

One-step Surface Doping of Organic Nanofibers to Achieve High Dark Conductivity and Chemiresistor Sensing of Amines

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Supporting Information

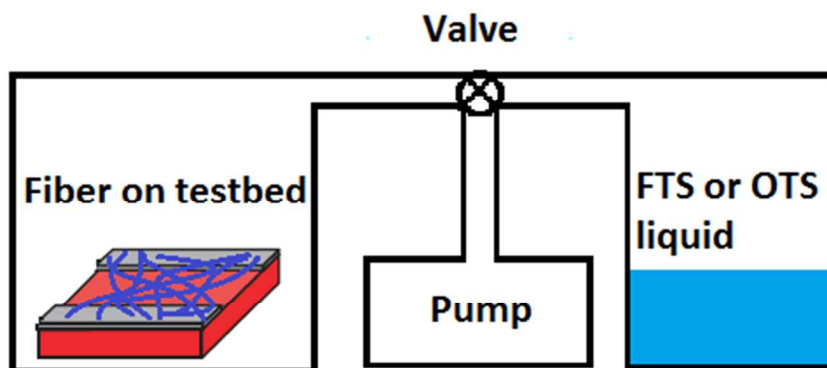


Figure S1. Diagram of the vapor deposition setup.

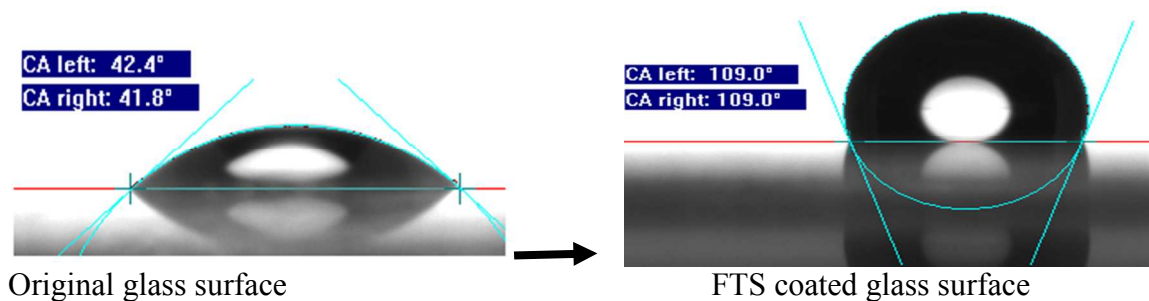


Figure S2. Contact angle measurement of pristine and FTS modified glass slides. The pristine glass surface is hydrophilic, with a contact angle of 42°. After FTS treatment, the contact angle dramatically increased to 109°, which is consistent with the literature.¹

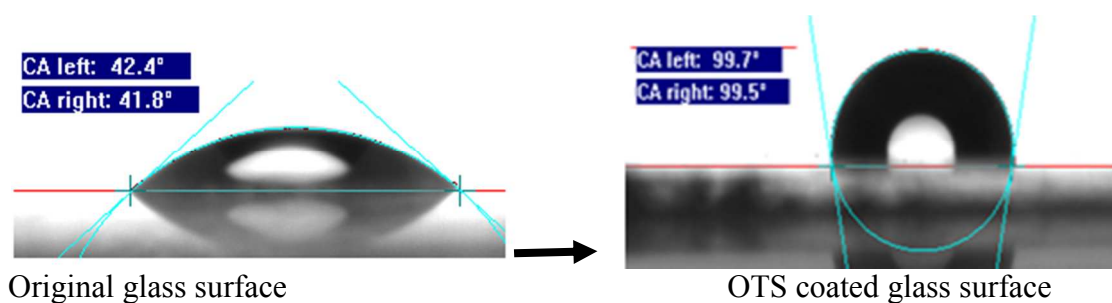


Figure S3. Contact angle measurement of pristine and OTS modified glass slides. OTS treatment increased the contact angle from 42° to 99°.

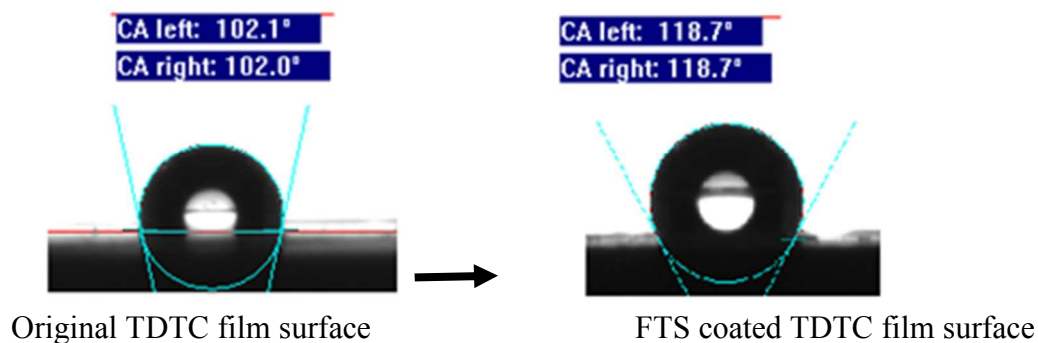


Figure S4. Contact angle measurement of pristine and FTS modified TDTC film. FTS treatment increased the contact angle from 102° to 118°.

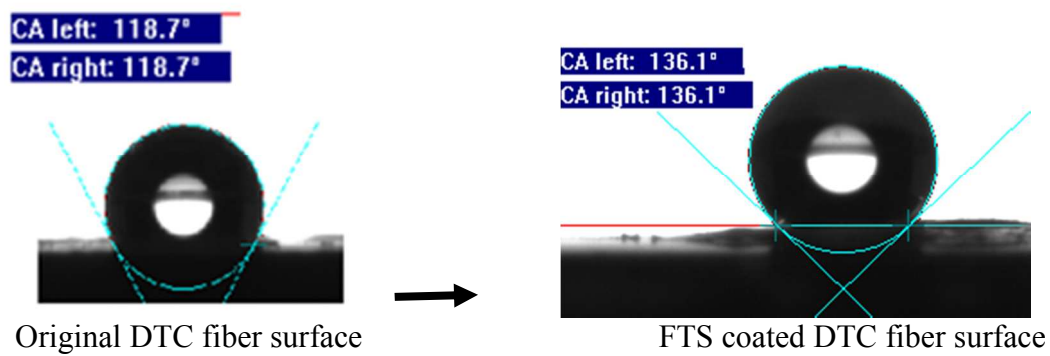


Figure S5. Contact angle measurement of pristine and FTS modified DTC nanofibers. FTS treatment increased the contact angle from 118° to 136°.

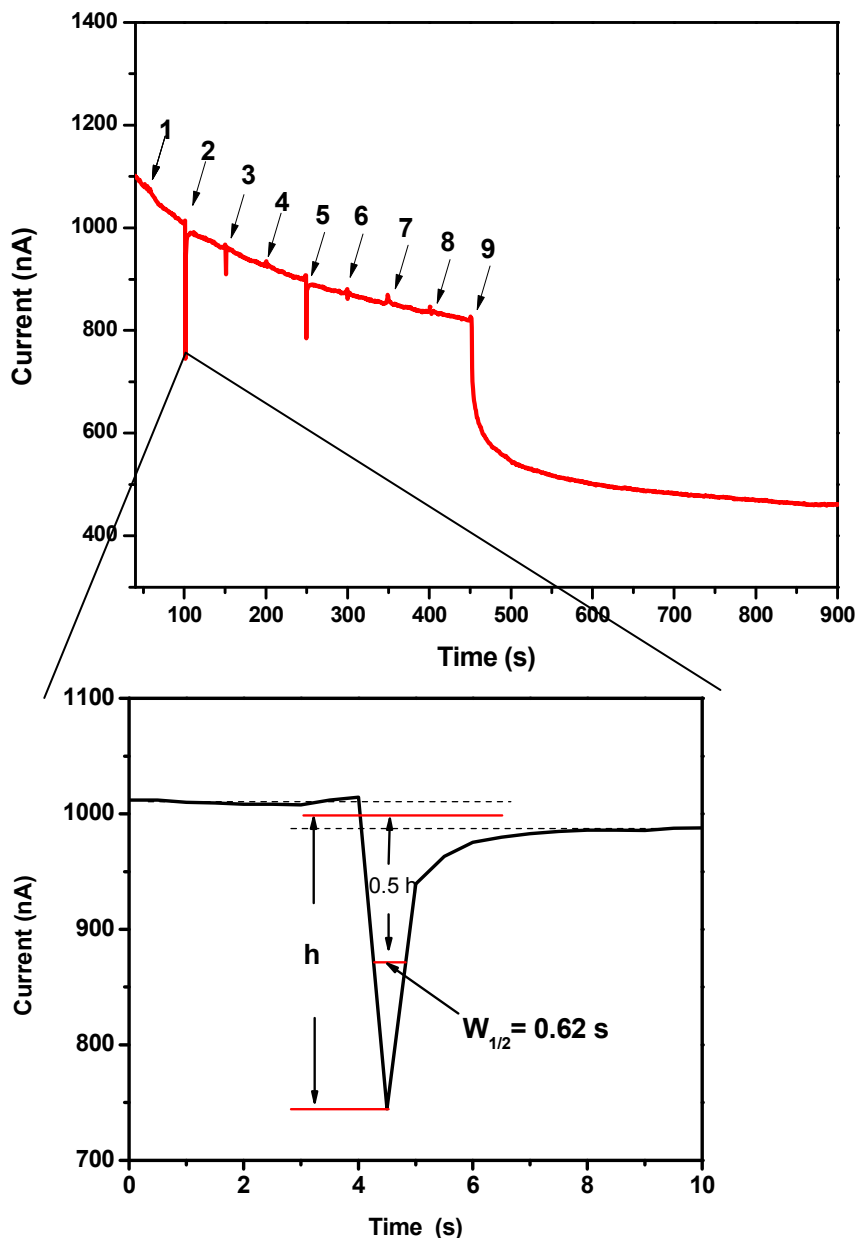


Figure S6. Electrical current measured over the FTS modified DTC nanofibers upon successive exposure to aniline and common organic solvent vapors: 1. air flow, 2. 410 ppm acetone, 3. 350 ppm chloroform, 4. 75 ppm toluene, 5. 350 ppm THF, 6. 150 ppm ethanol, 7. 260 ppm hexane, 8. 140 ppm nitromethane, 9. 8 ppm aniline. The spike signals caused by acetone, chloroform and THF are likely due to the nonspecific solvent effect (e.g., surface desorption of oxygen, commonly observed for other nanomaterial sensors), though this quick, reversible response (in time range of only 0.6 sec) can be easily distinguished from the response of amines. The rapid recovery of the spike signal caused by the solvent vapor is consistent with the weak, non-specific physical adsorption of the solvent molecules on the nanofiber, which can be desorbed quickly upon re-exposure to clean air. In comparison, the electrical current response to aniline vapor was almost irreversible in the time course of experiment, which is apparently due to the strong binding between amine and the nanofiber.

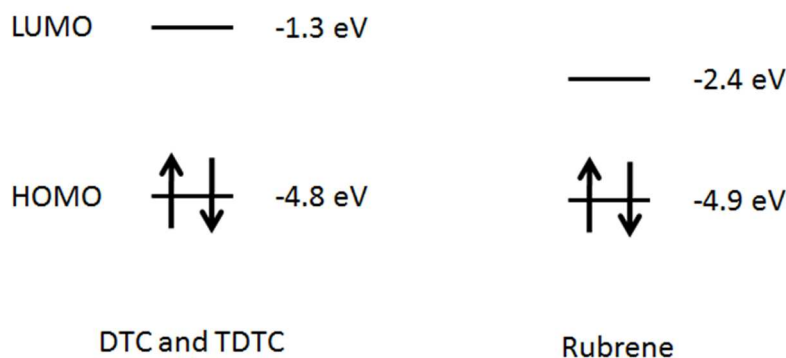


Figure S7. Molecular orbital energy levels of DTC, TDTC and rubrene. Geometry optimization and energy calculations were performed with density-functional theory (B3LYP/6-311g**//B3LYP/6-31g*) using Gaussian 09 package. The direct electron transfer between the rubrene and FTS molecules has been proven in the previous literature with electron spin resonance experiments.² Since the HOMO levels of DTC are even slightly higher than rubrene, the direct electron transfer between DTC and FTS molecules is thus expected.

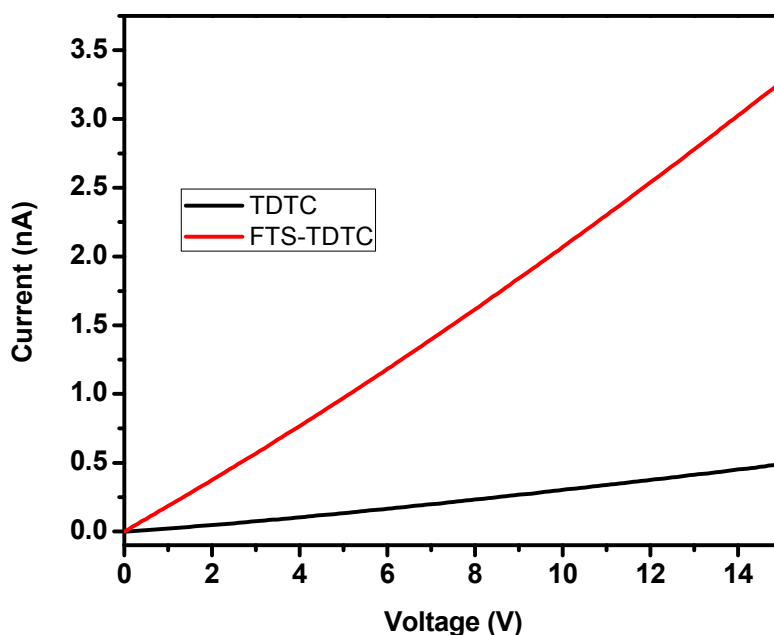


Figure S8. Current-Voltage (I-V) curves for bare TDTC film and FTS-coated TDTC film. Thin films were deposited on a gold electrode pair with a gap of 5 μm and width of 10 μm . The conductivity of FTS-coated TDTC film shown only a few-fold increase compared with the pristine TDTC film.

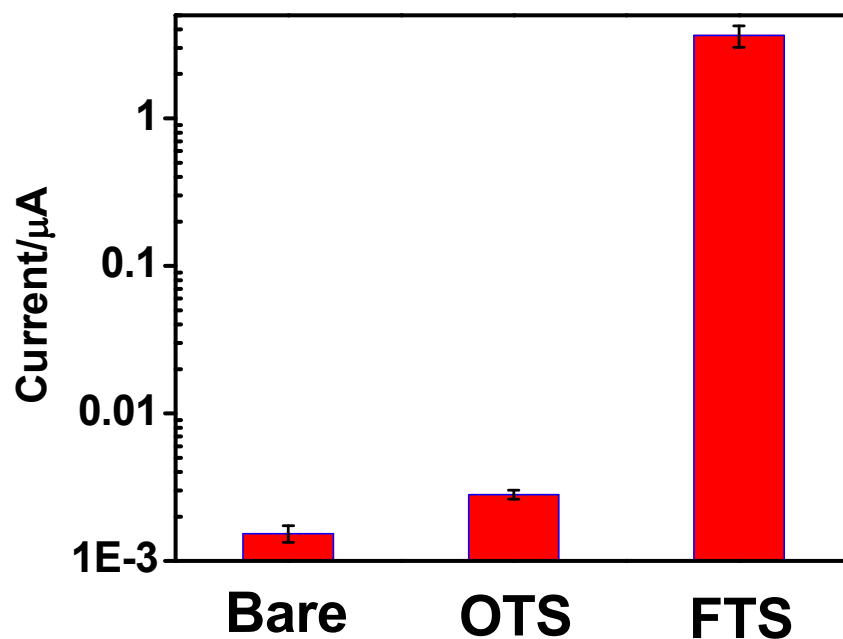


Figure S9. Comparison of the conductivity of bare, OTS and FTS coated DTC nanofibers. The nanofibers were deposited onto the same electrodes as in Figure 1 using the same drop-casting method as described in the Experimental Section. For each case the nanofibers were deposited onto 3-5 electrodes and measured for the I-V curve as shown in Figure 1; the electrical current value measured under a bias voltage of 30 V was used for the conductivity comparison shown in this plot, for which the small error bar reflects the slight variation between different devices thus fabricated.

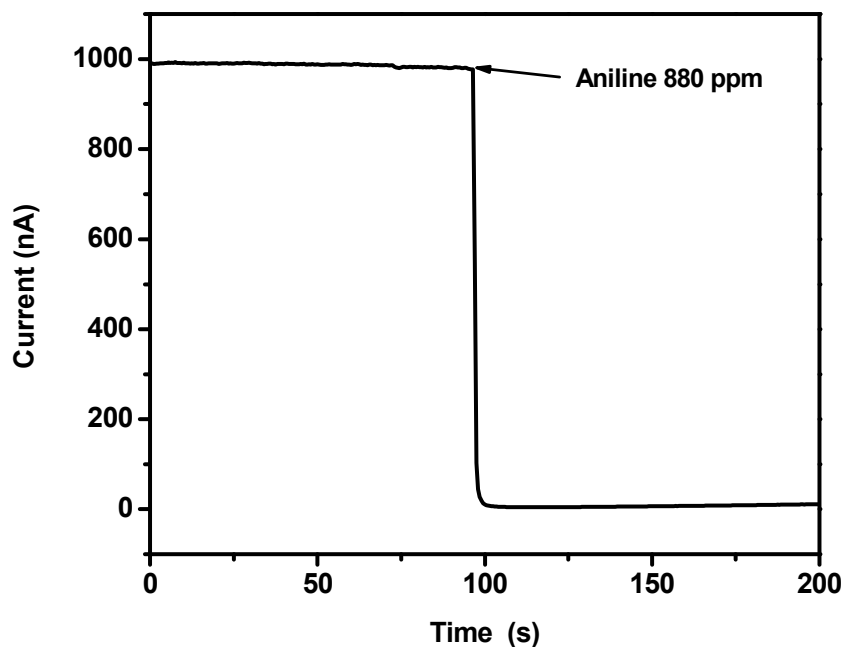


Figure S10. Electrical current measured over the FTS modified DTC nanofibers upon exposure to the saturated vapor of aniline under ambient condition (880 ppm). Nanofibers were deposited on the electrodes with a gap of 5 μm and width of 10 μm and measured under 30 V bias. Under this high vapor pressure, the electrical current was apparently decreased to zero level, indicating that the sensor was saturated with the aniline vapor.

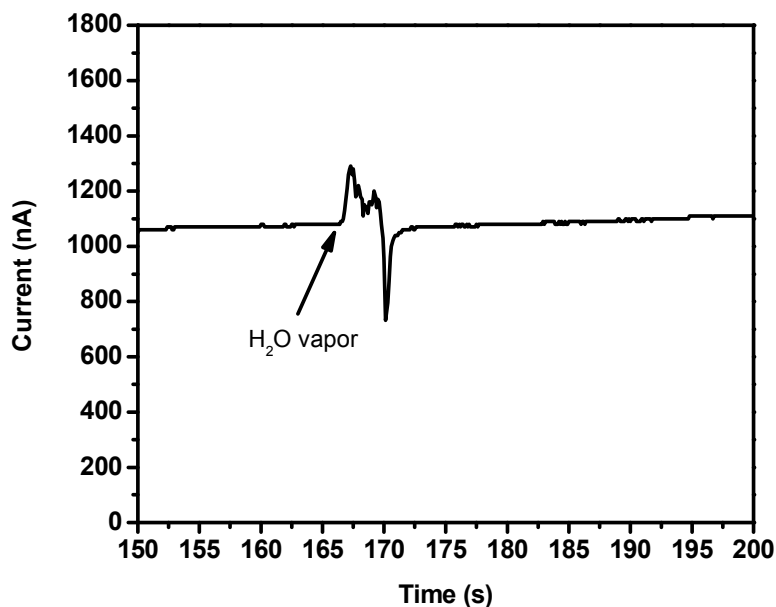


Figure S11. Electrical current measured over the FTS modified DTC nanofibers upon exposure to saturated water vapour (23000 ppm). Nanofibers were deposited on the same electrodes with a

gap of 5 μm and width of 10 μm and measured under 30 V bias. As observed for the organic solvent vapor, exposure to high concentration water vapor causes spike-like fluctuation of electrical current due to some non-specific interfacial interaction, though the signal fluctuation was very fast (only 5 seconds), and completely reversible, which can be easily distinct from the response to aniline and other amines vapor.

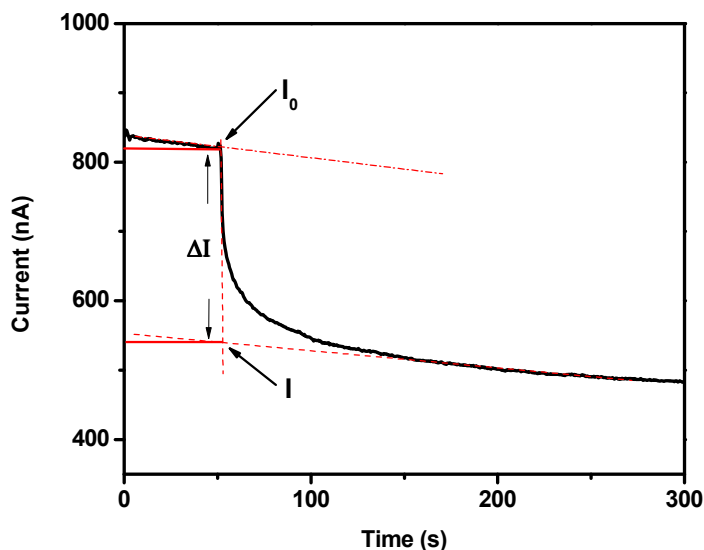


Figure S12. A plot showing how to get the current change ($\Delta I = I_0 - I$) from the current (I) vs. time (s) curve. This method considers the slow drifting of the baseline. The data presented in this plot are from Figure S6, upon exposure to 8 ppm aniline. Using the same method, we can get the ΔI values for the case of exposure to 880 ppm (Figure S10) and 80 ppb (Figure 3).

Langmuir fitting of the current change (ΔI) vs. vapor concentration of aniline:

Using the method presented in Figure S12, the current change ($\Delta I = I_0 - I$) can be obtained for the various vapor concentrations (pressures) of aniline, 0, 80 ppb, 8 ppm and 880 ppm, as presented in the table below:

vapor pressure of aniline	Relative current change observed ($(I_0 - I)/I_0$)
0	0
0.08	0.23
8	0.35
880	0.97 (close to 100%, sensor likely saturated)

Assuming an equilibrium was reached upon exposure to aniline vapor (which is reasonable considering the strong surface binding of aniline), the data shown in the above table should

follow the Langmuir adsorption model. First, the surface adsorption of aniline (i.e., surface density, X) is related to the vapor pressure of aniline as described by the Langmuir Equation,

$$X = \frac{k \cdot [\text{aniline}]}{1 + k \cdot [\text{aniline}]}$$

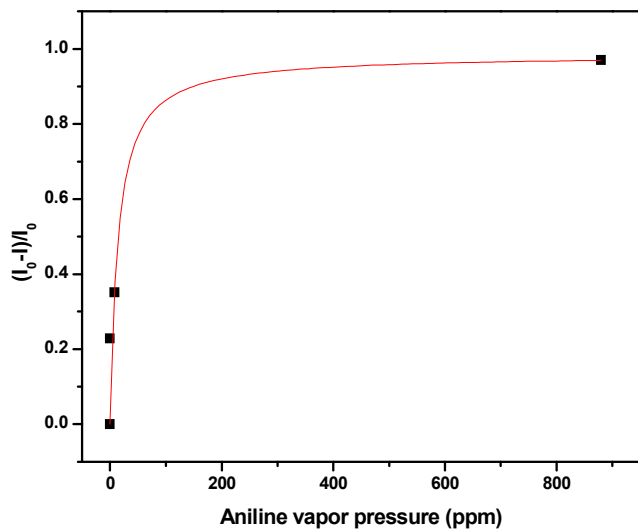
Where k is a constant, $[\text{aniline}]$ is the vapor pressure (concentration) of aniline.

The decrease in electrical current is proportional to the surface density of aniline molecules. Then, we have

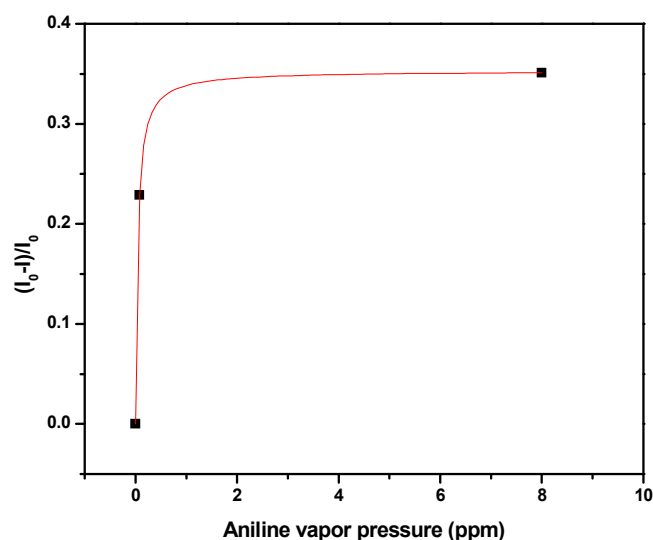
$$\Delta I/I_0 = \frac{a \cdot k \cdot [\text{aniline}]}{1 + k \cdot [\text{aniline}]}$$

Where a is a proportional constant.

Fitting this equation with all the four data points in the table above gives the plot shown below:



However, considering the fact that the sensor was likely saturated under high vapor pressure of aniline (880 ppm, see Figure S10), which led to close to 100% decrease in current, we decided to fit the three data points in low vapor concentration range (as shown in the plot below), which gives $a=0.35$, $k=23$ with a $R^2=1$.



The standard derivation of the electrical current measurements under vapor pressure of 80 ppb (Figure 3), 8 ppm (Figure S6) and 880 ppm (Figure S10) was (on average) about 1 nA. If we set the threshold of detectable current change at a value three times of the standard derivation, that's $\Delta I = 3$ nA, the corresponding detection limit can be determined by using the above fitting (by setting I_0 at a regular level of 1000 nA). This gives a detection limit of aniline vapor at 0.38 ppb.

Amine type	Names	Vapor pressure	Conductivity change
Aliphatic	Dodecylamine	18.4 ppm	-25%
	Trihexylamine	7.5 ppm	-10%
Aromatic	Triphenylamine	455 ppb	-60%
	2,4,6-Tri-tert-butylaniline	65 ppb	-30%
	4-Aminobiphenyl	1.1 ppm	-30%
	4-Dodecylaniline	200 ppb	-25%
	aniline	80 ppb	-25%

Table S1. Comparative sensing tests against the vapor of varying organic amines. The FTS modified DTC nanofibers used are the same as that in Figure 3. Each amine was tested on a freshly made new device. Similar to the response to aniline, the nanofibers demonstrate

significant conductivity modulation upon one-time exposure to diluted vapor of both aliphatic and aromatic amines, indicating that the reported nanofiber composite functions as a general amine sensor, in the similar manner as n-type semiconductor chemiresistors.

References:

- (1) Kobayashi, S.; Nishikawa, T.; Takenobu, T.; Mori, S.; Shimoda, T.; Mitani, T.; Shimotani, H.; Yoshimoto, N.; Ogawa, S.; Iwasa, Y. *Nat. Mater.* **2004**, *3*, 317-322.
- (2) Calhoun, M. F.; Sanchez, J.; Olaya, D.; Gershenson, M. E.; Podzorov, V. *Nat. Mater.* **2008**, *7*, 84-89.