

PHYSICAL PROPERTIES OF 2D HETEROJUNCTION THIOPHENE-FULLERENE STRUCTURE FOR ORGANIC PHOTOVOLTAICS

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1. Introduction

Organic semiconductors are promising materials in the field of photovoltaics. One of the well-tried methods for deposition of organic layers on solid substrates is the Langmuir method. Langmuir monolayers are Monomolecular layers formed on the surface of a liquid subphase. These monolayers are formed as a result of a self-organized process at the air/water interface. . The structures are primarily characterized through isotherm measurements where thermodynamic quantities, temperature and surface pressure, can be easily controlled; surface pressure by a moving barrier over the surface. In the presence of two constituents in the mixture, properties of the system depend on the mixture molar ratio.

In this communication the possibility of determining the monolayer properties of a binary system consisting of oligothiophene and fullerene is discussed. We focused on mechanical and thermodynamic properties of the monolayer. In this combination of materials polymer acts as a donor and fullerene is an acceptor in p-n-like heterojunction formed at material boundary. Physical aspects of this device were studied in [1] after the evidence of photoinduced electron transfer from the excited state of a conducting polymer onto fullerene (C₆₀). Because a single polymer layer device presents low efficiency due to the mechanism of charge generation and transport, the use of a C₆₀ molecule, which has a high electron affinity value, sublimed onto the polymer (donor) in a bilayer heterojunction or mixed in the polymer film (blend) in a bulk heterojunction, increased dramatically the efficiency of the photovoltaic devices [2].

The goal of this paper is to find the conditions under which mixture forms spatially distributed interfaces between domains of components what is necessary for exciton splitting and subsequent charge transport. The behavior of substances in the system is determined by molecular interactions in the materials.

2. Materials

Fullerene (PCBO) - [6,6]-Phenyl C₆₁ butyric acid octyl ester, 99% - was purchased from Sigma-Aldrich Co. Oligothiophene hexamer (OTH) – 3,3'-bis-decyl[2,2';5'.2'';5'';2''';5''';2'''';2''''']sexithiophene-5,5''''-didaroxilic acid was synthesized as described in [3]. Both materials were dissolved in chloroform at a concentration of 0.5 mmol/l. Subphase used was bidistilled deionised water (18 MΩ.cm).

3. Method

Langmuir trough model 611M (NIMA Technology, Coventry, UK) was used in monolayer experiments. Working areas of the trough used were 600 cm² (max) and 75 cm² (min). Surface pressure was measured using the Wilhelmy method with a filter paper plate. It turned out that some properties of the mixture changes along with time the mixture is left to stabilize. To

eliminate the time dependence all samples were measured after 40 minutes after mixing. After spreading the material to the subphase/air interface the solvent was left to evaporate for 15 minutes to reach stability of the monolayer. Monolayers were compressed at constant speed of $2 \text{ cm}^2 / \text{min}$. The trough was thermostated by a recirculating cooler FL 300 (Julabo Labortechnik, Germany) with an accuracy of $0.1 \text{ }^\circ\text{C}$. The experiments were carried out at temperatures of $22 \text{ }^\circ\text{C}$.

4. Results

The mechanical properties of monolayers are determined by isotherm (π -A) measurement of 2D film on the surface of water. The shape of this curve reveals phase transitions during the compression process. Measured curves for mixtures of various molar ratios of OTH and PCBO are shown in Fig. 1.

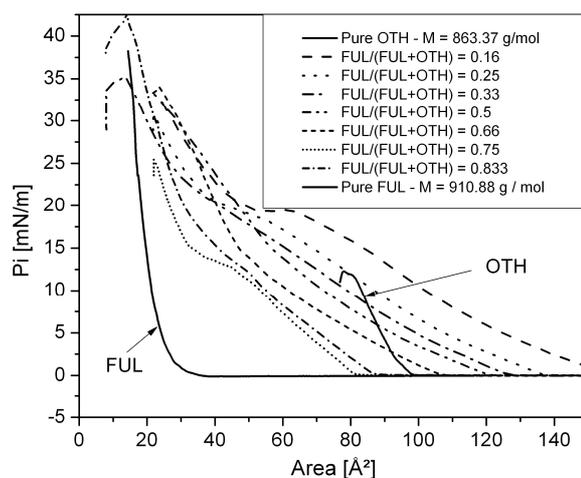


Fig.1: Pressure-area compression isotherms of mixtures with various OTH/PCBO molar ratios

As we can see the limiting areas per molecule for OTH and PCBO are ca. 80 \AA^2 and 35 \AA^2 , respectively. No clear transition from the liquid - expanded to the liquid - condensed phase is visible (transition typical for long-chained molecules like OTH). The noticeable feature is that pure OTH collapses at a very low value of surface pressure, $\pi \sim 12 \text{ mN/m}$.

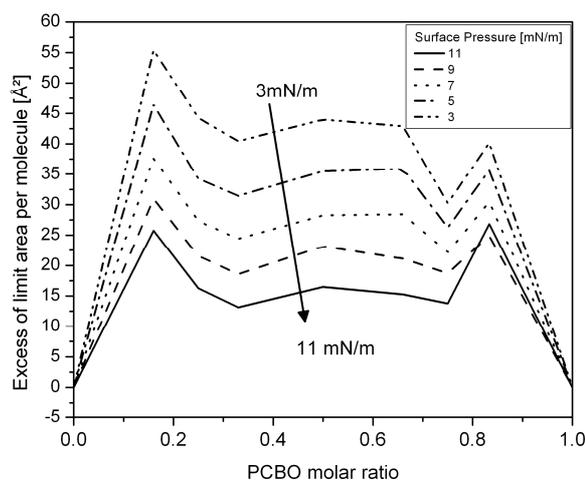


Fig.2: Excess area as a function of PCBO/OTH molar ratio at various levels of surface pressures

An important parameter for possible domain formation inside the mixture is represented by miscibility of components. This is obtained from values of the area per molecule for various molar ratios at the same surface pressure. For noninteracting molecules this dependence would be a straight line between points of the area for the pure constituents. The deviations from this line indicate the excess area which characterizes repulsive or attractive interactions between the molecules of components [4]. The excess areas for various molar ratios of the OTH/PCBO mixture are shown in Fig. 2. In all cases the average excess area is positive. This implies decreased miscibility of the components. It indicates that molecules do not mix homogeneously but form domains. These domains may not contain only pure components. This may suggest small clusters of individual oligothiophene molecules being attached with a certain number of PCBO forming more complicated structures due to intermolecular forces.

The molecular interactions in a two-component monolayer can be evaluated by a more detailed examination of the thermodynamics of the system. Such an analysis originated from Goodrich [5]. The variations of the Gibbs' free energy of a system containing a monolayer is given by

$$\left(\frac{\partial G}{\partial A}\right)_{T,P,n} = \gamma \quad (3)$$

where γ is the surface tension and A is the interfacial area. If we have a mixed monolayer with both components (1 and 2) constrained to remain in the surface, and variations of surface pressure are achieved by moving a barrier, at constant T and P , we have

$$dG = -Ad\pi \quad (4)$$

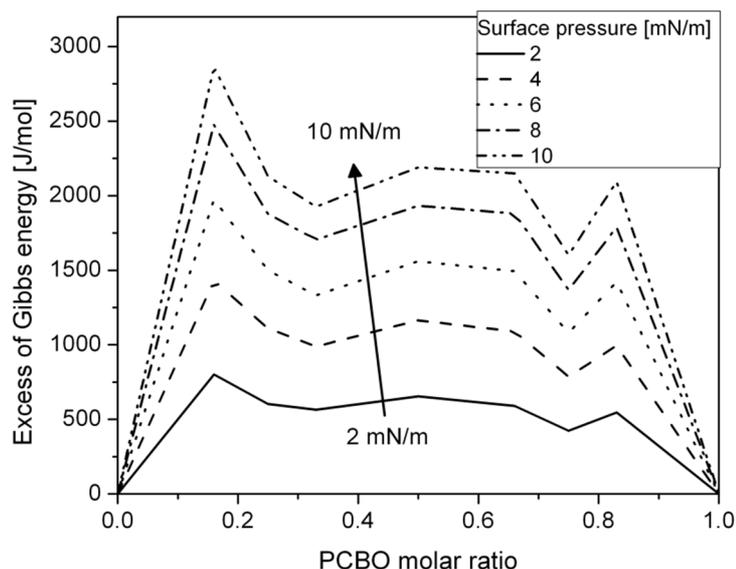


Fig.3 Excess of Gibbs energy as a function of PCBO molar ratio for various values of surface pressure.

It is often useful to consider the excess Gibbs' free energy of mixing, above that found for an ideal mixed film

$$\Delta G = \int_0^{\pi} (A_{12} - x_1 A_1 - x_2 A_2) d\pi \quad (5)$$

The value of ΔG provides information whether the particular interaction is energetically favorable ($\Delta G < 0$) or not ($\Delta G > 0$), while for $\Delta G = 0$ ideal mixing takes place. The value of ΔG as a function of the PCBO/OTH molar ratio for various values the surface pressure is presented in Fig. 3.

Deeper insight into structures formed inside the mixture can be obtained by optical microscopy. For this purpose the mixture of 1:1 ratio was deposited onto a Si substrate. Resulting dark field microscope images are shown in Fig. 4. The horizontal size of a snapshot is ca. 300 μm . We can clearly see domains of two different structures. Further measurements are needed to identify respective materials of this binary mixture in the microscope viewfield.

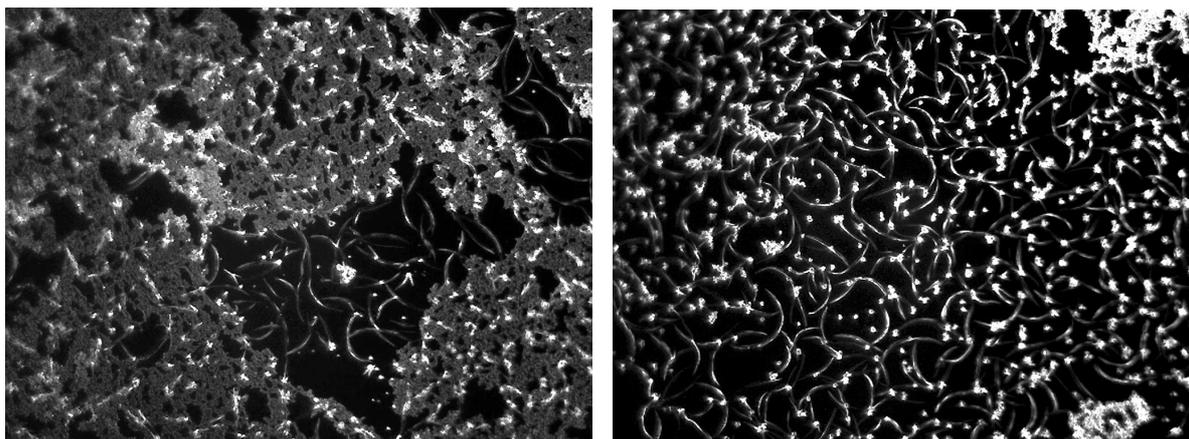


Fig. 4: Dark field surface microscope image of the structures formed by 1:1 OTH/PCBO mixture deposited onto Si substrate.

This finding is in good agreement with the results on the excess area and provides a convincing evidence on the phase separation in these molecular systems which are of fundamental relevance for the performance of organic photovoltaic devices.

Acknowledgement

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References:

- [1] N. S. Sariciftci and A. J. Heeger: *Int. J. Modern Phys. B*, **8**, 237 (1994).
- [2] G. Yu, J. Gao, J. C. Hummelen, F. Wuld, and A. J. Heeger: *Science*, **270**, 1789 (1995).
- [3] G. Čík, Z. Végh, F. Šeršeň, J. Krištín, B. Lakatoš, P. Fejdi: *Synth. Met.*, **149**, 31 (2005).
- [4] R. Maget-Dana: *Biochim. Biophys. Acta*, **1462**, 109 (1999).
- [5] F. C. Goodrich: *International Congress of Surface Activity*, 8591 (1957)
- [6] G. L. Gaines: *Insoluble Monolayers at the Liquid-Gas Interface*, Wiley-Interscience, New York (1966).