

Supporting Information

Catalyst + Chemodosimeter → Chemosensor: Incorporation of a catalytic functionality in an indicator displacement assay to realize reversible chemosensing detection

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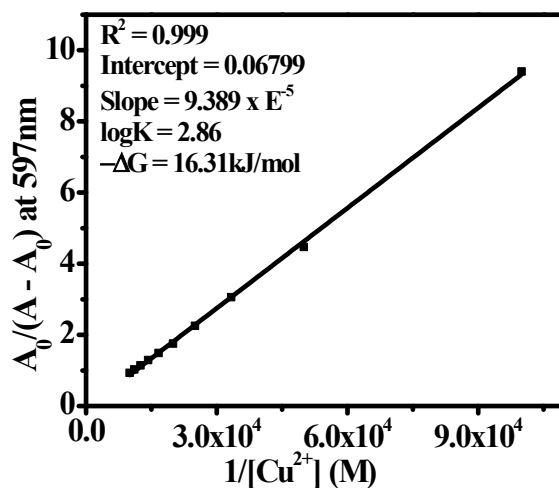
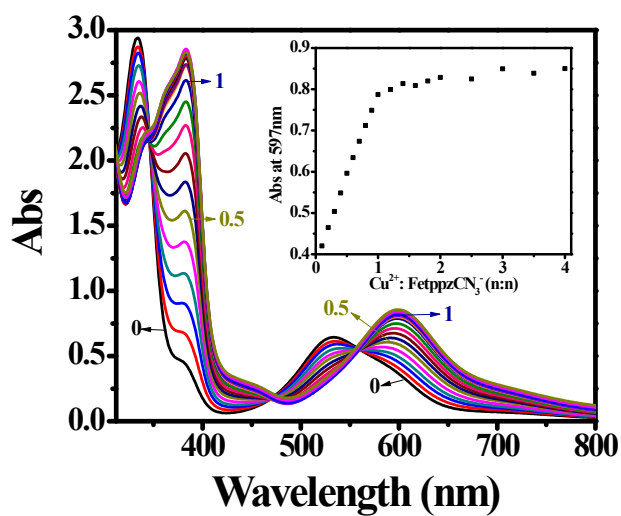
EXPERIMENTAL

Materials and Physical instrumentation. $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, 2,3,5,6-tetra(2'-pyridyl)pyrazine (tppz), benzyltriphenylphosphonium bromide (BTPPC), and potassium cyanide were obtained from Aldrich. CuCl_2 was obtained from Fluka. A Vario EL CHN analyzer was used to conduct the elemental analyses. Infrared spectra in the $500\text{--}4000\text{ cm}^{-1}$ range were recorded using a Perkin Elmer Model Frontier FTIR spectrometer using KBr pellets. UV-vis spectra were recorded on a Cary 50 ultraviolet-visible spectrophotometer. Ion chromatographic studies were conducted by using a 930 Compact IC Flex (Metrohm, Switzerland) system with a Metrosep A Supp 7-250/4.0 column; aqueous Na_2CO_3 (3.6 mM with pH 10.7) was used as the mobile phase at a flow rate of 0.7 mL/min, while the operation temperature and pressure were 323 K and 11.1 MPa, respectively. The retention time of OCN^- was found to be 13.44 min. Electrospray mass spectrometry (ESI-MS) was performed using a Waters Synapt G2-Si Ion Mobility Quadrupole MS system.

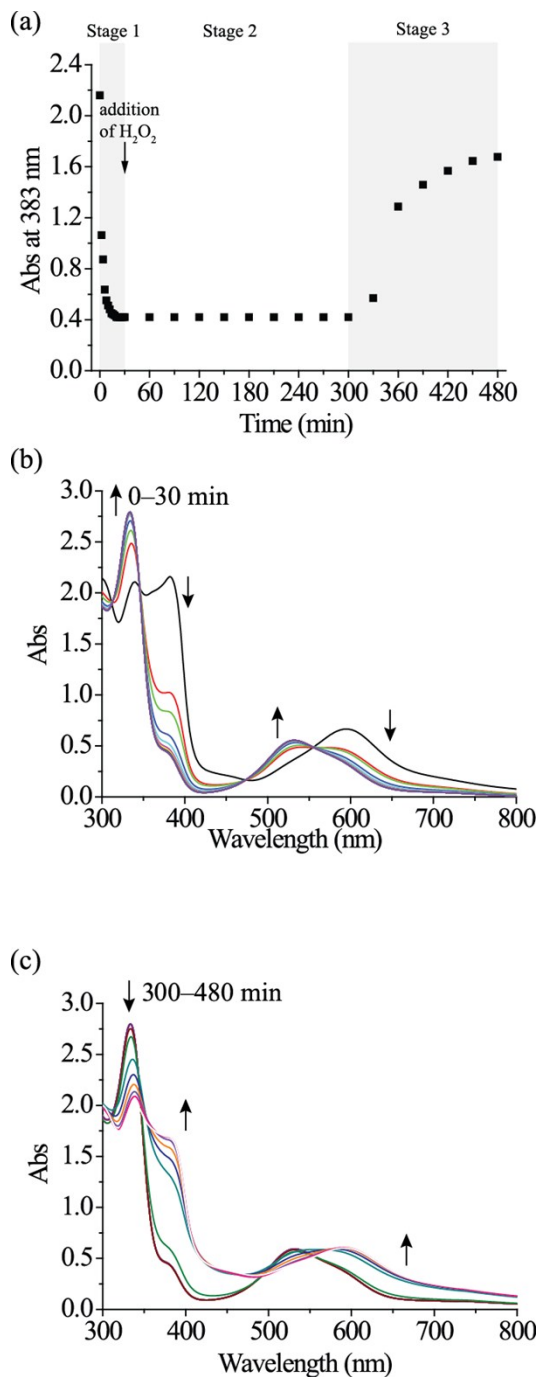
UV-Vis Spectroscopic Titrations. Phosphate buffer (pH 7, 0.02 M) was used in all the UV-vis spectroscopic titrations. Except for NH_4SCN and NaN_3 , all the anions (CN^- , SO_4^{2-} , HCO_3^- , HPO_4^{2-} , CH_3COO^- , NO_3^- , NCO^- , and Cl^-) used in the titrations were potassium salts. All the UV-vis spectroscopic measurements were taken after equilibrium was reached. Receptor-substrate interaction was analyzed by using Benesi–Hildebrand equations.⁸

Binding Properties of (i) Complex 1 Toward CN^- , (ii) Cu^{2+} toward CN^- , and (iii) $[\text{Fe}(\text{tppz})(\text{CN})_3]^-$ Toward Cu^{2+} . For the binding properties of (i) and (ii), a series of CN^- solutions ($0\text{--}1.0 \times 10^{-3}\text{ M}$) was mixed with the receptor solution (complex 1 or Cu^{2+} : $1.0 \times 10^{-4}\text{ M}$). While the binding properties of (iii) were evaluated with the titration of $[\text{Fe}(\text{tppz})(\text{CN})_3]^-$ solutions ($1.0 \times 10^{-4}\text{ M}$) by Cu^{2+} ($0\text{--}4.0 \times 10^{-4}\text{ M}$). All the titrations were carried out in the phosphate buffer at 298 K. The changes in the UV-vis spectra of the resulting mixtures were plotted as functions of the mole fraction of the analyte. The binding constants⁸ and method detection limits⁹ were evaluated from the spectroscopic changes.

[BTTPC][Fe(tppz)(CN)₃]. The complex was synthesized by modification of a reported method.¹¹ An aqueous ethanolic solution of (NH₄)₂Fe(SO₄)₂·6H₂O (392 mg, 1 mmol in deionized water:ethanol, v:v, 1:1, 50 mL) was added dropwise to a solution of 2,3,5,6-tetra(2'-pyridyl)pyrazine (tppz) (776 mg, 2 mmol in deionized water:ethanol, v:v, 1:1, 50 mL). The mixture was stirred and refluxed for 3 h. [Fe(tppz)₂]SO₄ was obtained by slow evaporation of the solvents. The purple solids obtained and KCN (650 mg, 10 mmol) were re-dissolved and stirred in water (50 mL) for 1 h. During the reaction, tppz ligand (~350 mg) was precipitated out as a white solid. Excess benzyltriphenylphosphonium bromide (BTTPC) (2.16 g, 5 mmol, 50 mL) in a hot aqueous solution was slowly added to the stirred mixture. The dark-blue solids precipitated out were collected by filtering, washed with deionized water, and air-dried at room temperature (800 mg, 91.4%). IR (KBr): $\nu_{\text{C}\equiv\text{N}} = 2077$ and 2107 cm^{-1} . High-resolution ESI-MS (negative mode): m/z 522.0898 {Fe(tppz)(CN)₃}⁻ (calculated mass: 522.0875 amu); ¹H NMR (500 MHz, d₆-DMSO) δ : 8.89 (d, J = 5.0 Hz, 2H), 8.75–8.76 (m, 2H), 8.18–8.21 (m, 2H), 8.13 (d, J = 7.5 Hz, 2H), 7.90 (m, 3H), 7.73–7.75 (m, 8H), 7.67 (m, 6H), 7.65 (m, 2H), 7.39 (m, 2H), 7.30 (m, 1H), 7.22–7.25 (t, 2H), 7.00 (d, J = 8.5 Hz, 2H), 6.96 (m, J = 9.5 Hz, 2H), 5.13 (d, J = 16 Hz, 2H). ¹³C NMR (500 MHz, D₆-DMSO): 117.44, 118.13, 124.07, 124.90, 125.06, 125.30, 127.82, 128.84, 128.86, 128.86, 130.07, 130.17, 130.79, 130.83, 133.70, 133.96, 134.04, 135.15, 138.31, 147.21, 149.42, 150.05, 151.18, 152.64, 155.02, 155.46, 156.03. Anal. calc. for C₅₂FeH₃₈N₉P·6H₂O: C, 63.48; H, 5.12; N, 12.81. Found C, 64.04; H, 5.17; N, 12.47.



S. Figure 1. (a) UV–Vis spectroscopic titrations of [BTTPC][Fe(tppz)(CN)₃] (1×10^{-4} M) with CuCl₂ ($0\text{--}4 \times 10^{-4}$ M) and (b) the slope and y-intercept are 9.39×10^{-5} M and 0.068, respectively, $\log K = 2.86$. All the experiments were carried out in pH 7 phosphate buffer (0.02 M) at 298 K.



S.Figure 2. (a) The absorbance changes at 383 nm of the mixture containing complex **1** (1×10^{-4} M), CN⁻ (1×10^{-3} M), and H₂O₂ (2×10^{-3} M) with respect to the reaction time. The UV-Vis spectra of the above-mentioned reaction (b) from the 0-30 min, and (c) from 300-480 min. All the experiments were carried out in deionized water at 298 K.