Photochemical CO_2 Reduction and Formic Acid Dehydrogenation Promoted by a Pentanuclear Cobalt Complex

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To solve energy and environmental problems, demand for the production of hydrogen gas in a clean manner is increasing. In this context, formic acid can be regarded as an excellent hydrogen career, and the production of formic acid from earth-abundant source and the dehydrogenation of formic acid to produce hydrogen have attracted considerable attention in recent years.

In this work, we developed a novel pentanuclear cobalt complex ($[Co_5OH(bpp)_6]^{3+}$, **Co5**, Hbpp = 3,5-bis(2-pyridyl)pyrazole, **Fig. 1**) and investigated it catalytic activity for the production and dehydrogenation of formic acid. Visible light irradiation of a solution containing **Co5**, $Ir(ppy)_3$ (Hppy = 2-phenylpyridine) as a photosensitizer and BIH (1,3-dimethyl-2-phenyl-2,3-dihydro-1*H* -benzo[d]imidazole) as a sacrificial electron donor under CO_2 resulted in the formation of carbon monoxide and formic acid.[1] Furthermore, irradiation of visible light to a solution containing **Co5**, $Ir(ppy)_3$, BIH and formic acid (500 *eq. vs.* **Co5**) under Ar atmosphere resulted in the formation of H_2 (**Fig. 2**). Therefore, we demonstrate that **Co5** works as a bicatalyst that promote both photochemical CO_2 reduction and formic acid dehydrogenation.

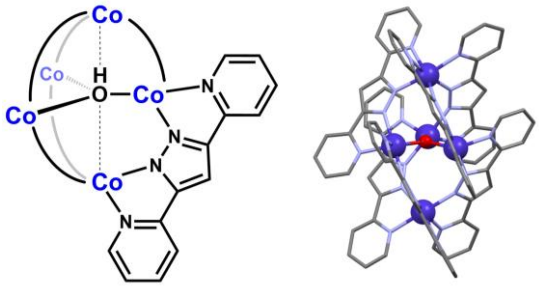

Fig. 1 Structure of the pentanuclear cobalt complex (**Co5**).

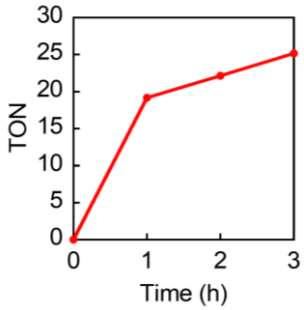

Fig. 2 Photochemical H_2 evolution in the presence of **Co5**, $Ir(ppy)_3$, BIH, and formic acid.

1) T. Akai, M. Kondo, S. K. Lee, H. Izu, T. Enomoto, M. Okamura, Y Saga, S. Masaoka, *Dalton Trans.*, **2020**, *49*, 1384.

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