Large-scale QM/MM calculations of the $CaMn_4O_5$ cluster in the oxygen evolving complex of photosystem II: comparisons with EXAFS structures

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Large-scale QM/MM calculations were performed to elucidate the optimized geometric structures of the $CaMn_4O_5$ cluster in the S_i (i = 0-3) states of the oxygen evolving complex (OEC) of photosystem II (PSII). The optimized Mn-Mn, Ca-Mn and Mn-O distances by the QM/MM starting from the high-resolution XRD structure were consistent with those of the EXAFS experiments by the Berkeley and Berlin groups. The QM/MM calculations removed out the significant discrepancy among the XRD, XFEL and EXAFS, providing an extended trimer model that was applicable for explanation of the recent EPR results.

In the first MD refinement procedure, we performed a simulated annealing run to construct the hydrogen bond networks around the OEC. We then cut out a spherical region for the hybrid quantum mechanics/molecular mechanics (QM/MM) calculations with a 30 Å radius around the $O_{(5)}$ atom in the OEC. The QM/MM model contains about 380 QM atoms and about 17,000 MM atoms as shown in the poster. The hybrid DFT (UB3LYP) with basis set I; LANL2DZ for Mn and Ca; 6-31G(d) for C, H, O and N was used for the QM part, and the AMBER-99 force field was applied for the MM part. An electronic embedding scheme was adopted, hydrogen link atoms were used for the QM-MM boundary, and no cut-off for the non-bonded interactions was used in the QM-MM interactions. During the QM/MM energy minimization procedure, all the atoms within 18 Å distances around a QM center (original $O_{(5)}$ position in the OEC) were allowed to move, while all other atoms remained frozen.

The NWChem 6.1 program package was used for all the QM/MM calculations at IMS, Riken and Tsukuba University. More details of the QM/MM model are given in the paper [1].

[1] M. Shoji, *Molecular Physics*, 113, 359 (2015).