Electronic Supplementary Information for:

Real-Time Structural Evolution at the Interface of an Organic Transistor During Thermal Annealing

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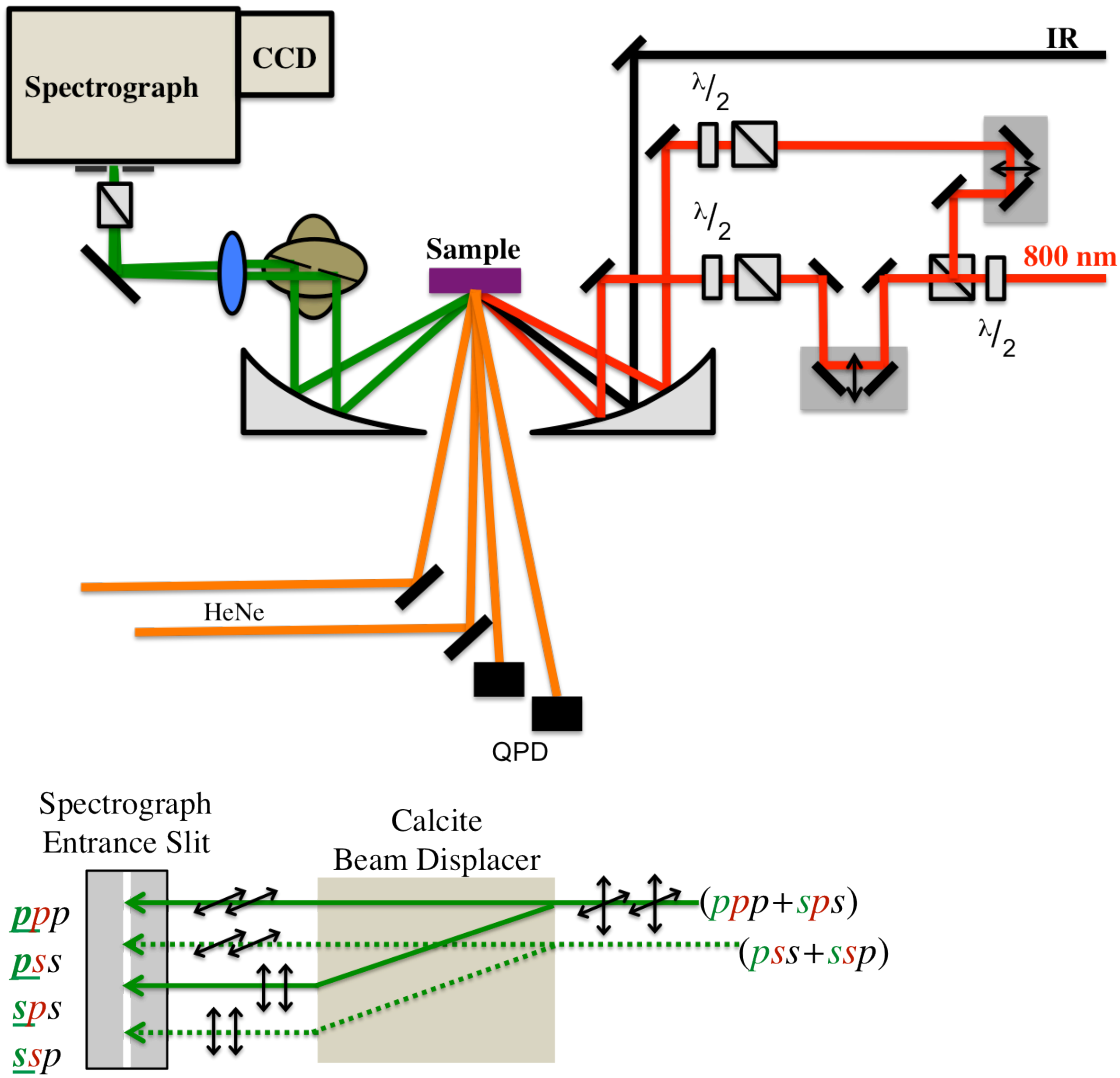

Figure S1. Schematic of the PM-VSFG instrument used in these studies. Red lines indicate the 800 nm beams (*s* and *p* polarized), black line indicates the mixed polarization MIR beam, orange lines are the two alignment HeNe paths, and green shows the direct of the VSFG signals. Just before the spectrograph is the beam displacer optic, shown in expanded view below. The two mixed polarization VSFG beams are filtered into 4 beams covering all four necessary polarization combinations to completely characterize the $\chi^{(2)}$.

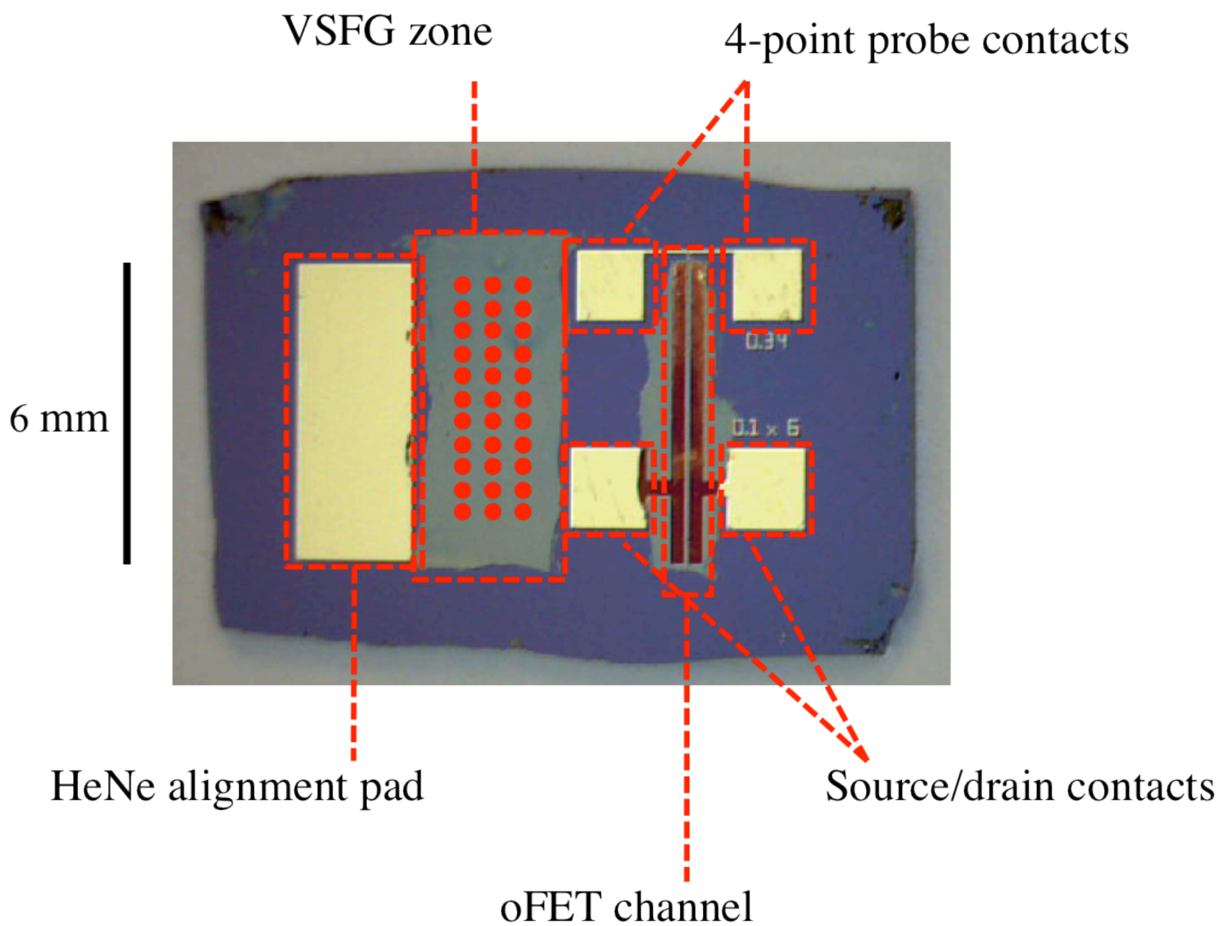

Figure S2. Labeled photo of a sample used for PM-VSFG studies. The rectangular pad on the left is used for aligning the sample and maintaining its alignment during the annealing process. The pad reflects the HeNe beams to the QPDs. The VSFG zone shows the portion of the sample where the PM-VSFG beams overlap. The 33 red spots indicate approximately where the laser spots are focused for the spectra collected at a given temperature. The sample was translated to a new spot for each temperature point to prevent film degradation by the irradiation. With this scheme we found that returning to the same spots on a subsequent pass yielded the same spectrum. The electrical connections are made to the source and drain contact pads, the gate is on the underside of the device. The four-point probe contacts were not used in this study. In this diagram, it is clear that the electrical and optical measurements are spatially separated, which was necessary to avoid degradation. P3HT is spin-coated over the entire VSFG zone and oFET channel, and then carefully removed in interstitial regions.

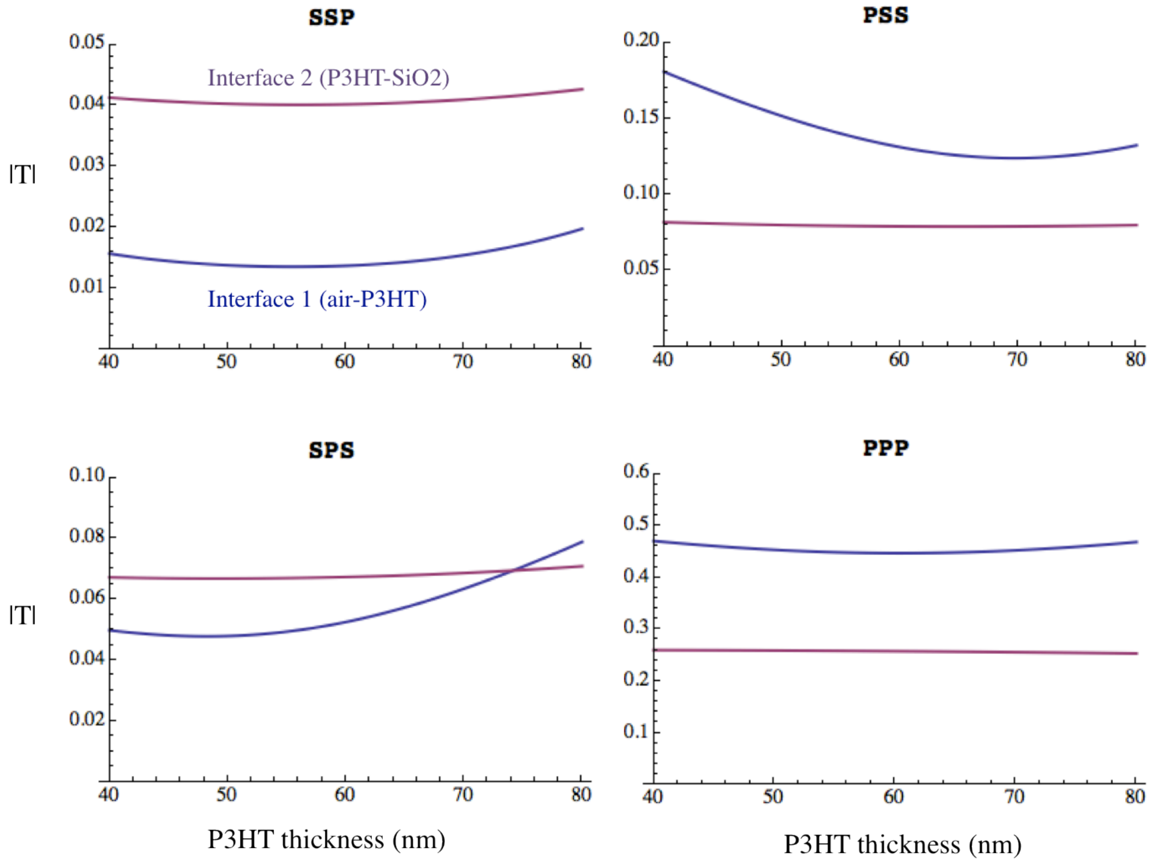

Figure S3. Transfer coefficients for SFG generated from a multilayer stack according to references 42 and 42. Here the dielectric thickness is 250 nm and the P3HT thickness is 60 nm. Input beam angles are those in the Experimental section, and the optical constants for P3HT are given in reference 12. The important observation here is that the buried interface signal is favored in the *ssp* and *sps* polarization combinations by factors of 3 and 1.3, respectively. We also note that the *pss* combination has transfer coefficients that favor the P3HT/air interface, however, we find that the VSFG spectral behaviors show that the pss/ssp ratio behaves similarly to the sps/ssp ratio (see Figure S8).

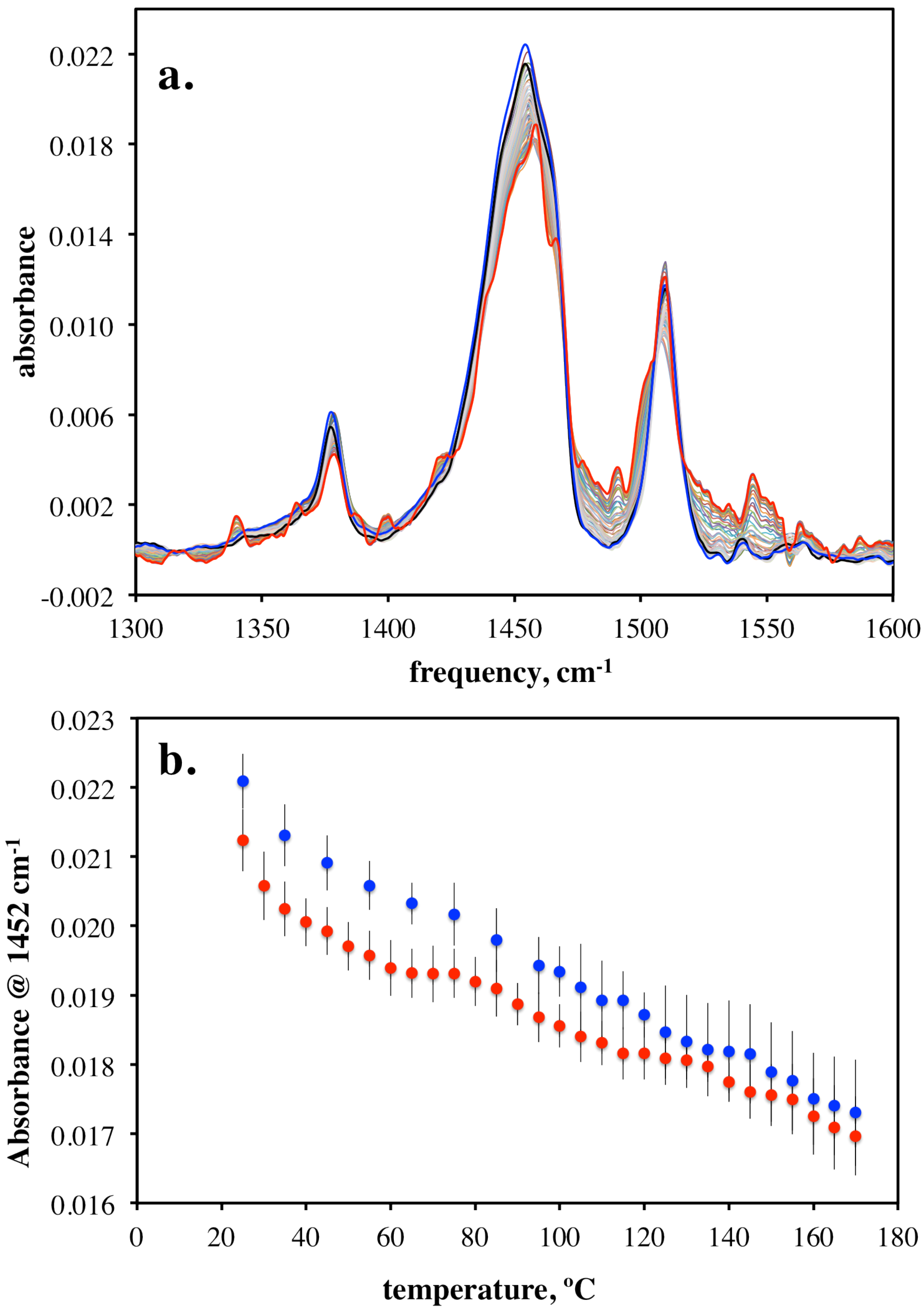

Figure S4. a) FTIR spectra in the C=C stretching region during annealing in dry air showing the changes as the film goes from 25 °C (black) to 170 °C (red) and cools back to 25 °C (blue). b) The absorbance at 1452 cm^{-1} as a function of temperature. Within the noise, the spectra change reversibly with temperature. For comparison to Figure 3, the scale bar in that figure is 5 mOD whereas the change in the plot above is less than 1 mOD from beginning to end.

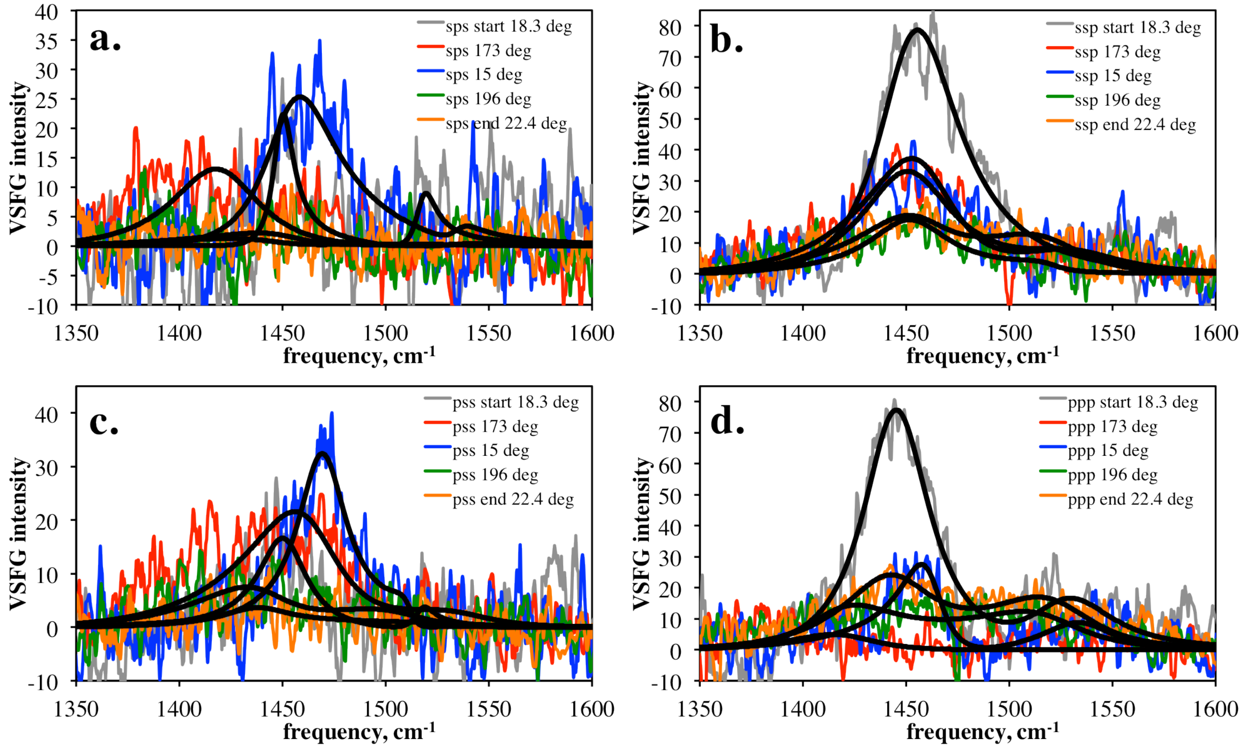

Figure S5. PM-VSFG spectra collected from DP3HT on bare SiO_2 dielectric at 18.3 °C → 173 °C → 15 °C → 196 °C → 22.4 °C. Shown are a) *sps*, b) *ssp*, c) *pss*, and d) *ppp* polarization combinations. At a given temperature, spectra for all four polarization combinations were collected simultaneously by the PM-VSFG method. Solid black overlaid lines are the best fit curves to the data using the equations described in the text.

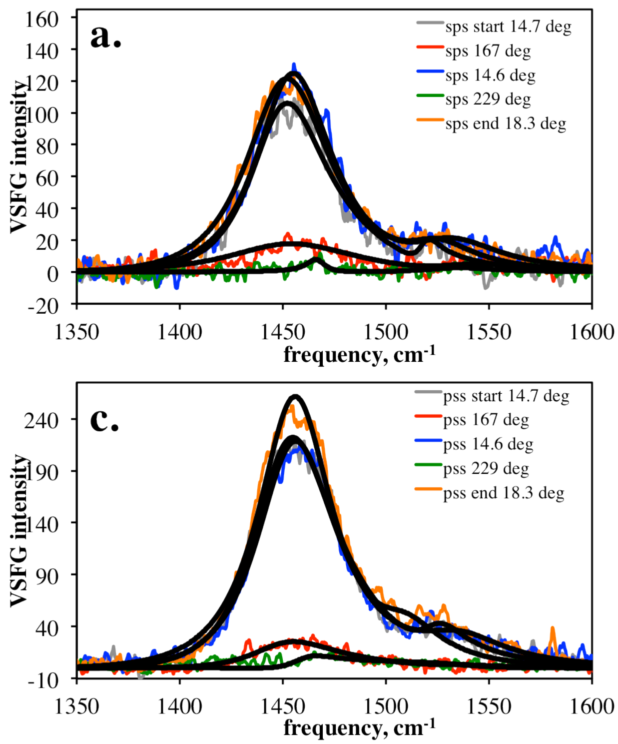

Figure S6. PM-VSFG spectra collected from DP3HT on Fluoro coated silica dielectric at 14.7 °C → 167 °C → 14.6 °C → 229 °C → 18.3 °C. Shown are a) *sps*, b) *ssp*, c) *pss*, and d) *ppp* polarization combinations. At a given temperature, spectra for all four polarization combinations were collected simultaneously by the PM-VSFG method. Solid black overlaid lines are the best fit curves to the data using the equations described in the text.

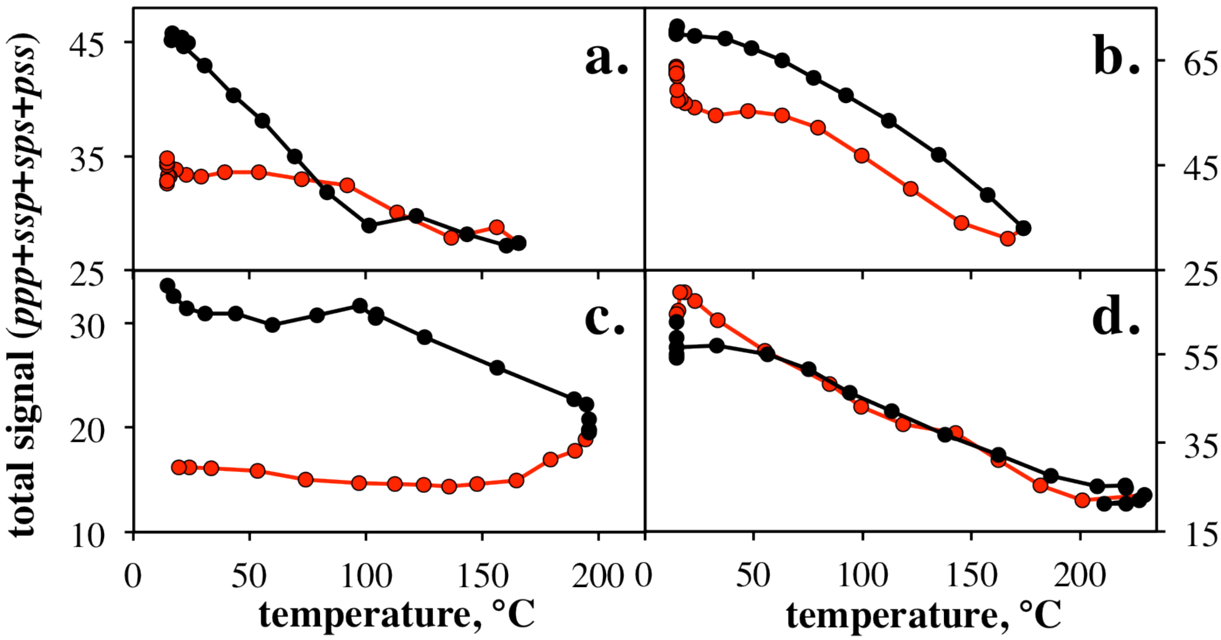

Figure S7. Total VSFG signals for the C=C ν_S including contributions (A/Γ) from all four polarization combinations (*sps*, *ssp*, *pss*, and *ppp*). In main text, we chose to not include the *ppp* polarization since it has contributions from multiple tensor elements, some of which duplicate information contained in the other three combinations. Here we show that the trends described in the text are unchanged by including the *ppp* C=C A/Γ values in the sum. In all frames, the black markers show the heating scan and the red show the cooling scan. Frames a) and c) show the data for bare SiO_2 dielectric for the first and second annealing cycles, respectively; frames b) and d) show the Fluoro data for first and second annealing cycles, respectively.

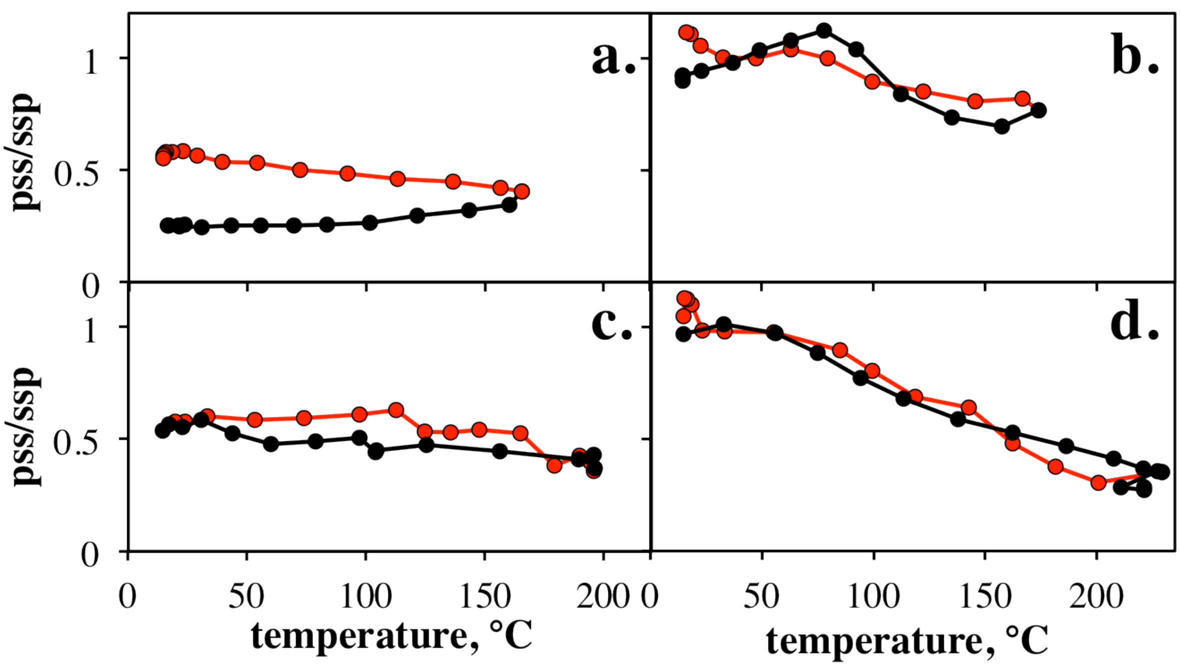

Figure S8. *Pss*/*ssp* ratios showing the same trends as the *sps*/*ssp* ratios in the main text. In all frames, the black markers show the heating scan and the red show the cooling scan. Frames a) and c) show the data for bare SiO_2 dielectric for the first and second annealing cycles, respectively; frames b) and d) show the Fluoro data for first and second annealing cycles, respectively.

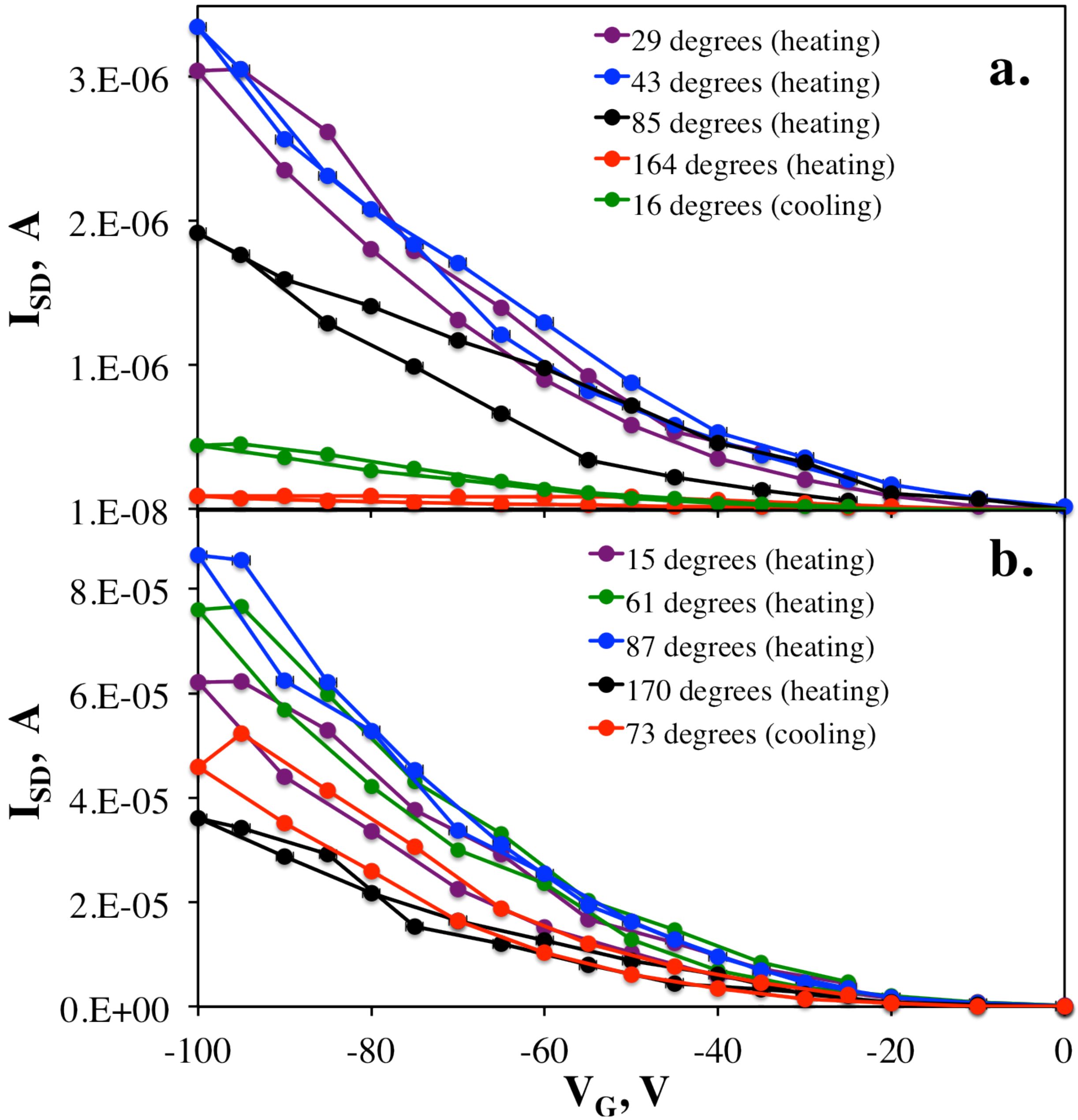

Figure S9. Representative transfer characteristics for P3HT oFETs measured during in-situ annealing on a) bare SiO_2 and b) Fluoro functionalized dielectric. These data were collected during the in-situ VSFG annealing process while the background scan was being acquired (IR beam blocked). A transfer scan of this type was collected at each temperature, for clarity selected temperatures during the heating scans are shown along with one scan during the cooling process.

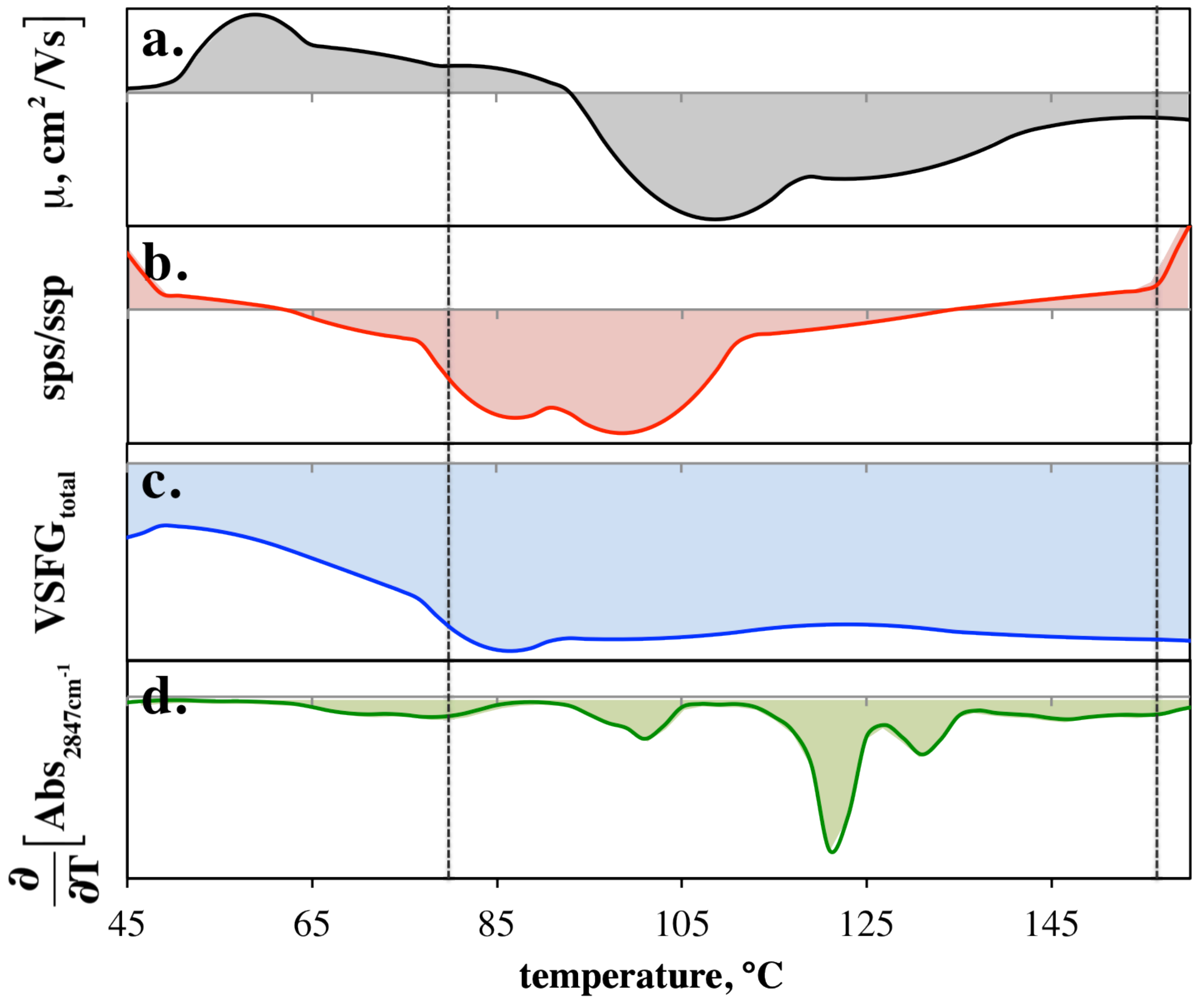

Figure S10. Temperature derivatives of data from the first heating scan for P3HT on Fluoro dielectric showing d/dT of the a) hole mobility, b) *sps*/*ssp* ratio, c) total VSFG signal (*pss*, *sps*, *ssp* contributions), and d) FTIR absorbance at 2847 cm^{-1}. In each frame, the horizontal grey line indicates zero, and the vertical dashed lines show the DSC transitions from Figure 1.