

SUPPLEMENTAL INFORMATION FOR

Thin Film and Bulk Phases Co-nucleate at the

Interfaces of Pentacene Thin Films

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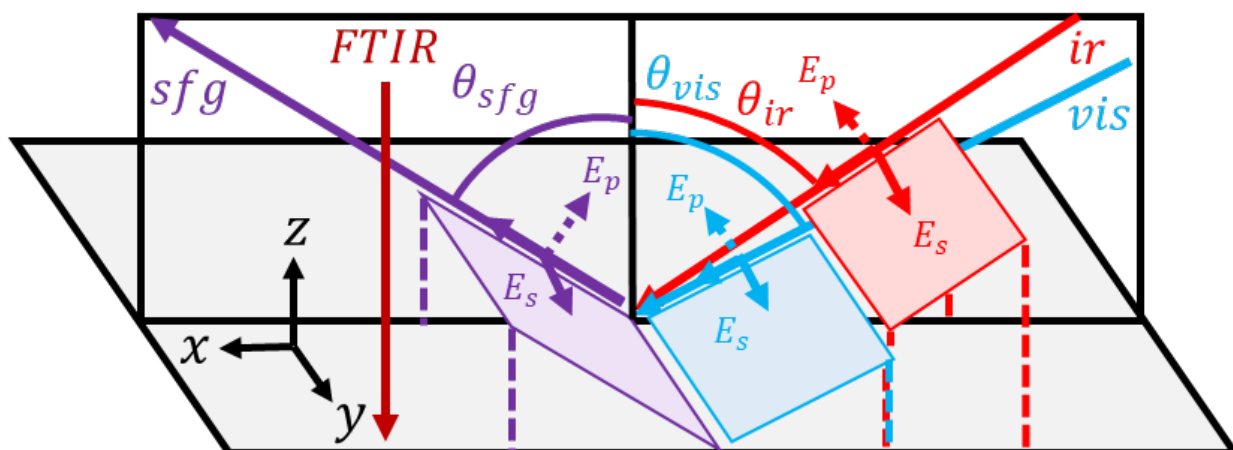


Figure S1. Geometry of the FTIR and VSFG experiments where the sample lies in the xy plane. The ssp experiment will probe the z direction, while the sps experiment will probe the y direction.

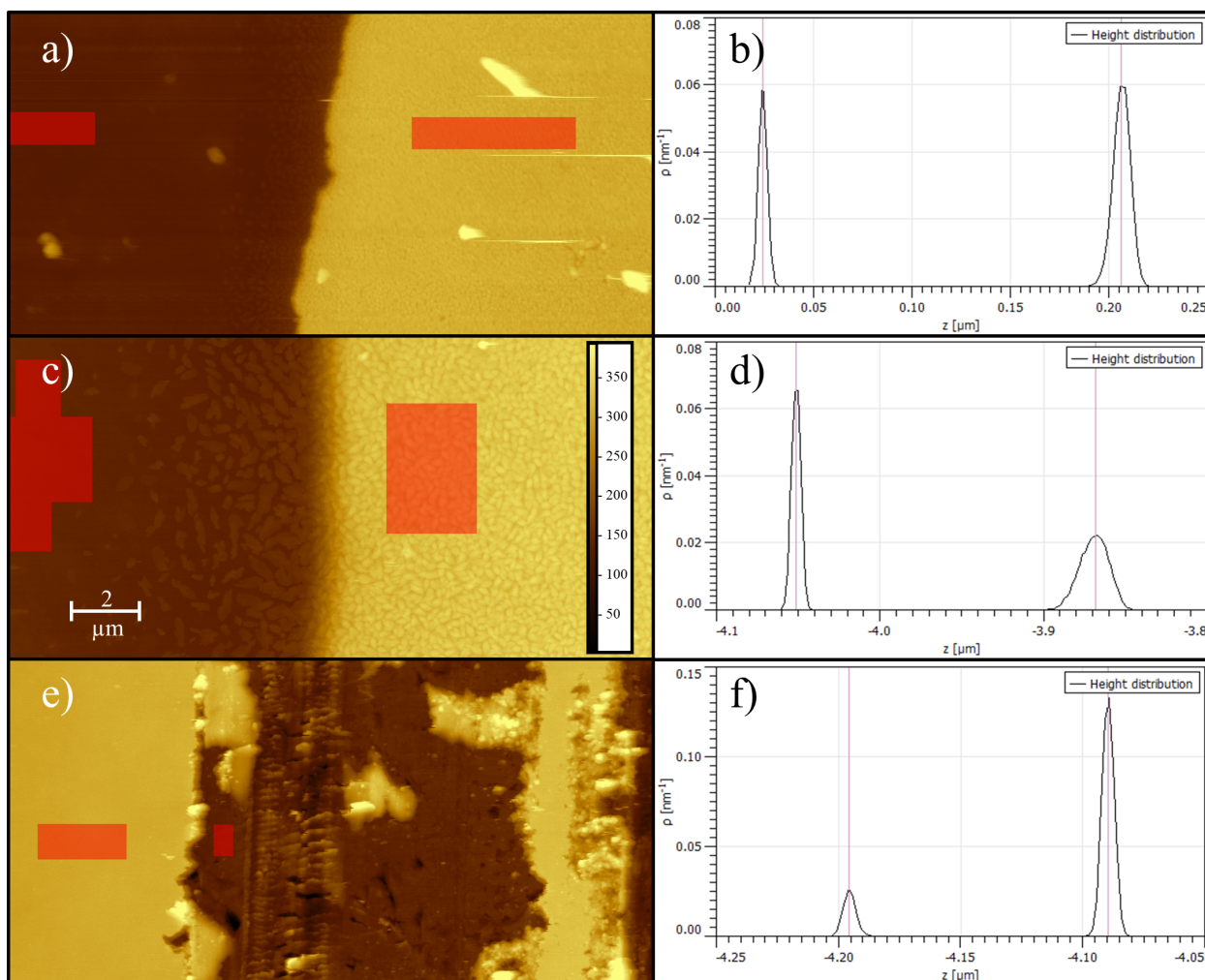


Figure S2. AFM topography images of samples with an QCM-measured deposition thicknesses of 200 nm with substrate temperatures of a) 28 °C, c) 125 °C (inset height scale for all images in nm), and e) 150 °C during deposition, and associated height distribution plots (b, d, f).

Using AFM we determined the height difference between the substrate and the sample to solve for the true sample thickness (Figure S2). We calculated the step differences between the red highlighted boxes to be 182, 183, and 106 nm respectively for the samples deposited at substrate temperatures of 28 °C, 125 °C, and 150 °C. Deposition will be linear, so a sample with an expected thickness of 100 nm will have half the listed values above as a true thickness.

Table S1. XRD measured standard deviation, amplitude, and area under each Gaussian for each (001) peak for samples on CaF₂ windows with different substrate temperatures during deposition.

	Thin-Film Phase			Bulk Phase		
	Amp.	std. deviation	Area	Amp.	std. deviation	Area
28 °C	19730	0.13	6380	0	0.00	0
125 °C	27990	0.14	10018	7801	0.19	3752
150 °C	324	0.20	162	1150	0.16	451
160 °C	0	0.00	0	1081	0.17	466

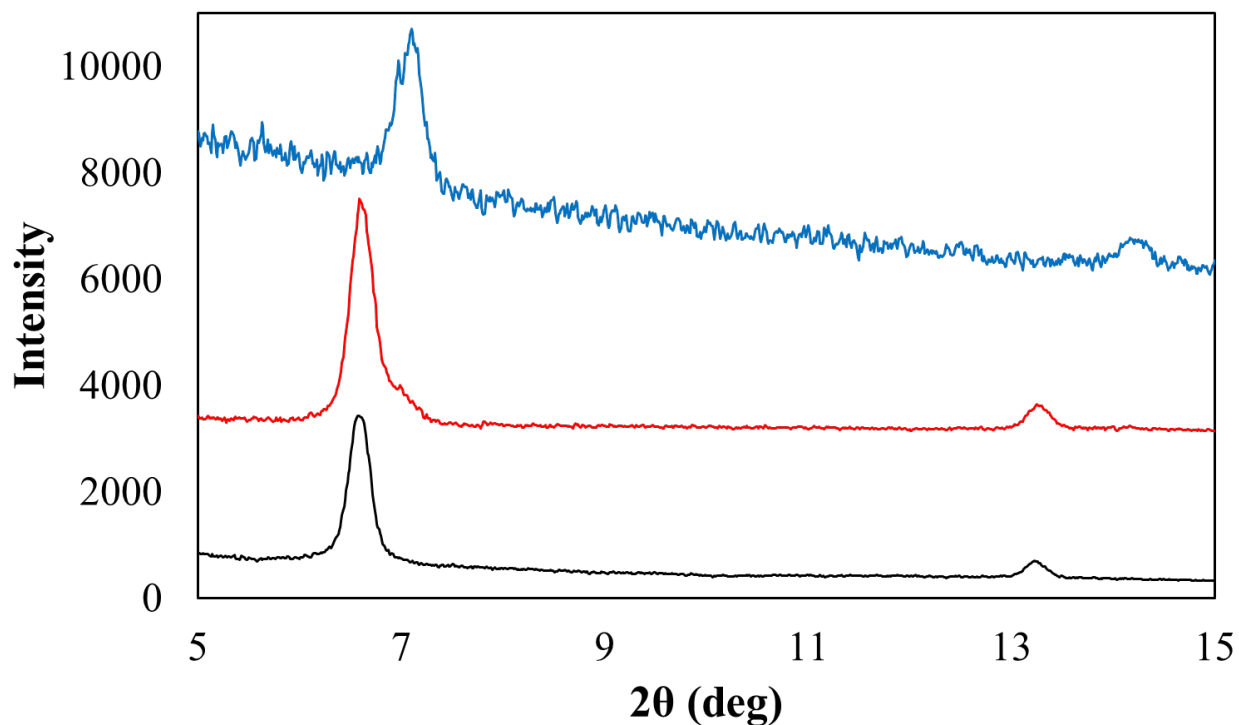


Figure S3. XRD measurements of pentacene deposited on SiO₂ wafers with substrate temperatures of 28 °C (black), 125 °C (red), and 150 °C (blue) during deposition.

Table S2. Experimental and theoretical frequencies of pentacene and pentacenequinone vibrational modes.

Mode	Pentacene		Pentacenequinone	
	Experimental Frequency (cm ⁻¹)	Theoretical Frequency (cm ⁻¹)*	Experimental Frequency (cm ⁻¹)	Theoretical Frequency (cm ⁻¹)*
CH (z)	904	879.6	913	911.5
CH (z)			937	938.2
Ring str. (y)			959	977.3
CO (x)			1615	1601.7
Ring str. (x)	1624	1617.3		
CO (y)			1673	1682.3
CH (x)	3013	3036.5		
CH (x)	3027	3040.8		
CH (x)		3042.5		
CH (y)	3042	3046.2		
CH (x)	3053	3059.4	3046	3063.0
CH (y)	3072	3071.0		3074.2

*A scaling factor of 0.9581 was applied.¹⁻³

Table S3. FTIR measured HWHM (cm^{-1}), amplitude ($\times 10^3$ au), and center frequency (cm^{-1}) for each C–H vibrational mode for samples on CaF_2 windows with different substrate temperatures during deposition.

			28 °C	125 °C	150 °C	160 °C
Mode	Frequency	HWHM	Amp.	Amp.	Amp.	Amp.
$\nu_1(\text{CH})$	3013.1	8.3	0.00333	0.00355	0.00269	0.00207
$\nu_2(\text{CH})$	3027.4	10.8	0.00382	0.00469	0.00479	0.00477
$\nu_3(\text{CH})$	3042.0	6.4	0.00459	0.00526	0.00680	0.00718
$\nu_4(\text{CH})$	3052.6	5.6	0.00771	0.00738	0.00766	0.00753
$\nu_5(\text{CH})$	3072.0	11.3	0.00032	0.00027	0.00126	0.00109

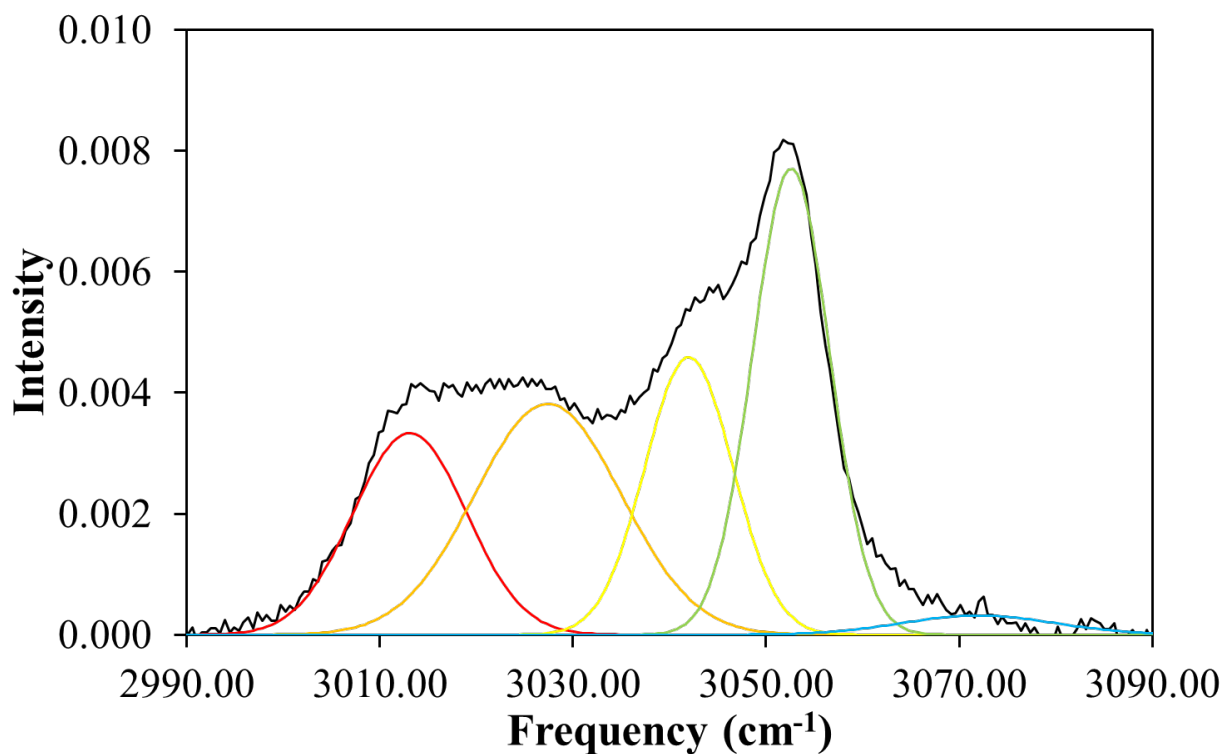
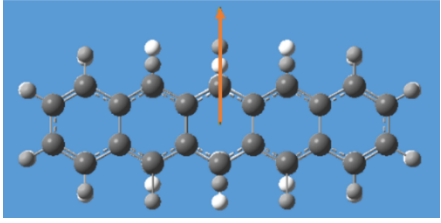
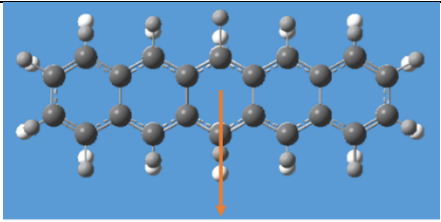
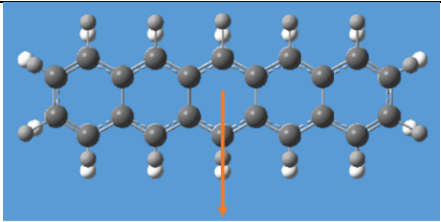
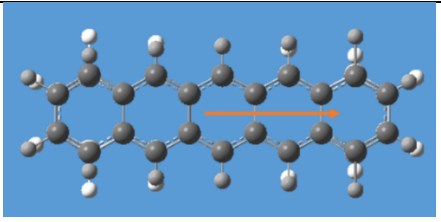
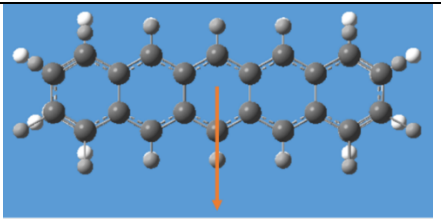
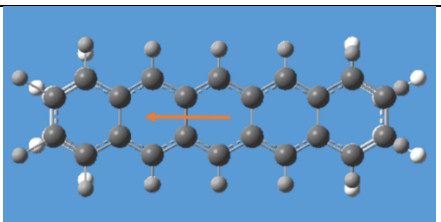


Figure S4. Example deconvolution of sample deposited at 28 °C fit using five Gaussians.

Table S4. Extremes (dark and light) of the vibrational movements for pentacene C–H modes as determined by B3LYP/6-31G (d,p). The orange arrow is the derivative of the dipole movement.

Mode	Frequency (cm ⁻¹)	Frame
$\nu_1(\text{CH})$	3013	
$\nu_2(\text{CH})$	3027	
		
$\nu_3(\text{CH})$	3042	
$\nu_4(\text{CH})$	3053	
$\nu_5(\text{CH})$	3072	

Raman spectroscopy was performed on a Witec Alpha 300R confocal Raman microscope with a UHTS300 spectrometer and DV401 CCD detector at the University of Minnesota Characterization Facility. A 785.112 nm diode laser coupled with a 600 g/mm grating was used to acquire spectra. Light was collected and focused with a Nikon 100 \times objective. The spectral resolution of the instrument was *ca* 4 cm⁻¹.

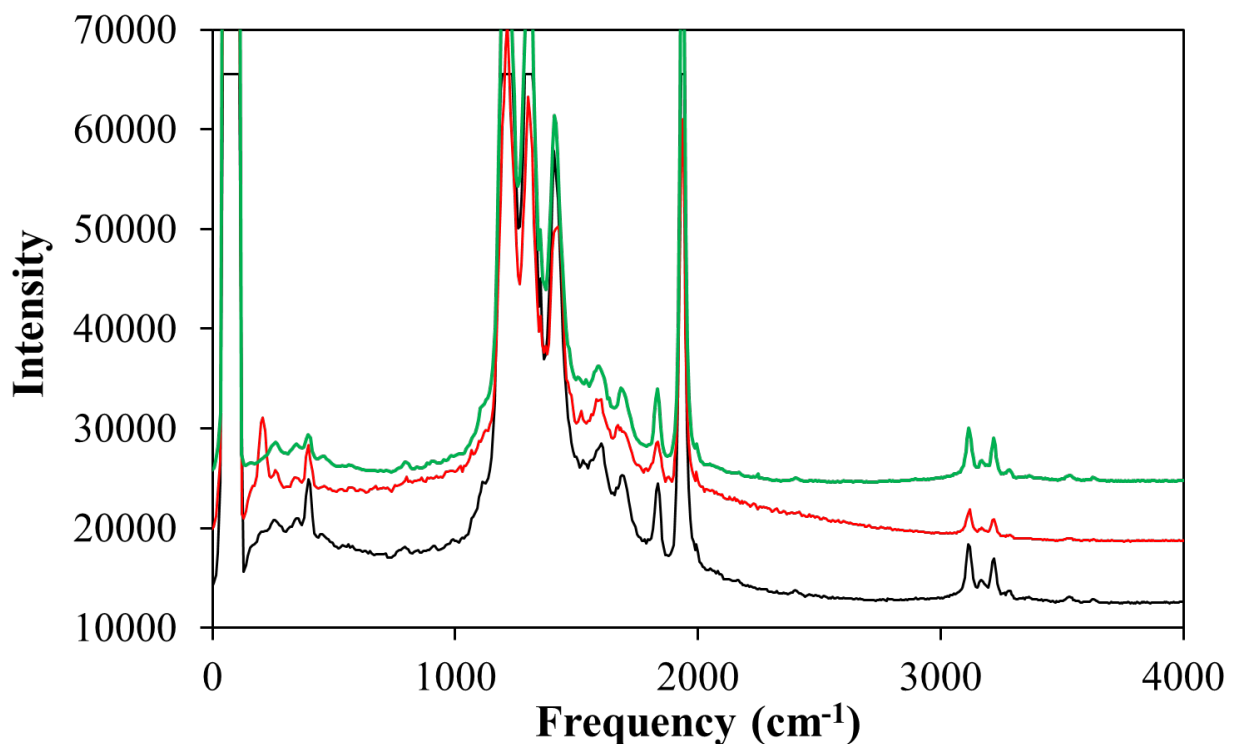


Figure S5. Raman spectra for pentacene deposited on CaF₂ windows with substrate temperatures of 28 °C (black), 125 °C (red), and 160 °C (green) during deposition.

REFERENCES

1. Pople, J. A.; Scott, A. P.; Wong, M. W.; Radom, L., Scaling Factors for Obtaining Fundamental Vibrational Frequencies and Zero-Point Energies from HF/6-31G* and MP2/6-31G* Harmonic Frequencies. *Isr. J. Chem.* 1993, *33*, 345-350.
2. Wong, M. W., Vibrational Frequency Prediction Using Density Functional Theory. *Chem. Phys. Lett.* 1996, *256* (4-5), 391-399.
3. Scott, A. P.; Radom, L., Harmonic Vibrational Frequencies: An Evaluation of Hartree-Fock, Møller-Plesset, Quadratic Configuration Interaction, Density Functional Theory, and Semiempirical Scale Factors. *J. Phys. Chem.* 1996, *100*, 16502-16513.