

# The Electronic Structures of active site of Sweet Potato

## Purple Acid Phosphatase

*Kenichi Koizumi,<sup>\*</sup> <sup>a,b</sup> Kizashi Yamaguchi,<sup>c</sup> Haruki Nakamura,<sup>b</sup> and Yu Takano<sup>b</sup>*

<sup>a</sup> Japan Biological Information Research Center, Aomi, Koto-ku, Tokyo 135-0064,  
Japan

<sup>b</sup> Institute for Protein Research, Osaka University, Suita, Osaka 565-0871, Japan

<sup>c</sup> Center for Quantum Science and Technology under Extreme Conditions, Osaka  
University, Toyonaka, Osaka 560-8531, Japa

E-mail: [koizumi@protein.osaka-u.ac.jp](mailto:koizumi@protein.osaka-u.ac.jp)

Purple acid phosphatase (PAP) catalyzes the phosphate ester under acidic condition (pH range from 4 to 7), which includes a binuclear metal center. The enzymes distinguished from other acid phosphatase by their characteristic purple color, due to the presence of a tyrosine residue ligated to ferric iron. The purple color is due to charge transfer between Fe(III) and tyrosine residue occurring at around 560 nm. The mammalian PAPs are regarded as target proteins for the treatment of osteoporosis. The bridging ligand between a Fe–Mn binuclear metal center is suggested to be nucleophile in the reaction. Therefore, the type of bridging ligand is essential for discussing the reaction mechanism. Strong antiferromagnetic coupling indicated a  $\mu$ -oxo bridge in sweet potato PAP in spite of  $\mu$ -hydroxo bridge centers of other PAPs. In this study, the electronic structure and magnetic interaction of the active site of sweet potato PAP have been studied using the hybrid DFT methods (UB3LYP and UB2LYP). UB3LYP showed reasonably good agreement with the experimental magnetic coupling constant. Calculation results clearly indicated a  $\mu$ -oxo bridge in the binuclear center. Analyses of natural orbitals and spin density distribution implied the asymmetric spin delocalization on the bridging oxygen. The mechanism and pathway of antiferromagnetic interaction between Fe(III) and Mn(II) were discussed using chemical indices introduced with the occupation numbers of singly occupied natural orbitals (SONOs).