Supporting Information

# Thermochemical Hole Burning on TEA(TCNQ)<sub>2</sub> Charge-Transfer Complex Using Single-Walled Carbon Nanotube STM Tips

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#### TG-MS analyses of the TEA(TCNQ)<sub>2</sub> crystal

The thermal decomposition behavior of  $TEA(TCNQ)_2$  crystals was studied by the thermogravimetry combined with mass spectrometry (TG-MS). As shown in Figure 1S, the TG curve shows that  $TEA(TCNQ)_2$  begins to decompose at ca. 195 °C and the weight loss between 195 and 220 °C is about 11%. Analysis of the gases evolved during decomposition with MS reveals the formation of ions having a mass-to-charge ratio (m/z) of 26, 27, 58, 86, and 101 amu. The ions at masses 26 and 27 are identified as the cyano groups cleavage to partial TCNQ and the ions at masses 58, 86 and 101 amu are characteristic peaks of triethylamine, which indicated that the possible decomposition mechanism involves the initial cleavage of cyano groups from TCNQ moiety and the subsequent vaporization of the low boiling point component, triethylamine.



**Figure 1S.** TG-MS curves of TEA(TCNQ)<sub>2</sub> single crystal. The numbers correspond to the mass-tocharge ratio of ions detected from the gaseous products. TG curve, left-hand ordinate.

#### SEM image of the edge of a SWNT STM tip



**Figure 2S.** Typical SEM image of the shortened SWNTs standing on the edge of a gold wire tip. The SWNTs are indicated by arrows.

High-resolution STM image of HOPG with a SWNT tip



**Figure 3S.** High-resolution STM image of HOPG with a SWNTs tip. Imaging conditions: 0.80 nA, 0.1 V, constant-current mode.



#### Section analysis of hole written on different planes of TEA(TCNQ)<sub>2</sub> crystal

**Figure 4S.** Section analysis of hole written on the *ab*-plane (a) and the *bc*-plane (b) of TEA(TCNQ)<sub>2</sub>, respectively. Writing condition: a commercial Pt/Ir tip, 8 V × 100  $\mu$ s; Imaging condition: 0.10 nA, 0.1 V, constant-current mode.



Hole array written by voltage pulses of different duration with a SWNT tip

**Figure 5S.** STM image of a hole array written with a SWNTs tip by voltage pulses of different duration from 100  $\mu$ s to 980  $\mu$ s at a fixed amplitude of 5 V. The smallest hole is ca. 3.4 nm in diameter created by 5 V × 140  $\mu$ s.

Hole array written on the TEA(TCNQ)<sub>2</sub> in high-purity N<sub>2</sub> atmosphere



**Figure 6S.** STM image of a hole array written on the TEA(TCNQ)<sub>2</sub> surface in high-purity N<sub>2</sub> atmosphere. Writing condition: a Pt/Ir tip, 8 V  $\times$  100 µs; Imaging condition: 0.10 nA, 0.1 V, constant-current mode.