Supporting Information

A novel coumarin based molecular switch for dual sensing of Zn(II) and Cu(II)

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Fig. S11. Change in emission spectrum of H₂L-Cu²⁺ upon gradual addition of EDTA (40 μM) in 1:1, v/v CH₃CN:H₂O.
Fig. S12. Mole ratio plot of Zn$^{2+}$ to the receptor H$_2$L

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Fig. S14. Job’s plot diagram of the receptor (H₂L) for Zn²⁺ (where ΔF indicates the change of emission intensity at 466 nm)

Fig. S15. Job’s plot diagram of the receptor (H₂L) for Cu²⁺
**Determination of detection limit:**

The detection limit was calculated based on the fluorescence titration. To determine the S/N ratio, the emission intensity of H$_2$L without any analyte was measured by 10 times and the standard deviation of blank measurements was found to be 2.6756×10$^{-3}$.

The limit of detection (LOD) of H$_2$L for Zn$^{2+}$ and Cu$^{2+}$ was determined from the following equation: $LOD = K \times \sigma$ Where $K = 3$ in this case and $\sigma = (S_b)/(S)$; $S_b$ is the standard deviation of the blank solution; $S$ is the slope of the calibration curve.

From the linear response curve of H$_2$L for Zn$^{2+}$ graph we get slope = 4.11821×10$^7$. Thus using the formula we get the LOD = 1.94×10$^{-8}$ M.

![Graph](image)

**Fig. S16.** Linear response curve of H$_2$L at 465 nm depending on the Zn$^{2+}$ concentration.

From the linear response curve of H$_2$L for Zn$^{2+}$ graph we get slope = -9.5×10$^6$, Thus using the formula we get the LOD = 1.87×10$^{-9}$ M.
Fig. S17. Linear response curve of H$_2$L at 485 nm depending on the Cu$^{2+}$ concentration.

**Determination of binding constant from Fluorescence titration data:**

Binding constant was calculated according to the Benesi-Hildebrand equation. $K_a$ was calculated following the equation stated below.

\[
\frac{1}{(F - F_0)} = \frac{1}{K_a(F_{\text{max}} - F_0)} \left\{ [M^{n+}]^c \right\} + \frac{1}{[F_{\text{max}} - F_0]}
\]

Here $F_0$, $F$ and $F_{\text{max}}$ indicate the emission in absence of, at intermediate and at infinite concentration of metal ion respectively. The binding constant $K_a$ is determined from the ratio of intercept and slope of Benesi-Hildebrand plot. Plot of $1/(F - F_0)$ vs $1/[Zn^{2+}]^2$ gives a straight line indicating 1:2 complexation between H$_2$L and Zn$^{2+}$.

For the determination of binding constant of Cu$^{2+}$ the equation modifies to

\[
\frac{1}{(F - F_0)} = \frac{1}{K_a(F_{\text{min}} - F_0)} \left\{ [M^{n+}]^c \right\} + \frac{1}{[F_{\text{min}} - F_0]}
\]

Here $F_0$, $F$ and $F_{\text{min}}$ indicate the emission in absence of, at intermediate and at infinite concentration of metal ion respectively. The binding constant $K_a$ is determined from the ratio of intercept and slope of Benesi-Hildebrand plot. Plot of $1/(F - F_0)$ vs $1/[Cu^{2+}]^2$ gives a straight line indicating 1:2 complexation between H$_2$L and Cu$^{2+}$. 
Fig. S18. Determination of association constant of H$_2$L for Zn$^{2+}$ from fluorescent titration data

\[ y = 2.77729 \times 10^{-13} x + 0.00051 \]

\[ R^2 = 0.9992 \]

Fig. S19. Determination of association constant of H$_2$L for Cu$^{2+}$ from fluorescent titration data

\[ y = -4.25555 \times 10^{-13} x - 0.00577 \]

\[ R^2 = 0.99738 \]
Fig. S20. Change in emission spectrum of H$_2$L (20 µM) upon addition of Na$^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$, Mn$^{2+}$, Fe$^{3+}$, Cr$^{3+}$, Al$^{3+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Cd$^{2+}$ and Hg$^{2+}$ (40 µM) in CH$_3$CN:H$_2$O (1:1, v/v, pH=7.2).
Fig. S21. Optimized structure of H$_2$L-Zn$^{2+}$ complex by DFT/B3LYP/6-31G(d,p)/LANL2DZ method

Fig. S22. Optimized structure of H$_2$L-Cu$^{2+}$ complex by DFT/UB3LYP/6-31G(d,p)/LANL2DZ method
Fig. S23. Contour plots of some selected molecular orbitals of H₂L.

Fig. S24. Contour plots of some selected molecular orbitals of H₂L-Zn²⁺ complex.
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Table S1. Vertical electronic transitions calculated by TDDFT/B3LYP/CPCM method for chemosensor H$_2$L, H$_2$L-Zn$^{2+}$ and H$_2$L-Cu$^{2+}$ complexes

<table>
<thead>
<tr>
<th>Compds.</th>
<th>$\lambda_{\text{excitation}}$ (nm)</th>
<th>Osc. Strength (f)</th>
<th>Key transition</th>
<th>Character</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$L</td>
<td>338.4</td>
<td>0.7214</td>
<td>HOMO $\rightarrow$ LUMO</td>
<td>ILCT</td>
</tr>
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<td>H$_2$L-Zn$^{2+}$</td>
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<td>0.6960</td>
<td>HOMO $\rightarrow$ LUMO</td>
<td>ILCT</td>
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<tr>
<td>H$_2$L-Cu$^{2+}$</td>
<td>482.0</td>
<td>0.0175</td>
<td>HOMO($\beta$) $\rightarrow$ LUMO+1($\beta$)</td>
<td>LMCT</td>
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<td></td>
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<td></td>
<td>HOMO($\beta$) $\rightarrow$ LUMO($\beta$)</td>
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<tr>
<td></td>
<td>358.9</td>
<td>0.2016</td>
<td>HOMO-1($\beta$) $\rightarrow$ LUMO+2($\beta$)</td>
<td>ILCT</td>
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