Electronic supplementary information for:

Galactose Oxidase models: Insights from ^{19}F NMR spectroscopy

By Fabien Michel, Sylvain Hamman, Christian Philouze, Carlos Perez Del Valle, Eric Saint-Aman, and Fabrice Thomas.

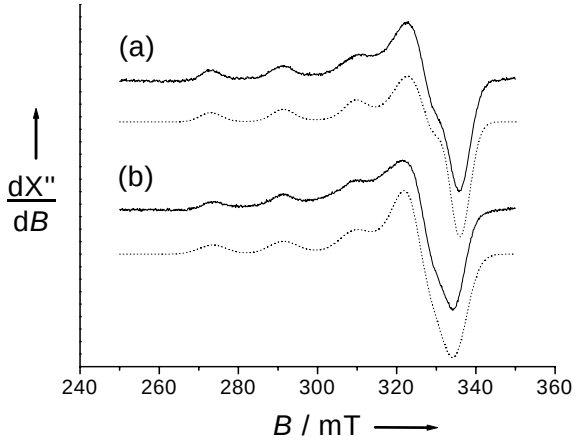

Fig S1: X-Band EPR spectra (solid lines) of 2 mM CH_3CN solutions of (a) $[Cu^{II}(HL^{CF3})(CH_3CN)]^{2+}$ and (b) $[Cu^{II}(L^{CF3})(CH_3CN)]^{+}$. Dotted lines represent simulations using the parameters: $g_{xx} = g_{yy} = 2.054$, $g_{zz} = 2.240$, $A_{xx} = A_{yy} = 2$ mT, $A_{zz} = 18.2$ mT ($[Cu^{II}(HL^{CF3})(CH_3CN)]^{2+}$) and $g_{xx} = g_{yy} = 2.064$, $g_{zz} = 2.242$, $A_{xx} = A_{yy} = 0.5$ mT, $A_{zz} = 17.8$ mT ($[Cu^{II}(L^{CF3})(CH_3CN)]^{+}$). Microwave freq. 9.413 GHz (a) 9.417 (b), power: 20 mW; Mod. Freq. 100 kHz, amp. 0.0987 mT; T = 100 K.

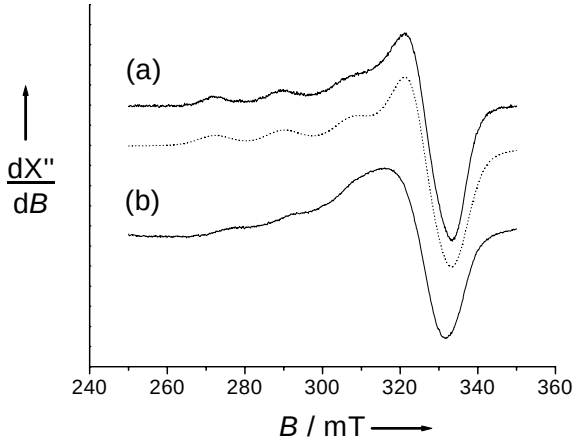

Fig S2: X-Band EPR spectra (solid lines) of 1 mM CH_3CN solutions of (a) $[Cu^{II}(HLq^{OMe})(CH_3CN)]^{2+}$ and (b) $[Cu^{II}(Lq^{OMe})(CH_3CN)]^{+}$. Dotted lines represent a simulation using the parameters: $g_{xx} = g_{yy} = 2.063$, $g_{zz} = 2.253$, $A_{xx} = A_{yy} = 0.5$ mT, $A_{zz} = 17.6$ mT. The spectrum of $[Cu^{II}(Lq^{OMe})(CH_3CN)]^{+}$ was too broad to obtain accurate spin Hamiltonian parameters by simulation. Microwave freq. 9.412 GHz (a) 9.418 (b), power: 20 mW; Mod. Freq. 100 kHz, amp. 0.0555 mT (a) 0.393 mT (b); T = 100 K.

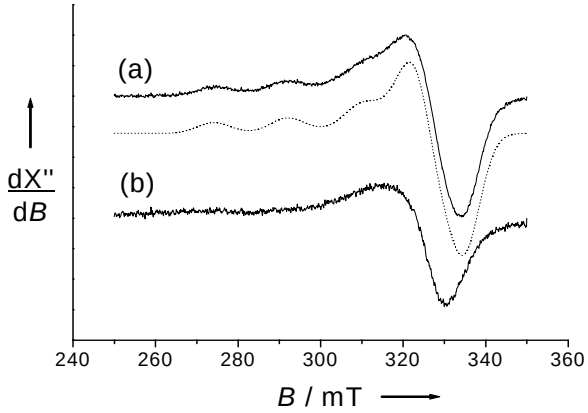

Fig S3: X-Band EPR spectra (solid lines) of 1 mM CH_3CN solutions of (a) $[Cu^{II}(HLq^{NO2})(CH_3CN)]^{2+}$ and (b) $[Cu^{II}(Lq^{NO2})(CH_3CN)]^{+}$. Dotted lines represent a simulation using the parameters: $g_{xx} = g_{yy} = 2.063$, $g_{zz} = 2.238$, $A_{xx} = A_{yy} = 0.5$ mT, $A_{zz} = 17.8$ mT. The spectrum of $[Cu^{II}(Lq^{NO2})(CH_3CN)]^{+}$ was too unresolved to obtain accurate spin Hamiltonian parameters by simulation. Microwave freq. 9.418 GHz (a) 9.420 (b), power: 20 mW; Mod. Freq. 100 kHz, amp. 0.197 mT (a) 0.0987 mT (b); T = 100 K.

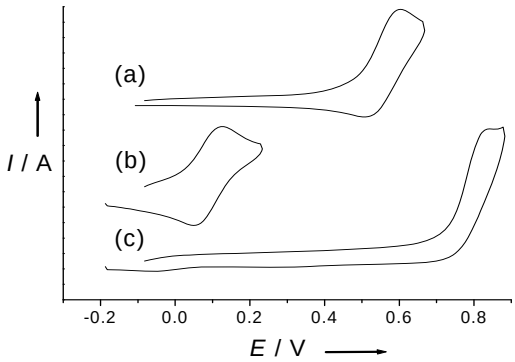

Fig S4: CV curves of 1 mM CH_3CN solutions (containing 0.1 M TBAP) of (a) $[Cu^{II}(L^{CF3})(CH_3CN)]^{+}$, (b) $[Cu^{II}(Lq^{OMe})(CH_3CN)]^{+}$, (c) $[Cu^{II}(Lq^{NO2})(CH_3CN)]^{+}$. T = 298 K, scan rate = 0.1 $V.s^{-1}$. Potentials are given relative to the Fc/Fc^{+} redox couple.

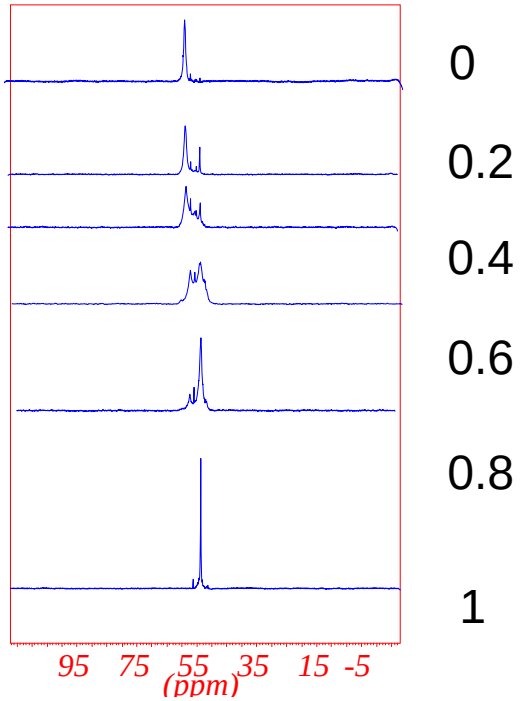

Fig S5: Titration of $[Cu^{II}(HLq^{OMe})(CH_3CN)]^{2+}$ (60 mM) with NEt_3; ^{19}F NMR spectra were recorded in (CD_3CN : CH_3CN) (1 : 4) at 293 K. The numbers correspond to the molar equivalents of base added; intensities are normalized.

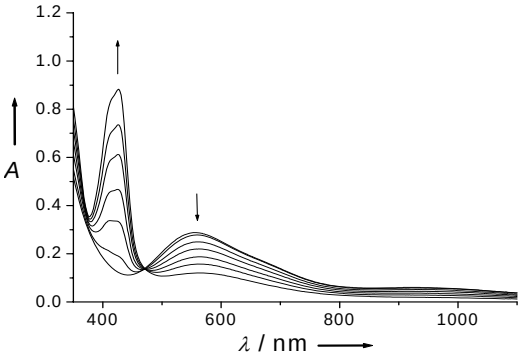

Fig S6: Titration of $[Cu^{II}(Lq^{OMe})(CH_3CN)]^{+}$ (0.3 mM) by 0 to 1 copper molar equivalent of copper(II) perchlorate. Arrows indicate spectral changes upon addition of copper; spectra recorded in CH_3CN at 238 K (l = 1.000 cm).