

Supporting Information for:

Electrical probing and tuning of molecular physisorption on graphene

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METHODS

Fabrication and characterization of graphene sensor devices. The graphene field effect transistors were fabricated on a silicon substrate with 60 nm thermal oxide. Single layer graphene film was first grown using the chemical vapour deposition (CVD) method on copper foils¹. After growth, one side of the copper foil was spin-coated with 950 PMMA A2 (Microchem) and the foil was then baked at 180⁰C for 1 min. Graphene on the uncoated side was removed by O₂ plasma etch (25 sec). To etch away the copper, the sample was placed in 0.1 M ammonium persulfate (Sigma-Aldrich) for over 12 hours. In the next step, PMMA-coated graphene was transferred from solution onto the 60 nm thermal oxide substrate. The substrate was allowed to dry (~1 day) and PMMA was removed by placing the die in acetone and then IPA for 15 min each. Photolithography was used to define the source and drain electrodes of the FET, after which metal contacts (0.5 nm titanium/ 100nm gold) were deposited followed by lift-off technique to complete the patterning. The graphene channel was defined using photolithography and 25 sec O₂ plasma etch. Devices in this study have graphene channel width of 1-2 μm , and length of 1-5 μm .

The graphene devices were characterized by DC electrical transport measurements. The current-voltage (I - V_g) transfer curve for devices used for temperature-dependence study are shown in Figure S4. The graphene channels are p-doped initially and the corresponding charge neutrality points, V_D can be used to determine the Fermi level, E_F at each gate voltage, V_g using the expression²,

$$E_F = \hbar v_F \sqrt{\pi n} \quad \text{Equation S1,}$$

where \hbar is the Planck constant, and v_F the Fermi velocity in graphene. n is the charge density of graphene given by $n = | \frac{C_{bg}(V_g - V_D)}{e} |$, where $C_{bg} (= \frac{\epsilon_{SiO_2} \epsilon_0}{d})$ is the back-gate capacitance for graphene device on silicon oxide ($\epsilon_{SiO_2} = 4$) of thickness, $d = 60$ nm.

Graphene nanoelectronic heterodyne detection setup. To operate the graphene transistor as a heterodyne sensor we follow Ref [20] of main text. An AC drive voltage, \tilde{V}^ω with a typical amplitude of $|\tilde{V}^\omega| = 10$ mV and frequency of 100 kHz, was provided by a HP 8648B signal generator (Santa Clara, CA). \tilde{V}^ω was then amplitude modulated (AM) at $\frac{\omega_m}{2\pi} = 1.4342$ kHz using the reference signal from a SR810 lock-in amplifier (Stanford Research Systems, Sunnyvale, CA), before it was delivered to the source terminal of the graphene transistor via a bias-tee as shown in Figure S5. The DC bias voltage, V_{sd} was maintained at 0 V throughout the measurements. The mixing current was measured at $\omega_m/2\pi$ using the lock-in amplifier. During temperature dependent desorption measurements, the gate, V_g^{DC} is held to ground.

Integration of graphene sensor with gas chromatography (GC). The graphene sensor die was capped with a silicon flow channel 400 mm deep by 400 mm wide, fabricated by a deep reactive ion etch of a patterned silicon wafer for 30 min. The flow channel was aligned to the centre of the die and secured by epoxy glue (Norland optical adhesive 81) at the edges. Vapour molecules are delivered to the graphene FET through a 70 cm long column (part no. 10029, inner diameter 250 μ m, from Restek, Bellefonte, PA, USA) with a linear speed of 8 mL/min and using helium as the carrier gas.

Temperature dependent measurement setup. For temperature dependent desorption measurement, the graphene sensor die was mounted on top of a solid state cooler (Vktech

TEC1-12706) using a silver paste (Artic Silver 5 thermal compound). The temperature of the solid state cooler was controlled by a DC power supply (Yihua-YH305D) and was calibrated using a K-type thermocouple (Amico) at each voltage.

DISCUSSION

Transport measurement for graphene transistor covered with 1, 2-Dichlorobenzene (DCB). In Fig. 4G (main text), we observe that the peak mixing current increases only slightly even with a ΔE_F shift of ~ 200 meV. One possible explanation for this could be screening of the back gate due to a layer of DCB covering the graphene channel. To study this, we carried out transport measurement on DCB decorated graphene transistor (Figure S6). We casted a drop of 1, 2 - DCB on the active area of device and allowed it to dry. Transport curves taken after 5 hours' drying time show shift of the Dirac point but the slopes remain constant. The shift of the transfer curves suggest n-doping of graphene from the absorption of DCB, but the constant slopes suggest that the back gate is still effective. These results confirm that the electric field screening from DCB molecules is not the reason for the weak gate tuning of DCB desorption dynamics. Similar weak dependence of peak mixing current on ΔE_F is observed for chlorobenzene as shown in Figure S3.

SUPPORTING FIGURES

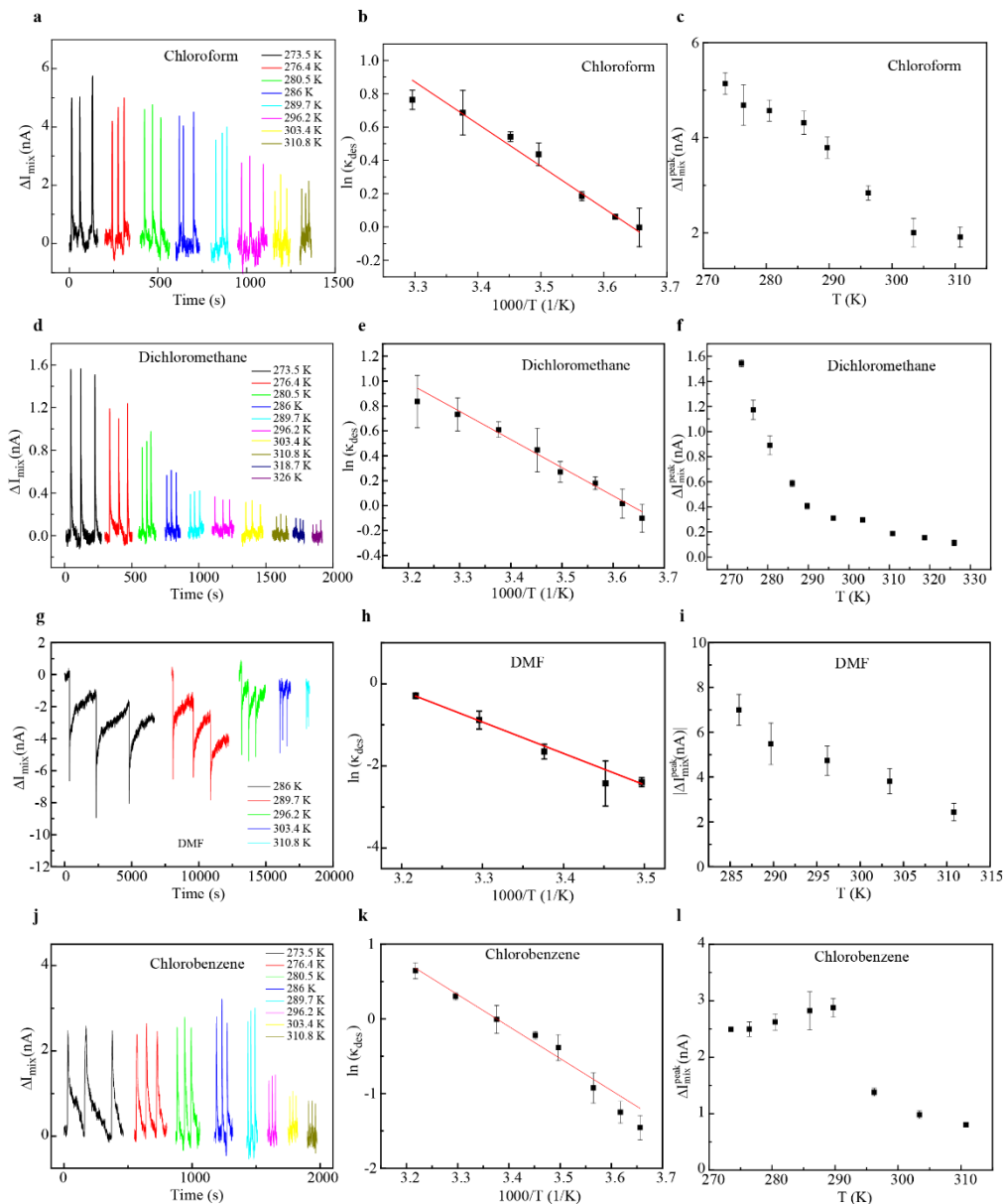


Figure S1. Temperature dependent desorption for small molecules. Temperature dependence of graphene sensor responses to repeated doses of chloroform (1.428 μg), dichloromethane (1.329 μg), DMF (28 ng) and chlorobenzene (109 ng) are shown in **a, d, g, j**, respectively. **b, e, h, k** show the Arrhenius plot of desorption rate constants at each temperature obtained from exponential fits to the desorption curves in **a, d, g, j**, respectively. Linear fits to these curves are shown in red. **c, f, i, l** show the peak response of graphene sensor from **a, d, g, j** respectively, plotted against temperature. Error bars show the standard deviation over 3 runs. For DMF, we chose a smaller temperature range as at lower temperatures desorption was extremely slow (\sim hours).

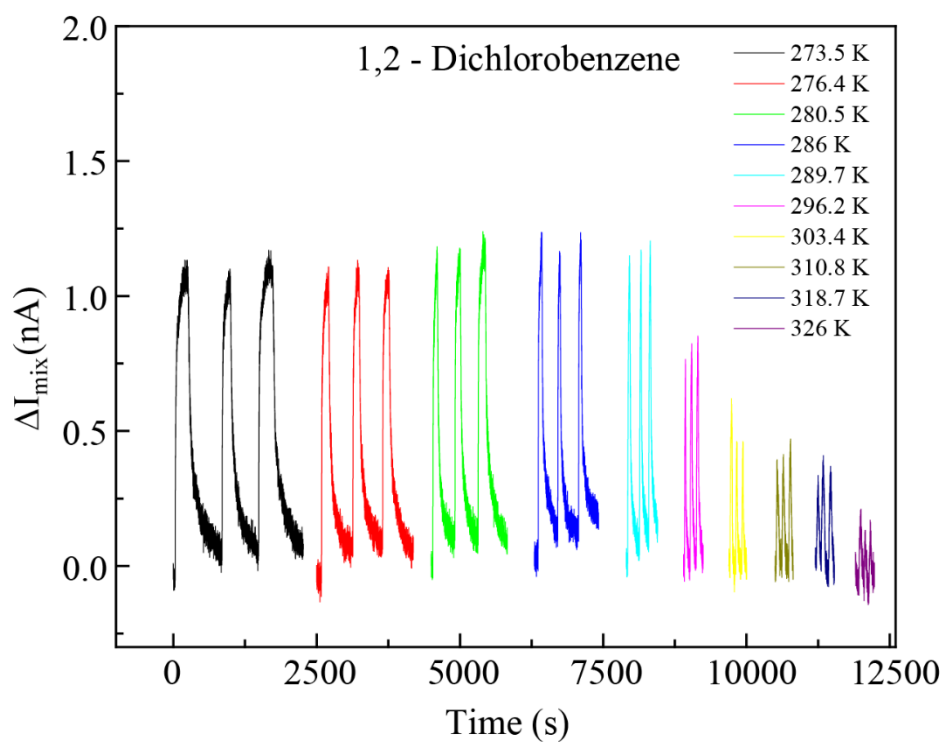


Figure S2. Temperature dependent desorption for 1, 2 – Dichlorobenzene. Temporal response of graphene sensor to repeated doses of 130 ng 1, 2 - Dichlorobenzene injection at different temperatures.

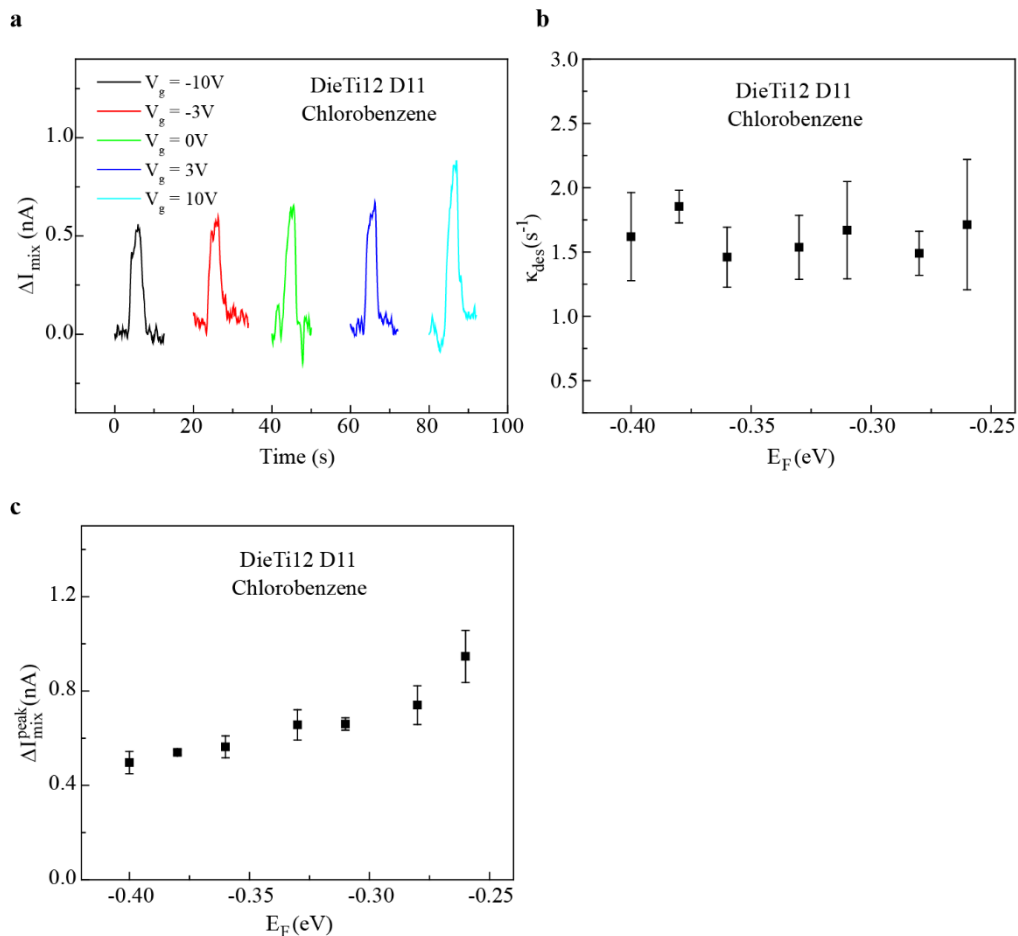


Figure S3. Gate dependence for chlorobenzene-graphene interaction. **a**, Mixing current response for 54.5 ng chlorobenzene at different back-gate voltages. **b**, Desorption rate obtained from the exponential fits to the desorption curves in **a**, plotted against graphene Fermi level shift. **c**, Peak mixing current response at different gate voltages plotted against Fermi level shift of graphene. The device dimensions are $L = 2 \mu\text{m}$ and $W = 2 \mu\text{m}$. Error bars show the standard deviation over 3 runs.

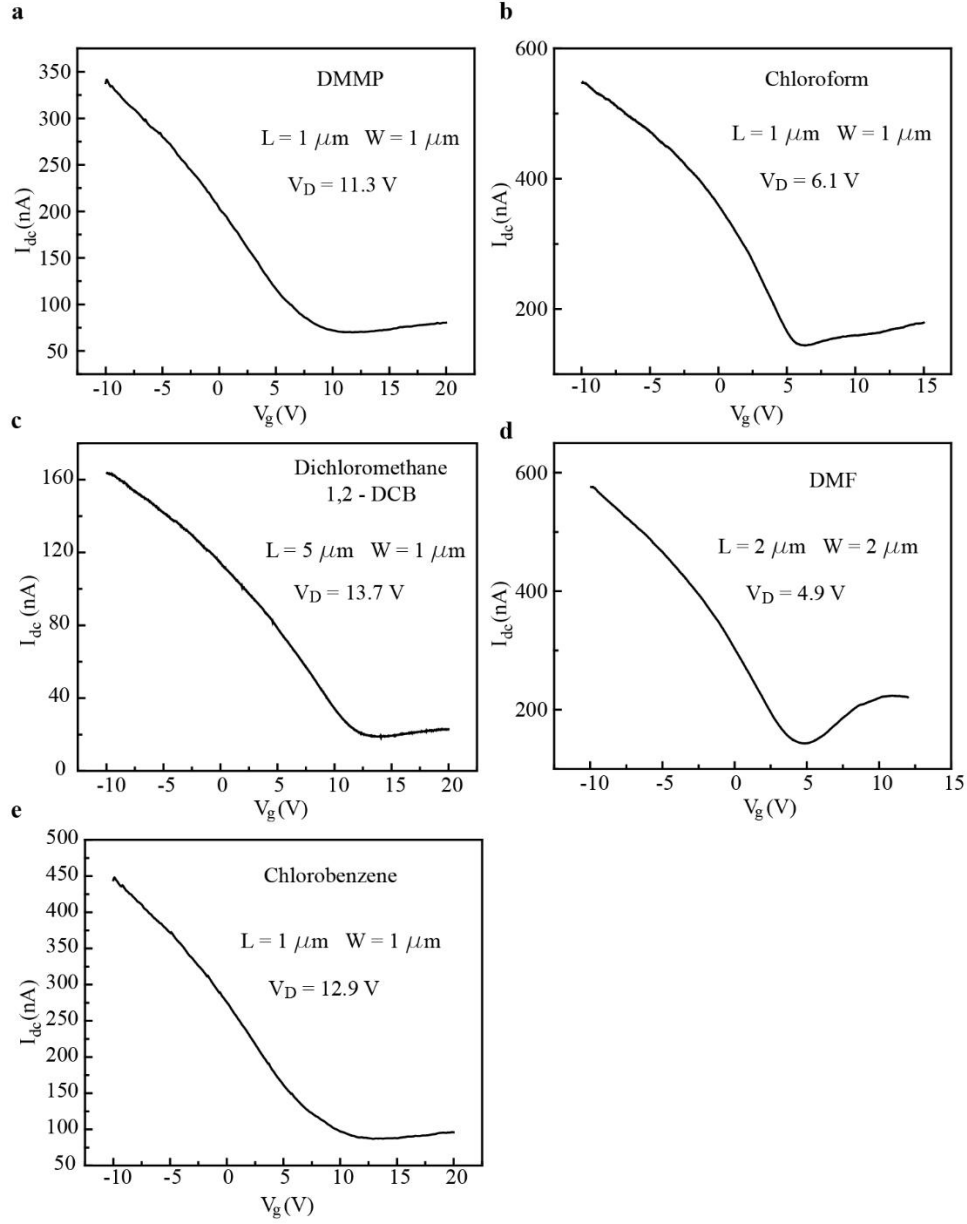


Figure S4. DC electrical transport characteristics for the devices used for temperature dependent measurements. a, DMMP, **b,** chloroform, **c,** dichloromethane and 1, 2 - DCB, **d,** DMF and **e,** chlorobenzene. The device dimensions and the charge neutral Dirac point voltage (V_D) are shown in the figure for each device. The source-drain voltage, $V_{sd} = 1 \text{ mV}$.

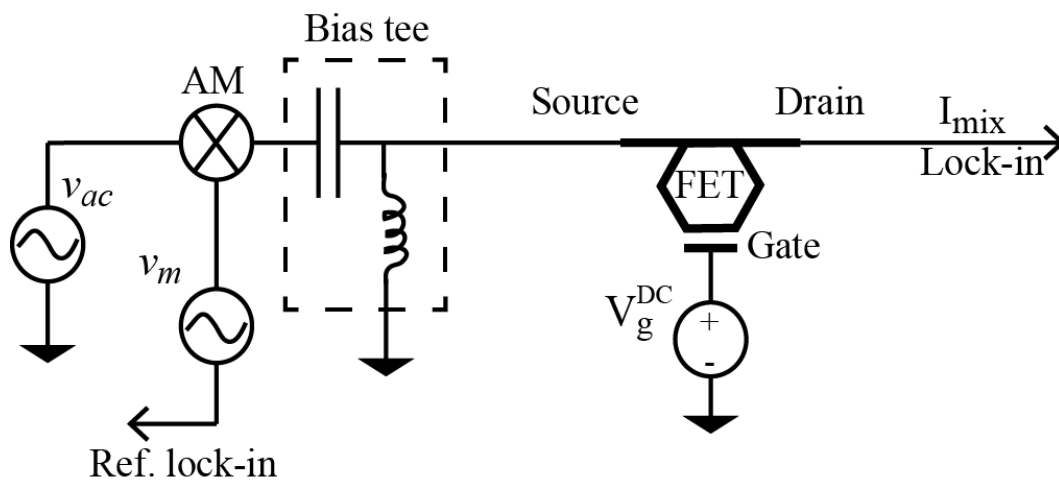


Figure S5. Nanoelectronic heterodyne measurement setup used to study molecular physisorption on graphene. The AC excitation voltage, v_{ac} , is 10 mV for all measurements in this work, except for chloroform temperature-dependence measurement where $v_{ac} = 15$ mV.

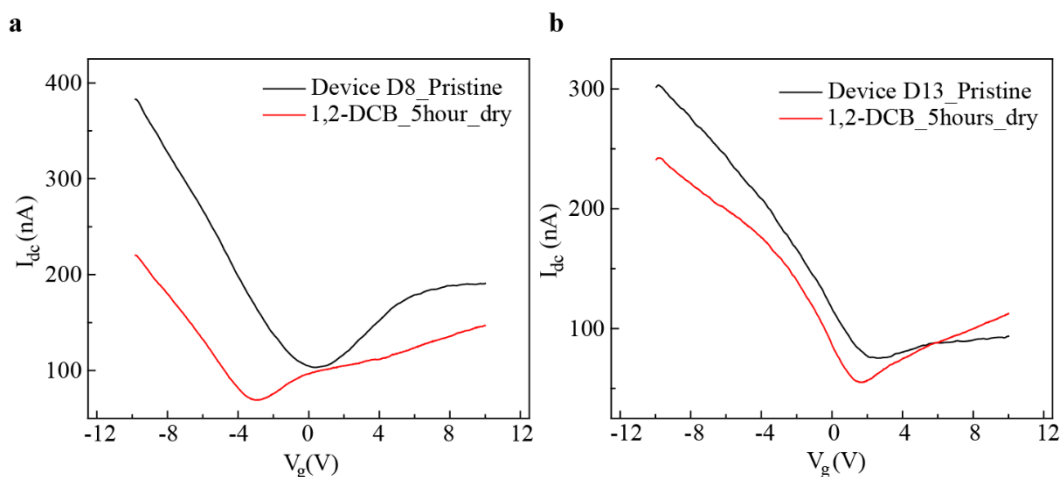


Figure S6. Transport measurement for 1, 2-Dichlorobenzene treated graphene. a, b, I - V_g measurement for two devices before (black) and after (red) 1, 2-Dichlorobenzene (DCB) treatment. The source-drain voltage, $V_{sd} = 1$ mV.

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