

UC Berkeley

UC Berkeley Previously Published Works

Title

Molecular Self-Assembly in a Poorly Screened Environment: F4TCNQ on Graphene/BN

Permalink

<https://escholarship.org/uc/item/4hw9v68v>

Journal

ACS Nano, 9(12)

ISSN

1936-0851

Authors

Tsai, Hsin-Zon

Omrani, Arash A

Coh, Sinisa

et al.

Publication Date

2015-12-22

DOI

10.1021/acs.nano.5b05322

Peer reviewed

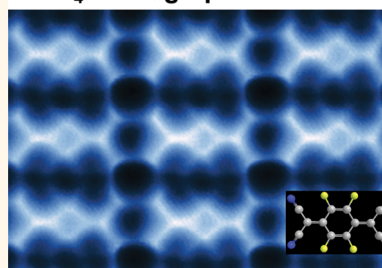
Molecular Self-Assembly in a Poorly Screened Environment: F₄TCNQ on Graphene/BN

Hsin-Zon Tsai,^{†,¶} Arash A. Omrani,^{†,¶} Sinisa Coh,^{†,*,¶} Hyungju Oh,^{†,‡} Sebastian Wickenburg,^{†,‡} Young-Woo Son,^{†,‡,§} Dillon Wong,[†] Alexander Riss,[†] Han Sae Jung,[†] Giang D. Nguyen,[†] Griffin F. Rodgers,[†] Andrew S. Aikawa,[†] Takashi Taniguchi,^{||} Kenji Watanabe,^{||} Alex Zettl,^{†,‡,⊥} Steven G. Louie,^{*,†,‡} Jiong Lu,^{*,†,‡,□} Marvin L. Cohen,^{*,†,‡} and Michael F. Crommie^{*,†,‡,⊥}

[†]Department of Physics, University of California, Berkeley, California 94720, United States, [‡]Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States, [§]Korea Institute for Advanced Study, Seoul 130-722, Korea, ^{||}National Institute for Materials Science, 1-1 Namiki, Tsukuba, 305-0044, Japan, [⊥]Kavli Energy NanoSciences Institute at the University of California, Berkeley and the Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States, [□]Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore, and [□]Centre for Advanced 2D Materials and Graphene Research Centre, National University of Singapore, 6 Science Drive 2, Singapore 117546, Singapore. [¶]H.-Z. Tsai, A. A. Omrani, and S. Coh contributed equally.

ABSTRACT We report a scanning tunneling microscopy and noncontact atomic force microscopy study of close-packed 2D islands of tetrafluoro-tetracyanoquinodimethane (F₄TCNQ) molecules at the surface of a graphene layer supported by boron nitride. While F₄TCNQ molecules are known to form cohesive 3D solids, the intermolecular interactions that are attractive for F₄TCNQ in 3D are repulsive in 2D. Our experimental observation of cohesive molecular behavior for F₄TCNQ on graphene is thus unexpected. This self-assembly behavior can be explained by a novel solid formation mechanism that occurs when charged molecules are placed in a poorly screened environment. As negatively charged molecules coalesce, the local work function increases, causing electrons to flow into the coalescing molecular island and increase its cohesive binding energy.

F₄TCNQ/graphene/BN



KEYWORDS: molecular self-assembly · graphene · hexagonal boron nitride (BN) · scanning tunneling microscopy (STM) · noncontact atomic force microscopy (nc-AFM) · density functional theory (DFT)

Surface functionalization *via* molecular self-assembly is a potentially useful technique for tuning the properties of graphene layers.^{1–3} Previous studies have shown that functionalization *via* tetrafluoro-tetracyanoquinodimethane (F₄TCNQ) adsorbates is particularly effective at p-doping graphene^{4–7} (as well as other substrates^{8–13}) through the transfer of electrons from the substrate to the adsorbed molecules. These studies, however, were performed using spatially averaged techniques and so were not able to determine local molecular self-assembly characteristics. Locally resolved scanning tunneling microscopy (STM) measurements of F₄TCNQ molecules deposited onto graphene/Ru(0001) also indicate charge transfer of electrons from graphene to F₄TCNQ and provide some structural information.¹⁴ These measurements reveal that F₄TCNQ molecules on graphene/metal do not assemble into islands, but rather

repel each other due to interaction between their electronegative outer atoms^{14,15} (in contrast to F₄TCNQ adsorption on bare metal surfaces, which induces significant rearrangement of surface atoms^{16,17}). However, because the graphene used in these previous STM measurements was supported by a bulk metal, it created a highly screened environment where long-range Coulomb interactions are damped. The local behavior of charged molecules on a poorly screened graphene surface that supports long-range Coulomb interactions has not been explored.

Here we report a combined STM, non-contact atomic force microscopy (nc-AFM), and theoretical investigation into the self-assembly characteristics of F₄TCNQ molecules on a graphene substrate supported by insulating hexagonal boron nitride (BN). This provides a nearly ideal setting to study molecular self-assembly on isolated graphene

* Address correspondence to
sglouie@berkeley.edu,
chmluj@nus.edu.sg,
mlcohen@berkeley.edu,
crommie@berkeley.edu.

Received for review August 25, 2015
and accepted October 20, 2015.

Published online October 20, 2015
10.1021/acsnano.5b05322

© 2015 American Chemical Society

in a poorly screened environment as BN is a wide-band-gap insulator that only weakly interacts with graphene.^{18–21} We observe that, unlike previous measurements of F₄TCNQ on graphene supported by metals, F₄TCNQ molecules on graphene/BN assemble into tightly packed 2D islands. This unexpected result can be explained by a unique self-assembly mechanism that is based on heterogeneous lateral charge transfer driven by local work function differences.

RESULTS AND DISCUSSION

F₄TCNQ molecules (Figure 1a) were deposited onto graphene/BN in ultrahigh vacuum (UHV) using a Knudsen cell evaporator. Molecular deposition was performed while electrically grounding the graphene layer at room temperature. The sample was then cooled to 4.5 K and imaged with both STM and nc-AFM using a CO-molecule-functionalized tip. The nc-AFM, which detects the frequency shift of a qPlus resonator in constant height mode, allows high-resolution imaging of individual chemical bonds and atomic-scale structure.^{22,23}

At low molecular coverage (below 0.1 monolayer (ML)), the majority of molecules deposited on graphene are isolated and typically separated from each other by more than 4 nm, as shown in the STM topographic image in Figure 1b. This observation is consistent with earlier studies of F₄TCNQ deposited onto graphene/metal.^{14,15} However, at higher coverage (above 0.2 ML), we observe that molecular adsorbates can coalesce into close-packed islands (Figure 2a, larger scale STM images can be found in Figure S1). High-resolution nc-AFM imaging (Figure 2b) shows that F₄TCNQ molecules within such islands are oriented in a planar rectangular geometry parallel to the underlying graphene (the molecular island unit cell is 1.25 ± 0.03 nm $\times$ 0.78 ± 0.03 nm). Molecular packing in the island is about 50 times denser than when the molecules are isolated at 0.1 ML coverage. Faint lines observed between adjacent molecules are likely caused by tilting of the CO molecule at the tip apex, as described in previous work.^{24,25}

We now discuss the mechanism for F₄TCNQ island assembly in 2D. We first used density functional theory (DFT) to confirm the known 3D crystal structure of bulk F₄TCNQ. Our calculation agrees well with the crystal structure determined previously using X-ray diffraction^{26,27} and reveals a large binding energy between molecular units in the 3D bulk crystal (1.6 eV per molecule, as shown in Figure 3a). A natural assumption would be that the same attraction mechanism that works for the bulk (driven by electrostatic and van der Waals interactions) is responsible for the formation of self-assembled 2D islands. To test this assumption, we used DFT to calculate the total energy of F₄TCNQ molecules in the absence of a substrate constrained to the same 2D planar geometry that we observed in our nc-AFM images (Figure 2b). Surprisingly, we found that the calculated interaction between molecules under these conditions is

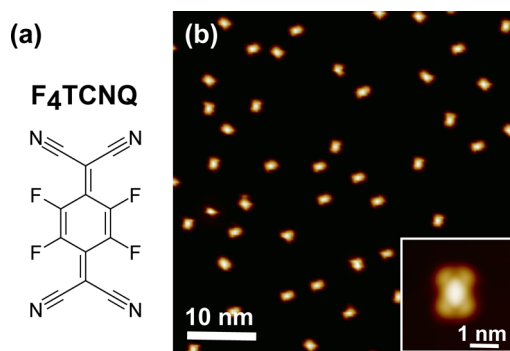


Figure 1. (a) Chemical structure of the F₄TCNQ molecule. (b) STM topography of F₄TCNQ molecules deposited onto graphene/BN at low coverage (below 0.1 monolayer). Inset shows close-up view of a single F₄TCNQ molecule. STM tunneling parameters are $V_s = 2$ V, $I_t = 5$ pA, and $T = 4.5$ K.

repulsive rather than cohesive. This can be seen in Figure 3b, which shows the total energy per molecule of a 2D island as a function of intermolecular distance. This curve exhibits a negative energy-vs-distance slope, thus implying that 2D island formation is energetically unfavorable for F₄TCNQ under these conditions.

This result indicates that the graphene substrate must play an important role in 2D island formation for F₄TCNQ molecules. In order to understand the effect of the graphene substrate, we performed an *ab initio* DFT calculation of the total energy of a 2D F₄TCNQ island supported by a single layer of graphene (*i.e.*, homogeneous molecular coverage in a periodic array). Inclusion of graphene in the simulation results in partial electron transfer from the graphene to the F₄TCNQ molecules. Each molecule in an island thus forms an electric dipole with the electron-depleted patch of graphene directly underneath the molecule (the dipole points down into the plane). The resulting dipole–dipole interactions between neighboring molecule–graphene complexes are repulsive and island formation becomes even less favorable than without graphene, as seen in the calculated energy-vs-distance curve of Figure 3c. Despite this repulsion, electron transfer from graphene into the molecules results in very strong binding of the molecules to the graphene (more than 1.8 eV per molecule, as shown in Figure 3c).

The calculations discussed so far were performed under fixed-electron-number conditions, a common constraint for DFT calculations. However, in a real molecular island surrounded by pristine graphene, the total number of electrons per molecule is not necessarily constant since island formation creates work function heterogeneity and leads to lateral transfer of screening charge (*i.e.*, electrons flow from low work function areas to regions having higher work function^{28–30}). As a result, the real experimental system is better described within a fixed-electrochemical-potential picture. Here the electrically grounded graphene sheet surrounding the island acts as an electron reservoir at fixed electrochemical potential.

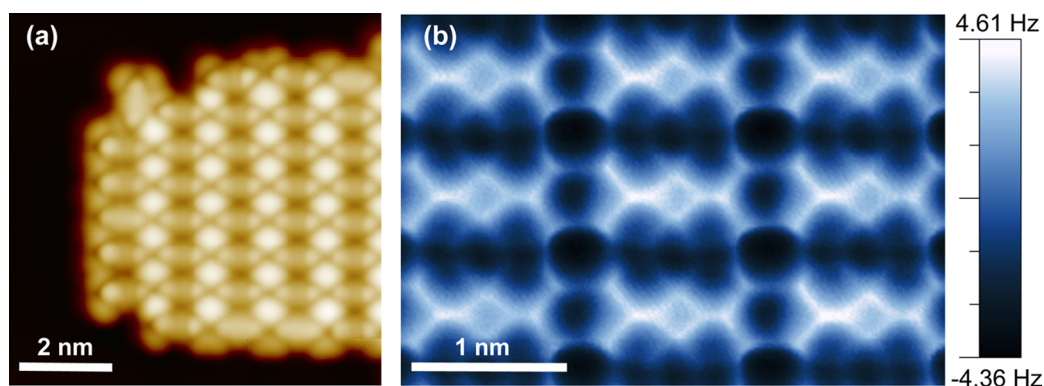


Figure 2. (a) STM and (b) nc-AFM images of an F_4TCNQ 2D island on graphene/BN. The nc-AFM image resolves individual chemical bonds within the F_4TCNQ molecules and shows that molecules within the island lie flat on the surface in a close-packed rectangular lattice. STM tunneling parameters are $V_s = 2$ V, $I_t = 5$ pA, and $T = 4.5$ K. AFM measurement parameters are $f_0 = 28.7$ kHz, amplitude = 60 pm, $Q = 10^5$, and $T = 4.5$ K.

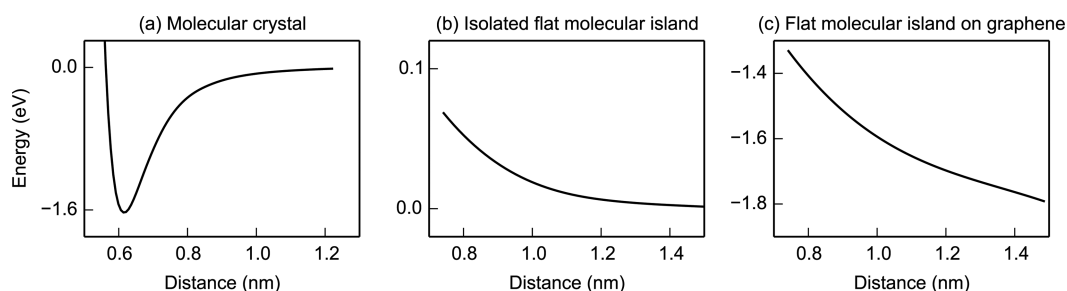


Figure 3. Calculated total energy per F_4TCNQ molecule as a function of the shortest distance between molecules for (a) a bulk molecular crystal, (b) an isolated, flat 2D molecular island having the same structure as in Figure 2b, and (c) the same as (b) but with a graphene substrate.

While *ab initio* techniques cannot directly treat this case of a large island surrounded by pristine graphene (as pictured in Figure 2a), they can be used to treat homogeneous systems having different overall electron density and work functions. We can thus model the real heterogeneous (*i.e.*, not periodic) system by comparing different homogeneous (*i.e.*, periodic) systems with varying work functions. We applied this technique by simulating homogeneous systems where graphene was subjected to different molecular coverages and where the overall charge carrier density was varied by hand (each individual calculation had a fixed number of electrons). This provides a method for taking into account the fact that (since F_4TCNQ molecules p-dope graphene) the local work function increases as islands assemble, thus causing electrons to flow into an island as molecules are packed more densely (in order to keep the electrochemical potential constant).

To illustrate this technique, we performed two separate DFT calculations of the work function above F_4TCNQ molecules on graphene as a function of intermolecular separation (shown in Figure 4a), each with a different number of charge carriers. In the first calculation (black curve) each molecule–graphene complex is charge neutral. In the second calculation (red curve) each complex has an excess of electrons that are

allowed to redistribute within the entire molecule–graphene assembly until reaching the ground state (one extra electron per each 36 carbon atoms in graphene, roughly one extra electron per molecule at full coverage). Here the vacuum energy above the island is set to zero, and so the work function is equivalent to the negative of the electrochemical potential. As expected, the work function above an island strongly increases for both the neutral and charged cases as the molecules are brought closer to each other (a similar dependence has been found earlier and was assigned to depolarization effects^{31,32}). The work function in the charged case is overall lower compared to the neutral case, reflecting the increase in electrochemical potential that occurs as carrier density of the molecule–graphene complex is increased.

Figure 4b shows the calculated total energy of the F_4TCNQ molecules vs molecule–molecule separation for the same neutral and doped systems. The neutral case is identical to what is shown in Figure 3c and results in overall binding of the molecules to graphene (negative energy) but an increasing energy with increased molecular density. For the doped case we see similar behavior, except that there is a net decrease in the total energy, reflecting the increased binding energy of the molecule–graphene complex as electrons are added to the system.

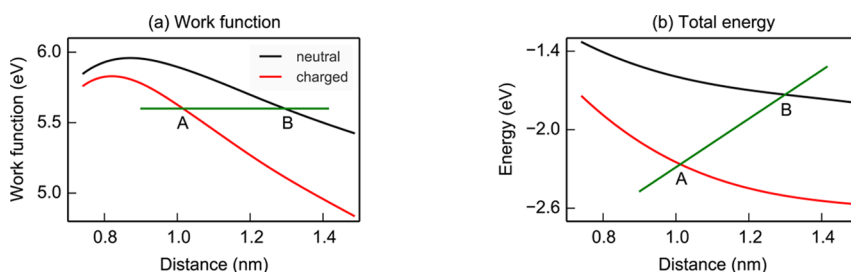


Figure 4. (a) Calculated work function relative to the vacuum level above an F_4TCNQ molecular assembly on graphene as a function of the shortest distance between molecules for both the neutral case (black line) and the electron-doped case (red line). (b) Calculated total energy per F_4TCNQ molecule on graphene as a function of the shortest distance between molecules for both the neutral case (black line) and the electron-doped case (red line). Green line shows hypothetical constant electrochemical potential (see text).

The origin of the attractive force driving island assembly of charged molecules on isolated graphene can be deduced from the curves shown in Figure 4. To see this, it is useful to imagine F_4TCNQ molecules on a graphene surface with a particular fixed hypothetical electrochemical potential, as indicated by the green line (the island formation mechanism is not sensitive to the precise value of the electrochemical potential). To achieve this particular electrochemical potential at a large intermolecular distance as indicated by point B in Figure 4a, the island has to be charge neutral since the green line crosses the neutral-island configuration (black line) at B. However, at a shorter intermolecular distance (point A) the island has to absorb excess electrons from the reservoir and becomes charged (red line) in order to achieve the same electrochemical potential as at B (as required by thermodynamic equilibrium). Since the total energy of a molecule–graphene complex is lower at the corresponding charge state and distance of A than at B (Figure 4b), we conclude that within a fixed electrochemical potential picture it is energetically favorable for the molecules to be closer to each other and to form a stable island (this can also be seen from the positive energy-vs-distance slope of the line connecting point A to point B in Figure 4b).

The island cohesion mechanism demonstrated in Figure 4 for fixed electrochemical potential can intuitively be understood as follows: as negatively charged

molecules coalesce into an island, there is an increase in the local work function above the island (Figure 4a) that causes additional electrons to flow into the island. These additional electrons cause the total energy of the molecule–graphene complexes to decrease (Figure 4b), resulting in island cohesion. This mechanism is not applicable to adsorbates on highly metallic substrates because of the high density of states in these substrates compared to graphene. In these systems electric fields induced by charge transfer are screened, and charge transfer induced by work function differences does not lead to reduced total energy. This explains why close-packed island formation has not been seen for F_4TCNQ molecules adsorbed onto graphene/Ru(0001).¹⁴

CONCLUSIONS

In conclusion, we find that F_4TCNQ molecules aggregate into close-packed islands on graphene/insulator, unlike their behavior on graphene/metal. This behavior is explained by a new type of island formation mechanism driven by lateral charge screening induced by long-range Coulomb interactions. We expect this island formation mechanism to apply to other molecular adsorbate systems that exhibit charge transfer in poorly screened environments. For such systems the work function above deposited molecules will strongly vary with intermolecular distance, causing additional charge transfer and increased binding as island density increases.

METHODS

The graphene/BN sample was fabricated using a graphene monolayer grown *via* CVD on copper foil.³³ Hexagonal boron nitride flakes were exfoliated onto heavily doped silicon wafers covered by a 285 nm thermal oxide, and graphene was transferred on top of the BN using a poly(methyl methacrylate) (PMMA) stamp.³⁴ Electrical contact was made to the graphene by depositing Ti (10 nm thick)/Au (30 nm thick) electrodes using a stencil mask technique. F_4TCNQ molecules were evaporated from a Knudsen cell held at 90 ± 5 °C onto a graphene/BN surface held at room temperature (island formation was facilitated by predeposition of a very dilute, inert seed layer to act as surface nucleation points, *e.g.*, *via* low coverage of 10,12-pentacosadiynoic acid (PCDA)). STM/nc-AFM imaging was done in a qPlus-equipped commercial Omicron LT-STM/AFM

at $T = 4.5$ K using tungsten tips. WSxM software was used to process all STM and nc-AFM images.³⁵

We performed first-principles density functional theory calculations using a Quantum-ESPRESSO package.³⁶ All calculations used the PBE exchange–correlation functional with a van der Waals correction (vdW-DF2³⁷). We used ultrasoft pseudopotentials from the GBRV database³⁸ with 40 and 200 Ry kinetic energy cutoffs for wave function and charge density, and our Brillouin zone sampling is equivalent to 24×24 points in the graphene primitive unit cell. Electron doping was achieved in the simulations by creating carbon pseudopotentials with a noninteger core charge to compensate for an energy divergence in the case of an infinite island.

Conflict of Interest: The authors declare no competing financial interest.

Acknowledgment. This research was supported by the Director, Office of Science, Office of Basic Energy Sciences of the U.S. Department of Energy (DOE), contract no. DE-AC02-05CH11231 Nanomachine program (STM imaging, sample synthesis, theory) and Molecular Foundry (graphene growth, growth characterization), and by National Science Foundation grant DMR-1206512 (device characterization). Computational resources were provided by the DOE at Lawrence Berkeley National Laboratory's NERSC facility. D.W. was supported by the Department of Defense (DoD) through the National Defense Science & Engineering Graduate Fellowship (NDSEG) Program, 32 CFR 168a. A.A.O. acknowledges support from the Swiss National Science Foundation (SNSF) Postdoctoral Research Fellowship under Grant No. P2ELP2-151852. J.L. acknowledges fellowship support from the National Research Foundation, Prime Minister Office, Singapore, under its Medium Sized Centre Programme and CRP award no. R-144-000-295-281. A.R. acknowledges fellowship support by the Austrian Science Fund (FWF): J3026-N16. K.W. and T.T. acknowledge support from the MEXT Japan Elemental Strategy Initiative (synthesis of BN crystals) and JSPS Grant-in-Aid for Scientific Research on Innovative Areas no. 25107004 (characterization of BN crystals). T.T. acknowledges support from a JSPS Grant-in-Aid for Scientific Research on Innovative Areas no. 25106006 (development of high pressure BN synthesis instrumentation). We acknowledge Vitor M. Pereira for useful discussions.

Supporting Information Available: The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.5b05322.

Additional figure (PDF)

REFERENCES AND NOTES

- Hong, G.; Wu, Q.-H.; Ren, J.; Wang, C.; Zhang, W.; Lee, S.-T. Recent Progress in Organic Molecule/graphene Interfaces. *Nano Today* **2013**, *8*, 388–402.
- Macleod, J. M.; Rosei, F. Molecular Self-Assembly on Graphene. *Small* **2014**, *10*, 1038–1049.
- Mali, K. S.; Greenwood, J.; Adisoejoso, J.; Phillipson, R.; De Feyter, S. Nanostructuring Graphene for Controlled and Reproducible Functionalization. *Nanoscale* **2015**, *7*, 1566–1585.
- Chen, W.; Chen, S.; Qi, D. C.; Gao, X. Y.; Wee, A. T. S. Surface Transfer P-Type Doping of Epitaxial Graphene. *J. Am. Chem. Soc.* **2007**, *129*, 10418–10422.
- Coletti, C.; Riedl, C.; Lee, D. S.; Krauss, B.; Patthey, L.; von Klitzing, K.; Smet, J. H.; Starke, U. Charge Neutrality and Band-Gap Tuning of Epitaxial Graphene on SiC by Molecular Doping. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2010**, *81*, 235401.
- Wang, X.; Xu, J.-B.; Xie, W.; Du, J. Quantitative Analysis of Graphene Doping by Organic Molecular Charge Transfer. *J. Phys. Chem. C* **2011**, *115*, 7596–7602.
- Song, J.; Kam, F.-Y.; Png, R.-Q.; Seah, W.-L.; Zhuo, J.-M.; Lim, G.-K.; Ho, P. K. H.; Chua, L.-L. A General Method for Transferring Graphene onto Soft Surfaces. *Nat. Nanotechnol.* **2013**, *8*, 356–362.
- Koch, N.; Duhm, S.; Rabe, J. P.; Vollmer, A.; Johnson, R. L. Optimized Hole Injection with Strong Electron Acceptors at Organic-Metal Interfaces. *Phys. Rev. Lett.* **2005**, *95*, 237601.
- Romaner, L.; Heimel, G.; Brédas, J.-L.; Gerlach, A.; Schreiber, F.; Johnson, R. L.; Zegenhagen, J.; Duhm, S.; Koch, N.; Zojer, E. Impact of Bidirectional Charge Transfer and Molecular Distortions on the Electronic Structure of a Metal-Organic Interface. *Phys. Rev. Lett.* **2007**, *99*, 256801.
- Qi, D.; Chen, W.; Gao, X.; Wang, L.; Chen, S.; Loh, K. P.; Wee, A. T. S. Surface Transfer Doping of Diamond (100) by Tetrafluoro-Tetracyanoquinodimethane. *J. Am. Chem. Soc.* **2007**, *129*, 8084–8085.
- Furuhashi, M.; Yoshinobu, J. Charge Transfer and Molecular Orientation of Tetrafluoro-Tetracyanoquinodimethane on a Hydrogen-Terminated Si(111) Surface Prepared by a Wet Chemical Method. *J. Phys. Chem. Lett.* **2010**, *1*, 1655–1659.
- Schlesinger, R.; Xu, Y.; Hofmann, O. T.; Winkler, S.; Frisch, J.; Niederhausen, J.; Vollmer, A.; Blumstengel, S.; Henneberger, F.; Rinke, P.; et al. Controlling the Work Function of ZnO and the Energy-Level Alignment at the Interface to Organic Semiconductors with a Molecular Electron Acceptor. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2013**, *87*, 155311.
- Yu, L.; Zubair, A.; Santos, E. J. G.; Zhang, X.; Lin, Y.; Zhang, Y.; Palacios, T. High-Performance WSe₂ Complementary Metal Oxide Semiconductor Technology and Integrated Circuits. *Nano Lett.* **2015**, *15*, 4928–4934.
- Stradi, D.; Garnica, M.; Díaz, C.; Calleja, F.; Barja, S.; Martín, N.; Alcamí, M.; Vázquez de Parga, A. L.; Miranda, R.; Martín, F. Controlling the Spatial Arrangement of Organic Magnetic Anions Adsorbed on Epitaxial Graphene on Ru(0001). *Nanoscale* **2014**, *6*, 15271–15279.
- Barja, S.; Garnica, M.; Hinarejos, J. J.; Vázquez de Parga, A. L.; Martín, N.; Miranda, R. Self-Organization of Electron Acceptor Molecules on Graphene. *Chem. Commun.* **2010**, *46*, 8198–8200.
- Faraggi, M. N.; Jiang, N.; Gonzalez-Lakunza, N.; Langner, A.; Stepanow, S.; Kern, K.; Arnau, A. Bonding and Charge Transfer in Metal-Organic Coordination Networks on Au(111) with Strong Acceptor Molecules. *J. Phys. Chem. C* **2012**, *116*, 24558.
- Katayama, T.; Mukai, K.; Yoshimoto, S.; Yoshinobu, J. Reactive Rearrangements of Step Atoms by Adsorption and Asymmetric Electronic States of Tetrafluoro-Tetracyanoquinodimethane on Cu(100). *Phys. Rev. B: Condens. Matter Mater. Phys.* **2011**, *83*, 153403.
- Xue, J.; Sanchez-Yamagishi, J.; Bulmash, D.; Jacquod, P.; Deshpande, A.; Watanabe, K.; Taniguchi, T.; Jarillo-Herrero, P.; LeRoy, B. J. Scanning Tunneling Microscopy and Spectroscopy of Ultra-Flat Graphene on Hexagonal Boron Nitride. *Nat. Mater.* **2011**, *10*, 282–285.
- Decker, R.; Wang, Y.; Brar, V. W.; Regan, W.; Tsai, H.-Z.; Wu, Q.; Gannett, W.; Zettl, A.; Crommie, M. F. Local Electronic Properties of Graphene on a BN Substrate via Scanning Tunneling Microscopy. *Nano Lett.* **2011**, *11*, 2291–2295.
- Järvinen, P.; Hämmäläinen, S. K.; Banerjee, K.; Häkkinen, P.; Ijäs, M.; Harju, A.; Liljeroth, P. Molecular Self-Assembly on Graphene on SiO₂ and H-BN Substrates. *Nano Lett.* **2013**, *13*, 3199–3204.
- Riss, A.; Wickenburg, S.; Tan, L. Z.; Tsai, H. Z.; Kim, Y.; Lu, J.; Bradley, A. J.; Ugeda, M. M.; Meaker, K. L.; Watanabe, K.; et al. Imaging and Tuning Molecular Levels at the Surface of a Gated Graphene Device. *ACS Nano* **2014**, *8*, 5395–5401.
- Gross, L.; Mohn, F.; Moll, N.; Liljeroth, P.; Meyer, G. The Chemical Structure of a Molecule Resolved by Atomic Force Microscopy. *Science* **2009**, *325*, 1110–1114.
- Schuler, B.; Liu, W.; Tkatchenko, A.; Moll, N.; Meyer, G.; Mistry, A.; Fox, D.; Gross, L. Adsorption Geometry Determination of Single Molecules by Atomic Force Microscopy. *Phys. Rev. Lett.* **2013**, *111*, 106103.
- Hapala, P.; Kichin, G.; Wagner, C.; Tautz, F. S.; Temirov, R.; Jelínek, P. Mechanism of High-Resolution STM/AFM Imaging with Functionalized Tips. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2014**, *90*, 085421.
- Hämmäläinen, S. K.; van der Heijden, N.; van der Lit, J.; den Hartog, S.; Liljeroth, P.; Swart, I. Intermolecular Contrast in Atomic Force Microscopy Images without Intermolecular Bonds. *Phys. Rev. Lett.* **2014**, *113*, 186102.
- Emgea, T. J.; Maxfield, M.; Cowana, D. O.; Kistenmachera, T. J. Solution and Solid State Studies of Tetrafluoro-7,8,8-Tetracyano-*p*-Quinodimethane, TCNQF₄. Evidence for Long-Range Amphoteric Intermolecular Interactions and Low-Dimensionality in the Solid State Structure. *Mol. Cryst. Liq. Cryst.* **1981**, *65*, 161–178.
- Goetz, K. P.; Fonari, A.; Vermeulen, D.; Hu, P.; Jiang, H.; Diemer, P. J.; Ward, J. W.; Payne, M. E.; Day, C. S.; Kloc, C.; et al. Freezing-in Orientational Disorder Induces Crossover from Thermally-Activated to Temperature-Independent Transport in Organic Semiconductors. *Nat. Commun.* **2014**, *5*, 5642.
- Ishii, H.; Sugiyama, K.; Ito, E.; Seki, K. Energy Level Alignment and Interfacial Electronic Structures at Organic/Metal and Organic/Organic Interfaces. *Adv. Mater.* **1999**, *11*, 605.

29. Xu, Y.; Hofmann, O. T.; Schlesinger, R.; Winkler, S.; Frisch, J.; Niederhausen, J.; Vollmer, A.; Blumstengel, S.; Henneberger, F.; Koch, N.; et al. Space-Charge Transfer in Hybrid Inorganic–Organic Systems. *Phys. Rev. Lett.* **2013**, *111*, 226802.
30. Ashcroft, N. W.; Mermin, N. D. Surface Effects. In *Solid State Physics*; Brooks/Cole, Cengage Learning, 1976; p 353.
31. Natan, A.; Kronik, L.; Haick, H.; Tung, R. T. Electrostatic Properties of Ideal and Non-Ideal Polar Organic Monolayers: Implications for Electronic Devices. *Adv. Mater.* **2007**, *19*, 4103–4117.
32. Chen, Z.; Darancet, P.; Wang, L.; Crowther, A. C.; Gao, Y.; Dean, C. R.; Taniguchi, T.; Watanabe, K.; Hone, J.; Marianetti, C. A.; et al. Physical Adsorption and Charge Transfer of Molecular Br₂ on Graphene. *ACS Nano* **2014**, *8*, 2943–2950.
33. Li, X.; Cai, W.; An, J.; Kim, S.; Nah, J.; Yang, D.; Piner, R.; Velamakanni, A.; Jung, I.; Tutuc, E.; et al. Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils. *Science* **2009**, *324*, 1312–1314.
34. Reina, A.; Son, H.; Jiao, L.; Fan, B.; Dresselhaus, M. S.; Liu, Z.; Kong, J. Transferring and Identification of Single- and Few-Layer Graphene on Arbitrary Substrates. *J. Phys. Chem. C* **2008**, *112*, 17741–17744.
35. Horcas, I.; Fernández, R.; Gómez-Rodríguez, J. M.; Colchero, J.; Gómez-Herrero, J.; Baro, A. M. WSXM: A Software for Scanning Probe Microscopy and a Tool for Nanotechnology. *Rev. Sci. Instrum.* **2007**, *78*, 013705.
36. Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Chiarotti, G. L.; Cococcioni, M.; Dabo, I.; et al. QUANTUM ESPRESSO: A Modular and Open-Source Software Project for Quantum Simulations of Materials. *J. Phys.: Condens. Matter* **2009**, *21*, 395502.
37. Lee, K.; Murray, E. D.; Kong, L.; Lundqvist, B. I.; Langreth, D. C. Higher-Accuracy van Der Waals Density Functional. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2010**, *82*, 081101.
38. Garrity, K. F.; Bennett, J. W.; Rabe, K. M.; Vanderbilt, D. Pseudopotentials for High-Throughput DFT Calculations. *Comput. Mater. Sci.* **2014**, *81*, 446.