

Redox-active Ligands as Protons, Electrons, and Hydrogen Poolers

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Molecular hydrogen is one of candidates as clean energy carrier.¹ Because of the difficulty in the storage of hydrogen, the development of hydrogen-storage/-evolution materials is strongly desired. Among a several options, utilization of organic compounds, known as organic hydrides, are one of the most fascinating way.² However, even in the previous excellent examples, high temperature and precious-metal-based catalysts are necessary in the hydrogen evolution reaction (HER). Therefore, the creation of a HER at moderate temperature with use of nonprecious-metal catalysts is an important issue.

Previously, we reported important reactions of nonprecious-metal complexes with redox-active ligands.³ For example, Fe(II) complex with *o*-phenylenediamine (opda), e.g., [Fe^{II}(opda)₃][ClO₄]₂, was reported to show the photochemical HER at room temperature (Figure 1).⁴ In this reaction, redox-active opda ligands were found to act as proton/electron pooler forming oxidized ligands *semi*-benzoquinodimine (s-bqdi) or *o*-benzoquinodimine (bqdi) after the photochemical HER. These photo-induced multi-electrons and protons transfer reactivity of nonprecious-metal complexes with redox-active ligands arose our expectations for the creation of small molecule activations such as MeOH and CO₂ (Figure 1).

We herein report our recent progresses on designing photochemical MeOH dehydrogenation and CO₂ fixation based on nonprecious-metal complexes with redox active ligands, together with investigations on the elucidation of their detailed mechanisms (Figure 1).⁵

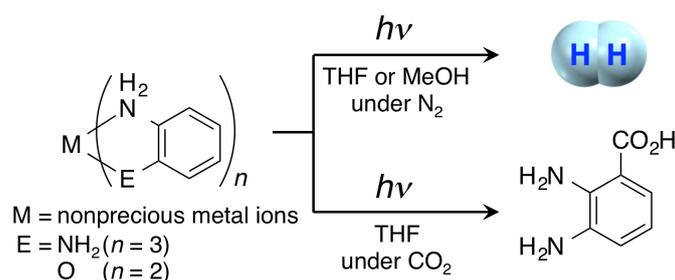


Figure 1. Photochemical HER, MeOH dehydrogenation, and CO₂ fixation assisted by nonprecious metal complexes with redox-active ligands.

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