Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information (ESI) for

Highly Sensitive Iridium(III) Complex-Based Long Life-Time Phosphorescent Probe for Thiopheol

*Li Xiong, Lin Yang, Shuai Luo, Yan Huang, and Zhiyun Lu**

Key Laboratory of Green Chemistry and Technology (Ministry of Education), College of Chemistry, Sichuan University, Chengdu 610064, China

E-mail: luzhiyun@scu.edu.cn

Table of Contents

1. The absorption properties of **Ir-NH$_2$** and **Ir-DNBS**. 2

2. The emission spectra of **Ir-NH$_2$**, **Ir-DNBS** and **Ir-DNBS** + thiophenol. 2

3. Photophysical data of **Ir-DNBS** and **Ir-NH$_2$**. 3

3. Sensitivity studies of **Ir-DNBS** to thiophenol under ambient condition. 3

4. Kinetic studies on the reaction of **Ir-DNBS** with thiophenol under nitrogen condition. 4

5. Kinetic studies on the reaction of **Ir-DNBS** with thiophenol under ambient condition. 4

6. Ionic activity effect studies on the phosphorescence response of **Ir-DNBS** toward thiophenol. 5

7. PH effect studies on the phosphorescence response of **Ir-DNBS** toward thiophenol. 5

8. Photochemical stability studies of **Ir-DNBS** and **Ir-NH$_2$**. 5

9. Transient photoluminescence tests of **Ir-DNBS**, **Ir-NH$_2$** and **Ir-DNBS** + 5 equiv thiophenol. 6

10. Reagents and Apparatus. 6

11. Determination of Quantum Yield. 7

12. Kinetics Constant and Half-time Calculations. 7

13. Determination of Thiophenol in Water Samples. 7

14. Synthetic details to **Ir-DNBS** and **Ir-NH$_2$**. 8

15. NMR spectra of **Ir-NH$_2$** and **Ir-DNBS**. 13

16. HR-MS spectra of **Ir-NH$_2$**, **Ir-DNBS** and **Ir-DNBS** in the presence of thiophenol. 16

17. Reference. 16

1. The absorption properties of Ir-NH2 and Ir-DNBS.

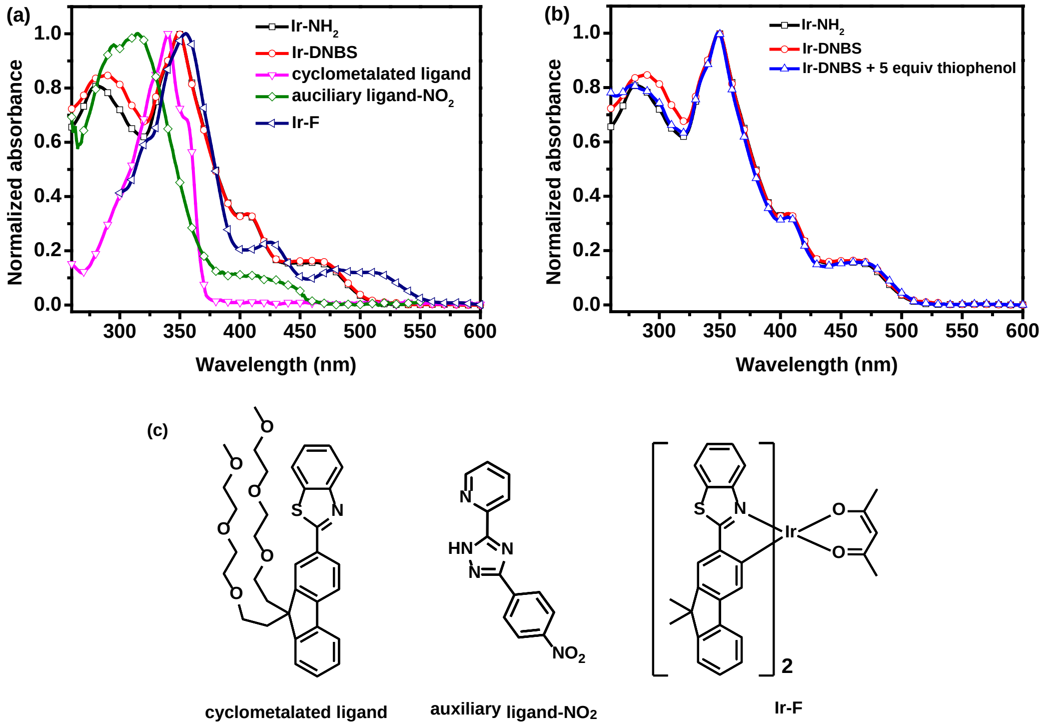


Figure S1. a) Normalized absorption spectra of **Ir-NH$_2$** (5 μM), **Ir-DNBS** (5 μM) in 40% acetonitrile/PBS (0.01 M, pH = 7.4) and cyclometalated ligand (5 μM) in acetonitrile, auxiliary ligand-NO$_2$ (5 μM) in DMSO and **Ir-F** (10 μM) in 2-MeTHF; b) normalized absorption spectra of **Ir-NH$_2$** (5 μM), **Ir-DNBS** (5 μM), **Ir-DNBS** (5 μM) + 5 equiv thiophenol in 40% acetonitrile/PBS (0.01 M, pH = 7.4); c) molecular structure of free cyclometalated ligand, auxiliary ligand-NO$_2$ and **Ir-F**.

2. The PL emission spectra of Ir-NH2, Ir-DNBS and Ir-DNBS + thiophenol.

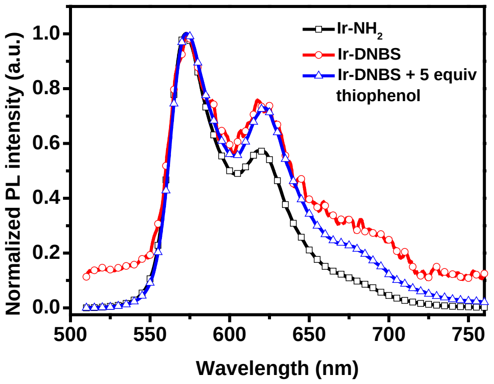


Figure S2. Normalized PL emission spectra (λ_{ex} = 420 nm) of **Ir-NH$_2$** (5 μM), **Ir-DNBS** (5 μM) and **Ir-DNBS** (5 μM) in presence of 5 equiv thiophenol in 40% acetonitrile/PBS (0.01 M, pH = 7.4).

3. Photophysical data of Ir-DNBS and Ir-NH$_2$.

Table S1. Photophysical data of **Ir-DNBS** and **Ir-NH$_2$**.

Compound	$\lambda_{\text{abs max}}$ (nm) (log ε)^a	$\lambda_{\text{PL max}}$ (nm)^a	$\Phi_{\text{PL}}{}^b$	average lifetime τ in nitrogen^a	average lifetime τ in air^a
Ir-DNBS	289(5.07), 349(5.14), 406(4.67), 463(4.37)	573, 620(sh)	0.001	31.0 ns	18.7 ns
Ir-NH$_2$	281(5.00), 349(5.09), 405(4.62), 463(4.29)	573, 620(sh)	0.21	2.07 µs	512.3 ns

[a] UV-Vis absorance, PL emission spectra, and lifetime are determined in 5 μM 40% acetonitrile/PBS (0.01 M, pH = 7.4) solution at 298 K. [b] The PL quantum yields are determined in nitrogen de-aerated 5 μM acetonitrile solution at 298K, using rhodamine B (Φ_F = 0.69 in ethanol) as reference, under excitation of 420 nm.

3. Sensitivity studies of Ir-DNBS to thiophenol under ambient condition.

Under air conditions, for the 5 μM **Ir-DNBS** samples, their phosphorescence intensity (PI) values at 577 nm show good linear correlation with the concentration of thiophenol in the range of 0−10 μM (Figure S3b). The slope k of the phosphorescence spectral titration results of the 5 μM **Ir-DNBS** sample with thiophenol was calculated to be 77.15 × 10^6 M^{-1} (R^2 = 0.9993). The standard deviation (S.D.) of our fluorescence spectrophotometer was calculated to be 0.1016 through 11 measurements on the PI value of $I_{577\ \text{nm}}$ of aerated solution of 5 μM **Ir-DNBS** in the absence of thiophenol. According to the equation LOD = 3 × S.D./k, the LOD of **Ir-DNBS** toward thiophenol was determined to be 3.9 nM under ambient condition.

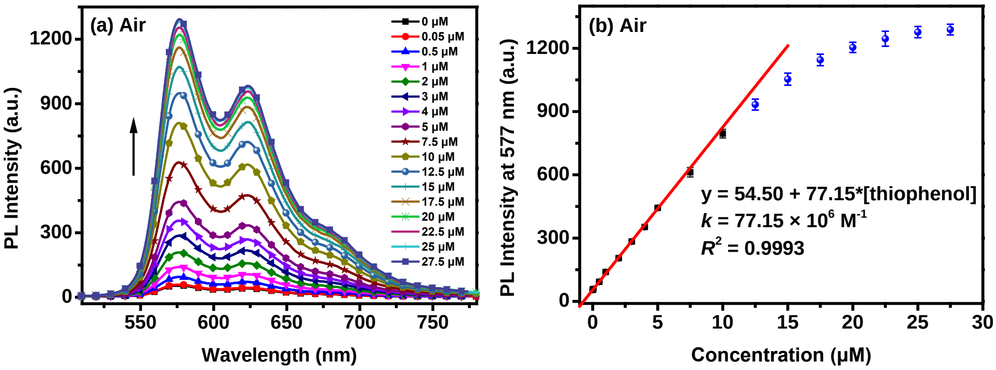


Figure S3. (a) Phosphorescence spectra (λ_{ex} = 420 nm, slits: 10/15) of 5 μM **Ir-DNBS** in the presence of different concentration of thiophenol in 40% acetonitrile/PBS (0.01 M, pH = 7.4) under ambient condition and (b) the correlation between phosphorescence intensity of 5 μM **Ir-DNBS** at 577 nm and concentration of thiophenol in 40% acetonitrile/PBS (0.01 M, pH = 7.4) under ambient condition.

4. Kinetic studies on the reaction of Ir-DNBS with thiophenol under nitrogen condition.

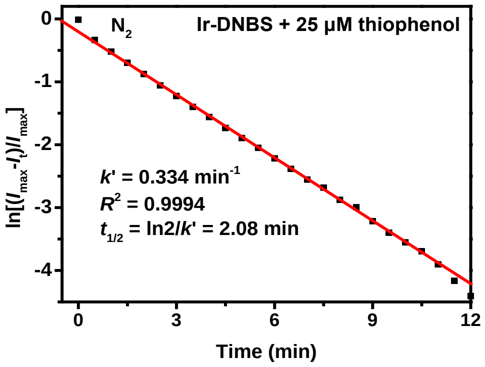


Figure S4. The fitted first order reaction kinetic constant of **Ir-DNBS** (5 μM) with thiophenol (25 μM) in 40% acetonitrile/PBS (0.01 M, pH = 7.4) under nitrogen condition according to the phosphorescence measurement.

5. Kinetic studies on the reaction of Ir-DNBS with thiophenol under ambient condition.

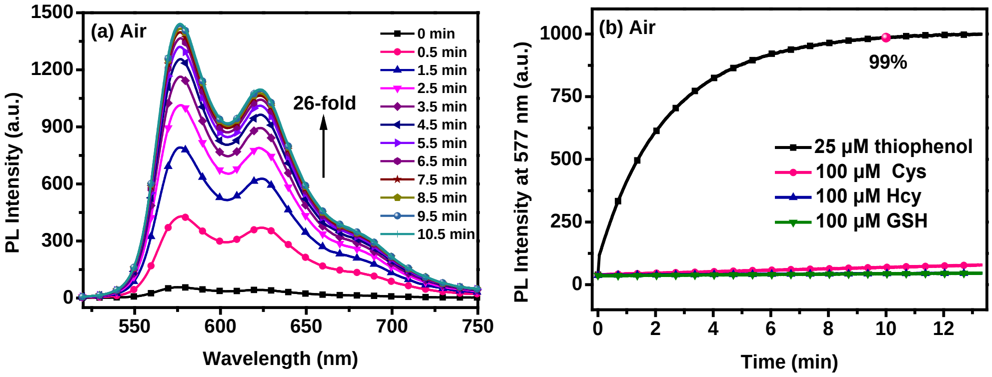


Figure S5. (a) Phosphorescence spectra (λ_{ex} = 420 nm, slits: 10/15) of 5 μM **Ir-DNBS** in the presence of 25 μM thiophenol at different reaction time in 40% acetonitrile/PBS (0.01 M, pH = 7.4) under ambient condition. (b) Phosphorescence enhancement profile of phosphorescence intensity at 577 nm of **Ir-DNBS** (5 μM in 0.01 M 40% acetonitrile/PBS, pH = 7.4) in the presence of thiophenol (5 equiv) or thiol species (20 equiv) under ambient condition.

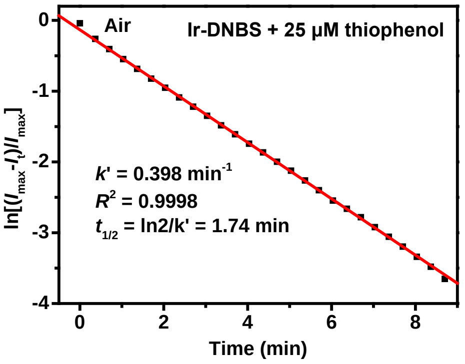


Figure S6. The fitted first order reaction kinetic constant of **Ir-DNBS** (5 μM) with thiophenol (25 μM) in 40% acetonitrile/PBS (0.01 M, pH = 7.4) under ambient condition according to the phosphorescence measurements.

6. Ionic activity effect studies on the phosphorescence response of Ir-DNBS toward thiophenol.

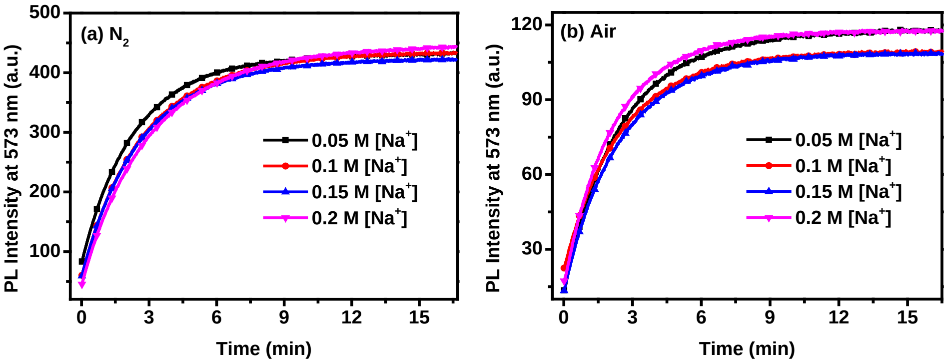


Figure S7. Phosphorescence enhancement profile (λ_{ex} = 420 nm, slits: 10/5) at $I_{573\text{ nm}}$ of **Ir-DNBS** (5 μM) with thiophenol (5 equiv) in 40% acetonitrile/PBS (0.01 M, pH = 7.4) with different concentration of Na^+ under nitrogen (a) and ambient (b) conditions.

7. PH effect studies on the phosphorescence response of Ir-DNBS toward thiophenol.

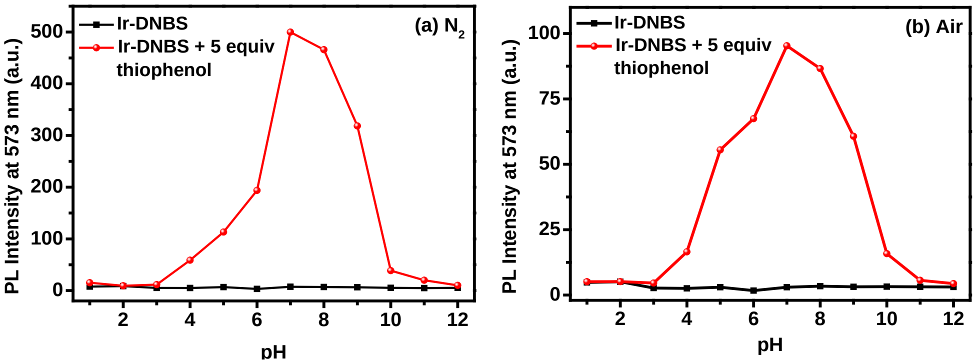


Figure S8. PH-dependent phosphorescence intensity ($I_{573\text{ nm}}$) of 5 μM **Ir-DNBS** in the absence or presence of 25 μM thiophenol in 40% acetonitrile/PBS (0.01 M, pH = 7.4) under nitrogen (a) and ambient (b) conditions (λ_{ex} = 420 nm, slits: 10/5).

8. Photochemical stability studies of Ir-DNBS and Ir-NH₂.

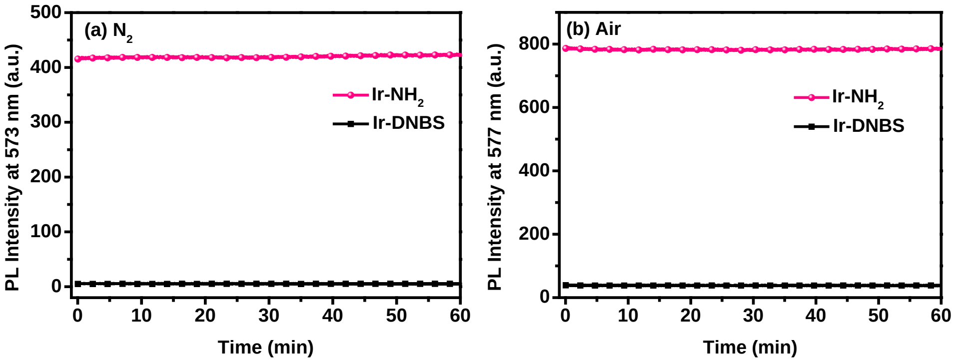


Figure S9. (a) The correlation between phosphorescence intensity of 5 μM **Ir-DNBS** or **Ir-NH_2** at 573 nm ($I_{573\text{ nm}}$) and time in 40% acetonitrile/PBS (0.01 M, pH = 7.4) under nitrogen condition (λ_{ex} = 420 nm, slits: 10/5); and (b) the correlation between phosphorescence intensity of 5 μM **Ir-DNBS** or **Ir-NH_2** at 577 nm ($I_{577\text{ nm}}$) and time in 40% acetonitrile/PBS (0.01 M, pH = 7.4) under ambient condition (λ_{ex} = 420 nm, slits: 10/15).

9. Transient photoluminescence tests of Ir-DNBS, Ir-NH$_2$ and Ir-DNBS + 5 equiv thiophenol.

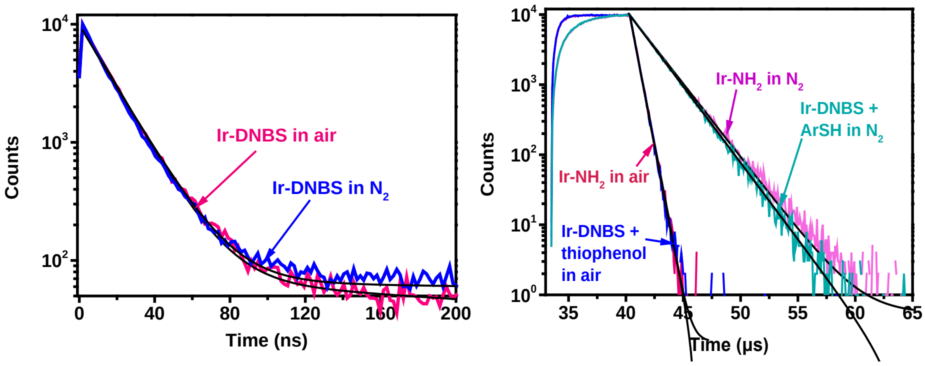


Figure S10. Phosphorescence decay curves of **Ir-DNBS** (5 μM), **Ir-NH$_2$** (5 μM) and **Ir-DNBS** (5 μM) + thiophenol (25 μM) in 40% acetonitrile/PBS (0.01 M, pH = 7.4) under nitrogen and ambient condition.

Table S2. The phosphorescence lifetime data of **Ir-DNBS**, **Ir-NH$_2$**, **Ir-DNBS** + 5 equiv thiophenol in 40% acetonitrile/PBS (0.01 M, pH = 7.4).

Compd.	Solvent	λ_{em} (nm)	Life time	Content (%)	χ^2
Ir-DNBS	Air saturated	573	15.5 ns 423 ns	99 1	1.18
	N$_2$ saturated	573	16.2 ns 2.04 μs	99 1	1.28
Ir-NH$_2$	Air saturated	573	512.3 ns	100	1.04
	N$_2$ saturated	573	2.07 μs	100	1.13
Ir-DNBS + thiophenol	Air saturated	573	500.4 ns	100	1.09
	N$_2$ saturated	573	1.99 μs	100	1.03

10. Reagents and Apparatus.

Unless otherwise described, all materials and solvents were obtained from commercial suppliers and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE II-400 MHz spectrometer and TMS was used as an internal standard. All chemical shift data are reported in the standard δ notation of parts per million. UV/Vis absorption spectra were recorded on a Perkin–Elmer Lambda 950 UV/Vis Spectrometer. Fluorescent emission spectra were measured using a Perkin–Elmer LS 55 fluorescence spectrophotometer. High-resolution MS (HR-MS) spectra were measured on a Shimadzu LCMSIT-TOF. pH values were measured using a PHS-3E pH meter. Melting points were determined by a SG ERR melting point instrument without further correction. Double distilled water was used to prepare the buffer solutions.

11. Determination of Quantum Yield.

The relative phosphorescence quantum yields of **Ir-DNBS** and **Ir-NH$_2$** were determined in dilute nitrogen-saturated acetonitrile solutions on a Perkin–Elmer Lambda 950 UV/Vis Spectrometer and a Perkin–Elmer LS 55 fluorescence spectrophotometer with reference to rhodamine B ($\Phi_F = 0.69$ in ethanol[1]). The phosphorescence quantum yields of **Ir-DNBS** and **Ir-NH$_2$** were determined as 0.001 and 0.21 respectively according the equation $\Phi_s = \Phi_r \times F_s/F_r \times A_r/A_s \times (n_s/n_r)^2$, where r and s represent the standard and sample; F is the integrated area of the photoluminescence intensity; A is the absorbance at 490 nm, n is the refractive index of the solvent.

12. Kinetics Constant and Half-time Calculations.

By analysing the time-dependent phosphorescence intensity variations of **Ir-DNBS** in the presence of thiophenol under nitrogen or air conditions, the quasi-first order reaction kinetic constant k' and half-time $t_{1/2}$ were obtained according to the formulae (1) and (2).

$$ln\left[{(F_{\max} - F_t)}/{F_{\max}}\right] = -k't \tag{1}$$

$$t_{1/2} = \ln 2/k' \tag{2}$$

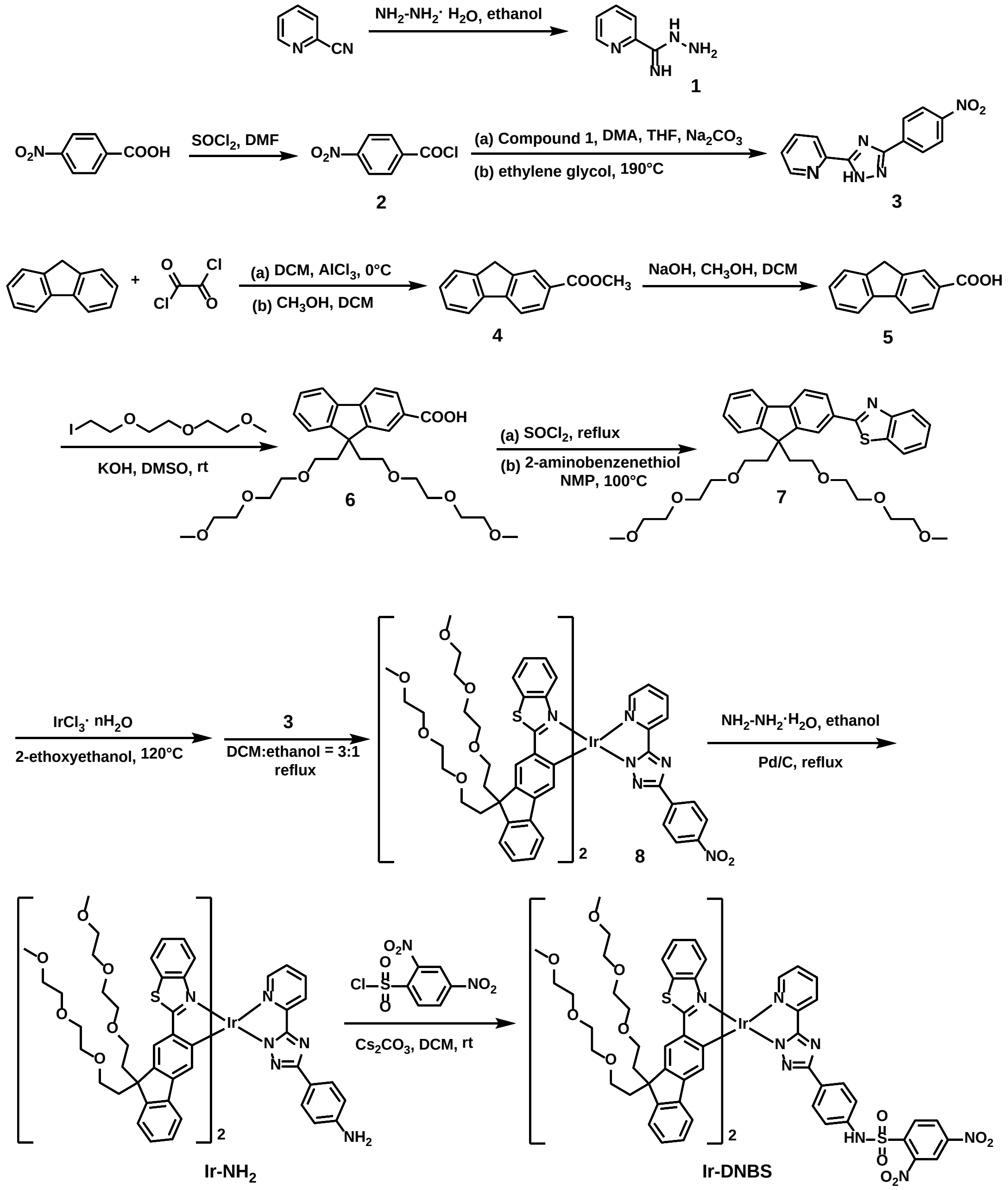
Here, $F_{\max}$ and F_t represent the maximum fluorescence intensity and the fluorescence intensity at time t at the maximum emission wavelength, respectively. k' is the quasi-first order kinetic constant, $t_{1/2}$ is the half-time of the reaction of **Ir-DNBS** with thiophenol.

13. Determination of Thiophenol in Water Samples.

The level of thiophenol in water samples was determined using the standard addition method (often referred to as “spiking” samples) according to previous publications.[2] The crude water samples (50 mL) obtained respectively from Jinjiang River, East Lake of Chengdu and the tap water in Chengdu city were adjusted using a 40% acetonitrile sodium phosphate buffer (0.01 M, pH = 7.4). And aliquots of the water samples were then spiked with different concentrations of thiophenol (1, 2, or 4 μM) that had been accurately prepared. The resultant samples were further treated with probe **Ir-DNBS** to give the final mixtures (3.0 mL) containing probe **Ir-DNBS** (final concentration = 5 μM) and thiophenol (final concentration = 1, 2, 4 μM). The solutions were incubated for 10 min at room temperature, and the phosphorescence spectra were measured on a Perkin–Elmer LS55 fluorescence spectrophotometer. The results (Table S1) were reported as the mean ± standard deviation of triplicate experiments.

14. Synthetic details to Ir-DNBS and Ir-NH_2.

Scheme S1. Synthetic routes to the objective compounds Ir-DNBS and the proposed probing species Ir-NH_2.



Synthesis of picolinimidohydrazide (1).[3]

2-cyanopyridine (5.2 g, 50 mmol) was heated and melted in a 25 mL two-necked flask, and hydrazine hydrate (3.44 g, 55 mmol) was added dropwise into the reaction flask under argon gas. Ethanol was slowly added dropwise to the turbid system until it became clarify. Then, the reaction solution was stirred at room temperature overnight and then filtered, washed with ice petroleum ether to afford a white solid 5.45 g without further purification.

Synthesis of 4-nitrobenzoyl chloride (2).[4]

The mixture of *p*-nitrobenzoic acid (8.36 g, 50 mmol) and 25 mL of thionyl chloride was added to a 50 mL reaction flask, and 5 drops of dry DMF were added dropwise. The reaction solution was refluxed at 75°C for 2 h and then thionyl chloride was distilled out to obtain a yellow solid 7.42 g without purification.

Synthesis of 3-(4-nitrophenyl)-5-phenyl-1*H*-1,2,4-triazole (3).

Compound **1** (5.45 g, 40 mmol) and Na_2CO_3 (4.8g, 45 mmol) were added in a 250 mL reaction flask under argon conditions. After adding 40 mL DMA/THF (3/1, v/v) solution, the mixture was stirred at 0°C for 20 min, then added 20 mL DMA solution of compound **2** (7.42 g, 40 mmol) and stirred at room temperature overnight. When stopped, the reaction mixture was filtered, washed with a little ethanol, and dried to get a brick red intermediate. Degassed ethanol (150 mL) was added in a reaction flask within the intermediate under argon gas, and then refluxed at 190°C for 1 h. Cooled down the reaction solution and filtered, washed with ethanol and dried, compound **3** was obtained as beige flake solid (2.2 g, yield: 16%). ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 15.17 (s, 1H, NH), 8.76−8.75 (m, 1H, ArH), 8.38 (d, J = 9.2 Hz, 2H, ArH), 8.35 (d, J = 9.2 Hz, 2H, ArH), 8.21 (d, J = 8.0 Hz, 1H, ArH), 8.05 (t, J = 7.6 Hz, 1H, ArH), 7.60−7.57 (m, 1H, ArH). HR-MS (ESI): *m/z* $[M + Na]^+$ 290.0636, Calcd: 290.0648.

Synthesis of methyl 9*H*-fluorene-2-carboxylate (4).

The mixture of fluorene (4 g, 24.36 mmol), DCM (120 mL) and oxalyl chloride (3.86 g, 30.45 mmol) was stirred in ice bath for 20 min, then added $AlCl_3$ (4.87 g, 36.54 mmol) and stirred at room temperature overnight. After being poured into 100 mL ice water, the reaction mixture was stirred vigorously for 15 min, extracted with DCM, washed with saturated salt water and dried over anhydrous sodium sulfate. After the removal of the solvent under reduced pressure, the residue was dissolved in 200 mL DCM/methanol (1/1, v/v), and stirred at room temperature overnight. The reaction mixture was poured into 100 mL water, extracted with DCM, washed with saturated salt water and dried over anhydrous sodium sulfate. After the removal of the solvent under reduced pressure, the crude product was subject to column chromatography (eluent: PE:DCM = 4:1) to afford a white solid (2.8 g, yield: 51%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.22 (s, 1H, ArH), 8.09 (d, J = 8.0 Hz, 1H, ArH), 7.85 (d, J = 6.4 Hz, 1H, ArH), 7.83 (d, J = 8.0 Hz, 1H, ArH), 7.59 (d, J = 7.6 Hz, 1H, ArH), 7.42 (t, J = 7.2 Hz, 1H, ArH), 7.37 (t, J = 7.2 Hz, 1H, ArH), 3.95 (s, 2H, CH_2), 3.94 (s, 3H, CH_3). HR-MS (ESI): *m/z* $[M + H]^+$ 225.0910, Calcd: 225.0910.

Synthesis of 9*H*-fluorene-2-carboxylic acid (5).

The mixture of compound **4** (2.56 mg, 11.4 mmol), NaOH (1.83 mg, 45.6 mmol) and 100mL DCM/methanol (9/1, v/v) was stirred at room temperature overnight. The pH of the solution was adjusted to 3 with 1M HCl/methanol solution. The mixture was extracted with DCM, washed with saturated salt water and dried over anhydrous sodium sulfate. After the removal of the solvent under reduced pressure, compound **5** was obtained as a white solid (2.75 g, yield quantification). ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 12.89 (s, 1H, COOH), 8.16 (s, 1H, ArH), 8.03−7.98 (m, 3H, ArH), 7.65 (d, J = 7.6 Hz, 1H, ArH), 7.44 (t, J = 7.2 Hz, 1H, ArH), 7.40 (t, J = 7.2 Hz, 1H, ArH), 4.01 (s, 2H, CH_2). HR-MS (ESI): m/z $[M-H]^-$ 209.0607, Calcd: 209.0608.

Synthesis of 9,9-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-9*H*-fluorene-2-carboxylic acid (6).

The mixture of compound **5** (4 g, 18.94 mmol) and KOH (15.94 g, 284.1 mmol) was dissolved in 100 mL DMSO, stirred at room temperature until the color of mixture changed to purple, and then transferred to a dropping funnel. Under argon gas, 1-iodo-2-(2-(2-methoxyethoxy)ethoxy)ethane (11.4 g 41.6 mmol) was dissolved in 50 mL DMSO, and purple mixture was dropped and stirred at room temperature overnight. The pH of the reaction solution was adjusted to 4 with 1M HCl solution. The mixture was extracted with DCM, washed with saturated salt water and dried over anhydrous sodium sulfate. After the removal of the solvent under reduced pressure, the crude product was subject to column chromatography to afford compound **6** as a yellow liquid (4.79 g, yield: 50%). ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 12.95 (s, 1H, COOH), 8.10 (s, 1H, ArH), 7.98−7.90 (m, 3H, ArH), 7.62 (m, 1H, ArH), 7.41 (m, 2H, ArH), 3.44−3.39 (m, 4H, CH2), 3.32−3.30 (m, 4H, CH_2), 3.23−3.21 (m, 4H, CH_2), 3.18 (s, 6H, CH_3), 3.08−3.05 (m, 4H, CH_2), 2.68−2.58 (m, 4H, CH_2), 2.43−2.30 3.18 (m, 4H, CH_2).

Synthesis of 2-(9,9-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-9*H*-fluoren-2-yl)benzo[*d*]thiazole (7).

A mixture of compound **6** (8.63 g, 17.17 mmol) and 30 mL of $SOCl_2$ was refluxed at 80°C for 3 h in a reaction flask equipped with an exhaust gas treatment unit. The reaction system was cooled and the $SOCl_2$ was removed by distillation under reduced pressure to obtain a yellow solid as intermediate.

A mixture of 2-aminobenzenethiol (3.23 g, 25.77 mmol) and 30 mL NMP was stirred at room temperature in a reaction flask equipped with an exhaust gas treatment unit. The above yellow intermediate was dissolved in 30 mL NMP, and added into the reaction solution in ice bath. After that, the reaction mixture was heated to 100°C and reacted for 5 h. The pH of the reaction solution was adjusted to 7～8 with 7 M ammonia solution after the reaction solution was poured into 50 mL water. The mixture was extracted with DCM, washed with water to neutral, and dried over anhydrous sodium sulfate. After the removal of the solvent under reduced pressure, the crude product was subject to column chromatography (PE:EA = 4:1) to afford compound **7** as a reddish brown liquid (4.72 g, yield: 46%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.19 (s, 1H, ArH), 8.11 (d, J = 8.0 Hz, 1H, ArH), 8.10 (d, J = 8.0 Hz, 1H, ArH), 7.94 (d, J = 8.0 Hz, 1H, ArH), 7.79 (d, J = 8.0 Hz, 1H, ArH), 7.76−7.74 (m, 1H, ArH), 7.52 (t, J = 8.0 Hz, 1H, ArH), 7.47−7.45 (m, 1H, ArH), 7.42 (d, J = 8.0 Hz, 1H, ArH), 7.39−7.37 (m, 2H, ArH), 3.50−3.47 (m, 4H, CH_2), 3.44−3.42 (m, 4H, CH_2), 3.40−3.36 (m, 8H, CH_2), 3.30 (s, 6H, CH_3), 3.22−3.18 (m, 4H, CH_2), 2.82−2.78 (m, 4H, CH_2), 2.56−2.43 (m, 4H, CH_2). HR-MS (ESI): *m*/*z* $[M + H]^+$ 592.2726, Calcd: 592.2727.

Synthesis of bis[2-(9,9-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-9*H*-fluoren-2-yl)benzo[*d*]thiazole-*N*,*C*^{2}]iridium(III)(2-(3-(4-nitrophenyl)-1*H*-1,2,4-triazol-5-yl)pyridine) (8).

The mixture of $IrCl_3 \cdot nH_2O$ (0.59 g 1.66 mmol) and compound **7** (2.36 g 3.99 mmol) was dissolved in 60 mL ethylene glycol ether/water (3/1, v/v) solution under argon gas, and refluxed at 120°C for 24 h. The reaction mixture was cooled, concentrated under reduced pressure, mixed with compound **3** (0.53 g, 1.99 mmol) and 40 mL DCM/ethanol (3/1,v/v) in a reaction flask, and refluxed at 70°C for 10 h. The reaction system was extracted with DCM, washed with water, and dried over anhydrous sodium sulfate. After the removal of the solvent under reduced pressure, the crude product was subject to column chromatography (DCM:methanol = 200:1) to afford compound **8** as an orange solid (1.94 g, yield: 23%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.25 (d, J = 8.8 Hz, 2H, ArH), 8.23 (d, J = 7.2 Hz, 1H, ArH), 8.14 (d, J = 8.8 Hz, 2H, ArH), (m, 3H, ArH), 8.14 (d, J = 8.8 Hz, 2H, ArH), 7.88 (d, J = 8.0 Hz, 1H, ArH), 7.87 (d, J = 8.0 Hz, 1H, ArH), 7.83 (d, J = 7.2 Hz, 2H, ArH), 7.82 (d, J = 8.4 Hz, 2H, ArH), 7.33 (d, J = 7.2 Hz, 1H, ArH), 7.32 (d, J = 7.2 Hz, 2H, ArH), 7.30−7.28 (m, 1H, ArH), 7.22 (t, J = 8.0 Hz, 1H, ArH), 7.20−7.17 (m, 1H, ArH), 7.15−7.13 (m, 4H, ArH), 7.11−7.09 (m, 1H, ArH), 7.06−7.04 (m, 1H, ArH), 6.99 (t, J = 8.0 Hz, 1H, ArH), 6.88 (d, J = 8.4 Hz, 1H, ArH), 6.86 (s, 1H, ArH), 6.81 (s, 1H, ArH), 6.28 (d, J = 8.4 Hz, 1H, ArH), 3.59−3.57 (m, 4H, CH_2), 3.55−3.52 (m, 4H, CH_2), 3.51−3.48 (m, 4H, CH_2), 3.42−3.40 (m, 4H, CH_2), 3.40−3.39 (m, 4H, CH_2), 3.38−3.35 (m, 4H, CH_2), 3.33 (s, 3H, OCH_3), 3.31 (s, 3H, OCH_3), 3.27 (s, 6H, OCH_3), 3.25−3.22 (m, 4H, CH_2), 3.07−2.84 (m, 8H, CH_2), 2.72−2.68 (m, 4H, CH_2), 2.48−2.42 (m, 4H, CH_2), 2.36−2.31 (m, 4H, CH_2). HR-MS (ESI): *m*/*z* $[M + 2Na]^{2+}$ 842.7620, Calcd: 846.7622.

Synthesis of bis[2-(9,9-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-9*H*-fluoren-2-yl)benzo[*d*]thiazole-*N*,*C*^{2}]iridium(III)(4-(5-(pyridin-2-yl)-1*H*-1,2,4-triazol-3-yl)aniline) (Ir-NH_2).

A mixture of Compound **8** (507 mg, 0.31 mmol), 20 mg Pd/C, 15 mL ethanol and 5 mL hydrazine hydrate was reacted at 85°C for 10 h. Then, the reaction mixture was cooled and filtered to recycle Pd/C, washed with water, extracted with DCM, dried over anhydrous sodium sulfate. After the removal of the solvent under reduced pressure, the crude product was subject to column chromatography (EA:methanol = 40:1) to afford orange solid (228.4 mg, yield: 46%). M.p.: 96.5−98.4°C。 ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ 8.24 (d, *J* = 6.8 Hz, 1H, ArH), 7.88 (d, *J* = 8.4 Hz, 2H, ArH), 7.87 (d, *J* = 7.2 Hz, 2H, ArH), 7.84 (s, 1H, ArH), 7.81 (s, 1H, ArH), 7.80 (s, 1H, ArH), 7.78 (m, 2H, ArH), 7.33−7.30 (m, 4H, ArH), 7.21−7.17 (m, 2H, ArH), 7.16−7.14 (m, 3H, ArH), 7.10 (t, *J* = 7.6 Hz, 1H, ArH), 7.06−7.04 (m, 1H, ArH), 7.00 (d, *J* = 8.0 Hz, 1H, ArH), 6.97 (t, *J* = 7.6 Hz, 1H, ArH), 6.83 (d, *J* = 7.6 Hz, 2H, ArH), 6.62 (d, *J* = 8.8 Hz, 2H, ArH), 6.26 (d, *J* = 8.4 Hz, 1H, ArH), 3.58−3.56 (m, 4H, CH$_2$), 3.51−3.46 (m, 8H, CH$_2$), 3.42−3.35 (m, 12H, CH$_2$), 3.33 (s, 3H, OCH$_3$), 3.31 (s, 3H, OCH$_3$), 3.27 (s, 6H, OCH$_3$), 3.25−3.20 (m, 4H, CH$_2$), 3.06−2.88 (m, 8H, CH$_2$), 2.71−2.66 (m, 4H, CH$_2$), 2.45−2.42 (m, 4H, CH$_2$), 2.35−2.30 (m, 4H, CH$_2$). ^{13}C NMR (400 MHz, CDCl$_3$, ppm) δ 180.7, 180.1, 150.2, 150.0, 149.9, 149.8, 149.6, 149.5, 146.3, 143.5, 143.1, 143.0, 142.6, 140.5, 140.0, 139.7, 139.5, 138.4, 131.4, 130.8, 128.5, 128.1, 127.9, 127.5, 127.3, 127.2, 127.0, 125.4, 125.0, 124.9, 124.8, 124.6, 123.7, 123.7, 122.96, 122.94, 122.9, 122.2, 121.3, 121.2, 121.0, 120.8, 120.77, 120.7, 120.6, 120.5, 120.4, 118.1, 114.9, 71.9, 71.8, 71.76, 70.6, 70.5, 70.47, 70.4, 70.38, 70.3, 70.28, 70.2, 70.0, 69.8, 67.6, 67.3, 67.2, 67.1, 59.0, 58.9, 58.88, 50.5, 50.47, 39.9, 39.7, 39.65, 39.6. HR-MS (ESI): *m*/*z* [M + H + Na]$^{2+}$ 816.7843, Calcd: 816.7842.

Synthesis of bis[2-(9,9-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-9*H*-fluoren-2-yl)benzo[*d*]thiazole-N,C^2]iridium(III)(2,4-dinitro-N-(4-(5-(pyridin-2-yl)-1*H*-1,2,4-triazol-3-yl)phenyl)benzenesulfonamide) (Ir-DNBS).

A mixture of compound **Ir-NH$_2$** (200 mg, 0.12 mmol), 2,4-dinitrobenzenesulfonyl chloride (165 mg, 0.65 mmol), Cs$_2$CO$_3$ (40.4 mg, 0.12 mmol) and 20 mL DCM was stirred at room temperature under argon gas overnight. The reaction mixture was poured in water, extracted with DCM, and dried with anhydrous sodium sulfate. After the removal of the solvent under reduced pressure, the crude product was subject to column chromatography (EA:methanol = 50:1) to afford a orange solid (97 mg, yield: 43%). M.p.: 104.7−106.1°C. ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ 8.53 (s, 1H, ArH), 8.25 (d, *J* = 8.4 Hz, 1H, ArH), 8.18 (d, *J* = 8.4 Hz, 1H, ArH), 7.98 (d, *J* = 8.4 Hz, 1H, ArH), 7.97 (d, *J* = 8.8 Hz, 2H, ArH), 7.86 (d, *J* = 8.0 Hz, 2H, ArH), 7.83−7.78 (m, 4H, ArH), 7.34−7.31 (m, 3H, ArH), 7.28 (d, *J* = 7.2 Hz, 1H, ArH), 7.23−7.20 (m, 1H, ArH), 7.20−7.18 (m, 1H, ArH), 7.17−7.15 (m, 3H, ArH), 7.13−7.08 (m, 4H, ArH), 7.04 (t, *J* = 8.0 Hz, 1H, ArH), 6.97 (t, *J* = 7.6 Hz, 1H, ArH), 6.88−6.85 (m, 2H, ArH), 6.78 (s, 1H, ArH), 6.27 (d, *J* = 8.4 Hz, 1H, ArH), 3.60−3.56 (m, 4H, CH$_2$), 3.55−3.52 (m, 4H, CH_2), 3.51−3.49 (m, 4H, CH_2), 3.42−3.35 (m, 12H, CH_2), 3.30 (s, 6H, OCH_3), 3.27 (s, 6H, OCH_3), 3.25−3.23 (m, 4H, CH_2), 3.08−2.85 (m, 8H, CH_2), 2.72−2.67 (m, 4H, CH_2), 2.46−2.42 (m, 4H, CH_2), 2.36−2.31 (m, 4H, CH_2). ^{13}C NMR (400 MHz, $CDCl_3$, ppm) δ 180.8, 180.3, 163.8, 163.7, 154.8, 152.8, 150.1, 150.0, 149.9, 149.8, 149.78, 149.7, 149.3, 148.34, 148.3, 143.6, 143.2, 143.0, 142.7, 140.3, 140.0, 139.6, 139.4, 138.4, 137.6, 133.9, 133.8, 131.9, 131.3, 130.9, 128.3, 128.2, 128.0, 127.3, 127.03, 127.0, 126.5, 125.4, 125.1, 124.9, 124.6, 123.0, 122.97, 122.7, 122.3, 121.2, 121.0, 120.7, 120.3, 120.2, 118.0, 71.9, 71.86, 71.8, 71.76, 70.5, 70.3, 70.29, 70.1, 67.6, 67.4, 67.2, 67.1, 59.0, 58.9, 58.8, 50.6, 50.4, 39.8, 39.7, 39.65, 39.5. HR-MS (ESI): *m*/*z* $[M + H + Na]^{2+}$ 931.7664, Calcd: 931.7659.

15. NMR spectra of Ir-NH_2 and Ir-DNBS.

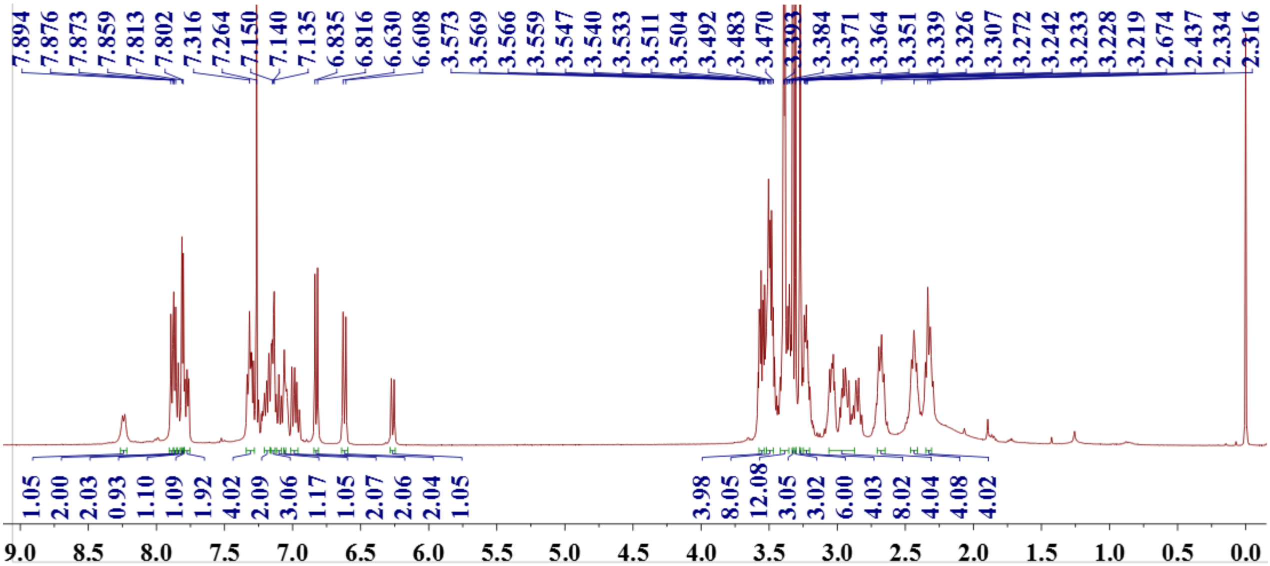


Figure S11. ^{1}H NMR spectrum of **Ir-NH_2** (400 MHz, $CDCl_3$, 298 K).

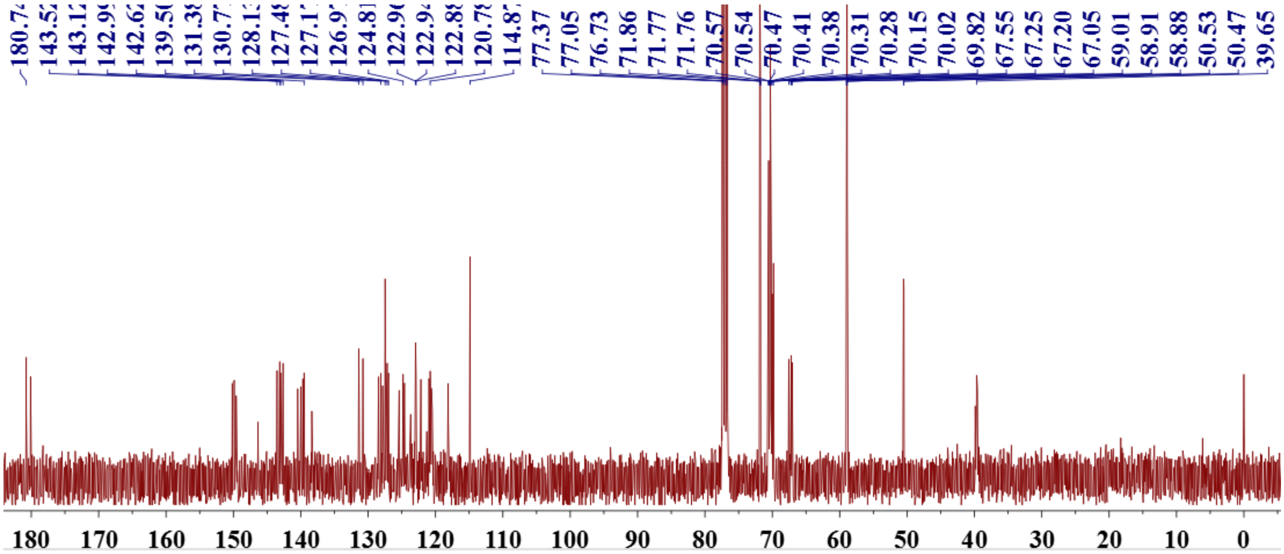


Figure S12. ^{13}C NMR spectrum of **Ir-NH$_2$** (400 MHz, CDCl$_3$, 298 K).

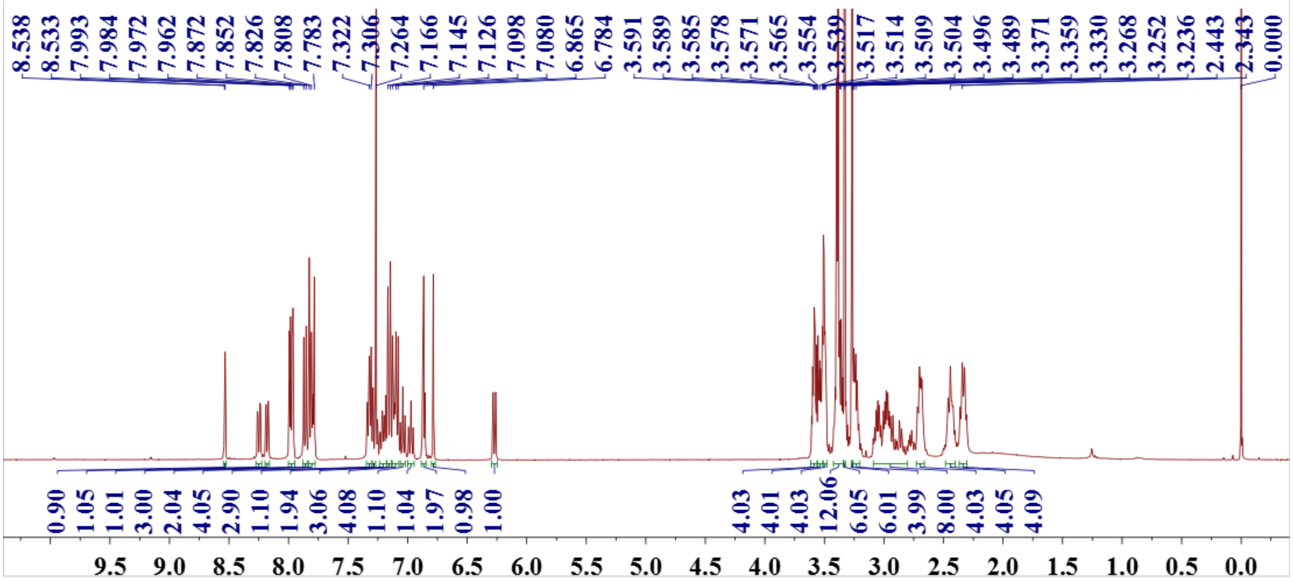


Figure S13. ^{1}H NMR spectrum of **Ir-DNBS** (400 MHz, CDCl$_3$, 298 K).

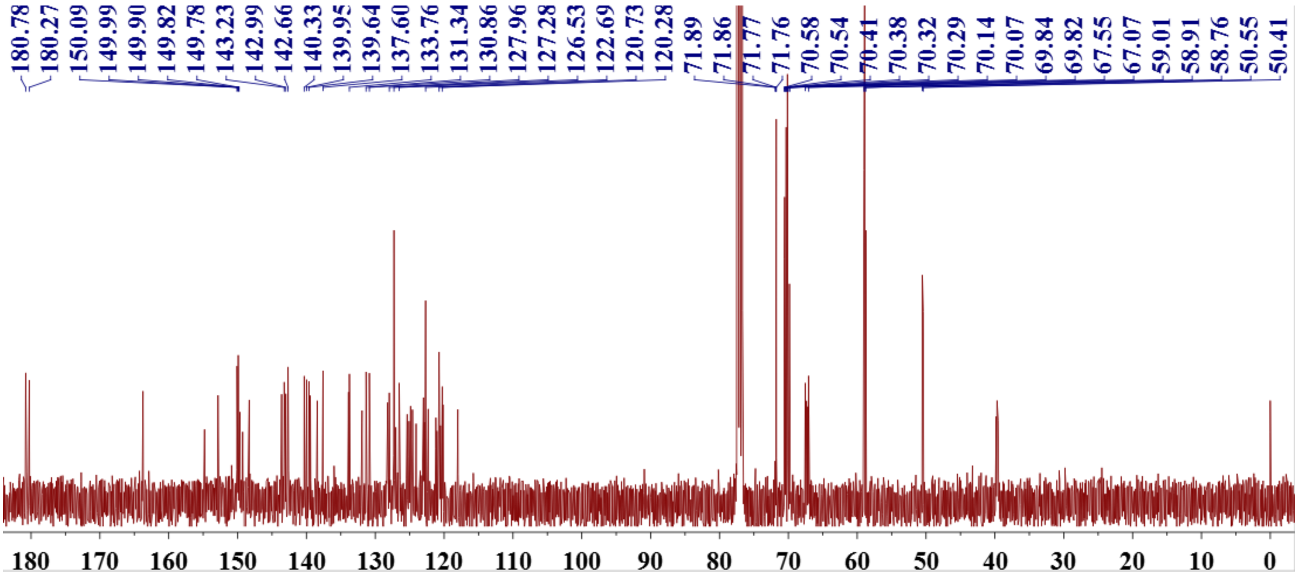


Figure S14. ^{13}C NMR spectrum of **Ir-DNBS** (400 MHz, $CDCl_3$, 298 K).

16. HR-MS spectra of Ir-NH2, Ir-DNBS and Ir-DNBS in the presence of thiophenol.

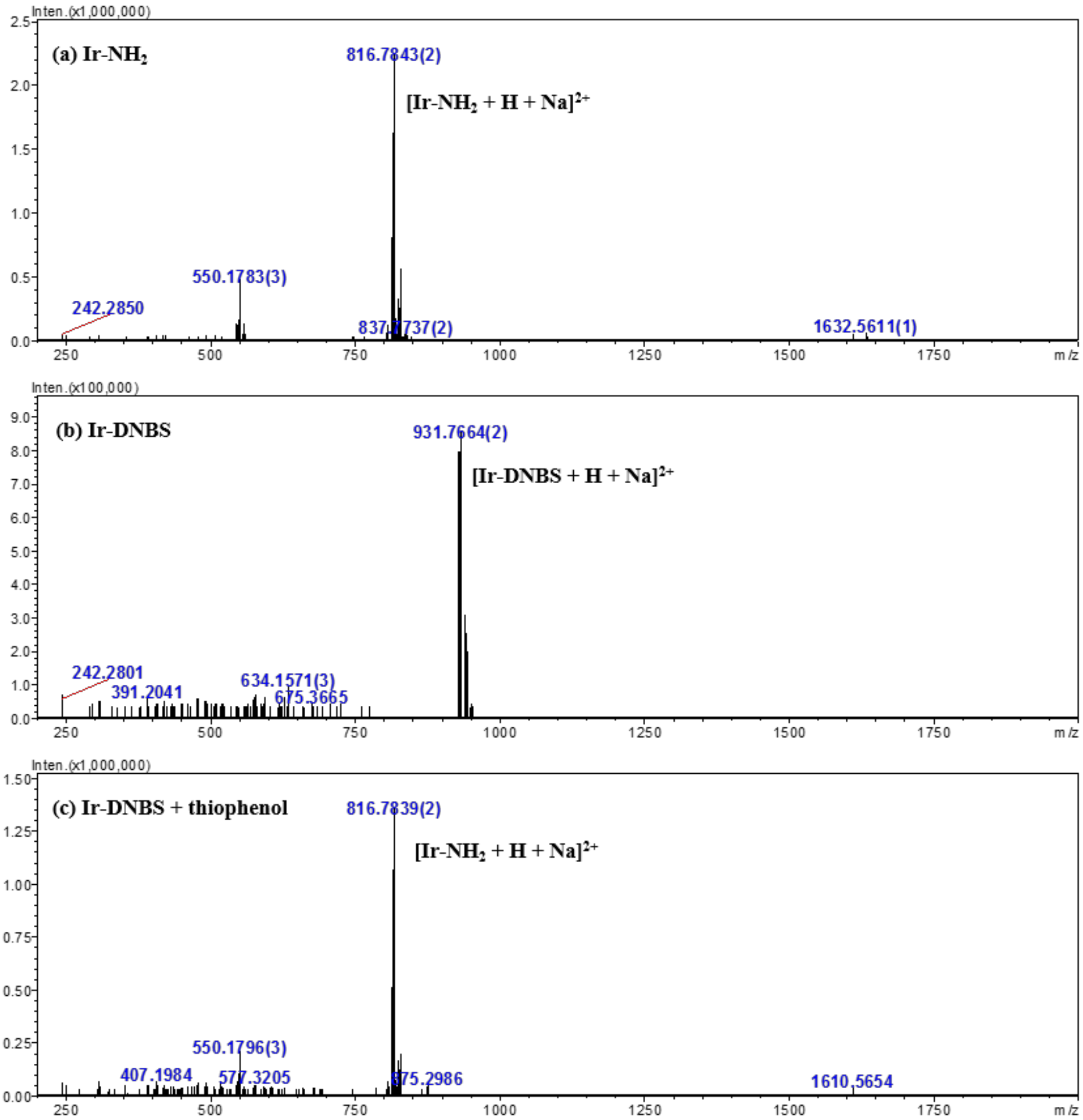


Figure S15. ESI-MS spectra of **Ir-NH$_2$**, **Ir-DNBS** and **Ir-DNBS** + thiophenol.

17. Reference.

[1] Chen, H.; Zhao, Q.; Wu, Y.; Li, F.; Yang, H.; Yi, T.; Huang, C. Selective phosphorescence chemosensor for homocysteine based on an iridium(III) complex. *Inorg. Chem.* **2007,** *46*, 11075−11081.

[2] Sun, Q.; Yang, S.-H.; Wu, L.; Yang, W.-C.; Yang, G.-F.; Yang, G.-F. A highly sensitive and selective fluorescent probe for thiophenol designed via a twist-blockage strategy. *Anal. Chem.* **2016,** *88*, 2266−2272.

[3] Zvirzdinaite, M.; Garbe, S.; Arefyeva, N.; Krause, M.; Stück, R.; Klein, A. Palladium(II) complexes of ambidentate and potentially cyclometalating 5-aryl-3-(2′-pyridyl)-1,2,4-triazine ligands. *Eur. J. Inorg. Chem.* **2017**, 2011−2022.

[4] Copley, G.; Oh, J.; Yoshida, K.; Shimizu, D.; Kim, D.; Osuka, A. Intramolecular electron transfer reactions in *meso-(4-nirophenyl)*-substituted subporphyrins. *Chem. Commun.* **2016**, *52*, 1424−1427.