

Supplementary information for

Nano-encapsulation of a far-red absorbing phthalocyanine into

poly(benzylmalate) biopolymers and modulation of their

photodynamic efficiency

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Contents

Characterization spectra for polymeric materials PMLABe₇₃ and PEG_{42-b}-PMLABe₇₃ ...	3
Figure S1. ¹ H NMR spectrum (400 MHz, CD ₃ COCD ₃) of PMLABe₇₃ and PEG_{42-b}-PMLABe₇₃	3
Figure S2. ¹ H NMR spectrum (400 MHz, CD ₃ COCD ₃) of PEG_{42-b}-PMLABe₇₃	3
Figure S3. SEC chromatogram (THF, 40°C, polystyrene standards, RI detector) of PMLABe₇₃	4
Figure S4. SEC chromatogram (THF, 40°C, polystyrene standards, RI detector) of PEG_{42-b}-PMLABe₇₃	4
Characterization spectra for ZnPc(SO₂Prop)8	5
Figure S5. FT-IR spectrum of ZnPc(SO₂Prop)8	5
Figure S6. ¹ H NMR spectrum of ZnPc(SO₂Prop)8	5
Figure S7. MALDI-MS spectrum of ZnPc(SO₂Prop)8	
Preparation of calibration curve for E.E.....	7
Figure S8. A: UV-vis spectra of ZnPc(SO₂Prop)8 in a 9/1 THF/water mixture. B: Calibration curve.....	7
Materials and Methods for UV-visible and Fluorescence measurements.....	8
UV-visible spectra of nanoparticles in water.....	9
Figure S9. UV-vis spectra (water) of ZnPc(SO₂Prop)8 -loaded PMLABe₇₃ nanoparticles (red) and ZnPc(SO₂Prop)8 -loaded PEG_{42-b}-PMLABe₇₃ nanoparticles (blue) with different loading ratios: 1 wt% (dot), 5 wt% (dash) and 10 wt% (line). Phthalocyanine concentrations: 2-8 μM.....	9
Fluorescence spectra of disrupted nanoparticles.....	10
Figure S10. Absorbance (line), fluorescence emission (dashes) and excitation (dots) spectra of ZnPc(SO₂Prop)8 -loaded PMLABe₇₃ disrupted nanoparticles (red), of ZnPc(SO₂Prop)8 -loaded PEG_{42-b}-PMLABe₇₃ disrupted nanoparticles (blue) and of ZnPc(SO₂Prop)8 (black), with different loading ratios.....	10
Figure S11. Dark toxicity and PDT effect of empty PMLABe₇₃ and PEG_{42-b}-PMLABe₇₃ nanoparticles.....	11
Figure S12. Dark toxicity and PDT effect of non-encapsulated ZnPc(SO₂Prop)8	11
References.....	12

Characterization spectra for polymeric materials

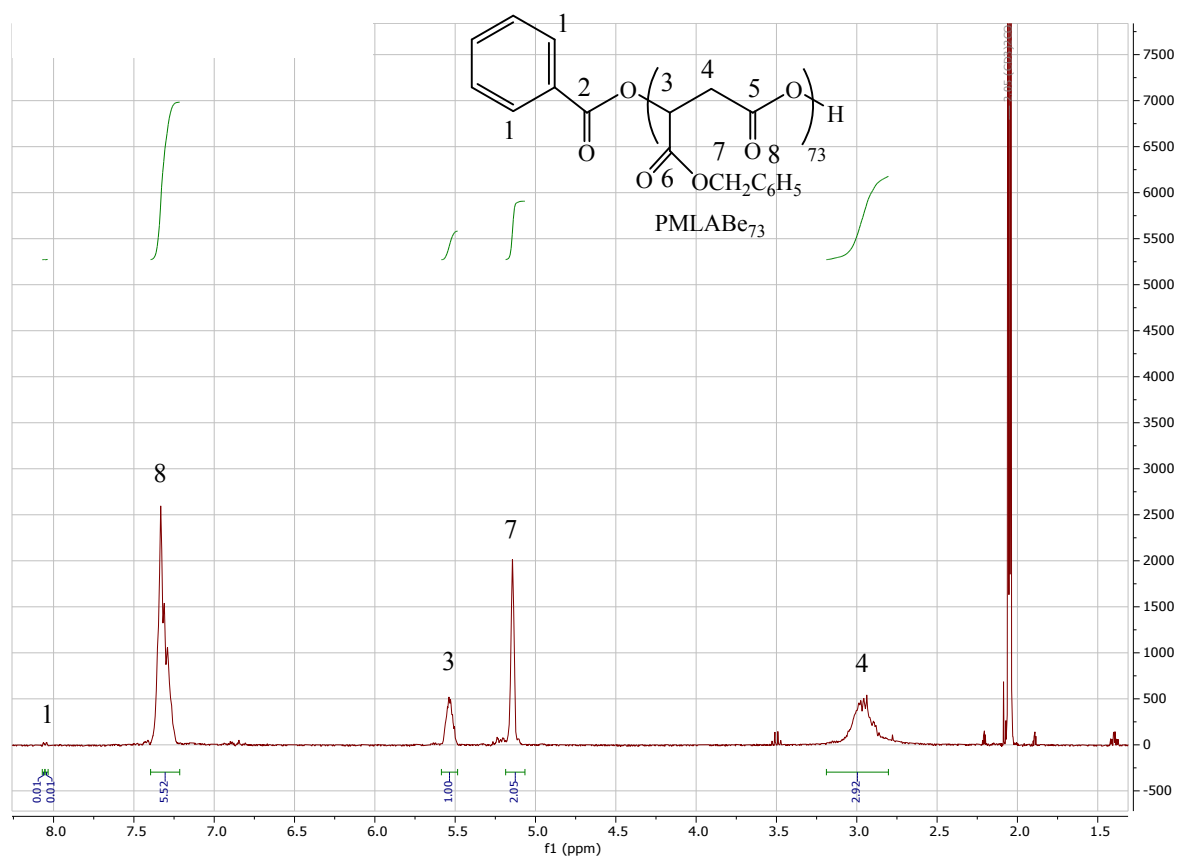


Figure S1. ¹H NMR spectrum (400 MHz, CD₃COCD₃) of PMLABe₇₃ and PEG₄₂-*b*-PMLABe₇₃.

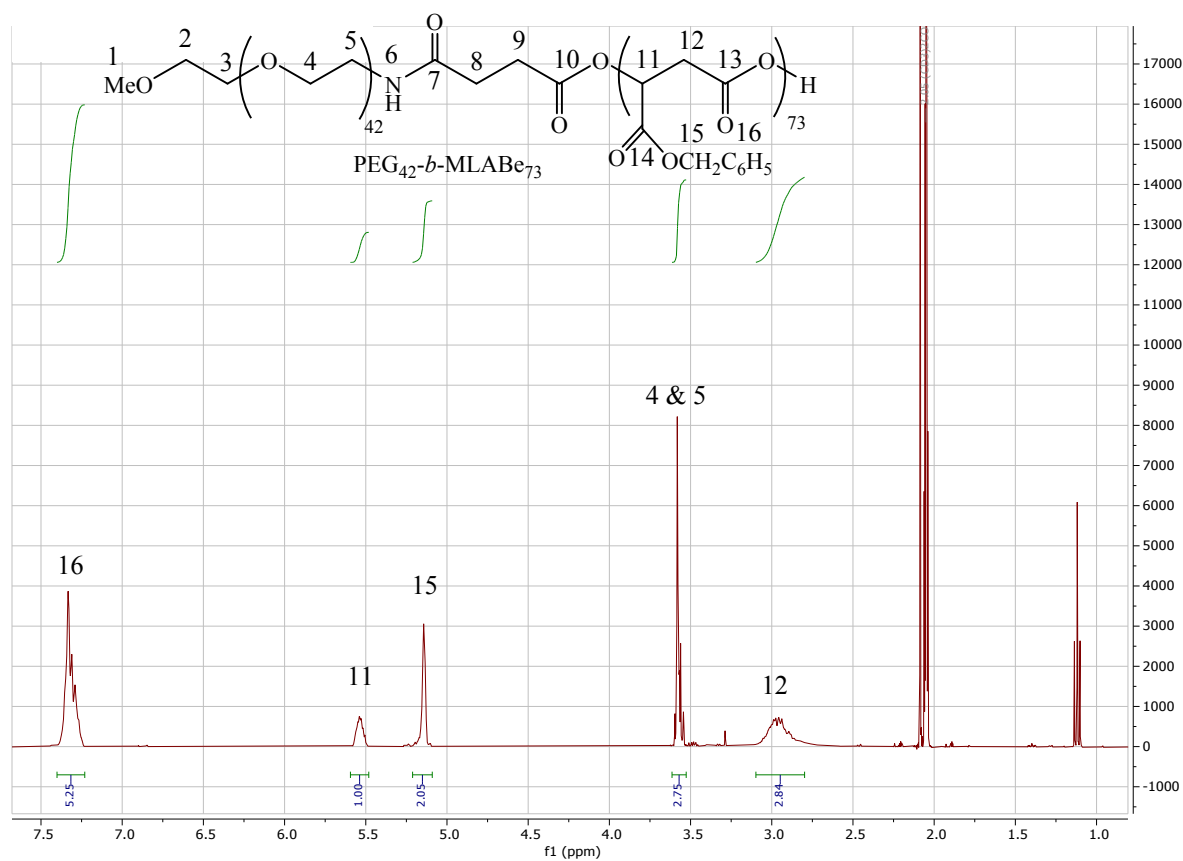


Figure S2. ¹H NMR spectrum (400 MHz, CD₃COCD₃) of PEG₄₂-*b*-PMLABe₇₃.

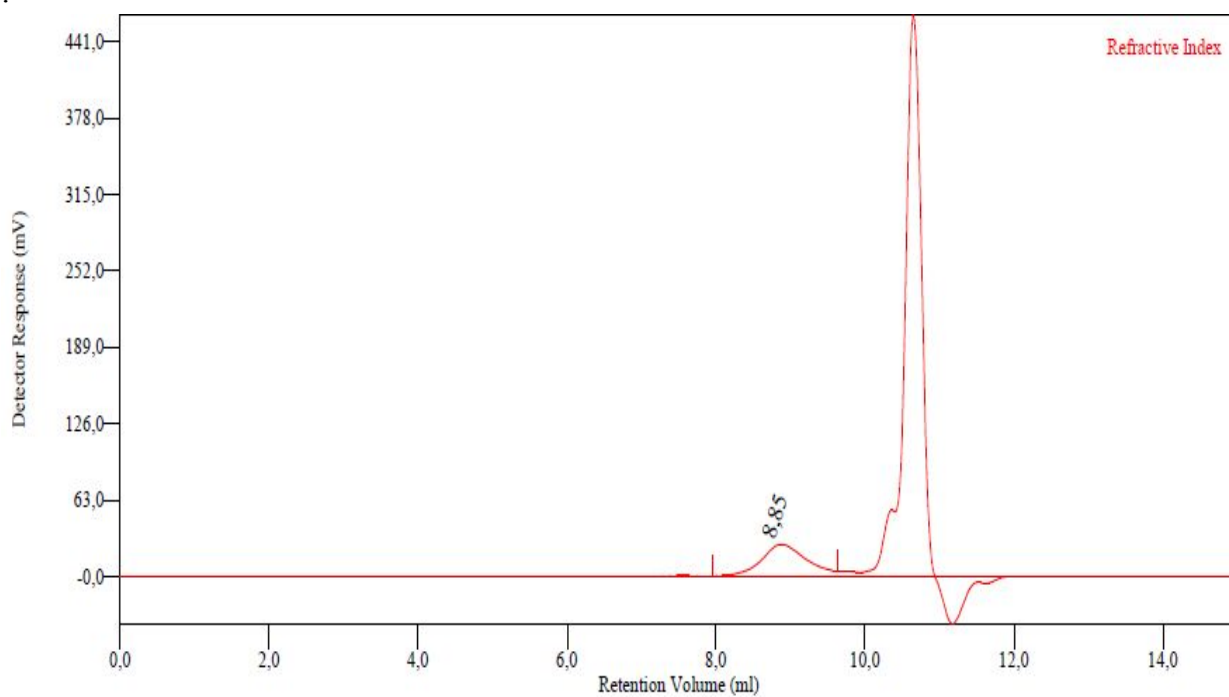


Figure S3. SEC chromatogram (THF, 40°C, polystyrene standards, RI detector) of **PMLABe₇₃**.

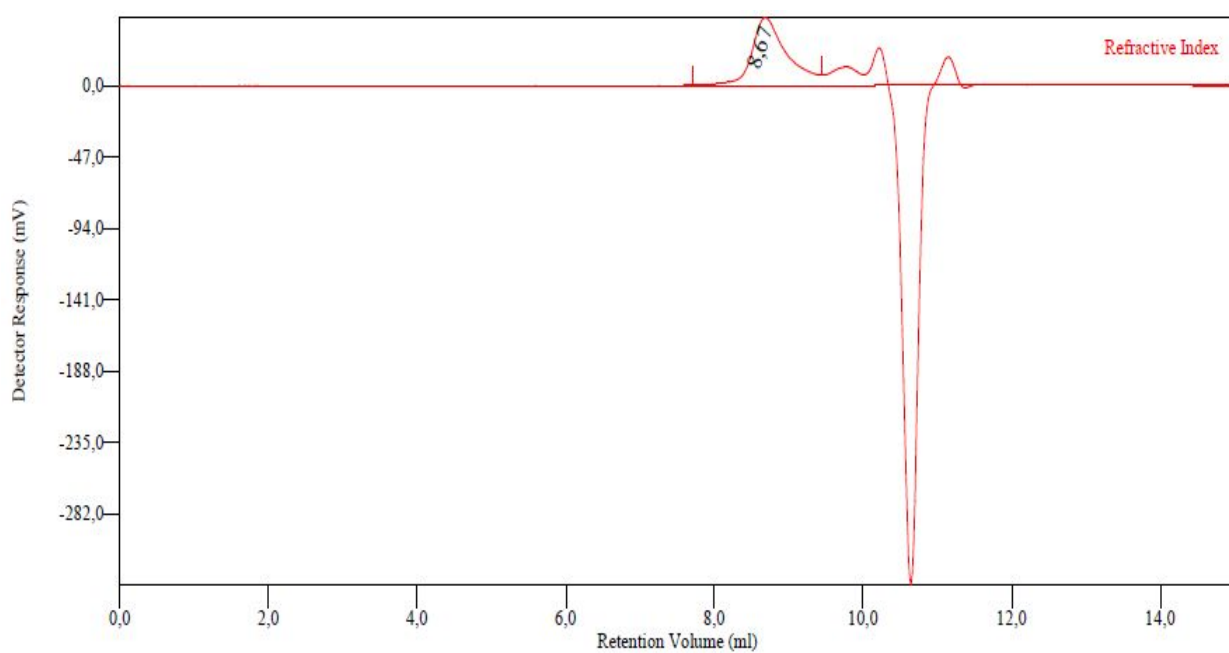


Figure S4. SEC chromatogram (THF, 40°C, polystyrene standards, RI detector) of **PEG₄₂-b-PMLABe₇₃**.

Characterization spectra for ZnPc(SO₂Prop)₈

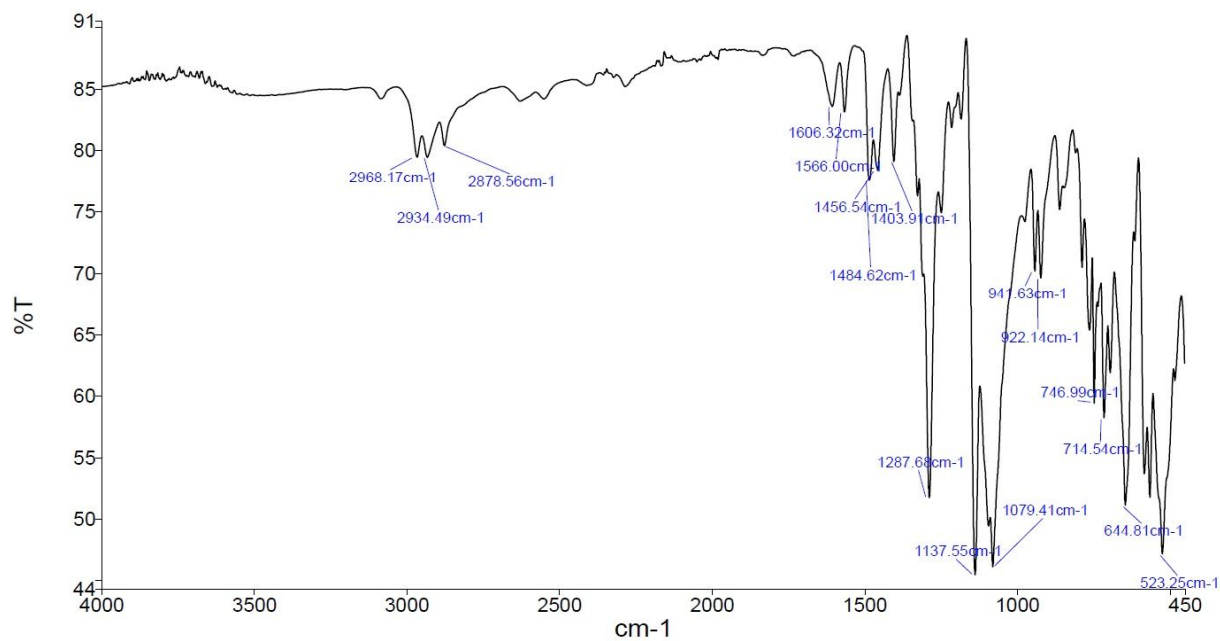


Figure S5. FT-IR spectrum of ZnPc(SO₂Prop)₈

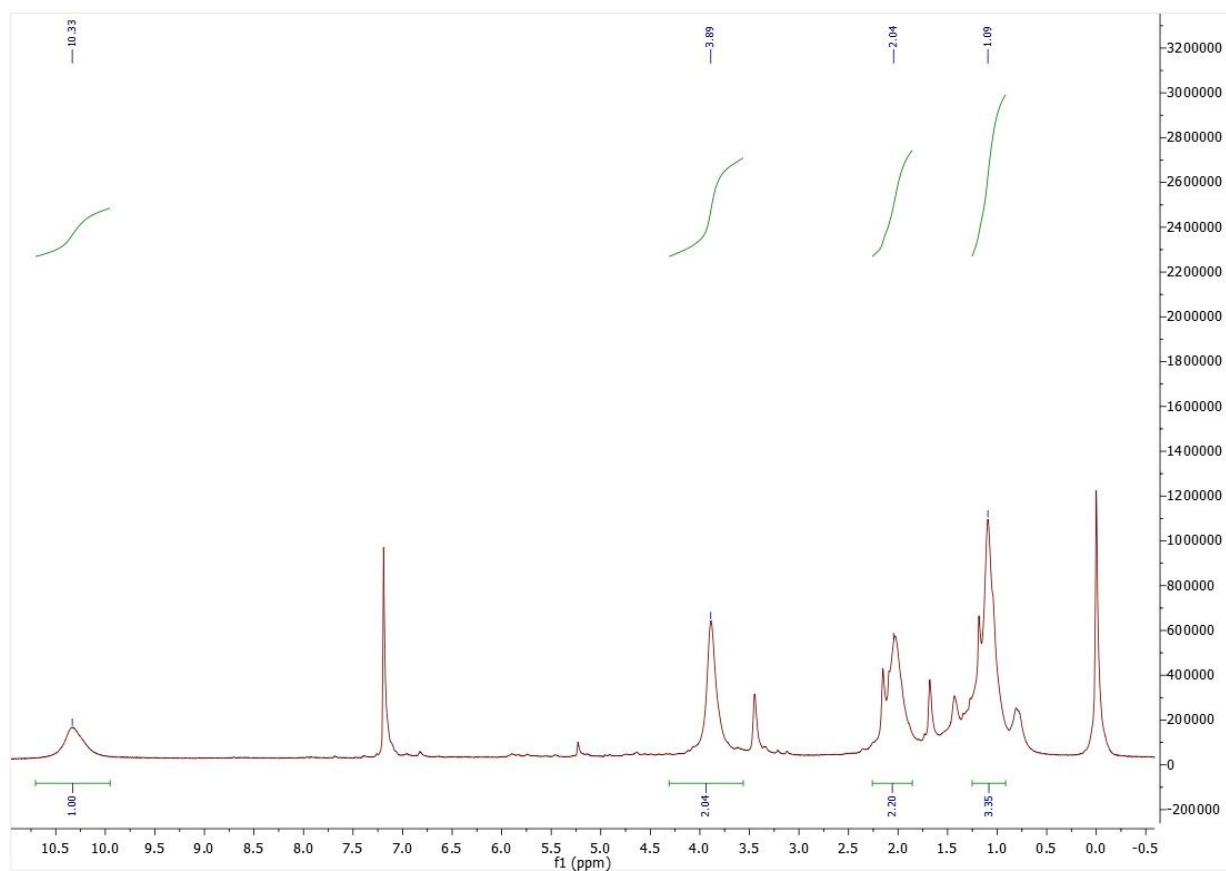


Figure S6. ¹H NMR spectrum of ZnPc(SO₂Prop)₈ (CDCl₃)

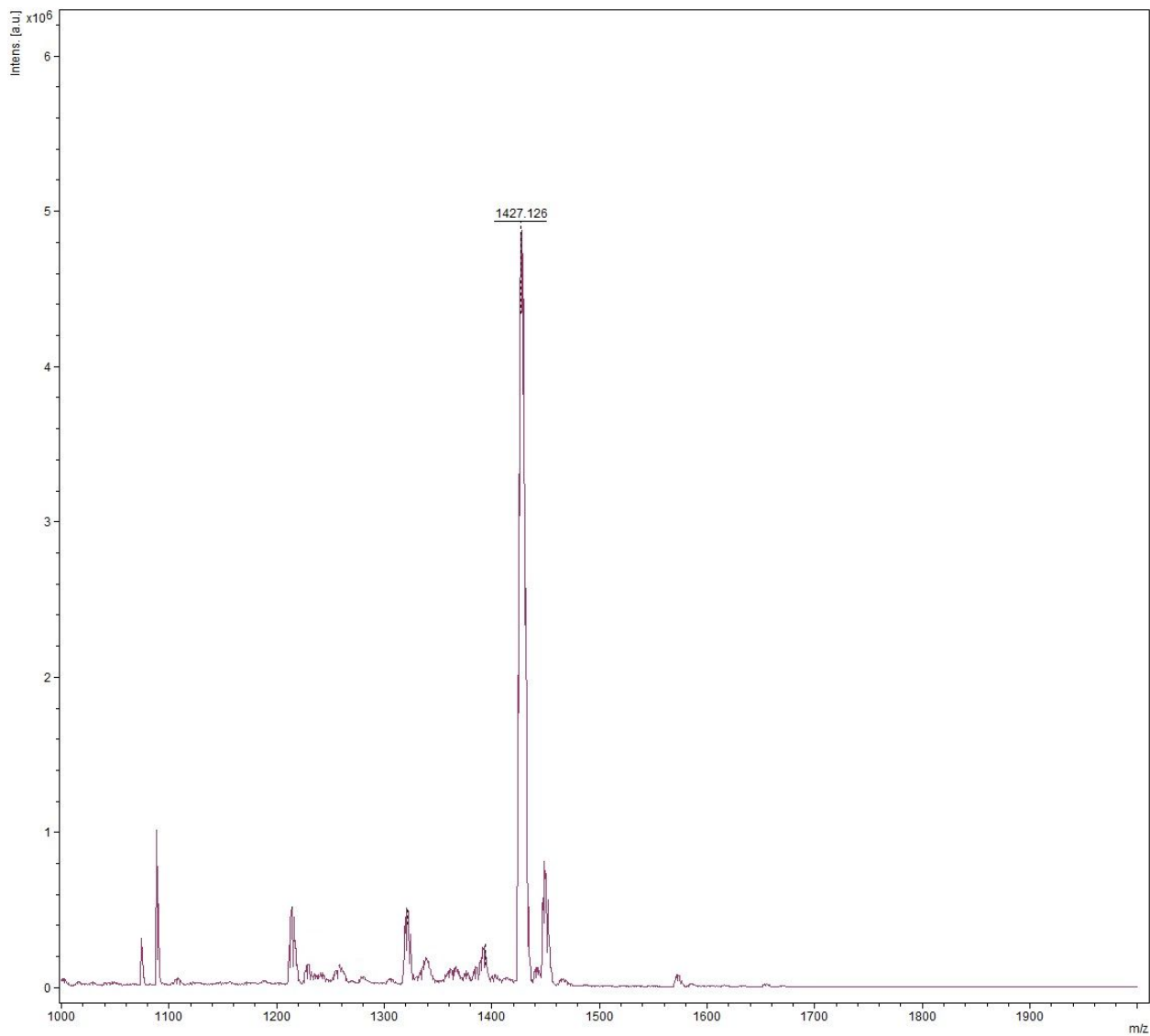


Figure S7. MALDI-MS spectrum of ZnPc(SO₂Prop)₈

Preparation of calibration curve for E.E.

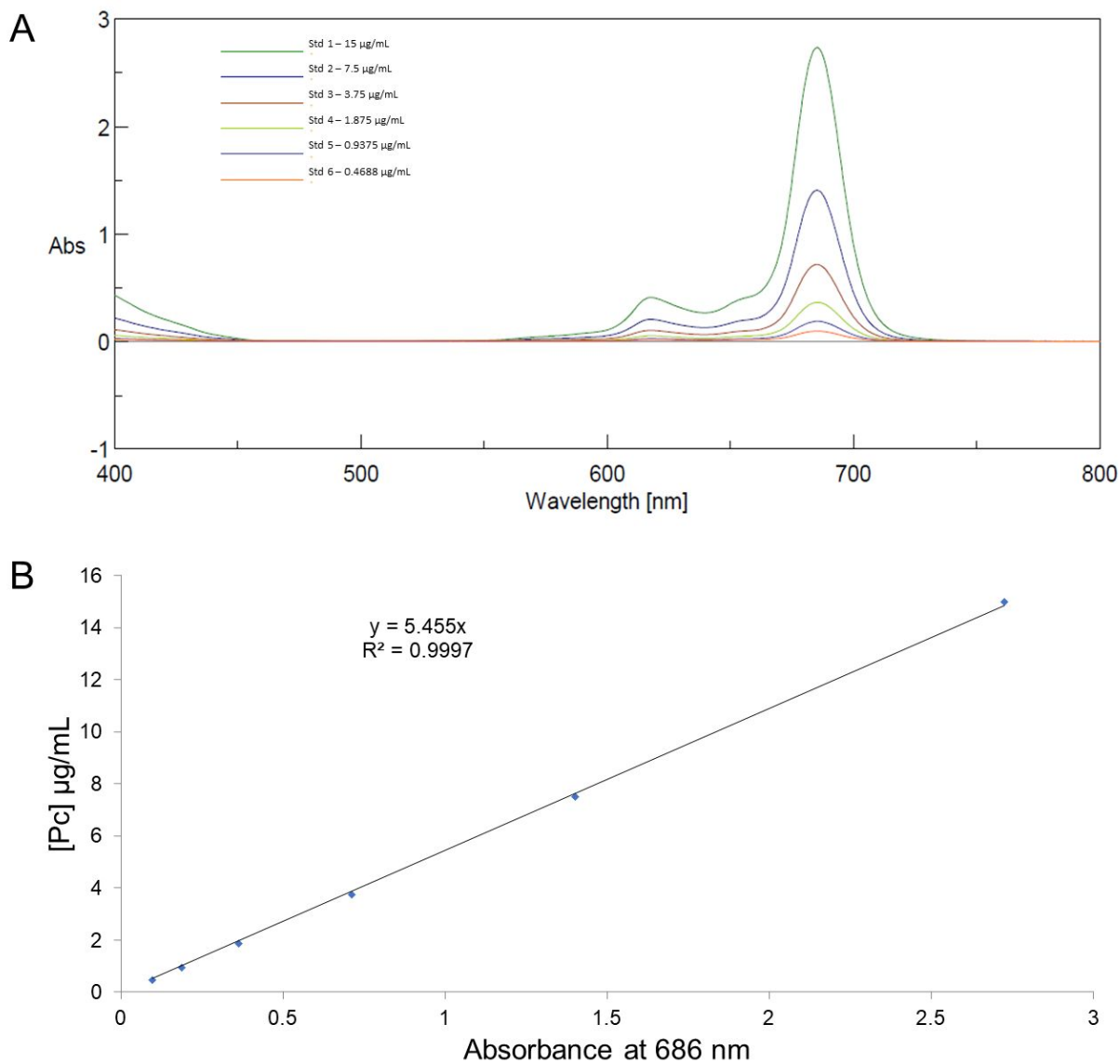


Figure S8. A: UV-vis spectra of **ZnPc(SO₂Prop)**8**** in a 9/1 THF/water mixture. B: Calibration curve.

Materials and Methods for UV-visible and Fluorescence measurements

Ground state electronic absorption

Absorption spectra were recorded at room temperature on a Shimadzu 2600 UV-vis spectrometer using a 1 cm path length quartz cuvette between maximum range 300 and 1100 nm in THF. Solutions were freshly prepared in spectrophotometric grade solvents. Molar extinction coefficients (ϵ) were determined by measurement of the absorption solutions of differing concentration for each compound, followed by determination of the slope.

Fluorescence

Steady-state fluorescence excitation and emission spectra in THF were recorded by using a Varian Cary Eclipse spectrofluorometer using 10 mm path length cuvettes at room temperature.

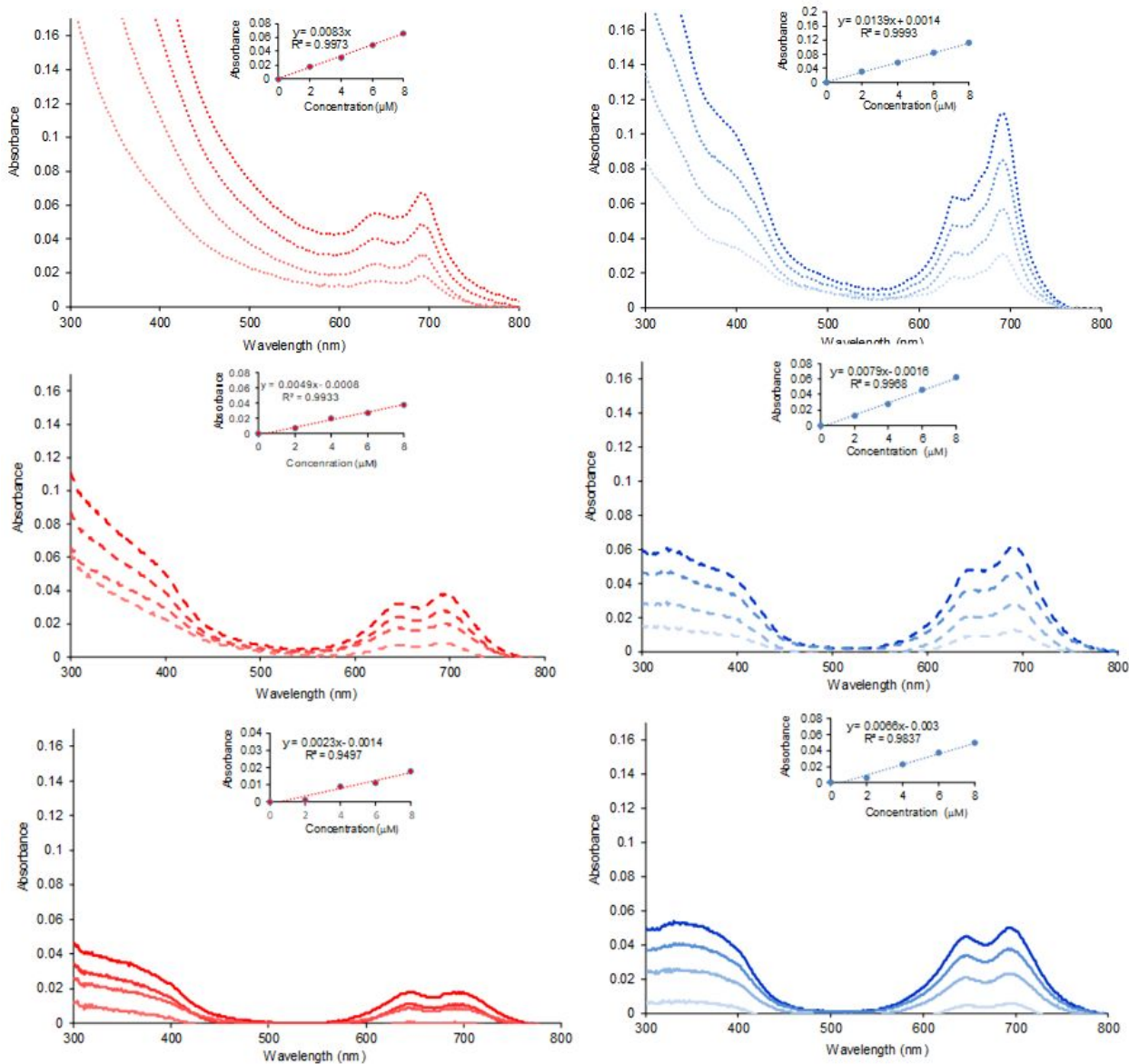


Figure S9. UV-vis spectra (water) of **ZnPc(SO₂Prop)₈**-loaded **PMLABe₇₃** nanoparticles (red) and **ZnPc(SO₂Prop)₈**-loaded **PEG₄₂-*b*-PMLABe₇₃** nanoparticles (blue) with different loading ratios: 1 wt% (dot), 5 wt% (dash) and 10 wt% (line). Phthalocyanine concentrations: 2-8 μM .

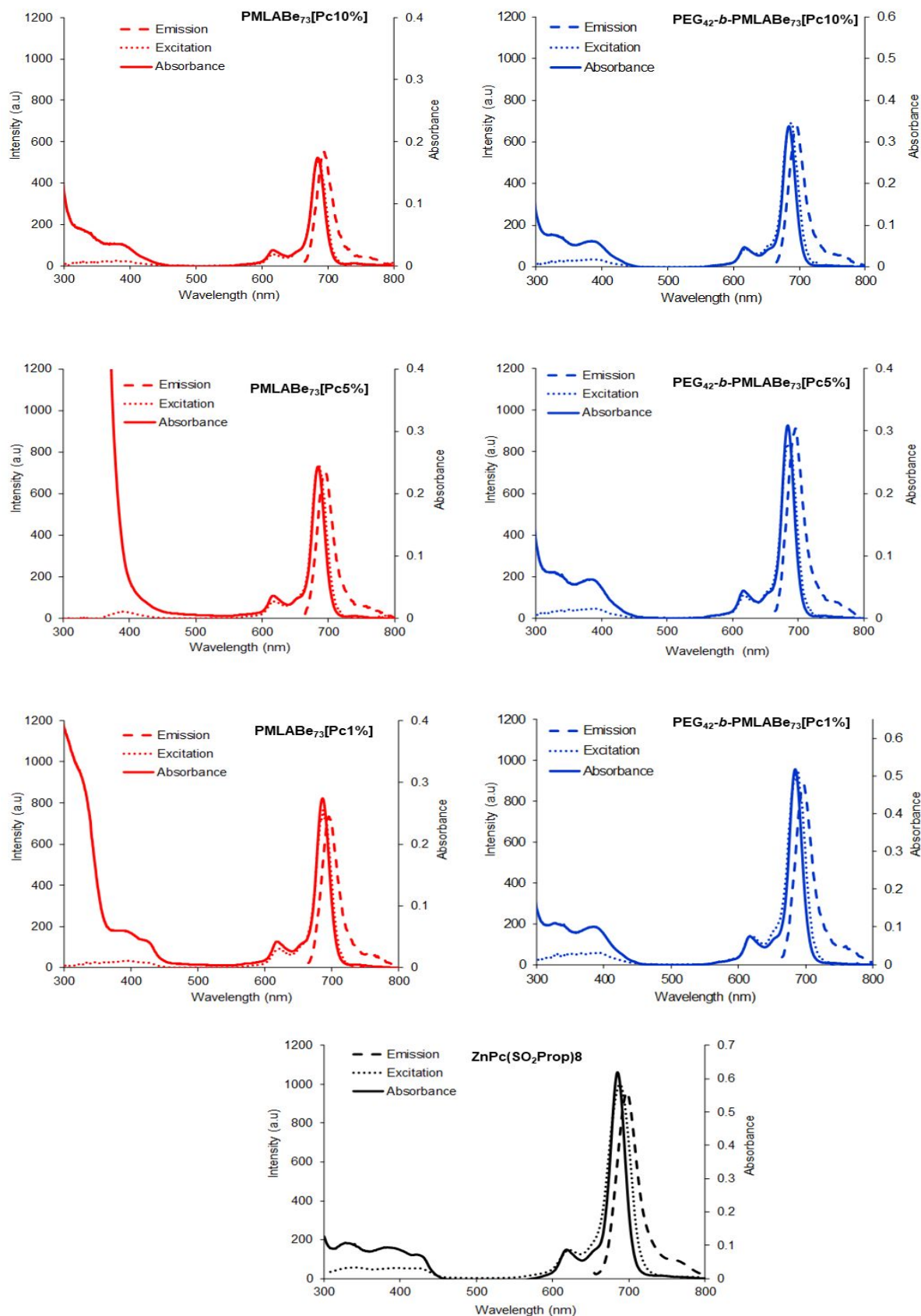


Figure S10. Absorbance (line), fluorescence emission (dashes) and excitation (dots) spectra (in THF) of **ZnPc(SO₂Prop)8**-loaded **PMLABe₇₃** disrupted nanoparticles (red), of **ZnPc(SO₂Prop)8**-loaded **PEG₄₂-b-PMLABe₇₃** disrupted nanoparticles (blue) and of **ZnPc(SO₂Prop)8** (black), with different loading ratios.

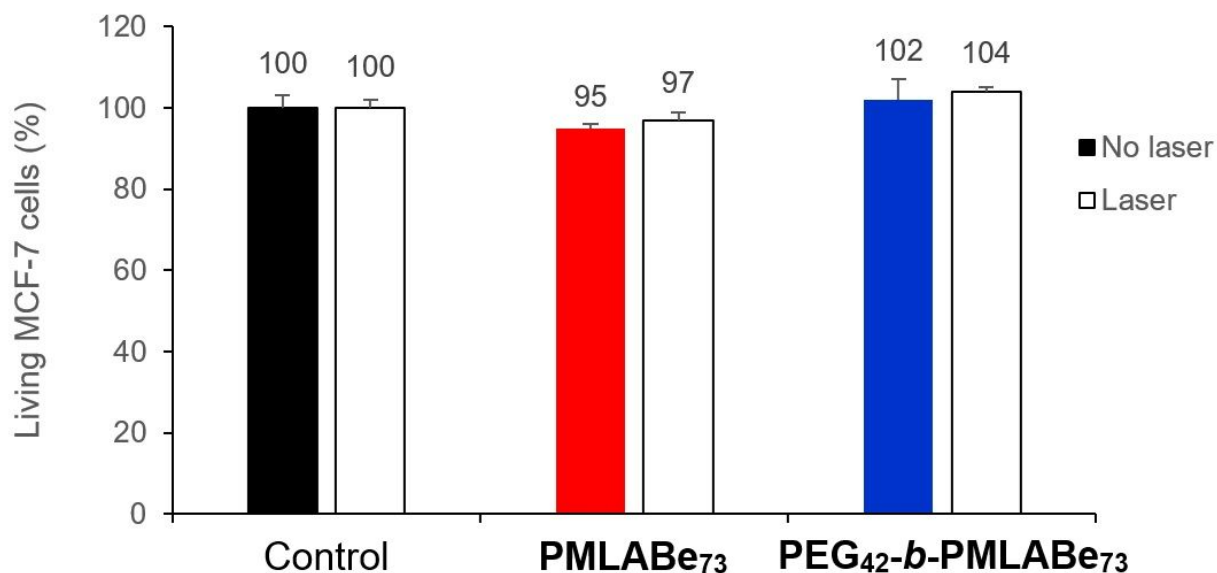


Figure S11. Study of PDT effect of empty PMLABe₇₃ and PEG_{42-b}-PMLABe₇₃ nanoparticles, incubated 24 h at 50 µg.mL⁻¹ with MCF-7 cells. Cells were irradiated with continuous laser for 20 min at 650 nm. Data are presented as (mean ± SD), n=3.

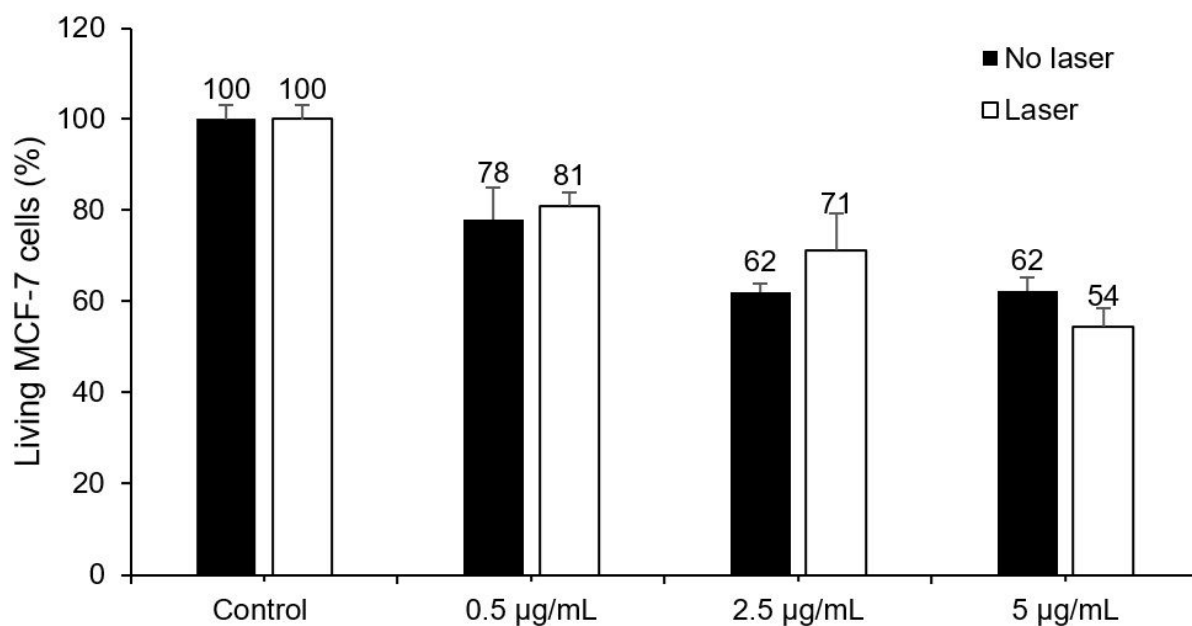


Figure S12. Study of PDT effect of non-encapsulated ZnPc(SO₂Prop)**8** on MCF-7 cells treated with 0.5 µg/mL, 2.5 µg/mL and 5 µg/mL for 24 h. Cells were irradiated with continuous laser for 20 min at 650 nm. Data are presented as (mean ± SD), n=3.

References

- [1] Williams, A. T. R.; Winfield, S. A.; Miller, J. N. Relative Fluorescence Quantum Yields Using a Computer-Controlled Luminescence Spectrometer. *Analyst*, **1983**, 108 (1290), 1067–1071.
- [2] Ogunsipe, A.; Maree, D.; Nyokong, T. Solvent effects on the photochemical and fluorescence properties of zinc phthalocyanine derivatives. *Journal of Molecular Structure*. **2003**, 650, 131-140.