Investigation of Solubility−Field Effect Mobility Orthogonality in Substituted Phenylene−Thiophene Co-oligomers

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We report here on our investigations of structure−property correlations in soluble organic semiconductors. To develop formulations for mass printing of semiconductor films, a series of alkoxy- and alkyl-disubstituted symmetric phenylene thiophene co-oligomers (disubstituted-PTTP) were systematically synthesized to achieve high solubility in common organic solvents. Solubilities of up to 40% by weight in tetrahydrofuran at room temperature were achieved by introducing branching at various positions on the terminal chains, and by silyloxy or hydroxy functionalization of the chains. Concomitant with the solubility increase, however, mobilities and I_{on}/I_{off} ratios of these materials in TFT devices fall several orders of magnitude. X-ray diffraction of the semiconductor films reveals increasing tilt of the molecular orientation on the substrate with an increase in steric crowding near the PTTP core. This indicates that π-stacking of these molecules along the channel between the source and drain is hampered and leads to the observed inverse interdependence of solubility and the field effect mobility.

Introduction

While plastic electronics has been a promising technology for the last several years, only recently has it achieved a sustained level of urgency.[1−5] Commercialization of several plastic electronic products such as flexible displays, RFID tags and smart cards, and photovoltaic elements are expected by the turn of the decade. The most significant impact of this technology is the estimated cost savings,[4,6−8] thus opening new markets for inexpensive, disposable circuitry that can reach grass-root levels in architectures difficult to realize inexpensively in silicon. For example, with use of plastic RFIDs, it is expected that item level tagging (as against case level or pallet level) will be achievable at a cost of only pennies per tag.[9]

To achieve this goal, however, the tags should be amenable to mass production using conventional techniques and still achieve the requisite performance standards. Ever so often, a material emerges in the literature as a promising organic semiconductor with very high performance characteristics (high mobility, low threshold voltage, etc.), only for it to place unreasonably high demands on the method of manufacture that makes mass production virtually impossible.[10−15] Subtractive techniques such as lithography, and batch processing such as vapor deposition, that most of these reported materials require reduce throughput significantly and hence offset the performance benefits of these materials over their solution-processible counterparts. The latter class affords the capability for mass production by printing techniques such as gravure, offset, or flexography. By proper choice of solvent combinations, solution-processible semiconductors can be incorporated into inks for roll-to-roll production of semiconductor films, maintaining the high throughput that is necessary for commercial viability.

With solution-processible semiconductors there are two distinct classes, each offering its own advantages in realizing a printed device. Polymers such as derivatives of poly(thiophene)s,[16−18] poly(fluorene)s,[19,20] and poly(arylamine)-

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s[21] offer greater mechanical strength, adhesion, and plasticity, improved rheological properties for ink formulations, and a wider tolerance for film-processing conditions. Well-defined small molecules, on the other hand, such as α,ω-substituted sexithiophenes,[22] substituted pentacenes,[23,24] and substituted phenylene thiophene co-oligomers,[25,26] exhibit higher charge-carrier mobilities due to better structural ordering, and in general are more amenable to scale-up while maintaining high purity and reproducible quality. With the inherent polydispersity of polymers and limited purification methods for them on a commercial scale seen as drawbacks, we have chosen to explore the small-molecule class extensively.

In designing such a semiconductor that can be mass-printed, an important parameter for consideration is the solubility limit of the semiconductor in the solvent (ink). Both the stability of an ink composition and the maximum film thickness obtainable from an ink are directly related to the percent solids content. As a thumb rule for mass printing with these small molecules, a minimum of 5% solids content in a stable ink is needed to achieve smooth films of the requisite thickness of ca. 100 nm.

A promising class of small molecules are the phenylene thiophene co-oligomers[27] that can be suitably derivatized to afford solution processibility[25,26] and even appreciable n-type field effect activity.[26] In particular, the [5,5′]-bisphenyl-[2,2′]-bithiophene (PTTP) family is attractive: p-type mobilities as high as 0.3 cm^2/V·s have been reported for the dihexyl-PTTP.[28] As the authors report, among the phenylene thiophene co-oligomers, this particular sequence of PTTP affords the best combination of mobilities and I_{on}/I_{off} ratio owing both to its molecular geometry[25] and energy levels.[27]

Here, we report on a series of alkyl and alkoxy derivatives of the PTTP family (Figure 1), systematically introducing branching, changing the length and position of the branches, and introducing functional groups such as siloxanes and hydroxyls on the terminal hydrocarbons.[29] Each of these has been characterized for its solubility limit in THF (where the molecules generally showed the highest solubility) and was used to fabricate transistors on silicon/silicon dioxide wafers. Mobilities were obtained for both vapor-deposited (sublimed) and solution-deposited semiconductor films. With use of X-ray diffraction on the sublimed films, an attempt to correlate the solubility−mobility interplay, and to understand the structure−property relations governing this interplay, is made.

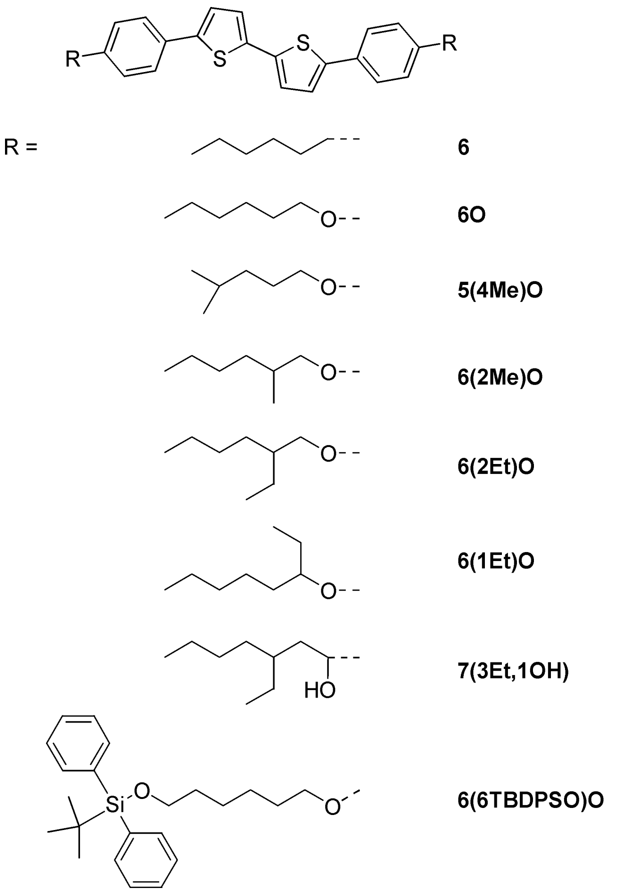

Figure 1. Structures and nomenclature of the various PTTP derivatives.

Experimental Section

Elaborate synthesis, yields, and characterization data for all the molecules are provided as Supporting Information.

General Procedure for Preparation of 5,5′-Bis[4-(alkyloxy)-phenyl]-[2,2′]-bithiophene. 2-[4-(Alkyloxy)-phenyl]-thiophene (6.00 mmol) was dissolved in anhydrous tetrahydrofuran (10 mL) under an argon atmosphere. Then *n*-BuLi (2.5 M in hexanes, 2.64 mL, 6.60 mmol) was added at −50 °C via syringe. The solution was stirred for 45 min at this temperature. A solution of iron(III)-acetylacetonate (2.12 g, 6.00 mmol) in anhydrous tetrahydrofuran (10 mL) was added at −50 °C within 15 min. The mixture was then allowed to warm to room temperature and heated to reflux for another 2 h. After the reaction was cooled, solvents were removed under reduced pressure and the residue was filtered through a short silica pad using toluene as eluent. The crude product was dissolved in refluxing toluene and then methanol (30 mL) was added to precipitate it out. The precipitate was filtered and recrystallized from toluene/methanol to give a yellow solid.

Film Preparation for Thin Film Transistors. Heavily n-doped silicon wafers (with a 3000 Å thermally grown silicon oxide layer) were used as the substrate for depositing the PTTP films for XRD characterization and also to fabricate bottom-gate transistors. The substrates were cleaned by standard piranha etching (3:1 concen-

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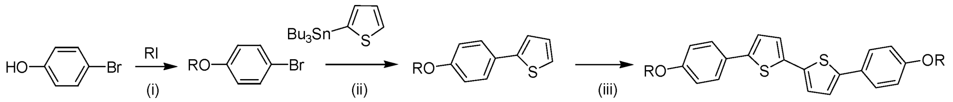
Scheme 1. Synthesis of Dialkoxy-PTTPs[a]



[a] (i) K_2CO_3, NaI, DMF, 100 °C, 14 h; (ii) $Pd(PPh_3)_4$, DMF, 100 °C, 16 h; (iii) *n*-BuLi, $Fe(acac)_3$, THF, 60 °C, 2 h.

trated sulfuric acid and hydrogen peroxide solution) and dried and used without any further surface treatment. In two sets of experiments, 50 nm of each PTTP semiconductor was sublimed (pressure $<10^{-6}$ Torr) onto these wafers while the substrates were maintained at room temperature and at 70 °C, respectively. Films were also prepared by liquid-phase deposition onto wafer maintained at 115 °C from dilute xylene solutions (400 ppm) following the procedure described by Mushrush et al.[25] Unlike the dihexyl PTTP, where optimized deposition temperatures and solvent were reported, no attempt was made to optimize the deposition conditions like temperature or solvents for any of the molecules and the conditions for dihexyl-PTTP were used as a standard.

TFTs were fabricated by evaporating gold source/drain electrodes onto the semiconductor films to form channels with $W/L = 20$ (channel length $L =$ ca. 315 μm). The current−voltage characteristics of these devices were collected by driving source-drain voltages from 0 to −100 V in 1 V decrements for each source-gate voltage, which was varied from 0 to −100 V in 20 V decrements. The devices were fabricated and tested under ambient conditions. All the devices exhibited typical p-type characteristics, and the mobility was extracted from the saturation regime.

For the SAXS measurements, the above sublimed films were probed in areas with no gold deposition. Cu Kα radiation (30 kV, 15 mA) was used and a scan range of 2.5° to 30° (2θ) was recorded.

Results and Discussion

Katz and co-workers[25] have reported on the synthesis and characterization of a series of mixed phenylene−thiophene oligomers and singled out the dihexyl-PTTP (**6**) as a material possessing a combination of good mobility, high I_{on}/I_{off} ratios, and good stability. Mobilities on the order of 10^{-2} $cm^2/V{\cdot}s$ can be reproducibly achieved with this material through casting films onto heated substrates from a very dilute (400 ppm) solution. Also, the synthesis of this particular molecule involves two steps and is straightforward to scale-up, making it attractive for commercialization. However, the solubility of this molecule is limited to a maximum of 1% in common solvents like tetrahydrofuran, chloroform, and xylenes and is thus not amenable for use as an ink for mass printing.

A strategy toward improved solubility[30] is to tune the terminal groups of this molecule while retaining the core phenylene−thiophene sequence. The semiconducting properties of the material evidently stem from the PTTP core, and small alterations to the terminal groups are expected to have minimal impact on the electronic level. New PTTP-based materials specifically targeting higher solubility have been designed and synthesized. The molecules designed in this study are shown in Figure 1, along with the nomenclature used for them.

Table 1. Solubility Limit at Room Temperature of the PTTP Derivatives in THF

compound	solubility limit (wt %) in THF at RT
6	1
6O	0.06
5(4Me)O	0.5
6(2Me)	6
6(2Et)O	8
6(TBDPSO)O	31
6(1Et)O	33
7(3Et,1OH)	39

A general synthesis scheme for the alkoxy derivatives is shown in Scheme 1. To synthesize the various PTTP derivatives, *p*-bromophenol was transformed into the alkoxy-derivatized analogues by a standard Williamson ether synthesis. Since the 2-fold Stille coupling as described by Mushrush et al.[25] resulted in low yields and/or made isolation of the pure molecule difficult, a modified synthetic approach was used. The 1-bromo-4-alkoxy benzene was reacted via a Stille coupling with tri-*n*-butylstannyl thiophene to form the 2-[4-alkyloxy phenyl]-thiophene. An oxidative coupling of this 2-[4-alkyloxy phenyl]-thiophene using an Fe^{3+} species[31] yielded the desired symmetric dimer in good purity and reasonable yield.

As can be seen from the structures, the materials were chosen to represent as wide a design space as possible, while maintaining the overall length of the molecule roughly constant. In most of these cases, for reasons of ease of synthesis, alkoxy groups were the preferred aliphatic chains rather than alkyl. As a control to rule out electronic effects, the alkoxy version of the dihexyl PTTP (**6**), viz. dihexyloxy PTTP (**6O**), was also synthesized and characterized in TFTs. **6O** shows mobilities nearly identical to **6** for films sublimed or deposited from solution, providing us a basis for comparison of the different PTTP derivatives. However, it should be noted that the solubility of the **6O** was much poorer (600 ppm in THF) than **6** and hence this molecule was not further characterized.

The PTTPs were soluble in all common organic solvents more polar than hexane and less polar than methanol to various degrees, and THF was found to be the best solvent for this class of materials. The solubility limit in THF for each of these molecules is listed in Table 1 and spans a wide range of less than 1% to nearly 40%.

Bulky silyl ether groups at the end of the chain, such as the *tert*-butyldiphenylsiloxy unit in **6(6TBDPSO)O**, have a dramatic effect on solubility, and up to 30% solubility of this compound in THF is achieved. In a comparison of the solubilities of **6(2Et)O** (8% in THF) and **6(2Me)O** (6% in THF), it is also apparent that the solubility improves as the

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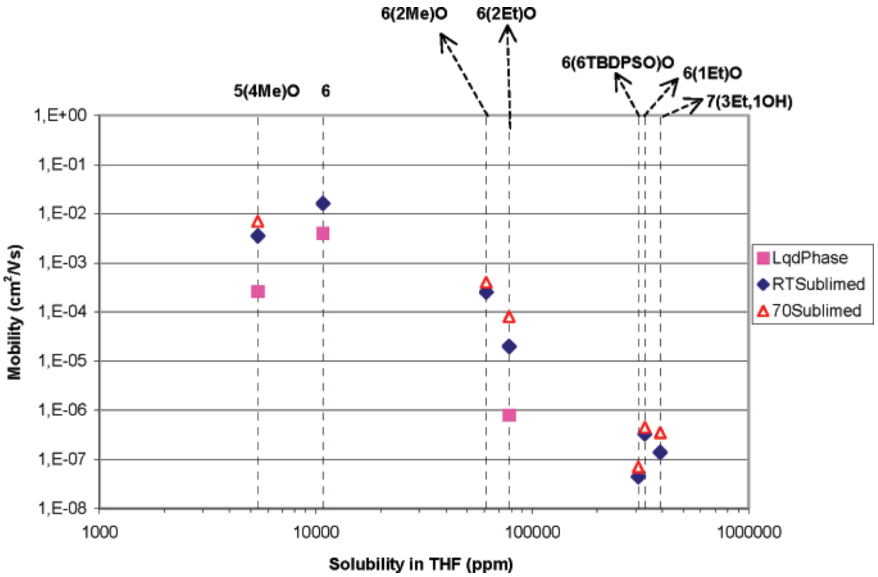

Figure 2. Field effect mobilities for the PTTP derivatives as a function of solubility limit.

Table 2. p-Type Field Effect Mobilities and I_{on}/I_{off} Ratios for Top Contact TFTs from the PTTP Derivatives[a]

	sublimed film (70 °C)		sublimed film (RT)		liquid-phase deposited	
compound	mobility ($cm^2/V{\cdot}s$)	I_{on}/I_{off}	mobility ($cm^2/V{\cdot}s$)	I_{on}/I_{off}	mobility ($cm^2/V{\cdot}s$)	I_{on}/I_{off}
6			1.6×10^{-2}	3000	4×10^{-3}	200
6O	1.4×10^{-2}	15000	2.8×10^{-2}	12000	1.2×10^{-3}	350
5(4Me)O	7×10^{-3}	4000	3.5×10^{-3}	1800	2.6×10^{-4}	100
6(2Me)O	4×10^{-4}	250	2.5×10^{-4}	300	no FET	no FET
6(2Et)O	8×10^{-5}	75	2×10^{-5}	30	8×10^{-7}	3
6(1Et)O	4.5×10^{-7}	3	3.3×10^{-7}	3	no FET	no FET
7(3Et, 1OH)	3.5×10^{-7}	3	1.4×10^{-7}	25	no FET	no FET
6(6TBDPSO)O	7×10^{-8}	2	4.4×10^{-8}	3	no FET	no FET

[a] Devices were made on Si/SiO_2 substrates with Au S/D electrodes.

length of the branch increases. More pronounced is the effect of the branching position on the solubility. Branching closer to the core creates a greater steric impediment to molecular packing and can hence lead to further improvement in solubility. Indeed, 1-ethyl hexyloxy terminals (in **6(1Et)O**) result in a solubility of 33%, a more than 4-fold improvement over the corresponding 2-ethyl hexyloxy terminals (**6(2Et)O**).

In an all-printed process, where the electrodes, the semiconductor, dielectric, and the gate are sequentially deposited, solvent orthogonality between successive layers is important to maintain the integrity of the films. A formulation of the semiconductor which is alcohol-based is hence potentially attractive, and one design of the terminal groups included hydroxy functionalization on the branch. This compound (**7(3Et, 1OH)**) showed solubilities of up to 1% in cyclohexanol and also the highest solubility in THF (39%) within this series.

These molecules were then used to fabricate TFTs, both by sublimation and by liquid-phase deposition as described earlier, and their electrical properties were characterized (Table 2). The mobilities of the molecules spanned orders of magnitude from 10^{-2} $cm^2/V{\cdot}s$ to less than 10^{-7} $cm^2/V{\cdot}s$. The mobilities of each PTTP derivative were highest for the films sublimed onto hot wafers (70 °C), and the mobilities from liquid-phase deposited films were consistently the lowest (and in some cases not detectable). This is consistent with results that Mushrush et al. have published for **6**.[25] The I_{on}/I_{off} ratios for these devices also follow the same trend with values ranging from 4000 for the **5(4Me)O** to less than 3 for the **6(6TBDPSO)O** in the sublimed films.

The mobilities of the molecules were plotted against their solubility limit (Figure 2). Empirically, we see a strong inverse power-law dependence of the mobility of the sublimed films with the solubility of the semiconductor, with an exponent of −2.8. Also, concomitant with the drop in mobility, the drop in I_{on}/I_{off} ratios across the samples implies that this is chiefly driven by dramatic lowering of the on current, with little effect on the off current. This implicates structural disorder due to increased steric hindrance on the core and not electronic effects from the various substitutions as the underlying mechanism for the poor mobilities. We believe that differences in crystal packing and/or molecular orientation of the semiconductors on the wafers lead to the differences in the observed mobilities. Increasing the bulkiness of the substitution by introducing branching units, especially nearer to the core, while making the compound more soluble also disturbs the crystal order and orientation needed for efficient charge carrier transport across the molecules.

To investigate the morphology of the semiconductors, the sublimed films were characterized by X-ray diffraction. All the molecules showed strong signals up to multiple orders, consistent with the crystalline nature of the films (Table 3).

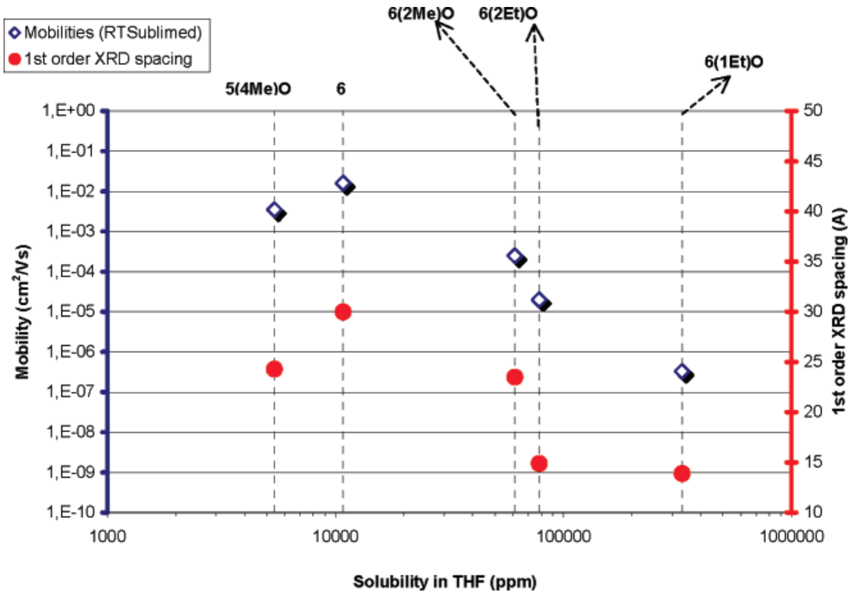

Figure 3. Correlation between *d*-spacing, solubility limit, and FET mobilities in the PTTP derivatives.

Table 3. First-Order *d*-Spacing from Sublimed PTTP Derivatives

compound	*d*-spacing from XRD (first order)	other order peaks observed
5(4Me)O	RT, 24.3 Å	2, 3, 5, 6
	70 °C, 23.8 Å	2, 3, 5, 6
6(2Me)O	RT, 23.5 Å	2, 3
	70 °C, 23.2 Å	2, 3
6(2Et)O	RT, 14.9 Å (a), 21.47 (b), 16.2 (c)	2 (a), 3 (a)
	70 °C, 14.7 Å (a), 21.5 (b), 19.1 (c)	2 (a), 3 (a); 2 (b)
6(1Et)O	RT, 13.9 Å	2, 3
	70 °C, 13.8 Å	2, 3

However, the first-order *d*-spacings vary from ca. 14 Å in the 1-ethyl hexyloxy derivative (**6(1Et)O**) to ca. 30 Å in the hexyl derivative (**6**).

For the 2-ethyl hexyloxy derivative (**6(2Et)O**), in addition to the first-, second-, and third-order peaks corresponding to 14.8 Å, a peak at 21.5 Å is obtained for the films sublimed onto substrates at RT. While this suggests that our assignment of the first-order peak might need to be revised to ca. 43−44 Å, so that the 21.5 Å and the 14.8 Å could then be assigned as second and third order, respectively, scans from $2\theta = 1.5°$ ($d \sim 55$ Å) reveal no additional peaks. Also, 43 Å is relatively too large for a molecule of length ∼33 Å. The only likely explanation is that the molecule is polymorphic, and at room temperature at least two crystal structures coexist in the film. A weak peak just above noise level at 16.2 Å is also discerned, pointing to possibly more than two structures. Support for the presence of polymorphs is obtained from films of this material sublimed onto wafers maintained at 70 °C. A second-order peak of the 21.5 Å (at 10.8 Å) can be discerned. In addition, a new stronger peak at 19.1 Å replaces the 16.2 Å.

The peaks for all the samples measured are sharpened for films sublimed onto the wafers at 70 °C, resolving even higher orders, indicating that the crystalline nature of the film is enhanced. Consistent with this effect, we typically observe approximately a 2-fold increase in the observed FET mobilities for films sublimed on to hot wafers with respect to films deposited onto substrates at room temperature. Importantly, this also implies that a change in percent crystallinity alone cannot fully explain the several orders of magnitude differences that we observe in mobilities across the various derivatives.

The mobilities obtained by all three deposition methods described follow the same trend (possibly explained away by crystallinity) across the derivatives, possibly explained away by crystallinity.[25] This allows us to use mobility data from any of the above deposition methods to compare the different derivatives. Since both X-ray diffraction data and transistor mobilities could be easily obtained on a single sublimed film, this provides a more direct and reliable comparison.

Plotted in Figure 3 is the first-order X-ray spacing against the solubility limit, superimposed with the observed mobilities (sublimed films onto wafers at RT) versus solubility limit. It should be noted here that all the molecules plotted have approximately the same molecular length (∼33 Å). Since this class of molecules prefers a vertical alignment to the substrate, this implies that the *d*-spacing can directly be related to the degree of tilting the molecules undergo with respect to the substrate, with a smaller *d*-spacing correlating to a larger tilt from the substrate normal.

Not surprisingly, the smallest tilt is seen in the linear alkyl derivative (**6**) and the largest in the 1-ethyl hexyloxy derivative (**6(1Et)O**). **6(1Et)O** has bulky branching that is also closest to the core. To accommodate the larger volume of the aliphatic chain in comparison with the aromatic moiety in a unit cell, the molecule tilts further on the substrate. Since carrier transport through the molecules is primarily through hopping across the π-stacks,[32] molecules aligned nearly perpendicular to the substrate (so that the π-stacking direction is co-incident with the TFT channel) should exhibit the

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highest mobilities. Consistent with this, as seen in Figure 3, the mobility in the sublimed films closely tracks the trend in the *d*-spacings, with good qualitative agreement pointing to a fundamental structure−property relationship.

Conclusions

A strong orthogonal interdependence between solubility and mobility in small molecule semiconductors, which allows rational design of new semiconductor materials for optimal device performance in mass-printed electronics, is reported. The solubility of the PTTP derivatives was tuned by introducing branching of differing lengths and at various positions of the terminal aliphatic chains. Functional groups like TBDPSO and hydroxy groups were also introduced into the chain. Introducing branching on the chains near the aromatic core heavily influences solubility, by sterically impeding the tendency of the molecules to pack closer. Highly soluble PTTPs were thus synthesized with solubilities up to 40% in THF, and these were further characterized for TFT performance.

Concomitant with the solubility increase by use of the branched chains, the mobility (and the I_{on}/I_{off} ratio) of these semiconductors in a transistor falls exponentially over several orders of magnitude. Since the dramatic effect on mobilities and I_{on}/I_{off} ratios track each other, this is not likely to be an electronic effect. Instead, we propose that the morphological difference due to increased steric hindrance on the core, in conjunction with the accompanying structural disorder, is the underlying cause for the poor mobilities. To understand this structural origin of the orthogonality between solubility and mobility, thin films of the neat semiconductors were characterized by SAXS. The observed first-order *d*-spacings, which relates to the tilt angles of the molecules on the substrate, correlate very well with the mobilities. This suggests that efficienct π-stacking of these molecules along the semiconducting channel between the electrodes is hampered by the increasing tilt, making carrier transport between the source and drain electrodes difficult. An important structure−property correlation in solution-processible organics, which has strong implications for development of mass-printed electronics, has thus been established.

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Supporting Information Available: Synthesis details. This material is available free of charge via the Internet at http://pubs.acs.org.

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