Electronic Supplementary Information (ESI):

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

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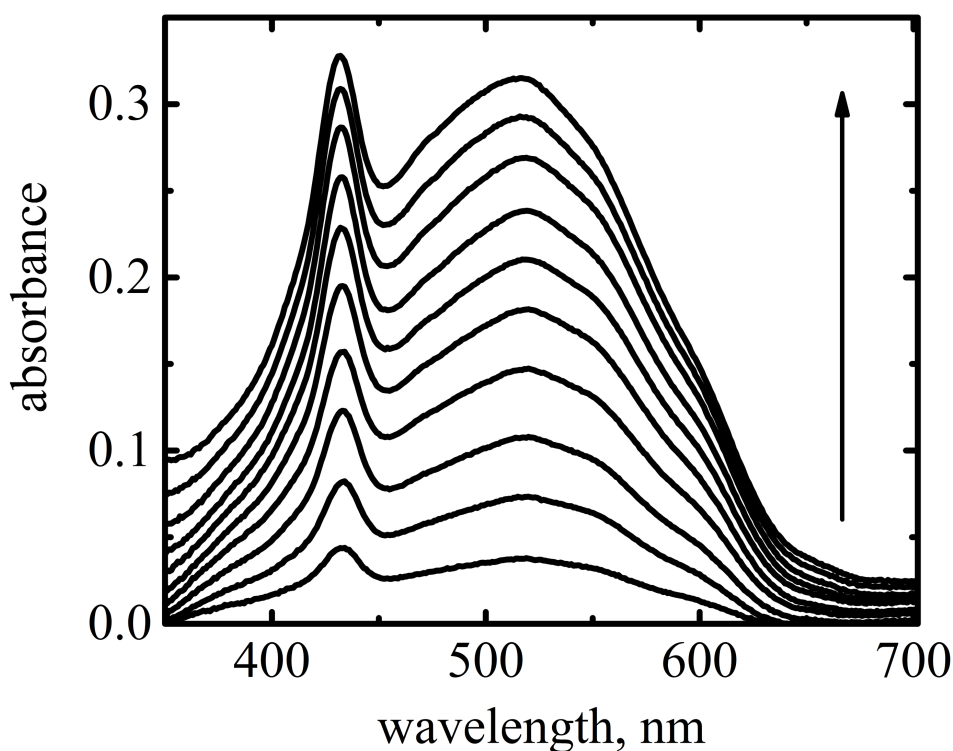
Absorption spectra

Figure S1. Steady-state absorption spectra of **PHT/PF** bilayers (from 1 to 10).

Derivation of kinetic equations

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

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

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.

If we denote n_2 as the number of the CS dyads, (P+-F-) in the double-layer structure, then $n_2 = 2n_1$. This is valid also in experimental conditions, because absorbances of the PF monolayer and the PF|PF double layers are so low as 0.025 and 0.05.

If we assume that inter-layer CS complexes are formed by recombination of a hole and an electron between two vertically overlapping CS dyads,

(P+-F-) | (P+-F-) → (P+ -F | P-F-).
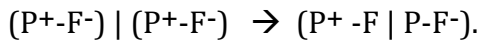
Then each formation of an inter-layer CS complex in the double-layer structure needs absorptions of two photons, one by both PF dyad, and thus this reduces the number of CS dyads by a factor $2n_2^2$:

$$n_2^1 = 2n_1 - 2n_2^2$$

or

$$n_2^1 = 2n_1 - 2n_2^2 = 2(n_1 - n_2^2)$$

Thus

$$PV_2 \propto 2(n_1 - n_2^2)l + n_2^2 kl = l\left[2n_1 + (k-2)n_2^2\right]$$

As

$$PV_1 \propto n_1 l$$

then

$$\frac{PV_2}{PV_1} = \frac{\left[2n_1 + (k-2)n_2^2\right]}{n_1} = 2 + (k-2)\frac{n_2^2}{n_1}$$

$$(2)$$

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. From Table 1,

$$\frac{PV_2}{PV_1} = 3.2$$

thus

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

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 thus assume, that first the double-layered CS complexes are formed 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 $t = (l + 2d)/l$, 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.

When the double-layered CS complexes (n_2^2) are formed, each complex uses two CS dyads, and when the triple-layered CS complexes (n_3^3) are formed, each complex uses in addition one CS dyad. Thus, n_2^1 get a value

$$n_2^1 = n_2 - 2n_2^2 - n_3^3 = 2n_1 - 2n_2^2 - n_3^3$$

Because the formation of each triple-layered CS complex reduces the number of one double-layered CS complex (n_2^2), those number reduces in the PV_3 - equation to a value

$$n_2^2 \rightarrow n_2^2 - n_3^3$$

Substituting n_2^1 and n_2^2 to the PV_3 -equation, one obtains

$$PV_3 \propto (2n_1 - 2n_2^2 - n_3^3)l + (n_2^2 - n_3^3) + n_3^3 tl$$
$$= 2n_1 l - n_2^2(k-2)l - n_3^3(1+l-t)l$$

and

$$\frac{PV_3}{PV_1} = 2 + (k-2)\frac{n_2^2}{n_1} + (t-k-1)\frac{n_3^3}{n_1}$$

Because $(t-1) = 2(k-1)$ then

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

(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.
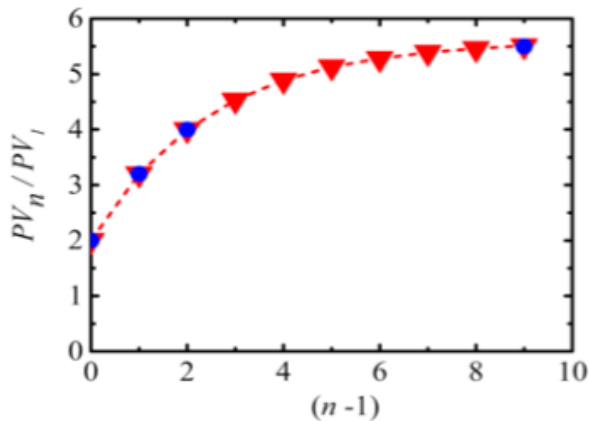

Fig. 7 Relative photo-voltage ratios PV_n/PV_1 as a function of $(n-1)$, where n is number of monolayers in films. Blue circles at $n = 0$, 1, and 9 are experimental results. At $n = 2$, PV_3/PV_1 is estimated to be, 4.0. After this, values for red triangles are calculated by using eq. (9).

By using the value

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

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

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

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), remains 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, $a = (k\text{-}2)\,(n_2^2/n_1) \approx (k\text{-}2) = (3.2 - 2) = 1.2$, 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 $(n - 1) = 0$.