

## DIRECT STM OBSERVATION OF ELECTRON STRUCTURE MODIFICATION OF NAPHTHACENEQUINONE MOLECULES CAUSED BY PHOTOISOMERISATION

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Light induced conformational transformations of the naphthacenequinone (NQ) molecules are observed by scanning tunneling microscopy (STM). NQ molecules packed in Langmuir - Blodgett (LB) film are shown to form stable ordered structures on a surface of highly oriented pyrolytic graphite (HOPG). The distinct peak in local density of electronic states is detected which is characteristic for the 2-dimensional character of conductivity. Additional sub-band of empty electronic states has been found for NQ molecules in form *A* and not found in form *B*. The constant height STM images of individual molecules in form *A* demonstrate an additional structure that indicates the conformational transition of NQ molecules. This transition is connected with the transfer of the phenoxy group from one oxygen to another.

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1. Photochromic molecules attract considerable and permanent interest due to their capability for reversible changing of their absorption and fluorescent spectra under irradiation at different wavelengths. In view of the development of new generation of ultra-high density 3 dimensional optical data storage based on the use of photochromic molecules it is important to clarify fundamental mechanisms that lead to modification of fundamental characteristics of photochromic molecules (especially organized in Langmuir - Blodgett (LB) films) under exposure to light. Properties of the photochromic molecules embedded either into polymeric matrices or other media (liquid crystals, solutions etc.) essentially depend on their environment. LB technique permits to produce photochromic molecular structures packed with ultra high density on the surface of a substrate. LB films are typical two-dimensional (single layer films) or three-dimensional (multilayer films) ordered assemblies. Evidently, one expects that photochromic molecules incorporated in highly ordered LB films should exhibit the behaviour that is not typical for free molecules or solutions. However, very little is known about physical aspects of photochromic reactions in LB films.

Photochromic compounds deposited on a substrate by LB (Langmuir - Sheffer) technique are an interesting and attractive object for investigations by different methods. Optical properties of molecular layers of spiropyrans and photochromic reaction kinetics of spiropyran molecules in LB layers on stearic acid were investigated [1-3]. The possibility of photochromic reaction in diarylethenes and salicylideneanilines LB films has been demonstrated [4, 5]. Similar results are presented in refs. [6, 7].

For particular molecules photo isomeric changes can be observed by means of precise methods based on scanning probe microscopy (such as scanning tunnel mi-

croscopy/spectroscopy – STM/STS, scanning force microscopy – SFM etc.). These methods in principle allow one to study electronic properties [8,9] and topology of particular molecules and their variations, caused by external optical irradiation, on a substrate surface with atomic resolution. The major advantage of STM methods is its high resolution (it permits to resolve much smaller details than optical wavelength). Recently, the possibility of the direct STM real-space analysis of molecular shape has been demonstrated [10]. The authors have identified two different conformations of the Cu-tetra (3,5 di-*t*-butylphenyl) porphyrin (Cu-TBPP) molecule deposited on the metal substrate in two metastable forms characterised by different shapes of the molecules. However until present moment direct observation of reversible modification of molecular structure by STM under optical radiation have not been observed.

In this paper we have demonstrated, to the best of our knowledge for the first time, the direct STM registration of photochromic reaction in LB films under exposure to light. The direct reaction (*formA* → *formB*) of naphthoquinone (NQ) molecules ordered in LB films is caused by 400 nm light and reverse reaction (*formB* → *formA*) is initiated by 480 nm light. The conformational transformations of individual molecules in LB layer have been observed before and after direct photoreaction. Our main findings are as follows:

1) the distinct peak is found in tunnel local density of electronic states of 6-phenoxy-5, 12-naphthacenequinone molecules [11] ordered in LB films. Such a peak is inherent in both *A* and *B* forms and is indicative of two-dimensional (2D) character of film conductivity. The shape of the differential conductivity curves is shown to be significantly modified after direct photoisomerization;

2) for molecules in the *A* form the additional sub-band in the range of unoccupied electronic states of LB films is detected;

3) the tunnel current flowing through the individual molecule falls from ~ 0.1 nA to ~ 0.04 nA when molecules undergo the transition from *A* to *B* form;

4) constant height images of individual molecule in the form *A* demonstrate an additional fine structure that points to the conformational transition of molecules from *A* to *B* form. This transition is connected with the transfer of the phenoxy group from one oxygen atom to another and probably leads to shutdown of some of tunneling channels.

2. To study electronic properties of NQ molecules and their possible conformational modifications during photochemical reactions we used STM and STS techniques. Molecules were deposited on a highly oriented pyrolytic graphite (HOPG) substrate using Langmuir-Sheffer technique to form different numbers of ordered molecular layers. Expected modification of NQ molecular structure under transition from para-form (*form A*) to ana-form (*form B*) and backward is shown in Fig.1. Variations of molecular properties in multilayer thin films caused by light irradiation change the initial density of electronic states which is detected in our STM and STS experiments.

The photochemical reaction was initiated by light passed through interference filter with transmission maximum at 400 nm for the direct reaction (*A* → *B*) and at 480 nm for the reverse reaction (*B* → *A*). We used the incandescent lamp as a light source. After filtering the light, passed through multimode optical fiber, was used to illuminate STM tunneling junction. Typical light intensity on the sample was about 1 mW/cm<sup>2</sup>. This scheme allowed to follow the changes of electronic properties of NQ molecules in

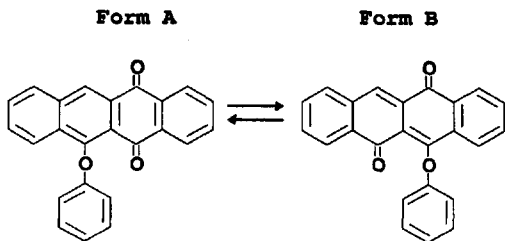


Fig.1. Schematic structure of two conformational forms (*A* and *B*) of 6-phenoxi-5,12-naphthacenequinone molecules which occurs during photocoloration ( $A \rightarrow B$ ) and photobleaching ( $B \rightarrow A$ ) reactions

processes of forward and backward phototransitions by means of STM and STS methods in situ.

LB film was deposited on the HOPG substrate under pressure of 5 mN/m. Average transfer coefficient  $\langle k \rangle$  was equal to 0.84.

All the measurements were performed using home-build STM with atomic resolution and maximum scan range  $5 \times 5 \mu m$  in ambient conditions. STM tips were mechanically cut from PtIr or Au wires. We have used STM to obtain constant current (topography) as well as constant height images. Spectroscopic data ( $I(V)$  and hardware  $dI/dV(V)$ ) were acquired then at the chosen point of the surface [12].

We have found that LB films of NQ molecules (from 1 to 40 monolayers) are capable to form stable ordered structures on a HOPG surface. Area occupied by each molecule is of order of  $20\text{-}23 \text{ \AA}^2$  which is in a good agreement with the value of  $27 \text{ \AA}^2$ , obtained from  $\pi - S$  isotherm at the deposition pressure. Distance between molecular rows is about of  $5.8\text{-}6.0 \text{ \AA}$  and that between molecules in the row is  $3.8 \text{ \AA} - 4.0 \text{ \AA}$ .

Tunneling conductivity curves measured for LB films with different number of layers always have revealed a peak in vicinity of zero of bias voltage. In strong binding approximation this points to the 2D character [13] of LB film conductivity and to the existence of long-range interaction between molecules (see Fig.2a).

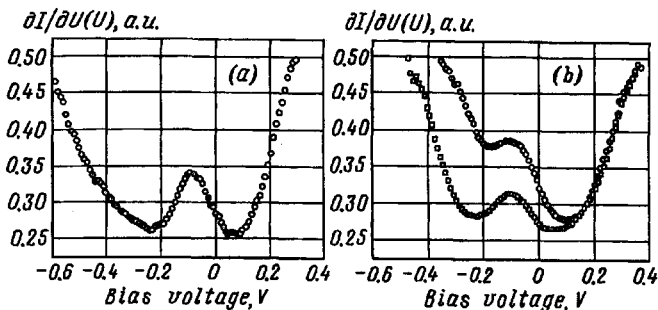


Fig.2. (a) Dependence of LB film differential conductivity on tunneling voltage (3 monolayers). The LB film was under exposure to the natural light during few days. (b) Dependence of differential conductivity of LB film on tunneling voltage (3 monolayers) before and after direct photoreaction;  $\circ$  - A-form;  $\square$  - B-form

Another set of experimental data is concerned with investigations of tunneling conductivity behaviour during photoreactions. Substantial variation in the local density of electronic states (LDOS) for direct photoreaction has been observed for three-layer LB film. It is found that the shape of the differential conductivity curve is significantly modified during photoisomerization. Upper graph depicted in Fig.2b shows strong asymmetry of the curve for form *A*. There exist additional contribution to LDOS at  $U_t < 0$  compared to form *B*, while the dependencies of LB film conductivity of *A* and *B* forms at  $U_t > 0$

are rather similar. Such additional contribution points to the origination of additional sub-band in the range of empty electronic states.

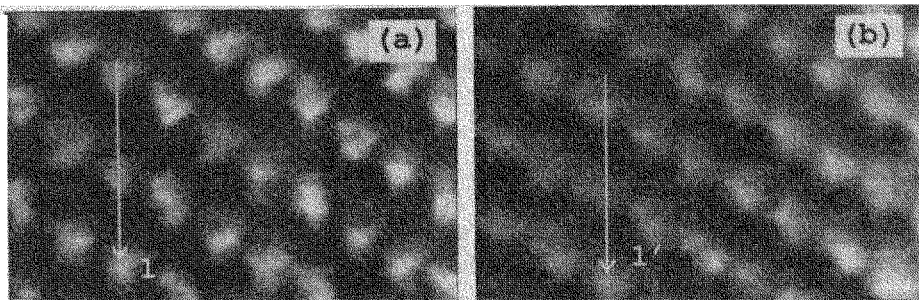


Fig.3. STM current images of the same portion of 3-layer naphthacenequinone LB films. (a) form A,  $I_t(x, y)$ :  $3.4 \text{ nm} \times 2.2 \text{ nm} \times 0.14 \text{ nA}$ , (b) form B,  $I_t(x, y)$ :  $3.3 \text{ nm} \times 2.5 \text{ nm} \times 0.08 \text{ nA}$

We have also studied the STM current images of individual molecules in NQ LB films. STM constant height images of 3-layer LB film corresponding to A and B forms of NQ are presented in Fig.3. Images (a) and (b) represent the selected site of the surface before and after direct photoreaction. Both pictures are registered under the same tunneling conditions:  $U_t = -150 \text{ mV}$ ;  $I_t = 0.4 \text{ nA}$ . In these experiments we have found the noticeable difference in STM current images of every molecule in LB layer for form A and B. These distinctions clearly seen from Fig.4, where crosssections of images from Fig.3, which are taken along  $1 - 1'$  direction, are presented. As seen from Fig.4 STM constant height image of 6-phenoxi-5,12-naphthacenequinone molecules in form A has  $\sim 0.1 \text{ nA}$  amplitude, while the current amplitude for molecules in form B is  $\sim 0.04 \text{ nA}$ . Besides, the STM current image of molecules in form A possesses an additional fine structure (see peak shifted to the edge of the molecule image). This peculiarity is connected either with topological conformational transition of molecule or with the occurrence of additional tunneling channel after molecular conformation.

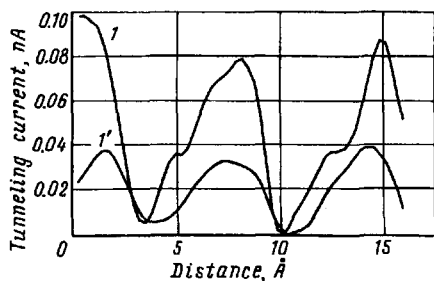


Fig.4. STM current image cross-sections according to arrows in Fig.3. Curves 1, 1' correspond to directions 1, 1' in Fig.3

The direct ( $A \rightarrow B$ ) and reverse ( $B \rightarrow A$ ) transitions of molecules caused by changing of light frequency can be understood by analysing the behaviour of driven non-linear oscillator. The driven non-linear oscillator model has been successfully used to describe the vibration molecular spectrum in external radiation field [14]. One can use double-well potential with simplest non-linearity  $\sim \gamma X^4$ ;  $X$  is configuration parameter. According to the semiclassical approach based on quasi-energy formalism there are two stable states (1 and 2) for driven oscillator in each well A and B, if the radiation frequency

$\nu$  is close enough to unperturbed molecular frequency  $\nu_0$ . The most probable state 1 or 2 (with small and high energy) is determined by the parameter  $\beta = \gamma J / (\nu - \nu_0)^3$ ,  $J$  is the intensity of external light,  $\gamma$ -nonlinearity, which can be slightly differ for wells  $A$  and  $B$ ,  $\nu_0$ -unperturbed molecular frequency, which can also different for wells  $A$  and  $B$ . If  $\beta$  is greater than critical value, the driven non-linear oscillator occupies the state 2 with high energy. For light wavelength  $\lambda_1 = 400$  nm parameter  $\beta$  is bigger than critical value for well  $A$ , but is smaller than critical value for well  $B$ . So, direct conformational transition  $A \rightarrow B$  occurs from high energy state 2 in well  $A$  to low energy state 1 in well  $B$ . Changing the light wavelength from  $\lambda_1 = 400$  nm to  $\lambda_2 = 480$  nm one changes the value of parameter  $\beta$ . Now  $\beta > \beta_c$  for well  $B$  (high energy state 2 is occupied in well  $B$ ) and  $\beta < \beta_c$  for well  $A$ . Reverse conformational transition  $B \rightarrow A$  occurs from high energy state in well  $B$  to low energy state in well  $A$ . The analytical expression for occupation numbers of non-linear oscillator in each well  $A$  and  $B$  can be obtained from the system of kinetic equations in quasi-energy formalism and will be published elsewhere. To our opinion, the observed transition is due to oxygen bonding transfer that leads to occurrence of additional tunneling channel and, in ordered molecular system of LB film, to occurrence of additional sub-band.

3. We have demonstrated the direct observation of differential conductivity changes of NQ LB films under photochemical reaction by STM/STS methods. Unusual behaviour of the differential conductivity of the molecular film probably corresponds to additional sub-band in the range of unoccupied electronic states of the sample as a result of photoreaction and can be referred to conformational modification of naphthacenequinone molecules. The distinction in the STM constant height images of individual NQ molecules in different forms has been found that demonstrates the conformation transition during photoisomerization.

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