Supporting Information

Amphiphilic Trismethylpyridylporphyrin-Fullerene (C$_{70}$) Dyad: An Efficient Photosensitizer under Hypoxia Condition

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Preparation and Characterization of the water-soluble PC$_{70}$ and the water-soluble Trismethylpyridylporphyrin (Scheme S1).

C$_{70}$ was synthesized by arc-discharged graphite under a helium atmosphere and isolated by high performance liquid chromatography (HPLC). PC$_{70}$ was prepared as following. Briefly, one equivalent of terephthalaldehydic acid methyl ester, 3 eq of pyridine-4-aldehyde, and 4 eq of pyrrole were reacted in propionic acid for 1.5 h, and the resultant mixture was separated through a silica gel. 5-(4-methoxycarbonylphenyl)-10,15,20-tris(4-pyridyl)-porphine was obtained, then LiAlH$_4$ was used to reduce the ester group to primary hydroxyl group at room temperature. Subsequently a Swern oxidation reaction was applied to oxidize the primary hydroxyl group to aldehyde group, the final product named 5-(4-Formylphenyl)-10,15,20-tris(4-pyridyl)-porphine (abbr. D-TMPyP) was purified by silica gel column chromatography. After that, D-TMPyP and sarcosine were added to a solution of C$_{70}$ in bromobenzene, which was refluxed in an argon atmosphere for 1 h and then evaporated under reduced pressure. The crude product was subjected to silica gel column chromatography. The obtained final product was mixed with methyl tosylate and refluxed in argon atmosphere for 1 h and then passed through an anion-exchange resin repeatedly to yield Trismethylpyridylporphyrin-C$_{70}$ as a chloride salt. Water-soluble porphyrin was prepared by the same method. Characterization of The obtained compounds were characterized by $^1$H NMR spectrometry, matrix-assisted laser desorption/ionization-time of flight
mass (MALDI-TOF) spectrometry, UV-Visible absorption spectroscopy, and dynamic light scattering (Nano-ZS ZEN3600, Malvern Instruments, Germany).

The $^1$H NMR (400 MHz) measurement of PC$_{70}$ was performed in DMSO-d$_6$. Due to existence of a variety of isomers, the spectroscopy has several sets of peaks (Fig. S1B). Furthermore, MALDI-TOF-MS ($\alpha$-cyano-4-hydroxy cinnamic acid as the matrix) exhibits m/z (%): 1571 (M$^+$) (Fig. S1A).

![Scheme S1 Preparation of PC$_{70}$ and D-TMPyP](image-url)
**Fig. S1** CHO-TMPyP $^1$H-NMR (400MHz, CDCl$_3$, 298K) $\delta$: 10.41 (1H, s), 9.07, 9.06 (6H, d, $J =$ 4.32 Hz), 8.87, 8.86 (8H, d, $J =$ 5.12 Hz), 8.41, 8.39 (2H, d, $J =$ 7.92 Hz), 8.33, 8.31 (2H, d, $J =$ 7.96 Hz), 8.17, 8.16 (6H, d, $J =$ 5.56 Hz), -2.88 (2H, s);

**Fig. S2** $^1$H NMR(400 MHz, CDCl$_3$) for C$_{70}$-TMPyP
**Fig. S3** MALDI-TOF-MS spectrum of PC\textsubscript{70}: 1571 (M\textsuperscript{+}).

**Fig. S4** The $^1$H NMR spectrum of PC\textsubscript{70} in DMSO-$d_6$. 
Fig. S5 OH-TMPyP $^1$H-NMR (400MHz, CDCl$_3$, 298K) $\delta$: 9.06, 9.05 (6H, d, $J = 4.44$ Hz), 8.93-8.82 (8H, m), 8.21-8.16 (8H, m), 7.80, 7.79 (2H, d, $J = 7.72$ Hz), 5.10 (2H, s), -2.88 (2H, s);

Fig. S6 MALDI-TOF-MS spectrum of D-TMPyP: 706 (M$^+$.)
**Fig. S7** The $^1$H NMR spectrum of D-TMPyP in DMSO-$d_6$.

**Fig. S8** Fluorescence spectra of PC$_{70}$ excited by different excitation wavelengths from 360 to 480 nm. The Fluorescence intensity was increased firstly and then decreased.
Fig. S9 Fluorescence spectra of PC$_{70}$ and D-TMPyP excited at 420 nm. The fluorescence intensity of PC$_{70}$ was decreased compared to D-TMPyP which indicated the interaction between D-TMPyP and C$_{70}$.

Fig. S10 Chemical trapping measurements of the $^{1}$O$_2$ quantum yield of PC$_{70}$. A) Photodegradation of Na$_2$-ADPA with PC$_{70}$. B) The absorption spectrum of PC$_{70}$. C) The decomposition rate constants of Na$_2$-ADPA by PC$_{70}$. D) Photodegradation of Na$_2$-ADPA with RB. E) The absorption
spectrum of RB. F) The decomposition rate constants of Na₂-ADPA by RB.

**Fig. S11** A) A part of the simulative structure of PC₇₀ via self-assembly. B) TEM image of PC₇₀.

**PDT treatment and cell viability assays:**

**Fig. S12** Cell viability of A549 cells incubated with gradient concentrations of D-TMPyP for 3 h and subsequently exposed to light irradiation for 10 min at a power density of 17 mW·cm⁻².

Confocal images after staining with PI, Dil, and Hoechst 33258.
**Fig. S13** Confocal images of A549 cells stained with Dil and Hoechst 33258 after treated with 2 μM of PC70 for 3 h and subsequently exposed to irradiation for 1, 5, 10 min, respectively. The images from left to right represent fluorescence images, bright field images and merged images, respectively.

**Fig. S14** Viability of A549 cells incubated with NaN3 (10 mM), mannitol (10 mM), and SOD (50 units) for 3 h without light irradiation.
Fig. S15 The electron spin-resonance (ESR) spectroscopy of PC<sub>70</sub> and D-TMPyP were detected under different conditions. A) PC<sub>70</sub> under air-saturated conditions, B) D-TMPyP under air-saturated conditions, C) PC<sub>70</sub> under N<sub>2</sub>-saturated conditions and D) D-TMPyP under N<sub>2</sub>-saturated conditions. All of the ordinates are consistent.