Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

S1. Spectroscopic studies of standard porphyrins in diverse media

In order to perform the qualitative analysis of porphyrins synthesized after incubation of the bacterial cells with 5-ALA at different time periods, the fluorescence excitation and emission spectra of standard porphyrins were measured. The standard porphyrins included coproporphyrin I (CP I), uroporphyrin I (UP I) and protoporphyrin IX (PP IX). Identical quantities of the three porphyrins were examined in selected media, which involved solvents and bacterial cell suspensions diluted with PBS to compare the spectroscopic characteristics with samples from the fraction I, and the same suspensions diluted by adding HCl (a final concentration of 1.5 M) – to compare with those from the fraction II. Autofluorescence background of control samples was subtracted from all spectra before normalization.

Normalized fluorescence excitation and emission spectra of the three standard porphyrins in each medium are shown in Fig. S1. In PBS, all standard porphyrins possessed the broad Soret bands with traces of metalloporphyrins (Fig. S1 A,B). The peak positions of CP I and UP I in the fluorescence emission spectra were independent of an excitation wavelength, and both the corresponding spectra showed the highest intensity under excitation at 390 nm. It is notable that the fluorescence emission spectrum of UP I is red-shifted versus that of CP I. PP IX yielded the negligible fluorescence intensity in PBS, in consistence with expectations for a high degree of aggregation. The addition of HCl to the samples changed the general shape of the spectra. The fluorescence emission of porphyrins was stronger under excitation at 405 nm than that at 390 nm in comparison with the emission spectra in PBS (as indicated by fluorescence intensity ratios shown in the legend). In acidic media all spectra of standard porphyrins exhibited the sharp Soret bands and characteristic porphyrin fluorescence emission bands, which were blue-shifted in comparison to those in PBS, in consistence with spectroscopic properties typical for a monomeric dicationic form.

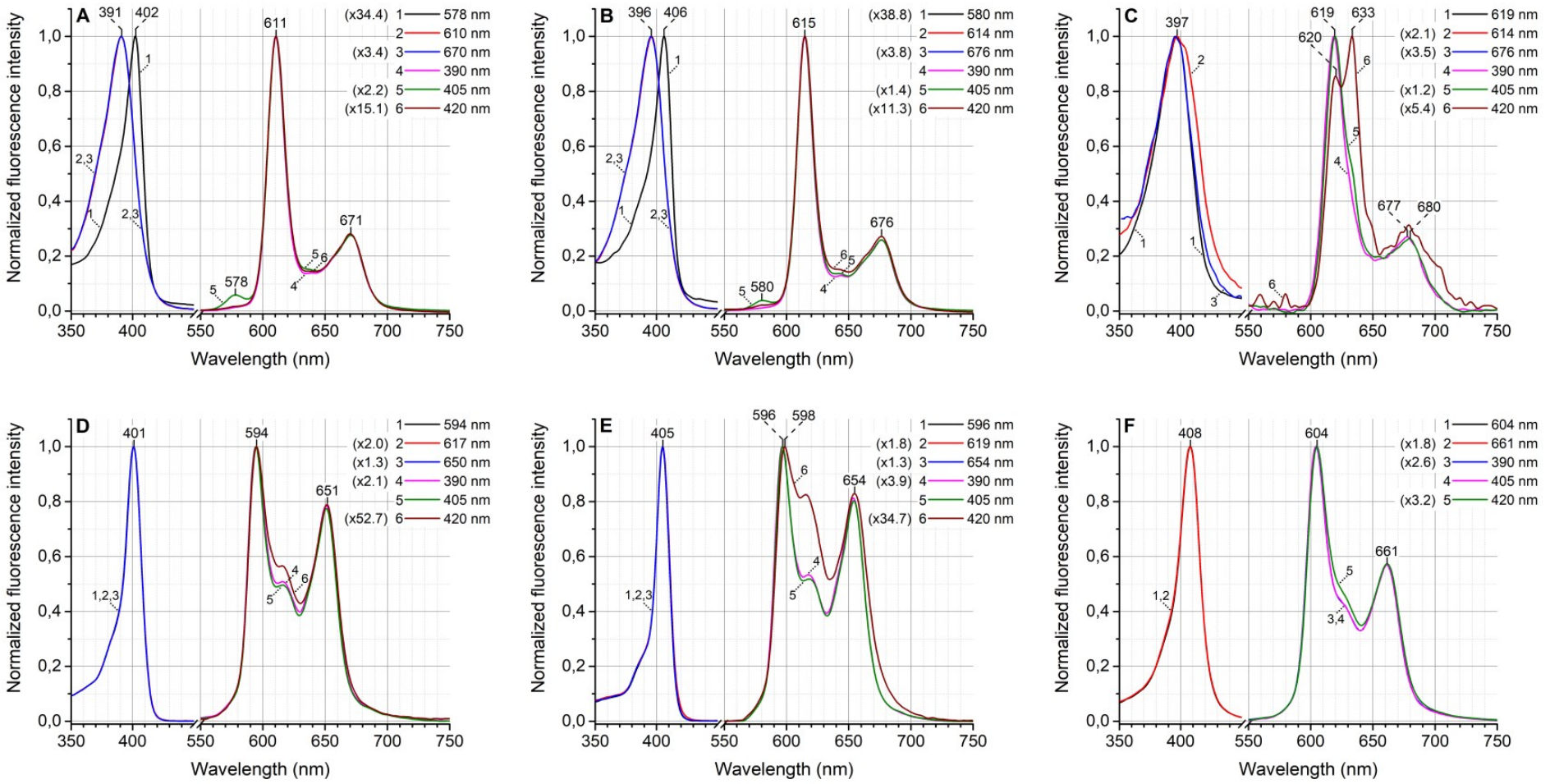

Fig. S1. Normalized fluorescence excitation and emission spectra observed in the samples of the bacterial cell suspensions after incubation of the bacterial culture with standard coproporphyrin I (A,D), uroporphyrin I (B,E), protoporphyrin IX (C, F) (c = 2 · 10^{-6} M) in PBS (A,B,C) and in PBS with 1.5 M HCl (D,E,F). Wavelengths used for excitation and registration of corresponding spectra are denoted in the legend.

S2. Modeling of fluorescence spectra of porphyrins

The fluorescence spectra of porphyrins being measured in the samples of both resuspended bacterial cells and supernatants after two incubation periods were further modeled using the fluorescence spectra of standard porphyrins that had been recorded under the same conditions. The modeling of the same sample's spectra that had been recorded at two excitation wavelengths was made in the following way: the corresponding fluorescence spectra of each standard porphyrin were used for parallel fitting at the ratio of intensities being calculated from the fluorescence excitation spectrum at the same two wavelengths that were used for the fluorescence excitation of the samples. The residual spectrum was obtained for each excitation wavelength by subtracting the sum of the spectra of standard porphyrins from the registered spectrum.

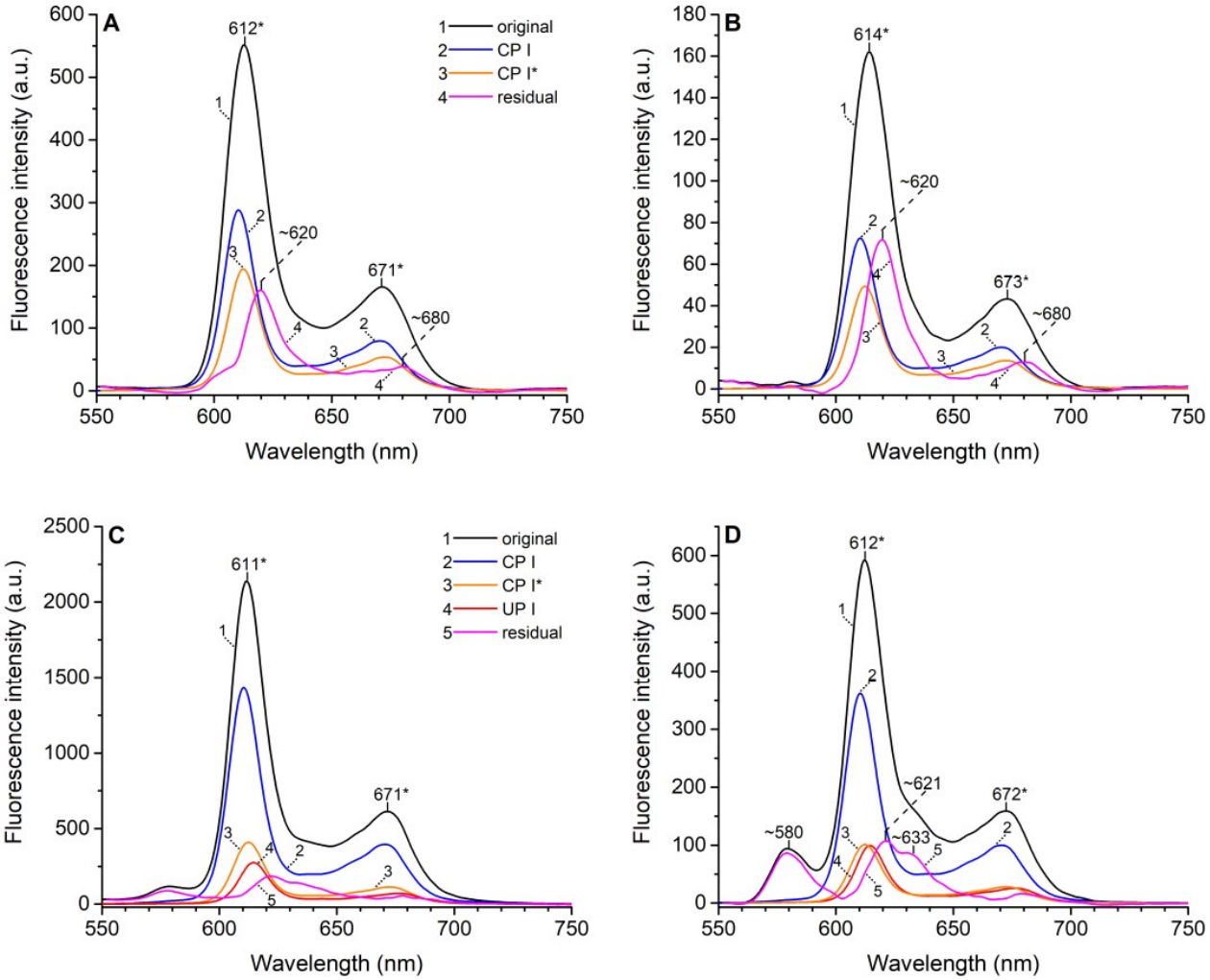

Fig. S2. Modeling of fluorescence emission spectra detected in the samples of the supernatants after incubation of the bacterial culture with 5-ALA (fraction I) for 4 h (A,B) and 20 h (C,D) in PBS; excitation at 395 nm – (A,C) and at 410 nm – (B,D).

Since the modeling of the spectra using the fluorescence spectrum of standard coproporphyrin I does not yielded the accurate correspondence, the spectrum was deliberately shifted for 2 nm to resemble the spectral position of the coproporphyrin isomer III[S1] and was marked as CP I*. The value of the fluorescence intensity ratio for it at the used excitation wavelengths was left the same as that obtained for coproporphyrin isomer I.

S1. Melø, T. B. & Reisaeter, G. Photodestruction of endogenous porphyrins in relation to cellular inactivation of Propionibacterium acnes. *Z. Naturforschung C J. Biosci.* **41,** 867–872 (1986).

S3. Evaluation of porphyrins accumulation

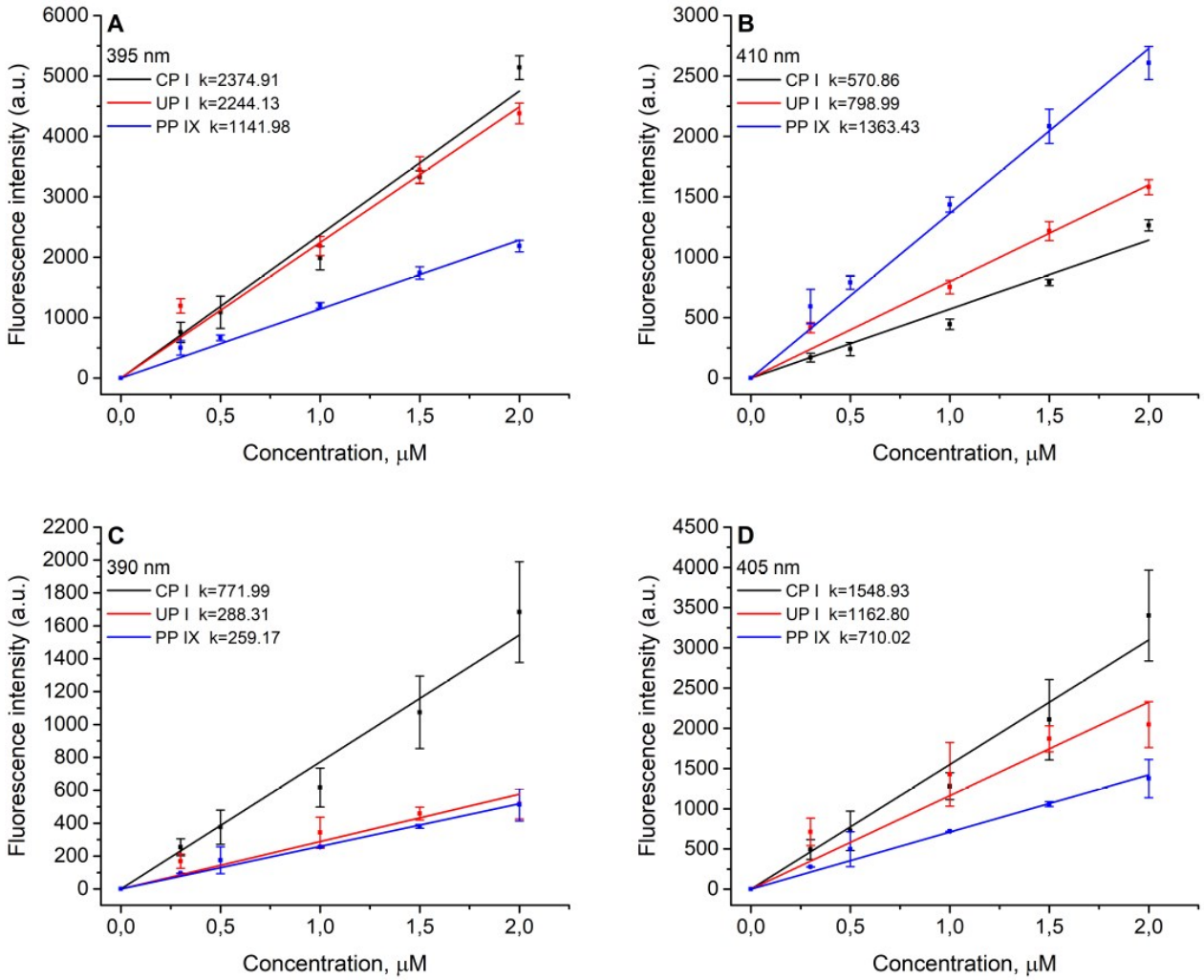

Fig. S3. The dependence of the fluorescence intensity on the concentrations of standard porphyrins being obtained in the bacterial cell suspensions of the fraction I (A,B) and the fraction II (C,D). The excitation wavelengths and linear regression coefficients are indicated in the legend. Error bars show SD.

The small volumes of stock solutions of standard porphyrins were added into the bacterial cell suspensions to obtain five different concentrations, in triplicate, and then the samples were incubated for 30 min at 37°C. The additional SDS (to get 4 % v/v) was supplemented in the case of samples with protoporphyrin IX. The Figure S3 shows the intensity values of the major fluorescence band for both fractions, which were measured using two excitation wavelengths. The linear regression fit was made using OriginPro 9.1 software.

Table S1. The calculated concentrations of standard porphyrins present in the bacterial cells and the supernatants for both fractions*

Standard porphyrins	Fraction I							
	Cells				Supernatant			
	4 h		20 h		4 h		20 h	
	395 nm	410 nm	395 nm	410 nm	395 nm	410 nm	395 nm	405 nm
UP I	9.30 ± 0.43 nM	9.24 ± 0.41 nM	6.35 ± 0.29 nM	6.31 ± 0.28 nM	-	-	122.55 ± 5.72 nM	124.27 ± 5.56 nM
CP I	6.39 ± 0.28 nM	6.23 ± 0.36 nM	3.84 ± 0.17 nM	3.74 ± 0.22 nM	121.30 ± 5.26 nM	126.84 ± 7.32 nM	603.71 ± 26.20 nM	634.24 ± 36.61 nM
PP IX	Not performed	48.97 ± 1.55 nM	Not performed	Not performed	-	-	Not performed	Not performed
	Fraction II							
	Cells				Supernatant			
	4 h		20 h		4 h		20 h	
	390 nm	405 nm	390 nm	405 nm	390 nm	405 nm	390 nm	405 nm
UP I	8.18 ± 0,67 nM	8.56 ± 0.81 nM	122.51 ± 10.02 nM	128.10 ± 12.12 nM	-	-	88.09 ± 7.21 nM	92.04 ± 8.71 nM
CP I	Not performed	Not performed	Not performed	Not performed	Not performed	9.37 ± 0.48 nM	Not performed	37.54 ± 1.92 nM
PP IX	11.62 ± 0.38 nM	11.70 ± 0.45 nM	-	-	-	-	-	-

* - The calculation is based on the spectral modeling and the obtained calibration data (Fig. S3).