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PHOTOCHEMISTRY
AND MAGNETOCHEMISTRY

Photoinduced Vectorial Electron Transfer in Multilayered Langmuir–Blodgett Films of Porphyrin and Phtalocyanine Derivatives

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Abstract—A series of new phtalocyanines and phtalocyanine–fullerene dyads was synthesized. The dyads were transferred to solid substrates in the form of the Langmuir–Blodgett films. Poly(hexylthiophene) (PHT) and/or phtalocyanine (B6PH) were used as secondary electron donors in the multilayered structures, together with molecules of phtalocyanine-fullerene (B6PF) or porphyrin–fullerene (DHD6ee) dyads in a matrix of octadecylamine (ODA) molecules in a ratio of 1 : 9. Directed photoinduced electron transfer in films was studied by means of the time-resolved Maxwell displacement charge method. It was established that the addition of a monolayer of molecules of the secondary B6PH donor to a monolayer of molecules of the DHD6ee/ODA (1 : 9) dyad resulted in a thirty-fold increase in the sample's photovoltaic response; it did not, however, change the recombination rate of the charges as compared to a single monolayer of the dyad molecules. In the case of bilayer samples consisting of B6PF/ODA (1 : 9) and PHT/ODA (3 : 2) monolayers, both quantities increased. The absorption of visible light over a wide spectral range was achieved via the use of three-component (PHT, B6PH and DHD6ee) multilayered structures. The relative sensitivities of the samples to excitation radiation were assessed and the efficiencies of their transformation of light energy to electric potential were compared. The largest sensitivity values were obtained for three-component samples prepared from PHT, B6PH, and DHD6ee monolayers in which the sensitivity value was 500 times larger than that for a separate monolayer of DHD6ee dyad molecules.

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INTRODUCTION

Over the last ten years, much attention has been devoted to studying directed photoinduced electron transfer in organic molecules [1–4]. Different donor–acceptor (D–A) molecular systems have been studied with the aim of using such molecules in the form of thin-film structures capable of transforming sunlight into electric energy. Several methods for preparing molecular films have been developed. One is the Langmuir–Blodgett (LB) method, which allows one to create monomolecular films with D–A dyads of uniform orientation on the surface of a solid substrate [5]. Charge separation between the donor and acceptor parts of dyad molecules can occur in a film upon photoexcitation [6].

Fullerenes having excellent electron acceptor properties are often used in the synthesis of D–A dyads [1–4, 6, 7]. However, fullerene absorbs light weakly in the visible range of the solar spectrum. To increase the efficiency of the conversion of light energy in D–A systems, dyes with properties of good electron donors and a high absorption of visible light were used. Several studies have been done with films of D–A dyads on a base of fullerene prepared by the LB method [8–12]. Dyads of phytochlorin fullerene and porphyrin-fullerene have convincingly exhibited photoinduced charge separation, both in solutions and in solid films [11, 12]. Photoinduced intramolecular electron transfer in films has been studied by means of the time-resolved Maxwell displacement charge (TRMDC) method first described in 1993 [13, 14]. Interlayer directed photoinduced electron transfer in alternating LB structures of phytochlorin fullerene dyad and polymer poly(3-hexylthiophene) was studied in detail in [15]. In bilayer structures consisting of a monolayer of phytochlorin–fullerene dyad molecules and a monolayer of diacetylene alcohol molecules, the amplitude of photovoltaic response and the kinetics of the recombination of carriers in a state of separated charges depend on the degree of polymerization (the dose of UV irradiation) of the diene monomers and the type of formed polydiacetylene [16, 17].

Porphyrin chromophores effectively absorb light in a rather narrow region of the blue part of the spectrum. The absorption region can be expanded by replacing the donor porphyrin molecules in a dyad with phtalocyanine molecules, or a monolayer of phtalocyanine molecules can be used as the layer of the secondary electron donor in a bilayer film structure [18].

This study was aimed at preparing and studying LB films consisting of phtalocyanine molecules and phtalocyanine-fullerene and porphyrin-fullerene dyads in order to expand the spectral absorption region of the film structures, allowing us to increase their sensitivity to sunlight. The TRMDC method was used to study directed photoinduced electron transfer in mono- and multilayer LB films. The relative sensitivities of samples to excitation radiation were assessed from the results of photovoltaic measurements.

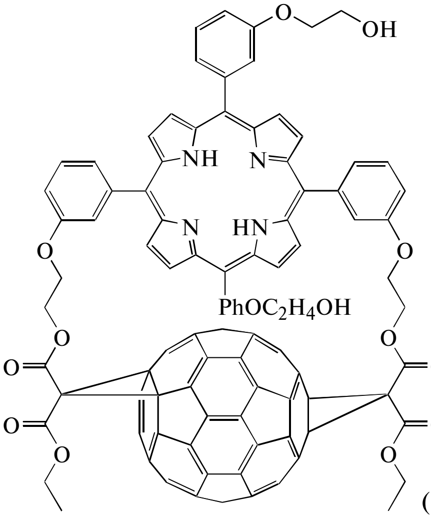
EXPERIMENTAL

Reactants and Methods

Chloroform of analytical grade (Merck, Germany) was used to prepare and deposit the solutions needed to obtain Langmuir films. Octadecylamine ODA (purity, 99%) was purchased from Sigma, while regioregular poly(3-hexylthiophene) PHT was purchased from Aldrich Chemicals. The other reactants and solvents used in synthesis were also purchased from Aldrich Chemicals and were used without preliminary purification, if not specified otherwise. Nuclear magnetic resonance (NMR) spectra were measured on a Varian Mercury (300 MHz) spectrometer in deuterochloroform, with tetramethylsilane as an internal reference. Mass spectra were obtained on a time-of-flight Waters LCT Premier XE mass spectrometer with electrospray ionization.

Synthesis

The structures of the studied phtalocyanine molecules and dyads are described below. The synthesis and properties of porphyrin-fullerene dyad DHD6ee (**1**), phtalocyanine-fullerene dyad B4P2F (**2**), and phtalocyanine ZnPH4 (**3**) were described earlier in [19, 20].



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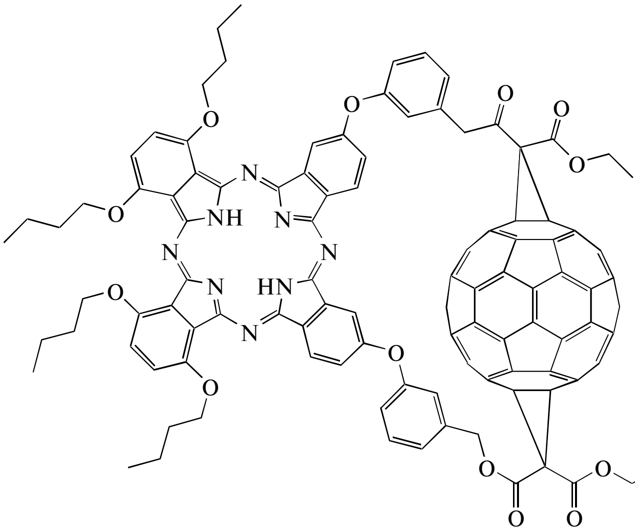

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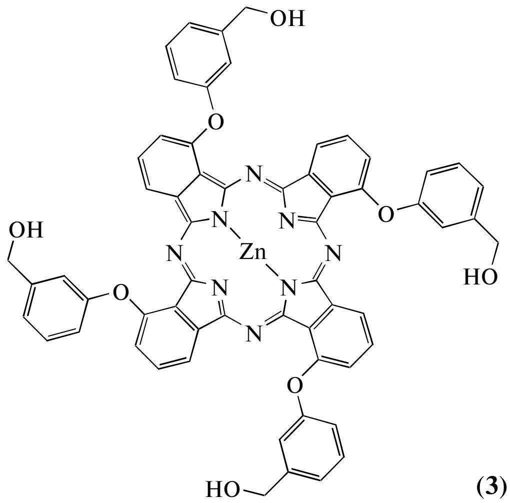

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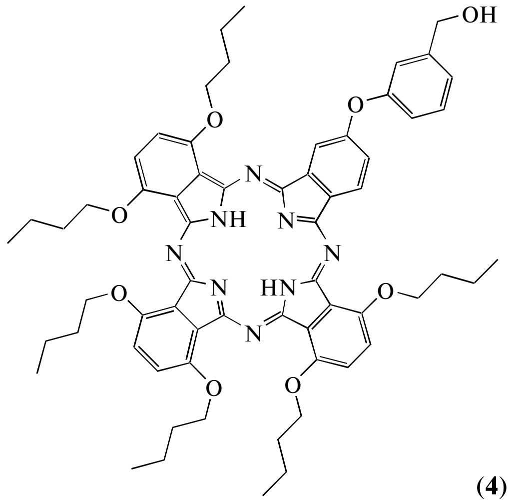

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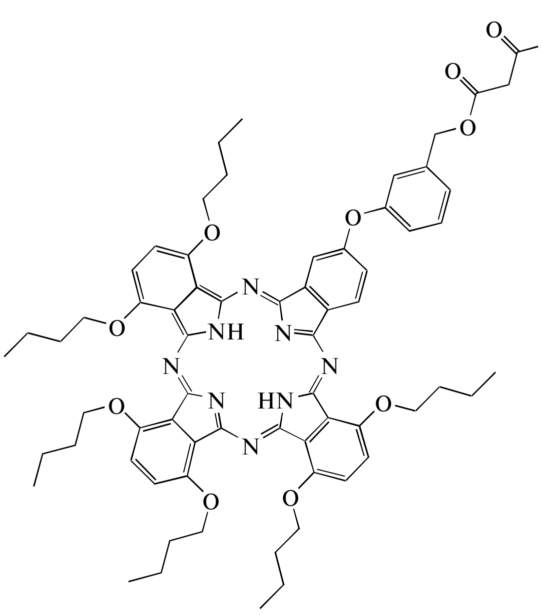

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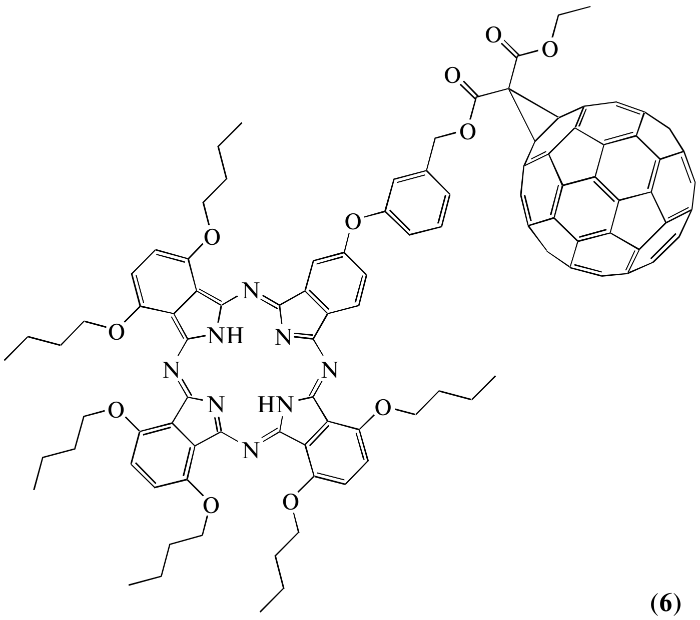

(6)

1,4,5,8,9,12-Hexabutoxy-14-[3-(hydroxymethyl) [phenoxy] phtalocyanine B6PH (4). 4 [3-(Hydroxymethyl) phenoxy] phtalonitrile (245 mg, 1 mmol), 2,5-dibutoxyphtalonitrile (270 mg, 1 mmol) and lithium shots (37 mg, 5.1 mmol) were suspended in 7 ml 1-pentanole. The reaction mixture was heat at reflux for 12 h under argon flow. A dark green solution was cooled and evaporated under vacuum. The obtained resinous residue was dissolved in 70 ml of chloroform, washed out with 100 ml of 10% hydrochloric acid, and then washed out three times with 100 ml of water. The organic layer was collected, and the solvent was evaporated at +70°C. The mixture of reaction products was chromatographically separated on Silica 100 silica gel (Merck.) A mixture of phtalocyanines was obtained by gradient elution (chloroform, chloroform/ethanol 19/1), and was then separated repeatedly on silica gel. Three phtalocyanine fractions (A (17 mg), B (52 mg), and C (73 mg)) were obtained by gradient elution (chloroform, chloroform/acetonitrile 475/25, chloroform/ acetonitrile 275/25, chloroform/ethanol 380/25). The R_f parameters for the A, B, and C fractions on thin-layer chromatography (TLC) (aluminum plates with Merck Silica gel 60 F254 silica gel) were 0.86, 0.73, and 0.52, respectively. By ^{1}H NMR spectra, we identified the A fraction as 1,4,5,8,9,12-octabutoxyphtalocyanine, the C fraction as a mixture of 1,4,5,8-tetrabutoxy-10,14-bis [3-(hydroxymethyl) phenoxy] phtalocyanine regioisomers, and the B fraction as the target product 1,4,5,8,9,12-hexabutoxy-14 [3-(hydroxymethyl) phenoxy] phtalocyanine. The ^{1}H NMR spectrum (δ, ppm, J, Hz) was 9.08 (d, J = 8.2, 1H, 16-H), 8.68 (s, 1H, 13-H), 7.68 (d, J = 2.1, 1H, 15-H), 7.62–6.97 (m, 10H, phtalo-H, Ar-H), 4.93–4.76 (m, 8H, 4,5,8,9-$OCH_2C_3H_7$), 4.72 (s, 1H, $ArCH_2OH$), 4.58 (t, J = 6.4, 2H, 1-$OCH_2C_3H_7$), 4.50 (t, J = 6.4 Hz, 2H, 12-$OCH_2C_3H_7$), 2.2–0.8 (m, 42H, $OCH_2C_3H_7$), –0.2 (s, 2H, NH); hydroxyl protons $ArCH_2OH$ were not resolved. Mass spectra m/z calculated for $C_{63}H_{72}N_8O_8$ $(M + H)^+$, 1069.5552; found, 1069.5555, 1070.5680.

1,4,5,8,9,12-Hexabutoxy-14-[3-(ethylmalonate-oxymethyl) phenoxy]-phtalocyanine (5). Ethylmalonyl chloride (0.007 ml, 0.05 mmol) and triethylamine (0.008 ml, 0.005 mmol) was added to a solution of 1,4,5,8,9,12-hexabutoxy-14 [3-(hydroxymethyl) phenoxy] phtalocyanine (21 mg, 0.018 mmol) in 4 ml of dichloromethane. The reaction mixture was stirred for 14 h at room temperature. After the usual work-up, the reaction mixture was separated on silica gel (eluent chloroform) and the main green fraction was collected to yield 20 mg (91%) of 1,4,5,8,9,12-hexabutoxy-14-[3-(ethylmalonateoxymethyl)-phenoxy] phtalocyanine (5). The ^{1}H NMR spectrum (δ, ppm, J, Hz) was 9.24 (d, J = 8.2, 1H, 16-H), 8.68 (d, J = 2, 1H, 13-H), 7.78 (dd, J_1 = 2, J_2 = 8.2, 1H, 15-H), 7.66–7.10 (m, 10H, phtalo-H, Ar-H), 5.27 (s, 1H, $ArCH_2OR$), 4.86 (t, J = 7, 8H, 4,5,8,9-$OCH_2C_3H_7$), 4.67 (t, J = 6.4, 2H, 1-$OCH_2C_3H_7$), 4.56 (t, J = 6.4, 2H, 12-$OCH_2C_3H_7$), 4.15 (q, J = 7.2, 2H, OCH_2CH_3), 3.44 (s, 2H, (c, 2H, $OCOCH_2COO$), 2.48–1.43 (m, 24H, $OCH_2C_2H_4CH_3$), 1.30–0.93 (m, 21H, CH_3), 0.02 (s, 2H, NH). Mass spectra m/z calculated for $C_{68}H_{78}N_8O_{11}$ $(M + H)^+$, 1183.5868; found, 1183.6012, 1184.5710.

B6PF Dyad. Fullerene C_{60} (8 mg, 0.011 mmol), iodine (3.5 mg, 0.014 mmol) and 1.4,5.8,9.12-hexabutoxy-14-[3-(ethylmalonateoxymethyl) phenoxy] phtalocyanine (12 mg, 0.01 mmol) was dissolved in 60 ml of toluene in an ultrasound bath and stirred under argon for 15 min. 1,8-Diazabicyclo[5.4.0] undec-7-ene (DBU) (0.0042 ml, 0.03 mmol) was added to the solution and the reaction mixture was stirred for 3 h protected from light. The solvent was evaporated and the mixture of products was separated on silica gel (eluent, chloroform), and the main green fraction was collected. The solvent was evaporated and the dry residue was washed with pentane to yield 10 mg (52%) of B6PF dyads. The ^{1}H spectrum (δ, ppm, J, Hz) was 9.26 (d, $J = 8.2$, 1H, 16-H), 8.87 (d, $J = 2$, 1H, 13-H), 7.79 (dd, $J_1 = 2$, $J_2 = 8.2$, 1H, 15-H), 7.67–7.14 (m, 10H, phtalo-H, Ar-H), 5.56 (s, 1H, $ArCH_2OH$), 4.86 (broadened t, $J = 7$ Hz, 8H, 4,5,8,9-$OCH_2C_3H_7$), 4.67 (t, $J = 6.4$, 2H, 1-$OCH_2C_3H_7$), 4.53 (t, $J = 6.4$, 2H, 12-$OCH_2C_3H_7$), 4.48 (q, $J = 7.2$, 2H, OCH_2CH_3), 2.51–0.83 (m, 45H, $OCH_2C_2H_4CH_3$, OCH_2CH_3), 0.07 (with, 2H, NH). Mass spectra m/z: calculated for $C_{128}H_{76}N_8O_{11}$ $(M + H)^+$, 1902.5745; found, 1902.4778, 1903.4824.

Preparation of Films

KSV LB 5000 and LB Minitrough System devices (KSV Ltd.) were used to measure isotherms of the compression and formation of monolayers and their transfer to solid substrates. Milli-Q water containing phosphate buffer (0.5 mmol Na_2HPO_4 and 1 mmol NaH_2PO_4) of pH 7 was used as a subphase. The temperature of the subphase was kept within the limits of $19 \pm 0.5°C$. The films were transferred to quartz plates in order to perform spectroscopic studies. Plates were preliminarily purified according to the standard technology [5] and were then plasma annealed in a nitrogen atmosphere at low pressure for 15 min on a PDC-23G device (Harrick). Samples for photoelectric measurements were prepared on glass plates covered with a semi-transparent layer of indium and tin oxide (ITO) with a resistance of about 10 Ω. These substrates were purified with acetone and chloroform in an ultrasonic bath (30 min in each solvent) and were then annealed for 10 min in plasma immediately before they were used to deposit monolayers. Deposition of 9 or 10 ODA layers on the ITO surface prevented any interaction between the active layers and the ITO electrode. Deposition of 20 or 21 ODA layers on the structure protected the active layers from direct contact with the upper electrode (a drop of liquid InGa metal).

Spectroscopic Study

Stationary absorption spectra of the layered structures were recorded on a Shimadzu UV-3600 spectrophotometer.

Photoelectric Measurements

Photoinduced directed electron transfer in the films was studied by the TRMDC method. Samples were excited with a pulse (10 ns) from a titanium-sapphire laser (CF125, SOLAR TII, Belarus) at wavelengths of around 770 (basic harmonic) and ~430 nm (second harmonic), the pumping of which was performed by the second harmonic of a Nd:YAG laser with a modulated Q factor (LF114, SOLAR TII, Belarus). The system's time resolution was determined by the excitation pulse width and was 10 ns. The samples for photoelectric measurements had the following structure: glass plate/ITO electrode/9–10 ODA layers/active layers/20–21 ODA layers/InGa electrode. A monolayer of molecules was transferable from the surface of the water subphase to a solid substrate by moving the latter either from water to air (upward), or in the opposite direction (downward). This allowed us to obtain film structures with opposite orientations of the molecules of donor–acceptor dyads with respect to the electrode's ITO surface and different sequences of monolayers in the samples. Since the dark conductivity of the samples was very low ($R_{\text{sample}} > 10^{10}$ Ω), they may be considered as condensers with capacities of 100–200 pF. Due to the high input resistance of the preamplifier (100 MΩ or 10 GΩ), the TRMDC measurements were performed in the photovoltaic mode at time intervals of 10 ns to 10 ms or 1.0 s, respectively. The measured TRMDC signals reflected the photoinduced motion of electrons in the layered structures in the direction normal to the film surface. Signal amplitudes were proportional to the quantity of charges and their displacement in the direction of the normal to the film surface. Signal decay over time was determined by the recombination of the state with the separated charges in the films under investigation.

RESULTS AND DISCUSSION

Films and Isotherms

Langmuir films were formed on the surface of a water subphase containing phosphate buffer. The solution of the molecules in chloroform ($c = 0.2$–0.35 mmol) was distributed on this surface. The conditions of the formation of monolayers of PHT/ODA and DHD6ee/ODA mixtures and their transfer to the solid substrates were described earlier in [12, 15]. For other substances under study, the speed of the compression (formation) of the Langmuir monolayer was 15 cm^2/min. Monolayers were transferred to the solid substrates at the speeds of the motion of the latter: 7 mm/min (downward) and 5 mm/min (upward). Figure 1 shows the isotherms of the dependence of the surface pressure on the area on the molecule (P-A) for phtalocyanines (B6PH, ZnPH4), phtalocyanine fullerene dyads (B6PF, B4P2F), and the mixture of B6PF molecules with molecules of the ODA matrix. Shapes of the PA isotherms for 100% phtalocyanine, B6PH and B6PF dyads were typical for the expanded monolayers with an acceptable value of the average area per one molecule of about 150 Å^2. The isotherm of the mixture of B6PF (10 mol %) and ODA (90 mol %) molecules exhibited higher collapse pressure and the presence of the condensed state of the monolayer over an interval of surface pressure from 25 to 40 mN/m. The areas per molecule obtained for 100% phtalocyanine

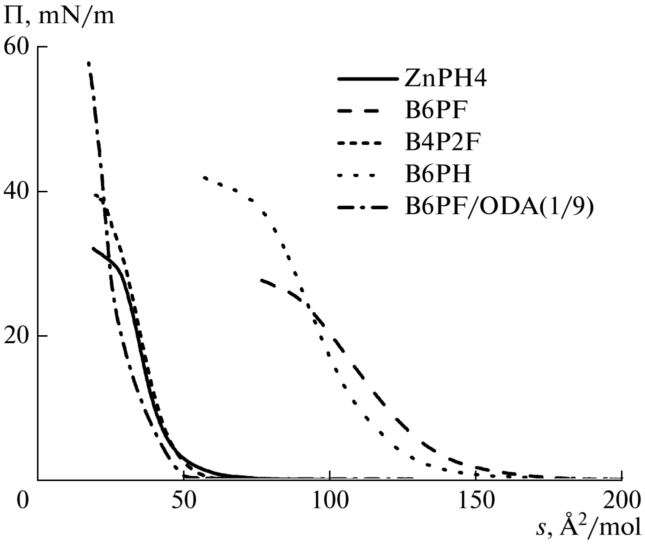

Fig. 1. PA isotherms of compression for the compounds under study; *s* is area.

ZnPH4 and B4P2F dyad were much smaller than those expected for the phtalocyanine monocycle lying on the water surface, meaning that the films formed on the subphase surface were not monolayers of homogeneously oriented molecules.

The films formed of the B6PH, B6PF, and B4P2F molecules were transferable by LB method to the solid substrates at a surface pressure of 18–20 mN/m in the layer. It was possible to obtain multilayered LB films only in the case of B6PH molecules. The transfer coefficient of the monolayers to the substrate was 0.8–1.0. A multilayered structure of the B4P2F dyad was obtained upon the transfer of layers to the substrate by the Langmuir–Schaefer (LS) method. The same method was applied in preparing mono- and multilayer films of the B6PF dyad. Langmuir monolayers of a mixture of molecules of the B6PF dyad (10 mol %) and the matrix (ODA) were transferred to the solid substrates by LB method in the form of a Y-type structure at a surface pressure of 30 mN/m; the transfer coefficient was close to unity.

Absorption Spectra

Figure 2 shows steady state absorption spectra of the substances transferred to the quartz plates by the LB and LS methods. The wide Q-bands of the phtalocyanine free base cover the region from 600 to 850 nm. The absorption band of ZnPH4 was narrower, with two maxima at 640 and 710 nm. The wide Q-bands of free compounds base indicate greater interaction between their chromophores. The use of these compounds allowed us to expand the visible light absorption region of the films.

Figure 3 shows the absorption spectra of the LB film of the B6PF (10 mol %) dyad depending on the number of monolayers. Absorption is proportional to the number of transferred layers, indicating the reproducibility of monolayer quality. A distinctive feature of the absorption spectrum of the LB film of molecules of porphyrin–fullerene dyad DHD6ee (10 mol %) is the presence of a narrow Soret band with its maximum at 436 nm [12]. The absorption spectrum of the LB film of polymer PHT (60 mol %) is a wide band with its maximum at 540 nm [15].

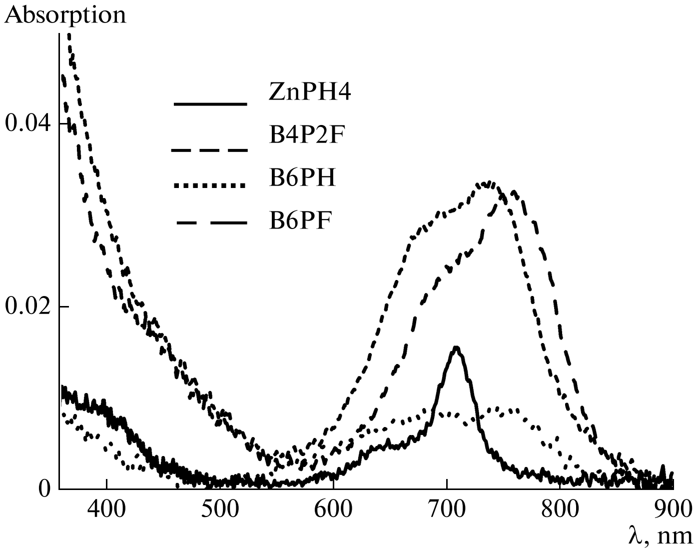

Fig. 2. Absorption spectra of monolayer films of the compounds under study.

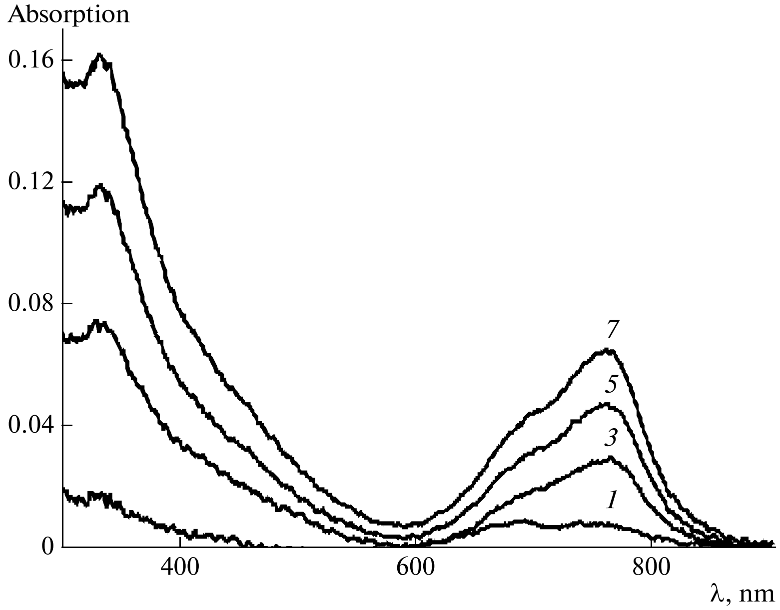

Fig. 3. Absorption spectra of the LB layers (curve numbers denote number of monolayers), prepared from a mixture of the molecules of the B6PF dyad and ODA matrix in the molar ratio of 1 : 9.

Photovoltaic (TRMDC) Measurements

Intralayer electron transfer. It is well known that the sign of photovoltaic response depends on the orientation of the donor–acceptor complex with respect to the surface of the ITO electrode [11]. The measured TRMDC signal therefore depends on the structure and amphiphilic properties of the dyad molecules. The photovoltaic responses have opposite signs for the monolayers of porphyrin–fullerene (DHD6ee) and phtalocyanine–fullerene (B6PF) dyads, though the transfer of films to the substrates occurs in the same direction of their motion through the monolayer formed on the surface of the liquid subphase (e.g., from the subphase to the air). This means that DHD6ee and B6PF dyads have opposite orientations to the subphase surfaces. In the Langmuir monolayer of DHD6ee molecules, the porphyrin (donor) parts of the dyads are closer to the water's surface, while the fullerene (acceptor) parts of these dyads are closer to water in the case of B6PF molecules. The molecules of both dyads were mixed with the ODA molecules in a ratio of 1 : 9, and the films were prepared by the LB method.

The photovoltaic signals of the monolayer films consisting of B6PF/ODA (1 : 9) molecules and transferred to the substrates by their motion upward and downward deposition are shown in Fig. 4. Pulse excitation was performed at a wavelength of 760 nm. Amplitudes and kinetics of these samples' TRMDC signals were similar to those measured earlier for DHD6ee/ODA (1 : 9) monolayers [12].

Interlayer electron transfer. The monolayer of polyhexylthiophene (PHT) in the matrix of the ODA (3 : 2) molecules was successfully used earlier as the secondary electron donor in bilayer structures consisting of monolayers of phytochlorin–fullerene dyad (PF, 30 mol %) and PHT [15], with interlayer directed photoinduced electron transfer being observed in such structures. The distance between the separated charges and the lifetime of this state increased in comparison to a monolayer of PF dyad molecules taken separately. Here, bilayer structures consisting of a monolayer of B6PF (10 mol %) dyad molecules and a monolayer of PHT polymer (60 mol %) were studied. Samples with two types of structure were prepared:

glass / ITO / ODA(10) / B6PF(1 upward) / PHT (1 downward)/ ODA(21)/InGa

and glass/ITO/ODA(10)/PHT(1 upward)/B6PF (1 downward)/ODA(21)/InGa.

Figure 5 shows the photovoltaic responses of such structures. The excitation of primary donor phtalocyanine occurred at a wavelength of 764 nm. The amplitude of the responses of such bilayer structures were five times larger than those for samples with a single monolayer of B6PF (10 mol %) dyad molecules. The differences between the bilayer and monolayer samples in their signal amplitudes and decay times were confirmed in [15] by the two-step mechanism of directed photoinduced electron transfer in a bilayer sample. Primary donor phthalocyanine is first photoexcited and transferred an electron to the fullerene, and an electron from secondary donor polythiophene is then spontaneously transferred to the phtalocyanine cation. The increase in the distance between the separated charges results in an increase in the amplitude of the photovoltaic response, while the migration of holes in the polymer layer increases the time of charge

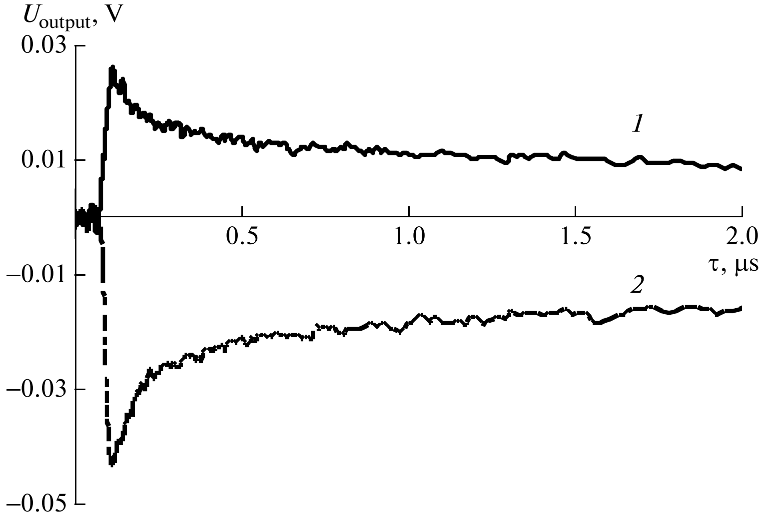

Fig. 4. Photovoltaic signals from monolayers of a mixture of B6PF/ODA (1 : 9) molecules with opposite orientations of dyads on the substrates: (*1*) upward, (*2*) downward.

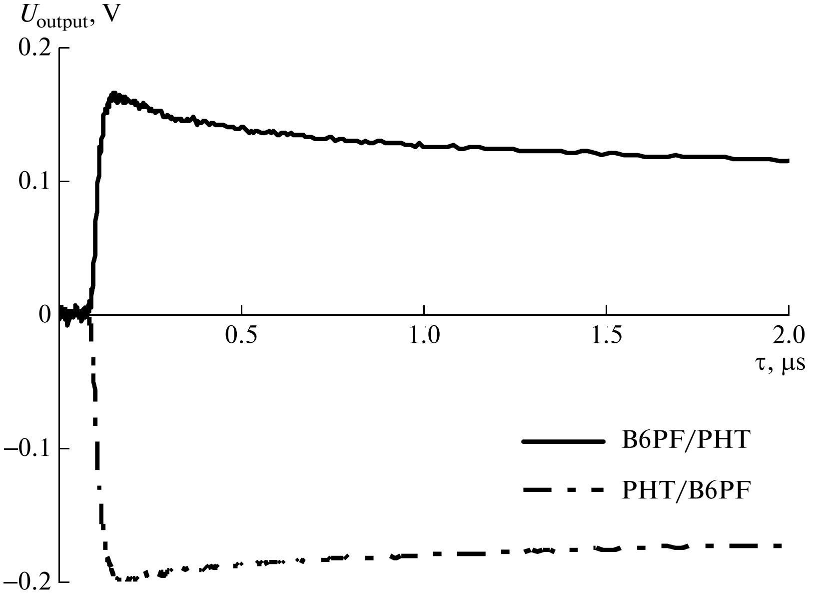

Fig. 5. Photovoltaic responses from two types of bilayer samples: B6PF/ODA–PHT/ODA (positive signal), PHT/ODA–B6PF/ODA (negative signal).

recombination. Samples with repeated bilayer structures were prepared in order to increase the distances between the separated charges even more.

Repeated bilayer structures. Three samples with PHT–B6PF active bilayer numbers of 1, 2, and 10 were prepared under identical experimental conditions. The samples had the following structure: glass/ITO/ODA (10)/[PHT (1 upward)/B6PF (1 downward)]$_n$/ODA (21)/InGa, where n is the number of bilayers in the structure.

Comparative TRMDC measurements of these samples were performed upon light pulse excitation of primary donor phtalocyanin at a wavelength of 764 nm. For the samples with one and two active bilayers, the energy density of optical excitation was 3.75 μJ/cm^2, while it was 1.12 μJ/cm^2 for the sample with 10 bilayers. Figure 6 shows the photovoltaic signals of these samples. The signal amplitude was proportional to the number of bilayers. We may assume that the measured photovoltaic signal in the experiment was the sum of signals from each bilayer. Charge

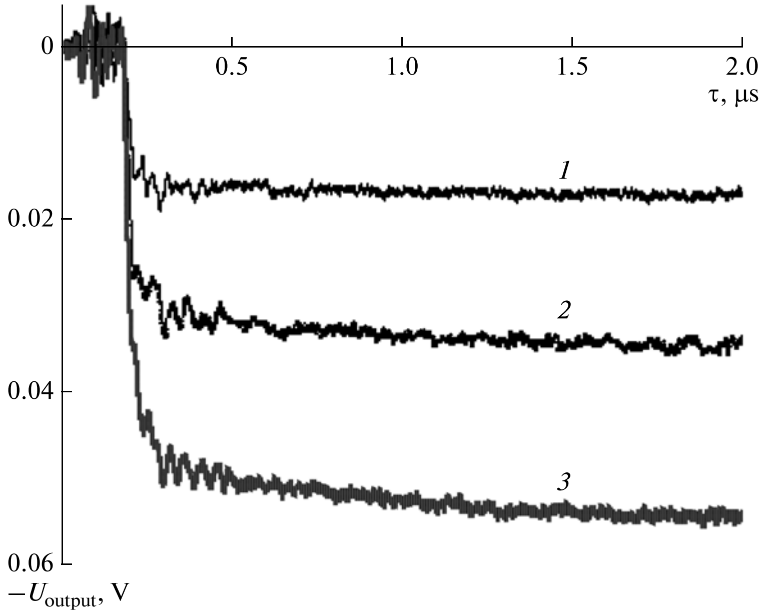

Fig. 6. Photovoltaic signals from samples of bilayer structure PHT/ODA–B6PF/ODA (*1*), repeated on the substrates 2 (*2*) and 10 times (*3*). See text for details.

separation occurred in each bilayer between the PHT and B6PF layers as a result of light excitation, and there was no charge transfer between the bilayers. Figure 7 shows the photovoltaic signal for the sample with 10 bilayers measured over two time intervals. The lifetime of the state with separated charges is noticeably longer than the single-bilayer sample. The signal amplitude decreased by almost half 2 ms after the excitation pulse was switched off, while the signal decreased by a factor of 10 in the single-bilayer sample. This indicates the possibility of the electrons transitioning not only inside the bilayers, but also between the bilayers. The time recombination of the charges increases both due to their migration along the polymeric polythiophene chains and as a result of the transition of charges from one bilayer to another.

The dependence of the photovoltaic response of the sample with 10 PHT–B6PF bilayers on the energy density of optical excitation ($\lambda = 764$ nm) is shown in Fig. 8. The signal increased linearly to a value of 15 μJ/cm^2, and it remained unsaturated at 80 μJ/cm^2. According to the data obtained by studying phtalocyanine films in [21], signal saturation can be expected at an excitation density exceeding 100 μJ/cm^2, due to exciton–exciton annihilation between phtalocyanine chromophores. Under the conditions of this study, the highest excitation density at which signal intensity reached the limit of the preamplifier's linear response region was 80 μJ/cm^2.

Phtalocyanine layer as the secondary donor. Two types of samples were obtained by the transfer of DHD6ee (10%) (downward)/B6PH (100%) (upward) or B6PH (downward)/DHD6ee (upward) bilayers to substrates covered with ITO film. As in the previous experiments, the active bilayers were insulated from the ITO and InGa electrodes by ODA multilayers. Upon light excitation of the porphyrin chromophores ($\lambda = 436$ nm, $E = 150$ μJ/cm^2) the two types of samples exhibited photovoltaic signals of opposite sign and the same amplitude (Fig. 9). Upon excitation of secondary donor phtalocyanine ($\lambda = 766$ nm, $E = 150$ μJ/cm^2), the shapes of the photovoltaic responses remained virtually the same and their amplitudes were one-third of those where porphyrin was excited.

The application of external electric voltage (±0.5 V) to samples barely influenced the amplitude of the measured signal (~10%), indicating a rather high homogeneity in the orientation of donors and acceptors in the film.

The photovoltaic response of the bilayer B6PH–DHD6ee structure was 30 times greater than the analogous response from a separate monolayer of the dyad ($\lambda = 436$ nm). However, the signal decay was the same in both cases. The addition of a B6PH (100%) monolayer to a monolayer of the DHD6ee (10 mol %) dyad did change the form of the photovoltaic response in the time scale of 0–2 ms. Considering that the speed of charge recombination in the monolayer of the dyad should be controlled by the motion of electrons within the monolayer between the macrocycles, we may conclude that there was no migration of charges in the layer of the secondary donor in the bilayer sample. The addition of a B6PH monolayer thus considerably increases the photovoltaic signal from the monolayer of the dyad, but does not change the recombination rate of the charges. At the same time, the addition of a

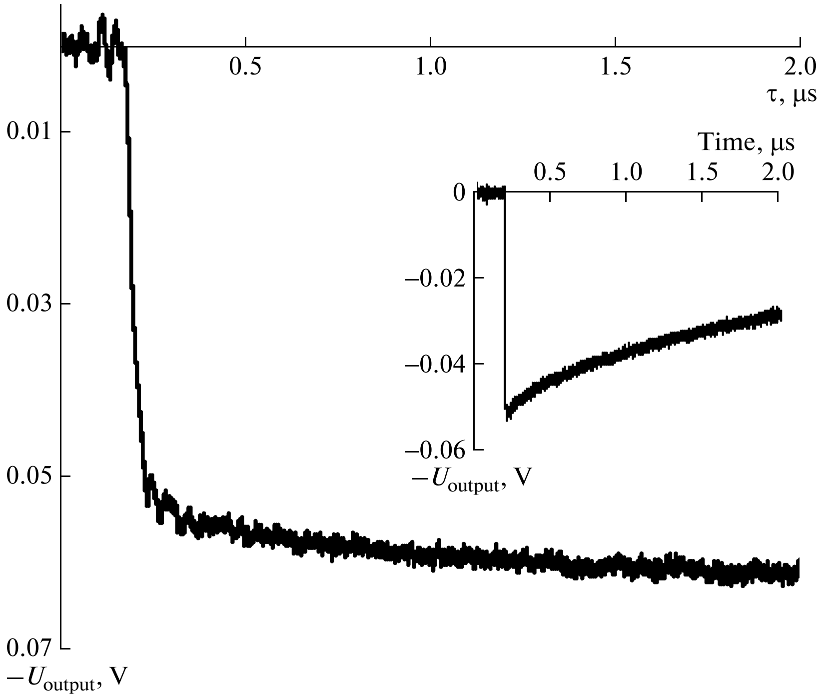

Fig. 7. Photovoltaic signals from a (PHT/ODA–B6PF/ODA) × 10 sample.

monolayer of PHT polymer (60 mol %) to the monolayer of the B6PF (10 mol %) dyad results in a noticeable increase in the time constant of the recombination of charges, due to their migration along the polymer chains.

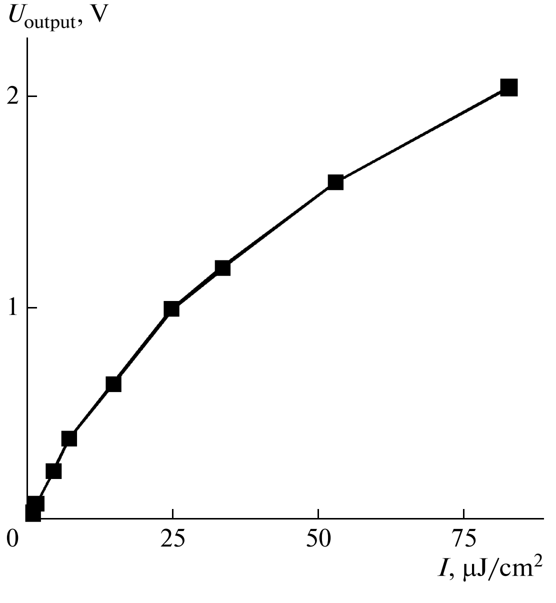

Fig. 8. Dependence of the amplitude of photovoltaic response on the energy density of optical excitation (λ = 763 nm) for a sample with (PHT/ODA–B6PF/ODA) × 10 structure.

Three-component layered structures. To increase the distance between the separated charges and the lifetime of each state, a monolayer of PHT polymer (60 mol %) is added to the bilayer structure DHD6ee–B6PH. Samples with the following structure were prepared by the LB method: ITO/ODA (9)/PHT (downward, upward)/B6PH (downward)/ DHD6ee (upward)/ODA (20)/InGa.

The photovoltaic responses were measured upon the excitation of either primary donor porphyrin (λ = 436 nm) or secondary donor phtalocyanine (λ = 767 nm). The signal amplitude of each sample was three times greater than that from the bilayer structure upon excitation at 767 nm. However, the difference was even more noticeable upon the excitation of the primary donor (λ = 436 nm) (Fig. 10). In our experiment, the density of the excitation energy for the bilayer sample was 5.3 times greater than that for the sample with the addition of a PHT layer. As a result, the signal amplitude of the three-component sample was 15 times greater than the one of the bilayer and almost 500 times greater than the one from the monolayer of DHD6ee (10 mol %) dyad molecules. We can explain such an increase in signal amplitude by the presence of a three-step directed photoinduced charge transfer. The first step was the intramolecular electron transfer from the photoexcited primary donor porphyrin to the fullerene. The second and third steps were the intermolecular transitions of the electron, first from phtalocyanine to the porphyrin cation and then from the polythiophene to the phtalocyanine cation.

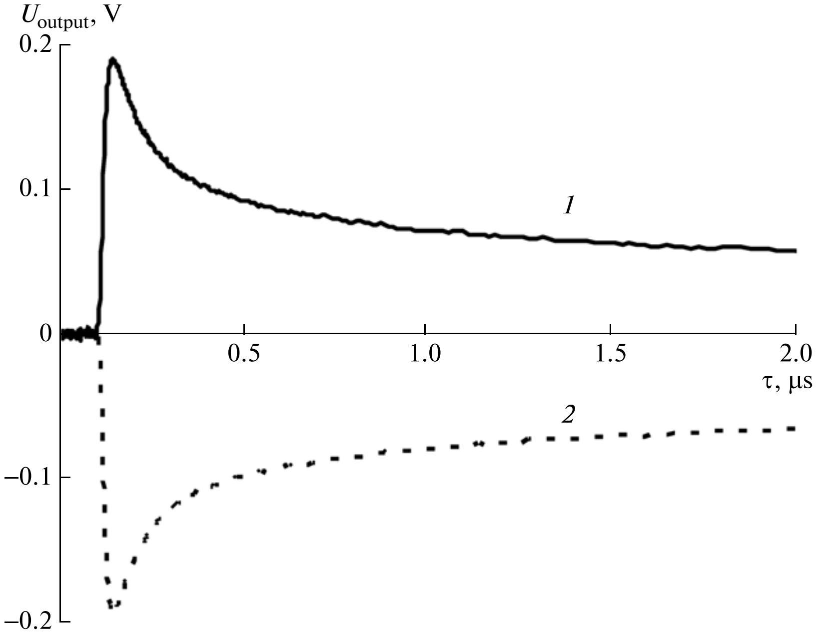

Fig. 9. Photovoltaic signals ((λ = 436 nm) from two types of bilayer samples: DHD6ee/ODA–B6PH (*1*); B6PH–DHD6ee/ODA (*2*).

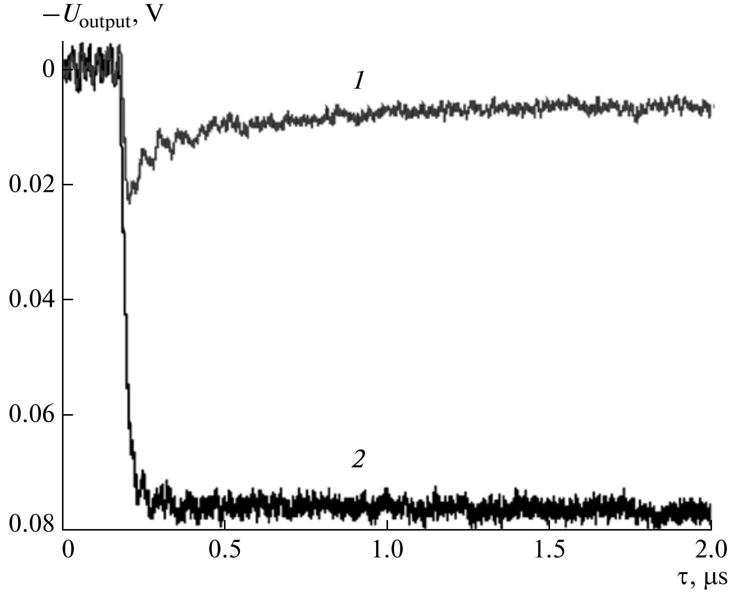

Fig. 10. Photovoltaic signal from the bilayer LB structure B6PH–DHD6ee/ODA (*1*) and its change upon the addition of two PHT/ODA monolayers (*2*).

The electrons were thus finally located on fullerene and the holes were on polythiophene. Therefore, the lifetime of the charge separated state in the sample considerably exceeded those for the monolayer and bilayer samples.

Relative sensitivity of samples. The samples were compared by calculating their relative sensitivity to the excitation radiation. The amplitudes of the photovoltaic responses were normalized by the excitation energies. Figure 11 summarizes the obtained results. In the alternating structures, the sensitivity of the samples was higher upon excitation of the primary donors (porphyrin in DHD6ee or phtalocyanine in B6PF). For the bilayer B6PH/DHD6ee and PHT/B6PF samples, the results of the measurements were the same. The highest sensitivity values were obtained for the samples prepared using three

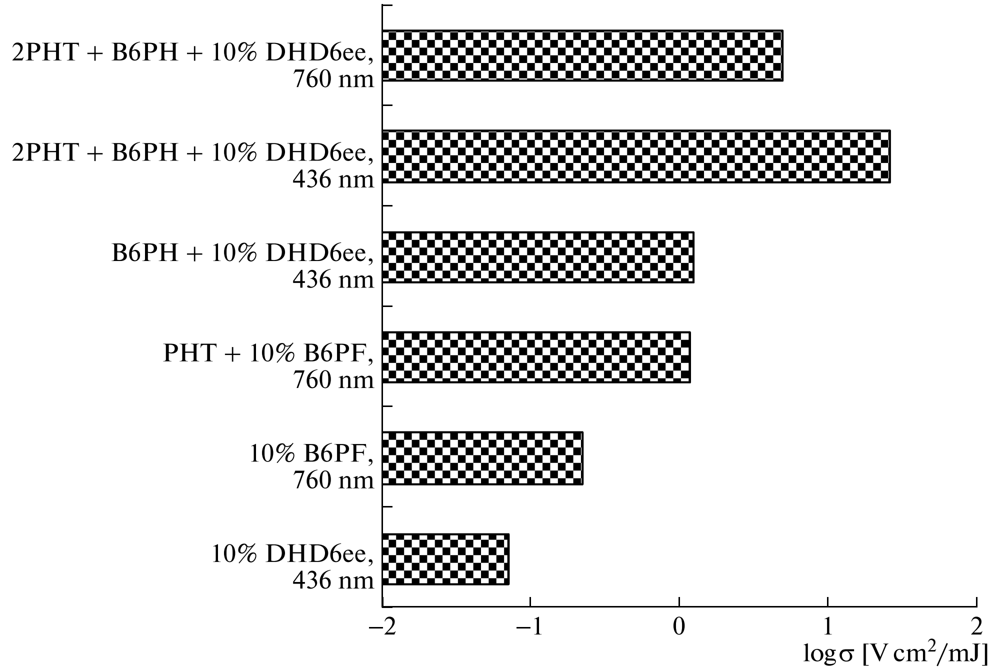

Fig. 11. Relative sensitivity (σ) of samples with different compositions to excitation laser radiation, as calculated from the results of photovoltaic measurements.

active compounds: DHD6ee, phtalocyanine B6PH, and polythiophene PHT dyads. Upon optical excitation of the primary donor at a wavelength of 436 nm, the sensitivity of the samples was as high as 27 V cm^2/mJ.

CONCLUSIONS

Molecular films of phtalocyanines and phtalocyanine fullerene, porphyrin–fullerene dyads, and polythiophene were thus prepared using the Langmuir–Blodgett method. The multilayered structures were created in order to expand the light absorption region of these films. The amplitudes of the samples' photovoltaic responses were measured. The signals were recorded by the TRMDC method in the timescale from nanoseconds to milliseconds. The addition of a layer of secondary electron donor consisting 100% of phtalocyanine B6PH molecules to the monolayer of molecules of the porphyrin–fullerene DHD6ee (10 mol %) dyad resulted in a noticeable increase in the sample's photovoltaic response, but it did not affect the charge recombination rate. The highest efficiency of the conversion of light into electric potential was exhibited by samples in which there were simultaneously present the layers of polythiophene, phtalocyanine, and porphyrin–fullerene dyads.

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