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Photoelectric Conversion of a Novel Langmuir–Blodgett Film

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ABSTRACT

The photoelectric conversion of a novel Langmuir–Blodgett (LB) film consisting of 3.4.9.10-perylenetetracarboxylic diimides (PTCDI) and amphiphilic zinc phthalocyanine (AmZnPc) were investigated. The results show that the PTCDI molecules were embedded in the cavity between the long alkyl chains of AmZnPc in the monomolecular layer of LB film. The V_{oc} *of the monomolecular layer of a mixture of PTCDI (E) and AmZnPc was as high as 145 mV. Copyright © 1997 Elsevier Science Ltd*

Keywords: perylenetetracarboxylic diimide, phthalocyanine, LB film, open-circuit voltage, short-circuit current, monomolecular layer.

INTRODUCTION

The photo-electric conversion of thin solid films, including LB films of organic molecules containing extended conjugated systems, is a subject of particular interest with respect to molecular structure and film structure in the development of thin film devices. In particular, the combination of phthalocyanine (Pc) and 3.4.9.10-perylenetetracarboxylic diimide (PTCDI) in a dual-layer organic solar cell closely mimics the properties of the inorganic P–N junction solar cell.[1,2]

In a previous communication, the photovoltage properties of PTCDI solid film were discussed with respect to the Dember effect.[3] More recently, a new

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approach has been developed for the formation of mixed film using the LB technique. This method allows the functional molecules to be arranged in a highly ordered structure on a solid substrate, and offers the possibility of practical applications in photoelectric devices.

We report here the photovoltaic behaviour of some new mixed LB films comprising a series of perylene derivatives (PTCDI) and phthalocyanines with long alkyl chains (AmZnPc). The structure–property relationships of these new mixed LB films, and their absorption characteristics, are also reported.

EXPERIMENTAL

Preparation of the mixed LB film

The synthesis and purification of PTCDI and of the Pc compound have been previously reported;[4] their structures are shown in Fig. 1. Chloroform (A.R.) was purchased from a Beijing chemical factory and was used as received.

The materials were mixed in the solid state and subsequently dissolved in chloroform to a concentration of approximately 1×10^{-4} mol/litre. The solution was spread onto a purified water subphase (pH 5.6–5.8, obtained after three deionizations). A solution of equimol AmZnPc and of PTCDI in chloroform were used to form the film on an ITO glass (indium tin oxide coated glass) surface. When the PTCDI was diluted with AmZnPc, a uniform stable floating film was formed and Y-type deposition was obtained on the ITO substrate. All the clean substrates for this work were hydrophilic in nature and were maintained in an isopropanol solution. The monolayer film was prepared at a constant surface pressure of 20 mN/m and the subphase temperature was kept at room temperature. The LB film balance was obtained with a Jielin JC-1 (Jielin University, China) equipped with an electronically controlled dipping device; electronic spectra of the LB films were recorded on a Shimadzu UV-120-02 spectrophotometer.

Measurement of the photo-electric conversion properties

The PTCDI and AmZnPc molecules, using the LB technique, were deposited onto an ITO conductive glass as a working electrode, with 0.1 mol/litre of H_2SO_4 (aq solution) as a supporting electrolyte, an SCE (saturated calomel electrode), and a Pt foil as a reference; a counter electrode was used to measure the open-circuit voltage (V_{oc}) and the short-circuit current (I_{sc}). Measurements were made of the current–voltage characteristics of the film in the dark, and under irradiation from broadly focused white light from a 250 W tungsten halide lamp equipped with a 7 cm water filter to separate

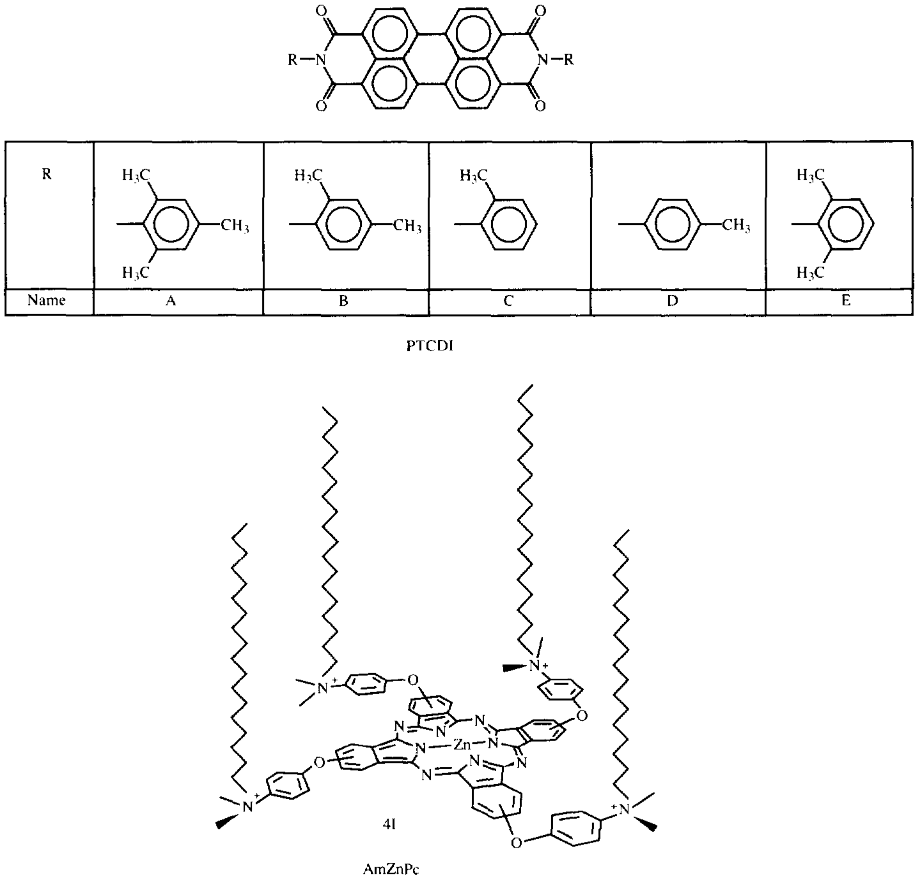

Fig. 1. Structural formulae of 3.4.9.10-perylenetetracarboxylic diimide (PTCDI) and amphilic zinc phthalocyanine (AmZnPc).

heat. The intensity of the incident light was 75 mW cm^{-2}; V_{oc} and I_{sc} values were measured using a Model GDM-8045 digital metre. Lifetimes were measured by the time-correlated single-photon counting technique using a Photochemical Research Associates Horiba-NAES Model 1100 lifetime fluorometer.

RESULTS AND DISCUSSIONS

Properties and structure of the LB films

Figure 2 shows the surface pressure–area (π–A) isotherms at room temperature for the monomolecular layer of equimolar mixed PTCDI and AmZnPc

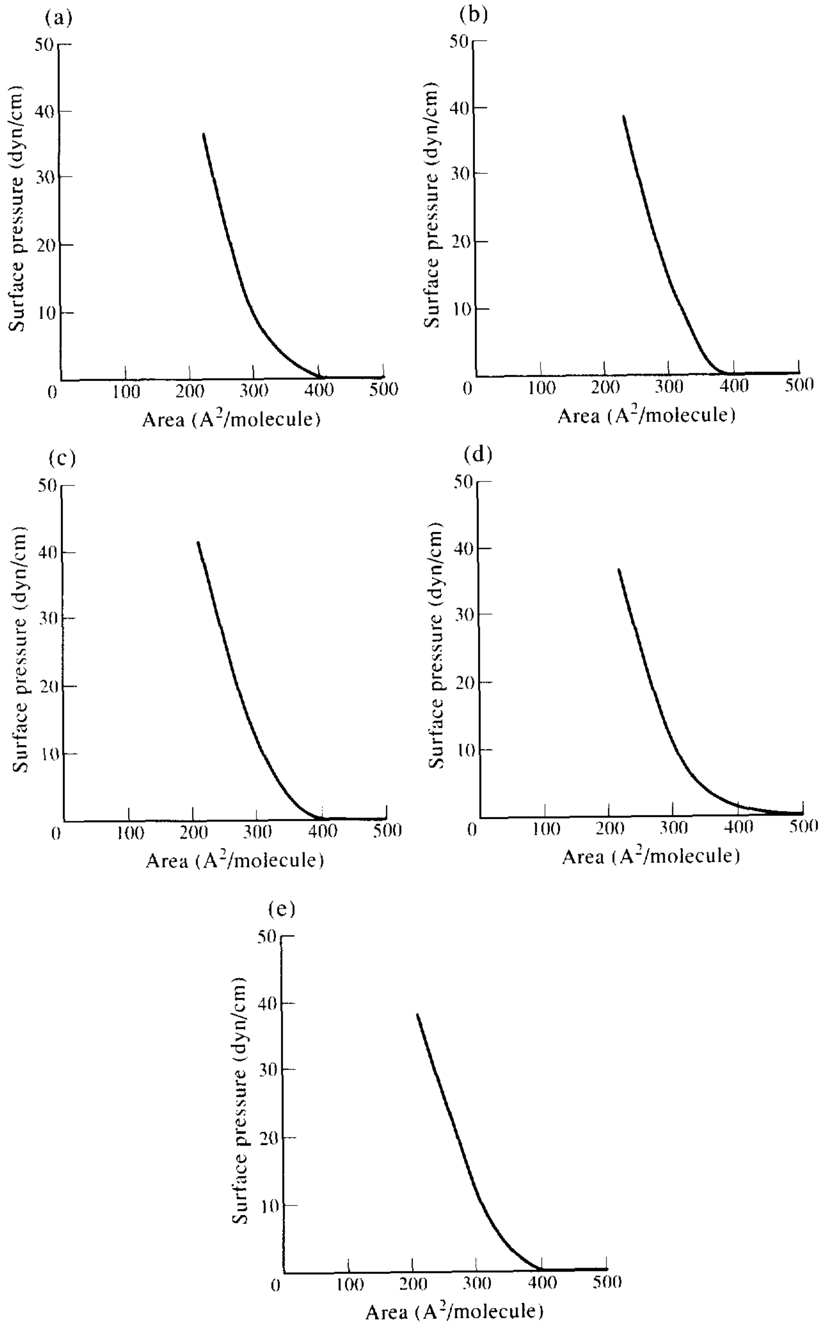

Fig. 2. Surface pressure–area isotherm of equimolar PTCDI and AmZnPc spread from 1.0×10^{-4} M chloroform solution.

sprea in chloroform on an aqueous subphase. The isotherm shows that there are distinct phase transitions and an abrupt slope, which implies that a well-condensed mixed monolayer was formed. From the π–A isotherms, it is also apparent that the mixed monolayers collapsed at over 40 mN/m. Extrapolating the isotherm to the abscissa, the area per molecule of the mixed film was calculated to be A: 324.3 Å^2; B: 317.1 Å^2; C: 323.8 Å^2; D: 321.2 Å^2; E: 320.0 Å^2, which is similar to the area per molecule 310 Å^2 of the individual AmZnPc film. This phenomenon suggests that the PTCDI molecules were embedded into the cavity between the long alkyl chains of the AmZnPc into one layer of the film, which protects the PTCDI molecule from interlayer aggregation. From the CPK (Corey–Pauling–Koltum) molecular model, the AmZnPc would fill a square 18.8 Å on one side and occupy a minimum area of about 354 Å^2 per molecule in a plane. It seems that the AmZnPc molecule is orientated with the plane of the macroring to the water surface with an angle of 32° for the individual AmZnPc film, and of 28° for the mixed film during compression.

Absorption spectra of mixed LB film

The shapes of the absorption curves were very similar for each molecule; at approximately 1×10^{-4} mol/litre concentration, the maximum absorption wavelength of compounds A–E in DMF were 527, 526, 525, 525 and 526 nm, respectively. AmZnPc had a strong narrow absorption band in the range of 650–710 nm, together with a weaker vibrational coupled satellite band at 610 nm. These results show that there is no obvious interaction between the PTCDI, and that AmZnPc exists in solution mainly as a monomer.

In contrast, in the mixed PTCDI + AmZnPc LB film, the soret band of the PTCDI moiety shows a peak at 546, 549, 549, 549 and 549 nm within one layer. They are thus red-shifted more than 20 nm compared with PTCDI in DMF. In addition, the absorbance of the PTCDI soret band at 549 nm, and of the AmZnPc Q band at 694 nm of the deposited films when plotted against the number of layers, resulted in a linear relationship, as show in Fig. 3.

Photo-electric conversional behaviour of mixed LB film

The open-circuit voltage (V_{oc}) and the short-circuit current (I_{sc}) only monomolecular layer LB films were determined in dilute H_2SO_4. The results are shown in Table 1; the intensity of the incident light was 75 mW/cm^2.

In order to investigate the photovoltaic behaviour of the mixed monolayer, and to confirm the contribution of PTCDI and AmZnPc (which act as electron acceptor and electron donor in the mixed molecule system), the open-circuit voltage and short-circuit current were measured with one

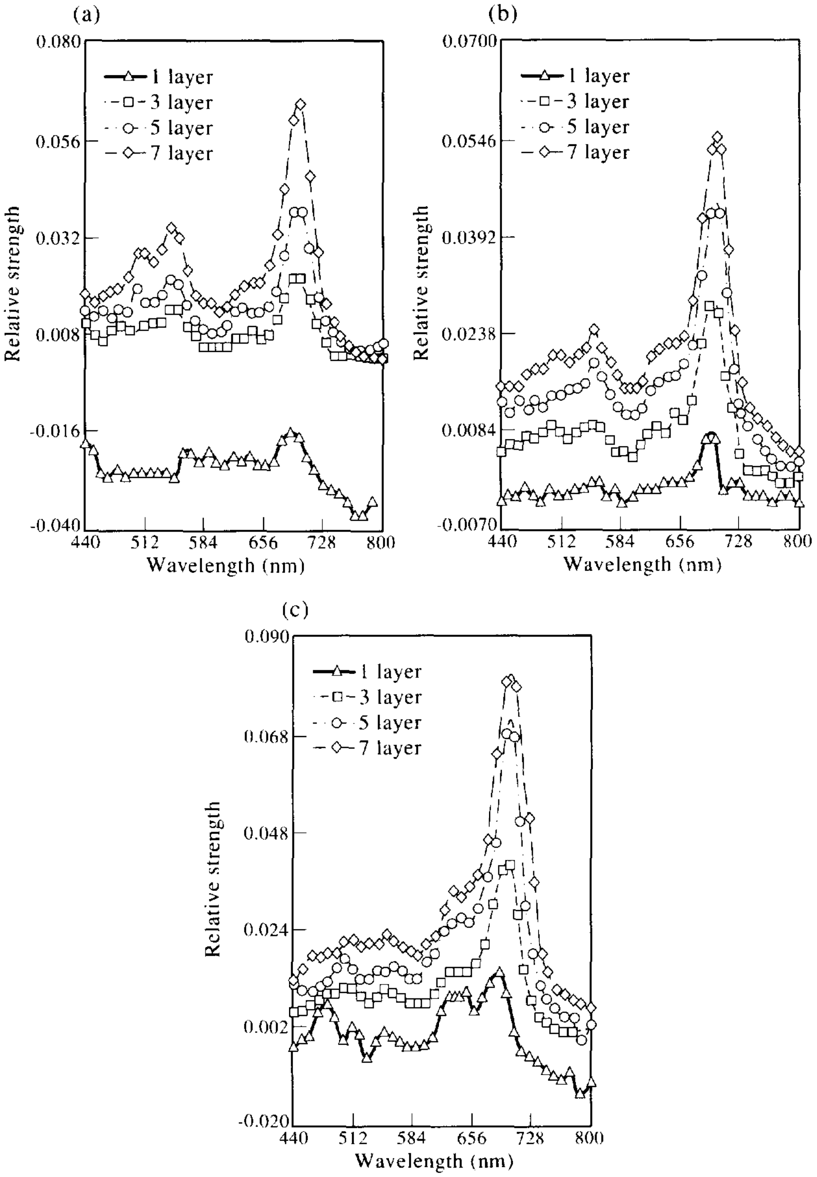

Fig. 3. Electronic absorption spectra of multilayers in mixed PTCDI + AmZnPc film.

monolayer of mixed compound (both PTCDI and AmZnPc which were modified on ITO electrode surface) and the results are shown in Table 1. Comparison of the V_{oc} and I_{sc} results of the mixed compound and of the monomolecular PTCDI[5] clearly indicates that rather higher values of V_{oc} were obtained for mixed compound. This shows that the charge separation efficiency of the mixed compound has been enhanced, allowing a complete

TABLE 1
Photo-electric Conversional Behaviour of the Monolayer LB Film

Compound	*A*	*B*	*C*	*D*	*E*
V_{oc} (mV)	46	63	71	92	145
I_{sc} (μA/cm^2)	0.01	0.02	0.01	0.03	0.03

charge transfer from the electron donor AmZnPc to the electron acceptor PTCDI. Therefore, the intermolecular charge-separated state having a long lifetime was formed, i.e. the fluorescence lifetime of mixed compound A–E with AmZnPc in DMF are 7.95, 7.84, 7.68, 7.36 and 7.26 ns, respectively. The observed short-circuit current mainly arose from excitation of the photosensitizer, i.e. the perylene moiety.

On the other hand, we consider that the mixed compound LB film formed is similar to the P–N junction of organic solar cell. Because PTCDI molecule is embedded in the cavity of the long alkyl chains of AmZnPc, and the AmZnPc molecular planer is deposited on the substrate, the PTCDI molecule planer is nearly the AmZnPc molecular plane. Thus, the P–N junction is formed.

CONCLUSIONS

The photoelectric behaviour of mixtures of PTCDI and AmZnPc were investigated by the LB film technique. From the surface pressure–area isotherms and electronic spectra data, it can be concluded that the PTCDI molecules are embedded in the cavity between the long alkyl chains of the AmZnPc in the monomolecular layer of the LB film. The macro-ring of AmZnPc is oriented nearly parallel to the surface of the substrate, giving the largest area per molecule for any PCTDI studied to date in LB films.

The mixed compounds exhibited high open-circuit photovoltages compared to the PTCDI. The V_{oc} of the mixture of compound E and AmZnPc, with only a monomolecular layer, is as high as 145 mV. This shows that the mixed compound has a good photoelectric behaviour. The short-circuit current mainly arose from the PTCDI moiety.

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