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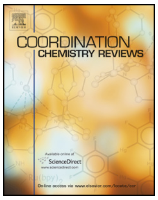

Review

Time-resolved X-ray absorption spectroscopy for the study of molecular systems relevant for artificial photosynthesis

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ABSTRACT

Transition metal coordination compounds have a rich photochemistry and are interesting candidates as both light harvesters (photosensitizers) and catalysts in photocatalytic systems. Knowledge of electronic and molecular structure of excited states of photosensitizers and intermediates of catalysts is a key topic for rational design of systems for artificial photosynthesis. We describe recent advances in the field of time-resolved X-ray absorption spectroscopy that provide information on local structure around metal centers, their orbital structure and oxidation state, and thereby insights into the mechanisms of their photochemical reactions. Photosensitizers with metal centers, multicomponent molecular catalytic systems, and supramolecular model sensitizer-catalysts with two metal centers are used as examples to demonstrate the possibilities of the technique. We overview different experimental methods that can be used to investigate intermediates with lifetimes in the range from hundreds of picoseconds to hundreds of microseconds. Theoretical methods to extract the structural and electronic information from X-ray absorption near edge structure spectroscopy (XANES) are also discussed.

1. Introduction

1.1. General principles

A technology to use the energy of sunlight to produce fuels is highly desirable for replacing fossil fuels with a renewable energy source without a carbon dioxide footprint [1]. The

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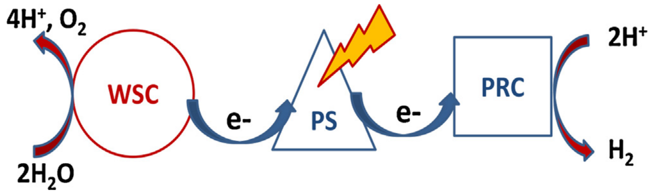

Fig. 1. Schematic picture of an artificial photosynthesis assembly consisting of a light collecting photosensitizer (PS), a proton reducing catalyst (PRC) and a water splitting catalyst (WSC).

promising approach for achieving this goal is to mimic photosynthesis and develop molecular catalysts for water splitting and hydrogen evolution. The field of research on molecular systems that convert light to the energy of chemical bonds [2,3] is known as artificial photosynthesis.

Investigation of light interaction with transition metal complexes is a classical branch of photochemistry. In this context a vast number of complexes based on different transition metals and organic ligands have been synthesized and characterized [4,5]. They have a multitude of excited electronic states of various character, metal to ligand charge transfer (MLCT), ligand to metal charge transfer (LMCT), metal centered (MC) and ligand centered (LC), and these states come with different multiplicities – singlets, triplets, quintets. The order of these states depends on metal and nature of ligands. It leads to a great variation of excited state relaxation patterns and properties of the molecules in the lowest excited states. Therefore, some molecules are strong light emitters whereas others have very weak light absorption or emission. The excited state lifetime of transition metal complexes varies from picoseconds to microseconds. Some metal–ligand combinations lead to photochemically very stable complexes, while other combinations result in high photochemical activity with for instance ligand dissociation or light induced electron transfer. By combining two (or more) transition metal complexes with different excited state properties, either bimolecularly or supramolecularly, a variety of excited state energy and electron transfer processes can be achieved. The synthetic simplicity of many complexes implies that a broad spectrum of constructs with widely differing electron and energy transfer characteristics can be built. This possibility is an important basis for the use of transition metal complexes as building blocks in photocatalytic molecular systems [6,7]. A detailed knowledge of excited state properties and reaction mechanisms is essential for the construction of complexes with desired and optimized functionality. With the increasing demand from the society for alternative energy solutions the development of transition metal complexes optimized for application in artificial photosynthesis has attracted special attention.

The net result of photosynthesis is splitting of water by extracting electrons that are used to reduce carbon dioxide to carbohydrates. Molecular oxygen is formed as a by-product. The most simple artificial photosynthesis process would be splitting of water into molecular oxygen and hydrogen consists of two half-reactions – the oxidative O_2 evolving reaction and reduction of protons generating H_2. As illustrated in Fig. 1 the two reactions generally require different catalysts and are often studied separately. The photosensitizer and the catalyst are two principal components of any photocatalytic reaction (Fig. 1). There are examples of single component systems [8], but they are rare and outside the scope of this review. The photosensitizer absorbs the light and converts this energy into a charge separated state. The photophysical processes leading to this state are usually fast. They occur on the time scale from tens of femtoseconds (fs) to hundreds of picoseconds (ps) and include intersystem crossing, rapid structural rearrangements, internal conversion and vibrational relaxation. The charge received by the catalyst from the photosensitizer is used to drive the desired reaction. In studies of the hydrogen generation half-reaction, the initial state of the photosensitizer is generally recovered by a sacrificial electron donor agent; correspondingly, for the water oxidation reaction a sacrificial electron acceptor would be used. In a complete photocatalytic system the two half-reactions are coupled and the electrons extracted from water are used to reduce the substrate forming the fuel, e.g. protons forming molecular hydrogen (H_2) (Fig. 1).

The reaction of H_2 evolution requires two electrons and two protons. A few intermediate states of the catalyst are usually involved in such a reaction. First, the catalyst receives an electron from the photosensitizer and interacts with the first proton forming a hydride intermediate. It is usually described as a two-step process, but in some cases a concerted proton-coupled electron transfer has been suggested [9]. The following reaction steps depend significantly on the catalysts and conditions and can include either interaction of two intermediates, reduction of the catalyst by the second electron coming from the photosensitizer or interaction of intermediate with the second proton. More detailed descriptions of proposed reaction mechanisms for different catalysts can be found in recent reviews [6,7,10–14].

Multicomponent and supramolecular strategies can be used to combine photosensitizer and catalyst into a functioning photocatalytic system [7,15–17]. The system is called multicomponent if it contains photosensitizer and catalyst that are not chemically bond with each other and dissolved in the same solution. Therefore the diffusion of the components in the solution controls the charge transfer. Such bimolecular process is slow, usually occurring in the time range from hundreds of nanoseconds to microseconds. Multicomponent systems sometimes contain an additional compound – an electron relay – that quenches the excited state of the photosensitizer and delivers the electrons to the catalyst [15,18]. For efficient reaction, the excited state lifetime of the photosensitizer has to be at least hundreds of nanoseconds.

The alternative is a supramolecular assembly of photosensitizer and catalyst [3,7,17,18]. In this case the two components are chemically bound to each other. We use an operational and rather general definition of a supramolecular system. A system containing a few functional units is supramolecular if the interaction energy between units is small compared to all other relevant energy parameters, regardless of the nature of the bonds that link the units [19]. This means that the photosensitizer-catalyst system is supramolecular if light absorption leads to an excited state localized on only one unit, or causes electron transfer between them. Supramolecular systems have to be distinguished from large molecules that have excited states substantially delocalized over the entire system. With a rationally designed chemical bridge between the photosensitizer and the catalyst in a supramolecular system [20], the speed of electron transfer can be dramatically increased in comparison with multicomponent systems, to values in the picosecond range [21,22], or even faster. This implies that the excited state lifetime of the photosensitizer for such a system can be significantly shorter than in a multicomponent system. The main challenge with a supramolecular assembly is the back electron transfer that can be also fast [23,24] and significantly decrease the photocatalytic performance of the molecular device. The supramolecular approach, however, does not exclude completely the effects of diffusion limited processes. As mentioned above, two electrons are required for production of molecular hydrogen. Therefore, the light absorbing unit has to be electron-replenished and in an entirely molecular approach this step is an intermolecular reaction. This means that the intermediate species have either to wait for a second photon and achieve a second light-driven electron transfer process, or react with another complex in the same state for the reaction to proceed. Both processes are slow.