

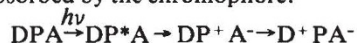
Photochemistry

A quantum step towards artificial photosynthesis

from J. Barber

ACCORDING to an article by Moore and colleagues published in this issue of *Nature* (see p.630), one of the major obstacles to the development of an artificial photosynthetic system has been overcome. For many years the goal of photochemists has been to provide an artificial system that mimics the unique properties of natural photosynthetic reaction centres — particularly their striking ability to facilitate a very rapid and efficient light-induced separation of charge without a significant back-reaction. To date, it has proved difficult to make model systems which do not suffer from high back-reaction rates; now Moore and colleagues seem to have achieved success.

Several different types of reaction centre are found in photosynthetic organisms. Higher plants and algae, which use water as a source of electrons and protons to reduce carbon dioxide and which produce oxygen as a by-product, contain two different types of reaction centre, known as photosystem one and photosystem two. Photosynthetic bacteria, which do not oxidize water, but oxidize more reducing substances such as H₂S and organic acids and therefore do not produce oxygen, contain only one type of reaction centre. Despite these differences, all photosynthetic reaction centres consist of a chromophore (P), which absorbs light energy, and a closely associated electron donor (D) and acceptor (A). The organization of these three components allows the following sequence of events to occur when a photon is absorbed by the chromophore:



The D⁺PA⁻ state is further stabilized by rapid secondary electron transfer processes. P is always a chlorophyll molecule but the chemical nature of D and A varies, with A most often being a quinone. For photosystem one and the bacterial system, D is a metalloprotein, either plastocyanin or cytochrome *c*; the nature of the primary electron donor in the photosystem two reaction centre is unknown but under certain circumstances can be the carotenoid β-carotene. Unlike photosystem one and two, functional reaction centres of photosynthetic bacteria have been isolated free of their light-harvesting proteins and subjected to detailed physical and chemical studies.

With these preparations it has been shown that P⁺A⁻ formation occurs within 100 picoseconds of an excitation flash from an ultrafast laser. The back-reaction is 100 times slower than the forward reaction; normally the P⁺A⁻ radical pair will be

quickly converted to D⁺PA⁻ which then has a much longer lifetime.

Moore and his co-workers have succeeded in synthesizing a very stable molecule which mimics the photochemical properties of natural reaction centres. Their molecule consists of three covalently linked entities: a chromophore (P), a donor (D) and an acceptor (A). The chromophore used is tetraarylporphyrin which has a structure and light-absorption properties comparable to those of chlorophyll. The acceptor is a quinone and the donor is a substituted β-carotene.

Because D and A are spatially separated by the porphyrin, the tripartite molecule has some remarkable properties. Flash spectroscopy shows that D⁺PA⁻ is generated within 200 picoseconds and has a long lifetime — charge recombination occurs on a microsecond time scale. The quantum yield for its formation is also very high and, in certain conditions, can reach 25 per cent. The energy stored in the charge complex is at least 1 V; the conversion of energy is thus remarkably efficient given that only 1.8 eV is available from the absorbed photon. Surprisingly, the

stabilized charge-transfer complex is generated from the singlet state of the excited porphyrin, with triplet states occurring only when the quinone is chemically reduced before illumination. In this situation, the porphyrin triplet is converted in 20 nanoseconds to a less reactive carotenoid triplet by a protective mechanism very reminiscent of a process seen in photosynthetic tissue. In nature, carotenoids not only function to quench chlorophyll triplets but also serve as light-harvesting pigments. Interestingly, Moore and colleagues have found that in their molecular triad, 10 per cent of light energy directly absorbed by the β-carotene moiety is transferred to the porphyrin.

Clearly Moore and colleagues have synthesized a very interesting molecule which, like photosynthetic reaction centres, can efficiently use the singlet energy of an excited porphyrin molecule to bring about stabilization of positive and negative charges to store chemical potential energy. Not only does the molecular triad give a convenient synthetic system for studying very fast photochemical reactions similar to those which occur in photosynthesis, but it could perhaps be exploited in a solar cell in which the molecule would catalyse further secondary reactions which generate a usable chemical or electrical fuel. □

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100 years ago

PROFESSOR Ruskin's utterances are perhaps to be taken least seriously when he is himself most serious, and probably he was never more in earnest than in his jeremiad on modern clouds, delivered at the London Institution on the 4th and 11th inst. Probably none of the readers of *Nature* have been terrified by the storm cloud of the nineteenth century, but should it be otherwise we hasten at once to their relief. Twenty years before the date fixed by Mr. Ruskin for the first appearance of his portentous "plague-cloud", the writer of the present article commenced a series of observations on the forms and structures of clouds, followed a few years later by such daily charts of wind and weather as could be constructed from the data, somewhat meagre, that were then accessible. As might be expected, cyclone and anticyclone were then as they are now. The dimensions and densities of the cloud layers have not altered, neither has our moral degeneracy nor the increased smoke of our manufacturing towns developed any new form of cloud. Neither (until the phenomenal sunrises and sunsets of the last three months) has *Nature*, in painting the clouds, employed upon her palette any fresh tints, whatever artists may have done. Further, we have not observed, nor met with any one, except Mr. Ruskin, who has observed, that the wind during the last thirteen

years has adopted a "hissing" instead of a "wailing" tone.

Admiration ought ungrudgingly to be bestowed on one who has done good service as an art critic and as a contributor to English literature. The sympathy, moreover, which, denied to those who are in advance of their age, is naturally accorded to the archaic type of mind, is enhanced by the attractiveness of a personality whose idealism is as lofty as that of Mr. Ruskin. But we maintain that there is a further sentiment which contributed to the applause which Mr. Ruskin's audiences bestowed upon him. Speaking generally, "broadly and comfortably", as he would say, Mr. Ruskin is not a representative man, yet he represents a certain spirit of Philistinism (for it merits this name), which is far from being unpopular, and which shows itself in opposition to scientific culture. He is the spokesman of that mental attitude which misinterprets the province of science and affects to misunderstand the plainest utterance of the physicist. "The first business", he says, "of scientific men is to tell you things that happen, as, that if you warm water it will boil". "The second and far more important business is to tell you what you had best do under the circumstances — put the kettle on in time for tea." "But if beyond this safe and beneficial business they ever try and explain anything to you, you may be confident of one of two things — either that they know nothing (to speak of) about it, or that they have only seen one side of it, and not only have not seen, but usually have no mind to see, the other".

From *Nature* 29, 353, 14 February 1884.