Chemical Probes for Water-Oxidation: Synthetic Manganese Complexes in Photoactivation of Water Splitting Complex and as Exogenous Electron Donors to Photosystem II

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Photoactivation of the water splitting enzyme was performed with 13 different synthetic manganese complexes and characterized by oxygen evolution yield, thermoluminescence and chlorophyll fluorescence induction kinetics. The efficiency of different compounds in photoactivation correlated with the rate of linear electron transport in the presence of these compounds. The organic ligands, associated with the manganese ions, do not prevent the photoactivation of the water splitting complex (WOC). Photoactivation with different manganese complexes depended on the number of the Mn-ions in the complex, their valence state and the nature of their donor atoms. The most efficient restorations were achieved by using tetrameric complexes having a dimer+dimer structure, complexes containing Mn(II) ions, and having 4–6 oxygen and 0–2 nitrogen atoms as donor atoms. Further, the effectiveness of photoactivation depended largely on the structure of the complexes. Our data support the notion that WOC in intact thylakoids requires the cooperation and well determined arrangement of all four manganese ions, and argue against the hypothesis that two manganese ions are sufficient for water splitting. Photoactivation by some complexes led to anomalous flash-oxygen patterns, which are explained by a modified/perturbed water splitting complex.