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A new series of mixed phenylene–thiophene oligomers with terminal n-perfluorooctyl groups has been synthesized. These compounds are 2,5-bis(4-n-perfluorooctoylphenyl)-thiophene (DFO–PTP, 1), 5,5′-bis(4-n-perfluorooctoylphenyl)-2,2′-bithiophene (DFO–PTTP, 2), 5,5′-bis(4-n-perfluorooctoylphenyl)-2,2′,5′,2′′-terthiophene (DFO–PTP 3), 3,5,5′-bis(4-n-perfluorooctoylphenyl)-2,2′,5′,2′′,5′,2′′′-quaterthiophene (DFO–PTP, 4), and 1,4-bis[5-(4-n-perfluorooctoylphenyl)-2-thienyl]benzene (DH–PTTP, 5). These systems have been characterized by 1H and 19F NMR, elemental analysis or HRMS, optical absorption and emission spectroscopies, differential scanning calorimetry, and thermogravimetric analysis. Vacuum-deposited films were characterized by optical absorption and emission spectroscopy, X-ray diffraction, scanning electron microscopy, and field effect transistor measurements. As thin films, all of the fluorinated compounds are n-type semiconductors with carrier mobilities ranging from ≈10−6 to ≈0.1 cm2 V−1 s−1, depending on the substrate deposition temperature. Furthermore, these films exhibit very large current on/off ratios (up to ≈105) due to substantially suppressed off-currents. Particularly interesting is straightforwardly synthesized DFO–PTTP (2), which displays a combination of high mobility, high current on/off ratio, and reversible, tunable, and stable memory effects.

Introduction

Organic thin film transistors (OTFTs)1 based on molecular and polymeric materials have been proposed for a large number of civilian and defense applications, such as flexible/bendable displays, low-cost electronic paper, RF–ID elements, and smart textiles, as well as smart memory/sensor elements in the automotive and transportation industries.2–4 The principal factors motivating OFET development are the lower cost and simpler packaging requirements vs silicon-based technologies, compatibility with flexible substrates, amenability to small, specialized production runs, and suitability for large-area depositions. Furthermore, conformal coverage on nonplanar surfaces can be easily achieved, enabling new applications and uses. Most of the known organic small molecules and almost all known (semi-
conducting polymers are hole-transporting (p-type) materials. For these materials, hole field effect mobilities and $I_{on}/I_{off}$ ratios surpassing those of amorphous silicon ($\mu \approx 1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, $I_{on}/I_{off} > 10^6$) have been demonstrated. On the other hand, despite the recent important progress, n-type materials are far less developed. Therefore, the discovery of new n-type semiconductors is crucial for the success of this new technology considering the importance of organic p–n junctions, bipolar transistors, and complementary integrated circuits in modern device functions. In particular, the complementary circuit, which is comprised of both p- and n-type materials, is a fundamental component of modern electronics because of the low static power dissipation (the transistors are “on” only during switching). There are several reasons (largely phenomenological) why only a limited numbers of n-type materials have been discovered so far: (1) most conjugated aromatic cores tend to be better hole than electron transporters, for reasons that are not well understood; (2) the mobilities of most known n-type semiconductors have been relatively low; (3) the performance of current n-type materials is easily degraded in air; (4) as a consequence of factor 3, specialized instrumentation is required to accurately assay the n-type activities of new structures; (5) “organic” design guidelines to envision high-mobility air-stable n-type compounds are lacking; and (6) satisfactory charge injection models for electrode–organic semiconductor interfaces are lacking.

The thin-film transistor (TFT) is a relatively simple device, composed of three electrodes (source, S; drain, D; and gate, G), a semiconducting material, and a dielectric material, deposited on an appropriate substrate. The drain–source (D–S) electrodes provide the contacts to the semiconductor. Most organic semiconductors have been studied in a “top” TFT configuration, where the D–S electrodes (usually Au) are deposited on top of the semiconductor layer, usually deposited on SiO$_2$. However, the simplest and most manufacturable device configurations will require optimized semiconductor performance in “bottom” TFT geometries, in which the semiconductor is deposited on a patterned D–S substrate. In either configuration, the device is turned on only when a voltage is applied between the S–G electrodes. Key TFT parameters include the field-effect mobility ($\mu$) and the on/off ratio ($I_{on}/I_{off}$), which quantify the average charge carrier drift velocity per unit electric field and D–S current gain when the device is turned on, respectively. Applications require the field-effect mobility and on/off ratio to be as high as possible.

In a recent series of papers, we showed that substitution of a perfluoroalkyl for an alkyl substituent switches the majority carrier from holes to electrons in several oligothiophene series. Both $\alpha$- and $\beta$-dihexyl-substituted oligothiophenes (up to six thiophene units) are p-type semiconductors, while the analogous $\alpha$- and $\beta$-diperfluorohexyl-substituted oligothiophenes display n-type behavior. Substitution with strong electron-withdrawing perfluoroalkyl groups increases the core ionization potential in comparison to the dihexyl-substituted analogues, as well as enhancing volatility and thermal stability. At the same time, we also investigated a new class of soluble and processable dihexyl-substituted phenylene–thiophene oligomers and found that these compounds exhibit high device p-channel mobilities and on/off ratios, as well as a substantial stable and read–write tunable memory effect as solution-cast films. In this contribution, we discuss the synthesis and characterization of a new family of mixed phenylene–thiophene oligomers (1–6, Chart 1) functionalized with perfluorocetyl chains. With the exception of FET applications, their lasing and...
amplified spontaneous emission,\textsuperscript{11} and as electroluminescent materials,\textsuperscript{12} phenylene–thiophene oligomers and polymers have received little attention.\textsuperscript{13} To our knowledge, fluorocarbon-functionalized phenylene and thiophene–phenylene derivatives have never been studied as FET semiconductor materials. The goal of the present work is to preserve the high TFT performance parameters, frontier molecular orbital energy tuning, and solution processability of the phenylene–thiophene oligomer family (7–12, Chart 1), while introducing the aforementioned advantages of fluorocarbon substitution.

All of the new compounds have been characterized by UV–visible spectroscopy, photoluminescence, differential scanning calorimetry, and thermogravimetric analysis, and the corresponding evaporated films have been studied by UV–visible spectroscopy, photoluminescence, X-ray diffraction, scanning electron microscopy, and FET measurement characteristics. We show that this family represents an interesting example where transport characteristics of known p-type cores can be tuned by proper molecular functionalization. Indeed, all of the new fluorooctyl-substituted phenylene–thiophene oligomers are n-type semiconductors, with FET electron mobilities approaching 0.1 cm\( ^2 \) V\(^{-1}\) s\(^{-1}\) [for DFO–PTTP (2)] and very high \( I_{on}/I_{off} \) ratios (~10\(^7\)). Furthermore, compound 2 exhibits an exceptionally high, reversible, tunable, and stable memory effect, with a considerable threshold voltage shift toward depletion (less positive value) after applying a (negative) writing voltage.

### Experimental Section

For the general synthetic procedures and reagents, see the Supporting Information. The compounds 5,5′- dibromo-2,2′-bithiophene and 5,5′- dibromo-2,2′,5′,2′-terthiophene were prepared from the bromination by N-bromosuccinimide (in DMF) of 2,2′-bithiophene (room temperature) and 2,2′,5′,2′- terthiophene, respectively, according to known procedures.\textsuperscript{14} The reagents 5,5′-bis(tri-n-butylstannyl)-2,2′-bithiophene and 2,5-bis(tri-n-butylstannyl)thiophene were synthesized according to a known procedure.\textsuperscript{15} The compound 1,4-bis(2-thienyl) benzene was prepared from the Ni(II)-catalyzed coupling of the Grignard reagent 2-thienylmagnesium bromide with 1,4-dibromobenzene\textsuperscript{10} or by the transition-metal-catalyzed coupling of the Grignard reagent 2-thienylmagnesium bromide with 1,4-dibromobenzene.\textsuperscript{16} The reagent 2,5-bis(4-bromophenyl)thiophene was synthesized by the Pd(0)-catalyzed coupling of 2,5-dibromothiophene with 4-bromo-2,5-bis(tri-n-butylstannyl)bithiophene and 2,5-bis(tri-n-butylstannyl)thiophene synthesized according to a known procedure. The compound 1,4-bis(2-thienyl) benzene was prepared from the Ni(II)-catalyzed coupling of the Grignard reagent 2-thienylmagnesium bromide with 1,4-diodobenzene\textsuperscript{10} or by the transition-metal-catalyzed coupling of 2-thienylzinc chloride with 1,4-dibromobenzene.\textsuperscript{16} The reagent 2,5-bis(4-bromophenyl)thiophene was synthesized by the Pd(0)-catalyzed coupling of 2,5-dibromothiophene with 4-bromo-2,5-bis(tri-n-butylstannyl)bithiophene and 2,5-bis(tri-n-butylstannyl)thiophene synthesized according to a known procedure.\textsuperscript{14} \( ^{1}H \) and \( ^{19}F \) NMR (400 MHz) spectra were measured in CDCl\(_3\) or CD\(_3\)CN on a Varian Mercury 400 (room temperature) or a Varian VXR300 (high temperature) instrument. Chemical shifts were referenced to solvent peaks. Emission and absorption spectra were obtained with a Cary 1 ultraviolet–visible spectrometer and a PTI QM2 fluorescence instrument. Thermal analysis was performed with a TA Instruments DSC 2920 differential scanning calorimeter (N\(_2\) atmosphere) and a TA

\begin{table}[h]
\centering
\begin{tabular}{|c|c|}
\hline
& \textbf{Chart 1} \\
\hline
1 (DFO-PTP) & \( R = n-C_8F_{17} \) \\
2 (DFO-PTP) & \( R = n-C_8F_{17} \) \\
3 (DFO-PTP) & \( R = n-C_8F_{17} \) \\
4 (DFO-PTP) & \( R = n-C_8F_{17} \) \\
5 (DFO-PTP) & \( R = n-C_8F_{17} \) \\
6 (DFO-PTP) & \( R = n-C_8F_{17} \) \\
7 (DH-PTP) & \( R = n-C_6H_{13} \) \\
8 (DH-PTP) & \( R = n-C_6H_{13} \) \\
9 (DH-PTP) & \( R = n-C_6H_{13} \) \\
10 (DH-PTP) & \( R = n-C_6H_{13} \) \\
11 (DH-PTP) & \( R = n-C_6H_{13} \) \\
12 (DH-PTP) & \( R = n-C_6H_{13} \) \\
\hline
\end{tabular}
\end{table}


\textsuperscript{15} Wei, Y.; Yang, Y.; Yeh, J.-M. Chem. Mater. 1996, 8, 2659.


Instruments SDF 2960 simultaneous DTA–TGA instrument (10−2 Torr) at ramp rates of 10 °C/min (DSC) and 1.5 °C/min (TGA).

**Synthesis of Diperfluoroocetyl-Substituted Phenylene-Thiophene Oligomers.** Preparation of 1-Bromo-4-n-perfluoroocetylbenzene (13). To a mixture of 1-bromo-4-iodobenzene (11.9 g, 42.1 mmol), copper bronze (5.9 g, 93 mmol), and 2,2′-bipyridyl (0.46 g, 2.9 mmol) in dry DMSO (100 mL) at 70 °C under nitrogen was slowly added a solution of 1-iodoperfluorooctane over a period of 4 h. The reaction was then stirred at this temperature for 3 days and then quenched with water (200 mL). Ethanol (200 mL) was added, and the reaction was filtered through Celite. The layers were separated, and the aqueous phase was extracted several times with ether. The organic portions were then combined, dried over MgSO4, filtered through Celite. The layers were separated, and the transparent yellow solid precipitates from solution. After filtering to remove the impurity, the remaining solution was again concentrated in vacuo and after standing for several hours separated into two phases. The top layer contained 1-bromo-4-iodobenzene and residual DMSO, and the bottom layer was primarily product. These were separated, and the product was purified by column chromatography (hexanes) to get 13.1 g, colorless solid (54%). 

**Preparation of 2,2′-Bis(4-n-perfluoroocetyl)thiophene (DFO−PTP, 1).** A mixture of 1-bromo-4-n-perfluoroocetylbenzene (3.1 g, 5.5 mmol), 2,5-bis(1-n-perfluorobutylstannyl)thiophene (1.8 g, 2.7 mmol), and tetraakis(triphenylphosphine) palladium(0) (0.20 g, 0.17 mmol) in dry toluene (80 mL) was heated under nitrogen at 80 °C overnight. It was then cooled to 0 °C and filtered. The reaction mixture was then cooled on ice and filtered to isolate the yellow precipitate. This solid was washed several times with cold hexane and methanol. The crude product was then purified by gradient vacuum sublimation to give a shiny yellow solid (0.9 g, 31%), mp 193−194 °C. 

**Preparation of 5,5′-Bis(4-n-perfluoroocetyl)-2,2′-bithiophene (DFO−PTT, 2).** A mixture of 1-bromo-4-n-perfluoroocetylbenzene (2.5 g, 4.4 mmol), 5,5′-bis(1-n-perfluorobutylstannyl)-2,2′-bithiophene (1.6 g, 2.2 mmol), and Pd[PPh3]4 (0.09 g, 0.08 mmol) in dry DMSO (30 mL) was heated under nitrogen at 90 °C overnight. It was then cooled to 0 °C and filtered. The collected solid was washed several times with methanol and ether and dried under vacuum to give 2.4 g of light-yellow solid (96%). Purification by gradient vacuum sublimation afforded 1.85 g yellow solid (74%), mp 264 °C. 

**Preparation of 1-(Tri-n-perfluoroocetyl)-4-n-perfluoroocetylbenzene (14).** General procedures for the stannylation of thiophene derivatives are reported elsewhere. The lithium salt of 1-bromo-n-perfluoroocetylbenzene is very poorly soluble; however, the bath temperature during n-butyllithium addition was maintained at −40 °C to −60 °C, and after complete addition, the bath temperature was occasionally raised as high as 0 °C, at which point precipitation prevented adequate stirring. After standard workup, the crude product (light-yellow liquid) was used for subsequent reactions. 

**Preparation of 5,5′-Bis(4-n-perfluoroocetyl)-2,2′,5′,2′-terthiophene (DFO−PT−P, 3).** A mixture of 1-(tri-n-butylstannyl)-4-n-perfluoroocetylbenzene (3.6 g, 4.6 mmol), 5,5′-dibromo-2,2′-5′,2′-terthiophene (2.1 g, 2 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.25 g, 0.21 mmol) in dry DMSO (100 mL) was heated under nitrogen at 90 °C for 2 days. The reaction mixture was then cooled on ice, and the precipitate was washed with copious amounts of ether, methanol, and vacuum-dried to give 1.65 g dark red solid (63%). The crude product was then purified by gradient vacuum sublimation to give 0.31 g of a light-orange solid (12%), mp 290 °C. 

**Preparation of 2-Bromo-5-(4-n-perfluorooctylphenyl)thiophene (15).** A mixture of 1-bromo-4-n-perfluoroocetylbenzene (4.8 g, 4.6 mmol), 2-(tri-n-butylstannyl)thiophene (3.17 g, 8.49 mmol), and tetraakis(triphenylphosphine)palladium(0) (0.25 g, 0.21 mmol) in dry DMSO (100 mL) was heated under nitrogen at 90 °C for 2 days. The reaction mixture was then cooled on ice, and the precipitate was washed with copious amounts of ether, methanol, and vacuum-dried to give 1.65 g dark red solid (63%). The crude product was then purified by gradient vacuum sublimation to give 0.31 g of a light-orange solid (12%), mp 290 °C. 

**Preparation of 5,5′-Bis(4-n-perfluoroocetyl)-2,2′,5′,2′-terthiophene (DFO−PT−P, 3).** A mixture of 1-(tri-n-butylstannyl)-4-n-perfluoroocetylbenzene (3.6 g, 4.6 mmol), 5,5′-dibromo-2,2′-5′,2′-terthiophene (2.1 g, 2 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.25 g, 0.21 mmol) in dry DMSO (100 mL) was heated under nitrogen at 90 °C for 2 days. The reaction mixture was then cooled on ice, and the precipitate was washed with copious amounts of ether, methanol, and vacuum-dried to give 1.65 g dark red solid (63%). The crude product was then purified by gradient vacuum sublimation to give 0.31 g of a light-orange solid (12%), mp 290 °C. 

**Preparation of 2-Bromo-5-(4-n-perfluorooctylphenyl)thiophene (16).** At room temperature and in the absence of light, N-bromosuccinimide (1.1 g, 6.2 mmol) was added to the solution of 2-(4-n-perfluoroocetyl)phenylthiophene (3.2 g, 5.6 mmol) in DMP (100 mL) and stirred for several hours. The reaction mixture was then poured into water (200 mL), and then extracted with ether (3 × 50 mL). The organic phase was then washed with water (2 × 50 mL), dried over MgSO4, filtered, and concentrated in vacuo to give a yellow-light, fluffy solid. The crude product was purified by column chromatography (hexanes) to give 4.3 g white solid (88%). HRMS (EI, CDCl3): m/z 1242.1429 (M+ 1242.1444). Anal. Calcd for C40H14S3F34: C, 38.85; H, 1.14; F, 52.23. Found: C, 40.07; H, 1.22; F, 48.98. 

**Preparation of 2-Bromo-5-(4-n-perfluorooctyl)thiophene (17).** A mixture of 1-bromo-4-n-perfluoroacetylbenzene (4.8 g, 4.6 mmol) and 2-bromo-2′-(4-n-perfluorooctyl)phenylthiophene (3.17 g, 8.49 mmol) in dry DMSO (100 mL) was heated under nitrogen at 90 °C overnight. It was then cooled to 0 °C and filtered. The reaction mixture was then cooled on ice, and the precipitate was washed with copious amounts of ether, methanol, and vacuum-dried to give 1.65 g dark red solid (63%). The crude product was then purified by gradient vacuum sublimation to give 0.31 g of a light-orange solid (12%), mp 290 °C.
ladium(0) (0.2 g, 0.2 mmol) in dry DMF (50 mL) was heated under nitrogen at 85 °C for 2 days. The reaction mixture was then filtered, and the precipitate was washed with copious amounts of ether, hexane, and methanol and dried to give 1.59 g of yellow-green solid (66%). The crude product was then purified by gradient sublimation to give 0.32 g of bright, gold-yellow solid (13%), mp 297 °C.\(^{1}\)H NMR (C\(_2\)D\(_2\)Cl\(_4\), 120 °C): \(\delta 7.80\) (d, 4H, \(J = 7.2\) Hz), 7.72 (s, 4H), 7.66 (d, 4H), 7.44 (d, \(J = 4.0\) Hz), 7.40 (d, 2H). 19F NMR (C\(_2\)D\(_2\)Cl\(_4\), 120 °C): \(\delta -80.98\) (3F), \(-109.96\) (2F), \(-120.65\) (2F), \(-121.30\) (6F), \(-122.26\) (2F), \(-125.60\) (2F). Anal. Calcd for C\(_{42}\)H\(_{16}\)S\(_2\)F\(_{34}\): C, 40.99; H, 1.31; F, 52.49. Found: C, 40.90; H, 1.26; F, 52.45.

**Attemped Preparation of 2,5-Bis[(4-n-perfluorooctyl)phenyl]-thiophene (DFO-PPTPP, 16).** A mixture of 1-(tri-n-butylstannyl)-4-perfluorooctylbenzene (4.6 mmol), 2,5-bis(4-bromophenyl)-thiophene (0.87 g, 2.2 mmol), and tetrakis(triphenylphosphine)-palladium(0) (0.2 g, 0.2 mmol) in dry toluene or DMF was heated under nitrogen at 80–100 °C for a period of 1–3 days. The reaction was then poured onto 150 mL of water, and the entire mixture was filtered. The organic filtrate was then separated, washed with 200–400 ppm, 10\(^{-4}\)–10\(^{-2}\) M). Evaporated films were \(~500\) Å thick (as determined by an observed in situ quartz crystal monitor). For FET device fabrication, top-contact electrodes (500 Å) were deposited by evaporating gold (pressure \(<10^{-5}\) Torr); channel dimensions were 100/50 \(\mu\)m (L) by 5.0 mm (W). The silicon oxide capacitance is \(~6\) nF/cm\(^2\) for 300 nm SiO\(_2\).

**Thin Film Characterization.** Thin films (500 nm) were analyzed by X-ray film diffractometry (XRD), using standard techniques, with monochomated Cu K\(_\alpha\) radiation. All \(\theta–2\theta\) scans were calibrated with the reflection of the Si(100) substrates. Films were coated with 3 nm of sputtered Au before analysis by scanning electron microscopy (SEM) using a Hitachi S4500 FE microscope. Electrical measurements were performed using a home-built coaxial probe station and a Hewlett-Packard 4155A semiconductor parametric analyzer.

**Results and Discussion**

**Synthetic Strategies.** The new phenylene–thiophene oligomers 1–5 were synthesized as shown in Scheme 1. As in the case of the dihexyl-substituted analogues 7–12, the diperfluorooctyl-substituted compounds 1–5 are straightforwardly synthesized from readily available starting materials. Perfluorooctyl-functionalization of the phenyl ring is accomplished by coupling the iodophenyl–cuprate complex (from 1-bromo-4-iodobenzene and copper bronze) with perfluorooctyl iodide in
dry dimethyl sulfoxide (DMSO). Next, the 1-perfluorooctyl-4-bromobenzene (13) was converted to the key stannyl building block 12 in quantitative yield by reaction of the lithium derivative of 13 with n-Bu3SnCl. All of the ring—ring coupling reactions were performed according to the Stille protocol, using Pd[PPh3]4 as the catalyst and the appropriate bromophenyl or bro- mothiophene derivatives with the corresponding tri-n-butylstannyl phenyl or thiophene reagents. All these coupling reactions can be carried out in either DMF or toluene as the solvent without greatly affecting yields. Intermediates 13, 15, and 16 were purified by column chromatography on silica gel (hexanes), and all tri-n-butylstannyl intermediates can be used as crude materials in subsequent reactions. Under similar reaction conditions, the fluorocarbon-substituted derivative 6 is not formed. It has been shown that stannylbenzenes are not as active as stannylthiophenes, in particular for palladium-catalyzed coupling reactions with halobenzenes and triflates.20 The Suzuki–Miyaura cross-coupling has been demonstrated to be a valuable methodology for (oligo, poly)phenylenes, and in principle it could be a valuable alternative for the synthesis of 6.21 All perfluorooctyl-substituted systems 1–5 are purified by gradient vacuum sublimation.

**Thermal Properties of Compounds 1–5.** Capillary melting points and DSC transition temperatures for compounds 1–5 are summarized in Table 1. The melting points of 1–5 show the expected increase with subsequent thiophene unit additions to the backbone structure. Melting points of the diperfluorooctyl-substituted oligomers are substantially higher than those of the dihexyl-substituted analogues for smaller oligomers (PTP and PTTP core structures), but very close to the dihexyl analogues for larger oligomers (PT3P, PT4P, and PTPTTP core structures). A similar trend was observed when comparing perfluorohexyl- and hexyl-substituted oligothiophenes,7b but here the differences in the melting points of the smaller oligomers are more pronounced (~50 °C difference between DFO–PTP and DH–PTP), doubtless due to introduction of the longer perfluorooctyl versus hexyl chains. Compounds 1–5 all exhibit reversible thermal transitions in the DSC plots (Figures 1 and S1). In the cases of DFO–PT3P (3) and DFO–PTPTTP (5), the largest transition in the heating segment corresponds to an overlap of two transitions, which can be clearly distinguished separately in the cooling segment. For the former system, the large transition at 293

* The thermal transition with the largest enthalpy change in the DSC plot.

![Figure 1. DSC traces (scan rate is 10 °C/min under N2; 2nd heating cycle) for (A) DFO–PTPTTP (5), and (B) DFO–PT3P (4).](image)

![Figure 2. Thermogravimetric analysis plots for diperfluorooctyl-substituted phenylene—thiophene oligomers 1–5.](image)
Table 2. Absorption Maxima ($\lambda_{\text{max}}$, nm), Fluorescence Maxima ($\lambda_{\text{f}}$, nm),$^a$ and Optical Band Gaps ($E_{\text{gap}}$, eV; THF Solution and 500-Å Films on Glass)$^b$ for Phenylene–Thiophene Compounds 1–5 and 7–11

<table>
<thead>
<tr>
<th>compd</th>
<th>$\lambda_{\text{max}}$</th>
<th>$\lambda_{\text{f}}$</th>
<th>$E_{\text{gap}}$</th>
<th>$\lambda_{\text{max}}$</th>
<th>$\lambda_{\text{f}}$</th>
<th>$E_{\text{gap}}$</th>
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<tr>
<td>DFO–PT–(1)</td>
<td>336</td>
<td>382, 401$^a$</td>
<td>3.3</td>
<td>318</td>
<td>412$^a$, 440</td>
<td>3.3</td>
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<td>DFO–PT–(2)</td>
<td>386</td>
<td>439, 464</td>
<td>2.9</td>
<td>342</td>
<td>478, 509$^a$</td>
<td>2.9</td>
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<tr>
<td>DFO–PT–P(3)</td>
<td>412</td>
<td>477$^a$, 504</td>
<td>2.7</td>
<td>364</td>
<td>555$^a$, 578</td>
<td>2.6</td>
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<tr>
<td>DFO–PT–P(4)</td>
<td>436</td>
<td>505$^a$, 539</td>
<td>2.6</td>
<td>375</td>
<td>574$^a$, 616</td>
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<tr>
<td>DFO–PT–PT–P(5)</td>
<td>384</td>
<td>436$^a$, 460</td>
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<tr>
<td>DH–PT–(7)</td>
<td>330</td>
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<td>306</td>
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<tr>
<td>DH–PT–(8)</td>
<td>373</td>
<td>436, 460$^a$</td>
<td>2.9</td>
<td>332</td>
<td>523, 559$^b$</td>
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<tr>
<td>DH–PT–P(9)</td>
<td>408</td>
<td>472$^a$, 503</td>
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<td>2.6</td>
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<tr>
<td>DH–PT–P(10)</td>
<td>432</td>
<td>498$^a$, 536</td>
<td>2.6</td>
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<tr>
<td>DH–PT–PT–P(11)</td>
<td>378</td>
<td>432$^a$, 458</td>
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<td>320</td>
<td>512$^a$, 545</td>
<td>2.9</td>
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</table>

$^a$ Excitation wavelength is $\lambda_{\text{max}}$. Absolute fluorescence maxima are denoted with an asterisk. $^b$ Band gaps are estimated as the point of intersection of the normalized absorption and emission spectra. Band gap values in parentheses were estimated at 10% of absorption onset. $^c$ For compounds 8–11 from ref 4a. $^d$ For films of 8 and 9, emission was not observed (n.o.).

Optical Properties of 1–5 in Solution and as Thin Films. Optical absorption and emission maxima and optical band gaps for diperfluoroalkyl-substituted compounds 1–5 and, for comparison, the corresponding dihexyl-substituted compounds 7–11 (in solution and as thin films on glass substrates) are summarized in Table 2. Graphical representations of the UV–visible spectra in THF solution are shown in Figure S3. Within the fluorinated series, the addition of successive thiophene units to the backbone structure (1 → 4) results in a bathochromic shift of the UV–visible absorption maximum both in solution (336 to 436 nm) and in the solid state (318 to 375). A similar trend is observed in the alkyl-substituted series (7 → 10).$^{44a}$ Note that the absorption maxima of 1–4 are red-shifted (4–13 nm) with respect to that of 7–10, which is the opposite of the behavior observed for fluoroalkyl/alkyl-substituted oligothiophenes.$^{7b}$ This result can be explained by considering the enhanced charge transfer from the electron-rich thiophene to the electron density-depleted fluoroalkyl-substituted phenyl ring. The quinoidal resonance structure (b) where the sulfur electron pair is delocalized to the external phenyl ring is more stabilized for series 1–4 than in series 7–10, a result which should increase molecular planarity and $\pi$-conjugation and therefore shift the absorption maxima of the $\pi \rightarrow \pi^*$ transition to the red. This effect is less important in the oligothiophene series (and overcome by the donor/hyperconjugative effect of alkyl substituents)$^{7b,f}$ since a resonance structure of type a is already planar. That there is considerably reduced conjugation between thiophene-phenyl vs thiophene-thiophene rings is evident from the $\lambda_{\text{max}}$ red-shift on going from PT–P-type cores 5 and 11 to the corresponding $\pi$ isoelectronic PT–P systems 3 and 9. The thin-film optical absorption maxima of both series are blue-shifted with respect to the solution values (Figure 3A), indicating formation of J-type aggregates as previously observed in the unsubstituted thiophene-phenylene series.$^{13d}$

The photoluminescence spectra of both series reveal similar trends in emission characteristics. The solid-state spectra of diperfluoroalkyl-substituted series 1–5 are shown in Figure 3B. A bathochromic shift of the emission maxima is seen as the oligomer core size increases, consistent with the optical absorption. Note that strong emission is readily observed for all 1–5 films, whereas films of the alkyl-substituted analogues 7–11 exhibit either far weaker or negligible emission. This result is consistent with our previous findings that fluorocarbon substitution greatly increases solid-state oligothiophene PL efficiencies.$^{7b,f}$ Energy gaps were estimated from the intersection of normalized UV–visible and photoluminescence spectra. In the two cases where emission is not observed (films of 9 and 10), the energy gaps were estimated as the wavelength at which the intensity is $\sim$10% of the maximum absorption. Table 2 shows these estimated band gaps, both from solution
Table 3. Mobilities ($\mu$, cm$^2$ V$^{-1}$ s$^{-1}$), On/Off Ratios ($I_{on}/I_{off}$), and Threshold Voltages ($V_T$, V) for Vacuum-Deposited Films of Diperfluorooctyl-Substituted Phenylene–Thiophene Oligomers 1–5 at Various Growth Temperatures ($T_D$, °C)

<table>
<thead>
<tr>
<th>compd</th>
<th>$T_D$</th>
<th>$\mu$</th>
<th>$I_{on}/I_{off}$</th>
<th>$V_T$</th>
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<tbody>
<tr>
<td>DFO-PTP</td>
<td>25</td>
<td>0.0002</td>
<td>$1 \times 10^4$</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>na</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DFO-PTTP</td>
<td>25</td>
<td>0.0002</td>
<td>$3 \times 10^5$</td>
<td>31</td>
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<tr>
<td></td>
<td>80</td>
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<tr>
<td></td>
<td>90</td>
<td>0.0030</td>
<td>$3 \times 10^6$</td>
<td>51</td>
</tr>
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<td></td>
<td>100</td>
<td>0.0060</td>
<td>$5 \times 10^6$</td>
<td>53</td>
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<td></td>
<td>110</td>
<td>0.074</td>
<td>$6 \times 10^6$</td>
<td>55</td>
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</tr>
<tr>
<td></td>
<td>90</td>
<td>0.0039</td>
<td>$5 \times 10^6$</td>
<td>61</td>
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<td></td>
<td>110</td>
<td>0.0035</td>
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<td>57</td>
</tr>
<tr>
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<td>90</td>
<td>na</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>0.0003</td>
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<tr>
<td></td>
<td>120</td>
<td>0.0013</td>
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<td></td>
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<td>55</td>
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<td>DFO–PTPTP</td>
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<tr>
<td></td>
<td>90</td>
<td>0.0011</td>
<td>$5 \times 10^6$</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>0.0002</td>
<td>$1 \times 10^6$</td>
<td>70</td>
</tr>
</tbody>
</table>

and film data, for the two series of compounds. For a given core size, band gaps are essentially the same for both dihexyl-4a and diperfluorooctyl-substituted oligomers (in solution and in solid films) as well as for the unsubstituted systems.13d,e This trend was also observed in the dihexyl- and diperfluorohexyl-substituted oligothiophene series;7b upon fluoroalkyl substitution, the HOMO and LUMO energy levels for a given nT core are stabilized to the same extent, meaning that the differences in energy remain very similar.

Thin Film Transistor Behavior of Compounds 1–5. Table 3 summarizes the mobilities and on/off ratios of films of 1–5 deposited at various substrate temperatures ($T_D$). Top-contact TFT devices [100 and 50 μm channel lengths ($L$) and 5.0 mm channel widths ($W$)] were fabricated on p-doped Si/SiO$_2$ substrates. Mobilities ($\mu$) were calculated in the saturation regime using the relationship $\mu_{sat} = (2I_{dsd})/[W(C_{ox}(V_{gs} - V_{th}))^2]$, where $I_{dsd}$ is the source–drain saturation current; $C_{ox}$ is the oxide capacitance, $V_{gs}$ is the gate voltage, and $V_{th}$ is the threshold voltage. The latter can be estimated as the $x$ intercept of the linear section of the plot of $V_{gs}$ vs $I_{ds}$ (at $V_{sd} = 100$ V). Current on/off ratios ($I_{on}/I_{off}$) from $V_{gs} = 0 \to 100$ V were determined at $V_{sd} = 100$ V. Measurements were performed either under vacuum (~$10^{-5}$ Torr) or under an argon atmosphere without significant differences in measured FET characteristics.

Typical current–voltage characteristics for a film of compound 2 are shown in Figure 4. Note the positive gate and source–drain voltages, which indicate n-type charge transport. Evaporated films of compounds 1–3 exhibit electron mobilities in the range of $10^{-4}$–$10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ when deposited at 25 °C, whereas those of longer oligomers 4 and 5 exhibit negligible and very low values, respectively. Unlike the dihexyl-substituted analogues 7–11, where hole mobilities change at the very most by a factor of $10^\pm$ with $T_D$, the electrical characteristics of the diperfluorooctyl-substituted compounds 1–5 are strikingly sensitive to the film growth temperature. Thus, the electron mobilities of films of the DFO-substituted compounds deposited at higher temperatures are $10^2$–$10^4$ times greater than those of films deposited at 25 °C. Despite the short core length and considering the reduced intramolecular $\pi$-conjugation with respect to 3T (as judged by comparing $\lambda_{max}$ values), the compound DFO–PTP (1) affords FET-active films when deposited at room temperature. Interestingly, film growth at 50 °C affords inactive films, and higher growth temperatures cannot be explored due to the high volatility of this compound. Variations in film morphology can explain such behavior (vide infra). The mobility of DFO–PT2P (2) films deposited at 110 °C reaches the respectable value of ~0.1 cm$^2$ V$^{-1}$ s$^{-1}$, whereas the maximum mobilities of the remaining oligomers 3–5 are ~0.001–0.004 cm$^2$ V$^{-1}$ s$^{-1}$. It is interesting to note the PTTP-type core structures 2 and 8 exhibit the greatest carrier mobilities in both series. A similar trend was observed for alkyl- and fluoroalkyl-substituted quaterthiophenes, which both have the greatest carrier mobilities in the respective oligothiophene series.7b Therefore, it appears that fluoroalkyl versus alkyl substitution alters the majority carrier sign but has little influence on the “intrinsic” core charge transport capabilities. The on/off ratios of 1–5, and as seen for the corresponding systems 7–11, follow a similar trend with $T_D$. For the dihexyl series 7–11, films deposited at various substrate temperatures usually exhibit $I_{on}/I_{off}$ ratios of the same order of magnitude (typically $10^3$–$10^5$). The only exception is found for compound 7, which displays an on/off ratio 1 order of magnitude higher when deposited at higher temperatures. On the other hand, the $I_{on}/I_{off}$ ratios for the perfluorooctyl-substituted series vary over many orders of magnitude, with the most striking being DFO–PT2P, where the field-effect current enhancement increases from 0 to ~$10^7$ when going from $T_D = 90$ to 140 °C. Note that the $I_{on}/I_{off}$ ratios of 1–5 are extremely high (see Table 3), generally $10^2$–$10^4$ times larger than those of the 7–11 series, despite the observed lower on-currents. This result is clearly a consequence of the extremely low device off-currents, ranging in the
Table 4. Observed and Calculated d-Spacings (Å) and Tilt Angle (Φ, deg) from X-ray Diffraction θ–2θ Scans on 500 Å Films of Phenylene–Thiophene Oligomers 1–5

<table>
<thead>
<tr>
<th>compd</th>
<th>d-spacing (Å)</th>
<th>obsd°</th>
<th>calcd</th>
<th>Φ°</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFO–PTP (1)</td>
<td>29.0</td>
<td>39</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>DFO–PTPP (2)</td>
<td>32.1°, 28.8</td>
<td>43</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>DFO–PT–P (3)</td>
<td>39.3, 34.0°, 27.6</td>
<td>47</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>DFO–PT (4)</td>
<td>39.3</td>
<td>50</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>DFO–PTTP (5)</td>
<td>47.8, 37.6, 33.4°, 28.1, 24.6</td>
<td>47</td>
<td>45</td>
<td></td>
</tr>
</tbody>
</table>

Films grown at a substrate temperature of 50 °C (1) and 90 °C (2–5). The strongest reflection is denoted by an asterisk. For the strongest reflection.

$10^{-11}–10^{-13}$ A level (for 100 µm × 5 mm devices), probably because the oligomers in this study are not particularly electron deficient compared to other n-channel compounds, and therefore exhibit strong resistance to n-type doping.

As seen in Table 3, the carrier mobilities (and maximum source–drain currents) for films of the DFO-substituted series grown at room temperature are low, and the current–voltage characteristics do not exhibit the typical plateau in the saturation regime. Figure S4 illustrates this behavior for DFO–PTTP (2). For a gate voltage ($V_g$) of 100 V, the maximum source–drain current ($I_{sd}$) of ~25 nA occurs at a source–drain voltage ($V_{sd}$) of only 35 V and then gradually decreases to ~18 nA at $V_{sd}=100$ V. Similar results are obtained for films of 3 and 5 deposited at 25 °C, with maximum source–drain currents ($I_{sd}$) occurring in the range of $V_{sd}=25–55$ V. Because the films deposited at higher substrate temperatures do not exhibit such features in the current–voltage plots, decomposition or degradation of the films is unlikely. Rather, a change in the distribution of trap energetics upon operating the device appears to be a more reasonable explanation. Maximum currents for high-$T_D$-deposited films are in the range of hundreds/thousands of nanoamps, whereas those for 25 °C-deposited films are only tens or even tenths of nanoamps, making them more susceptible to experimental variations and more difficult to measure reliably.

**X-ray Diffraction. Film Microstructure for Compounds 1–5.** In contrast to the X-ray film diffraction studies of the other oligothiophene and oligothiophene–phenylene series, the determination of interplanar d-spacings in the present case is not as straightforward. For three of the compounds (2, 3, 5), the corresponding films exhibit multiple families of reflections in the θ–2θ scans (and thus multiple d-spacings). The observed d-spacings for films of diperfluorooctyl-substituted phenylene–thiophene oligomers 1–5 are summarized in Table 4. The simplest case is for films of DFO–PTP (1) and DFO–PT$_3$P (4), in which only one strong set of reflections is observed in the θ–2θ scans (Figure 5). For films of DFO–PTP (1), the first reflection appears at θ = 3.0°, corresponding to a d-spacing of 29 Å. Several higher order reflections in this set are observed as well (second through fifth, seventh, and ninth). For DFO–PT$_3$P (4) films, the calculated d-spacing is 39.1 Å (2θ = 2.25°). In addition, however, a cluster of weak peaks in the 18.2°-19.0° 2θ range are observed (expanded inset of Figure 5B). These small peaks correspond to a d-spacing range of 4.9–4.7 Å, which is close to the 4.6 Å d-spacing observed in the unsubstituted phenylene–thiophene oligomers and attributed to the lateral separation between neighboring molecules. A possible interpretation of these weak reflections observed in Figure 6, then, is that some portion of the DFO–PT$_3$P film adopts a parallel microstructure, in which the long molecular axes are aligned parallel to the substrate surface. Such an alignment motif is...
expected to exhibit much lower in-plane mobility than perpendicular alignment for rodlike organic oligomers. However, it seems highly unlikely that such a small relative proportion of the film that is aligned in a parallel fashion could be the sole explanation for TFT inactivity in the case of 90° film deposition. It is interesting that films of DFO–PTTP (1) and DFO–PT3P (3) deposited at high temperatures (50 and 90 °C, respectively), which appear to be the most highly textured in the XRD, are also TFT-inactive at these deposition temperatures (Table 3).

Films of DFO–PTTP (2) and DFO–PT3P (3) exhibit two and three dominant sets of reflections, respectively, with one of them being by far predominant. Therefore, films of both materials are highly textured. The 0–2θ scan of a DFO–PTTP (5) film is more complex and is shown in Figure 6. When the lower 2θ region of the plot is expanded (Figure 6B), there are at least five reflections, the second of which (at 2θ = 2.35°) overlaps somewhat with the third at 2.65°. This second peak, marked with an arrow in Figure 6A, corresponds to the five higher order reflections, also marked with arrows (Figure 7A). Interestingly, no apparent higher order reflections corresponding to the other low-angle peaks (1.85°, 2.65°, 3.15°, and 3.60°) are detected. It appears that the DFO–PTTP molecules exhibit several orientations in the 90 °C vacuum-deposited film and that the films are less textured compared to the other systems previously discussed. However, the DFO–PTTP films exhibit respectable mobilities at this deposition temperature.

An estimation of the molecular length of oligomers 1–5 can be achieved by simply adding the lengths of the unsubstituted oligomers to the estimated lengths of two perfluorooctyl chains (26.14 Å each). The latter chain length is determined as the sum of the length of a perfluorooctyl chain (from the crystal structure of perfluorohexyl-substituted 3T and 4T), two diperfluoromethylene carbon–carbon bonds (from the same crystal structure), and the van der Waals radius of fluorine (1.35 Å). These calculated oligomer lengths are also given in Table 4. The largest experimentally determined d-spacings for 1–4 are 8–10 Å less than the corresponding calculated molecular length values, except for that of 5, which is very close to the estimated length. These are larger differences than those observed in comparing hexyl- and perfluorohexyl-substituted oligothiophenes (≤4.2 Å) but similar to those observed for the dihexyl-substituted analogues 7–12 (6–10 Å). Estimation of the molecular tilt angles for the preferred orientation (strongest reflection set) with respect the substrate normal leads to a value range of 39–45°, which is impressively close considering the variation in core lengths and bond connectivities in molecules 1–5. Indeed, the phenylene–thiophene core structure, depending on the position and relative number of phenylene and thiophene units, is known to assume a variety of related molecular shapes, such as straight, bent, or zigzag. Some phenylene–thiophene oligomers have been shown to pack in a fashion similar to analogous all-thiophene systems; however, the greater variation in molecular shape due to incorporation of phenylene units could conceivably lead to packing motifs not observed for all-thiophene systems. An example of the former case is the single-crystal structure of the bent molecule 2,5-bis(4-biphenylyl)thiophene, or PPTPP, which is the unsubstituted analogue of compound DH–PPTTP (12). Interestingly, PPTPP (like unsubstituted oligothiophenes and the diperfluorohexyl-substituted 3T and 4T) in fact packs in layers in the well-known herringbone structure. However, phenylene–thiophene (P–T) oligomers with different P:T ratios might exhibit completely different crystal structures, which could explain the different molecular arrangements on the substrate surface. While X-ray diffraction analysis is an important tool for interpreting the TFT performance of various films, of greater importance for this family of compounds is the film morphology. This is discussed in the following section.

**Figure 7.** Scanning electron micrographs (bar indicates 2 μm) of 500 Å thick films grown on HMDS-treated Si/SiO2 substrates of (A) DFO–PTTP (2), Td = 25 °C. (B) DFO–PTTP (2), Td = 90 °C. (C) DFO–PTTP (5), Td = 90 °C. (D) DFO–PT3P (3), Td = 25 °C.

for films of other fluorocarbon-functionalized semiconductors, which in part explains the lower mobility (by an order of magnitude) of DFO–PTTP (2) versus π isoelectronic 6,12-diperfluorohexylquaterthiophene \((\mu \sim 0.2 \, \text{cm}^2 \, \text{V}^{-1} \, \text{s}^{-1} \) at \(T_D \sim 90 \, ^\circ \text{C}\)). Films of DFO–PTTP (5) (Figure 7C) adopt a morphology similar to those of DFO–PTTP films when deposited at 25 °C. Deposition on 90 °C substrates leads to an increase in the grain size as well, as it does for DFO–PTTP, but in the case of DFO–PTTP films, the larger grains become less rodlike and more leaflike and curled on the edges. These microstructural features may explain the reduced mobility of DFO–PTTP films at this \(T_D \) (0.001 \( \text{cm}^2 \, \text{V}^{-1} \, \text{s}^{-1} \)) with respect to DFO–PTTP (0.03 \( \text{cm}^2 \, \text{V}^{-1} \, \text{s}^{-1} \)). An image of a DFO–PTTP film deposited at 90 °C is shown in Figure 7D.

DFO–PT3P (3) films display a quite different morphology from those of DFO–PTTP and DFO–PTPTP films. For room temperature deposition, features are extremely small and not well interconnected. When the deposition temperature is increased to 90 °C, however, the films exhibit sparse, small circular features that appear to be tubelike. This is shown for DFO–PT3P in Figure 8A. Again, the higher substrate temperature for growth leads to a contiguous and smooth film, and this correlates well with the observed mobility, which is 2 orders of magnitude greater for 90 °C-deposited films than for those grown at 25 °C.

As discussed previously, DFO–PTP (1) films grown on 25 °C substrates exhibit electron mobilities comparable to or even greater than those of the films of the other phenylene–thiophene of this study (2–5) deposited under identical conditions. When DFO–PTP films are deposited onto 50 °C substrates, however, they are TFT-inactive. While \(t \sim 20 \) scans indicate that the films are highly textured, scanning electron microscopy reveals that DFO–PTP grows vertically in ridgelike plates. Thus, DFO–PTP films deposited on 25 °C substrates (Figure 8B) display a smooth surface with ridgelike crystallites protruding from the surface, whereas film deposition at 50 °C (Figure 8C) leads to very large ridges normal to the substrate surface, with little or no deposition in the areas between them. The large open regions in films produced at \(T_D = 50 \, ^\circ \text{C}\) explain the TFT inactivity of the films.

Finally, films of DFO–PT4P deposited in the 25–90 °C temperature range are TFT-inactive. The films of this compound exhibit an FET effect only when grown at very high temperatures. X-ray diffraction studies do not explain this observation, since the films are textured and already exhibit a single set of strong reflections for 90 °C depositions. However, the morphology of DFO–PT4P films is quite different from the others described above. For \(T_D < 90 \, ^\circ \text{C}\), DFO–PT4P films grow as small, rodlike, completely disconnected plates (not shown). However, when the deposition temperature is increased, it becomes clear that DFO–PT4P films grow as highly interconnected networks of ridges, as shown in Figures 8D and the inset. Thus, the reason for the dramatic increase in mobility observed for films of this compound can be correlated with dramatic, growth-temperature-dependent changes in morphology.

**Nonvolatile Memory Characteristics of DFO–PTTP (2) Films.** The nonvolatile transistor memory element is a central device in conventional silicon electronics but has only very recently been shown to have potential in organic transistors. In such devices, a voltage is placed between the gate and the semiconducting layer, and via a charge storage mechanism not completely clarified, the effective gate voltage is then altered from the applied gate voltage \(V_{ag}\). The resulting polarization creates additional electronic states within the device, and the effective threshold voltage can be altered in a controlled manner for real-world applications where available gate voltage is limited. We have shown previously that p-type DH–PTTP (8) exhibits, besides the greatest mobility, the largest memory effect in the alkyl-substituted thiophene-phenylene series. Therefore, an interesting question is whether any members of the present class of phenylene-thiophene compounds exhibit such properties and, if so, with which magnitude. The only other organic n-type semiconductor where the memory phenomenon was investigated was \(N,N^\prime\)-bis(1H,1H-perfluoroctyl)naphthalene-1,4,5-tricarboxylic diimide, where a moderate \(V_t\) shift \((\sim 10 \, \text{V})\) is observed on an SiO2 dielectric. Since DFO–PTTP (2) has an identical core to 8 and exhibits the largest mobility in the fluorinated series, we concentrated initial efforts on this system. Furthermore, since DFO–PTTP-based devices exhibit high \(V_t\) values \((30–60 \, \text{V} \, \text{depending on} \, T_D \, \text{and} \, I_D)\), this compound is an ideal candidate to reveal large current variations upon writing.

Writing voltages \((V_w)\) were applied to DFO–PTTP films between the source and gate electrodes, and before and after writing, the FET characteristics were measured and compared. It is found that DFO–PTTP (2) exhibits an exceptionally large current modulation by applying a writing voltage (vide infra). This is an interesting system because of the reversibility and predictability of the effects of the applied writing voltage. The memory effect [measured in terms of the

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applying the writing voltage. The current ratio was recorded immediately (1 s) after the current ratio by PTTP (V ratio of maximum current at Figure 9. Histogram showing memory effect tunability of DFO–PTTP films on SiO2 substrates with various applied writing voltages and times. Each bar represents the ratio of the maximum current (Vg = 40 V, Vsd = 60 V) after the indicated writing/erase voltage is applied to the same maximum current before the writing voltage is applied.

Figure 9: Histogram showing memory effect tunability of DFO–PTTP films on SiO2 substrates with various applied writing voltages and times. Each bar represents the ratio of the maximum current (Vg = 40 V, Vsd = 60 V) after the indicated writing/erase voltage is applied to the same maximum current before the writing voltage is applied.

That devices based on SiO2 dielectrics exhibit a very large ratio of maximum currents has been observed previously. For instance, typical ratios for DH–PTTP (2)-based devices on Si/SiO2 are in the range of 225–500, but the effect disappears almost instantaneously. However, for the present devices based on DFO–PTTP, the effect of writing persists for longer than 10 min! Figure 10A (and inset) shows the current ratio decay for a typical device, which appears to follow an exponential function. Note that after as long as 5 min, a current gain due to writing of ~100 times is recorded. With such a time scale, the charge storage dissipation process is slow enough that the same device could be operated many times without substantial changes in the FET I–V characteristics. Figure 10B shows current–voltage plots for a device BW and AW after 5 min. Note that in order to completely reverse the memory effect in these devices, a positive erase voltage must be applied. We observed ~10 times larger currents even in devices tested 35 min after writing. Figure 10 shows that 12 min after writing by applying an erase voltage to the device, the current ratios can be brought back close to the original value.

We previously proposed a possible mechanism for this memory effect in which static charges induced by the writing voltage (in form of isolated monopole or oriented dipoles) are injected between the semiconductor and gate electrode, either in the bulk of the dielectric and/or at one or both dielectric interfaces. This phenomenon results in a shift in the electrical potential between the gate and the semiconductor and alters the charge distribution in the transistor. Our recent results on a “floating gate” configuration suggest that, at least for DH–PTTP, most of the charge is stored at the dielectric–semiconductor interface. The results presented here confirm that hypothesis and go beyond. Since SiO2 has modest charge storage capability, the large and persistent memory effect likely involve charge accumulation at the dielectric–semiconductor interface and possibly involves the bulk fluorinated semiconductor. Probably the greater stability of the stored charge is due to the presence of the longer fluorocarbon chains, considering that Teflon is outstanding in its ability to retain charge. The study of the remaining fluorinated systems as well as implementation of dielectric materials with greater storage capabilities than SiO2 (glass resin, TOPAS, P4MS) will provide additional insight into the mechanism of the charge process.

Conclusions

A new family of diperfluoroctyl-substituted phenylene–thiophene oligomers, 1–5, has been synthesized
and characterized by optical absorption and photoluminescence spectroscopies, differential scanning calorimetry, and thermogravimetric analysis. Vacuum-evaporated films of 1–5 have been studied by UV-visible and photoluminescence spectroscopy, X-ray diffraction, scanning electron microscopy, and electrical (TFT) characteristics. All five compounds are thermally stable, exhibit reversible thermal transitions, and sublime quantitatively, and smoothly at temperatures well below their melting points.

X-ray diffraction shows that vapor-deposited films of 1–5 are textured but exhibit much weaker or multiple sets of reflections than the corresponding dihexyl-substituted analogues 7–11. Morphological characterization (by SEM) of films of 2, 3, and 5 reveals that, when grown on room-temperature substrates, the surfaces are relatively featureless but that crystallites increase in size when the deposition temperature is increased. For compound 1, ridgelike vertical features form at 50 °C, leaving areas with no deposition between them. Presumably, the resulting poor interconnectivity of the grains renders films of 1 TFT-inactive at this growth temperature. Films of compound 4 exhibit much smaller features than those of 1–3 and 5 when deposited at room temperature, but for deposition temperatures greater than 90 °C, the crystallites form highly interconnected networks, which is a key requisite for efficient charge transport. FET experiments prove that films of 1–5 are n-type semiconductors, with electron mobilities that strongly depend on the growth temperature. This is principally a consequence of film morphological changes rather than dramatic alterations in film microstructure with T_d. The mobilities of films deposited at elevated substrate temperatures are 2–4 orders of magnitude greater than for room-temperature growth. The greatest field-effect performance is observed for DFO-PTTP (2), which exhibits a mobility of ~0.1 cm² V⁻¹ s⁻¹ and an I_on/I_off ratio of ~10⁷. To our knowledge, this compound also exhibits the largest transistor memory effect ever reported for an organic material, with a current gain of ~100× and 10× times persisting 5 and 35 min after writing, respectively. These results warrant both additional investigation as well as efforts to understand/optimize charge accumulation, storage, and dissipation for this class of semiconductors.

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Supporting Information Available: General synthetic procedures and reagents and figures showing DSC traces for 4 and 5, TGA for 7–11, UV–vis for 1–5 and 7–11, and I vs V plots for a thin film of 2 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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