Quinones as Reversible Electron Relays in Artificial Photosynthesis

<u>M. Mosberger</u>¹, A. Rodenberg¹, M. Orazietti¹, C. Bachmann¹, B. Probst¹, R. Alberto^{1*}, P. Hamm^{1*}

¹University of Zurich, Winterthurerstrasse 190, 8057 Zurich.

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 hydroguinones are excellent electron acceptors, thus efficiently inhibiting any productive electron transfer reactions in the reductive halfproton system photocatalytic reduction reaction to H_2 . А featuring а reversible hydroguinone/guinone shuttle system that overcomes this limitation will be presented along with a kinetic analysis of the system elucidating the faith of the guinone species as well as the bottle neck of the system.^[4]

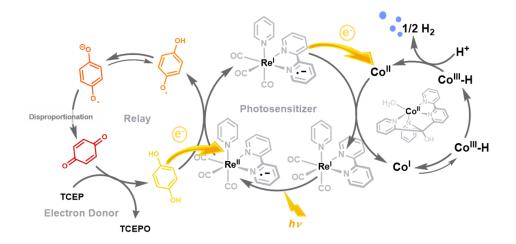


Fig. 1: Reductive half reaction of artificial photosynthesis with TCEP as sacrificial electron donor, a quinone-based relay, a Ru-photosensitizer and a Co-based water reduction catalyst (WRC).

[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. Orazietti, M. Mosberger, R. Alberto, P. Hamm et al, *ChemPhysChem*, **2016**, 17, 1321-1328.