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Molecular assemblies for solar energy conversion – Biomimetic approach

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Excitation energy migration followed by electron transfer forms the main components of natural photosynthesis. An understanding of these aspects is essential to reenact the primary processes in laboratory under conditions that are precisely repeatable. Here we describe the state of understanding of the natural process and several model systems designed to harvest solar energy and conversion to useful form of chemical energy. The molecular assemblies constituting the model systems offer a great advantage in terms of better comprehension of the mechanistic aspects and yield valuable information on the design of molecular photonic devices.

NATURAL photosynthesis represents efficient energy conversion process. Excitation energy and electron transfer reactions form important primary processes in

the natural photosynthesis. The transduction of light energy to chemical energy has been carried out by green plants and bacteria and in this process approximately 3.0×10^{21} J of free energy is stored annually. An effective way to understand the mechanism of these primary processes is to conceptualize a photosynthesis unit (PSU), a composite of an antenna protein and a reaction centre (RC) protein. The antenna system is a light-harvesting pigment protein complex (LHC) comprising an ensemble of chlorophyll molecules which harvests the light energy extending from near-UV to near-IR. The radiant energy is transferred to specialized chlorophyll molecules called RC where the actual charge separation (CS) occurs. This trapped energy in the RC initiates a series of electron transfer reactions mediated through cytochromes till the final reductant NADPH is formed leading to the synthesis of ATP. Plant and bacterial systems have a judicious combination of LHC and RC. This is essential since the cross-section for the absorption of light by chlorophyll (Chl) molecule is small and thus if each RC contains a few Chl molecules, the turnover will be small even

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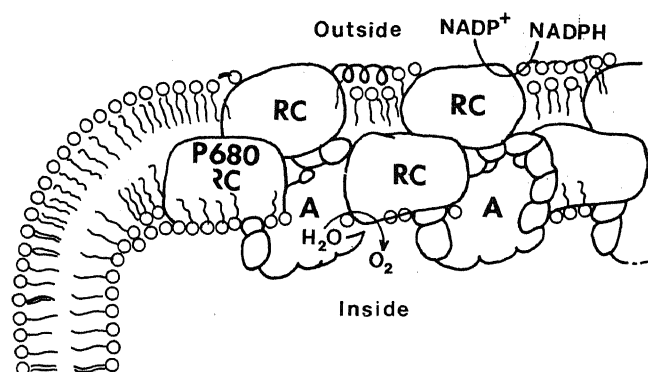


Figure 1. Schematic representation of reaction centre. 'A' represents reaction centre and antenna proteins consisting of chlorophyll *a/b* for PS I and PS II complexes.

under bright sunlight. The antenna system provides a viable support and permits the RC to function effectively under extreme conditions. The LHC and RC are intimately associated with a membrane (Figure 1). The necessity of the membrane can be visualized as follows. It provides support to the components and possible orientational features for efficient light harvesting and conversion. Secondly, the membrane affords the enzyme ATP synthetase which is driven by the membrane potential, i.e. the electrical potential and the chemical potential (H^+). The stored energy in the membrane exists in redox energy and ATP, synthesized by the membrane protein. The RCs are hydrophobic and consist of several pigment molecules associated with easily reducible quinones and iron-sulphur proteins. The organization of these components is very critical to avoid any wasteful charge recombination reactions.

Light harvesting systems

Two categories of LHS exist¹. Oxygen-evolving organisms contain Chl *a*, Chl *b* or bacteriochlorophyll, B.Chl *a* and B.Chl *b*. The auxiliary system consists of Chl *b*, phycobilins, carotenoids and Chl *c* pigments. In higher plants and algae, the LHC are intrinsic proteins embedded within the thylakoid membrane of the chloroplasts². Interestingly, in the photosynthetic bacteria the bulk of the light harvesting Chl is located outside the membrane in specialized organelles called chlorosomes. The antenna is usually heterogeneous and includes small ensemble of pigment units comprising of a few Chl and less number of auxiliary pigments such as carotenoid molecules. These are closely associated with RC protein spatially to accomplish efficient energy transduction and rapid electron transfer. In nature, there exists a variety of antenna systems consisting of repeating units, each unit with different composition and organization of pigments. However, functionally all the



Figure 2. Structure of green photosynthetic bacterium *Prostheochloris acustruuii*. The bacteriochlorophyll molecules are shown in ellipsoids. Numbers 1, 3, 4, 6 and 7 denote histidine on the axial ligand to Mg(II) while in 5 and 2, the Mg(II) is bound to peptide and water respectively.

systems behave in a similar fashion, that is transducing light energy within 100 ps with nearly 100% efficiency.

A general picture regarding the pigment organization in a few LHC, viz. the green photosynthetic bacterium³, cyanobacterium⁴, and Chl *a/b* protein complexes from chloroplasts⁵, is available in the literature. The detailed picture of the water-soluble bacteriochlorophyll light harvesting system of the green bacterium *Chlorobium* reveals many interesting features⁴ (Figure 2). The complex contains 21 B.Chl *a* molecules distributed evenly over three identical subunits. Each subunit consists of 7 B.Chl *a* molecules arranged in a specific orientation with an average distance of ~ 12 Å. The planes of B.Chl *a* molecules are more or less parallel and all the 21 B.Chl *a* molecules are involved in the energy transfer. Interestingly, the entire protein assembly have 3-fold axis of symmetry ensuring absorption of light energy in all the directions. It is recognized that the arrangement of B.Chl molecules allows alignment of the transition moment dipoles to maximize the efficiency of energy transfer, viz. inductive resonance. The different conformations of the pigments impose distinct photophysical properties thereby permitting efficient intrapigment excitation energy transfer in these systems.

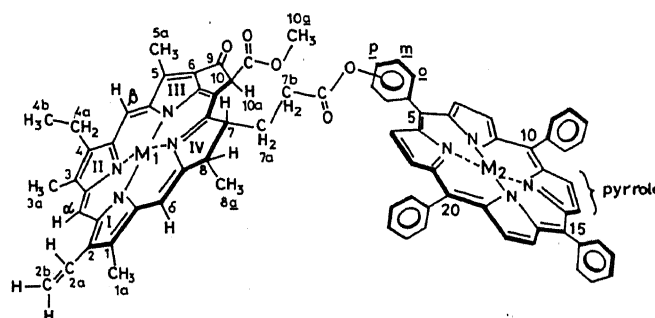
Model studies

Studies on the rate constants of energy transfer and steady-state spectroscopic data on the LHCs suggest

strong coupling between the pigment molecules. Despite this, Forster's weak coupling approach seems to explain the observed ultrafast rates adequately. One of the main problems has been the estimation of survival time of the exciton states. This, in principle, is governed by the relative strength of the exciton coupling and vibronic coupling. Association of large number of pigment/dye molecules results in both the red and blue shift of the absorption bands relative to the absorption of independent pigment molecules. Though there are no straightforward methods of predicting the lifetime of the exciton states in the red or blue-shifted aggregates, a short lifetime is found for the blue-shifted aggregates⁶. The short relaxation may arise from the fast internal conversion to the low-lying excited state followed by efficient nonradiative deactivation of this state⁷. There are systems where subpicosecond kinetics have shown excitonic spectral shifts similar to that observed for bacterial antenna systems. Model studies are essential to understand some of these processes. Biomimetic approach seems to be the most appropriate course of study. Owing to the close structural similarity between porphyrin and chlorophyll, porphyrin systems have been chosen by many workers to construct models to illustrate energy transfer mechanisms. Two methodologies have been adopted to organize the porphyrin molecules favourable for maximum excitation energy transfer. Self-assemblage of porphyrin molecules is often accomplished by proper choice of solvent (often non-polar solvents to promote aggregation of porphyrins). Alternately, porphyrins endowed with functional groups in the peripheral positions associate extensively in solution owing to coordinative interactions⁸. The self-assembling system results in the red-shifted absorption bands similar to that observed in LHCs. Photophysical studies in these system are limited to ascertain the existence of excitation energy transfer. Nevertheless, these systems afford an important model for the excitation energy transfer studies.

A class of bisporphyrins bearing ethylene oxide groups $(\text{CH}_2\text{O})_n$ of varying lengths ($n = 0$ to 3) have been reported by Jeyakumar and Krishnan⁹. It is demonstrated that the efficiency of energy transfer is maximum when the two porphyrin units are separated by diethylene glycol bridge. Singlet and triplet energy transfers have been illustrated in the hybrid porphyrin dimers bearing Zn(II) in one of the units^{10,11}. Most of these studies are confined to covalently linked bisporphyrin systems. They have the inherent disadvantage of existing in several conformers thereby inducing uncertainty in the magnitude of distal separation and fixed orientational feature. In addition, the bisporphyrins exhibit absorption bands which are often akin to the absorption spectrum of the individual components. These systems are very elegant but far removed from the LHCs of the photosynthetic systems.

Heterodimers consisting of two different chromophores are of recent interest in the model studies. These have the advantage of being spectrally-distinct. Mala Raghavan and Krishnan¹² reported an interesting porphyrin-pheophorbide system in which the orientation of the porphyrin is varied by linking the pheophorbide unit to one of the positions (*o*, *m* or *p*) of the meso-aryl rings of the porphyrin (Figure 3). The authors demonstrated efficient energy transfer from the porphyrin to pheophorbide. Time-resolved fluorescence studies have shown that the rate of energy transfer is in the order of 10^{11} s^{-1} with Forster critical distance of $\sim 40 \text{ \AA}$. The growth of the bleach at 675 nm monitored at different time intervals suggests that energy transfer is complete within 40 ps (the time-constant of the instrument). They have proposed that the path *a* is more likely since the triplet-triplet energy transfer proceeds at much slower rate (10^9 s^{-1}). This study is of interest since the authors fail to observe any biexponential decay (in the order of ps) to detect any conformer or the quenched porphyrin. Tran-Thi *et al.*¹³ reported another interesting heterodimer comprising porphyrin and phthalocyanine. This is one of the few studies where solvent dependency on the rates of excitation energy transfer has been



\underline{p} and \underline{m} , $M_1 = 2H$, $M_2 = 2H$ Free base dimers
 \underline{p} and \underline{m} , $M_1 = 2H$, $M_2 = \text{Zn(II)}$, Mono-metallated dimers
 \underline{p} and \underline{m} , $M_1 = M_2 = \text{Zn(II)}$, bis-metallated dimers
 $\underline{p}, \underline{m}$ denote the positions at 5(Ar) to which pheophorbide is attached.

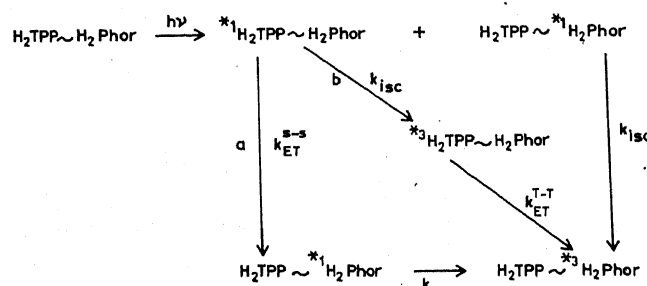


Figure 3. Structures of covalently linked chlorophyllide-tetraphenyl porphyrin and a possible scheme of excitation energy transfer in covalently linked chlorophyll porphyrin systems.

investigated. Time-resolved studies in toluene have shown that energy transfer occurs both from the singlet and triplet manifold of the porphyrin to the phthalocyanine with an estimated singlet lifetime of the porphyrin at 260 ps and a rate of singlet-singlet energy transfer of $3.3 \times 10^9 \text{ s}^{-1}$. However, in polar solvents such as dimethyl sulphoxide, a biexponential decay with two lifetime components at 0.33 ns and 2.8 ns is observed. It is suggested that in this solvent the short component essentially arises from charge transfer state and the energy transfer is inefficient. The difference in behaviour in the different solvent seems to arise from the possible existence of different conformers.

Reaction centre

The concept of RC is central to the function of the photosynthetic act. This complex is hydrophobic in nature and located in the membrane. It was earlier speculated that a series of photoinduced electron transfer reactions occur within the RC complex essentially to accomplish the formation of the reductant NADPH. The nature of the pigments and reductants and their organization in a variety of RC complexes have been obtained by spectral data. With the successful isolation of single crystals of the RC complex of the purple bacteria (*Rhodospseudomonas viridis* and *Rhodobacterium sphaeroides*) and the remarkable three-dimensional structure of these systems¹⁴, many speculations concerning the organization and the role of the pigments have been set aside. The structure of the membrane protein (Figure 4) has the following essential features. The primary donor is dimeric in nature in which two bacteriophyll molecules are intimately associated with one another. The other pigments B.Chl and bacteriopheophytin (B.Pheo) are arranged sequentially along with a quinone and terminating with an iron centre. There exists a two-fold symmetry between the primary donor and Fe centre with the disposition of the pigments on either side of the axis. The initial electron transfer occurs between the primary donor to the B.Pheo to the quinone in about 200 ps. There has been an intense debate as regards the role played by the B.Chl positioned between the primary donor and B.Pheo in the initial reaction. The dynamics of the electron transfer reactions occurring in the bacterial RC complex is a subject of immense interest, especially in view of the remarkable structural details that are available from the X-ray structure. The polypeptide chains hold the two B.Chl molecules in the primary donor without any specific interactions though the B.Chl molecules exhibit pronounced tendency to form dimers and aggregates in solutions depending on the polarity of the solvent¹⁵. Several interesting studies are available on the RC complex in recent years.

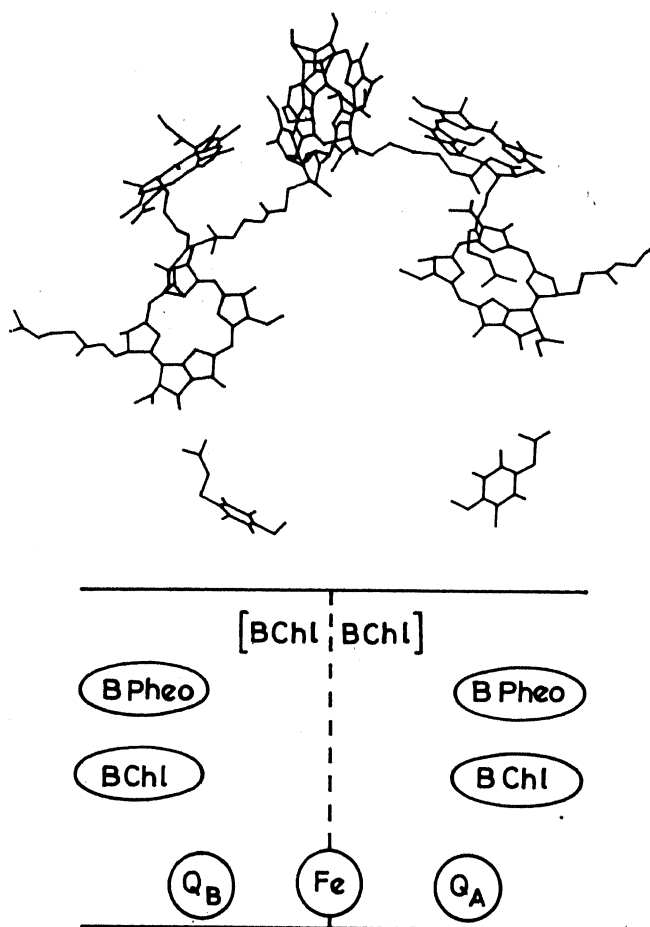


Figure 4. Structure of membrane bound reaction-centre protein complex of *Rhodospseudomonas viridis*. Disposition of the pigments and acceptors are shown schematically.

Model reactions

The organization of the primary donor and auxiliary acceptors in the RC complex is intriguing in many respects. The obvious feature of this being the near unity of quantum efficiency of the primary reaction and the absence of any wasteful charge recombination reaction. The primary donor is a dimeric chlorophyll and the reason for this choice is unknown. It is thought that the dimer acts as a trap for the excitation energy received from the antenna. It is recognized that the migration of excitation energy within the antenna from one Chl molecule to another Chl molecule takes place at about 0.1 ps per step till this reaches the final step in the RC. If there exists no processes in less than 0.1 ps in the RC, the excitation energy would be returned to the antenna resulting in an unsuccessful event. The recent experiments of hole burning experiments and other studies on purple bacterial RC systems have shown that the excited state resulting from the burning of the Qy

transition of the primary donor is in resonance with the internal CT state¹⁶. This internal CT state of the dimer has an estimated lifetime of 25 ps. The primary electron transfer step involving the donor (dimeric Chl) and pheophytin happens in about 2 ps. Interesting questions arise as to the route of the electron from the excited dimer to the porphyrin and the role of the Chl positioned between the donor and acceptor pheophytin. Arguments have been put forward to implicate the Chl molecule as an intermediate state where the electron resides in about 3.5 ps and then transfer to the pheophytin occurs in about 0.9 ps so that no accumulation of reduced pheophytin occurs. The sequential electron transfer proceeds much faster in forward direction relative to the slower reverse reaction, except in a few cases, e.g. photoinhibition where the charge recombination takes place.

The biomimetic model studies involve many approaches. One of the approaches is to mimic the dimeric chlorophyll (primary donor) part and understand the mechanism of intramolecular CT coupled state for the primary energy trapping. Several interesting models consisting of chlorophyll, chlorophyllide and porphyrin dimers have been synthesized and studied^{17,18}. These studies have provided invaluable insight into the charge delocalization mechanism within the molecular entity.

The photoinduced electron transfer studies have been modelled using covalently linked donor-acceptor systems. These involve a diad, consisting of a donor and an acceptor or triad, donor and two acceptors and tetrad and others. The donor normally involves a porphyrin and diverse acceptors have been extensively studied and the results that have accumulated are very impressive. A few studies bearing chemically modified porphyrins have been employed as acceptors. Several excellent reviews detailing the model studies have appeared in the literature¹⁹. Here we shall consider systems of recent interest and focus attention on the elucidation of the dependence of various parameters that lead to enhanced

rates. It has been known that the rate of electron transfer within a donor-acceptor system primarily depends upon (i) distal separation between the donor and acceptor, (ii) orientational features of donor *vis-à-vis* acceptor relative to one another, (iii) the nature of the covalent linkage, and (iv) the nature of the media. The covalently linked systems often contain either a sigma network (consisting of saturated hydrocarbon groups) or occasionally, a pi system. The orientational features are often derived from spectroscopic data²⁰. The detailed solvent dependence study has been carried out only in a few systems²¹. Often Marcus' theory²² has been invoked to explain the observed results with a fair amount of success. In many of these systems, when the distance is known the orientational features are uncertain thus leading to various misgivings. The results of these studies point out that the observed rate is in the order of 10^9 to 10^{10} s^{-1} very similar to the rates in the photosynthetic process.

Gust and coworkers²³ have accomplished more or less ideal systems bearing pigments and acceptors organized in a certain manner so as to produce sequential electron transfers. These systems are of interest. They are often designated as triads, tetrads and so on to designate the number of acceptors covalently attached to the pigment centre. Recently, a multi-component system involving carotenoid, porphyrins and two quinones has been reported²⁴ (Figure 5). They are able to demonstrate that on selective laser excitation produced a singlet excited state of the porphyrin followed by electron transfer to a quinone and charge migration to carotenoid with great facility. The rates of these reactions and the quantum yields of these processes have been determined using diverse spectral techniques. There have been many attempts to mimic the RC complexes by careful design including that of the primary donor, the dimeric pigment molecules. This aspect has been illustrated by Maruyama and Osuka²⁵. The authors from their study on elegantly synthesized tetrad and pentad systems involving porphyrins and acceptors have demonstrated a

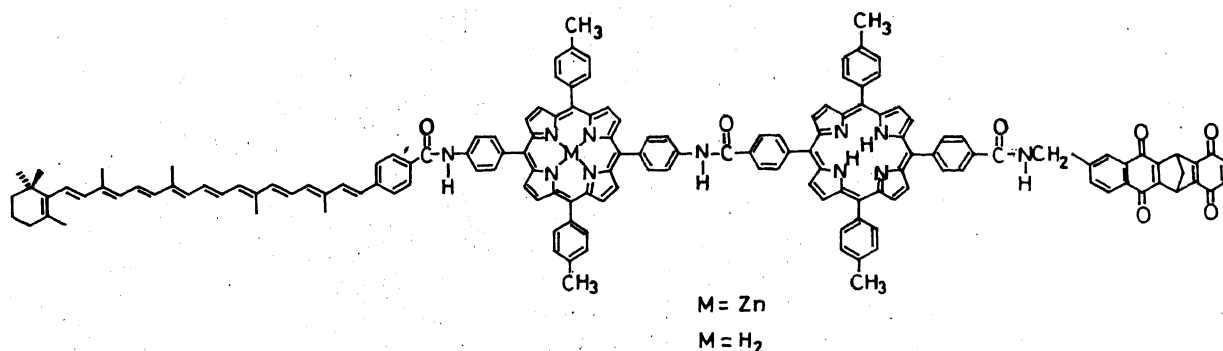


Figure 5. A multicomponent covalently bound donor-acceptor system involving porphyrins, amide, bisquinone and a carotenoid.

linear dependence of distal separation between the donor and acceptor on the rates of intramolecular electron transfer.

Future directions

Intelligent design of molecular components aimed at increasing efficiency of charge transfer and charge separation events form the basic approach. It has become increasingly evident that excitation energy migration in antenna systems and model studies require investigations into femtosecond time domain with wide tunability of laser pulse wavelength. A quantitative understanding of the exciton migration in the ensemble of identical pigments should soon emerge from these studies. Improved design of molecular systems to illustrate the mechanism of exciton migration is necessary to augment research in the photosynthesis antenna systems. It is known that certain plant pigments and dyes do aggregate in solution, however, the type of the aggregates and extent of aggregation are not well understood. A knowledge of this would become available from the photophysical studies on the Langmuir-Blodgett films of these molecules. Studies on certain dye molecules illustrate that *J* aggregates which exhibit red-shifted absorption band (relative to the monomer absorption band) have a longer excited state lifetime, a situation ideally suited for exciton migration for efficient light harvesting²⁶. The rate constants for site-to-site energy migration are often described in terms of weak incoherent mechanism and the occupation probabilities are obtained from the Master equation²⁷. Simulation studies have been proved to be partly successful in the elucidation of the mechanistic aspects. In addition to Forster's critical distal parameter, orientational features of the pigment molecules play an important role in governing the rates of intramolecular energy transfer. In obliquely aligned transition dipoles (of the pigments), it has been shown that geometrical factor (k^2/R^6) bears a linear dependence on the experimental rates of intramolecular energy transfer. Apparently, this seems to be the only study describing the geometric factor dependence on the rates. Many more studies would be necessary to exploit some of these molecular systems for electronic devices, such as relay and memory systems.

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Multielectron transfer water oxidation catalysts as models for photosynthetic oxygen evolving centre

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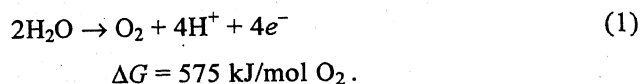
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Oxygen evolution is one of the most important processes in photosynthesis. Several proposals have been made to elucidate the role of manganese ions and the mechanism involved in photosynthetic oxygen evolution. Metal oxides such as RuO_2 , PtO_2 , etc have been initially reported as oxygen-evolving catalysts. However, redox chemistries and mechanisms associated with such catalysts were difficult to evaluate and they are non-specific. Although several manganese complexes are reported as models, the manganese model complexes show that they are active for water oxidation only in the heterogeneous state since each metal centre in such systems acts as one-electron oxidant only and the four-electron water oxidation is efficiently coupled in the heterogeneous system. In recent times, by choosing proper chemical model systems, the

mechanism of oxygen evolution as a model for water oxidation centre in photosystem II has been studied. The report of dimer $[(\text{bpy})_2(\text{H}_2\text{O})\text{Ru}-\text{O}-\text{Ru}(\text{H}_2\text{O})(\text{bpy})_2]^{4+}$ with aquo ligands has shown the way to look for molecular catalysts which are well characterized. In a further understanding, polynuclear metal complexes like Ru-red and Ru-brown are found to be efficient catalysts for water oxidation. Although monomeric $[\text{Ru}(\text{bpy})_2(\text{H}_2\text{O})_2]^{2+}$ could not oxidize water, it was found that other monomeric ruthenium complexes are active for water oxidation as two-electron oxidant in both homogeneous as well as in heterogeneous systems. The visible light splitting of water with such catalysts has been achieved by a system mimicking photosystem II. In this review we present artificial model systems for photosynthetic oxygen evolution.

SOLAR energy conversion is becoming increasingly important and urgent as an alternative new energy resource since the global environmental problems such as CO_2 increase have come to be serious. Photosynthesis is an excellent photochemical model for achieving artificial solar energy conversion systems, for which water oxidation is the most important primary step to provide electrons to the whole system to produce energy-rich reduction compounds¹⁻⁴. Water oxidation in

photosystem II of the green plant photosynthesis is the essential reaction to pump electrons from water molecules to biological systems (eq. (1)).



To achieve photosynthesis, a minimum of 475 kJ energy per mol of evolved oxygen (or per consumed carbon dioxide) must be introduced in the system. The ability of green plants to produce molecular oxygen from water using sunlight energy is a mystery which remains to be

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