



Short communication

Synthesis and characterisation of heterotrinnuclear transition metal complexes for biomimetic proton reduction

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ABSTRACT

Selected structural, spectroscopic, electrochemical and photochemical properties of novel heterotrinnuclear [FeFe]-hydrogenase enzyme model compounds carrying a catalytic iron sulfur cluster site directly coupled to different transition metal subunits are reported. Typical metal-to-ligand charge transfer (MLCT) chromophores based on electron donating copper(I), rhenium(I) and tungsten(0) complex fragments were selected to provide both long-wavelength spectral sensitization and photoredox activity. Photoinduced one-electron transfer from the MLCT donor subunit to the diiron acceptor site could be observed with an efficient steady-state accumulation of the corresponding charge-separated state. The reduced iron site of these deeply coloured heterotrinnuclear [FeFe]-hydrogenase model systems has been shown to be electrocatalytically active for proton reduction in the presence of trifluoroacetic acid (TFA). However, a successful visible-light powered system for catalytic hydrogen release in homogeneous solution could not be achieved, and the reaction remained stoichiometric with all of the systems investigated.

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The development of noble-metal free water-splitting devices for sustainable production of solar fuels is a vibrant research field at the crossroads of photochemistry, catalysis and materials science. Efficient accumulation of hydrogen-based reduction equivalents in both natural and artificial photosynthesis requires robust long-wavelength absorbing sensitizers for light-harvesting. In this context, one of the most difficult steps is to collect multiple electrons released from the excited-state species involved, and to store them as electron pairs by forming new energy-rich chemical bonds [1]. To better compete with unproductive processes such as back electron transfer to the starting compounds, this challenging task usually requires the involvement of additional catalysts. For the generation of gaseous hydrogen as a fuel, the combination of two electrons and two protons has to be achieved at a common active site. In the biosphere, the necessary proton coupled multielectron transfer steps are catalyzed by hydrogenase enzymes [2,3], which can accelerate both the heterolytic cleavage and the formation of H₂ molecules according to Eq. (1):



As part of our ongoing efforts to establish the novel field of light-driven enzyme models (artificial photoenzymes [4]), we have introduced several earth-abundant molecular systems for the construction

of hydrogen evolving catalysts potentially acting as multielectron transfer photosensitizers [4–6]. In the first generation of these examples, a simple modular strategy was chosen for coupling an iron-based hydrogenase mimic to different photoredox active donor subunits by offering a free diimine coordination site. The neutral parent compound [5], containing a biomimetic Fe₂(CO)₆ dithiolato subunit as the catalytically active site (cat) and a central 1,2-bis(arylimino)acenaphthene (BIAN) ligand system for chelating other metal complex donor fragments (M) is schematically shown in Fig. 1. The aryl substituents R of the 1,2-diimine complexes can be varied to fine-tune the electronic structure and to achieve additional features such as water solubility of these organometallic compounds [7–9]. Here, we report on some of our results obtained with the first heterotrinnuclear complexes of the thiolate functionalized dipp-BIAN ligand system, where R = 2,6-diisopropylphenyl and M = W⁰(CO)₄, Re^I(CO)₃Cl or Cu^I(CH₃CN)₂⁺. Further details on preparation and characterisation of these compounds can be found in the supporting information.

Synthesis, structure and spectroscopic data of the modified dipp-BIAN-ligand (L) containing a catalytic [FeFe]-hydrogenase model site and a free 1,2-diimine coordination subunit have already been described before [5]. This proton to hydrogen converting redox catalyst L acts as a chelating moiety for the modular construction of dyad architectures based on multinuclear transition metal complexes. As an example for such a system carrying a third metal center, the molecular structure and the optical properties of the heterotrinnuclear tungsten-diiron donor acceptor system L[W⁰(CO)₄] (1) are given in Fig. 2.

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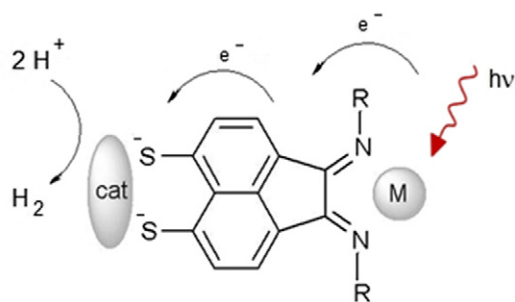


Fig. 1. Modular approach for constructing [FeFe]-hydrogenase enzyme models based on a bifunctional bridging ligand designed for coupling a hydride forming and proton reducing two-electron catalyst (left side) to various photoredox-active complexes (M) with highly reducing excited state properties suitable for powering vectorial electron flow (right side).

As expected, coupling donor fragments (**M**) such as closed shell transition metal moieties with a d^6 or d^{10} electron configuration to the free coordination site of the diiron catalyst (**L**) gives rise to long-wavelength spectral sensitization and improved light-harvesting by introducing additional absorption features in the visible spectral region. For example, the trinuclear compound **1** shown in Fig. 2 is dark green in solution, which is attributed to a broad metal-to-ligand charge transfer ($^1\text{MLCT}$) absorption band with a maximum at 640 nm characteristic for the $[\text{W}^0(\text{CO})_4(\text{BIAN})]$ chromophore. Notably, a weak feature assigned as a singlet-triplet absorption peak populating the $^3\text{MLCT}$ state occurs at 710 nm (Fig. 2). This spin-forbidden transition obviously becomes partially allowed by a significant degree of spin-orbit coupling in the presence of the heavy tungsten atom. It should be mentioned that as an alternative assignment, a MMCT band cannot be completely ruled out, although electrochemical data of the complex subunits [5,12] suggest that tungsten oxidation (+0.22 V) and diiron reduction (-1.58 V) in a direct optical charge transfer transition would require a slightly higher photon energy of 1.80 eV corresponding to 689 nm.

With other low-valent donor fragments such as $\text{Cu}^1(\text{CH}_3\text{CN})_2^+$ or $\text{Re}^1(\text{CO})_3\text{Cl}$, the corresponding $^1\text{MLCT}$ absorption bands are observed at 440 and 490 nm in acetonitrile solution, respectively (see Supporting Information). These charge transfer bands are further red-shifted in less polar solvents such as dichloromethane (negative solvatochromism), which has been reported before with other copper and rhenium BIAN-R derivatives [10,11]. All complexes **1–3** also show a more or less identical absorption band pattern between 350 and 450 nm, which is assigned to electronic excitations within the BIAN diiron complex moiety **L**, and in addition a narrow UV-peak occurs in the 300 nm region (Fig. 2), which has been attributed to a $\sigma\sigma^*$ transition involving the metal-metal bond of the catalytic [FeFe]-site [5]. These spectroscopic features are consistent with the presence of a largely

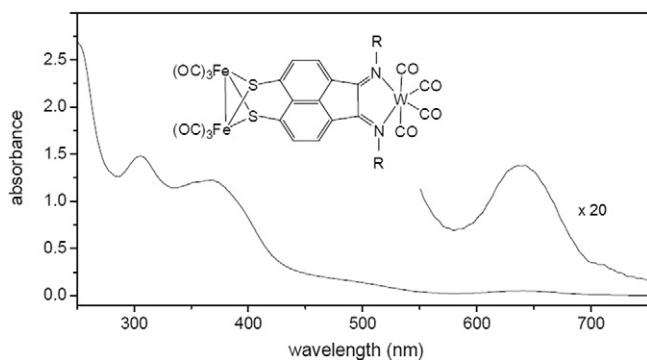


Fig. 2. Electronic absorption spectrum of a 5×10^{-5} M solution of complex **1** in acetonitrile (298 K, 1 cm cell). The thiolate functionalized BIAN-R ligand structure connecting a catalytic diiron site with the low-valent tungsten carbonyl donor fragment is also shown (R = 2,6-diisopropylphenyl = dipp).

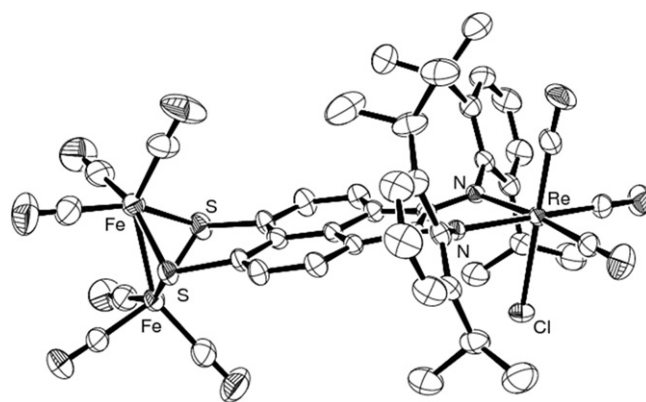


Fig. 3. Molecular structure of complex **2** (ORTEP; displacement ellipsoids at the 50% probability level; H-atoms are omitted for clarity).[†] Crystallographic data: The rhenium complex **2** was crystallized from a diethylether solution by slow evaporation of the solvent at 8 °C. Formula $\text{C}_{49}\text{H}_{48}\text{ClFe}_2\text{N}_2\text{O}_{10}\text{ReS}_2$, M_w 1222.36, monoclinic, $P2_1/c$, a 19.197(1), b 17.118(1), c 16.874(1) Å, β 109.824(2) °, V 5216.5(6) Å³, Z 4, T 300 K, ρ (calc) 1.556 g cm⁻³, R_1 (all data) 0.025, wR_2 (all data) 0.061. The full crystallographic information in CIF format has been deposited with the Cambridge Crystallographic Data Centre (CCDC 1517720).

unperturbed diiron subunit of ligand **L** even after a metallation at the opposite 1,2-diimine site.

A similar picture is obtained by comparing the detailed structural properties of the free BIAN-R diiron complex moiety **L** [5] with some of the new heterotrinnuclear systems derived thereof. In Fig. 3, the X-ray structure of the rhenium diiron complex **2** is displayed. Upon binding of the transition metal donor fragment $\text{Re}^1(\text{CO})_3\text{Cl}$, the arylated 1,2-diimine motif of the free ligand **L** merely switches from a *syn-anti*-[5] to an *anti-anti*-configuration, whereas the remaining core of the diiron complex stays largely unmodified. As usually observed in many other related examples, the $\text{Re}(\text{I})$ atom adopts a pseudo-octahedral configuration which is composed of a facial arrangement of the three carbonyl C atoms, an axial chlorido ligand, and two equatorial N atoms of a chelating 1,2-diimine ligand, provided in the present case through the BIAN-R entity of the [FeFe]-hydrogenase model compound **L**.

Encouraged by these results, we also tested out the notional ability of the thiolate bridged iron carbonyl site of the trinuclear system **2** to function as an electrocatalyst for proton reduction in solution, similar to what had been observed before for the free ligand system **L** [5]. Indeed, as reported in Fig. 4, the rhenium compound **2** shows a significant current

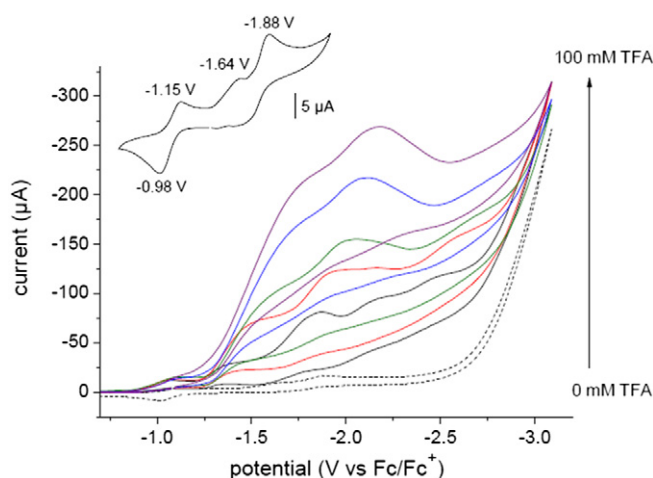


Fig. 4. Cyclic voltammograms of 0.85 mM complex **2** in N_2 -purged DCM solution with increments of added TFA: 0, 20, 40, 60, 80, 100 mM. Inset: Enlarged excerpt of the voltammogram of **2** in the absence of TFA (0.1 M NBu_4PF_6 , 50 mV s^{-1} scan rate, glassy carbon working electrode of surface area 0.0707 cm^2).

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