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Article

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Molecular Arrangement and Charge Transfer in C₆₀/Graphene Heterostructures

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Abstract

Charge transfer at the interface between dissimilar materials is at the heart of electronics and photovoltaics. Here we study the molecular orientation, electronic structure, and local charge transfer at the interface region of C₆₀ deposited on graphene, with and without supporting substrates such as hexagonal boron nitride. We employ *ab initio* density functional theory with van der Waals (vdW) interactions, and experimentally characterize interface devices using high-

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3 resolution transmission electron microscopy and electronic transport. Charge transfer between
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5 C₆₀ and the graphene is found to be sensitive to the nature of the underlying supporting substrate
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7 and to the crystallinity and local orientation of the C₆₀. Even at room temperature, C₆₀ molecules
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9 interfaced to graphene are orientationally locked into position. High electron and hole mobilities
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11 are preserved in graphene with crystalline C₆₀ overlayers, which has ramifications for organic
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13 high-mobility field-effect devices.
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18 KEYWORDS: graphene, C₆₀, organic semiconducting molecules, fullerenes, interfacial charge
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20 transfer
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24 C₆₀ and graphene are, in their own right, fascinating low dimensional materials with
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26 spectacular properties. The high electron affinity and unusual phonon modes of C₆₀ have
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28 rendered it an important nanomaterial for electronic applications, and the ultrafast charge transfer
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30 dynamics and an energetically favorable LUMO level for many donor organic semiconductors
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32 have established C₆₀ as an excellent electron acceptor for organic solar cells.^{1,2} When combined
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34 with strong charge transfer from alkali metals, the phonon modes in C₆₀ drive superconductivity
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36 at surprisingly high temperature.³ The related carbon allotrope graphene displays phenomenal
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38 electron and hole mobilities even at room temperature, and the conductance can be readily gated
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40 by an external electric field or altered *via* adsorbed chemical species. It is likely that many
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42 applications of graphene will involve heterostructures. Indeed, the interfacing of graphene to
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44 other low-2D materials *via* van der Waals forces is a rapidly expanding field of research.^{4,6,20}
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49 The interfacing of C₆₀ and graphene is of particular interest. For example, charge transfer
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51 between C₆₀ and graphene affects the graphene electronic transport.²⁷⁻³⁰ Adding gating electric
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53 fields^{7,8} allows further functional possibilities on the control of interface properties such as
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energy barriers, magnetism^{9,10} and electron-hole dynamics.^{11,4} The ability to fine-tune the charge transfer state of C₆₀ interfaced to graphene (*e.g.* with reversible electrostatic gating) is thus central to the development of novel electrochemical and optoelectronic prototypes. Devices based on organic molecule/graphene interfaces, which utilize the tunable Fermi level in graphene, have already shown promise.¹²⁻¹⁴ In particular, the C₆₀/graphene heterostructure is known to form a Schottky junction.¹³

In this report we investigate the C₆₀/graphene interface *via ab initio* density functional theory (DFT) calculations, transmission electron microscopy, and electronic transport experiments, at cryogenic temperature and at room temperature. The graphene is either suspended or supported on different substrates, including hexagonal boron nitride (h-BN). We determine the most favorable molecular orientations of the C₆₀s, the interface band structure, the intrinsic charge transfer (which is highly dependent on C₆₀ deposition process and substrate type), and the graphene electron and hole mobilities. The theoretical and experimental evidence suggests that C₆₀ molecules at the interface remain firmly locked to the graphene lattice even at room temperature, in sharp contrast to the freely rotating behavior of C₆₀s in undoped molecular crystals.

Results and discussion:

We first examine theoretically the most favorable geometrical arrangements of crystalline close-packed C₆₀ on graphene on different substrates at low temperatures, and the associated interfacial band structure and charge transfer. Figs. 1a,b show schematic representations respectively of C₆₀ on suspended graphene, and C₆₀ on graphene supported by h-BN. The C₆₀ film is assumed to be crystalline with a well-ordered periodic lattice and a 4x4 superstructure is defined. In the nomenclature of ref. 13, the C₆₀ lattice is oriented 28° with respect to the

graphene lattice, *i.e.* it is aligned with the armchair direction. Due to the highly spherical shape of the C_{60} molecule several possible molecular arrangements for C_{60} on graphene are possible, with different interaction energies and different local charge transfer.

As in ref. 13, we consider nine representative orientations of C_{60} on graphene (Fig. 1c). We perform first-principles density functional theory calculations including van der Waals (vdW) dispersion forces (the calculation approach differs somewhat from that of ref. 13; see *Methods* for details). If vdW interactions are excluded (using the PBE functional approach, see *Methods*), then the most energetically favorable configuration of C_{60} on graphene is the Hexagon/Hole alignment. However, if vdW interactions are included (using the DRSLL functional approach), then, as presented in Fig. 1d (open bars), the most energetically favorable configuration is the Hexagon/Bridge alignment (right-hand-most open bar), with an interaction energy of about 1.1 eV/ C_{60} . We note that the vdW term is significant, with a jump in interaction energy of roughly 1 eV/ C_{60} , as shown previously.¹³ If an h-BN support is added to the graphene (see Fig. 1b), the interaction energy (including vdW interactions) between graphene and C_{60} is further enhanced by ~ 0.25 - 0.33 eV, as seen by comparing the open and filled bars in Fig. 1d. With an h-BN supporting substrate, the most energetically favorable configuration at low temperatures of C_{60} on graphene remains Hexagon/Bridge (Fig. 1d, right-hand-most filled bar), with an interaction energy of about 1.45 eV/ C_{60} .

Different molecular orientations of C_{60} on graphene give different magnitudes of charge transfer between the C_{60} and graphene. We use first principles DFT simulations to evaluate the magnitude and sign of the charge transfer. Even though DFT is known to underestimate band gaps and frontier orbitals (HOMO, LUMO), we will show below that our calculations reproduce closely the magnitudes and trends observed in the experiments for the large systems used in the

supercell. The system size is too large for higher levels of theory, *e.g.* GW or hybrid functional, to be employed. We consider first the case of C₆₀ on suspended graphene. Fig. 2a shows the calculated charge transfer from C₆₀ to graphene for the different C₆₀ orientations, as a function of n_o , the externally induced graphene charge density (as might result from external electric field gating). With zero external gating ($n_o = 0$), the charge transfer is negative in the range 0.03-0.07 electrons/C₆₀ (this corresponds to a change in charge density in the graphene of 4.3-10.1x10¹²/cm²). For all molecular orientations, with no external gating, C₆₀ on suspended graphene acts as an electron acceptor, as expected. With increasing n_o in the negative direction, the charge transfer between C₆₀ and graphene increases, with the Dimer/Hole orientation giving a slightly bigger effect. With increasing n_o in the positive direction, external gating compensates the intrinsic charge transfer, with a zero crossing at about $n_o = +20 \times 10^{12}/\text{cm}^2$. Beyond this, external gating overcomes the intrinsic charge flow and the C₆₀ is forced to donate electrons to the graphene.

Figs. 2b and 2c show respectively the influence of external gating (again expressed as n_o) on the graphene electronic density of states and Fermi level shift, for the C₆₀/graphene hybrid system assuming a Dimer/Hole configuration. Similar results are obtained for the other orientations. The effect of electrostatic gating on the electronic band structure is displayed in Figs. 2d-f, which clearly show the charge doping effect at the Dirac point and the rigid shift-like effect of the electric gating on C₆₀ and graphene bands. Once the C₆₀/graphene interface is created, at no bias regime $n_o=0$, the HOMO of the C₆₀ layer (faint red in Fig. 2e) is sufficiently lower in energy relative to the Fermi level and charge transfer takes place from graphene to C₆₀. At finite bias (Fig. 2d, 2f), the potential difference between graphene and C₆₀ drives the position of the fullerene states closer (for $n_o < 0$) or away (for $n_o > 0$) from the Fermi level by several tenths

of meV's. This particular arrangement of graphene and C_{60} states drives the system to a band alignment where most of the states are bias-dependent allowing further control on the electronic structure.

Figs. 3a and 3b contrast, for C_{60} /graphene with $n_0=0$, the charge transfer and induced dipole moment $|P(\text{Debye})|$ for the selected C_{60} orientations. The induced dipole moments are all in the range ~ 0.3 - 0.5 Debye, with no obvious correlation to the induced charge densities. For C_{60}/G , the charge transfer increases with increasing magnitude of dipole moment but there is much scatter in the data (see Fig. S5a). There appears to be no correlation between the C_{60} adsorption orientation dependence of the dipole moment, charge transfer and interaction energies. Fig. 3c shows the zero bias charge difference density plot for the Dimer/Hole configuration for the C_{60} /graphene heterostructure.

We now turn to the additional influence of a supporting h-BN substrate on the charge transfer from C_{60} to graphene. Fig. 3d shows the predicted charge transfer from C_{60} to graphene for the different molecular orientations of C_{60} , all for the bias-free condition $n_0 = 0$. In all cases the charge transfer is negative (electrons again flow from graphene to C_{60}), and the Dimer/Hole orientation has the maximum charge transfer. The orientation with the maximum charge transfer (Dimer/Hole) is different from the orientation with the strongest interaction energy (Hexagon/Bridge), which implies that more charge transfer does not necessarily cause stronger molecular interaction. The interaction of C_{60} with the substrate is an interplay between vdW interaction at the C_{60} /graphene interface and charge rearrangement at the graphene/h-BN interface. Hence, it is possible that the vdW interaction is not determined solely by charge transfer. As the spread in interaction energies among the C_{60} molecular orientations is small

(0.020-0.100 eV), it is possible to establish more than one C_{60} molecular orientation. Due to this complication, further study is needed to exactly determine the tradeoff between the driving forces in this system. Remarkably, the addition of the h-BN substrate reduces the maximum (bias-free) charge transfer by roughly one order of magnitude from that of the C_{60} /graphene configuration (Fig. 3a). Fig. 3e shows the corresponding induced dipole moment $|P(\text{Debye})|$. Interestingly, with an h-BN substrate present, the polarizations for the nine molecular arrangements can be separated into two groups, delineated by a threshold polarization $|P(\text{Debye})|_{\text{thresh}} = 0.10$, as indicated by the dotted line in Fig. 3e. Results for the group above threshold are displayed with blue bars and give sizeable charge transfer in the range of $0.01\text{-}0.28 \times 10^{12} \text{ /cm}^2$ ($0.07\text{-}2 \times 10^{-3} \text{ e/C}_{60}$). Results of the group below threshold are displayed in purple and give charge transfers 3 orders of magnitude lower. For C_{60} /G/h-BN, there is no clear correlation between charge transfer and dipole moment (see Fig. S5b). The only notable qualitative trend is that the group of molecular orientations with large dipole moments corresponds to the group with large charge transfer and the same goes for the group of small dipole moments and charge transfer. The greatest charge transfer is obtained from the Dimer/Hole configuration ($1.8 \times 10^{-3} \text{ e/C}_{60}$). The charge transfer varies significantly across the C_{60} configurations due to the importance of the carbon bond between two hexagons of the C_{60} cage, namely 6:6. According to the chemistry of C_{60} ,^{16,17} 6:6 bonds are preferential sites for functionalization for several compounds as the degree of electron delocalization varies (double bond) and higher reactivity is present, mainly due to the increase of π electron density at this bond.

Although h-BN is often considered to be an ideal, inert substrate for graphene,¹⁸ our results clearly show that it has a profound effect on heterostructure charge transfer and polarizability. Fig. 3f presents the charge difference density plot at zero bias for the Dimer/Hole configuration

for C₆₀/graphene/h-BN. The stronger charge transfer for C₆₀ on the suspended graphene with no underlying h-BN (Fig. 3c) is strikingly evident. Prior to forming the interface with C₆₀, the induced dipole moment at the graphene/h-BN heterostructure is $|P(Debye)| \approx 0.33$ (see Figure S4). After forming the interface with C₆₀, charge rearrangement takes place and the value reduces to below $|P(Debye)| \approx 0.10$. The difference in electronic character for the p_z -orbitals between h-BN, polar, and graphene, covalent, is one of the main driving-forces for such modifications of the interfacial polarization dipole. No appreciable modifications (<0.10 Å) of the value of the interlayer distance between graphene and C₆₀ are observed due to this charge rearrangement once monolayer or few-layers h-BN are introduced. This suggests the active electronic role of the h-BN substrate in limiting the amount of carriers that participates in the interfacial charge separation.

We note that the theoretical studies described above are performed in the low temperature ($T=0$) regime. The question arises what influence higher temperature might have on the results. For example, it is well known that in (undoped) crystalline C₆₀, the C₆₀ molecules freely rotate at room temperature.^{1,2} Near 260K the C₆₀s rotate almost freely, and in the range 260K to 90K they execute jumps. Below 90K, the C₆₀s are substantially frozen in place.¹ On the other hand, for alkali-doped C₆₀, the situation is quite different. Here the C₆₀s are locked into specific orientations with respect to the alkali ions, even at room temperature. X-ray diffraction studies on K₃C₆₀ clearly find the absence of C₆₀ free rotations.³ For K₃C₆₀ and Rb₃C₆₀, the C₆₀s orient themselves so that the electron-rich C=C bonds face the K⁺ and Rb⁺ ions for charge transfer. Combined with effects of molecular repulsion, C₆₀ molecules are fixed to one of the two energetically stable orientations and switch between the two with thermal energy.^{1,2} For ions with smaller ionic radii, such as Li⁺ and Na⁺, the ion-C₆₀ repulsion is much weaker, but the C₆₀s

are still locked to a few energetically stable orientations and jump between them with thermal energy.^{1,2,5}

We have examined theoretically the situation for C₆₀ on graphene where the pure C₆₀ becomes “doped” (*i.e.* charged) by virtue of interaction with the (possibly gated) graphene. In this case the C₆₀s that reside at the interface with graphene are substantially locked into position even at room temperature as demonstrated using *ab initio* molecular dynamics simulations at 300K (see SI and movies for details). Hence, the charge transfer and band structure calculations presented above are relevant also for finite temperature. Theoretical simulations predict no temperature dependence of charge transfer up to 300K.

We now turn to experiment. We explore the following heterostructure: multilayer crystalline C₆₀ on monolayer graphene on multilayer h-BN. Fig. 4c shows schematically a cross-section of our typical device-like structure, here assuming crystalline C₆₀ and an h-BN support. Fig. 4d shows an optical image of a functioning device.

We have found that the crystallinity of the C₆₀, and the associated device electronic characteristics, are highly sensitive to C₆₀ deposition conditions. If the C₆₀ is evaporation-deposited under only modest (1×10^{-4} torr) “uncontrolled” vacuum conditions, an amorphous C₆₀ film typically results (see Fig. S1). On the other hand, if the C₆₀ deposition is performed under more controlled UHV conditions, highly crystalline C₆₀ films are readily obtained. Figs. 4a,b exemplify the high degree of C₆₀ crystallinity of our UHV-prepared samples. For these TEM-compatible samples, 15nm of C₆₀ is deposited on suspended graphene at 1.4×10^{-10} torr. Excellent crystallinity is observed with a grain size ranging from ≈ 100 nm to 200nm, where the projected lattice images of the stacked layers of C₆₀ indicate a triangular pattern for the organization of the molecules (inset in Fig. 4a). The crystalline structure is confirmed with electron diffraction as

shown in Fig. 4b. The outermost spots (blue circles) correspond to the Bragg reflections for the lattice plane (0-110) of graphene (with 2.1 Å-spacing).¹⁵ The inner spots (red circles) correspond to Bragg reflections for the lattice plane (111) of C₆₀ (with 8.73 Å-spacing), which correspond to a close packed plane with a 2D triangular lattice. This result is consistent with previous results for C₆₀ thin films¹³. Substrate heating is crucial for achieving highly crystalline C₆₀ films¹³ (see Methods).

A controlled deposition of the crystalline C₆₀ thin film is essential for quantifying the charge transfer between graphene and C₆₀ (see Fig. S1). Figs. 5a,b show R vs V_g data for high quality crystalline C₆₀/graphene/h-BN heterostructures constructed under UHV conditions (1.4x10⁻¹⁰ torr), with a C₆₀ thickness of order 50nm. C₆₀ here behaves as an electron acceptor. The room temperature data of Fig. 5a indicate a charge transfer from graphene to C₆₀ of 0.2x10¹²/cm², or Δρ=0.14x10⁻² e/C₆₀ transferred from graphene to C₆₀. Fig. 5b shows similar data for the same device, but for T=4.2K. The charge transfer is again 0.2x10¹²/cm² or Δρ=0.14x10⁻² e/C₆₀, in agreement with Δρ theoretically calculated for the dimer/hole C₆₀ orientation for a C₆₀/graphene/h-BN heterostructure (see Fig. 3d). As predicted by molecular dynamics simulations, the absence of temperature dependence results in experimental observation of very close charge transfer values at 4.2K and 300K.

The carrier mobility is derived from the resistance plots of Figs. 5a,b. Knowing the aspect ratio of the sample, the measured resistivity is converted to conductivity and using the Drude model ($\sigma = ne\mu$), the mobility of the sample is deduced.³¹ Simple inspection of the slope of the resistance near the charge neutrality point (Figs. 5a,b) indicates that the high electron and hole mobilities of graphene in the graphene/h-BN devices are largely preserved after C₆₀ deposition. Table 1 shows that both electron and hole mobilities remain within a factor of two after C₆₀

deposition. The room temperature ($T=300\text{K}$) data suggest that both the electron and hole mobilities are slightly depressed upon C_{60} deposition, while the 4.2K data suggest a depression in the hole mobility, and an increase in the electron mobility, upon C_{60} deposition. The increase in electron mobility upon C_{60} deposition is surprising, and points to a possible modest annealing effect on the graphene during the (elevated temperature) C_{60} deposition.

Conclusion:

In summary, C_{60} /graphene constitutes a van-der-Waals heterostructure with exciting possibilities for electronic devices and charge transfer applications. We have shown through first-principles calculations that charge transfer between C_{60} and graphene depends on C_{60} orientation, and, critically, on the presence or absence of an underlying h-BN substrate. The C_{60} orientation with the strongest interaction energy is Hexagonal/Bridge, but the orientation with the greatest charge transfer and dipole moment is Dimer/Hole. C_{60} s at the graphene interface are orientationally locked into position and do not rotate, even at room temperature. External gating can change the C_{60} from an electron acceptor to an electron donor. Crystalline C_{60} /graphene/h-BN devices maintain the high mobility intrinsic to suspended graphene, and have a charge transfer consistent with the Dimer/Hole C_{60} configuration. Our findings suggest that the combination of *ab initio* density functional theory calculations and electronic transport experiments can be effective in the search for other substrates that enhance the range of tunable charge transfer at the C_{60} /graphene interface.

Methods:

Fabrication of the hBN-graphene-C₆₀ heterostructure and electronic transport measurements

Graphene was mechanically exfoliated from natural graphite on methyl methacrylate (MMA) polymer. Single graphene flakes were selected and transferred on hexagonal boron nitride (h-BN), which was previously deposited by mechanical exfoliation on a Si/SiO₂ wafer. Transfer was done following the procedure described in.²⁰ Metallic electrodes were deposited using a silicon shadow mask,²¹ avoiding the use of e-beam resist and further contamination of the surface. After the deposition of the electrodes, the sample was annealed in a H₂/Ar atmosphere at 350 °C for three hours in order to clean the surface from any organic contamination. Finally, C₆₀ was deposited in ultrahigh vacuum ($P=1.4 \times 10^{-10}$ torr) using a low temperature effusion cell. The sample was slowly heated up from room temperature to 156 °C at a rate of 0.5 K/min. This slow rate protects the integrity of the electrical contact to graphene. Deposition of C₆₀ was done at 0.1 Å/s heating the effusion cell at 332 °C and holding the sample temperature at 156 °C during deposition. Measurements were performed in a vacuum probe station before and after the deposition of C₆₀, at $P=1 \times 10^{-8}$ Torr at 300K and at a lower vacuum at 4.2K. Two terminal differential resistance measurements were done with a lock-in amplifier applying a small AC current of 10nA. The carrier density was controlled by applying a DC voltage to the doped silicon.

vdW *ab initio* calculations

Calculations were based on *ab initio* density functional theory using the SIESTA method²² and the VASP code.^{23,24} Results presented in the manuscript were produced using the VASP code, while SIESTA was used to perform initial tests at large number of atoms in the unit cell. The

generalized gradient approximation²⁵ along with the DRSLL²⁶ functional, which includes vdW dispersion forces, were used in both methods, together with a double-polarized basis set in Siesta, and a well-converged plane-wave cutoff of 500 eV in VASP. We used a Fermi-Dirac distribution with an electronic temperature of $k_B T = 20$ meV. Additional details are provided in the Supplementary Material.

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Supplementary Material

The supplementary material is available free of charge online *via* the internet at <http://pubs.acs.org>.

References

- (1) Prassides, K.; Margadonna, S. In *Fullerenes: Chemistry, Physics and Technology*; Kadish, K. M.; Ruoff, R. S., Eds; John Wiley & Sons Inc., 2000; pp. 249-251, 555–610.
- (2) Dresselhaus M. S.; Dresselhaus, G.; Eklund, P. C. In *Science of Fullerenes and Carbon Nanotubes*; Academic Press Inc, 1996; pp 184-197, 243-246
- (3) Stephens, P. W.; Mihaly, L.; Lee, P. L.; Whetten, R. L.; Huang, S.-M.; Kaner, R.; Deiderich, F.; Holczer, K. Structure of Single-Phase Superconducting K₃C₆₀. *Nature* **1991**, 351, 632-634.

- (4) Hebard, A. F.; Rosseinsky, M. J.; Haddon, R. C.; Murphy, D. W.; Glarum, S. H.; Palstra, T. T. M.; Ramirez, A. P.; Kortan, A. R. Superconductivity at 18 K In Potassium-Doped C_{60} . *Nature* **1991**, 350, 600-601.
- (5) Yildirim, T.; Fischer, J. E.; Harris, A. B.; Stephens, P. W.; Liu, D.; Brard, L.; Strongin, R. M.; Smith, A. B. Orientational Phase Transition in Na_xC_{60} ($1 < x < 3$). *Phys. Rev. Lett.* **1993**, 71, 1383-1386.
- (6) Geim, A. K.; Grigorieva, I. V. Van der Waals Heterostructures. *Nature* **2013**, 499, 419-425.
- (7) Geim, A. K. Graphene: Status and Prospects. *Science* **2009**, 324, 1530-1534.
- (8) Geim, A. K.; Novoselov, K. S. The Rise of Graphene. *Nat. Mater.* **2007**, 6, 183-191.
- (9) Santos, E. J. G. Carrier-Mediated Magnetoelectric Coupling in Functionalized Graphene. *ACS Nano* **2013**, 7, 9927-9932.
- (10) Santos, E. J. G. Magnetoelectric Effect in Functionalized Few-Layer Graphene. *Phys. Rev. B* **2013**, 87, 15540-15547.
- (11) Li, Z. Q.; Henriksen, E. A.; Jiang, Z.; Hao, Z.; Martin, M. C.; Kim, P.; Stormer, H. L.; Basov, D. N. Dirac Charge Dynamics in Graphene by Infrared Spectroscopy. *Nat. Phys.* **2008**, 4, 532-535.
- (12) Ojeda-Aristizabal, C; Bao, W.; Fuhrer, M. S. Thin-Film Barristor: A Gate-Tunable Vertical Graphene-Pentacene Device. *Phys. Rev. B* **2013**, 88, 035435.
- (13) Kim, K.; Lee, T. H.; Santos, E. J. G.; Jo, P. S.; Salleo, A.; Nishi, Y.; Bao, Z. Structural and Electrical Investigation of C_{60} -Graphene Vertical Heterostructures. *ACS Nano* **2015**, 9, 5922-5928.
- (14) Lee, C. H.; Schiros, T; Santos, E. J. G.; Kim, B.; Yager, K. G.; Kang, S. J.; Lee, S.; Yu, J.; Watanabe, K.; Taniguchi, T.; Hone, J.; Kaxiras, E.; Nuckolls, C.; Kim, P. Epitaxial Growth of Molecular Crystals on Van der Waals Substrates for High-Performance Organic Electronics. *Adv. Mater.* **2014**, 26, 2812-2817.
- (15) Meyer, J. C.; Geim, A. K.; Katsnelson, M. I.; Novoselov, K. S.; Booth, T. J.; Roth, S. The Structure of Suspended Graphene Sheets. *Nature* **2007**, 446, 60-63.
- (16) Prato, M.; Lucchini, V.; Maggini, M.; Stimpfl, E.; Scorrano, G.; Eiermann, M.; Suzuki, T.; Wudl, F. Energetic Preference in 5,6 and 6,6 Ring Junction Adducts of C_{60} : Fullerooids and Methanofullerenes. *J. Am. Chem. Soc.* **1993**, 115, 8479-8480.
- (17) Fagan, P.; Calabrese, J. C.; Malone, B. Metal Complexes of Buckminsterfullerene (C_{60}). *Acc. Chem. Res.* **1992**, 23, 134-142.

- (18) Dean, C. R.; Young, A. F.; Meric, I.; Lee, C.; Wang, L.; Sorgenfrei, S.; Watanabe, K.; Taniguchi, T.; Kim, P.; Shepard, K. L.; Hone, J. Boron Nitride Substrates for High-Quality Graphene Electronics. *Nat. Nanotechnol.* **2010**, 5, 722-726.
- (19) Withers, F.; Del Pozo-Zamudio, O.; Mishchenko, A.; Rooney, A. P.; Gholinia, A.; Watanabe, K.; Taniguchi, T.; Haigh, S. J.; Geim, A. K.; Tartakovskii, A. I.; Novoselov, K. S. Light-Emitting Diodes by Band-Structure Engineering in Van der Waals Heterostructures. *Nat. Mater.* **2015**, 14, 301-306.
- (20) Zomer, P. J.; Dash, S. P.; Tombros, N.; van Wees, B. J. A Transfer Technique for High Mobility Graphene Devices on Commercially Available Hexagonal Boron Nitride. *Appl. Phys. Lett.* **2011**, 99, 232104-232109.
- (21) Bao, W.; Liu, G.; Zhao, Z.; Zhang, H.; Yan, D.; Deshpande, A.; LeRoy, B.; Lau, C. N. Lithography-Free Fabrication of High Quality Substrate-Supported and Freestanding Graphene Devices. *Nano Res.* **2010**, 3, 98-102.
- (22) Soler, Jose M.; Artacho, E.; D Gale, J.; Garcia, A.; Junquera, J.; Orderjon, P.; Sanchez-Portal, D. The SIESTA Method for ab *Initio* Order-N Materials Simulation. *J. Phys.: Condens. Matter* **2002** 14, 2745-2779.
- (23) Kresse, G.; Hafner, J. Ab *Initio* Molecular Dynamics for Open-Shell Transition Metals. *Phys. Rev. B* **1993** 48, 13115-13118.
- (24) Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab *Initio* Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B* **1996** 54, 11169-11186.
- (25) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, 77, 3865-3868.
- (26) Dion, M.; Rydberg, H.; Schroder, E.; Langreth, D. C.; Lundqvist, B. I. Van der Waals Density Functional for General Geometries. *Phys. Rev. Lett.* **2004**, 92, 246401-246405.
- (27) Bautista-Flores C., Sato-Berrú R. Y.; Mendoza D. Charge Transfer in the Fullerene C₆₀-Few Layer Graphene System and the Existence of Negative Photoconductivity. *Appl. Phys. Lett.* **2014**, 105, 191116.
- (28) Jnawali, G.; Rao, Y.; Beck, J. H.; Petrone, N.; Kyminis, I.; Hone, J.; Heinz, T. F. Observation of Ground- and Excited-State Charge Transfer at the C₆₀/Graphene Interface. *ACS Nano* **2015**, 9, 7175-7185.

- (29) Wang, R.; Wang, S.; Wang, X.; Meyer, J. A. S.; Hedegard, P.; Laursen, B. W.; Cheng, Z.; Qiu, X. Charge Transfer and Current Fluctuations in Single Layer Graphene Transistors Modified by Self-Assembled C₆₀ Adlayers. *Small* **2013**, 9, 2420.
- (30) Chaturbedy, P.; Ramakrishna Matte, H.S.S.; Voggu, R.; Govindaraj, A.; Rao, C.N.R. Self-Assembly of C₆₀, SWNTs and Few-Layer Graphene and Their Binary Composites at the Organic-Aqueous Interface. *J. Colloid Interface Sci.* **2011**, 360, 249-255.
- (31) Novoselov, K.S.; Geim, A.K.; Morozov, N.; Jiang, D.; Zhang Y.; Dubonos S. V.; Grigorieva, I.V.; Firsov, A. A. Electric Field Effect in Atomically Thin Carbon Films. *Science* **2004**, 306, 666-669.

Table 1

	Before C ₆₀ deposition			After C ₆₀ deposition		
T(K)	μ_h (cm ² /Vs)	μ_e (cm ² /Vs)	Peak position (cm ⁻²)	μ_h (cm ² /Vs)	μ_e (cm ² /Vs)	Peak position (cm ⁻²)
4.2	12,300	5,100	-0.086±0.002	6,150*	10,200*	0.095±0.002
300	4,700	5,830	-0.095±0.003	2,530	4,600	0.121±0.003

Table 1. Parameters from electronic transport measurements, for a C₆₀/G/h-BN device.

Figures

Figure 1. Schematic representation of (a) C_{60} molecules on graphene (C_{60}/G), and (b) C_{60} molecules on graphene supported by h-BN ($C_{60}/G/h\text{-BN}$). The relative separation between C_{60} , graphene, and h-BN has been initially converged. (c) Optimized molecular configurations between C_{60} and graphene resulting from a computational screening at different starting geometries. For clarity, C_{60} molecules (violet atoms) are only shown near the graphene surface (faint pink) with the rest of the other atoms hidden. (d) Interaction energies per C_{60} molecule calculated with vdW interactions included, for the different configurations shown in (c). The interaction energy is defined in terms of the adsorption energies, between C_{60} and G, or G/h-BN heterostructure: $E_i = E[C_{60}] + E[A] - E[C_{60}/A]$, where $A = G, G/h\text{-BN}$. The open bars are for C_{60}/G , while the solid blue bars are for $C_{60}/G/h\text{-BN}$.

Figure 2. First-principles density functional theory calculations for C₆₀/graphene (C₆₀/G)

interfaces. (a) Calculated charge transfer (in electrons per C₆₀ interfacial molecule) to graphene as a function of the external electric field (E_{ext}) induced-carrier density in graphene (n_0). Both scales are represented along the x-axis. All nine C₆₀/graphene geometries presented in Fig. 1(c) are represented, with several data curves superposed on top of each other at the present density scale. The black curve shows the average of all configurations. The green curve (Dimer/Hole) has a slightly larger charge transfer at large values of n_0 . A cut through the data set at $n_0=0$, with

the different configurations identified, is presented in Fig. 3a. Positive $\Delta\rho$ means that electrons are transferred from C_{60} to graphene, which can occur with sufficient gate bias (*i.e.* high enough positive n_0). (b) Variation of the density of states at the Fermi level as a function of n_0 for the Dimer-Hole configuration of C_{60}/G . Similar results are also observed for the other interface geometries (not shown). (c) Variation of the Fermi level of the combined C_{60}/G system as a function of n_0 . Notice that the position of the Fermi level is relative to that at zero bias where a finite charge transfer is already observed. Positive (negative) bias shifts upward (downward) in energy the Fermi level (insets). (d)-(f) Electronic band structures of the C_{60}/G heterostructure with a Dimer/Hole configuration at different gate bias. Graphene states are highlighted in blue and C_{60} bands in faint red. Fermi level is shown by the dashed-line in each panel.

Figure 3. vdW-DFT calculations for total interfacial charge transfer, induced dipole moment, and charge difference density for the C₆₀/G and C₆₀/G/h-BN systems, all for n₀=0. (a) Charge transfer and (b) induced dipole moment for C₆₀/G. The dipole moment vector points from C₆₀ to graphene. (c) Charge difference density for C₆₀/G assuming a Dimer/Hole orientation. (d) Charge transfer and (e) induced dipole moment for C₆₀/G/h-BN. In (d), data for the hatched purple open bars have been amplified by 10² for readability. The dashed horizontal red line in (e) delineates an induced dipole threshold of 0.1 Debye. Dipole data above this are plotted in

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3 solid blue, while data below this are plotted in hatched purple (see text). (f) Charge difference
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5 density for C₆₀/G/h-BN assuming a Dimer/Hole orientation. For (c) and (f), blue and red
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7 isosurfaces represent positive and negative charges, respectively.
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Figure 4. (a) TEM image of a ~15nm thick C₆₀ film deposited on suspended graphene under UHV conditions. High crystallinity is clearly observed (scale bar 10nm). The inset is a blow-up of the region outlined by the yellow box, and highlights the close-packed structure of the C₆₀s (bright dots correspond to the projected lattice images of the C₆₀ molecular columns). (b) Electron diffraction for C₆₀ deposited on suspended graphene under UHV conditions. Graphene (blue circles) and C₆₀ (red circles) diffraction spots are identified (scale bar 2nm⁻¹) (c) Schematic representation of C₆₀/G/h-BN device used for transport measurements. The device can be electrically probed prior to, and after, C₆₀ deposition. (d) Optical image of a G/h-BN

heterostructure contacted with Cr/Au electrodes prior to C₆₀ deposition. The dotted lines indicate the border of the graphene (blue) and h-BN (pink) flakes (scale bar 20 μm).

Figure 5. Gate voltage dependence of the resistance of graphene/h-BN devices before (dotted line, blue) and after (solid line, red) deposition of $\approx 15\text{nm}$ high crystallinity C_{60} . Deposition conditions are identical to samples in Figure 4. Samples are measured at (a) 300K and (b) 4.2K. Shift of peak to the right indicates hole doping of the graphene by the C_{60} . Mobilities extracted from gate voltage dependence and presented in Table 1.

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