## Exploring the molecular mechanisms of photosynthesis by ab initio molecular dynamics

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The understanding of the molecular mechanisms and the catalytic strategies photosynthetic proteins in plants and bacteria offers many challenges to theoretical biophysicists. These mechanisms includes the capture of light by antenna systems, the primary charge separation that convert the photon energy into chemical energy, and the subsequent cascade of biochemical processes leading to the formation of stable high-energy organic products that can be stored in the living organisms. One fundamental step of such mechanisms is the conversion of the electronic excitations into chemical energy used to perform the light-driven transformation of water molecules into molecular oxygen and hydrogen equivalents, i.e. water splitting. This water oxidation in photosynthetic organisms occurs through a series of intermediate steps S0-S4 of the so-called Kok-Joliot's cyle in the Oxygen Evolving Center of Photosystem II (PSII), recently crystallised at atomic resolution [1]. The four electrons necessary for the water splitting reaction are subsequently removed by a radical tyrosine (Tyrz) from the Mn<sub>4</sub>CaO<sub>5</sub> core, where they are accumulated to perform the more difficult catalytic step: the formation of molecular oxygen. Beyond their interests in biophysics, the comprehension of photosynthetic water splitting mechanisms may also inspire artificial devices [2,3].

By means of Quantum Mechanics / Molecular Mechanics (QM/MM) calculations, we were able to rationalize previously puzzling experiment [4,5] and to understand the complex proton-coupled-electron-transfer mechanisms along the way to water spitting [6]. In the present contribution we will focus on the very early events following the first charge separation which is occurring in the so-called P680 complex, composed by two four chlorophylls which have a twofold pseudo-symmetry. The photo-induced electron transfer is supposed to leave an oxidising hole shared between two particular chlorophylls,  $P_{D1}$  and  $P_{D2}$ , which form the so-called "special pair" of chlorophylls of PSII. This charged pair of chlorophylls is known to be stable for about a hundred of ns before in turn it oxidizes in normal conditions one of the two pseudo-symmetry in the charge distribution of the oxidised special pair, in agreement with several experiments. We have also characterised the origin and the dynamics of this asymmetry, pointing out the key role of the mutual orientation of the chlorophylls and of the protein environment.

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## Figure

Quantum Mechanics / Molecular Dynamics simulation of the special pair of chlorophylls of Photosystem II.