

## Quantum Chemical Calculations of Cobalt Phthalocyanines: Electrocatalysis for the O<sub>2</sub> Reduction

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Complexes comprised of phthalocyanine and a transition metal in center macro-cyclics have been expected as cathode catalysts in the air electrode, because a few metallo-macrocyclic complexes are known to reduce O<sub>2</sub> to water by the direct four-electron steps. Recently, we found that the catalytic system comprised of phthalocyanines with the electron-withdrawing groups such as cyano group (CoPc(CN)<sub>8</sub>) is able to promote the electro-reduction of O<sub>2</sub>. [1-3] Although some mechanistic interpretations of the catalytic activity for the O<sub>2</sub> reduction have been proposed, it is not clear yet. In order to clarify the electrocatalytic reduction of O<sub>2</sub> by cobalt phthalocyanines, we carried out the molecular orbital calculations by the density functional theory (DFT) for substituted cobalt phthalocyanines. The structures of substituted phthalocyanines are shown in Figure 1. All calculations were carried out by B3LYP/LANL2DZ level on Gaussian 03 program package.

The optimized calculations suggest that the unsubstituted CoPc keeps the D<sub>4h</sub> symmetry, while substituted CoPcs possess the D<sub>2h</sub> symmetry due to Jahn-Teller effect. The SOMO levels of Co(II)Pc series lie in lower level by increasing the property of electron withdrawing, as shown in Figure 2. Co(II)Pc(CN)<sub>8</sub> can be expected to have the highest electro-activity for the O<sub>2</sub> reduction. This trend was also observed for Co(I)Pc series. These calculated results demonstrate that the redox potentials for CoPcs shift to more positive potentials with increasing the property of electron-withdrawing. The plot of the redox potential vs. SOMO level gave a good correlation as shown in Figure 3. The SOMO levels of Co(II)Pc series are located in lower level than those of Co(I)Pc series. The SOMO-SOMO gap between Co(II)Pc series and O<sub>2</sub> becomes smaller as the intensity of the electron-withdrawing becomes stronger. So CoPcs with strong electron-withdrawing groups such as Co(II)Pc(CN)<sub>8</sub> may easily interact with oxygen molecule. The present results support previous experimental results that Co(II)Pcs with strong electron-withdrawing groups (e.g. -CN) may interact favorably with oxygen molecule and promote the O<sub>2</sub> reduction.

### References:

- [1] K. Arihara, L. Mao, P. A. Liddell, E. Marino-Ochoa, A. L. Moore, T. Imase, D. Zhang, T. Sotomura, T. Ohsaka, *J. Electrochem. Soc.*, in press.
- [2] L. Mao, K. Arihara, T. Sotomura, T. Ohsaka, *Chem. Commun.*, 2818 (2003).
- [3] L. Mao, K. Arihara, T. Sotomura, T. Ohsaka, *Electrochim. Acta*, **49**, 2515 (2004).

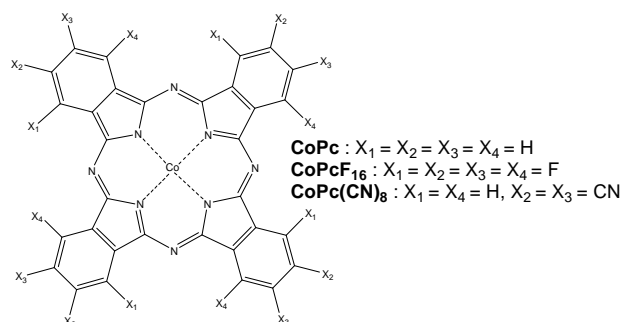


Figure 1. Chemical structures of CoPcs.

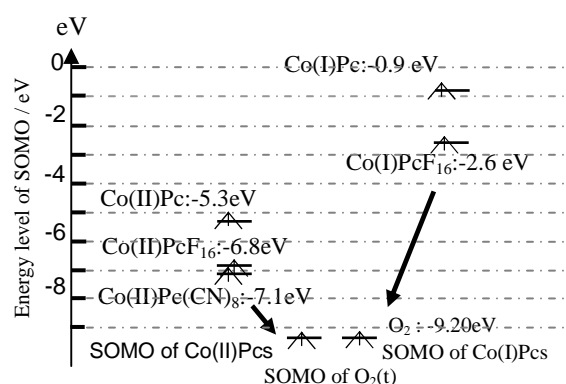


Figure 2. SOMO levels of Co(II)Pc series, Co(I)Pc series, and triplet O<sub>2</sub> molecule calculated by B3LYP/LANL2DZ.

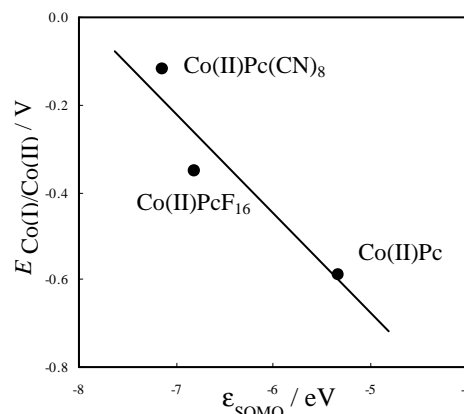


Figure 3. Plot of Co(II)/Co(I) redox potentials of CoPcs vs. the energy of the SOMO of Co(II)Pcs.