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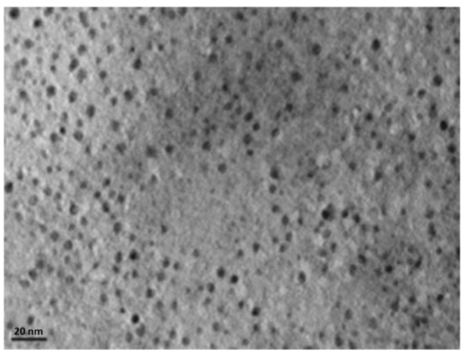
Electronic Supplementary Information

Enhanced Photodynamic Selectivity of Nano-Silica-Attached Porphyrins Against Breast Cancer Cells

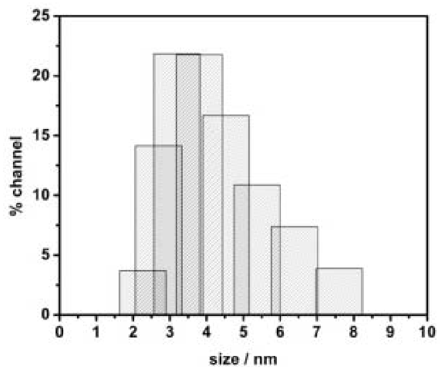
Wenbing Li, Wentong Lu, Zhen Fan, Xianchun Zhu, Aisha Reed, Brandon Newton, Yazhou Zhang, Shavelle Courtney, Papireddy T. Tiyyagura, Shufang Li, Ebonie Butler, Hongtao Yu, Paresh C. Ray and Ruomei Gao*

Department of Chemistry and Biochemistry, Jackson State University, Jackson Mississippi 39217

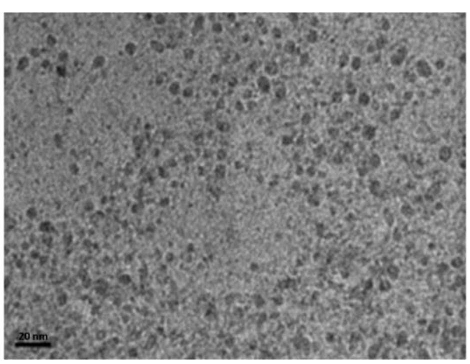
Nanoparticle size measurements



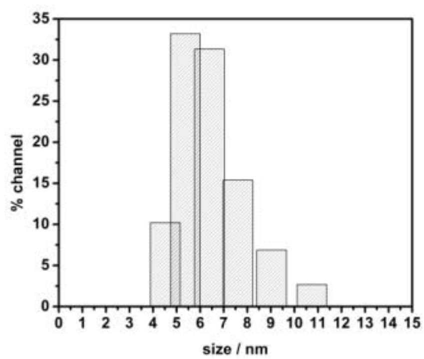
(a)



(b)



(c)



(d)

Figure S1. TEM images and nanoparticle size analysis for SiO_2 (a, b) and SiO_2-TMPyP (c, d)

Calculation of SiO_2 nanoparticle concentration

SiO_2 molarity is reported in terms of SiO_2 nanoparticles (C_{SiO2}) to better reflect experimental conditions. The nanoparticle concentration is calculated according to Eq. 1, using a SiO_2 density (d_{SiO2}, g/cm^3) of 2.6 g/cm^3 and an average diameter (ϕ_{SiO2}, nm) of 4.0 nm.

$$C_{SiO_2} = \frac{\dfrac{C_{SiO_2,\,g/L}}{d_{SiO_2,\,g/cm^3}} \Big/ \dfrac{4}{3}\pi\left(\dfrac{\phi_{SiO_2,\,nm}}{2}\times 1\times 10^{-7}\right)^3}{6.02\times 10^{23}} \qquad (1)$$

Adsorption of TMPyP onto SiO_2 nanoparticles.

The absorbance spectra and calibration curve for TMPyP loaded onto SiO_2 nanoparticles are shown in Figure S2. An average of 6.0 nm for SiO_2-TMPyP was used for calculations in this paper. All of the experiments were carried out at ambient temperature. In a typical preparation, TMPyP (2.5×10^{-5} M) was loaded onto SiO_2 (1.8 g/L or 3.4×10^{-5} M in terms of particle concentration). The molar ratio of TMPyP over SiO_2 is estimated to be $2.5\times10^{-5}/3.4\times10^{-5}$ = 0.74. We therefore conclude that under our experimental conditions, an average of one TMPyP molecule was loaded per SiO_2 particle.

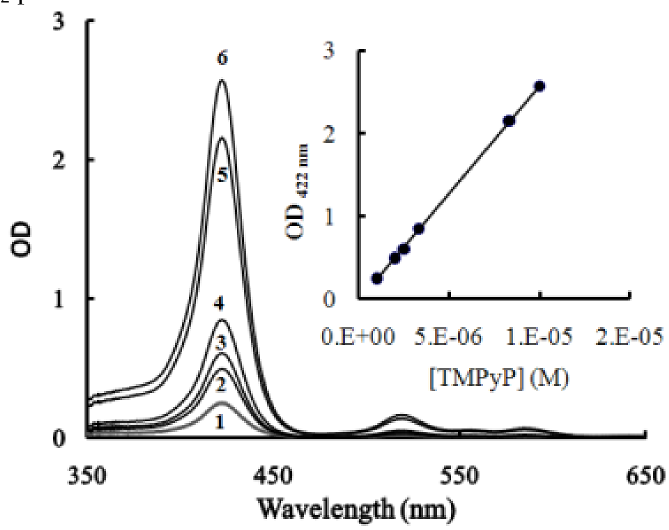


Figure S2. Absorption spectra and calibration curve of TMPyP adsorbed on SiO_2 nanoparticle (0.17 M) surface at pH 8. Spectra were measured against a pH 8 aqueous NaOH solution; 1-6: 1.0×10^{-6}, 2.0×10^{-6}, 2.5×10^{-6}, 3.3×10^{-6}, 8.3×10^{-6} and 1.0×10^{-5} M TMPyP, respectively. Insertion: calibration curve of absorbance at 426 nm vs. 1.0×10^{-6}-1.0×10^{-5} M TMPyP adsorbed on SiO_2 nanoparticles, giving an extinction coefficient of 2.3×10^5 M^{-1} cm^{-1}

Determination of bimolecular total quenching rate constants of $^1O_2$ removal (k_T) by Stern-Volmer analysis.

The k_T were determined by Stern-Volmer analysis for free TMPyP, SiO_2 and SiO_2-TMPyP nanoparticles at pH 8 and pH 6. Measurements were carried out in D_2O at an excitation wavelength of 532 nm using TSPP as a sensitizer. Our data indicated that the kinetics of $^1O_2$ luminescence decay at 1270 nm followed Stern-Volmer equation of $k = k_d + k_T[Q]$, where k is the observed first-order rate constant of $^1O_2$ decay after a laser pulse and k_d is the observed first-order solvent deactivation rate constant of $^1O_2$ in the absence of a quencher. Changes in the $^1O_2$ lifetime were observed with the addition of free TMPyP, SiO_2 and SiO_2-TMPyP nanoparticles to solutions. Stern-Volmer plots show a good linear correlation between k and quencher concentrations [Q]. k_T values could then be derived from slopes of the straight lines.

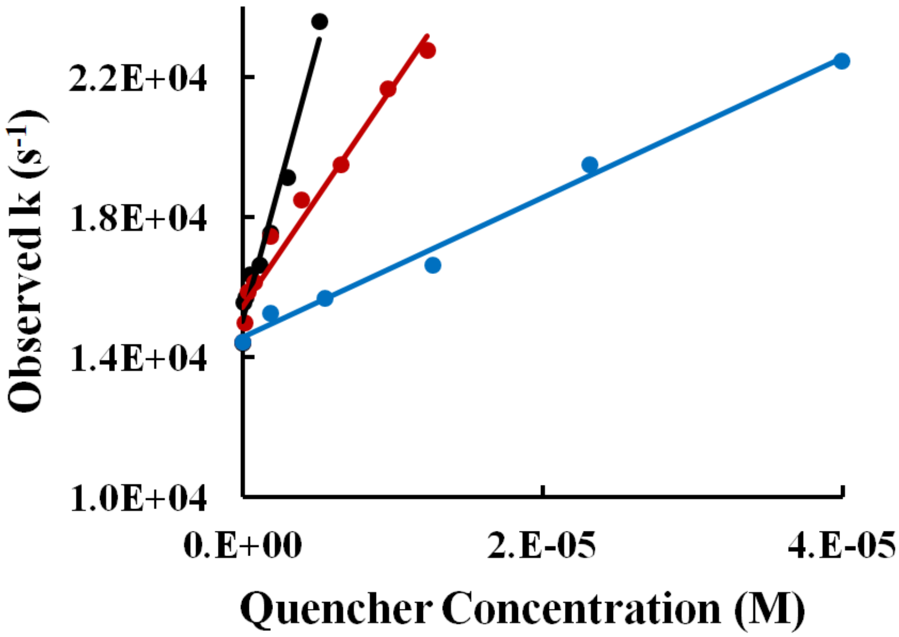


Figure S3. Stern-Volmer plots for the luminescence quenching of $^1O_2$ by SiO_2 nanoparticles (black dots), SiO_2-TMPyP (red dots) and free TMPyP (blue dots). Solid lines are theoretical simulation using linear least-square fitting method. The experiments were carried out at an excitation wavelength of 532 nm using *meso*-Tetra(4-sulfonatophenyl)porphine dihydrochloride (TSPP) as a sensitizer in pH 8 D_2O solutions.

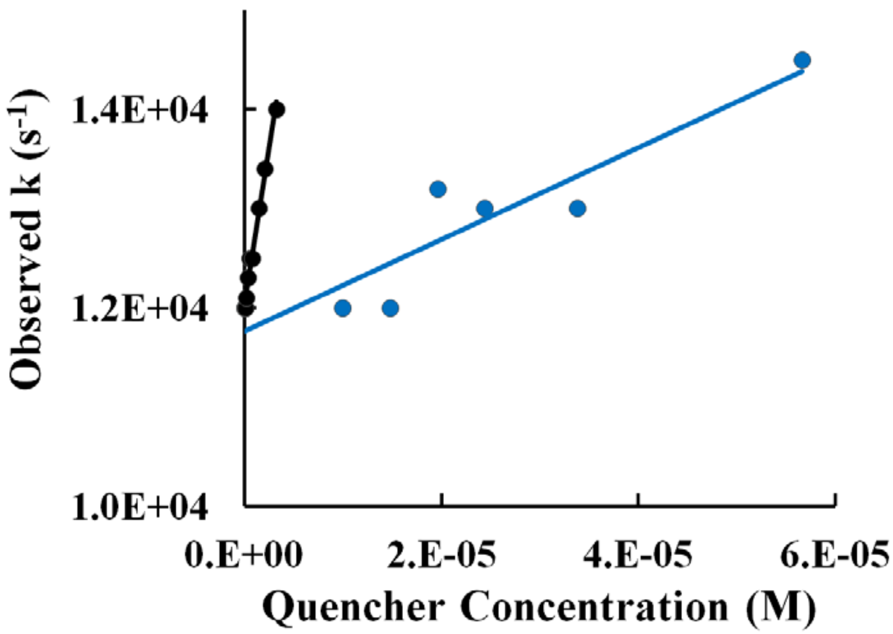


Figure S4. Stern-Volmer plots for the luminescence quenching of $^1O_2$ by SiO_2 nanoparticles (black dots) and free TMPyP (blue dots). Solid lines are theoretical simulation using linear least-square fitting method. The experiments were carried out at an excitation wavelength of 532 nm using *meso*-Tetra(4-sulfonatophenyl)porphine dihydrochloride (TSPP) as a sensitizer in pH 6.0 D_2O solutions.

MTT assay results for Figure 6:

	Exp. Trial #	**Sample 1** drak control cells only	**Sample 2** dark control cells+SiO2-TMPyP	**Sample 3** 20 min irradiation cells only	**Sample 4** 20 min irradiation cells+SiO2-TMPyP
pH 7.4	1.00	1.36	0.92	0.95	0.64
	2.00	0.71	0.70	0.86	0.48
	3.00	0.92	0.93	0.92	0.64
	Average	1.00	0.85	0.91	0.59
	S.D.	0.33	0.12	0.04	0.10
pH 6.0	1.00	1.14	0.65	0.72	0.31
	2.00	0.89	0.91	0.73	0.42
	3.00	0.96	0.82	0.93	0.32
	Average	1.00	0.79	0.79	0.35
	S.D.	0.13	0.13	0.12	0.06