Supporting Information

# A Molecular Binuclear Nickel (II/III) Schiff Base complex for Efficient HER Electrocatalysis

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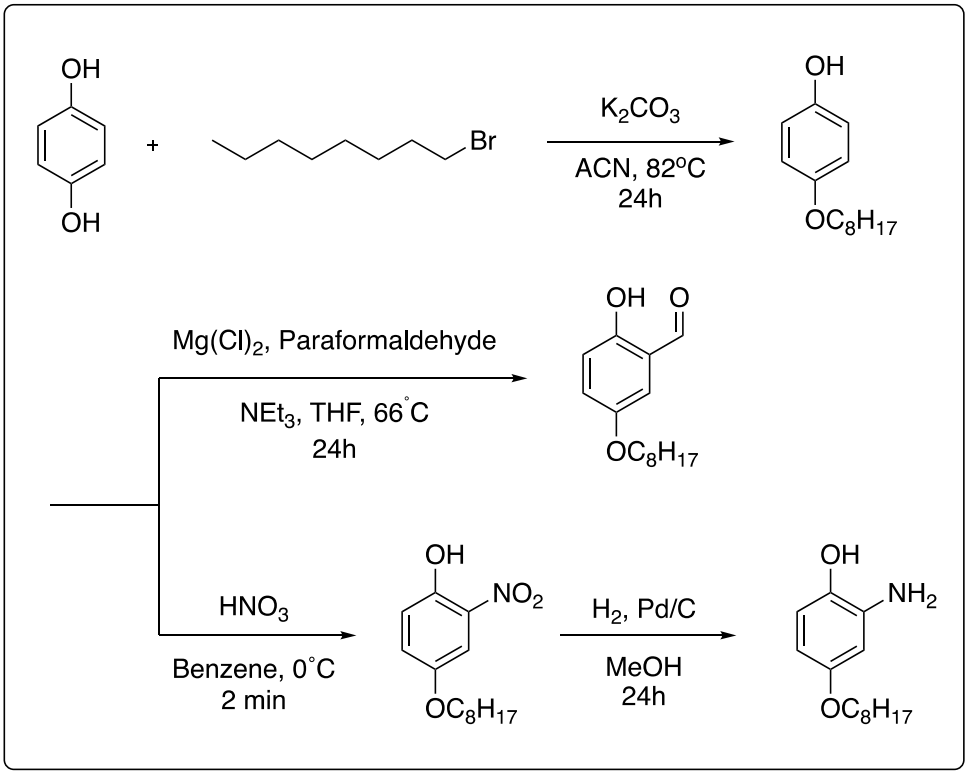
**Table of Contents**

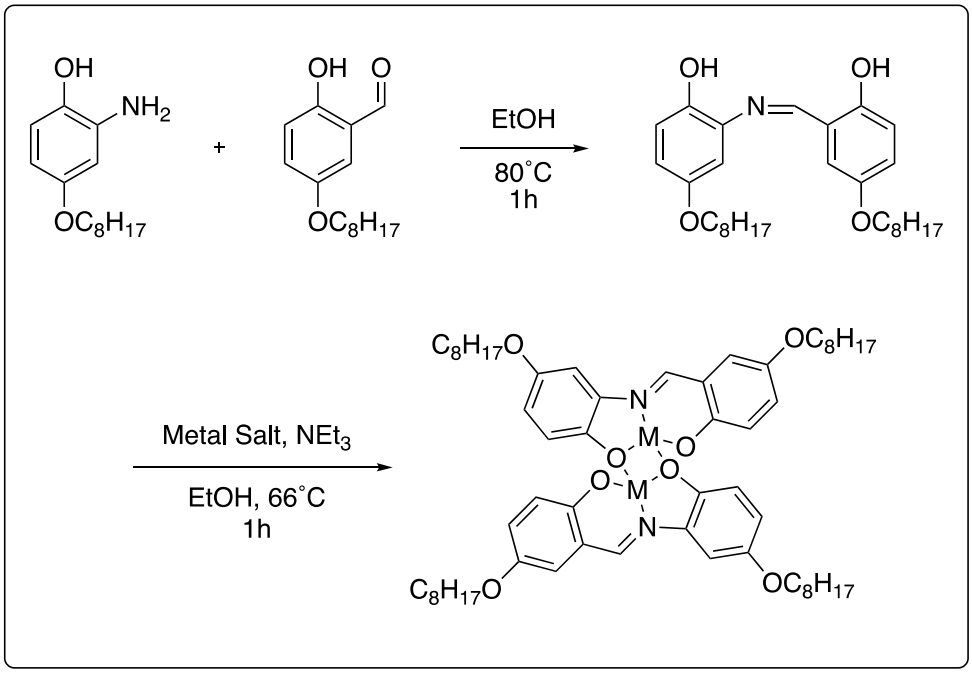


## 1. Materials and Methods

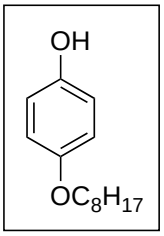
Chemicals were purchased from Fluka, Alfa Aesar, Sigma-Aldrich, and Merck. Commercially available hydroquinone was purchased from Sigma-Aldrich. 4-(octyloxy)phenol[1], 2-hydroxy-5-(octyloxy)benzaldehyde[2], 2-nitro-4-(octyloxy)phenol[3], 2-amino-4-(octyloxy)phenol[3], (Z)-2-((2-hydroxy-5-(octyloxy)benzylidene)amino)-4-(octyloxy)phenol[4], and $[Ni]_2[L]_2$[4,5] were synthesized according to reported literature procedures. DCM was obtained using a M. Braun Inert Gas System GmBH where it is stored over molecular sieve MB-SPS-7 under argon atmosphere. NMR solvents were purchased from Sigma-Aldrich. TLC was performed on Macherey-Nagel silica gel 60 (0.20 mm) with fluorescent indicator UV254 on aluminium plates and on Merck aluminium oxide 60 (0.20 mm) with fluorescent indicator UV254 on aluminium plates. For chromatography, silica-gel columns were prepared with silica-gel 60 (0.070-0.20 mesh) from Grace and aluminium oxide 60, basic, activity level II from Acros. $^{1}H$ and $^{13}C$ NMR spectra were recorded on a Bruker DRX 500 MHz spectrometer and a Bruker Advance 300 MHz NMR spectrometer. Chemical shifts are given in parts per million (ppm) on the delta scale ($\delta$) and are referenced to the used deuterated solvent for $^{1}H$-NMR. High resolution mass spectra were obtained using an Agilent 6520 Q- TOF mass spectrometer with an ESI source and an Agilent G1607A coaxial sprayer and a Thermo Fisher Scientific LTQ Orbitrap XL with an Ion Max API Source. MALDI-TOF was measured on a . UV-Vis absorption spectra were collected on a Varian CARY 300 Bio spectrophotometer from 200 to 900 nm.

## 2. Synthesis Procedures



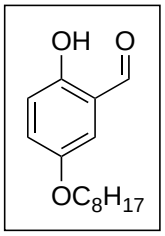

**Synthesis of 4-(octyloxy)phenol:**




Hydroquinone (4.0 g, 36.3 mmol) and potassium carbonate (5.0 g, 36.3 mmol) were added to a flame dried round bottom flask with a magnetic stir bar and dissolved in acetonitrile (100 mL) before being left to stir at room temperature for 30 minutes. After, 1-bromooctane (7.0 g, 36.3 mmol) was added drop wise and refluxed at 82°C for 24 h. Reaction mixture was then left to cool to room temperature before filtered through glass frit and washed with dichloromethane. The crude product was evaporated to dryness before

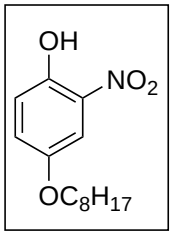
purification via column chromatography (silica, EtOAc/heptane, [1:4]) to provide 4-(octyloxy)phenol (3.23 g, 40%) as a dark brown solid. $R_f$=0.5, $^1$H-NMR (300 MHz, CDCl3, 25°C): δ= 6.82 (m, 4H, Ar-H), 4.68(s, 1H, Ar-OH), 3.90 (t, *J* = 6.6 Hz, 2H, -$OCH_2$-), 1.75 (m, 2H, -$OCH_2\underline{CH_2}$-), 1.38-1.25 (m, 10H, -$OCH_2CH_2\underline{(CH_2)_5}$), 0.90 (m, 3H, -$OCH_2CH_2(CH_2)_5\underline{CH_3}$).

**Synthesis of 2-hydroxy-5-(octyloxy)benzaldehyde:**



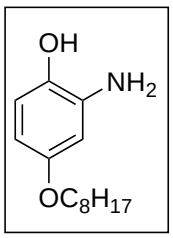

Magnesium chloride (1.7 g 17.9 mmol) and paraformaldehyde (0.9 g, 30.0 mmol) were added to a flame dried round bottom flask with a magnetic stir bar and dissolved in THF (100 mL). Triethylamine (1.8 g, 17.8 mmol) was then added, and solution was left to stir at room temperature for 10 minutes. After, 4-(octyloxy)phenol (1.1 g, 5 mmol) was added and refluxed at 66˚C for 24 h. Reaction mixture was then left to cool before diluted with ether, and washed with 1M HCl. Mixture as dried with magnesium sulfate and evaporated under reduced pressure to afford 2-hydroxy-5-(octyloxy)benzaldehyde (1.1 g, 88%) as a brown oil. $^1$H-NMR (300 MHz, CDCl3, 25°C): δ= 10.62 (s, 1H, -OH), 9.82 (s, $^1$H, -CHO), 7.12 (dd, *J* = 9.0, 3.1 Hz, 1H, Ar-H), 6.98 (d, *J* = 3.1 Hz, 1H, Ar-H), 6.90 (d, J = 9.1 Hz, 1H, Ar-H), 3.92 (t, *J* = 6.6 Hz, 2H, -$OCH_2$-), 3.90 (t, 2H, -$OCH_2$-), 1.75 (m, 2H, -$OCH_2\underline{CH_2}$-), 1.38 - 1.25 (m, 10H, -$OCH_2CH_2\underline{(CH_2)_5}$), 0.90(m, 3H, -$OCH_2CH_2(CH_2)_5\underline{CH_3}$).

**Synthesis of 2-nitro-4-(octyloxy)phenol:**



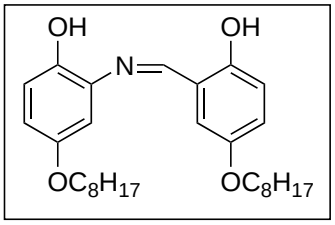

4-(octyloxy)phenol (3.0 g, 13.0 mmol) was added to benzene (100 mL) in a flame dried round bottom flask with a magnetic stir bar. Once cooled to 0˚C, 56% aqueous nitric acid solution (13 mmol) was added slowly and vigorously stirred for 2 minutes. The reaction mixture was then quenched with water after which the organic phase was dried with magnesium sulfate and evaporated to reveal the crude product as an orange powder. Impurities were removed via column chromatography (silica, EtOAc/heptane, [1:20]) to provide 2-nitro-4-(octyloxy)phenol (1.94 g, 56%) as an orange solid. $R_f$=0.4, $^1$H-NMR (300 MHz, CDCl3, 25°C): δ= 10.33 (s, 1H, -OH), 7.50 (d, *J* = 3.07, 1H, Ar-H), 7.22 (dd, $J_1$ = 3.13, $J_2$ = 3.04, 1H, Ar-H), 7.08 (d, *J* = 9.17, 1H, Ar-H), 3.94 (t, 2H, -$OCH_2$-), 1.75 (m, 2H, -$OCH_2\underline{CH_2}$-), 1.50-1.25 (m, 10H, -$OCH_2CH_2\underline{(CH_2)_5}$), 0.90(m, 3H, -$OCH_2CH_2(CH_2)_5\underline{CH_3}$).

**Synthesis of 2-amino-4-(octyloxy)phenol:**



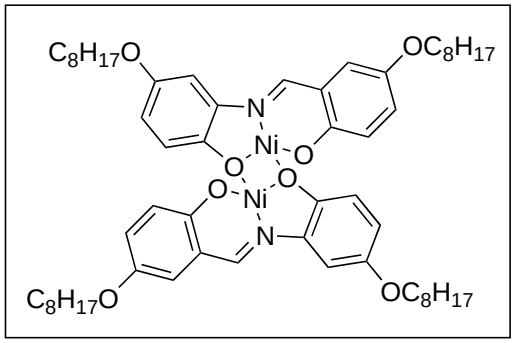

In a flame dried round bottom flask equipped with a stir bar, a solution of 2-nitro-4-(octyloxy)phenol (1.3 g, 4.8 mmol) and 10% Pd/C (51 mg) in MeOH (50 mL) were placed under hydrogen atmosphere. The reaction mixture was left to stir for 24 h. After, the catalyst was filtered off and evaporated to reveal 2-amino-4-(octyloxy)phenol (0.99 g, 89%) as a dark red solid. ($^1$H-NMR (300 MHz, CDCl3, 25°C): δ= 6.65 (d, *J* = 8.47, 1H, Ar-H), 6.35 (d, *J* = 2.77, 1H, Ar-H), 6.21 (dd, $J_1$ = 2.79, $J_2$ = 2.78, 1H, Ar-H), 3.87 (m, 2H, -$NH_2$), 3.94 (t, 2H, -$OCH_2$-), 1.75 (m, 2H, -$OCH_2\underline{CH_2}$), 1.50-1.25 (m, 10H, -$OCH_2CH_2\underline{(CH_2)_5}$), 0.90(m, 3H, -$OCH_2CH_2(CH_2)_5\underline{CH_3}$).

**Synthesis of (Z)-2-((2-hydroxy-5-(octyloxy)benzylidene)amino)-4-(octyloxy)phenol:**




2-amino-4-(octyloxy)phenol (0.4 g, 1.68 mmol) was dissolved in ethanol (20 mL) in a flame dried round bottom flask equipped with a magnetic stir bar. Then, 2-hydroxy-5-(octyloxy)benzaldehyde (0.42 g, 1.68 mmol) was added dropwise to the reaction mixture and refluxed for 1 h at 80˚C. After, the reaction was left to cool and evaporated to dryness before purification via column chromatography (silica, EtOAc/heptane, [1:5]) (Z)-2-((2-hydroxy-5-(octyloxy)benzylidene)amino)-4-(octyloxy)phenol (0.55 g, 69%) as a black solid. ($^1$H-NMR s(300 MHz, $CDCl_3$, 25°C): δ= 8.61 (s, 1H, -CH=N-), 7.03 (dd, $J_1$ = 9.0, $J_2$ = 2.8 Hz, 1H, Ar-H), 7.00 (d, $J$ = 7.5 Hz, 1H, Ar-H), 6.90 (m, 2H, Ar-H), 6.79 (dd, $J$ = 8.8, $J_2$ = 2.8 Hz, 1H, Ar-H), 6.72 (d, $J$ = 2.8 Hz, 1H, Ar-H), 3.92 (m, 4H, -$OCH_2$ -), 1.75 (m, 4H, -$OCH_2\underline{CH_2}$ -), 1.50-1.25 (m, 20H, -$OCH_2CH_2(\underline{CH_2})_5$), 0.90(m, 6H, -$OCH_2CH_2(CH_2)_5\underline{CH_3}$). $\lambda_{max}$ nm: 386. FTIR ($cm^{-1}$): 2985, 2940, 2895, 2830, 1622, 1492, 1454, 1299, 1241, 1126, 1036, 808, 735, 563, 464.

**Synthesis of $[Ni]_2[L]_2$ Complex:**




(Z)-2-((2-hydroxy-5-(octyloxy)benzylidene)amino)-4-(octyloxy)phenol (0.1 g, .2 mmol) and triethyl amine (1.5 equiv.) are dissolved in ethanol (20 mL) in a flame dried round bottom flask equipped with a magnetic stir bar. After, a solution of nickel (II) acetate hexahydrate (50 mg, 0.2 mmol) in ethanol (20 mL) is added dropwise to the round bottom flask and refluxed for 1 h at 65˚C. The reaction mixture was cooled before filtering to obtain the $[Ni]_2[L]_2$ as a dark red precipitate. The crude, solid complex was washed with hot ethanol twice to remove any impurities, revealing the pure $[Ni]_2[L]_2$ complex (70 mg, 33%). MALDI-TOF *m/z*: calcd. For $C_{58}H_{82}N_2Ni_2O_8^+$ 1051.478; found [M+H]+: 1051.165. FTIR ($cm^{-1}$): 2920, 2852, 1600, 1545, 1489, 1468, 1262, 1202, 1151, 1046, 809, 512. Elemental Analysis: Anal. Calcd: C: 66.18, H: 7.85, N: 2.66%. Found: C: 65.26, H: 7.27, N: 2.55%.

**3. Analytical Data**

**4-(octyloxy)phenol:**

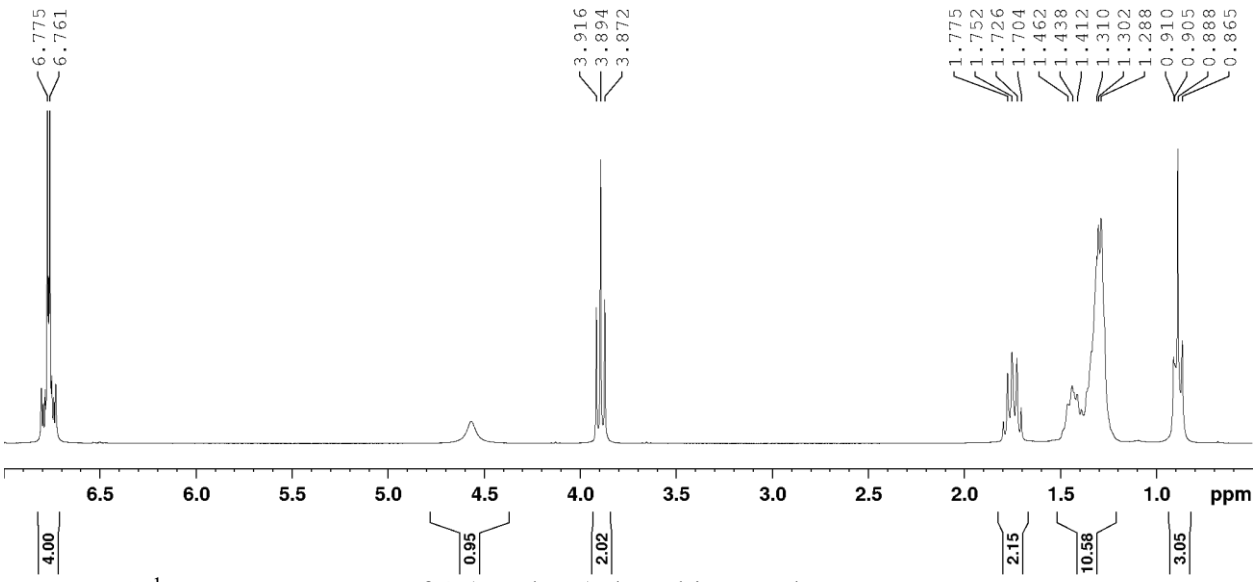



**Figure S1**. $^{1}$H-NMR spectrum of 4-(octyloxy)phenol in $CDCl_3$.

**2-hydroxy-5-(octyloxy)benzaldehyde:**

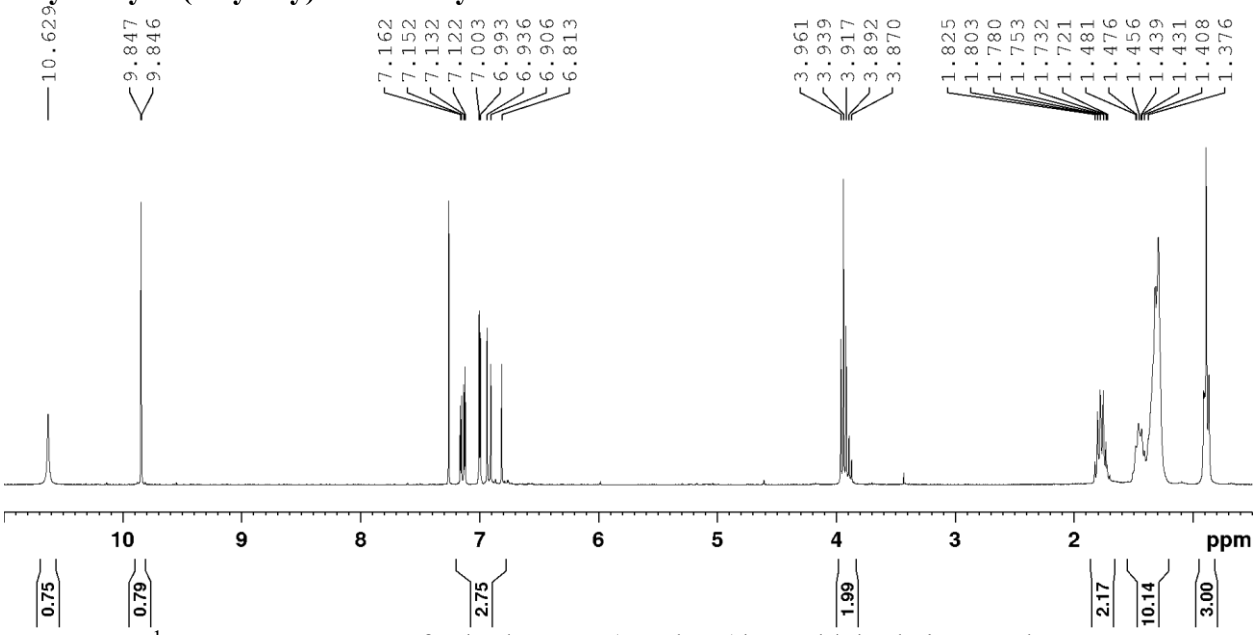



**Figure S2**. $^{1}$H-NMR spectrum of 2-hydroxy-5-(octyloxy)benzaldehyde in $CDCl_3$.

**2-nitro-4-(octyloxy)phenol:**

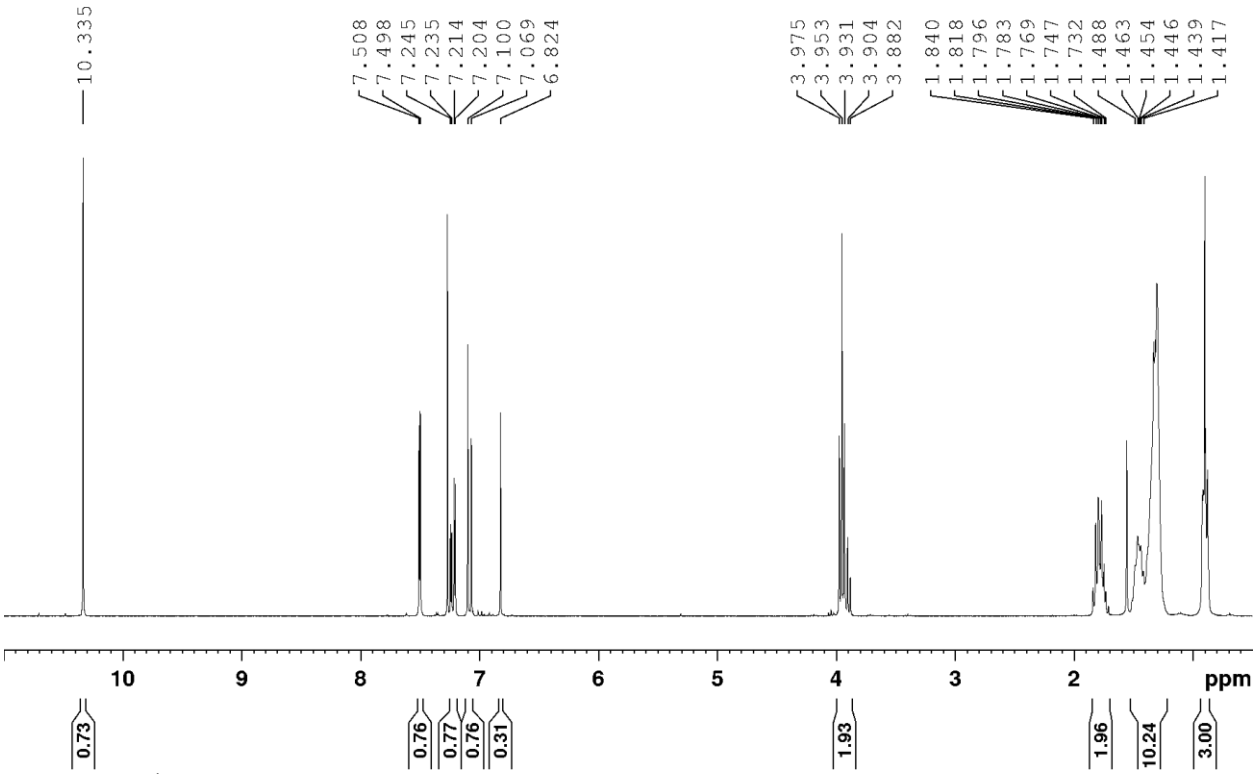



**Figure S3**. $^{1}$H-NMR spectrum of 2-nitro-4-(octyloxy)phenol in $CDCl_3$.

**2-amino-4-(octyloxy)phenol:**

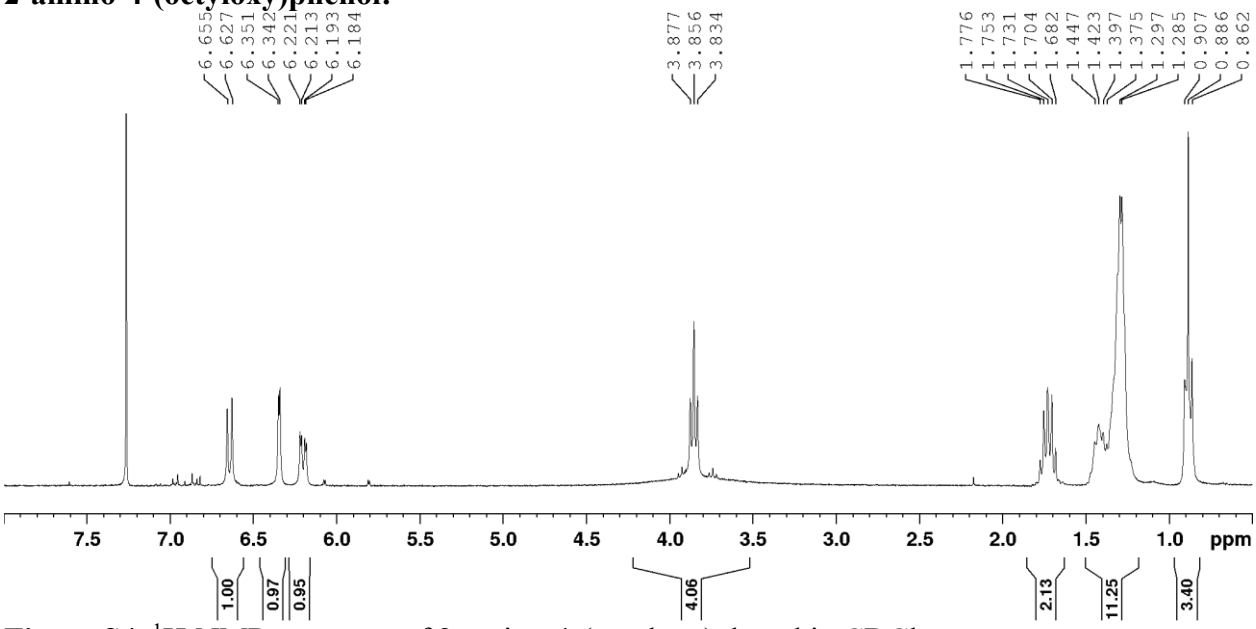



**Figure S4**. $^{1}$H-NMR spectrum of 2-amino-4-(octyloxy)phenol in $CDCl_3$.

**(Z)-2-((2-hydroxy-5-(octyloxy)benzylidene)amino)-4-(octyloxy)phenol:**

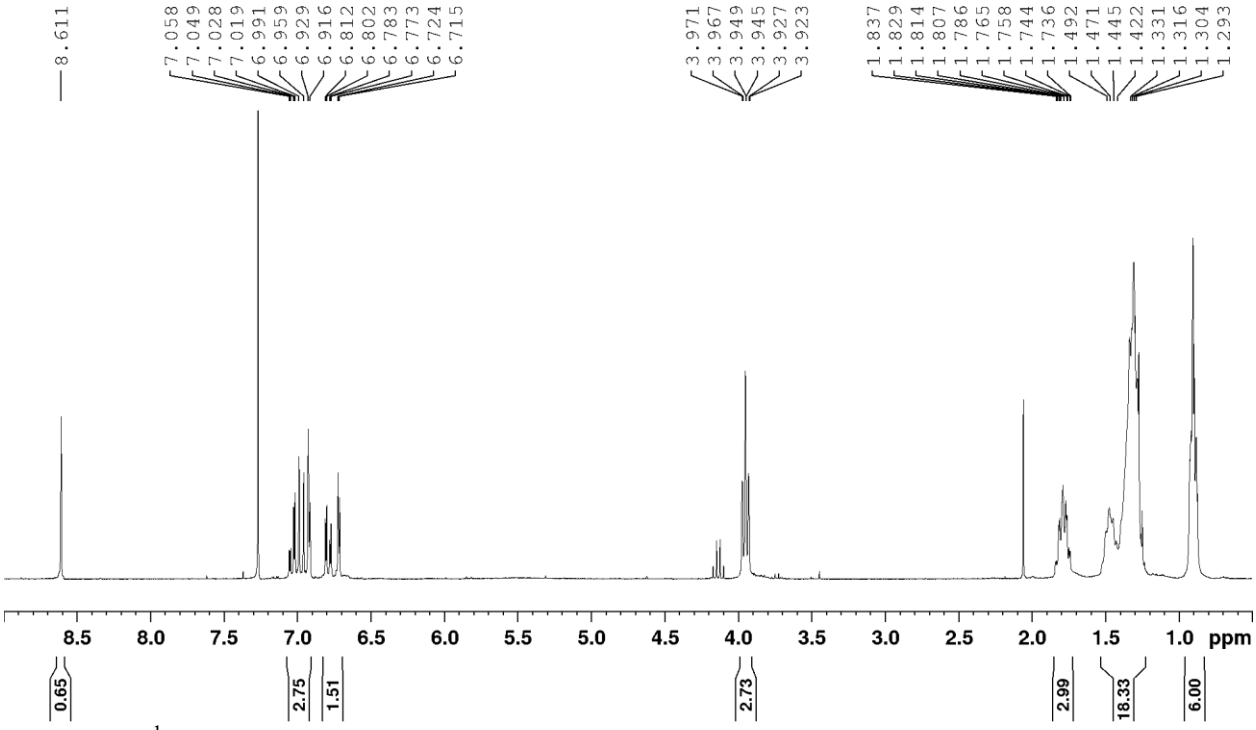



**Figure S5**. $^{1}$H-NMR spectrum of (Z)-2-((2-hydroxy-5-(octyloxy)benzylidene)amino)-4-(octyloxy)phenol in $CDCl_3$.

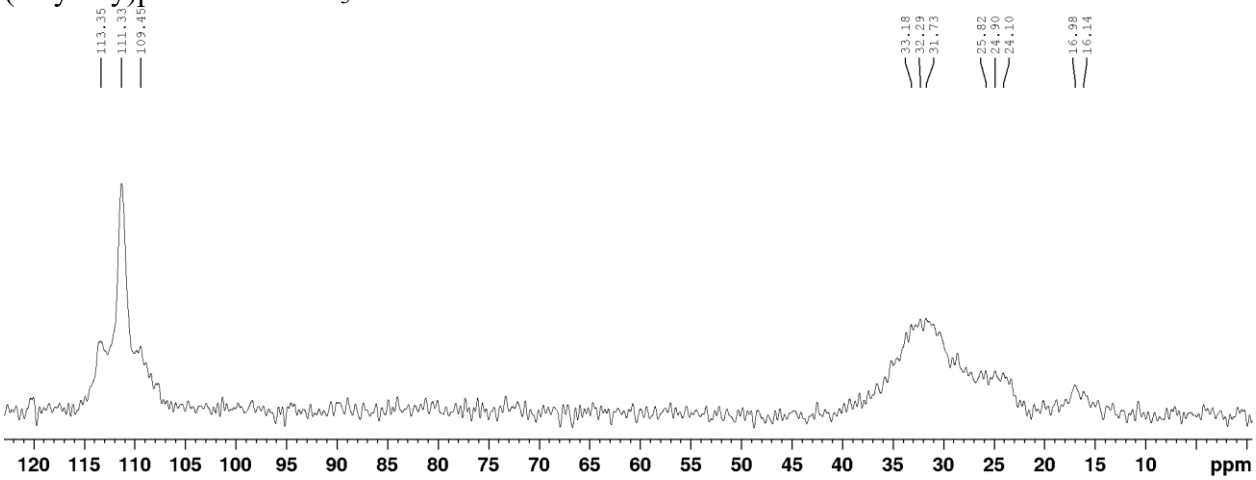



**Figure S6**. $^{13}$C NMR spectrum of $[Ni]_2[L]_2$ **2**.

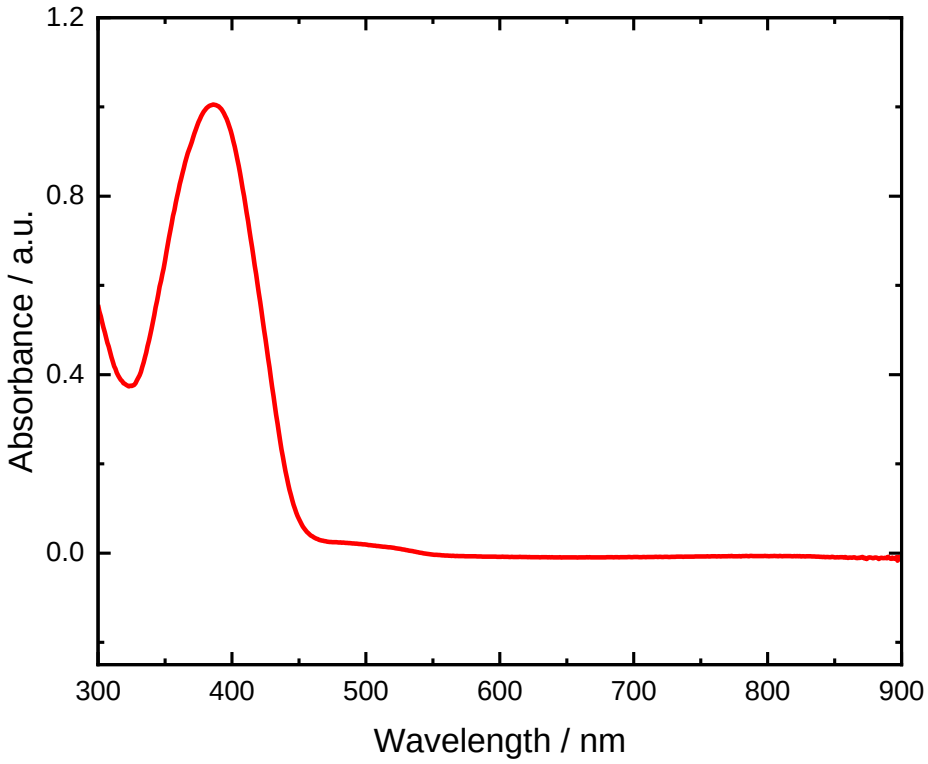



**Figure S7**. UV-VIS spectrum of (Z)-2-((2-hydroxy-5-(octyloxy)benzylidene)amino)-4-(octyloxy)phenol **1** in $CH_2Cl_2$.

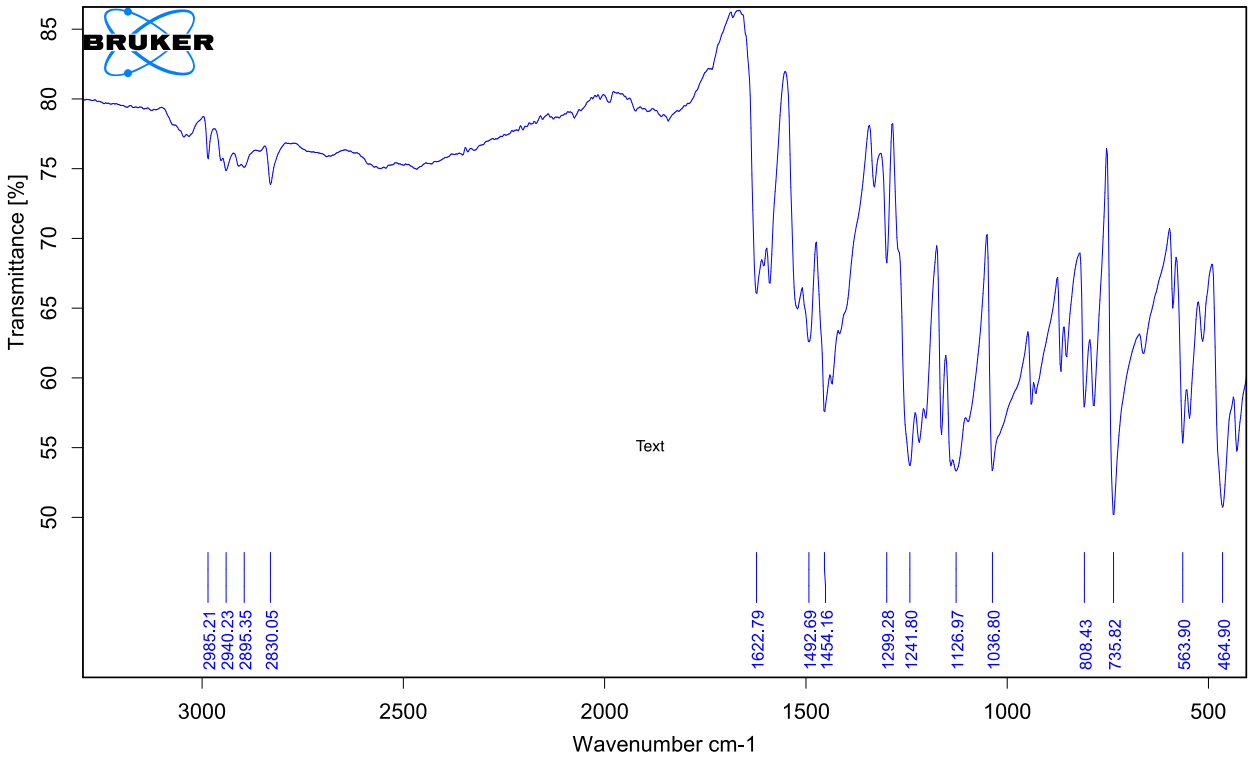



**Figure S8**. FTIR spectrum of (Z)-2-((2-hydroxy-5-(octyloxy)benzylidene)amino)-4-(octyloxy)phenol **1**.

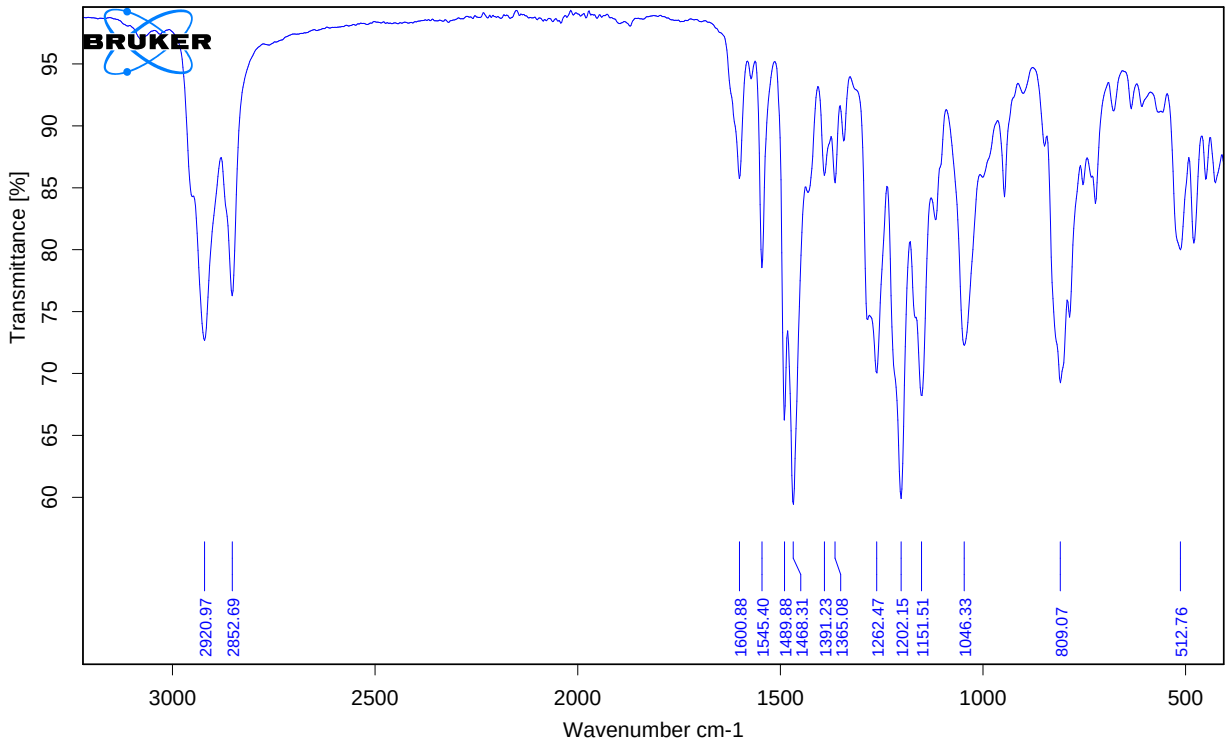



**Figure S9**. FTIR spectrum of $[Ni]_2[L]_2$ **2**.

## 4. Electrochemical Characterization

For electrode preparation, a solution of 0.8 mL isopropanol (IPA) and 0.2 mL high purity water (18 MΩ) containing 0.25 mg carbon black (CB) and 0.25 mg $[Ni]_2[L]_2$ **2** were added together with 10 µL Nafion. The mixture was sonicated in an ultrasonic cleaner for 1 hour. The suspension was applied to the surface of carbon paper (1$cm^2$) via spray coating apparatus.

**Procedure of Catalyst-Loaded Electrodes and Electrolyte**

Electrocatalytic HER studies were carried out by using Vertex.5A Ivium Technologies B.V in a conventional three-electrode configuration, using catalyst coated onto carbon paper as the working electrode, platinum wire as the counter electrode, and Ag/AgCl as the reference electrode. Before all measurements, electrolyte was purged for at least 30 minutes using Argon gas. CVs were recorded in 0.5 M $H_2SO_4$ solution at 50 mV $s^{-1}$ scan rate. LSVs were measured with a scan rate of 10 mV $s^{-1}$.

The equation for Faradaic efficiency:

$FE\%$ = (amount of product × n × F)/Q × 100

n = Number of electrons involved in formation of 1 product molecule F = Faradaic constant Q = Amount of charge passed through the working electrode

**Characterization by Electrochemical Impedance Spectroscopy (EIS) – Method**

The electrochemical impedance spectroscopy (EIS) was measured using a potentiostat model Vertex.5A Ivium Technologies B.V. The impedance spectrum was recorded for all experiments in the frequency range of $10^6$ Hz to 0.1 Hz with a perturbation amplitude of 10 mV. The aim of this characterization is the investigation of $[Ni]_2[L]_2$ for HER electrolysis. To realize the measurements 0.5M $H_2SO_4$ were employed for HER. For the determination of the cell parameters, first two platinum electrodes were measured in a one cell

compartment with the corresponding electrolyte as a control experiment to determine the electrolyte resistance. Afterwards, the setup was transferred to a H-cell configuration with Nafion membrane in between. By this way the resistance of the membrane is found and immediately subtracted from the electrolyte resistance. Next, one platinum electrode was replaced by a carbon paper electrode as a working electrode. Finally, the carbon paper coated with the $[Ni]_2[L]_2$ catalyst was set as working electrode, to evaluate the complete electrochemical cell by EIS. All fitted and calculated impedance data are summarized in the table S5. The bode plot for the two-electrode system is shown in the manuscript. Based on EIS, the applied electrochemical cells were characterized in detail indicating negligible losses of the systems.

Equation for overpotential calculations:

$E_{RHE} = E_{Ag/AgCl} + 0.197 + 0.059 * pH$

For electrochemically active surface area (ECSA),

$i_c = \nu C_{dl}$

$A_{ECSA} = C_{dl}/C_s$

catalysts were loaded on carbon paper electrodes. The ECSA values can be calculated using the equations below: in which i is the charging current, v is the scan rate, and C is the specific capacitance (12000 uF/cm$^2$)[6].

**Table S1:** Cell parameter extracted via electrochemical impedance measurements for HER

| WE | CE | $R_{Sol}$ / Ω | $R_{carrier}$ / Ω | R / $[Ni]_2[L]_2$ **2** Ω | $R_{Me}$ / Ω | C / F | CPE-T | CPE-P |
|---|---|---|---|---|---|---|---|---|
| Pt | **Pt** | **3.23E+00** | **3.840E+04** | **-** | **1.40E+01** | **-** | **1.511E-04** | **9.433E-01** |
| Cp | **Pt** | **3.23E+00** | **6.020E+04** | **-** | **1.40E+01** | **-** | **3.384E-05** | **9.645E-01** |
| $[Ni]_2[L]_2$ **2** | **Pt** | **3.23E+00** | **5.922E+04** | **1.257E+02** | **1.40E+01** | **4.386E-06** | **7.727E-05** | **8.151E-01** |

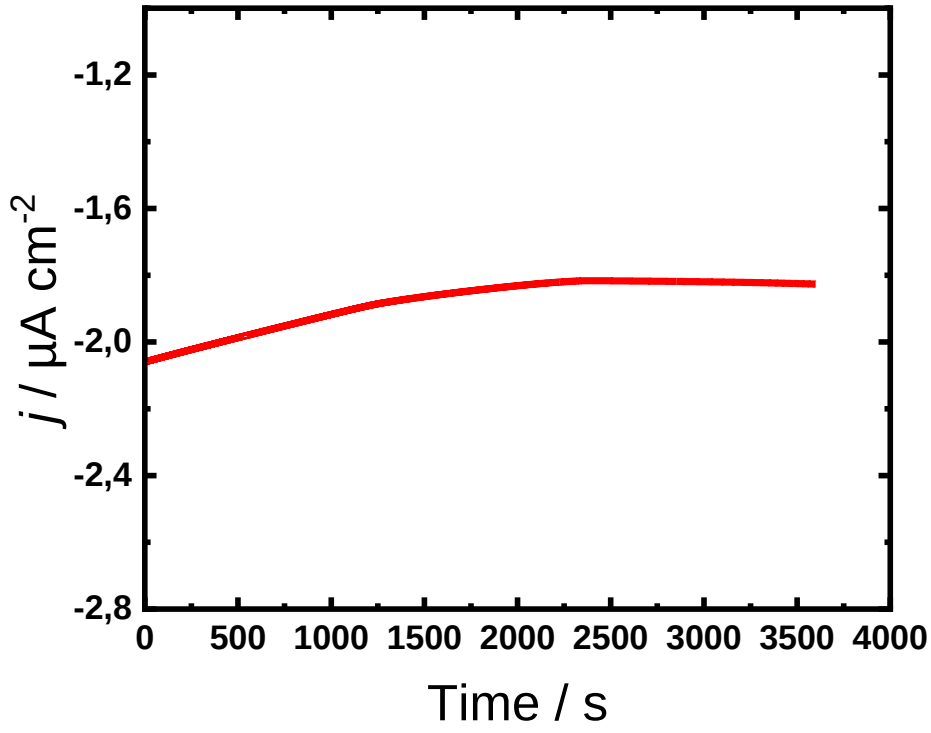



**Figure S10.** Chronoamperometric measurement of $[Ni]_2[L]_2$ **2** at 400 mV vs. RHE for 1 hr.

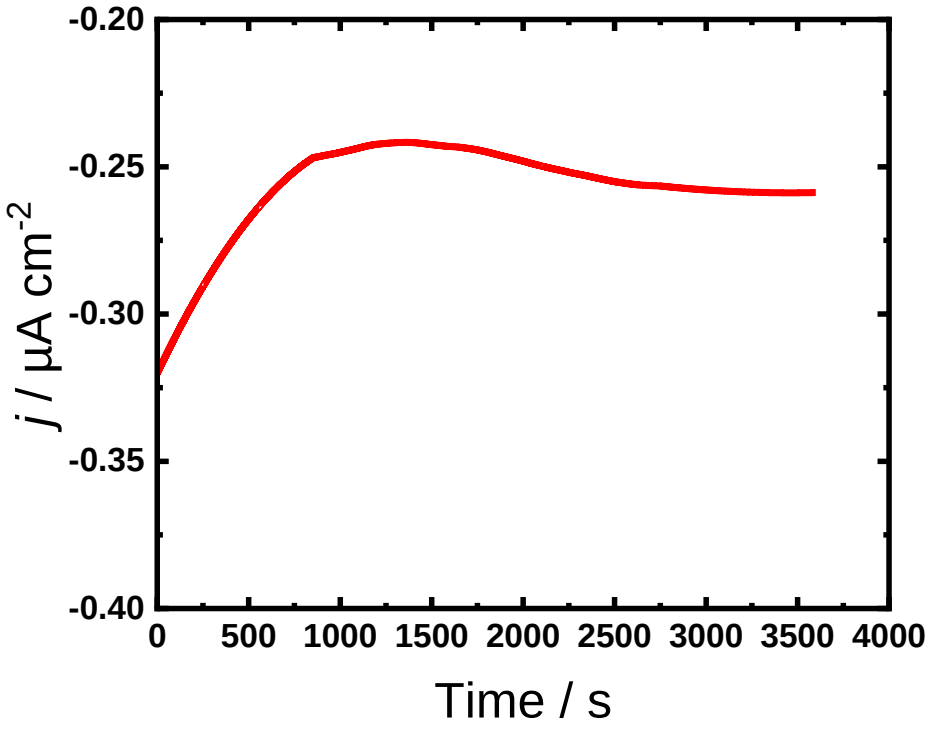



**Figure S11.** Chronoamperometric measurement of carbon black on carbon paper at 400 mV vs. RHE for 1 hr.

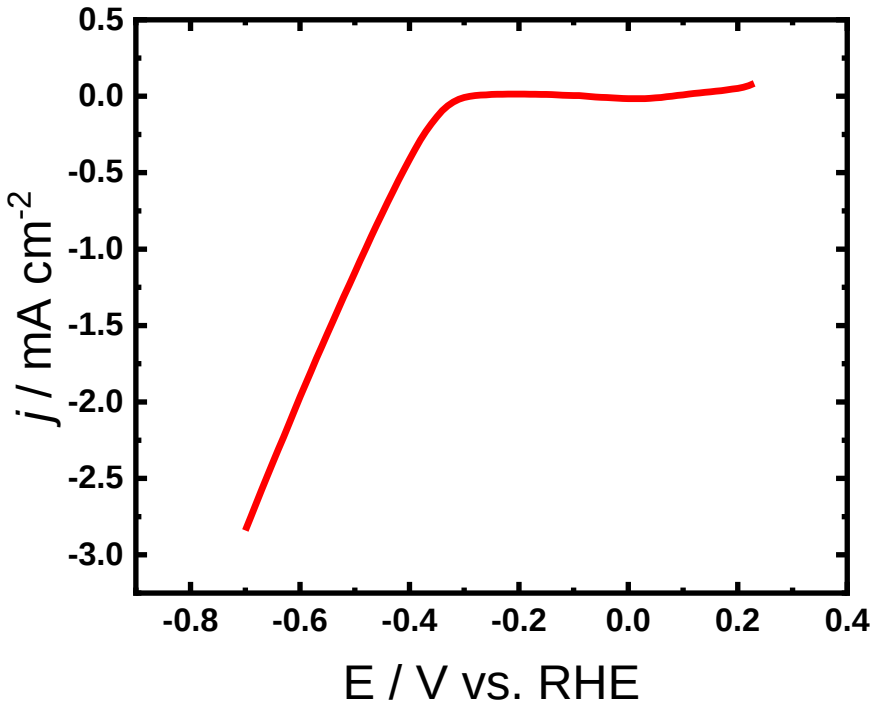



**Figure S12.** LSV measurement of $[Ni]_2[L]_2$ **2** from 0.2 to -0.7 V vs. RHE.

| Potential (V vs RHE) | $FE_{H2}$ ( % ) | | |
|---|---|---|---|
| | 5 min | 30 min | 60 min |
| -0.02 | - | - | 45% |
| -0.4 | - | - | 100% |
| -0.67 | 40% | 82% | 90% |

**Table S2:** Faradaic efficiencies of $H_2$ production after chronoamperometry using $[Ni]_2[L]_2$ **2** as WE.

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Some M(II) Complexes with ONO Tridentate Schiff Base N-Salicylidene-o-Aminophenol (SaphH2). *J. Mol. Struct.* **2012**, *1010*, 130–138, doi:10.1016/j.molstruc.2011.11.043.
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