Supporting Information

A highly selective and sensitive probe for colorimetric and fluorogenic detection of Cd\(^{2+}\) in aqueous media

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General method of UV-vis and fluorescence titration:

By UV-vis method

UV-vis spectra were recorded on a JASCO V-530 spectrophotometer using a dissolution cell of 10 mm path and the fluorescence spectra were recorded on a PTI spectrophotometer using a fluorescence cell (10 mm). For UV-vis titrations, stock solution of receptor was prepared (c = 6 x 10^{-6} ML^{-1}) in CH₃OH-H₂O (1:4 v/v) in the presence of HEPES buffer solution (pH 7.1). For fluorescence titrations, stock solution of receptor was prepared (c = 3 x 10^{-6} ML^{-1}) in CH₃OH-H₂O (1:4 v/v) in the presence of HEPES buffer solution (pH 7.1). The solution of the guest cations using their perchlorate salts in the order of 2 x 10^{-5} M were prepared in deionised water. Solutions of various concentrations containing host and increasing concentrations of cations were prepared separately. The spectra of these solutions were recorded by means of UV-vis methods. Binding constant was calculated according to the Benesi-Hildebrand equation. $K_a$ was calculated following the equation stated below.

$$\frac{1}{(A-A_0)} = \frac{1}{K(A_{max}-A_0)} [M^{x+}]^n + \frac{1}{[A_{max}-A_0]}$$

Here $A_0$ is the absorbance of receptor in the absence of guest, $A$ is the absorbance recorded in the presence of added guest, $A_{max}$ is absorbance in presence of added $[M^{x+}]_{max}$ and $K$ is the association constant. The association constant ($K$) could be determined from the slope of the straight line of the plot of $1/(A-A_0)$ against $1/[M^{x+}]$ and is found to be $1.656 \times 10^{-5}$ M.

![Figure S1: Benesi-Hildebrand plot from absorption titration data of receptor (6 µM) with Cd^{2+}.](image-url)
**General procedure for drawing Job plot by UV–vis method**

Stock solution of same concentration of the receptors and the guest were prepared in the order of ca. \(1.0 \times 10^{-5}\) ML\(^{-1}\) CH\(_3\)OH-H\(_2\)O (1:4, v/v). The absorbance in each case with different host–guest ratio but equal in volume was recorded. Job plots were drawn by plotting \(\Delta I X_{\text{host}}\) vs \(X_{\text{host}}\) (\(\Delta I\) = change of intensity of the absorbance spectrum during titration and \(X_{\text{host}}\) is the mole fraction of the host in each case, respectively).

**By fluorescence method:**

The binding constant value of Cd\(^{2+}\) with receptor has been determined from the emission intensity data following the modified Benesi–Hildebrand equation,

\[
\frac{1}{\Delta I} = \frac{1}{\Delta I_{\text{max}}} + \frac{1}{K[C]} \left(\frac{1}{\Delta I_{\text{max}}} - \frac{1}{\Delta I}\right)
\]

Here \(\Delta I = I - I_{\text{min}}\) and \(\Delta I_{\text{max}} = I_{\text{max}} - I_{\text{min}}\), where \(I_{\text{min}}, I,\) and \(I_{\text{max}}\) are the emission intensities of receptor considered in the absence of Cd\(^{2+}\), at an intermediate Cd\(^{2+}\) concentration, and at a concentration of complete saturation where \(K\) is the binding constant and \([C]\) is the Cd\(^{2+}\) concentration respectively. From the plot of \([1 / (I_{\text{min}} - I)]\) against \([C]^{-1}\) for receptor, the value of \(K\) has been determined from the slope. The association constant \((K_a)\) as determined by fluorescence titration method for the receptor with Cd\(^{2+}\) is found to be \(6.808 \times 10^5\) M\(^{-1}\) (error < 10%).

![Benesi–Hildebrand plot from fluorescence titration data of receptor (3 µM) with Cd\(^{2+}\).](image)

**Figure S2:** Benesi–Hildebrand plot from fluorescence titration data of receptor (3 µM) with Cd\(^{2+}\).
Determination of detection limit:

The detection limit (DL) of RQ for Cd$^{2+}$ was determined from the following equation:

$$DL = K \times \frac{Sb1}{S}$$

Where $K = 2$ or $3$ (we take $3$ in this case); $Sb1$ is the standard deviation of the blank solution; $S$ is the slope of the calibration curve.

**For UV-vis:**

From the graph, we get slope = 43180.32, and $Sb1$ value is 0.010213

Thus using the formula we get the Detection Limit = $7.09 \times 10^{-7}$ M i.e. RQ can detect Cd$^{2+}$ in this minimum concentration through UV-vis method.

**For Fluorescence:**

From the graph we get slope = $1.44 \times 10^{12}$, and $Sb1$ value is 94366.66

Thus using the formula we get the Detection Limit = $1.97 \times 10^{-7}$ M i.e. RQ can detect Cd$^{2+}$ in this minimum concentration through fluorescence method.
ESI MS spectra of compound B:

Figure S3: ESI TOF mass spectra of the compound B.
$^1$H NMR spectra of the compound B:

Figure S4: $^1$H NMR (300 MHz) spectra of compound B in CDCl$_3$. 

^1\text{H} \text{NMR} \text{ spectra of the receptor:}

Figure S5: ^1\text{H} \text{NMR (300 MHz) spectra of the receptor in CDCl}_3.
ESI MS spectra of the receptor:

Figure S6: ESI TOF mass spectra of the receptor.
$^{13}$C NMR spectra of the receptor:

Figure S7: $^{13}$C NMR (100 MHz) spectra of the receptor in CDCl$_3$. 

Figure S8: Expansion mode of the $^{13}$C NMR spectra of the receptor in CDCl$_3$. 
IR spectra of the receptor and its Cd$^{2+}$ complex:

![IR spectra graph]

Figure S9: FT IR spectra of the receptor and its complex with Cd$^{2+}$. 
ESI-MS of Cd$^{2+}$ complex of the receptor:

Figure S10: ESI TOF mass spectra of the Cd$^{2+}$ complex of the receptor.
UV-vis titration spectra of the receptor with different guest cations in CH$_3$OH-HEPES buffer solution (1:4, v/v, pH= 7.1):
Fluorescence emission spectra of the receptor with different guest cations in CH$_3$OH-HEPES buffer solution (1:4, v/v, pH = 7.1):

- **Co$^{2+}$**
- **Cr$^{3+}$**
- **Cu$^{2+}$**
- **Fe$^{3+}$**
- **Hg$^{2+}$**
- **Mn$^{2+}$**