

第90回有機元素化学セミナー / The 90th Organoelement Seminar Series

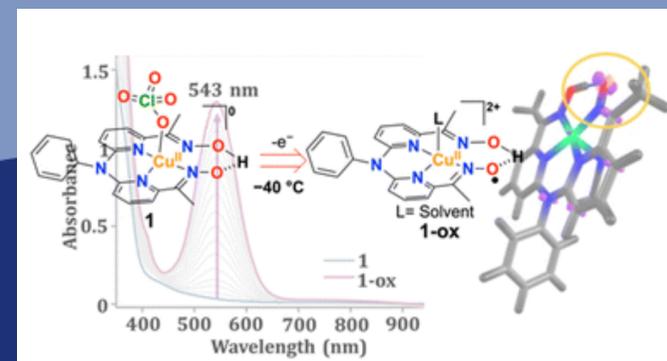
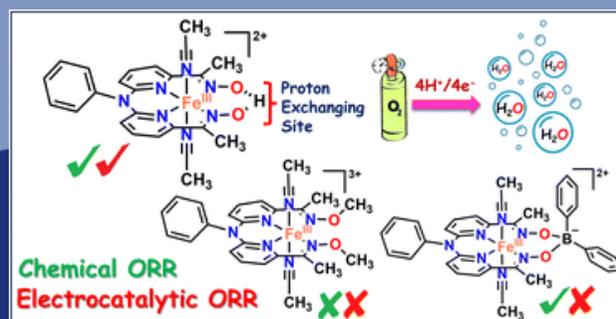
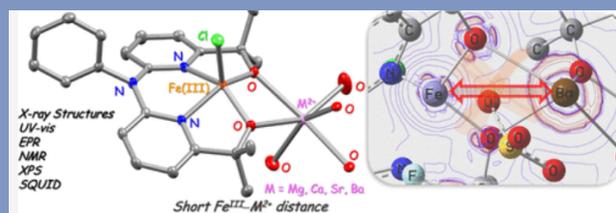
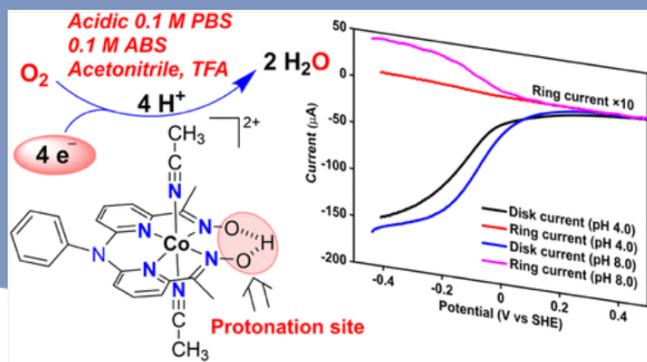


Prof. **Sayantan Paria**

(Indian Institute of Technology Delhi, India)

website URL: <https://sites.google.com/view/paria-research-group/>

"Exploring the Scaling Relationship for Oxygen Reduction Reaction Using Molecular Cobalt Complexes"



We are pleased to inform you that Dr. Sayantan Paria, an accomplished researcher from the Indian Institute of Technology Delhi, will be delivering a seminar at our institution. Dr. Paria is recognized for his work in molecular electrocatalysis, with a focus on the spectroscopic characterization and reactivity of high-valent transition metal intermediates. In this seminar, he will highlight recent developments in small-molecule transformation reactions, particularly those involving proton-coupled electron transfer processes, and discuss their mechanistic features and potential applications in energy-relevant catalysis.

16:30-17:30, June 9th (Mon.), 2025@Room WL1-301 (Lecture Theater, West Bld. 1, Science Tokyo)

Host: Yuma Morimoto (Sch. of Sci.) (yuma.morimoto@chem.sci.isct.ac.jp)

Exploring the Scaling Relationship for Oxygen Reduction Reaction Using Molecular Cobalt Complexes

Sayantana Paria

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The development of an efficient earth-abundant catalyst for the oxygen reduction reaction (ORR) is crucial, considering the importance of the reaction in fuel cell technology.¹ It has been shown in a series of molecular Fe(porphyrin) complexes that the turnover frequency (TOF) of ORR increases with increasing the effective overpotential (η_{eff}), which is often referred to as a ‘molecular scaling relationship’. Likewise, TOF also increases with decreasing the $E_{1/2}$ of the redox couple that initiates the catalysis (such as for ORR, CO₂ reduction, etc.). Thus, a catalyst can be defined as effective if it exhibits a high TOF value without altering the $E_{1/2}$ or η_{eff} . A careful design of a catalyst is, therefore, required to break the scaling relationship. In this study, a family of Co^{III} complexes (**1-8**) having a bis-pyridine-dioxime ligand architecture at the primary coordination sphere and a non-identical secondary coordination sphere (SCS) has been synthesized and characterized.² The electrocatalytic ORR activity of these catalysts has been explored in acetonitrile in the presence of trifluoroacetic acid (TFAH) and in a 1:1 TFAH/CF₃COO⁻ buffer solution. All the complexes were found to be selected for 4e⁻/4H⁺ reduction of O₂. A linear free energy relationship (LFER) for this series of catalysts was explored, which showed an increase in turnover frequency (TOF) with increasing effective overpotential (η_{eff}). However, Co^{III} catalysts embedded with *ortho*-NHMe₂⁺-C₆H₄- and *ortho*-OMe-C₆H₄- groups at the SCS don’t follow the LFER trend and exhibited >1000 and >250 times higher TOF than the values expected, considering their positions in the log(TOF)/ η_{eff} correlation in the buffer solution. Kinetic studies established similar kinetics for all the Co catalysts, and we propose that the protonation of the Co^{III}(O₂[•]) is the rate-determining step. Apparently, the presence of -NHMe₂⁺ or -OMe groups at the SCS creates proton relay sites, which assist in protonating the Co^{III}(O₂[•]) intermediate and cause the rate enhancement. The study enlightens the ligand design strategy for developing efficient molecular ORR catalysts that can break scaling relationships.

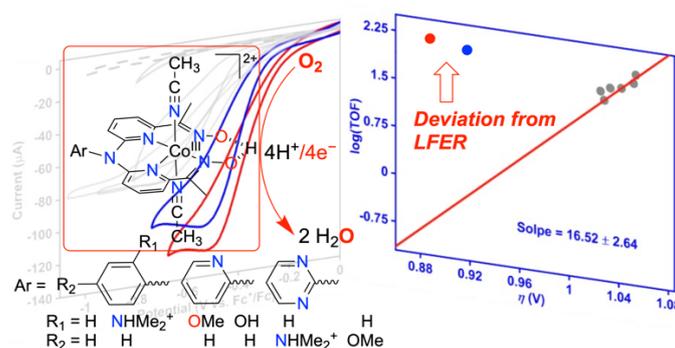


Figure 1. Linear free energy relationship for oxygen reduction reaction catalyzed by a series of Co^{III} complexes.

References

- 1 M. L. Pegis, C. F. Wise, D. J. Martin and J. M. Mayer, *Chem. Rev.*, 2018, **118**, 2340-2391.
- 2 (a) A. Das, A. Ali, G. Gupta, A. Santra, P. Jain, P. P. Ingole, S. Paul and S. Paria, *ACS Catal.*, 2023, **13**, 5285-5297; (b) A. Das, A. Santra, A. Kumari, D. Ghosh and S. Paria, *J. Am. Chem. Soc.*, 2025, **147**, 6549-6560; (c) A. Santra, A. Das, S. Kaur, P. Jain, P. P. Ingole and S. Paria, *Chem. Sci.*, 2024, **15**, 4095-4105.

Bio-Sketch

Dr. Sayantan Paria

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About speakers

Dr. Sayantan Paria completed his doctoral studies under the supervision of Prof. Tapan Kanti Paine at IACS Kolkata in December 2012. In April 2013, he joined the research group of Prof. Shinobu Itoh at Osaka University, Japan. After spending approximately three years in Japan, he moved to Spain to work as a postdoctoral fellow in Prof. Antoni Llobet's research group, where he continued his research on molecular electrocatalysis from May 2016 to March 2017. In April 2017, Dr. Paria joined the Indian Institute of Technology Delhi as an Assistant Professor and was promoted to Associate Professor in December 2022. His research interests include molecular electrocatalysis and the spectroscopic characterization and reactivity studies of high-valent transition metal-containing reaction intermediates.

Research Interests

His area of research includes electrocatalysis using transition metal-containing small molecules, spectroscopic characterization, and proton-coupled electron transfer reactivity studies of metastable reaction intermediates involved in small molecule transformation reactions.

Awards and Honors

1. Early Career Research (ECR) Award, 2018, Government of India
2. JSPS Postdoctoral Fellowship (2014-2016)
3. Postdoctoral fellowship from ICIQ International Postdoctoral Mobility Programme (ICIQ-IPMP) (2016-2017)
4. Humboldt Postdoctoral Fellowship (not joined)