

# Supplementary Materials: Electrochemical conversion of the lignin model veratryl alcohol to veratryl aldehyde using manganese(III)-Schiff base homogeneous catalysts

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## 1. Experimental details for materials and methods

### 1.1 Chemical and Reagents

All the starting materials (Aldrich) and solvents (Probus) used for the synthesis were of commercially available reagent grade and were used without further purification.

### 1.2 Physical measurements

Elemental analyses were performed on a Carlo Erba Model 1108 CHNS-O elemental analyzer. The IR spectra were recorded as KBr pellets on a Bio-Rad FTS 135 spectrophotometer in the range of 4000–400  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectra were recorded on a Bruker AC-300 spectrometer using  $\text{DMSO-d}_6$  (296 K) as solvent and  $\text{SiMe}_4$  as an internal reference. The EPR experiments were performed on a Bruker X-band EPR spectrometer Elexsys580 using a parallel-mode resonator ER 4116DM and an Oxford cryostat ESR900. The electro-spray mass spectra of the compounds were obtained on a Hewlett-Packard model LC-MSD 1100 instrument (positive ion mode, 98:2  $\text{CH}_3\text{OH-HCOOH}$  as mobile phase, 30 to 100 V). Room-temperature magnetic susceptibilities were measured using a digital measurement system MSB-MKI, calibrated using mercury tetrakis(isothiocyanato)cobaltate(II)  $\text{Hg}[\text{Co}(\text{NCS})_4]$  as a susceptibility standard. Variable-temperature magnetic data were obtained with a Quantum Design MPMS SQUID susceptometer. Sample was a 3 mm diameter pellet molded from ground crystalline sample. Electronic spectra were recorded on a Cary 230 spectrometer. Conductivities of  $10^{-3}$  M solutions in DMF were measured on a Crison microCM 2200 conductivimeter.

Cyclic voltammetry was performed using an EG&G Princeton Applied Research model 273 potentiostat, controlled by EG&G PAR model 270 software. A Metrohm model 6.1204.000 graphite disc was used as working electrode. A saturated calomel electrode was used as reference and a platinum wire as an auxiliary electrode. Measurements were made with ca.  $10^{-3}$  M solutions of complexes in DMF using 0.1  $\text{mol dm}^{-3}$  tetraethylammonium perchlorate as a supporting electrolyte.

### 1.3 Synthesis of the complexes

$\text{Mn}_2\text{L}^2(\text{H}_2\text{O})_2(\text{DCA})_2$  (**1**). 0.42 mmol (0.15 g) of  $\text{H}_2\text{L}^2$  was dissolved in methanol (40 mL) and 0.42 mmol (0.12 g) of  $\text{Mn}(\text{CH}_3\text{COO})_2$  was added to the initial yellow solution which changed to brown. The mixture was gently heated and stirred for 30 min, and then 0.42 mmol (0.04 g) of  $\text{NaN}(\text{CN})_2$  in 10 mL of methanol was added. The mixture was stirred until evaporation of half of its volume, and then it was left to crystallization by slow evaporation. The crystals were isolated by filtration and washed with diethyl ether.

$\text{MnL}^3(\text{H}_2\text{O})_2(\text{ClO}_4)$  (**3**). 1.99 mmol (1.00 g) of  $\text{H}_2\text{L}^3$  was dissolved in 100 mL of a 1:1 methanol-ethanol mixture and 1.99 mmol (0.72 g) of  $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  was added to the initial yellow solution which changed to green (CAUTION: Although no problems have been encountered in this work, perchlorates are potentially explosive and should be handled in only small quantities and with care!). After stirring for ten minutes, 3.98 mmol (0.16 g) of NaOH, dissolved in a small quantity of water, was added, and the mixture turned dark. The progress of the reaction was followed by TLC for three

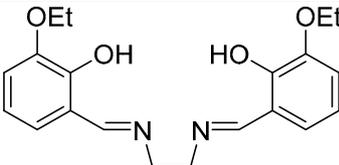
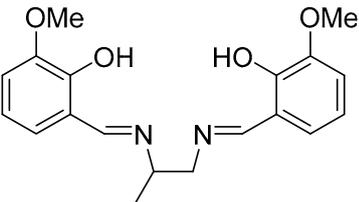
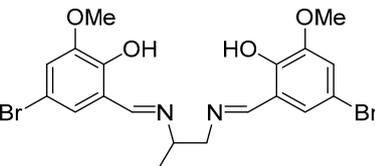
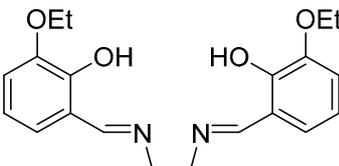
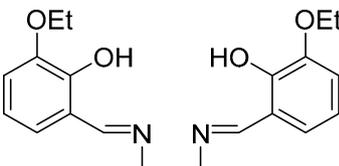
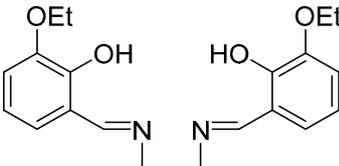
days and the mixture was then filtered. The complex was obtained from the filtrate as a brown solid after crystallisation. It was isolated by filtration and washed with diethyl ether and dried in air.

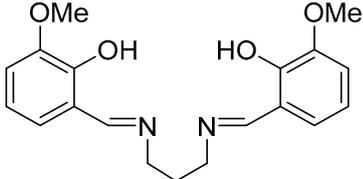
$\text{Mn}_2\text{L}^4_2(\text{H}_2\text{O})_2(\text{DCA})_2$  (**5**), 0.41 mmol (0.15 g) of  $\text{H}_2\text{L}^4$  was dissolved in methanol (40 mL) and 0.41 mmol (0.11 g) of  $\text{Mn}(\text{CH}_3\text{COO})_2$  was added to the initial yellow solution which changed to brown. The mixture was gently heated and stirred for 30 min, and then 0.41 mmol (0.04 g) of  $\text{NaN}(\text{CN})_2$  in 10 mL of methanol was added.

$\text{MnL}^4(\text{H}_2\text{O})_2(\text{ClO}_4)$  (**6**),  $\text{H}_2\text{L}^4$  (1.62 mmol, 0.6 g) was dissolved in methanol (40 mL) and  $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (1.62 mmol, 0.59 g), dissolved in methanol was added to the initial yellow solution, which changed to green. After stirring for 10 min,  $\text{NaOH}$  (3.24 mmol, 0.13 g), dissolved in a small quantity of water, was added and the mixture turned black. The progress of the reaction was followed by TLC for three days and the mixture was then filtered. The complex was obtained from the filtrate as a brown solid after crystallisation. It was isolated by filtration and washed with diethyl ether and dried in air.

## 2. Table

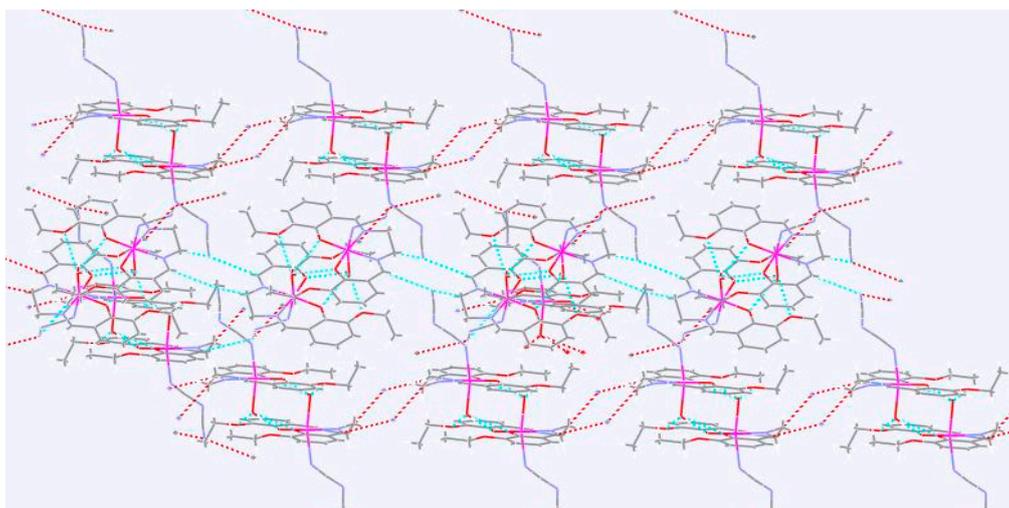
**Table S1.** Compound formula, structure of the Schiff base ligand and reference.

| Complex | Formula  | Schiff base ligand   | Reference <sup>a</sup> |
|---------|--|--|------------------------|
| 1       | $\text{Mn}_2\text{L}^1_2(\text{H}_2\text{O})_2(\text{N}(\text{CN})_2)_2$               |   | This work              |
| 2       | $\text{MnL}^2(\text{H}_2\text{O})_2(\text{NO}_3)(\text{CH}_3\text{OH})$                |  | Ref. 26 (2)            |
| 3       | $\text{MnL}^3(\text{H}_2\text{O})(\text{ClO}_4)$                                       |  | This work              |
| 4       | $\text{Mn}_2\text{L}^1_2(\text{H}_2\text{O})_4(\text{NO}_3)_2(\text{CH}_3\text{OH})_2$ |  | Ref. 17 (4)            |
| 5       | $\text{Mn}_2\text{L}^4_2(\text{H}_2\text{O})_2(\text{N}(\text{CN})_2)_2$               |  | This work              |
| 6       | $\text{MnL}^4(\text{H}_2\text{O})_2(\text{ClO}_4)$                                     |  | This work              |

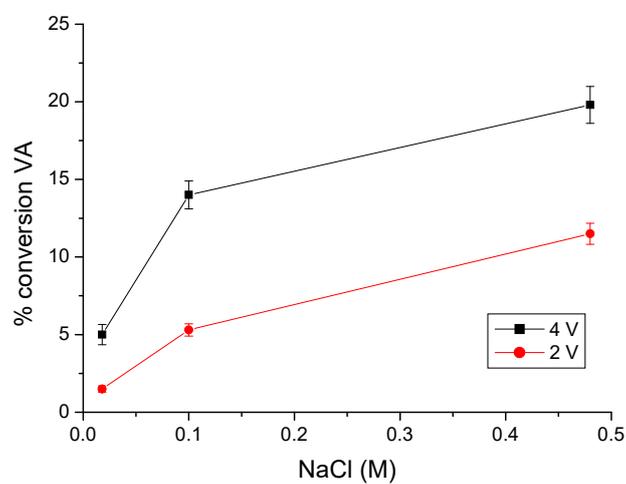
|   |   |  |             |
|---|---|--|-------------|
| 7 | $\text{MnL}^5(\text{H}_2\text{O})_2(\text{N}(\text{CN})_2)$ |  | Ref. 27 (3) |
|---|---|--|-------------|

<sup>a</sup>In parentheses, compound number in the reference

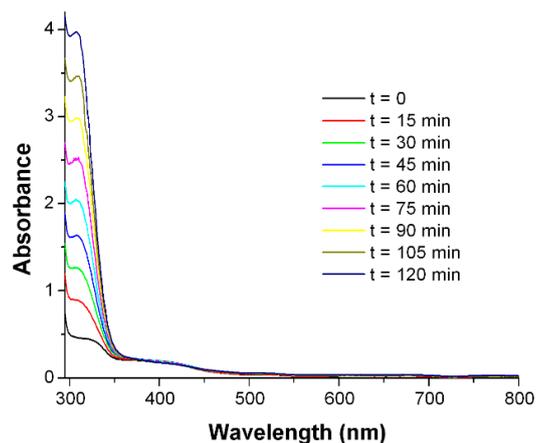
### 3. Figures



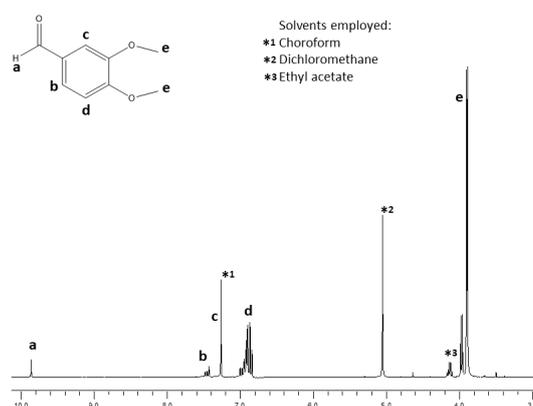
**Figure S1.** Stick diagram for 1 showing the hydrogen bonding network.



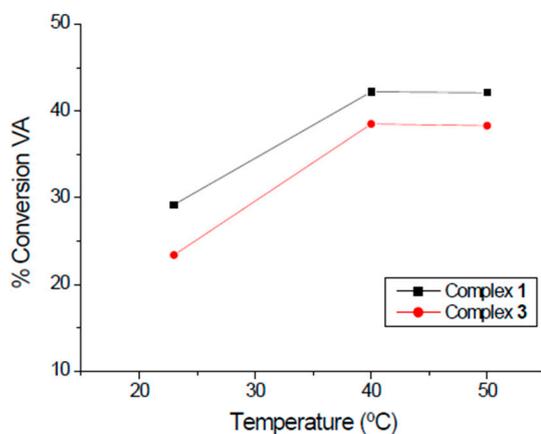
**Figure S2.** Conversion of veratryl alcohol to veratryl aldehyde catalysed by 1 using different NaCl concentrations. Conditions: 23 °C; pH 7.0; results after 60 min.



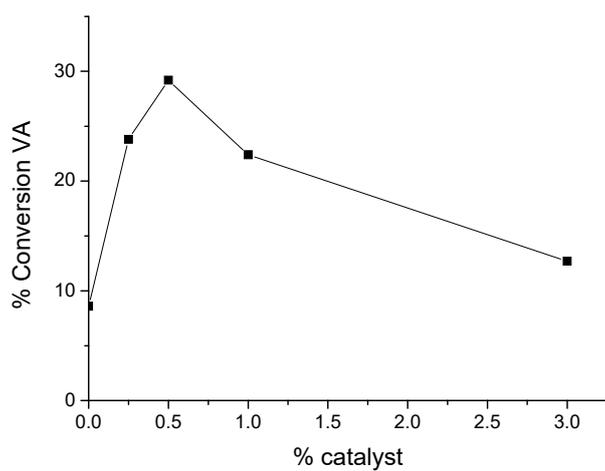
**Figure S3.** Evolution over time of the UV-Vis spectra in the electrochemical cell using **1** as catalyst. The formation of veratryl aldehyde is followed by its characteristic absorption band at 310 nm. Conditions: 4 V; 40 °C; pH 8.25; 0.48 M NaCl; initial veratryl alcohol concentration =  $1 \times 10^{-3}$  M.



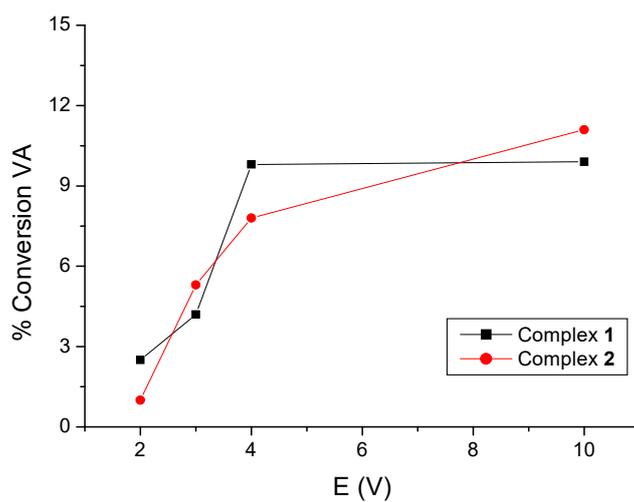
**Figure S4.**  $^1\text{H}$  NMR spectrum (in  $\text{CDCl}_3$ ) of the veratryl aldehyde isolated product after electrocatalytic oxidation of veratryl alcohol.



**Figure S5.** Conversion of veratryl alcohol to veratryl aldehyde at different temperature using catalysts **1** and **3**. Conditions: 4 V; 0.48 M NaCl; pH 8.25.



**Figure S6.** Conversion of veratryl alcohol to veratryl aldehyde using different concentrations of catalyst 1. Conditions: 4 V; 0.48 M NaCl; 23 °C; pH 8.25.



**Figure S7.** Conversion of veratryl alcohol to veratryl aldehyde at different potentials. Conditions: 0.1 M NaCl; 23 °C; pH 7.0; 1% catalyst.