Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting information

for

A Photoacoustic Zn^{2+} Sensor Based on a Merocyanine/Xanthene-6-ol Hybrid Chromophore and Its Ratiometric Imaging in Mice

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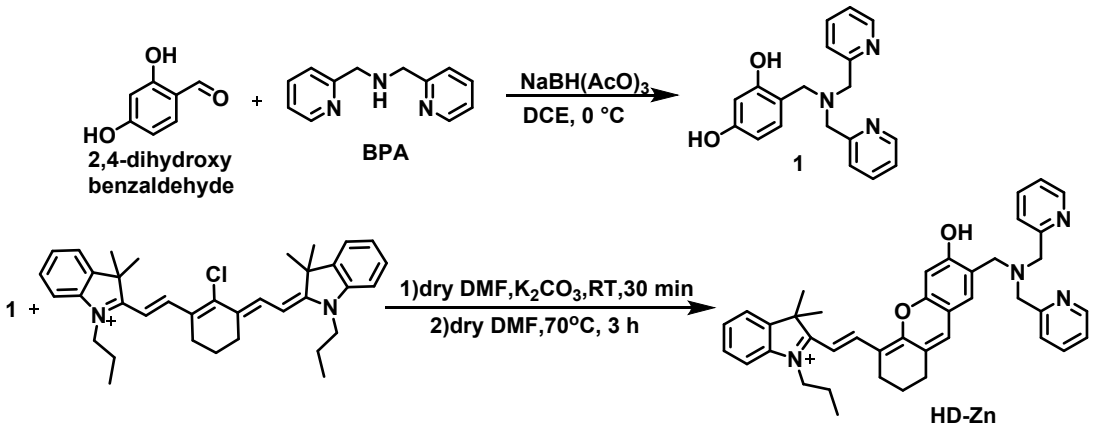
Content



Scheme S1. Synthesis of **HD-Zn**.

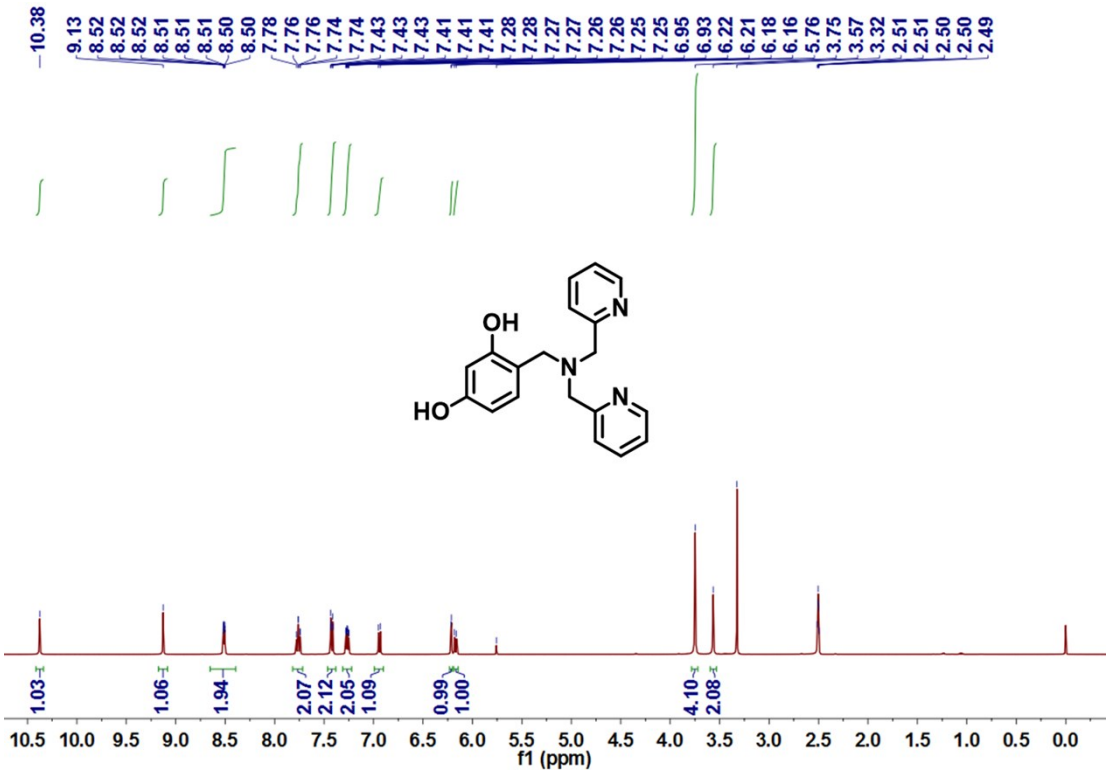


Fig. S1 ^{1}H NMR spectrum of compound **1** in DMSO-d_6.

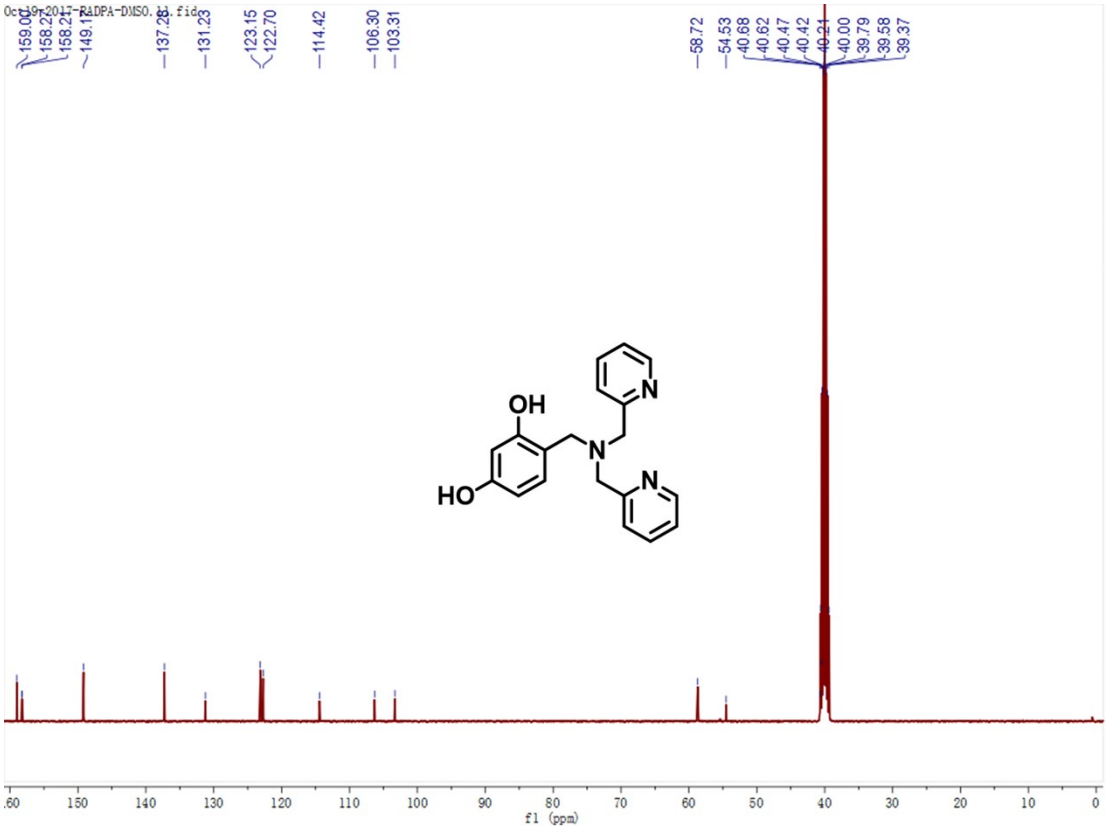


Fig. S2 ^{13}C NMR spectrum of compound **1** in DMSO-d_6.

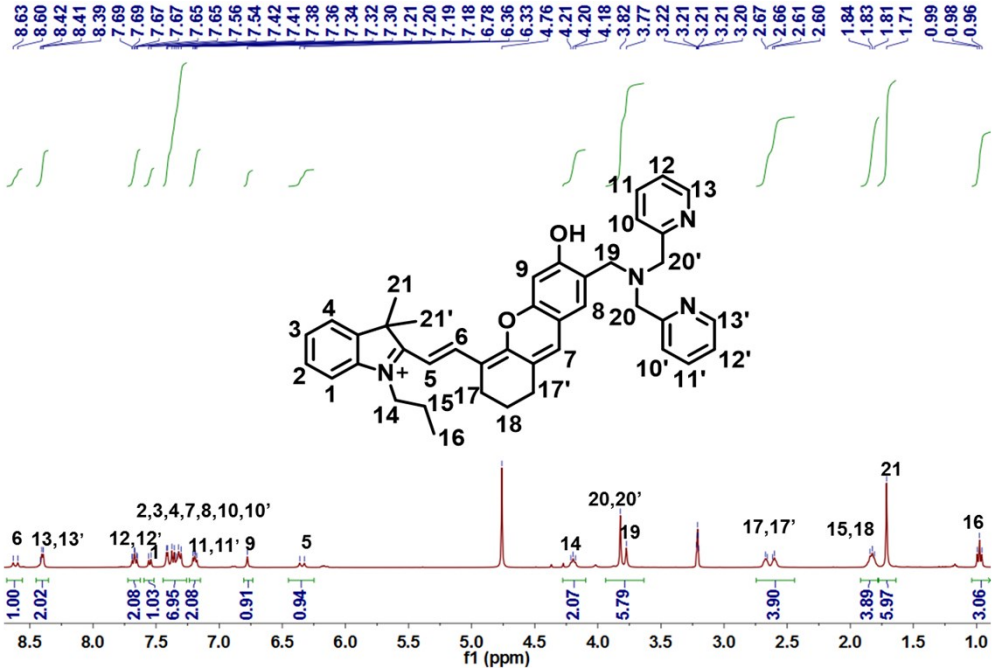


Fig. S3 ^{1}H NMR spectrum of **HD-Zn** in CD_3OD.

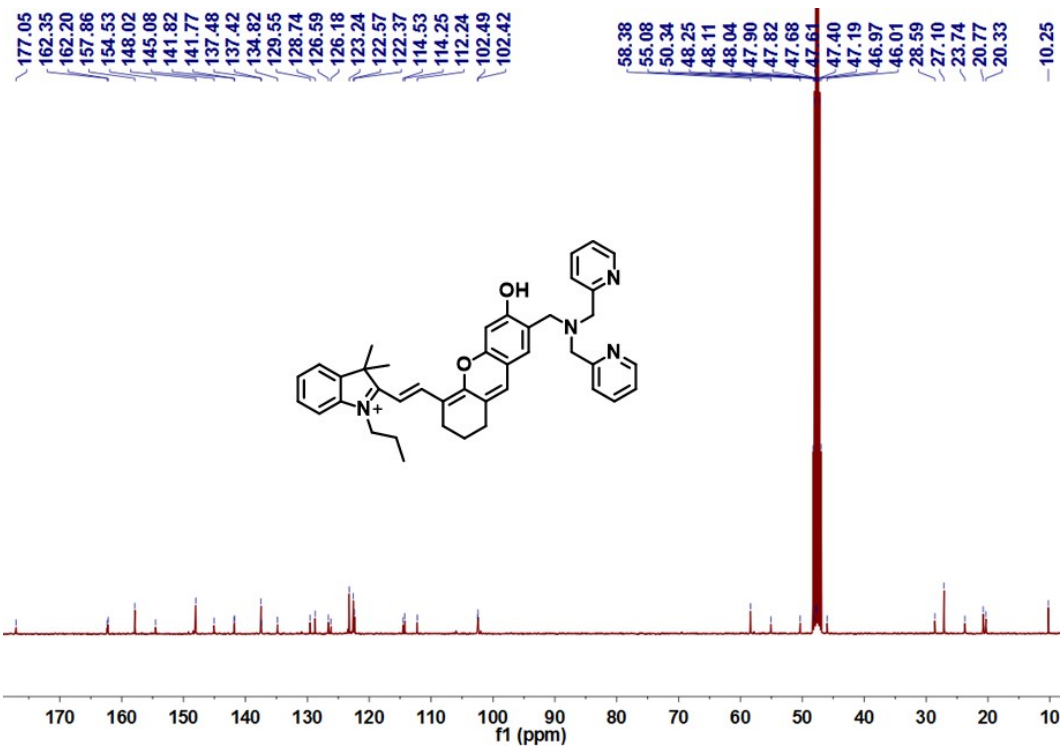


Fig. S4 ^{13}C NMR spectrum of **HD-Zn** in CD_3OD.

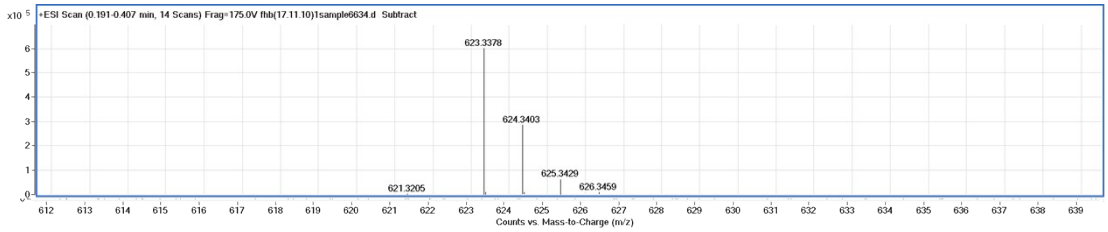


Fig. S5 HR-MS spectrum of **HD-Zn**.

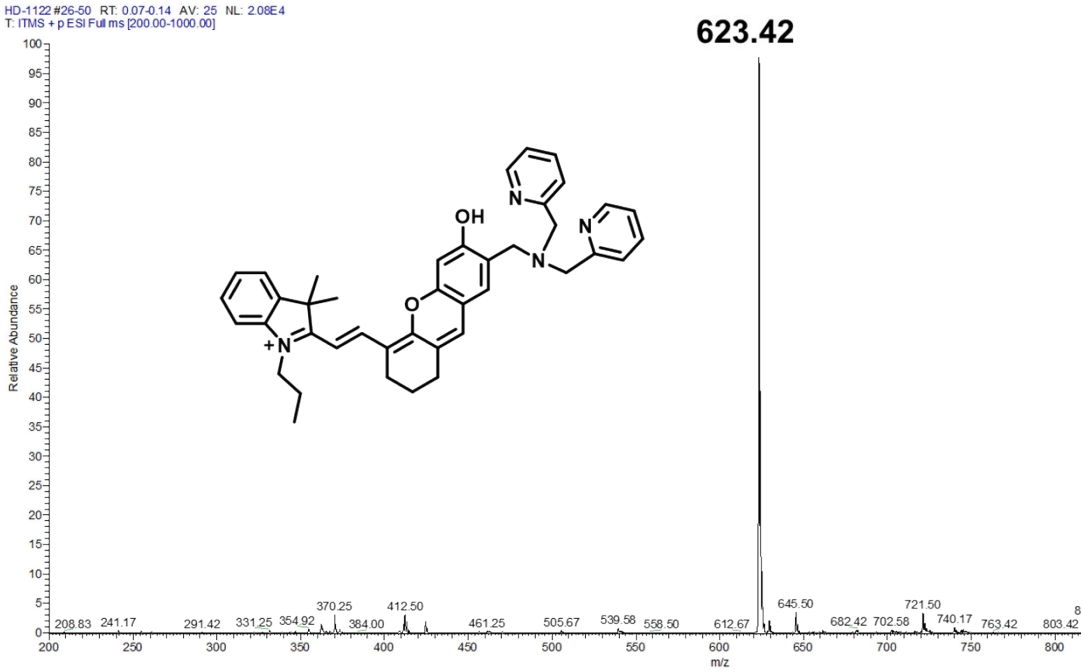


Fig. S6 ESI-MS spectrum of **HD-Zn**.

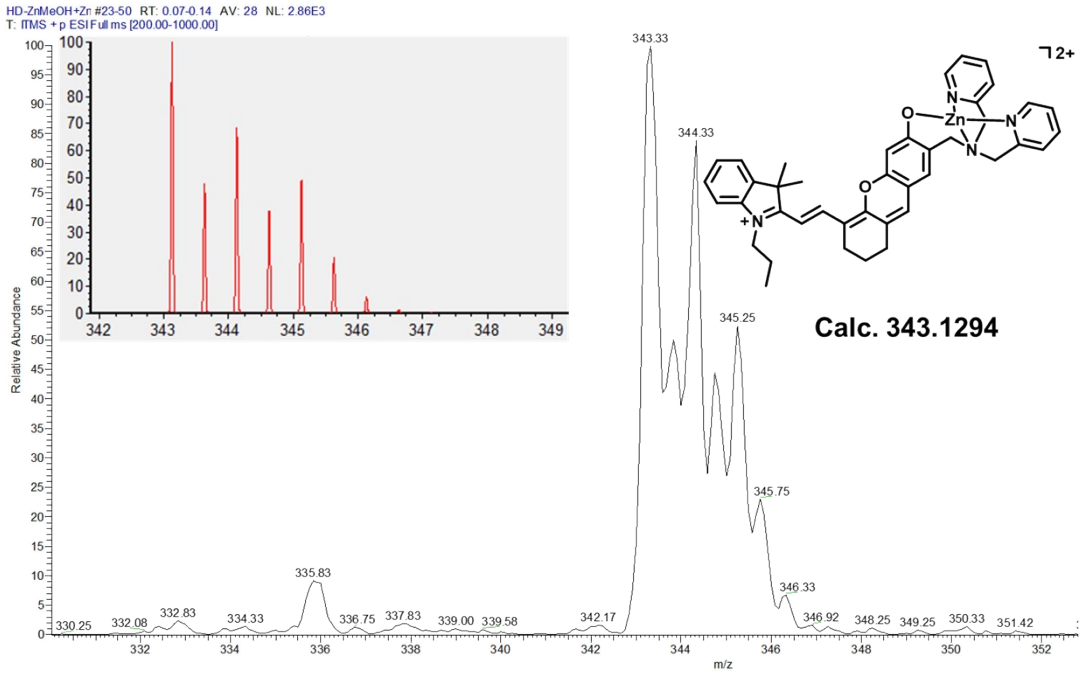


Fig. S7 HR-MS spectrum of **HD-Zn** in the presence of 1 eq Zn^{2+}.

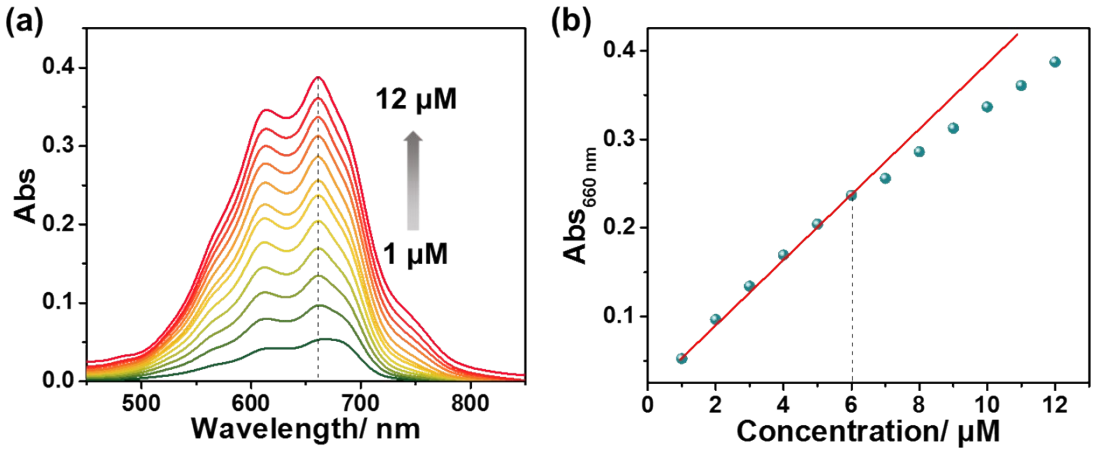


Fig. S8 (a) Absorption spectra of **HD-Zn** (1-12 μM) in HEPES containing 0.5% DMSO; (b) Absorbance profile of **HD-Zn** at different concentration based absorbance at 660 nm.

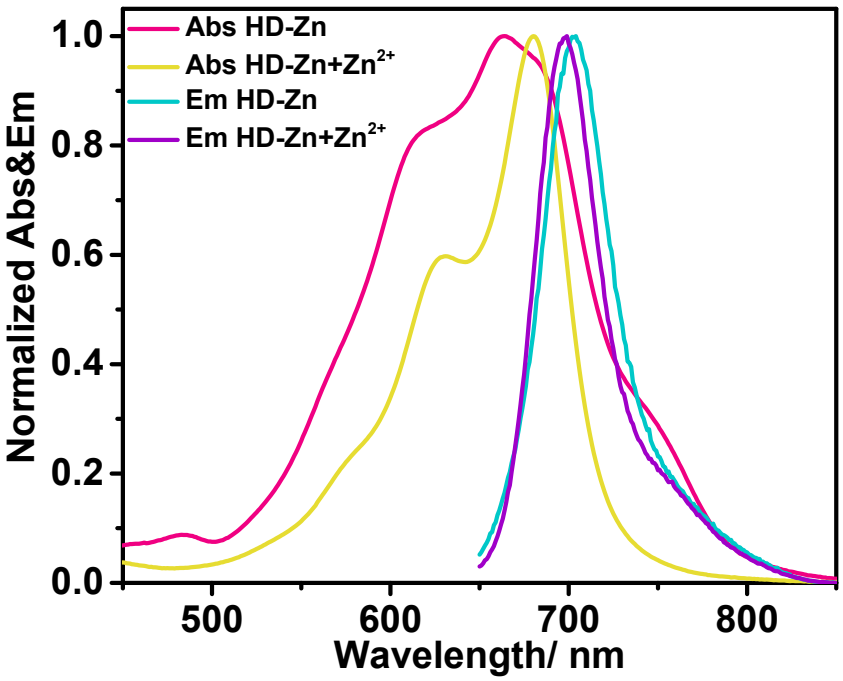


Fig. S9 Normalized absorption and emission spectra of **HD-Zn** (5 μM) in HEPES (50 mM, 100 mM KNO_3, pH 7.4, 0.5 % DMSO) in the absence or presence of Zn^{2+}, λ_{ex} = 633 nm.

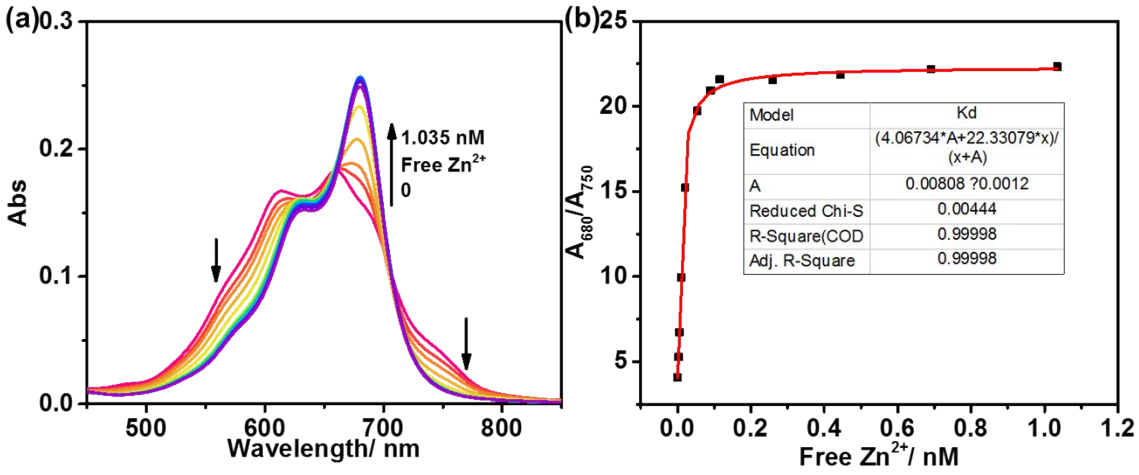


Fig. S10 (a) Absorption spectra of 5 μM **HD-Zn** in a series of Zn^{2+} buffer solutions; (b) zinc binding isotherm based on absorbance ratio A_{680}/A_{750} and its fitting for dissociation constant determination. The concentrations of zinc ion were buffered using in aqueous EGTA buffer (50 mM, 100 mM KNO_3, pH 7.4, 10 mM EGTA).

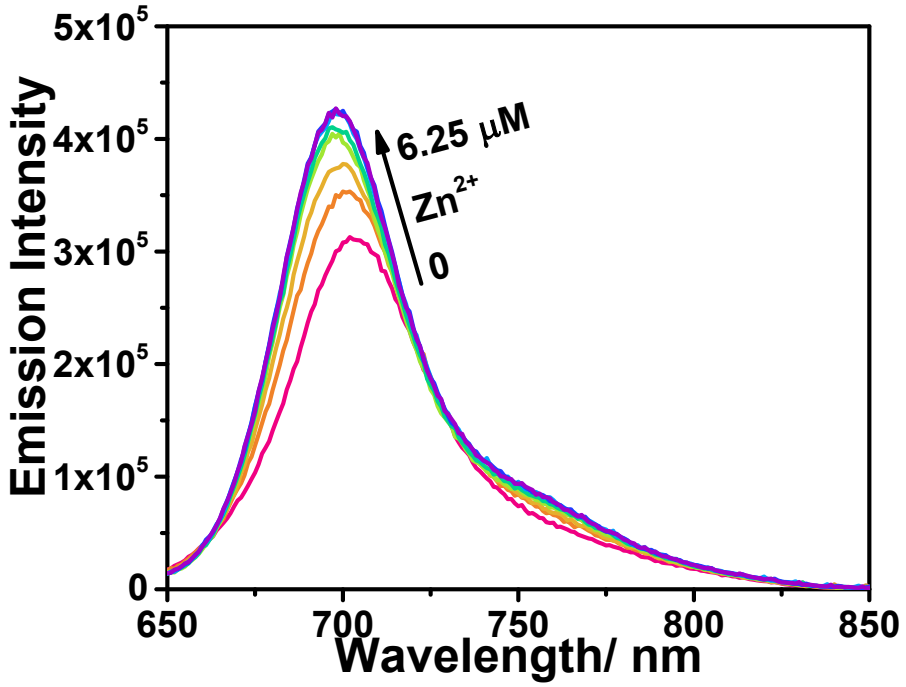


Fig. S11 Fluorescence spectra of **HD-Zn** (5 μM) upon titration with Zn^{2+} (0- 6.25 μM) in HEPES buffer (50 mM, 100 mM KNO_3, pH 7.4, 0.5 % DMSO), λ_{ex} = 633 nm.

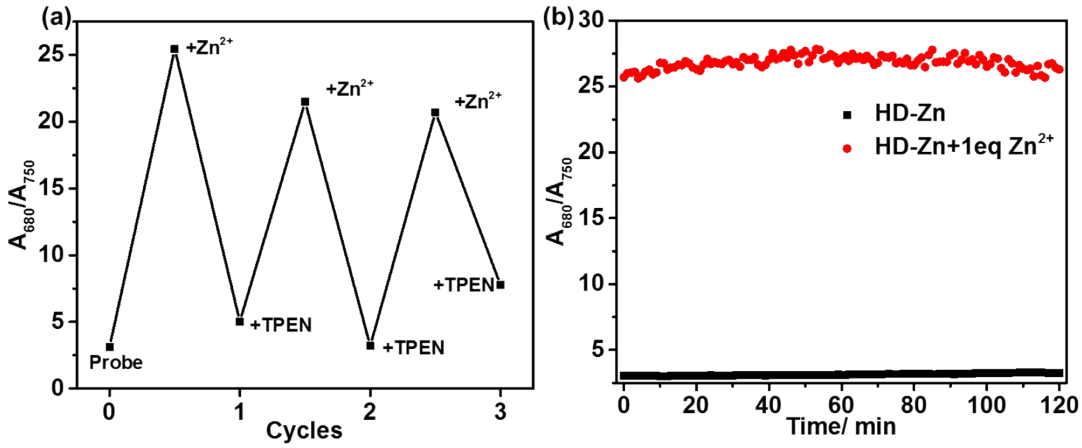


Fig. S12 (a) Reversible Zn^{2+} sensing behavior of **HD-Zn** (5 μM) in HEPES buffer (50 mM, 100 mM KNO_3, pH7.4). Zn^{2+} (10 μM) and TPEN (10 μM) were added alternately, and absorption was determined after each addition; (b) Absorbance ratio A_{680}/A_{750} of **HD-Zn** (5 μM) in the absence and presence of Zn^{2+} in 2 h.

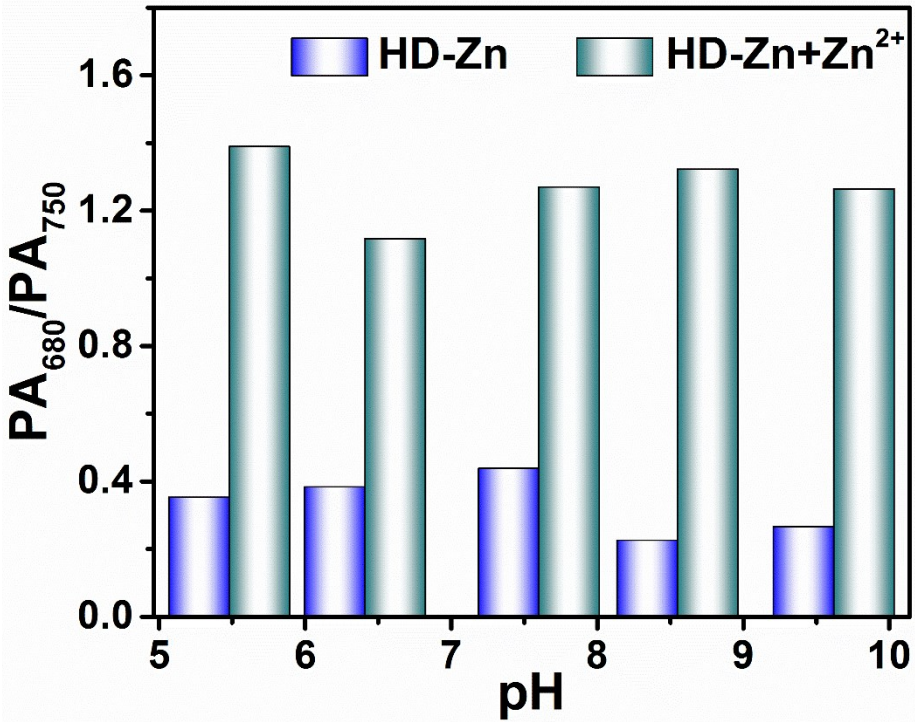


Fig. S13 PA_{680}/PA_{750} ratios of **HD-Zn** (20 μM) determined in aqueous solutions with or without 1.2 equiv Zn^{2+} at different pH.

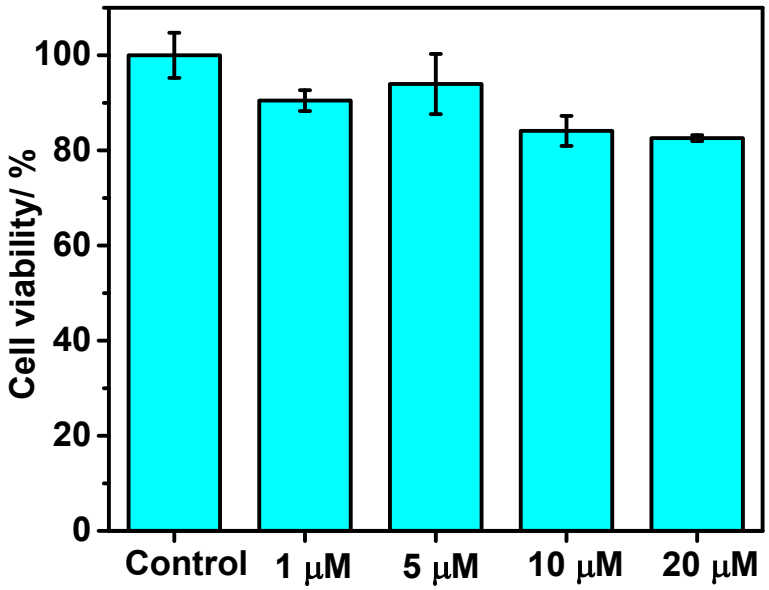


Fig. S14 MTT assay of MCF-7 cells incubated with **HD-Zn** in 12 h.

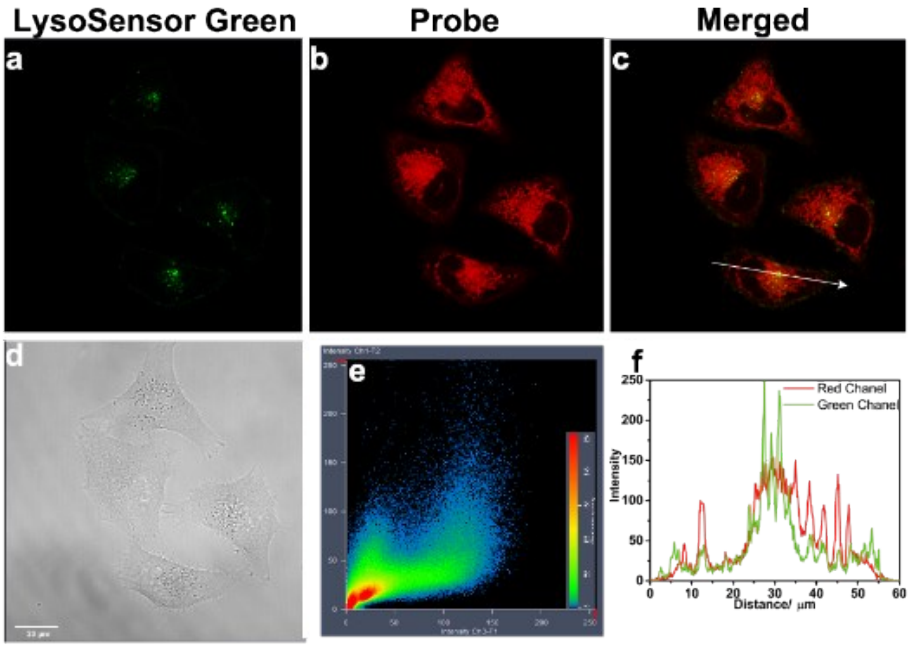


Fig. S15 Confocal fluorescence images of MCF-7 cells incubated with LysoSensor Green DND-189 (1 μM, 20 min) and **HD-Zn** (5 μM, 10 min) in sequence at 37°C. (a) Fluorescence image obtained with the band path 490–580 nm upon excitation at 488 nm (LysoSensor channel); (b) fluorescence image obtained with the band path 640–750 nm upon excitation at 633 nm (**HD-Zn** channel); (c) merge image of LysoSensor and **HD-Zn** channel images; (d) bright field image; (e) intensity correlation plot of LysoSensor channel and **HD-Zn** channel. (f) Fluorescence profile along white lines randomly across MCF-7 cells.

Table S1. Selected parameters for the calculated singlet states of **HD-Zn** and its Zn^{2+} complex. [a]

Compound	Elecreonic transition	Energy, eV/λ, nm	*f* [b]	Composition[c]	CI[d]
HD-Zn	$S_0 \rightarrow S_1$	2.25/550	0.8759	H→L	0.70504
	$S_0 \rightarrow S_2$	2.83/438	0.0008	H-1→L	0.70469
	$S_0 \rightarrow S_3$	3.30/376	0.4200	H-2→L	0.66792
	$S_0 \rightarrow S_4$	3.41/364	0.1361	H-3→L	0.66337
	$S_0 \rightarrow S_5$	3.77/329	0.0001	H-4→L	0.61815
	$S_0 \rightarrow S_6$	3.79/327	0.0179	H-8→L	0.39074
	$S_0 \rightarrow S_7$	3.80/326	0.0209	H-8→L	0.42235
	$S_0 \rightarrow S_8$	3.84/323	0.0018	H-5→L	0.61846
	$S_0 \rightarrow S_9$	3.94/315	0.0046	H-7→L	0.56751
	$S_0 \rightarrow S_{10}$	4.05/306	0.1992	H→L+1	0.66697
HD-Zn /Zn^{2+} complex	$S_0 \rightarrow S_1$	2.01/617	0.8020	H→L	0.70628
	$S_0 \rightarrow S_2$	3.11/399	0.5108	H-1→L	0.67810
	$S_0 \rightarrow S_3$	3.15/394	0.0010	H→L+1	0.68110
	$S_0 \rightarrow S_4$	3.20/387	0.0017	H→L+2	0.68330
	$S_0 \rightarrow S_5$	3.40/365	0.1372	H-2→L	0.68603
	$S_0 \rightarrow S_6$	3.70/335	0.0015	H-3→L	0.68548
	$S_0 \rightarrow S_7$	3.78/328	0.0455	H→L+3	0.57972
	$S_0 \rightarrow S_8$	3.82/324	0.0246	H-5→L	0.50257
	$S_0 \rightarrow S_9$	3.85/322	0.2224	H→L+4	0.58710
	$S_0 \rightarrow S_{10}$	3.87/321	0.0033	H→L+5	0.69400

[a] Parameters were calculated by TDDFT/B3LYP/6-311G(d) (water was used as solvent), based on the optimized ground-state geometries using the method Hartree-Fock/6-311G(d) basis set. [b]Oscillator strength. [c]H, HOMO (highest occupied molecular orbital) and L, LUMO (lowest unoccupied molecular orbital). [d] Coefficient of the wavefunction for each excitations.