

Electronic Supplementary Information (ESI)

Electrochemical Synthesis of Biobased Polymers and Polymer Building Blocks from Vanillin

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1. Product analysis of the divanillin synthesis

The product structure was confirmed by LC-DAD-MS, elemental analysis and FT-IR. LC-DAD-MS analysis of first batch synthesis of divanillin is shown in Fig. S1. First peak was assigned to remaining vanillin (4.9 wt.-% determined by GC-FID) and second peak was assigned to divanillin.

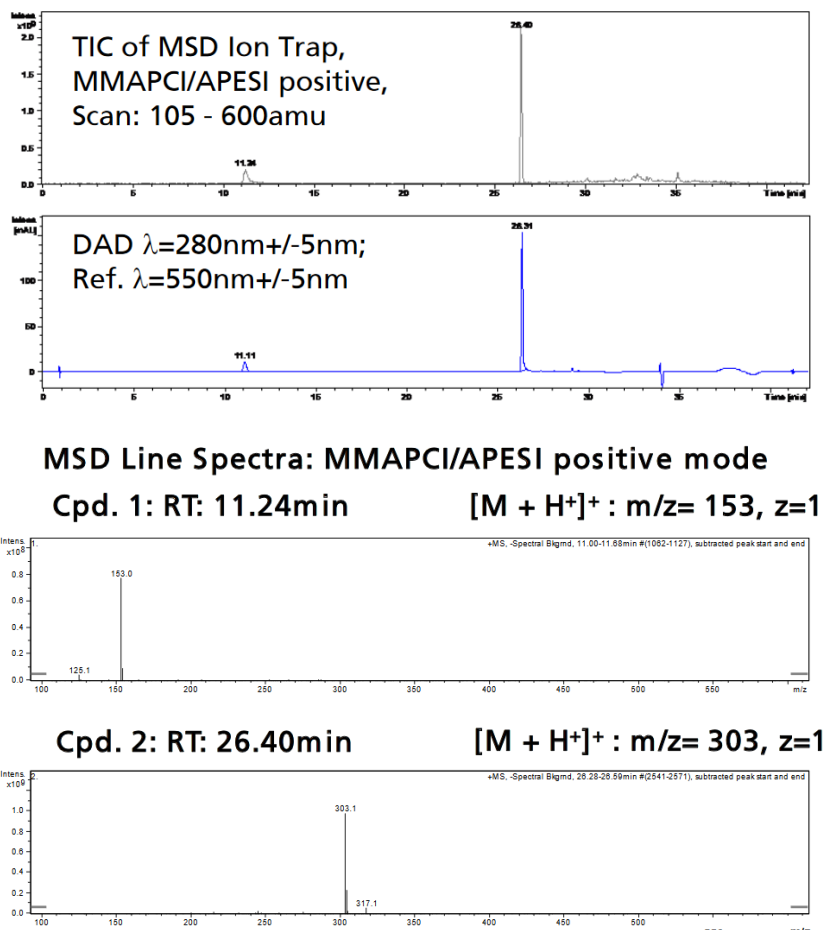


Fig. S1 LC-DAD-MS spectra of divanillin. Set-up - Kinetex C8, 2.6 μm , 100 \AA , 3 mm x 100 mm
A: Acetic acid-0.05%; B: Methanol; Gradient, 0-42 min, 0.5 ml min⁻¹, T: 45 °C; MMAPCI/APESI pos.

Elemental Analysis (CHO) for divanillin (Found: C, 62.6; H, 5; O, 32.3. Calc. for C₁₆H₁₄O₆:
C, 63.6; H, 4.7; O, 31.8%).

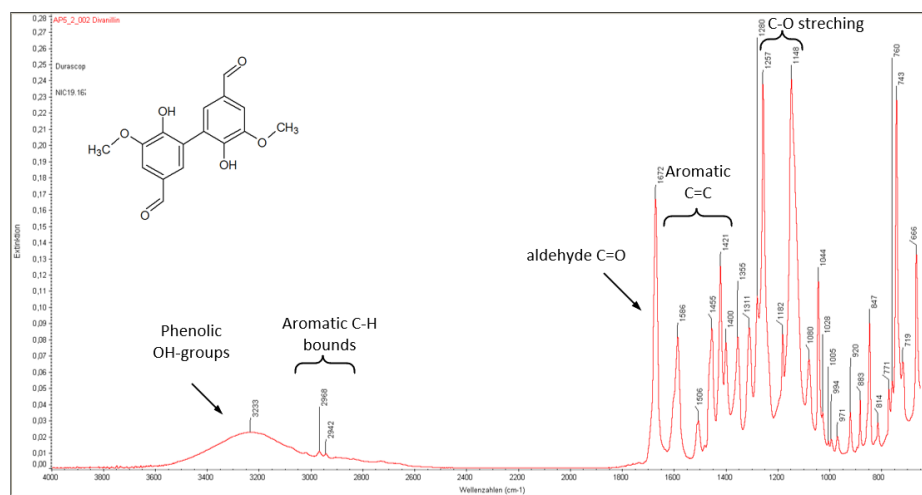


Fig. S2 FT-IR spectrum of divanillin, ATR-mode.

2. Electrochemical reduction of vanillin at GC

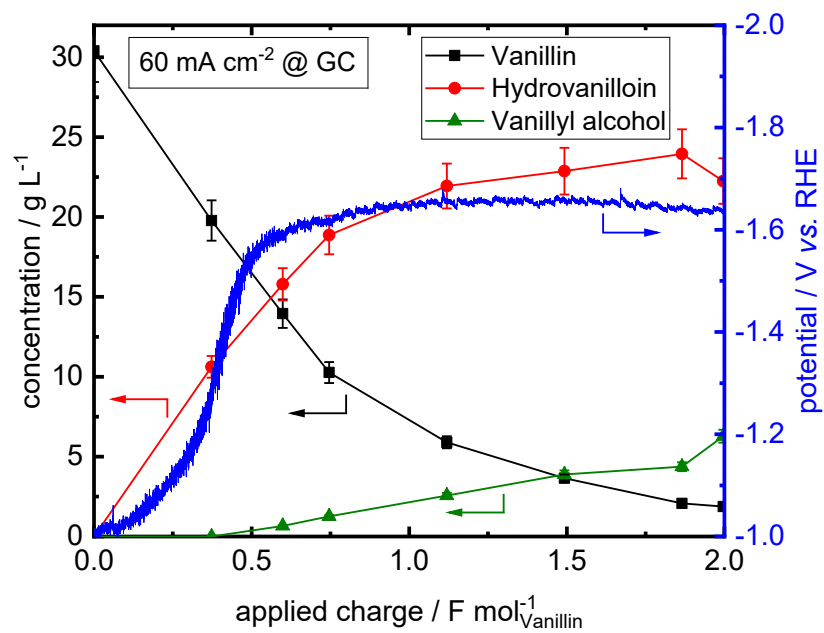


Fig. S3 Potential and concentration course of the electrochemical vanillin reduction at GC at 60 mA cm⁻². Analysis was carried out by capillary electrophoreses coupled with UV-Vis detection.

3. Isolation and identification of the product of the electrochemical vanillin reduction

Table S1 Isolated product yields after an applied charge of 2 F mol⁻¹ at different current densities and at different cathode materials.^a

Cathode material	Current density (mA cm ⁻²)	Isolated product yield ^b after an applied charge of 2 F mol ⁻¹ (%)
Zn	30	72.4
	60	64.0
	100	48.6
Pb	30	71.7
	60	69.8
	100	57.7
GC	30	69.1
	60	62.4
	100	50.0

^aElectrolysis was performed under following conditions - catholyte: 0.2 M Vanillin in 1 M sodium hydroxide, anolyte: 1 M sodium hydroxide, room temperature, catholyte stirred at 250 rpm. ^bIsolation of the product was carried out by titrating the catholyte to pH = 2 with 1 M HCl followed by filtration, washing and drying.

The isolated product was identified by HPLC-DAD-MSD, FT-IR and ¹H-, ¹³C- and 2D-NMR (HSQC, ¹³C/¹H) as pure hydrovanilloin. Exemplary spectra of isolated hydrovanilloin synthesized at a Zn cathode at 30 mA cm⁻² with an applied charge of 2 F mol⁻¹ are shown in Fig.S4-S6. In the HPLC-DAD-MSD spectra, however, two product peaks were observed. The first peak was assigned to hydrovanilloin showing a molecule signal with a monoisotopic mass of 306 g mol⁻¹ and a signal with a monoisotopic mass of 288 g mol⁻¹ due to water fragmentation from the pinacol group. The second peak solely shows the water fragmented signal with a monoisotopic mass of 288 g mol⁻¹, which would correspond to 1,2-bis(4-hydroxy-3-methoxyphenyl)ethanon being in keto-enol tautomeric equilibrium with 1,2-bis(4-hydroxy-3-methoxyphenyl)hydroxyethene. We suspect that dissolution of the isolated product in methanol for HPLC-DAD-MSD analysis leads to the water fragmentation. The ¹H-, ¹³C- and 2D-NMR (HSQC, ¹³C/¹H) spectra of the same product reveal that peak 2 of the HPLC-DAD-MSD spectra is an artefact, as no water fragmentation is observed. Since the reductive electrochemical coupling of vanillin by pinacolization is a stereoselective reaction, two forms, namely the DL-form and the meso-form, are possible. The ratio between these two forms can be calculated by the methoxy groups signals or the C α -H α / C α' -H α' signals in the aliphatic region of hydrovanilloin in the ¹H-NMR spectra. The methoxy group signals were assigned to 3.67 ppm (meso-form) and 3.61 ppm (DL-form) and the C α -H α / C α' -H α' signals to 4.47 ppm (meso-form) and 4.41 (DL-form). A meso- to DL-form ratio of 78% is calculated.

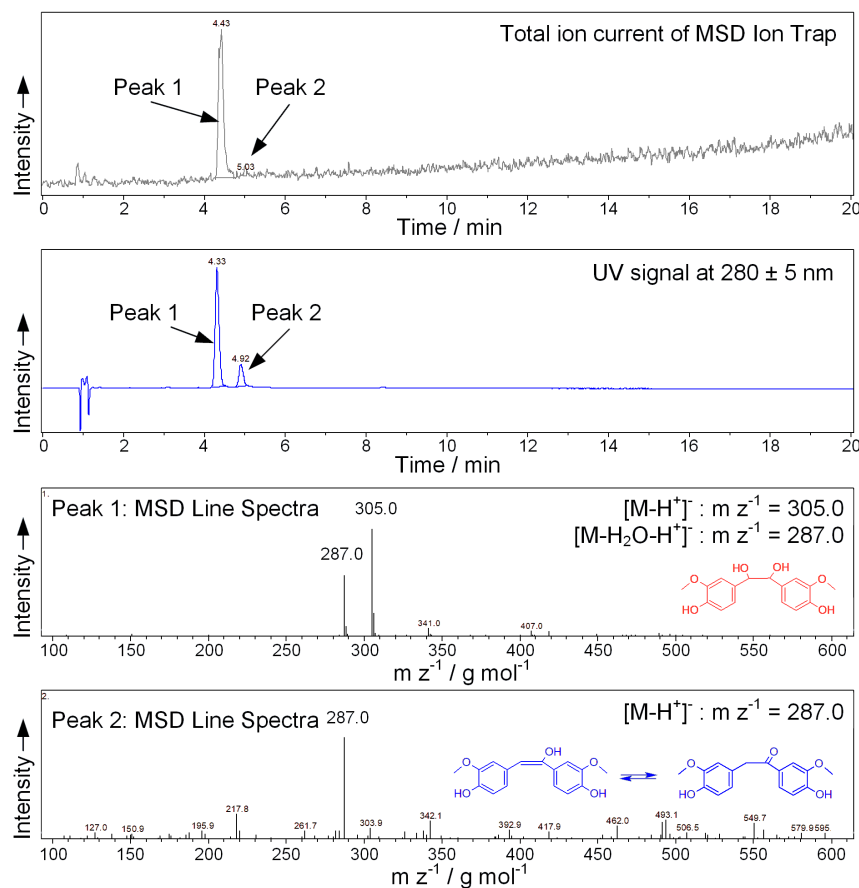


Fig S4 HPLC-UV-MSD spectra of the isolated product dissolved in MeOH for analysis. (Vanillin concentration 0.2 M in 1 M sodium hydroxide solution, Zn cathode, 30 mA cm⁻², 2 F mol⁻¹, catholyte stirred at 250 rpm, RT)

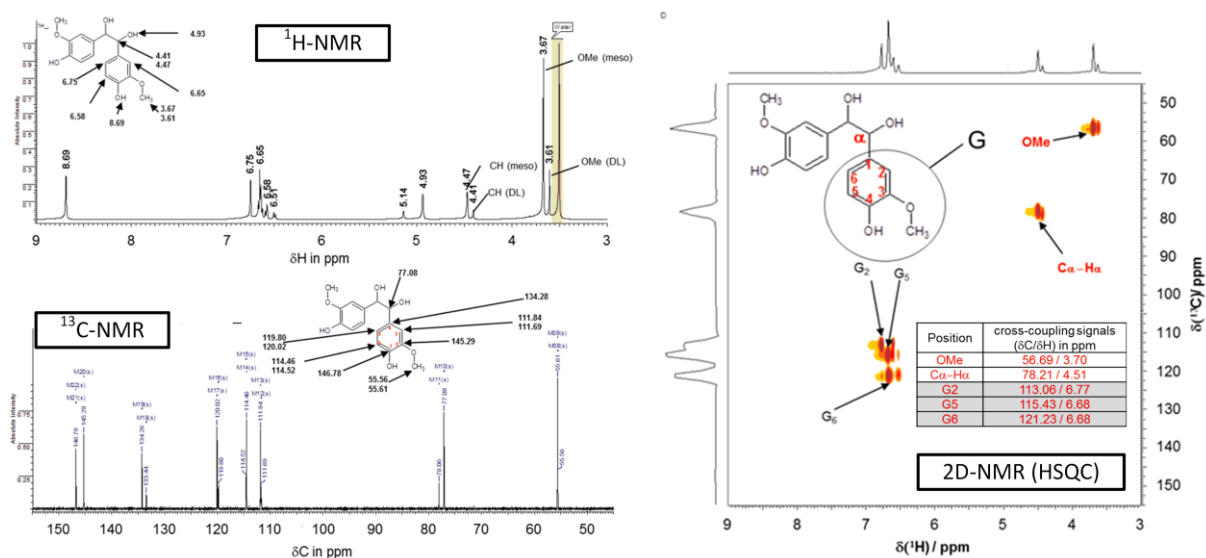


Fig S5 ¹H-, ¹³C- and 2D-NMR (HSQC, ¹³C/¹H) spectra of the isolated product dissolved in DMSO-d₆ recorded on a Bruker AVANCE spectrometer operating at 500 MHz. (Vanillin concentration 0.2 M in 1 M sodium hydroxide solution, Zn cathode, 30 mA cm⁻², 2 F mol⁻¹, catholyte stirred at 250 rpm, RT)

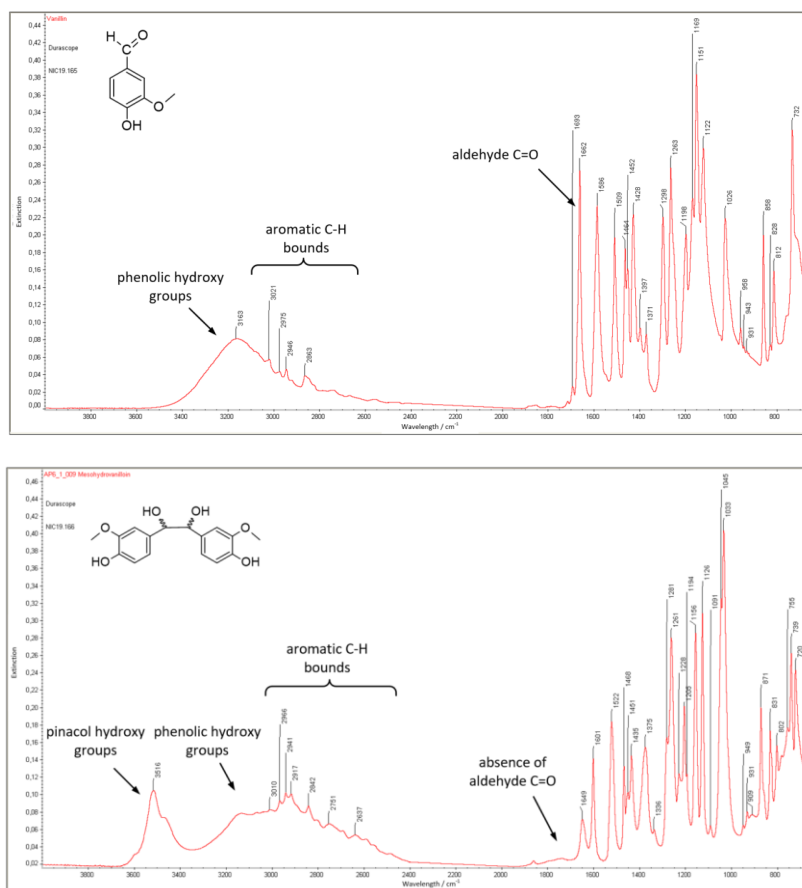


Fig. S6 FT-IR spectra of vanillin and hydrovanillin, ATR-mode.

4. Electrochemical synthesis of polyvanillin

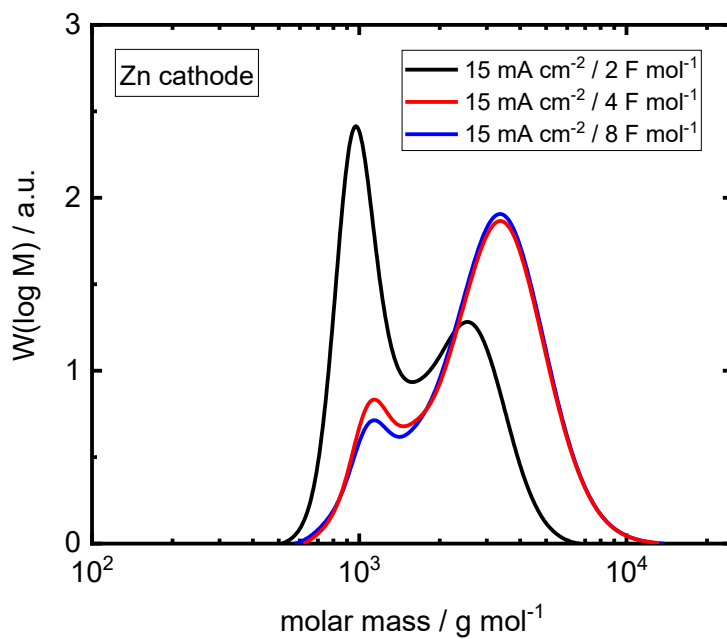


Fig. S7 Molecular weight distribution of isolated polyvanillin determined by SEC (calibrated versus pullulan standard) after different amount of applied charges at a current density of 15 mA cm⁻² (run 1-3).

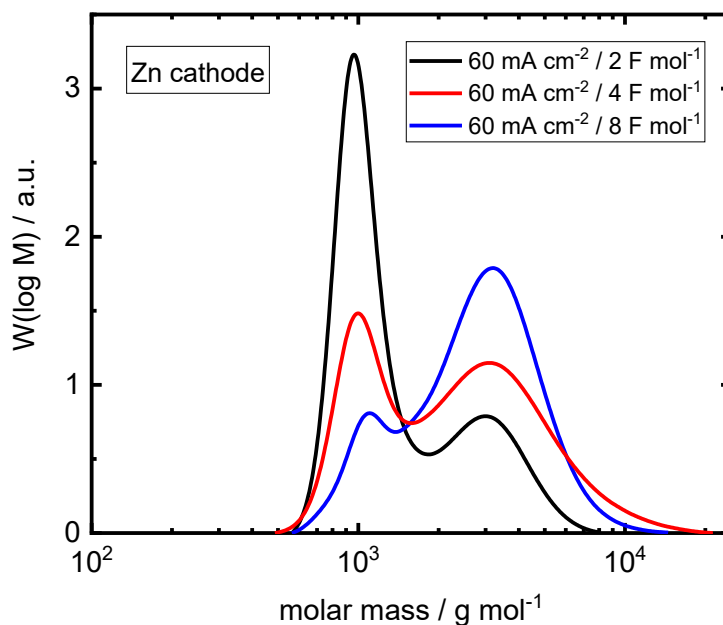


Fig. S8 Molecular weight distribution of isolated polyvanillin determined by SEC (calibrated versus pullulan standard) after different amount of applied charges at a current density of 60 mA cm⁻² (run 7-9).

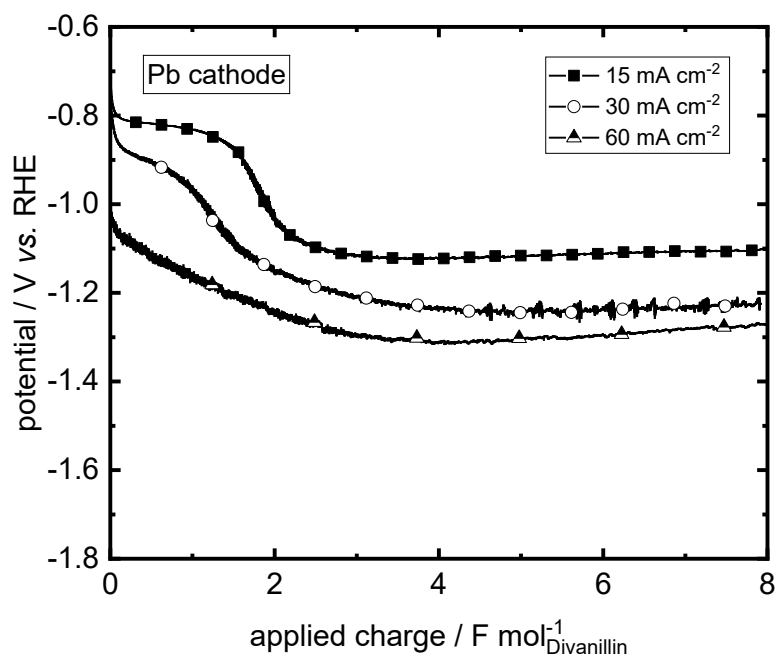


Fig. S9 Potential-charge plots of the electrochemical divanillin reduction at a Pb cathode (5 cm²). Electrolysis was performed under following conditions – anode: Ni-foam, catholyte: 0.1 M divanillin in 1 M sodium hydroxide (first batch of divanillin), anolyte: 1 M sodium hydroxide, room temperature, catholyte stirred at 250 rpm.

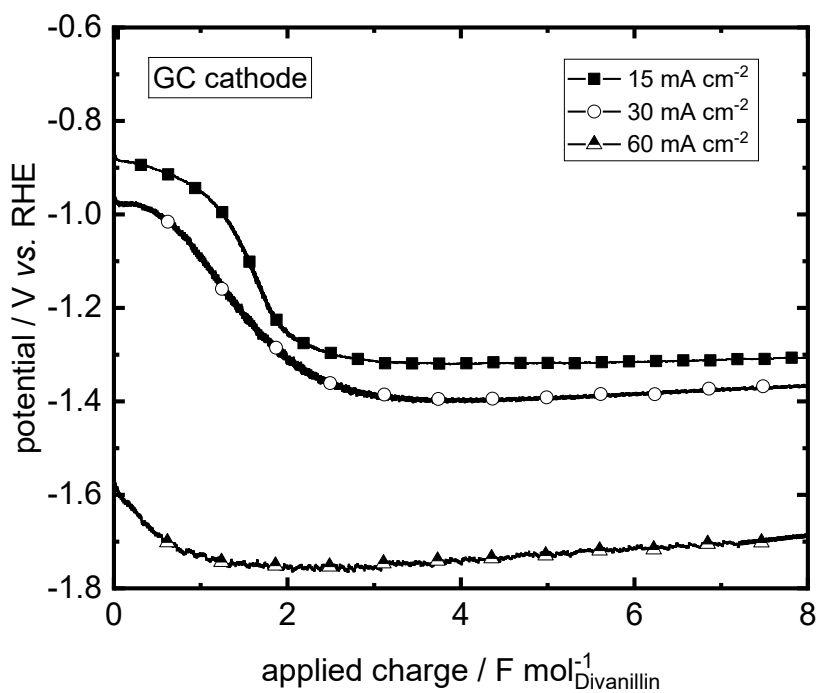


Fig S10 Potential-charge plots of the electrochemical divanillin reduction at a GC cathode (5 cm²). Electrolysis was performed under following conditions – anode: Ni-foam, catholyte: 0.1 M divanillin in 1 M sodium hydroxide (first batch of divanillin), anolyte: 1 M sodium hydroxide, room temperature, catholyte stirred at 250 rpm.

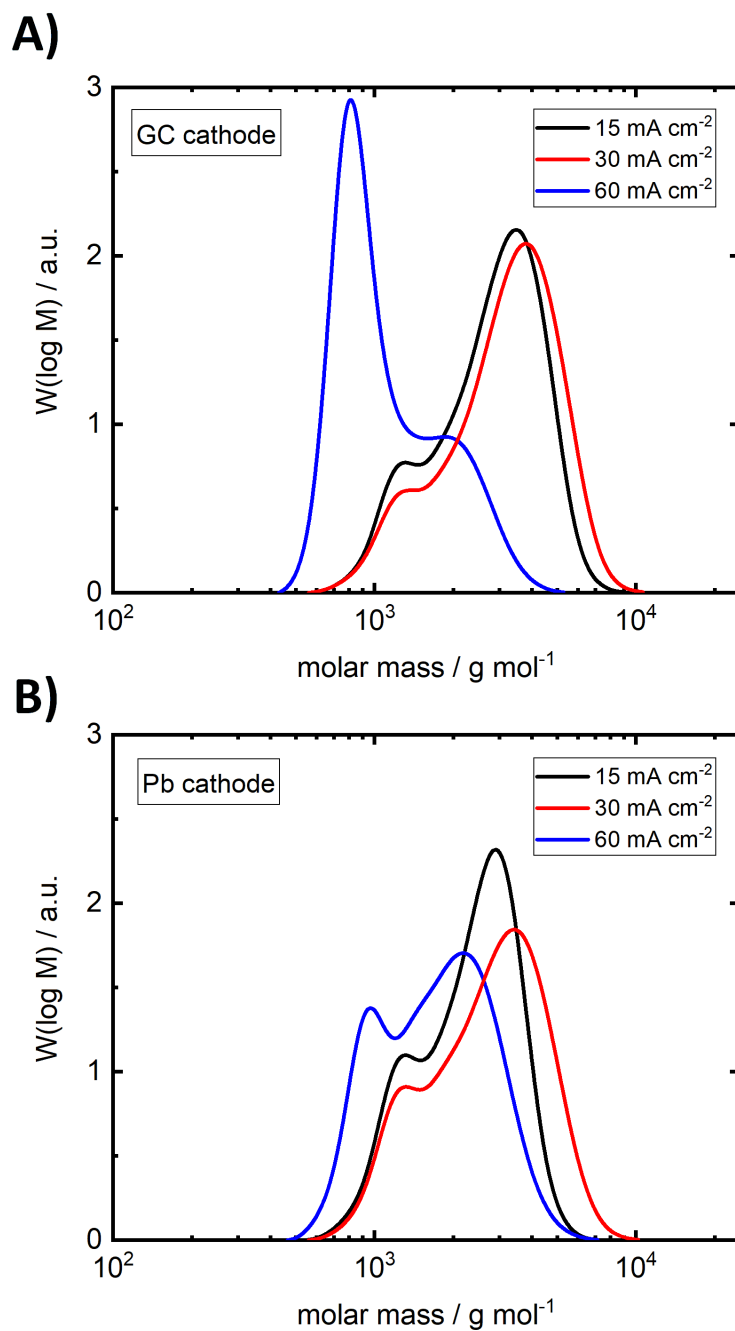


Fig S11 MWDs of isolated polyvanillin synthesized at a glassy carbon cathode (A) and a Pb cathode (B). Electrolysis was performed under following conditions – applied charge: 8 F mol^{-1} , catholyte: 0.1 M divanillin in 1 M sodium hydroxide (first batch of divanillin), anolyte: 1 M sodium hydroxide, room temperature, catholyte stirred at 250 rpm, isolated products were analyzed by SEC. SEC was calibrated versus pullulan standard.

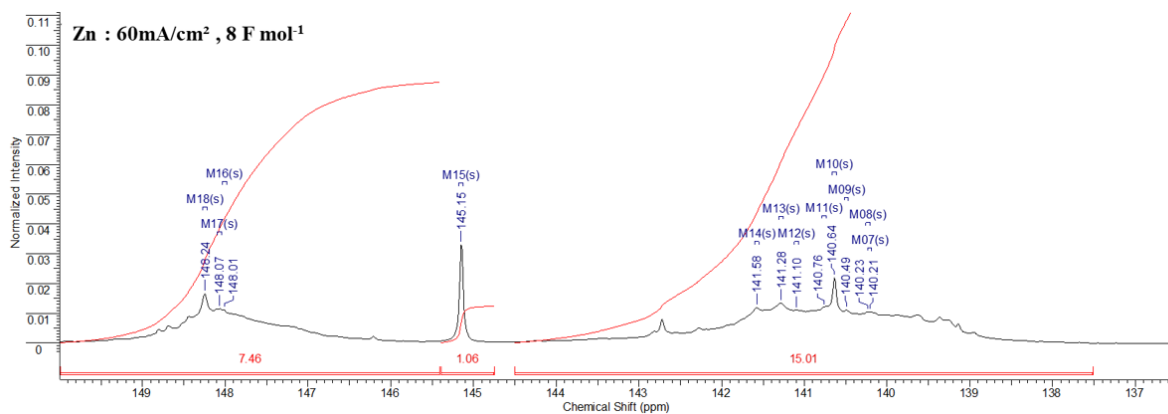


Fig. S12 ³¹P-NMR analysis of the polyvanillin sample generated by electrochemical pinacolization of 5,5'-bis-vanillin at a Zn-cathode at a current density of 60 mA cm⁻² and an applied charge of 8 F mol⁻¹, after in-situ labelling with 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (Cl-TMDP) in pyridine / CDCl₃ = 1.6 / 1 (v / v). Chemical shifts are reported relative to the sharp signal (132.2 ppm) originating from the reaction between traces of H₂O and Cl-TMDP. Internal standard: Cyclohexanol (peak: 145.15 ppm); integration region for aliphatic hydroxy groups: 150.0-145.4 ppm and for total phenolic hydroxy groups: 144.5 – 137.5 ppm.