Supporting Information

Porphyrins as ITO photosensitizers:

Substituents control photo-induced electron transfer direction

Yulia Furmansky, Hela Sasson, Paul Liddell, Devens Gust, Nurit Ashkenasy and Iris Visoly-Fisher

1. Absorption spectra

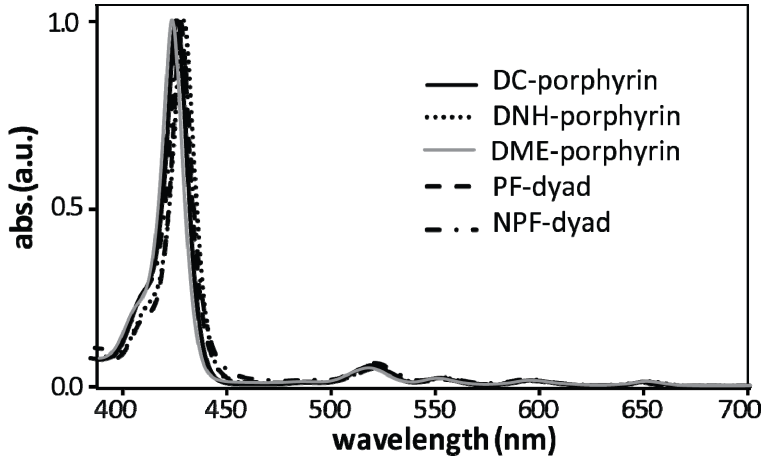

Figure S1: Normalized absorption spectra of solutions of porphyrin derivatives in chloroform (**PF-** and **NPF-dyads**), THF (**DC-porphyrin**) and toluene (**DNH-porphyrin**).

TABLE S1: Extinction coefficients in solution and wavelengths of the wavelength of Soret band absorption maxima of the porphyrin derivatives in solution, and in multi- and monolayer films.

	Soret band in solution * (nm)	Soret band in multilayers (nm)	Soret band in monolayers (nm)	Extinction coefficient (1/M*cm)
DC-porphyrin	418 [a]	435	420	150000 [a]
DNH-porphyrin	422 [b]	429	423	350000 [b]
TMP-porphyrin	421 [c]	422	NA	115000 [c]
PF-dyad	420 [c]	433	423	500000 [c]
NPF-dyad	420 [c]	436	423	450000 [c]

The measurements were performed in [a]THF, [b]toluene, [c]chloroform solutions

2. Cyclic voltammetry

TABLE S2: Redox potentials [V] vs. Fe/Fe^{+} for porphyrin derivatives.

Compound	P/P^{+} [b]	P/P^{-}	$C60/C60^{-}$
DNH-porphyrin	+0.38	-2.02	-
DC-porphyrin	+0.55	-1.85	-
PF-dyad	+0.43	-2.09	-1.15
NPF-dyad	+0.53	-1.94	-1.05

[b] Irreversible processes.

3. SPS and CPD

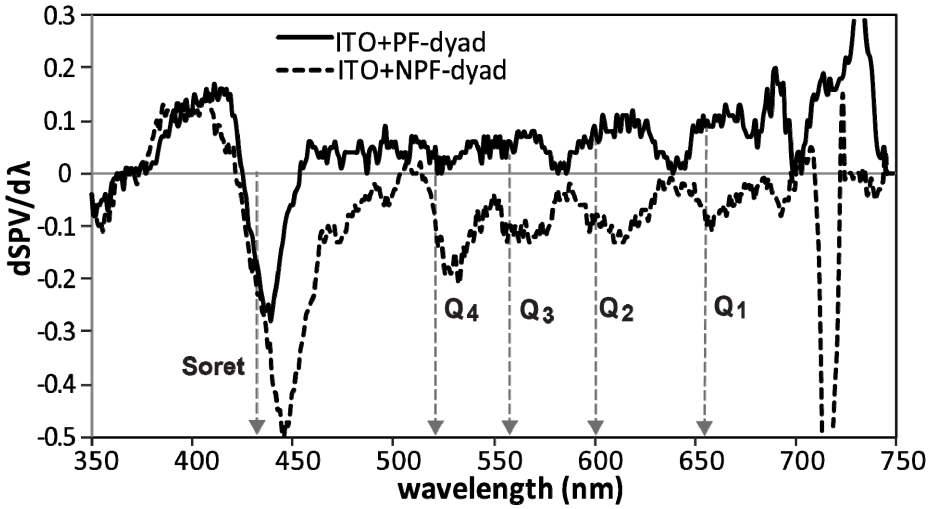

Figure S2: SPV derivative as a function of wavelength for **PF-** and **NPF-dyads**. The arrows indicate the wavelengths corresponding to absorption maxima, showing that the derivatives nullifies (corresponding to local SPV peaks) when the illumination approaches the absorption maxima.

To elucidate changes in the band bending of the bare- and modified- ITO, CPD values before and after illumination by a Xe lamp (290W) were compared (Table S3). Intensity dependent measurements indicated that photosaturation was not obtained, suggesting that the light intensity was insufficient to flatten the bands. Therefore only relative changes in band bending could be detected. A 140 mV smaller SPV was observed for **DNH-porphyrin**-modified ITO compared to bare ITO, indicating an decrease of at least 140 meV in the ITO band bending upon adsorption of DNH-porphyrin, which is sufficient to promote electron transfer from the **DNH-porphyrin** to ITO (scheme 3). Furthermore, the **DNH-porphyrin**-

modified ITO sample shows a significantly smaller work function, compared to other modified and bare ITO (Table S3), further confirming that **DNH-porphyrin** adsorption induces reduction in the ITO surface band bending. A reduced change in SPV upon absorption in the ITO could also be observed in SPS of **DNH-porphyrin** monolayer films (Figure S3a), suggesting that the first adsorbed monolayer determines the band bending of the ITO. The same trend was observed in measurements using super-bandgap, 340 nm monochromatic illumination (35 µW, Figure S3b), indicating that the lower SPV signal in **DNH-porphyrin**/ITO is due to light absorption at the ITO layer itself.

TABLE S3: Summary of surface work function and band bending measurements for monolayer modified samples.

Sample	Work function (eV) [a]	Band bending (meV) [b]
bare ITO	5.09±0.03	360±90
ITO+DNH-porphyrin	4.91±0.06	220±10
ITO+DC-porphyrin	5.02±0.04	275±5
ITO+PF-dyad	5.07±0.04	310±30
ITO+NPF-dyad	5.00±0.03	330±20

[a] Sample work function = CPD_{dark} + 5.01 eV (the work function of the gold probe).

[b] The band bending was calculated as the difference in CPD before and after illumination with Xe lamp (290W).

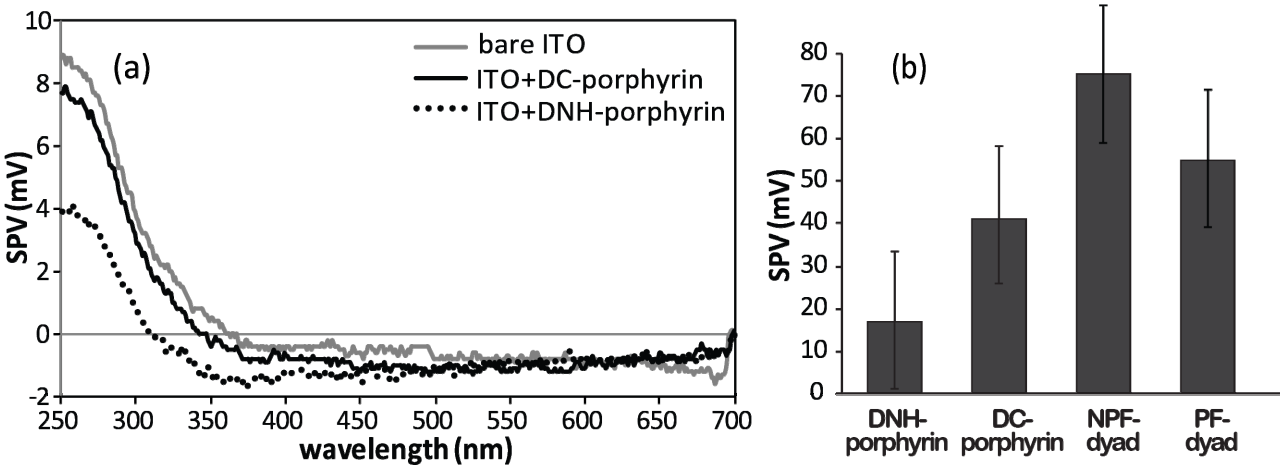

Figure S3: (a) SPS of bare ITO, **DC-** and **DNH-porphyrin** monolayers on ITO, showing SPV as a function of illuminating wavelength. (b) Photovoltage response of different monolayer samples upon illumination with monochromatic 340 nm light (35µW).

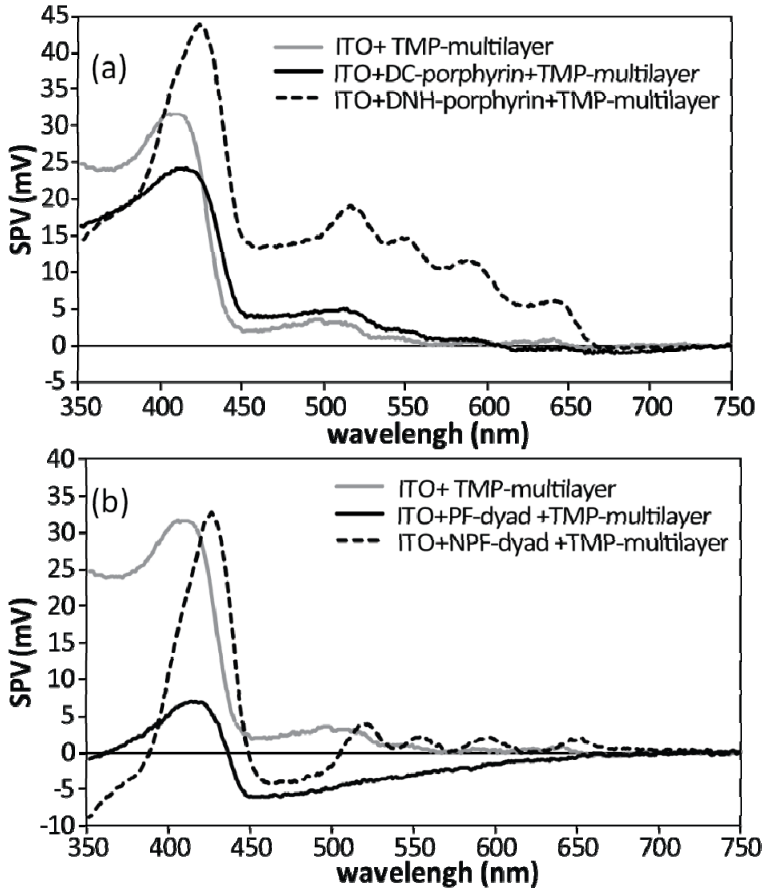

Figure S4: SPS spectra of **TMP-porphyrin** multilayers adsorbed on ITO modified with (a) **DC-** and **DNH-porphyrin** monolayers, and (b) **PF-** and **NPF-dyad** monolayers.