Phosphinatophenylporphyrins tailored for high photodynamic efficacy

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Content

Figure S1-S9. NMR spectra of 2\textsubscript{a-c}.
Figure S10-S12. Electrospray ionization-mass spectra of 2\textsubscript{a-c}.
Figure S13-S15. Electrospray ionization-mass spectra of 3\textsubscript{a-c}.
Figure S16. Absorption spectra of 3\textsubscript{a-c} in PBS.
Figure S17. Titration of TPPS and 3\textsubscript{a-c} with HSA in PBS.
Figure S18. Kinetics of the porphyrins triplet states of 3\textsubscript{a-c}.
Figure S19. Phosphorescence of O\textsubscript{2}($\Delta_g$) produced by 3\textsubscript{a-c} and TPPS in D\textsubscript{2}O.
Figure S20. Flow cytometry histograms.
Table S1. IC\textsubscript{50} values of 3\textsubscript{a-c} and TPPS for HeLa and MRC-5 cells irradiated with a 150 W halogen lamp or 525 nm light.
Figure S1. $^1$H NMR (CDCl$_3$) spectrum of compound 2a.

Figure S2. $^{31}$P{H} NMR (CDCl$_3$) spectrum of compound 2a.
Figure S3. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl$_3$) spectrum of compound 2a.

Figure S4. $^1\text{H}$ NMR (CDCl$_3$) spectrum of compound 2b.
Figure S5. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl$_3$) spectrum of compound 2b.

Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl$_3$) spectrum of compound 2b.
Figure S7. $^1$H NMR (CDCl$_3$) spectrum of compound 2c.

Figure S8. $^{31}$P{$^1$H} NMR (CDCl$_3$) spectrum of compound 2c.
Figure S9. $^{13}$C{$^1$H} NMR (CDCl$_3$) spectrum of compound 2c.
Figure S10. Electrospray ionization-mass spectrum of 2a in the positive mode (top) and high-resolution mass spectrum (bottom).
Figure S11. Electrospray ionization-mass spectrum of 2b in the positive mode (top) and high-resolution mass spectrum (bottom).
Figure S12. Electrospray ionization-mass spectrum of 2c in the positive mode (top) and high-resolution mass spectrum (bottom).
Figure S13. Electrospray ionization-mass spectrum of 3a in the positive mode (top) and high-resolution mass spectrum (bottom).
Figure S14. Electrospray ionization-mass spectrum of 3b in the positive mode (top) and high-resolution mass spectrum (bottom).
Figure S15. Electrospray ionization-mass spectrum of 3c in the positive mode (top) and high-resolution mass spectrum (bottom).
Figure S16. Absorption spectra of 3a, 3b and 3c in PBS.

![Absorption Spectra](image)

Figure S17. Titration of TPPS and 3a-c with HSA in PBS: A) Changes of the Soret bands of porphyrins after addition of HSA; B) Difference absorption spectra; C) Corresponding binding isotherms at 422 nm. Arrows indicate absorption changes after the addition of HSA.

In a simple binding equilibrium assuming 1:1 stoichiometry, the relationship between the observed absorption changes and experimental parameters is as follows:

\[
\Delta A = \frac{\Delta A_{\text{max}} K_b [\text{HSA}]}{1 + K_b [\text{HSA}]},
\]

where \( \Delta A \) is the absorbance change after the addition of HSA at a selected wavelength, \( \Delta A_{\text{max}} \) is the maximum absorbance change, i.e., all porphyrin molecules are bound to HSA, \( K_b \) is the binding constant, and [HSA] is the equilibrium molar concentration of free HSA given by the equation:

\[
[HSA] = \frac{(c_{\text{HSA}} K_b - c_{\text{porph}} K_b - 1)/2K_b + \sqrt{(c_{\text{porph}} K_b - c_{\text{HSA}} K_b + 1)^2 + 4 c_{\text{HSA}} K_b}}{2K_b},
\]

where \( c_{\text{HSA}} \) is the total HSA concentration and \( c_{\text{porph}} \) is the total porphyrin concentration.

A nonlinear fit to the binding isotherms affords binding constant \( K_b \). The estimated error is 15%.

Figure S18. Kinetics of the porphyrins triplet states of 3a-c monitored by transient absorption at 460 nm in oxygen-, air- and argon-saturated PBS. Excited at 420 nm.
Figure S19. Phosphorescence of $\text{O}_2(\Delta_g)$ produced by 3a-c and TPPS in D$_2$O after excitation at 420 nm (solutions with matched absorbance, $A = 0.400$). The sharp signal at the beginning of kinetic traces is due to porphyrin short-lived fluorescence (fluorescence lifetime of $\sim$10 ns). Red lines represent single exponential fits to experimental data.
Figure S20. Flow cytometry histograms: (A) HeLa cells incubated with 0.625, 1.25, 2.5, 5 or 10 µM 3c for 24 h (darkening tones of green); (B) HeLa cells incubated with 0.625µM 3c for 0, 2, 18 or 24 h (from light green to dark green). (C) HeLa cells incubated with porphyrins 3a (grey), 3b (orange), 3c (green), TPPS (red) for 24 hours (porphyrins concentrations are 1.25 µM). Black color is a control.
Table S1. IC\textsubscript{50} values of 3a-c and TPPS for HeLa and MRC-5 cells irradiated with a 150 W halogen lamp (45 mW cm\textsuperscript{-2}) or 525 nm light (9 mW cm\textsuperscript{-2}).

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