

Photoinduced interlayer electron transfer in alternating porphyrin–fullerene dyad and regioregular poly(3-hexylthiophene) Langmuir–Blodgett films

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Abstract

Alternating Langmuir–Blodgett (LB) bi-layer structures containing a donor–acceptor (DA) dyad layer and a layer of conducting polymer were used to study interlayer vectorial photoinduced electron transfer (VPET). The used porphyrin–fullerene dyads were known to be capable of VPET, from the porphyrin to fullerene moiety, as a LB monolayer structure. The DA dyad and the poly(3-hexylthiophene), PHT, layers were deposited as adjacent LB monolayers in order to promote the secondary electron transfer from the polymer to the porphyrin cation, the product of the primary electron transfer. The VPET reaction was studied with the time-resolved Maxwell displacement charge (TRMDC) method both in the photovoltage (PV) and photocurrent (PC) modes. The PHT monolayer at the side of the porphyrin moieties lengthened the charge separation (CS) distance. Because of PHT the photovoltage amplitudes were increased and the recombination kinetics of the charge-separated state was delayed. The electron transfer direction in the bi-layer system was determined by the orientation of the DA dyad. The charge separation in the system took place with yield close to unity.

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1. Introduction

Design and study of molecular systems capable for intramolecular photoinduced electron transfer have importance when new types of organic photovoltaic (PV) materials are searched [1–3]. Efficient photoinduced charge separation (CS) is an essential event for the light-to-electricity conversion. The efficient intramolecular CS can be achieved by using donor–acceptor (DA) molecules in which the electron donor and acceptor moieties have been linked covalently together [4–7]. In addition to dyads, more advanced molecular systems, such as triads and tetrads, have been synthesized and their electron transfer properties studied [8–13]. In fabrication of DA dyads two very widely used compounds are fullerene and porphyrin [1,14–19]. The studies have shown that the intramolecular charge transfer in this kind of DA molecules takes place with high yield in dilute solutions [14,20]. To utilize the intramolecular charge separation in light conversion one has to immobilize the DA molecules as ordered molecular films. A widely used method

to assemble molecular monolayers and deposit them to form a solid multilayer structure is the Langmuir–Blodgett (LB) technique [21]. Although the technique sets specific requirements for the molecules and thereby limits its applicability, the LB technique is a powerful and inexpensive method to engineer different molecular interfaces. The defined orientation of the DA molecules in an LB monolayer enables a vectorial charge transfer in the system [22–24]. Yamazaki and co-workers have studied the electric field effect on the photoinduced vectorial interlayer energy and electron transfer processes in LB films by fluorescence method [25,26].

A molecular photovoltaic device can be imagined to consist of series of interacting layers with different functions [24]. The principal part of the device is the donor–acceptor interface where the primary photoinduced charge separation takes place. The charges generated in the DA interface should be quickly evacuated from each other and delivered to the electric circuit to avoid losses due to the charge recombination. A simplest device working as presented consists of three functional layers placed in between electrodes: a hole transport layer, a donor–acceptor layer and an electron transport layer. For this structure one can count several reactions and processes which take place in the device after the photoexcitation. Those are the

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primary charge separation in the donor–acceptor layer, electron capture and electron transport by the electron transport layer, and the electron transfer to the anode, and analogously, the hole capture, transport and transfer to the cathode by the hole transfer layer. A coherent performance of all these functions is essential for the operation of the device. Due to the complex function of the device it is important to study and analyze carefully all the processes involved. In the present work, the model samples were prepared in order to study the processes mentioned above, and specially the primary CS in the DA layer and the hole capture by the hole transport layer.

Previously we introduced donor–acceptor dyads composed of porphyrin and fullerene moieties covalently linked together with two molecule chains [15]. The dyads have polar groups either in the porphyrin or in the fullerene end of the molecule to enable the LB film fabrication. When the dyads were incorporated into the LB films, the photoinduced vectorial electron transfer was observed in direction from porphyrin to fullerene [27]. For the monolayers consisting of dyads having the hydrophilic groups in the porphyrin end of the molecule the recombination of charges obeyed a power law, $N_{CS}(t) \sim t^{-b}$, with $b \approx 0.25$. In addition, the photoinduced charge separation was considerably longer living in films than in solution [20,27]. In this work the monolayer of the dyad with the hydrophilic groups in the porphyrin end was deposited on a secondary electron donating, or hole transport layer, conducting polymer. The polymer was polyhexylthiophene (PHT) which is known to have a p-type semiconductor character [28]. The main focus of the present paper is on the characterization of the electron donation and the hole capture process by means of the time-resolved Maxwell displacement charge (TRMDC) method.

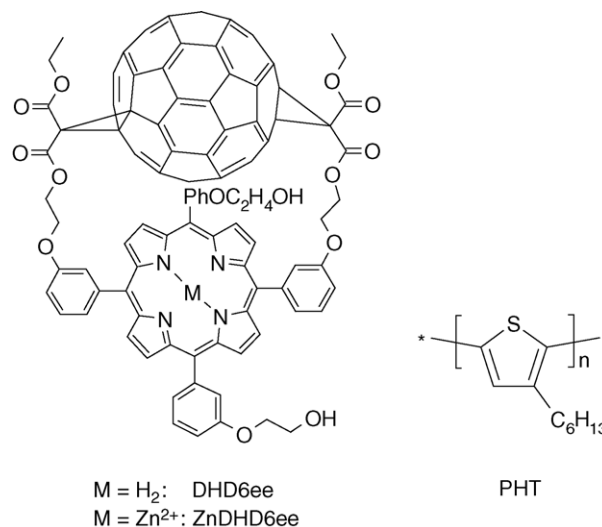
2. Materials and methods

2.1. Materials

Chloroform of analytical grade (Merck) was used for solution preparation and spreading solvent without any further purification. Matrix molecule for the LB film, octadecylamine (ODA), was of 99% grade (Sigma). The synthesis for the studied dyad molecules is described elsewhere [15]. The structures for the dyads, DHD6ee and its zinc derivative, and the regioregular poly(3-hexylthiophene), PHT, are presented in Scheme 1. PHT was purchased from Aldrich and was of 98.5% grade. The chloroform solutions were prepared to have concentrations of approximately 1 mg ml^{-1} of dyad or ODA and 0.2 mg ml^{-1} of PHT. The spreading solutions were diluted from these stock solutions to the total concentration $\leq 1.0 \text{ mM}$.

2.2. Sample preparation

The LB 5000 and LB Minitrough systems (KSV Instruments, Helsinki, Finland) were used for the isotherm measurements and the film depositions. The subphase was a phosphate buffer containing $0.5 \text{ mM Na}_2\text{HPO}_4$ and $0.1 \text{ mM NaH}_2\text{PO}_4$ ($\text{pH} \sim 7$) in ion-exchanged Milli-Q water. The subphase temperature was adjusted with a thermostat to $18 \pm 0.5^\circ\text{C}$. Samples for spec-



Scheme 1.

troscopic studies were deposited onto quartz substrates which were cleaned by the standard procedure [21] and plasma etched for 15 min in a low-pressure nitrogen atmosphere with plasma cleaner PDC-23G (Harrick). For the photoelectrical measurements glass slides covered by semitransparent ITO electrode with sheet resistance approximately 10Ω per square were used. The glasses with ITO electrodes were cleaned in ultrasonic bath first in acetone and then in chloroform and plasma etched in nitrogen for 10 min prior to use.

The film formation and the deposition conditions for the dyads are described in details elsewhere [27]. In this work the dyad concentrations in LB film preparation were 10 and 18 mol% in ODA for DHD6ee and ZnDHD6ee, respectively. The dyad monolayer deposition was done at the surface pressure of 15 mN m^{-1} with deposition rates of 5 mm min^{-1} in both directions. For the LB deposition of PHT it was mixed with ODA at concentration of 60 mol%, counted per PHT monomer unit. The PHT deposition pressure was 20 mN m^{-1} and the deposition rates were 7 and 4 mm min^{-1} for the water-to-air (up) and air-to-water (down) depositions, respectively [23].

A general structure of the sample for electrical measurements was ITO|insulating ODA layers|active layers|insulating ODA layers|top electrode, where the top electrode was either a drop of indium–gallium liquid allow (InGa) or a solid evaporated aluminum electrode. When aluminum electrodes were evaporated onto sample, the ITO electrode was removed from half of the substrate by 50% aqua regia at 50°C prior to any other operations. Eleven layers of ODA were deposited onto the ITO slides to prevent interactions between the active layers and the ITO electrode. After the active layer deposition, 12 ODA layers were deposited onto the sample in order to prevent interactions between the active molecules and the InGa electrode. When Al electrodes were evaporated the active layers were covered with 20 protective ODA layers.

Thermal evaporation of Al top electrodes was done in high vacuum ($p < 10^{-5} \text{ mbar}$) with BOC Edwards Auto 306 coating system. The used evaporation source was a tungsten filament. The Al deposition rate was $0.1\text{--}0.3 \text{ nm s}^{-1}$ and the thickness of

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