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14. ABSTRACT The objective of this research was to develop the chemistry for the synthesis of a new class of pentacene and tetracene containing polymers and oligomers. These materials were designed to have low bandgap and high charge carrier mobility. The general synthetic routes were developed for this class of materials. The synthesized new molecules and polymers were used for structural property relation studies to understand the effect of molecular structure on solid state packing, energy level and absorption. New molecular design rules were found for high performance electron transporting materials. A general correlation between charge carrier type and the molecular orbital energy levels was obtained for the first time using the large number of compounds synthesized.					
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Title: Synthesis, Morphological and Electrical Characterization of Solution Processable Low Bandgap Organic Materials

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Agreement number: FA9550-06-1-0126

Note: All results in this final report have been published or are in preparation for publication. Therefore, executive summaries are included below. Technical details can be found in the corresponding publications.

Ph.D Thesis of Ming Lee Tang (available through Stanford University library)

Title: Structure-property relationships for organic transistors: from holes to electrons to ambipolar behavior

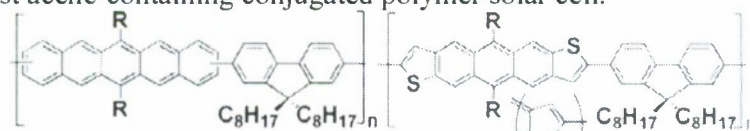
Abstract: Organic transistors offer the potential for low-cost, large area, flexible electronic applications. However the structure-property relationships that govern thin film packing and hence mobility are not clear, even for small molecules. In this dissertation, I investigate these relationships by designing, synthesizing and characterizing a family of acenes. I have designed a new conjugated core, tetraceno[2,3-*b*]thiophene that is more stable and easily functionalized than pentacene, the workhorse of organic transistors, but retains its high mobility. By incorporating various functional groups on this core, I am able to show that by increasing the van der Waals forces between molecules, intermolecular interaction is increased, and hence thin film mobility. By adding other functional groups like halogen atoms, I am able to induce electron transport by lowering molecular orbital energy levels. Hole and electron mobilities from 0.1-0.6cm²/Vs are measured for a series of acenes. This is interesting, because ambipolar organic thin film transistors consisting of a single material having high and balanced hole and electron mobilities are rare, with pentacene being the sole exception. Lastly, a series of 20 acenes are examined with respect to their frontier orbital energy levels and carrier type. In accordance with theory, molecules with higher energies only transport holes, while molecules relatively low in energy (like perfluoropentacene) are solely electron transporting. Molecules with energy levels in between are ambipolar. This is the first time the transition between charge carrier type is directly correlated with the measured HOMO/ LUMO levels in the field of organic transistors.

Okamoto, Toshihiro; Jiang, Ying; Qu, Fei; Mayer, Alex C.; Parmer, Jack E.; McGehee, Michael D.; Bao, Zhenan.

Synthesis and Characterization of Pentacene- and Anthradithiophene-Fluorene Conjugated Copolymers Synthesized by Suzuki Reactions.

Published in **Macromolecules** (2008), 41(19), 6977-6980.

Abstract: We have synthesized new types of pentacene- and anthradithiophene-dialkylfluorene conjugated copolymer via Suzuki cross-coupling polymerization. The polymer chemical structures and molecular weights were characterized by ^1H NMR, ^{13}C NMR, and gel permeation chromatography (GPC). Fundamental properties, such as electrochemical and optical behavior, were studied using cyclic voltammetry (CV) and UV-vis absorption (UV-vis) to estimate the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels as well as their optical bandgaps. Both polymers exhibit relatively low bandgaps and their high solubility in common halogenated organic solvents. They were successfully incorporated into photovoltaic cells, giving a power efficiency up to 0.68%. This is the first acene-containing conjugated polymer solar cell.



Polymer 1	Polymer 2
$M_n = 36\,400$, PDI = 3.21	$M_n = 58\,000$, PDI = 2.30
Optical bandgap: 1.78 eV	Optical bandgap: 1.98 eV

Okamoto, Toshihiro; Senatore, Michelle L.; Ling, Mang-Mang; Mallik, Abhijit B.; Tang, Ming L.; Bao, Zhenan.

Synthesis, characterization, and field-effect transistor performance of pentacene derivatives.

Published in **Advanced Materials** (2007), 19(20), 3381-3384.

Abstract: We have synthesized and characterized several new asymmetric and symmetric pentacene derivatives with electron-withdrawing groups, such as bromo, cyano, and trifluoromethyl. These substituents resulted in better oxidative stability and lower HOMO-LUMO gaps. Their thin-film FET performance was measured by using a top contact configuration. The best device performance was measured for 2,3-Br₂P, which exhibited a mobility as high as $0.22\text{ cm}^2\text{V}^{-1}\text{ s}^{-1}$ and an on/off ratio greater than 10^5 . Most remarkably, these devices showed good stability, even with exposure to air and ambient light for more than three months, whereas pentacene devices measured under the same conditions quickly degraded. Further investigations probing the effect of these substitutions on molecular packing and film growth behavior are underway.

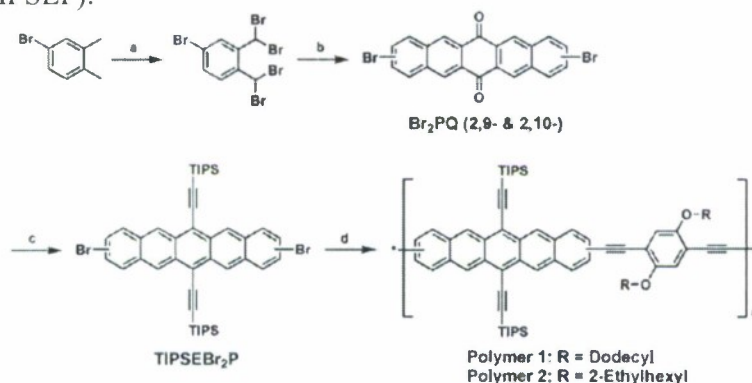
Okamoto, Toshihiro; Bao, Zhenan.

Synthesis of Solution-Soluble Pentacene-Containing Conjugated Copolymers.

Published in the **Journal of the American Chemical Society** (2007), 129(34), 10308-10309.

Abstract: We have synthesized new-type of pentacene copolymers containing linear- and branched-dialkoxyphenyldiethynylene units via a modified Sonogashira coupling reaction at room temperature to prepare low-band gap polymers ($<1.7\text{ eV}$). The structures of polymers were confirmed by ^1H NMR and the molecular weights were determined by

size exclusion chromatography. The electrochemical and optical properties of the polymers were studied using cyclic voltammetry and UV-vis absorption to estimate the HOMO and LUMO levels as well as their optical bandgaps. Branch-type pentacene copolymer **2** exhibited good solubility in common organic solvents as well as good film-forming ability, while linear-type polymer **1** has poor solubility owing to stronger interaction between polymer chains. Notably, in terms of optical stability, our pentacene copolymers exhibit much better stability in solution than TIPS-ethynyl substituted pentacene (TIPSEP).



Tang, Ming L.; Reichardt, Anna D.; Okamoto, Toshihiro; Miyaki, Nobuyuki; Bao, Zhenan.

Functionalized asymmetric linear acenes for high-performance organic semiconductors.

Published in *Advanced Functional Materials* (2008), 18(10), 1579-1585.

Abstract: A series of compounds from the tetraceno[2,3-*b*]thiophene and the anthra[2,3-*b*]thiophene family of semiconducting molecules has been made. Specifically, synthetic routes to functionalize the parent molecules with bromo and then hexyl groups are shown. The bromo- and hexyl-functionalized tetraceno[2,3-*b*]thiophene and anthra[2,3-*b*]thiophene were characterized in the top-contact thin-film transistor (TFT) geometry. They give high mobilities, ranging from 0.12 cm² V⁻¹ s⁻¹ for -*n*-hexylanthra[2,3-*b*]thiophene to as high as 0.85 cm² V⁻¹ s⁻¹ for -bromotetraceno[2,3-*b*]thiophene. Notably, grain size increases, going from the shorter anthra[2,3-*b*]thiophene core to the longer tetraceno[2,3-*b*]thiophene core, with a corresponding increase in mobility. The transition from undesirable 3D to desirable 2D thin-film growth is explained by the increase in length of the molecule, in this case by one benzene ring, which results in an increase in intralayer interactions relative to interlayer interactions.

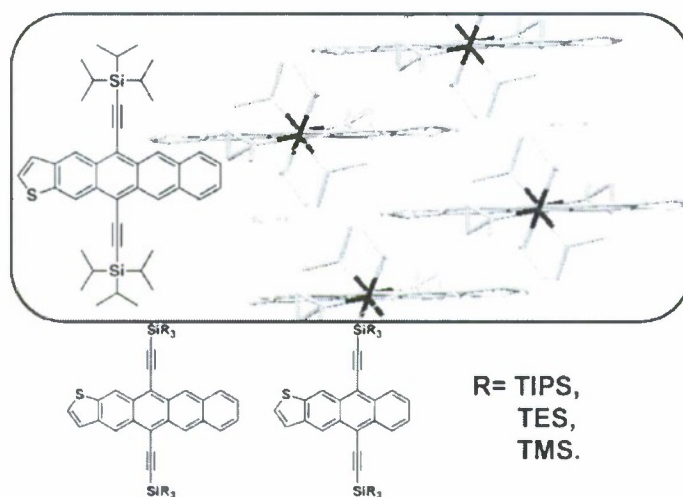
Tang, Ming L.; Reichardt, Anna D.; Siegrist, Theo; Mannsfeld, Stefan C. B.; Bao, Zhenan.

Trialkylsilyl-ethynyl-Functionalized Tetraceno[2,3-*b*]thiophene and Anthra[2,3-*b*]thiophene Organic Transistors.

Published in *Chemistry of Materials* (2008), 20(14), 4669-4676.

Abstract: A series of ethynyl-substituted molecules with the tetraceno[2,3-*b*]thiophene

and anthra[2,3-*b*]thiophene core have been synthesized. The aim was to investigate the impact of differently bulky side-chain substituents on the packing of the molecule in thin film and hence its thin-film transistor (TFT) mobility. Three R groups were used, namely, the tri-isopropyl-, triethyl-, and trimethylsilylethynyl groups. We did not observe a direct correlation between substituent size and TFT mobility. However, the 5,12-bis(triisopropylsilylethynyl)tetraceno[2,3-*b*]thiophene has a mobility as high as $1.25 \text{ cm}^2/\text{V}\cdot\text{s}$, the 5,12-bis(trimethylsilylethynyl)tetraceno[2,3-*b*]thiophene has a mobility of about $0.00616 \text{ cm}^2/\text{V}\cdot\text{s}$, while 5,10-bis(triethylsilylethynyl)anthra[2,3-*b*]thiophene and 5,10-bis(trimethylsilylethynyl)anthra[2,3-*b*]thiophene have a mobility of $10^{-4} \text{ cm}^2/\text{V}\cdot\text{s}$ on phenylsilane- and octadecyltrichlorosilane-treated surfaces respectively.

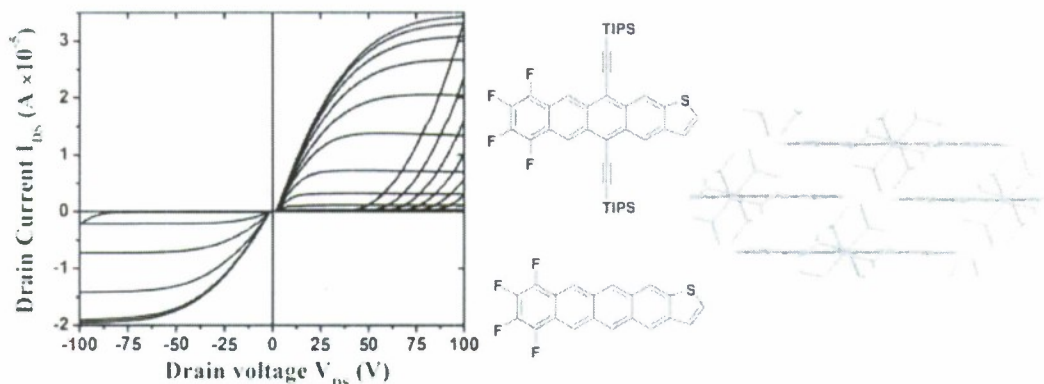


Tang, Ming L.; Reichardt, Anna D.; Miyaki, Nobuyuki; Stoltenberg, Randall M.; Bao, Zhenan.

Ambipolar, High Performance, Acene-Based Organic Thin Film Transistors.

Published in the *Journal of the American Chemical Society* (2008), 130(19), 6064-6065.

Abstract: We present a high performance, ambipolar organic field-effect transistor composed of a single material. Ambipolar molecules are rare, and they can enable low-power complementary-like circuits. This low band gap, asymmetric linear acene contains electron-withdrawing fluorine atoms, which lower the molecular orbital energies, allowing the injection of electrons. While hole and electron mobilities of up to 0.071 and $0.37 \text{ cm}^2/\text{V}\cdot\text{s}$, respectively, are reported on devices measured in nitrogen, hole mobilities of up to $0.12 \text{ cm}^2/\text{V}\cdot\text{s}$ were found in ambient, with electron transport quenched. These devices were fabricated on octadecyltrimethoxysilane-treated surfaces at a substrate temperature of 60°C .

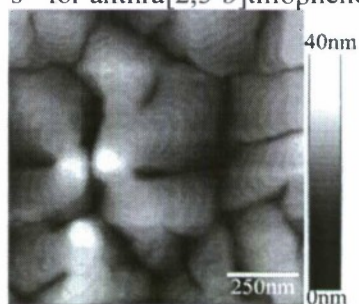
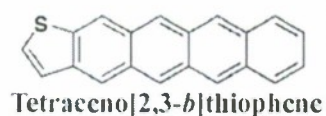
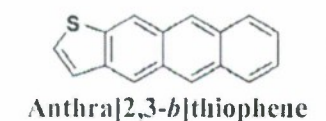


Tang, Ming L.; Okamoto, Toshihiro; Bao, Zhenan.

High-Performance Organic Semiconductors: Asymmetric Linear Acenes Containing Sulphur.

Published in the **Journal of the American Chemical Society** (2006), 128(50), 16002-16003.

Abstract: Two new linear acenes with fused thiophene units have been synthesized. These acenes have conjugation lengths between anthracene and pentacene. Thin films of these linear molecules were characterized by ultraviolet spectroscopy, X-ray diffraction, atomic force microscopy (AFM), and field-effect transistor measurements. Submonolayer AFM studies show growth that greatly resembles pentacene, while thin-film growth is dendritic. Mobilities as high as $0.47 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ have been found for the tetraceno[2,3-*b*]thiophene and are as high as $0.15 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for anthra[2,3-*b*]thiophene.



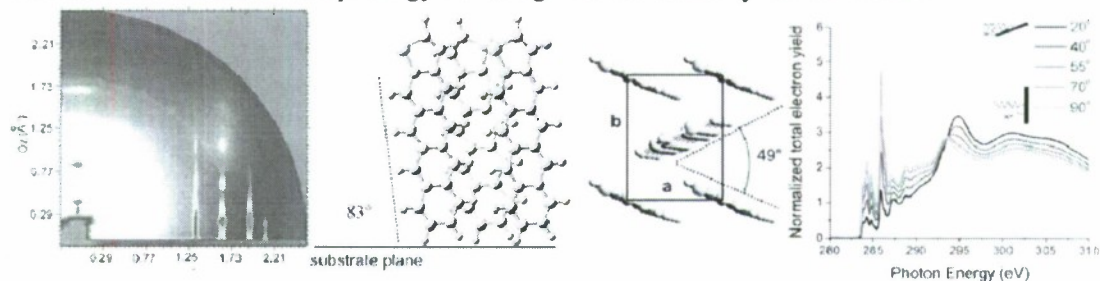
Yuan, Quan; Mannsfeld, Stefan C. B.; Tang, Ming L.; Toney, Michael F.; Luening, Jan; Bao, Zhenan.

Thin Film Structure of Tetraceno[2,3-*b*]thiophene Characterized by Grazing Incidence X-ray Scattering and Near-Edge X-ray Absorption Fine Structure Analysis.

Published in the **Journal of the American Chemical Society** (2008), 130(11), 3502-3508.

Abstract: Understanding the structure–property relationship for organic semiconductors

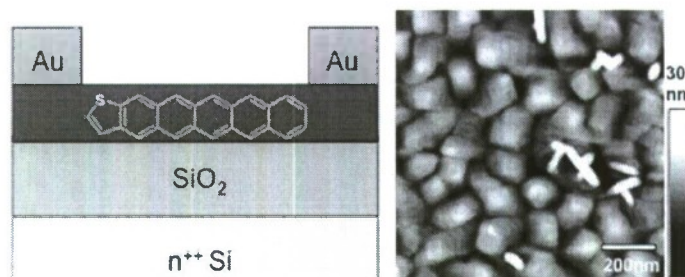
is crucial in rational molecular design and organic thin film process control. Charge carrier transport in organic field-effect transistors predominantly occurs in a few semiconductor layers close to the interface in contact with the dielectric layer, and the transport properties depend sensitively on the precise molecular packing. Therefore, a better understanding of the impact of molecular packing and thin film morphology in the first few monolayers above the dielectric layer on charge transport is needed to improve the transistor performance. In this Article, we show that the detailed molecular packing in thin organic semiconductor films can be solved through a combination of grazing incidence X-ray diffraction (GIXD), near-edge X-ray absorption spectra fine structure (NEXAFS) spectroscopy, energy minimization packing calculations, and structure refinement of the diffraction data. We solve the thin film structure for 2 and 20 nm thick films of tetraceno[2,3-*b*]thiophene and detect only a single phase for these thicknesses. The GIXD yields accurate unit cell dimensions, while the precise molecular arrangement in the unit cell was found from the energy minimization and structure refinement; the NEXAFS yields a consistent molecular tilt. For the 20 nm film, the unit cell is triclinic with $a = 5.96 \text{ \AA}$, $b = 7.71 \text{ \AA}$, $c = 15.16 \text{ \AA}$, $\alpha = 97.30^\circ$, $\beta = 95.63^\circ$, $\gamma = 90^\circ$; there are two molecules per unit cell with herringbone packing ($49\text{--}59^\circ$ angle) and tilted about 7° from the substrate normal. The thin film structure is significantly different from the bulk single-crystal structure, indicating the importance of characterizing thin film to correlate with thin film device performance. The results are compared to the corresponding data for the chemically similar and widely used pentacene. Possible effects of the observed thin film structure and morphology on charge carrier mobility are discussed.



Tang, Ming L.; Mannsfeld, Stefan C. B.; Sun, Ya-Sen; Becerril, Héctor A.; Bao, Zhenan.
Pentaceno[2,3-*b*]thiophene, a hexacene analog for organic thin film transistors.

Under revision for the **Journal of the American Chemical Society**.

Abstract: Hexacene and larger fused rings remain elusive targets for chemists. Here, we report a hexacene-like molecule containing six linearly fused rings, specifically a pentacene molecule fused with a terminal thiophene ring, pentaceno[2,3-*b*]thiophene. It can be purified and isolated as a purple-black powder at ambient conditions. This molecule has a low HOMO-LUMO gap of 1.75eV in *o*-DCB, and an optical bandgap of 1.58eV in thin film. Top contact organic thin film transistors (OTFTs) were made, and atomic force microscope (AFM) reveals dendritic thin film growth characteristic of pentacene. An OTFT mobility of $0.574\text{cm}^2/\text{Vs}$ was measured for pentaceno[2,3-*b*]thiophene under nitrogen.

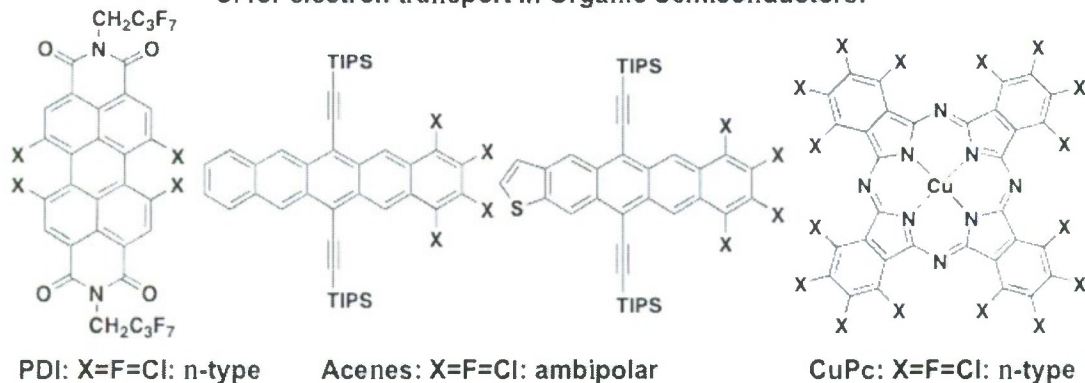


Tang, Ming L.; Oh, Joon H.; Reichardt, Anna D.; Bao, Zhenan.

Chlorination: A general route towards electron transport in organic semiconductors.
Journal of the American Chemical Society (2008), submitted.

Abstract: We show that adding chlorine atoms to conjugated cores is a general, effective route towards the design of *n*-type air-stable organic semiconductors. We find this to be true for acenes, phthalocyanines and perylene tetracarboxylic diimide (PDI) based molecules. This general finding opens new avenues in the design and synthesis of organic semiconductors. We compared a series of fluoro and chloro functionalized acenes, phthalocyanines and PDI based molecules. The acenes synthesized showed high and balanced ambipolar transport in the top-contact organic field effect transistor (OFET) geometry. The electron-withdrawing halogen groups lowered the LUMO and the charge injection barrier for electrons, such that electron and hole transport occurred simultaneously. If the chlorine added does not distort the planarity of the conjugated core, we found that the chloro functionalized molecules tend to have a slightly smaller HOMO-LUMO gap and a lower LUMO level than the fluoro containing molecules, both from calculations and cyclic voltammetry measurements in solution. This is most likely due to the fact that Cl contains empty 3d orbitals that can accept π -electrons from the conjugated core, while F does not have energetically accessible empty orbitals for such delocalization.

Cl for electron transport in Organic Semiconductors:



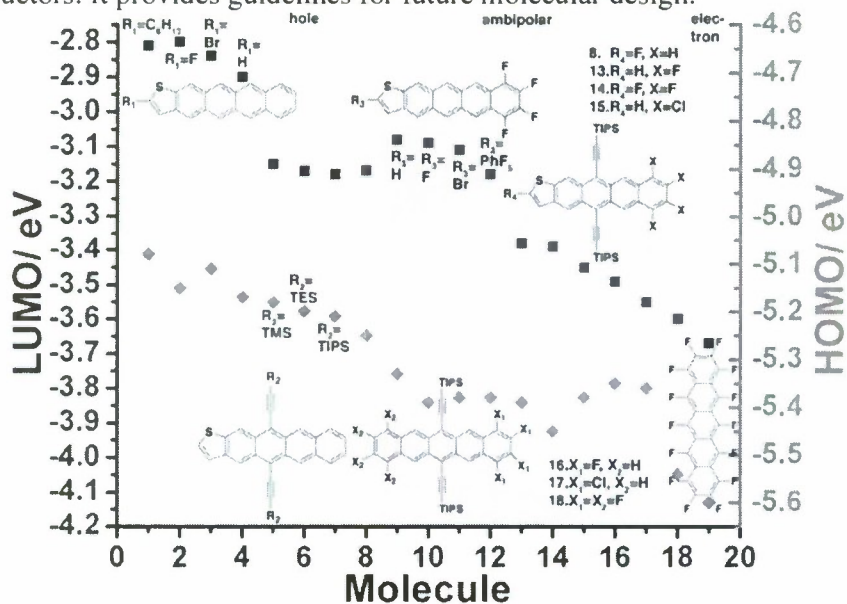
Tang, Ming L.; Reichardt, Anna D.; Wei, Peng; Bao, Zhenan.

Correlating Carrier Type with Frontier Molecular Orbital Energy Levels in

Organic Thin Film Transistors of Functionalized Acene Derivatives.

Journal of the American Chemical Society (2008), submitted.

Abstract: We investigate the relationship between the charge carrier type in organic thin film transistors (OTFTs) and molecular energy levels. We examine a series of functionalized acenes that collectively have their HOMOs range from -4.9eV to -5.6eV and LUMOs range from -2.8eV to -3.7eV, as measured by cyclic voltammetry. Placed together, these 19 molecules allow us to chart the transition from OTFTs that display only hole transport, to ambipolar, to solely electron transport. Specifically, we note that for octadecyltrichlorosilane (OTS) treated substrates, with top contact gold electrodes, electron injection occurs when the LUMO < -3.15eV, while hole injection ceases when the HOMO < -5.6eV. Ambipolar transport prevails when molecules have HOMO/ LUMO levels within the aforementioned range. This is seen across channel lengths ranging from 50-150 μ m and using only gold as electrodes. This empirical plot is the first time such a detailed study has been made on the onset of charge injection for a class of organic semiconductors. It provides guidelines for future molecular design.

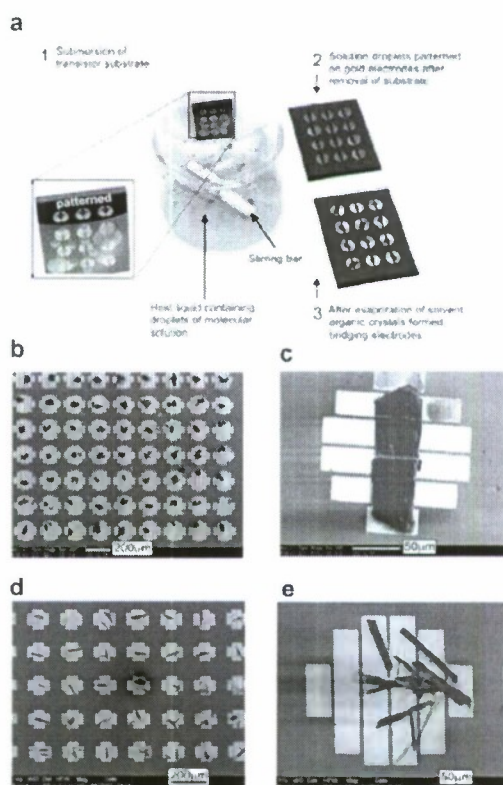


Stefan C. B. Mannsfeld, Armon Sharei, Shuhong Liu, Mark E. Roberts, Iain McCulloch, Martin Heeney, and Zhenan Bao

Highly efficient patterning of organic single crystal transistors from solution phase.
Adv. Mater. 20, 4044-4048, 2008.

One way to pattern crystals based on solvent dewetting is to pattern the semiconductor solution and then grow crystals from it. The schematic of this approach is illustrated in Figure 1a. In this method, an emulsion of a saturated organic semiconductor solution in water is formed in a beaker with a stirring bar. Then a transistor substrate, with electrode regions lyophilic and background lyophobic, is dipped into the emulsion and pulled out. Upon removal of the substrate, droplets of the molecular solution adhere to the gold electrode pads exclusively. After evaporation of the solvent, patterned crystals are formed only on the electrode regions. It was found that the presence of liquid vortex generated by

the stirring bar significantly improve the selectivity of the molecular solution droplet. Without the stirring, a significant amount of solution droplets was deposited in the OTS-treated regions. The shearing force exerted on the substrate surface by the vortex was believed to strip off small droplets that adsorbed on the lyophobic surface regions and trim larger droplets that cover several electrodes down to the exact size of a single electrode pad. Using this technique, large arrays of cyclohexyl-substituted quaterthiophene (CH-4T) (Fig. 1b-c) and trimethylsilyl-substituted quaterthiophene (TMS-4T) (Fig. 1d-e) single crystal FETs were fabricated. The patterned single crystals FETs exhibited superior performance: the highest mobility of TMS-4T transistors was $0.11 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, while the highest mobility of CH-4T transistors was $0.02 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Besides excellent device performance, this technique also offers several other advantages over existing techniques, such as the cleanliness and selectivity of the crystal patterns, the patterning speed, and the ultra-small amount of material required. This patterning method may be particularly useful for depositing crystals of small organic semiconductors whose high tendency to crystallize makes it difficult to form uniform films. The method furthermore allows fine control over the crystallization conditions by choice of initial concentration and host liquid temperature.



a) Schematic illustrating the patterning process. A wettability-patterned substrate (gold electrodes lyophilic, background lyophobic) is dipped into a beaker containing a host liquid and small amounts of the molecular solution dispersed by a stirring bar (1). After removal of the substrate from the beaker, droplets of molecular solution are patterned onto the gold electrodes (2), leading to formation of bridging crystals (3) after

evaporation of the solvent. b-e) SEM images of solution-patterned single crystal transistors of CH-4T (b,c) and TMS-4T (d,e) showing clearly faceted crystals.

H.A. Becerril, M. Roberts, Z.H. Liu, J. Locklin, Z. Bao

High Performance Organic Thin Film Transistor Through Solution Sheared Deposition of Small Molecule Organic Semiconductors

Adv. Mater. 20, 2588-2594, 2008.

We have demonstrated a simple solution-shearing (SS) process capable of depositing 20–50nm films of aligned, ribbon-like, millimeter-long organic semiconductor crystals on planar substrates. The main process variables, including temperature, concentration and shearing rate can be adequately controlled for depositing various semiconductor materials on surface-modified silicon oxide and polymer surfaces. We found that without optimizing the SS process for an individual material, top-contact OTFTs prepared with SS semiconductors have mobilities that are comparable and, more often, superior to those of drop-cast devices. In spite of the aligned nature of the SS films, we observed little mobility anisotropy and we are currently investigating the molecular orientation within the SS-deposited crystals. Due to its relative simplicity, extremely-low material quantity requirements, and scalability potential, we expect that the SS technique can be useful as a tool for fabricating high performance OTFTs from solution and rapidly evaluating libraries of organic semiconductors in search for the elusive high-mobility candidates.

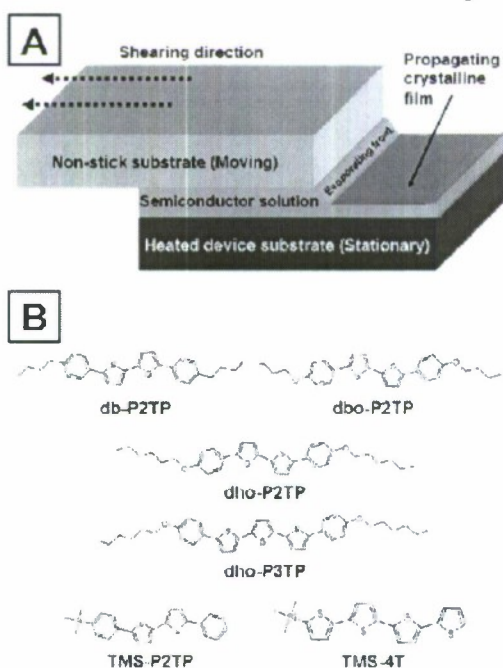


Figure 1. Schematic illustration of the SS method (A), and library of organic semiconductor compounds screened by solution shearing (B).

A. Briseno, S. Mannsfeld, C. Reese, J. M. Hancock, Y. Xiong, Z. Bao, S. A. Jenekhe, Y. Xia

Perylenediimide Nanowires and Their Use in Fabricating Field-Effect Transistors and Complementary Inverters.
Nano Lett. 7, 2847-2853, 2007.

Perylenetetracarboxydiimide (PTCDI) nanowires self-assembled from commercially available materials are demonstrated as the n-channel semiconductor in organic field-effect transistors (OFETs) and as a building block in high-performance complementary inverters. Devices based on a network of PTCDI nanowires have electron mobilities and current on/off ratios on the order of 10^{-2} cm²/Vs and 10^4 , respectively. Complementary inverters based on n-channel PTCDI nanowire transistors and p-channel hexathiapentacene (HTP) nanowire OFETs achieved gains as high as 8. These results demonstrate the first example of the use of one-dimensional organic semiconductors in complementary inverters.

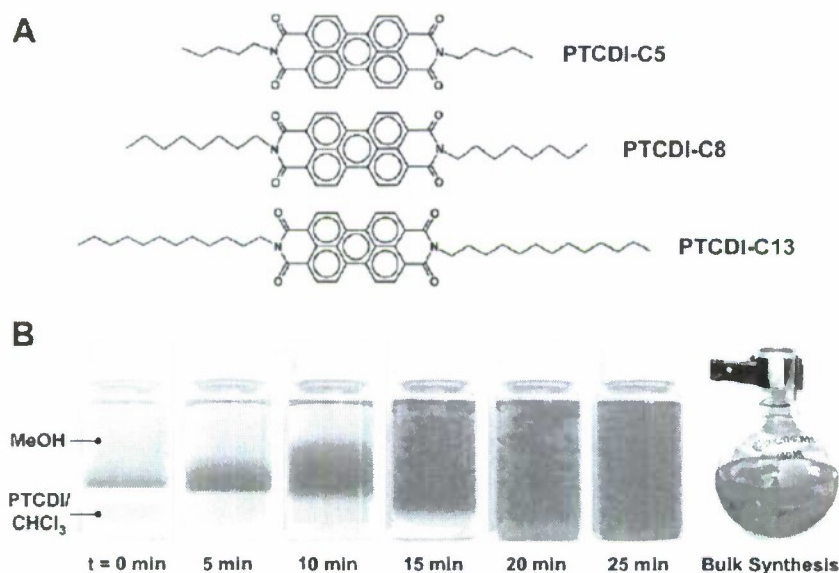


Figure 1. (A) Chemical structures of the three perylenetetracarboxydiimide (PTCDI) derivatives of varying dialkyl chain lengths synthesized as n-type semiconductor NWs using a solution-phase method. (B) A series of optical photographs detailing the interfacial self-assembly of PTCDI nanostructures. The top layer of the vial is methanol, and bottom layer is PTCDI dissolved in chloroform (~ 1.5 mg/mL). The last picture frame illustrates a 500 mL flask containing a large quantity of PTCDI-C₃ NWs that were also synthesized in ~ 25 min.

S. Liu, S.C.B. Mannsfeld, M.C. LeMieux, H.W. Lee, Z. Bao
Organic semiconductor-carbon nanotube bundle bilayer field effect transistors with enhanced mobilities and high on/off ratios.
Appl. Phys. Lett., 92, 053306, 2008.

Most of the single crystals used so far for the fabrication of organic FETs have been grown using the physical vapor transport (PVT) method. In this approach, the starting material is placed in the highest temperature region of the reactor, and crystal growth

occurs downstream within a narrow range in the temperature-gradient furnace. In 2006, we reported a technique which employs the PVT method to fabricate large arrays of patterned organic single crystals, where rough thin-film domains of octadecyltriethoxysilane (OTS) were microcontact-printed onto a clean Si/SiO₂ surface and the nucleation of vapor-grown organic single crystals was restricted to the printed OTS domains. As a further investigation of this concept, in this work, patterned single-walled carbon-nanotube (SWNT) bundles were utilized as templates to study the selective nucleation and growth of various organic semiconductor single crystals. With SWNT bundles as templates, several organic semiconductor materials were successfully patterned, including p-type pentacene, tetracene, sexiphenylene, and sexithiophene, as well as n-type tetracyanoquinodimethane (TCNQ). This study suggests that the selective growth of crystals onto patterned carbon nanotubes is most likely due to the coarse topography of the SWNT bundles. Moreover, it was observed that the crystals nucleated from SWNT bundles and grew onto SWNT bundles in a conformal fashion. The crystal growth can be directly applied onto transistor source-drain electrodes and arrays of organic single-crystal field effect transistors are demonstrated. The results demonstrate the potential of utilizing carbon nanotubes as nucleation templates for patterning a broad range of organic materials for applications in optoelectronics.

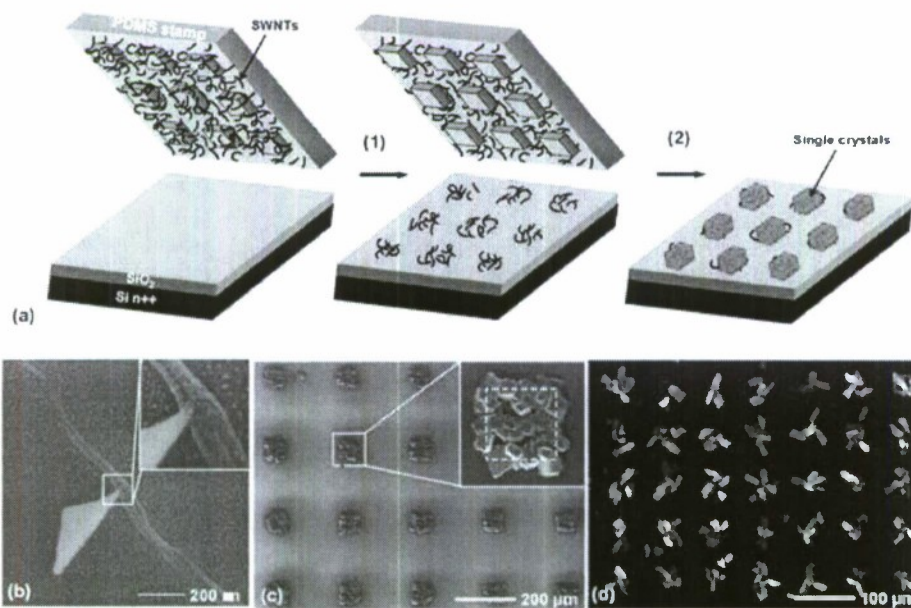


Figure. a) Schematic procedure for patterning organic single crystals. (1) SWNT bundles on a relief-patterned PDMS stamp are transferred from the PDMS stamp to a hydrophilic Si/SiO₂ substrate; (2) molecular crystals are vapor-grown onto the SWNT-patterned regions. b) Scanning electron microscopy (SEM) image of pentacene crystals nucleated from SWNT bundles. (c-d) Images of patterned single crystal arrays of pentacene (c) (SEM) and sexithiophene (d) (cross-polarized optical micrograph).

S. Sista, Y. Yao, Y. Yang, M.L. Tang, Z. Bao

Enhancement in open circuit voltage through a cascade-type energy band structure.

Appl. Phys. Lett. 91, 223508, 2007.

In this paper, we report a method to increase the open-circuit voltage V_{OC} of an organic solar cell by inserting an interfacial layer between the donor and acceptor layers to form a cascade-type energy band structure. We demonstrate its feasibility using a recently reported asymmetric pentacene derivative, tetraceno[2,3-*b*]thiophene (TT) as a donor material, C60 as an acceptor material, and copper phthalocyanine (CuPc) as the sandwich layer. The V_{OC} was increased from 0.3 V for the device with no CuPc sandwich layer to 0.56 V for 13 nm thick CuPc layer. The power conversion efficiency (PCE) of the device with 13 nm CuPc layer was 1.53% and the fill factor (FF) was 0.64, in comparison to TT/C60 device which had a PCE of 0.78% and a FF of 0.52.

C.C. Reese, Z. Bao

Detailed characterization of contact resistance, gate-bias dependent field-effect mobility, and short-channel effects with microscale elastomeric single-crystal field-effect transistors.

Adv. Func. Mater., in press.

The Organic Field-effect Transistor (OFET) has proven itself invaluable as both the fundamental element in organic circuits and the primary tool for the characterization of novel organic electronic materials. Crucial to the success of the OFET in each of these venues is a working understanding of the device physics that manifest themselves in the form of electrical characteristics. As commercial applications shift to smaller device dimensions and structure/property relationships become more refined, the understanding of these phenomena become increasingly critical. Here, we employ high-performance, elastomeric, photo lithographically patterned single-crystal field-effect transistors as tools for the characterization of short-channel effects and bias-dependent parasitic contact resistance and field effect mobility. Redundant characterization of devices at multiple channel lengths under a single crystal allow the morphology free analysis of these effects, which is carried out in the context of a device model previously reported. The data show remarkable consistency with our model, yielding fresh insight into each of these phenomena, as well as confirming the utility of our FET design.

C. Reese, Z. Bao

Overestimation of the field-effect mobility via transconductance measurements and the Origin of the output / transfer characteristic discrepancy in organic field-effect transistors.

J. Appl. Phys. in press.

Paramount to the rational design of electronic materials is the accurate characterization of their intrinsic properties. In particular, many applications of conducting and semiconducting soft materials have been driven by the development of materials with high, bias-stable field-effect mobility. Here, we demonstrate the effect of parasitic resistance and bias-dependent mobility on device electrical characteristics. Specifically, we analyze the two of the most commonly employed test algorithms - the output and transfer curves - via a closed-form analysis. The analysis exhibits characteristics endemic to those published in literature, such as effective mobilities with maxima with respect to

gate voltage that may lead to overstatements of mobility by manyfold. Furthermore, analysis reveals that common overestimation relative to intrinsic and output-estimated mobilities is caused solely by gate-bias-dependent mobility, and parasitic resistance can only lead to an underestimation of the effective mobility. We introduce a method for accurate mobility estimation and a dimensionless variable for evaluating the importance of contact resistance.

C.C. Reese, M.E. Roberts, S.R. Parking, Z. Bao

Isotropic Transport in an Oligothiophene Derivative for Single-crystal Field-effect Transistor Applications

Angew. Chem. submitted.

We apply our high resolution single crystal measurement experimental technique to an α -substituted oligothiophene, trimethyl-[2,2';5',2";5",2''']quaterthiophen-5-yl-silane (4T-TMS), whose asymmetric, building-block structure specifies a symmetric planar motif through steric interactions, yet allows the electronically active cores to pack closely. Furthermore, we carry out electronic structure calculations in order to correlate microscopic intermolecular interactions to macroscopic electronic properties, and employ these results to evaluate both the utility of the 4TTMS crystal and develop a general design rule for organic crystalline semiconductors based on symmetry considerations. Combined with the previously reported results for rubrene, these data reveal a key detail about charge transport in molecular materials: four-fold rotational symmetry of molecular interactions gives symmetric transport, while two-fold yields two-fold symmetric anisotropic transport. This is a non-trivial conclusion that further confirms the model invoked previously, where the measured field-effect mobility is determined by $\mu_{\text{FET}} = \mu_i n_i u_j$, where $n_i = n_j$ is the direction of applied field and normal vector to the plane of carrier collection, and indices are summed in accordance with Einstein notation. In other words, on the length-scale of the field-effect measurement, diffusive-type transport is observed, free of manifestations of the discrete intermolecular interactions assumed to dictate transport. This conclusion is key for the design of molecular materials, especially for those used in circuits where crystal orientation cannot easily be specified. In order to guarantee consistent material performance, four-fold symmetry must be achieved. This symmetry, along with ease and quality of crystal formation and relatively good performance, make 4TTMS a good candidate for these applications. Furthermore, the correlation between experimentally observed anisotropy of field-effect mobility with the symmetry of electronic interactions – as estimated using quantum chemical calculations – suggests that the *a priori* prediction of orientation-dependent properties is indeed possible.

C.C. Reese, M.E. Roberts, S.R. Parkin, Z. Bao

Tuning of crystalline solid-state order and charge transport via building-block modification of oligothiophenes

J. Am. Chem. Soc. submitted.

We study the family of α -substituted oligothiophene derivatives in order to determine the effects of terminal substituent density on the packing of the electronically active core units. The molecules consist of an aromatic oligothiophene core, functionalized at the terminal positions with electronically inactive trimethylsilane (TMS) groups. In addition

to imparting solubility, the substituent TMS groups yield layer-by-layer ordering of the aromatic cores. By isolating the functionalization to the terminal positions, the TMS groups are isolated to between the bc-planes that dominate charge transport. Furthermore, this motif allows us to study specifically the steric effects of the TMS groups on the in-plane packing of the aromatic core. Our previous thin film structure studies showed that end substitution on the aromatic molecule with less bulky linear alkyl chains did not change the molecular packing motif. We have shown that the orientation and proximity of organic semiconductor molecules in the solid-state may be tuned using a terminal building-block-type modification, resulting in substantial quantitative and qualitative differences in their electronic properties. Specifically, the addition of a terminal, electronically inactive TMS group results in crystal packing that directly reflects the steric considerations of their interlayer confinement. This is indirectly manifested in the tilt and offset of the oligothiophene cores responsible for charge transport within the bc-plane: mono and di-substituted quaterthiophenes showed less and more tilt/offset, respectively, than their unsubstituted counterpart. These differences were apparent in their intermolecular electronic interactions, as measured macroscopically via electrical characterization and calculated using quantum chemical calculations and the resolved crystal structures. The predicted and measured trend was coincident, with $4T > 4TTMS > 4T2TMS$ in terms of charge transport efficiency. While the data are insufficient to apply the general conclusion to the oligomers 3T and 5T, electrical comparison of the monoTMS series, in particular between 5TTMS and 5T2TMS, suggests that the trend holds. Furthermore, structural comparisons of analogues varying only in core length have demonstrated identical motifs. This work demonstrates that substantial modification of the intermolecular interactions may be effected by the proper tuning of electronically inactive terminal groups, subtly tuning longitudinal offset of the aromatic cores. Furthermore, the correlation of these results with direct calculation suggests that solid-state tuning via steric interactions with predictable results is indeed possible.

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