

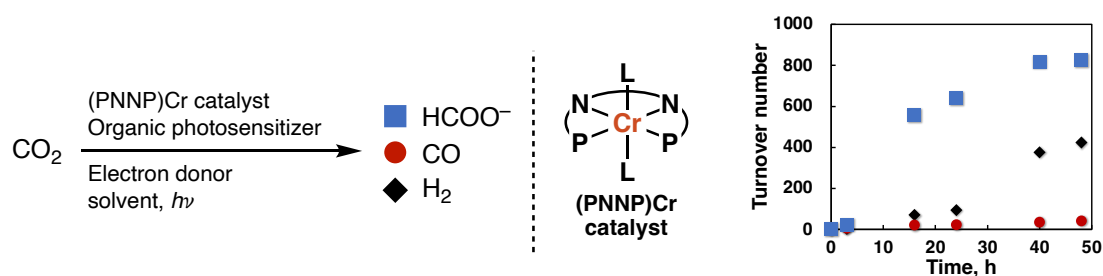
## Earth-Abundant Systems for Photocatalytic CO<sub>2</sub> Reduction using Chromium Complexes Supported by Ferrocenyl Groups for Improving the Performance

(<sup>1</sup>Graduate School of Science, Nagoya University, <sup>2</sup>IMCE, Kyushu University, <sup>3</sup>IRCCS, Nagoya University) ○ Taku Wakabayashi,<sup>1</sup> Jieun Jung,<sup>1</sup> Yohei Kametani,<sup>2</sup> Yoshihito Shiota,<sup>2</sup> Kazunari Yoshizawa,<sup>2</sup> Susumu Saito<sup>1,3</sup>

**Keywords:** Carbon Dioxide, CO<sub>2</sub> Reduction, Chromium Complex, Photocatalysis, DFT Calculation

Solar energy continues to attract attention as it has potential to convert carbon dioxide (CO<sub>2</sub>) into renewable feedstocks, such as carbon monoxide for Fischer-Tropsch chemistry and formic acid for direct formic acid fuel cells. Ideally, this solar-to-fuel conversion should be realized in a catalytic system consisting entirely of inexpensive metals for practical application to industrially viable devices. In this regard, various earth-abundant systems have been reported for photocatalytic CO<sub>2</sub> reduction. On the other hand, only a few reported systems have been known to exhibit catalytic ability for formate production so far.<sup>1</sup>

We previously reported photocatalytic systems for CO<sub>2</sub> reduction using Ir,<sup>2</sup> Ru,<sup>3</sup> and Fe<sup>4</sup> complexes bearing PNNP-type tetradentate ligands, where the bulky PNNP ligands may control the stereochemistry at the central metal. In our subsequent study, we herein introduce the synthesis and application of novel chromium (Cr) complexes bearing ferrocene-attached PNNP-type ligands for photocatalytic CO<sub>2</sub> reduction. By combining Cr complexes with an organic photosensitizer under visible-light irradiation, the earth-abundant photocatalytic systems exhibited conversion of CO<sub>2</sub> into formate with high reactivity and selectivity. To the best of our knowledge, this is the only known Cr homogeneous molecular catalyst for CO<sub>2</sub> photoreduction. The reaction mechanism has been investigated in detail by mechanistic and computational studies.



1) R. Cauwenbergh, S. Das, *Green Chem.* **2021**, 23, 2553. 2) a) K. Kamada, J. Jung, T. Wakabayashi, K. Sekizawa, S. Sato, T. Morikawa, S. Fukuzumi, S. Saito, *J. Am. Chem. Soc.* **2020**, 142, 10261. b) K. Kamada, J. Jung, Y. Kametani, T. Wakabayashi, Y. Shiota, K. Yoshizawa, S. H. Bae, M. Muraki, M. Naruto, K. Sekizawa, S. Sato, T. Morikawa, S. Saito, *Chem. Commun.* **2022**, 58, 9218. 3) K. Kamada, H. Okuwa, T. Wakabayashi, K. Sekizawa, S. Sato, T. Morikawa, J. Jung, S. Saito, *Synlett* **2022**, 33, 1137. 4) T. Wakabayashi, K. Kamada, K. Sekizawa, S. Sato, T. Morikawa, J. Jung, S. Saito, *Organometallics* **2022**, 41, 1865.