

Organic Field-Effect Transistors

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1 Motivation

Over the past twenty years, research into the applications of organic semiconductors (OSCs) has intensified rapidly. Though their electron mobility is much lower than that of typical semiconductors, OSCs show promise in low-cost, flexible, lightweight, and environmentally-friendly semiconductor applications. Their hole mobility was found to be comparable to that of amorphous silicon (a-Si), with values exceeding $1.0 \text{ cm}^2/\text{Vs}$ [1]. Their high hole mobility has led to p-type semiconductor applications in organic light-emitting diodes (OLEDs), photovoltaic cells, and organic field-effect transistors (OFETs). Due to space constraints, this paper will focus solely on OFETs.

2 Principles of Operation

Transistors are the fundamental building block in modern circuitry, and are used as either signal amplifiers or on/off switches. The field effect is a phenomenon in which the conductivity of a semiconductor changes due to the application of an electric field normal to its surface [2]. The electric field is applied via a metallic gate in the device. OFETs are composed of three terminals, the source, drain, and gate, as well as a semiconductor layer and an insulating layer between the semiconductor and gate (Figure 1). The insulator can be made of a variety of dielectric materials, though SiO_2 is a common choice. Many of the OFETs are organic thin-film transistors (OTFTs), in which the semiconductor layer is approximately two-dimensional, due to the linear structure of many of the OSCs used today.

A voltage is applied to the gate to control the amount of current flow between the source and drain. In a p-type OFET, which is the most common variety of OFET due to the relatively high hole mobility in OSCs, a negative voltage greater in magnitude than the threshold voltage of the semiconductor material is applied between the gate and the source (Equation 1). This

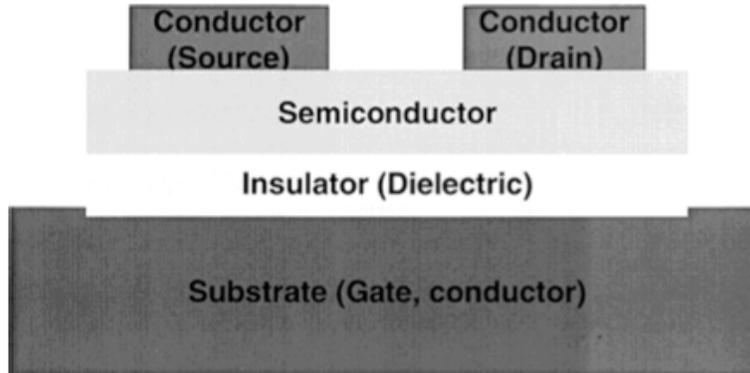


Figure 1: Typical structure of a thin-film field-effect transistor. [3]

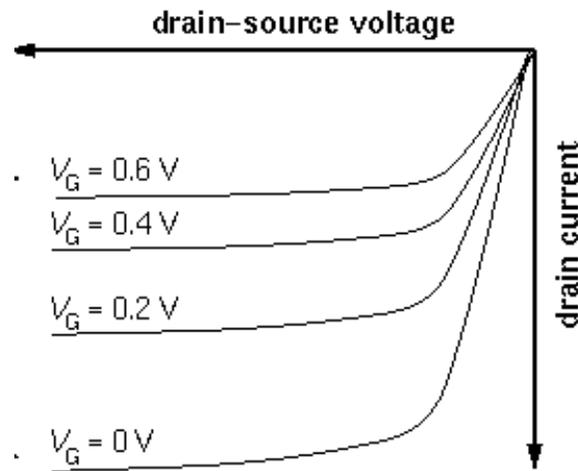


Figure 2: Typical current-voltage behavior for a p-type FET. [4]

$$V_{GS} < -V_t \quad (\text{Equation 1})$$

voltage causes a p-type channel to form at the semiconductor-insulator interface. A negative voltage is also applied between the drain and the source, causing a holes to flow from the source to the drain. This behavior is equivalent to a negative current flowing from the drain to the source. As the magnitude of the drain-source voltage is increased, the magnitude of the drain-source current also increases until “pinch-off,” at which point the p-channel pinches closed on one side and the drain current saturates at its max-

imum value. The magnitude of the saturation current depends on the applied gate-source voltage (Figure 2). Though p-type OFETs are much more common than n-type OFETs, some n-type OFETs have been researched. In the case of n-type OFETs, the current-voltage behavior is similar, but the values are in the first quadrant instead of the third due to the opposite charge of electrons and holes [2].

OFET research generally seeks to optimize two important values, the carrier mobility and the on/off current ratio. Carrier mobility is directly proportional to semiconductor conductivity, and is thus directly related to the performance of the device. Mobilities in the range of 0.1 to 1.0 cm^2/Vs are considered fairly good, but these values have only been achieved for hole mobility, and lower values are frequently reported [5]. The on/off current ratio is the ratio of the saturation current when V_{GS} is high to the leakage current when V_{GS} is zero. Increasing this ratio is important in the switch-like behavior of OFETs. On/off ratios as high as 10^8 have been reported for some OFETs [6], though reported values are generally lower.

3 Materials Choices

All OSCs under consideration today contain a high density of aromatic rings due to the electron delocalization inherent in aromatic structures. Aromatic rings contain alternating single and double bonds that lead to overlapping p orbitals, which form π -bonds. In π -bonds, electrons delocalize and are shared between the atoms on the ring’s backbone (Figure 3). Similar to conduction due to a delocalized “sea of electrons” in metals, free movement of delocalized π electrons in organic compounds allows organic molecules to conduct electricity and behave as semiconductors.

The molecules used in the active semiconductor layer of OFETs are generally linear or two-dimensional structures due to the planar conformation of aromatic rings, though some 3D structures have been proposed [5]. The semiconductor compounds can be either small molecules or polymers exhibiting a variety of conformations. The major categories of OSC discussed here, which are primarily p-type, approximately planar molecules, are linearly-fused benzene rings, linearly-fused thiophenes, a large set of variants incorporating these two structures, structures incorporating carbazoles, and discotic molecules. Though some OSC structures do not fall within those categories, a complete discussion of all materials researched for use in OFETs is not

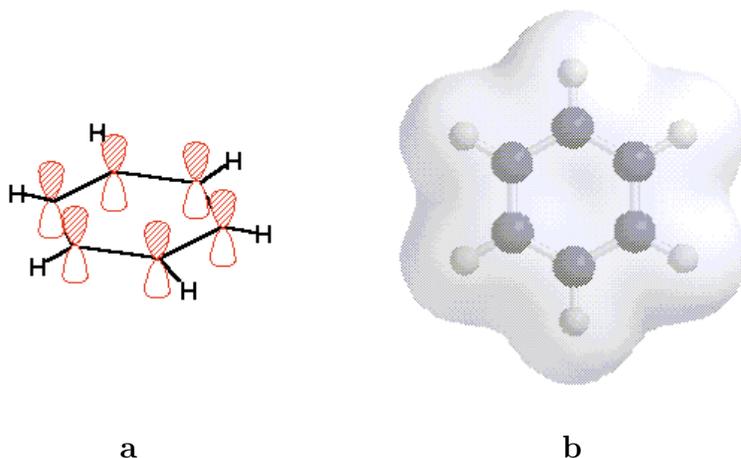


Figure 3: p orbitals in a benzene ring (Figure 3a) leading to electron delocalization (Figure 3b). [7]

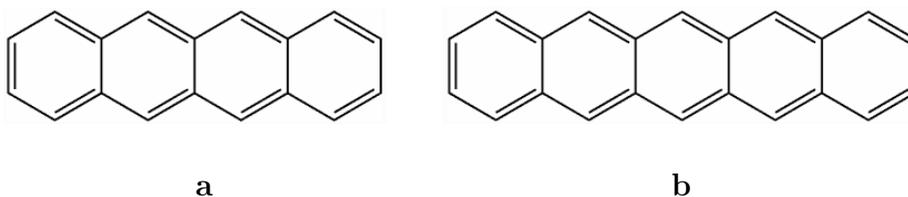


Figure 4: Two linearly-fused benzene chains, tetracene (Figure 4a) and pentacene (Figure 4b). [8]

within the scope of this paper.

Linear fused chains of benzene rings such as tetracene and pentacene are some of the most common materials used in OFETs. Their structures are simple (Figure 4), and their performance has been highly-researched. Thin films of tetracene grown through vacuum sublimation have resulted in hole mobility values up to $0.15 \text{ cm}^2/\text{Vs}$ [9], while hole mobility in OFETs using pentacene grown through thermal evaporation in a vacuum has reached values as high as $2.2 \text{ cm}^2/\text{Vs}$ [10]. The reason for the higher carrier mobility in pentacene is likely the greater molecule length, which allows more space for carrier movement than is available in tetracene. In addition to having an excellent mobility value, the on/off current ratio for pentacene OFETs

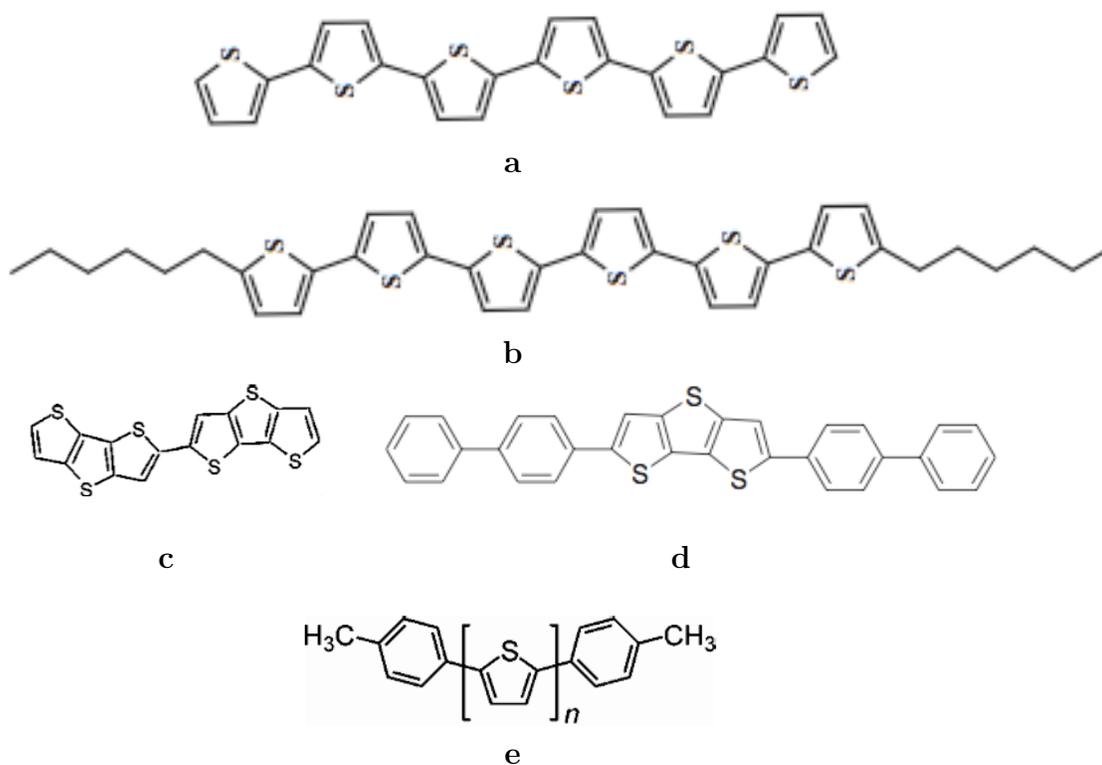


Figure 5: A variety of thiophene-based OSCs, sexithiophene (Figure 5a), hexyl-substituted sexithiophene (Figure 5b) [12], bis(dithienothiophene) (Figure 5c) [6], a thiophene-benzene oligomer (Figure 5d) [13], and tolyl-substituted thiophene (Figure 5e) [14].

can reach 10^8 [10], indicating its ability to function very well as a switch. The success of linearly-fused benzene rings is likely due to the overlap of π -orbitals in close-packed, highly-crystalline regions of the material, which is thought to strongly affect field-effect mobility [11].

Linear thiophene oligomers and thiophene derivatives (Figure 5) constitute another popular class of materials for use in OFETs. Sexithiophene (Figure 5a) deposited through thermal evaporation yields modest values for carrier mobility around $0.1 \text{ cm}^2/\text{Vs}$ and an on/off current ratio around 10^3 [12]. However, the addition of alkyl chains to the end of the sexithiophene, as in hexyl-substituted sexithiophene (Figure 5b) increases both the mobility and the on/off ratio. The ideal length of alkyl chain was found to be

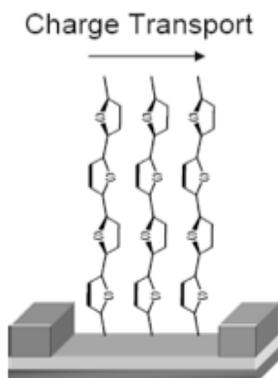


Figure 6: Ideal arrangement of oligothiophene molecules for maximum hole mobility and on/off current ratio [5].

the shortest chain investigated, ethyl. Ethyl-substituted sexithiophene exhibited an elevated hole mobility of $1.1 \text{ cm}^2/\text{Vs}$ and an on/off current ratio of 10^4 [12]. The reason for this change is that the ethyl chains attach themselves to the growth substrate, causing the vertical orientation of thiophene molecules. Ordered stacking of π -conjugated molecules leads to maximum carrier mobility along the direction of stacking, yielding maximum performance [5]. However, as the alkyl chains are not conductive, minimizing their length improves the performance of the OFET.

In some cases, thiophene-based OSCs exhibit exceptionally high on/off ratios, but relatively low carrier mobility. Fused thiophene chains (Figure 5c) deposited by vacuum sublimation were found to have on/off ratios up to 10^8 , but have hole mobilities of only $0.02\text{-}0.05 \text{ cm}^2/\text{Vs}$ [6]. Tolyl-substituted thiophene (Figure 5e) grown by vacuum deposition was found to exhibit an even higher on/off ratio of 10^9 in the case of $n = 2$ and possess the additional property of being highly stable in air, but have a hole mobility of only $0.03 \text{ cm}^2/\text{Vs}$ [14]. This behavior is useful in cases where the on/off ratio is more important than the mobility, in many display and memory applications.

A variety of other thiophene-based OFETs demonstrate behavior in between that of the ethyl-substituted oligothiophene and the materials with exceedingly high on/off ratios. Certain thiophene-benzene oligomers (Figure 5d) exhibit mobilities up to $0.42 \text{ cm}^2/\text{Vs}$ and on/off current ratios up to 5×10^6 [13]. However, the scope of this paper does not allow for in-depth discussion of such materials.

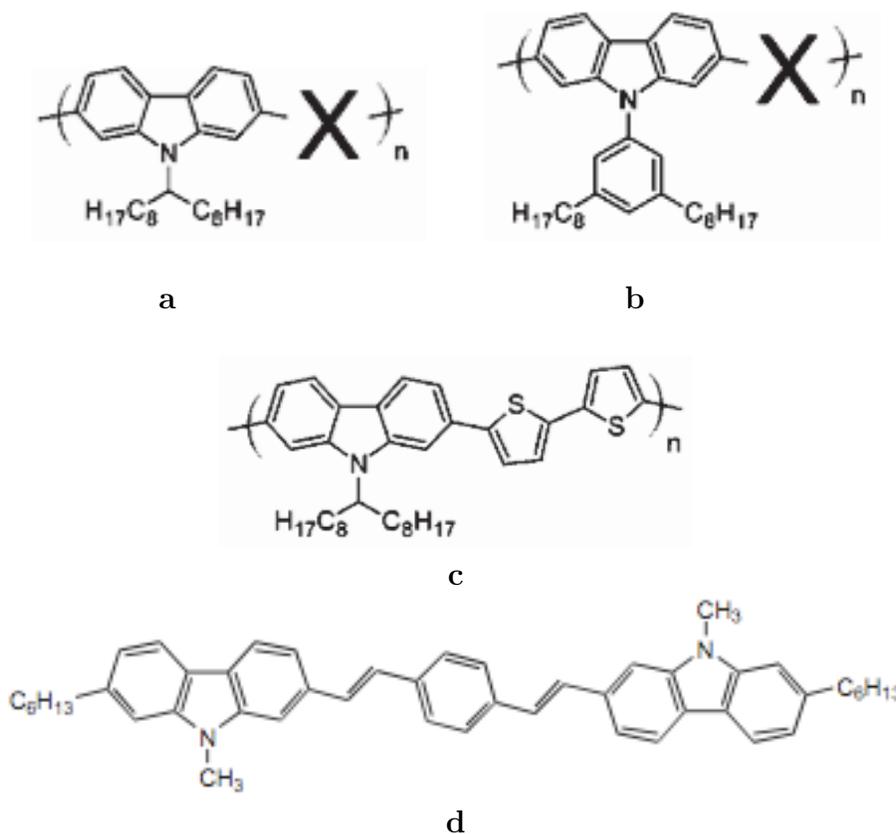


Figure 7: A selection of carbazoles: generic carbazoles (Figure 7a, b), P4 (Figure 7c) [15], and RCPCR (Figure 7d) [16].

Carbazoles (Figure 7), another material class currently being investigated for use in OFETs, have a variety of desirable properties. RCPCR (Figure 7d) is a good candidate for crystalline thin films, because it maintains a trans-configuration during deposition. This property is favorable because ordered structures will lead to π -bond stacking, as was the case in ethyl-substituted thiophene, which will result in higher carrier mobilities. Thermal analysis of RCPCR also indicated thermal stability up to 415°C [16]. Other carbazole derivatives have lower mobilities and on/off ratios of $2.0 \times 10^{-3} \text{ cm}^2/\text{Vs}$ and 5×10^4 , respectively, but can be deposited onto devices via solution processing [15]. Chemical solution processing is an intriguing technique because it could make OFET manufacturing simpler and more cost-effective to perform on a large scale than physical deposition techniques currently allow.

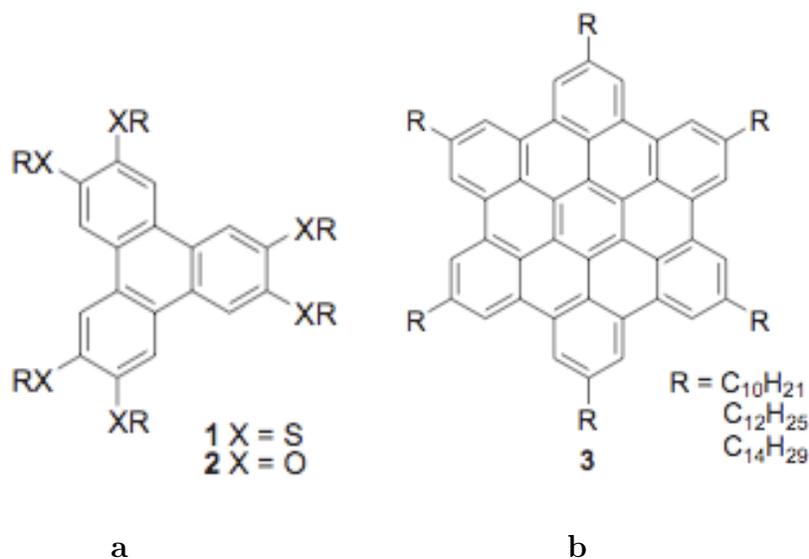


Figure 8: Three examples of discotic OSCs: hexahexylsulfanyltriphenylene (Figure 8a, X=S), hexabutyloxytriphenylene (Figure 8a, X=O), and hexabenzocorone (Figure 8b) [5].

Discotic molecules (Figure 8) have attracted attention as OFET semiconductors because they self-assemble into columns, facilitating charge transport along the column. Mobility values up to 0.10 cm²/Vs have been recorded for hexahexylsulfanyltriphenylene (Figure 8a, X=S), and values greater than 0.01 cm²/Vs have been recorded for hexabutyloxytriphenylene (Figure 8a, X=O). Recently, hole mobilities exceeding 1.0 cm²/Vs have been recorded for the crystal phase of hexabenzocorone (Figure 8b), though its liquid crystal phase also yields values in the range of 0.50 cm²/Vs [5].

4 Present Limitations and Future Research

Though intense research into p-type OFETs has resulted in promising carrier mobilities and on/off current ratios, there are significant problems requiring further research. One notable issue is the poor electron mobility in OSCs, limiting the effectiveness of n-type OFETs. Modern circuitry uses both p-type and n-type transistors, so developing an effective n-type OFET is an

important area for future research. One solution could be the cyanation of materials currently used in p-type OFETs. A large concern during the production of n-type OFETs is the instability of radical anions in air. Adding functional groups with high electron affinities to p-type semiconductors, such as pentacene, helps overcome the air instability. In addition to high electron affinities, the performance of n-type OFETs requires large electronic couplings and fairly small internal reorganization energies. Theoretical studies have predicted that all of these requirements could be fulfilled through cyanation of pentacene, oligothiophenes, oligopyrroles, and oligofurans, which have already been researched as p-type semiconductors [17]. Investigating these predictions is a potential area of future research.

Another area of research, mentioned briefly in the discussion of carbazoles, is the desirability of solution-processible OSCs. The current methods of physical semiconductor deposition, such as vacuum sublimation and thermal evaporation, are less cost-effective than methods using soluble organic semiconductor compounds combined with large-scale stamping and printing [18]. Poly(3-hexylthiophene) has been found to have good solubility, and was used in one of the first solution-processed OFETs [19]. Carbazoles have also been shown to be soluble and solution-processable, but their carrier mobilities and on/off current ratios are not ideal [15]. Future work may attempt to find soluble OSCs with better electronic properties.

One of the major problems facing OFETs today is the anisotropy inherent in most of the OSCs due to their linear nature. The conductivity of linear OSCs can change depending on the direction of the applied voltage in relation to the orientation of the molecules. Thus, optimizing the performance of OFETs requires either excellent control of molecule orientation during deposition or an isotropic alternative to linear OSCs. As has been discussed, some control of molecular orientation within OSCs has been a topic of ongoing research. However, 3D OSCs have been proposed as an alternative solution. 3D structures could be synthesized by attaching conjugated oligomers to a central node. A recent trend towards this outlook is suggested by the emergence of pseudo-3D systems based on triphenylamine (TPA) [5], though fully-isotropic organic “silicon substitutes” have not yet been discovered.

Another area of related research is into the design of fully-organic FETs, in which all parts of the transistor are composed of organic materials, not just the semiconductor. Such devices have potential applications in extremely cheap and flexible circuits with applications in RFID tags, electronic price

tags, and electronic paper [20].

In conclusion, OFET research over recent decades has led to very promising p-type devices based on a wide selection of OSCs ranging from simple oligomers such as pentacene to complex discotic and functionalized compounds. Problems relating to electron mobility, chemical deposition techniques, and anisotropy still limit OFETs. However, if these obstacles are overcome, OFETs could be used to create cost-effective, flexible, lightweight, and environmentally-friendly circuits.

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