

Photoelectric Conversion of Perylenetetracarboxylic Diimides in Langmuir–Blodgett Films

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ABSTRACT

This article reports the photoelectric conversion of 3, 4, 9, 10-perylenetetracarboxylic diimides (PTCDI) in multilayers of Langmuir–Blodgett (L–B) films using the photoelectrochemistry technique and absorption spectroscopy. The rate of electron transfer caused by five different PTCDI molecules was determined and the results demonstrate the photoelectric conversion properties of PTCDI molecules in L–B films.

1 INTRODUCTION

Derivatives prepared from 3, 4, 9, 10-perylenetetracarboxylic dianhydride (PTCDA) and diimides (PTCDI) have useful semiconductive and photoconductive properties, and have also been reported as functional dyes.^{1,2} In most cases, PTCDI are not ideally suited to thin film deposition by the L–B technique. However, we have obtained high-quality monolayer and multilayers by mixing the PTCDI with a long-chain fatty acid. In a previous communication the photovoltage properties of PTCDI solid film were discussed with respect to the Dember effect.³ The L–B technique is a suitable method for

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studying the photoelectric conversion with the help of absorption spectrum and special devices. There are two approaches involved in this, the first part pertaining to the structure properties of the PTCDI in an L-B film, and the second to photoelectrochemical aspects of formation of the L-B film, which may result in important differences between aggregation and the L-B layer.

2 EXPERIMENTAL

2.1 Preparation of L-B films

The synthesis and purification of the PTCDI (Table 1) have been previously reported;⁴ stearic acid was obtained from Sigma.

The materials were mixed in the solid state and subsequently dissolved in chloroform to a concentration of approximately 1×10^{-4} mol litre⁻¹. The solution was spread onto a purified water subphase (pH 5.6–5.8) obtained after three deionizations. The molar ratio of the PTCDI to stearic acid was 1:3, to form the film onto an ITO (indium tin oxide coated) glass surface. When the PTCDI was diluted with stearic acid, a uniform stable floating film was formed and Y type deposition was obtained on the ITO substrate. All clean substrates thus obtained were hydrophilic and were kept intact in isopropanol. The monolayer film was prepared at a constant surface pressure of 20 mN m⁻¹ and the subphase temperature was controlled at room temperature. L-B film balance was obtained by a JieLin JC-1 (made in JieLin University, China) equipped with an electronically controlled dipping device. Electronic spectra of the L-B films were recorded on a Shimadzu UV-120-02 spectrophotometer.

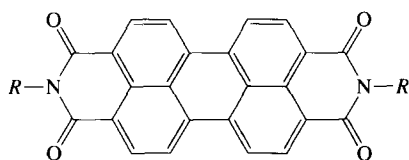


Table 1
Structure of 3,4,9,10-Perylenetetracarboxylic Diimides

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	A	B	C	D	E

2.2 Measurement of properties of photoelectric conversion

The PTCDI molecule with aid of the L-B technique was deposited on ITO conductive glass as a working electrode, with 0.1 mol litre⁻¹ of H₂SO₄ (aqueous solution) as a supporting electrolyte, an SCE and a Pt foil as a reference, and a counter electrode was used to measure the open circuit voltage (V_{oc}) and short circuit current (I_{sc}). The current-voltage characteristics of the film in the dark and under irradiation of broadly focused white light from a 250-W metal halide-lamp (75 m W cm⁻²) were measured using a Model GDM-8045 digit meter.

3 RESULTS AND DISCUSSIONS

3.1 The properties and structure of monolayer

The absorption spectra of the mixed PTCDI and stearic acid are shown in Fig. 1; since the shape of the absorption curves were very similar for all molecules, only the spectra of compounds A, C and E are shown. At approximately 1×10^{-4} mol litre⁻¹ concentration, these compounds in DMF showed λ_{max} at 527 nm, 525 nm and 526 nm respectively, values which are characteristic of monomer absorption. This contrasts with the absorption spectrum of L-B films, which have maxima at 560 nm, 570 nm and 550 nm, respectively. The surface pressure-area (π -A) isotherms of the PTCDI are shown in Fig. 2. From these isotherms it is apparent that the monolayers of compounds A, B, C and E collapse at about 40 mN m⁻¹, while that of compound D collapses at 33 mN m⁻¹. The results are in accord with structural features, in that the phenyl substituent directly bound to the PTCDI moiety is oriented nearly perpendicular to the latter portion.⁵ Their longitudinal translation is appreciably smaller than the transverse shift when bulky *ortho*-substituents are present in the phenyl ring; the packing is so strongly perturbed that the stacks are either extremely expanded or a pronounced transverse shift avoids any overlapping of the molecules. Because of this, the angle between the two rings of compound E is larger than that in compound D; the solubility of compound E is greater than compound D, and this results in L-B film structure from compound E and stearic acid being able to completely spread onto the water surface. From the π -A isotherms, the per-molecular areas of the compounds are: A:111.72 Å²; B:89.23 Å²; C:91.94 Å²; D:96.21 Å²; E:95.69 Å². These results show that the per-molecular areas are of a similar order, except for compound A, and have the same deposited form in the L-B film. On the other hand, the π -A isotherms of compound A and D are smooth curves, different to those of the other compounds.

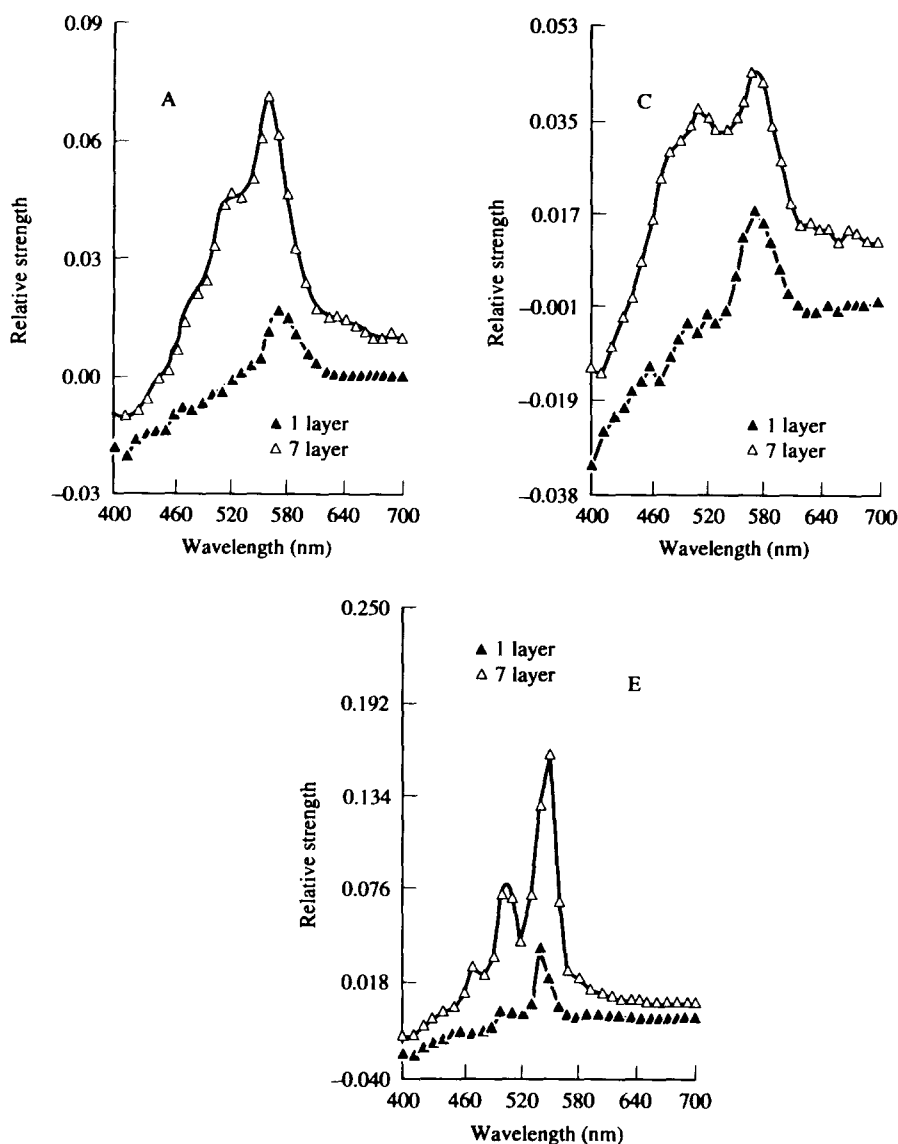


Fig. 1. Electronic absorption spectra of multilayers of PTCDI in mixed L-B film: \blacktriangle , 1 layer on each side of ITO substrate; \triangle , 7 layers per side.

3.2 Photoelectric conversion properties of mixed L-B film

The open circuit voltage (V_{oc}) and short circuit current (I_{sc}) consisting of one-layer and seven-layer L-B films, respectively, were determined in dilute H_2SO_4 . The results are shown in Table 2; the light intensity is 75 mW cm^{-2} .

The results in Table 2 clearly demonstrate the photoelectric conversion properties of the mixed L-B films. It is apparent that compounds **B** and **C** have

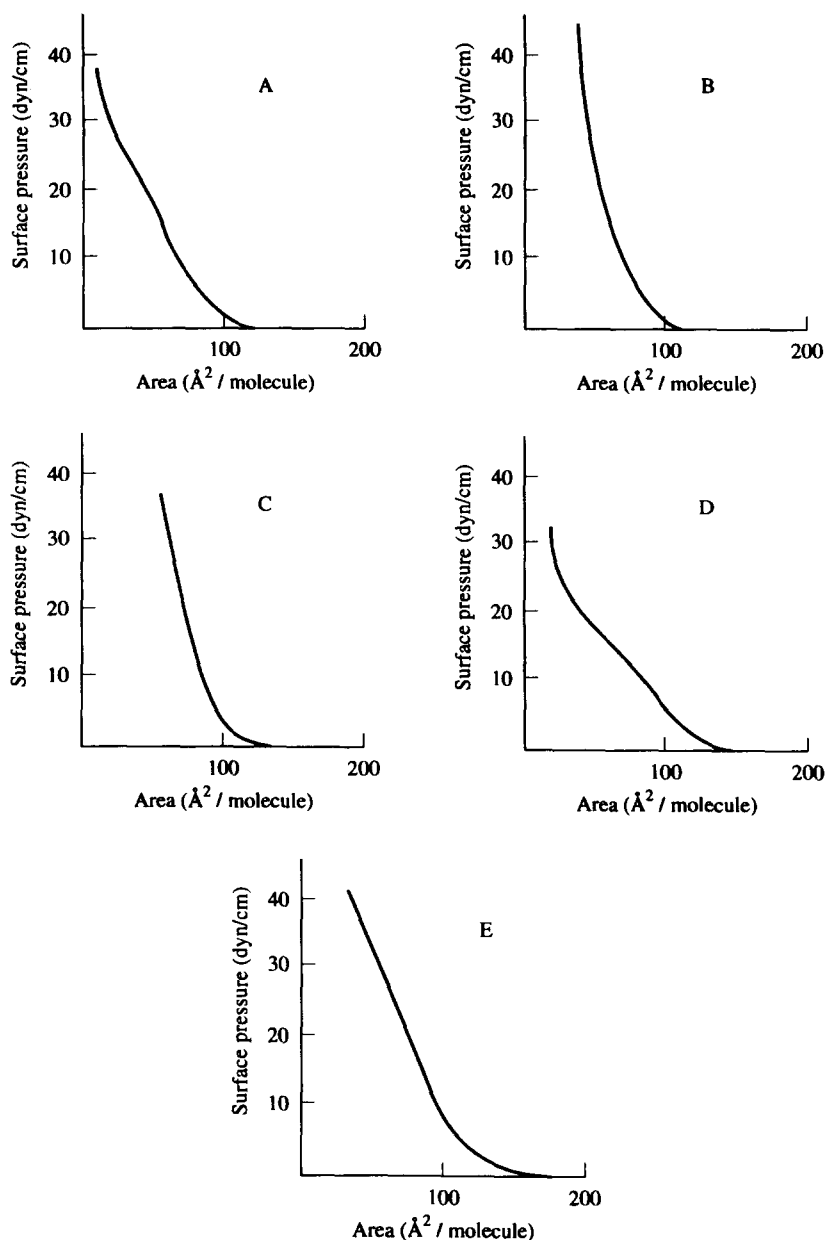


Fig. 2. Surface pressure-area isotherms of PTCDI spread from 1.0×10^{-4} M chloroform solution.

the best photoelectric conversion properties, and that the electron transfer is minimal when compounds **B** and **C** completely form a film. The structure of the compounds is in accord with the small angle between the two rings of the molecule, thus making the distance between the two molecules very small.

TABLE 2
Photoelectric Conversion Properties of Mixed L-B films

Compound	A		B		C		D		E	
	1-layer	7-layer	1-layer	7-layer	1-layer	7-layer	1-layer	7-layer	1-layer	7-layer
V_{oc} (mV)	30	76	77	95	34	123	16	61	29	141
I_{sc} ($\mu A\ cm^{-2}$)	0.02	0.03	0.03	0.1	0.14	0.44	0.02	0.03	0.02	0.03

The lifetimes of compounds A–E in chloroform were measured at 5.88 ns; 5.81 ns; 5.37 ns, 5.98 ns and 6.04 ns respectively. Since these values are almost the same it can be concluded that the factor which principally affects the photoelectric conversion properties is the influence of the chemical structure of the compounds on the film structure.

4 CONCLUSIONS

Multilayers of mixed PTCDI molecules with stearic acid may be readily built-up on an ITO substrate using the L–B technique. Typical properties and structure of the monolayers, and photoelectric conversion properties of the mixed L–B film, were observed in the films. As a result, the V_{oc} value of compound E reached 141 mV and the I_{sc} of compound C reached $0.44\ \mu A\ cm^{-2}$ under intense light irradiation of $75\ mW\ cm^{-2}$. These results indicate the possibility for improving the photoelectric conversion properties when further new compounds are evaluated.

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