Molecular catalytic system for efficient water splitting

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Chapter 6

General Discussion and Outlook

ABSTRACT

The future perspectives of this research dissertation regarding water oxidation catalysis, oxygen evolving complexes and electro-assisted surface immobilized catalytic assemblies are presented in this chapter. A glance at my current work and upcoming research projects is described in section 6.2. Finally, the future outlook of water splitting catalysis by molecular complexes for stand alone solar to clean fuel conversion system is described along with integrated photo-electrochemical systems.

6.1. GENERAL DISCUSSION AND OUTLOOK

Being a young scientist, my enthusiasm has always been fueled by the desire to contribute something new for future energy supply and renewable materials. For this research work, my interest was focused on water splitting catalysis with the specific aim to contribute to the design, synthesis and testing of new molecular complexes for oxygen evolution, and full cell electrochemical water oxidation into molecular hydrogen and oxygen on surface immobilized catalytic assemblies. This chapter presents a number of novel opportunities that can be explored along this line, based on the results presented in the previous chapters.

6.2. FUTURE WORK

6.2.1. Dinuclear Complexes for Water Oxidation

One of the future directions worth studying would be the development of water oxidation catalysis with two iridium centers involved and the mechanism of O-O bond formation during the dioxygen generation process. In a first step to demonstrate the viability of this approach, some dinucleating nitrogen based ligands have been prepared that can accommodate two metal centers (Fig. 6.1). These ligands can also be extended with anchoring groups to implement electrochemical devices and photocatalytic systems.

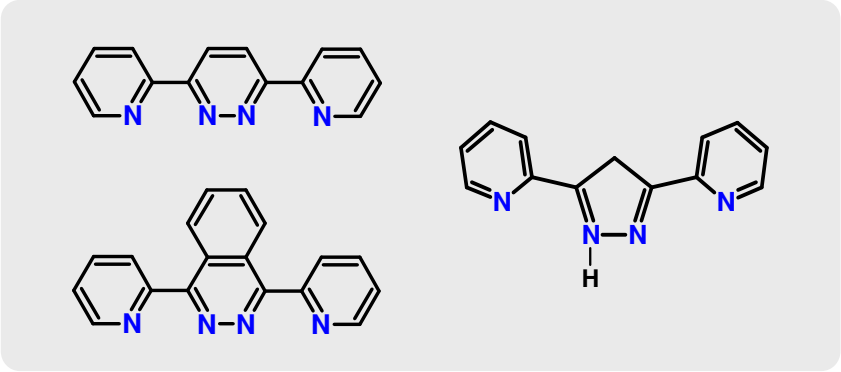

Figure 6.1. (left) A 3,6-bis(2-pyridyl)pyridazine, 3,6-bis(2-pyridyl)phthalazine, and **(right)** a Hbpp ligand [2,2′-(1H-pyrazole-3,5-diyl)bis(pyridine)] for dinuclear complexes.

6.2.2. Water Splitting via Tunneling Linker

Another avenue that can be explored is to introduce an alkyl tunneling barrier between the catalytic site and the electron sink (electrode) to increase the residence time of charge in the complex for enhanced catalysis. There are different ways to position alkyl chain modified catalyst molecules on a solid surface. In Fig. 6.2, an alkyl wire with a length of C_{12}-C_{19} is connected to the catalyst molecules while it has an electrode anchoring group on the other side of the chain. Since it is an insulating material, the alkyl layer provides a tunneling bridge that delays the backflow of electrons. This will also present a working model of a device that can modulate the rate of electron flow by adjusting the length of the alkyl chain [1].

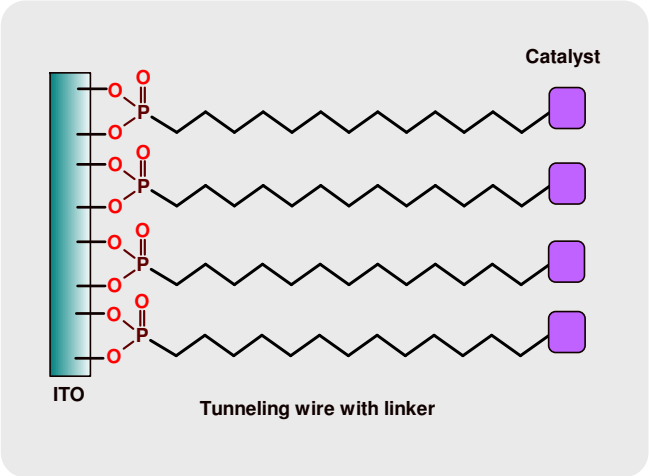

Figure 6.2. Alkyl chain with anchoring units modified catalyst-electrode assembly for electro-driven water splitting system.

6.2.3. Chromophore Sensitized Photo-Electrocatalytic Oxygen Evolving Assembly

Recently, it has been shown that a linker modified electrochemical water oxidation system can be extended with synthetic photo sensitizer molecules like Ru-$(bpy)_3$ (bpy is 2,2′-bipyridine) [2,3]. One difficulty for optimization is a very close proximity of the catalytic site to the photo harvesting molecule. Separating the two elements by a bridge or a tunneling barrier may enhance the performance of the light harvesting molecule by allowing it to act as an organometallic photovoltaic (PV) unit that can extract electrons from the catalyst when exposed to light. A chromophore sensitized catalytic assembly is under preparation and this line can be pursued for the development of a photo-electrocatalytic device system for light and electricity driven oxygen evolution in aqueous solution.

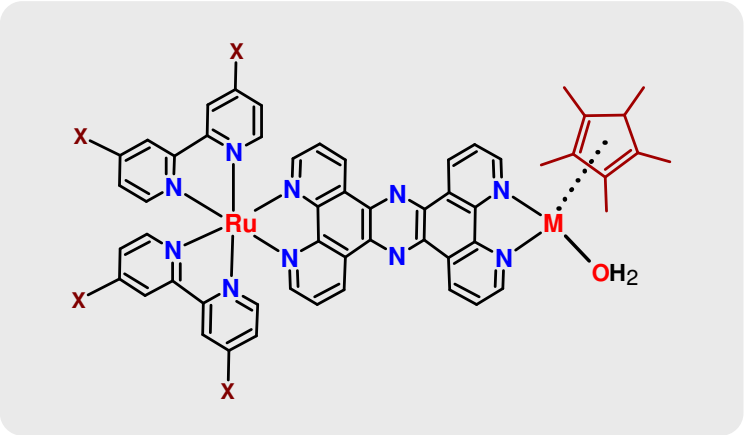

Figure 6.3. A chromophore sensitized water splitting catalyst for photo-electrocatalytic oxygen generation (X= COOH or PO_3H_2; M = Ru, Ir).

A Ru-$(bpy)_3$ type sensitizer with the mono ruthenium or iridium catalysts as shown in Figure 6.3, can be used in photoanode systems operating at moderate overpotential when exposed to visible light. The system may be integrated with a photocathode PV system with a hydrogen generation molecular catalyst or a thin layer of platinum.

6.2.4. The Artificial Leaf: Integrating Water Splitting Catalysts with a Multi-Junction Solar Cell

Recently, progress has been reported in the development of multi-junction solar cells with a thin coating of a water splitting catalyst [4,5]. Miller *et al*. reported that a composite oxide material coated on an ITO layer on a triple-junction silicon solar cell can operate at ~7.8 % efficiency for solar to hydrogen conversion and efficiencies of 4.7 % and 2.5 % were obtained recently with a cobalt phosphate catalyst, both in a wired and in a wireless configuration using a ternary alloy system at the cathode for proton reduction [6,7]. The corrosion protection of such PV based systems during water oxidation and oxygen evolution is an important issue to be addressed for future solar to fuel conversion applications.

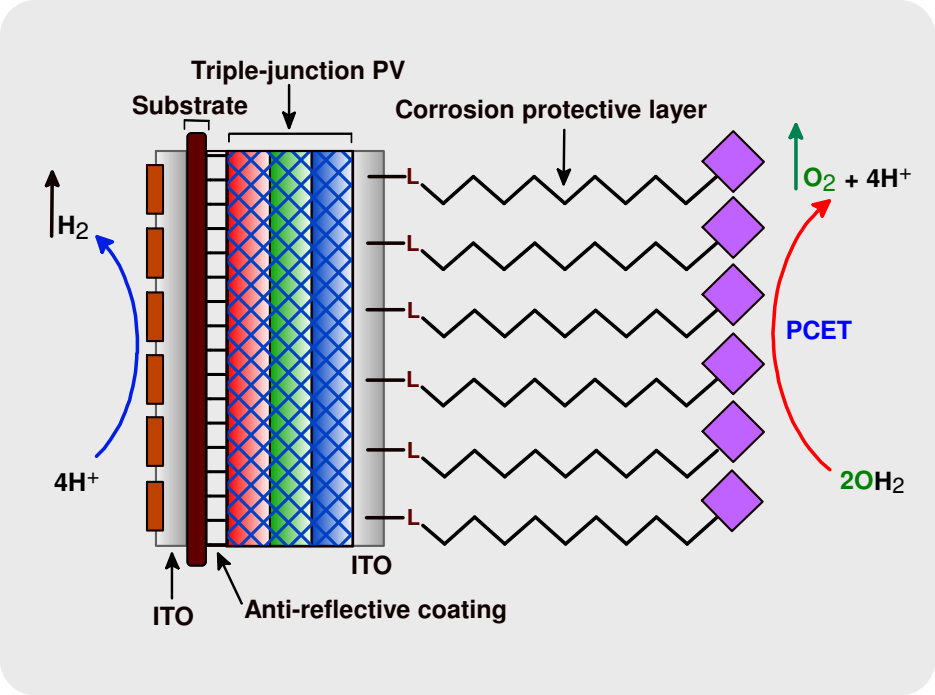

Figure 6.4. Water splitting catalysts can be attached to a molecular layer integrated with a Multi-Junction solar cell for corrosion protective coating/tunnelling bridge in Artificial Leaf configurations for stand-alone water oxidation and hydrogen production (L= COOH or PO_3H_2).

Another follow-up to the research presented in this thesis is the development of an integrated molecular system with a triple-junction solar cell, where the catalyst will be modified with a corrosion protective layer or anti corrosion coating for deposition on the PV surface, for photo-electrochemical water splitting. The other side of the device is wired or coated with hydrogen reduction catalysts or a thin platinum film for H_2 generation (Figure 6.4). Such photo-electrocatalytic devices are suitable for stand-alone applications, since they allow the conversion of sunlight to fuel using water as the raw material without the need for an external energy source.

This work is targeted to explore new materials and designs for the artificial man-made apparatus that makes use of natural resources like water and sun light for clean fuel production. The bottom line is that water splitting catalysis for solar to fuel conversion offers a potential alternative for future green energy supplies based on renewable materials. The electrochemical water splitting systems with molecular catalysts have potential application in *e.g.* rooftop devices to make personalized energy carriers. The proposed "Artificial Leaf" will soon be the future outcome of the present day technology and efforts in this field. Cheap and easy accessible hydrogen will not only serve as fuel for transportation but also as driving force for green power generation.

REFERENCES

01- C. C. Page, C. C. Moser, X. Chen and P. L. Dutton, *Nature* **1999**, *402*, 47–52.

02- Z. Chen, J. J. Concepcion, J. W. Jurss and T. J. Meyer, *J. Am. Chem. Soc.* **2009**, *131*, 15580–15581.

03- J. J. Concepcion, J. W. Jurss, P. G. Hoertz and T. J. Meyer, *Angew. Chem. Int. Ed.* **2009**, *48*, 9473–9476.

04- O. Khaselev and J. A. Turner, *Science* **1998**, *280*, 425–427.

05- M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori and N. S. Lewis, *Chem. Rev.* **2010**, *110*, 6446–6473.

06- R. E. Rocheleau, E. L. Miller and A. Misra, *Energy & Fuels* **1998**, *12*, 3–10.

07- S. Y. Reece, J. A. Hamel, K. Sung, T. D. Jarvi, A. J. Esswein, J. J. H. Pijpers and D. G. Nocera, *Science* **2011**, DOI: 10.1126/science.1209816.