

Oxidation of water is the main challenging step to produce H<sub>2</sub> from water-splitting reaction. This particular reaction is energetically uphill process ( $\Delta G^\circ = +113.38$  kcal/mol), and it involves removal of multiple protons and electrons along with slow kinetics of formation of an oxygen-oxygen bond. Therefore, to build hydrogen-based energy economy by splitting of water using sunlight, it is necessary to understand the water oxidation reaction at molecular level in order to design an efficient water oxidation catalyst (WOC). With this concern, the research works presented in this thesis are focused on developing new mononuclear Ru-based WOCs and exploration of their water oxidation activities with mechanistic details. The thesis comprises of six chapters. The **Chapter 1** provides a general overview of molecular water oxidation catalysis including background theory, general factors to design efficient catalysts and mechanistic insights. It also includes a brief literature overview of the developed molecular WOCs, particularly Ru-based, in last forty years. The **Chapter 2** describes the synthetic procedures of various ligand- and Ru-precursors, general instrumentation and techniques, and details of computational methods used for the whole research work. The **Chapter 3** reports Ce(IV) driven water oxidation activities of two mononuclear Ru<sup>II</sup>-aqua complexes supported by neutral polypyridyl based pentadentate ligand frameworks. The effect of electronic perturbation on catalytic performances by changing the ligand scaffold is described here. Electrochemical, spectroscopic and kinetic studies establish a mechanism where a formal ruthenium(VI)-oxo species acts as an active intermediate, triggering O–O bond formation via water nucleophilic attack pathway. Furthermore, the deactivation pathway of catalyst under catalytic condition has been investigated. The **Chapter 4** describes Ce(IV)-driven water oxidation activity of a mononuclear ruthenium(III) complex supported by an anionic, redox-non-innocent ligand. Mechanistic investigations by spectroscopic, electrochemical, kinetics and computational studies reveal that reaction proceeds through formation of a high-valent formal Ru<sup>VII</sup> species, where the redox active ligand participates to accumulate the oxidation equivalents in cooperation with metal centre, thereby metal ion needs to reach V oxidation state at the most. Based on kinetic studies, an unconventional pathway for O-O bond formation via heterometallic radical coupling interactions between the oxygen atoms of a hydroxocerium(IV) ion and a metal oxyl moiety has been demonstrated. In **Chapter 5**, an unusual functionality of a strategically placed dangling carboxylic group in a Ru-complex towards O-O bond formation to promote water oxidation via oxide relay pathway has been described. Isotope labelling experiment using <sup>18</sup>O-labelled water has been performed to establish the mechanism. The presence of pendant carboxylic group enormously enhances the catalytic rate that is compared with another Ru(II) complex having similar coordination environment, but, without a dangling carboxylic group. In **Chapter 6**, an overall summary and final remarks of research outcome are stated.