Supporting Information

Photo induced NO release of $[Fe_2(\mu\text{-}SL)_2(NO)_4]$ complexes and their protein adducts: insights from structure, cytotoxicity and photodynamic studies

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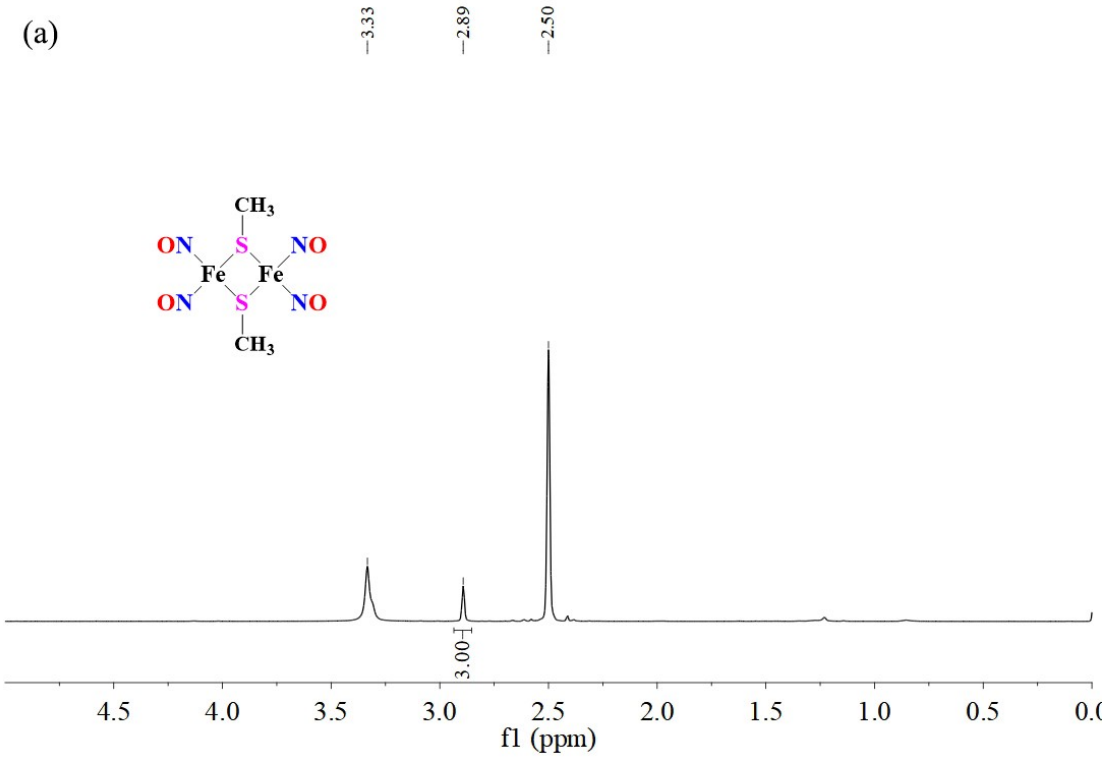
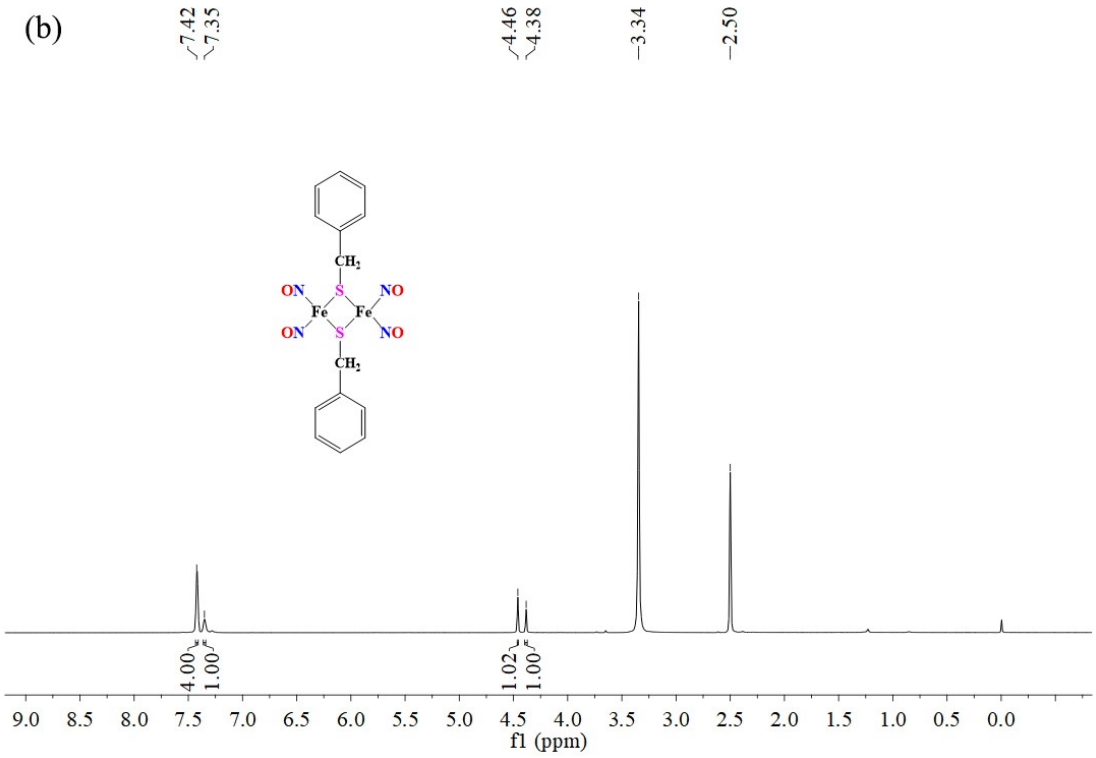
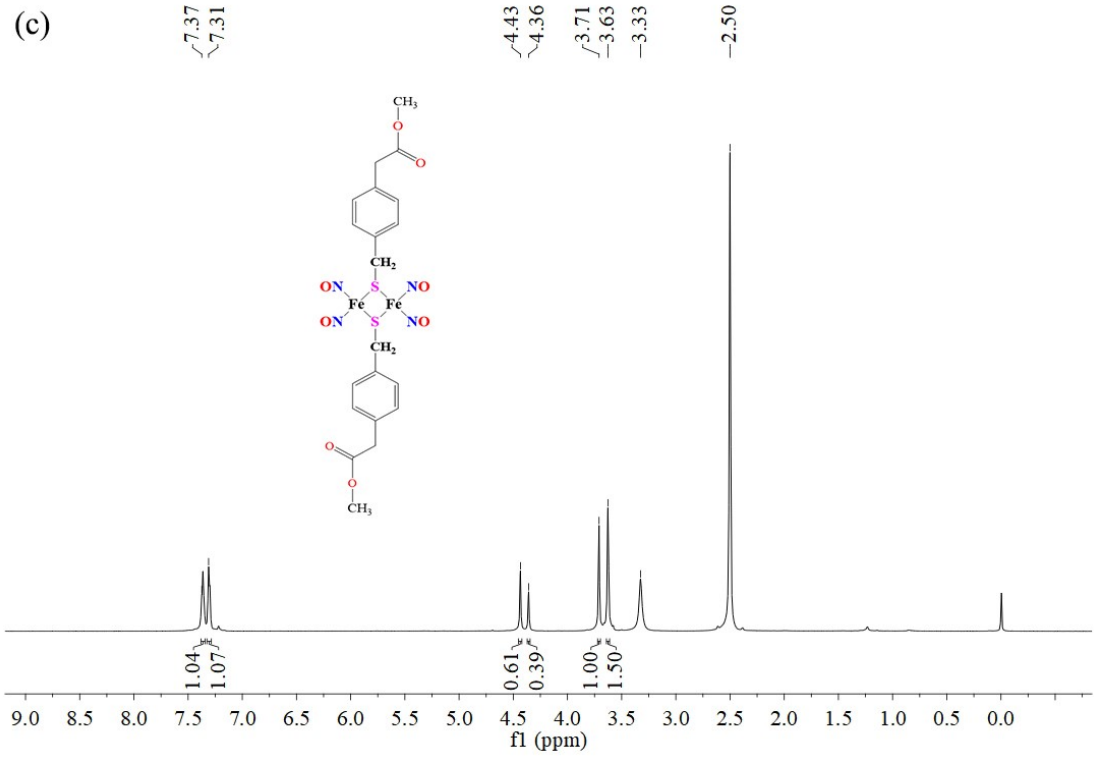
(a)


3.33
2.89
2.50
CH3
ON
S
NO
Fe
Fe
ON
S
NO
CH3
3.00
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

(b)


7.42
7.35
4.46
4.38
3.34
2.50
CH2
ON
S
NO
Fe
Fe
ON
S
NO
CH2
4.00
1.00
1.02
1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

(c)


7.37
7.31
4.43
4.36
3.71
3.63
3.33
2.50
CH3
O
O
CH2
ON
S
NO
Fe
Fe
ON
S
NO
CH2
O
O
CH3
1.04
1.07
0.61
0.39
1.00
1.50
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

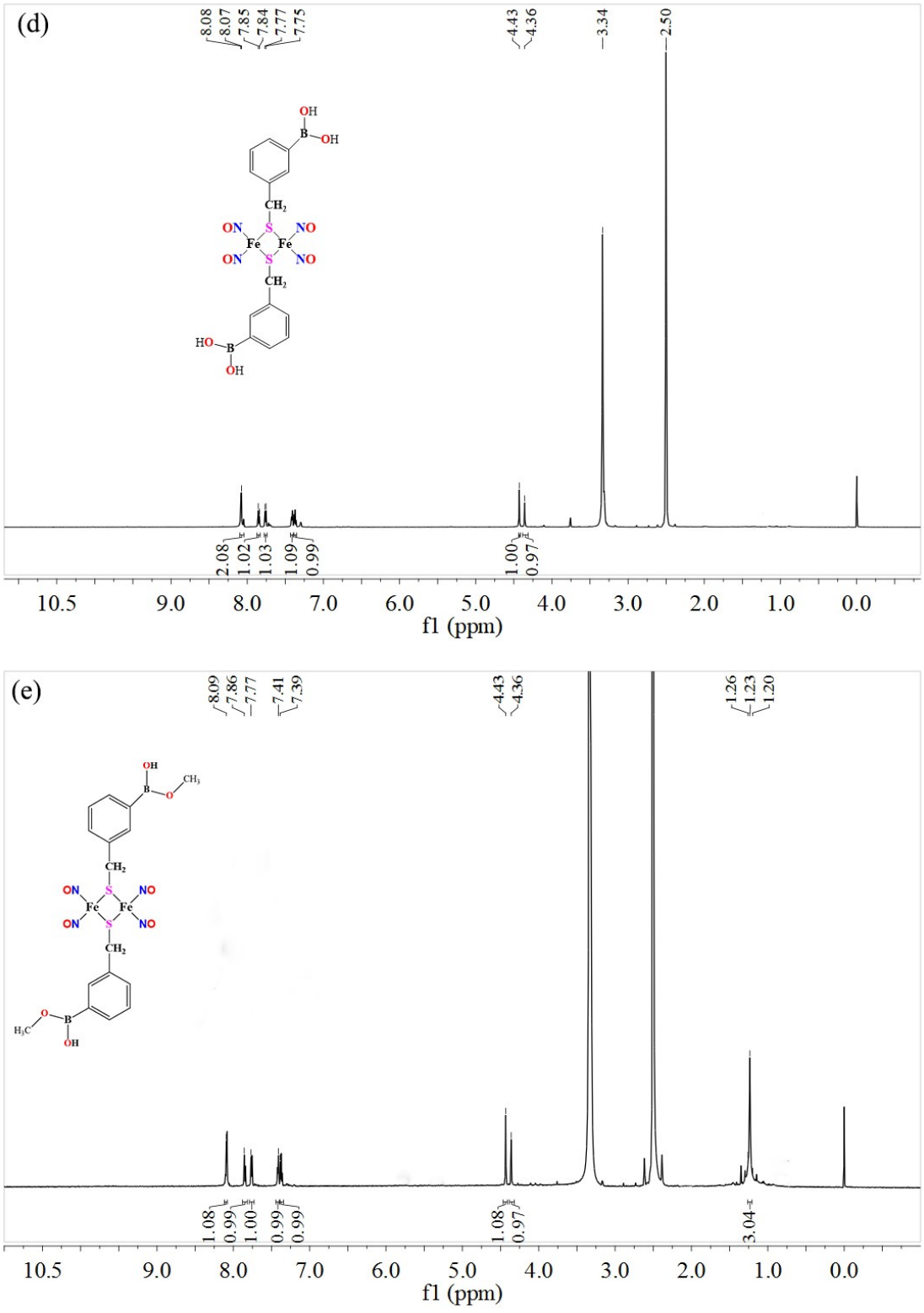
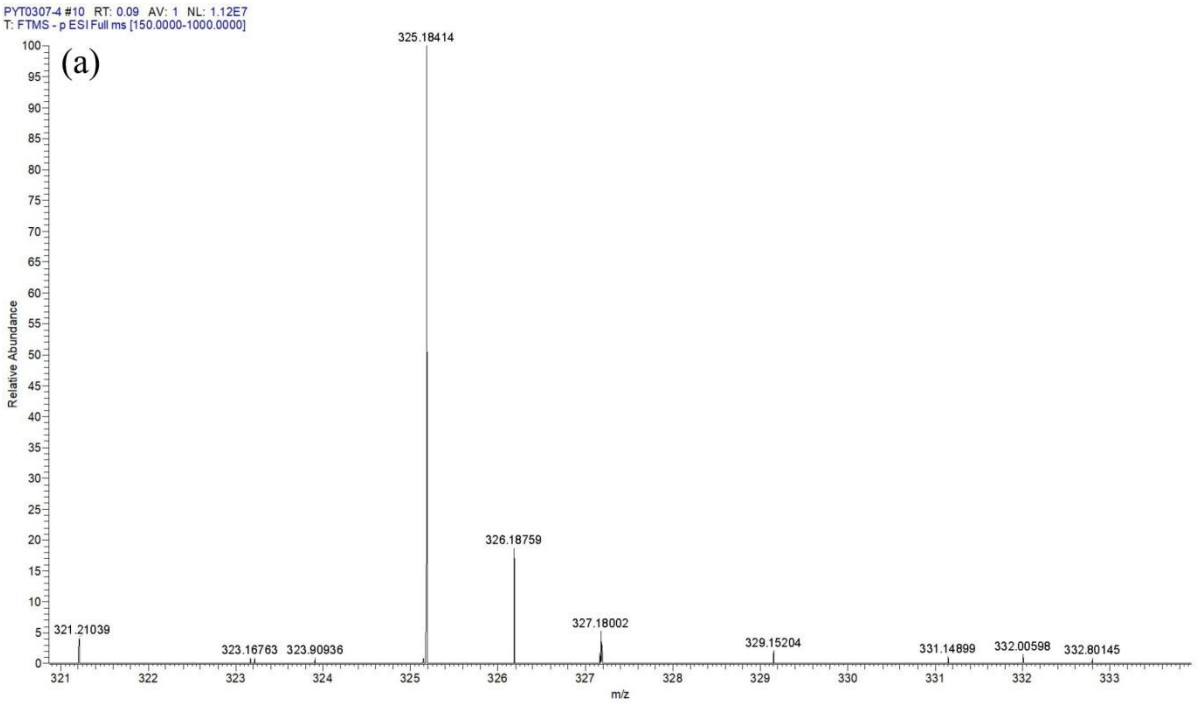


Fig. S1. ^{1}H NMR spectrum (600 MHz) of the four complexes: (a) complex **1**, (b) complex **2**, (c) complex **3**, (d) complex **4**, (e) crystallized complexes **4**.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(a)
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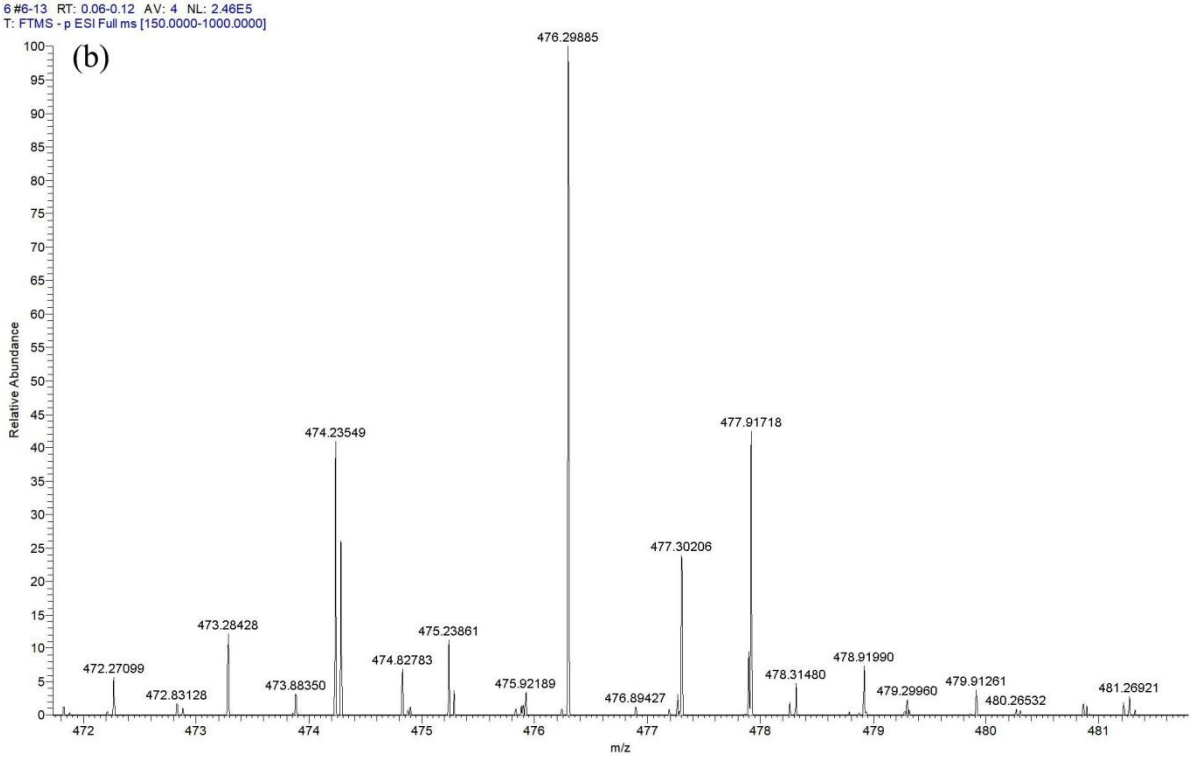
326.18759
321.21039
323.16763
323.90936
327.18002
329.15204
331.14899
332.00598
332.80145
Relative Abundance
m/z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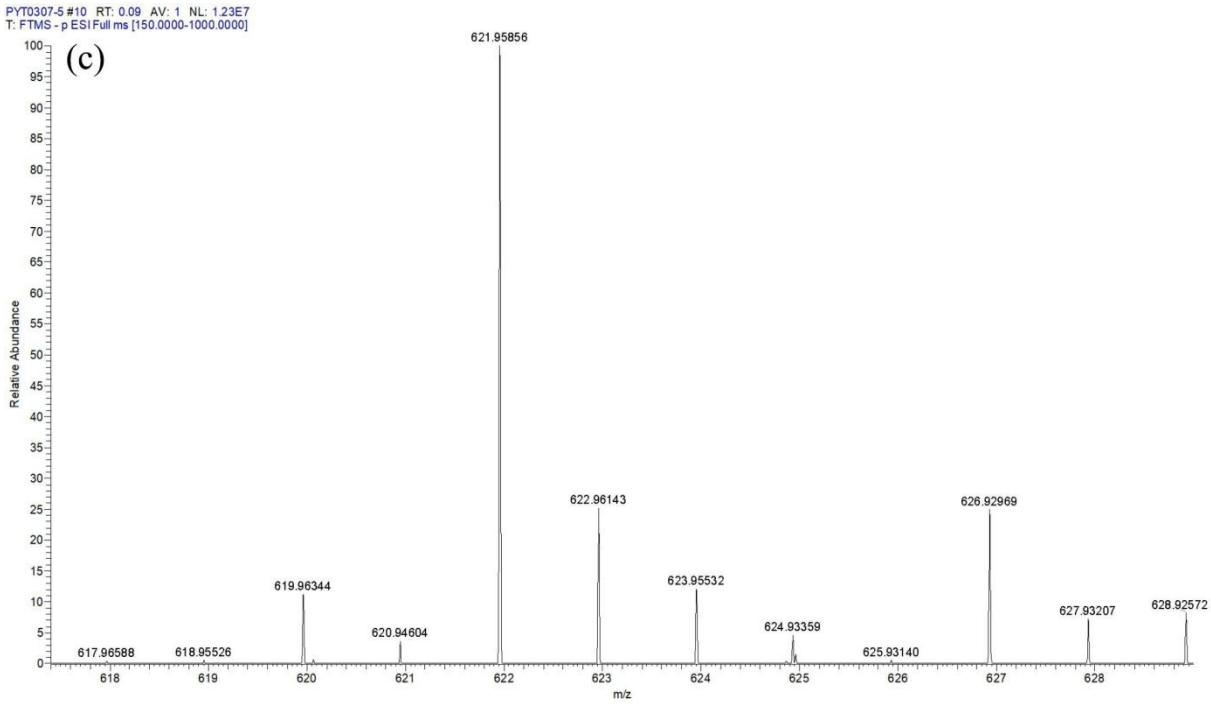
(b)
476.29885
474.23549
477.91718
477.30206
473.28428
475.23861
474.82783
472.27099
472.83128
473.88350
475.92189
476.89427
478.91990
478.31480
479.29960
479.91261
480.26532
481.26921
Relative Abundance
m/z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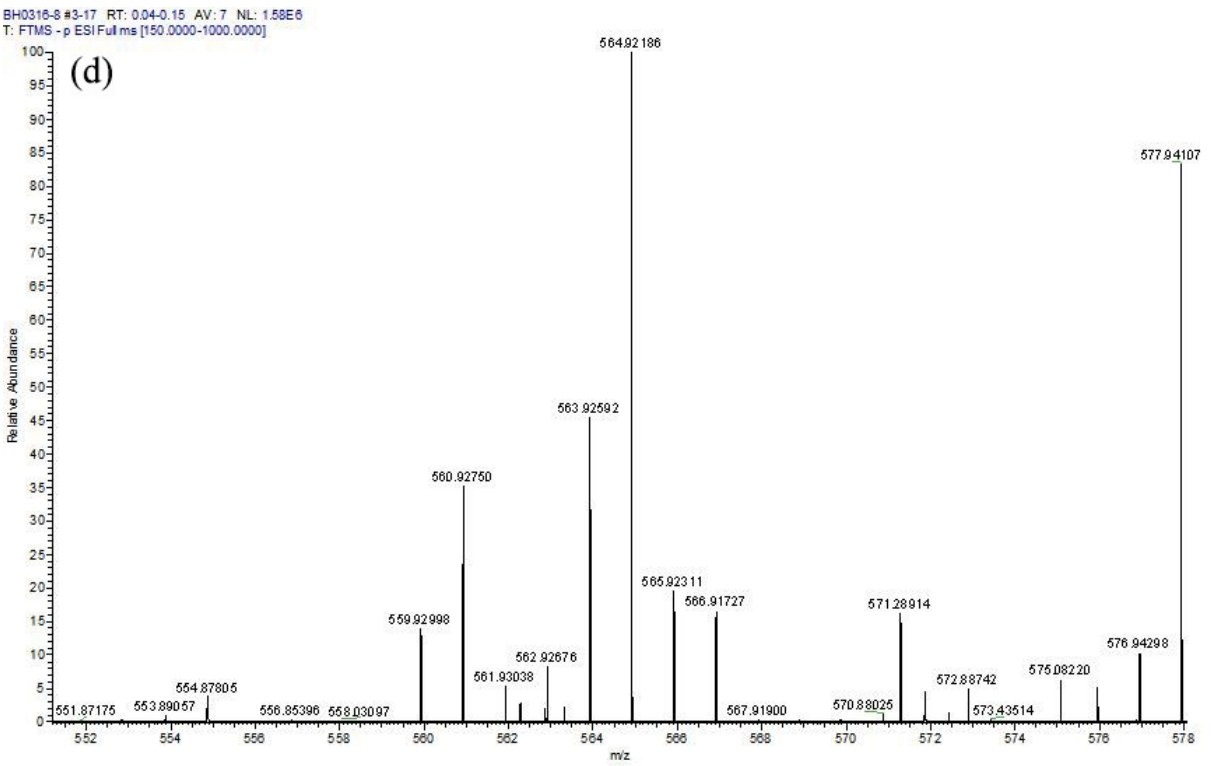
(c)
621.95856
622.96143
626.92969
619.96344
623.95532
627.93207
628.92572
620.94604
624.93359
617.96588
618.95526
625.93140
Relative Abundance
m/z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(d)
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577.94107
563.92592
560.92750
565.92311
566.91727
571.28914
559.92998
576.94298
562.92676
561.93038
572.88742
575.08220
554.87805
551.87175
553.89057
556.85396
558.03097
567.91900
570.88025
573.43514
Relative Abundance
m/z

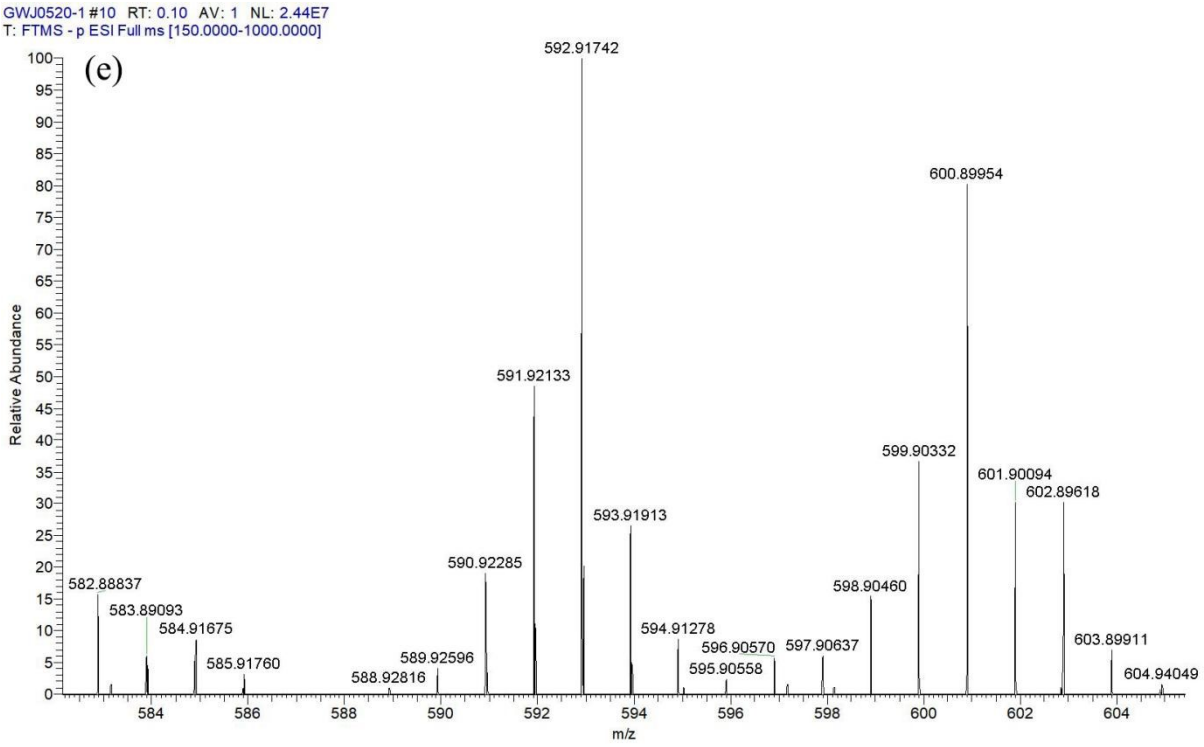

Fig. S2. ESI-MS spectra of the four complexes in CH_3OH: (a) complex **1**, (b) complex **2**, (c) complex **3**, (d) complex **4**, (e) crystallized complexes **4**.

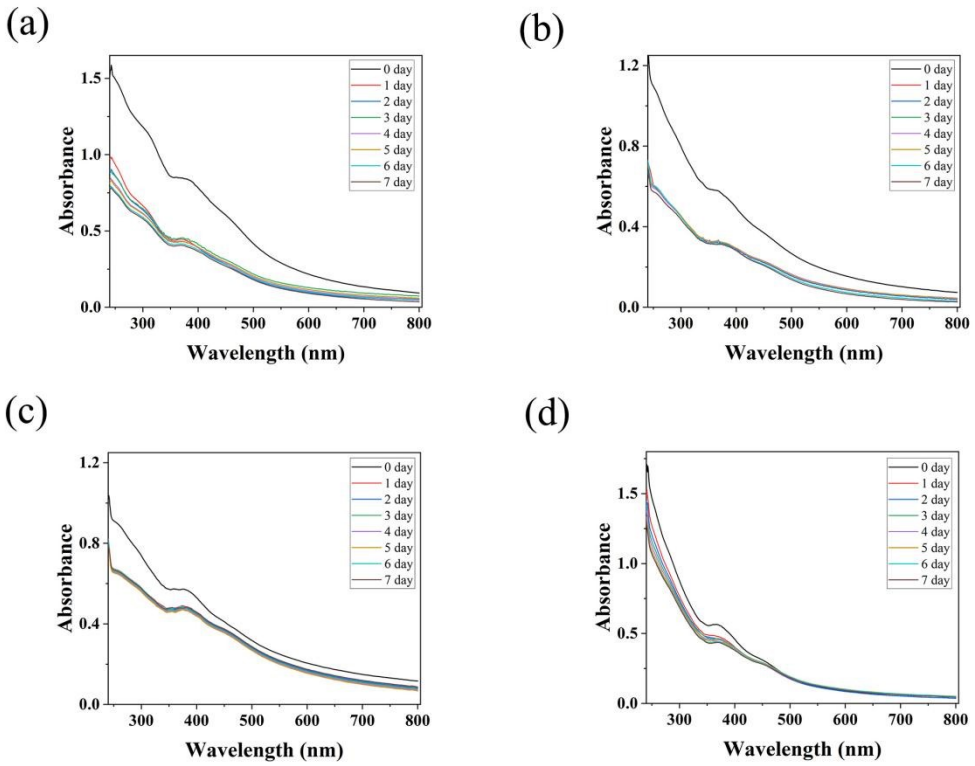

Fig. S3. UV-vis spectra of complexes **1–4** in PBS buffer (5% DMSO) for 7 days: (a) complex **1**, (b) complex **2**, (c) complex **3**, and (d) complex **4**.

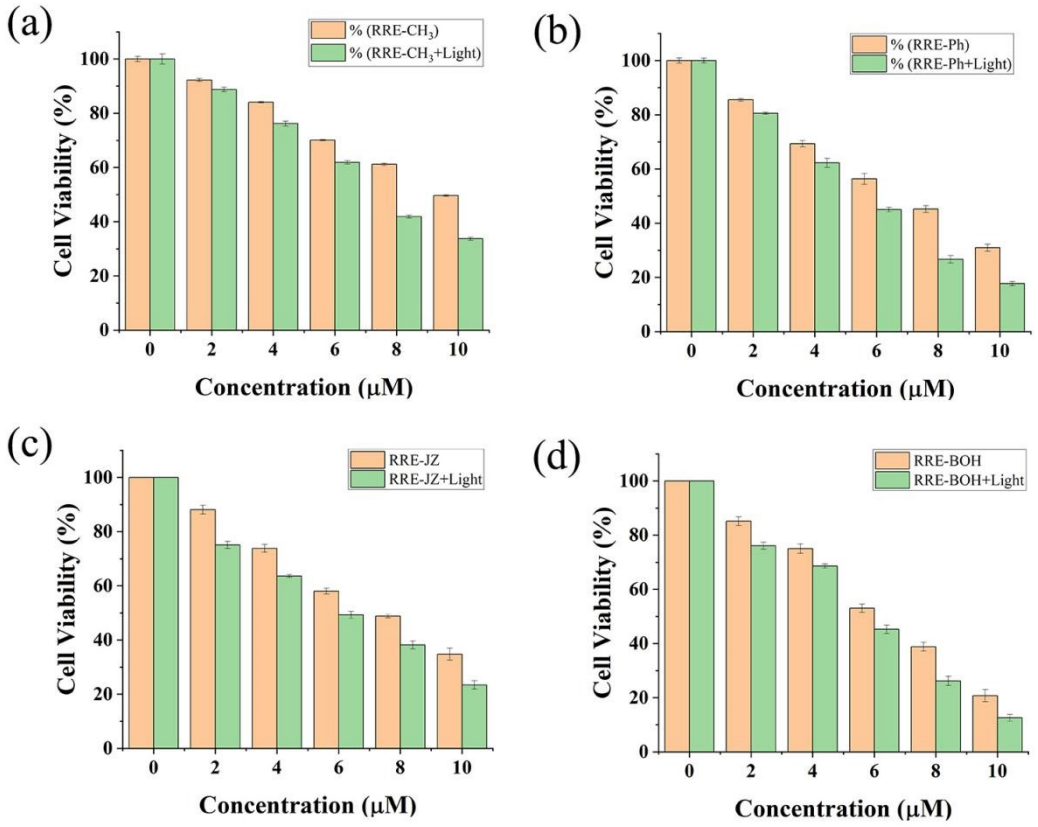

Fig. S4. Cell viability of HeLa cells incubated with complexes **1–4** at various concentrations for 24 h under dark and light irradiation: (a) complex **1**, (b) complex **2**, (c) complex **3**, and (d) complex **4**.

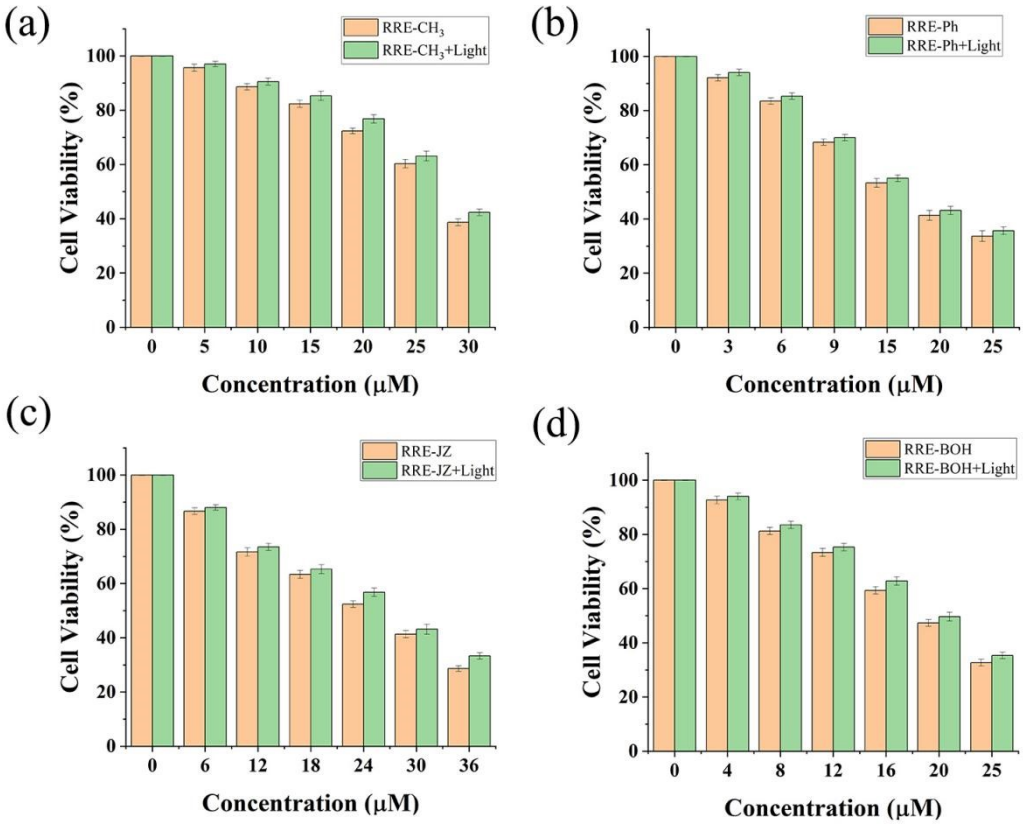

Fig. S5. Cell viability of HL7702 cells incubated with complexes **1–4** at various concentrations for 24 h under dark and light irradiation: (a) complex **1**, (b) complex **2**, (c) complex **3**, and (d) complex **4**.

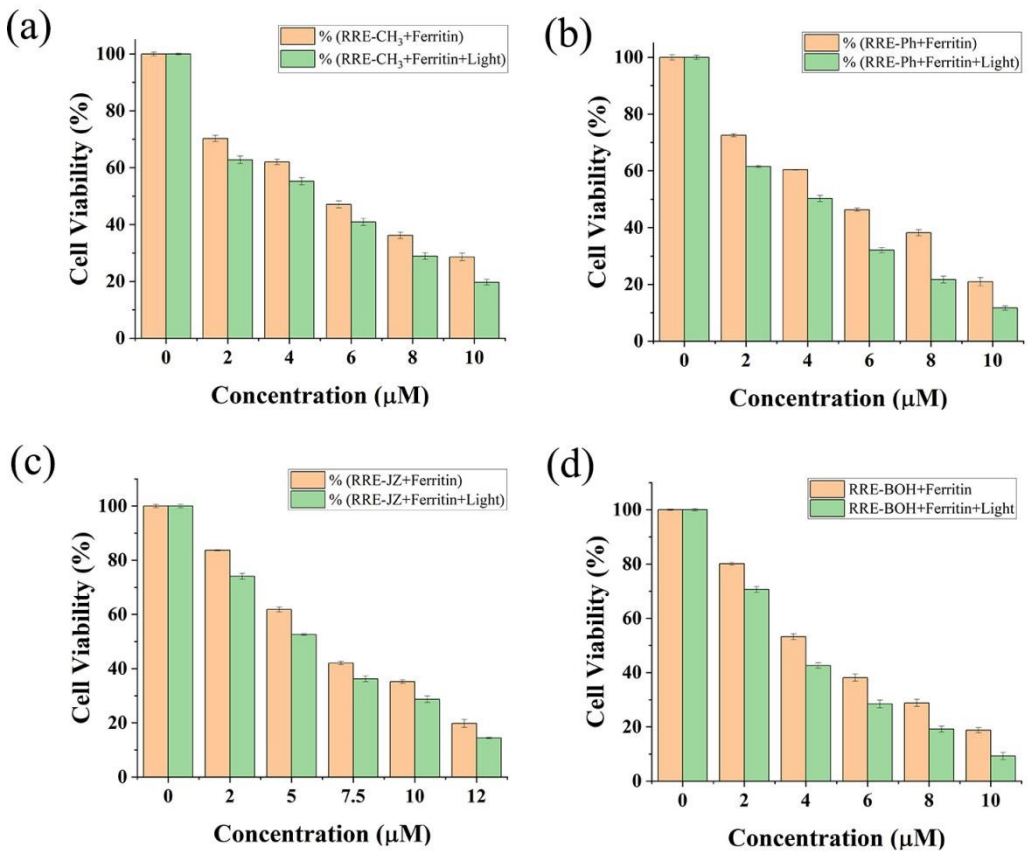

Fig. S6. Cell viability of HeLa cells incubated with ferritin complexes **1–4** adducts at various concentrations for 24 h under dark and light irradiation: (a) adduct **1**, (b) adduct **2**, (c) adduct **3**, and (d) adduct **4**.

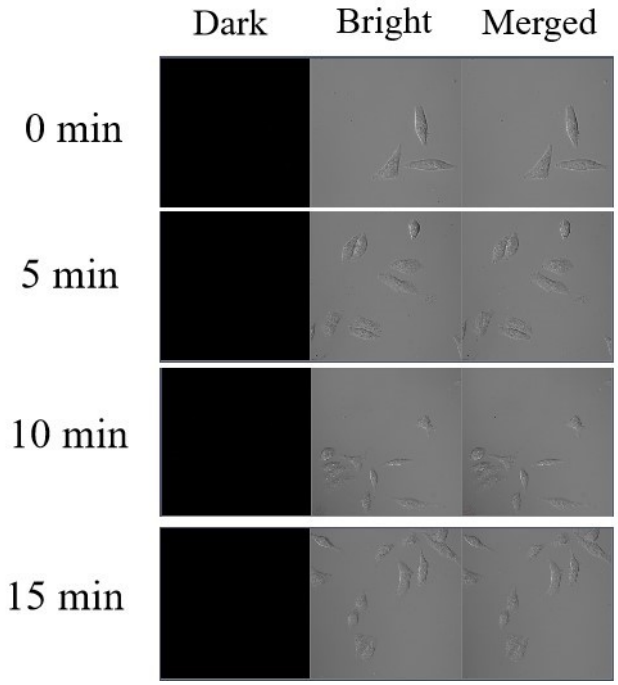

Fig. S7. Red confocal microscopy images of HeLa cells treated with DAX-J2 for 0, 5,10 and 15 min under an LED light (420 nm). Excitation was performed with a 561 nm laser, and the emission wavelength was recorded in the range of 579–701 nm.

Table S1. Crystallographic data and refinement statistics for the four nitrosyl iron-sulfur complexes.

	1	**2**	**3**	**4'**
Chemical formula	$C_2H_6Fe_2N_4O_4S_2$	$C_{14}H_{14}Fe_2N_4O_4S_2$	$C_{20}H_{22}Fe_2N_4O_8S_2$	$C_{16}H_{20}B_2Fe_2N_4O_8S_2$
Formula weight	325.92	478.11	622.23	593.80
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P*-1	$P2_1/c$	$C2/c$	$P2_1/c$
a (Å)	7.0639(4)	7.142(4)	35.2604 (13)	5.0645(2)
b (Å)	8.7633(8)	16.668(11)	5.0790 (2)	23.6415(8)
c (Å)	9.5289(8)	7.986(5)	16.1563 (6)	10.1545(4)
α (°)	89.048(7)	90	90	90
β (°)	68.641(7)	93.36(2)	115.6664 (11)	95.0247(10)
γ (°)	89.088(6)	90	90	90
V (Å^3)	549.25 (8)	949.1 (10)	2607.90 (17)	1211.15(8)
Z	4	2	4	2
Temperature (K)	293 K	298 K	273 K	298 K
DX (g cm^{-3})	1.971	1.673	1.585	1.628
F (000)	324.0	484.0	1272.0	604.0
Theta range (°)	4.6-28.9°	2.8-27.6°	2.9–28.3°	2.7-28.5°
***R* [$F^2 > 2\ \sigma(F_2)$]**	0.040	0.052	0.028	0.029
w*R* (F^2)	0.119	0.093	0.076	0.074
S	1.07	1.01	1.02	1.05
Δ > max, Δ > min (e Å^{-3})	0.66, -0.61	0.42, -0.40	0.31, -0.28	0.27, -0.22

Table S2. Selected bond distances (Å) and bond angles (°) of complex **1**.

Fe1—N1	1.669 (3)	O1—N1	1.162 (4)
Fe1—N2	1.666 (4)	O2—N2	1.155 (5)
Fe1—S1	2.2513 (12)	S1—C1	1.825 (4)
O1—N1—Fe1	169.7 (4)	O2—N2—Fe1	171.0 (3)
Fe1—S1—Fe1^{i}	73.54 (4)	S1—Fe1—S1^{i}	106.46 (4)

Table S3. Selected bond distances (Å) and bond angles (°) of complex **2**.

Fe1—N1	1.665 (3)	O1—N1	1.169 (3)
Fe1—N2	1.666 (3)	O2—N2	1.161 (4)
Fe1—S1	2.2567 (16)	S1—C1	1.839 (3)
O1—N1—Fe1	169.5 (3)	O2—N2—Fe1	167.6 (3)
Fe1—S1—Fe1^{i}	73.95 (4)	S1—Fe1—S1^{i}	106.05 (4)

Table S4. Selected bond distances (Å) and bond angles (°) of complex **3**.

Fe1—N1	1.6640 (19)	O1—N1	1.161 (2)
Fe1—N2	1.6649 (18)	O2—N2	1.157 (2)
Fe1—S1	2.2485 (6)	S1—C1	1.845 (2)
O1—N1—Fe1	172.40 (18)	O2—N2—Fe1	171.9 (2)
Fe1—S1—Fe1^{i}	73.018 (19)	S1—Fe1—S1^{i}	106.984 (19)

Table S5. Selected bond distances (Å) and bond angles (°) of complex **4'**.

Fe1—N1	1.6653 (16)	O1—N1	1.161 (2)
Fe1—N2	1.6703 (17)	O2—N2	1.155 (2)
Fe1—S1	2.2546 (5)	S1—C1	1.8444 (18)
O1—N1—Fe1	170.52 (18)	O2—N2—Fe1	170.3 (2)
Fe1—S1—Fe1^{i}	73.188 (15)	S1—Fe1—S1^{i}	106.810 (15)

Table S6. In vitro cytotoxic IC_{50} values (μM) for complexes 1–4 and their Ferritin complex adducts against HeLa cells under dark and light irradiation.

Adducts		**1**	**2**	**3**	**4**
HeLa	Light (-)	5.03 ± 0.25	4.87 ± 0.41	6.13 ± 0.19	4.46 ± 0.65
	Light (+)	4.02 ± 0.32	3.25 ± 0.26	4.75 ± 0.39	3.36 ± 0.72