Let there be light — but not too much

Green plants have an in-built protection system that prevents their photosynthetic machinery from being damaged by excessive levels of light. Researchers have now demonstrated a similar mechanism in an artificial molecular system.

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It is hoped that artificial photosynthetic systems will one day be able to harness some of the energy in sunlight for applications such as solar energy, optoelectronics and molecular machines. For this to happen, however, these systems must be able to harvest the light, separate the electrons and ‘holes’ formed when the light is absorbed, and then transport these charges to places where they are needed (which for plants are the catalytic sites where the oxidation of water and reduction of carbon dioxide occur). Notable progress has been made in all of these areas, but researchers have still not developed components that are both efficient and robust, and, moreover, these different components have not been integrated into a working system.

An issue that is often overlooked is self-regulation and repair. Consider, for example, photosynthesis in green plants: this process is optimized for the conversion of solar energy into chemical potential at ambient light levels, but it is also able to adapt to changing light conditions, such as sudden increases in brightness that would, in the absence of a protection mechanism, lead to the production of significant quantities of toxic free radicals in the cells.

Plants have developed an intricate defence mechanism that dissipates the excess energy in the form of heat, thus minimizing irreversible damage to the photosynthetic cells. This is a complicated mechanism but, in simple terms, a fall in pH triggers chemical changes in the photosynthetic pigments that shift the absorption to the red part of the solar spectrum. This results in the photons being trapped, and, as a net result, less solar energy is converted into chemical potential.

On page 280 of this issue, Devens Gust, Tom Moore, Ana Moore and co-workers at Arizona State University (ASU) have now demonstrated a similar protection mechanism in an artificial photosynthetic system. Building on their previous work, the ASU team has developed a self-regulating molecular nonlinear transducer in which two antennae harvest the light, a porphyrin molecule acts as an electron donor, a fullerene molecule accepts electrons, and a photochromic group regulates the overall system (Fig. 1).

This photochrome — and the way that it changes shape depending on the light conditions — is central to the protection mechanism. Under ambient conditions and low levels of illumination it adopts a closed form. It is safe to assume that this closed form has no impact on the transfer of charge and energy in the rest of the system (that is, between the antennae, porphyrin and fullerene). However, when exposed to light in the blue–green and ultraviolet regions of the spectrum, the photochrome photoisomerizes to form an open isomer, which does have a significant influence on the rest of the system, as we shall see below. At ambient temperatures, it reverts to the closed form.

So how does the system work? When solar photons are absorbed by the antennae, the excitation energy migrates to the porphyrin molecule, exciting it from its ground state to a higher energy singlet state. Photo-induced charge transfer from the porphyrin to the fullerene then occurs with a time constant of 2 ns, leading to the formation of...
of a charge-separated radical ion pair state (in other words, the fullerene has a negative charge and the porphyrin has a positive charge). At low levels of white light, when the photochrome is in a closed form, a large fraction (82%) of the energy absorbed by the antennae is stored as an electrochemical potential.

However, as the level of illumination level increases, the conversion efficiency falls, reaching a value as low as 27%, because the fraction of the photochromes that are open increases. This reduction in efficiency happens because the open form quenches the lifetime of the excited state from 2 ns to 33 ps and, moreover, the energy is mostly dissipated in the form of heat rather than being used to transfer the electron from the porphyrin to the fullerene. Subsequently, decreasing the intensity of illumination returns the efficiency to its initial value of nearly 82%.

Molecular self-regulation will be required for many applications of nanotechnology, in particular in applications in which the components must continuously adapt both to changing external environments and to the function of neighbouring devices. Although self-regulation is crucial to biological functions in general, it has been difficult to engineer it into synthetic systems at the molecular level. However, this marvellous work by the ASU team shows that it can be done.

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References

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