Mechanistic aspects of solar energy harvesting with organic heterocycles

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Impressive progress has recently been achieved in photocatalytic water splitting with organic polymers consisting of pyridine, *s*-triazine or heptazine (tri-*s*-triazine) building blocks.[1,2] In addition to efficient hydrogen evolution in the presence of sacrificial electron donors, stoichiometric splitting of pure water with visible light has been reported.[3] However, the fundamental mechanistic principles of the photoinduced reaction and the catalytic cycle are currently not understood.

We have recently obtained first-principles computational evidence that water splitting with organic heterocycles can be understood as a molecular photochemical reaction taking place in hydrogen-bonded chromophore-water complexes [4,5]. Water is oxidized homolytically by a light-driven electron transfer from water to the chromophore, followed by proton transfer. Via a conical intersection of the potential-energy surface of the resulting charge transfer state with the electronic ground state, pyridinyl, triazinyl or heptazinyl radicals and OH radicals are generated in their electronic ground states. It is shown that the excess hydrogen atom of the chromophore radicals can be photodetached by a second photon, which regenerates the chromophores. A water molecule is thus catalytically decomposed into H and OH radicals in a biphotonic process (sequential absorption of two photons). The proposed photochemical reaction scheme within hydrogen-bonded complexes of heterocycles with water [4,5] is very different from the traditional paradigm of photocatalytic water splitting, which assumes the separation of electrons and holes in semiconducting materials or molecular donor-acceptor complexes over substantial time scales (microseconds) and distances (micrometers) [6].

In the second part of the talk, it is shown that the biphotonic reaction mechanism exists also in hydrogen-bonded clusters of DNA bases with water. We have recently discovered that photoexcited adenine[7], guanine and cytosine can abstract hydrogen atoms from water molecules in hydrogen-bonded clusters, yielding hydrogenated DNA-base radicals. The excess hydrogen atom of these radicals can be photodetached by the absorption of another photon, which regenerates the DNA base. The RNA/DNA bases may thus have been the photocatalysts for water splitting by UV light at the very beginning of biological photosynthesis.

References

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