Electrochemical CO_2 Reduction by a Framework Catalyst Based on Copper Porphyrin Complex Bearing Pyrene Moieties

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The electrochemical 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 catalysts 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 a novel supramolecular framework catalyst using a copper(II) porphyrin complex bearing pyrene moieties as the catalyst modules.

The target molecule **CuBPPy** (Figure a), 5,10,15,20-tetrakis(4-(7-(tert-butyl)pyren-2-yl)phenyl)porphyrinato copper (II), was synthesized by inserting copper into the free-base porphyrin, 5,10,15,20-tetrakis(4-(7-tert-butyl)pyren-2-yl)phenyl)porphyrin (**HBPPy**). By the simple recrystallization in *o*-dichlorobenzene and DMF, the framework catalyst (**FC1**) structure was obtained and its structure was confirmed via X-ray diffraction (Figure b). It was observed that the CH-π interactions between the pyrene units stabilizes the porous structure. Then, the light absorption, gas adsorption, and electrochemical properties of **FC1** were all studied. Finally, the catalytic ability of **FC1** for CO_2 reduction was investigated, both in photochemical and electrochemical systems, and formic acid is observed as the main product.

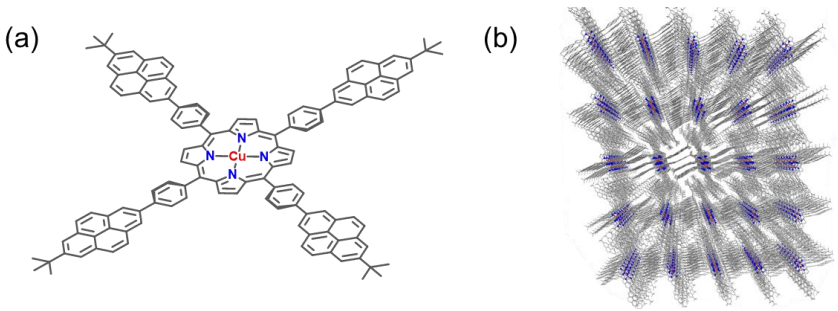

Figure (a) Chemical structure of **CuBPPy**. (b) Framework structure of **FC1**.

References: [1] (a) T. Itoh, M. Kondo, M. Kanaike, S. Masaoka, *CrystEngComm*. **2013**, *15*, 6122. (b) M. Tasaki, M. Kondo, S. Masaoka, et al. *Small*. **2021**, *17*, 2006150. (c) K. Kosugi, M. Kondo, S. Masaoka, et al. *J. Am. Chem. Soc.*, **2023**, *145*, 10451.