

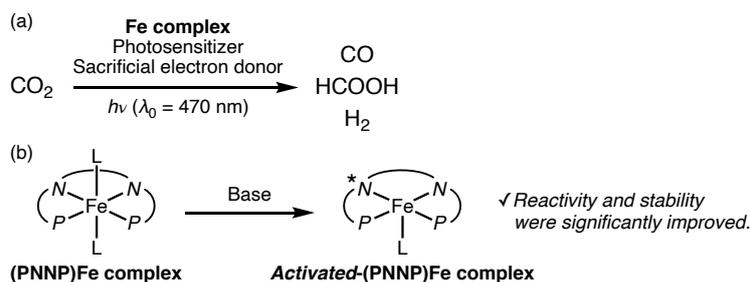
## Activation of a PNNP-ligated Fe complex with a base to facilitate photocatalytic CO<sub>2</sub> reduction

(<sup>1</sup>Graduate School of Science, Nagoya University, <sup>2</sup>RCMS, Nagoya University) ○ Taku Wakabayashi,<sup>1</sup> Kenji Kamada,<sup>1</sup> Jung Jieun,<sup>1</sup> Susumu Saito,<sup>1,2</sup>

**Keywords:** Carbon dioxide, Iron complex, Photoreaction, Transient absorption spectroscopy, Reduction reaction

Carbon dioxide (CO<sub>2</sub>) could be a ubiquitous raw material in terms of cheapness and low toxicity to achieve a sustainable society. There is a great demand to use earth-abundant metals instead of noble metals for the integration of the catalysts into economically viable devices. We have recently reported iridium<sup>1</sup> and ruthenium<sup>2</sup> complexes bearing PNNP-type tetradentate ligands for photocatalytic CO<sub>2</sub> reduction. They both worked as self-photosensitized reduction catalysts, converting CO<sub>2</sub> into formic acid (HCO<sub>2</sub>H) and carbon monoxide (CO) with high reactivity and stability under visible light irradiation in the presence of 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[*d*]imidazole (BIH) as a sacrificial electron donor. We anticipate that the introduction of a bulky PNNP ligand prevents catalyst deterioration and promotes efficient catalysis. However, as mentioned above, it is necessary to use earth-abundant base metals instead of precious metals in an attempt to implement technologies based on CO<sub>2</sub> utilization.

Herein, we have developed a novel iron complex bearing a PNNP-type tetradentate ligand. This complex was found to convert CO<sub>2</sub> into CO mainly under blue light irradiation in the presence of Ir(ppy)<sub>3</sub> (tris(2-phenylpyridinato)iridium(III)) as a photosensitizer and BIH as a sacrificial electron donor (Scheme 1 (a)). The catalytic ability and durability were significantly improved by pre-activation of the Fe complex with the addition of a base (Scheme 1 (b)). Employing this catalyst activation, the turnover number for more reduced carbon products increased more than four times in 24 h light irradiation. The catalytic mechanism was interrogated in detail by picosecond laser flash photolysis measurements.



**Scheme 1. (a) CO<sub>2</sub> photoreduction and (b) activation of an Fe complex by adding a base.**

1) K. Kamada, J. Jung, T. Wakabayashi, K. Sekizawa, S. Sato, T. Morikawa, S. Fukuzumi, S. Saito, *J. Am. Chem. Soc.* **2020**, *142*, 10261. 2) K. Kamada, H. Okuwa, T. Wakabayashi, K. Sekizawa, S. Sato, T. Morikawa, J. Jung, S. Saito, *Synlett* (Invited for a Cluster to honor Prof. Shunichi Fukuzumi on the occasion of his 70th birthday) **2022**, Article ASAP. DOI: 10.1055/a-1709-0280 (accessed 2022-1-11).