

Supporting Information

Gate-Tunable Dirac Point of Molecular Doped Graphene

Pablo Solís-Fernández,[†] Susumu Okada,[§] Tohru Sato,^{||} Masaharu Tsuji,[†] Hiroki Ago^{†,‡,}*

[†]Institute for Materials Chemistry and Engineering, Kyushu University, Fukuoka 816-8580,
Japan

[§]Graduate School of Pure and Applied Sciences, University of Tsukuba, Ibaraki 305-8571,
Japan

^{||}Department of Molecular Engineering, School of Engineering, Kyoto University, Kyoto
615-8510, Japan

[‡]PRESTO, Japan Science and Technology Agency (JST), Saitama 332-0012, Japan

Cascade measurements.

To better understand the effects of piperidine on the FET characteristics, the FET devices were subjected to successive sweeps of the gate voltage, which for brevity will be referred to as cascades. The dependence of the drain-source current to the applied gate voltage (transfer characteristics) of the FET are measured in a conventional way. This measurement consists of two consecutive sweeps of the gate voltage from a maximum value (V_G^+) to a minimum gate value (V_G^-), and then in the reverse direction. These are referred as backward and forward sweepings, respectively. To obtain a cascade, the transfer characteristics are measured repeatedly, but on each iteration V_G^- is gradually decreased (V_G^+ is kept fixed). The cascade will consist on the group of either forward or backward curves of each iteration, which allows to observe the evolution of transfer characteristics (and specially the position of the *CNP*) with the minimum gate voltage applied.

Stability of the doping effects of piperidine.

The stability of the doping effects in ambient and humid conditions was tested. When the sample is brought to air, the n-doping largely decreases, as the *CNP* appeared ~ 40 V closer to 0 V (blue curve of Fig. S8a). The decrease of the n-doping in air is probably induced by the interaction of the piperidine with water molecules present in air, decreasing the effectivity of piperidine to dope the graphene. However, if the sample is brought back to vacuum after 24 h in air the *CNP* slowly shifts back again, although it does not completely recover to the previous position even after extended periods in vacuum (red curve of Fig.

S8a). Similar results have been observed in the case of molecular doping with other amine-containing molecules, showing that the doping level decreases after a few days of exposition to air.¹ We should note that even though the n-doping have slightly diminished after exposing the FET to air, the effectivity of the gate voltage for shifting the *CNP* remains practically uncompromised. This can be seen in Fig. S8b, where the slopes of the *CNP* versus the applied V_G^- retain similar values for large V_G^- .

For further understanding of the doping stability, the functionalized graphene was exposed to more severe conditions by immersion in H₂O and IPA baths for different periods of time. Fig. S8c shows the resistance plots of a FET in vacuum, after being immersed 10 minutes (blue curve) and 5 hours (red curve). As the bath time increases, the *CNP* shifted closer to 0 V, while SEM images show that the large aggregations of piperidine disappeared from the graphene (Fig. S9). In fact, the *CNP* of unstressed devices lies closer to zero than before the exposition to the piperidine, reaching even positive values after the long washing (points for the smallest V_G^- over -90 V in Fig. S8d, and blue curve of Fig. S9). Accordingly, Raman spectra show that the values for the *FWHM*(*G*) and the *2D/G* after washing are larger than before the exposition to piperidine (Fig. 2b,c of the main text). The positions of the *G* and *2D* bands are also closer to those commonly found in the literature for pristine graphene on SiO₂ (1580 and 2670 cm⁻¹ respectively).² This seems to indicate that graphene is closer to a neutral doping state after washing than it was before the functionalization, for which some unintentional p-dope existed (Fig. 1b of the main text). However, even at these lower coverages of piperidine, the effect of the gate voltage in the shift of the *CNP* is still evident (Figs. S8d and S9d,e), although it have decreased from

~ 100 V before washing to ~ 30 V (Fig. 3c of the main text). It should be noted that after washing only one maximum appears in the resistance plot, as opposed to the two maxima observed during the first functionalization stages (Fig. 1c,d of the main text). This indicates a homogeneous coverage of piperidine after washing, as most probably the piperidine not directly contacting the graphene results easier to remove by washing than that in contact with graphene. Interestingly, both homogeneous and inhomogeneous coverages at low piperidine concentrations can be attained.

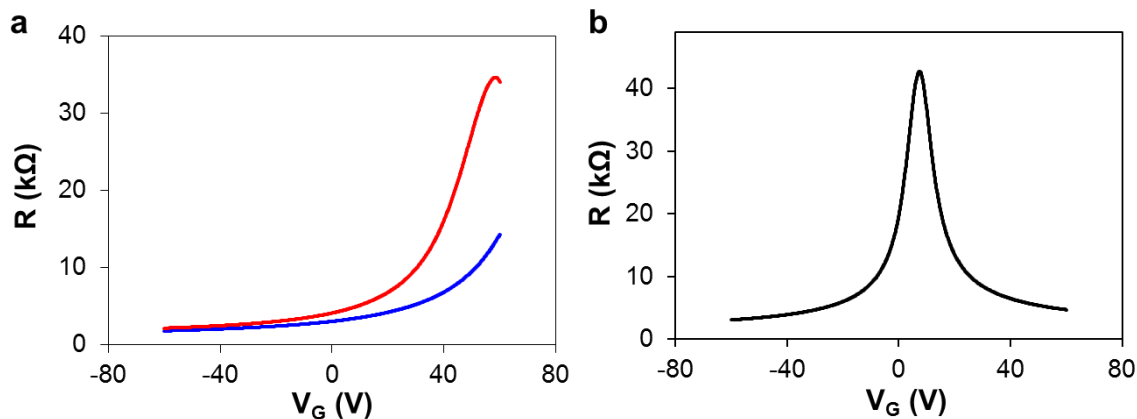


Figure S1. Resistance dependence on gate voltage of pristine graphene. (a) An as-prepared graphene FET (blue curve), with the *CNP* located far beyond 60 V. After annealing in vacuum at 523 K for 2h (red curve), the *CNP* appears below 60 V. More prolonged annealing times can recover even more the position of the *CNP*. However, as Raman measurements were conducted at ambient pressure, the annealing of the FETs was only conducted until the *CNP* was visible within the gate voltage range, to allow for a better comparison between the different characterization techniques. (b) Device from a different sample showing almost no initial doping. We note that the fundamental results and main conclusions of this work do not essentially depend on the unintentional doping state of the graphene.

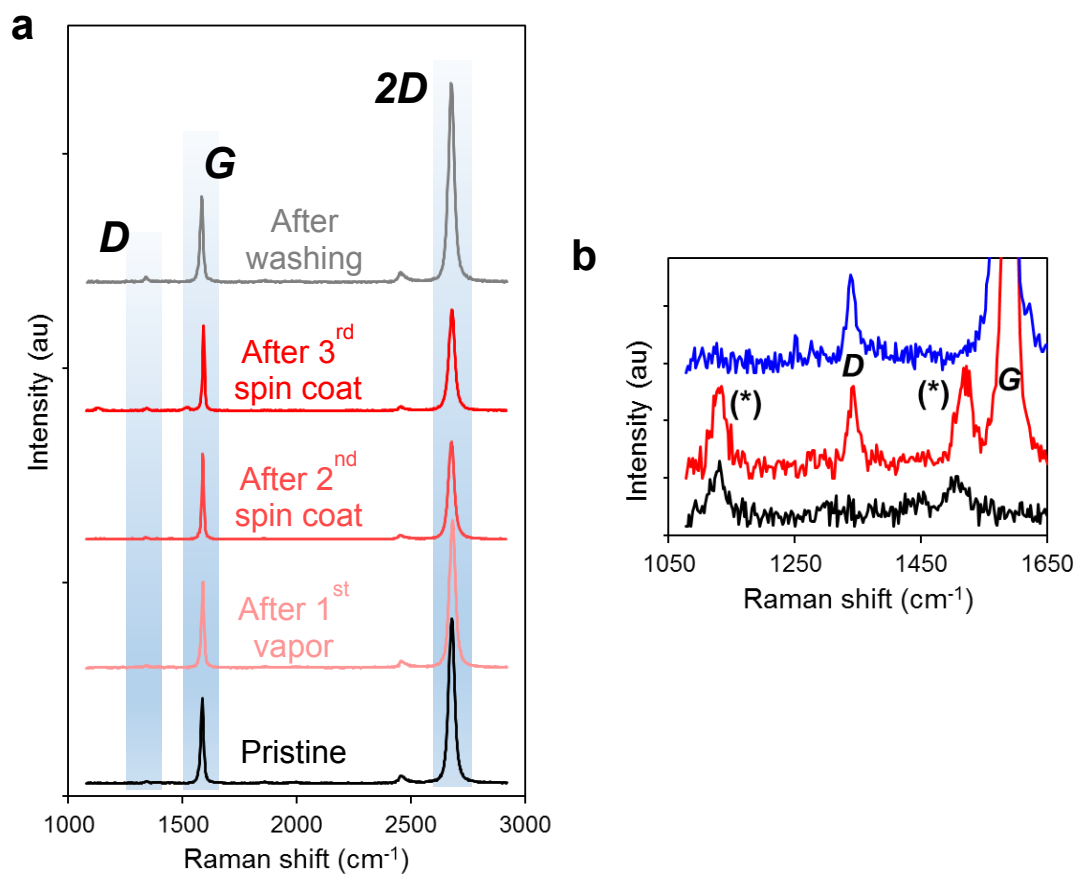


Figure S2. (a) General Raman spectra of graphene after different stages of exposure to piperidine, with the position of the *D*, *G* and *2D* bands indicated. (b) Enlarged region of the general spectra after the 3rd spin coat (50%), showing the apparition of piperidine-related bands marked with (*) ($\sim 1130\text{ cm}^{-1}$ and $\sim 1520\text{ cm}^{-1}$). Red spectrum is collected at the graphene, and black spectrum over the bare SiO_2 . Blue spectrum corresponds to graphene after washing in $\text{H}_2\text{O}/\text{IPA}$.

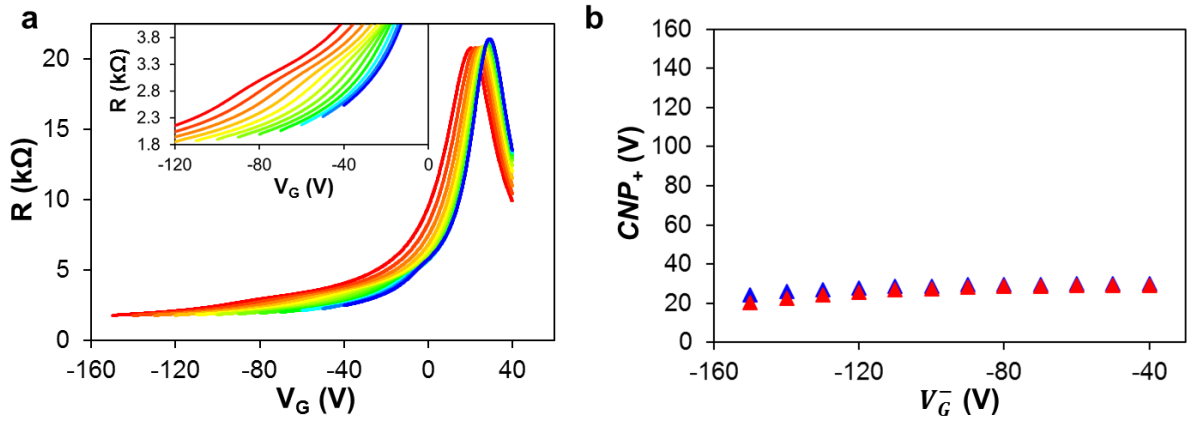


Figure S3. Cascade measurements in a FET with low piperidine coverage. (a) Forward sweepings of the cascades, with the minimum applied gate (V_G^-) stepping from the initial -40 V (blue curves) to -150 V (red curves). Inset in (a) shows an enlargement of the incipient CNP_- and its dependence with V_G^- . (b) Corresponding position of the CNP for each V_G^- , with blue and red markers corresponding to the backward and forward sweepings, respectively. The total shift of the CNP is ~ 9 V, slightly larger than that of pristine graphene (< 3 V).

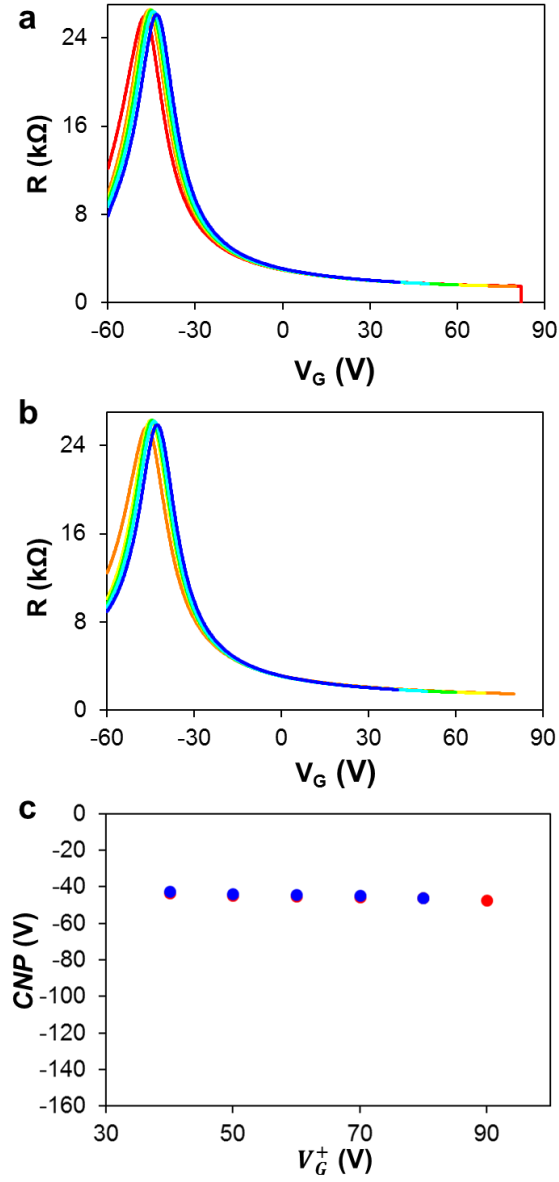


Figure S4. Cascade collected in a graphene FET exposed to piperidine. In this occasion V_G^- was kept constant, while V_G^+ increased from 40 V (blue curves) to 90 V (red curves). The sweeping order was also reverted, collecting first the forward sweepings (a) and immediately after the backward sweepings (b). The FET broke at ~ 82 V (red curve in forward sweepings). (c) Variation of the CNP with V_G^+ .

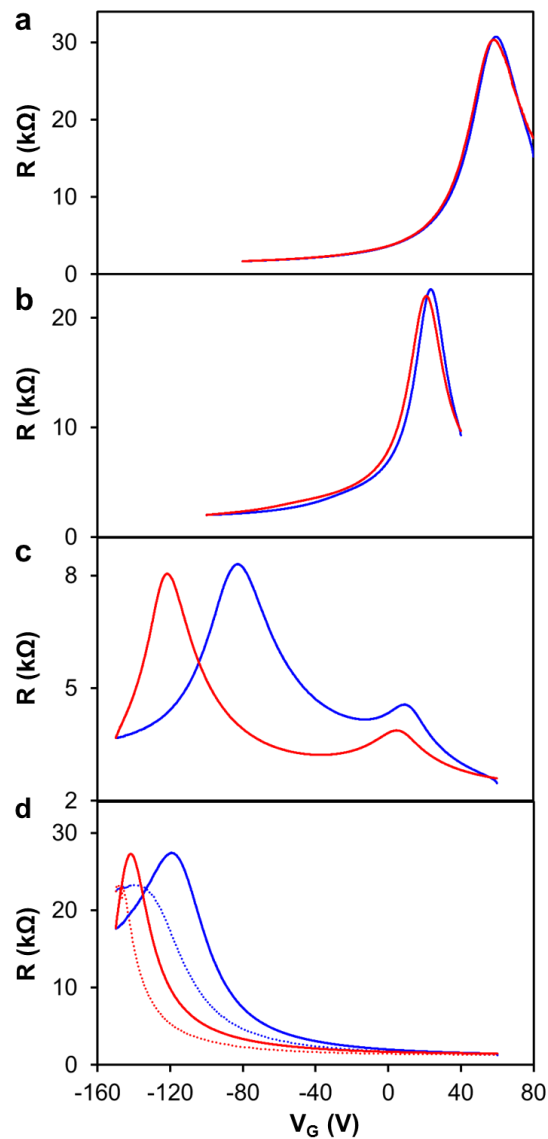


Figure S5. Resistance dependence on the gate voltage of the same graphene-FET as in Fig. 1 of the main text, after being stressed by applying a larger negative voltage (V_G^-). Hysteresis in this case is higher than that of the unstressed measurements. Curves correspond to pristine graphene (a), and with increasing concentrations of piperidine from low (b) to large (d). Shown in (d) are the curves before (dotted lines) and after annealing in vacuum (393K / 2h) (full lines). Blue and red curves correspond to the backward and forward sweeping, respectively.

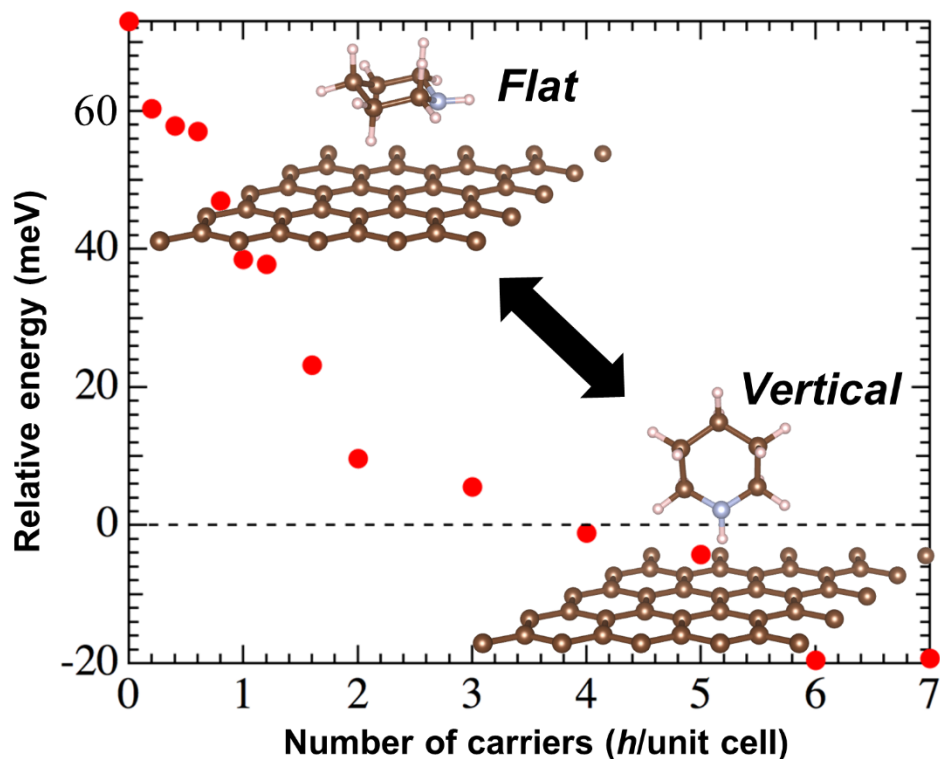


Figure S6. First-principles DFT calculation of the difference in the adsorption energy of piperidine on graphene for two representative configurations as a function of the hole carrier density induced on the system by a vertical electric field. The studied unit cell contains 32 atoms of C and one piperidine molecule. The vertical axis represents the difference in energies $E_{Vert} - E_{Flat}$. E_{Vert} denotes the energy of the system when the piperidine is oriented vertically to the graphene plane and with the amine group pointing towards it, while E_{Flat} is the energy when the piperidine molecule lies parallel to the graphene plane. While in the absence of an electric field the *Flat* configuration is the most stable, but the situation reverts when an electric field is applied.

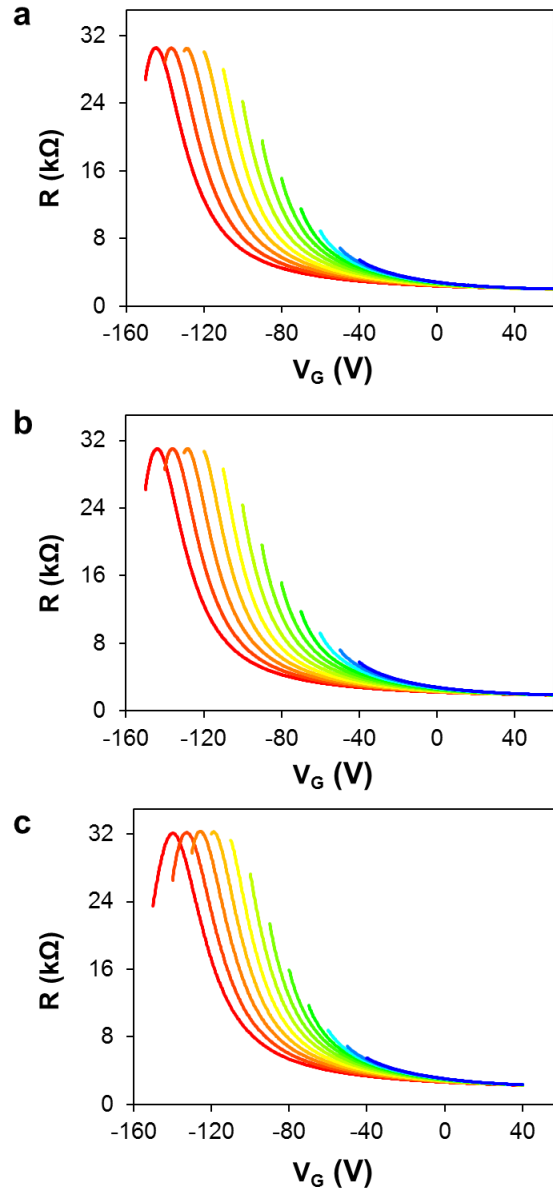


Figure S7. Cascade collected in a same graphene FET at different sweep speeds: (a) low (~ 8.4 V/s), (b) normal (~ 20 V/s) and (c) high (~ 45 V/s). The sweep speed does not have a large impact on the tuning of the doping level of graphene, with differences of the *CNP* position being below 5 V.

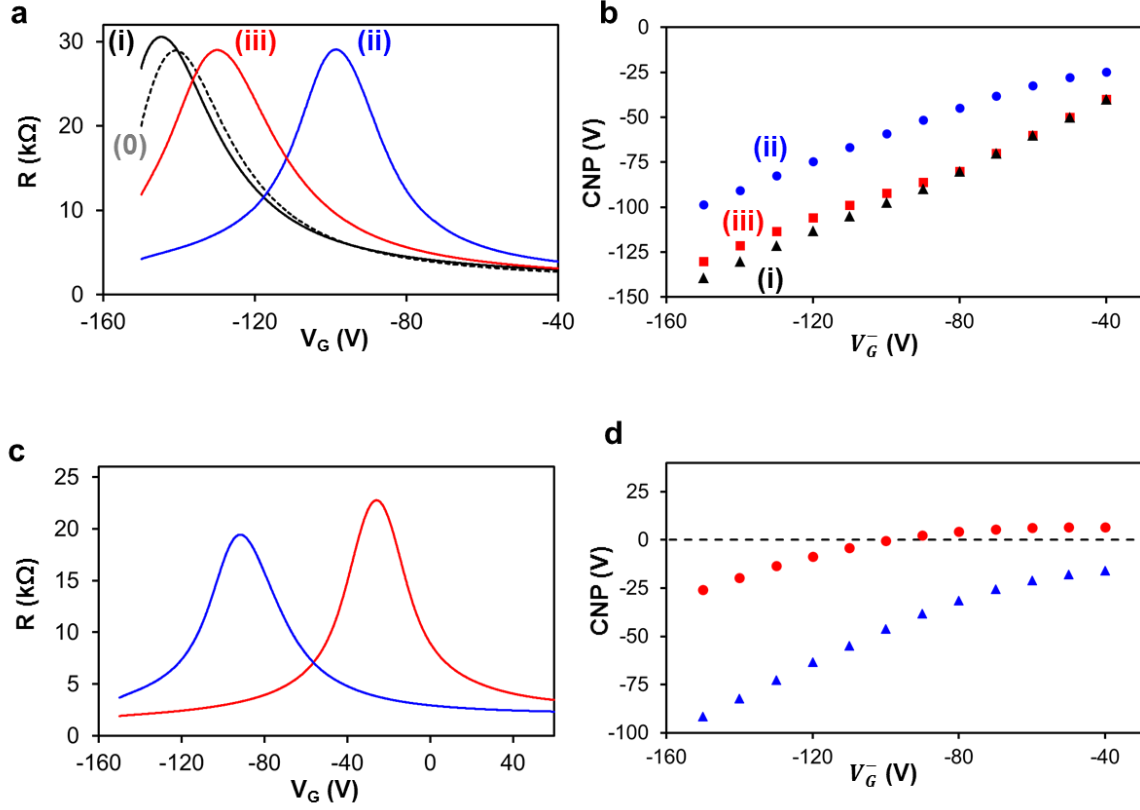


Figure S8. (a) Resistance curve (forward sweeps) of a FET stressed to $V_G = -150$ V in vacuum (0), after 2 weeks in vacuum (i), in air (ii), and back to vacuum (iii). (b) Evolution of CNP_- versus V_G^- for each case shown in (a). (c) Resistance curves (forward) of a FET stressed to $V_G = -150$ V, after being washed 5 minutes in H_2O and IPA (blue curve) and after being washed for several hours (red curve). Measurements were done in vacuum. (d) Dependence of the CNP position with V_G^- for the forward sweepings after being washed for 5 minutes (blue triangles) and after several hours of washing (red circles).

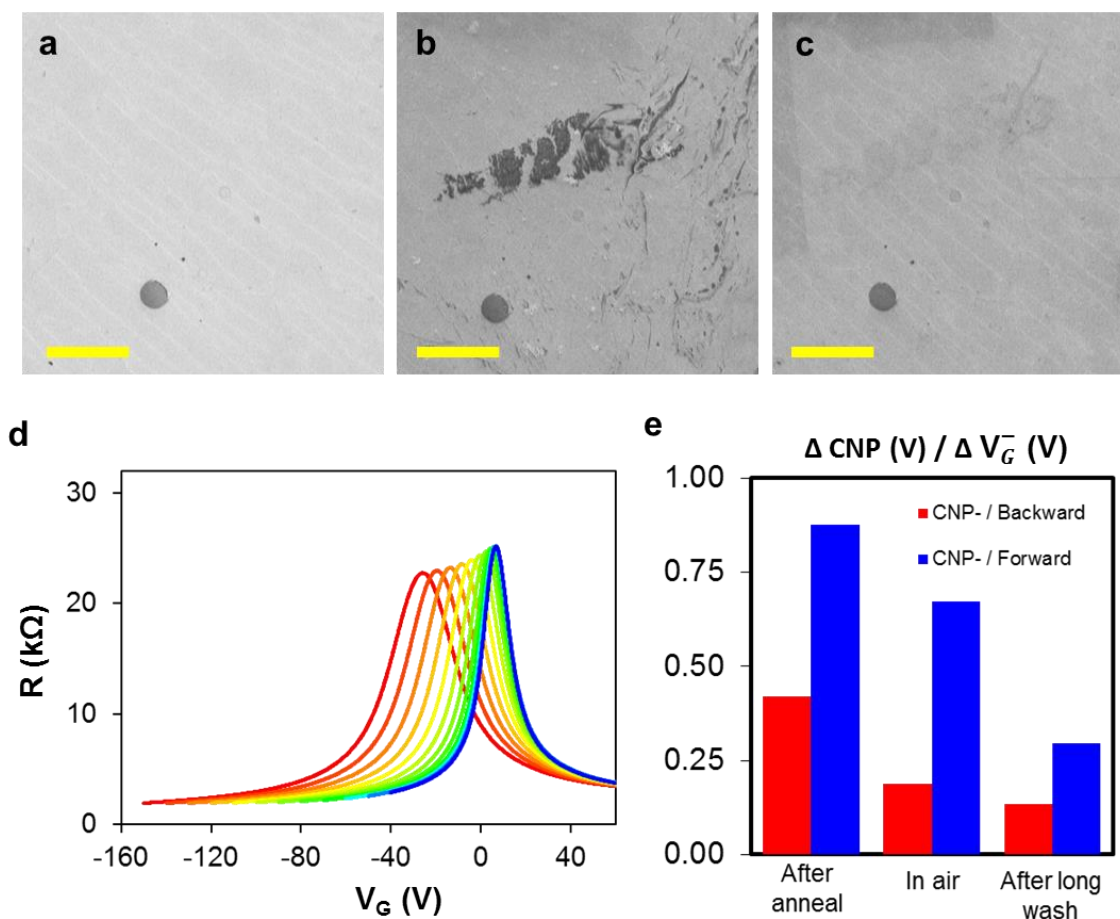


Figure S9. (a) SEM images of the same area of graphene (a) before, (b) after the 3rd spin coat with piperidine, and (c) after washing by immersion for 5 minutes in H₂O and IPA, successively. Scale bars represent 50 μm . Images in (a) and (b) are enlarged versions of those of Fig. 1b and 1e of the main text, respectively. (d) Forward cascade of a FET that has been washed in H₂O/IPA for several hours. (e) Ratio of the *CNP* shifts and the variations of V_G^- causing them for both sweep directions after the final doping, in air, and in vacuum after washing the sample for several hours.

References:

1. Kim, Y.; Ryu, J.; Park, M.; Kim, E. S.; Yoo, J. M.; Park, J.; Kang, J. H.; Hong, B. H. Vapor-Phase Molecular Doping of Graphene for High-Performance Transparent Electrodes. *ACS Nano* **2014**, *8*, 868–874.
2. Yokota, K.; Takai, K.; Enoki, T. Carrier Control of Graphene Driven by the Proximity Effect of Functionalized Self-Assembled Monolayers. *Nano Lett.* **2011**, *11*, 3669–3675.