Electronic Supplementary Information

Synthesis of vanillin *via* a catalytically active Cu(II)-Metal Organic Polyhedron

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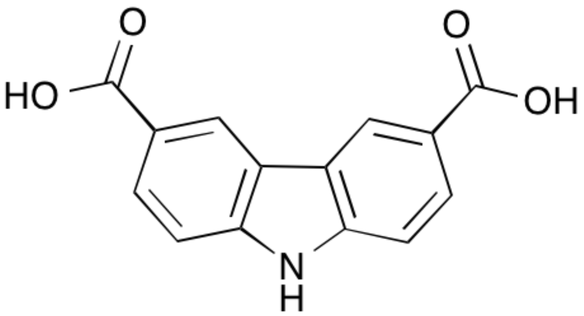
1. Experimental

All reagents and solvents were used as received from commercial suppliers without further purification. Powder X-ray diffraction (PXRD) data were collected under ambient conditions on a Bruker AXD D8 Advance diffractometer operated at 160 W (40 kV, 40 mA) for Cu Kα1 (λ= 1.5406 Å). Thermal gravimetric analysis (TGA) was performed under N_2 at a heating rate of 2 °C/min using a TA Instruments Q500HR analyser. Inductively coupled plasma mass spectrometry was conducted on a Varian model ICP spectrometer. IR spectra were recorded using a Bruker TENSER 27 FT-IR spectrophotometer. Gas chromatography (GC) was performed using a Innowax column (30 mX 0.25 mm ID and 0.25 thickness) with a N_2 flow of 0.2 mL/min, FID 230 ^{o}C, heating ramp of 10 oC from 50 to 230 ^{o}C. For high-resolution mass spectrometry (HMRS), the samples were dissolved or diluted in 100% Acetonitrile acidified with 0.1% formic acid. HR-ESI-MS was performed on a micrOTOF II instrument with an ESI-Sprayer source (Bruker Daltonics, Bremen, Germany). The mass spectrometer was controlled by the Compass 1.5 for micrOTOF software package (Bruker Daltonics, Rheinstetten, Germany). The instrument was operated on positive mode, and mass detection was performed in the full scan mode in the range of 50-3000 m/z. The used capillary voltage was 4500, end plate offset +500 V. The drying gas (N_2) flow rate was 10 L/min, and the drying gas temperature was 210°C. Cyclic voltammetry experiments *(CVs)* were carried out in a CH Instruments CHI1030C potentiostat in a 10 mL cell with the CPE as working electrode, a platinum wire as counter electrode and a Ag^0|AgCl reference electrode. All experiments were carried in a 0.1 M KNO_3 at 100 mV/min in a potential range from -0.6 to 0.6 V.

Catalytic protocol

Activated catalyst (MOP **1**), 0.005 g (0.4 mol%), suspended in THF (10 mL) was mixed with 3 mL of H_2O_2 (50 wt% in H_2O), 0.025 mL of acetonitrile and 0.50 g (2.57 X10^{-3} mol) of ferulic acid (dissolved in 40 mL of THF). The reaction mixture was heated to reflux for 3 h. After the reaction was finished, the catalyst was recovered by filtration; the filtrate was extracted with ethyl acetate and washed with a saturated solution of NH_4Cl. The combined organic phases were dried with anhydrous Na_2SO_4, filtrated and concentrated under vacuum. Finally, the residue was purified by column chromatography (AcOEt-hexane 5:95).



Scheme S1: *9H*-carbazole-3,6-dicarboxylic acid (H_2L^1) ligand used for the synthesis of MOP **1**.

2. Powder X-ray Diffraction Patterns

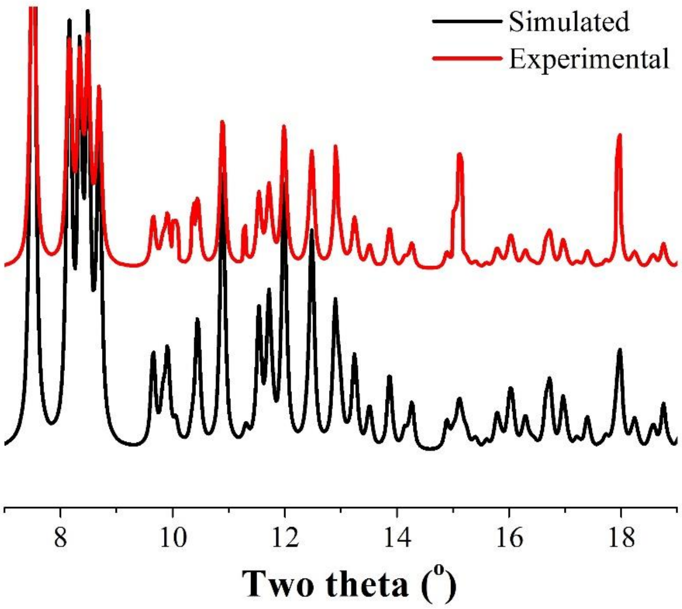


Fig. S1: PXRD patters of calculated (black) and as-synthesised (red) MOP **1**.

3. TGA plot

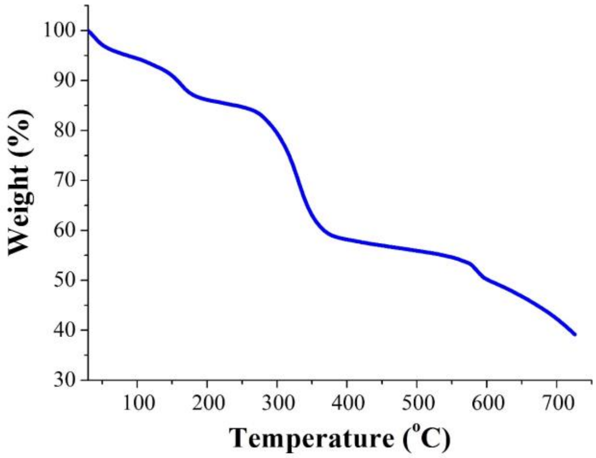


Fig. S2: Thermal gravimetrical analysis of as-synthesised MOP **1**.

4. FTIR experiments

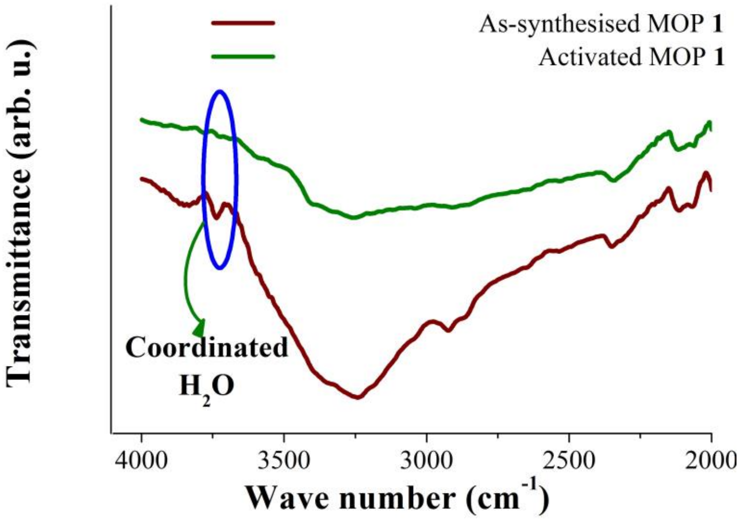


Fig. S3: FTIR spectra of MOP **1** at 25 °C. As-synthesised (wine line) and activated at 150 °C under vacuum (10^{-3} bar, gren line), emphasising the fade of coordinated H_2O molecules.

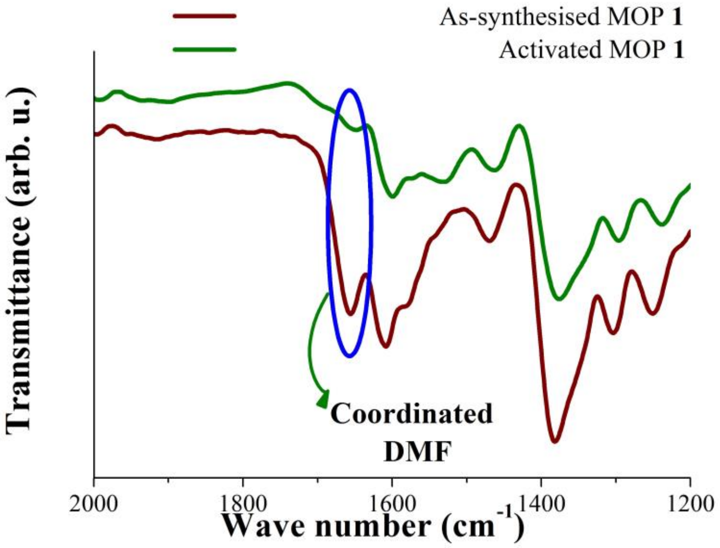


Fig. S4: FTIR spectra of MOP **1** at 25 °C. As-synthesised (wine line) and activated at 150 °C under vacuum (10^{-3} bar, gren line), emphasising the fade of coordinated DMF molecules.

5. Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Each of the 5 hot filtrates (coming from the catalytic reactions) were combined with OPTIMA grade nitric acid (180 µL) and OPTIMA grade sulphuric acid (180 µL). The mixture was heated to 90 °C for 2 h in an open container in a dust-free environment. The resulting solutions were diluted to 5.0 mL using 2% OPTIMA grade nitric acid. These stock solutions were diluted to 1:100 (v/v) with 2% nitric acid and analysed relative to a 50 ppb germanium internal standard on a Varian model ICP spectrometer using He collision gas mode.

Results

Analysis was done in CCT mode. The instrument passed its performance check. No analytes were observed to have tripped to analogue at any concentration measured and thus no cross calibration was necessary. A good calibration line was obtained for all elements. The washout samples are fine, indicating that there is no problem with carryover in this experiment. Cu was not found on samples 1 to 10. The detection limit of the Varian model ICP spectrometer was approximately from 0.4 ppm to 1 ppb.

6. ^{1}H-NMR and ^{13}C-NMR Spectra

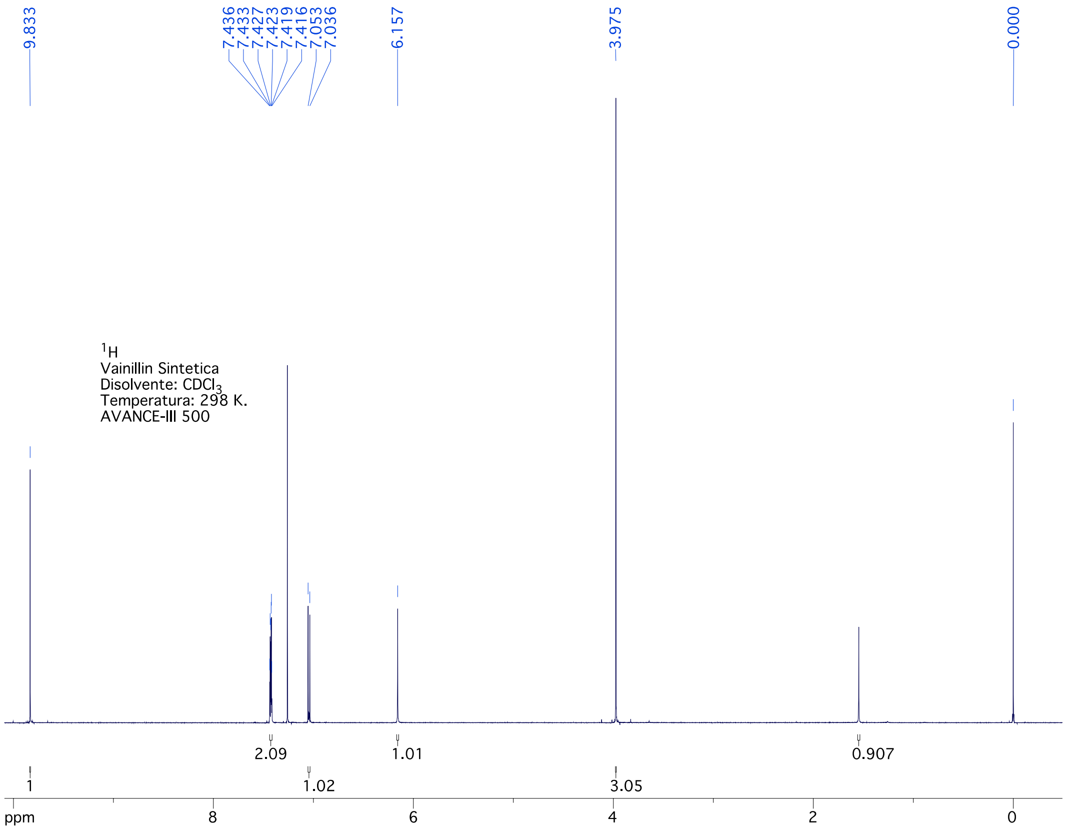


Fig. S5: ^{1}H-NMR spectrum of vanillin after column chromatography purification on silica gel.

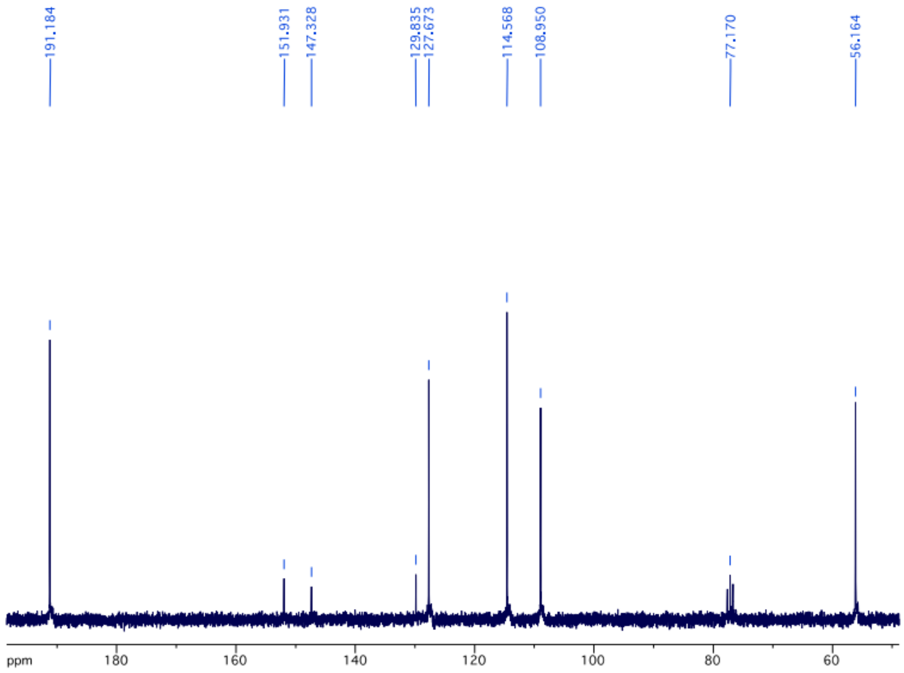


Fig. S6: ^{13}C-NMR spectrum of vanillin after column chromatography purification on silica gel.

7. PXRD of the catalyst after the reaction

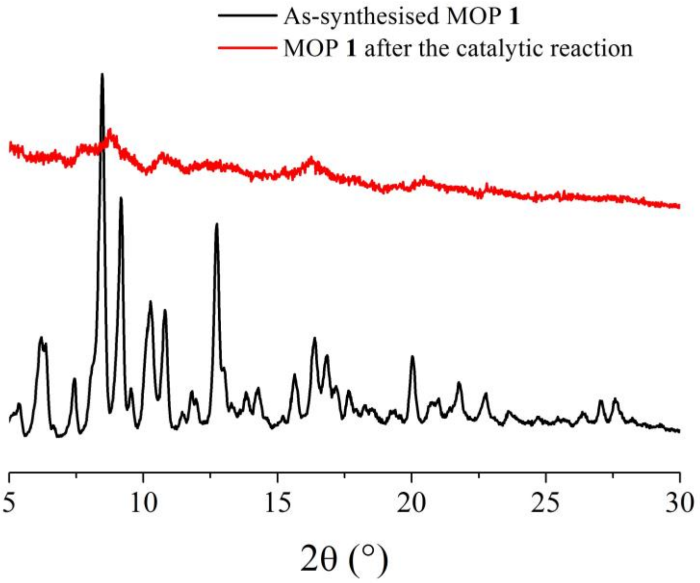


Fig. S7: PXRD of the as-synthesised MOP **1** and after the catalytic reaction experiment on MOP **1**.

8. Recyclability of the catalyst MOP 1

Activated catalyst (MOP **1**), 0.05g (50 mg, 0.4 mol%), suspended in THF (10 mL) was mixed with 3.0 mL of H_2O_2 (50 wt% aqueous), 0.025mL of acetonitrile and 0.50g ($2.57X10^{-3}$ mol) of ferulic acid (dissolved in 40 mL of THF). The reaction mixture was heated to reflux for 3 h. After the reaction was finished, the catalyst was recovered by filtration; the filtrate was extracted with ethyl acetate and washed with a saturated solution of NH_4Cl. The combined organic phases were dried with anhydrous Na_2SO_4, filtrated and concentrated under vacuum. Finally, the residue was purified by column chromatography (AcOEt-hexane 5:95).

Cycle	Activated Catalyst (mg)[*]	Reaction Yield (%)
1	50	60
2	50	55
3	48	49
4	47	44
5	47	40

[‡] Cyc. 0 corresponds to only the activated MOP **1** before any catalytic reaction.

[*] The mass loss from Cycle 0 to Cycle 5 was due the manipulation of the catalyst during the filtration, activation and sonication processes. In each case, we adjusted the rest of the reactants accordingly with the amount of activated catalyst. The reaction yield was obtained after isolation of the vanillin by column chromatography purification.

9. HMRS experiments

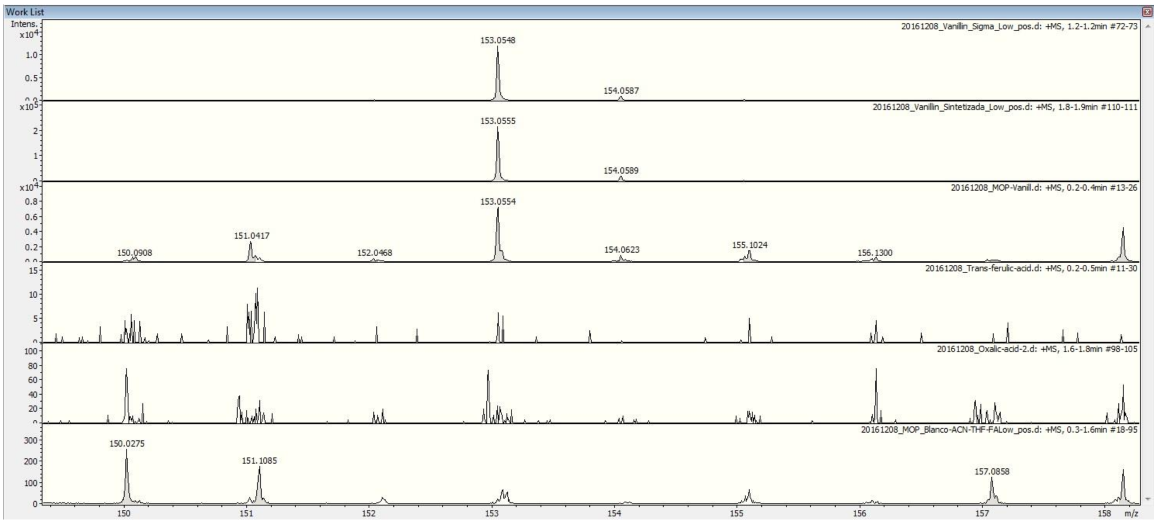


Fig. S8: HMRS spectra for vanillin in the bulk of the solution: m/z calcd. for: $C_8H_9O_2$ = 153.0546, found: 153.0554, 3rd spectrum top-down.

10.Cyclic voltammetry experiments (CVs)

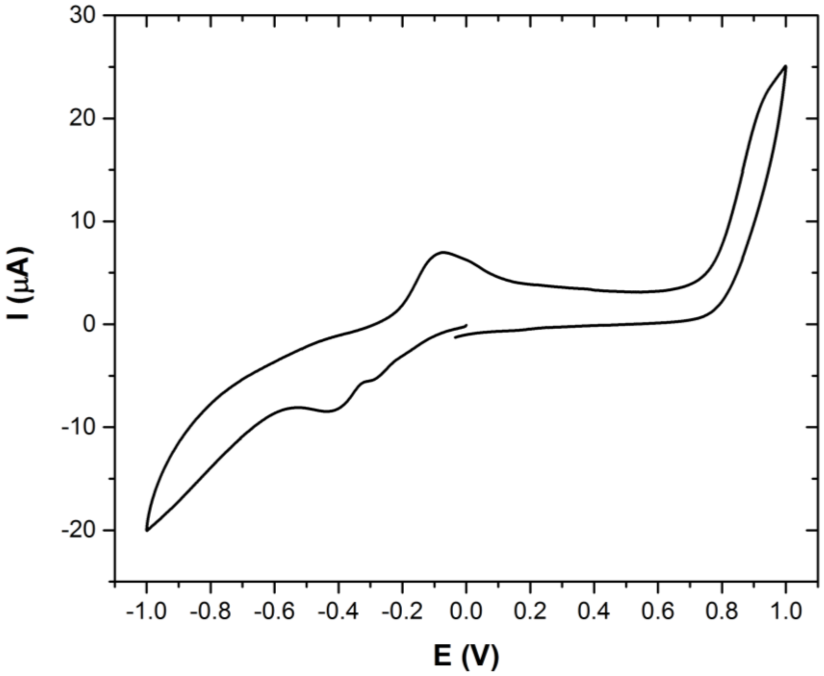


Fig. S9: Cyclic voltammetry experiment of MOP**1**@CPE.

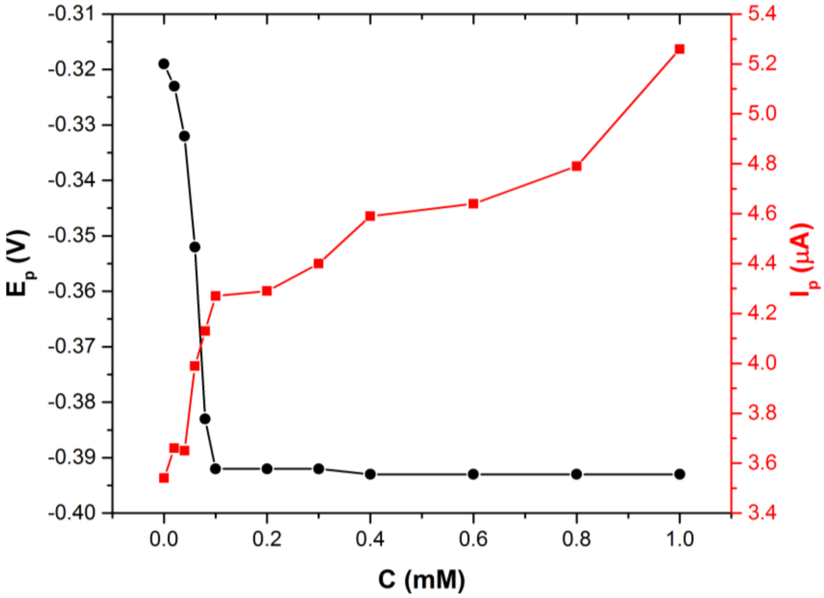


Fig. S10: Reduction peak potential and current for Cu(I) to Cu(0) (from 0.02 to 1 mM H_2O_2).