SUPPLEMENTARY INFORMATION

Pentacene Monolayer Trapped between Graphene and Substrate

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The Parameters for Kinetic Monte Carlo (kMC)

Pentacene Interactions

Sublimation is a critical phenomenon in our simulation. With nearest-binding model, the molecules should sublime at the sublimation temperature. For pentacene, it's a challenging task because of the complex $\pi-\pi$ interaction, which is configuration related [1]. For simplicity, we employ nearest-neighbor model where the molecules is isotropic in-plane, but with different out-of-plane interaction. In-plane square lattice model is well-suited for standing-out pentacene molecules [2]. Apart from previous abstract models, which adopt deliberately chosen parameters with respect to the ratio of interaction parameters to $k_B T$ [3, 4], to get a reasonable mobility at the working temperature, we estimate the overall nearest-binding energy used in the system from the sublimation temperature 372 ℃ [5]. We assumed that detailed balance is reached at the sublimation temperature. More specifically, the sublimation rate of molecules from the bulk is equal to the condensation rate from gas phase.

In our model, the evaporation rate is with respect to the moving of molecules in gas phase. In the kMC model, the waiting time for sublimation to occur Δt_{sub} is represented as below.

$$\Delta t_{sub} = 5 \cdot \frac{S_0}{S} \cdot e^{2\Delta E_{NB}} \cdot \Delta t \quad \text{(S1)}$$

Here S_0 is the area for one pentacene molecule, S is the total surface area of interest, ΔE_{NB} is the sum of all nearest-binding energy of one pentacene molecule to the surrounding, factor 2 before $\Delta E_{binding}$ represents that the molecule should hop twice to escape the surface potential (there's a huge possibility for molecules one step away from the surface to jump back into the bulk while two steps away is safe according to the nearest-neighbor binding scenario), the factor 5 before $\frac{S_0}{S}$ means the second hopping step is directly away from the surface rather than moving parallel to the surface, and Δt is the waiting time for gas molecule to move one lattice constant.

To bridge this model with molecular kinetics theory, we represent Δt as below.

$$\Delta t = a_0 / v_{rms} \quad \text{(S2)}$$

Where a_0 is the lattice constant used for the lattice model, 0.7 nm, and v_{rms} is the root mean square velocity for gas molecules for simplicity. Here, root means square is using to represent the Brownian motion.

The collision rate A for gas molecules to bulk pentacene with area S is represent by molecular kinetics as below assuming ideal gas.

$$A = \frac{n}{4} \cdot \sqrt{\frac{8}{3\pi}} \cdot v_{rms} \quad \text{(S3)}$$

By detailed balance, we have:

$$\Delta t_{sub} = \frac{1}{A} \quad \text{(S4)}$$

Here we can calculate $\Delta E_{NB} = 0.1501\ eV$. Decomposing the binding energy into in-plane term (J_{in}) and out-of-plane term J_{out} according to the calculated surface energy [6], we got $J_{in} = 0.03325\ eV$ and $J_{out} = 0.00866\ eV$.

The Hamaker Constants

The Hamaker constants used include that of graphene-pentacene, graphene-mica, and mica-pentacene. We calculate the Hamaker constants by adapting that from the method of Lifshitz [7], where the imaginary dielectric response functions are reconstructed by simplified Ninham-Parsegian representations [8, 9]. Necessary optical data for graphite is adopted from the handbook [10], while the dielectric response function of muscovite mica is directly adapted from [8]. The ultraviolet contribution of dielectric response function for pentacene is calculated from [11] and the infrared from [12].

Because the distance between graphene layers in graphite is 0.34 nm [13], and that between graphene-mica is 0.49 nm [14], we assume the distance between pentacene and mica is 0.49 nm and that between pentacene and graphene is 0.34 nm. Therefore, the binding energy for different interfaces per pentacene atom area is calculated to be $E_{pen-mica} = 0.0162\ eV$, $E_{\ pen-\mathrm{graphene}} = 0.0639\ eV$ and $\mathrm{E_{graphene-mica}} = 0.0529\ eV$. Therefore, the dimensionless Hamaker constants used are $A_{sub} = 0.0162\ eV$, $A_{cover} = 0.0639\ eV$ and $A_{inter} = 0.0529\ eV$.

The Pentacene Orientation

Very thin pentacene film deposit on inert, flat surfaces is reported to be in thin film phase (1.54 nm) with the long axis perpendicular to the surface, because (001) surface is thought to be of lowest surface energy [15]. Calculation demonstrated that the energies of other surfaces are at least 51.6% higher than that of (001) surface. Mica is reported to be of this case [16]. While graphene is of big π-conjugated structure, the interaction between graphene (or HOPG) and pentacene is very weak, the second layer and roughness of the substrate greatly influence the pentacene stacking of the first layer, where slightly rougher HOPG surface gives thin film phase [17]. Thin film phase of pentacene is found on graphene covered SiO_2 [18], indicating the dominant role SiO_2 plays for monolayer pentacene stacking. Therefore, in the case discussed in this paper, the inert, flat mica surface requires pentacene to contact with it through the lowest surface energy, e.g., (001) surface, which out competes the weak interaction between pentacene and graphene.

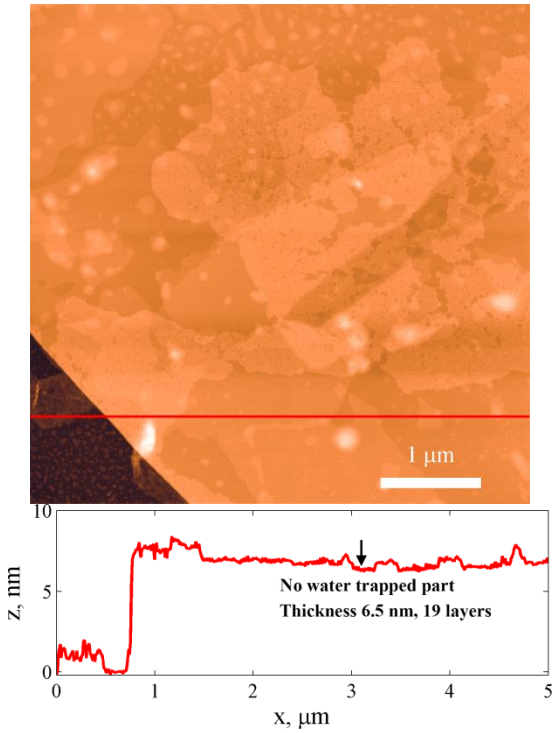

Figure S1 The AFM height profile of FLG before transfer to the pentacene covered mica substrate for sample in Figure 1. The overall thickness is 6.5 nm, which corresponds to totally 19 layers of graphene.

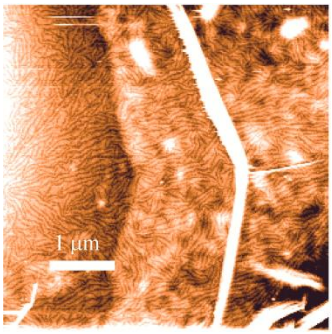

Figure S2 Dense stripe pattern formed between graphene and silica surface.

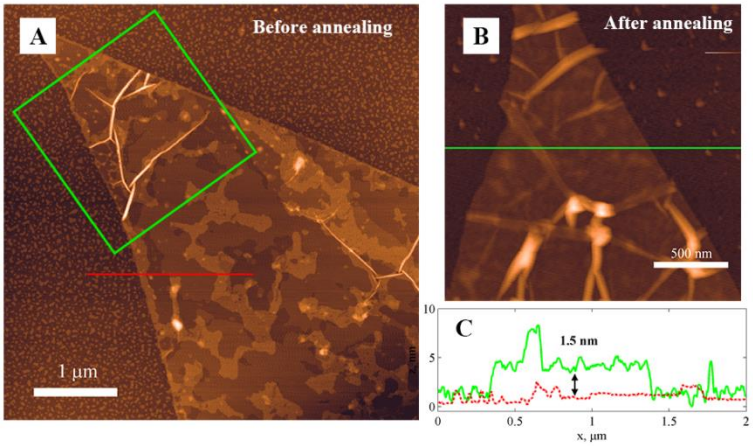

Figure S3 The AFM profile of bilayer graphene before and after monolayer trapping. A) Bilayer graphene on bare mica substrate. B) Bilayer graphene after pentacene monolayer trapping, at the location indicated by the green box in A). C) Height profile comparison.

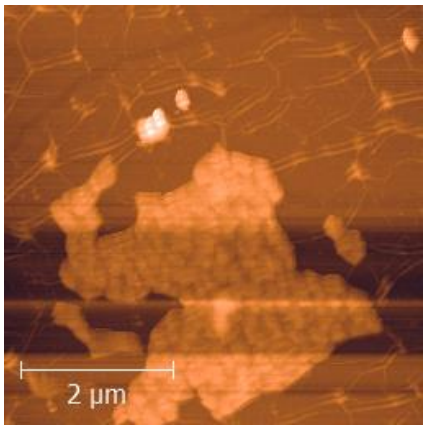

Figure S4 A lot of wrinkles will be created for monolayer graphene upon annealing.

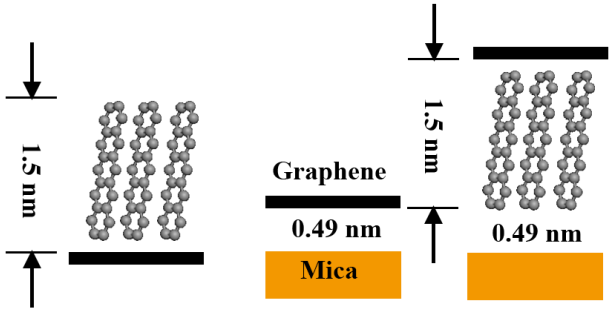

Figure S5 The measured pentacene thickness. Assuming the distance between pentacene and mica is the same as that of graphene and mica (0.49 nm), the measured distance is exactly the thickness of pentacene on graphene.

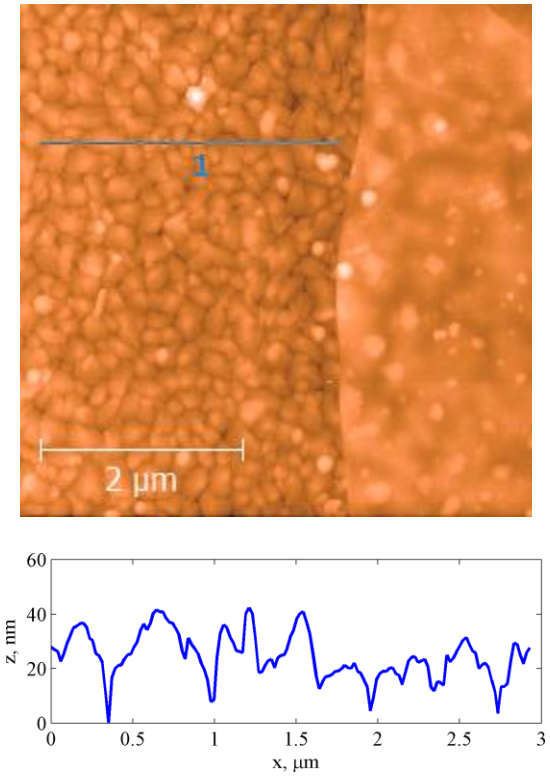

Figure S6 The profile of original pentacene film.

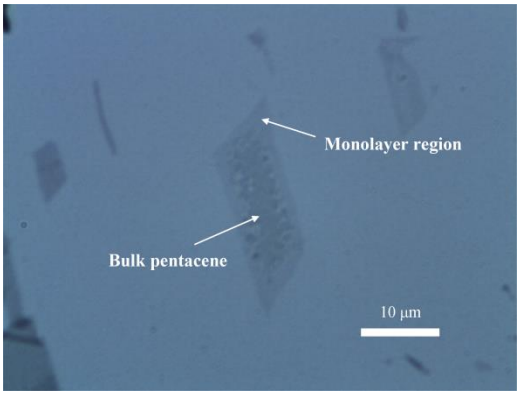

Figure S7 The overall optical image of a typical trapped pentacene sample. The monolayer region is about 2 μm in this figure.

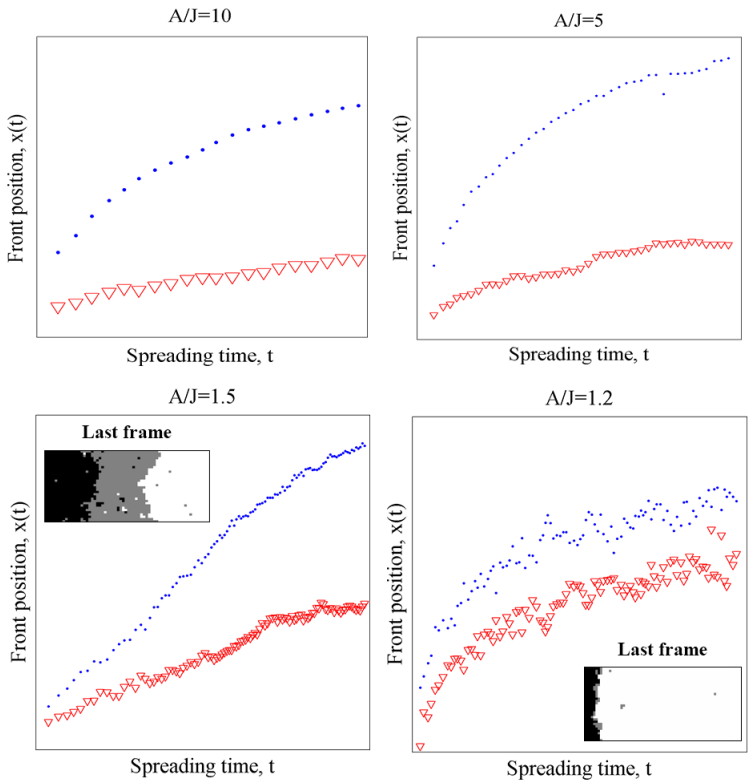

Figure S8 The spreading curves for different A to J parameters. Blue dots curves indicate the growth of the first layer. Red triangle curves indicate the growth of the second layer. First layer is preferred to spread until A/J ratio down to 1.5 and not to spread at $\mathrm{A/J} = 1.2$. In all simulations, we adjust temperature to maintain $\mathrm{J/k_B}T = 1$.

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