Supporting information 1. Equipment used

A Bruker Vertex 70-Ram II Raman spectrometer (equipped with a 1064 nm Nd:YAG laser and liquid nitrogen cooled germanium detector) was used to collect Raman data. Elemental analyses were carried out on a Vario EL III MicroCube CHNS Analyzer. Mass spectral data were collected with a Bruker AutoFLEX III Smartbeam TOF/TOF Mass spectrometer. The instrument was operated in negative ion mode using an m/z range of 400–3000 amu. The voltage of the ion sources were set at 19 and 16.7 kV for ion sources 1 and 2, respectively, while the lens was set at 8.50 kV. The reflector 1 and 2 voltages were set at 21 and 9.7 kV, respectively. The spectra were acquired using alpha-cyano-4- hydroxycinnamic acid as the MALDI matrix, using a 337 nm nitrogen laser. ¹H NMR spectra were obtained using a Bruker AVANCE 300 MHz NMR spectrometer in acetone.

Dynamic light scattering (DLS) experiments were done on a Malvern Zetasizer nanoseries, Nano-ZS90. Ground state electronic absorption spectra were recorded at room temperature using on a Shimadzu UV-2550 spectrophotometer and a 1 cm pathlength cuvette. Fluorescence emissions spectra were recorded on a Varian Eclipse spectrofluorometer. Fluorescence lifetimes were measured using a time correlated single photon counting setup (TCSPC) (FluoTime 300, Picoquant GmbH) with a diode laser (excitation source: LDH-P-485 with 10 MHz repetition rate, 88 ps pulse width). Photo-irradiations for singlet oxygen studies were done using a General Electric Quartz line lamp (300W). A water filter was used to filter off infrared radiations. This means irradiation encompassed both the Q and Soret bands. Light intensity was measured with a POWER MAX5100 (Molelectron detector incorporated) power meter and was found to be 9.43×10^{18} photons s⁻¹ cm⁻².

The absorbance of the cells was measured at an excitation wavelength of 450 nm using a Synergy 2 multi-mode microplate reader (BioTek1).

For biological photo-irradiation, samples were enclosed in a box is to ensure that no unwanted ambient light can reach the samples, thus invalidating the results observed. At the very top, a 420 nm mounted LED (M420L3 purchased from Thorlabs) is shone into the box through a hole. The LED is connected to a T-cube LED driver (LEDD1B purchased from Thorlabs), which is used to regulate the current it receives, further details have been reported¹.

2. Procedure for in vitro dark toxicity and PDT

For *In vitro* dark cytotoxicity studies, the MCF-7 carcinoma cells were cultured using Dulbecco's modified Eagle's medium (DMEM) containing 4.5 g/L glucose with L-glutamine (0.11 g/L) and phenol red, supplemented with 10% (v/v) heat-inactivated fetal calf serum (FCS) (50 mL), and 100 unit/mL penicillin-100 µg/mL streptomycin-amphotericin B. The cells were grown in 75 cm² vented flasks (Porvair[®]) and incubated at 37 °C and 5 % CO₂ with humidified atmosphere. Once 90- 100 % cell confluence was achieved, determined through microscopic examination, the cells were rinsed with Dulbecco's modified phosphate buffer saline (DPBS). Cells were passaged through routine trypsinisation. Routine viability and cell enumeration was performed using the trypan blue dye exclusion assay (0.4 % trypan blue solution) using a hemocytometer. Cells were seeded at a cell density of 10,000 cells/well in supplemented DMEM containing phenol red in 96-well tissue culture plates (Porvair[®]) and incubated in a humidified atmosphere at 37 °C and 5 % CO₂ for 24 h to foster cell attachment to the wells. The attached cells were rinsed with 100 µl DPBS once, followed by administration of 100 µl supplemented DMEM containing gradient concentrations of 0-120 µg/ml. Vehicle controls were performed with fresh supplemented medium or medium containing comparable amounts of DMSO (1% (v/v), for porphyrins and the conjugates.

After 24 h incubation with supplemented DMEM with phenol red, cell proliferation neutral red reagent (WST-1) was used to quantify the surviving cells. The WST-1 assay was used to assess the toxicity and cell proliferation as per manufacturer's instructions (Roche) using a Synergy 2 multi-mode microplate reader (BioTek[®]) at a wavelength of 450 nm. The percent cell viability was determined using equation 1:

% cell viability =
$$\frac{Absorbance \ sample \ at \ 450 \ nm}{Absorbance \ control \ at \ 450 \ nm} \times 100$$
 (1)

where the absorbance of sample is the cells containing TMPP, TMPP-GQDs, ZnTMPP, GaCITMPP, ZnTMPP-GQDs and GaCITMPP-GQDs of control is the placebo cells containing 1% DMSO.

The photodynamic therapy effects of the different complexes were investigated by incubating cells as explained above with varying concentration of TMPP, TMPP-GQDs, ZnTMPP, GaClTMPP, ZnTMPP-GQDs and GaClTMPP-GQDs. The difference is that after incubation for 24 h and then washing with DPBS, the DMEM used did not contain phenol red. The photo-irradiations were performed using a 420 nm mounted LED (M420L3 purchased from Thorlabs), The irradiation time was 300 s to result in irradiation doses of 40 J/cm². After irradiation, the media was replaced with a fresh one containing phenol red. The absorbance of the cells was measured at an excitation wavelength of 450 nm using a Synergy 2 multi-mode microplate reader (BioTek1) discussed above. There were no changes in the spectra of the porphyrins following irradiation for PDT studies, hence confirming stability.

The Statistical analysis, the data obtained from the three independent triplicate experiments were analysed with a 3 way factorial ANOVA Anova (analysis of variance) to determine the statistical differences between the *in vitro* cytotoxicity and photodynamic effect of the photosensitizers on MCF-7 cancer cells. TukeyHSD posthoc test was used to determine the mean differences in *vitro* photodynamic effect of the photosensitizers on MCF-7 cancer cells. p-value of s <0.05 was considered significant.

3. Photochemical and photophysical parameters

3.1. Fluorescence quantum yield

Fluorescence quantum yields (Φ_F) were determined by comparative methods², equation 1.

$$\Phi_{\rm F} = \Phi_{\rm F}^{\rm Std} \frac{\rm F \, A^{\rm Std} \, n^2}{\rm F^{\rm Std} \, A \, (n^{\rm Std})^2} \tag{1}$$

where F and F^{Std} are the areas under the fluorescence curves for sample and standard, respectively. A and A^{Std} are the absorbances of the sample and reference at the excitation wavelength, respectively. *n* and *n^{Std}* are the refractive indices of

the solvent used for the sample and standard, respectively. ZnTPP in DMF was used as a standard (\mathcal{P}_F^{Std}) = 0.033³ when exciting where porphyrins absorb, quinine sulphate in 0.1 M H₂SO₄ (Φ_F = 0.52)⁴ was employed where the GQDs absorb. The Φ_F and fluorescence lifetimes are represented as $\Phi_{F(Porp)}$ and $\tau_{(Porp)}$ when exciting where porphyrins absorb, and $\Phi_{F(GQDs)}$ and $\tau_{(GQDs)}$ when exciting where GQDs absorb.

GQDs fluorescence quantum yields upon coordination ($\Phi_{F(GQDs)}^{conjugate}$) to porphyrins is given by equation 2

$$\Phi_{F(GQDs)}^{conjugate} = \Phi_{F(GQDs)} \cdot \frac{F^{conjugate}}{F_{(GQDs)}}$$
(2)

where $\Phi_{F(GQDs)}$ (the fluorescence quantum yield of the GQDs alone) was used as the standard, $F_{(GQDs)}$ is the fluorescence intensity of the GQDs alone and $F^{Conjugate}$ is the fluorescence intensity of the GQDs coordinated to the porphyrins at the excitation of wavelength of 340 nm.

3.2. Singlet oxygen quantum yield (Φ_{Δ}) .

The singlet oxygen quantum yields in DMF porphyrins and GQDs-porphyrin conjugates were evaluated using equation (3)

$$\Phi_{\Delta} = \Phi_{\Delta}^{\text{Std}} \frac{W \cdot I_{\text{abs}}^{\text{Std}}}{W^{\text{Std}} \cdot I_{\text{abs}}}$$
(3)

where $\Phi_{\Delta}^{\text{Std}}$ is the singlet oxygen quantum yield for the standard standard (ZnTPP in DMF ($\Phi_{\Delta}^{\text{Std}}$ = 0.53)⁵), W and W^{std} are the DPBF photobleaching rates in the presence of porphyrin derivatives under investigation and the standard, respectively. I_{abs} and $I_{\text{abs}}^{\text{Std}}$ are the rates of light absorption by the porphyrin derivative and standard, respectively. A similar equation may be derived for the use of ADMA as a quencher.



S1. NMR spectra of TMPP



S2. Mass spectra of TMPP







S4. Mass spectra of ZnTMPP

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