

# Photodimerization of P2VB on Au(111) in Solution Studied with Scanning Tunneling Microscopy

Guang-Zheng Yang, Li-Jun Wan,\* Qing-Dao Zeng, and Chun-Li Bai\*

*Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China*

*Received: June 10, 2002; In Final Form: February 20, 2003*

Photodimerization of 1,4-bis( $\beta$ -pyridyl-2-vinyl)benzene (P2VB) has been investigated on Au(111) in solution by using electrochemical scanning tunneling microscopy (ECSTM). Both reactant and product form ordered molecular adlayers on the substrate. Higher resolution STM images reveal the structural details before and after photochemical reaction. A dimeric structure is observed after UV irradiation. The size of a dimer is consistent with its chemical structure. On the basis of STM images, the photoinduced [2+2] cycloaddition reaction occurred in P2VB adlayer is discussed.

## Introduction

The photopolymerization of crystalline conjugated diolefins and diacetylenes has been intensively investigated with special emphasis on structural and geometric requirements in determining reactivity.<sup>1–11</sup> The unique relation of structure to reactivity has led to labeling those reactions as “topochemical” wherein the structure of the products is dictated by the geometry and proximity of the reactive sites of the precursors in the lattice.<sup>2,6</sup> Through the pioneering work of Schmidt and co-workers, the prerequisites for photochemical [2+2] reactions in the solid state are now well established.<sup>5,12</sup> That is, with few exceptions,<sup>13</sup> the double bonds of neighboring molecules in the olefin crystal arrange in a parallel fashion and make contact at a distance of 4.2 Å or less.<sup>14</sup> The reactions investigated generally involved minimal molecular reorganization. In the topochemical reaction, the geometrical relation of reactant to product is very important for speculating the reaction mechanism in the molecular level. In particular, the symmetrical relationship is important in the discussion of the spatial restriction of the molecules during the solid-state chemical reactions. 2,5-Distyrylpyrazine (DSP), 1,4-bis( $\beta$ -pyridyl-2-vinyl)benzene (P2VB), and diacetylenes are typical examples where the symmetry of the molecular packing is unchanged before and after the reaction in the solid state. In these cases, the reactions proceed homogeneously through the bulk materials, and the single crystalline polymeric materials are obtained.<sup>1,15</sup>

By repeated intermolecular [2+2] cyclodimerizations, diolefins can be photochemically converted to a linear high polymer crystal. It is of particular interest both in theory and in application to extend these studies on photopolymerization of diolefins in solution. Self-assembled monolayers (SAMs) of organic molecules on solid substrates have attracted much attention because of their potential applications from surface wettability control, lubrication, sensors, nanodevice and lithography.<sup>16–19</sup> Reactions in solution often differ from those in solid state, and reactions in surface also differ from those in bulk crystal. Now the processes that occur at the surface have promised to give novel insight by recent developments in the field of scanning probe techniques. A great deal of investigation

on the reactivity of organic compounds at various interfaces has been carried out with atomic or molecular resolution by scanning probe microscopy (SPM) such as STM and AFM.<sup>13,20–22</sup>

Because photopolymerization of P2VB is a polyphotonic reaction, it is possible with suitable selection of the wavelength of irradiating light to control the formation of molecular scaffolding such as dimer or polymer.<sup>23</sup> Scheme 1 illustrates the reactions forming dimer (b) and polymer (c). When the wavelength is longer than 400 nm, a dimer is obtained. In this Letter, we report an STM investigation of photodimerization of P2VB on the Au(111) surface in 0.1 M HClO<sub>4</sub> solution under ultraviolet (UV) irradiation. The structures of P2VB monomer and dimer obtained after UV irradiation have been observed by ECSTM. The results should supply useful information for understanding the photopolymerization reaction on the surface in solution.

## Experiment

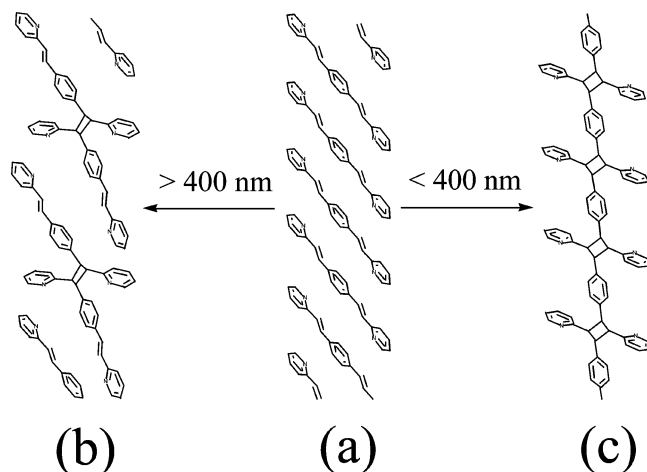
Single-crystal beads of Au were prepared at the end of a Au wire (99.99% in purity, 0.8 mm in diameter) by the method described in the literature.<sup>24</sup> Au(111) facets that formed on a gold single-crystal bead in an octahedral configuration were directly used for STM observation. Before STM experiment the Au single-crystal bead was annealed in a hydrogen–oxygen flame, quenched in ultrapure water saturated with hydrogen, then thoroughly rinsed with pure 0.1 M HClO<sub>4</sub>, and transferred to an electrochemical cell with a drop of water to protect against contamination. The electrochemical cell contained a reversible hydrogen electrode (RHE) in 0.1 M HClO<sub>4</sub> and a Pt counter electrode. The electrolyte, 0.1 M HClO<sub>4</sub> was prepared with HClO<sub>4</sub> (Cica-Merck, Japan, Ultrapure grade) and Milli-Q water. P<sub>2</sub>VB was synthesized according to the method described in the literature.<sup>3</sup> P2VB solution was sonicated for 10 min to achieve saturation (ca.  $4 \times 10^{-5}$  M).

The photodimerization was carried out by using a deuterium lamp (300 mA, 80 V) with a monochromator to filter out the output of the lamp. The wavelength used here was 410 nm. The light was conducted to the Au(111) facet by a fiber.

In situ STM measurements were carried out with Nanoscope E electrochemical STM (Digital Instruments). The STM tips used were made from electrochemically etched tungsten wire in a diameter of 0.25 mm. To minimize faradic currents, the

\* Corresponding author. Tel. & Fax: +86-10-62558934. E-mail: wanlijun@iccas.ac.cn.

**SCHEME 1: Schematic Illustration of Solid Photopolymerization Reaction of Diolefins, (a) Monomer, (b) Oligomer, and (c) Polymer**

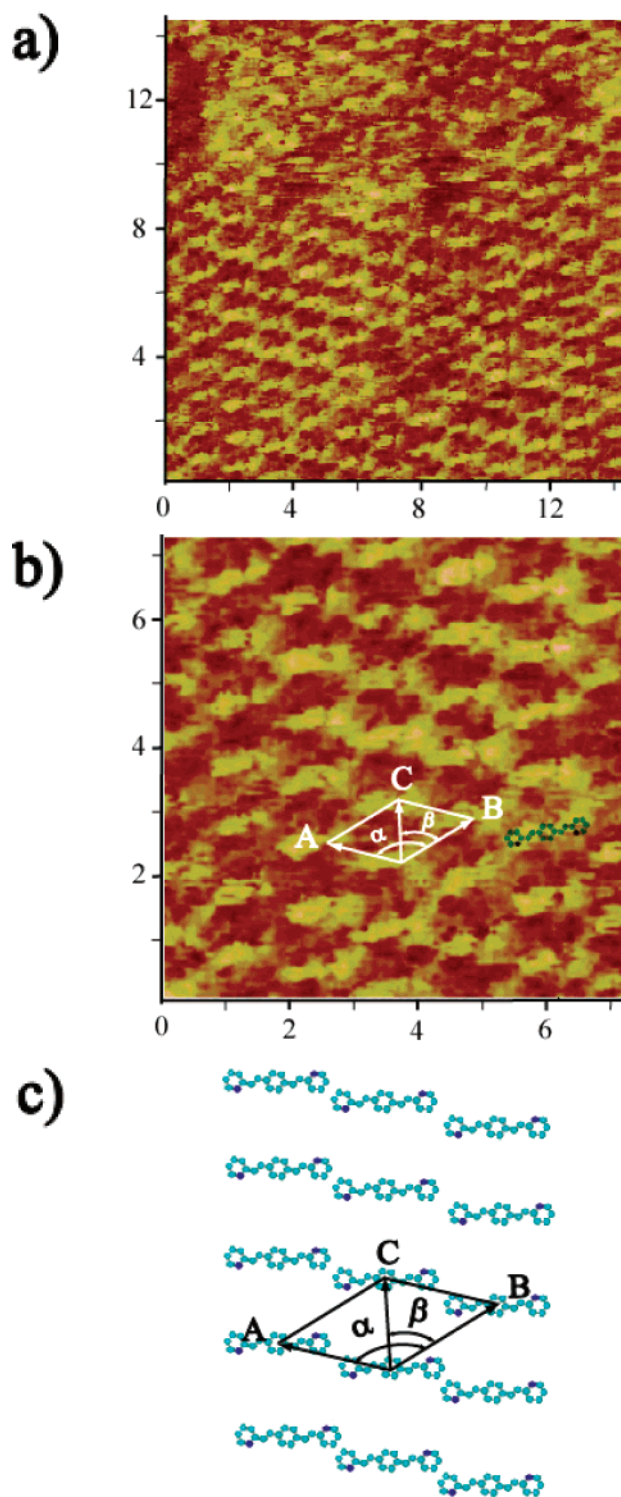


sidewall of the tips was coated with clear nail polish. The STM images were obtained while and after Au(111) was being irradiated. To avoid the effect of tip shadow on UV irradiation, different scanning directions and angles were used during STM imaging. All images are raw data without further processing. The images were obtained in the constant-current mode with a tunneling current of 500 pA. The electrode potential of Au(111) was held at 0.44 V vs RHE. All molecular models were optimized with Heperchem software package (version 6.0).

### Results and Discussion

A drop of saturated P2VB solution was directly added into electrochemical cell after atomically flat (111) terraces ( $>200$  nm) could be clearly imaged by STM in 0.1 M HClO<sub>4</sub> solution. A P2VB monolayer is formed on the Au(111) surface. Figure 1a shows a typical image of the monolayer in a large scale. Although several defects are observed in the image, it is clear that the molecules cover the Au(111) surface and form a long-range ordered adlayer. Individual molecule in linear configuration can be resolved. Figure 1b is a higher resolution image showing the details of the adlayer. Each molecule appears in a rodlike contour  $1.52 \pm 0.02$  nm long and  $0.28 \pm 0.02$  nm wide. P2VB is a typical conjugated diolefin. In the STM image a linear configuration can be clearly seen. A schematic illustration for a P2VB molecule is drawn in Figure 1b. The molecular rows extend along **A**, **B**, and **C** directions, as indicated by the arrows in Figure 1. The repeat distances along molecular rows in **A**, **B**, and **C** directions are measured to be ca. 1.60, 1.02, and 1.00 nm with experimental error  $\pm 0.02$  nm. One of molecular rows in the **A** direction is along the close-packed directions of the Au(111) lattice. The internal angle  $\alpha$  between **A** and **B** is ca.  $133 \pm 2^\circ$ , the internal angle  $\beta$  between **C** and **B** is ca.  $60 \pm 2^\circ$ . On the basis of the STM images, a structural model for this adlayer is proposed in Figure 1c.

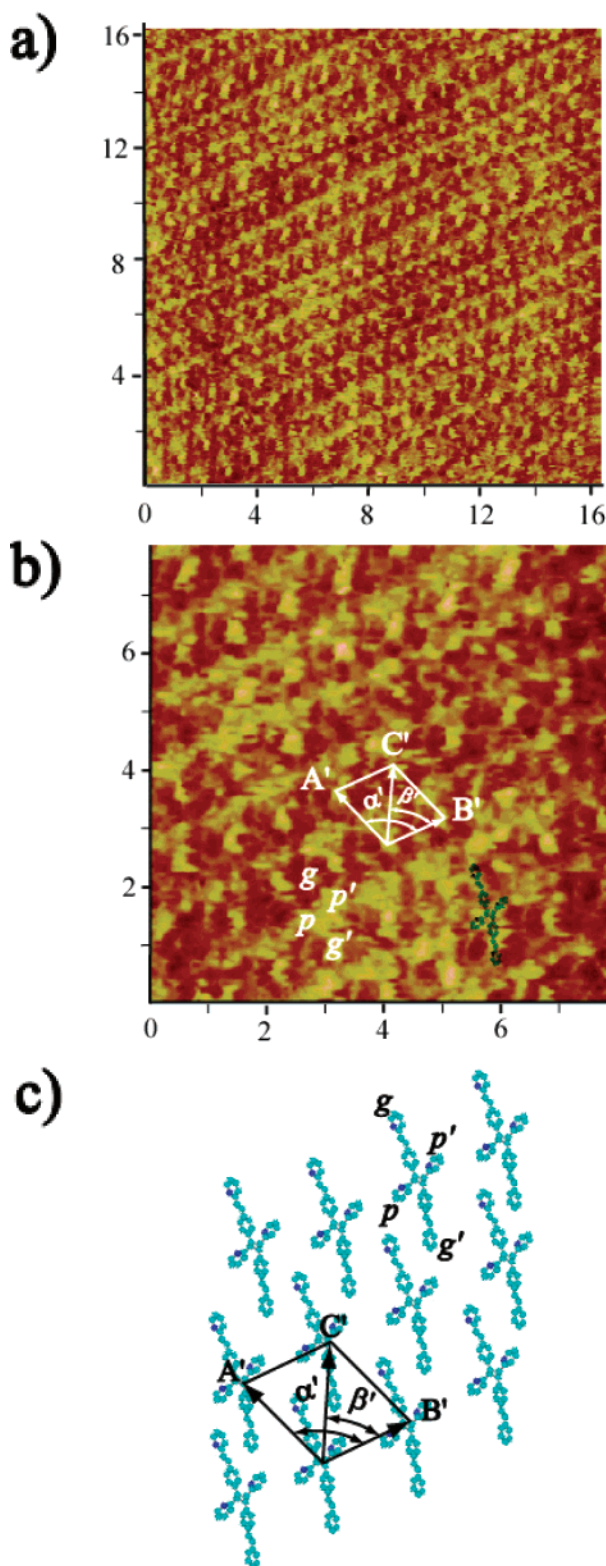
After the STM images of the reagent were obtained, UV light was introduced to irradiate the P2VB adlayer. Although STM scanning was continued during the irradiation process, only distorted image could be seen due to molecular motion and reaction.<sup>25</sup> The steady images were acquired after 55 min irradiation. Figure 2a is a typical STM image of irradiated P2VB adlayer. A well-defined adlayer is clearly observed. However, the packing arrangement of the adlayer and the molecular appearance reveals a quite different structure from that shown in Figure 1a. The high-resolution STM image is shown in Figure



**Figure 1.** (a) Large scale and (b) high-resolution STM images of the P2VB adlayer on the Au(111) electrode in 0.1 M HClO<sub>4</sub> with a setpoint of 500 pA. (c) Proposed structural model for the monolayer.

2b. It can be seen that the molecular rows extend in three directions, **A'**, **B'**, and **C'**. The repeat distances along the **A'**, **B'**, and **C'** directions are 1.41, 1.1, and 1.43 nm with experimental error  $\pm 0.2$  nm. The internal angle  $\beta'$  is  $60 \pm 2^\circ$ , the same as that in the reagent adlayer, whereas  $\alpha'$  decreases to  $110 \pm 2^\circ$ . The different structure and molecular arrangements indicate the change in the irradiated adlayer. On the other hand, the new feature of the image is regular clusters. Each cluster consists of four spots marked by **p** and **p'**, **g** and **g'** with different brightness, three brighter and one (**g**) darker. By comparing the





**Figure 2.** (a) Large scale and (b) high-resolution STM images of the P2VB photoreaction product adlayer on the Au(111) electrode in 0.1 M HClO<sub>4</sub> with a setpoint of 500 pA. (c) Proposed structural model for the monolayer.

STM image and chemical structure, one can see that a cluster corresponds to a photodimerized product of P2VB molecule, as shown in Scheme 1b. Under scrutiny, it can be concluded that four spots in Figure 2b correspond to four conjugate groups of dimer because of the formation of four-cycle rings. Two spots, indicated by **p** and **p'** in the **B'** direction, are ascribed to the

two pyridine rings in a dimer. The other two longer spots, indicated by **g** and **g'**, are ascribed to the  $\beta$ -pyridylstyryl moiety in the dimer. A molecular structure of a dimer is outlined in Figure 2b. The sizes in a dimer are measured to be ca.  $2.1 \pm 0.02$  and  $1.1 \pm 0.02$  nm along the longer and shorter axes, respectively. The measured distances are consistent with the optimized dimer structure between two  $\beta$ -pyridylstyryl groups and two pyridine rings. The different orientations of two  $\beta$ -pyridylstyryl groups with respect to the Au(111) surface result in the brightness difference in STM images. The brighter one marked **g** is assumed to be vertical to the electrode surface, whereas the darker one marked **g'** is parallel to the surface. On the basis of STM results, a structural model for the adlayer consisting of P2VB dimers is proposed in Figure 2c. The model can explain the observed adlayer.

The photochemical reaction has been intensively studied.<sup>26–34</sup> As a result, it is known that the reaction in solution is different in a metal surface because the metal may quench the excited state. Studies of the photochemistry of a monolayer on a metal surface have demonstrated that the excited state is not completely quenched by the metal, although the observed reaction quantum yields may be lower than either in solution or in the solid state.<sup>30–35</sup> An example is the photodimerization of self-assembled monolayers of *cis*- and *trans*-4-cyano-4'-(10-mercaptopodecoxy)stilbene on gold.<sup>35</sup> In the present study, the photoyield on the P2VB adlayer should be lower than that in solution due to the quenching effect of the Au(111) surface. However, it is possible from the STM observation that the dimerization can occur not only in solution also on P2VB adlayer on substrate surface. The details on photo yield on surface should be investigated by other techniques.

In summary, we have investigated the photoreaction of P2VB molecules on the Au(111) surface in 0.1 M HClO<sub>4</sub>. P2VB monomer adsorbs on the Au(111) surface and forms a well-defined adlayer. After UV irradiation a dimeric structure with regular molecular rows is observed on the Au(111) surface. A higher resolution STM image reveals the structural details of the adlayers and individual molecules. The distances in a dimer are ca.  $2.1 \pm 0.02$  and  $1.1 \pm 0.02$  nm along the longer and shorter axes, respectively, consistent with the chemical structure. The structural models proposed for the two adlayers are consistent with the experimental results.

**Acknowledgment.** Financial support from National Natural Science Foundation of China (Nos. 20025308, 20177025, and 20103008), National Key Project on Basic Research (Grant G2000077501), and the Chinese Academy of Sciences are gratefully acknowledged.

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