

## 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<sub>2</sub>O to O<sub>2</sub> 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.<sup>[1,2]</sup> 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.<sup>[3]</sup> 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<sub>2</sub>. 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.<sup>[4]</sup>

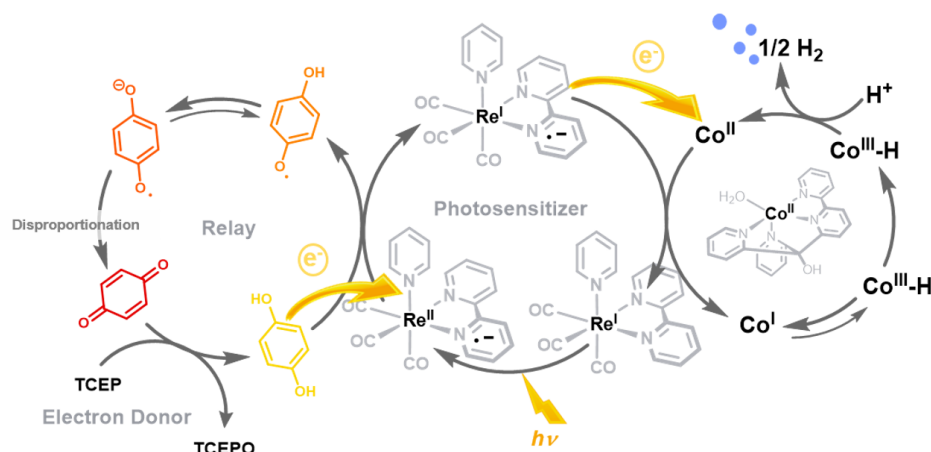


Fig. 1: Reductive half reaction of artificial photosynthesis with TCEP as sacrificial electron donor, a quinone-based relay, a Ru-photosensitizer and a Co-based water reduction catalyst (WRC).

[1] B. Probst, M. Guttentag, A. Rodenberg, P. Hamm, R. Alberto, *Inorg. Chem.*, **2011**, 50, 3404–3412.

[2] M. Guttentag, A. Rodenberg, B. Probst, P. Hamm, R. Alberto et al, *Eur. J. Inorg. Chem.*, **2012**, 2012, 59–64.

[3] S. Berardi, M. Guttentag, C. Richmond, T. Stoll, A. Llobet et al, *Chem. Soc. Rev.*, **2014**, 43, 7501–7519.

[4] A. Rodenberg, M. Oraziotti, M. Mosberger, R. Alberto, P. Hamm et al, *ChemPhysChem*, **2016**, 17, 1321–1328.