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Supporting Information

Reduction of protons assisted by a hexanuclear nickel thiolate metallacrown: protonation and electrocatalytic dihydrogen evolution

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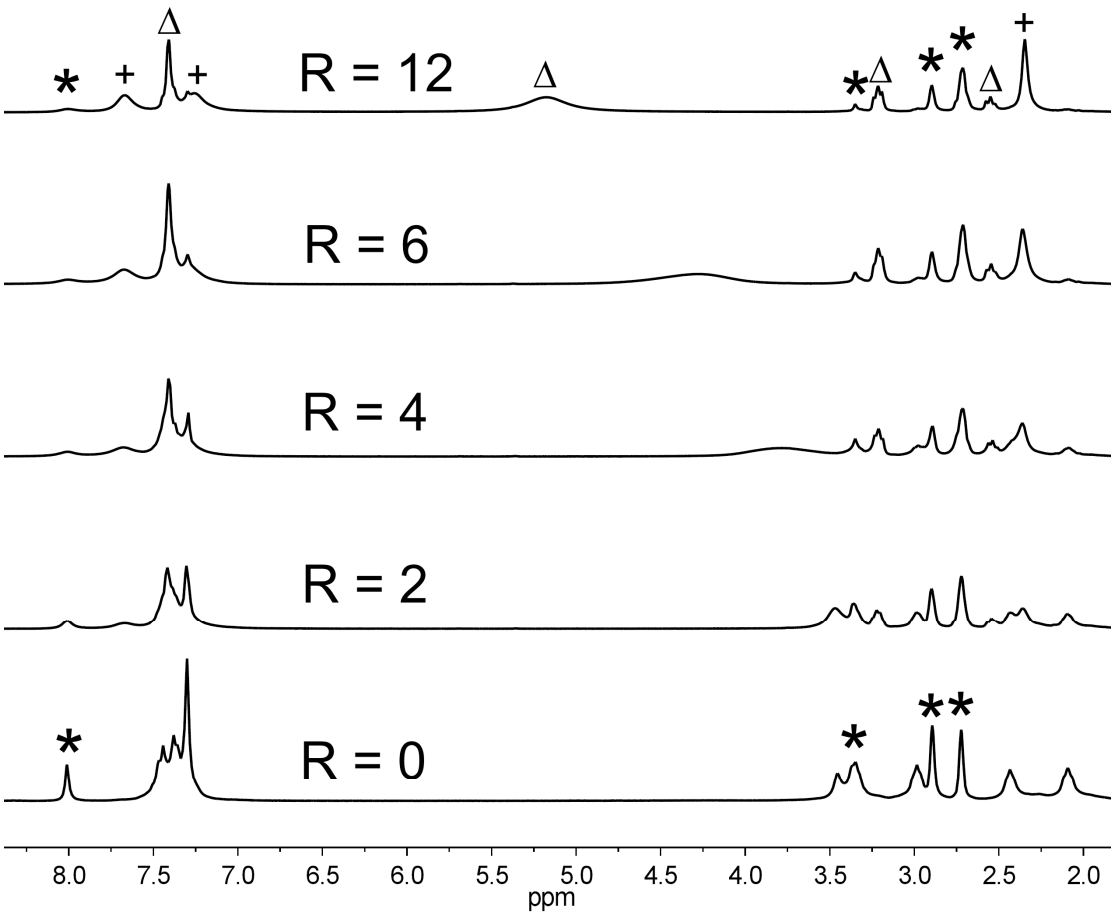

Figure S1. ^{1}H NMR of the $[Ni_6L_{12}]$ in DMF-d_7 solution upon the addition of a solution of $TsOH{\cdot}H_2O$ in DMF-d_7 in various Ni to H^+ ratios. R = $[H^+/Ni]$. Δ, signals from protonated $[Ni_6L_{12}]$; +, signals from TsO^- anions; ✱, signals from the residual protons of the solvent.

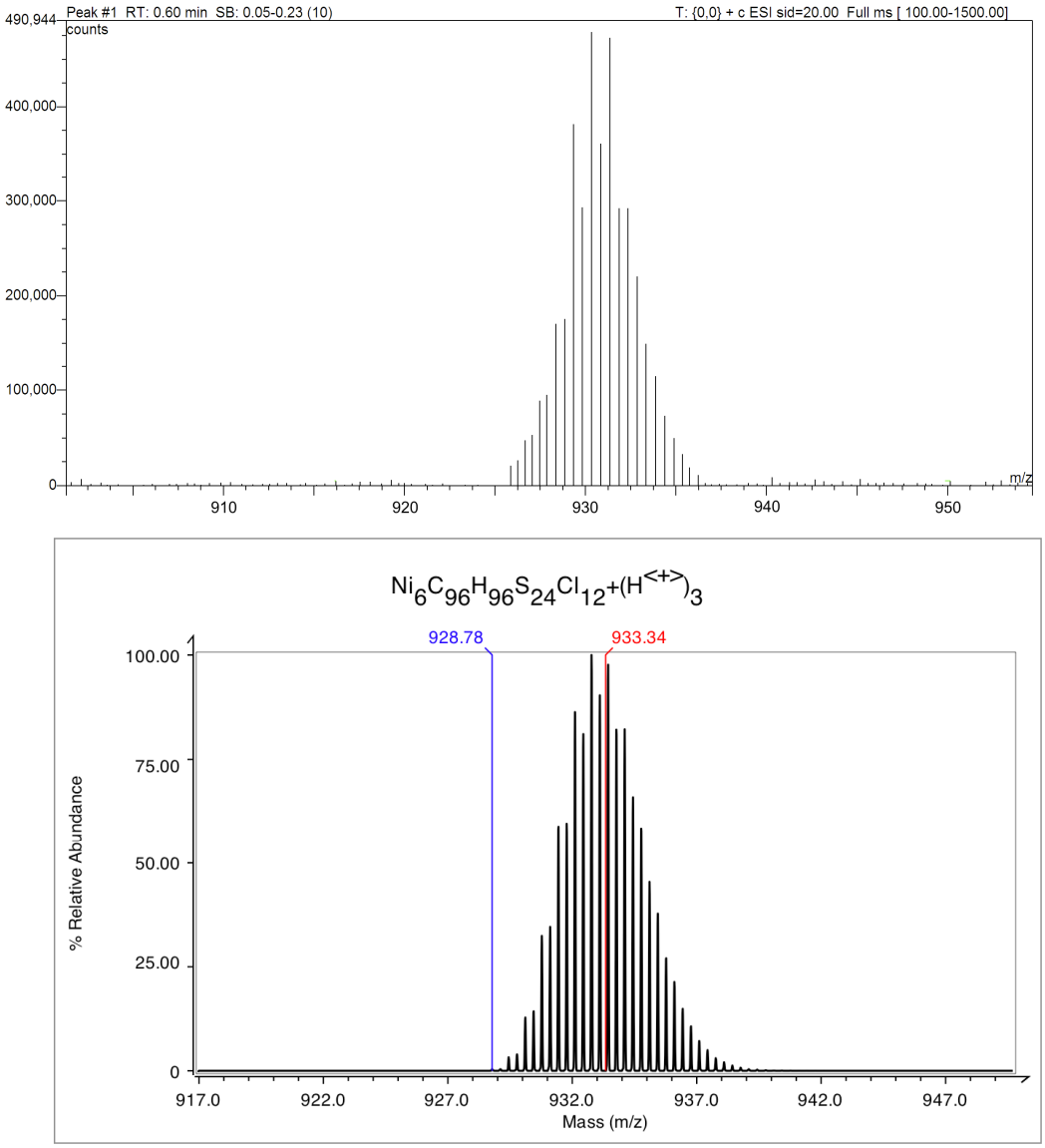

Figure S2. Positive ion MS(ESI) spectrum of $[Ni_6L_{12}]$ in a diluted solution of trifluoromethanesulfonic acid in dichloromethane showing the $[M+3H^+]^{3+}$ signal (top) and the isotopic distribution pattern simulated for $[Ni_6C_{96}H_{96}S_{24}Cl_{12}]+3H^+$ (bottom).

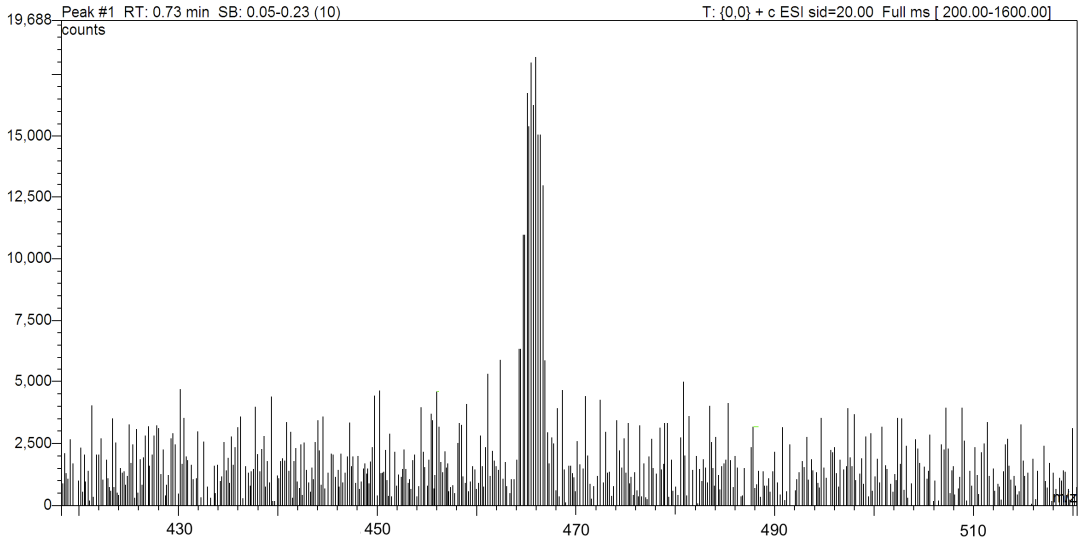

Figure S3. Experimental ESI-MS of $[Ni_6L_{12}]$ in a diluted solution of DCl in dichloromethane showing the $[M+6D^+]^{6+}$ signal.

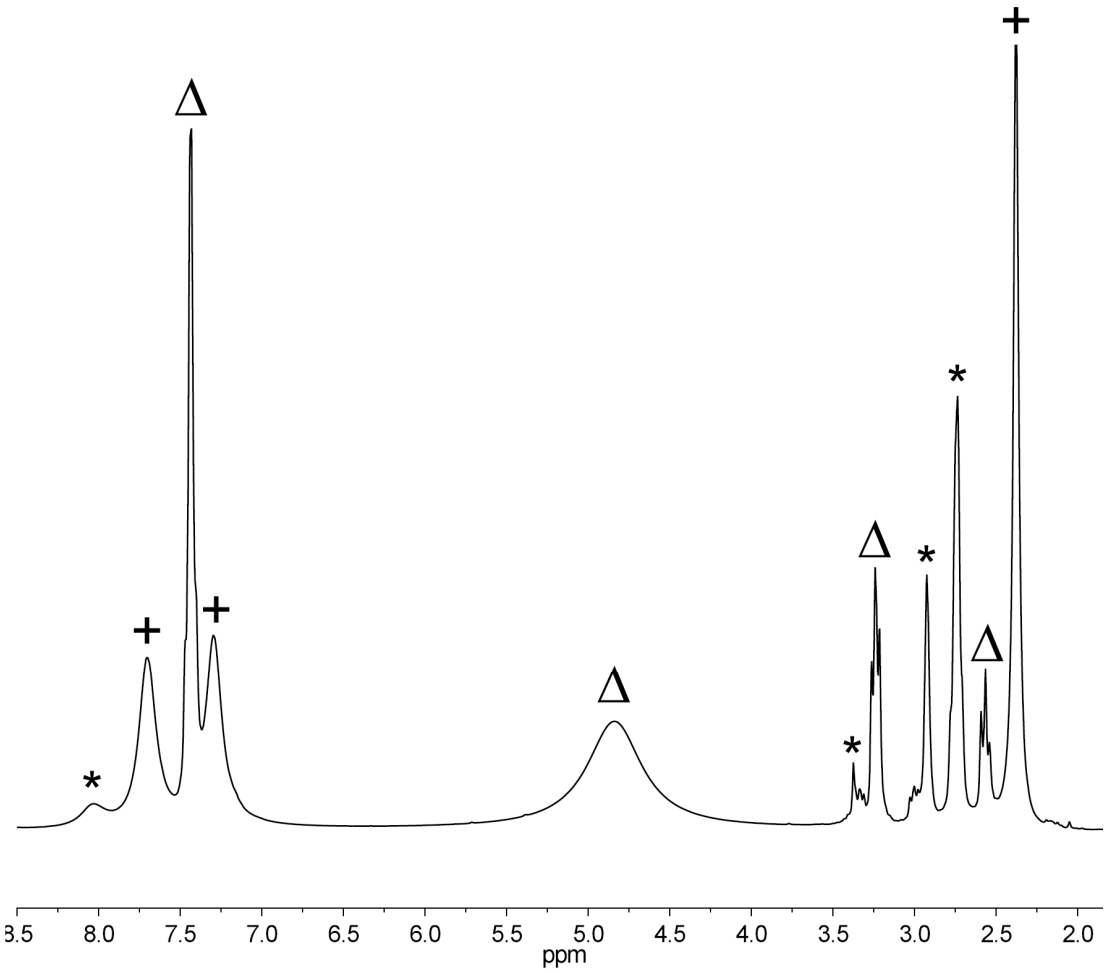

Figure S4. ^{1}H NMR of protonated $[Ni_6L_{12}]$ in DMF-d7 solution after two days of the addition of $TsOH \cdot H_2O$ to the $[Ni_6L_{12}]$. Δ, signals from protonated $[Ni_6L_{12}]$; +, signals from TsO^- anions; ✱, signals from residual protons of the solvent.

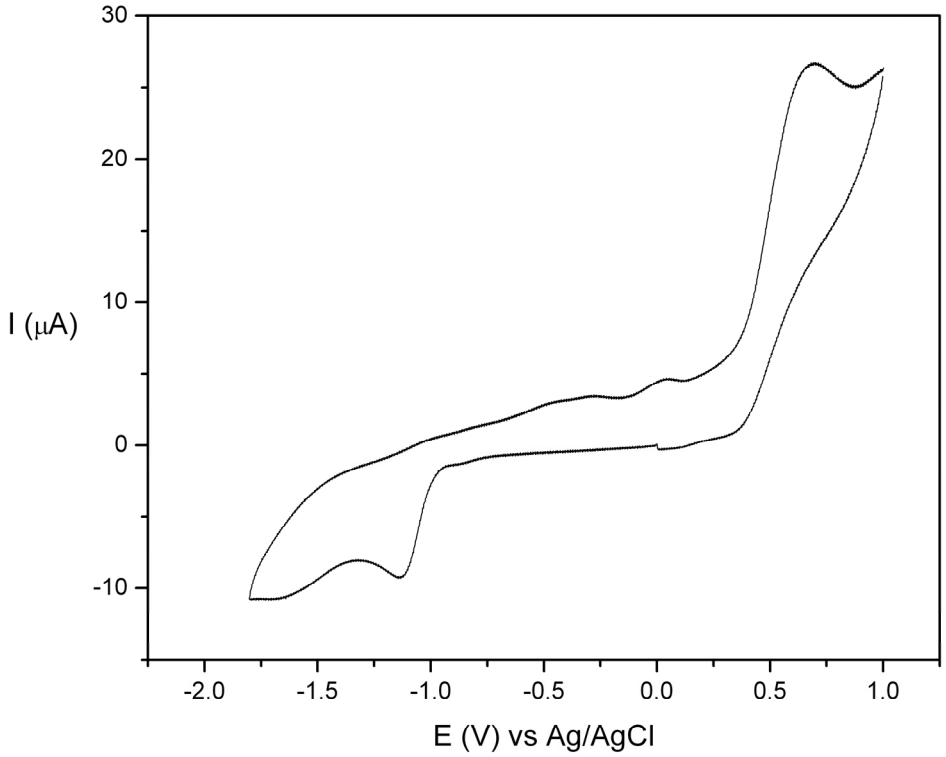

Figure S5. Cyclic voltammogram of $[Ni_6L_{12}]$ (0.5 mM in DMF + 0.1 M *n*-Bu_4NPF_6) at a steady glassy carbon working electrode with a Pt wire auxiliary electrode. Scan rate 200 mV/s.

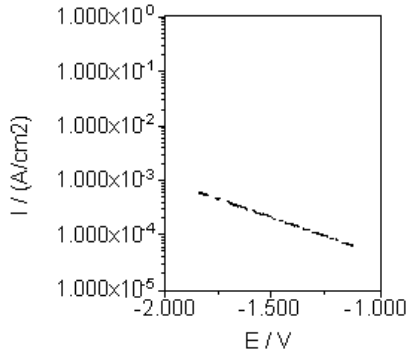

Figure S6. Tafel plot of the proton reduction cyclic voltammogram recorded using the $[Ni_6L_{12}]$ immobilized edge plane pyrolitic graphite electrode.

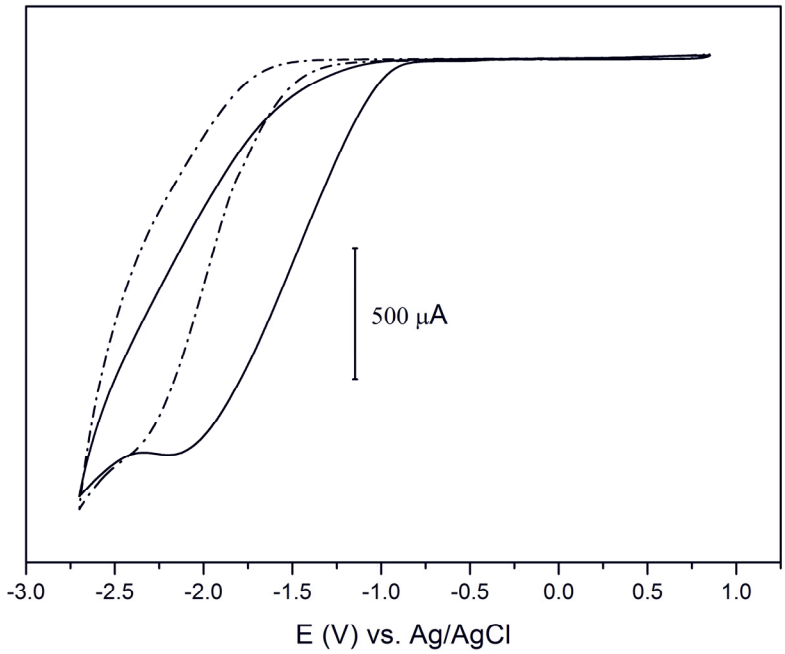

Figure S7. CV of a 0.1 M solution of dichloroacetic acid containing 0.1 M n-Bu_4NPF_6 on a $[Ni_6L_{12}]$-immobilized static edge plane pyrolitic graphite electrode with a Pt wire auxiliary electrode (see experimental section for the details of immobilization). Scan rate 200 mV/s. (——) First scan; (·–·–·) after 30 scans.