Atomic Force Microscopy Characterization of Room-Temperature Adlayers of Small Organic Molecules through Graphene Templating

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Supporting Information

Materials and Methods

Materials. Anhydrous inhibitor-free tetrahydrofuran (THF, ≥99.9%, water content <0.002%) and anhydrous cyclohexane (99.5%, water content <0.001%) were purchased from Sigma-Aldrich. These reagents were used as supplied and stored in a glove-box purged with nitrogen. Muscovite mica (Grade V1; round disks of diameter 10 mm) was obtained from Ted Pella. Kish graphite was obtained from Covalent Materials US Inc.

Sample preparation. Samples were prepared in a glove-bag (Sigma-Aldrich AtmosBag) that was purged and protected under a continuous flow of ultra-high purity argon, in which the relative humidity (RH) was controlled to be <2%. Humidity was monitored using a Fluke 971 temperature humidity meter. All experiments were performed at room temperature (22±2 °C). Mica disks were first heated in air at 200 °C for 10 min to remove absorbed moisture, and then transferred into the glove-bag. The mica surface was cleaved in the glove-bag and exposed to organic vapors for ~10 s to ~1 min. The partial pressure of organic molecules at the mica surface, which determines the surface coverage at equilibrium, was adjusted by varying the distance between the vapor source and the mica surface. Graphene sheets were deposited onto the mica surface through the standard method of mechanical exfoliation (Novoselov *et al.* 2005; Lui *et al.* 2009) of Kish graphite, thus sealing and preserving the adlayers of organic molecules.

Identification of graphene layers. Monolayer graphene sheets were identified through optical microscopy and confirmed by spatially resolved Raman spectroscopy (Xu *et al.* 2010). Raman spectra were recorded with a Renishaw M1000 Micro Raman spectrometer system using a 514.5 nm laser beam and a 2400 lines per mm grating. A confocal optical microscope with a ×100 objective lens was used to record spectra with a spatial resolution of 2 μm. No noticeable D peak was observed in the Raman spectra (Fig. S1), indicating high-crystalline order of our samples.

Atomic Force Microscopy. All AFM images were acquired under tapping mode on a Digital Instrument Nanoscope IIIA at ambient conditions. A sharp TESP tip (Veeco) with a radius of end of 8 nm was used. Typical values for the force constant and resonance frequency were 42 N/m and 320 kHz respectively. Height calibrations were performed using the step heights of freshly cleaved graphite samples. Due to the super-flatness of the samples, sometimes the laser interference pattern along the slow-scan axis was hard to avoid, which is more noticeable in large-area scanning and have a period of twice the wavelength of the laser. This is caused by the constructive interference of laser reflected from the sample surface and

that reflected from the cantilever. The broad stripe-like features seen in Fig. 2a and Fig S7ab were due to this effect.

References for Materials and Methods

Lui, C. H., Liu, L., Mak, K. F., Flynn, G. W. and Heinz, T. F. (2009). "Ultraflat graphene." *Nature* **462**, 339.

Novoselov, K. S., Jiang, D., Schedin, F., Booth, T. J., Khotkevich, V. V., Morozov, S. V. and Geim, A. K. (2005). "Two-dimensional atomic crystals." *Proc. Natl. Acad. Sci. U. S. A.* **102**, 10451.

Xu, K., Cao, P. G. and Heath, J. R. (2010). "Graphene visualizes the first water adlayers on mica at ambient conditions." *Science* **329**, 1188.

Supplementary Figures, with Additional Discussion in the Captions

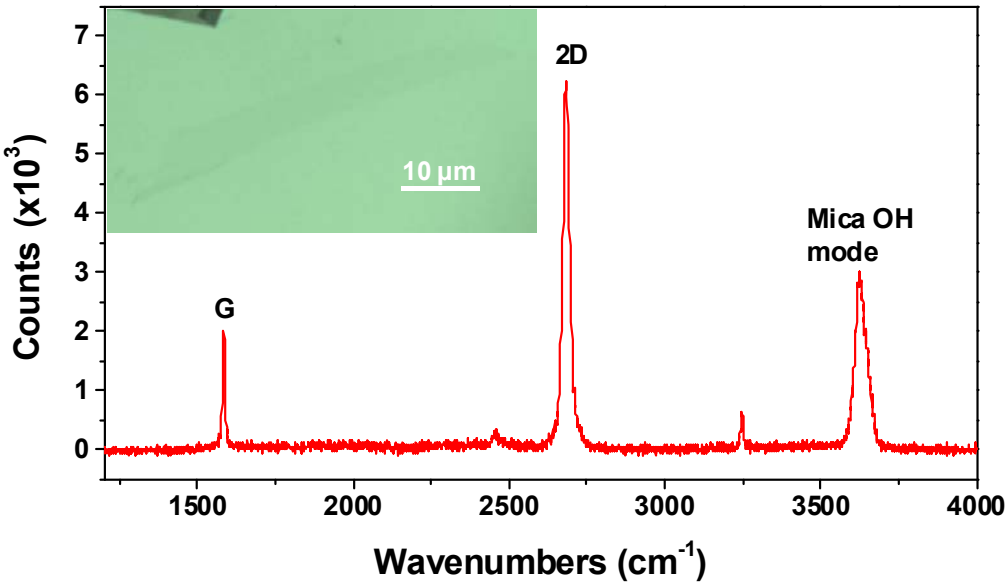

Fig. S1. Raman spectrum of a monolayer graphene sheet deposited on a mica surface that was in equilibrium with a THF vapor. Inset: transmission optical image of the graphene sheet at the center. The 2D and G bands of graphene and the OH mode of mica are labeled. Similar Raman spectra were also observed for monolayer graphene sheets deposited on mica surfaces that were in equilibrium with cyclohexane vapors.

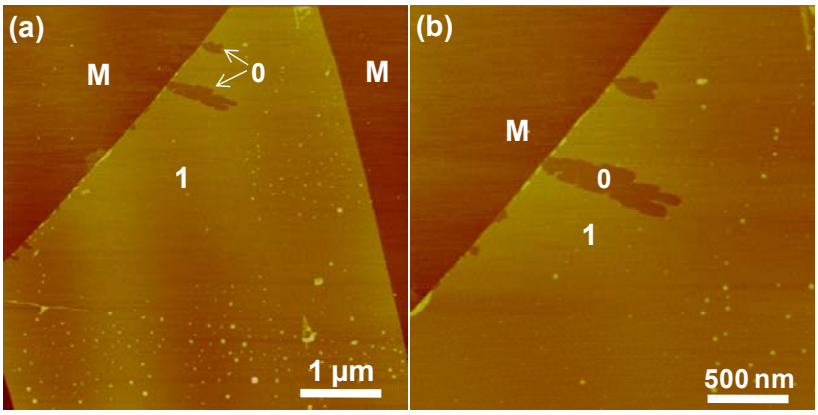

Fig. S2. Graphene on top of a near-complete monolayer of THF adlayer on mica (a), and a close up of the edge (b), where the adlayer is missing. M labels the mica surface, while 0 and 1 label regions where monolayer graphene is on top of 0 and 1 adlayers of THF on mica, respectively. No second adlayer is observed before the first adlayer is completed.

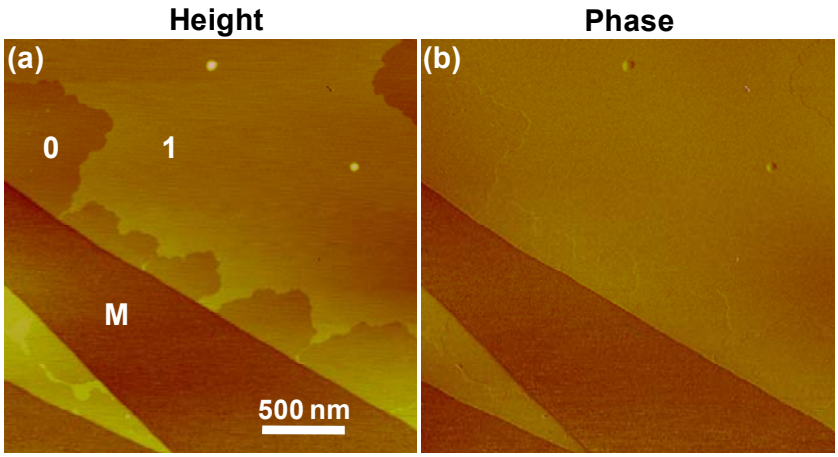

Fig. S3. AFM height (a) and phase (b) images for monolayer graphene sheets deposited on a mica surface that was in equilibrium with a cyclohexane vapor, corresponding to Fig. 3a in the main text. M labels the mica surface, while 0 and 1 label regions where monolayer graphene is on top of 0 and 1 adlayers of cyclohexane on mica, respectively. Significant phase difference is observed between the mica and graphene surfaces, reflecting the difference in surface properties. By comparison, the same phase is observed for the flat islands and other parts of graphene, indicating the AFM tip is interacting with the same surface (graphene), and the islands are cyclohexane adlayers underneath graphene.

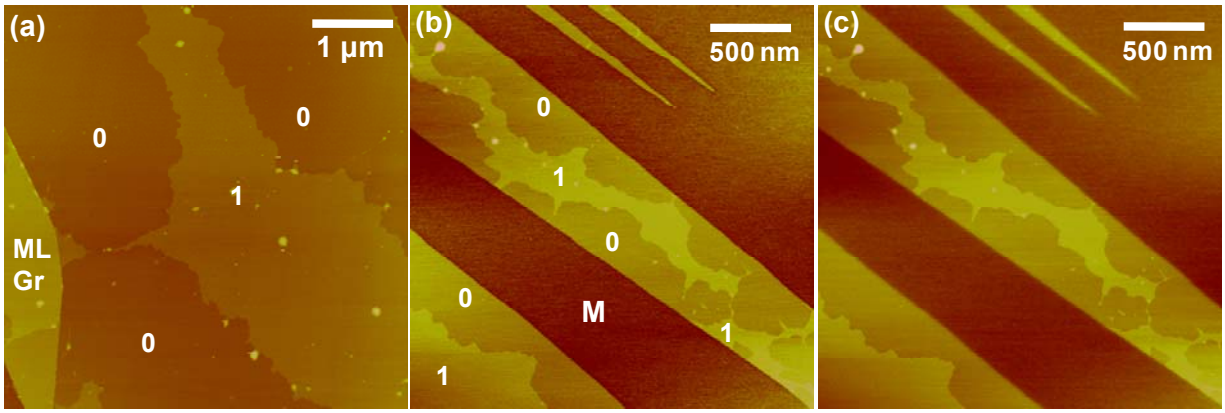

Fig. S4. Cyclohexane adlayers tend to form large, continuous islands on the mica surface. M labels the mica surface, while 0 and 1 label regions where monolayer graphene is on top of 0 and 1 adlayers of cyclohexane on mica, respectively. "ML Gr" labels multilayer graphene. **(a,b):** At reduced surface coverage, the adlayers tend to form narrow "necks" as opposed to isolated small islands, suggestive of weak molecule-substrate interactions. **(c):** The same area as (b), but imaged after the sample was stored at ambient conditions for 2 months. All adlayer structures, including the narrow necks, remain unchanged.

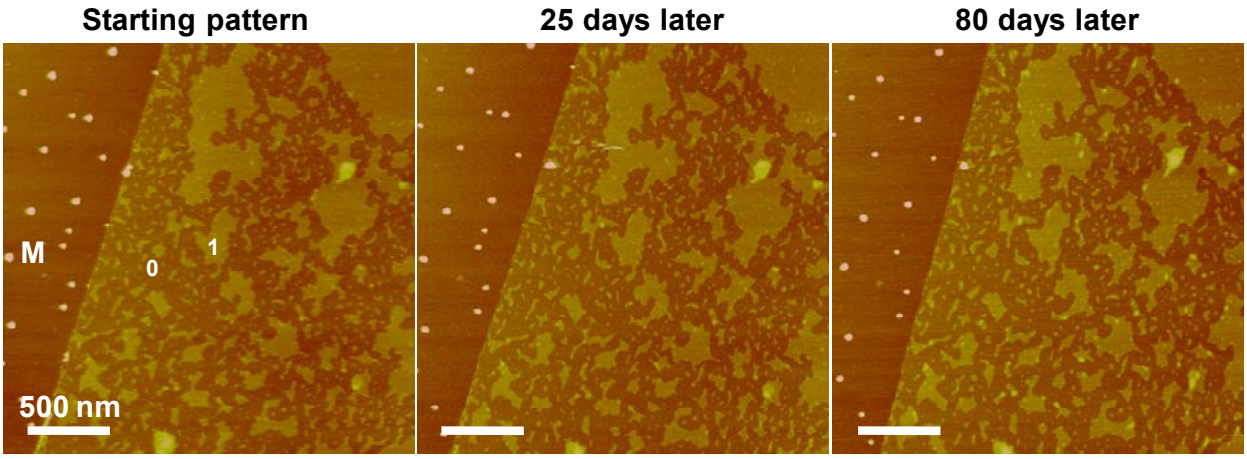

Fig. S5. Graphene-templated water adlayers are stable for months under ambient conditions without significant structural changes. Left: AFM image of a monolayer graphene sheet deposited on mica at ambient conditions (~40% RH). Center: The same sample, after being kept at ambient conditions for 25 days. Right: The same sample, after being kept at ambient conditions for 80 days. M labels the mica surface, while 0 and 1 label regions where monolayer graphene is on top of 0 and 1 adlayers of water on mica, respectively.

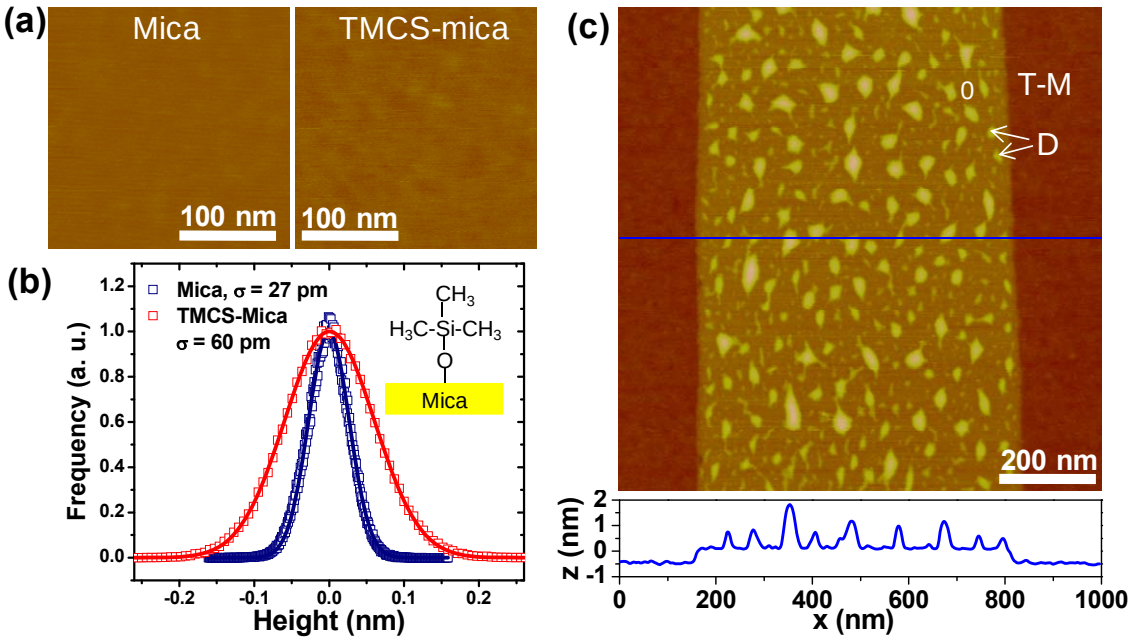

Fig. S6. Water adsorption on TMCS-functionalized mica surfaces at ambient conditions.

As a control experiment, we utilized graphene templating to characterize the water adsorption on mica surfaces that were rendered somewhat hydrophobic (and slightly rougher) via chemical functionalization with trimethylchlorosilane (TMCS). The surface functionalization was carried out through vapor deposition. Freshly prepared mica surfaces were first exposed to an environment with controlled RH of 35±2% for about 5-10 min. The mica substrates were then quickly transferred into a sealed reaction vessel containing a beaker filled with about 5 ml of purified TMCS liquid and allowed to react for about 30-60 min. The TMCS-functionalized mica surface was then equilibrated with ambient air (~40% RH) for ~10 min before graphene was deposited. The water contact angles of fresh mica and TMCS-functionalized mica were measured, via contact-angle goniometry, to be ~0° and 40°, respectively.

(a): AFM images indicate a uniform surface passivation of mica by TMCS. However, the functionalized surface, although still very flat, is rougher that what is observed for freshly cleaved mica. **(b):** Height histograms of a fresh mica surface and a TMCS-functionalized mica surface. The measured RMS roughness of fresh mica (27 pm) is likely limited by the noise of AFM, whereas the roughness of TMCS-functionalized mica surface is significantly higher (60 pm). There is, however, no evidence that TMCS functionalization introduces etch pits or other large defects into the mica. The inset is a simple molecular drawing of TMCS-functionalized mica. **(c):** Graphene-templating reveals that under ambient conditions (~40% RH), water adsorbs as nanometer-sized droplets on the relatively hydrophobic TMCS-functionalized mica surface. "T-M" labels TMCS-functionalized mica surface, "0" labels where monolayer graphene is in direct contact with the TMCS-functionalized mica surface, and "D" points to two droplets. A cross-sectional profile is given for the blue line, which indicates the droplets have varying heights on the order of ~1-2 nm. These results contrast with the flat 2D islands typically observed for adlayers on fresh (hydrophilic) mica surfaces.

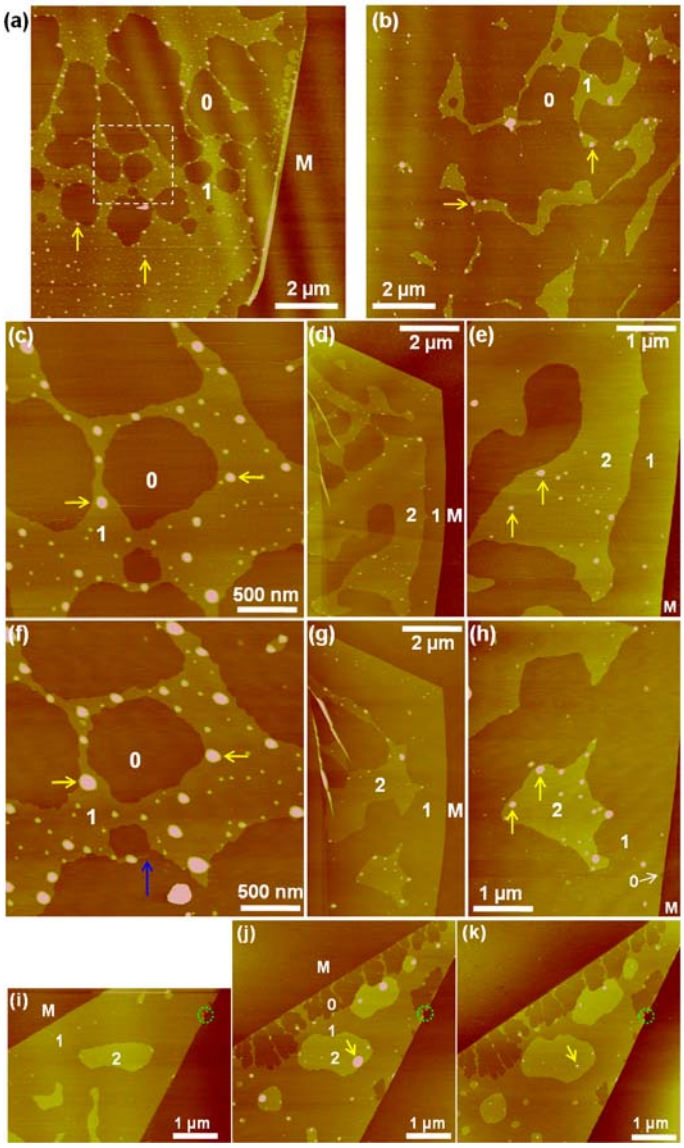

Figure S7. AFM images of graphene-templated THF adlayers reveal both structural and dynamical information. These images represent a more complete series of what is presented in Figure 2 in the main text. M labels the mica surface, and 0, 1, and 2 label regions where monolayer graphene is on top of 0, 1, and 2 adlayers of THF, respectively. Yellow arrows point to droplets. (a)-(e) were taken within a few hours after graphene sheets were deposited. **(a)**: The case in which the trapped adlayer is a submonolayer. **(b):** Another sample with very low surface coverage of THF. **(c):** Zoom-in of the square in (a). **(d):** Another sample showing the second THF adlayer on top of the first. **(e):** Zoom-in of the second adlayer in (d). **(f-h):** The same areas as (c-e), after the samples were kept at ambient conditions for 2 months. **(i-k):** Another sample freshly prepared (i), and after being kept at ambient conditions for 60 days (j) and 68 days (k), illustrating processes in which droplets revert back to islands. The green circles mark a defect on the graphene edge, which served as a reference point for aligning the images.

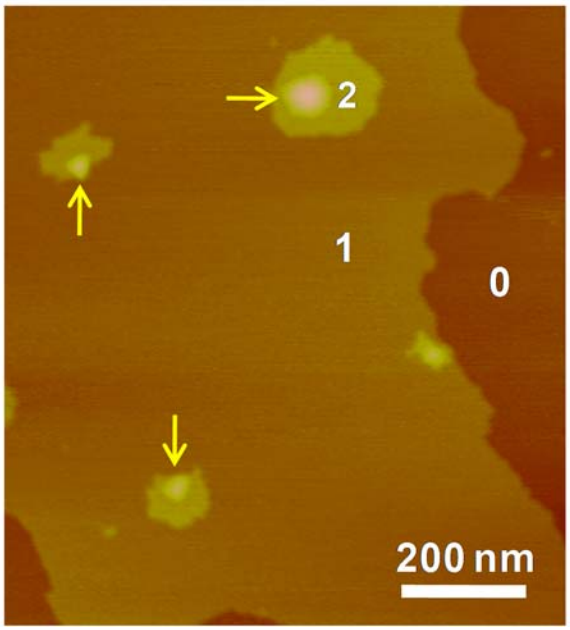

Figure S8. AFM images of a graphene-templated cyclohexane adlayer. The labels 0, 1, and 2 indicate regions where monolayer graphene is on top of 0, 1, and 2 adlayers of cyclohexane, respectively. Yellow arrows point to droplets. This particular image reveals the second cyclohexane adlayers.