

## Accepted Manuscript

### Photochemical Reactivity of a Binuclear Fe(I)-Fe(I) Hydrogenase Model Compound with Cyano Ligands

Andrew Hunt, Jacob Barrett, Meghan McCurry, Carmen Works

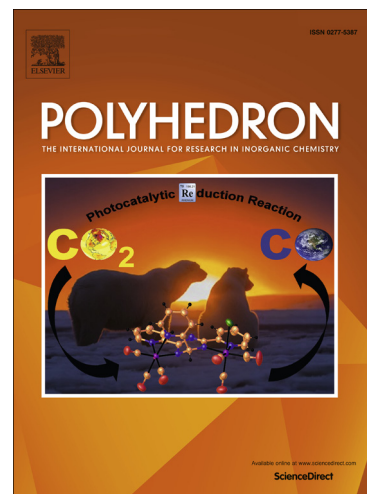
PII: S0277-5387(16)00008-5  
DOI: <http://dx.doi.org/10.1016/j.poly.2016.01.004>  
Reference: POLY 11766

To appear in: *Polyhedron*

Received Date: 30 September 2015  
Accepted Date: 4 January 2016

Please cite this article as: A. Hunt, J. Barrett, M. McCurry, C. Works, Photochemical Reactivity of a Binuclear Fe(I)-Fe(I) Hydrogenase Model Compound with Cyano Ligands, *Polyhedron* (2016), doi: <http://dx.doi.org/10.1016/j.poly.2016.01.004>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



## Photochemical Reactivity of a Binuclear Fe(I)-Fe(I) Hydrogenase Model Compound with Cyano Ligands

Andrew Hunt, Jacob Barrett, Meghan McCurry and Carmen Works\*

Sonoma State University, 1801 E. Cotati Ave, Rohnert Park CA 94928

\*Corresponding author. Tel: 707 664 3084, email: works@sonoma.edu

### 1. Introduction

The detrimental effects of fossil fuel usage on our global ecosystem as well as ever increasing energy demand has inspired much research towards the development of clean and renewable fuels for a sustainable future. Hydrogen is seen as an ideal carbon-free energy source as its only combustion product is water. Photoelectrochemical generation of hydrogen is a promising alternative storage method for solar energy in the form of chemical energy [1]. Unfortunately the best catalysts for hydrogen generation and usage are based on the rare noble metal platinum, presenting a serious economic obstacle for the large-scale (megatonne) production of H<sub>2</sub> necessary to meet a portion of our energy demand. Fortunately, nature has provided efficient and robust noble metal free hydrogen producing enzymes, which serve as inspiration for many synthetic mimics.

Hydrogenase enzymes efficiently catalyze the reversible oxidation of molecular hydrogen, and gaseous carbon monoxide is a competitive enzyme inhibitor for hydrogen activation or generation of hydrogen at the enzyme active site [2-5]. There is no clear biological significance for CO inhibition, but the process is photochemically reversible [5]. The active site of iron-iron hydrogenase is a unique organometallic dinuclear Fe-Fe complex with carbon monoxide and cyanide ligands and is referred to as the H-cluster in the enzyme active site. Scheme 1 illustrates both the unique active site core (H-cluster) of the enzyme, where X is thought to be a nitrogen and important in proton activation, and model compounds (left) of the bimetallic enzymatic system. The H-cluster is tethered to a ferridoxin type cluster (F-cluster) which functions as an electron source or sink depending on the reaction direction. The details of the catalytic mechanism are not fully understood, but molecular hydrogen possibly binds to the iron on the H-cluster, in the active site pocket of the enzyme, replacing a labile water molecule [3]. It is also proposed that protons can bind to the metal centers through an oxidative addition and generate either a terminal or bridging hydride [6]. The organometallic core of the active site has inspired the synthesis of several inorganic structural mimics of the H-cluster (Scheme 1) both to mimic the activity of the enzyme and also to understand binding and activation of either molecular hydrogen or protons.

Download English Version:

<https://daneshyari.com/en/article/7764564>

Download Persian Version:

<https://daneshyari.com/article/7764564>

[Daneshyari.com](https://daneshyari.com)