Quinones as Reversible Electron Relays in Artificial Photosynthesis

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The ultimate source of electrons for photocatalytic hydrogen production is water. The four-electron oxidation of two H_2O to O_2 involves several steps associated with a high kinetic overpotential. So far, this prevented its widespread use as an electron donor in full, molecular water splitting systems. Therefore, the two half-reactions in artificial photosynthesis are commonly studied using sacrificial agents. On the reductive side, irreversible or semi-reversible electron donors such as tertiary amines or ascorbic acid were applied.[1,2] This practice was established to study the half-reaction individually, without interference of the oxidative side. However, this concept has little practical significance.

In contrast, nature uses a completely reversible electron relay in the form of the hydroquinone/quinone system to shuttle electrons between PSII and PSI.[3] Compared to the oxidized form of tertiary amines and ascorbate, oxidized hydroquinones are excellent electron acceptors, thus efficiently inhibiting any productive electron transfer reactions in the reductive half-reaction to H_2. A photocatalytic proton reduction system featuring a reversible hydroquinone/quinone shuttle system that overcomes this limitation will be presented along with a kinetic analysis of the system elucidating the faith of the quinone species as well as the bottle neck of the system.[4]

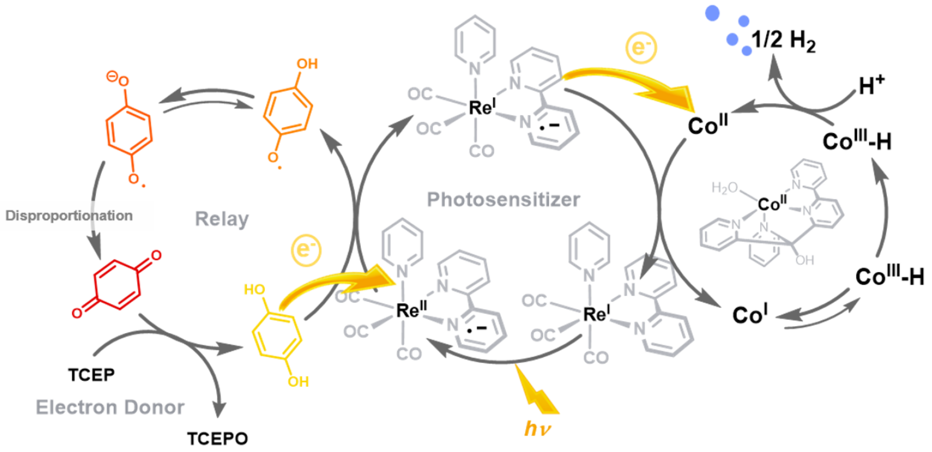

Fig. 1: Reductive half reaction of artificial photosynthesis with TCEP as sacrificial electron donor, a quinone-based relay, a Ru-photosensitizer and a Co-based water reduction catalyst (WRC).

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