

Dr. Indresh Kumar Pandey

Area of Interest

Organic Chemistry: (i) *Catalytic-Transfer-hydrogenation of amide, carbamates, urea derivatives, polyurethanes and carbon-dioxide*

(ii) *Bio-inspired hydrogenase enzymes for proton reduction and hydrogen evolution, N-heterocyclic carbene complexes*

(iii) *Electrocatalytic CO₂ reduction, water oxidation, Organometallic chemistry*



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Education:

Ph.D.: (*Delhi University 2011-2016*) **Topic:** *Bio-inspired hydrogenase enzymes for proton reduction and hydrogen evolution*

2004-2006: *Master of Science in Organic Chemistry 1st Division, Gorakhpur University, India.*

2001-2004: *Bachelor of Science in Chemistry with 1st Division, Gorakhpur University, India.*

Postdoctoral –Fellow

- *Ph.D; C.N.U, Seoul South Korea in 2011*
 - *Postdoctoral Fellow at Department of Chemistry IISER Bhopal 2017-2019 (Prof. Joyanta Choudhury)*
 - *Postdoctoral Fellow at Department of Chemistry B.H.U. 2019-2022 (Prof. D.S Pandey)*
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Research Experience

- *Research Associate at Department of Chemistry IARI; 2016 – 2017, Delhi.*
 - *Project Assistant at National Physical Laboratory 2009 to 2010 Delhi.*
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Teaching Experience

- *Assistant professor at DDU Gorakhpur University Nov. 2022*
- *Assistant professor at Gujrat Public Service commission; August 2022*
- *Assistant Professor on a contractual basis at St. Andrew's College Gorakhpur, from 2007 - 2009.*

Experimental -Skills

- Synthesis of air sensitive catalyst on milligram scale.
- Ex-situ and in-situ synthesis of compounds using standard schlenk line techniques
- Handling of glove box for inert reactions
- X-ray single crystal structure solution
- Handling of cyclic- voltametry and electro-catalytic studies

Characterization techniques

- NMR, ESI-MASS
- FT-IR
- UV-Vis
- Cyclic-voltametry

Achievements & Awards

- NET-LS (Lecturer) CSIR in December 2009
- JRF (Junior Research Fellowship) UGC-CSIR in 2010
- NET-SRF (Senior Research Fellowship) UGC-CSIR in 2013
- National Postdoctoral Fellowship DST- SERB (N-PDF), India in 2017
- D. S. Kothari Postdoctoral Fellowship, University Grant Commission, India 2019
- BEST- ACS poster award

Members of professional bodies

- Life Time Member of Chemical Research Society of India (CRSI)
- Life Time Member of Indian Carbon Society of India

Administrative work

- Proctorial Board at DDU Gorakhpur
- ICT cell member at DDU Gorakhpur
- Supridentet of sports college DDU Gorakhpur

Publications:

- 1) Biphenol-based tetradentate N_2O_2 donor scaffold binuclear Zn(II) and trinuclear Cu(II) Complexes: Synthesis, Structure, Characterizations, and catalytic cyanosilylation of aldehydes at room temperature, Adelew Estifanos Filkale, **Indresh Kumar Pandey** and Ray Butcher, *Inorg. Chimica Acta.*, 2024, **559**, 12180
- 2) Binuclear cobalt(II) complexes: synthesis, structure, characterizations and catalytic applications in acceptor-less dehydrogenation (AD) of primary alcohols into aldehydes, Adelew Estifanos Filkale, **Indresh Kumar Pandey** and Ray Butcher, *New J. Chem.*, 2023, **47**, 19657-1967
- 3) Silver Cluster of Pentamethylene-Functionalized Bis-Limidazolium Dication Ligands and its Application in A_3 Coupling Reactions, **Indresh Kumar Pandey**, Priti Malhotra,

Pooja Sharma, Ranjeev Kumar and Prakash Chandra., SSRN: (Submitted) 2023; <http://dx.doi.org/10.2139/ssrn.4584175>

- 4) *An Imidazolylidene-Based Mesoionic Carbene–Mn (I) Complex and Its Catalytic Potential in N-Heteroarene Hydrogenation*, Ravi Kumar, Madhusudan K. Pandey, **Indresh K. Pandey**, Abhishek Kumar and Dr. Joyanta Choudhury, *Eur. J. Inorg. Chem.*, 2023, 26, 2875-2882.
- 5) *Ru (II) half-sandwich complexes of N-heterocyclic carbene (NHCs); investigation toward electrochemical water oxidation*, **Indresh Kumar Pandey**, Pooja Sharma, *Chem. Commun.*, (Submitted) 2023.
- 6) *Acid-assisted Hydrogenation of CO₂ to methanol using Ru(II) and Rh(III) RAPTA-type catalysts under mild conditions*, Pooja Sharma, **Indresh Kumar Pandey**, Abhinav Kumar, Sanjay Kumar Nigam P. Rath and Manoj Trivedi, *Chem. Commun.*, 2021, 57, 8941–8944.
- 7) *Switching Site-Reactivity in Hydrogenase Model Systems by Introducing a Pendant Amine Ligand*, **Indresh Kumar Pandey**, Tashika Agarwal, Shaikh Mobin; Matthias Stein, Sandeep Kaur-Ghumaan, *ACS Omega* 2021, 6, 4192-420.
- 8) *Electrocatalytic CO₂ Reduction with a Half-Sandwich Cobalt Catalyst: Selectivity towards CO*, **Indresh Kumar Pandey**, Abhishek Kumar, and Joyanta Choudhury, *Chem. Asian J.*, 2020, 15, 904-919.
- 9) *Intramolecular Stabilization of a Catalytic [FeFe] Hydrogenase Mimic Investigated by Experiment and Theory*, **Indresh Kumar Pandey**, Firasat Hussain, Matthias Stein, and Sandeep Kaur-Ghumaan, *Dalton Trans.*, 2018, 47, 4941-4949.
- 10) *Synthesis and Electrocatalysis of Diiron Monothiolate Complexes: Small Molecule Mimics of the [FeFe] Hydrogenase Enzyme*, M. Natarajan, **Indresh Kumar Pandey**, and Sandeep Kaur-Ghumaan, *Chem. Select.*, 2017, 2, 1637–1644.
- 11) *Diiron complexes [Fe₂(CO)₅(μ-Mebdt)L] containing a chelating phosphine ligand L=(Oxydi-2,1-phenylene)bis(diphenylphosphine): Bioinspired [FeFe] hydrogenase model complexes*, **Indresh Kumar Pandey**, F.Hussain and Sandeep Kaur-Ghumaan, *Chem. Select.*, 2016, 1, 5671–5678.
- 12) *Diiron benzenedithiolate complexes relevant to the [FeFe] hydrogenase active site*, **Indresh Kumar Pandey**, S. M. Mobin, N. Deibel, B. Sarkar, and S. Kaur-Ghumaan, *Eur. J. Inorg. Chem.*, 2015, 17, 2875-2882.
- 13) *Hydrogen generation: Aromatic dithiolate-bridged metal carbonyl complexes as hydrogenase catalytic site models*, **Indresh Kumar Pandey**, M. Natarajan, and Sandeep Kaur-Ghumaan, *J. Inorg. Biochem.*, 2015, 143, 88-110.
- 14) *Effect of dispersion conditions on the mechanical properties of multi-walled carbon nanotubes based epoxy resin composites* P. Garg, B. P. Singh, G. Kumar, T. Gupta,

Indresh Kumar Pandey, R. K. Seth, R. P. Tandon, and R. B. Mathur, *J. Polym. Res.*, 2011, 18, 1397-1407.

- 15) *Designing of multiwalled carbon nanotubes reinforced low-density polyethylene nanocomposites for suppression of electromagnetic radiation*", B. P. Singh, Prabha, P. Saini, T. Gupta, P. Garg, G. Kumar, and **Indresh Kumar Pandey**, S. Pande, R. K. Seth, S. K. Dhawan and R. B. Mathur, **J. Nanopart. Res.*, 2011, 13, 7065-7074.
- 16) *4, 5-Bis [(phenylmethyl)thio]benzene-1,2-dicarbonitrile*", **Indresh Kumar Pandey** and S. Kaur-Ghumaan, **Acta Cryst., Sec E*, 2016, Accepted.
- 17) *Manjul Gondwal, Sarita Kalakoti, Rakesh Kumar Verma, Bhanu Pratap Singh Gautam, **Indresh Kumar Pandey**, Girijesh Kumar Verma "Environmental Hazards in the Himalaya" in Edited By. Deepak Pant, Sanjesh Kumar, Gurpreet Singh, "Natural Hazards in Himalaya" Published by "The Shambhavi. M. Associates" Printed at: Aargon Press, Delhi ISBN: 978-81-951370-2-2, 2023*
- 18) *Half –Sandwich Ruthenium (II) NHC based metal complexes for anticancer activity*, **Indresh Kumar Pandey**, Pooja Sharma, *Dalton Trans.* , (Submitted) 2024.
- 19) *Zinc metal complexes of tetrazole based derivatives as high energy density materials: An insight from Quantum Chemical Studies*; **Indresh Kumar Pandey**, Pooja Sharma, *New J. Chem* (Submitted) 2024

Paper in Conferences :

1. *Hydrogenase biomimetics: Dinuclear Iron Carbonyl Complexes with Bridged Benzenedithiolate Ligand*", at the symposia on *Advanced Biological Inorganic Chemistry (SABIC)*, The Stadel Salt Lake, Kolkata, January 7-11, 2017.
2. *Dinuclear Iron Carbonyl Complexes with Monodentate Phosphine Ligands: Active Site Models of the [FeFe] Hydrogenase Active Site*", **10th Mid-Year CRSI Symposium in Chemistry**, National Institute of Technology and Bharathidasan University, Tiruchirappalli, July 23-25, 2015.
3. *Dihydrogen Evolution Catalyzed by Binuclear Iron Carbonyl Complexes with Bridged Benzenedithiolate Ligand*", **17th CRSI National Symposium in Chemistry**, CSIR-National Chemical Laboratory, Pune, February 6-8, 2015.
4. *Attended a workshop on the 2nd Indo-German Workshop on Supra-molecular Chemistry*, organized by the Department of Chemistry, University of Delhi, Delhi, 30th March 2015.
5. *Attended a workshop on Electronic Structure, Atomistic and Statistical Modeling in Chemistry, Materials and Life Sciences*, University of Delhi, Royal Society of Chemistry

London (North India Section), and Schrodinger GmbH, Bangalore, Delhi, October 8-10, 2014.

6. Attended a workshop on Molecular Characterization Techniques, organized by Sophisticated Instrument Centre (SIC) IIT-Indore, under the Continuing Education Program (CEP), IIT-Indore, March 7-8, 2014.
7. Mono and di-phosphine substituted diiron complexes as models for the [FeFe] hydrogenase active site," **20th ISCB International Conference Chemistry and Medicinal Plants in Translational Medicine for Health Care**, Department of Chemistry, University of Delhi, Delhi, March 1-4, 2014.
8. "Diiron Carbonyl Complexes as Catalyst for Proton Reduction: Pertinence to the [FeFe] Hydrogenase Enzymes," **Modern Trends in Inorganic Chemistry (MTIC XV)**, IIT Roorkee, Roorkee, December 13-16, 2013.
9. Hydrogen generation from protons by Diiron Carbonyl Complexes: Development of Alternative Renewable Energy Resources", **International Workshop on Green Initiatives in Energy, Environment & Health**, organized by Green Chemistry Centre of Excellence, The Energy and Resources Institute (TERI), Green Chemistry Network Centre, Delhi University, Gautam Buddha University and Green Chemistry Network, sponsored by Royal Society of Chemistry, London (North India Section), Delhi, December 2-3, 2013.
10. Catalytic hydrogen evolution from diiron carbonyl complexes with pertinence to the [FeFe] hydrogenase Enzymes," **National Symposium on Electrochemical Science & Technology (NEST)**, Indian Institute of Science (IISc), Bengaluru, August 23-24, 2013.
11. Effect of Functionalization and Dispersion Conditions on the Mechanical Properties of Multi-walled Carbon nanotubes based Epoxy resin Composites," **First Asian International Carbon Conference (FACC-2009)**, organized by National Physical Laboratory (NPL, CSIR) Indian Habitat Center, Delhi, November 25-27, 2009.

Date: 16.03.2024

Gorakhpur

Summary of Ph.D. work

Design and development of catalyst is one of the important contemporary challenges in the context of energy and environment for catalytic reduction of proton/ CO₂ or – a renewable and economical C1 feedstock – to high-value products and/or utilizable fuels (C. Hepburn and co-workers *Nature*, 2019, 575, 87-97). The alarming issue of escalating CO₂ concentration (>400 ppm) in the atmosphere and overconsumption of fossil fuels adds renewed relevance to the above challenge. Concerning this, Chemically/electrocatalytic proton/CO₂ reduction strategy holds promise because of its suitability toward storing intermittent electrical energy and its modularity toward converting proton and CO₂ to desirable products (such as H₂, CO, HCO₂H/HCO₂⁻, C₂O₄²⁻ etc.) based on variables such as applied potential. Besides, a significant choice of relatively inexpensive and abundant first-row transition metals (e.g., Mn, Fe, Co, Ni) in combination with suitable ligands, is preferred over noble metal (e.g., Pt, Re, Ru, Rh, Ir)-based counterparts, considering practicality and sustainability (S. L. Hooe and Co-workers *ACS Catalysis*, 2020, 10, 1146-1151). My thesis work has been conceived with the above background to address the rational design of catalysts in the context of reduction of proton/ CO₂ or – a renewable and economical C1 feedstock – to high-value products and/or utilizable fuels.

1) A highly efficient homogeneous catalyst system for production of CH₃OH from CO₂ using single molecular defined Ruthenium and Rhodium RAPTA-type catalysts [Ru(g6-p-cymene)X₂(PTA)](X= I(1), Cl(2); PTA = 1,3,5-triaza-7-phosphaadamantane) and rhodium catalysts [Rh(C₅Me₅)X₂(PTA/PTA-BH₃)] (X = Cl(3), H(4) and PTA-BH₃, H(5)) developed in acidic media under mild conditions. A TON of 4752 is achieved using a [Ru(-p-cymene)I₂(PTA)] catalyst which represents the first example of CO₂ hydrogenation to CH₃OH using single molecular defined Ru and Rh RAPTA-type catalysts.

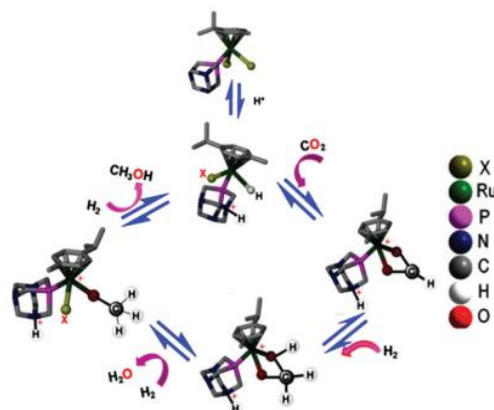
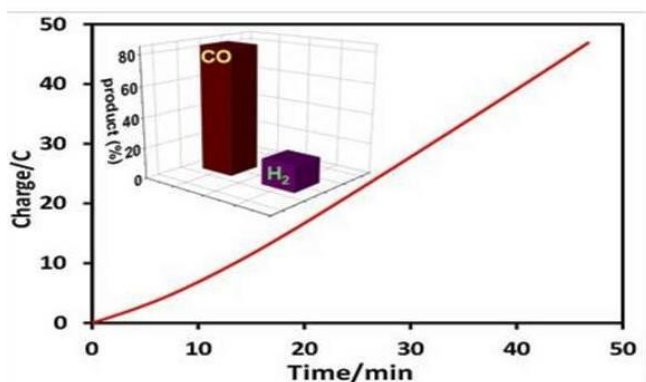
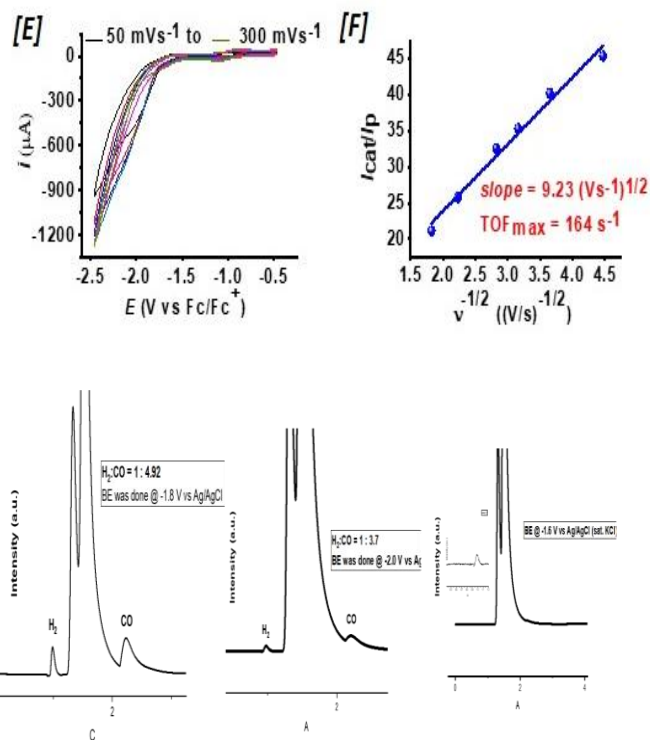


Figure 1. Plausible mechanism for the hydrogenation of CO₂ catalyzed by the Ru [Ru(-p-cymene)I₂(PTA)] [Rh(C₅Me₅)X₂(PTA/PTA-BH₃)]; *Chem. Communication*, 2020, 15, 904-919.

2. A) Electrocatalytic CO₂ Reduction with Half-Sandwich Cobalt Catalyst: Selectivity towards CO

We present herein for the first time a potentially active novel piano stool Cp*Co (III)-half-sandwich catalyst system after Artero's systems (*J. Am. Chem. Soc.* 2017, 139, 3685) for electrocatalytic CO₂ reduction for CO-

selectivity, as against **HCO₂H**-selectivity (**Artero's catalyst**) in aqueous acetonitrile solution (**Figure 1 A**). In addition to an electron-donating Cp* ligand (Cp* = pentamethylcyclopentadienyl), the catalyst featured a proton-responsive pyridyl-benzimidazole-based N, N-bidentate. Owing to the presence of a relatively electron-rich Co center, the reduced Co(I)-state was made prone to activate the electrophilic carbon center of CO₂. At the same time, the proton-responsive benzimidazole scaffold was susceptible to facilitate proton-transfer during the subsequent reduction of CO₂. The above factors rendered the present catalyst active toward producing CO as the major product over the other potential 2e/2H⁺ reduced product HCOOH, in contrast to the only known similar half-sandwich CpCo(III)-based CO₂-reduction catalysts which produced HCOOH selectively. This catalytic system exhibited Faradaic efficiency (FE) of ~70% while the overpotential for CO production was found to be 0.78 V as determined by a controlled-potential electrolysis.



[A] Co-based catalysts for CO₂ electroreduction: previous work
[CpCo^{III}(PPI)]⁺-half-sandwich type: **HCO₂H**-selective; operates via Co(I)
 [Artero, *J. Am. Chem. Soc.* **2017**, *139*, 3685]

[B] this work
[Cp*Co^{III}(NN)(solvent)]²⁺-half-sandwich type
 CO-selective; operates via Co(I)

Figure 2. [A] Artero Catalyst (*J. Am. Chem. Soc.* **2017**, *139*, 3685); [B] this work ; *Chem. Asian J.*, **2020**, *15*, 904-919.

c) Diiron Benzenedithiolate Complexes Relevant to the [FeFe] Hydrogenase Active Site

Here (**Figure 2**), we demonstrated that the reaction of benzene dithiol with metal iron carbonyl [Fe₃(CO)₁₂] gives, Hexa carbonyl bridged benzdithiolate diiron, [Fe₂(CO)₆(μ-bdt)] precursor. Further, this [Fe₂(CO)₆(μ-bdt)], the precursor was treated with phosphine ligands such as PPh₃, PPh₂Me, PPh₂H which are sigma donor and pi acceptor. Treatment of metal precursor, [Fe₂(CO)₆(μ-

bdtd)] with these phosphine ligands yielded a series of both mono and disubstituted complexes; $[\text{Fe}_2(\text{CO})_5(\mu\text{-bdtd})(\text{PPh}_3)]$ (1), $[\text{Fe}_2(\text{CO})_4(\mu\text{-bdtd})(\text{PPh}_3)_2]$ (2), $[\text{Fe}_2(\text{CO})_5(\mu\text{-bdtd})(\text{PPh}_2\text{Me})]$ (3) $[\text{Fe}_2(\text{CO})_4(\mu\text{-bdtd})(\text{PPh}_2\text{Me})_2]$ (4), $[\text{Fe}_2(\text{CO})_5(\mu\text{-bdtd})(\text{PPh}_2\text{H})]$ (5) and $[\text{Fe}_2(\text{CO})_4(\mu\text{-bdtd})(\text{PPh}_2\text{H})_2]$ (6). These complexes mimic the active site of [FeFe]hydrogenase and were investigated as a catalyst for proton reduction. Complexes 1, 3, and 5 were found to be potentially active catalysts in electrocatalytic proton reduction in the presence of two distinct acids, HClO_4 , and $\text{CF}_3\text{CO}_2\text{H}$ of varying strengths.

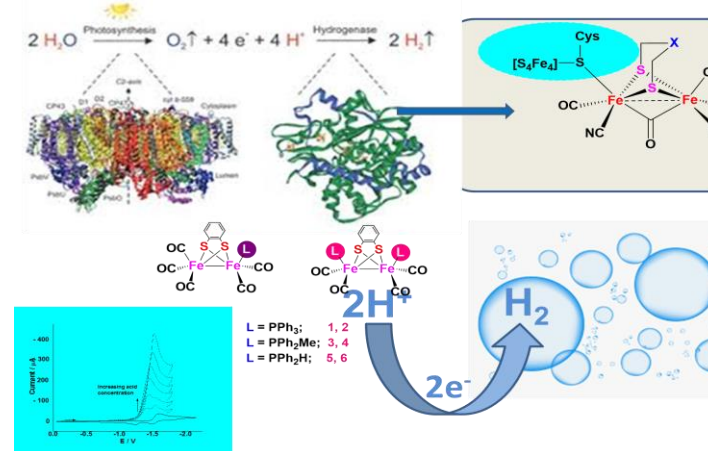


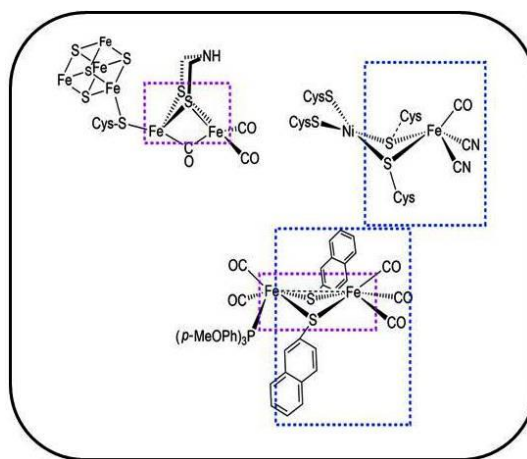
Figure 3. Electrocatalytic proton reduction is shown by catalysts 1-3 from out of six synthesized catalysts.

Eur. J. Inorg. Chem., 2015, 17, 2875-2882.

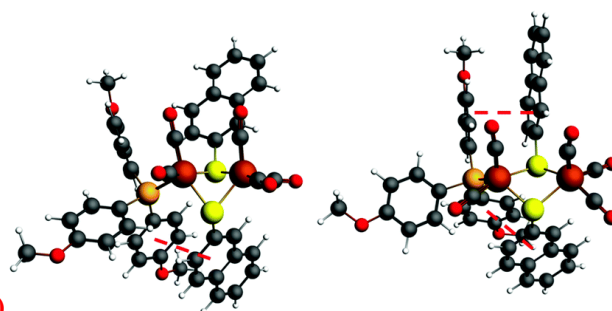
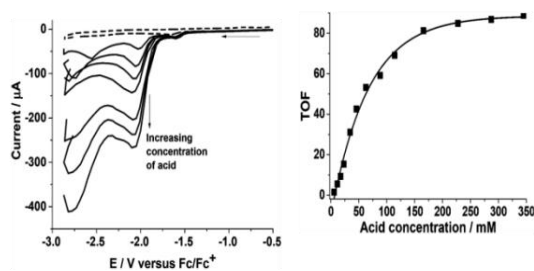
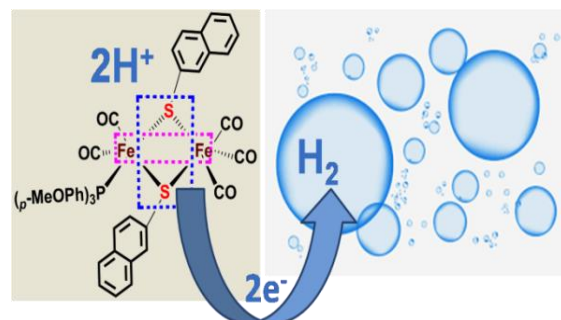
d) Intramolecular stabilization of a catalytic [FeFe]-hydrogenase mimic investigated by experiment and theory

Here, we have designed and synthesized the mono-substituted complex $[\text{Fe}_2(\text{CO})_5(\mu\text{-naphthalene-2-thiolate})_2(\text{P}(\text{PhOMe-}i>p)_3)]$ taking after the structural principles from both [NiFe] and [FeFe]-hydrogenase enzymes. The bridging naphthalene thiolates in the synthesized complexes resemble μ -bridging cysteine amino acids of [NiFe] and [FeFe]-hydrogenase enzymes. However, one of the naphthyl moieties of this catalyst forms π - π stacking interactions with the terminal bulky phosphine ligand and was proofed from the crystal structure and DFT calculations. This interaction stabilizes the reduced and protonated forms of the catalyst during

electrocatalytic proton reduction in the presence of acetic acid and hinders the rotation of the phosphine ligand. The intramolecular π - π stabilization, electrochemistry, and the mechanism of the hydrogen evolution reaction were investigated using computational approaches (Figure 3). Moreover, this catalyst was investigated for electrocatalytic reduction of proton in different acid concentrations and was found active at low overpotential.



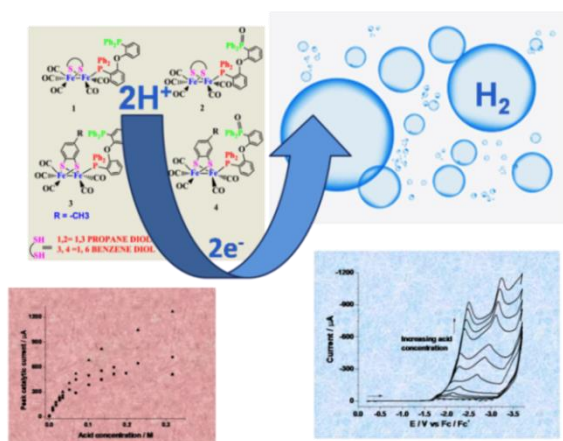
(A)



(B)

Figure 4. [A] Active sites ('H-cluster') of the [FeFe]-hydrogenase (top left) and the [NiFe]-hydrogenase (top right) enzymes. The $[\text{Fe}_2(\text{CO})_5(\mu\text{-naphthalene-2-thiolate})_2(\text{P}(\text{PhOMe-}p)_3)]$ complex (below) takes up design principles from both catalytic centers. [B] catalyst demonstrated the $\pi\text{-}\pi$ stabilization in DFT calculation. *Dalton Trans.*, 2018, 47, 4941-4949.

e) Complexes $[\text{Fe}_2(\text{CO})_5(\text{m-pdt}/\text{Mebdt})(\text{L})]$ Containing Chelating Diphosphine Ligand: Bioinspired [FeFe] Hydrogenase Model Complexes



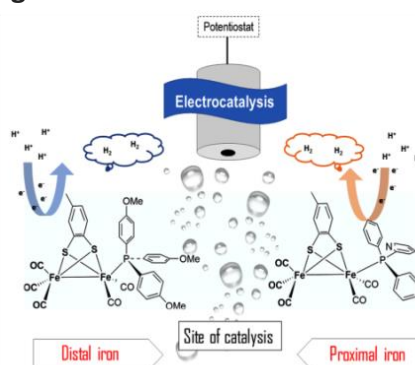
$\text{L}=(\text{Oxydi-2,1-phenylene})\text{bis}(\text{diphenylphosphine})$

Figure 5. Catalyst **1-4** of $[\text{Fe}_2(\text{CO})_5(\text{m-pdt}/\text{Mebdt})(\text{L})]$ and their catalysis on proton reduction, *Chem. Select.*, 2016, 1, 5671-5678.

In the same line, in the development of hydrogen-generating catalysts, here we have tried to investigate the significant effect of a catalyst on the reduction potential of a proton by incorporating a large bite angle of bis phosphine ligand flanked with one oxygen atom. This motivation initiated our studies on the reaction of $[\text{Fe}_2(\text{CO})_6(\text{m-pdt})]$ and $[\text{Fe}_2(\text{CO})_6(\text{m-Mebdt})]$ with this chelating phosphine ligand. Moreover, the purpose of using this chelating phosphine ligand was to attach the phosphine ligand simultaneously to both the iron atoms or investigate the formation of the tetra-iron complex. Both the alkyl (pdt) and

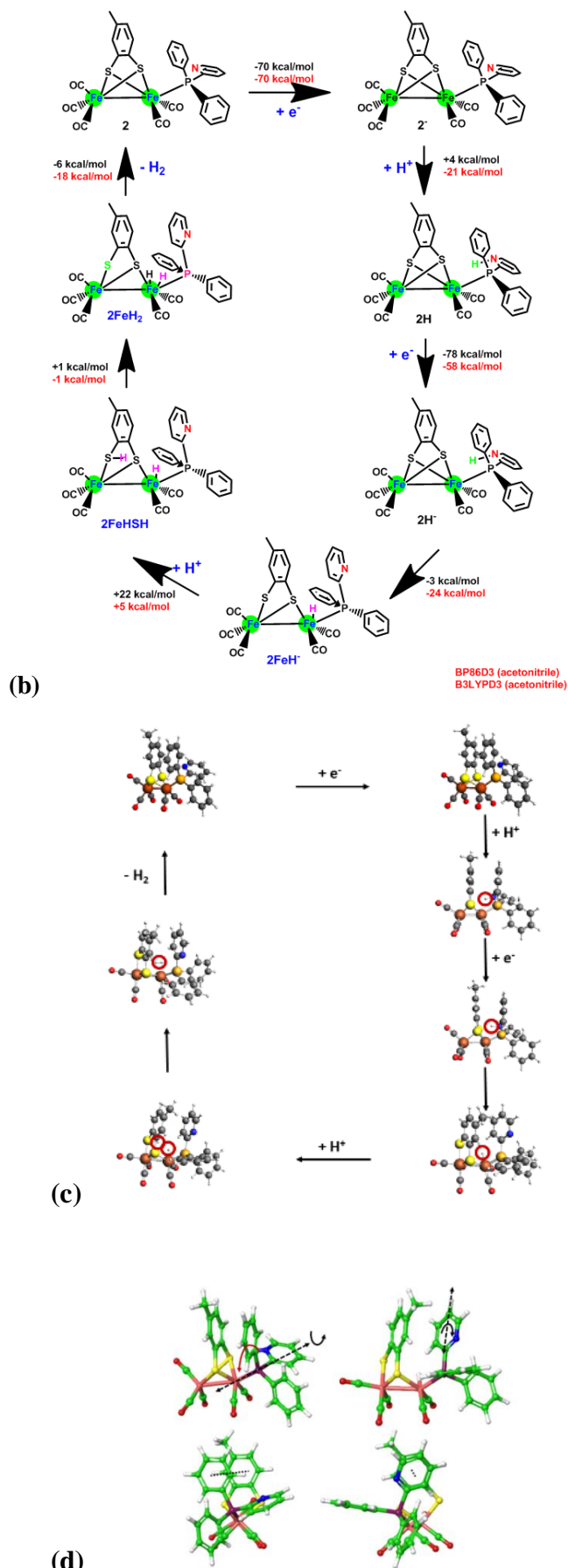
aromatic (Mebdt) dithiolate-bridged complexes were synthesized for comparison. The following diiron complexes, $[\text{Fe}_2(\text{CO})_5(\text{m-pdt})(\text{k}^1\text{-L})]$ **1** and $[\text{Fe}_2(\text{CO})_5(\text{m-Mebdt})(\text{k}^1\text{-L})]$ **3** were successfully investigated for electrocatalytic proton reduction. $[\text{Fe}_2(\text{CO})_5(\text{m-pdt})(\text{k}^1\text{-LO})]$ **2** and $[\text{Fe}_2(\text{CO})_5(\text{m-Mebdt})(\text{k}^1\text{-LO})]$ **4** were obtained as mono-oxidized side products during the synthesis of **1** and **3**.

f) (i) ; Switching Site-Reactivity in Hydrogenase Model Systems by Introducing a Pendant Amine Ligand



Here, two binuclear complexes $[\text{Fe}_2(\text{CO})_5(\mu\text{-Mebdt})(\text{P}(\text{PhOMe-}p)_3)]$ **1** and $[\text{Fe}_2(\text{CO})_5(\mu\text{-Mebdt})(\text{PPh}_2\text{Py})]$ **2** were studied for their proton reduction activity using cyclic voltammetry technique. Through DFT studies the role of terminal phosphines ligands without/with pendant amines in influencing site reactivity during chemical (C) and electrochemical (E) steps of the catalytic cycle has been elucidated. Complex **1** with a $\text{P}(\text{PhOMe-}p)_3$ phosphine moiety (devoid of pendant amine group) showed a distal iron atom HER activity while for complex **2** with PPh_2Py phosphine substituent (with a pendant amine group), the pyridine nitrogen lone pair acted as the primary site for protonation with HER activity at the proximal iron atom.

(a)



ACS Omega 2021, 6, 4192-420

Figure 6; Here DFT study revealed that (b) and (c) demonstrated ECEC mechanism for acid-assisted proton reduction and in figure (d) demonstrated that Intramolecular proton transfer of the pyridinium

proton from 2H^- (left) to the proximal iron atom Fe_p to yield 2FeH^- (right). This transfer is accompanied by a phosphine ligand rotation to bring the pyridine into the stacking position with Mebdt , and a pyridine ring rotation around the C2-C5 axis.

ii) Synthesis and Electrocatalysis of Diiron Monothiolate Complexes: Small Molecule Mimics of the [FeFe]Hydrogenase Enzyme

Here we have tried to synthesize monothiolate-bridged complexes without a linker to explore the catalytic properties of catalyst for proton reduction. However, many dithiolate-bridged complexes mimicking the [FeFe] hydrogenase active site have been reported. Though complexes without linker bridging between the iron of the type $[\text{Fe}_2(\text{m-SR})_2(\text{CO})_6]$ ($\text{R}=\text{any aromatic, an alkyl group}$) have been known since 1965, but systematic studies are yet to be required with these monothiolate-bridged complexes without a linker between the sulphur atoms. However, in such type of complexes homo-association is significantly responsible for the stabilization of the anionic species generated during the two-electron reduction process. Besides, the starting neutral complex is recovered by repeating second re-oxidation at more positive potentials. This type of recovery has been reported for the $[\text{Fe}_2(\text{m-SEt})_2(\text{CO})_6]$ complex as well. This is, however, not the case for most of the reported dithiolate-bridged complexes. Hence, to explore the chemistry of monothiolate-bridged molecules complexes $[\text{Fe}_2(\text{m-SCH}_2\text{Ph})_2(\text{CO})_6]$ **1** $[\text{Fe}_2(\text{m-SCH}_2\text{Ph})_2(\text{CO})_5(\text{P}(\text{PhOMe-}p)_3)]$ **2** and $[\text{Fe}_2(\text{m-SEt})_2(\text{CO})_5(\text{P}(\text{PhOMe-}p)_3)]$ **3** have been synthesized and investigated. The catalytic aspects of these complexes have been studied in the presence of acetic and trifluoroacetic acids and were found active toward proton reduction.

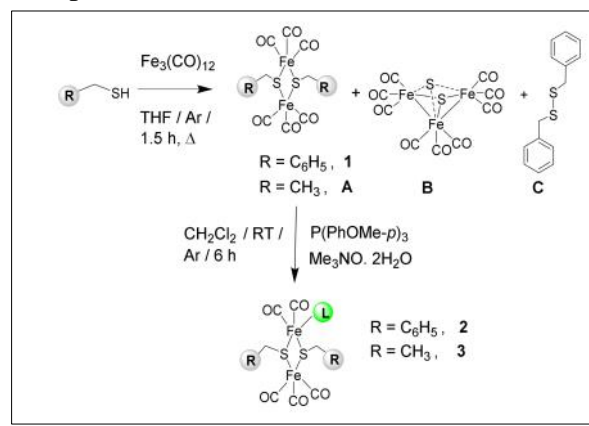


Figure 7. Synthetic scheme of catalyst **2** and **3**

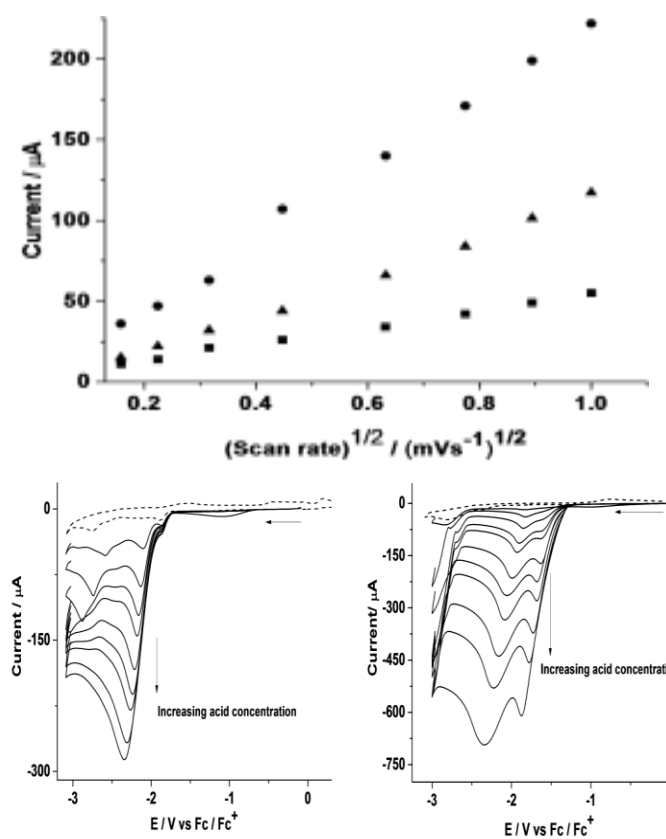


Figure 8. Catalyst **2** and **3** and their catalysis on proton reduction *Chem. Select.*, 2017, 2, 1637–1644.