Substituent Effects of Bipyridine Ligands on Oxygen Reduction Reaction Catalyzed by Dinuclear Cobalt Complexes

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Four-electron oxygen reduction reaction (4e$^-$-ORR) is a key step of natural and artificial energy conversion systems. In nature, cytochrome *c* oxidase containing Fe-Cu dinuclear complex as an active center efficiently catalyzes 4e$^-$-ORR in the respiration process. Therefore, the studies of ORR catalyst based on transition-metal complex has been of interest over the past few decades.[1] Previously, we reported dinuclear cobalt polypyridyl complexes bridged by xanthene (**1**), anthraquinone and anthracene[2] as effective 4e$^-$-ORR catalysts. Among them, **1** indicated the highest selectivity (96%) and TOF (5.6×10^2 s^{-1}) for chemical 4e$^-$-ORR. However, **1** required relatively large overpotential of 630 mV for electrochemical ORR.

In this paper, we discuss effects of bipyridine substituents on electrochemical ORR catalyzed by dinuclear cobalt complexes bridged by 1,8-bis(terpyridyl)xanthene (**1**-**6**, Figure 1). Linear sweep voltammetry (LSV) using the complex catalyst modified on glassy carbon (GC) as a working electrode in O_2-saturated phosphate buffer (pH 1.0) showed a catalytic wave at the potential under 0.27 (**1**), 0.24 (**2**), 0.27 (**3**), 0.26 (**4**), 0.23 (**5**), 0.32 (**6**) V vs. SCE (Figure 2). The onset potantial of **6** was more positive than those of **1**–**5**, suggesting that overpotential of ORR was affected by proton relay rather than electron-donating and -withdrawing effects of bipyridine ligands.

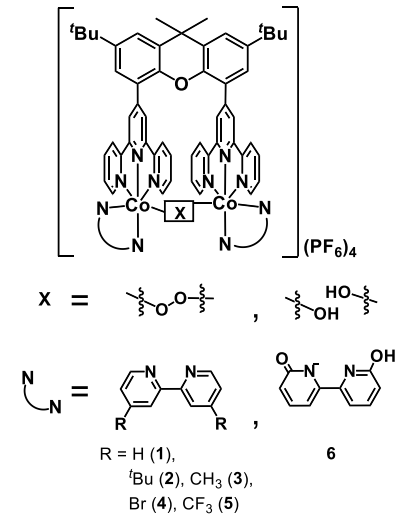

Figure 1. Structures of the xanthene-bridged dinuclear cobalt polypyridyl complexes.

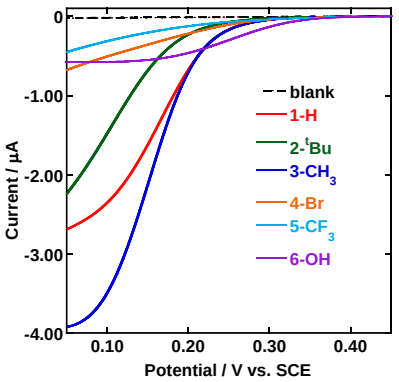

Figure 2. LSVs using a GC modified with complex catalysts (3.0 nmol cm^{-2}) in O_2-saturated phosphate buffer (pH 1.0). Scan rate: 10 mV s^{-1}.

References

1) M. L. Pegis, C. F. Wise, D. J. Martin, J. M. Mayer, *Chem. Rev.* **2018**, *118*, 2340.
2) T. Wada, H. Maki, T. Imamoto, H. Yuki, Y. Miyazato, *Chem. Commun.* **2013**, *49*, 4394.