Hybrid DFT Calculations of Artificial and Native Water Splitting Systems　A Spin Hamiltonian Model for Radical Intermediates

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Abstract

The nature of chemical bonds of putative ruthenium (Ru)-quinine(Q) complex(**1**) mononuclear[Ru(trpy)(3,5-t-Bu_2Q)(OH_2)(trpy=2,2':6',2''-terpyridine, 3,5-di-tert-butyl -1,2-benzoquinone)(**2**) and binuclear [Ru_2(btpyan)(3,6-di-Bu_2Q)$_2$(OH_2)](SbF_6)$_2$ (btpyan= 1,8-bis(2,2':6',2''-terpyrid-4'-yl)anthracene,3,6-t-Bu_2Q=3,6-di-tert-butyl-1,2-benzoquin one) (**3**) were investigated by broken-symmetry (BS) hybrid density functional (DFT) methods. BS DFT computations for **3** have elucidated that the closed-shell structure (**3b**): Ru(II)-quinone (Q) complex is less stable than the open-shell structure (**3bb**) consisted of Ru(III) and semiquinone (SQ) fragments. These computations have also elucidated eight different electronic and spin structures of tetraradical intermediates generated in the course of water splitting reaction. The Heisenberg spin Hamiltonian model for these species has been derived to elucidate six different effective exchange interactions (J) for four spin systems. Six J values have been determined using total energies of the eight (or seven) BS solutions for different spin configurations. The natural orbital analysis of these BS DFT solutions have also been performed to elucidate the natural orbitals and their occupation numbers that are useful for lucid understanding of the nature of chemical bonds of these Ru complexes (**1**, **2** and **3**). Implications of the computational results are discussed in relation to proposed reaction mechanisms of water splitting reaction in artificial photosynthesis systems, and similarity between artificial and native water splitting systems [1,2].

1)　words: Ruthenium complexes, Artificial and native models, Water splitting reaction, Spin Hamiltonian, Radical Intermediates