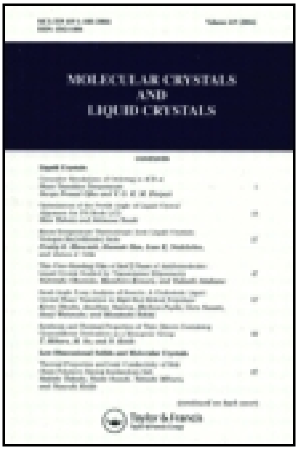

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# Organized Langmuir-Blodgett Monolayers and Multilayers Based on Semi-Amphiphilic Binuclear Phthalocyanine: AFM Investigation and Photovoltaic Characteristics

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# Organized Langmuir-Blodgett Monolayers and Multilayers Based on Semi-Amphiphilic Binuclear Phthalocyanine: AFM Investigation and Photovoltaic Characteristics

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A water-soluble binuclear cobalt phthalocyanine-sulphonate was used to prepare LB films by semi-amphiphilic technique. Atomic force microscopy (AFM) was applied to investigate the surface morphology of $C_{18}NH_2$-OME/bi-CoPc LB multilayer on silicon substrate and surface photovoltage spectra (SPS) was used to study the interfacial charge transfer properties.

*Keywords:* binuclear phthalocyanine; LB films; AFM; photovoltage

## INTRODUCTION

Much attention has been focused on organizing phthalocyanines into ordered thin-film assemblies, such as Langmuir-Blodgett (LB) films, which may be useful in application such as molecular devices. Leznoff, C. C. [1] is the first one to put planar binuclear phthalocyanine in LB films. However, few works about studies of water-soluble planar binuclear phthalocyanine by LB technique has been reported. Atomic force microscopy (AFM) is proving to be a valuable characterization tool for studying the surface of monolayer and multilayer LB films.[2] The method allows direct observation of the surface morphology of organic layers. In this work, we introduce a kind of water-soluble binuclear phthalocyanine (Scheme 1, bi-CoPc) into LB films by semi-amphiphilic technique and use AFM and SPS to investigate the properties of this assembly.

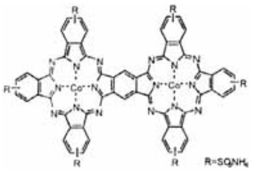
## EXPERIMENTAL

The preparation of LB films was reported in another publication (*in press, Langmuir*). LB monolayers of octadecylamine ($C_{18}NH_2$)-Methyloctadecanate (OME)/bi-CoPc ($C_{18}NH_2$ : OME = 1:4 and 1:1) on ITO were used for SPS measurements. The principle of SPS measurement was described in detail elsewhere.[3] A five-layer-LB film on silicon substrate was used for AFM investigation. AFM was carried out in air with a commercial system (Park Scientific Instruments). A 100 μm scanner was applied for surface inspection. Cantilever 220 μm long with an integrated pyramidal tip (nominal spring constant 0.03 N/m) was used in contact mode for all measurements.

## RESULTS AND DISCUSSION

### AFM Investigation of LB Multilayer

A 5-layer $C_{18}NH_2$-OME/bi-CoPc LB film was deposited at a surface pressure of 30 mN/m on a hydrophilic silicon substrate. On inspection of the large scan area (10 μm×10 μm) of the 5-layer film, the image appears to be flat and homogeneous (Figure 1) and the image is found to be stable and unchanged over long periods of observation. The RMS. roughness of this film is 0.579 nm and the average roughness is 0.473 nm. Moreover, this film is considerably stable that the AFM image taken on this film stored in air at room temperature for 30 days shows no obviously change compared with Figure 1. This confirms the strong interaction between bi-CoPc and substrate.



SCHEME 1
Chemical structure of bi-CoPc.

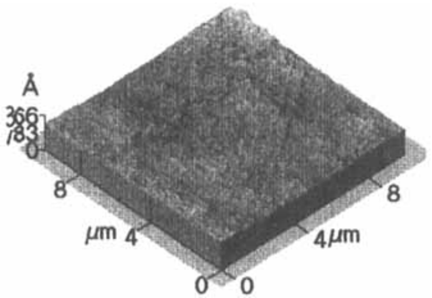


FIGURE 1 AFM image of a 5-layer LB films of $C_{18}NH_2$-OME/bi-CoPc deposited onto a hydrophilic silicon substrate (stored in air for 2 days).
See Color Plate VII at the back of this issue.

## Surface Photovoltage Spectra of Monolayer

The SPS of $C_{18}NH_2$-OME/bi-CoPc monolayers deposited on ITO substrates with different external electric field are shown in Figure 2. The irradiated electrode was defined as ITO(I) which $C_{18}NH_2$-OME/bi-CoPc monolayer deposited on it and the back one was defined as ITO(II). When the external electric field is 0 V, low photovoltage response can be observed. When a d. c. electric field is applied on the sample, there is a strong photovoltage response at about 340 nm (near the Soret-band). As the external electric field is made more positive, a positive photovoltage response can be observed. On reversing the external electric field, a negative photovoltage can be induced.

The illumination on the bi-CoPc surface make the electron in ground state (HOMO) excited to high energy level (LUMO). When the external electric field is made more positive (+ 1.0 V), the energy level of ITO(I) becomes lower and the injection of electrons from bi-CoPc to ITO(I) interface is made more easily, the efficiency of charge separation is higher now. This effect will increase the photovoltage response in ITO(I)/bi-

CoPc/ITO(II) heterostructure (Figure 2, curve b). On reversing the external electric field, the energy level of ITO(I) is raised and the electrons move toward ITO(II) interface, the direction of photovoltage response is changed (Figure 2, curve c). The photovoltage response values to the negative and positive electric field are different for the monolayers of $C_{18}NH_2$ :OME = 1:4 and 1:1. Our previous work had confirmed that the order of hydrocarbon chains in LB films of 1:4 is much higher than that of 1:1. So the SPS results indicate that when the hydrocarbon chains in the monolayer are organized into highly ordered structure (1:4), the charge transfer efficiency is higher than that of the lower ordered structure (1:1).[4]

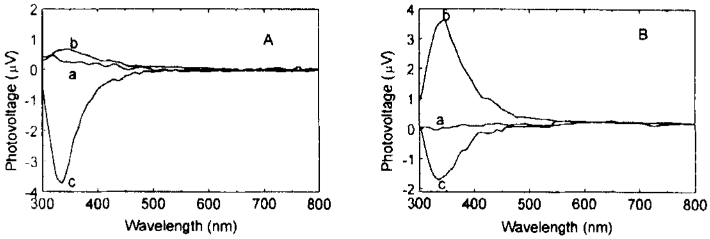


FIGURE 2 SPS of LB monolayers on ITO substrates: (A) $C_{18}NH_2$ : OME =1:4; (B) $C_{18}NH_2$ : OME =1:1 (a) E = 0 V, (b) E = + 1 V, (c) E = -1 V.

## Acknowledgement

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