Electronic Supplementary Material (ESI) for Nanoscale Advances.

Supporting Information

Regulation of photo triggered cytotoxicity in electrospun nanomaterials: role of photosensitizer binding mode and polymer identity

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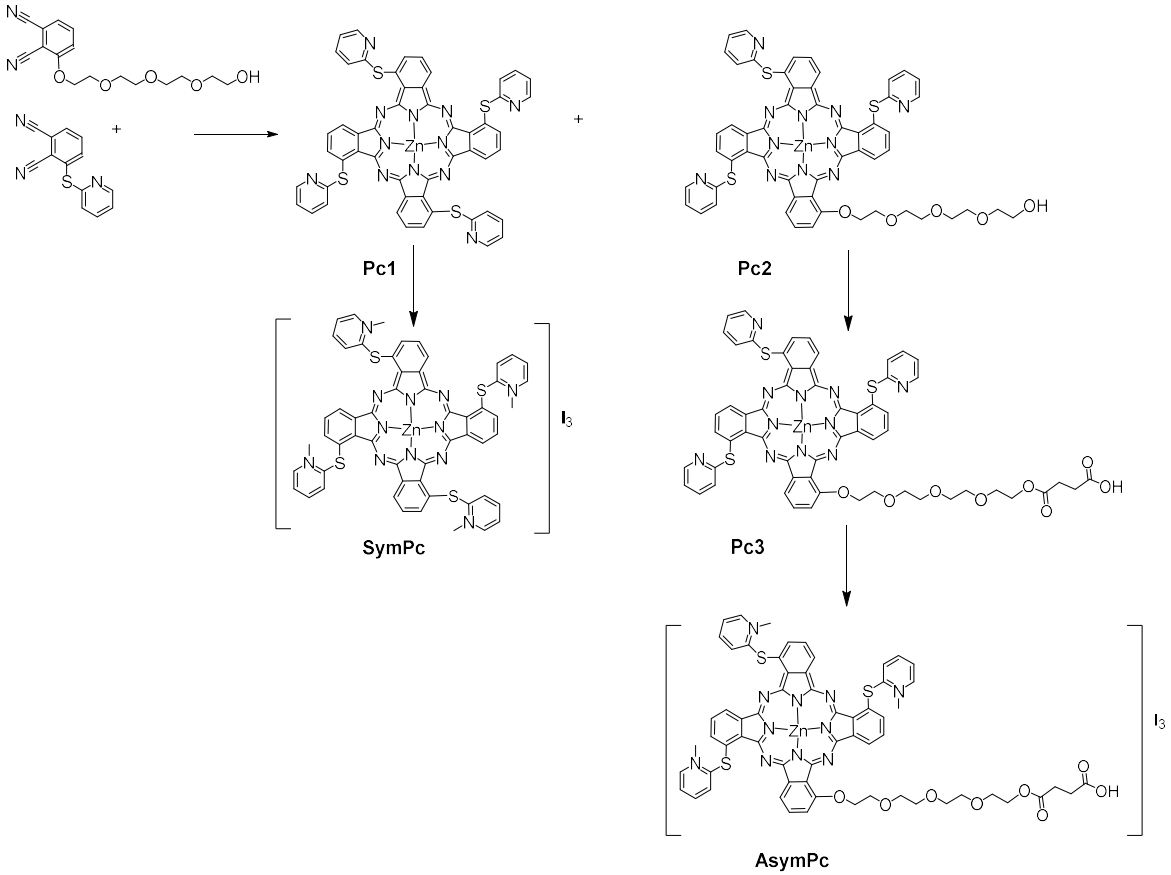
Inhalt

1. Synthesis



Scheme S1*. Synthetic pathway towards SymPc and AsymPc.*

Pc1 and **Pc2** were synthesized as described previously.[1]

1.1 Synthesis of SymPc

Pc1 (53.5 mg, 0.05 mmol, 1.00 eq.) was dissolved in DMF (ca 1 mL) and MeI was added in excess. The reaction was stirred at 50◦C overnight (18h). DCM (200 mL) was added and stirred for 1 h at room temperature. The green solid was collected. Molecular Formula: $C_{56}H_{40}N_{12}S_4Zn$ Yield: 57.6 mg, 0.05 mmol, 100% FT-MS (CH_3CN/H_2O):$[M]^{4+}$: calc.: m/z = 268.04128, found: m/z = 268.04120; $[M+I]^{3+}$: calc.: m/z = 399.69005, found: m/z = 399.69008; $[M+2I]^{2+}$: calc.: m/z = 662.98758, found: m/z = 662.98808. ^{1}H-NMR (DMSO−d6, 400 MHz, 300 K): 9.42-7.60 (m, 28 H, H-aromatic), 5.03-4.33 (m, 12 H).

1.2 Synthesis of Pc3

Pc2 (57.5 mg, 0.05 mmol, 1.00 eq.) and succinic anhydride (8.3 mg, 0.08 mmol, 1.60 eq.) were dissolved in DMF (10 mL) and heated to 50 ◦C. Molecular Formula: $C_{59}H_{45}N_{11}O_8S_3Zn$ 30 Yield: 60.0 mg, 0.05 mmol, 100% MALDI-TOF-MS (DCTB-$CHCl_3$):[M]: calc.: m/z = 1096.19 , found: m/z = 1196.06.

1.3 Synthesis of AsymPc

Pc3 (57.1 mg, 0.05 mmol, 1.00 eq.) was dissolved in DMF (as little as possible) and MeI was added in excess. The reaction was stirred at 50 ◦C over night (18h). DCM (200 mL) was added and stirred for 1 h at room temperature. The green solid was collected. Molecular Formula: $C_{62}H_{54}N_{11}O_8S_3Zn$ Yield: 57.6 mg, 0.05 mmol, 100% FT-MS (CH_3CN/H_2O):

[1]Galstyan, A.; Riehemann, K.; Schä Fers Acd, M.; Faust, A.; Schäfers, M.; Faust, A. A Combined Experimental and Computational Study of the Substituent Effect on the Photodynamic Efficacy of Amphiphilic Zn(II)Phthalocyanines. *J. Mater. Chem. B* **2016**, *4* (4), 5683–5691..

$[M+I]^{3+}$: calc.: m/z = 380.08112, found: m/z = 380.08110; $[M+2I]^{2+}$: calc.: m/z = 633.57418, found: m/z = 633.57456; $[M+3I]^{+}$: calc.: m/z = 1394.05339, found: m/z = 1394.05440. ^{1}H-NMR (DMSO−d6 d6, 400 MHz, 300 K): δ (ppm) = 9.57-6.96 (m, 24 H, H-aromatic), 5.29-3.34 (m, 32 H, H-aliphatic).

2. Photophysical characterization

2.1 Absorption spectra

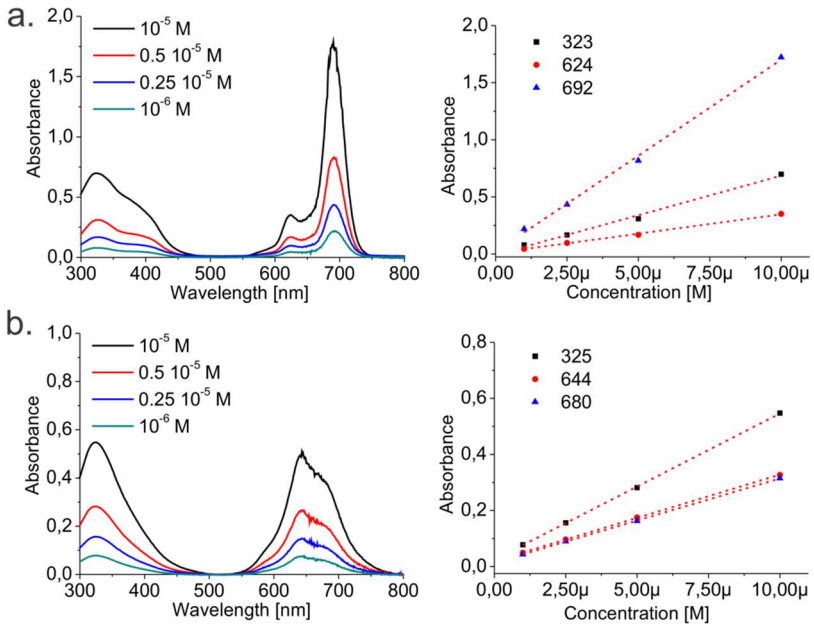


Figure S1. *UV-Vis absorption spectra of different SymPc concentrations (a) in DMF and (b) in H_2O and corresponding linear fits of absorption maxima.*

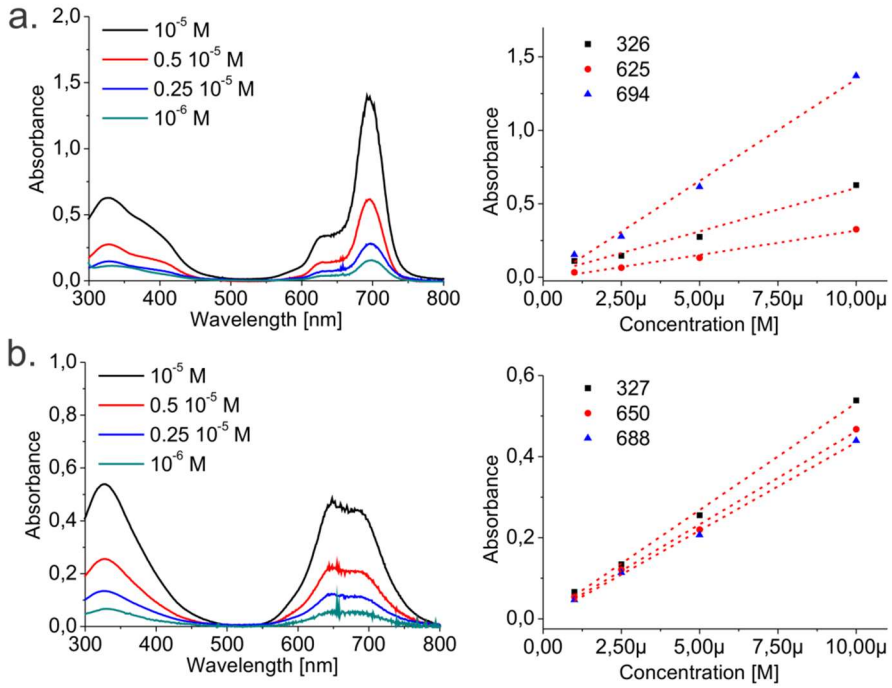


Figure S2. *UV-Vis absorption spectra of different AsymPc concentrations (a) in DMF and (b) in H_2O and corresponding linear fits of absorption maxima.*

2.2 Singlet oxygen quantum yields

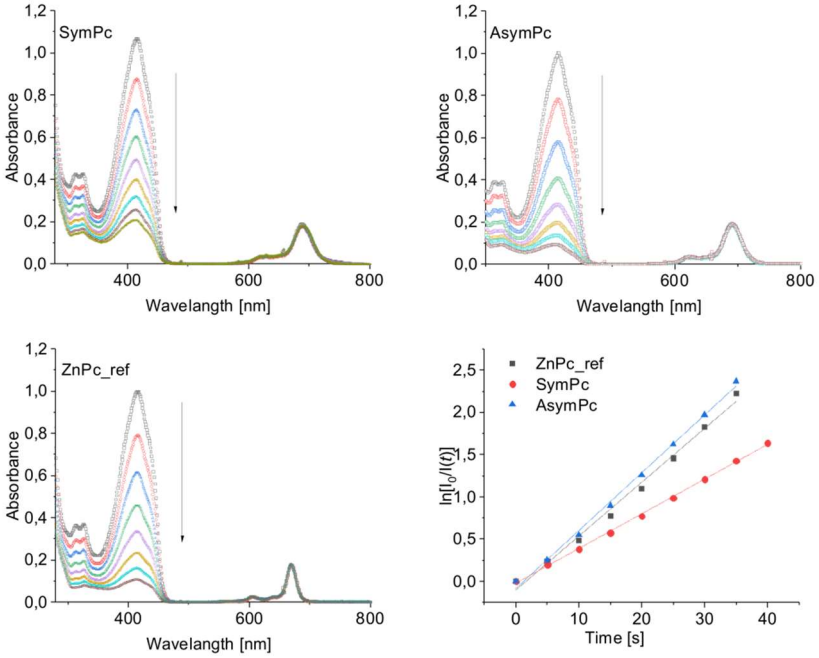


Figure S3. *Time-dependent decomposition of DPBF photosensitized by SymPc, AsymPc and unsubstituted ZnPc as reference in DMF upon irradiation with light from projector lamp filtered through a cut-off filter for λ > 610 nm and corresponding first-order plots.*

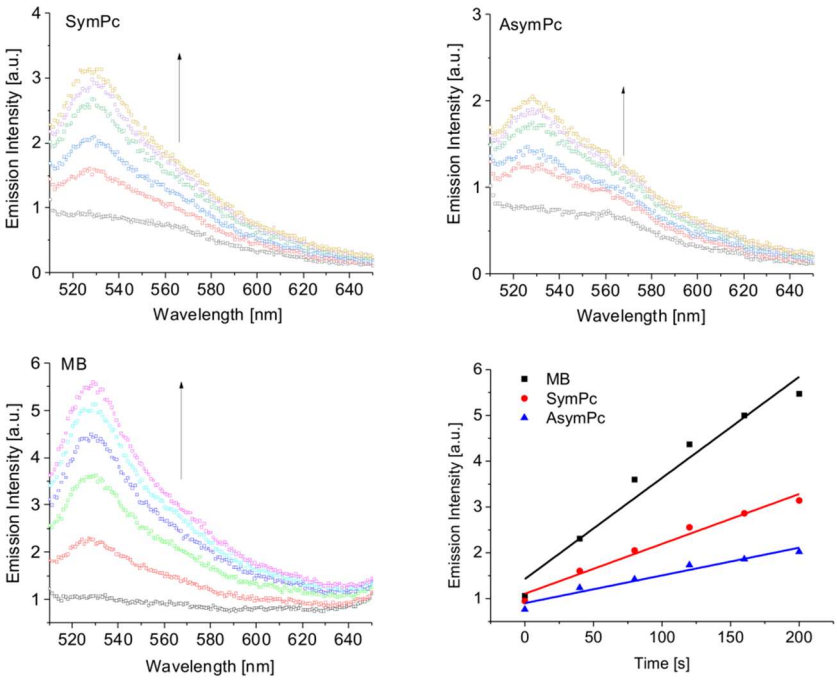


Figure S4. *Changes in the emission spectra of DCFDA photosensitized by SymPc, AsymPc and unsubstituted ZnPc as reference in H_2O upon irradiation with light from projector lamp filtered through a cut-off filter for λ > 610 nm and corresponding first-order plots.*

2.3 Evaluation of photosensitizers concentration in nanofibers

UV-Vis spectroscopy was used to determine the PS loading. To obtain a constant area of approximately 113 cm^2, samples were randomly cut from the mat at different locations using a 12 cm diameter hole punch. The samples were washed with 70% ethanol solution (1 x 1 mL) and water (3 x 1 mL) to remove unbound PS and then heated at 100°C for 1 h in a 1 mL DMF-H_2O 1:1 mixture in case of PVA-based NFs and in DMF for PAN and PCL based NFs.

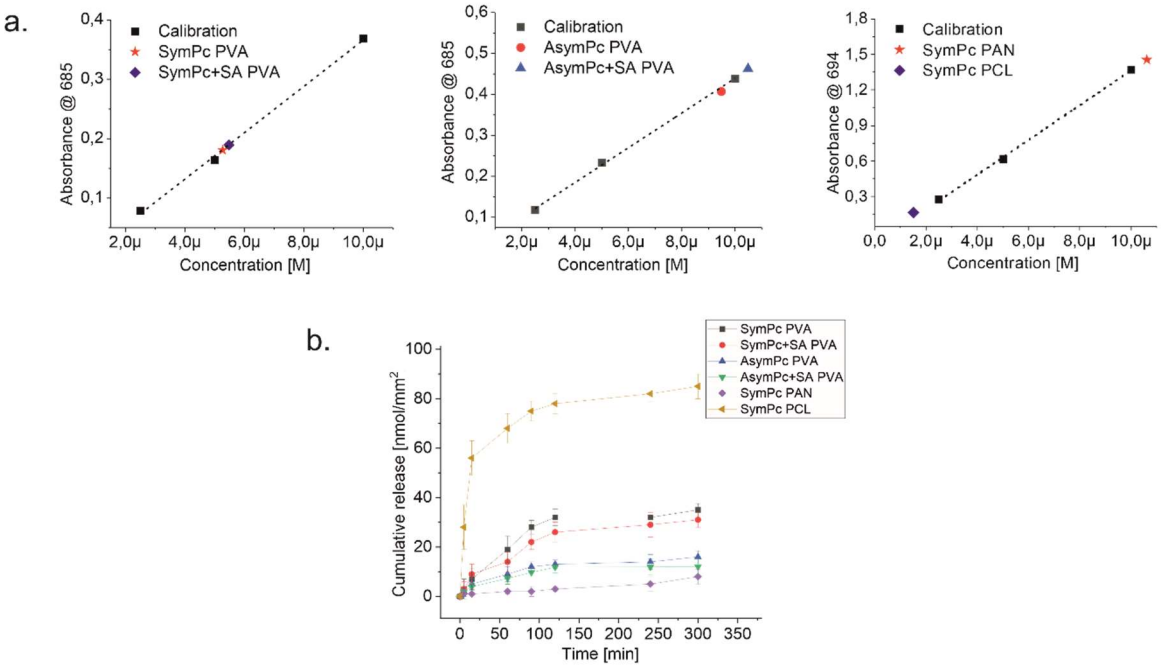


Figure S5. *a) Calibration curves for spectrophotometric UV-vis determination of PS concentration and absorbances of PSs found NFs after washing with 70% EtOH and H_2O, b) Release of PS from NFs in H_2O.*

2.4 Structural characterization of bair PVA, PAN and PCL nanofibers

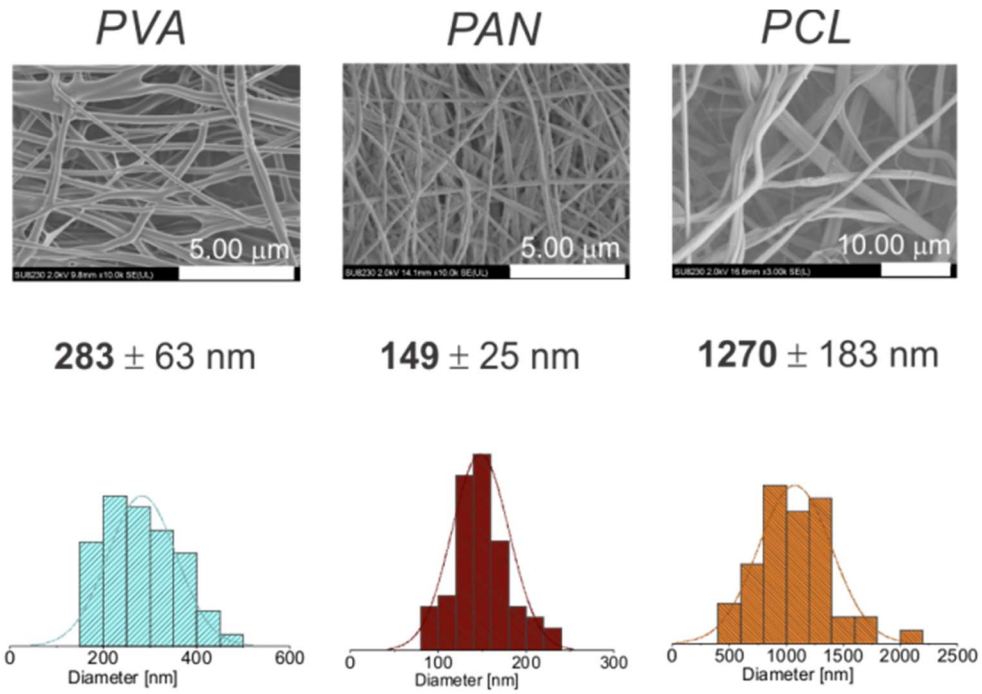


Figure S6. *SEM images and* fiber size distribution of bair PVA, PAN and PCL photosensitizers concentration in nanofibers.

3. Photobiological Studies

3.1 Viability of bacteria treated with SymPc and AsymPc

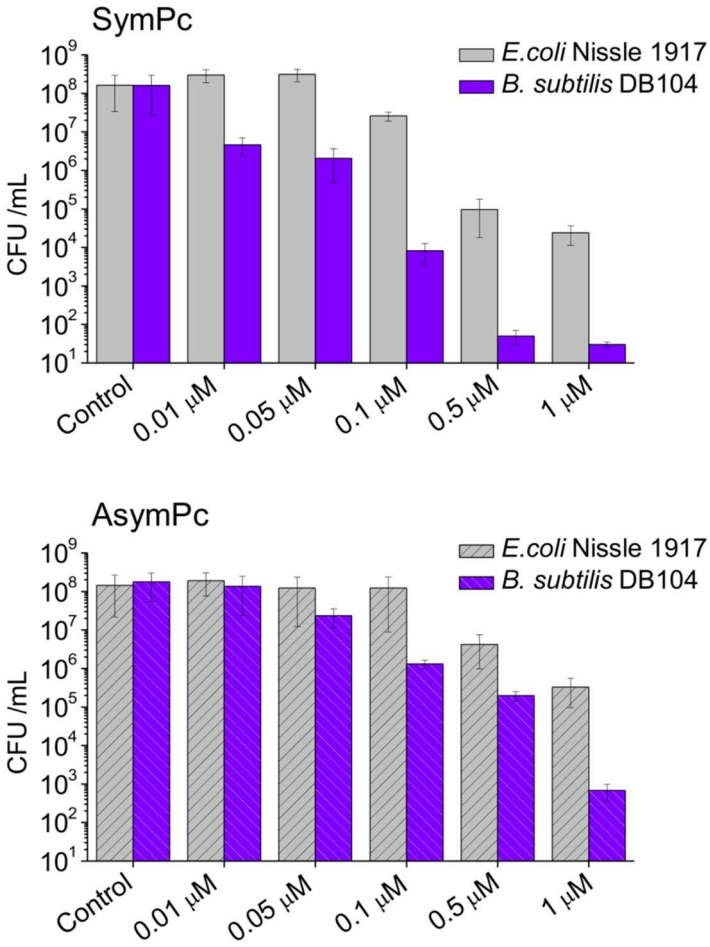


Figure S7. *Viability of B. subtilis DB104 and E. coli Nissle 1917 treated with corresponding amount of SymPc or AsymPc for15 min in dark and irradiation with total light dose of 9 J/cm^2.*

3.2 Determination of the viability of bacteria adhered to nanofibers

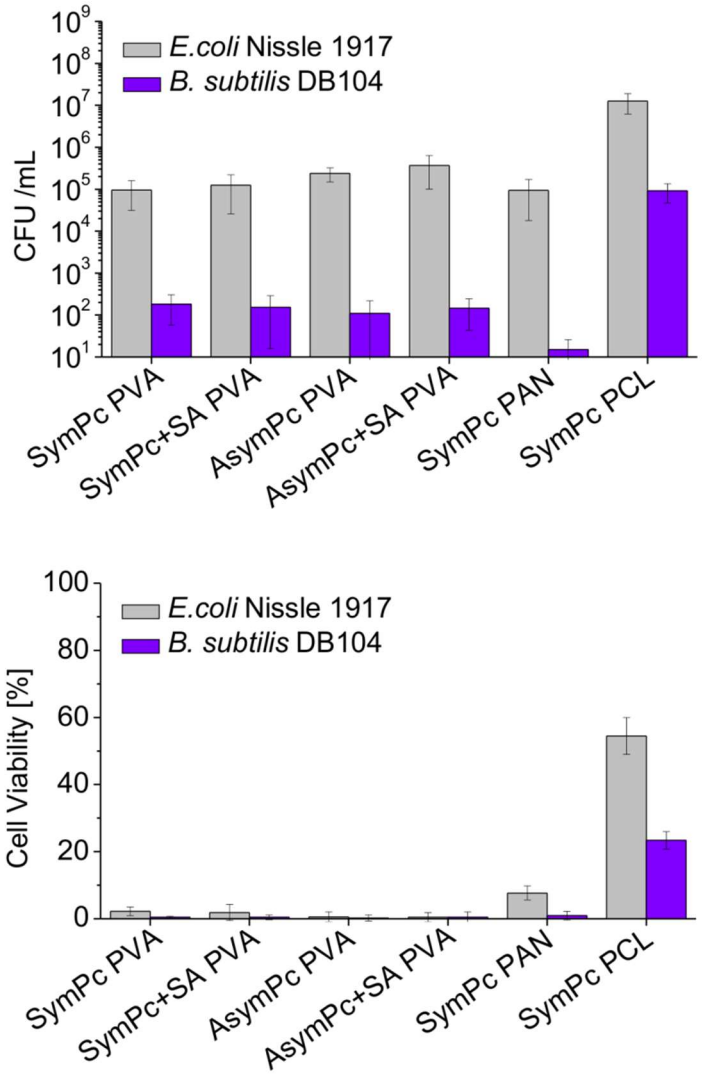


Figure S8. *Viability of B. subtilis DB104 and E. coli Nissle 1917 attached to the NFs (incubation 1h in dark) determined using CFU counting and XTT assay.*

3.3 Viability of bacteriophages treated with SymPc and AsymPc

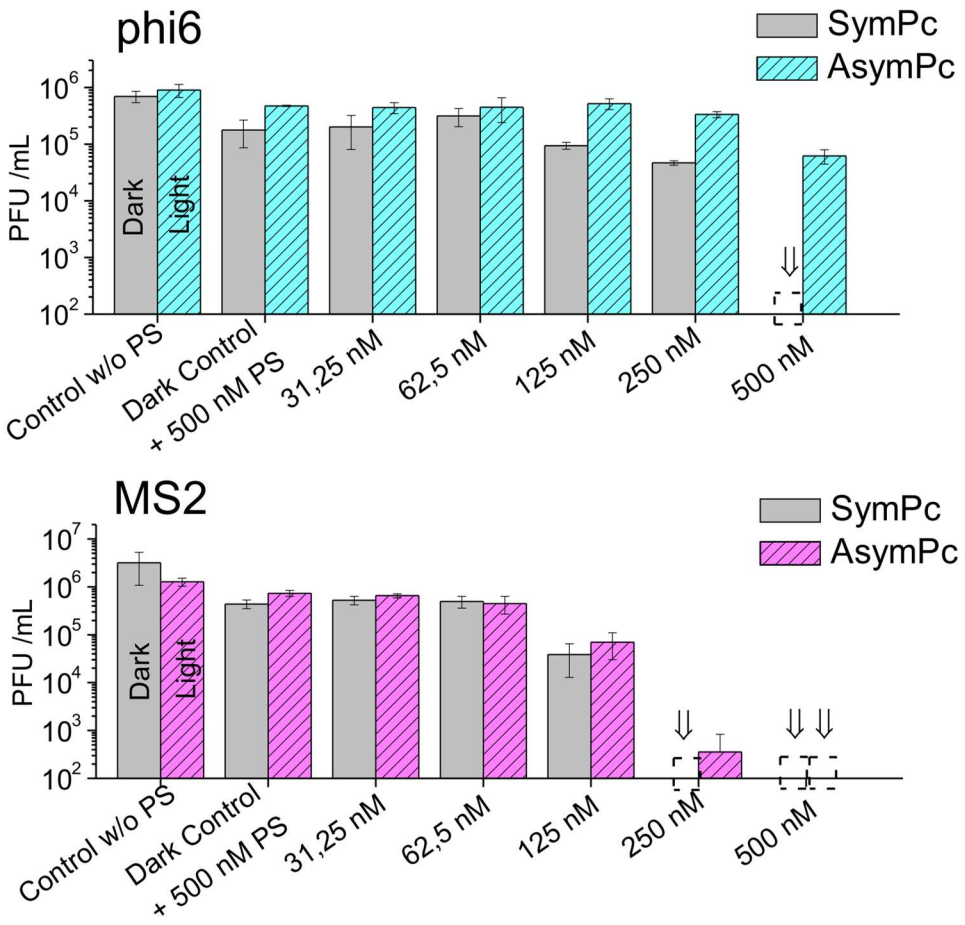


Figure S9. *Viability of phi6 and MS2 treated with corresponding amount of SymPc or AsymPc for15 min in dark and irradiation with total light dose of 6 J/cm^2.*

4. FT-IR and Mass Spectra

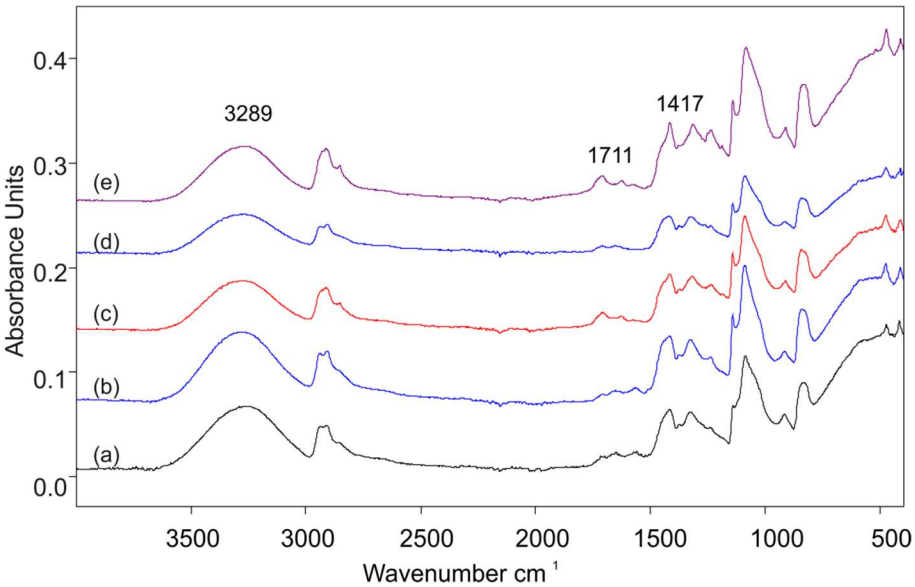


Figure S10. *FT-IR spectra of PVA (a), SymPc PVA (b), SymPc+SA PVA (c), AsymPc PVA (d) and AsymPc+SA PVA (e).*

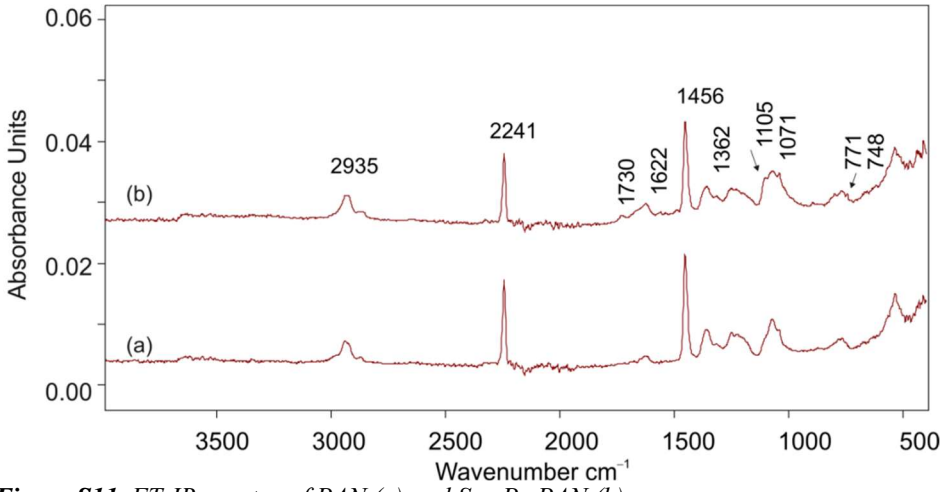


Figure S11. *FT-IR spectra of PAN (a) and SymPc PAN (b).*

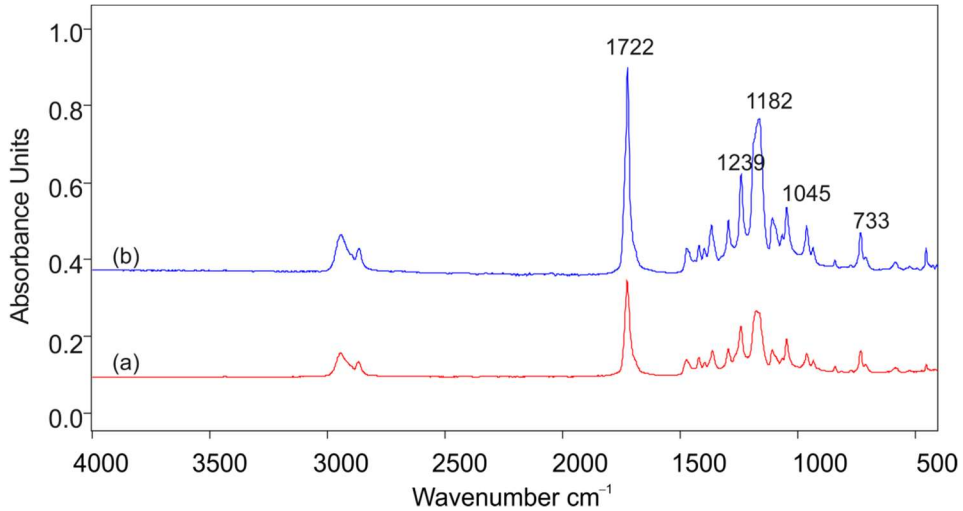


Figure S12. *FT-IR spectra of PCL (a) and SymPc PCL (b).*

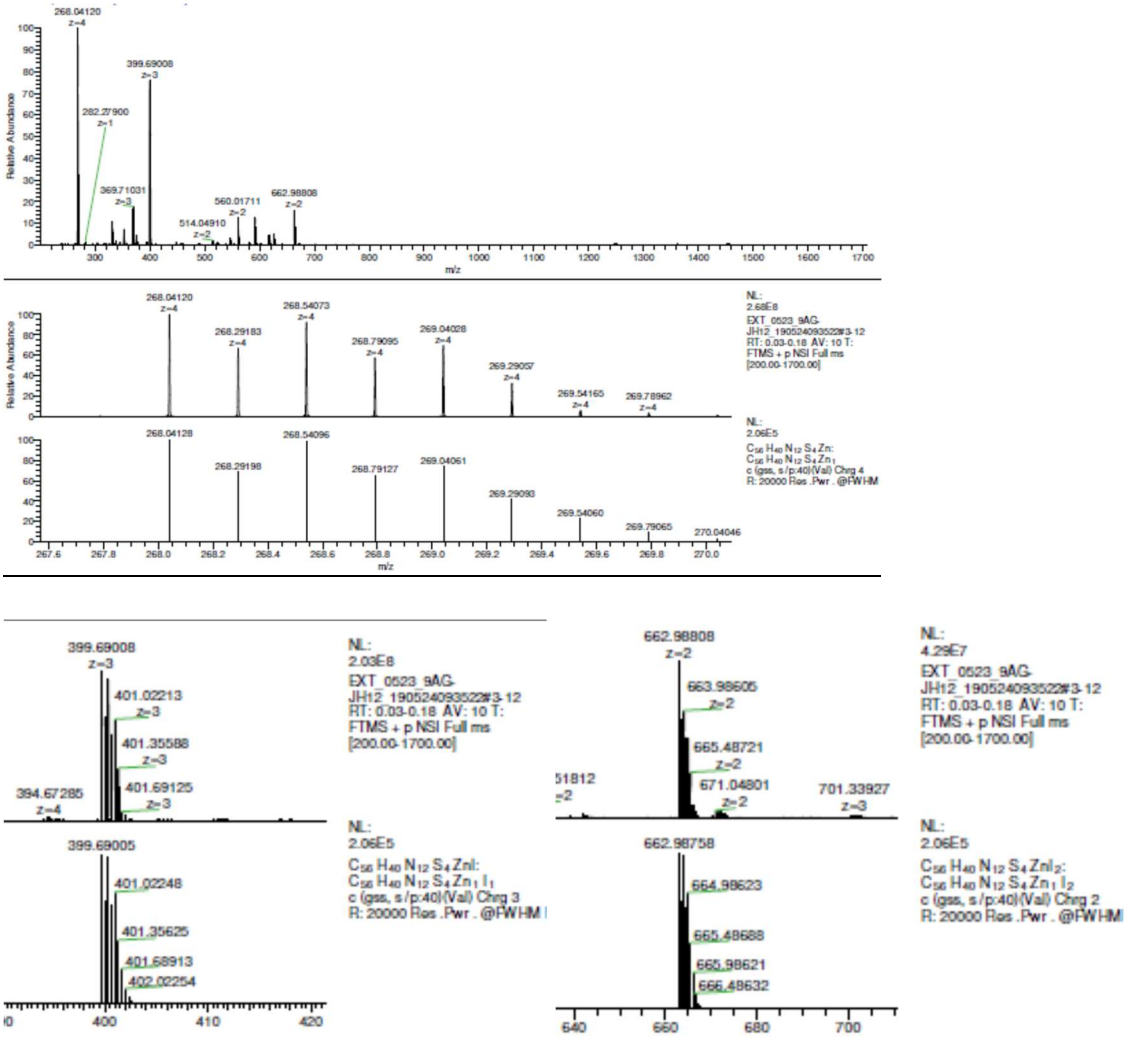


Figure S13. *Mass spectra of* ***SymPc***.

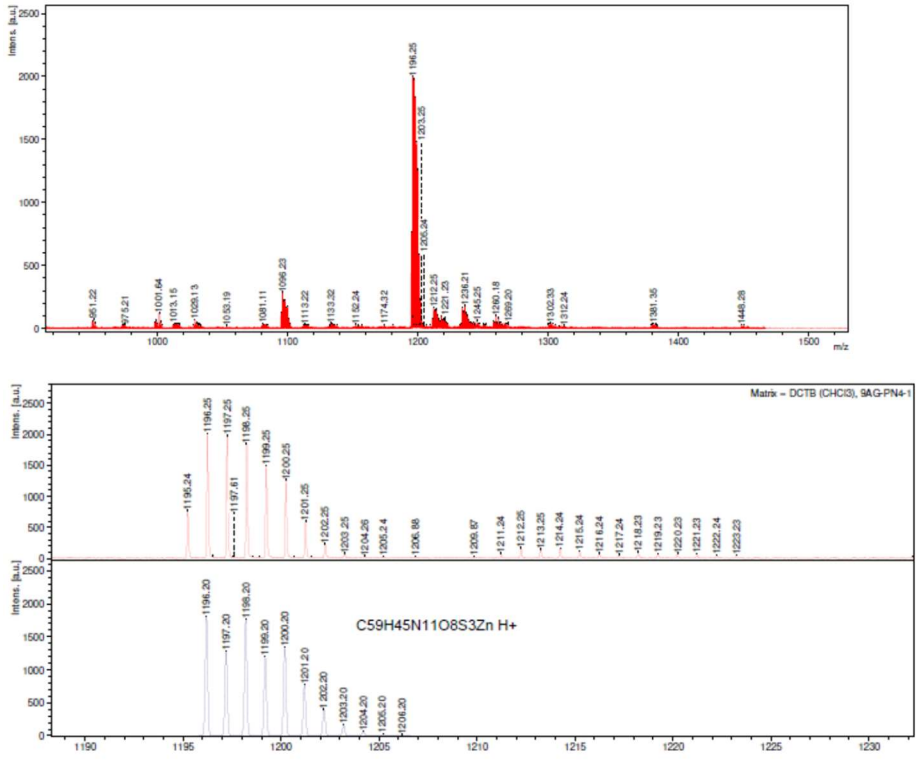


Figure S14. *Mass spectra of* ***Pc3***.

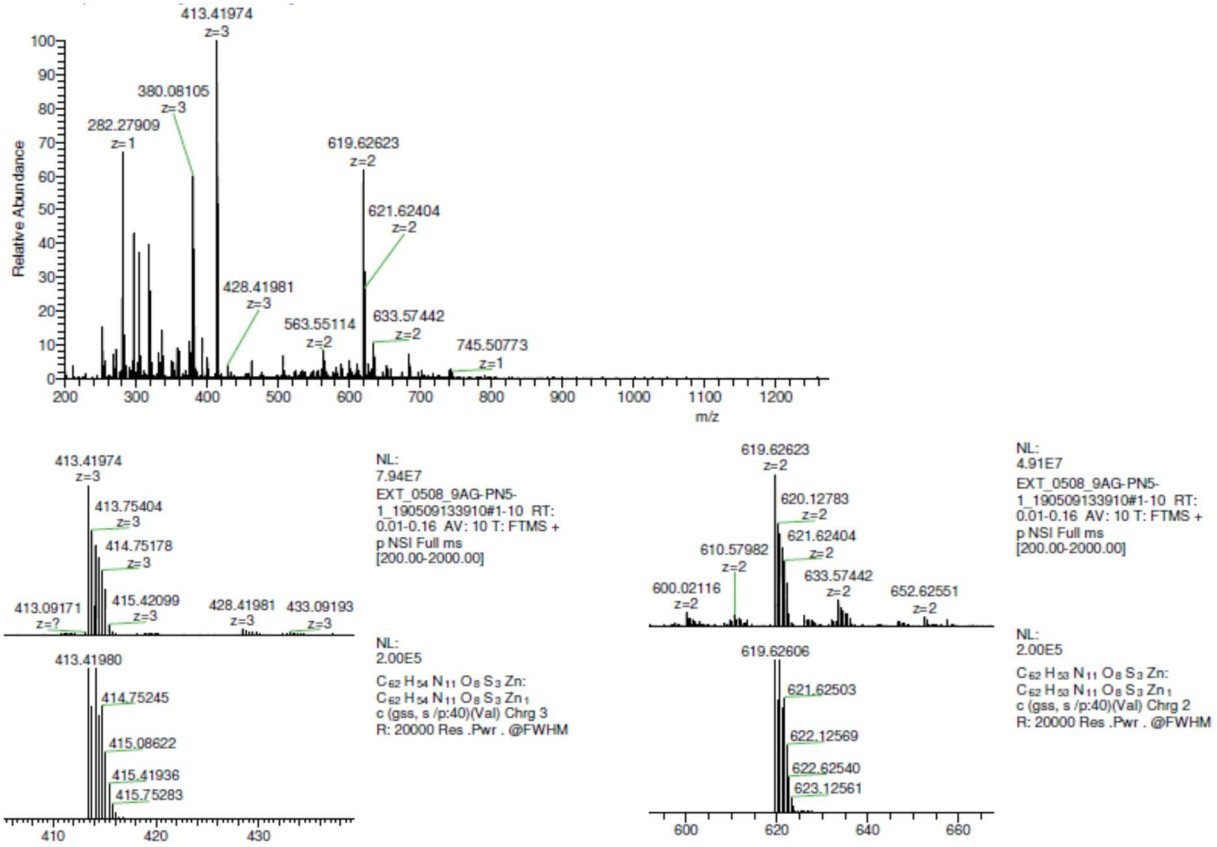


Figure S15. *Mass spectra of* ***AsymPc***.