Supporting Information

A Singlet Oxygen Self-Reporting Photosensitizer for Cancer Phototherapy

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Chemicals and Apparatus

The general chemicals used in this study were analytically pure and purchased from Energy Chemical Co., J&K Scientific Ltd., or Aldrich Chemical Co. The **Rh-NBSe** and **Rh-NBSe-1** was dissolved in dimethyl sulfoxide (DMSO, Cell Culture Reagent) to get 3 mM stock solution. ^{1}H NMR and ^{13}C NMR spectra of all compounds were detected by Bruker Avance Ⅲ 500 spectrometer. Mass spectrometric (MS) data were obtained with LTQ Orbit rap XL or TOF MALDI-MS instruments. Fluorescence measurements were performed on a VAEIAN CARY Eclipse fluorescence spectrophotometer (Serial No. FL0812-M018). Confocal laser scanning microscope (CLSM) images were

performed on Olympus FV1000-IX81 confocal laser scanning microscope. Small animals' fluorescence imaging was carried out by Night OWL II LB983 living imaging system.

Fluorescence Self-Reporting Titration

After dissolving in PBS (0.5 mM), the fluorescence spectra (Rh moiety, Ex: 550 nm) of Rh-NBSe and Rh-NBSe-1 were scanned, then the solutions in cuvette were irradiated by 660 nm red light (20 mW/cm^2) for a series of time, and recorded the fluorescence spectrum, respectively.

Singlet Oxygen Quantum Yield (Φ_Δ) Calculation

The Φ_Δ of PSs were detected using 1, 3-diphenlisobenzofuran (DPBF, λex = 415 nm) as the singlet oxygen capture agent with 660 nm red light (3 mW), and methyl blue (**MB)** as the standard (Φ_Δ= 0.57 in DCM). The absorption spectrum of DPBF at interval of 15s were obtained, and the yields were calculated by the following equations:

$$\Phi_\Delta = \Phi_{\Delta S}\left(\frac{k}{k_S}\right)\left(\frac{F_S}{F}\right) \quad F = 1 - 10^{-O.D.}$$

Where *S* is standard MB, and the *k* is the slope of decrease speed, $\boldsymbol{\Phi_{\Delta S}}$ is the singlet oxygen quantum yield of MB, F is the absorbance correction factor, and the O.D. is absorbance at 660 nm.

Cell Culture

Animal stage IV human breast cancer cells 4T1 were maintained in RPMI 1640 medium and supplemented with 1% penicillin-streptomycin and 10% FBS at 37ºC under the atmosphere of 5% CO_2 and 95% air.

Subcellular Localization

4T1 cells were incubated with 1 μM **Rh-NBSe** for 30 min, after washing twice by PBS, Mito Tracker Green (Ex: 488 nm, Em: 500-540 nm), LysoTracker Green DND 26 (100 nM) (Ex: 488 nm, Em: 500-540 nm) and Hoechst 33342 (2 mg/mL) (Ex: 405 nm, Em: 440-480 nm) were used to label mitochondria, lysosome and nucleus, respectively. After twice washing with PBS, the cells were then imaged with CLSM.

Intracellular Singlet Oxygen Detection

The ROS production in 4T1 cells was detected using 2,7-Dichlorodi-hydrofluorescein diacetate **(**DCFH-DA**)** (Ex: 488 nm, Em: 480-520 nm). The cells were incubated with following treatments: group 1, control; group 2, 1 μM **Rh-NBSe** without irradiation; group 3, 1 μM **Rh-NBSe** with 1 min irradiation (660 nm, 20 mW/cm^2) and group 4, 1 μM **Rh-NBSe-1** with 1 min irradiation (660 nm, 20 mW/cm2). After treatments, the CLSM imaging was performed to give the level of intracellular ROS.

MTT Assays and Cell Viability Calculation

4T1 cells were plated at 10000 cells per well in a 96-well cell culture plate, followed by incubation at 37ºC for 24 h. Then different concentration (0-2.5 μM) of **Rh-NBSe** medium were prepared in plate. After 30 min incubation, the cells were subjected to different light dose (0, 6, 12 J/cm^2) by 660 nm LED red light. The cells were incubated overnight at incubator and then cleaned the medium. Next, 5 mg/mL MTT solution in PBS was added to each well. After 4 h, the medium were removed out carefully, and 200 μL DMSO was added to each well to dissolve blue formazan. And the absorbance of 490 nm was measured with a Bio-Rad microplate reader and the cell viability was obtained by the following equation:

$$cell\ viability\ (\%) = \left(OD_{ps} - \frac{OD_{blank\ control}}{OD_{control}} - OD_{blank\ control} \right) \times 100\%$$

Fluorescence Self-Reporting Detection in Cells

The 4T1 cells were incubated with 1 μM **Rh-NBSe** or 1 μM **Rh-NBSe-1** for 30 min. The initial fluorescent imaging in 4T1 were obtained using CLSM (Ex:561 nm, Em:570-620 nm), then the 35 mm cell dishes was exposed to 660 nm red LED light for different time, and the fluorescence imaging were obtained simultaneously.

Tumor Imaging of Rh-NBSe in Vivo

All animal operations were in accordance with institutional animal use and care regulations approved by the Model Animal Research Center of Dalian Medical University. Specific female Balb/c mice, 5-6 weeks of age, were obtained from Laboratory Animal Center of Dalian Medical University. Then, 3×10^6 4T1 cells were injected subcutaneously into the selected armpit positions to establish the breast tumor model of Balb/c mice. Tumors were allowed to grow to about 100 mm^3. For detection of tumor targeting accumulation, **Rh-NBSe** and **Rh-NBSe-1** was injected intravenously into tumor bearing mice, and fluorescence imaging was observed at different post-injection time by small animal's fluorescence imaging.

Fluorescence Self-Reporting Detection in Tumor

To research self-reporting property in tumor, the **Rh-NBSe** and **Rh-NBSe-1** was compared by peritumoral injection (100 μL x 0.5 μM). After 1h diffusion, the mice with injection of the two PSs were imaged using small animals' fluorescence imaging to get the initial fluorescence imaging, then the tumor sites were irradiated with 660 nm LED light for 5 min (50 mW/cm^2), and recorded the after fluorescence in tumor.

PDT evaluation for mice

In order to evaluate the PDT efficacy of **Rh-NBSe** in vivo, all mice were divided into five groups and performed with different treatments. Each group contained six mice, PBS and PSs were injected by tail vein injection. After 2 h post-injection, tumor region was irradiated with 660 nm red xenon lamp at a power density of 50 mW/cm^2 for 8 min. The tumor volume of all mice was measured using a vernier caliper for 14 days after different treatments, and calculate the tumor volume (V) according to the greatest longitudinal diameter (L) and the greatest transverse diameter (D).

$$V = L \cdot D^2/2.$$

Moreover, after 21 day post-treatment, the mice were euthanized, and tumor tissues of mice were harvested for histological analysis by means of hematoxylin-eosin (H&E) staining.

Synthesis

Synthesis of compound **2**

Nitrogen was purged in EtOH (10 mL) for 15 min, NaOH (0.44 g, 11 mmol) and 3-mercapto-1-propanol (1 g, 11 mmol) were added and the reaction was stirred at 0 ^{o}C ice bath for 30 min while the flask was sealed. Then, cis-1,2-dichloroehylene (0.502 g, 0.55 mmol) in degassed EtOH (1 mL) was added and the reaction was reflux for 18 h. After cooling to RT, extracted with petroleum ether (PE) and brine. The organic layer was collected and dried with Na_2SO_4, and then evaporated under reduced pressure. The product was purified by silica gel column chromatography using EtOAc/hexanes (50:50, v/v) as mobile phase, to give reseda oil (0.973 g, 85%). HRMS (ESI): m/z for

$C_8H_{17}O_2S_2^+$ ([M+H]$^+$): calc. 209.0664; found 209.0664; $C_8H_{16}O_2S_2Na^+$ ([M+Na]$^+$): calc. 231.0484; found 231.0492.

Synthesis of compound 4

Compound **2** (790 mg, 3.79 mmol) was dissolved in DCM (15 mL), 1.7 mL Et_3N was added into reactions and stirred for 10 min, then p-toluenesulfonyl chloride (TsCl, 1.45g, 7.58 mmol) was dissolved in DCM (5 mL) and added dropwise at 0 ^oC, the reaction was finished after 12 h at r.t. Extracted with PE and brine, the organic was collected and dried with Na_2SO_4, and then evaporated under reduced pressure. The product was purified by silica gel column chromatography using DCM/hexanes (150:75, v/v) as mobile phase, to give transparent oil compound **3** (1.03 g, 52.5%). HRMS (ESI): m/z for $C_{22}H_{28}O_6S_4Na^+$ ([M+Na]$^+$): calc. 539.0661; found 539.0662. The compound **3** (500 mg, 0.97 mmol) was dissolved in DMSO (10 mL) and then NaN_3 (630 mg, 9.7 mmol) was added for 4 h. The reaction mixture was extracted with PE and brine, the organic was collected and dried with Na_2SO_4, and then evaporated under reduced pressure to give the compound **4** for next step reaction.

Synthesis of compound **Rh**

The compound **6** was synthesised as reference.[1] Then a mixture of **6** (570mg, 3 mmol), 3-(diethylamino)phenol (990 mg, 6 mmol), p-TsOH(78 mg, 0.45 mmol) and acetic acid (15 mL) was heated at 70 ^oC and stirred for 7 h. The reaction mixture was cooled to r.t., and the pH was adjusted to above 7.0 with 10% NaOH solution. The precipitate was filtered and washed with water (30 mL). The solid was dissolved in CH_2Cl_2 (30 mL)

,to which chloranil (366 mg, 1.5 mmol) was added. The mixture was stirred for 2 h. After removal of the solvent, the residue was purified by column chromatography to give an amaranthine solid (500 mg, yield 34.5%). ^{1}H NMR (500 MHz, DMSO) δ 7.51 (s, 1H), 7.50 (s, 1H), 7.35 (s, 1H), 7.33 (s, 1H), 7.30 (s, 1H), 7.29 (s, 1H), 7.17 (d, *J* = 2.1 Hz, 1H), 7.15 (d, *J* = 2.2 Hz, 1H), 6.97 (d, *J* = 2.1 Hz, 2H), 4.97 (d, *J* = 2.1 Hz, 2H), 3.66 (q, *J* = 6.9 Hz, 7H), 3.39 (s, 1H), 1.21 (t, *J* = 7.1 Hz, 14H). HRMS (ESI): m/z for $C_{30}H_{33}N_2O_2^+$ ([M]$^+$): calc. 453.2537; found 453.2536.

Synthesis of compound **Rh-N$_3$**

The compound **4** was obtained by a click reaction, the **Rh** (60 mg, 0.12 mmol) and compound **4** (310 mg, 1.2 mmol) was dissolved in component solvent ($CHCl_3$: EtOH:H_2O=12 mL:1 mL:1 mL), then $CuSO_4 \cdot 5H_2O$ (18 mg, 0.07 mmol) and sodium ascorbate (29 mg, 0.14 mmol) was successively added under nitrogen atmosphere. The reaction was completed after 24 h at r.t., the reagent was extract with DCM and the organic layers was dried over $MgSO_4$, the crude product was obtained after removal of the solvent. The **Rh-N$_3$** was purified by column chromatography to give an amaranthine solid (75 mg, yield 83.8%). ^{1}H NMR (500 MHz, MeOD) δ 8.19 (d, *J* = 10.3 Hz, 1H), 7.52 – 7.45 (m, 4H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 9.6 Hz, 1H), 6.99 (s, 1H), 6.22 (d, *J* = 8.1 Hz, 1H), 6.14 (d, *J* = 8.0 Hz, 1H), 5.37 (s, 2H), 4.60 (t, *J* = 6.2 Hz, 2H), 3.71 (dd, *J* = 13.8, 6.7 Hz, 8H), 3.45 – 3.41 (m, 2H), 2.82 – 2.74 (m, 2H), 2.71 (t, *J* = 6.8 Hz, 2H), 2.27 (dt, *J* = 14.0, 7.1 Hz, 2H), 1.88 – 1.84 (t, 2H), 1.34 (t, *J* = 7.0 Hz, 12H). HRMS (ESI): m/z for $C_{38}H_{47}N_8O_2S_2^+$ ([M]$^+$): calc. 711.3258; found 711.3252.

Synthesis of **8**

Under nitrogen atmosphere, the 3-I-phenyl-diethylamine (550 mg, 2.0 mmol) and Se (320 mg, 78.96 mmol) was added into DMSO, then CuO (79.5 mg, 1.0 mmol) and KOH (225 mg, 4.0 mmol) was separated added, the reaction was completed after 3 h at 90 ^{o}C. After cooled 30 min, the DMSO was removed by vacuum pump, and the product was purified by column chromatography to give brown oil (386 mg, yield 85%). HRMS (ESI): m/z for $C_{20}H_{29}N_2Se_2^+$ ($[M+H]^+$): calc. 457.0656; found 457.0660.

Synthesis of **9**

To a stirred solution of 1M HCl (100 mL) was added the compound **8** (1.5 g, 3.3 mmol), the $NaNO_2$ (500 mg, 7.26 mmol) in 5 mL water was followed dropwise into reaction mixture, orange precipitate was observed. The reaction was completed after 30 min, the crude products was obtained after extracted using ethyl acetate, the compound **9** was purified by recrystallization of isopropanol to get orange solid (1.52g, yield 90%). HRMS (ESI): m/z for $C_{10}H_{13}N_2OSe^+$ ($[M/2]^+$): calc. 257.0193; found 257.0202.

Synthesis of **10**

To obtain the N-propargyl-naphthylamine, the 1-naphthylamine (3.0 g, 21 mmol) was dissolved in DMF, then the 3-propargyl bromide (2.5 g, 21 mmol) and K_2CO_3 (2.9 g, 21 mmol) was added, after stirred 2 h at r.t., the reaction was completed. After removed the solvents, the products was purified by column chromatography to get colorless oil (2 g, yield 52.5%). MS (ESI): m/z for $C_{13}H_{12}N^+$ ($[M+H]^+$): calc. 182.09; found 182.08.^{1}H NMR (400 MHz, MeOD) δ 7.97 (d, J = 9.4 Hz, 1H), 7.75 (d, J = 9.4 Hz,

1H), 7.42 – 7.38 (m, 2H), 7.32 (t, *J* = 7.9 Hz, 1H), 7.21 (d, *J* = 8.2 Hz, 1H), 6.74 (d, *J* = 7.5 Hz, 1H), 4.10 (d, *J* = 2.2 Hz, 2H), 2.52 (t, *J* = 2.4 Hz, 1H).

Synthesis of **NBSe**

The compound **9** (230 mg, 0.45 mmol) and **10** (236 mg, 1.3 mmol) was dissolved in CF_3CH_2OH, the reaction was refluxed at 90 ℃ for 2 h under N_2 atmosphere. After cooled to r.t., the 1M HCl was dropped into the mixture. After removed the solvents, the **NBSe** was obtained by column chromatography to got bule solid (94 mg, yield 46%). HRMS (ESI): m/z for $C_{23}H_{22}N_3Se^+$ ($[M]^+$): calc. 420.0973; found 420.0967.

Synthesis of compound **Rh-NBSe**

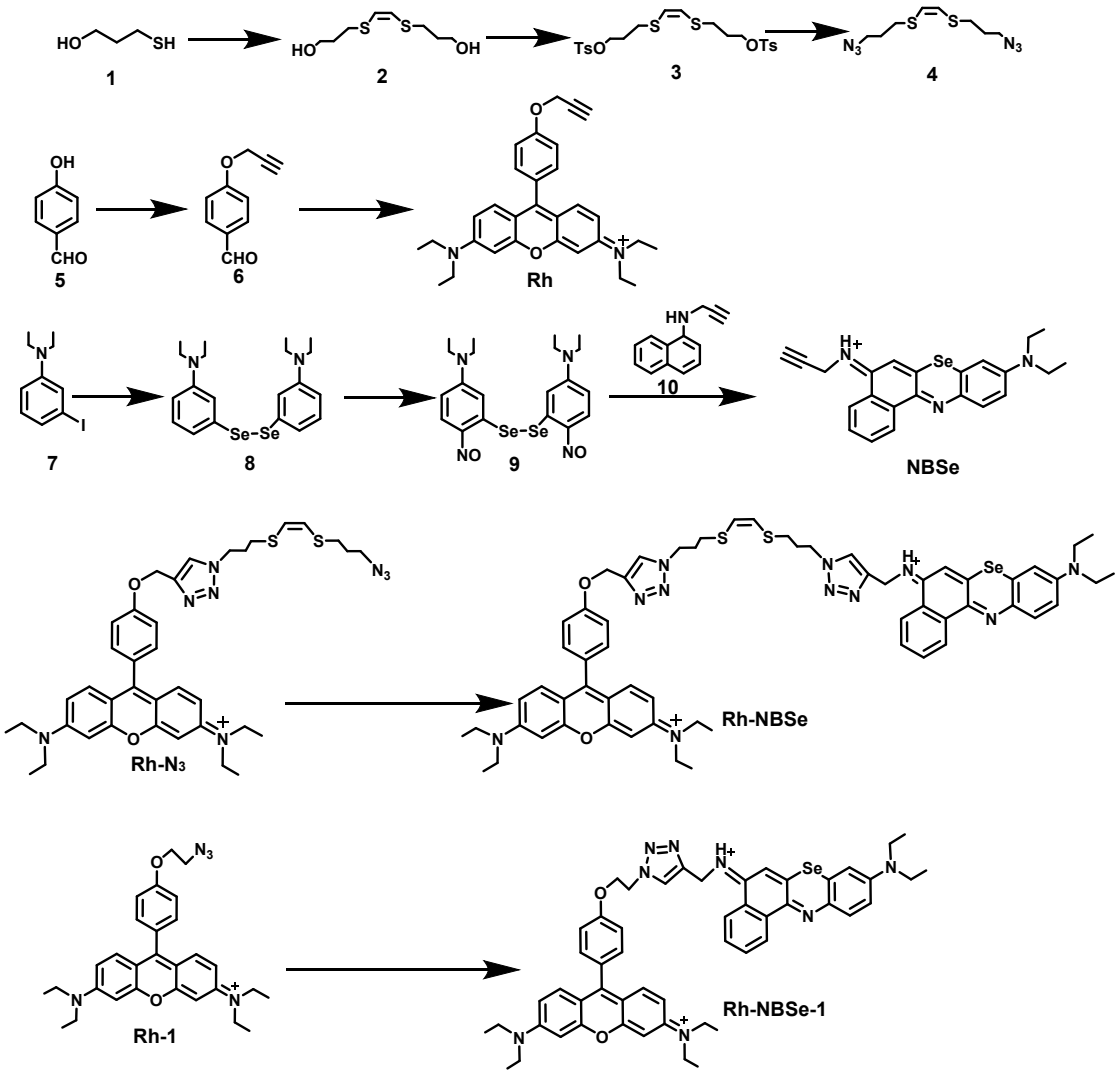
The NBSe was synthesised as reference, the target product **Rh-NBSe** was obtained by click reaction. **Rh-N_3** (40 mg, 0.054 mmol) and **NBSe** (36.5 mg, 0.080 mmol) was dissolved in component solvent ($CHCl_3$:EtOH:H_2O=12 mL:1 mL:1 mL), then $CuSO_4 \cdot 5H_2O$ (8 mg, 0.032 mmol) and sodium ascorbate (13 mg, 0.065 mmol) was successively added under nitrogen atmosphere. The reaction was completed after 24 h at r.t., the reagent was extract with DCM and the organic layers was dried over $MgSO_4$, the crude product was obtained after removal of the solvent. The product was purified by column chromatography to give a purple solid (45 mg, yield 70%). ^{1}H NMR (500 MHz, MeOD) δ 9.05 (d, *J* = 8.0 Hz, 1H), 8.30 (d, *J* = 8.1 Hz, 1H), 8.16 (s, 1H), 8.14 (s, 1H), 8.10 (d, *J* = 9.5 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 4.5 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.57 (d, *J* = 2.8 Hz, 1H), 7.40 – 7.35 (m, 4H), 7.29 (dd, *J* = 8.6, 6.5 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 1H), 7.08 (d, *J* = 9.6 Hz, 1H), 7.01 (d, *J* = 2.5 Hz, 1H),

6.99 (d, *J* = 2.5 Hz, 1H), 6.87 (d, *J* = 2.4 Hz, 2H), 5.36 – 5.29 (m, 2H), 4.96 (s, 2H), 4.54 – 4.43 (m, 4H), 3.68 (dq, *J* = 25.2, 7.1 Hz, 12H), 2.67 – 2.56 (m, 4H), 2.28 – 2.18 (m, 4H), 1.34 (t, *J* = 7.1 Hz, 6H), 1.31 – 1.29 (t, 12H). ^{13}C NMR (500 MHz, MeOD) δ 160.03, 157.93, 157.14, 155.59, 155.45, 152.11, 151.08, 143.17, 142.30, 140.22, 139.08, 134.48, 132.86, 131.71, 131.40, 130.51, 129.45, 128.89, 128.41, 125.58, 125.13, 124.50, 124.29, 123.96, 123.69, 122.15, 117.20, 115.00, 114.96, 113.87, 112.88, 108.16, 105.92, 95.96, 61.19, 50.14, 48.58, 48.44, 48.37, 45.66, 45.46, 38.69, 35.15, 34.55, 34.35, 31.67, 30.54, 30.40, 30.03, 29.35, 29.25, 29.07, 28.93, 26.71, 24.49, 23.94, 22.34, 19.93, 13.05, 11.86, 11.52. HRMS (ESI): m/z for $C_{61}H_{69}N_{11}O_2S_2Se^{2+}$ ($[M]^{2+}$): calc. 565.7116; found 565.7119. $C_{61}H_{68}N_{11}O_2S_2Se^{+}$ ($[M-H]^{+}$): calc. 1130.4159; found 1130.4177.

Synthesis of compound **Rh-NBSe-1**

The Rh-1 was synthsised as reference.[2] The **Rh-NBSe-1** was obtained from **Rh-1** and **NBSe**, **Rh-1** (50 mg, 0.093 mmol) and **NBSe** (42 mg, 0.093 mmol) was dissolved in component solvent ($CHCl_3$:EtOH:H_2O=12 mL:1 mL:1 mL), then $CuSO_4 \cdot 5H_2O$ (14 mg, 0.056 mmol) and sodium ascorbate (22 mg, 0.11 mmol) was successively added under nitrogen atmosphere. The reaction was completed after 24 h at r.t., the reagent was extract with DCM and the organic layers was dried over $MgSO_4$, the crude product was obtained after removal of the solvent. The product was purified by column chromatography to give a purple solid (68 mg, yield 76%). ^{1}H NMR (500 MHz, MeOD) δ 8.70 (dd, *J* = 22.8, 7.6 Hz, 1H), 8.38 (s, 1H), 8.23 (d, *J* = 6.6 Hz, 1H), 7.77 (dd, *J* = 17.8, 10.3 Hz, 1H), 7.77 (dd, *J* = 17.8, 10.3 Hz, 1H), 7.66 (d, *J* = 7.0 Hz, 2H), 7.60 (d,

J = 6.7 Hz, 1H), 7.36 (s, 1H), 7.15 (d, *J* = 14.6 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 9.5 Hz, 2H), 6.83 (s, 2H), 4.94 (s, 1H), 4.93 – 4.91 (t, 2H), 4.63 – 4.60 (t, 2H), 3.62 (dd, *J* = 16.0, 8.3 Hz, 12H), 1.32 – 1.28 (t, 18H). ^{13}C NMR (500 MHz, MeOD) δ 161.52, 159.28, 158.15, 156.84, 153.56, 152.45, 144.75, 144.57, 140.41, 139.29, 136.14, 135.92, 134.34, 134.23, 132.91, 132.77, 131.89, 130.86, 130.31, 126.45, 126.13, 125.69, 125.62, 123.64, 118.51, 116.30, 115.23, 114.07, 109.56, 107.25, 97.40, 68.29, 51.55, 47.06, 46.92, 39.84, 36.56, 33.07, 31.96, 30.83, 30.74, 30.64, 30.60, 30.47, 30.33, 28.11, 26.93, 25.90, 25.35, 23.74, 14.44, 13.24, 12.97. HRMS (ESI): m/z for $C_{52}H_{56}N_8O_2S_2Se^{2+}$ ($[M]^{2+}$): calc. 452.1840; found 452.1831.



Scheme S1 Synthesis routes of **Rh-NBSe** and **Rh-NBSe-1**.

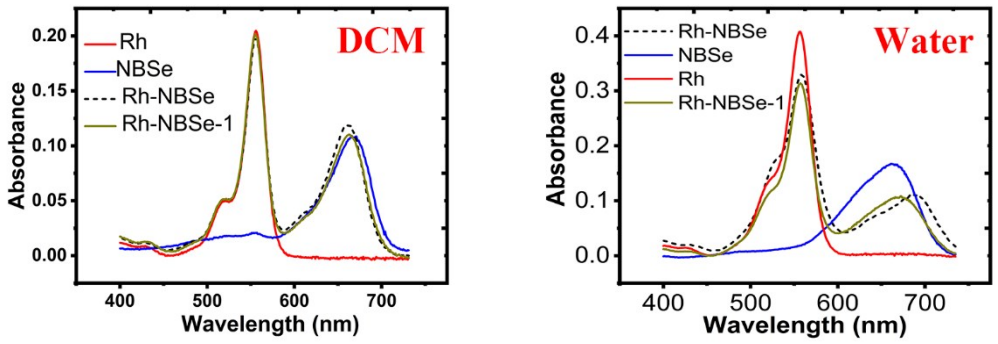
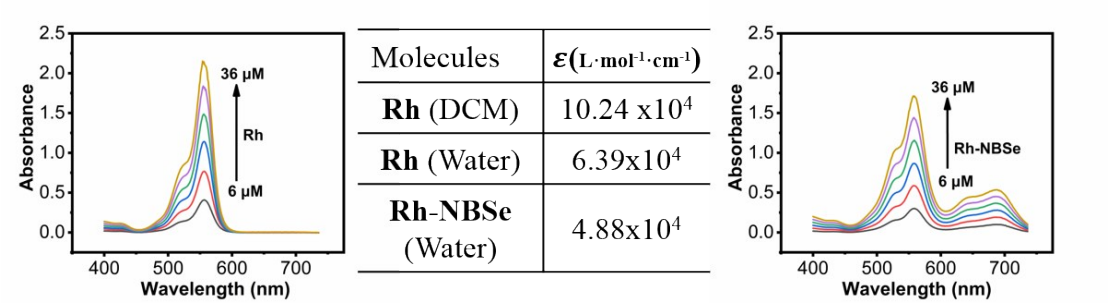


Fig. S1 Absorption spectra of **Rh**, **NBSe**, **Rh-NBSe**, and **Rh-NBSe-1** in DCM (2 μM) and in water (6 μM), respectively.



Molecules	ε(L·mol^{-1}·cm^{-1})
Rh (DCM)	10.24 x10^4
Rh (Water)	6.39x10^4
Rh-NBSe (Water)	4.88x10^4

Fig. S2 Step-up absorption in water ranged of 6-36 μM, which left is **Rh** and right is **Rh-NBSe**.

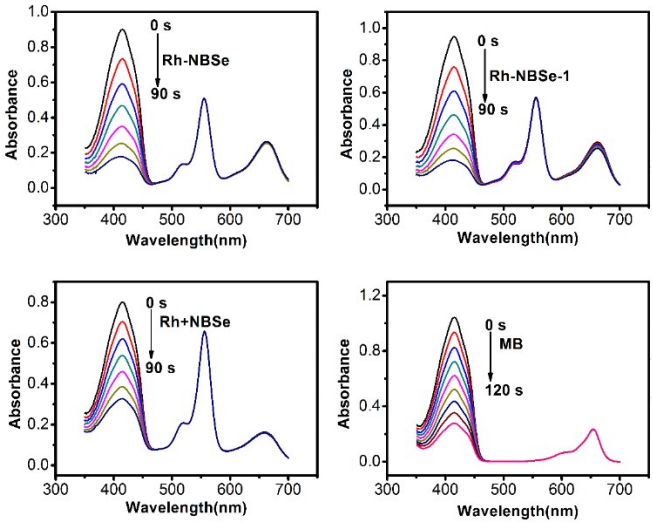


Fig. S3 Singlet oxygen quantum yield mesurement of **Rh-NBSe**, **Rh-NBSe-1**, **Rh**+**NBSe** and **MB** (reference). And the **DPBF** is scavenger of $^1O_2$, which maximum absorption is 415 nm. All the samples are irradiated by 660 nm (3 mW/cm^2) light at a interval of 15s, and record the absorption spectra.

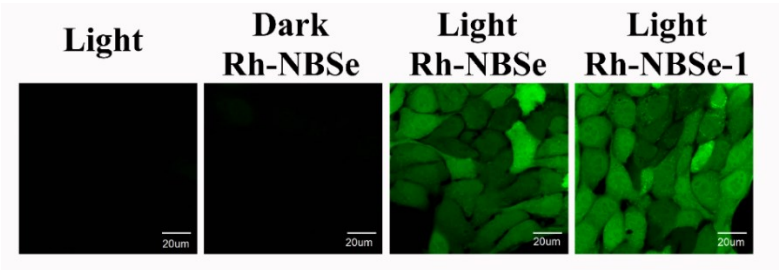


Fig. S4 Intracellular ROS detection using DCFH-DA kit. All cells of light group are treated by 660 nm light (20 mW/cm^2) for 1 min, then imaged with CLSM. Ex: 488 nm, Em: 500-540 nm.

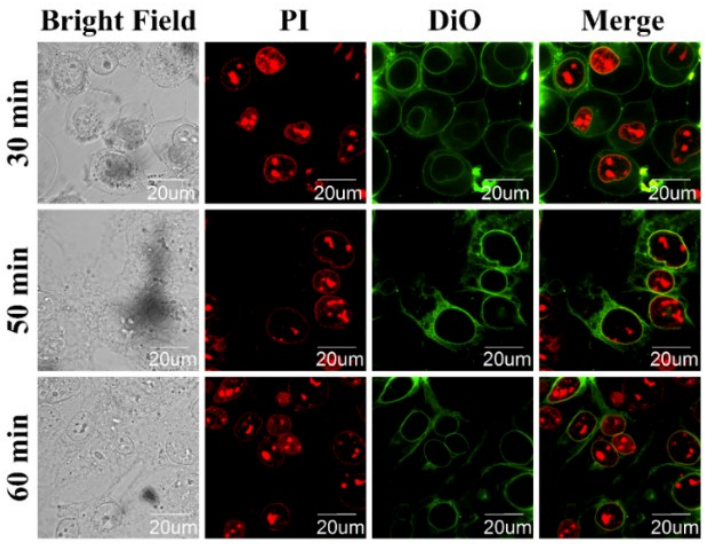


Fig. S5 Cellular morphologic change labeled with DiO and PI. DiO is membrane dyes, Ex: 488 nm, Em: 500-540 nm. And PI is nuclear dyes, which labeled death cells, Ex: 488 nm, Em: 620-700 nm.

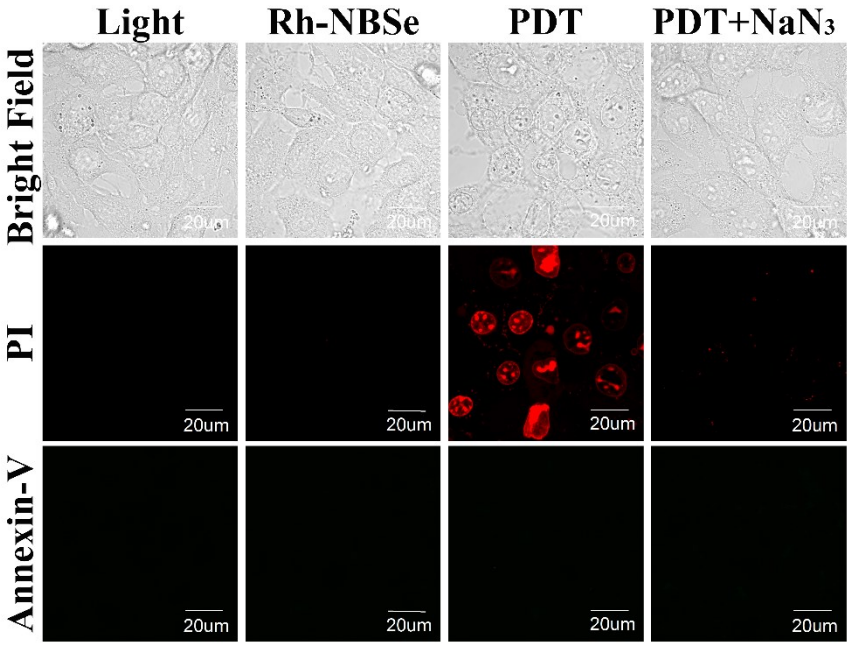


Fig. S6 Apoptosis/necrosis detection in 4T1 using AnnexinV-FITC/PI. The FITC-labelled recombinant human Annexin V particularly bind to phosphatidylserine that appears on the outer surface of the cell membrane of apoptotic cells. Ex: 488 nm, Em: 500-540 nm.

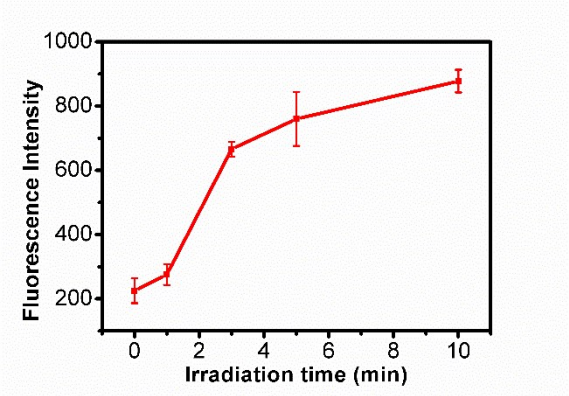


Fig. S7 Self-reporting fluorescence increase followed by irradiation time. Data were analyzed by CLSM. Data were shown as mean ± SD (n = 3).

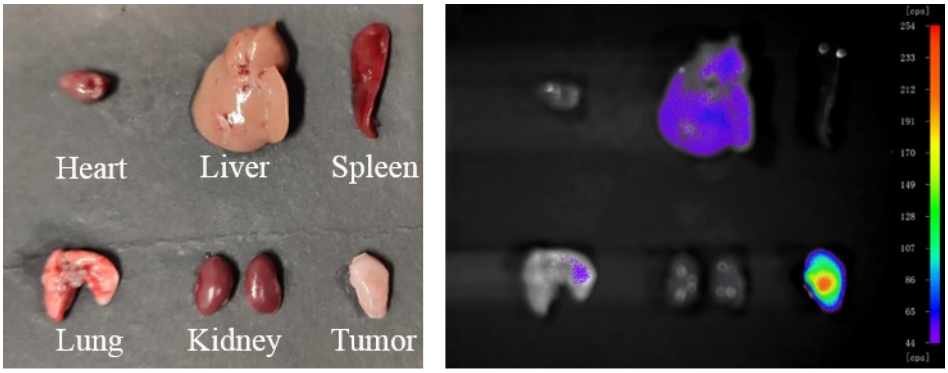


Fig. S8 Fluorescence of main tissues and tumor after 24h post-injection (tail-vein). Ex: 550 nm, Em: 600 nm.

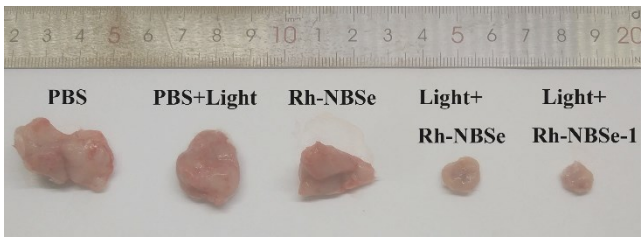


Fig. S9 Picture of solid tumors of different groups.

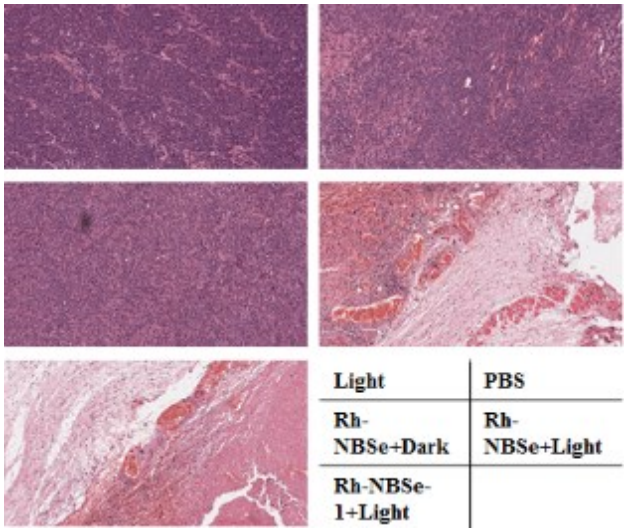


Fig. S10 Histological analysis of tumors of different groups.

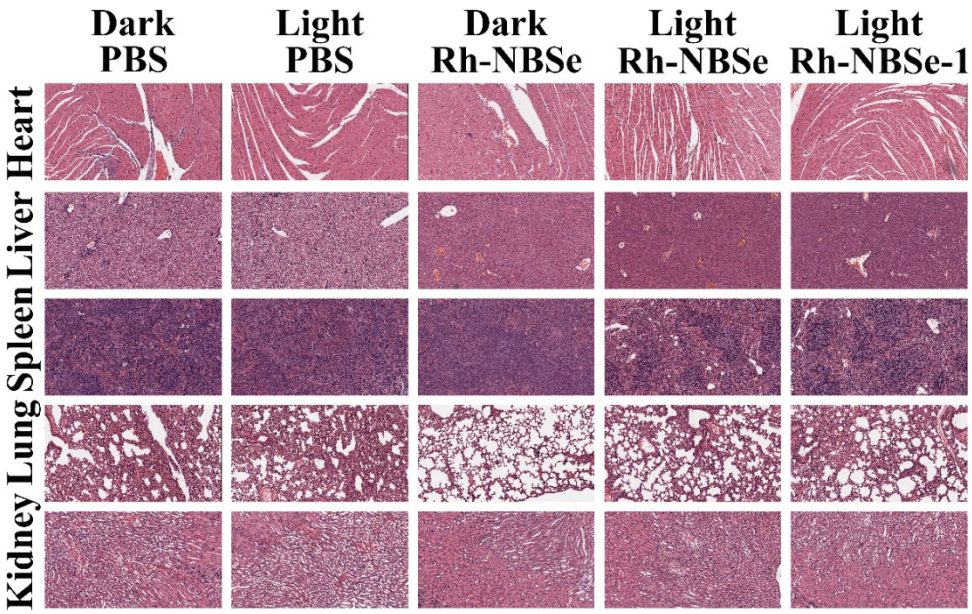


Fig. S11 Histological analysis of major organs (heart, liver, spleen, lung and kidney).

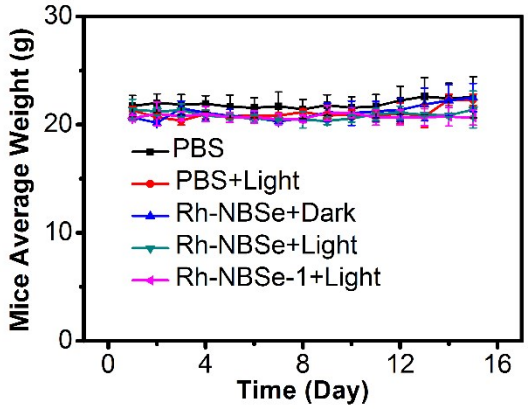


Fig. S12 Mice average weight record post-irradiation. Data were shown as mean ± SD (n = 5)

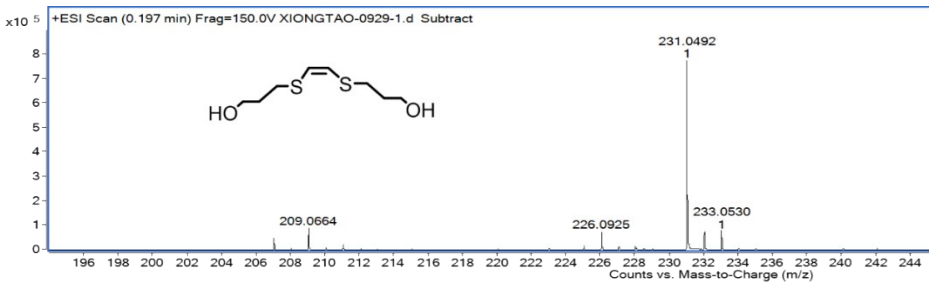


Fig. S13 HRMS (ESI) of structure **2**.

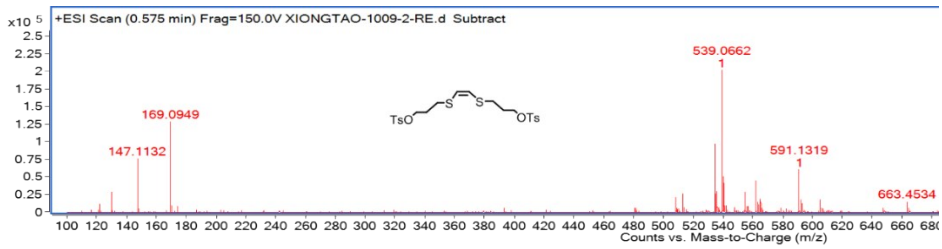


Fig. S14 HRMS (ESI) of structure **3**.

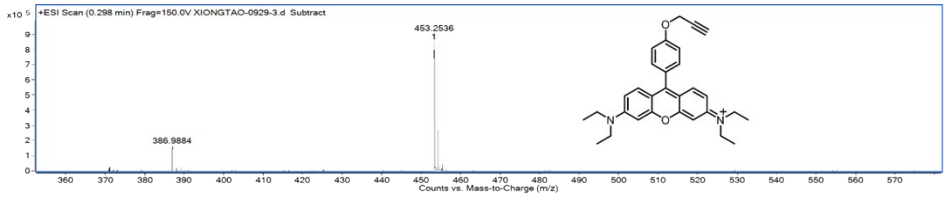


Fig. S15 HRMS (ESI) of **Rh**.

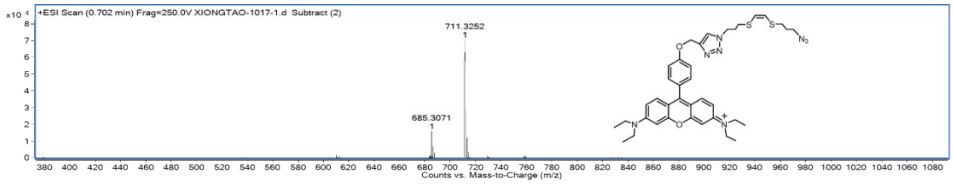


Fig. S16 HRMS (ESI) of **Rh-N_3**.

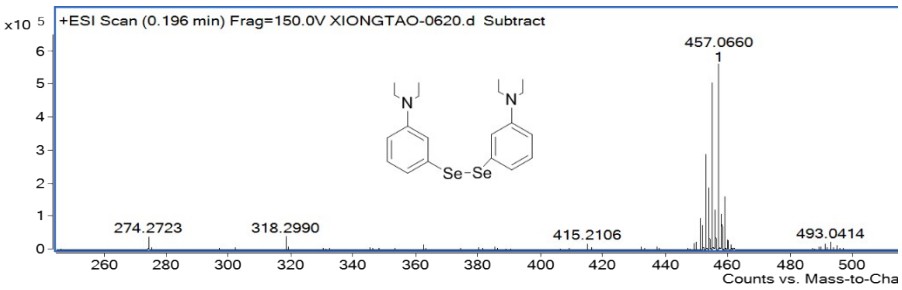


Fig. S17 HRMS (ESI) of structure **8**.

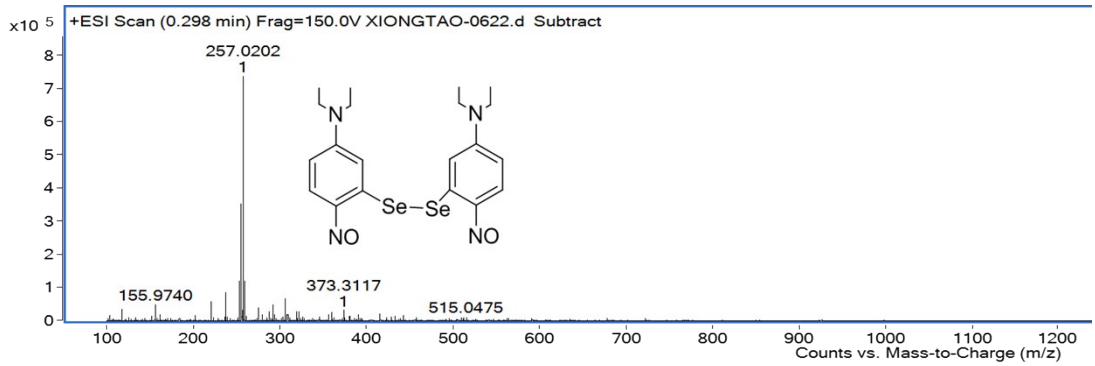


Fig. S18 HRMS (ESI) of structure **9**.

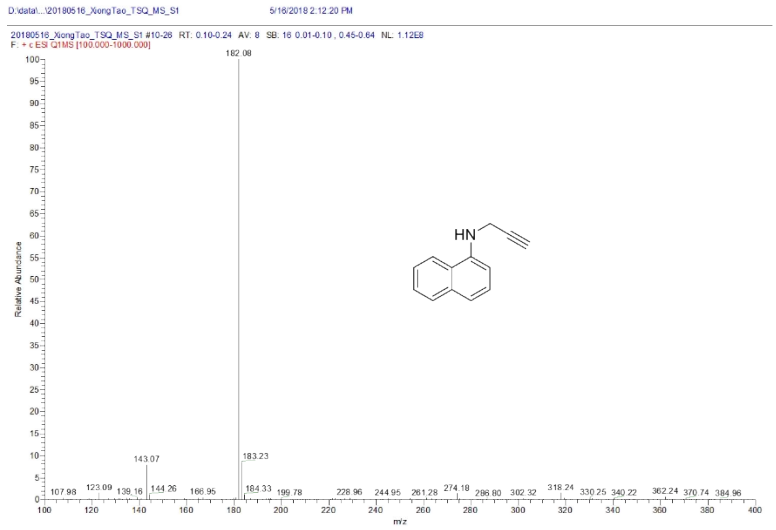


Fig. S19 HRMS (ESI) of structure **10**.

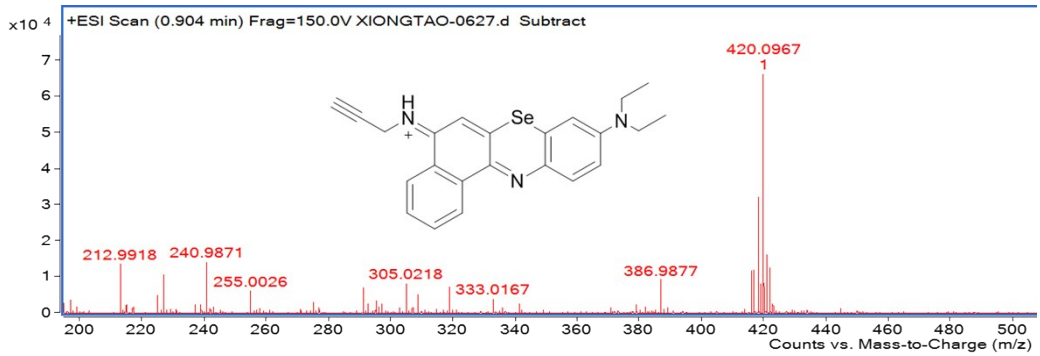


Fig. S20 HRMS (ESI) of structure **NBSe**.

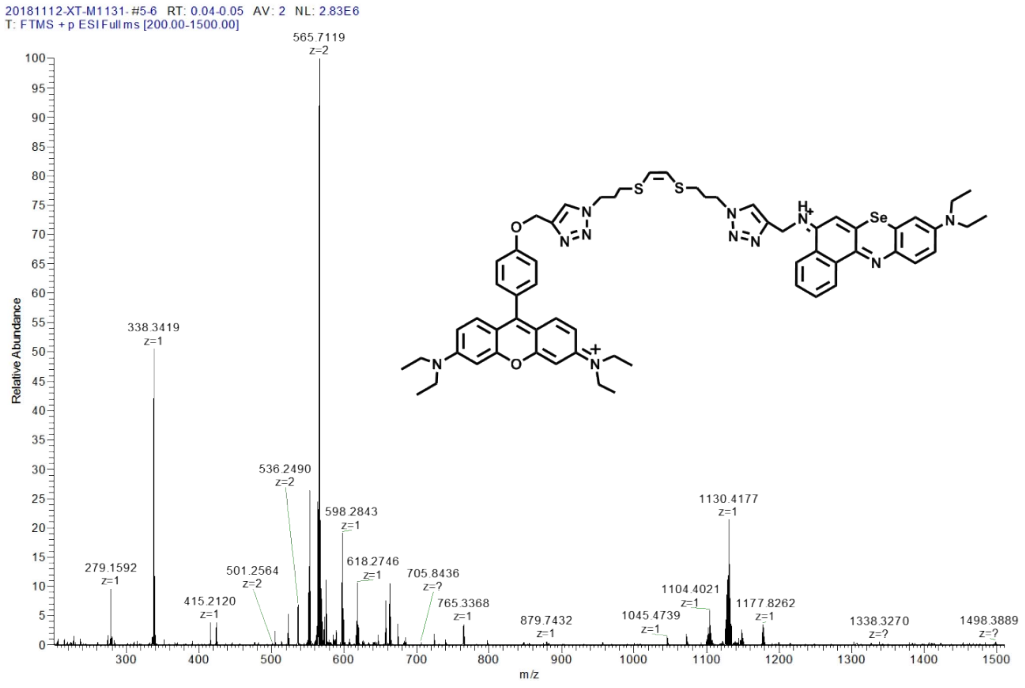


Fig. S21 HRMS (ESI) of structure **Rh-NBSe**.

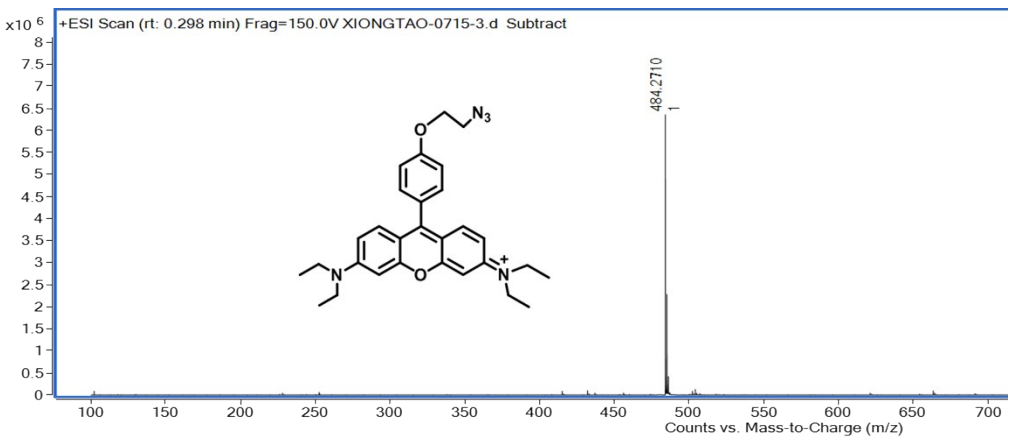


Fig. S22 HRMS (ESI) of **Rh-1**.

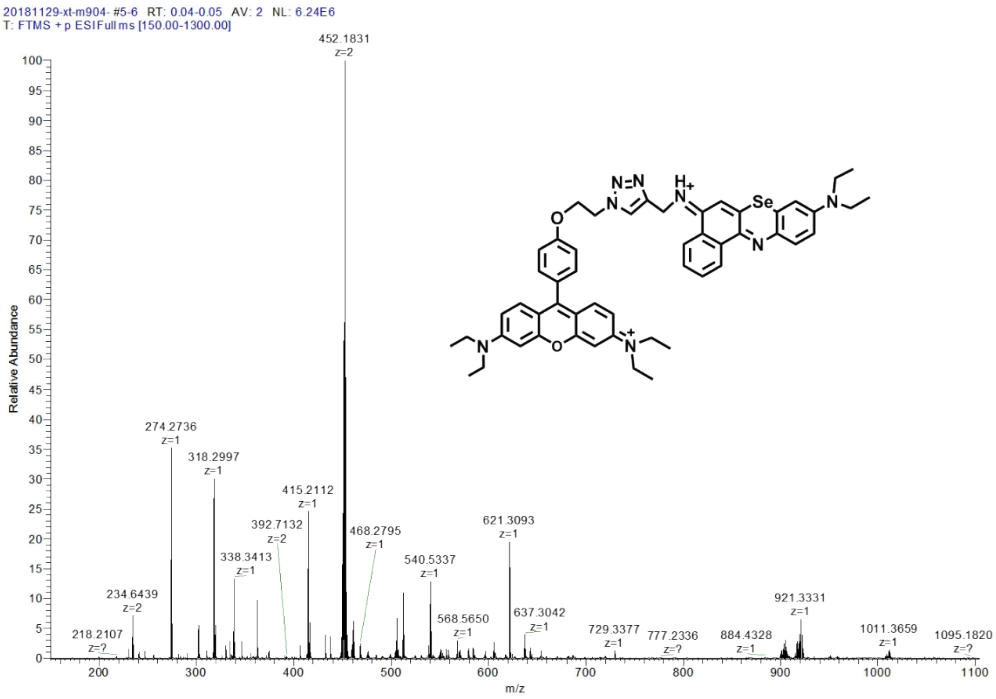


Fig.S 23 HRMS (ESI) of **Rh-NBSe-1**.

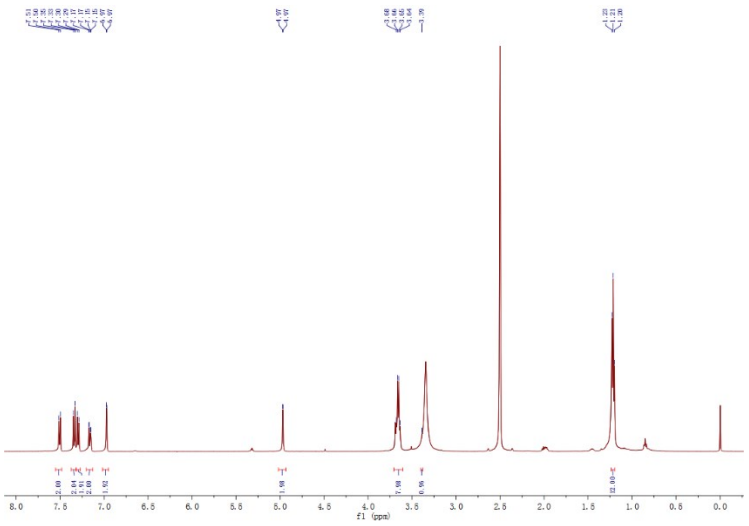


Fig. S24 [1]HNMR of **Rh**.

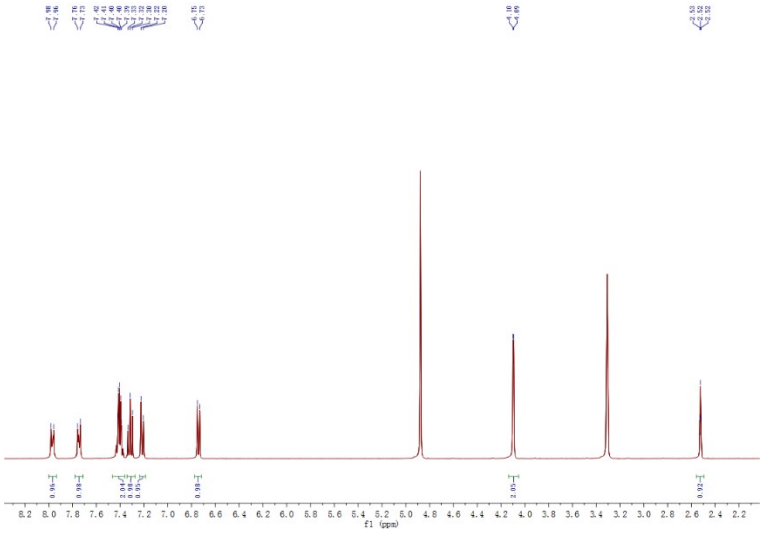


Fig. S25 [1]HNMR of structure **10**.

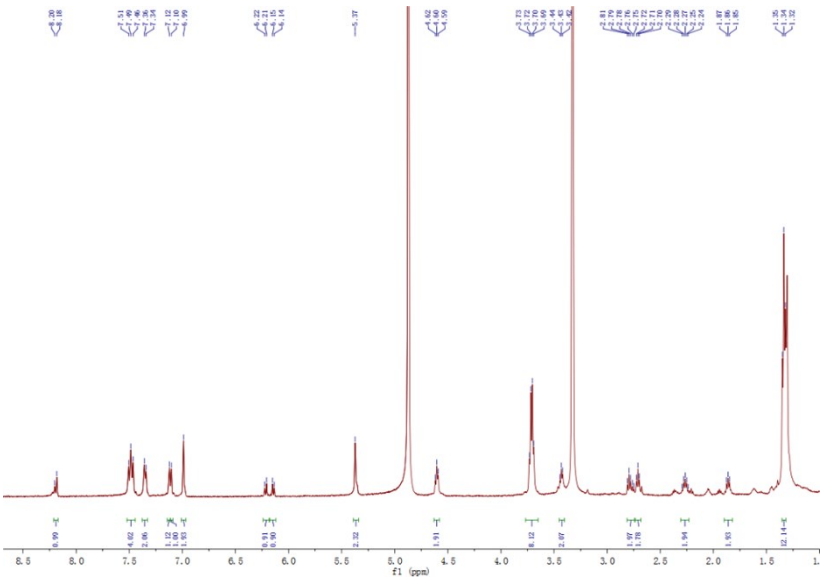


Fig. S26 [1]HNMR of **Rh-N_3**.

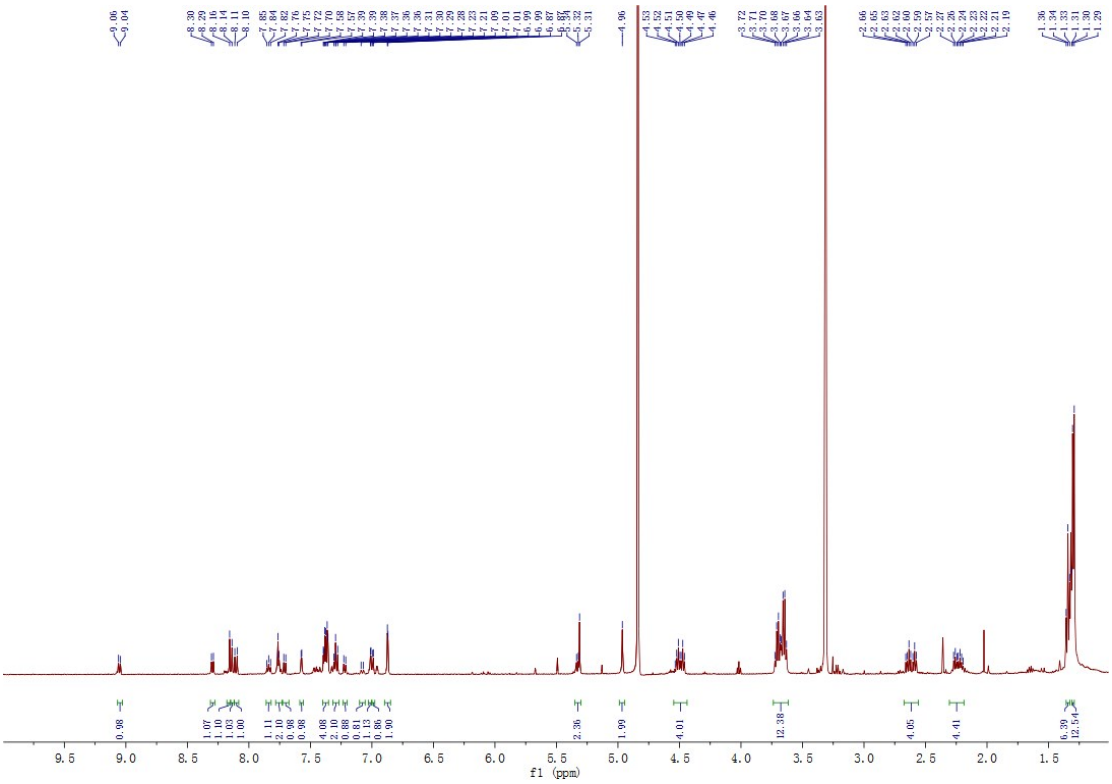


Fig. S27 ^{1}HNMR of **Rh-NBSe**.

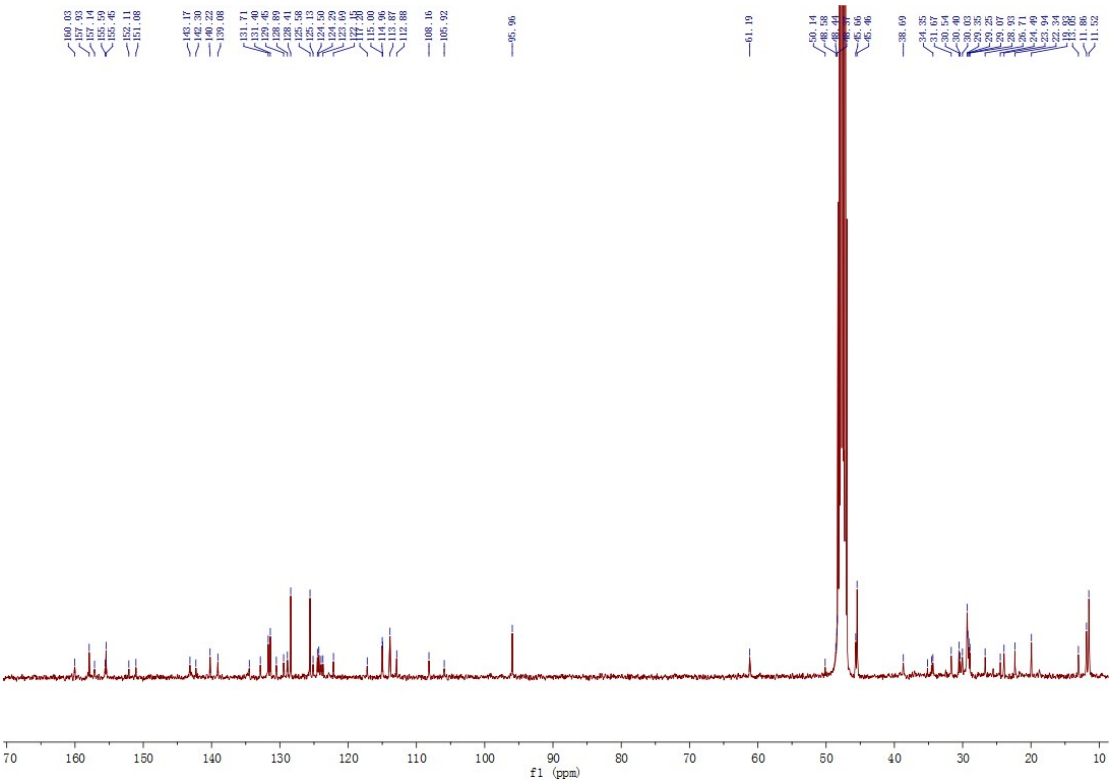


Fig. S28 ^{13}CNMR of **Rh-NBSe**.

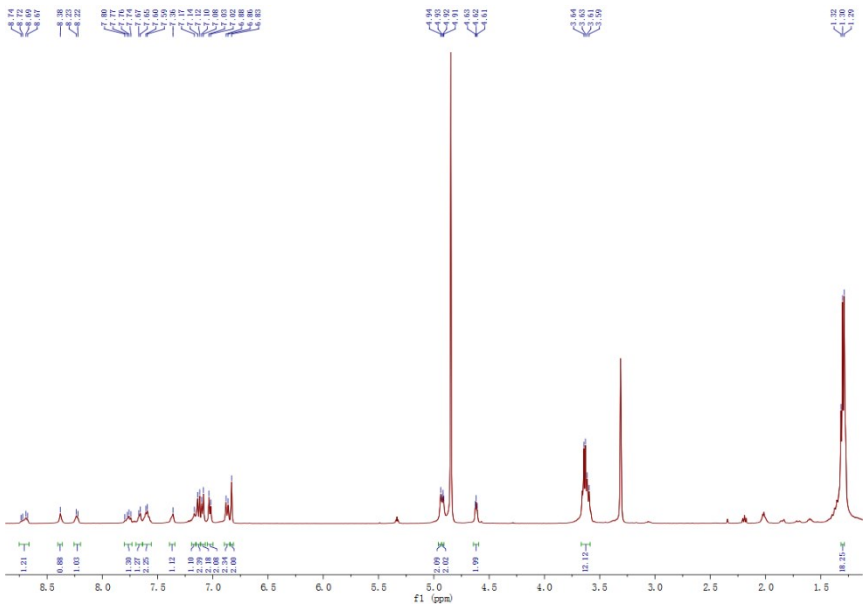


Fig. S29 [1]HNMR of **Rh-NBSe-1**.

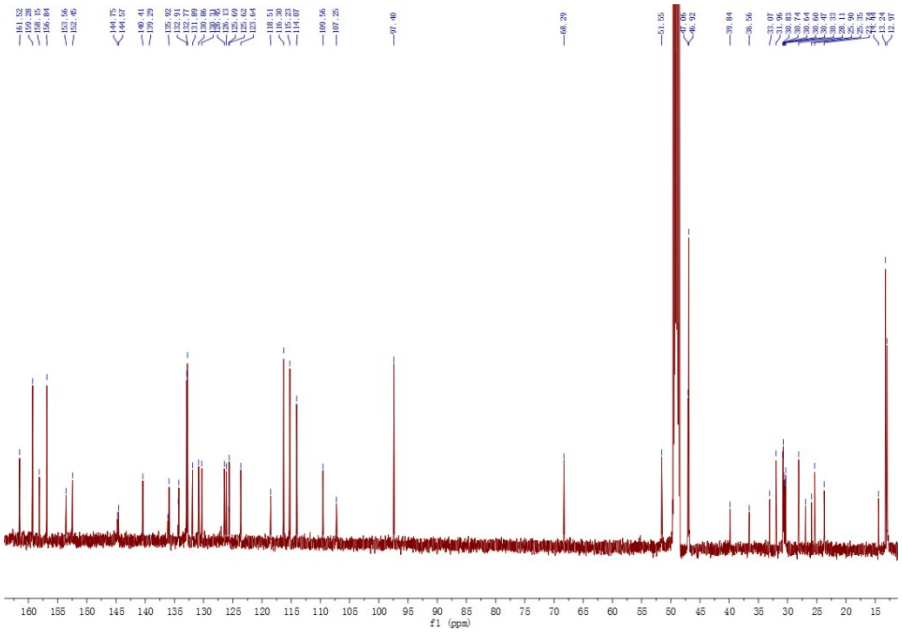


Fig. S30 [13]CNMR of **Rh-NBSe-1**.

Reference

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2. Li, M.; Long, S.; Kang, Y.; Guo, L.; Wang, J.; Fan, J.; Du, J.; Peng, X. *J. Am. Chem. Soc.* **2018**, *140*, 15820-15826.