Photocatalytic CO_2 reduction by multinuclear rhenium complexes having metal centers separated by various distances

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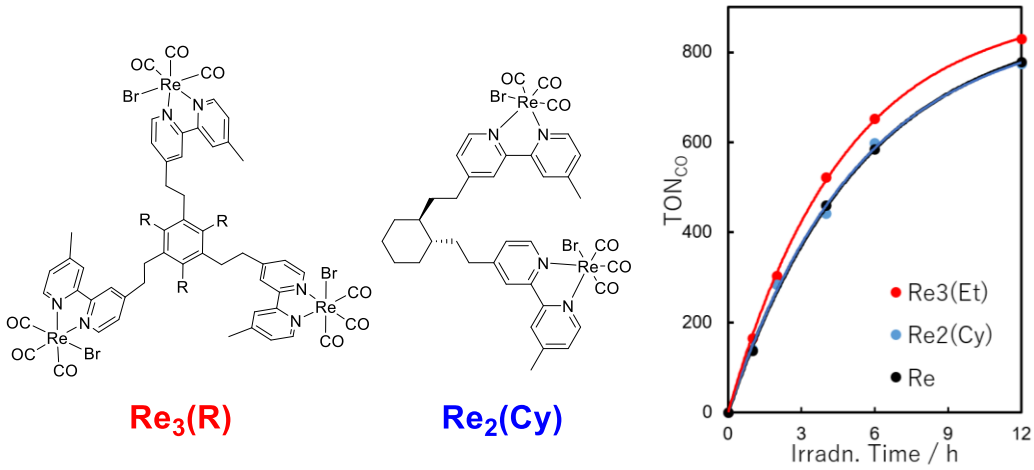
Photocatalytic CO_2 reduction using sunlight can be one of the candidates for building a sustainable society by recycling CO_2 to produce useful carbon compounds. Among photocatalysts for CO_2 reduction, rhenium(I) complexes have been investigated intensively, because they exhibit peculiar properties such as the high efficiency as well as the high selectivity for CO_2 reduction to CO.[1] We have found that some dinuclear rhenium complexes composed of two neighboring metal centers exhibited higher photocatalytic ability for CO_2 reduction. Herein, we will report new multinuclear rhenium(I) complexes having metal centers separated by various distances, such as **Re_3(R)** and **Re_2(Cy)** shown below, with various degrees of restricted conformations due to alkyl chains.

Multidentate ligands, composed of three or two bipyridine units linked with linkers comprising mesitylene, cyclohexane and so on, were synthesized, which were converted into the corresponding multinuclear rhenium(I) complexes. The photophysical, electrochemical, and photocatalytic properties were investigated. The ground state and excited state of multinuclear complexes are comparable to those of the corresponding mononuclear rhenium(I) complex. On the other hand, these multinuclear complexes displayed different CO_2 reduction performance under and electrochemical and photocatalytic conditions. For example, these complexes could reduce CO_2 at a lower overpotential than a mononuclear complex. Moreover, under photocatalytic reaction conditions using a photosensitizer absorbing visible light, the photocatalytic CO_2 reduction ability of some multinuclear complexes were found to be higher than a mononuclear complex owing to the proximity of metal centers and the conformation.



1) Kuramochi, Y.; Ishitani, O.; Ishida, H. *Coord. Chem. Rev.* **2018**, *373*, 333–356.