Electron transfer in oriented donor-acceptor dyads, intralayer charge migration, and formation of interlayer charge separated states in multi-layered Langmuir-Schäfer films

Alexander Alekseev[a], Alexander Efimov[b], Vladimir Chukharev[b], Artem Ivanov[a] and Helge Lemmetyinen[b*]

Photoinduced intra- and interlayer electron transfer (ET) of doubly bridged donor-acceptor molecule, porphyrin-fullerene dyad (PF), was studied in single- and multi-layered Langmuir-Schäfer (LS) films and in LS films, where PF and an efficient electron donating polymer polyhexyltiophene (PHT) formed a bilayer PHT/PF and multi-layered PHT/PF structures. The ET through layers were investigated by a method, which measures the photovoltaic (PV) response proportional to the number of charge-separated (CS) states and to the CS distance between the electrons and holes formed in pulsed photo-excitation. Primary conclusions were, that ET starts as formations of CS dyads (P^+F^-) in single-layers, continues as long-range intra-layer charge migrations following interlayer CS between two adjacent monolayers. Quantitative conclusions were, that the interlayer ET efficiency is 100 % in the bi-layered PF structure (2PF), where two CS dyads in adjacent layers forms CS complexes (P^+F/PF^-) and that the probability to form longer or higher order of CS complexes follows an expression of a convergent geometric series, with a converting factor of 2/3. In the PHT/PF bilayer structure the ET efficiency was one order of magnitude higher, than that for the 2PF structure due to the ET from the CS dyads to ground state electron donor PHT, with an acceptor density, much higher than that of (P^+F^-).

Introduction

Photoinduced electron transfer plays a central role in many areas of science and chemical technology. In biological photosynthesis a sunlight absorption is followed by a series of electron transfers. These fast processes develop a large separation of positive and negative charges known as photosynthetic reaction centres. By mimicking the light harvesting ability of green plants, chemists have attempted to copy the events in photosynthesis with several types of model compounds or molecular systems. This is used for harnessing solar energy.

For an electron transfer (ET) reaction to happen the electron donor, D, and the acceptor, A, have to be or to diffuse to a short distance. For photoinduced ET in solutions this needs a high concentration of quencher molecules and/or long lifetimes for the excited donor or acceptor, which cannot always be arranged. Many natural and artificial ET reactions take place, however, in more or less organized assemblies or

[a]Prokhorov *General Physics Institute, Russian Academy of Sciences, Vavilova str. 38, 119991 Moscow, Russia*
[b]*Faculty of Engineering and Natural Sciences, Tampere University, Korkeakoulunkatu 8, 33720 Tampere, Finland*
E-mail: helge.lemmetyinen@gmail.com

supramolecular structures and in viscous soft or even solid environments. There the influence of external factors such as solvent and temperature is changed and, in some cases, loosed their importance.

Strategies to design and synthetize molecular devices for ET in molecular electronic devices has emerged and evidenced to successful. One of the selected strategies is to synthetize and use electron donor and acceptor moieties, which have more or less controlled distances and mutual orientations by linking donor and acceptor pairs covalently by single or double bonds, molecular chains, or rigid bridge, forming a D-A dyad with a well-defined and fixed mutual orientation and distance of the donor and acceptor moieties.[1]

For efficient ETs to take place both the acceptors and donors should be powerful in their functions. One natural selection is fullerene as an acceptor and porphyrin derivatives as donors. The first successful syntheses of fullerene and porphyrin containing donor-acceptor dyads and their photochemical characterizations were carried more than two decades ago.[2] Desired charge separated (CS) states were formed in polar solvents. For a dyad with a short (two carbons) linker the charge separation took place in few picoseconds and the lifetime of the CS state were 50 and 250 ps for a zinc porphyrin and a free-base porphyrin donors, respectively[2c]. Dyads with longer separation[2b] of the donor and acceptor showed longer lifetimes of the CS state extended to 500 ps. Not only the time constants of the charge separation and recombination were affected by the dyad geometry, but also a gradual distortion of the absorption spectrum was observed.[2a,b] These results have encouraged researchers in synthesis of new fullerene-based D-A dyads and in thorough investigation of the photodynamics of the dyads.

During the last few decades we have studied photoinduced ET reactions of a series of pheophytin-, phthalocyanine-, and porphyrin-fullerene dyads, in which the donor and acceptor moieties are covalently linked to each other[1g,h,3]. The common feature for all of these compounds is that a π–π interaction in the D-A pair could have an important role in the ET reaction. Practically in all studied molecules the donor-acceptor pairs form an intramolecular exciplex, (D-A)*, as a transient state before the formation of a CS state or a tight ion pair. When the center-to-center distance of the donor and acceptor pair is short (7 – 11 Å)[3d,l,p,4], both the exciplex formation and the primary electron transfer following it, are extremely fast with rate constants of 7 – 23 x 10^{12} s^{-1} and 40 – 1400 x 10^{9} s^{-1}. The rates become slower when the distance and orientational fluctuations increase.

When the D-A dyads were organized as single molecular layer on a solid substrate, basically the same phenomena as in solutions were observed. The exciplex emission was observed for several dyad molecules but having faster formation and slower decay rates than in solutions. The CS states were formed via the exciplex state and had lifetimes in microsecond timescale. A comprehensive review on ET reactions of D-A pairs in solutions, solid phase and organized molecular films was published by us a decade ago.[3y]

When the D-A dyads were assembled as multimolecular layers, this resulted in more complex charge separation and recombination dynamics. Characteristic for the ET in organized assemblies were intralayer interactions, which opened a possibility of for charge migrations both in the acceptor and in the donor layers, after the primary intramolecular exciplex formation and charge separation. Because film deposition procedures are possible to repeat several times for the same or different film system, layers of same or different molecules could be deposited on top of another. This offered a tool to build multifunctional molecular films.

Due to the parallel orientation of the D-A-molecules in the molecular films, the electrons appear, after the photoexcitation, on one side of the layer and the holes on the other. Thus, by adding a layer of secondary electron donors or acceptors to the structure, the distance of the charge separation increases and can be partly controlled. This was demonstrated first by utilizing a polyhexylthiophene polymer, PHT, and a phytochlorin-fullerene dyad as the secondary donor layer yielding bi-layer structures such as PHT|PF, in which the distance of the charge separation increased gradually, and thus the lifetime was also extended to

a millisecond time domain.[3h] Due to the better organization, and thus better optical end electrical properties, the yield of the ET was estimated to be close to unity. With more complex system the CS states had lifetimes in several second time domains. These were important results considering possible applications and motivated us to study different types of molecular structures, based on these ideas and experiments, for constructing efficient all organic solar cell structures.

As a result of several years' work, although we were able to obtain as high values as 15-20 % and 22-38 % for external and internal quantum yields[3x,6], respectively, the power conversion efficiencies remained at its peak on level 4-5 %. In this paper we will give a quantitative explanation why the efficient ET of idealistic D-A dyads reduce their affections for a cooperative work in multi-layered structures.

Experimental section

Molecular structures of used compounds are shown in Fig. 1. The synthesis of the dyad is published earlier.[5] The PHT polymer was commercially available (Sigma Aldrich) and used without additional purification.

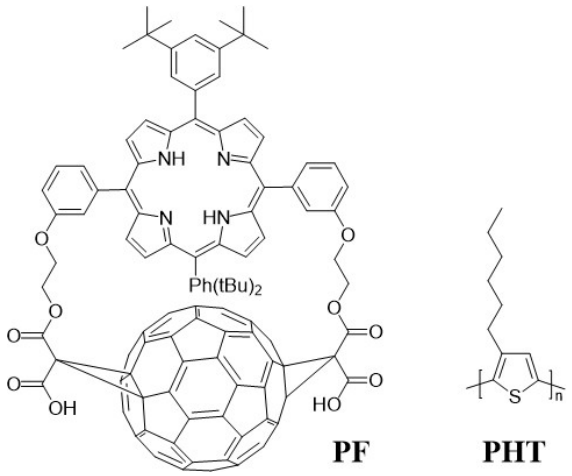


Fig. 1 Chemical structures of studied compounds, doubly bridged porphyrin-fullerene dyad, PF, and polyhexyl-thiophene polymer, PHT.

The studied molecular films were prepared by spreading a solution of the studied compounds in an evaporating solvent onto water surface. After the solvent evaporates, the monomolecular layer produced is compressed until a quasi-solid one molecule thick film is formed (Langmuir-layer). In a Langmuir-Schäfer (LS) technique the floating monolayer is transferred to a solid substrate by putting down a hydrophobic substrate horizontally so that it contacts the hydrophobic ends of the floating monolayer, and then lifting away the plate with the deposited molecular film. The multilayered films were prepared by repeating the putting down and lifting up procedures several times. Alternate films were prepared by changing the type of monolayer between each deposition.

The 0.36 mM of PF or 0.5 mM of PHT in chloroform solutions were spread onto an aqueous subphase surface with pH ≈ 7 (phosphate buffer: 0.5 mM Na_2HPO_4 and 0.1 mM NaH_2PO_4 in Milli- Q water). More information on these compound preparations by LS or LB methods are presented elsewhere.[5]

Two series of sample structures were prepared and studied. The first one consisted of 1, 2 or 10 LS monolayers of PF dyad alone. The second series incorporated a hole transporting layer of PHT, and it followed our previous observation of the photovoltage response increase in bilayer structure of PHT/PF *vs* PF monolayer solely.[8] Therefore, the second series consisted of a bilayer PHT/PF and film consisting of 10 superimposed PHT/PF films.

The steady state absorption spectra of the samples were measured after each PF layer deposition by a Shimadzu UV-3600 spectrophotometer. Fig. 2 presents the spectra of studied PF layers.

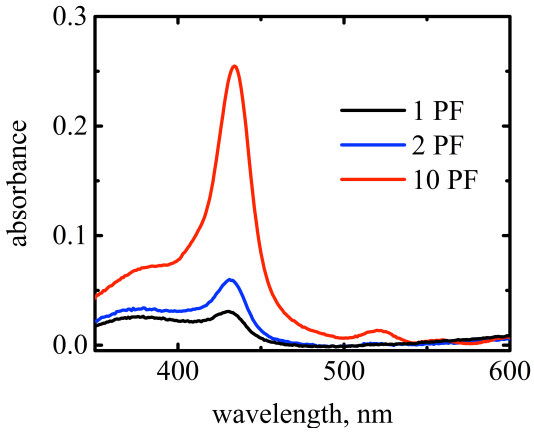


Fig. 2 The absorption spectra of PF, 2PF, and 10PF samples.

The absorption spectra of PHT/PF were measured after each bi-layer depositions (Fig. S1). The qualities of the films were monitored by recording the transfer ratio during each monolayer deposition. The transfer ratio values for each monolayer on a substrate were close to unity. The absorption bands of compounds had the maxima at 430 nm (PF, Soret band of the porphyrin moiety) and around 540 nm (PHT). The multilayer film absorption spectra were essentially the sum of the monolayer absorbances, demonstrating low or negligible electronic interaction between the layers. The preparation and quality characterization of mono- and multilayered LS- and LB-films of several PF types and PF/PHT molecular films are quantitative studied by Vuorinen[3o,q], Tolkki[3z], and Vivo[6].

The thicknesses of PF and PHT monolayer were estimated previously to be 2.5 and 3 nm, respectively.[6]

The time resolved Maxwell displacement charge (TRMDC) method was used to study the vectorial photoinduced electron transfer (VPET) in film structures.[7] Before the layers deposition the ITO plates were cleaned in ultrasonic bath following the procedure described elsewhere.[3x] The organic monolayers are transferred onto a glass substrate, covered by ITO film electrode. The other electrode was a drop of a liquid metal InGa. 11 layers of octadecylamine (ODA) were deposited onto ITO substrates by LB method prior to the active layers, and 20 ODA layers were deposited on top of the active layers to prevent the direct contact of functional film with electrodes for photovoltage measurements. In all cases, the expected direction of photoexcited electron transfer was from ITO to InGa electrode due to the dyad molecule orientation on a substrate and the layer sequence in the PHT/PF samples. The samples had extremely low conductivity ($R_s > 10^{10}$ Ohm) in a darkness and could be considered as capacitors. The input impedance of the preamplifier was large (100 MΩ). The TRMDC measurements were done in a photovoltaic mode in a time scale from 10 ns to 10 ms. The PV signals appeared due to electron movement in active layers in a direction from one electrode to another. The signal sign indicated the direction of charges displacement in a sample: from ITO towards InGa electrode, a negative sign, and *vice versa*. The signal amplitude is proportional to a number of CS states and CS distance between the electrons and holes. The high sensitivity of the method and the time resolution limited by the width of the light excitation pulse and the time response of the electronic detection system (~20 ns) allow to study the charge transfer process both in a single monolayer and in multilayered structures.[3]

The optical excitation of the samples in a pulsed mode was carried out at a wavelength of 434 nm using the second harmonic of titanium-sapphire laser pumped by the second harmonic of a Q-switched Nd:YAG laser (532 nm). The excitation pulse duration was 10 ns. Before a set of measurements, the laser was tuned to the desired wavelength and energy and allowed to become stabilized. Its energy was checked by averaging 20 pulses with a power meter using a pulse measuring head. A set of neutral filters with measured transmittances were used for selecting the desired energies. After a series of experiments the energy was re-checked. If the energy was changed more than 10 %, the series was repeated after tuning the laser again.

The studied samples had the following structure: ITO / ODA (11 layers) / active layers / ODA (20 layers) / InGa liquid metal drop electrode.

Results

PV-response. In Fig. 3a the curve 1 represents the PV signal of a single PF layer, where inter-layer electron transfers cannot take place. Thus, one can see only fast formations of CS-states of PF, a small portion of recombination of the P^+F^- -state (< 0.1 μs), and a delayed electron and/or hole jumping as an increased life-time of the photo voltage signal.

Curve 2, in Fig. 3a, represents the PV signal of 10PF monolayers. In this case inter-layer electron transfers between two adjacent layers, can take place, in addition to intra-layer transitions. Here, one can see first the very fast formation of the CS-states of PF, but also a slow (≈ 3 μs) increase in the (negative) intensity of the PV signal. This increase in the PV

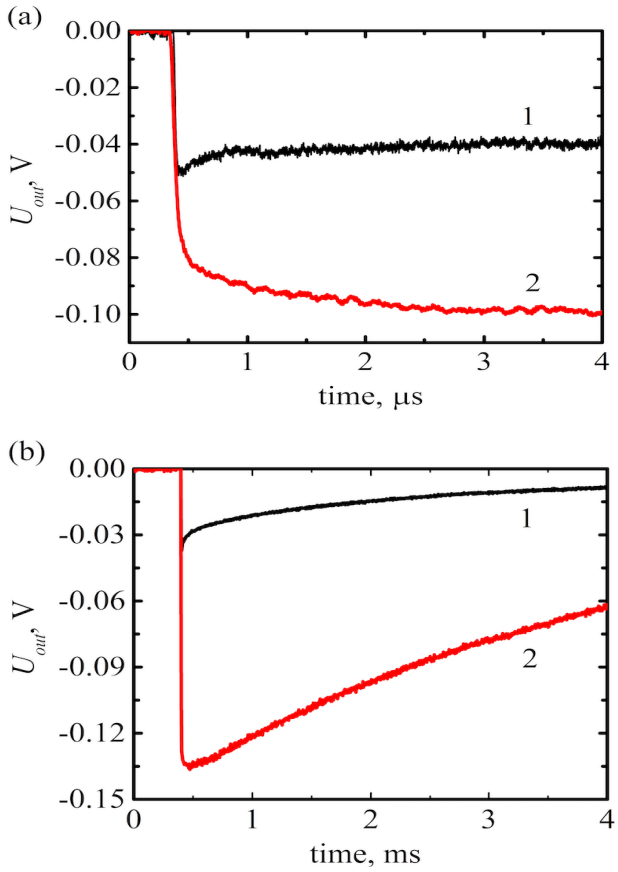


Fig. 3 Photo-voltage signals of PF (black curves) and 10PF (red curves) samples in (a) microsecond and (b) millisecond timescales. The excitation densities were 30 and 1.9 μJ cm^{-2}, for PF and 10PF samples, respectively.

signal corresponds to the averaged increased distances of the positive and negative charges, e.g. an inter-layer electron transfer.

The curves 1 and 2, in Fig. 3b, represent the CT-decays of the PF monolayer and that of 10PF, respectively. The former decay is somewhat faster. Similarly, as the formations of the PV signals in multi-layered systems, the decays are also delayed due to electron/hole migrations.

Fig. 4 presents the PV responses for all PF samples in a faster time-scale but normalized with the intensities at delay corresponding to the instrumental time resolution, which can be seen as the rise during the first 30 ns. Then the response of the mono-layered sample starts to decay, as in Fig. 3a, but the responses of the 2PF and 10PF samples still grow. A longer lasting rise time of the 10 PF sample can be interpreted in favor of intralayer charge transfers, followed by the formation interlayer CS states.

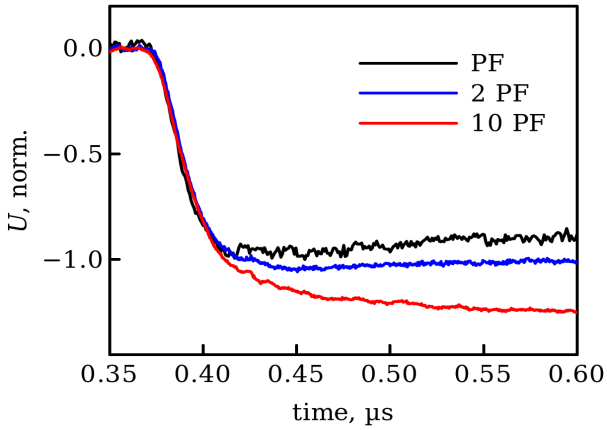


Fig. 4 Normalized photo-voltages of PF, 2PF, and 10PF samples showing starting decay (PF), short-living growth and decay (2PF), and long-living growing (10PF) due to increased number and distance of interlayer CS.

The rising of the 10PF sample continues (Fig. 3a, curve 2) roughly 4 ms after the 2PF sample starts to decay demonstrating clearly, that the interlayer CS processes continue longer in multi-layered structures.

The photovoltaic responses of PHT/PF and 10(PHT/PF) bi-layers, measured during first 4 ms after switching off the optical excitation pulse, are presented in Fig. 5. The photovoltaic response of the PHT/PF layers were significantly higher for both

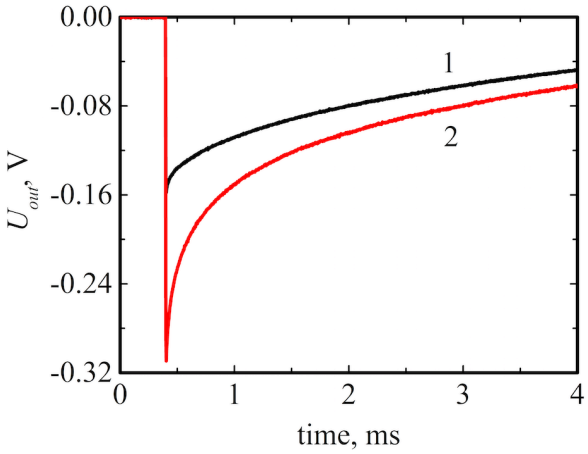


Fig. 5 Decays of PHT/PF and 10(PHT/PF) samples in millisecond timescale. The excitation densities are 1.9 μJ cm^{-2}.

samples compared to the pure PF samples (Fig. 3b), but decays were faster. The faster decays of PHT/PF samples indicate less intra-layer charge migrations than in pure PF samples.

Normalization of photovoltage signals. In this work the measured parameters were the photovoltage (*PV*) signal responses created in studied mono- or multi-layered molecular films. The excitation light pulse initiates charge transfers in each separate film and the signal measured is proportional to the density of the generated charges and to the average distances of the charge shifts in direction perpendicular to the film plane. When the photo-induced processes created for the same DA compound in solutions the longest-living transient decayed to the ground state in less than 0.5 ns[3l], but in the present work PV-signals were obtained to last several milliseconds. However, placing the same dyad in LB film supported by matrix molecules such as octadecylamine (mole fraction 90 %), the charge recombination kinetics changed from an exponential to a distributed one.[8] In solid films each dyad is fixed to its local environment and adopts its particular conformation state, which results in a broad distribution of the charge separation times, from picoseconds to nanoseconds. In the present work the layers were formed solely from dyad molecules leading to enhanced intermolecular interactions and further prolongation of the lifetime of the charge separation, in particular due to carrier migration in the layers. As the result, the PV-signals were obtained to last several milliseconds. The close distance in a solid structure between the dyad molecules increase the possibility for the electrons to jump from a fullerene anion to a neighbor ground state fullerene and for the holes from porphyrin cation to porphyrin. In a bi- or multi-layer systems the interlayer electron transfers are possible. How efficient these transfers are is the main focus of the present work.

Comparison of photo-voltage signals between monolayers and multilayers, with thicknesses from 2 nm to 20 nm caused signal responses so different in their intensities that the use of different excitation pulse energies was obligate, within the limits of the measurement instruments. On the other hand, if the same excitation densities were used, the sample absorbances were very different, which resulted in different number of photons absorbed by the molecular films.

The purpose was to obtain relative values of the efficiencies of the photo-voltage signal for each measured sample system, which then can be compared in more accurate way. The absorptions of each sample should be taken into account, when the excitation energies vary. From experimental data one can calculate the energies absorbed by each sample. The calculated values of I_{na} (μJ cm^{-2}) are presented in Table 1.

Using the *PV* signal values and the corresponding excitation light intensities, I_{na}, for all the sample systems, one can calculate the relative efficiencies, PV'_n/I_{na}, for the CS processes in all studied monolayer and multilayer systems. This value describes the photo-voltage efficiency for each studied system in units of V/μJ cm^{-2}.

The comparison between the efficiencies of each layer system can be done dividing the calculated efficiencies, PV'_n/I_{na}, with n = 2, 10, 1/1, and 10(1/1), with that of PV'_1/I_{1a}. The ratios of these relative CS efficiencies are presented as ratio PV_n/PV_1 in the last column of Table 1.

Table 1 Experimental quantities for determining the relative photo-voltage efficiencies. A_{434} = absorbance at 434 nm, PV'_n = measured photo-voltage, I_{no} = excitation density, I_{na} = absorbed excitation density, PV'_n/I_{na} = normalized photo-voltage efficiency, $PV_n/PV_1 = PV'_n/I_{na}/PV_1/I_{1a}$ = relative photo-voltage efficiency, n = number of monolayers.

Sample		A_{434}	PV'_n/ V	I_{no}/ μJ cm^{-2}	I_{na}/ μJ cm^{-2}	PV'_n/I_{na} V/μJ cm^{-2}	PV_n/PV_1
PF	n = 1	0.025	0.050	30.0	1.68	0.030	-
2PF	n = 2	0.050	0.085	8.2	0.89	0.096	3.2
10PF	n = 10	0.250	0.137	1.9	0.83	0.165	5.5
PHT/PF	n = 1/1	0.044	0.90	8.2	0.79	1.162	38
10(PHT/PF)	n = 1/1	0.320	0.97	2.3	1.20	0.808	27

Effect of the excitation intensity. The dependence of the PV signals on the excitation intensities are presented in Fig. 6. The lowest energy used was 0.2 μJ/cm² at which the signal was PV = 10 mV. The excitation density dependence was tested for 10PF layers. The response looks to be linear through the whole excitation range.

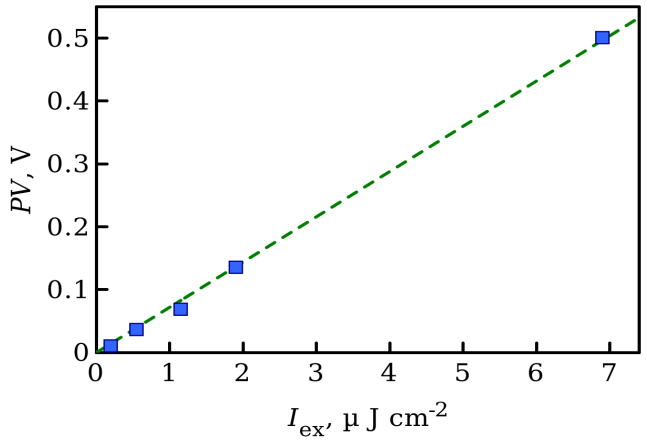


Fig. 6 Dependence of photo-voltage signal intensities on excitation density for 10PF sample.

The mechanism how the multi-layered CS complexes are formed from mono-layered CS dyads depends on the carrier densities in both interacting adjacent layers, because it needs one photon in both layer in order to form one CS complex in a double-layer structure. Experiments do not show any sign of the second order reactions down to excitation density as low as 0.2 μJ cm^{-2}. Unfortunately, measurements at lower excitation densities yielded very low PV signal. Thus, the density of carriers in the layer does not limit the CS to occur.

In order to reach a saturation level roughly half of dyes should become excited. For a porphyrin chromophore this needs a excitation density of around 1 mJ cm^{-2} at 434 nm. Thus, at low densities, (2-30 μJ cm^{-2}) as used in the present study, less than one dyad from 5000 becomes excited. In other words, in a monolayer there are, in average, 50-70 non-excited dyads between two excited dyads. Thus, an interlayer CS is only possible if electrons or holes, or both, can travel along the layer. Electron migration is known to be an efficient in fullerene solid films and PF-like dyads are shown to be conductive in solid films.[9]

Discussion

Charge separation in PF-films

Charge migrations. Because only a low growth of the PV response was observed in bi-layer structures, (Fig. 4) the present study suggests that carrier migration is fast, about 100 nm in a microsecond. A bigger growth was observed for 10PF sample (Fig. 3a and 4) for a period of few microsecond due to a cascade type of interlayer reactions. For the 10PF sample the time resolved rise caused a roughly 30 % increase in the total PV response, whereas this was 40-fold the response of a PF monolayer.

As a summary of the present and earlier studies following conclusions can be done for developing more accurate models for CS in mono- and multi-layered film structures:

1. In principle, already in a double-layer structure one could expect a dependence of PV responses on the square of the excitation density at the low excitation limit, since the interlayer charge transfer depends on carrier density in both adjacent layers. However, no quadratic dependence was observed at excitation densities < 10 μJ cm^{-2} (Fig. 6).
2. At high excitation densities, where most of the dyads become excited, one could expect saturation behaviour. In present work, apparently, the saturation limit was not reached, because the used low excitation density.
3. The highest used excitation density was 50 times larger than the lowest. Thus, at the low excitation densities the probability to excite any molecule is less than 2 % compared to the high excitation intensity.
4. At low excitation intensity, if an excited molecule forms a charge separated state, a probability to have another excited PF molecule in an adjacent layer at close distance is << 2%.
5. A corollary from the previous statements is that, because the low density of CS dyads in both adjacent monolayers, an interlayer charge transfer can occur only after a long distance intralayer charge migration[1h,3v,8b,10],

until a hole and an electron, in adjacent layers, reach an overlapping location and form an intralayer CS state.

6. Furthermore, because there is a linear PV dependence on the excitation intensities at all used intensities, the probabilities of the inter-layer charge transfers are the same in all single layer and the carriers can move along the initial layer, jumping from one dyad to another. The number of these jumps can be close to 100 or larger.
7. There are charge migrations[8b] already in a monolayer and the PV response has an intra-layer CS nature rather than an intramolecular. In photo-voltage experiments, however, the instrument is measuring the projection of the CS signal perpendicular to the instrument's electrodes.

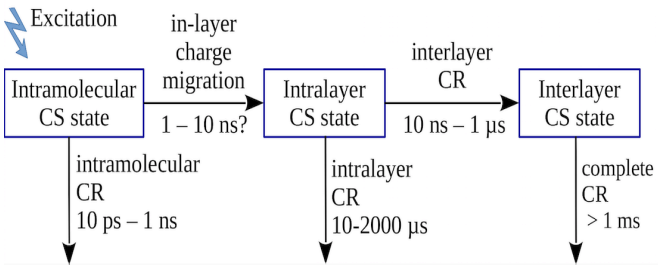
In order to observe long-living and high-intense CS complexes it is evident, that their formations in two adjacent PF layers should be more efficient than the recombination of a primary intra-molecular CS dyad. A simple explanation could be, that the rate of the ET from a negative charged fullerene to any neutral fullerene moieties surrounding it is faster than the intramolecular charge recombination. As soon as this ET takes place, the intramolecular charge recombination is blocked.

The PF molecule was quantitatively studied in solutions by V. Chukharev *et al.*[3l] It was found that the exciplex and the CS transients were formed in 100 fs and 10 ps, one after another, and that the CS state recombined to the ground state in less than 0.5 ns. Comparing those results with the present work, with a time resolution of roughly 100 ns, one could not expect high PV responses.

When the PF compound was studied[8] with the femtosecond pump–probe instrument in LB films, with 1/10 mol-% ratios of PF in an octadecylamine matrix, the first observed transient, formed almost instantly, had an absorption shape resembling to that of the exciplex and that of the CS states in solutions. The decay had a fast and a slow component, with lifetimes of roughly 5 ps and 1 ns. The same transients were observed[10] by the nanosecond flash–photolysis and by transient photo-voltage measurements indicating that the exciplex decayed to the CS state, rather than to the ground state. The CS state had a lifetime longer than 10 ms.

The electron and hole jumping lead to formations of the intralayer CS states, increase the distances of the charges, and thus increase the lifetime of the CS states. The CS recombination rate depends exponentially on the distance between the charges and even a moderate increase in the CS distance, e.g. an electron shift from one fullerene to another at close proximity, would result in a gradual increase of the CS state lifetime by a few orders in magnitude, as is observed in monolayers (Fig. 3, curves 1). In a bi- or multilayer systems the interlayer ET are possible (Fig. 3, curves 2) after those of the intralayer.

Intramolecular/-layer *vs.* interlayer CS. The fact that PV responses were observed with a instrumental time resolution of 100 ns and it decayed in a microsecond time domain means that there is a dominating alternative process for intramolecular CS state relaxation in PF samples in LS films. This is the charge migration, which converts intramolecular CS state to an intralayer CS state, in which electrons and holes reside in another dyad molecules. The essential steps of the excited state relaxations are outlined in Scheme 1.

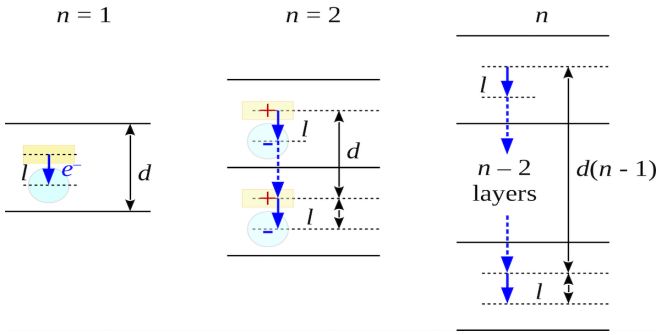


Scheme 1 Intramolecular, intralayer and interlayer CS steps in multi-layered molecular PF films.

The intramolecular CS state can relax "in place" through the intramolecular CR or yield a longer-lived intralayer CS state. The formation efficiency of the intralayer CS state depends on the ratio the rate constants of these two reactions. Probably both of present work the LS films were consisted of PF molecules solely, support strongly the blocking of

the CS recombination reaction in molecular films. The close distance between the dyad molecules in solid films increase both the rate and the probability for the electrons to jump from a fullerene anion to a neighbour ground state fullerene and for the holes from a porphyrin cation to neutral porphyrin moiety. Thus, the 100-fold duration of the excitation light pulses in the present work, does not influence on formation mechanisms of the final CS states. When the intralayer electron and hole transfers processes have blocked the intramolecular CS recombination reactions the reaction continues to the final long-living CS states. These processes are non-exponential, and reaction time constants can be taken as rough estimations only. However, as soon as the intralayer CS state is formed it has a long lifetime (10 μs – 2 ms), because the increased geometrical distance between charges and their low density. The photo-voltage signals intensity remains the same in time, as can be seen from the PV decay profile of the monolayered PF sample (Fig. 3a). Therefore, in multilayered PF samples the interlayer charge separation is a quantitative reaction. This reaction is a non-exponential, as well, and one can expect that it takes place in 10 ns – 1 μs time domain. There is only a low time resolved growth of the PV signal of the 2PF sample (Fig. 4). In a microsecond time domain, in the 10PF sample interactions of the CS states between adjacent layers can result in longer distances of the charges in perpendicular to the layer surface and thus higher PV responses (Fig 4). Though in the latter case one can expect a cascade of interlayer charge transfer reactions with contributes to a relatively slow rise of the signal.

Kinetic mechanism modelling. Apparently, an interlayer ET is responsible for the sharp growth of the PV response on switching from a monolayer to a bi-layer sample (Table 1). Only intralayer CS are possible in a monolayer, whereas interactions of the CS states in adjacent layers can result in longer distances of the charges and thus higher PV responses. This is illustrated in Scheme 2.



Scheme 2 The effect of intra- and interlayer charge separations on charge distances and photo-voltage responses in mono-, bi- and multi-layered structures of PF films.

The CS distances in the monolayer is determine by the formed charge distance in the DA dyad, *l*, where the PV response is proportional to $PV_1 \sim l$. In the bi-layer structure the same excitation density generates intralayer CS states in both layers, and this alone should double the PV response, because $PV_2 \sim 2l$.

However, the charge recombination (CR) at the layer interface, or the recombination of the fullerene anions and the porphyrin cations, would result in a decrease of the total number of charges, but simultaneously increase the CS distance to $l + d$, where *d* is the layer thickness. This makes PV response proportional to $PV_2 \sim d + l$. Since $d > l$, the net result is an increase in the PV response, compared to the case, where no interlayer CS takes place.

Extending this model to *n*-layer case, the relative gain in the PV response under the condition of the same number of carriers generated in each layer is

$$R_n = \frac{PV_n}{PV_1} = \frac{d(n-1)+l}{l} \qquad (1)$$

R_n is a liner function of *n*. It also gives the maximum possible value for each R_n, where all primary formed CS dyads form CS complexes in a *n*-layered film structure.

According equation (1), $PV_1 \approx l$ and $PV_2 \approx (d + l)$ and, if one assumes that *x* % from primary formed CS dyad form CS complexes in a double-layer, then

$$\frac{PV_2}{PV_1} = \frac{l(1-x)+(d+l)x}{l} = 1 + x\frac{d-l}{l} = 3.2$$

The value PV_2/PV_1 = 3.2 is taken from Table 1. In order to estimate the ratio of d/l, one can assume further that x = 1, which is valid only in the case, in which the formation of CS complexes is 100 % in the double-layer structure. Thus, value of d would be d = 2.2 l. Notable, this is based on the assumption of 100 % formation of CS complexes.

Ratio PV_2/PV_1. Let's consider the processes taking place in the studied films in detail, by constructing a kinetic equation for each PV_n/PV_1, elaborating that first for the double-layer systems, PV_2/PV_1. The obtained photo-voltage signal amplitudes are proportional to the product of number of the CS states and distances of the charges in the corresponding CS state. Thus

$$PV_1 \propto n_1 l$$
$$PV_2 \propto n_2^1 l + n_2^2 kl$$

where n_1 is the number of intra-molecular CS dyads, (P^+-F^-), in the monolayer system, n_2^1 is the number intra-molecular CS dyads in each monolayer of the double-layer structure, and n_2^2 is the number of the inter-layer CS complexes in the double-layer structure.

Furthermore, if l is the distance between the charges in intramolecular CS dyads and d is the thickness of the monolayer, then $k = (l + d)/l$, is the proportionality factor for the increased distance in inter-layer CS complexes (Scheme 2).

If inter-layer CS complexes are formed by recombination of a hole and an electron between two vertically overlapping CS dyads, then each formation of an inter-layer CS complex in the double-layer structure needs absorptions of two photons, one by both PF dyad, and simultaneously reduces the number of CS dyads. When these reactions are taken into account in the number of n_2^1, the ratio PV_2/PV_1 obtains the formula (2) (see details in **Electronic Supplementary Information (ESI)**) with the experimental PV_2/PV_1 -value of 3.2 (**Table 1**):

$$\frac{PV_2}{PV_1} = 2 + (k-2)\frac{n_2^2}{n_1} = 3.2 \qquad (2)$$

and

$$\frac{n_2^2}{n_1} = \frac{1.2}{(k-2)} \qquad (3)$$

The constant 2, in eq. (2) indicates, that if in a bi-layer structure both layers absorb same number of photons and there is no formation of inter-layer CS complexes, the photo-voltage would be 2 times higher than that of monolayer. The second term in eq. 2 indicates how much the formation of bi-layered CS complexes would increase the photo-voltage signal.

If all intra-layer CS dyads would transform to inter-layer CS complexes, then n_2^2/n_1 = 1 and $k = (l + d)/l$ = 3.2, this gives a value d = 2.2 l, as was obtained when the equation (1) was applied with 100 % CS complexes formation.

The value d = 2.2 l is in good agreement with the geometry of the PF dyad. The measured[3e] layer thickness is roughly d = 2.5 nm, which gives l = 1.1 nm. This value is roughly the same as reported earlier for complete charge separation distance for a similar dyad system.[3n,4] A good agreement with these experimental facts supports the 100 % CS complex formation.

The ratio PV_3/PV_1. Following the same analogical procedure as above one can construct a kinetic equation for the ratio for PV_3/PV_1. We assume, that the double-layered CS complexes are formed first and from those, the triple-layered CS complexes, in recombination reactions with CS dyads in adjacent layers:

$$PV_3 \propto n_2^1 l + n_2^2 kl + n_3^3 tl$$

Here $t = (l + 2d)/l$ (Scheme 2), is the proportionality factor for the increased distance of charges in triple-layered CS complexes. n_3^3 is the number of the inter-layer CS complexes in the triple-layered structure.

The formations of double-layered (n_2^2) and triple-layered (n_3^3) CS complexes effect on concentrations of n_2^1 and n_2^2 in the PV_3 equation above and the PV_3/PV_1 ratio obtains the formula (4) (see details in **ESI**):

$$\frac{PV_3}{PV_1} = 2 + (k-2)\frac{n_2^2}{n_1} + (k-2)\frac{n_3^3}{n_1} \qquad (4)$$

The third term in this sum expression indicates how much the formations of triple-layered CS complexes would change the total photo-voltage in addition to that of bi-layered CS complexes.

We do not have experimental value for PV_3/PV_1 – ratio, but it is possible to estimate graphically quite accurate. Using eq. (4) and values PV_n/PV_1 (Table 1), and presenting the values of 2, PV_2/PV_1 = 3.2 and PV_{10}/PV_1 = 5.5 as function of (n - 1), we get a curve through three blue circles with (n – 1) -values of 0, 1, and 9, respectively (Fig. 7). The fourth blue circle, with a value (n - 1) = 2, should correspond the photo-voltage of PV_3/PV_1. A justification for using (n - 1) will be given below.

An estimation PV_3/PV_1 = 4.0 looks satisfactory, because variations upward or downward cannot be wide, as one can see from Fig. 7. In addition, the estimation is scientifically acceptable because it is based on experimental results and we have both a theory and a mathematically derived equation based on this theory.

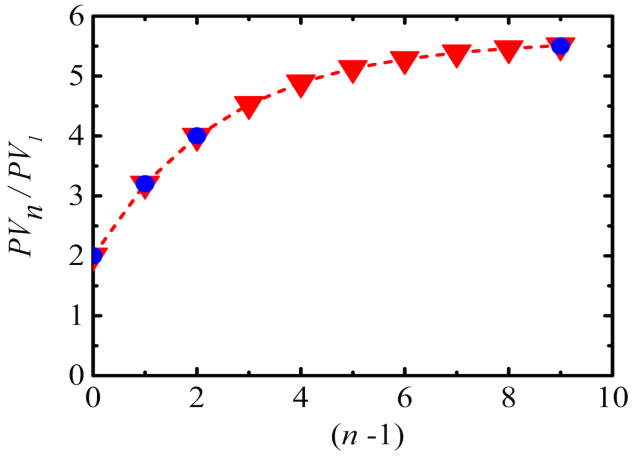


Fig. 7 Relative photo-voltage ratios PV_n/PV_1 as a function of (n-1), where n is number of monolayers in films. Blue circles at n = 0, 1, and 9 are experimental results. At n = 2, PV_3/PV_1 is estimated to be, 4.0. After this, values for red triangles are calculated by using eq. (9).

By using the value

$$\frac{PV_3}{PV_1} = 4.0$$

and substituting eq. (3) to eq. (4) one obtains

$$\frac{n_3^3}{n_1} = \frac{0.8}{(k-2)} \qquad (5)$$

As a minor corollary, proportionality factors k and t can be related to the layer thickness d and charge distance, l, in the PF dyad. Because k = (l + d)/l = 3.2, then d = 2.2 l, where d = 2.5 nm. Thus l = 1.14 nm. Furthermore, t = 2k -1 = 5.4 Those parameters fit well with molecular dimensions of PF and the structure of multilayered PF films.

Formation efficiencies of *n*-layered CS complexes. Analogical with eq. (2) and (4) it can be shown, that

$$\frac{PV_n}{PV_1} = 2 + (k-2)\frac{n_2^2}{n_1} + (k-2)\frac{n_3^3}{n_1} + (k-2)\frac{n_4^4}{n_1} + \ldots \qquad (6)$$

The ratio of n_3^3/n_2^2 = 2/3 as can be seen from equations (3) and (5). Supposing, intuitively, that the ratios of all two subsequent terms in equation (6), remain as constant, 2/3, then

$$\frac{PV_n}{PV_1} = 2 + (k-2)\frac{n_2^2}{n_1} + (k-2)\frac{n_2^2}{n_1}\left(\frac{2}{3}\right) + (k-2)\frac{n_2^2}{n_1}\left(\frac{2}{3}\right)^2 + (k-2)\frac{n_2^2}{n_1}\left(\frac{2}{3}\right)^3 + (k-2)\frac{n_2^2}{n_1}\left(\frac{2}{3}\right)^4 + \ldots. \qquad (7)$$

The equation (7) has a form of a convergent geometric series

$$S = c + a + aq + aq^2 + aq^3 + ag^4 + \ldots, \qquad (8)$$

where c = 2 is a constant, a = (k - 2) (n_2^2/n_1) ≈ (k - 2) = (3.2 - 2) = 1.2, and q = 2/3.

The 1st term of the series (7) is a = (k - 2) = 1.2. When a constant c = 2 is added to a, the total effect of the 1st term on the PV response is 3.2, which corresponds to the experimental photo-voltage ratio of PV_2/PV_1. Thus (n – 1), where n is the number of layers of studied films, corresponds the orders of the terms of the series (7), and justifies its use as the abscissa in Fig. 7. Furthermore, because constant c = 2 belongs to each partial sum, PV_n/PV_1, of the series (7), it can be used in the graphic presentation as the constant, when (n – 1) = 0.

Finally, we have to test if the assumption, that the ratio of two subsequent terms is q = 2/3, is valid for eq. (7) and (8), we calculate the sum of the 9 first terms of this series, or the value of PV_{10}/PV_1:

$$\frac{PV_{10}}{PV_1} = 2 + S = 2 + \frac{a(1-q^9)}{(1-q)} = 2 + 3.51 = 5.51 \qquad (9)$$

This value 5.51 is exactly the experimental value, PV_{10}/PV_1 = 5.5, in Table 1 and Fig. 7. This confirms convincingly the correctness of the kinetic model presented above. Furthermore, all other partial sums of the series, PV_n/PV_1, were calculated and marked as red triangles in Fig. 7. This support the theory and verify the accuracy of the estimation of value PV_3/PV_1 = 4.0.

The effect of each term of the series, or effect of any *n*-layered CS complex can thus be calculated. For example, the effect of PV_5/PV_1 on the total *PV* -response is $u = aq^{5-1} = 1.2(2/3)^4 = 0.24$ (4.4 %), and that of the 10th layer, $u = 0.047$ (0.85 %). In addition, the maximum sum of the present infinite series (7), is $S = 2 + a/(1-q) = 5.60$, which also fits with the curve in Fig. 7. Thus, the portion of 10 PF layers is 98 % from the possible maximum value.

Charge separation in PHT/PF-films

In PHT/PF samples the hole transporting PHT is adjacent to the porphyrin moiety of the PF layer. The reaction can be described simply by a scheme

$$(T \mid P^*\text{-}F) \rightarrow (T \mid P^+ \text{ - } F^-) \rightarrow (T^+ \mid P \text{ - } F^-),$$

where T represents the thiophene-moieties in a PHT film.

The reactions increase the PV responses close of 40 and 10 times compared to PF mono- and bi-layers, respectively (Table 1) though the 2PF sample has a higher absorption than the PHT/PF sample. This has a straightforward explanation of efficient hole transfer from the porphyrin moiety of the PF layer to the PHT layer. There are two reasons, first PHT is deposited right on top of porphyrin side of the PF layer and is in close proximity to porphyrin. Secondly, PHT is a strong hole accepting layer due to its redox properties. Actually, it has been shown that at the interface of PHT and phthalocyanine, macrocyclic molecules with properties close to that of porphyrins, the hole transfer takes place in 30 ps.[11]

It was concluded above in chapter *Charge separation in PF-films,* that an interlayer charge transfer can occur only after a long distance intralayer charge migration following a primary intramolecular CS state, and that before charges participate in an interlayer charge transfer, they can move along the initial layer, jump from one dyad to another, and the number of the jumps can be close to 100 or larger, and that there must be charge migration already in a mono-layer. This all is due to a low density of CS dyads in any monolayer. However, there is no need for the charge migration in a PHT/PF sample, because the high tiophene-moiety density in the PHT layer. The intramolecular CS state of PF can relax directly to the interlayer CS state. As it has been shown the charge migration in a PF monolayer is very fast and its rate competes with the charge recombination in the CS dyads. From Fig. 3 and 5 we concluded that the faster decays of PHT/PF samples indicate less intra-layer charge migrations than in pure PF samples.

Thus, if any charge migration takes place in a monolayer, they are still surrounded by electron accepting tiophene-moieties. All these properties increase the PV responses of mono- and double-layer structures of PHT/PF 38- and 28-folds, respectively, compared to pure PF monolayer.

The explanation for high PV responses in PHT/PF films, compared to PF films is straightforward. If the lifetimes of the intralayer CS state of PF dyad (Scheme 1) are $\tau^o_{SC} = 1/k_{SC}$ and $\tau^r_{SC} = 1/(k_{SC} + k_r[T])$ for the PF monolayer and PHT/PF double-layer, respectively, where [T] is the density of the tiophene-moieties in the PHT layer, then the ratio of the lifetimes is, Table 1,

$$\frac{\tau^o_{SC}}{\tau^r_{SC}} = \frac{k_{SC} + k_r[T]}{k_{SC}} = 1 + \frac{k_r[T]}{k_{SC}} = 38$$

$$k_r[T] = 37k_{SC}$$

Simply the rate for the CS complex formation is 37 times faster than the recombination of the SC state of

the PF dyad, where its lifetime is increased due to the charge migration.

For the 10PHT/PF sample the structure of the film is 5[T | P-F || T | P-F], which could, in principle, yield a structure 5[T^+| P - F^- || T^+| P - F^-], which potentially could yield further to a structure 5[T^+| P - F|| T| P - F^-] and to an increased CT distance, as in 2PF and 10PF samples. Fullerene is, however, a very strong electron acceptor and PHT strong electron donor and electron transfer from F^- to T^+ is very improbable. A probable reason for the decreased efficiency is, that in a state [T | P-F || T* | P-F], which is possible with the 430 nm excitation (compare the absorptions of 2PF and 10(PHT/PF in Table 1) the ET takes place from T* to PF in a process (T | P-F || T* | P-F) → (T | P-F^- || T^+ | P-F). This yields a PV signal to opposite directions and reduces the total efficiency compared to single (T | P*-F) and (T* | P-F) layers. This also indicates, that it is reasonable to handle each double layer (T | P-F) in the 10(PHT|PF) sample as separate from each other.

Conclusions

Photoinduced intra- and interlayer electron transfer (ET) of doubly bridged porphyrin-fullerene (PF) dyad molecules was studied in mono and multi-layered Langmuir-Schäfer films, as well as films, where the PF dyad and an efficient electron donating polymer polyhexyltiophene (PHT) formed a bilayer PHT/PF or an alternating structure of 10 PHT/PF bilayers.

Excitation intensities were so low, that samples didn't saturate. The highest used excitation density was 50-fold compared to the lowest. Thus, the probability to excite any molecule is less than 1/50 compared to the high excitation intensity and the probability to have another excited PF molecule in an adjacent layer of the excited one at close distance is << 2%. It was shown that the intramolecular charge migration can compete with the fast intramolecular charge recombination in laterally densely packed PF layers, and results in formations of long-living intralayer CS states. The charge carriers, before they participate in an interlayer charge transfer, can move along the initial layer, jumping from one dyad to another. The number of these jumps is 100 or more. Thus, interlayer charge transfers occur after a long distance intralayer charge migration. Furthermore, due to the linear PV dependence on the excitation intensities, the efficiencies of the interlayer charge transfers are the same in all single layer.

The interlayer ET efficiency is 100 % for the bilayer PF structure (2PF), where two CS dyads (P^+F^-) in adjacent layers form a double-layered CS complex (P^+F-PF^-). In a 10PF structure there are nine combinations of PF bilayers, from which eight bilayers can basically start to form triple-layered CS complexes and so on. These all reduce the increase of the total PV responses, because simultaneously with the formation of one longer CS complex from a shorter PV complex and one CS dyad, the number of two charged pairs reduces to one charged pair. The density of the CS dyads (P^+F^-) reduces in one of the adjacent PF layers, as well.

It was shown, that each increase of the number of the CS dyads (P^+F^-) in formed CS complexes follows a formula of a convergent geometric series, where the first member of the series has a value a = 1.2, and a converting factor a value q = 2/3. The sum of (n - 1) first terms, where n = number of PF layers in the sample is

$$S = \frac{a(1-q^{n-1})}{(1-q)}$$

which corresponds exactly the experimental values at each value of n:

$$\frac{PV_n}{PV_1} = 2 + S = 2 + \frac{a(1-q^{n-1})}{(1-q)}$$

For the PHT/PF bilayer the ET efficiency is one magnitude of order higher, than that for the 2PF structure. The reason is, that in this case CS dyads (P^+F^-) interact with a ground state electron donor PHT, with an acceptor density, much higher than that of (P^+F^-) dyads.

In alternating PHT/PF layers, there is no ET between bi-layer films. Furthermore, the PV ratio, PV_{10}/PV_1, for the 10(PHT/PF) system was less than that for the PHT/PF system. The reason is that in n(PHT/PF) structures reactions as (T | P-F || T* | P-F) → (T | P-F^-

|| T^+ | P-F) take place between each adjacent bilayers, which competes with the opposite direction of the PV compared to that in bilayer (T | P*-F) → (T^+| P - F^-). Here T is the tiophene moiety in the PHT polymer.

Although the interlayer ET efficiency is high for the bilayer PF structure (2PF), the efficiency decreases by factor 2/3 in each formations of triple- and higher multi-layer structures. E.g. in a film structure 5PF, the 5^{th} layer acts as ET layer only with an efficiency of 4.3 %. This is one reason for low yield in solar cell applications, when multilayered PF films were used solely. The efficiencies of the formation of interlayer CS state in PF and 2PF films can be increased gradually by adding a special hole transporting layer, such as PHT used in this study, or some electron transporting layer. In those cases, the bi-layer structures should, however, act as efficient ET layers.

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