ELECTRONIC SUPPLEMENTARY INFORMATION

A fluorescent sensor with a detection level of pM for Cd\(^{2+}\) and nM for Cu\(^{2+}\) based on different mechanisms

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Experimental section
Measurements

UV-vis spectra were recorded on a Shimadzu 3100 spectrometer. Fluorescence measurements were carried out using an Edinburgh Instruments Ltd-FLS920 fluorescence spectrophotometer. $^1$H NMR spectra were recorded on a Bruker AV III 400 MHz NMR spectrometer and $^{13}$C NMR spectra were recorded on a Bruker AV III 100 MHz NMR spectrometer with tetramethysilane (TMS) as an internal standard. Infrared spectra were recorded using a Bruker Vertex 70 FT-IR spectrometer with KBr pellets.

Sample preparation

All tests described in this paper were carried out at room temperature (25 °C) with distilled water. In the experiments of titration with various metal ions, the sensor was dissolved in HEPES acetonitrile-H$_2$O (9:1) buffer solution to afford the test solution (1 × 10^{-5} M). Stock solutions (1 × 10^{-5} M) of the mental salts of LiCl, NaCl, KCl, MgCl$_2$, CaCl$_2$, BaCl$_2$, NiCl$_2$, CuCl$_2$, ZnCl$_2$, CdCl$_2$, HgCl$_2$, PbCl$_2$, AgNO$_3$, MnCl$_2$, FeCl$_3$, CoCl$_2$, CrCl$_3$, SrCl$_3$, AlCl$_3$, CuCl$_2$, Cu(NO$_3$)$_2$, CuSO$_4$ and (COOHCOO)$_2$Cu in water were prepared. Stock solutions (1 × 10^{-5} M) of the anion salts of CH$_3$COONa, NaBF$_4$, NaF, NaCl, NaBr, NaI, NaNO$_3$, NaNO$_2$, Na$_2$S, NaHSO$_3$, Na$_2$S$_2$O$_3$, NaSO$_4$, Na$_3$PO$_4$, Na$_2$HPO$_4$, NaH$_2$PO$_4$, Na$_4$P$_2$O$_7$, ATP, ADP and AMP in water were prepared. Stock solutions (1 × 10^{-5} M) of the anion acids of Glycine, Leucine, Isoleucine, Valine, Proline, Phenylalanine, Methionine, Tryptophan, Cysteine, Asparagine, Tyrosine, Aspartic acid, Glutamic acid, Lysine, Arginine, Histidine and Glutamine in water were prepared.

Calculation of quantum yield
The quantum yield of sensor $L$ was determined according to the following equation:

$$
\phi_u = \phi_s \frac{F_u A_u n_u^2}{F_s A_s n_s^2}
$$

where $\phi$ is fluorescence quantum yield; $F$ is integrated area under the corrected emission spectra; $A$ is the absorbance at the excitation wavelength; $n$ is the refractive index of the solution; the subscripts $u$ and $s$ refer to the unknown and the standard, respectively. Rhodamine B in ethanol solution was used as the standard, which has a quantum yield of 0.97.

Synthesis

N-{2-[bis(pyridin-2-ylmethyl)amino]ethyl}benzimidazo[2,1-a]benz[de]isoquinoline-7-one-12-carboxamide ($L$). Compound 1 (Benzimidazo[2,1-a]benz[de]isoquinoline-7-one-12-carboxylic acid) and compound 2 (Benzimidazo[2,1-a]benz[de]isoquinoline-7-one-12-carbonyl chloride) were prepared according to our previous work.\(^1\) Compound 2 (0.20 g, 0.60 mmol) was suspended in 20 ml chloroform and then equimolar N,N-bis(pyridin-2-ylmethyl)ethane-1,2-diamine (0.145 g, 0.60 mmol) was added dropwise. The mixture was stirred at room temperature for 1h. Then the organic mixture was washed with $\text{Na}_2\text{CO}_3$ solution (5%) (50 ml×3), and dried over anhydrous $\text{Na}_2\text{SO}_4$. After removing the solvent by evaporation at reduced pressure, the crude product $L$ was obtained. The crude product was then washed with methanol (30 ml×3) and get the pure compound $L$. Yield: 0.29 g, 90%. Ms (ESI): m/z = 562.2226 [M+Na]$^+$. FTIR (KBr, cm$^{-1}$): 1720 (C=O), 1230 (C-N). \(^1\)H NMR (400 MHz, CDCl$_3$): 9.93 (t, 1H), 8.83 (dd, 1H), 8.69 (m, 2H), 8.50 (m, 2H), 8.33 (td, 2H), 8.16 (d, 1H), 7.87 (m, 1H), 7.60 (m, 4H), 7.35 (td, 2H), 7.03 (m, 2H), 4.06 (s, 4H), 3.88 (q, 2H), 3.03 (t, 2H). \(^1\)C NMR (400 MHz, CDCl$_3$): δ 164.86, 160.59, 149.36, 148.99, 141.10, 136.41, 135.75, 132.66,
132.21, 131.93, 128.15, 127.19, 125.38, 123.13, 122.83, 121.97, 119.56, 118.86, 60.36, 53.75, 37.70. Element analysis for $\text{C}_{19}\text{H}_{10}\text{N}_{2}\text{O}_{3}$ (%): C 73.54, H 4.89, N 15.55, O 5.91 calculated C 73.59, H 4.87, N 15.60, O 5.94.

**Scheme S1.** Synthetic routes of L. Conditions: (i) CH$_3$COOH, at 118°C for 20 h; (ii) CH$_2$Cl$_2$, at room temperature overnight; (iii) CHCl$_3$, at room temperature for 1 h.
**Figure S1.** Absorption spectra of L (1×10^{-5} M) in acetonitrile-H_{2}O (9:1) containing HEPES (0.01 M, pH=7.4) buffer solution in the presence of various metal ions (Li^{+}, Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Ag^{+}, Mn^{2+}, Fe^{3+}, Co^{3+}, Cr^{3+}, Sr^{3+} and Al^{3+}).

**Figure S2.** Changes in the absorption spectra of L (1×10^{-5} M) in acetonitrile-H_{2}O (9:1) containing HEPES (0.01 M, pH=7.4) upon titration with Cd^{2+} (1×10^{-5} M).

**Figure S3.** Change ratio of absorbance of L (1×10^{-5} M) upon addition of Cd^{2+} (1×10^{-5} M) in
acetonitrile-H$_2$O (9:1) containing HEPES (0.01 M, pH=7.4) at 25 °C. Absorbance is monitored at 387 nm.

**Figure S4.** Changes in the fluorescence spectra of L (1×10$^{-5}$ M) in acetonitrile-H$_2$O (9:1) containing HEPES (0.01 M, pH=7.4) as the concentration of Cd$^{2+}$ (1×10$^{-11}$ M) increased from 0 to 10$^{-10}$ M. Insert: Change ratio of fluorescence of L (1×10$^{-5}$ M) upon addition of Cd$^{2+}$ (1×10$^{-11}$ M). Excitation is at 370 nm.

**Figure S5.** Change ratio of fluorescence of L (1×10$^{-5}$ M) upon addition of Cd$^{2+}$ (1×10$^{-5}$ M) in
acetonitrile-H$_2$O (9:1) containing HEPES (0.01 M, pH=7.4) at 25 °C. Excitation is at 370 nm, and emission is monitored at 501 nm.

**Figure S6.** Job’s plot of the L$^+$Cd$^{2+}$ complex in acetonitrile-H$_2$O (9:1) containing HEPES (0.01 M, pH=7.4) at 25 °C. The total concentration of L and Cd$^{2+}$ was 0.1 mM. Excitation is at 370 nm, and emission is monitored at 501 nm.

**Figure S7.** Metal ion selectivity profiles of L ($1\times10^{-5}$ M) in the presence of various metal ions in acetonitrile-H$_2$O (9:1) containing HEPES (0.01 M, pH=7.4) at 25 °C: (black bars) fluorescence intensity at 501 nm in the presence of 3 equiv. of (Li$^+$, Na$^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, Ba$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Hg$^{2+}$, Pb$^{2+}$, Ag$^+$, Mn$^{2+}$, Fe$^{3+}$, Co$^{2+}$, Cr$^{3+}$, Sr$^{3+}$ and Al$^{3+}$); (red bars) fluorescence intensity in the
presence of 1 equiv. of \( \text{Cd}^{2+} \) followed by (3 equiv. of \( \text{Li}^+ \), \( \text{Na}^+ \), \( \text{K}^+ \), \( \text{Mg}^{2+} \), \( \text{Ca}^{2+} \), \( \text{Ba}^{2+} \), \( \text{Zn}^{2+} \), \( \text{Hg}^{2+} \), \( \text{Pb}^{2+} \), \( \text{Ag}^+ \), \( \text{Mn}^{2+} \), \( \text{Fe}^{3+} \), \( \text{Co}^{2+} \), \( \text{Cr}^{3+} \), \( \text{Sr}^{3+} \) and \( \text{Al}^{3+} \); 1 equiv. of \( \text{Cu}^{2+} \), \( \text{Ni}^{2+} \)). Excitation is at 370 nm.

**Figure S8.** Fluorescence spectra of L-\( \text{Cd}^{2+} \) complex (1×10^{-5} M) in acetonitrile-\( \text{H}_2\text{O} \) (9:1) containing HEPES (0.01 M, pH=7.4) buffer solution in the presence of various anions (Ac\(^-\), BF\(_4^-\), F\(^-\), Cl\(^-\), Br\(^-\), I\(^-\), NO\(_3^-\), NO\(_2^-\), S\(^2-\), HSO\(_3^-\), S\(_2\)O\(_3\)\(^2-\), SO\(_4^{2-}\), PO\(_4^{3-}\), HPO\(_4^{2-}\), H\(_2\)PO\(_4^-\), PPI, ATP, ADP, AMP). Excitation wavelength is at 370 nm.

**Figure S9.** Changes in the fluorescence spectra of L-\( \text{Cd}^{2+} \) in acetonitrile-\( \text{H}_2\text{O} \) (9:1) containing HEPES (0.01 M, pH=7.4) upon titration with PPI (1×10^{-5} M). Insert: the concomitant on-off color change under UV light. Excitation is at 370 nm.
Figure S10. Change ratio of fluorescence of L-Cd$^{2+}$ ($1\times10^{-5}$ M) upon addition of PPi ($1\times10^{-5}$ M) in acetonitrile-H$_2$O (9:1) containing HEPES (0.01 M, pH=7.4) at 25 °C. Excitation is at 370 nm, and emission is monitored at 501 nm.

Figure S11. Reversible switching of the emission of L by repeated addition of Cd$^{2+}$ and PPi. Excitation is at 370 nm, and emission is at 501 nm.
Figure S12. Fluorescence spectra of L-Cd$^{2+}$ complex ($1 \times 10^{-5}$ M) in acetonitrile-H$_2$O (9:1) containing HEPES (0.01 M, pH=7.4) buffer solution in the presence of various amino acids (Glycine, Leucine, Isoleucine, Valine, Proline, Phenylalanine, Methionine, Tryptophan, Cysteine, Asparagine, Tyrosine, Aspartic acid, Glutamic acid, Lysine, Arginine, Histidine, Glutamine). Excitation wavelength is at 370 nm.

Figure S13. The fluorescence intensity of L at various pH values at room temperature in acetonitrile-H$_2$O (9:1) solution.
Figure S14. Absorption spectra of L \((1\times10^{-5} \text{ M})\) in water containing HEPES \((0.01 \text{ M}, \text{pH}=3.5)\) buffer solution in the presence of various metal ions \((\text{Li}^+, \text{Na}^+, \text{K}^+, \text{Mg}^{2+}, \text{Ca}^{2+}, \text{Ba}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Cd}^{2+}, \text{Hg}^{2+}, \text{Pb}^{2+}, \text{Ag}^+, \text{Mn}^{2+}, \text{Fe}^{3+}, \text{Co}^{2+}, \text{Cr}^{3+}, \text{Sr}^{3+} \text{and Al}^{3+})\).

Figure S15. Changes in the absorption spectra of L \((1\times10^{-5} \text{ M})\) in water containing HEPES \((0.01 \text{ M}, \text{pH}=3.5)\) upon titration with Cu\(^{2+}\) \((1\times10^{-5} \text{ M})\).
Figure S16. Change ratio of fluorescence of L upon addition of Cu\(^{2+}\) (1×10\(^{-5}\) M) in water containing HEPES (0.01 M, pH=3.5) at 25 °C. Excitation is at 370 nm, and emission is monitored at 515 nm.

Figure S17. Metal ion selectivity profiles of L (1×10\(^{-5}\) M) in the presence of various metal ions in water containing HEPES (0.01 M, pH=3.5) at 25 °C: (black bars) fluorescence intensity at 515 nm in the presence of 3 equiv. of (Li\(^+\), Na\(^+\), K\(^+\), Mg\(^{2+}\), Ca\(^{2+}\), Ba\(^{2+}\), Ni\(^{2+}\), Zn\(^{2+}\), Cd\(^{2+}\), Hg\(^{2+}\), Pb\(^{2+}\), Ag\(^+\), Mn\(^{2+}\), Fe\(^{3+}\), Co\(^{2+}\), Cr\(^{3+}\), Sr\(^{3+}\) and Al\(^{3+}\)); (red bars) fluorescence intensity in the presence of 1 equiv. of Cu\(^{2+}\) followed by (3 equiv. of Li\(^+\), Na\(^+\), K\(^+\), Mg\(^{2+}\), Ca\(^{2+}\), Ba\(^{2+}\), Ni\(^{2+}\) Zn\(^{2+}\), Cd\(^{2+}\), Hg\(^{2+}\), Pb\(^{2+}\), Ag\(^+\), Mn\(^{2+}\), Fe\(^{3+}\), Co\(^{2+}\), Cr\(^{3+}\), Sr\(^{3+}\) and Al\(^{3+}\)). Excitation is at 370 nm.
Figure S18. Fluorescence intensity of L upon addition of 1 equiv of Cu$^{2+}$ in the presence of 3 equiv of other metal ions (Li$^+$, Na$^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, Ba$^{2+}$, Ni$^{2+}$, Zn$^{2+}$, Cd$^{2+}$, Hg$^{2+}$, Pb$^{2+}$, Ag$^+$, Mn$^{2+}$, Fe$^{3+}$, Co$^{2+}$, Cr$^{3+}$, Sr$^{2+}$ and Al$^{3+}$) in water (9:1) containing HEPES (0.01 M, pH=3.5) at 25 °C. Excitation is at 370 nm.

Figure S19. Fluorescence intensity of L in the presence of 1 equiv of CuCl$_2$, Cu(NO$_3$)$_2$, CuSO$_4$ and Cu(CH$_3$COO)$_2$ in water containing HEPES (0.01 M, pH=3.5) at 25 °C. Emission is at 515 nm, and excitation is at 370 nm.
Figure S20. $^1$H NMR spectra of L in CDCl$_3$.

Figure S21. $^{13}$C NMR spectra of L in CDCl$_3$. 
Figure S22. The mass spectrum of L+Na.

References