Supplementary Information for:

Self-Assembled Organic Monolayers on Epitaxial Graphene with Enhanced Structural and Thermal Stability

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Section S1: Sample Preparation Details

The substrates used in all experiments were prepared from 6H-SiC(0001) n-type single crystal wafers (Cree, Inc.), doped with nitrogen to a resistivity of $0.070 \,\Omega \cdot \text{cm}$. Prior to introduction into the vacuum chamber, the samples were cleaned ultrasonically with acetone and isopropanol. Once loaded into the UHV environment, the samples were heated by direct current to ~550 °C and degassed for a minimum of 8 hours. After outgassing, the SiC samples were subjected to a series of brief anneals at or below 1100 °C in order to remove the native oxide layer as well as any persistent adsorbates from the ambient environment preceding substrate

graphitization. Atomically pristine epitaxial graphene surfaces were subsequently prepared by flashing the samples between 1300 °C and 1350 °C for several 1 minute intervals. Finally, the current through the resistively heated graphitized substrates was slowly reduced over the course of several minutes before allowing the samples to reach thermal equilibrium with the room temperature UHV chamber.

PTCDI (98% purity, Alfa Aesar) and PTCDA (97% purity, Sigma-Aldrich) were purchased and used without further purification. Each molecule was loaded independently into alumina-coated tungsten sublimation modules before being introduced into the UHV environment. In an effort to remove gas phase impurities from the source material, the molecules were each thoroughly degassed below their respective sublimation temperatures for time periods exceeding 8 hours. Self-assembled monolayers of PTCDI and PTCDA were subsequently prepared by resistively heating the alumina boats above this temperature threshold to sublimate the source material onto epitaxial graphene substrates that were maintained at room temperature. Molecular coverage was controlled by varying the sample exposure time while keeping the source temperature and source-sample distance parameters constant. In particular, PTCDI was deposited by applying a constant current of 5.6 A to the tungsten filament within the alumina boat for 4.5 minutes in order to establish a steady molecular flux. The epitaxial graphene samples were then positioned in line-of-sight of the sublimation module and exposed for ~90 seconds to achieve full monolayer coverage. The corresponding maximum background UHV chamber pressure during PTCDI deposition was 2.6 x 10⁻⁹ Torr. Following PTCDI deposition, the substrates were post-annealed at 60 °C for 1 hour to promote thermodynamically favorable molecular reorganization and uniform coverage across the sample surface. An analogous experimental methodology was utilized to produce PTCDA monolayers on epitaxial graphene with the details of the procedure having been described elsewhere.¹ The removal of both PTCDI and PTCDA self-assembled monolayers and the associated restoration of atomically clean graphene surfaces are readily achieved by annealing the samples at ~550 °C overnight.

Section S2: STM Characterization of PTCDI Step Edge Interactions

Observations of the various interactions that occur between the step edges of the EG/SiC(0001) surface and the deposited PTCDI molecules are useful for gaining deeper insight into the formation and growth of the PTCDI adlayer. As shown in Fig. SI-1a, the PTCDI monolayer grows continuously over the graphene sheet, with each molecular domain traversing the atomic step without disruption. Detailed examination of Fig. SI-1a further demonstrates that the ability of the film to propagate across step edges is not correlated strongly with specific substrate orientations as we note the presence of two distinct molecular domains within this image that exhibit the same step-crossing behavior, even though their molecular orientations are at a slight angle with respect to one another. Additionally, as shown in Fig. SI-1b, we observe that the PTCDI molecules exhibit a tendency to accumulate along step edges at sub-monolayer coverages. This behavior appears to play an important role under full monolayer conditions as well (Fig. SI-1c), where we observe that the angle between the two neighboring PTCDI domains on the lower terrace is 118°, which corresponds precisely to the angle between the flat sides of the adjoining step edges. Taken as a whole, these observations suggest the following model for PTCDI self-assembly on the EG/SiC(0001) surface: During the initial stages of deposition, individual PTCDI molecules diffuse freely across the surface occasionally interacting with other adsorbates and topographic features on the substrate. As more PTCDI is deposited onto the surface, the molecules preferentially collect along step edges until stable molecular islands are

formed, where the growing domains adopt a crystallographic orientation influenced by the step edge where the molecules originally accumulated. These islands continue to propagate across the EG surface as additional PTCDI is sublimated onto the substrate, growing seamlessly over step edges and surface defects, while maintaining the orientation templated by the step edge where the domain nucleated, until encountering other PTCDI islands, resulting in the formation of well defined molecular domain boundaries.



Fig. SI-1 (a) High-resolution STM image showing the PTCDI monolayer continuously following the underlying graphene sheet over a SiC step edge ($V_s = -0.9$ V and $I_t = 0.04$ nA). (b) STM image of a submonolayer coverage of PTCDI on epitaxial graphene that displays the molecules accumulating along the step edges of two distinct terraces ($V_s = -1.0$ V and $I_t = 0.03$ nA). (c) Large-area scan exhibiting the boundary formed between two PTCDI domains with different crystallographic orientations, where the direction of the *a* lattice vector for each domain is indicated by a solid blue arrow ($V_s = -1.0$ V and $I_t = 0.06$ nA). The angular configuration of each domain is coincident with the angles of the nearby step edges.

Section S3: STM Characterization of PTCDI Island Edge Stability



Fig. SI-2 (a) STM image of a submonolayer coverage of PTCDI on epitaxial graphene ($V_s = -1.0 \text{ V}$ and $I_t = 0.06 \text{ nA}$). The individual PTCDI island shown in this image depicts the formation of an ordered domain boundary with well-defined molecular edges. (b) Large-area scan displaying the domain boundary between two PTCDI islands that have different angular orientations with respect to the underlying substrate, where the direction of the *a* lattice vector for each domain is indicated by a solid blue arrow ($V_s = -1.0$ V and $I_t = 0.05$ nA). The edges of each island are crisp and irregularly shaped. (c) High-resolution STM image of the molecularly defined edge of a PTCDI island next to a region of exposed graphene ($V_s = -1.0 \text{ V}$ and $I_t = 0.03$ nA).

Section S4: X-ray Reflectivity Experimental Details and Supplementary Data

Following molecular deposition and STM validation of organic adlayer quality, samples were transferred between vacuum environments and temporarily subjected to ambient conditions such that the relative thermal stability of PTCDA versus PTCDI on EG/SiC(0001) could be quantified at the macroscopic level using XRR characterization techniques. In particular, temperature-dependent high-resolution XRR measurements were performed in vacuum (base pressure ~10⁻⁷ Torr) at the Advanced Photon Source endstation 5ID-C.² X-rays of

energy $E_{\gamma} = 15.00$ keV were selected using a double-crystal Si(111) monochromator, while a Rh-coated mirror was used for harmonic rejection and focusing. The incident beam was collimated to 0.2 mm (vertical) \times 1 mm (horizontal), providing an incident flux of 10¹¹ photons/s at the sample surface. Scattered X-rays in the vicinity of the specular condition were collected using a CCD detector. Experimental details on XRR data acquisition, extraction, and uncertainty estimation are fully described elsewhere.³⁻⁴ XRR data is presented as a function of the SiC reciprocal lattice index (SiC r.l.u.), $L = 2Sin(\frac{2\theta}{2})\frac{c_{SiC}}{\lambda}$, where 2θ is the scattering angle, $\lambda = 0.827$ Å is the X-ray wavelength, and $c_{SiC} = 15.12$ Å is the lattice parameter for 6H-SiC. Substrates were radiatively heated via exposure of the back of the sample to a nude tungsten filament, while temperature was monitored using a K-type thermocouple affixed to the sample surface. The sample temperature was not observed to deviate by more than ± 5 °C during each measurement. XRR measurements were taken in 25 °C heating steps for the EG/SiC control sample and 15 °C heating steps for molecular adlayer samples until no changes in scattering were observed, where we note that typical equilibration time for each temperature step was 45 ± 5 minutes. XRR data in the range of interest (L = 3 - 6 SiC r.l.u.) were acquired over 15 minutes for each designated temperature.

The epitaxial graphene control sample was heated from 35 °C to 250 °C and displayed only small variations in scattered intensity over the temperature range of experimental interest; indicating that any changes observed for the molecular adsorbate samples could be reliably attributed to changes in molecular film coverage. For the case of PTCDA/EG/SiC(0001), the sample was heated from 35 °C to 290 °C. At the starting temperature, T = 35 °C, the peak position is at L = 4.5 SiC r.l.u., and little change in scattered intensity is observed until T = 185 °C, when the peak begins to weaken, broaden, and shift to lower *L*. This behavior continues

until T = 260 °C, at which point there are no further changes in the XRR. Similarly, the PTCDI sample was heated from 35 °C to 320 °C. For PTCDI/EG/SiC(0001), little change in the lineshape parameters are observed until T = 220 °C, at which point the same trends (e.g., reduction in peak intensity, broadening, shifting of position to lower L) observed for PTCDA are seen for PTCDI. At T = 290 °C, all the PTCDI molecules are desorbed and no further changes in the XRR develop. After each of the samples was thermally ramped, they were subsequently cooled to room temperature for a final XRR post-desorption control measurement. The results of this control measurement demonstrated that the EG/SiC(0001) sample remained essentially identical throughout the experiment, whereas the PTCDA/EG/SIC(0001) and PTCDI/EG/SIC(0001) samples underwent significant and irreversible changes consistent with the thermal desorption of an adsorbed molecular layer. The subtle differences that are observed between the last measurements collected at elevated temperature and the control measurements taken upon return to room temperature are attributed to an increase in the Debye-Waller factor as temperature is increased.



Fig. SI-3 (a) XRR results for a clean EG/SiC(0001) surface as a function of substrate temperature. The observed intensity and L value for both the nominal EG(0002) peak decreases only slightly over the temperature range of interest, which is attributed to the increased

Debye-Waller contribution. The stability of this peak indicates that the epitaxial graphene layers are structurally insensitive to temperature changes within this low temperature regime while being heated within a high vacuum environment. (b-c) XRR results for PTCDA and PTCDI self-assembled adlayers on EG/SiC(0001) surfaces as a function of substrate temperature. The PTCDA/EG(0002) and PTCDI/EG(0002) peaks decrease in intensity and shift toward lower *L* as the sample temperatures are increased, indicating the thermally induced desorption of the organic adsorbates.

Section S5: Derivation of X-ray Reflectivity Data Analysis

In order to simplify and streamline the XRR data analysis presented in the main text, we assert that the coverage (Θ) of the molecular film layers is correlated with the square root of the reflected intensity at the momentum transfer $q_z = 4\pi Sin(2\theta/2)/\lambda$ (expressed in terms of $L = c_{SiC} q_z/2\pi$ in the main text). This approach is validated below:

The total structure factor (F_{Tot}) is the summation of the bulk truncated SiC(0001) unit cell $(F_{u.c.})$, epitaxial graphene (EG) film (F_{EG}) , and self-assembled molecular adlayer $(F_{adlayer})$ structure factors:

$$F_{Tot} = F_{u.c.}F_{CTR} + F_{EG} + F_{adlayer}$$
(S1)

where the structure factor *F* for a general layer is:

$$F(q_z) = \sum_m o_m f_m e^{iq_z \, z_m} \, e^{-\frac{1}{2}(q_z u_m)^2} \tag{S2}$$

and the CTR structure factor is:

$$F_{CTR}(q_z) = \frac{1}{1 - e^{iq_z c_{SiC}}}$$
(S3)

Here, *m* is the index for each atomic layer, f_m is the form factor for the layer, u_m is the layer's vibrational amplitude, z_m is the layer position, and o_m is the layer occupancy. Because desorption of the PTCDA and PTCDI layers are thermally induced, the structure factor possesses a temperature dependence in addition to its q_z dependence. However, in the temperature range of experimental interest, we expect only the occupancy of each molecular layer to change (via desorption). We do not expect significant influence on the molecular film *d*-spacing and vibrational amplitude as the thermal expansion and Debye-Waller contributions should be minimal over this temperature range. The layer occupancy is therefore the only component that exhibits a strong dependence on the substrate temperature. Accounting for this, and defining a structure factor, $\gamma(q_z) = F_{u.c.}F_{CTR} + F_{EG}$, we can rewrite the expression for the total structure factor as follows:

$$F_{Tot}(q_z, T) = \gamma(q_z) + f_P(q_z) \sum_m o_m(T) e^{iq_z z_m}$$
(S4)

Here we note that each molecular layer in the second to last term possesses only PTCDA or PTCDI (denoted subscript *P*) and that we have neglected the vibrational amplitude. Then, if we choose the index m = 0 to coincide with the first molecular adlayer, we find:

$$F_{Tot}(q_z, T) = \gamma(q_z) + f_P(q_z) \sum_{m=0}^{N} o_m e^{im(q_z \, d_P)}$$
(S5)

for N molecular adlayers with PTCDA and PTCDI *d*-spacing = d_P . The reflected intensity $I(q_z, T) = |F_{Tot}(q_z, T)|^2 = F_{Tot}F_{Tot}^*$ where * denotes the complex conjugate, and therefore:

$$I(q_{z},T) = |\gamma(q_{z})|^{2} + \gamma(q_{z})f_{P}^{*}(q_{z})\sum_{m=0}^{N}o_{m}(T)e^{-im(q_{z}d_{P})}$$

$$+ \gamma^{*}(q_{z})f_{P}(q_{z})\sum_{m=0}^{N}o_{m}(T)e^{im(q_{z}d_{P})}$$

$$+ |f_{P}(q_{z})|^{2}\sum_{m=0}^{N}o_{m}(T)e^{im(q_{z}d_{P})}\sum_{m=0}^{N}o_{m}(T)e^{-im(q_{z}d_{P})}$$
(S6)

Referring to the assumption that the *d*-spacing for the molecular films are temperature independent (i.e., the molecules are desorbing but the layer is not expanding) allows us to analyze the reflected intensity at a single q_z associated with the PTCDA/PTCDI *d*-spacing of $d_p = \sim 3.35$ Å: $q_{z_P} = \frac{2\pi}{d_P} \sim 1.88$ Å⁻¹; $L \sim 4.5$ SiC r.l.u. The expression S6 therefore simplifies to:

$$I(q_{z_{P}},T) = |\gamma(q_{z_{P}})|^{2} + \gamma(q_{z_{P}})f_{P}^{*}(q_{z_{P}})\sum_{m=0}^{N}o_{m}(T) + \gamma^{*}(q_{z})f_{P}(q_{z})\sum_{m=0}^{N}o_{m}(T) + |f_{P}(q_{z})|^{2}\sum_{m=0}^{N}o_{m}(T)\sum_{m=0}^{N}o_{m}(T)$$
(S7)

The total coverage for the PTCDA and PTCDI films at a specified temperature is defined as $\Theta(T) = \sum_{m=0}^{N} o_m(T)$. Appropriate substitution into equation S7 produces the following mathematical relationships:

$$I(q_{z_P}, T) = |\gamma(q_{z_P})|^2 + \gamma(q_{z_P})f_P^*(q_{z_P})\Theta(T) + \gamma^*(q_z)f_P(q_z)\Theta(T)$$

$$+ |f_P(q_z)|^2\Theta(T)^2$$
(S8)

$$I(q_{z_P}, T) = A + B \Theta(T) + C \Theta(T)^2$$
(89)

where A, B and C are real numbers, and the total molecular film coverage can be expressed as:

$$\Theta(T) = \frac{-B \pm \sqrt{B^2 - 4AC + 4CI(q_{z_P}, T)}}{2C}$$
(S10)

It is therefore possible to plot $\sqrt{I(T)}$ at q_{z_P} to yield values proportional to the total coverage of the PTCDA and PTCDI self-assembled molecular adlayers.

Furthermore, it is possible to plot $I(q_{z_P}, T)$ to explore the coverage of the PTCDA and PTCDI self-assembled molecular adlayers because the molecular coverage and reflected intensity is correlated. By this analysis, any temperature dependent event, such as those observed in Fig. SI-3, is associated with a molecular desorption event. Indeed, this interpretation is validated by the observed trends of $I(q_{z_P}, T)$ in Fig. SI-3 and agree with what is expected from a first-order Polanyi-Wigner desorption event.⁵

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