

## Multi-potential-step chronocoulo spectroscopy for electrocatalytic proton reduction by mononuclear ruthenium complexes

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Electrocatalytic proton reduction to  $H_2$  is a topic of worldwide interest as the need to solve energy and environmental issues. Molecular metal complexes are promising candidates for proton reduction catalysts, since their catalytic activity can be tuned via rational ligand design. An understanding of the redox reactions and catalytic aspects of the molecular catalysts is essential for improving their catalytic performance for proton reduction. A spectroelectrochemical technique is useful to directly observe the real change in the molecular catalysts in addition to the electrochemical data for current or charge for monitoring the reactions of molecular catalysts.<sup>1)</sup> In this study, we investigated electrocatalytic activities of *distal*-/*proximal*-[Ru(tpy)(L)(OH<sub>2</sub>)]<sup>2+</sup> isomers<sup>2)</sup> (tpy = 2,2':6',2''-terpyridine, L = 5-phenyl-2,8-di(2-pyridyl)-1,9,10-anthrydine) for proton reduction (Fig 1). Moreover, the catalytic mechanisms of both isomers were studied using a multi-potential-step chronocoulo spectroscopic (MPSCCS) technique (Fig 1).

UV-visible spectroscopic analysis of *distal*-/*proximal*-[Ru(tpy)(L)(OH<sub>2</sub>)]<sup>2+</sup> in acetonitrile (AN) showed that both isomers are stoichiometrically converted to *distal*-/*proximal*-[Ru(tpy)(L)(AN)]<sup>2+</sup> by exchange of the aqua ligand with solvent AN. The observed rate constants for the formation of *distal*-/*proximal*-[Ru(tpy)(L)(AN)]<sup>2+</sup> were estimated to be  $2.8 \times 10^{-2}$  and  $5.4 \times 10^{-2} \text{ min}^{-1}$ , respectively. Cyclic voltammograms (CVs) of *distal*-/*proximal*-[Ru(tpy)(L)(AN)]<sup>2+</sup> in dry AN under Ar exhibited three reversible reduction waves, assigned to three sequential one-electron reduction processes for both isomers. Addition of water changed the profile of the CVs for both isomers: large catalytic currents for proton reduction appeared. In the presentation, the proton reduction mechanisms of both isomers will be discussed based on the results obtained from the MPSCCS analysis.

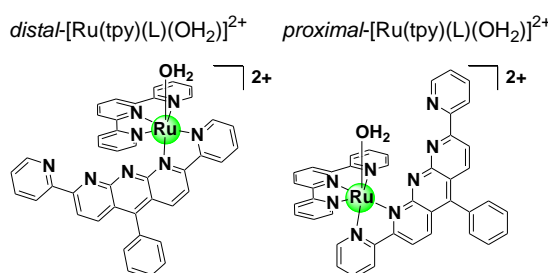


Fig 1. Structures of *distal* and *proximal* isomers of mononuclear Ru aquo complexes.

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