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Review

Photoinduced water oxidation using dendrimeric Ru(II) complexes as photosensitizers

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ABSTRACT

Following bio-inspired guidelines, solar-powered water oxidation can be exploited for hydrogen generation by direct photocatalytic water splitting. This reaction poses some formidable challenges at the interface of oxidation catalysis and photochemistry. Molecular innovation is expected to provide a decisive lead in the field of artificial photosynthesis. Key achievements include the discovery of novel transition metal catalysts, exhibiting oxygen-evolving activity upon multi-electron oxidation and the design of antenna-like sensitizers. The thermodynamic and photophysical requirements of the system are discussed herein. A successful combination is obtained with polynuclear dendrimeric Ru(II) polypyridine sensitizers, activating colloidal IrO_2 nanoparticles or a tetra-ruthenate polyoxometalate catalyst. In this latter case, an unprecedented quantum yield up to 30% is achieved, which holds great promise for the up-grade to functional materials and practical technology.

1. Introduction

Artificial photosynthesis is a Holy Grail of modern science [1–7]. Actually, the effective production of high-energy content chemical species, i.e. fuels, by exclusively using solar irradiation would revolutionize modern society, giving access to a virtually inexhaustible energy source, equally distributed on Earth. Search on artificial photosynthesis has therefore been extremely appealing in the last decades, and has become more and more urgent as the global energy demand is deemed to increase substantially in the very next future.

To develop synthetic systems capable of performing artificial photosynthesis, Nature is obviously the ideal model; analogous to the natural photosynthetic systems, a synthetic system capable of performing artificial photosynthesis should contain the following basic components: (i) light-harvesting antennae; (ii) charge separation units; (iii) multielectron transfer catalysts (see Fig. 1) [8,9]. Whereas the design of light-harvesting antenna systems as well as of charge separation units have been extensively pursued in the last decades, with quite remarkable results [5–13], the bottleneck of research in artificial photosynthesis has been the design of

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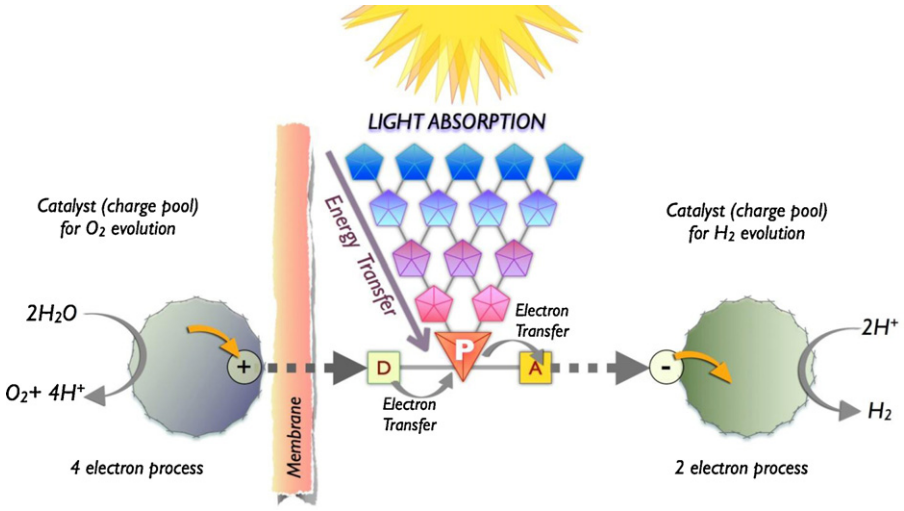

Fig. 1. Schematic representation of an artificial photosynthetic system.

synthetic catalysts capable of driving light-induced multielectron transfer processes, efficiently. In particular, as any scheme of artificial photosynthesis must include water oxidation, photo-driven production of molecular oxygen from water is the fundamental step that has to be pursued towards the achievement of an efficient artificial photosynthesis [14–17].

Water oxidation to molecular oxygen is indeed a quite complex reaction: it requires a four electron exchange, and orchestrating bond breaking-forming events as a new O–O bond should be the final outcome. Eq. (1) indicates that such a reaction requires a potential E (vs NHE) of 1.23 eV (at pH 0), whereas the global process highlighted in Eq. (2) is endoergonic by 4.92 eV (113.38 kcal).

$$2H_2O \rightarrow O_2 + 4e^- + 4H^+ \quad (E = +1.23 - 0.059 \times \mathrm{pH})\,\mathrm{V} \qquad (1)$$

$$2H_2O \rightarrow O_2 + 2H_2 \quad (\Delta G = +4.92\,\mathrm{eV}) \qquad (2)$$

In green plants and some bacteria, the quite complex reaction shown in Eq. (1) is performed by part of Photosystem II, known as the oxygen evolving complex (OEC), whose structure was finally clarified a few years ago [18]: this OEC is made of a cluster of four manganese and one calcium ion, held together by oxygen bridges. The five redox states which are sequentially involved in the overall four-electron process needed to perform water oxidation (the so-called Kok cycle [19]) are related to proton-coupled electron transfer steps [14,15,20]. The OEC is one of the more oxidizing natural systems. Even Nature finds water oxidation a quite difficult task: under ambient sunlight in the chloroplast, the OEC must be re-synthesized every half an hour owing to the oxidation damage it undergoes from the oxygen that itself has produced [17].

A synthetic, non-protein catalyst capable of oxidizing water as effectively as the OEC was prepared about 30 years ago [21]. This was the so-called "blue dimer", whose structural formula is shown in Fig. 2 (the "blue dimer" is compound b; in this figure other molecular catalysts, successively made, are shown). Once activated electrochemically or chemically, via a strong oxidizing agent (e.g., cerium salts), the blue dimer undergoes the stepwise loss of four electrons and four protons, producing an intermediate species that oxidizes water [21,22]. Unfortunately, the blue dimer loses its catalytic efficiency after a few cycles. However, the blue dimer paved the way to the discovery of other water oxidation catalysts, most of them still based on ruthenium centers [23–26]. In the last few years, also molecular catalysts based on iridium centers [27], as well as on cheaper metals such as manganese [28,29], cobalt [30], and iron [31] have been prepared. Interestingly, whereas most of the molecular catalysts reported are, inspired by the natural OEC, multimetallic species, some recent reports have suggested that also monometallic systems can behave as effective catalysts [27,31–33]. Among such monometallic species, even osmium compounds have been introduced [34].

Beside the molecular catalysts mentioned above, colloidal systems have also been employed as catalysts for water oxidation:

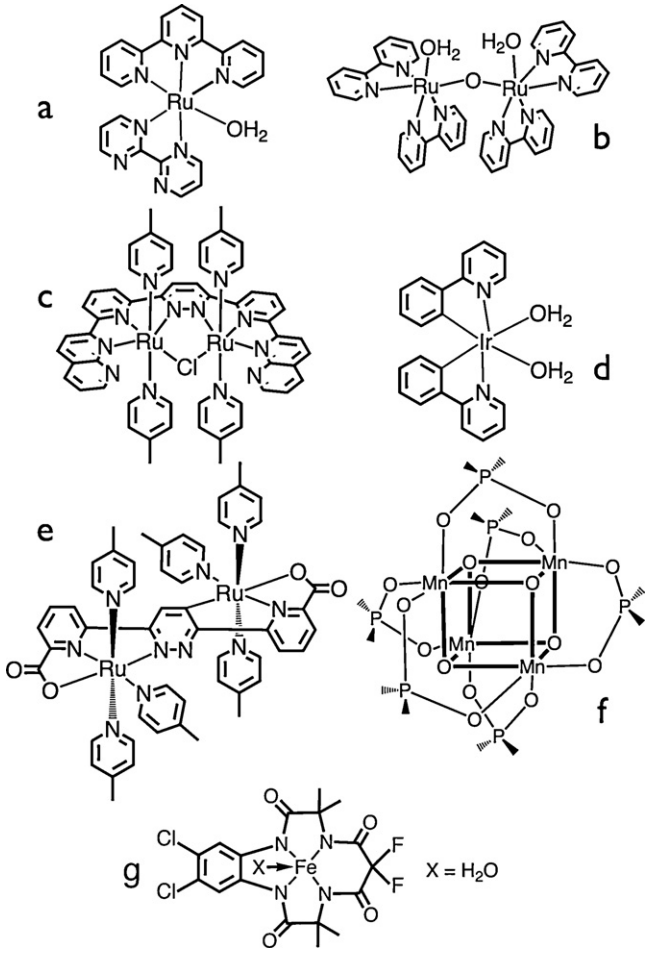

Fig. 2. Some examples of molecular catalysts for water oxidation. The "blue dimer" is compound b. Charges of the ionic species are omitted. For details, see Refs. [32] (for compound a); [21] (b); [33] (c); [27] (d); [24b] (e); [29] (f); [31] (g).