Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

An AIE-active type Ⅰ photosensitizer based on *N*, *N*′-diphenyl-dihydrophenazine for high-performance photodynamic therapy under hypoxia

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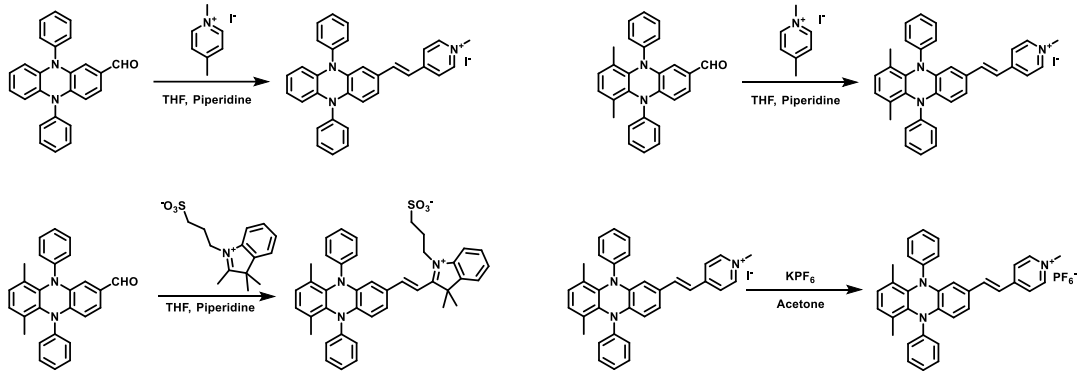
Contents

Reagents and Measurements

1, 4-dimethylpyridin-1-ium iodide, tetrahydrofuran (THF), 3-(2,3,3-trimethyl-3H-indol-1-ium-1-yl) propane-1-sulfonate, dichloromethane, piperidine, acetic acid were all purchased from Energy Chemical. All reagents were bought from commercial sources (Energy Chemical, Sigma-Aldrich, Adamas-beta) and used without further processing. All solvents were purified and dried before using by standard methods. The solvents used in spectrum analysis were of HPLC grade. The solutions for analytical studies were prepared with deionized water treated using a Milli-Q System (Billerica, MA, USA). Hecho S5000 LED cold-light fountain provides the white light irradiation. The synthesis of the compound **DMP-CHO** and **DP-CHO** were prepared as reported in the literature[1] and the synthetic routes of **DMPpy** and **DMPSI** were similar to **DPpy**.

Preparation of DMPpy, DPpy, DMPSI and DMPpy-PF_6 molecules

Scheme S1 Synthesis routes of DMPpy, DPpy, DMPSI, and DPSI



Synthesis of DMPpy and DPpy. These compounds are prepared from **DMP-CHO** and **DP-CHO** (100 mg, 0.256 mmol), 1,4-dimethylpyridin-1-ium iodide (60 mg, 0.256 mmol) and 2 drops piperidine were dissolved in 10mL THF in the flask under nitrogen atmosphere at 70 °C After 8 hours of reflux, the reaction was complete. After filtered and spin-dried, the crude product was separated by silica column with DCM/ EtOH (v:v = 10:1).

(E)-4-(2-(6,9-dimethyl-5,10-diphenyl-5,10-dihydrophenazin-2-yl)vinyl)-1-methylpyridin-1-ium (**DMPpy**): Yield = 32.2%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.87 (d, *J* = 6.6 Hz, 2H), 8.22 (d, *J* = 6.5 Hz, 2H), 8.10 (d, *J* = 16.2 Hz, 1H), 8.05 (s, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.70 – 7.66 (m, 1H), 7.63 (d, *J* = 16.3 Hz, 1H), 7.19 (q, *J* =

8.5 Hz, 4H), 7.11 (q, *J* = 7.9 Hz, 2H), 7.03 (d, *J* = 7.9 Hz, 2H), 6.98 – 6.92 (m, 3H), 6.88 (t, *J* = 7.2 Hz, 1H), 4.26 (s, 3H), 2.13 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (151 MHz, DMSO) δ 151.91, 146.05, 144.98, 144.46, 142.19, 140.35, 139.45, 139.22, 131.41, 130.27, 128.55, 127.63, 126.82, 125.45, 125.10, 124.69, 122.81, 122.37, 121.92, 120.80, 118.46, 115.89, 46.35, 43.14, 21.58, 20.96, 17.29, 16.72. HRMS ESI (m/z). $[M]^+$: calcd. for $C_{34}H_{30}N_3$ 480.2434; Found, 480.2430.

(E)-4-(2-(5,10-diphenyl-5,10-dihydrophenazin-2-yl)vinyl)-1-methylpyridin-1-ium (**DPpy**): Yield = 45.1%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.71 – 8.60 (m, 2H), 7.99 (d, *J* = 5.2 Hz, 2H), 7.75 (q, *J* = 8.0 Hz, 4H), 7.60 (q, *J* = 7.3 Hz, 2H), 7.48 (t, *J* = 7.1 Hz, 5H), 6.78 (d, *J* = 9.0 Hz, 1H), 6.65 (s, 1H), 6.33 – 6.29 (m, 2H), 5.76 (s, 1H), 5.55 (d, *J* = 8.3 Hz, 1H), 5.51 (d, *J* = 5.6 Hz, 1H), 5.47 (d, *J* = 7.2 Hz, 1H), 5.32 (t, *J* = 4.6 Hz, 1H), 4.14 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.14, 133.32, 131.97, 131.65, 130.30, 129.07, 128.96, 128.28, 125.62, 124.79, 124.39, 123.49, 122.72, 47.73. HRMS ESI (m/z) $[M]^+$: calcd. for $C_{32}H_{26}N_3$ 452.2121; Found, 452.2126.

Synthesis of DMPSI. DMPSI was prepared from **DMP-CHO** (100 mg, 0.256 mmol), 3-(2,3,3-trimethyl-3H-indol-1-ium-1-yl)propane-1-sulfonate (72 mg, 0.256 mmol) and 2 drops piperidine were dissolved in 10mL THF in the flask under nitrogen atmosphere at 70 °C. After 8 hours of reflux, the reaction was complete. After filtered and spin-dried, the crude product was separated by silica column with DCM/ EtOH (v:v = 10:1).

(E)-3-(2-(2-(6,9-dimethyl-5,10-diphenyl-5,10-dihydrophenazin-2-yl)vinyl)-3,3-dimethyl-3H-indol-1-ium-1-yl)propane-1-sulfonate (**DMPSI**): Yield = 10.8%. ^{1}H NMR (400 MHz, DMSO-d6) δ 8.56 (d, *J* = 16.2 Hz, 2H), 8.31 (dd, *J* = 8.6, 1.5 Hz, 1H), 8.03 – 8.00 (m, 1H), 7.96 – 7.86 (m, 2H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.62 (td, *J* = 4.5, 1.9 Hz, 2H), 7.34 – 7.29 (m, 2H), 7.26 – 7.19 (m, 5H), 7.14 – 7.02 (m, 6H), 6.92 (t, *J* = 7.2 Hz, 1H), 4.89 (t, *J* = 7.5 Hz, 2H), 2.24 – 2.17 (m, 2H), 2.16 – 2.14 (m, 3H), 2.02 – 1.96 (m, 2H), 1.87 (s, 3H), 1.84 (s, 6H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 184.92, 156.79, 152.26, 150.80, 147.94, 147.11, 144.35, 144.17, 143.90, 142.02, 135.42, 133.96, 132.80, 132.74, 132.66, 132.53, 132.43, 132.38, 132.15, 130.44, 127.67, 126.29, 125.89,

125.62, 124.96, 120.31, 118.34, 114.95, 59.35, 58.18, 55.41, 50.46, 48.72, 43.36, 43.24, 43.10, 42.97, 42.83, 42.69, 42.55, 42.41, 29.06, 27.98, 21.94, 21.84, 20.55, 14.54. HRMS ESI (m/z) $[M+Na]^+$: calcd. for $C_{41}H_{39}N_3O_3SNa$ 676.2610; Found, 676.2600.

Synthesis of DMPpy-PF_6. DMPpy (100 mg, 0.165 mmol) was dissolved in 10 ml acetone. Then 5 ml of saturated solution of potassium hexafluorophosphate (KPF_6) was added in the solution at 40-50 °C. After 8 hours of reflux, the reaction was complete. After filtered and spin-dried, the crude product was washed three times with deionized water to remove KPF_6 to give a brown solid **DMPpy-PF_6**.

(E)-4-(2-(6,9-dimethyl-5,10-diphenyl-5,10-dihydrophenazin-2-yl)vinyl)-1-methylpyridin-1-ium hexafluorophosphate (**DMPpy-PF_6**): Yield = 98%. ^{1}H NMR (400 MHz, CD_3CN) δ 8.44 (d, *J* = 6.8 Hz, 2H), 8.01 (d, *J* = 6.8 Hz, 2H), 7.98 (d, *J* = 1.8 Hz, 1H), 7.88 (d, *J* = 16.4 Hz, 1H), 7.72 (d, *J* = 8.3 Hz, 1H), 7.65 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.41 (d, *J* = 16.4 Hz, 1H), 7.19 – 7.10 (m, 6H), 7.00 (d, *J* = 7.8 Hz, 2H), 6.95 (d, *J* = 7.9 Hz, 2H), 6.90 (d, *J* = 7.3 Hz, 1H), 6.86 (t, *J* = 7.3 Hz, 1H), 4.19 (s, 3H), 2.19 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (151 MHz, CD_3CN) δ 154.11, 147.49, 147.18, 146.46, 145.32, 144.20, 141.96, 141.27, 141.06, 133.41, 132.64, 132.45, 129.68, 128.94, 128.25, 126.94, 126.64, 124.33, 123.18, 122.80, 121.84, 118.82, 116.67, 47.80, 17.89, 17.37. HRMS ESI (m/z). $[M]^+$: calcd. for $C_{34}H_{30}N_3$ 480.2434; Found, 480.2442.

Fluorescence Quantum Yield Measurement

The fluorescence quantum yield (η) of titled compounds in aqueous medium was determined using a fluorescence comparison protocol. Freshly prepared Rhodamine 6G (RDM 6G) was used as standard (η = 0.95 in water).[2] Firstly, the absorption spectra of titled compounds and RDM 6G in water were recorded by a spectrometer (Shimadzu RF-6000). Secondly, the photoluminescence spectra of the corresponding samples were measured by a fluorescence spectrometer at the same excitation wavelength. The photoluminescence intensities were calculated by wavelength integration. The η value of titled compounds was finally calculated by the following equation:

$$\eta_1 = \eta_0 \frac{A_0 F_1 n_1^2}{A_1 F_0 n_0^2}$$

where, A is the absorbance at the excitation wavelength, F is the photoluminescence intensity, n is the refractive index of the solvent, and the subscripts 1 and 0 represent the sample and the standard.

Reactive oxygen species generation measurement *in vitro*

The reactive oxygen species (ROS) generation measurement of **DMPpy**, **DPp**y, **DMPSI** in buffer solution (1/99: DMSO/ PBS) under white light irradiation (10 mW·cm^{-2}) was detected using 2′,7′-dichlorodihydrofluorescein diacetate (DCFH-DA) as a commercial probe. DCFH-DA was hydrolyzed to DCFH for testing. The concentration of DCFH was 2 μM and the concentration of phenazine-based photosensitizers was 10 μM. The fluorescence increase of DCFH-DA at 520 nm was recorded at di□erent irradiation time to obtain the ascent rate of the photosensitizing process.

The Singlet oxygen ($^1O_2$) generation measurement of **DMPpy** in buffer solution (1/99: DMSO/ PBS) under white light irradiation (10 mW·cm^{-2}) was detected using 9,10-Anthracenediyl-bis(methylene)dimalonic Acid (ABDA) as a commercial probe. The concentration of ABDA was 100 μM and the concentration of **DMPpy** was 10 μM. The fluorescence decrease of ABDA at 380 nm was recorded at di□erent irradiation time to obtain the ascent rate of the photosensitizing process.

The superoxide radicals ($O_2^{-\cdot}$) generation measurement of **DMPpy** in buffer solution (1/99: DMSO/ PBS) under white light irradiation (30 mW·cm^{-2}) was detected using dihydrorhodamine123 (DHR123) as a commercial probe. The concentration of DHR123 was 10 μM and the concentration of **DMPpy** was 10 μM. The fluorescence increase of DHR123 at 530 nm was recorded at di□erent irradiation time to obtain the ascent rate of the photosensitizing process.

The hydroxyl radicals (·OH) generation measurement of **DMPpy** in buffer solution (1/99: DMSO/ PBS) under white light irradiation (30 mW·cm^{-2}) was detected

using 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) as the ·OH indicator in ESR measurement. Samples were prepared by mixing 10 μL, 1 mM of **DMPpy**, in water and 25 μL of DMPO (100 mM) in water, respectively. EPR signals were recorded by adding samples through a capillary tube under a white light irradiation at 30 $mW \cdot cm^{-2}$ for 1 minutes.

Theoretical Calculation

Methodology: Geometry optimizations were carried out on the molecules in the vacuum phase, using the software Avogadro to enter the starting geometry. The molecules were distorted to form various conformations, and then the global minimum of the potential energy surface was found through structural optimization. Frequency calculations were performed on the optimized geometry to distinguish whether they are in a minimum state or a transition state on the potential energy surface. Finally, in the transition state structure, the bond length and bond angle were distorted in the vibration direction, and the structure was re-optimized until only positive frequencies were obtained. All calculations were performed using the Gaussian 16 program[3] with the (TD)M06-2X-D3 function[4] and the standard 6-311G (d,p) basic settings in the Gaussian 16 program.[5]

Cell Culture

Hela cell line was provided by Feringa Nobel Prize Scientists Joint Research Center, East China University of Science and Technology. The culture media contain 10% fetal bovine serum (FBS) and 1% penicillin-streptomycin (PS). All cells were cultured in an incubator at 37 °C with humidified environment containing 5% CO_2.

Cellular Imaging

Cells were seeded in confocal cell dishes and cultured in the incubator. When the cell confluence reached around 70%, fresh culture medium containing **DMPpy** (10 μM) was added into the cell dishes. After incubation for 1 h, cells were washed with 1× PBS

and co-stained for 30 min with Mito Tracker Green (2 μM), BODIPY 505/515 (5 $\mu g \cdot mL^{-1}$) or Lyso Tracker Green (. Afterward, cells were washed with 1× PBS and taken for confocal fluorescence imaging (Nikon A1R). The excitation laser was at 490 nm and the emissions were collected within 500-530 nm for for commercial fluorophores. The excitation laser was at 490 nm and the emissions were collected within 650-750 nm for **DMPpy**. The Pearson's correlation coefficient was calculated by ImageJ.

Cytotoxicity of DMPpy in cells under normoxia and hypoxia

The Hela cells were planted in 96-well plate (5000 per well) for 16 h, and another 8 h under normoxic (21 % O_2) or hypoxic (8 % and 1 % O_2) atmosphere. After 24 h, the **DMPpy** at different concentrations was added and continued to incubate 4 h under normoxic (21 % O_2) or hypoxic (8 % and 1 % O_2) atmosphere. After that, the cell culture media was replaced with 100 μL fresh medium. Subsequently, the cells were irradiated upon white light for 0-20 min (30 $mW \cdot cm^{-2}$). After irradiation, the cells were again incubated for 12 h. Then, 100 μL CCK-8 solution (0.1 $mg \cdot mL^{-1}$) in DMEM was added to each well. After 4 h of incubation, the absorbance value of each well was recorded with a microplate reader at 450 nm. The cell viability rate was calculated by the following equation:

The cytotoxicity was evaluated by Cell Counting Kit 8 (CCK-8) assays. Cells were seeded in 96-well plates and cultured in standard 0.2 mL DMEM medium containing 10% FBS (Invitrogen, Calsbad, CA, USA) and 1% antibiotics (penicillin, 10000 $U \cdot mL^{-1}$, streptomycin 10 $mg \cdot mL^{-1}$) for 24 h (37 °C, 5% CO_2). For the *in vitro* dark cytotoxicity study, Hela cells were seeded in 96-well plates (1×10^4 cells per well) and cultured overnight. Fresh culture media containing varied concentrations of **DMPpy** were added into the cell wells and incubated for 24 h. Afterward, fresh culture medium was added into the cell dishes after washing with 1× PBS for three times. For the *in vitro* phototoxicity study, the Hela cells were then treated with various concentrations (0-32 μM) of DMPpy in the dark for 24 h and then irradiated for 0-10 min. The white light irradiation source intensity was 30 $mW \cdot cm^{-2}$. After incubation, absorbance was measured on a multifunctional microplate reader (Synergy H1, BioTek Instruments,

America) at 450 nm. The relative cell survival rate (%) was calculated by the following formula: cell survival rate = ($OD_{treated}/OD_{control}$) × 100%. Each concentration of **DMPpy** contained 6 cell wells.

Intracellular ROS detection.

2′,7′-dichlorodihydrofluorescein diacetate (DCFH-DA) was employed as the intracellular ROS indicator, which can be converted to DCFH and emits bright green fluorescence in the presence of ROS. Hela cells were planted onto 35 mm confocal dishes at a density of 1×10^5 cells and cultured for 24 h at 37 °C under 5% CO_2. The cells were then incubated with 10 μM **DMPpy** for 4 h. After rinse with PBS, the cells were incubated with 1 μM DCFH-DA for another 30 min. The cells were washed with PBS and exposed to irradiation for 10 min with white light (30 $mW\cdot cm^{-2}$). After irradiation, confocal fluorescence imaging was used to observe the intracellular ROS level. The excitation wavelength for DCF was 488 nm and emission wavelength collected from 500 nm to 550 nm. In order to simulate hypoxic environment (8% and 1% O_2), Anaero Pack-Anaero and Anaero Pack-Micro Aero (Mitsubishi Gas Chemical Company, Japan) were used. Hela cells were planted onto 35 mm confocal dishes at a density of 1×10^5 cells and cultured for 16 h under normoxic condition, and then the cells were incubated for another 8 h at 37 °C under hypoxic. Other operations were same to that in normoxic condition.

Intracellular $O_2^{-\cdot}$ detection.

The detection of $O_2^{-\cdot}$ was performed using the similar procedure described for the detection of ROS, except that DHE (10 μM) was used as the $O_2^{-\cdot}$ probe. The red fluorescence signal of cells was collected by CLSM.

Calcein-AM/PI staining of Hela cells.

Hela cells were planted onto 35 mm confocal dishes at a density of 1×10^5 cells for 24 h at 37 °C under 5% CO_2. Hela cells incubated with different following treatments: group 1, untreated; group 2, incubated with 10 μM **DMPpy** for 4 h followed

by white light at a light dose of 30 mW·cm^{-2} for 0-20 min. Before imaging, each group was stained with 2 μM Calcein-AM and 8 μM PI for 30 min. Then the fluorescence images of Calcein-AM/PI within Hela cells were detected using confocal microscopy with the excitation wavelength of 488 nm, capture emission region from 500 nm to 550 for green channel, 600-640 nm for red channel.

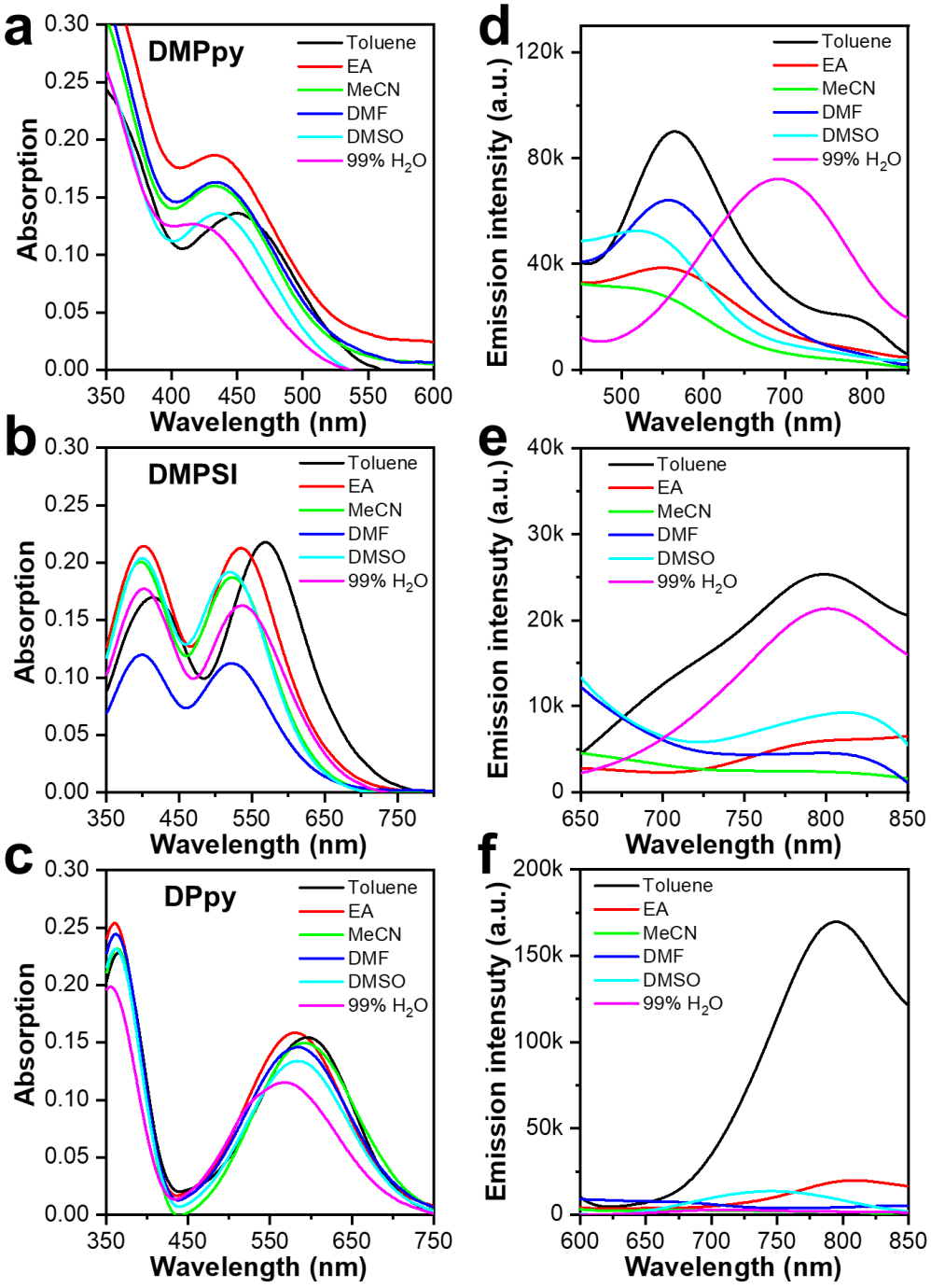


Fig. S1 The UV absorption and fluorescence spectra of a, d) **DMPpy**; b, e) **DMPSI** and c, f) **DPpy** in different solvents. 99% H_2O is DMSO/H_2O = 1:99 (v/v)

Table S1. The experimental optical characteristics for the titled compounds.[a]

Dye	Absorption	Emission		Stokes shift (cm^{-1})	Molar Absorption Coefficient
	λ_{exp} (nm)[b]	λ_{exp} (nm)[b]	η (%)	E_{exp}[b]	ε ($L \cdot mol^{-1} \cdot cm^{-1}$)
DMPpy	**430**	**700**	**4.1**	> 8970	13241
DMPSI	**540**	**795**	**1.2**	> 5523	16263
DPpy	**580**	**710**	**0.2**	> 3156	11029

[a]Data were catched in aqueous solution (1/99: DMSO/ H_2O) in an ordinary temperature. λ_{exp} = experimental absorption onsets or emission peaks, E_{exp} = experimental Stokes shift. [b]The experimental values are obtained from the absorption and the emission peaks.

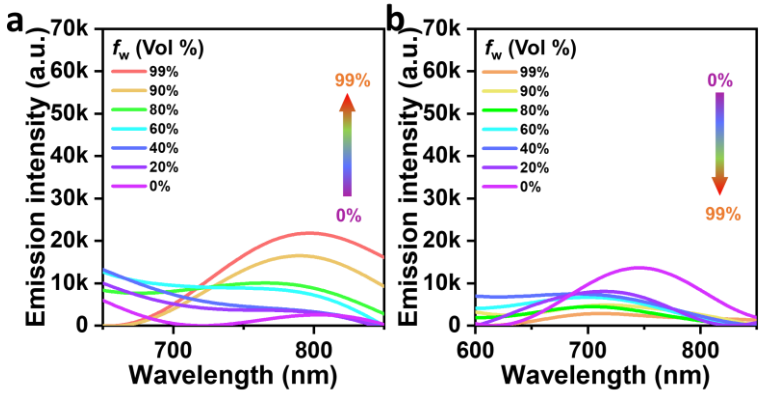


Fig. S2 PL spectra of (a) **DMPSI** and (b) **DPpy** in DMSO/water with different f_w values.

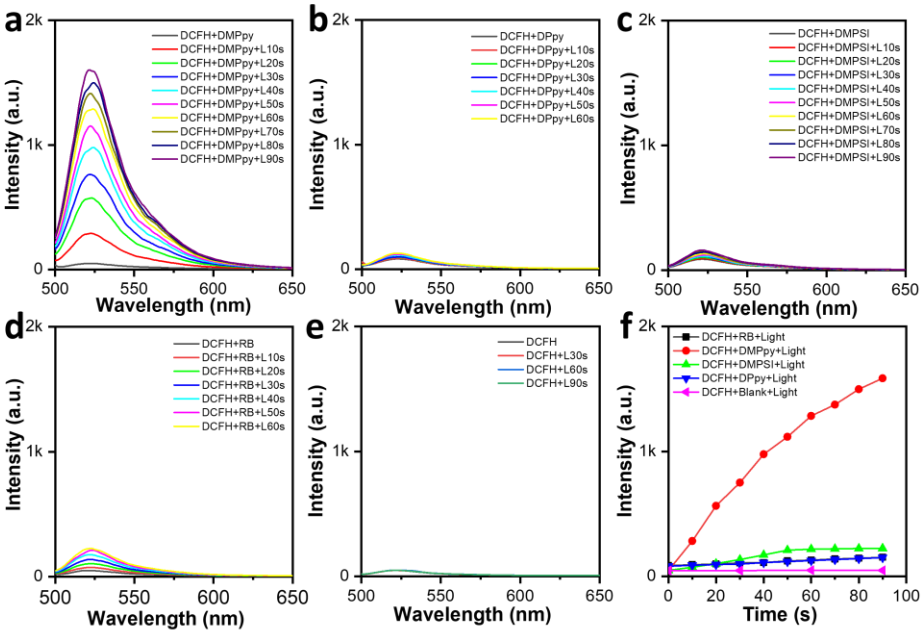


Fig. S3 PL spectra of DCFH-DA (2 μM) in the presence of (a) **DMPpy**, (b) **DPpy**, (c) **DMPSI**, (d) RB and (e) blank under the irradiation with different time in DMSO/PBS: (v/v= 1:99). (f) The fluorescence change curves of DCFH-DA under various conditions with different time. Compounds concentration: 10 μM. White light: 30 $mW \cdot cm^{-2}$.

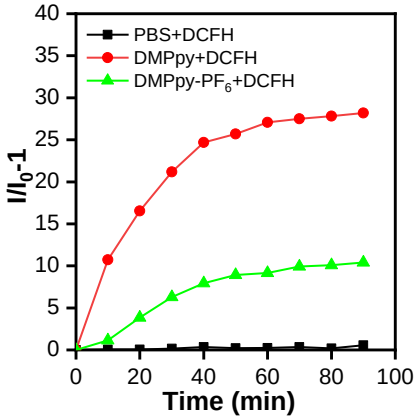


Fig. S4 Plot of the relative emission intensity (I/I_0-1) of the DCFH (2 μM) solution containing **DMPpy** or **DMPpy-PF$_6$** (10 μM) versus the irradiation time. Compounds concentration: 10 μM. White light: 30 mW·cm^{-2}.

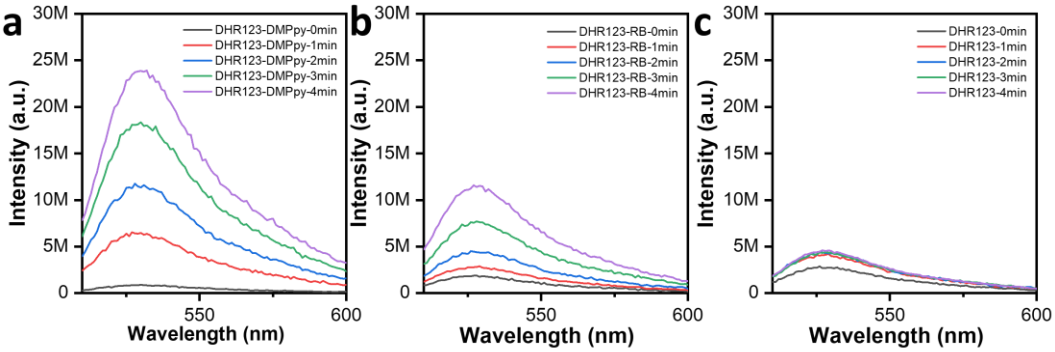


Fig. S5 PL spectra of DHR 123 (10 μM) in the presence of (a) **DMPpy**, (b) **RB**, (c) blank under the irradiation with different time in DMSO/PBS: (v/v= 1:99). Compounds concentration: 10 μM. White light: 30 mW·cm^{-2}.

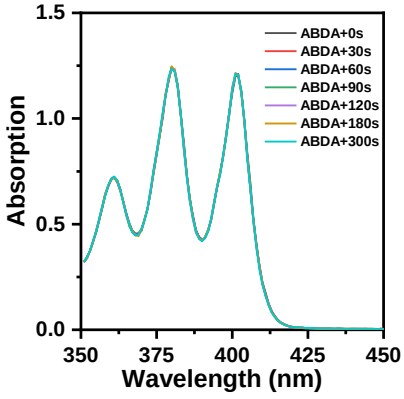


Fig. S6 UV-vis spectra of ABDA under the irradiation with different time in DMSO/PBS (v/v = 1/99). White light: 30 mW·cm^{-2}.

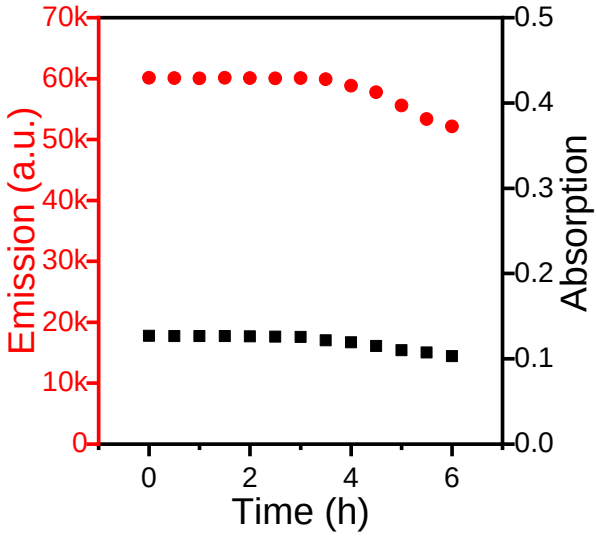


Fig. S7 Photostability of the **DMPpy** under white light irradiation with different time in DMSO/PBS (v/v = 1/99). White light: 30 mW·cm^{-2}.

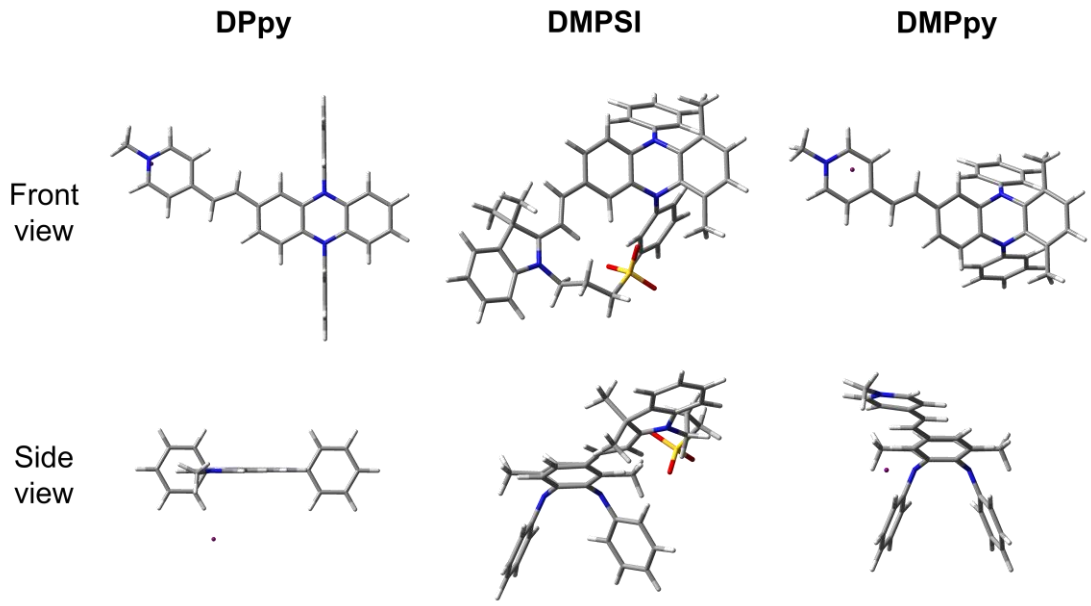


Fig. S8 Full optimized S_0 structures of **DPpy**, **DMPSI** and **DMPpy** from two perspectives, calculated at the M06-2X-D3/6-311G(d,p) level.

Biological Experiments

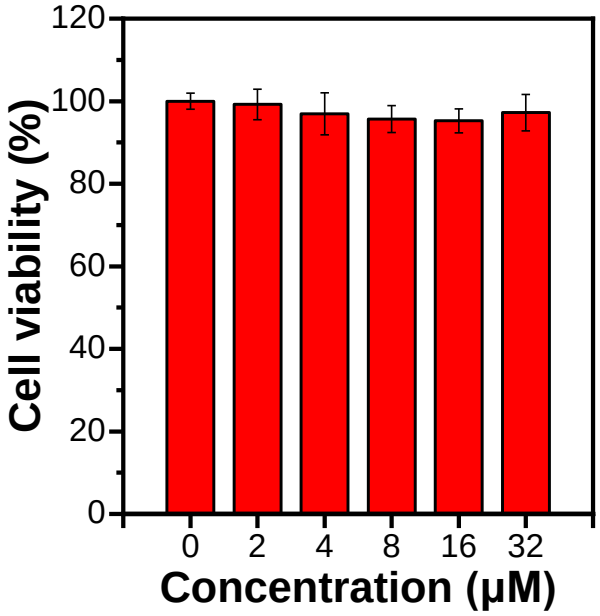


Fig. S9 Relative viabilities of 293T cells after incubation with various concentrations of **DMPpy** for 24 h in dark.

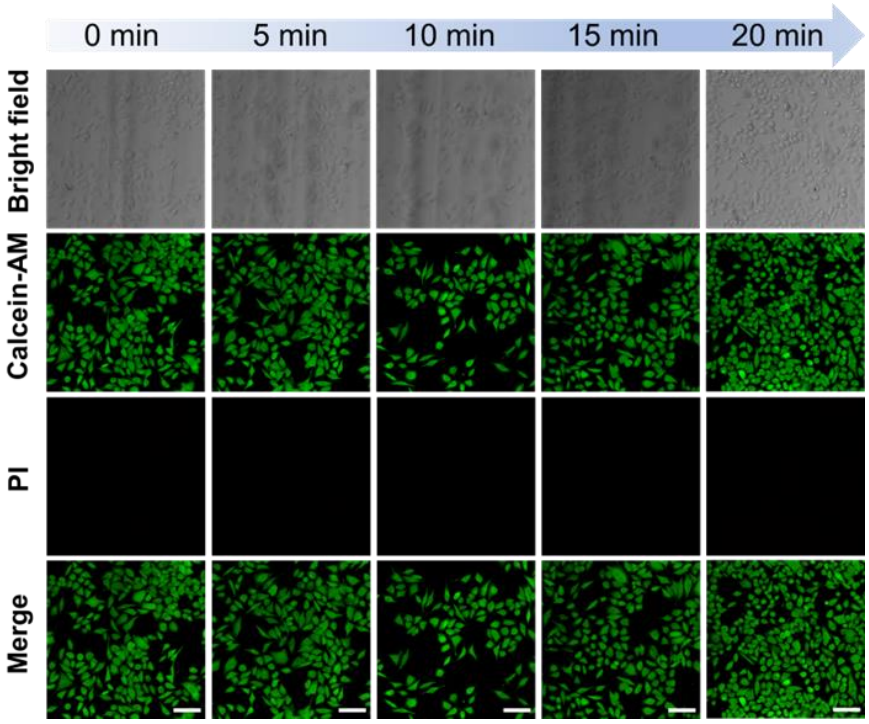


Fig. S10 CLSM images of Hela cells costained with Calcein-AM/PI incubated with PBS after irradiation for 0-20 min under normoxia (21 % O_2). [PI] = 1 μM , E_x = 488 nm, E_m = 600 – 650 nm; [Calcein-AM] = 1 μM, E_x = 488 nm, E_m = 500 – 560 nm. White light: 30 mW·cm^{-2}. Scale bar = 100 μm.

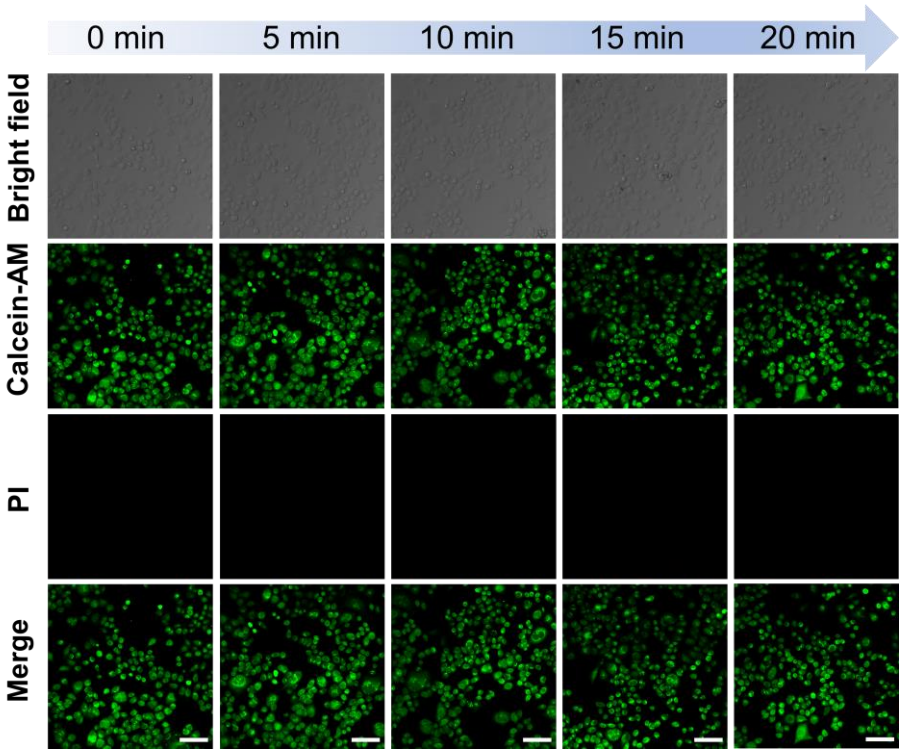


Fig. S11 CLSM of Hela cells costained with Calcein-AM/PI incubated with PBS after irradiation for 0-20min under hypoxia (8 % O_2). [PI] = 1 μM , E_x = 488 nm, E_m = 600 – 650 nm; [Calcein-AM] = 1 μm, E_x = 488 nm, E_m = 500 – 560nm. White light: 30 mW·cm^{-2}. Scale bar = 100 μm.

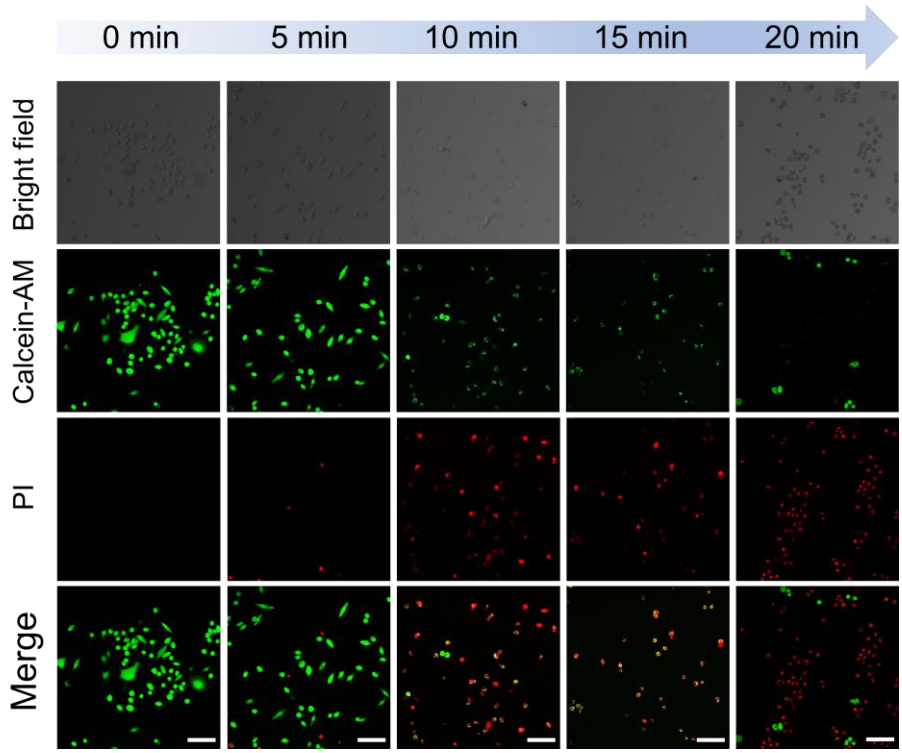


Fig. S12 CLSM images of Hela cells costained with Calcein-AM/PI incubated with **DMPpy** after irradiation for 0-20min under hypoxia (1 % O_2). [PI] = 1 μM , E_x = 488 nm, E_m = 600 – 650 nm; [Calcein-AM] = 1 μM, E_x = 488 nm, E_m = 500 – 560 nm. White light: 30 mW·cm^{-2}. Scale bar = 100 μm.

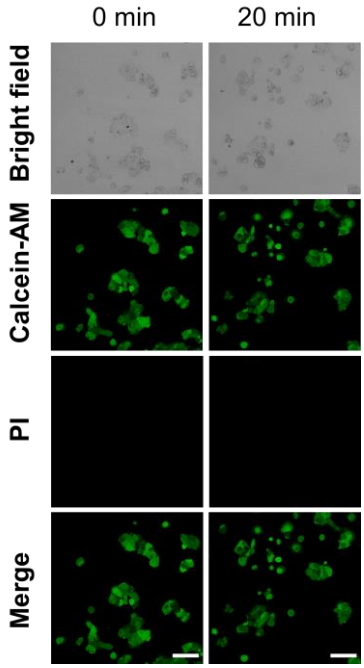


Fig. S13 CLSM iamges of MCF-7 cells costained with Calcein-AM/PI incubated with PBS after irradiation for 0 and 20 min under hypoxia (1 % O_2). [PI] = 1 μM , E_x = 488 nm, E_m = 600 – 650 nm; [Calcein-AM] = 1 μM, E_x = 488 nm, E_m = 500 – 560 nm. White light: 30 mW·cm^{-2}. Scale bar = 100 μm.

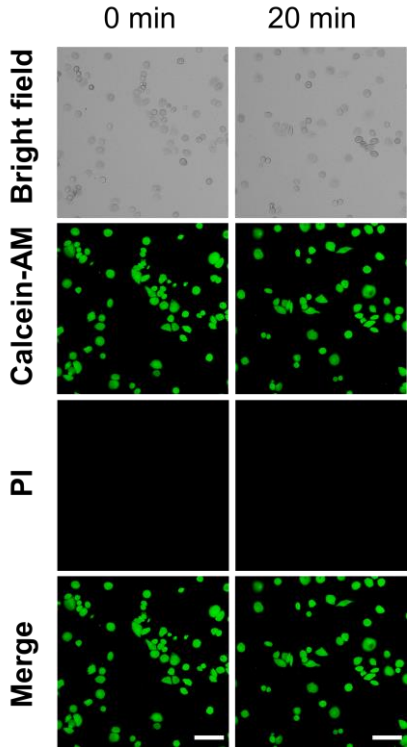


Fig. S14 CLSM iamges of A549 cells costained with Calcein-AM/PI incubated with PBS after irradiation for 0-20 min under hypoxia (1 % O_2). [PI] = 1 μM , E_x = 488 nm, E_m = 600 – 650 nm; [Calcein-AM] = 1 μM, E_x = 488 nm, E_m = 500 – 560 nm. White light: 30 mW·cm^{-2}. Scale bar = 100 μm.

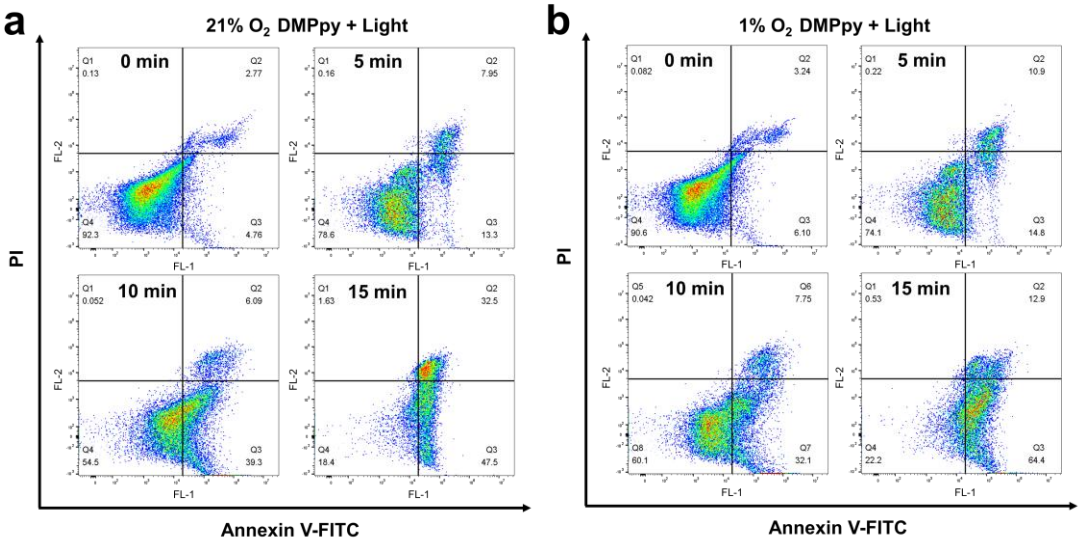


Fig. S15 Flow cytometry profiles for Hela cells treated with **DMPpy** under (a) 21% O_2 or (b) 1% O_2, irradiated for different periods and stained with Annexin V-FITC and PI. White light: 30 mW·cm^{-2}. [**DMPpy**] = 10 μM

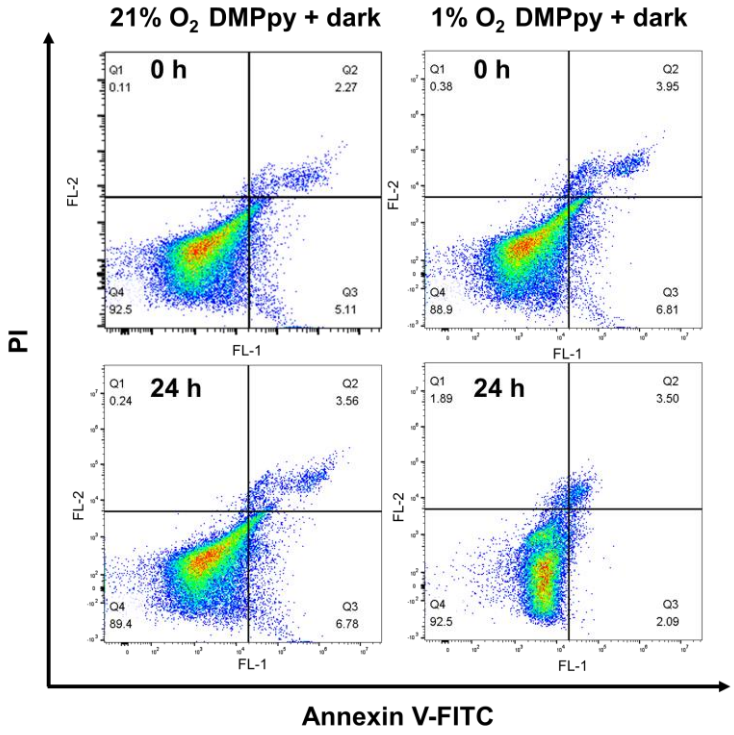


Fig. S16 Flow cytometry profiles for Hela cells treated with **DMPpy** under 21% O_2 or 1% O_2, in dark for 24 h and stained with Annexin V-FITC and PI. [**DMPpy**] = 10 μM.

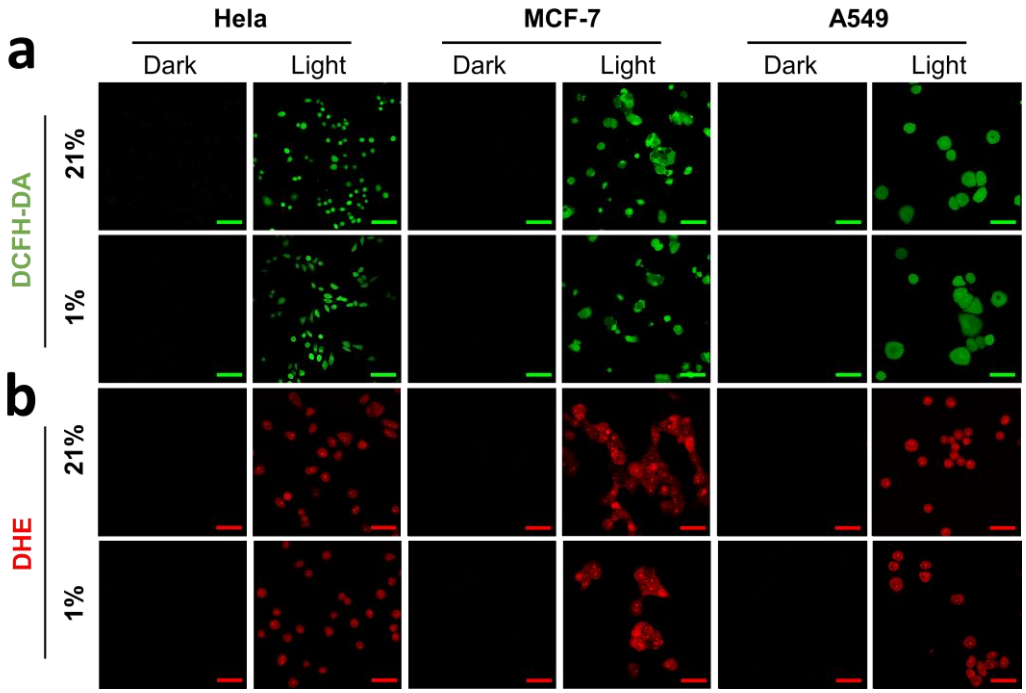


Fig. S17 (a) CLSM images of three types of cells stained with DCFH-DA + DMPpy in normoxia (21 % O_2) and extremely hypoxia (1 % O_2) under dark or light for 10min; (b) CLSM images of three types of cells stained with DHE + DMPpy in normoxia (21 % O_2) and extremely hypoxia (1 % O_2) under dark or light for 10min; [DCFH-DA] = 10 μM, Ex = 488 nm, Em = 500–530 nm; [DHE] = 10 μM, Ex = 488 nm, Em = 590–630 nm. White light: 30 mW·cm^{-2}. Scale bar = 50 μm.

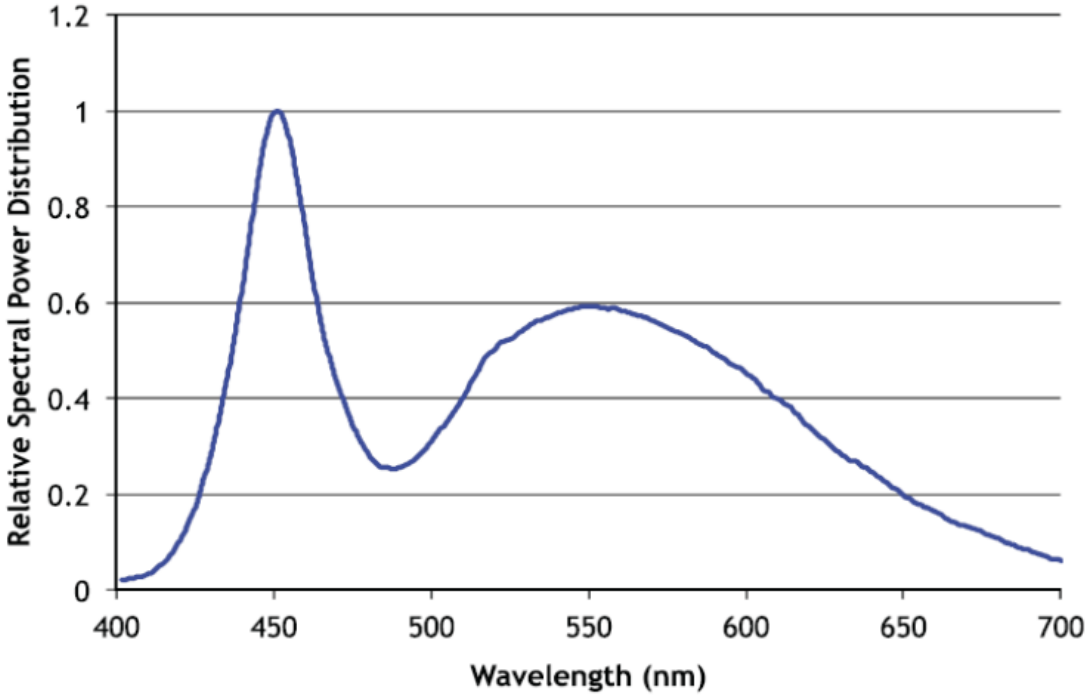


Fig. S18 White spectrum of the light source S5000.

Original Spectral Copy of New Compounds

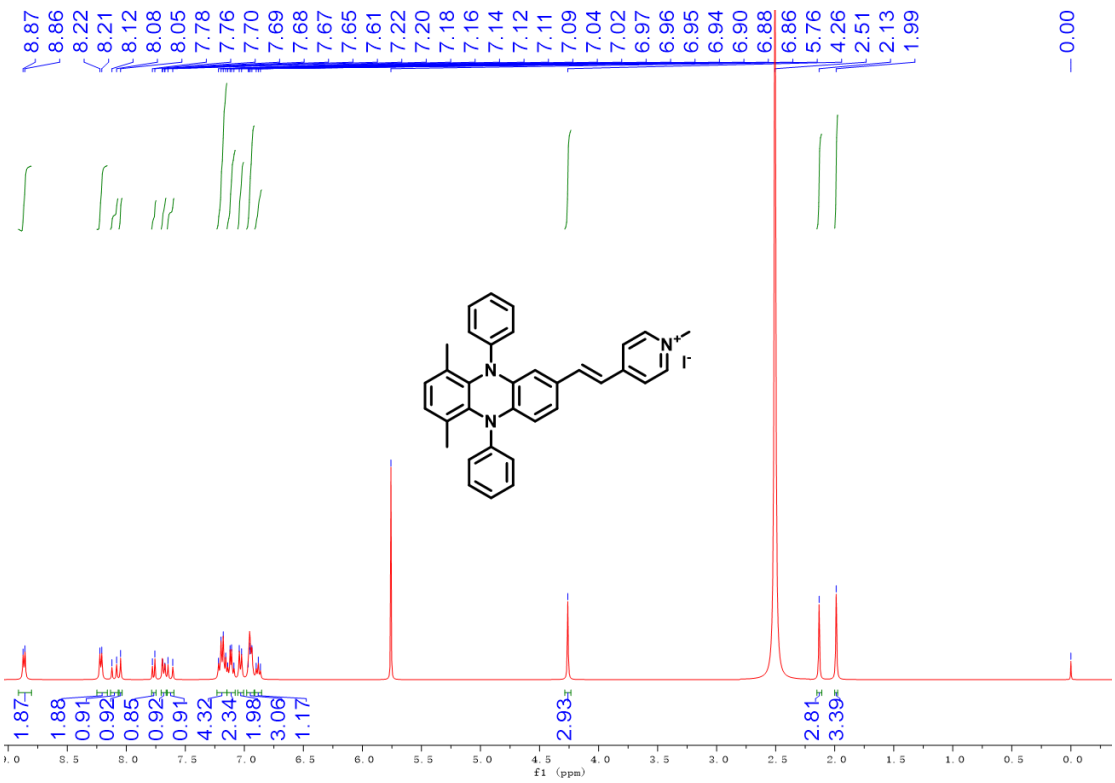


Fig. S19 ^{1}H NMR spectrum of **DMPpy** in DMSO-d_6.

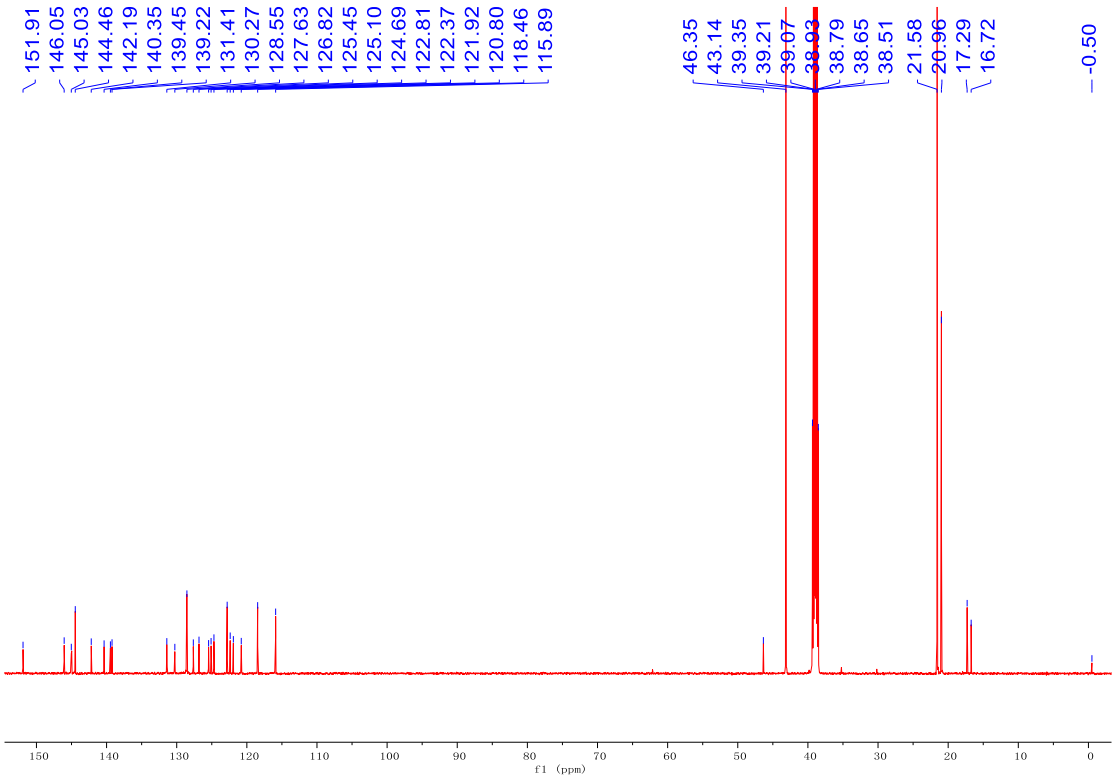


Fig. S20 ^{13}C NMR spectrum of **DMPpy** in DMSO-d_6.

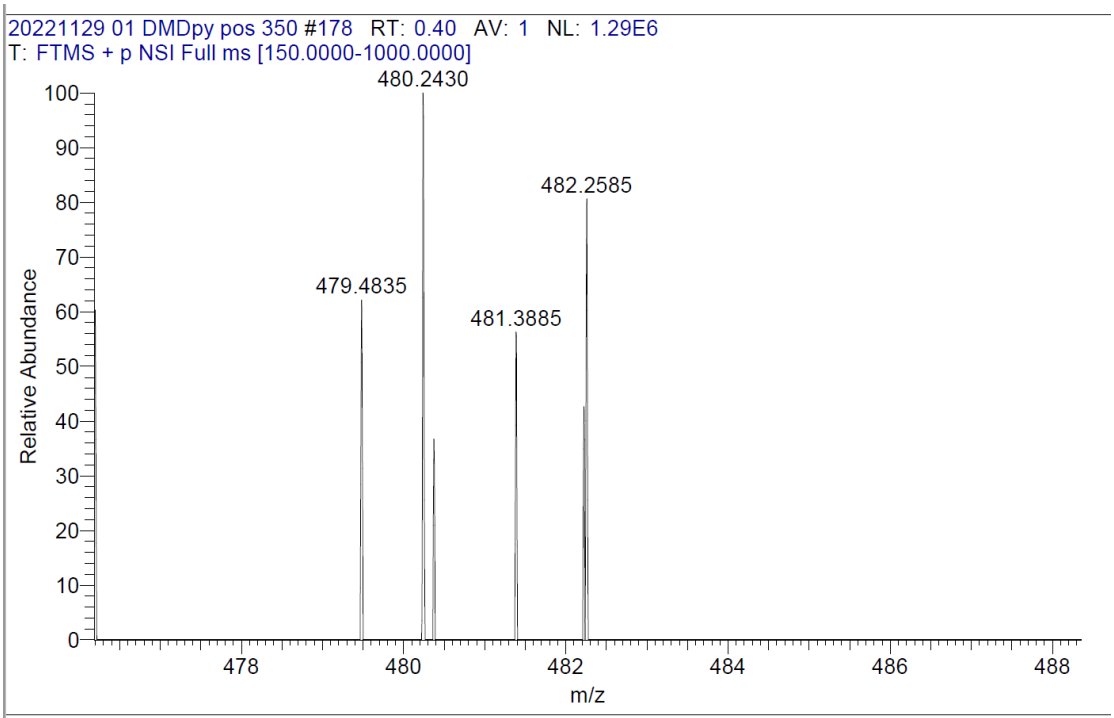


Fig. S21 High resolution mass spectrum of compound **DMPpy**.

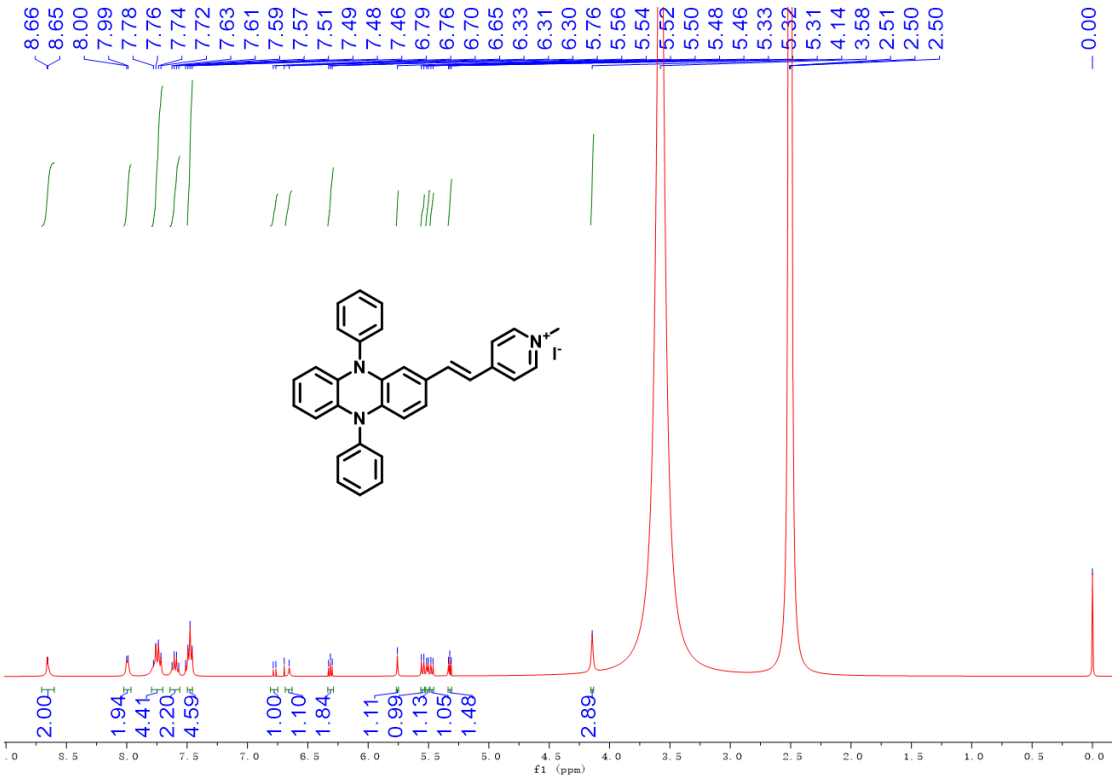


Fig. S22 ^{1}H NMR spectrum of **DPpy** in DMSO-d_6.

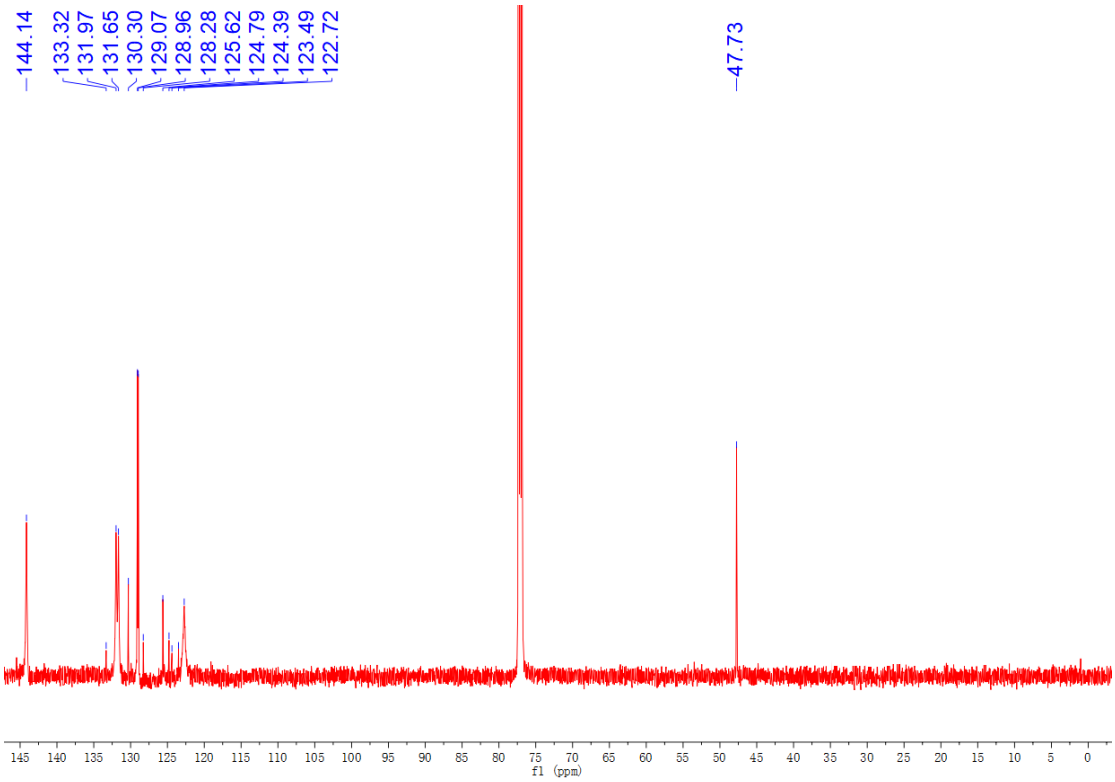


Fig. S23 ^{13}C NMR spectrum of **DPpy** in $CDCl_3$.

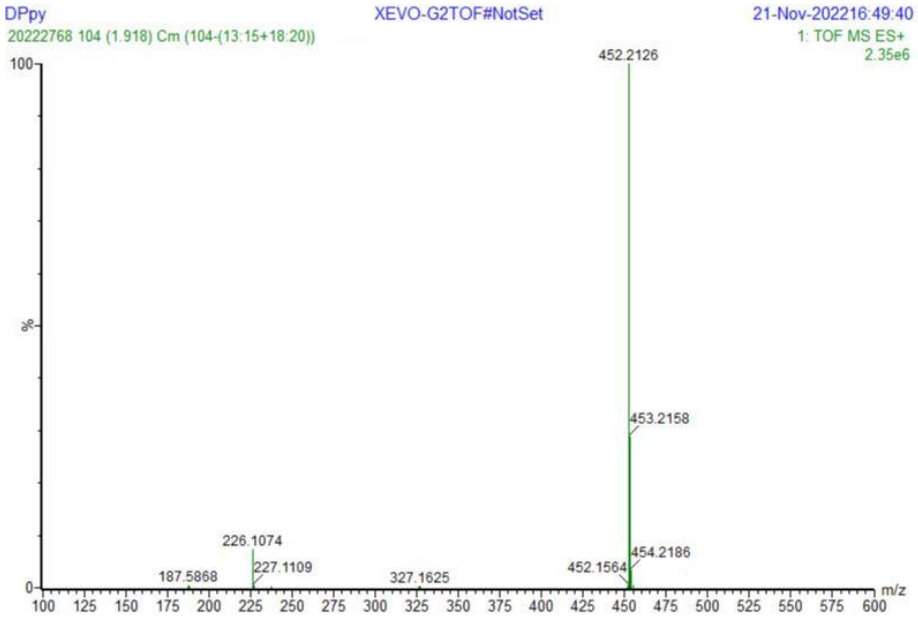


Fig. S24 High resolution mass spectrum of compound **DPpy**.

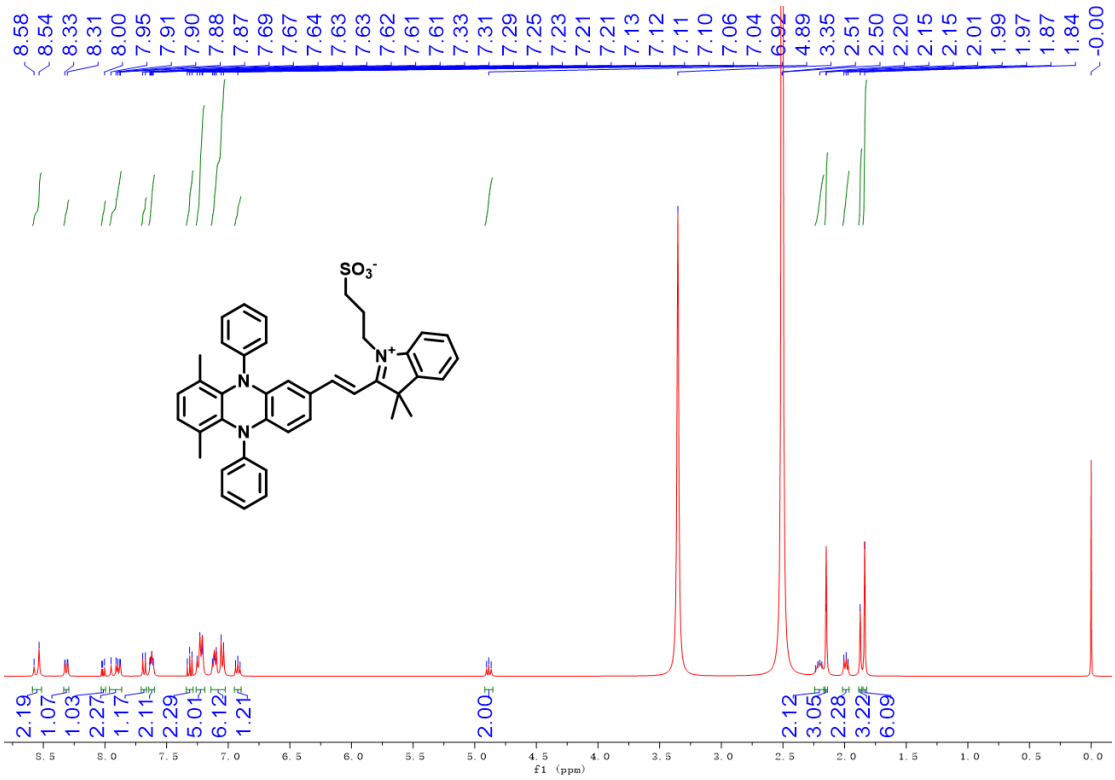


Fig. S25 ^{1}H NMR spectrum of **DMPSI** in DMSO-d_6.

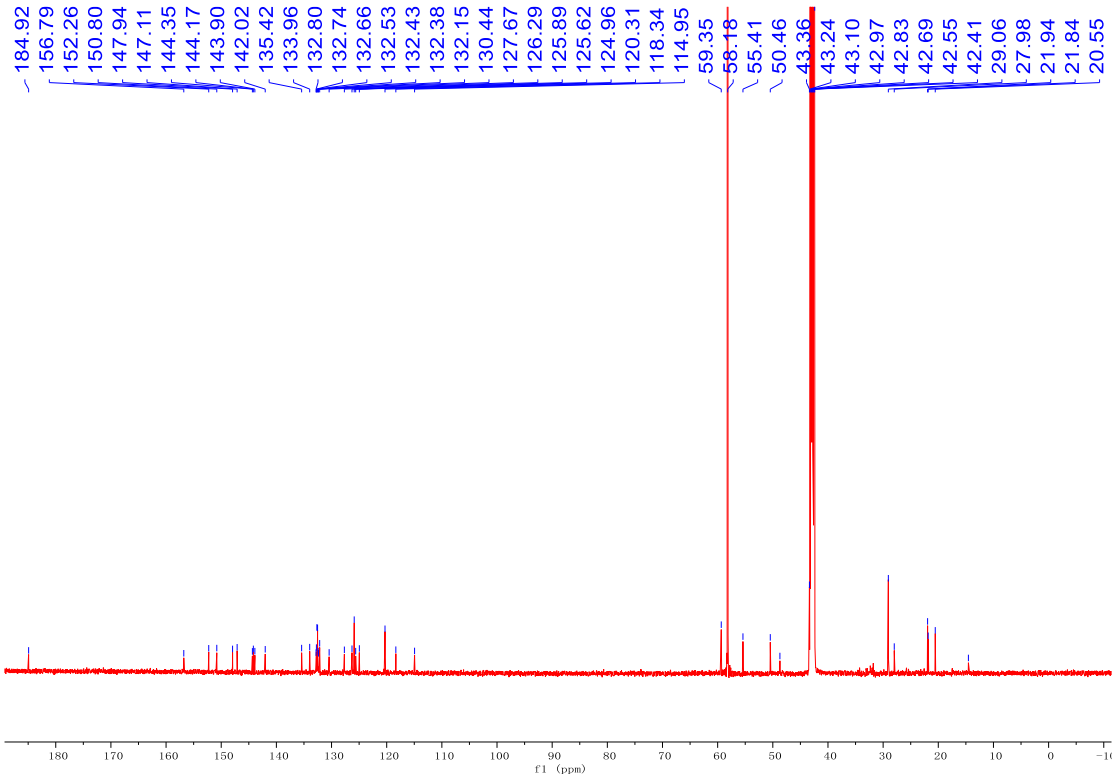


Fig. S26 ^{13}C NMR spectrum of **DMPSI** in DMSO-d_6.

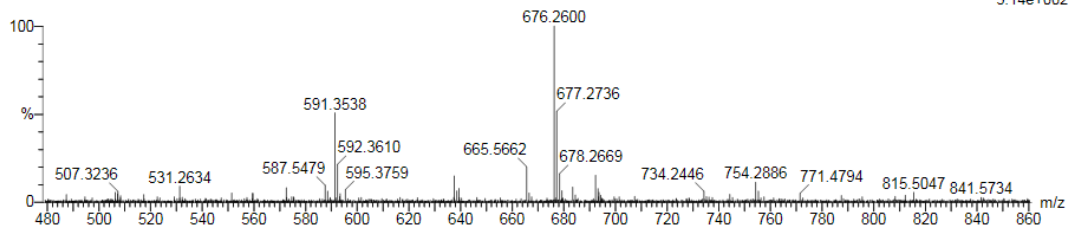
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
45 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-41 H: 0-39 N: 0-3 O: 0-3 S: 0-1 Na: 0-1

JIANLI-HUA
HL-LSF-A12 110 (1.255)

1: TOF MS ES+
3.14e+002



Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
676.2600	676.2610	-1.0	-1.5	23.5	38.4	0.0	C41 H39 N3 O3 S Na

Fig. S27 High resolution mass spectrum of compound **DMPSI**.

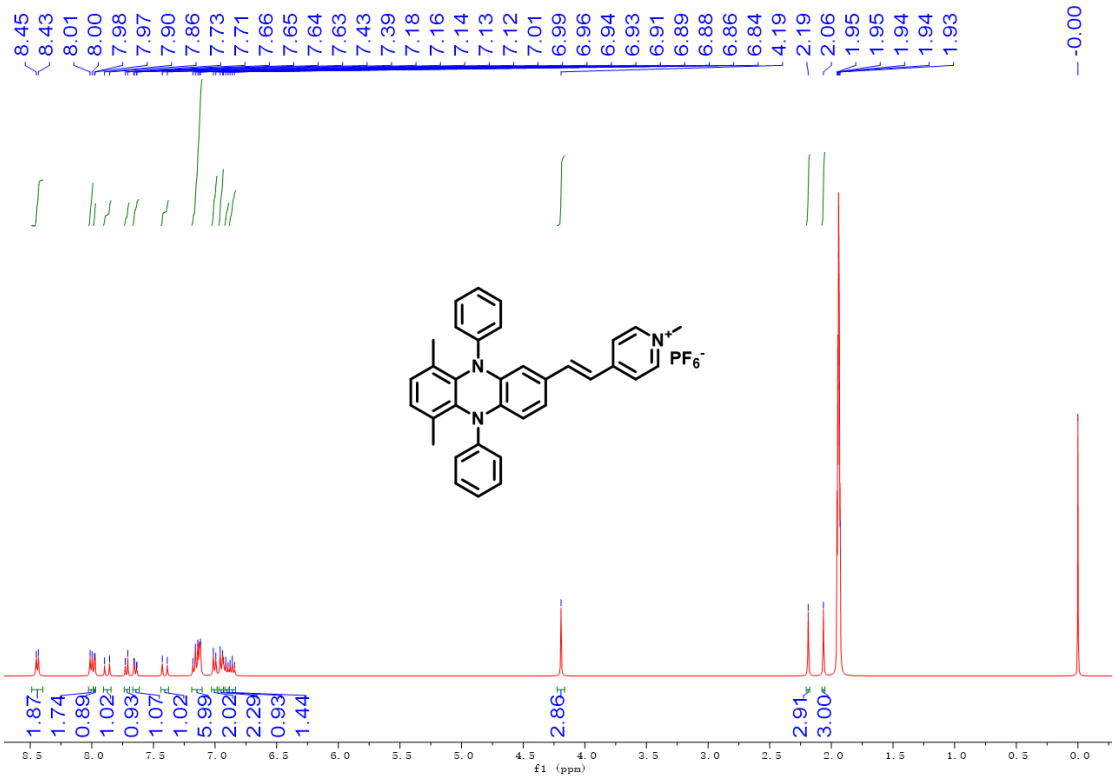


Fig. S28 ^{1}H NMR spectrum of **DMPpy-PF_6** in CD_3CN.

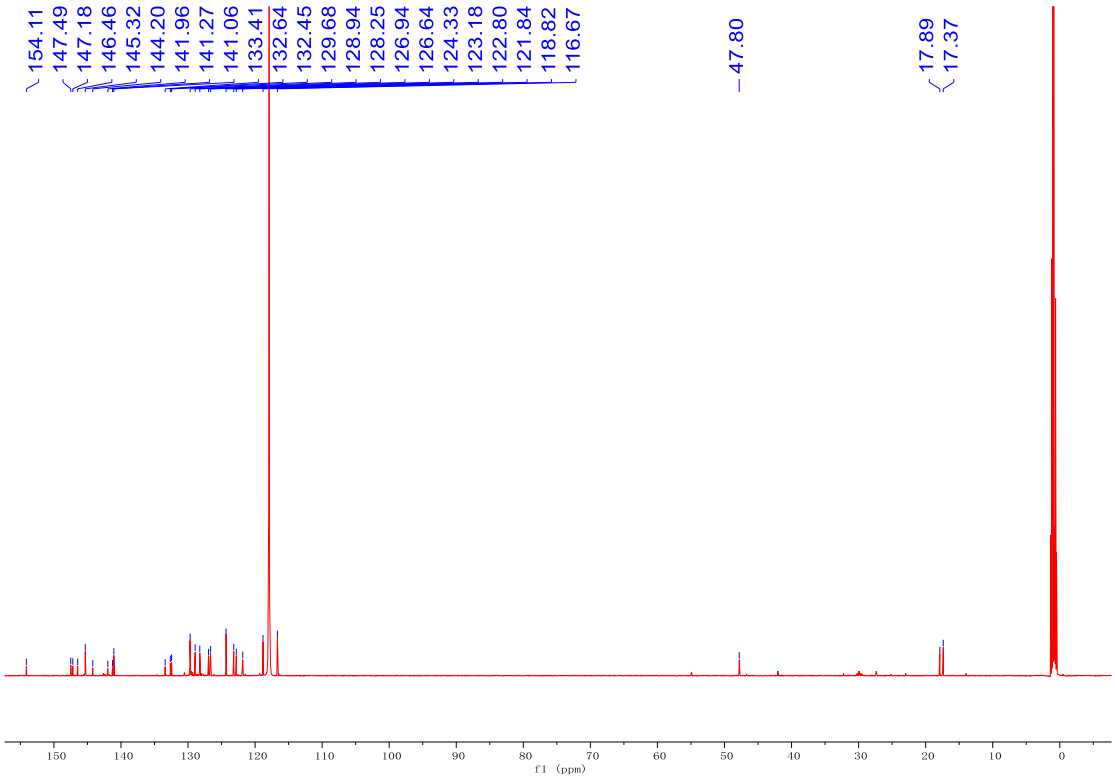


Fig. S29 ^{13}C NMR spectrum of **DMPpy-PF$_6$** in CD_3CN.

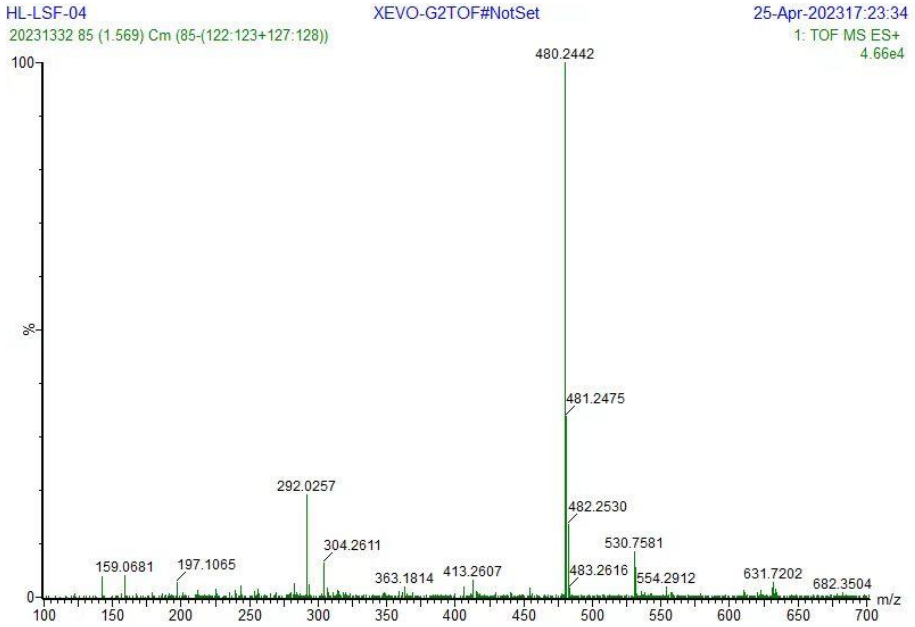


Fig. S30 High resolution mass spectrum of compound **DMPpy-PF$_6$**.

Reference

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