Supporting Information

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

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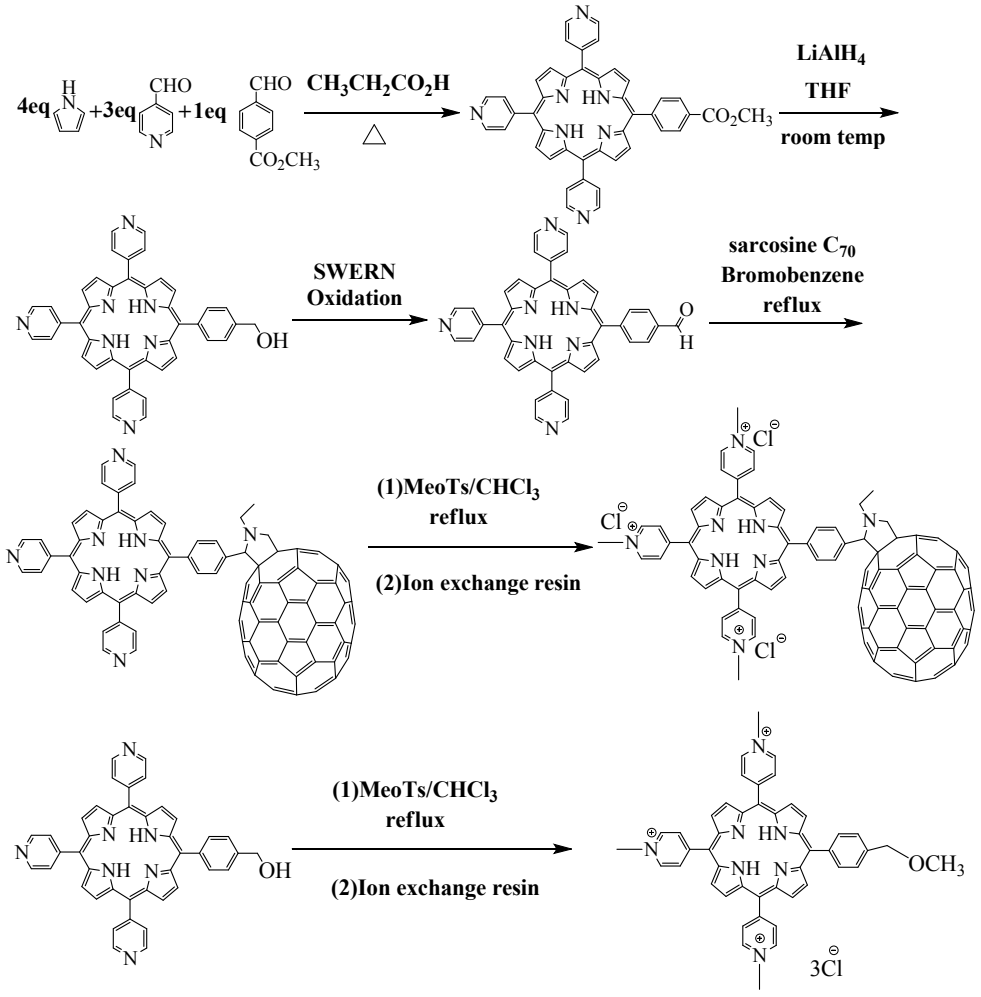
Preparation and Characterization of the water-soluble PC_{70} and the water-soluble Trismethylpyridylporphyrin (Scheme S1).

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 ^1H 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 (α-cyano-4-hydroxy cinnamic acid as the matrix) exhibits m/z (%): 1571 (M^+) (Fig. S1A).



Scheme S1 Preparation of PC_{70} and D-TMPyP

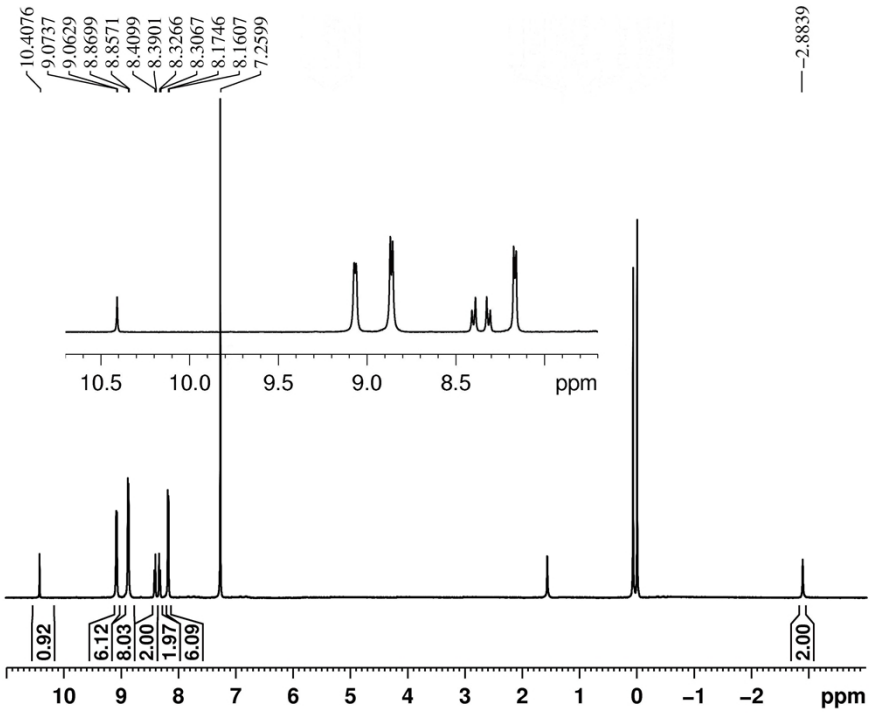


Fig. S1 CHO-TMPyP ^{1}H-NMR (400MHz, $CDCl_3$, 298K) δ: 10.41 (1H, s), 9.07, 9.06 (6H, d, J = 4.32 Hz), 8.87, 8.86 (8H, d, J = 5.12 Hz), 8.41, 8.39 (2H, d, J = 7.92 Hz), 8.33, 8.31 (2H, d, J = 7.96 Hz), 8.17, 8.16 (6H, d, J = 5.56 Hz), -2.88 (2H, s);

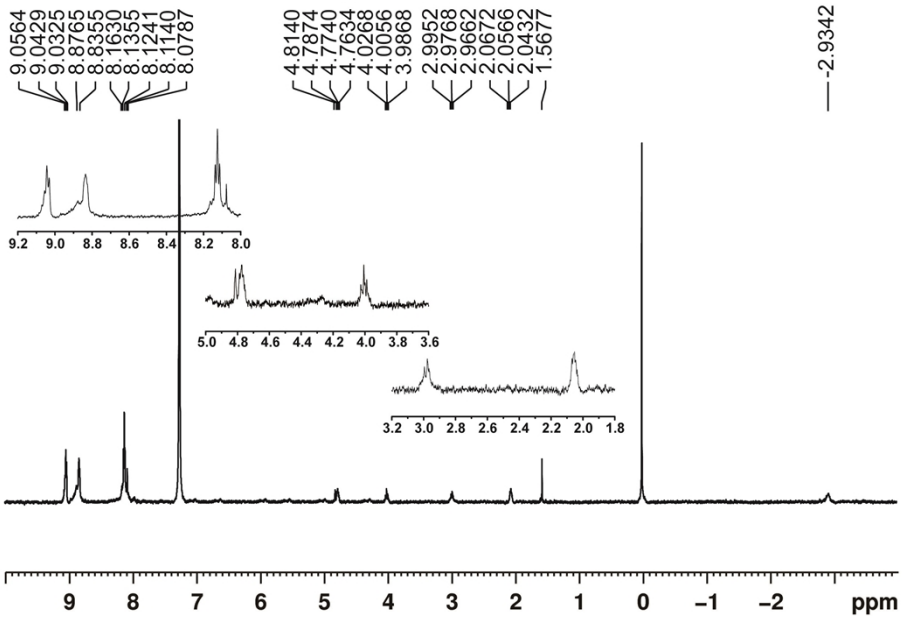


Fig. S2 ^{1}H NMR(400 MHz, $CDCl_3$) for C_{70}-TMPyP

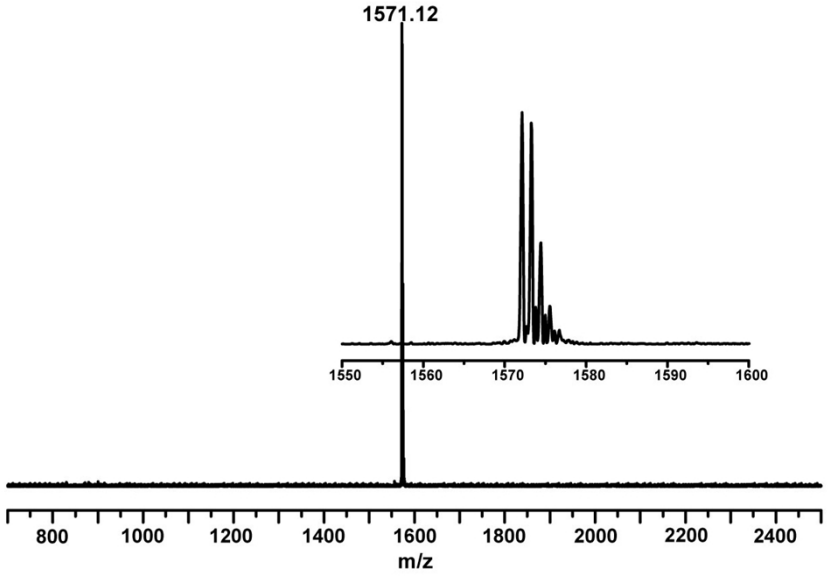


Fig. S3 MALDI-TOF-MS spectrum of PC_{70}: 1571 (M^+).

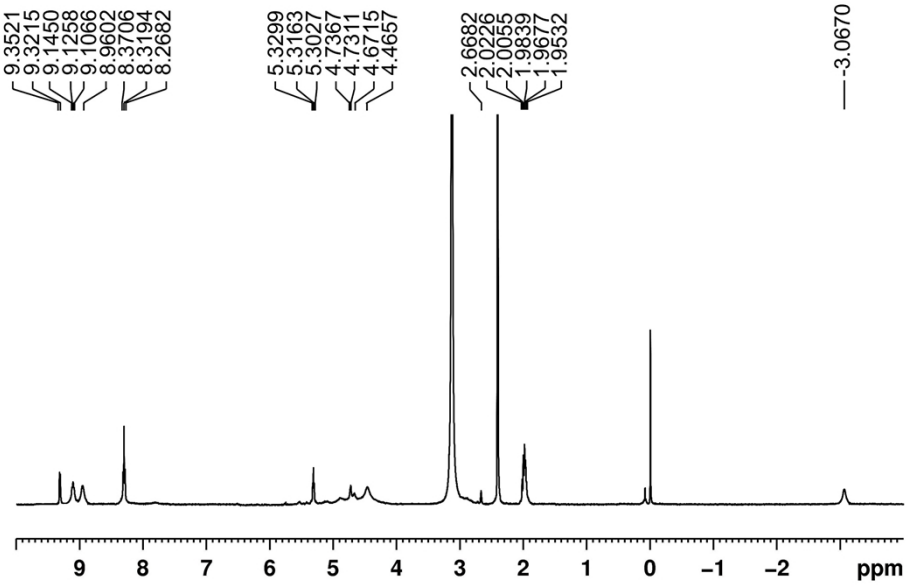


Fig. S4 The ^1H NMR spectrum of PC_{70} in DMSO-d_6.

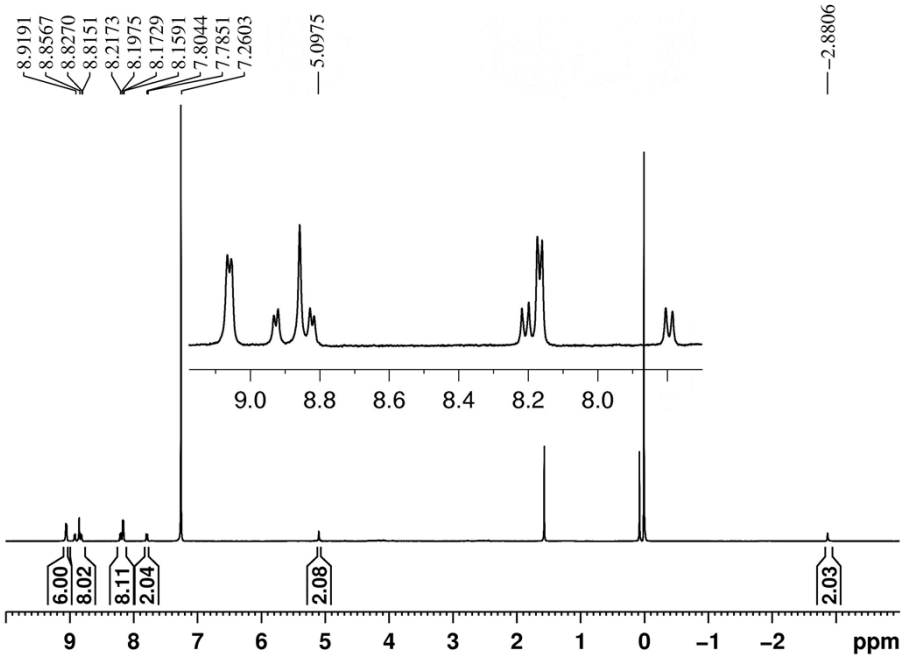


Fig. S5 OH-TMPyP ^{1}H-NMR (400MHz, $CDCl_3$, 298K) δ: 9.06, 9.05 (6H, d, J = 4.44 Hz), 8.93-8.82 (8H, m), 8.21-8.16 (8H, m), 7.80, 7.79 (2H, d, J = 7.72 Hz), 5.10 (2H, s), -2.88 (2H, s);

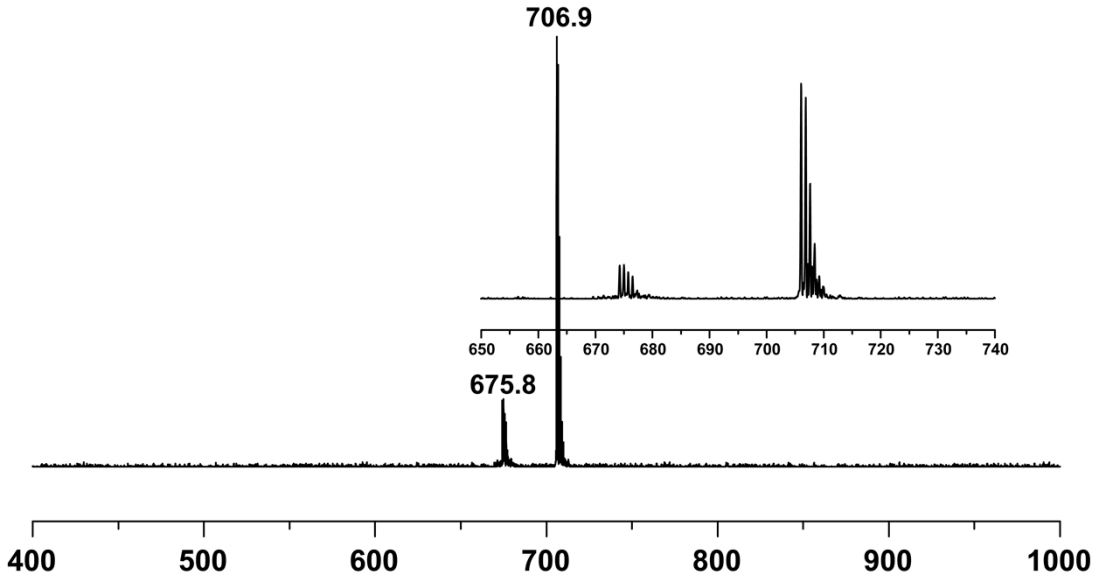


Fig. S6 MALDI-TOF-MS spectrum of D-TMPyP: 706 (M^+).

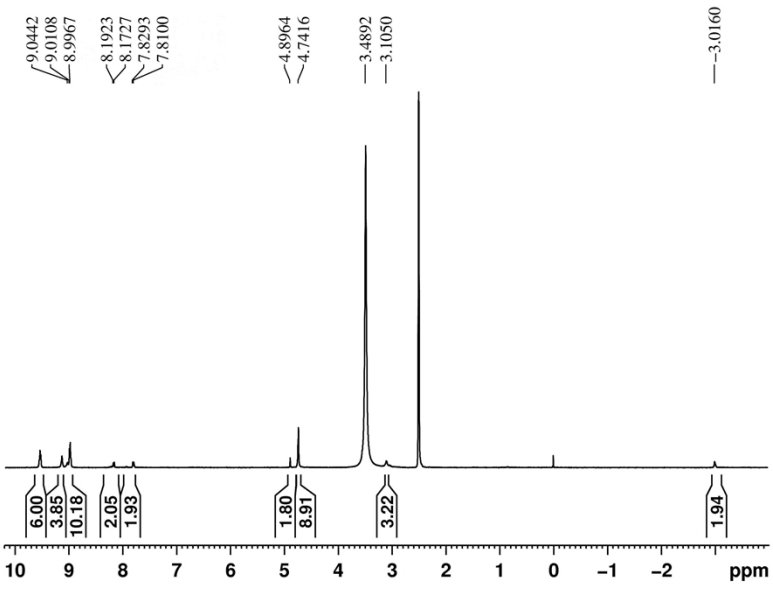


Fig. S7 The ^{1}H NMR spectrum of D-TMPyP in DMSO-d_6.

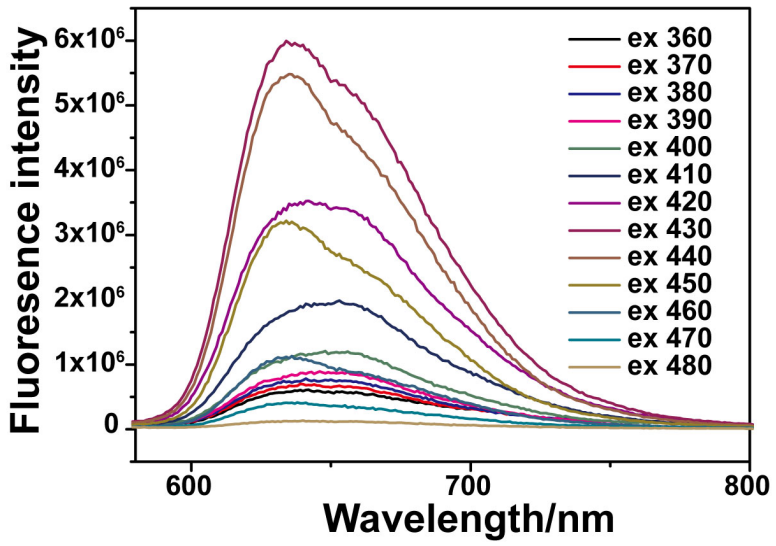


Fig. S8 Fluorescence spectra of PC_{70} excitated by different excitation wavelengths from 360 to 480 nm. The Fluorescence intensity was increased firstly and then decreased.

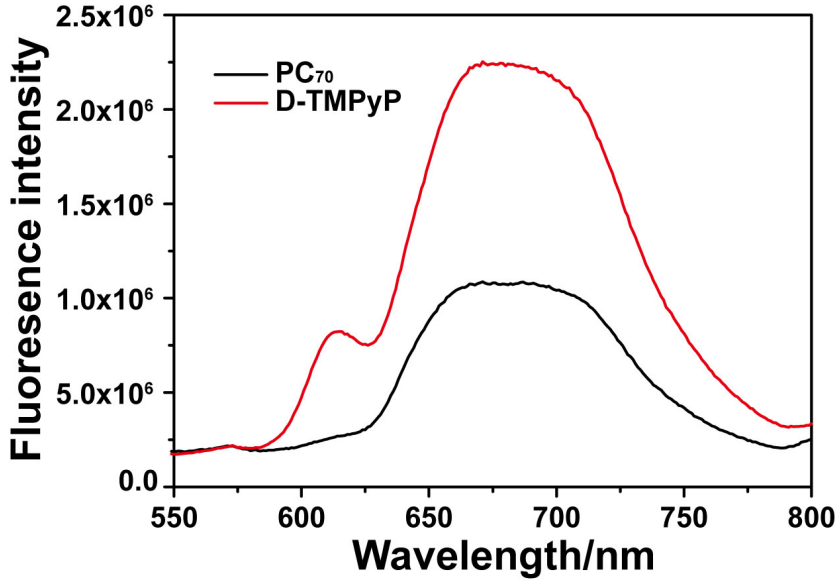


Fig. S9 Fluorescence spectra of PC_{70} and D-TMPyP excitated at 420 nm. The fluorescence intensity of PC_{70} was decreased compared to D-TMPyP which indicated the interaction between D-TMPyP and C_{70}.

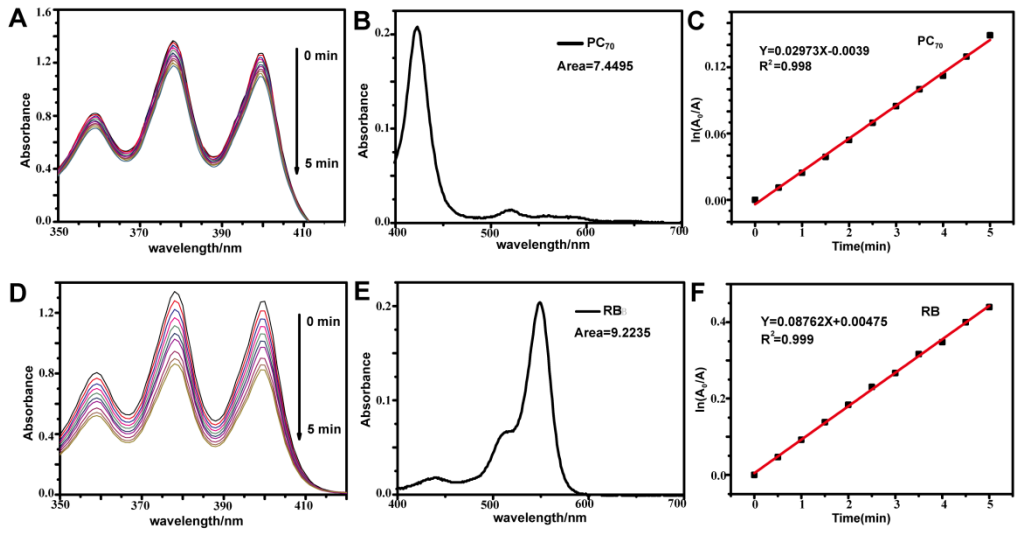


Fig. S10 Chemical trapping measurements of the $^1O_2$ quantum yield of PC_{70}. A) Photodegradation of Na_2-ADPA with PC_{70}. B) The absorption spectrum of PC_{70}. C) The decomposition rate constants of Na_2-ADPA by PC_{70}. D) Photodegradation of Na_2-ADPA with RB. E) The absorption

spectrum of RB. F) The decomposition rate constants of Na_2-ADPA by RB.

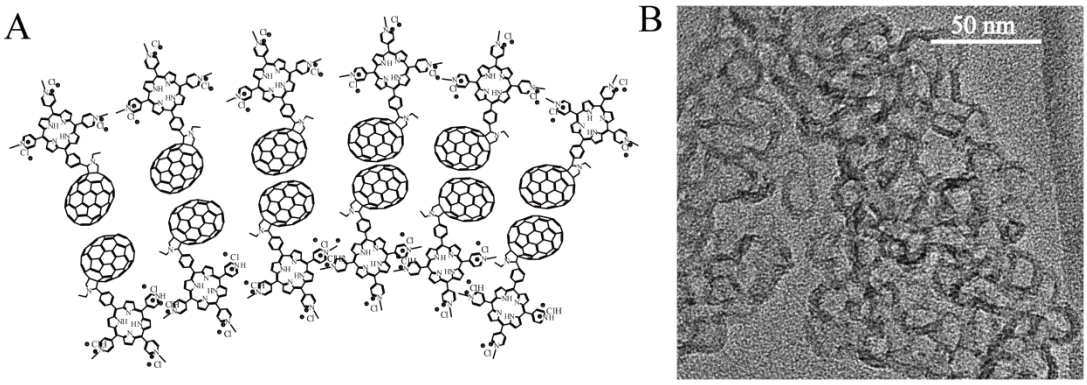


Fig. S11 A) A part of the simulative structure of PC_{70} via self-assembly. B) TEM image of PC_{70}.

PDT treatment and cell viability assays:

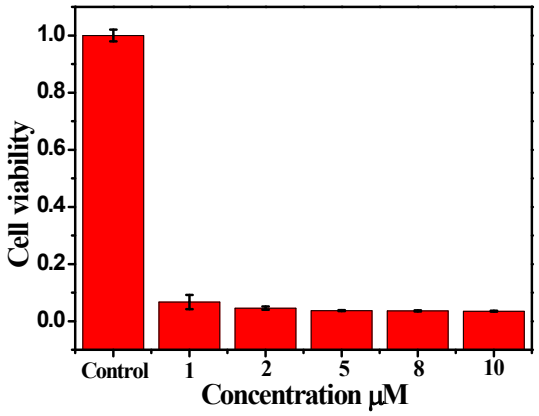


Fig. S12 Cell viability of A549 cells incubated with gradient concentrations of D-TMPyP for 3 h and subsequently exposed to light irradiation for 10 min at a power density of 17 $mW \cdot cm^{-2}$.

Confocal images after staining with PI, Dil, and Hoechst 33258.

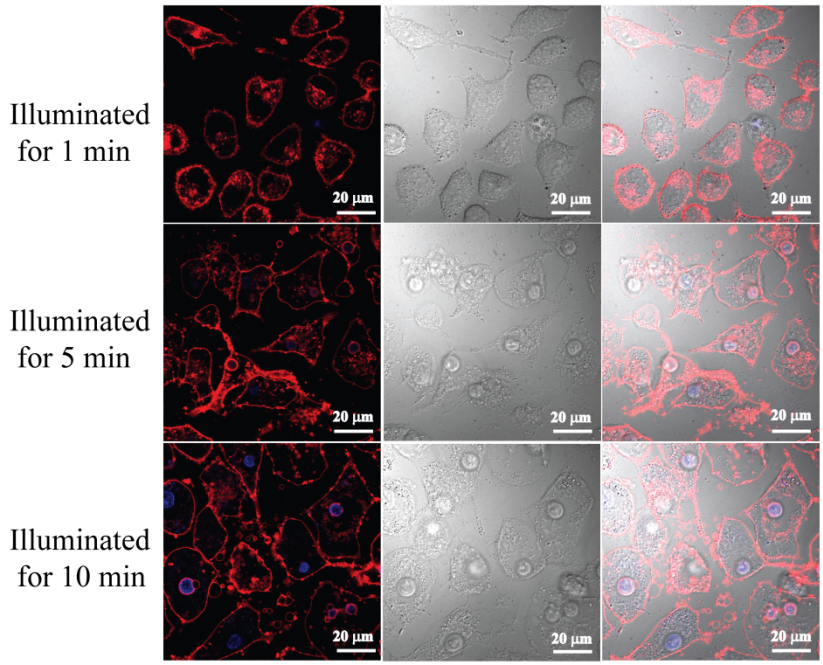


Fig. S13 Confocal images of A549 cells stained with Dil and Hoechst 33258 after treated with 2 μM of PC_{70} for 3 h and subsequently exposed to irradiation for 1, 5, 10 min, respectively. The images from left to right represent fluorescence images, bright field images and merged images, respectively.

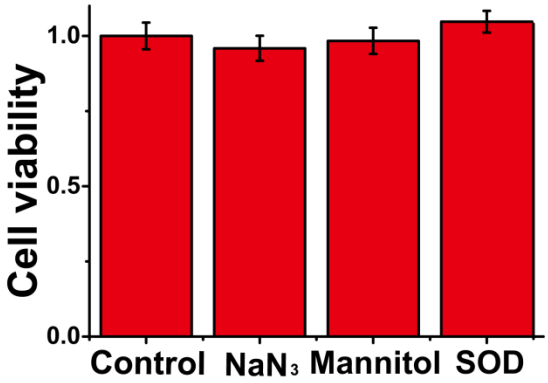


Fig. S14 Viability of A549 cells incubated with NaN_3 (10 mM), mannitol (10 mM), and SOD (50 units) for 3 h without light irradiation.

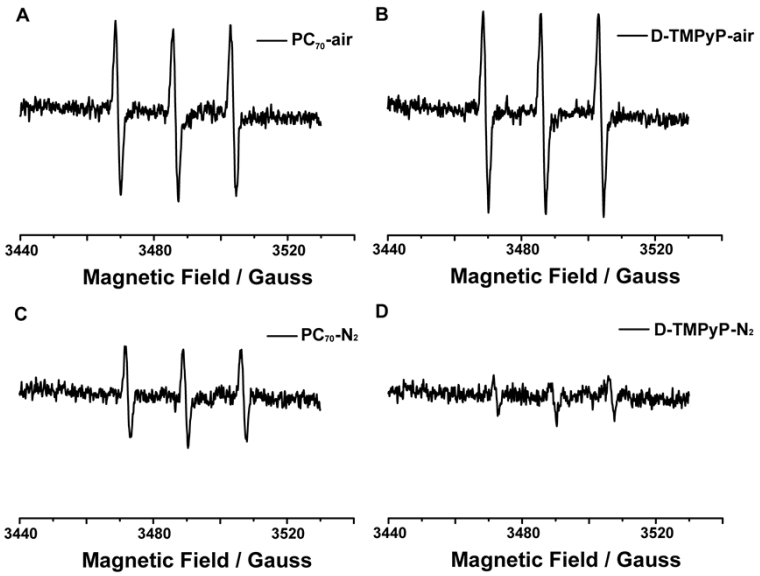


Fig. S15 The electron spin-resonance (ESR) spectroscopy of PC_{70} and D-TMPyP were detected under different conditions. A) PC_{70} under air-saturated conditions, B) D-TMPyP under air-saturated conditions, C) PC_{70} under N_2-saturated conditions and D) D-TMPyP under N_2-saturated conditions. All of the ordinates are consistent.