## Supporting information for Chemical Communications

# Selective and sensitive "turn-on" fluorescent Zn<sup>2+</sup> sensors based on di- and tripyrrins with readily modulated emission wavelengths

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#### **Experimental Section**

#### General

Commercial available solvents and reagents were used as received. Deuterated solvents for NMR measurements were available from Aldrich. UV-Vis absorption spectra were recorded by a Varian Cary 100 spectrophotometer and fluorescence spectra were recorded on a Varian Cray Eclipse fluorescence spectrophotometer, with a quartz cuvette (path length = 1 cm); both spectrophotometers were standardized. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were obtained using a Bruker AM 400 spectrometer with tetramethylsilane (TMS) as the internal standard. Mass spectra (MS) were carried out on an TOF MS instrument. Column chromatography was carried out in air using silica gel (200-300 mesh). Reactions were monitored by thin-layer chromatography. PD2,<sup>1</sup> PD3,<sup>2</sup> D1<sup>3a</sup> and D4<sup>3b</sup> were prepared according to reported methods.



Scheme S1 Synthesis of sensors D2 and D3.

Preparation of compound (D2).<sup>3c</sup> PD2 (340 mg, 1 mmol) was dissolved in 250 mL of CH<sub>2</sub>Cl<sub>2</sub>, then DDQ (340 mg, 1.5 mmol) was added. The mixture was stirred at room temperature for 30 min and then directly purified by silica gel column (Eluent: CH<sub>2</sub>Cl<sub>2</sub> : PE=1:1) to afford the crude product D2 which was recrystallized from CH<sub>2</sub>Cl<sub>2</sub> and *n*-hexane (251 mg, yield: 74.2%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, Bruker 400 MHz, 298K):  $\delta$  12.76 (b, 1H, CHO-H), 9.72 (s, 1H, Pyrrolic-NH), 8.16 (s, 1H, Pyrrolic- $\alpha$ H), 6.90 (d, 1H, J =4.4 Hz, Pyrrolic), 6.71 (d, 1H, J =4.8 Hz, Pyrrolic), 6.65 (d, 1H, J =4.8 Hz, Pyrrolic), 6.26 (d, 1H, J =4.0 Hz, Pyrrolic). <sup>13</sup>C NMR (CDCl<sub>3</sub>, Bruker 100 MHz, 298K):

 $\delta$  180.49, 163.74, 153.16, 139.27, 136.07, 133.60, 128.51, 119.91, 119.65. HRMS: obsd 339.0562 , calcd for  $C_{16}H_8F_5N_2O~([M+H~]^+)$ : 339.0557.

Preparation of compound (D3). <sup>3c</sup> PD3 (500 mg, 1.2 mmol) was dissolved in 300 mL of CH<sub>2</sub>Cl<sub>2</sub>, then DDQ (409 mg, 1.8 mmol) was added. The mixture was stirred at room temperature for 1 h and then directly purified by silica gel column (Eluent: CH<sub>2</sub>Cl<sub>2</sub>) to afford the crude product D3 which was recrystallized from CH<sub>2</sub>Cl<sub>2</sub> and *n*-hexane (205 mg, yield: 41.2%). <sup>1</sup>HNMR: (CDCl<sub>3</sub>, Bruker 400 MHz, 298K):  $\delta$  12.89 (s, 1H, pyrrolic-NH), 8.16 (s, 1H, pyrrolic), 7.93 (t, 2H, Ph-H), 7.59 (t, 1H, Ph-H), 7.5 (t, 2H, Ph-H), 6.8 (d, 1H, *J* = 4.0 Hz, pyrrolic), 6.71(d, 1H, *J* = 4.4 Hz, pyrrolic), 6.64 (d, 1H, *J* = 4.8 Hz, pyrrolic), 6.27 (d, 1H, *J* = 4.0 Hz, pyrrolic). <sup>13</sup>C NMR (CDCl<sub>3</sub>, Bruker 100 MHz, 298K):  $\delta$  185.10, 163.39, 152.76, 138.49, 137.88, 135.28, 133.44, 132.38, 129.08, 128.47, 128.13, 122.36, 119.63, 119.23. HRMS: obsd 415.0874, calcd for C<sub>22</sub>H<sub>12</sub>F<sub>5</sub>N<sub>2</sub>O ([M+H]<sup>+</sup>): 415.0870.

#### Sensor D4 applied in aqueous solution

In order to test sensor D4 as a potential biological fluorescent sensor, we investigated its performance in aqueous solution. All measurements were carried out in HEPES buffer (DMF/50mM HEPES, 4:1, v:v, pH 7.2). The concentration of sensor D4 was fixed at  $1 \times 10^{-5}$  M. As shown in Figure S7a, the binding behavior is similar to that observed in DMF. Upon addition of Zn<sup>2+</sup> (0–1.2eq.), the peak centered at 528 nm decreases gradually with a new sharp peak developed at about 616 nm. D4 shows weak fluorescence, but the fluorescence intensity was greatly enhanced with a maximal emission at 629 nm upon addition of Zn<sup>2+</sup> (Fig. S7b). When various metal ions were added respectively to the solution of D4, only Zn<sup>2+</sup> greatly enhanced its fluorescence intensity (Fig. S7c). These results suggest that D4 is a promising candidate for biological imaging. Competition experiments also give inspiring results as shown in Figure S7d, with the fluorescence intensity almost unaffected by other ions. All these results prompted us to further investigate its possible applications in bioimaging.

### Crystallography

Single crystals suitable for X-ray analysis of  $[Zn(D2)_2]$ ,  $[Zn(D3)_2]$ ·MeOH and  $[ZnD4(H_2O)_2]$ ·2MeOH were obtained by slow evaporation of a MeOH-H<sub>2</sub>O solution of the corresponding zinc complex at room temperature.

Crystal data for  $[Zn(D2)_2]$ :  $C_{32}H_{12}F_{10}N_4O_2Zn$ ,  $Mw = 739.83 \text{ g}\cdot\text{mol}^{-1}$ ,  $0.48 \times 0.46 \times 0.21 \text{ mm}^3$ , Monoclinic, C2/c, a = 56.690(5), b = 7.6550(8), c = 13.1551(12) Å,  $\beta = 92.7360(10)^\circ$ , V = 5702.3(9) Å<sup>3</sup>, F(000) = 2944,  $\rho_{calcd} = 1.724 \text{ Mg}\cdot\text{m}^{-3}$ ,  $\mu(Mo\cdotK\alpha) = 0.967 \text{ mm}^{-1}$ , T = 298(2) K, 13570 data were measured on a Bruker SMART Apex diffractometer, of which 5012 were unique ( $R_{int} = 0.0655$ ); 442 parameters were refined against Fo<sup>2</sup> (all data), final wR2 = 0.1570, S = 1.081, R1 (I > 2\sigma(I)) = 0.0729, largest final difference peak/hole = +0.615/-0.926 e Å<sup>-3</sup>. Structure solution by direct methods and full-matrix least-squares refinement against F<sup>2</sup> (all data) using SHELXTL.

[**Zn(D3)**<sub>2</sub>]·**MeOH**: C<sub>45</sub>H<sub>24</sub>F<sub>10</sub>N<sub>4</sub>O<sub>3</sub>Zn, Mw = 924.05 g·mol<sup>-1</sup>, 0.22 × 0.16 × 0.12 mm<sup>3</sup>, Monoclinic, C2/c, a = 28.864(2), b = 10.2060(10), c = 14.8521(13) Å, β = 115.894(2)°, V = 3936.0(6) Å<sup>3</sup>, F(000) = 1864,  $\rho_{calcd}$  = 1.559 Mg·m<sup>-3</sup>,  $\mu$ (Mo-K $\alpha$ ) = 0.720 mm<sup>-1</sup>, T = 298(2) K, 9831 data were measured on a Bruker SMART Apex diffractometer, of which 3460 were unique (R<sub>int</sub> = 0.0812); 290 parameters were refined against Fo<sup>2</sup> (all data), final wR2= 0.0840, S= 1.009, R1 (I > 2 $\sigma$ (I))= 0.0516, largest final difference peak/hole = +0.487/-0.344 e Å<sup>-3</sup>. Structure solution by direct methods and full-matrix least-squares refinement against F<sup>2</sup> (all data) using SHELXTL.

[ZnD4(H<sub>2</sub>O)<sub>2</sub>]·2MeOH:  $C_{28}H_{19}F_{10}N_3O_5Zn$ , Mw = 732.83 g·mol<sup>-1</sup>, 0.40 × 0.34 × 0.14 mm<sup>3</sup>, Orthorhombic, P2(1)2(1)2(1), a = 7.5070(8), b = 16.0921(17), c = 49.020(4) Å,  $\beta = 90^{\circ}$ , V = 5921.8(10) Å<sup>3</sup>, F(000) = 2944, Dc = 1.644 Mg·m<sup>-3</sup>,  $\mu$ (Mo-K $\alpha$ ) = 0.936 mm<sup>-1</sup>, T = 298(2) K, 29656 data were measured on a Bruker SMART Apex diffractometer, of which 10345 were

unique ( $R_{int} = 0.1375$ ); 852 parameters were refined against Fo<sup>2</sup> (all data), final wR2= 0.3127, S= 1.047, R1 (I > 2\sigma(I))= 0.1298, largest final difference peak/hole = +0.912/-0.891 e Å<sup>-3</sup>. Structure solution by direct methods and full-matrix least-squares refinement against F<sup>2</sup> (all data) using SHELXTL.

#### **DFT** calculations

All calculations were carried out by using the Gaussian03 program package.<sup>4</sup> The geometries of all compounds were optimized by density functional calculations employing the hybrid B3LYP function.<sup>5</sup> The LANL2DZ basis set<sup>6</sup> was used for Zn atom while the 6-31G\* basis set<sup>7</sup> was adopted to describe other atoms. Subsequent single-point calculations were performed with the same method and basis sets, but in a DMF solvent environment<sup>8</sup> represented by the polarizable continuum model. The calculated HOMO/LUMO energies are listed in Table S2. Molecular structures and molecular orbitals were visualized by the Gabedit software.<sup>9</sup>

## **Detection Limits<sup>10</sup>**

The detection limits of sensors D1-D4 were obtained according to the literature method. Take D4 as the example: Fluorescence changes during the titration of D4 (0.2  $\mu$ M) with Zn<sup>2+</sup> (0-0.6  $\mu$ M) in DMF is shown in Figure S18a. The enhancement of fluorescence intensity is clearly resolved and has a good signal to noise ratio. The intensity data normalized between the minimum intensity (free D4) and the maximum intensity (0.6  $\mu$ M Zn<sup>2+</sup> added) are shown in Figure S18a (inset). A linear regression curve was fitted to the five intermediate values (50 nM-0.25  $\mu$ M Zn<sup>2+</sup>) as shown in Figure S18b. The detection limit of D4 to Zn<sup>2+</sup> was calculated to be 46 nM.

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# **Tables and figures**

[ZnD4(H <sub>2</sub> O) <sub>2</sub> ]·2MeOH	Free ligand D4	
Dihedral angle between plane A and B: 5.98 (5)°	Dihedral angle between plane A and B: 9.97(1)°	
Dihedral angle between plane A and C: 8.66(8)°	between plane A and C: 8.66(8)° Dihedral angle between plane A and C: 26.12(4)°	
Dihedral angle between plane B and C: 3.98(3)°	Dihedral angle between plane B and C: 20.11(3)°	

**Table S1.** Dihedral angles for [ZnD4(H<sub>2</sub>O)<sub>2</sub>]·2MeOH and free D4, with the crystal information of free D4 adapted from the literature.<sup>3b</sup>

Table S2. Calculated HOMO/LUMO energies of free ligands and zinc complexes of sensors D1~D4.

Compound	E(HOMO)	E(LUMO)	ΔΕ
D1	-5.66	-2.48	3.18
D2	-6.07	-2.93	3.14
D3	-6.00	-2.89	3.11
D4	-5.50	-3.00	2.50
$[Zn(D1)_2]$	-5.57	-2.46	3.11
$[Zn(D2)_2]$	-5.81	-2.86	2.95
$[Zn(D3)_2]$	-5.68	-2.77	2.91
$[Zn(D4)(DMF)_2]$	-4.85	-2.49	2.36



190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

Fig. S2. The <sup>13</sup>C NMR spectrum of D2 in CDCl<sub>3</sub>.



Fig. S4. The <sup>1</sup>H NMR spectrum of D3 in CDCl<sub>3</sub>.









Fig. S7. a) Absorbance changes during the titration of D4 (10  $\mu$ M) with Zn<sup>2+</sup> in HEPES buffer (DMF/50mM HEPES, 4:1, v:v, pH 7.2). b) Fluorescence changes during the titration of D4 (10  $\mu$ M) with Zn<sup>2+</sup> in HEPES buffer (DMF/50mM HEPES, 4:1, v:v, pH 7.2). Excitation wavelength was fixed at 564 nm (one of the isosbestic points) during titration. c) Fluorescence spectra ( $\lambda_{ex} = 564$  nm) of D4 (10  $\mu$ M) in the presence of various metal ions in aqueous solution (DMF/50mM HEPES, 4:1, v:v, pH 7.2). d) White bars represent the addition of 1 equiv of metal ions (for Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, 100 equiv and Ca<sup>2+</sup>, 10 equiv) to a 10  $\mu$ M solution of D4. Black bars represent the addition of 1 equiv) to a 10  $\mu$ M solution of D4.



**Fig. S8.** a) Absorbance changes during the titration of D1 (10  $\mu$ M) with Zn<sup>2+</sup> in DMF. Inset: normalized absorbance changes at 494 nm as a function of the concentration of Zn<sup>2+</sup>. b) Fluorescence changes during the titration of D1 (10  $\mu$ M) with Zn<sup>2+</sup> in DMF. Excitation wavelength was fixed at 458 nm (one of the isosbestic points) during titration. c) Fluorescence spectra ( $\lambda_{ex} = 458$  nm) of D1 (10  $\mu$ M) in the presence of various metal ions in DMF. d) White bars represent the addition of 1 equiv of metal ions (for Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>,100 equiv and Ca<sup>2+</sup>, 10 equiv) to a 10  $\mu$ M solution of D1. Black bars represent the addition of 1 equiv of Zn<sup>2+</sup> mixed with 1 equiv of other metal ions (for Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>,100 equiv and Ca<sup>2+</sup>, 10 equiv) to a 10  $\mu$ M solution of D1.



**Fig. S9.** a) Absorbance changes during the titration of D2 (10  $\mu$ M) with Zn<sup>2+</sup> in DMF. Inset: normalized absorbance changes at 510 nm as a function of the concentration of Zn<sup>2+</sup>. b) Fluorescence changes during the titration of D2 (10  $\mu$ M) with Zn<sup>2+</sup> in DMF. Excitation wavelength was fixed at 449 nm (one of the isosbestic points) during titration. c) Fluorescence spectra ( $\lambda_{ex} = 449$  nm) of D2 (10  $\mu$ M) in the presence of various metal ions in DMF. d) White bars represent the addition of 1 equiv of metal ions (for Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>,100 equiv and Ca<sup>2+</sup>, 10 equiv) to a 10  $\mu$ M solution of D2. Black bars represent the addition of 1 equiv of Zn<sup>2+</sup> mixed with 1 equiv of other metal ions (for Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>,100 equiv and Ca<sup>2+</sup>, 10 equiv) to a 10  $\mu$ M solution of D2.



**Fig. S10.** a) Absorbance changes during the titration of D3 (10  $\mu$ M) with Zn<sup>2+</sup> in DMF. Inset: normalized absorbance changes at 515 nm as a function of the concentration of Zn<sup>2+</sup>. b) Fluorescence changes during the titration of D3 (10  $\mu$ M) with Zn<sup>2+</sup> in DMF. Excitation wavelength was fixed at 457 nm (one of the isosbestic points) during titration. c) Fluorescence spectra ( $\lambda_{ex} = 457$  nm) of D3 (10  $\mu$ M) in the presence of various metal ions in DMF. d) White bars represent the addition of 1 equiv of metal ions (for Na<sup>+</sup>, K<sup>+</sup>, 100 equiv and Ca<sup>2+</sup>, 10 equiv) to a 10  $\mu$ M solution of D3. Black bars represent the addition of 1 equiv of Zn<sup>2+</sup> mixed with 1 equiv of other metal ions (for Na<sup>+</sup>, K<sup>+</sup>, 100 equiv and Ca<sup>2+</sup>, 10 equiv) to a 10  $\mu$ M solution of D3.



**Fig. S11.** Images of sensors D1 $\sim$ D4 (10  $\mu$ M) in the absence (A, C) and presence (B, D) of 1 equiv. of Zn<sup>2+</sup> in DMF. A, B) bright field images, C, D) images taken under a portable UV lamp.



Fig. S12. X-ray crystal structure of  $[Zn(D2)_2]$  complex. a) top view, b) side view. Hydrogen atoms are omitted for clarity.



Fig. S13. X-ray crystal structure of  $[Zn(D3)_2]$ ·MeOH complex. a) top view, b) side view. Hydrogen atoms are omitted for clarity.



Fig. S14. Frontier orbital energy diagrams of [Zn(D1)<sub>2</sub>], [Zn(D2)<sub>2</sub>], [Zn(D3)<sub>2</sub>], and [Zn(D4)(DMF)<sub>2</sub>].



**Fig. S15.** a) Fluorescence changes during the titration of D1 (0.5  $\mu$ M) with Zn<sup>2+</sup> (0-1.5  $\mu$ M) in DMF, inset: Normalized intensity between the minimum intensity (free D1) and the maximum intensity (1.5  $\mu$ M Zn<sup>2+</sup> added). b) A plot of (I-I<sub>min</sub>)/(I<sub>max</sub>-I<sub>min</sub>) vs Log([Zn<sup>2+</sup>]), the calculated detection limit of sensor D1 is 1.1×10<sup>-7</sup> M.



Fig. S16. a) Fluorescence changes during the titration of D2 (0.4  $\mu$ M) with Zn<sup>2+</sup> (0-1.4  $\mu$ M) in DMF, inset: Normalized intensity between the minimum intensity (free D2) and the maximum intensity (1.4  $\mu$ M Zn<sup>2+</sup> added). b) A plot of (I-I<sub>min</sub>)/(I<sub>max</sub>-I<sub>min</sub>) vs Log([Zn<sup>2+</sup>]), the calculated detection limit of sensor D2 is 2.7×10<sup>-7</sup> M



Fig. S17. a) Fluorescence changes during the titration of D3 (0.3  $\mu$ M) with Zn<sup>2+</sup> (0-0.9  $\mu$ M) in DMF, inset: Normalized intensity between the minimum intensity (free D3) and the maximum intensity (0.9  $\mu$ M Zn<sup>2+</sup> added). b) A plot of (I-I<sub>min</sub>)/(I<sub>max</sub>-I<sub>min</sub>) vs Log([Zn<sup>2+</sup>]), the calculated detection limit of sensor D3 is 1.3×10<sup>-7</sup> M.



**Fig. S18.** a) Fluorescence changes during the titration of D4 (0.2  $\mu$ M) with Zn<sup>2+</sup> (0-0.6  $\mu$ M) in DMF, inset: Normalized intensity between the minimum intensity (free D4) and the maximum intensity (0.6  $\mu$ M Zn<sup>2+</sup> added). b) A plot of (I-I<sub>min</sub>)/(I<sub>max</sub>-I<sub>min</sub>) vs Log([Zn<sup>2+</sup>]), the calculated detection limit of sensor D4 is 4.6×10<sup>-8</sup> M.