

## Supporting Information for “Donor/Acceptor complex of Triphenylene and Trinitrotoluene on Au (111): A Scanning Tunneling Microscopy Study”

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### Experimental Section

TNT (1g/L in acetonitrile, Sigma-Aldrich) and TP (TCI) were used as received. Electrolyte solution was prepared with ultrapure HClO<sub>4</sub> (Aldrich Chemical Co., 99.999%) and Milli-Q water (Milli-Q, ≥ 18.2 MΩ, TOC < 4 ppb). Molecular models of TP adlayer were built in HyperChem 6.0 and Materials Studio 3.0. Theoretical calculations on structure of electrostatic potentials of TNT and TP were carried out with DMol 3 in Materials Studio 3.1 (Accelrys, San Diego, CA).

The preparation for the Au(111) crystal and electrolyte solution was the same procedure as reported in the literature.<sup>1</sup> Briefly, a well-defined Au(111) facet using for the STM experiments was prepared by crystallization of molten ball formed at the end of a Au wire (99.999%) in a hydrogen-oxygen flame.<sup>2,3</sup> For electrochemical measurements, a single-crystal Au(111) disk of ca. 8 mm in diameter and ca. 5 mm in height was used. Before each measurement, the Au (111) electrode was further annealed in a H<sub>2</sub>-O<sub>2</sub> flame and quenched in Mill-Q water saturated with H<sub>2</sub>.

Electrochemical measurements including cyclic voltammetry and stripping experiments were performed by the hanging meniscus method in a three-compartment electrochemical cell with using an EG&G Princeton Applied Research (PAR) advanced electrochemical system (PARSTAT 2263) controlled by a microcomputer with EG&G PARC M250 software as reported previously.<sup>4</sup> A reversible hydrogen electrode (RHE) and a platinum wire were used as reference and counter electrodes, respectively. The solutions were deaerated with high purity N<sub>2</sub> before experiments. All electrode potentials were reported with respect to the RHE in 0.1 M HClO<sub>4</sub>. All experiments were performed at room temperature (about 298 K).

Electrochemical STM experiments were carried out by using a NanoScope E microscope (Digital Instrument Inc., Santa Barbara, CA) in 0.1 M HClO<sub>4</sub>. The tunneling tips were prepared by electrochemical etching of a tungsten wire (0.25 mm in diameter) in 0.6 M KOH. To minimize faradic current, the sidewalls of the tips were sealed with transparent nail polish. All the STM images were collected in the constant-current mode.

Theoretical calculations on electronic density of molecular orbital and electrostatic potentials were carried out with DMol 3 in Materials Studio 3.1 (Accelrys, San Diego, CA).

### Additional STM images of TNT/TP complex

The coexistence of monolayer and bilayer structures was observed in STM image, as shown in Figure S1 A. In the right image of Figure S1 A, yellow and blue lines are marked to indicate the lattices of the lower and upper layers, respectively. It is shown that there is no rotation or shift of molecular lattices between the upper and the lower molecular adlayers, and the measured unit cell parameters are the same. It is indicated that the upper layer is overlapped perfectly on the first layer. The cross sectional profiles of the first and second layers along the line S-S' (Figure S1 B) supply direct evidence for the double layer structure. The apparent corrugation height of upper layer is about twice of that of the first layer.

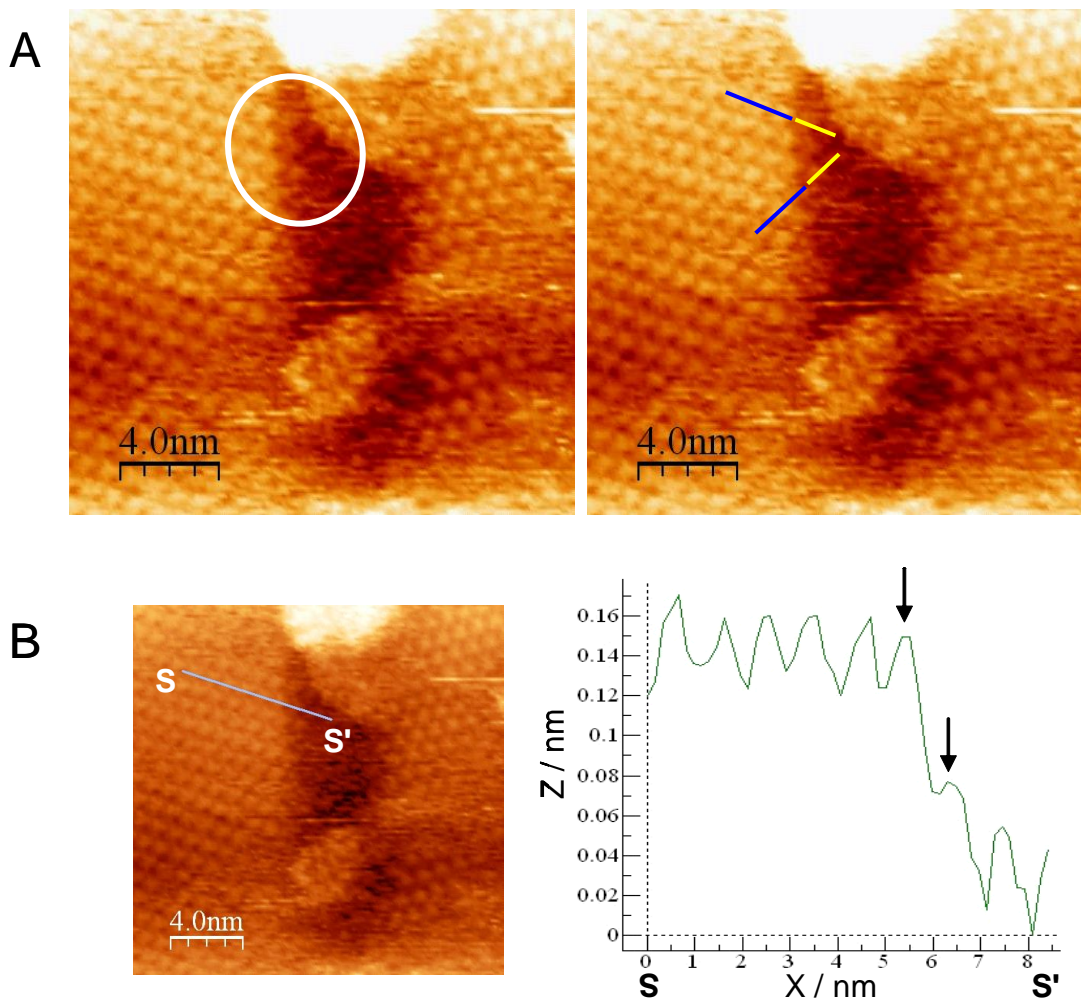


Figure S1. (A) STM image of double layer structure. ( $E=550$  mV,  $E_{tip}=430$  mV,  $I_t=3.1$  nA) In the left image of A, the coexistence of the monolayer and the bilayer is marked by white circle. In the right image of A, yellow and blue lines are drawn to mark the lattice directions of the lower layer and the upper layer, respectively. (B) Cross-sectional profile along S-S' line in the corresponding STM image.

### References:

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