Detection of Zn(II) ions by fluorescent pyrene-derived molecular probes

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Supplementary Material:

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UV-Vis experiments: The general procedure for the molar absorptivity of compounds **3a** and **3b** was carried out as follows. A stock solution (1.32×10^{-5} M) of compound **3a** was prepared by dissolving 0.5 mg in 50 mL of CH_3CN . Compound **3b** was prepared by dissolving 0.8 mg in 50 mL CH_3CN (2.12×10^{-5} M) and then 1 mL was transferred to the UV-Vis cell. From the stock solution six successive dilutions were carried out, Table S1, shows the molar absorptivity calculated for each new compound.

Table S1: molar absorptivity for compounds *ortho*-**3a** and *meta*-**3b** in CH_3CN ($\text{M}^{-1}\text{cm}^{-1}$).

	240 nm	274 nm	326 nm	340 nm
<i>ortho</i> - 3a	8.9×10^4	5.3×10^4	3.4×10^4	4.4×10^4
<i>meta</i> - 3b	5.3×10^4	3.4×10^4	2.0×10^4	2.6×10^4

Figure S1: Molar absorptivity of compounds **3a** and **3b** in CH_3CN .

Figure S2: Fluorescence titrations (CH_3CN , $\lambda_{\text{ex}} = 325$) between **3a** and **3b** upon addition of metal chloride salts ($\text{M} = \text{Hg(II)}$, Cu(II) , Fe(III) , Fe(II) , Al(III) , Cd(II) and Ni(II)). See figure S3 for the ZnCl_2 spectra.

Figure S3: Fluorescence titrations (CH₃CN, λ_{ex} = 325, addition of ZnX₂ (X = F⁻, Cl⁻, Br⁻, I⁻, NO₃⁻, CH₃CO₂⁻, SO₄²⁻, ClO₄⁻ and BF₄⁻)

Figure S4: Fluorescence titrations (CH₃CN, λ_{ex} = 325) between **3a** and **3b** upon addition of metal perchlorates salts (M = Cu(II), Fe(III), and Fe(II), Ca(II), Mg(II) and Na(I)). See figure S2 for the Zn(ClO₄)₂ spectra.

Figure S5: Fluorescence titrations (CH₃CN, λ_{ex} = 325) between **3b** and Zn(ClO₄)₂ in 1% H₂O.

Protocol to determine the concentration of Zn(II)_(aq) by **3b**.

In four parallel experiments, molecular receptor **3b** (3.8 mg, 5.0 μmol) was dissolved in 20 mL $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ (50:50). An aliquot of $\text{Zn}(\text{ClO}_4)_2$ (0.25, 0.5, 0.75 and 1.0) was added to each and the solution refluxed for 24 h. Solvent was removed by rotary evaporation and the solid was dried *in vacuo* and then at 100°C for several days to remove all solvent. A 50 μM solution of each sample was prepared in 100% CH_3CN and the fluorescence spectra recorded (see below). **CAUTION: perchlorate salts are potentially highly explosive and should be treated with extreme care even at the very low concentrations employed here.**

Figure S6: Fluorescence of **3b** and $[\mathbf{3b}\cdot\text{Zn}]^{2+}$ complexes.

Concentration of Zn^{2+} (mM)	Fluorescence intensity (421 nm)
0	0.14
0.07	0.06***
0.081	0.22
0.19	0.39
0.5	0.87

*** point ignored in calibration curve due to solubility

Table S2: Data for Zn(II) binding calibration curve.

Figure S7: Calibration curve generated from fluorescence data demonstrating a linear response.

IR data

Figure S8: ATR-IR data of **3a** on the addition of Zn(ClO₄)₂.

1D (3a and 3b) and 2D NMR (3b): Spectra of free receptor (3b):

Figure S9: ^1H NMR of receptor **3b** in a mixture of CHCl_3 : CH_3CN (1:1).

Figure S10: ¹³C NMR of receptor **3b** in a mixture of CHCl₃:CH₃CN (1:1).

Figure S11: HSQC of receptor **3b** in a mixture of CHCl₃:CH₃CN (1:1) full spectrum.

Figure S12: HSQC of receptor **3b** in a mixture of CHCl₃:CH₃CN (1:1) aromatic region.

Figure S13: COSY of receptor **3b** in a mixture of CHCl₃:CH₃CN (1:1) aromatic region.

Figure S14: ROESY of receptor **3b** in a mixture of CHCl_3 : CH_3CN (1:1) full spectrum.

Figure S15: ^1H NMR aromatic region (Bottom) receptor **3b** without the addition of $\text{Zn}(\text{ClO}_4)_2$ and (Top) upon the addition of five equivalents of $\text{Zn}(\text{ClO}_4)_2$ in a mixture of CHCl_3 : CH_3CN (1:1).

Figure S16: 2D TOCSY for receptor **3b** with the addition of $\text{Zn}(\text{ClO}_4)_2$ in a mixture of $\text{CHCl}_3:\text{CH}_3\text{CN}$ (1:1).

Figure S17: 2D TOCSY aromatic region receptor **3b** with the addition of $\text{Zn}(\text{ClO}_4)_2$ in a mixture of $\text{CHCl}_3:\text{CH}_3\text{CN}$ (1:1).

Figure S18: ROESY spectrum of **3b** after the addition of five equivalents of $\text{Zn}(\text{ClO}_4)_2$ in a mixture of $\text{CHCl}_3:\text{CH}_3\text{CN}$ (1:1).

Figure S19: ROESY expanded spectrum of **3b** after the addition of five equivalents of $\text{Zn}(\text{ClO}_4)_2$ in a mixture of $\text{CHCl}_3:\text{CH}_3\text{CN}$ (1:1).

Figure S20: ^1H NMR of receptor **3a** in DMSO (* dichloromethane, # acetone residual solvent)

Figure S21: ^1H NMR of receptor **3a** in DMSO.

Computational methods: Equilibrium geometries for the ligands (**3a** and **3b**) and their zinc complexes ($[\text{Zn}\cdot\mathbf{3a}](\text{ClO}_4)_2$ and $[\text{Zn}\cdot\mathbf{3b}](\text{ClO}_4)_2$) were determined by full conformational searches of the 676 possible structures (identified through the number of rotatable bonds) followed by molecular mechanics energy minimization methods (using the MMFF force field). No formal bonds between zinc and ligands or anions were introduced. Initial refinement was followed by geometry optimization at semiempirical PM3d level with the resulting structures used as input coordinates for density functional calculations (B3LYP/6-31G*). Calculations were made using Spartan '10 installed on a desktop computer equipped with Intel Xenon Dual Quad Core CPUs running at 2.33 GHz.¹

Table S3: Key interactions in angstroms (Å) and degrees (°).

	3a	3b	$[\text{Zn}\cdot\mathbf{3a}](\text{ClO}_4)_2$	$[\text{Zn}\cdot\mathbf{3b}](\text{ClO}_4)_2$
N-H	1.011	1.013	1.030	1.029
N-H'	1.012	1.012	1.023	1.027
triazoleH	1.079	1.078	1.077	1.078
triazoleH'	1.080	1.079	1.082	1.088
amide C=O	1.230	1.228	1.283	1.279
amide C=O'	1.232	1.233	1.282	1.286
triazole Zn···N	N/A	N/A	2.040	2.018
triazole Zn···N'	N/A	N/A	2.019	2.020
C=O···Zn	N/A	N/A	1.955	1.942
C=O'···Zn	N/A	N/A	1.924	1.949
anion···Zn	N/A	N/A	N/A	N/A
anion'···Zn	N/A	N/A	N/A	N/A
pyrene–pyrene distance	5.523	4.771	10.798	7.382
triazole N'···Zn···N	N/A	N/A	96.45	101.72
C=O'···Zn···O=C	N/A	N/A	115.43	110.64
anion'···Zn···anion	N/A	N/A	N/A	N/A
anion···Zn···O=C	N/A	N/A	N/A	N/A
triazole C=O···Zn···N	N/A	N/A	110.95	111.07
pyrene–pyrene angle	18.48	3.91	43.56	77.49

Job Plot and Limits of detection for [Zn·3a] and [Zn·3b]

Figure S22: mole fraction of Zn^{2+} in **3a** (LHS) and **3b** (RHS).

Figure S23: Calibration graph used to calculate the LoD for Zn(II) **3a**.

References:

1. *Spartan 10* Wavefunction Inc.: Irvine CA, 2010.