

TADF 有機分子を光増感剤 Mn(I)錯体を触媒として用いた CO₂ 還元光触媒反応

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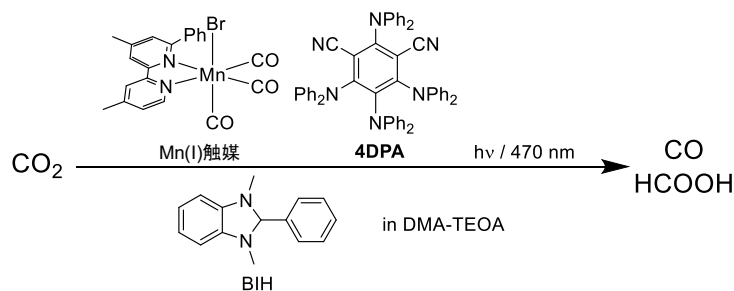
Photocatalytic CO₂ reduction using TADF organic molecules as photosensitizers and a Mn(I) complex as a catalyst. (¹*School of Science, Tokyo Institute of Technology*, ²*Dipartimento di Chimica Ciamician, Universita' di Bologna*, ³*Graduate school of Advanced Science and Engineering, Hiroshima University*) ○Rei Inoue,¹ Elena Bassan,² Francesco Calogero,² Simone Potenti,² Andrea Gualandi,² Pier Giorgio Cozzi,² Paola Ceroni,² Yusuke Tamaki,¹ Osamu Ishitani^{1,3}

Photocatalytic CO₂ reduction using metal complexes have attracted much attention. In most of the reported researches, rare metals such as Ru(II) are used as a central metal ion of photosensitizers to drive photochemical electron transfer from an electron donor to a catalyst. For developing photosensitizers composed of only abundant elements, in this study, we focus on organic molecules that exhibit thermally activated delayed fluorescence (TADF) with long excitation lifetimes¹, and developed photocatalytic CO₂ reduction systems. One of the TADF molecules, namely **4DPA**, with strong absorption of visible light and long excitation lifetime worked as a good photosensitizer in the visible light driven photocatalytic system for CO₂ reduction giving CO and HCOOH as main products in combination with a Mn(I) catalyst. (TON_{CO+HCOOH} > 650, Φ_{CO+HCOOH} = 22.8%)

Keywords : photocatalytic CO₂ reduction; TADF; Organic photosensitizer; Mn(I) complex

近年、金属錯体を用いた CO₂ 還元光触媒反応が盛んに研究されているが、多くの系では、光吸収により電子移動を駆動する光増感剤に Ru などの希少金属を用いている。

本研究では、可視光を吸収し、長い励起寿命を有する熱活性遅延蛍光(TADF)分子に着目し¹、これを光増感剤に用いた CO₂ 還元光触媒反応系の開発を試みた。いくつかの TADF 分子を用いて光触媒反応を行い、下式に構造を示す **4DPA** が光増感剤として優れていることを見出した。**4DPA** は 510 nm までの可視光を吸収し、72 μs の励起寿命を示した。**4DPA** を下式に示す Mn(I)触媒及び還元剤 BIH と組み合わせて 470 nm の可視光を照射することで、CO₂ が CO と HCOOH へと光触媒的に高効率で還元された (TON_{CO+HCOOH} > 650、Φ_{CO+HCOOH} = 22.8%)。



1) H. Uoyama, C. Adachi, *et al.*, *Nature*, **2012**, 492, 234-238.