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Donor/acceptor complex of triphenylene and trinitrotoluene on Au(111): a scanning tunneling microscopy study†

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The co-adsorption of trinitrotoluene (TNT), a typical π -electron acceptor, and triphenylene (TP), a typical π -electron donor, on a Au(111) surface was investigated by *in situ* Electrochemical Scanning Tunneling Microscopy (ECSTM). DFT calculations proved that parallelly stacked and well-overlapped TP and TNT molecules can form Donor–Acceptor dyads through intermolecular π – π charge transfer, which agree well with the experimental results in the present work.

Donor–acceptor (D–A) type charge-transfer complexes have raised much attention due to their potential application in molecular nanodevices and nanoelectronics.^{1–4} Organic molecules are in this respect very versatile, as their physical and chemical properties can be finely tuned by chemical design.⁵ In particular, the direct landing of the acceptor molecular nanostructures on the nanotemplate exclusively constructed from the donor molecules offers an ease of fabrication of organic donor/acceptor nanojunctions with well-ordered two-dimensional (2D) organization.⁶ Scanning tunneling microscopy (STM) can offer the spatial resolution to address individual chemisorbed or physisorbed conjugated molecules in highly ordered (mono)layers and to reveal their self-assembly behavior.^{7–10} The high spatial resolution of scanning probe microscopes also enables the detection of local electronic property changes resulting from intermolecular interactions such as π – π stacking,^{11,12} or charge-transfer complexes.^{13,14}

It is known that triphenylene (TP) and trinitrotoluene (TNT) molecules have electron rich and electron deficient structures, respectively. Especially, TP has complementary electronic density with TNT according to their electronic characteristics.¹⁵ There are significant π – π intermolecular interactions existing between them, which facilitate the molecule recognition of TP to TNT.^{15,16} However, to the best of our knowledge, there has been no report about co-adsorption and interaction behavior of TNT and TP on the electrode surface at an atomic and molecular level. In the present work, from STM observation, TNT molecules are found to overlap

on the TP adlayer to form a well-ordered adlayer of the TP–TNT complex on Au(111). DFT calculation shows that parallelly stacked and well-overlapped TP and TNT molecules can form Donor–Acceptor dyads through significant intermolecular π – π charge transfer. Furthermore, expanding from the single-component phase, the binary TP–TNT system provides further insight into the “bottom-up” approach to nanofabrication for device miniaturization and molecular electronics in the future.

Fig. 1 compares the cyclic voltammograms (CVs) of 6×10^{-6} M TNT on a bare and TP-modified Au(111) electrode in 0.1 M HClO₄ recorded at a scan rate of 50 mV s^{−1}. On a bare Au(111) electrode (black curve), three cathodic redox peaks of TNT associated with the irreversible reduction of the nitro groups to hydroxyamines, followed by conversion to amine groups, are found at 330, 260 and 230 mV, respectively. The redox pair at 0.6–0.7 V is due to the reversible oxidation/reduction of the hydroxyamino/nitroso group.¹⁰ As shown in the red curve, the intensities of these three reduction peaks of TNT decrease greatly on the TP-modified Au(111) electrode and the corresponding potentials are negatively shifted to 290, 210, and 140 mV, respectively. As a control experiment, the TP-modified Au(111) surface doesn't show any current peak in

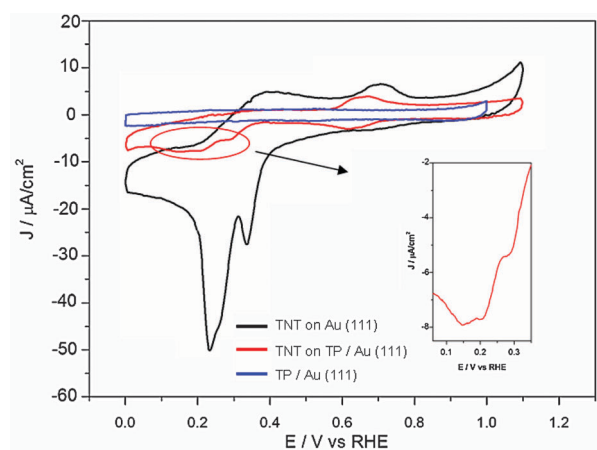


Fig. 1 Cyclic voltammograms of bare (black curve) and TP-modified (red curve) Au(111) electrode in a 0.1 M HClO₄ + 6×10^{-6} M TNT solution. An inset voltammogram is the expansion of the part marked with the red ring. Cyclic voltammogram of the TP-modified Au(111) electrode in 0.1 M HClO₄ (TNT free) is shown as a blue curve. Potential scan rate: 50 mV s^{−1}

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the TNT-free solution in the corresponding potential range (blue curve).

There are two possible mechanisms for the observed electrochemical behavior of TNT on the TP modified Au(111) electrode: (1) reduced adsorbed sites for TNT on Au(111) due to the presence of TP molecules, or (2) an interaction between TNT and TP molecules. If the adsorbed sites of TNT are blocked by the adsorbed layer of TP molecules, the CV result should be in line with the CV obtained at decreased surface concentration of TNT. However, from the experimental results, it has been observed that the potentials of redox peaks are shifted to the more positive potentials (data not shown) with decreased TNT concentration. In contrast, the redox potentials of TNT have been shifted negatively on the TP modified Au(111) surface. Therefore, the decreasing of adsorbed sites of TNT is not the primary reason. Another possibility is that the charge transfer from the electron rich molecule TP to the electron deficient molecule TNT changes the electronic structure of TNT, which results in a negative shift of the reductive potential of TNT. To further clarify the adlayer structure of the TNT/TP complex on Au(111), ECSTM is employed.

The adlayer structure of TP on Au (111) is investigated by *in situ* electrochemical STM. Fig. 2A shows a typical large-scale STM image of TP on Au (111) acquired under potential control of 550 mV in 0.1 M HClO₄. It is evident that the atomically flat terrace is covered by an ordered adlayer of TP.

The structural details can be seen in the high resolution STM image of Fig. 2B. It is clear that each TP molecule can be resolved as a cluster containing three bright spots. The cluster is measured to be 0.7 ± 0.1 nm, close to the size of TP molecules. The molecular rows cross each other at an angle of either 60° or

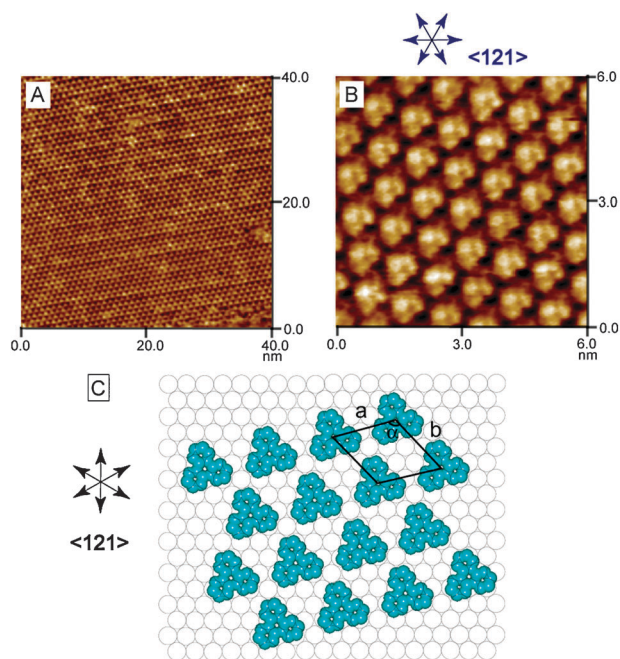


Fig. 2 (A) Large-scale ($E = 550$ mV, $E_{\text{tip}} = 387$ mV, $I_t = 6.4$ nA) and (B) higher resolution STM images of TP adlayer on the Au(111) surface. ($E = 550$ mV, $E_{\text{tip}} = 387$ mV, $I_t = 4.0$ nA). (C) Proposed structural model for the TP adlayer with a unit cell with a $(\sqrt{13} \times \sqrt{13})$ symmetry. The adlayer belongs to the $p3m1$ planar group.

120° with an experimental error of $\pm 2^\circ$. The repeated distances along molecular rows, A and B directions, are both 3.8 nm with an experimental error ± 0.2 nm, which are about $\sqrt{13}$ times of the underlying lattice. Compared to the underlying Au(111) lattice, a unit cell with a $(\sqrt{13} \times \sqrt{13})$ symmetry for the molecular adlayer could be concluded. It is proposed that the molecule lies flat on a three-fold hollow site of the Au (111) surface. A structural model for the self-assembly of the TP molecule on the Au (111) surface is proposed in Fig. 2C.

After the TP adlayer was imaged, indicating that TP molecules have been coated on the Au(111) surface successfully, a small amount of TNT solution was directly injected into the electrochemical cell. About an hour later, STM imaging was resumed to reveal the adlayer structure. Fig. 3A is a typical STM image showing the structure of adsorbed molecules in the adlayer, acquired at 550 mV in 0.1 M HClO₄. From the large scale STM image, a well-defined molecular array is seen to extend over the atomically flat terrace. Fig. 3B shows a higher-resolution STM image of TNT on the TP-modified Au (111) electrode. On the basis of the molecular orientation and intermolecular distance, the $(\sqrt{13} \times \sqrt{13})$ symmetry which is same as that of the TP molecules on Au (111) can be concluded.

As shown in Fig. 3B, each cluster can be recognized as a triangle composed of three spots. Among these three spots, two spots are brighter than the other one, which is different from the appearance of the TP molecule on Au(111). Interestingly, it should be noticed that there are many molecular defects which can be barely observed in the pure TP adlayer on Au(111) (Fig. 2A). Fig. 3C is a high-resolution STM image containing some molecular defects, as marked with two red rings. A careful observation indicates that there is one triangular molecule with dark contrast existing in every defect position. According to the shape and size of the dark triangular molecule

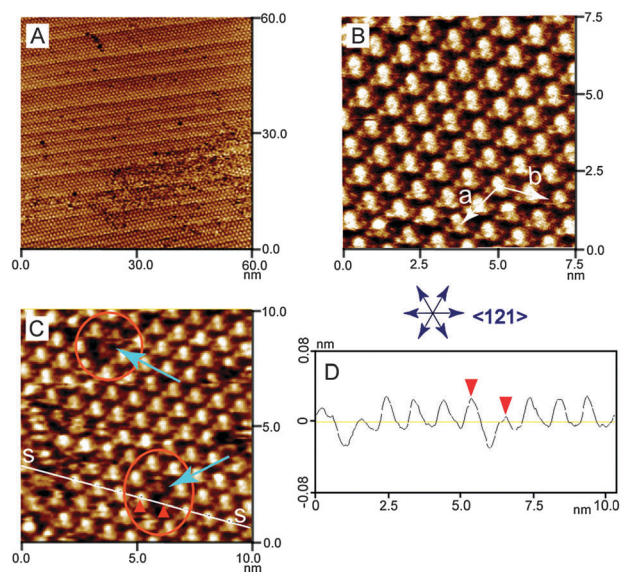


Fig. 3 (A) Large-scale STM image of the self-assembled TNT adsorbed on the TP-modified Au(111) surface ($E = 550$ mV, $E_{\text{tip}} = 381$ mV, $I_t = 7.88$ nA). (B) Higher resolution STM images of TNT and TP adlayer without and (C) with molecular defects on the Au(111) surface ($E = 550$ mV, $E_{\text{tip}} = 450$ mV, $I_t = 8.68$ nA). (D) Cross-sectional profile along S-S' line in (C).

in defect spots, the triangle can be attributed to the TP molecules on Au(111). Fig. 3D is the cross-section profile along the molecular row indicated by line S–S' in Fig. 3C, showing the corrugation height difference of the complex adlayer and defect spots. From the image characteristics and corrugation height, we assume that the TNT adlayer is grown epitaxially on the TP adlayer. The defects correspond to the spots where TNT does not form the complex structure with TP. Occasionally, the monolayer–bilayer step edge was observed in the STM image, as shown in Fig. S1 (see ESI†), which provides further evidence for the formation of bilayer structures. The stacked complex of TNT and TP on Au(111) is structurally reminiscent of the 1 : 1 complex of trinitrobenzene and TP in the solid state.¹⁵ We note that the STM image of the TNT/TP complex is different from that of the TNT adlayer on the Au(111) surface,¹⁰ indicating that the electron structure of TNT has been changed upon complexation.

We further performed theoretical modelling based on density functional theory (DFT) calculation. The optimized configurations for the TNT-TP complex in the lowest energy is shown in Fig. 4A with both top and side views. The result indicates that the TNT molecule can form a stable complex with the TP molecule through π – π stack interaction. A structural model for the self-organization of the TP–TNT complex on the Au(111) surface is proposed in Fig. 4B.

Fig. 5 shows the electrostatic potentials of TNT, TP, and the TP–TNT complex, in which the yellow and the blue regions represent negative charge and positive charge, respectively. It is shown that the TNT and TP molecules possess opposite charge distribution in their aromatic cores, as is shown in Fig. 5A and B. In the case of the TP–TNT complex, the negative charge is almost transferred from the TP molecule to TNT, as is shown in Fig. 5C. The electrostatic potentials analyses theoretically prove that TP is a good donor to TNT and significant intermolecular π – π charge transfer induces the formation of the TP–TNT

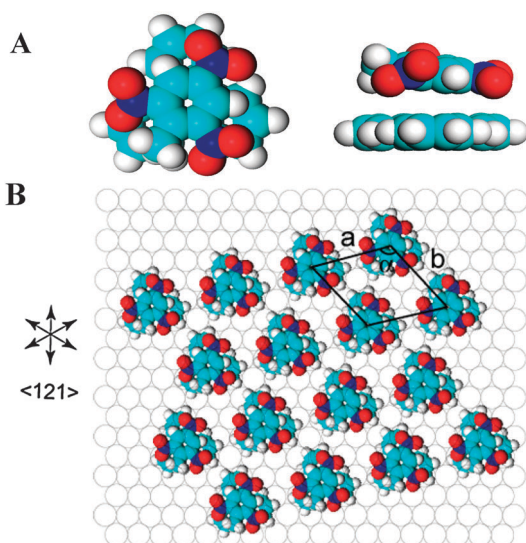


Fig. 4 (A) Top (left) and side (right) views of the TP–TNT complex model calculated by DFT. (B) Proposed structural model for the TP–TNT complex adlayer on Au(111). A unit cell with a $(\sqrt{13} \times \sqrt{13})$ symmetry is overlaid. Due to low symmetry of the TP–TNT complex, the adlayer belongs to the p1 planar group.

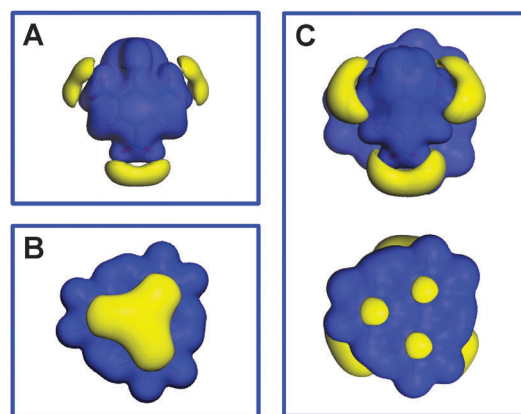


Fig. 5 Structure of electrostatic potentials of (A) TNT, (B) TP and (C) TP–TNT complex with front (top) and back (down) views.

Donor–Acceptor complex. Moreover, the change of electrostatic potentials in the TP–TNT complex compared with that of the single molecules calculated by DFT further elucidates the interaction between TNT and TP.

In the present work, the electrochemical behaviour and adsorption structure of TNT on TP modified Au(111) were studied. TNT molecules grow epitaxially on the TP adlayer and form the TP–TNT complex adlayer based on the STM results. Both experimental and DFT calculations indicate that the TP–TNT complex consists of parallelly stacked TNT and TP molecules through significant intermolecular π – π charge transfer. This result provides a simple way to fabricate organic donor/acceptor nanojunctions on the electrode surface, which is a key issue in the design of molecular nanodevices.

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