INTRAMOLECULAR ELECTRON TRANSFER ENABLES EFFICIENT CO_2 PHOTOREDUCTION BY A (PNNP)Mn CATALYST

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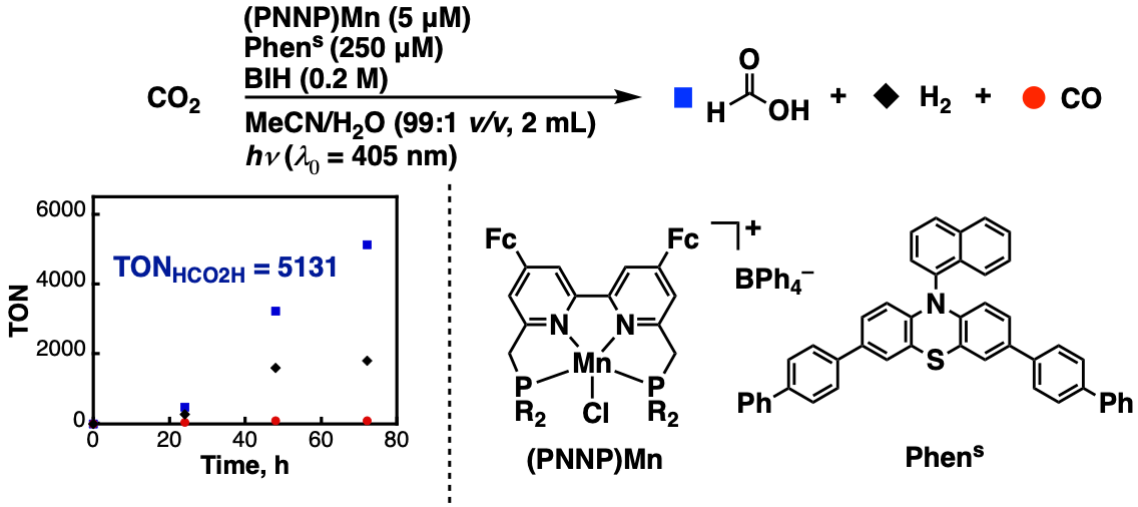
Photocatalytic carbon dioxide (CO_2) reduction is an attractive strategy for addressing global carbon emissions by converting CO_2 into value-added chemical fuels. Among the possible products, formic acid (HCO_2H), which could be produced from CO_2 reduction as a platform chemical such as a fuel in a direct formic acid fuel cell, can be provided as a valuable energy storage source. Previously, we reported that iridium complexes[1] bearing PNNP-type ligands exhibit excellent activity for CO_2 photoreduction. However, developing efficient, selective, and earth-abundant molecular catalysts for this transformation remains a challenge. To address these limitations, we report here new manganese (Mn) complexes coordinated with ferrocenyl-substituted PNNP ligands, which demonstrate high reactivity for the photocatalytic reduction of CO_2 to HCO_2H.

The photocatalytic performance of the Mn complexes was evaluated under visible-light irradiation (λ_0 = 405 nm) in the presence of an organic photosensitizer and a sacrificial electron donor, 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[*d*]imidazole (BIH), under a CO_2 atmosphere. Incorporation of the ferrocenyl moiety markedly enhances catalytic efficiency by facilitating intramolecular electron transfer and stabilizing key reaction intermediates. Compared to their non-ferrocenyl counterparts, these ferrocenyl-containing Mn systems exhibit higher turnover numbers (TON_{HCO2H} > 5131) for the formation of HCO_2H. To elucidate the underlying mechanism, we employed various analytical techniques, including transient absorption, electron paramagnetic resonance, and density functional theory calculations. In particular, we aim to clarify the effect of the ferrocenyl group on this reaction. Particular attention was given to clarifying the role of the ferrocenyl group in facilitating electron transfer and modulating the electronic structure of the catalytic center.



Scheme 1. CO_2 photoreduction using a (PNNP)Mn complex

[1] Kamada, K.; Jung, J.; Wakabayashi, T.; Sekizawa, K.; Sato, S.; Morikawa, T.; Fukuzumi, S.; Saito, S. *J. Am. Chem. Soc*. 2020, *142*, 10261.