Ambient Photodoping of p-Type Organic Nanofibers: Highly Efficient Photoswitching and Electrical Vapor Sensing of Amines

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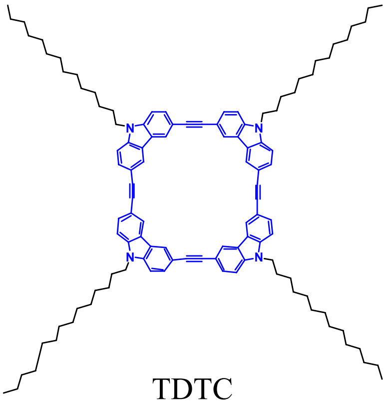
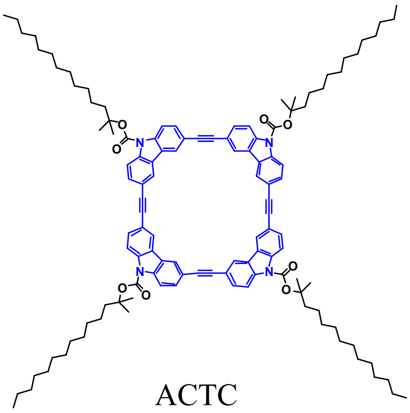
Supporting Information



TDTC



ACTC

Synthesis and fabrication of nanofibers. TDTC and ACTC were synthesized by following the previous method.[1-3] All nanofibers were fabricated by injecting 0.4 mL chloroform solution of TDTC or ACTC (0.15 mM) into 3 mL ethanol in a test tube with stirring and then aging for 2 days in refrigeratory. The nanofibers thus formed can be transferred and cast onto glass surface by pipetting.

Structural and property characterizations. UV-vis absorption and fluorescence spectra were measured on a PerkinElmer Lambda 25 spectrophotometer and LS 55 fluorometer, respectively. SEM measurement was performed with a FEI NanoNova 6300 microscope, and the samples were directly drop-cast on a silica substrate. The FEI NanoNova is a high resolution SEM allowing for direct imaging of non-conducting materials with feature size down to 2 nm. The X-ray diffraction was carried out with a Philips X'Pert XRD instrument. TEM measurement was performed on a JEOL 2010 instrument (LaB6, operated at 200 kV). Electron diffraction patterns were recorded using a CCD camera under controlled electron dose with low illumination intensity to reduce radiation damage of the sample. All the measurements were performed at room temperature using a 300 nm diameter probe.

Photocurrent and vapor sensing measurements. Electrical current measurements of the nanofibers were performed with an Agilent 4156C Precision Semiconductor Parameter Analyzer coupled with a Signatone S-1160 Probe Station housed in a metallic shielding box under ambient condition. The micro-gap electrodes were fabricated by photolithography on a silicon wafer covered with a 300-nm thick SiO_2 dielectric layer. The gold electrode pair is 14 μm long and 4 μm wide, on to which appropriate amount of nanofibers were deposited by drop-casting, followed by air-drying in the dark. A tungsten lamp (Quartzline, 21V, 150W) and Mercury lamp (Newport, 200 W) was used as the white light source and UV light source, respectively. The light is guided into the probe station through a glass or quartz optical fiber, followed by focusing on the sample through the objective lens. The vapor sensing measurements were carried out by directly blowing diluted aniline or other common organic vapor onto nanofibers by a syringe.

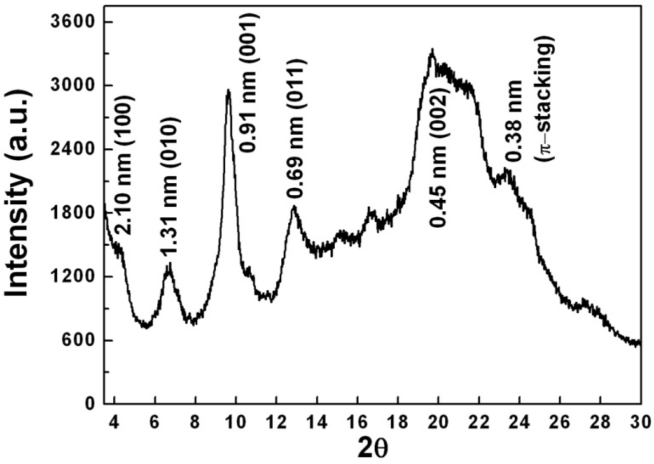


Fig. S1 XRD spectrum of the TDTC nanofibers (d-spacing = 0.38 assigned to π-π interaction[2]).

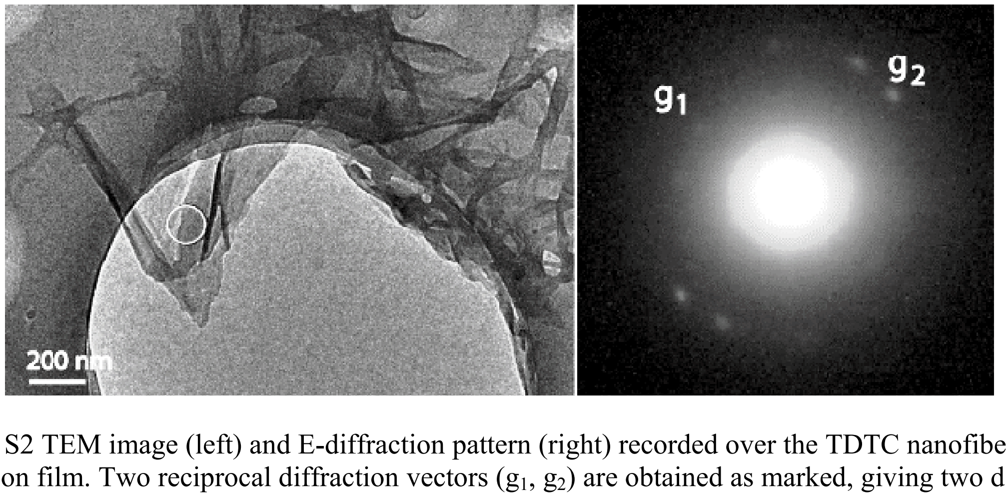


Fig. S2 TEM image (left) and E-diffraction pattern (right) recorded over the TDTC nanofibers cast on a carbon film. Two reciprocal diffraction vectors (g_1, g_2) are obtained as marked, giving two d-spacings, d1 = 0.94 nm and d2 = 1.24 nm.

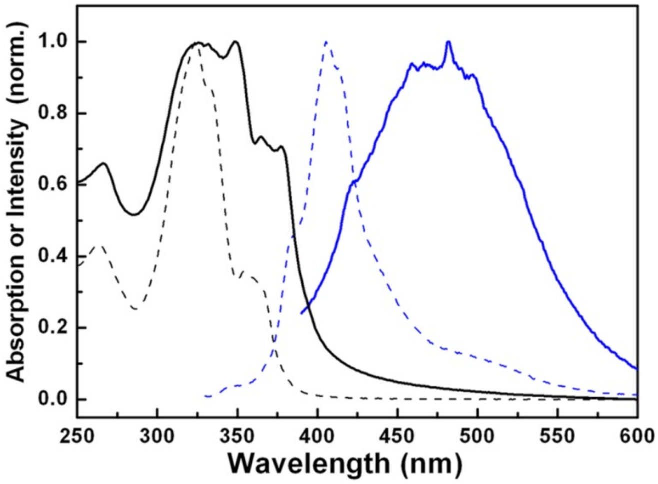


Fig. S3 The absorption (black) and fluorescence (blue) spectra of TDTC in chloroform solution (dashed) and the nanofiber state (solid).

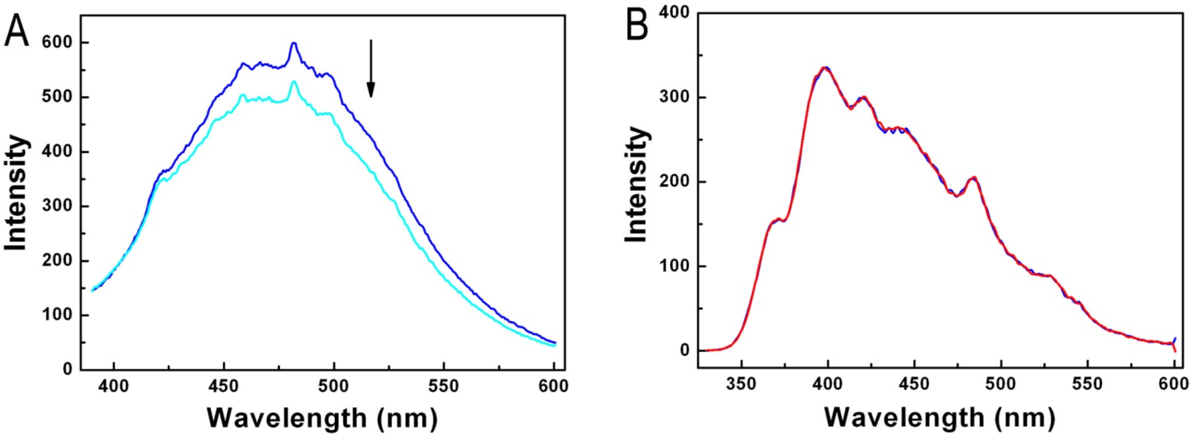


Fig. S4 A) Fluorescence emission spectra of TDTC nanofibers under argon gas (blue) and ambient condition (cyan); B) Fluorescence emission spectra of ACTC nanofibers under argon gas (red) and ambient condition (blue).

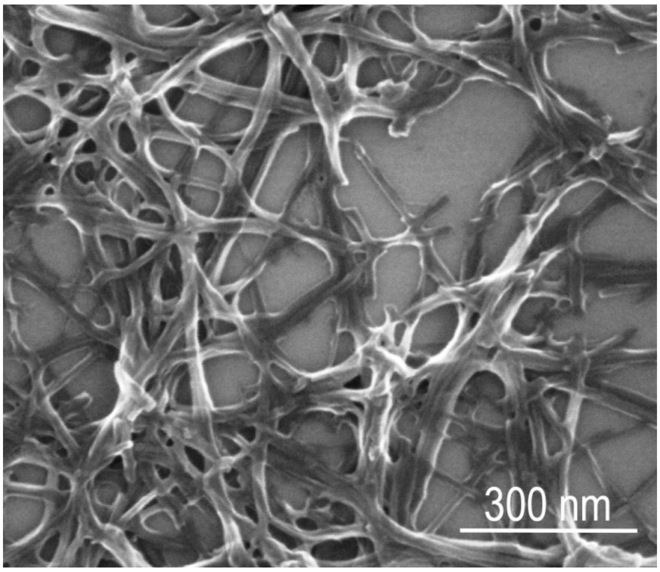


Fig. S5 A SEM image of the nanofibers fabricated from ACTC.

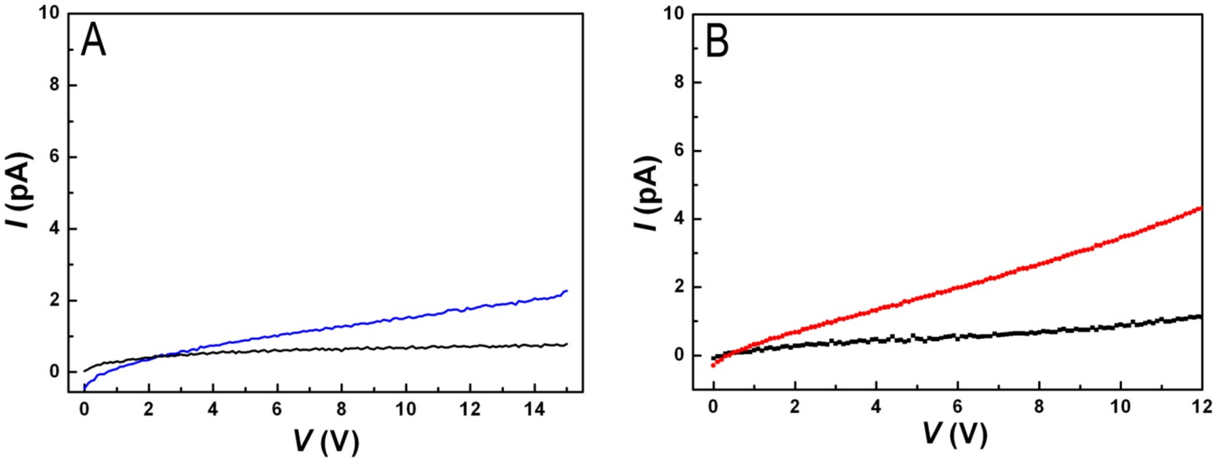


Fig. S6 A) I-V curves measured over ACTC nanofibers in the dark (black) and under the irradiation of white light at power density of 0.3 mW/mm^2 (blue); (B) I-V curves measured over ACTC nanofibers in the dark (black) and under the irradiation of UV light (from a mercury lamp) at power density of 2 mW/mm^2 (red).

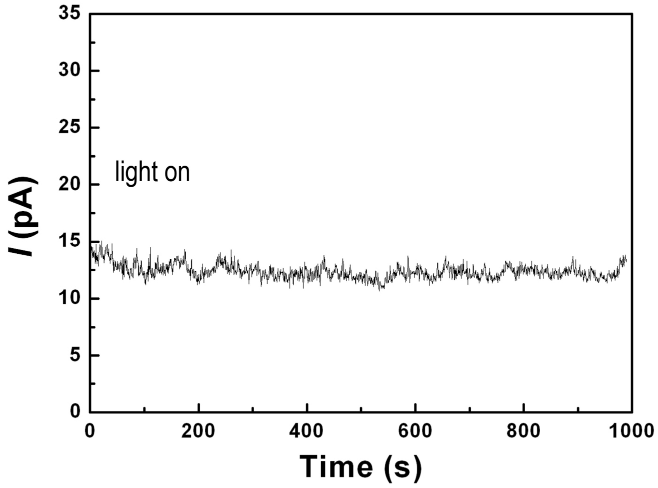


Fig. S7 Photocurrent change (at 10V) of TDTC film with time following argon gas introduction (monitored 25 min after argon gas started)

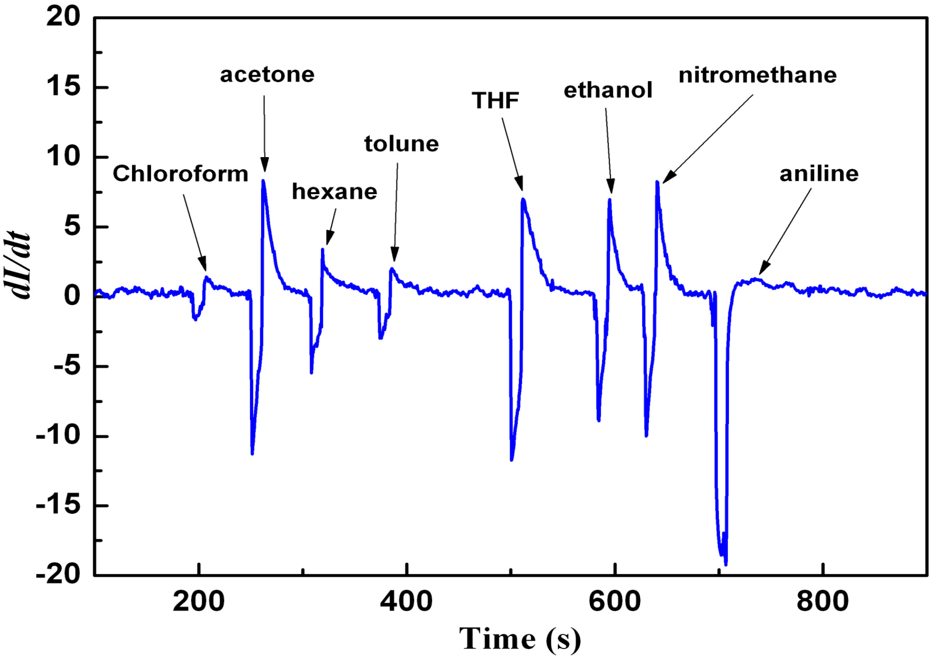


Fig. S8 First order differentiation of Figure 3B (dI/dt vs. time) showing the different response to aniline as compared to the 7 reference reagents vapor: while quite symmetric "pulse" signal was observed for all the reference reagents, the response to aniline remained asymmetric with negligible signal on the positive side. Such an observation can be used to distinct amines from other common liquids or solvents as discussed in the context.

References:

1. Naddo, T.; Che, Y.; Zhang, W.; Balakrishnan, K.; Yang, X.; Yen, M.; Zhao, J.; Moore, J. S.; Zang, L. *J. Am. Chem. Soc.* **2007,** 129, 6978-6979.
2. Balakrishnan, K.; Datar, A.; Zhang, W.; Yang, X.; Naddo, T.; Huang, J.; Zuo, J.; Yen, M.; Moore, J. S.; Zang, L. *J. Am. Chem. Soc.* **2006,** 128, 6576-6577.
3. Zhang, W.; Moore, J. S. *Angew. Chem. Int. Ed.* **2006,** 45, 4416-4439.