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Supporting Information

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Single-crystal Organic Nanowires of Cu-TCNQ: Synthesis, Patterning, Characterization and Device Applications

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Experimental Section

Nanowire growth: a 50 nm thin film of Cu was deposited with e-beam evaporation onto substrates (Si, glass and PET foil). TCNQ powders were loaded into a ceramic boat and the substrate with Cu film was placed on the top of the ceramic boat with the Cu film-coated side facing down. The boat with substrates was placed into a 2" quartz tube that was inserted into a tube furnace. The reaction temperature and time were precisely controlled. The temperature was first increased to 120 °C and then kept at that temperature for 2 h. Finally, the temperature was decreased to the room temperature. In the process, the argon gas flow rate was kept at 50-80 standard cubic centimeters per minute (sccm).

Characterization: SEM observations were performed with a Hitachi S4700. TEM measurements were performed with a Hitachi HF2000 (operated at 200 kV) and a JEOL 2010F (operated at 200 kV). Samples were prepared by dropping a methanol solution of suspended Cu-TCNQ nanowires onto a carbon film-coated Cu TEM grid, or by directly growing nanowires on a pure Cu TEM grid in TCNQ vapor in Ar for 2 hours. The Raman spectra of the Cu-TCNQ nanowires were recorded by a Renishaw 1000 confocal microRaman spectrometer utilizing an excitation wavelength of 633 nm.

Nanowire patterning: Patterned Cu thin films on substrates were fabricated using photolithography and e-beam lithography methods. For the quadrangle and line patterns (Fig.2a and 2b), SPR 220 3.0 was used as photoresist. The resist was spun with 4000 rpm for 1 minute, then baked at 120°C for 90 s. Exposure was carried out on a Karl Suss contact aligner for 7 s. Post-exposure bake was done at 120°C for 90 s. The wafer was then developed in CD 26 for 2 min. After descum for 30 s, 50 nm-thick Cu was deposited onto the wafer through e-beam metal evaporation, then lifted off with acetone.

For the patterned Cu nanodots, the Si substrate was spun165 nm thick PMMA (2%). An array of different diameters (100 or 300 nm) holes was then patterned using e-beam lithography and the pattern was developed using MIBK: IPA (1:3). After several seconds of reactive ion etching (RIE) (50 sccm, 95 W), different thicknesses (10, 50, 100 nm) of Cu were deposited through e-beam evaporation and the pattern was lifted off using acetone. This process forms 100 nm or 300 nm diameter islands of Cu on a Si substrate, from which the Cu-TCNQ nanowires were grown.

Patterned arrays of Cu-TCNQ nanowires were grown on the substrate with pre-patterned Cu islands using the above mentioned method.

Device fabrication and testing: The cross-point memory device was fabricated through the following process. First the bottom Ti (20 nm)/Cu (100 nm) electrode was evaporated onto a PET plastic substrate in a vacuum of 10^{-5} Torr using a shadow mask. Then the Cu-TCNQ nanowire network active layer was grown on the patterned plastic substrate. Finally, the device was completed by deposition of aluminum electrodes on the nanowires. The top and bottom electrodes had a linewidth of 0.2 mm and were aligned perpendicularly to form the cross-point device structure. The *I-V* curves of the device were tested in air with an HP4156 semiconductor parameter analyzer using a probe station. The voltage for the write-erase-read cycles was generated and the current on the device was read with a Keithley 6430 Source Meter.

Figure S1

The molecular structure of TCNQ is shown below. TCNQ can easily react with Cu to form the charge transfer complex Cu-TCNQ:

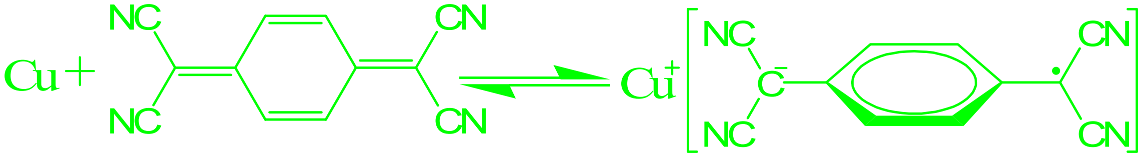

Figure S2
Cu-TCNQ organic nanowires grown at 120°C for 2 hours in argon gas onto evaporated Cu films on the following substrates: (a), glass. (b), Si wafer. (c), PET foil. (d), Cu foil. Digital photographs of Cu-TCNQ nanowires mats on substrates of: (e), glass, (f), Si (g), PET.

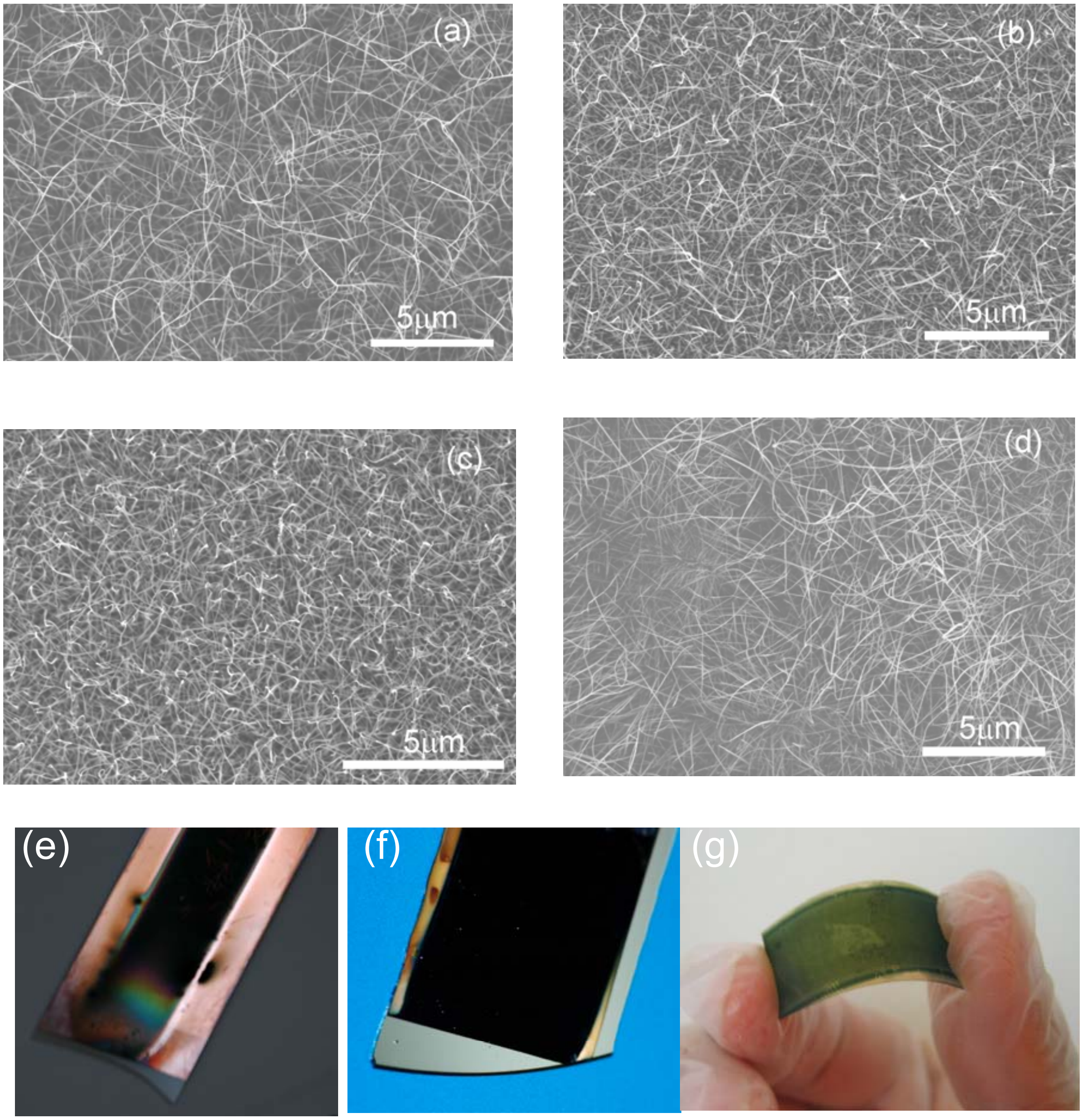

Figure S3

The thickness of the Cu film has a significant influence on the morphology of the Cu-TCNQ nanostructures. The nucleation sites for growth on silicon substrates are Cu islands on the substrate and growth appears to proceed through a simple chemical reaction. $Cu(solid) + TCNQ(vapor) \rightarrow TCNQ - Cu$. As the reaction proceeds, the nanowires grow longer and longer on the nucleation sites until one of the reactants are depleted or some other growth interruption occurs. By limiting the amount of Cu, short nanowires can be grown. When the Cu film is 1 nm thick, the seeds grow only into 150 nm-diameter nanorods less than 300 nm tall. With increasing thickness of the Cu thin film, the Cu-TCNQ nanostructure morphology evolves from nanorods (Fig 3a) to nanocones (Fig 3b), to nanoneedles (Fig 3c), and finally to nanowires up to 20 μm (Fig 3d).

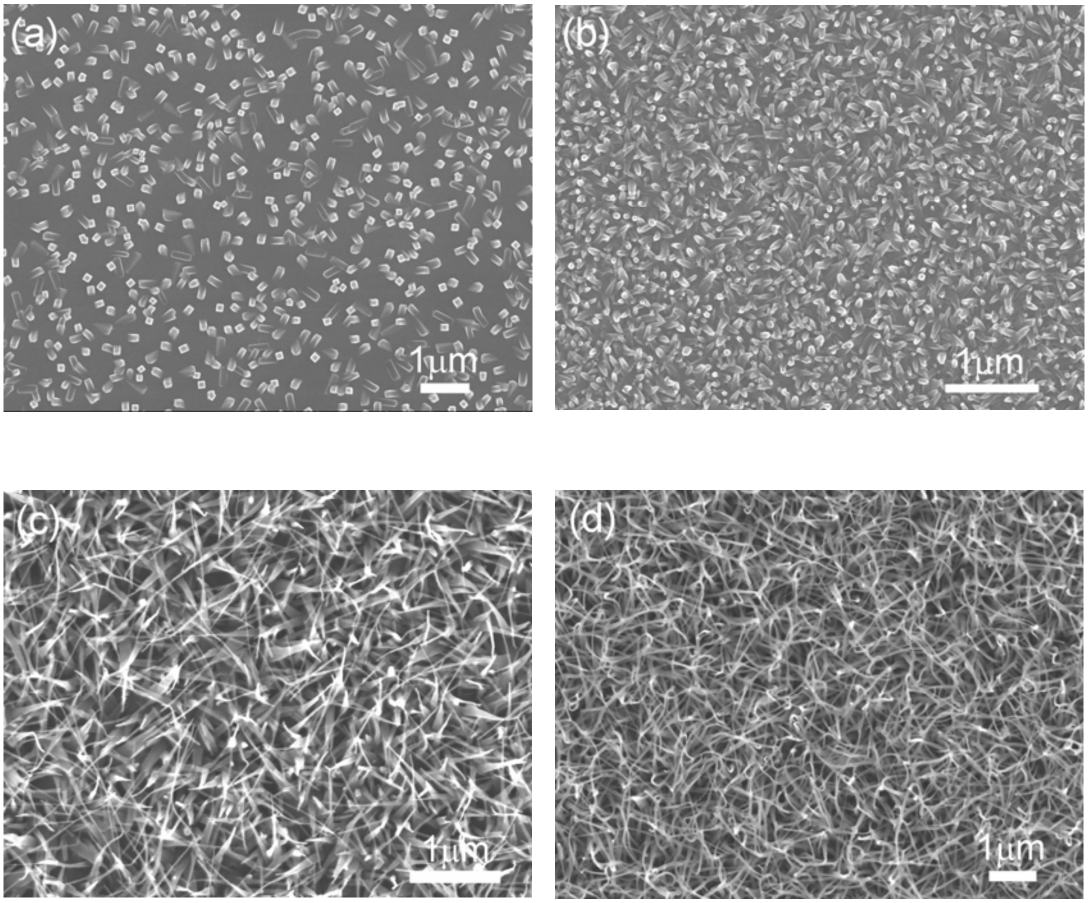

Figure S4

3D graphical representation of the structure of Cu-TCNQ nanowires looking along from the *a* axis (Cu, yellow; C, gray; N, blue). The crystal structure is monoclinic, space group *Pn*, *a* = 3.8878(8)Å, *b* =11.266(2) Å, *c* = 11.266(2) Å, β= 90.00(3)°, *V*= 493.5(2) $Å^3$, *Z*= 2.

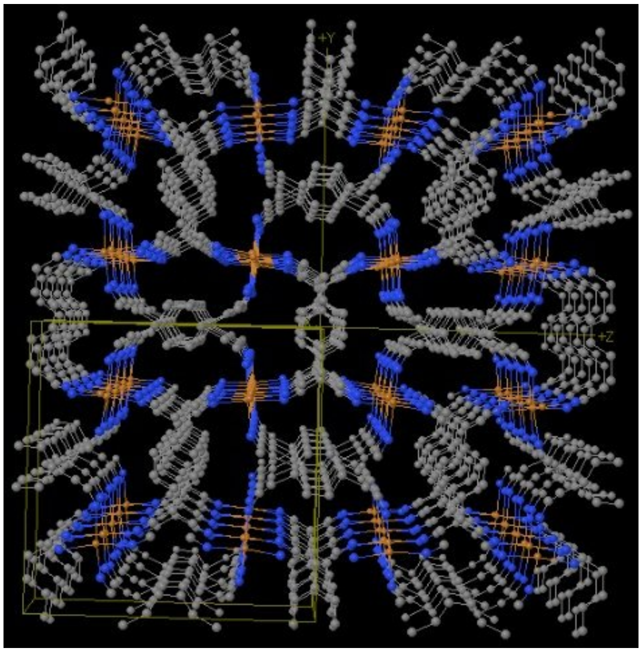

Figure S5

The SEM images of the Cu-TCNQ nanowires grown for different times, the scale bar is 500 nm.

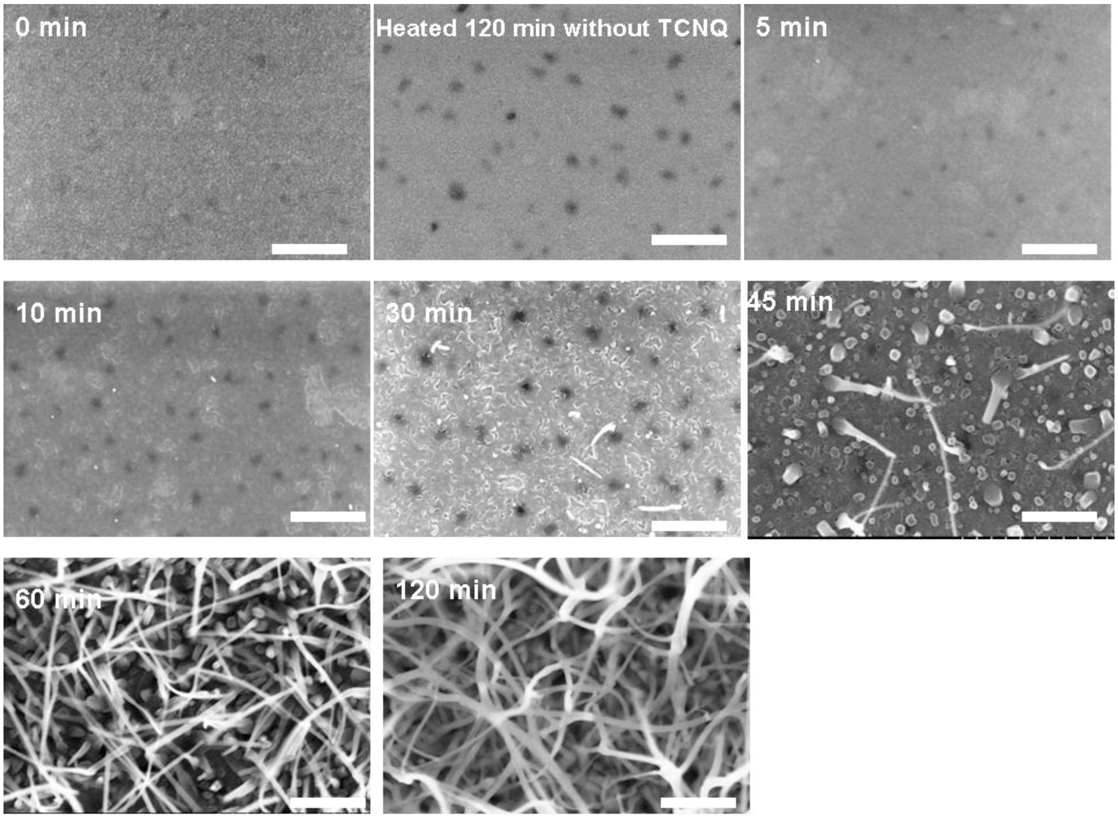

Figure S6

The Raman spectra of the Cu-TCNQ nanowires grown for different times. Inset is the Raman spectra intensity of Cu-TCNQ at different growth times. There are three different growth stages. At the first 30 mins, layers of Cu-TCNQ film form on the Cu surface by chemical reaction. Subsequently, islands of Cu-TCNQ appear and form the nuclei for subsequent, rapid nanowire growth. At last, the Cu-TCNQ nanowires grow successfully from the nuclei on the base.