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# Competition between electrocatalytic CO<sub>2</sub> reduction and H<sup>+</sup> reduction by Cu(II), Co(II) complexes containing redox-active ligand



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ARTICLE INFO	A B S T R A C T		
A R T I C L E I N F O Keywords: Transition metal complex Redox-active ligand Electrocatalysis	A benzimidazole derivative ligand ( $L^1$ ) and its corresponding transition metal complexes $ML^1Cl_2$ ( $M = Cu$ (1), Co (2)) have been synthesized and characterized by a combination of X-ray crystallography, PXRD, electrochemistry, spectral (IR, UV–vis) techniques and DFT calculations. The electrocatalytic activity of the two complexes for CO <sub>2</sub> reduction was investigated without and with proton source. Bulk electrolysis of the two complexes demonstrates that there is a competition between CO <sub>2</sub> and H <sup>+</sup> reduction during the electrocatalytic process, leading to a low Faradaic efficiency for CO evolution but a high FE for H <sub>2</sub> evolution. The reason of the serious competition reaction of hydrogen generation in the process of catalytic CO <sub>2</sub> reduction have been investigated. Studies show that the catalytic effect could be due to a synergy effect between the redox active ligand $L^1$ and metal ions (Cu (II) (1) and Co (II) (2)), while the formation of hydride complex [M(I)L <sup>1o</sup> -H <sup>o</sup> -] <sup>1-</sup> might be the crux in the selectivity between CO <sub>2</sub> reduction and H <sub>2</sub> evolution, and the process of electrocatalytic reduction of CO <sub>2</sub> could have promoted H <sup>+</sup> reduction.		

# 1. Introduction

The release of carbon dioxide (CO<sub>2</sub>) by burning unprecedented amount of fossil fuels to meet the growing energy demand has caused an ever-increasing emission of anthropogenic CO<sub>2</sub> into the atmosphere, [1–3] which further leads to series of negative consequences such as global climate change, and eventually disorganizing the earth's ecosystem.[4,5] Therefore, searching for new, green, and sustainable energy sources such as H<sub>2</sub> to replace traditional fossil fuels is an urgent issue of worldwide concern. On the other side, CO2 is an ideal C1 feedstock, which can be converted into energy-rich compounds[6] such as carbon monoxide, formic acid, methanol, etc. However, due to the thermodynamic and kinetic reasons, there are still many obstacles for the conversion of CO<sub>2</sub> and H<sub>2</sub> evolutions.[7–9] Accordingly, the exploration of economical and practical catalysts like non-noble transition metal complexes characteristic with high catalytic efficiency, selectivity and stability, has attracted large amounts of researcher's interests.[10] Electrochemical and photochemical catalysis are promising ways for CO2 reduction and H2 evolution among many strategies.[11,12]However, compared with photocatalytic method, electrocatalysis is a great indirect way to utilize the clean energy such as solar energy, wind energy, and nuclear energy, which can greatly broaden the use of renewable energy.[13] In recent years, a number of non-noble transition metal complexes with excellent electrocatalytic performance have been reported as  $CO_2$  reduction or  $H_2$  evolution catalysts.[14–19]

In the process of electrocatalytic CO<sub>2</sub> reduction reaction (eCO<sub>2</sub>RR), the parallel competing reaction of H<sub>2</sub> evolution is usually a critical issue. [20] Therefore, several efforts have devoted to figure out the competition between CO<sub>2</sub> reduction and H<sup>+</sup> reduction which is very significant for promoting electrocatalytic CO<sub>2</sub> reduction.[21–23] Peters reported a Co<sup>III</sup> electrocatalyst coordinated by a tetradentate N4 ligand which is possibly the key for the preferential reduction of CO<sub>2</sub> over H<sub>2</sub> evolution. [24,25] Trovitch and Jones et al. illustrated that during the electrocatalytic CO<sub>2</sub> reduction by a manganese complex [(PDI)Mn(CO)]<sup>+</sup> (PDI = 2,6-bis(4- methoxyphenylmethylimine)pyridine), H<sub>2</sub> evolution can be enhanced by CO<sub>2</sub>, which could produce proton source in the formation of carbonic acid, [26] while, two [Ni(pdi)]<sup>2+</sup> catalysts studied by Rochford and Groysman may have the similar behaviors with the Mn(I) complex.[17]

It is well known that redox active and electron-rich benzimidazole

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Received 17 April 2021; Received in revised form 7 July 2021; Accepted 30 July 2021 Available online 3 August 2021 0020-1693/© 2021 Elsevier B.V. All rights reserved. derivatives has excellent biological properties, [27-30] and Tamaki et al found that benzimidazole derivative (1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole, BIH) was a very suitable electron donor in photocatalytic reduction of carbon dioxide.[31]Additionally, benzimidazole derivatives transition metal complexes have also been extensively studied due to their excellent properties.[32,33] Such as benzimidazole-based imine-linked copper complexes have a selectivity in the detection of cyproheptadine and thiabendazole drug molecules.<sup>[15a]</sup> Benzimidazole derivatives have displayed superior antimicrobial activity[34] and acted as anti-inflammatory agents,[35] etc. On the one hand, Benzimidazoles have been previously identified as promising hydride donors[36-39] due to their characteristic conformation and an anomeric effect. [40] On the other hand, it can be widely used as N-N chelating ligands, analogous in many ways to bipyridine. [41] However, very few of them have been investigated as CO<sub>2</sub> reduction catalysts. [42,43]

For the reasons above, in this work, we have successfully synthesized and crystallized a new benzimidazole derivative ligand 2-(6-methoxypyridin-2-yl)-1-((6-methoxypyridin-2-yl)methyl)-6-nitro-1*H*-benzo[*d*] imidazole ( $L^1$ ) and two transition metal complexes ML<sup>1</sup>Cl<sub>2</sub> (M = Cu (1), Co (2)) containing ligand  $L^1$  with distorted tetrahedral geometry, and systematically explored their electrochemical behaviors. Both of the two complexes display electrocatalytic reactivity for CO<sub>2</sub> reduction along with H<sub>2</sub> evolution. Coupled with DFT calculations the probable mechanism of electrocatalytic CO<sub>2</sub> reduction competing with H<sub>2</sub> evolution for the two compounds were also interpreted.

#### 2. Results and discussion

#### 2.1. Synthesis

The synthesis routes of the ligand  $L^1$  and the two complexes 1 and 2 are shown in Scheme 1. Herein, the novel benzimidazole derivative ligand was prepared by 4-nitro-o-phenylenediamine and 6-methoxypyridine-2-carboxaldehyde in a molar ratio of 1: 2 in good yield (44%). As the proposed mechanism for the synthesis of ligand  $L^1$  depicted in Scheme S1, the overall reaction takes place in two steps: at first, two amino groups on 4-nitro-o-phenylendiamine react with two aldehyde groups on two 6-methoxypyridine-2-carboxaldehydes proceeding



Scheme 1. Synthesis routes of ligand L<sup>1</sup> and complexes 1 and 2.

through a condensation reaction to form one bis-Schiff base, and then intramolecular redox reaction occurs, leading to the formation of benzimidazole geometry which is a thermodynamically stable structure. The two novel complexes  $CuL^1Cl_2$  (1) and  $CoL^1Cl_2$  (2) were both prepared with benzimidazole derivative  $L^1$  and transition metal chlorides,  $CuCl_2.2H_2O$  and  $CoCl_2$ , respectively, but under different reaction conditions.

In the synthesis of complex 1, a mixture of dichloromethane and methanol as the reaction solvent and room temperature are required. But for complex 2 is isolated in acetonitrile solution and under high temperature. The purity of the as-synthesized  $L^1$  is verified by its crystal structure (Fig. 1) and NMR spectrum (Figure S1), while compounds 1 and 2 were verified by comparing their theoretical and experimental powder X-ray diffraction (PXRD) patterns (Figure S2). For the two compounds, the peak positions of the diffraction in both patterns are all in good agreement, which confirms that the crystalline phases of all the as-prepared samples are all uniform.



**Fig. 1.** Crystal structures of ligand  $L^1$  (a), complexes 1 (b) and 2 (c), all at 50% probability ellipsoids. Color code: blue, N; red, O; gray, C; green, Cl; cyan, Cu; magenta, Co. Hydrogen atoms have been omitted for clarity of the scan rate. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

# 2.2. Crystal structure determinations of the ligand $L^1$ and complexes 1 and 2

A summary of the main crystallographic information of  $L^1$ , 1 and 2 is given in Table S1. The selected bond lengths of 1 and 2 are listed in Table 1. Single crystal structures of  $L^1$ , 1 and 2 were shown in Fig. 1.

Crystallographic structural analysis reveals that the ligand  $L^1$  crystallizes in the triclinic crystal system and space group *P*-1(2). In the large conjugated structure, the pyridine ring containing N1 is perpendicular to the plane formed by benzimidazole and the other pyridine ring containing N2, which is very conducive for the transfer of electrons within the molecule.

Crystallographic structural analysis reveals that complexes **1** and **2** crystallize in the triclinic *P*-1(2) and monoclinic *P*-1–21/n-(14) space group, respectively. The center transition metal ions (Cu (II) and Co (II)) in **1** and **2** are both four coordinated with two N atoms (N1 and N2) from the ligand  $L^1$  and two chloride ions (Cl1 and Cl2) to form distorted tetrahedral geometry. The bond lengths Cu–N, Cu–Cl, and Co–N, Co–Cl are comparable to those of the other reported tetrahedral Cu (II) [44,45] and Co (II) complexes. [46,47]

#### 2.3. IR and UV-Vis spectra

As shown in Figure S3, the FT-IR spectra of complexes (1 and 2) and the free ligand  $L^1$  were investigated. It can be found that the IR spectra of complexes 1 and 2 are very close to ligand  $L^1$ , especially in the range of 1200–700 cm<sup>-1</sup>. However, the strong band at 1471 cm<sup>-1</sup> for ligand  $L^1$  is assigned to the stretching vibration corresponding to v(C=N) in benzimidazole,[48] which increase to 1489 cm<sup>-1</sup> in complex 1 and 1486 cm<sup>-1</sup> in complex 2. The v(C=N) band undergoes a blueshift in the spectra of the two complexes as compared to free ligand  $L^1$ , which can be attributed to the coordination of the benzimidazole nitrogen to the metal center.[49,50] The most important bands which appeared in the 429 cm<sup>-1</sup> for complex 1 and 431 cm<sup>-1</sup> for complex 2 belong to the stretching vibration peak of v(M-N) coordination bond,[51] confirming that the complexes formation and representing further evidence for the coordination of the ligands through nitrogen atoms.

The UV–vis spectra of the complexes (1 and 2) and the free ligand  $L^1$  were collected at room temperature in DMF. As depicted in Figure S4, Complex 1 is light yellow and complex 2 is light blue in color and both of them have two bands: one in the UV region (1: 322 nm, and 2: 320 nm) and one in the visible region (1: 402 nm, and 2: 403 nm), while ligand  $L^1$  is colorless and only exhibits two major peaks in the UV region at 313 nm ( $\pi$ - $\pi^*$ ) and 343 nm (n- $\pi^*$ ). Upon the coordination with metal ions (Cu (II) (1) and Co (II) (2)), both the absorption intensities at 313 nm and 343 nm are enhanced, which indicates the formation of the L-Cu<sup>2+</sup> or L-Co<sup>2+</sup> complexes[52].

In order to explore the formation of complexes in DMF solutions, we have synthesized complexes  $ML_2$  (M = Cu (3), Co (4)) and analyzed the complexes by UV–vis. The ligand-to-metal molar ratios used in the experiments were 2:1 for ligand with M = Cu(II) (3) or Cu(II) (4). Compared with complexes 1 and 2, the UV–vis spectra of complexes 3 and 4 have one band redshift (3: 338 nm; 4: 353 nm) and one band blueshift(3: 368 nm; 4: 387 nm), indicating that complexes 1 and 2 bound by only one imidazole ligand in DMF solution.

Table 1The selected bond length (Å) for complexes 1 and 2.

1		2		
Cu (1)-N (1)	2.051(2)	Co (1)-N (1)	2.079(3)	
Cu (1)-N (2)	1.968(2)	Co (1)-N (2)	2.015(4)	
Cu (1)-Cl (1)	2.209(8)	Co (1)-Cl (1)	2.230(13)	
Cu (1)-Cl (2)	2.204(8)	Co (1)-Cl (2)	2.211(14)	

# 2.4. Electrochemistry under argon saturation

The cyclic voltammograms (CVs) for the ligand  $L^1$  obtained in 0.1 M <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub>/DMF solution under argon (Ar) at different scan rates are presented in Fig. 2a. Overall, the voltammograms consist of one irreversible reduction peak at the potential of -0.96 V and one quasi-reversible reduction peak at the potential of -1.42 V versus Fc<sup>+/0</sup>. (all the potentials are versus Ferrocene due to the DMF solvent), which could be assigned to the continuously reduction of  $L^1$  affording two radical anions  $[L^{1\bullet}]^-$  and  $[L^{1\bullet\bullet}]^{2-}$ . Thus, it can be postulated that the large  $\pi$ -system of benzimidazole unit of  $L^1$  enables multiple-electron transfer as other  $\pi$ -acidic ligand [53–56] bipyridine, terpyridine, diamine, etc. Fig. 3 and Fig. 4 show the cyclic voltammogram (CV) plots of complexes 1 and 2 recorded in DMF solution under Ar. These two complexes exhibit similar electrochemical behavior based on the data summarized in Table 2.

In general, the two complexes display both ligand-based and metalbased redox processes. The first two reduction processes occur at about -0.97 V, -1.55 V, and -0.98 V, -1.72 V for complexes 1 and 2, respectively, which could be due to the reduction of the benzimidazole ligand  $L^1$  by comparing the reduction potentials of the ligand itself. The results are also consistent with the DFT analysis, that the LUMOS (lowest unoccupied molecular orbital) for complexes 1 and 2 are primarily based on ligand  $L^1$  (Fig. 5, the whole frontier molecular orbital surfaces of 1 and 2 are illustrated in Figure S5, Tables S2 and S3).

While the third and fourth reductions at about -1.97 V and -2.06 V for complex 1 should be Cu localized, which could be assigned to successive reductions of Cu<sup>II</sup> to Cu<sup>I</sup> and Cu<sup>I</sup> to Cu<sup>0</sup>, respectively. Whereas, the third reduction potential at about -2.16 V for complex 2 could be



**Fig. 2.** (a) Cyclic voltammetry of 2.5 mM ligand  $L^1$  under 1 atm Ar at scan rate range from 50 to 400 mV s<sup>-1</sup>; (b) The linear plots of peak cathodic currents versus the square root.



**Fig. 3.** (a) Cyclic voltammetry of 2.5 mM complex 1 under 1 atm Ar at scan rate range from 50 to 400 mV s<sup>-1</sup>; (b) The linear plots of peak cathodic currents versus the square root of the scan rate.

ascribed to  $\text{Co}^{II}/\text{Co}^{I}$  couple. These ligand and metal centered reduction assignments are well in agreement with other transition metal complexes with redox-active ligands. [57–59] As Fig. 2b, 3b and 4b indicated, the fitting curves of cathodic peak currents at varies scan rates for  $L^1$ , 1 and 2 all increase linearly versus the square root of the scan rate, illustrating that the currents are controlled by diffusion of the compounds to the surface of the working electrode.

# 2.5. Study on electrocatalytic reduction in the presence of $CO_2$

The electrocatalytic activity of complexes 1 and 2 was investigated for the reduction of  $CO_2$  under Ar and saturated  $CO_2$  at different scan rate. To intuitive display the better electrochemical performance under  $CO_2$  than under Ar atmosphere, only the CVs with scan rate of 100 mV s<sup>-1</sup> been displayed.

Fig. 6a and 6b illustrate a comparison of the CVs of **1** and **2** in the presence and absence of CO<sub>2</sub>, respectively, showing that upon bubbling CO<sub>2</sub>, both compounds **1** and **2** display two reduction peaks with close potential values at -1.0 V, -2.06 V vs. Fc<sup>+/0</sup>, and -1.03 V, -2.17 V vs. Fc<sup>+/0</sup> (the scaning rate is 100 mV/s), respectively, which suggests that the two complexes exhibit similar process for the electrochemical reduction of CO<sub>2</sub>. Notably, the cathodic peak currents were observed largely enhanced at the two electrons transfer redox potentials for both of the two complexes. As shown in Figure S6, compared with L<sup>1</sup>, CuCl<sub>2</sub>, CoCl<sub>3</sub> with and without HAc in the DMF solution, complexes **1** and **2** with the addition of HAc showed largely enhanced currents under the same conditions, suggesting that it's the complex that plays a catalytic role in the electrocatalytical process. Nonetheless, by employing control



**Fig. 4.** (a) Cyclic voltammetry of 2.5 mM complex **2** under 1 atm Ar at scan rate range from 100 to 600 mV s<sup>-1</sup>; (b) The linear plots of peak cathodic currents versus the square root of the scan rate.

#### Table 2

The reduction potentials of complexes **1** and **2** and ligand  $L^1$  under 1 atm Ar at 100 mV s<sup>-1</sup> in a 0.1 M <sup>*n*</sup>Bu<sub>4</sub>NPF<sub>6</sub> DMF supporting electrolyte.

	1st	2nd	3rd	4th
Complex 1 Complex 2	-0.97 -0.98	$-1.55 \\ -1.72$	$-1.97 \\ -2.17$	-2.11 -
Ligand L <sup>1</sup>	-0.96	-1.42	-	-



Fig. 5. LUMO of complexes 1 (a) and 2 (b) (iso value = 0.02).

potential electrolysis (CPE) experiments, at the two potentials of the two complexes, namely E = -1.0 V, -2.06 V for complex **1**, and E = -1.03 V, E = -2.17 V for complex **2**, only at the latter potentials of the two complexes, CO and H<sub>2</sub> were detected by GC analysis (Due to the presence of residual water in DMF, the residual water in unopened DMF solution determined by Karl-fisher titration is 3.32%. <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> and on



**Fig. 6.** Cyclic voltammetry of complexes **1** (a) and **2** (b) in the presence (red) and absence (blue) of  $CO_2$  recorded at 100 mV s<sup>-1</sup> at glassy carbon in a 0.1 M <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> DMF supporting electrolyte. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the glass of the cell which can hardly removed, H<sub>2</sub> also evolved at the cathode along with CO formation[6].), which suggest that only the latter reduction wave of the two complexes is correspond to the electrocatalytic reduction of CO2 or the evolution of H2. In addition, the cyclic voltammetry experiments for complexes 1 and 2 under saturated carbon dioxide atmosphere in DMF solution were also recorded at different scan rates shown in Figure S7. It can be found that all the CV plots at different scan rates repeated well with no evolution of new oxidative or the reductive waves, which assures the reproducibility and stability of complexes 1 and 2 for electrocatalytic CO<sub>2</sub> reduction. Meanwhile, the relationship between concentrations of the complex and the catalytic current peaks were also investigated (Figure S8), which reveals that the catalytic currents at the cathode potentials -2.06 V (for complex 1) and -2.17 V (for complex 2) both have linear dependence relationship with catalyst concentrations, proving that the rate determining step in the catalysis is the first order.

To further explore the electrocatalytic ability of  $CO_2$  reduction for the two complexes, a series of CPE experiments were recorded for 3 h in DMF solution with 0.1 M <sup>*n*</sup>Bu<sub>4</sub>NPF<sub>6</sub> under saturated  $CO_2$  using a fluorine doped tin oxide (FTO) glass with a surface-area of 1.0 cm<sup>2</sup> as the working electrode in a gas-tight cell, meanwhile, the gaseous products in the headspace of the electrochemical cell was analyzed by gas chromatography (GC).

As depicted in Fig. 7 by the black line, the current densities are very small at the potentials of -2.06 V without complexes 1 or 2 during the electrolysis, and there was barely any CO or H<sub>2</sub> detected, which reveals



**Fig. 7.** CPE with 2.5 mM complexes **1** (blue line) and **2** (violet line), blank experiment without **1** or **2** (black line), and rinse tests for complexes **1** (red line) and **2** (olive line) on an FTO working electrode  $(1.0 \text{ cm}^2)$ . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

that no catalysis occurred. In addition, rinse tests were performed on the FTO glass electrode after electrocatalysis for complexes 1 and 2, which reveals that the current densities are similar with results of the blank test before the catalysis, indicating that the two complexes are both great homogeneous catalysts (Fig. 7, the red and olive lines). X-ray photoelectron spectroscopy (XPS) confirmed that there have been no metaloxide formed after the whole electrolysis (Figure S9, ESI), which revealed that the two complexes are both quite stable during the 3 h electrolysis. The almost linear curves of the CPE indicate that catalysts 1 and 2 remain stable in solution during the whole catalytic process (Fig. 7). By comparing the scanning electron microscopy (SEM) of FTO electrodes before and after CPE of complexes 1 and 2, it is found that there is no film electrodeposited on the glass electrode (Figure S10, ESI). Besides, the in situ UV-vis spectroelectrochemistry was performed during the controlled potential electrolysis (Figure S11, ESI), and no insignificant difference was observed in the electron spectrogram, which further confirms that complexes 1 and 2 have high catalytic stability. In addition, the NMR studies of the liquid phase after 3 h CPE in DMF shows no evidence of other CO<sub>2</sub> reduction products such as formic acid in the liquid phase.

After analyzing by gas GC, the Faradaic efficiency (FE) of CO and  $H_2$  evolution for complex 1 at applied potentials -2.06 V, and for complex 2 at -2.17 V is calculated according to eq (2):

$$FE(\%) = 2nF/Q \tag{2}$$

where n is the number of moles of CO or  $H_2$ , F is the Faradaic constant, Q is the total charge passed. As depict in Fig. 8, at the first 30 min of CPE, the Faradaic efficiency of CO (black) and  $H_2$  (red) formation for complex 1 is 5%, and 38%, respectively. The FE for CO keeps stable during the whole electrolysis, but the FE for  $H_2$  increases to 45% at the point of 150 min, and then decreases to 42% at the end of the electrolysis. For complex 2, the Faradaic efficiency of CO (blue) formation is only 0.5%, but the FE for  $H_2$  (magenta) could reach to 97%, which suggests that complex 2 is a valuable catalyst for  $H_2$  evolution.

The electrochemical CO<sub>2</sub> reduction by complexes **1** and **2** is possible owing to the reductive disproportionation of CO<sub>2</sub> to produce CO and  $CO_3^{2^-}$  (2CO<sub>2</sub> + 2e<sup>-</sup> = CO + CO<sub>3</sub><sup>2^-</sup>(a)), which is usually caused in the absence of proton donor, or due to the assists of the proton to generate CO and H<sub>2</sub>O (CO<sub>2</sub> + 2H<sup>+</sup> + 2e<sup>-</sup> = CO + H<sub>2</sub>O (b)). In order to figure out the electrochemical mechanism, CO<sub>2</sub> reduction activity of complexes **1** and **2** was also investigated in the presence of a proton donor CH<sub>3</sub>COOH (HAc) in the DMF solution with 0.1 M <sup>*n*</sup>Bu<sub>4</sub>NPF<sub>6</sub>.

As shown in Fig. 9, upon addition of 3.5 mol/L HAc in the solution under saturated CO<sub>2</sub> atmosphere, the intensities of the catalytic currents



Fig. 8. The Faradaic efficiency of CO and  $H_2$  formation for complexes 1 and 2 in the presence and absence of a proton donor HAc (3.5 mol/L) in the DMF solution with 0.1 M  $^nBu_4NPF_6$ .



**Fig. 9.** CVs of complexes **1** (a) and **2** (b) in the presence of a proton donor HAc in the DMF solution with 0.1 M  $^{n}$ Bu<sub>4</sub>NPF<sub>6</sub>.

at the potential of E = -2.06 V for complex **1**, and E = -2.17 V for complex **2** increase by almost 100% compared with the CV without HAc. The linear sweep voltammetry (LSV) of complexes **1**(a) and **2** (b) at different concentrations of acetic acid are shown in Figure S12. As for complex **1**, the Faradaic yield for CO increases to 10% compared with the FECO = 5% without HAc (Fig. 8 olive curve), and the FE for H<sub>2</sub> is calculated as 60% at first, and then declined to around 45% at the end of the electrolysis (Fig. 8 navy curve). As for complex **2**, the Faradaic yield

for CO increases to 1.0% compared with the FECO = 0.5% without HAc (Fig. 8 violet curve), and the FE for H<sub>2</sub> is about 94% at the end of the electrolysis (Fig. 8 purple curve). The experimental result indicates that the addition of the proton donor acetic acid can promote the electrocatalytic reduction of CO<sub>2</sub> by complexes 1 and 2, which suggests that the catalytic CO<sub>2</sub> reaction for complexes 1 and 2 could be a proton-coupled electron transfer (PCET) process.[60–62] Moreover, there is no CO product detected in another CPE experiment under the same condition except using argon instead of carbon dioxide in either complex 1 or 2, suggesting that the CO product is not from the reduction of DMF, but from the reduction of CO<sub>2</sub>. Futheremore, there is no H<sub>2</sub> product detected, suggesting that CO<sub>2</sub> is necessary to reduce protons.

We propose a similar mechanism for both complexes 1 and 2 to explain the results in Scheme 2 and Scheme S2. Here, we take complex 1 as an example to illustrate the process. The lowest unoccupied molecular orbitals (LUMO) of complex 1 are mainly located on the ligand  $L^1$ , indicating that the first one electron reduction occurs at the ligand L<sup>1</sup> after the departure of the two chlorine ions, generating [Cu(II)DMFL<sup>1•-</sup>] (1a) in DMF solution. In fact, in this process, an electron enters the empty LUMO of the lowest lying  $\pi^*$  orbital of the redox-active benzimidazole ligand  $L^1$ , which is reduced to be radical anion  $L^{1-}$  acting as an electron reservoir for catalytic reduction of CO<sub>2</sub>.[63,64] Then, CO<sub>2</sub> is nucleophilically attacked to form the CO2 adduct intermediates [Cu(II)  $(L^{1 \bullet -})^{-}CO_{2}]^{+}$  (1b). After the second electron reduction happened on the metal center, a proton-coupled electron transfer (PCET) process happens to form  $[Cu(I)(L^{1\bullet-}) (COOH)]^{1-} (1c)$  with a COOH<sup>-</sup> group coordinated. Finally the C-O bond of the carboxyl group cleavage to release CO, along with H<sub>2</sub> generated, both of which may be resulting from the cooperation of the noninnocence radical anion benzimidazole ligand L<sup>1</sup> and the metal ion.[65] In addition, the evolution of H<sub>2</sub> may because a transition state copper/cobalt hydride complex  $ML^{1}H(1d)$  (M = Cu (1), Co (2)) is formed in the process of CO<sub>2</sub> releasing, which has been well proved by previous reported CO<sub>2</sub> reduction studies.[66,67] Therefore, the formation of hydride complex [M(I)L<sup>1•-</sup>H<sup>•-</sup>]<sup>1-</sup> before CO<sub>2</sub> reduction may play an essential role in the competition between  $CO_2$  reduction and H<sub>2</sub> evolution electrocatalysis.



Scheme 2. Proposed reaction mechanism for the electrocatalytic reduction of  $CO_2$  in the presence of complex 1 in DMF.

#### 3. Conclusion

In this report, we have successfully synthesized a novel benzimidazole derivative ligand 2-(6-methoxypyridin-2-yl)-1-((6-methoxypyridin-2-yl) methyl)-6-nitro-1*H*-benzo[*d*]imidazole (L<sup>1</sup>) and its corresponding transition metal complexes  $M L^{1}Cl_{2}$  (M = Cu (1), Co (2)). Upon combining cyclic voltammetry, bulk electrolysis with coulometry potential as well as complementary DFT calculations, it is found that the two complexes can electrocatalytic CO2 reduction and H2 evolution due to synergy effect between the redox-active ligand L<sup>1</sup> and transition metal (Cu (1), Co (2)). However, the selective  $CO_2$  reduction was not achieved, on the other hand, the high selectivity for H<sub>2</sub> evolution with Faradaic efficiency = 97% by complex 2 is very promising. The addition of proton donor HAc can enhance the electrocatalytic reduction of CO<sub>2</sub>, but no effect on the H<sub>2</sub> evolution, revealing a proton-coupled electron transfer (PCET) process. Based on these investigations, incorporating with some DFT calculations, the electrocatalytic mechanism was explored. And we found that the formation of transition metal hydride complex [M(I)  $L^{1\bullet-}H^{\bullet-}]^{1-}$  before CO<sub>2</sub> reduction might be the crux in the competition between CO<sub>2</sub> reduction and H<sub>2</sub> evolution. Further work is underway to explore potential transition metal complexes containing redox-active ligand catalysis with high selectivity of CO<sub>2</sub> reduction against the competing H<sub>2</sub> evolution.

# 4. Experimental section

# 4.1. General procedures

Unless otherwise stated, all manipulations were carried out under aerobic conditions, and all chemicals were commercially available and used as supplied without further purification, carbon dioxide and argon were purchased from Deihai Gases Corporation.

# 4.2. Synthesis of ligand 2-(6-methoxypyridin-2-yl)-1-((6methoxypyridin-2-yl) methyl)-6-nitro-1H-benzo[d]imidazole (L<sup>1</sup>)

The ligand  $L^1$  was synthesized according to published procedure with some modification. [42] Under N2 atmosphere, 6-methoxypyridine-2-carboxaldehyde (2 g, 14.6 mmol) was slowly added dropwise to 4-nitro-phenylendiamine (1.12 g, 7.3 mmol) in acetonitrile turbid solution (40 mL). The mixture was heated to reflux at 80 °C for 24 h, then cooled to room temperature, and filtered to give a yellow precipitate. The solid was washed with cold acetonitrile 3-5 times, and then dried in vacuo. The crude product was recrystallized from methanol/dichloromethane (V: V = 1: 2) to give the yellowish crystals. Yield: 1.26 g (44%). Calc. (Found) for C<sub>20</sub>H<sub>17</sub>N<sub>5</sub>O<sub>4</sub>: C, 61.38(61.40); H, 4.35(4.31); N, 17.90 (17.83) %. IR (KBr disk, cm-1): 3292 (m), 3101 (w), 2996 (w), 1606 (m), 1573 (m), 1521 (s), 1471 (s), 1411 (m), 1330 (s), 1272 (w), 1230 (w), 1145 (w), 1025 (s), 983 (m), 883 (m), 809 (s), 742 (m), 553 (w), 431 (w). 1H NMR (DMSO- $d_6$ , 400 MHz):  $\delta$  (ppm)  $\delta$  8.31 (s, 1H), 8.07 (s, 2H), 7.91 (s, 1H), 7.78 (s, 1H), 7.65 (s, 1H), 7.51 (s, 1H), 7.30 (s, 1H), 7.20 (s, 1H), 7.04 (s, 1H), 6.76 (t, J = 38.6 Hz, 1H), 5.76 (s, 2H), 3.90 (s, 3H), 3.78 (s, 3H). (Figure S1)

# 4.3. Synthesis of $CuL^1Cl_2$ (1)

A solution  $CuCl_2 \cdot 2H_2O(0.170 \text{ g}, 1 \text{ mmol})$  in methanol (5 mL) was added to a solution of  $L^1(0.391 \text{ g}, 1 \text{ mmol})$  in dichloromethane (10 mL). The mixture was stirred at room temperature for 12 h. The resulting solution was filtered, and the filtrate was kept for evaporation at RT for about 7 days to give X-ray-quality light yellow crystals at room temperature. Yield: 0.295 g (56%). Calc. (Found) for C20H17Cl2CuN5O4: C, 45.64(45.59); H, 3.23(3.17); N, 13.31(13.39) %. IR (KBr disk, cm-1): 3369 (s), 2942 (m), 2831 (w), 1604 (s), 1579 (s), 1527 (s), 1467 (s), 1425 (m), 1344 (s), 1303 (s), 1268 (w), 1027 (s), 877 (w), 806 (m), 740 (m), 563 (w), 437 (w).

# 4.4. Synthesis of $CoL^1Cl_2$ (2)

A solution CoCl<sub>2</sub> (0.129 g, 1 mmol) in CH<sub>3</sub>CN (5 mL) was added to a solution of L<sup>1</sup> (0.39 g, 1 mmol) in CH<sub>3</sub>CN (10 mL). The mixture was stirred under reflux for 12 h. After cooling to room temperature, the resulting solution was filtered, and all volatiles were removed under reduced pressure to yield blue solid, which was washed with diethyl ether and dried. X-ray-quality blue crystals were grown by vapor diffusion of diethyl ether onto a saturated acetonitrile solution at 2 °C. Yield: 0.245 g (47%). Calc. (found) for C20H17Cl2CoN5O4: C, 46.05 (46.10); H, 3.26(3.33); N, 13.43(13.46) %. IR (KBr disk, cm-1): 3390 (m), 3103 (m), 2941 (w), 2846 (w), 1606 (s), 1575 (s), 1525 (s), 1471 (s), 1425 (m), 1342 (s), 1305 (s), 1135 (w), 1039 (m), 877 (w), 806 (m), 742 (w), 566 (w).

## 4.5. Physical measurements

Infrared spectra (2 wt% sample in KBr pellets) were recorded on a Nicolet 170SX spectrometer in the 4000–400 cm-1 region. Elemental analyses (C, H and N) of the catalysts were performed on a model 2400 PerkinElmer analyzer. Powder X-ray diffraction (XRD) data were measured with a RIGAKU DMAX2500PC diffractometer with Cu-Ka radiation (k = 1.54056 Å). Nuclear Magnetic Resonance (NMR) spectra were acquired on a 300 MHz Bruker Avance spectrometer at 298 K, in which 0.5 mL electrolyte was mixed with 0.2 mL CD<sub>3</sub>Cl<sub>3</sub> (deuterated chloroform) was added as internal standard. UV–vis absorption spectra were measured by a TU-1800 (Beijing Purkinje General Instrument Ltd.) equipped with a photomultiplier tube detector.

# 4.6. X-Ray crystallographic data collection and refinement of the Structures.

Single crystals of  $L^1$ , **1** and **2** were mounted on a Bruker APEX-II CCD X-ray single-crystal diffractometer, and all data were collected at 173 K with graphite monochromated MoKu radiation ( $\lambda = 0.71073$  Å) in I > 2 $\sigma$  (I) diffraction spots and reduced by the SAINT v8.34A program, and absorption corrections were applied using program SADABS2014/5. The structures were solved by ShelXT program and refined by full-matrix least-squares techniques based on F2 with all observed reflections performed with the SHELXL program.[68] Molecular graphics: Olex2.[69] All the structures were refined by the full-matrix least squares method on  $F^2$  with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were generated geometrically. CCDC numbers for  $L^1$ , **1** and **2** are 1854595, 1581406, and 1835472, respectively.

# 4.7. Electrochemical measurements and electrolysis product analysis

All electrochemical experiments were tested by a CHI660E electrochemical analyzer to study their electrocatalytic properties and performed in a single chamber three-electrode reactor. 0.1 M solution of nBu<sub>4</sub>NPF<sub>6</sub> in dry N, N-dimethlyformamine (DMF) was used as supporting electrolyte. Cyclic voltammogram (CV) experiments were performed with a 3 mm-diameter glassy carbon working electrode, which was carefully polished using diamond paste, and ultrasonically rinsed in absolute ethanol and deionized water, then dried before use. There was about 10 mL of solution in the electrolytic cell, and the concentration of the complexes in the solution was about 2.5 mmol/L. The counterelectrode was a platinum wire and the reference electrode was Ag/ AgCl electrode. Control potential electrolysis (CPE) were performed with F-doped tin oxide (FTO) conducting glass substrates (1 cm  $\times$  1 cm, active surface area was 1.0 cm2) as the working electrode, which was obtained from Zhuhai Kaivo Optoelectronic Corp. They were pre-treated by dipping it in 5 wt% NaOH in ethanol for several hours, and then cleaning with water, ethanol, and water successively. Before each experiment the solution was purged with Ar or CO<sub>2</sub> for 30 min at room

#### temperature.

The in situ UV–Vis spectroelectrochemistry were carried out by applying a constant potential of -2.06 V and -2.17 V vs. Fc<sup>+/0</sup> for the complexes **1** and **2**, respectively, and recorded by using a UV-1800 UV–vis spectrophotometer (Shimadzu). In situ spectroelectrochemical studies were performed using a quartz cuvette of 1 cm path length assembled as an electrochemical cell, containing a platinum gauze, a platinum wire and an Ag/AgCl (saturated KCl) electrode as working, counter and reference electrode, respectively.The headspace gas samples (2 mL) generated by CPE experiments were extracted using a lure lock-type air-tight syringe and injected into a gas chromatography instrument (GC, Shimadzu GC-2014) equipped with a flame ionization detector (TCD, Shimadzu) to perform analysis for quantifying H<sub>2</sub>. Ultra-high purity Ar was used as carrier gas to detect CO and and H<sub>2</sub>. The liquid products were analyzed by NMR (Bruker AVANCE III HD).

# 4.8. Density functional theory calculations

Quantum-mechanical calculations were carried out using the Gaussian 09 program package, using the B3LYP hybrid functional [70,71] and the "double- $\xi$ " quality LanL2DZ[72] basis sets were used for transition metals (Cu and Co) and 6-311G (d, p) basis sets were used for non-metal atoms.[73] Atom coordinates used in the calculations were from crystallographic data, and a molecule in the unit cells was selected as the initial model.

#### CRediT authorship contribution statement

Ning-Ning Shi: Data curation, Formal analysis, Investigation, Methodology, Project administration, Resources, Software, Supervision, Validation, Visualization, Writing–original draft, Writing–review & editing. Xiao-Meng Yin: Supervision, Validation, Resources, Software. Wei-Song Gao: Conceptualization, Data curation, Investigation. Jin-Miao Wang: Conceptualization, Investigation, Methodology. Shi-Fu Zhang: Conceptualization, Investigation, Methodology. Yu-Hua Fan: Conceptualization, Data curation, Formal analysis, Methodology, Validation. Mei Wang: Conceptualization, Data curation, Funding acquisition, Investigation, Project administration, Resources, Supervision, Validation, Visualization, Writing–review & editing.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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# Appendix A. Supplementary data

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