POLYMORPHISM AND CATALYTIC CONTROL IN BIOLOGICAL WATER OXIDATION

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The complexity of the geometric and electronic structure of the natural water oxidizing complex, a tetramanganese–calcium cluster embedded in Photosystem II, combined with the absence of direct observations on catalytically active intermediates, means that very few mechanistic aspects of biological water oxidation are sufficiently well understood.[1] Physical methods that report on the local electronic structure of the catalyst have been the primary and most reliable source of information on the semi-stable "pre-catalytic" states of the catalyst. However, it is only in recent years that this information has been cast into atomistic structural models and transformed into actual knowledge.[2–5] This transformation was made possible by the development of quantum chemical methods and models that focus on magnetic and spectroscopic observables relating to spin states, EPR parameters, optical absorption profiles, and X-ray absorption spectroscopy, in combination with critical analysis of structural data from crystallography and EXAFS regarding the architecture of the enzyme. Here I will discuss the fundamental contributions of quantum chemistry in uncovering a fundamental feature of biological water oxidation, a form of structural polymorphism that is functionally crucial in controlling and directing reactivity.[6–7] These studies manage to unify disparate experimental observations and revise previous computational models of reactivity that neglected spectroscopic constraints.

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