Electron Supplementary Information

A highly efficient and selective turn-on fluorescent sensor for Cu\textsuperscript{2+} ion based on calix[4]arene bearing four iminoquinoline subunits on the upper rim

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To a solution of calix[4]arene 3 or 5 (0.3 mmol) in a mixture of CH₂Cl₂ (6 mL) and glacial acetic acid (6 mL) was added 100% HNO₃ (2 mL) for 3 at 0 °C and 65% HNO₃ (0.4 mL) for 5 at room temperature. The reaction mixture was stirred for 3~7h and subsequently poured into water (30 mL). The water layer was extracted with CH₂Cl₂ (2×25 mL). The combined organic layers were washed with water (2×25 mL) and then evaporated to obtain a solid residue. The crude reaction products were further purified by recrystallization from CH₂Cl₂ and CH₃OH to give the pure compounds.

Yield: 84 %. Mp: 199-200 °C. ¹H NMR (CDCl₃, 300 MHz): δ 7.58 (s, 8H), 4.65 (d, J = 14.0 Hz, 4H), 4.22 (t, J = 4.4 Hz, 8H), 3.75 (t, J = 4.7 Hz, 8H), 3.38 (d, J = 14.0 Hz, 4H), 3.37 (s, 12H). ¹³C NMR (CDCl₃, 75 MHz): δ 161.5, 143.1, 135.5, 124.0, 74.3, 71.6, 58.7, 30.9. MALDI-TOF MS: m/z 837.3 (M+H)+. Anal. Calcd. for C₄₀H₄₄N₄O₁₆: C, 57.41; H, 5.30; N, 6.70. Found C, 57.20; H, 5.15; N, 6.82.

Yield: 43 %. Mp: 174-175 °C. ¹H NMR (CDCl₃, 300 MHz): δ 7.65 (s, 4H), 6.54-6.59 (m, 6H), 4.56 (d, J = 13.7 Hz, 4H), 4.28 (d, J = 4.8 Hz, 4H), 4.07 (d, J = 4.8 Hz, 4H), 3.81 (d, J = 3.8 Hz, 4H), 3.76 (d, J = 3.8 Hz, 4H), 3.41 (d, J = 13.7 Hz, 4H), 3.41 (s, 6H), 3.37 (s, 6H). ¹³C NMR (CDCl₃, 75 MHz): δ 162.5, 155.6, 142.6, 136.8, 133.4, 128.7, 123.7, 123.3, 73.8, 73.5, 71.9, 71.7, 58.7, 58.6, 30.8. MALDI-TOF MS: m/z 747.5 (M+H)+. Anal. Calcd. for C₄₀H₄₆N₂O₁₂: C, 64.33; H, 6.21; N, 3.75. Found C, 64.10; H, 6.30; N, 3.81.

To a solution of tetraaminocalix[4]arene (143 mg, 0.2 mmol) in a mixture of CH₂Cl₂ (6 mL) and CH₃CH₂OH (6 mL) were added 2-quinolinecarboxaldehyde (126 mg, 0.8 mmol) and 5 Å molecular sieve. The mixture was stirred for one night at room temperature and then filtered. The filtrate was concentrated under reduced pressure, and the resulting residue was purified by recrystallization from CH₂Cl₂ and CH₃OH to give the pure compound 1 (173 mg) in 68% yield. Mp: 278-279 °C. ¹H NMR (CDCl₃, 300 MHz): δ 8.56 (s, 4H), 8.04 (d, J = 8.5 Hz, 4H), 7.98 (d, J = 8.4 Hz, 4H), 7.64 (t, J = 8.5 Hz, 4H), 7.56 (t, J = 8.7 Hz, 4H), 7.44 (t, J = 7.1 Hz, 8H), 4.63 (d, J = 13.4 Hz, 4H), 4.23 (t, J = 5.1 Hz, 8H), 3.89 (t, J = 5.2 Hz, 8H), 3.46 (s, 12H), 3.31 (d, J = 13.5 Hz, 4H). ¹³C NMR (CDCl₃, 75 MHz): δ 158.4, 156.1, 155.2, 147.6, 145.0, 135.8, 135.5, 129.5, 129.4,
25,26,27,28-Tetrakis(ethoxymethoxy)-5,17-diiminoquinoline calix[4]arene (2)

It was synthesized by the similar method as 1. Yield: 80%. Mp: 168-169 °C. \(^1\)H NMR (CDCl\textsubscript{3}, 300 MHz): \(\delta\) 8.51 (s, 2H), 8.03 (d, \(J = 8.4 \text{ Hz}, 2\)H), 7.97 (d, \(J = 8.5 \text{ Hz}, 2\)H), 7.64 (t, \(J = 8.5 \text{ Hz}, 2\)H), 7.52 (t, \(J = 8.6 \text{ Hz}, 2\)H), 7.49 (t, \(J = 7.3 \text{ Hz}, 2\)H), 6.79 (s, 4H), 6.74-6.64 (m, 6H), 4.56 (d, \(J = 13.7 \text{ Hz}, 4\)H), 4.28 (d, \(J = 4.8 \text{ Hz}, 4\)H), 4.07 (d, \(J = 4.8 \text{ Hz}, 4\)H), 3.81 (d, \(J = 3.8 \text{ Hz}, 4\)H), 3.76 (d, \(J = 3.8 \text{ Hz}, 4\)H), 3.41 (s, 6H), 3.37 (s, 6H), 3.26 (d, \(J = 13.7 \text{ Hz}, 4\)H). \(^{13}\)C NMR (CDCl\textsubscript{3}, 75 MHz): \(\delta\) 157.6, 156.6, 156.5, 155.2, 147.6, 144.1, 135.9, 135.8, 134.8, 129.3, 128.5, 128.4, 127.6, 127.0, 122.5, 121.6, 118.4, 73.1, 72.7, 71.7, 71.7, 58.6, 58.5, 45.5, 30.4. MALDI-TOF MS: \(m/z\) 965.5 (M+H\(^+\)). Anal. Calcd. for C\(_{60}\)H\(_{60}\)N\(_4\)O\(_8\): C, 76.47; H, 6.27; N, 5.81. Found C, 76.20; H, 6.35; N, 5.72.

(2) General procedures for the absorption and fluorescence experiments

The absorption and fluorescence experiments reported in this paper were carried out in CH\(_3\)CN. The resolution was set at 1 nm, \(\lambda_{\text{ex}}\) is 335 nm, and the excitation and emission slit widths were 10 nm. The samples were performed with a series of 1.0×10\(^{-5}\) M HPLC acetonitrile solutions of compounds 1 and 2. Metal perchlorates were performed with 1.0×10\(^{-3}\) M. The sample was performed with 1.0×10\(^{-5}\) M.

(3) Job plot for compound 1 and Cu\(^{2+}\)

![Job plot for compound 1 and Cu\(^{2+}\)](image)

Figure S1. Job plot for 1 and Cu(ClO\(_4\))\(_2\): \([1] + [\text{Cu}^{2+}] = 1.0 \times 10^{-5} \text{ mol L}^{-1}\) in CH\(_3\)CN. \(\lambda_{\text{ex}} = 335 \text{ nm, } \lambda_{\text{em}} = 412 \text{ nm.}\)
Figure S2. Absorption spectra of 1 (1 × 10⁻⁵ M) in the presence of Cu(ClO₄)₂ in CH₃CN. [Cu²⁺]: 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 11.0, 12.0×10⁻⁶ M.

Figure S3. Absorption spectra of 1 (1 × 10⁻⁵ M) in the presence of Zn(ClO₄)₂ in CH₃CN. [Zn²⁺]: 2.0, 4.0, 6.0, 8.0, 10.0, 12.0, 14.0, 16.0, 18.0, 20.0, 24.0, 26.0×10⁻⁶ M.
(5) Fluorescent titration of 1 with Zn$^{2+}$

Figure S4. (a) Fluorescence emission spectra of 1 (1 × 10$^{-5}$ M) in the presence of Zn(ClO$_4$)$_2$ in CH$_3$CN. [Zn$^{2+}$]: 10.0, 20.0, 30.0, 40.0, 50.0, 60.0, 70.0, 80.0, 90.0, 100.0, 110.0, 120.0, 130.0, 140.0, 150.0, 160.0, 200, 250 ×10$^{-5}$ M. $\lambda_{\text{ex}}$ = 335 nm. (b) Plot of $I/I_0$ versus [Zn$^{2+}$].

(6) Fluorescent titration of 2 with Cu$^{2+}$

Figure S5. (a) Fluorescence emission spectra of 2 (1.0 × 10$^{-5}$ M) in the presence of Cu(ClO$_4$)$_2$ in CH$_3$CN. [Cu$^{2+}$]: 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 12.0, 15.0, 20.0, 30.0, 50.0 ×10$^{-5}$ M. $\lambda_{\text{ex}}$ = 335 nm. (b) Plot of $I_f$ versus [Cu$^{2+}$].
Figure S6. Plot of I_f versus metal ion concentration. [I] = 1 × 10^{-5} M, \lambda_{ex} = 335 nm, \lambda_{em} = 412 nm. M^{n+} represent Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Fe^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Ag^+, Hg^{2+}.
The ESI-MS spectra of 1-Cu\textsuperscript{2+} and 1-Zn\textsuperscript{2+}
(9) The $^1$H NMR titration of compound 1 with Zn$^{2+}$

Figure S7. The $^1$H NMR (298K, 600MHz) titrations of compound 1 (2×$10^{-3}$ M) with Zn$^{2+}$ in the mixture solution of CDCl$_3$ and CD$_3$CN (1:1). a-e: [Cu$^{2+}$]: 0, 0.5, 1.0, 1.5, 2.0×$10^{-3}$ M.
The 1H NMR and 13C NMR spectra of compounds 1, 2, 4, 6.

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