

**Electro- and Photocatalytic Hydrogen Evolution
from Water Supported by octahedral Ni₆L₁₈ based
connected 1D coordination cages**

A Thesis

Submitted to
Indian Institute of Science Education and Research
Pune in partial fulfillment of the requirements for the
BS-MS Dual Degree Programme

by

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Certificate

This is to certify that this dissertation entitled “**Electro- and Photocatalytic Hydrogen Evolution from Water Supported by octahedral Ni₆L₁₈ based connected 1D coordination cages**” towards the partial fulfilment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research, Pune represents study/work carried out by **K Sravan Kumar** at Indian Institute of Science Education and Research under the supervision of **Dr. Ramamoorthy Boomishankar**, Associate Professor, Department of Chemistry, during the academic year 2018-2019.



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Declaration

I hereby declare that the thesis entitled “**Electro- and Photocatalytic Hydrogen Evolution from Water Supported by octahedral Ni₆L¹₈ based connected 1D coordination cages**” submitted for the fulfilment of the BS-MS dual degree programme at Indian Institute of Science Education and Research (IISER), Pune has not been submitted by me to any other University or Institution. This work was carried out at Indian Institute of Science Education and Research (IISER), Pune, India under the supervision of Dr. Ramamoorthy Boomishankar.



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Dedicated to my Family

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Contents

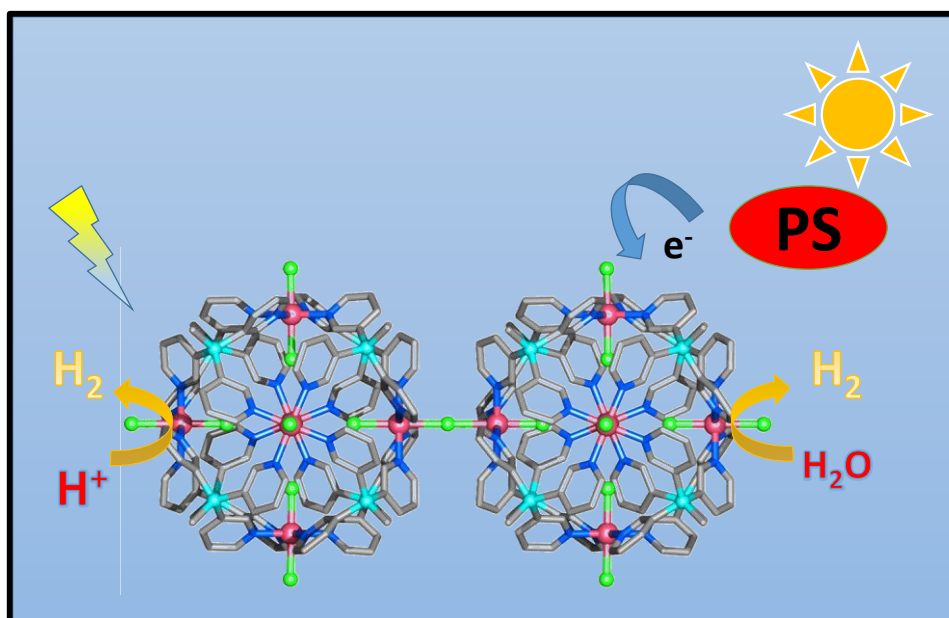
| | |
|-----------------------------------------------|-------|
| Abstract..... | 9 |
| Chapter 1..... | 9-27 |
| Introduction..... | 10-15 |
| Materials and Methods..... | 15 |
| Synthesis of Ligand L ¹ | 15-16 |
| Synthesis of 1D Nickel coordination cage..... | 16-17 |
| Results and Discussion..... | 17-22 |
| 1.1 Crystal structure..... | 17-19 |
| 1.2 Electrochemical studies..... | 19-21 |
| 1.3 Photocatalytic studies..... | 21-23 |
| Conclusion..... | 24 |
| Bibliography..... | 25-27 |

List of Figures/Schemes

| | |
|-----------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Figure 1 | <i>Scheme for water splitting reaction. Proton reduction reaction (Red), Water oxidation (blue) and overall reaction (Black).</i> |
| Figure 2 | <i>Scheme for natural photosynthesis</i> |
| Figure 3 | <i>Possible mechanism for HER mediated by metal complexes. E is electrochemical step and C is chemical step.</i> |
| Figure 4 | <i>(a) Scheme for synthesis of N-Donor silane tripodal ligand L¹. (b) ¹H NMR spectrum of L¹. (c) ²⁹Si NMR of L¹ showing a single peak around 12.69 ppm</i> |
| Figure 5 | <i>(a) Scheme for synthesis of 1D Nickel coordination cages (1) by using 3 eq of L¹ and 4eq of NiCl₂.6H₂O. (b) Out of plane XRD patterns of 1 (Blue) and simulated (Black). (c) Thermogravimetric analysis of 1 showing stability till 300 °C.</i> |
| Figure 6 | <i>(a) Crystal structure of 1D Nickel coordination cage (1) solved in P4/n space group. C (grey), N (dark blue), Si (cyan), Ni (dark pink), Cl (green). (b) View of 1 along 4-fold axis. (c) View of 1 along 3-fold axis.</i> |
| Figure 7 | <i>(a) UV-Visible spectrum of 1 in solid form (Red). (b) UV-Visible spectrum of 1 in water (Blue) and after 17days (green) revealing high stability of 1 in water.</i> |
| Figure 8 | <i>(a) Scan rate dependent cyclic voltammetry of 1 in acetonitrile solution. (b) Cyclic voltammetry of 1 in BR buffer solution at pH 4. (c) Cyclic voltammetry of 1 in BR buffer solution at pH 4 by increasing potential window, we observed sharp decline in catalytic current after -1.2V due to hydrogen evolution. (d) Linear shift voltammetry of 1 in BR buffer solution by varying pH values.</i> |
| Figure 9 | <i>(a) Pourbaix diagram of 1 in BR buffer solution using differential pulse Voltammetry showing pH dependence of both Ni⁺²/Ni⁺¹ and Ni⁺³/Ni⁺² redox couples. (b) Cyclic Voltammetry of 1 by varying concentrations of acetic acid (3.4mM, 7.8mM, 10.2mM, 13.6mM and 17mM).</i> |
| Figure 10 | <i>Kinetic plot of light driven Hydrogen evolution vs Time (h) of 100µM, 150µM, and 200 µM concentration of 1 in the presence of 0.5mM [Ru(byp)₃]⁺² as PS and 0.3M ascorbic acid. 1 was highly stable even after 70 hours in water rendering maximum turnover number of around 1230 of Hydrogen in 69 hours</i> |
| Figure 11 | <i>Comparative data of various Nickel polypyridine complexes and present work</i> |

Abstract

Recently, there is gradual increase in demand for renewable energy due to global energy crisis and hydrogen production from water offers a promising approach. Herein, we report the design and synthesis of an octahedral Ni_6L^{18} based one dimensional coordination network derived from a N-donor tripodal silane ligand $\text{MeSi}(3\text{-py})_3$ and study of their electrocatalytic and photocatalytic activity for hydrogen evolution from water. The 1-D cage (**1**) is highly soluble in water and organic solvents like acetonitrile, methanol etc. The UV-Visible studies reveals that the complex is highly stable in solution. The electrochemical analysis of **1** in aqueous BR buffer solution have revealed that it exhibits two quasi reversible redox couples $\text{Ni}^{2+}/\text{Ni}^{+1}$ and $\text{Ni}^{3+}/\text{Ni}^{+2}$. Further, the Pourbaix diagram and pH dependent LSV studies reveal that **1** exhibits the proton coupled electron process (PCET) which is vital for proton reduction reaction. Further, acetic acid dependent cyclic voltammetry were performed which revealed the TOF of 53s^{-1} for the H_2 evolution reaction from water catalyzed by **1**. Remarkably, the photocatalytic activity performed for 69hr using $100\mu\text{M}$, $150\mu\text{M}$, and $200\mu\text{M}$ concentrations of **1**, $[\text{Ru}(\text{byp})_3]^{+2}$ as PS and ascorbic acid as sacrificial electron donor resulted in a TON of 1230.



Introduction

In recent years, there is a gradual development in the utilization of renewable resources, sunlight, and water, which offers a promising solution to the challenging global energy crisis. Sunlight can be used as a source for electricity by converting it into chemical energy which can be further transformed into power by using a fuel cell technology with high efficiencies, thereby avoiding the emission of greenhouse gases. Nonetheless, sunlight is also a potential source of energy by the generation of hydrogen, a prominent energy-dense carbon-free fuel, by a water splitting process.¹⁻²In natural photosynthesis, plants utilize sunlight for synthesizing carbohydrates from hydrogen, produces oxygen and even fossil fuels *via* a series of photochemical reactions which encourages the scientific community to incline their research towards the field of photosynthesis.³⁻⁵

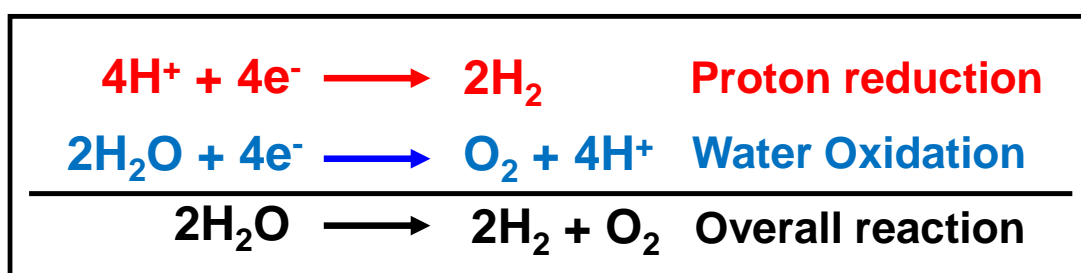


Figure 1. Scheme for water splitting reaction. Proton reduction reaction (Red), Water oxidation (blue) and overall reaction (Black).

The whole photosynthetic process involves two essential process Photosystem I (P700) and Photosystem II (P680), several cofactors and a unique enzyme, the hydrogenase.⁴ It includes several steps like light harvesting, spatial charge separation process, multielectronic redox catalysis which produces hydrogen and oxygen at enzymatic sites like metal clusters in hydrogenase enzyme. Firstly, the sunlight is absorbed by pigments which converts the wide range of visible light into chemical energy in photosystem II. Before charge recombination occurs, the electron transfer process will drive the electrons to PS I. Finally, a second light harvesting process occurs at PS I which provides additional energy to the electrons which were transported from PS II for either CO₂ fixation (by Calvin cycle) or hydrogen production in the hydrogenase enzyme. The second harvesting process is induced to reduce several electron acceptors such as phylloquinone and ferredoxin,

also reducing the cofactor NADP⁺ (nicotinamide adenine dinucleotide phosphate) to NADPH (biological hydrogen), thereby oxidizing PS I.⁶ The cofactor NADPH is used as both electron and proton source for CO₂ reduction into carbohydrates in the Calvin cycle.⁷ Electrons from PS II helps in regenerating oxidized Photosystem I by several electron relays such as plastoquinone, cytochrome f and plastocyanine. The natural photosynthetic process is so far the most efficient and fascinating process which can interconvert photons to hydrogen in low thermodynamic overpotentials.⁸ Understanding this scheme of the biological photosynthetic process is very necessary for designing new novel molecular systems which are capable of achieving high efficiencies. Significant achievements had been reported in utilizing hydrogenases in water splitting applications and their catalytic mechanisms have been studied at molecular level.⁹⁻¹⁰

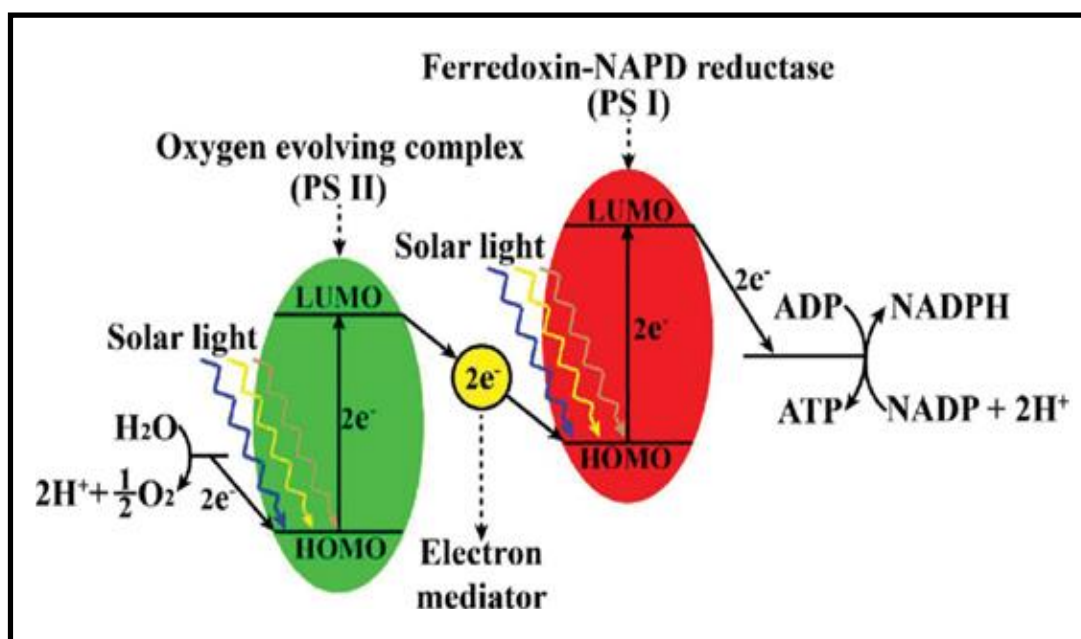


Figure 2. Scheme for natural photosynthesis

Spurred by this, scientists are trying to develop new types of systems which are capable of utilizing the sunlight to generate energy which can replace carbon-based fuels with carbon-free fuels. Efficient solar cells and solar based water splitting systems are majorly in demand and will provide clean energy. As solar cells are capable of directly converting solar energy into electrical energy but do not have the luxury to store it while solar based water splitting systems can store the energy in the form of chemical bonds which is more efficient and reliable.¹¹ This advantage in

energy storage through water splitting has attracted greater attention for the past few decades. Chemical water splitting driven by solar energy includes two half-cell reactions namely Hydrogen evolution reaction (HER) and Oxygen evolution reaction (OER). The water splitting processes can be achieved in two major pathways: electro catalytic, and photocatalytic water splitting. As water splitting process requires a proton reduction catalyst (PRC) for reducing the energy barrier of 237kJ/mol, a plethora of materials as PRC's have been investigated which includes metal oxides, semiconductors, transition metal-ligand complexes, etc. In this thesis, we will restrict our discussion to hydrogen evolution reaction (HER) by electrocatalytic and photocatalytic water splitting employing transition metal-ligand complexes as PRC's.

In the literature, several homogenous and heterogeneous metal catalysts made up of noble metals like Pt, Ru, Rh, etc., have been extensively studied shows promising PRC activities.¹²⁻¹⁴ However, the lack of abundance of these high-cost metals renders their real-life applications ineffective. Motivated by the exquisite examples of catalysts made up of earth-abundant metals in the form of naturally existing enzymes like hydrogenases, researchers are immensely inclined to develop non-noble metal based synthetic PRC's especially those containing Fe, Ni, Co, Mn ions. The tendency of these metal ions to exhibit variable oxidation states and coordination sites in addition to their low cost enables them as a potential candidate as the catalyst for proton reduction reactions.¹⁵⁻¹⁷ The solubility and stability of metal-complexes in aqueous solutions or in a mixture of aqueous-organic solutions is a striking feature during hydrogen generation which benefits the reduction of organic additives in the environment and maintaining high substrate concentrations.¹⁸ Besides, it helps in electrocatalytic systems by lending protons in the solution which is a prime requirement for Proton-coupled electron transfer process (PCET).

Scientists have deduced a possible mechanism for HER mediated by metal complexes based on theoretical and experimental studies. We can attribute the reduction and protonation events as the electron transfer (E) and chemical (C) steps, respectively. Usually, in a HER reaction, there are two pathways which are possible. Firstly, in the homolytic pathway where two metal hydrides complexes undergo reductive elimination to form H₂. Secondly, in the heterolytic pathway in

which a single metal hydride complex extracts a naked proton and generates H₂. It can be concluded that in both the pathways, two protons (protonation) and two electrons (reduction) are involved in a HER reaction as shown in figure 3.

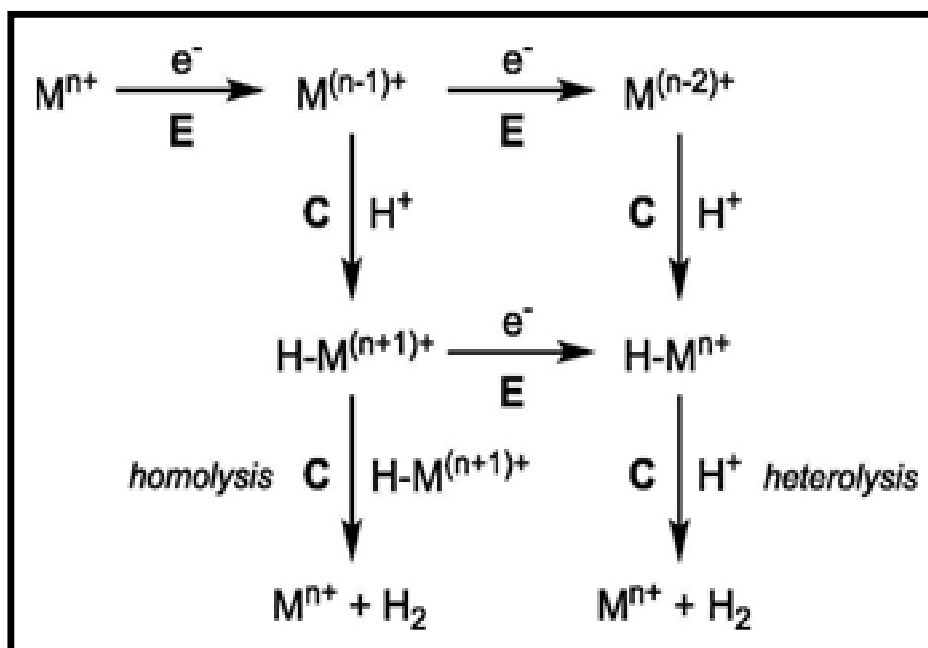


Figure 3. Possible mechanism for HER mediated by metal complexes. *E* is electrochemical step and *C* is chemical step.

Over the years, cobalt- and nickel-based metal complexes are widely studied ascribing to their high performance in catalytic activity in HER. But nickel is relatively more earth-abundant and bio-relevant than cobalt and hence has stimulated intense catalytic studies on nickel complexes than the cobalt complexes.¹⁹ On the other hand, strategic ligand design and alteration also plays a vital role in catalytic experiments as ligand tends to stabilize low oxidation state of the metal center thereby minimizing the overpotential necessary for HER. Sulfur and phosphine based ligands which have π - back donating nature show promising activity in this aspect.²⁰⁻²¹ Also, the addition of redox-active ligands like pyridine moieties helps in lowering the overpotential and aids in increasing the catalytic activity. In here, we will restrict our discussion to Nickel based complexes utilizing pyridyl-based ligands.

Different polypyridyl based metal complexes are suitable for HER as pyridine donor ligands are not only water stable but also stabilize low oxidation state of the metal. Sun and co-workers initially developed Nickel-based polypyridyl complexes in 2014 for these applications.²² They have synthesized different polypyridyl based nickel

complexes employing stoichiometric ratios of different amine moieties to pyridine. Electrochemical studies performed in neutral water furnished that one with diamine and tripyridine Nickel complex to be the most active catalyst with a stable performance of 60 h in controlled potential electrolysis at 830mV overpotential and a quantified evolution of 3.08×10^5 mol of H_2 with faradaic efficiency of approximately 91%. Dubois and co-workers have showed both electro and photocatalytic activities of Nickel bis diphosphine complexes are stable but rendered relatively low TOF's.²³⁻²⁵ So, in a recent work of Eisenberg and co-workers, they have experimentally proved that nickel complexes coordinated by combination of sulfur and N- donor ligand showed excellent photocatalytic activity giving TON's around 5000.²⁶ Despite offering excellent catalytic activity by these pyridyl based ligands as H_2 -evolving Nickel catalysts, it is still a challenging task for designing ligands which offers the requisite square pyramidal or planar coordination geometries to metal ions. Recently, Boomishankar and co-workers have shown proton reduction activities in water from a self-assembled M_6L_8 type octahedral discrete cage for Co(II) ions supported from N-donor tripodal silane ligand $MeSi(3-py)_3$.²⁷ The Co(II) in this cage is coordinated with four pyridyl groups from four different silanes ligands in an equatorial fashion. The axial coordinations are furnished by a chloride ion tightly trapped inside the cage framework and an exo-cage aqua-ligand which is amenable for easy replacement during catalytic reactions. This cage complex exhibits both electrocatalytic proton reduction having TOF of $16h^{-1}$ and photocatalytic water splitting with TOF value of $20.50 h^{-1}$. Inspired by the PRC activities of this Co (II) cage and the self-assembling capability of the tripodal silane ligand, we set out to explore the potential of an iso-structural Ni (II) cage based on this ligand.

Herein, we report a one dimensional Nickel (II) coordination cage derived from the ligand $MeSi(3-py)_3$. While the Ni^{+2} favours the formation of a similar octahedral cage framework, both axial coordination in this cage is provided by chloride ions which helps the cage to propagate as a one-dimensional connected cage framework. The framework of cages is soluble in water as well as in organic solvents like methanol, acetonitrile, etc., and hence was used for proton reduction activity in aqueous solutions. The electrochemical studies indicate that 1-D Nickel cage exhibits catalytic behavior and can act as an efficient proton reduction catalyst in both aqueous and non-aqueous solutions with a maximum Turnover frequency of $53s^{-1}$

for the electrocatalytic hydrogen evolution. These results signify that the Ni(II) cage exhibits better electrocatalytic activity than the iso-structural Co(II) cages. Due to possibility of conjugation via Si atom in 1D cage, we have rationalized that it might accept electrons from photosensitizer upon exposing to light. The photocatalytic studies of 1D nickel cage was carried out in presence of $[\text{Ru}(\text{bpy})_3]^{+2}$ as photosensitizer and ascorbic acid (H_2A)/ ascorbate (A^-) as sacrificial electron donor and we detected a very high turnover number of 1230 using a $100\mu\text{M}$ solution of **1** as a catalyst.

Materials and Methods

All chemicals used for synthesis were purchased from Sigma-Aldrich and used as received without any further purification. TLC analysis was done on aluminium plates with silica gel 60 F254; Column chromatography was done on 200-300 mesh silica gel. ^1H NMR spectra were recorded on Bruker Advanced 400 MHz DPX spectrometer using 1,1,1,1-tetramethyl silane (TMS) as an internal standard. Water was deionized using Millipore synergy system ($18.2\text{ M}\Omega\text{ cm}$ resistivities) and was stored under argon atmosphere. UV-Visible absorption measurements were carried out in Shimadzu UV-2600 spectrophotometer. Thermogravimetric analysis (TGA) analysis was obtained from Perkin-Elmer STA 1000 instrument. The powder X-ray diffraction (PXRD) data were obtained from a Bruker-D8 Advance diffractometer. Electrochemical measurements were carried out with a CH-electrochemical analyser, Model 1100A, using a glassy-carbon-disk electrode (diameter 3mm) as the working electrode, platinum wire as the counter electrode, and SCE (saturated calomel electrode) as a reference electrode in KNO_3 and 0.1M TBAP (Tetrabutyl ammonium perchlorate) as supporting electrolyte. Aqueous solution measurements were carried out in Britton Robinson Buffer (BR buffer) and acetonitrile solvent for non-aqueous solution measurements. For photocatalytic measurements we have used Pressure transducer (PXM409-002BAUSBH).

Synthesis of ligand ($\text{MeSi}(\text{3-py})_3$) L^1 :

The Ligand L^1 was synthesized according to scheme in figure 1a. In here, a stirred solution of 3-Bromopyridine (9.84g, 6mmol) in dry diethyl ether (100mL) and

dropwise addition of n-BuLi (26mL, 6.6mmol) under $-78\text{ }^{\circ}\text{C}$ in nitrogen atmosphere leads to a thick yellow colored solution. Under same reactions condition subsequent addition of Methyl TrichloroSilane (2.54g, 2mmol) to the stirred solution after 1 hour leads to orange colored solution which is then slowly brought to room temperature and kept at stirring for 12 hours as shown in scheme 1. The resulting reaction mixture was diluted using diethyl ether and extracted with distilled water. The organic phase was washed with brine solution, dried over Na_2SO_4 , and concentrated to yield 2g of clear yellow-red oily product. The crude product was purified through column chromatography using 2% Methanol in Dichloromethane to give 1.5g of L^1 as a white solid (65%).²⁸ Further, the ligand synthesized was confirmed by ^1H NMR and ^{29}Si NMR as shown in figure 1(b and c).

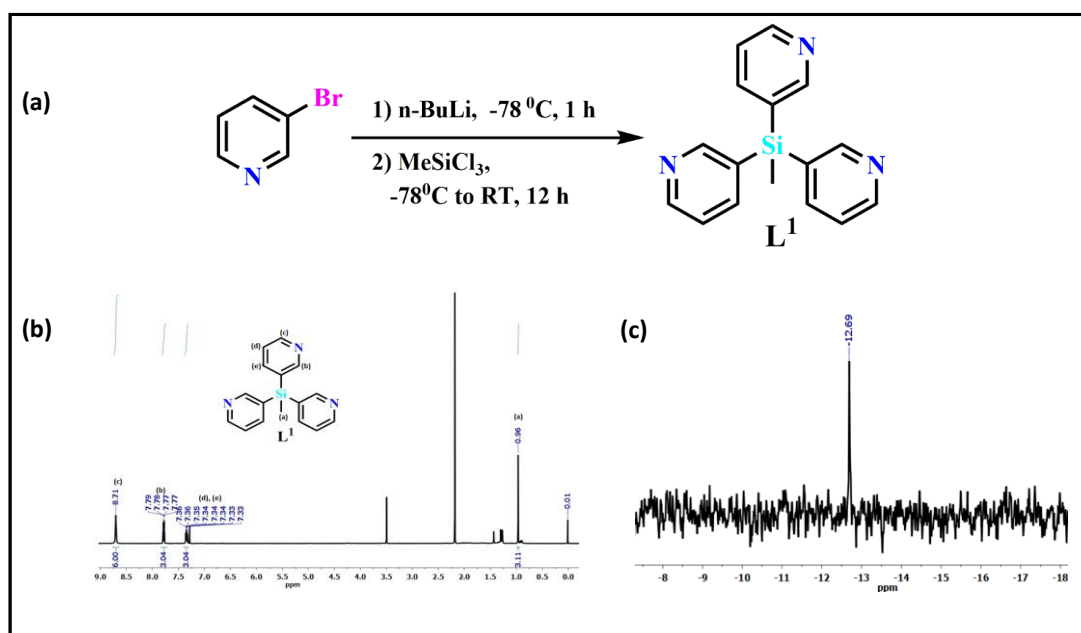


Figure 4.(a) Scheme for synthesis of N-Donor silane tripodal ligand L^1 . (b) ^1H NMR spectrum of L^1 .(c) ^{29}Si NMR of L^1 showing a single peak around 12.69 ppm.

Synthesis of 1-D Nickel coordination cages (1)

To the stirred methanolic solution of L^1 , a methanolic solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ was added dropwise at room temperature. The resultant solution was kept for slow evaporation and blue coloured crystals of **1** was obtained after one week. The phase purity of the crystals of **1** was determined by power X-ray diffraction and TGA

analysis reveals that the 1D Nickel coordination cage starts decomposing after 300°C as shown (Figure 5c).

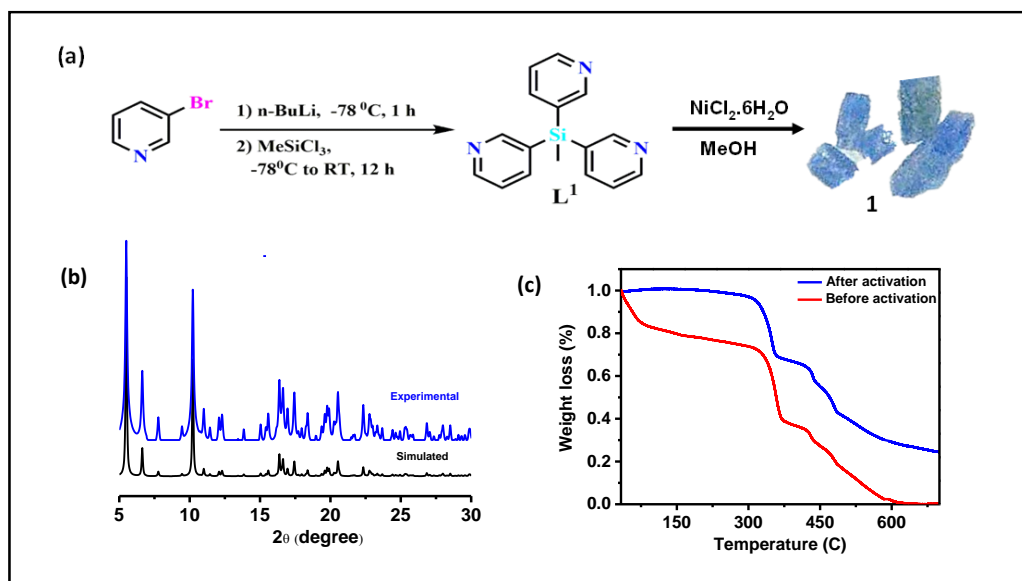


Figure 5. (a) Scheme for synthesis of 1D Nickel coordination cages (**1**) by using 3 eq of L¹ and 4eq of NiCl₂·6H₂O. (b) Out of plane XRD patterns of **1** (Blue) and simulated (Black). (c) Thermogravimetric analysis of **1** before (red) and after (blue) activation

Results and Discussion

1.1 Crystal Structure of 1:

The single crystal X-ray diffraction analysis revealed that **1** was crystallized in the tetragonal P4/n space group. The X-ray analysis revealed that there is a formation of self-assembled one-dimensional cage connected framework of formula [Ni^{II}₆L₁₈Cl₁₂]₃₂H₂O. The presence of solvated water molecules has been confirmed by the TGA analysis which amounts to a sharp 20% weight loss at 85°C (figure5c). Each cage motif consist of a Ni₆L₁₈ core where the Ni²⁺ ions are equatorially connected with four N pyridyl atoms of four different ligands and two axially coordinated chloride ions in a distorted octahedral geometry. One among the six outer cage axial chloride ions is shared between two Ni²⁺ centres from the two adjacent cages and give rise to a connected-cage one dimensional coordination architecture (figure 6a). Each Ni₆L₁₈ motif exhibits three crystallographically imposed 4-fold axes passing through two opposite Ni²⁺ centers along z-axis and four 3-fold axes passing through the opposite pairs of eight ligand Si–Me groups (figure 6b,c).

The Ni-N distances range from 2.080 to 2.130 Å; and the Ni-Cl distances ranging from 2.335 to 2.573 Å. Due to densely packed structure, further guest encapsulation experiments in intrinsic cavities were found to be difficult. However, formation of 1D cage along the z-axis led to some extrinsic cavities which accommodates the solvated molecules of water.

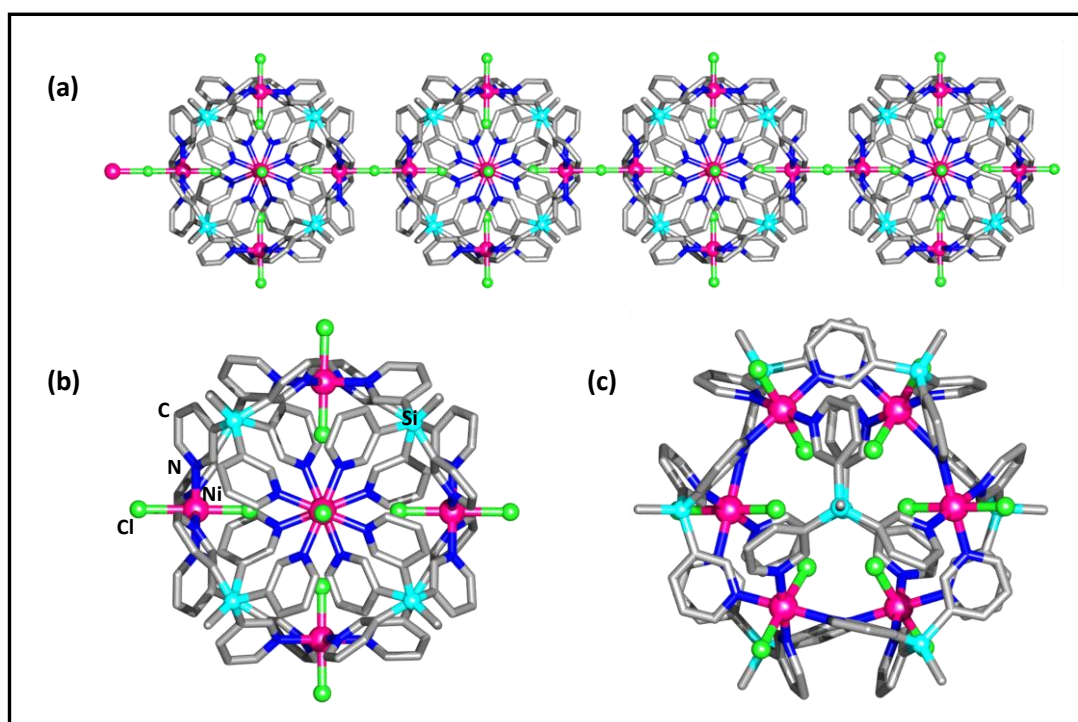


Figure 6. (a) Crystal structure of 1D Nickel coordination cage (**1**) solved in $P4/n$ space group. C (grey), N (dark blue), Si (cyan), Ni (dark pink), Cl (green). (b) View of **1** along 4-fold axis. (c) View of **1** along 3-fold axis.

Further, the UV-Visible spectral studies in the solid state and in aqueous medium suggest that the 1D Nickel cage (**1**) exhibits two maxima approximately at 392nm and 615nm attributing to ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (P) and ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (F) type d-d transitions, respectively. The spectrum after 17 days reveals that the 1D cage is highly stable in the solution and exhibit similar absorbance pattern as that of the freshly made sample (Figure 7).

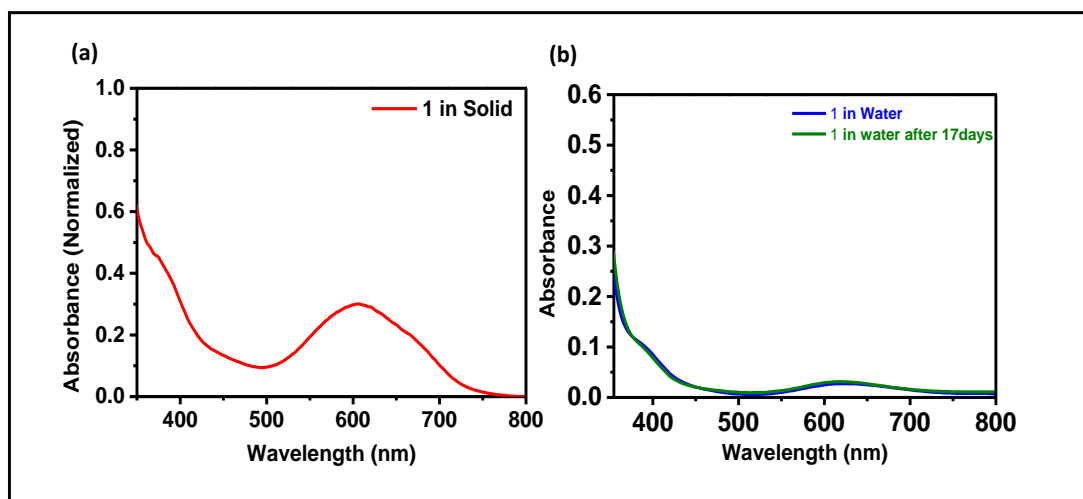


Figure 7. (a) UV-Visible spectrum of **1** in solid form (Red). (b) UV-Visible spectrum of **1** in water (Blue) and after 17days (green) revealing high stability of **1** in water.

1.2 Electrochemical studies

The electrochemical studies of **1** have been performed in both aqueous and non-aqueous solutions. The scan rate dependent cyclic voltammogram of the **1** in MeCN solvent exhibits the two quasi-reversible redox peaks at 0.90 V and -0.42 V for the Ni²⁺/Ni³⁺ and Ni¹⁺/Ni²⁺ couples, respectively (figure 8a). Sweeping further towards cathodic potentials around -1.3V reveals an irreversible peak which we assigned as ligand-centered process as shown previously. Further, cyclic voltammogram of **1** in BR buffer solution reveals two quasi-reversible redox peaks for Ni²⁺/Ni³⁺ and Ni¹⁺/Ni²⁺ couples at 0.167 V and -0.356 V, respectively (figure 8b). Increasing the potential window from 1.0V to -1.5V shows a sharp decline in the catalytic current with an over potential of -438 mV that corresponds to the hydrogen evolution from water (figure 8c).

We further explored the pH dependence of catalytic activity of **1** in aqueous BR buffer solution in acidic region where the catalytic proton reduction usually occurs. The DPV measurements were carried out by varying the pH ranging from 2.2 to 8.5, which reveals the pH dependence of redox activity. The pourbaix diagram shows that both Ni²⁺/Ni³⁺ and Ni¹⁺/Ni²⁺ redox couples show the pH dependence of potential, albeit a pH independent behavior of the Ni¹⁺/Ni²⁺ redox couple around pH 4.2 to 5.1 showing only the electron transfer attributes in this range (figure 9a). This pH dependence of potentials indicates involvement of proton coupled electron transfer process which is vital for the proton reduction process. The Linear shift voltammetry

(LSV) of **1** was studied under varying pH conditions show the linear decrease in the potentials with a slope of approximately -0.059V/pH indicating the involvement of the Proton-Coupled Electron Transfer (PCET) process, which is an essential step for the H_2 evolution reactions (figure8d).

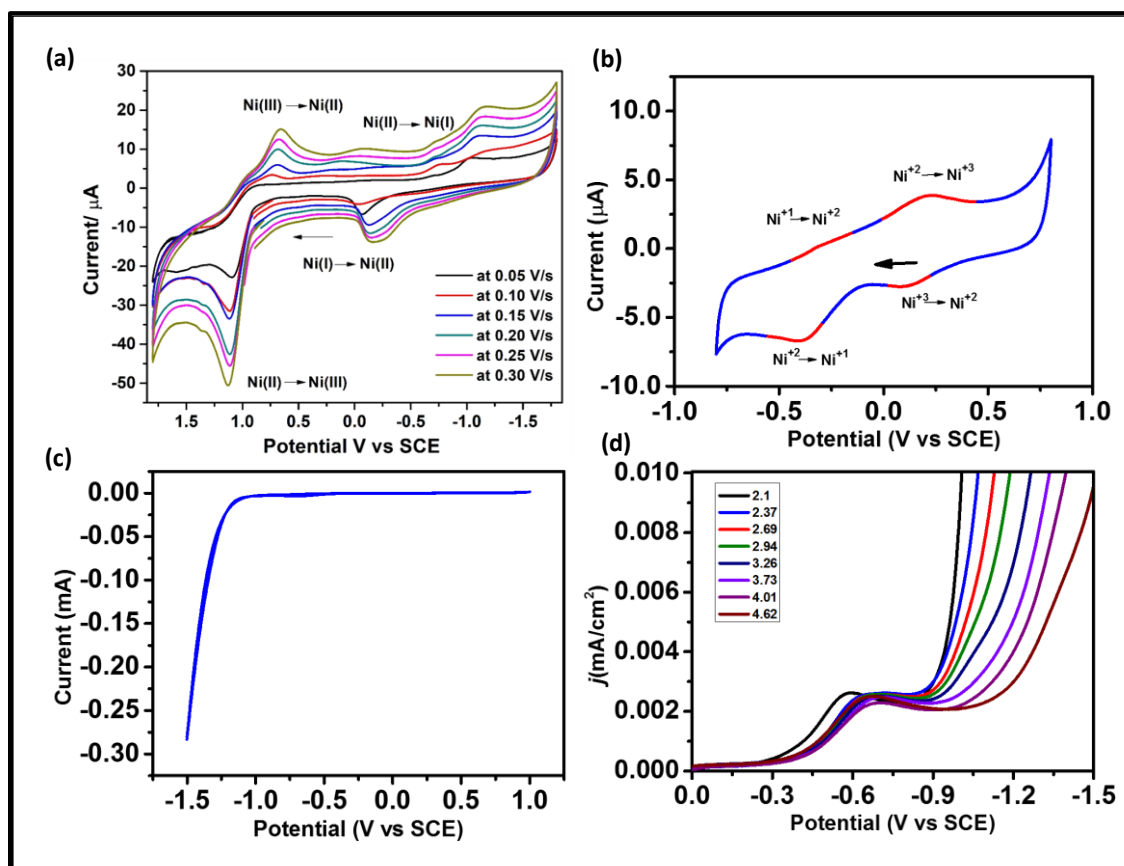


Figure 8. (a) Scan rate dependent cyclic voltammetry of **1** in acetonitrile solution showing two redox couples. (b) Cyclic voltammetry of **1** in BR buffer solution at pH 4 exhibits two redox couples $\text{Ni}^{2+}/\text{Ni}^{3+}$ and $\text{Ni}^{1+}/\text{Ni}^{2+}$ (highlighted with red). (c) Cyclic voltammetry of **1** in BR buffer solution at pH 4 by increasing potential window, we observed sharp decline in catalytic current after -1.2V due to hydrogen evolution. (d) Linear shift voltammetry of **1** in BR buffer solution by varying pH values revealing that **1** undergoes proton couples electron transfer process.

Furthermore, we carried out cyclic voltammetry of **1** in acetonitrile solution in the presence of varied concentrations of acetic acid. These experiments show a progressive increase in the catalytic currents for the $\text{Ni}^{2+}/\text{Ni}^{1+}$ redox couple with increase in the acetic acid concentrations (figure 9b). Using the formula given in equation 1, we have calculated the rate constant for hydrogen evolution where i_p

attributes to catalytic current in the absence of acetic acid and i_c attributed to catalytic peak current in the presence of acetic acid, n is the number of electrons transferred, R is the gas constant, T is temperature and F is the Faraday constant. The rate constant or turnover frequency of 1D cage was found to be around $53s^{-1}$.

$$\frac{i_c}{i_p} = \frac{n}{0.4463} \sqrt{\frac{RTk}{Fv}} \quad \rightarrow \text{Equation 1}$$

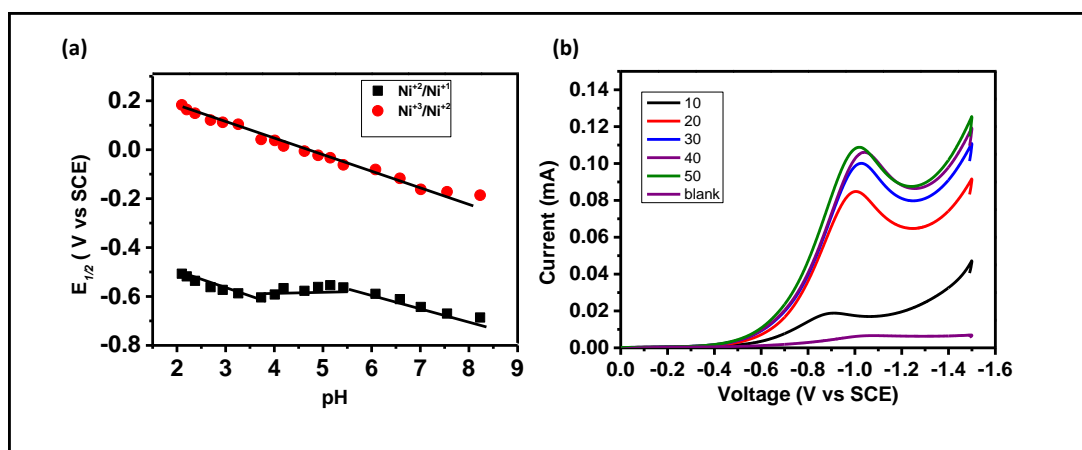


Figure 9. (a) Pourbaix diagram of **1** in BR buffer solution using differential pulse voltammetry showing pH dependence of both Ni^{2+}/Ni^{+1} and Ni^{3+}/Ni^{2+} redox couples. (b) Cyclic Voltammetry of **1** by varying concentrations of acetic acid (3.4mM, 7.8mM, 10.2mM, 13.6mM and 17mM).

1.3 Photocatalytic Studies

Inspired by the results of electrocatalytic activity of **1**, we envisioned that the self-assembly of **1** might show photocatalytic activity the presence of $[Ru(byp)_3]^{+2}$ as a photosensitizer (PS), and ascorbic acid (AA) as a sacrificial electron donor. In this experiment, a pressure transducer was fitted to a 33mL round bottomed flask capped with septum from other side and a magnetic bead inside. Adding 0.5mM $[Ru(byp)_3]^{+2}$, 0.3M ascorbic acid and 0.3 sodium ascorbate inside the RB flask which was then dipped into a temperature controlled water-jacketed beaker surrounded by 469nm wavelength blue LED's as a light source to the PS. The pressure generated was further used for calculating the number of moles of hydrogen gas evolved using the formula $PV = nRT$. The hydrogen generated vs time profile using 100 μ M, 150 μ M, and 200 μ M concentration of catalyst **1** exhibits a high turnover number of 1230 for 69 hours and maximum turnover frequency obtained for was calculated to

be 18h^{-1} . This attributes that **1** is highly stable thermodynamically but kinetically slow in releasing the hydrogen gas (figure 10).

Further studies are in progress for the photocatalytic H_2 evolution reactions from water under different concentrations of the catalyst with the aim of boosting the turnover number. A comparative analysis of the catalytic efficiency of **1** with that of other well-known Ni^{2+} catalysts are given Table 1. The better performance of **1** in comparison with other known complexes can be gleaned from the fact that most of the best performing catalysts are known in mixed organic-aqueous medium, whereas **1** shows a high turnover number in pure water (figure 11).

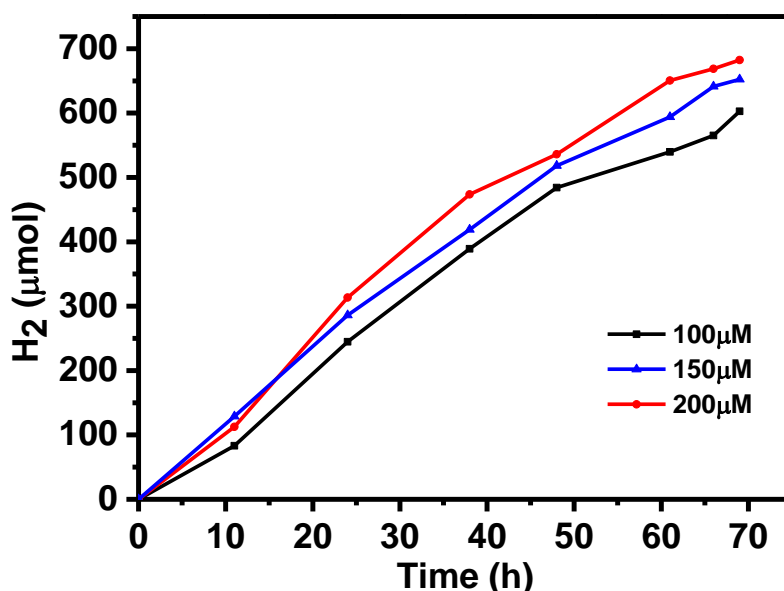


Figure 10. Kinetic plot of light driven Hydrogen evolution vs Time (h) of $100\mu\text{M}$, $150\mu\text{M}$, and $200\mu\text{M}$ concentration of **1** in the presence of 0.5mM $[\text{Ru}(\text{byp})_3]^{+2}$ as PS and 0.3M ascorbic acid. **1** was highly stable even after 69 hours in water rendering maximum turnover number of around 1230 of Hydrogen in 69 hours

| Catalyst | PS and SR | Medium | TON | Longevity (h) | reference |
|--------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------|-----------------------------------------------|-------------|---------------|---------------------|
| Ni(L) ₂ (H ₂ O) ₂](BF ₄) ₂ L=2-(2-pyridyl)-1,8-naphthyridine) (2.5μM) | FI(2.0mM), TEA (5%v/V) | EtOH/H ₂ O at pH 10.5 | 3220 | 24 | 22 |
| [Ni(L') ₃](BF ₄) ₂ , L'=2-(2-pyridyl)quinoline), (10.0μM) | FI(2.0mM), TEA (5%v/V) | EtOH/H ₂ O at pH 10.5 | 685 | 24 | 22 |
| Ni ^{II} (L ^{N₂Py₃})(MeCN)](ClO ₄) ₂ | FI(2.0mM), TEA (5%v/V) | EtOH/H ₂ O at pH 12.0 | 3500 | 24 | 29 |
| Nickel(II) phthalocyanine (NiPc) | [Ir(dfppy) ₂ (dcbpy) (0.5mM) and TEOA (0.2M) | CH ₃ CN/H ₂ O at pH 9.0 | 520 | 12 | 30 |
| Present work (1) | [Ru(bpy)₃]²⁺ (0.5mM) and AS (0.3M) | H₂O at pH 4.0 | 1230 | 70 | Present work |

Figure 11. Comparative data of various Nickel polypyridine complexes and present work

Conclusions

In conclusion, we report here for the first time a self-assembled one dimensional Ni(II) containing coordination network made up of connected cage architectures using polypyridyl ligands as linkers. Due to variable oxidation states and octahedral coordination geometry of Ni(II), **1** was shown to exhibit catalytic behavior in water. The electrochemical and photocatalytic studies reveals that **1** can behave as an efficient molecular catalyst. Additionally, pH dependent electrochemical studies reveals that **1** exhibits proton coupled electron transfer process which is vital for proton reduction. We have also determined rate constant or TOF of **1** by acid dependent cyclic voltammetry in acetonitrile which gives a TOF of 53s^{-1} . Further, photocatalytic experiment of a $100\mu\text{M}$ of **1** in the presence of $[\text{Ru}(\text{byp})_3]^{+2}$ as PS and ascorbic acid as electron donor exhibits a significantly high TON of 1230 for H_2 in 69 hours. These results reveals that **1** is thermodynamically very stable and can act as a potential candidate for proton reduction reaction in water.

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