

Electrochemical Polymerization and Electrocatalytic Water Oxidation of a Carbazole-Tethered Cobalt Phthalocyanine

(¹Graduate School of Engineering, Osaka University, ²JST PRESTO)

○ Li Shangxing,¹ Hikaru Iwami,¹ Mio Kondo,^{1,2} Shigeyuki Masaoka¹

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Increasing energy requirement and environment awareness have promoted extensive research on the development of alternative energy conversion with high efficiency. As a key reaction in such schemes, four electron oxidation of water ($2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$) is critical for artificial photosynthesis. In nature, this reaction is efficiently catalyzed in photosystem II in cooperation of the catalytic center and charge transporters. However, the development of artificial catalytic systems for water oxidation in which the catalytic center is surrounded by charge transporters remains challenging.

In this context, we have previously reported electrocatalysts that successfully integrate catalytic centers and charge transporters into a single system.¹⁾ In this study, we extended our approach to phthalocyanine derivatives. A carbazole-tethered cobalt phthalocyanine complex **Co(czPc)** was synthesized and characterized by elemental analysis and some spectroscopic techniques.

Co(czPc) polymerized by electrochemical oxidation via the dimerization of carbazole moiety to afford a polymeric material, **poly-Co(czPc)**. UV-Vis-NIR absorption measurement suggested that *J* aggregation of the phthalocyanine core in the polymer state. Subsequently, the effect of the introduction of biscarbazole group was analyzed by electrochemical impedance spectroscopy. As a result, **poly-Co(czPc)** exhibited high charge transporting ability compared with drop-casted **Co(tBuPc)**, which does not possess biscarbazole moieties. In addition, **poly-Co(czPc)** showed catalytic ability for the electrochemical water oxidation reaction in neutral buffer solution, and the product of the reaction was determined to be dioxygen by gas chromatography. Moreover, **poly-Co(czPc)** produced larger amount of the product and Faradaic efficiency than nonpolymeric system, **Co(tBuPc)**. The present study showed that the introduction of conductive backbone into molecule-based catalysts can enhance their catalytic ability, and this strategy has wide applicability to molecular catalysts.

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- 2) S. Li, H. Iwami, M. Kondo, S. Masaoka, *submitted*.

