Supporting Information

Exciplex-exciplex energy transfer and annihilation in solid films of porphyrin-fullerene dyads

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1. Samples

Langmuir-Blodgett film preparation was described in ref. [8].

Drop casted films were prepared using roughly 1 mM chloroform solution of the dyad. A drop of the solution (30-50 μL) was spread on glass surface leaving roughly 5 mm spot after solvent evaporation. The most homogeneous parts of the films were used for pump-probe measurements.

2. Pump-probe measurements

The same pump-probe instruments as was used previously to study dyads in solutions [6] was employed in solid films measurements. The second harmonic (420 nm) of the amplified Ti:sapphire mode-locked pulses (50 fs) was used for the excitation. White continuum generated by the pulses at fundamental wavelength (840 nm) were used to form the probe and reference beams. The probe and reference beam spots at the sample was approximately 0.3 mm in diameter. Typical time resolution was 150 fs (FWHM).

3. Absorption and emission spectra

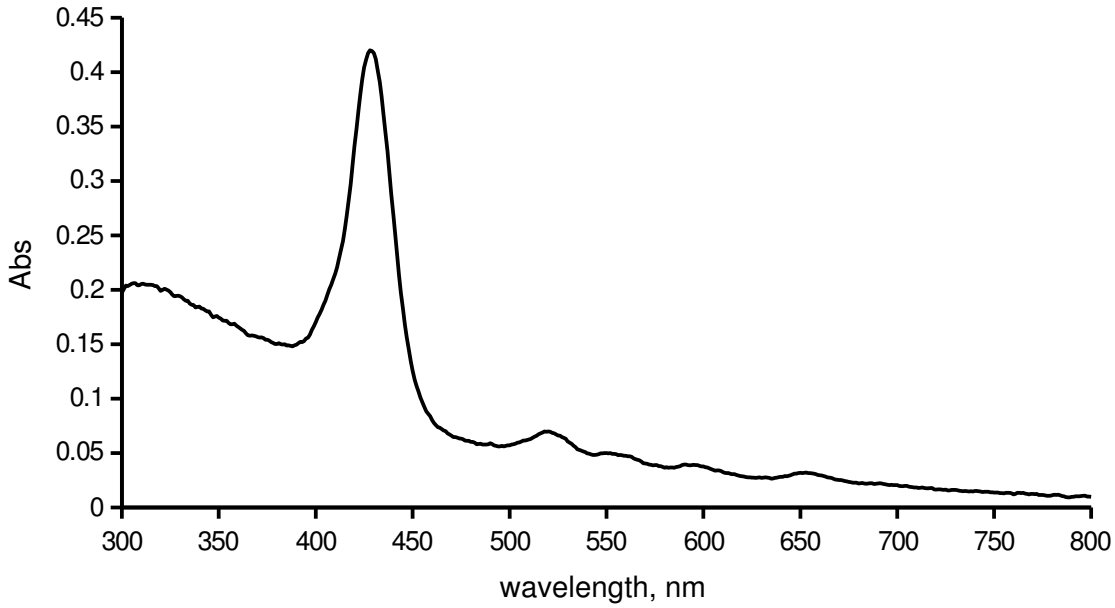

Fig. S1. Absorption spectrum of 62 layers LB film of PF dyads in octadecylamine matrix at 10 mol-% concentration.

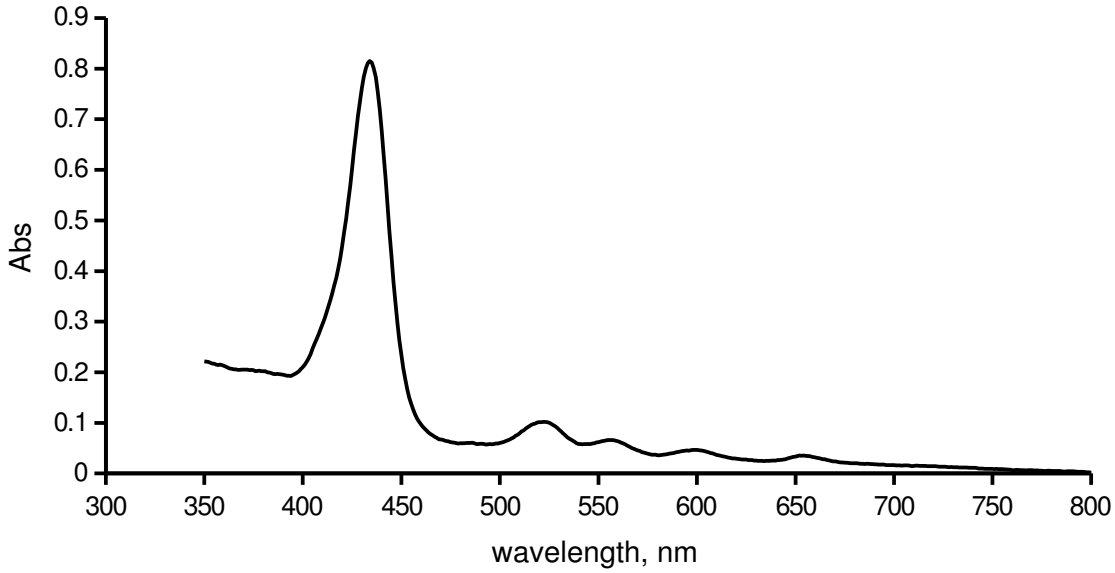

Fig. S2. Absorption spectrum of drop casted film of PF dyads.

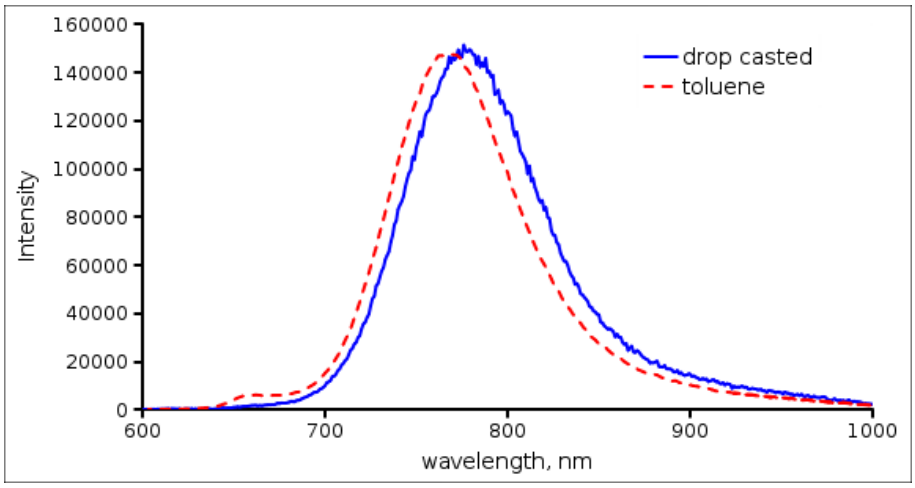

Fig. S3. Exciplex emission spectra of PF drop casted film (solid line) and PF toluene solution (dashed line). A weak band at 660 nm presents residual emission of the porphyrin locally excited singlet state. This band is almost totally quenched in drop casted films.

4. Exciplex emission decays

Time correlated single photon counting method was used to study emission decays of the films. The samples were excited by a pulsed laser diode (LDH-P-C-405B, PicoQuant GmbH) at 405 nm. The time resolution was roughly 70 ps. The decays obtained for PF drop casted film are presented in Fig. S4. At porphyrin fluorescence wavelength (~660 nm) only a fast, not resolved in time relaxation can be seen. At longer wavelengths the average emission lifetime approaches 1 ns. Although the lifetime probably overestimated as decays were not exponential and the fast decay components may be

unresolved with this measurement method.

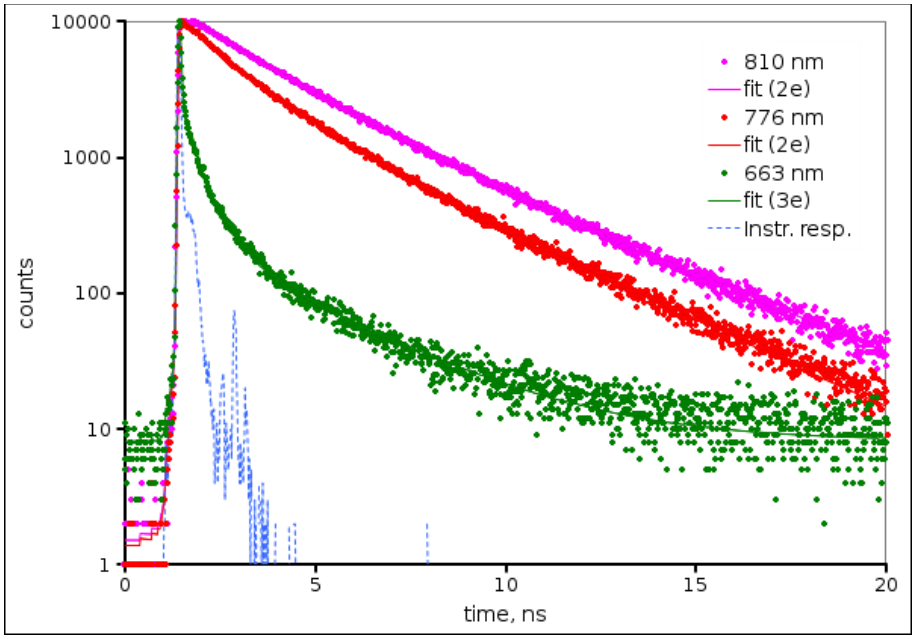

Fig. S4. Emission decays of PF dyad in drop casted film (dots). The instrument response function is shown by the dashed blue line.

The faster up-conversion instrument cannot be used to study the exciplex emission decay since the exciplex has rather low emission quantum yield, typically 10^{-3} - 10^{-4}.

5. Pump-probe measurements of LB multilayer films

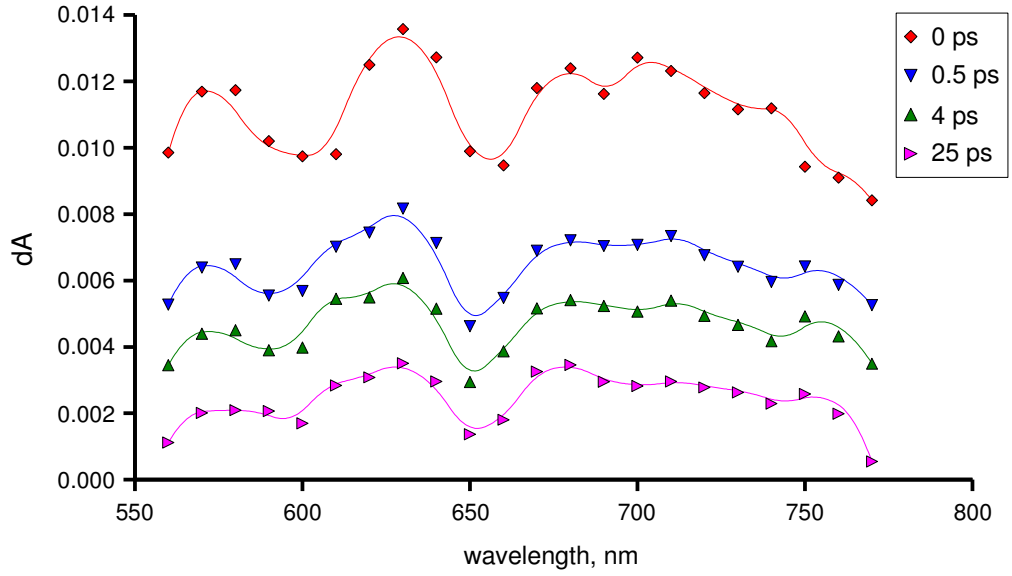

Fig. S5. Transient absorption spectra of 62 layers 10 mol-% PF film in octadecylamine matrix at different delay times. Excitation density was roughly 2 mJ cm^{-2}. As in the case of the drop casted

films (Fig. 1) the signal decays gradually during first few picoseconds but the shapes of the spectra remain virtually the same.

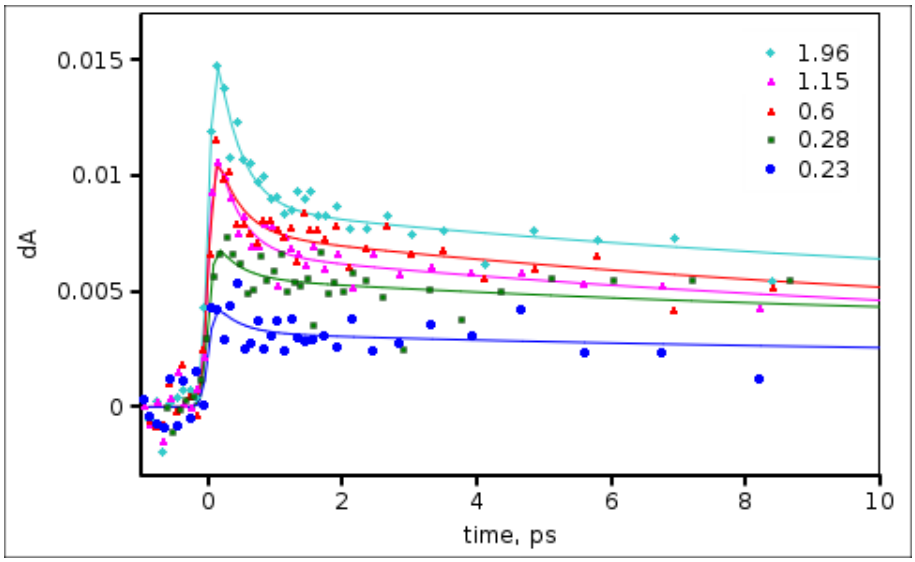

Fig. S6. Transient absorption decays at 700 nm of multilayer LB film measured at different excitation densities (indicated on the plot in mJ cm^{-2}). The solid lines present results of bi-exponential data fits. The fits with combination of the fast second order and slow exponential decays gave no statistically reliable improvement of the mean square deviation, which is due to lower absorption, and thus lower signal-to-noise ratio achieved for LB films as compared to that for drop casted films. Nevertheless, the excitation density dependence of the decay profiles follows the same trend as for the drop casted films. At ~0.3 mJ cm^{-2} excitation density a fast decay component appears and its relative intensity increases with increasing the density.

6. Dependence on the excitation density

6.1. Rate constants

The transient absorption decays of drop casted film at 700 nm were fitted using combination of a fast second order and slow exponential components. The exponential lifetime was kept constant for all excitation densities (140 ps). The second order rate was the free fit parameter. The best fit rates were:

***excitation density*, mJ/cm^2**	***rate*, ps^{-1}**
0.4	0.8±0.7
0.6	0.9±0.6
1.1	1.3±0.8
2.0	1.8±0.9

6.2. Transient absorption amplitudes

For a relatively transparent sample the dependence of the transient absorption signal, *A*, on the

excitation density, I, can be expressed as

$$A = A_0(1 - \exp(-I/I_0))$$

where A_0 is the maximum signal intensity and I_0 is the saturation energy density. In the absence of inter-chromophore interaction the saturation density can be expressed in terms of the chromophore absorption cross section, σ, and excitation photon energy, $h\nu$, $I_0 = h\nu/\sigma$. The inter-chromophore excitation annihilation reduces the maximum signal intensity by factor n, which is the number of chromophores involved in the annihilation reaction. The efficient saturation density is also lower by factor n in the presence of annihilation. Then, the transient absorption signal at a delay time long enough for annihilation to complete is

$$A_{long} = \frac{A_0}{n}[1 - \exp(-\frac{n I}{I_0})]$$

The data in Fig. 2 were fitted using a fast second order and slow exponential decay components. The amplitude of the exponential component is A_{long} in the frame of this model. The amplitude of the second order component is $A_{2nd} = A - A_{long}$, i. e. the total signal minus long-lived signal. This model was used to draw the trend lines in Fig. 3. The only adjustable parameter for the modeling was n,[1] which was found to be roughly 4.

1 The saturation excitation density was calculated assuming molar absorption of the dyad at excitation wavelength, 420 nm, to be 150 000 M^{-1} cm^{-1}, as estimated from the absorption spectrum.