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Unravelling the Role of –OCH₃ Positional Isomerism and Dihedral Angle in Ni(II)-dppe Dithiolates for Enhanced Heterogeneous Electrocatalytic Oxygen Evolution Reaction (OER)

Devyani Srivastava,^a Aparna Kushwaha,^a Ratna Chauhan,^b Suresh W. Gosavi,^c Sarfaraz Ahmed,^d
Gabriele Kociok-Köhn,^{e*} Abhinav Kumar ^{a*}

^a Department of Chemistry, Faculty of Science, University of Lucknow, Lucknow 226007, India.

Email: abhinavmarshal@gmail.com

^b Department of Environmental Science, Savitribai Phule Pune University, Pune-411007, India.

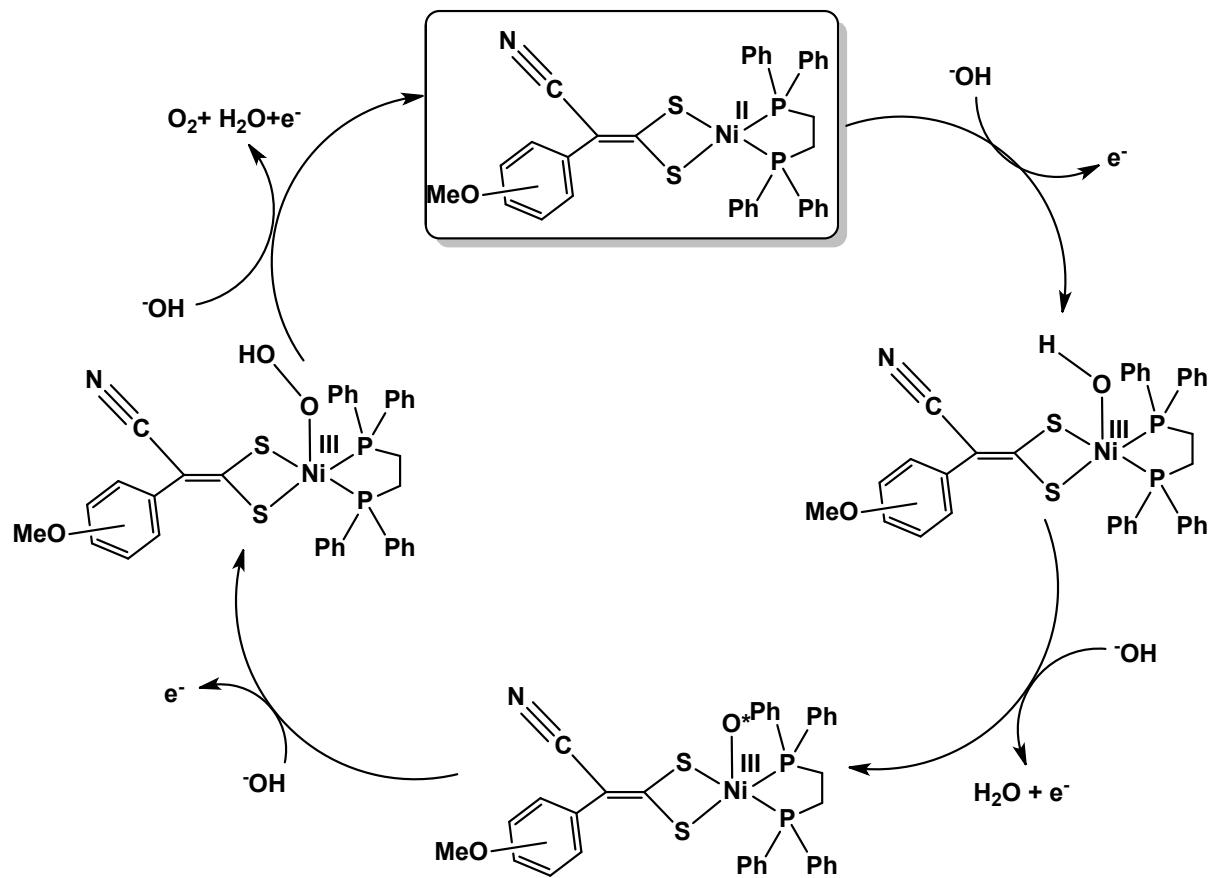
^c Department of Physics, Savitribai Phule Pune University, Pune-411007, India.

^d Department of Pharmacognosy, College of Pharmacy, King Saud University, P.O. Box 2457 Riyadh 11451, Saudi Arabia

^e Physical Structure Characterization, University of Bath, Claverton Down, Bath, BA2 7AY, UK.

Email: chsgk@bath.ac.uk

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Scheme S1. The plausible mechanistic pathway for dppe appended Ni(II)-dithiolate electrocatalysed OER.

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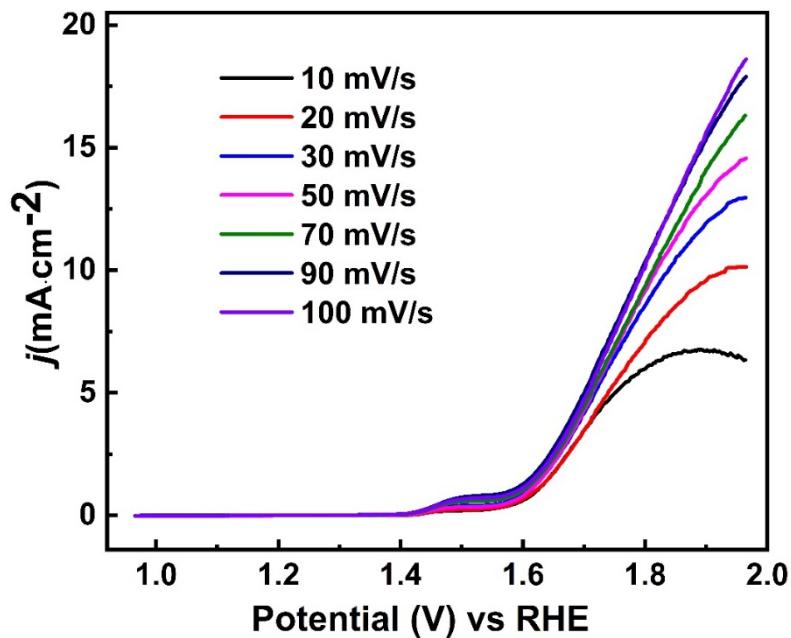


Fig. S1 Linear sweep voltammograms for Ni-L1 at different scan rates

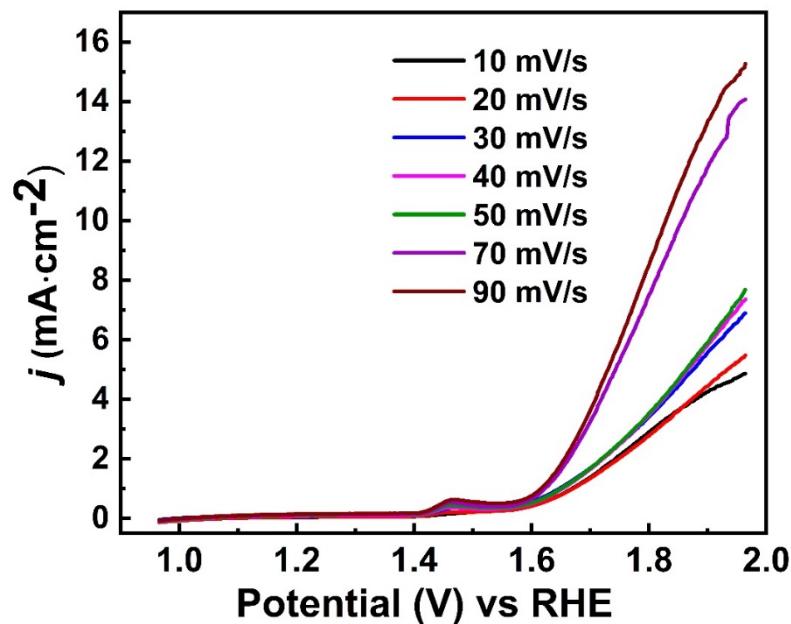


Fig. S2 Linear sweep votammograms for Ni-L2 at different scan rates

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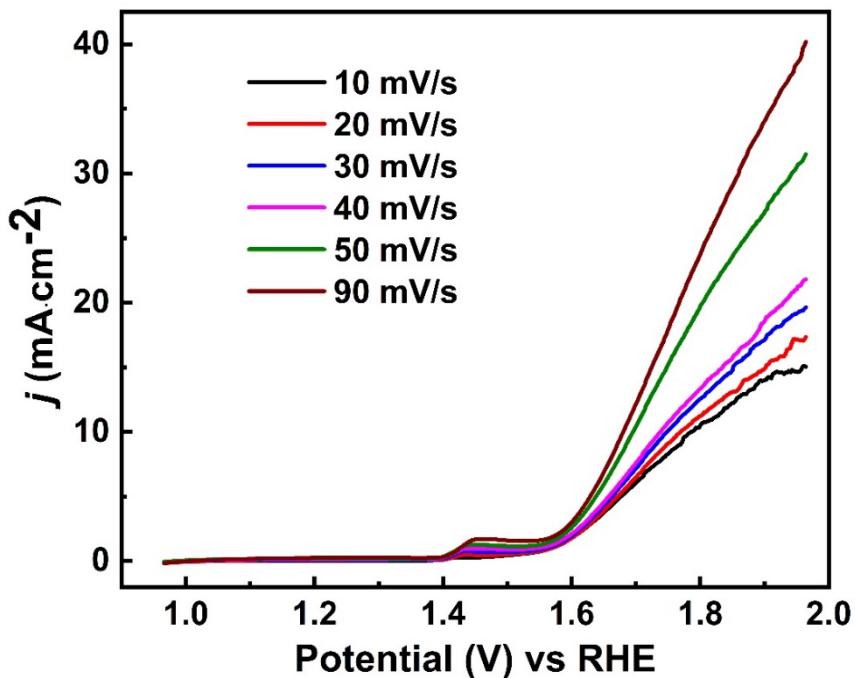


Fig. S3 Linear sweep voltammograms for Ni-L3 at different scan rates

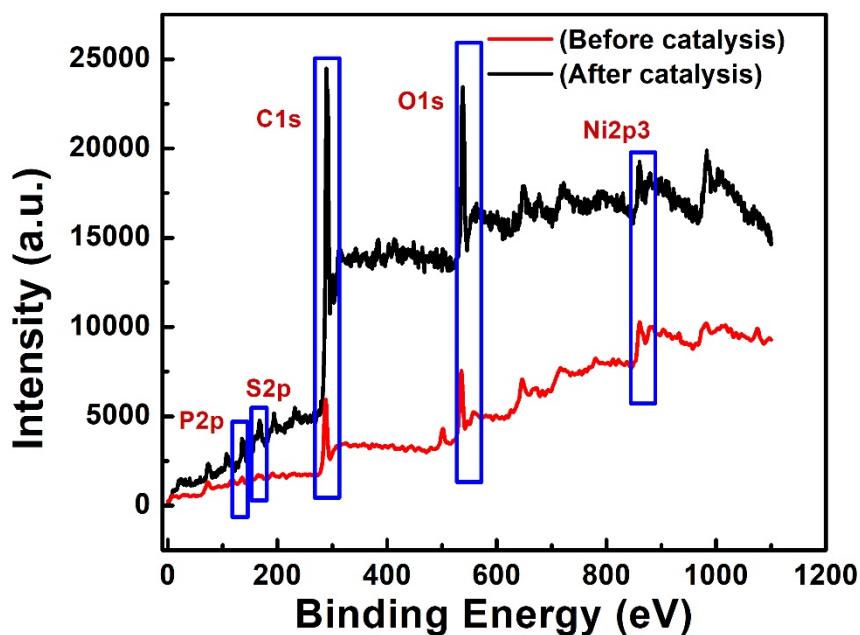


Fig. S4 XPS spectra for Ni-L3 before and after OER electrocatalysis.

Table S1 The OER electrocatalytic performances of some previously reported analogous complexes.

Electrocatalyst	Supporting	Onset Potential	Potential (V) at 10	Ref.
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	Electrolyte	(V)	mV·cm⁻²	
Ni-L1	0.1M KOH	1.58	-	This work
Ni-L2	0.1M KOH	1.59	1.60	This work
Ni-L3	0.1 M KOH	1.56	1.49	This work
Ni-mtsq	0.1 M KOH	1.54	-	1
Nidtsq	0.1 M KOH	1.50	1.38	2
1	0.1 M KOH	1.69	-	3
Ni-1	0.1 M KOH	1.49	1.05	4
Ni-2	0.1 M KOH	1.55	1.43	4
Ni-3	0.1 M KOH	1.52	1.12	4
Ni-4	0.1 M KOH	1.57	1.13	4
GC _{rde} /Nf-1	1 M KOH	1.72	1.82	5
GC _{rde} /Nf-2	1 M KOH	1.52	1.58	5
GC _{rde} /Nf-3	1 M KOH	1.57	1.67	5
GC _{rde} /Nf-4	1 M KOH	1.56	1.65	5
GCE/Nf/Complex-1	0.1M KOH	-	-	6
GCE/Nf/Complex-2	0.1M KOH	-	1.73	6
GCE/Nf/Complex-3	0.1M KOH	-	1.68	6

1. D. Srivastava, A. Kushwaha, G. Kociok-Köhn, S. W. Gosavi, R. Chauhan, A. Kumar and M. Muddassir, The supramolecular frameworks and electrocatalytic properties of two new structurally diverse tertiary phosphane-appended nickel(II) and copper(I) thiosquarates. *CrystEngComm*, 2023, **25**, 6822-6836. <https://doi.org/10.1039/D3CE00817G>
2. A. Kushwaha, D. Srivastava, G. Kociok-Köhn, Y. Padwal, R. Chauhan, S. Gosavi, M. Muddassir and A. Kumar, Insights into the supramolecular and molecular

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electrocatalytic properties of 1,2-bis(diphenylphosphine)ethane appended nickel(II) 1,2-dithiosquare for oxygen and hydrogen evolution reactions. *New J. Chem.*, 2024, **48**, 3717-3728. <https://doi.org/10.1039/D4NJ00247D>

3. A. Singh, A. Singh, G. Kociok-Köhn, K. C. Molloy, A. K. Singh, A. Kumar, M. Muddassir, Ni(II) dithiolate anion composites with two-dimensional materials for electrochemical oxygen evolution reactions (OERs). *New J. Chem.*, 2021, **45**, 16264–16270. <https://doi.org/10.1039/D1NJ02644E>
4. A. Kushwaha, D. Srivastava, G. Kociok-Köhn, S. W. Gosavi, R. Chauhan, S. Ahmed, A. Kumar, Supramolecular and electrocatalytic OER properties of new heteroleptic fluoro- and trifluoromethyl-substituted Ni(II)-dithiolates: effects of substituents and dihedral angle on the electrocatalytic performance. *New J. Chem.*, 2024, **48**, 15856–15865. <https://doi.org/10.1039/D4NJ03502J>
5. Anamika, D. K. Yadav, K. K. Manar, C. L. Yadav, K. Kumar, V. Ganesan, M. G. B. Drew, N. Singh, New Heteroleptic [Ni(II) 1,1-Dithiolate-Phosphine] Complexes: Synthesis, Characterization and Electrocatalytic Oxygen Evolution Studies. *Dalton Trans.*, 2020, **49**, 3592-3605. <https://doi.org/10.1039/C9DT04923A>
6. M. K. Gond, S. K. Pandey, U. K. Chaudhari, P. K. Sonker, M. K. Bharty, V. Ganesan, B. Prashanth, S. Singh, Synthesis, crystal structures and electrocatalytic water oxidation by Mn(II), Co(II) and Ni(II) complexes of thiophene-2-carbohydrazide. *J. Mol. Struct.*, 2022, **1270**, 133886. <https://doi.org/10.1016/j.molstruc.2022.133886>