

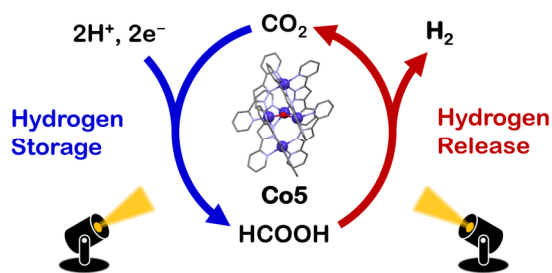
Photochemical Hydrogen Production based on HCOOH/CO₂ cycle Catalyzed by Pentanuclear Cobalt Complex

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With the increasing demand for energy and the rapid depletion of fossil fuels, the development of renewable and environmentally friendly energy sources has become essential. Given this background, significant research efforts have focused on the liquid organic hydrogen carrier formic acid, which is a low-toxicity liquid under ambient conditions. Therefore, efficient catalysts for the production of formic acid and its conversion into hydrogen are required for utilisation of formic acid as a hydrogen carrier.

In this work, we developed a novel pentanuclear cobalt complex ($[\text{Co}_5\text{OH}(\text{bpp})_6]^{3+}$, **Co5**, Hbpp = 3,5-bis(2-pyridyl)pyrazole) and investigated its photocatalytic activity for the production and dehydrogenation of formic acid (**Fig.**). The photoirradiation of a solution containing **Co5**, a photosensitizer and a sacrificial electron donor in a CO₂ atmosphere resulted in the formation of formic acid, carbon monoxide, and hydrogen.¹ Surprisingly, the evolution of hydrogen was completely suppressed in an Ar atmosphere, indicating that CO₂ is required for the generation of hydrogen. The photoirradiation of a solution containing **Co5**, a photosensitizer, a sacrificial electron donor and formic acid in an Ar atmosphere resulted in the formation of hydrogen and CO₂. Therefore, the first catalytic cycle for hydrogen production based on the photochemical two-electron reduction of CO₂ and the dehydrogenation of formic acid was demonstrated.² Under the optimized conditions, the turnover frequency (TOF) of **Co5** for the dehydrogenation reaction of formic acid was higher (229 h⁻¹) than those reported for other molecular catalysts that operate under photoirradiation at ambient temperature. In addition, mechanistic studies were performed to elucidate the underlying mechanism of the catalytic cycle.



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

2) T. Akai, M. Kondo, Y. Saga and S. Masaoka, *Chem. Commun.*, **2022**, accepted, DOI: 10.1039/D1CC06445B.