

# 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<sub>41</sub>-b-PEO<sub>205</sub>, Mw=19K, PDI=1.05, about 90% quaternized) used in this work was prepared according to previously reported procedures.<sup>1</sup> Other reagents and solvents were of analytical grade and used without further purification. Ultrapure water was used throughout the work.

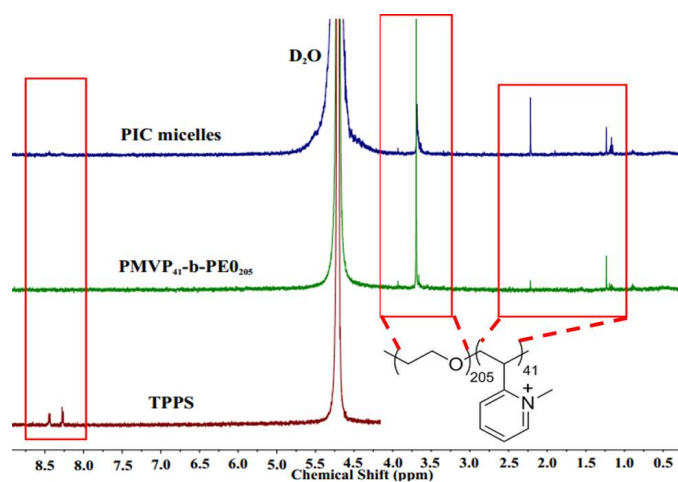
#### Sample Preparation

The electrostatic micelles were obtained by simply mixing PMVP<sub>41</sub>-b-PEO<sub>205</sub> 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.

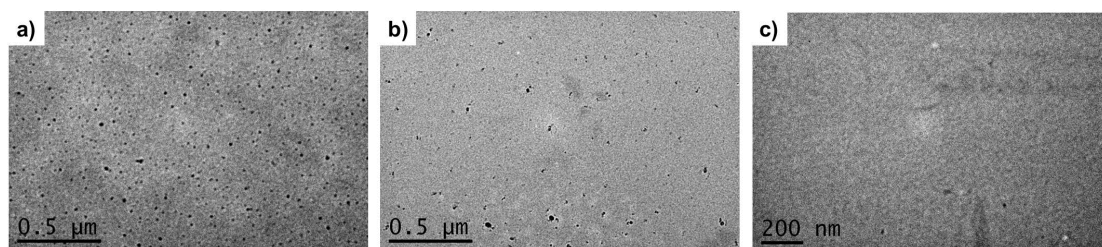
#### Characterization of PIC micelles

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. <sup>1</sup>H spectra were measured on a Bruker-500 MHz NMR spectrometer and recorded in D<sub>2</sub>O.

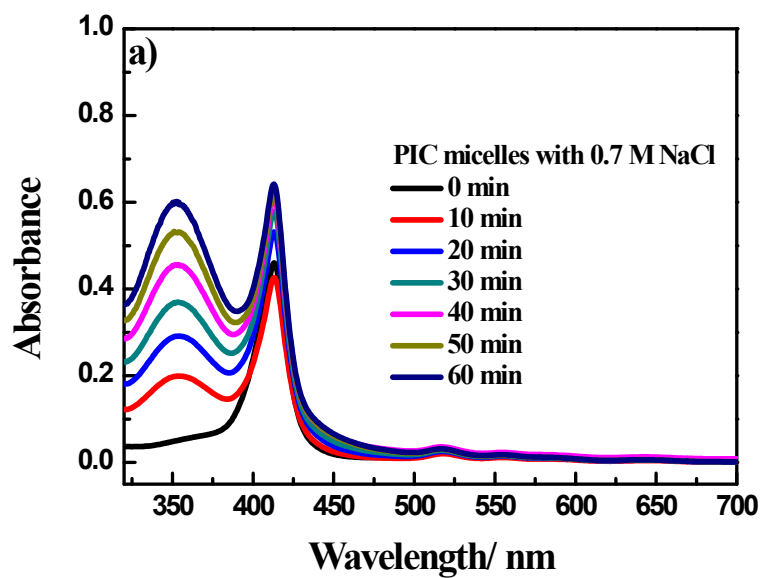
For FF-TEM measurements, in the freezing procedure, a drop of sample was placed on copper grids, the sample-loaded copper was frozen by plunging this into liquid nitrogen. Aggregate structures were believed to be preserved and “solidified” by this procedure. Fracturing and replication were carried out 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).

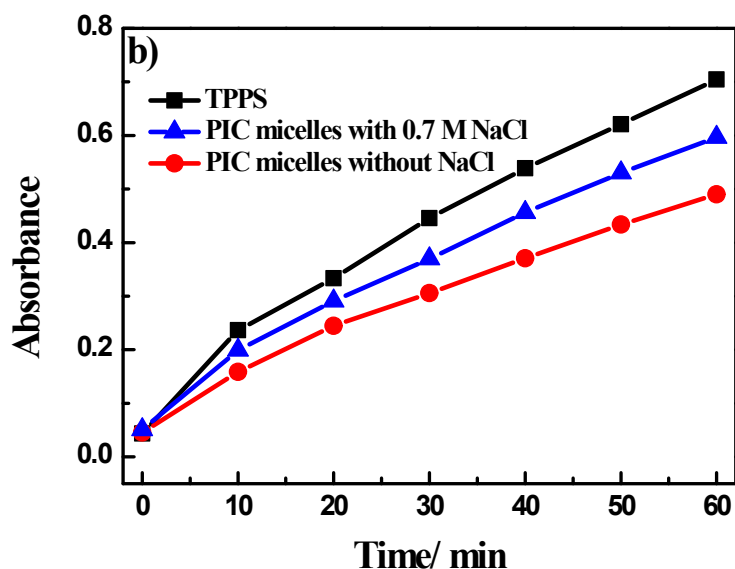


**Fig. S1.**  $^1\text{H}$  NMR spectrum of TPPS,  $\text{PMVP}_{41}\text{-b-PEO}_{205}$  and the PIC micelles recorded in  $\text{D}_2\text{O}$ .

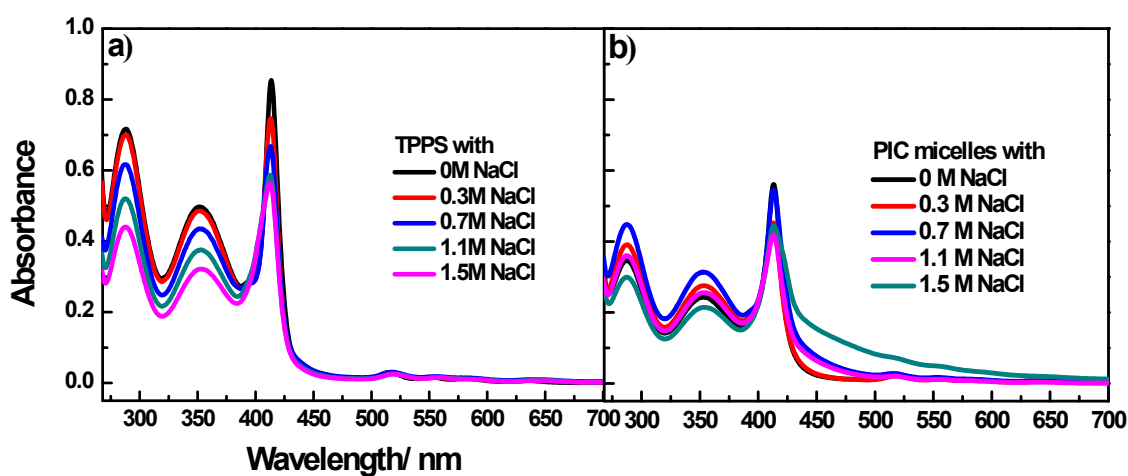


**Fig. S2.** The TEM images of TPPS/  $\text{PMVP}_{41}\text{-b-PEO}_{205}$  PIC micelles. (a) without NaCl; (b) with 0.7 M NaCl and shows the amount of PIC micelles is decrease seriously; (c) with 1.5 M NaCl and shows PIC micelles are disassembled.





**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

1.M. Biesalski, D. Johannsmann and J. Ruhe, *Journal of Chemical Physics*, 2004, **120**, 8807-8814.