

Article

Electrocatalytic Hydrogen Evolution of Transition Metal (Fe, Co and Cu)–Corrole Complexes Bearing an Imidazole Group

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Abstract: The study of the hydrogen evolution reaction (HER) by non-noble transition metals is of great significance for the production of hydrogen energy. In this work, a new 5,15-bis-(pentafluorophenyl)-10-[4-(1H-imidazole) phenyl]-corrole and its metal complexes (metal = Co, Cu, Fe) were synthesized and used for electrocatalyzed HER in DMF organic solvent and aqueous media. The prepared cobalt corrole showed the best catalytic performance in both media. Its turnover frequency (TOF) and catalytic efficiency (C.E) could reach 265 s^{−1} and 1.04 when TsOH was used as the proton source in a DMF solvent. In aqueous media, its TOF could also reach 405 h^{−1}. The catalytic HER may go through an EECEC or ECEC (E: electron transfer, C: chemical step) pathway for these catalysts, depending on the acidity and concentration of the proton source. The present work successfully demonstrates that imidazole at a meso-phenyl group may improve the electrocatalytic HER activity of transition metal corroles.

Keywords: corrole; hydrogen evolution; electrocatalysis; cobalt; copper; iron



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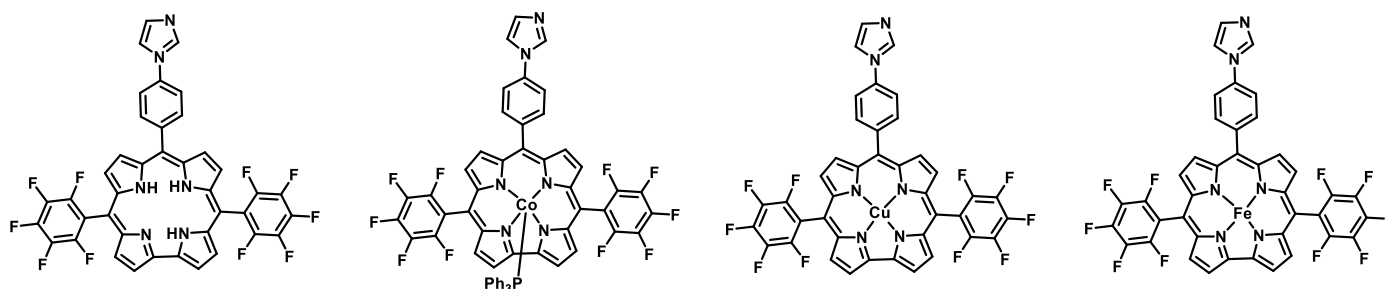
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1. Introduction

With the continuous consumption of non-renewable fossil fuels and environmental pollution caused by their combustion, exploring new sustainable and environmentally friendly energy has become the focus of scientific research. Hydrogen energy is the most promising renewable energy because of its high calorific value and pollution-free combustion [1,2]. A variety of methods have been reported for producing hydrogen, with the electrocatalytic hydrogen evolution reaction (HER) being particularly significant [3–5]. Due to the slow reaction kinetic of HER, the reaction usually needs to be facilitated by the addition of a catalyst. Platinum-based catalysts have excellent catalytic performance for HER; however, their high cost and scarcity limit their wider application [6–8]. Therefore, exploring earth-abundant catalysts that effectively catalyze HER is crucial.

Currently, many low-cost transition metals have been used in catalytic HER studies, including cobalt [9,10], copper [11–13], nickel [14], iron [15], etc. Macrocyclic molecular catalysts have also been used for HER due to their unique chemical structure and tunable activity [16–18]. Metal porphyrins have been extensively used in electrocatalytic HER [19–21]. Corrole is a class of trianionic macrocyclic ligand in the porphyrin family. It has the capacity to stabilize encapsulated metal with higher oxidation [22]. This is conducive to electrocatalytic hydrogen evolution by lowering the overpotential [23]. Recently, lots of studies have focused on metal–corrole electrocatalysts in HER [21,24,25]. The catalytic properties of metal corroles may be modulated by modifying the groups at their meso-positions [26]. It has been found that the strong electron-withdrawing groups such as pentafluorophenyl [27], cyanophenyl [28], and nitrobenzene [29] could enhance the catalytic HER ability of metal–corrole catalysts. In addition, the introduction of proton relay groups such as amine [30], hydroxyl [31], and sulfonic acid groups [32] is also

effective at enhancing the catalytic ability of the catalysts. Previously, we have reported the electrocatalytic HER activity of metal-corrole complexes bearing pentafluorophenyl [24], nitro [29], hydroxyl [31], and ethoxycarbonyl [33] substituents. The imidazole moiety, as a group with both electron-withdrawing as well as strong proton transfer ability [34,35], may improve the electrocatalytic HER activity of metal-corrole catalysts. In this work, we have prepared a new corrole bearing 4-(1H-imidazole) phenyl group at the 10- position and two strong electron-withdrawing pentafluorophenyl groups at the 5- and 15- positions and its Co, Cu, and Fe complexes (Scheme 1). The results show that the three new metal corroles have good electrocatalytic ability for proton reduction in both organic and aqueous media, with cobalt corrole having the best performance.



Scheme 1. The structure of the investigated metal corroles.

2. Results and Discussion

2.1. Synthesis and Characterization

The freebase corrole 5,15-bis-(pentafluorophenyl)-10-[4-(1H-imidazole) phenyl]-corrole (PFIC) was synthesized by modifying the previous method [36]. Metal-corrole complexes were obtained by reacting freebase corrole with different metal salts under certain conditions. All four corroles were synthesized and characterized by ultraviolet-visible spectroscopy (UV-vis), high-resolution mass spectroscopy (HRMS), X-ray photoelectron spectroscopy (XPS), and nuclear magnetic resonance (NMR). All characterization data are listed in Section 3 and the figures are listed in the ESI (Figures S1–S14).

2.1.1. UV-Vis of Freebase Corrole and Metal Complexes

The UV-vis absorption spectra of the freebase corrole and metal complexes are shown in Figure S1. Like the previously reported freebase corrole compound [37], the PFIC has a strong, sharp characteristic absorption peak at about 410 nm (Soret band) and two weaker broad absorption peaks at about 550–650 nm (Q band). PFIC-Co, PFIC-Cu, and PFIC-Fe exhibit the normal Soret and Q absorption bands of metal-corrole complexes. PFIC-Co exhibits a split Soret band and a red-shifted Q band; this is caused by the axial binding of the triphenylphosphine ligand. Such changes can prove that the metal has successfully coordinated with freebase corrole to form metal complexes [38].

2.1.2. Structural Characterization by Single-Crystal X-ray Diffraction

Single-crystal X-rays can clearly reveal the molecular structure of corrole complexes. The single-crystal structure of PFIC-Cu illustrates that it contains an imidazole moiety and exhibits that the Cu ion has successfully coordinated with the four N atoms at the corrole's center. Also, the Cu ion is in the same plane as the corrole macrocycle (Figure 1). Specific crystal data are detailed in Table S1. The crystal data accurately demonstrate that the lengths of these four Cu-N bonds range from 1.87 to 1.89 Å and that they have an average length of 1.883 Å, which happens to be in agreement with the electronic structure of d^8 Cu^{III} [39]. Otherwise, the large angles of $\angle \text{N1-Cu-N3}$ and $\angle \text{N2-Cu-N4}$ produced by the coordinating atoms are 166.0° and 167.7° , respectively, indicating that the Cu is slightly off-center. The PFIC-Cu's crystallographic information can be obtained for free at the Cambridge Crystallographic Data Centre; its CCDC identifier is 2301493.

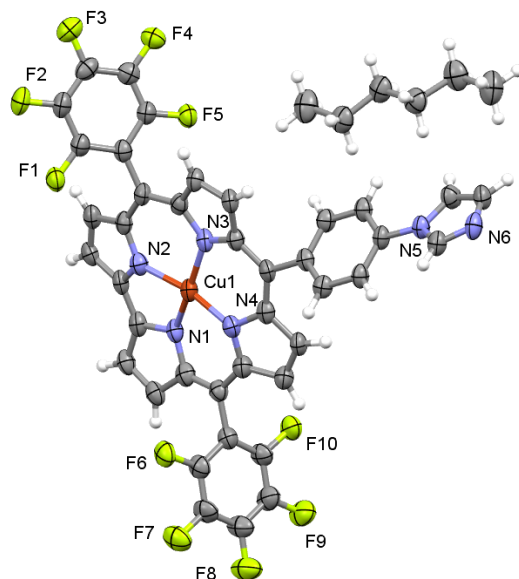


Figure 1. Thermal ellipsoid plots (50% probability) of the X-ray structure of PFIC-Cu.

2.1.3. X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy can effectively detect the elemental distribution of metal complexes. Figure 2a exhibits the full spectrum of PFIC-Co, showing the corresponding signals of Co, N, F, P, and O. In Figure 2b, the peaks of Co 2p^{3/2} and Co 2p^{1/2} are at 780.7 and 795.6 eV [40], which exactly correspond to the Co^{III} oxidation state. Due to the existence of imidazole groups, N can be classified into four categories based on the spectra of N 1s: Graphitic-N, Pyrrolic-N, Co-N, and Pyridinic-N. The corresponding peaks are at 401.1, 400.2, 399.3, and 398.5 eV, respectively [41]. Similarly, the peaks of each element in the spectra of PFIC-Cu and PFIC-Fe are assigned and shown in Figures S13 and S14.

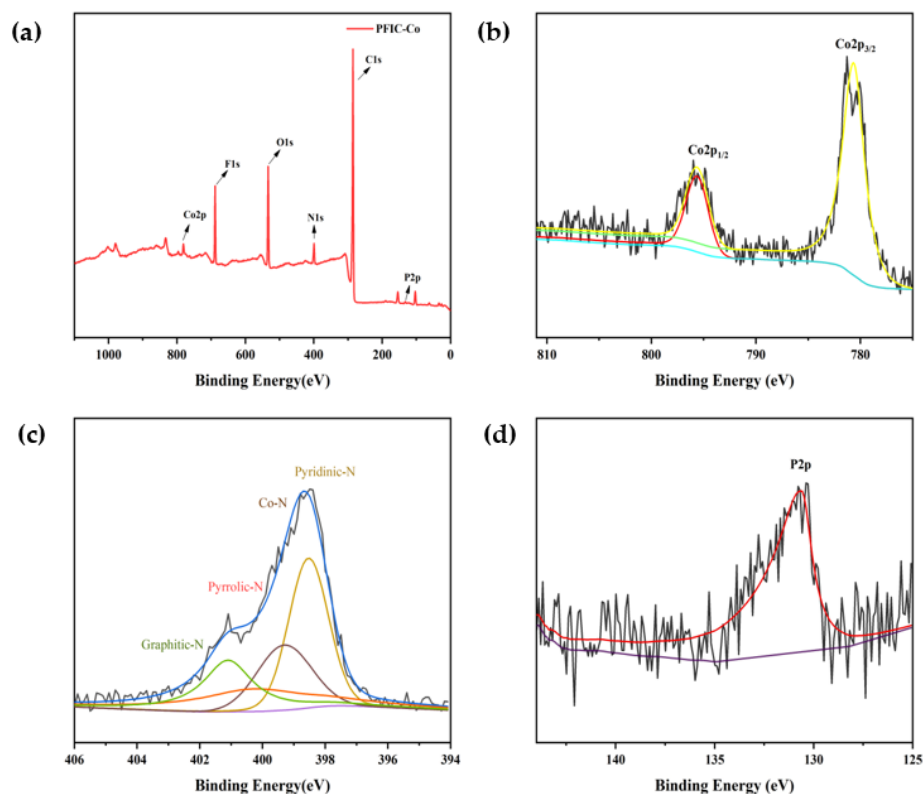


Figure 2. XPS survey spectrum of PFIC-Co (a); XPS spectra of Co 2p (b), N 1s (c), and P 2p (d).

2.2. Cyclic Voltammetry Studies

In the test, all cyclic voltammetry (CV) tests were carried out in N, N-dimethylformamide (DMF) with 0.1 M TBAP as the supporting electrolyte under N₂ atmosphere at a scan rate of 100 mV s^{−1} and a catalyst concentration of 1.0 mM; the working electrode was 3.00 mm glassy carbon, while the counter electrode was a graphite rod, with Ag/AgNO₃ serving as the reference electrode. The results are presented in Figure 3. PFIC-Co exhibited an irreversible redox peak and a reversible redox peak in the scanning range from 0 to 2.5 V vs. ferrocene. The first reduction peak, attributed to the reduction of Co^{III} to Co^{II}, took place at −0.84 V. This phenomenon was irreversible, since the -PPh₃ (triphenylphosphine) axial ligand was lost during the reduction process [42]. For PFIC-Cu, two redox peaks appeared at −0.25 and −2.21 V (E_{1/2}), which are attributed to Cu^{III}/Cu^{II} and Cu^{II}/Cu^I. Similarly, for PFIC-Fe, its Fe^{III}/Fe^{II} and Fe^{II}/Fe^I reduction potentials were −0.97 and −2.14 V (E_{1/2}). The redox peak potentials of all the compounds are summarized in Table 1. A comparison of the M^{II}/M^I redox potentials of the three substances shows that PFIC-Co has a more positive potential compared to PFIC-Cu and PFIC-Fe. Furthermore, we also tested the CVs of metal corroles with different scans. The results indicate a positive linear relationship between the redox peak current values of metal corroles and the square root of the scanning speed (Figure S15), implying the electron process to be diffusion-controlled [43].

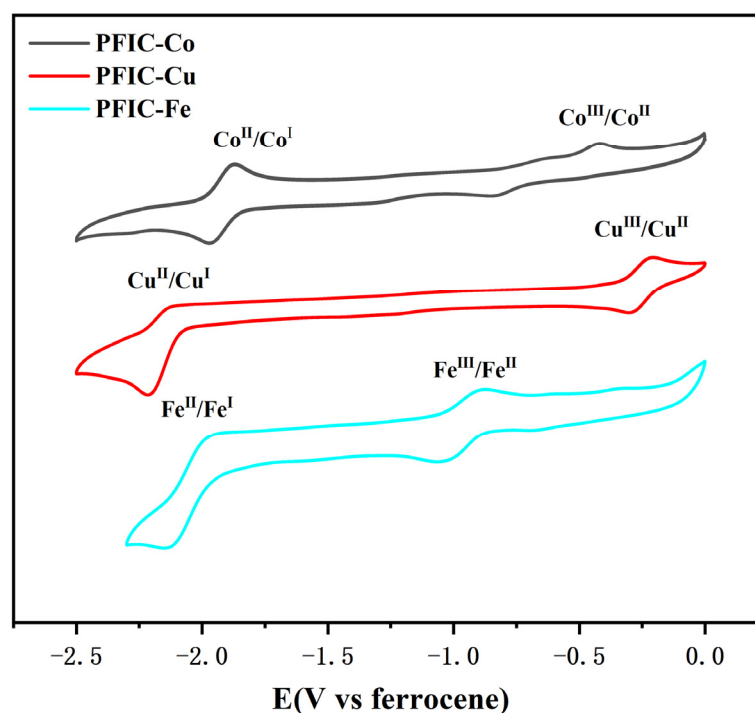


Figure 3. CVs of the metal complexes PFIC-Co, PFIC-Cu, and PFIC-Fe (1.0 mM) in DMF (0.1 M TBAP).

Table 1. Redox potentials of metal corroles.

Complex	M ^{III} /M ^{II}		M ^{II} /M ^I
	Ox 1/V	Red 1/V	Red 2/V
PFIC-Co	−0.43	−0.84	−1.97
PFIC-Cu	−0.21	−0.30	−2.21
PFIC-Fe	−0.89	−1.05	−2.14

2.3. Electrocatalytic Activity of Metal Corroles in DMF

In general, the catalytic pathway and the catalytic performance of the catalyst for the HER are closely related to the proton source. The HER catalytic activities of these three metal corroles were tested using acetic acid (AcOH, pKa 13.2 in DMF [44]), trifluoroacetic acid (TFA, pKa 3.5 in DMF [45]), and p-toluene methanesulfonate (TsOH, pKa 2.6 in DMF [44]) as the proton source in DMF.

Firstly, CV tests were performed in an environment where AcOH was the proton source. As shown in Figure 4, with increasing acid equivalents, the CVs of the three complexes gradually became irreversible and the peak currents gradually increased, indicating the presence of a proton reduction process. This was indicated by the gradual disappearance of the second oxidation peaks and the increase in the current of the second reduction peaks. We suggest that the irreversibility is due to the formation of M-H intermediate species in the catalyzing HER, which makes the CV irreversible. It can be seen that the first reduction peak remains almost invariant for all metal corroles, indicating that this step is only the metal reduction process without the involvement of proton reduction reaction. Furthermore, the peak current near the M^{II}/M^I increases with the increase in AcOH concentration and reaches a maximum when the acid concentration reaches 32 eq. The position of the reduction also shifts negatively, indicating the involvement of M(I) species in the HER [31].

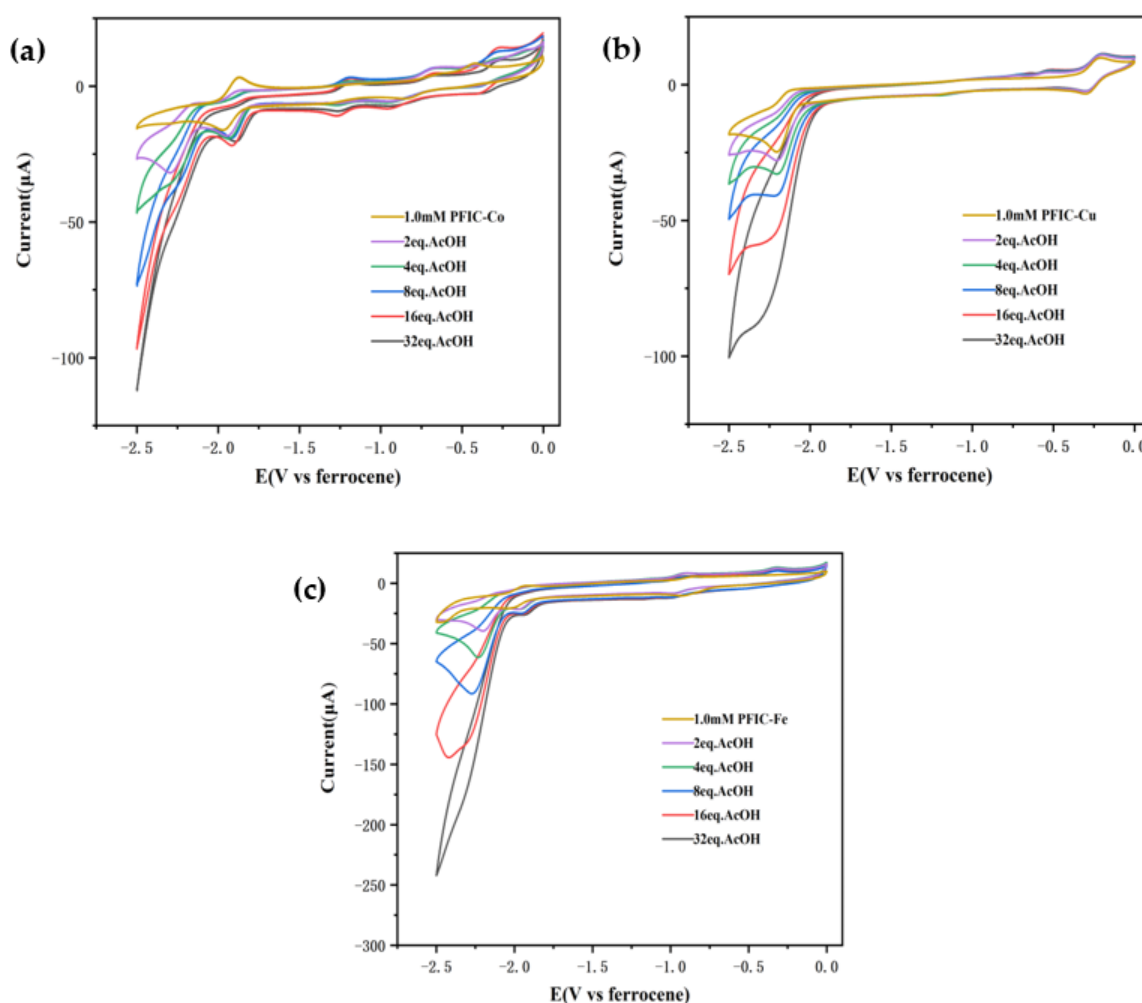


Figure 4. CV curves of compounds PFIC-Co (a), PFIC-Cu (b), and PFIC-Fe (c) (1.00 mM) with increasing AcOH content (0–32 equiv.).

Figure 5 shows the CVs of three metal corroles in catalyzing proton reduction when using TFA as the proton source. Compared to the AcOH proton source, there is a notably stronger catalytic peak current (-2.5 V) at the equivalent acid concentrations. With an increase in acid concentration, there are no changes observed in the first reduction peaks, while the second redox peak (M^{II}/M^I) progressively loses its reversibility. This also implies that $M(I)$ serves as the active center of catalytic proton reduction. It can be found that the catalytic current of PFIC-Fe is the largest, followed by PFIC-Cu and finally PFIC-Co. However, the maximum catalytic current alone is not a comprehensive measure of catalytic performance, and i_{cat}/i_p values can be introduced to measure catalytic performance (The i_{cat} is the peak catalytic current in presence of acid and the i_p is the peak current without an acid proton source. The i_{cat}/i_p ratio may reflect the catalytic activity of the catalysts).

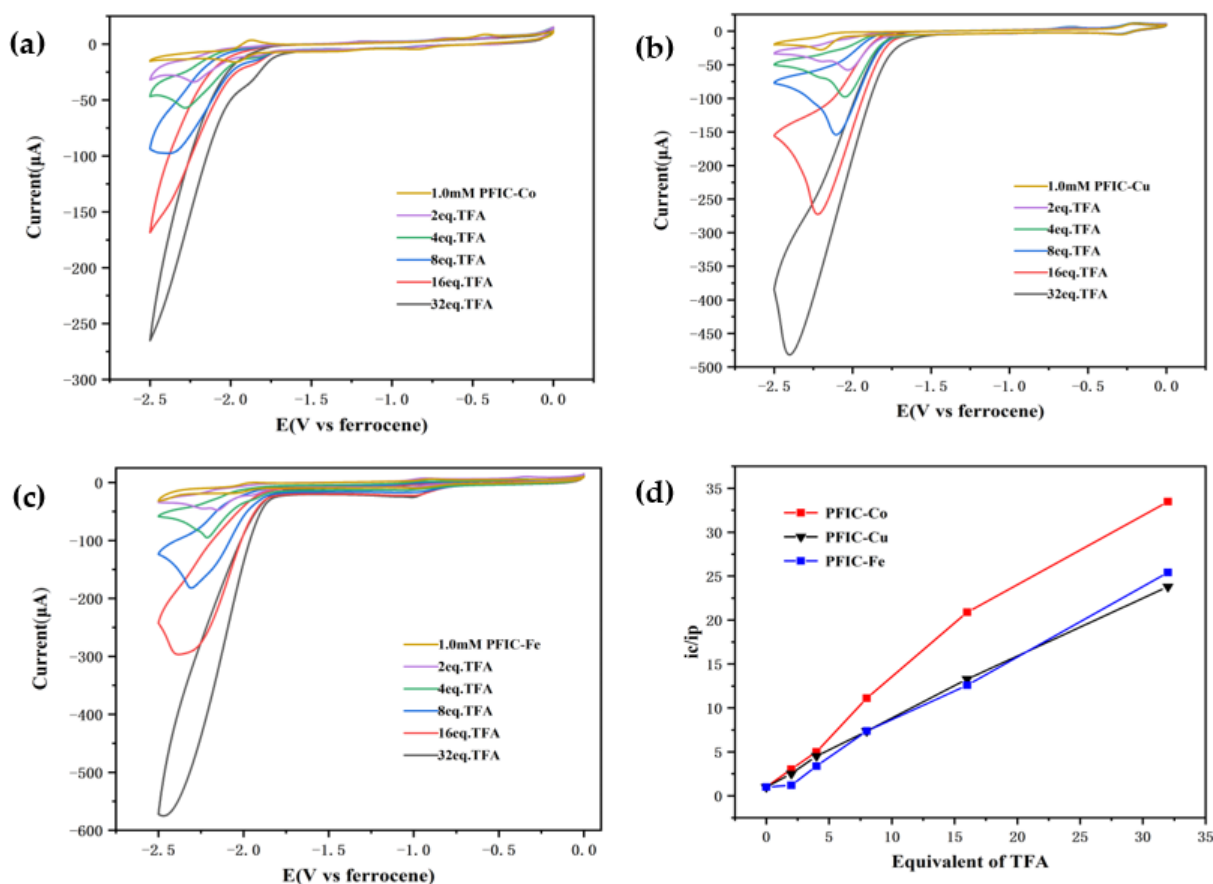


Figure 5. CVs of metal corroles (a–c), 1.0 mM) in different concentrations of TFA (0–32 eq.), and variation of i_{cat}/i_p values in DMF solutions containing different concentrations of TFA (d).

The i_{cat}/i_p is calculated and presented in Figure 5d; it can be seen that i_{cat} increases almost linearly with the increasing acid concentration. PFIC-Co has the largest value of i_{cat}/i_p , followed by PFIC-Fe and PFIC-Cu. Overpotential is a parameter that can be used to characterize the catalytic property. The overpotential (η) is defined by Equations (1) and (2) [44]; PFIC-Cu exhibits the lowest overpotential of 715 mV, followed by PFIC-Co (813 mV) and PFIC-Fe (898 mV). It can be observed that the catalyst catalyzes the HER differently at different acid concentrations. In the case of PFIC-Co, at low TFA concentration, a reduction peak appeared immediately after the second reduction peak (Co^{II}/Co^I), indicating that Co^I was further protonated to form $Co^{III}-H$. $Co^{III}-H$ was then additionally reduced and protonated to form Co^{II} . When the concentration of TFA increased to a certain value, the overpotential shifted to the positive direction and only one reduction peak appeared, indicating that, at this time, Co^{II} was the active center of proton reduction, and followed by

the direct formation of $\text{Co}^{\text{IV}}\text{-H}$ species via the protonation of Co^{II} [28], which could then be reduced to $\text{Co}^{\text{III}}\text{-H}$ and finally complete the hydrogen evolution via the Heyrovsky process.

$$\eta = E_{\text{HA}}^0 - E \quad (1)$$

$$E_{\text{HA}}^0 = E_{\text{H}^+}^0 - \left(\frac{2.303RT}{F} \right) \text{pK}_{\text{aHA}} \quad (2)$$

E_{HA}^0 is the standard electrode potential of H^+/H_2 , $E_{\text{H}^+}^0$ is the standard potential for the solvated proton–dihydrogen couple $E_{\text{H}^+}^0 = -0.62$ V in DMF, pK_{aHA} is the dissociation constant of acid in solvent, and $E_{\text{TFA}}^0 = -0.83$ V is calculated using Equation (2) [33].

From Figure 6, it can be seen that when using TsOH as the proton source, we can find that the catalytic process of the three catalysts is the same as TFA. This also indicates that the catalytic pathways of the catalysts are the same in these two proton sources. In comparison with using TFA as the proton source, the peak current and the $i_{\text{cat}}/i_{\text{p}}$ become larger for the same acid equivalent, which is due to the smaller pK_{a} value of TsOH.

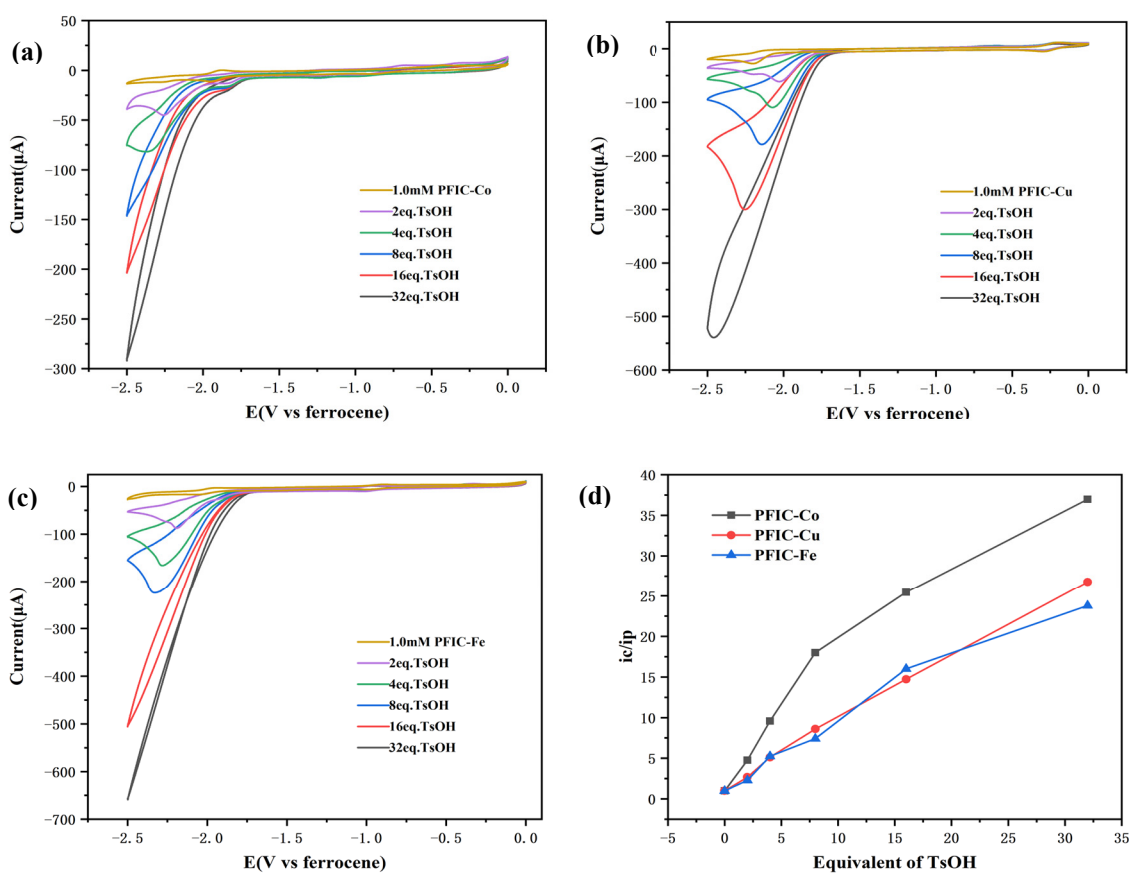


Figure 6. CVs of metal corroles ((a–c), 1.0 mM) in different concentrations of TsOH (0–32 eq.), and variation of $i_{\text{cat}}/i_{\text{p}}$ values in DMF solutions containing different concentrations of TsOH (d).

The CVs of bare GC electrode without catalysts and in the presence of catalysts under the same acid concentration is shown in Figure S16. The results clearly show that the sharp catalytic current increasing is indeed a result of the electrocatalysis of the molecular catalysts. The catalytic efficiency (C.E) and turnover frequency (TOF) were calculated by using the following Equations (3) and (5), respectively [45]:

$$\text{C.E} = \frac{i_{\text{cat}}/i_{\text{p}}}{C_{\text{HA}}/C_{\text{cat}}} \quad (3)$$

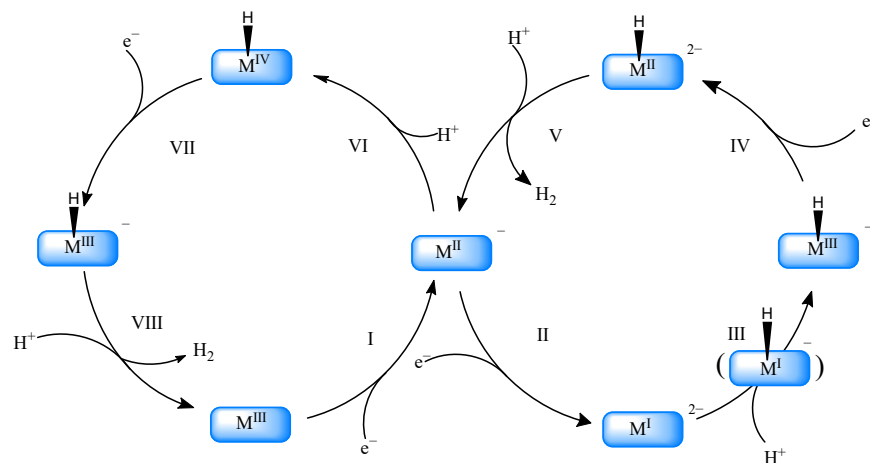
$$k_{\text{obs}} = k[\text{H}^+]^x \quad (4)$$

$$k_{\text{obs}} = 1.94v \left(\frac{i_{\text{cat}}}{i_p} \right)^2 \quad (5)$$

where i_{cat} is the peak current in acid and i_p is the peak current in non-acid. C_{HA} denotes the concentration of organic acid, C_{cat} refers to the concentration of the catalyst, v denotes the scanning rate, and k_{obs} represents the rate constant or turnover frequency (TOF) of the catalytic reaction. The TOFs of PFIC-Co, PFIC-Cu, and PFIC-Fe in TsOH (32 equiv.) are calculated to be 265 s^{-1} , 138 s^{-1} , and 109 s^{-1} , respectively. PFIC-Co has the largest TOF, indicating that it has the best catalytic activity. Other parameters of the three corroles at TFA and TsOH are summarized in Tables S2 and S3. To compare the HER activity of PFIC-Co, PFIC-Cu, and PFIC-Fe with other molecular electrocatalysts, the previously reported HER activities of some transition metal molecular electrocatalysts are summarized in Table S4 [28,31,46–50]. The table shows that the performance of these molecular catalysts is diverse. The overpotentials of these catalysts are generally around 800 mV, which is at the same level as that of our catalysts. The TOF, on the other hand, varies from high to low, with an average level of around 150 s^{-1} , where the highest can reach up to 1350 s^{-1} and the lowest is only 13 s^{-1} . It can be seen that these three metal-corrole catalysts show good catalytic performance. However, there is still a gap compared to the state-of-the-art molecular electrocatalysts.

2.4. Possible Catalytic Pathways for Hydrogen Production

Electrochemical hydrogen production pathways are generally inseparable from proton transfer and electron transfer processes, and most of the active center is metal [51]. Based on previous reports on electrocatalytic hydrogen production by metal corroles [47,48], the speculated catalytic pathways of the current system are depicted in Scheme 2. For PFIC-Co, when the proton source is the weak acid AcOH, $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$ gradually becomes irreversible with the increase in acid concentration, suggesting that Co^{I} is involved in the HER. The formed $\text{Co}^{\text{I}}\text{-H}$ may rapidly convert to $\text{Co}^{\text{III}}\text{-H}$, followed by subsequent reduction to form $\text{Co}^{\text{II}}\text{-H}$ at a more negative potential. The final protonation of $\text{Co}^{\text{II}}\text{-H}$ leads to hydrogen release and finishes the catalytic cycle, so the possible catalytic pathway is EECEC (E: electron transfer, C: proton transfer, I-II-III-IV-V, in Scheme 2). When using low concentrations of TFA or TsOH as a proton source, the possible catalytic pathway for hydrogen production is also EECEC. However, at high concentrations, the active center changes to Co^{II} , which is first protonated to $\text{Co}^{\text{IV}}\text{-H}$, and then $\text{Co}^{\text{IV}}\text{-H}$ is subsequently reduced to $\text{Co}^{\text{III}}\text{-H}$. Finally, $\text{Co}^{\text{III}}\text{-H}$ acquires a proton to produce H_2 , so the possible catalytic pathway is ECEC (I-VI-VII-VIII). For PFIC-Fe, the possible catalytic pathways are consistent with PFIC-Co. However, as for PFIC-Cu, at low acid concentrations in all acids, the active center is Cu^{I} , so the possible catalytic pathway is EECEC. Whereas at high concentrations, the active center is Cu^{II} and the possible catalytic pathway is ECEC.



Scheme 2. Suggested pathways for the Fe, Co, and Cu corrole catalysts in electrocatalytic HER.

2.5. Electrocatalytic Proton Reduction in Neutral Aqueous Media

The catalytic properties and catalytic pathways of metal corroles in organic systems have been explored above. From the point of view of practical application, further investigation of the catalytic process of catalysts for HER in aqueous solutions is necessary. We carried out electrochemical studies using three metal corroles as catalysts in a buffer solution of pH = 7 containing 0.25 M phosphate. In this system, Ag/AgCl was utilized as the reference electrode, while the remaining electrode systems corresponded to that of the organic phase system. Due to the low solubility of organic molecules in pure water, a co-solution of acetonitrile and water was used ($V_{\text{water}}/V_{\text{acetonitrile}} = 3/2$). As shown in Figure 7, a negligible current was produced in the absence of any catalyst, with the overpotential at approximately -1.14 V versus the reversible hydrogen electrode (RHE). After the addition of $5.0 \mu\text{M/L}$ of catalysts to the buffer solution (10 mL), it was found that the catalytic current increased significantly and the overpotential shifted positively to some extent. Among them, the catalytic current of PFIC-Co was the highest (0.91 mA) and the overpotential was positively shifted by 380 mV. The results suggest that the three catalysts exhibit effective catalytic activity in a neutral aqueous solution. In addition, Figure S17 demonstrates the effect of different catalyst concentrations on catalytic performance, and it was found that the catalytic current gradually increased with the increase in catalyst dosage. And we also conducted controlled potential electrolysis (CPE) experiments for the three catalysts at different overpotentials (738 mV–1138 mV), according to Equation (6) [52]. From Figure S18, it can be found that the TOF increases as the overpotential increases. When the overpotential reaches 1138 mV, the TOFs of PFIC-Co, PFIC-Cu, and PFIC-Fe are 405, 310, and 272 h^{-1} , respectively. Also, the Faraday efficiency of electrocatalytic hydrogen evolution could be calculated using Equations (7) and (8) [53,54]. It turned out that the Faraday efficiencies of PFIC-Fe, PFIC-Cu, and PFIC-Co were 89.8%, 91.3%, and 94.7%, respectively. The Faraday efficiencies of some transition metal complexes reported previously are summarized in Table S5 [55,56]. The table shows that most of the complexes have a Faraday efficiency of up to 85% or more, with the lowest being 74% and the highest being up to 98%. This shows that these three catalysts have good hydrogen production ability. In addition, the stability of the three catalysts was tested using chronoamperometry (Figure S19). These metal corroles exhibited good stability over long periods of electrolysis.

$$\text{TOF} = \frac{\Delta C}{F \times n_1 \times n_2 \times t} \quad (6)$$

$$\text{pH}_{\text{theoretical}} = 14 + \lg \frac{\sum I t}{F V} \quad (7)$$

$$\text{FE}(\%) = \text{AVG} \left(\frac{\text{pH}_{\text{practical}}}{\text{pH}_{\text{theoretical}}} \right) \quad (8)$$

where ΔC represents the increase in charge compared to the blank (without catalyst), with F representing the Faraday constant, n_1 being the number of electrons required for the production of 1 mol of H_2 ($n_1 = 2$ in this electrolysis), n_2 indicating the mol of catalyst used, and t representing the electrolysis time. $\text{pH}_{\text{theoretical}}$ stands for theoretical pH value, I is the current intensity, V is the electrolyte volume, and $\text{pH}_{\text{practical}}$ represents the practical pH value.

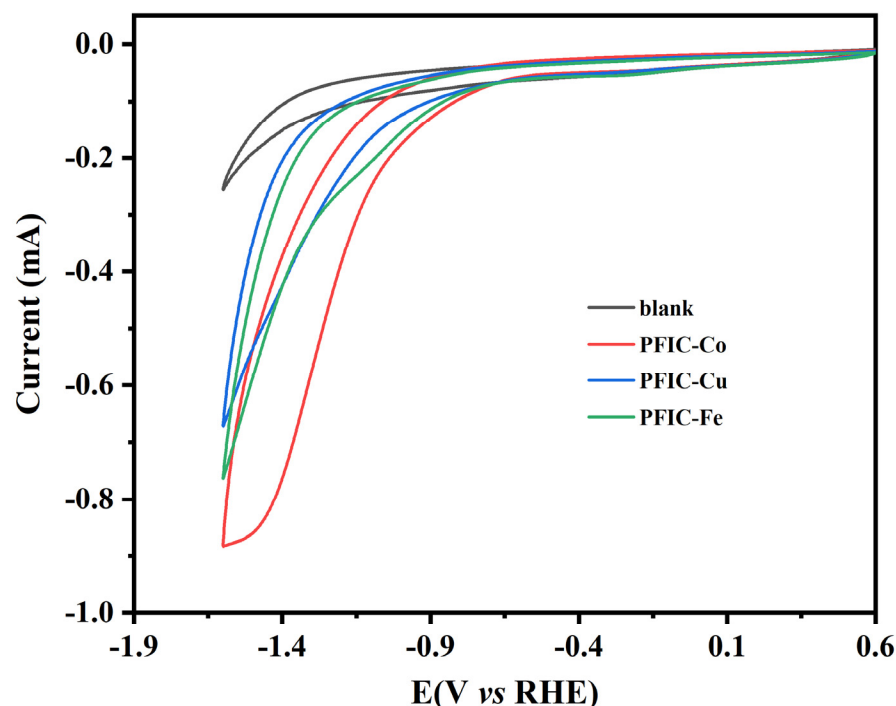


Figure 7. CVs of metal corroles (5.0 μ M) in aqueous neutral medium.

3. Materials and Methods

All reagents were purchased commercially, are of high purity, and can be used without further purification. UV-visible spectra were measured using a Hitachi U-3010. High-resolution mass spectrometry was performed with a Bruker maxis impact mass spectrometer that utilized an electrospray (ESI) source. The Bruker Advance III 400 MHz spectrometer was utilized to detect ^1H -NMR, ^{31}P NMR, and ^{19}F NMR spectra in CDCl_3 ($\delta = 7.26$ ppm) solvent at room temperature. Additionally, X-ray photoelectron spectroscopy (XPS) was recorded using an Axis Ultra-DLD spectrophotometer. Single Crystal X-ray Diffraction was measured using the Rigaku XtalAB PRO MM007DW. The CVs were measured with a CHI-660E electro-chemical analyzer in a DMF system and TBAP as a supporting electrolyte under N_2 protection for 30 min. The CPE experiments took place in a two-room electrolytic cell filled with a blend of acetonitrile and water (2:3 ratio) mixed with 0.1 M KCl as the electrolyte. Ag/AgCl electrodes served as the reference electrodes, with a GC plate (10×10 mm) used as the working electrode in one room, while a platinum wire was placed in another room.

Synthesis of 5,15-bis-(pentafluorophenyl)-10-[4-(1H-imidazole)phenyl]-corrole

Freebase corrole was synthesized using an improved method published in the literature. First, 160 mL of freshly steamed pyrrole and 2.8 g of pentafluorobenzaldehyde were mixed homogeneously, followed by the addition of 120 μL of trifluoroacetic acid (TFA) as a catalyst, and the reaction was carried out for 45 min at room temperature. Next, 240 μL of ethylenediamine was added to stop the reaction. The extra pyrrole was removed through distillation under reduced pressure at 140°C , resulting in an oily product. To obtain a purer product, the crude product was separated via column chromatography with eluents of CH_2Cl_2 and Hex ($V_{\text{DCM}}/V_{\text{Hex}} = 3:1$). The dipyrromethane was obtained at a yield of 83%. Next, dipyrromethane (1.25 g, 4 mmol) and 4-(1H-Imidazol-1-yl) benzaldehyde (344 mg, 2 mmol) were dissolved in 300 mL of DCM, followed by the addition of 460 μL of trifluoroacetic acid, and the reaction was carried out for 4 h at an ambient temperature protected from light. Immediately thereafter, 920 μL of triethylamine and DDQ (1.18 g, 4 mmol) was added. After 1 h of reaction, the crude product was obtained by removing the DCM using a rotary evaporator, followed by separating the resulting product through a

first-column chromatography (silica gel: 100 mesh, eluent: DCM) to eliminate the DDQ. Then, the product was once again isolated using column chromatography with silica gel (400 mesh) and an eluent of dichloromethane and ethyl acetate in a ratio of 3:1, and the reddish-orange portion of the product solution was collected and the solvent was removed by rotatable evaporation under vacuum to give purple product (200 mg, yield: 11%). ^1H NMR (500 MHz, Chloroform- d) δ 9.13 (s, 2H), 8.78–8.64 (m, 4H), 8.58 (s, 2H), 8.34 (d, J = 8.6 Hz, 2H), 7.95 (s, 1H), 7.82 (d, J = 7.8 Hz, 2H), 7.61 (s, 1H), 7.38 (s, 1H). ^{19}F NMR (471 MHz, Chloroform- d) δ −137.90 (4F), −152.58 (2F), −161.67 (4F). HRMS (ESI) $[\text{M} + \text{H}]^+$, calculated for $\text{C}_{40}\text{H}_{19}\text{F}_{10}\text{N}_6$: 773.1506, found: 773.1520.

Synthesis of cobalt 5,15-bis-(pentafluorophenyl)-10-[4-(1H-imidazole)phenyl]-corrole

Freebase corrole (50 mg, 65 μmol) and NaOAc (60 mg, 732 μmol) were dissolved in 30 mL of ethanol and stirred for 5 min at room temperature, followed by the addition of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (50 mg, 200 μmol) and triphenylphosphine (100 mg, 382 μmol), and the reaction was continued for two hours. Then, 30 mL of dichloromethane and 30 mL of water were added to extract, and the organic phase was collected and dried using sodium sulfate. Column chromatography using CH_2Cl_2 as the eluent was used to further purify the raw material obtained. The resulting product was recrystallized using CH_2Cl_2 and Hex for further purification. The clean substance (red-brown powder) was obtained by recrystallizing, resulting in a 75% yield of 53.13 mg. ^1H NMR (500 MHz, Chloroform- d) δ 8.69 (d, J = 39.8 Hz, 2H), 8.22 (s, 2H), 8.00 (t, J = 35.0 Hz, 4H), 7.72–7.31 (m, 7H), 7.04–6.88 (m, 3H), 6.57 (d, J = 35.2 Hz, 6H), 4.66–4.36 (m, 6H). ^{19}F NMR (471 MHz, Chloroform- d) δ −136.71–−138.45 (4F), −154.44 (2F), −161.88–−164.84 (4F). HRMS (ESI) $[\text{M} + \text{H}]^+$, calculated for $\text{C}_{58}\text{H}_{31}\text{CoF}_{10}\text{N}_6\text{P}$: 1091.1515, found: 1091.1551.

Synthesis of copper 5,15-bis-(pentafluorophenyl)-10-[4-(1H-imidazole)phenyl]-corrole

Freebase corrole (56 mg, 72 μmol) was dissolved in 50 mL of ethanol, and NaOAc (60 mg, 732 μmol) was added, stirred at room temperature for 10 min and then $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (70 mg, 350 μmol) was added, followed by the reaction for 1.5 h, and the liquid was dried completely to acquire the unfinished product, which was later divided using column chromatography, and CH_2Cl_2 was used as the eluent to obtain the purer product. A yellow-black powder (45 mg, yield: 75.1%) was obtained. ^1H NMR (500 MHz, Chloroform- d) δ 8.05–7.95 (m, 2H), 7.84 (d, J = 40.3 Hz, 4H), 7.47–7.40 (m, 2H), 7.35 (d, J = 2.7 Hz, 1H), 7.23 (s, 2H), 7.17–7.05 (m, 3H), 6.99 (s, 1H). HRMS (ESI) $[\text{M} + \text{H}]^+$, calculated for $\text{C}_{40}\text{H}_{16}\text{CuF}_{10}\text{N}_6$: 833.0567, found: 833.0570.

Synthesis of iron 5,15-bis-(pentafluorophenyl)-10-[4-(1H-imidazole)phenyl]-corrole

The freebase corrole weighing 50 mg (65 μmol) and ferrous chloride tetrahydrate weighing 2.389 g (13 mmol) were combined with 30 mL DMF and reacted for 6 h at 140 $^\circ\text{C}$ in a nitrogen-protected atmosphere. Waiting until the reaction solution had cooled down to room temperature, we extracted it with CH_2Cl_2 (50 mL) and H_2O (50 mL). Then, we collected the organic phase and washed it with saturated brine. Finally, we dried it with Na_2SO_4 . The product was then purified by chromatography in a similar procedure to the preparation of cobalt corrole with CH_2Cl_2 as the eluent. Finally, a dark brown solid was obtained (52 mg, yield: 82%). HRMS (ESI) $[\text{M} + \text{H}]^+$, calculated for $\text{C}_{40}\text{H}_{16}\text{FeF}_{10}\text{N}_6$: 826.0621, found: 826.0629.

4. Conclusions

In summary, the new 5,15-bis-(pentafluorophenyl)-10-[4-(1H-imidazole)phenyl]-corrole containing an imidazole moiety and its cobalt, copper and iron complexes had been synthesized and well characterized. Their reactivity for electrocatalytic proton reduction in different media was also investigated. The three prepared metal corroles showed good catalytic performance in both aqueous and organic phase media. The Co corrole exhibited the best performance with a TOF of up to 265 s^{-1} in DMF (TsOH proton source). We also explored the catalytic proton reduction in organic solvents with different acids as the proton

source for each catalyst. It turned out that the electrocatalytic HER by these metal corroles may proceed via two competing ECEC and/or EECEC pathways depending on the acid proton sources used.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal14010005/s1>, Figure S1: UV-vis spectrum of PFIC and PFIC-Co, PFIC-Cu and PFIC-Fe in CH₂Cl₂; Figure S2: ¹H NMR spectrum of 5,15-bis-(pentafluorophenyl)-10-[4-(1H-imidazole)phenyl]-corrole; Figure S3: ¹⁹F NMR spectrum of 5,15-bis-(pentafluorophenyl)-10-[4-(1H-imidazole)phenyl]-corrole; Figure S4: ¹H NMR spectrum of cobalt 5,15-bis-(pentafluorophenyl)-10-[4-(1H-imidazole)phenyl]-corrole; Figure S5: ¹⁹F NMR spectrum of cobalt 5,15-bis-(pentafluorophenyl)-10-[4-(1H-imidazole)phenyl]-corrole; Figure S6: ³¹P NMR spectrum of cobalt 5,15-bis-(pentafluorophenyl)-10-[4-(1H-imidazole)phenyl]-corrole; Figure S7: ¹H NMR spectrum of copper 5,15-bis-(pentafluorophenyl)-10-[4-(1H-imidazole)phenyl]-corrole; Figure S8: ¹⁹F NMR spectrum of copper 5,15-bis-(pentafluorophenyl)-10-[4-(1H-imidazole)phenyl]-corrole; Figure S9: High resolution mass spectrum of 5,15-bis-(pentafluorophenyl)-10-[4-(1H-imidazole)phenyl]-corrole; Figure S10: High resolution mass spectrum of cobalt 5,15-bis-(pentafluorophenyl)-10-[4-(1H-imidazole)phenyl]-corrole; Figure S11: High resolution mass spectrum of copper 5,15-bis-(pentafluorophenyl)-10-[4-(1H-imidazole)phenyl]-corrole; Figure S12: High resolution mass spectrum of iron 5,15-bis-(pentafluorophenyl)-10-[4-(1H-imidazole)phenyl]-corrole; Figure S13: XPS survey spectrum of PFIC-Cu (a); XPS spectra of Cu 2p (b) and N 1s (c) and F 1s (d) of PFIC-Cu; Figure S14: XPS survey spectrum of PFIC-Fe (a); XPS spectra of Fe 2p (b) and N 1s (c) and F 1s (d) of PFIC-Fe; Figure S15: Plots of metal corrole complexes Co, Cu, and Fe (a–c, 1.0 mM) for sweep rate (v) variations of 100–400 mV/s and peak currents (i_p) versus square root of the sweep rate (v_{1/2}) for the reduction and first oxidation peaks (d–f); Figure S16: Comparison of CV test between bare GC and PFIC-Co, PFIC-Cu and PFIC-Fe at high acid concentration; Figure S17: CV plots (0.00–5.00 μM) of different concentrations of metallacorrole complexes (PFIC-Co(a), PFIC-Cu(b), PFIC-Fe(c)) in a mixed system of acetonitrile and water (pH = 7); Figure S18: (a) Charge increase for PFIC-Co (5.00 μM), (b) Charge increase for PFIC-Cu (5.00 μM), (c) Charge increase for PFIC-Fe (5.00 μM) at different overpotentials; Figure S19: Catalytic current versus time obtained from 4 h CPE with 5.00 μM (a) PFIC-Co, (b) PFIC-Cu (c) PFIC-Fe in buffer solution at −1.04 V vs. RHE; Table S1: Crystal data and structure refinement for PFEC-Co; Table S2: Catalytic performance parameters of three metal complexes in TFA system; Table S3: Catalytic performance parameters of three metal complexes in TsOH system; Table S4: HER activity for transition metal corroles in organic solvent by using organic acids as proton; Table S5: Faraday efficiency of transition metal complexes in nature homogeneous aqueous solution. [28,31,52–58].

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