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Perspective

Solution-Processable Organic Semiconductors for Thin-Film Transistors: Opportunities for Chemical Engineers

Yueh-Lin (Lynn) Loo
Dept. of Chemical Engineering and Center for Nano- and Molecular Science
and Technology, University of Texas, Austin, TX 78712

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Introduction: Thin-Film Transistors as Building Blocks for Circuits in Flexible Displays

Imagine households with wallpapers whose patterns and colors we can change at the click of a switch. Imagine newspapers and books whose contents automatically update daily or on request. Or imagine a disposable strip that monitors a child's temperature and dispenses the minimum amount of medication for fever relief. Central to these applications will be electronic devices that are based on organic molecules and polymers. Compared to silicon or germanium, organic molecules and polymers — with a wide range of functionalities as building blocks — are chemically versatile, and can be synthesized in large quantities at moderate reaction conditions. They are mechanically flexible, and can be easily melt- or solution processed over large areas. The combination of these unique attributes has fueled research and development in organic electronics, with hopes that, one day, we can realize the low-cost, large-area, mechanically-flexible applications mentioned earlier.

This review focuses on the materials development for the organic thin-film transistor — a small, yet critical, component that makes the realization of these applications possible. The organic thin-film transistor has been proposed as the fundamental unit for backplane driving circuits in flexible displays and low-cost memory applications. In an active matrix-type display, for example, arrays of organic thin-film transistors — each individually controllable — would turn on and off the corresponding pixels. An organic thin-film transistor is shown in Figure 1. This device consists of sequentially-deposited layers of conductors (gate, source and drain electrodes), an insulator (gate dielectric), and an organic semiconductor. This device architecture — known as the bottom-contact geometry — resembles that of a silicon transistor, with the exception that the semiconductor is exposed and deposited last. Since the organic semiconductor is frequently chemically- and mechanically fragile, depositing it last eliminates its exposure to the various solvents and chemical environments that are needed to define the other device components.

The thin-film transistor effectively functions as a switch; biasing the gate electrodes switches the transistor between its ''on'' and ''off'' states. Specifically, when a bias is applied on the gate electrode, charges accumulate at the organic semiconductor-dielectric interface capacitively, as illustrated in Figure 1. It is this charge accumulation layer that allows charge carriers to flow from the source to the drain when a bias is applied between the two electrodes. The organic semiconductor layer therefore plays the role of an insulator in the absence of any gate bias, while allowing current to flow between the source and drain electrodes only in the presence of an electric field induced by an applied gate bias. Analogous to a valve in fluid flow, the gate voltage thus controls the flow of current between the source and drain electrodes in these devices. Depending on the nature of the organic semiconductor — p-channel characteristics if it has a tendency to transport holes, and n-channel characteristics if it has a tendency to transport electrons — the gate electrode must be biased negatively or positively to induce hole- or electron transport, respectively.

In order for thin-film transistors to be successfully incorporated as driving circuits in display applications, they need to exhibit high current output, good switching speeds, and high contrast between the ''on'' and ''off'' states. These requirements translate to several important parameters that are used to characterize organic thin-film transistors, including the mobility (also known as the charge-carrier mobility or the field-effect mobility; this quantity measures the average

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Y-L Loo's e-mail address is lloo@che.utexas.edu.

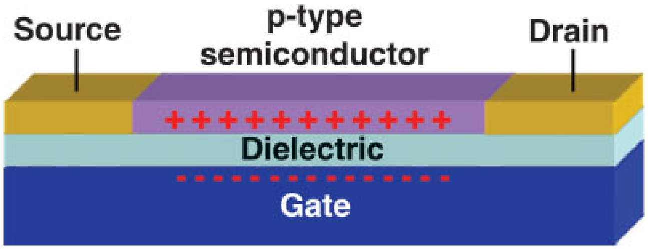

Figure 1. A bottom-contact thin-film transistor.

charge-carrier drift velocity per unit electric field, and has units of $cm^2/V\text{-}s$); the threshold voltage (which measures the voltage required to turn ''on'' the transistor); and the on/off current ratio (a measure of contrast between the device ''on'' and ''off'' states). Because the threshold voltage is controlled by subtleties of the organic semiconductor-dielectric interface that are neither well understood nor under control, the community has — to a large extent — used mobility and on/off current ratio as the primary and secondary benchmarks for thin-film transistor performance. For display applications, organic thin-film transistors in driving circuits need to exhibit a minimum mobility of 0.1 $cm^2/V\text{-}s$, and an on/off current ratio of at least 10^3.

Organic Semiconductors: An Overview

Given the promise of organic thin-film transistors, significant research effort has been dedicated to the design and synthesis of environmentally-stable organic semiconductors that exhibit high mobility. Figure 2 contains the chemical structures of representative organic semiconductors. For example, pentacene (Figure 2a), an organic semiconductor with p-channel characteristics, has been reported to exhibit mobilities of order 1 $cm^2/V\text{-}s$.[1] This value is comparable to the mobilities exhibited by amorphous silicon thin-film transistors and exceeds the requirements for driving circuits in display applications. Thin-film transistors made with numerous other organic semiconductors with p-characteristics, including anthracene, oligo-thiophenes, copper phthalocyanine (Figure 2b), etc., have been reported to exhibit mobilities of order $10^{-3} - 10^{-1}$ $cm^2/V\text{-}s$. While organic semiconductors with p-channel characteristics have been explored extensively, organic semiconductors that exhibit n-channel characteristics are also needed to realize p-n junctions and complementary logic circuits. Organic semiconductors more typically exhibit p-, rather than n-channel characteristics, because of their low oxidizing and high-reducing potentials. As such, a common practice to realize organic semiconductors with n-characteristics is to modify existing materials with strong electron-withdrawing groups, like -CN, -F, and -Cl, to lower their lowest

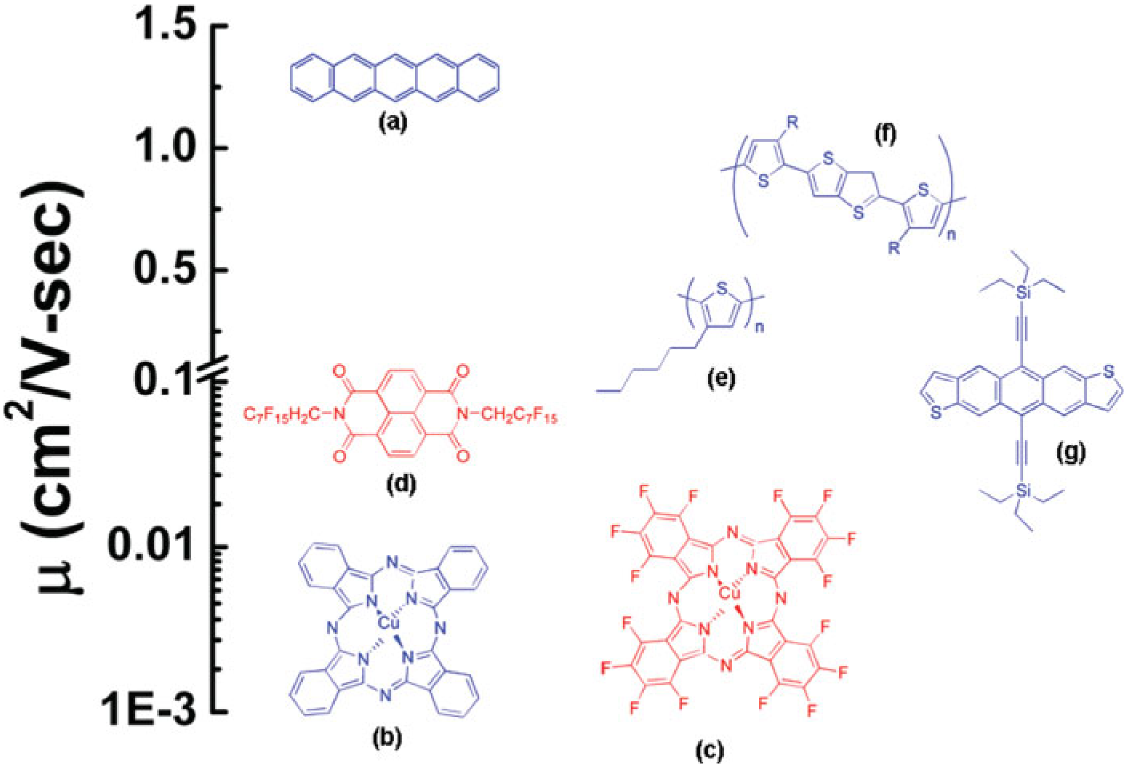

Figure 2. Charge-carrier mobilities of thin-film transistors based on organic semiconductors.

Organic semiconductors with p-characteristics are colored blue, while those that exhibit n-characteristics are colored red: (a) pentacene, (b) copper phthalocyanine, CuPC, (c) fluorinated copper phthalocyanine, FcuPC, (d) fluorinated naphthalene diimide, F-NDI; (e) regioregular poly(3-hexyl thiophene), P3HT; (f) poly(2,5-bis(3-alkylthiophen-2-yl) thieno[3,2-b]thiophene), PBTTT, and (g) triethylsilylethynyl anthradithiophene, TES ADT.

unoccupied molecular orbital (LUMO) energy levels for aiding electron injection and electron transport. For example, substituting fluorines for hydrogens along the periphery of copper phthalocyanine (Figure 2c), can alter the organic semiconductor from having p-channel to having n-channel characteristics; devices made with fluorinated copper phthalocyanine exhibit a typical electron mobility of 10^{-2} cm^2/V-s.[2] By attaching perfluoroalkyl chains to oligothiophenes, the electronic character can also be altered so they transport electrons instead of holes.[3] More recently, families of fluorinated organic semiconductors based on naphthalene diimide (Figure 2d) and perylene diimide that are environmentally stable and exhibit electron mobilities of order 10^{-2} – 10^{-1} cm^2/V-s[4] have also been reported.

There is thus a wide variety of organic semiconductors that satisfy the performance criteria of thin-film transistors. The majority of these organic semiconductors, however, need to be deposited on a device platform by thermal evaporation in a high-vacuum chamber. To truly realize the low-cost aspects of organic electronics, organic semiconductors must be deposited from solution with more economical and versatile techniques, such as spin coating, drop casting, ink-jet printing and screen printing. This need has in turn driven the development of solution-processable organic semiconductors. To date, there are three classes of solution-processable organic semiconductors: polymer semiconductors, soluble organic semiconductor precursors, and organic semiconductors with solubilizing side chains. This review highlights recent advances and developments of soluble electrically-active polymers and organic molecules for thin-film transistor applications.

Polymer Semiconductors

Early solution-processable organic semiconductors were largely based on substituted oligomers or polymers. By incorporating electrically-active repeat units along a continuous backbone and introducing solubilizing alkyl side chains, polymer semiconductors are soluble in common organic solvents, and have excellent film formability when spun or cast from dilute solutions. Among the first polymers to exhibit field-effect characteristics was poly(3-alkyl thiophene), or P3HT ($<10^{-5}$ – 10^{-4} cm^2/V-s)[5]. This early P3HT was amorphous because its synthesis did not allow the controlled placement of the alkyl side chains. While the amorphous nature of P3HT films has been suggested to limit the mobility of these materials, experiments conducted on P3HT of varying alkyl side chain lengths suggested a strong correlation between side chain length and mobility.[6] Specifically, thin-film transistors with spun films of poly(3-butylthiophene) exhibit a mobility of 1×10^{-4} cm^2/V-s while analogously processed thin-film transistors with poly(3-decylthiophene) exhibit a mobility of 6×10^{-7} cm^2/V-s. The decrease in mobility likely stems from an increase in the average spacing between the electrically-active moieties on neighboring polymer chains, which effectively increases the intermolecular charge transport spacing. This comparison provided initial evidence that the mobility is limited by intermolecular transport and implicates the importance of molecular organization within the organic semiconductor thin film on device characteristics.

The mobility of P3HT thin-film transistors increased dramatically with the discovery of routes to control the placement of the alkyl side chains.[7] For example, thin-film transistors fabricated with regioregular P3HT (e in Figure 2) with > 98.5% head-to-tail linkages routinely exhibit mobilities in the range of 0.05 – 0.1 cm^2/V-s.[8] When spun from chloroform solutions, these materials tend to adopt a microcrystalline morphology consisting of two-dimensional (2-D) conjugated layers with strong π-π interchain interactions separated by layers of insulating alkyl chains. On a silicon dioxide dielectric surface, these lamellae are oriented edge-on so the π-π stacking direction is in-plane. This orientation facilitates fast in-plane charge transport between the source and drain electrodes at the polymer semiconductor-dielectric interface. More recently, polythiophene derivatives, such as poly(2,5-bis(3-alkylthiophen-2-yl)thieno[3,2-b]thiophene), or PBTTT (Figure 2f), have been designed to contain chemical moieties that can pack with closer π-π intermolecular interactions, so they can assemble into large crystalline domains on crystallization from a liquid crystal phase. Thin-film transistors containing PBTTT routinely exhibit a hole mobility between 0.2 – 0.6 cm^2/V-s when the devices are tested in nitrogen.[9]

As the organic electronics community is quickly discovering, the molecular characteristics of the electrically-active components alone do not govern the electrical performance of devices comprised of these materials. The way in which the organic semiconductor is deposited can dramatically alter the way in which polymer chains pack, which can in turn alter its electrical characteristics. For example, drop casting (slow solvent evaporation) instead of spin coating (almost instantaneous solvent evaporation) P3HT on the same thin-film transistor platforms can induce the molecules to adopt an edge-on rather than a face-on orientation, thereby increasing the mobility in these devices by more than an order of magnitude.[10] This instance, along with many others reported in the literature, implies the ability to exert significant morphological control — which influences device characteristics — through proper channels of processing.

The ease with which polythiophenes can be synthesized has prompted scientists to copolymerize other conjugated monomers (e.g., fluorene) with thiophene in the hope of accessing a wider range of structure and properties. Copolymers containing thiophene and fluorene units typically exhibit liquid-crystalline characteristics, and with proper substrate alignment, thin-film transistors comprising these copolymers can exhibit mobilities of order 10^{-4} – 10^{-3} cm^2/V-s.[11] In addition to providing main chain rigidity, the incorporation of fluorene units is reported to enhance the stability of the polymer against oxidative doping. Thiophene units have also been incorporated in donor-acceptor-type conjugated copolymers recently. The copolymerization of donor and acceptor-type moieties along a single backbone allows one to tune the electronic and optoelectronic properties of the resulting copolymer through manipulating the extent of intramolecular charge transfer. Indeed, high-electron mobility and ambipolar-type thin-film transistors, based on thiophene-containing conjugated copolymers have been reported.[12]

Blending two or more electrically-active materials to achieve the desired properties is a straightforward alternative to copolymerization. By incorporating an air-stable polymer semiconductor, poly(benzobisimidazobenzophenanthroline), BBL, that exhibits n-characteristics with copper phthalocyanine (Figure 2b; p-characteristics), Babel and coworkers[13] were able to fabricate ambipolar thin-film transistors that transport both holes and electrons. The hole mobilities were reported to be 10^{-6} – 10^{-4} cm^2/V-s and electron mobilities 10^{-6} – 10^{-5} cm^2/V-s for the range of compositions explored. As with P3HT homopolymers and copolymers, processing history was shown to dramatically influence the blend morphology and, accordingly, the blend electrical characteristics. In another example, Goffri and coworkers[14] examined thin-film transistors consisting of polymer blends of regioregular P3HT and polyethylene. Polyethylene, a commodity plastic that is available at low-cost and has excellent film forming and mechanical properties, is added to control film morphology. Specifically, when the blend is cooled from the melt, polyethylene crystallizes first. This crystallization induces phase separation of the blend; P3HT is selectively expelled to the air-polymer and the polymer-dielectric interfaces. When cast and annealed on a device platform, only minute quantities of P3HT (as low as 3% of total polymer concentration) are needed. The bulk of the polymer film, consisting of polyethylene, effectively encapsulates the P3HT at the organic semiconductor-dielectric interface, resulting in mechanically- and environmentally-robust, high-performance thin-film transistors.

Soluble Organic Semiconductor Precursors

While polymer semiconductors have excellent film formability, they are generally amorphous or semicrystalline and exhibit a significant amount of kinetically-trapped disorder in the solid state. Organic small molecules, on the other hand, tend to exhibit high-levels of crystallinity. Since molecular order in the organic semiconductor thin film is correlated with device mobility, there exists a strong drive to develop solution-processable, small-molecule organic semiconductors that adopt a highly ordered structure on solidification. One such common route entails the development of solution-processable organic semiconductor precursors. These precursors can be readily dissolved in common organic solvents and spun down on dielectric surfaces to form a uniform thin film before they are thermally,[15] or irradiatively,[16] converted to the fully conjugated forms that can subsequently crystallize. For example, a pentacene precursor was synthesized by Diels-Alder chemistry using *N*-sulfinylamide as the heterodienophile. This product is highly soluble in chlorinated organic solvents, as well as tetrahydrofuran and dioxane. On annealing at 150 – 200°C, the precursor reverts back to pentacene, yielding thin-film transistors with mobilities in the range of 0.1 – 0.8 cm^2/V-s.[17] Other examples of solution-processable organic semiconductor precursors include that of tetrabenzoporphyrin, which upon reverting back to the electrically-active form yields thin-film transistors with a mobility of 0.017 cm^2/V-s.[18] Thin-film transistors containing substituted sexithiophene, whose ester groups are removable by thermolysis at 150 – 260°C, were reported to exhibit a mobility of 0.07 cm^2/V-s. The thermal conversion of ester-substituted sexithiophene back to its electrically-active form was tracked by synchrotron-based near-edge X-ray absorption fine structure spectroscopy;[19] DeLongchamp and coworkers observed a loss in the carbonyl signal that is associated with the ester side groups upon annealing. Simultaneously, structural rearrangement where the sexithiophene molecules become perpendicular to the substrate yields a morphology that is frequently correlated with high-mobilities in thin-film transistors.

Organic Semiconductors with Solubilizing Side Chains

While soluble precursors of organic semiconductors are attractive from a processing standpoint, the preparation of these soluble precursors is often synthetically challenging, and technically-demanding annealing steps (i.e., high-temperatures or high UV flux), are required to convert the material back to its original electrically-active form. Chemically modifying small-molecule organic semiconductors by attachment of flexible side chains or bulky groups that do not degrade their electrical properties represents a preferred alternative to achieve solution processability, enhance film formability and improve chemical stability against oxidation and photo-doping. Katz and coworkers,[20] for example, added alkyl side chains to anthradithiophene to promote solubility and processability; thin-film transistors with solution-deposited hexylanthradithiophene exhibit mobilities of 0.01 – 0.02 cm^2/V-s.

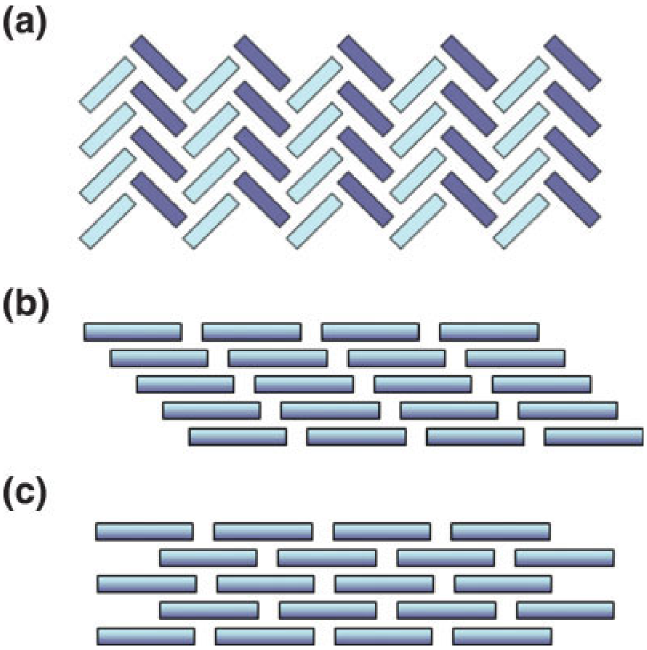

Figure 3. Packing motifs for acene organic semiconductors; the rectangles represent the electrically-active core of individual molecules: (a) herringbone arrangement; (b) 1-D slip-stack arrangement; (c) 2-D "brickwork" arrangement.

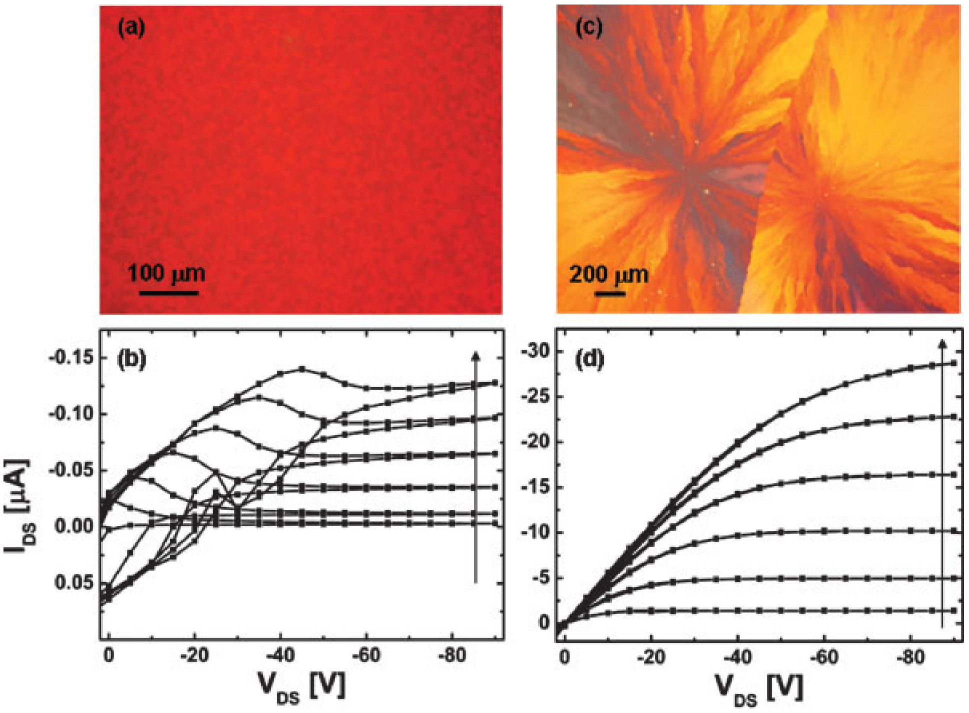

Figure 4. Optical micrograph of spin-cast TES ADT (a), and its thin-film transistor electrical characteristics (b), when the same transistor is exposed to dichloroethane vapors, TES ADT crystallizes (c), and the electrical characteristics of the thin-film transistor improve dramatically (d).

Here, the source-drain current, I_{DS}, is plotted against the source-drain voltage, V_{DS}, with increasing gate voltage (arrow indicates direction of increase). The gate voltage was increased in increments of −10V from 0 to −50V. Negative gate voltages were used to turn on the transistor because TES ADT has p-channel characteristics. Before solvent-vapor annealing, the thin-film transistor exhibits low-source-drain currents and significant current-voltage hysteresis on cycling. The source-drain currents increase dramatically with solvent-vapor annealing; this increase translates to a higher mobility and a higher on/off current ratio. Solvent-vapor annealing also removes traps at the charge transport interface, as evinced by the removal of current-voltage hysteresis in (d).

More recently, Anthony[21] developed substituted organic semiconductor derivatives bearing two trialkylsilyl groups at the central ring of the electrically-active acene cores. Not only did the silylation of acene molecules (e.g., anthracene, pentacene, etc.) dramatically increase solubility, the addition of bulky alkylsilyl groups on the central ring drastically influenced the packing of the molecules. In the solid state, the unsubstituted acene molecules tend to pack in a herringbone-type configuration (Figure 3a) to promote C-H…π type contacts. The addition of alkylsilyl side groups to the central ring enhances π-π overlap between molecules, so the substituted molecules typically exhibit 1-D slipped stack or 2-D ‘‘brickwork’’ type arrangement, as shown in Figures 3b and c, respectively. In these arrangements, the intermolecular characteristic spacing is 3.5Å, and there exists extensive contact between the π faces of neighboring molecules. Not surprisingly, mobilities upward of 0.17 cm^2/V-s have been reported for thin-film transistors with spin-cast tri-isopropylsilyl-substituted pentacene (TIPS pentacene).[22]

Another silylated molecule that has generated a lot of attention lately is triethylsilylethynyl anthradithiophene, or TES ADT[23] (g in Figure 2). Like TIPS pentacene, TES ADT adopts a 2-D ‘‘brickwork’’ type arrangement in the solid state. Thin-film transistors with drop-cast TES ADT have been reported to exhibit charge-carrier mobilities of 1 cm^2/V-s.[23] Thin-film transistors fabricated with spin-cast TES ADT, on the other hand, exhibit mobilities that are at least two to three orders of magnitude lower.[24] The optical micrograph of a spin-cast TES ADT film, and its corresponding electrical characteristics when incorporated into a thin-film transistor are shown in Figures 4a and b, respectively. Like all other solution-processed organic semiconductors, the electrical characteristics of TES ADT are highly variable and depend heavily on the details of the processing conditions (0.002 ± 0.002 cm^2/V-s). We developed a simple and straightforward solvent-vapor annealing process to enhance the electrical characteristics of spin-cast TES ADT thin films.[24] Specifically, exposing spin-cast thin films of TES ADT that were originally amorphous to dichloroethane vapors allows drastic structural rearrangement on the dielectric surface; TES ADT completely crystallizes after 2 minutes of exposure to dichloroethane vapors. Figure 4c contains an optical micrograph that reveals large, crystalline grains of TES ADT upon exposure to dichloroethane vapors. Correspondingly, the mobility and on/off current ratios of TES ADT thin-film transistors improve by more than two orders of magnitude; mobilities $>$ 0.1 cm^2/V-s can be routinely obtained from spin cast TES ADT following solvent vapor annealing with dichloroethane (Figure 4d).

The addition of triethylsilylethynyl side groups to the central ring of anthradithiophene also has profound effects on its materials properties. While TES ADT does pack in a 2-D ''brickwork'' type arrangement, its intermolecular π-orbital overlap is limited to the edges of the molecule (because of the bulkiness of the triethylsilylethynyl groups).[21] The van der Waals interactions that hold TES ADT together in its crystalline state are thus unusually weak and can be overcome easily. Indeed, calorimetry experiments carried out on TES ADT indicate a low-melting temperature ($\approx 160^\circ$C), and a small melting endotherm (≈ 26 J/g). Consequently, TES ADT does not recrystallize easily on cooling from the molten state. It is this unique property of TES ADT that has enabled its patterning in thin-film transistor fabrication. More specifically, selective UV irradiation in the presence of dichloroethane vapors can cause TES ADT to dewet from the substrate surface. We are therefore able to use this dewetting phenomenon to pattern the active channel of TES ADT thin-film transistors and simultaneously crystallize the material within the channel regions to obtain devices with high mobility, minimal parasitic leakage currents, and low off currents.[25] Coupled with optimized methods for establishing efficient electrical contact with TES ADT,[26] arrays of high-performance thin-film transistors can be routinely and reproducibly fabricated.

The introduction of solvent not only simplifies organic semiconductor processing, it brings an added dimension of tunability with which the morphology and structure of the electrically-active material can be manipulated. Stingelin-Stutzmann and coworkers[27] reported the addition of a vitrifying agent (technically, not a solvent but a plasticizing agent) that suppressed the crystallization of rubrene during processing. Controlled crystallization of the organic semiconductor in a subsequent step resulted in thin-film transistors with mobilities as high as 0.7 cm^2/V-s, and an on-off current ratio $>10^6$.

Outlook and Opportunities for Chemical Engineers

The field of organic electronics, in particular, organic thin-film transistors, has seen tremendous progress in the last decade. The advent of more advanced synthetic techniques has enabled the design and synthesis of environmentally-stable and solution-processable organic semiconductors that exhibit excellent electrical characteristics. Yet, numerous challenges — in terms of fundamental understanding and technological progress — remain to be overcome before commercial applications can be truly realized. Long-standing fundamental questions, such as how charge transport is influenced by molecular structure and packing, will have to be addressed. Device reliability and stability against the environment are standing technological issues that still challenge this field.

Processing-Structure-Function Relationships of Soluble Organic Semiconductors

Despite the promising library of organic semiconductors available to us, the electrical characteristics of thin-film transistors made with the same organic semiconductor can range from being on par with those of amorphous silicon devices, to being inferior depending on the details of processing. Clearly, the processing methodologies dramatically influence the growth habit of the organic semiconductor, which can in turn affect its electrical characteristics. Yet, until recently, the morphological details of organic semiconductor thin films have been neglected. Chemical engineers are equipped with the know-how to address how processing influences structure and morphology and, accordingly, electrical properties of these materials. Established and emerging structural characterization tools, including electron microscopy, atomic force microscopy, X-ray diffraction and scattering, near-edge X-ray absorption fine structure spectroscopy,[28] and infra-red spectroscopy[29] will aid in the elucidation of structure over several length scales. For example, we recently showed that the electrical conductivity of polymer-acid-templated polyaniline[30] can be improved by more than an order of magnitude when the molecular weight of the polymer acid template is reduced.[31] The increase in electrical conductivity is accompanied by drastic structural changes, including increases in the crystallinity and conjugation length of polyaniline. With processing-structure-function relationships at hand, chemical engineers are positioned to be the ''middle men'' who can interface between the organic synthetic chemists and the device physicists and electrical engineers. Specifically, we are equipped to develop the design rules and guidelines which will make inexpensive, high-performance electronic devices a reality.

Characterization and Manipulation of the Organic Semiconductor-Dielectric Interface

While it is generally agreed upon that the charge transport occurs within the first several nanometers of the organic semiconductor layer at the organic semiconductor-dielectric interface, the majority of the characterization has been carried out in the bulk. Pentacene, for example, adopts an orthorhombic crystal structure in thin films. In thicker films, however, pentacene adopts a triclinic crystal structure.[32] Yet, the majority of the morphological characterization of pentacene is carried out on the triclinic form. Because the bulk structure may not be representative of the underlying structure at the organic semiconductor-dielectric interface, it is imperative that we understand the initial structural development at that relevant interface to address charge transport issues. To examine the relevant interface, Chabinyc and coworkers[33] have developed a delamination technique that allows one to ''peel'' the organic semiconductor from the dielectric interface. The use of synchrotron-based near-edge X-ray absorption fine structure spectroscopy allows one to probe the ensemble-average molecular orientation of organic semiconductors adsorbed on surfaces, and should shed light on how charge transport is influenced by molecule organization.

Given that charge transport is governed by the organic-semiconductor-dielectric interface, there have been some reports where the dielectric surface is modified in attempts to improve the electrical characteristics of thin-film transistors. Chemically modifying the dielectric surface with self-assembled monolayers, for example, can dramatically improve thin-film transistor device characteristics, which have been speculated to originate from specific interactions between the polymer semiconductor and the self-assembled monolayer. More recently, there have been reports of modifying device characteristics through the systematic modification of the dielectric surface with self-assembled monolayers having different chemical functionalities.[34] Furthermore, Panzer and Frisbie[35] demonstrated the use of a polyelectrolyte gate dielectric to achieve unprecendented charge carrier densities in organic thin-film transistors. Despite the numerous examples listed earlier, the complexity of the organic semiconductor-dielectric interface is not at all understood and remains an active area of research. The breadth of chemical engineering education and training coupled with our traditional focus on thermodynamics, kinetics and transport put us in a position to tackle these issues.

Developing Processing and Patterning Methodologies for Organic Electronics

Organic semiconductors are mechanically- and chemically fragile species. As such, conventional photolithography processes that were originally developed for fabricating silicon transistors are not compatible for fabricating organic thin-film transistors. Frequently, the photoresists, developers, and etchants that are used to define the metal source and drain electrodes interact with the organic semiconductor, resulting in devices with inferior electrical characteristics. There therefore exists a strong drive to develop patterning strategies that are compatible with organic semiconductors for fabricating organic thin-film transistor arrays. For example, nanotransfer printing[36] (nTP) is a solventless process for defining metallic components that is compatible with organic semiconductors. Soft-contact lamination[37] (ScL) allows efficient electrical contact to be established between organic semiconductors and metallic electrodes that are defined on a separate elastomeric substrate. More recently, the development of solvent-based metal and dielectric formulations have also enabled all-printed circuits. Chemical engineers appreciate the fragility of the materials and the organic semiconductors' susceptibility to degradation. Coupled with the interdisciplinary nature of modern chemical engineering education, including exposure to nanotechnology and nanofabrication, we are poised to make an impact in this arena.

Molecular and Multiscale Modeling of Structure and Transport Properties

Given the complexities of charge transport within a structurally heterogeneous organic medium, the field will unquestionably benefit from molecular and multiscale modeling, an area where chemical engineers already have made a significant impact.[38] Modeling over multiple length scales will not only address the fundamental charge transport processes, which are quantum-mechanical in nature, but should also relate chain packing and molecular orientation at relevant interfaces to macroscopic electrical properties of the material[39]. Using quantum-chemical calculations, for example, Bredas and coworkers showed how the interchain transfer integral — a quantity that measures the ease with which a charge is transferred between two interacting molecules and is therefore directly correlated with mobility — can be extremely sensitive to molecular packing.[40] The ability to predict structure-function relationships of electrically-active organic molecules and polymers from first principles will undoubtedly aide the rational design of these materials.

Conclusions

Organic electronics is a field that is rapidly expanding. Given the promising library of electrically-active materials now available to us, chemical engineers are positioned to rapidly advance this field. We have a molecular perspective when examining materials, an aspect that is sorely needed in organic electronics. Fundamental understanding of processing-structure-function relationships of electrically-active materials is essential to realizing the high-performance organic thin-film transistors needed for display applications.

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