

Title:

**STRUCTURE AND ELECTRONIC PROPERTIES
OF SELF-ASSEMBLED MACROCYCLE
AND POLYMER MULTILAYERS**

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STRUCTURE AND ELECTRONIC PROPERTIES OF SELF-ASSEMBLED MACROCYCLE AND POLYMER MULTILAYERS

Lin Song Li and Alexander D. Q. Li*

1. INTRODUCTION

Layer-by-layer (LBL) self-assembly technique has been widely used to fabricate artificial thin films for a number of potential applications with several advantages (Decher, 1997; Lenahan et al., 1998; Kaschak et al., 1999). First, many materials with charges can be chosen as building blocks for this simple approach to thin-film fabrication; this includes conducting polymers, optical chromophores, metal complexes, or semiconductor nanoparticles. Second, LBL self-assembly processes are much simpler when compared to the Langmuir-Blodgett technique, or chemical/physical vapor depositions (Liu et al., 1997; Li et al., 1998; Lütt, et al., 1998; Dante et al., 1999; Kim et al., 1999; Liu et al., 1999; Ostrander et al., 2001). Finally, by controlling length scale at the nanometer level, LBL approach can be used to construct materials with designed properties for applications in electronics, photonics, and optoelectronics. Since the interfaces between each layer become the key linkages for multilayers and therefore interface properties are crucial to the self-assembled systems (Li et al., 1998; Schlenoff et al., 1998).

The Kelvin Probe, as a non-contact, non-destructive vibrating capacitor device, has been used to measure the work function difference, or for non-metals, the surface potential, between a conducting specimen and a vibrating tip (Lüth, 1993; Baikie and Estrup, 1998). Measuring surface potentials of organic monolayers on conducting or semiconducting solids has been carried out successfully (Bruening et al., 1994; Bruening et al., 1995; Bruening et al., 1997; Bastide et al., 1997; Cohen et al., 1997;

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Cohen et al., 1999; Kronik and Shapria, 1999; Cohen et al., 2000). Studies on monitoring work function change *in situ* were also reported (Hamma and Cabarrocas, 1999; Tadayyon et al., 1999). Cahen D. and co-workers reported surface work function control of a semiconductor through molecular modification of its surfaces (Bruening et al., 1995; Bruening et al., 1997; Bastide et al., 1997; Cohen et al., 1997; Cohen et al., 1999; Cohen et al., 2000). Their results indicated that surface electric properties were a function of molecular modifiers in systems composed of chemisorbed monolayers of dicarboxylic acids on CdTe, CdSe, CuInSe₂, GaAs and InP. Recently, we employed Kelvin probe technique to measure work functions of organic and polymeric multilayers grown on conductive substrates (Li et al., 2000). The results indicated that the variation of the work function, as multilayers of PDDA [poly(dimethyldiallylammonium chloride)] and NiPc are self-assembled, is periodic.

In this chapter, we choose to assemble multilayer thin films using positively charged oligomeric viologen and negatively charged nickel phthalocyanine (NiPc) on a conductive oxide (Figure 1). Due to their interesting chemical structure and electronic properties, phthalocyanines have received considerable attention as constituents in optoelectronic devices (Hanack and Lang, 1994; Smolenyak et al., 1999), such as a single molecular dye Schottky barrier or hole conductors (p-type layers) in heterojunction devices. Conversely, viologens are electron acceptors (Kelly and Rodgers, 1994; Gong et al., 2000; Le et al., 2000), which seem ideal when coupled with electron-rich phthalocyanines. We hope that the study of the effect of self-assembled multilayers on the work function will provide insightful information on materials design and lead to the control of electronic properties on surfaces through molecular engineering.

2. EXPERIMENTAL SECTION

2.1. Materials Synthesis

Oligo(hexylene-4,4'-bipyridinium dibromide), or OHBP, was synthesized in our laboratory according to the following procedures. Bipyridine (0.8698 g) was mixed with 1,6-dibromohexane (1.3587 g) in approximately 2 mL of ethanol. The clear transparent mixture was then heated to 100 °C for about 24 hours. After reaction, a yellow solid was collected and washed with more ethanol, yielding 2.223 g (yield: 100%) of product—oligo(hexylene 4,4'-bipyridinium dibromide), or oligomeric viologen. ¹H NMR (DMSO-d₆), δ 1.35 (m, 4H), 2.03 (m, 4H), 4.71 (m, 4H), 8.78 (d, 4H), 9.53 (d, 4H). The average degree of polymerization is 11. NiPc was purchased from Aldrich and used without further purification.

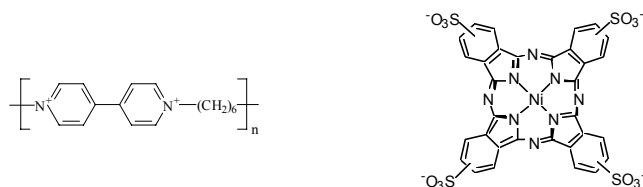


Figure 1. Molecular structures of oligo(hexylene 4,4'-bipyridinium dibromide), or OHBP (left) and nickel phthalocyaninetetrasulfonic acid tetrasodium salt, or NiPc (right).

2.2. Preparation of Self-Assembled Multilayers

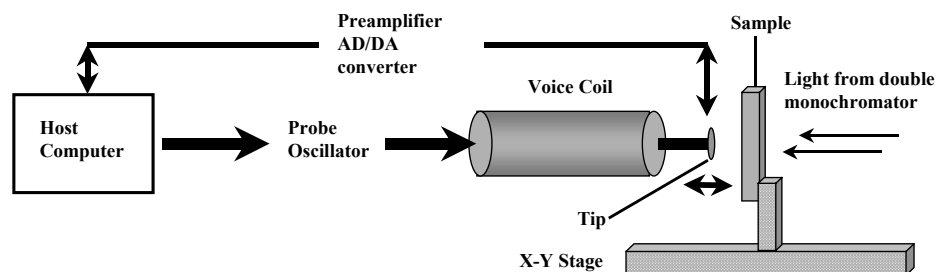
Positively charged OHBP and negatively charged NiPc were used for preparing self-assembled bilayers. The concentrations of OHBP polymer and NiPc aqueous solution were 50 mM and 1 mM, respectively. The ITO substrates (resistivity $\leq 40 \Omega/\text{cm}^2$) were purchased from Delta Technologies Company. Before using them, they were cleaned for 10 min by ultrasonication in an acetone solution. Then, the substrates were rinsed several times in deionized water and dried by N_2 . Immediately after drying, the substrates were immersed in the OHBP solution for about 5 min. The attractive force between positively charged OHBP polymer and negatively charged (OH-terminated) ITO surface is expected to coat the ITO surface with an OHBP monolayer. The coated sample then was washed with deionized water to remove all of the non-adsorbed materials and dried under N_2 for measurements. Then, the OHBP-coated substrate was immersed in a NiPc aqueous solution for another 2 min, followed by washing with deionized water. At this time, an OHBP-NiPc bilayer was formed on the ITO substrate. It was dried under N_2 again for further measurements. Repeating the above steps, additional bilayers of OHBP and NiPc were deposited and a multilayer began to emerge on the ITO substrate.

2.3. Instrumentation and Measurements

All infrared spectra of OHBP-NiPC multilayers were collected on a Bio-Rad FT-IR spectrometer (Mode FTS-40) equipped with a MCT detector at 2 cm^{-1} resolution. The measurements were carried out at an external reflection configuration, polarized within the incident plane at a grazing angle of 70 degree. UV-visible spectra were collected with a Varian Cary 1C instrument.

A commercial Kelvin probe system (KP-6500 Digital Kelvin Probe System, McAllister Technical Services) was used to measure work function changes. This apparatus measures the contact potential difference (CPD) between a reference plate and the sample's surface. CPD is defined as the work function of the reference plate connected to the preamplifier minus the work function of the sample, i.e. $\phi_m - \phi_{\text{sam}}$ (where ϕ_m is the work function of the reference plate (a constant), and ϕ_{sam} is the work function of sample). By comparing the work function before and after deposition of OHBP or NiPc onto an ITO substrate, the change in work function, $\Delta\phi$, after the deposition is obtained. The probe plate is made of stainless steel with a diameter of 10 mm. It was electrically connected via ground to the sample during the measurement with an accuracy of 2.5 mV. The typical distance between the reference plate of the probe and the sample was less than $\sim 1\text{mm}$ at 100 Hz oscillation frequency (Li et al., 2000). A CPD measurement was obtained by the Kelvin Probe system under ambient conditions each time after the new monolayer (OHBP or NiPc) was deposited onto the ITO substrate.

Surface photovoltage spectroscopy (SPS) measurements were carried out on a home-built setup (Scheme 1). ITO was chosen as the substrates that were illuminated through the transparent backside by monochromatic light, which was obtained by passing light from a 450 W xenon lamp through a double-prism monochromator (SPEX FL3-21). The Kelvin probe was employed to pick up the photovoltage signal. Photo-induced surface photovoltage spectra were obtained by scanning the wavelength of the incident light through the UV and visible range (250 - 710 nm) at a typical scanning rate of 20 nm/min. The raw SPS data were not corrected for the spectrum of the xenon lamp.



Scheme 1. Setup diagram for the measurements of surface photovoltage spectroscopy using Kelvin probe.

3. RESULTS AND DISCUSSION

ITO surfaces always show negatively charged characteristics due to the formation of dangling Sn-O⁻ bonds. Other likely contributions of the negative charges can be attributed to the formation of a typical *n*-type depletion layer on bare ITO. Therefore, in an aqueous solution, positively charged OHBP forms a monolayer on the substrate surfaces through self-organization or association of charge pairs, a process that assembles solution-solvated oligomers into monolayer films. Similarly, negatively charged NiPc macrocycles will bind to the dispersed positively charged oligomeric viologen monolayer. Multilayer thin films can be obtained by alternately dipping the substrate into the solutions of OHBP and NiPc. In the following discussions, we first establish the formation and structure of the OHBP and NiPc multilayers through optical absorption and surface infrared studies. Subsequently, we will monitor the evolution of the surface physical properties as each organic layer (OHBP or NiPc) is assembled.

3.1. UV-vis Measurements on Multilayer Thin Films

UV-vis spectra of OHBP-NiPc multilayers are shown in Figure 2. All the spectra exhibit the characteristic α and β absorption at 634 and 670 nm due to the π - π^* electronic transitions in NiPc molecules. The absorption at 274 and 343 nm are due to π - π^* electronic transitions in viologens. The growth of the film was monitored by measuring the absorption of both OHBP at 274 nm and NiPc at 634 nm. An approximate linear relationship between the optical absorption and the number of depositions was observed. This suggests that about the same amount of OHBP and NiPc macrocycle were deposited with each dipping if orientation effect of the chromophores is ignored. This assumption is generally acceptable because charge-charge interactions have little preference to molecular orientation.

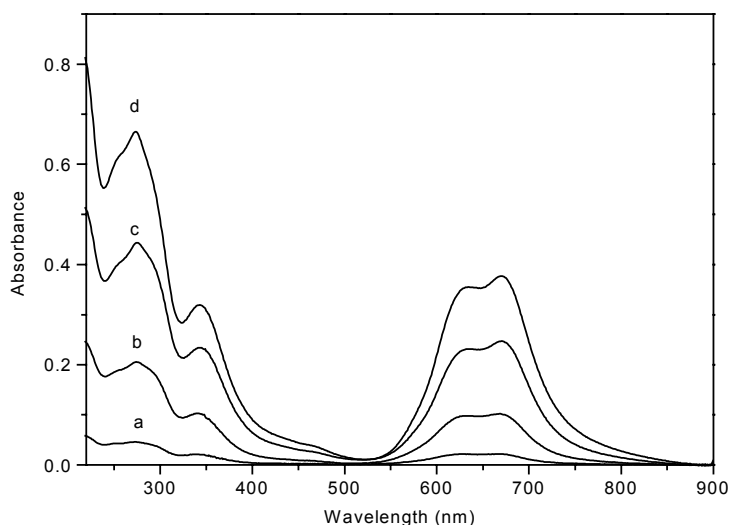


Figure 2. Optical absorption of (a) 3 layer-pairs of OHBP-NiPc; (b) 9 layer-pairs of OHBP-NiPc; (c) 15 layer-pairs of OHBP-NiPc; (d) 21 layer-pairs of OHBP-NiPc on quartz substrates.

3.2. Grazing Angle FTIR Studies on Self-assembled Multilayers

To understand the self-assembled multilayer better, we have carried out FTIR measurements on both self-assembled films and bulk materials using grazing angle (70 degrees) external reflection of the IR beam from conductive ITO surfaces in a p-polarized geometry. In this configuration, only those IR vibration modes that have a non-zero component along the surface normal will be measured. FTIR spectroscopy of NiPc drop-casted film on ITO was reported by us previously (Li et al., 2000). There are four bands at 1240 (s, ν_{as}), 1202 (s, ν_{as}), 1106 (w, ν_s), and 1030 (w, ν_s) cm^{-1} attributed to the sulfonate groups on NiPc (Colthup et al., 1975; Stymne et al., 1979; Watanabe et al., 1983; Enokida and Hirohashi, 1991; Fukui et al., 1991;). The macrocycle in-plane vibrations of C-N or C-C stretching modes bands are located at 1602, 1520, 1489, 1327, and 1089 cm^{-1} , and the 1160 cm^{-1} band is due to the C-H in-plane bending mode. On surfaces, the in-plane vibration modes of the NiPc are suppressed while the sulfonate bands remain strong ($\sim 1200 \text{ cm}^{-1}$). These results indicate that NiPc disk-like molecules are mostly lying flat on the surfaces in the drop-casted thin films.

Band assignment of OHBP is based on the model compound methyl viologen or bipyridinium (Christensen and Hammett, 1989; Bae et al., 1991). The bands at 3122 and 3044 cm^{-1} are due to the aromatic Ar-H. Aliphatic C-H vibrations located at 2935 and 2863 cm^{-1} , are assigned as asymmetric and symmetric methylene stretching modes, respectively. The methylene bending vibrations are located at 1468 and 1450 cm^{-1} . The bending vibrations of C-H from aromatic rings are located at 1348, 1233, and 1177 cm^{-1} . The vibrations of C=N or C=C stretching modes including ring modes are located at

1639, 1556, 1508, and 1252 cm^{-1} , and the 834 cm^{-1} band is due to the N-alkyl stretching mode. The 1639 cm^{-1} band is characteristic of the pyridinium ring breathing mode, confirming the formation of oligomeric viologen.

For self-assembled multilayers, the surface IR spectra of $N = 9, 18$ where N is the number of deposited OHBP-NiPc bilayers, are shown in Figure 4. With $N = 9$ OHBP-NiPc bilayers, OHBP bands at 2925, 2858, 1638, and 811 cm^{-1} , and NiPc bands at 1198 and 1033 cm^{-1} become visible. For the $N = 18$ sample, the bands belonging to OHBP and NiPc in the range of 1750 to 700 cm^{-1} are more distinct. Comparing with the bulk vibration information, a new band at 1227 cm^{-1} belonging to NiPc emerged; this band is originally from sulfonate groups and responsible for the formation of salt bridges of $\text{—SO}_3^-\cdots\text{Py}^+\text{—R—}$, which indicated the binding between OHBP and NiPc. In OHBP, both aromatic Ar-H and aliphatic C-H vibrations experienced considerable shift. For example, a blue shift of 14 cm^{-1} from 3059 cm^{-1} to 3044 cm^{-1} occurred in the Ar-H mode. Both aliphatic C-H shifted from 2925 and 2858 cm^{-1} to 2935 and 2863 cm^{-1} , corresponding to red shifts of 10 cm^{-1} and 5 cm^{-1} , respectively. We believe that these shifts are also due to the formation of charge pairs ($\text{—SO}_3^-\cdots\text{Py}^+\text{—R—}$) between viologens and NiPc sulfonates. The intensity of the OHBP bands at 2925 and 1638 cm^{-1} and that of the NiPc bands at 1326 and 1033 cm^{-1} were monitored during multilayer deposition. These four bands increased linearly with deposition number N , suggesting that materials deposited during each cycle was approximately constant. This observation is consistent with those of optical absorption studies.

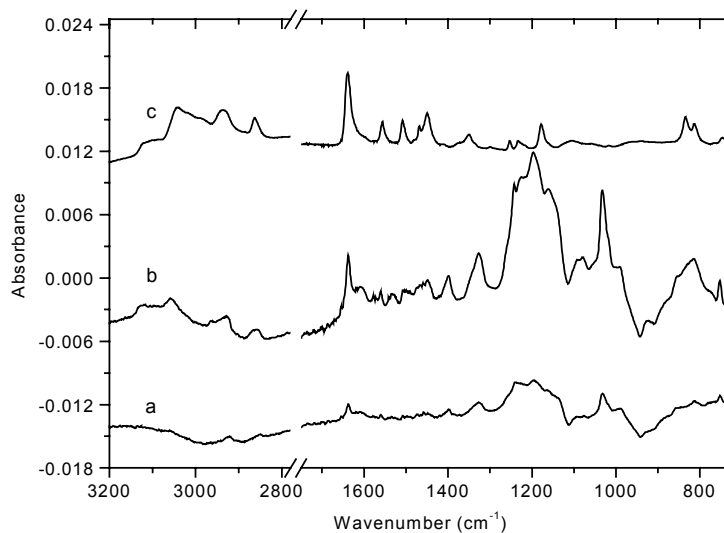


Figure 3. External grazing angle reflection (p-polarized; 70°) of infrared absorption spectra of self-assembled OHBP-NiPc multilayers on ITO substrates. (a) $N = 9$ bilayer; (b) 18 bilayer; (c) OHBP drop casted films onto an ITO substrate.

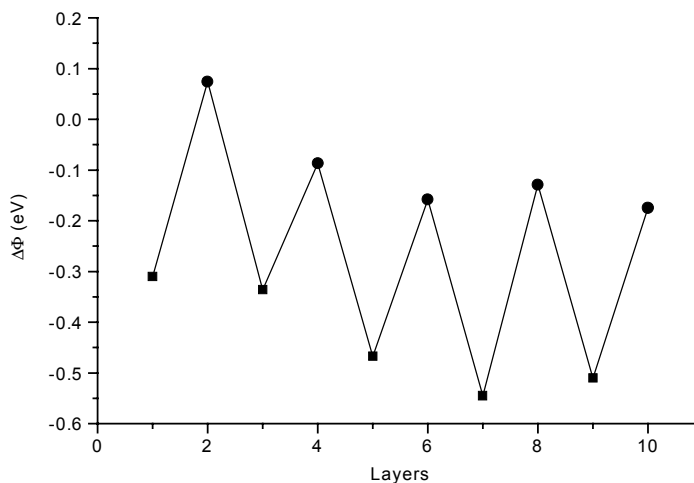


Figure 4. Surface work function (ϕ eV) dependence on the terminating layer of OHBP (square) or NiPc (circle) versus the number of total individual layers (i.e., the number of OHBP layers plus NiPc layers).

3.3. Kelvin-Probe Measurements on Multilayer Thin Films

Contact potential differences (CPDs) were measured after each deposition of viologen oligomers or NiPc layer on ITO. The surface work function values vs N , indicating that the surface potential of ITO electrodes changed after the deposition of OHBP or NiPc is shown in Figure 4. After a single layer of viologen oligomers was deposited onto an ITO substrate, its CPD value increased by ~ 300 mV (work function decreased by 0.3 eV) in reference to blank ITO. After deposition of NiPc onto OHBP-coated ITO, the CPD value decreased to around 50 mV (work function increased by 0.05 eV) in reference to blank ITO. Subsequent deposition of OHBP and NiPc layers continue the trend on increasing and decreasing the CPD by ~ 400 mV. The oscillation of the work function with layer deposition demonstrates that the relationship between surface potential and layer deposition (whether OHBP or NiPc) is periodic; therefore, that the surface work function of a multilayer is the same in an ideal situation regardless of the number of bilayers in the structure. We attribute this result to the reproducibility and consistency of the bilayer structure previously observed with UV-vis and FTIR.

Work function change can be due to modification in electron affinity and/or an alteration in band bending at surfaces/interfaces (Bruening et al., 1994; Kronik and Shapira, 1999). Therefore the total change in surface potential is equal to the sum of the modulation in band bending and electron affinity. Since the interaction between OHBP and ITO oxide are weak charge-charge bindings, we expect that changes in the work function from deposition of oppositely charged oligomers or macrocycles on ITO result predominantly from electron affinity contribution. We expect band bending if the self-assembled monolayers have ligand properties that alter the density of the surface states

(Bruening et al., 1995). The presence of a dipole layer, interacting weakly with surfaces, affects the electron affinity of the substrate only. Both band bending and electron affinity can be changed simultaneously if a dipole layer interacts strongly with surfaces (Bruening et al., 1997; Cohen et al., 1997; Cohen et al., 1999).

Due to the formation of a typical *n*-type depletion layer on bare ITO, there are some negative charges on the surface of ITO, thus promoting the growth of a positively charged viologen monolayer through electrostatic attractions (Moons et al., 1997; Li et al., 2000). The formation of OHBP on ITO surfaces generates a dipole at the inorganic-organic interface, pointing towards ITO, thus lowering the electronic affinity and decreasing its work function. In other words, it is easier for the surface-localized electrons to transfer into the vacuum from the Fermi level after the formation of OHBP/ITO dipole layers. When the negatively charged NiPc layer is deposited on top of a previous OHBP layer, another new dipole layer at the interface of OHBP and NiPc, pointing away from ITO, forms. The net interfacial dipoles of OHBP/ITO and NiPc/OHBP cancel each other mostly, and the net CPD values shift back to 50 mV, close to the blank reference ITO CPD value. This same effect keeps repeating itself as deposition of OHBP-NiPc multilayers continues. If this modification of the work function were mainly due to an alteration of ITO band bending, we would not have observed the oscillation pattern of CPD values. Therefore, we concluded that this oscillating pattern in the work function was mainly due to modulation in ITO's electron affinity. These results reveal that a Kelvin probe is a very effective tool for monitoring the surface physical properties as multilayer growth is evolving.

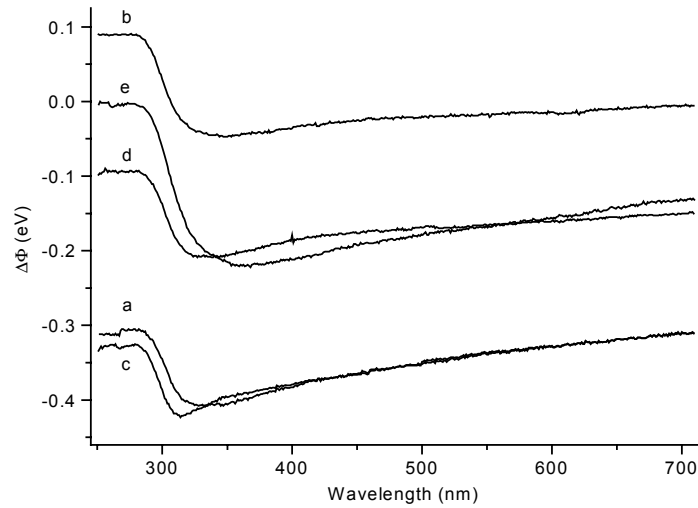


Figure 5. Surface photovoltage spectra (SPS) dependence on the terminating layer of OHBP and NiPc. (a) OHBP/ITO; (b) NiPc-OHBP/ITO; (c) OHBP-NiPc-OHBP/ITO; (d) NiPc-OHBP-NiPc-OHBP/ITO; (e) blank ITO.

3.4. Surface Photovoltaic Effects due to Formation of OHBP-NiPc Multilayers

Surface photovoltage measurement (SPV) is a very sensitive tool to measure the charge redistribution on semiconductor surfaces, buried interfaces, and heterojunctions. Here, we use surface photovoltage spectroscopy (SPS) to study the photovoltaic behaviors of OHBP-NiPc multilayers on ITO (Figure 5). The photo-excited electron-hole pairs will migrate under the intrinsic electric field at the interface, thus changing band bending. Therefore, SPS has been chosen to monitor the band bending change of ITO at the inorganic-organic interface under UV-vis illumination with or without OHBP and NiPc layer modification in this study.

For reference purposes, blank ITO's SPS was employed as the baseline (curve e in Figure 5). It has more than 200 mV photovoltaic response when excited at the band gap (350 nm) of ITO ($E_g = 3.7 - 4.3$ eV) (Gerfin and Grätzel, 1996; Hamberg and Granqvist, 1986; Moons et al., 1997), and about 140 mV response when excited at 650 nm. Its negative photovoltaic response value indicates a typical *n*-type material with an upward band bending near the surface. After one layer of electron-accepting oligomeric viologens is assembled, the photovoltaic response is significantly decreased to 105 mV at 350 nm. The reduction of the photovoltaic effect is almost the same at 650 nm (curves a and e are parallel to each other). This result indicates that surface states have been altered after the deposition of electron accepting OHBP molecules under light illumination. When we grow a NiPc layer and form the first OHBP-NiPc bilayer on ITO, about 30 mV photovoltaic response at 350 nm was recovered. However, the recovery of photovoltaic effects is 80 mV at 650 nm. The same effect keeps repeating as the deposition of the second OHBP-NiPc bilayers, with the exception that we are losing photovoltaic response with each addition of electron acceptor viologens. The significance of this result is that photo-induced band bending can be really changed by chromophoric monolayer modification on surfaces.

Actually, the total change in surface work function ($\Delta\phi$) for a semiconductor comes from two terms, the change in electron affinity related to surface dipole, $\Delta\chi$, and the change in band bending, ΔV (Bruening et al., 1994):

$$\Delta\phi = \Delta\chi \pm \Delta V \text{ ("+" for n-type; "-" for p-type)} \quad (1)$$

Because ITO forms an *n*-type depletion layer, we have $\Delta\phi$ that equals the sum of $\Delta\chi$ and ΔV . Without light illumination (labeled with superscript (1)), we measured the surface work function change [Eq. (2)], which is shown in Figure 5.

$$\Delta\phi^{(1)} = \Delta\chi^{(1)} + \Delta V^{(1)} \quad (2)$$

With light illumination (labeled with superscript (2)), we measured a photo-induced effect on the change of surface work function [Eq. (3)], which is plotted in Figure 6.

$$\Delta\phi^{(2)} = \Delta\chi^{(2)} + \Delta V^{(2)} \quad (3)$$

Since we expect the electron affinity will remain constant with or without light illumination, i.e., $\Delta\chi^{(1)} = \Delta\chi^{(2)}$, we can deduce the photo-induced band bending change $\Delta\Delta V = \Delta V^{(2)} - \Delta V^{(1)} = \Delta\phi^{(2)} - \Delta\phi^{(1)}$. Accordingly, we have calculated the photo-induced

band bending change $\Delta\Delta V$ at the ITO band gap (350 nm) and in the red region of the spectrum (650 nm). For bare ITO substrates, we have $\Delta\Delta V(350 \text{ nm}) = -215 \text{ meV}$ and $\Delta\Delta V(650 \text{ nm}) = -143 \text{ meV}$, which confirms that excitation at the band gap has a more pronounced photovoltaic effect. After the formation of a viologen monolayer, the $\Delta\Delta V(350 \text{ nm})$ and $\Delta\Delta V(650 \text{ nm})$ values shift to -105 meV and -20 meV . When a bilayer of OHBP-NiPc is formed, the photo-induced band bending values are $\Delta\Delta V(350 \text{ nm}) = -137 \text{ meV}$ and $\Delta\Delta V(650 \text{ nm}) = -100 \text{ meV}$. The second bilayer repeats the same trend. Figure 6 shows the plot of $\Delta\Delta V(\lambda)$ against excitation wavelength λ after the correction from blank ITO, and it is clear that the photo-induced band bending change depends on the terminal layer of the self-assembled multilayers of OHBP-NiPc. In other words, the photo-induced band bending change is also a periodic function of the self-assembled layers, oscillating between two approximate values corresponding to the characteristics of viologen and NiPc.

4. CONCLUSIONS

Our results from optical absorption and surface external reflection FTIR reveal that we can grow self-assembled multilayers consisting of electron acceptors like OHBP and donors like NiPc. In order to investigate the evolution of the surface physical properties of self-assembled multilayers, we applied Kelvin probe techniques and surface photovoltage spectroscopy to monitor the growth of self-assembled OHBP and NiPc systems. Kelvin probe results indicate that the surface electronic potential is very sensitive to the presence of self-assembled molecular layers on surfaces. We find that there is an approximately constant gap of 350 meV between the surface work function of OHBP and NiPc terminated self-assembled multilayers. In other words, the surface work function or surface electronic potentials is a periodic function of the terminating layer, oscillating between $\sim 450 \text{ mV}$ for OHBP layers and $\sim 100 \text{ mV}$ for NiPc layers. On the other hand, the photo-induced effects can be also correlated to the terminating layer of the OHBP-NiPc system. This shows that the self-assembled layers also control the photo-induced effects to some extent. Over the whole excitation spectrum (300-710 nm), the photo-induced band bending change oscillates between two values mostly governed by the properties of the terminating layer of the self-assembled systems.

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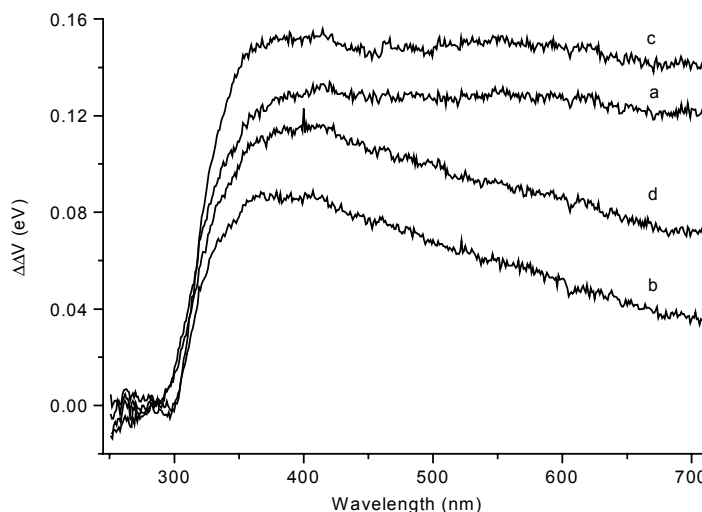


Figure 6. $\Delta\Delta V$ (mV) dependence on the excitation wavelength λ after the correction from ITO, i.e. $\phi_{\text{sam}} - \phi_{\text{ITO}}$: (a) OHBP/ITO; (b) NiPc-OHBP/ITO; (c) OHBP-NiPc-OHBP/ITO; (d) NiPc-OHBP-NiPc-OHBP/ITO.

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