Electronic Supporting Information

Synthesis of a Pyridyl-Append Calix[4]arene and its Application to the Modification of Silver Nanoparticles as an Fe$^{3+}$ Colorimetric Sensor

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The procedure of synthesis of 4-propynoxypyridine

A suspension of 4-hydroxy pyridine (0.57 g, 6 mmol) and anhydrous potassium carbonate (1.66 g, 12 mmol) in acetone (20 mL) was stirred for 0.5 h at room temperature. Then a solution of 3-bromopropyne (1.3 mL, 12 mmol) dissolved in acetone (5 mL) was slowly added. The reaction mixture was stirred for 2 h at 50 °C. The cooled reaction mixture was filtered and washed with acetone. The filtrate were removed under vacuum and the residue was further purified by column chromatography eluting with ethyl acetate/methanol (v/v = 5:1); Yield: 95%. ¹H NMR (600 MHz, CDCl₃): δ 7.45 (d, J = 7.2 Hz, 2H, PyH), 6.42 (d, J = 7.2 Hz, 2H, PyH), 4.60 (s, 2H, OCH₂Py), 2.65 (s, 1H, CCH).

![Graph](image_url)

**Fig. S1.** The plot of 1/I versus mole fraction of Fe³⁺. Fluorescence spectra of 2 (5×10⁻⁵ M) with various equivalents of Fe³⁺ in CH₃CN (0 -1.2 equiv).
**Fig. S2.** Job’s plots of 2 toward Fe$^{3+}$ in CH$_3$CN solution at an invariant total concentration of 10$^{-5}$ M. (Excitation 285nm)

**Fig. S3** The MALDI-TOF mass spectrum of the 2·Fe$^{3+}$ complex.

**Fig. S4** Photographs of the fluorescence responses (2 (5×10$^{-4}$ M) in the absence and presence of 1.0 equiv Fe$^{3+}$ in CH$_3$CN under UV light (λex = 254 nm).
**Fig. S5.** The fluorescence changes of 2 (10⁻⁵ M) toward 5.0×10⁻⁵ M Fe³⁺ in the presence of 1.0×10⁻⁴ M other ions. I₀ is fluorescence emission intensity at 313 nm for free 2, and I is the fluorescent intensity upon addition of other metal ions with the existence of Fe³⁺.

**Fig. S6.** The partial ¹H NMR spectra of (c) 2 (5 mM) in CD₃CN and in the presence of (b) 1.0 equiv and (a) 2.0 equiv of Fe(ClO₄)₃.
**Fig. S7.** The optimized structure of the 2·Fe$^{3+}$ complex

**Fig. S8.** The photographic images (A), UV-vis spectra (B) of 2-Ag NPs on the increasing time (10-60 min) under the ultraviolet light at $\lambda_{max} = 365$nm. (C) The stability of the 2-Ag NPs (the absorbance intensity at 414 nm).

**Fig. S9** Size distribution of TEM images of 2-Ag NPs.
Fig. S10 FT-IR spectra of (a) calix[4]arene 2 and (b) 2-Ag NPs

Fig. S11 $^1$H NMR of calix[4]arene 2 and 2-Ag NPs in CDCl$_3$. 
**Fig. S12** The UV-vis spectra of 2-Ag NPs, in the presence of different 0.2 mM alkali metal ions and alkaline earth metal ions (Li⁺, Na⁺, K⁺, Cs⁺, Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺) in methanol solutions.

**Fig. S13** The photographic images (A), UV-vis spectra (B) and the dependence of the R values (A₃₆₄/A₄₁₄) of (C) of 2-Ag NPs on the increasing concentration of Fe³⁺ (2.5-250 μM). Typically, 0.5 mL of various concentrations of Fe³⁺ were added into 1.5 mL 2-Ag NP solutions, and the combined solution mixed well for 30 min and then tested.
Fig. S14 NMR and HDMS spectra of compounds 2