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Supporting Information for

Molecular engineering to achieve AIE-active photosensitizer with NIR emission and rapid ROS generation efficiency

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Experimental Section

Materials and Methods

Unless stated otherwise, all analytical grade chemicals used in this paper were purchased from Energy Chemical, Macklin, or Sigma as received without further. Superdry dichloromethane (DCM) and methanol (MeOH) with molecular sieves were purchased from Macklin. DCFH, DHR123, ABDA, and Rose Bengal were purchased from Bidepharm and used as received. Cell culture medium (DMEM/HIHG GLUCOSE) and fetal bovine serum (FBS) were purchased from Cytiva and Every Green. Mitotracker Green and Cell Counting Kit-8 were purchased from Beyotime.

^{1}H NMR (500 MHz) and ^{13}C NMR (500 MHz) spectra were recorded on a 500 MHz Bruker Avance spectrometer with Chloroform-d or Dimethyl sulfoxide-d6 as the solution. High-resolution mass spectra (HRMS-ESI) were measured on the matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometer. The photophysical characteristics of the **DBP**, **TBP,** and **TBP-SO_3** in DMSO were determined with FL-4600 fluorescent spectrophotometer and Cary 500 UV-vis-NIR spectrophotometer for photoluminescence (PL) spectra (5.0×10^{-5} M) and absorption spectra (1.0×10^{-5} M), respectively. The photoluminescence quantum yields (PLQYs) of their solid and solution were determined in an integrating sphere. Excited-state lifetimes of these solids and solutions were determined with the Edinburgh FLSP920 spectrofluorimeter. Cellular fluorescence images were taken using a Zeiss laser scanning confocal microscope and analyzed using ZEN 2.6 software. Cytotoxicity Assay was received by Infinite 200 Pro (Tecan). White light source for ROS generation experiment comes from a commercial LED light with 23.4 mW/cm^2 neutral white light. The model number is NVC-EXTT9029.

X-ray crystallography

Single-crystal X-ray diffraction experiments for **DBP**, **TBP** and **TBP-SO_3** were carried out on a Bruker Apex II CCD diffractometer with graphite-monochromated Cu Kα radiation (λ ¼ 1.5418 Å).

Theoretical calculations

The ground state (S_0) geometries of three materials in isolated state were optimized at the theoretical level of B3LYP/6-31g(d). Energies of the first singlet and triplet excited states were calculated based on the optimized S_0 at TD-B3LYP/6-31g(d), and the calculation for isolated state was conducted in DMSO environment. All these calculations were manipulated by the Gaussian 09 suite.[1] The calculation of the SOC matrix elements was carried out in ADF2017 program package[2] with B3LYP at all electron TZP basis set and all the relativistic effects were considered for all atoms using the zeroth-order regular approximation (ZORA) method.[3]

ROS generation measurement

DCFH (Dichlorofluorescein) was used as the ROS indicator of **DBP**, **TBP**, **TBP-SO$_3$** and a commercial standard photosensitizer, Rose Bengal upon light irradiation. The fluorescence of each sample (2 μM) was firstly set as blank. Then, 40 μM of DCFH was mixed with each sample (DMSO/PBS (v:v) = 1/99) in a dark room, and the fluorescence of the sample was measured at once. The sample mixture was then irradiated under white light (23.4 mW/cm^2) at intervals of 5 s until 120 s. DCFH aqueous solution without AIEgens was subjected to irradiation. The fluorescence of DCF was excited at 480 nm and collected within 500−650 nm.

Dihydrorhodamine 123 (DHR123) was employed to evaluate type I (free radical-dominated) ROS generation of **DBP**, **TBP**, **TBP-SO$_3$** and a commercial standard photosensitizer, Rose Bengal upon light irradiation. The fluorescence of the sample (2 μM) was firstly set as blank. Then, 3 μM of DHR123 was mixed into the sample (DMSO/water (v:v) = 1/99) in a dark room, and the fluorescence of the sample was measured at once. The sample mixture was then irradiated under white light (23.4 mW/cm^2) at intervals of 1 min until 10 min. DHR123 aqueous solution without AIEgens was subjected to irradiation. The fluorescence of DHR123 was excited at 480 nm and collected within 500−650 nm.

ABDA (9,10-Anthracenediyl-bis(methylene)dimalonic acid) was employed to

evaluate $^1O_2$ generation of **DBP**, **TBP**, **TBP-SO$_3$** and a commercial standard photosensitizer, Rose Bengal upon light irradiation. The absorbance of the sample (2 μM) was firstly set as blank. Then, 100 μM of ABDA was mixed to the sample (DMSO/water (v:v) = 1/99) in a dark room, and the absorbance of the sample was measured at once. The sample mixture was then irradiated under white light (23.4 mW/cm^2) at intervals of 1min until 10 min. The absorption of ABDA at 378 nm was recorded at various irradiation times to obtain the decay rate of photosensitizing process. The absorbance change of ABDA alone in 10 min light irradiation time was also measured as a control.

Cell culture and Cell imaging

HeLa cells were cultured in Dulbecco's minimal essential medium (DMEM) containing 10% FBS in a 5% CO_2 humidity incubator at 37℃. HeLa cells were seeded on a 35 mm Petri dish at a density of 8000–10 000 cells per dish for 24 h. After being incubated under certain conditions, the cells were washed with Stroke-physiological saline solution three times and subjected to imaging analysis using a Zeiss Laser Scanning Confocal Microscope.

For the lipid droplet co-localization imaging HeLa cells were treated with 50 μM oleic acid for 3 h co-stained, then the cells were washed with Stroke-physiological saline solution three times. After incubation with 1 μM **DBP**, **TBP** and 0.5 mM BODIPY Green for 30 min, the cells were washed with Stroke-physiological saline solution three times again and subjected to imaging analysis using a Zeiss Laser Scanning Confocal Microscope. **DBP** was excited at 561 nm and its emission was collected in the range of 600–740 nm; **TBP** was excited at 488 nm and its emission was collected in the range of 600–740 nm; BODIPY was excited at 405 nm or 488 nm and its emission was collected in the range of 490–550 nm The Pearson correlation coefficient (R) was determined by the ZEN 2.6 software.

For the endoplasmic reticulum HeLa cells were seeded and cultured at 37 ℃ in a 35 mm glass-bottomed dish. After incubation with **TBP-SO$_3$** and ER-Tracker red

(100 nM) for 30 min, the cells were washed with Stroke-physiological saline solution three times and subjected to imaging analysis using a Zeiss Laser Scanning Confocal Microscope. The **TBP-SO_3** was excited at 488 nm and its emission was collected in the range of 650-740 nm. ER - Tracker red was excited at 561 nm and the emission filter was 550-600 nm. The R was determined by the ZEN 2.6 software.

DCFH-DA was employed to detect the ROS generation inside cells under light irradiation. Hela cells were cultured in the plates at 37℃ with DMEM without FBS. Following incubation with **DBP** (2 μM), **TBP** (2 μM) and **TBP-SO_3** (2 μM) for 30 min in the dark room, DCFH-DA (30 μM) was added into the cells. After 20 min incubation, cells were washed thrice with Stroke-physiological saline solution. The fluorescence images of DCFH-DA were acquired using CLMS. The white light (30 mW/cm^2) was utilized as a illuminant for ROS excited and the emission was collected at 500-530 nm. For $O_2^{\bullet-}$ detection, HeLa cells were incubated with 2 μM of AIEgens and 10 μM dihydroethidium (DHE) for 30 min. After being washed by Stroke-physiological saline solution for three times, cells were irradiated with white light at a power density of 30 mW cm^{-2} for 10 min. Then, the red fluorescence was immediately observed using Zeiss Laser Scanning Confocal Microscope with the excitation wavelength of 561 nm, and emission collection wavelength from 570-630 nm. In addition, Singlet Oxygen Sensor Green (SOSG) was also applied as the indicator to detect $^1O_2$ generation. Hela cells with 2 mL DMEM were incubated with different materials 2 μL (DBP, TBP and TBP-SO_3) and 2 μL SOSG for 30 min, and the final concentrations were 2 μM. After being washed by PBS two times and adding DMEM 2 mL, cells were irradiated by white light at a power density of 30 mW cm^{-2} for 10 min. Then, the green fluorescence was immediately observed using an inverted fluorescent microscope with the excitation wavelength of 488 nm, and emission collection wavelength from 510-535 nm.

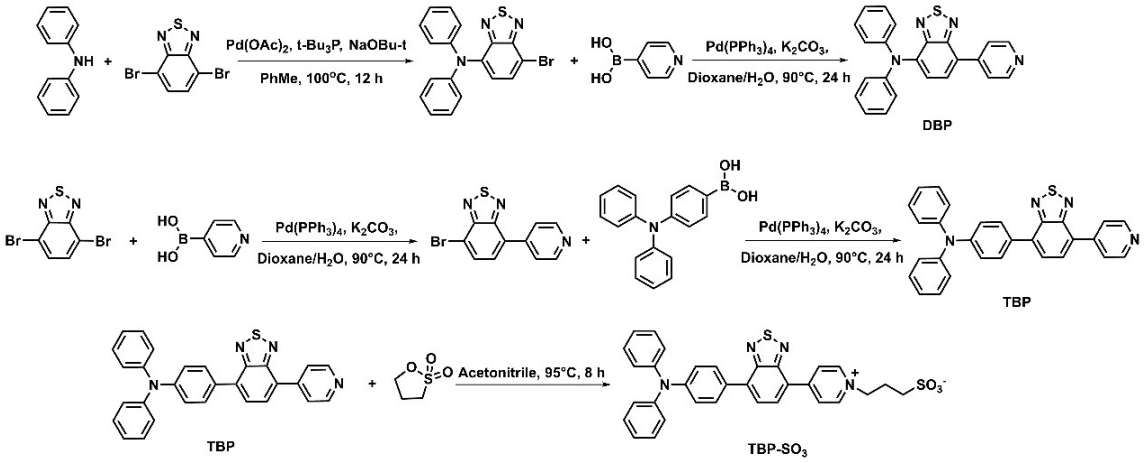
Cytotoxicity Assay

Cell Counting Kit-8 (CCK-8) assay was utilized to quantitatively measure the cytotoxicity of **DBP**, **TBP** and **TBP-SO_3** based on HeLa cell line. HeLa cell lines were seeded in DMEM and 10% FBS media in a 96-well round-bottom microplate with a density of 1×10^4 cells per well. The gens (**DBP**, **TBP** and **TBP-SO_3**) were added at different concentrations of 0, 1, 2, 5, 10, 20, 30 and 40 μM after replacing the medium, and was incubated with different cell lines respectively for 30 min, followed by irradiation with white light for 10 min (30 mW/cm^2), and another array of plates with cells were kept in the dark as the control. After 24 h incubation, 10 μL CCK-8 was added into each well. 1 hour later, the absorption of each well at 450 nm was recorded via Infinite 200 Pro. Each trial was performed with 4 wells in parallel.

Bacteria Culture and Assessment of Antibacterial Activity

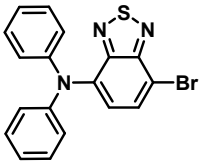
A single bacteria colony on solid agar plate was transferred to 5 mL corresponding liquid culture medium and grown for 10-12 h at 37 °C with a shaking speed of 200 rpm. The antimicrobial activities of **TBP-SO_3** to bacteria were evaluated by the traditional surface plating method. For the antibacterial activity of **TBP-SO_3** in dark, PBS solution of *S. aureus* (~1×10^9 CFU mL^{-1}) was treated with 10 μM of **TBP-SO_3** for 20 min at 37°C, respectively. Next, the bacteria suspensions were serially diluted by 10^4 fold with PBS. 100 μL diluted bacteria were spread on the corresponding solid agar plate and then incubated for 14-16 h at 37°C. The antibacterial activity of **TBP-SO_3** on the bacteria was evaluated according to the reduced ratio of colonies. The bacteria colonies on the agar plates were counted and the reduced ratio was calculated based on the equation [(A - B)/A] × 100%, where A is the mean number of bacteria colonies in the control sample (without **TBP-SO_3**), and B is the mean number of bacteria after incubated with the **TBP-SO_3**. The results were repeated for three times. As to antibacterial activity of **TBP-SO_3** under light, the bacteria were treated under the same conditions as the experiment in the dark except for that the samples were incubated for 5 min in the dark and then irradiated under white light (50 mW/cm^2) for 20 min.

Synthesis and characterization



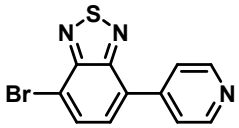
Scheme S1. Synthetic route for **DBP**, **TBP** and **TBP-SO_3**.

Synthesis of 7-bromo-N,N-diphenylbenzo[c][1,2,5]thiadiazol-4-amine.



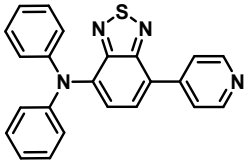
4,7-Dibromobenzo[c]-1,2,5-thiadiazole (1.57 g, 5.34 mmol) and diphenylamine (0.90 g, 5.34 mmol) was solubilized with 20 mL toluene (PhMe). Then $Pd(OAc)_2$ (0.03 g, 0.13 mmol), t-Bu_3P (0.55g, 2.67 mmol) and NaOBu-t (0.65g, 8.68 mmol) were added to the mixture. The solution was heated at 100°C under the nitrogen atmosphere for 12 h. After cooling to room temperature, the mixture was extracted with dichloromethane (DCM) three times and dried over anhydrous Na_2SO_4. The solvent was concentrated under reduced pressure. The concentrate was purified by silica gel column chromatography with DCM and petroleum ether (PE) (1:5, v/v) to afford the desired product as the orange solids. Yield: 60%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.92 (d, J = 7.8 Hz, 1H), 7.28 (t, J = 8.8 Hz, 4H), 7.09-7.05 (m, 3H), 7.01-7.00 (m, 4H).

Synthesis of 4-bromo-7-(pyridin-4-yl)benzo[c][1,2,5]thiadiazole.



A mixture of 4,7-dibromobenzo[c][1,2,5]thiadiazole (1.00 g, 3.40 mmol), pyridin-4-ylboronic acid (0.42 g, 3.42 mmol), $Pd(pph_3)_4$ (0.16 g, 0.14 mmol) and K_2CO_3 (2.35 g, 17.03 mmol) were ere solubilized with 60 mL 1,4 – dioxane/H_2O (3:1, v/v). The solution was heated at 90°C under the nitrogen atmosphere for 12 h. After cooling to room temperature, the mixture was extracted with dichloromethane (DCM) for three times and dried over anhydrous Na_2SO_4. The filtrate was concentrated under reduced pressure. The concentrate was purified by silica gel column chromatography with DCM and ethyl acetate (EAC) (3:1, v/v) to afford the desired product as the yellow solids. Yield: 45%. ^{1}H NMR (500 MHz, chloroform-d) δ 8.79 (d, J = 6.0 Hz, 2H), 7.99 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 4.5 Hz, 2H), 7.71 (d, J = 7.5 Hz, 1H).

Synthesis of DBP.



DBP

A mixture of 7-bromo-N,N-diphenylbenzo[c][1,2,5]thiadiazol-4-amine (0.10 g, 0.26 mmol), pyridin-4-ylboronic acid (0.05 g, 0.41 mmol), $Pd(pph_3)_4$ (0.02 g, 0.02 mmol) and K_2CO_3 (0.24 g, 1.70 mmol) were ere solubilized with 20 mL 1,4 – dioxane/H_2O (3:1, v/v). The solution was heated at 90°C under nitrogen atmosphere for 12 h. After cooling to room temperature, the mixture was extracted with dichloromethane (DCM) for three times and dried over anhydrous Na_2SO_4. The filtrate was concentrated under reduced pressure. The concentrate was purified by silica gel column chromatography with DCM and EAC (4:1, v/v) to afford the desired product as red solid. Yield: 45%.^{1}H NMR (500 MHz, DMSO-d_6) δ 8.71 (d, J = 5.5 Hz, 2H), 8.04 – 7.98 (m, 3H), 7.31 (m, 4H), 7.22 (d, J = 8.0 Hz, 1H), 7.11 (t, J = 7.0 Hz, 2H), 7.07 – 7.00 (m, 4H). ^{13}C NMR (126 MHz, DMSO-d6) δ 154.39, 151.15, 150.38, 147.56, 144.38, 140.67,

130.56, 129.92, 125.13, 124.61, 124.25, 123.52, 123.09. ESI HRMS: calcd. for $C_{23}H_{16}N_4S$: 380.4690, fond: 381.1168.

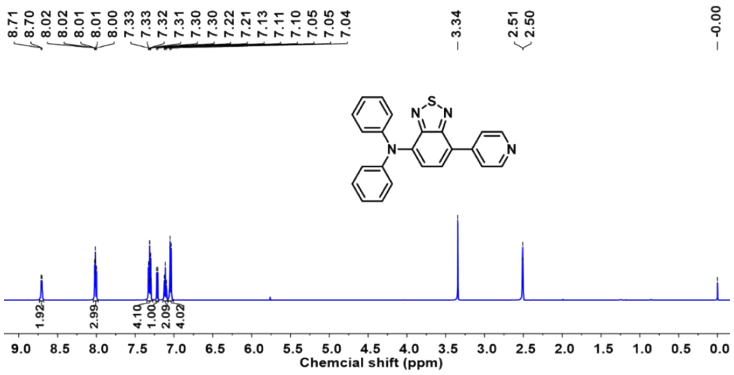


Figure S1. ^{1}H NMR spectrum of compound **DBP**.

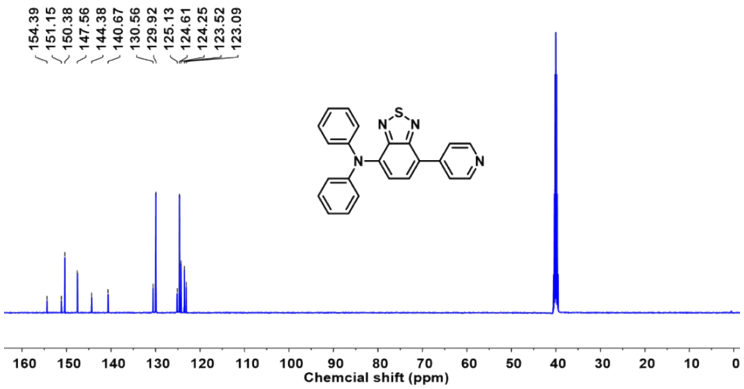


Figure S2. ^{13}C NMR spectrum of compound **DBP**.

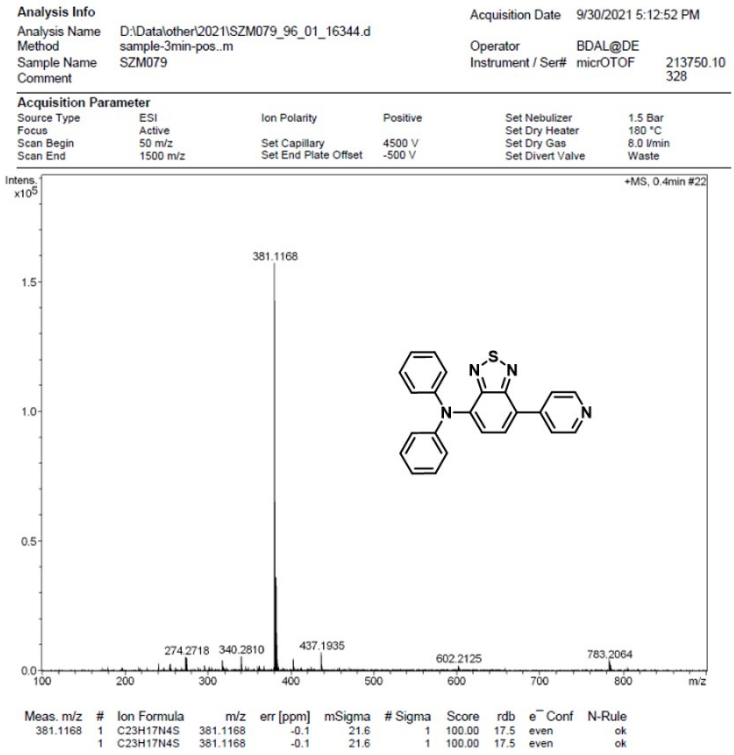
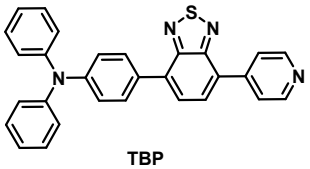


Figure S3. HRMS spectrum of compound **DBP**.

Synthesis of TBP.



TBP

A mixture of 4-bromo-7-(pyridin-4-yl)benzo[c][1,2,5]thiadiazole (0.10 g, 0.34 mmol), (4-(diphenylamino)phenyl)boronic acid (0.10 g, 0.34 mmol), $Pd(pph_3)_4$ (0.02 g, 0.02 mmol) and K_2CO_3 (0.35 g, 2.50 mmol) were ere solubilized with 17 mL THF/H_2O (15:2, v/v). The solution was heated at 70°C under nitrogen atmosphere for 8 h. After cooling to room temperature, the mixture was extracted with dichloromethane (DCM) for three times and dried over anhydrous Na_2SO_4. The filtrate was concentrated under reduced pressure. The concentrate was purified by silica gel column chromatography with DCM to afford the desired product as red solid. Yield: 36%.^{1}H NMR (500 MHz, DMSO-d_6) δ 8.75 (d, J = 5.5 Hz, 2H), 8.13 (d, J = 7.5 Hz, 1H), 8.07 (d, J = 6.0 Hz, 2H), 7.99 – 7.96 (m, 3H), 7.39 – 7.36 (m, 4H), 7.14 – 7.10 (m, 8H). ^{13}C NMR (126

MHz, DMSO-d_6) δ 153.78, 153.49, 150.45, 148.27, 147.28, 133.97, 130.80, 130.41, 130.20, 128.90, 127.59, 125.24, 125.13, 124.20, 123.92, 123.86, 122.52, 122.15. ESI HRMS: calcd. for $C_{29}H_{20}N_4S$: 456.5670, fond: 457.1481. The characteristic of TBP was same as reported work.[4]

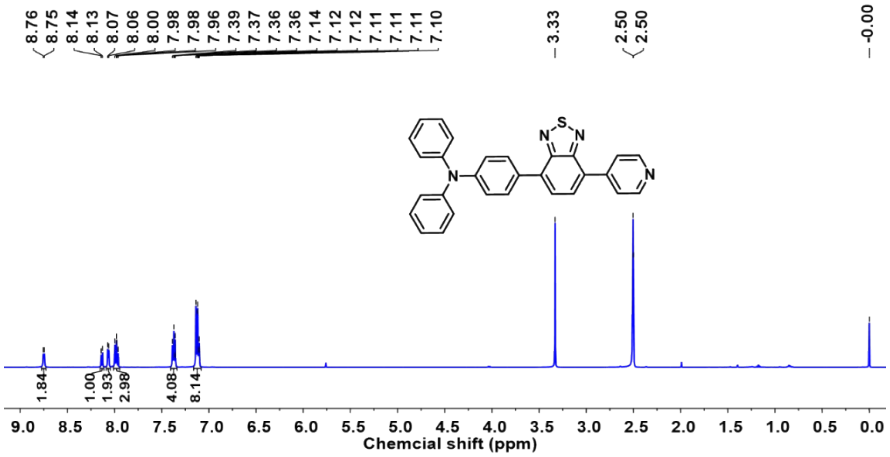


Figure S4. [1]H NMR spectrum of compound **TBP**.

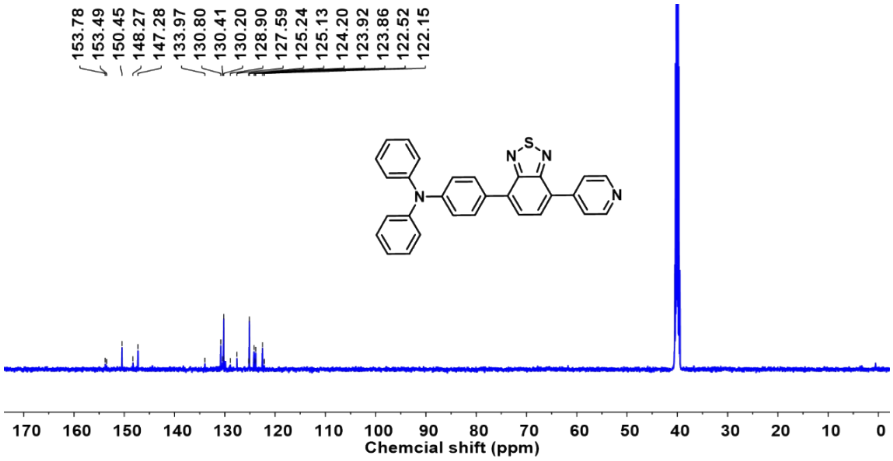


Figure S5. [13]C NMR spectrum of compound **TBP**.

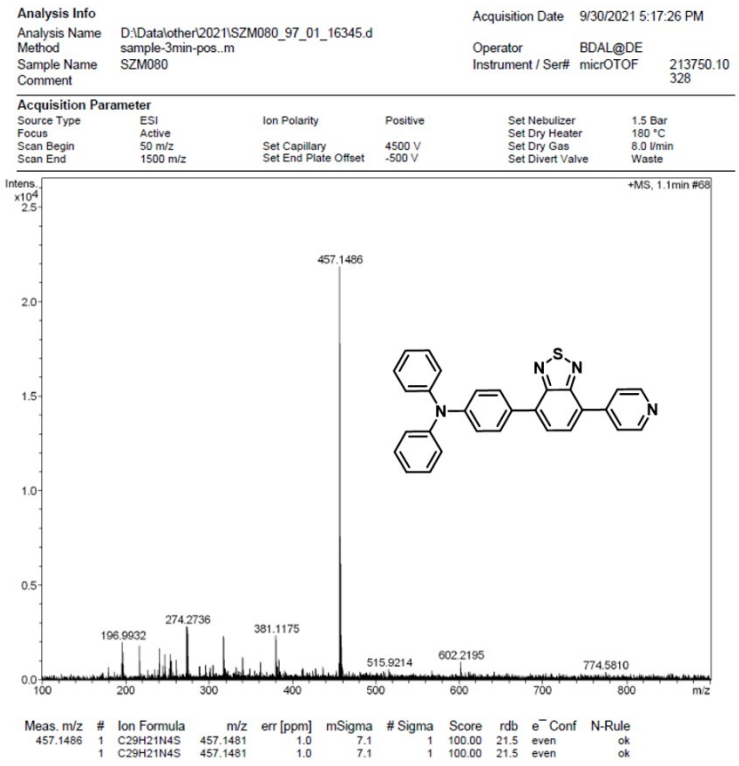
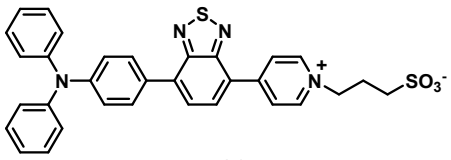


Figure S6. HRMS spectrum of compound **TBP**.

Synthesis of TBP-SO3.



To an oven dried round bottom flask sealed with rubber stopper, **TBP** (0.73 g, 1.60 mmol) and 1,2-oxathiolane 2,2-dioxide (0.20 g, 1.6 mmol) were added, followed by the addition of dry acetonitrile (10 mL). The reaction mixture was reflxed at 95°C for 8 h. After cooling to room temperature, the mixture was extracted with dichloromethane (DCM) for three times and dried over anhydrous Na_2SO_4. The filtrate was concentrated under reduced pressure. The concentrate was purified by silica gel column chromatography with DCM and Methanol (MeOH) (30:1, v/v) to afford the desired product as deep red solid. Yield: 65%. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.22 (d, J = 6.5 Hz, 2H), 8.88 (d, J = 7.0 Hz, 2H), 8.48 (d, J = 7.5 Hz, 1H), 8.05 – 8.02 (m, 3H), 7.38 (t, J = 7.5 Hz, 4H), 7.16 – 7.09 (m, 8H), 4.79 (t, J = 7.0 Hz, 2H),

2.50 (s, 2H), 2.34 – 2.29 (m, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 153.65, 153.11, 151.92, 148.84, 147.06, 145.24, 136.67, 132.67, 131.10, 130.25, 129.49, 127.17, 126.81, 125.42, 124.73, 124.50, 121.94, 59.50, 47.53, 27.80. ESI HRMS: calcd. for $C_{32}H_{26}N_4O_3S_2^-$ $[M + Na]^+$: 601.6953, fond: 601.1339.

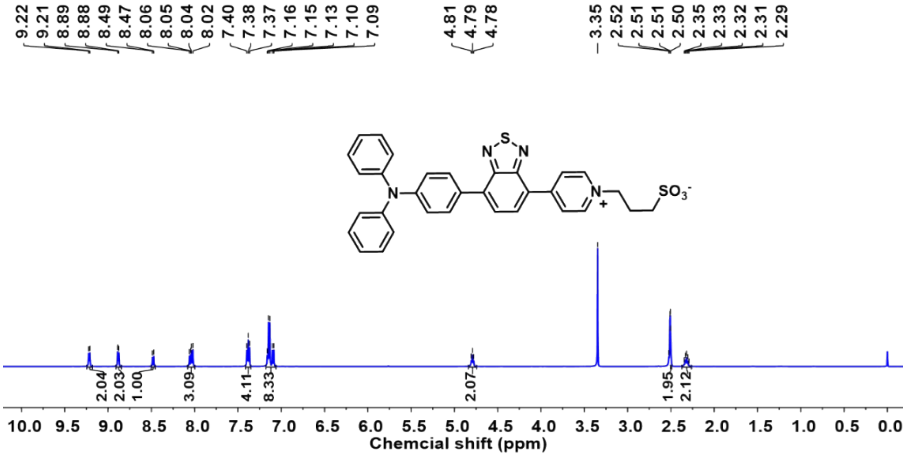


Figure S7. ^{1}H NMR spectrum of compound **TBP-SO$_3$**.

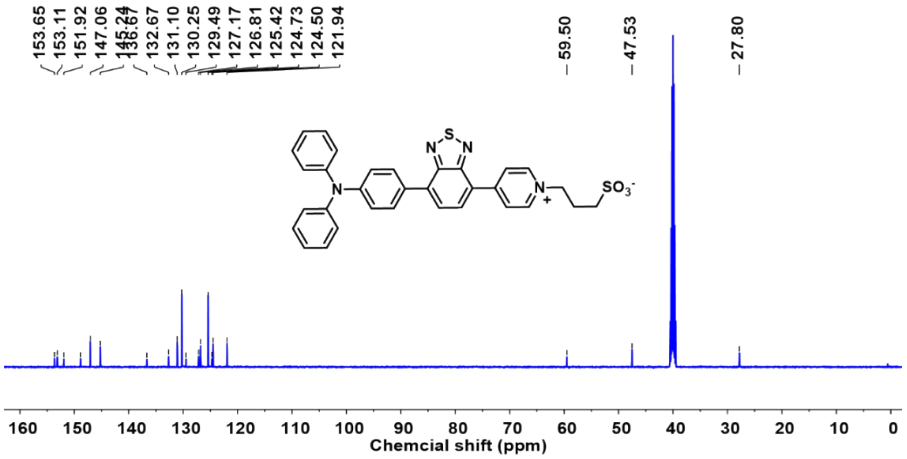


Figure S8. ^{13}C NMR spectrum of compound **TBP-SO$_3$**.

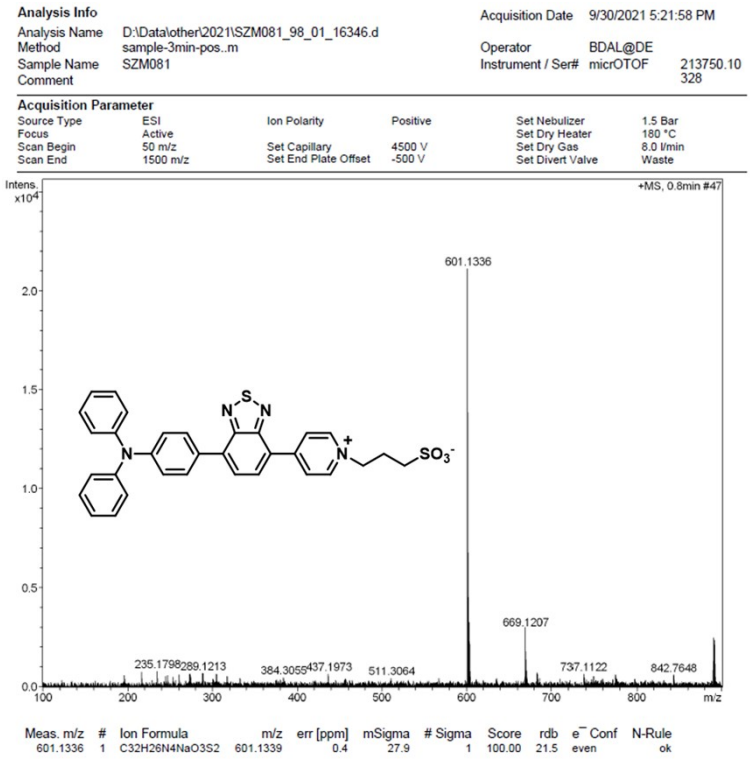


Figure S9. HRMS spectrum of compound **TBP-SO3**.

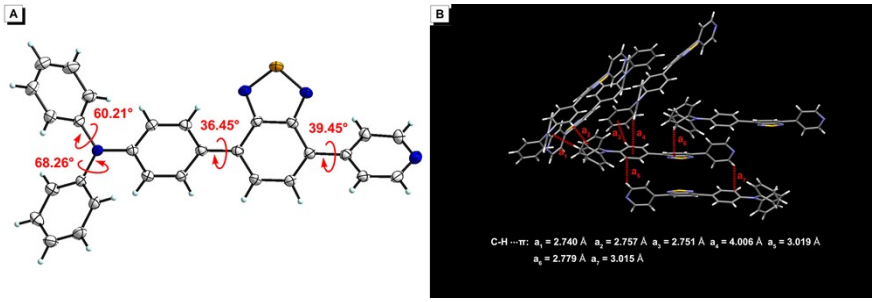


Figure S10. Single crystal structure (A) and molecular stacking structure (B) of **TBP**.

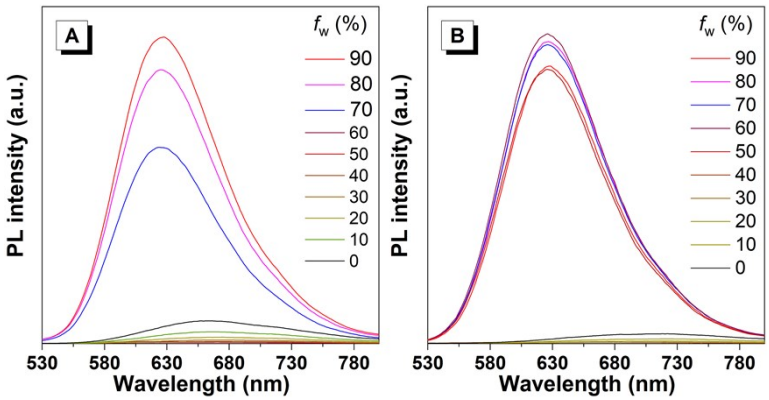


Figure S11. PL spectra of **DBP** (5×10^{-5} M) (A) and **TBP** (5×10^{-5} M) (B) in DMSO/H_2O mixtures with different H_2O fractions.

Table S1. Crystal data and structure refinement for **DBP**, **TBP** and **TBP-SO_3**.

Empirical formula	$C_{23}H_{16}N_4S$ **DBP**	$C_{29}H_{20}N_4S$ **TBP**	$C_{64}H_{50}N_8O_6S_4$ **TBP-SO3**
Temperature	295K	295K	173K
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/n$	P-1
a/Å	11.3157(7)	9.7827(12)	9.1035(3)
b/Å	15.2990(8)	9.9281(12)	10.9040(4)
c/Å	22.1575(14)	23.760(3)	30.0685(11)
α/°	90	90	87.972(2)
β/°	103.527(4)	98.562(7)	84.880(2)
γ/°	90	90	78.020(2)
Volume	3729.5(4) Å^3	2282.0(5) Å^3	2907.64(18) Å^3
Z	8	4	2
ρ_{calc}	1.355 g/cm^3	1.329 g/cm^3	1.320 g/cm^3
μ	1.660 mm^-1	1.452 mm^-1	1.986 mm^-1
F(000)	1584	952	1204
Reflections collected	25130	27253	42552
Independent reflections	6124 [R_{int}=.1013, R_{sigma}=0.0779]	3780 [R_{int}=0.0423, R_{sigma}=0.0291]	9596 [R_{int}=0.0611, R_{sigma}=0.0495]
Data/restraints/parameters	6124/0/505	3780/0/307	9596/6/766
Goodness-of-fit on F^2	1.022	1.094	1.040
Final R indexes [I>=2σ (I)]	R_1=0.0609, wR_2=0.1147	R_1=0.0403, wR_2=0.0949	R_1=0.1049, wR_2=0.2829
Final R indexes [all data]	R_1=0.1156, wR_2=0.1349	R_1=0.0479, wR_2=0.0997	R_1=0.1277, wR_2 = 0.3042

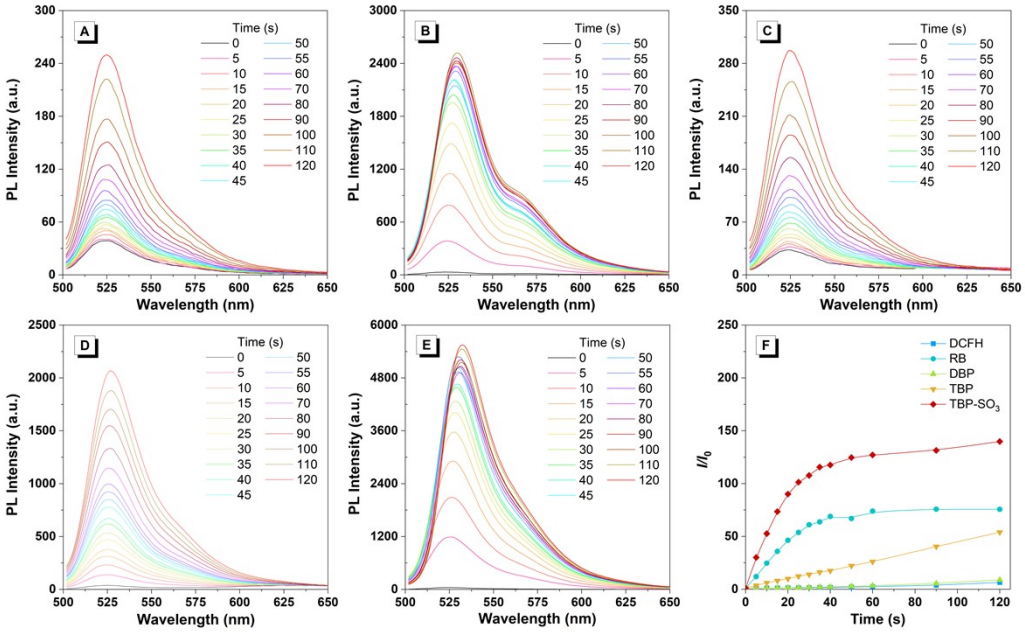


Figure S12. Fluorescence spectra for ROS of Ctrl (A), Rose Bengal (B), **DBP** (C), **TBP** (D), **TBP-SO$_3$** (E), and I/I_0 (F) with white light irradiation using DCFH as fluorescence probe. Gens concentration (2×10^{-6} M), DCFH concentration (4×10^{-5} M), white light irradiation (400−700 nm, 23.4 mW/cm^2).

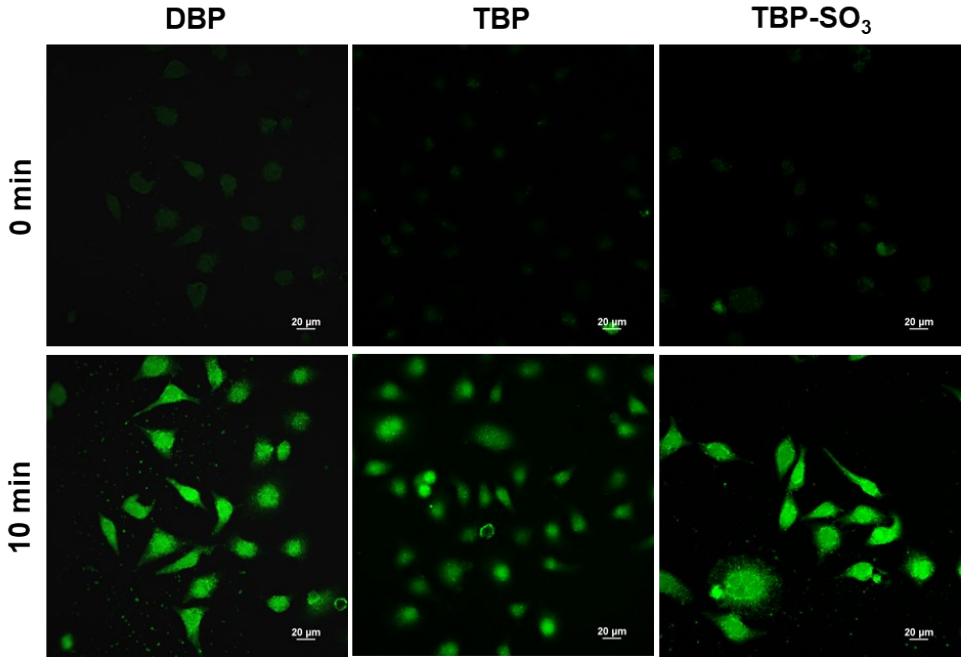


Figure S13. Intracellular ROS level using DCFH as the indicator in HeLa cells incubated with **DBP**, **TBP,** and **TBP-SO$_3$**.

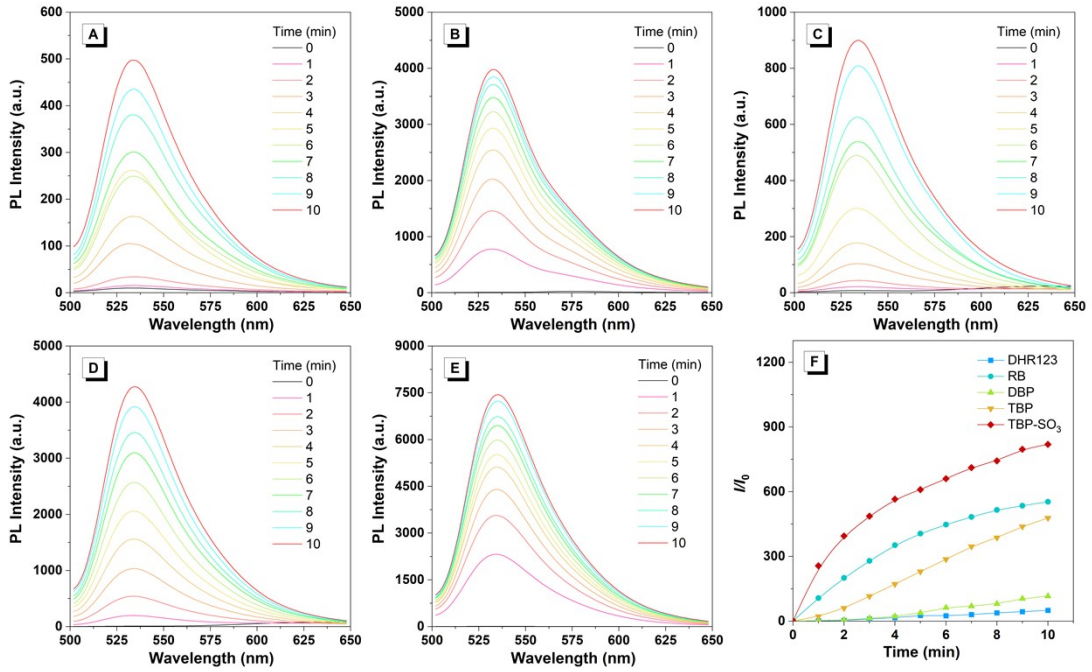


Figure S14. Fluorescence spectra for ROS of Ctrl (A), Rose Bengal (B), **DBP** (C), **TBP** (D), **TBP-SO$_3$** (E), and I/I_0 (F) with white light irradiation using DHR123 as fluorescence probe. Gens concentration (2×10^{-6} M), DHR123 concentration (3×10^{-6} M), white light irradiation (400−700 nm, 23.4 mW/cm^2).

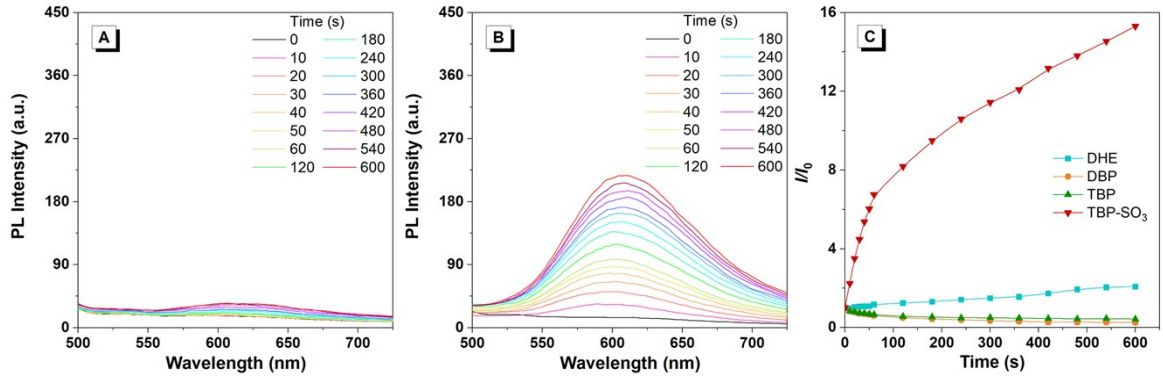


Figure S15. The fluorescence spectra of Ctrl (A) and **TBP-SO$_3$** (B) upon different white light irradiation times. (C) The fluorescence intensity changes (I/I_0) at 610 nm in presence of DHE and RNA versus irradiation time. AIEgen concentration is 2×10^{-6} M and DHE concentration is 1×10^{-5} M, respectively.

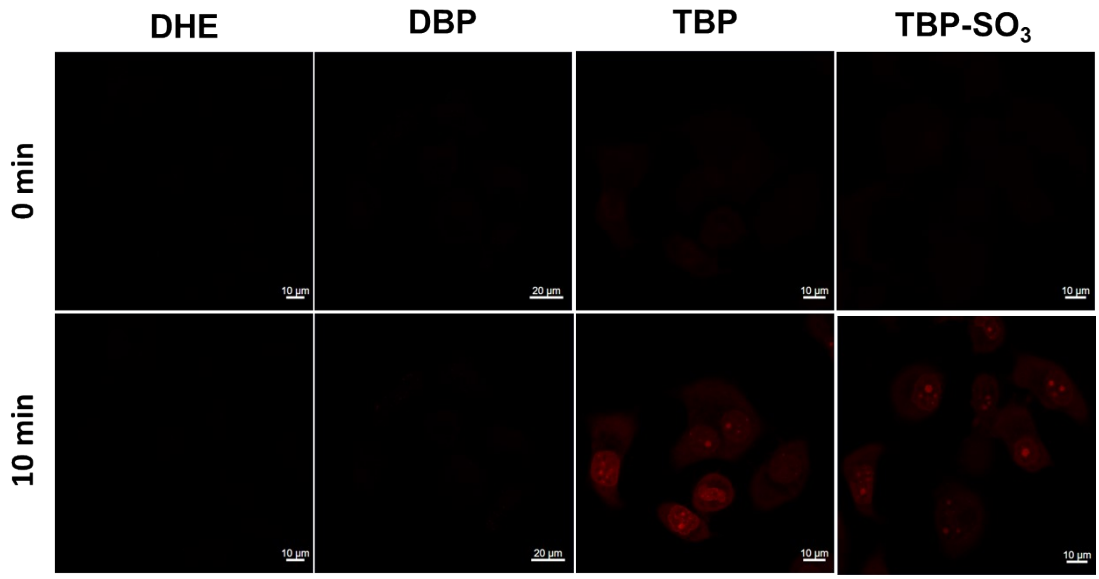


Figure 16. Intracellular $O_2^{\bullet-}$ level using DHE as the indicator in HeLa cells incubated with **DBP**, **TBP,** and **TBP-SO$_3$**.

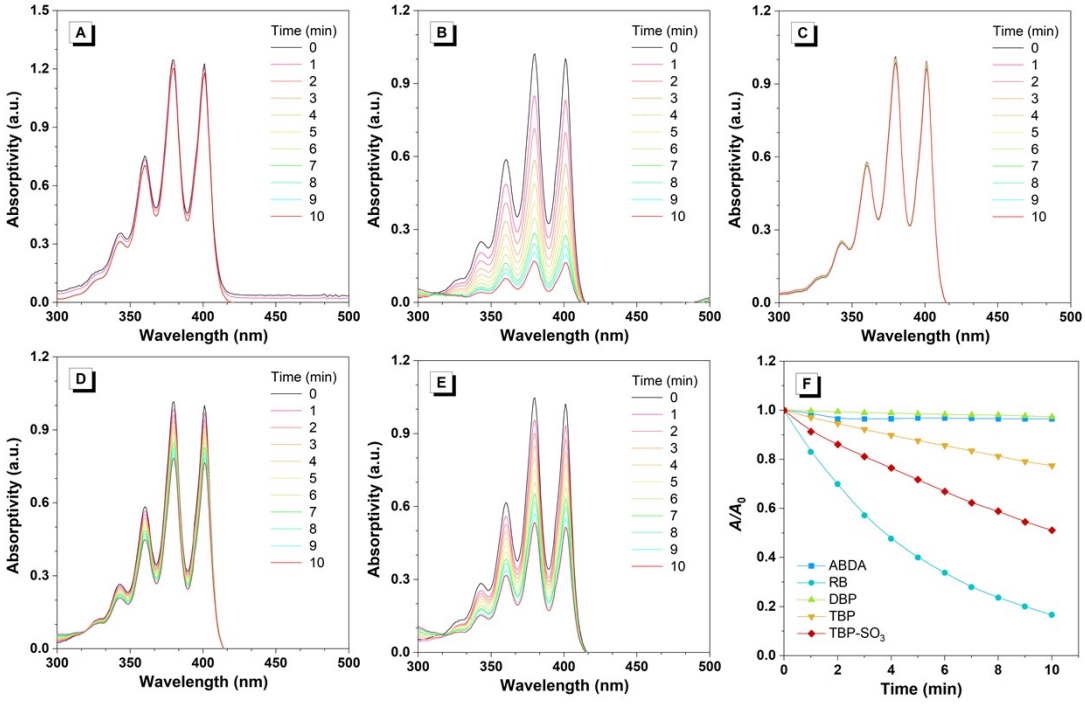


Figure S17 Absorbance spectra for $^1O_2$ of Ctrl (A), Rose Bengal (B), **DBP** (C), **TBP** (D), **TBP-SO3** (E), and A/A_0 (F) with white light irradiation using ABDA as fluorescence probe. Gens concentration (2×10^{-6} M), ABDA concentration (1×10^{-4} M), white light irradiation (400−700 nm, 23.4 mW/cm^2).

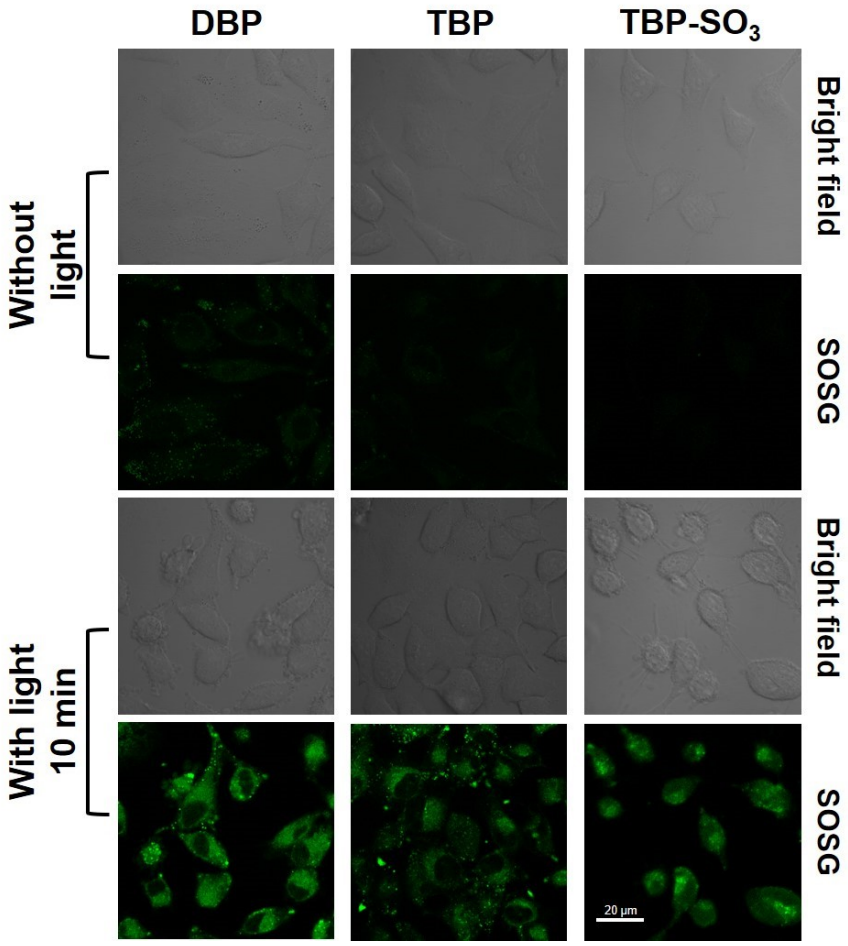


Figure S18. Intracellular $^1O_2$ level using SOSG as the indicator in HeLa cells incubated with **DBP**, **TBP,** and **TBP-SO$_3$**.

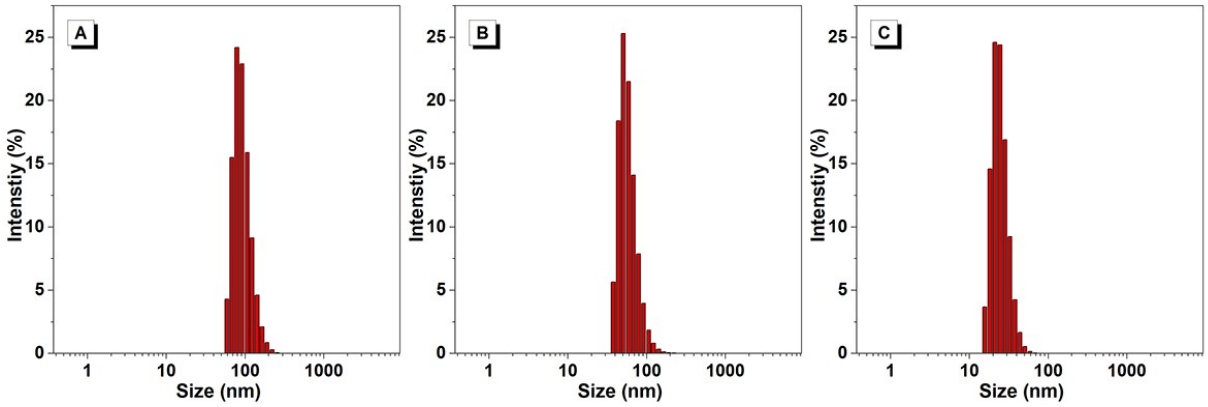


Figure S19. DLS imagings for nanoparticles **DBP** (A), **TBP** (B), and **TBP-SO$_3$** (C).

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