Inorganic Chemistry Communications 21 (2012) 147–150

Contents lists available at SciVerse ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Design, synthesis and characterization of a modular bridging ligand platform for bio-inspired hydrogen production

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ARTICLE INFO

Article history:
Received 6 March 2012
Accepted 20 April 2012
Available online 28 April 2012

Keywords:
Multielectron transfer
Non-innocent ligands
Redox relays
Hydrogenase models
Iron catalysis

ABSTRACT

Synthesis and characterization of a novel type of ambident bridging ligands joining together the functional prerequisites for visible-light absorption, photoinduced electron transfer and catalytic proton reduction is presented. This class of compounds consists of a chromophoric 1,2-diimine-based π-acceptor site and a rigid polyaromatic dithiolate chelator. Due to the presence of a common conjugated linker moiety with an intrinsic two-electron redox reactivity and a suitable orbital coupling of the subunits, a favourable situation for vectorial multielectron transfer from attached electron donors to a catalytic acceptor site is provided. As an example for the application of this kind of bifunctional ligand systems, a [FeFe]-hydrogenase enzyme model compound is prepared and structurally characterized. Electrocatalytic hydrogen formation with this complex is demonstrated.

Due to its unexcelled energy density, hydrogen is an attractive fuel medium for the chemical storage of renewable energy. The search for more advanced H_2-releasing electro- and photocatalytic systems based on earth-abundant materials therefore represents a basic research area of paramount importance [1–4]. In living organisms, [FeFe]-hydrogenase enzymes belong to the most efficient class of catalysts for the reversible splitting of hydrogen into protons and electrons. Within the last few years, there has been a remarkable progress in understanding the structure and function relationships of hydrogenase active sites and synthetic analogues based on a functional Fe_2S_2-core [5–7]. Both native enzymes and bio-inspired iron thiolate complexes have been combined directly or indirectly with various photosensitizers in order to achieve visible-light driven proton reduction and H_2-release with such types of catalysts [8–13].

Since hydrogen formation in protic media is a net two-electron process, a fundamental requirement for all such systems is the efficient coupling of reducing-equivalents to the active site, thus avoiding problems with destructive side reactions and back-electron transfer. For this purpose, the native hydrogenases are wired to additional iron-sulfur clusters acting as covalently linked redox relays [14]. Thus, it is quite surprising that this important functional feature has only recently been addressed in the design of synthetic hydrogenase model compounds [15]. Following rational guidelines for the development of artificial model enzymes [4,16], we are presenting here a novel type of bio-inspired H_2-releasing catalyst system consisting of a functional core unit (Scheme 1) that electronically couples a reversible redox cofactor for multielectron transfer chemistry with a rigid polyaromatic dithiolate site for the attachment of robust iron-hydrogenase enzyme mimetics [17–20]. The central acenaphthene-based core **1** of the novel class of bridging ligands presented here is obtained in three steps following published procedures (Scheme 2) [21,22]. We have chosen this kind of linker subunit as a starting point for the design of functionalized derivatives of bis(arylimino)acenaphthene systems (BIAN-R) such as **2**, which can be readily modified in their electronic and solubility properties by a variation of the aromatic substituents R (Scheme 1) [23,24]. BIAN-R ligands are a non-innocent organic cofactors that can be exploited as redox relays for the acceleration of biomimetic two-electron transfer chemistry [4]. The corresponding orange- to red-colored compounds (Fig. 1) are acting as strong π-acceptor chelates forming stable coordination compounds with a variety of transition metals and main group elements.

Especially, complex formation with non-precious-metal donor fragments such as MLCT-chromophores based on copper or other earth-abundant and environmentally benign elements is an attractive option that can readily broaden the long-wavelength spectral sensitization range of such systems for an optimized performance in the context of solar energy utilization [4,25].

In addition to the functional 1,2-diimine subunit, the periphery of the novel bridging ligand platform has been equipped with an electronically coupled dithiolate binding site. This further modification was carried out to enable efficient charge injection from a chemically, electro- or photochemically reduced BIAN-R moiety in a dyad architecture with attached electron acceptor systems such as semiconductor surfaces, nanoparticles or molecular redox catalysts.

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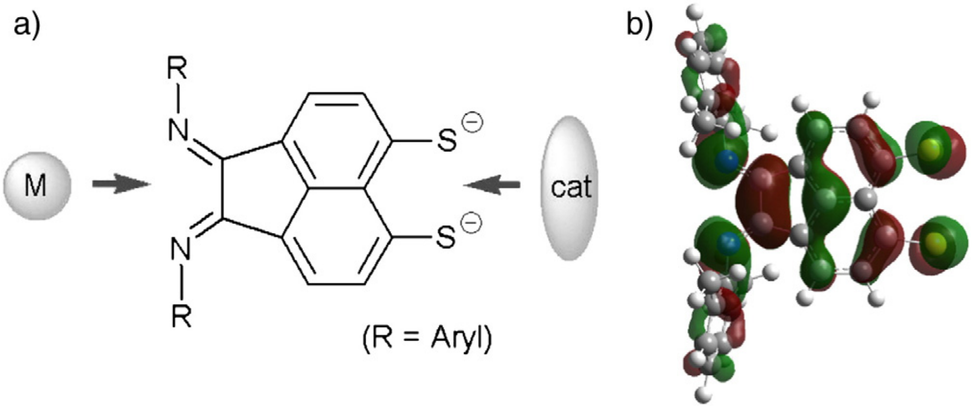
doi:10.1016/j.inoche.2012.04.034



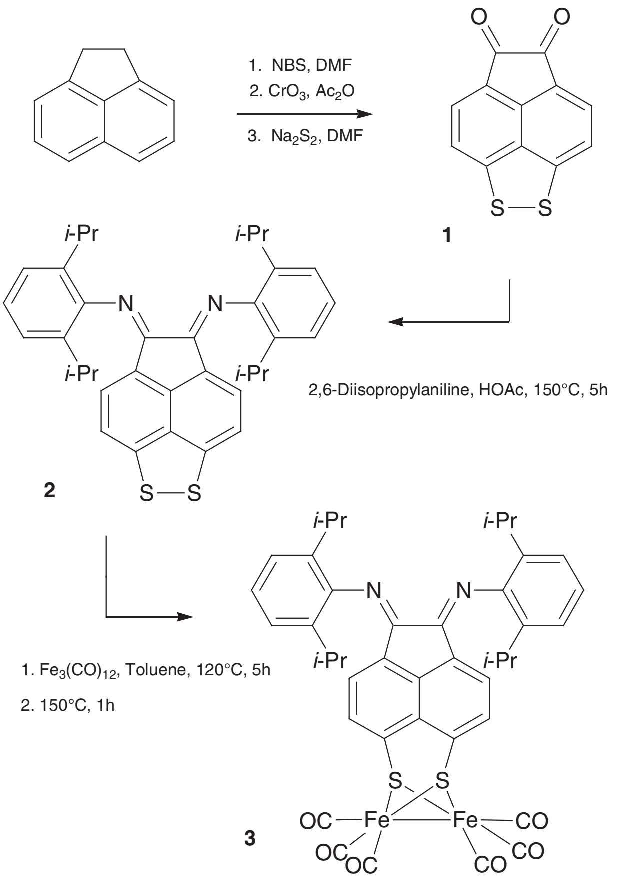
Scheme 1. a) Structural features of 1,2-diimine-fused naphthalene dithiolate ligands including possible sites for functionalization (R), coordination of metal-based donor fragments (M), and binding of catalytic subunits (cat) such as iron-hydrogenase model compounds to accept injected charges. b) π*-acceptor orbital (LUMO) of the bridging ligand demonstrating the degree of electronic communication between the two binding sites.

We decided to demonstrate this potential by coupling the precursor system **2** to a dinuclear iron carbonyl fragment in order to obtain a functional model compound for an iron-hydrogenase active site. For this purpose, a toluene solution of **2** was metallated with $Fe_3(CO)_{12}$ and the crude product was purified by recrystallization to yield the diiron cluster compound **3** (Scheme 2) as a deep red crystalline material.

The intraligand ππ*-absorption bands of the substituted BIAN-R derivative **2** in the UV and visible range are slightly blue-shifted upon metallation (Fig. 1), while an additional spectral feature occurs at 306 nm, which is attributed to the σσ*-absorption involving the metal-metal bond present in the diiron species **3**. The infrared spectrum of the iron-complex displays a set of three carbonyl bands in the 1980–2080 cm^{-1} region (Fig. 2), which is consistent with the properties of similar [FeFe]-hydrogenase model systems carrying electron donating substituents [17]. The energetic range of the CO-stretching vibrations, which are slightly shifted to lower frequencies compared to compounds with an isolated carbonyl core [9,17], indicates a significant degree of electronic communication between the diiron moiety and the appended 1,2-diimine fragment, thus confirming an orbital coupling of the linked subunits (Scheme 1).

The molecular structure of complex **3** is dominated by a regular Fe_2S_2-butterfly core with an Fe-Fe distance of 2.509(1) Å attached to the planar acenaphthene moiety of the BIAN-R ligand (Fig. 3). Further details on selected bond lengths and angles of compounds **1** and **3** are reported in the Supporting Information of this work.

Electrochemical properties of the iron carbonyl complex **3** were studied by cyclic voltammetry at 298 K in DCM solution. On the cathodic scan, the voltammogram of **3** (200 μM, 0.1 M Bu_4NPF_6, 50 mVs^{-1} scan rate) displays a quasi-reversible primary reduction wave with a peak potential of −1.58 V versus Fc^+/Fc, which is in a typical range for the reduction of a dithiolate bridged $Fe_2(CO)_6$



Scheme 2. Synthesis of compounds 1–3 from acenaphthene.

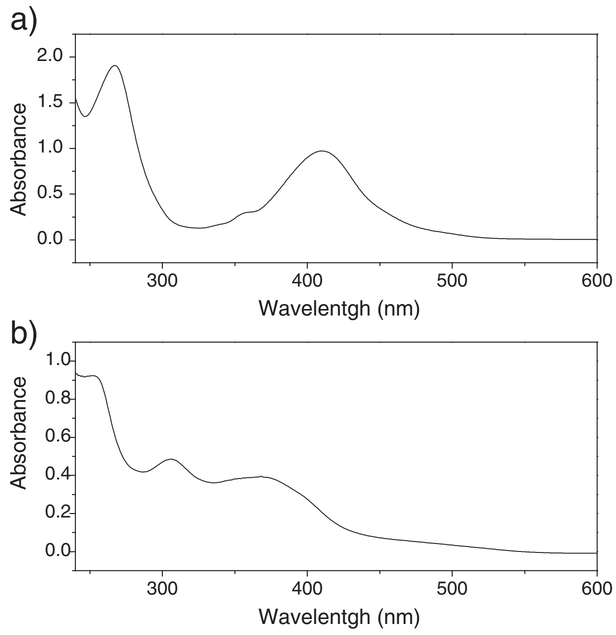


Fig. 1. Electronic absorption spectra of a) 7.0×10^{-5} M compound **2** and b) 2.0×10^{-5} M complex **3** in DCM-solution (298 K, 1-cm cell).

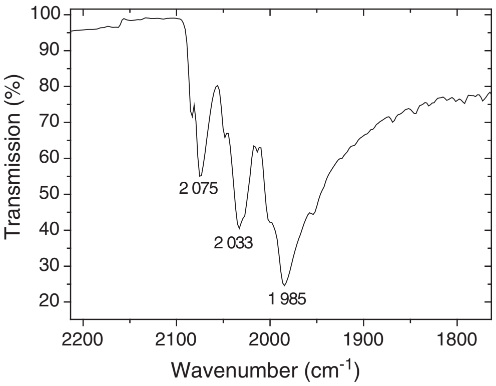


Fig. 2. ATR-FTIR spectrum of the iron carbonyl complex **3** in the solid state at 298 K.

moiety not carrying strongly electron withdrawing groups [7,26]. A second irreversible reduction process occurs at −1.90 V, which is tentatively assigned to the aromatic 1,2-diimine core of the complex. The corresponding free BIAN-R ligand shows a chemically reversible reduction wave with a cathodic peak potential at −2.14 V versus Fc^+/Fc [27]. In biomimetic hydrogenase model systems favouring the net transfer of two electrons to the bimetallic iron site via sequential one-electron steps, the first reduction process leads to a d^7–d^8 precursor compound, which similar to other metal-based mixed valent systems [3,28] represents a key-intermediate for the catalytic release of hydrogen [26]. Therefore, we also investigated the electrochemical response of DCM solutions of the iron carbonyl complex **3** in the presence of acetic acid [29,30] as shown in Fig. 4.

While without compound **3** no reduction wave occurs in the monitored potential window, the over-voltage for proton reduction from AcOH is significantly lowered in the presence of the reduced diiron complex. The observed dependence of the current on the acid concentration together with the large anodic potential shift of several hundreds of mV clearly demonstrates that **3** can serve as a catalyst for H_2-generation in DCM solution.

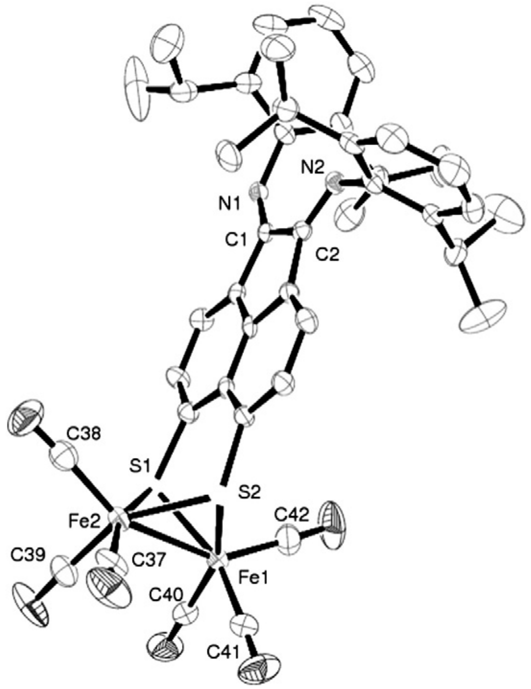


Fig. 3. Molecular structure of the 1,2-diimine-functionalized [FeFe]-hydrogenase model compound **3** (ORTEP; displacement ellipsoids at the 50% probability level; H-atoms are omitted for clarity).

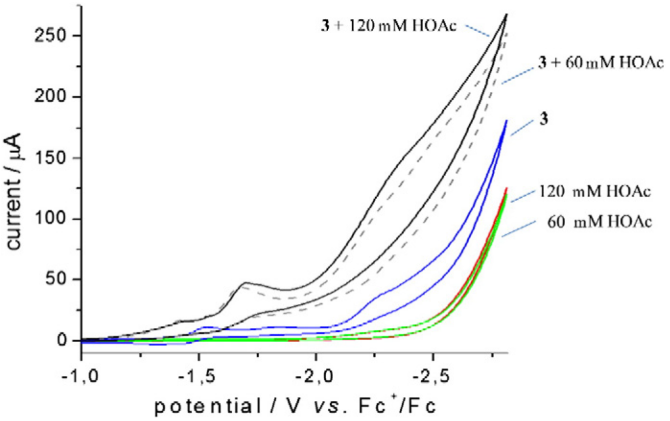


Fig. 4. Cyclic voltammograms of acetic acid (0, 60 and 120 mM) dissolved in N_2-purged DCM in the absence and presence of 200 μM diiron complex **3** indicating electrocatalytic behaviour for hydrogen production (0.1 M Bu_4NPF_6, 50 mVs^{-1} scan rate).

Thus, the additional beneficial features such as an extended chromophoric π-electron system and the further metal complex docking site attached to our novel catalyst system does not seem to interfere negatively with its efficient function as an artificial hydrogenase model compound.

In summary, we have introduced a novel versatile type of bridging ligand that provides a favourable orbital communication between covalently linked 1,2-diimine and rigid dithiolate chelator subunits. The compound is deeply coloured and integrates a readily tunable molecular architecture with an intrinsic two-electron redox reactivity. These advantageous properties can be exploited to combine the complementary functions of visible-light absorption and multielectron transfer catalysis in a synergistic manner. As a first example of the latter reactivity, the promising electrocatalytic properties of a novel biomimetic [FeFe]-hydrogenase model compound based on this bifunctional ligand system have been investigated. Further studies are currently underway to modify the features of such compounds by a systematic variation of substituents R and by binding additional metal complex fragments to the 1,2-diimine coordination site of the BIAN-R subunit of the compounds (Scheme 1) to demonstrate the broad potential of these systems as novel multielectron transfer photosensitizers for artificial photosynthesis and bio-inspired photoredox catalysis [4].

Acknowledgement

Financial support of this work by the Austrian Science Fund FWF project P21045: “Bio-inspired Multielectron Transfer Photosensitizers” is gratefully acknowledged.

Appendix A. Supplementary material

Supplementary data to this article can be found online at doi:10.1016/j.inoche.2012.04.034.

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