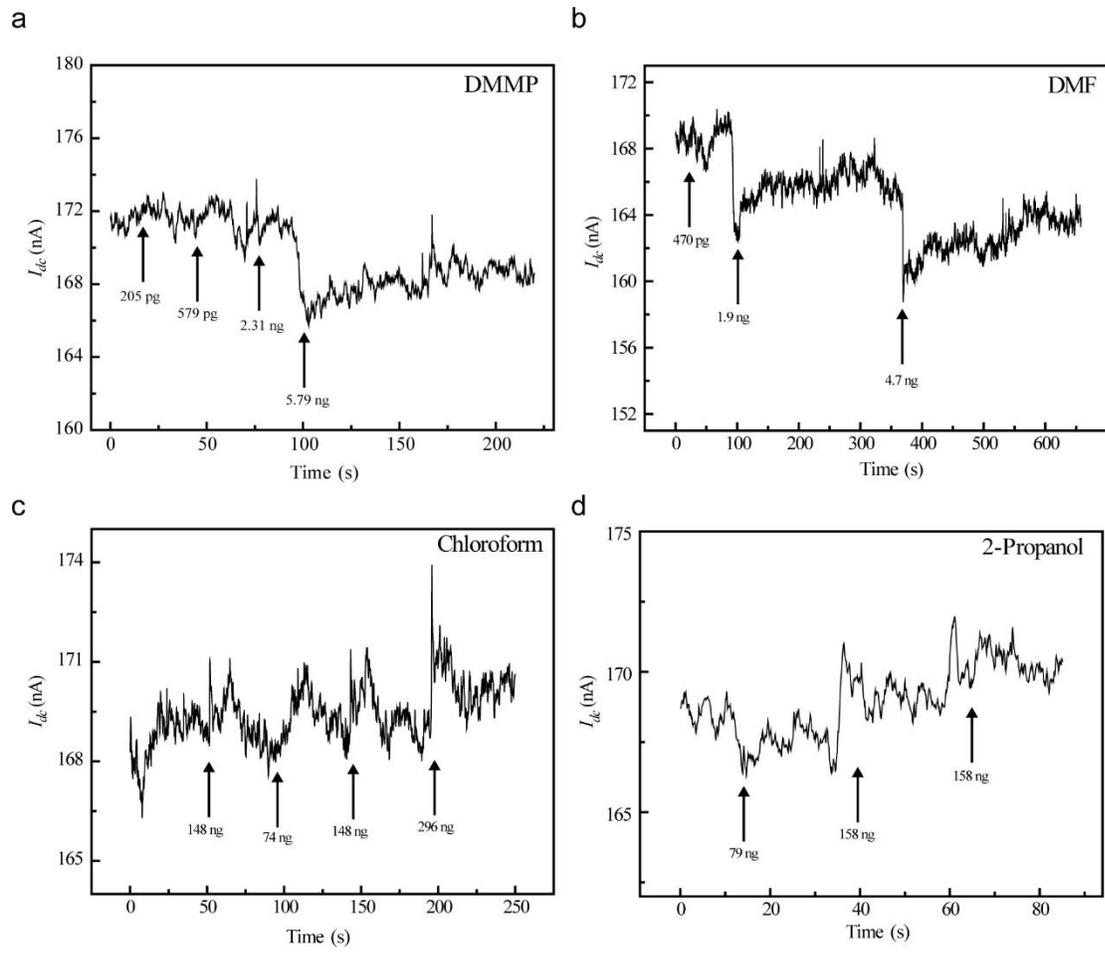
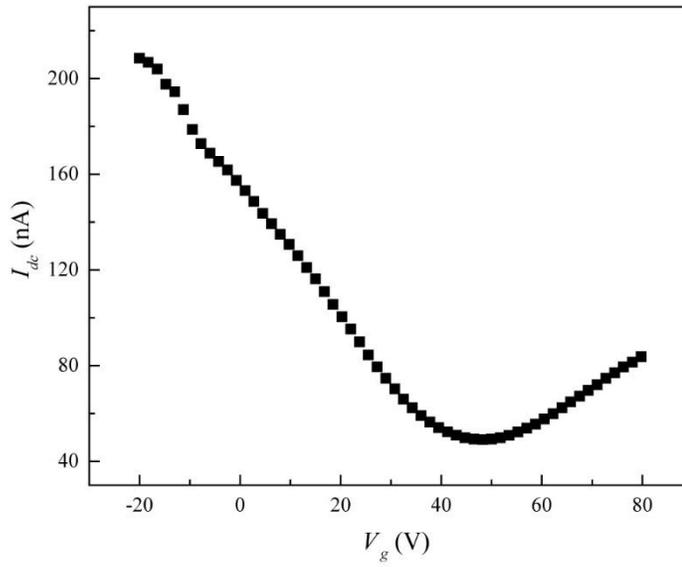


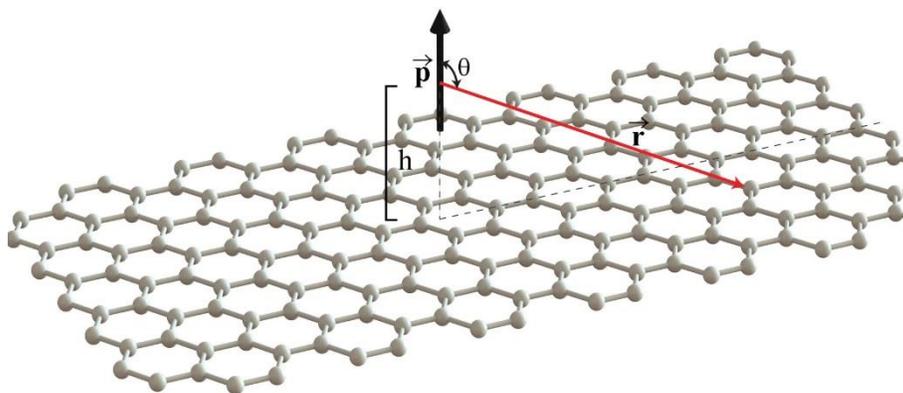
**Supplementary Figure 1.** Time trace of background mixing current reveals a  $3\sigma$  noise floor of  $\sim 0.12$  nA for our proof-of-principle graphene heterodyne sensor.



**Supplementary Figure 2.** DC sensing of vapour analytes using the same GrFET for (a) DMMP, (b) DMF, (c) chloroform, and (d) 2-propanol. The conventional DC detection method using the same GrFETs is much less responsive in both response time and sensitivity.



**Supplementary Figure 3.** Current-Gate voltage transfer curve for the graphene transistor used in Fig. 2 and Fig. 3. Channel length and width were 7  $\mu\text{m}$  and 2  $\mu\text{m}$ , respectively. DC source-drain bias voltage was 1 mV.



**Supplementary Figure 4.** Model of a surface adsorbed molecule located above a graphene film with the dipole moment,  $\vec{p}$ , perpendicular to the graphene surface.

Analyte	Dipole moment (D)	Boiling point (°C)	Smallest injected mass (ng)	FWHM (s) (averaged over triplicates)	Concentration at minimum injected mass (ppm)
Pentane	0	36	-	-	-
Hexane	0	69	-	-	-
Benzene	0	80	-	-	-
Toluene	0.37	111	172	1.61	210
1,4-Dioxane	0.45	101	52	2.1	50
Chloroform	1.04	61	74	0.68	164
Chlorobenzene	1.54	131	5.5	0.75	12
Dichloromethane	1.6	40	66	1	139
2-Propanol	1.66	82	39	1.12	105
Ethanol	1.69	79	15	0.9	65
Acetone	2.88	56	15	0.8	58
DMMP	3.62	181	0.205	6.83	0.043
DMF	3.82	153	0.944	2.54	0.92

**Supplementary Table 1.** Summary of 13 vapour analytes tested using graphene heterodyne sensors.

## Supplementary Note 1: Vapour sensing procedures

For vapour sensing, each analyte was injected individually at the GC injection port, except for Fig. 4 where a mixture of eight analytes was injected together. The injection oven temperature was set at 250 °C and flow pressure was set at 7.6 psi which corresponded to a carrier gas flow rate of 8 mL/min. Mass of each injected analyte was calibrated using the GC splitter and flame ionization detector (FID).

For Fig. 4, a 7.2 m long CP-SIL-5-CB column (part no. CP8510, inner diameter 250 µm, from Varian, a division of Agilent Santa Clara, CA), and a 2.8 m long Carbowax column (part no. 12523, inner diameter 250 µm, from Restek, Bellefonte, PA) paired with temperature and flow programming were used to achieve rapid separation of the mixture of eight analytes. The oven temperature was initially set to 32 °C, after 36 seconds it was ramped to 45 °C at a rate of 50 °C/min where it was held for 24 seconds before being ramped up to 80 °C at 100 °C/min. After being held at 80 °C for 12 seconds the temperature was increased to 110 °C at 50 °C/min and held there until all the analytes were eluted from the column. Similarly, the flow pressure, and hence flow rate, was also varied to enhance separation. The flow pressure was initially maintained at 15 psi for 30 seconds and was then ramped at a rate of 30 psi/min to 19 psi and held there till the end of the run.

A Y-split was used to split the analytes separated by the CP-SIL-5-CB and Carbowax columns in a 50-50 ratio, and simultaneously deliver the analytes to both the graphene heterodyne sensor and the FID. A pair of 70 cm long guard columns were used to deliver the separated analytes from the Y-split to the respective detectors. The FID oven temperature was set at 300 °C, while the graphene sensor was held at ambient temperature.

All the analytes used in this work were purchased from Sigma-Aldrich (St Louis, MO) and had purity greater than 97%. The polarity and boiling point of each analyte is listed in Supplementary Table 1. Supplementary Table 1 also shows the minimum injected mass detected experimentally, the average full width at half maximum of three runs at the minimum injected mass, and the theoretical detection limit based on the sensor noise level.

### **Supplementary Note 2: Vapour concentration calculation**

This calculation converts the injected analyte mass into the vapour concentration in the GC channel that the graphene sensor is exposed to. The concentration,  $C$ , in ppm or ppb is given by:

$$C = \frac{m}{nM} \times 10^6, \quad (1)$$

where  $m$  is the mass of the analyte,  $M$  is the molecular weight of the analyte, and  $n$  is the number of moles of helium that flows over the sensor in a given period of time, which can be determined by:

$$n = yt \times 10^{-3} \times \frac{1}{24}, \quad (2)$$

where  $y$  is the flow rate of helium, through the guard column, in L/s,  $t$  is the full width at half maximum of the analyte detection peak, and ideal gas law dictates that 1 mole of helium occupies 24 litres.

Experimental data for gas flow reveals a flow rate of 8 mL/min or  $0.133 \times 10^{-3}$  L/s. The full width half maximum of DMMP detection peak is 6.83 seconds. Using these values we find that  $n = 0.0379$  moles. Further considering  $M = 124$  g/mol for DMMP, we calculate that  $m = 3$  pg of DMMP (the detection limit) corresponds to a concentration of  $C = 0.64$  ppb. The same

method is also employed for all other analytes used in the experiment. The corresponding minimum concentrations detected by the sensors are shown in Supplementary Table 1.

### Supplementary Note 3: Graphene nanoelectronic heterodyne sensing model

The DC current-voltage relation for a transistor is given as:

$$I = \frac{\mu W}{L} [C_g (V_g - \frac{1}{2}V)] \cdot V, \quad (3)$$

where  $C_g$  is the gate capacitance,  $V_g$  is the DC gate voltage,  $V$  is the DC bias voltage, and  $C_g (V_g - \frac{1}{2}V)$  gives the charge per unit area within the graphene channel induced by the effective gate voltage,  $V_g^{eff} = V_g - \frac{1}{2}V$ . When molecules are adsorbed on graphene surface, they induce additional charge in the graphene channel and thus modify the transistor current:

$$I = \frac{\mu W}{L} [C_g (V_g - \frac{1}{2}V) + Q_m] \cdot V, \quad (4)$$

where  $Q_m$  is the molecule induced charge per unit area inside the graphene channel. Importantly, since vapour molecules are charge neutral,  $Q_m$  is zero unless there is charge transfer between molecule and graphene or under imperfect screening. This is the fundamental reason why pristine graphene DC sensors have low sensitivity toward most vapour molecules<sup>1</sup>.

A time varying AC excitation at  $\omega$ ,  $\tilde{V}^\omega$ , will modulate the channel potential and generate charge density modulation due to electrostatic coupling with gate. In addition,  $\tilde{V}^\omega$  can also excite the adsorbed molecules, which in turn produce a dipole-induced charge density modulation at  $\omega$ ,  $\tilde{Q}_m^\omega$ . Thus, the heterodyne mixing current (the fourth term in Eq. (1)) can be expressed as:

$$I_{mix} = \frac{\mu W}{L} [C_g (-\frac{1}{2}\tilde{V}^\omega) + \tilde{Q}_m^\omega] \cdot \tilde{V}^\omega. \quad (5)$$

The first term inside the square bracket is the contribution from the inherent gate response and is accounted as the background current. The second term, however, is related to the molecular

dipole-induced charge perturbation in graphene. Hence, we can measure the changes in mixing current due to molecular absorption as the sensor signal:  $\Delta I_{mix} = \frac{\mu W}{L} \tilde{Q}_m \tilde{V} \omega$ . This is Eq. (3) in the main text.

To calculate  $\tilde{Q}_m^\omega$ , we first examine a single molecule with a dipole moment,  $\vec{\mathbf{p}}$ , adsorbed on the centre of graphene surface. For simplicity, we assume the molecule-graphene vertical distance is  $h$ , and the dipole moment is perpendicular to the graphene surface (Supplementary Figure 4). The electric field on graphene due to the molecular dipole can be expressed as

$$\vec{\mathbf{E}}_{Gr} = \frac{1}{4\pi\epsilon_0} \left[ \frac{3(\vec{\mathbf{p}} \cdot \hat{\mathbf{r}})\hat{\mathbf{r}} - \vec{\mathbf{p}}}{r^3} \right], \quad (6)$$

where  $\vec{\mathbf{r}}$  is a point on graphene from  $\vec{\mathbf{p}}$ ,  $\hat{\mathbf{r}}$  is its unit vector, and the angle between  $\vec{\mathbf{r}}$  and  $\vec{\mathbf{p}}$  is  $\theta$ .

This local electric field polarizes graphene:

$$\vec{\mathbf{p}}_{Gr} = \alpha_{Gr} \vec{\mathbf{E}}_{Gr} = \frac{\alpha_{Gr}}{4\pi\epsilon_0} \left[ \frac{3(\vec{\mathbf{p}} \cdot \hat{\mathbf{r}})\hat{\mathbf{r}} - \vec{\mathbf{p}}}{r^3} \right], \quad (7)$$

where  $\alpha_{Gr}$  is graphene's polarizability and  $\vec{\mathbf{p}}_{Gr}$  is the molecular dipole induced graphene dipole moment at  $\vec{\mathbf{r}}$ . The macroscopic polarization normal to graphene surface,  $\vec{\mathbf{P}}_{Gr}^Z$ , can be obtained by integrating  $\vec{\mathbf{p}}_{Gr}$  over the entire graphene lattice. The unit area can be calculated as  $dA = 2\pi r \sin \theta \frac{-h}{\cos^2 \theta} d\theta$ , while the number of carbon atoms within this unit area is given by  $\frac{2 dA}{A_{uc}}$ , with  $A_{uc} = 0.051 \text{ nm}^2$  being the unit cell area of graphene. Hence, we have:

$$\begin{aligned} \vec{\mathbf{P}}_{Gr}^Z &= \frac{1}{W \times L \times t} \int_{\pi}^{\pi - \cos^{-1}(\frac{2h}{W})} \frac{\alpha_{Gr}}{4\pi\epsilon_0} \left[ \frac{3(\vec{\mathbf{p}} \cdot \hat{\mathbf{r}})\hat{\mathbf{r}} - \vec{\mathbf{p}}}{r^3} \right] \frac{2}{A_{uc}} 2\pi r \sin \theta \frac{-h}{\cos^2 \theta} d\theta \\ &= \frac{1}{W \times L \times t} \frac{\alpha_{Gr}}{4\pi\epsilon_0} \frac{4\pi}{A_{uc}} \frac{p}{h} \int_{\pi}^{\pi - \cos^{-1}(\frac{2h}{W})} -\sin \theta (3 \cos^2 \theta - 1) d\theta \end{aligned}$$

$$\begin{aligned} &\approx \frac{1}{W \times L \times t} \frac{\alpha_{Gr}}{4\pi\epsilon_0} \frac{4\pi}{A_{uc}} \frac{p}{h} \frac{2h}{W} \\ &= \frac{1}{W^2 \times L \times t} \frac{\alpha_{Gr}}{4\pi\epsilon_0} \frac{8\pi}{A_{uc}} p \end{aligned}$$

with  $t$  being the thickness of the graphene film. For simplicity, we only add up all atoms within the radius of  $W/2$  (assuming  $W < L$ ) in the integration.

An AC driving voltage at  $\omega$  will cause the molecular dipole to oscillate at the same frequency, introducing charge density fluctuation on graphene. Here we include a proportional quantity,  $\gamma(\tilde{V}^\omega, \omega)$ , to account for the degree of dipole excitation,  $\gamma(\tilde{V}^\omega, \omega)p$ . The amount of dipole perturbation at  $\omega$  would depend on the strength of the AC drive voltage compared with the binding strength between molecule and graphene. If the molecule is in free space, then one would expect the entire molecule to flip following  $\tilde{V}^\omega$ , *i.e.*,  $\gamma = \cos \omega t$ . Hence, the oscillating molecular dipole induced charge density fluctuation on graphene can be estimated by:

$$\tilde{Q}_m^\omega = \gamma(\tilde{V}^\omega, \omega) \vec{\mathbf{P}}_{Gr}^Z = \gamma(\tilde{V}^\omega, \omega) \frac{1}{W^2 \times L \times t} \frac{\alpha_{Gr}}{4\pi\epsilon_0} \frac{8\pi}{A_{uc}} p. \quad (8)$$

We emphasize that since graphene is not an ideal metal, Supplementary Equation S8 only serves for order of magnitude calculation. From Supplementary Equation S5 and Supplementary Equation S8, we obtain the sensing signal for a single molecule:

$$\Delta I_{mix} = \frac{\mu W}{L} \gamma(\tilde{V}^\omega, \omega) \frac{1}{W^2 \times L \times t} \frac{\alpha_{Gr}}{4\pi\epsilon_0} \frac{8\pi}{A_{uc}} p \tilde{V}^\omega = \frac{\gamma(\tilde{V}^\omega, \omega) \mu}{W \times L^2 \times t} \frac{\alpha_{Gr}}{4\pi\epsilon_0} \frac{8\pi}{A_{uc}} p \tilde{V}^\omega. \quad (9)$$

If  $n = \frac{N}{WL}$  is the areal density of the surface adsorbed molecules, we have:

$$\Delta I_{mix} = \frac{\gamma(\tilde{V}^\omega, \omega) \mu}{L \times t} \frac{\alpha_{Gr}}{4\pi\epsilon_0} \frac{8\pi}{A_{uc}} n p \tilde{V}^\omega, \quad (10)$$

for quantitative measurement of analyte concentration in the vicinity of graphene sensor. For better noise rejection, we use AM modulation and measure the mixing current change at the modulation frequency.

#### **Supplementary Note 4: Estimation of the sensor detection limit**

We first estimate the sensor detection limit using Eq. (S9). For a typical device, we use  $L = W = 1 \mu\text{m}$ ,  $t = 0.34 \text{ nm}$ ,  $\mu = 1000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ , and  $\alpha_{Gr} = 0.9 \text{ \AA}^3$  (in CGS unit, ref. 2). A single DMMP molecule with  $p = 3.62$  Debye is adsorbed on graphene surface. For simplicity, we assume the molecular dipole is partially excited at  $\tilde{V}^\omega = 20 \text{ mV}$ , with  $\gamma = 0.1 \times \cos \omega t$ . Using Eq. (S9), we estimate a sensor signal on the order of  $\sim 3 \text{ fA}$  for a single DMMP molecule. Using a  $3\sigma$  noise floor of  $0.12 \text{ nA}$ , we estimate a detection limit of  $\sim 10^4$  molecules for our proof-of-principle devices.

We can also compare this number with estimation from concentration calculation. Using the molecule weight of  $124 \text{ g/mol}$  and the mass density of  $1.145 \text{ g/mL}$  (liquid), we estimate that the inter-molecule distance is approximately  $0.57 \text{ nm}$  for liquid DMMP. Therefore, the maximal number of DMMP molecules adsorbed and closely packed on a  $1 \mu\text{m}$  ( $W$ )  $\times$   $1 \mu\text{m}$  ( $L$ ) graphene surface is approximately  $3 \times 10^6$ . We further assume that  $23.2 \text{ ng}$  of injected DMMP molecules saturate the graphene surface and form a liquid layer, which generates a sensing signal of approximately  $6 \text{ nA}$  (see Fig. 2c). Using a  $3\sigma$  noise floor of  $0.12 \text{ nA}$ , we can estimate that the *upper limit* of detectable DMMP molecules on the graphene sensor surface is approximately  $6 \times 10^4$ , agreeing with the detection limit estimated from Supplementary Equation S9.

We would like to emphasize that this detection limit can be readily improved to  $\sim 100$  molecules by reducing the device channel length from  $1 \mu\text{m}$  to  $0.1 \mu\text{m}$ . Furthermore, by reducing

the noise floor through better design of measurement circuitry, coupled with the adoption of higher quality graphene transistor or carbon nanotube transistor, one could push the detection limit into single molecule regime.

### **Supplementary References**

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- 2 Yu, E. K., Stewart, D. A. & Tiwari, S. Ab initio study of polarizability and induced charge densities in multilayer graphene films. *Phys. Rev. B* **77**, 195406 (2008).