Synthetic Chemistry for Ultrapure, Processable, and High-Mobility Organic Transistor Semiconductors

HOWARD E. KATZ,* ZHENAN BAO, AND
SYLVAIN L. GILAT

Bell Laboratories, Lucent Technologies,
600 Mountain Avenue, Murray Hill, New Jersey 07974

ABSTRACT

An essential aspect of the development of organic-based electronics is the synthetic chemistry devised for the preparation of the semiconductor materials responsible for the activity of organic field-effect transistors. Access to organic semiconductors in sufficient purity and variety has led to breakthroughs in solid-state physics and circuit realization. In this Account, we review the synthetic methods that have been most useful for preparing a range of semiconductors, including thiophene-based oligomers, several kinds of fused rings, and polymers. The tradeoff between process efficiency and target purity is emphasized.

There is growing recognition of the opportunity to fabricate low-cost and/or large-area electronic components from organic-based circuits.[1] Such circuits are not predicted to replace silicon technology where high device density, speed, and stability under extreme conditions are vital. Rather, they may play a role in applications such as identification tags, smart cards, and display drivers that are intended for single or short-term use, very large-scale manufacture, low-resolution architectures, or plastic sub-

Howard E. Katz is Distinguished Member of Technical Staff at Bell Laboratories-Lucent Technologies. He prepared his Ph.D. thesis under Professor Donald Cram at UCLA in the area of artificial enzymes. At Bell Laboratories, he initially explored "converse" host–guest chemistry, where anions were bound to multidentate Lewis acidic receptors. His subsequent scientific activities have been aimed at new organic materials synthesized with methods developed specifically for electronics- and optics-related targets. These accomplishments have been recognized through numerous invited appearances, articles, and appointments, including full membership on the Defense Science Research Council, the University of Illinois Lane Lectureship, and the Case Western Reserve Frontiers Lectureship.

Zhenan Bao received her Ph.D. degree in chemistry from the University of Chicago in 1995, where she investigated palladium-catalyzed reactions for the synthesis of functional conjugated polymers and their applications as electro-optical materials. She joined Bell Laboratories of Lucent Technologies (Murray Hill, NJ) as a Member of Technical Staff in 1995. Her current research interests include rational design and synthesis of organic and polymeric semiconductors for thin-film field-effect transistors and light emitting diodes, nonlithographical patterning of optoelectronic devices, and self-assembled molecular structures and microobjects. She has authored more than 50 publications, given more than 30 invited talks and seminars, and held four U.S. patents.

Sylvain L. Gilat is currently a Principal Scientist in Physical Chemistry at Galileo Laboratories, a start-up company developing pharmaceutical and nutritional products to treat and prevent cardiovascular disease and diabetes. Dr. Gilat was a Member of Technical Staff at Bell Laboratories–Lucent Technologies from 1998 to 2000, where he helped set up a molecular electronics program. Prior to joining Bell Laboratories, Dr. Gilat was a postdoctoral fellow at UC Berkeley and Cornell University, where he developed an energy transfer system within dendrimers. Dr. Gilat holds a Ph.D. from Collège de France, Paris, and an engineering degree in Physics & Chemistry from ESPCI, Paris.

strates. The main logic units in these circuits are field-effect transistors (FETs), comprising a gate electrode, a gate dielectric, a semiconductor, and source/drain electrodes.[2] The device is generally in an insulating state until a gate voltage is applied (relative to the source), which establishes a "channel" of charge at the semiconductor–dielectric interface, turns the device on, and allows conductivity between the source and drain (Figure 1). (Other conceivable active organic electronic devices include rectifiers, photoconductors, photovoltaics, and the commercially important light-emitting diodes, which are outside the scope of this Account.)
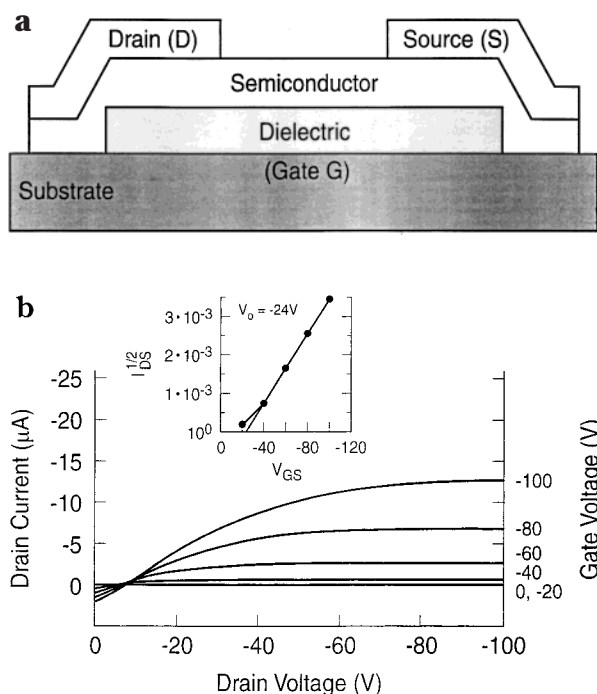
FETs can be viewed partly as capacitors, with the gate and semiconductor functioning as parallel plate electrodes. As long as the semiconductor has accessible orbitals for the injection of charge and is sufficiently continuous, the gate–source voltage charges the capacitor. "Accessible orbitals" are roughly defined as highest occupied orbitals below 1.5 V vs standard calomel electrode (for electron removal or "hole" injection) or lowest unoccupied orbital levels more positive than -1 V for electron injection. The layer of charge on the semiconductor side provides carriers for the current flowing between the source and the drain, provided the semiconductor forms a continuous film with intermolecular π-overlap in a direction parallel to the intended current flow. For a given quantity of formal charging of the capacitor (the event that switches the device "on"), the source–drain conductivity is governed by the mobility of the carriers in the semiconductor. If the injected charges reside in local potential minima, or "traps", they will be "stuck" and relatively high voltages will be needed to dislodge them. Such traps can be due to oxidizable or reducible chemical impurities, grain boundaries, inhomogeneities at the dielectric interface, or crystallographic defects, and they result in low mobility. Conversely, impurities functioning as dopants can introduce extrinsic charge carriers that are not controlled by the gate voltage. If the doping level is too high, the device does not display its intended switching function, but rather acts as a poorly modulated resistor. For liquid crystal displays, a mobility of >0.1 cm^2/(V·s) and an on/off current ratio (calculated as the ratio of the highest and lowest saturation currents in a plot such as that shown in Figure 1b) of 10^6 are considered adequate.[3] For some low-level logic circuits, these requirements can be relaxed. Amorphous silicon and a few outstanding organic semiconductors meet these specifications. Recent experiments on organic semiconductor single crystals indicate that several materials display mobilities orders of magnitude higher when defect-free and observed at low temperatures in inert atmospheres.[4]

For low-cost processing, all of the elements of the FET should be deposited and patterned using techniques such as printing, stamping, casting, and rapid sublimation or thermal transfer. This is in contrast to the much more capital-intensive processes associated with patterning and

FIGURE 1. (a) Schematic diagram of a "top contact" FET. The gate electrode lies at the substrate−dielectric interface. The alternative "bottom contact" geometry has the source and drain on the semiconductor−dielectric interface. (b) Drain current versus drain voltage of a bis(benzodithiophene) FET with W/L = 10, deposited at a substrate temperature of 100 °C. The inset shows the plot of the square root of drain voltage versus gate voltage, used to calculate threshold voltage and mobility. The flatter parts of the curves, at the right of the main plot, indicate saturation currents. Reprinted with permission from ref 28 (1997).

deposition on silicon, and the subsequent interconnection and packaging. While printed wires and solution-deposited polymer dielectrics are well established, the need for semiconductors that meet both the performance and processing requirements has driven the investigation of organic semiconductors. These generally fall into two classes: conjugated polycyclic compounds of molecular weight <1000, and polyheterocycles with much higher average molecular weight. Complex circuits incorporating hundreds of transistors have been demonstrated,[1,5] including some using low-power complementary logic (requiring both electron and hole transport). FET arrays driving dozens of pixels in concert have also been produced and integrated with the appropriate display materials.[6] Furthermore, some of the semiconductors have been deposited under mild conditions with simple techniques, making these materials promising for use in inexpensive reel-to-reel production schemes.

An important and underappreciated aspect of organic semiconductor research is synthesis. While several prototypical semiconductors are commercially available, including the polyacenes and phthalocyanines, and others can seemingly be synthesized via trivial one-step conversions, optimized materials are likely to require more complex synthetic methods. In the case of polymers, control of regiochemistry, molecular weight distribution, and end groups will be necessary to ensure the needed

chain overlaps and orientation. All of the organic semiconducting materials, including those synthesized by supposedly trivial means, will need to be in highly purified forms, as impurities affect a host of physical properties, especially the on- and off-conductance, that bear on the ultimate utility of the compositions. In many cases, the choice of synthetic sequence is governed by the overriding consideration of final product purity, and the most direct pathways are not necessarily the ones most likely to ensure pure products.

In this Account, we highlight the synthetic methods that have been key to our ability to prepare a wide range of organic semiconductors, including heterocyclic oligomers, linear fused rings, two-dimensional fused rings, and polymers. Because of our ability to generate a "library" of semiconductors, we have been able to relate their properties to structural differences and match certain semiconductors to specific applications. A wealth of new physical phenomena has been uncovered by studying sets of these compounds and is described in separate publications. In addition, many of the performance issues related to the actual FETs have been delineated in recent reviews.[7] Therefore, despite the relevance of this field to physics and physical chemistry, this paper will focus almost exclusively on organic synthesis. Relevant thiophene chemistry has been reviewed by Bauerle,[8] and the influence of ordering on the performance of these compounds has been reviewed by Fichou.[9]

There are a few essential kinds of steps relevant to the preparation of organic semiconductors, namely ring synthesis, ring linkage, substituent attachment, and refinement. These are of varying importance among the classes of compounds considered. Obviously, compounds based on widely available heterocycles such as thiophene do not require ring synthesis, while others are based on entirely new heterocycles whose synthesis was problematic. Linking and substitution reactions may be chosen from a voluminous literature and include the Stille, Suzuki, and Kumada organometallic coupling reactions, among others.[10] These must often be tuned because of specific and unexpected side reactions associated with particular backbones, or the need to avoid a particularly deleterious byproduct. While few of the reactions discussed here are entirely new, their selection and use are often quite material-specific. Our intent is to guide those in the organic device community toward useful pathways.

Heterocyclic Oligomers

Oligomers of 2,5-linked thiophene rings (Figure 2) may be synthesized directly via classic coupling reactions. For example, α-terthiophene **1b** may be oxidatively coupled with $FeCl_3$[11] or deprotonated and then dimerized with $CuCl_2$[12] to give the prototypical semiconductor α-sexithiophene (α-6T, **2b**). The first method can result in isomeric impurities and the retention of iron residues, while the second method causes minor but perceptible chlorination of the product. Although significantly active molecular solid-based FETs were originally demonstrated with α-6T
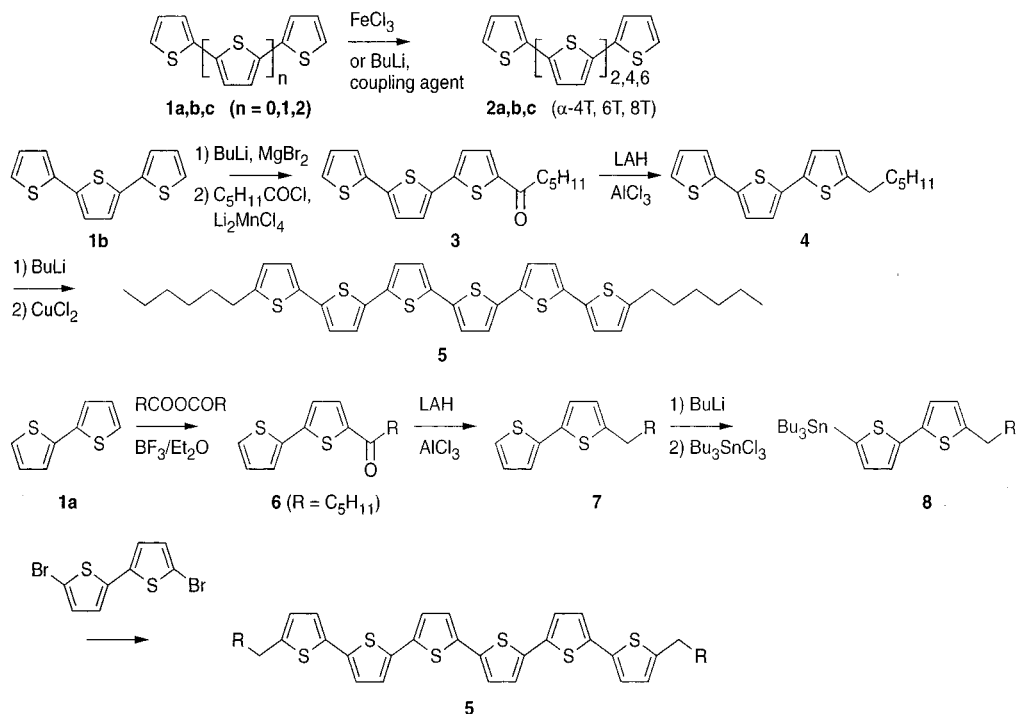
FIGURE 2. Synthetic routes to thiophene oligomers.

made using these reactions, their performance was not optimal. Because we expected device performance to be sensitive even to low levels of chemical inhomogeneities, we invested some effort in optimizing an alternate coupling reaction and subsequent purification steps. We lithiated terthiophene in tetrahydrofuran and then performed oxidative coupling at low temperature with ferric acetylacetonate.[13] This reagent does not supply a substituting electrophile and leaves relatively soluble organometallic byproducts. These byproducts and small-molecule impurities were removed by repeated triturations with a series of solvents, and then the desired product was extracted from high-molecular-weight impurities and intractable inorganics. Filtration of the extract and crystallization provided a somewhat refined product, which was further purified by vacuum sublimation. This last step ensures that the sublimation process carried out during device fabrication employs only material that is volatile and stable under sublimation conditions. Using this specially handled material, obtained in 20–30% yield, on/off ratios above 10^6 versus zero gate were demonstrated for the first time,[14] as was bandlike low-temperature hole transport.[15]

The desire for maximum purity of every intermediate has guided our protocols for preparing oligothiophenes with substitution at the terminal 5-carbons. For example, we generally do not employ alkyl halides or alkylthiophenes as reagents for the preparation of nonpolar thiophenes where there is any chance that unreacted starting materials or side products could be present in product mixtures. Since all of the reaction components would tend to have similar low polarities, their chromatographic separation would be tedious and unreliable. Instead, we prefer to introduce substituents with oxygen-

ated functionalities, such as carbonyls and alkoxy groups, as polar intermediates. Starting materials, monosubstituted and disubstituted products, and oxygenated reagents usually have contrasting polarities and may be eluted one at a time from silica gel columns. Further transformations, including reductions and deprotections, are often quantitative or nearly so, and give products that again are easily separated by chromatography. The target semiconductors are then obtained by coupling reactions of these functionalized precursors and can be isolated on the basis of the semiconductors' larger molecular size.

We first employed this logic in developing alternative syntheses of dihexyl-α-6T, **5**. 5-Hexanoylterthiophene **3** was prepared from lithiated terthiophene **1b** and hexanoyl chloride and then purified, reduced to give **4**, and dimerized.[16] The resulting product had a much higher on/off ratio (including depletion mode) than had been reported for material derived from commercial hexylthiophene and bithiophene[17] and was suitable for liquid-phase deposition. More conveniently, 5-hexanoylbithiophene **6** was obtained by simple Friedel–Crafts acylation with hexanoic anhydride, reduced to give **7**, and Stille-coupled to 5,5′-dibromobithiophene.[18] This latter approach is more general and allows for the incorporation of shorter and nonthiophene central units, or even a central single bond (dialkylquaterthiophenes). Side chains other than hexyl can also be incorporated, provided the corresponding anhydrides or acid chlorides are available. For example, we have prepared didodecyl- and dioctadecyl-α-6T.[18] The latter compound has FET activity even though a large volume fraction consists of insulating polyethylene-like chains, a tribute to the two-dimensional nature of the mobility in crystalline layered structure domains of these compounds.
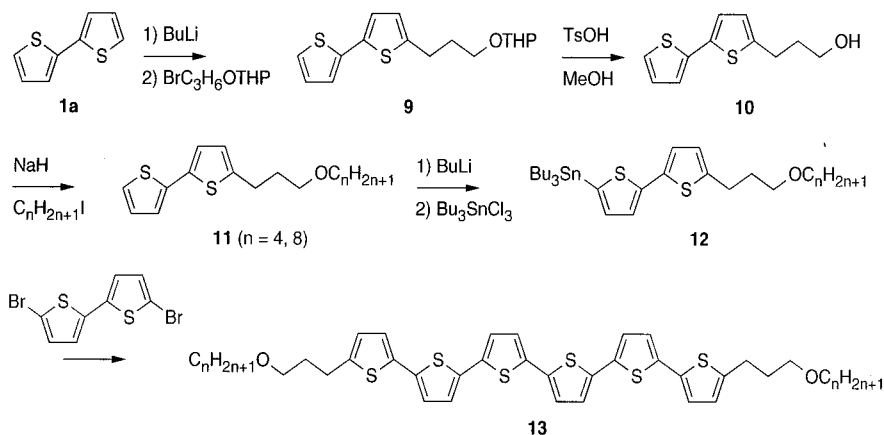
FIGURE 3. Preparation of oxy-functionalized thiophene oligomers.
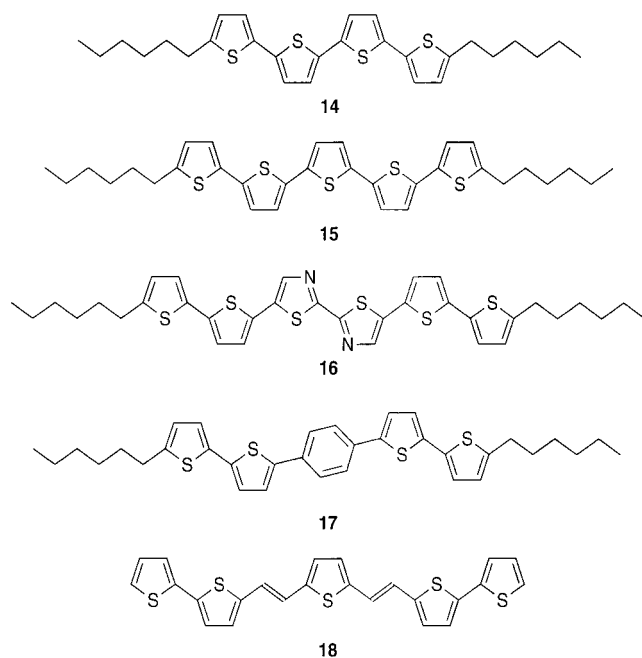

FIGURE 4. Shorter and mixed-subunit thiophene oligomers.

Another kind of side chain that we have appended to thiophene oligomers is alkoxyalkyl[18] (Figure 3), where one of the methylene units of an alkyl chain is replaced by an ether oxygen. The key polar intermediate is tetrahydropyran (THP)-protected 5-hydroxypropylbithiophene **9**, readily available because THP-protected 3-bromopropanol may be purchased and used to alkylate 5-lithiobithiophene. Subsequent removal of the THP group, to give **10**, and further elaboration from the OH terminus to give compounds such as **11** and **12** are facile and could, in principle, lead to an enormous variety of functionalized oligothiophene derivatives. We have observed enhanced solubility of the thiophene hexamer with butoxypropyl end substituents (**13**, $n = 4$) relative to the dialkyl analogues.[18]

Contrary to our expectations, we found that dihexyl-α-4T[19] **14** and 5T[20] **15** (Figure 4) had mobilities as high as or higher than those of the 6Ts. This is advantageous because of the greater solubility and volatility of the shorter oligomers that allow easier deposition of films.[21] The shorter compounds are also slightly less prone to atmospheric doping, which diminishes the on/off ratio

and alters the threshold voltage (the gate voltage where an FET is decidedly on). Another means of improving environmental stability without shortening the molecule is to incorporate a less oxidizable central subunit. We chose bithiazole for this purpose.[20] Thiazole was dimerized and iodinated by standard methods to give 5,5′-diiodo-2,2′-bithiazole. Because of the modular nature of our $2 + 2 + 2$ coupling reactions, it would be possible to attach arbitrarily 5-substituted bithiophenes to bithiazole by Stille coupling to the diiodide. We prepared bis(hexylbithienyl)-bithiazole **16** and showed that its on/off ratio is higher than that of the all-thiophene analogue, and its threshold voltage is markedly less susceptible to drift.[20] These effects are attributable to the substitution of *just two atoms* in an otherwise identical pair of molecules.

Preliminary results suggest that similar beneficial effects are obtained by employing 1,4-phenylene, inserted through the use of diiodobenzene, as the central subunit in place of the bithiazole, as in **17**.[22] Internal double bonds, on the other hand, were found to decrease compound stability, although one thienylenevinylene oligomer, *all-trans*-2,5-bis(2-(2,2′-bithien-5-yl)ethenyl)thiophene **18**, synthesized using Wittig chemistry, has a measured mobility of 0.008−0.012 cm²/(V·s) as an evaporated film and 0.0014 cm²/(V·s) when spin-coated.[23]

Linear Fused Rings

Pentacene **20** is one of the most widely studied organic FET semiconductors.[24] It is easily synthesized via quinone **19**[25] (Figure 5), is commercially available, and displays the highest mobility in an easily realizable device. Recently, pentacene has even been coaxed to display ambipolar mobility (high mobilities for both holes and electrons).[4] However, pentacene is only moderately stable to oxygen as a dense solid and is considerably unstable as a high-surface-area solid or dispersion, or under illumination. Pentacene is also very high melting and virtually insoluble, even in hot aromatic solvents. It was attractive to combine the molecular shape of pentacene, which leads to a favorable crystal packing geometry and orientation, with thiophene end groups that would increase stability and also provide points of attachment for solubilizing substit-
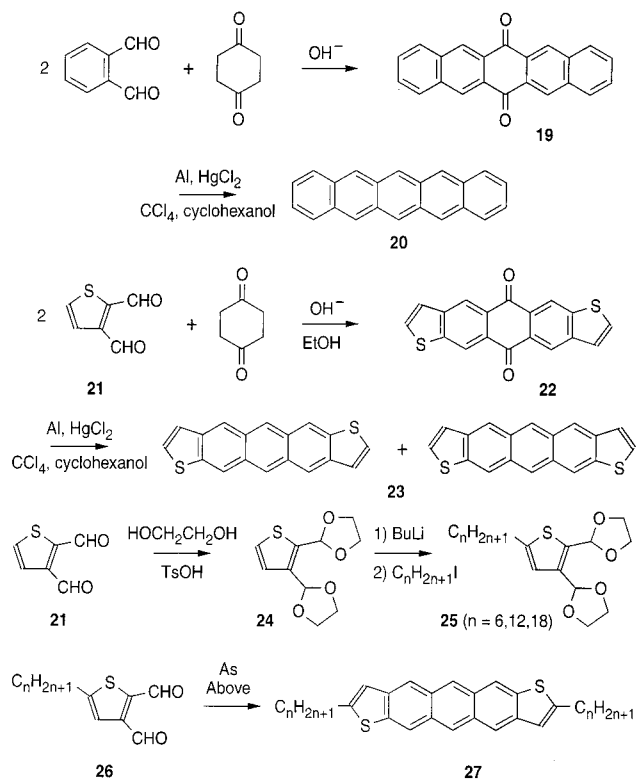
FIGURE 5. Syntheses of pentacene and anthradithiophenes.

uents. This led us to consider anthradithiophenes, whose parent compound had never been reported, though its dione precursor had been described.

The synthesis of unsubstituted anthradithiophene **23** via quinone **22** was analogous to that of pentacene.[26] It was presumably obtained as a mixture of syn and anti isomers since the reaction should not have favored either of them, and there was no obvious way to separate them. The compound is lighter in color and more environmentally stable than pentacene. Its field-effect mobility is an order of magnitude lower than that of pentacene, about 0.1 cm²/(V·s), but its on/off ratio is higher versus zero gate. A highly ordered thin-film morphology was observed and is consistent with the electrical characteristics.[26]

To attach solubilizing groups, the precursor dialdehyde **21** was protected as the bis acetal **24**, alkylated in high yield to give **25**, and deprotected to form **26**. From this point, the synthesis of the anthradithiophene ring is the same, and just as for the thiophene oligomers, a wide variety of end substituents could conceivably be attached in this way. Hexyl, dodecyl, and octadecyl disubstituted derivatives were made (structure **27**), and the first two had higher mobilities than the parent compound, with increased solubility.[26] The third still had significant activity, even though it consisted mostly of nonconjugated carbons. The dihexyl derivative could be cast under certain conditions as an active film from solution, while pentacene has only been solution cast as a Diels–Alder adduct.[27]

The performance of linear, fused ring compounds was further explored using a shorter unit, benzodithiophene (**28**, Figure 6) as a building block for the synthesis of a

variety of other planar structures. Benzodithiophene can be synthesized exclusively as its anti isomer through a previously described four-step synthesis.[28] In our hands, this synthesis, from commercially available 2,3-dibromothiophene and 3-thiophene carboxaldehyde, proceeded in an overall yield of 60% after recrystallization from ethanol. Iron(III) acetylacetonate (vide supra) proved to be the reagent of choice for the oxidative dimerization of the lithiated **28** to give **29**, in 78% yield. Other oxidative agents were tried for this reaction but gave either low yields or byproducts. The dimer was purified by vacuum sublimation to give a bright yellow compound with remarkable stability in air below 400 °C, and mobility of 4×10^{-2} cm²/(V·s) when the evaporated on a substrate at 100 °C.[28]

Prompted by our observations of other alkylated semiconductors, compounds **30**, **32**, **35**, and **41** (Figures 6 and 7) were also synthesized.[29] In an initial attempt to functionalize the α positions of benzodithiophene, we found that, not surprisingly, electrophilic substitution[30] using NBS led to a complex mixture of products having similar retention times on silica gel. Therefore, the direct lithiation of **28** was vital to its elaboration. The reaction conditions were optimized (LDA at −78 °C for 30 min followed by the addition of the electrophile and slow raising of the temperature to ambient) to yield mono- and difunctionalized products in roughly equal amounts in a single step after conventional and reversed-phase chromatography (Figure 6). Alternatively, either α-hexylbenzodithiophene **31** or α-bromobenzodithiophene **33** could be obtained as the sole product in about 60% yield when only 1 equiv of LDA was used. In this case, the compounds were isolated through alternate triturations in ethanol and acetonitrile. Oxidative dimerization of **31** was achieved according to the same procedure used on unsubstituted benzodithiophene **28** to give the dimer **32** as a bright yellow compound (78% yield) with stability similar to that of the unsubstituted compound **29**.

Functionalization of the benzodithiophene building block with the 2-(5-hexyl)-thienyl substituent was achieved through a Suzuki coupling.[31] 2-Iodo-5-hexylthiophene **36** was synthesized from the commercially available 2-hexylthiophene (LDA/THF/−78 °C, 30 min, excess I₂, quantitative) and was readily transformed into the corresponding boronic ester **37** using pinacol borane in dioxane.[32] The Suzuki coupling between **33** and **37** was optimized in DMF with PdCl₂(dppf) as a catalyst and K₃PO₄ as a base to yield the highly fluorescent asymmetric product **38** in 87% yield.

Various iodinations of **38** gave complex mixtures, including **39**. Fortunately, the reaction of **38** with LDA followed by 1,2-dibromoethane gave a single product, **40**, in 51% isolated yield. The symmetric benzodithiophene derivative **35** bearing two side hexylthiophene rings could be obtained in 83% yield from **40**, under Suzuki coupling reaction conditions. Alternatively, **35** was derived from **34** in 74% yield (Figure 6).

Compounds **30** and **35** display considerable solubility in common organic solvents. Dimer **32** displays a solubil-
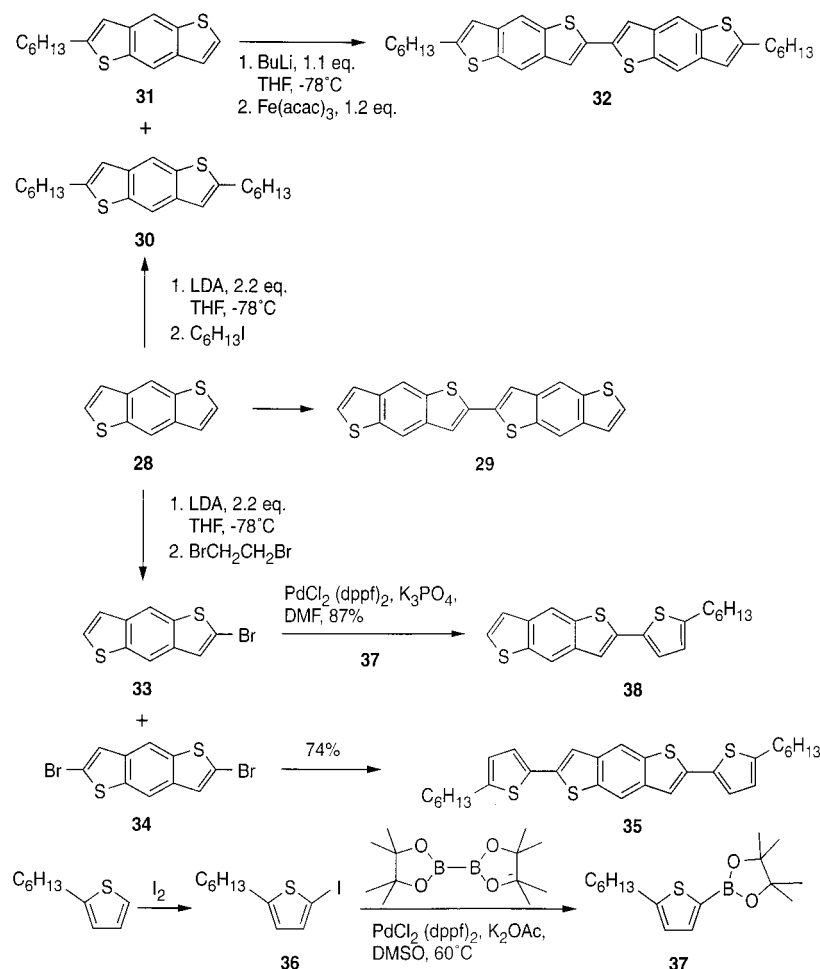
FIGURE 6. Lithiation and subsequent reactions of benzodithiophene.

ity barely sufficient for ^{1}H NMR in chlorobenzene. Not surprisingly, the solubility of the longest molecule **41**, obtained by dimerization of lithiated **38**, is very low ($<10^{-6}$ M^{-1}). The mobility of holes reached 1.6×10^{-2} cm^2/(V·s) when **32** was evaporated on a substrate at room temperature, with an on/off ratio of 5000. The charge mobility in a thin film of **36** cast from chlorobenzene displayed a moderate value of 1.2×10^{-3} cm^2/(V·s). An evaporated thin film of the insoluble molecule **41** displayed a charge mobility of 1.0×10^{-3} cm^2/(V·s). X-ray diffraction data also indicate that the preferred orientation of the dimer molecules is perpendicular to the substrate.

Two-Dimensional Fused Ring Compounds

The simplest two-dimensional fused rings that we have employed are NTCDI derivatives **43**. They are synthesized trivially from NTCDA **42** and amines[33] (Figure 8) and can be easily purified by sublimation. Some of these compounds have the rare characteristic of high electron mobility.[34] The incorporation of fluoroalkyl groups on the side chains greatly stabilizes NTCDI solids for electron transport in air by a mechanism that is not yet fully understood.[35] Ring substitution by fluorine or other small electron-withdrawing groups would also be desirable but remains an unresolved challenge.

The family of phthalocyanines **44** is another type of two-dimensional fused ring system (see Figure 9 for general structures). They are commonly used as organic semiconductors in numerous applications, such as solar cells, light emitting diodes, and nonlinear optical materials.[36] Most of the unsubstituted phthalocyanines, coordinated with different metals, are commercially available and can be easily purified by vacuum sublimation. The most common and best performing phthalocyanine for p-channel transistors is the copper phthalocyanine (CuPc). Mobility as high as 0.02 cm^2/(V·s) and an on/off ratio greater than 10^5 have been reported.[37] The rare earth bis-(phthalocyanines) were also shown to have relatively high p-type mobility (ca. 0.015 cm^2/(V·s)).[38] In addition, n-type behavior was observed under vacuum.[38]

Phthalocyanines can be made soluble by substitutions with alkyl and alkoxyl side chains.[36] The *tert*-butyl-substituted copper phthalocyanines have good solubility in various organic solvents, such as chloroform and toluene, and are also volatile enough for vacuum sublimation. However, the crystallinity of these compounds is significantly reduced in sublimed and cast films due to the bulky *tert*-butyl groups and irregularity in substitution.[39] Most of the other substituted phthalocyanines with longer linear alkyl and alkoxy side chains (e.g., hexyl or higher) are not sufficiently volatile for vacuum sublima-
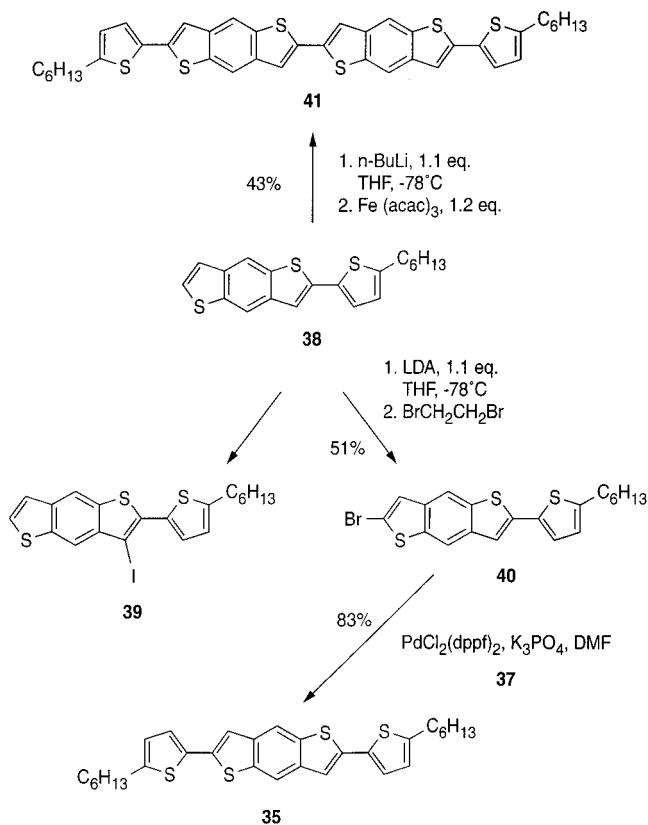
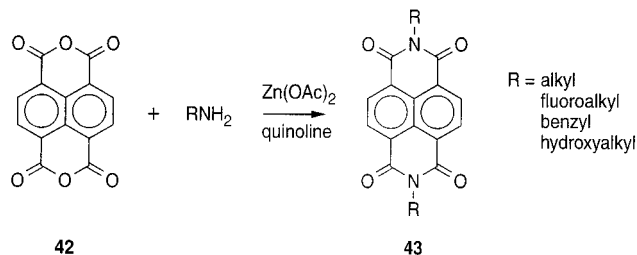**FIGURE 7.** Reactivity of the benzodithiophene compound **38**.

FIGURE 8. One-step synthesis of NTCDI compounds.

tion. Therefore, their purification tends to be more difficult. Column separation sometimes degrades them. Relatively low mobilities were measured for octa-octoxy copper phthalocyanine cast from solution despite the high crystallinity of the film. The low mobility has been attributed to possible trapping by impurities.[39]

The energy levels of phthalocyanine derivatives can be tuned by substitution with electron-withdrawing groups to give n-channel semiconductors.[40] Several phthalonitrile derivatives with perfluoro and perchloro substitution are readily available, and they can be used to form the corresponding phthalocyanines by following standard literature procedures (refluxing in a high-boiling-point organic solvent together with metal salts)[41] (Figure 9). The perfluorinated metallophthalocyanines are easily purified by vacuum sublimation, and highly ordered semiconductor films can be prepared.[42] The best transistor performance was reported with the copper complex. The perchlorinated phthalocyanine showed surprisingly low crystallinity, and the resulting films had very low field-effect mobility. 2,3,9,10,16,17,23,24-Octacyano copper
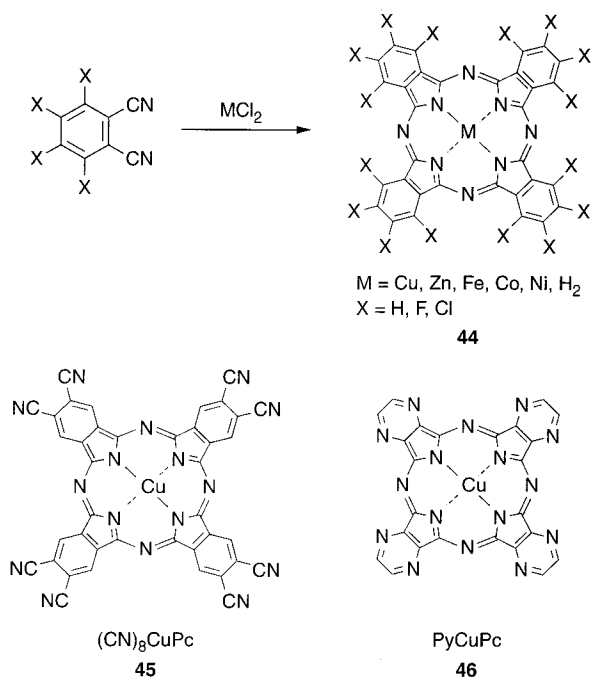

FIGURE 9. Synthesis and chemical structures of phthalocyanines and derivatives.

phthalocyanine (CN$_8$CuPc) **45** and copper tetra(pyrazino-[2,3])-5,10,15,20-tetraazaporphyrine (PyCuPc) **46** can be synthesized using similar procedures.[41,43] In the case of CN$_8$CuPc, a dilute solution has to be used during synthesis to prevent polymerization.[43] Neither of the last two phthalocyanines could be sublimed for purification and transistor evaluation.

Polymeric Semiconductors

Polymeric materials offer advantages of easy processing from solution and good film-forming properties. The family of polythiophene derivatives are the most studied polymers for transistor application. The low-mobility electrochemically polymerized polythiophene was used in the first organic field-effect transistor.[44] Solution-soluble regiorandom poly(3-alkylthiophene)s **52** used for transistor studies are usually prepared using FeCl$_3$ oxidative polymerizations from 3-alkylthiophenes **51**. Low mobilities were again reported and were attributed to the random structures and amorphous morphology in the solid state.[45] Attempts have been made to improve the molecular ordering of regiorandom poly(3-alkylthiophene)s by using Langmuir–Blodgett (LB) films.[46,47] However, a large amount of surfactant has to be incorporated in order to form stable LB films, and the resulting devices showed poor performance.[46]

Regioregular poly(3-alkylthiophene)s **53** (Figure 10) have been shown to have properties very different from their corresponding regiorandom polymers, such as smaller band gaps, better ordering and crystallinity in their solid states, and substantially improved electroconductivities.[48] The field-effect mobility of regioregular poly(3-hexylthiophene) (P3HT) is among the highest reported for polymer transistors.[49−51] The polymer backbones adapt a
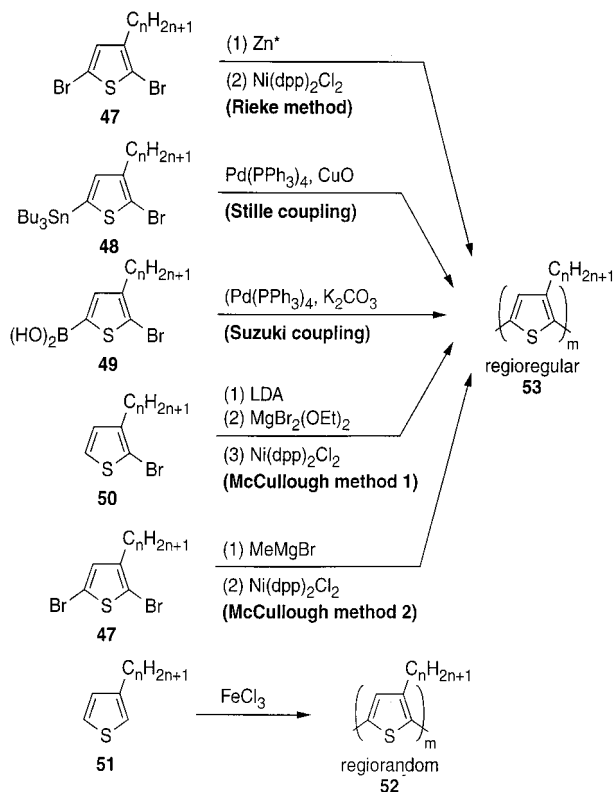
FIGURE 10. Synthetic methods for regioregular and regiorandom poly(3-alkylthiophene)s.

FIGURE 11. Regioregular polythiophenes with various side chains.

preferred orientation in thin films such that the hexyl side chains may be close to normal to the substrate and the backbone is essentially parallel to the substrate.[49−52] Such preferred orientation might account for the relatively high mobilities in P3HT, since it would place the transport direction (i.e., that between thienyl rings) parallel to the substrate.

There are several synthetic approaches for preparing regioregular poly(3-alkythiophene)s (Figure 10).[53] The Rieke method involves the reaction of 3-alkyl-2,5-dibromo-thiophene **47** with activated zinc followed by a nickel(0)-catalyzed polycondensation reaction. High-molecular-weight polymers with reasonable polydispersity can be obtained with properly controlled reaction conditions.[54] Other methods employ **48−50** as starting materials. McCullough and co-workers rely on the coupling reactions of the Grignard products from 3-alkyl-2-bromothiophene or 3-alkyl-2,5-dibromothiophene[55,56] to give high-molecular-weight regioregular poly(3-alkylthiophene)s with good yields. All the purified polymers prepared using the above methods give similar transistor performance. The purification is done simply by precipitation and reprecipitations in methanol, acetone, and hexane. The Stille and Suzuki couplings give regioregular poly(3-alkylthiophene)s with weight-averaged molecular weight less than 10 000.[57,58] The transistor devices fabricated with P3HT synthesized from the Stille reaction had slightly lower field-effect mobilities (about 0.007 cm²/(V·s)).[59] This may be related to the higher tendency of side reactions, potentially causing more defects in the polymer and disturbing the ordering of polymer in the resulting film.
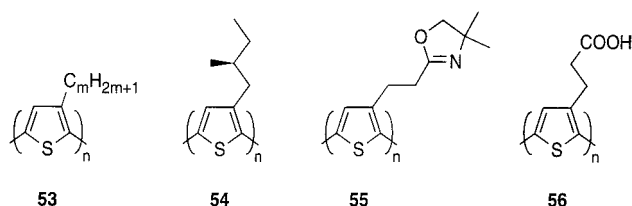
Regioregular polythiophenes with various side chains can be readily prepared using the McCullough approaches (**53−56**, Figure 11). The nature of the side chains has a great impact on transistor performance.[49,50,60] First, the length of linear alkyl substituents needs to be between 3 and 12 carbons.[60] If the alkyl chain is too long, the film matrix could be dominated by the insulating alkyl substituents, resulting in low mobilities of the films. On the other hand, if the alkyl chain is too short, the polymer has low solubility, and it is difficult to form uniform smooth films. Second, the bulkiness of the side chains has a direct effect on the morphology and field-effect mobility of the polymer.[50] Poor molecular ordering and low crystallinity have been observed for regioregular polythiophenes with bulky or carboxylic-substituted side chains (**55** and **56**), and the resulting transistor devices also showed low field-effect mobilities (less than 10^{-5} to 10^{-4} cm²/(V·s)).[50] In another example, a chiral alkyl-substituted regioregular polythiophene (**54**) has shown better crystallinity. However, the $\pi-\pi$ overlap distance between the polythiophene backbones increases substantially (i.e., to ca. 4.3 vs 3.8 Å for regioregular poly(3-hexylthiophene) (PHT) after the introduction of methyl branches in the side chains. The field-effect mobility of this polymer is reasonably high compared to those of many solution-processable conjugated polymers (i.e., of the order of 10^{-3} cm²/(V·s)) but is still an order of magnitude lower than that of regioregular PHT.[50] These results indicate that the nature of the side chains has a critical impact on the self-assembly, crystallization, and semiconducting properties of regioregular poly(3-alkylthiophene) derivatives. High crystallinity and high transistor performance are obtained only with regioregular polythiophenes that contain non-sterically hindered linear side chains.

Other types of conjugated polymers have also been investigated for transistor applications (Figure 12). Some examples include poly(2,5-dialkylphenylene-*co*-phenylene)s (**57**), poly(2,5-dialkylphenylene-*co*-thiophene)s (**58**), poly-(2,5-dialkylphenylene vinylene)s (**59**), and the dialkoxyl derivatives of the above polymers (**60−62**).[59] They were all prepared from palladium(0)-catalyzed Stille reactions.[61] However, very low (less than 10^{-4} cm²/(V·s)) or no field-effect mobilities have been found. Recently, Sirringhaus and co-workers reported the transistor performance of a liquid crystalline polymer. It is an alternating copolymer of a bithiophene and a dioctylfluorene (**63**), and enhanced mobility was reported through chain alignment in its liquid-crystalline phase. A mobility of 0.01−0.02 cm²/(V·s) for devices parallel to the alignment direction was obtained, while it was 5−8 times lower for devices perpendicular to the alignment direction. Another
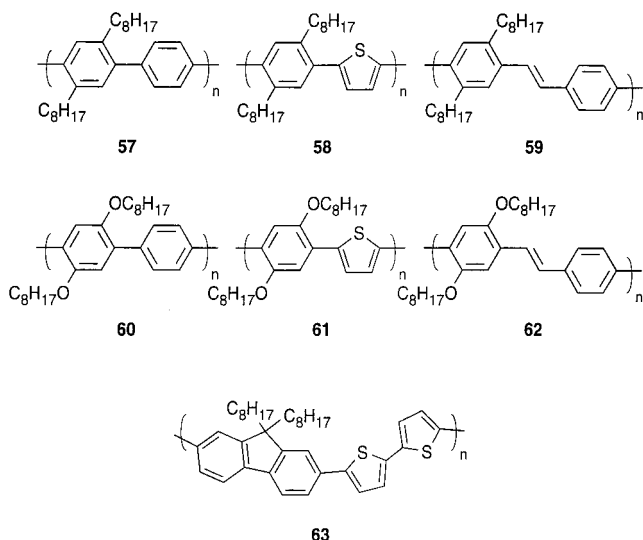
FIGURE 12. Examples of conjugated polymers studied for field-effect transistors.

polymeric system involves a soluble precursor polymer which can undergo subsequent chemical reactions to give the desired conjugate polymer such as poly(thienylene vinylene) ($\mu = 0.22$ cm^2/(V·s)).[63] Even though high field-effect mobilities have been reported, the on/off ratios often suffer due to partial doping of the material. Similarly, high mobilities and low on/off ratios have been reported for polypyrrole and polyaniline.[64,65]

Conclusion

A substantial body of synthetic chemistry has been developed for the preparation and tuning of organic semiconductors. The availability of these synthetic techniques has been vital to the advancement of the field of organic electronics, providing the means for understanding the solid-state physics on one hand, and exploring applications on the other hand. Having developed a multiplicity of useful reactions and procedures ensures the availability of a variety of semiconductor structures, so structure–activity relationships can be ascertained, and rich combinatorial arrays can be produced. Work on heterocyclic ring synthesis has made anthradithiophenes, benzodithiophenes, and halogenated phthalocyanines available. In synthesizing oligomers, a surprising dependence of linkage reaction outcomes on connection points has been noted. Elaboration of end substituents has enabled control of film morphology, solution processing, and interaction with environmental vapors. In addition, valuable purification protocols are made possible by the appending of suitably polar functional groups.

For large-area components, the regioregular polymers are advantageous because of their film-forming capabilities. Where high on/off ratio and resistance to air doping are important, the shorter oligomers and fused thiophenes would perform best. The fluorinated phthalocyanine and NTCDI derivatives combine air stability with n-channel operation, enabling complementary logic circuit fabrica-

tion. Medium length substituents increase the likelihood that a given compound will form a high-mobility film from solution.

Future work will focus on more complex devices and device responses, including some that could only be demonstrated with organic materials as the active elements. For example, the covalent bonding of receptor sites within the interacting distance of the FET channel can lead to new sensing mechanisms, exploration of which is currently in progress.

References

(1) Drury, C. J.; Mutsaers, C. M. J.; Hart, C. M.; Matters, M.; de Leeuw, D. M. Low-cost All-polymer Integrated Circuits. *Appl. Phys. Lett.* **1998**, *73*, 108–110. Garnier, F.; Hajlaoui, R.; Yassar, A. All-polymer Field-effect Transistor Realized by Printing Techniques. *Science* **1994**, *265*, 1684–1686.

(2) Katz, H. E.; Bao, Z. The Physical Chemistry of Organic Field-effect Transistors. *J. Phys. Chem. B* **2000**, *104*, 671–678.

(3) Sirringhaus, H.; Wilson, R. J.; Friend, R. H.; Inbasekaran, M.; Wu, W.; Woo, E. P.; Grell, M.; Bradley, D. D. C. Mobility Enhancement in Conjugated Polymer Field-effect Transistors through Chain Alignment in a Liquid Crystalline Phase. *Appl. Phys. Lett.* **2000**, *77*, 406–408. Sirringhaus, H.; Tessler, N.; Friend, R. H. Integrated Optoelectronic Devices Based on Conjugated Polymers. *Science* **1998**, *280*, 1741–1744.

(4) Schon, J. H.; Berg, S.; Kloc, Ch.; Batlogg, B. Ambipolar Pentacene Field-effect Transistors and Inverters. *Science (Washington, D.C.)* **2000**, *287*, 1022–1025.

(5) Crone, B.; Dodabalapur, A.; Lin, Y.-Y.; Filas, R. W.; Bao, Z.; LaDuca, A.; Sarpeshkar, R.; Katz, H. E.; Li, W. Large-scale Complementary Integrated Circuits Based on Organic Transistors. *Nature* **2000**, *403*, 521–523. Klauk, H.; Jackson, T. N. Pentacene organic thin-film transistors and Ics. *Solid State Technol.* **2000**, *43*, 63–72, 75–77.

(6) Rogers, J. A.; Bao, Z.; Baldwin, K.; Dodabalapur, A.; Crone, B.; Katz, H. E.; Raju, V. R.; Amundson, K.; Ewing, J.; Drziac, P. *Proc. Nat. Acad. Sci.*, in press.

(7) Katz, H. E.; Dodabalapur, A.; Bao, Z. Oligo- and Polythiophene Field-effect Transistors. In *Handbook of Oligo- and Polythiophenes*; Fichou, D., Ed.; Wiley-VCH: Weinheim, 1998. Horowitz, G. Organic Field-effect Transistors. *Adv. Mater.* **1998**, *10*, 365–377. Brown, A. R.; Jarrett, C. P.; de Leeuw, D. M.; Matters, M. Field-effect Transistors Made from Solution-processed Organic Semiconductors. *Synth. Met.* **1997**, *88*, 37–55. Garnier, F. Thin film Transistors Based on Organic Conjugated Semiconductors. *Chem. Phys.* **1998**, *227*, 253–262. Bao, Z.; Rogers, J. A.; Katz, H. E. Printable Organic and Polymeric Semiconductor Materials and Devices. *J. Mater. Chem.* **1999**, *9*, 1895–1904.

(8) Bauerle, P. The Synthesis of Oligothiophenes. In *Handbook of Oligo- and Polythiophenes*; Fichou, D., Ed.; Wiley-VCH: Weinheim, 1998.

(9) Fichou, D. Structural order in conjugated oligothiophenes and its implications on optoelectronic devices. *J. Mater. Chem.* **2000**, *10*, 571–558.

(10) Wu, R.; Schumm, J. S.; Pearson, D. L.; Tour, J. M. Convergent Synthetic Routes to Orthogonally Fused Conjugated Oligomers Directed toward Molecular Scale Electronic Device Applications. *J. Org. Chem.* **1996**, *61*, 6906–6921. Wei, Y.; Yang, Y.; Yeh, J.-M. Synthesis and Electronic Properties of Aldehyde End-Capped Thiophene Oligomers and Other α,ω-Substituted Sexithiohenes. *Chem. Mater.* **1996**, *8*, 2659–2666.

(11) Fichou, D.; Horowitz, G. G.; Garnier, F. Eur. Pat. Appl. EP,402,-269, 1990; FR Appl. 89/7,610, 1989.

(12) Fichou, D.; Teulade-Fichou, M.-P.; Horowitz, G.; Demanze, F. Thermal and Optical Characterization of High Purity α-octithiophene. *Adv. Mater.* **1997**, *9*, 75–80.

(13) Katz, H. E.; Torsi, L.; Dodabalapur, A. Synthesis, Materials Properties, and Transistor Performance of Highly Pure Thiophene Oligomers. *Chem. Mater.* **1995**, *7*, 2235−2237.

(14) Dodabalapur, A.; Torsi, L.; Katz, H. E. Organic Transistors: Two-Dimensional Transport and Improved Electrical Characteristics. *Science* **1995**, *268*, 270−271.

(15) Torsi, L.; Dodabalapur, A.; Rothberg, L. J.; Fung, A. W. P.; Katz, H. E. Intrinsic Transport Properties and Performance Limits of Organic Field-Effect Transistors. *Science* **1996**, *272*, 1462−1464. Torsi, L.; Dodabalapur, A.; Rothberg, L. J.; Fung, A. W. P.; Katz, H. E. Charge transport in oligothiophene field-effect transistors. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1998**, *57*, 2271−2275.

(16) Katz, H. E.; Dodabalapur, A.; Torsi, L.; Elder, D. Precursor Synthesis, Coupling, and TFT Evaluation of End-Substituted Thiophene Hexamers. *Chem. Mater.* **1995**, *7*, 2238−2240.

(17) Garnier, F.; Yassar, A.; Hajlaoui, R.; Horowitz, G.; Deloffre, F.; Servet, B.; Ries, S.; Alnot, P. Molecular Engineering of Organic Semiconductors: Design of Self-assembly Properties in Conjugated Thiophene Oligomers. *J. Am. Chem. Soc.* **1993**, *115*, 8716−8721.

(18) Katz, H. E.; Laquindanum, J. G.; Lovinger, A. J. Synthesis, Solubility, and Field-Effect Mobility of Elongated and oxa-Substituted α,ω-Dialkyl Thiophene Oligomers. Extension of "Polar Intermediate" Synthetic Strategy and Solution Deposition on Transistor Substrates. *Chem. Mater.* **1998**, *10*, 633−638.

(19) Katz, H. E.; Lovinger, A. J.; Laquindanum, J. G. α,ω-Dihexylquaterthiophene: a Second Thin Film Single-Crystal Organic Semiconductor. *Chem. Mater.* **1998**, *10*, 457−459.

(20) Li, W.; Katz, H. E.; Lovinger, A. J.; Laquindanum, J. G. Field-effect Transistors Based on Thiophene Hexamer Analogues with Diminished Electron Donor Strength. *Chem. Mater.* **1999**, *11*, 458−465.

(21) Garnier, F.; Hajlaoui, R.; El Kassmi, A.; Horowitz, G.; Laigre, L.; Porzio, W.; Armanini, M.; Provasoli, F. Dihexylquaterthiophene, a Two-dimensional Liquid Crystal-like Organic Semiconductor with High Transport Properties. *Chem. Mater.* **1998**, *10*, 3334−3339.

(22) Katz, H. E., unpublished results.

(23) Dimitrakopoulos, C. D.; Afzali-Aradakani, A.; Furman, B.; Kymissis, J.; Purushothaman, S. *trans-trans*-2,5-Bis-[2-{5-(2,2′-bithienyl)}-ethenyl]thiophene: Synthesis, Characterization, Thin Film Deposition, and Fabrication of Organic Field-effect Transistors. *Synth. Met.* **1997**, *89*, 193−197.

(24) Klauk, H.; Gundlach, D. J.; Nichols, J. A.; Jackson, T. N. Pentacene Organic Thin-film Transistors for Circuit and Display Applications. *IEEE Trans. Electron Devices* **1999**, *46*, 1258−1263. Dimitrakopoulos, C. D.; Brown, A. R.; Pomp, A. Molecular Beam Deposited Thin Films of Pentacene for Organic Field Effect Transistor Applications. *J. Appl. Phys.* **1996**, *80*, 2501−2508. Horowitz, G.; Fichou, D.; Peng, X.; Garnier, F. Thin-film transistors Based on alpha-conjugated Oligomers. *Synth. Met.* **1991**, *41−43*, 1127−1130. Laquindanum, J. G.; Katz, H. E.; Lovinger, A. J.; Dodabalapur, A. Morphological Origin of High Mobility in Pentacene Thin Film Transistors. *Chem. Mater.* **1996**, *8*, 2542−2544.

(25) Goodings, E. P.; Mitchard, D. A.; Owen, G. Synthesis, Structure, and Electrical Properties of Naphthacene, Pentacene, and Hexacene Sulfides. *J. Chem. Soc., Perkin Trans. 1* **1972**, *11*, 1310−1314.

(26) Laquindanum, J. G.; Katz, H. E.; Lovinger, A. J. Synthesis, Morphology, and Field-effect Mobility of Anthradithiophenes. *J. Am. Chem. Soc.* **1998**, *120*, 664−672.

(27) Brown, A. R.; Pomp, A.; de Leeuw, D. M.; Klaassen, D. B. M.; Havinga, E. E.; Herwig, P.; Muellen, K. Precursor Route Pentacene Metal−insulator-semiconductor Field-effect Transistors. *J. Appl. Phys.* **1996**, *79*, 2136−2138.

(28) Laquidanum, J. G.; Katz, H. E.; Lovinger, A. J.; Dodabalapur, A. Benzodithiophene Rings as Semiconductor Building Blocks. *Adv. Mater.* **1997**, *9*(1), 36−37. Note that the structures of the prefused intermediates given in this reference are incorrect.

(29) Gilat, S.; Katz, H. E.; Li, W. Searching for New Soluble Organic Semiconductors: Unexpected Reactivity of Substituted Benzodithiophenes. Presented at the 218th National Meeting of the American Chemical Society, New Orleans, LA, August 1999; ORGN-241.

(30) Gronowitz, S.; Dahlgren, T. Some Electrophilic Substitution Reactions of Benzo[1,2-b:4,3-b′]dithiophene and benzo[2,1-b:3,4-b′]dithiophene. *Chem. Scr.* **1977**, *12*, 97−101.

(31) Miyaura, N. In *Advances in Metal−Organic Chemistry*; Liebeskind, L. S., Ed.; Jai Press: London, 1998; Vol. 6, p 187.

(32) Murata, M.; Watanabe, S.; Masuda, Y. Novel Palladium(0)-Catalyzed Coupling Reaction of Dialkoxyborane with Aryl Halides: Convenient Synthetic Route to Arylboronates. *J. Org. Chem.* **1997**, *62*, 6458−6459.

(33) Rademacher, A.; Maerkle, S.; Langhals, H. Soluble Perylene Fluorescent Dyes with Higher Photostability. *Chem. Ber.* **1982**, *115*, 2927−2934.

(34) Katz, H. E.; Johnson, J.; Lovinger, A. J.; Li, W. Naphthalenetetracarboxylic Diimide-based n-Channel Transistor Semiconductors: Structural Variation and Thiol-enhanced Gold Contacts. *J. Am. Chem. Soc.* **2000**, *122*, 7787−7792. Katz, H. E.; Lovinger, A. J.; Johnson, J.; Kloc, Ch.; Siegrist, T.; Li, W.; Lin, Y.-Y.; Dodabalapur, A. A Soluble and Air-stable Organic Semiconductor with High Electron Mobility. *Nature* **2000**, *404*, 478−481.

(35) Katz, H. E.; Siegrist, T.; Schon, J. H.; Kloc, Ch.; Batlogg, B.; Lovinger, A. J.; Johnson, J. Solid State Structural and Electrical Characterization on N-benzyl and N-alkyl Naphthalene 1,4,5,8-Tetracarboxylic Diimides. *Chem. Phys. Chem.* **2001**, in press.

(36) Moser, F. H. *Phthalocyanines*; CRC Press: London, 1983.

(37) Bao, Z.; Lovinger, A. J.; Dodabalapur, A. A Highly Ordered Vacuum-Deposited Thin Films Of Metallophthalocyanines And Their Applications In Field-Effect Transistors. *Adv. Mater.* **1997**, *9*, 42−44. Bao, Z.; Lovinger, A. J.; Dodabalapur, A. Soluble And Processable Regioregular Poly(3-Hexylthiophen) For Thin Film Field-Effect Transistor Applications With High Mobility. *Appl. Phys. Lett.* **1996**, *69*, 3066−3068.

(38) Guilland, G.; Sadoun, M. A.; Maitrot, M.; Simon, J.; Bouvet, M. Field-Effect Transistors Based On Intrinsic Molecular Semiconductors. *Chem. Phys. Lett.* **1990**, *167*, 503−505.

(39) Bao, Z.; Lovinger, A. J., unpublished results.

(40) Schlettwein, D.; Wohrle, D.; Karmann, E.; Melville, U. Conduction Type Of Substituted Tetraazaporphyrins And Perylene Tetracarboxylic Acid Diimides As Detected By Thermoelectric-Power Measurements. *Chem. Mater.* **1994**, *6*, 3−5.

(41) Jones, J. G.; Twigg, M. V. A fluorinated Iron Phthalocyanine. *Inorg. Chem.* **1969**, *8*, 2018−2019. Schlettwein, D.; Wohrle, D.; Jaeger, N. I. Reversible Reduction and Reoxidation of Thin Films of Tetrapyrazinotetraazaporphyrines. *J. Electrochem. Soc.* **1989**, *136*, 2882−2890.

(42) Bao, Z.; Lovinger, A. J.; Brown, J. New Air-Stable N-Channel Organic Thin Film Transistors. *J. Am. Chem. Soc.* **1998**, *120*, 207−208.

(43) Wohrle, D.; Meyer, G.; Wahl, B. Polymere Phthalocyanine und ihre Vorstufen, 1. Reaktive Oktafunktionelle Phthalocyanine aus 1,2,4,5-Tetracyanbebzol. *Makromol. Chem.* **1980**, *181*, 2127−2135.

(44) Tsumura, A.; Koezuka, H.; Ando, T. Macromolecular Electronic Device: Field-effect Transistor with a Polythiophene Film. *Appl. Phys. Lett.* **1986**, *49*, 1210−1212.

(45) Assadi, A.; Svensson, C.; Willander, M.; Inganas, O. Field-Effect Mobility Of Poly(3-Hexylthiophene). *Appl. Phys. Lett.* **1988**, *53*, 195−197.

(46) Paloheimo, J.; Kuivalainen, P.; Stubb, H.; Vuorimaa, E.; Yli-Lahti, P. Molecular Field-effect Transistors Using Conducting Polymer Langmuir−Blodgett Films. *Appl. Phys. Lett.* **1990**, *56*, 1157−1159.

(47) Xu, G. F.; Bao, Z.; Groves, J. T. Langmuir−Blodgett Films Of Regioregular Poly(3-Hexylthiophene) As Field-Effect Transistors. *Langmuir* **2000**, *16*, 1834−1841.

(48) Fichou, D. In *Handbook of Oligo- and Polythiophenes*; Fichou, D., Ed.; Wiley-VCH: Weinheim, 1998.

(49) Bao, Z.; Dodabalapur, A.; Lovinger, A. J. Soluble And Processable Regioregular Poly(3-Hexylthiophen) For Thin Film Field-Effect Transistor Applications With High Mobility. *Appl. Phys. Lett.* **1996**, *69*, 4108−4110.

(50) Bao, Z.; Lovinger, A. J. *Chem. Mater.* **1999**, *11*, 2607−2612.

(51) Sirringhaus, H.; Tessler, N.; Friend, R. H. Integrated Optoelectronic Devices Based On Conjugated Polymers. *Science* **1998**, *280*, 1741−1743.

(52) Sirringhaus, H.; et al. Two-Dimensional Charge Transport In Self-Organized, High-Mobility Conjugated Polymers. *Nature* **1999**, *401*, 685−688.

(53) McCullough, R. D. The chemistry of Conducting Polythiophenes: from Synthesis to Self-assembly to Intelligent Materials. *Adv. Mater.* **1998**, *10*, 1−24.

(54) Chen, T. A.; Wu, X.; Rieke, R. D. Regiocontrolled Synthesis Of Poly-(3-Alkylthiophenes) Mediated By Rieke Zinc: Their Characterization And Solid-State Properties. *J. Am. Chem. Soc.* **1995**, *117*, 233−244.

(55) McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. Design, Synthesis, And Control Of Conducting Polymer Architectures: Structurally Homogeneous Poly(3-Alkylthiophenes). *J. Org. Chem.* **1993**, *58*, 904−912.

(56) Loewe, R. S.; Khersonsky, S. M.; McCullough, R. D. A Simple Method To Prepare Head-To-Tail Coupled, Regioregular Poly(3-Alkylthiophenes) Using Grignard Metathesis. *Adv. Mater.* **1999**, *11*, 250−252.

(57) Malenfant, P. R. L.; Frechet, J. M. J. Dendrimers As Solubilizing Groups For Conducting Polymers: Preparation And Characterization Of Polythiophene Functionalized Exclusively With Aliphatic Ether Convergent Dendrons. *Macromolecules* **2000**, *33*, 3634–3640.

(58) Bidan, G.; De Nicola, A.; Enee, V.; Guillerez, S. Synthesis And UV–Visible Properties Of Soluble Regioregular Oligo(3-Octylthiophenes), Monomer To Hexamer. *Chem. Mater.* **1998**, *10*, 1052–1058.

(59) Bao, Z., unpublished results.

(60) Bao, Z.; Feng, Y.; Dodabalapur, A.; Raju, V. R.; Lovinger, A. High-Performance Plastic Transistors Fabricated By Printing Techniques. *Chem. Mater.* **1997**, *9*, 1299–1301.

(61) Bao, Z. N.; Chan, W. K.; Yu, L. P. Exploration Of The Stille Coupling Reaction For The Syntheses Of Functional Polymers. *J. Am. Chem. Soc.* **1995**, *117*, 12426–12435.

(62) Sirringhaus, H.; Wilson, R. J.; Friend, R. H.; Inbasekaran, M.; Wu, W.; Woo, E. P.; Grell, M.; Bradley, D. D. C. Mobility Enhancement In Conjugated Polymer Fets Through Chain Alignment In A Liquid-Crystalline Phase. *Appl. Phys. Lett* **2000**, *77*, 406–408.

(63) Fuchigami, H.; Tsumura, A.; Koezuka, H. Polythienylenevinylene Thin-Film Transistor With High Carrier Mobility. *Appl. Phys. Lett.* **1993**, *63*, 1372–1374.

(64) Kuo, C. T.; Chen, S. A.; Hwang, G. W.; Kuo, H. H. Field-Effect Transistor With The Water-Soluble Self-Acid-Doped Polyaniline Thin Films As Semiconductor. *Synth. Met.* **1998**, *93*, 155–160.

(65) Kou, C. T.; Liou, T. R. Characterization Of Metal-Oxide-Semiconductor Field-Effect Transistor (MOSFET) For Polypyrrole And Poly-(N–Alkylpyrrole)s Prepared By Electrochemical Synthesis. *Synth. Met.* **1996**, *82*, 167–173.