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Regulating donor configuration to develop AIE-active type I photosensitizers for lipid droplet imaging and high-performance photodynamic therapy under hypoxia

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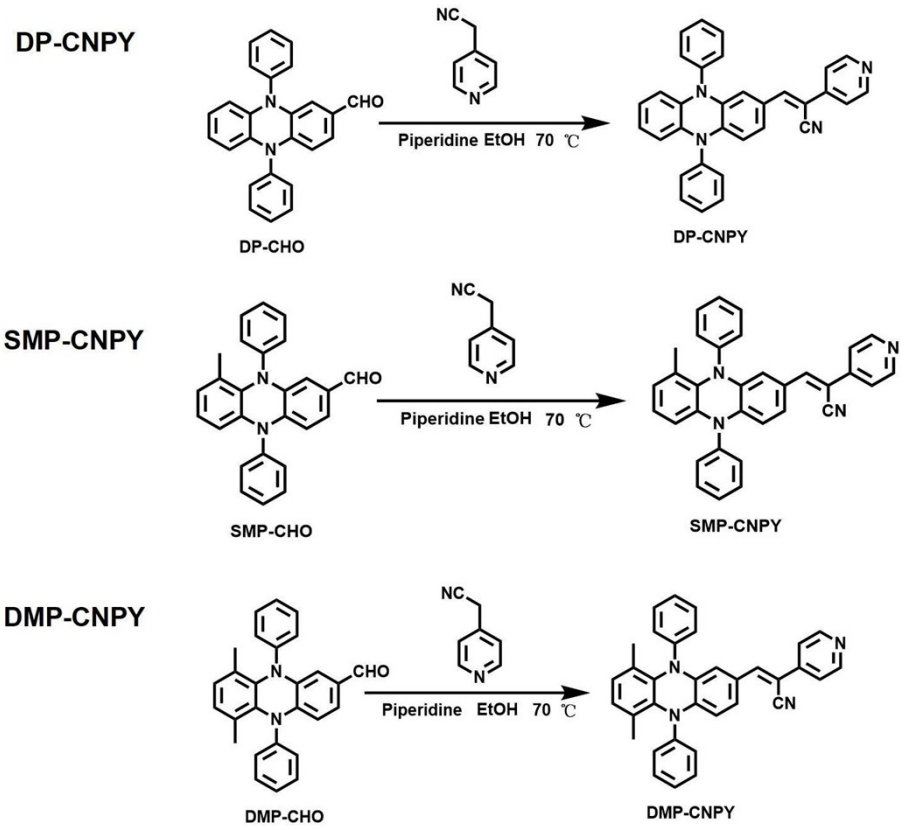
Reagents and measurements

2-(pyridin-4-yl) acetonitrile, ethanol (EtOH), dichloromethane, piperidine, 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). The synthesis of the compound **DMP-CHO** and **DP-CHO** were prepared as reported in the literature.



Scheme S1. Synthesis of **DP-CNPY**, **SMP-CNPY** and **DMP-CNPY**.

Synthesis of **DP-CNPY**, **SMP-CNPY** and **DMP-CNPY**. These compounds are prepared from DP-CHO (100 mg, 0.256 mmol), SMP-CHO (112 mg, 0.256 mmol) and DMP-CHO (116 mg, 0.256 mmol), 2-(pyridin-4-yl) acetonitrile (30 mg, 0.256 mmol) and 2 drops piperidine were dissolved in 10 mL EtOH 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).

(Z)-3-(5,10-diphenyl-5,10-dihydrophenazin-2-yl)-2-(pyridin-4-yl) acrylonitrile (**DP-CNPY)**: Yield = 78.32%. ^{1}H NMR (400Hz, DMSO-d_6) δ 8.54 (d, J = 5.6 Hz, 2H), 7.72 (dt, J = 14.4, 7.9 Hz, 6H), 7.54 – 7.42 (m, 7H), 6.89 (d, J = 6.9 Hz, 1H), 6.41 (s, 1H), 6.37 – 6.27 (m, 2H), 5.59 – 5.46 (m, 3H). ^{13}C NMR (151 MHz, Benzene-d_6) δ 150.22, 142.97, 131.82, 131.36, 130.76, 128.00, 125.71, 122.51, 121.33, 119.16, 113.33, 112.16. HRMS ESI (m/z). [M]+: calcd. for $C_{32}H_{23}N_4$ 463.1923; Found, 463.1929.

(Z)-3-(9-methyl-5,10-diphenyl-5,10-dihydrophenazin-2-yl)-2-(pyridin-4-yl) acrylonitrile (**SMP-CNPY)**: Yield = 80.53%. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.65 (d, J = 5.3 Hz, 2H), 8.11 (d, J = 2.2 Hz, 1H), 7.67 – 7.50 (m, 6H), 7.36 – 7.31 (m, 2H), 7.30 – 7.22 (m, 5H), 7.07 (tt, J = 7.1, 1.5 Hz, 1H), 6.85 (d, J = 7.4 Hz, 2H), 6.25 (d, J = 8.6 Hz, 1H), 6.17 (dd, J = 7.3, 2.3 Hz, 1H), 2.10 (s, 3H). ^{13}C NMR (101 MHz, Methylene Chloride-d_2) δ 150.74, 144.71, 129.62, 129.49, 129.43, 127.94, 127.88, 127.65, 120.59, 120.25, 117.89, 54.40, 54.13, 53.86, 53.59, 53.32, 18.71, 17.96. HRMS ESI (m/z). [M]+: calcd. for $C_{33}H_{25}N_4$ 477.2079; Found, 477.2076.

(Z)-3-(6,9-dimethyl-5,10-diphenyl-5,10-dihydrophenazin-2-yl)-2-(pyridin-4-yl) acrylonitrile (**DMP-CNPY)**: ^{1}H NMR (400 MHz, Chloroform-d) δ 8.72 – 8.67 (m, 2H), 8.14 (d, J = 2.0 Hz, 1H), 7.77 (dd, J = 8.5, 2.0 Hz, 1H), 7.73 (s, 1H), 7.61 – 7.58 (m, 2H), 7.56 (d, J = 8.5 Hz, 1H), 7.19 (dt, J = 15.4, 7.5 Hz, 4H), 7.08 (d, J = 7.7 Hz, 2H), 7.01 (dd, J = 12.4, 8.2 Hz, 5H), 6.98 – 6.90 (m, 1H), 2.16 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (101 MHz, Methylene Chloride-d_2) δ 150.74, 144.71, 129.62, 129.49, 129.43, 127.94, 127.88, 127.65, 120.59, 120.25, 117.89, 54.40, 54.13, 53.86, 53.59, 53.32, 18.71, 17.96. HRMS ESI (m/z). $[M]^+$: calcd. for $C_{34}H_{27}N_4$ 491.2230; Found, 491.2236.

Fluorescence quantum yield measurement

The fluorescence quantum yield (η) of titled compounds in aqueous medium was determined using a fluorescence comparison protocol. Freshly prepared RDM 6G was used as standard (η = 0.95 in water). Firstly, the absorption spectra of titled compounds and RDM 6G in water were recorded by a spectrometer (Agilent Carry 4000). 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 **DP-CNPY**, **SMP-CNPY**, **DMP-CNPY** in buffer solution (DMSO/ PBS=1/99) under white light irradiation (30 mW · cm^{-2}) was detected using 2', 7'-dichlorodihydrofluorescein diacetate (DCFH-DA) as a commercial probe. The concentration of DCFH-DA was 2 μM and the concentration of DHP-based photosensitizers was 2 μM. The fluorescence increase of DCFH-DA at 520 nm was recorded at different irradiation time to obtain the ascent rate of the photosensitizing process.

The singlet oxygen ($^1O_2$) generation measurement of three compounds in buffer solution (DMSO/ PBS=1/99) under white light irradiation (30 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 three compounds was 10 μM. The absorption decrease of ABDA at 380 nm was recorded at different irradiation time to obtain the ascent rate of the photosensitizing process.

The superoxide radicals ($O_2^{-\bullet}$) generation measurement of three compounds in buffer solution (DMSO/PBS = 1/99) under white light irradiation (30 mW·cm^{-2}) was detected using dihydrorhodamine 123 (DHR123) as a commercial probe. The concentration of DHR123 was 10 μM and the concentration of three compounds was 10 μM. The fluorescence increase of DHR123 at 530 nm was recorded at different irradiation time to obtain the ascent rate of the photosensitizing process.

The hydroxy radicals (• OH) generation measurement of three compounds in buffer solution (DMSO/PBS=1/99) under white light irradiation (30 mW·cm^{-2}) was detected using HPF as a

commercial probe. The concentration of HPF was 10 μM and the concentration of three compounds was 10 μM. The fluorescence increase of HPF at 525 nm was recorded at different irradiation time to obtain the ascent rate of the photosensitizing process.

Measurement of singlet oxygen quantum yield

The $^1O_2$ quantum yield of **DP-CNPY**, **SMP-CNPY, DMP-CNPY** in water upon light irradiation (30 mW cm^{-2}) was determined using 9,10-anthracenediyl-bis(methylene) diatonic acid（ABDA）as an indicator and Rose Bengal (RB) as the reference photosensitizer and calculated using the following equation

$$\Phi_{sample} = \Phi_{RB} \frac{K_{sample} \times A_{RB}}{K_{RB} \times A_{sample}}$$

where K_{sample} and K_{RB} are the decomposition rate constants of ABDA in the presence of the sample and RB, respectively. A_{sample} and A_{RB} represent the integration area of absorption bands ranging from 400 to 800 nm of the sample and RB, respectively. Φ_{RB} is the $^1O_2$ quantum yield of RB (Φ_{RB} = 0.75 in water). The natural logarithm of the absorbance ratio (A_0/ A) of ABDA at 380 nm was plotted against irradiation time and the slope is regarded as the decomposition rate. The concentration of ABDA and three compounds was 100 x 10^{-6} M and 1 x 10^{-5} M, respectively. $K_{DP\text{-}CNPY}$, $K_{SMP\text{-}CNPY}$, $K_{DMP\text{-}CNPY}$ and K_{RB} were calculated as 0.000113, 0.000610, 0.000134, 0.0023, $A_{DP\text{-}CNPY}$ and A_{RB} at 550 nm were 0.0891 and 0.0134, $A_{SMP\text{-}CNPY}$ and A_{RB} at 450 nm were 0.0334 and 0.0139, respectively, and $A_{DMP\text{-}CNPY}$ and A_{RB} at 420 nm were 0.0548 and 0.0136 (Fig. 3b; Fig. S4), respectively. The $^1O_2$ quantum yields of three compounds in water were 0.54%, 8.28% and 1.08%, respectively.

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[2] with the (TD)M06-2X-D3 function[3] and the standard 6-311G (d, p) basic settings in the Gaussian 16 program.[4]

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 ℃ 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 **SMP-CNPY** NPs (60 μg • mL^{-1}) was added into the cell dishes. After incubation for 1 h, cells were washed with 1× PBS and co-stained for 30 min with BODIPY 505/515 (5 μg·mL^{-1}) or Lyso Tracker Green (2 μM). 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 commercial fluorophores. The excitation laser was at 490 nm and the emissions were collected within 650-750 nm for **SMP-CNPY** NPs. The Pearson's correlation coefficient was calculated by ImageJ.

Cytotoxicity of SMP-CNPY NPs 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 **SMP-CNPY** NPs 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·cm^{-2}). After irradiation, the cells were again incubated for 12 h. Then, 100 μL CCK-8 solution (0.1 mg·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·mL^{-1}, streptomycin 10 mg·mL^{-1}) for 24 h (37 ℃, 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 **SMP-CNPY** NPs 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, 30, 60, 90 and 120 μg • mL^{-1}) of **SMP-CNPY** NPs in the dark for 24 h and then irradiated for 0-10 min. The white light irradiation source intensity was 30 mW·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 **SMP-CNPY** NPs 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 DCF and emits bright green fluorescence in the presence of ROS. 4T1 cells were planted onto 35 mm confocal dishes at a density of 1×10^5 cells and cultured for 24 h at 37 ℃ under 5% CO_2. The cells were then incubated with 60 μg • mL^{-1} **SMP-CNPY** NPs 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·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 ℃ under hypoxic.

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 60 μg • mL^{-1} **SMP-CNPY** NPs for 4 h followed by white light at a light dose of 30 $mW \cdot cm^{-2}$ 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.

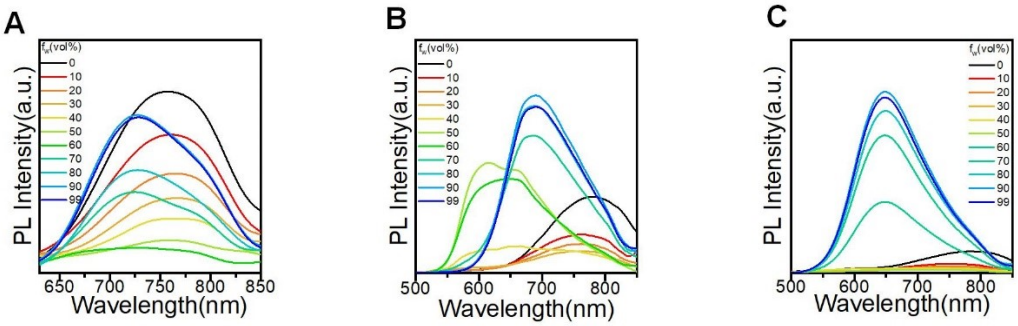


Fig. S1. PL spectra of **DP-CNPY** (A), **SMP-CNPY** (B) **and DMP-CNPY** (C) in a mixture of DMSO/water with different values.

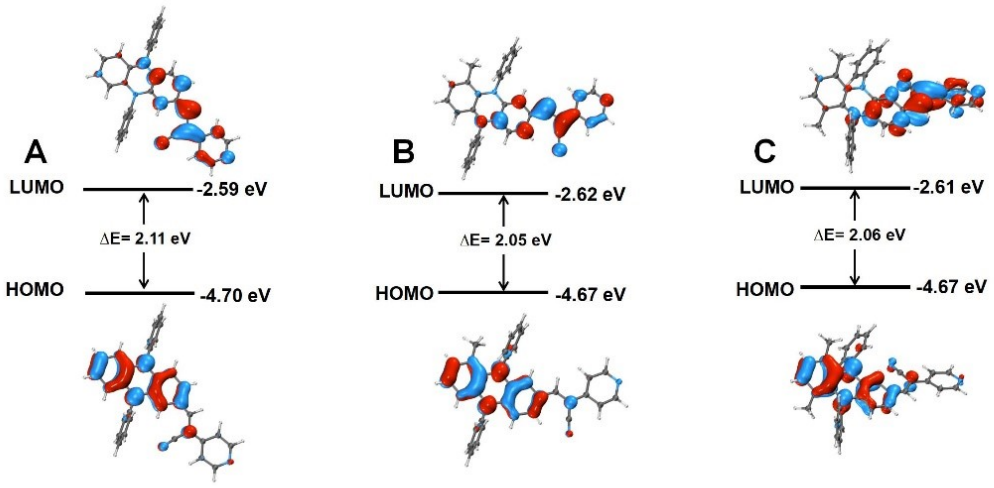


Fig. S2. HOMO-LUMO energy levels at the optimized S_1 geometries (A) **DP-CNPY, (B) SMP-CNPY, (C) DMP-CNY.**

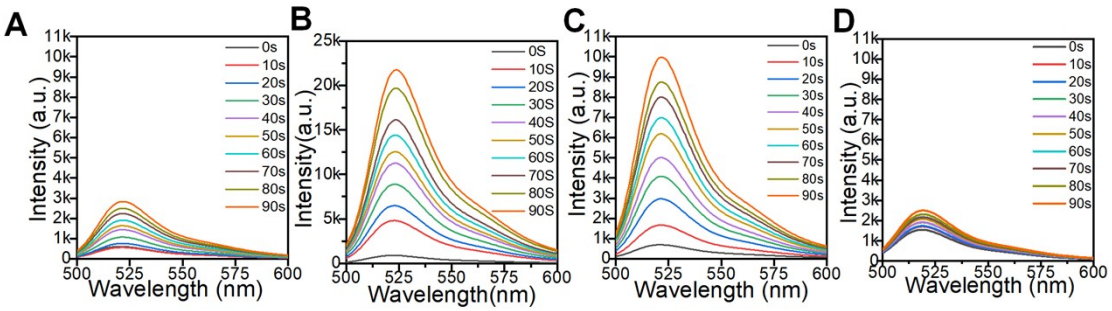


Fig. S3. PL spectra of DCFH-DA mixed with PSs in solution and aggregates under light irradiation for different time, (A-D) **DP-CNPY**, **SMP-CNPY**, **DMP-CNPY**, DCFH-DA in DMSO/PBS mixture (v/v = 1:99). [PSs] = 10 × 10^{-6} M, [DCFH-DA] = 5×10^{-6} M, white light power: 30mW· cm^{-2}.

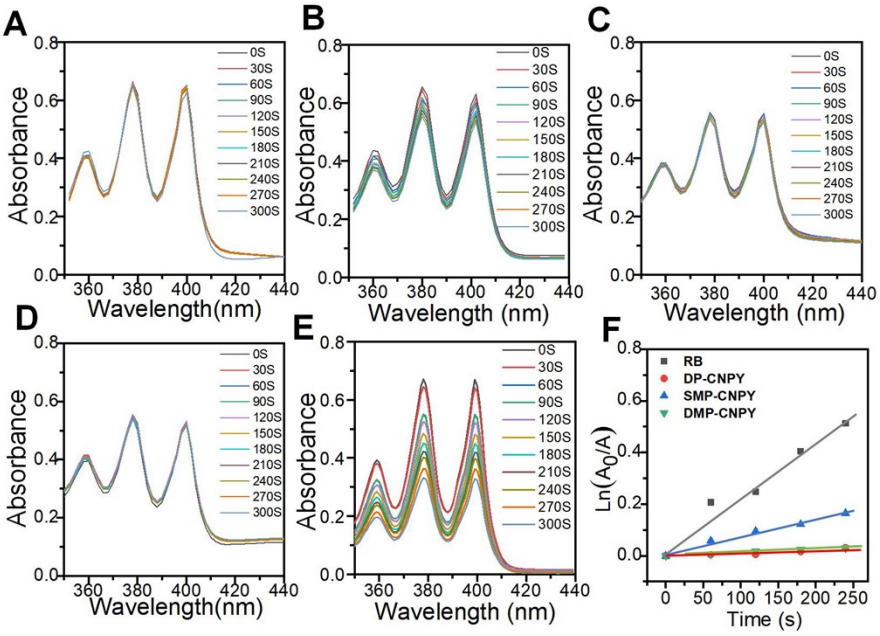


Fig. S4. Absorption spectra of ABDA mixed with PSs solution under light irradiation for different time: (A-E) **DP-CNPY**, **SMP-CNPY**, **DMP-CNPY**, ABDA, RB in DMSO/PBS mixture (v/v = 1:99). [PSs] = 10×10^{-6} M, [ABDA] = 10×10^{-5} M, white light power: 30 mW· cm^{-2}. (F) The natural logarithm of absorbance ratio of ABDA at 380 nm in **DP-CNPY, SMP-CNPY, DMP-CNPY**, RB solution for different durations with the same light irradiation.

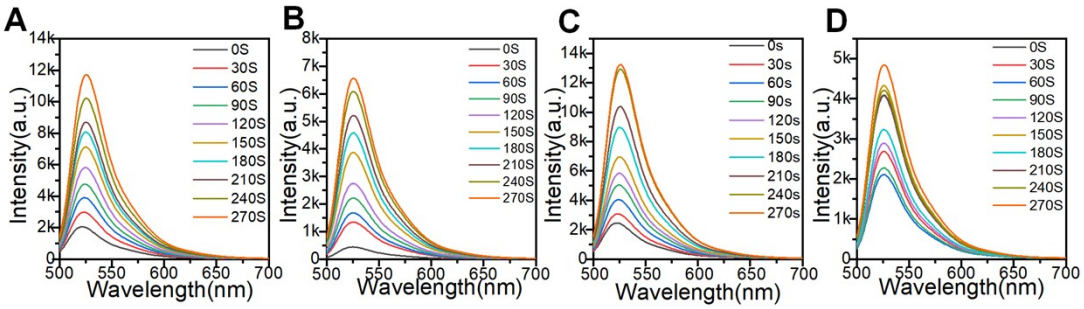


Fig. S5. PL spectra of DHR123 mixed with PSs in solution and aggregates under light irradiation for different time, (A-D) **DP-CNPY**, **SMP-CNPY**, **DMP-CNPY**, DHR123 in DMSO/PBS mixture (v/v = 1:99). [PSs] = 10×10^{-6} M, [DHR123] = 10×10^{-6} M, white light power: 30mW·cm^{-2}.

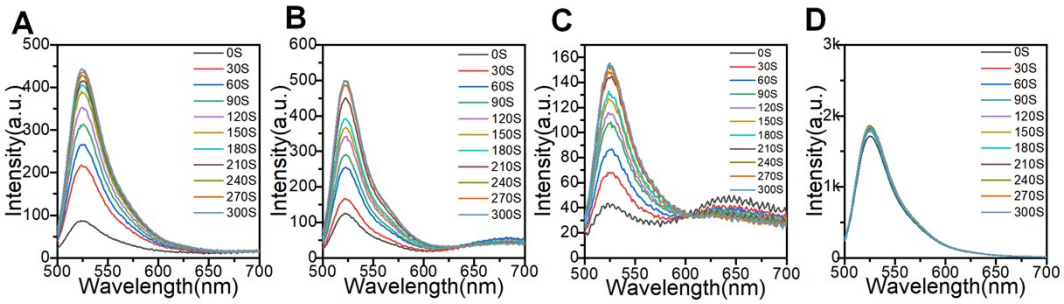


Fig. S6. PL spectra of HPF mixed with PSs in solution and aggregates under light irradiation for different time, (A-D) **DP-CNPY**, **SMP-CNPY**, **DMP-CNPY**, HPF in DMSO/PBS mixture (v/v=1:99). [PSs] = 10 × 10^{-6} M, [HPF] = 10×10^{-6} M, white light power: 30mW·cm^{-2}.

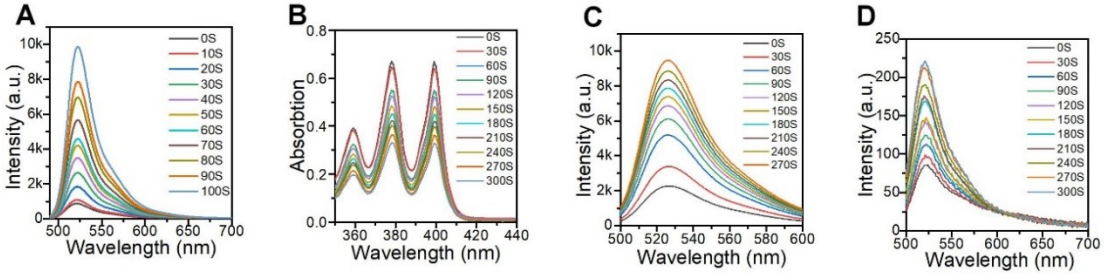


Fig. S7. PL spectra of DCFH-DA(A), DHR123(C), HPF(D) and absorption spectra of ABDA(B) mixed with **RB** in solution and aggregates under light irradiation for different time. [**RB**] = 10 × 10^{-6} M, [DCFH-DA] = 5×10^{-6} M, [ABDA] = 10 × 10^{-5} M, [DHR123] = 10×10^{-6} M, [HPF] = 10×10^{-6} M, white light power: 30mW·cm^{-2}.

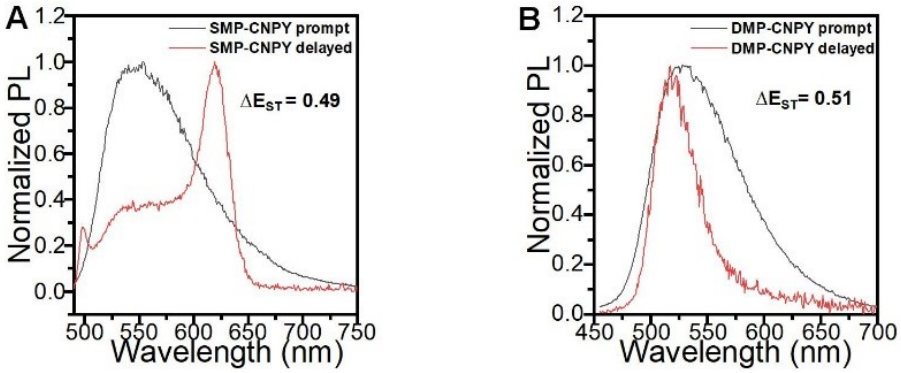


Fig. S8. Low-temperature fluorescent and phosphorescent spectra of emitters in 2Me-THF: (A) **SMP-CNPY**, (B) **DMP-CNPY.** Concentration: 10^{-5} M.

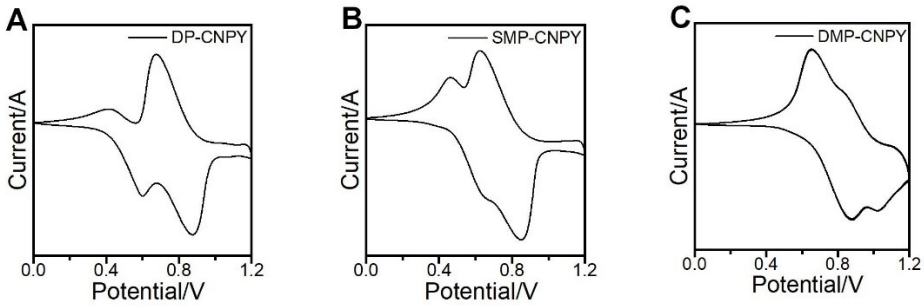


Fig. S9. Cyclic voltammetry gram of **DP-CNPY** (A), **SMP-CNPY** (B), **DMP-CNPY** (C) in DCM.

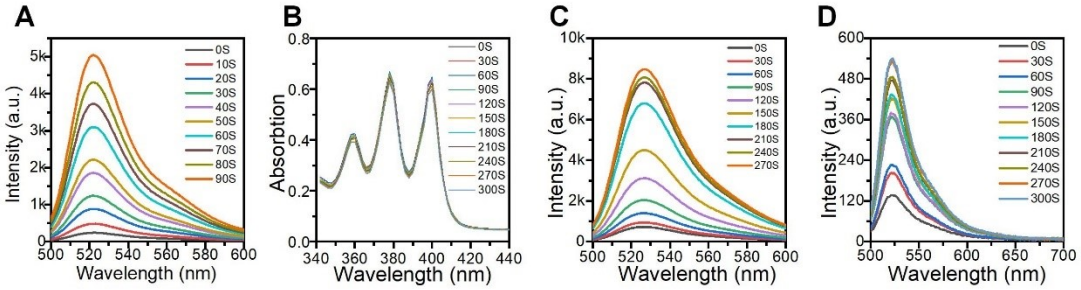


Fig. S10. PL spectra of DCFH-DA (A), DHR123 (C), HPF (D) and absorption spectra of ABDA (B) mixed with **SMP-CNPY** NPs in solution and aggregates under light irradiation for different time. [**SMP-CNPY** NPs] =60 μg·mL^{-1}, [DCFH-DA] = 5×10^{-6} M, [ABDA] = 10 × 10^{-5} M, [DHR123] = 10×10^{-6} M, [HPF] = 10×10^{-6} M, white light power: 30mW·cm^{-2}.

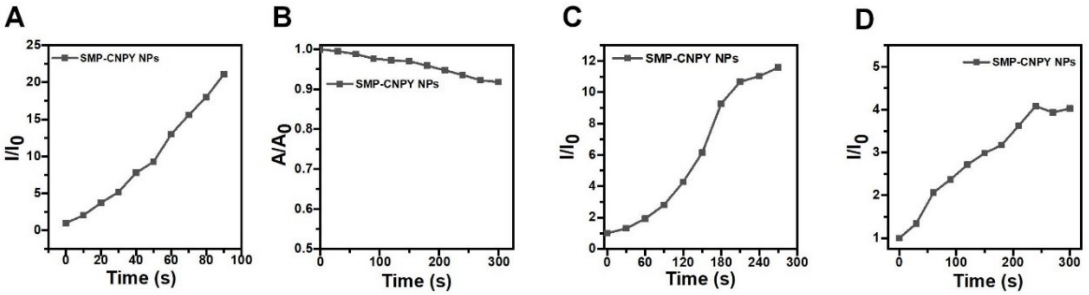


Fig. S11. Line chart of DCFH-DA(A), DHR123(C), HPF(D) and absorption spectra of ABDA(B) mixed with **SMP-CNPY** NPs in solution and aggregates under light irradiation for different time. [**SMP-CNPY** NPs] = 60 μg·mL^{-1}, [DCFH-DA] = 5×10^{-6} M, [ABDA] = 10 × 10^{-5} M, [DHR123] = 10×10^{-6} M, [HPF] = 10×10^{-6} M, white light power: 30mW·cm^{-2}.

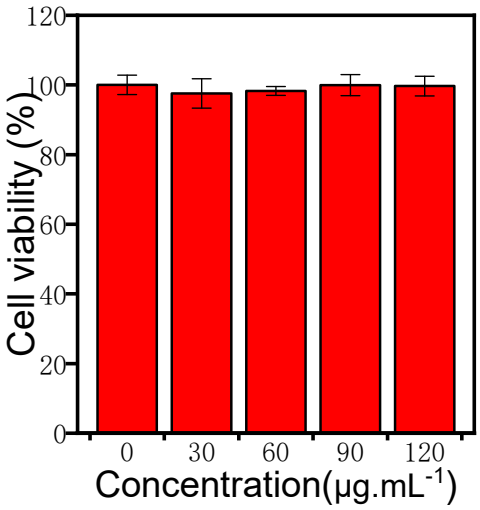


Fig. S12. Relative viabilities of 4T1 cells after incubation with various concentrations of **SMP-CNPY** NPs for 24 h in dark.

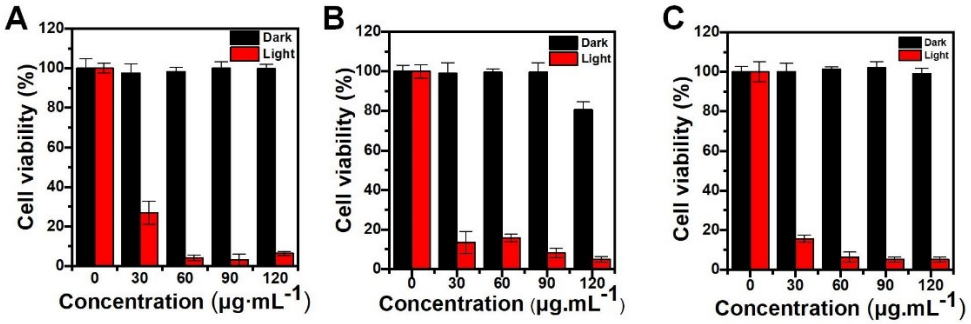


Fig. S13. Cell viability of **SMP-CNPY** NPs (0, 30, 60, 90 and 120 μg.mL^{-1}) treated Hela (A) A549 (B) 4T1 (C) cells under light irradiation or in the dark under normal (21% O_2), time: 15min，White light: 30 mW·cm^{-2}.

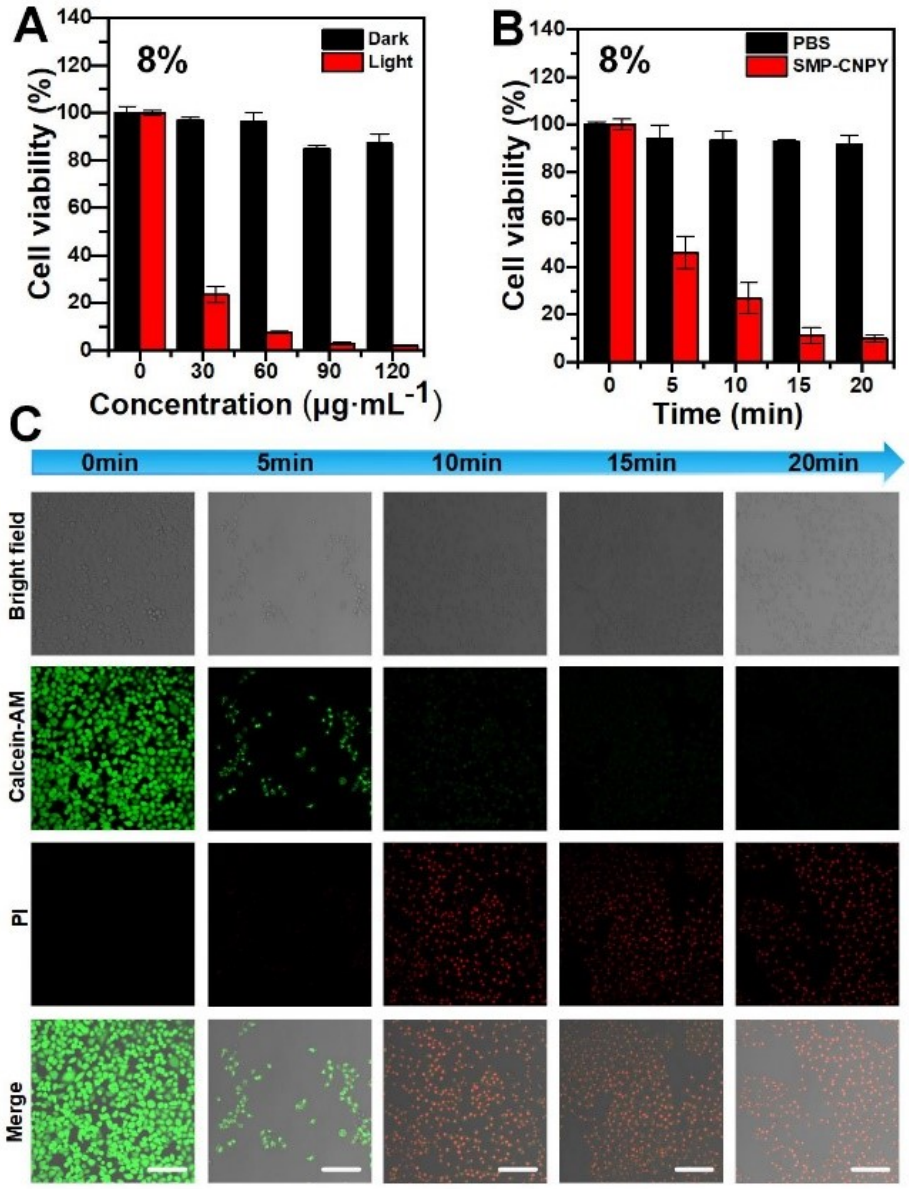


Fig. S14. (A) Cell viability of Hela cells co-incubated with **SMP-CNPY** NPs (0, 30, 60, 90, and 120 μg·mL^{-1}) under light exposure or dark conditions, hypoxic conditions (8%); (B) Cell viability after 0–20 minutes of irradiation of HeLa cells co-cultured with SMP-CNPY NPs (60 μg.mL^{-1}), hypoxic conditions (8%); (C) CLSM image of HeLa cells co-incubated with SMP-CNPY NPs (60 μg·mL^{-1}) after 0-20 minutes of light and then stained with Calcein-AM(1μM)/PI(1μM), hypoxic condition (8%), White light: 30 mW·cm^{-2}. Scale bar = 100 μm.

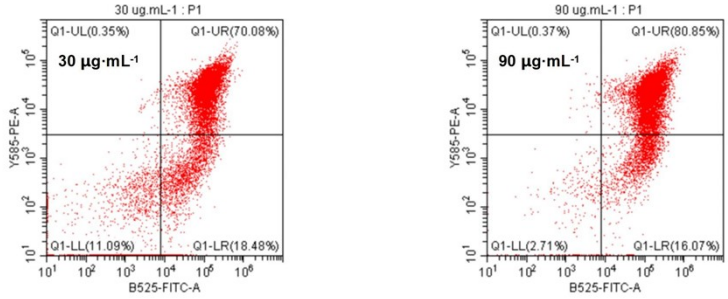


Fig. S15. Flow cytometry profiles for 4T1 cells treated with **SMP-CNPY** under 21% O_2 irradiated for different periods and stained with Annexin V-FITC and PI. White light: 30 mW·cm^{-2}. [**SMP-CNPY**] = 30，90 μg·mL^{-1}

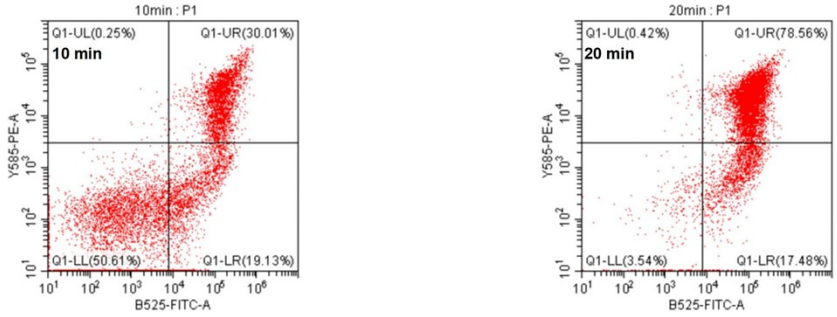


Fig. S16. Flow cytometry profiles for 4T1 cells treated with **SMP-CNPY** under 21% O_2 irradiated for different time and stained with Annexin V-FITC and PI. White light: 30mW·cm^{-2}. [**SMP-CNPY**] = 60 μg·mL^{-1}

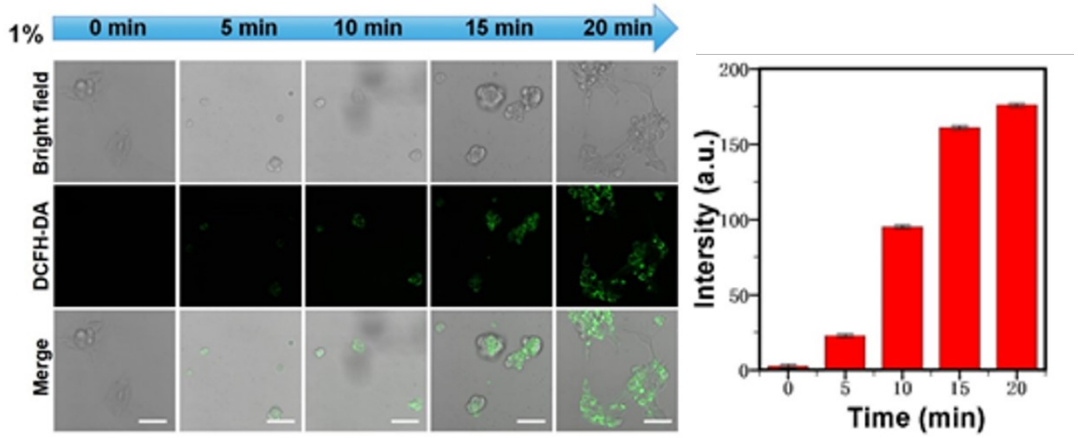


Fig. S17. CLSM images of 4T1 cells stained with DCFH-DA + SMP-CNPY NPs (60 μg·mL^{-1}) in extremely hypoxia (1 % O_2) under dark or light for 5, 10, 15, 20 min; [DCFH-DA] = 10 μM, Ex = 488 nm, Em = 500–530 nm. Scale bar = 50 μm. Average intracellular fluorescence intensity after different times of white light irradiation.

Table S1. Solution (Soln): DMSO, concentration 10^{-5} M, a) Absolute PLQY measured using an integrating sphere; b) fluorescence lifetime; Kr = Φ_F/τ ; Knr = $(1-\Phi_F)/\tau$

Compounds	λ_{abs}	λ_{em}	Φ_F[a] (%)		τ[b] (ns)		K_r (10^7 s^{-1})		K_{nr} (10^7 s^{-1})	
	Soln	Soln	Soln	Powder	Soln	Powder	Soln	Powder	Soln	Powder
DP-CNPY	550	760	0.66	7.61	1.10	6.59	0.60	1.15	90.31	14.02
SMP-CNPY	450	750	4.48	13.27	1.25	2.00	3.58	6.64	89.27	43.27
DMP-CNPY	420	750	1.70	6.03	2.17	0.78	0.78	1.00	45.30	15.61

Table S2. E^{OX} and $E^{OX\ vs\ NHE}$ for **DP-CNPY**, **SMP-CNPY** and **DMP-CNPY**.

	E^{OX} [eV]	$E^{OX\ VS\ NHE}$ [eV]
DP-CNPY	0.524	0.614
SMP-CNPY	0.546	0.636
DMP-CNPY	0768	0.858

Table S3. The energy levels, oscillator strengths (f) and orbital transition analyses of all compounds in ground state. Optimization and excitation were calculated at the (TD) M06-2X-D3/6-311G(d,p) level.

Compounds	Composition	*f*	E_{HOMO}	E_{LUMO}	ΔE
DP-CNPY	97.9% H→ L	0.4320	-4.80 eV	-2.42 eV	2.38 eV
SMP-CNPY	97.0% H→ L	0.3950	-5.40 eV	-2.50 eV	2.90 eV
DMP-CNPY	98.5% H→ L	0.1159	-5.50 eV	-2.66 eV	2.84 eV

Table S4. Calculated emission characteristics of all compounds in the local minimum of the excited state, calculated at the TD-M06-2X-D3/6-311G(d,p) level.

Compounds	Composition	*f*	E_{HOMO}	E_{LUMO}	ΔE
DP-CNPY	99.1% H→ L	0.5519	-4.70 eV	-2.59 eV	2.11 eV
SMP-CNPY	99.1% H→ L	0.4134	-4.67 eV	-2.62 eV	2.05 eV
DMP-CNPY	99.0% H→ L	0.4702	-4.67 eV	-2.61 eV	2.06 eV

Table S5. Crystal data and structure refinement for **DP-CNPY**.

Identification code	2307743	
Empirical formula	C32 H22 N4	
Formula weight	462.53	
Temperature	294.00 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 7.5597(5) Å	α= 90°.
	b = 17.6192(10) Å	β= 92.283(4)°.
	c = 18.0498(11) Å	γ = 90°.
Volume	2402.3(3) $Å^3$	
Z	4	
Density (calculated)	1.279 Mg/m^3	
Absorption coefficient	0.597 mm^{-1}	
F(000)	968	
Crystal size	0.2 x 0.1 x 0.1 mm^3	
Theta range for data collection	3.507 to 68.243°.	
Index ranges	-8<=h<=9, -21<=k<=18, -21<=l<=21	
Reflections collected	28969	
Independent reflections	4289 [R(int) = 0.1141]	
Completeness to theta = 67.679°	98.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7531 and 0.5541	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4289 / 0 / 326	
Goodness-of-fit on F^2	1.045	
Final R indices [I>2sigma(I)]	R1 = 0.0834, wR2 = 0.1665	
R indices (all data)	R1 = 0.1657, wR2 = 0.2011	
Extinction coefficient	0.0011(3)	
Largest diff. peak and hole	0.204 and -0.186 $e.Å^{-3}$	

Table S6. Crystal data and structure refinement for **SMP-CNPY.**

Identification code	2307746	
Empirical formula	$C_{33}H_{24}N_4$	
Formula weight	476.56	
Temperature	293.00 K	
Wavelength	1.54178 Å	
Crystal system	Tetragonal	
Space group	$P4_12_12$	
Unit cell dimensions	a = 9.5261(2) Å	α= 90°.
	b = 9.5261(2) Å	β= 90°.
	c = 54.7827(17) Å	γ = 90°.
Volume	4971.3(3) $Å^3$	
Z	8	
Density (calculated)	1.273 Mg/m^3	
Absorption coefficient	0.591 mm^{-1}	
F(000)	2000	
Crystal size	0.18 x 0.16 x 0.11 mm^3	
Theta range for data collection	3.227 to 68.528°.	
Index ranges	-11<=h<=11, -11<=k<=11, -65<=l<=64	
Reflections collected	110107	
Independent reflections	4571 [R(int) = 0.0941]	
Completeness to theta = 67.679°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7531 and 0.5178	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4571 / 0 / 335	
Goodness-of-fit on F^2	1.070	
Final R indices [I>2sigma(I)]	R1 = 0.0509, wR2 = 0.1275	
R indices (all data)	R1 = 0.0557, wR2 = 0.1321	
Absolute structure parameter	0.43(19)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.157 and -0.271 $e.Å^{-3}$	

Table S7. Crystal data and structure refinement for **DMP-CNPY**.

Identification code	2307751	
Empirical formula	$C_{34}\ H_{26}\ N_4$	
Formula weight	490.59	
Temperature	294.00 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P121/c 1	
Unit cell dimensions	a = 20.5630(14) Å	α= 90°.
	b = 9.8980(10) Å	β= 91.320(4)°.
	c = 12.9388(9) Å	γ = 90°.
Volume	2632.8(4) $Å^3$	
Z	4	
Density (calculated)	1.238 Mg/m^3	
Absorption coefficient	0.572 mm^{-1}	
F(000)	1032	
Crystal size	0.18 x 0.17 x 0.11 mm^3	
Theta range for data collection	2.149 to 68.545°.	
Index ranges	-24<=h<=24, -11<=k<=11, -15<=l<=15	
Reflections collected	35400	
Independent reflections	4770 [R(int) = 0.0542]	
Completeness to theta = 67.679°	98.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7531 and 0.5897	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4770 / 0 / 346	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0468, wR2 = 0.1266	
R indices (all data)	R1 = 0.0506, wR2 = 0.1301	
Extinction coefficient	0.0225(18)	
Largest diff. peak and hole	0.165 and -0.169 $e.Å^{-3}$	

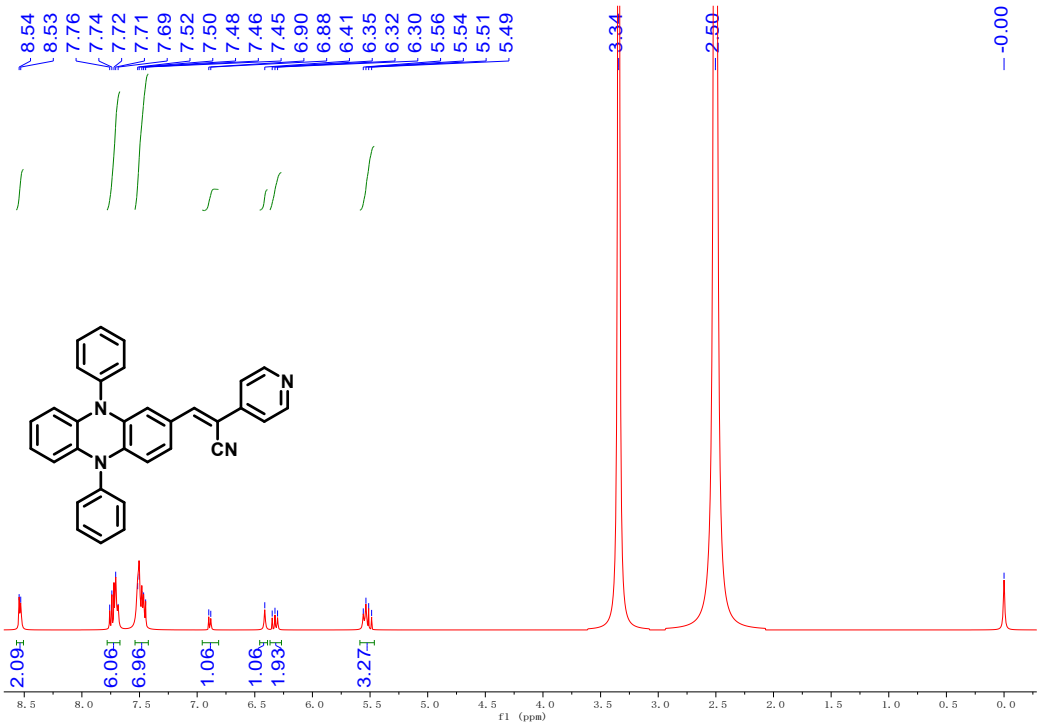


Fig. S18. ^{1}H NMR spectrum of **DP-CNPY** in DMSO-d_6

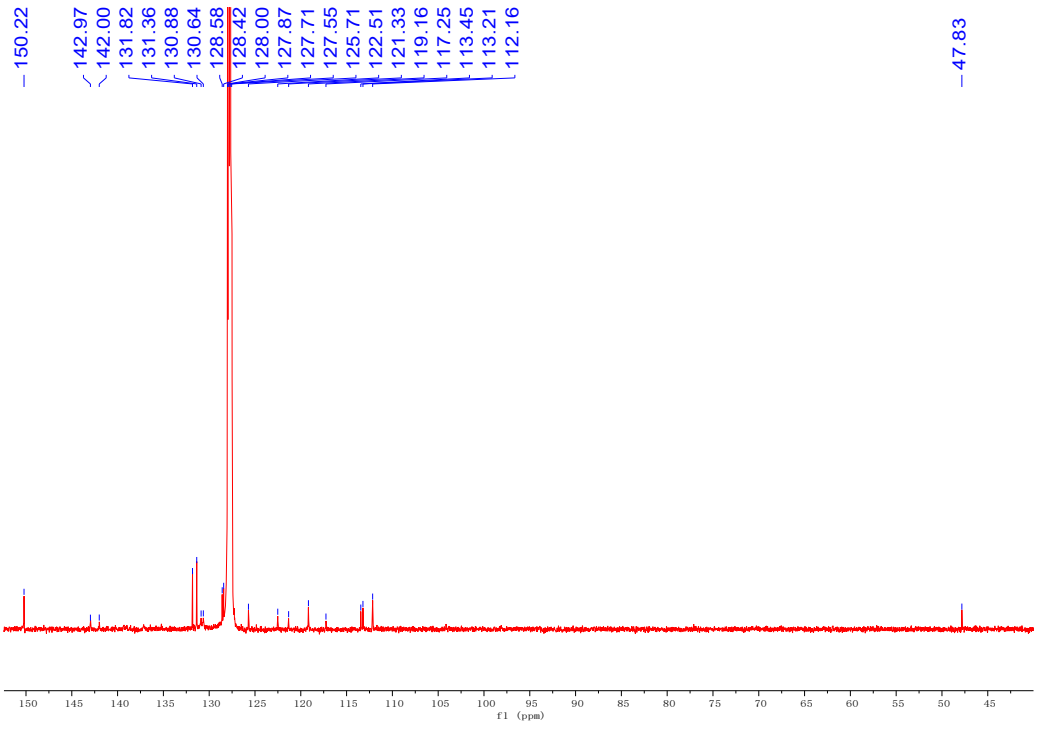


Fig. S19. ^{13}C NMR spectrum of **DP-CNPY** in C_6D_6

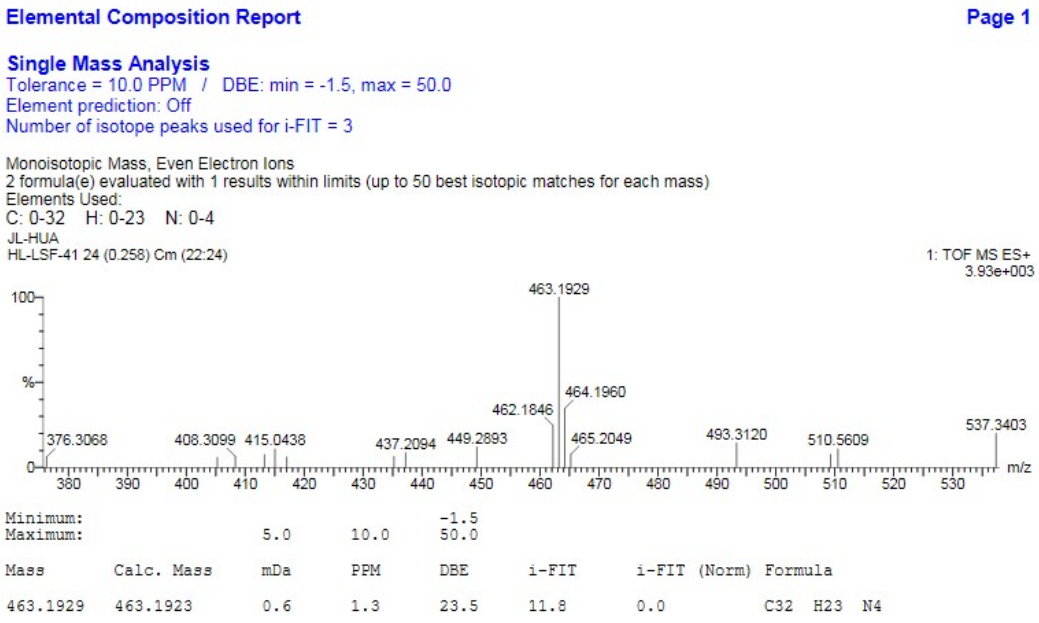


Fig. S20. High resolution mass spectrum of compound **DP-CNPY**.

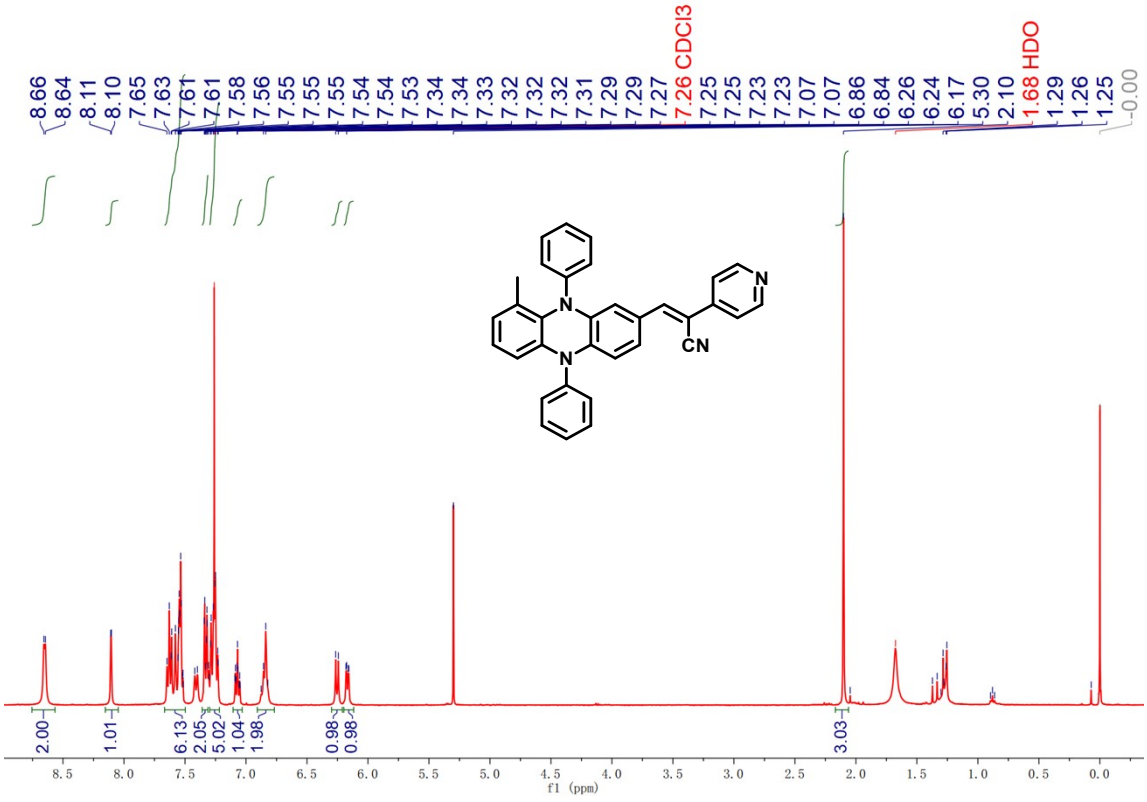


Fig. S21. ^{1}H NMR spectrum of **SMP-CNPY** in $CDCl_3$

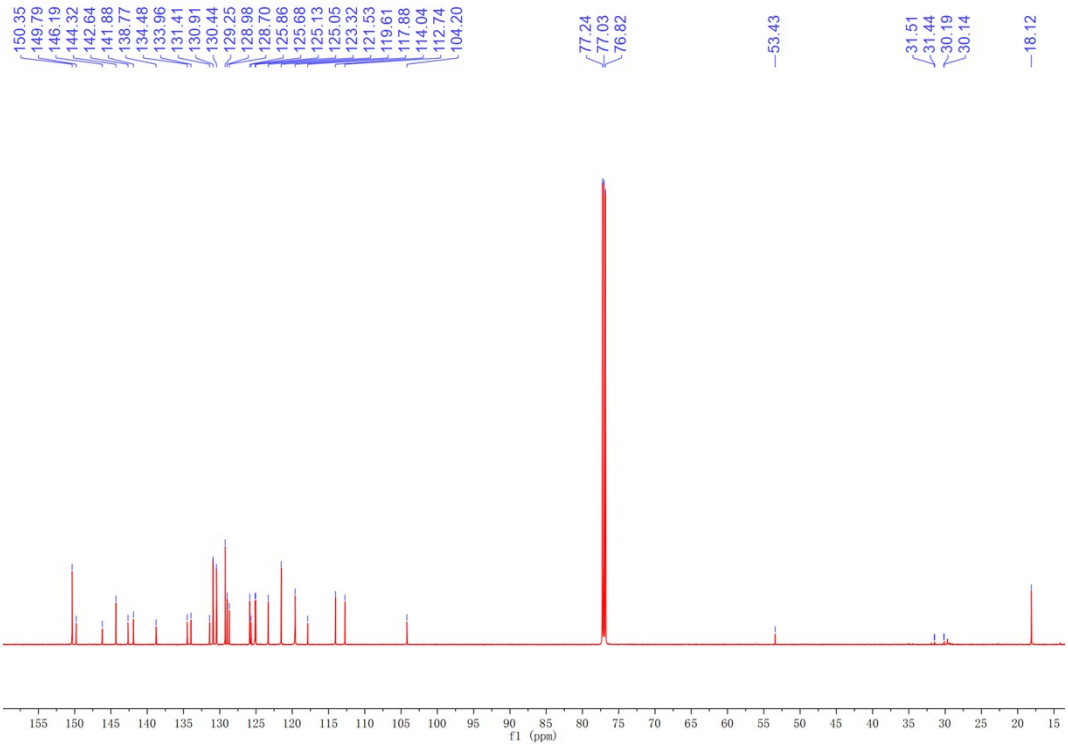


Fig. S22. ^{13}C NMR spectrum of **SMP-CNPY** in $CDCl_3$

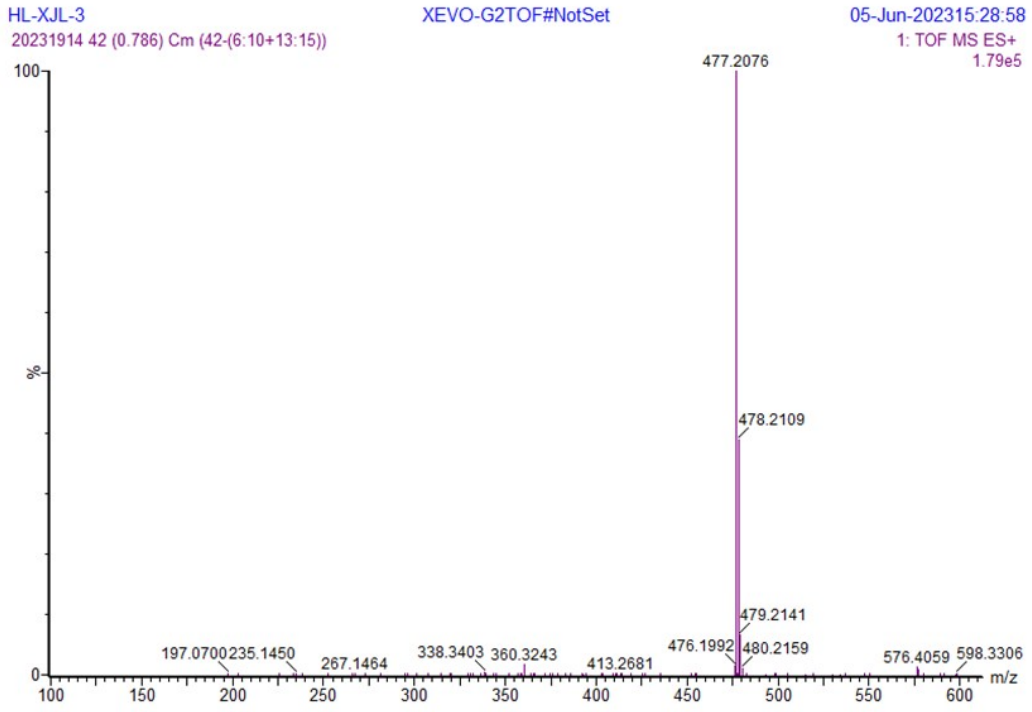


Fig. S23. High resolution mass spectrum of compound **SMP-CNPY**.

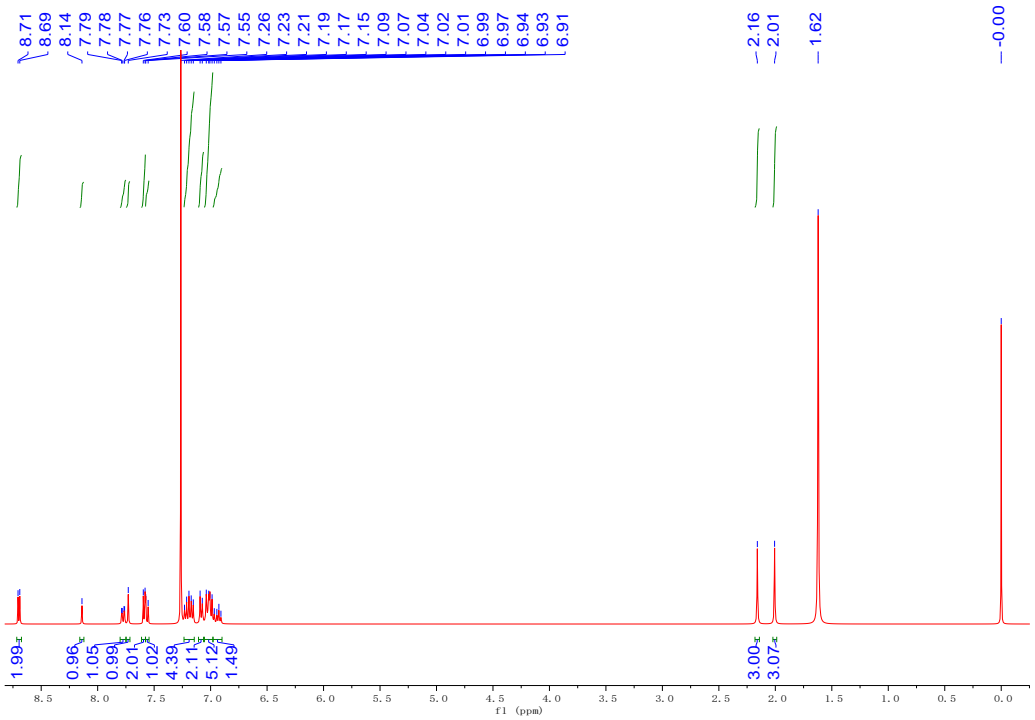


Fig. S24. ^{1}H NMR spectrum of **DMP-CNPY** in $CDCl_3$

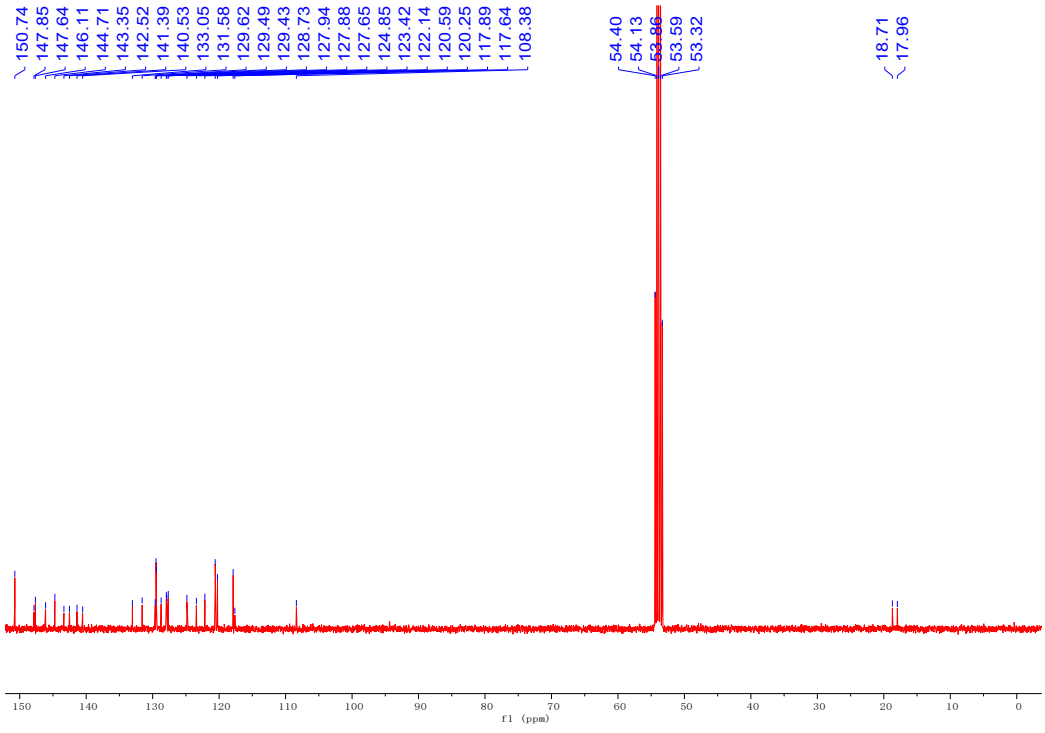
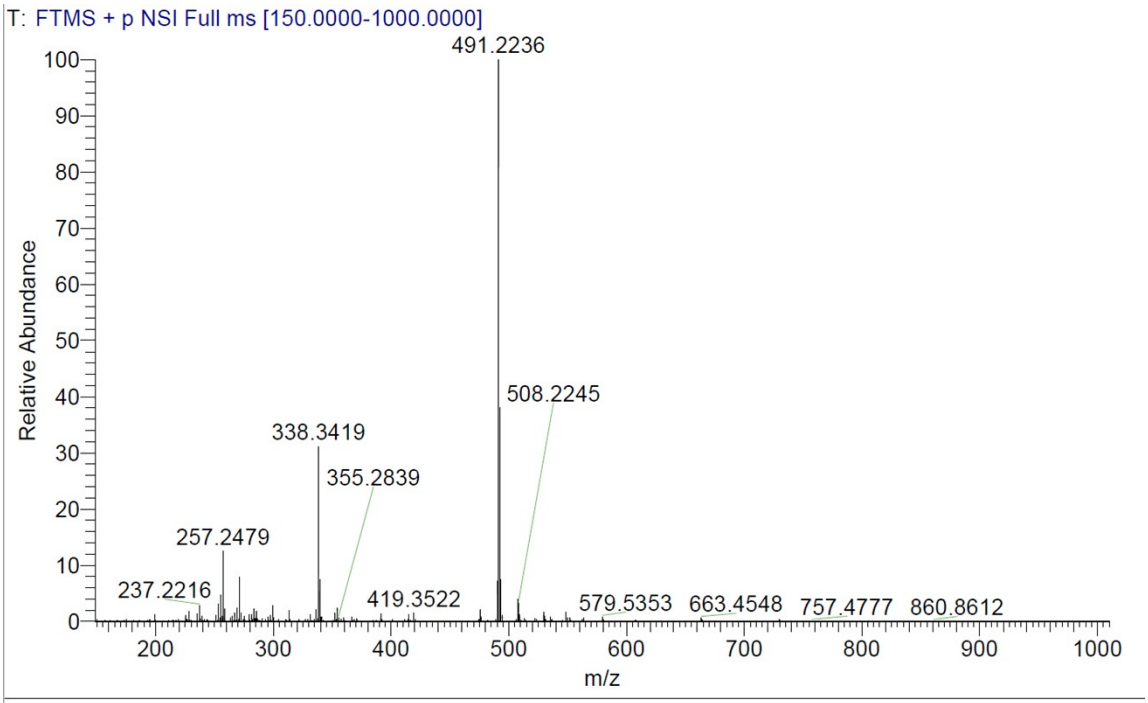


Fig. S25. ^{13}C NMR spectrum of **DMP-CNPY** in $CDCl_3$



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m/z= 467.9009-504.8383

m/z	Intensity	Relative	Theo. Mass	Composition
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Fig. S26. High resolution mass spectrum of compound **DMP-CNPY**.