Highly selective and efficient electroreduction of CO₂ in water by quaterpyridine derivative-based molecular catalyst noncovalently tethered to carbon nanotubes

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Abstract
A disubstituted quaterpyridine based cobalt complex non-covalently tethered to multiwalled carbon nanotube (MWCNT) substrate, forming a hybrid catalyst, Co-qpyCOOH/CNT, catalyzed the conversion of CO₂ to CO under aqueous conditions. At an optimal and uniform loading, it exhibited remarkable catalytic activity, near-exclusive selectivity, and high stability towards the formation of CO. At a mere cathodic potential of −0.65 V versus RHE (η = 0.54 V), it achieved a high partial current density of −6.7 mA/cm² and a F.E.CO = 100%. In addition, with 20 h of stable operation, hydrogen evolution remained practically undetected. Its hybrid structure due to noncovalent immobilization on MWCNT imparted the intrinsic activity and much-needed stability in performance whereas –COOH groups may stabilize the intermediates by acting as H-bond donors, promoting catalytic activity. Tethering to a conductive solid substrate and tuning of the second sphere of coordination played an important role in its performance to achieve desired reduction product with high selectivity and activity.

KEYWORDS
carbon dioxide reduction, cobalt complex, disubstituted quaterpyridine, heterogeneous molecular catalysis, second coordination sphere

1 | INTRODUCTION
The rapidly increasing concentration of carbon dioxide in the atmosphere is a global concern.¹ Researchers have been trying to resolve this issue by developing materials and deploying techniques which can sequester CO₂ from the atmosphere or point sources and could either store it for the long term or convert it to useful chemicals, closing the carbon cycle. Electrochemical reduction of CO₂ holds immense potential due to its ease of handling, recyclability of...
materials, mild operating conditions, and ability to adapt for various desirable end products. Molecular catalysts, a class of catalysts for carbon dioxide reduction reaction (CO2RR), are being actively explored due to a great deal of control over their structure and molecular level utilization of catalytic sites, allowing researchers to deploy them in various innovative ways. Among the plethora of molecular catalysts, including porphyrins, phthalocyanines, and other macrocyclic molecules, polypyridyl catalysts have received significant attention over the past decades. While bipyridine and terpyridine based molecular catalysts have been studied for a wide variety of electrochemical applications (oxygen reduction reaction [ORR], CO2RR, etc.) in great detail, with various electrolytes, transition metal atoms, and substitution on the basic structure, higher polypyridine based molecular catalysts have been gaining traction over the past decade or so. Notably, quaterpyridine based molecular catalysts have shown great catalytic activity towards hydrogen evolution reaction (HER), oxygen evolution reaction [OER], and CO2RR. Among one of the earlier studies, Leung et al.11 deployed a cobalt-based quaterpyridine complex, driven by visible light, to act both as hydrogen evolving and oxygen-evolving molecular catalyst. In the following years, Guo et al.12 showed that the same quaterpyridine ligand, with Fe and Co as central metal atoms, could also behave as a photocatalyst and selectively convert CO2 to CO with a high turnover number (TON). An early study in 2018 by Cometto et al.13 further proved that iron- and cobalt-based quaterpyridine complexes were suitable for homogeneous electrochemical catalysis (with weak Bronsted acids) towards CO2RR. It also emphasized that Co outperformed Fe due to a deactivation pathway associated with catalysis by Fe. Recently, Wang et al.14 adopted a heterogeneous form of cobalt quaterpyridine and a highly efficient and selective hybrid molecular catalyst, immobilized on multiwalled carbon nanotubes (MWCNTs), was shown to operate in near-neutral aqueous conditions. Building on the existing literature, some recent reports have evaluated the performance of mono- or disubstituted covalently tethered quaterpyridine complexes for photocatalytic CO2RR.15,16 So far, however, most of these studies have remained limited to photocatalysis or homogeneous electrocatalysis. Inspired by these literature articles, we chose a disubstituted derivate of quaterpyridine ligand for our investigation. While cobalt is well-known for its electrocatalytic activity for CO2 reduction when used with organic ligands, MWCNT is typically considered a robust substrate for immobilization via π-π stacking. Besides, MWCNT acts as a conductive support, improving the catalytic activity and its highly conjugated structure allows to proceed via more facile noncovalent immobilization, eliminating the need of sophisticated coupling techniques for the tethering of the electrocatalyst. Furthermore, it has been known that the secondary coordination sphere in a molecular catalyst can play a role in the performance enhancement towards CO2RR.17,18 Substitution with carboxylic acid, amine, or hydroxy group on the parent molecule has been demonstrated to improve the catalytic performance by stabilization of intermediates through H-bonding or by their tendency to act as proton donors.19 In this study, a benzoic acid disubstituted cobalt complex was synthesized and non-covalently tethered to MWCNT substrate, forming a hybrid catalyst Co-qpyCOOH/CNT. This heterogenized molecular catalyst was evaluated for CO2RR in aqueous conditions, wherein, MWCNT enabled an efficient electron transfer, catalytic cobalt sites coupled with the substituted ligand catalyzed the conversion of CO2 to CO. To the best of our knowledge, 2,2′:6′,2′′′:6′′′-quaterpyridine-4′,4′′-bis-(4-benzoic acid) based cobalt complex has not been studied so far, for electrochemical application towards CO2RR, under purely aqueous conditions.

### 2 | EXPERIMENTAL SECTION

#### 2.1 | Chemicals

2,2′:6′,2′′′:6′′′-quaterpyridine-4′,4′′-bis-(4-benzoic acid) (98%) was purchased from HetCat. Cobalt acetate tetrahydrate, KHCO3 (99.7%), and anhydrous DMF were purchased from Sigma-Aldrich. Multi-walled carbon nanotubes (>95%, OD: 10–20 nm, 3.06 wt% –OH) were purchased from US Research Nanomaterials. Nafion perfluorinated resin solution (5 wt% in mixture of lower aliphatic alcohols and water) and Nafion N117 ion-exchange membrane were bought from Sigma-Aldrich while Toray Paper 060 carbon fiber paper (CFP) was procured from Fuel Cell Store. Solvents like methanol and diethyl ether were purchased from Sinopharm Chemical Reagent Co., Ltd. Gases used for electrochemical measurements and gas chromatography (GC) were purchased from Air Liquide. Electrolyte solutions for electrochemical performance testing were prepared using de-ionized (DI) water produced by Milli-Q Gradient A10 system (18.2 MΩ/cm, Millipore).

#### 2.2 | Synthesis

37.2 mg (0.068 mmol, 1 eq.) of ligand 2,2′:6′,2′′′:6′′′-quaterpyridine-4′,4′′-bis-(4-benzoic acid) was added to 40 ml DMF and dissolved completely with sonication. It was followed by dissolution of 20.2 mg cobalt acetate tetrahydrate (0.081 mmol, 1.2 eq.). Round bottom flask (RBF) and reflux setup were degassed and protected with argon atmosphere and the reaction mixture was stirred...
and heated to reflux at 120°C for 12 h. After cooling down to room temperature, cobalt complex was precipitated using diethyl ether. The obtained precipitate was washed with a small amount of methanol and diethyl ether to remove excess cobalt salt and rinse off DMF. Product (Cobalt (II) complex) was obtained by drying in a vacuum oven at 60°C for overnight.

For the preparation of Cobalt (II) complex hybrid with carbon nanotubes, 25 mg of MWCNT was dispersed in 30 ml of DMF. To each batch of such dispersion, a given amount of cobalt complex (37.5–6 mg) dissolved in 10 ml of DMF, was added. Each of these MWCNT dispersions was then sonicated for 30 min followed by vigorous stirring for 24 h. Each batch was centrifuged at 9000 r/min to remove the catalyst solution. Subsequently, each of these was subjected to three cycles of dispersion in 15 ml DMF followed by washing to remove loosely bound catalyst molecules. Finally, they were washed with 300 ml of DI water to remove DMF and were dried in a vacuum oven at 60°C to obtain Co-qpyCOOH loaded MWCNT (Figure S1).

2.3 Material characterization

High-angle annular dark-field-scanning transmission electron microscopy (HAADF-STEM), FEI Talos F200, field-emission TEM at 200 kV, was used for the imaging and elemental mapping. UV-visible spectra were collected using Shimadzu UV-1800 spectrophotometer. Quartz cuvettes were used, and qualitative spectra were recorded in the range of 800 nm to 267 nm. FTIR spectra using KBr pellets were recorded with Thermo Scientific Nicolet iS50 FTIR Spectrometer from 4000 cm⁻¹ to 400 cm⁻¹ wavenumbers. Kratos AXIS Supra XPS, equipped with an automated dual anode (Al/Ag Kα) X-ray monochromatic source, was used at the in-house central facility for the surface analysis of Co-qpyCOOH/CNT_25. Peak positions were calibrated by applying an energy offset. ICP-MS testing was performed using Agilent 7700 s with a detection limit of 1 ppb. Sample digestion was carried out using aqua regia at 220°C for 2 h. HPLC analysis was conducted on Agilent 1260 Infinity, equipped with Aminex HPX-87H Ion Exclusion Column (Bio Rad) and 5 mmol/L sulfuric acid as mobile phase.

2.4 Preparation of catalytic ink and electrodes

Catalyst inks were prepared in DMF using carbon nanotubes loaded with varying amounts of cobalt complex and Nafion (5 wt%) as a binder. Briefly, 8 mg of hybrid catalyst was dispersed in 1.95 ml DMF and was subjected to 5 min of sonication followed by the addition of 0.05 ml Nafion. Highly homogeneous catalyst ink was obtained by sonication of this mixture for 3 h in a water bath. All the inks for electrochemical testing were prepared by the above procedure. These were labeled as Co-qpyCOOH/CNT_37.5, Co-qpyCOOH/CNT_25, Co-qpyCOOH/CNT_12.5, and Co-qpyCOOH/CNT_6 wherein the number denotes the amount of cobalt complex added during the hybrid synthesis. The actual amount of the cobalt complex loading was assessed by ICP-MS.

Each piece (25 mm × 5 mm) of carbon fiber paper (CFP) was coated by drop-casting 100 μl of the catalytic ink, covering a geometric area of 0.5 cm², which translates to loading of approximately 0.8 mg/cm² (CNT basis). After drying each CFP under an IR lamp, they were kept in a vacuum oven at 60°C for an overnight duration to remove residual DMF before the electrochemical testing.

2.5 Electrochemical setup

A custom-made H-type cell with a Nafion N117 ion-exchange membrane separating the two compartments was used for the electrocatalytic testing for CO₂RR. For each electrochemical test, a freshly prepared working electrode and electrolyte (0.1 mol/L aqueous KHCO₃) were used. A platinum plate, Ag/AgCl (saturated KCl) electrode, and carbon fiber paper were used as a counter, reference, and working electrode, respectively. The current was controlled by CHI660E potentiostat/galvanostat workstation (at ambient temperature) and the gaseous product analysis for the electrochemical experiments was carried out using Agilent 7890B gas chromatograph (GC) system. CO₂ (or Ar) gas was delivered at an average rate of 9 ml/min to the GC system. The gas-phase composition was analyzed by GC every 12.33 min (including post run) using Hayesep Q and Molsieve 5 Å columns. Among the gaseous products, both H₂ and CO were analyzed by a thermal conductivity detector (TCD3 and TCD1, respectively). Figure S2 shows the representative peaks recorded by the GC corresponding to H₂ and CO formation. Electrochemical impedance spectroscopy (EIS) measurements were carried out on Autolab PGSTAT302N potentiostat workstation at room temperature.

2.6 Linear sweep voltammetry (LSV)

Linear Sweep voltammetry was performed using the above-mentioned setup of instruments, electrodes, and electrolytic cell. The electrolyte in the cathode compartment was bubbled with CO₂ or Ar for at least 30 min to ensure complete
saturation. The electrolyte was continuously stirred by using a magnetic stirrer and the gas flow rate was kept constant at 9 ml/min, both during the saturation period and the entire duration of electrochemical measurements. All measurements were made at room temperature and applied potentials were referenced to a reversible hydrogen electrode (RHE) based on the below equation.

\[ E_{\text{RHE}} = E_{\text{Ag/AgCl}} + (0.059 \times X) + E_{\text{Ag/AgCl}}^0 \]  

where \( E_{\text{Ag/AgCl}}^0 = 0.197 \).

### 2.7 Controlled potential electrolysis (CPE)

Electrolyte solution was saturated with CO2 for a minimum of 30 min. The gas flow rate was maintained at 9 ml/min while the solution was continuously stirred, for the entire testing duration. At each potential, gaseous products were collected every 12.33 min and the faradaic efficiency (F.E.) results obtained were calculated by taking the mean of third to fifth injections to ensure that an equilibrium has been attained in the headspace of the cell. Potential drops that is, iR corrections (85%) which account for the electrolyte resistance, were recorded and used for Tafel slope calculations.

### 2.8 Turnover frequency (TOF) calculations from CPE

Intrinsic performance of the Co sites in the hybrid catalyst was measured using turnover frequency, calculated using below mentioned formula, with two-electron pathway for the production of CO. Number of cobalt sites was obtained from ICP-MS measurements.

\[ \text{TOF (h}^{-1}) = \left( \frac{j_{\text{CO}} A}{2Fm} \right) \times 3600 \]  

where \( j_{\text{CO}} \) (A/cm²) is partial current density corresponding to CO₂RR to CO; \( A \) (cm²) is geometrical surface area of the coated electrode; \( F \) (s·A/mol) is Faraday constant (96485.3 s·A/mol); \( m \) (mol) is the amount of cobalt sites.

### 2.9 Stability test

Stability of Co-qpyCOOH/CNT-25 hybrid catalyst was evaluated at −0.65 V versus RHE in 0.1 mol/L KHCO₃ electrolyte for a duration of 20 h (2 cycles, 10 h each).

### 3 RESULTS AND DISCUSSION

As illustrated in Figure S1, hybrid catalyst was prepared by immobilization of quaterpyridine-based cobalt complex on MWCNT and was characterized for its physical features besides its electrochemical performance. Briefly, Co-qpyCOOH was prepared by refluxing qpyCOOH with Co(OAc)₂-4H₂O in DMF under inert conditions. The as-prepared cobalt complex was immobilized onto MWCNT to obtain Co-qpyCOOH/CNT. Additional details on catalytic ink and electrode preparation have been provided in the supporting information.

Carbon nanotubes loaded with the cobalt complex were imaged using high-angle annular dark-field-scanning transmission electron microscopy (HAADF-STEM) to visually represent the morphology of the substrate and immobilization of the catalyst in the form of its constituent elements. Figure S3A and S3B represent the bright field (BF) and dark field images, respectively, of a small section of entangled mass of carbon nanotubes. As the MWCNTs were not subjected to any destructive pre-treatments (horn-sonication or oxidizing acids), their integrity remained intact, as can be observed from these images. Their porous structure offers a large surface area for the π–π stacking of the molecular catalyst. Energy dispersive X-ray (EDX) analysis of this section for select elements (C, N, and Co) showed a uniform dispersion of the catalytic sites, rendering the high conductivity and activity (discussed in subsequent sections) to the hybrid structure (Figure S3C–E).

Figure 1A shows UV-vis spectra, recorded for cobalt acetate, quaterpyridine-derivative ligand, and its cobalt complex. The free ligand showed absorbance peaks in the UV-region corresponding to π–π* and n–π*, as is usually exhibited by polypyridyl ligands. Its corresponding cobalt complex showed similar peaks, with a slight red-shift, indicating an interaction between the coordinating N-atoms and central metal atom. A broad but weak absorbance band was also observed in the visible region which corresponds to spin forbidden metal to ligand charge transfer (MLCT). This observation established that the quaterpyridine ligand had undergone the reaction to yield a coordinated species. The spectrum of the cobalt salt showed some absorbance in the visible region, but no special features were observed, unlike the free ligand and its coordinated species.

Fourier transform infrared spectroscopy (FTIR) technique was used as another complementary method to confirm the formation of coordinated cobalt complex. Figure 1B shows the transmittance plots for both the ligand and its complex. qpyCOOH exhibited a broad and strong band centered between 3400 and 3450 cm⁻¹, originating from O–H stretching from water molecules.
absorbed by KBr and also from the O–H groups in the carboxylic acid of benzoic acid substitution. Bending vibration from O–H bends was also recorded at 1016 cm\(^{-1}\) and 1475 cm\(^{-1}\). Sharp band at 1703 cm\(^{-1}\) was attributed to C=O stretching whereas band due to \(\nu(C-O)\) was observed at 1250 cm\(^{-1}\). Aromatic C=C pyridine ring stretching vibration was recorded at 1383 cm\(^{-1}\) and aromatic C–H stretching bands at 3000–3100 cm\(^{-1}\). Spectrum of Co-qpyCOOH exhibited almost all these bands with small shifts in wavenumbers due to metal atom interactions whereas some peaks disappeared from the spectrum, suggesting successful complexation with the cobalt salt.

X-ray photoelectron spectroscopy (XPS) was employed to examine the surface composition of the hybrid electrocatalyst Co-qpyCOOH/CNT\(_{25}\) developed for this study. Figure S4 shows a broad scan and narrow scans of C 1 s, N 1 s, O 1 s, and Co 2p. The scans of individual elements were analyzed and resolved into constituent peaks to detect and confirm the presence of surface-immobilized species (Figure 2). Peaks for N, O, and Co were calibrated based on an energy offset of 0.45 eV, which was used to shift the peak for C–C bond in the C 1 s survey. The peak for C–C/C=C was centered at 284.8 eV (correction reference) whereas the peak at 285.2 eV was attributed to C=N bonds of the skeleton structure of the molecular catalyst. Further deconvolution of peaks resulted into a series of peaks at 286.3 eV and 289.2 eV corresponding to C–O and O=C=O (carboxylate group), respectively of the substrate and/or the catalyst. An additional peak at 291.1 eV was attributed to \(\pi-\pi^*\) transition from delocalized \(\pi\)-electrons (Figure 2A).\(^{20-23}\)

Narrow scan of N 1 s exhibited two peaks, centered at 399.8 eV and 402.2 eV, which were assigned to pyridinic-N species and graphitic-N (Figure 2B). Possible source for the contribution from graphitic nitrogen may be residual DMF or nitrogen atoms substituting terminal carbon atoms in graphitic layer in the carbon nanotube substrate.\(^{20,21,24}\)

XPS survey of O 1 s core levels has been shown in Figure 2C which deconvolutes into two peaks at 531.7 eV and 533.7 eV, corresponding to carbonyl and hydroxy structures.\(^{25}\)

Scan of Co 2p core levels shows the appearance of two major peaks at 781.6 eV and 796.9 eV, which were assigned to 2p\(_{1/2}\) and 2p\(_{1/2}\) core levels, respectively. Simultaneously, two more satellite features appeared at 786.7 eV and 802.1 eV, confirming the presence of cobalt metal atom in a valence state of +2 in its coordinated form (Figure 2D).\(^{26}\)

In a series of assessments made to evaluate the electrochemical performance of the hybrid catalyst Co-qpyCOOH/CNT\(_{25}\) towards CO\(_2\)RR, first was based on polarization/linear sweep voltammetry (LSV) curves, as shown in Figure S5. The electrocatalyst was subjected to a reduction potential up to \(-0.8\) V versus RHE (reversible hydrogen electrode) at a scanning rate of 5 mV/s. Under argon saturated electrolyte (pH = 8.34), current density was primarily driven by HER, and onset of activity was observed at an overpotential of 0.29 V. Thereafter, the hybrid catalyst was tested in a CO\(_2\) saturated electrolyte (pH = 6.8) while keeping all other conditions at par. A relatively lower onset overpotential was recorded at 0.24 V, but a much higher catalytic current density was observed, originating from CO\(_2\)RR. Intrigued by this remarkable performance, this electrocatalyst was further tested for its activity, selectivity, robustness, and other intrinsic properties.

Molecular catalyst Co-qpyCOOH was immobilized on the carbon nanotubes by means of \(\pi-\pi\) interactions between them. Due to the nonspecific nature of noncovalent
bonding, it becomes imperative to optimize the amount of catalyst used, to alleviate the issue of aggregation, which may adversely affect the performance due to the unavailability of a fraction of catalytically active sites on the electrode surface. A series of catalytic inks were prepared by progressively increasing the amount of catalyst added to the MWCNT dispersion. Total current densities, faradaic efficiencies, and partial current densities were measured by performing chronoamperometric tests from $-0.45 \text{ V}$ to $-0.65 \text{ V}$ versus RHE, as shown in Figure 3. Total current density showed a monotonous increase with increasing reductive potentials for all the samples. Furthermore, when these samples were compared to assess the impact of loading, the overall current density increased with the increasing amount of molecular catalyst used. Co-qpyCOOH/CNT_6 could attain a maximum current density of $-3 \text{ mA/cm}^2$ at $-0.65 \text{ V}$ versus RHE whereas Co-qpyCOOH/CNT_25 could reach $-6.7 \text{ mA/cm}^2$ at the same potential. Co-qpyCOOH/CNT_12.5 showed an intermediate level of current density across all tested potentials. It was observed that the current density of Co-qpyCOOH/CNT_25 was quite comparable to Co-qpyCOOH/CNT_37.5, indicating a plateauing of performance. Comparison of faradaic efficiency (F.E.) data showed that $\text{H}_2$ and CO were the only gaseous products detected. Based on faradaic efficiency measurements, CO$_2$RR dominated the catalytic activity and only a very small amount ($\leq 1\%$) of $\text{H}_2$ formed (Figure 3B), proving the extremely selective behavior of the hybrid catalyst. At $-0.45 \text{ V}$ versus RHE, the F.E.CO ranged between 75--83\% for various samples, while F.E.$\text{H}_2$ still remained low, possibly due to lower accuracy at lower reduction currents and corresponding lower amounts of gases at such a low overpotential. HPLC analysis of the electrolyte detected no peaks of formic acid, ruling out the possibility of its formation at this potential. At subsequent potentials ($-0.55 \text{ V}$ vs. RHE onwards), F.E.CO reached and maintained nearly 100\% for all samples. Therefore, partial current density towards formation of CO ($j_{CO}$) was practically identical to total current density (Figures 3A and 3C).

Despite the near-exclusive selectivity exhibited toward the formation of CO across all the samples, current density decreased consistently with the reduction of the molecular catalyst added. Therefore, considering the high current density output and an extremely selective
performance of Co-qpyCOOH/CNT_25, it was chosen as an optimized hybrid catalyst for further evaluation of other parameters.

The optimized hybrid catalyst was subjected to more detailed performance evaluation. Even though the onset potential towards CO2RR was about $-0.35$ V versus RHE ($\eta = 0.24$), we started chronoamperometric testing from $-0.45$ V versus RHE as the currents were too low for lower reduction potentials and expectedly, the gaseous products formed were also on a lower side. The hybrid catalyst showed approximately 79% and 95% F.E.CO at $-0.45$ V and $-0.5$ V versus RHE, respectively (Figure 3D). For subsequent potentials, up to $-0.75$ V versus RHE, F.E.CO increased to nearly 100% and remained at that level for the entire testing range. In parallel, current density, with majority of contribution from CO2RR, rose from $-1$ mA/cm$^2$ to $-10.41$ mA/cm$^2$, as applied reduction potential increased from $-0.45$ V to $-0.75$ V versus RHE. Evidently, HER, even though considered as a competing reaction in aqueous conditions, remained negligible. Such remarkable performance towards carbon dioxide reduction proves its exceptionally high selectivity and activity.

Benzoic acid substituted on parent molecular catalysts have not been studied much for their role towards carbon dioxide reduction in homogeneous or heterogeneous conditions. Most studies have primarily utilized this group as a linker for covalent immobilization (e.g., amide linkage) on a substrate or synthesize a MOF for photocatalytic and/or electrocatalytic applications for CO2RR.15,23,27,28 However, the effects exerted by second-sphere substituents seem to play a significant role as suggested by several recent reports.17,29–31 Therefore, it is imperative to consider those effects which may contribute to the efficiency of -COOH decorated molecular catalysts. Based on mechanism studies, molecular catalysts substituted with hydroxyl (-OH), amino (-NH$_2$), carboxylic (-COOH) groups have been shown to behave as proton donors or H-bond donors during CO$_2$ adsorption by central metal atom and its subsequent conversion to *COOH.19,32,33 Furthermore, the positions of substitution (ortho vs. para vs. meta) of these groups have also been observed to affect the ultimate performance of catalysts.34 A recent 2021 report, comparing the performance of aromatic and aliphatic substitution with -COOH group, further highlights the nuanced

![Figure 3](image-url)
differences of performance based on environment in which CO₂RR is performed. Benzoic group may not be a better choice than the phenolic group due to its relatively low pKₐ and the fact that weak Bronsted acids tend to promote catalytic activity, but it may still play the dual role of proton-donor and H-bond donor, rendering it the ability to perform well in near-neutral and even low pH conditions. Sulfonic-acid groups on the other hand have extremely low pKₐ and have been shown to adversely affect the catalytic performance.

Nonetheless, its exceptional performance under near-neutral aqueous conditions, makes it comparable to some of the best-known heterogeneous electrocatalysts in the literature (Table 1). With a near-unity faradaic efficiency (CO) and a mere overpotential requirement of 0.54 V (−0.65 V vs. RHE) to attain a partial current density of −6.7 mA/cm², it ranks better than many of the listed entries across all parameters. It lags behind some of the very high-performing state-of-the-art electrocatalysts in terms of current density, however, it still achieved 100% F.E.(CO) at marginally higher overpotentials in 0.1 mol/L KHCO₃ electrolyte. The differences in current densities may somewhat be bridged with CO₂RR carried under higher concentrations (e.g., 0.5 mol/L KHCO₃) of electrolyte. Furthermore, the parent molecule-based hybrid catalyst (entry 2) performed extremely well with a high current density (−10 mA/cm²) at a remarkably low overpotential of 0.34 V (−0.45 V vs. RHE) and that too at a very low catalyst loading. Our study further highlights that quaterpyridine based electrocatalysts hold potential to be used as hybrid materials for CO₂RR. With more focus on their structural and operational environment optimization, they may even outshine many high-performing catalysts based on porphyrins and phthalocyanines.

It is worth noting that the high performance observed from our study was carried out using traditional H-cell. Integrating this hybrid molecular catalyst with a GDE and deploying a flow cell which utilizes moist CO₂ may help attain much higher current density which is up to 10–20 times higher and may exhibit stability lasting several days. The strategy to use a flow cell with a GDE coated with an electrocatalyst to attain industrially relevant performance has been successfully demonstrated not only with certain molecular catalysts but also with covalent organic frameworks (COFs). It is worth noting that these electrolyzer setups utilize moist CO₂ and therefore, use a three-phase system instead of a two-phase one. This improves the gas diffusion at the Table 1: Comparison of Co-qpyCOOH/CNT with covalently or non-covalently immobilized CO-selective CO₂ reduction electrocatalysts working in aqueous media

| Catalyst                  | Potential [V versus RHE] | Current density [j(mA/cm²)] | F.E.(CO) [%] | Electrolyte  | Reference |
|---------------------------|--------------------------|-----------------------------|--------------|--------------|-----------|
| Co-qpyCOOH/CNT            | −0.65                    | 6.7                         | ~100         | 0.1 mol/L KHCO₃ | This study |
| [Co(qpy)]²⁺/MWCNT          | −0.45                    | 10                          | 100          | 0.5 mol/L NaHCO₃ | 14        |
| CoPP@CNT                  | −0.6                     | 25.1                        | 98.3         | 0.5 mol/L NaHCO₃ | 37        |
| CoTPyPP/CNT               | −0.6                     | ~7.9                        | 94.7         | 0.5 mol/L KHCO₃ | 38        |
| Co¹²CPY/CNT               | −0.7                     | ~10.74                      | ~96          | 0.1 mol/L KHCO₃ | 39        |
| NapCo@SNG                 | −0.8                     | ~2.37                       | 97           | 0.1 mol/L KHCO₃ | 40        |
| NapCo@SNG                 | −0.7                     | ~1.26                       | 95           | 0.1 mol/L KHCO₃ | 40        |
| CoPc2                     | −0.676                   | ~19.5                       | 93           | 0.5 mol/L NaHCO₃ | 27        |
| CoPc/CNT (2.5%)           | −0.63                    | ~10.0                       | 92           | 0.1 mol/L KHCO₃ | 41        |
| CoPc-CN/CNT (3.5%)        | −0.63                    | ~15.0                       | 98           | 0.1 mol/L KHCO₃ | 41        |
| CoPc/CNT                  | −0.61                    | 20                          | ~90          | 0.5 mol/L KHCO₃ | 42        |
| Perfluorinated CoPc       | −0.8                     | ~4.4                        | 93           | 0.5 mol/L KHCO₃ | 43        |
| CoPc-P4VP                 | −0.73                    | 2.0                         | 89           | 0.1 mol/L NaH₄PO₄ | 44        |
| STPyP-Co                  | −0.62                    | 6.6                         | 96           | 0.5 mol/L KHCO₃ | 45        |
| COF-367-Co                | −0.67                    | 3.3                         | 91           | 0.5 mol/L KHCO₃ | 46        |
| CAT₃py/CNT                | −0.59                    | 0.24                        | 93           | 0.5 mol/L KHCO₃ | 47        |
| CoCAT-COOOH               | −0.62                    | ~0.16                       | 95           | 0.5 mol/L NaHCO₃ | 48        |
| CoPc/O₂C                  | −0.73                    | 2.7                         | 94           | 0.1 mol/L NaHCO₃ | 49        |
interfaces and helps to attain high current densities. It has recently been shown that the wettability at the interfaces of three-phase systems plays an important role in controlling the gas diffusion, eventually helping to improve and realize industrial benchmarks.

It has been observed for several electrocatalysts that despite an excellent performance towards CO$_2$RR, kinetics may remain sluggish due to several reasons, including mass transport limitations. To get insights into the intrinsic activity and reaction mechanics of heterogenized electrocatalyst Co-qpyCOOH/CNT$_{25}$, Tafel slope was calculated. iR correction (85%) was employed with $R = 28 \, \Omega$ (experimentally determined) to account for the potential drop due to electrolyte resistance. A linear fit analysis of plot between log ($j_{CO}$) and potential (overpotential) provided a Tafel slope of 132 mV/dec (Figure 4A). This value is clearly close to the theoretical value of 118 mV/dec, therefore, rate-determining step (RDS) is the transfer of first electron, leading to the formation of adsorbed *COO$^-$. This low Tafel slope also indicates that mass transfer limitations were non-existent, further implying that aggregate formation was minimized at this optimized concentration, correlating to its high activity. Figure S6 shows the plots obtained from electrochemical impedance spectroscopy, highlighting the fact that the charge transfer resistance was very low for the hybrid electrocatalyst, leading to better electrocatalytic kinetics.

Turnover frequency (TOF) value is an important factor which is used to benchmark the performance of a molecular catalyst. The number of cobalt sites on the hybrid electrocatalyst Co-qpyCOOH/CNT$_{25}$ was calculated by using ICP-MS. Equation (2) with $[Co^{2+}]$ (mg/L) = 0.54547 and $[Co^{2+}]$ (mol) on electrode = 1.8746 × 10$^{-8}$ was used to calculate the TOF at each potential with an assumption that all the cobalt atoms were contributing to the catalytic activity. Figure 4B shows the plot between the reduction potentials and TOF. The TOF values increased with the increasingly applied potential and could attain a maximum value of 5178 h$^{-1}$ at $-0.75$ V versus RHE. Such high TOF also indicates towards an efficient and uniform dispersion of the immobilized molecular catalyst on the surface, which may enable the availability of catalytic sites on the surface during the CO$_2$RR.

As mentioned above, structural and operational environment, plays a very important role and dictates the performance of these molecular catalysts. A recent study by Sun et al. compared two different molecular catalysts, that is, Co(II)CPY/CNT, made of phenanthroline subunits and Co-TPP/CNT, made of pyrrole subunits. Under similar operating conditions, they showed that Co(II)CPY/CNT outperformed the pyrrole-based electrocatalyst. A computational analysis explained this on the basis of synergistic effect between the ligand and cobalt, better delocalization of electrons, high electron density on N-atoms, and a significant role played by $d_{Z^2}$ orbital. It’s interesting to observe that simple polypyridine-based electrocatalysts, perform extremely well, often outperforming, when competing against well-studied porphyrins and phthalocyanines, as can be observed from the various entries listed in Table 1. Quaterpyridine based electrocatalysts have shown near unity selectivity, highly stable performance, and fast reaction kinetics as evidenced by Tafel slopes. It is plausible as well as worth exploring if a structural difference based on pyridine versus pyrrole subunit could give rise to such competing performances.

For molecular catalysts’ industrial relevance, their robustness under operating conditions would play an important role, therefore, it was crucial to assess the aforementioned hybrid catalyst for its stability under operating conditions. Co-qpyCOOH/CNT$_{25}$ was subjected to a potential of $-0.65$ V versus RHE for two cycles of operation, each 10 h long, in carbon dioxide saturated 0.1 mol/L KHCO$_3$ electrolyte. An exceptional stability was shown (Figure S7) by this hybrid catalyst with a current density between $-6.8$ mA/cm$^2$ and $-8.4$ mA/cm$^2$ and F.E.CO = $\sim 100\%$ across the 20-h operation.

**FIGURE 4** (A) Tafel slope and (B) turnover frequency of hybrid catalyst Co-qpyCOOH/CNT$_{25}$
4 CONCLUSION

A disubstituted quaterpyridine based cobalt complex was synthesized and noncovalently tethered to MWCNT to yield a hybrid catalyst. Besides its structural characterization, it was evaluated for its electrochemical performance towards CO₂RR. At an optimal and uniform loading of the molecular catalyst on MWCNT, as evident from its HAADF-STEM images, it exhibited remarkable catalytic activity, near-exclusive selectivity, and stability towards formation of CO. At a cathodic potential of −0.65 V versus RHE (η = 0.54 V), it achieved a partial current density of −6.7 mA/cm² and a F.E.ₐₐ = 100%. In addition, it achieved 20 h of stable operation, while HER remained practically undetected. Its exceptional performance under near-neutral aqueous conditions makes it state-of-the-art and comparable among some of the best-known heterogeneous electrocatalysts in the literature. Its hybrid structure due to noncovalent immobilization on a conductive substrate imparted intrinsic activity and much-needed stability in performance whereas -COOH groups may stabilize the intermediates by acting as H-bond donors, promoting catalytic activity. Given the complexities involved in heterogeneous molecular catalyst structures, computational analysis is much needed for screening of such potential catalysts as well as for unraveling of precise mechanisms.

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CONFLICTS OF INTEREST

The authors declare no conflicts of interest.

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