Coordination Chemistry Reviews 374 (2018) 15–35

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

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

Review

Photochemistry of iron complexes

Juan Chen, Wesley R. Browne *

Molecular Inorganic Chemistry, Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747AG Groningen, The Netherlands

ARTICLE INFO

Article history:
Received 10 May 2018
Accepted 12 June 2018

Keywords:
Iron
Photochemistry
Photoreduction
Photooxidation
Photocatalysis

ABSTRACT

Although iron is among the most abundant of the bio-essential transition metals and its coordination chemistry is of central importance to bio-inorganic and bioinspired chemistry, its photochemistry has been overshadowed by ruthenium polypyridyl complexes since the 1970s. The photochemistry of iron complexes is nevertheless rich and presents a multitude of opportunities in a wide range of fields. Here, we review the state of the art and especially recent progress in the photochemistry of iron complexes, focusing on aspects of relevance to environmental, biological and photocatalytic chemistry.

Contents

1. Introduction

Photochemistry is a small but essential branch of chemistry, recognized for example, as the basis for the "molecular machines" honored by the 2016 Nobel prize for chemistry [1,2], and is central to most life on this planet. At its most basic level, photochemistry is the conversion of electromagnetic radiation to chemical energy [3] and enables induction of chemical transformations with spatial and temporal control [1]. The chemical transformations and changes in reactivity form the basis of "photodynamic therapy" treatments in medicine [4] and in photo(redox)catalysis [5], and

---

* Corresponding author.
E-mail address: w.r.browne@rug.nl (W.R. Browne).

https://doi.org/10.1016/j.ccr.2018.06.008
0010-8545/

hence exploring new photochemical processes in both organic and inorganic molecular systems opens opportunities in medicine, materials and chemical reactivity.

The range of organic and inorganic compounds of interest to photochemistry is limited due primarily to the requirement that an accessible electronically excited state is either dissociative or is sufficiently long-lived to engage in energy or electron transfer, or to react with other compounds [6]. From an inorganic perspective, this demand has mostly limited attention to transition metal complexes such as those of chromium, ruthenium, and iridium [7,8]. In the case of iron complexes, the lowest excited states are metal centered (e.g., $e_g \leftarrow t_{2g}$) and are displaced with respect to the ground state facilitating rapid radiationless deactivation, and hence quenching photochemical reactivity. Nevertheless there are iron complexes that show significant photochemistry, but the design of new photoreactive complexes presents the challenge of identifying and understanding the approaches available to achieving photoreactivity. In this review, we will discuss the known photochemistry of iron complexes and categorize the various reaction classes to build a picture of the state of the art.

The reported iron complexes are mostly coordinated with organic ligands in an octahedral or, less often, tetrahedral coordination environment and the photochemistry reported to date correlates with formal oxidation state, spin state, as well as the ligand structure. Hence, we will begin our discussion by introducing electronic structures and the electronic configurations of iron complexes in their various oxidation states.

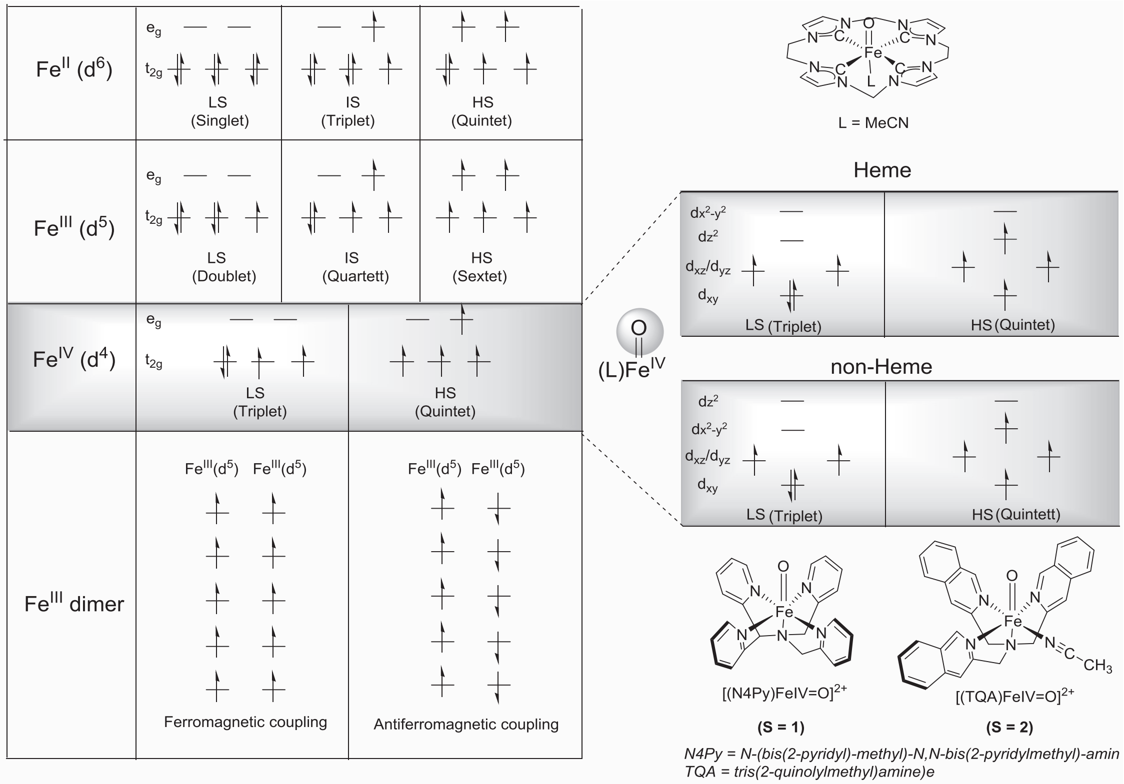
The earliest, and perhaps the best-documented, photochemical reactions are the photo-assisted Fenton and photo-induced decarboxylation reactions, both of which are of relevance to environmental and materials science (see Section 3.1 and Section 3.2). The photochemically induced release of small molecules, a field of growing importance, is dominated by:

- The release of N_2, for example, from porphyrin-ligated Fe^{III} azide complexes used to generate high valent iron complexes.
- H_2 evolution, for example, through reductive elimination from Fe-hydride complexes, which holds potential in energy storage.
- CO-release, mainly from Fe-CO complexes, which is of importance in CO-related cytoprotection, anti-inflammation, and vasodilatory therapeutic treatments.

Iron is a bio-essential element and its complexes are well recognized as candidates in photometallodrugs in cancer treatment, specifically DNA cleavage and photocytotoxicity as shown by the series of iron complexes discussed in Section 3.4. Last but not least, photocatalytic reactions using iron complexes are seeing increasing attention, with both heme and non-heme iron complexes as photo-catalysts in the oxidation of organic substrates. This area is discussed in the final section of this review.

2. Electronic structures and photophysics in iron complexes

The known oxidation states of iron range from Fe^0 to Fe^{VI}, all of which have been observed experimentally. Its cations have dominated the field of transition metal oxidation chemistry, due to its great importance in both bioinorganic and synthetic chemistry. The chemistry of iron is enriched by the number of accessible spin states; including high-, intermediate-, and low-spin iron complexes. In bioinorganic and biomimetic chemistry, the majority of iron complexes are in an octahedral or pseudo-octahedral environment. Scheme 1 illustrates the energetic ordering of the d orbitals and the electronic configurations of the oxidation states from Fe^{II} to Fe^{IV} in octahedral environments. Fe^0, Fe^V, and Fe^{VI} are not included due to the lack of reports on photoactivity of their complexes. Low-spin Fe^{II} complexes are the only diamagnetic members of this series of possible oxidation and spin states with the rest



Scheme 1. (left) Oxidation and spin states of iron complexes in an octahedral geometry and (right) the ground state occupation of d-orbitals of oxo-iron(IV) complexes in pseudo-octahedral geometry for non-heme and heme complexes (structures shown are the representative for each class).