SMALL-MOLECULE ORGANIC SEMICONDUCTORS

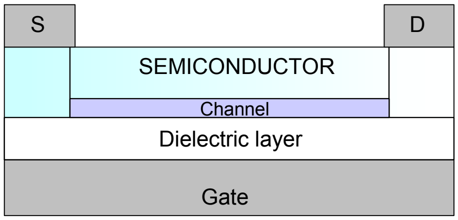
Reported by Nandita Madhavan April 01, 2002

INTRODUCTION

The term “organic semiconductors” is used to describe organic materials which possess the ability of conducting electrons. The electronic conductivity of these materials lies between that of metals and insulators, spanning a broad range of 10^{-9} to 10^{3} Ω^{-1} cm^{-1}. Historically, the study of conductivity of organic compounds can be traced back to 1906, when the photoconduction of solid anthracene was discovered.[1] However, interest in this field lapsed during the next four decades until the early 1950s, when a considerable amount of research was devoted to understanding the charge transport properties of semiconductors. The potential of these materials for practical applications was under-appreciated until the late 1980s, when the use of organic semiconductors in electronic devices such as light emitting diodes (LEDs) and field effect transistors (FETs) was envisioned. The interest in the study of FETs in particular stems from the fact that these devices are easier to fabricate than traditional silicon based transistors that require rigorous processing techniques. Processing techniques for fabrication of FETs can be improved by replacing silicon with organic semiconductors. Incorporation of functional groups in organic semiconductors can improve their solubility in organic solvents and facilitate formation of semiconductor thin films by cost-effective solution deposition techniques. Another advantage of solution techniques is the broad range of compounds that could be used in FETs. This contrasts with the conventional vapor deposition techniques that require the semiconductor to be sublimable. This report aims to illustrate the application of fundamental principles of synthetic and physical organic chemistry in the development of organic semiconductors for FETs.

BASIC CHARACTERISTICS OF FIELD EFFECT TRANSISTORS

A typical FET (Figure 1) is composed of three electrodes (gate, source and drain), a dielectric layer, and a semiconducting layer. In the absence of a gate voltage this device is in an “off” state and no conductivity is observed between the source and drain. Upon application of a gate voltage, a “channel” of charge is formed facilitating flow of current between the source (S) and the drain (D). Depending on the nature of the semiconductor and electrodes used, the channel formed can be n-type, where electrons are the charge carriers, or p-type where holes (electron deficient species) function as carriers. The



p- type: S extracts electrons
n-type : S injects electrons

Figure 1. Schematic diagram of FET: S = Source, D = Drain electrode

performance of an FET is gauged by the mobility (μ) of charges in the semiconductor and the drain-source current ratio between the "on" and the "off" states. High values of μ (> 0.1 cm^2/Vs) and on/off ratios (> 10^6) are desirable for practical application of FETs in circuits.[2] The mobility of organic semiconductors is dependent on the degree to which the charge-accepting orbitals of neighboring molecules overlap. In contrast to inorganic semiconductors, where charges move within a three-dimensional covalent network, organic semiconductors rely upon weak van der Waals interactions among discrete molecular constituents for charge transport. Fabrication of efficient FETs based on organic compounds requires a thorough understanding of the charge migration pathway in these molecules.

Factors affecting performance of FETs.

The characteristics of FETs are deeply influenced by the nature of the semiconductor used. As illustrated in Figure 1 the electrode injects electrons into the semiconductor in an n-channel FET. Therefore, the semiconductor should possess an accessible low energy LUMO in order to accommodate the extra electron. Electron-withdrawing groups such as cyano or fluoro are incorporated in semiconductors in order to lower its LUMO energy level, and to improve n-channel conductivity. Similarly in a p-channel device, a HOMO of high energy is desirable for ease of removal of electrons by the electrode.

An important factor affecting the performance of FETs is the morphology of the semiconductor thin film used in the device. Thin films are composed of grains the average size of which is directly proportional to the temperature used for casting the film. The mobility is found to increase with an increase in temperature owing to an improved morphological homogeneity of the film. However, beyond an optimal temperature the mobility is found to decrease owing to discontinuities in the film created by an increase in intergranular spaces when the grain size becomes very large.[3] The mobility is also dependent on the packing of the organic molecules in the film, and is maximum when the direction of π- overlap coincides with the direction of current flow.

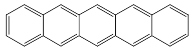
CLASSIFICATION OF ORGANIC SEMICONDUCTORS

Known organic semiconductors can be broadly classified into two groups on the basis of their molecular weight: conjugated polycyclic compounds of molecular weight less than 1000, and heterocyclic polymers with molecular weight greater than 1000.[4] Polymers are useful materials for semiconductors because of the ease with which they form thin films with large surface area. However, their poor solubility in organic solvents and loss of mobility upon functionalization to enhance solubility has motivated researchers to investigate the use of small molecules as semiconductors. An advantage of small molecules is more facile control of charge transport by modification of various molecular parameters. For example, the ability of these molecules to pack into well-organized polycrystalline films leads to higher mobility compared to polymeric semiconductors. Small-molecule organic semiconductors may further be classified as linear, two-dimensional fused ring compounds, and heterocyclic oligomers.

LINEAR FUSED RING COMPOUNDS

Pentacene

Pentacene **1** is known to have the highest thin film mobility among organic semiconductors and also a strikingly high single crystal mobility of 2 cm^2/Vs, which makes it a widely studied organic FET semiconductor. The high mobility of pentacene is a result of significant orbital overlap from edge-to-face interactions among the molecules in their crystal lattice. Interactions of this kind are characteristic of a herringbone geometry as illustrated in Figure 2. Pentacene is commercially available or can be readily synthesized in the laboratory.[5] Most FETs fabricated with pentacenes exhibit p-channel activity. An exception was found when pentacene crystals were designed to show both p- and n-channel conductivity by employing an aluminum oxide dielectric layer.[6] However, the instability of pentacene in air and its low solubility in organic solvents prompted researchers to prepare functionalized pentacene derivatives.



1

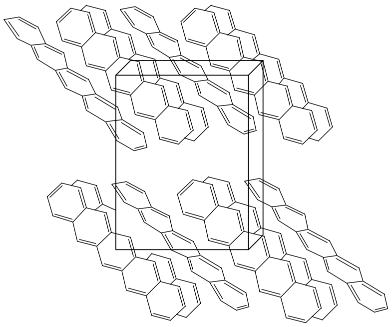
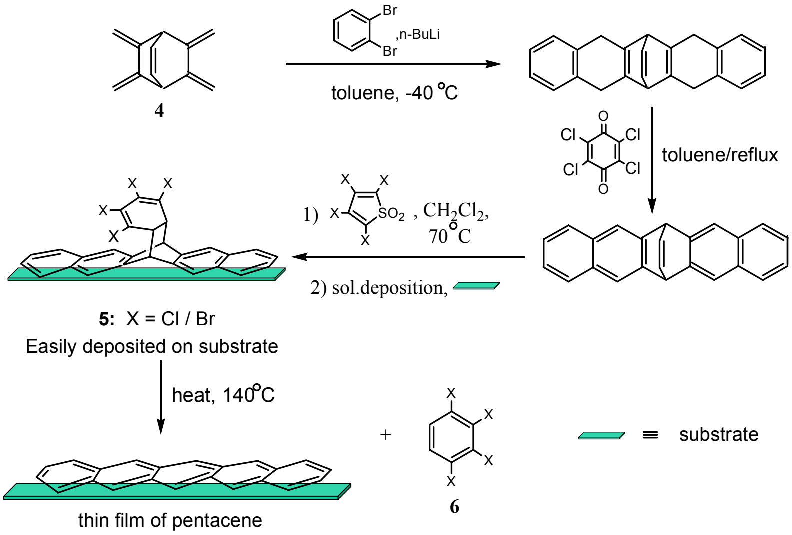


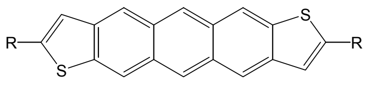
Figure 2. Herringbone motif found in pentacene crystals

Scheme 1

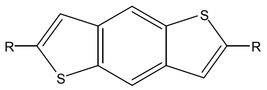


Müllen and co-workers used the "precursor route" to cast thin films of pentacene by cost-effective solution deposition techniques. The strategy involved generation of pentacene in situ from pre-formed films of soluble precursors.[7] Precursor **5** was synthesized starting from the Pentaene **4** as shown in Scheme 1 and then cast into thin films from a solution of methylene chloride or toluene. The resulting film was then heated to 140 °C, at which temperature it underwent the retro Diels Alder reaction to yield pentacene. This reaction was thermodynamically driven by the formation of the low energy tetrahalo benzene derivative **6**, which was eliminated as a by-product in the process. The mobility of the FETs fabricated using this technique was about 0.1 cm^2/Vs, which is relatively high considering the fact that solution deposition techniques were used which are less accurate than vapor deposition techniques normally used.

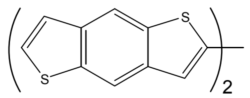
An alternate approach taken by Katz and co-workers for enhancing the stability of pentacene involved synthesizing heterocyclic analogs fused with thiophene rings.[8] The thiophene rings allow greater intra- and intermolecular overlap between the π-conjugated units and also provide sites for attachment of solubilizing alkyl chains. Therefore, anthradithiophene **7** and its alkyl derivatives **8 – 10** were synthesized as mixtures of the *syn* and *anti* isomers and their FET characteristics were studied. The alkylated derivatives **8** and **9** exhibited a higher mobility (greater than 0.1 cm^2/Vs) in comparison to unsubstituted **7** (0.09 cm^2/Vs) and the dioctadecyl derivative **8** (0.06 cm^2/Vs). The lower mobility of derivative **10** can be explained on the basis of X-ray crystallographic data that indicate a low degree of order for dioctadecyl **10** in the solid state. Additionally, the solubility of the dihexyl derivative **8** in organic solvents was exploited in casting thin films using the solution deposition technique, and the mobility in an FET was measured. However, the morphology of the film formed was not regular and the mobility measured was low. Other thiophene derivatives of pentacene studied include benzodithiophene **11** and its derivatives **12** and **13**.[9] Field effect measurements performed on the dimer **13** showed μ = 0.04 cm^2/Vs when the deposition temperature was 100 °C. Although none of the above compounds proved to be superior to pentacene with regard to mobility, the potential for improved processibility via side-chain modification is promising.



syn and anti isomers
7 R = H
8 R = C_6H_{13}
9 R = $C_{12}H_{25}$
10 R = $C1_8H_{37}$



11 R = H
12 R = Long alkyl chains

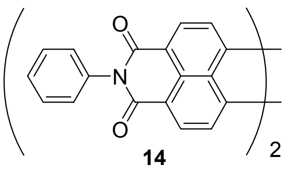


13

TWO-DIMENSIONAL FUSED RING COMPOUNDS.

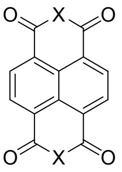
Naphthalene derivatives.

A majority of the classical organic semiconductors were known to exhibit p-channel activity, which challenged researchers to develop n-type organic semiconductors. Since it was known that an n-type organic semiconductor can be made by introduction of imide groups, semiconductor properties of the perylene derivative **14** were studied.[10] FETs fabricated from diimide **14** possessed n-channel activity with a mobility on the order of 10^{-5} cm^2/Vs. However, the performance of the FET rapidly degraded over time which was attributed to the instability of **14** in air. Therefore, synthesis and fabrication of more stable FETs showing n-channel activity was desirable.

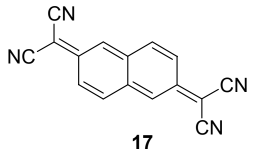


14

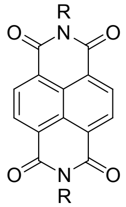
Naphthalene dianhydride **15** has been shown to possess electron acceptor properties by electrochemical measurements, making it an ideal material for n-channel FETs.[11] Although the extent of conjugation in **15** is less than that in the perylene diimide **14** and the crystal structure of **15** indicates only partial intermolecular overlap, it has an accessible LUMO for electron injection that explains its n-channel activity. The mobility for an FET fabricated with anhydride **15** at 55 °C was on the order of 10^{-3} cm^2/Vs.[12] FETs prepared using diimide **16** and the cyano derivative **17** showed a mobility on the order of 10^{-4} and 10^{-5} cm^2/Vs respectively. The n-channel activity of these semiconductors is of considerable interest despite the low μ values.



15: X = O,
16: X = NH



17



18 R= $CH_2C_7F_{15}$
19 R= $CH_2C_3F_7$
20 R= C_8H_{17}
21 R= $CH_2C_6H_4CF_3$

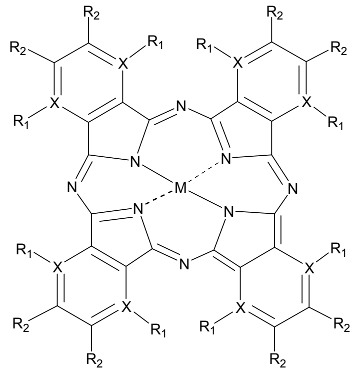
The alkyl derivatives **18, 19,** and **20** of the diimide were synthesized in order to improve processing and also to study the effect of fluoro substituents on the field-effect characteristics.[13] The fluoroalkyl diimides **18** and **19** showed FET activity , whereas non-fluorinated **20** did not. This difference was attributed to the stabilization of the molecular orbitals of these compounds by electronegative fluoro groups and to a denser packing of the fluorinated compounds in the herringbone geometry as compared to **20**. Katz and co-workers studied the FET characteristics of a number of derivatives of dimide **16** and the best on/off ratio was exhibited by the N-trifluoromethylbenzyl imide **21**.[14]

Phthalocyanine derivatives

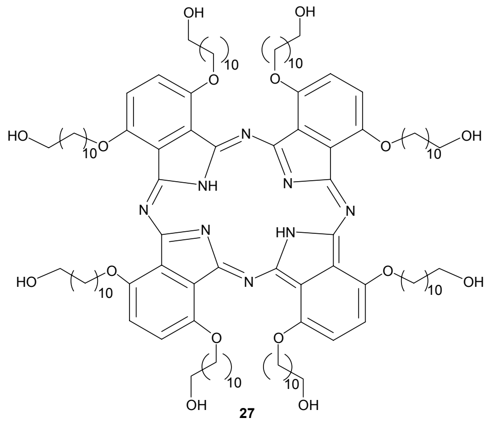
The semiconducting properties of phthalocyanines was first observed in 1948.[15] However, their use in transistors was limited by the low mobility of these metal complexes. Nevertheless, a relatively high mobility (0.02 cm^2/Vs) was reported for a p-channel FET fabricated from a commercially available Cu-phthalocyanine **22** at high deposition temperatures (125 °C).[15]

A dramatic change in the FET characteristics was observed with metallophthalocyanine derivatives **23-26** bearing electron-withdrawing groups. The FETs behaved like n-channel semiconductors instead of p-channel semiconductors.[16] This reversal of channel activity is a result of the change in the LUMO energy level of the molecule caused by the electron-withdrawing groups, making the orbital more accessible for electron injection. The best mobility, around 0.02 cm^2/Vs was exhibited by the fluorinated derivative **23** (M = Cu) at 125 °C and an on/off ratio of 5×10^4 was observed.

Another approach used by Davidson and co-workers involved a modified orientation of phthalocyanine molecules in thin films by functionalization with hydrophilic groups (**27**).[17] The hydroxyl groups around the periphery of the phthalocyanine ring act as anchors owing to attraction with the substrate, making the rings lie in an orientation that enhances the electronic conductivity between the FET electrodes.

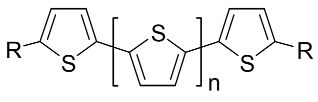


22 $R_1 = R_2 = H$, X = C, M = Cu
23 $R_1 = R_2 = F$, X = C, M = Cu, Zn, Fe, Co
24 $R_1 = R_2 = Cl$, X = C, M = Fe
25 $R_1 = H$, $R_2 = CN$, X = C, M = Cu
26 $R_1 = R_2 = H$, X = N, M = Cu



27

HETEROCYCLIC OLIGOMERS

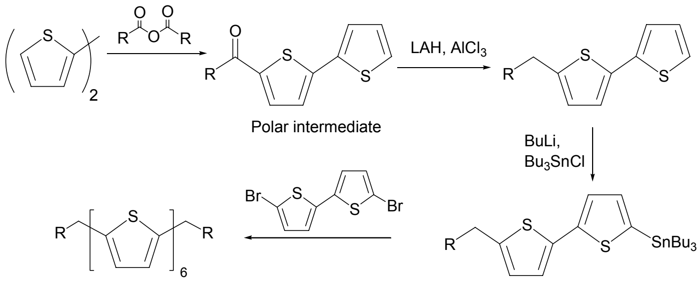


28 R = H, n=4
29 R = *n*-hexyl, n=4
30 R = H, n=2
31 R = H, n=3

Oligomers of 2,5-linked thiophene rings especially the hexamer **28**, show p-type semiconductor properties. Garnier and co-workers demonstrated that attachment of long alkyl *n*-hexyl chains (**29**) at the terminii of these oligomers improved the mobility of FETs by enhancing the self-organization of these molecules in the thin film.[18] The mobility could be further increased by an order of magnitude using high temperatures (280 °C) for film-deposition.[19] The smaller oligomers, **30** and **31** have better mobility and on/off ratios owing to their lower susceptibility to atmospheric doping.

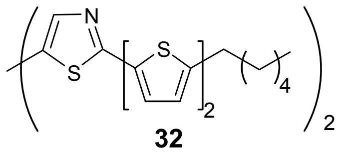
Katz and co-workers improved the FET characteristics of these oligomers by developing a synthesis that allowed more efficient purification of intermediates. They hypothesized that the non-optimal performance of FETs fabricated using thiophene oligomers was caused by contamination with chemical impurities (`2 %). The purity of the oligomers was compromised because the intermediates and impurities formed have similar polarities, making purification difficult. Therefore polar carbonyl and alkoxy groups were introduced in order to increase the polarity of the intermediates (Scheme 2).

Scheme 2



These intermediates could be easily purified via column chromatography , reduced and then subjected to Stille coupling to give the dialkyl thiophene oligomers.[20] Although, the mobility of **29** prepared by this method was not improved, the on/off ratio was due to increased purity of the semiconductor.

Another method used for improving the on/off ratio of these oligomers was incorporation of a less easily oxidizable central subunit (**32**), which would prevent doping and hence conductivity in the off state. Thiazole rings were employed for this purpose, and it was found that though there was a decrease in mobility , the on/off ratio was significantly improved.



32

FUTURE APPLICATIONS

Fabrication of low-cost electronic components from organic-based circuits is of great interest in the field of microelectronics, and organic semiconductors have an important role to play in the assembly of these circuits. Even though these organic analogs are not predicted to replace silicon technology in which high device speed and precision are required, they are likely to replace amorphous silicon in applications such as identification tags, smart cards, and display drivers that are intended for short-term use and large-scale manufacture. As a long-term application one can envision the application of these semiconductors in fabrication of nanoelectronic devices or what is often referred to as “molecular electronics”.

CONCLUSION

Chemical tunability of organic semiconductors make them attractive materials for fabrication of FETs. Basic principles of physical organic chemistry have been employed to modify the FET characteristics by incorporation of alkyl chains, and electron-withdrawing groups. On the other hand, the “precursor route” and the “polar intermediate” route used synthetic organic chemistry as a tool to improve FET characteristics. Future work will involve fabrication of more complex devices for practical applications using organic semiconductors.

REFERENCES

(1) Okamato, Y.; Brenner, W. *Organic Semiconductors.* Reinhold Publishing Corporation: New York; 1964.

(2) Katz, H. E.; Bao, Z. *J. Phys. Chem. B.* **2000**, *104*, 671.

(3) Garnier, F.; Horowitz, G.; Fichou, D.; Yassar, A. *Synth. Met.* **1996**, *81*, 163.

(4) Katz, H. E.; Bao, Z.; Gilat, S. J. *Acc. Chem. Res.* **2001**, *34*, 359.

(5) Goodings, E. P.; Mitchard, D. A.; Owen, G. *J. Chem. Soc., Perkin Trans. 1* **1972**, *11*, 1310.

(6) Schön, J. H.; Berg, S.; Kloc, Ch.; Batlogg, B. *Science* **2000**, *287*, 1022.

(7) Herwig, P.; Müllen, K. *Adv. Mater.* **1999**, *11*, 480.

(8) Laquindanum, J. G.; Katz, H. E.; Lovinger, A. J. *J. Am. Chem. Soc.* **1998**, *120*, 664.

(9) Laquindanum, J. G.; Katz, H. E.; Lovinger, A. J.; Dodabalapur, A. *Adv. Mater.* **1997**, *9*, 36.

(10) Horowitz, G.; Kouki, F.; Spearman, P.; Fichou, D.; Nogues, C.; Pan, X.; Garnier, F. *Adv. Mater.* **1996**, *8*, 242.

(11) De Luca, C.; Giomini, C.; Rampazzo, L. *J. Electroanal. Chem.* **1990**, *280*, 145.

(12) Laquindanum, J. G.; Katz, H. E.; Dodabalapur, A.; Lovinger, A. J. *J. Am. Chem. Soc.* **1996**, *118*, 11331.

(13) Katz, H. E.; Lovinger, A. J.; Johnson, J.; Kloc, C.; Siegrist, T.; Li, W.; Lin, Y. –Y.; Dodabalapur, A. *Nature* **2000**, *404*, 478.

(14) Katz, H. E.; Johnson, J.; Lovinger, A. J.; Li, W. *J. Am. Chem. Soc.* **2000**, *122*, 7787.

(15) Bao, Z.; Lovinger, A. J.; Dodobalapur, A. *Appl. Phys. Lett.* **1996**, *69*, 3066.

(16) Bao, Z.; Lovinger, A. J.; Janelle, B. *J. Am. Chem. Soc.* **1998**, *120*, 207.

(17) Davidson, K.; Jones, R.; McDonald, S. *Synth. Met.* **2001**, *121*, 1399.

(18) Garnier, F.; Yassar, A.; Hajlaoui, R.; Horowitz, G.; Deloffre, F.; Servet, B.; Ries.; Alnot, P. *J. Am. Chem. Soc.* **1993**, *115*, 8716.

(19) Servet, B.; Horowitz, G.; Ries, S.; Lagorsee, O.; Alnot, P.; Yassar, A.; Deloffre, F.; Srivastava, P.; Hajlaoui, R.; Lang, P.; Garnier, F. *Chem. Mater.* **1994**, *6*, 1809.

(20) (a) Katz, H. E.; Dodabalapur, A.; Torsi, L.; Elder, D. *Chem. Mater.* **1995**, *7*, 2238., (b) Katz, H. E.; Laquindanum, J. G.; Lovinger, A. J. *Chem. Mater.* **1998**, *10*, 633.