Development of Functional Metal Complexes for Artificial Photosynthesis

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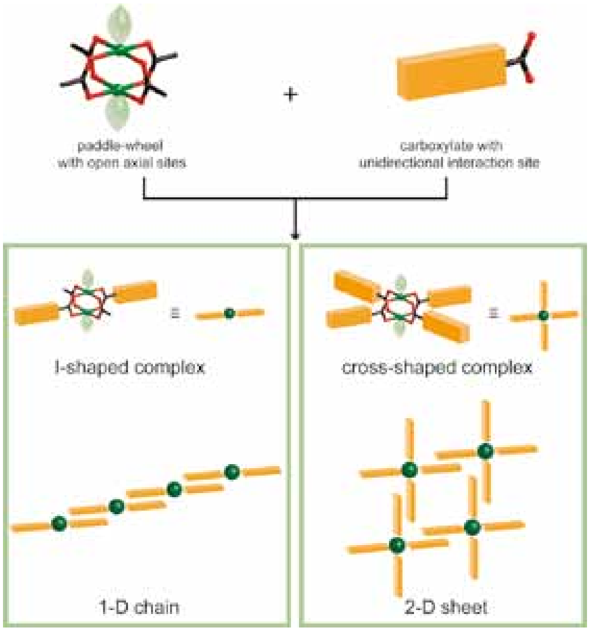
1. Controlled Self-Assembly of Paddle-Wheel Dimers via Multipoint Arene-Perfluoroarene Interactions[1)]

Control over the self-assembling process of metal complexes is of key importance to construct supramolecular materials in which desirable bulk properties emerge as a consequence of specific intermolecular orientations. Paddle-wheel complexes which are described as M_2L_4 (M = metal ion, L = monoanionic bidentate ligand) attract much attention because of their highly symmetric (D_{4h}) structures suitable for the construction of continuous structures. Moreover, the existence of free coordination sites at the axial positions (open axial sites) and their Lewis acidity play a crucial role in catalysis or selective guest recognition. Therefore, the construction of continuous structures of paddle-wheel units with open axial sites is of significance to develop functional materials.

In this study we firstly report the self-assembly of Rh(II) and Cu(II) paddle-wheel complexes with open axial sites controlled via *unidirectional* interaction realized by multipoint arene-perfluoroarene interactions (Scheme 1). Two kinds of paddle-wheel dimers, the I-shaped complex (**1**), which has only two *unidirectional* interaction sites and is expected to one-dimensional chain assembly, and the cross-shaped complex (**2**), which has four *unidirectional* interaction sites in one molecule and is expected to have two-dimensional sheet-structure, are chosen to examine the molecular arrangements in the crystalline state (Scheme 1).



Scheme 1. Schematic illustration of I- and cross-shaped paddle-wheel complexes with open axial sites and their self-assembled structures.

In the crystal packing structures of **1** and **2**, intermolecular multipoint arene-perfluoroarene interactions are observed. **1** is arranged in one-dimensional chain due to face-to-face overlap of phenylene and perfluorophenyl rings. Interchain stacking are stabilized by π–π interactions between perfluorophenyl rings to form the two-dimensional sheet structure. In the crystal packing structures of **2**, an infinite two-dimensional square-grid sheet structure is formed via multipoint arene-perfluoroarene interaction between ligands.

Moreover, porous structure was formed by the stacking of the two dimensional sheets via π–π interaction between ligands along the *a* axis and open axial sites are oriented to the channel.

The results presented in this contribution offer a new strategy to assemble paddle-wheel units of various metal ions with open axial sites at room temperature. This can be a powerful tool to construct supramolecular structures applied for heterogeneous catalytic system or sensor.

2. Photoinduced Hydrogen Evolution from Water by a Simple Platinum(II) Terpyridine Derivative[2)]

Hydrogen energy has been one of the most important targets as a renewable clean energy. Particularly, hydrogen generation based on water splitting by solar energy has attracted considerable attention for many years. Up to now, photochemical hydrogen production catalyzed by metal complexes has been extensively studied using a so-called three-component system consisting of tris(2,2’-bipyridine)ruthenium(II) ($Ru(bpy)_3^{2+}$) as a photosensitizer, methylviologen (N,N’-dimethyl-4,4’- bipyridinium, MV^{2+}) as an electron relay, and ethylenediaminetetraacetic acid disodium salt (EDTA) as a sacrificial electron donor, for which colloidal platinum was often employed as a H_2-evolving catalyst. Previously, we reported on the photochemical hydrogen production from water catalyzed by $[PtCl(terpy)]^+$ (terpy = 2,2’:6’,2”-terpyridine) in the presence of EDTA, where the platinum(II) complex is known to serve as a photosensitizer as well as a H_2-evolving catalyst. Thus this work was considered as the first example of ‘bifunctional single-component photocatalysts’ driving visible light-induced H_2 production from water (Figure 1).

In this work, we reported the novel platinum(II) complex (PV^{2+}) as the first example of ‘trifunctional single-component photocatalysts’ for visible light-induced H_2 production from water (Figure 1).

The H_2-evolving activity of PV^{2+} evaluated in the presence of EDTA showed that the stability of the PV^{2+} catalyst during the photolysis is much higher than that of the parent compound $[PtCl(tpy)]^+$. This is due to the improved electron-accepting ability of PV^{2+} compared with $[PtCl(tpy)]^+$. It is also found that the photolysis of PV^{2+} first generates a one-electron-reduced species (PV^+) as an initial photoproduct and this further undergoes a photoinduced process leading to H_2 generation from water. Therefore, this is the first demonstration of Z-scheme photosynthesis within the family of artificial molecular systems, although these two-step reductive quenching processes do not perfectly match with the oxidative ones in natural photosynthesis. The present study also demonstrates that the PHE activity can be dramatically enhanced by the presence of a Pt^{II}-based molecular co-catalyst, such as *cis*-$[PtCl_2(NH_3)_2]$.

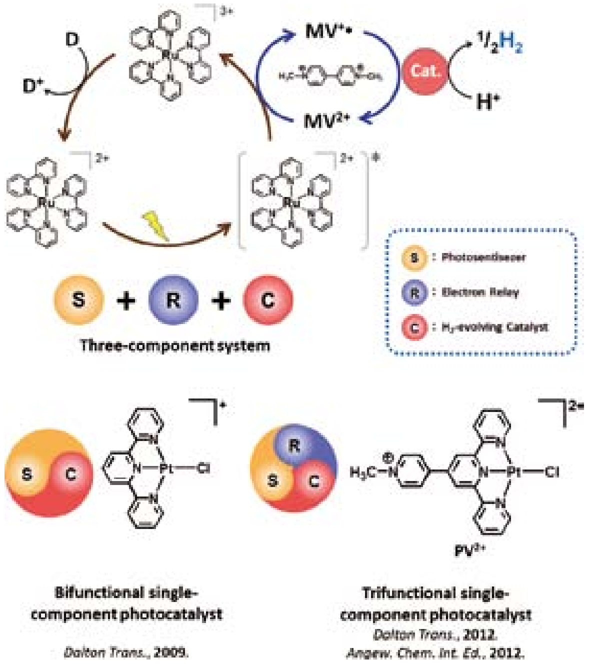


Figure 1. Three-component, bifunctional single-component and trifunctional single-component photocatalysts for hydrogen production from water.

References

1) T. Itoh, M. Kondo, M. Kanaike and S. Masaoka, *CrystEngComm* **15**, 6122–6126 (2013).
2) M. Kobayasi, S. Masaoka and K. Sakai, *Angew. Chem., Int. Ed.* **51**, 7431–7434 (2012).

Awards

NAKAMURA, Go; FY2013 (the 4th) Sokendai President’s Award (2013).
NAKAMURA, Go; Student Poster Award, 2nd CSJ Chemistry Festa (2012).
YOSHIDA, Masaki; Student Poster Award, 2nd CSJ Chemistry Festa (2012).
MURASE, Masakazu; Student Poster Award, 2nd CSJ Chemistry Festa (2012).
OKAMURA, Masaya; Student Poster Award, 2nd CSJ Chemistry Festa (2012).

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