Electronic Supplementary Material (ESI) for Dalton Transactions.


# A Protein Scaffold Enables Hydrogen Evolution for a Ni-bisdiphosphine Complex

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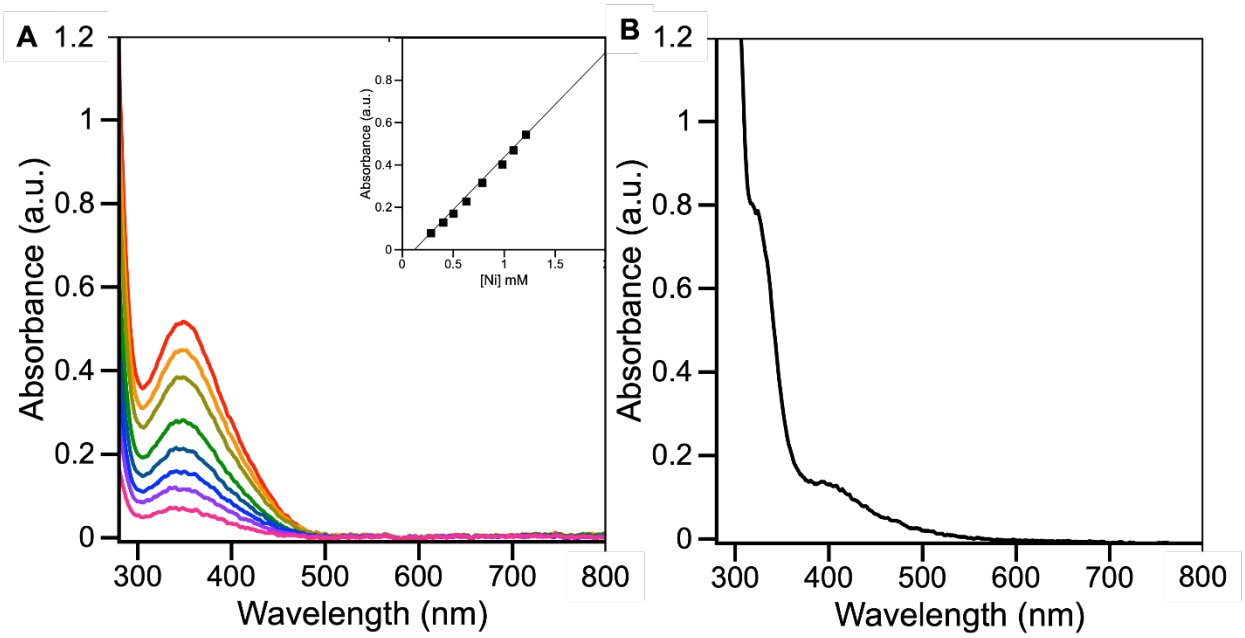


**Figure S1**. Absorbance spectra of [**NGly**] in 0.1 M HEPES at pH 7 (A), the data used to calculate the extinction coefficient (inset of A), and [Ni(PN$^{Gly}$P)$_2$]⊂LmrR following assembly (B).

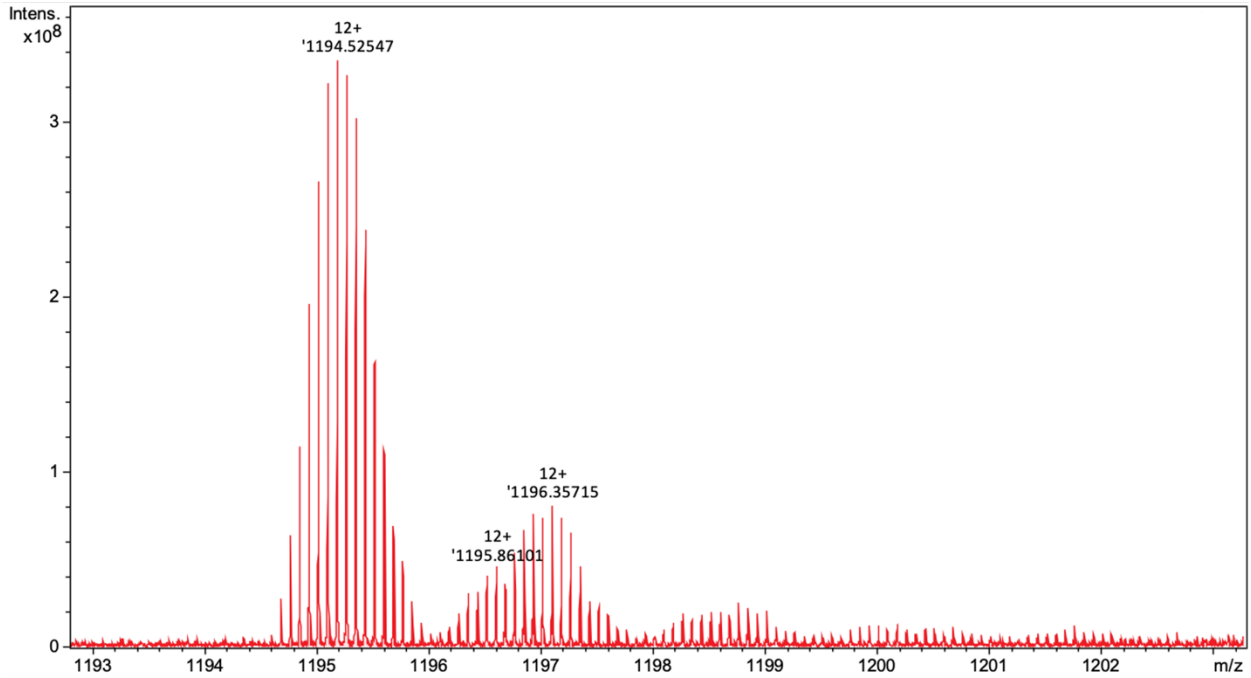


**Figure S2**. Expanded view of the ESI data from [Ni(PN$^{Gly}$P)$_2$]⊂LmrR showing the calculated and found masses of LmrR monomer + (PN$^{glycine→maleimide}$P) ligand + Ni + 2H: calculated 14345.1, found 14345.2. A mass for LmrR + (PN$^{glycine→maleimide)}$P ligand + H, calculated = 14187.20, was found = 14187.13.The mass for the ligand was calculated using the in situ formed amide bond with the maleimide group. The phosphine atoms of the PNP ligand are extremely air sensitive and are expected to dissociate from the Ni center via oxidation of the phosphine ligands. The mass at 14345.2 was found in very low abundance (1%) due to rapid dissociation of the Ni atom after exposure of the sample to $O_2$ for the ESI measurements.

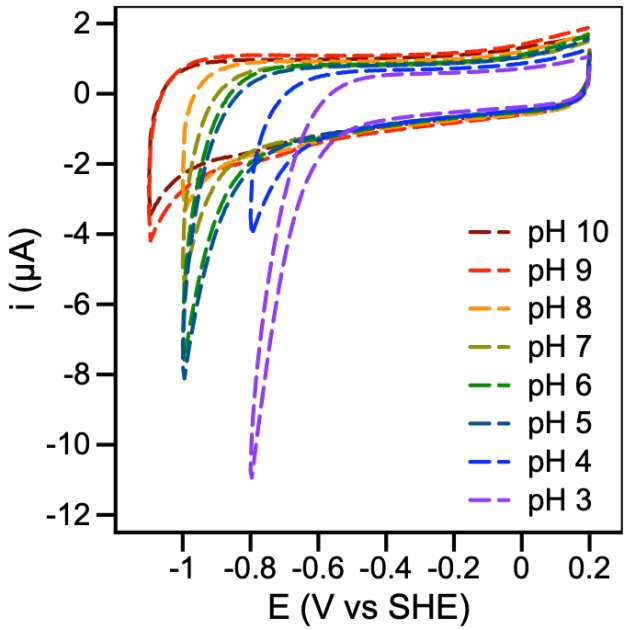


**Figure S3**. Electrochemical response of EPPG electrode in the respective phosphate buffer solutions titrated to the designated pH using phosphoric acid, or by mixing mono/di-basic sodium phosphate solids in water.

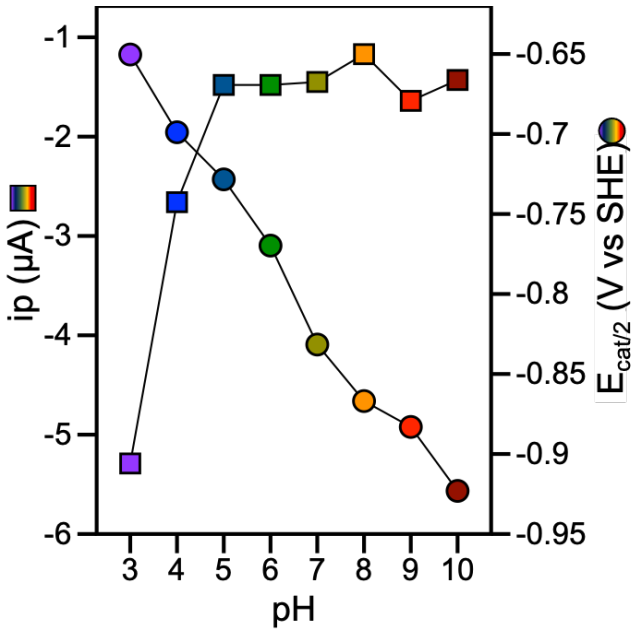


**Figure S4**. Peak catalytic currents (squares) and the $E_{cat/2}$ values (circles) obtained from the background subtracted linear sweep voltammograms resulting from a film of $[Ni(PN^{Gly}P)_2]$⊂LmrR on an EPPG electrode surface. Peak currents are observed to stabilize above pH 5, suggesting protonation of the metal or nearby residue may be of importance. As expected, the $E_{cat/2}$ shifts cathodically as the pH increases and the [proton] diminishes, requiring an increased driving force to complete the reaction. Points are connected to visualize the trend and are not a fit to the data. Data points correlate to pH and are colored to match those of Figure 2, with the following color scheme: pH 3.0 (purple), 4.0 (navy), 5.0 (blue), 6.0 (green), 7.0 (asparagus), 8.0 (orange), 9.0 (red), 10.0 (crimson).

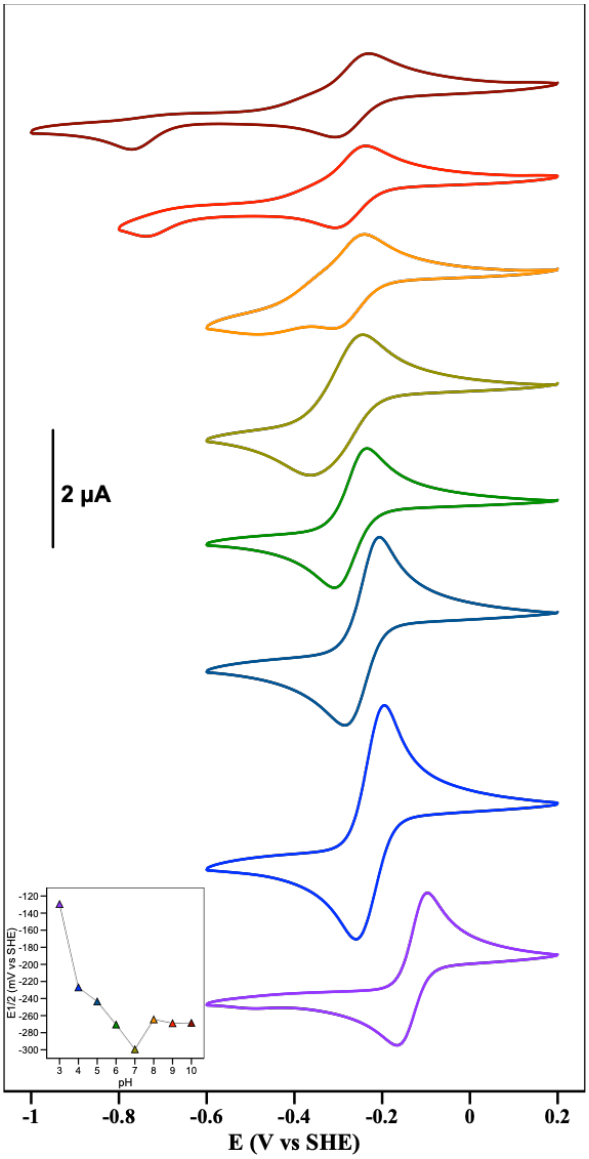


**Figure S5.** Cyclic voltammograms of [Ni($PN^{Gly}P$)$_2$] in 0.1 M phosphate buffer from pH 3 (bottom, purple) to pH 10 (top, crimson) focused on the reversible $Ni^{2+/0}$ couple. Inset: Observed $E_{1/2}$ values. Colors used for the cyclic voltammograms match those of the inset to designate the pH value: pH 3.0 (purple), 4.0 (navy), 5.0 (blue), 6.0 (green), 7.0 (asparagus), 8.0 (orange), 9.0 (red), 10.0 (crimson). At no point was a current increase observed at any pH, indicating that this complex is not a catalyst for hydrogen evolution.