

## Double hybrid density functional calculations of the $\text{CaMn}_4\text{O}_5$ cluster in the $S_3$ state of oxygen evolving complex in photosystem II

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Double hybrid density functional theory (DFT) calculations under the broken-symmetry (BS) approximation have been performed for elucidation of several reaction intermediates<sup>1)</sup> consisted of the  $\text{CaMn}_4\text{O}_5$  cluster and amino acid residues in the  $S_3$  state of oxygen evolving complex (OEC) of photosystem II (PSII). Full geometry optimizations of the intermediates were performed with BS UB3LYP/DZVP method and total energies were calculated with double hybrid BS DFT/TZVP method. The relative stabilities of the intermediates in OEC of PSII were found to be variable with the weights of MP2 and van der Waals components in the double hybrid DFT scheme, indicating characteristic behaviors of strongly correlated electron systems (SCES) where orbital, spin and charge degrees of freedom play important roles for reasonable descriptions of the electronic and spin states. Implications of the computational results are discussed in relation to possible mechanisms of the O-O bond formation in water oxidation in OEC of PSII.

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2) H. Isobe, M. Shoji, J.-R. Shen, K. Yamaguchi, *Inorg. Chem.*, **55**, 371 (2016).