Supplemental Information for
Suppress Singlet Oxygen Formation from 5,10,15,20-Tetrakis(4-sulfonatophenyl)porphyrin Using Polyion Complex Micelles

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Experimental Section

Materials
5,10,15,20-Tetrakis(4-sulfonatophenyl)porphyrin (TPPS) was purchased from Alfa Aesar China (Tianjin) and used as received. Diblock polyelectrolyte poly (N-methyl-2-vinylpyridinium iodide)-b-poly (ethylene oxide) (PMVP\textsubscript{41}-b-PEO\textsubscript{205}, Mw=19K, PDI=1.05, about 90% quaternized) used in this work was prepared according to previously reported procedures.\textsuperscript{1} Other regents and solvents were of analytical grade and used without further purification. Ultrapure water was used throughout the work.

Sample Preparation

The electrostatic micelles were obtained by simply mixing PMVP\textsubscript{41}-b-PEO\textsubscript{205} and TPPS solutions in neutral aqueous solution. The final charge ratio of the block polymer and TPPS were 4:1 to reach charge neutral mixing and the concentrations are kept constant (20 µM and 5 µM, respectively). After stirring, the resulting micelle solutions were stored in dark place for about 12 h at ambient temperature for further characterizations.

Characterization of PIC micelles

The PIC micelles were characterized by transmission electron microscopy (TEM, JEM-100CX, 100 kV) for FF-TEM images and FEI Tecnai G2 T20 (120 kV) for others, freeze-fracture apparatus (BalzersBAF400, -140°C), the UV-vis absorbance measurements were carried out on a UV-1800 SHIMADZU spectrophotometer in the range of 200–700 nm. A Hitachi F-7000 fluorescence spectrometer was used to measure the fluorescence emission of PIC micelles and TPPS solutions. \textsuperscript{1}H spectra were measured on a Bruker-500 MHz NMR spectrometer and recorded in D\textsubscript{2}O.

For FF-TEM measurements, in the freezing procedure, a drop of sample was placed on copper grids, the sample-loaded copper was frozen by plunging this into liquid nitrogen. Aggregate structures were believed to be preserved and "solidified" by this procedure. Fracturing and replication were carried out in a freeze-fracture apparatus (BalzersBAF400, Germany) at -140°C. Pt/C was deposited at an angle of 45° to shadow the replicas, and C was deposited at an angle of 90° to consolidate the replicas. The resulting replicas were examined in a JEM-100CX electron microscope. TEM micrographs were obtained with a JEM-100CX II transmission electron microscope (working voltage of 80–100 kV).
Fig. S1. $^1$H NMR spectrum of TPPS, PMVP$_{41}$-b-PEO$_{205}$ and the PIC micelles recorded in D$_2$O.

Fig. S2. The TEM images of TPPS/ PMVP$_{41}$-b-PEO$_{205}$ PIC micelles. (a) without NaCl; (b) with 0.7 M NaCl and shows the amount of PIC micelles is decrease seriously; (c) with 1.5 M NaCl and shows PIC micelles are disassembled.
Fig. S3. (a) UV-vis absorption spectra at different irradiation time for the PIC micelles in the presence of 0.7 M NaCl. (b) Kinetics of tri-iodide formation versus irradiation time in the solution of TPPS and PIC micelles. The absorbance at $\lambda = 353$ nm was compared between free TPPS, the PIC micelles without and with 0.7 M NaCl. The concentration of iodide (KI) was kept constant of 0.05 M for all the measurements.

Fig. S4. UV-vis absorption spectra of (a) TPPS and (b) PIC micelles in the presence of NaCl of various concentrations. The concentration of iodide is 0.1 M (KI) for both cases and the solutions were irradiated for 10 min before spectral measurements.

Reference