Supporting Information:

Effect of co-adsorbate and hole transporting layer on the photoinduced charge separation at TiO$_2$-phthalocyanine interface

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1 Solid samples

Figure S1: Electron microscopy (FE-SEM) cross-section images prepared by screen-printing (top) and spin-coating (bottom). The bottom (light) layers are FTO, thin dark layers on top of FTO are TiO$_2$ compact layers, gray layers in the middle are mesoporous TiO$_2$ films and a lighter layer on top of TiO$_2$ films is access of spiro-MeOTAD.
2 Absorption spectra

Absorption spectrum (in the Q-band region) of the Pc at low concentration in ethanol is presented in Figure S2.

![Absorption spectrum](image)

Figure S2: Absorption spectrum of the Pc in ethanol at 0.8 µM concentration measured in 1 cm cuvette.

It was found that a better solvent for self-assembled monolayer (SAM) deposition on TiO₂ is t-BuOH:MeCN = 1:1 mixture (vol:vol), which was used in this study. Absorption spectra of the Pc and mixed Pc:CDCA samples in this mixture at concentrations used for SAM deposition (roughly 50 µM) are shown in Figure S3. It can be noted that the Pc is somewhat aggregated, and addition of CDCA reduces the aggregation significantly already in solution.

For the solid samples, the steady state absorption spectra were recorded sequentially for substrates with TiO₂ nanoparticle films before SAM deposition, after deposition of the Pc or Pc:co-adsorbate SAM, and then after deposition (spin coating) or the hole-transporting material. The spectra of TiO₂ substrates were subtracted form the latter two. Figure S4 presents the spectra of the sample with Pc:CDCA = 1:10.

The Q-band region of the absorption spectra consists roughly of two broad bands, and was fitted to two Gaussian band shape:
Figure S3: Absorption spectra of the Pc and PC:CDCA mixtures in $t$-BuOH:MeCN mixed solvent. Pc concentration is roughly 50 $\mu$M, measured in 1 mm cuvettes. Dotted lines are bi-Gaussian fits of the Q-band areas of the Pc:CDCA = 1:200 mixture.

Figure S4: Absorption spectra for the Pc:CDCA = 1:10 sample before (blue) and after (red) the deposition of the spiro-MeOTAD hole-transporting material. Absorption of the TiO$_2$ substrate was subtracted from the spectra. Dotted lines are the bi-Gaussian fits of the Q-band area.

$$A(\lambda) = a_1 \exp \left( -\frac{(\lambda - \lambda_1)^2}{2\Delta \lambda_1^2} \right) + a_2 \exp \left( -\frac{(\lambda - \lambda_2)^2}{2\Delta \lambda_2^2} \right)$$  \hspace{1cm} (1)$$

where $\lambda_1$ and $\lambda_2$ are the band positions, $\Delta \lambda_1$ and $\Delta \lambda_1$ are the band widths, and $a_1$ and $a_2$ are the band intensities, respectively.
The fit results for the absorption spectra are summarized in Table S1.

Figure S5: Absorption spectra for the Pc:OA = 1:10 sample before (blue) and after (red) deposition of the spiro-MeOTAD hole-transporting material. Absorption of the TiO$_2$ substrate was subtracted from the spectra. Dotted lines are the bi-Gaussian fits of the Q-band areas.

Table S1: Results of the decomposition of the spectra in the Q-band region on two Gaussian bands. $a_1$, $\lambda_1$, $\Delta \lambda_1$, $a_2$, $\lambda_2$ and $\Delta \lambda_2$ are the fit parameters in eq. 1, $a_1/a_2$ is the ratio of the band intensities taken as the measure of aggregation, $f_1/f_2$ is the ratio of the oscillator strengths calculated as the ratio of areas under the bands, and $A_{rel}$ is the relative absorbance of the sample.

| sample | $a_1$ | $\lambda_1$ | $\Delta \lambda_1$ | $a_2$ | $\lambda_2$ | $\Delta \lambda_2$ | $a_1/a_2$ | $f_1/f_2$ | $A_{rel}$ |
|--------|-------|-------------|-----------------|-------|-------------|-----------------|----------|----------|----------|
| Pc in EtOH | 0.026 | 633         | 43              | 0.158 | 677         | 10              | 0.16     | 0.67     |          |
| SAMs without Spiro | | | | | | | | |
| Pc | 1.15  | 622         | 27              | 0.98  | 687         | 28              | 1.18     | 1.02     | 1        |
| Pc:CDCA = 1:10 | 0.543 | 624         | 24              | 0.652 | 682         | 23              | 0.83     | 0.79     | 0.48     |
| Pc:CDCA = 1:50 | 0.150 | 635         | 27              | 0.240 | 683         | 15              | 0.62     | 1.01     | 0.16     |
| Pc:CDCA = 1:100 | 0.102 | 636         | 18              | 0.206 | 684         | 16              | 0.50     | 0.54     | 0.09     |
| Pc:OA = 1:10 | 0.860 | 632         | 31              | 0.856 | 692         | 20              | 1.00     | 1.40     | 0.77     |
| Pc:OA = 1:100 | 0.250 | 635         | 28              | 0.387 | 690         | 17              | 0.65     | 1.01     | 0.24     |
| covered by Spiro | | | | | | | | |
| Pc | 1.599 | 633         | 19              | 1.449 | 680         | 18              | 1.10     | 1.01     | 1        |
| Pc:CDCA = 1:10 | 0.558 | 641         | 36              | 0.874 | 686         | 13              | 0.64     | 1.67     | 0.55     |
| Pc:CDCA = 1:50 | 0.070 | 640         | 31              | 0.160 | 688         | 14              | 0.44     | 0.91     | 0.08     |
| Pc:OA = 1:10 | 1.012 | 636         | 25              | 1.077 | 684         | 17              | 0.94     | 1.31     | 0.78     |
| Pc:OA = 1:100 | 0.317 | 636         | 26              | 0.535 | 685         | 16              | 0.59     | 0.88     | 0.29     |
3 Estimation of Pc to co-adsorbate ratio on the surface of TiO$_2$

Assuming that the area occupied by single molecule, Pc, CDCA or OA, on the surface of TiO$_2$ is the same independent of was it deposited along or as a mixture, the area per Pc in mixed layers can be calculated as

$$S_m = S_{Pc} + c_r S_{ads}$$  \hspace{1cm} (2)

where $S_{Pc}$ and $S_{ads}$ are the mean molecular areas occupied by Pc and co-adsorbate (CDCA or OA) single molecule on TiO$_2$, and $c_r$ is the relative molecular concentration of the co-adsorbate on TiO$_2$ surface, or the ratio of number of co-adsorbate to Pc molecules. The sample absorption in the red part of the spectrum depends solely on the density of Pc molecules. The ratio of the mean molecular area per Pc in mixed film to that in pure Pc film is

$$r = \frac{S_m}{S_{Pc}} = \frac{S_{Pc} + c_r S_{ads}}{S_{Pc}} = 1 + c_r \frac{S_{ads}}{S_{Pc}}$$  \hspace{1cm} (3)

The relative absorption of mixed sample is inversely proportional to $r$, or

$$A_{rel} = \frac{A_m}{A_{Pc}} = r^{-1}$$  \hspace{1cm} (4)

which gives

$$A_{rel}^{-1} = \frac{A_{Pc}}{A_m} = 1 + c_r \frac{S_{ads}}{S_{Pc}}$$  \hspace{1cm} (5)

Since absorption spectra of samples with different concentrations of co-adsorbate are different, direct comparison of the absorption intensity is meaningless. Instead, the areas under Q-bands were calculated as $A = a_1 \Delta \lambda_1 + a_2 \Delta \lambda_2$ (see eq. (1)), and used to calculate
relative absorbances of the mixed samples, as presented in Table S1 in the last column ($A_{rel}$). The dependence of $1/A_{rel}$ on relative concentration of co-adsorbates in solutions used for sample sensitization, $c_{sol}$, is presented in Fig. S6. An average of 8 co-adsorbate free samples was used as a reference, $A_{Pc}$, but all 8 data points are shown at $c_{sol} = 0$.

![Graph showing relative decrease of Pc absorption in films with co-adsorbates (CDCA or OA) as function of the relative concentration of the co-adsorbate in solution used for the TiO$_2$ sensitization.](image)

Figure S6: Relative decrease of Pc absorption in films with co-adsorbates (CDCA or OA) as function of the relative concentration of the co-adsorbate in solution used for the TiO$_2$ sensitization. Absorption intensities of 8 sample without co-adsorbates (denote as Pc in the plot) were averaged and used as reference. Dotted lines are linear approximations of the dependences.

The dotted lines in Fig. S6 present slopes of dependences, which are 0.1 for CDCA and 0.03 for OA, respectively. According to eq. (5) the slope must be $S_{ads}/S_{Pc}$ if relative concentration of co-adsorbates in the layer and sensitization solution is the same. A rough estimation of the mean molecular areas, $S_{ads}$ and $S_{Pc}$ can be obtained from molecular modelling or Langmuir monolayer studies of similar compounds.\(^1\) In a tightly packed molecular monolayers one can expect the areas to be roughly 1, 0.4 and 0.3 nm$^2$ for Pc, CDCA and OA, respectively. Therefore the ratio $S_{ads}/S_{Pc}$ can be expected to be in the range 0.2–0.5, or few times larger than that obtained from the plot in Fig. S6. Apparently the relative concentration of adsorbate in the film is few times lower than that in the solution, $c_{sol} > c_{m}$. It seems that the date of Pc binding to TiO$_2$ is few times higher than that for CDCA, and for CDCA it is higher than for OA.
4 Transient absorption measurements

Figure S7: Time-resolved transient absorption spectra for the Pc:CDCA = 1:10 sample. Spectra were corrected for the group velocity dispersion and instrument response. Excitation wavelength was 695 nm.

4.1 Effect of co-adsorbate on the electron injection yield

The question of practical importance is the yield of the electron injection into TiO$_2$. It can be approached by comparing the spectra of the singlet excited state (as the measure of the number of absorbed photons) to that of the Pc cation (as the measure of the number of injected electrons, at least in the case of non-aggregated samples, as discussed above). Unfortunately, there are no wavelengths at which only Pc* or Pc$^+$ would have an absorption band. As a reasonable compromise one can use absorption in the range 580–600 nm shortly after excitation (0.01–0.02 ps delay) as the measure of Pc*. For measuring Pc$^+$, the band at 860 nm at sufficiently long delay time can be used, though keeping in mind that intra-aggregate Pc$^+$ are also contributing to the absorption at this wavelength, and thus this will give an overestimation for aggregated samples. For the Pc:CDCA = 1:50 sample, 2 ps seems to be a reasonable choice to estimate the “primary” electron injection efficiency as at this time the visible part of the spectrum does not keep features of the Pc* and the signal
at 860 nm is still relatively strong. The absorption ratio \((A_{(Pc^+)/A_{(Pc^-)}})\) is 0.74 (860 nm absorption at 2 ps to 590 nm absorption at 0.02 ps). For the Pc:CDCA = 1:10 sample the similar approach gives a ratio of 0.45, but the spectrum at 2 ps retains a band around 990 nm, meaning that part of the signal at 860 nm is due to \(Pc^+\)–\(Pc^-\) pairs but not the electrons injected to TiO\(_2\). Therefore, the efficiency of electron injection of the Pc:CDCA = 1:10 sample is not higher than 60% of that of the Pc:CDCA = 1:50 sample. For the CDCA-free sample the ratio drops to 0.4 and the anion feature at 990 nm is even stronger than for the Pc:CDCA = 1:10 sample. Thus the relative efficiency of the electron injection into TiO\(_2\) is < 50% for the co-adsorbate-free sample. For the Pc:OA = 1:10 sample the absorption ratio \((A_{(Pc^+)/A_{(Pc^-)}})\) is 0.55, or close to that of Pc:CDCA = 1:10 sample, but there is the problem of not well resolved spectrum of the singlet excited state.

Following this estimation guideline, the relative yield of injected electrons in the Pc:CDCA = 1:50 sample is roughly 10% at 200 ps delay time and it drops slightly more to roughly 8% at the longest studied delay of 6 ns. At this delay time the injected electrons are definitely “free” electrons in the conduction band and not bound to surface cations.

![Figure S8: Normalized transient absorption decays of TiO\(_2\)|(Pc:CDCA=1:50)|Spiro at a few characteristic wavelengths. The delay time scale is linear until 2.4 ps and logarithmic after that. Symbols are measured data and solid lines are fits.](image-url)
Figure S9: Decay component spectra for the TiO$_2$|Pc|Spiro sample obtained with six-exponential fit.

Figure S10: Time resolved transient absorption spectra for the Pc:CDCA = 1:10 sample with spiro-MeOTAD. The spectra are corrected for the group velocity dispersion and instrument response. Excitation wavelength was 695 nm.
Figure S11: Decay component spectra for the Pc:CDCA = 1:10 sample with spiro-MeOTAD obtained with six-exponential fit.

Figure S12: Time resolved transient absorption spectra for the Pc:OA = 1:10 sample with spiro-MeOTAD. The spectra are corrected for the group velocity dispersion and instrument response. Excitation wavelength was 695 nm.
Figure S13: Decay component spectra for the Pc:OA = 1:10 sample with spiro-MeOTAD obtained with six-exponential fit.

5 Photocurrent measurements and conversion efficiency estimations

5.1 Estimation of photon to electron conversion quantum yield

The average absorptances, $a_{av}$, were calculated as integral values of absorptance spectra ($a(\lambda) = 1 - 10^{-OD(\lambda)}$) in the range 550–750 nm. Example spectra are presented in Figure S14 for Pc:CDCA samples (covered by spiro-MeOTAD) with different relative concentration of CDCA.
Figure S14: Absorptance \( (a = 1 - 10^{-OD}) \) spectra of samples with different Pc:CDCA ratios (indicated on the plot. Vertical dotted lines are placed at 550 and 750 nm to indicate interval in which the average absorptance was calculate (see text for details).

Knowing excitation power density, \( P_{650} \), short circuit current, \( I_{sc} \), average absorptances, \( a_{av} \), and the wavelength band width, \( \Delta \lambda \), one can estimate the quantum yield of photon to electron conversion, \( \phi \), assuming the band width \( \Delta \lambda \) is reasonably narrow. The relation between the photon and electron fluxes is

\[
\phi a \frac{P_{650} \Delta \lambda}{h \nu} = \frac{I_{sc}}{e}
\]

where \( h \nu = \frac{hc}{\lambda} \) is the photon energy, and \( e \) is the electron charge. Thus the quantum yield is

\[
\phi = \frac{I_{sc}hc}{eaP_{650}\lambda \Delta \lambda}
\]

### 5.2 Dependence of efficiency on relative concentration of CDCA

The dependence of short circuit current \( (I_{sc}) \) on the relative concentration of CDCA \( (c_{rel}) \) is shown in Fig. S15a together with the samples without co-adsorbate \( (c_{rel} = 0) \). The highest current was obtained for Pc:CDCA = 1:10 sample, though statistically there is on significant difference between 1:10 and 1:20 samples. In fact, a few samples were prepared for each concentration and the \( I_{sc} \) value deviation from sample to sample was up to 30%.
Also up to 20% variation of absorptances was observed for similarly prepared samples. To some extend sample absorptance can be used as the measure of Pc surface density in the samples. Therefore Fig. S15b presents dependence of $I_{sc}$ on sample absorptance averaged in the 550–750 nm range.

![Graph S15a](image)

![Graph S15b](image)

Figure S15: Dependence of the short circuit current, $I_{sc}$, on (a) relative concentration of CDCA, $c_{rel}$, and (b) and average sample absorptance in the 550–750 nm range, $a_{aver}$.

It is interesting to notice some correlation between $I_{sc}$ and $a_{aver}$ for the samples with the same composition (e.g. without co-adsorbate) in Fig. S15b. One can also notice that the highest photocurrent is generated by samples with average absorptance in the range 0.2–0.4, which looks as optimum for 2 µm thick samples. This absorptance is typical for 1:10–20 Pc:CDCA samples, and estimated absorbed photon to electron conversion efficiency for this samples is around 40%. This efficiency can be increased by increasing concentration of CDCA, but this also result in fast decrease of the decrease of the sample absorptance and overall decrease of the photocurrent.

References

(1) Jurak, M.; Golabek, M.; Holysz, L.; Chibowski, E. Properties of Langmuir and solid supported lipid films with sphingomyelin. *Advances in Colloid and Interface Science* 2015, 222, 385–397.