THE USE OF FERROELECTRICS AND DIPEPTIDES AS INSULATORS IN ORGANIC FIELD-EFFECT TRANSISTOR DEVICES

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FIELD-EFFECT TRANSISTOR DEVICES

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Nomenclature

FET – field-effect transistor

FeFET – ferroelectric field-effect transistor

LED – light emitting diode

PV – photovoltaic

MIS – metal-insulator-semiconductor

MFM – metal-ferroelectric-metal

MIM – metal-insulator-metal

AFM – atomic force microscopy

SEM – scanning electron microscope

XRD – x-ray diffraction

DLS – dynamic light scattering

EIS – electrochemical impedance spectroscopy

C-V – capacitance-voltage

G-V – conductance-voltage

G-f – conductance-frequency

P-E – polarization-electric field

I-V – current-voltage
$V_g$ – gate voltage

$V_{ds}$ – drain-source voltage

$V_{Th}$ – threshold voltage

$\Delta V_{Th}$ – threshold voltage shift

$I_{ds}$ – drain-source current

$\mu_{\text{sat}}$ – saturation charge carrier mobility

$I_{\text{on}}/I_{\text{off}}$ – current on/off ratio

$W/L$ – width/length of the drain-source channel

$E_C$ – coercive field

$P_R$ – remnant polarization

$P_S$ – saturation polarization

$\Delta V_{FB}$ – flat band voltage shift

HOMO – highest occupied molecular orbital

LUMO – lowest unoccupied molecular orbital

PVDF – polyvinylidene fluoride

PVDF-TrFe – polyvinylidene fluoride-trifluoroethylene

PVDF-HFP – polyvinylidene fluoride-hexafluoropropylene

PVP – poly-4-vinyl phenol
PGMEA – propylene glycol monomethyl ether acetate

PMMA – polymethyl methacrylate

FF – L,L-diphenylalanine

FF-MNS – L,L-diphenylalanine micro/nanostructures

PCL - polycaprolactone

DP10-PPV – poly-2,3-diphenyl-5-decyl-1,4-phenylenevinylene

PVPh-HEM – poly-4-vinylphenol-co-2-hydroxyethyl methacrylate

PVA – polyvinyl alcohol

SiO₂ – silicon dioxide

DNTT – dinaphtho[2,3-b:2',3'-f]thieno[3,2-b]thiophene

TIPS-pentacene – 6,13-bis(triisopropylsilylethynyl)pentacene

PC – propylene carbonate

BTAc – butyl acetate

DMSO – dimethyl sulfoxide

DMF – dimethyl formamide

MEK – 2-butanone (methyl ethyl ketone)

HFIP – 1,1,1,3,3,3-hexafluoro-2-propanol

MCP – 4-mercaptopyridine
EDC – 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide

NHS – N-hydroxysuccinimide

PBA – 1-pyrenebutanoic acid

Urs – urease

wt% - weight percent (measure of solution concentration)
Abstract

While the electrical transport characteristics of organic electronic devices are generally inferior to their inorganic counterparts, organic materials offer many advantages over inorganics. The materials used in organic devices can often be deposited using cheap and simple processing techniques such as spincoating, inkjet printing, or roll-to-roll processing; allow for large-scale, flexible devices; and can have the added benefits of being transparent or biodegradable.

In this manuscript, we examine the role of solvents in the performance of pentacene-based devices using the ferroelectric copolymer polyvinylidene fluoride-trifluoroethylene (PVDF-TrFe) as a gate insulating layer. High dipole moment solvents, such as dimethyl sulfoxide, used to dissolve the copolymer for spincoating increase the charge carrier mobility in field-effect transistors (FETs) by nearly an order of magnitude as compared to lower dipole moment solvents. The polarization in Al/PVDF-TrFe/Au metal-ferroelectric-metal devices also shows an increase in remnant polarization of ~20% in the sample using dimethyl sulfoxide as the solvent for the ferroelectric. Interestingly, at low applied electric fields of ~100 MV/m a remnant polarization is seen in the high dipole moment device that is nearly 3.5 times larger than the value observed in the lower dipole moment samples, suggesting that the degree of dipolar order is higher at low operating voltages for the high dipole moment device.

We will also discuss the use of peptide-based nanostructures derived from natural amino acids as building blocks for biocompatible devices. These peptides can be used in a bottom-up process without the need for expensive lithography.
Thin films of L,L-diphenylalanine micro/nanostructures (FF-MNSs) were used as the dielectric layer in pentacene-based FETs and metal-insulator-semiconductor diodes both in bottom-gate and top-gate structures. It is demonstrated that the FF-MNSs can be functionalized for detection of enzyme-analyte interactions. This work opens up a novel and facile route towards scalable organic electronics using peptide nanostructures as scaffolding and as a platform for biosensing.
1 Introduction

Since the discovery of the highly conductive organic polymer polyacetylene in 1977 by A.J. Heeger, H. Shirakawa, and Alan G. MacDiarmid (who won the 2000 Nobel Prize in Chemistry), there has been a rapid growth in the study of organic electronics. The term organic electronics refers to semiconductor devices in which the semiconducting layer is made of an organic material. Here, organic means carbon-based, and another commonly used description is plastic electronics. These carbon-based materials get their conductive properties from significant overlap of the π-orbitals in the material, allowing for the transport of charge. Many devices have been manufactured, such as organic field-effect transistors (FETs), organic light emitting diodes (LEDs), and organic photovoltaics (PVs).

While the electrical transport characteristics of organic electronic devices are generally inferior to their inorganic counterparts, organic materials offer many advantages over inorganics. Many of the materials used in organic devices are polymers or small molecules that can be deposited using simple processing techniques such as spincoating, inkjet printing, or roll-to-roll processing. This allows for large-scale, flexible devices and cheaper manufacturing.

This work begins in Chapter 2 with an introduction to organic electronics, discussing the operating principles of metal-insulator-semiconductor (MIS) and FET devices along with the materials used in this work and their properties. An overview of ferroelectricity is also contained in this section. Chapter 3 discusses the particular processing and measurement conditions for the devices. Chapter 4 begins the discussion of results with ferroelectric organic FETs using the polymer
polyvinylidene fluoride-trifluoroethylene (PVDF-TrFe) as the ferroelectric material and pentacene as the organic semiconductor. Chapter 5 describes ferroelectric organic FET devices using either a different semiconductor or a different copolymer of polyvinylidene fluoride. Chapter 6 contains a discussion of organic FETs fabricated using pentacene and the nanostructured dipeptide L,L-diphenylalanine (FF) as the insulating material. Chapter 7 contains suggestions of future work to further characterize PVDF-TrFe and FF.
2 Introduction to Organic Electronics – Devices and Materials

2.1 Metal-insulator-semiconductor diodes

An MIS diode is essentially a capacitor where one plate is a metal, the other is a semiconductor, and they are separated by an insulating material. Before we discuss the working principles of the MIS device, we should make some definitions for an ideal, p-type (majority carrier is a positive hole) MIS capacitor. $E_F$ is the Fermi level (the highest occupied energy state, on average) of both the metal and the semiconductor. $\phi_m$ is the work function of the metal and the distance from $E_F$ to the vacuum level. $\phi_s$ is the work function of the semiconductor and assumed to be equal to $\phi_m$ for an ideal MIS capacitor. $E_i$ is the intrinsic level of the semiconductor. And $\phi_F$ is the energy difference between $E_i$ and $E_F$. An energy level diagram for this MIS device is shown in Fig. 2.1 (a) in flat band conditions, meaning no potential is applied to the diode.
We will connect the semiconductor to ground and the metal to a potential source for the following discussion. If we apply a negative potential to the metal electrode, a negative charge will accumulate on the metal plate. This induces a positive charge on the semiconductor surface near the insulator that is equal in magnitude due to the mobile positive charges. The Fermi level of the metal is raised by $qV$ when a potential of $-V$ is applied and the energy bands of the semiconductor bend near the semiconductor-insulator interface to accommodate the extra holes that have been accumulated. This scenario is called accumulation and is shown in Fig. 2.1 (b).
If we now apply a positive potential to the metal plate, a net positive charge will result on its surface. This causes the holes in the semiconductor to move away from the semiconductor-insulator interface, leaving a net negative charge on its surface. As shown in Fig. 2.1 (c), the energy bands of the semiconductor bend downward, and this situation is called depletion. If the positive potential is increased, these bands bend farther, causing $E_i$ to fall below the $E_F$, as can be seen in Fig. 2.1 (d). This is called inversion mode, where the semiconductor is now as n-type as it was p-type under no bias (i.e. $E_i$ is $\varphi_F$ below $E_F$ during inversion and is $\varphi_F$ above $E_F$ under no bias), and conduction of charges becomes possible in an n-type fashion (majority negative electrons). The inversion mode is what allows for the operation of FETs in inorganic MIS devices. Organic FETs don’t have an inversion mode, however, and operate in accumulation mode. The lack of an inversion mode is due to inherently low electron mobility and a high degree of negative charge trapping in organic semiconductors coupled with very long relaxation times for negative carriers.

MIS devices can be considered to be made up of three capacitors. The first, $C_e$, is the capacitance due to exchange of charge between the semiconductor-insulator interface states and the energy bands of the semiconductor. The second, $C_s$, is capacitance due to the semiconducting layer and is in parallel with $C_e$. The last, $C_i$, is the capacitance due to the insulating layer and is in series with the other two. The equivalent capacitor is shown in Fig. 2.2. We can find the voltage dependent capacitance of this equivalent capacitor using the equation:

$$C = \frac{dQ}{dV} = \frac{C_i(C_s + C_e)}{C_s + (C_s + C_e)} \quad \text{Eq. 2.1}$$
The voltage dependence of total capacitance allows us to extract a great deal of information for MIS devices and we will need \( C_i \) for our treatment of FET devices.

**Fig. 2.2.** Equivalent circuit of an MIS capacitor.

### 2.2 Field-effect transistors

The field effect transistor is a three terminal semiconducting device in which conduction between two of the terminals is modulated by the third. An electric potential applied to the third terminal allows charge to be accumulated and create a conducting channel between the first two terminals. In this way, the third terminal is called the gate electrode, because it “gates” the transfer of charge between the other two electrodes. The first two terminals are called the source and the drain. In an ideal transistor, there are two distinct states: “on” where current is being conducted between the source and the drain, and “off” where no current is conducted.

Based on the placement of these electrodes, FET devices can have one of a few structure classifications. The gate electrode will always be separated from the semiconducting layer by an insulating layer called the dielectric. The source and
drain electrodes will always be in direct contact with the semiconductor because they must inject and extract charge. The gate can be placed either above or below the insulator resulting in the top-gate or bottom-gate denotation, respectively. The source and drain can be placed either in contact with the insulator or be separated from the insulator by the semiconducting layer, giving the name of bottom contact or top contact. Fig. 2.3 shows all 4 device geometries. Both bottom-gate, top contact and top-gate, bottom-contact geometries have been examined in this work.

Fig. 2.3. The different device structures of an FET: (a) Bottom-gate, Top-contact, (b) Bottom-gate, Bottom-contact, (c) Top-gate, Bottom-contact, (d) Top-gate, Top-contact.

We will consider bottom-gate, top-contact devices for a discussion of device operation. In an FET, two voltages are applied with respect to a grounded source electrode in order to modulate the current between source and drain. The voltage applied to the gate, called gate voltage ($V_g$), draws charges to the dielectric-semiconductor interface and forms a conducting channel along this interface between the source and drain via an electric field through the dielectric layer. The
voltage applied to the drain electrode, called drain-source voltage ($V_{ds}$), drives mobile charges in the conducting channel between the source and drain to form a current. The conducting channel has a length, $L$, between the source and drain and a width, $W$, defined by the edge of the electrodes, perpendicular to the direction of current. Fig. 2.4 shows typical device architecture and application of voltages.

![Fig. 2.4. Bottom-gate FET with applied voltages labeled.](image)

Unlike inorganic FETs, which operate in inversion mode, organic FETs operate in accumulation. Most organic semiconductors are p-type, so accumulation mode occurs at negative applied gate voltages. As $V_g$ becomes more negative, the device will "turn on." The minimum $V_g$ that causes the device to turn on, meaning mobile charges are accumulated, is called the threshold voltage, $V_{Th}$. At gate voltages beyond $V_{Th}$ (more negative) current can be measured between the source and drain called drain-source current, $I_{ds}$. The magnitude of this current is dependent both upon $V_g$ and $V_{ds}$. 

8
We can model this drain-source current if we know how much charge is accumulated in the conduction channel between the source and drain. Let us define the x-direction as along the length of the channel, L, from the source to the drain and the y-direction as along the width of the channel, W. Conduction occurs along the dielectric-semiconductor interface, so we can treat the region made up of the gate electrode, dielectric, and dielectric-semiconductor surface between source and drain as a capacitor whose thickness is the thickness of the dielectric. We will make an assumption for long-channel FETs, as all devices examined in this work are, that the vertical electric field (originating from $V_g$) is much larger than the horizontal electric field (resulting from $V_{ds}$). This leads to treating the conduction channel as infinitely thin meaning all charge resides on the semiconductor/dielectric interface. In this way, we have a two-dimensional electron gas between our source and drain along the interface. So then the charge on the lower surface of the semiconductor (in the conduction channel) is:

$$Q(x, y) = C_0 [V_g - V_{Th} - V(x)]$$  \hspace{1cm} \text{Eq. 2.2}$$

Where $C_0$ is the capacitance per unit area of the dielectric and $V(x)$ is the potential along the conduction channel such that at the source, $x = 0$ and $V(0) = 0$ and at the drain, $x = L$ and $V(L) = V_{ds}$. We can then use the drift equation to define the current in the conduction channel as:

$$I(x, y) = Q(x, y) \mu \frac{dv}{dx}$$  \hspace{1cm} \text{Eq. 2.3}$$
For long-channel FETs, the accumulated charge along the y-direction should be completely uniform, so we can immediately integrate over y from 0 to the full width, W, and be left with:

\[ I_{ds}(x) = WQ(x)\mu \frac{dV}{dx} \]  
Eq. 2.4

Where \( I_{ds}(x) \) is the drain-source current as a function of position along the length of the channel. It is equivalent to write \( Q(x) \) as \( Q(V) \) because the only position dependent parameter of \( Q \) is \( V(x) \). We are now ready to integrate over the length of the channel. Remember that \( V(x=0) = 0 \) and \( V(x=L) = V_{ds} \).

\[ \int_{0}^{L} I_{ds}(x) \, dx = W\mu \int_{0}^{V_{ds}} Q(V) \, dV \]  
Eq. 2.5

We can substitute our expression for \( Q(x) = Q(V) \) that we defined in Eq. 2.1 and be left with:

\[ \int_{0}^{L} I_{ds}(x) \, dx = W\mu \int_{0}^{V_{ds}} C_{0}[V_{g} - V_{th} - V(x)] \, dV \]  
Eq. 2.6

This integration gives us:

\[ I_{ds} = \frac{W\mu C_{0}}{L} \left[(V_{g} - V_{th})V_{ds} - \frac{V_{ds}^2}{2}\right] \]  
Eq. 2.7

Now, for sufficient gate voltage \( V_{g} > V_{th} \), increasing \( V_{ds} \) will lead to a linear increase \( I_{ds} \). This regime is referred to as the linear regime. Increasing \( V_{ds} \) beyond a point \( (V_{ds} = V_{g} - V_{th}) \) results in a “pinching-off” of the current, where current no longer increases, but is instead constant as \( V_{ds} \) continues to be increased. When \( V_{ds} > V_{g} - V_{th} \), a depletion region forms near the drain because of the local difference in potential between \( V(x) \) and \( V_{g} \). Mobile charge carriers are still able to
travel across this depletion region because of the high electric field between the pinch-off point and the drain electrode, but their motion is now space-charge-limited and the current is said to be saturated. In this saturation regime, current is constant. The $V_{ds}$ that causes the onset of saturation, and subsequently the magnitude of the saturation current, increases as the gate voltage is increased. These distinct regimes are shown in Fig. 2.5. We can describe the saturation current by substituting $V_{ds} = V_g - V_{Th}$ into Eq. 2.7:

$$I_{ds(sat)} = \frac{WC_0}{2L} \mu(V_g - V_{Th})^2$$

Eq. 2.8

**Fig. 2.5.** (a) Onset of a conducting region once $V_g > V_{Th}$ resulting in linear regime (b) “Pinching-off” of conduction region at $V_{ds} = V_g - V_{Th}$ (c) Saturation regime when $V_{ds} > V_g - V_{Th}$ (d) A typical output curve from a pentacene-based organic FET marking the linear regime (a), pinch-off point (b), and saturation regime (c).

Using this definition of saturation current, we can solve for the saturation charge carrier mobility, $\mu_{sat}$.
\[ \mu_{sat} = \frac{2L}{WC_0} \left( \frac{d\sqrt{I_{ds}}}{dV_g} \right)^2 \]  

Eq. 2.9

Equipped with these equations, we can begin to characterize the performance of FET devices. There are two important measurements techniques used to evaluate FETs: the output and the transfer. These two measurements monitor \( I_{ds} \) as one of the two controlling voltages is changed. Sample curves of the transfer and output are shown in Fig. 2.6 (a) and (b), respectively.

**Fig. 2.6.** (a) Transfer and (b) Output curves of a typical pentacene-based organic FET device.

The output characteristics measure \( I_{ds} \) as a function of \( V_{ds} \) at several, fixed, gate voltages. Here, \( I_{ds} \) increases linearly with \( V_{ds} \) until the saturation point is reached, after which current stays constant. The magnitude of this saturated output current increases as \( V_g \) is increased because the saturation point moves to a higher (in magnitude) voltage at larger gate voltages.
The transfer characteristics measure the drain-source current with respect to changing gate voltage at a fixed drain-source voltage. The chosen $V_{ds}$ is called the operating voltage and is usually selected in the saturation regime. When operated in the saturation regime, as $V_g$ is swept to larger magnitudes, $I_{ds}$ will increase quadratically, as indicated by Eq. 2.8. There are four important parameters that can be extracted from the transfer curves: saturation mobility, threshold voltage, on/off current ratio, and subthreshold swing. It is convenient to plot the square root of $I_{ds}$ vs. $V_g$ so that $\mu_{sat}$ can be extracted from Eq. 2.9. A linear fit of the square root transfer characteristics can be used to find the slope to be inserted into Eq. 2.9 and the intersection along the $V_g$ axis will give the threshold voltage, $V_{Th}$. The $I_{on}/I_{off}$ ratio is the ratio of the on current to the off current and is defined as the current measured when the gate voltage is equal to the operating voltage of the device (i.e. $V_g = V_{ds}$) divided by the minimum current of the device. $I_{ds}$ vs. $V_g$ is often plotted on a logarithmic scale to easily see the quadratic relationship between the two and to find $I_{on}/I_{off}$.

The logarithmic plot is also useful to find the subthreshold swing, which can be used to estimate the trap density in the semiconductor. The subthreshold region of the transfer curves is located below $V_{Th}$ where Eq. 2.8 insinuates current abruptly becomes zero. In reality, this is not the case and there is still conduction below $V_{Th}$ originating from weak accumulation in the conduction channel. The current in the subthreshold region comes from diffusion of current and is generally linear when we plot log($I_{ds}$) vs. $V_g$. The inverse of this slope is called subthreshold swing (SS).
\[ SS = \frac{\partial v_g}{\partial (\log(I_{ds}))} \]  

Eq. 2.10

A smaller value for \( SS \) means that a small change in the input bias will considerably modulate the output current. Some of the best devices exhibit \( SS \) as low as 70 mV/decade.\(^1\)

The maximum trap charge density of FET devices can then be estimated using the relationship\(^2\)

\[ N_{\text{trap}}^{\max} \approx \left\lfloor \frac{qSS\log(e)}{k_B T} - 1 \right\rfloor \frac{C_0}{q} \]

Eq. 2.11

Here, \( q \) is elementary charge, \( SS \) is the subthreshold swing, \( e \) is the natural exponential, \( k_B \) is the Boltzmann constant, \( T \) is temperature, and \( C_0 \) is the insulator capacitance.

### 2.3 Organic materials

#### 2.3.1 Semiconductors

Organic semiconducting materials are carbon based materials that have the ability to conduct an electrical current. For this reason, organic electronics are sometimes called plastic electronics. Most organic semiconductors are single crystals, small molecules, or conjugated polymers that have a high density of double bonds, or \( \pi \) bonds, between the carbons, allowing for charge transport. Charge transport in organic molecules does not occur in the same manner as it does in inorganic semiconductors. Inorganic semiconductors have a band-to-band transfer mechanism, while organic molecules rely on a thermally assisted hopping
mechanism via a Gaussian distribution of electronic states. In this way, charge transport in organic semiconductors is very dependent on packing of semiconductor polymer chains or small molecules and the density of structural defects. Band to band transfer is much faster due to the available energy sites all having the same energy, while hopping transport requires charge carriers to change levels in order to move across the material. The fastest hopping transport occurs when there is a very tight distribution of available energy states and defects in the semiconductor are minimized.

Conjugated π bonds are the source of electrical conductivity in organic molecules. Conjugation means that the carbons in the organic molecule have alternating single and double carbon-carbon bonds. This alternation leads to a phenomenon called resonance in which it is equivalent to interchange the single bonds and double bonds when drawing the molecules. This symmetry indicates an equal sharing of electron density between the carbon sites. The most common example of resonance (and the most common molecular group in organic semiconductors) is the benzene ring, a ring of six carbons with three alternating double bonds. Fig. 2.7 shows the two different choices of double bond placement in parts (a) and (b) and a common representation of the delocalization of electrons among all six carbons in part (c).
The four valence electrons of carbon have the special ability to become hybridized, meaning they can be rearranged in the 2s and 2p orbitals in order to form either single bonds (sp$^3$ hybridized), double bonds (sp$^2$ hybridized), or triple bonds (sp hybridized). The nomenclature comes from the ratio of orbital character in each hybrid orbital (i.e. sp hybridized is the combination of one 2s orbital and one 2p$_x$ orbital, 50 % of each; sp$^2$ hybridized is made up of the 2s orbital and the 2p$_x$ and 2p$_y$ orbital, 33 % s and 67% p; sp$^3$ hybridized is made up of the 2s, 2p$_x$, 2p$_y$, and 2p$_z$ orbitals, 25 % s and 75 % p).

**Fig. 2.7.** Resonance of Benzene.

**Fig. 2.8.** sp$^2$ hybridization of carbon.
We are mostly concerned with sp\textsuperscript{2} hybridization, the one that forms double bonds, as it is the most common in organic semiconductors. The 2s, 2p\textsubscript{x} and 2p\textsubscript{y} orbitals combine to form three new orbitals while the 2p\textsubscript{z} orbital remains unaffected. Fig. 2.8 shows a schematic of the sp\textsuperscript{2} hybridized orbital. The three hybridized orbitals form three single bonds in a planar fashion 120° apart. The 2p\textsubscript{z} orbital is then involved in a double bond along one these three single bond directions. The in-phase combination of electrons in the 2p\textsubscript{z} orbitals of neighboring carbon atoms combine to form a \pi orbital. This \pi orbital is a molecular orbital describing bonding between atoms, not an atomic orbital describing the placement of electrons in an atom as we have been talking about until now. The two 2p\textsubscript{z} electrons from neighboring atoms now lie in the highest occupied molecular orbital (HOMO). The next highest molecular orbital (in energy) is empty and is called the lowest unoccupied molecular orbital (LUMO). It is formed by the out-of-phase combination of the two 2p\textsubscript{z} orbitals and is labeled the \pi^* orbital, or anti-bonding orbital. Fig 2.9 shows the in-phase (\pi) and out-of-phase (\pi^*) combinations of the 2p\textsubscript{z} orbitals in ethylene.
For highly conjugated systems, such as benzene rings, the π and π* orbitals are delocalized across the molecule/polymer. These are the HOMO and LUMO levels of the molecule or polymer. The transfer of electrons (or, more commonly, holes) in organic semiconductors occurs in one of these two levels (LUMO for electrons, HOMO for holes). In this way, it is possible to compare these two energy levels to the valence and conduction bands in inorganic semiconductors. It becomes easier to discuss organic FETs using these similarities.
Fig. 2.10. Energy bands at the metal/semiconductor interface. \( E_F \) is the Fermi energy of the source/drain material, \( \phi_m \) is the work function of the metal, and \( \Delta \) is the charge injection barrier between metal and semiconductor.

The HOMO level is important for another reason in FET device fabrication. In order to ensure good injection of positive charge from the source electrode (and charge collection at the drain), the HOMO level of the organic semiconductor must match well with the Fermi level of the chosen source and drain materials. It is favorable for the charge injection barrier to be as low as possible between the materials. Fig. 2.10 shows a schematic of the energy level diagram for this process.

The semiconductors used in this work are pentacene, dinaphtho[2,3-b:2',3'-f]thieno[3,2-b]thiophene (DNTT), and 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-pentacene). Pentacene is a small molecule semiconductor that has been
extensively studied because of its ability to provide high charge carrier mobility for an organic semiconductor.\textsuperscript{3,4} It is generally deposited using thermal evaporation, as are most small molecule semiconductors. It is an aromatic hydrocarbon comprised of five fused benzene rings, shown in Fig. 2.11. It forms polycrystalline films in a herringbone packing structure. The film forms single crystal islands on the surface of the dielectric, generally dendritic in shape.\textsuperscript{5}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{pentacene.png}
\caption{Molecular structure of pentacene.}
\end{figure}

DNTT is another small molecule semiconductor that has only recently begun to be used in FET devices (c. 2007).\textsuperscript{6} DNTT is a highly $\pi$-extended heteroarene with six fused aromatic rings. It has a relatively low-lying HOMO level and a large HOMO-LUMO gap. It forms good FET devices that are stable in air and have high charge carrier mobility close to 2 cm$^2$V$^{-1}$s$^{-1}$.\textsuperscript{1,7} Its structure is shown in Fig. 2.12.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{DNTT.png}
\caption{Molecular structure of DNTT.}
\end{figure}
TIPS-pentacene is a variation of pentacene in which two triisopropylsilylethynyl acetylene groups have been added to the center benzene ring on pentacene, shown in Fig. 2.13. The addition of the isopropyl groups allows pentacene to be dissolved in many organic solvents while also increasing the carrier mobility of pentacene FETs.\(^8\) The increase in mobility comes from the steric hindrance introduced by the long sidechains. The packing of TIPS-pentacene molecules is restricted, such that greater \(\pi-\pi\) overlap is enforced. This increased \(\pi-\pi\) overlap allows for easier transfer of charge between pentacene molecules. Also, the presence of grain boundaries is greatly reduced in this solution processable thin film of TIPS-pentacene as compared to thermally evaporated, small molecule pentacene. Increasing the solubility of pentacene allows for much simpler device fabrication, as spincoating or dropcasting can now be employed rather than thermal evaporation, which requires equipment that is vastly more complex and expensive than spincoating setups. This cheap, facile fabrication is one of the most attractive aspects of organic FET technology.

Fig. 2.13. Molecular structure of TIPS-pentacene.
2.3.2 Insulators

The use of both metal oxide and organic polymer dielectrics is common in organic FETs. Each has advantages and disadvantages. Oxides typically have higher dielectric constants, which is useful for FET device applications because a high dielectric constant means an increased capacitance, which translates to a larger magnitude of charge accumulated in the conduction channel at lower applied gate voltages. It is important to have low operating voltages in order to reduce the power consumption of transistors. However, it has been shown that the use of SiO$_2$ as the insulating layer in pentacene devices leads to an increase in threshold voltage shift ($\Delta V_{Th}$), a decrease in $\mu_{sat}$, and an increase in operating voltage.$^9$

Organic FETs are being actively developed for applications in large-area flexible electronics.$^{10,11}$ A requirement for such applications is that both the semiconducting layer and the gate dielectric layer be solution processable. Organic insulators have become very common for use in organic FETs due to their ability to create low-operating voltage, stable devices.$^{12,13}$ Getting away from oxide dielectrics, such as SiO$_2$ and Al$_2$O$_3$ in organic FETs is not only cost-effective, but has tremendous advantages for improving carrier mobility and stability of devices.$^{14}$ However, organic insulators suffer from the fact that they have inherently low dielectric constants. This can make it difficult to accumulate sufficient charge for conduction. Much effort has gone into modification of the dielectric-semiconductor interface; appropriate gate dielectrics that are free of electron-trapping groups, such as hydroxyl or silanol, have allowed the
demonstration of $n$-channel organic FETs,\textsuperscript{15} which is otherwise not observable with oxide dielectrics. In order to achieve stable and low-operating voltage organic FETs, the dielectric surface should be hydrophobic and the insulator must provide a relatively high capacitance, which is often a challenge with many polymer dielectrics because of their inherently low dielectric constant. Thus, other strategies involving solvent manipulation have been used.\textsuperscript{47,48}

The main advantage of the organic dielectric is the ease of fabrication. Most polymer dielectrics are easily soluble in common organic solvents, which allows them to be used in simple application techniques such as spincoating or dropcasting. This allows for the manufacturing of devices in ambient conditions, further improving ease of fabrication. Device fabrication with polymer dielectrics is generally cheaper, simpler, and faster because large-scale manufacturing techniques like roll-to-roll printing can be employed. Polymer dielectrics are also much less brittle under mechanical stress. Flexible, large-scale devices are easily realized in all-organic FETs (FETs in which both the dielectric and semiconductor are organic materials). Table 2.1 provides a list of solvents used to dissolve the insulators in this work along with their solvent properties.

All devices discussed in this work are of the all-organic variety. Three different organic insulators have been used. The first of these is poly-4-vinylphenol (PVP). PVP is one of the most widely used insulators for organic FET devices because of its ability to provide high carrier mobility, stable devices.\textsuperscript{16,17} The monomer is an ethylene with one of the carbons containing a 4-phenol group. The “4” in 4-phenol refers to the position of the OH group on the phenyl group. The “1”
position is the carbon connected to the ethylene group and the carbons are numbered around the 6-carbon ring in order to give the lowest number to the other attached groups. “4” is directly opposite the “1” position. The backbone of the polymer chain is formed by these ethylene groups. A schematic of the poly-4vinylphenol group is shown in Fig. 2.14. The other three dielectrics used in this study are polyvinylidene fluoride-trifluoroethylene, polyvinylidene fluoride-hexafluoro propylene, and L,L-diphenylalanine, all of which will be discussed in more detail at a later point in this manuscript.

![Molecular structure of poly-4-vinylphenol.](image)

**Fig. 2.14.** Molecular structure of poly-4-vinylphenol.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dipole Moment (D)</th>
<th>Dielectric Constant</th>
<th>Boiling Point (°C)</th>
<th>Solubility parameter (MPa)$^{1/2}$</th>
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</thead>
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<td>26.7</td>
</tr>
<tr>
<td>Dimethyl Formamide</td>
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<td>19.1</td>
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<tr>
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<td>2.38</td>
<td>110</td>
<td>18.2</td>
</tr>
</tbody>
</table>

**Table 2.1.** Properties of various solvents used in this work.
2.4 Ferroelectrics

2.4.1 Explanation of ferroelectricity

Ferroelectricity is a phenomenon occurring in certain materials that arises from separation of charge. It refers to a spontaneous electric polarization that can be manipulated upon the application of an electric field. The name ferroelectricity comes from an analogy to ferromagnetism (the presence of a permanent magnetic moment), which was discovered prior to ferroelectricity.

In a ferroelectric material, each molecule or unit cell has an individual electric dipole. The origin of this dipole comes from a lack of a center of symmetry in the unit cell of a crystal lattice or monomer of a polymer. Each noncentrosymmetric crystal, except those belonging to point group 43, can be polarized by mechanical stress; these materials are called piezoelectric. This polarization leads to a change in the surface charge density of the material. Some piezoelectric materials can also experience a change in surface charge density due to a change in temperature; these materials are called pyroelectric. The materials which are both piezoelectric and pyroelectric whose dipoles can be manipulated by an external electric field are called ferroelectric.

The magnitude of each individual dipole depends on the amount of charge that is displaced, q, and the distance by which the charge is separated, δ. When you have a number of dipoles per unit volume, N, a macroscopic polarization for the material occurs called \( \vec{P} \), with \( \vec{P} = Nq\vec{\delta} \). Note that both \( \vec{P} \) and \( \vec{\delta} \) are vectors, so the magnitude of polarization increases when separation of charge for individual dipoles is along the same direction.
Let’s imagine a single dipole, oriented upward, sandwiched between two plates of a parallel plate capacitor (Fig. 2.15 (a)). The small electric field created by the dipole will cause the free charges in the plates of the capacitor to rearrange. There will be an excess of positive charge on the upper plate surface, and negative charges will have moved away from the upper plate. In the bottom plate, negative charges will be attracted toward the surface of the plate, leaving an excess of positive charges farther away from the plate surface (Fig. 2.15 (b)). If we connect these plates with a conducting wire, we would measure a current flowing between the plates to balance this separation of charge (Fig. 2.15 (c)). However, charge on the surface of the two plates will remain in order to cancel the electric field created by the dipole. This allows us to measure a non-zero electric potential between the two capacitor plates, even though there is no applied bias (Fig. 2.15 (d)).

**Fig. 2.15.** (a) Dipole between plates of a capacitor. (b) Rearrangement of charge in capacitor plates. (c) Measureable current due to dipole. (d) Remaining voltage across capacitor plates to cancel electric field from dipole.
Now, we add a second dipole. Depending on the orientation of this second dipole, our inherent electric field will either be canceled (when we add the second dipole antiparallel to the first) or be doubled in magnitude (if we add the second dipole parallel to the first). In the first case, the potential across the plates disappears, because there is no electric field between the plates (Fig. 2.16 (a)). In the second case, the potential between the capacitor plates will double in magnitude, because the electric field between the plates has doubled (Fig. 2.16 (b)). This concept can be applied to any number of dipoles we place between the capacitor plates. But in reality, these dipoles don’t simply line up parallel or antiparallel. They can have any orientation depending on the alignment of the crystal lattice or the polymer that makes up the set of dipoles. Thus, we get a relationship for the total polarization that looks like:

$$
\vec{P} = \sum_{i}^{\text{all}} N q_i \vec{\delta}_i
$$

Eq. 2.12

Fig. 2.16. (a) Antiparallel addition of dipoles and (b) parallel addition of dipoles between the plates of a capacitor.

In order to align dipoles and increase the total polarization, an exterior electric field is applied to the material. As the magnitude of the applied field
increases, the number of individual dipoles that align along the direction of the field increases. This alignment remains, even after the electric field is removed. The direction of the dipoles can be switched by applying a bias in the opposite direction. This leads to an asymmetric curve in polarization versus electric field measurements. This scenario is described in Fig. 2.17.

Fig. 2.17. (a) Unaligned dipoles in a ferroelectric material. (b) A bias is applied to align the dipoles. (c) Dipole alignment remains after electric field is removed. (d) Asymmetric polarization resulting from dipole alignment.

So how can we take advantage of these permanent dipoles and the ability to arrange them as we please? One way is to use these materials in a sensor. Because ferroelectrics are both pyroelectric and piezoelectric, they make good temperature and pressure sensors. In piezoelectric materials, a change in applied force or pressure corresponds to a change in surface charge density, which can be measured as a current or potential across the ferroelectric material. A change in temperature causes a similar change in surface charge for pyroelectric materials.

Ferroelectrics can also be used as memory storage devices by taking advantage of the hysteresis in the polarization versus electric field loop. One of the most common device architectures is the metal-ferroelectric-metal (MFM)
capacitor. Because the alignment of individual dipoles in a ferroelectric can remain after removal of bias, a non-symmetric polarization is induced when voltage is swept from positive to negative vs. negative to positive; polarization is bias-direction-dependent. Therefore, measuring the displacement field while sweeping voltage gives insights into how the dipoles are aligned, allowing information to be stored in the form of either a high displacement field or a low displacement field. The high and low configurations are equivalent to the computational “1” and “0.” However, polarization is switched during each measurement. Thus, this type of readout is destructive because a “rewrite” process is required after each measurement. Another type of memory device based on ferroelectric materials is the FET. These devices use a non-destructive readout, and as such, have smaller power consumption than the MFM devices because no rewrite process is required. A bistability, which is created by applying a gate voltage to align the dipoles, observed in the magnitude of drain-source current is used to distinguish between the two states. Moreover, ferroelectric-based FETs offer a great platform for probing the nature of polarization on the charge transport mechanism.\textsuperscript{18,19}

2.4.2 PVDF, PVDF-TrFe, and PVDF-HFP

Polyvinylidene fluoride (PVDF) and its copolymer polyvinylidene fluoride-trifluoroethylene (PVDF-TrFe) are some of the most common ferroelectric materials used for organic ferroelectric FETs.\textsuperscript{20,21} This is due to the relatively high remnant polarization, fast switching times, and good thermal stability of the
polymer. PVDF is also a high-k polymer dielectric, which makes it attractive for use in electronic devices.

The VDF monomer is made up of two carbon atoms, one of which has two hydrogens bonded to it, the other containing two fluorine atoms. Many of the bulk properties of PVDF come from the orientation of the hydrogens and fluorines with respect to each other. There are four conformations of the PVDF polymer: α, β, δ, and γ. The α-phase is paraelectric and is the most easily attainable due to it being kinetically favored. The α-phase has the conformation trans-gauche (TG⁺TG⁻). This means that the two pairs of hydrogen are 180 degrees apart. The fluorine pairs are both 120 degrees apart from the hydrogen pairs and 180 degrees apart from each other. The β phase is ferroelectric and is the most widely studied. β-PVDF is in the all-trans conformation (TTTT) in which the bonds on each successive carbon are 180 degrees away from the previous ones. So all of the hydrogen bonds are in the same direction and all of the fluorine bonds are along the same direction. The ferroelectric properties of β-PVDF come from the differing electronegativity of hydrogen and fluorine, which gives rise to a dipole for each molecule oriented perpendicular to the polymer chain. The γ-phase is also polar and has a confirmation in between that of α and β. There are three trans followed by a gauche (TTTG⁺TTTG⁻). The δ-phase is a ferroelectric version of the α conformation. The structure is identical to the α-phase and the ferroelectric properties are induced by poling the PVDF layer with a high electric field that ensures neighboring chains orient identically. The four polymorphs of PVDF, along with the PVDF-TrFe copolymer are shown in Fig. 2.18.
The copolymer PVDF-TrFe has the advantage of being ferroelectric directly after solution processing of the film, while PVDF requires additional measures such as stretching of the polymer or controlled heating of the film to ensure the all-trans configuration.\textsuperscript{26,27} The extra fluorine in the TrFe monomer prevents the polymer from forming the trans-gauche α phase so long as the molecule is above 11\% TrFe.\textsuperscript{28} This ease of fabrication is the main motivation for using the PVDF-TrFe copolymer for ferroelectric devices. The β phase is the most attractive for applications in ferroelectric electronics because it has the strongest piezoelectric and pyroelectric qualities.\textsuperscript{29}

Another copolymer of PVDF that has been shown to be polar is polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP). However, the α-phase is still more thermodynamically favorable for the PVDF-HFP copolymer. Preparation in the β-phase is often achieved by stretching films at elevated temperatures. Recently, the β-phase has been shown to exist directly after solution processing if the PVDF-HFP solution has a hydrated salt, Mg(NO\textsubscript{3})\textsubscript{2}*6H\textsubscript{2}O, introduced before spincoating\textsuperscript{30} or if they are prepared with zirconium-doped barium titanate.\textsuperscript{31} Here, we use the PVDF-HFP film with no further processing, so it is largely in the α-phase. Fig. 2.19 shows PVDF-HFP.
Fig. 2.18. (a) α-PVDF, (b) β-PVDF, (c) γ-PVDF, (d) δ-PVDF, (e) and (f) PVDF-TrFe. The α-phase and δ-phase have two chains to demonstrate the difference in paraelectricity and ferroelectricity.

Fig. 2.19. Molecular structure of PVDF-HFP.
2.5 Dipeptides

2.5.1 Diphenylalanine

The nanostructures obtained from biomolecules are attractive due to their biocompatibility, ability for molecular recognition, and ease of chemical modification. Peptide-based self-assemblies derived from natural amino acids are superior building blocks for biocompatible and other devices as they can be used in a bottom-up process without any need for expensive lithography.\textsuperscript{32,33,34,35} By mimicking the structures occurring in nature, peptide materials play a unique role in a new generation of hybrid materials. Phenylalanine-containing polypeptides have amphiphilic properties that help in their self-assembly and result in a variety of well-defined structures, such as nanorods, nanotubes, and nanospheres.\textsuperscript{36,37} Such molecular self-assembly are a result of various inter/intramolecular interactions: van der Waals, electrostatic, and hydrogen bonds. The self-assembly mechanism further depends on the preparation conditions, such as concentration, pH, and temperature.\textsuperscript{38,39} Additionally, due to the ease of manipulating peptide nanostructures on various substrates for active materials, one can conjure up new functionalities in electronic devices.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{diagram.png}
\caption{Molecular structure of the dipeptide \textit{L,L}-diphenylalanine.}
\end{figure}
We have chosen to use the dipeptide L,L-diphenylalanine (FF). A dipeptide is simply two amino acid groups connected by a peptide bond. FF is two propionic acid groups (two carbons with a carboxylic acid group), each with a phenyl ring, connected by an NH group (the peptide bond). Its structure is shown above in Fig. 2.20. There are several processes that can form nanostructures from these FF monomers including: solvent-vapor exposure, physical vapor deposition, and electrospinning. The solvent-vapor method involves spincoating a solution of FF monomers to form a thin film. The thin film is then placed in a vapor environment at elevated temperatures for about 12 hours in which the vapor has a tendency to promote strong hydrogen bonds (such as water, isopropanol, or analine). Nanostructuring begins with FF monomers congregating to form 6-member rings with an approximate diameter of 1 nm. Hydrogen bonds then form between rings to form long ring stacks. These ring stacks will then pack into the P6\textsubscript{1} hexagonal crystal structure. After a sufficient number of layers are formed by these packed ring stacks, the layers will roll up to form the final product of a nanotube with an interior diameter of about 120 nm and a length on the order of a few micrometers. This process is described in Fig. 2.21.
The L,L-diphenylalanine micro/nanostructures (FF-MNSs) have a good thermal and chemical stability.\textsuperscript{36} The solid-vapor phase synthesis results in a dense network of horizontal FF-MNSs on different substrates. Such a network provides not only scaffolding for other active materials, but also enhances the substrate surface area that may be used for applications in sensors, transistors, and solar cells. Another unique property of peptide nanostructures is their ferroelectric nature,\textsuperscript{32,40,41} which may be manipulated using thermal annealing. The piezoelectric hexagonal form of FF-MNSs is known to show an irreversible phase transition at ~ 140 °C to a less-polar orthorhombic structure.\textsuperscript{42}

Peptide nanostructures pave the way for a novel class of dielectrics in both bottom-gate and top-gate organic FET architectures, with applications in biosensing and piezoelectric devices. Top-gate organic FETs with polymer dielectrics are often a challenge with low-cost spincoating techniques, since the solvents used for dissolving the polymer dielectric degrade the underlying organic
semiconductor layer. The solvents used for dispersing peptide nanostructures are usually orthogonal to the organic semiconducting layer, and thus provide a simple fabrication route towards top-gate organic FETs. The hydrophilic and hydrophobic nature of the surface of FF-MNS can be controlled by changing their phase. It was recently shown that the surface of hypercin conjugated FF-MNSs in the hexagonal phase is more hydrophobic than the surface of the orthorhombic phase.\textsuperscript{37,43} The high surface area and the hydrophobic nature of the hexagonal phase of FF-MNSs provide a superior organic molecular/polymer-dielectric interface.
3 Techniques

3.1 Fabrication

3.1.1 Spincoating

Spincoating is a common method employed to deposit uniform films of organic, polymer dielectric materials as well as some polymer organic semiconductors. In order for a material to be spincoated, it must exhibit good solubility for a chosen solvent. The spincoating process generally goes as follows: (1) the polymer to be deposited is dissolved in some solvent, (2) some volume of the solution is dropped onto the substrate either before it begins to rotate or after it is rotating at some slow spin rate, (3) the substrate is allowed to continue to rotate at a few thousand rotations per minute (RPM) while the film spreads to a uniform thickness.

There are many factors that dictate the quality and thickness of spincoated films. Concentration of the polymeric solution, volume of solution used for spincoating, spin speed, temperature of the substrate, vapor pressure, and qualities of the solvent (such as boiling point and viscosity) all affect the formation of films. Thinner films result from lower concentration, smaller volume, faster spin speed, and lower boiling point of solvent. Following the spincoating, it is customary to thermally anneal the films in order to drive off the solvent and increase the crystallinity and uniformity of the film.

Spincoating for this work was performed on one of two spincoaters. For the diphenylalanine work, spincoating was carried out on a Laurel Technologies
Corporation WS-400B-6NPP/LITE/8K spincoater in ambient conditions with a slow stream of N\textsubscript{2} gas over the substrate and subsequently annealed in an oven in ambient conditions. All other films (PVP, PVDF-TrFe, PVDF-HFP and TIPS-pentacene) were spincoated inside a N\textsubscript{2} glove box atmosphere on a Specialty Coating Systems ModelP-6708D spincoater. These films were also annealed inside the glove box. More experimental details for film formation are contained in their respective sections.

3.1.2 Thermal Evaporation

Thermal evaporation is a form of physical vapor deposition commonly employed in the manufacturing of organic FET devices. It involves heating solid materials to the point that they sublime and travel to some target substrate where they can deposit to form a film. The process is only suitable for metals and small organic molecules because the high temperatures used to achieve film growth typically break down heavy organic polymers before they can sublime. The procedure for thermal evaporation usually follows the steps: (1) the material to be deposited is heated to the point that individual molecules/atoms have sufficient thermal energy to leave the surface; (2) these individual molecules/atoms travel to the substrate; (3) the molecules/atoms deposit and arrange themselves onto the surface of the target to form a film.

The mean free path of atoms in a gas is described by \(^{44}\)

\[
\lambda = \frac{k_BT}{\sqrt{2}\pi a^2 P}
\]

Eq. 3.1
Where $k_B$ is the Boltzmann constant, $T$ is temperature, $d$ is the average diameter of the molecules in the hard-sphere model, and $P$ is the pressure. Because the individual molecules/atoms must cover some distance (usually 10s of cm) during thermal evaporation, it is important to carry out the process under vacuum conditions to minimize the number of scatterings/interactions of the material as it travels from source to target. Decreasing the pressure during deposition will also increase the mean free path of the molecules/atoms by reducing the number of collisions that occur along its path, which must be longer than the distance from the source to the substrate.

Thermal evaporation was used to form the gate electrode (aluminum), source and drain electrodes (gold), and the small molecule semiconductor layer (both pentacene and DNTT). In order to achieve vacuum conditions, a rotary pump (roughing pump) was used in conjunction with a turbomolecular pump. Pressure during deposition of all materials was around $10^{-6}$ mbar. Sublimation of the material was accomplished by resistive heating of either a molybdenum boat (in the case of the metal electrodes) or a quartz crucible (in the case of the semiconductors) that held the material. The power delivered to the boat or crucible was controlled in order to select the deposition rate. Gold was deposited at a rate of 3 Å/s, pentacene and DNTT at a rate of 0.3 Å/s, and aluminum at a rate of 2.5 Å/s. The thickness of the layer is monitored by a quartz crystal balance during deposition.

The thermal evaporation of gold must be done through a shadow mask in order to define the channel length and width. Two different masks have been
fashioned using laser ablation and the patterns as well as the device dimensions are shown in Fig. 3.1.

**Fig. 3.1.** Two different gold top-contact shadow masks used for thermal evaporation containing both FET source/drain terminals and circular pads for MIS C-V measurements.

### 3.2 Characterization

#### 3.2.1 MIS capacitance-voltage measurements

Capacitance versus voltage (C-V), conductance versus voltage (G-V), and conductance versus frequency (G-f) characteristics were measured from MIS structures with an HP 4284A LCR meter. During the C-V and G-V measurements, a DC voltage is applied with a small AC voltage signal superimposed on top while the capacitance or the conductance is monitored. A program was developed in LabVIEW to control the application of voltage and sensing of capacitance or
conductance. The magnitude of the AC signal was 200 mV and the frequency of the signal was usually in the range of 5-10 kHz for all measurements presented in this work. The DC signal is then swept from positive bias to negative bias and from negative to positive (usually $\approx \pm 10$ V). The number of steps and range of applied bias can be selected in the LabVIEW program. During these sweeps, capacitance or conductance is measured and recorded for each DC voltage applied. During the G-f measurements, a DC bias selected in the depletion region is kept constant while the frequency of the AC signal is swept from 10 Hz to 1 MHz while conductance is recorded. The experimental setup is shown in Fig 3.2 below.

![Experimental setup diagram](image)

**Fig. 3.2.** MIS Capacitance and Conductance experimental setup.

### 3.2.2 Field-effect transistors

The organic FET characteristics were measured at room temperature in ambient atmosphere with two source meters, a Keithley 2400 and a Keithley 236, configured together using two separate programs written in LabVIEW, one
program for the output characteristics and one for the transfer. The two source meters are used in tandem because two voltages must be sourced, $V_{ds}$ and $V_g$, and two currents must be measured, $I_{ds}$ and the gate leakage current $I_g$. For both output and transfer measurements, the Keithley 236 is in charge of sourcing $V_{ds}$ and measuring $I_{ds}$ while the Keithley 2400 sources $V_g$ and measures $I_g$. For output measurements, the program can set the Keithley 236 to sweep any $V_{ds}$ range with any desired number of data points for a set $V_g$ to be sourced by the Keithley 2400. A new gate voltage is then set and the same $V_{ds}$ sweep is performed. The number and step size of gate voltages can also be set to select how many $V_{ds}$ sweeps occur during a measurement. For each $V_{ds}$, the $I_{ds}$ is measured by the Keithley 236 and recorded during each sweep at a new $V_g$. The program for the transfer characteristics is quite similar to the output program. A single $V_{ds}$ can be selected to be sourced by the Keithley 236 and the number of points and range of $V_g$ to be sourced by the Keithley 2400 can be set for the sweep. $I_{ds}$ is then measured and recorded by the Keithley 236 and $I_g$ is recorded by the Keithley 2400 for each data point. Fig. 3.3 shows a schematic of the experimental setup.

**Fig. 3.3.** Experimental setup for FET measurement.
3.2.3 **Metal-ferroelectric-metal**

Metal-Ferroelectric-Metal (MF-M) capacitors have been characterized using a modified Sawyer-Tower to monitor switching current. An oscillating voltage with a sawtooth shape is applied across a reference resistor and the MFM capacitor sample that have been placed in series. The voltage drop across the resistor is measured and then converted to current as a function of time, I(t). Because the resistor and MFM capacitor are in series, the current across them should be the same. The experimental setup is shown in Fig. 3.4.

![Experimental setup for polarization measurements on MFM capacitors.](image)

**Fig. 3.4.** Experimental setup for polarization measurements on MFM capacitors. Figure provided by Anagh Bhaumik, Missouri State University, Springfield, MO, USA.

Once I(t) is known, an integration over time is used to find the accumulated charge on the capacitor. This charge and the area of the capacitor is used to find the polarization (P) using the following relation:
\[ P = \frac{Q}{A} = \frac{\int I(t)dt}{A} \]  \hspace{1cm} \text{Eq. 3.2}

The P-V curves of the MFM capacitor are then obtained by integrating the current-time data for different applied voltages using Origin Pro 8.5.1. The P-V hysteresis loops must then be centered along the y-axis, as drift of the current often occurs. As the voltage increases, the MFM capacitor starts to show hysteresis characteristics, and the polarization saturates at higher voltages. The coercive voltage is defined as the voltage where \( \frac{dP}{dV} \) reaches a maximum. Physically, this corresponds to the ferroelectric dipoles “flipping” their orientation. In theory, \( \frac{dP}{dV} \) should approach infinity for ideal ferroelectric capacitors as polarization should abruptly change from positive to negative or vice versa when the dipoles flip. In practice, this transition is slightly slower and there is a marginal shift away from a vertical transition in the P-V curves during switching.

The area under the \( I(t) \) peaks is proportional to the total switched polarization and the position of the peak maximum corresponds to the coercive voltage. The asymmetry observed in switching current for two states of polarization represents the imprint in the sample which is a characteristic property of fabricated ferroelectric thin film devices. This suggests that films of ferroelectrics can have unipolar character, strongly preferred polarization direction in their as-grown state, and that the direction of the unipolarity correlates with the sense of the imprint. Imprint results from trapped charges, charge defects, and other defect dipole complexes, as well as stress gradients.\textsuperscript{45,46} The sharpness of the switching current is a hallmark of a superior ferroelectric material.
Another important feature of the P-V loops is the polarization remaining at no applied electric field. This polarization is defined as remnant polarization ($P_R$). It is a result of the magnitude and orientation of the inherent ferroelectric dipoles of the material that remain after the removal of the applied electric field. A better orientation of dipoles means a higher remnant polarization. In general, the remnant polarization tends to increase when the applied field increases, because at higher applied fields it becomes more likely for a higher percentage of dipoles to become aligned. These dipoles do not flip back until a minimum electric field required to reorient the dipoles, defined as the coercive field ($E_C$), of the opposite polarity is reached.

The maximum polarization reached by the MFM capacitor is defined as the saturation polarization ($P_S$). For ideal MFM capacitors, the ratio of $P_R$ to $P_S$ should approach unity; the polarization at zero applied bias should be nearly the same as the polarization at large applied fields. When $P_R/P_S$ is one, there is a distinct state of polarization, making it easier to distinguish between the opposite polarities.

### 3.2.4 Atomic force microscopy

Atomic Force Microscopy (AFM) is a measurement that uses a cantilever with a very fine tip to probe the surface of materials with a resolution on the atomic scale. The process involves dragging a very sharp tip at the end of a flexible cantilever across the surface of the sample while monitoring the minute changes in force between the tip and surface using an optical probe. The tip is moved by a piezoelectric system with high precision while its position is recorded using a laser.
focused on the back of the cantilever whose reflection is incident on a photodiode detector that transforms the information to a 2D image. AFM is commonly employed for both conducting and insulating surfaces.

AFM can be performed in 3 different operating modes. The first mode is called contact mode. The force on the tip is held constant as it drags across the surface and this force is monitored by the laser positioning system to create the image. Contact mode is most commonly used for hard surfaces, but is difficult to employ for soft, liquid, or polymer surfaces because the dragging motion tends to damage the surface and distort the image through interactions of surface tension in liquids or trapped electrostatic charges. The second mode is called non-contact where the tip hovers over the surface and interacts using van der Waals and other weak forces. This mode is the least commonly employed because of the weak signals from surface features. The third mode is called tapping mode in which the tip is in contact with the surface only occasionally. The cantilever is provided a constant driving force where it oscillates near a resonant frequency (usually a few hundred kHz). The amplitude of oscillations is constantly monitored by the laser/photodiode system. Tapping mode is used for surfaces that contact mode has trouble imaging. As all of our sample are polymers or soft, organic compounds, we have employed the tapping mode for all AFM images presented in this work.
3.2.5 Scanning electron microscopy

Scanning Electron Microscope (SEM) microscopy is a non-invasive, non-destructive technique often employed to examine the surface characteristics of materials in the subnanometer range. Electrons are focused on the surface of some sample, they interact with the atoms in the sample at this location, the beam is scanned across the surface by raster coils to probe different regions, and scattered electrons are collected by a detector to form an image. It is a sensitive tool to probe topography as well as composition of the sample surface.

An SEM is made up of an electron source (most commonly a field emission gun or tungsten filament) that emits electrons in a beam, one or two condenser lenses that govern the intensity of the electron beam, an objective lens that focuses the electron beam on the surface of the sample, scanning coils that control the placement of the beam, and an electron detector connected to a cathode ray tube (CRT) display. SEM microscopy is generally carried out under vacuum conditions to limit the interaction of electrons (both incident and scattered) with ambient gas molecules. One of the important limitations of SEM is charging effects. Samples that are insulating or poor conductors tend to trap electrons that do not escape from the sample surface and can cause bright spots in images that prevent accurate reproduction of topography. Many solutions such as conductive coatings or addition of charge transfer paths have been devised to overcome this limitation.

There are four important parameters of the electron beam that govern the quality of the image. The electron probe current ($i_p$) is a measure of the number of electrons incident on the sample surface per unit time; electron probe
convergence ($\alpha_p$) is the angle that the edge of the electron beam makes with the vertical and is the largest contributor to aberration and depth of focus control; electron probe diameter ($d_p$) is the diameter of the beam at the sample surface and is limited by probe current and convergence angle; and the accelerating voltage ($V_{\text{acc}}$) is the energy given to incident electrons which controls the interaction volume (essentially the depth or size of the region where electron interactions occur in the sample). Controlling these four parameters and understanding the trade-offs between them are the most important part of SEM operation.

There are several different signals that can be detected from the interaction of electrons in the material. These signals are a result of either elastic or inelastic scattering of electrons and include secondary electrons, backscattered electrons, x-ray photons, and Auger electrons. Backscattered electrons are electrons that have undergone elastic collisions within the material and subsequently exit the surface of the material and constitute the largest percentage of interactions. Secondary electrons are conduction electrons in the sample that have been excited enough by the electron beam to exit the surface of the sample. X-ray photons occur when beam electrons interact with core electrons in the material, causing a relaxation of higher energy electrons that will then emit a photon during this transition. Auger electrons occur when an electron in a higher energy level interacts with one of these high-energy x-rays due to relaxation causing the electron to be emitted.

The different signals occur from different regions of the interaction volume, because the different electrons each have a different depth that they are capable
of escaping the surface from. Secondary electrons come from a very small region near the surface of the material. Due to this very small volume, secondary electrons provide the best resolution of surface features. The secondary electrons are low in energy, so their signal must be enhanced by an Everhart-Thornley photomultiplier detector before being displayed on the CRT display. Backscattered electrons have a much larger volume that they can escape from. The depth from which these backscattered electrons originate is strongly linked to the atomic number of atoms they scatter from, so backscattering is often used to provide information on the chemical composition of different regions of the sample. X-rays come from a region even deeper than backscattered electrons and are used in elemental analysis because each element has a unique x-ray spectrum.
4 The role of solvents in PVDF-TrFe/pentacene based field-effect transistor performance

4.1 Motivation

Recent work on the effect of solvents used to dissolve the gate insulating layer for spin casting has shown that a large dipole moment solvent enhances the performance of pentacene and other FETs with non-ferroelectric insulators.\textsuperscript{47,48,49} High dipole moment solvents help reorganize the dipolar field in the polymer dielectric layer, modifying the interaction between the dielectric dipoles, and thus improving the switching frequencies and the saturation mobility of long channel organic FETs.\textsuperscript{47} Solvents may also act to increase the crystallinity of the dielectric without complex annealing processes. Furthermore, the use of high dipole moment solvents leads to a higher stability for MIS diode devices highlighted by a decrease in flat band voltage shift ($\Delta V_{FB}$).

An extensive study of the differences in device performance based on solvent choice for PVP and polymethyl methacrylate (PMMA) MIS and FET devices was performed by Ukah, et. al.\textsuperscript{48} A drastic improvement in charge carrier mobility, lower operating voltages, better stability against bias stress, and faster switching times were achieved by using a high dipole moment solvent in both PVP/pentacene and PMMA/pentacene devices. This allows for the use of thin, low-\textk dielectrics to be used in all-organic FET devices and MIS diodes. FET mobility results are shown in Table 4.1 below. These enhancements have been attributed to an improved
dipolar orientation in the dielectric layers that have been dissolved in high-dipole moment solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dipole moment (Debye)</th>
<th>FET mobility PMMA (cm²/Vs)</th>
<th>V_{Th} (V)</th>
<th>FET mobility PVP (cm²/Vs)</th>
<th>V_{Th} (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>0.38</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anisole</td>
<td>0.99</td>
<td>0.001</td>
<td>-8.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Butyl acetate</td>
<td>1.84</td>
<td>0.04</td>
<td>-2.7</td>
<td>0.09-0.2</td>
<td>-1.6</td>
</tr>
<tr>
<td>Propylene carbonate</td>
<td>4.90</td>
<td>0.1-0.2</td>
<td>-1.0</td>
<td>1</td>
<td>1.0</td>
</tr>
<tr>
<td>Dimethyl sulfoxide</td>
<td>4.10</td>
<td></td>
<td></td>
<td></td>
<td>-1.3</td>
</tr>
</tbody>
</table>

Table 4.1. Properties of Solvents used for dissolving PMMA and PVP, and their corresponding pentacene FET charge carrier mobilities and threshold voltages.

It is reasonable to question if the improvement in device performance is a result of some amount of solvent remaining in the dielectric film after annealing. To confirm that this is not the case, two high temperature annealing studies were conducted on PVP based devices. The first study involved changing the temperature used for annealing after spincoating a solution of PVP dissolved in propylene carbonate (PC). Three devices were baked for one hour under nitrogen atmosphere, one at 100 °C, one at 140 °C, and the final at 170 °C. Detailed MIS diode characterization of these devices was performed. All devices performed nearly identically, with similar capacitance-voltage and conductance-voltage characteristics, density of interface traps, and flat band voltage shift. This indicates that 100 °C is sufficient to purge the solvent from the dielectric film after spincoating.
The second study compared two devices using PVP dissolved in dimethyl sulfoxide (DMSO) (4 wt%). Solutions of PVP were spincoated onto aluminum coated glass slides using 6 drops of solution and a rotation of 5000 RPM for 60 seconds. The first device was baked at 100 °C in a nitrogen atmosphere for one hour and the second device was annealed under vacuum for four hours at 130 °C. Again, all devices performed the same, yielding similar charge carrier mobilities ($\approx 8 \times 10^{-2}$ cm$^2$V$^{-1}$s$^{-1}$), $I_{on}/I_{off}$ ($\approx 10^3$), and $V_{Th}$ ($\approx -1.4$ V). Fig. 4.1 shows the output and transfer curves of the baked and vacuum-annealed devices. These results confirm that the solvent is driven off and only the dielectric film remains, thus the improvement in device performance is a result of the reorganization of the dipolar field in the dielectric film due to high dipole moment solvents rather than the presence of the solvent in the film. Device parameters are shown in Table 4.2.

<table>
<thead>
<tr>
<th>Annealing method</th>
<th>$\mu_{sat}$ (cm$^2$V$^{-1}$s$^{-1}$)</th>
<th>$I_{on}/I_{off}$</th>
<th>$V_{Th}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 °C, baked</td>
<td>.08-.09</td>
<td>$10^3$</td>
<td>-1.4</td>
</tr>
<tr>
<td>130 °C, vacuum annealed</td>
<td>.06-.08</td>
<td>$10^3$</td>
<td>-1.4</td>
</tr>
</tbody>
</table>

**Table 4.2.** Summary of device characteristics for PVP/pentacene FETs using DMSO with different annealing conditions.
Owing to the fact that conduction in FET devices occurs along the dielectric-semiconductor interface, it is important to improve the contact between the two layers as much as possible. In general, a smoother dielectric surface (i.e. low root-mean-square surface roughness) results in a better device performance. To see if the improvement in FET charge carrier mobility resulting from the use of a high dipole moment solvent in PVP-Pentacene devices comes from an improved surface, SEM images of thin PVP films on aluminum-coated glass spincoated from 3 different solvents were taken. PVP was dissolved in butyl acetate (BTAc), DMSO, and PC. The samples were prepared by evaporating 60 nm of Aluminum onto three one-inch-by-one-inch glass slides. Each dielectric was added by
spincoating 5 drops of solution at 5000 rpm for 60 seconds on top of the aluminum layer. The surface morphology of PVP-BTAc, PVP-DMSO, and PVP-PC films was examined using a Hitachi S-4700 cold field emission SEM at the University of Missouri Electron Microscopy Core Facility. The SEM images were taken with accelerating voltages of 1 keV and beam currents of 10 µA. The low accelerating voltages were used due to the thin (approximately 70 nm) films. The images indicate no difference in the formation of the dielectric layers. The layers are nearly indistinguishable and quite uniform. SEM images of these three devices are shown in Fig. 4.2.

![SEM images](a) PVP-BTAc (b) PVP-DMSO and (c) PVP-PC.

**Fig. 4.2.** Scanning electron microscope images of (a) PVP-BTAc (b) PVP-DMSO and (c) PVP-PC.
4.2 PVDF-TrFe/pentacene field effect transistors

After observing the improvement of FET device characteristics using high dipole moment solvents with paraelectric dielectrics, we have extended this concept to examine the role of solvent choice in the performance of ferroelectric, PVDF-TrFe based FETs, MIS diodes, and MFM structures. In particular, $\mu_{\text{sat}}$ and $I_{\text{on}}/I_{\text{off}}$ improve by an order of magnitude in pentacene ferroelectric FETs (FeFETs) when PVDF-TrFe is dissolved in a high dipole moment solvent. The remnant polarization in MFM devices also significantly improves with the use of high dipole moment solvents.

Solutions of PVDF-TrFe (75/25 molar ratio) were made using solvents with varying dipole moments (D). Solutions of PVDF-TrFe dissolved in DMSO (4.1 D at 20°C), dimethyl formamide (DMF) (3.8 D at 20°C) and 2-butanone (MEK) (2.7 D at 20°C) at concentrations of 2.4 wt%, 4.3 wt%, and 1.5 wt%, respectively, were heated on a hot plate at 80 °C until completely dissolved. The solutions were spincoated (2000 rpm) on Al-coated glass slides in a nitrogen glove box and the films were annealed for one hour at 135 °C. Pentacene was thermally evaporated to an approximate thickness of 60 nm on top of the PVDF-TrFe films. Gold top contacts were then thermally evaporated with varying channel lengths and widths for FETs and differing diameters for circular MIS devices. For the MFM devices, gold top contacts were evaporated through the shadow mask directly onto the PVDF-TrFe films. Two batches of pentacene FeFETs with more than 10 devices from each solvent were tested.
The polarization versus applied electric field (P-E) hysteresis loops of PVDF-TrFe MFM capacitors are shown in Fig. 4.3 for the three different solvents. The leakage currents were at least three orders of magnitude lower than the displacement current. The dielectric film thicknesses were inferred from capacitance measurements of MFM and MIS devices (in the accumulation region) and further confirmed with a reflectometer. Using the typical relative permittivity ($\varepsilon_F$) of 16 reported in literature, the thicknesses of the films were found to be 190 nm, 200 nm, and 300 nm for DMSO, DMF, and MEK solvents, respectively. $P_R$ is found to be the largest for the DMSO sample (5.6 $\mu$C/cm$^2$), which is about 20% higher compared to PVDF-TrFe films dissolved in MEK and DMF. Additionally, $P_R/P_S$ for DMSO is 0.75, DMF is 0.68, and MEK is 0.73, indicating that the DMSO device shows a better ferroelectric nature compared to the other two. The coercive field ranges from 52 MV/m to 74 MV/m, as shown in Table 4.3, with the lower value for the MEK sample.

Fig. 4.3. Polarization-electric field hysteresis curves for Al/PVDF-TrFe/Au ferroelectric capacitors where the ferroelectric layer was dissolved in (a) DMSO, (b) DMF, and (c) MEK. The thickness of the films was slightly different as mentioned in the text, and the measurements were performed at 1 kHz.
Table 4.3. Pentacene MFM characteristics for different solvents used to dissolving PVDF-TrFe.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dipole Moment (D)</th>
<th>Coercive Field (MV m(^{-1}))</th>
<th>Remnant Polarization ((\mu)C cm(^{-2}))</th>
<th>(P_R/P_S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSO</td>
<td>4.1</td>
<td>69.0</td>
<td>5.6</td>
<td>0.75</td>
</tr>
<tr>
<td>DMF</td>
<td>3.8</td>
<td>74.0</td>
<td>4.6</td>
<td>0.68</td>
</tr>
<tr>
<td>MEK</td>
<td>2.7</td>
<td>52.0</td>
<td>4.9</td>
<td>0.73</td>
</tr>
</tbody>
</table>

Fig. 4.4. I-V measurements for PVDF-TrFe MFM devices dissolved in (a) DMSO, (b) DMF, and (c) MEK.

The current-voltage characteristics of the same MFM capacitors are shown in Fig. 4.4. Current vs. voltage measurements for the three different solvents were
recorded for different applied voltages at 1 kHz to better comprehend the switching current. The sharpness of the switching current is indicative of better ferroelectric thin films. The full-width-half-max FWHM of the current pulse shown as an inset in Fig. 4.4 can be qualitatively assessed for understanding polarization switching characteristics. A decrease in the FWHM indicates a more square hysteresis in the P-E loop, which is a requirement for better ferroelectric devices. The DMSO based devices exhibit the smallest FWHM of the current pulse which means it has the sharpest switching in the P-E loops.

Fig. 4.4 represents the current response with the applied voltage of the ferroelectric capacitor. It is clear to see that with the increase in the applied voltage, the switching current is predominantly sharper and attains larger values. The sharp features of the current pulse for the DMSO sample rule out the possibility of any leakage current which could enhance the polarization values to be calculated by integrating the current pulse. The time integration of the current response is used for determination of the polarization values.

The displacement ($D$) is the sum of both linear and ferroelectric polarization, and from Maxwell’s equation we know that $D = \varepsilon_0 \varepsilon_F E + P(E)$, where $\varepsilon_0$ and $\varepsilon_F$ are the vacuum and relative permittivity, respectively; $E$ is the electric field and $P(E)$ is the ferroelectric polarization. As long as the applied field is lower than the coercive field, only the linear dielectric polarization contributes, which would result in no hysteresis and thus no ferroelectric polarization. The displacement curves in Fig. 4.3 were measured from an unpolarized state in all three cases. It is clearly seen that the DMSO based sample shows a hysteresis in its displacement even at the
lowest measured voltage, indicating that the dipoles in the copolymer are more ordered initially, even before an electric field is applied. We found a similar behavior in non-ferroelectric based pentacene FETs where DMSO and another high dipole moment solvent, propylene carbonate, yielded the best switching times, indicative of an improved dipolar orientation. From the polarization curves it can thus be inferred that dissolving ferroelectric dielectrics in a high dipole moment solvent results in low-operating voltage devices since the ferroelectric response can be measured at lower voltages.

In order to see if the performance of PVDF-TrFe pentacene FETs also depends on solvent polarity, the transistor characteristics and capacitance-voltage (C-V) features were measured from un-optimized FETs and MIS structures. In these devices no additional steps were taken for improving the surface roughness of the copolymer films.

Fig. 4.5 shows the current-voltage (I-V) output and transfer characteristics from pentacene FeFETs where DMSO and MEK were used to dissolve the dielectric layer. The FeFETs exhibit good current modulation with distinct linear and saturation regimes, and could be operated well below -3 V, with threshold voltages around -1.0 V for all three devices. These are typical characteristics of many devices that were measured from each of the solvents. The electrical parameters of the FeFETs were obtained from the saturation regime by using $\mu_{sat} = \frac{2L}{WC_0} \left( \frac{\partial \sqrt{I_{ds}}}{\partial V_g} \right)^2$, as defined in Sec. 2.2. Note, for the transfer characteristics, the gate voltage was swept up to $V_{ds}$, which was selected in the
saturation regime. The range of $\mu$ obtained for the FeFETs are $0.013-0.017 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, $0.005-0.008 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, and $0.005-0.007 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for DMSO, DMF, and MEK samples, respectively. These results clearly show an increase in carrier mobility with DMSO, which has the highest dipole moment. Table 4.3 lists FeFET properties for all three solvents.

**Fig. 4.5.** (a,b) Output and (c,d) transfer characteristics of pentacene FeFETs where the PVDF-TrFe layer was dissolved either in DMSO or MEK. The W/L ratio is 10.

However, the values of mobility reported here are lower than those for state-of-the-art pentacene devices utilizing organic, non-ferroelectric materials as the
gate dielectric. Pentacene devices using non-polar organic dielectrics have been shown to have p-type mobilities ≈2 cm²V⁻¹s⁻¹.⁴⁷,⁴⁹,⁵⁰ Typical values of mobility reported for bottom gate ferroelectric PVDF-TrFe/pentacene devices are 0.005-0.05 cm²V⁻¹s⁻¹.⁵¹,⁵²,⁵³ The decreased mobility for ferroelectrics is attributed to the high surface roughness of PVDF-TrFe,⁵⁴ (as can be seen in our AFM images), as well as the more conductive nature of PVDF-TrFe compared to other paraelectric dielectrics such as PVP or PMMA. The high surface roughness also contributes to a low $I_{on}/I_{off}$ of the current because of a high leakage between gate and drain. Some groups have solved the surface roughness and leakage problems by inverting the device stack, adding another insulating layer, or mechanically stretching the PVDF-TrFe layer.⁵⁴,⁵⁵,⁵⁶ However, inverting the device is not an accessible resolution for pentacene due to the small number of mutually orthogonal solvents for pentacene and PVDF-TrFe; all reported top-gate devices used polythiophene as the semiconducting material. Mechanical stress has been effectively used to reduce surface roughness of PVDF-TrFe for improved pentacene mobilities of 0.1 cm²V⁻¹s⁻¹ in bottom-gate FET structures.⁵⁴ Patterning the gate in a bottom-gate architecture has also improved pentacene mobility to 0.18 cm²V⁻¹s⁻¹.⁵⁷

Since the goal of this work was to mainly study the role of solvent polarity on the PVDF copolymer and its impact on device performance, the device fabrication strategy was kept to the simplest. We point out that high dipole moment solvents such as DMSO and DMF improve $I_{on}/I_{off}$, and DMSO further improves other pentacene FET characteristics. It is difficult to gauge the extent of structural changes of pentacene, if any, at the interface solely from x-ray diffraction and AFM.
measurements. As pointed out earlier, switching frequencies of pentacene FETs improve with non-ferroelectric dielectrics dissolved in high dipole moment solvent, which is an indication of a re-organization of the dipolar field in the dielectric layer.

The I-V characteristics of pentacene FeFETs display the typical hysteresis in measured current, which arises from the polarization state of the ferroelectric layer. Fig. 4.6 (a) through (c) show representative I-V hysteresis curves from DMSO, DMF, and MEK based pentacene FeFETs. These devices were from another batch with slightly higher operating voltages, compared to the electrical characteristics of FeFETs shown in Fig. 4.5. The gate bias was swept from positive to negative voltage until the leakage current was still small, and swept back to positive voltages. The interface traps become filled with holes at large negative gate biases in excess of the coercive fields. This trap-filling results in an increase in the conductivity, and measured current, which depends both on carrier density and carrier mobility. The increased conductivity remains even after the removal of the gate bias, allowing for a non-destructive readout using a small drain-source voltage to measure either a high or low conductivity. Polarization can be reversed by applying a positive gate bias equal to the coercive field, which returns the device to the off state. The maximum changes in $V_{Th}$ for all three solvents are similar. Again, one observes a higher hysteresis at lower voltages for the DMSO device.
Fig. 4.6. Transfer curves for pentacene FeFETs for selected values of gate bias sweeps where the PVDF-TrFe was dissolved in (a) DMSO, (b) DMF, and (c) MEK.

SS and $N_{trap}^{max}$ were estimated for the three different solvents using the relationships defined in Eqs. 2.10 and 2.11. Our results are similar to reported values\textsuperscript{58} and all FET characteristics are summarized in Table 4.4.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dipole Moment (D)</th>
<th>FET Mobility (cm$^2$V$^{-1}$s$^{-1}$)</th>
<th>$I_{on}/I_{off}$</th>
<th>SS (V/decade)</th>
<th>$N_{trap}^{max}$ (cm$^{-2}$) ($\times 10^{13}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSO</td>
<td>4.1</td>
<td>0.013-0.017</td>
<td>$10^3$</td>
<td>2.0</td>
<td>1.90</td>
</tr>
<tr>
<td>DMF</td>
<td>3.8</td>
<td>0.005-0.008</td>
<td>$10^2$</td>
<td>1.7</td>
<td>1.65</td>
</tr>
<tr>
<td>MEK</td>
<td>2.7</td>
<td>0.005-0.007</td>
<td>10</td>
<td>2.4</td>
<td>1.31</td>
</tr>
</tbody>
</table>

Table 4.4. FeFET characteristics of PVDF-TrFe/pentacene devices using different solvents to dissolve PVDF-TrFe.

C-V measurements were performed on MIS structures with all three solvents. Fig. 4.7 shows C-V hysteresis of the three PVDF-TrFe/pentacene MIS devices. The DMSO based MIS structure shows the largest hysteresis with a shift in the flat-band voltage ($\Delta V_{FB}$) of 1.9 V. $\Delta V_{FB}$ for the DMF and MEK samples were 1.2 V and 0.9 V, respectively. All measurements were taken from an unpolarized state and the coercive voltage was not reached. The C-V hysteresis again shows
that large dipole moment solvents result in a higher polarization of the PVDF-TrFe layer.

**Fig. 4.7.** Hysteresis in C-V measurements for PVDF-TrFe/pentacene MIS diodes using (a) DMSO, (b) DMF, and (c) MEK.

In summary, our study presents a proof of concept that high dipole moment solvents improve pentacene FeFET characteristics, which is most likely due to a better orientation of the polymer chains in PVDF-TrFe, and thus an improved semiconductor-ferroelectric interface. Molecular dynamics simulations of other polymer dielectrics show an enhancement in the end-to-end polymer chain distance with increasing dipole moment of the surrounding solvent molecules. It is conceivable that PVDF-TrFe, which is mainly in an all-trans conformation, remains in a more extended polymer chain in solution with high dipolar solvents. The extended conformation of the chains in solution is further maintained upon spincoating and baking. The P-V measurements demonstrate that DMSO, with the highest dipole moment, results in a higher remnant polarization in PVDF-TrFe-based MFM devices. This work opens up a facile processing route for spincoating PVDF-TrFe and other ferroelectric dielectric films for improved organic FETs and memory devices.
4.3 AFM and XRD on PVDF-TrFe and PVDF-TrFe/Pentacene Devices

4.3.1 AFM on PVDF-TrFe films

Again, because the performance of FET devices depends so strongly on the interface between the dielectric and semiconductor, the surface of the PVDF-TrFe film was examined using atomic force microscopy (AFM). For this study, nine samples were prepared. Each sample had thermally annealed aluminum (~60 nm) on a 0.5”x0.5” glass slide. Three solutions of PVDF-TrFe (75/25 molar ratio) were prepared: one dissolved in DMSO (4.1 wt%), one dissolved in DMF (3.9 wt%), and one dissolved in MEK (1.6 wt%). All nine slides have PVDF-TrFe spincoated on top of the aluminum, three each of the three different solvents. The spincoating recipe was the same for all solvents. Three drops of solution were placed on the stationary slide. The slide was then rotated at a speed of 1600 RPM for 50 seconds. Samples were then placed directly into an oven to bake at 135 °C for 90 minutes. Three samples were left with only PVDF-TrFe film, one of each solvent. Three of the samples, one of each solvent, then had 6 nm of pentacene thermally evaporated on top of the PVDF-TrFe. The final three samples, one of each solvent, had 58 nm of pentacene thermally evaporated onto the ferroelectric.

AFM images of all nine films were taken using the tapping mode on a Nanosurf Flex-Axiom AFM at the LME/LNLS (Laboratory of Electron microscopy of the Brazilian Synchrotron Light Laboratory, Campinas, Brazil). Fig. 4.8 shows the comparison of PVDF-TrFe films using DMSO, DMF, or MEK as the solvent used for spincoating. As stated earlier, PVDF-TrFe is known to form thin films with
relatively high surface roughness as compared to many typical organic dielectrics. An area of 3×3 µm² was examined for each film. The RMS roughness of the films are 2.70 nm for DMSO, 6.49 nm for DMF, and 3.43 nm for MEK. The surfaces of films formed using DMSO and MEK have very similar characteristics. They both form large, homogeneous domains, whereas the DMF sample appears to have a more varied domain size with smaller domains dominating.

**Fig. 4.8.** 3×3 µm² area AFM images of PVDF-TrFe films dissolved in (a) DMSO, (b) DMF, and (c) MEK.

### 4.3.2 AFM on pentacene/PVDF-TrFe

**Fig. 4.9.** 3×3 µm² area AFM images of 6 nm of pentacene thermally evaporated on top of PVDF-TrFe films dissolved in (a) DMSO, (b) DMF, and (c) MEK.
An image of a 3×3 μm² area of 6 nm thickness pentacene on top of the three PVDF-TrFe films is shown in Fig. 4.9. Again, the pentacene film on PVDF-TrFe (DMF) exhibits the highest RMS roughness (9.54 nm) and the DMSO and MEK samples show similar, smaller roughness (4.47 nm and 3.50 nm, respectively). Images of a 10×10 μm² area of the final set of samples with 60 nm of pentacene on top of PVDF-TrFe films is shown in Fig. 4.10. These films appear to be almost identical, with the typical dendritic features of pentacene present in all three. It is challenging to differentiate the films as the dendrites are of very similar size in all three samples.

**Fig. 4.10.** 10×10 μm² area AFM images of 60 nm of pentacene thermally evaporated on top of PVDF-TrFe films dissolved in (a) DMSO, (b) DMF, and (c) MEK.

It is difficult to come to any conclusion about the origin of FET device improvement based on these AFM images of surface morphology. The devices using DMSO and MEK are the two that perform most differently, yet they have the most similar morphological characteristics. It is likely that the different solvents are the genesis of some other modifications in the ferroelectric films – such as
improved dipolar order or a change in crystallinity causing larger ferroelectric dipoles or more desirable orientation of these dipoles – that causes device enhancement. Surface morphology is not the only contribution to device performance; the orientation of dipoles near the surface of the semiconductor/dielectric interface also have a strong effect on the interface transport properties in organic FETs. High dipole moment solvents tend to improve the dipolar order, as indicated by the work of Ukah, et. al.\textsuperscript{48} Transient C-V measurements performed on long-channel (50 μm) PVP/pentacene FET devices show an improved switching time for high dipole moment devices. Long-channel, top-gate pentacene FETs using patterned PVP dissolved in PC as the dielectric yield a bandwidth frequency $\omega_T \sim 75$ kHz at 5V, which is among the highest achieved switching frequency for long-channel organic FETs.

4.3.3 XRD on pentacene/PMMA

X-ray diffraction (XRD) has been employed in order to examine the structural characteristics of pentacene on insulators that have been fabricated using solvents of differing dipole moment during spincoating. Pentacene thin films ($\sim 15$ nm) grown on PMMA (dissolved in three different solvents) were characterized. The XRD patterns shown in Fig. 4.11 contains a series of (00k') lines. The film consists of mainly one phase with a first order diffraction peak at 5.6°, corresponding to a lattice separation of 15.8 Å. PC and DMSO have a higher dipole moment compared to BTAc. The XRD peak positions and widths are similar for all three suggesting that the structural differences are minimal.
4.3.4 Effect of annealing time on pentacene/PVDF-TrFe

Another AFM study of the effect of annealing time on surface morphology for PVDF-TrFe dissolved in either DMSO or MEK was also performed. Oliveira et al. found that piezoelectric response and degree of crystallinity increased with increasing annealing time at an annealing temperature near the Curie temperature. Solutions of PVDF-TrFe dissolved in DMSO (4.2 wt%) and MEK (1.7 wt%) were spincoated onto aluminum coated (60 nm) 0.5”×0.5” glass slides. Three drops of solution were placed on the substrate before rotating at 1600 RPM for 45 seconds. The slides were then annealed in a nitrogen atmosphere at 135 °C for either 1 hour or 3 hours. Images were taken using a Digital Instruments Nanoscope IIIa MMAFM-2 AFM. 5×5 μm² area AFM images of the different samples are shown in Fig. 4.12. The samples annealed for 1 hour exhibit similar surface roughness to the 3 hour samples (8.3 nm vs. 6.1 nm for MEK; 6.7 nm vs. 4.8 nm for DMSO).
6.8 nm for DMSO). For both solvents, it appears that larger, more defined crystals are formed by the PVDF-TrFe film when annealed for only 1 hour.

Fig. 4.12. 5×5 µm² area AFM images of PVDF-TrFe films annealed for different amounts of time at 135 °C. (a) DMSO, 1 hr; (b) MEK, 1 hr; (c) DMSO, 3 hr; (d) MEK, 3 hr.

These two different annealing times have also been compared in FET devices. The 1 hour annealing results are from the devices discussed earlier in Sec. 4.2, so they have the same preparation conditions. The 3 hour annealed devices were made using 4.0 wt% DMSO, 4.0 wt% DMF, and 1.4 wt% MEK solutions. These solutions were spincoated onto 1”×1” aluminum coated glass by adding 6 drops of solution to the wafer after spinning had begun and were then allowed to spin at 1900 RPM for 60 seconds. The films were then immediately annealed in a nitrogen atmosphere at 135 °C for 3 hours. 60 nm of pentacene was thermally evaporated on top of the PVDF-TrFe films followed by 50 nm of gold
through a shadow mask to be used as the top contacts. The performance of both sets of devices are quite comparable. There is a decrease in mobility accompanied by a slightly higher $I_{\text{on}}/I_{\text{off}}$ for the 3 hour devices as well as a larger hysteresis in the I-V transfer characteristics. This increase in $\Delta V_{\text{Th}}$ is likely a result of slightly different film thicknesses and different applied gate biases rather than a consequence of the different annealing times. The amount of polarization for the ferroelectric dipoles comes from the applied electric field, so thinner films have better orientation of dipoles at lower applied voltages. Table 4.5 summarizes the similarities in FET performance.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\mu_{\text{sat}}$ (cm$^2$V$^{-1}$s$^{-1}$) 1 hr</th>
<th>3 hr</th>
<th>$I_{\text{on}}/I_{\text{off}}$ 1 hr</th>
<th>3 hr</th>
<th>Max. $\Delta V_{\text{Th}}$ (V) 1 hr</th>
<th>3 hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSO</td>
<td>.013-.017</td>
<td>.008-.001</td>
<td>$10^3$</td>
<td>$10^2$</td>
<td>5</td>
<td>4.5</td>
</tr>
<tr>
<td>DMF</td>
<td>.005-.008</td>
<td>.001-.002</td>
<td>$10^2$</td>
<td>$10^3$</td>
<td>7.5</td>
<td>4</td>
</tr>
<tr>
<td>MEK</td>
<td>.005-.007</td>
<td>.002-.003</td>
<td>10</td>
<td>$10^2$</td>
<td>5.5</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 4.5. Comparison of PVDF-TrFe (1 hr annealing)/Pentacene to PVDF-TrFe (3 hr annealing)/Pentacene devices.

Both AFM and XRD measurements indicate that there is very little structural or morphological differences between devices using different solvents for spincoating the dielectric. This means that the differences in FET characteristics have some other origin. The work by Oliviera$^{28}$ indicating an improved piezoelectric response of PVDF-TrFe with increased annealing times sounds favorable, but the accompanying decrease in crystal size likely has an adverse effect when combined with the domains of pentacene. The growth of pentacene, and subsequently FET performance, has been shown to be highly dependent on surface roughness and
surface chemistry of the insulating layer. Higher surface roughness and a more hydrophilic surface both tend to degrade carrier transport. It is also known that higher mobility is correlated to larger pentacene domains. Formation of pentacene from thermal annealing occurs by the formation of nucleation sites as the first few molecules move around the surface of the substrate. The crystals of pentacene are grown from these nucleation sites. The smaller PVDF-TrFe crystal size promotes a more dense distribution of nucleation sites, leading to smaller pentacene domains. Thus, it is expected that the samples annealed for 1 hr would have better FET performance since they exhibit smaller surface roughness and larger crystals.

### 4.4 Photocurrent on PVDF-TrFe/pentacene field-effect transistors

PVDF-TrFe/Pentacene devices for photocurrent measurements were manufactured by dissolving PVDF-TrFe in DMSO (8.0 wt%), DMF (8.0 wt%), or MEK (3.0 wt%). A patterned aluminum gate was deposited using thermal evaporation through a shadow mask onto a 1”×1” glass slide. Eight drops of the PVDF-TrFe solutions were dropped onto the patterned Al glass slides and then spincoated at 1600 RPM for 60 seconds. The samples were then annealed at 135 °C in a nitrogen atmosphere for 3 hours. Pentacene was thermally annealed to a thickness of 60 nm through a patterning mask before 50 nm of gold was evaporated through a shadow mask for the top contacts.
In addition to PVDF-TrFe/pentacene FET devices, we have also examined PVP/pentacene devices. A 5 wt% solution of PVP in propylene glycol monomethyl ether acetate (PGMEA) along with 2 wt% of crosslinking agent PMMF was prepared for spincoating. The PVP film was formed by spincoating at 5000 RPM for 60 seconds on top of 60 nm of Al before annealing in a nitrogen atmosphere at 180 °C for one hour. Pentacene was then thermally evaporated to a thickness of 60 nm before 50 nm gold top contacts were thermally evaporated through a shadow mask.

Transient photocurrent measurements on organic FETs provide information on charge transport phenomena, trap/release processes, trap distribution, and depolarization processes.\textsuperscript{18,62,63} The experiment consists of operating a transistor in either the accumulation or the depletion mode and alternating between illumination and dark conditions on the conduction channel to generate photocarriers while measuring the resulting current as a function of time and illumination. A figure of the experimental setup is shown in Fig. 4.13 below.
When light is incident on the semiconductor, so long as the energy of the photon is larger than the bandgap of the semiconductor, an exciton pair will be generated when an electron is promoted from the valence to the conduction band upon the transfer of energy from the photon. This leaves a hole behind and this electron-hole pair can either recombine to form another photon or separate and form a photocurrent. In an FET structure, where we apply an electric field across the semiconductor using the drain-source voltage, this electron-hole pair tends to separate due to the force from the electric field on the charges. When using a p-type semiconductor (as most organic materials are), the hole has a much higher intrinsic mobility than the electron.

The low mobility of electrons leads to electron trapping in the semiconductor. When illumination is removed, no new photocarriers are being generated and the measured current begins to decay due to recombination of
photocarriers as well as a redistribution of the in-built field created by the separation of these carriers. This process is initially very fast as carriers that are near each other recombine, but the rate of recombination quickly declines due to the spatial separation of holes from trapped electrons.\textsuperscript{64,65} It is more difficult for photocarriers separated by a large distance to recombine.

Because we are in an FET geometry, we can also tune the current using the gate voltage. The retention of photogenerated current is dependent on the gate voltage.\textsuperscript{65} Upon photoexcitation in depletion, negative carriers are immediately trapped, while the more mobile holes move toward the interface, where charge conduction occurs for a transistor. Because of the in-built field at the interface due to the positive $V_g$, holes exit the depletion region and the photogenerated positive carriers are not allowed to approach the interface. The holes generated in the bulk move towards a minimum potential region determined by these drift-diffusion processes to produce a current and the negative charges remain localized in traps. On termination of illumination, charges that are near to each other recombine rapidly. The decay process slows because the negative charges are not mobile, so the recombination cross-section shrinks. The trapped negative charges screen the gate voltage, leading to a metastable dark current that is higher than the dark current before any illumination. This metastable current state persists for many hours.

The current decay rate can be increased by operating the transistor in the accumulation mode.\textsuperscript{66} Applying a negative $V_g$ promotes an increased recombination rate as negative charges in the bulk de-trap. Positive photocarriers
will also be drawn toward the interface, where recombination with electrons trapped in low-energy traps near the interface is much easier due to their new proximity. This leads to a rapid decrease in excess charge carriers, returning the current to its initial, pre-illumination dark current value.

The magnitude of increase in current due to illumination is also dependent on the gate voltage used during illumination. As you increase the negative gate bias (accumulation for p-type materials), the rate of increase in current increases. This is attributed to higher drift/diffusion rates for positive photocarriers towards the conduction channel.

The PVP/pentacene devices show a slightly different response to illumination than what is discussed in the literature. At low positive gate voltages (depletion) the current initially increases quite rapidly and then slowly declines. At higher gate voltages, the initial rapid increase is still seen, followed by a region of slower increase in current. Regardless of gate voltage, there is a very rapid, nearly instant, decrease in current upon removal of incident light and then the off current remains constant. The off current appears to be a square wave, quite different from the behavior displayed in literature. Fig. 4.14 shows the behavior of current when subjected to light at different gate voltages.
Fig. 4.14. Current of a PVP/pentacene FET under illumination in the depletion region at (a) low gate voltages and (b) higher gate voltages.

The work by Ukah involving varying the thickness of PVP films in FET structures indicates that thinner films generally have a lower trap density than thicker films.\textsuperscript{48} Our films are on the order of 75 nm thick, which is in the low-trap range shown by Ukah. Because the transport of photocarriers is highly dependent on trap density, the shape of PVP photocurrent curves are qualitatively different to what is seen in our PVDF-TrFe devices. If negative charges are less often trapped, then they are more readily available for recombination and current will decline much more rapidly upon termination of illumination.

Another feature of the PVP rise currents is the change in shape at higher applied $V_g$. The PVP monomer is slightly polar due to the hydroxy group on the phenyl ring. At large applied gate voltages, this contributes to a marginal polarization of the dielectric film. This polarization causes an additional electric field near the semiconductor/dielectric interface. The electric field allows for the detrapping of positive charges near the interface that can then enter the conduction channel and increase the measured photocurrent.
In our ferroelectric FETs, at low gate voltages, the photoresponse slowly changes upon the introduction or termination of luminescence. Modeling this current response in PVDF-TrFe/pentacene films will give information on the density and depths of traps in FET devices when using different solvents. We have illuminated the conduction region between source and drain of the PVDF-TrFe/pentacene devices using a 532 nm laser diode incident at an approximate power of 12 mW. The drain-source voltage has been set to -4 V for each measurement.

It can be seen in Fig. 4.15 that the photoresponse is slightly different for the different solvents, with differing rise times for all. The rise currents have been fit to a simple exponential curve:

\[ I_{\text{rise}}(t) = I_{\text{ini}} + I_{\text{max}} \left[ 1 - e^{-\frac{t}{\tau_{\text{rise}}}} \right] \]  

Eq. 4.1

Where \( I_{\text{rise}}(t) \) is the photocurrent as a function of time, \( I_{\text{ini}} \) is the initial value of the photocurrent before illumination, \( I_{\text{max}} \) is the maximum value of the current, and \( \tau_{\text{rise}} \) is the time constant related to photocarrier generation. After fitting of the illumination data in the depletion region at \( V_g = +4 \) V to Eq. 4.1, it is found that \( \tau_{\text{rise}} \) is similar for DMSO and DMF, while the MEK has a slower increase in current. This trend indicates that the higher dipole moment solvents serve to improve the dipolar order at the semiconductor/dielectric interface in two ways: (i) decreased trapping near the interface and (ii) increased mobility of positive photocarriers. The lower trap density allows for current to increase more rapidly, as generated carriers are less often trapped near the conduction channel. The increased mobility allows
generated photocarriers to more easily separate and move towards the conduction channel.

The decay has a slightly different behavior, and is unable to be fit with a single exponential function. We will use the function employed by Dutta and Narayan to describe the decay currents:  

\[ I_{\text{decay}}(t) = I_{\text{ini}} - I_{\text{dec}} \ln \left( \frac{t}{\tau_{\text{decay}}} \right) \]  

Eq. 4.2

\( I_{\text{ini}} \) is the initial current before decay, \( \tau_{\text{decay}} \) is the time constant related to carrier lifetime, and \( I_{\text{dec}} \) is linearly proportional to hole mobility, the Bohr radius of positive carriers, and a gate voltage-dependent parameter, \( Q \), describing the density of trapped negative charges which is position dependent. The equation is derived using an assumption that the recombination process for photocarriers shows a persisting trapped negative charge carrier density that is exponentially dependent on position.

\[ \frac{dn(x, t)}{dt} = -[n(x, t)]e^{-\frac{2x}{a}} \]  

Eq. 4.3

Here, \( n(x, t) \) is the trapped charge density at a position \( x \) and a time \( t \), \( x \) is distance away from the channel-bulk interface, and \( a \) is the Bohr radius of positive charges. The last assumption for Eq. 4.2 is that the initial trap density, \( n(x, 0) \), is not uniform, but is inversely proportional to position such that \( n(x, 0) = Q/x \).

Decay current fits to Eq. 4.2 show that the carrier lifetime is similar for all three solvents. This suggests that the trap density and initial photocarrier charge density in the bulk is similar for each of the three devices. Decay processes are
dominated by the recombination of carriers which is limited by the spatial separation of positive carriers near the conduction channel and negative carriers trapped in the bulk. The similarity in decay rates between the three solvents shows that the bulk trap distribution is more or less identical regardless of the solvent used for fabrication of the PVDF-TrFe layer.

While the rate of illumination current rise is more dependent on interface trapping and mobility of hole carriers making their way into the conduction channel, the dark current decays are more dependent on bulk trapping. Differences in rise times during illumination and similarities during decay times point toward an improved interface as the source of FET device improvement with solvent choice, while the bulk properties of pentacene are unaffected by the change in solvent used to spincoat PVDF-TrFe. The photocurrent time constant results are summarized in Table 4.6 and the photocurrent curves as well as the fits to Eq. 4.1 and Eq. 4.2 are shown in Fig 4.15.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\tau_{\text{rise}}$ (s)</th>
<th>$\tau_{\text{decay}}$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSO</td>
<td>$10.15 \pm 0.11$</td>
<td>$86.63 \pm 0.11$</td>
</tr>
<tr>
<td>DMF</td>
<td>$8.46 \pm 0.60$</td>
<td>$88.80 \pm 0.07$</td>
</tr>
<tr>
<td>MEK</td>
<td>$15.47 \pm 0.25$</td>
<td>$86.99 \pm 0.16$</td>
</tr>
</tbody>
</table>

**Table 4.6.** Comparison of decay times ($\tau_{\text{decay}}$, in seconds) for PVDF-TrFe/pentacene devices from Eq. 4.2. $V_g = +4$ V, $V_{ds} = -4$ V, Laser power = 12 mW.
Fig. 4.15. Comparison of photocurrent for PVDF-TrFe/pentacene devices with three different solvents. Experimental data is the solid line and the fits are dashed lines. Characteristic time constants are shown as well.

The dependence of photocurrent decay on gate voltage has also been inspected for the PVDF-TrFe devices. Data was gathered by switching illumination at gate voltages of 0 V, +2 V, +4 V, +6 V, +8 V, and +10 V, in that order. Just prior to each measurement, the devices were poled using -8 V gate voltage during an output measurement. Again we have used 532 nm laser light with an incident power of 15.7 mW and a $V_{ds}$ of -4 V.

Fig. 4.16 shows that the photoresponse of the three PVDF-TrFe/pentacene FETs exhibit a similar trend when $V_g$ is changed. Upon illumination at low gate voltages, the photocurrent slowly increases and nearly saturates after 60 seconds. As the gate voltage is increased, this behavior changes and the photocurrent will immediately saturate and reach some equilibrium value upon illumination.
Dutta and Narayan have attributed the $V_g$ dependence of photocurrent to a rearrangement of the in-built field in the semiconductor layer due to the generation of photocarriers. When using a ferroelectric insulator such as PVDF-TrFe, the strong ferroelectric dipoles in the insulator also serve to rearrange the field near the interface of the semiconductor. Depending on the orientation of these dipoles, transport of majority carriers into the conduction channel is either more or less difficult. We believe the abrupt change in illumination current behavior of PVDF-TrFe at higher positive gate voltages is due to a competition between the field originating from the rearrangement of dipoles in the ferroelectric film and the in-built field from the separation of trapped negative photocarriers from the more mobile positive photocarriers in the bulk of the semiconductor. The combination of the fields creates an equilibrium region in which positive carriers are drawn to. Current is confined to a smaller region when the ferroelectric field is introduced resulting in a space-charge limited current that is saturated. The curves from the DMF sample in Fig. 4.16 (b) show that even as $V_g$ is increased, there is no change in the illumination current, giving merit to this explanation.

Fig. 4.16. Photoresponse of (a) DMSO, (b) DMF, and (c) MEK PVDF-TrFe/pentacene FETs with changing gate voltage.
Table 4.7 shows the behavior of decay times as a function of gate voltage from a fit to Eq. 4.2. Each solvent shows the same trend of an initial decrease in decay time with increasing $V_g$, followed by an increase to a value above the initial, zero bias condition. A longer decay time translates to a longer photocarrier lifetime. The initial decrease in photocarrier lifetime can be explained by the manner in which the experiment was performed. Photocurrent curves were taken starting at zero applied bias and increasing $V_g$ in the positive direction for each iteration. Prior to these photocurrent measurements, the device was poled during an FET output measurement to $V_g = -8$ V. This means that the dipoles in PVDF-TrFe were initially oriented upward (i.e. negative pole nearest to the semiconductor/dielectric interface). This serves to draw excess positive photocarriers into the conduction channel. During the dark portion of the photocurrent measurements when no new carriers are being generated, the current will decay more rapidly because of the propensity of holes to enter the current channel and leave the device.

At higher positive $V_g$, the PVDF-TrFe film will be poled in the opposite direction, meaning the dipoles will flip and the more positive pole will be near the semiconductor. This new orientation of the ferroelectric dipoles serves to prohibit holes from entering the conduction channel, meaning they spend more time in the bulk, extending the carrier lifetime and slowing the decay in current.
<table>
<thead>
<tr>
<th></th>
<th>DMSO</th>
<th>DMF</th>
<th>MEK</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 V</td>
<td>86.95 ± 0.15</td>
<td>81.07 ± 0.45</td>
<td>85.91 ± 0.23</td>
</tr>
<tr>
<td>+2 V</td>
<td>82.17 ± 0.36</td>
<td>88.46 ± 0.18</td>
<td>75.08 ± 0.66</td>
</tr>
<tr>
<td>+4 V</td>
<td>81.70 ± 0.24</td>
<td>90.72 ± 0.10</td>
<td>74.07 ± 0.58</td>
</tr>
<tr>
<td>+6 V</td>
<td>88.33 ± 0.06</td>
<td>90.88 ± 0.05</td>
<td>80.41 ± 0.34</td>
</tr>
<tr>
<td>+8 V</td>
<td>90.82 ± 0.04</td>
<td>90.88 ± 0.03</td>
<td>87.88 ± 0.16</td>
</tr>
<tr>
<td>+10 V</td>
<td>91.10 ± 0.02</td>
<td>91.21 ± 0.02</td>
<td>89.92 ± 0.03</td>
</tr>
</tbody>
</table>

**Table 4.7.** Comparison of decay times ($t_{\text{decay}}$, in seconds) from a fit to Eq. 4.2 for PVDF-TrFe/pentacene devices using different solvents for PVDF-TrFe at different gate voltages.
5 Effect of solvent on other insulator/semiconductor combinations

5.1 Motivation

We have seen an improvement in FET device performance due to an increased dipole moment of solvent used for insulator spincoating in many systems. However, each of these systems has involved pentacene as the semiconductor layer. So we introduce a new active layer in DNTT while keeping PVDF-TrFe as the insulator. We have also only observed FET improvement in one ferroelectric system, so we have used another ferroelectric polymer in PVDF-HFP with pentacene. The device structures and dimensions have been kept identical for these new systems. The trend of increased FET mobility with higher dipole moment is again observed in these new combinations.

5.2 PVDF-TrFe/DNTT field-effect transistors

Electrical Characterization of PVDF-TrFe FET devices using dinaphtho[2,3-b:2',3'-f]thieno[3,2-b]thiophene (DNTT) as the active layer have also been carried out. DNTT devices were manufactured by dropping 6 drops of PVDF-TrFe solution dissolved in DMSO (4.2 wt%) or MEK (1.6 wt%) onto 1”×1” Al-coated glass slides and then spincoating at 1600 RPM for 45 seconds. Samples were then annealed at 135 °C in nitrogen atmosphere for 3 hours. DNTT was thermally annealed to a thickness of 40 nm before 40 nm of gold was evaporated through a shadow mask for the top contacts.
Device characteristics are similar to pentacene results, although devices are slightly less reliable than their pentacene counterparts. The charge carrier mobilities of both pentacene and DNTT devices are nearly identical, however, the $I_{on}/I_{off}$ and threshold voltage shifts of DNTT samples are inferior to the pentacene devices. The results are summarized in Table 5.1. FET transfer characteristics for DMSO and MEK samples are shown in Fig. 5.1 below. CV hysteresis curves are also shown in Fig. 5.2.

![Graphs showing FET transfer characteristics for PVDF-TrFe/DNTT devices using (a) DMSO, (c) MEK. Transfer curves for PVDF-TrFe/DNTT devices using (b) DMSO, (d) MEK.](image)

**Fig. 5.1.** Output curves for PVDF-TrFe/DNTT devices using (a) DMSO, (c) MEK. Transfer curves for PVDF-TrFe/DNTT devices using (b) DMSO, (d) MEK.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dipole Moment (D)</th>
<th>FET Mobility (cm²V⁻¹s⁻¹)</th>
<th>$I_{on}/I_{off}$</th>
<th>SS (V/decade)</th>
<th>$N_{trap}^{max}$ (cm⁻²) (*10¹³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSO</td>
<td>4.1</td>
<td>0.012-0.017</td>
<td>10²</td>
<td>1.9</td>
<td>1.62</td>
</tr>
<tr>
<td>MEK</td>
<td>2.7</td>
<td>0.005-0.008</td>
<td>10</td>
<td>4.9</td>
<td>2.77</td>
</tr>
</tbody>
</table>

**Table 5.1.** Comparison of FET results for PVDF-TrFe/DNTT devices.
Fig. 5.2. CV hysteresis of PVDF-TrFe/DNTT MIS devices.

5.3 PVDF-HFP/pentacene field-effect transistors

Electrical Characterization of pentacene MFM and FET devices using polyvinylidene fluoride-hexafluoro propylene (PVDF-HFP) as the ferroelectric insulator have also been carried out. PVDF-HFP devices were manufactured by dropping 7 drops of PVDF-HFP solution dissolved in DMSO (4.0 wt%), or MEK (3.5 wt%) onto 1”×1” Al-coated glass slides and then spincoating at 1700 RPM for 60 seconds. Samples were then annealed at 135 °C in a nitrogen atmosphere for 2 hours. Pentacene was thermally annealed to a thickness of 60 nm for FET devices and MFM devices were left as is. 50 nm of gold was evaporated through a shadow mask for the top contacts on both FET and MFM devices.

The polarization versus applied electric field (P-E) hysteresis loops of PVDF-HFP MFM capacitors are shown in Fig. 5.2 for the two different solvents. The dielectric film thicknesses were inferred from capacitance measurements of the MFM devices. Using the typical relative permittivity ($\varepsilon_R$) of 12 reported in
literature, the thicknesses of the films were found to be 100 nm for DMSO and 320 nm for MEK solvents. The remnant polarization ($P_R$) is found to be largest for the DMSO sample (1.0 $\mu$C/cm$^2$), which is about 6x higher compared to PVDF-HFP films dissolved in MEK. The shape of these polarization curves are markedly different from the polarization curves of PVDF-TrFe shown in Fig 4.3. The hysteresis is quite small and the transition from one polarity to the other is far from sharp. This indicates that the ferroelectric properties of the HFP copolymer are inferior to those of the TrFe copolymer without post fabrication treatment, as mentioned in Sec. 2.4.

![Polarization-electric field hysteresis curves](image)

**Fig. 5.3.** Polarization-electric field hysteresis curves for Al/PVDF-HFP/Au ferroelectric capacitors where the ferroelectric layer was dissolved in (a) DMSO and (b) MEK. The measurements were performed at 1 kHz.

Pentacene-based FET devices using PVDF-HFP as the insulating layer performed quite similarly to PVDF-TrFe/pentacene devices. They exhibit slightly improved $I_{on}/I_{off}$ and the MEK devices have an improved charge carrier mobility. However, due to the slightly less ferroelectric nature of the HFP copolymer, the threshold voltage shifts are much smaller ($\approx$1 V), even at large applied gate bias.
Output and transfer characteristics of PVDF-HFP-based FETs are shown in Fig. 5.4 and current-voltage hysteresis in the transfer curves is shown in Fig. 5.5. The improved $I_{on}/I_{off}$ and FET mobility indicate that PVDF-HFP would be a good high-k organic insulator, although it is probably not suited to ferroelectric applications, at least without any post-fabrication treatment to improve its ferroelectricity. Table 5.2 shows the important FET parameters for PVDF-HFP/pentacene devices.

**Fig. 5.4.** Output and transfer characteristics of PVDF-HFP/pentacene devices using (a,b) DMSO and (c,d) MEK.
Fig. 5.5. I-V hysteresis characteristics of PVDF-HFP/pentacene devices using (a) DMSO and (b) MEK.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\mu_{\text{sat}}$ (cm$^2$V$^{-1}$s$^{-1}$)</th>
<th>$I_{\text{on}}/I_{\text{off}}$</th>
<th>Max. $\Delta V_{\text{Th}}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSO</td>
<td>0.008–0.011</td>
<td>$10^3$</td>
<td>1.0</td>
</tr>
<tr>
<td>MEK</td>
<td>0.001–0.017</td>
<td>$10^3$</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Table 5.2. Comparison of FET results for PVDF-HFP/pentacene and PVDF-TrFe/pentacene devices.

5.4 Dynamic light scattering on PMMA solutions

Exploring the role of solvents in device performance is one of the aspects of this research. In order to paint a clearer picture of what processes cause the improvement in FET characteristics, it is important to understand what these polymer insulators look like while still in solution. In order to do this, dynamic light scattering (DLS) was performed.

DLS is an optical technique used to find the average molecular weight ($M_w$), mean-squared radius of gyration ($<R_G^2>$), and second virial coefficient ($A_2$) of polymers in
Scattering intensity will be measured for several dilute concentrations of the solution at a constant detector angle and for several detector angles for the same concentration of solution. The reason for these two sets of measurements are to correct for scattering interference phenomena resulting from large particle size (intramolecular interference) and from non-ideal, or inhomogeneous, solutions (intermolecular interference). For large molecules, scattering can occur from different parts of the same molecule or polymer chain. When this occurs, there is interference from the different path lengths of scattered light to the detector. The only angle where this path length is the same is at 0°. Unfortunately, the scattering intensity is drowned out by the intensity of the primary beam at 0°. Therefore it is necessary to measure scattering intensity at several angles and extrapolate to 0° scattering angle. For solutions that are not infinitely dilute, scattering can occur from different macromolecules. The scattered beams from different molecules can interfere at the detector. In order to correct for this interference, scattering intensity is measured for several different concentrations of solution at the same detector angle and then extrapolated to infinite dilution (conc. = 0). The equations of these two extrapolations are given by

Conc. = 0

\[ \frac{kc}{R_\theta} = \frac{1}{M_W} \left[ 1 + \frac{16\pi^2}{3\lambda^2} n_0^2 (R_0^2) \sin^2 \left( \frac{\theta}{2} \right) \right] \]  \hspace{1cm} \text{Eq. 5.1}

Θ = 0

\[ \frac{kc}{R_\theta} = \frac{1}{M_W} + 2A_2c \]  \hspace{1cm} \text{Eq. 5.2}
Here, c is the solution concentration, λ is the laser wavelength in air, \( n_0 \) is the index of refraction of the solvent, and θ is the detector angle. k is a constant depending on the polymer, solvent, and temperature and is defined as

\[
k = \frac{2\pi^2 n_0^2}{\lambda^4 N_A} \left( \frac{dn}{dc} \right) (1 + \cos^2 \theta)
\]

Eq. 5.3

\( N_A \) is Avogadro’s number and \( \frac{dn}{dc} \) is the change in refractive index of the solution with concentration. This value is defined for many solute/solvent combinations and is most commonly measured using a differential refractometer.

\( R_\theta \) is called the Rayleigh ratio and is independent of the incident light intensity and distance to the detector and is defined using the constant k, solution concentration, and molecular weight:

\[
R_\theta = kM_W c
\]

Eq. 5.4

Fig. 5.6. Schematic of the dynamic light scattering experiment.

The extrapolation of the two curves given by Eqs. 5.1 and 5.2 are placed onto the same graph, called a Zimm plot, in order to find the average molecular weight (\( \bar{M}_w \)), mean-squared radius of gyration (\( \langle R_G^2 \rangle \)), and second virial coefficient (\( A_2 \)). The intercept of the \( \theta = 0^\circ \) line and the conc. = 0 line both give \( \bar{M}_w \), the slope
of the conc. = 0 line can give $\langle R_G^2 \rangle$, and the slope of the $\theta = 0^\circ$ line gives $A_2$. The most interesting of these constants for our purposes is the mean-squared radius of gyration. This constant is related to how “stretched-out” the molecule is.

Molecular dynamics simulations are an effective tool to examine the characteristics of polymers in different environments. Tung, et. al. carried out MD simulations on PMMA polymer chains in the presence of different solvent molecules.\textsuperscript{59} They selected solvents of different molecular weights and dipole moments. They found a strong correlation between increasing dipole moment of the solvent and increasing mean-square end-to-end distance, a quantity similar to $\langle R_G^2 \rangle$, of PMMA polymers in solution. We have performed DLS measurements on PMMA in both MEK and toluene.

The dipole moment of MEK is 2.7 D and toluene has a dipole moment of 0.375 D. Solutions for DLS were created by dissolving PMMA in one of the two different solvents to a concentration of 1.0 wt%. Solutions were then diluted to concentrations of 0.8, 0.6, 0.4, and 0.2 wt% by adding the appropriate amount of solvent and then placing the new solution on a hot plate at 45 °C for approximately 30-45 minutes while the previous concentration was being measured. The solvent was always filtered through a 0.22 μm PTFE filter to ensure purity.

The detection system consisted of an ALV/CGS-3 Compact Goniometer System, an ALV/LSE Light Scattering Electrons and Multiple Tau Digital Correlator, and a 633 nm laser diode. The solutions to be measured were placed in a glass cuvette in the detection system in an index matching vat filled with very pure toluene. The detector was swept from 30° to 150° in 30° steps. At each
detector angle, 2 measurements of 60 seconds each were taken and then averaged to record the scattered intensity.

Fig. 5.7. Zimm plots for PMMA dissolved in (a) MEK and (b) Toluene.

The Zimm plots for both solvents are shown in Fig. 5.6. Analysis of this data gives a radius of gyration \( \langle R_G^2 \rangle^{1/2} \) of PMMA of 98 nm when dissolved in MEK and of 40 nm when dissolved in toluene, which is a trend that is in line with the findings of Tung et. al. Table 5.3 gives some \( \langle R_G^2 \rangle^{1/2} \) values found in literature for comparison. If the elongation of the polymer chain in solution is transferred to a more spread out polymer when the thin film is formed from spincoating, an improved dipolar order is expected as more of the PMMA side groups will be oriented in the same direction.

<table>
<thead>
<tr>
<th>Polymer/solvent combination</th>
<th>Chloroform</th>
<th>Toluene</th>
<th>MEK</th>
<th>DMF</th>
<th>Methanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP10-PPV\textsuperscript{68}</td>
<td>38 nm</td>
<td>35 nm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVPh-HEM\textsuperscript{67}</td>
<td></td>
<td></td>
<td>113 nm</td>
<td>115 nm</td>
<td></td>
</tr>
<tr>
<td>PVA\textsuperscript{69}</td>
<td></td>
<td></td>
<td>162 nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polystyrene\textsuperscript{69}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>109 nm</td>
</tr>
<tr>
<td>PMMA (this work)</td>
<td>41 nm</td>
<td>98 nm</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.3. Comparison of some \( \langle R_G^2 \rangle^{1/2} \) from literature of various polymer/solvent combinations.
The use of diphenylalanine nanostructures as an insulating material for pentacene field-effect transistors

6.1 Motivation

Another group of molecules that exhibits strong piezoelectric qualities is peptides. These materials are attractive for many other reasons than their ferroelectric response. Peptides are biocompatible and able to be used for molecular recognition. Many peptides can be easily manufactured or manipulated. Side groups can be changed strategically to fine-tune material parameters. Perhaps the most useful attribute of peptides is there propensity to create structures through self-assembly, such as nanotubes or nanospheres. Self-assembly allows peptides to be used as scaffolding or as a blueprint for other materials such as the active layer in an FET or LED. For these reasons, we have examined the dipeptide FF in conjunction with pentacene to determine its efficacy as an insulator in FET devices. We have also demonstrated that FF can be used as a base for protein detection.

6.2 Fabrication of FF devices

All reagents used were of analytical grade. Sulfuric acid, absolute ethanol, methanol, potassium dihydrogen phosphate and urea were purchased from Synth (Brazil). Aniline, 4-mercaptopyridine (MCP), L,L-diphenylalanine, 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC), N-hydroxysuccinimide (NHS), 1-pyrenebutanoic acid 97%, and urease type III (EC. 3.5.1.5, from Jack Bean, 15.000 – 50.000 U g⁻¹) were obtained from
Sigma-Aldrich (USA). With the exception of aniline, which was distilled prior to use, all reagents were used as received. All solutions were prepared using ultrapure water from a MilliQ® system (resistivity >18 MΩ cm⁻¹).

Fresh stock solutions were prepared by dissolving the lyophilized form of the peptide in HFIP at a concentration of 50 mg mL⁻¹. The peptide solution was then dropped onto aluminum coated glass substrates (50 µL) and spincoated at 1000 rpm for 30 seconds. The substrates that contained the films were placed on an elevated platform in an uncovered Petri dish that contained 20 mL of the appropriate solvent (isopropanol in our case) such that only the vapor reached the film. The entire setup was covered with aluminum foil and placed on a hot plate at 80° C. The incubation time was 720 min, after which a layer of FF-MNSs was formed on the substrates. The FF-MNSs were used as the dielectric layer in organic FETs.

FF-MNSs were functionalized in order to study enzyme-analyte interactions. A gold electrode was placed in a 100 mmol L⁻¹ MCP solution for 2 hours to coat the metallic surface with a thiol layer. The self-assembly of FF-MNSs was performed directly on the substrates using a variation of the solid-vapor phase approach proposed by Ryu and Park.70 This method was also detailed in a previous work.71 Functionalization of FF-MNSs was achieved by drop-casting 15 µL (7.0 mmol L⁻¹) of 1-pyrenebutanoic acid (PBA) in ethanol solution onto the FF-MNSs/MCP/Au electrode. The layer was then washed with water to remove the non-adsorbed PBA and dried at room temperature. For the protein immobilization, 15 µL of a solution containing 30 mg mL⁻¹ of urease (Urs) + 50 mmol L⁻¹ of EDC + 50 mmol L⁻¹ of NHS in a phosphate buffer with a pH of 6.5 (10 mmol L⁻¹) was drop-cast with PBA-
modified FF-MNSs/MCP/Au electrodes for two hours at room temperature. Excess reagents were removed by washing with the phosphate buffer and the electrode was tested immediately in an electrochemical cell.

In order to prepare bottom-gate organic FET structures, we first thermally evaporate 60 nm of aluminum onto 1"x1", organically cleaned glass microscope slides as the gate electrode. We have fabricated both bulk FF devices (with no nanostructures) and devices with FF-MNSs as the dielectric layer. Using the nanostructuring procedure discussed in Section 2.2, FF-MNS films were deposited on Al coated glass substrates. For the bulk FF films, the peptide compound was dissolved in HFIP (50 mg/ml) and spincoated on Al coated glass substrates. The bulk FF films were left at room temperature in a nitrogen glove box for a few hours before adding the pentacene layer on top. The thickness of the bulk FF dielectric layer is estimated to be ~500 nm when using the accumulation capacitance of the MIS device and assuming a dielectric constant of 3.6. 40 This result was further confirmed by reflectometry. The thickness of the FF-MNS dielectric layer varied between 500 – 600 nm. Pentacene films (with 60 nm thickness) were thermally evaporated on top of bulk FF and FF-MNS layers, followed by thermal evaporation of a 40 nm thick layer of gold through a shadow mask containing both FET and capacitor structures for the top contacts.

Top-gate devices were prepared by depositing 40 nm of gold through a shadow mask onto 1"x1" organically cleaned glass microscope slides. This was followed by thermal evaporation of 60 nm of pentacene. FF-MNSs were formed using identical spincoating and nanostructure processes as in bottom-gate devices for
the dielectric layer. This layer was thicker (~ 800 nm) compared to the bottom-gate devices. A thin strip of aluminum was deposited through a shadow mask to a thickness of 60 nm on top of this dielectric layer to act as the gate electrode.

6.3 Characterization tools

The SEM images were obtained using a JEOL FEG-SEM JSM 6330 F and a JEOL LV-SEM microscope at the LME/LNLS (Laboratory of Electron microscopy of the Brazilian Synchrotron Light Laboratory, Campinas, Brazil).

The Raman spectra were collected by an Invia Renishaw spectrometer attached to a microscope with a ×50 lens. The system is equipped with two lasers, a 785 nm diode laser and a 514 nm argon ion laser.

Electrochemical impedance spectroscopy (EIS) was performed using a µAutolab Fra 2, Type III potentiostat/galvanostat. pH measurements were obtained with a Metrohm-Pensalab 827 pH meter equipped with combined glass electrodes. All electrochemical measurements were performed in a conventional three-electrode electrochemical cell. The FF-MNSs/MCP/Au assembly was the working electrode (geometrical surface area = 0.07 cm²), Pt wire was used as the auxiliary electrode and a saturated calomel electrode (SCE) was used as the reference electrode.

EIS was performed in the presence of 5 mmol L⁻¹ [Fe(CN)₆]³⁻/⁴⁻ and 0.1 mol L⁻¹ KCl by applying an alternating current voltage with 5 mV amplitude in a frequency range from 1.0 Hz to 100 kHz. The electrolyte solution was purged with high-purity
nitrogen for at least 15 min prior to each electrochemical experiment and a nitrogen environment was then maintained for the solution in the cell during the measurement process.

6.4 As-Iαs diphenylalanine metal-insulator-metal capacitors

As a prelude to using FF-MNS as a dielectric layer in an organic FET, we wanted to make sure that the FF layer itself acts as a good dielectric layer. Bottom-gate structures using bulk FF film, as discussed in the Experimental Section, were used.

Fig. 6.1 shows the transfer and output characteristics; the inset of Fig. 6.1 (a) shows the capacitance-voltage characteristics of a pentacene MIS device with bulk FF as the dielectric layer. The charge carrier mobility is extracted by using the standard saturation regime FET current-voltage (I-V) characteristics \( \mu_{\text{sat}} = \frac{2L}{WC_0} \left( \frac{d\sqrt{I_d}}{dV_g} \right)^2 \), as defined in Sec. 2.2. \( I_{\text{on}}/I_{\text{off}} \) and \( \mu_{\text{sat}} \) are \( 10^3 \) and \( 4 \times 10^{-2} \) cm\(^2\)V\(^{-1}\)s\(^{-1}\), respectively. As discussed in the next section, these devices result in a catastrophic breakdown upon bias stress.
Fig. 6.1. (a) Transfer and (b) output characteristics from pentacene organic FETs using FF film as the dielectric layer. The inset in (a) shows the capacitance vs. voltage characteristics at 5 kHz from an MIS structure.

6.5 Comparison of annealed and non-annealed FF-MNS films – phase and morphology

Raman spectroscopy is a sensitive tool for probing self-assembly in biological macromolecules. For organic semiconductors this technique is particularly informative on chemical composition, segmental orientation, conformational distribution, and phase identification.\textsuperscript{72} Both Raman and infrared (IR) signatures from FF nanostructures are well known,\textsuperscript{73,74} and can be used to determine the phase and other electronic effects (for functionalized tubes). The 1000 cm\textsuperscript{-1} Raman peak is the strongest in FF and FF-MNS, which arises from a ring deformation mode. There are clear differences between the Raman spectra of the annealed vs.
non-annealed films (Fig. 6.2). New peaks are seen at 660 and 1507 cm$^{-1}$ in the annealed sample. Also, the 1200 cm$^{-1}$ region in the annealed FF-MNS sample shows additional Raman peaks. Due to a change in the structural symmetry of FF-MNSs from P6$_{1}$ in the hexagonal phase to P2$_{2}$$\text{I}$$2_{1}$ in the orthorhombic phase,$^{71}$ it is conceivable that silent Raman modes in the hexagonal phase become observable in the orthorhombic phase. The 1507 cm$^{-1}$ is seen in FTIR; it is likely that this peak becomes Raman active in the orthorhombic phase. One could also apply such symmetry arguments to the 1200 cm$^{-1}$ region, which mainly arise from C-H bending modes. However, full scale ab initio calculations of the vibrational frequencies of the two phases of FF-MNSs are required to ascertain the exact origin of the peaks.

![Raman spectra](image_url)

**Fig. 6.2.** Raman spectra of non-annealed (black) and annealed (blue) FF-MNS film.
Since the performance of an organic FET is critically dependent on the semiconductor-dielectric interface, high resolution SEM images were obtained from neat FF-MNS films as well as from pentacene deposited FF-MNS films. The growth conditions and substrates chosen for this study were identical to the organic FET fabrication conditions. In order to minimize gate current leakage in the devices, the non-annealed FF-MNS film was deposited from a high concentration so as to form a dense network of nanostructures. Fig. 6.3 shows SEM images of (a) annealed and (b) non-annealed FF-MNS films that were deposited on Al coated glass substrates. In non-annealed FF-MNS films (Fig. 6.3 (b)), the self-assembly process may not be complete and there appears to be a resemblance to the amorphous phase in which there are large planar structures rather than tube-like structures. Upon annealing, clear micro/nanotape-like structures are seen in the SEM images (Fig. 6.3(a)). The annealing of the films was carried out at 150 °C for one hour, resulting in the orthorhombic phase. X-ray diffraction measurements from non-annealed and annealed FF-MNSs clearly show the two different phase formations; the hexagonal phase with P6\textsubscript{1} symmetry changes to an orthorhombic phase with P2\textsubscript{2}1\textsubscript{2}1\textsubscript{2}1 symmetry upon annealing.\textsuperscript{71}
Fig. 6.3. SEM images of (a) annealed and (b) non-annealed FF-MNS films. Isopropanol vapor was used to promote the nanostructuring of FF. The film was annealed at 150° C for one hour in (a).

Since pentacene was vacuum evaporated on top of the FF-MNS films in bottom gate organic FETs, we have analyzed the morphology of these films in detail. Keeping in mind that the process of thermal deposition of the semiconductor layer can reach moderately high temperatures on the substrate and further promote penetration of the material into the underlying layer, Fig. 6.4 gives us clues as to how the underlying FF-MNS film may be modified upon the deposition of the pentacene film. The SEM image (top view) in Fig. 6.4 is from an identical non-annealed FF-MNS film as the one shown in Fig. 6.3 (b) but with a thin film of pentacene (~ 60 nm) deposited on top. It clearly shows that the morphology of the FF layer changes compared to the non-annealed pristine film; there is formation of self-assembled structures upon which pentacene coats itself. The inset shows a section of the pentacene film where the FF-MNS layer was absent and the pentacene layer was grown on Al. Although typical dendritic features are not seen
in the inset, the SEM image of pentacene grown on Al resembles the growth of pentacene on other cross-linked polymer dielectrics.\textsuperscript{48}

\textbf{Fig. 6.4.} SEM image of a pentacene coated non-annealed FF-MNS film grown on Al coated glass. The inset shows a section of the pentacene films that was grown just on Al (with no FF-MNS layer underneath).

\textbf{6.6 Bottom Gate FF-MNS/pentacene and bottom-gate as-is FF/pentacene field effect transistors}

Both pentacene MIS and organic FET devices were fabricated using FF-MNSs as the dielectric layer in a bottom-gate architecture. The FF-MNS layer was spincoated and self-assembled on Al coated glass as discussed in the Section 6.1. These micro/nanostructures were in the hexagonal phase, confirmed by Raman scattering. The inset of Fig. 6.5 (a) shows the capacitance vs. voltage curve at 5 kHz from an MIS diode; a slight hysteresis is seen. The accumulation capacitance
of 7.6 nF cm\(^2\) is similar to what was seen for the bulk film, suggesting that the thicknesses of the dielectric layers are similar. The output characteristics (Fig. 6.5 (b)) show an increased modulation in output current compared to the bulk FF film based organic FET. Using the saturation region FET characteristics, \(I_{\text{on}}/I_{\text{off}}\) and \(\mu_{\text{sat}}\) were determined to be \(10^3\) and \(5.5 \times 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}\), respectively.

**Fig. 6.5.** (a) Transfer and (b) output characteristics from pentacene organic FETs using non-annealed FF-MNSs as the dielectric layer. The inset in (a) shows the capacitance vs. voltage characteristics at 5 kHz from an MIS structure.

The order of magnitude decrease in p-type charge carrier mobility with FF-MNSs compared with bulk FF film may be attributed to the morphology of pentacene. Due to the high surface roughness of the FF-MNS layer, the pentacene layer does not show its typical large dendritic features\(^{48}\) although the crystalline nature of pentacene appears to be similar to pentacene films deposited on other substrates, as inferred from Raman scattering (Fig. 6.6).
In order to see whether the crystalline structure of pentacene is retained when deposited on FF-MNSs, we measured the Raman spectra from two vacuum evaporated pentacene films (grown under identical condition), one on non-annealed FF-MNS film and the other on a PVDF dielectric layer using a high resolution micro-Raman system. The Raman peak positions and widths are identical in both cases. As seen in Fig. 6.6, the strongest Raman peaks in pentacene are in the 1100-1500 cm\(^{-1}\) region. The C–C aromatic stretch vibration lies in the 1340–1400 cm\(^{-1}\) range. The two peaks at 1160 and 1178 cm\(^{-1}\) are related to the motion of the H atoms at the end and the side of the molecule. The 1371 cm\(^{-1}\) peak is seen as the strongest C–C stretching vibration.

The overall intensity of the Raman spectrum is stronger from the pentacene film grown on FF-MNSs compared to PVDF, indicative of the fact that the underlying nanostructures in FF increase the surface area, and thus the overall

**Fig. 6.6.** The Raman spectra of pentacene grown on non-annealed FF-MNSs and PVDF films. The inset shows the low energy region between 200-100 cm\(^{-1}\).
scattering cross section. Comparing the two Raman spectra, we can conclude that the crystalline nature of pentacene on FF-MNSs is retained.

Annealing the FF-MNS layer such that it is in the orthorhombic phase does not improve the device performance in terms of carrier mobility and $I_{on}/I_{off}$. There is a slight change in the thickness of the FF-MNS layer upon annealing, also seen in the metal-insulator-metal (MIM) performance (Fig. 6.7), which coincides with a slightly higher leakage in the I-V characteristics in pentacene organic FETs. The gate leakage current was at least one order of magnitude lower than $I_{ds}$ for all bottom-gate organic FETs.

![Graph](image.png)

**Fig. 6.7.** Capacitance vs. voltage of MIM structures with non-annealed (black) and annealed (blue) FF-MNS films.
Fig. 6.8. Operational stability of (a) an annealed FF-MNS based organic FET and (b) a bulk FF based organic FET. The transfer characteristics were measured after applying a bias of $V_g = V_{ds} = -6$ V for varying stress times.

To investigate the bias-stress effect in organic FETs, which is typically manifested as a change in threshold voltage ($V_{Th}$) and/or hysteresis in the output current characteristics, we applied $V_g = V_{ds} = -6$ V for set times and the I-V transfer characteristics were measured after each interval. The organic FETs were subjected to a total of 3600 s of bias stress. Fig. 6.8 (a) shows the transfer characteristics of an annealed FF-MNS/pentacene organic FET. A shift of ~ 0.5 V is observed in $V_{Th}$ after 1 hr of bias stress for the FF-MNS device, while the as-is FF devices has a $\Delta V_{Th}$ of over 120 V. Bias stress investigations with similar time scales on SiO$_2$-based pentacene organic FETs typically show large $V_{Th}$ shifts, and can be further correlated to structural changes. Similar bias stress measurements were also conducted on pentacene organic FETs using bulk FF as the dielectric layer (Fig. 6.8 (b)); surprisingly after 30 min of bias stress the devices completely breakdown.
Although organic FETs fabricated with bulk FF films perform slightly better than with FF-MNS films, it is clear from the bias stress analysis that FF nanostructures make the devices far more robust compared to bulk FF when subjected to a sustained electric field. Furthermore, bias stress measurements were also performed on non-annealed FF-MNS/pentacene organic FETs. These devices did not perform as well as the annealed FF-MNS films but were better than the bulk FF devices. As seen in the SEM images (Fig. 6.4), the pentacene growth promotes a nanostructuring effect in non-annealed FF-MNS films. The bias stress results indicate that a significant portion of the bulk of the non-annealed FF-MNS film may not have the same nanoscale morphology as the surface, as is evident from Fig. 6.9. We have obtained preliminary cross-sectional SEM images, where the sample was manually sliced. These images show that the top layer from pentacene grown on non-annealed FF-MNS has nanostructures with tube-like shapes with lengths on the order of microns, whereas the layers below seem to have more planar, tape-like microstructures.

The above results clearly show that as long as FF is in the form of nanostructures, they can withstand the stress due to the applied electric field (~ $10^5$ V/cm) because of their larger surface area compared to bulk FF. For robust working devices, it is important that FF be highly nanostructured, opening up several applications where one may use FF-MNSs as scaffolds for solution processable conjugated polymers/oligomers to improve the stability and alignment preferences of the organic semiconductor itself.
Fig. 6.9. Cross-sectional SEM images from the pentacene/FF-MNS (non-annealed) interface. (Left) the top layer was in focus; (right) the layers below the top are in focus.

6.7 Top-gate FF-MNS/pentacene field-effect transistors

A large challenge lies in top-gate pentacene and other vacuum evaporated organic semiconductor based organic FETs. In such structures, polymer dielectrics are typically used and the solvent incompatibility, especially with pentacene, is a major problem. Most organic solvents used for dissolving the polymer dielectric damage the pentacene layer. There are a few reports of top gate pentacene organic FETs;\textsuperscript{78,79,80} however, in most cases the gate dielectric is not simply spincoated on top of the pentacene layer but rather lift-off, lamination, or other techniques are used for incorporating the gate dielectric layer.

Fig. 6.10 shows the transistor I-V characteristics from top-gate pentacene organic FETs with FF-MNSs as the dielectric layer. Higher operating voltage
compared to bottom-gate architecture devices is most likely due to a higher thickness of the FF-MNS layer (~800 nm). $I_{on}/I_{off}$ and $\mu_{sat}$ were determined as $10^2$ and $2.5 \times 10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$, respectively. We point out that all our measurements are performed in air and even after a few days, the I-V characteristics of both bottom-gate and top-gate devices do not degrade. Since the FF-MNS (mainly the hexagonal phase) layer is hydrophobic, the impact of air and moisture in such devices is minimal.

Fig. 6.10. (a) Transfer and (b) output characteristics from a top-gate FF-MNS based pentacene organic FET. The inset in (a) shows the capacitance vs. voltage characteristics at 5 kHz from an MIS structure.

Organic FETs are being routinely used for biosensing applications. Organic FETs are being routinely used for biosensing applications. The top-gate organic FET architecture demonstrated above is a practical approach for applications in sensing, such as enzyme-analyte and antibody-antigen interactions. Functionalizing FF-MNSs is relatively straightforward and can be readily used in top-gate organic FETs. In the next section we demonstrate a
potential application of functionalized FF-MNSs in urease detection using electrochemical methods.

### 6.8 Functionalization of FF-MNSs for enzyme-analyte detection

The assembly process of PBA onto FF-MNSs/MCP/Au electrodes has been monitored by electrochemical impedance spectroscopy (EIS). The aromatic pyrenyl moiety interacts with the aromatic-like structure of the FF-MNS walls through irreversible \( \pi-\pi \) stacking at the FF-MNS and PBA interface.\(^{84}\) The carboxylic acid functional groups from the PBA-modified FF-MNS surface were used for the covalent coupling of complementary amino groups of the protein urease (Urs). In this case, the carboxylic acid residues were functionalized to an active ester using carbodiimide and NHS reagents prior to the coupling of the functionalized monolayer associated with the electrode to the protein.\(^{85}\)
Fig. 6.11. Electrochemical impedance spectroscopy for the different electrodes: FF-MNSs/MCP/Au (black), PBA/FF-MNSs/MCP/Au (blue), and Urs/PBA/FF-MNSs/MCP/Au (red) in 0.1 mol L\(^{-1}\) KCl containing 5 mmol L\(^{-1}\) \([\text{Fe(CN)}_6]^{3-/4-}\) as the probe. The solid lines are fit to the equivalent circuit shown in the inset.

The impedance features of electrodes in the presence of equimolar \([\text{Fe(CN)}_6]^{3-/4-}\) at different steps of the functionalization process. Significant differences in the impedance spectra were observed during stepwise modification of the electrodes. To obtain more detailed information about the interfacial electrical properties between the electrodes and the electrolyte, the Randles circuit (inset of Fig. 6.11) was chosen to fit the obtained impedance data.\(^{86,87}\) In the Randles circuit, it is assumed that the resistance for charge transfer \((R_\text{et})\), depicted as \(R_2\), is parallel to the interfacial capacitance \((C_1)\) giving rise to a semicircle in the complex plane plot of \(Z_m\) (imaginary part of the impedance) against \(Z_r\) (real part of the impedance). We note that in this circuit the diffusion
impedance can be neglected. $R_{\text{et}}$ for the FF-MNSs/MCP/Au electrode was estimated to be $\sim 6 \, \Omega$ and increased to $60 \, \Omega$ when the electrode was modified with PBA; peripheral carboxylate-groups, which produced negative charge, decrease the electron-transfer for the $\text{[Fe(CN)]}_6^{3/-4}$ molecules. It is also seen that the capacitance increases by almost a factor of 3 for the fully functionalized FF-MNSs, most likely due to the presence of an excess of negative charge generated on the surface, resulting in a pH change of the electrolyte solution (6.5) in comparison to the $\text{pK}_\text{PB} = 4.8$. Furthermore, the assembly of Urs on the functionalized electrode produced an insulating layer on the electrode surface that acts as a barrier to the interfacial electron transfer. This was reflected by an increase of $R_{\text{et}}$ to over 200 k$\Omega$. The results demonstrate that PBA and subsequently the protein, Urs, were successfully immobilized on the surface of modified electrode. SEM images of the electrode with FF-MNSs were taken before and after functionalization with PBA and Urs, as shown in Fig. 6.12. Although the morphology of FF-MNSs remain unchanged, functionalized FF-MNSs show the presence of a polymeric film layer on the surface of the tubes, which can be assigned to PBA and Urs self-assembled arrays adsorbed preferentially along the longitudinal direction of the nanotubes. The peptide assemblies appear homogeneously spread across the electrode surface, fully covering the substrate. The coverage with tapes/tubes, whose lengths are in the micrometer range, can be assessed by visual inspection. In these low-magnification images, we observe that the structures are densely distributed onto the electrode, forming an intricate network. We observe that PBA and Urs are adsorbed preferentially along the
longitudinal direction of the tapes/tubes (Fig. 6.12 C and D) after functionalization of FF-MNSs.

**Fig. 6.12.** SEM images of FF-MNSs/MCP/Au electrodes obtained under aniline vapor (A) and (B) before, as well as (C) and (D) after functionalization with PBA and Urs.

Since the capacitance and $R_{\text{ef}}$ of FF-MNSs change significantly upon functionalization and further interaction with the protein (Urs), functionalized FF-MNSs may serve as an excellent dielectric in top-gate organic FETs providing a simple device architecture for enzyme-protein detection. Such applications are currently being explored.

Peptide nanostructures have a great potential in organic electronics, either as scaffolds which can help align conjugated polymers/molecules or as active materials when functionalized. Our work reports for the first time the use of
diphenylalanine peptide nanostructures as the gate dielectric in organic FETs. We show that for organic FETs to withstand a bias-stress effect, the nanostructured morphology of the peptide layer is essential. FF-MNSs further allow a simple fabrication of top-gate pentacene organic FETs, which could pave the way for enzyme–analyte sensing applications in the future. Using electrochemical methods we demonstrate that functionalized FF-MNSs are very sensitive in protein (Urs) detection. Electrochemical impedance spectroscopy shows that both interfacial capacitance and charge transfer resistance change significantly when the FF-MNS layer is functionalized with pyrenebutanoic acid and upon interaction with Urs. A second method using square wave voltammetry was also used to show the efficacy of FF-MNSs in Urs detection. Functionalized FF-MNSs in top-gate organic FETs are thus a viable platform for future applications in protein-analyte detection.

6.9 FF-MNS/TIPS-pentacene field-effect transistors

FF-MNS devices using TIPS-pentacene as the semiconductor were fabricated and characterized. The nanostructuring for the FF-MNS layer was achieved in the same way described in Sec. 6.1. A solution of TIPS-pentacene was made by dissolving 4.3 mg of the semiconductor in 0.49 mL of toluene (1.0 wt%). This TIPS-pentacene solution was spincoated on top of the FF-MNS layer by dropping 10 drops of the solution onto a substrate that was already spinning at 1600 RPM. After the solution was applied, the sample continued to spin at 1600 RPM for 60 seconds and then was immediately placed in an oven to anneal at 90 °C for 20
minutes in a nitrogen atmosphere. Gold top contacts were then thermally evaporated through a shadow mask to a thickness of 50 nm.

The electrical characteristics of this FF-MNS/TIPS-pentacene, bottom-gate FET were then examined. It was found that the performance of the device is nearly the same as its pentacene counterpart having $\mu_{\text{sat}}$ of $1.8 \times 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, $I_{\text{on}}/I_{\text{off}}$ of $10^2$, and a threshold voltage of -2.7 V. The important advantage of this TIPS-pentacene device over the FF-MNS/pentacene device is the ease of fabrication. Both the dielectric and the semiconductor layer were spincoated, allowing for cheap and large scale manufacturing of devices. The output and transfer curves for the FF-MNS/TIPS-pentacene device are shown in Fig. 6.13.

![Output and Transfer curves](image)

**Fig. 6.13.** (a) Output and (b) Transfer curves of TIPS-pentacene on FF-MNS.
7 Suggested Future Work

7.1 PVDF-TrFe in solution – dynamic light scattering and molecular dynamics simulations

We wish to expand the DLS study to PVDF-TrFe in solution. However, we are limited in our accuracy due to a lack of information about the dn/dc values for PVDF-TrFe in our three solvents of interest: DMSO, DMF, and MEK. Use of a differential refractometer to find the dn/dc values is needed in order to continue with the study.

Another interesting experiment involves molecular dynamics studies of PVDF-TrFe in the three different solvent environments. A change in solvent environment has been shown to illicit a change in polymer chain conformation in PMMA/solvent molecular dynamics studies. A comparison of DLS data to molecular dynamics data should give some information about the formation of PVDF-TrFe thin films.

7.2 PVDF-TrFe with other semiconductors – flexible, all solution-processable field-effect transistors using TIPS-pentacene

FET and MFM devices using PVDF-TrFe as the insulator can be fabricated on flexible indium tin oxide (ITO) coated substrates in order to probe the piezoelectric qualities of the PVDF-TrFe film. The piezoelectricity of PVDF-TrFe can be exploited in sensors and actuators because of the changing polarization response
at different applied pressures or bending radii.\textsuperscript{89,90} Flexible FET devices have also been fabricated to study the effect of bending radius and bending cycle fatigue on P3HT transistors.\textsuperscript{91}

The goal is to study the piezoelectric response from PVDF-TrFe MFM capacitors as a function of bending radius for the three solvents DMSO, DMF, and MEK. It has been shown that the piezoelectric response is better and the manipulation of dipoles is easier for more crystalline, better ordered films.\textsuperscript{89,92,93} Therefore better piezoelectric qualities are expected for the DMSO sample, based on the indication from MFM and FET measurements of its improved polarization qualities and dipolar order.

FET devices should use the solution-processable semiconductor TIPS-pentacene because it has shown good performance in flexible devices.\textsuperscript{94,95,96} TIPS-pentacene has the added bonus of allowing for an all-solution-processable organic FET, which is desirable for large scale or printed devices. The drain-source current of flexible FET devices should be monitored as a function of bending radius, and performance of devices using the three different solvents can then be compared.

An additional advantage of flexible devices is the simplicity in transferring to an all-printed device using techniques like roll-to-roll printing or inkjet printing. These methods have recently been successfully administered to polymer films.\textsuperscript{97,98,99} This allows for a facile, scalable, and precise fabrication of devices. Additionally, our group has demonstrated an improvement in PVP/TIPS-pentacene FET and MIS diode performance for printed PVP as compared to a spincoated insulating film.\textsuperscript{100}
7.3 Diphenylalanine – nanotube alignment and examination of ferroelectric phase

Future improvement in organic FET performance can be achieved by aligning the nanotube structures and reducing the thickness of the FF-MNS layer. This will greatly reduce the surface roughness and improve the interface between the conjugated molecule/polymer and the dielectric layer. Since many of the solvents used for dissolving organic semiconductors are orthogonal to the FF-MNS layer, pentacene may be easily replaced by other solution-processable conjugated polymers, such as TIPS-pentacene, as already demonstrated.

Better alignment of the nanotubes has been explored. Electrospun films of FF have been fabricated from a solution of FF dissolved in HFIP along with polycaprolactone (PCL), which was used to increase the viscosity of the solution for electrospinning. Electrospinning is a method of forming thin films in which a very dense network of fibers is deposited onto the substrate. The process involves a solution being allowed to drip out of a syringe equipped with a small gauge needle. The substrate is spun at a few thousand RPM while a large potential (usually about 20 kV) is applied between the needle and the substrate. This large potential causes the droplets coming out of the needle to turn into a spray with a well-defined cone shape. The very small drops of solution in the resulting mist are then accelerated from the needle to the substrate by the large applied voltage and a continuous stream of solution is formed out of the spray. This allows the deposited fibrils to have good alignment and complete coverage of the device.
We employed a homemade electrospinning apparatus comprised of a syringe capped by a 12 gauge needle to allow for controlled drip rate of the FF/PCL solution, a hard disc drive (HDD) that holds the substrates which was connected to a voltage source to vary the spin speed of the HDD, and a transformer so that a large potential can be applied between the needle and HDD. We used 1300 RPM spin speed for the substrates. The needle and HDD (with the substrates) are placed 15 cm apart and a potential of 22 kV is applied between them. One lead of the transformer is attached to the hard drive and to an external ground. The other lead is attached to the needle on the syringe. The system was allowed to run in this state for 5 minutes until a dense network of FF nanotubes was formed (shown in Fig. 7.1).

![Electrospun films of diphenylalanine at (a) 2,000x magnification and (b) 20,000x magnification.](image)

**Fig. 7.1.** Electrospun films of diphenylalanine at (a) 2,000x magnification and (b) 20,000x magnification.
While alignment of the nanotubes was not achieved, the dense coverage of the FF should improve FET device performance by reducing the leakage current of the devices. If better alignment of the nanotubes were to be achieved, the ferroelectric phase of FF could be more easily examined.

Both bottom-gate and top-gate FF-MNS/pentacene devices should be prepared in the ferroelectric phase. The FET and MIS characteristics can be examined for both sets of devices. This would be one of the first examples of a ferroelectric, top-gate pentacene device.
References


9 N.B. Ukah, Low Dielectric Constant-Based Organic Field-Effect Transistors and Metal-Insulator-Semiconductor Capacitors, University of Missouri–Columbia, 2012.


100 K. Gooden, A. Laudari, G. Knotts, S. Guha, Flexible and Printed Electronics 1, 015004 (2016).
Publications


Vita

Grant Cooper Knotts was born Kansas City, Missouri in 1989. He obtained a Bachelor’s of Science degree in Physics and a Bachelor’s of Science in Chemistry in 2011 from the University of Missouri-Kansas City. Upon graduation, he began his graduate school work at the University of Missouri-Columbia. He began working for Dr. Suchi Guha in the spring of 2012 and obtained a Master’s of Science in Physics in May of 2014.

In January of 2013, Grant was married to Paige Knotts and they are expecting their first child in June of 2016.