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#### ACCEPTED MANUSCRIPT

# Unravelling electron transfer processes at photosystem 2 embedded in an Os-complex modified redox polymer

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#### **Abstract**

In the development of semi-artificial biophotovoltaic assemblies, deeper understanding of electrochemical processes is required to achieve functional and efficient devices. Evaluation of photosystem 2 embedded in an Os-complex modified redox polymer using scanning photoelectrochemical microscopy (SPECM) provides insight into the intricate electrochemical processes of the immobilized protein complex and its electrical communication pathways with the redox tethers of the polymer matrix. The use of local irradiation during a SPECM array scan prevents sample inactivation prior to analysis. Moreover, the simultaneously possible collection of partially reduced oxygen species in the form of hydrogen peroxide confirms the presence of competing charge transfer pathways involved in the reduction of oxygen at the chlorophyll pigments upon irradiation of the sample. In addition, evaluation of photocurrent in the presence of an inhibitor that blocks the terminal plastoquinone Q<sub>B</sub> binding site of the photosystem reveals electrochemical communication between the intermediate plastoquinone Q<sub>A</sub> and the redox polymer. The obtained information proves to be relevant for further design and optimization of devices for technological applications.

**Keywords:** scanning (photo)electrochemical microscopy, photosystem 2, redox polymers, biophotovoltaics, DCMU

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