Supporting Information

Porphydin oriented self-assembled nanostructures for efficient exciton dissociation in high-performing organic photovoltaics

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Additional text and Figures

1. Porphyrin materials synthesis and characterization

1.1 Synthetic procedure of the water soluble porphyrin derivatives used in this study. 

The porphyrin utilized in this study, meso-tetrakis(1-methylpyridinium-4-yl)porphyrin chloride \([\text{H}_2\text{TMPyP}]^{4+}\text{Cl}^-\) (porphyrin 1), and its zinc (II) derivative \([\text{ZnTMPyP}]^{4+}\text{Cl}^-\) (porphyrin 2), were synthesized following a condensation reaction according to literature procedures (Fig. S1). The starting materials were generally used as received (Aldrich) without any further purification, unless otherwise stated. All reactions were performed under an argon atmosphere and monitored by thin-layer chromatography (TLC) (silica, CH$_2$Cl$_2$/MeOH). Column flash chromatography was performed on a silica gel column.

![Synthetic scheme of porphyrins 1 and 2.](image)

**Figure S1.** Synthetic scheme of porphyrins 1 and 2.
1.2 FTIR measurements. Evidence for the formation of hydrogen bonds in aggregates of porphyrin I was provided by IR absorption spectra of the isolated molecules (recorded in solutions with concentration $10^{-6}$ M) and comparing them with those obtained from the respective aggregated films (Fig. S2). According to literature reports, the formation of weak hydrogen bonds such as C–H···N causes a blue shift in the frequency of the C–H stretching mode.\textsuperscript{2,3} The spectral region around 3000 cm\textsuperscript{-1} was focused on, because the frequencies of the C–H stretching modes, which are affected by the intermolecular C–H···N hydrogen bonds, are in this region. It can be observed that, the main peak in free molecules spectrum appears in a frequency of 2930 cm\textsuperscript{-1}. This main peak is attributed to the C–H vibrational modes at the neighbours of the nitrogen atoms in the pyridine rings. A blue shift of the main peak in the actual film’s spectrum (to 3030 cm\textsuperscript{-1}) was observed, owing probably to the formation of the intermolecular hydrogen bonds, as has been previously reported for molecules with nearly similar structure.\textsuperscript{4} The fact that the porphyrin I molecules have the nitrogen atoms in the pyridine rings at the outer side of the molecule, strengthens the argument that they indeed can be connected by the intermolecular C–H···N hydrogen bonds, forming aggregates in which molecules adopt a face-to-face orientation.\textsuperscript{4}
Figure S2 FTIR spectra of porphyrin 1 monomer (in solution) and aggregates (in film).

On the contrary, FTIR spectra of porphyrin 2 (Fig. S3) exhibited no differences in the region of interest, indicating the formation of a different bonding network. In the case of this molecule, the aggregation may be attributed to coordination between zinc atoms of one molecule and nitrogen atoms of a neighboring molecule, as in the case of other Zn-metallated porphyrins with similar structure.\(^5\)
Figure S3 FTIR spectra of porphyrin 2 monomer (in solution) and aggregates (in film).

2. Porphyrins as cathode interlayers: interfacial study

2.1 UV-vis absorption measurements. We first tried to indentify if porphyrins 1 and 2 still exhibit aggregates with a face-to-face and edge-to-edge orientation, respectively, when are spin coated on top of the P3HT:PCBM layer. UV-vis absorption spectra of P3HT:PC$_{71}$BM (1:0.8 % w/w in chloroform solution) films spin coated on a quartz substrate were recorded (Fig. S4) before and after the insertion of porphyrin layers, spin coated from their methanol solutions with concentration as high as 4.0 % w/v, in order to exhibit relatively high absorption in the area in which P3HT strongly absorbs. From Figure S4 it is evident that the porphyrin 1 self-assembles into aggregates with a face-to-face orientation still exhibits when
inserted on top of the photoactive layer (the porphyrin’s Soret band appears at approximately 405 nm), while porphyrin 2 exhibits aggregates with an edge-to-edge molecular orientation.

![Figure S4 UV-vis absorption of porphyrins 1 and 2 aggregates on top of P3HT:PC71BM.](image)

**Figure S4** UV-vis absorption of porphyrins 1 and 2 aggregates on top of P3HT:PC71BM.

In the case of porphyrin layers inserted on top of the photoactive layer (with a thickness of 100 nm) via spin-coating from solutions with concentration 0.7 % w/v (device operation conditions), all UV-vis absorption (Fig. S5) and fluorescence (Fig. S6) spectra were quite similar. The UV-vis absorption spectra exhibited the characteristic peaks of the P3HT spectrum with a small but not worth mentioned red-shift in the case of those with the porphyrins coatings (Figure S5). It is obvious that the enhanced device operation is not due to higher absorption after porphyrins insertion.
**Figure S5** UV-vis absorption spectra of P3HT:PC$_{71}$BM films with and without the porphyrin layers inserted on top of them *via* spin-coating.

**Figure S6** Fluorescence spectra of P3HT:PC$_{71}$BM films with and without the porphyrin layers inserted on top of them *via* spin-coating.
2.2 AFM study. The surface morphology of the porphyrin I films deposited from their methanolic solutions on P3HT:PC71BM films was also studied by atomic force microscopy (AFM) (Fig. S7). The concentration of the porphyrin solution was progressively increased (0.4 %, 0.7 % and 1 % w/v), whereas the spin speed remained constant at 2000 rpm. The results show the 2D and 3D AFM topographic images along with the respective statistical data obtained upon processing these images. The main result derived by comparing these images is that the deposition of the porphyrin layer smoothens the underlying film of the bulk heterojunction blend, which possesses slightly higher peak-to-valley height and roughness than the porphyrin-modified films. This clearly demonstrates that the porphyrin noanoaggregates are uniformly arranged on the organic substrate. Moreover, upon increasing the concentration of the porphyrin solution, the surface morphology remains smooth but the aggregates seem to become larger. This can be extracted by the histogram of the 1 % w/v porphyrin I film, which shows a shift of the heights distribution to higher values, thus presenting in this case a negative skewness compared to nearly zero skewness values for the lower concentrations, namely a relatively symmetrical distribution of the aggregates heights. Finally, the low coefficient of kurtosis calculated for the films spin-coated from the more dilute solutions is indicative of the round-shaped aggregates formed under these deposition conditions. The effect of spin-speed on surface morphology of porphyrin I films deposited from a 0.7 % w/v solution in methanol over a P3HT:PC71BM film was investigated with AFM and the results are depicted in the 2D and 3D images of Fig. S8 along with the relevant statistical analysis. It turns out that the increase in the spin speed does not lead to a monotonous altering of the surface properties. In particular, the smoothest surface with the lowest peak-to-valley height difference occurs for the intermediate spin speeds of 2000 and 4000 rpm. Lower and higher speeds seem to result in the formation of larger aggregates disrupting slightly the film uniformity.
Figure S7 Surface morphology study of porphyrin 1 on P3HT:PC$_{71}$BM: the influence of solution concentration.

The surface morphology of the porphyrin 2 films deposited from different concentration methanolic solutions (all spin-coated at the same spin speed of 2000 rpm) on P3HT:PC$_{71}$BM underlayer was investigated with AFM and the results are presented in the 2D and 3D images of Fig. S9 along with the relevant statistical analysis. Upon comparing the Zn-porphyrin films spin-coated from 0.2 %, 0.4 %, 0.7 % and 1 % w/v solutions, it can be deduced that the
observed trend of the surface roughness is not monotonous as was observed in the case of the porphyrin \( I \) films (see Figure S7 above), owing probably to the different solubilities of the two porphyrins in methanol and also the different stacking geometries that are being formed in the Zn-porphyrin.

**Figure S8** Surface morphology studies of porphyrin \( I \) on P3HT:PC\(_{71}\)BM: the influence of spin coating conditions.

Therefore, in this case, an optimum concentration can be picked out, i.e. 0.7 % w/v, by taking into account primarily the smaller size and more homogeneous distribution of the nanoaggregates and not strictly the absolute values of the lowest peak-to-valley height and surface roughness. To this end, it is noteworthy that the surface skewness switches from
positive values in low concentrations to a negative value in the most concentrated solution, indicating a transition of the aggregates size distribution towards larger values upon increasing the concentration of the methanolic solution.

**Figure S9** Surface morphology study of porphyrin 2 on P3HT:PC$_{71}$BM: the influence of solution concentration.
References


