Electrochemical and Photochemical CO₂ Reduction by Rhenium Porphyrin Complexes

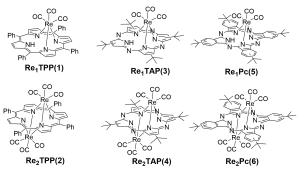
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CO₂ reduction has attracted much attention as it enables to convert CO₂ to useful chemicals and construct sustainable carbon neutral system. Rhenium-bipyridine complexes have been reported to exhibit catalytic activity in the electrochemical and photochemical CO₂ reduction.^{1),2)} In those cases, the tricarbonyl rhenium(I) ([Re(CO)₃]⁺) unit is regarded as important roles in the expression of the catalytic activity. Meanwhile, porphyrinic complexes such as metalloporphyrins and metallophthalocyanines have been also known to work as catalysts for the CO₂ reduction.³⁾ The large π -conjugated system of the macrocyclic ligands could contribute to catalyze the reaction at low overpotentials.

In this study, we investigated the catalytic activities toward the electrochemical and photochemical CO_2 reduction of the 6 complexes constituted by a combination of the $[Re(CO)_3]^+$ unit(s) and the porphyrinic ligand (TPP: tetraphenylporphyrin, TAP: tetraazaporphyrin, Pc: phthalocyanine).⁴⁾⁻⁶⁾ In the cyclic voltammograms under CO_2

atmosphere, the catalytic currents attributed to the CO_2 reduction were observed in complexes 1 - 5. The large current increase occurred at the second reduction potential in all cases. The catalytic current increased in the order of TAP < Pc < TPP, and with the decreasing number of the [Re(CO)₃]⁺ unit. In addition to these behaviors, the photocatalytic



activities of the rhenium complexes will be discussed in the presentation.

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