

Biomimetic Chemical Sensors using Nanoelectronic Read out of Olfactory Receptor Proteins

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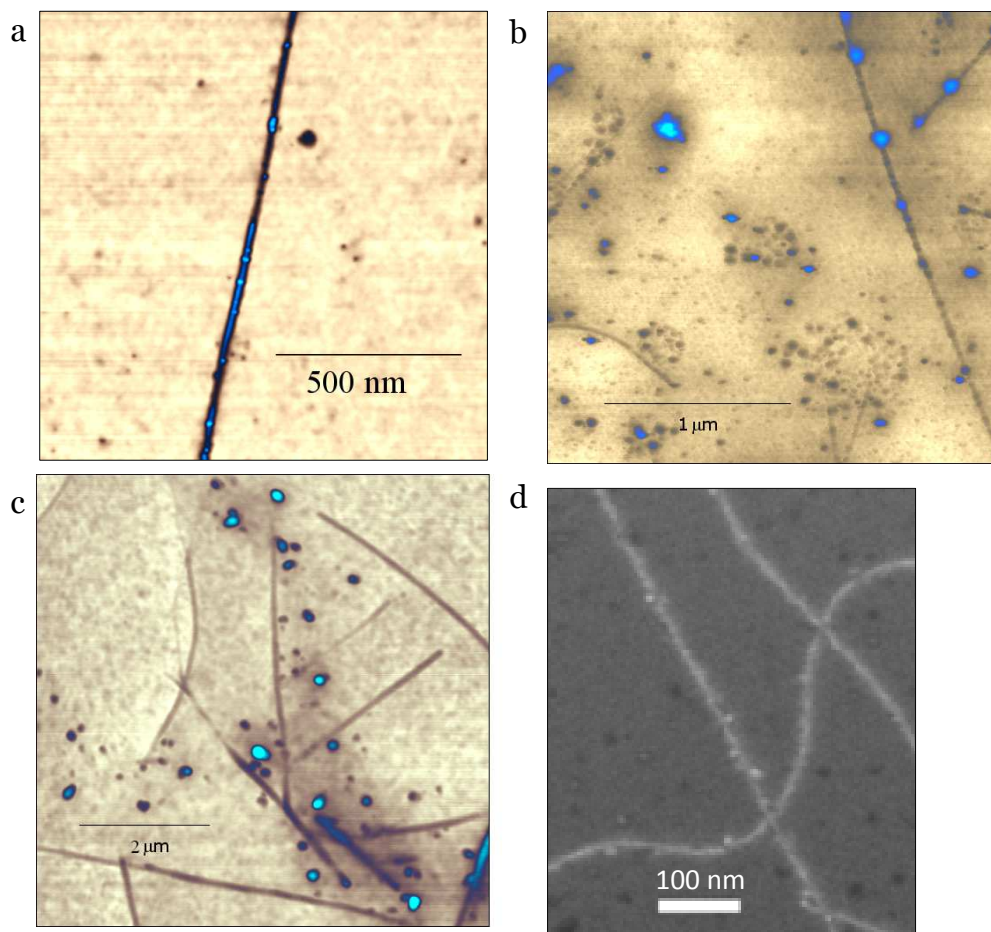
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Supplementary Data

1. Non-specific binding of micelles to functionalized NTs

Multiple AFM and SEM experiments were done to examine the binding of His-tagged proteins and micelles to functionalized and unfunctionalized nanotubes. The results are summarized in Supplementary Figure 1.

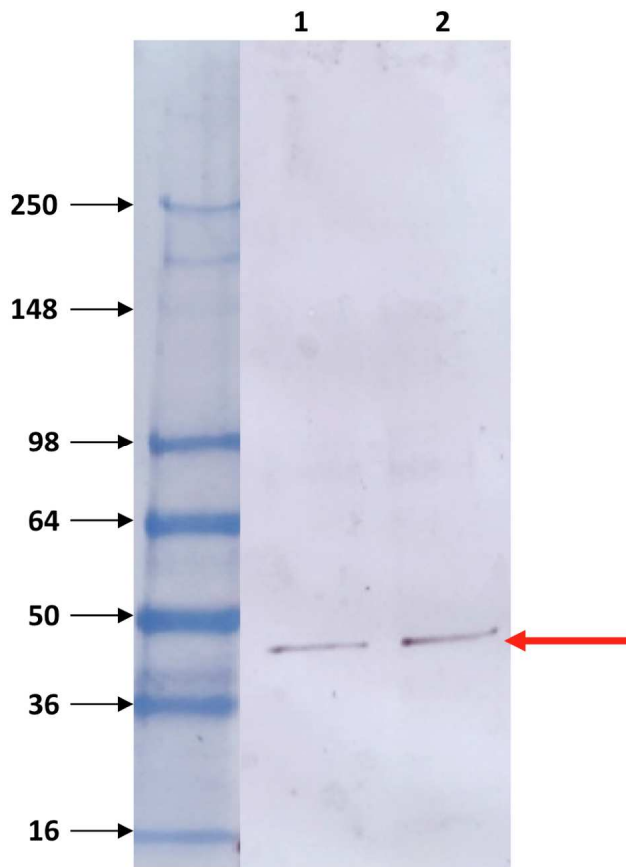


Supplementary Figure 1 (a) Water soluble, His-tagged proteins selectively bind to Ni-NTA functionalized carbon nanotubes. 20 nm height color scale. (b) Digitonin micelles containing His-tagged proteins also selectively bind to Ni-NTA functionalized carbon nanotubes. 30 nm height color scale. (c) Digitonin micelles do not preferentially bind to un-functionalized carbon nanotubes. 30 nm height color scale. (d) SEM image of His-tagged gold beads attached to Ni-NTA modified NTs. In each case, we find binding site densities of ~ 5 -10 sites/ μm of nanotube length.

We conducted numerous control experiments using identical incubation and washing protocols to confirm that binding between mORs and the nanotube was controlled by the Ni-NTA:His-tag interaction. We confirmed that empty digitonin micelles and empty nanodiscs have no affinity for Ni-NTA modified nanotubes. We also exposed Ni-NTA functionalized devices to proteins *without* His-tags and confirmed that no bound proteins remain after the wash protocol. The proteins for these experiments were commercially obtained protein G; we did not use the mORs since these were all His-tagged, and were not designed for His-tag removal. It is expected that the Ni-NTA:His-tag interaction will properly orient the protein on the nanotube, but this has not been verified through a structural measurement.

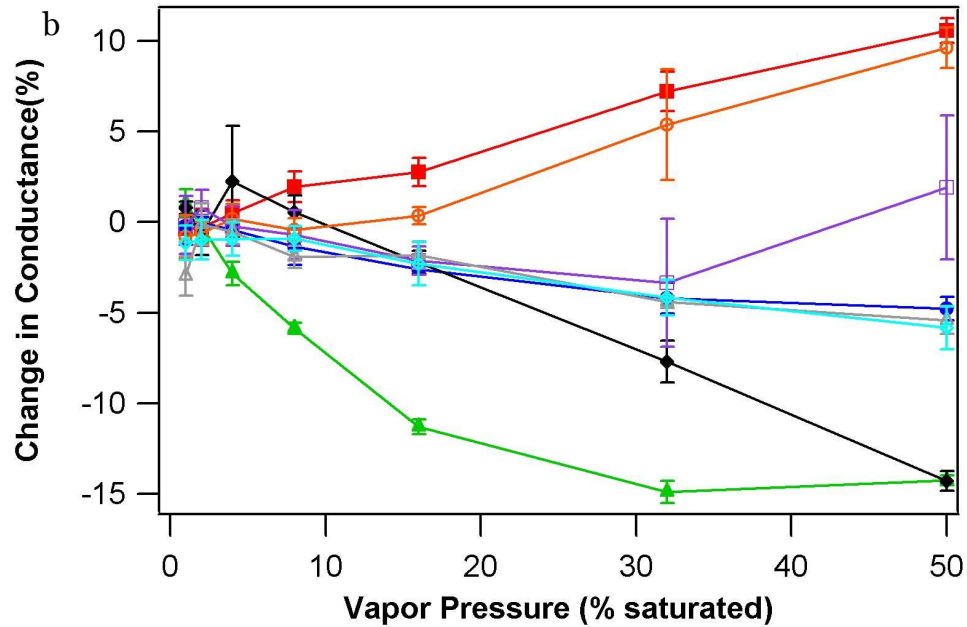
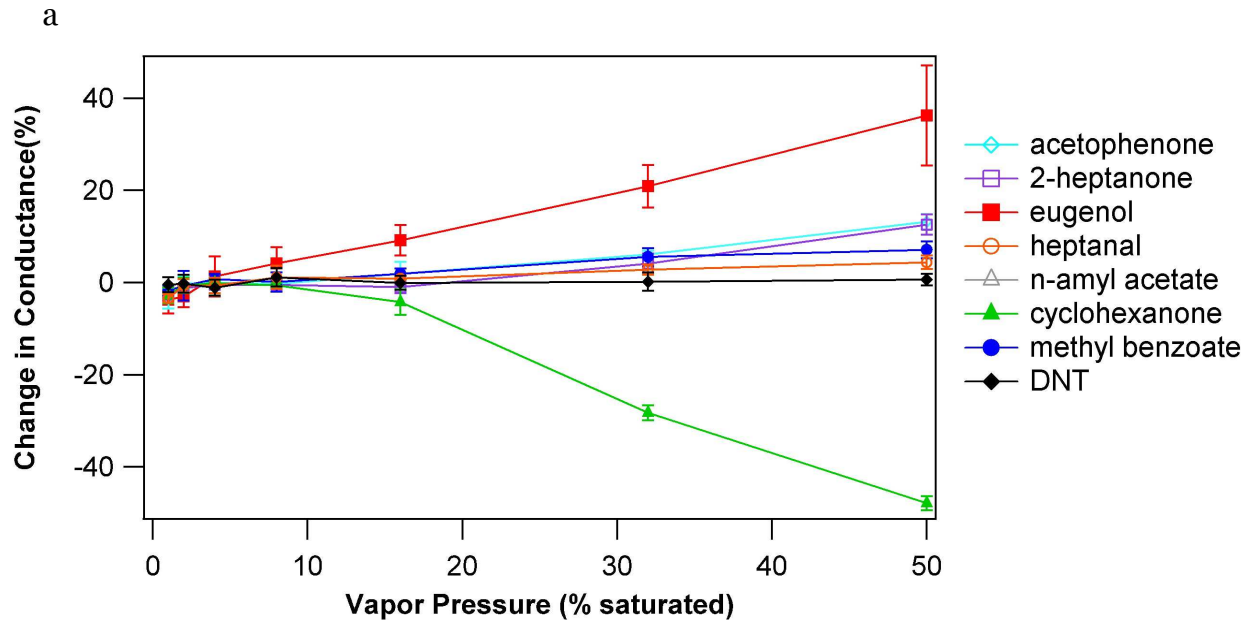
2. Western blot analysis after receptor purification on Ni magnetic beads.

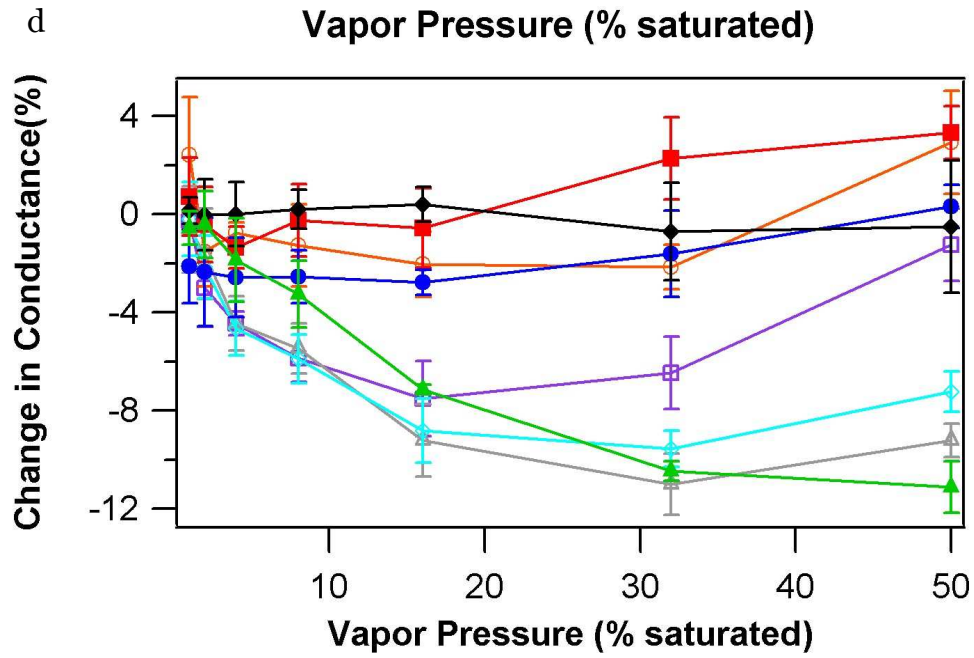
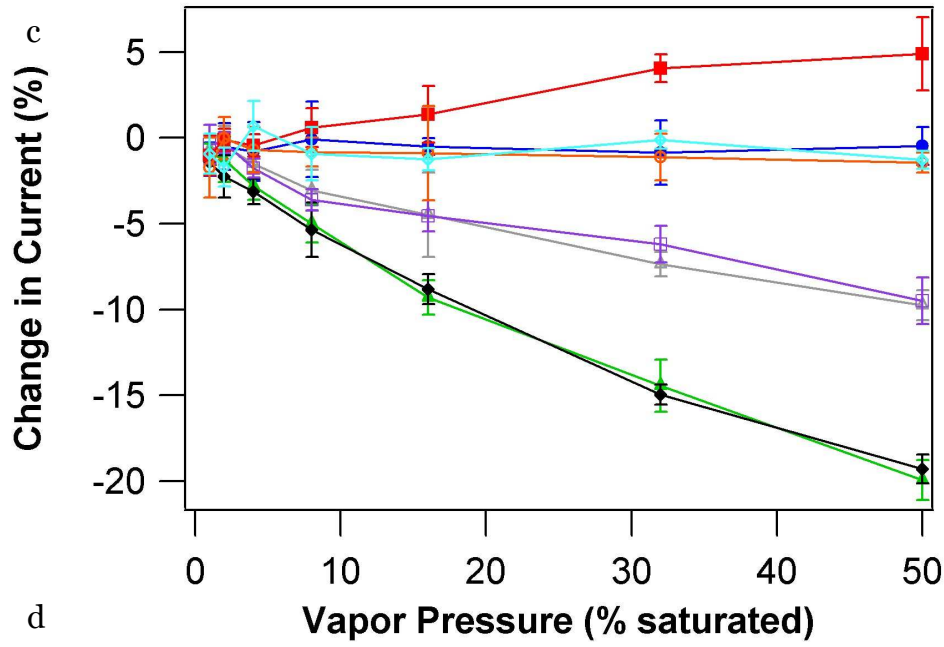
The correct molecular weight of each expressed mOR in the purified fractions was verified by Western blot analysis using antibody for His-tag or V5 epitope. Supplementary Figure 2 shows an example of Western blot for mOR 174-9.

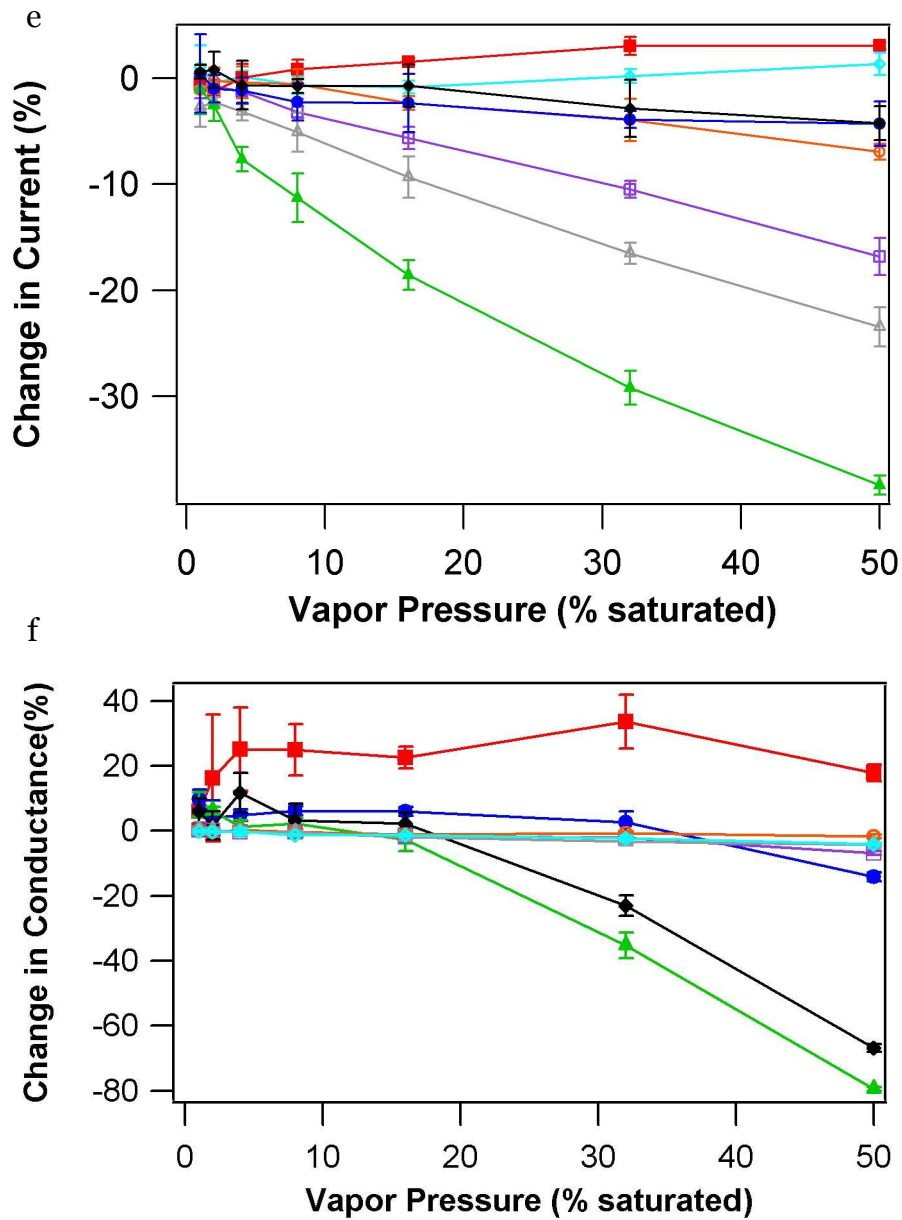


Supplementary Figure 2. Western blot analysis of purified mouse olfactory receptor (mOR) 174-9 (~40 kDa, red arrow). The receptor was purified using Ni magnetic beads and diluted 10 fold (line 1) and 25 fold (line 2). Western blot analysis was performed using Bio-Rad kit (chromogenic detection) probing the V5 epitope with anti-V5 antibody. The V5 epitope is a sequence in the recombinant mOR located upstream of the natural mOR sequence and downstream of the His tag.

3. Summary of NT response data



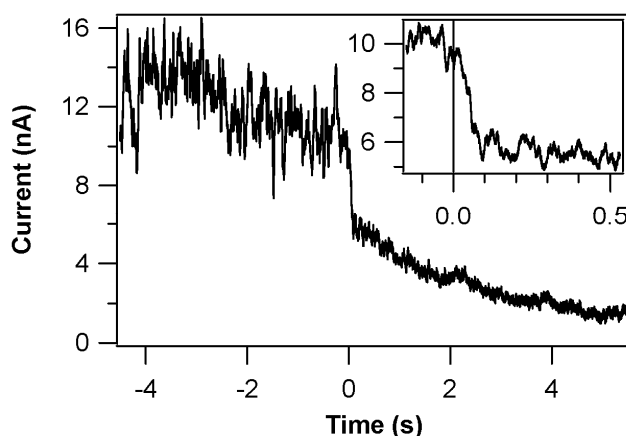




Supplementary Figure 3. Data summarizing responses across all functionalized device types, all odorants, and all concentrations used in the experiments. (a) mOR 174-9 in digitonin micelles. (b) mOR 174-9 in nanodiscs. (c) mOR 203-1 in digitonin micelles. (d) mOR 203-1 in nanodiscs. (e) mOR 256-17 in digitonin micelles. (f) mOR 256-17 in nanodiscs.

4. Control Experiment to Determine Response Time of the Measurement Apparatus

The chamber used for measurements of the responses of NT Devices to odorant vapors is described in detail above. The speeds of gas introduction and flushing have been well characterized over several years of chemical sensing measurements on functionalized carbon nanotubes and more recently, with graphene^{1,2}. These earlier measurements demonstrate that the intrinsic response time of the measurement apparatus is below 100 ms. Here we show an example of how a NT device that was functionalized with single stranded DNA (ssDNA) responds upon exposure to the odorant dimethylmethylphosphonate (DMMP). Other than the chemical treatment of the nanotube device and the odorant used, the measurement is performed identically to those presented in the main paper. A ~40 % decrease in the device current occurs within 100 ms.



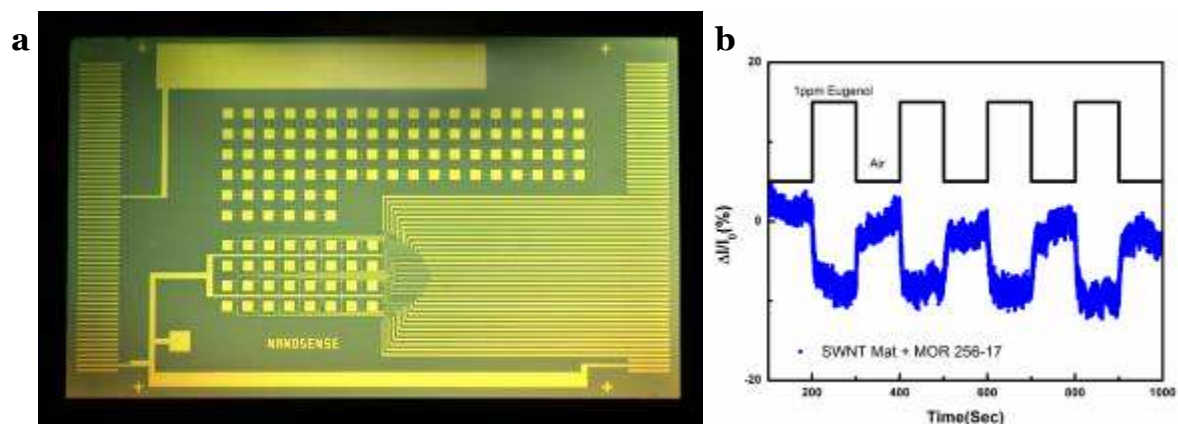
Supplementary Figure 4 Current response of a single-stranded DNA functionalized NT transistor to DMMP at 1500 ppm in the same chamber as was used for the mOR experiments. We typically observe a very rapid response in the first 0.1 seconds for NT devices functionalized with ssDNA, in contrast to the much slower response (~10-30 seconds) observed for the mOR-functionalized NT devices discussed in the main text.

5. Arrays of mOR-NT Devices

The chip in Supplementary Figure 4 is an array of 32 nanotube transistors functionalized with mOR-25-17 in digitonin micelles, sharing a common drain and back gate. The transistors consist of networks of nanotubes, unlike the few (1-3) tube devices discussed in the main paper. Flexible printed circuits (flex tabs) were used to interface the chip to a computer-controlled custom electronic system for signal conditioning and data acquisition. Fabrication was done on a 4" wafer using a commercially obtained 6" CVD furnace system to grow carbon nanotubes.

Device responses upon exposure to odorant vapors were collected as described in the main text, except that the total flow was 1000 sccm, and breathing grade air was used as

the carrier gas for all flows. For the data shown below, the precise concentration of eugenol was verified using an FTIR spectrometer.



Supplementary Figure 5 (a) Image of an array of mOR-functionalized NT devices used to establish the potential for large-scale production. (b) Response of one such device upon exposure to eugenol vapor at a concentration of 1 ppm. Sensing data are % change from background current, as in the main paper.

1. Staii, C., Chen, M., Gelperin, A. & Johnson, A. T. DNA-decorated carbon nanotubes for chemical sensing. *Nano Letters* 5, 1774-1778 (2005).
2. Lu, Y., Goldsmith, B. R., Kybert, N. J. & Johnson, A. T. C. DNA-decorated graphene chemical sensors. *Applied Physics Letters* 97, 083107 (2010).