

EFFECT OF SELF-ORGANIZATION IN 2D MOLECULAR SYSTEMS PERSPECTIVE FOR ORGANIC PHOTOVOLTAICS

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Properties of monolayer films of the amphiphilic molecules using the Langmuir method were studied. We focused on binary systems of organic molecules to form self-organized structures suitable for application in photovoltaics. The studied materials were fullerene nanoparticles as acceptor and oligothiophene polymer as donor in organic molecular heterojunction structure. Mechanical as well as thermodynamic quantities were evaluated for characterizing the 2D molecular binary system at various molar ratios. The formation of self-assembled domains was visualized by AFM and fluorescence microscopy.

Key words: Langmuir monolayers, fullerene, oligothiophene, organic solar cells, molecular self-organization

1 INTRODUCTION

Langmuir monolayers are monomolecular layers formed on the surface of a liquid, mostly water. Due to the method of pouring of amphiphilic material mixture on the water surface these monolayers form structures as a result of a self-organized process. Organic molecules constituting the monolayer are amphiphilic and they spontaneously spread at the air/water interface. The Langmuir monolayer is a very suitable model for the study of self-organization in two dimensions. Structures are primarily characterized through isotherm measurements. A pair of 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, the properties of the system depend on the mixture molar ratio.

In this communication we focus on monolayer properties of a binary system consisting of oligothiophene and fullerene: their mechanical and thermodynamic properties in a monomolecular layer. This combination of materials is perspective in organic photovoltaic cells. The research involving polymer (donor) and fullerene (acceptor) heterojunctions became intense in the area of photophysics and device physics [1,2] 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 [3]. It was found that, besides tailoring electronic properties, the bulk film morphology of the blend is crucial for the photovoltaic performance.

The goal of this paper is to find the conditions under which mixture forms spatially distributed interfaces between domains of components. Interfaces are necessary for exciton splitting and subsequent charge transport. The intermolecular interactions play essential role in an intimate mixing of the components. These phenomena are studied here in a two-dimensional molecular structure, using the monolayer formed at the air/water interface as a model molecular system. The phase separation is visualized by fluorescence microscopy techniques on a monolayer transferred from the water surface onto a solid silicon substrate by the Langmuir-Blodgett technology.

2 MATERIALS AND METHOD

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'';5''',2''',2''']sexithiophene-5,5''-didaroxilic acid was synthesized as described in [4].

Both materials were dissolved in chloroform at a concentration of 0.5 mmol/l. The subphase used was bidistilled deionised water (18 M.cm, ELIX 5, Millipore, USA). OTH-PCBO mixture monolayers were formed by spreading of approx. 100l of the solution with mixed materials on the water surface in the Langmuir trough using a microsyringe (Hamilton, USA).

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). The measurement of surface tension was carried out using the Wilhelmy balance equipped with a filter paper plate. After spreading 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 cm²/min. The trough was

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thermostated by a recirculating cooler FL 300 (Julabo Labortechnik, Germany) with accuracy of 0.1 °C. The experiments were carried out at temperatures of 22 °C.

A transfer of the monolayer onto a solid substrate was carried out in a LB trough by vertical dipping at surface pressure of 10 mN/m. Two types of monolayers were used: pure oligothiophene and oligothiophene-fullerene mixture at 1:1 molar ratio.

3 RESULTS AND DISCUSSION

The essential characterization of monolayers is based on the measurement of surface pressure (π) observed versus area per molecule (A) of the 2D film on the surface of water. The shape of the A curve reflects phase transitions during the isothermal compression of the system. Measured isotherms for mixtures of various molar ratios of OTH and PCBO are shown in Fig. 1.

As we can see the limiting areas per molecule for OTH and PCBO are cca 80 Å² and 35 Å², respectively. The isotherm curves show no visible transition from the liquid expanded to the liquid - condensed phase, what we would expect for long-chained molecules like OTH, when chains change their alignment. We can observe very low value of surface pressure at which pure OTH collapses, $\pi \approx 12$ mN/m. A theoretical value of the area occupied by a thiophene monomer in a monolayer assuming that the thiophene rings lie parallel to the surface is approximately 45 Å². If we compare the calculated area with the value obtained from the experiment it comes out that the thiophene hexamer backbone is tilted by cca 35 °C from the normal.

Further parameter of a mixture is represented by miscibility of components. This is obtained from values of area per molecule for various molar ratios at the same surface pressure. In a case of non-interacting molecules of two compounds this dependence would be straight line between points of area for the pure constituents. The deviation from this dependence is the excess area and as a function of OTH/PCBO ratio characterizes repulsive or attractive interactions between the molecules of components [5]. For the materials where components behave like an ideal mixture the excess area of the mixture, ΔA , defined as

$$\Delta A = A_{12} - x_1 A_1 - x_2 A_2$$

is equal to zero. A_{12} is the molecular area in the mixed monolayer at temperature T and surface pressure π , whereas A_1 and A_2 are molecular areas in the two single component monolayer and x_1 and x_2 are molar ratios of the pure components in the mixture ($x_1 + x_2 = 1$). The excess areas for various molar ratios of the OTH/PCBO mixture are shown in Fig. 2. In all cases the average area occupied by one molecule in a monolayer is higher than that given by the mixing rule. This reveals decreased miscibility of the components in a mixture. The effect is mostly pronounced at both sides of the PCBO molar ratio interval. It indicates that molecules form domains

instead of homogenously mixing with the molecules of other component. The domains may not contain only pure components, this may suggest small clusters of individual oligothiophene molecules being attached with a certain number of PCBO molecules in the prevailing pure PCBO phase forming more complicated structures due to intermolecular forces.

Elastic modulus is a parameter determining rigidity of a monolayer

$$|E| = -A \left(\frac{\partial \pi}{\partial A} \right)_T$$

where π stands for surface pressure, A – is the area per molecule and T – is temperature. Elastic modulus as a function of area is sensitive to phase transitions. The maximum value reached illustrates the elasticity of the monolayer [6].

The measurement data for the maximum values of elasticity modulus for different PCBO/OTH ratio are presented in the insert of Fig. 3. We can see that even the smallest fraction of PCBO causes elastic modulus of mixture to drop significantly. The similar behaviour can be seen also at the other side of the PCBO ratio interval. A rigid pure PCBO monolayer becomes less compact by adding even a small amount of the other component.

The deeper insight into the interactions in 2D molecular systems can be found from the application of the ordinary phase rule on this system [7]. If temperature and external pressure are constant, assuming 2 surface phases (PCBO and OTH) the number of degrees of freedom $F=3-q$, where q is the number of surface phases which are in equilibrium with each other. We will use the phase rule in the region of critical collapse, but it is also applicable for 2D phase transitions (L-S or LE-LC transition). If the two components are miscible, then two phases are in equilibrium. Therefore, $q = 2$ and system has still one degree of freedom. If the two components are immiscible then $q = 3$ and the system has no degree of freedom. Therefore, when two components are immiscible, mixed monolayers will possess the unvaried mechanical properties (being in equilibrium with bulk phase) at the same surface pressure, regardless of composition. If components are miscible, collapse pressure will vary with the composition. In this binary mixture this PCBO phase is more fragile which determines elastic modulus of a monolayer as a whole.

The molecular interactions in a two-component monolayer can be evaluated by a more detailed examination of the system thermodynamics. Such an analysis originated from Goodrich [8].

The variations of the Gibbs free energy of a system containing a monolayer is given by

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

where γ is the surface tension and S is the interfacial area. If we have a mixed monolayer with both components (1 and 2) constrained to remain in the surface, and

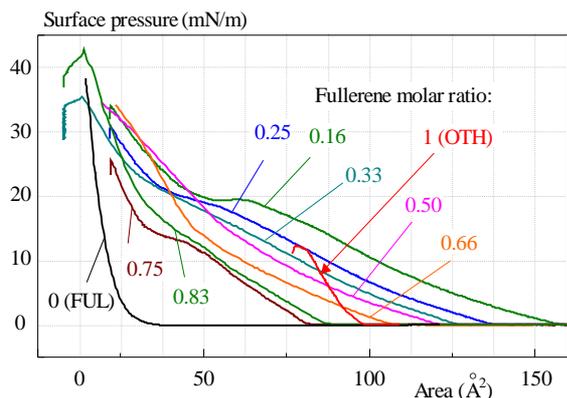


Fig. 1. Pressure-area compression isotherms of mixture for various PCBO molar ratios

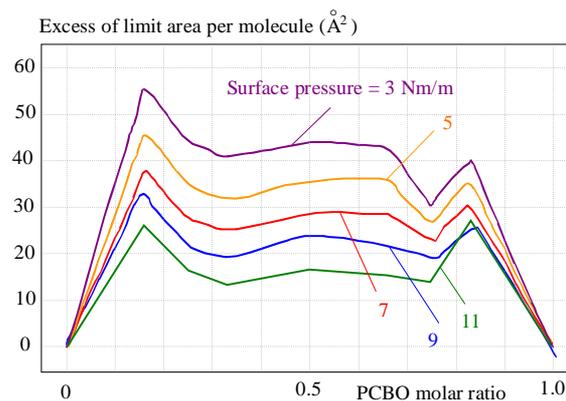


Fig. 2. Excess area as a function of PCBO molar ratio for different levels of surface pressures

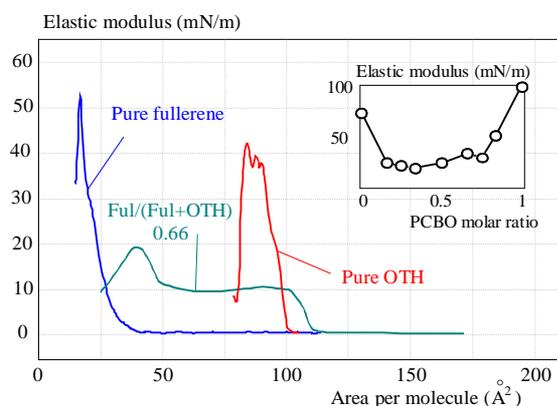


Fig. 3. Elastic modulus as a function of area per molecule. Maximum elastic modulus *vs* PCBO molar ratio is shown in the inset

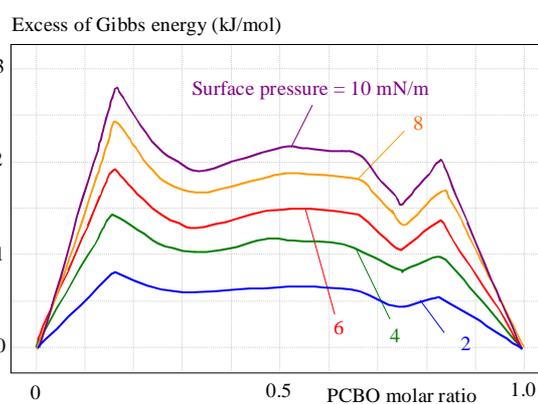


Fig. 4. Excess of Gibbs energy as a function of PCBO molar ratio for various values of surface pressure

variations of surface pressure are achieved by moving a barrier, at constant T and P , we have

$$dG = -Ad\pi$$

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

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

The value of ΔG provides information whether the particular interaction is energetically favourable ($\Delta G < 0$) or not ($\Delta G > 0$), while for $\Delta G = 0$ ideal mixing takes place. The value of ΔG as a function of PCBO/OTH molar ratio for different values of π is shown in Fig. 4.

The behaviour of ΔG (see Fig.4) is analogous to that observed for the excess area. Along the whole interval of the molar ratio the excess of Gibbs energy has positive values, which means that the pair interaction between the different molecules (OTH PCMO) is weaker than that between the identical molecules. The difference in energies estimated from Fig. 4 depending on the surface pressure varies between 500–2500 J/mol, which corresponds to binding energy at the order of magnitude of 0.01 eV, which is a value typical of van der Waals forces. The weaker the interaction between the molecules of different type the larger spacing between them and this is

also the cause of the positive deviation in the area per molecule observed upon mixing in the monolayer, *ie* the positive values of the excess area as shown in Fig. 2.

This finding provides convincing evidence on phase separation in these 2D molecular systems which are of fundamental relevance for the performance of organic photovoltaic devices.

Figure 7 illustrates creation of oligothiophene clusters in oligothiophene-fullerene mixture (1:1 mol/mol) on a Si substrate prepared by the Langmuir-Blodgett method. The fluorescence image shows brighter areas which represent oligothiophene clusters. Fullerene molecules do not emit light in the selected fluorescent wavelength band (547 to 718nm). The image is therefore completed by optical microscopy. Darker foamy areas correspond to fullerene nanoparticles.

Phase separation is proven by fluorescence microscopy. In Fig. 5 the structures of pure oligothiophene on Si substrate are shown. The sample was prepared by vertical depositing a single monolayer by the Langmuir-Blodgett method. The material forms chain-like clusters of approx. 20nm length. In Fig. 6 fluorescence spectra of oligothiophene material are shown from a detail of the same sample recorded at various spots.

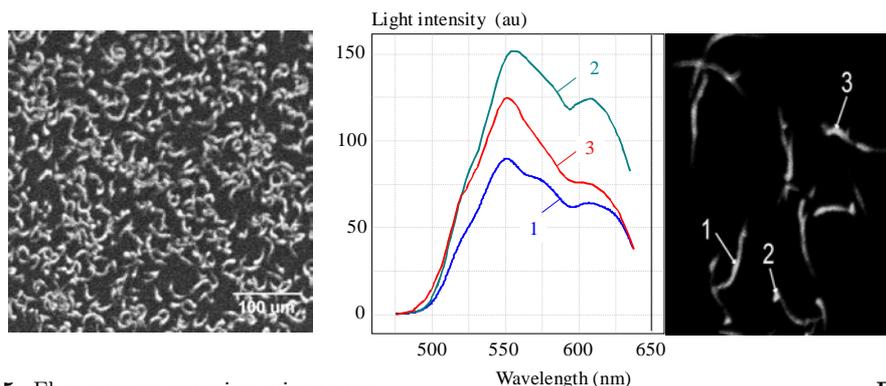


Fig. 5. Fluorescence scanning microscopy image of pure oligothiophene deposited on silicon substrate by the Langmuir-Blodgett method; ZEISS axiovert 200M with confocal head LSM 510 Meta, laser excitation wavelength 458 nm

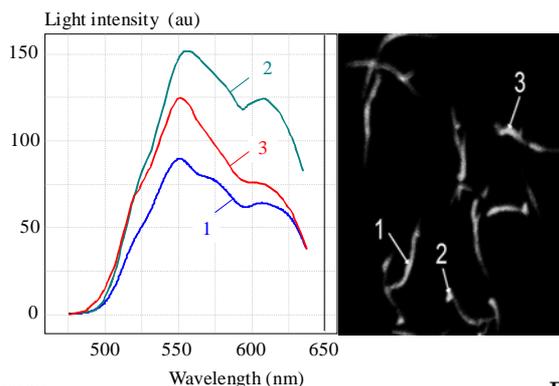


Fig. 6. Fluorescence spectra of microscopic oligothiophene clusters formed on Si substrate after deposition of Langmuir-Blodgett monolayer

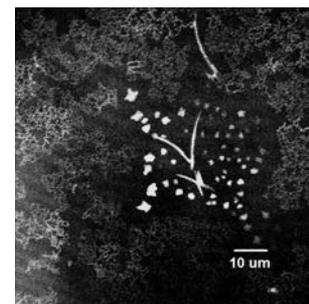


Fig. 7. Fluorescence scanning microscopy image of oligothiophene-fullerene 1:1 mixture deposited on silicon substrate by the Langmuir-Blodgett method. ZEISS axiovert 200M with confocal head LSM 510 Meta, laser excitation wavelength 458 nm. Fluorescence filter 547 to 718nm

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