

models to more complex biological systems will thus be even more challenging. However, it is important to remember that virtually all of our understanding of multivalent interactions has ultimately come from studying simplified systems such as these. Furthermore, artificial systems that are inspired by nature often present exciting opportunities for developments in materials and nanoscience⁵.

The walking mechanism of the divalent ligand is reminiscent of the way myosin V walks along actin filaments as it transports vesicles through cells⁶. Of course, it should be remembered that the directional motion observed with the adamantyl ligands is

distinct from that in the myosin system. Whereas myosin is a true molecular machine that is driven forward by chemical change, the fluorescent ligands take their direction from a thermodynamic need for disorder. Nevertheless, movement along a concentration gradient is also important in biological systems, for example chemotactic movement towards metabolites or away from toxins is essential for the survival of microorganisms. Research to control the directional movement of molecules along concentration gradients is underway⁷, and the insight provided by this study leaves us but a hop, skip and jump from understanding these systems too. □

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PHOTOCHEMICAL CO₂ REDUCTION

Towards an artificial leaf?

Photosynthesis in plants converts energy from the Sun into chemical fuel in the form of glucose. Now, a strategy to combine carbon dioxide reduction and photochemical water splitting, using a recyclable hydrogen donor, offers the opportunity to develop non-biomimetic photosynthesis.

Josef Michl

It seems to be encoded in human DNA that a foreseeable future crisis is not to be considered significant until it is at the door. Those of us who teach are reminded of this feature of the human psyche twice a year, when a term-end examination announced early in the semester is then ignored for months until it suddenly becomes worthy of serious overnight efforts during the exam week! Our collective attitude to the rather unpleasant issue of climate change — a change that is very likely to result from ever increasing levels of carbon dioxide in the atmosphere — is very similar. We are happy to pay some lip service but continue to burn fossil fuels with abandon because there are always sufficient immediate financial and economic needs to trump any long-term considerations. Unless the unlikely and almost inconceivable happens — the cost of carbon-neutral renewable energy becomes competitive with or even lower than the cost of energy from fossil fuels — then the outcome of this is predictable.

The amount of usable energy that reaches the Earth in the form of solar radiation dwarfs the amount of renewable energy potentially available from all the other sources combined. It is therefore easy to conclude that, in the long run, civilization as we know it can only survive if we learn how to harvest solar energy and store it in the

form of fuels much more cheaply than we are able to at present.

Combining the photochemical splitting of water¹ with the reduction of carbon dioxide to create a transportable fuel is one of the obvious ways to proceed². The oxygen from water can be released into the atmosphere and the hydrogen combined with the carbon dioxide to form a fuel such as formic acid, formaldehyde, methanol or their equivalents. The sum effect of this is to set up a system for artificial photosynthesis — albeit that the energy is stored in a form different from the sugars produced by plants. If the fuel formed is burned, the previously released oxygen is consumed and carbon dioxide is released back into the atmosphere, for an overall carbon-neutral process.

Although it sounds simple, the design of an inexpensive system to combine water splitting and carbon dioxide reduction is an enormously difficult undertaking. Even green plants, after aeons of evolution, only perform this task (Fig. 1a) with an efficiency of a few per cent. Could we do better in the few years or decades that are left at our disposal? An important step forward on this difficult path is described³ by Barry Carpenter and his collaborators in *Nature Chemistry*.

Rather than attempt to combine these two processes, Carpenter and colleagues propose that there are advantages to keeping

the steps separate, and suggest the use of a recyclable redox agent. This allows them to rely on known chemistry and to propose the use of mutually incompatible conditions for the two processes. In a first step — and the step that their article addresses — carbon dioxide is photochemically reduced to formic acid. The hydrogen comes from the dehydrogenation of a tricyclic tertiary amine reaction partner.

The design of the tertiary amine is the key. Most photochemical CO₂ reduction processes require some kind of sacrificial electron donor. The majority of research, however, has been directed towards the development of new metal catalysts for this process, and most simply use a stoichiometric quantity of triethylamine (or similar). The role of the amine is first to provide an electron — producing a radical cation. With a simple amine such as triethylamine, a number of reaction routes are then possible in the process — the amine further provides a proton and a hydrogen atom — producing a variety of highly reactive intermediates such as imines and enamines and eventually resulting in a complex mixture of waste products.

Applying their knowledge of the ways in which reactive radical cations decay^{4,5}, Carpenter and co-workers designed a tricyclic amine such that the resulting radical cation (Fig. 1b) would form only

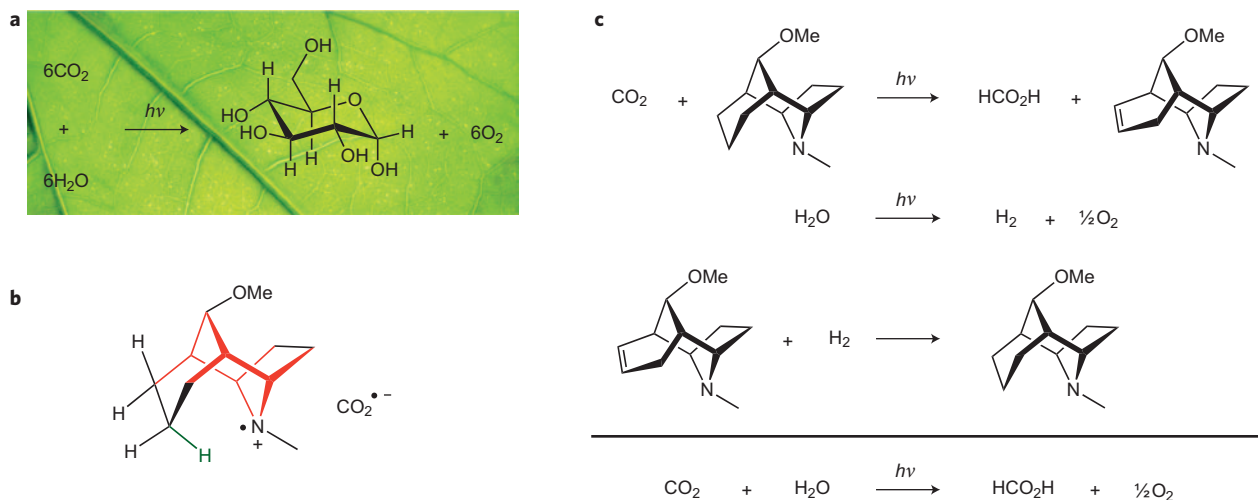


Figure 1 | Non-biomimetic photosynthesis. **a**, Photosynthesis in plants. **b**, The amine radical cation formed from Carpenter and colleagues' tricyclic amine as the initial intermediate during photochemical CO_2 reduction. Formation of double bonds at the bridgehead positions (red) is prohibited. A transannular hydrogen (green) is ideally placed for eventual formation of an alkene. **c**, Proposed use of a tricyclic tertiary amine as the stoichiometric reducing agent in a photochemical reduction of carbon dioxide. The amine can be regenerated using hydrogen — potentially produced in a separate photochemical water-splitting reaction. The sum of the processes is the production of a transportable chemical fuel (formic acid) from carbon dioxide and light.

one product — an alkene. The bridged tricyclic structure of the amine prevents formation of the highly reactive imines and enamines as it would require the formation of double bonds at bridgehead positions (in contradiction of Bredt's rule). Furthermore, the cage-like structure places a transannular C–H bond in close proximity to the amine radical cation, and the hydrogen atom abstraction ultimately leads to the formation of a stable alkene.

They then showed that hydrogenation of this alkene, catalysed fairly typically with a Pd catalyst, allowed the regeneration of the original amine. Hypothetically, the hydrogen for this step could be obtained from photochemical water splitting in an entirely

separate process, but the sum of the processes is the generation a transportable fuel (formic acid) from carbon dioxide using light — non-biomimetic photosynthesis (Fig. 1c).

Carpenter and co-workers have introduced a new concept for artificial photosynthesis, designed a suitable recyclable amine, synthesized it, and demonstrated that the whole scheme should work. They do not claim to have developed a practical system. What they have accomplished is the introduction of a new principle and a demonstration of its feasibility. Much further development of the concept is needed before anything like a commercially viable artificial leaf can be built. May it happen in time! □

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ENERGY TRANSFER

On the right path

Controlled energy-transfer on a molecular scale is a goal in many areas of science, from artificial photosynthesis to molecular electronics. Now, DNA origami has been used to direct the transfer of energy from an excited input dye down one of two paths by precisely arranging a mediator dye.

Bo Albinsson

Communication in the molecular world is inherently short range, for example one molecule can specifically 'recognize' another if they are within collision distance. There are, however, exceptions. Fluorescence resonance energy transfer (FRET) is one of the names used to describe the transport of electronic excitation energy

governed by long-range Coulomb interaction. To some people the 'F' stands for Förster after Theodor Förster who in 1948 made the first quantitative description of FRET in terms of easily accessible spectroscopic parameters. He showed that organic and inorganic dyes can transfer excitation energy over distances up to almost 100 Å — a distance far beyond

the size of the molecules themselves¹. The term "a spectroscopic ruler" was first used in the late 1960s by Stryer and Haugland², and since then FRET has been used in numerous studies to estimate distances between chromophores attached to a wide variety of (macro)molecules in materials and biological sciences.