Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Nitrooelfin-modified Cyclometalated iridium(III) complexes for tunable detection of biothiols with deep-red emission

Table S1. Comparison with recent Ir(III)-based probes for biothiols

Entry	Reference	Sensing phase	LOD	Linear range	response time
1	**This work**	**DMSO/HEPES=1:1**	**Ir1: 47.6 nM** **Ir2: 232 nM**	**10-80 μM** **25-150 μM**	**80s** **1min**
2	Rsc. Adv., 2017,7(83):52621-52625	DMSO/HEPES=4:1	9.7 μM	50-450 μM	—
3	J. Inorg. Biochem. 2017, 177, 412-422	KPI/MeOH=1:1	—	—	—
4	Sci. Technol. Adv. Mat., 2016, 17, 109–114	DMSO/HEPES=9:1	1.67 μM	4-40 μM	—
5	Chem.Commun., 2016,52, 4450-4453	DMSO/HEPES=4:1	0.78 μM	2.5 -80 μM	10 min
6	Opt. Express, 2016, 24, 28247–28255	CH_3CN/H_2O=3:2	—	—	—

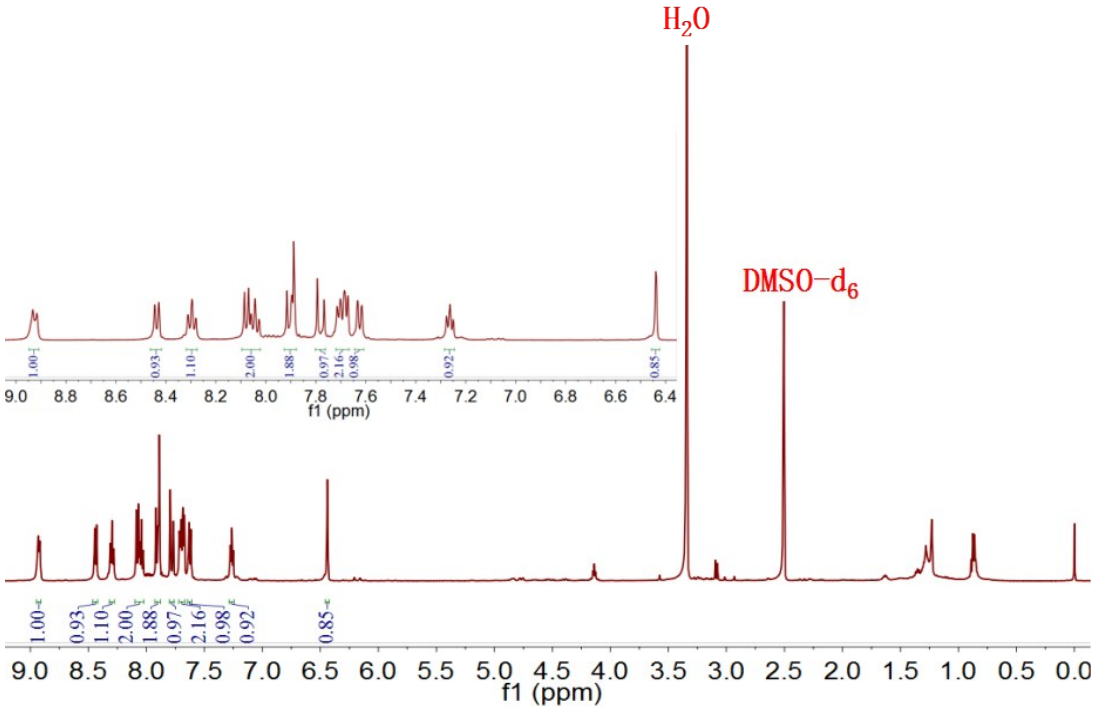

Fig S1. ^{1}H NMR spectrum of **Ir1** in DMSO-d_6.

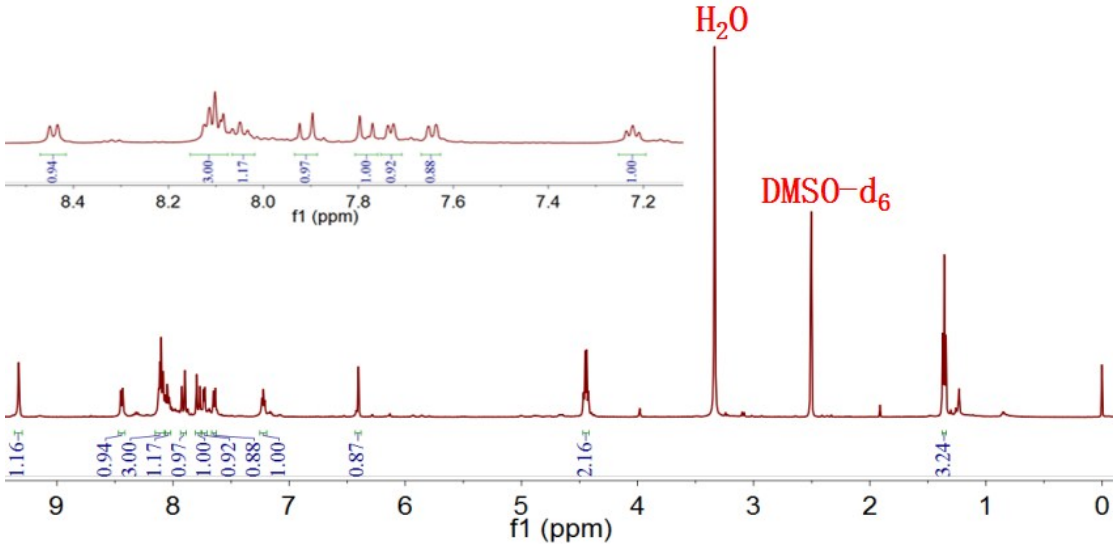

Fig S2. ^{1}H NMR spectrum of **Ir2** in DMSO-d_6.

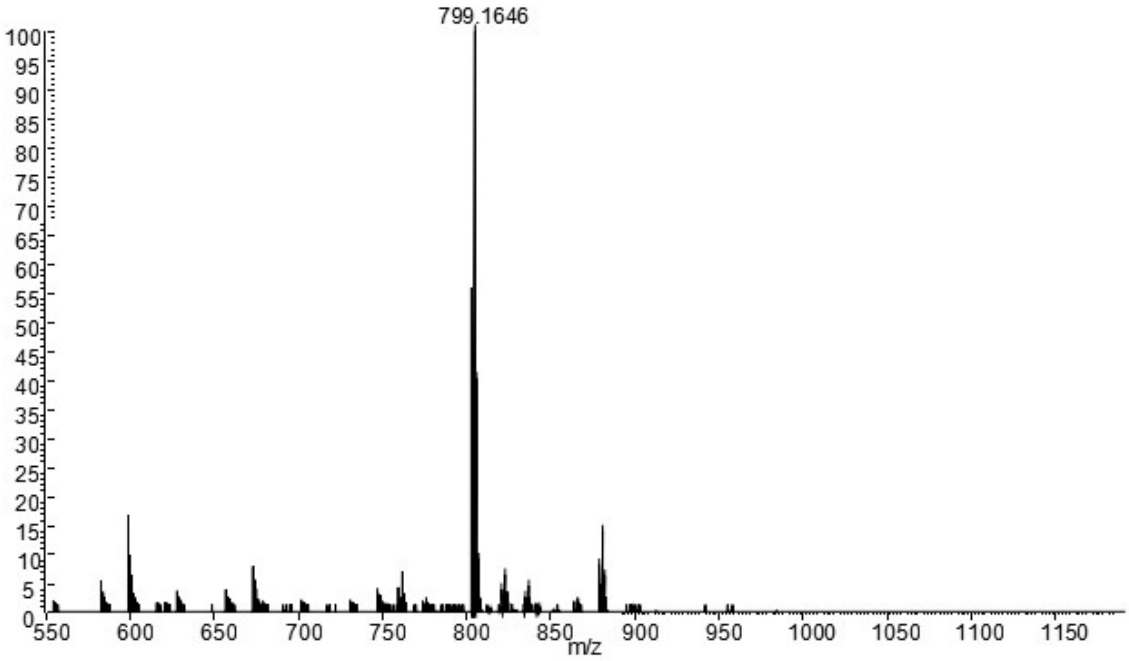

Fig S3. HRMS spectrum of **Ir1** in CH_3CN.

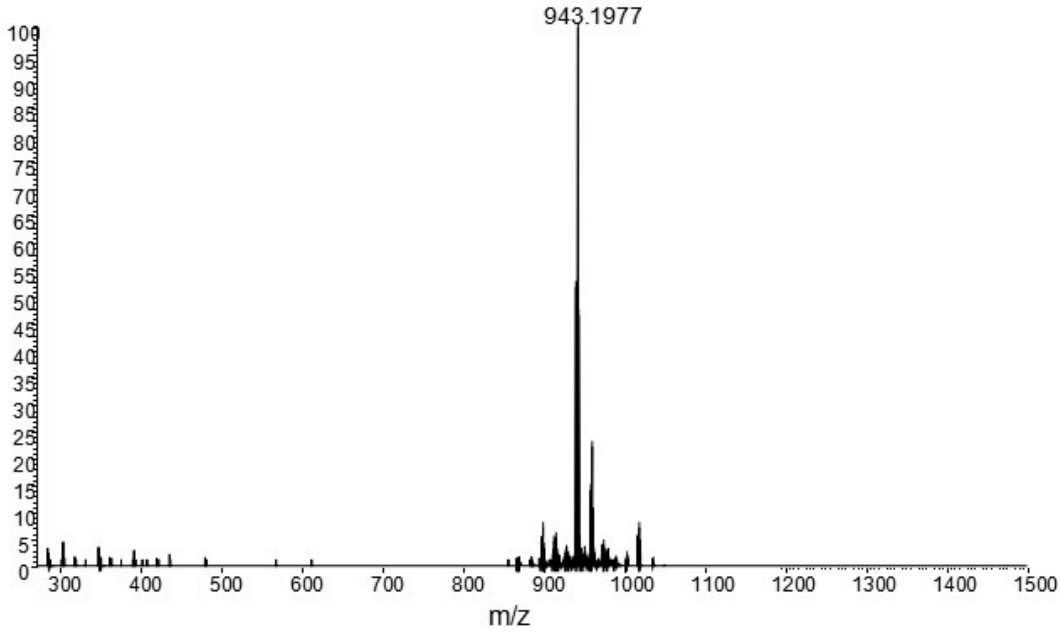

Fig S4. HRMS spectrum of **Ir2** in CH_3CN.

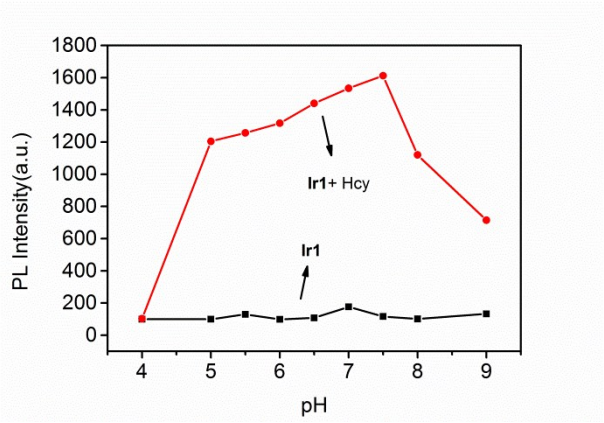

Fig S5. PL intensity of **Ir1** (10 μM) at 571nm in the presence and absence of Hcy under different pH. λ_{ex}=380 nm.

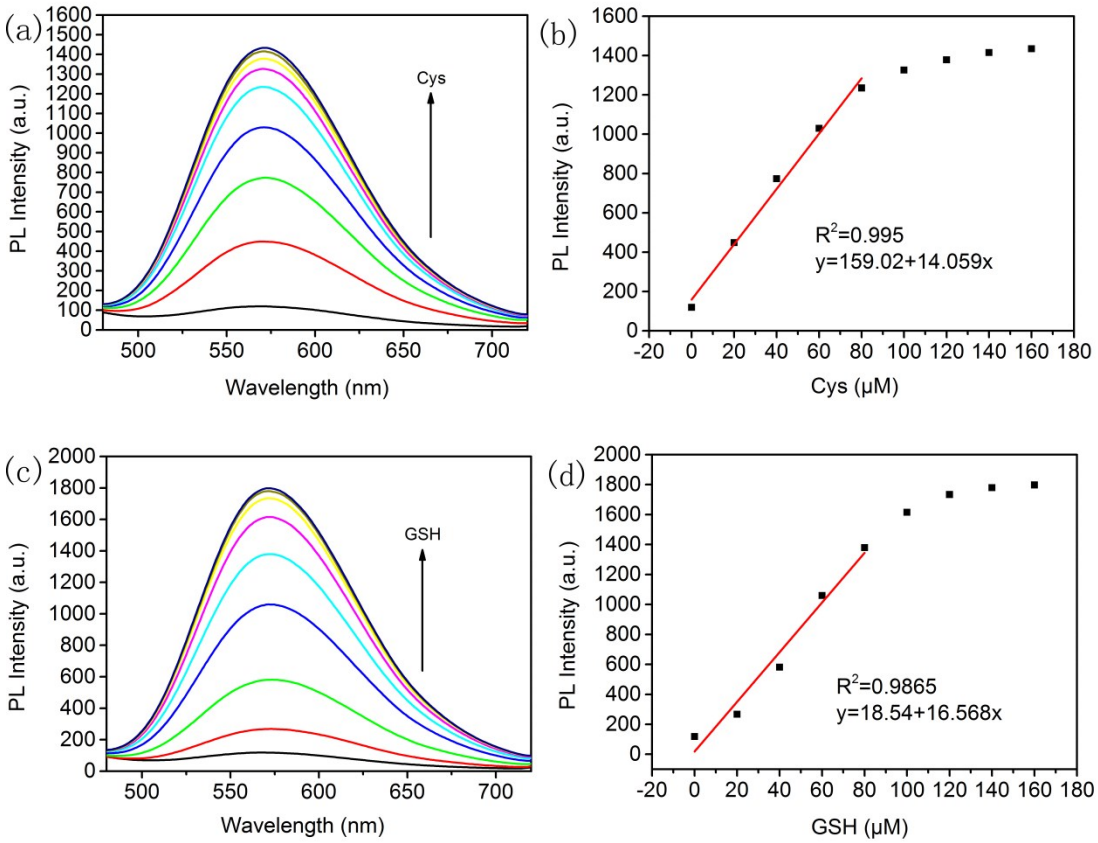

Fig S6. PL spectra of **Ir1** (10 μM) upon addition of Cys (a) and GSH (c) (0-160 μM) in DMSO/HEPES buffer solution (pH=7.4, 1:1, v/v); corresponding plot of PL intensity at 571 nm versus concentration of Cys (b) and GSH (d). λ_{ex}=380 nm.

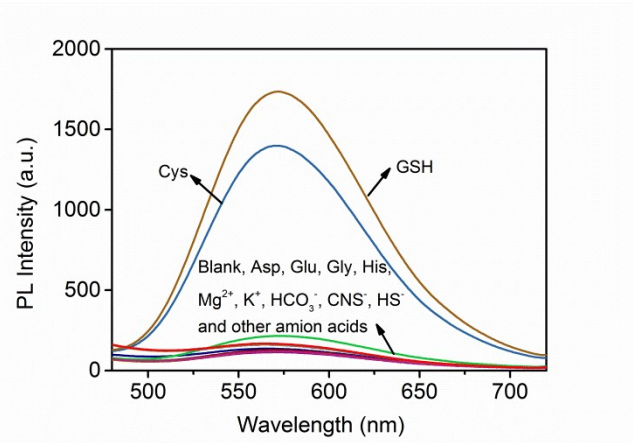

Fig S7. PL intensity of **Ir1** (10 μM) with various analytes (1 mM) including Asp, Glu, Gly, His, Lys, Thr, Mg^{2+}, K^{+}, HCO_3^{2-}, CNS^{-}, HS^{-}, Ala, Arg, Phe, Pro, Ser, Trp, Tyr, GSSG, Cys and GSH in DMSO/HEPES buffer solution (pH=7.4, 1:1, v/v).

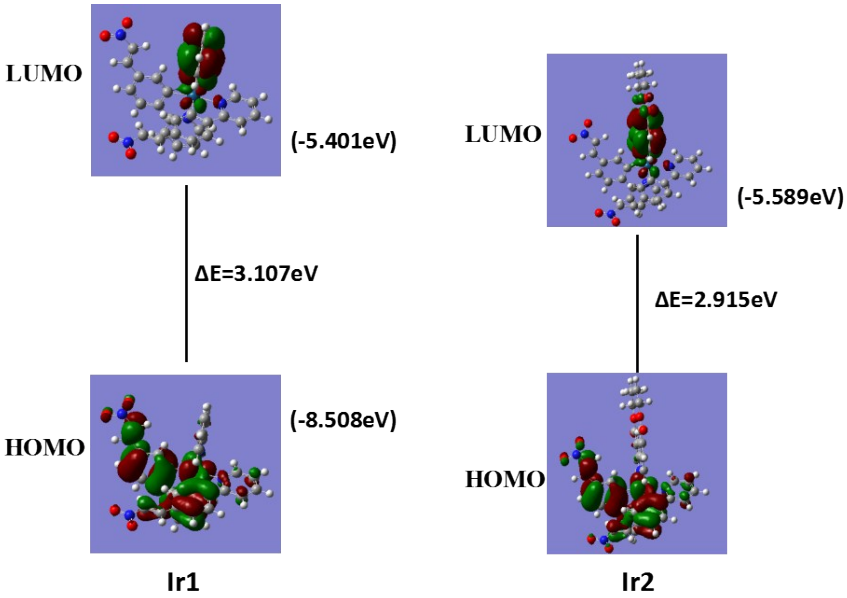

Fig S8. HOMO and LUMO Distributions of **Ir1** and **Ir2**.

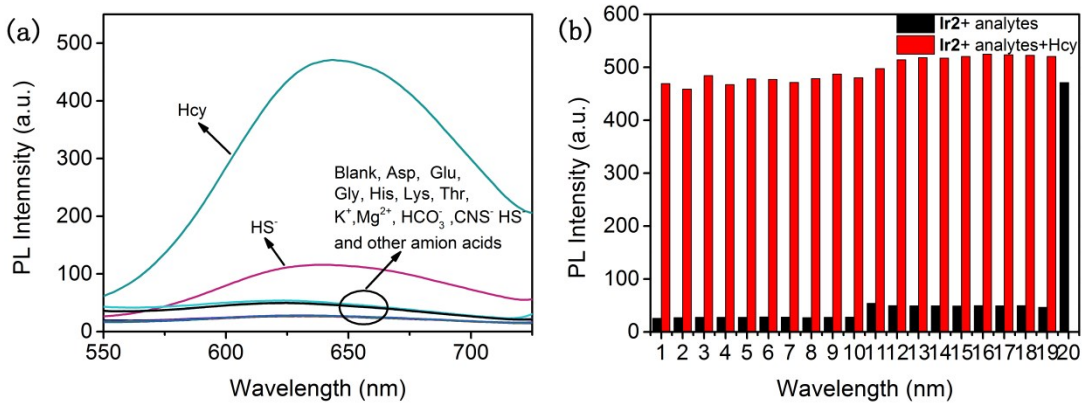

Fig S9. (a) PL intensity of **Ir2** (50 μM) in the presence of various analytes. (b) PL intensity of **Ir2** (50 μM) at 643 nm upon addition of Hcy and various analytes (1 mM) in DMSO/HEPES buffer solution (pH=7.4, 1:1, v/v) (1-Asp, 2-Glu, 3-Gly, 4-His, 5-Lys, 6-Thr, 7-Mg^{2+}, 8-K^{+}, 9-HCO_3^{2-}, 10-CNS^{-} and 11-HS^{-}, 12-Ala, 13-Arg, 14-Phe, 15-Pro, 16-Ser, 17-Trp, 18-Tyr, 19-GSSG, 20-Hcy respectively, 300 μM.). λ_{ex}= 380 nm.

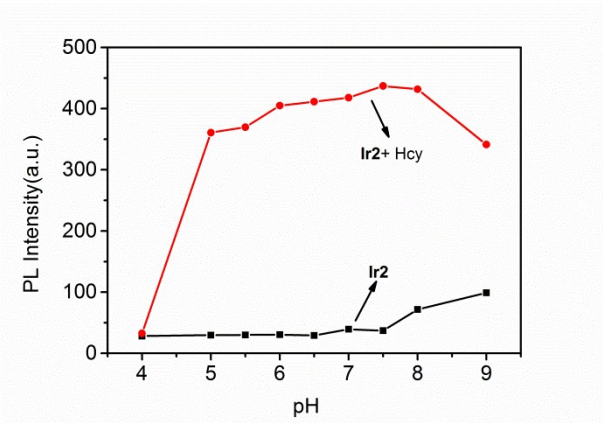

Fig S10. PL intensity of **Ir2** (50 μM) at 643 nm in the presence and absence of Hcy under different pH. λ_{ex}=380 nm.

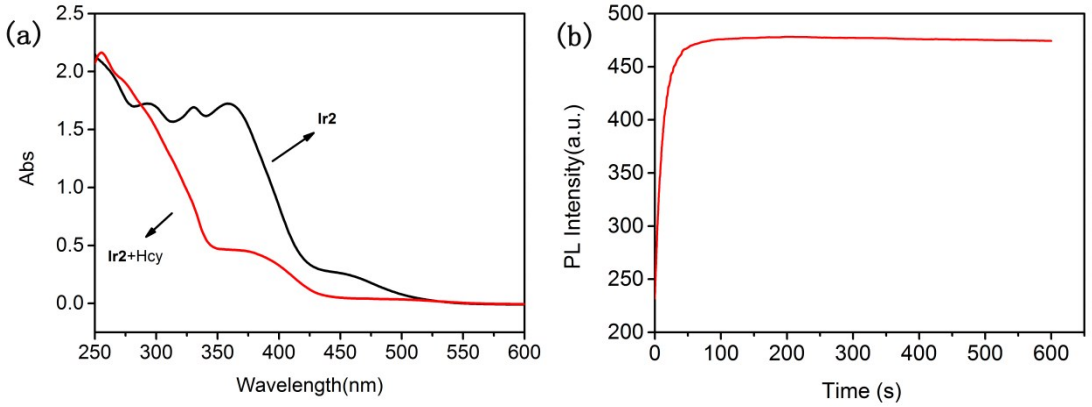

Fig S11. (a) Absorption spectra of **Ir2** (50 μM) in presence of Hcy in DMSO/HEPES buffer solution (pH=7.4, 1:1, v/v). (b) Time-dependent PL intensity of **Ir2** at 643 nm in presence of 6 equiv. λ_{ex}= 380 nm.

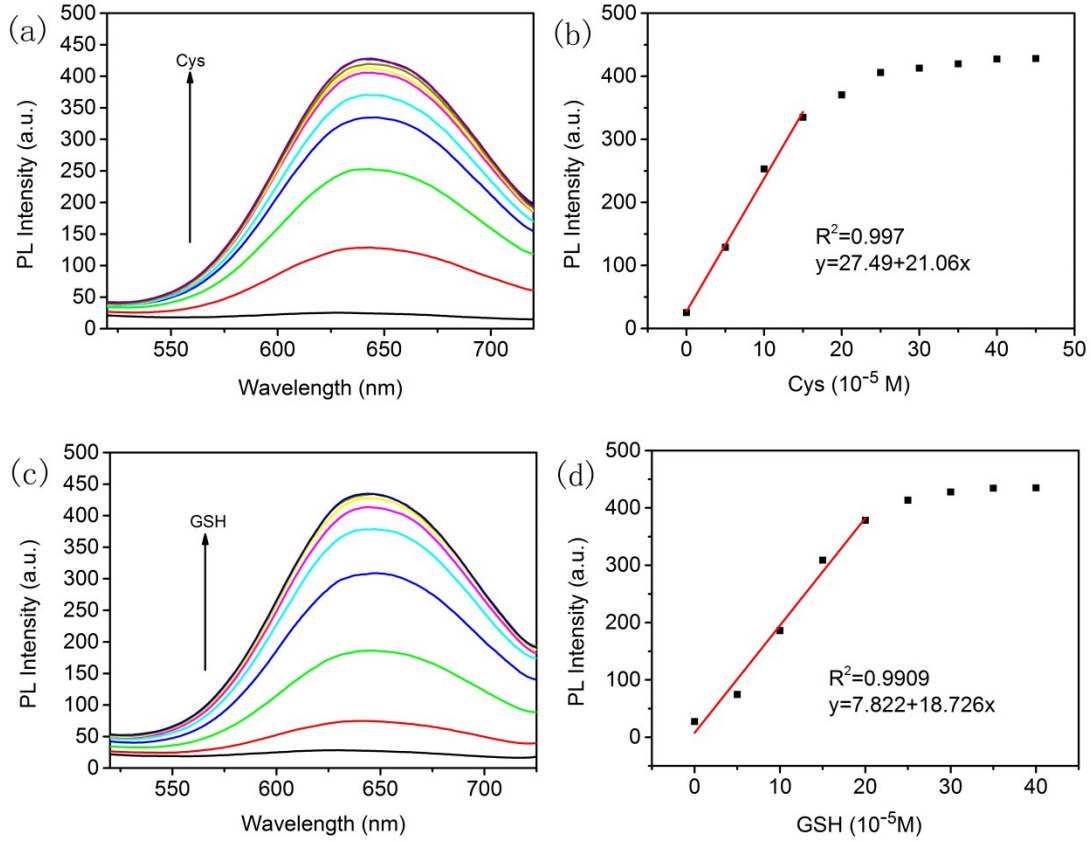

Fig S12. PL spectra of **Ir2** (50 μM) upon addition of Cys (a) (0-450 μM) and GSH (c) (0-400 μM) in DMSO/HEPES buffer solution (pH=7.4, 1:1, v/v); corresponding plot of PL intensity at 643 nm versus concentration of Cys (b) and GSH (d). λ_{ex}=380 nm.

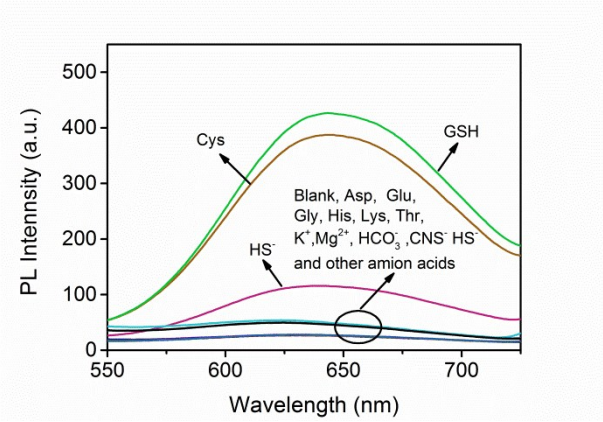

Fig S13. PL response of **Ir2** (50 μM) with various analytes (1 mM) including Asp, Glu, Gly, His, Lys, Thr, Mg^{2+}, K^{+}, HCO_3^{2-}, CNS^{-}, HS^{-}, Ala, Arg, Phe, Pro, Ser, Trp, Tyr, GSSG, Cys and GSH in DMSO/HEPES buffer solution (pH=7.4, 10mM, 1:1, v/v).

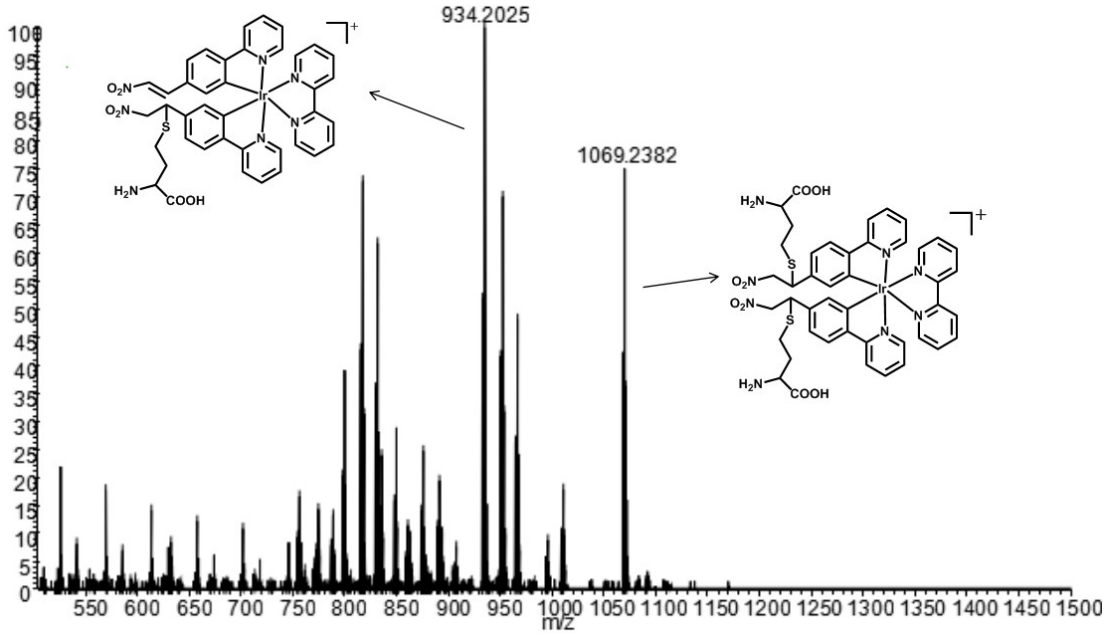

Fig S14. HRMS spectrum of **Ir1** (10μM) in the presence of Cys (5equiv.) for 3 min in the CH_3CN/D_2O solution (1:1, v/v).

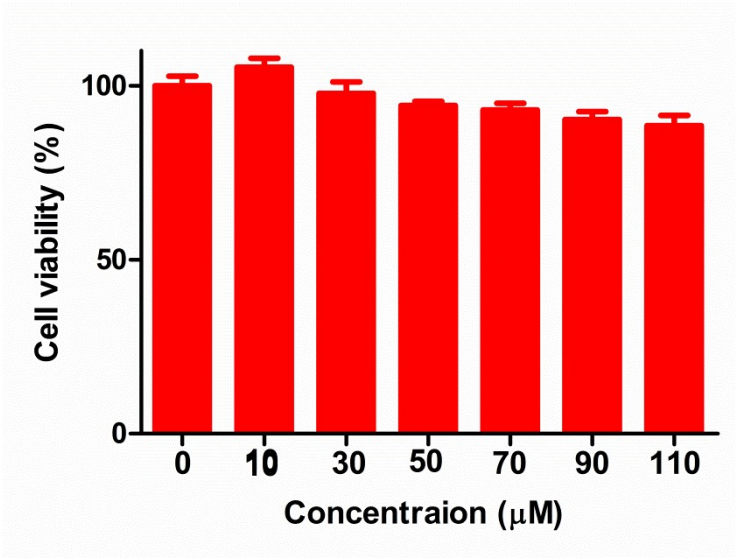

Fig S15. MTT result of **Ir2** with HeLa cells. The cytotoxicity of probes was assessed with a 3–(4,5–dimethyl–2–thiazolyl)–2,5–diphenyl–2–H–tetrazolium bromide (MTT) assays towards HeLa cells. The cells were seeded in 96–well plates at about 10000 cells per well in 100 μL DMEM, and incubated at 37 oC in 5% CO_2 atmosphere for 24 h. After removing culture medium, **Ir2** diluted in DMSO (100 μL) were added to cell wells with various concentrations of 0, 10, 30, 50, 70, 90 and 110 μM. The cells were incubated for another 24 h. After the incubation, the culture medium was removed and DMEM (200 μL) was added into cell wells. Then 20 μL of 5 mg/mL MTT assays were added to cell wells and cells were incubated for another 4 h, followed by removal of the culture medium containing MTT and addition of 150 μL of DMSO to each well to dissolve the formazan crystals formed. Finally, the plates were shaken for 5 min. The absorbance of the solution was measured on a Bio–Rad 680 microplate reader at 490 nm. Cell viability (%) was calculated based on the following equation: (Asample/Acontrol) × 100 %, where Asample and Acontrol denote as absorbencies of the sample well and control well, respectively.

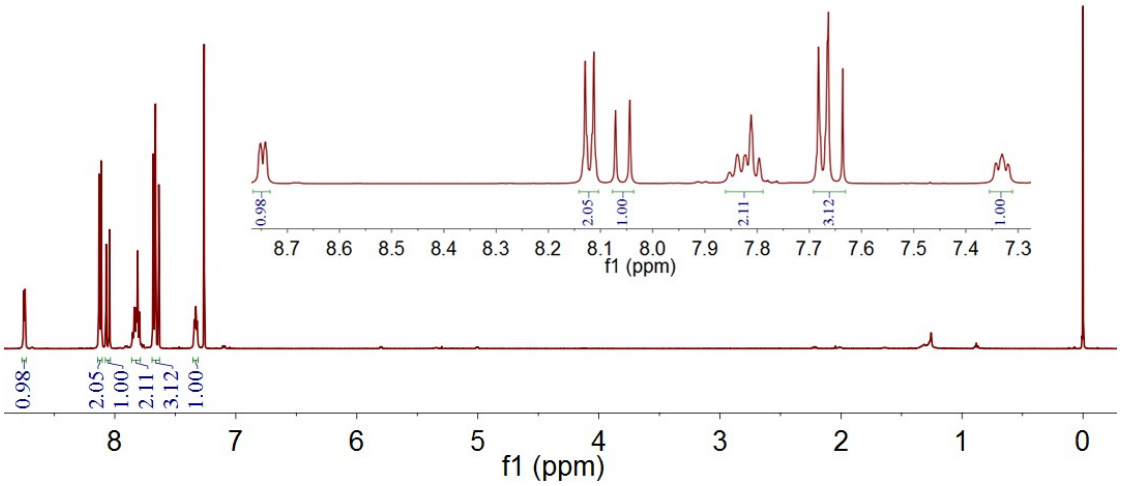

Fig S16. ^{1}H NMR spectrum of compound **1** in $CDCl_3$.

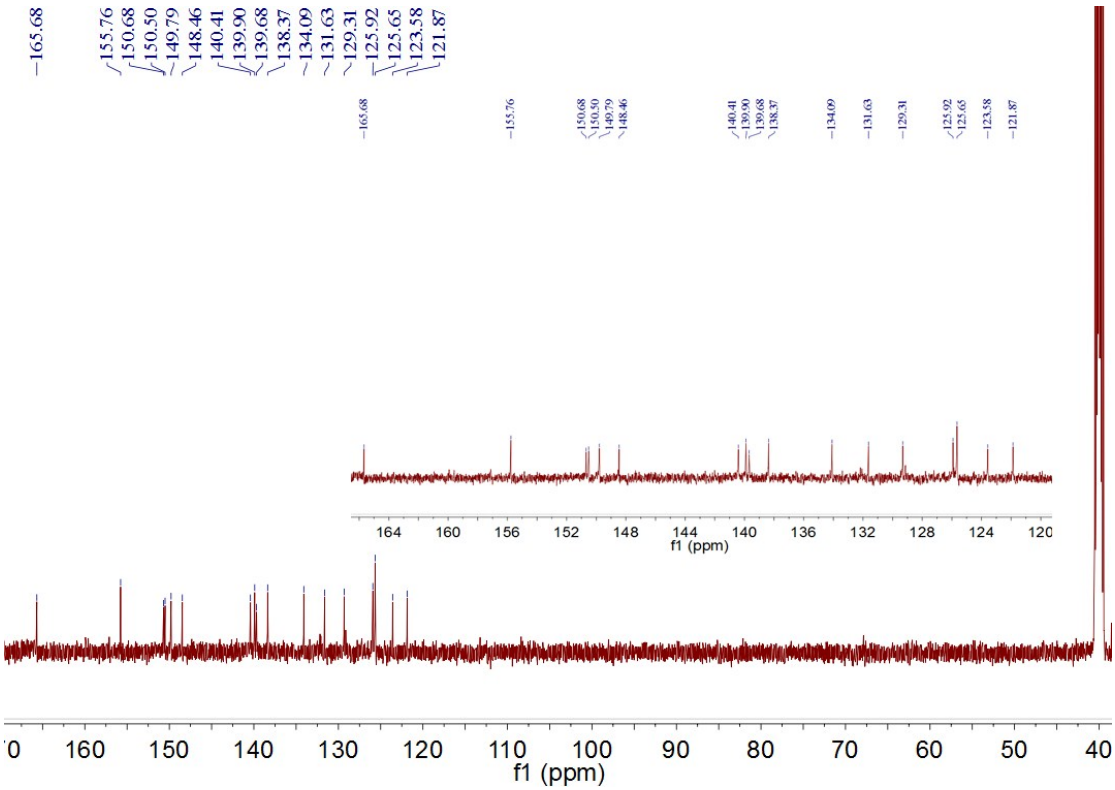

Fig S17. ^{13}C NMR spectrum of **Ir1** in DMSO.

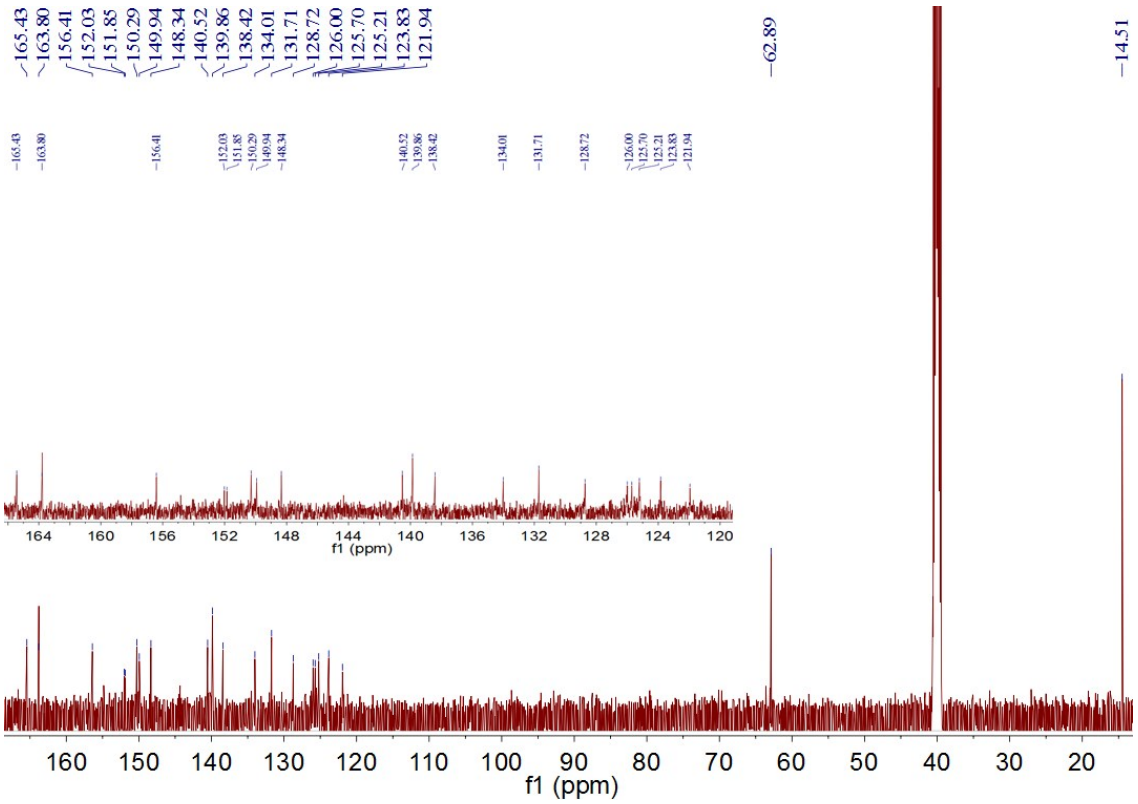

Fig S18. ^{13}C NMR spectrum of **Ir2** in DMSO-d_6.

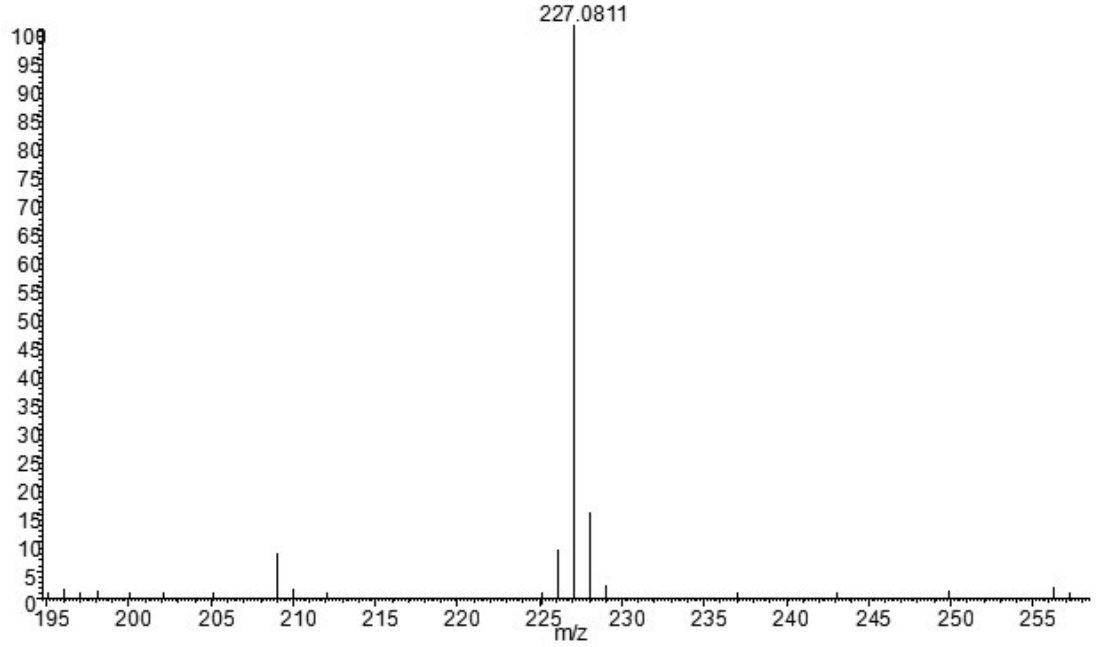

Fig S19. HRMS spectrum of compound **1** in CH_3CN.