# **Supporting Information**

# for

# Peripheral nucleic bases boost H<sub>2</sub> production by synthetic molecular catalysts in water

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<i>Entry P</i>	age No
General methods & synthetic procedures.	3-6
Electrochemical Evaluation	5
Photocatalytic H <sub>2</sub> production	6
Calculation of Faradic Efficiency	7
Scheme 1: Scheme for the Synthesis of Complex C1-C3	5
Figure S1: <sup>1</sup> H NMR spectrum of complex C1	8
Figure S2:. <sup>1</sup> H NMR spectrum of complex C2.	9
Figure S3: <sup>1</sup> H NMR spectrum of complex C3.	9
Figure S4: HRMS spectra of C1-C3	10
Figure S5: FTIR data for the solid complexes (C1-C3).	10
Figure S6: UV-Visible spectrum of complexes C1-C3	11
Figure S7: UV-Vis data of C1 with TFA addition	11
Figure S8: CV data recorded in DMF and acid addition study	12
Figure S9: Spectroelectrochemistry data of complex C1 in pH 7	12
<b>Figure S10.</b> Plot of $i_p$ vs. square root of scan rate.	13
<b>Figure S11:</b> Plot of $i_{cat}$ vs. square root of scan rate.	13
Figure S12: CV of C1 and C2 at different scan rate in pH 6.0	14
Figure S13: Bulk electrolysis and GC data recorded for the complexes C1-C3.	14
Figure S14: Simplified CV for measuring TOF and OP	15
Figure S15: Comparative CV data recorded at different pH for C2 and C3	15
Figure S16. Two-dimensional (2D) EXSY spectrum (NMR) for C1 complex.	16
Figure S17. Two-dimensional (2D) EXSY spectrum (NMR) for C3 complex.	17
<b>Figure S18:</b> LSV recorded for Co(DMG)pyridine and C1 after addition of D <sub>2</sub> O	17
Figure S19: pH titration of complexes C1 and C2.	18
Figure S20: Proton inventory test for C2 at pH 6.0.	18
Figure S21: Rinse test of complexes C1, C2 & C3 at pH 5.0.	19
Figure S22: CV recorded Before/After bulk Studies for C1-C3	19
Figure S23: UV-Vis spectra recorded Before/After bulk Studies for C1-C3	20
Figure S24: SEM image and EDS spectra of plastic chip working electrode.	20
Figure S25: TON of hydrogen production during photocatalytic study	21
Figure S26: Gas Chromatography data post photocatalytic studies	21
<b>Figure S27:</b> Showcasing a comparison of Cobaloxime based molecular catalyst having different biomolecules as outer co-ordination sphere.	ng
Table S1 Elemental Analysis of complexes (C1 C3)	22
Table S1. Deficient and Plantysis of complexes (C1-C3).         Table S2. Optical absorbance data of complexes (C1-C3) recorded in DMF	23

<b>Table S3</b> . The $E_{Co^{III/II}}$ and $E_{cat/2}$ values for C1-C3 recorded at variable pH condition	ons. 23
Table S4. Collective data for selected molecular cobalt complexes for H <sub>2</sub> production from	pure
aqueous medium under different conditions	24
Table S5. Comparative data for cobaloxime based complexes for H <sub>2</sub> production from pure	aqueous
medium under different conditions	24
Table S6: TON calculated for C1-C3 for electrocatalytic and photocatalytic HER	25
References	25-26

#### 1. Materials and methods

Reagents were purchased from commercially available sources, and were used without any further purification. Millipore water (18.2 MQ.cm at 298K) was used for all the studies and analysis. Optical absorption spectra were recorded on JASCO V-750 spectrometers using 1 cm path length. FTIR spectra of the solid complexes were recorded on the Perkin Elmer (Spectrum-Two) instrument. Nuclear Magnetic Resonance Spectra (NMR) were recorded at ~300K temperature using a Bruker Avance III 500 MHz Ascent FT spectrometer with working frequencies of 500 MHz for <sup>1</sup>H. Cyclic voltammetry (CV) studies were carried out using Metrohm Auto lab PGSTAT 204 potentiostat. The measurements were carried out in aqueous buffer using 0.1M 2-(N-Morpholino)ethane sulfonic acid, hydrate (MES) in millipore water, using 0.1M anhydrous sodium sulphate as supporting electrolyte. The electrochemical analysis was carried out using a standard three electrode system, with 1 mm glassy carbon disc as working electrode, Ag/AgCl (in 3M KCl) as reference electrode and platinum wire as counter electrode. All the potentials are reported Vs  $K_4$ Fe(CN)<sub>6</sub> (E = +0.363V at SHE) which was added as an internal standard. pH of the solutions used were adjusted using ORION STAR A111 pH Meter (Thermo Scientific). Bulk experiments (BE) were done using four-neck glass vessel where three of the necks were occupied by 23 cm coiled Pt electrode as counter electrode, Ag/AgCl (in 3M KCl) as reference electrode, and graphite plastic chip as working electrode, out of four neck one left was sealed with rubber septum, was used for N<sub>2</sub> purging and for gas collection over headspace (Via gas tight syringe VICI made) with constant stirring. The headspace gas was collected and, analysed using (CIC Dhruva) Gas chromatography (GC) instrument equipped with a TCD detector and 5 A° molecular sieve column for separation of the gases with Argon as carrier. The GC instrument was calibrated using the standard 1%, 5% and 10% H<sub>2</sub> gases available.

#### 2. Synthetic Procedures:

The complex Co(dimethylglyoxime)<sub>2</sub>Cl<sub>2</sub> and ligands Adenine(CH<sub>2</sub>)Pyridine (L1), Cytosine(CH<sub>2</sub>)Pyridine(L2), Thymine(CH<sub>2</sub>)Pyridine(L3) were synthesized according to previously reported literature.<sup>1,2</sup> Further metalation of ligands L1 to L3 to yield complex C1-C3 respectively was carried out according to the following procedure.

#### Synthesis of C1-C3:

360 mg of Co(dmg)<sub>2</sub>Cl<sub>2</sub> was taken in 15mL of dry methanol under an inert atmosphere. 139ul of triethylamine (TEA) was added to the above suspension and stirred until a clear dark brown solution was obtained. After 5 minutes of stirring, 1 equivalent amount of ligand L1 was added to the above solution and the reaction mixture was left to stir under inert atmosphere. Formation of a light brown precipitate was observed after few hours. After 8 hours of stirring the precipitate was collected via filtration and washed with diethyl ether. It was further dried under vacuum. (Yield= 623 mg, 73 % w.r.t Cobaloxime) <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  18.40 (s, 2H), 8.16 (s, 1H), 8.06 (s, 1H), 7.96 (d, *J* = 5.0 Hz, 2H), 7.32 (s, 2H), 7.23 (d, *J* = 5.0 Hz, 2H), 5.41 (s, 2H), 2.30 (s, 12H). UV-Vis in DMF ( $\lambda_{max}$  in nm,  $\varepsilon$  in parentheses M<sup>-1</sup>cm<sup>-1</sup>): 270(10640), 360(1765) FTIR (in KBr,  $\upsilon$  in cm<sup>-1</sup>): 513 (Co-N pyridine), 434 (Co-Cl). HRMS (ESI, positive mode) m/z for [M+H]<sup>+</sup> ion [C<sub>19</sub>H<sub>24</sub>Cl<sub>1</sub>Co<sub>1</sub>N<sub>10</sub>O<sub>4</sub>] calculated: 551.1075, obtained: 551.1075

C2 was synthesized in a similar process as above using L2 ligand (Yield= 615.6 mg, 71 % w.r.t Cobaloxime).

<sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  18.44 (s, 2H), 7.97 (d, *J* = 5 Hz, 2H), 7.63 (d, *J* = 10 Hz, 1H), 7.25 (d, *J* = 5 Hz, 2H), 5.73 (d, *J* = 10 Hz, 1H), 4.83 (s, 2H), 2.32 (s, 12H).

UV-Vis in DMF ( $\lambda_{max}$  in nm,  $\epsilon$  in parentheses M<sup>-1</sup>cm<sup>-1</sup>): 267(23116), 355(1917)

FTIR (in KBr, v in cm<sup>-1</sup>): 515 (Co-N pyridine), 434 (Co-Cl). HRMS (ESI, positive mode) m/z

for [M+H]<sup>+</sup> ion [C<sub>18</sub>H<sub>24</sub>Cl<sub>1</sub>Co<sub>1</sub>N<sub>8</sub>O<sub>5</sub>] calculated: 527.0962, obtained: 527.0963

C3 was synthesized in a similar process as above using L3 ligand (Yield= 604.8 mg, 68 % w.r.t Cobaloxime).

<sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  18.43 (s, 2H), 11.38 (s, 2H), 7.96 (d, J = 10 Hz, 1H), 7.50 (s,2H), 7.32 (d, J = 10 Hz, 1H), 4.84 (s, 2H), 2.31 (s, 12H), 1.73 (s, 3H). UV-Vis in DMF ( $\lambda_{max}$  in nm,  $\varepsilon$  in parentheses M<sup>-1</sup>cm<sup>-1</sup>): 260(12387),304(7069) FTIR (in KBr,  $\upsilon$  in cm<sup>-1</sup>): 515 (Co-N pyridine), 426 (Co-Cl). HRMS (ESI, positive mode) m/z for [M-Cl]<sup>+</sup> ion [C<sub>1</sub>9H<sub>2</sub>5Co<sub>1</sub>N<sub>7</sub>O<sub>6</sub>] calculated: 506.1191, obtained: 506.1191





#### 3. Electrochemical Evaluation:

The electrocatalytic behavior of the three catalyst was analyzed using cyclic voltammetry technique. All the complexes were studied in aqueous medium where 0.1 M MES was used for preparing the pH solution and sodium hydroxide solution was used to adjust the pH of the solution from pH 4-pH 7. 0.1 M Na<sub>2</sub>SO<sub>4</sub> was used as supporting electrolyte. CVs were performed using 1mm glassy carbon disc as working electrode, Ag/AgCl (in 3M KCl) as reference electrode and Pt-wire as counter electrode. All potentials reported here are against SHE. Studies were carried out using 3mL of 0.5mM catalyst solution. The electrochemistry

setup consists of a glass cell (capacity 5mL), covered with PTFE cap with four openings. Three were used for dipping electrodes and the remaining one for purging nitrogen. Bulk electrolysis study was performed using a four neck glass vessel of 60 mL capacity, the three openings were used for the three electrodes and the fourth one was used for nitrogen purging and gas collection. Plastic chip with an active area dimension of 1 cm× 1 cm was used as working electrode, Ag/AgCl in 3M KCl as reference electrode, coiled platinum wire as counter electrode.

#### 4. *Photocatalytic* H<sub>2</sub> *Production*:

Photocatalytic H<sub>2</sub> Production studies were carried out at in aqueous buffer medium in a Schlenk flask of capacity 28 mL. 0.5mM Eosin-Y stock solution was prepared as photosensitizer and from that solution the required conc. was prepared by dilution. Similarly, 1mM freshly prepared catalyst concentration was prepared and from it the required concentration was prepared for the experiment. All the experiments were performed at pH 5 using 0.1M (MES) buffer unless stated otherwise. Total volume of reaction mixture was 10 mL, 10% TEOA (v/v) was used as sacrificial electron donor (SED). The photocatalytic experiments were carried out using 40W Kessil KSPR160L- 518nm LED bulb as light source. Before each experiment the sample was purged with Argon gas for 30 min to degas amount of O<sub>2</sub> present. During the experiment, 0.5 mL of headspace gas was collected and injected into the GC instrument via VICI made Leur-lock gas tight syringe over period of time.

Evaluation of a catalyst is done mainly by two parameters, Turnover frequency (TOF) and Overpotential (OP) Requirement. The  $k_{obs}$  for electrocatalytic H<sub>2</sub> production at different pH was calculated by following Equation S1:

$$\frac{i_{cat}}{i_p} = \frac{n}{0.4463} \sqrt{\left(\frac{RTk_{obs}}{Fv}\right)}$$

Here,  $i_p$  represents stoichiometric current for the cobalt-based redox process and  $i_{cat}$ , catalytic current signifying H<sub>2</sub> evolution. The  $k_{obs}$  represents the pseudo-first-order rate constant for the reaction, which can be translated to TOF. While R, T, F, and v define the universal gas constant, temperature in the Kelvin scale, the Faraday constant, and scan rate in Vs<sup>-1</sup> unit, respectively.

The overpotential was measured using Equation S2:

$$OP = E_{H^+/H_2} - E_{cat/2}$$

OP is defined as the difference between the potential where the half-maxima of the catalytic current is achieved and the equilibrium potential for  $H^+/H_2$  ( $^{E}_{H^+}/H_2$ ) at the experimental conditions ( $E_{cat/2}$ ).

## Current efficiency of C1 at pH 5:

Overall charge passed during the catalytic HER = 4.674 C

Theoretical amount of hydrogen expected =  $4.674 \text{ C}/(96485 \text{ C} \times 2) \text{ moles} = 0.024 \text{ m moles}$ 

Experimentally hydrogen detected in headspace by GC=0.022 m moles

Faradic efficiency of C1 =  $(0.022/0.024) \times 100 \% = 91\%$ 

### Current efficiency of C2 at pH 7:

Overall charge passed during the catalytic HER = 3.151 C

Theoretical amount of hydrogen expected = 3.151 C/(96485 C x 2) moles = 0.016 m moles

Experimentally hydrogen detected in headspace by GC= 0.0147 m moles

Faradic efficiency of C2= (0.0147/ 0.016) X 100 % = 92%

## Current efficiency of C3 at pH 7:

Overall charge passed during the catalytic HER = 1.587 C

Theoretical amount of hydrogen expected =  $1.587 \text{ C}/(96485 \text{ C} \times 2) \text{ moles} = 0.008 \text{ m moles}$ 

Experimentally hydrogen detected in headspace by GC= 0.0070 m moles

Faradic efficiency of C3= (0.0070/ 0.008) X 100 % = 87.5%



Supplementary Figures:

Figure S1: <sup>1</sup>H NMR spectrum of complex C1 recorded in d<sup>6</sup>-DMSO at 298 K. The inset highlights the NMR signal distribution in  $\delta$  5.0-8.5 ppm.



Figure S2: <sup>1</sup>H NMR spectrum of complex C2 recorded in d<sup>6</sup>-DMSO at 298 K. The inset highlights the NMR signal distribution in  $\delta$  4.5-8.5 ppm.



**Figure S3:** <sup>1</sup>H NMR spectrum of complex C3 recorded in d<sup>6</sup>-DMSO at 298 K. The inset highlights the NMR signal distribution in  $\delta$  4.5-11.5 ppm.



**Figure S4:** Mass spectra (ESI-MS mode) of (A)C1 (B) C2 and (C) C3 recorded in methanol. The green spectra indicate the m/z peaks in simulated mass while the red spectra indicate m/z peaks observed in mass peaks for the complexes.



**Figure S5:** FTIR data for the solid complexes (C1-C3). Data were recorded at room temperature by preparing KBr pellet scanning from 400-4000 cm<sup>-1</sup>. The stretching frequency of Co-N(py) axial bond and Co-Cl bond are highlighted in grey trace.



**Figure S6:** UV-Visible spectrum of complexes (C1: Red trace; C2: Green trace; C3: Blue trace) recorded in DMF. Inset figure depicts the d-d transition for the three complexes. Data were recorded at room temperature. Assignment of above transitions are mentioned in Table S1.



**Figure S7:** UV-Vis study of C1 in DMF (red trace) after TFA addition (10% v/v) (blackbrown trace) and Co(DMG)<sub>2</sub>Cl<sub>2</sub> core (pink trace). No changes in LMCT band around ~360 nm were observed on acid addition, which confirms that axial ligand is still bound to the cobaloxime core in acidic media.



**Figure S8: (A)**The cyclic voltammograms recorded for C1-C3 under inert atmosphere. A 1mm glassy carbon disc, a Pt wire, and Ag/AgCl (in 3M KCl) was used as working, counter, and reference electrode respectively. CV was recorded with a scan rate of 0.5 V/s. The potential values were referenced using an internal standard, ferrocene (green trace). The

horizontal arrow indicates the initial scan direction. **(B)** Cyclic voltammograms recorded for C1 following the addition of 10% TFA(trifluoroacetic acid) as proton source to the sample present in DMF solution under  $N_2$  atmosphere. Increase in catalytic current is observed upon acid addition.



**Figure S9**. Spectroelectrochemistry data for C1 in water pH 7.0 (A) Gradual changes in optical spectrum for C1 is observed with time, when potential was held at -0.3V vs. SHE, Band at ~ 500 nm and ~600 nm gradually increases with time (B) Change in optical spectra, when potential was held at -0.9 V vs. SHE, band at ~600 nm gradually decreases with time. A 3 mm glassy carbon rod was used as working electrode, Pt wire as counter electrode and Ag/AgCl (in 3M KCl) as reference electrode, respectively. The experiment was done at room temperature.



Figure S10: Plot of  $i_p$  vs. square root of scan rate. Linear increase in the current with scan rate shows the stoichiometric nature of the signal.



Figure S11: Plot of  $i_c$  vs. square root of scan rate. The plateau current observed designates scan rate independent region. All rates were measured in this scan independent region.



**Figure S12:** Cyclic voltammogram data recorded at different scan rate: (A) for complex C1 (B) for complex C2. Data were recorded at pH 6.0 in buffered aqueous solution (0.1 M MES buffer) in the presence of  $0.1 \text{ M Na}_2\text{SO}_4$  electrolyte under inert conditions at RT. All data were recorded at 1 Vs<sup>-1</sup> scan rate at room temperature using 0.5mM of each complex and three electrode setup. The horizontal arrow depicts the initial scan direction.



**Figure S13:** Chronocoulometry data recorded for complexes C1-C3 (50  $\mu$ M). Data were recorded at aqueous pH 5.0 buffer(in buffered aqueous solution (0.1 M MES buffer) in the presence of 0.1 M Na<sub>2</sub>SO<sub>4</sub> electrolyte under inert conditions at RT), applying potential of -0.90 V vs. SHE. The data is recorded using a 1 cm x 1 cm plastic chip electrode as working electrode, Coiled Pt-wire as counter electrode and Ag/AgCl (in 3M KCl) as reference electrode in a 4 necked flask of volume 60mL. Figure beside represents Gas Chromatography (GC) data recorded after injecting 0.5 mL of head space gas in the GC instrument using leurlock gas-tight syringe after 7200 sec.



**Figure S14:** Simplified cyclic voltammogram for measuring (A) Turn Over Frequency (TOF) and (B) overpotential requirement (OP).



Figure S15: Comparative cyclic voltammogram data recorded at different pH: (A) for complex C2 (B) for complex C3. Data were recorded at pH 7.0 to pH 2.0 in buffered aqueous solution (0.1 M MES buffer) in the presence of 0.1 M Na<sub>2</sub>SO<sub>4</sub> electrolyte under inert conditions at RT. (pH 7.0: red trace; pH 6.0: blue trace; pH 5.0: green trace; pH 4.0: violet trace; pH 3.0 brown trace; pH 2.0 sky blue trace). All data were recorded at 1 Vs<sup>-1</sup> scan rate at room temperature using 0.5mM of each complex and three electrode setup. The horizontal arrow depicts the initial scan direction.



**Figure S16:** The two-dimensional (2D) EXSY spectrum (NMR) recorded for C1 complex in d<sub>6</sub>-DMSO at 300 K with 500 msec mixing time. The cross peaks are connected by dotted lines between



amine (NH), oxime(N-OH) and water, to display the sign of proton exchange between various functional groups as following: oxime/water (black trace), oxime/NH (Red trace), water/ NH (green).

**Figure S17:** The two-dimensional (2D) EXSY spectrum (NMR) recorded for C3 complex in  $d_6$ -DMSO at 300 K with 500 msec mixing time. The cross peaks are connected by dotted lines between amine (NH), oxime(N-OH), enolic -OH and water, to display the sign of proton exchange between various functional groups as following: oxime/water (black trace), enolic OH/water (Red trace), water/ NH (Brown trace), enolic OH/oxime (Green trace).



**Figure S18:** LSV data recorded for (A) Co-*bis*-(dimethylglyoxime)pyridine [Co(DMG)Pyridine] (10.0 mM) (B) for complex C1 (0.5 mM). Data were recorded at pH 7.0 (black trace), after addition of  $50\mu$ L D<sub>2</sub>O (red trace), and addition of  $100\mu$ L D<sub>2</sub>O (blue trace) under inert conditions at the room temperature. All data were recorded at 1 Vs<sup>-1</sup> scan rate at

room temperature using 0.5mM of each complex and three electrode setup. The horizontal arrow depicts the initial scan direction. Very minimal to no changes were observed in the TOF



of Co(DMG)Pyridine complex after addition of  $D_2O$ . Whereas, in case of complex C1, huge change in Co(II) centric catalytic current is observed after addition of  $D_2O$ .

**Figure S19:** pH titration data for complexes C1 and C2 in water. 5 mL aqueous solution of each complex with concentration 1mM was taken. Necessary amount of HCl was added to the solution to achieve pH~3. 2  $\mu$ L of 0.1 M NaOH was added dropwise, and corresponding pH was measured. The pKa values of 4.52 and 4.28 presumably correspond to N1 of C1 and N3 of C2 respectively. pKa of ~10 corresponds to the primary amine group. The pKa of the oxime group in nucleobase appended complex is found to be around ~7 from the above data.



Figure S20: Proton Inventory Studies of C2 (black circle), where the comparative catalytic rates  $\begin{bmatrix} D_2 O \end{bmatrix}$ 

in H<sub>2</sub>O/D<sub>2</sub>O mixture and water  $\binom{K_n/K_{H_2O}}{(M_2O)}$  was plotted against  $n = \frac{1}{[H_2O] + [D_2O]}$ . All measurements were conducted at -1.0V vs. SHE. All reported values are averaged from three or more independent measurements for standard deviation calculations.



**Figure S21:** The run 1 (black trace) is a complete cyclic voltammograms recorded for C1-C3 with a full scan ranging from 0.4 V to -1 V. The electrode was polished and cleaned after this run. The run 2 (red trace) is a scan of the same complex in the same solution, where only a cathodic scan from 0.4 V to -0.9 V (where maximum catalytic current is recorded) is taken. The electrode was only rinsed with deionized water (no polishing) and was used for run 3. Then this electrode was used for run 3 in a different aqueous solution (pH 5.0), which did not contain any complex. The third run (blue trace) was performed in that blank solution, where the cathodic scan was started at -0.9V and continued to -1V before returning back to 0.4V. Origination of no significant reduction current was observed in the third run in the cathodic stretch, which signifies no heterogeneous species was forming during the catalytic H<sub>2</sub> production.



**Figure S22:** Cyclic voltammogram of the complexes before (Black trace) and after (Red trace) bulk studies for complex C1 (A), C2 (B) and C3 (C) at pH 5.0 aqueous solution in buffered aqueous solution (0.1 M MES buffer) in the presence of 0.1 M Na<sub>2</sub>SO<sub>4</sub> electrolyte under inert conditions at RT. The bulk electrolysis of corresponding complex was done at -0.9 V (*vs.* SHE) for 7200 sec.



**Figure S23:** UV-Vis spectra of the complexes before (Black trace) and after (Red trace) bulk studies for complex C1 (A), C2 (B) and C3 (C) at pH 5.0 aqueous solution in buffered aqueous solution (0.1 M MES buffer) in the presence of 0.1 M Na<sub>2</sub>SO<sub>4</sub> electrolyte under inert conditions at RT. The bulk electrolysis of corresponding complex was done at -0.9 V (*vs.* SHE) for 7200 sec.



**Figure S24:** SEM image and EDS spectra of plastic chip working electrode (A) before and (B) after chrono coulometric experiment. The Bulk electrolysis data was recorded at -0.90 V *vs*. SHE of complexes C1-C3 at pH 5.0 for 7200 secs using Ag/AgCl reference electrode, Pt coil as counter electrode and plastic chip as working electrode. The active size of the plastic chip electrode was 1 x 1 cm and it was rinsed with water (NOT polished) before the SEM and EDS experiments after the bulk electrolysis. No trace of cobalt was found onto the working electrode.



Figure S25: Photocatalytic H<sub>2</sub> production recorded for C1-C3 complexes under irradiation with monochromatic light laser ( $\lambda$ =518 nm) in a buffered aqueous solution (pH 5.0) with 50 µM catalyst, 0.5 mM conc. of Eosin-Y (PS), and sacrificial electron donor 10% triethanolamine (TEOA). C1 (Black square), C2 (Red circle), and C3 (blue triangle) along with blank (Green inverted triangle, containing only PS and TEOA) showing the TON of H<sub>2</sub> production over a period of 6 hours.



**Figure S26:** Gas Chromatography data for Complex C1-C3 recorded after photocatalytic studies. Standard Control 1%  $H_2$  (green trace). PS: Photosensitizer, TEOA (sacrificial electron donor, (SED)). Three control experiments were performed to demonstrate essential presence of a PS, catalyst molecule, and SED for significant  $H_2$  production under photo-irradiation.



**Figure S27:** Showcasing a comparison of Cobaloxime based molecular catalyst having different biomolecules as outer co-ordination sphere.

Complex	C	1	Н		N	
Complex	Experimental	Theoretical	Experimental	Theoretical	Experimental	Theoretical
C1	41.43 %	42.17 %	4.39 %	4.39 %	25.43 %	25.31 %
C2	41.05 %	41.83 %	4.59 %	5.07 %	21.27 %	21.83 %
C3	42.12 %	42.71 %	4.65 %	4.89 %	18.10 %.	17.56 %

 Table S1. Elemental analysis data of complexes (C1-C3).

**Table S2**. Optical absorbance data of complexes (C1-C3) recorded in DMF with possible assignments of transitions. The molar extinction ( $\varepsilon$ ) values are given in the parentheses.

Complex	π- π* λ <sub>max</sub> /nm (ε /M <sup>-1</sup> cm <sup>-1</sup> )	LMCT λ <sub>max</sub> /nm (ε /M <sup>-1</sup> cm <sup>-1</sup> )	<i>d-d</i> λ <sub>max</sub> /nm (ε / M <sup>-1</sup> cm <sup>-1</sup> )
C1	270(10640)	360(1765)	540 (76)
C2	267(23116)	355(1917)	550 (95)
C3	260(12387)	304(7069)	516 (168)

**Table S3**. The  $E_{Co^{III/II}}$  and  $E_{cat/2}$  values for C1-C3 recorded at variable pH conditions.

	C	1	C	2	C	3
рН	E <sub>Co</sub> III/II (mV)	E <sub>cat/2</sub> (mV)	E <sub>Co</sub> III/II (mV)	E <sub>cat/2</sub> (mV)	E <sub>Co</sub> <sup>III/II</sup> (mV)	E <sub>cat/2</sub> (mV)
7	-85	-913	-	-	-150	-946
6	-53	-830	-25	-803	-90	-827
5	-52	-784	-66	-752	-75	-778
4	-29	-774	-84	-718	-85	-743
3	-45	-680	-61	-714	-	-
2	34	-663	2	-595	-	-

Sr. No	Molecular Cobalt catalyst		Electrocatalytic HER			
		TOF	OP	TON	Working	
		(S <sup>-1</sup> )	(mV)		Medium	
1	Co(Iminopyridine)	2.2 h <sup>-1</sup>	450	-		3
2	Co(DmgBF <sub>2</sub> ) <sub>2</sub> (CH <sub>3</sub> CN) <sub>2</sub>	-	442	5x10 <sup>5</sup> (7h)	pH 2.2	4
3	CoGGH	-	600	310 (2.5h)	pH 8	5,6
4	Ht-CoM61A	-	830	1.1x10 <sup>5</sup>	pH 7	7
				(6h)		
5	CoMC6*a	680		2.3x10 <sup>5</sup>	рН 6.5	8,9
				(3h)		
6	Co-salen tyrosine	190	775	-	pH 2.0	10
7	CoMP11-Ac	-	852	2.5x10 <sup>4</sup>	pH 7	11,12
				(4h)		

**Table S4**. Collective data for selected molecular cobalt complexes for  $H_2$  production from pure aqueous medium under different conditions.

**Table S5**. Comparative data for molecular cobalt complexes with  $Co(dmg)_2Cl$  as core for  $H_2$  production from pure aqueous medium under similar conditions.

Sr. No	Molecular Cobalt catalyst	Electrocatalytic HER			Ref
		TOF (s <sup>-1</sup> )	OP (mV)	Working Medium	
1	Co(dma) Cl(nyridina)	930	515	pH 7	13
		60	465	pH 5	13
2	Co(dmg) <sub>2</sub> Cl(4-pyridine	8830	507	pH 7	
	tyrosine)	860	490	pH 5	13
3	Co(dmg) <sub>2</sub> Cl(4-pyridine	2670	517	pH 7	
	picity fatalistic)	300	475	рН 5	14
4	Co(dmg) <sub>2</sub> Cl(4-ethylamine	3800	457		
	pyrianc)			рН 5	15
5	$Co(dmg)_2Cl(1-Imidazole$	3280	454	pH 7	
	acette actury	1300	476	pH 5	
6	Co(dmg) <sub>2</sub> Cl(4-Imidazole	4925	428	pH 7	
	accirc acid)	666	429	pH 5	
7	Co(dmg) <sub>2</sub> Cl(Histidine)	4525	477	pH 7	
		1587	460	pH 5	
8	$C_{1}(1) C_{1}(1) \cdots C_{n}(1)$	3960	494	рН 6	16
	$Co(dmg)_2CI(1son1aZ1d)$	1951	489	рН 5	1
9	Co(dmg) <sub>2</sub> Cl(vitamin B <sub>6</sub> )	1370	373	pH 7	17

		77	400	рН 5	
10	Co(dmg) <sub>2</sub> Cl(4-pyridine	8400	465	рН б	18
	Dopannic)	1800	425	pH 5	
11	Co(dmg) <sub>2</sub> Cl(4-pyridine Adenine) C1	44200	479	рН 5	This work
12	Co(dmg) <sub>2</sub> Cl(4-pyridine Cytosine) <b>C2</b>	15800	463	pH 5	
13	Co(dmg) <sub>2</sub> Cl(4-pyridine thymine) C <b>3</b>	27300	479	pH 5	

**Table S6**. TON calculated for Complex C1-C3 in pH 5 using 50  $\mu$ M catalyst concentration for Photocatalytic HER.

Sr.No	TON	C1	C2	C3
1	Electrocatalytic	44	30	14
2	Photocatalytic(TON vs. Cat)	241±5	234±5	150±5

Each data is calculated from a replicate of three experiments Photocatalytic TON reported after 6 hours

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