Tuning Charge Transport in PVDF-Based Organic Ferroelectric Transistors: Status and Outlook

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organic field-effect transistors (FETs) for nonvolatile memory application was demonstrated more than 15 years ago. The ferroelectric dielectric polyvinylidene fluoride (PVDF) and its copolymers are most widely used for such applications. In addition to memory applications, polymer ferroelectrics as a dielectric layer in organic FETs yield insights into interfacial transport properties. Advantages of polymer ferroelectric dielectrics are their high dielectric constant compared to other polymer dielectrics and their tunable dielectric constant with temperature. Further, the polarization strength may also be tuned by externally poling the ferroelectric dielectric layer. Thus, PVDF and its copolymers provide a unique testbed not just for investigating polarization



induced transport in organic FETs, but also enhancing device performance. This article discusses recent developments of PVDFbased ferroelectric organic FETs and capacitors with a focus on tuning transport properties. It is shown that FET carrier mobilities exhibit a weak temperature dependence as long as the dielectric is in the ferroelectric phase, which is attributed to a polarization fluctuation driven process. The low carrier mobilities in PVDF-based FETs can be enhanced by tuning the poling condition of the dielectric. In particular, by using solution-processed small molecule semiconductors and other donor–acceptor copolymers, it is shown that selective poling of the PVDF-based dielectric layer dramatically improves FET properties. Finally, the prospects of further improvement in organic ferroelectric FETs and their challenges are provided.

KEYWORDS: ferroelectric dielectric, organic semiconductor, transport, poling, field-effect transistors

1. INTRODUCTION

Although the discovery of the piezoelectric effect in polyvinylidene fluoride (PVDF) dates back 50 years,¹ and its structural and ferroelectric properties were heavily investigated in the early 1980s,²⁻⁴ its application in organic electronic devices came only much later. Ferroelectricity, analogous to ferromagnetism, arises because of spontaneous electric polarization which can be reoriented by an external electric field. PVDF and its copolymers such as PVDF trifluoroethylene (PVDF-TrFE) play an increasingly central role in memory applications,⁵⁻⁹ wearable electronics,¹⁰⁻¹² and pressure and other sensors.^{13–18} Figure 1 provides a snapshot of the technological applications of PVDF and its copolymers. Applications in actuators and memory devices predominantly arise from its ferroelectric and piezoelectric properties. PVDFbased ferroelectrics have been hailed as an important group of materials for advancing the Internet of things;¹⁰ in particular, they provide a viable path toward sustainable smart sensors. A number of applications exploit the piezoelectric nature of PVDF; for instance, energy harvesting materials or sensors that are incorporated in the human body. The memory

applications, demonstrated via two-terminal capacitor architectures or three-terminal transistors, exploit the ferroelectric properties of PVDF and its copolymers. Moreover, the phase transition between the ferroelectric phase and the paraelectric phase at high temperatures, characterized by the Curie temperature, provides a tuning knob for the dielectric constant. The focus of this Spotlight on Application is in the use of PVDF-TrFE as a ferroelectric dielectric in thin film transistors where the transport properties may be tuned via temperature and electrical poling conditions. Temperature allows a systematic tuning of charge transport in organic transistors with the change in dielectric constant of PVDF-TrFE, without having to change the dielectric material. Changing the polarization condition of the PVDF-TrFE dielectric layer by

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Figure 1. Applications of PVDF-based copolymers in thin film electronics.

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an electric field allows the transistor properties to be enhanced in some geometries.

In addition to exploiting its ferroelectric and piezoelectric properties, due to its robust chemical resistance and high thermal stability, PVDF is heavily used as membranes for gas separation and pollutant removal. We direct the readers to a review article on the application of PVDF as membranes;¹⁹ these aspects of PVDF are not discussed in this article.

Memory storage applications are often based on metalferroelectric-metal (MFM) capacitors, where a nonsymmetric polarization is induced with an external voltage. Displacement field versus voltage sweeps in such capacitors yield information on the alignment of dipoles. As the polarization switches sign during the measurement, the readout is destructive. Another memory device that may be based on ferroelectrics is the fieldeffect transistor (FET).²⁰ It is important to note here that ferroelectric materials are not a requirement for FETs, but they do create new pathways for device application. Organic FETs comprising semiconducting conjugated polymers or small molecules are core building elements of electronic circuits,²¹ and have seen significant performance improvement since they were first introduced in the 1980s.²² A majority of the organic memory devices have utilized PVDF and its copolymers as a gate dielectric in ferroelectric FETs.²³⁻²⁷ Because no rewrite process is required, these devices use a nondestructive readout and consume less power compared to MFM capacitors.²⁸



Figure 2. Chemical structure and spectroscopic fingerprint of PVDF. (a) Schematic representation of unpoled PVDF-TrFE. It has crystalline domains with directed dipole moments in an amorphous matrix. (b) Application of a vertical electric field while heating the film just above the ferroelectric-paraelectric transition temperature results in (c) an alignment of the net dipole moment. Schematic representation of (d) α PVDF, (e) β PVDF, and (f) β PVDF-TrFE (75:25). (g) Raman spectrum of PVDF-TrFE (75:25). (h) FTIR spectrum of PVDF-TrFE (75:25).

PVDF and its copolymers provide avenues for lowoperating-voltage organic FETs. Unlike metal oxide semiconductor FETs (MOSFETs), which operate in the inversion region, organic FETs mostly operate in the accumulation region.²⁹ Hence, metal contacts with an appropriate work function must be chosen to match the HOMO/LUMO level of the organic semiconductor for efficient charge injection. The injected charges accumulate at the semiconductor-dielectric interface, which is governed by the dielectric capacitance (C), where $C = \frac{\varepsilon_0 \kappa A}{d}$; κ being the dielectric constant, with ε_0 the permittivity of free space, A the area of the capacitor, and d is the thickness of the dielectric. A high value of C, therefore, ensures low operating voltage FETs and can be achieved either by the use of a high κ dielectric or by decreasing the thickness of the dielectric layer. Although oxide dielectrics have some of the highest values of κ , they are not ideal for flexible FETs. Moreover, the oxide-organic semiconductor interfaces are known to trap charges, making it especially difficult to achieve n-type FETs.³⁰ A recent review by Wang et al. provides a comprehensive overview of organic FETs using polymer-based gate dielectrics.³¹ The dipole moment of solvents is seen to indirectly impact the capacitance value. Polymer dielectrics such as poly(methyl methacrylate) (PMMA) and poly(4vinylphenol) (PVP) have $\kappa < 4$, but dissolving them in high dipole moment solvents results in thin (<70 nm) and pinhole free films. Such dielectric films in organic FETs can achieve operating voltages well below 2 V.^{32,33} Organic ferroelectric dielectrics such as PVDF-TrFE with $\kappa > 8$ at room temperature provide an alternate route toward enhancing capacitance values, offering a path toward low-operating-voltage organic FETs.

Achieving intrinsic carrier mobility of the specific organic semiconductor in an FET architecture is quite challenging because the semiconductor—dielectric interface dictates charge transport. It has been observed that employing the same organic semiconductor but altering the dielectric layer may result in vastly different carrier mobilities in FETs.^{34,35} Because of the inherent disorder (in the electronic states) of conjugated molecules or polymers,³⁶ contribution from electron phonon interaction,³⁷ and the dynamic coupling of charge carriers to the electronic polarization at the semiconductor-dielectric interface,^{38,39} quantifying transport in organic FETs poses a complex problem. Organic ferroelectrics provide a few solutions to this problem.

This paper is organized as follows: Section 2 focuses on structure-property relationship of PVDF and its copolymers, followed by a brief discussion of applications in memory and sensing in Section 3. In Section 4, the nuances of temperature-dependent transport in small molecule-based FETs using ferroelectric and nonferroelectric dielectrics are provided. This section is followed by the effect of electrical poling of PVDF-TrFE in organic FETs in Section 5. Finally, expected future developments in the area of organic ferroelectric FETs are discussed.

2. PVDF AND ITS COPOLYMERS: STRUCTURE

Ferroelectric materials have no center of symmetry and the appearance of spontaneous polarization causes a strain, resulting in their piezoelectric behavior. As known from oxide ferroelectric materials such as $BaTiO_3$, their crystallinity is a key factor to ferroelectricity. This holds true for polymer ferroelectrics as well. Ferroelectric homopolymers such as

PVDF are semicrystalline in nature and organize into crystalline lamellae with folded chains interwoven within amorphous layers.³ Much of their structural and ferroelectric properties were determined in the 1970s and 1980s.^{2–4} PVDF and its copolymers belong to a class of polymers with crystalline dipolar domains surrounded by a noncrystalline matrix, as schematically shown in Figure 2a. Application of an electrical field during the crystallization process, which occurs at the ferroelectric—paraelectric transition temperature, orients the dipoles, shown in Figure 2 b, c. The orientation of molecular dipoles in an applied field is called poling, and by varying the direction of the electric field, the dipoles may be aligned either parallel or perpendicular to the film plane.

The net dipole moment arises from the backbone chain conformation of the molecule. At least four different phases have been identified. The two predominant phases are the paraelectric (α) phase and the ferroelectric (β) phase.⁴ The α phase has a backbone conformation of alternating transgauche configuration (TG⁺TG⁻) and the β phase is the all trans configuration (TTTT). These two phases are represented in Figure 2 d, e with the arrows denoting the direction of the dipole moment. As seen for the α phase, the individual dipole moments cancel out due to the backbone conformation. The ferroelectricity of the β phase arises from the differences in electronegativity of hydrogen and fluorine atoms, giving rise to a dipole moment for each molecule in a perpendicular direction to the backbone. The γ phase has a chain conformation in between the α and β phases. The δ phase is a polar analog of the α phase, and its ferroelectric properties were experimentally determined a few years ago.⁴⁰ In this article, we focus on the α and β phases.

The additional fluorine atom in the TrFE monomer, shown in Figure 2 f, prevents the polymer from being in the transgauche α phase as long as the molecule is above 11% TrFE.⁴¹ The representation here is a 75:25 PVDF-TrFE, which is most frequently used. Unlike PVDF, the advantage of the copolymer, PVDF-TrFE, is that it is ferroelectric directly after spincasting the film. The competition between the shortrange van der Waals interaction of the molecular dipoles and the long-range dipole-dipole interactions between the chains dictate the ferroelectric phenomenon in PVDF-TrFE. The β phase in PVDF-TrFE may be further enhanced by thermal annealing above the ferroelectric-paraelectric phase transition temperature. The Raman and FTIR spectra from PVDF-TrFE confirm the backbone chain conformation, and thus the β phase. The 840 cm⁻¹ vibrational peak in the Raman and FTIR spectra (Figure 2g, h) is assigned to the CF_2 group and appears only when the backbone is in the all-trans conformation. The 1285 cm⁻¹ Raman peak is from the coupling of the CF₂ stretching and skeletal C-C stretching modes, and the 1400 cm^{-1} band in the FTIR spectrum is assigned to the CF₂ bending modes. There are several other binary copolymers of PVDF, such as PVDF-HFP with hexafluoropropylene (HFP), PVDF-CTFE with chlorotrifluoroethylene (CTFE) and even ternary copolymers with PVDF-TrFE. Details of their structure and dielectric properties are found in ref 42.

2.1. X-ray Diffraction and Morphology. Kepler and Anderson had shown that the application of an external electric field polarizes the β phase in PVDF.² By following the intensity of the (110) and (200) planes as a function of the sample orientation, they verified that the ferroelectric phase is due to a field induced orientation of the dipoles on the chains and not due to the orientation of the dipoles associated with the

amorphous phase. There are several excellent articles on X-ray diffraction (XRD) studies from PVDF and its copolymers, highlighting the different phases.^{43–48}

Figure 3 shows the XRD data of PVDF-TrFE films of approximate thickness 800 nm for unpoled and vertically poled



Figure 3. Structure and morphological properties of PVDF-TrFE. (a) Grazing-incidence XRD from unpoled and poled PVDF-TrFE films. (b) SEM image of unpoled PVDF-TrFE film. (c) SEM image of a V-poled PVDF-TrFE film. Reproduced with permission from ref 49. Copyright 2018 American Physical Society.

films.⁴⁹ The poling conditions will be discussed in greater detail when we show the results of polarization modulation in FETs in Section 5. The vertical poling condition is accomplished by applying an external electric field ($\sim 1 \times 10^8 \text{ V/m}$) to the PVDF-TrFE film sandwiched between two

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electrodes for half an hour. The 2θ peak at ~20° is from the (200) or (100) reflections of the β /ferroelectric (FE) phase. The indexing of the (001) and (400/220) Bragg peaks is based on ref 47. The shoulder at 19° is a signature of the paraelectric (PE) phase. The intensity of the 20° peak is enhanced upon electrical poling, thus signaling an increase in the β phase. The increase in polarization of (upon poling) originates from reorientation of the dipoles in the crystalline phase by an electric field rather than orientation of the dipoles of the amorphous (PE) phase.⁴³⁻⁴⁵

The surface morphology of the ferroelectric films is clearly seen to change upon poling as shown in the scanning electron microscope (SEM) images (Figure 3 b, c). The vertically poled film shows clear domains >1 μ m representing ferroelectric domains. There is some signature of domains in the unpoled film but not as pronounced as in a vertically poled film.

The noncentrosymmetric structure responsible for the ferroelectric nature of materials is also responsible for its nonlinear optical property. Second harmonic generation (SHG), where the fundamental light doubles in frequency, is a measure of broken symmetry. We direct the readers to several works on SHG from PVDF-TrFE films, which have been used to confirm the ferroelectric phase since the late 1980s.^{50–52}

3. APPLICATIONS IN MEMORY AND SENSING

Both MFM capacitors and ferroelectric FETs using PVDF and its copolymers have been heavily utilized in memory



Figure 4. Polarization versus voltage loops from MFM capacitors. (a) Schematic of a Sawyer–Tower circuit. (b) Typical polarization versus electric field for a PVDF-TrFE based MFM capacitor. (c) Polarization versus voltage hysteresis loops for Al/PVDF-TrFE/Au MIM capacitors, where PVDF-TrFE was dissolved either in DMSO, DMF, or MEK solvents. Reproduced with permission from ref 55. Copyright 2014,AIP Publishing. (d) AFM images of PVDF-TrFE films deposited from different solvents.



Figure 5. Output voltage and current of (a) piezoelectric, (b) pyroelectric, and (c) triboelectric nanogenerators using PVDF-TrFE dissolved in four different solvents: THF, MEK, DMF, and DMSO. Reproduced with permission from ref 56. Copyright 2017 Wiley.

applications. A recent review by Stadlober et al. on the application of PVDF based materials in the Internet of things provides exhaustive examples of sensing and sustainability.¹⁰ The piezoelectric behavior in these materials controls their application in sensing since an applied force can change the surface charge density. We further direct the readers to the review by Naber et al. on organic nonvolatile memory devices based on PVDF, where two-terminal capacitors and diodes, and three-terminal FETs are discussed.⁵ The low-voltage switching of PVDF-TrFE capacitors has made it attractive for integration in flexible memory circuits with printable contacts and conductive polymer interface layers.⁵³

PVDF-based films are not without disadvantages. The metal-polymer interface in diode architectures and the thickness of the layer can impact switching times during endurance tests.⁵ Additionally, the inherent dipolar disorder results in surface roughness which manifests itself as gate leakage currents when used as a dielectric layer in FETs. In the next few sections, while demonstrating several applications of PVDF-TrFE in FETs and capacitors, we show that solvent treatment, electrical poling, and adding buffer layers are a few strategies for overcoming some of these issues.

3.1. MFM Capacitors. A tell-tale sign of a ferroelectric capacitor is the hysteresis in polarization versus voltage (P-V)loops as shown in Figure 4. These measurements are typically performed using a Sawyer-Tower circuit, as schematically shown in Figure 4a, where an oscillating voltage is applied across a resistor in series with the MFM and the voltage drop is converted as a time varying current. Knowing the time-varying current and the area of the capacitor, the polarization versus voltage (or electric field) loops can be achieved, as shown in the plot in Figure 4b. Upon removal of the bias, the dipoles remain aligned resulting in a remnant polarization (P_R) , and in the case of robust ferroelectrics, this value is usually close to the saturation polarization (P_S) . The coercive field (E_C) is the minimum field required to switch $P_{\rm R}$. Measuring the displacement field while sweeping the voltage sheds light on the alignment of the dipoles; information is stored as a high displacement field or a low displacement field, equivalent to a

Boolean "1" or "0". Because the polarization is switched during each measurement, the readout here is destructive. There are several reports on charge displacement versus applied voltage measurements from PVDF-TrFE MFM devices.^{5–8} The saturation polarization in PVDF-TrFE and other PVDF-based copolymers is an order of magnitude smaller than inorganic ferroelectric materials such as lead zirconate titanate.⁵⁴

3.2. Solvent Dependence of PVDF-TrFE in MFM Capacitors and Sensors. Knotts et al. performed P-Vloops from PVDF-TrFE MFM capacitors where the ferroelectric dielectric was dissolved in solvents of various dipole moments.⁵⁵ Figure 4c plots the P-V curves for Al/PVDF-TrFE/Au capacitors. PVDF-TrFE was dissolved in solvents with varying dipole moments (D) prior to casting them as films. These solvents include dimethyl sulfoxide (DMSO) (4.1 D), dimethylformamide (DMF) (3.8 D), and 2-butanone (MEK) (2.7 D). The thicknesses of the films were approximately 190, 200, and 300 nm for DMSO, DMF, and MEK solvents, respectively. The remnant polarization was found to be the largest for DMSO (5.6 μ C/m²) and the coercive field varies between 52 and 74 MV/m, the lower value being for MEK. We note that the displacement (D) arises both from linear and ferroelectric polarization: $D = \varepsilon_0 \varepsilon E + P(E)$, where ε_0 and ε are vacuum and relative permittivities, respectively. E is the external electric field and P(E) is the ferroelectric polarization. If E is lower than E_{C} only the linear component of the dielectric polarization contributes. The MFM capacitor where DMSO is used as the solvent shows a hysteresis in the displacement at the lowest field, indicating that there is some ordering of the dipoles even before the field is applied.55

The improved properties with high dipole moment solvents are believed to be due to an extended chain conformation in solution which is maintained after processing the films. There is some correlation with the morphology of the films; AFM studies show the least surface roughness from films when DMSO is used as the solvent (Figure 4d). Moreover, pentacene FETs with PVDF-TrFE as the dielectric show

improved performance when the PVDF-TrFE films were prepared with high D solvents.⁵⁵ It should be pointed out that the usage of high D solvents in dissolving nonferroelectric dielectrics has also been beneficial for improving device performance of organic diodes and FETs.^{32,33}

A solvent-dependent study of PVDF-TrFE was later conducted and extended by Kim et al., where they observed high piezoelectric and pyroelectric properties from PVDF-TrFE films along with enhanced power output from triboelectric generators based on PVDF-TrFE dissolved in a high dipole moment solvent.⁵⁶ In this work, they use a fourth solvent, tetrahydrofuran (THF) with a low dipole moment (1.75 D), and find higher values of piezoelectric, pyroelectric, and triboelectric properties when DMSO is used for dissolving PVDF-TrFE. In particular, the work focuses on nanogenerators (NGs) which harvest energy from piezoelectric, triboelectric, and pyroelectric phenomena. By fabricating flexible PVDF-TrFE NGs, the performance enhancement due to solvents was investigated. Figure 5 shows the output voltage and current for piezoelectric, pyroelectric, and triboelectric NGs. The piezoelectric NG was bent upward with a curvature of 5 mm such that a tensile strain could be applied. The pyroelectric NGs were tested in a temperature range of 23-36 °C, and the triboelectric NG was operated in contact separation mode. In each case when PVDF-TrFE is dissolved in DMSO, which has the highest D compared to the other solvents used, the power output performance was observed to be the highest.

The above examples demonstrate that using high dipole moment solvents for dissolving PVDF-based dielectrics significantly improves device performance. In many scenarios, the high dipole moment solvents further help in the processing of thin dielectric layer, which enhances the stability of MIS diodes and FETs. Such a strategy of using high D solvents, thus opens up a facile processing route for spincasting PVDF-TrFE and other ferroelectric dielectric films for organic electronics.

4. TEMPERATURE-DEPENDENT TRANSPORT IN PVDF-TRFE-BASED FET

This section presents temperature tuning of the dielectric constant of PVDF-TrFE and its impact on FET transport. Because the Curie temperature of PVDF-TrFE (for the specific VDF/TrFE ratio used) is ~400 K, it allows sweeping the dielectric from its ferroelectric phase to the paraelectric phase with a wide range of dielectric constants. This provides a novel way of tuning an organic FET using the same dielectric film. Prior to discussing temperature-dependent transport in PVDF-TrFE based organic FETs, we provide a brief overview of charge transport models and how to extract essential FET parameters from current–voltage characteristics.

4.1. FET Transport Properties and Current–Voltage Characteristics. Disordered systems such as amorphous and organic semiconductors, in general, are characterized by both extended and localized states, and the transport of carriers is described in terms of a hopping mechanism between disordered-localized states.⁵⁷ The charges in organic semiconductors are polaronic (short-range Holstein),⁵⁸ and their transport as a function of temperature has been described by several models–variable range hopping,⁵⁹ delocalized charge transport,⁶⁰ multiple trapping and release,^{61,62} and other hybrid models.⁶³ The process of carrier transport becomes even more complex in FETs because of additional interfaces such as the semiconductor-dielectric boundary, where electronic polarization and both short- and long-range lattice

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fluctuations play a role. Section 4.3 discusses these aspects of transport as a function of temperature and polarization in detail.

FET carrier mobility (μ) , on-off current ratio, and threshold voltage $(V_{\rm th})$ are usually obtained from the saturation region of the transconductance region. $V_{\rm th}$ signals the operating voltage of the device; hence, low-operatingvoltage FETs have $V_{\rm th}$ values close to 0 V. In the saturation region

$$\mu = \frac{2L}{WC_i} \left(\frac{\partial \sqrt{I_{\rm DS}}}{\partial V_{\rm G}} \right)^2 \tag{1}$$

where C_i is the dielectric capacitance, W is the channel width, L is the channel length, V_G is the gate voltage, and I_{DS} is the drain current, and V_{DS} is the drain-source voltage. Recently, there have been several reports on whether the FET mobilities should be extracted from the saturation or the linear region of the transconductance curve,^{64,65} where the linear region carrier mobility is given by

$$\mu_{lin} = \frac{L}{WC_i V_{\rm DS}} \frac{\partial I_{\rm DS}}{\partial V_{\rm G}} \tag{2}$$

One should note that for short channel FETs, the contact resistance affects the linear region more than the saturation region.⁶⁶ Device simulation at the molecular level suggests that mobilities obtained from the saturation and linear region are similar as long as the energetic disorder of the semiconductor is less than 50 meV.⁶⁷ Further, a reliability factor, *r*, for carrier mobilities has been defined.⁶⁴ The *r* factor is based on the ideal Shockley FET equations with $V_{\rm th} = 0$ V. Because the polarization condition of the ferroelectric layer dictates the value of $V_{\rm th}$ an ideal *r* factor of ~100% is not expected in ferroelectric FETs. Another metric for FET performance is the subthreshold swing, which is given by

$$SS = \frac{dV_{GS}}{d(\log I_{DS})}$$
(3)

A small value of SS is preferred as it implies that a small change in the input bias can considerably modulate the output current and enhance switching speeds. A typical value for a MOSFET is 60 mV/decade.

4.2. Role of the Gate Dielectric Layer. Using the same organic semiconductor layer but changing the dielectric layer or changing even the processing condition of the dielectric layer in FETs can vastly alter the performance of devices. More than 10 years ago, it was shown that carrier mobilities of singlecrystal rubrene FETs decrease as the dielectric constant (κ) of the gate insulator increases.³⁴ This was attributed to Fröhlich polarons, which arises from a long-range interaction between the charge carriers and the longitudinal optical (LO) phonons of the dielectric layer. One would expect this interaction to be further enhanced with additional polarization effects of the gate dielectric.

The dynamic coupling of the charge carriers to the electronic polarization at the semiconductor-dielectric interface is schematically shown in Figure 6 a. This coupling results from an image force at the interface and from the Coulomb interaction of the charge carriers with the surface phonons of the dielectric (schematically shown by the red charges). An immediate consequence of such an interaction would be to decrease the carrier mobility, which can be understood on the



Figure 6. Role of the dielectric layer in TIPS-pentacene FETs. (a) Schematic of ferroelectric FET. The dynamic coupling of the charge carriers at the semiconductor-dielectric interfaces is illustrated. Reproduced with permission from ref 68. Copyright 2015 AIP Publishing. (b) Schematic of FET architectures. The top device is a bottom gate PVDF-TrFE. The dipoles denote unpoled or poled conditions. The device in the middle depicts a dual FET with PVDF-TrFE or PVP as bottom gate and CYTOP as top gate. The device at the bottom shows a bilayer structure of combined gate dielectrics. (c) Chemical structure of pentacene and TIPS-pentacene. (d) Average carrier mobility of TIPS-pentacene FETs with different gate dielectrics. Reproduced with permission from ref 35. Copyright 2019 AIP Publishing.

basis of a renormalization of the transfer integral and an increase in the effective mass of the carriers.³⁹ Shown in Figure 6b are typical FET configurations with top-contact geometries. The architecture in the middle device of Figure 6b serves as dual gate geometry. Here, the semiconducting film remains the same and the FET operation takes place either by using the top or the bottom gate dielectric. Bilayer dielectrics such as PVDF-TrFE/SiO₂ or other oxides serve as testbeds for probing transport where the interface between the semiconducting and the ferroelectric layer is similar to a single-layer device (top-contact architecture in Figure 6b) but because the ferroelectric layer is not gated, the effect of dielectric polarization is not observed in transport properties.

Using a small molecule semiconductor, 6,13-bis-(triisopropylsilylethynyl)pentacene (TIPS-pentacene) (Figure 6c), as the active layer, a clear trend of decreasing carrier mobility with increasing κ of the gate dielectric is seen in Figure 6d. These carrier mobilities were extracted from the saturation region of the transconductance region. Vertical poling of the PVDF-TrFE film results in improved carrier mobilities compared to unpoled PVDF-TrFE. The impact of poling is presented in Section 5. Other nuances such as organic versus inorganic oxide dielectrics also play a role. Because oxide dielectrics can trap charges, FETs with SiO₂ as the gate dielectric show lower mobilities compared to polyvinylphenol (PVP), although PVP and SiO₂ have similar values of κ .

The value of κ increases from 5 (at 200 K) to 25 (at 390 K) in PVDF-TrFE. We note that the Curie temperature (T_c) for 75:25 PVDF-TrFE is ~390 K. By using the same dielectric, temperature may be used as a tuning parameter for monitoring polarization-induced transport. Senanayak et al. have shown that the carrier mobility remains suppressed in PVDF-TrFE/

poly(3-hexylthiophene) (P3HT) FETs as long as the temperature is below ${T_{\rm c}}^{69}$

4.3. Tuning Transport with Temperature in Pentacene/PVDF-TrFE FETs. 4.3.1. Comparison of Ferroelectric and Nonferroelectric Dielectrics. Figure 7 a, b shows the



Figure 7. Ferroelectric versus nonferroelectric dielectrics in temperature-dependent transport. Transfer curves of pentacene FETs at different temperatures with (a) PMMA and (b) PVDF-TrFE as the dielectric layer. The insets show the threshold voltage as a function of temperature. (c) Comparison of pentacene FET charge carrier mobilities with PMMA (black squares) and PVDF-TrFE (red circles) dielectrics. The blue triangles represent the dielectric constant of PVDF-TrFE as a function of temperature. Reproduced with permission from ref 68. Copyright 2015 AIP Publishing.

transfer curves of two pentacene FETs as a function of temperature with PMMA and PVDF-TrFE dielectric layers. Because PMMA degrades, the temperature-dependent measurements were performed only until 350 K. The measurements with PVDF-TrFE were carried out beyond T_c until 440 K. Because of a decreased trapped charge density, $V_{\rm th}$ (insets in Figure 7a, b) decreases with increasing temperature. The PVDF-TrFE based FET shows a discontinuity at T_{c} , beyond which there is a sharp decrease in $V_{\rm th}$. The carrier mobilities, obtained from the saturation region, are plotted in Figure 7c along with the variation in κ of PVDF-TrFE as a function of temperature. Although both PMMA and PVDF-TrFE show activated transport, clear differences are seen. The carrier mobility of the pentacene FET is suppressed as long as PVDF-TrFE is in the ferroelectric phase. Beyond T_{cr} when PVDF-TrFE is in the paraelectric phase, a sharp rise in mobility is observed with increase in temperature. For a thermally activated hopping process, the carrier mobility may be modeled as'

$$\mu = \mu_0 \exp\left(-\frac{\Delta}{k_{\rm B}T}\right) \tag{4}$$

with μ_0 being the mobility in the absence of any traps, Δ is the activation energy, $k_{\rm B}$ is the Boltzmann constant, and *T* is the temperature.



Figure 8. Activation energies and Fröhlich polaron parameters. (a) Arrhenius plots of pentacene FET mobilities for varying thickness of the PVDF-TrFE dielectric layer. (b) Schematic of single and bilayer FETs. (c, d) Comparison of pentacene FET mobilities for single layer and bilayer devices with PVDF-TrFE thicknesses of 20 and 500 nm, respectively. (e) Mobility of Fröhlich polarons as a function of temperature for three different thicknesses of the PVDF-TrFE layer in pentacene FETs. The bold line is a fit to the strongly coupled Fröhlich polaron discussed in the text. Adapted with permission from ref 68. Copyright 2015 AIP Publishing.

The data pose a few questions: does the polarization strength vary with the thickness of the PVDF-TrFE layer? Is there a way to disentangle the thermal process from the polarization contribution (due to Fröhlich polarons) to the carrier mobility? These insights may be obtained by changing the thickness of the PVDF-TrFE film and by comparing μ_{FET} from single-layer devices to bilayer dielectric layers.

4.3.2. Thickness Dependence of the Ferroelectric Layer. We first look at the Arrhenius plots of pentacene FET mobilities for varying thickness of the PVDF-TrFE layer. Figure 8a plots the mobilities in the temperature range while the dielectric is still in the ferroelectric phase (200-400 K). The thickness of the pentacene layer remains unchanged. The data is fit with eq 4 to obtain Δ , which is seen to decrease with the thickness of the dielectric layer. Concomitantly, μ_{FET} is found to increase with thicker dielectric films. These results suggest that there are two competing effects as long as the dielectric remains ferroelectric: activated hopping, which enhances μ_{FET} with temperature, and a higher coupling of the carriers due to the formation of surface Fröhlich polarons with increasing κ as the temperature increases until T_c . The activation energies inferred from thickness dependent transport show that thinner dielectric films induce stronger polarization fields, thus, lowering the values of μ_{FET} compared to thicker dielectric films. MOSFETs show a similar effect of reduced μ_{FET} when high κ dielectrics are used, and this effect in the literature has been coined as "remote phonon scattering".^{71,72}

An ideal scenario to disentangle the effect of Fröhlich polarons from the total contribution of transport that also includes the Holstein polarons is to use an air gap as the dielectric and then compare the mobility from the ferroelectric dielectric and the air-gap FET. Such an approach was used for rubrene single crystals for comparing the contribution of Fröhlich polarons from dielectrics of varying values of κ .³⁴ This approach is clearly problematic for thin films. For obtaining the

contribution of Fröhlich polarons in P3HT FETs, Senanayak et al. used the concept of a bilayer device⁶⁹ where the ferroelectric dielectric is in series with another nonferroelectric dielectric. We show it schematically for pentacene FETs in Figure 8b. The pentacene–PVDF-TrFE interface, as far as the morphology is concerned, is not changed compared to the single-layer device, although the influence of any polarization fluctuation is absent in such bilayer devices, as the PVDF-TrFE layer is in series with the gated SiO₂ dielectric layer. The bilayer device is thus representative of thermally activated hopping because of the Holstein polaron, whereas the singlelayer PVDF-TrFE is dominated by the Fröhlich polarons. By using Matthiessen's rule, we can express the FET mobility as

$$\mu_{\text{FET}} = \left(\frac{1}{\mu_{\text{p}}} + \frac{1}{\mu_{\text{bilayer}}}\right)^{1}$$
, where μ_{p} is the contribution from

Fröhlich polarons (polarization fluctuation dependent mobility) and μ_{bilayer} is the mobility of the bilayer FET, representative only of Holstein polarons.

Figure 8c, d show the FET mobilities as a function of temperature from single-layer PVDF-TrFE FETs and bilayer FETs for two different PVDF-TrFE layer thicknesses (20 and 500 nm). The first observation here is the bilayer device shows an exponential increase in FET mobility for the entire temperature range, similar to other nonferroelectric dielectrics. A second observation, which we saw earlier, is that the FET mobility is suppressed in single-layer PVDF-TrFE FETs, and this reduction in mobility is higher for the thinner dielectric. Figure 8 e shows the extracted values of μ_p , obtained using Matthiessen's rule, for three different dielectric thicknesses. The data can be modeled by the strongly coupled Fröhlich polaron model:⁵⁸

$$\mu_{\rm p} = \frac{ea^2\omega_{\rm s}}{8k_{\rm B}T} \exp\left(-\frac{\Delta_p}{k_{\rm B}T}\right) \tag{5}$$



Figure 9. Electrical poling and polarization properties of MFM capacitors. (a, b) Schematic of poling a PVDF-TrFE film vertically and laterally, respectively. Arrows denote the polarization direction in the film after poling. (c) Capacitance–voltage sweeps and the (d) corresponding tan δ values from an unpoled, lateral (L) poled, and vertical (V) poled PVDF-TrFE film. (e) Capacitance–voltage sweeps after L-poling a V-poled PVDF-TrFE film. Reproduced with permission from ref 49. Copyright 2018 American Physical Society.

In eq 5, ω_s is the frequency of surface phonons of the dielectric, Δ_p is the hopping barrier of the polarons, and *a* is the hopping length. For details on the fitting parameters, see ref 68; *a* varies between 2 and 5 Å, and the average hopping barrier was found to be approximately 90 meV. Both ferroelectric and nonferroelectric based pentacene FETs show activated transport. However, the charge carrier mobility shows weak temperature dependence in the ferroelectric phase, which is a signature of a transport phenomenon driven by polarization fluctuation.

4.4. Role of the Organic Semiconductor Layer. We briefly touch upon other temperature-dependent studies from organic/polymeric FETs with PVDF-TrFE. As mentioned earlier, the dominant contribution to transport in P3HT/ PVDF-TrFE FETs is a polarization fluctuation process.⁶⁹ This was the first demonstration of the impact of coupling of charge carriers to the polarization field on carrier mobility in a solution-processable polymer FET. Photoexcitation measurements in the depletion mode of the FETs further revealed distinct responses when PVDF-TrFE is in the ferroelectric phase, indicating different transport regimes.

TIPS-pentacene/PVDF-TrFE FETs have been used for determining the nature of temperature-dependent carrier mobility.^{35,73} Because TIPS-pentacene films can crack around 340 K, the full extent of the tunability of κ in PVDF-TrFE until T_c cannot be exploited in these FETs. A band-like behavior, $\frac{d\mu}{d\tau}$ < 0, is observed beyond 200 K with unpoled PVDF-TrFE. dΤ Bulk transport from two-terminal TIPS-pentacene diodes show discrete trap space-charge limited conduction (SCLC) behavior; the carrier mobilities obtained from two-terminal devices also display $\frac{d\mu}{dT}$ < 0 beyond 180 K. Other dielectrics such as Al_2O_3 ($\kappa = 10$), where the dielectric constant is comparable to PVDF-TrFE and other low κ dielectrics all show hopping transport in TIPS-pentacene FETs with $\frac{d\mu}{dT} > 0$. Additionally, thermally activated hopping transport is observed when the dipoles are prealigned in the PVDF-TrFE film via electrical poling. The band-like transport with unpoled PVDF-TrFE in TIPS-pentacene FETs is related to the nature of discrete traps, which lie close to the mobility edge in TIPSpentacene. Polarization fluctuation in unpoled PVDF-TrFE reduces the trap depth, and this process manifests transport via discrete traps, resulting in carrier transport akin to band-like behavior beyond a certain temperature.³⁵

Thus far, it is seen that the usage of PVDF-TrFE dielectrics in organic FETs decreases the value of carrier mobility (at room temperature) compared to other low- κ dielectrics. However, by appropriately poling the dielectric layer, enhanced carrier mobilities and low-operating-voltage organic FETs have been realized. In Section 2, we touched on electrical poling of ferroelectric dielectrics with regard to alignment of the dipole moment. In Section 5, we discuss the modulation of transport properties in FETs by changing the poling condition of the ferroelectric dielectric layer. Additionally, we will present a few optical techniques such as charge-modulated reflectance imaging that have been used in the literature to visualize polarization reversal in ferroelectric transistors.

5. ELECTRICAL POLING OF THE PVDF-TRFE LAYER

5.1. Metal-Ferroelectric-Metal and Metal-Ferroelectric-Semiconductor Capacitors. Capacitance–voltage (C-V) measurements from MFM capacitors show strong hysteresis due to polarization reversal, which is again an indicator of a ferroelectric film. Such butterfly loops in PVDF-based MFMs have been observed in several investigations.^{74,75} External electrical poling of the PVDF-TrFE layer changes the orientation of dipoles, and is an effective means of tuning the polarization strength. The method of vertical poling the PVDF-TrFE film was shown in Figure 2. It turns out that the exact poling direction—whether the films are vertically or laterally poled—influences the C-V loops.

Figure 9 a, b show some of the strategies for external poling of the PVDF-TrFE film.⁴⁹ The vertical (V) poling condition for C-V and FET measurements was achieved by the application of an external electric field of $\sim 1 \times 10^8$ V/m. This was realized by placing a temporary top electrode on top of a spin-coated PVDF-TrFE film during the crystallization process. Lateral (L) poling was achieved by depositing Al

strips, at a separation of 2 mm, on top (or bottom) of the PVDF-TrFE film and by applying $\sim 1 \times 10^5$ V/m for 15 min while heating the film at 135 °C. Figure 9c shows the C-Vcurves from three MFM capacitors with the same thickness (120 nm) of the PVDF-TrFE layer but with different poling conditions: V-poled, L-poled, and unpoled. The V-poled device has the highest value of capacitance, followed by unpoled and L-poled films. The coercive voltage, where polarization switching occurs, is at ~ 7 V for the unpoled film. The tan δ value (Figure 9d), which indicates the dissipation factor, is relatively low for these MFM devices. The presence of lateral electrodes on substrates with MFM capacitors have the advantage that the polarization condition of V-poled or unpoled devices may be modulated even after the FETs are fabricated. Figure 9e demonstrates the impact of laterally poling an existing V-poled film on the C-V characteristics. The L-poling was achieved by applying a lateral voltage on prefabricated electrodes on the film for 15-20 min prior to the C-V sweeps. One observes a decrease in the accumulation capacitance with an increase in the L-poling voltage.

C-V measurements from metal-insulator-semiconductor (MIS) diodes, the two-terminal analogue of FETs (Figure 10a, inset), further provide insights into trap states, nature of



Figure 10. Capacitance-voltage characteristics from pentacene MIS diodes with (a) PMMA and (b) PVDF-TrFE dielectric layers. The inset in a shows a schematic of the device.

doping, and other interfacial properties at the semiconductordielectric interface.^{76,77} The capacitance can be changed by accumulating, depleting, and inverting charges at the semiconductor-dielectric interface by sweeping the bias voltage. The inversion region is typically not observed from organic MIS diodes due to the long relaxation of minority carriers in organic semiconductors.⁷⁷ Such C-V curves from MIS structures are also indicators of the ferroelectric polarization. Shown in Figure 10 are representative C-V curves from pentacene MIS diodes using similar thicknesses for a nonferroelectric dielectric, PMMA, and PVDF-TrFE. Taking into account the differences in the dielectric constant of the two dielectrics, the accumulation capacitance is seen to scale accordingly. Since these pentacene MIS diodes are p-type, the accumulation occurs when the bias voltage is swept to negative values. Unlike PVDF-TrFE, the C-V curve shows no hysteresis when PMMA is used as the dielectric layer. The clockwise direction of hysteresis in the PVDF-TrFE based MIS diode can be understood in terms of requiring a high positive voltage to deplete the charges in the reverse direction. Unfortunately, the hysteresis seen in the CV curve for organic MIS diodes is not always conclusive whether the dielectric is ferroelectric or not. Thicker nonferroelectric dielectrics with organic semiconductors often show hysteresis in CV characteristics, which may arise from slowly polarizing dipole charges or interface charges.³² Hence, the signature of ferroelectric polarization in MIS diodes or FETs should rely on other techniques as well. Recently, charge modulation reflectance and nonlinear optical spectroscopy have proved to be a powerful visualization platform for polarization reversal in organic FETs and MIS diodes; we discuss these processes in the next section.

5.2. Detecting Polarization Reversal in PVDF-TrFE FETs via Optical Modulation. Charge modulation spectroscopy, an alternate technique to DC current-voltage measurements, has been used to investigate the transport properties in FETs and MIS diodes.⁷⁸⁻⁸⁰ Typically, a small AC bias is applied to the gate electrode which modulates the charges at the semiconductor-dielectric interface. The modulating charges further varies the transmittance or the reflectance signals from the sample. Nonlinear optical effects also provide avenues for visualizing charge distribution in devices. As mentioned earlier, SHG is a measure of broken symmetry. An in-plane electric field may be an effective mechanism for breaking the symmetry in otherwise symmetric molecular or other systems. Electricfield-induced SHG (EFISHG), described as a $\chi^{(3)}$ effect, was observed in Si-SiO₂ metal oxide semiconductor (MOS) interfaces due to subinterface inversion symmetry breaking. Si-SiO₂ buried interfaces with external DC electric fields provided a mechanism for the observation of EFISHG and proved to be an effective way of mapping the charge distribution at the interface in MOS devices.^{82–86} EFISHG has provided a visualization tool for carrier injection and transport in the area of organic FETs.⁸⁷⁻⁸⁹ EFISHG generated signals have been used to correlate polarization reversal processes and the underlying charges in the semiconducting layer in PVDF-TrFE-based MIS structures.90

Iwamoto and co-workers have extensively used EFISHG and charge modulation spectroscopy (CMS) to probe electric field distribution in organic FETs and MIS structures.^{90,91} They performed CMS from ITO/PVDF-TrFE/pentacene/Au MIS diodes, where the reflectance spectrum, $\frac{\Delta R}{R} = \frac{I_{\lambda} - I_{\lambda 0}}{I_{\lambda 0}}$, was measured from the devices by biasing from -60 to 60 V. These measurements were performed by sweeping from negative to positive voltages, and vice versa. While sweeping from negative to positive voltages, -60 V was used as the reference spectrum $(I_{\lambda 0})$ and whereas sweeping from positive to negative voltages, +60 V was used as the reference spectrum. The CMS results are shown in Figure 11a, b and the experimental setup is shown in Figure 11c.90 The modulation of the CMS spectra with wavelength is due to an increase or decrease in absorption. Along with the CMS spectrum in Figure 11a, the absorption spectrum of pentacene is depicted as a dotted line where the four arrows denote absorption peaks at 540, 580, 630, and 670 nm. The voltage dependences of the CMS spectra are shown in Figure 11d at four different wavelengths, corresponding to the four absorption peak positions in pentacene. The optical modulation at 540 and 580 nm are similar to butterfly like loops seen in C-V characteristics of MFM structures (Figure 9). Upon illumination, excitons created in the pentacene layer dissociate into polarons (holes and electrons). These interfacial charges respond to the polarization reversal of the PVDF-TrFE layer. The voltage dependence of the CMS at 630 and 670 nm has been attributed to an electric field modulation in the pentacene layer. This wavelength region in pentacene has contributions from the Davydov states, which are affected due to

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Figure 11. CMS $(-\Delta R/R)$ from PVDF-TrFE/pentacene MIS diode. (a) CMS were measured from -60 V to +60 V with the reference spectrum at V = -60 V. The dashed line depicts the absorption spectrum of pentacene. (b) CMS spectra were measured from +60 V to -60 V with the reference spectrum at V = +60 V. (c) Experimental setup of CMS. (d) Voltage dependence of CMS at four wavelengths corresponding to the four peaks (depicted by the arrows in a) in the absorption spectrum of pentacene. Reproduced with permission from ref 90. Copyright 2017 AIP Publishing.



Figure 12. Polarization rotation of the PVDF-TrFE layer by 90° . (a) Device schematic showing the position of the lateral electrodes which was used for applying a lateral voltage to V-poled FETs. (b) Chemical structure of DNTT and transfer curves of DNTT/PVDF-TrFE FETs for V-poled, unpoled, and L-poled condition of the ferroelectric layer. (c) Chemical structure of pentacene and transfer curves of pentacene/PVDF-TrFE FETs for V-poled, unpoled, and L-poled condition of the ferroelectric layer. (d) Transfer characteristics of a V-poled DNTT FET subjected to two different lateral voltages. (e) Schematic transfer curves of PVDF-TrFE-based FETs for different poling conditions. The L-poled FETs show a slightly positive $V_{\rm th}$ and a high current at zero gate bias condition (depicted by the circle). The orientation of the dipoles in PVDF-TrFE as a result of the poling conditions is shown. Reproduced with permission from ref 49. Copyright 2018 American Physical Society.

spontaneous polarization. This work highlights that combining CMS with EFISHG from ferroelectric-based MIS diodes is an effective means of obtaining information on the carrier energetics in organic devices.

5.3. Polarization Rotation of the Ferroelectric Layer in FETs. MOSFETs based on ferroelectric oxides have benefitted from the prospect of tuning the polarization in the oxide layer, enabling fast switching and low-power operation.^{92,93} The spontaneous polarization in MOSFETs not only controls the channel conductance but may be further reoriented with an external field.^{94,95} Along the same lines, a theoretical prediction by Qi and Rappe analyzed the effect of polarization rotation on the performance of MOSFETs using BaTiO₃ as the gate dielectric.⁹⁶ They found that polarization rotation by 90° changes the surface potential of the Si substrate, resulting in SS < 60 mV/decade.

The above studies on MOSFETs motivated us to explore the effect of polarization rotation in organic FETs.⁴⁹ These studies were conducted using PVDF-TrFE and small molecule semiconductors such as dinaphtho[2,3-b:2',3'-f]thieno[3,2-b]thiophene (DNTT), pentacene, and TIPS-pentacene. All FETs in this study were low-operating voltage devices, well-below the coercive voltage of PVDF-TrFE, ensuring that during FET operation there was no polarization rotation in the dielectric layer. The PVDF-TrFE films after spin-coating were either V- or L-poled as shown in Figure 9a, b before depositing the organic semiconductor film and the contact electrodes. Some V-poled FETs were fabricated with two additional lateral electrodes as shown in Figure 12a, so that a lateral field could be applied to reorient the polarization direction by 90° and monitor its effect on transport.

Figure 12b, c show the transfer curves for DNTT and pentacene FETs. In each case the transfer curves from three FETs are shown for when the dielectric layer was unpoled (black), V-poled (red), and L-poled (yellow). The SS and μ_{FET} extracted from the saturation region of each of these FETs are listed in Table 1. The V-poled devices are the best with the

 Table 1. Electrical Parameters for DNTT and Pentacene

 PVDF-TrFE FETs for Different Poling Conditions of the

 Ferroelectric Dielectric^a

| semiconductor | dielectric poling condition | subthreshold swing (mV/dec) | $(\times 10^{-3} \text{ cm}^2/(\text{V} \text{ s}))$ |
|----------------------------------|--------------------------------|--------------------------------|--|
| DNTT | V-poled | 403 ± 5 | 11.3 ± 0.2 |
| | Unpoled | 1000 ± 8 | 6.0 ± 0.1 |
| | L-poled | 1700 ± 11 | 5.0 ± 0.1 |
| Pentacene | V-poled | 600 ± 4 | 2.9 ± 0.1 |
| | Unpoled | 1100 ± 7 | 1.6 ± 0.2 |
| | L-poled | 1140 ± 9 | 1.5 ± 0.1 |
| ^{<i>a</i>} Adapted from | ref 49. | | |

lowest vales of off-current and SS. The unpoled FETs performed better than the L-poled FETs, suggesting that the unpoled PVDF-TrFE film has some amount of ordering in the vertical direction. The FET performance is further tunable upon changing the polarization direction by 90° in the PVDF-TrFE layer, as seen in Figure 12d. These transfer curves are from an original V-poled DNTT FET where a lateral field was applied for approximately 15 min prior to measuring the transfer curves. While increasing the lateral field, which orients the dipoles in the horizontal direction, a clear degradation in FET properties is observed. It is worth pointing out that a similar behavior is seen in MFM diodes. Note that in Figure 9e, the accumulation capacitance decreases after a lateral field is applied.

The effect of polarization rotation on FET properties can be understood by the schematic shown in Figure 12e. Because the semiconductors used here are p-type, the V-poling direction plays a role. The overall dipole moment should point downward for a high accumulation of charges. The L-poling direction in PVDF-TrFE was chosen such that the dipole moment pointed toward the drain electrode. L-poling induces a spontaneous parallel electric field and a slightly positive threshold voltage; hence, even under the absence of any gate voltage there is a considerable drain-source current. The high off currents in L-poled FETs can also be understood from charge modulation reflectance measurements in pentacene/ PVDF-TrFE FETs; a minority carrier injection is observed when the interface is positively polarized.⁹¹

The above example shows that V-poling the ferroelectric dielectric improves FET performance. PVDF-based ferroelectrics, however, have other issues: surface roughness, dipolar disorder, and higher conductivity in PVDF (approximately 1×10^{-12} S/m) compared to other polymer nonferroelectric dielectrics.⁹⁷ Typically, these attributes result in high-gate-leakage current in FETs. In order to reduce the gate leakage current and further enhance FET performance, we have developed a method of judiciously combining V-poling and L-poling the PVDF-TrFE layer, which is presented in the next section.

5.4. Textured-Poling of PVDF-TrFE Films in TIPS-Pentacene FETs. The PVDF-TrFE films were grown on substrates that were equipped with two lateral electrodes at the bottom flanking the central gate electrode, schematically shown in Figure 13 a. After V-poling, a lateral field is applied



Figure 13. Textured-poling of PVDF-TrFE films in TIPS-pentacene FETs. (a) Representation of the FET geometry with two lateral electrodes on either side of the central gate electrode. Schematics of vertical and textured poling of the ferroelectric layer are shown on the right. (b) Optical image of a typical TIPS-pentacene FET. (c) Transfer characteristics from a V-poled PVDF-TrFE/TIPS-pentacene device. (d) Transfer characteristics from a textured poled PVDF-TrFE/TIPS-pentacene device. The gate leakage currents are shown in red. Reproduced with permission from ref 98. Copyright 2019 Wiley.

from the underside of the PVDF-TrFE films. This geometry ensures that the lateral field penetrates only a part of the dielectric film from below and does not induce any lateral polarization at the top of the dielectric layer close to the semiconductor (TIPS-pentacene layer) as long as the lateral field is not too high. Details of the poling conditions are found in ref 98. We refer to this combination of V-poling and Lpoling from beneath the PVDF-TrFE layer as textured-poling.

Figure 13b shows an optical image of a TIPS-pentacene FET (with PVDF-TrFE as the dielectric). The channel lengths of the devices were either 50 or 100 μ m. The transfer sweeps from the V-poled and textured-poled FETs (Figure 13c, d) clearly demonstrate a higher performance from the textured-poled device. One sees an improvement in the on-current and a reduction in the vertical gate-source current upon textured-

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Figure 14. Device simulation, cross-sectional TEM images of poled PVDF-TrFE. (a) Electric field simulation within a dielectric layer. The inset shows the device geometry and the region of interest in top of the gate electrode. The blue curve is the field distribution within the dielectric slab. (b) Cross-sectional TEM images from a textured poled PVDF-TrFE film of thickness ~300 nm. The zoomed-in region near the electrode marked by the blued box is shown in c. (d) Cross-section TEM image from an unpoled PVDF-TrFE films. Reproduced with permission from ref 98. Copyright 2019 Wiley. (e) Optical image of an off-centered polymer FET. (f) Transfer characteristics after L-poling a V-poled (PVDF-TrFE) off-centered TIPS-pentacene FET. Reproduced with permission from ref 98. Copyright 2019 Wiley.

poling. Since saturation is reached by -4 V, the transfer sweeps are shown only up to this value. A major benefit seen upon textured-poling is that the vertical (gate-source) current becomes independent of the gate voltage unlike the V-poled FET, where the gate-source current can dramatically increase when swept to higher voltages. The textured-poled FETs on average yield $\mu = 1 \text{ cm}^2/(\text{V s})$, on/off ratios of 1×10^5 , and SS values close to 200 mV/decade. The best vertically poled FET yield $\mu = 0.08 \text{ cm}^2/(\text{V s})$, on/off ratio of 1×10^4 , and SS of 350 mV/decade. Details of this work are found in ref 98. It is conceivable that by changing the processing condition for depositing the semiconductor layer in conjunction with textured poling will further enhance FET properties. It was shown by Lee et al. that controlling the residual solvent in TIPS-pentacene FETs improves FET properties.⁹⁹ Another approach used with TIPS-pentacene has been to blend it with polystyrene; FETs fabricated with such blends show carrier mobilities >8 cm²/(V s).¹⁰⁰

The presence of lateral electrodes allows a lateral electric field to be applied to any V-poled device for achieving textured-poling even after device fabrication. For the thickness of PVDF-TrFE used in ref 98, applying $\sim 1 \times 10^4$ V/m electric field in the lateral direction further improves the FET performance of V-poled devices. A question that occurs for textured-poling is the optimum value of the lateral field for achieving best performing FETs. We know from the previous section that a lateral field applied from the top of the dielectric increases the off current (Figure 12); hence, the magnitude of the field from below should be such that it does not penetrate the entire bulk of the dielectric layer.

5.4.1. Field Penetration in the Dielectric Layer. As apparent from the geometry of the FETs (Figure 13a), when a lateral field is applied, the electric field at the center of the gate electrode (central) must be strictly zero from Gauss's law. Simulation of the electric field distribution using a dielectric slab with a similar κ as PVDF-TrFE provides a few clues.⁹⁸

Figure 14a shows the electric field distribution between the two electrodes. The inset shows a scaled down device architecture that was used for the simulations and the region of interest. The blue field lines show a small penetration of the field in the dielectric layer, roughly 1/3 the value near the edge that falls off closer to the center of the electrode.

Cross-sectional TEM images are challenging because of the additional charging of the dielectric layer by the e-beam itself. Figure 14b, c show the cross-sectional TEM images from textured films grown on Al-coated glass. The initial TEM image from the textured poled film (Figure 14b) shows a layer of approximately 30-40 nm region near the electrode with a different morphology, which is darker in color (blue box). Repeated measurements, however, show that this region grows because of additional charging (Figure 14c). Hence, based only on TEM images, it is difficult to quantify the extent of the lateral poling in textured-poled PVDF-TrFE films. Figure 14d shows the initial cross-sectional TEM image from an unpoled film, which has no differences in morphology near the Al electrode. However, it should be pointed out that repeated measurements result in changing the color/morphology near the electrode because of additional charging effects from the electron beam.

Although the TEM images are not entirely conclusive in correlating the magnitude of the applied lateral field to the extent of the penetration of the electric field into the dielectric layer, it is safe to assume that if 1/3-1/4 of the PVDF-TrFE layer is approximately laterally poled from below, carrier mobilities of FETs are significantly enhanced. For PVDF-TrFE film thicknesses (~300 nm) used in ref 98, a lateral electric field of 1×10^4 V/m significantly improves device properties. An additional constraint is the exact placement of the channel region of the FET on the central electrode. If the devices are off-centered such as in Figure 14e, the penetration depth of the electric field is higher compared to near the center (Figure 14a, inset). The image shown here is an example from a polymer

FET. For such devices, we note that a lateral electric field of 1×10^5 V/m for a V-poled TIPS-pentacene FET can easily degrade the transfer characteristics (Figure 14f).

5.4.2. Textured-Poling: Application in Polymer-Based FETs. To check whether there is a universality in improving FET performance with textured-poled PVDF-TrFE dielectrics, further experiments have been conducted using a conjugated donor-acceptor (D-A) polymer. Copolymers of diketopyrrolopyrrole (DPP) are attractive due to their high carrier mobilities and stable performance in organic FETs.¹⁰¹⁻¹⁰⁶ One such D-A copolymer, DPP-DTT, with donor moiety of dithienylthieno[3,2-b]thiophene (DTT) and an acceptor moiety of *n*-alkyl DPP (Figure 15 a), has shown p-type carrier



Figure 15. (a) Chemical structure of DPP-DTT. (b) Transfer and output (inset) characteristics from a V-poled PVDF-TrFE/DPP-DTT FET. (c) Transfer and output (inset) characteristics from a textured-poled PVDF-TrFE/DPP-DTT FET.

mobilities >5 cm²/(V s) in FET architectures with modified SiO_2 dielectrics.^{104,107} The DPP-DTT polymer dissolved in a

mixture of chloroform and dichlorobenzene (5 mg/mL) was spin-coated on top of V-poled and textured-poled PVDF-TrFE films with evaporated Au as top contact source and drain electrodes. The transfer and output curves of representative devices are shown in Figure 15b, c. Although the SS values are similar for both V-poled and textured-poled FETs, the carrier mobility of textured-poled FETs are an order of magnitude higher than V-poled devices. The V-poled devices tend to suffer more from leakage currents. The average value of μ is 0.05 and 0.5 $\text{cm}^2/(\text{V s})$ for V-poled and textured-poled DPP-DTT FETs, respectively. Although the textured-poled DPP-DTT FETs show carrier mobilities which are an order of magnitude smaller than those obtained with Si/SiO_2 ¹⁰⁴ the operating voltages here are lower by at least a factor of 3 for top-contact FETs. The operating voltages for the DPP-DTT FETs were still lower than the coercive voltage (for the particular thickness of the PVDF-TrFE layer), ensuring that there is no spontaneous polarization reorientation during transistor operation.

5.4.3. FETs and Inverter Circuits Based on PVDF and Its Copolymers. The examples above demonstrate that textured-poled PVDF-TrFE dielectric has the potential in enhancing transport properties in organic/polymeric FETs. It could provide a path toward improving long-channel printable FETs without any nanopatterning techniques along with the benefit of low-operating voltages. Different mechanisms for solution shearing¹⁰⁸⁻¹¹¹ and novel printing methods¹¹² for depositing the semiconducting layer are expected to further benefit textured-poled ferroelectric FETs.

On the one hand, the high κ values of PVDF and its copolymers allow low-voltage-operating FETs; on the other hand, the high dipolar disorder results in overall low performance of FETs. In addition to external poling of the dielectric layer as we have developed, other groups have developed strategies of using buffer layers and combination of

| Table 2. FET Properties of Va | arious Organic Semiconductors | Using PVDF-Based | Copolymers as the I | Dielectric Layer |
|-------------------------------|-------------------------------|------------------|---------------------|------------------|
|-------------------------------|-------------------------------|------------------|---------------------|------------------|

| semiconductor | $I_{\rm on}/I_{\rm off}$ | carrier mobility $(cm^2/(V s))$ | ref |
|---------------------------|---|--|---|
| C8-BTBT | $\sim 1 \times 10^{6}$ | 4.6 | 75 |
| C8-BTBT | $\sim 1 \times 10^4$ | 0.55 | 75 |
| РЗНТ | 1×10^{4} | 0.01 | 69 |
| РЗНТ | | 0.08 | 115 |
| РЗНТ | 1×10^{5} | 2.3 | 116 |
| Anthracene | 1×10^{5} | 1.1 | 117 |
| F8T2 | 1×10^4 | 10^{-4} | 118 |
| PC12TV12T | 1×10^{4} | 0.45 | 114 |
| pBTTT-C16 | 1×10^{6} | 0.40 | 119 |
| DPP-DTT | | 1.2 | 120 |
| pentacene | 1×10^{5} | 0.12 | 121 |
| pentacene | 1×10^4 | 0.0064 | 122 |
| pentacene | $\sim 1 \times 10^3$ | 3.3 | 123 |
| pentacene | 1×10^{3} | 0.017 | 55 |
| TIPS-pentacene | $\sim 1 \times 10^4$ | 0.65 | 124 |
| TIPS-pentacene | 1×10^{5} | 1.0 | 98 |
| DNTT | 1×10^{2} | 0.01 | 49 |
| rubrene | $\sim 1 \times 10^4$ | 12 | 113 |
| ZnO^{b} | 1×10^{4} | 0.36 | 125 |
| P(NDI2OD-T2) ^b | 1×10^4 to 1×10^6 | 0.7 | 115 |
| 2DPP-TEG ^b | | 1.5 | 102 |
| P(NDI2OD-T2) ^b | 1×10^{3} | 0.27 | 114 |
| | semiconductor C_8 -BTBT C_8 -BTBT $P3HT$ $P3HT$ $P3HT$ $P3HT$ Anthracene $F8T2$ $PC12TV12T$ $pBTTT-C16$ $DPP-DTT$ $pentacene$ $pentacene$ $pentacene$ $pentacene$ $pentacene$ $TIPS-pentacene$ $TIPS-pentacene$ $DNTT$ $rubrene$ ZnO^b $P(ND12OD-T2)^b$ $2DPP-TEG^b$ $P(ND12OD-T2)^b$ | semiconductor I_{on}/I_{off} C_8 -BTBT ~1 × 10 ⁶ C_8 -BTBT ~1 × 10 ⁴ P3HT 1 × 10 ⁴ P3HT 1 × 10 ⁵ Anthracene 1 × 10 ⁵ F8T2 1 × 10 ⁴ PC12TV12T 1 × 10 ⁴ PBTTT-C16 1 × 10 ⁶ DPP-DTT pentacene pentacene 1 × 10 ⁵ pentacene 1 × 10 ³ pentacene 1 × 10 ³ TIPS-pentacene 1 × 10 ³ DNTT 1 × 10 ² rubrene ~1 × 10 ⁴ ZnO ^b 1 × 10 ⁴ P(ND12OD-T2) ^b 1 × 10 ⁴ P(ND12OD-T2) ^b 1 × 10 ³ | semiconductor I_{on}/I_{off} carrier mobility $(cm^2/(V s))$ C_8 -BTBT~1 × 10^64.6 C_8 -BTBT~1 × 10^40.55P3HT1 × 10^40.01P3HT1 × 10^52.3Anthracene1 × 10^51.1F8T21 × 10^410^{-4}PC12TV12T1 × 10^60.45pBTTT-C161 × 10^60.40DPP-DTT1.2pentacene1 × 10^50.12pentacene1 × 10^50.12pentacene1 × 10^50.0064pentacene1 × 10^33.3pentacene1 × 10^51.0DNTT1 × 10^20.01rubrene~1 × 10^40.65TIPS-pentacene1 × 10^51.0DNTT1 × 10^60.72DO ^b 1 × 10 ⁴ to 1 × 10 ⁶ 0.72DPP-TEG ^b 1.5P(NDI2OD-T2) ^b P(NDI2OD-T2) ^b 1 × 10 ³ 0.27 |

^aThe mobility values are mainly from the saturation region. ^bn-type.

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other polymer dielectrics for enhancing FET properties with PVDF-based copolymers. We highlight some of these works from several research groups which also demonstrate n-type FETs and inverter circuits using PVDF. Table 2 lists the FET properties using PVDF and its copolymers as the dielectric layer with different organic semiconductors. It should be pointed out that the actual geometries differ in terms of whether they are top or bottom contact FETs. Demonstrated in the work by Sun et al., a thin PMMA layer on PVDF-TrFE can act as a buffer layer that preserves the ferroelectricity but reduces the inherent polarization fluctuation, thus enhancing p-type carrier mobility in dioctylbenzothienobenzothiophene (C8-BTBT) FETs.⁷⁵ Another approach has been to control the chain conformation of PVDF-based copolymers by crosslinking, resulting in FET mobilities of $>1 \times 10 \text{ cm}^2/(\text{V s})$ in rubrene single crystals.¹¹³

Along with the demonstration of n-type FETs with PVDF-TrFE, complementary inverter circuits have also been achieved.^{114,115} Baeg et al. show a gain of 25 in their printed inverter circuits using blended PVDF-TrFE and PMMA as the dielectric layer. Using poled PVDF-TrFE films as the dielectric layer, Senanayak and Narayan obtain a gain of 36 and switching response of 4 MHz with their inverter circuits.¹¹⁵

6. CONCLUSION AND PERSPECTIVES

The tunability of the dielectric constant with temperature and the prospect of polarization rotation in polymer ferroelectrics allow independent parameters for tuning interfacial transport in organic FETs and enhancing device properties. Because the polaronic nature of charge carriers in organic semiconductors is coupled with disorder effects,³⁶ both local and nonlocal electron-phonon coupling are required to describe transport.³⁷ The Fröhlich polarons, which in semiconductor physics are defined in the context of polar crystals where the LO phonons can induce an oscillating macroscopic polarization,¹²⁶ are seen to play a role in FET transport when high- κ -dielectric insulators are used. PVDF-TrFE with its temperature-dependent κ provides a mechanism for describing transport in the presence of such electron-phonon interactions. However, as we have seen in the example of pentacene FETs there are limitations in extracting just the Fröhlich polaron component from current-voltage characteristics. Along with the longrange Fröhlich polarons, the Holstein polarons dominate transport. The approach thus far used for thin film organic FETs has been to use a bilayer FET with a combination of PVDF-TrFE and a nonferroelectric dielectric. 68,69 The ideal situation for distinguishing the Fröhlich polarons in the presence of ferroelectric dielectrics would be to compare the transport properties of ferroelectric FETs to an FET with an air-gap which uses the same semiconductor material. Using the air gap as an insulator in FETs has been shown with single crystals³⁴ but clearly becomes challenging for thin films.

Temperature-dependent studies from TIPS-pentacene FETs with PVDF-TrFE were less conclusive about Fröhlich polarons because the temperature range is limited to about 300 K in order for the organic semiconductor layer to remain intact, and the full polarization effect of the ferroelectric layer is not exploited. However, these studies shed light on another phenomenon, namely, the connection between the nature of trap states and transport highlighted by $\frac{d\mu}{dT} < 0$ above a certain temperature.^{35,73} The presence of discrete traps in TIPS-pentacene along with polarization fluctuation in the ferro-

electric dielectric layer manifests itself as a band-like transport. It is conceivable that other π -conjugated polymers and molecules with discrete trap states show temperature-dependent transport akin to TIPS-pentacene and the polarization fluctuation inherent to PVDF-TrFE help reveal the different regimes in transport.

PVDF-TrFE-based capacitors and FETs provide a novel route for using optical modulation and nonlinear techniques to visualize carrier energetics and polarization reversal processes.^{90,91} Techniques such as EFISHG, which are independent of contact resistance issues, will further clarify the trends in carrier mobility with temperature, for example, whether the semiconductor shows an activated transport or a band-like transport and how is it related to the trap states in FET architectures.

Recent trends in organic FETs are directed toward high-speed transistors 127,128 and low contact resistance. 129,130 In the quest for GHz frequency organic transistors, the contact resistance, channel length, and parasitic capacitance are found to be more pertinent parameters compared to only seeking high carrier mobilities.¹²⁷ There have been a few studies that show contact resistance of organic FETs to be lower than 100 Ω cm. 128,129,131 Several of these approaches require treating the Au electrodes with self-assembled monolayer (SAM) of pentafluorobenzenethiol but they typically work for bottomcontact geometries. The poling condition needed for PVDF-TrFE films limits the FET geometry to being top-contact, and thus SAM modification of the electrodes is not a viable route toward reducing contact resistance in these ferroelectric FETs. There have been efforts in using a buffer layer on top of the ferroelectric film for suppressing polarization fluctuation at the semiconductor-insulator interface, thus enhancing FET properties.^{75,132} Contact doping has been shown to be an effective means of reducing the contact resistance, especially for top-contact FETs.¹³³ Using strategies of contact doping and buffer layers may further improve FET properties based on textured-poling the PVDF-TrFE layer.

The poled FETs shown here operate in a low-voltage regime such that during normal transistor operation, $V_{\rm DS}$ and $V_{\rm G}$ were not responsible for any additional polarization rotation, and the impact of V-poling, L-poling, and textured-poling could be independently verified. This limited the usage of high performing single crystal organic semiconductors, which typically need high operating voltages for FET operation. The textured-poled FETs suggest that the lateral poled region below the V-poled region in the PVDF-TrFE layer remains sufficiently pinned even when a high gate voltage is applied. Hence, such a poling treatment may allow the use of highperforming solution-processable or single-crystalline organic semiconductors in the future even though the operating voltages may be high.

Scaling down FETs with reduced channel lengths may enhance the effect of polarization rotation such that during normal operation one may benefit from V-poling; however, such strategies involve expensive nanopatterning techniques. Textured-poling the ferroelectric layer improves FET performance, opening up the prospect of achieving high carrier mobilities without nanopatterning. The example of TIPSpentacene FET shown here, without any specific processing of the semiconducting layer and only utilizing the strategy of textured-poling of the PVDF-TrFE layer, demonstrate carrier mobilities of 1 cm²/(V s). Additional processing of the semiconducting film along with strategies enumerated above for reducing contact resistance will further boost FET performance using textured-poled PVDF-TrFE dielectrics, ensuring low-voltage operation and simple fabrication routes.

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Notes

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