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

Supporting information

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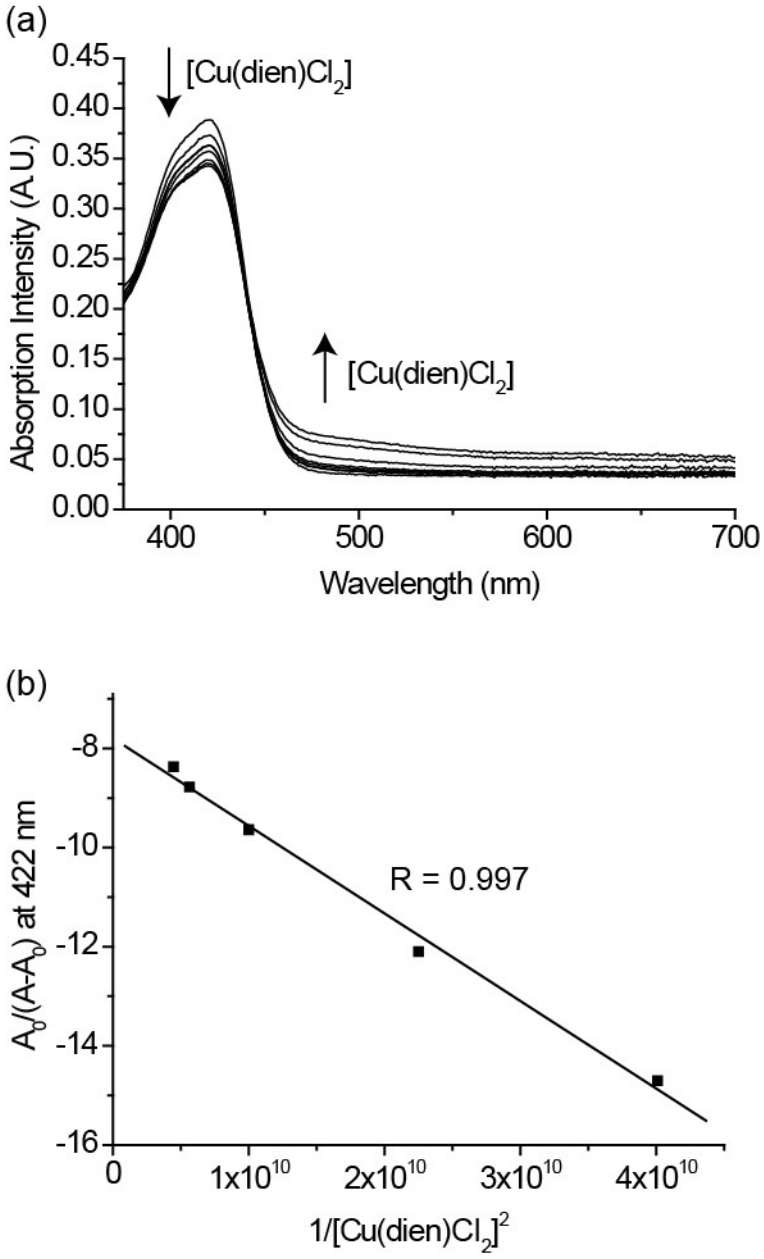
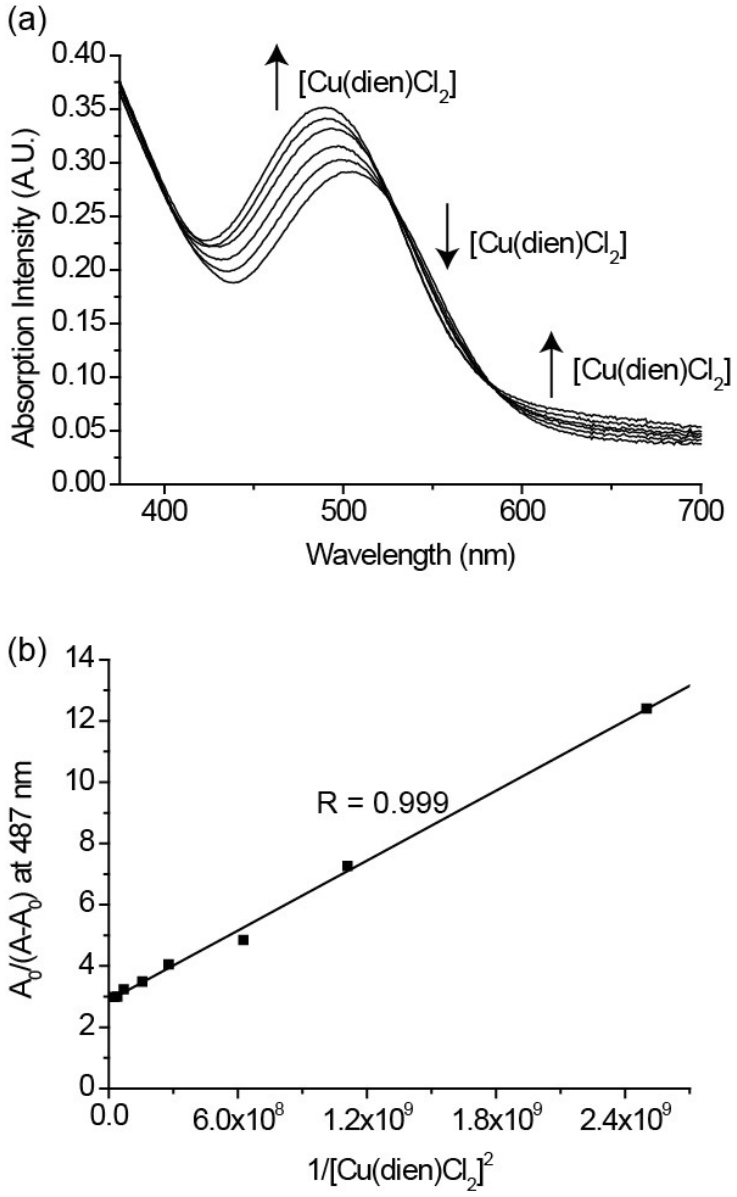
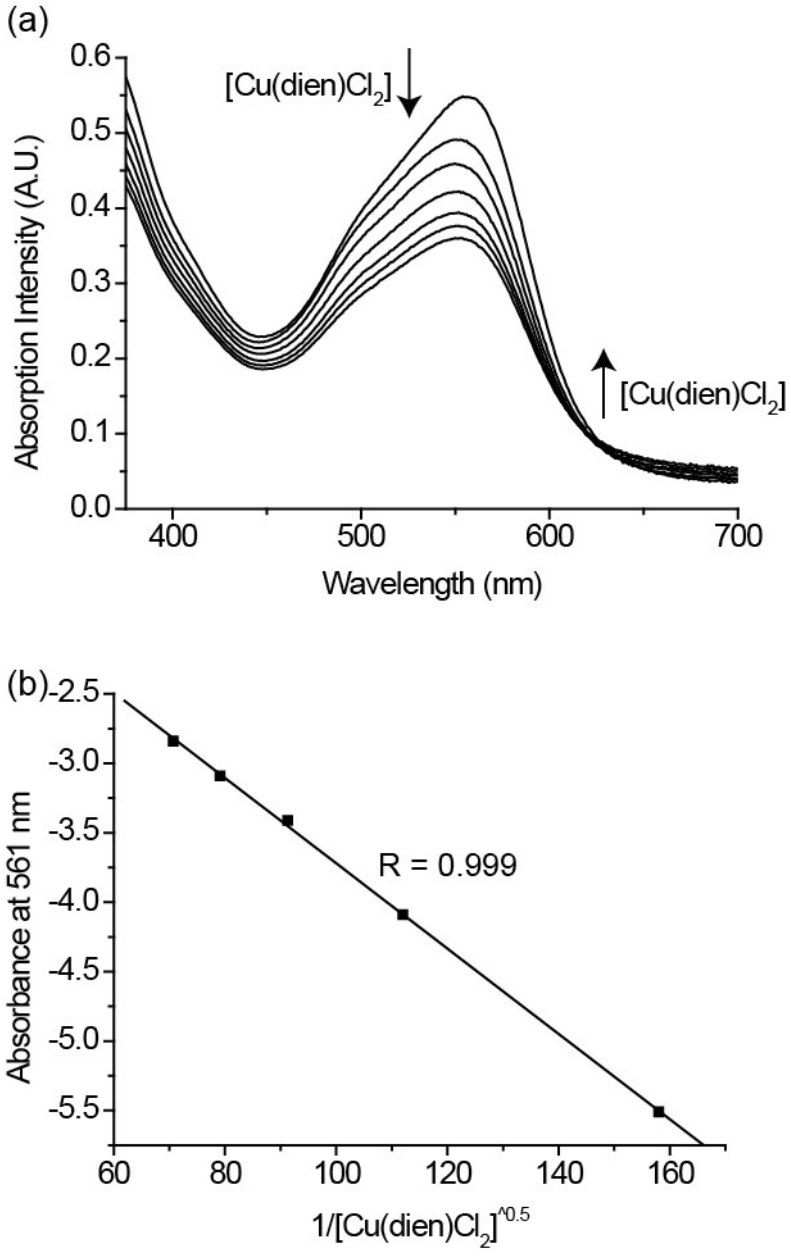


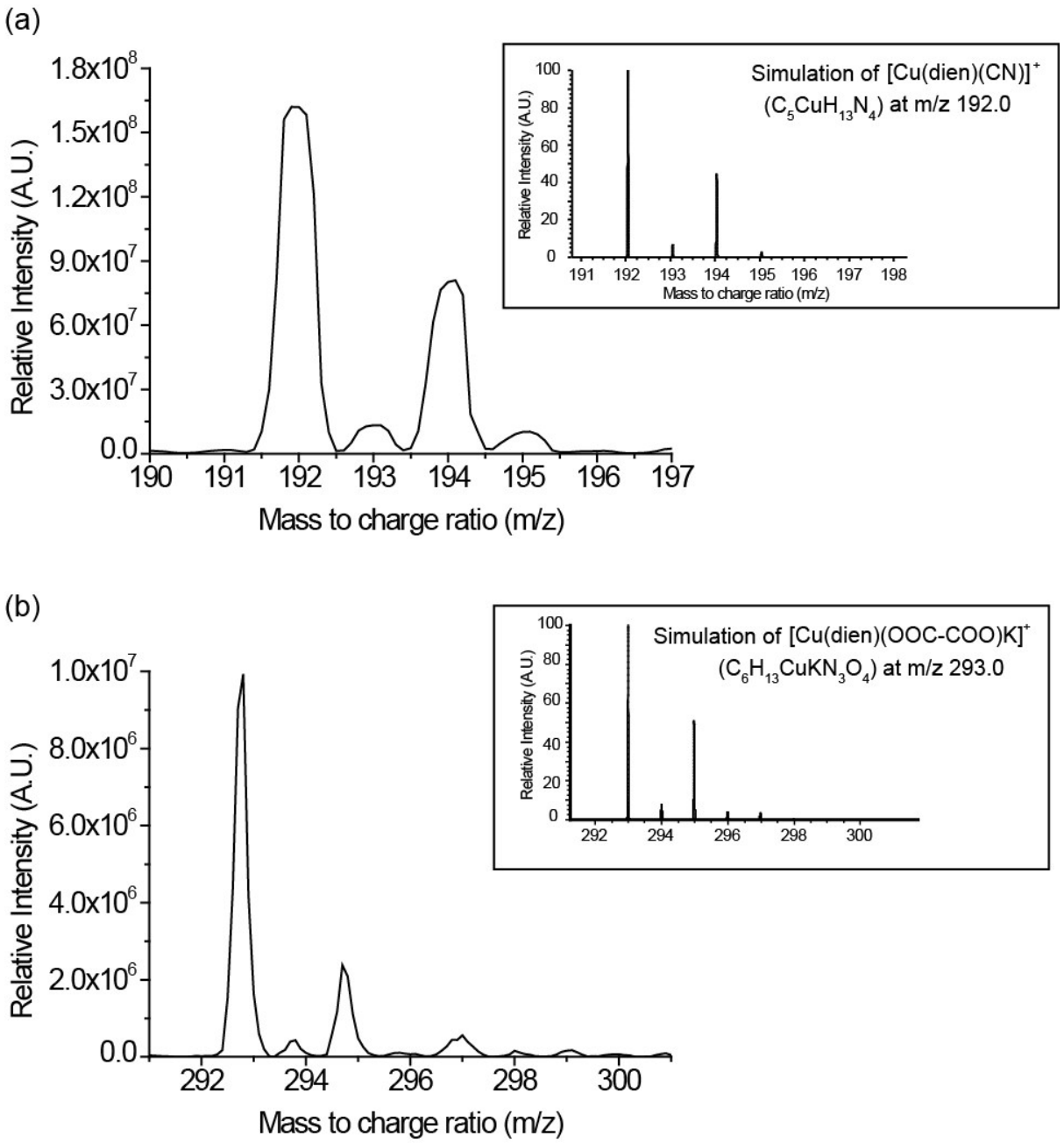
SI.Figure 1. (a) Spectroscopic titrations of $K_4[Fe^{II}(CN)_6]$ (3.3×10^{-4} M) by $Cu^{II}(dien)Cl_2$ (0 to 2×10^{-5} M) (b) The slope and y-intercept are -1.77×10^{-10} M and -7.79 respectively of the best fitted $A_0/(A-A_0)$ *versus* $1/\{[Cu^{II}(dien)Cl_2]\}^2$ plot with log $K = 5.32 \pm 0.008$ 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 [Fe^{II}:Cu^{II}]. All the titrations were performed in HEPES buffer at pH 7.4 at 298 K.



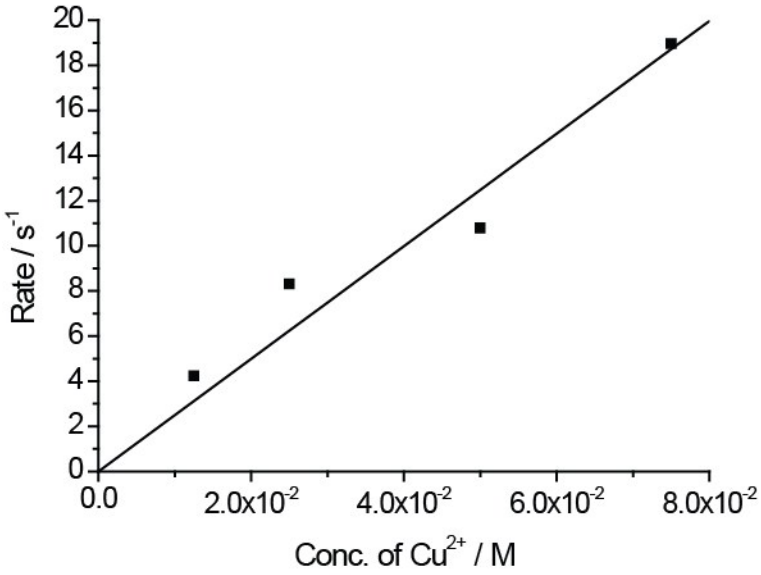
SI.Figure 2. (a) Spectroscopic titrations of $K_2[Fe^{II}(^tBubpy)(CN)_4]$ (5×10^{-5} M) by $Cu^{II}(dien)Cl_2$ (0 to 2×10^{-4} M) (b) The slope and y-intercept are 3.80×10^{-9} M and 2.88 respectively of the best fitted $A_0/(A-A_0)$ *versus* $1/\{[Cu^{II}(dien)Cl_2]\}^2$ plot with log $K = 4.44 \pm 0.001$ 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.



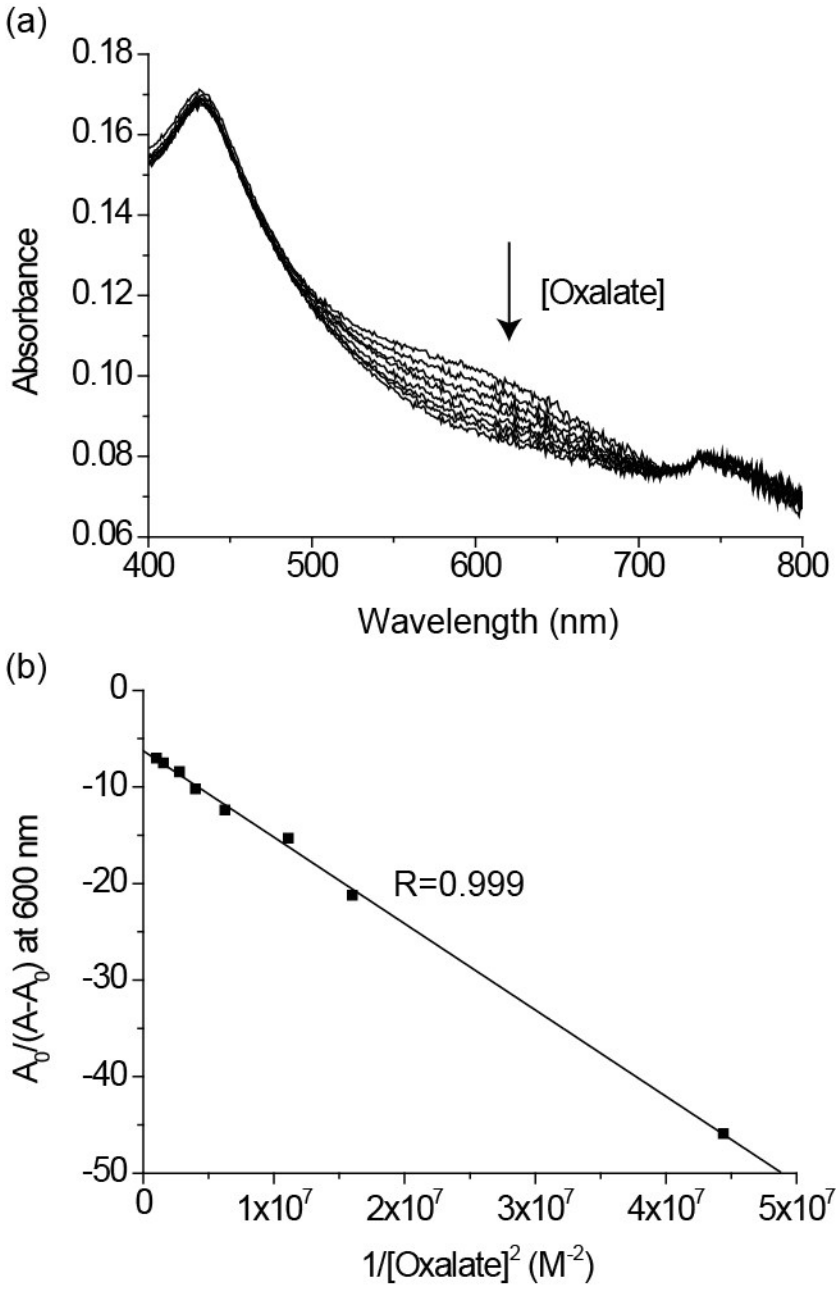
SI.Figure 3. (a) Spectroscopic titrations of $Fe^{II}(^{t}Bubpy)_2(CN)_2$ (5×10^{-5} M) by $Cu^{II}(dien)Cl_2$ (0 to 1×10^{-4} M) (b) The slope and y-intercept are -3.07×10^{-2} M and 6.51×10^{-1} respectively of the best fitted $A_0/(A-A_0)$ *versus* $1/\{[Cu^{II}(dien)Cl_2]^{0.5}\}$ plot with log $K = 2.65 \pm 0.001$ at 561 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}: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.



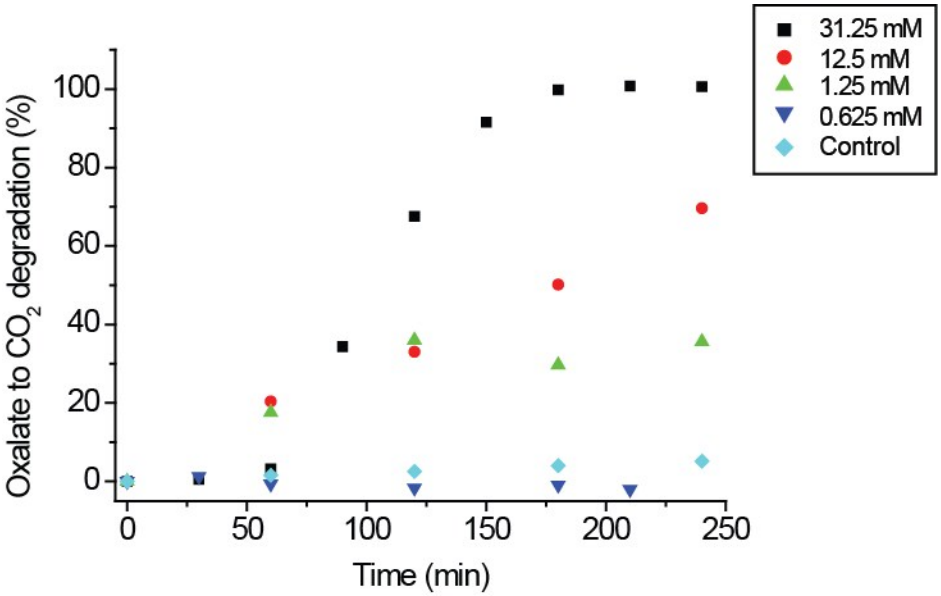
SI.Figure 4. Electrospray mass spectra of (a) "complex **1** / **2** or **3**-cyanide-mixture" and *(inset)* the simulation of $[Cu^{II}(dien)(CN)]^+$ (*m*/*z* 192.0); and (b) "complex **1**/ **2** or **3**-oxalate-mixture" and *(inset)* the simulation of $[Cu^{II}(dien)(OOC–COO)(K)]^+$ (*m*/*z* 293.0).The mass spectra were performed in aqueous methanol.



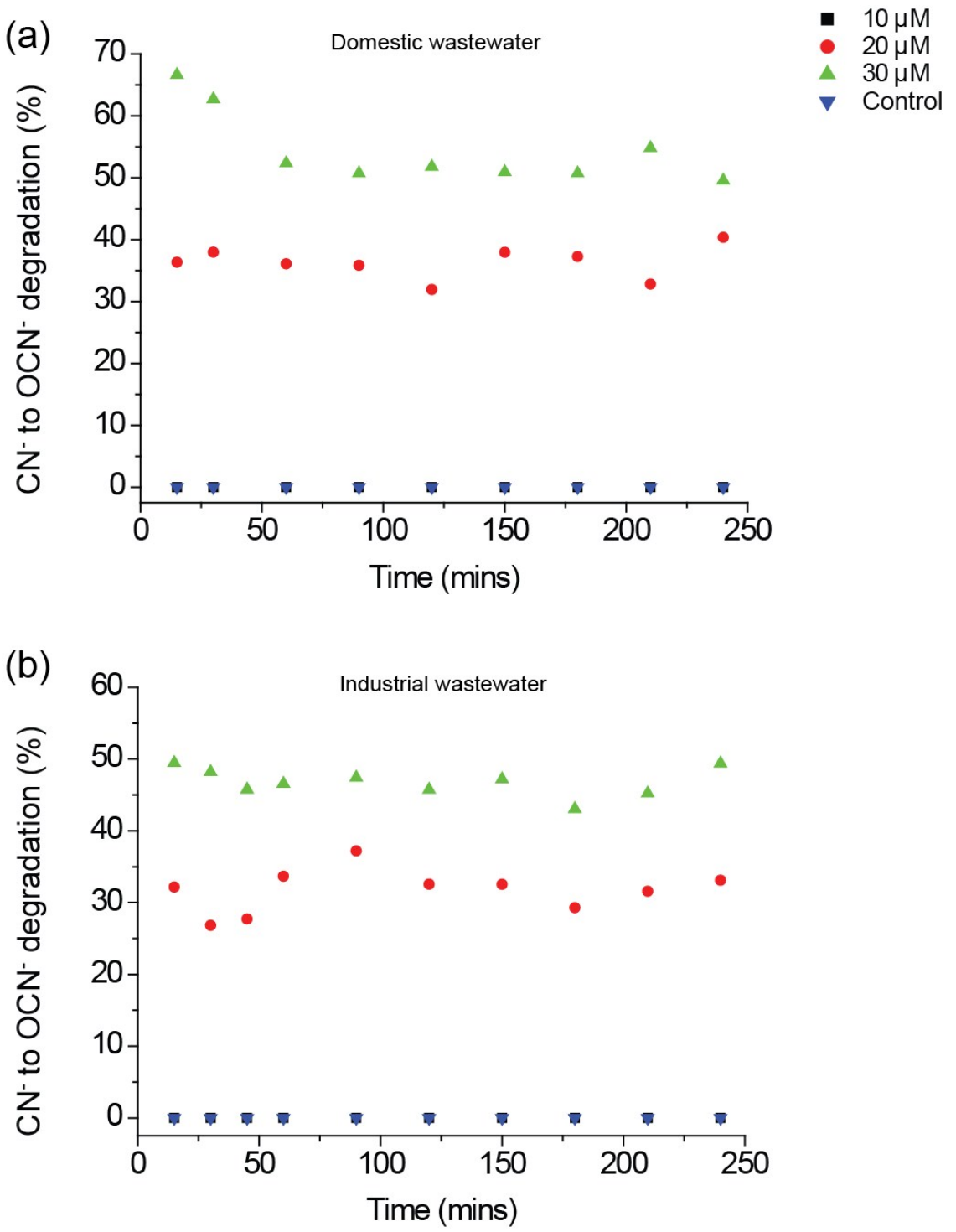
SI.Figure 5. Kinetic plot of apparent association rate constant k_{obs} (s^{-1}) *versus* Cu^{2+} concentration. The rate constant value was calculated from the slope (249.5 $M^{-1}s^{-1}$) of the curve (y =mx). All the k_{obs} data were retrieved from Sarla, M.; Pandit, M.; Tyagi, D. K.; Kapoor, J. C. *J. Hazard. Mater.* **2004**, *B116*, 49-56.



SI.Figure 6. (a) UV–vis spectroscopic titrations of $Cu^{II}(dien)Cl_2$ (5×10^{-4} M) with oxalate (0 to 1×10^{-3} M). (b) The slope and y-intercept are -8.95×10^{-7} M and -6.25×10^{-1} respectively of the best fitted $A_0/(A-A_0)$ *versus* 1/[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** (6.25×10^{-4} M) against time. The formation of CO_2 in the absence of catalyst (✹). All the experiments were performed with H_2O_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.