge transport in organic TFT devices. Over the entire T_D range examined here, the TTA films deposited on OTS substrates exhibit reflections having the same 2θ values (Figure S4). As the deposition temperature (T_D) is increased, the peaks become sharper and their intensities increase. The consistency in reflection positions indicates the presence of a single polymorph and growth orientation across the T_D range. The increase in relative intensity of the higher order peaks on going from room temperature to higher growth temperatures indicates enhanced long range order. The effect of surface treatment is not as obvious as the effect of substrate temperature on the XRD data (Figure S5).

2.5. Organic Thin Film Transistor Fabrication and Characterization

Thin film transistors were fabricated in bottom gate-top contact configurations. Highly doped p-type (100) silicon wafers were used as gate electrodes as well as substrates, and 300 nm thermally grown SiO_2 on the Si was used as the gate insulator. Organic semiconductor thin films (50 nm) were vapor-deposited onto the Si/SiO₂, HMDS-treated, and OTS-treated substrates as described previously. Then, 50 nm gold source and drain electrodes were vapor-deposited at 2×10^{-6} Torr through a shadow mask in a high vacuum deposition chamber. Devices were fabricated with typical channel lengths of 100 µm and a channel width of 2000 µm. Current–voltage (*I–V*) transfer and output plots were measured for each device under vacuum and in air. To illustrate the precision of each measurement, the reported data are an average of at least five devices tested on different regions of the semiconductor film. Key device performance parameters such as field-effect carrier mobility (μ), threshold voltage (V_T), and on-to-off current ratio (I_{on}/I_{off}), were extracted using standard procedures.^[56] The results are summarized in **Table 3**.

DFP-TTA and **DFP-DTT** exhibit good n-type charge transport. **DFP-TTA** exhibits electron mobility $\mu_e = 0.30 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $I_{on}/I_{off} = 2.9 \times 10^7$ for films grown on an OTS-coated substrate at 25 °C (**Figure 7A**, B). **DFP-DTT** exhibits $\mu_e = 0.05 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $I_{on}/I_{off} = 10^7$ for films grown on an HMDS-coated substrate at 25 °C.^[25] The relatively low electron injection barriers evident in the HOMO-LUMO energy diagram (Figure 4) doubtless contribute to this high n-type charge transport. As discussed in the single-crystal structural analysis, the differences in core sizes



Figure 6. Comparison of the θ -2 θ XRD scan of a **DFP-TTA** film grown at 50 °C on an OTS-coated substrate (A) with the simulated powder pattern (B).

Table 3. TFT device performance of TTA materials in this study.



Compound		Substrate Surface Treatment	-	Vacuum				Air			
	Substrate Temperature T _D (°C)		Carrier Sign	Mobility μ (cm ² V ⁻¹ s ⁻¹) ^{a)}		Threshold Voltage V⊤ (V)	I _{on} /I _{Off}	Mobility μ (cm ² V ⁻¹ s ⁻¹)		Threshold Voltage V _⊤ (V)	I _{on} /I _{Off}
F F	25	Bare	Ν	$(6.7 \pm 1.0) \times 10^{-3}$	$(7.7 \times 10^{-3})^{b)}$	72 ± 14	$(4.1 \pm 1.9) \\ \times 10^4$	NA ^{c)}			
F		HMDS	Ν	0.04 ± 0.01	(0.05)	56 ± 7	$(3.2 \pm 0.2) \\ imes 10^6$	NA			
s s		OTS	Ν	$\textbf{0.29}\pm\textbf{0.01}$	(0.30)	56 ± 5	$(1.8 \pm 1.5) \times 10^{7}$	NA			
	50	Bare	Ν	$(7.6 \pm 0.0) \\ imes 10^{-3}$	$(7.6 imes 10^{-3})$	47 ± 0	$(5.3 \pm 0.0) \\ \times 10^7$	NA			
	F	HMDS	Ν	0.05 ± 0.02	(0.08)	57 ± 5	$(2.8 \pm 1.1) \times 10^{7}$	NA			
F F FP-TTA		OTS	Ν	0.03 ± 0.00	(0.03)	44 ± 2	$(3.4 \pm 2.0) \\ \times 10^5$	NA			
	25	Bare	Ρ	0.04 ± 0.00	(0.04)	$-(19 \pm 0)$	$(1.5 \pm 0.0) \\ \times 10^{6}$	0.04 ± 0.00	0.04	-(17±1)	$(4.7 \pm 2.7) \times 10^5$
∫_s		HMDS	Ρ	0.07 ± 0.00	(0.07)	$-(17 \pm 0)$	$(3.3 \pm 0.0) \\ \times 10^{6}$	$\textbf{0.08} \pm \textbf{0.01}$	0.09	$-(18 \pm 2)$	$(1.3 \pm 0.2) \\ \times 10^{6}$
s j=(OTS	Ρ	0.11 ± 0.01	(0.11)	$-(13 \pm 4)$	$(4.3 \pm 4.0) \times 10^7$	0.11 ± 0.02	0.13	$-(19 \pm 6)$	$\begin{array}{c} (4.8\pm0.2) \\ \times10^6 \end{array}$
S 5 DP-TTA	50	Bare	Ρ	$\textbf{0.05} \pm \textbf{0.01}$	(0.06)	$-(19 \pm 4)$	$(1.9 \pm 1.2) \\ \times 10^{5}$	0.04 ± 0.00	0.05	$-(16 \pm 2)$	$(1.3 \pm 0.5) \\ \times 10^5$
		HMDS	Ρ	0.10 ± 0.00	(0.10)	$-(10 \pm 1)$	$(4.0 \pm 3.6) \\ imes 10^{6}$	0.10 ± 0.01	0.11	$-(14 \pm 1)$	$(2.4 \pm 1.3) \times 10^{6}$
		OTS	Ρ	0.21 ± 0.00	(0.21)	$-(22 \pm 0)$	$(1.1 \pm 0.0) \\ \times 10^{6}$	$\textbf{0.16} \pm \textbf{0.05}$	0.19	$-(25 \pm 13)$	$(1.1 \pm 1.0) \times 10^{7}$
DBS-TTA	25	Bare	Ρ	$(2.3 \pm 0.4) \times 10^{-5}$	(2.8 × 10 ⁻⁵)	$-(25 \pm 4)$	$(8.3 \pm 8.2) \times 10^3$	$(1.2 \pm 0.1) \times 10^{5}$	(1.3×10 ⁻⁵)	-(15 ± 0)	$(2.0 \pm 1.0) \times 10^2$
		HMDS	Ρ	$(2.6 \pm 0.4) \times 10^{-4}$	(3.0×10^{-4})	$-(42 \pm 3)$	$(3.7 \pm 2.4) \times 10^4$	$\begin{array}{c}(2.9\pm0.5)\\\times10^4\end{array}$	(3.4×10 ⁻⁴)	$-(34 \pm 2)$	$(3.1 \pm 1.6) \times 10^3$
		OTS	Ρ	(4.1 ± 0.9) × 10 ^{−4}	(5.0×10^{-4})	$-(45 \pm 4)$	$(5.7 \pm 1.9) \times 10^3$	$(4.2 \pm 0.6) \\ \times 10^4$	(4.8×10^{-4})	$-(41 \pm 5)$	$(5.7 \pm 2.5) \times 10^3$
	50	Bare	Ρ	(2.3 ± 0.1) × 10 ⁻⁵	(2.4 × 10 ⁻⁵)	$-(31 \pm 2)$	$(1.0 \pm 0.8) \\ \times 10^4$	$(1.0 \pm 0.1) \times 10^{5}$	(1.1×10 ⁻⁵)	-(10±4)	$(2.6 \pm 0.2) \times 10^2$
		HMDS	Ρ	(6.7 ± 2.1) × 10 ^{−4}	(8.5×10^{-4})	-(42 ± 6)	$(1.5 \pm 0.9) \\ \times 10^{5}$	$\begin{array}{c} (6.8\pm0.5)\\ \times10^4 \end{array}$	(7.3×10^{-4})	$-(39 \pm 4)$	$(2.7 \pm 1.6) \times 10^4$
		OTS	Ρ	$(8.6 \pm 0.3) \times 10^{-4}$	(8.8×10 ⁻⁴)	-(44 ± 11)	$(4.2 \pm 3.0) \times 10^4$	$(7.3 \pm 0.8) \\ \times 10^4$	(8.2×10 ⁻⁴)	-(40 ± 8)	$(2.4 \pm 0.2) \times 10^4$
	110	Bare	Ρ	$(5.0 \pm 0.3) \times 10^{-4}$	$(5.5 imes 10^{-4})$	$-(32 \pm 4)$	$(1.3 \pm 0.4) \times 10^4$	$(4.1 \pm 0.3) \\ \times 10^4$	(4.4×10^{-4})	$-(22 \pm 3)$	$(2.2 \pm 1.1) \times 10^3$
		HMDS	Ρ	$(1.6 \pm 0.1) \times 10^{-3}$	(1.7×10 ⁻³)	$-(34 \pm 4)$	$(4.1 \pm 1.8) \times 10^4$	$(1.3 \pm 0.0) \times 10^3$	(1.4×10 ⁻³)	$-(36 \pm 1)$	$(5.8 \pm 2.9) \times 10^3$
		OTS	Ρ	(1.8 ± 0.5) $\times 10^{-3}$	(1.9 × 10 ⁻³)	$-(12 \pm 5)$	$(5.9 \pm 2.6) \times 10^4$	$(2.1 \pm 0.2) \times 10^3$	(2.3 × 10 ⁻³)	$-(29\pm3)$	$(1.5 \pm 0.1) \times 10^4$

^{a)}The average values obtained for at least 5 devices; ^{b)}The maximum mobility recorded; ^{c)}Not active.

of **DFP-DTT** (Figure 5B) versus **DFP-TTA** (Figure S3B) can be correlated with the lower mobility of **DFP-DTT**. DFT calculations predict the reorganization barrier for electron transport in the case of **DFP-DTT** to be 0.33 eV, slightly greater than the corresponding one for tetrathienoacene derivative **DFP-TTA**,

0.28 eV (Table S2). This factor, among others, likely contributes to the mobility differences in these two bis(perfluorophenyl) derivatives.

In marked contrast to the above **DFP-TTA** and **DFP-DTT** results, neither **DBS-TTA** nor **DBS-DTT** exhibit the anticipated

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Figure 7. Transfer and output plots of OTFT devices fabricated from TTA films grown on an OTS-coated substrate: (A) transfer plot; (B) output plot. **DFP-TTA**, substrate temperature = 50 °C, μ = 0.30 cm² V⁻¹ s⁻¹, V_T = 60 V, I_{on}/I_{off} = 2.9 × 10⁷ in vacuum. (C) transfer plot; (D) output plot. **DP-TTA**, substrate temperature = 50 °C, μ = 0.21 cm² V⁻¹ s⁻¹, V_T = -22V, I_{on}/I_{off} = 1.1 × 10⁶ in vacuum (E) transfer plot; (F) output plot. **DBS-TTA**, substrate temperature = 110 °C. μ = 1.9 × 10⁻³ cm² V⁻¹ s⁻¹, V_T = -5 V, I_{on}/I_{off} = 4.7 × 10⁴ in vacuum. Channel width = 2000 μ m, channel length = 100 μ m.

n-type charge transport, despite having the lowest-lying LUMOs in this series. Instead, they exhibit p-type charge transport. Thus, **DBS-TTA** achieves $\mu = 0.0019 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $I_{on}/I_{off} = 4.7 \times 10^4$ on OTS-coated substrates for T_D = 110 °C (Figure 7E, F), and **DBS-DTT** exhibits $\mu = 0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $I_{on}/I_{off} = 10^5$ for films grown on HMDS-coated substrates at 90 °C.^[30] To understand the reversed polarity of the charge transport in these perfluorophenyl and benzothianolyl derivatives, we optimized the molecular geometries of the corresponding radical anions using DFT computation, and their charge distributions are shown in Figure S6. Upon injection of an electron into **DBS-TTA**, 63% of the charge is localized in the external electron-withdrawing groups while only 37% of the remaining charge is delocalized over the conjugated tetrathienoacene skeleton. In contrast, the negative charge on **DFP-TTA** is more uniformly distributed, with the external electron-withdrawing substituents bearing ca. 44% of the charge and the central conjugated fused

unit the remaining 56%. The more evenly delocalized charge in the perfluorophenyl derivative likely stabilizes the injected charge to a greater extend, thus facilitating electron transport even though the DBS-TTA LUMO energy is lower in energy. These contrasting results can be ascribed to the different nature (σ -inductive vs. π -mesomeric) of the two electron-withdrawing substituents, as discussed above. The situation for the DBS-TTA radical cation is very different, and we find that the positive charge is evenly distributed, with ca. 47% located in the external substituent groups and the remaining 53% on the conjugated tetrathienoacene core (Figure S6), probably favoring hole transport within the thin film. The theoretical calculations also show that DBS-TTA has the smallest reorganization energy within the series (Table S2), with the reorganization energy for hole transport less than that for electron transport (0.214 eV vs. 0.282 eV, respectively). Note that the present results for DBS-TTA and DBS-DTT are in accord with other observations

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that appending electron-withdrawing thiazole units to oligothiophene skeletons seldom enhances electron mobility.^[57] In fact, as shown here for **DBS-TTA** vs. **DP-TTA**, lower hole mobilities are usually obtained versus the corresponding oligothiophenes.

As expected from the HOMO-LUMO energy diagram (Figure 4), **DP-TTA** and **DP-DTT** exhibit good p-type charge transport. Since the work function of the gold electrode is about -5.0 eV, these materials have the lowest hole injection barrier in the series: **DFP-TTA** (0.66 eV) < **DBS-TTA** (0.55 eV) < **DP-TTA** (0.35 eV) and **DFP-DTT** (0.84 eV) < **DBS-DTT** (0.61 eV) < **DP-DTT** (0.47 eV). As a result, **DP-TTA** exhibits $\mu = 0.21$ cm² V⁻¹ s⁻¹ and $I_{on}/I_{off} = 1.1 \times 10^6$ on OTS-coated substrates at 50 °C (Figure 7C, D). Note that **DP-DTT** grown at 70 °C exhibits $\mu = 0.42$ cm² V⁻¹ s⁻¹ and $I_{on}/I_{off} = 5 \times 10^6$ on OTS-coated substrates.^[22]

The effect of substrate temperature and surface treatment are also well reflected in the device performance. As the film crystallinity is enhanced by increasing the substrate temperature, the device performance is substantially enhanced. For **DP-TTA** devices, the parameters $\mu = 0.11 \text{ cm}^2\text{V}^{-1} \text{ s}^{-1}$ and $I_{on}/I_{off} = 2.8 \times 10^7$ for room temperature growth change to $\mu = 0.21 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $I_{on}/I_{off} = 1.1 \times 10^6$ for films grown at 50 °C on OTS-coated substrates. For **DBS-TTA** devices, $\mu = 5.0 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $I_{on}/I_{off} = 3.8 \times 10^4$ for room temperature growth changes to $\mu = 1.9 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $I_{on}/I_{off} = 4.7 \times 10^4$ for 110 °C growth on OTS-coated substrates.

Organic self-assembled monolayer (SAM) treatment of gate dielectric surfaces is known to enhance TFT performance by minimizing surface charge traps and by increasing the microstructural order of semiconductor growth.^[58] Thus, growth on HMDS and OTS SAM-treated Si/SiO2 substrates yields significantly enhanced device performance than on bare Si/SiO₂ substrates. OTS surface treatment particularly enhances OTFT performance versus the other treatments for the TTA semiconductors. For example, **DFP-TTA** devices exhibit $\mu = 0.30$ cm² V⁻¹ s⁻¹ and I_{on}/I_{off} = 2.9 × 10⁷ on OTS for 25 °C growth, but μ = 0.05 cm² V⁻¹ s⁻¹ and $I_{on}/I_{off} = 3.1 \times 10^6$ on HMDS, compared to $\mu = 0.0077$ cm² V⁻¹ s⁻¹ and $I_{on}/I_{off} = 2.7 \times 10^4$ on bare SiO₂. DP-TTA and DBS-TTA OTFTs follow the same pattern. One possible explanation for the superior device performance on OTS SAMs versus HMDS SAMs is the high structural quality of the OTS SAMs. If long alkyl chains in OTS molecules are tightly packed and vertically aligned, the SAM has order approaching in-plane crystallinity which enhances the interconnectivity of initial semiconductor film growth as well as the film crystallinity.^[59-61] To understand the origin of these device performance variations induced by substrate temperature during semiconductor growth and dielectric surface treatment, the surface morphology of semiconductor films was next examined by tapping mode AFM.

2.6. Semiconductor Film Morphology and TFT Performance

The surface morphology of organic semiconductor thin films is often used to evaluate crystalline microstructure based on grain sizes. The highest carrier mobilities are generally obtained for films having the appropriate balance of large grain size and space-filling grain connectivity. AFM images of the TTA films clearly reflect the influence of surface morphology on device performance. The most distinctive effect on surface morphology is substrate temperature (T_D; Figures S7, S8, S9). As the substrate temperature is increased, semiconductor molecules diffuse more rapidly, and are captured in islands facilitating grain growth. Therefore, films deposited at higher temperatures exhibit larger grain sizes. For example, 50 nm thick DFP-TTA films have small ball-shaped grains with diameters of 100 nm - 200 nm for room temperature growth and become web-like 2-3 µm long wire meshes in films grown at 50 °C (Figure S7). DP-TTA films exhibit the largest grain sizes in the series. While small gains with 100-200 nm diameters grow at room temperature, the grains grow in pentacene-like ordered crystalline structures^[62-64] with 2-3 µm diameters as the substrate temperature is increased to 50 °C (Figure S8). DBS-TTA exhibits relatively small grains compared to DFP-TTA and DP-TTA, reflecting the highest molecular weight and melting temperature in the series. These grains evolve from small facets with 20-40 nm diameters to 200-300 nm wide balls at 110 °C growth temperature (Figure S9). XRD data shown in Figure S4 verify that the crystallinity increases along with these film morphology changes. TFT parameters summarized in Table 3 indicate corresponding device performance enhancement as well.

While bulk film morphology evolution satisfactorily explains the effects of substrate temperature on semiconductor film crystallinity, it does not correlate well with dielectric surface treatment. Thus, 50 nm thick TTA film morphologies do not vary greatly for the three different types of substrates. Even the XRD data do not exhibit significant differences related to surface treatment (Figure S5). If the bulk film morphologies are similar, the key factors defining device performance on these three substrates may involve variations in the interface microstructure. To investigate possible differences in molecular level interface microstructure, the surface morphologies of the TTA semiconductor films having submonolayer thicknesses were next investigated on these three substrates.

AFM images of sub-monolayer TTA films grown on the different substrates clearly explain the origin of the device performance differences as a function of dielectric surface treatment (Figure 8). In general, TTA semiconductors grow in large, widely spaced domains on bare Si/SiO₂ along with large empty boundary regions. On the other hand, these materials form small grains with greater nucleation densities on HMDS and OTS SAMs, resulting in tightly integrated film structures. The most densely populated small grains grow on OTS-coated Si/SiO₂ and the SAM plays an important role in modulating charge transport. DFP-TTA forms the most densly populated film structure on the OTS SAM (Figure 8A). This tightly integrated initial semiconductor film growth structure achieves the highest n-type device performance on OTS SAM-deposited gates. Note that DP-TTA films exhibit smaller, but densely populated grains on OTS SAMs compared with the HMDS SAMs and the bare SiO₂ surface (Figure 8B). DBS-TTA also exhibits the same trend with widely dispersed grain patches on bare SiO₂ (Figure 8C). In contrast, DBS-TTA forms webs of microwire structures on HMDS and OTS SAMs. However, the wire diameters are much smaller on OTS SAMs than on HMDS SAMs. These tightly integrated initial semiconductor layers



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Figure 8. Sub-monolayer (1.5 nm) film morphologies of TTA films on the three different Si/SiO₂ substrates indicated. A. **DFP-TTA** grown at 25 °C, B. **DP-TTA** grown at 50 °C, C. **DBS-TTA** grown at 110 °C (tapping mode, topography, 10 μ m × 10 μ m).

composed of small but highly crystalline grains must have enhanced charge transport on OTS SAMs to achieve the best device performance among the substrates examined here. In short, interface semiconductor film microstructures, very different from bulk film morphologies, indicate that the superior device performance for growth on OTS SAMs originates from well-connected as well as highly crystalline initial semiconductor film growth in the dielectric-semiconductor interfacial region.

3. Conclusions

In this contribution, we established that tetrathiophenes with proper electron-withdrawing functional groups offer

considerable potential as versatile n-type organic semiconductors. The TTA building block can now be obtained via an efficient one-pot synthetic route and the first TTA-based n-channel molecule is one result of this study. Enlarged TTA cores are effective in reducing the bandgap and introducing n-type properties. Solid-state packing motifs revealed in single crystal analysis, substrate temperature dependence of film growth, and semiconductor–gate dielectric interface morphology are all shown to be critically importanct factors in optimizing TFT performance. We believe the newly designed one-pot synthetic routes offer a scalable way to produce practical building blocks for n-type organic semiconductors, and are now currently pursuing these molecular design strategies further by incorporating other building blocks into perfluorophenyl-functionalized molecular structures.



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Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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