

Supramolecular Framework Catalyst Constructed by Iron Porphyrin Complexes for Photochemical CO₂ Reduction

(¹Graduate School of Engineering, Osaka University, ²JST PRESTO) ○ Kento Kosugi,¹ Chiharu Akatsuka,¹ Mio Kondo,^{1,2} Shigeyuki Masaoka¹

Keywords: CO₂ Reduction; Supramolecular Framework Catalyst; Photochemistry; Reaction Field; Porphyrin

Molecule-based porous crystalline photocatalysts without noble metals are one of the most attractive systems for visible-light-driven CO₂ reduction. However, reports on this class of photocatalysts are still limited and their activities are quite low compared to those containing noble metals. Here, we report an iron-complex-based porous crystalline photocatalyst for CO₂ reduction with high activity, selectivity, and stability.

A key to our success is the introduction of the concept of supramolecular framework catalyst,¹ which are constructed by the self-assembly of discrete catalyst modules bearing catalytic site and intermolecular interaction sites via noncovalent interactions. Important feature of supramolecular framework catalysts is that three essential components for light-driven CO₂ reduction,

(i) photosensitizer, (ii) reaction field, and (iii) catalytic sites, can easily be incorporated into their structures in ordered fashion. In this study, we employed **FeBPPy** as a molecular module (Figure 1). **FeBPPy** contains an iron porphyrin scaffold, which can function as a catalytic site for CO₂ reduction, with pyrene moieties, which serve as both light-harvesting units and non-covalent interaction sites, at the *meso* positions. By a simple recrystallization technique, **FeBPPy** are self-assembled into the supramolecular framework catalyst (**FC1**).²

Photocatalytic CO₂ reduction of **FC1** was conducted under visible-light irradiation (400 ≤ λ ≤ 750 nm) in a CO₂ saturated MeCN containing the suspension of **FC1** as a photocatalyst, 0.2 M TFE as a proton source and 0.2 M BIH as a sacrificial electron donor. After 24 h, the formation of CO (697.3 mmol g⁻¹, selectivity 99.9%) was confirmed. The production rate was 29,100 μmol g⁻¹ h⁻¹, which is more than 100 times higher than those of current best-in-class porous-crystalline-solid-based photocatalysts without noble metals. The performance of the **FC1** is also excellent in terms of apparent quantum yield for CO production (0.596% at 400 nm) and stability (up to 96 h).³ The details of the control experiment, durability test, and mechanistic investigation will be discussed in the presentation.

1) T. Itoh, M. Kondo, M. Kanaike, S. Masaoka, *CrystEngComm*. **2013**, *15*, 6122. 2) M. Tasaki, Y. Okabe, H. Iwami, C. Akatsuka, K. Kosugi, K. Negita, S. Kusaka, R. Mastuda, M. Kondo, S. Masaoka. *Small*. **2021**, *17*, 2006150. 3) K. Kosugi, C. Akatsuka, H. Iwami, M. Kondo, S. Masaoka, *submitted*.

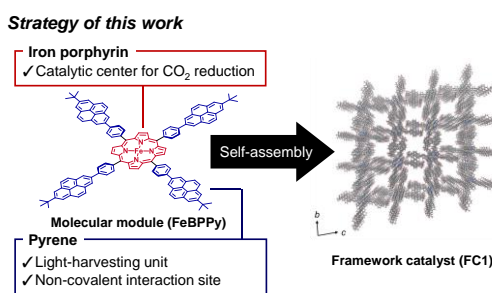


Figure 1. Structure and features of **FeBPPy** and **FC1**.