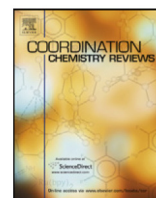




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Review

Design and photochemical study of supramolecular donor–acceptor systems assembled via metal–ligand axial coordination



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ABSTRACT

The natural photosynthetic light energy harvesting functional nano-architectures, organized exclusively by non-covalent interactions, have inspired the design of artificial supramolecular donor–acceptor systems held solely by self-assembly methods. Various non-covalent interactions have been employed to design such supramolecular conjugates. The present review highlights recent progress made toward the design and photochemical study of energy-harvesting systems assembled by metal–ligand axial coordination. Due to the remarkable photophysical and photochemical properties of porphyrins and phthalocyanines, and importantly, their ability to form metal–ligand coordination bonds, they have been widely used as sensitizers in the construction of donor–acceptor conjugates of this class. Both fullerene and non-fullerene molecules, functionalized with nitrogenous ligands that are capable of donating a pair of electrons to the central metal atom of tetrapyrrolic macrocycles, have commonly been used as electron acceptors. The significance of endohedral fullerenes and carbon nanotubes in mimicking natural photosynthesis by stabilizing the light induced charge-separated states in supramolecular multicomponent donor–acceptor assemblies held via metal–ligand axial coordination interaction is a burgeoning area of research. Particular attention has also been given to the generation of long-lived charge-separated states, in addition to the design principles and characterization of donor–acceptor systems assembled by metal–ligand axial coordination.

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1. Introduction

The major challenge for the 21st century is the search for carbon free clean energy that is abundant, renewable, and can replace the

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currently used fossil fuel derived energy [1–5]. The main reasons to detest fossil fuels are their limited sources and the production of air polluting carbon containing gases, which have displayed adverse effects both in the environment as well as in human health. The non-renewable property of fossil fuels is another main reason to find alternatives. Apparently, harvesting sun energy is the answer for fulfilling the increasing energy demand, which is directly proportional to the increasing world population. Annually, about 120,000 TW (1 TW = 10^{12} Watts) of solar energy, which is about 8,000 times the total global energy requirement, hits the Earth's surface. However, the disperse nature of sun light mandates efficient methods of light energy harvesting and techniques to fulfill the necessity of renewable and clean energy demand for the next generation. In this context, the natural photosynthetic process stands out as one of the most prominent and reliable methods to harvest light energy. For millions of years, green plants and some bacteria have been harvesting light energy and converting it into chemical energy to perform their physiological activities. This establishes a grand challenge to the scientific community, at this point, to design and deploy such biomimetic materials to harvest light energy efficiently. Out of various existing and deployable artificial photosynthetic schemes [6–16], this review focuses on the design and study of energy harvesting supramolecular donor–acceptor systems comprising metal–ligand axial coordination.

The first review on photoactive donor–acceptor systems based on metal–ligand axial coordination was published by us in 2005 covering mainly metal tetrapyrrole–fullerene systems [17]. Since then, a few reviews and monographs have appeared in the literature [10,18–33]. In addition, nanocarbons beyond fullerenes, viz., carbon nanotubes and endohedral fullerenes, have also been employed [11,34–36]. To keep things in perspective and current, this review highlights work done since 2009. Along with nanocarbons, key examples of other electron acceptors used in building such donor–acceptor are also discussed. As reviewed here, the supramolecular donor–acceptor systems assembled using axial coordination binding motif have resulted in novel systems exhibiting photoinduced energy and electron transfer events in a controlled fashion.

The following sections in the introduction provide the necessary background for the review topic.

1.1. The natural photosynthetic process

The natural photosynthetic process is a series of events where green plants utilize light energy, first, to oxidize water into molecular oxygen and to generate four electrons. In the second step, CO_2 is subsequently reduced into the energetic biomolecules, hydrocarbons and sugars, by utilizing electrons generated in the first step. The process of photosynthesis is multifaceted and is challenging to elucidate all of the individual steps [37–41]. Thanks to impressive advances in X-ray crystallography, it has been possible to solve the structure of membrane proteins involved in photosynthesis. The first crystal structure resolved was that of photosystem II (PSII) from the thermophilic cyanobacteria. This helped to understand the mechanistic details of light harvesting, charge separation, and catalysis events. The primary events occurring in PSII of aerobic cyanobacteria largely follows in other photosynthetic living organisms. The first step of the process involves gathering sufficient light energy through the light energy harvesting complexes [42]. One single light harvesting complex II (LHCII) consists of around 200 chlorophylls (Chls) and 50 carotenoids (Cars) as shown in Fig. 1. The chlorophylls exclusively collect photons from light and transfer them to the reaction center. The major role of carotenoids during this process is to protect the photosynthetic apparatus from photo-damage [43].

In P_{680} , PSII chlorophylls upon photoexcitation transfer an electron to an acceptor system, which is subsequently involved in reducing carbon dioxide. This is the site where the light harvesting,

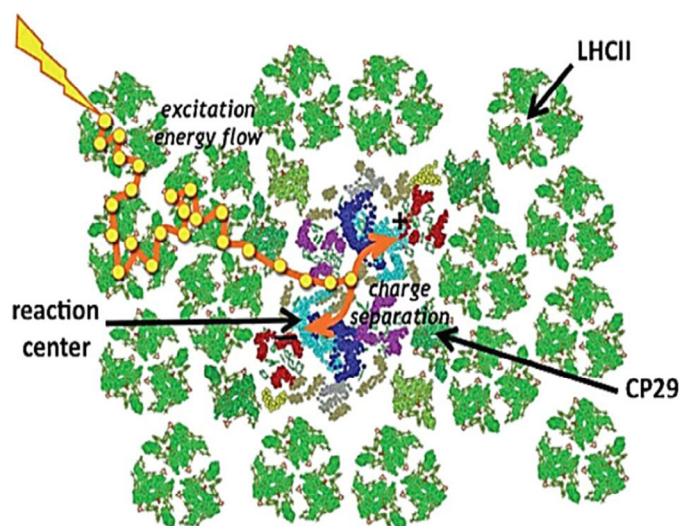


Fig. 1. Structure of light harvesting center II (LHCII) showing the excitation energy migration from antennae to reaction center (reproduced with permission from Ref. [42]).

charge separation, charge stabilization, and electron transfer take place. The excited state of the primary donor P_{680} rapidly transfers an electron to ChlD1, pheophytin (PheoD1), and eventually to the first acceptor, plastoquinone A (Q_A), and then to the final acceptor, plastoquinone B (Q_B), to stabilize the charge-separated states. After protonation, the acceptor, plastoquinone B (Q_B) forms plastoquinol, $\text{QH}_2(\text{B})$, and releases from PS(II) into the matrix, which mediates the electron transfer between PSI and PSII. The oxidized form of P_{680}^+ , which acts as a strong oxidant now gets an electron from a Mn_4Ca -cluster in the oxygen evolving complex (OEC). After the abstraction of four consecutive electrons from OEC, two molecules of water get oxidized to generate one molecule of O_2 and four protons. The structure of OEC has been determined by X-ray crystallography and consists of four manganese and one calcium atom that are held together by μ -oxo and hydroxy ligands in a cubane like arrangement. The mechanism behind the oxidation of water by OEC, which is triggered by absorbed light energy, has been extensively studied, and found that the OEC cycle undergoes five oxidation cycles denoted by $\text{S}_0, \text{S}_1, \dots, \text{S}_4$ in the Kok cycle. The S_0 state is the most reduced state, also known as the resting state of the OEC catalyst, whereas the S_4 state is the most oxidized state. Molecular oxygen gets liberated during the process of S_0 – S_4 conversion of OEC catalyst [43].

1.2. Artificial photosynthesis

The role of natural photosynthesis is to convert sunlight into other forms of energy and store it in the form of carbohydrates and lipids in green plants. The artificial photosynthetic process inspired from nature is a technique where sunlight is converted into other forms of energy, viz., electricity and fuels. In principle, a typical artificial photosynthetic system must be comprised of the following components: an antenna, which is basically a collection of chromophores that absorb sunlight efficiently throughout the solar spectrum and transfer that energy to another component called the reaction center. The reaction center is where the absorbed excitation energy drives efficient photoinduced electron transfer to an electron acceptor to generate charge-separated states. Thus, a reaction center can be considered a nanoscale photovoltaic device. Additionally, the reaction center could be coupled to a water oxidation catalyst and a proton reduction catalyst for water-to-hydrogen conversion, or schemes of similar nature [44–46].

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