Influence of Molecular Structure and Film Properties on the Water-Stability and Sensor Characteristics of Organic Transistors

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Low-voltage organic thin-film transistors were fabricated to investigate the stability of organic semiconductors in water and determine the critical parameters for aqueous phase chemical detection. We showed that the molecular structure, alkyl-chain length, and thin-film morphology strongly influence the electrical characteristics in water. Highly two-dimensional films of alkyl-substituted semiconductors greatly reduced the influence of water on the electrical characteristics. The sensitivity and response times of OTFT sensors were also impacted by the thin-film structure of the organic semiconductor. OTFT sensors were used to detect 10 parts per billion cysteine and 40 ppm TNT in aqueous solutions.

Introduction

Organic thin-film transistors (OTFTs) have superior attributes for electronic sensors in part owing to the use of organic materials, which can double as the charge transport layer and the detection media.[1−6] This unique advantage arises from the ability to impart specific functionality on the active semiconductor material and enhance its sensitivity to specific materials. In addition to this fundamental advantage, the semiconductor film morphology can be controlled to modulate the interaction between the target molecules and the transistor-critical semiconductor-dielectric interface.[7] OTFTs are ideal for inexpensive, single use sensors due to their compatibility with flexible, large area substrates and simple solution-processing methods.[3,8,9]

OTFT based electronic sensors benefit from the simple design and ease of fabrication. Their basic components include a thin organic semiconductor film, an insulating layer, and three metal electrode terminals. The insulator layer separates the gate electrode from the semiconductor, and the source and drain electrodes are deposited either on the organic semiconductor (top-contact) or the insulating layer (bottom-contact). Operating as an electronic switch, the current flow between the source and drain is modulated by the bias (V_G) applied to the capacitively coupled gate electrode. Analyte binding (or interaction) is detected by a change in the electrical output, which depends on the analyte composition, concentration, and the OTFT bias conditions.[2]

OTFT sensors have been demonstrated for vapor sensing by monitoring the transistor output current change upon exposure to the analyte vapor.[10,11] The response mechanism is generally attributed to charge trapping or doping from analyte molecules diffusing through semiconductor grain boundaries.[12] Two approaches have been demonstrated to achieve selectivity toward analyte molecules: a "finger-print" approach[2,13] based upon the response of an array of multiple organic semiconductors and selectively functionalizing the active semiconductor material in order to target a specific analyte.[14,15] For the latter approach, organic semiconductors with hydroxyl-alkoxy side chains were used to enhance the OTFT response to phosphonate vapors compared to the alkyl substituted material[15] and side-chains with a chiral center were incorporated on another semiconductor molecule to discriminate between two enantiomers.[14]

OTFTs are generally incompatible with water, primarily due to high operating voltages and water-mediated material degradation and delamination.[16] Significant degradation of the device characteristics has been observed from OTFT operation in humid environments, especially when the active layer is a reactive material such as pentacene.[17,18] Recently, however, we demonstrated stable operation in water using a

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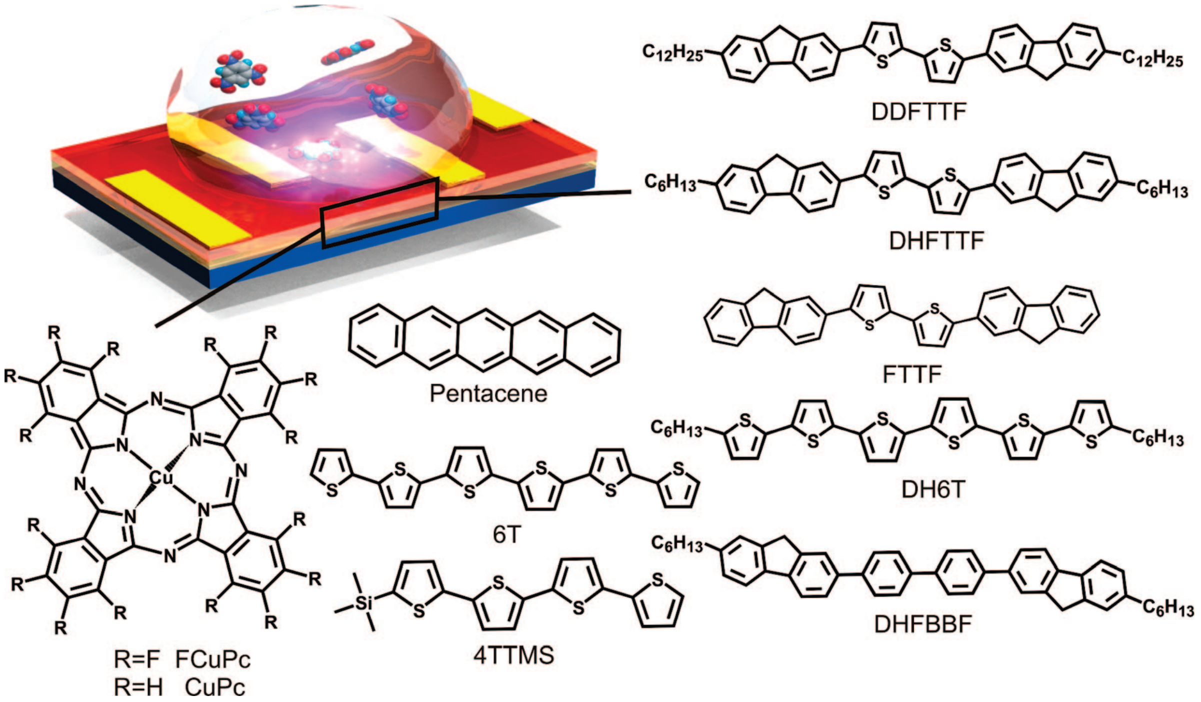

Figure 1. Schematic of an organic thin-film transistor with various common organic semiconductors.

low-voltage transistor enabled by a thin polymer dielectric layer and a stable fluorene-thiophene oligomer, DDFTTF, as the semiconductor.[19] The key to the stability in water is the ability to operate at low voltages and the use of an environmentally stable organic semiconductor. Further development of OTFT sensors functional in aqueous media has foreseeable benefits in health diagnostics, environmental monitoring,[20] and national defense.[21]

In this report, we investigate the influence of the organic semiconductor film properties, such as morphology and thickness, on their TFT stability in water and the sensor response to select analytes. A variety of common organic semiconductors, shown in Figure 1, were evaluated to access their operational stability in water. We show a strong correlation between the molecular structure and film morphology on the water stability and the sensor characteristics.

Experimental Section

Materials. All materials are purchased from Aldrich unless otherwise noted. Fluorene-thiophene oligomers, FTTF, DHFTTF, and DDFTTF,[22] trimethyl-[2,2′;5′,2′′;5′′,2′′′]quaterthiophen-5-yl-silane (4TTMS),[19] and DHFBBF[23] were synthesized according to previously reported methods. All organic semiconductors were purified by gradient sublimation under high vacuum at least twice before use, except hexadecafluoro-copper-phthalocyanine (FCuPc) and copper-phthalocyanine (CuPc), which were washed with acetone and methanol.

Device Fabrication. Polymer dielectric films were deposited on highly doped silicon substrates according to a previously reported method.[19] All semiconductor films, other than 4TTMS, were deposited by thermal evaporation (Angstrom Engineering, Inc.) at a rate of 0.3−0.5 Å/s under a pressure of 5.0×10^{-7} Torr. The substrate temperature (T_{sub}) was controlled by heating a copper block during deposition. 4TTMS films were deposited via drop-casting from a bromobenzene solution at 90 °C under a saturated solvent vapor,[24] and the residual solvent was removed under vacuum. The thickness and substrate temperature during deposition, T_{sub}, are shown in Table 1. For all devices, the top gold contacts were thermally evaporated in high vacuum at a rate of 1 nm/s while rotating the substrate holder. The electrode dimensions were defined by a shadow mask with a channel width (W) and length (L) of 1 mm and 50 μm, respectively.

Characterization. The electrical measurements were carried out in ambient using a Keithley 4200SCS semiconductor parameter analyzer and a standard probe station setup. Atomic force microscopy (AFM) was performed using a Digital Instruments Nanoscope IV operated in tapping mode (∼350 kHz frequency, Si tip).

Water-Stability Measurements. All OTFTs were characterized in water after testing under ambient conditions. A drop of deionized (DI) water was placed over the source (S) and drain (D) electrodes such that the entire channel was covered. Immediately after the addition of water, the S−D current (I_{DS}) was measured versus gate voltage (V_G) with an S−D bias of −0.6 V. The I_{DS}−V_G curves were repeated until no change in characteristics was observed. Next, the output characteristics (I_{DS}−V_{DS} for multiple V_G) were measured.

Sensor Measurements. A droplet of DI water (10 μL) was placed across the S−D electrodes (W/L = 2 mm/100 μm) as described above. The S−D current was measured versus time with a constant V_G and V_{DS}. V_G was set to −0.6 V while the V_{DS} was set to −0.3 or −0.5 V, depending on the I_{DS}−V_G curves for the

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Table 1. Electrical Characteristics of Various Organic Semiconductors under Ambient and Aqueous Conditions[a]

				ambient			water		
material	T_{sub} [°C]	thickness [nm]	V_G [V]	μ [cm^2/(V s)]	V_T [V]	on/off	μ [cm^2/(V s)]	V_T [V]	on/off
pentacene	65	40	1	1.5	0.02	5.0×10^4			
FCuPc	105	40	2	0.045	0.38	$2.7\ 10^3$			
CuPc	105	40	2	0.005	−0.52	3.3×10^3			
4TTMS	90	(soln)	2	0.09	−0.2	4.0×10^3			
6T	65	30	1	0.12	−0.38	1.5×10^3	0.18	0.36	9.00×10^1
DH6T	90	30	1	0.09	0.1	2.1×10^3	0.12	0.76	8.50×10^1
DHFBBF	90	30	2	0.013	−1.13	1.4×10^4			
FTTF	65	30	1	0.06	−0.28	9.4×10^3	0.34	0.42	3.49×10^2
DHFTTF	90	30	1	0.11	−0.06	7.9×10^3	0.14	0.38	3.35×10^2
DDFTTF	25	15	1	0.08	−0.28	1.9×10^4	0.06	0.85	1.10×10^2
DDFTTF	90	30	1	0.15	−0.04	1.2×10^4	0.17	0.68	3.10×10^2
DDFTTF	90	60	1	0.11	−0.13	9.4×10^3	0.1	0.51	1.20×10^2
DDFTTF	105	15	1	0.21	−0.3	1.1×10^4	0.18	0.38	3.20×10^2
DDFTTF	105	25	1	0.15	−0.34	3.4×10^4	0.26	0.31	7.90×10^2
DDFTTF	105	60	1	0.13	−0.18	5.0×10^3	0.14	0.44	1.30×10^2

[a] The performance in water is reported after the initial shift in electrical characteristics is stabilized.

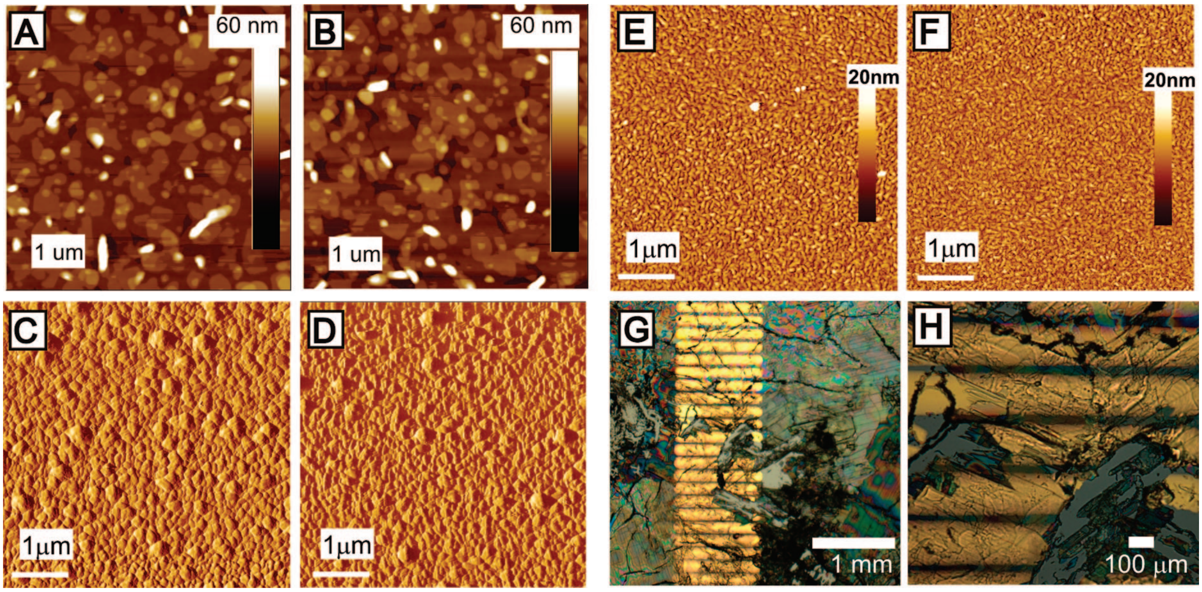

Figure 2. Influence of bias under water on the semiconductor film morphology. AFM images before/after bias under water for 15 nm DDFTTF (A/B), 40 nm pentacene (C/D), 40 nm FCuPc (E/F). A, B, E, and F are height images while C and D are amplitude images. Optical micrographs of 4TTMS are low (G) and high (H) magnification after bias under water.

particular semiconductor film. After establishing a baseline (60−90 s), a drop of analyte solution was added to the droplet of water. The measurement continued until no change in I_{DS} was observed.

Results and Discussion

A critical feature for the use of OTFTs as sensors in aqueous media is the stability of the organic semiconductor in water. Additionally, previous research has shown a strong dependence of sensor response on morphology and thickness of the organic semiconductor in vapor phase sensing;[4,25] therefore, it is also important to understand the influence of water on the electrical characteristics with similar changes in film properties. We have previously studied how the film morphology affects the electrical performance;[26,27] however, it is unclear how such morphological variations will impact the degree to which water influences these characteristics. The following section will discuss the electrical stability of OTFT operation in water based on various organic semiconductors.

The electrical characteristics of the OTFTs under ambient and aqueous conditions are summarized in Table 1. The maximum V_{DS} was limited to −0.6 V to reduce ionic conduction through the analyte solution. Although we observed ideal characteristics for all semiconductor materials in ambient conditions at $|V_{DS}|$ and $|V_G| \sim 0.6$ V, for many semiconductors no field effect is obtained in water for a variety of reasons. In the presence of water, there was a noticeable but small background current ($\sim 10^{-9}$ A) owing to ion transport through the solution. Therefore, materials with a low mobility, such as CuPc or FCuPc, showed only a small field effect and very low on/off ratios. The *n*-channel

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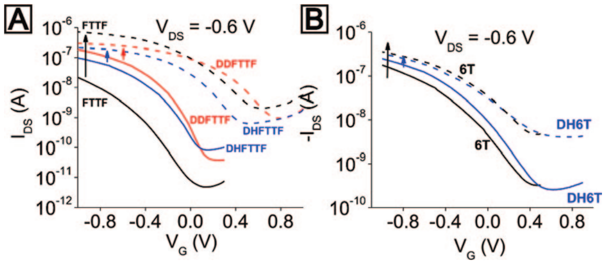

Figure 3. Change in transfer characteristics of FTTF and 6T derivatives in water. (A) Transfer characteristics in ambient (solid) and aqueous (dashed) conditions for FTTF (black), DHFTTF (blue), and DDFTTF (red). (B) Transfer characteristics in ambient (solid) and aqueous (dashed) conditions for 6T (black) and DH6T (blue).

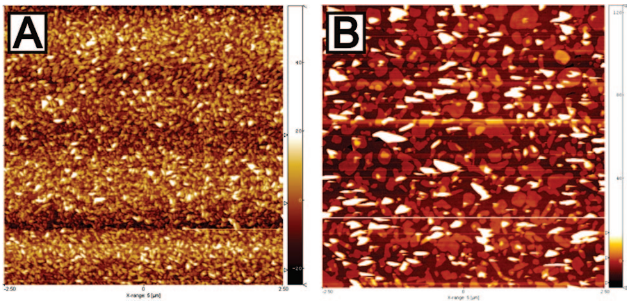

Figure 4. Fifteen nanometer DDFTTF film morphology with substrate deposition temperature. The films were deposited with a T_{sub} of 25 °C and a rate of 0.5 Å/s (A) and a T_{sub} of 105 °C and a rate of 0.2−0.3 Å/s (B).

material, FCuPc, showed some field effect, which is surprising due to the fact that it transports electrons that are more easily trapped by water molecules (online Supporting Information, Figure SI-1).[28] For materials that are unstable in ambient conditions, such as pentacene, the OTFT performance degraded too rapidly for useful operation in water, even though no morphological changes were observed. In general, the morphology of all thermally evaporated thin films tested remained unaffected by OTFT operation in water. Figure 2 shows the AFM of a few materials, DDFTTF (A,B), pentacene (C,D), and FCuPc (E,F), before and after electrical bias in water. Although the solution-deposited 4TTMS initially showed good electrical characteristics, the highly crystalline films gradually delaminated under water. While solution deposition is advantageous toward the realization of low-cost electronics, residual solvent at the dielectric interface may result in charge trapping and semiconductor delamination, as shown here. The influence of water on the output characteristics of these materials is shown in the online Supporting Information.

While many common organic semiconductors showed poor characteristics in water, we found that a variety of materials were stable, especially linear sexithiophene (6T) and thiophene-fluorene oligomer (FTTF) derivatives. The use of high performance semiconductors such as pentacene is preferred; however, these materials are not stable under atmospheric conditions, let alone water. Therefore, we turned to materials with improved ambient stability at the cost of slightly lower electronic performance, which were initially reported as a ambient stable alternatives to pentacene.[22,29] Here, we used 6T and FTTF derivatives to explain the impact of the semiconductor side chain and thin-film morphology on the responsiveness of the electrical characteristics to water environments.

Previously, we showed that OTFTs based on DDFTTF were extremely stable in water over 10 000 electrical cycles.[19] The stability was attributed to the close packing nature of the alkyl chains. When exposed to water, the device parameters changed in accordance with semiconductor doping: an increase in mobility, a decrease in on/off ratio, and a positive shift in threshold voltage. Similar doping effects were reported for polythiophene and pentacene films on a hygroscopic dielectric upon exposure to humidity.[30,31]

The influence of water on the transistor characteristics is well correlated with the alkyl side chain length for FTTF and 6T semiconductor cores. Figure 3 shows the change in transfer characteristics ($I_{DS}-V_G$) for FTTF (A) and 6T (B) derivatives. For each material evaluated, the exposure to water leads to a positive shift in threshold voltage and an increase in both the on and off current. The shift in electrical characteristics happens gradually as water penetrates the film and has been attributed to the hydronium ions accumulating at the semiconductor−dielectric interface by the negative gate voltage. For the FTTF derivatives, the shift in characteristics depends on the side chain length. The increase in mobility is the largest for FTTF (no side chains), still considerable for DHFTTF (hexyl chains) and the least for DDFTTF (dodecyl chains). The on−off ratio of each material depends only on the on-current, since the off-current arises mainly from the ionic transport through the water. A similar correlation is shown for 6T derivatives. The increase in carrier mobility of DH6T is less than that of 6T owing to the presence of the hexyl chains, which induce closer thin-film packing[29] and repel water from the dielectric interface.

An advantage of using organic thin-film transistors for chemical sensors is the ability to control the film morphology by the choice of molecular structure (side chains) and film growth conditions. Many studies have been conducted on correlating the growth conditions to the semiconductor film morphology and electrical performance for oligothiophene[29] and thiophene-fluorene oligomers.[26] In most cases, a higher substrate temperature during deposition, T_{sub}, and a lower molecular flux (i.e., deposition rate) lead to films with large two-dimensional grains and a high charge charier mobility, μ.[32] Conversely, depositions carried out at room temperature with a high molecular flux typically result in films with many three-dimensional grains. For the vapor sensing, the OTFT response has been well correlated with the number of grains boundaries; [4,25] however, it is unclear whether or not the film morphology will influence the electrical characteristics in a complex medium, such as water.

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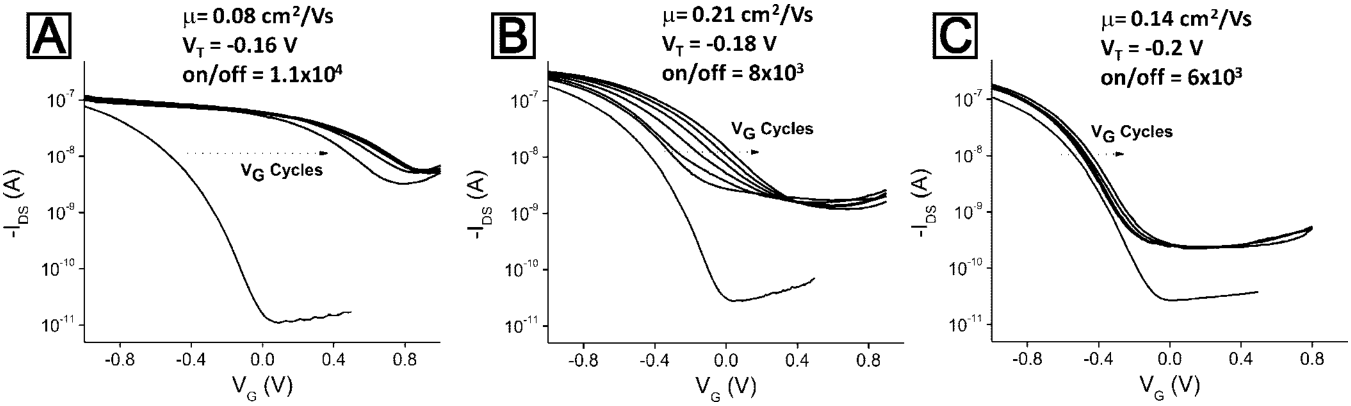

Figure 5. Influence of water on the transistor characteristics of DDFTTF thin films with morphology and thickness. The OTFT characteristics are shown in ambient (gray) and water (black) for DDFTTF films deposited at 25 °C and 0.5 Å/s to a thickness of 15 nm (A) and 105 °C and 0.3 Å/s to a thickness of 15 nm (B) and 25 nm (C).

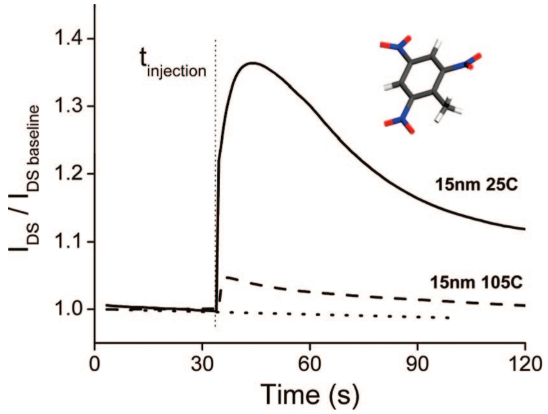

Figure 6. OTFT sensor response of two-dimensional (15 nm, 105 °C) and three-dimensional (15 nm, 25 °C) DDFTTF films to TNT.

For similar growth conditions, the morphology strongly depends on alkyl-chain length. Thin films of DH-6T were highly two-dimensional with large grains compared to films of 6T, which generally consisted of small grains with many boundaries. The morphological differences arising from the film molecular structure, in addition to the close-packing hydrophobic chains, could contribute to the change in transistor characteristics presented in Figure 3. OTFTs were fabricated with DDFTTF semiconductor films with varying morphology and thickness. Films with high grain densities were deposited using a T_{sub} of 25 °C and a rate of 0.5 Å/s, while films with larger and more two-dimensional grains were deposited using a T_{sub} of 105 °C and a rate of 0.2−0.3 Å/s to a thickness of 15 nm, 25 nm, and 60 nm. The morphology of the 15 nm films is shown by the AFM micrographs in Figure 4.

Upon exposure to water, the time to reach the steady-state transfer characteristics depends on the film morphology and thickness. The evolution of the $I_{DS}-V_G$ curves over time is shown in Figure 5, with the ambient characteristics shown in gray. Subsequent curves were recorded immediately after the addition of water with approximately 30 s between each measurement. Films with a high grain density (25 °C, 15 nm) underwent a rapid change in characteristics reach steady-state immediately after the addition of water. The change in characteristics for thin films with larger, two-dimensional grains (105 °C, 15 nm), however, occurred gradually over the period of a few minutes. The influence of water on the semiconductor properties can be reduced by increasing the thickness of the two-dimensional films deposited with a high T_{sub}, as shown in Figure 5C. These results are consistent with the picture of water penetrating the semiconductor film primarily by diffusion through the film grain boundaries.

The sensor characteristics, including response time and sensitivity, were evaluated for films with varying grain size and thickness. After adding a droplet of DI water (10 μL) to the OTFT channel region, a constant bias of $V_{DS} = -0.6$ V and $V_G = -0.3$ V was applied. The measured baseline reflects a slight drift in I_{DS} with time due to gate bias stress;[33,34] however, the initial current could be restored after removal of V_G. The baseline was established for a short period (~60 s), and then a small volume (2 μL) of analyte solution was added to the existing water droplet.

The influence of film morphology on sensor response time and sensitivity is shown using a 40 ppm (ppm) solution of 2,4,6-trinitrotoluene (TNT). No attempt was made here to detect lower concentration solutions; however, we have previously shown as low as 0.3 ppm for 2,4,6-trinitrobenzene (TNB).[19] As shown in Figure 6, the change in current, ΔI_{DS}, and response time is greater for the film with small grains than for film with large 2-D grains. The increase in current is attributed to the electron-withdrawing characteristics of the TNT molecules accumulating at the grain boundaries and interacting with the positive charge carrier traps. Thus, the film with greater number of smaller grains can accommodate more analyte molecules leading to a larger change in current. A similar correlation has been shown in the vapor phase for oligothiophene films to 1-pentanol.[25]

The OTFT sensor characteristics for TNT vary from typical sensor response curves, where a change in current is observed followed by saturation to a constant value. However, most sensor characteristics reported to date have been performed in the vapor phase rather than in a complex background, such as water. While the mechanism for the current change is not completely understood, the difference in response for films with different grain sizes exemplifies the importance of grain boundaries and diffusion and adsorption at these critical interfaces. After the initial increase, the current gradually decreases to a steady-state value greater than the baseline current, indicating that the

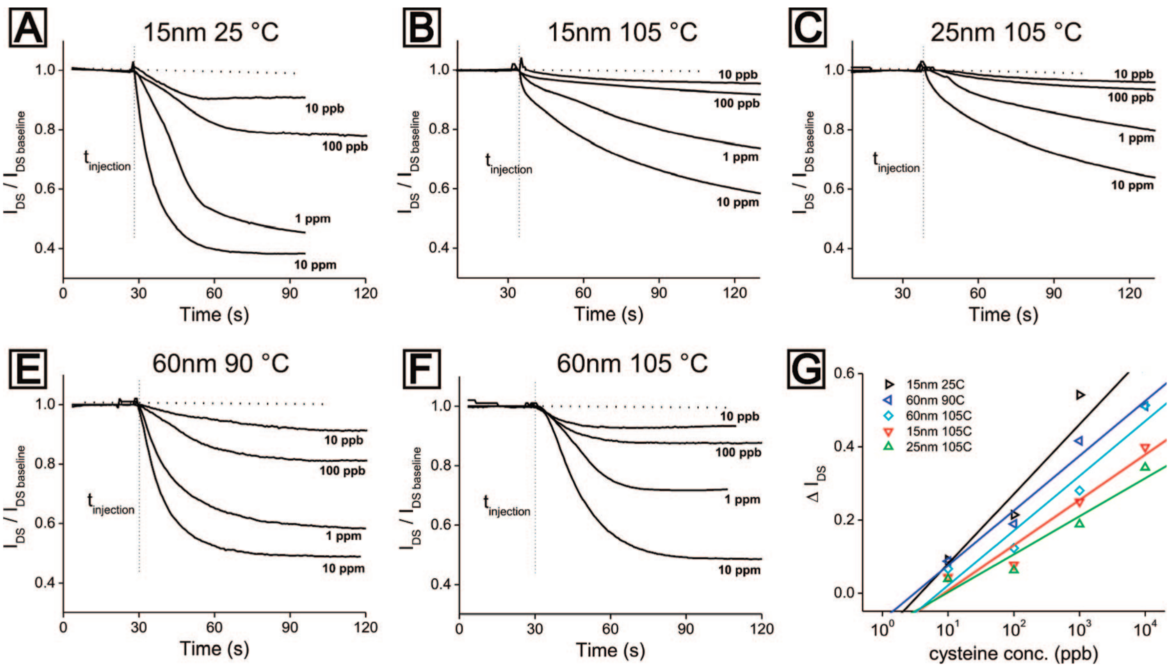

Figure 7. Sensor response and sensitivity to aqueous solutions of cysteine with film morphology and thickness. $I_{DS}/I_{DS\text{-baseline}}$ versus time is shown for DDFTTF films with the following thickness and T_{sub}: 15 nm 25 °C (A), 15 nm 105 °C (B), 25 nm 25 °C (C), 60 nm 90 °C (D), and 60 nm 105 °C (E). ΔI_{DS} is plotted versus cysteine concentration on a semilog plot (F). A line fit shows the detection limit for these films around 2−5 ppb.

analyte is indeed influencing the charge transport in the channel. The initial “overshoot” could be attributed to an initial nonuniform distribution of analyte in the solution resulting in adsorption and desorption of the analyte at the surface of the semiconductor film or analyte interactions at the electrode interfaces. The mechanism for analyte interaction in the presence of water is currently under investigation.

A more thorough evaluation of the OTFT sensor response with film morphology and thickness was performed using a model analyte, cysteine. Previously, we observed a strong I_{DS} response to aqueous solutions of cysteine down to 100 parts per billion (ppb) for 40 nm DDFTTF film deposited at a T_{sub} of 90 °C. In the following section, we evaluate the change source-drain current for the films previously described (3-D and 2-D), in addition to thicker (60 nm) semiconductor films.

The OTFT response, $I_{DS}/I_{DS\text{-baseline}}$, to cysteine solutions with a concentration down to 10 ppb is shown in Figure 7. For the thin semiconductor films, we observed a markedly greater ΔI_{DS} with a faster response time for the high grain density films. The change in current for the films comprised of more two-dimensional grain films deposited at 105 °C was much less, and saturation was only reached after significantly longer times. A larger response was observed for the 15 nm film compared to the 25 nm film revealing the thickness dependence. Thicker (60 nm) semiconductor films still show a strong response to cysteine solutions. The films deposited at a higher T_{sub} and containing larger grains shows a more delayed response immediately after the addition of the analyte. The total ΔI_{DS} after reaching saturation, however, is similar for both films. As previously suggested, the change in OTFT characteristics occurs through an interaction of the analyte molecules with the semiconductor molecules directly in the thin electrically active charge transport layer and bulk interaction within the film. Additionally, the large range of responses observed for different films suggests that the response is not contact related but caused by changes in the semiconductor channel.

The dependence of the OTFT response on the cysteine solution concentration is shown in Figure 7G. The sensitivity to analyte concentration changes can be determined from the slope of ΔI_{DS} ($\Delta I_{DS} = 1 - I_{DS\text{-saturation}}/I_{DS\text{-baseline}}$) when plotted versus the analyte concentration. As expected, the sensitivity significantly depends on morphology and grain boundary density and much less on thickness. Since the I_{DS} response mainly depends on the analyte’s electronic role in the conducting channel region, the ppb detection limits for cysteine are similar for each film; however, the overall response time varies with the film properties.

Conclusion

In this report, we discussed the stability of various organic semiconductors toward water and investigated the basic material requirements. The influence of molecular structure and side chain length on the stability in water was shown for FTTF and 6T derivatives. Furthermore, we showed the influence of water on OTFT characteristics with different morphologies and thicknesses. The OTFT response, ΔI_{DS}, was correlated with film morphology and thickness. While rough, nanocrystalline films display large $I_{DS} - V_G$ changes in water, their response to analytes is much greater than their two-dimensional counterparts. This works shows that trace chemicals can be electronically detected using organic transistors.

In addition to understanding the relationship between the film properties and the sensor characteristics in water, another important challenge facing organic transistor based sensors is the ability to discriminate between various analytes. While a few examples have been reported showing an increased sensitivity to a particular analyte by imparting functionality to the semiconductor layer, the fundamental explanation describing the change in current in response to a particular analyte is lacking. Strategies to achieve specificity for the OTFTs discussed here could be as straightforward as incorporating a sensor layer with enhanced specificity toward a particular analyte[14,15] or integrating a selective membrane on the surface of the OTFT to eliminate exposure to nontarget analytes. We are currently investigating such methods to achieve specificity using molecular and interface engineering.

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Supporting Information Available: Output characteristics of various organic semiconductors under ambient and aqueous conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

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