[FeFe]-Hydrogenase Mimics for Catalytic Hydrogen Evolution Reactions

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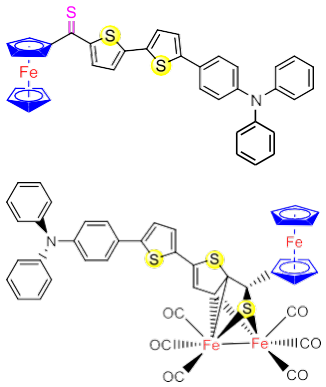
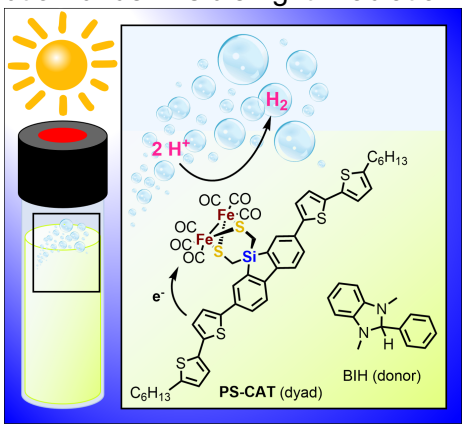
In a recent publication, we have investigated the use of a ferrocenyl α-thienyl thioketone as a proligand for the preparation of [FeFe]-hydrogenase H-cluster mimics.[1] This study showed the formation of *ortho*-metalated complex that resembles similar structures of complexes obtained in analogous reactions of aromatic thioketones together with the formation of unexpected arrangement of sulfur and iron atoms, resulting from the ring opening, i.e., dearomatization of the thiophene ring. In our continuing studies we focused on the reaction of the push-pull ferrocenyl α-thienyl thioketone with $Fe_3(CO)_{12}$ leading to a [FeFe]-hydrogenase mimic complex catalyzing the hydrogen evolution reaction under visible light irradiation (λ = 405 nm, TON ≈ 230).



The second part focusses on the photocatalytic production of hydrogen using [FeFe]-hydrogenase mimics. We designed a compact and precious metal-free photosensitizer-catalyst dyad (**PS-CAT**) for photocatalytic hydrogen evolution under visible light irradiation. **PS-CAT** represents a prototype dyad comprising π-conjugated oligothiophenes as light absorbers. **PS-CAT** and its interaction with the sacrificial donor 1,3-dimethyl-2-phenylbenzimidazoline were studied by steady-state and time-resolved spectroscopy coupled with electrochemical techniques and visible light-driven photocatalytic investigations. Operando EPR spectroscopy revealed the formation of an active $[Fe^{0.5}Fe^{0.5}]$ species – in accordance with theoretical calculations – presumably driving photocatalysis effectively (TON ≈ 210).[2,3]



References

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