Electronic Supporting information

Novel Selective Quinoline-based Fluorescent Probes for Zn^{2+}

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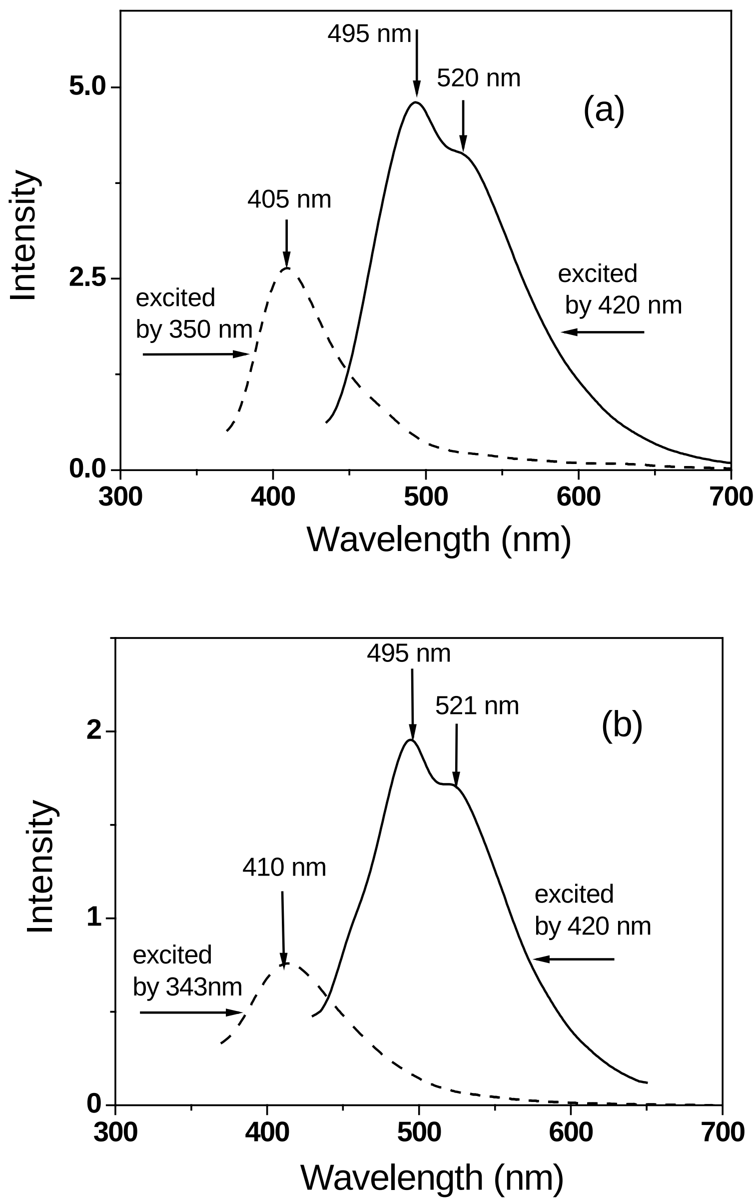

Figure S1. Fluorescence emission spectra at 293 K in DMSO-H_2O (80:20) (a) QB1 (1.0×10^{-4} mol/L) only and zinc perchlorate (2.0×10^{-3} mol/L) was added, respectively. (b) QB2 (1.0×10^{-5} mol/L) only and zinc perchlorate(1.5×10^{-4} mol/L) was added, respectively. The dashed line corresponds to the free chemosensors only and the solid line to the zinc complexes.

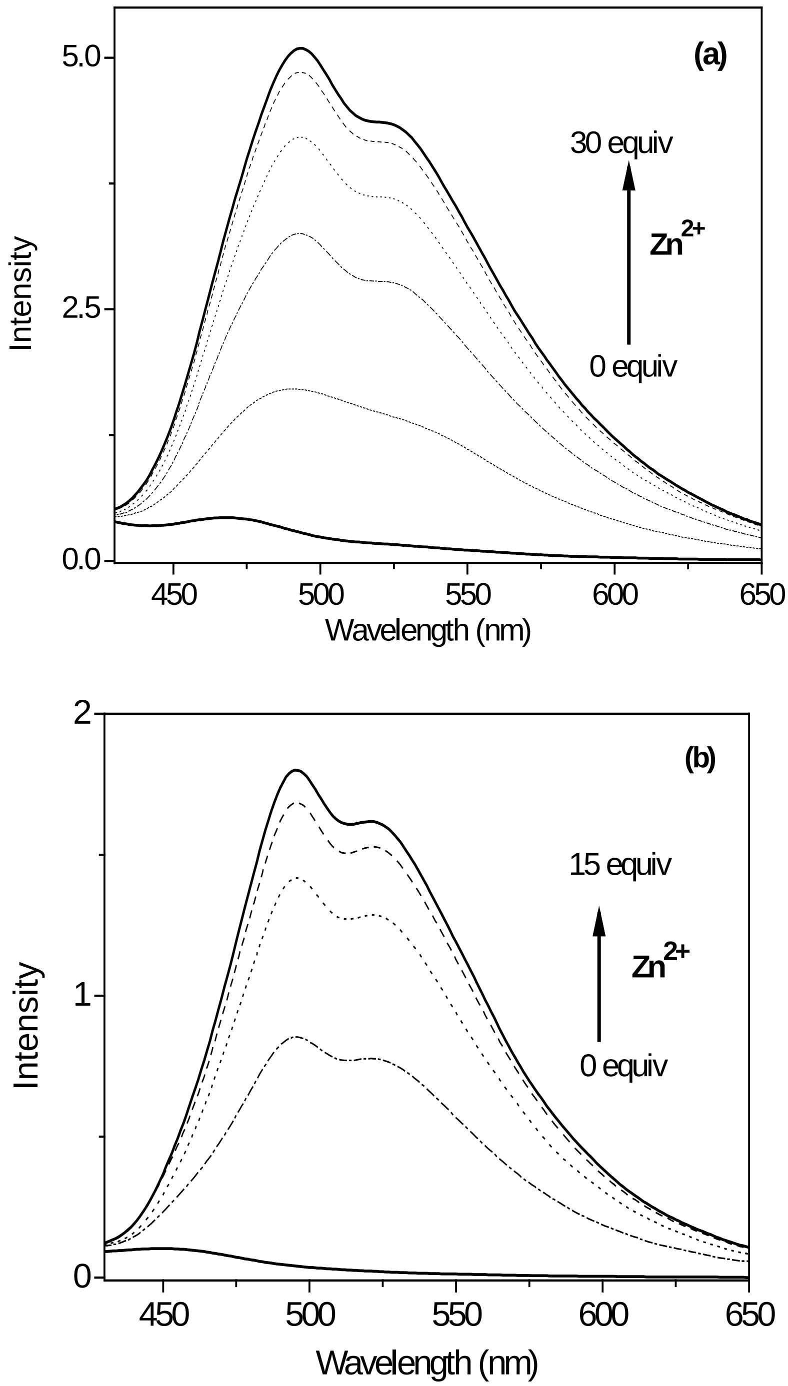

Figure S2. Luminescent titrations of receptors QB1 at 1.0×10^{-4} mol/L (a) and QB2 at 1.0×10^{-5} mol/L (b) with increasing concentration of Zn^{2+}. Excitation wavelength was 420 nm with 4 nm slit widths, and spectra were corrected.

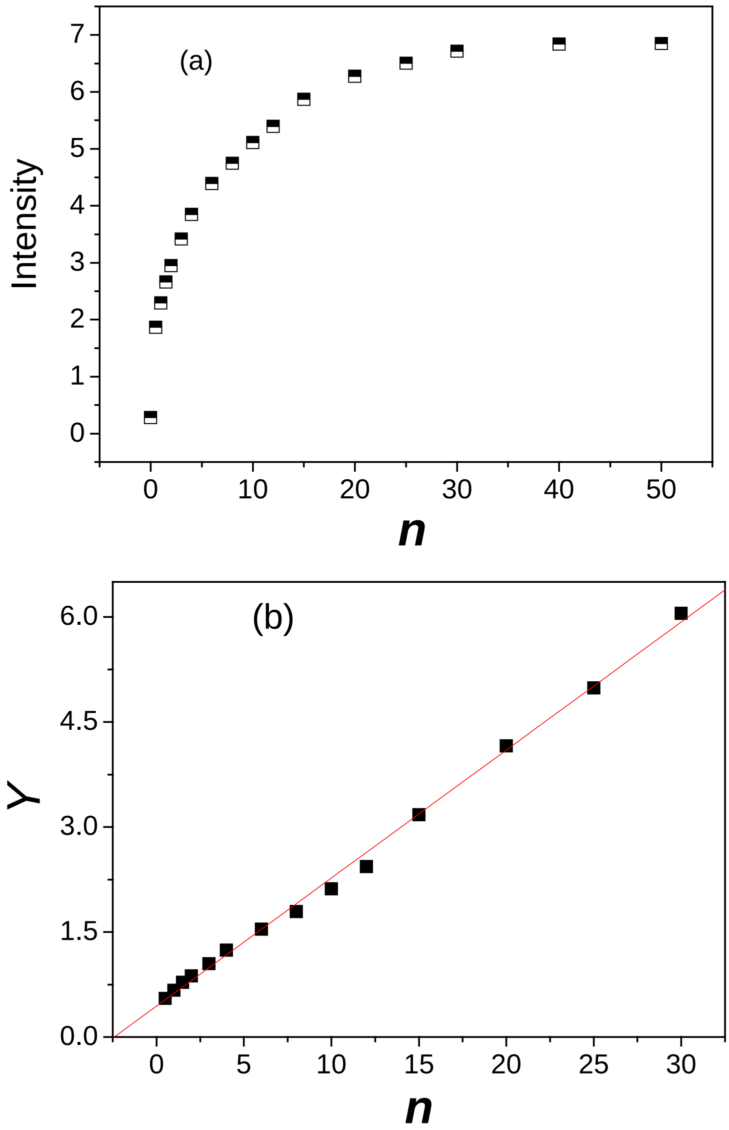

Figure S3. (a) Fluorescent intensity changes at 495 nm *vs* the equivalent molar ratio of Zn^{2+} added (Excitation wavelength at 420 nm with the concentration of QB1 being 1.0×10^{-4}M. (b) Plot for QB1-Zn^{2+} system with K_{ass} being calculated as 4.08×10^{9} M^{-3}.

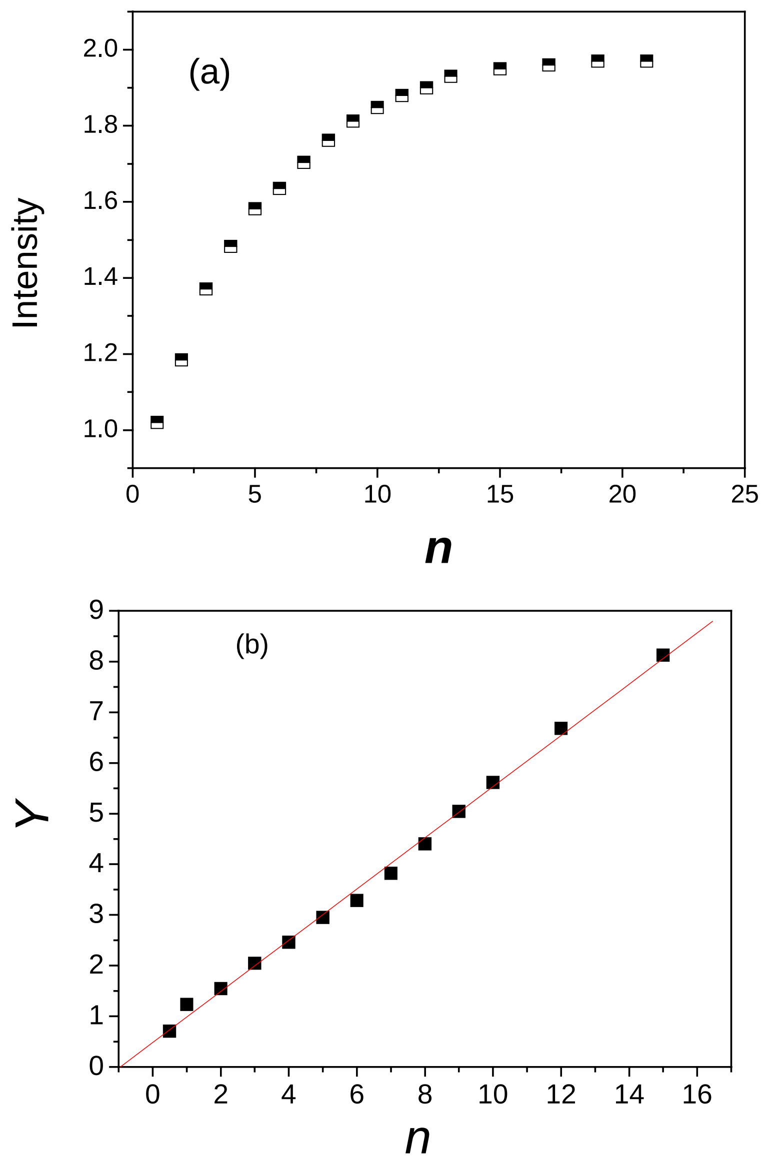

Figure S4. (a) Fluorescent intensity changes at 495 nm *vs* the equivalent molar ratio of Zn^{2+} added (Excitation wavelength at 420 nm with the concentration of QB2 being 1.0×10^{-5}M. (b) Plot for QB2-Zn^{2+} system with K_{ass} being calculated as 1.27×10^{14} M^{-3}.

Here, the linear fits for K_s of Zn-QB1 and Zn-QB2 are deduced as follows:

$$2\ Zn^{2+} + 2\ QB \rightleftharpoons Zn_2QB_2$$

ligand only	C_0		
nC_0 Zn^{2+} is added	$(n\text{-}x)\ C_0$	$(1\text{-}x)\ C_0$	$xC_0/2$

$$K_{ass} = \frac{[Zn_2QB_2]}{[Zn^{2+}]^2\ [QB]^2} \qquad (1)$$

The measurements are performed under the conditions where the fluorescent intensities of the free ligand is a constant A_0; After addition of a given amount of metal salt at a concentration of C_0, the fluorescent intensity becomes

$$A = a \times [\ C_0x/2\ ] + A_0 \qquad (2)$$

In the presence of an excess of salt, the fluorescent intensity reaches the saturate value A_{lim}:

$$A_{lim} = a \times [\ C_0/2\ ] + A_0 \qquad (3)$$

From eqs (2) and (3), it is easy to derive the usual equation:

$$\frac{A - A_0}{A_{lim} - A_0} = x \qquad (4)$$

From eqs (1) to (4), we can obtain the equation:

$$(2kC_0^3)^{1/2} \times \left(n - \frac{A - A_0}{A_{lim} - A_0} \right) = \frac{1}{A_{lim} - A} \times [(A - A_0) \times (A_{lim} - A_0)]^{1/2} \qquad (5)$$

For clarity, we set the value,

$$\frac{1}{A_{lim} - A} \times [(A - A_0) \times (A_{lim} - A_0)]^{1/2} = Y \qquad (6)$$

If $\boldsymbol{A_{1im}}$ cannot be accurately determined, it can be left as a floating parameter in the analysis. ***k*** can thus be obtained by a linear least-squares analysis of ***n*** versus ***Y.***

For chemosensor QB1, K_{ass} is calculated to be 4.08×10^9 $(mol/L)^{-3}$.

For chemosensor QB2, K_{ass} is calculated to be 1.27×10^{14} $(mol/L)^{-3}$.

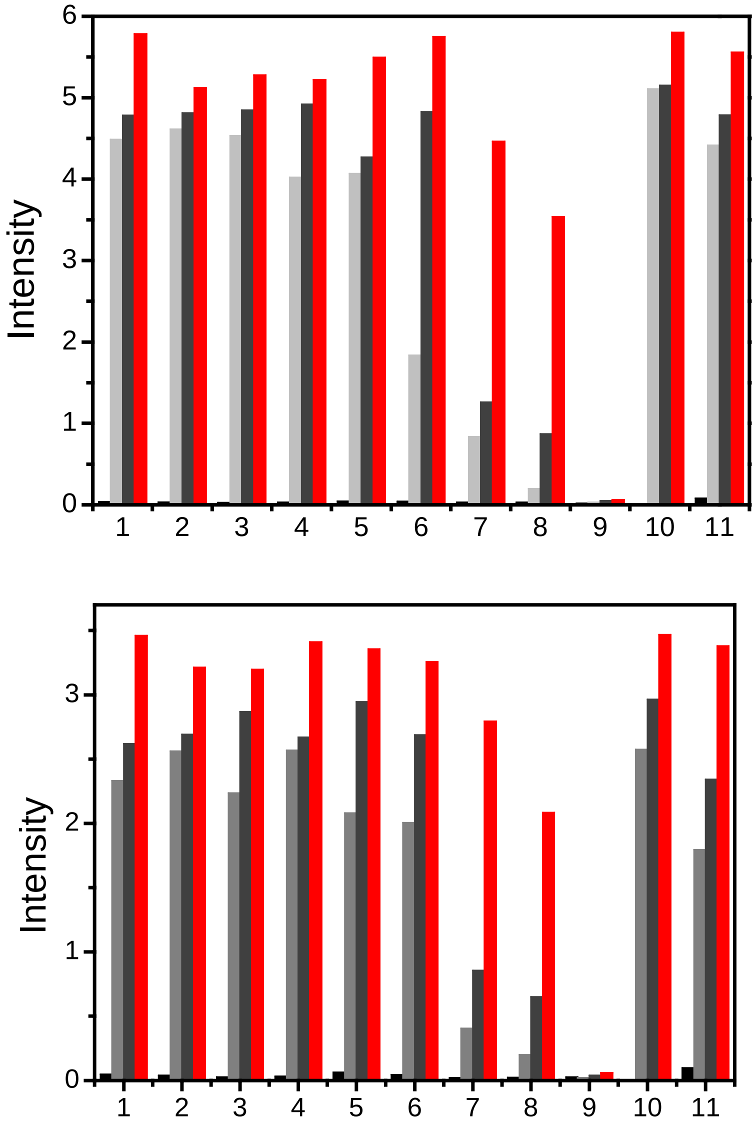

Figure S5. Selectivity of QB2 for Zn^{2+} over the metal ions of interest. Black bars: QB2 + 15 equiv cation of interest: 1, Na^{+}; 2, K^{+}; 3, Ca^{2+}; 4, Mg^{2+}; 5, Mn^{2+}; 6, Fe^{2+}; 7, Co^{2+}; 8, Ni^{2+}; 9, Cu^{2+}; 10, Zn^{2+}(0 equiv); 11, Cd^{2+}.. Light gray bars: addition of 1 equiv of Zn(II) to the solution containing QB2 and 5 equiv cation of interest. Dark gray bars: addition of 1 equiv of Zn(II) to the solution containing QB2 and 1 equiv cation of interest. Red bars: addition of 10 equiv of Zn(II) to the solution containing QB2 and 1 equiv cation of interest. Samples were excited at 420 nm, and the emission spectra were recorded. [QB] = 100 μM.

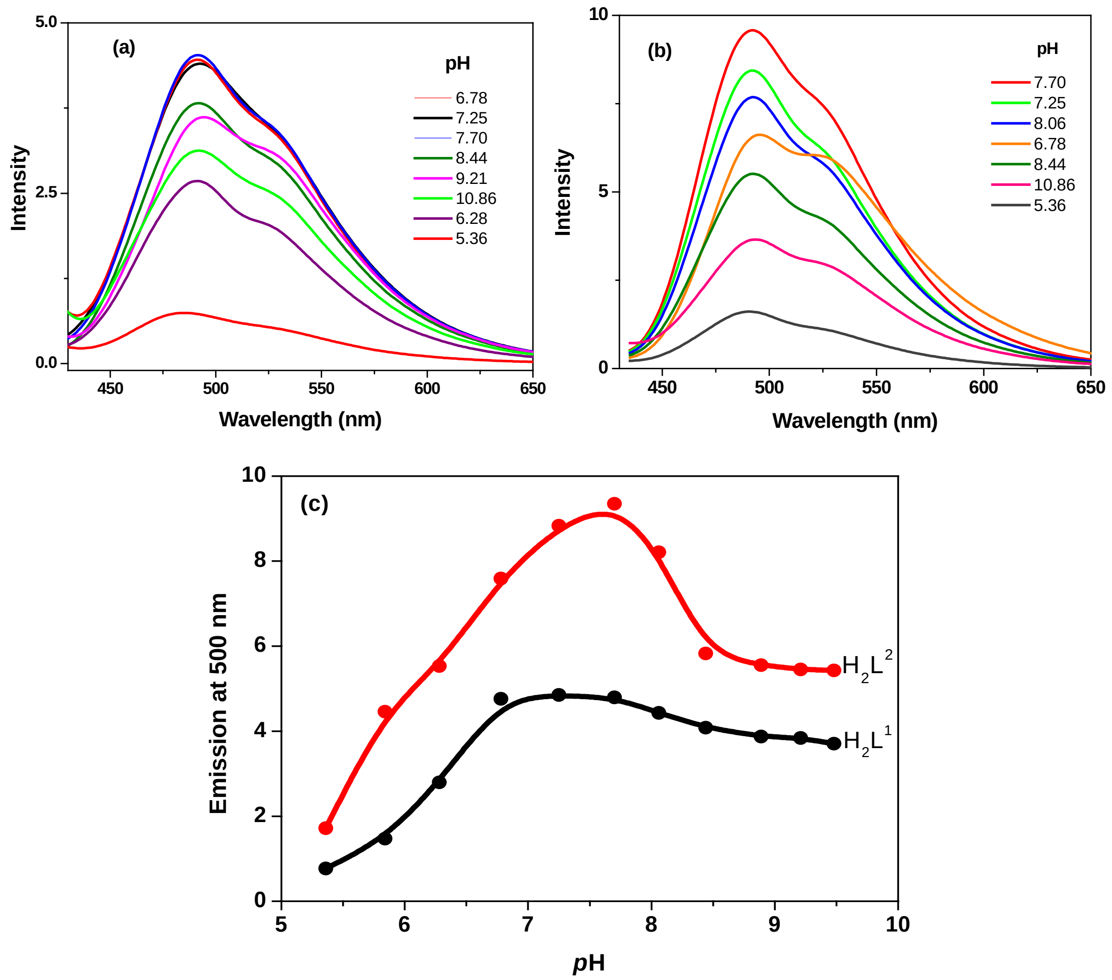

Figure S6. Changes in the emission spectra of (a) QB1 (50 μM) (b) QB2 (50 μM) against different pH (HEPES buffer or TRIS buffer) in DMSO – H_2O (v:v, 40:60) solutions upon addition of $Zn(ClO_4)_2 \cdot 6\ H_2O$ (0.75 mM) in water. (c) Emission intensity variations of QB with different pH after addition of Zn^{2+}, monitored at 420 nm.