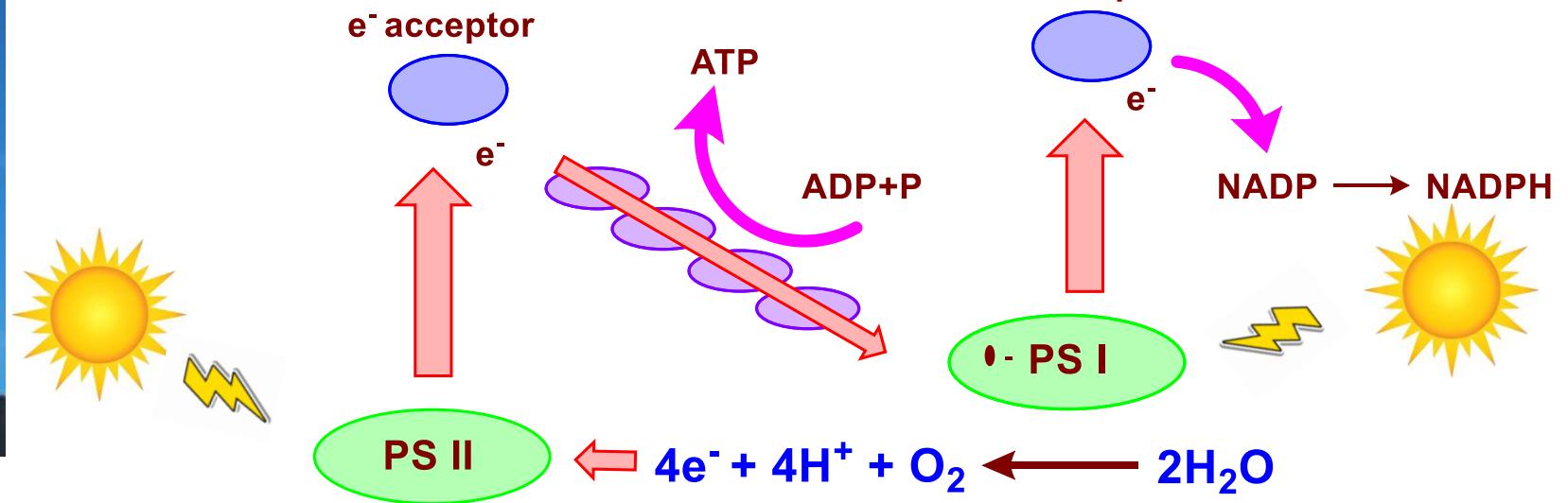
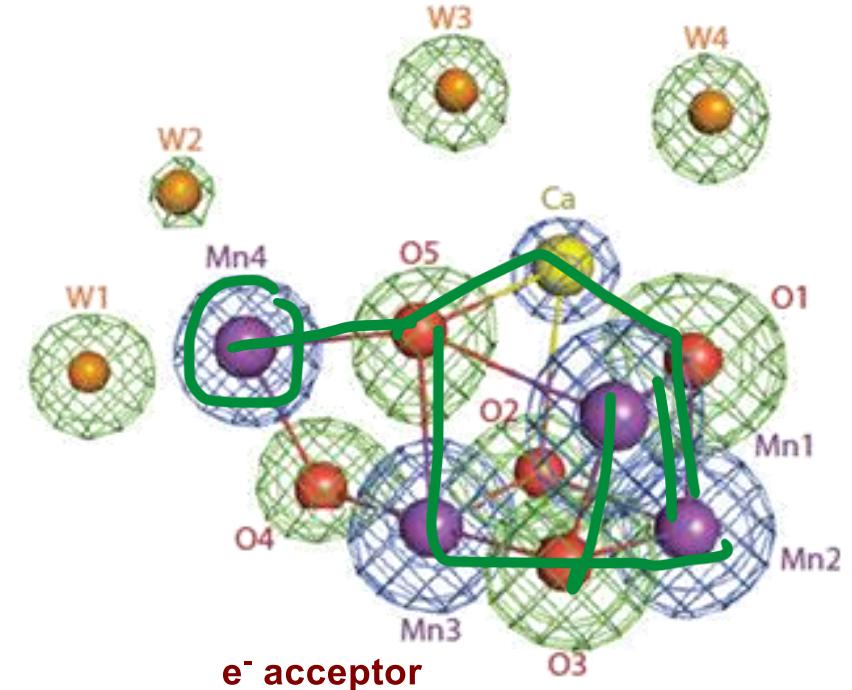


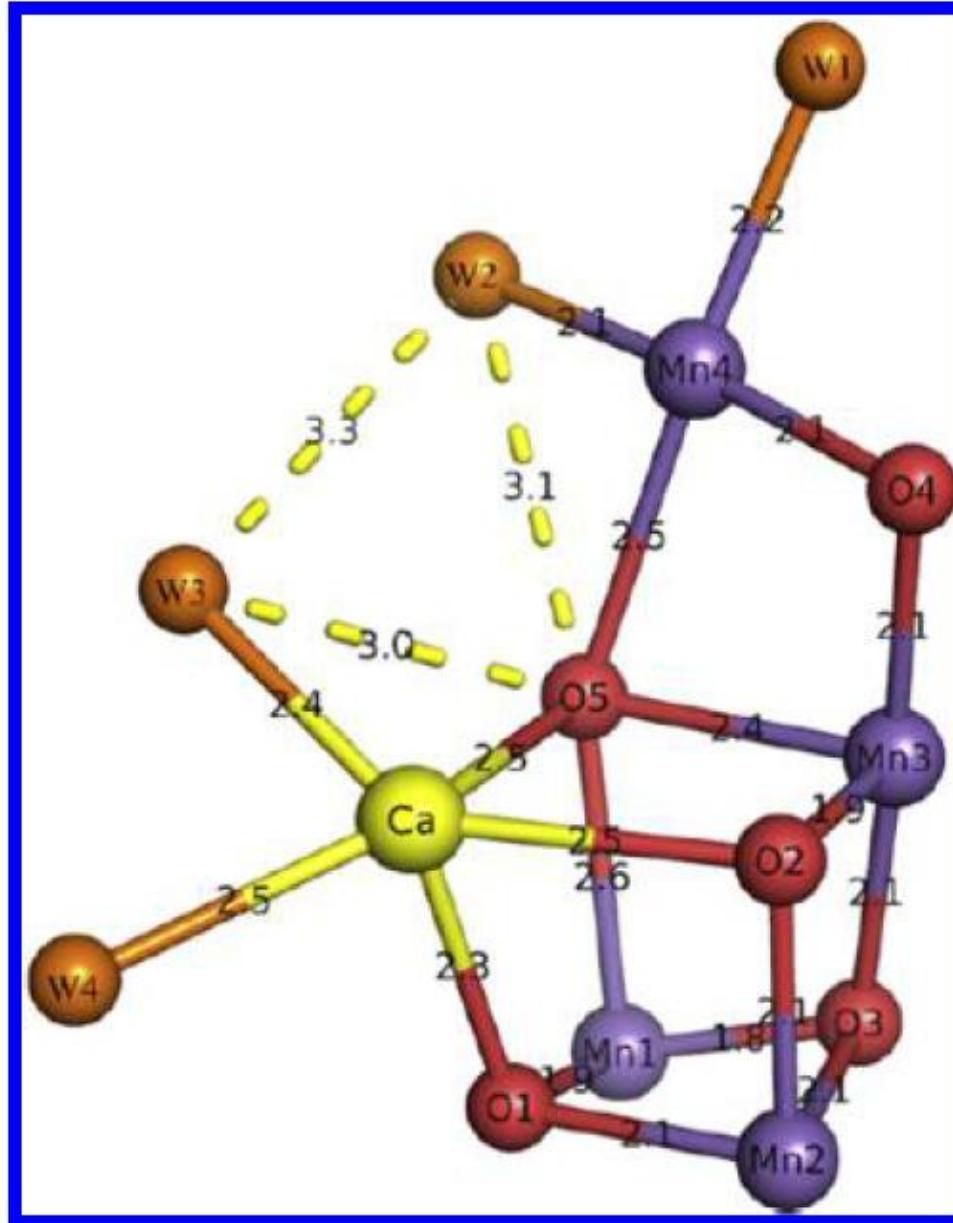
Water Oxidation: Non-renewable to Renewable Energy



Challenge!
Thermodynamic
Uphill process

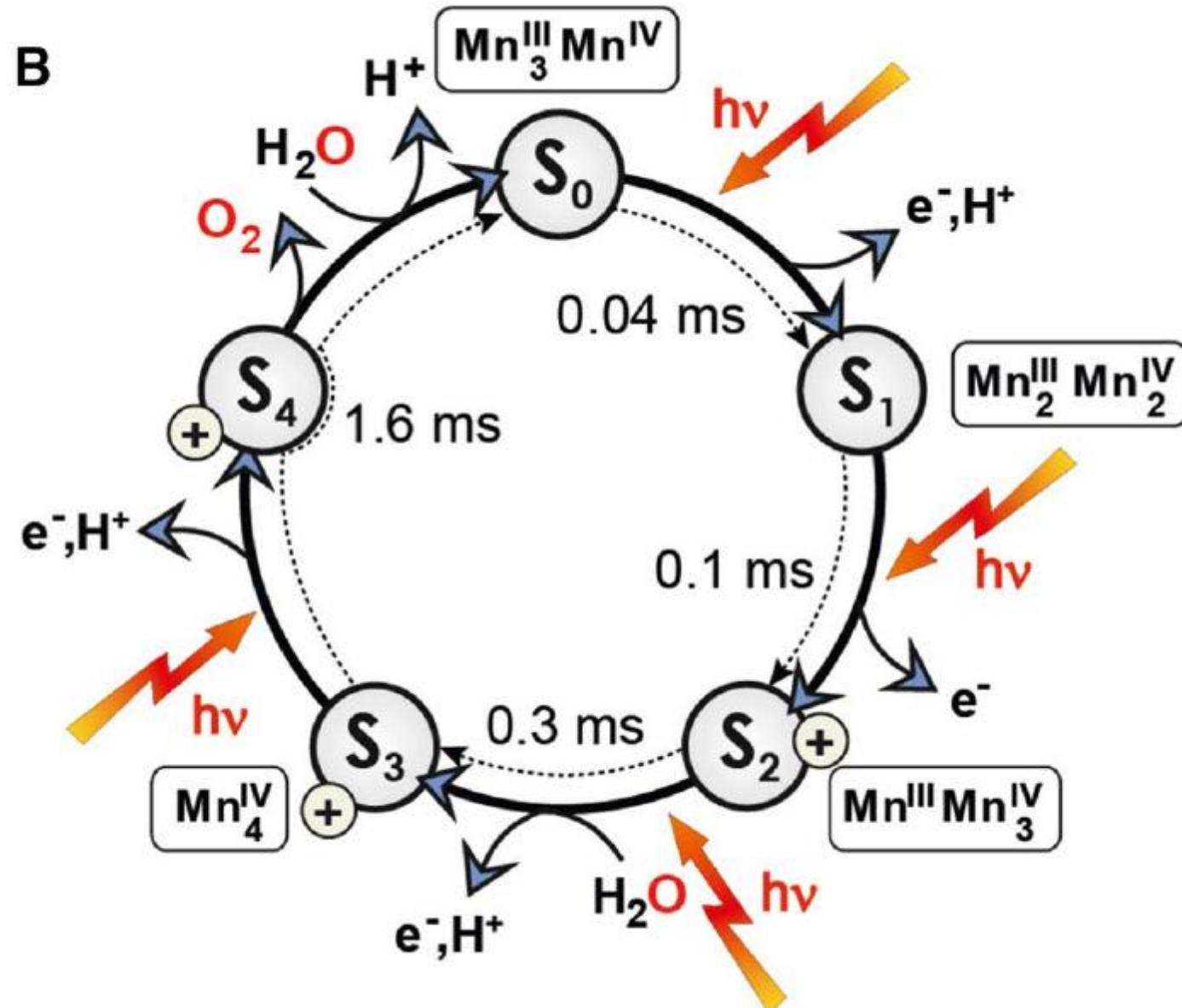


The Oxygen Evolving Complex

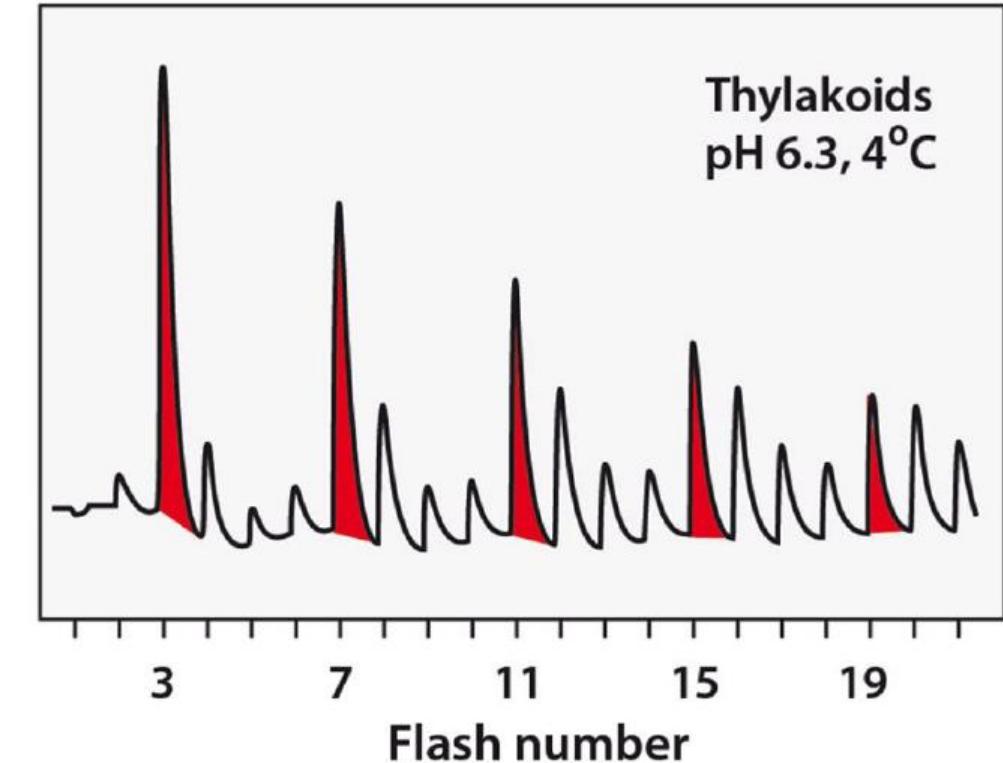


Water oxidation cycle (Kok cycle)

B

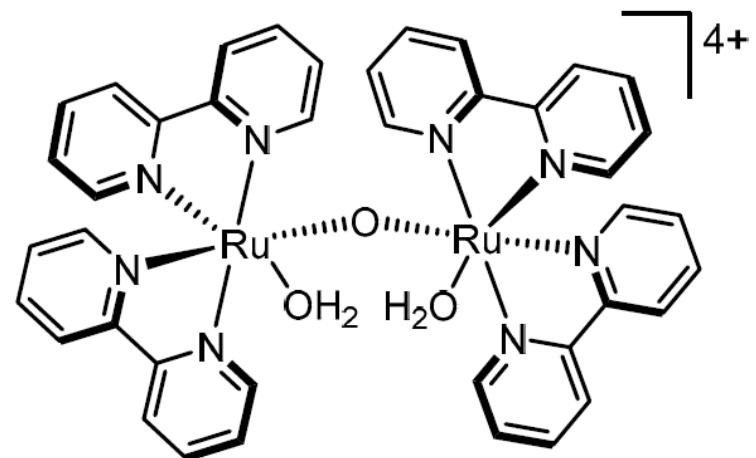


A

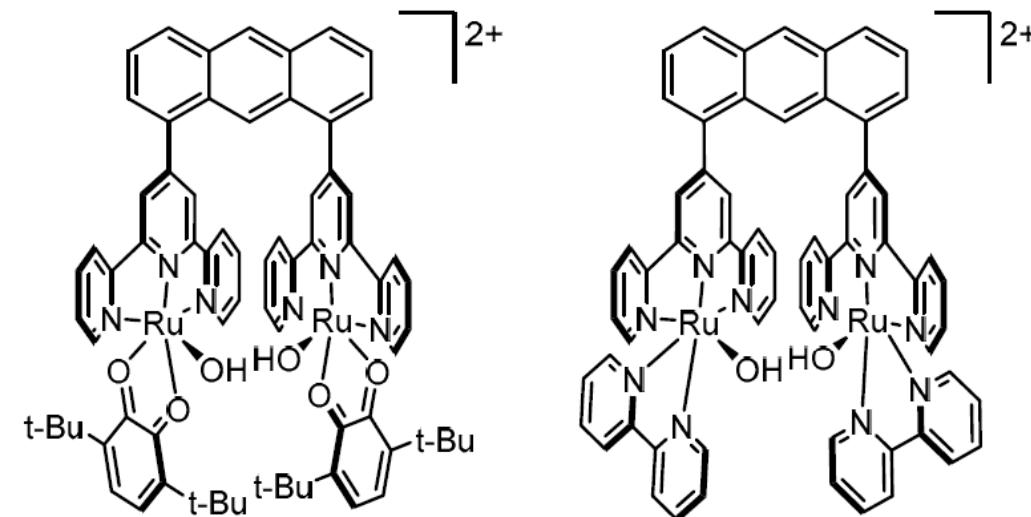


Release pattern of molecular measured polarographically following successive light flashes of spinach thylakoids at 4 °C. Note that O_2 release follows a 4-flash pattern (the starting dark stable state is S_1).

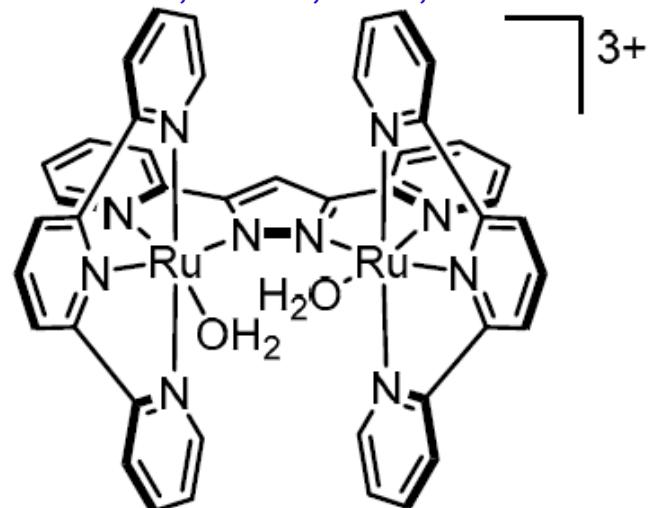
Photosystem II Inspired Ru-based Water Oxidation Catalysts



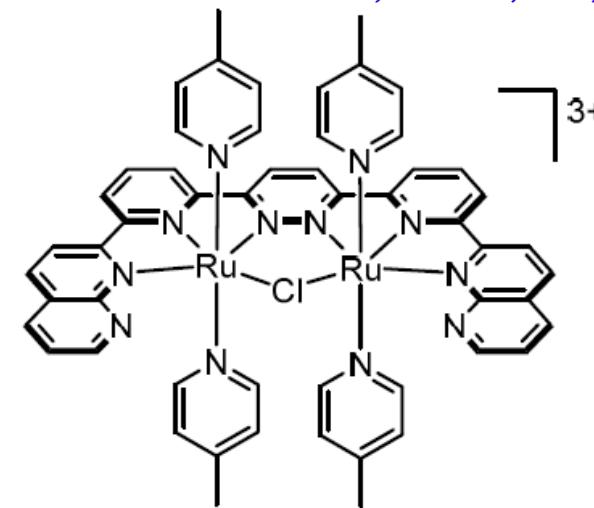
T. J. Meyer's group
JACS, 1982, 104, 4029



Tanaka's group
Angew. Chem. Int. Ed., 2000, 39, 1479

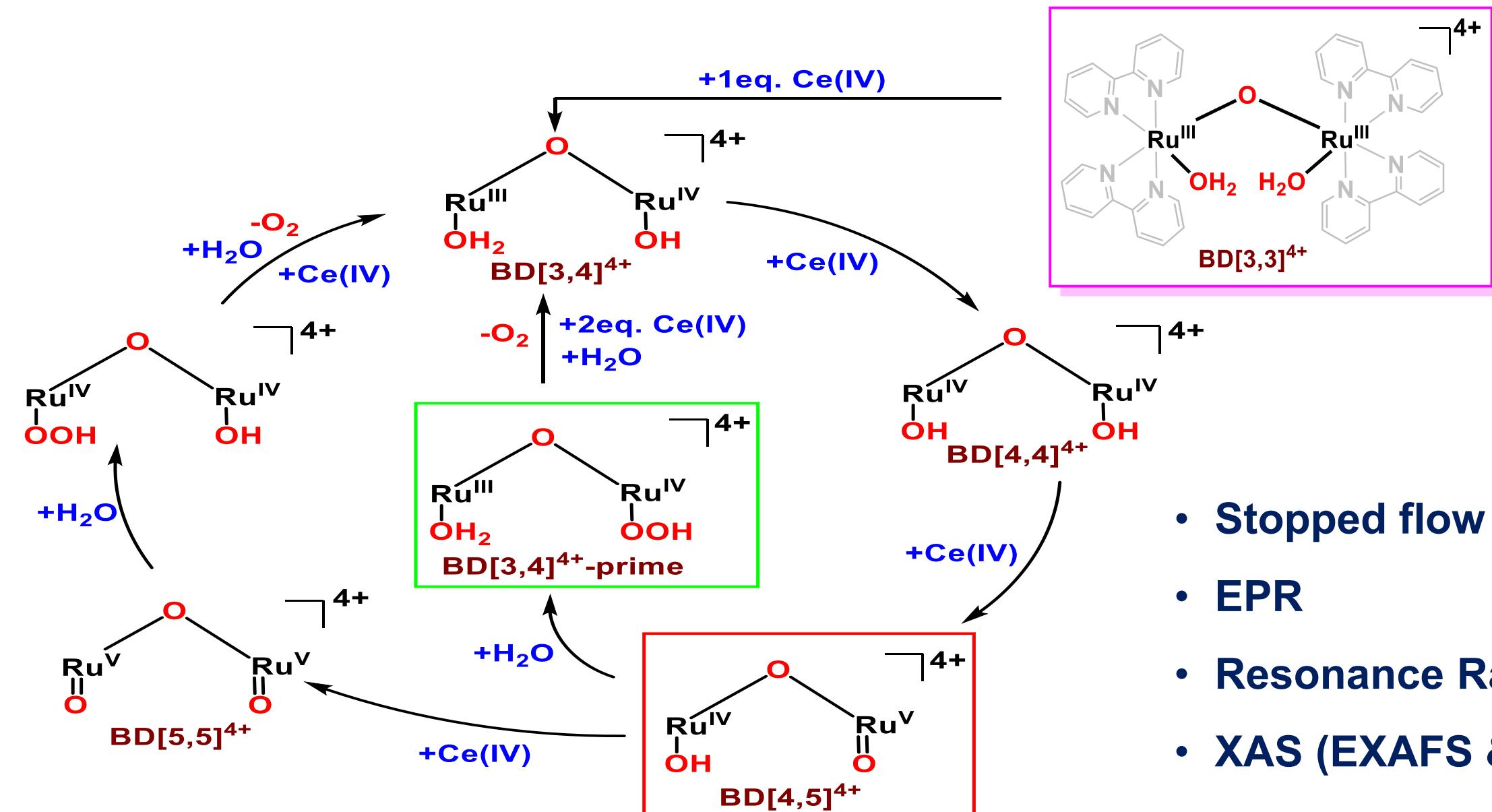


Llobet's group
JACS, 2004, 126, 7798



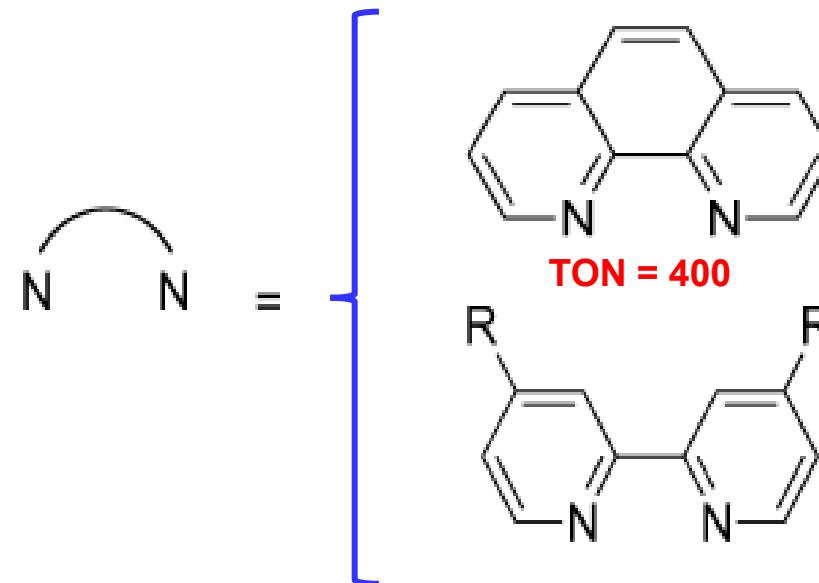
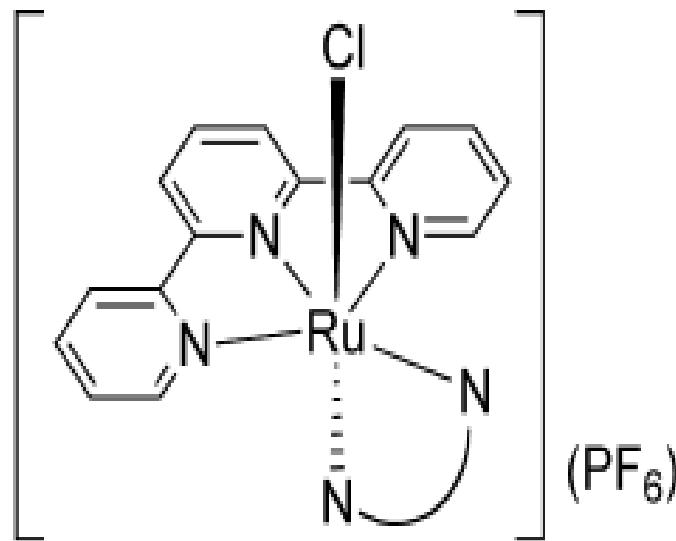
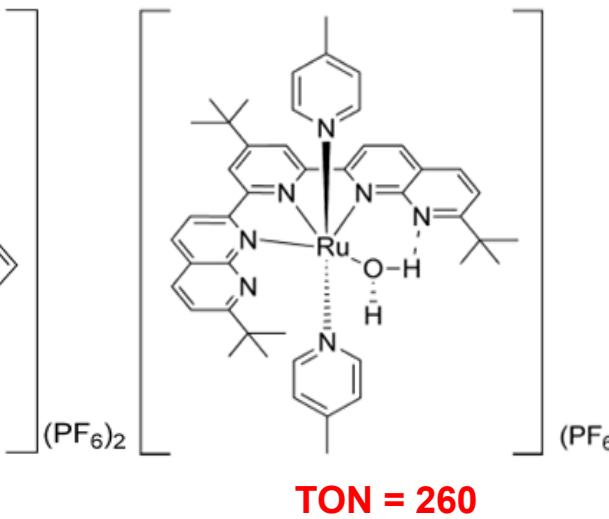
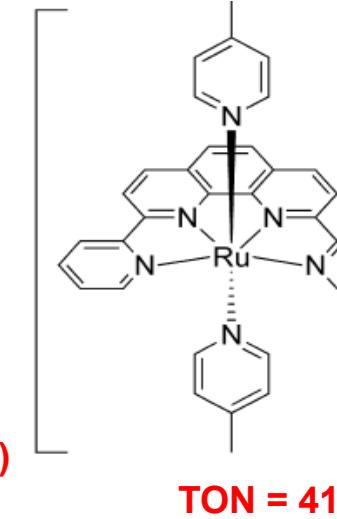
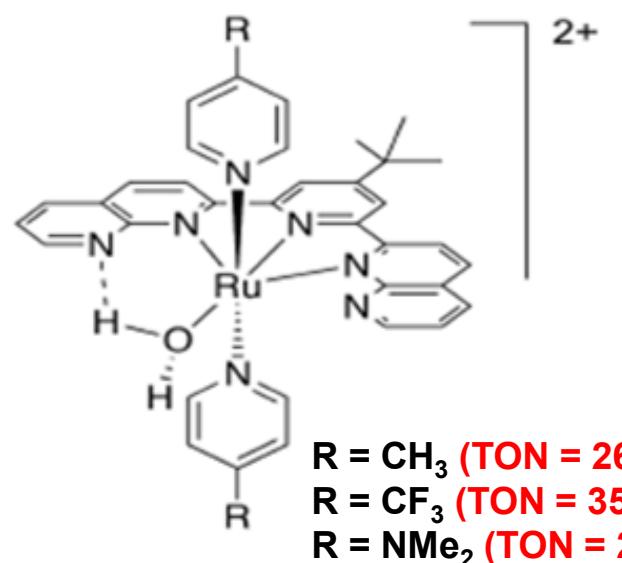
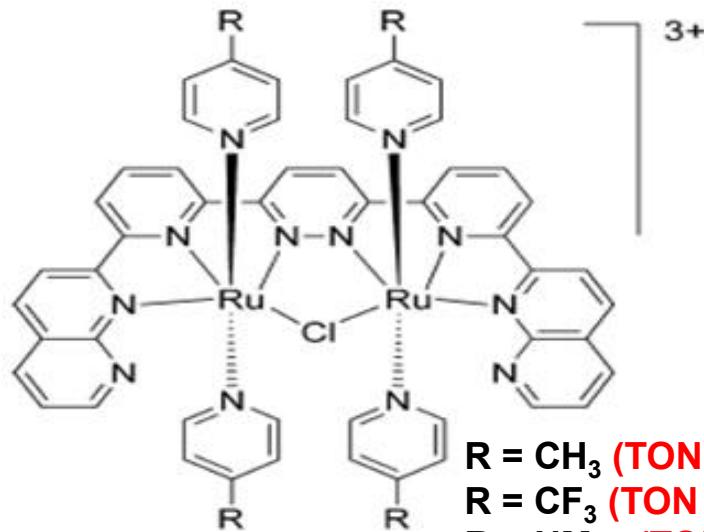
Thummel's group
JACS, 2005, 127, 12802

Mechanistic Study of Water Oxidation by Blue Dimer (BD)

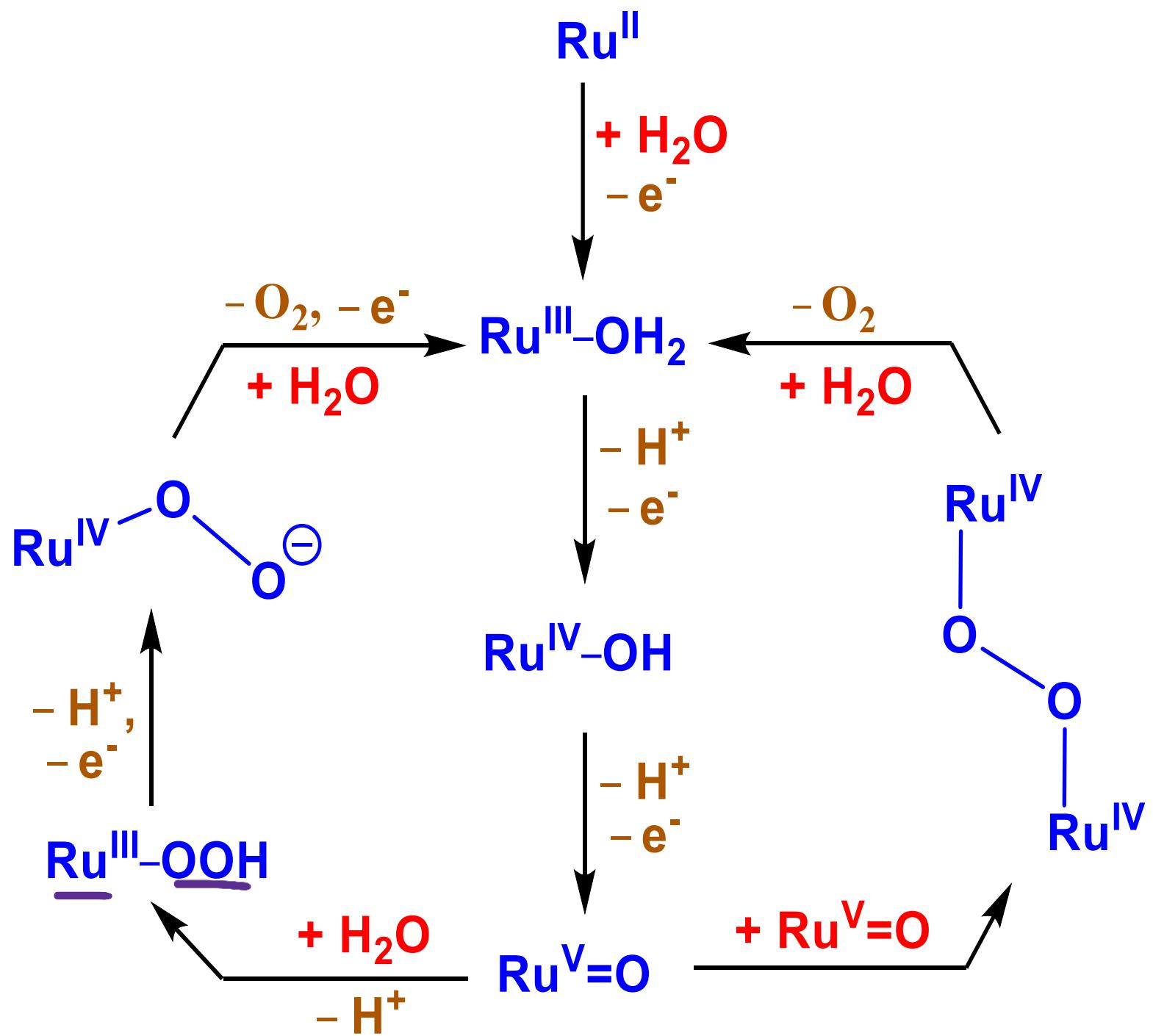


- Stopped flow Kinetics
- EPR
- Resonance Raman
- XAS (EXAFS & XANES)

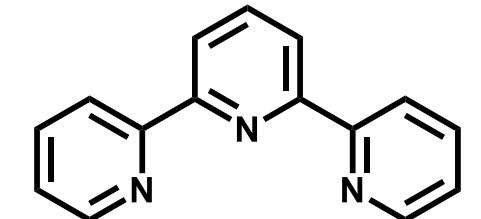
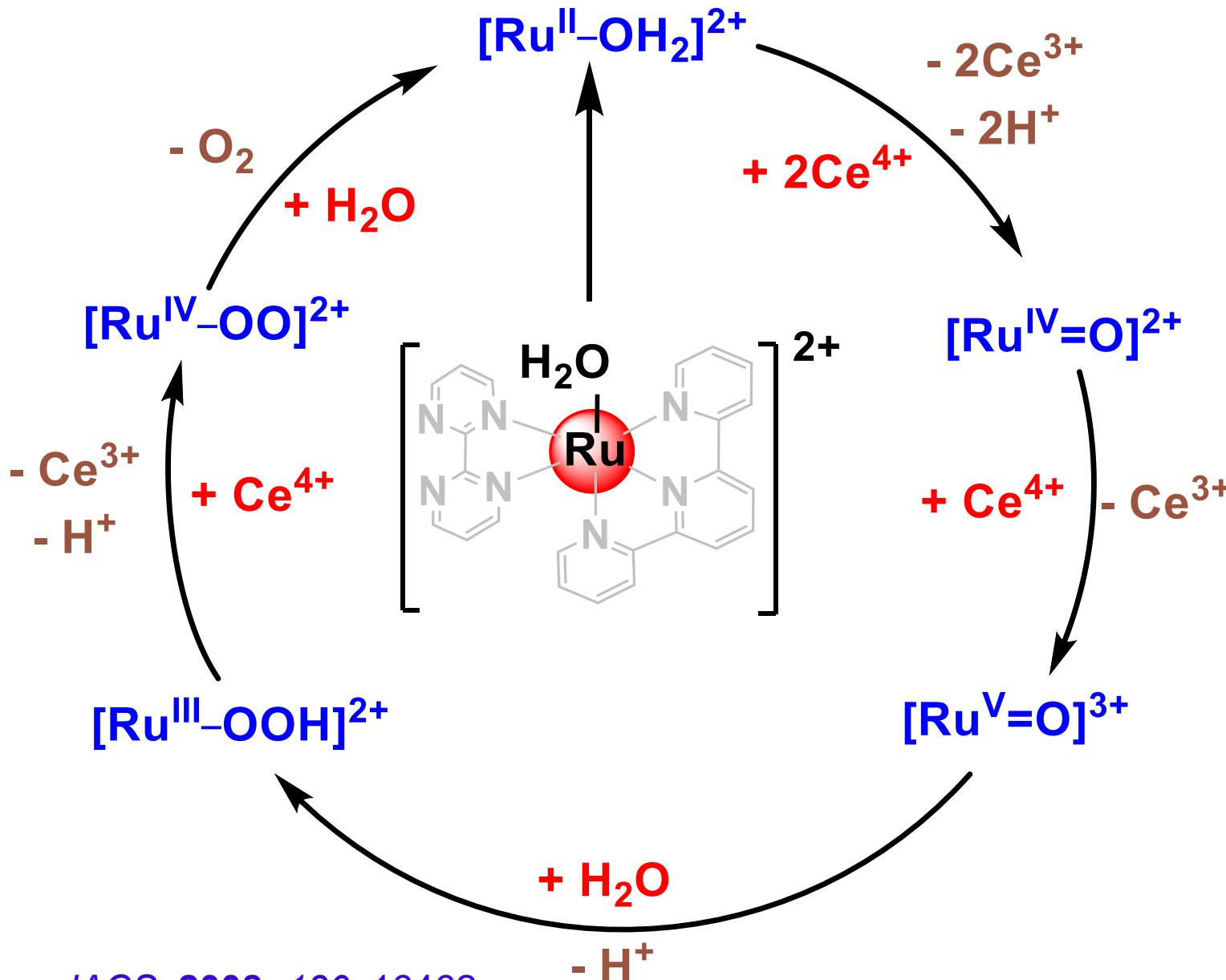
Is dimeric compound essential for Water Oxidation?



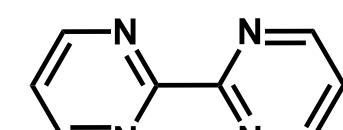
$\text{R} = \text{H}$ (TON = 390); $\text{R} = \text{Me}$ (TON = 190)
 $\text{R} = \text{OMe}$ (TON = 110); $\text{R} = \text{NO}_2$ (TON = 260)
 $\text{R} = \text{COOEt}$ (TON = 570)



Mechanistic Study of Water Oxidation

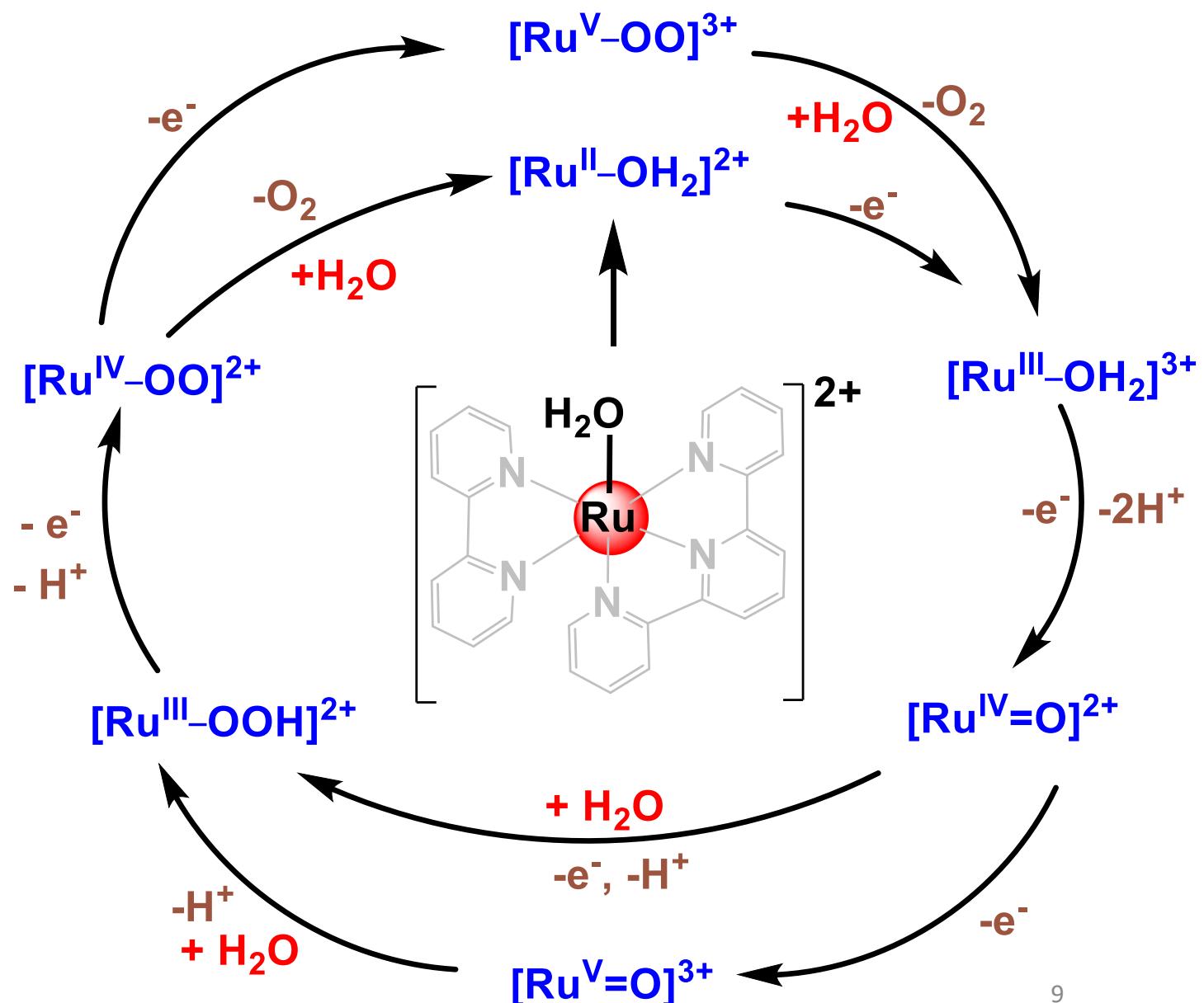
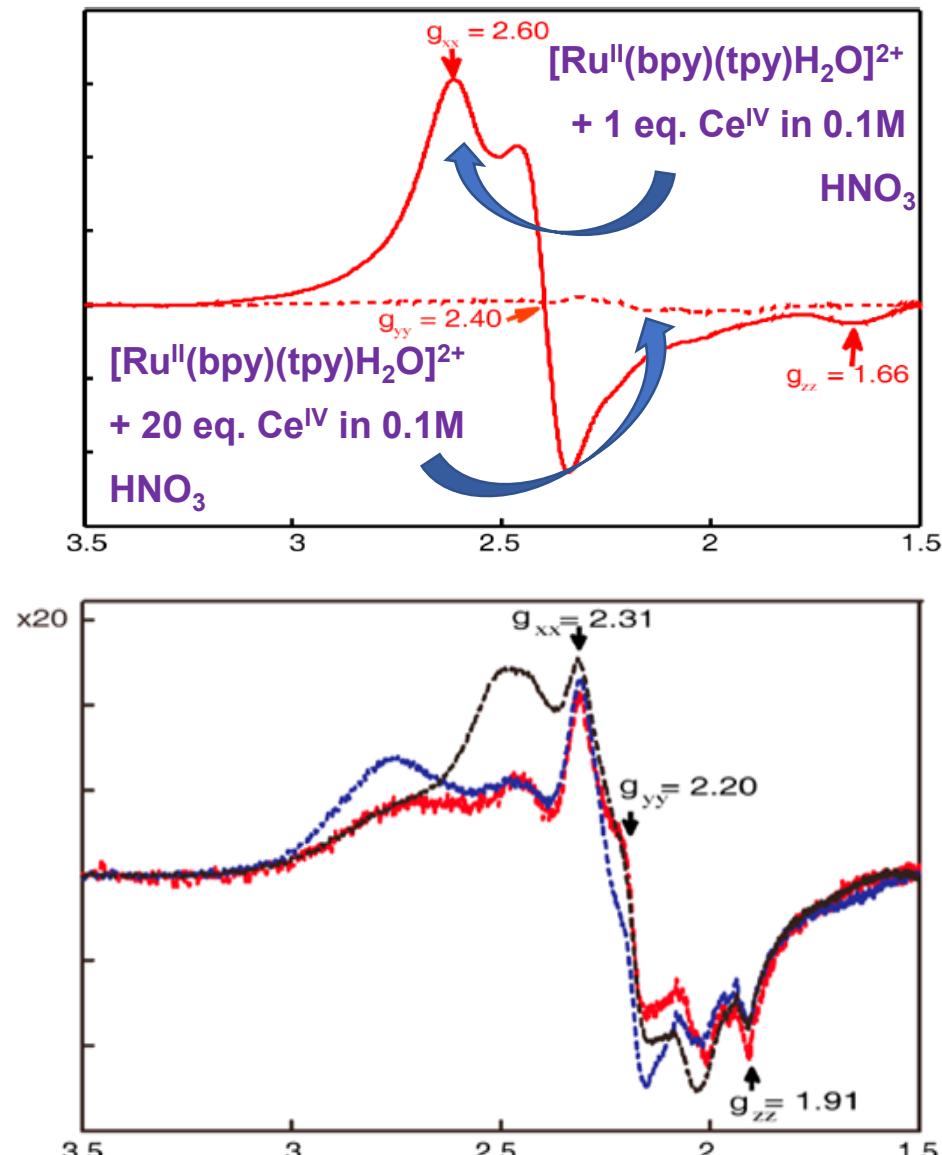


2,2':6',2''-terpyridine
(tpy)

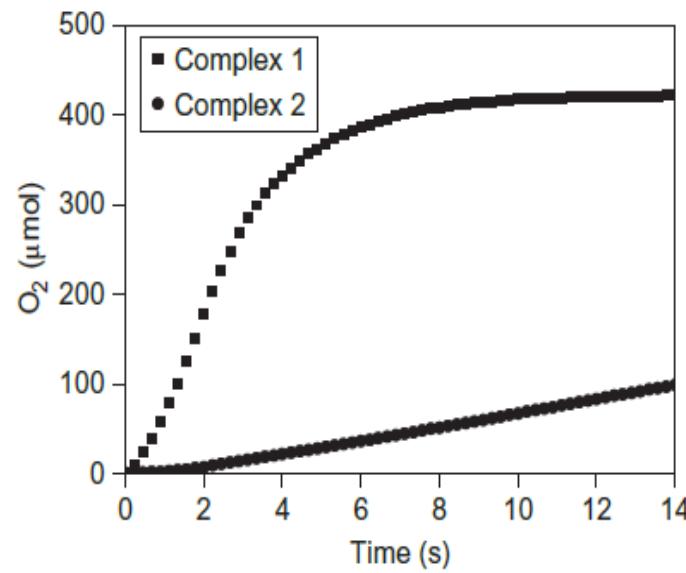
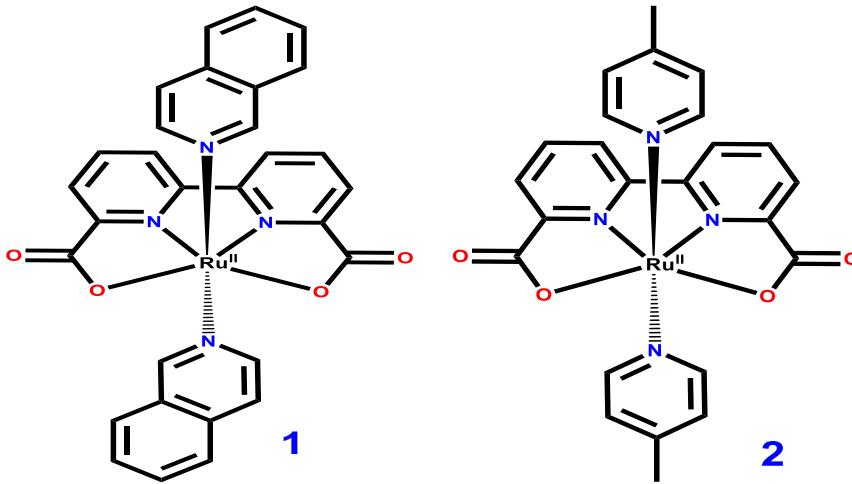


2,2'-bipyrimidine
(bpm)

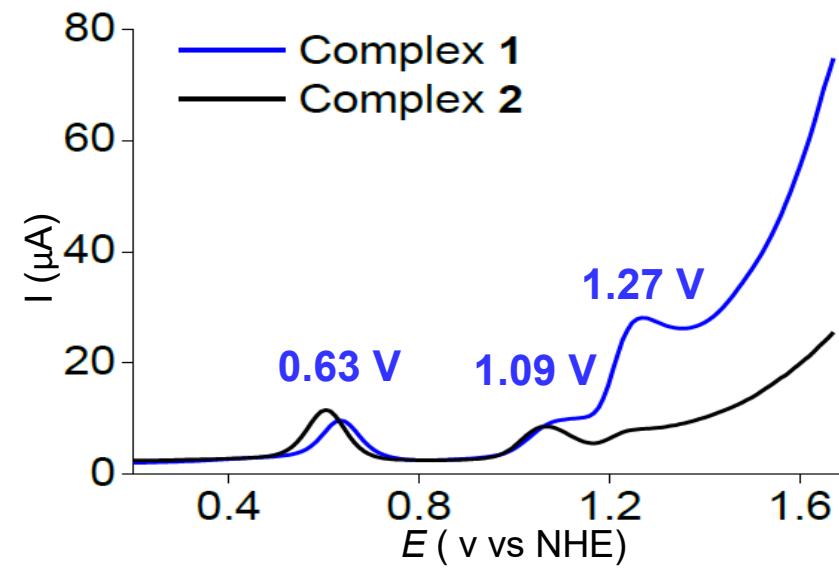
The active species: Ru^{IV}=O or Ru^V=O?



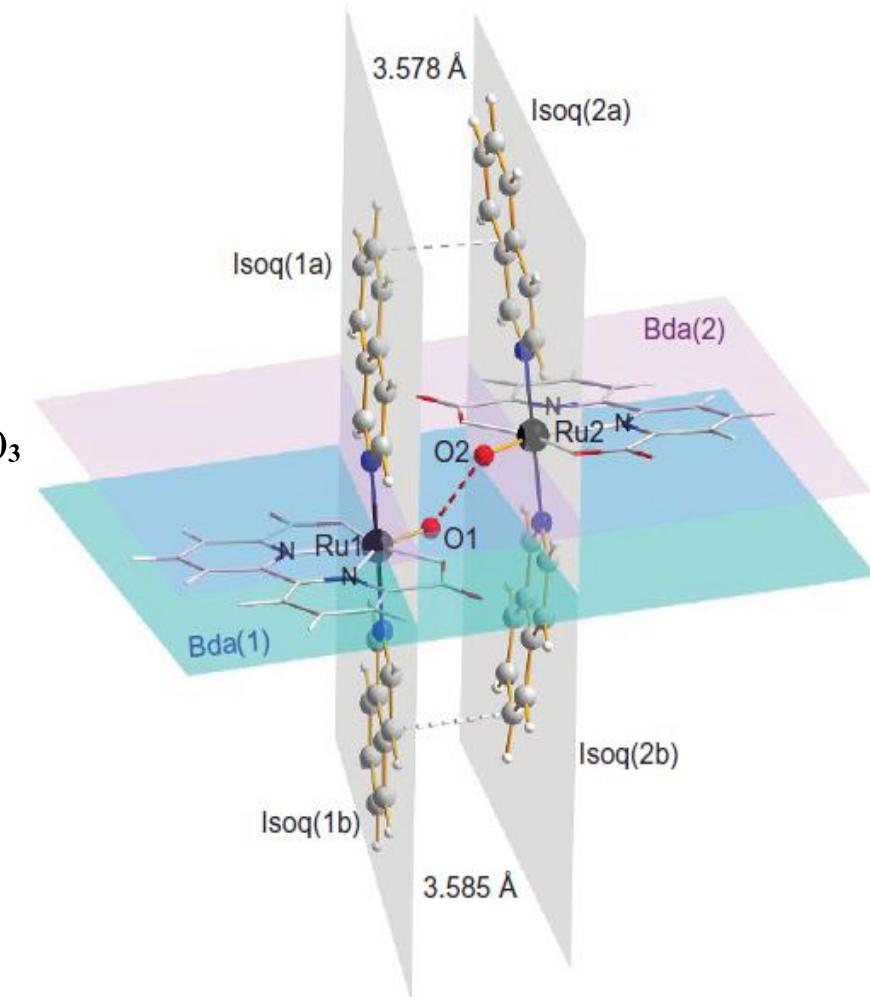
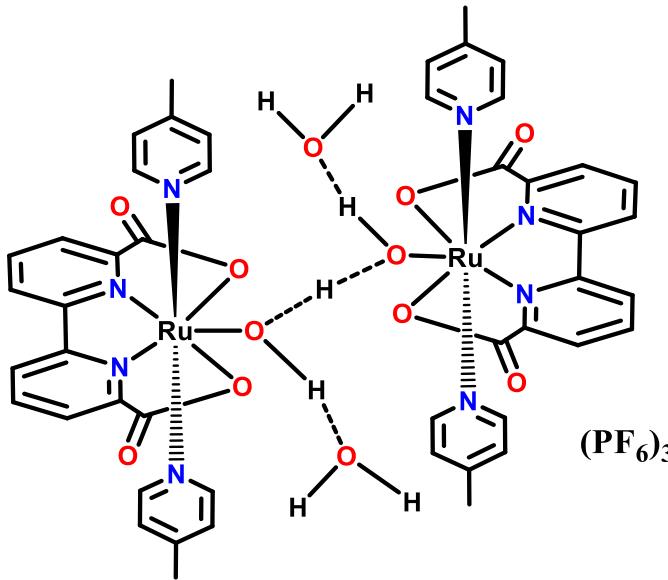
Effect of Dianionic ligands on Water Oxidation



Kinetic plots of oxygen formation



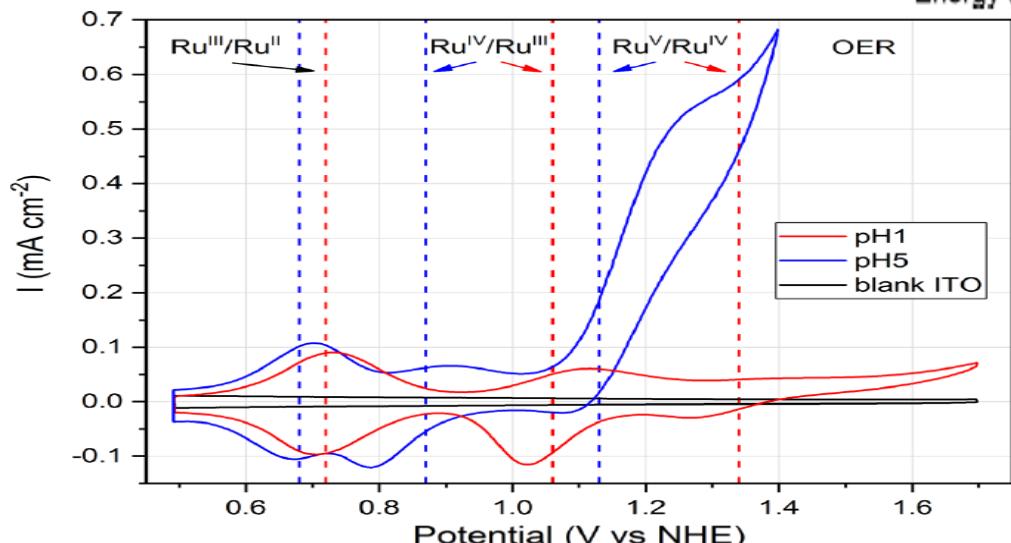
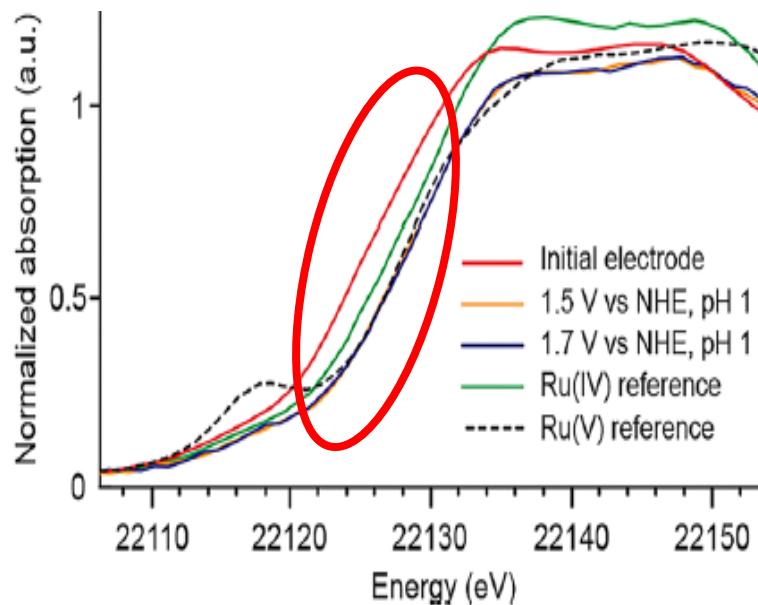
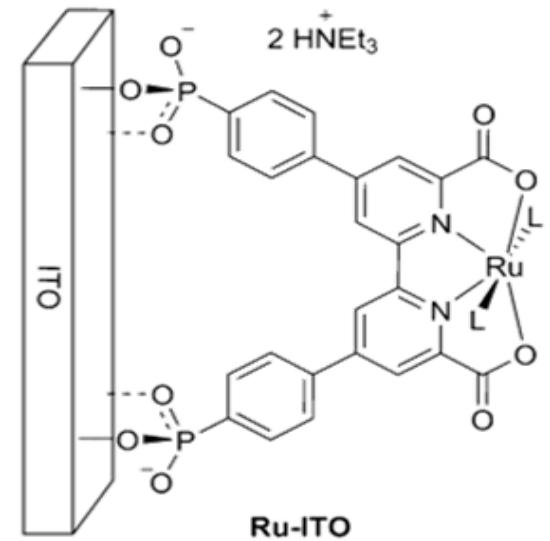
DPV of 1 and 2



TOF (1) = 303 s^{-1}

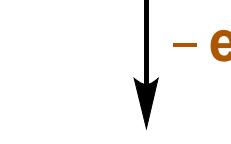
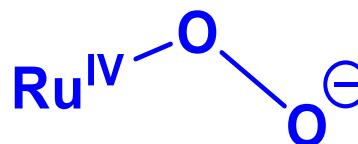
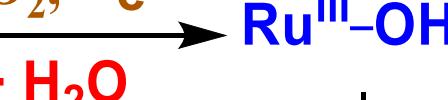
TOF (PS II) = 100 - 400 s^{-1}

Which path WNA or I2M?



CV of ITO and Ru-ITO electrodes

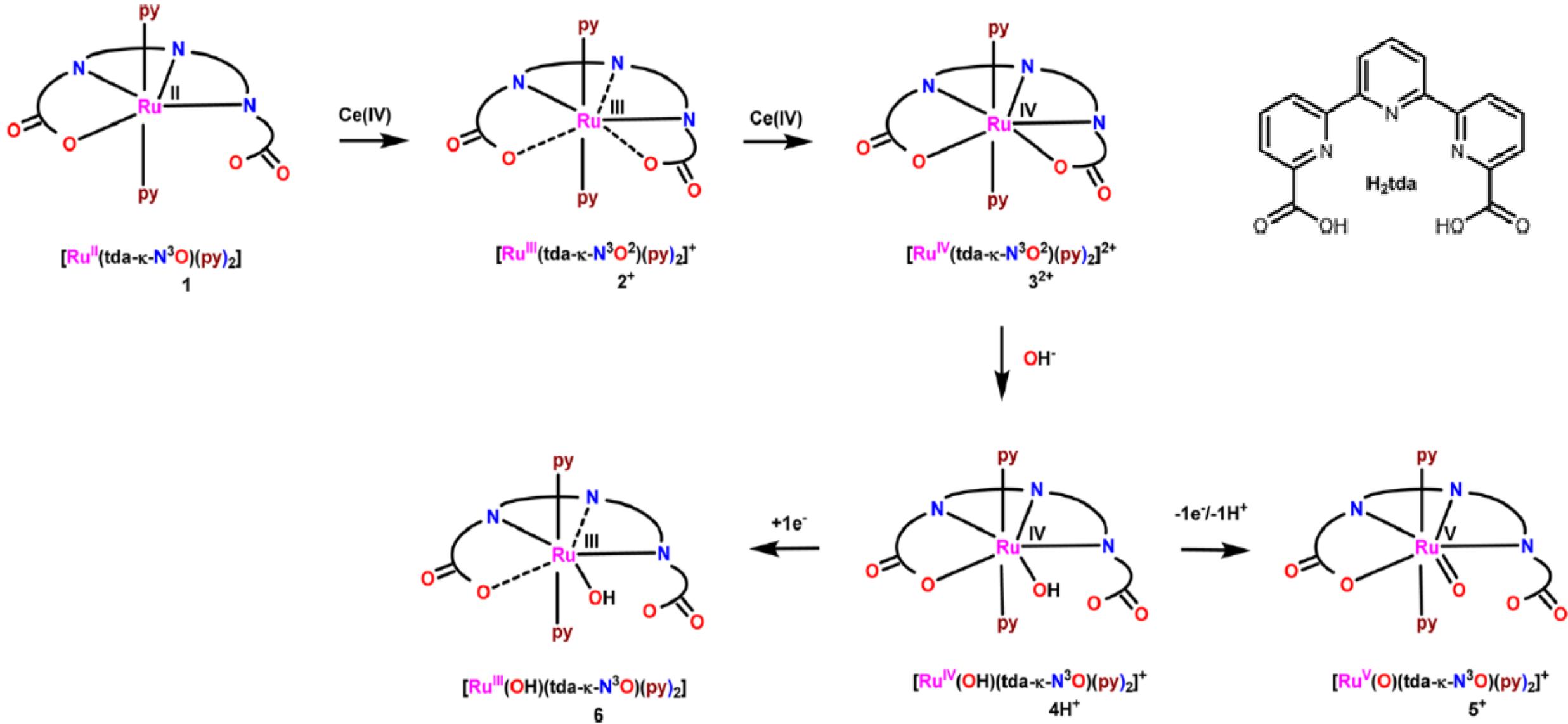
**Water Nucleophilic Attack (WNA)
preferred as Heterogenous Catalyst**



Intermolecular Oxo Radical coupling (I2M) path preferred as Homogenous Catalyst

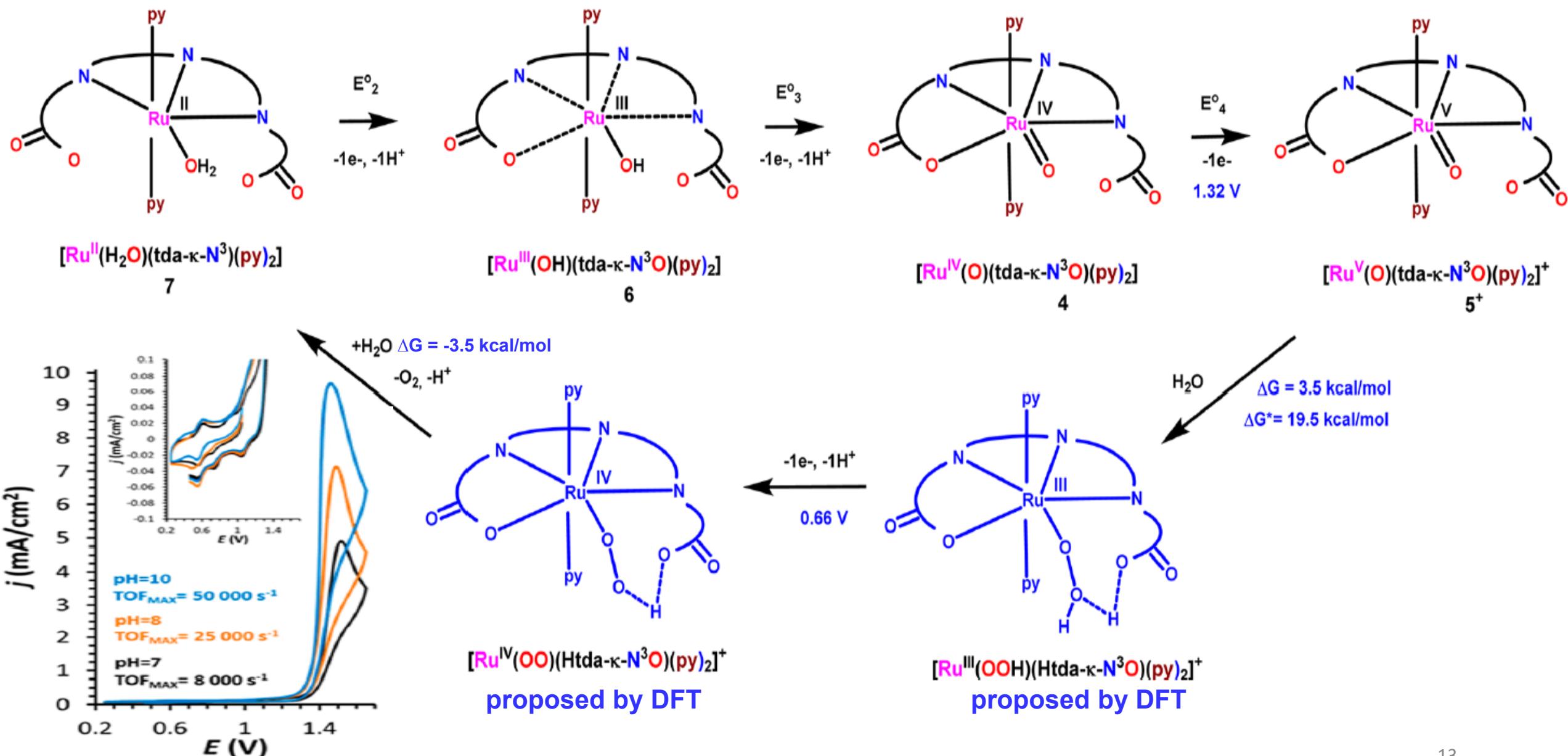


Dianionic ligand with Internal Basic site

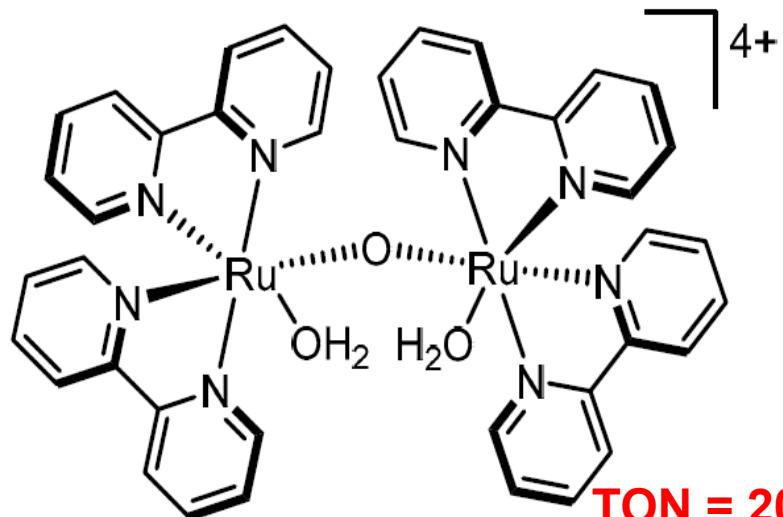


Broken lines indicates bonds that are simultaneously formed and broken at room temperature.

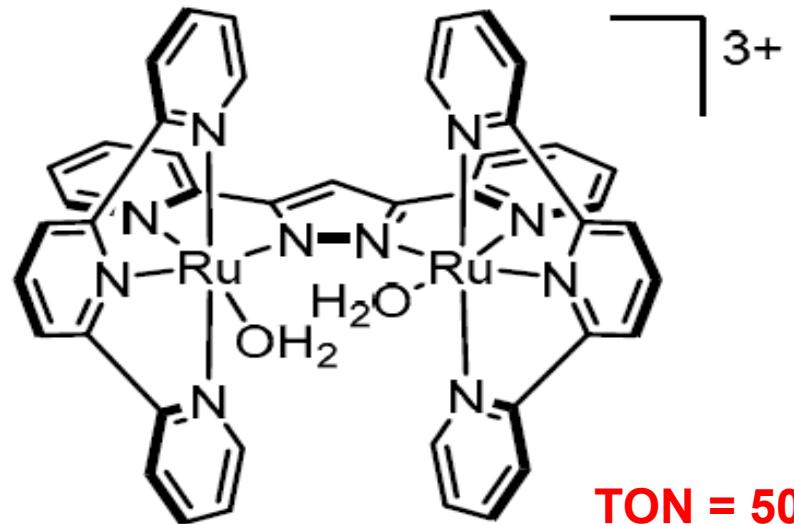
How Basic site makes Dramatic Change?



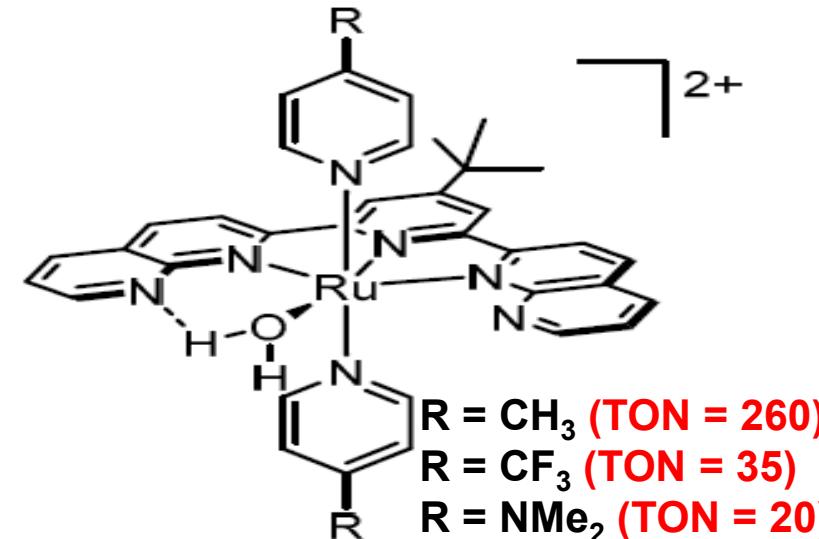
Conclusion



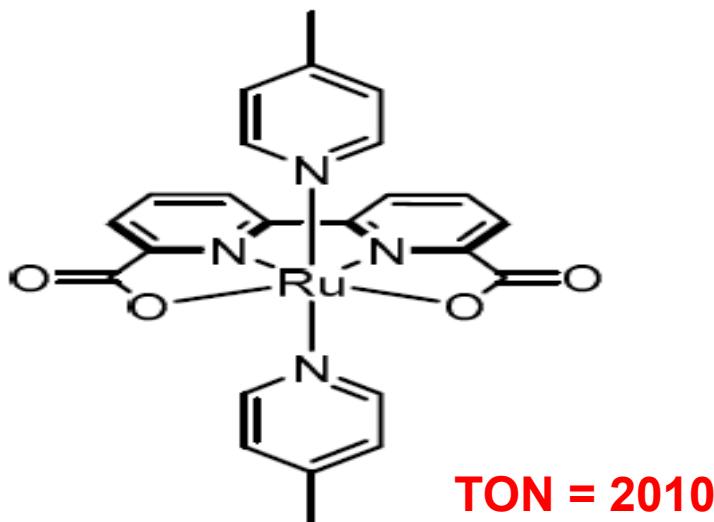
In 1982, First Ru-based WOC



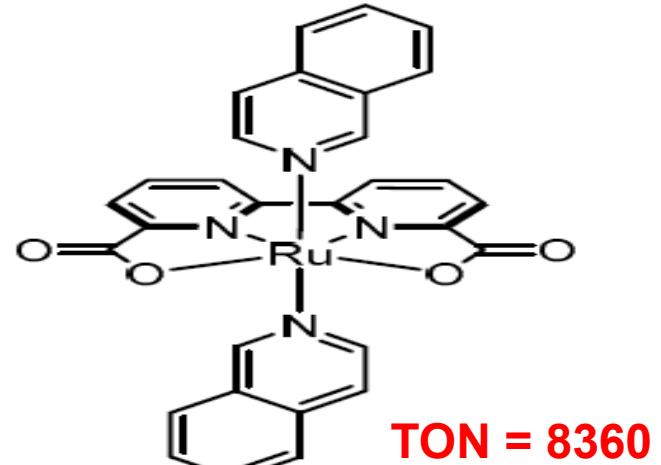
In 2004, With more Rigid Backbone
to favour I2M



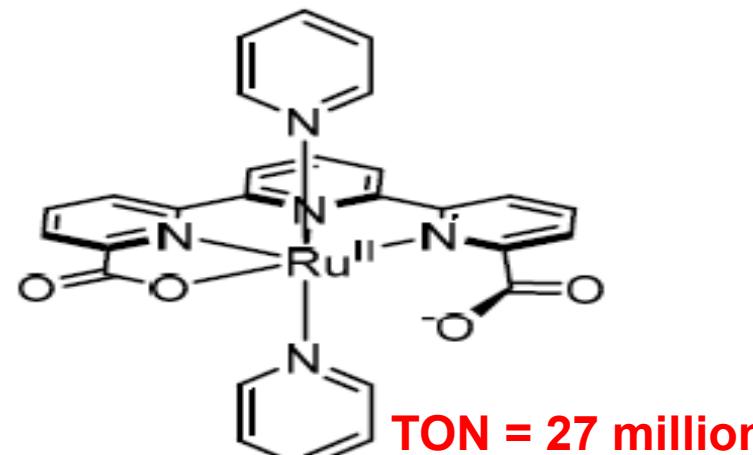
In 2005, One Metal Site is
Enough



In 2009, Evolution of
Anionic ligands



In 2012, **TOF = 303 s⁻¹**
(PS II, **TOF = 100 - 400 s⁻¹**)



In 2015, **TOF = 50000 s⁻¹**
at pH = 10