Supporting Information

for

A reaction-type receptor for the multi-feature detection of Hg^{2+} in water and living cells †

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Contents

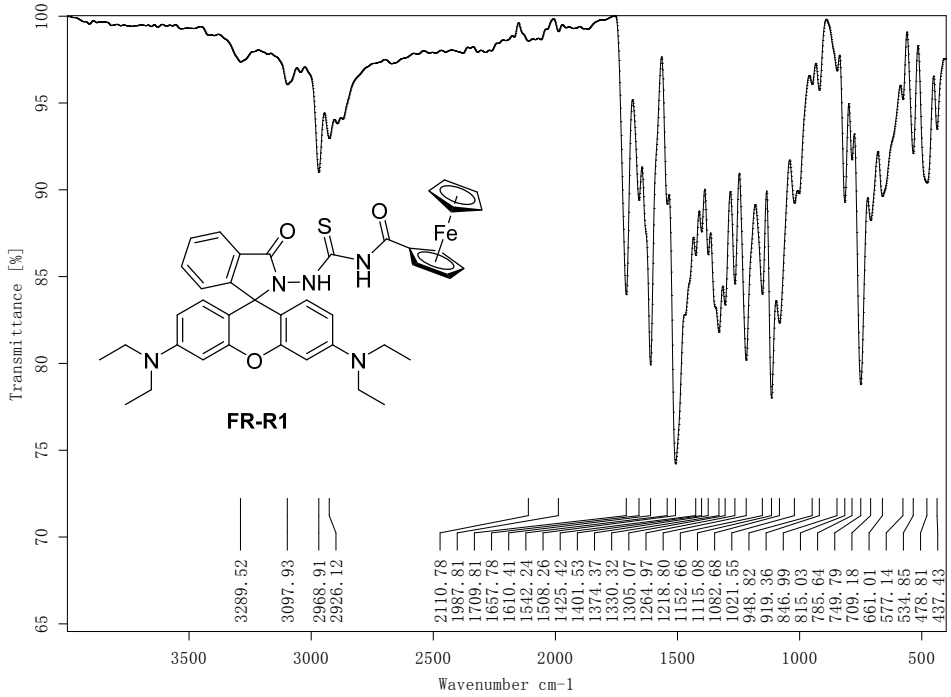


Fig. S1. FT-IR spectrum of **FR-R1**.

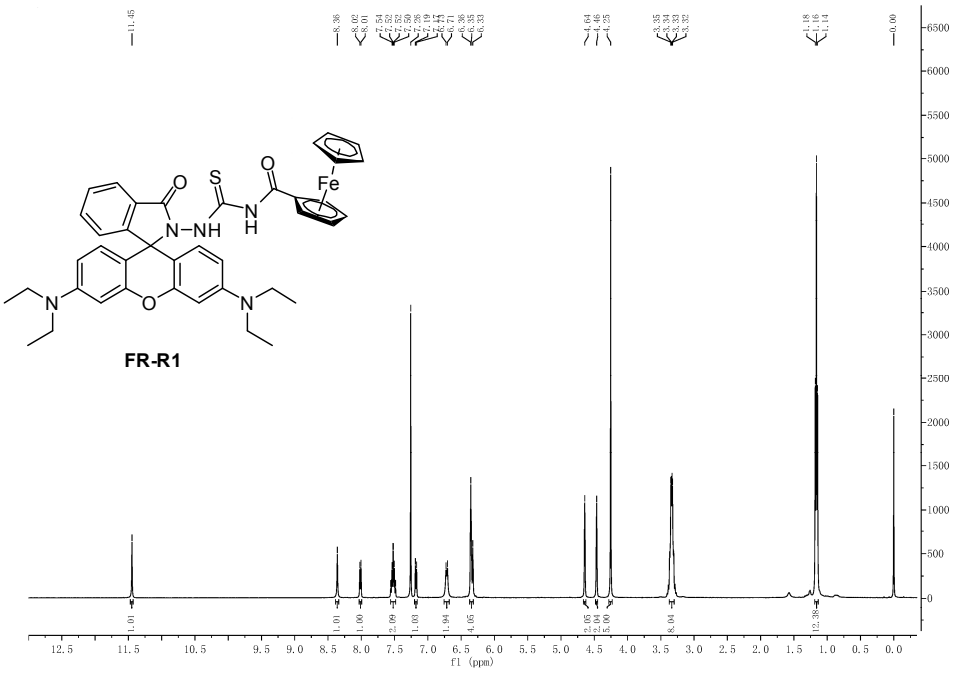


Fig. S2. ^{1}H NMR spectrum of **FR-R1** in $CDCl_3$.

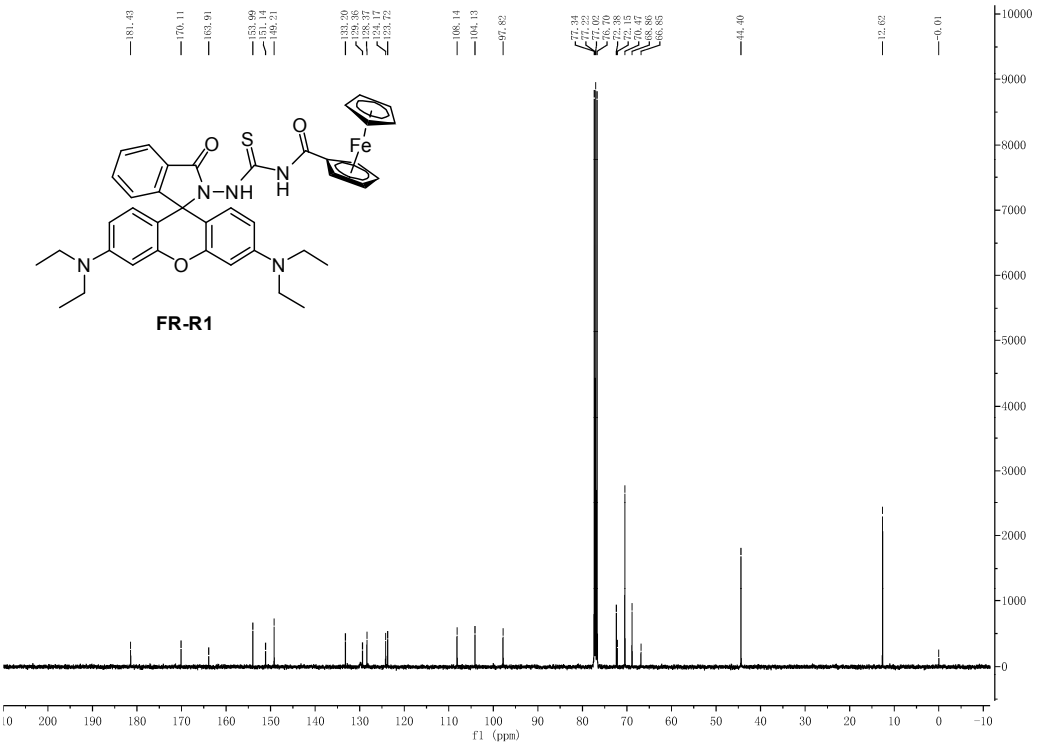


Fig. S3. ^{13}C NMR spectrum of **FR-R1** in $CDCl_3$.

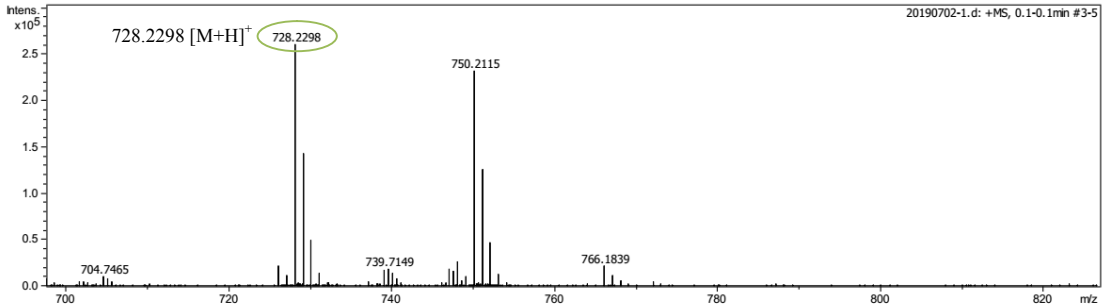


Fig. S4. HR-MS of **FR-R1**.

Table S1. Crystallographic and refinement data of **FR-R1**

Formula	$C_{40}H_{40}FeN_5O_3S{\cdot}CHCl_3$
*M*r	846.05
Temperature	150.00(10) K
Wavelength	1.54184 Å
Crystal system	Orthorhombic
Space group	$Pca2_1$
Unit cell dimensions	a = 30.8908(12) Å α = 90.00°
	b = 9.6600(3) Å β = 90.00°
	c = 12.8697(5) Å γ = 90.00°
Volume	3840.4(2) $Å^3$
Z	4
Density	1.463 mg/m^3
Absorption coefficient	5.956 mm^{-1}
F(000)	1756
Crystal size	0.26 x 0.19 x 0.09 mm
Theta range for data collection	4.47 to 70.95°
Limiting indices	-32<=h<=37, -11<=k<=8, -9<=l<=15
Reflections collected / unique	9435 / 4224 [R(int) = 0.040]
Completeness to theta = 25.68	99.8 %
Absorption correction	Muti-scan
Max. and min. transmission	1.00000 and 0.43673
Refinement method	Full-matrix least-squares on F^2
Data/ restraints /parameters	4918/ 1 / 491
Goodness-of-fit on F^2	1.029
Final R indices [I>2sigma(I)]	R_1 = 0.0728, wR_2 = 0. 2047
R indices (all data)	R_1 = 0.0864, wR_2 = 0. 1875
Largest diff. peak and hole	0.787 and -0.867 e. $Å^{-3}$

Table S2. Selected bond lengths (Å) and angles (°) for **FR-R1**

C10—C11	1.459(12)	C11—N5	1.385(10)
C11—O3	1.220(11)	C12—N5	1.413(10)
C12—N1	1.356(10)	C13—C14	1.488(11)
C12—S1	1.638(8)	C13—O4	1.230(9)
C13—N2	1.354(10)	C14—C19	1.386(11)
C14—C15	1.371(12)	C15—C16	1.379(12)
C16—C17	1.399(12)	C17—C18	1.386(12)
C18—C19	1.384(11)	C20—C21	1.497(10)
C19—C20	1.521(11)	C20—N2	1.525(8)
C20—C32	1.503(10)	C21—C26	1.401(10)
C21—C22	1.386(10)	C22—O1	1.387(8)
C22—C23	1.382(10)	C23—C24	1.392(10)
C24—C25	1.409(10)	C24—N3	1.376(10)
C25—C26	1.383(11)	C27—N3	1.457(10)
C29—N3	1.443(10)	C31—C32	1.380(11)
C31—O1	1.378(9)	C31—C36	1.401(10)
C32—C33	1.396(11)	C33—C34	1.357(12)
C34—C35	1.405(12)	C35—C36	1.387(11)
C35—N4	1.362(10)	C39—N4	1.468(11)
C37—N4	1.425(14)	N1—N2	1.377(9)
C9—C10—C11	130.9(7)	O3—C11—N5	122.1(8)
C11—C10—C6	121.5(8)	N1—C12—N5	112.5(7)
O3—C11—C10	121.4(8)	N5—C12—S1	120.8(6)
N5—C11—C10	116.4(7)	O4—C13—C14	127.5(8)
N1—C12—S1	126.7(6)	C15—C14—C13	129.4(8)
N2—C13—C14	106.2(6)	C19—C14—C13	108.0(7)
O4—C13—N2	126.3(8)	C14—C15—C16	117.7(8)
C15—C14—C19	122.4(8)	C18—C17—C16	121.4(8)

C15—C16—C17	120.4(8)	C18—C19—C14	120.3(8)
C19—C18—C17	117.5(8)	C19—C20—N2	97.9(6)
C14—C19—C20	112.3(7)	C21—C20—C32	111.5(6)
C18—C19—C20	127.4(7)	C32—C20—C19	110.1(6)
C21—C20—C19	114.0(6)	C22—C21—C20	121.7(6)
C21—C20—N2	112.2(6)	C26—C21—C20	122.7(7)
C32—C20—N2	110.3(6)	C23—C22—C21	123.2(6)
C22—C21—C26	115.4(7)	C21—C22—O1	122.3(6)
C23—C22—O1	114.4(6)	N3—C24—C23	121.0(7)
C22—C23—C24	121.2(7)	C23—C24—C25	116.6(7)
N3—C24—C25	122.4(6)	C25—C26—C21	122.4(7)
C26—C25—C24	121.1(6)	C32—C31—C36	122.3(7)
O1—C31—C32	123.2(6)	O1—C31—C36	114.5(7)
C31—C32—C20	121.3(7)	C31—C32—C33	115.6(7)
C33—C32—C20	123.1(7)	C34—C33—C32	123.4(8)
C33—C34—C35	120.9(8)	C36—C35—C34	116.9(7)
N4—C35—C34	120.8(8)	N4—C35—C36	122.2(8)
C35—C36—C31	120.9(8)	C11—N5—C12	128.5(7)
C12—N1—N2	122.3(6)	C13—N2—N1	119.1(6)
C13—N2—C20	114.6(6)	C24—N3—C27	122.2(7)
N1—N2—C20	118.6(6)	C29—N3—C27	116.7(7)
C24—N3—C29	120.6(6)	C35—N4—C39	120.9(8)
C35—N4—C37	121.5(8)	C31—O1—C22	118.5(6)
C37—N4—C39	117.4(7)		

Table S3. Hydrogen bond geometry (Å, º) for **FR-R1**

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(D–H···A)
N5–H5A···O4^{i}	0.86	2.29	3.132(2)	167.7
C9–H9···O4^{i}	0.98	2.19	3.111(2)	155.6
C25–H25···O3^{ii}	0.93	2.66	3.576(9)	170.9
C28–H28A···*Cg*1^{ii}	0.96	3.24	3.834(2)	121.6
C37–H37···C29^{iii}	0.93	2.71	3.591(16)	157.9
C3–H3···*Cg*2^{iv}	0.98	2.69	3.644(2)	165.3
C2–H2···Cl1^{v}	0.98	2.72	3.502(2)	137.4
C41–H41···S^{v}	0.98	2.81	3.653(12)	144.1
C41–Cl2···*Cg*3^{v}	1.75	3.36	4.654(12)	128.5

Symmetry codes: (i) 0.5 - x, y, 0.5 + z; (ii) x, 1 + y, z; (iii) x, -1 + y, z; (iv) 0.5 - x, -1 + y, 0.5 + z; (v) 0.5 - x, -1 + y, -0.5 + z. *Cg*1 and *Cg*2 are the centroids of C6−C10 and C14−C19 rings, respectively; *Cg*3 is the centroid of C21−C22 bond.

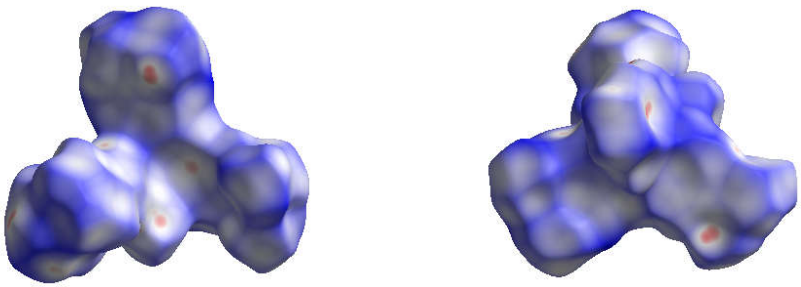


Fig. S5. Hirshfeld surfaces of **FR-R1** in different orientations.

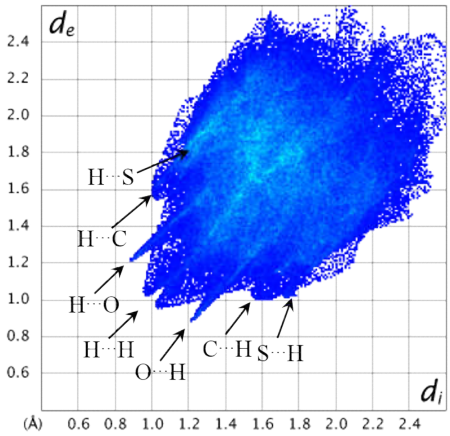


Fig. S6. Fingerprint plots of **FR-R1**.

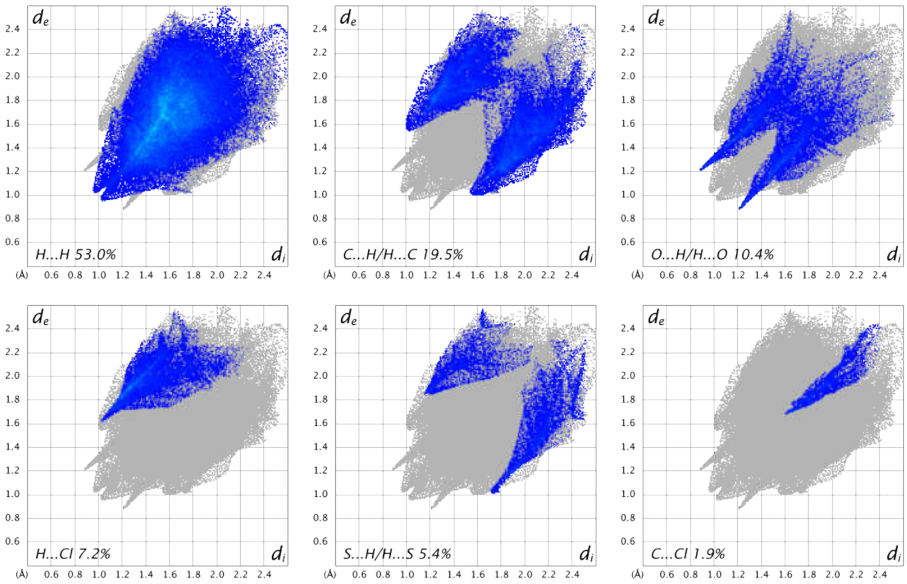


Fig. S7. Fingerprint plots of **FR-R1** resolved into the indicated intermolecular contacts.

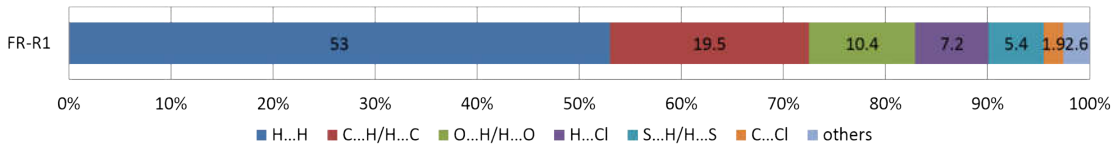


Fig. S8. Distribution (%) of intermolecular contacts from Hirshfeld surface analysis for **FR-R1**.

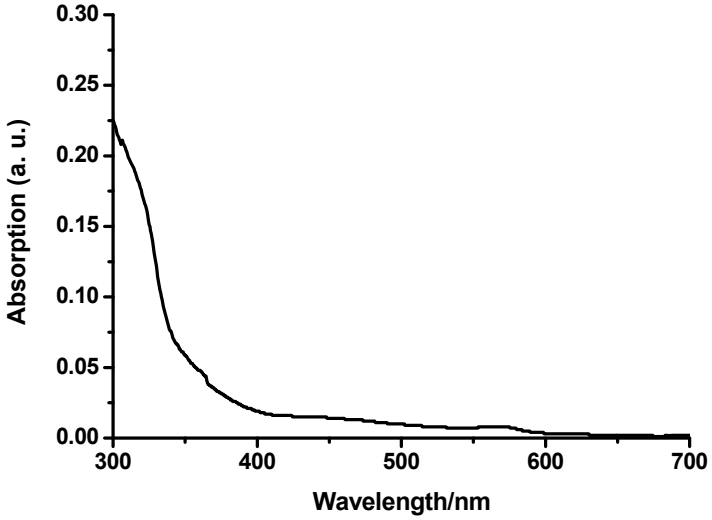


Fig. S9. UV-vis spectrum of **FR-R1** (10 μM) in H_2O/THF (4:1, v/v).

Table S4. UV-vis absorption of **FR-R1** (10 μM) at 569 nm in different solvents

Solvent	THF/H_2O (4:1, v/v)	THF	EtOAc	CH_2Cl_2	$CHCl_3$	DMSO	DMF
Abs.	0.013	0.011	0.006	0.008	0.009	0.116	0.155

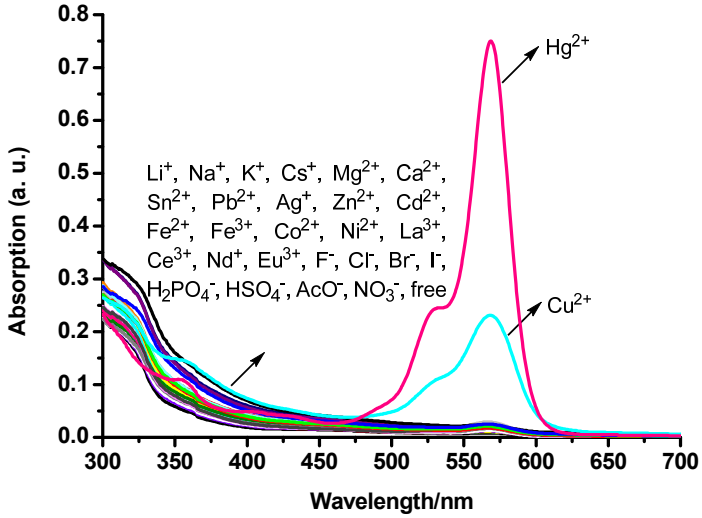


Fig. S10. UV-vis spectra of **FR-R1** (10 μM) in H_2O/THF (4:1, v/v) in the presence of various ions (50 μM).

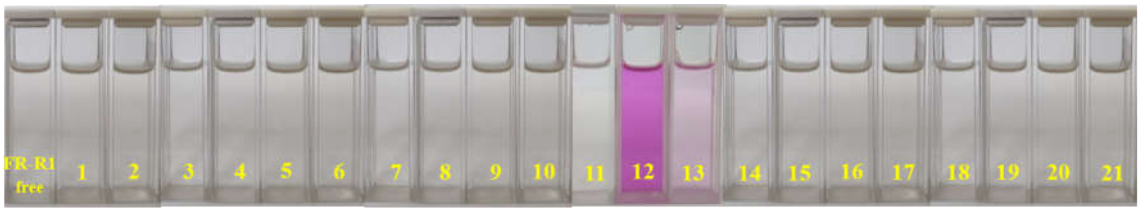


Fig. S11. Color changes of **FR-R1** (10 μM) in H_2O/THF (4:1, v/v) with different metal ions (50 μM) under visible light, where 1-21 are Li^+, Na^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}, Sn^{2+}, Pb^{2+}, Ag^+, Zn^{2+}, Cd^{2+}, Hg^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, La^{3+}, Ce^{3+}, Nd^+, and Eu^{3+}, respectively.

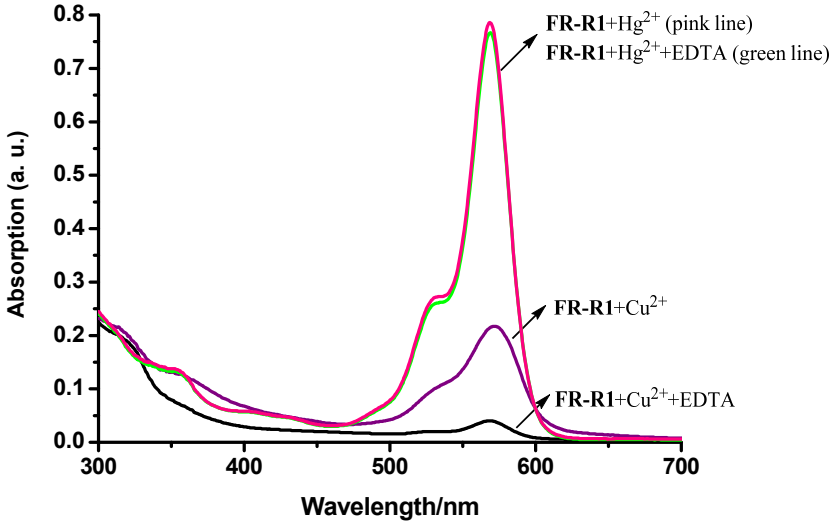


Fig. S12. Effects of EDTA (20 μM) on UV-vis spectra of **FR-R1** (10 μM) in H_2O/THF (4:1, v/v) with Hg^{2+} (10 μM) or Cu^{2+} (10 μM).

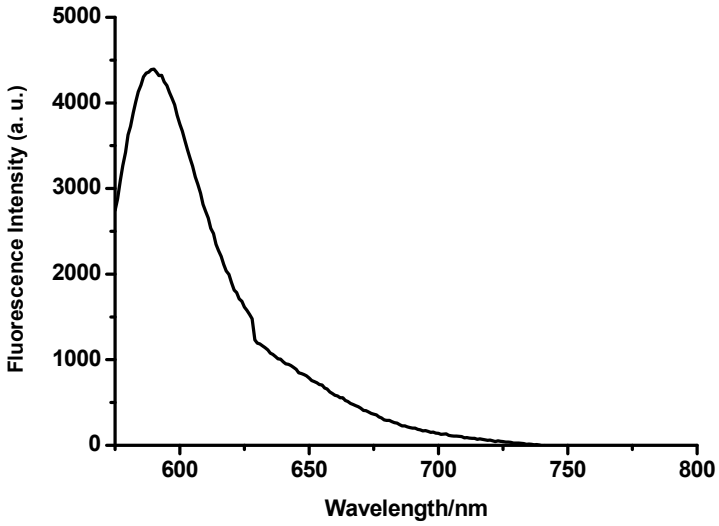


Fig. S13. Fluorescent spectrum of **FR-R1** (5 μM) in H_2O/THF (4:1, v/v). (λ_{ex} = 565 nm).

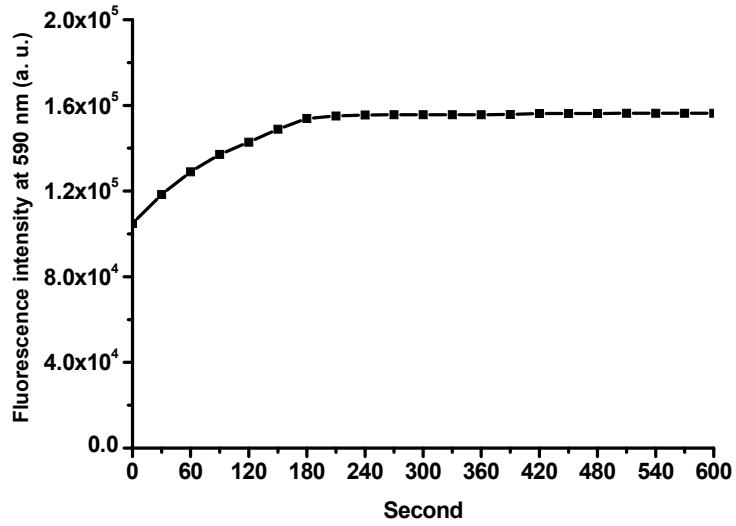


Fig. S14. Time response of **FR-R1** (5 μM) in H_2O/THF (4:1, v/v) to Hg^{2+} (10 μM).

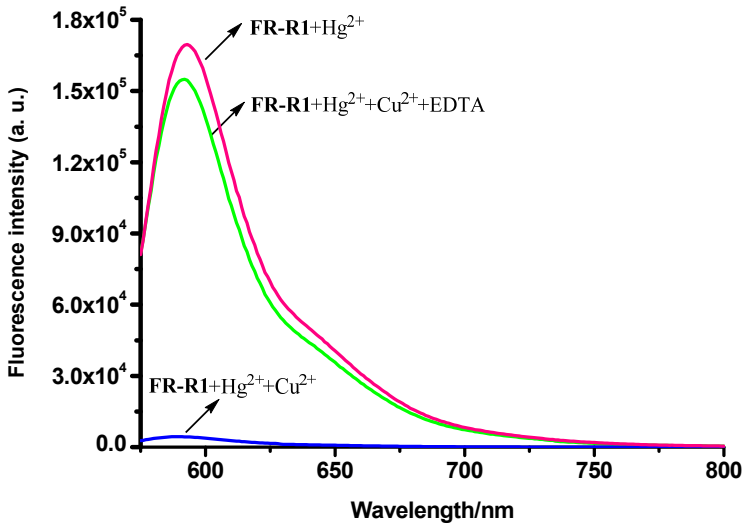


Fig. S15. Fluorescent spectra of **FR-R1** (5 μM) in H_2O/THF (4:1, v/v) with Hg^{2+} (5 μM) affected by Cu^{2+} (10 μM) or Cu^{2+} (10 μM) plus EDTA (20 μM). (λ_{ex} = 565 nm).

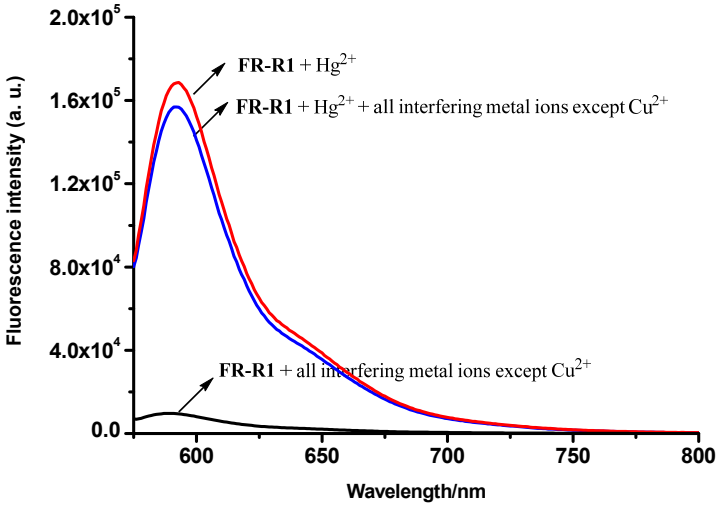


Fig. S16. Fluorescent spectra of **FR-R1** (5 μM) in H_2O/THF (4:1, v/v) with Hg^{2+} in the mixture of all interfering metal ions (except Cu^{2+}) at the same concentration of 5 μM. (λ_{ex} = 565 nm).

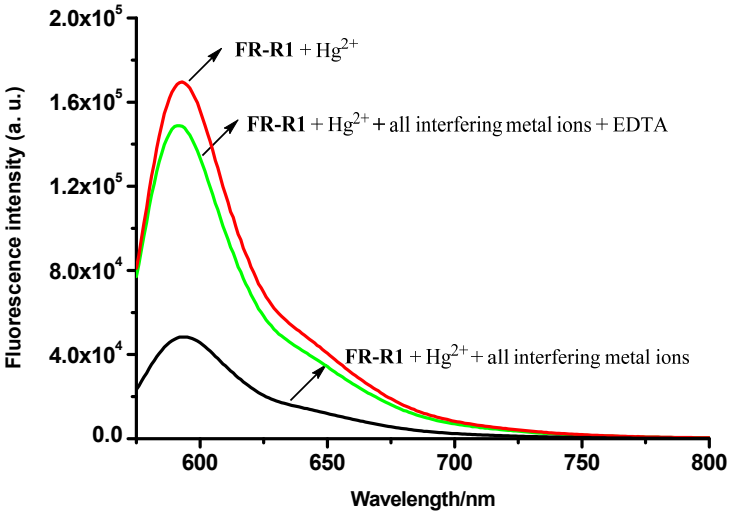


Fig. S17. Effects of EDTA (100 μM) on fluorescent spectra of **FR-R1** (5 μM) in H_2O/THF (4:1, v/v) with Hg^{2+} in the mixture of all interfering metal ions at the same concentration of 5 μM. (λ_{ex} = 565 nm).

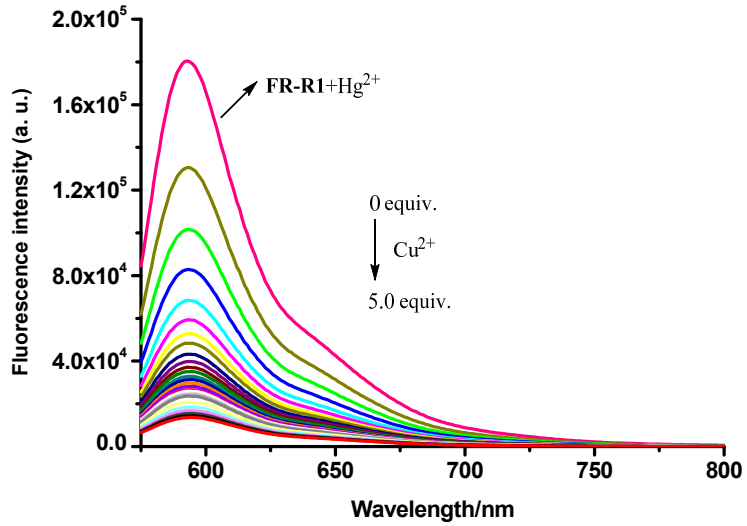


Fig. S18. Fluorescent spectra of **FR-R1** (5 μM) in H_2O/THF (4:1, v/v) with Hg^{2+} (5 μM) obtained during the titration of Cu^{2+} (0 to 5.0 equiv.). (λ_{ex} = 565 nm).

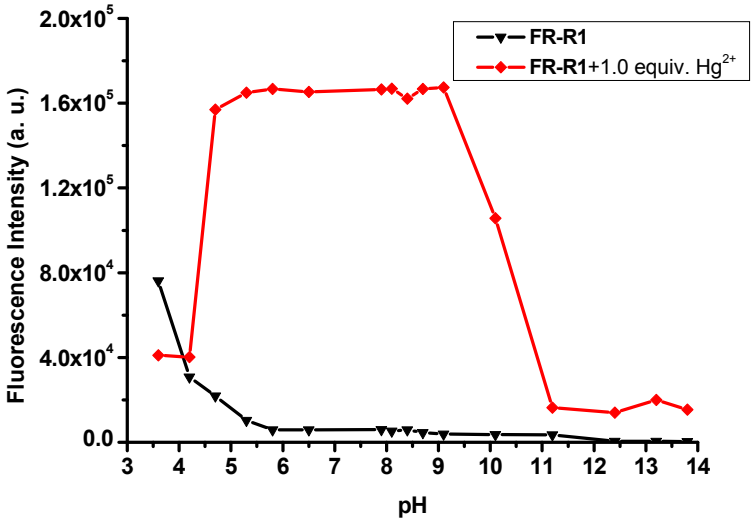


Fig. S19. Fluorescent intensity changes of **FR-R1** and [**FR-R1**+Hg^{2+}] in various pH values. pH was adjusted with 0.1 M HCl and 0.1 M NaOH aqueous solutions, λ_{ex} = 565 nm, λ_{em} = 590 nm, 5 μM for each sample in H_2O/THF (4:1, v/v) solution.

Table S5. CV data of **FR-R1** in the absence and presence of Hg^{2+} [a]

Compd.	E_{pa}/mV	E_{pc}/mV	E_{pa}-E_{pc}/mV	$E_{1/2}$/mV	I_{pa}/I_{pc}
FR-R1	768	661	107	715	1.92
FR-R1+Hg^{2+}	701	614	87	657	1.07

[a] Conditions: **FR-R1** (0.5 mM) in CH_2Cl_2/CH_3CN (1:9, v/v) containing 0.1 M *n*-Bu_4NPF_6, Pt disk working electrode, Pt auxiliary electrode, Hg/Hg_2Cl_2 reference electrode, and scan rate at 100 mVs^{-1}.

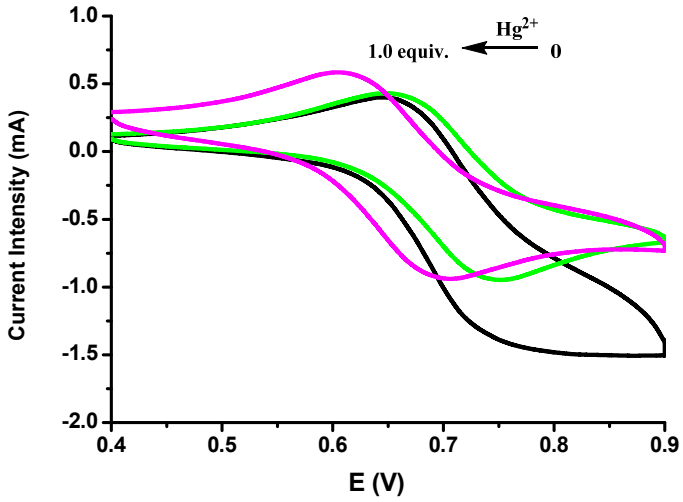


Fig. S20. CV assays of **FR-R1** (0.5 mM) in CH_2Cl_2/MeCN containing 0.1 M *n*-Bu_4NPF_6 as supporting electrolyte upon the addition of Hg^{2+} ions. Black, green and pink lines refer to **FR-R1**, **FR-R1** + 0.5 equiv. Hg^{2+} and **FR-R1** + 1.0 equiv. Hg^{2+}, respectively.

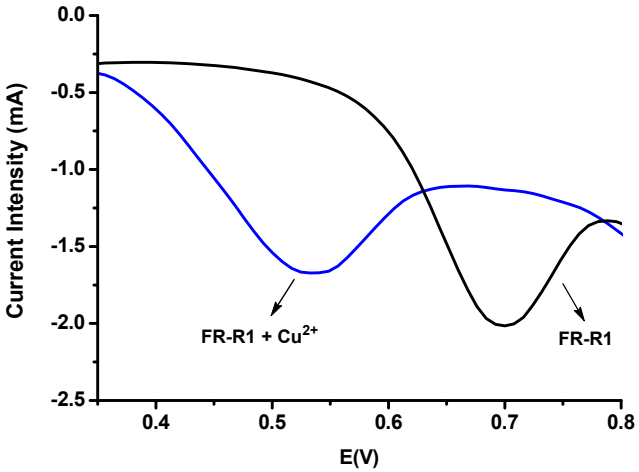


Fig. S21. DPV assays of **FR-R1** (0.5 mM) in H_2O/THF (1:9, v/v) containing 0.1 M *n*-Bu_4NClO_4 as supporting electrolyte upon the addition of Cu^{2+} 1.0 equiv.

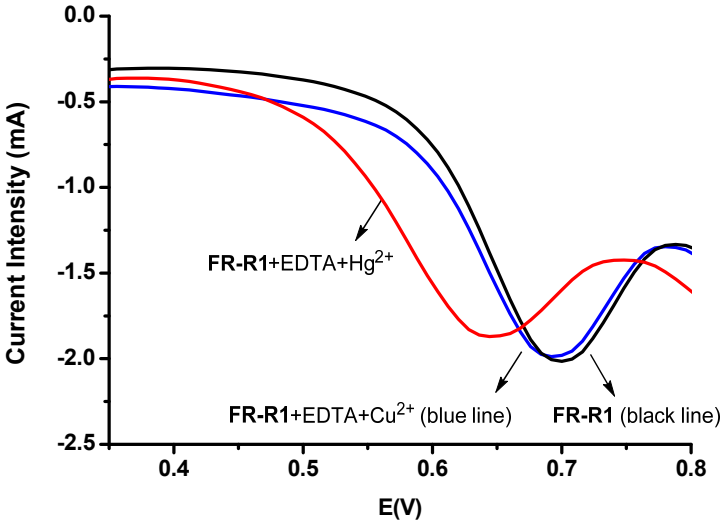
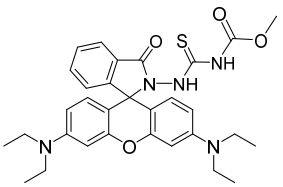
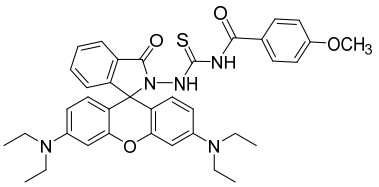
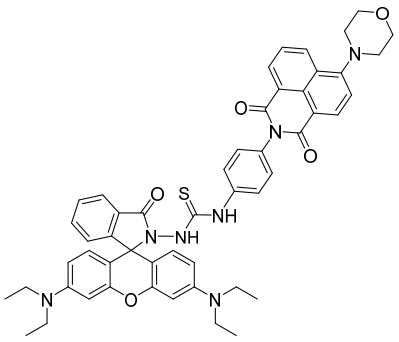
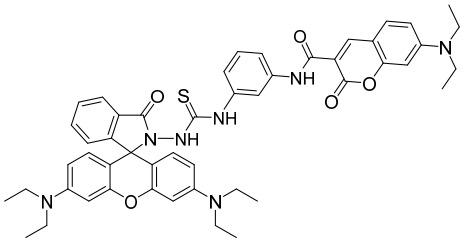
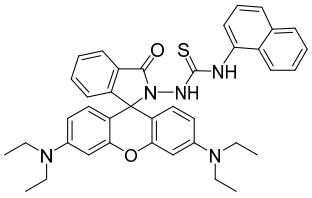
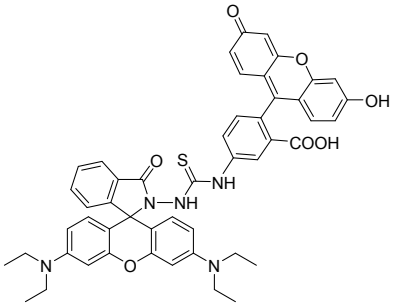
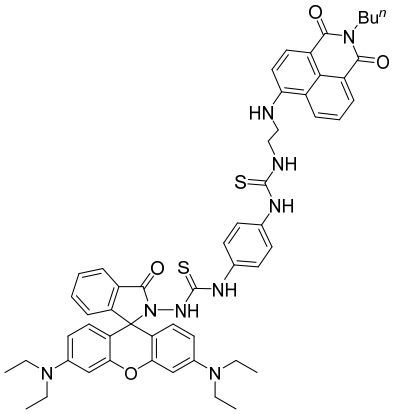
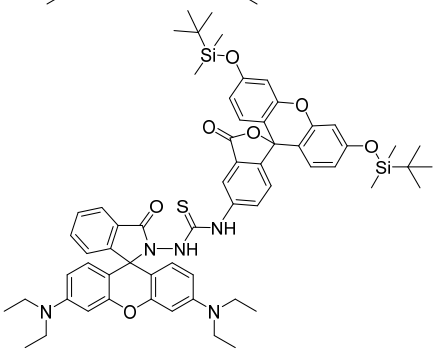
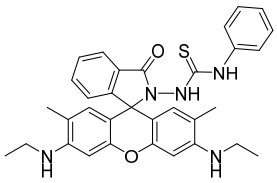
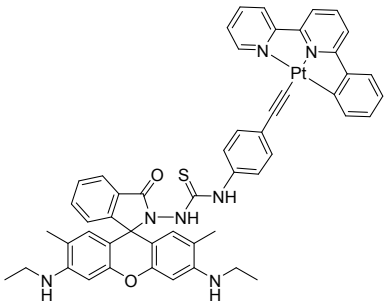
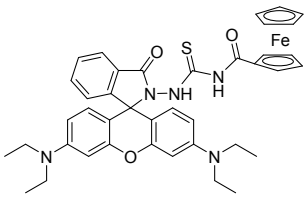


Fig. S22. DPV assays of **FR-R1** (0.5 mM) in H_2O/THF to Hg^{2+} (0.5 mM) and Cu^{2+} (0.5 mM) in the presence of EDTA (1.0 mM) with 0.1 M *n*-Bu_4NClO_4 as supporting electrolyte.

Table S6. Comparison of **FR-R1** with some analogs with different functional groups

Probe	Analysis medium	Detection limit	Ref.
	MeCN/H_2O = 1:1	9.97×10^{-7} M (0.2 ppm)	S1
	DMF/HEPES = 2:3	1.71×10^{-9} M	S2
	MeOH/H_2O = 2:1	3×10^{-8} M	S3
	EtOH/H_2O = 1:1	3.2×10^{-9} M	S4
	MeCN/HEPES = 0.6:100	6.9×10^{-9} M	S5
	MeCOMe/H_2O = 2:3	5×10^{-8} M	S6

	MeOH/H_2O = 1:2	1.68×10^{-7} M	S7
	Tris-HCl (0.01 M)/MeCN = 1:1	5.4×10^{-9} M	S8
	MeOH/H_2O = 1:4	9.97×10^{-9} M (2 ppb)	S9
	MeCN/HEPES = 1:1	4.87×10^{-7} M	S10
	THF/H_2O = 1:9	1.60×10^{-8} M	Our work

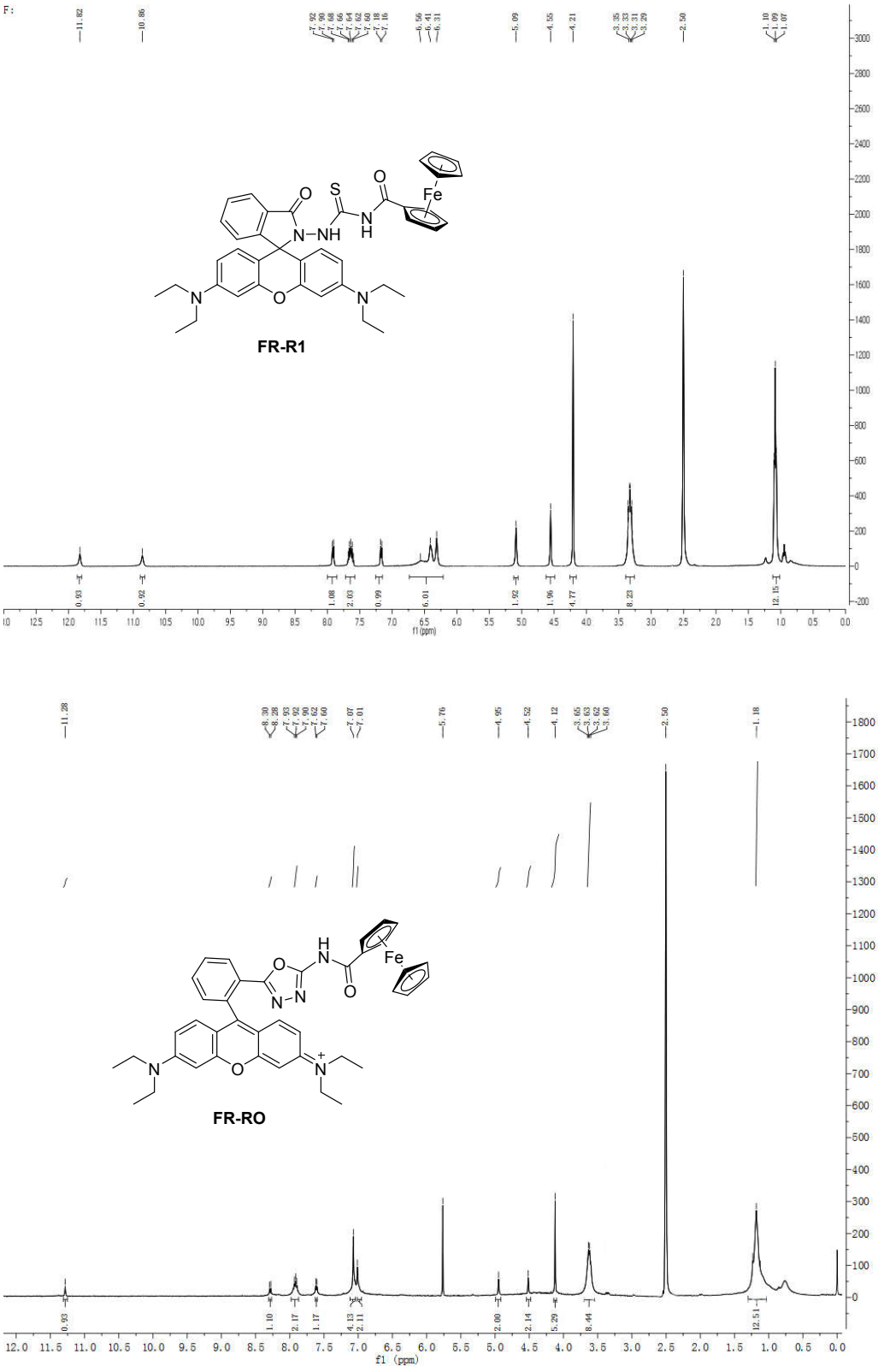


Fig. S23. ^{1}H NMR spectra of **FR-R1** and **FR-RO** in DMSO-d_6.

Table S7. Cartesian coordinates (Å) of the structures of **FR-R1** and **FR-RO**

FR-R1

C	5.02422002	-0.40393880	1.36476044
H	3.97319432	-0.37933464	1.62638336
C	5.85515073	0.72657393	1.10106710
H	5.53969346	1.76062397	1.11591903
C	7.16213942	0.25124883	0.77384828
H	8.01101577	0.86177607	0.49723887
C	7.13835613	-1.17508556	0.83038170
H	7.96596204	-1.83381840	0.60510799
C	5.81716469	-1.57824124	1.19418779
H	5.46768657	-2.59608062	1.29998107
C	5.09510880	0.64941679	-2.17879984
H	4.82784067	1.69324784	-2.10872660
C	6.36443869	0.10450520	-2.50764456
H	7.25771460	0.67033538	-2.73351837
C	6.27366410	-1.31993273	-2.43964304
H	7.08296117	-2.01726538	-2.60646453
C	4.94633851	-1.66543324	-2.06203456
H	4.58948439	-2.67416413	-1.90253776
C	4.20166069	-0.44062461	-1.90598032
C	2.84091583	-0.23518747	-1.37696363
C	1.05556369	-1.57588440	-0.22669293
C	0.34106204	-0.30050415	2.53235712
C	-0.74545347	0.01062101	3.49308464
C	-0.68091593	0.08511620	4.88279954
H	0.25410151	-0.11566166	5.39643766
C	-1.84623732	0.41892072	5.57292658
H	-1.83588927	0.48345684	6.65698327
C	-3.03692304	0.67142605	4.87514022
H	-3.93501717	0.92921007	5.42951198
C	-3.08940225	0.59741577	3.48018892
H	-4.01421016	0.79388630	2.94620309
C	-1.92569736	0.26439914	2.79374522
C	-1.71229893	0.13831252	1.28282663
C	-2.64786081	-0.86512987	0.63837424
C	-3.38146622	-0.56511744	-0.51058119
C	-4.22992644	-1.48816413	-1.12273776

H	-4.74418454	-1.15853484	-2.01505337
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C	-3.63845385	-3.09885435	0.56879853
H	-3.69187556	-4.08399074	1.01225589
C	-2.80270267	-2.16198939	1.15018038
H	-2.22695235	-2.44791245	2.02425520
C	-5.36335493	-5.06259946	-0.65216305
H	-6.32413491	-5.46430634	-0.99047211
H	-5.42343200	-5.02767562	0.44185611
C	-4.23373629	-6.01091829	-1.08168506
H	-3.25548691	-5.62529127	-0.78192180
H	-4.22298152	-6.14588611	-2.16728631
H	-4.36933278	-6.99513844	-0.61933420
C	-6.00048021	-3.36910657	-2.38232138
H	-6.39861222	-2.35188094	-2.28937860
H	-6.87375110	-4.02880033	-2.42125715
C	-5.20497854	-3.49947035	-3.69027343
H	-4.89521781	-4.53436941	-3.86315885
H	-4.30492967	-2.87888616	-3.67085542
H	-5.81965357	-3.18388769	-4.54087309
C	-2.57736964	1.66052385	-0.57814155
C	-1.81003937	1.48421811	0.57640045
C	-1.10796753	2.61171340	1.02948056
H	-0.50398063	2.52661929	1.92870958
C	-1.15542624	3.83511383	0.38236714
H	-0.58975316	4.65869499	0.79686311
C	-1.92644560	4.00299884	-0.79908090
C	-2.64864299	2.88196813	-1.24990912
H	-3.28290297	2.91657912	-2.12510000
C	-2.75564406	5.36344304	-2.69477765
H	-2.63229375	4.46961357	-3.31689944
C	-4.24965604	5.63457129	-2.46006746
H	-4.40166418	6.58114270	-1.93278675
H	-4.70810176	4.84065568	-1.86403700
H	-4.77958012	5.69181578	-3.41739831
C	-1.26776947	6.38763179	-0.95945220
H	-1.11835478	7.07445544	-1.79859357
H	-0.26309420	6.10124741	-0.62699339
C	-2.00386768	7.12005046	0.17241387

H	-2.18606957	6.45600736	1.02189787
H	-2.97060467	7.50231472	-0.16834047
H	-1.40795702	7.96918198	0.52520364
Fe	5.77969704	-0.49029534	-0.58284197
N	0.45603588	-0.41215761	0.14186495
H	0.90605722	0.44882691	-0.18890774
N	-0.28836806	-0.34426132	1.29248882
N	-5.26113193	-3.69967541	-1.16796582
N	-1.95457796	5.20972358	-1.48376177
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O	1.53166111	-0.47355340	2.73761887
N	2.12489388	-1.39878293	-1.11205233
H	2.55171492	-2.28181898	-1.35432743
S	0.65712168	-3.12160502	0.25179622
H	-2.32297867	6.18917932	-3.26923093

FR-RO

C	-6.24539133	-1.78346513	-0.85083267
H	-6.54040971	-2.35506356	0.01810127
C	-7.12522396	-1.20100703	-1.81237343
H	-8.20515715	-1.25043444	-1.79645462
C	-6.33381775	-0.50338867	-2.77270750
H	-6.70878052	0.06517256	-3.61239380
C	-4.96172588	-0.65365882	-2.40700270
H	-4.11617375	-0.23378969	-2.93478061
C	-4.90878048	-1.44634905	-1.21948460
H	-4.01501071	-1.72343310	-0.67673279
C	-6.49047490	1.01474355	1.02014573
H	-6.73214417	0.39999167	1.87475035
C	-7.39364351	1.55647259	0.07010214
H	-8.46506567	1.41348789	0.06363057
C	-6.64366611	2.28185559	-0.90577223
H	-7.04955045	2.79264879	-1.76767472
C	-5.26546753	2.18730289	-0.57304875
H	-4.45827251	2.65929558	-1.11710752

C	-5.16247515	1.40334078	0.63513617
C	-3.96337852	0.97191357	1.35642462
C	-1.50952692	0.85258075	1.06692585
C	0.06338431	0.57171678	2.48102110
C	1.06489302	0.35721847	3.48938378
C	1.03544765	0.42507508	4.88273200
H	0.12330886	0.67465671	5.41408917
C	2.22381831	0.15744314	5.56183006
H	2.24331480	0.19822742	6.64568852
C	3.39237167	-0.16295163	4.85768668
H	4.30498227	-0.36669845	5.40898673
C	3.41087159	-0.22716883	3.45810500
H	4.32190492	-0.47648991	2.92426047
C	2.23800444	0.03309589	2.76622177
C	2.04158687	0.01298921	1.23668982
C	2.82370222	1.05741292	0.49641024
C	3.31978345	0.80087149	-0.78888005
C	3.99316455	1.76408359	-1.53262050
H	4.34027164	1.46772357	-2.51241378
C	4.21684473	3.05926891	-1.01512953
C	3.69952744	3.32822859	0.28689540
H	3.82047077	4.30403595	0.73645867
C	3.03562904	2.35243144	1.00306562
H	2.66638503	2.60131510	1.99419432
C	5.14317473	5.35015016	-1.17679292
H	6.02832853	5.75501060	-1.67548076
H	5.41145550	5.26662813	-0.11809393
C	3.96820176	6.32108172	-1.35224539
H	3.05871658	5.94034366	-0.87853898
H	3.75020801	6.49073753	-2.41036216
H	4.20928382	7.28787569	-0.89820149
C	5.41617571	3.72541606	-3.07217597
H	5.86500083	2.72581499	-3.08515478
H	6.23603939	4.42277416	-3.26515213
C	4.36539211	3.84929893	-4.18353079
H	3.97866659	4.87011542	-4.24960546
H	3.51870724	3.17861869	-4.01229591
H	4.81109803	3.59367192	-5.15039618
C	2.70511217	-1.48071952	-0.68330173

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C	1.75266964	-2.52453061	1.24095211
H	1.35304528	-2.47238844	2.24996405
C	1.82580354	-3.75975641	0.62868186
H	1.49030455	-4.62751350	1.17955912
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C	2.79239013	-2.71236608	-1.32347708
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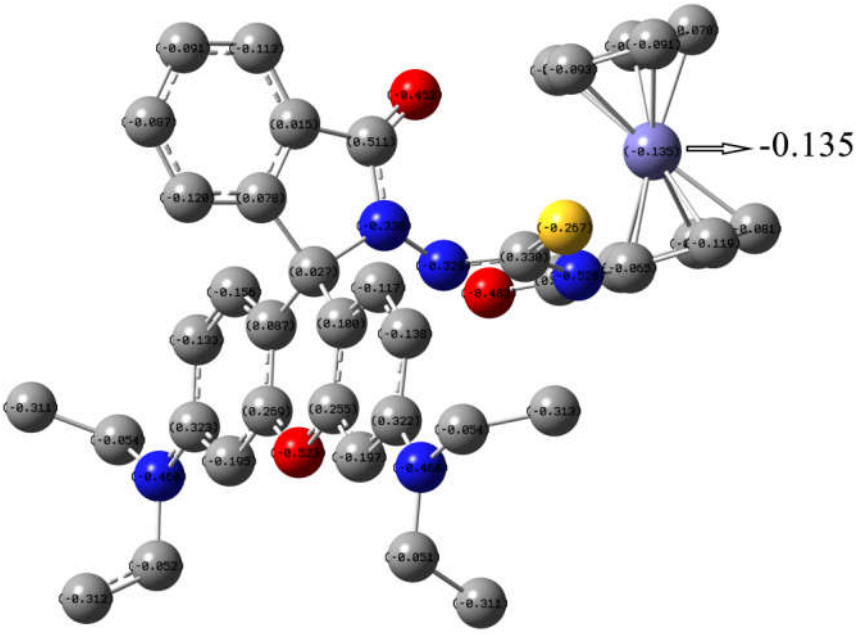
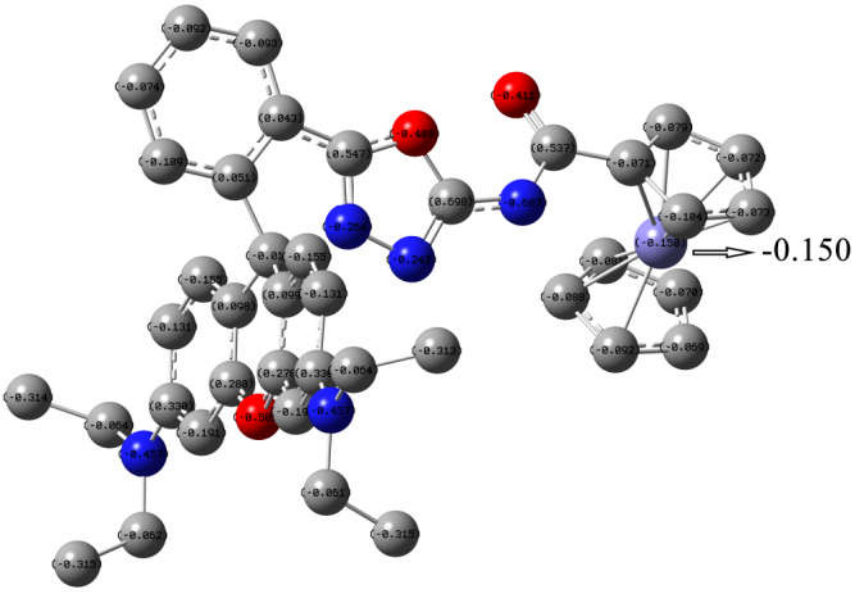
H	2.53729394	-4.39390730	-3.29416854
C	4.43855085	-5.31363201	-2.78628594
H	4.81884171	-6.20578680	-2.28106844
H	4.91536183	-4.44076769	-2.33152840
H	4.74875502	-5.36300906	-3.83519934
C	1.96752702	-6.34082966	-0.64662438
H	1.72799317	-7.07508188	-1.42066020
H	1.02943224	-6.15659126	-0.11111398
C	3.01696775	-6.92646753	0.30732298
H	3.29740426	-6.20985305	1.08447930
H	3.92520842	-7.21073070	-0.23096330
H	2.62021159	-7.82180162	0.79706450
Fe	-6.01361963	0.28480750	-0.87562550
N	-0.46397220	0.56654533	0.33109986
N	0.51970155	0.41300347	1.26722186
N	4.92025516	4.00694886	-1.72125374
N	2.37609238	-5.11130089	-1.33404360
O	3.18625473	-0.41746274	-1.40074642
O	-3.93741609	0.48034338	2.46471327
O	-1.23885263	0.86905613	2.42621768
N	-2.74400229	1.18150624	0.62390529
H	-2.80641199	1.29516104	-0.38064777
H	2.46776743	-6.13158583	-3.13428176



FR-R1



FR-RO

Fig. S24. The Mulliken charge values in **FR-R1** and **FR-RO**.

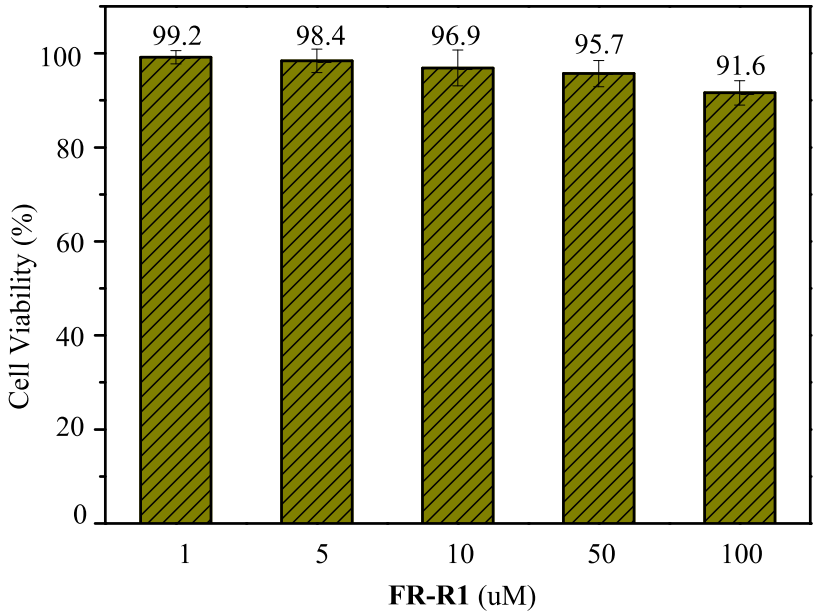


Fig. S25. The cytotoxicity of **FR-R1** on HeLa cells. The data are given as mean ± SD (n = 6).

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