Supporting Information

A Ratiometric Fluorescent Sensor with a Large Stokes Shift for Imaging Zinc Ion in Living Cells

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1. Synthesis of FQ1.

General Information. SeO₂, NaBH(OAc)₃, 4-nitrobenzyl bromide, 1,4-dioxane and metal salts were purchased from Alfa Aesar A Johnson Matthey Company and used as received. Di-2-picolylamine was purchased from J&K Chemical Ltd. Compound **1** was prepared according to known procedures.^{S1}

Dimethyl sulfoxide (DMSO), Tris(hydroxymethyl)aminomethane hydrochloride (Tris), 4-(2-hydroxyerhyl)piperazine-1-erhanesulfonic acid (HEPES), nitrilotriacetic acid (NTA) and N,N,N',N'-tetrakis-(2-pyridylmethyl)ethylenediamine (TPEN) were also purchased from Alfa Aesar. These materials were received and then used for spectrum measurement.

¹H and ¹³C NMR spectra were recorded on an AVANCE-400 spectrometer and referenced to internal TMS or solvent signals. Mass spectra (ESI) were obtained on LC-MS 2010.

CAUTION: Perchlorate salts with organic ligands can be potential explosive and should be handled with care.



Scheme S1 Synthesis of FQ1.

7-hydroxymethyl-8-hydroxy-quinoline (2). To 50% HCl solution (10 mL) was added **1** (0.27 g, 1 mmol). The mixture was heated at 60°C for 2 hours. After cooling, the solution was neutralized with 1 N NaOH to pH 5–6, and then extracted with methylene chloride (3 × 10 mL). Organic phases were combined and dried over Na₂SO₄. The filtrate was evaporated to generate crude residue, which was purified by recrystallization from the mixture of methylene chloride and hexane. ¹H NMR (400 MHz, CDCl₃, ppm) δ 8.03 (1H, d, *J* = 8.41 Hz), 7.44 (1H, d, *J* = 8.37 Hz), 7.31 (1H, d, *J* = 3.89 Hz), 7.29 (1H, d, *J* = 3.86 Hz), 4.94 (2H, *s*), 2.73 (3H, *s*). ¹³C NMR (100 MHz, MeOD, ppm): δ 158.0, 150.1, 138.8, 137.3, 127.5, 127.5, 124.1, 123.4, 118.3, 60.0, 24.9. Mass (ESI): m/z 188.0 (M–H⁺).

8-(4-nitrobenzyloxy)-7-hydroxymethyl-2-methyl-quinoline (3). A mixture of **2** (0.19 g, 1 mmol), 4-nitrobenzyl bromide (0.26 g, 1.2 mmol), K₂CO₃ (0.55 g, 4 mmol) and KI (17 mg, 0.1 mmol) in acetone (20 mL) was refluxed for 12 h. After cooling, the mixture was filtered to remove salts and the filtrate was evaporated to generate crude residue, which was purified by flash chromatography (silica gel) or recrystallization to give the desired products. Eluents: petroleum ether, containing 5-15% ethyl acetate, yield: 80%. ¹H NMR (400 MHz, CD₃Cl, ppm): δ 8.28 (2H, d, *J* = 8.52 Hz), 8.07 (1H, d, *J* = 8.40 Hz), 7.79 (2H, d, *J* = 8.44Hz), 7.58 (1H, d, *J* = 8.32 Hz), 7.51 (1H, d, *J* = 8.32 Hz), 7.32 (1H, d, *J* = 8.44 Hz), 5.65 (2H, s), 4.87 (2H, d, *J* = 6.16 Hz), 2.75 (3H, s), 2.04 (1H, t, *J* = 6.16 Hz). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 158.5, 151.3, 147.6, 145.5, 141.7, 136.4, 132.8, 128.61, 127.7, 126.0, 123.7, 123.5, 122.2, 61.3, 25.7. Mass (ESI): m/z 325.0 (M+H⁺), 347.0 (M+Na⁺).

8-(4-nitrobenzyloxy)-2-methyl-quinoline-7-carbaldehyde (4). A solution of **3** (0.65 g, 2 mmol) in dry methylene chloride (20 mL) was stirred at room temperature with 1.0 g of manganese dioxide. After 20 h, the mixture was filtered off and the solid was washed with methylene chloride. The combined organic phase was concentrated. The pure product was obtained by recrystallization from the mixture of ethyl acetate and hexane. yield: 95%. ¹H NMR (400 MHz, CDCl₃, ppm) δ 10.61 (1H, s), 8.29 (2H, d, *J* = 8.60 Hz),

8.10 (1H, d, J = 8.48 Hz), 7.87 (1H, d, J = 8.52 Hz), 7.76 (2H, d, J = 8.48 Hz), 7.58 (1H, d, J = 8.52 Hz), 7.43 (1H, d, J = 8.44 Hz), 5.84 (2H, s), 2.77 (3H, s). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 189.9, 159.2, 158.9, 147.8, 144.6, 142.1, 136.6, 131.9, 128.7, 127.6, 124.6, 123.8, 123.6, 122.4, 76.1, 25.6. Mass (ESI): m/z 322.9 (M+H⁺), 355.0 (M+Na⁺).

2-(4-nitrophenyl)-8-methylfuro[3,2-*h***]quinoline (5). 4** (0.64 g, 2 mmol), and KOH (0.44 g, 8 mmol) were stirred in DMF (8 mL) for 4 hours at 80°C. The solution was first acidified with 1 N HCl to pH 5–6, then extracted with DCM (5 × 10 mL). The organic phases were washed with water and brine, dried over Na₂SO₄. The solvents were evaporated to give crude product, which was purified by flash chromatography (silica gel) to give the desired products. Eluents: petroleum ether, containing 10% ethyl acetate, yield: 50%. ¹H NMR (400 MHz, CDCl₃, ppm) δ 8.35 (2H, d, *J* = 8.64 Hz), 8.20–8.15 (3H, m), 8.12 (1H, d, *J* = 8.12 Hz), 7.65 (1H, d, *J* = 8.44 Hz), 7.40 (1H, d, *J* = 7.24 Hz), 7.36 (1H, s), 2.87 (3H, s). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 159.8, 154.2, 150.0, 147.3, 136.8, 136.4, 136.0, 128.5, 127.6, 125.6, 125.4, 124.3, 123.9, 122.0, 119.6, 106.2, 25.6. Mass (ESI): m/z 305.1 (M+H⁺), 327.2 (M+Na⁺).

2-(4-aminophenyl)-8-methylfuro[3,2-*h***]quinoline (6). 5** (0.2 g, 0.6 mmol) was dissolved in ethanol and a solution of cupric sulfate (2 M aqueous solution, 40 μ L) is added. After the mixture is cooled to 0°C, sodium borohydride (0.11 g, 3 mmol) is added portion wise. Then the reaction mixture is stirred at room temperature and was monitored by TLC. Then the solvents were evaporated and the solid was diluted with ethyl acetate, washed with water and brine, dried over Na₂SO₄. The solvents were evaporated to give crude product, which was purified by flash chromatography (silica gel, DCM/10% ethyl acetate) to give the desired products. Yield: 80%: ¹H NMR (400 MHz, MeOD, ppm) δ 8.20 (1H, d, *J* = 8.36 Hz), 7.82 (2H, d, *J* = 8.48 Hz), 7.63 (1H, d, *J* = 8.40 Hz), 7.57 (1H, d, *J* = 8.42 Hz), 7.32 (1H, d, *J* = 8.37 Hz), 7.01 (1H, s), 6.81 (2H, d, *J* = 8.48 Hz), 2.75 (3H, s). ¹³C NMR (100 MHz, MeOD, ppm): δ 160.3, 159.8, 150.4, 148.6, 138.7, 136.6, 131.4, 127.5, 125.5, 124.0, 121.8, 121.0, 120.7, 116.1, 110.1, 24.5. Mass (ESI): m/z 274.9 (M+H⁺), 297.0 (M+Na⁺), 312.9 (M+K⁺).

2-(4-dimethylaminophenyl)-8-methylfuro[3,2-*h*]**quinoline** (7). To a mixture of **6** (0.3g, 1.1 mmol), Na₂SO₄ and formaldehyde (40% a.q., 3.5 mmol, 0.4 mL) in 1, 2-dichloroethane (10 mL) was added NaBH(OAc)₃ (0.76 g, 3.5 mmol) in portions. The resulting solution was stirred at room temperature overnight. The solution was first acidified with 1 N HCl to pH 4–5, and then neutralized with 1 N NaOH to pH 7–8. Organic phase was separated. Aqueous phase was extracted with DCM (3 × 10 mL). Organic phases were combined and dried over Na₂SO₄. The solvents were evaporated to give crude product, which was purified by flash chromatography (silica gel, petroleum ether/5% ethyl acetate) to give the desired products. Yield: 90%. ¹H NMR (400 MHz, CDCl₃, ppm) δ 8.11 (1H, d, *J* = 8.32 Hz), 7.93 (2H, d, *J* = 8.64 Hz), 7.65 (1H, d, *J* = 8.64 Hz), 3.04 (6H, s), 2.86 (3H, s). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 159.2, 158.3, 150.7, 148.4, 136.8, 136.4, 129.8, 126.7, 124.1, 122.9, 120.6, 119.3, 118.5, 112.1, 99.4, 40.5, 25.7. Mass (ESI): m/z 303.1 (M+H⁺), 325.2 (M+Na⁺).

Synthetic procedure for 8 and FQ1.

These compounds were prepared according to known procedures.^{S2}

2-(4-(dimethylamino)phenyl)furo[3,2-*h***]quinoline-8-carbaldehyde (8).** Yield: 60%. ¹H NMR (400 MHz, CDCl₃, ppm) δ 10.38 (1H, s), 8.35 (1H, d, *J* = 8.36 Hz), 8.00 (1H, d, *J* = 8.36 Hz), 7.92 (2H, d, *J* = 8.88 Hz), 7.82 (1H, d, *J* = 8.44 Hz), 7.66 (1H, d, *J* = 8.40 Hz), 6.98 (1H, s), 6.80 (2H, d, *J* = 8.88 Hz), 3.04 (6H, s). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 194.0, 159.2, 152.1, 151.0, 148.7, 137.8, 136.5, 130.7, 127.7, 126.8, 123.2, 123.0, 117.9, 115.9, 112.1, 99.3, 40.40. Mass (ESI): m/z 317.1 (M+H⁺), 349.1 (M+Na⁺).

2-(4-(dimethylamino)phenyl)-8-(bis(2-pyridylmethyl)amino)methylfuro[3,2-*h***]quin oline (FQ1).** Yield: 92%.¹H NMR (400 MHz, CDCl₃, ppm) δ 8.55 (2H, d, *J* = 4.60 Hz), 8.19 (1H, d, *J* = 8.40 Hz), 7.91 (2H, d, *J* = 8.60 Hz), 7.76–7.62 (6H, m), 7.55 (1H, d, *J* = 8.40 Hz), 7.15–7.12 (2H, m), 6.94 (1H, s), 6.78 (2H, d, *J* = 8.64 Hz), 4.17 (2H, s), 3.98 (4H, s), 3.01 (6H, s). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 160.2, 159.6, 158.3, 150.7, 149.2, 148.6, 136.9, 136.5, 136.2, 129.7, 126.6, 124.9, 123.2, 122.8, 122.1, 119.8, 119.2,

118.5, 112.1, 99.4, 60.8, 60.5, 40.4. Mass (ESI): m/z 500.2 (M+H⁺), 522.1 (M+Na⁺), 538.1 (M+K⁺).

Zinc Complexes of FQ1. FQ1 (18 mg) were dissolved in 6 mL of methanol containing 10% water. To this solution was added $Zn(ClO_4)_2$ (1 equiv) at room temperature. The mixture was shaken for 10 min. An aliquot of the above complex solution (1.0 mL) was drawn out and placed into a glass tube. Ethyl ether was then added carefully into the tube. After several days, crystals of zinc complex appeared and were ready for X-ray diffraction.

2. Crystallography of ZnFQ1.

Measurements were done on a Rigaku RAXIS-RAPID imaging plate diffractometer equipped with a CCD detector using Mo $K\alpha$ monochromatized radiation ($\lambda = 0.71073$ Å). Cell refinement and data reduction were accomplished by the RAPID AUTO program. The structure was then solved with direct methods and refined using SHELXTL-97 software package^{S 3}. All non-hydrogen atoms were refined anisotropically. Positions of hydrogen atoms attached to carbon atoms were fixed at their ideal positions.

Table S1. Crystallographic parameters for complex ZnFQ1.

Supplementary Material (ESI) for Chemical Communications

Compound	ZnFQ1
Formula	$C_{34}H_{39}N_5O_{12}Cl_2Zn$
Formula weight	845.97
Wavelength(Å)	0.71073
Crystal system	Triclinic
Space group	<i>P</i> -1
$T(\mathbf{K})$	113(2)
$a(\text{\AA})$	13.540(3)
$b(\text{\AA})$	15.622(3)
$c(\text{\AA})$	19.581(4)
α (°)	106.96(3)
$\beta(^{\circ})$	95.54(3)
$\gamma(^{\circ})$	110.83(3)
$V(\text{Å}^3)$	3608.9(12)
Ζ	4
$D(Mg/m^{-3})$	1.557
<i>F</i> (000)	1752
μ (Mo Ka)(mm ⁻¹)	0.900
θ range(°)	1.49 ~ 25.02
Goodness of fit on F ²	1.057
$R_1, wR_2 [I > 2\sigma (I)]$	0.0914, 0.2367
R indices (all data)	0.1271, 0.2744
$R = \sum F_0 - Fc / \sum F_0 , wR_2 =$	$\left\{\sum[w(F_0^2 - F_c^2)^2]/\sum[w(F_0^2)^2]\right\}^{1/2}$

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3. UV-visible Absorbance and Fluorometric Analysis.

UV-visible spectra were recorded on HITACHI 3010 UV-vis spectrometer. Fluorescence spectra were recorded using a HITACHI F-4500 spectrometer. The path length was 1 cm with cell volume of 3.0 mL. **FQ1** were dissolved in DMSO to obtain stock solutions. Quantum yields were determined to be 0.008 for the apo form and 0.005 for the zinc complex using quinine sulfate in 0.1 N H₂SO₄ (Φ = 0.54)^{S4}



Figure S1. Spectrochemical titration of **FQ1** upon the titration of Zn^{2+} (0.2, 0.4, 0.6, 0.8, 1.0, 1.2, and 1.6 equiv) in 10 mM Tris-HCl solution. a) UV–vis absorption (10 μ M) change at 350 nm and 405 nm. b) Fluorescence emission intensity (5 μ M, λ_{ex} = 405 nm) change at 540 nm and 620 nm.



Figure S2. Spectrochemical titration of FQ1 upon the titration of Zn^{2+} (0.2, 0.4, 0.6, 0.8, 1.0, 1.2, and 1.6 equiv) in 10 mM Tris-HCl solution. The ratios of I_{620nm}/I_{540nm} as a function of Zn^{2+} concentrations

4. Job's Plot⁸⁵.

A series of solutions containing **FQ1** and $Zn(ClO_4)_2$ were prepared such that the sum of the total metal and total **FQ1** concentration remained constant at 25 μ M. The molar fraction x of **FQ1** was varied between 0.1 and 1.0. The corrected absorbance $(A_{(L/M)}-A_{(L)})\bullet X_{(L)}$ of each solution at 320 and 350 nm were plotted against the molar fraction of the sample solution (Figure S3).



Figure S3. Job's plot for FQ1 in 10 mM Tris-HCl solution. The sum of the concentrations of ligand and Zn^{2+} is 25 μ M.

5. Determination of Apparent Dissociation Constant (K_d) with Zn^{2+} .

A series of HEPES (4-(2-hydroxyerhyl)piperazine-1-erhanesulfonic acid) solution (25 mM, pH = 7.4, 0.1 NaClO₄, 15% (V/V) DMSO) were prepared that contained 9 mM NTA (nitrilotriacetic acid) and 0–8.5 mM Zn(ClO₄)₂. The log*K* and p*K*a values were taken from literature^{S6}.

 $(\log K (ZnL) = 10.66 (20^{\circ}C, = 0.1) \text{ and } pK_{a1} = 9.73, pK_{a2} = 2.49, pK_{a3} = 1.89).$ Protonation constants must be corrected upward by 0.11 when working at 0.1 M ionic strength. Then, free Zn²⁺ concentration was calculated using the method described in ref. S7.

$$\begin{split} &[Zn^{2+}]_{\text{free}} = [Zn^{2+}]_{\text{total}} / ([K(ZnL)]\alpha_{\text{M}}[L]_{\text{free}}) \\ &\alpha_{\text{M}} = 1 + 10^{\text{pH-pKa1}} + 10^{2\text{pH-pKa1-pKa2}} + 10^{3\text{pH-pKa1-pKa2-pKa3}} \\ &[L]_{\text{free}} \approx [L]_{\text{total}} - [Zn^{2+}]_{\text{total}} \end{split}$$

 $[L]_{total}$ was set to 9mM, and $[Zn^{2+}]_{total}$ was varied from 0 to 8.5 mM. Thus, a series of $[Zn^{2+}]_{free}$ was obtained:

$[Zn^{2+}]_{total} (mM)$	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
$[Zn^{2+}]_{free}$ (nM)	0.36	0.76	1.21	1.73	2.33	3.02	3.85	4.84	6.05

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(m M)	5 0	5 5	6.0	65	7.0	75	0 0	0.5	

$[Zn^{2+}]_{total} (mM)$	5.0	5.5	6.0	6.5	7.0	7.5	8.0	8.5
$[Zn^{2^+}]_{free}$ (nM)	7.56	9.50	12.1	15.7	21.2	30.2	48.4	102.8

Normalized fluorescence intensities (510 nm) of 2.5 μ M FQ1 as a function of Zn²⁺ concentration were measured in HEPES buffer solution. Free Zn²⁺ concentrations were obtained by using 9 mM NTA/0–8.5 mM Zn(ClO₄)₂ buffer system The solutions were allowed to equilibrate at 20°C for 5 min after each addition. The fluorescence intensity data were fitted to [eq. 1] with 1:1 binding model, and K_d was calculated (Figure S4).

$$F = \frac{[Zn^{2+}]_{\text{free}} F_{\text{max}} + K_d F_{\text{min}}}{K_d + [Zn^{2+}]_{\text{free}}}$$
(1)

Where F = normalized fluorescence intensity, K_d = dissociation constant, F_{min} = fluorescence intensity of free ligand, F_{max} = fluorescence intensity of zinc-loaded sensor and $[Zn^{2+}]_{free}$ is the free Zn^{2+} concentration.

The values of apparent dissociation constants with Zn^{2+} was 21.2±1.2 nM ($R^2 = 0.9975$).



Figure S4. Fluorescence intensity ($\lambda_{ex} = 390 \text{ nm}$, $\lambda_{em} = 510 \text{ nm}$) of FQ1 (2.5 μ M) as a function of Zn²⁺ concentration.

6. Effect of pH on the Fluorescence Intensity



Figure S5. a) Fluorescence intensity ($\lambda_{ex} = 405 \text{ nm}$) of **FQ1** (5 μ M) as various pH values in 10 mM Tris-HCl solution. Intensity of **FQ1** and **ZnFQ1** were measured at 540 nm and 620 nm, respectively.



7. Selectivity Based on Fluorescence Intensity

Figure S6. a) Fluorescence spectra of **FQ1** (5 μ M) in the presence of various metal ions, followed by 1.0 equiv of Zn²⁺ in Tris-HCl buffer. b) White bars represent the fluorescence intensity **FQ1** (5 μ M) at 620 nm with no ion added; Gray bars represent the fluorescence intensity **FQ1** (5 μ M) at 620 nm in the presence of 1 equiv. of Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, Cd²⁺, Hg²⁺, Pb²⁺ and 200 equiv Mg²⁺, Ca²⁺, Na⁺, and K⁺; Black bars represent the fluorescence intensity at 620 nm of **FQ1** (5 μ M) in the presence of the indicated metal ions, followed by 1 equiv of Zn²⁺.

8. Confocal Fluorescence Microscopy.

An Olympus FV-1000 laser scanning microscopy system, based on an IX81 (Olympus, Japan) inverted microscope, was used for confocal fluorescence imaging. The microscope was equipped with a 405 nm Laser Head FV5-LD405-2, 50mw (Olympus, Japan) and UPLSAPO 40x/0.9 (Olympus, Japan) objective.

9. Cell Culture Methods.

NIH 3T3 and HEK 293 cells were obtained from Cell Culture Center, Institute of Basic Medical Sciences Chinese Academy of Medical Sciences; School of Basic Medicine Peking Union Medical College.

HEK293 cells were cultured in Dulbecco's modified Eagle's medium (DMEM, Hyclone) supplemented with 10% fetal calf serum (FCS, Hyclone), 1% penicillin (Hyclone) and 1% streptomycin (Hyclone) at 37°C in a 5/95 CO₂/air incubator. The cells were cultured 3 days before dye loading on a 35 mm diameter glass-bottomed coverslips. Then the cells were incubated with 10 μ M probe **FQ1** for 30 min at 37°C under 5% CO₂, washed with PBS three times and bathed in serum-free DMEM (2 mL) before imaging. Stock solution of Zn(ClO₄)₂ (10 mM) and sodium pyrithione (20 mM) in DMSO were diluted 10-fold with DMEM prior to addition and incubated for 10 min. Excitation wavelength of laser was 405 nm. Emissions were collected at 460–530 nm and 580–680 nm. Images were gathered and processed with Olympus FV10-ASW V0107A-1 software (Olympus, Japan)



Figure S7. Fluorescence images of intracellular Zn^{2+} in HEK 293 cells incubated with **FQ1** (10 μ M). HEK 293 cells incubated with **FQ1** (10 μ M) at 37°C for 30 min (Top); **FQ1** stained cells were exposed to 10 μ M Zn^{2+} and 20 μ M pyrithione at 25°C for 10 min (Bottom). a) Bright-field transmission images. b) Fluorescence images with emission collected at 460–530 nm. c) Fluorescence images with emission collected at 580–680 nm. d) Ratiometric images generated from b) and c).

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10. NMR Data





