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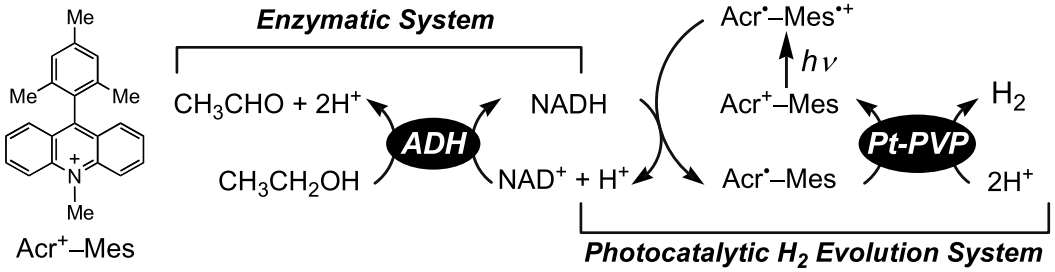
Bioinspired Artificial Photosynthetic Systems

The rapid consumption of fossil fuel has caused unacceptable environmental problems such as the greenhouse effect, which may lead to disastrous climatic consequences. Now renewable and clean energy resources are definitely required in order to deal with such global energy and environmental issues. Nature harnesses solar energy with photosynthesis for its production tasks, and fossil fuel is the product of photosynthesis. Thus, it is highly desirable to develop artificial photosynthetic systems for the production of hydrogen or other fuels by exploiting and applying the basic chemistry of photosynthesis, hopefully in a more efficient manner than natural systems.

We have been developing bioinspired artificial photosynthetic systems and working towards their application. First, multi-step electron-transfer systems composed of electron donor-acceptor ensembles were constructed, mimicking functions of the photosynthetic reaction center. However, a significant amount of energy is lost during the natural multi-step electron-transfer processes. As an alternative to conventional charge-separation functional molecular models based on multi-step long-range electron transfer within redox cascades, simple electron donor-acceptor dyads linked by covalent or non-covalent bonding have been developed to attain a long-lived and high-energy charge-separated state without significant loss of excitation energy. Such simple molecular dyads, capable of fast charge separation but extremely slow charge recombination, have significant advantages with respect to synthetic feasibility, providing a variety of applications including the construction of organic solar cells and the development of efficient photocatalytic systems for solar energy conversion.

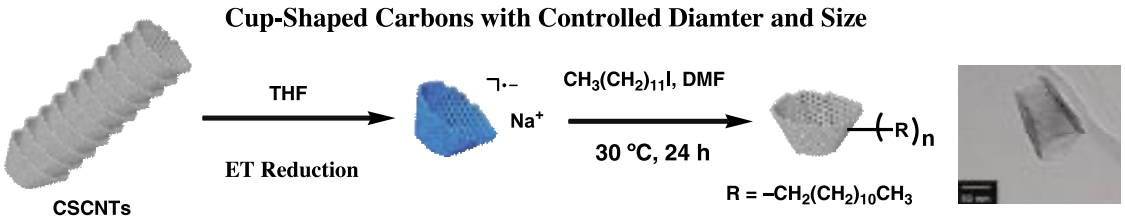
Highly efficient photocatalytic hydrogen-evolution systems *without electron mediators* such as methyl viologen (MV^{2+}) have been constructed using 9-mesityl-10-methylacridinium ion (Acr^{+}–Mes), poly(*N*-vinyl-2-pyrrolidone)-protected platinum nanoclusters (Pt-PVP) and NADH (*β*-nicotinamide adenine dinucleotide, reduced form), and these have been used as a photocatalyst, a hydrogen-evolution catalyst and an electron donor, respectively. The electron donor (NADH) is replaced by ethanol in the presence of the alcohol dehydrogenase (ADH) by which NADH is regenerated in photocatalytic hydrogen evolution.

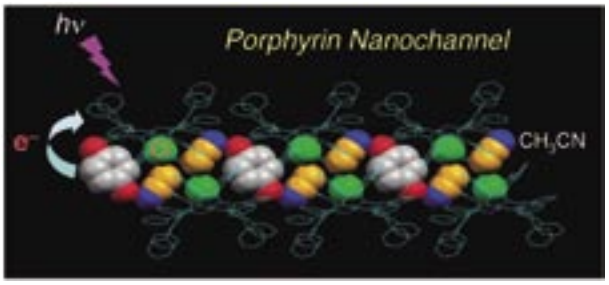


Novel organic solar cells have also been prepared using the quaternary self-organization of porphyrin (donor) and fullerene (acceptor) dye units by clusterization with gold nanoparticles on SnO_2 electrodes. The energy conversion efficiency of the OTE/SnO_2/ $(H_2PC15MPC+C_{60})_m$ electrode reaches as high as

1.5%, a value 45 times higher than that of the reference system.

Development of New Photofunctional Nanomaterials





We have developed new photofunctional nanomaterials. For example, the electron-transfer reduction of cup-stacked carbon nanotubes (CSCNTs) with sodium naphthalenide and their subsequent treatment with 1-iodododecane results in electrostatically destacking the CSCNTs to yield cup-shaped carbons with controlled diameter and size. Such nanocarbon materials can be readily functionalized with porphyrins. We have also developed a "porphyrin nanochannel" composed of a hydrochloride salt of a saddle-distorted dodecaphenylporphyrin (H_2DPP), [H_4DPPP]Cl_2 and electron donors. The porphyrin nanochannel provides an excellent opportunity to construct and develop porphyrin-based photofunctional materials.

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