

A Dissertation Submitted to Wuhan University of
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**Synthesis of bi- and tri-dentate ligand-based
transition
metal (VIIB) complexes for catalytic
oxidations**

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ABSTRACT

Clean and environmentally friendly energy resources that have the potential to meet the needs of present and future generations are very necessary for the life on our planet. Catalytic water oxidation into oxygen and protons is a crucial reaction to many sustainable energy storage schemes including water splitting for hydrogen production or the direct conversion of carbon dioxide into fuel. For practical application, water oxidation catalysts (WOCs) should be highly active, long-lived (*i.e.*, stable under the reaction conditions), and preferably made of earth-abundant elements. Further improvement of the artificial photosynthetic cells mostly depends on improving its components. WOCs have special prominence for improving artificial photosynthesis systems as water oxidation is the most difficult step of the whole process and considered to be the bottle-neck of making energy from the sun. Molecular catalysts for water oxidation are advantageous for their possible structure tuning aiming to catalyst activity optimization and most importantly the ability to study the reaction mechanisms, which will give the chance for precise catalyst engineering.

Here, we have developed water oxidation systems that are based on both ruthenium and cobalt metal ions. In ruthenium based molecular systems, the choice of a facial tridentate capping ligand (λ, ξ, ν -triazacyclononane) alongwith some other bidentate ligands (neutral and negatively charged) was found to be effective strategy to stabilize different ruthenium oxidation states. Our ruthenium catalysts provide some interesting findings that are summarized as follow:

1. While most of the reported ruthenium based WOCs are based on meridional tridentate ligands, here we introduced the facial tridentate ligand λ, ξ, ν -triazacyclononane ($[\text{Ru}(\lambda, \xi, \nu)\text{aneN}^{\nu}]$) as a possible strategy for constructing stable and efficient WOCs.

2. The catalysts revealed very good catalytic activities towards water oxidation with high turnover number (TON) reaching 1200 and high initial turnover frequency (TOF) of 0.2 s^{-1} in case of catalyst $[\text{Ru}(\lambda, \xi, \nu)\text{aneN}^{\nu}(\text{bpy})\text{Cl}]^{+}$ that is higher than its analogous structure $[\text{Ru}(\lambda, \xi, \nu)\text{aneN}^{\nu}(\text{bpy})\text{DMSO}]^{\nu+}$, which showed a TON of 60 .

3. Unexpectedly, the complexes incorporating the negatively charged ν -picolinate (pic) ligands *i.e.*, $[\text{Ru}(\lambda, \xi, \nu)\text{aneN}^{\nu}(\text{pic})\text{DMSO}]^{\xi+}$ and $[\text{Ru}(\lambda, \xi, \nu)\text{aneN}^{\nu}(\text{pic})\text{H}_2\text{O}]^{\nu+}$ showed very low catalytic activity that is due to picolinate ligand dissociation and the formation of the tri-aqua complex in both cases which was not active catalyst for water oxidation.

We also developed a cobalt based water oxidation catalyst, the catalyst address many points of the currently growing problems in the field. It is very simple that can even be generated *in-situ* from a bidentate ligand and commercially available cobalt salts. The structure of the catalysts are well designed to have two coordinated ligands and two available coordination sites for water coordination. The selection of a bidentate ligand that is based on triazole moiety avoids the use of complex structures of polydentate ligands that are not easy to synthesize and is very challenging to tune. The generated catalyst is very stable in aqueous medium for very long time, at least for several weeks, while some other reported catalysts decompose directly on dissolving to give free cobalt ions. The *in-situ* protocol enables the assembling of molecular catalyst film on different electrode materials. The high stability of the catalyst under strong oxidative conditions though its simple structure make the system is very attractive. The proof of the high stability of the *in-situ* generated complex and its high catalytic activity under neutral conditions which is based only on a bidentate ligand, shed light on the ability of small ligands, instead of a pre-synthesized polydentate ligands, to stabilize cobalt ions in lower as well as higher oxidation states. Here we present some interesting results of our cobalt based catalytic system:

1. It is active catalyst for both the photochemical and electrochemical water oxidation reaction in acetate buffer at near-neutral conditions (pH 7).
2. In electrochemical investigations, the catalyst was found to self-assemble a catalyst film on the surface of different electrodes such as GC, HOPG, and ITO electrodes.
3. The film was proved not to be cobalt oxide/hydroxide as normally expected but for the first time, a molecular cobalt complex incorporating the organic ligand bound to cobalt ions. The molecular nature of the deposited film was evidenced based on its SEM, Raman, FTIR, and XPS spectra results along with its physical properties.
4. The catalyst film exhibited an oxygen evolution peak current density around 9 mA cm⁻² on GCE at 1.49 V (vs. NHE) with more than 10 folds increase compared to cobalt salts only, also it showed current density of 2.1 mA cm⁻² on ITO electrode at 1.49 V (vs. NHE) for more than 11 hours of electrolysis. The deposited film on ITO electrode showed a stable current density of ~ 3 mA cm⁻² when used in a catalyst-free buffer solution of pH 7.
5. In the photochemical WO, the catalytic activity of the complex competes with some of the best WOCs reported so far in terms of stability and TON.
6. The homogenous identity of the catalyst in the photolysis process was evidenced

based on ESI-MS, DLS, FTIR, and ^1H NMR characterizations.