Photochemical CO_2 Reduction by Framework Catalysts Based on Metal Porphyrin Complexes Bearing Pyrene Moieties

([1]*Graduate School of Engineering, Osaka University*, [2]*JST PRESTO*) ○Marc Alec Dominic Ong Yau[1], Kento Kosugi[1], Maho Imai[1], Yutaka Saga[1], Mio Kondo[1,2], Shigeyuki Masaoka[1]
Keywords: CO_2 Reduction, Framework Catalyst, Photochemistry, Porphyrin, Metal Complex

The photochemical reduction of carbon dioxide (CO_2) to value-added carbon products is a promising approach to simultaneously address global environmental and energy demand issues. Therefore, extensive efforts have been made to develop photocatalysts for CO_2 reduction with high activity, selectivity and stability. In this context, molecule-based heterogeneous catalysts have attracted much attention since they satisfy the advantages of both homogeneous and heterogeneous systems. Our group recently introduced the concept of supramolecular framework catalyst[1], which is constructed by the self-assembly of discrete catalyst modules bearing catalytic sites and intermolecular interaction sites via noncovalent interactions, to construct a molecule-based heterogeneous catalyst. In this work, we aim to develop novel supramolecular framework catalysts using copper(II) and manganese(III) porphyrin complexes bearing pyrene moieties as the catalyst modules.

The syntheses started by first synthesizing the free-base porphyrin, 5,10,15,20-tetrakis(4-(7-tert-butyl)pyren-2-yl)phenyl)porphyrin (**HBPPy**). Then, the copper and manganese metals were inserted into **HBPPy**, and the target molecules 5,10,15,20-tetrakis(4-(7-(tert-butyl)pyren-2-yl)phenyl)porphyrinato copper (II), **CuBPPy** and 5,10,15,20-tetrakis(4-(7-(tert-butyl)pyren-2-yl)phenyl)porphyrinato manganese(III) chloride, **MnBPPy** were obtained (Figure a). The obtained complexes were characterized by UV-Vis spectroscopy and elemental analysis. The properties of their crystals were investigated via PXRD and solid-state UV-Vis spectroscopy. Both catalysts exhibited CO_2 reduction activity (CO_2 to HCOOH) under visible-light irradiation (Figure b). Their catalytic activities are comparable to the best-in-class among relevant noble-metal-free catalytic systems.

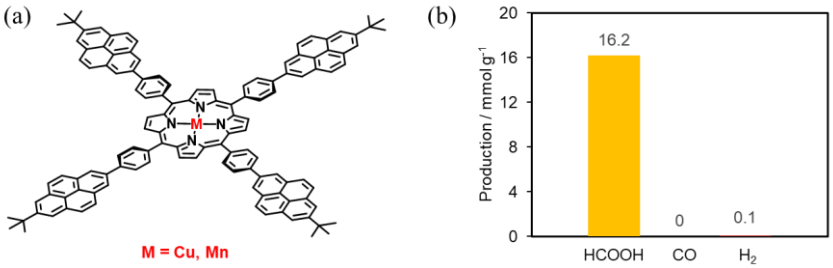

Figure (a) Chemical structure of **MBPPy**. (b) Photochemical CO_2 reduction by **MnBPPy** for 24 h.

References: [1] (a) T. Itoh, M. Kondo, M. Kanaike, S. Masaoka, *CrystEngComm*. **2013**, *15*, 6122. (b) M. Tasaki, Y. Okabe, H. Iwami, C. Akatsuka, K. Kosugi, K. Negita, S. Kusaka, R. Mastuda, M. Kondo, S. Masaoka. *Small*. **2021**, *17*, 2006150.