In silico study of reaction mechanisms and design principles for water oxidation catalysts

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SUMMARY

One of the key processes for sustaining life on earth is photosynthesis. In this process the sunlight, using water and carbon dioxide as raw materials, is converted into chemical energy and stored as carbohydrates. Mimicking the water oxidation reaction in an artificial device in order to be able to convert the sunlight in carbon-neutral fuels is considered one of the most important challenges for solving the world-wide energy and environmental problems. For this reason during the last decades the scientific effort on water splitting has been growing. During the first attempts the scientific community tried to understand and reproduce properly the natural oxygen evolving complex (OEC) of photosystem II, using the same kind of structure and metallic atoms. Over time other metals started to be used, as well as complexes with less than four metallic centers. Nowadays the knowledge of the process is much improved and it is possible to find mono-nuclear catalysts, while a broad range of atoms can be used as metallic centers. In my thesis I show the contribution of various computational methods for gaining understanding of the process and in

the development of new catalysts to optimize the water oxidation reaction.

In the introductory chapter a broad perspective on the photosynthetic process, emphasizing the role of the OEC, is presented. Also relevant literature information about the artificial devices and the different water oxidation catalysts is summarized. Then, in chapter **2**, the theoretical background of all methods used in this thesis is discussed.

The next two chapters contain a detailed study of the reaction pathways for two different classes of catalysts. In chapter **3** a di-manganese catalyst presented several years ago by Limburg *et al.* is studied. This work is performed with some of the most advanced molecular dynamics tools in order to obtain profound understanding of the catalysis mechanism. It is shown how a structural rearrangement, which takes place before the expected oxygen-oxygen bond formation, leads to an intermediate complex in which the two metallic centers are linked only by one oxygen bridge. This transient complex appears to be able to catalyze the water oxidation reaction. Also the possible mechanism involving this newly discovered intermediate is presented, pointing to the second oxyl radical as the proton acceptor that mediates the oxygen-oxygen bond formation reaction. Next, in chapter **4**, the catalyst analyzed is the $[(\text{benzene})\text{Ru}(\text{O})(\text{bpy})]^{2+}$. Two different possible reaction pathways are investigated. Based on the *in silico* studies it can be concluded that the pathway in which the incoming

water molecule first becomes a ligand of the metallic center, leading to a heptacoordinated intermediate, is not suitable. Instead the direct reaction between the oxo-ligand and the reactant water molecule is the most appropriate for this catalyst. This chapter also shows that including an explicit solvent environment in the simulations is crucial to reproduce properly the reaction pathway and the intermediates.

In chapter **5**, the same family of catalysts as in chapter **4** is used. This time a thermodynamic study is performed. From these calculations the free-energy profile for the whole catalytic cycle and the overpotential are obtained for each catalyst. This overpotential can be of use as it is one of the parameters that measures the performance of the catalyst. From this study it could be concluded that $[(cymene)Ru(OH_2)(bpy)]^{2+}$ represents the best option among the water oxidation catalysts of this class, followed closely by the $[(cymene)Mn(OH_2)(bpy)]^{3+}$. The second one, may be a very promising candidate for being part of an “artificial leaf”, due to the large earth abundance of the Mn metal.

Finally, in chapter **6**, a brief future perspective about the remaining open questions and the possible methodology that could be used for going deeper into the research is given.