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Supporting Information

Photothermal-triggered release of singlet oxygen from an endoperoxide-containing polymeric carrier for killing cancer cells

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1. Experimental Procedures

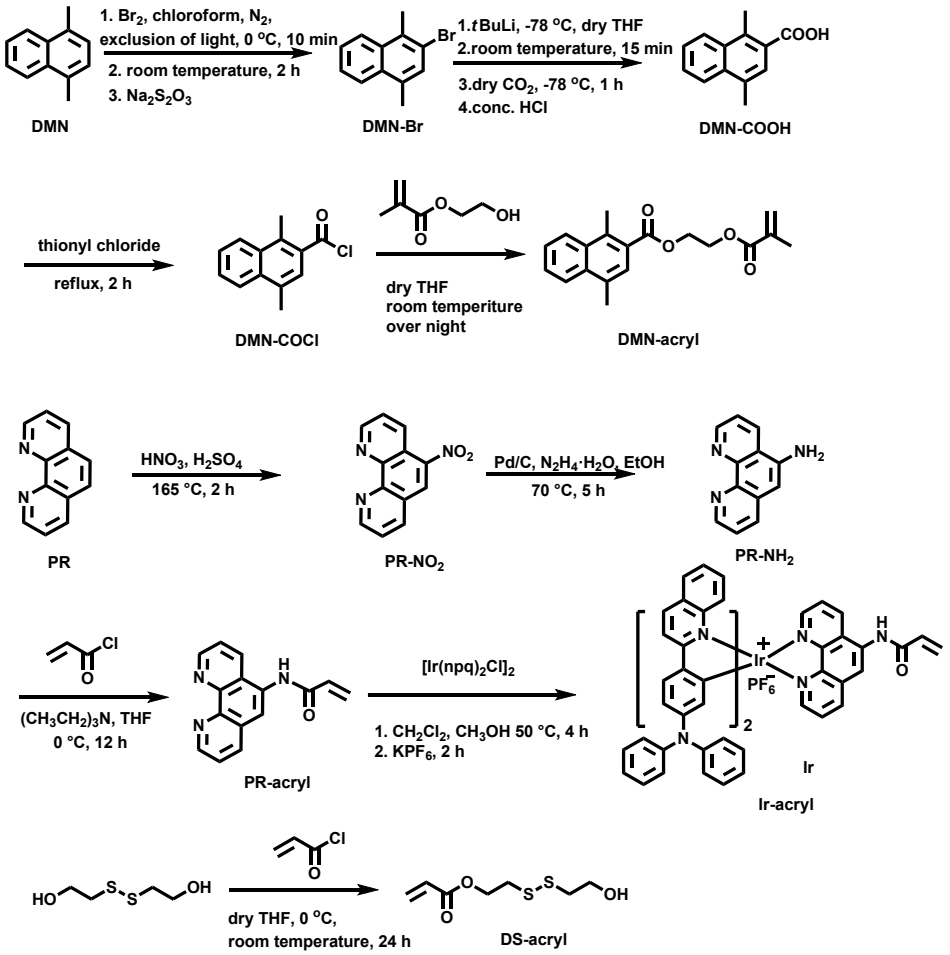
1.1 Materials and general methods

Materials:
All reagents and solvents were purchased from commercial sources and used directly without further purification. Deionized water was used to prepare all aqueous solutions.

Instruments:
NMR spectra were recorded on a nuclear magnetic resonance spectrometer (Bruker Ultra Shield Plus, 400 Hz) at 298 K using deuterated chloroform ($CDCl_3$) as solvent. Chemical shifts were given in ppm and referenced against external Me_4Si (^1H). The number-average molecular weight (M_n) of the polymers was characterized in tetrahydrofuran (THF) by gel permeation chromatography (GPC) at 308 K using polystyrene as standard. The UV-vis absorption spectra were obtained with an ultraviolet and visible spectrophotometer (Shimadzu UV-3600 UV-vis-NIR spectrophotometer). Luminescence spectra were obtained with a fluorescence spectrometer (Edinburgh FL 920 spectrophotometer). The particle size and morphology of AuNRs and AuNRs@PEG were characterized by the transmission electron microscope (TEM, JEOL JEM-2100, 200 kV). The average hydrodynamic size and zeta potential of AuNRs and AuNRs@PEG were measured via dynamic light scattering (DLS) on a zeta particle size analyzer (Brookhaven 90Plus). Oxygen concentration was controlled by flow counters (HORIBA STEC, SEC-E40JS, 60 SCCM) when preparing P1-SO. The excitation light source used to photoactivate the polymeric singlet oxygen carrier was a xenon lamp (CEL-HXF 300, 300 W) which was equipped with a band-pass filter (475 ± 20 nm). The excitation light source used to generate the photothermal effect of AuNRs@PEG was a power adjustable 808 nm semiconductor laser (Changchun Laser photoelectric technology co., LTD, MW-GX-808, 5W). Temperature was measured by a thermal infrared imager (FLIR E40). Cell viability was measured with an enzyme-linked immunesorbent assay (ELISA) reader. Confocal luminescence images were carried out by a laser scanning confocal microscopy (Olympus Fluo view FV1000) equipped with 20× objective lens.

1.2 Synthesis and characterization of the monomers and polymers

Synthesis of the monomers:
The synthetic routes of the monomers were shown in Scheme S1.



Scheme S1. Synthetic routes of the monomers (DMN-acryl, Ir-acryl and DS-acryl).

Synthesis and characterization of DMN-Br:

The DMN-Br was synthesized through a modified process according to the reported method.[1] The DMN (1.250 g, 8.000 mmol) was dissolved in chloroform (4 mL) in dark under nitrogen atmosphere. After the solution was cooled to 0 °C, Br_2 (1.342 g, 8.400 mmol) was added into the solution in 10 min. The reaction was then warmed to room temperature and stirred for 2 h. After that, chloroform (20 mL) and half saturated $Na_2S_2O_3$ solution (20 mL) was sequentially injected into the solution to dilute the reaction and neutralize the residual Br_2, respectively. The above mixture was further extracted by deionized water (20 mL). The organic layer was dried with Na_2SO_4 and then evaporated to remove the solvent. The residue was purified on a silica gel column using petroleum ether to give DMN-Br (1.410 g, yield 75%) as a colorless and transparent oily liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm): 8.07-8.03 (m, 1H), 7.98-7.95 (m, 1H), 7.58-7.52 (m, 2H), 7.49 (s, 1H), 2.78 (s, 3H), 2.64 (s, 3H).

Synthesis and characterization of DMN-COOH:

The DMN-COOH was synthesized through a modified process according to the reported method.[1] DMN-Br (1.410 g, 6.000 mmol) was dissolved in dry tetrahydrofuran (24 mL) under nitrogen atmosphere. After the solution was cooled to -78 °C, *t*BuLi (10 mL, 1.3 M, 13.000 mmol) was added into the solution in 20 min and stirred for another 20 min at -78 °C. The reaction was warmed to room temperature and then stirred for 15 min. Next, the reaction was cooled to -78 °C again and bubbled with dry CO_2, which was dried by passing over phosphorus pentoxide, for 2 h. After the solution was warmed to room temperature, ethyl acetate (18 mL) was injected into the solution. The solution was evaporated to remove the solvent. The residue was further dissolved in ethyl acetate (66 mL) and extracted by 0.25 M NaOH aqueous solution (5×18 mL). The water layer was washed by hexane (36 mL) and mixed with concentrated hydrochloric acid (6 mL) to generate a large amount of white precipitate. The precipitate was filtered off and washed by deionized water. Then the product was dried *in vacuo* to give DMN-COOH (1.092 g, yield 91%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm): 8.28-8.26 (m, 1H), 8.05-8.03 (m, 1H), 7.83 (s, 1H), 7.67-7.59 (m, 2H), 3.02 (s, 3H), 2.71 (s, 3H).

Synthesis and characterization of DMN-acryl:

DMN-COOH (200 mg, 1.000 mmol) was dissolved in thionyl chloride (5 mL) under nitrogen atmosphere. After the reaction was stirred at 40 °C for 2 h, the solvent was evaporated by vacuum oil pump for 1 h. Afterword the dry tetrahydrofuran (6 mL) was injected into the reaction to dissolve the residue. The reaction was further added with 2-hydroxyethyl methacrylate (1.3 g, 10.000 mmol) and stirred at room temperature overnight. The solution was evaporated to remove the solvent. The residue was dissolved in dichloromethane and then extracted by deionized water. The organic layer was dried with Na_2SO_4 and then evaporated to remove the solvent. The residue was purified on a silica gel column using petroleum ether and ethyl acetate (10:1, v/v) to give DMN-acryl (102 mg, yield 33%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm): 8.22-8.20 (m, 1H), 8.03-8.00 (m, 1H), 7.64-

7.56 (m, 3H), 6.19-6.18 (m, 1H), 5.62-5.61 (m, 1H), 4.63-4.61 (m, 2H), 4.54-4.52 (m, 2H), 2.90 (s, 3H), 2.68 (s, 3H), 1.98 (t, *J* = 1.2 Hz, 3H).

Synthesis and characterization of Ir-acryl:

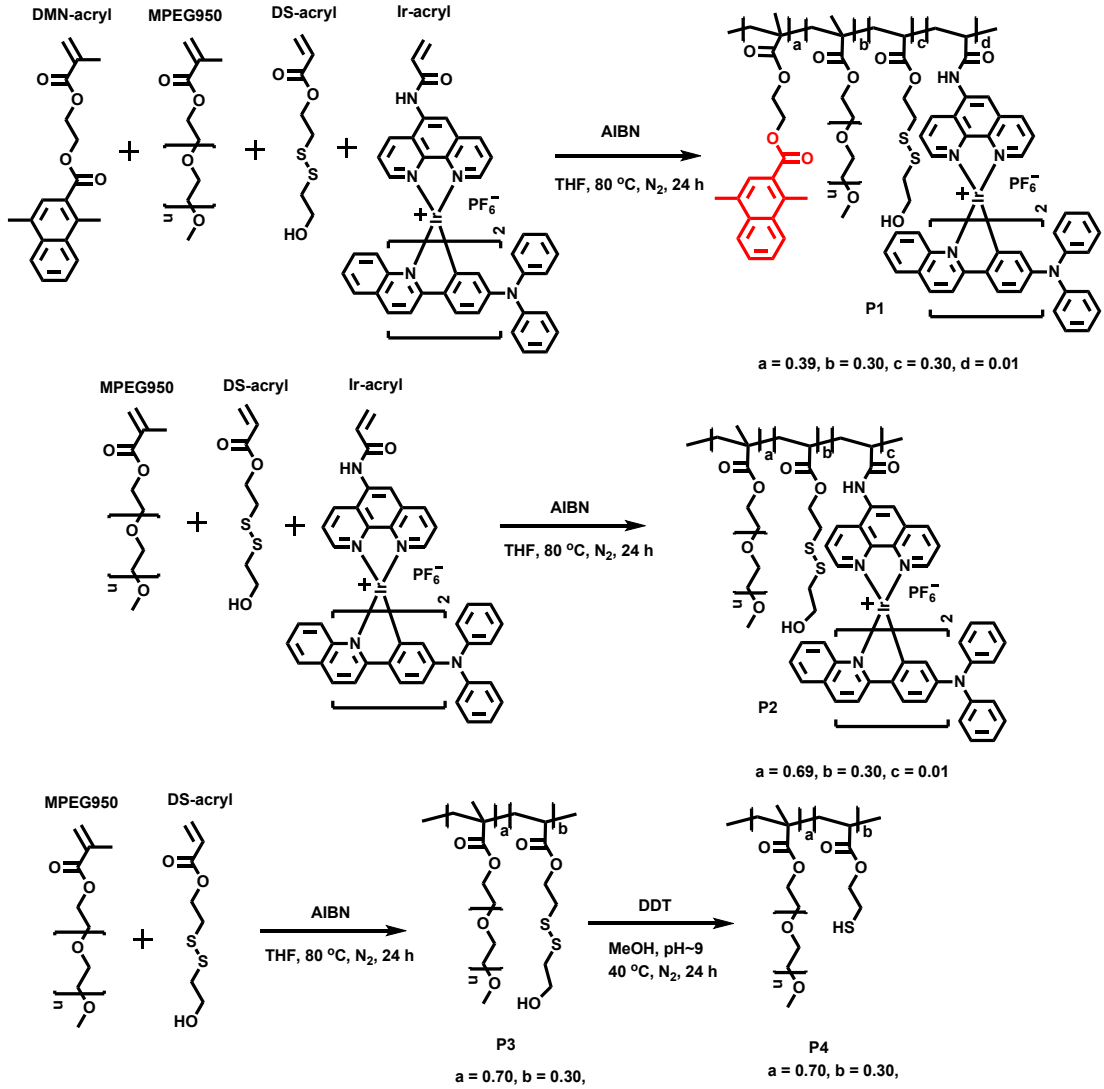
The Ir-acryl was synthesized through the reported method.[2] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) *δ* (ppm): 8.89 (dd, *J* = 1.2 Hz, 8.8 Hz, 1H), 8.797 (s, 1H), 8.55 (dd, *J* = 0.8 Hz, 5.2 Hz, 1H), 8.492 (s, 1H), 8.46 (dd, *J* = 1.2 Hz, 4.8 Hz, 1H), 8.219 (dd, *J* = 1.2 Hz, 8.4 Hz, 1H), 7.874 (dd, *J* = 5.2 Hz, 8.4 Hz, 1H), 7.808-7.631 (m, 7H), 7.440 (dd, *J* = 1.2 Hz, 8.0 Hz, 1H), 7.353 (d, *J* = 8.8 Hz, 1H), 7.155-7.106 (m, 2H), 7.001 (d, *J* = 8.8 Hz, 1H), 6.921-6.659 (m, 26H), 6.505-6.459 (m, 1H), 6.044 (dd, *J* = 2.4 Hz, 10.4 Hz, 2H), 5.842 (d, *J* = 1.6 Hz, 10.4 Hz, 1H).

Synthesis and characterization of DS-acryl:

Bis(2-hydroxyethyl) disulfide (2.888 g, 18.750 mmol) was dissolved in dry tetrahydrofuran (50 mL) under nitrogen atmosphere. After the solution was cooled to 0 °C, acryloyl chloride (1.131 g, 12.500 mmol) was added into the solution. The reaction was stirred at room temperature for 20 h. Finally, the solution was evaporated to remove the solvent and purified by silica gel column using petroleum ether, dichloromethane and ethyl acetate (8:2:1, v/v/v) to give DS-acryl (2.053 g, yield 79%) as a light yellow oily liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) *δ* (ppm): 6.47-5.86 (m, 3H), 4.44 (t, *J* = 6.4 Hz, 2H), 3.89 (t, *J* = 6.0 Hz, 2H), 2.97 (t, *J* = 6.8 Hz, 2H), 2.89 (t, *J* = 6.0 Hz, 2H), 2.18-1.92 (m, 1H).

Synthesis of the polymers:

The synthetic routes of the polymers were shown in Scheme S2.



Scheme S2. Synthetic routes of the polymers (P1-P4).

Synthesis and characterization of P1:

A mixture of DMN-acryl (49 mg, 0.156 mmol), MPEG950 (114 mg, 0.120 mmol), DS-acryl (25 mg, 0.120 mmol), Ir-acryl (5 mg, 0.004 mmol), 2,2-azobisisobutyronitrile (AIBN, 2 mg, 0.012 mmol) and nitrogen saturated tetrahydrofuran (2.5 mL) was refluxed under nitrogen atmosphere at 80 °C for 18 h. After the reaction was cooled to room temperature, diethyl ether (200 mL) was poured into the solution to get the orange emulsion. Then the emulsion was centrifuged (10000 r/min) for 15 min. The red oil liquid at the bottom of

the centrifuge tube was collected and successively washed and centrifuge (10000 r/min, 15 min) with tetrahydrofuran and diethyl ether for another 3 times. Finally, the residue was dried at 40 °C overnight and stored at -20 °C to give P1 (156 mg, 81%) as an orange red solid. GPC (THF, polystyrene standard): M_n = 11163, PDI = 1.36.

Synthesis and characterization of P2:
A mixture of MPEG950 (262 mg, 0.276 mmol), DS-acryl (25 mg, 0.120 mmol), Ir-acryl (5 mg, 0.004 mmol), 2,2-azobisisobutyronitrile (AIBN, 2 mg, 0.012 mmol) and nitrogen saturated tetrahydrofuran (2.5 mL) was refluxed under nitrogen atmosphere at 80 °C for 18 h. After the reaction was cooled to room temperature, diethyl ether (200 mL) was poured into the solution to get the orange emulsion. Then the emulsion was centrifuged (10000 r/min) for 15 min. The red oil liquid at the bottom of the centrifuge tube was collected and successively washed and centrifuged (10000 r/min, 15 min) with tetrahydrofuran and diethyl ether for another 3 times. Finally, the residue was dried at 40 °C overnight and stored at -20 °C to give P2 (220 mg, 75%) as an orange red solid. GPC (THF, polystyrene standard): M_n = 16888, PDI = 1.14.

Synthesis and characterization of P3:
A mixture of MPEG950 (266 mg, 0.280 mmol), DS-acryl (25 mg, 0.120 mmol), 2,2-azobisisobutyronitrile (AIBN, 2 mg, 0.012 mmol) and nitrogen saturated tetrahydrofuran (2.5 mL) was refluxed under nitrogen atmosphere at 80 °C for 18 h. After the reaction was cooled to room temperature, diethyl ether (200 mL) was poured into the solution to get the milk white emulsion. Then the emulsion was centrifuged (10000 r/min) for 15 min. The colorless transparent oil liquid at the bottom of the centrifuge tube was collected and successively washed and centrifuged (10000 r/min, 15 min) with tetrahydrofuran and diethyl ether for another 3 times. Finally, the residue was dried at 40 °C overnight and stored at -20 °C to give P3 (201 mg, 69%) as an white solid. GPC (THF, polystyrene standard): M_n = 18218, PDI = 1.84.

Synthesis and characterization of P4:
P3 (100 mg) and dithiothreitol (DTT, 15 mg, 0.097 mmol) was dissolved in methyl alcohol (2 mL). After the pH of the solution was adjusted to 9 by aqueous ammonia, the reaction was stirred at 40 °C for 2 h under nitrogen atmosphere. After the reaction was cooled to room temperature, diethyl ether (100 mL) was poured into the solution to get the milk white emulsion. Then the emulsion was centrifuged (10000 r/min) for 15 min. The colorless transparent oil liquid at the bottom of the centrifuge tube was collected and successively washed and centrifuged (10000 r/min, 15 min) with tetrahydrofuran and diethyl ether for another 3 times. Finally, the residue was dried at 40 °C overnight and stored at -20 °C to give P3 (201 mg, 69%) as an white solid. GPC (THF, polystyrene standard): M_n = 24129, PDI = 1.35.

1.3 Synthesis of AuNRs and AuNRs@PEG

Synthesis of AuNRs:
The synthesis of AuNRs was modified from the reported method.[3,4]

Preparation of Au seeds: Cetyltrimethyl ammonium bromide (CTAB, 364 mg, 1.000 mmol) was dissolved in 9.75 mL deionized water. $HAuCl_4$ (0.25 mL, 0.01 M) and ice-cold $NaBH_4$ aqueous solution (0.6 mL, 0.01 M) were added into the solution successively with vigorous stirring at room temperature. After the color of solution turned to yellowish-brown, the solution was further stirred for 10 min vigorously. The seeds solutions could be used immediately after 2 hours' standing at room temperature in dark.

Preparation of growth solution: CTAB (3.644 g, 10.000 mmol) was dissolved in deionized water (95 mL). Concentrated hydrochloric acid (83 μL), $HAuCl_4$ (455 μL, 0.11 M), $AgNO_3$ (100 μL, 0.10 M) and new prepared ascorbic acid (552 μL, 0.10 M) were successively added into the solution to give the colorless transparent aqueous solution.

Preparation of AuNRs: The seeds solution (240 μL) was added into the above growth solution. After vigorous stirring for 1 min, the solution was kept constant at 28 °C for 12 h. Finally, the CTAB stabilized AuNRs were collected by centrifugation (10000 r/min, 15 min) and washed for 2 times with deionized water and redispersed in deionized water (5 mL).

Synthesis of AuNRs@PEG:
The synthesis of AuNRs@PEG was referenced to the reported method.[4] The above prepared AuNRs was diluted with deionized water (95 mL). The aqueous solution of P4 (20 mL, 1 mg/mL) was added into the above solution. The mixture was further stirred at room temperature for 36 h. Finally, the AuNRs@PEG were collected by centrifugation (10000 r/min, 15 min) and washed for 3 times with deionized water and redispersed in deionized water (5 mL).

1.4 Preparation of P1-SO

To generate the singlet oxygen loaded polymer P1-SO, the DMSO solution of P1 was irradiated by a xenon lamp (λ_{ex} = 475 nm, 55 mW/cm^2) at room temperature for 3 4 h. The solution was bubbled with O_2 (50 mL/min) during the whole irradiation.

1.5 Cell culture

The cell lines HeLa (human cervical cancer) was provided from the Institute of Biochemistry and Cell Biology, SIBS, CAS (China). The cells were cultured in DMEM (Dulbecco's modified Eagle's medium) supplemented with 10% FBS (fetal bovine serum, Gibcco), 100 mg/mL streptomycin and 100 U/mL penicillin at 37 °C with 5% CO_2.

1.6 Cytotoxicity assay

The *In vitro* cell viability was measured through the methyl thiazolyltetrazolium (MTT) assays with HeLa cells. Cells were seeded into a 96-well cell culture plate at the density of 10^4/well at 37 °C with 5% CO_2 and 100% humidity for 24 h. Afterwards, the cells were incubated with the DMEM solutions of different concentration of P1 (10 μg/mL, 50 μg/mL and 100 μg/mL), P1-SO (10 μg/mL, 50 μg/mL and 100 μg/mL) and AuNRs@PEG (5 μg/mL, 10 μg/mL, 20 μg/mL, 40 μg/mL and 60 μg/mL) at 37 °C with 5% CO_2 and 100% humidity for another 24 h in dark. Then the cells were treated with MTT (10 μL/well, 5 mg/mL) and incubated for an additional 4 h at 37 °C under 5% CO_2. The medium was then replaced by dimethyl sulfoxide (DMSO, 150 μL/well). OD570 was monitored by an enzyme-linked immunesorbent assay (ELISA) reader. The following formula was used to calculate the inhibition of cell growth: Cell viability (%) = (mean of Abs. value of the treated group / mean Abs. value of the control group)×100%.

1.7 Cell imaging

HeLa cells were planted on confocal petri dish and allowed to adhere for 24 h. Then the cells were incubated with P1 (50 μg/mL) at 37 °C under 5% CO_2. The cells were viewed after different incubation period (0.5 h, 1.5 h, 7.5 h and 24 h) on confocal microscopy. (λ_{ex} = 488 nm, λ_{em} = 580-640 nm).

1.8 ROS detection

HeLa cells were planted on confocal petri dish and allowed to adhere for 24 h. The cells were incubated with AuNRs@PEG (20 μg/mL) for 24 h and successively incubated with P1-SO or P1 (50 μg/mL) for 6 h at 37 °C. Then the cells were treated with DCFH-DA (10 μM) at 37 °C for 30 min under 5% CO_2. After that, the cells were treated with 808 nm NIR light excitation (0.88 W/cm^2) for 20 min. The luminescence of DCF was viewed 20 min later using confocal microscopy (λ_{ex} = 488 nm, λ_{em} = 500-540 nm).

1.9 Annexin V-FITC/PI assay

HeLa cells were planted on confocal petri dish and allowed to adhere for 24 h. The cells were incubated with AuNRs@PEG (20 μg/mL) for 24 h and successively incubated with P1-SO or P1 (50 μg/mL) for 6 h at 37 °C. Then the cell was stained with 5 μL annexin V-FITC and 10 μL PI at room temperature for 10 min in dark. After that, the cells were treated with 808 nm NIR light excitation (0.88 W/cm^2) for 20 min. The luminescence of FITC and PI was viewed 7 h later by confocal microscopy in green channel (λ_{ex} = 488 nm, λ_{em} = 500-560 nm) and red channel (λ_{ex} = 488 nm, λ_{em} = 600-680 nm), respectively.

2. Supplementary Figures

The absorption peak located at 244 nm in the UV-Vis absorption spectrum of P1 and the bumps located at 8.15 ppm, 7.95 ppm and 7.56 ppm in the ^{1}H NMR spectrum of P1 matched well with those of DMN (Fig. S1 and Fig. S2), while these peaks were not observed in the corresponding spectra of the DMN-free counterpart P2, demonstrating that the DMN was successfully incorporated in the polymeric $^1O_2$ carrier P1. Furthermore, both of the absorption and emission spectra of P1 and P2 showed the specific peaks of Ir(III) complex (λ_{abs} = 451 nm, λ_{em} = 590 nm) (Fig. S1, Fig. S3 and Fig. S4). Some specific ^{1}H NMR peaks of Ir(III) complexe, PEG and DS could also be easily found in the ^{1}H NMR spectra of P1 and P2 (Fig. S2), indicating that these three monomers were incorporated in P1 and P2 successfully. The contents of Ir(III) complexes and DMN incorporated in P1 were calculated to be 2.05 w% and 10.12 w%, respectively, through the UV-Vis absorption and ^{1}H NMR spectra.

Fig. S1 UV-Vis absorption spectra of P1 (100 μg/mL), P2 (100 μg/mL), DMN-acryl (50 μM) and Ir-acryl (10 μM) in chloroform at 25 °C.

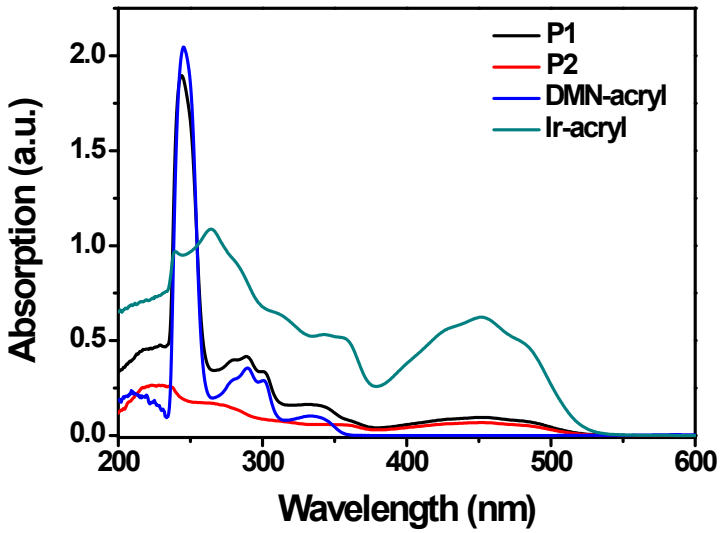


Fig. S2 ^{1}H NMR spectra of P1, P2, MPEG950, Ir-acryl, DMN-acryl and DS-acryl in deuterated chloroform.

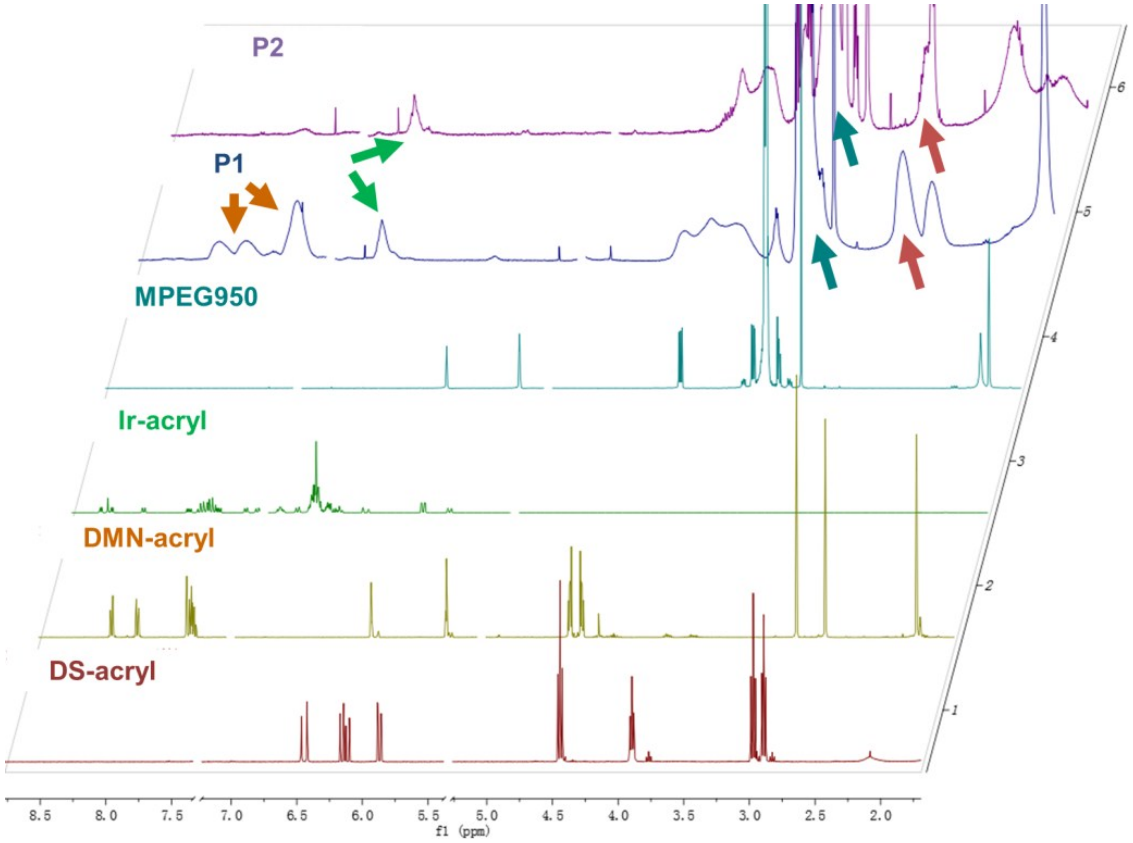


Fig. S3 a) UV-Vis absorption spectra of DMN-acryl (50 μM), Ir-acryl (10 μM), MPEG950 (10 μM) and DS-acryl (10 μM) in chloroform at 25 °C. b) Normalized UV-Vis absorption and emission spectra of Ir-acryl in chloroform at 25 °C. λ_{ex} = 488 nm.

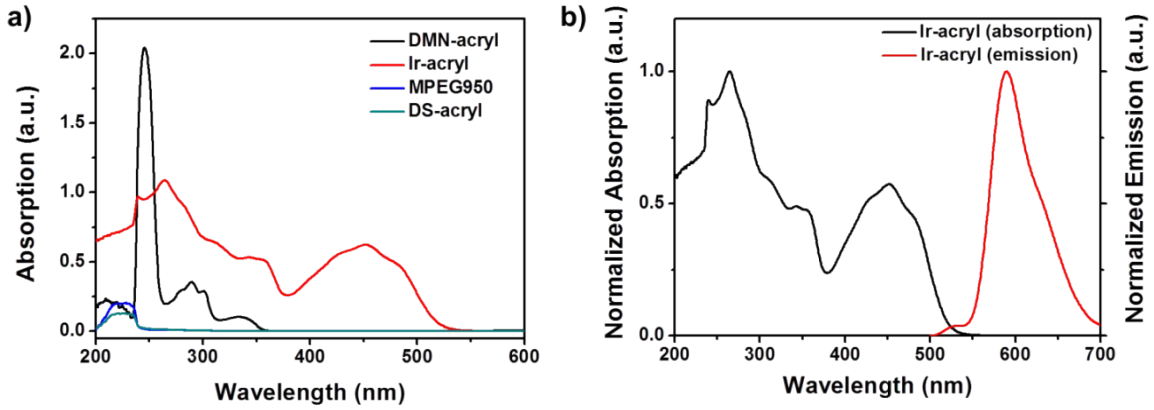


Fig. S4 Normalized UV-Vis absorption and emission spectra of P1 (100 μg/mL) and P2 (100 μg/mL) in chloroform at 25 °C. λ_{ex} = 488 nm.

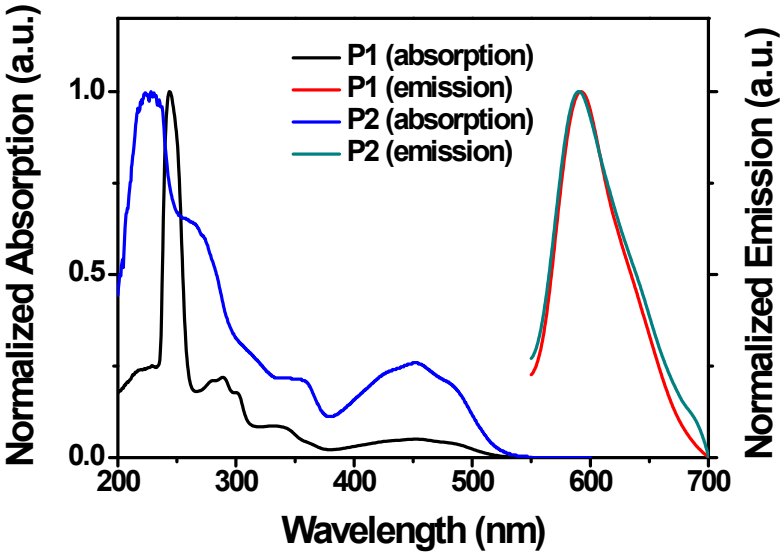


Fig. S5 The UV-Vis absorption spectra of the oxygen saturated solution (V_{CHCl3}:V_{CH3OH} = 99:1) mixed with DMN-acryl (5×10^{-5} M) and methylene blue (MB, 10^{-4} M) after different period of irradiation (λ_{ex} = 600 nm, 34 mW/cm^{-2}) by a xenon lamp at 25 °C. The solution of methylene blue (MB, 10^{-4} M) was served as reference during the measurement.

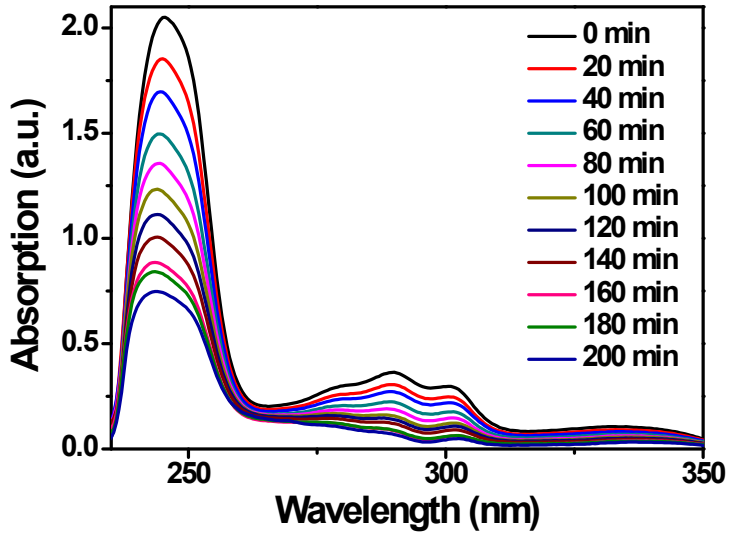


Fig. S6 TEM images of a,b) AuNRs and c,d) AuNRs@PEG.

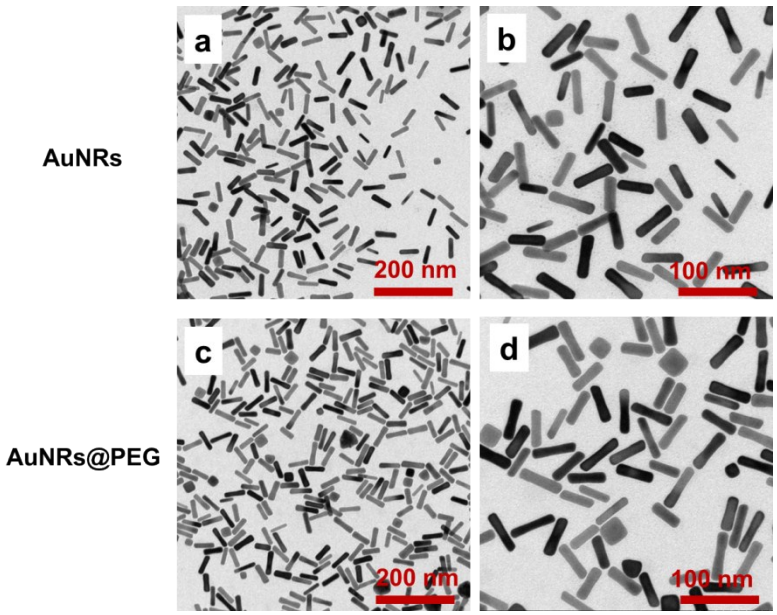


Fig. S7 Normalized UV-Vis absorption spectra of AuNRs and AUNRs@PEG in deionized water at 25 °C.

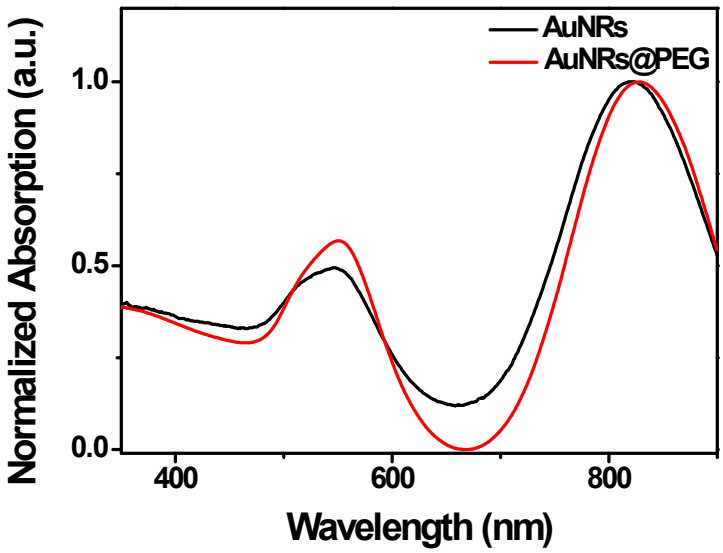


Fig. S8 Temperature increase of the aqueous solution of AuNRs@PEG with different concentrations (100 μg/mL, 50 μg/mL and 20 μg/mL) under 808 nm laser irradiation (0.88 W/cm²) for 30 min. The measurements and data collection were conducted at 37 °C.

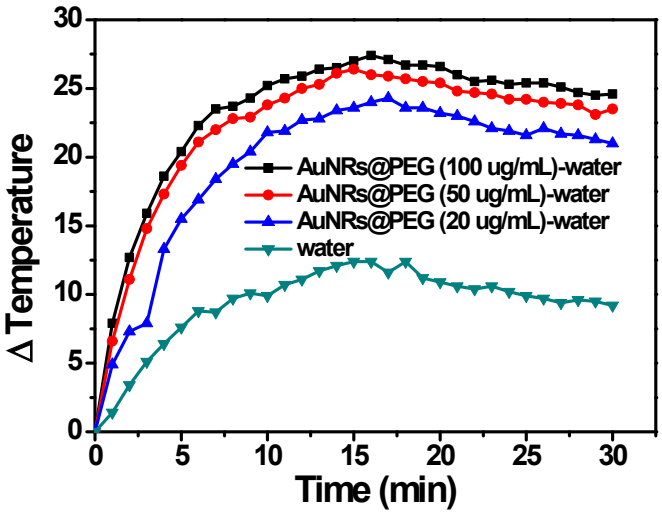


Fig. S9 *In vitro* cell viability of HeLa cells treated with a) P1, P1-SO and b) AuNRs@PEG at different concentrations at 37 °C for 24 h in dark.

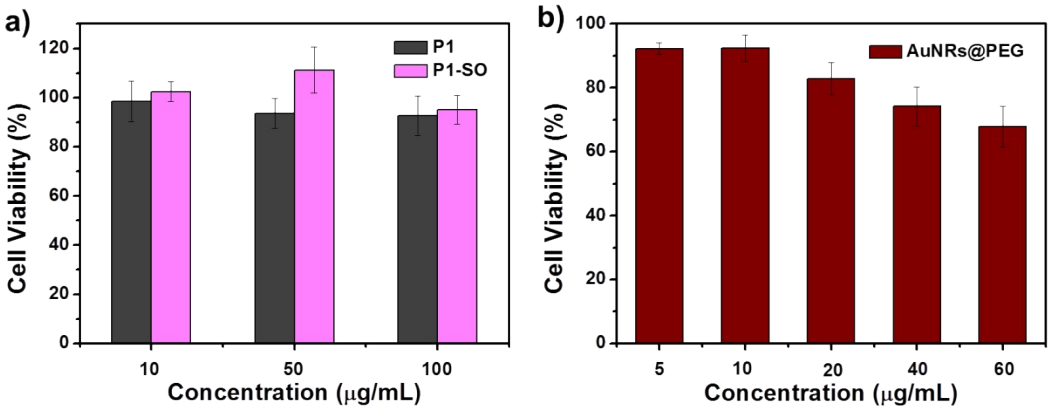


Fig. S10 Confocal microscopy images of HeLa cells which were incubated with P1 (50 μg/mL) for a) 0.5 h, b) 1.5 h, c) 7.5 h and d) 24 h. All the images share the same scale bar of 100 μm. Images were taken at 25 °C. λ_{ex} = 488 nm, λ_{em} = 580-640 nm.

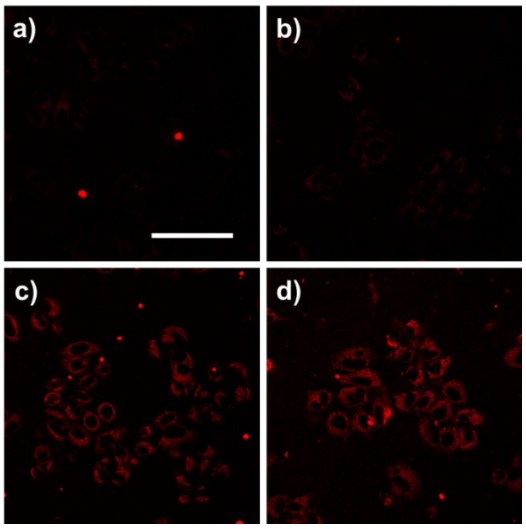


Fig. S11 Confocal microscopy images of HeLa cells treated with DCFH-DA. The cells were incubated with P1-SO (50 μg/mL) or P1 (50 μg/mL) for 6 h at 37 °C and then treated with DCFH-DA (10 μM) for 30 min at 37 °C in succession. The luminescence of DCF was viewed 20 min later in green channel (λ_{ex} = 488 nm, λ_{em} = 500-540 nm). All the images share the same scale bar of 100 μm. Images were taken at 25 °C.

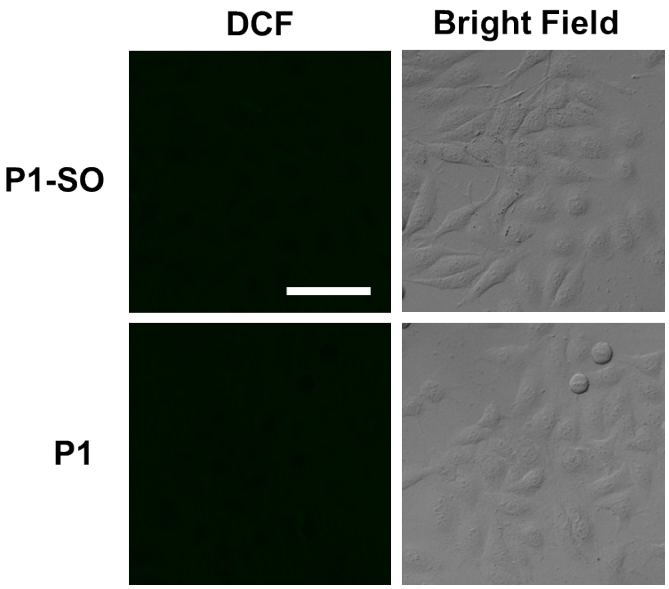
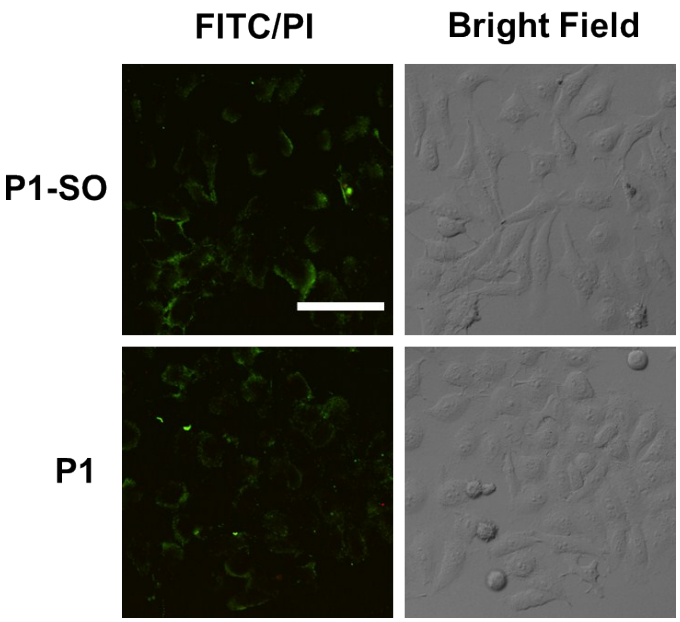


Fig. S12 Confocal microscopy images of HeLa cells stained with Annexin V-FITC and PI. The cells were incubated with P1-SO (50 μg/mL) or P1 (50 μg/mL) for 6 h at 37 °C and then treated with annexin V-FITC (5 μL) and PI (10 μL) at room temperature for 10 min in dark in succession. The luminescence of FITC and PI was viewed 7 h later in green channel (λ_{ex} = 488 nm, λ_{em} = 500-560 nm) and red channel (λ_{ex} = 488 nm, λ_{em} = 600-680 nm), respectively. All the images share the same scale bar of 100 μm. Images were taken at 25 °C.



3. Supplementary Tables

Table S1. Average hydrodynamic size and zeta potential of AuNRs and AuNRs@PEG.

	AuNRs	AuNRs@PEG
Average hydrodynamic size (nm)[a]	41.1 ± 0.4	56.9 ± 2.8
zeta potential (mV)[a]	20.83 ± 2.05	-13.30 ± 0.86

[a] The measurements were conducted at 25 °C .

References

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Author Contributions

Ms. Wen Lv (Ph. D candidate), lead contribution in investigation, synthesis, data collection, data analysis and writing of original draft;

Ms. Huiting Xia (graduate student), supporting contribution in synthesis and data collection;

Dr. Kenneth Yin Zhang, supporting contribution in writing and data analysis;

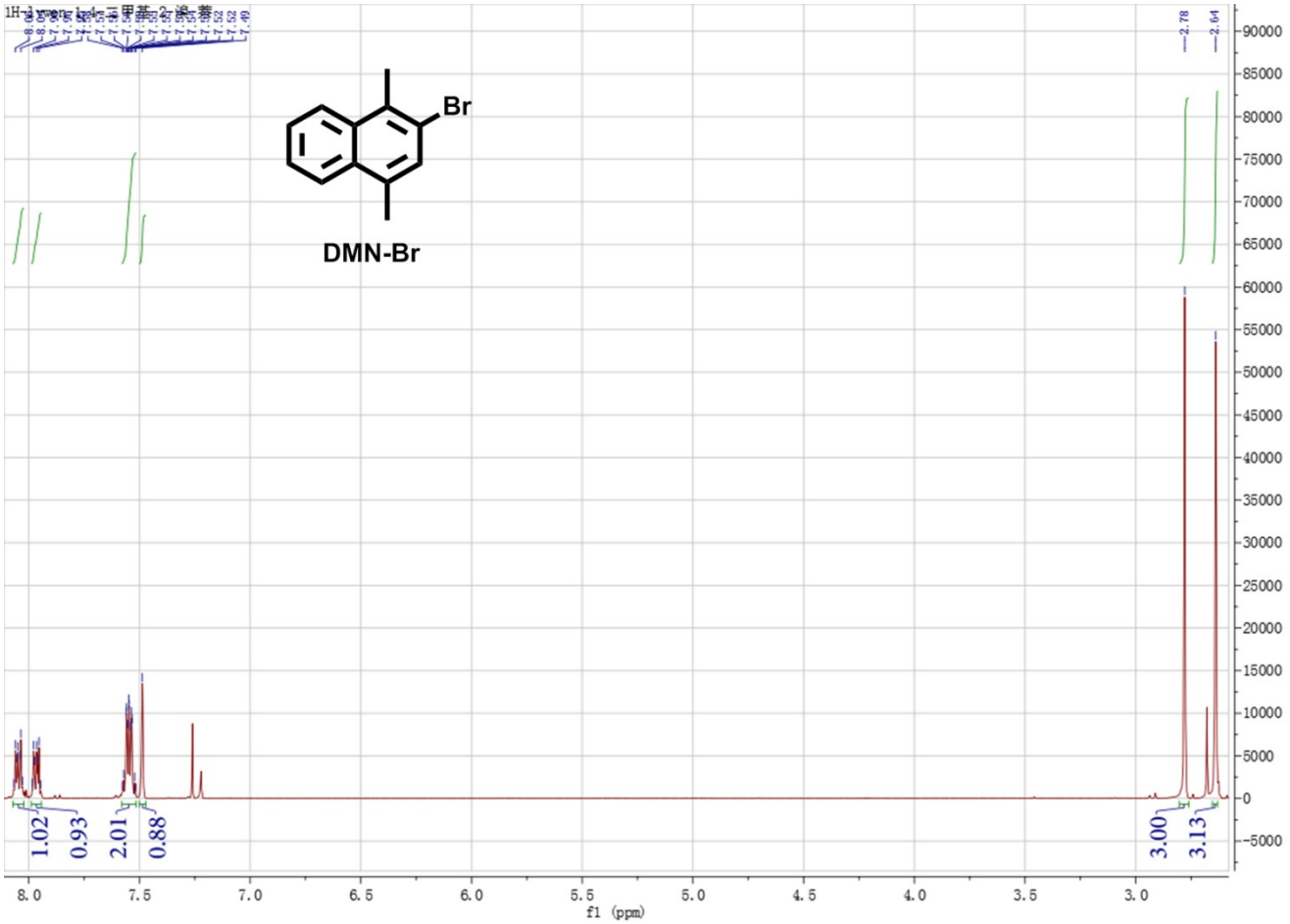
Mr. Zejing Chen, supporting contribution in synthesis;

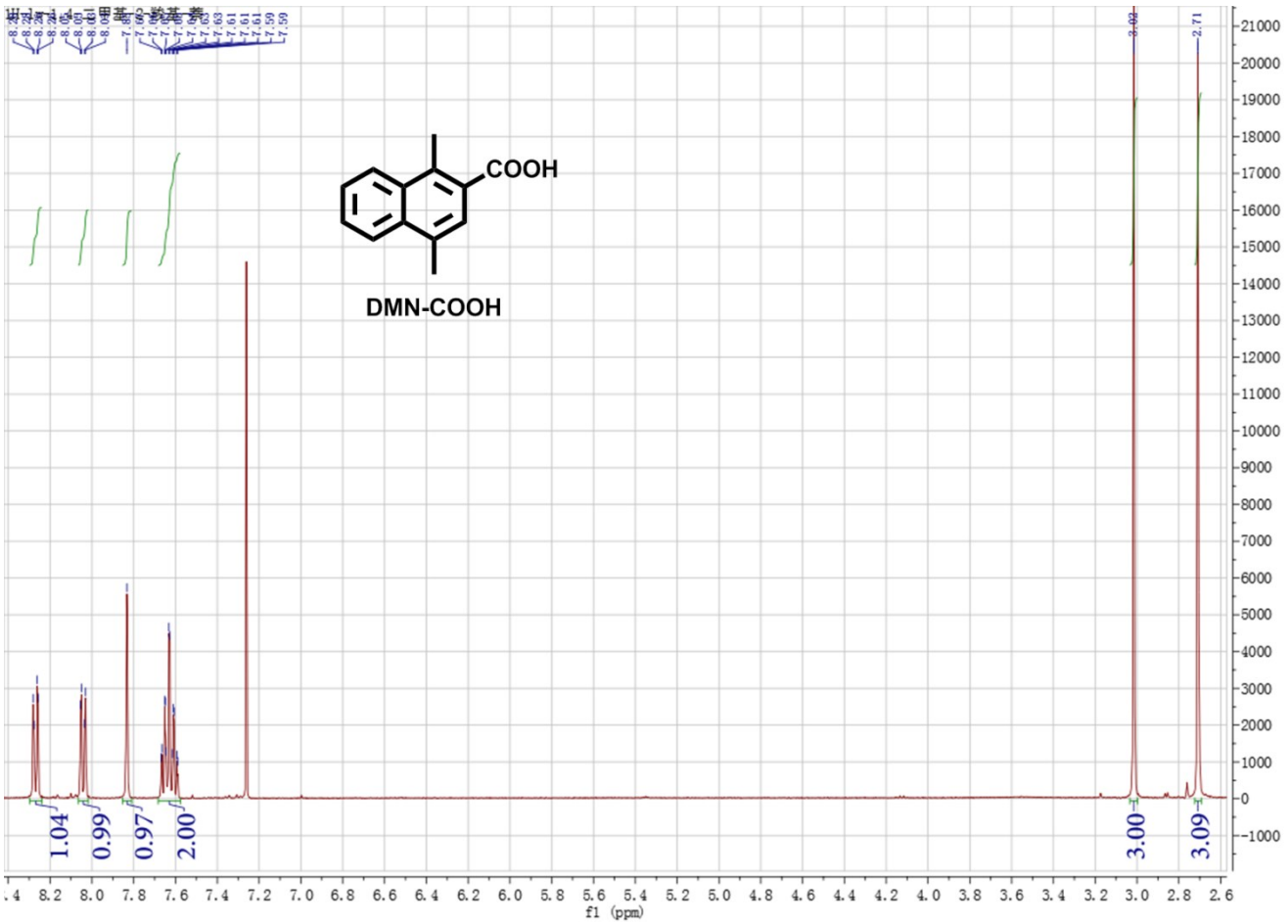
Professor Dr. Shujuan Liu, supporting contribution in project administration and data analysis;

Professor Dr. Wei Huang, supporting contribution in funding acquisition and writing;

Professor Dr. Qiao Zhao, lead contribution in funding acquisition and project administration; supporting contribution in design, data analysis and writing.

^{1}H NMR spectra

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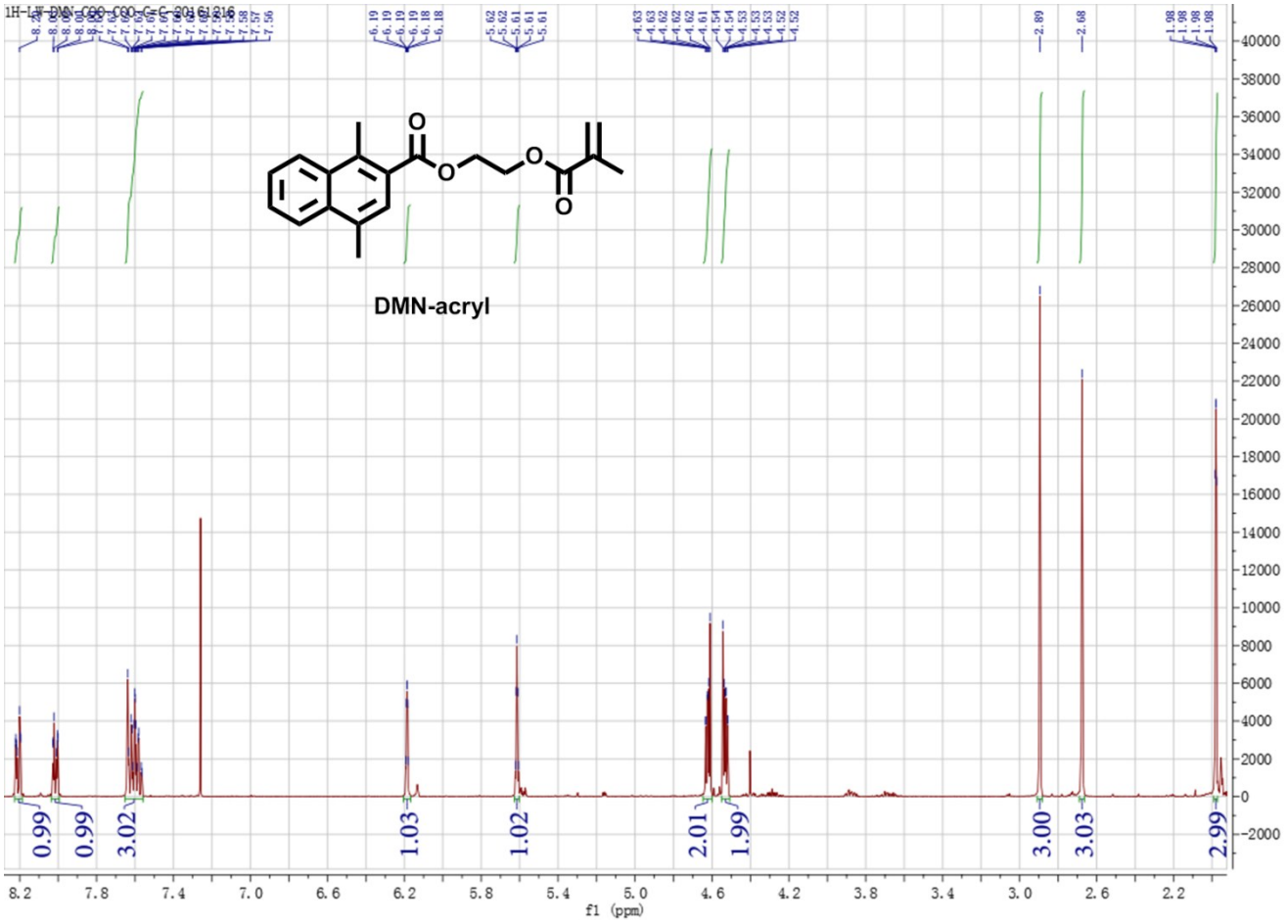
3.09
f1 (ppm)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O
O
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DMN-acryl
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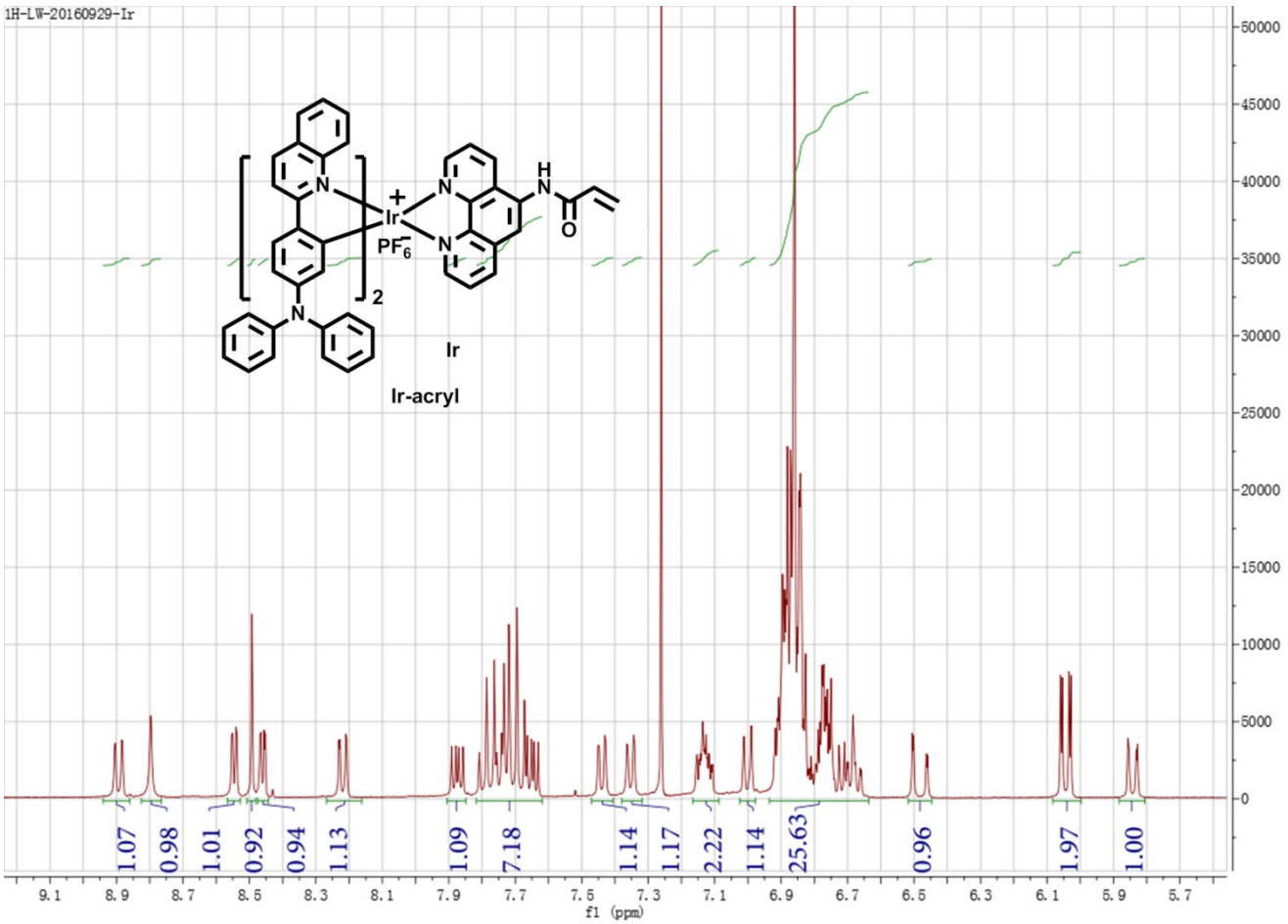
2.99
f1 (ppm)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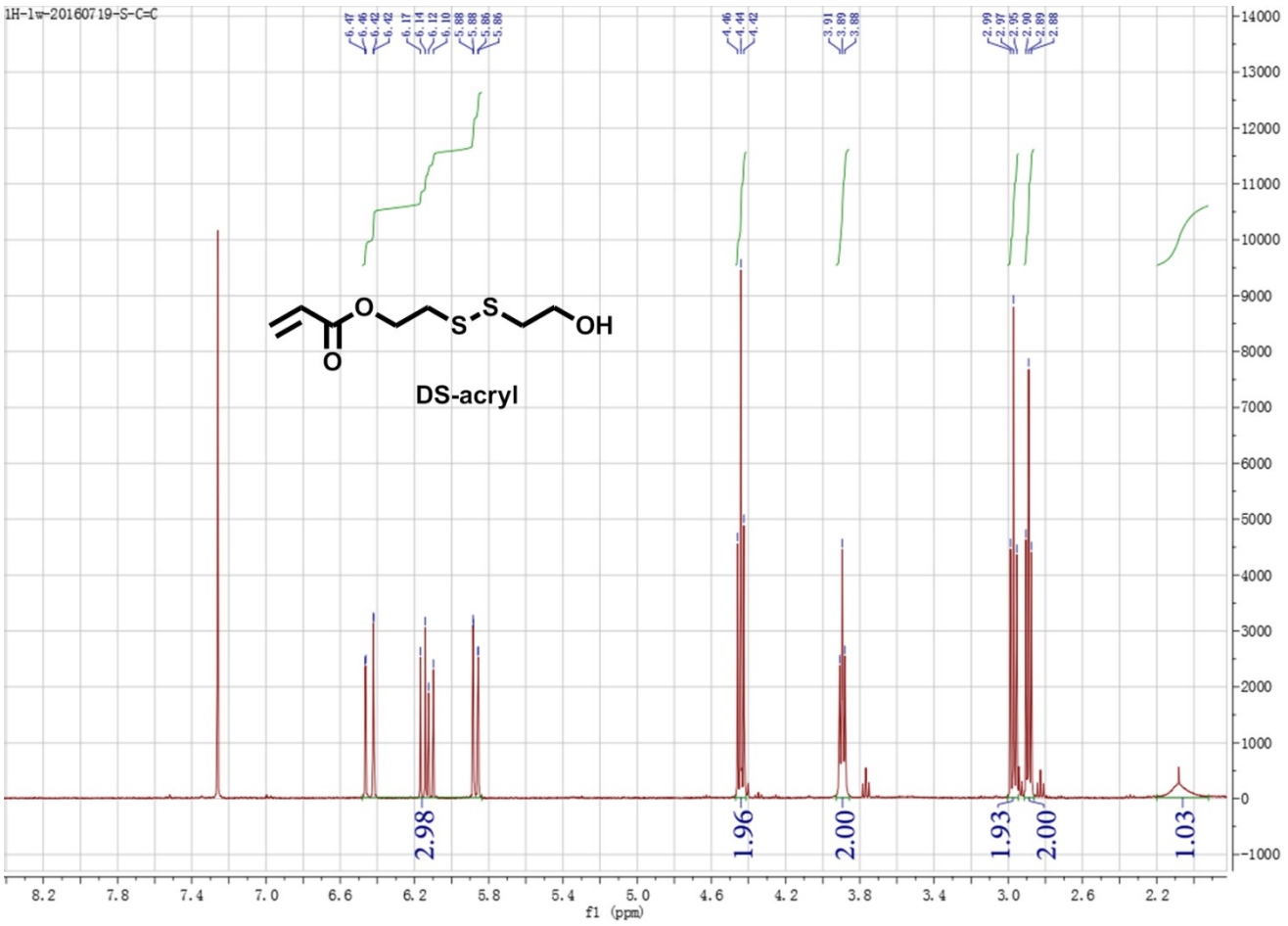
f1 (ppm)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