Supplementary Material

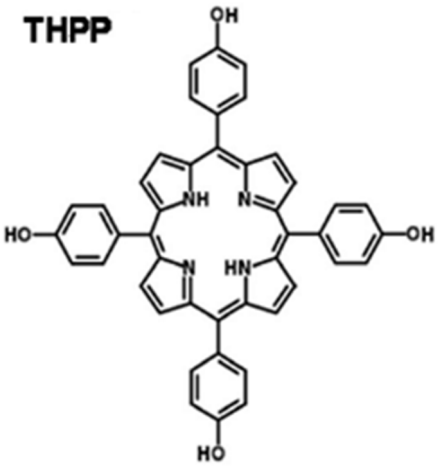

Figure S1. Chemical structure of THPP.

Characterization of the THPP.

^{1}H NMR (400 MHz, DMSO-doublet 6δ) was recorded on a Varian Gemini and a Bruker 300 MHz spectrometer at 300 MHz.

Mass spectrum (FAB) was determined using a mass-spectrometer Varian MAT 312 (Amex Lab, Bucuresti, Romania) (450°C, Tor, 70 eV) type operating in Electron Spray Ionization (ESI-MS) mode, Finnigan-Mat TSQ 700 type. The m/z values refer to the highest peak of the isotopic pattern ratio according to the natural abundance of the isotopes. [10].

High performance liquid chromatography (HPLC) was performed with an Agilent 1100 system (Agilent Technologies, Waldbronn, Germany), with a UV–visible diode-array detector, a degasser, and a liquid chromatography pump. An Agilent software was used to calculate peak areas. The sample 20 μL was injected into the HPLC system, at a flow rate of 1 mL/min. THPP was analyzed by HPLC on a Zorbax Eclipse XDB C18 (Agilent Technologies, Waldbronn, Germany), 150 mm × 4.6 mm × 5μm column with acetonitrile/water (7:3) as mobile phase (0.7 mL min^{-1}) in isocratic mode. Identification of compounds was achieved by comparing their retention times and UV spectra with those of standards stored in a data bank [55,56]. The detection limits ranged from 0.15–0.5mg L^{-1}. The reagents were provided of highest purity obtainable from Merck (Madison, NJ, USA), Fluka (Quaker Houghton, USA) and Scharlau SL (Barcelona, Spain) and were used without further purification.

Results

^{1}H NMR: 9.94 (singlet, 4H, ArOH), 8.86 (singlet, 8H, βH), 8.0 (doublet, 8H, ArH 2,6, J= 8.4 Hz), 7.21 (doublet, 8H, ArH3,5, J = 8.4 Hz), -2.88 (singlet, 2H, NH) The other peaks, corresponding to phenyl and pyrrole protons or to OH are resonating in low field region of 7.36–8.11ppm (orto-and meta-H-Ph), 8.98ppm (β-H-pyrrole), respectively to 10.01 ppm (OH). Found $(M + H)^+$ 678.253 C44H30N4O4 requires M + 1 = 678.250.

Mass spectrum: Molecular ion (M+) at m/e value of 678; m/e = 307 fragment, corresponding to the double charged ion of the meso-tetraphenyl porphyrin fragment; loss of water molecules and the appearance of remarkable abundant (55%) carbonylium fragments (m/e = 94) [10].

HPLC. Since in the chromatogram, no peaks attributed to the aggregated forms were observed (as in the NMR spectrum), nor impurities generated by the degradation or transformation of this form into other isomeric forms, we deduced that the THPP form with

which we performed the experiments was pure in compliance with the retention time at which this porphyrin was observed (8–10 min, depending on the used mobile phase).

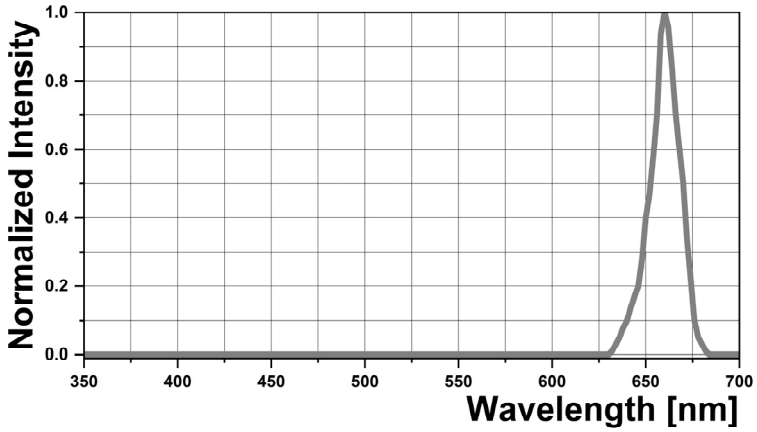

Figure S2. LED lamp emission spectrum.

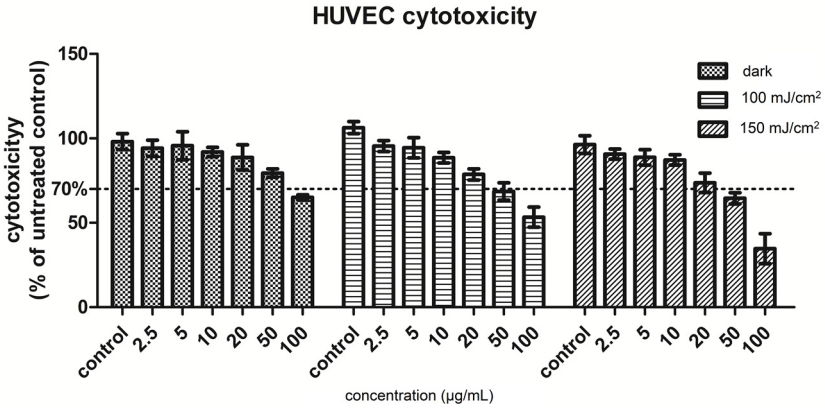

Figure S3. THPP cytotoxicity in HUVEC monocultures**.** Comparative cytotoxicity testing w/wo irradiation 100 mJ/cm^2 and 150 mJ/cm^2 of HUVEC monocultures exposed to THPP (concentration range 0–100µg/ml). Viability is expressed as % of untreated controls (mean ± SD, $n = 3$), toxicity limit is drawn at 70% of untreated control.

Table S1. Phototoxic indexes calculated for the melanoma co-cultures, following exposure to THPP alone in different concentrations and, respectively THPP mediated PDT, irradiation dose 100mJ/cm^2, data are presented as media ± SD, $n = 3$, for each THPP concentration.

THPP Concentration	WM35	M1-15	B16-F10
control	0.99 ± 0.007	1.001 ± 0.02	0.98 ± 0.01
1 µg/mL	1.03 ± 0.03	1.18 ± 0.005	1.12 ± 0.01
2.5 µg/mL	1.10 ± 0.05	1.18 ± 0.03	1.26 ± 0.03
5 µg/mL	1.17 ± 0.02	1.27 ± 0.005	1.25 ± 0.03
10 µg/mL	1.29 ± 0.04	1.44 ± 0.05	1.46 ± 0.02
20 µg/mL	1.76 ± 0.07	1.83 ± 0.08	1.94 ± 0.03
50 µg/mL	4.59 ± 0.28	2.65 ± 0.15	1.86 ± 0.05
100 µg/mL	3.78 ± 0.32	3.76 ± 0.21	1.51 ± 0.11

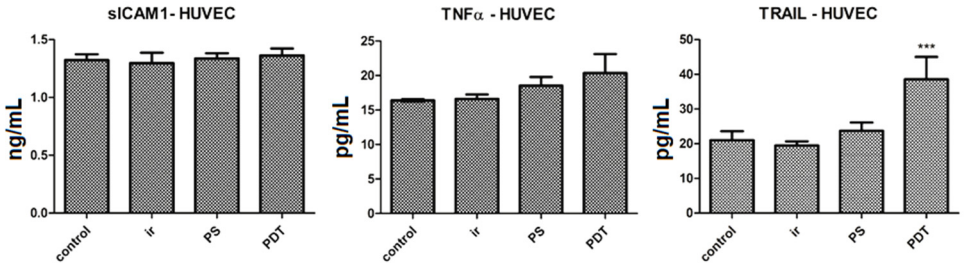

Figure S4. Inflammatory markers in HUVEC monoculture. ELISA measurement of sICAM1(ng/mL), TNF-α (pg/mL), TRAIL (pg/mL); Each bar represents mean ± standard deviation (n = 3). *** = p<1.0E-03, compared to control. 1 = control, 2 = irradiated (100 mJ/cm^2), 3 = THPP (15 μg/mL), 4 = PDT (THPP 15 μg/mL and irradiation 100 mJ/cm^2).