Synthetic models for the active site of hydrogenase enzymes are of interest as catalysts for the generation of hydrogen, a clean energy carrier. We have studied several models composing of a diironhexacarbonyl unit coupled to electroactive thiolate ligands (see figure). The thiolate ligands are derivatives of naphthalic anhydride. They were employed to modulate the redox properties of the iron-carbonyl core and as potential electron transport groups. Our models have been demonstrated to catalyze the electrochemical generation of molecular hydrogen from acetic acid at favorable overpotentials.