

# A Density Functional Theory Based Protocol to Compute the Redox Potential for Transition Metal Complexes

Toru Matsui<sup>1,2</sup>, Yasutaka Kitagawa<sup>1</sup>, Yasuteru Shigeta<sup>3</sup>, and Mitsutaka Okumura<sup>1</sup>

<sup>1</sup> Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, 560-0043 Japan.

<sup>2</sup> Advanced Institute for Computational Science, RIKEN, Kobe, 650-0047, Japan

<sup>3</sup> Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, Toyonaka, 560-8531 Japan.

E-mail: toru.matsui@riken.jp

Toward the design of new materials at molecular level, it is helpful to understand the property of a single molecule. The redox potential is one of the most fundamental quantities of transition metal complexes (TMCs), which clarifies whether the target molecule can easily take an electron or not. The importance of measuring the redox potential of TMC is not limited to inorganic chemistry. The redox potential is one of the key information for a metal cluster to understand its catalytic property. It is also meaningful to investigate the redox potential of significant metallo-proteins, which play a crucial role for electron transfer process in biomolecules.

Recently, we have proposed a scheme to evaluate redox potential of a wide variety of transition metal complexes by adding a charge-dependent correction term for a counter ion around the charged complexes, which is based on Generalized Born theory, to the solvation energy [1]. The mean absolute error (MAE) toward experimental redox potentials of charged complexes is considerably reduced from 0.81 V (Maximum error 1.22 V) to 0.22 V (Maximum error 0.50 V). We found a remarkable exchange-correlation functional dependence on the results rather than the basis set ones. Moreover, long-range corrected (LC)-DFT well reproduces the experimental standard hydrogen electrode potentials (4.44 V).

The combination of Wachters+f (for metal) and 6-31++G(d,p) (for other atoms) with the B3LYP functional gives the least MAE 0.15 V for the test complexes. This scheme is applicable to other solvents, and heavier transition metal complexes such as  $M_1(\text{CO})_5(\text{pncn})$  ( $M_1=\text{Cr, Mo, W}$ ),  $M_2(\text{mnt})_2$  ( $M_2=\text{Ni, Pd, Pt}$ ), and  $M_3(\text{bpy})_3$  ( $M_3=\text{Fe, Ru, Os}$ ) with the same quality.

## References

[1] T. Matsui, Y. Kitagawa, Y. Shigeta, and M. Okumura, *J. Chem. Theory Comput.* 9: 2974, 2013.