PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A

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Review

Cite this article: Cogdell RJ, Gardiner AT, Molina PI, Cronin L. 2013 The use and misuse of photosynthesis in the quest for novel methods to harness solar energy to make fuel. Phil Trans R Soc A 371: 20110603.
http://dx.doi.org/10.1098/rsta.2011.0603

One contribution of 15 to a Discussion Meeting Issue 'Can solar power deliver?'.

Subject Areas:
green chemistry, biochemistry, organometallic chemistry, photochemistry

Keywords:
photosynthesis, solar energy, artificial photosynthesis, biofuels, solar fuel, polyoxometalates

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The use and misuse of photosynthesis in the quest for novel methods to harness solar energy to make fuel

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This short review will illustrate that photosynthesis can provide a real contribution towards our sustainable, green fuel requirements in the future. However, it is argued that the focus on biofuels is misplaced and that, in the longer term, investment in artificial photosynthesis will prove much more beneficial.

1. Introduction

Photosynthesis is the only major chemical process on the planet that is able to use solar energy to produce fuel [1]. It, therefore, comes as no surprise that 'photosynthesis' is widely used both directly and indirectly as a source of renewable energy. An example of direct use is the conversion of the photosynthetic product sucrose (from sugar cane and sugar beet) into a fuel, usually ethanol [2]. Photosynthesis can also be used indirectly as an inspiration for novel approaches to achieve artificial photosynthetic energy conversion [3–6]. This short review will discuss the relative merits of these two approaches principally by considering the efficiency that each can potentially achieve for the conversion of incoming solar energy into the energy stored within a suitable fuel.

Most currently used methods of generating clean, renewable energy only produce electricity. Electricity has two inherent problems: the intermittency of the supply

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and difficulty of storage. In effect, electricity has to be used more or less at the same time that it is produced. Even if it was possible to efficiently store electricity, there would still be a need to produce dense, portable fuels for aviation and shipping. A major challenge for us now is to design systems that are capable of making fuels from solar energy as they represent flexible stored energy that can then be used on demand.

Efficiency is the key issue. The amount of solar energy arriving at the surface of the Earth each year is about 120 000 TW [7]. However, the amount per square metre is only about 200 W (this value changes depending on the geographical location but is a reasonable average value) [8]. In other words, solar energy is an abundant but relatively diffuse source of energy. Mankind currently uses about 14 TW per annum, and this has been predicted to rise to about 28 TW by 2050 [9]. If solar energy is to be harvested to provide a significant fraction of the required 14 TW then rather large areas of land must be turned over to 'farming' the Sun rather than producing food. Obviously, the lower the efficiency of the energy conversion process, the larger the area of land required will be and the bigger the potential problem will become persuading the public to accept this. This issue must be addressed now as it will be unforgivable if and when researchers develop effective strategies to convert solar energy into fuels that these are then rejected by the public and are, therefore, subsequently impossible to implement. The scientific community in this field must not repeat the same mistakes that were made with regard to handling the perceived problems involved with the genetic modification of crops. Too little attention is being paid to this issue at present.

2. Harnessing photosynthesis

What exactly is photosynthesis and how efficient can it be? Photosynthesis is the process by which plants, algae and some bacteria can use solar energy to remove electrons from water [10] and use them to reduce atmospheric carbon dioxide to carbohydrates. During water oxidation, oxygen is produced and this supplies all the oxygen we breathe [11,12]. The carbohydrates synthesized ultimately provide the major part of the energy required to support all life on the Earth. Moreover, primordial photosynthetic activity has provided all the fossils fuels that we now consume so greedily.

The all-encompassing term photosynthesis can in the first instance be broken down into two partial reactions, the light and the dark reactions [1]. The light reactions use solar energy to power the synthesis of adenosine triphosphate (ATP) and reduced nicotinamide adenine dinucleotide phosphate (NADP), i.e. energy and reductant. The subsequent dark reactions then consume these chemicals during the enzymatic reduction of carbon dioxide into carbohydrates. For plants, the dark reactions come in two versions depending on the family, called C3 [13] and C4 photosynthesis [14,15]. The overall efficiency of C3 photosynthesis depends on whether it is being carried out by plants or algae. The maximum measured efficiency for C3 plants growing in the field under optimal conditions in their mid-growing season has been estimated to be 3.5 per cent [16]. The efficiency is a little higher for C4 plants at 4.3 per cent [16] and even higher for some microalgae grown in small bioreactors at 5–7% [17]. It is instructive to compare these actual measured efficiencies with the maximum theoretically achievable efficiencies. These have been calculated to be 4.6 per cent for C3 plants and 6 per cent for C4 plants [16]. Unfortunately, for most crops, the actual efficiency is usually less than 1 per cent. In comparison, the overall efficiency of conversion of solar energy into electricity by standard silicon-based solar cells is typically 10–20% [8].

If natural photosynthetic systems are going to be used to produce fuels, such as bioethanol or biodiesel, then careful consideration must be given to the efficiency and detailed energy balance for each process. 'Energy balance' is defined as the ratio of energy available from the biofuel in question to the energy input required to operate the complete biofuel production process. Values greater than 1 mean that there is a net energy gain. The efficiency will dictate how much land will be needed to provide a given amount of fuel and a detailed energy balance will reveal the total energy produced compared with the amount expended

in its production. Hard data on real efficiencies determined for 'energy crops' in the field are difficult to find. More work has been carried out in determining energy balances. Typical energy balance values of some key biofuels range from approximately 1.3–1.5 for ethanol from corn in the USA, to 2.5 for biodiesel from Germany to 8 for ethanol from sugar cane in Brazil (http://ngm.nationalgeographic.com/2007/10/biofuels/biofuels-interactive). Clearly, if cellulose and lignin can be efficiently broken down into fermentable substrates, then these energy balances will increase [18,19]. At present, even though the production of first-generation biofuels does generate a positive energy balance their scalability is still limited by their overall low efficiency of solar energy conversion. These low efficiencies translate to land area requirements that cannot be reasonably sustained if production is significantly increased.

Is it possible to make natural photosynthesis more efficient? To answer this question, the reasons for the limits on photosynthetic efficiency must be explored. An excellent review on these subjects has recently been published by Blankenship *et al.* [7]. Any attempt to make photosynthesis more efficient requires an understanding of the various steps where energy losses occur between the absorption of light and the fixation of carbon dioxide. A typical crop plant only absorbs light in the visible region of the incident solar spectrum up to about 750 nm. This means that immediately about 50 per cent of the potential energy in the incident solar spectrum is unavailable and lost at this stage. A further approximately 25 per cent is lost owing to a combination of reflection, photochemical inefficiency (for example, part of the energy of blue photons is lost because all the productive photochemistry takes place in the long-wavelength red end of the spectrum) and thermodynamic limits [16]. The other losses reflect the costs of synthesizing carbohydrates and consequences of respiration/photorespiration. Some of these final loss processes reflect complications with the carbon dioxide fixation enzyme, ribulose-1,5-bisphosphate carboxylase oxygenase (RuBisCo) [20]. In many ways, this is a remarkable enzyme since it is able to fix carbon dioxide even though atmospheric levels of this gas are so low at 0.04 per cent. There are no artificial catalysts capable of fixing carbon dioxide that can operate at such low levels and at ambient temperature. Unfortunately, RuBisCo has a low affinity for carbon dioxide, which means that large amounts of this enzyme are needed (RuBisCo is the most abundant protein on the planet!). Even more importantly RuBisCo also reacts with oxygen in a process that effectively reverses the productive fixation reaction [21]. Up to about a quarter of the fixed carbon can be lost in this way [16]. The C4 adaptation in certain plants [22] is one of the ways that have evolved to try to overcome this problem, and the use of carboxysomes in some algae is another [23,24]. Both of these cases involve carbon dioxide-concentrating mechanisms that shift the outcome of the RuBisCo reaction in the direction of carbon dioxide fixation rather than the oxygenase reaction. Overcoming each of these efficiency bottlenecks is not straightforward and so, overall, the possibility of enhancing the efficiency of natural photosynthesis is rather limited but could be of benefit [16]. However, the current limits on the efficiency of photosynthesis call into question the strategy of using plants to produce bioethanol or biodiesel [25,26]. It is hard to see how the production of either of these fuels can be scaled up to provide a significant contribution to our current or future energy needs. The theoretical maximal yield obtainable from biofuels means that the land area required is just too prohibitive [26]. Moreover, ethanol *per se* is a poor choice of fuel because so much energy must be expended during the distillation process to obtain spirit that is sufficiently pure and suitable to be used as an additive for combustion engines. Indeed it follows, therefore, that producing a fuel that is non-miscible with water would be advantageous and a much better choice.

3. Artificial photosynthesis

Although challenging, a much more potentially fruitful way forward is to develop robust systems capable of artificial photosynthesis. These systems can be designed to abate or abrogate the limits and losses of natural photosynthesis, so could, in principle, be much more efficient. How can designing these systems be approached? The essence of photosynthesis can be broken down into four partial reactions as illustrated in figure 1. The first stage involves light harvesting.

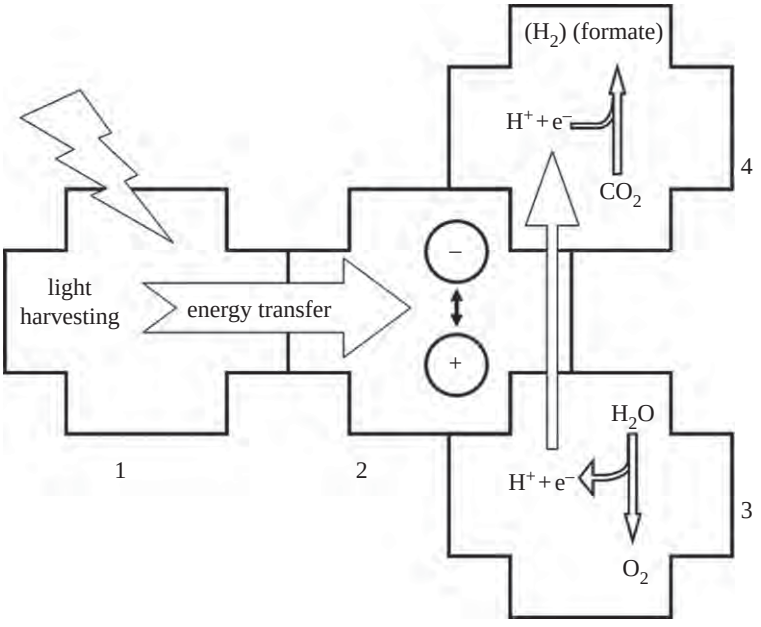

Figure 1. Schematic for the decomposition of photosynthesis into four working modules, each of which can be used in turn as the basis for constructing artificial systems capable of photosynthesis. Module 1 is a light-harvesting device (concentrator) that funnels energy into the reaction centre. In natural photosynthetic organisms, this module is equivalent to the antenna proteins. Module 2 is equivalent to the reaction centre and uses this incoming energy to separate charges across a membrane. The separated positive and negative charges can be then made to do work. Module 3 is the oxidative part of the system as the positive charge from the reaction centre is used to remove electrons from a suitable substrate, hopefully water. In plants, this function is performed by the oxygen evolving complex present in photosystem II. The electrons are then carried to module 4, where reduction of a suitable substrate occurs, which can be either protons to form hydrogen gas or CO_2 to form formate and then methanol. If all four modules can be combined in a functional system then the goal of synthesizing a working artificial photosynthetic device will be achieved.

In the second stage, this absorbed light energy is used to separate charge across a membrane. The positive charges are accumulated to allow water to be oxidized, and the negative charges are accumulated to allow the reductive synthesis of a fuel. A great deal of detailed structural and functional information is known about the different biological modules (pigment–protein complexes and enzymes) that catalyse these reactions and so it is possible to ask what design information can be gleaned by a careful examination of these modules and can this be used to make solar fuels?

There are several high-resolution X-ray crystal structures of light-harvesting complexes. A few of these are shown in figure 2 [27–29]. Strikingly, they are very diverse and at first glance there does not seem to be any clear conserved structural motives. This lack of commonality may appear at first to be a problem but is in reality a positive feature. The structural variability arises from the fact that the basic physics of energy transfer is rather tolerant. There are many ways to organize a group of pigments so that the protein scaffold holds them sufficiently close and at about the right orientation with respect to each other so that the resulting energy transfer reactions are very efficient [30]. Indeed, there have been many artificial light-harvesting analogues synthesized and they work rather well [3,31,32]. In the biological system, the charge separation reactions take place in membrane-bound, pigment–protein complexes called reaction centres. In contrast to light-harvesting complexes, the structures of the different types of reaction centres are all very similar [11]. This reflects the fact that the physics of electron transfer has very strict structural constraints [30]. These constraints have now been rather well understood and many excellent reaction centre analogues have been synthesized [33,34]. Construction of devices capable of mimicking the light-harvesting and charge separation reactions that occur in natural photosynthesis, however,

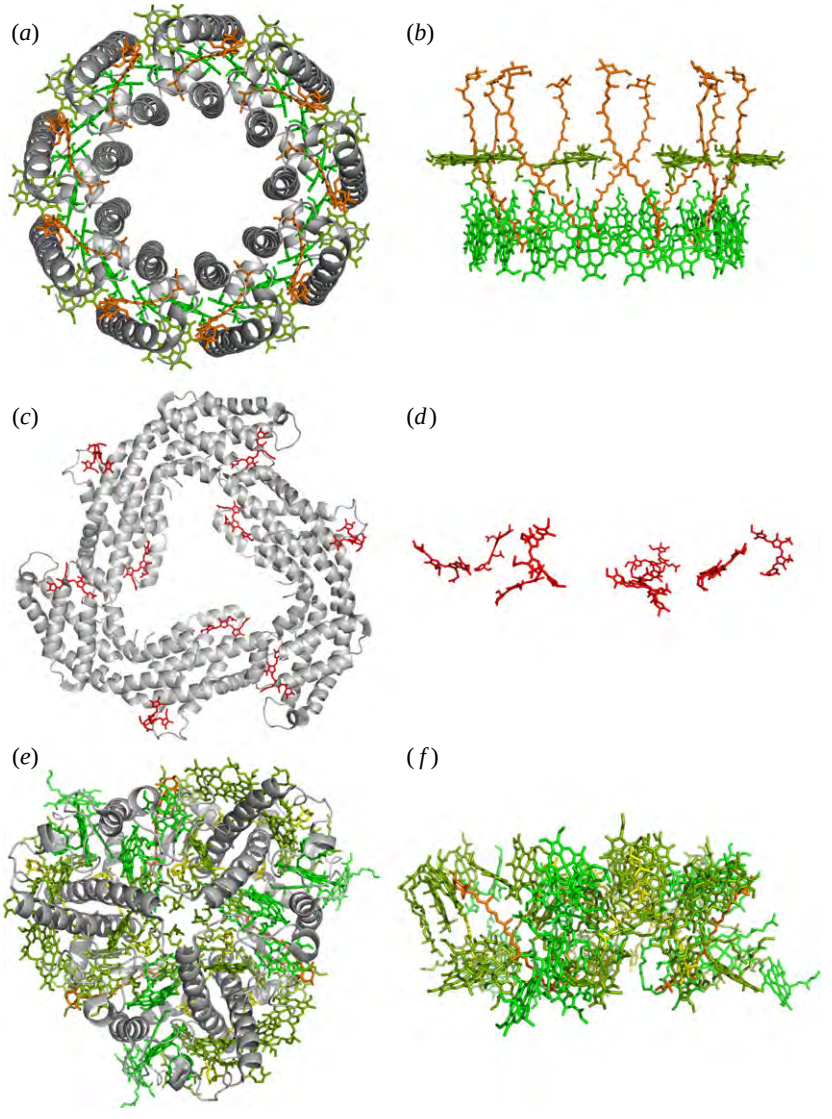

Figure 2. X-ray crystal structures of three different light-harvesting complexes and their corresponding pigment arrangement. (*a*) The LH2 complex from *Rhodopseudomonas acidophila* strain 10050 [27], pdb 1KZU, viewed from the cytoplasm perpendicular to the membrane plane. The protein chains are coloured grey with the β-polypeptide forming the outer ring and the α-polypeptides forming the inner ring. The B800 Bchl molecules are shown in olive green and the B850 Bchl molecules are bright green. The phytol chains have been removed for clarity. The carotenoid rhodopin glucoside is coloured orange. (*b*) View of the pigment arrangement in (*a*) with the protein scaffold removed. The B800 Bchl molecules are in the plane of the membrane and the excitonically coupled B850 molecules are oriented perpendicular to the membrane. Although the bacteriochlorin rings are at right angles to each other, their dipole moments are still aligned, enabling energy transfer to occur. The carotenoid molecule provides additional light-harvesting capacity and is intercalated within the protein chains, adding physical strength to the complex. (*c*) The phycocyanin hexameric rod structure from the cyanobacteria *Thermosynechococcus vulcanus* phycobiliprotein antenna [28]. The phycocyanin β and α proteins form a subunit that aggregates to form a trimer coloured in grey. In the native phycobilisome, the rods along with the allophycocyanin core and linker proteins form the light-harvesting antenna phycobiliproteins. Some cyanobacterial species also have additional phycoerythrocyanin rods. The phycocyanobillin chromophore molecules are shown in red. (*d*) Red phycocyanobillin chromophores with the phycocyanin hexamer removed, viewed perpendicular to (*c*). (*e*) The light-harvesting complex II (LHCII) trimer from spinach [29], pdb 1RWT. All proteins are coloured grey with the chlorophyll *a* coloured olive green, chlorophyll *b* bright green, lutein coloured yellow and xanthophyll coloured orange. (*f*) The LHCII pigments viewed perpendicular to (*e*) with the protein scaffold removed.

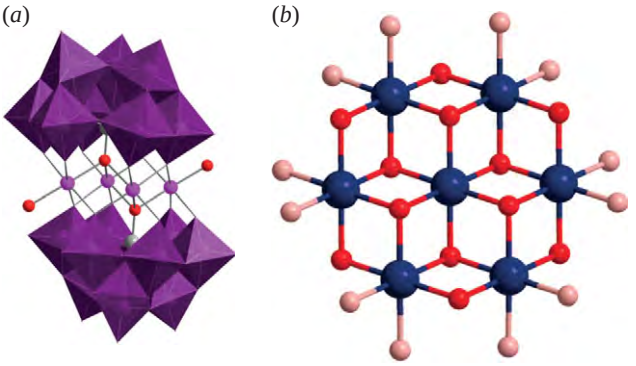

Figure 3. Structures of some newly developed catalysts capable of water oxidation. (*a*) $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$, a molecular catalyst composed of a $[Co_4O_4]$ core sandwiched between two polyoxotungstate ligands. The remarkable stability towards oxidative and hydrolytic degradation of this self-assembled polyoxometalate stems from the inorganic nature of its ligands [38]. Co atoms are pink; O/OH_2 (terminal), red; P, grey; and WO_6, purple octahedra. (*b*) Model of the probable structure of a water oxidation catalyst generated via electrodeposition of Earth-abundant elements from aqueous solutions containing phosphate and Co^{2+} (Co–Pi) [39]. This catalyst is extremely promising from an artificial photosynthetic viewpoint in that it is able to generate O_2 under ambient conditions in neutral aqueous solution.

requires detailed information not only on how individual antenna complexes and reaction centres function but also on how to assemble them in ordered supramolecular arrays. The natural system houses these arrays in the photosynthetic membranes where their organization is carefully controlled. This leads to efficient scale-up where the processes are regulated, protected and optimized. These issues have recently been thoroughly reviewed [35]. Even though there is now a detailed understanding of individual pigment–protein complexes, production is not yet possible of an artificial system with the required efficient supramolecular arrays that can replicate the scaled-up natural photosynthetic process. In contrast to the cases of the light-harvesting complexes and reaction centres, there is an even bigger lack of good artificial catalysts capable of either oxidizing water or reducing carbon dioxide at atmospheric concentrations and low temperatures.

Very recently, a rather high-resolution crystal structure of photosystem (PS) II from a thermophilic cyanobacterium has been described in which the structure of the manganese cluster, responsible for water splitting and oxygen evolution, can be clearly seen [36]. The storage of multiple charges (four are needed to produce one molecule of oxygen) prior to catalysis is a difficult reaction, especially true in this case because of the high redox potentials involved. A natural consequence of this is that under high-illumination conditions PSII typically only works for about 30 min, after which time it is damaged and has to be replaced [37]. A great deal of research is now being undertaken to try to find new and efficient catalysts capable of water oxidation. Figure 3 illustrates two of the more recently developed catalysts: a mixed metal anion belonging to the polyoxometalate [39] family and an amorphous material electrodeposited from simple metal salts in aqueous solution. Both catalysts contain cobalt–oxo cores in their structures. Perhaps the most promising example currently is the system described by Nocera and co-workers [40,41]. The key in this area of research is to develop catalysts that, as in biology, use cheap Earth-abundant metals so that the system can be easily and cost-effectively scalable [42]. The importance of this point is succinctly illustrated with reference to the metal platinum. Water can be split by electrolysis using platinum electrodes; however, this method is not viable for large-scale hydrogen production as there is simply not enough platinum on the Earth to allow this approach to be sufficiently scalable.

Hydrogenases catalyse the reversible oxidation of molecular hydrogen and play a key role in the energy metabolism of various micro-organisms [43]. There are also excellent high-resolution crystal structures of hydrogenases, and these along with various spectroscopic studies have

enabled many details of the reaction mechanisms and active sites to be established [44–46]. As hydrogenases are enzymes capable of reducing protons to release hydrogen, it is easily possible to envisage ways in which these enzymes, using the knowledge of the mechanism and active sites, could be used directly in some sort of bio-hybrid device. Unfortunately, there are at present no good artificial biomimetic analogues with anything approaching the catalytic capabilities of the natural enzymes. The major hurdle to realizing this potential has come from the unfortunate property of hydrogenases in that they are irreversibly inhibited by oxygen. However, the recent characterization of the structure of an oxygen-tolerant hydrogenase with a novel iron–sulfur centre may present a way out of this impasse [47] by inspiring the development of biomimetic H_2-producing catalysts that are capable of functioning in the presence of oxygen.

In Glasgow, UK, we are taking the artificial photosynthesis route and beginning by using biological photosynthetic complexes, as working modules, to try and explore design possibilities for the fabrication of small-scale systems capable of making solar fuels. It is quite clear that the biological modules will not have the required long-term stability, so in parallel we are working hard to synthesize robust inorganic analogues capable of carrying out each of the four stages of artificial photosynthesis described in figure 1.

4. Summary

Because of the non-sustainability and impracticality of continued fossil fuel use, 'green' alternatives are being urgently sought. Nevertheless, in the rush to find alternatives short-term solutions may only appear to be more 'green' than they turn out to be over the longer term. Photosynthetic solar energy conversion promises to be a virtually unlimited, sustainable 'green' resource that has great potential to fill the 'green' gap. However, the headlong rush to promote biofuels as an answer to the current energy problems seems to us to both ignore the inherent drawbacks of biofuels and waste the huge potential of photosynthetic energy conversion. Our view can be succinctly summed up by two very recent quotes from Walker: 'biofuels do not, at present, lead to any appreciable sparing of carbon dioxide emissions that could not be better accomplished by the most modest means of energy conservation' [25, p. 515] and 'in a world in which the population is set to increase by about 75 million each year, most biofuels might well come to be regarded as a lamentable misuse of land and water resources' [26, p. 323].

Artificial photosynthesis has many technical challenges to overcome but over the longer term promises to provide a cheap, scalable, 'green' fuel that will prove much more sustainable and genuine than the illusory benefits promised from biofuels.

The authors acknowledge financial support from EPSRC and the University of Glasgow.

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