Supporting Information

for

Amidofluorene-appended lower rim 1,3-diconjugate of calix[4]arene: synthesis, characterization and highly selective sensor for Cu$^{2+}$

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¹H NMR and ¹³C NMR spectra of compounds 1, 2, 3, 4 and L, HRMS of L, UV–vis and fluorescent titration spectra of L with Cu$^{2+}$ ion solutions
Spectroscopic and analytical data

Figure S1: $^1$HNMR (400 MHz in CDCl$_3$) of 1.
Figure S2: $^{13}$CNMR (100 MHz in CDCl$_3$) of 1.
Figure S3: $^1$HNMR (400 MHz in CDCl$_3$) of 2.
Figure S4: $^{13}$CNMR (100 MHz in CDCl$_3$) of 2.
Figure S5: $^1$HNMR (400 MHz in CDCl$_3$) of 3.
Figure S6: $^{13}$CNMR (100 MHz in CDCl$_3$) of 3.
Figure S7: $^1$HNMR (400 MHz in CDCl$_3$) of 4.
Figure S8: $^{13}$CNMR (100 MHz in CDCl$_3$) of 4.
Figure S9: $^1$HNMR (400 MHz in CDCl$_3$) of L.
**Figure S10:** $^{13}$CNMR (100 MHz in CDCl$_3$) of L.
Figure S11: HRMS (m/z) of L.
Figure S12: Absorption spectra of (L) \((1.0 \times 10^{-5}\text{M})\) and Absorption spectra of L \((1.0 \times 10^{-5}\text{M})\) with Cu\(^{2+}\) (100 equiv) in MeCN.
**Figure S13:** Absorption spectral in region 500–800 nm when L was titrated with varying amounts of Cu$^{2+}$ concentration.

**Figure S14:** (a) Fluorescence spectra obtained during the titration of L with Cu$^{2+}$ ion in MeCN. (b) Relative fluorescence intensity ($I-I_0$) as a function of [Cu$^{2+}$]/[L] mole ratio. Fluorescence intensity data for the complexes were plotted according to the Benesi-Hildebrand equation [1]: $1/(F - F_0) = 1/K_a \times (F_{\text{max}} - F_0) \times [M^{n+}] + 1/(F_{\text{max}} - F_0)$. 

5 eq of Cu$^{2+}$

0-100 eq of Cu$^{2+}$
Figure S15: Job plot for determining the stoichiometry of $L$ and $\text{Cu}^{2+}$ ($1.0 \times 10^{-4}\text{M}$) in MeCN. ($X =$ Mole fractions, $I =$ intensity of fluorescence).

$y = -15.935x + 154.38$

$R^2 = 0.9907$
Figure S16: Calibration curve (Hill Plot) of fluorescence intensity of L with Cu$^{2+}$ ion concentrations. The detection limit was determined from the fluorescence titration data based on a reported method [2,3]. The fluorescence spectrum of probe L was measured by 5 times repeat and the standard deviation of blank measurement was obtained. To gain the slope, the fluorescent intensity data at 365 nm was plotted as a function of the concentration of Cu$^{2+}$. The detection limit was calculated with the following equation:

Detection limit = $3\sigma/K$

Where $\sigma$ is the standard deviation of blank measurement, and K is the slope between the fluorescence versus Cu$^{2+}$ concentration. The fluorescent intensity at 365 nm has a good linearity with concentrations of Cu$^{2+}$ in the range from $1 \times 10^{-6}$ M to $10 \times 10^{-6}$ M. The linear equation was found to be $y = -15.935x - 154.38$ (R = 0.9907), where y is the fluorescent intensity at 365 nm and x represents the concentration of Cu$^{2+}$ added. So the detection limit for Cu$^{2+}$ was calculated to be $9.6 \times 10^{-8}$ M (detection limit = $3\sigma/K = (3 \times 0.513)/15.935 \times 10^{-6}$).

Reference: