Supplementary Material for the Manuscript

Synthesis, Magnetostructural Correlation and Catalytic Promiscuity of Unsymmetric Dinuclear Cu(II) Complexes: Models for Catechol Oxidases and Hydrolases

Renata E.H.M.B.Osório,[1] Rosely A. Peralta,[1] Adailton J. Bortoluzzi,[1] Vicente R. de Almeida,[1] Bruno Szpoganicz,[2] Franciele L. Fischer,[3] Hernán Terenzi,[3] Antonio S. Mangrich,[4] Dalva E. C. Ferreira,[5] Willian R. Rocha,[5] Wolfgang Haase,[6] Zbigniew Tomkowicz,[6,7], Ademir dos Anjos,[8] and Ademir Neves[1]*

Supplementary Material

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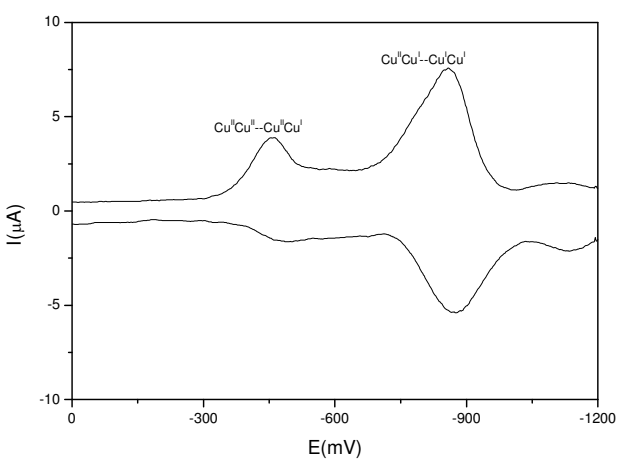
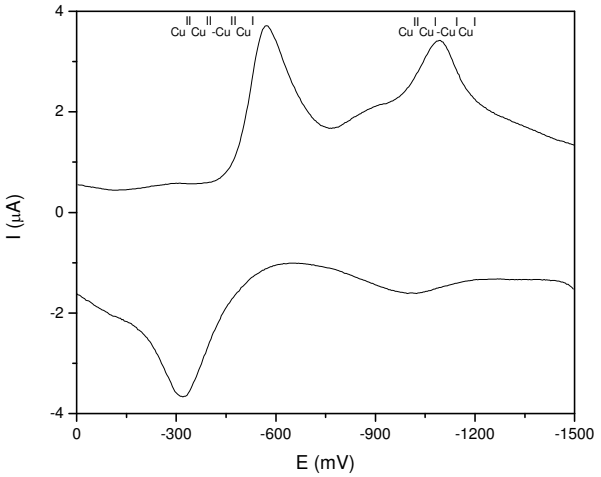
[*]Corresponding author: ademir@qmc.ufsc.br; tel.: +55 4837219219; fax: +55 4837219711



(a)



(b)

Figure S1. Square wave voltammograms of complexes **1** (a) and **2** (b) in CH_3CN, 0.1 $mol.L^{-1}$ [(TBA)PF_6]. Concentration of complexes – 5.0 x 10^{-4} $mol.L^{-1}$; platinum working electrode; platinum wire counter electrode; Ag/Ag^+ reference electrode. The Fc^+/Fc couple (E_0 = 400 mV *vs.* NHE) was used as the internal standard.[1]

1. Gagné, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.,* **1980**, *19*, 2855-2857.

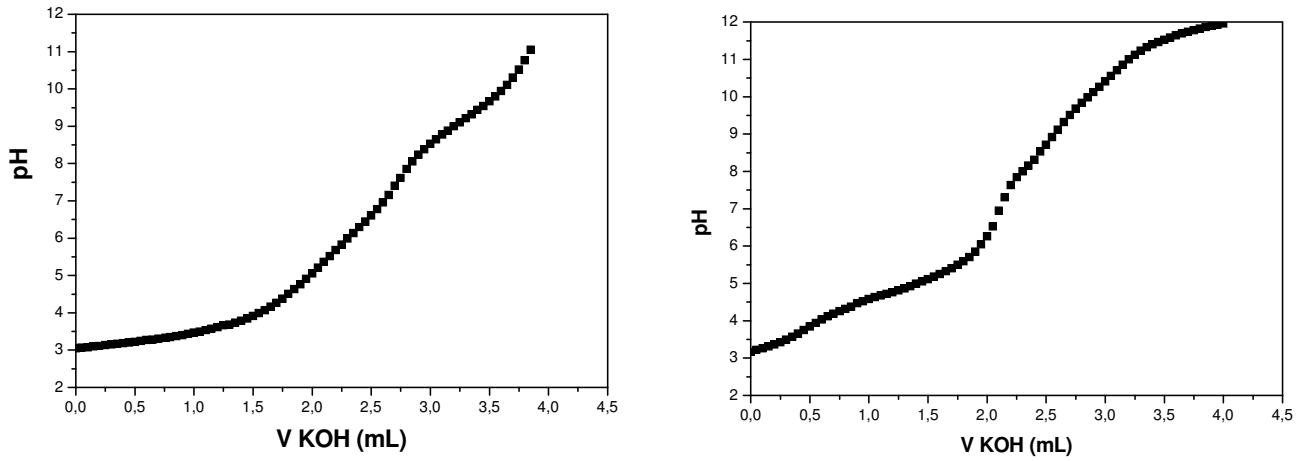


Figure S2. Potentiometric titration curves of complexes **1** (left) and **2** (right). Conditions: Complex = 0.05 mmol; [KCl] = 0.100 mol.L^{-1}; [KOH] = 0.100 mol.L^{-1}; in solution ethanol /water (70:30%v/v – 50 mL) at 25ºC.

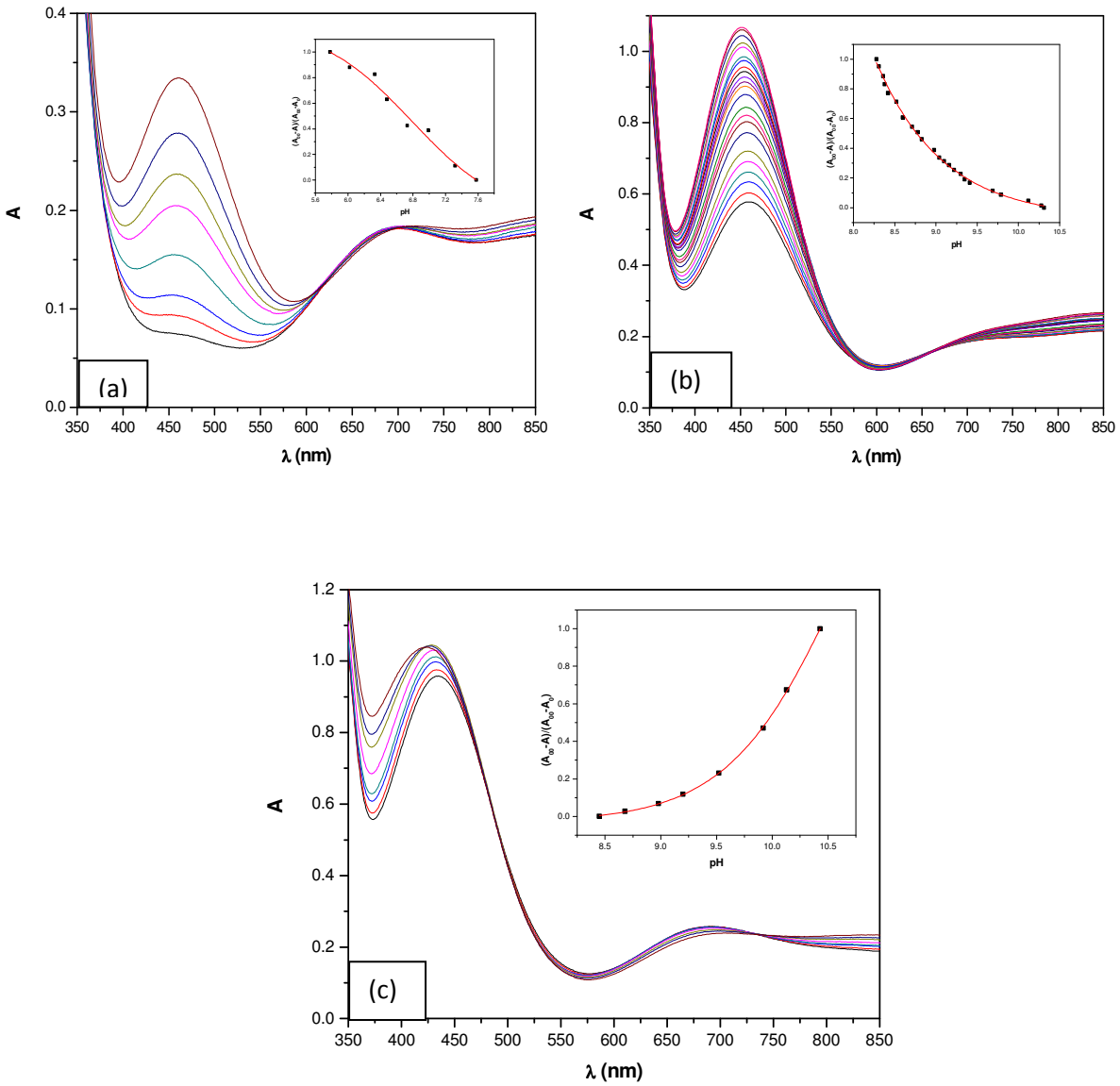


Figure S3. Spectrophotometric titration of **1** (a) (pH value: 5.68-7.58; pK_a = 6.48) and (b) (pH value: 8.28-10.31; pK_a = 8.17) **2** (c) (pH value: 8.45-10.43; pK_a = 10.64). Conditions: Complex = 0.05 mmol; [KCl] = 0.100 mol.L^{-1}; [KOH] = 0.100 mol.L^{-1}; in solution ethanol /water (70:30%v/v – 50 mL) at 25ºC.

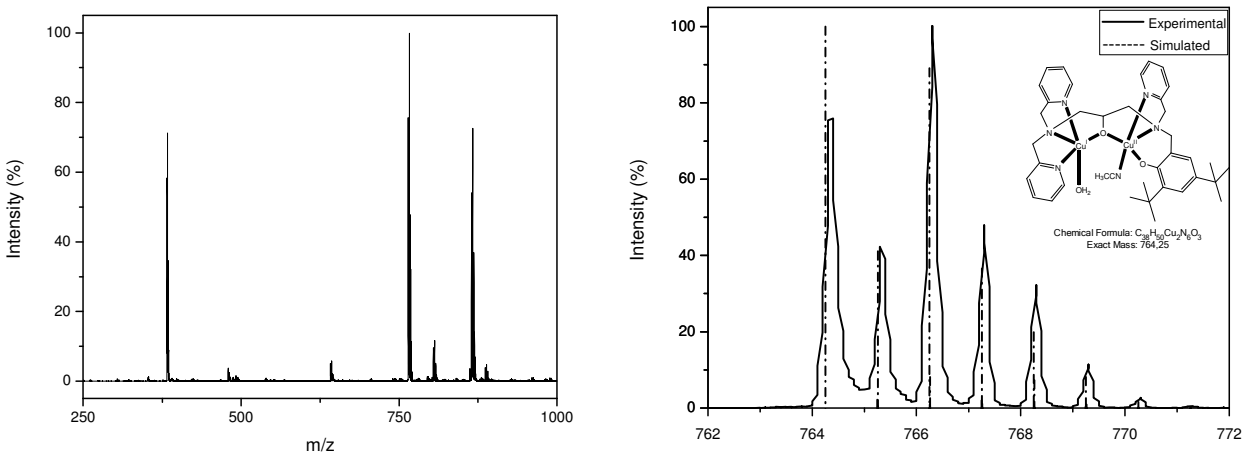


Figure S4. ESI-MS spectra of complex **1** in CH_3CN/water (50:50).

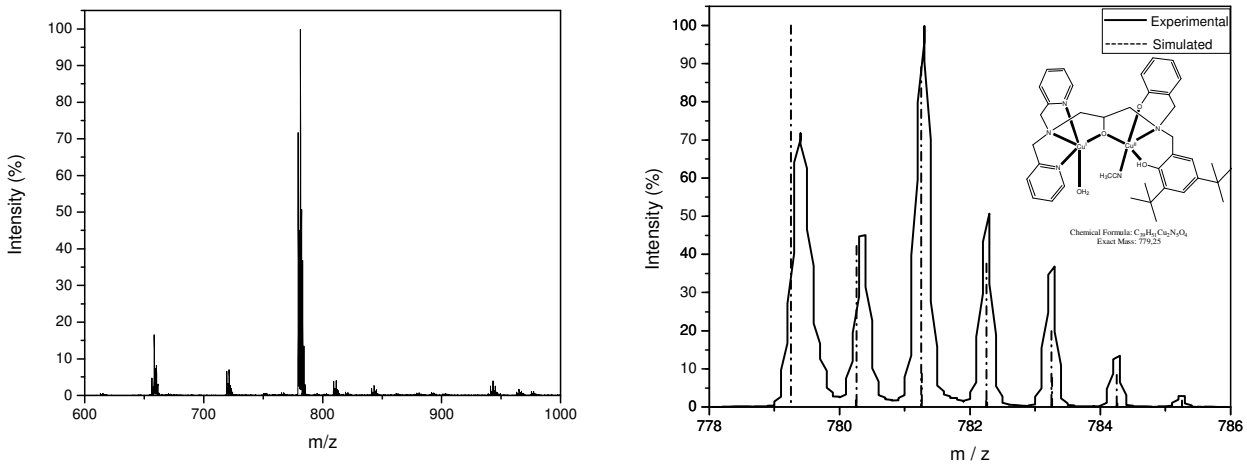


Figure S5. ESI-MS spectra of complex **2** in CH_3CN/water (50:50).

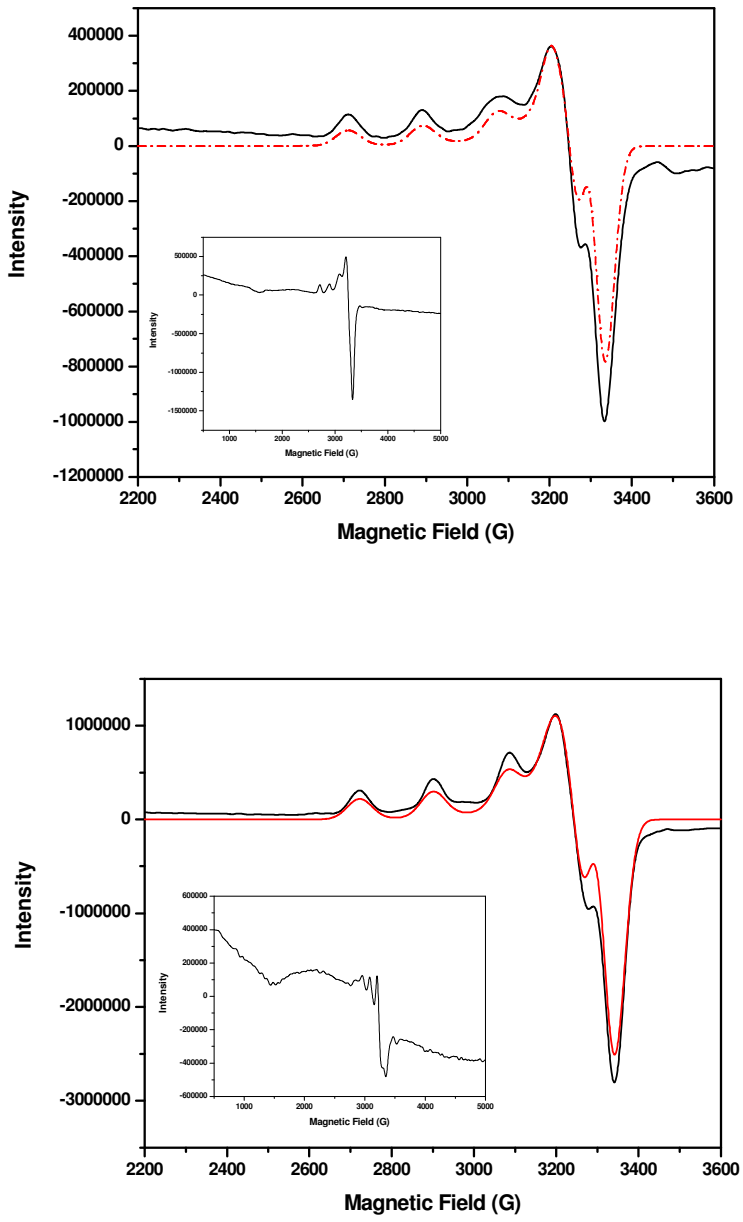


Figure S6. X-band EPR spectra of complexes **1**(top) and **2** (bottom) in acetonitrile/water (50:50) frozen solution at 77K, [buffer] = 0.05 mol.L^{-1} (HEPES pH 7.0). Experimental (black); simulated (red). Inset gives the EPR spectra showing the $\Delta M_S = \pm 2$ transitions.

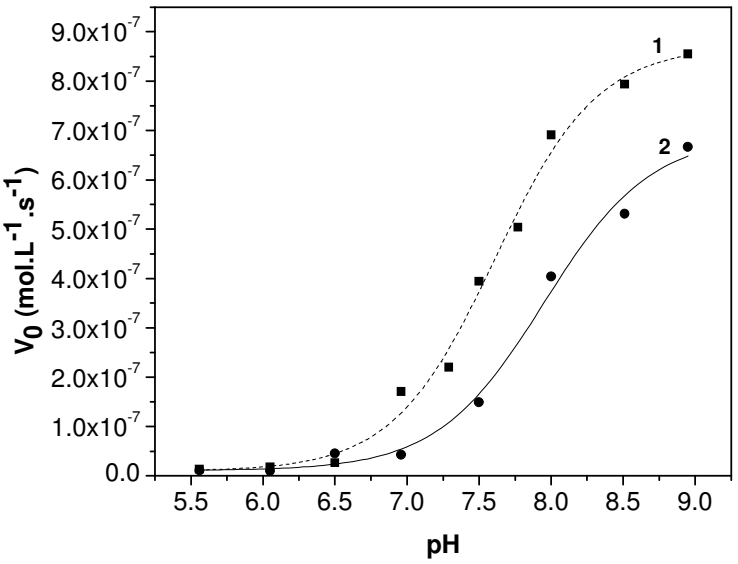


Figure S7. Dependence of the reaction rates on pH for the oxidation of 3,5-DTBC catalyzed by complexes **1** (■) and **2** (●) Conditions: [Complex] = 2.40 x 10^{-5} mol.L^{-1}; [3,5-DTBC] = 5.00 x 10^{-3} mol.L^{-1} for **1** and 2.00 x 10^{-3} for **2**; [Buffer] = 3.30 x 10^{-2} mol.L^{-1}; in solution CH_3OH / H_2O (32:1) at 25ºC.

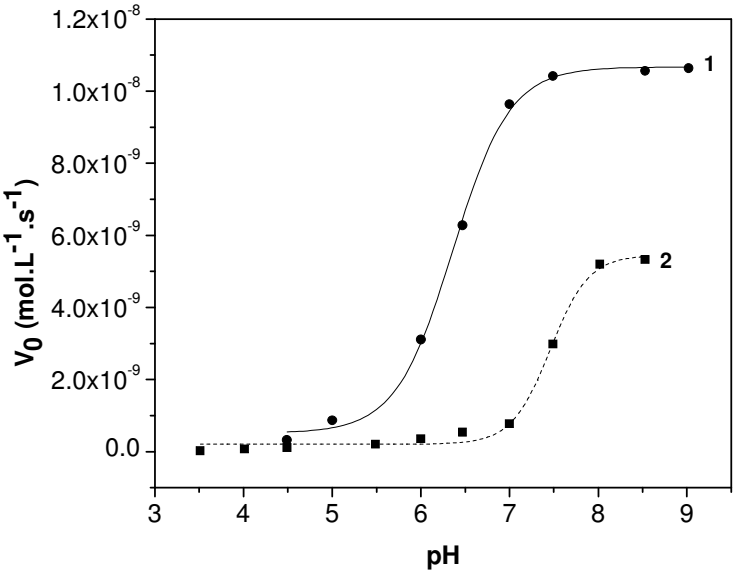


Figure S8. Dependence of the initial reaction rate on the pH in the hydrolysis of 2,4-BDNPP promoted by complexes **1** (•) and **2** (■). Conditions: solution CH_3CN/H_2O 1:1; [complex] = 4.0 x 10^{-5} mol.L^{-1}; [buffer] = 0.05 mol.L^{-1} (HEPES pH 8.0); *I* = 0.05 mol.L^{-1} ($LiClO_4$); [2,4-BDNPP] = 5.0 x 10^{-3} mol.L^{-1} (**1**) and 2.0 x 10^{-3} mol.L^{-1} (**2**)

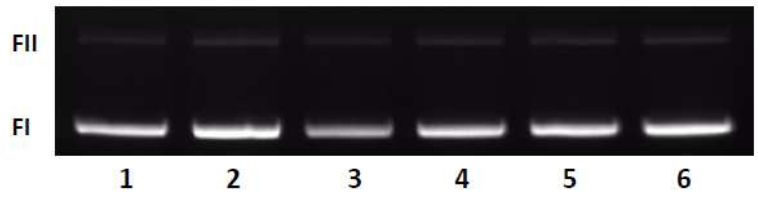


Figure S9. Cleavage of pBSK II (25 µM pb) by copper(II) chloride ($CuCl_2$) in 25 mmol.L^{-1} CHES buffer pH 9.0, where lane 1 is the DNA control and lanes 2-6 are DNA + $CuCl_2$ (10, 20, 30, 40 and 50 µmol.L^{-1}, respectively). Incubation: 6 h at 37 ºC.