

Probing Organic Field Effect Transistors In Situ during Operation Using SFG

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Organic field effect transistors (OFET) have attracted considerable attention recently as an enabling component for “organic” or “plastic” electronics.¹ Plastic electronics has several advantages over silicon-based electronics in terms of the possibility of low cost, roll-to-roll processing, and the development of electronics on flexible substrates.² However, considerable challenges in organic semiconductors, such as low mobility, irreproducible electrical characteristics, and long-term stability, need to be overcome for OFETs to gain widespread acceptance.

In previous spectroscopic studies, optical absorption, Raman, photoelectron spectroscopy, and second harmonic generation have been used to characterize the structure of the thin film semiconductors.^{3–8} During operation of the OFET, changes in the thin film occur in a very thin channel region near the gate dielectric; hence considerable information could be obtained if this interface were studied in situ. In this communication, we report results obtained using surface-sensitive IR+Visible Sum Frequency Generation (SFG)⁹ nonlinear optical spectroscopy on interfaces of OFETs during operation. We observe remarkable correlations between trends in the SFG spectra and electrical properties of the transistor, with varying gate voltage (V_G). These results suggest that field effects on electronic conduction in thin film organic semiconductor devices are correlated to interfacial nonlinear optical characteristics.

We integrated the SFG setup in our laboratory¹⁰ with a four-probe electrical measurement system. This system allowed us to simultaneously measure SFG spectra and source-drain currents (I_{SD}) while applying voltages across source-drain (V_{SD}) and gate electrodes. We fabricated OFETs with bottom gate and top gold electrodes using thin film deposition and evaporation through a shadow mask (Figure 1).

Four organic thin films, 5,5'-bis(4-hexylphenyl)-2,2'-bithiophene (6pttp6), pentacene, 4,4'-dihexylbiphenyl (DHB), that has the phenyl rings and hexyl side chains, similar to 6pttp6, but no thiophene rings), tetracontane (C_{40} , a linear alkane), and a control sample with bare silicon dioxide (SiO_2) were investigated. The first two organic films are p-channel semiconductors, while the latter two would be expected to be insulators.

To probe the p-channel interface of the organic thin films and the bare SiO_2 , SFG spectra were taken while V_G was tuned from -80 to $+80$ V, all at $V_{SD} = 0$ V. When a negative V_G was applied above the threshold, the 6pttp6 and pentacene OFETs operated in accumulation mode with carriers being predominantly positively charged (holes). For each voltage step, we averaged over 5 spectra, with 50 data acquisitions per point. To avoid damaging the organic film, the intensities of both the visible beam and IR beam were reduced to the minimum possible level. The optical beams were also moved to new locations within the same transistor device after every two spectra. No damage was observed during SFG spectral acquisition, and the SFG and I - V curves reported were reversible.

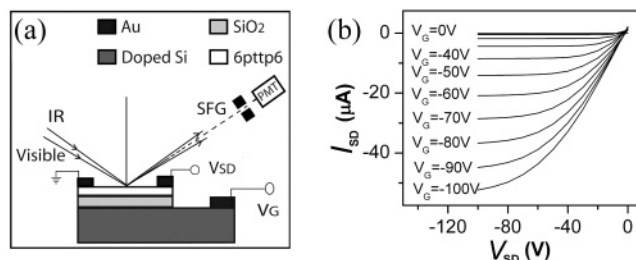


Figure 1. (a) Schematic diagram of the combined SFG and electrical probe station system. The OFET dielectric was a 300 nm thick thermally grown silicon dioxide film, and the gold contact pads were 50 nm thick with a transistor width/length ratio of approximately 23. (b) Typical electrical characteristics of the 6pttp6 OFET showing transistor action.

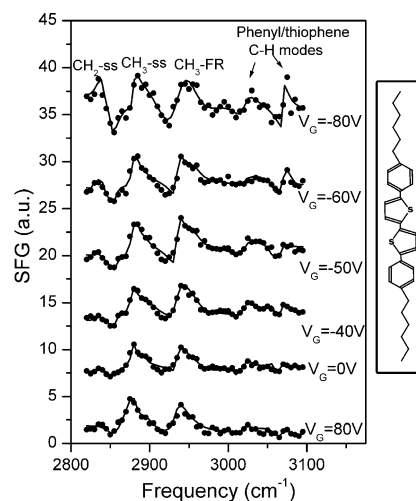


Figure 2. SFG spectra in ssp polarization (s-polarized SF output, s-polarized visible input, and p-polarized infrared input) of the 6pttp6 (molecular structure shown) OFET taken at different V_G . The black dots represent raw data points, while the solid line is a fit of the data to the expected SF signal intensity equation⁹ consisting of nonresonant and resonant terms.

There are several peaks in the SFG spectra of 6pttp6 (Figure 2). The important peaks have been assigned to the CH_3 -ss (symmetric stretch, 2880 cm^{-1}) from the end group of the molecule, the CH_2 -ss (2845 cm^{-1}) present on the backbone, and C-H modes from the phenyl and thiophene rings in the central part of the molecule (between 3000 and 3100 cm^{-1}).¹¹ Due to good signal-to-noise ratio for the CH_2 -ss and CH_3 -ss peaks, we represent characteristic changes in the molecule as a ratio of the two peaks. With increasing negative V_G , we observed an increase in the ratio of the CH_2 -ss peak to that of the CH_3 -ss peak intensity. No discernible change in the peak intensity ratio was observed at positive V_G . By fitting the spectra to the master SFG equation,⁹ we extracted the values of the peak strength/damping constant (A/Γ ; which is proportional to the product of the concentration and orientational average of the molecular chromophores) for each peak.

Since the semiconductor films are very thin (~ 50 nm), it is possible to get SFG signal from both the SiO_2 -semiconductor

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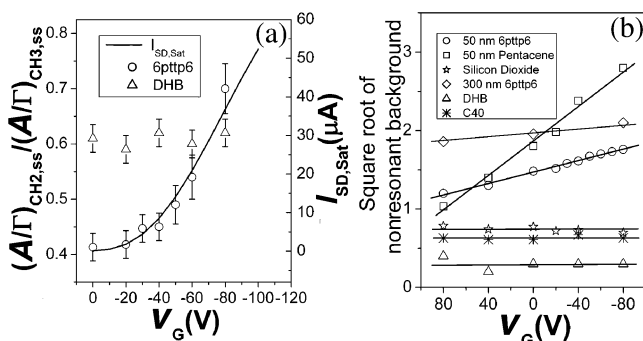


Figure 3. (a) A plot of the peak intensity ratio (points) for CH₂-ss and CH₃-ss and $I_{SD,sat}$ (solid line) measured on 6pttp6 and DHB OFETs plotted as a function of increasing negative V_G . (b) A plot of the square root of the nonresonant background versus V_G . The largest slope was observed for the pentacene OFET which has the highest carrier mobility.

interface, as well as from the semiconductor–air interface. Any anisotropy in the bulk can also contribute to the signal. To determine which interfaces were contributing to the change in the signal observed with V_G , we took SFG spectra using a thicker (~ 300 nm) 6pttp6 film. In this case, we observed that the increase in the peak intensity ratio of CH₂-ss/CH₃-ss with increasing negative V_G was approximately halved (as compared to the thin sample at similar I_{SD} values). If the SFG signal were coming predominantly from the semiconductor–air interface or the bulk, we would expect that the intensity change for the thick sample would have remained unchanged or increased, respectively. However, since this is not the case, although the total signal may include contributions from the air–semiconductor interface including interference effects, we are confident that the changes in the signal observed are from the SiO₂–semiconductor interface; the changes measured by SFG would then decrease (as observed) with increasing thickness since the IR beam is attenuated while passing through a thicker sample. Our results are consistent with the known fact that, in these organic OFETs, only the molecular layers nearest the dielectric interface are most affected by the electrical field.¹²

While we did observe transistor action (Supporting Information) and a change in the baseline of the SFG spectra with increasing negative V_G on pentacene OFETs, due to poor signal-to-noise ratio of the SFG spectra, we cannot comment on any relative peak intensity changes. We obtained good SFG spectra from DHB and C₄₀, with well resolved CH₂ and CH₃ peaks; however, we did not observe any transistor action nor any discernible change in the SFG peak ratio or the baseline with varying V_G on these OFETs. These results, along with the fact that we observed no CH₂/CH₃ peak intensity change for 6pttp6 and pentacene OFETs at positive V_G , suggest that the SFG peak ratio changes observed in 6pttp6 and pentacene with varying negative V_G are due to charges stabilized by the conjugated cores (occurs only at negative V_G) of these molecules.

For 6pttp6, the rise in the intensity ratio of CH₂-ss/CH₃-ss peaks with increasing negative V_G correlates remarkably well with the dependence of $I_{SD,sat}$ on V_G (Figure 3A). No measurable shift in the frequency of the SFG peaks (within the resolution of 5 cm⁻¹) was observed with varying V_G . Since the 6pttp6 film is polycrystalline (the long molecular axes lie roughly perpendicular to the surface¹³), with limited molecular motion, we do not expect a large change in molecular orientation with electric field. Such a large change would also likely affect both CH₂ and CH₃ peak intensities. We believe that the change observed only in the CH₂ peak intensity is due to a structural change in the alkyl chain due to the presence of the delocalized charge in the conjugated core of the molecule at negative V_G . One possible structural change is a trans-gauche conformational change of CH₂ groups that changes the local symmetry

within the alkyl chain and can increase the SFG CH₂ peak intensity.^{14,15} The charged conjugated core of the 6pttp6 molecule is expected to most significantly affect the CH₂ groups nearest it.

In Figure 3B, we plot the square root of the nonresonant background versus V_G . An increase was observed for thin and thick 6pttp6 and pentacene OFETs, and no change was observed for the insulators DHB, C₄₀, and SiO₂. We explain the increase by noting that, at high electric fields, a contribution to the SFG intensity can result from higher order susceptibility terms (field-induced SFG).¹⁶ Since the increase was much higher in the nonresonant background as compared to the increase in the intensity of individual resonant peaks (as can be seen in Figure 2), we believe that this field-induced SFG results primarily from electronic effects in the semiconductor. It is evident from the data that the increase in the SFG background measured on the OFETs depends on the field, as the increase in the thicker sample (the field is smaller in a thicker sample at the same applied V_G) was smaller than that in the thinner sample at the same V_G . Remarkably, the highest slope in the SFG background shift was observed for the pentacene OFET, which was also measured to have the highest carrier mobility. The field effective carrier mobility of the 50 nm 6pttp6 and pentacene OFETs studied was extracted from measured I – V curves to be 0.06 and 0.2 cm²·V⁻¹·s⁻¹, respectively. This suggests that factors that strongly influence the field response of the nonresonant background in SFG spectra (e.g., ordered domains of molecules with large higher order nonlinear susceptibilities) are correlated to high electronic mobility.

In conclusion, using SFG surface-sensitive spectroscopy, we have observed strong correlations between structure and electronic properties of organic semiconductors at the dielectric semiconductor interface. These correlations point to the possibility of using SFG spectroscopy to monitor electronic properties of OFETs. Additional experiments with other OFETs as well as temperature-dependent measurements are planned.

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Supporting Information Available: This section includes the chemical formulas of the organic thin films studied and the electrical characteristics measured on pentacene. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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