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Supporting Information

Non-sterical stabilization of one-electron-oxidized NiSalen complex by thiophene core

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General:

The NMR spectra were recorded on a Brucker Avance III 400 spectrometer (^{1}H: 400.13 MHz; ^{13}C: 100.61 MHz; chemical shifts are reported as parts per million (δ, ppm); the residual solvent peaks were used as internal standards: 7.28 and 2.51 ppm for ^{1}H in $CDCl_3$ and DMSO-*d*$_6$ respectively, 39.5 and 77.2 ppm for ^{13}C in $CDCl_3$ and DMSO-*d*$_6$; multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad; coupling constants, *J*, are reported in Hz). MALDI-TOF spectra were recorded on a Shimadzu Axima Resonance spectrometer. IR spectra were recorded on a FT-spectrometer Spectrum BX in KBr pellets. UV-Vis spectra were recorded on Shimadzu UV-1700 and UV-1800 spectrometers, luminescence spectra were recorded on Shimadzu RF-5301 spectrofluorimeter. Melting points were determined in open capillary tubes on Stuart SMP30 Melting Point Apparatus. Starting materials and reagents were purchased from commercial sources, solvents were distilled prior to use. Absolute THF, DMF and DCM were prepared according the literature.[1] All reactions were carried out under Ar, all reaction vessels were oven-dried prior to use. TLC was performed utilizing the Macherey-Nagel Alugram® SIL G/UV$_{254}$ plates, Macherey-Nagel silica 60 was used for column chromatography. Crystallographic studies were performed on an Agilent Xcalibur diffractometer.

Electrochemical measurements were carried out using a three-electrode cell consisting of a working electrode, a counter electrode (Pt plate) and a reference electrode (Ag wire in 0.1*M* $AgNO_3$ in MeCN), continuously purged with Ar gas (Lentekhgas extra pure, 99,998%). However, for consistency all the potentials are quoted *vs*. Ag/AgCl (*aq.* KCl sat.) reference electrode. The 0.1*M* solutions of $[Et_4N]^+[BF_4]^-$ in MeCN and $[Bu_4N]^+[BF_4]^-$ in 1,2-DCE were used as background electrolytes. Tetraalkylammonium salts were preliminary recrystallized from isopropyl alcohol and dried at 120^0 *in vacuo*. Solvents of HLPC grade were obtained from Aldrich and stored under pre-activated 3 Å molecular sieves. Potentiostat/galvanostat apparatus Autolab PGSTAT30 (Eco Chemie, Netherlands) and Elins P-30I (Russia) were used for voltammetric measurements.

XPS spectra were obtained for the 0.001*M* solution of initial or electrochemically oxidized forms of **[Ni(ThioSalEn)]** and 0.1*M* $[Et_4N]^+[BF_4]^-$ in MeCN, drop-casted on a platinum foil and dried overnight at room temperature under vacuum. Spectra were recorded using a Thermo Fisher Scientific Escalab 250Xi spectrometer with nonmonochromatic AlKa radiation (photon energy 1486.6 eV). A total energy resolution of the experiment was about 0.3 eV. Spectra of the samples were recorded in the constant pass energy mode at 20 eV, using a 650 mm diameter analysis area. During data processing of the XPS spectra, binding energy values were referenced to the C 1s peak (284.8 eV) from the adventitious contamination layer. Investigations were carried out at room temperature in an ultrahigh vacuum of the order of $1\ 10^{-9}$ mbar.

Synthesis of target compound:

3-methoxythiophene-2-carbaldehyde 1:

3-methoxythiophene (1.14 g, 11.2 mmol, 1 ml) solution in 15 ml of absolute THF was placed into the Schlenk flask. A solution of *n*-BuLi (2.5 N *in hexanes*, 11.3 mmol, 4.5 ml) was added dropwise for 1 h *via* syringe at RT. Reaction mixture was heated to reflux for 2 h, cooled to -10 ^{o}C and anhydrous DMF (12.9 mmol, 1 ml) was added dropwise *via* syringe. Resulting mixture was heated slowly to RT and stirred overnight. 10 ml of 10% w/w NH_4Cl were added carefully to the mixture, followed by extraction with ether. Organic layer was washed with water and brine and dried with anhydrous Na_2SO_4. Solvent was evaporated *in vacuo* and the residue was purified by column chromatography (silica gel, DCM as eluent) yielding the product **1** (617 mg, 4.35 mmol, 39%). The spectroscopic data was in accordance with literature.[2]

3-hydroxythiophene-2-carbaldehyde 2:

To a stirred solution of aldehyde **1** (617 mg, 4.35 mmol) in 30 ml of absolute DCM was added BBr_3 (0.45 ml, 4.7 mmol) at 0 ^{o}C. After stirring for 8 h at RT another portion of BBr_3 (0.1 ml, 1 mmol) was added and the reaction mixture was stirred overnight. Reaction mixture was quenched with several drops of MeOH, then with 10 ml of saturated aqueous NH_4Cl, filtered through the Celite® pad and extracted with DCM. Organic layer was washed with water and brine and dried with anhydrous Na_2SO_4. Solvent was evaporated *in vacuo* and the residue was purified by column chromatography (silica gel, DCM-EtOAc 20:1 as eluent) yielding the product **2** (410 mg, 3.2 mmol, 74%). The spectroscopic data was in accordance with literature.[2]

[Ni(ThioSalEn)]:

To a stirred solution of aldehyde **2** (410 mg, 3.2 mmol) in 7 ml of EtOH in sealable tube 1,2-diaminoethane (100 mg, 1.6 mmol) was added, resulted in immediate formation of creamy-red precipitate. After 10 min, fine powder of $Ni(OAc)_2{*}4H_2O$ (400 mg, 1.6 mmol) was added and mixture was homogenised for 5 min on US bath. Tube was sealed and heated to 85 ^{o}C for 1.5 h, then reaction mixture was cooled, green residue was separated by centrifugation, washed with 2 mt of cold EtOH and dried to give the desired product (350 mg, 1.04 mmol, 65%). Pure sample suitable for electrochemical experiments and spectroscopic characterization was obtained using the column chromatography (silica gel, PE-DCM 1:1 as eluent). Single crystal suitable for crystallographic studies was obtained by slow evaporation of MeCN solution of compound.
Green solid, mp 240 ^{o}C (dec.); ν_{max}(KBr) 3150-2800 (br), 1675, 1590, 1490, 1420, 1360, 1295, 1190, 1125, 1020, 760, 695, 635, 595, 475; UV-Vis (0.17 mM in MeCN) 269 (3.35), 315 (3.12), 402 (2.80); δ_H (400 MHz, DMSO-d_6) 7.67 (2H, arom, d, J = 5.3 Hz), 7.60 (2H, imine, s), 7.57 (2H, arom, d, J = 5.3 Hz), 3.26 (4H, ethylene, s, 4H); δ_C (100.6 MHz, DMSO-d_6) 169.6, 155.1, 134.2, 121.3, 109.4, 58.3; MS (MALDI): M^+, calcnd. for $C_{12}H_{10}N_2O_2S_2Ni$: 336.0 found: 336.2.

Electrochemistry:

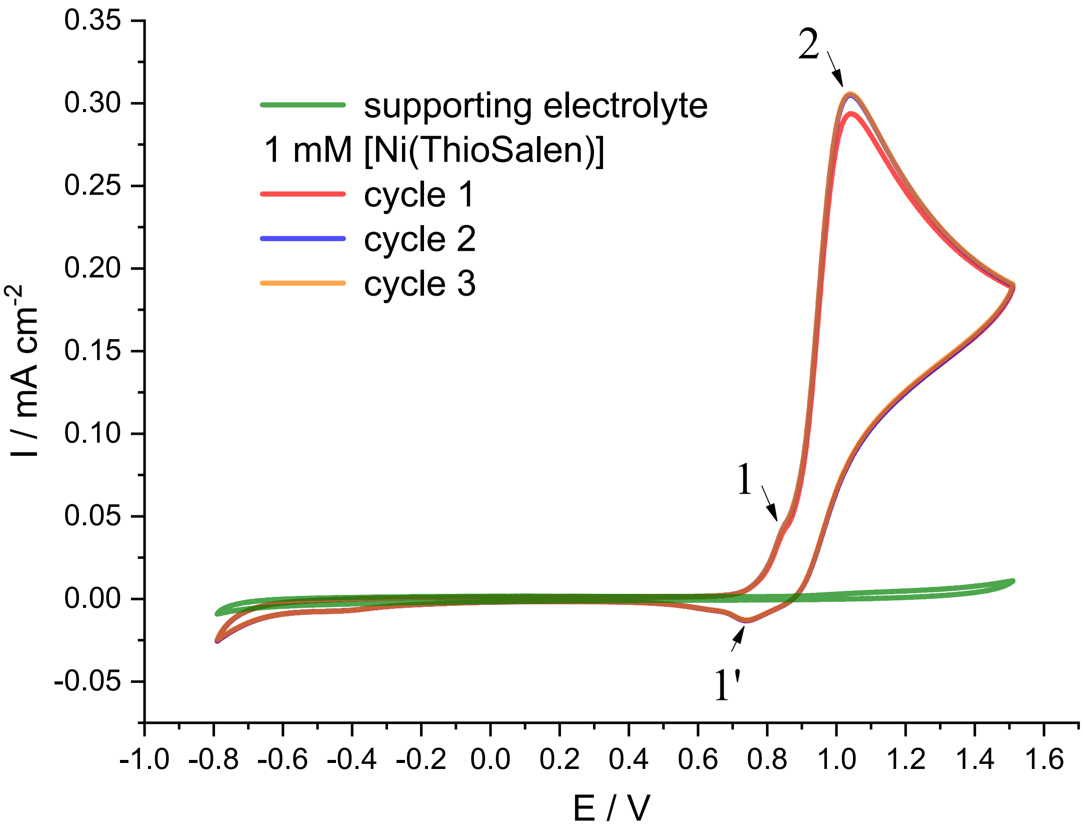

Figure S1 CVA of [Ni(ThioSalEn)] in 0.1 M $[Et_4N]^+[BF_4]^-$ in MeCN on ITO electrode, scan rate 50 mVs^{-1}.

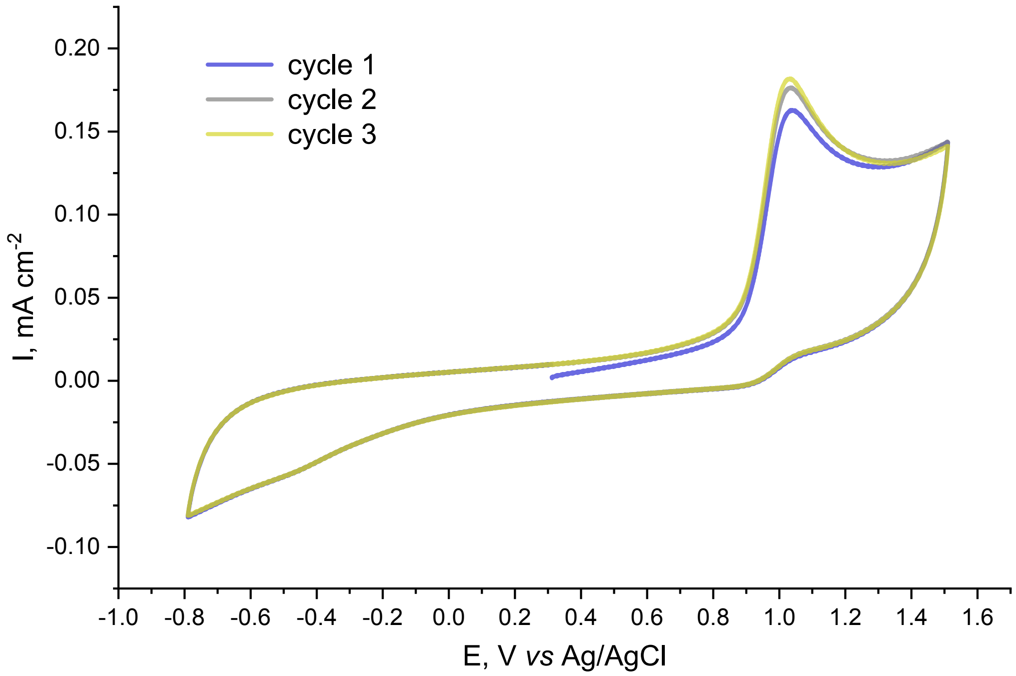

Figure S2 CV of [Ni(ThioSalEn)] in 0.1 M $[Et_4N]^+[BF_4]^-$ in MeCN on Pt electrode, scan rate 50 mVs^{-1}.

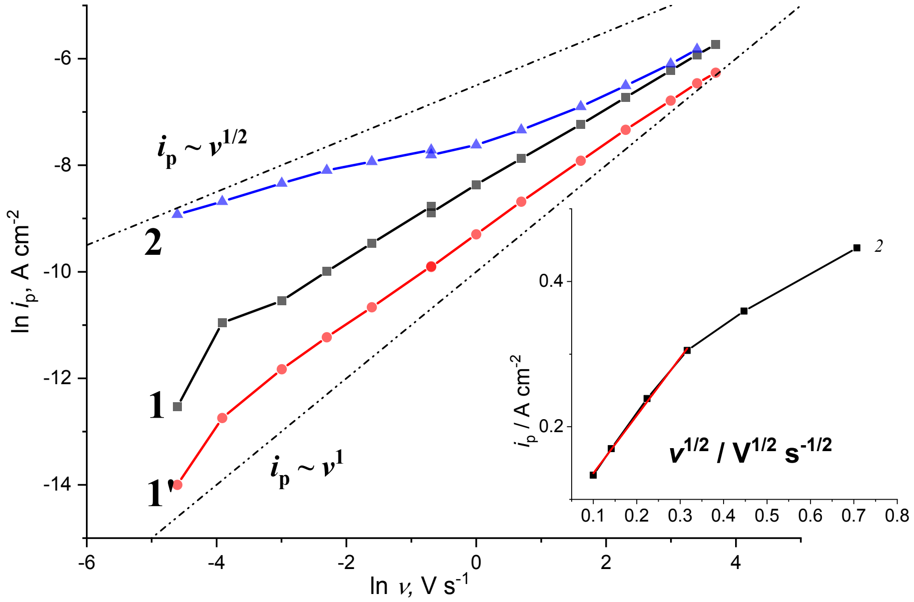

Figure S3 Log-log and square root (insert) representations of dependence of peak currents *vs*. scan rate for CVA of [Ni(ThioSalEn)] in 0.1 M $[Et_4N]^+[BF_4]^-$ in MeCN on ITO electrode, curves numbers correspond to peak notations on Fig. 2

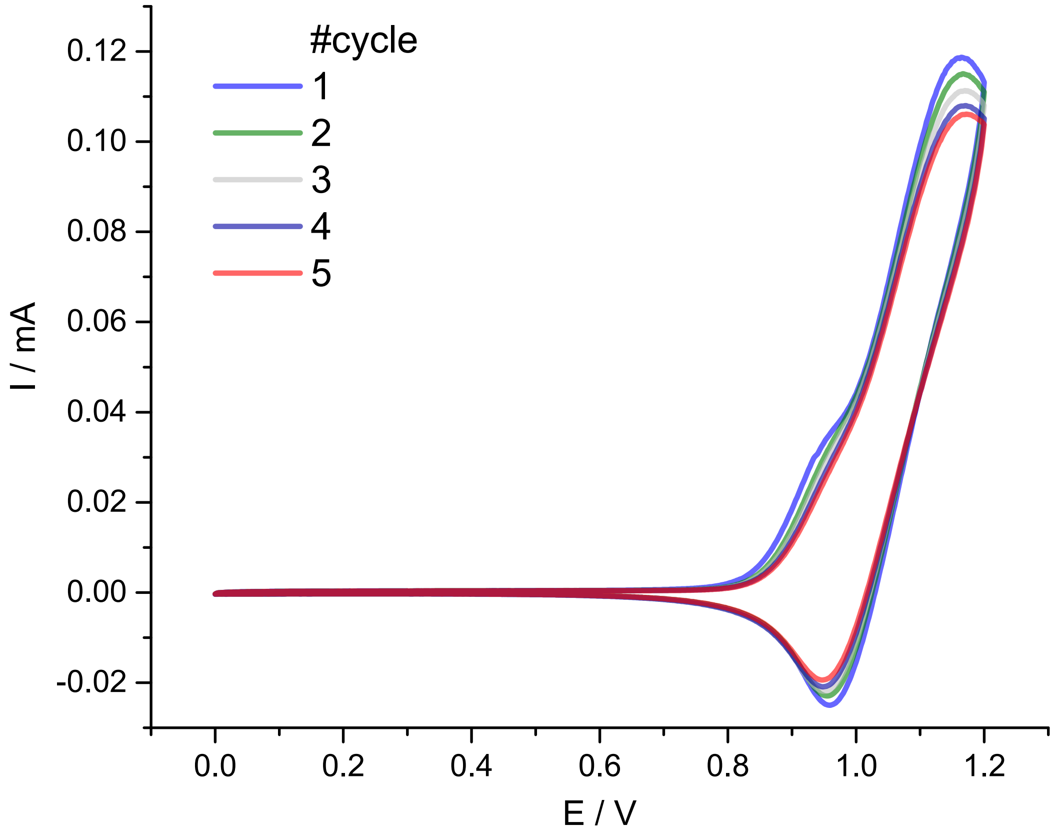

Figure S4 CVA of [Ni(ThioSalEn)] in 0.1M $[Bu_4N]^+[BF_4]^-$ in 1,2-DCE on ITO electrode, scan rate 50 mv/s.

Spectral data for [Ni(ThioSalEn)]:

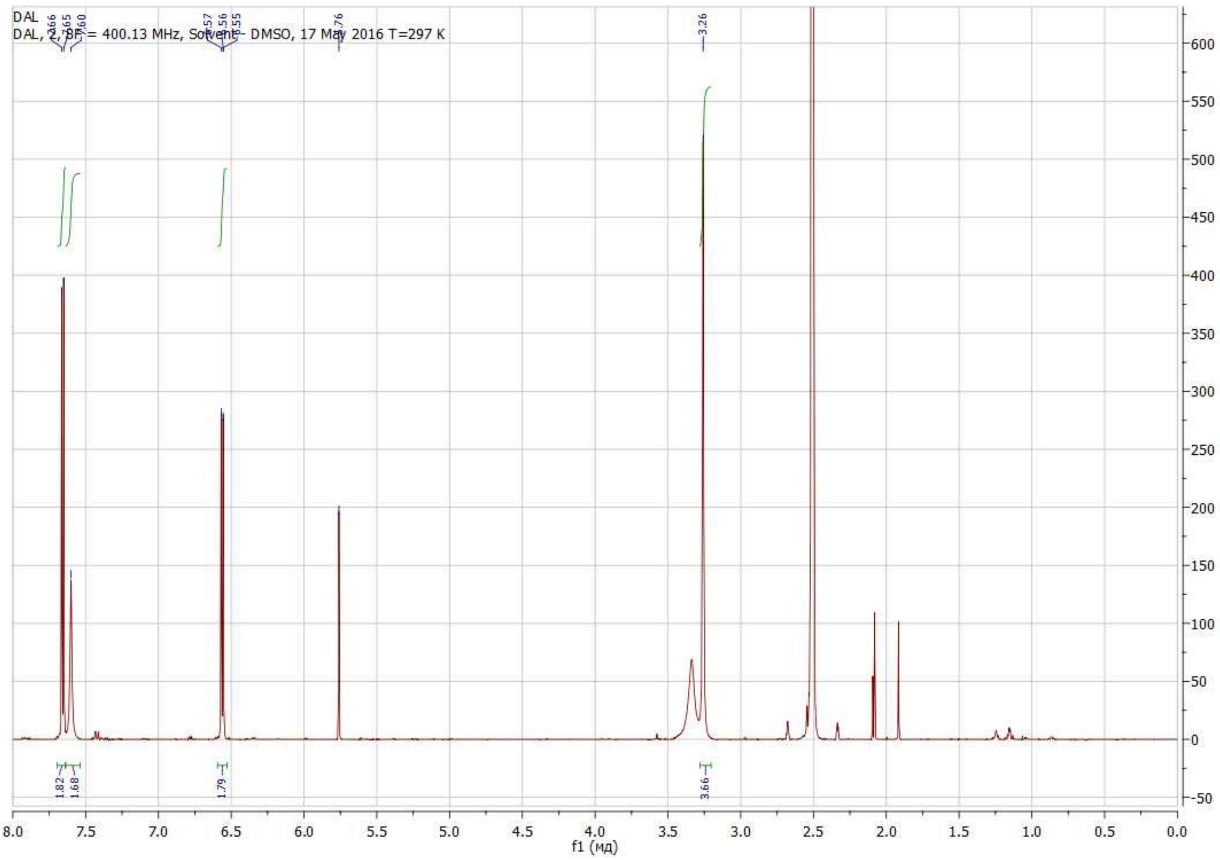

Figure S5 ^{1}H NMR spectrum of [Ni(ThioSalEn)], DMSO-d$_6$, 400 MHz

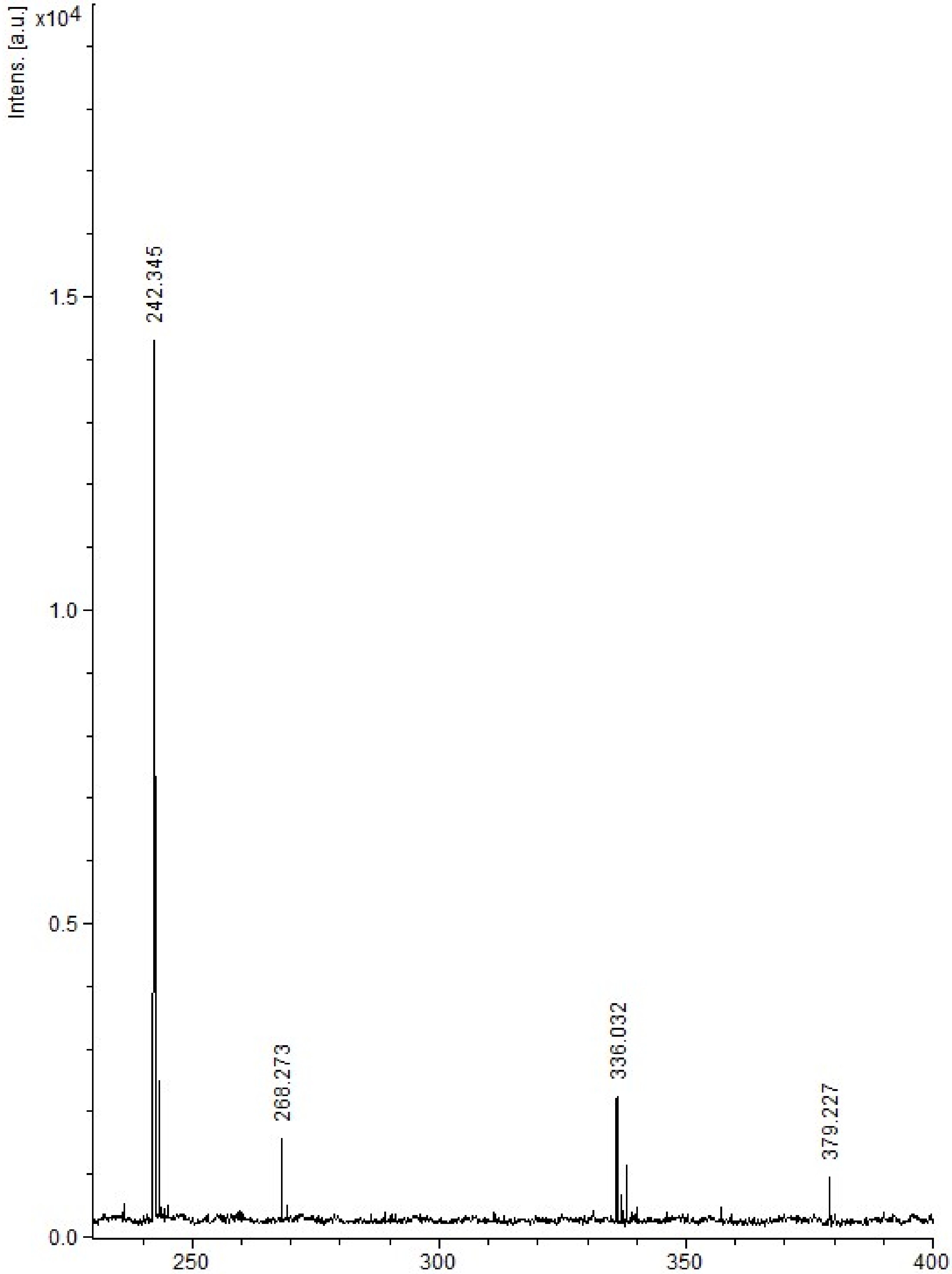

Figure S6 MALDI-TOF MS spectrum of [Ni(ThioSalEn)]

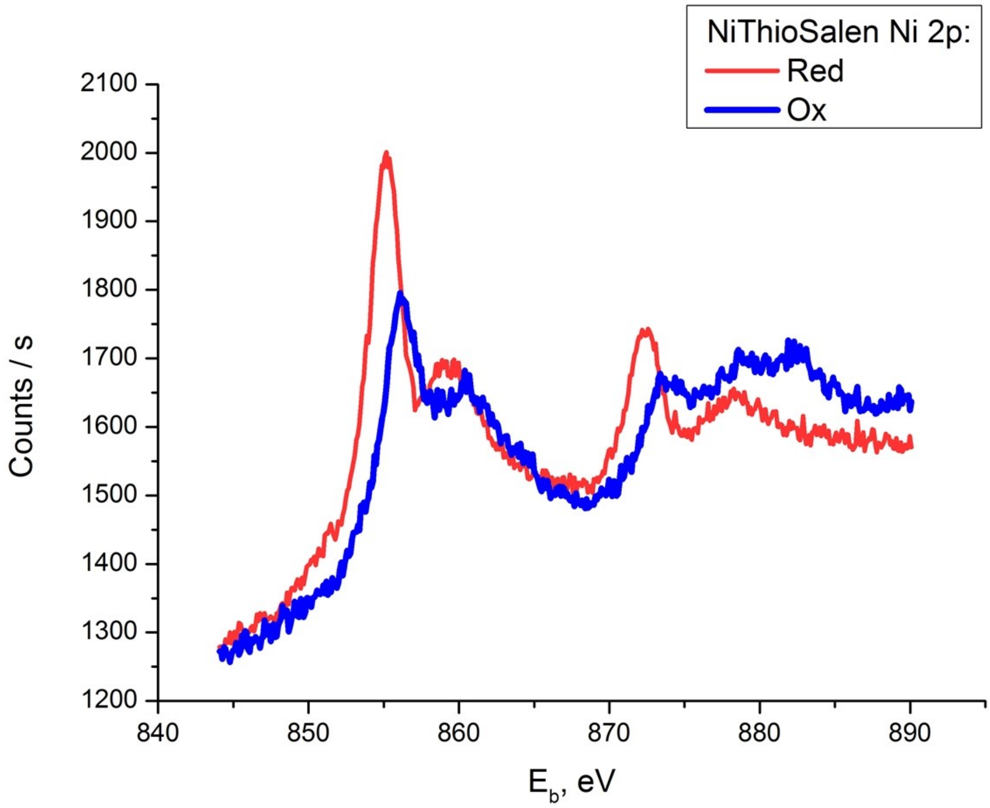

Figure S7 XPS Ni2p binding energies spectrum of initial (red) and oxidized (blue) [Ni(ThioSalEn)]

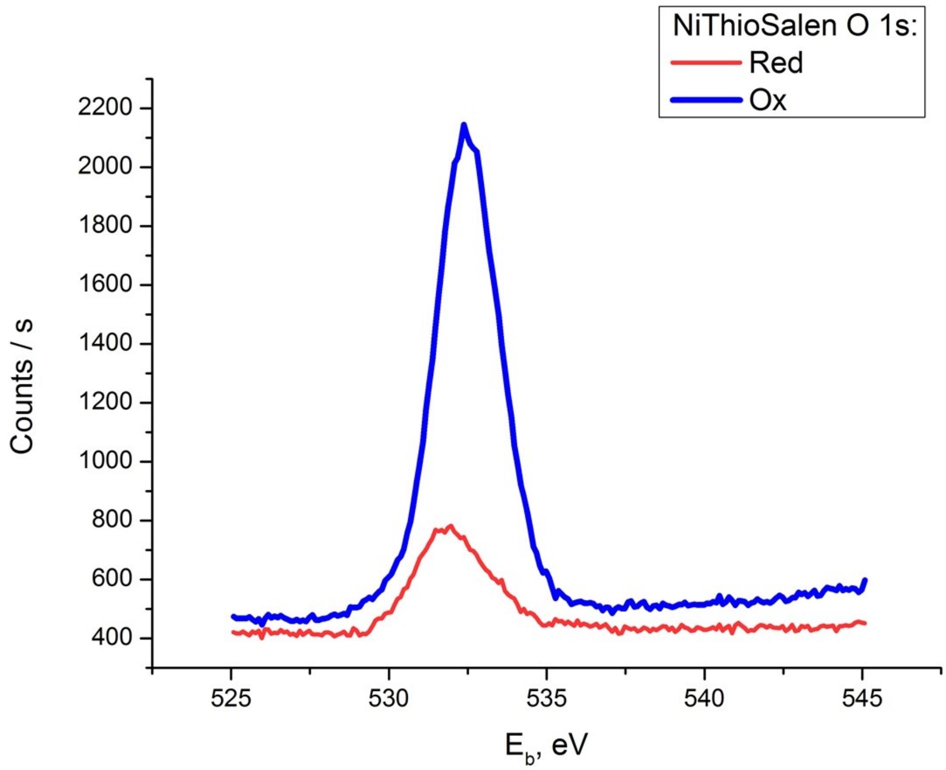

Figure S8 XPS O1s binding energies spectrum of initial (red) and oxidized (blue) [Ni(ThioSalEn)]

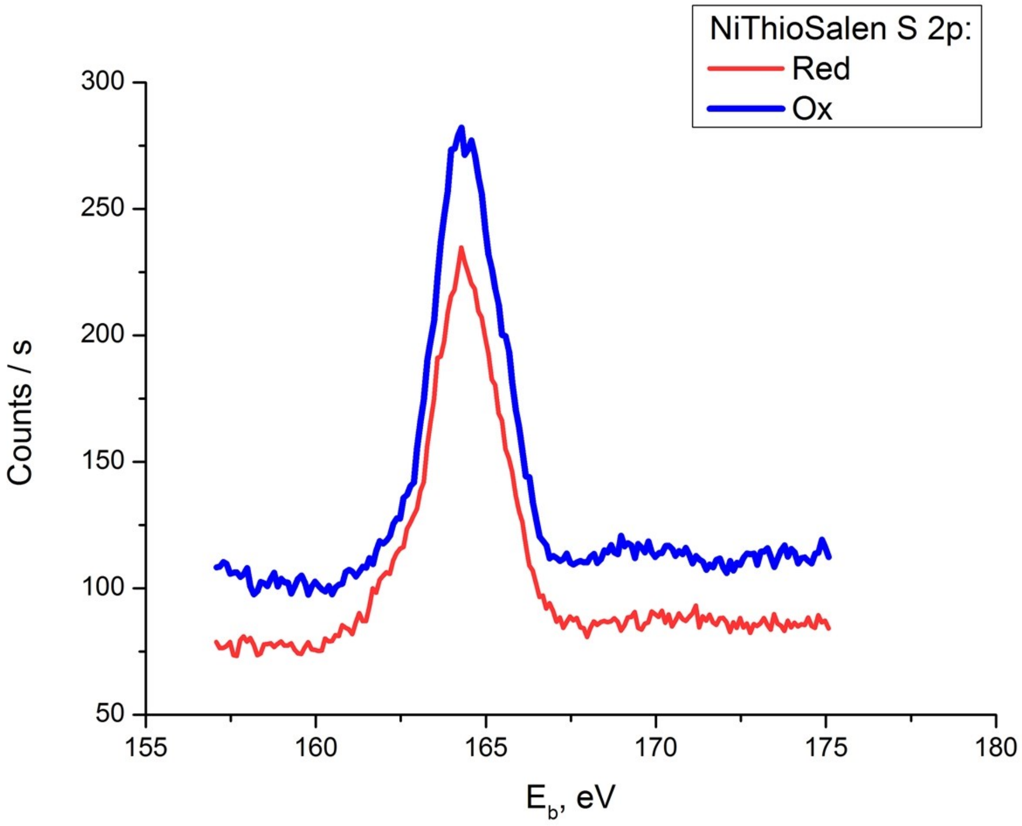

Figure S9 XPS S2p binding energies spectrum of initial (red) and oxidized (blue) [Ni(ThioSalEn)]

Table S1. Thermodynamics of formation of oxidized complexes with axially coordinated acetonitrile (DFT computational data for 298 K).

	ΔH, kJ/mol	ΔS, J/mol·K	ΔG, kJ/mol	$\Delta G_{½}$, kJ/mol
ox-[Ni(SalEn)(CH_3CN)$_2$]	–36	–254	+40	+2
ox-[Ni(ThioSalEn)(CH_3CN)$_2$]	–14	–258	+63	+24
ox-[Ni(ThioSalPhen)(CH_3CN)$_2$]	–93	–217	–28	–60
ox-[Ni(EDOTSalEn)(CH_3CN)$_2$]	–64	–280	+19	–23

The thermodynamic parameters in the table above were calculated from the ideal-gas partition functions obtained from CAM-B3LYP/6-311G* DFT calculations using C-PCM for solvent effects. The use of implicit solvent affects the energies (enthalpies) of molecules in solution, but the entropy, which is still obtained in the framework of the ideal gas approximation, is very likely to be significantly overestimated. Therefore, apart from the ΔG value ($\Delta G = \Delta H - T\Delta S$), an alternative $\Delta G_{½}$ metric ($\Delta G_{½} = \Delta H - ½T\Delta S$) is provided in Table S1 to illustrate the effects of using lower entropies, which are likely to be encountered in condensed phase, for the calculation of free energy differences. Since $\Delta G_{½}$ can be considered as a lower estimate of free energy, the actual Gibbs free energy change for the process in question is likely to be somewhere between ΔG and $\Delta G_{½}$.