

Supporting Information for
Discrimination of Alkyl and Aromatic Amine Vapors Using
TTF-TCNQ Based Chemiresistive Sensors

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Experimental Section

Materials. Tetrathiafulvalene (TTF), 7,7,8,8-tetracyanoquinodimethane (TCNQ), and the amines (butylamine, hexylamine, dodecylamine, triethylamine, benzylamine, cyclohexylamine, dibutylamine, aniline, o-toluidine, p-toluidine, N,N-dimethylaniline, and 4-fluoroaniline) were obtained from Sigma-Aldrich and used without further treatment. To make TTF-TCNQ microfibers, 1 mL of freshly made TCNQ solution (5 mM in acetonitrile) was mixed with 1 mL of freshly made TTF solution (5 mM in acetonitrile), wherein precipitation of the cocrystals of TTF-TCNQ occurred instantly. The microfibers suspension thus prepared was aged for about 5 min before being filtered or transferred to make chemiresistors.

UV-vis absorption spectral measurement. 1 mM stock solutions of TCNQ were prepared in toluene, chloroform and acetonitrile. 4 mL of each of the solutions was transferred into a quartz cuvette for UV-vis spectral measurement on an Agilent Cary 100 series spectrophotometer. Then 31.3 μL of hexylamine (the density is 0.766 g/mL at room temperature) or 23.5 μL of aniline (the density is 1.022 g/mL at room temperature) was injected quickly into each of the 4 mL TCNQ solutions, followed by shaking. After 1 min, the TCNQ and amine mixed solution was measured for UV-vis absorption spectra in comparison to the amine free solution as shown in Figure S4.

XRD and FTIR measurement. The TTF-TCNQ materials used for XRD and FTIR measurement were prepared via filtering the TTF-TCNQ microfibers suspension, followed by vacuum drying. A Bruker D2 Phaser XRD instrument was used to perform the XRD measurement. For FTIR measurement, KBr pellets containing TTF, TCNQ, TTF-TCNQ microfibers, and TTF-TCNQ microfibers mixed with dodecylamine were made and measured on a Nicolet Magna 750 Fourier transform infrared spectrometer equipped with a liquid-nitrogen-cooled mercury cadmium telluride detector. Pure were obtained from Sigma-Aldrich and used without further treatment. TTF-TCNQ microfibers were prepared following the method described above. Some of the

microfibers were used directly in preparing the KBr pellet for FTIR measurement. The rest of the microfibers were dispersed in chloroform under a few seconds of bath ultrasonication, followed by addition of dodecylamine at 1% (molar ratio) of the amount of TTF-TCNQ. Since chloroform is a poor solvent for TTF-TCNQ cocrystal, but a good solvent for dodecylamine, we expected that dodecylamine would be molecularly dispersed in the chloroform suspension of TTF-TCNQ microfibers, allowing for full surface access of dodecylamine to the microfibers. The mixture thus obtained was then fully dried overnight under ambient condition in a fume hood, and the resulted solid of TTF-TCNQ microfibers should be covered with sufficient dodecylamine. The dry mixture thus obtained was used to make a KBr pellet for IR measurement. The FTIR spectra recorded from the four samples above are shown Figure S7 below.

Sensor materials preparation. The sensor testing was performed with the similar methods as described in our previous work¹. The sensor chip was fabricated by depositing sensor material onto interdigitated electrodes (IDEs) patterned on a glass wafer. The IDEs have 20 gold finger pairs, with each pair about 5 mm in total width, 10 μm , or 100 μm in gap. The total area of IDEs is about 5 mm \times 5 mm in size. 5 mM acetonitrile solutions of TTF and TCNQ were prepared separately. To make TCNQ (or TTF) chemiresistive sensors, 0.2 mL of freshly made TCNQ (or TTF) solution in acetonitrile was drop-cast on the IDEs. To make TTF-TCNQ chemiresistors, 0.2 mL of the TTF-TCNQ microfibers suspension was transferred onto the IDEs via a drop-casting method. All IDEs coated were kept overnight under ambient condition before testing.

Senor testing experiments. In a typical vapor preparation, 10 mL liquid or 10 g solid of amines was sealed in a 4 L amber glass bottles for 1 day at room temperature to reach the gas/liquid, or gas/solid equilibrium states. Before the measurement, the saturated vapor was taken out with a 50 mL glass syringe and diluted with dry air. Different amines were diluted to about 100 ppm for easy comparison: butylamine (ca. 110 ppm, corresponding to 1/1000 dilution of saturated vapor), hexylamine (ca. 120 ppm, 1/100 of saturated vapor), dodecylamine (18 ppm, no dilution), triethylamine (ca. 100 ppm, 1/700 of saturated vapor), benzylamine (ca. 95 ppm, 1/10 of saturated vapor), cyclohexylamine (ca. 90 ppm, 1/150 of saturated vapor), dibutylamine (ca. 100 ppm, 1/25 of saturated vapor), aniline (ca. 100 ppm, 1/8 of saturated vapor), o-toluidine (ca. 100 ppm, 1/4 of saturated vapor), p-toluidine (ca. 100 ppm, 1/4 of saturated vapor), N,N-dimethylaniline (ca. 100 ppm, 1/13 of saturated vapor), and 4-fluoroaniline (ca. 100 ppm, 1/8 of saturated vapor). Then the syringe containing the diluted amines was mounted to a syringe pump (Model: NE-4000, New Era Pump System. Inc.) and fitted with a short needle. The needle end was fixed 1 cm away from the sensor materials deposited on IDEs by a holder. 5 mL of vapor was pumped at a speed of 110 mL/min in each exposure. For each amine four cycles of exposures were performed, and the time interval between two consequent exposures was 2 min. The resistance change (measured as current change) was recorded with an Agilent 4156C Precision Semiconductor Parameter Analyzer. The bias applied to pure TCNQ, pure TTF and TTF-TCNQ material were 10 V, 10 V and 0.1 V, respectively. All current-time curves were presented without baseline correction.

Supplementary figures

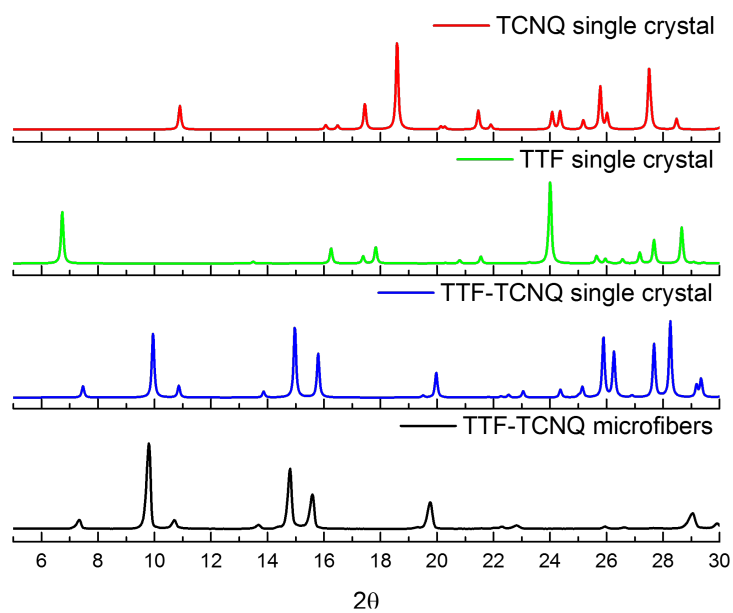


Figure S1. XRD spectra for TTF-TCNQ microfibrils, in comparison with the powder simulated XRD spectra from the single crystal structures of TCNQ², TTF³ and TTF-TCNQ⁴.

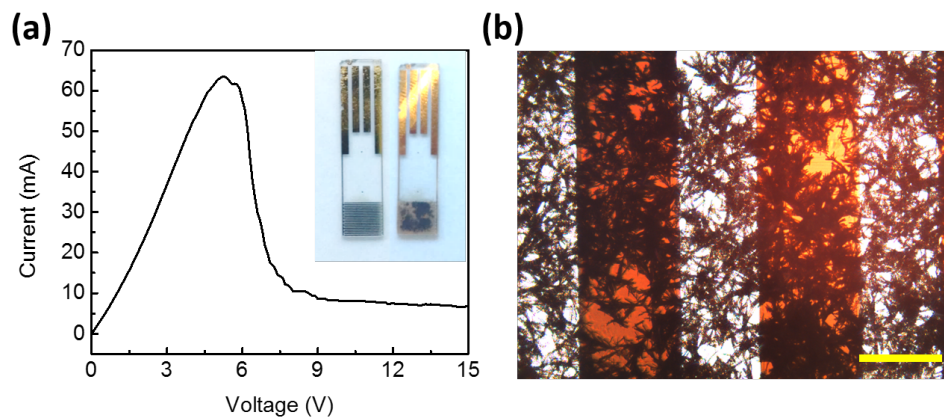


Figure S2. (a) A typical I-V curve measured on the TTF-TCNQ microfibers coated on the IDEs. Inset: The photos taken on the IDEs before (left) and after (right) coating of the TTF-TCNQ microfibers. (b) Optical microscope image of the TTF-TCNQ microfibers coated on the IDEs. Scale bar = 100 μm.

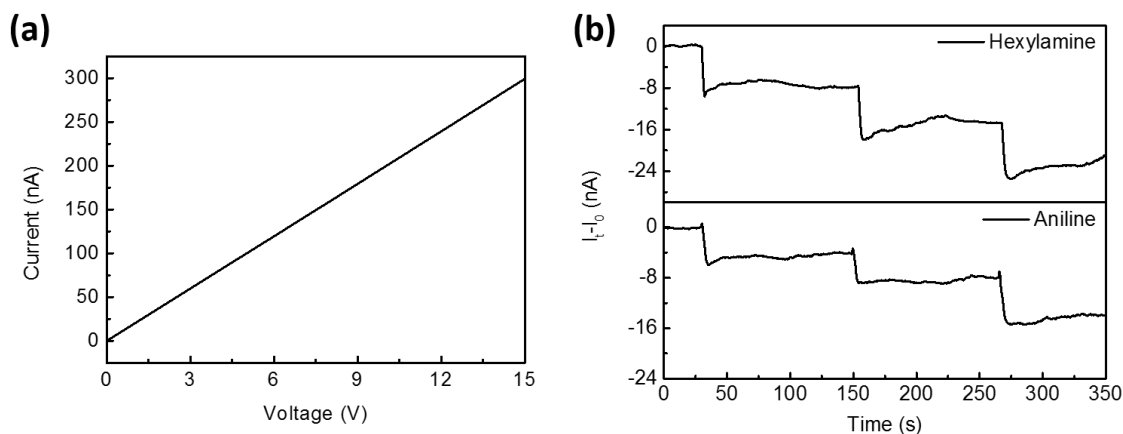


Figure S3. (a) A typical I-V curve measured on the TTF sample deposited on the same IDEs. (b) Change of electrical current of the TTF sample upon exposure to the vapor of hexylamine (120 ppm, top) and aniline (100 ppm, bottom) with 10 V bias voltage. Since all these responses were in the range of nA, combining that the TCNQ responses ranged within sub-nA (Figure 3), the contributions to the current response from the impurity of TTF or TCNQ (if any) can be excluded in TTF-TCNQ chemiresistors.

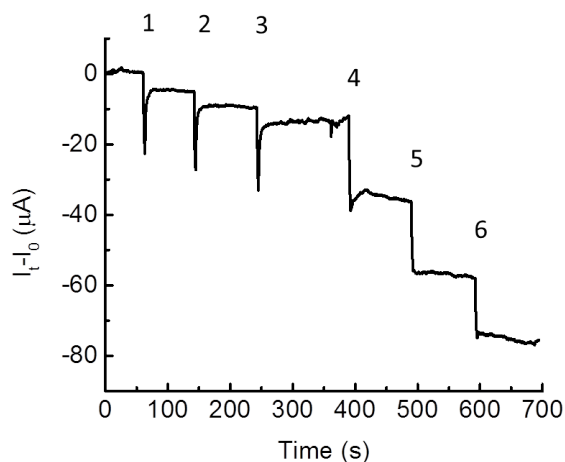


Figure S4. The current change of TTF-TCNQ fibers coated onto the IDEs measured upon 3 consequent exposures to ca. 100 ppm aniline vapor (labeled 1-3), followed by another 3 consequent exposures to ca. 120 ppm hexylamine vapor exposures (labeled 4-6). The current fluctuation between 3 and 4 was due to the operation of changing amine source.

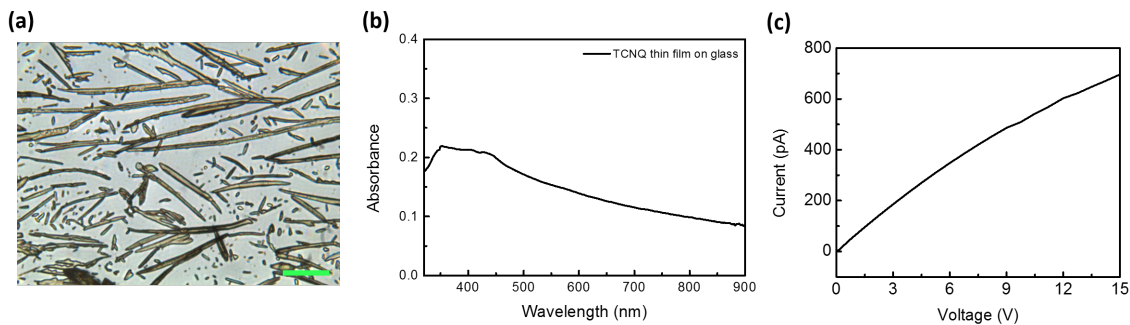


Figure S5. (a) Optical microscope image of TCNQ crystalline microfibers; scale bar = 50 μm . (b) UV-vis absorption of the TCNQ microfibers deposited on glass substrate, indicating no TCNQ anionic radicals formed. (c) An I-V curve measured for the TCNQ microfibers coated on the IDEs.

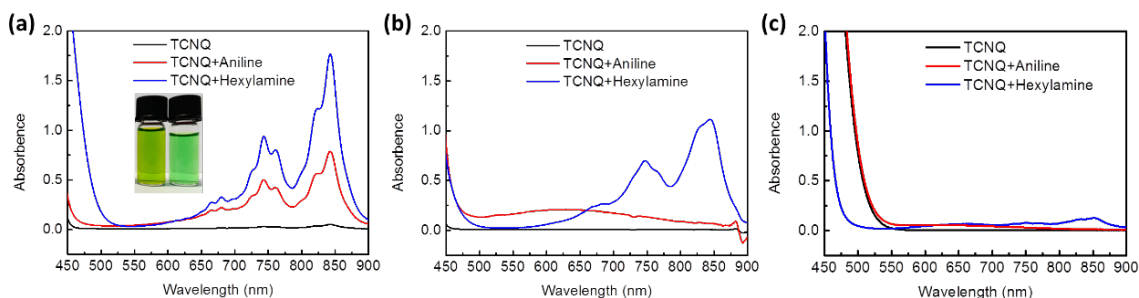


Figure S6. UV-vis absorption spectra of the solution of TCNQ (black), TCNQ mixed with aniline (red), and TCNQ mixed with hexylamine (blue) dissolved in (a) acetonitrile, (b) chloroform, and (c) toluene. Concentration of TCNQ was 1 mM, and amine was $6 \text{ g}\cdot\text{L}^{-1}$. Inset in (a): Optical photo of the acetonitrile solution of TCNQ (5 mM) mixed with $6 \text{ g}\cdot\text{L}^{-1}$ aniline (left) and hexylamine (right).

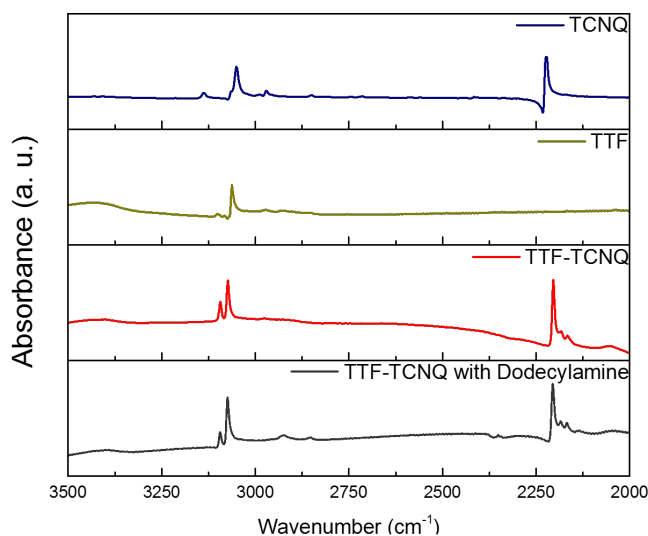


Figure S7. The FTIR spectra of TCNQ, TTF, TTF-TCNQ cocrystal microfibers, and TTF-TCNQ cocrystal microfibers mixed with 1% (molar) dodecylamine. The IR spectra of TTF, TCNQ and TTF-TCNQ cocrystal are well consistent with the previously reported spectra in *ChemCatChem* 2016, **8**, 2335–2339.⁵ The two peaks, $\nu=3062.4 \text{ cm}^{-1}$ and $\nu=3049.9 \text{ cm}^{-1}$, observed for neutral TTF and TCNQ respectively, are blue-shifted to $\nu=3093.3 \text{ cm}^{-1}$ and $\nu=3073.0 \text{ cm}^{-1}$ respectively in the 1:1 TTF-TCNQ cocrystal, and such blue-shift was also observed in *ChemCatChem* 2016, **8**, 2335–2339,⁵ and attributed to the formation of charge transfer complex between TTF and TCNQ. The area ratio of the two peaks obtained for TTF-TCNQ cocrystal is about 2.58 (I_{3073}/I_{3093} , baseline corrected). However, upon mixing with dodecylamine this ratio was more than doubled, increasing to 5.69, indicating that the molar ratio of TTF⁺ cations formed in TTF-TCNQ was reduced by more than 50%. That's to say, more than half of the TCNQ⁻ anions were formed by charge transfer interaction with dodecylamine instead. This IR observation

indicates that the surface adsorbed dodecylamine can effectively compete with TTF by forming charge transfer complex with TCNQ.

References

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