Catalyst Displacement Assay: A Supramolecular Approach for Design of Smart Latent Catalysts for Pollutant Monitoring and Removal

Supporting information


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SI.Figure 1. (a) Spectroscopic titrations of $K_4[\text{Fe}^{II}(\text{CN})_6]$ (3.3 $\times$ 10$^{-4}$ M) by $\text{Cu}^{II}(\text{dien})\text{Cl}_2$ (0 to 2 $\times$ 10$^{-5}$ M) (b) The slope and y-intercept are -1.77 $\times$ 10$^{-10}$ M and -7.79 respectively of the best fitted $A_0/(A-A_0)$ versus $1/[[\text{Cu}^{II}(\text{dien})\text{Cl}_2]]^2$ plot with log $K = 5.32 \pm 0.008$ at 422 nm. From fitting the curve with the ratio 1:2 Benesi-Hildebrand equation, the solvated form of the complex is deduced as 1:2 ratio of $[\text{Fe}^{II}:\text{Cu}^{II}]$. All the titrations were performed in HEPES buffer at pH 7.4 at 298 K.
Figure 2. (a) Spectroscopic titrations of K$_2$[Fe$^{II}$(Bubpy)(CN)$_4$] (5 x 10$^{-5}$ M) by Cu$^{II}$(dien)Cl$_2$ (0 to 2 x 10$^{-4}$ M) (b) The slope and y-intercept are 3.80 x 10$^{-9}$ M and 2.88 respectively of the best fitted $A_o/(A-A_o)$ versus $1/[[Cu^{II}$(dien)Cl$_2$]$^2$ plot with log $K = 4.44 \pm 0.001$ at 487 nm. From fitting the curve with the ratio 1:2 Benesi-Hildebrand equation, the solvated form of the complex is deduced as 1:2 ratio of [Fe$^{II}$:Cu$^{II}$]. All the titrations were performed in aqueous DMF (1:1 v/v) (1.50 mL of aqueous HEPES buffer at pH 7.4 + 1.50 mL of DMF) at 298 K.
SI.Figure 3. (a) Spectroscopic titrations of Fe^{II}(Bubpy)_2(CN)_2 (5 \times 10^{-5} \text{ M}) by Cu^{II}(dien)Cl_2 (0 to 1 \times 10^{-4} \text{ M}) (b) The slope and y-intercept are -3.07 \times 10^{-2} \text{ M} and 6.51 \times 10^{-1} \text{ respectively of the best fitted } A_o/(A-A_o) \text{ versus } 1/\{\text{[Cu}^{II}(\text{dien})\text{Cl}_2]^{0.5}\} \text{ plot with } \log K = 2.65 \pm 0.001 \text{ at } 561 \text{ nm. From fitting the curve with the ratio 0.5:1 Benesi-Hildebrand equation, the solvated form of the complex is deduced as 0.5:1 ratio of [Fe}^{II}:\text{Cu}^{II}]. All the titrations were performed in aqueous DMF (1:1 v/v) (1.50 mL of aqueous HEPES buffer at pH 7.4 + 1.50 mL of DMF) at 298 K.
**SI.Figure 4.** Electrospray mass spectra of (a) “complex 1 / 2 or 3-cyanide-mixture” and (inset) the simulation of $[\text{Cu}^{II}(\text{dien})(\text{CN})]^+$ ($m/z$ 192.0); and (b) “complex 1/ 2 or 3-oxalate-mixture” and (inset) the simulation of $[\text{Cu}^{II}(\text{dien})(\text{OOC–COO})(\text{K})]^+$ ($m/z$ 293.0). The mass spectra were performed in aqueous methanol.
SI. Figure 5. Kinetic plot of apparent association rate constant $k_{obs}$ (s$^{-1}$) versus Cu$^{2+}$ concentration. The rate constant value was calculated from the slope (249.5 M$^{-1}$s$^{-1}$) of the curve ($y = mx$). All the $k_{obs}$ data were retrieved from Sarla, M.; Pandit, M.; Tyagi, D. K.; Kapoor, J. C. J. Hazard. Mater. 2004, B116, 49-56.
SI.Figure 6. (a) UV–vis spectroscopic titrations of $\text{Cu}^\text{II}(\text{dien})\text{Cl}_2$ ($5 \times 10^{-4}$ M) with oxalate (0 to $1 \times 10^{-3}$ M). (b) The slope and y-intercept are $-8.95 \times 10^{-7}$ M and $-6.25 \times 10^{-1}$ respectively of the best fitted $A_0/(A-A_0)$ versus $1/[\text{oxalate}]^2$ plot with log $K = 6.84 \pm 0.002$ at 600 nm. All titrations were carried out in aqueous phosphate buffer pH 4 at 298 K.
SI. Figure 7. Formation of CO$_2$ with respect to different initial concentration of oxalate in the presence of complex 1 ($6.25 \times 10^{-4}$ M) against time. The formation of CO$_2$ in the absence of catalyst (○). All the experiments were performed with H$_2$O$_2$ (0.4 M) and pH 3 at room temperature and UV-vis irradiation under an open atmosphere.
SI. Figure 8. Conversion of cyanide to cyanate in real sample of (a) domestic wastewater (level I, untreated) and (b) industrial wastewater by 3 (2.0 × 10^{-4} M) in the presence of H_2O_2 (6.53 × 10^{-4} M) and spiked with (■) 10 μM, (●) 20 μM and (▲) 30 μM of cyanide. Control experiments (▼) were run in the absence of 3, but in presence of H_2O_2 (6.53 × 10^{-4} M) and spiked with 10 μM cyanide.
SI. Figure 9. Full range ESI-MS spectra of complexes 1-3. All the experiments were conducted in DI water/methanol.