C. R. Chimie 20 (2017) 209–220

Contents lists available at ScienceDirect

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Artificial, molecular-based light-harvesting antenna systems made of metal dendrimers and multibodipy species

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ARTICLE INFO

Article history:
Received 7 October 2015
Accepted 15 February 2016
Available online 11 April 2016

keywords:
Light-harvesting antenna
Energy transfer
Ru(II) polypyridine complexes
Bodipy dyes
Dendrimers
Os(II) polypyridine complexes

ABSTRACT

Artificial photosynthesis is expected to include the development of light-harvesting antenna systems, similarly to what Natural Photosynthesis does. Here some basic requirements for designing synthetic light-harvesting antennae are presented, together with the results obtained by our team in the last few decades on light-harvesting antennae based on metal dendrimers or made of multibodipy species.

1. Introduction

From the beginning of the industrial age, mankind uses the combustion of fossil fuels as the main source of energy, powering developments in agriculture, industry, transportation, communication, and medicine [1]. However, the supplies of fossil fuels are not limitless [1]. In fact, the average worldwide energy consumption is 16.2 TW [2,3], and this value is doomed to rise. Besides the foreseen shortage of fossil fuels expected in the near future, a probably even worse problem is represented by the huge amount of CO_2 released in the atmosphere by the combustion of fossil fuels: this CO_2 release is responsible for global important issues, like Earth's warming and climate change [4]. Moreover, it cannot be disregarded that fossil fuels are mainly concentrated in limited regions of Earth, that are also politically unstable (and these facts are sometimes connected), and climatic change is probably also one of the reasons for the massive emigration from the South of the world. Considering these global problems, one of the major challenges for science is to find a renewable source of energy which is environmentally clean, inexpensive, distributed, and abundant [5,6]. Most of the energy sources that can satisfy these requirements are connected, directly or indirectly, with solar energy; among these, direct sunlight is the most attractive. Compared with the other sources, sunlight energy is available everywhere and completely sustainable. Actually, we are lucky that *Spaceship Earth* [6], which is otherwise a closed system, receives an inexhaustible power flow from the Sun: 120,000 TW of electromagnetic radiation of various wavelengths. So, the quantity of energy that continuously arrives from the Sun largely exceeds human needs [6–8]. However, light energy is intermittent and too diffuse to be profitably and immediately used by our civilization at its

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http://dx.doi.org/10.1016/j.crci.2016.02.011

maximum potential, so it must be converted to some other type of energy for storage, and the most convenient way is to store it within chemical bonds. Indeed, this is what Nature did from the very beginning and allowed the birth of Life on Earth.

By mimicking natural photosynthesis, it is possible, in principle, to use sunlight to synthesize high-energy content chemicals (fuels) from low-energy content materials. A possible example is the preparation of molecular hydrogen and oxygen by a water splitting process [9]. Indeed, molecular hydrogen is considered one of the possible candidates to replace fossil fuels in the near future; it has several advantages, for example a high specific enthalpy value [10–12]. Moreover, technologies to store and transport hydrogen are available. The combustion of hydrogen regenerates water, releasing energy. The result is a sustainable cycle that is environmentally benign and generates no by-products [9,12]. Obviously, alternative chemical fuels from sunlight other than hydrogen and oxygen, like ammonia, CO, etc, can also be the object of artificial photosynthesis. In particular, a quite attractive field is photoreduction of CO_2.

Whatever the final desired product is, an artificial, molecular-based photosynthetic system inspired by natural, molecular photosynthesis can be schematized as in Fig. 1 [13]. It basically includes (i) an antenna system, (ii) a reaction center, and (iii) multielectron transfer catalysts.

(i) *The light-harvesting antenna system*. The antenna system is an assembly of a large number of chromophores. It has the role of collecting light energy and funneling it to a specific subunit (the energy trap) by a series of energy transfer processes. In essence, it converts light energy into electronic energy.

(ii) *The reaction center*. The reaction center contains the energy trap and some electron donor and acceptor subunits coupled to the energy trap so that a sequence of photoinduced electron transfer processes can take place starting from the excited state of the energy trap, with the ultimate goal of producing a charge-separated state. Basically, the reaction center has the role of converting electronic energy into redox energy.

(iii) *The multielectron transfer catalysts*. A single electron (or hole) is suitable to produce current, that is electricity, but to perform chemical reactions from low-energy content raw materials like water and carbon dioxide leading to high-energy content species like molecular hydrogen or reduced forms of CO_2, multielectron processes are required. In fact, sequences of single electron steps cannot be used, since the intermediate states would have a too high energy potential. The consequence is that electrons (or holes) must be collected by some charge pool devices and used to drive the multielectron transfer processes. Such charge pools are catalysts for multielectron transfer reactions. Both catalysts for reduction and for oxidation processes are needed. Basically, the multielectron catalysts use redox energy to produce chemical energy.

Here we will concentrate on light-harvesting antenna systems. In particular, after a chapter in which some main requisites for designing an artificial light-harvesting antenna are summarized, we shall briefly review the work we have done in this field during a period of 25 years, starting from our research on the design and the photophysical studies of light-harvesting antenna dendrimers made of multinuclear Ru(II) and Os(II) polypyridine subunits to the energy transfer processes occurring in various multibodipy systems arranged on different scaffolds. The mechanisms of the energy migration processes occurring in the studied systems will also be discussed. All the reported experiments and data refer to acetonitrile fluid solutions at room temperature, unless otherwise stated.

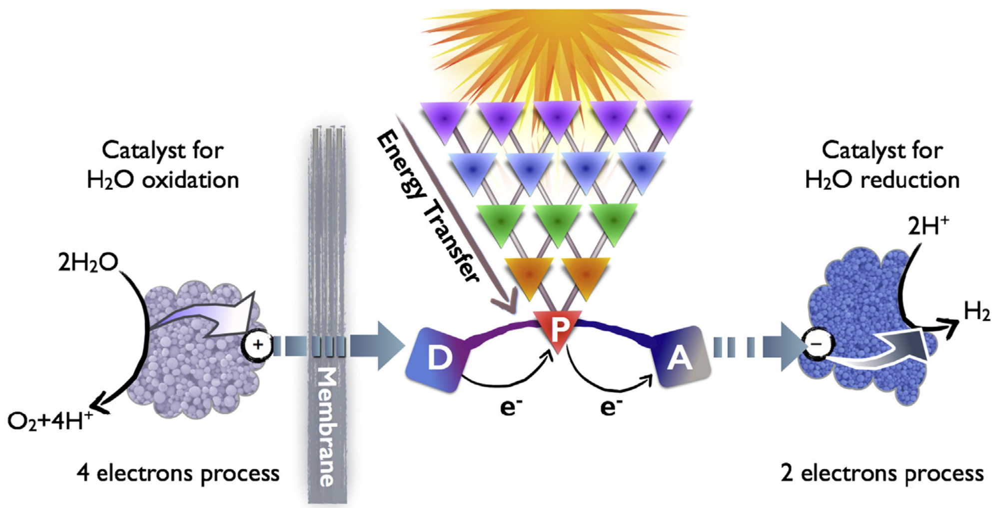

Fig. 1. Schematization of a possible artificial photosynthetic system. The colored triangles indicate the chromophores constituting the antenna systems; the D–P–A assembly corresponds to the reaction center; on the left and right extremes of the sketch, the multielectron transfer catalysts are represented.